

CHAPTER 3

CROSS-COUPLING WITH ORGANOSILICON COMPOUNDS

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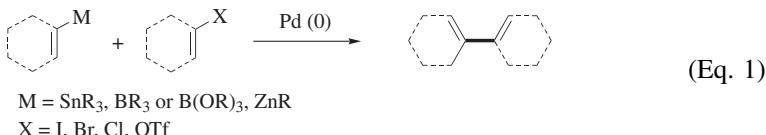
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INTRODUCTION

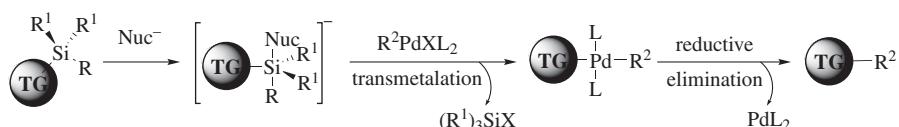
Silicon, an element widely used in many facets of organic chemistry,^{1–5} was not effectively employed in cross-coupling reactions until sixteen years after the first reported transition-metal-catalyzed coupling reactions by Corriu⁶ and Kumada.⁷ Most early developments in this field were achieved through the use of organoboron (1979),^{8–10} organozinc (1977),^{11,12} and organotin (1977)^{13–15} coupling partners (Eq. 1).



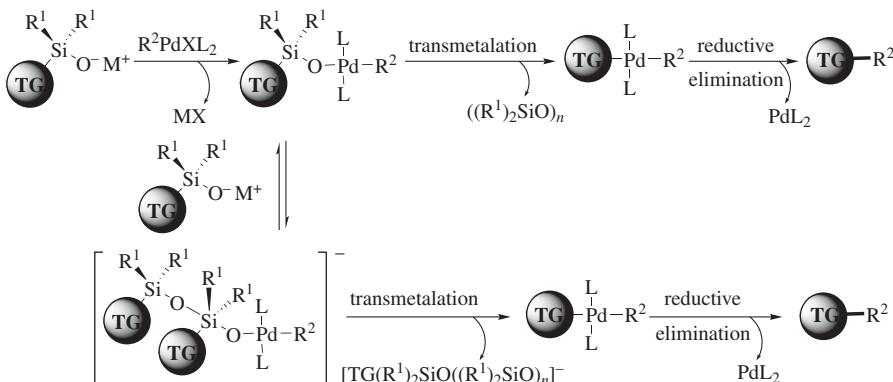
Environmentally benign and of low molecular weight, organosilicon functions possess many properties that make them the ideal donors of organic groups in cross-coupling reactions. However, despite silicon's location in Group 14 along with tin and with similar electronegativity (1.90 for silicon vs. 1.96 for tin),¹⁶ tetracoordinate organosilanes are less capable of transferring one of the attached organic groups to palladium compared with tetracoordinate organostannanes. Despite this limitation, pioneering efforts initiated by several research groups provided the framework on which modern organosilicon cross-couplings are based, namely, that appropriately substituted organosilicon compounds are capable of expanding their valence.^{17–20} Through the addition of an appropriate silicophilic Lewis base, an *in situ* generated pentacoordinate silane can effectively transfer an organic group (TG = transferable group, Scheme 1). This feature allowed for the rapid development of silicon cross-coupling methods that continues today.

In recent years, a new paradigm for silicon-based cross-coupling has been introduced that obviates the need for external activation of the silane. In this scenario, a silanolate salt serves as the carrier and the key transmetalation is facilitated through the formation of a discrete Si-O-Pd linkage. From there, the transferable group migrates with or without additional activation (Scheme 2).

In view of recent advances, organosilicon-based cross-coupling has now become a practical, viable, and in some cases, superior cross-coupling method compared with the more commonly employed organoboron, -zinc, and -tin couplings. The unique properties of organosilicon compounds provide a number of distinct advantages to their use as donors in transition-metal-catalyzed cross-coupling reactions: (1) silicon moieties can be introduced into organic substrates by many general and high-yielding methods for the construction of silicon-carbon bonds, (2) organosilicon reagents are chemically robust and allow isolation and purification of the products and are compatible with many functional groups, (3) silicon-containing byproducts of the coupling are of low molecular weight, are non-toxic, and are easily removed from reaction mixtures, and (4) a number of mild methods for the activation of the organosilicon moieties are now available that are compatible with many functional groups.

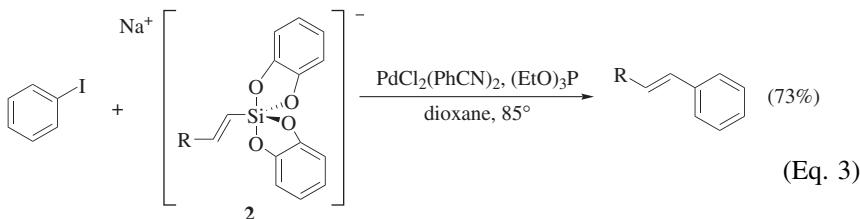
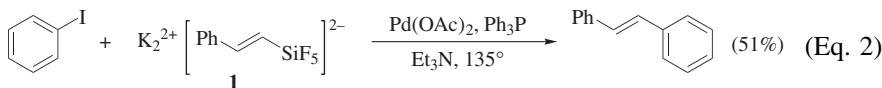


Scheme 1



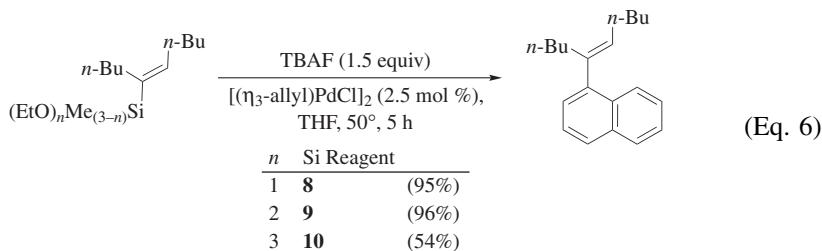
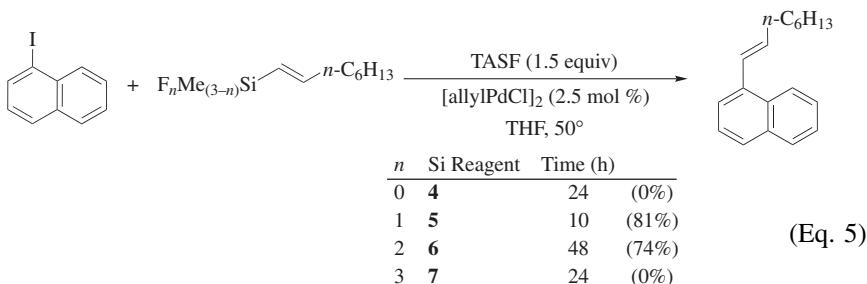
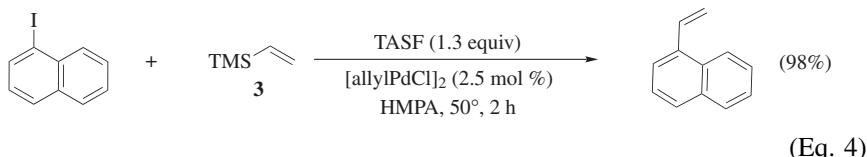
Scheme 2

One of the earliest reports of silicon cross-coupling involves the use of the dipotassium salt of pentafluorostyrylsilicate **1** (Eq. 2).²¹ Despite the harsh conditions employed, this reaction provided the first indication that higher-valent silanes could become viable donors in palladium-catalyzed cross-coupling reactions. This concept was further reinforced by the finding that a pentacoordinate silane, sodium alkenylbis(catecholato)silicate **2**, can effectively undergo coupling with several aryl iodides, albeit at elevated temperatures (Eq. 3).²²



The use of penta- and hexacoordinate silanes illustrates the kind of activation that is required to polarize the carbon-silicon bond sufficiently for a successful cross-coupling reaction. However, the technology at this stage was very limited in substrate scope and reaction efficiency. Beginning in 1988, a series of reports by Hiyama and Hatanaka demonstrated that such limitations can be overcome through the use of an additive to generate the requisite pentacoordinate siliconate moieties *in situ* (Eq. 4).²³ The substrate scope is significantly expanded when stable and easily synthesized tetracoordinate silanes are used. Nucleophilic fluoride sources are the additive of choice because of the high enthalpy of formation (159 kcal/mol) of a Si–F bond.²⁴ Yet this modification was not sufficient in all

cases. Whereas vinyltrimethylsilane **3** readily couples with electrophiles in the presence of a fluoride source [tris(dimethylamino)sulfonium difluorotrimethylsilicate or TASF], more substituted alkenyltrimethylsilanes such as **4** do not (Eq. 5).²⁵ The problem is overcome through the use of the corresponding fluorosilanes **5** and **6**, although **7** is unreactive. Alkoxy silanes **8** and **9** exhibit similar reactivity to fluorosilanes with tetra-*n*-butylammonium fluoride (TBAF) as the promoter, whereas the trimethoxysilane **10** is less active (Eq. 6).²⁶



Numerous reports highlighting many permutations of the fluoro- and chlorosilane cross-coupling with aryl, heteroaryl, alkenyl, allyl, and even alkyl halides (or pseudohalides) were published in the following years.^{27–30} As shown in Figure 1, this body of work encompassed a wide range of fluorosilane precursors, electrophiles, and even documented multicomponent permutations. These pioneering studies provide a glimpse into the prodigious potential of organosilicon cross-coupling, and therefore suggest that its continued refinement can match the efficiency, selectivity, and versatility of the more actively studied Suzuki-Miyaura coupling of organoboron compounds and the Stille-Migita-Kosugi coupling of organotin compounds.

The next major advance in the evolution of silicon-based cross-coupling was the serendipitous discovery by Denmark that organosilanols can serve as competent partners.^{31–35} Silanols are capable of facile cross-coupling under activation

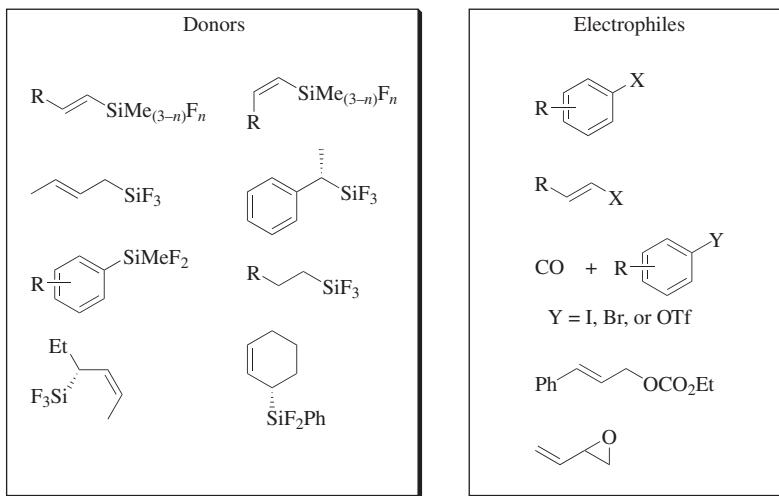
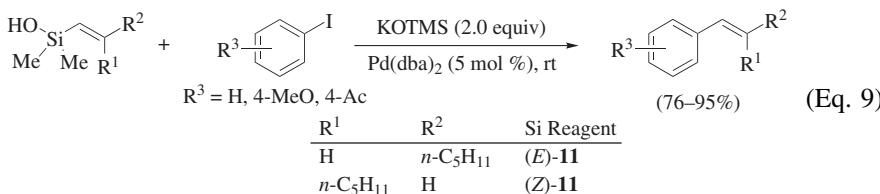
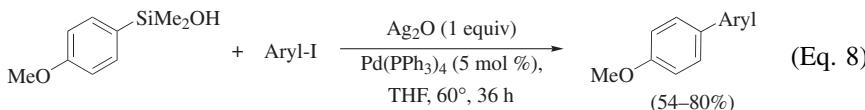
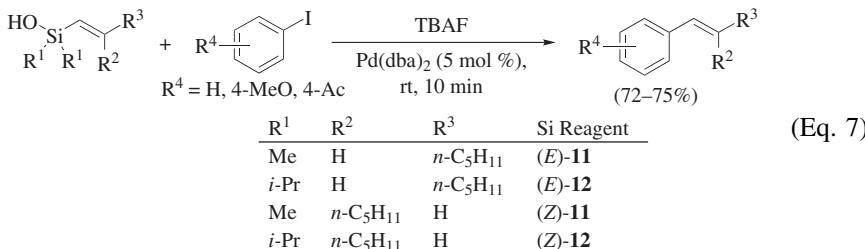
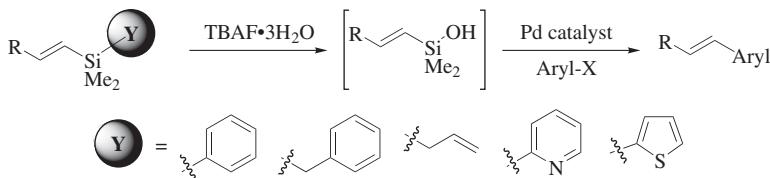


Figure 1. Permutations of organofluorosilane cross-coupling.

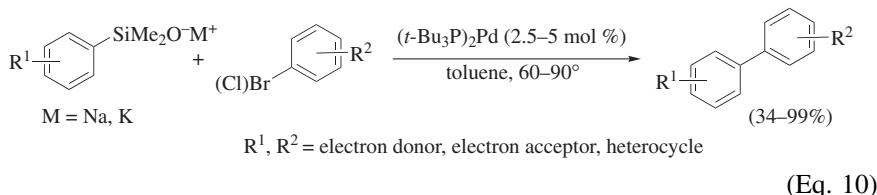
by TBAF, but in addition, other promoters such as silver oxide^{36,37} and potassium trimethylsilanolate³² are also effective activators (Eqs. 7–9).



The demonstration that organosilanols can effectively cross-couple with a variety of organic halides and pseudohalides led to two significant advances: (1) the



introduction of a myriad of silanol surrogates bearing more chemically robust groups (silacyclobutyl,^{38–40} phenyl,^{41,42} benzyl,^{43–45} allyl,^{46,47} 2-thienyl,^{48,49} and 2-pyridyl^{50–52}) that can be converted into silanols under the action of TBAF•3H₂O (Scheme 3), and (2) the discovery that the conjugate bases of organosilanols (alkali metal silanlates) are the active species under activation by Brønsted bases (Eq. 10).^{53,54} These silanolate salts can be generated *in situ* or prepared and stored as stable solids and are “self-activating” coupling partners.⁵⁵ The preparative advantages of the silanolate salts along with the unique mechanism with which they undergo cross-coupling will be described in detail in the following sections.



In contrast to the boron- and tin-based reagents, the diversity of silicon-based reagents that undergo successful cross-coupling is enormous. Silicon moieties bearing three carbon substituents, one, two, or three halogen substituents (both chlorine and fluorine) as well as one, two, or three oxygen substituents (hydroxy, alkoxy, and silyloxy) are all known to participate in cross-coupling reactions with various electrophilic partners. This remarkable diversity reflects the versatility of the silicon-based cross-coupling process. However, this diversity also constitutes an impediment to the practitioner interested in implementing this method, namely, how to select the appropriate precursor for a given transformation.

This chapter presents a thorough overview of the various combinations of transferable groups and organic electrophiles. The scope of the coverage is limited to the combination of silicon-bearing nucleophiles with halo or related electrophiles under catalysis by palladium or nickel complexes wherein the silyl halide (or pseudohalide) is lost. The literature is covered through 2008, with selected references from 2009 and 2010. A number of reviews of silicon-based cross-coupling reactions have already appeared that chronicle the development of the process from the earlier advances with fluoride activation^{27–30,56,57} to the more recent improvements^{58,59} including Brønsted base-activated silanols^{33–35,53,55,60–62} and their application in natural products synthesis.⁶³

MECHANISM

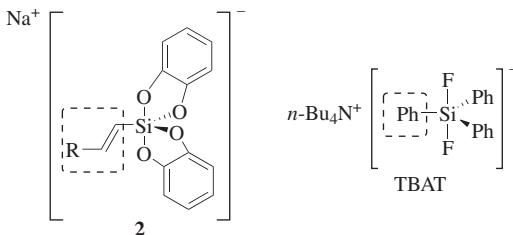
General Catalytic Cycle

The generally accepted mechanism for transition-metal-catalyzed cross-coupling reactions involve: (1) oxidative addition to an electrophilic halide or pseudo halide, (2) transmetalation from an organometallic donor, and (3) reductive elimination to generate a new C–X or C–C bond.⁶⁴ Although the oxidative addition of an organic halide to a Pd(0) complex is common among most coupling reactions, the transmetalation step is distinctive to the organometallic donor employed. After transmetalation has occurred, the diorganopalladium species suffers reductive elimination to form the product containing a new carbon–carbon bond and simultaneously regenerates the palladium(0) catalyst.^{65,66} The transmetalation step in the cross-coupling of organosilanes has been the subject of stereochemical, spectroscopic, kinetic, and computational studies. For the most part, these studies focus on the catalytic processes that involve activation by fluoride, although two more recent reports address the mechanism of transmetalation of alkali metal silanlates. These two preparatively distinct processes will be discussed separately.

Fluoride Activation via 10-Si-5 Intermediates

The generally accepted paradigm in the field of silicon-based cross-coupling is the necessity to generate a pentacoordinated silicate as a prerequisite for a successful coupling. This is not an unreasonable scenario because it is well known that silicon can readily expand its valency.^{17–20} Although there is no direct evidence for an “activation” step preceding a cross-coupling when a tetra-coordinate silane is employed in the presence of a nucleophilic promoter, there is some experimental data that lend support to this contention.⁶⁸

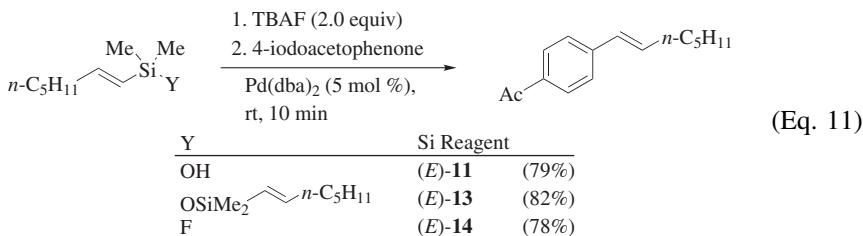
Indirect evidence for an activation step is found in the ability of pre-synthesized, stable, pentacoordinate silanes to transfer an organic group onto palladium. Two examples are the use of catecholsiliconates **2** for alkenyl transfer and the use of tetra-*n*-butylammonium triphenyldifluorosilicate (TBAT) as a phenylating reagent.^{21,69–71}



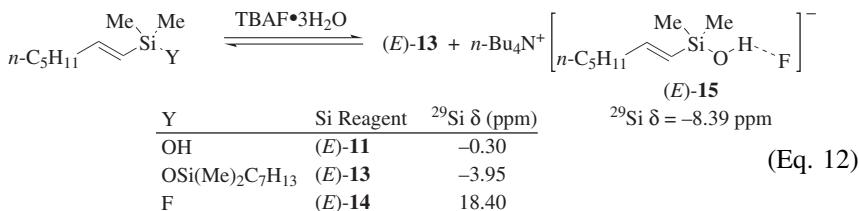
An early observation in the development of fluorosilane cross-coupling noted the effect of heteroatom substitution at silicon on the facility of coupling. In the cross-coupling between (1-octenyl)silylfluorides **5–7**, (Eq. 5) and 1-iodonaphthalene, fluoride substitution on silicon is essential for the coupling to proceed.

The reactivity of the silane decreases with increasing numbers of fluoride atoms, however, such that trifluorosilane (*E*)-7 is completely unreactive.²⁵ In a related experiment with alkoxysilanes, a similar effect was observed, with trialkoxysilane (*E*)-10 displaying reduced reactivity.²⁶

A number of investigations including quantitative evaluation of substituent effects,⁷² a Hammett study,⁷³ determination of a rate equation,⁷⁴ and spectroscopic identification of intermediates⁷⁵ provided crucial insights into the mechanistic details of the fluoride-promoted cross-coupling reactions. One of the first quantitative comparisons demonstrated that three different monofunctional silanes (silanol (*E*)-11; disiloxane (*E*)-13; and fluorosilane (*E*)-14) react nearly identically under the standard coupling conditions (Eq. 11).



The similarity of reaction rates and yields results from conversion of all three precursors into a more advanced, common reactive intermediate. ²⁹Si NMR analysis of a mixture of TBAF with either silanol (*E*)-11, disiloxane (*E*)-13, or fluorosilane (*E*)-14 show that only two species are formed almost immediately. One was identified as the disiloxane (*E*)-13 and the other species, (*E*)-15, is a hydrogen-bonded complex between the organosilanol and TBAF (Eq. 12). Subsequent kinetic analyses revealed the role of this intermediate in the cross-coupling pathway.



A cleverly designed Hammett study employing an intramolecular competition between aryl groups in a diaryldifluorosilane revealed a significant dependence on the substituents ($\rho = -1.5$), clearly indicating that the transmetalation step involves electrophilic attack of the arylpalladium(II) intermediate on the *ipso* carbon on the arylsiliconate complex.⁷³

Kinetic Analysis and Mechanistic Implications. The kinetic analysis of the TBAF-promoted coupling of (*E*)-11 with 2-iodothiophene revealed the following

overall rate equation (Eq. 13):

$$\text{rate} = k_{\text{obs}}[\text{SiOH}]^2[\text{TBAF}]^n$$

$$k_{\text{obs}} = k[\text{Pd}]^1$$

$$n = 1 \text{ at TBAF/SiOH} < 2; n = -1 \text{ at TBAF/SiOH} > 2$$
(Eq. 13)

The implications of this equation are detailed below in the context of the basic three-step catalytic cycle for palladium-catalyzed cross-coupling reactions.⁶⁴ The first-order rate constant dependence on palladium concentration is consistent with a mononuclear palladium entity participating in each turnover of the catalytic cycle. The zero order behavior in 2-iodothiophene is interpreted as a fast and irreversible oxidative insertion step of the palladium(0) species under the reaction conditions. The ease of this process is well documented and the predominant use of iodides in many of the early reports of cross-coupling chemistry has its origin in this behavior.⁶⁴

The positive correlation between the rate and silanol concentration strongly supports the conclusion that transmetalation is the rate-determining step, as it is in organotin coupling reactions.¹⁵ The unique second-order dependence on silanol concentration indicates that two silicon-based entities participate in the rate-determining transmetalation step. NMR spectroscopic studies revealed the rapid formation of a disiloxane from two molecules of silanol in the presence of TBAF and therefore suggest that the second-order dependence is due to such a disiloxane, not a silanol, undergoing transmetalation.

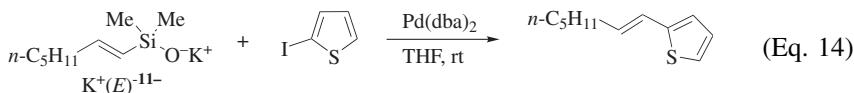
The striking divergence of rate dependence on fluoride concentration is indicative of a change in mechanism. ²⁹Si NMR spectroscopic studies showed that a hydrogen-bonded silanol-TBAF complex (*E*-15) is a thermodynamically stable intermediate formed by the interaction of TBAF·3H₂O with nearly any silyl precursor (Eq. 12). If such a complex were formed, then the process of conversion into a pentacoordinated fluoride-activated disiloxane (*E*-16) would release one molecule of TBAF for every two molecules of complex initially present (Scheme 4). The intermediacy of (*E*-16) and its role in the turnover-limiting, bimolecular transmetalation with the arylPdXL_n species is consistent with the kinetic data (second order in silanol, first order in arylPdX, no kinetic saturation observed) and also consistent with the observed rate dependence on TBAF. Spectroscopic studies showed that at low TBAF concentration, silicon is mostly in the form of disiloxane (*E*-13); however, at higher concentration the predominant species becomes (*E*-15). Direct formation of disiloxane (*E*-16) from (*E*-11) and resultant fluoride activation would be consistent with second-order behavior in silanol, and first-order behavior in TBAF. However, if all of the silane is present as (*E*-15), then an inverse dependence of the coupling rate on fluoride concentration is expected because one molecule of TBAF must dissociate prior to the rate-determining transmetalation step. Moreover, the mechanistic implications of these studies are also relevant to the TBAF-promoted coupling of fluoro-, hydrido-, and heterocyclic silanes, all of which form related species when mixed with TBAF. In addition, it is likely that hydroxide-activated cross-coupling reactions of monofunctional silanes proceed by a similar mechanism.

However, given the enormous number of competent silane precursors (Figure 3) it would be ill-advised to extrapolate the conclusions from these mechanistic studies to the details of other coupling processes.

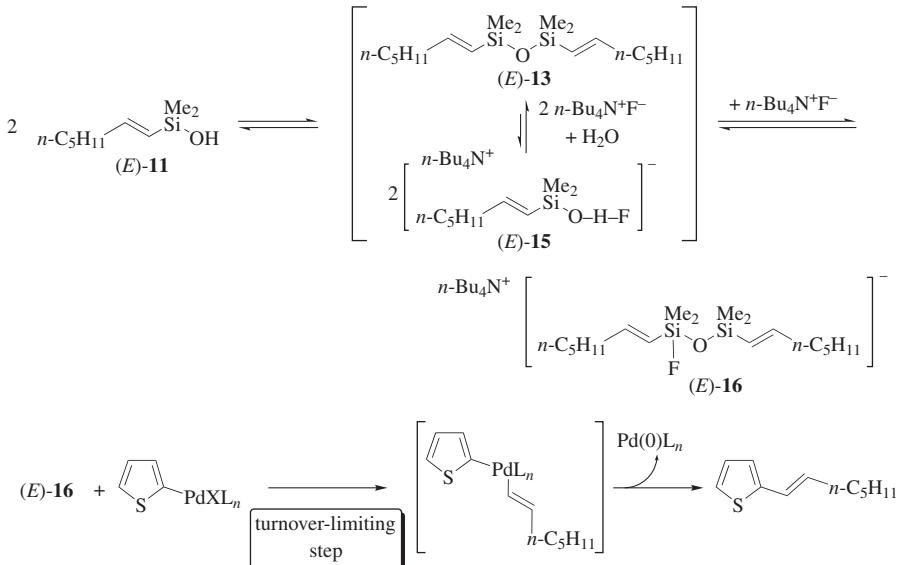
A recent computational study on the role of fluoride activation in the cross-coupling of vinyltrimethylsilane **3** with a vinylpalladium(II) complex concluded that prior activation of the silane is energetically prohibitive.⁷⁶ Rather, these authors concluded that a termolecular transmetalation transition structure assembly consisting of a complex between **3** and the vinylpalladium(II) species in which fluoride simultaneously activates the trimethylsilyl group is preferred.

Brønsted Base Activation via 8-Si-4 Intermediates

The mechanistic aspects of the fluoride-free cross-coupling reaction of organosilanols and their conjugate bases (Eqs. 9 and 10) have also been investigated.⁷⁷ The kinetic analysis examined the coupling of silanolate $\text{K}^+(E)\text{-11}^-$ to 2-iodothiophene, which is representative of the KOTMS-promoted cross-coupling of alkenylsilanols (Eq. 14). The derived rate equation is shown in Eq. 15.

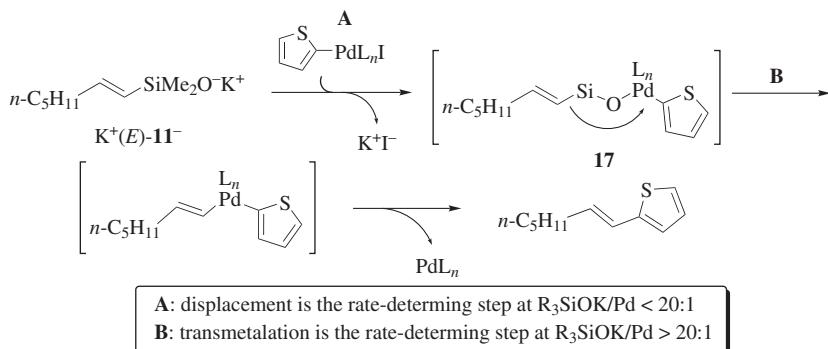


$$\begin{aligned} \text{rate} &= k_{\text{obs}}[\text{R}_3\text{SiOH}]^n \\ k_{\text{obs}} &= k[\text{Pd}]^1 \\ n &= 1 \text{ when } \text{R}_3\text{SiOK/Pd} < 20/1; n = 0 \text{ when } \text{R}_3\text{SiOK/Pd} > 20/1 \end{aligned} \quad (\text{Eq. 15})$$



The zero order rate dependence on 2-iodothiophene and the first-order dependence of the rate constant on palladium concentration are straightforward to interpret. As in the kinetic analysis of the TBAF-promoted system, these data are consistent with a fast and irreversible oxidative insertion of the palladium into the aryl iodide bond. Thus, the oxidative addition step is not interpreted to be the turnover-limiting step of this coupling.

The results of varying the silanolate concentration show two regions with distinct slopes. This behavior is interpreted as a change in the turnover-limiting step. It is immediately apparent that the mechanism diverges from that of the TBAF-promoted reaction. A change to zero order behavior in silanolate is evidence of an intramolecular transmetalation step. The proposed mechanism for this fluoride-free system is, therefore, shown in Scheme 5.



Scheme 5

The region of low silanolate concentration (below 20 equiv with respect to palladium) shows first-order behavior, which is interpreted as rate-determining formation of intermediate **17**. This slope levels to a zero order regime at higher silanolate concentrations, which lends support for a rate-determining intramolecular transmetalation from **17**. Because the concentration of palladium catalyst (0.05 equiv with respect to iodide) is static throughout the course of the reaction, a rate-determining intramolecular process involving this catalyst should exhibit a rate behavior independent of silanolate concentration.

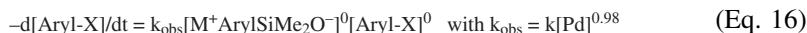
The analysis of silanolate order with a stoichiometric amount of palladium with respect to 2-iodothiophene also revealed a first-order dependence of the reaction rate on silanolate concentration.⁷⁷ This critical experiment rules out the possibility that an activated complex involving another molecule of silanolate (with **17** to generate a pentacoordinate silicon) is formed. In this latter case, second-order behavior would have been expected.

The demonstration that a neutral, tetracoordinate (8-Si-4) species is capable of rapid transmetalation to an arylpalladium(II) unit forces a revision of the belief that organosilicon donors all require prior activation as a pentacoordinate siliconate. This discovery illustrates the importance of the silicon-oxygen-palladium

linkage because it allows for an otherwise kinetically inaccessible transformation to occur. The divergence of mechanism from that of fluoride activation, wherein an intermolecular transmetalation from a fluoride-activated disiloxane is found to be rate-determining, is remarkable because two equally efficient room-temperature coupling systems can operate via different mechanisms.

Brønsted Base Activation via Both 8-Si-4 and 10-Si-5 Intermediates

The unambiguous demonstration that transmetalation can take place by via both neutral and (8-Si-4) and anionic (10-Si-5) intermediates comes from a recent study on isolated arylpalladium(II) arylsilanolate complexes.⁷⁸ The kinetic analysis of the cross-coupling of potassium arylsilanolates with aryl bromides catalyzed by $((t\text{-Bu})_3\text{P})_2\text{Pd}$ (Eq. 10) afforded little mechanistic insight (Eq. 16).



However, investigation of the stoichiometric process provided a unique insight into the species undergoing the critical transmetalation. Spectroscopic (^1H , ^{13}C , and ^{31}P NMR) and X-ray crystallographic analysis allowed the identification of the key, T-shaped, three-coordinate complex **20** (formed *in situ* from $\text{K}^+\text{18}^-$ and the oxidative addition product **19**, Figure 2), which undergoes transmetalation with a first-order decay (k_{obs} of $5.0 \times 10^{-4} \text{ s}^{-1}$) to form biaryl **21**. Although this result clearly proves the competence of an 8-Si-4 species to undergo transmetalation, it does not represent the reaction conditions for the catalytic process. In the presence of $\text{K}^+\text{18}^-$, **20** undergoes transmetalation ten-times faster (k_{obs} of $5.0 \times 10^{-3} \text{ s}^{-1}$). Moreover, the rate constant shows a first-order dependence on silanolate, further supporting the conclusion that an activated pathway has intervened. Thus, both pathways can be operative for a given precursor, providing that a palladium silanolate intermediate can be formed.

STEREOCHEMISTRY

Alkenylsilanes

Configurational Specificity. The cross-coupling of alkenylsilanes bearing many different silicon donor moieties with aryl and heteroaryl halides all proceed with high stereospecificity for the formation of geometrically defined alkenes at varying levels of substitution. Examples of (*E*)- and (*Z*)-2-monosubstituted alkenylsilanes are shown in Eqs. 5, 7, and 9. In addition, (*E*)- and (*Z*)-**1**, 2-disubstituted alkenylsilanols⁷⁹ and (*E*)- and (*Z*)-2,2-disubstituted alkenylsilanolate⁸⁰ undergo clean cross-coupling with high stereospecificity under mild conditions (Eqs. 17a, 17b). Even trisubstituted siloxanes (as in **22**,⁸¹ silanols (masked as in **24**),⁴⁵ and silanolates (as in **26**)⁸⁰ can produce tetrasubstituted alkenes (**23**, **25**, **27**) bearing a variety of groups or rings without loss of configurational purity of the starting silane (Eqs. 18a–18c).

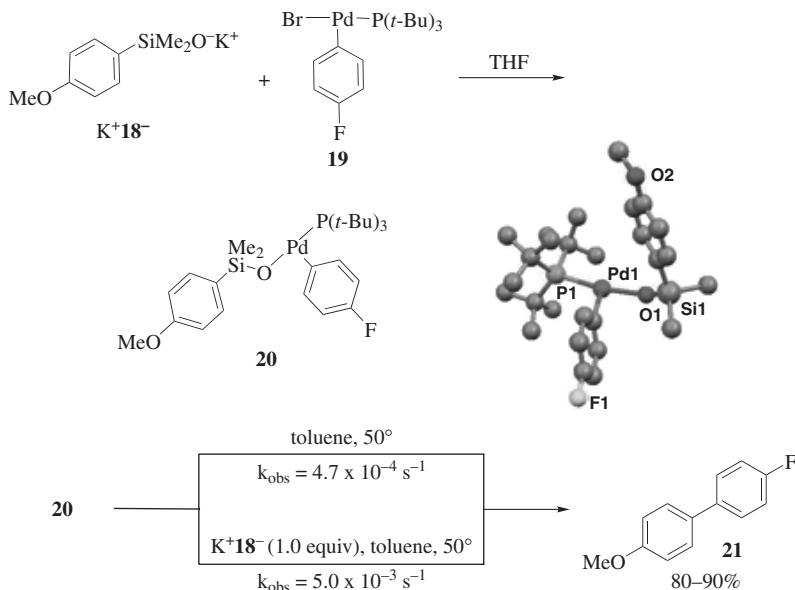
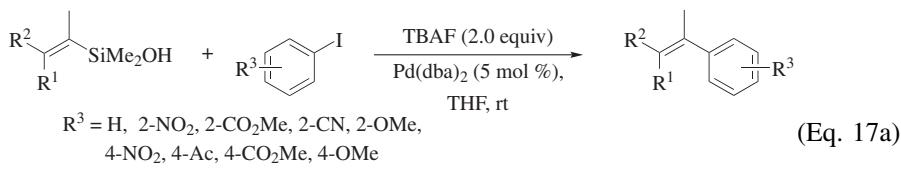
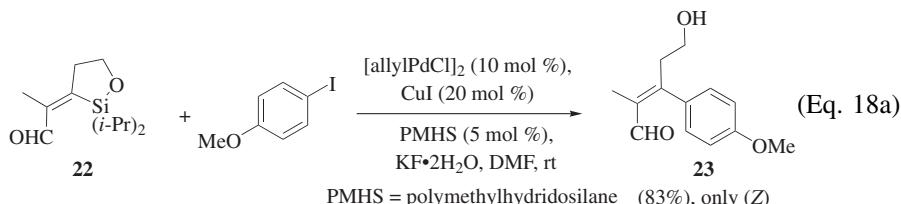
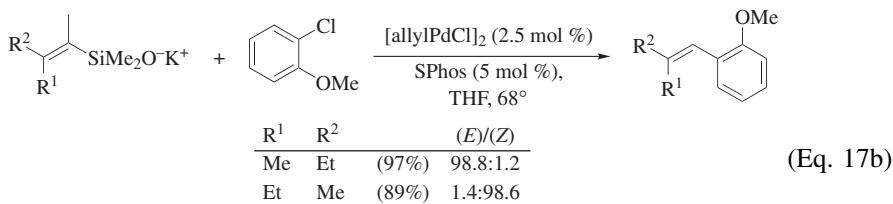
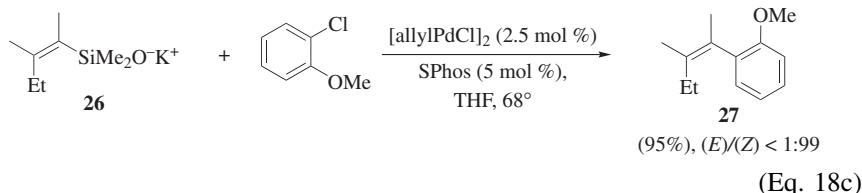
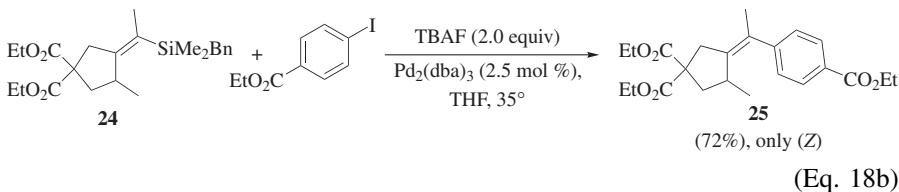


Figure 2. Formation and conversion of an isolable arylpalladium(II) silanolate complex.

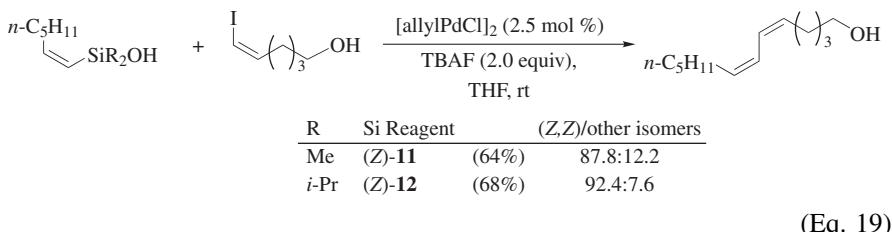


$\frac{\text{R}^1}{\text{H}}$	$\frac{\text{R}^2}{\text{CH}_2\text{OTHP}}$	(76–91%), only (<i>E</i>)
CH_2OTHP	H	(66–87%), only (<i>Z</i>)

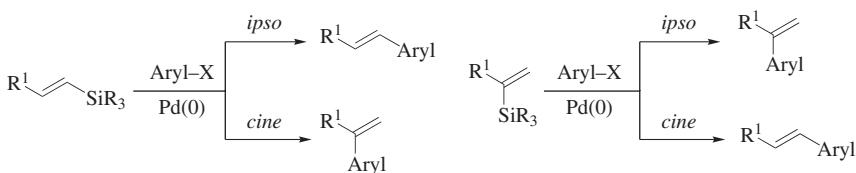




A slight erosion in the geometrical specificity is seen in the coupling of (*Z*)-alkenylsilanols ((*Z*)-**11**, (*Z*)-**12**) (and their surrogates) with (*Z*)-alkenyl iodides (Eq. 19).^{31,38} The selectivity can be improved by the use of the diisopropylsilanol.

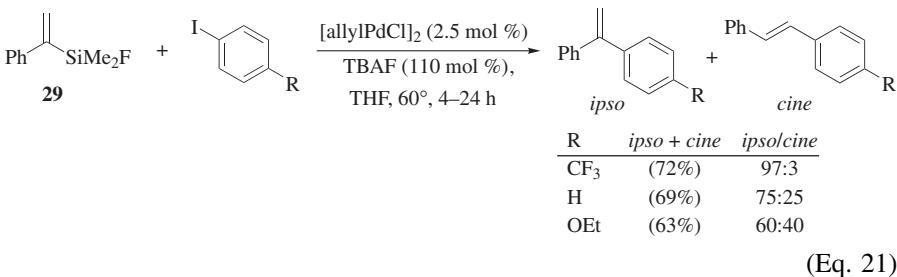
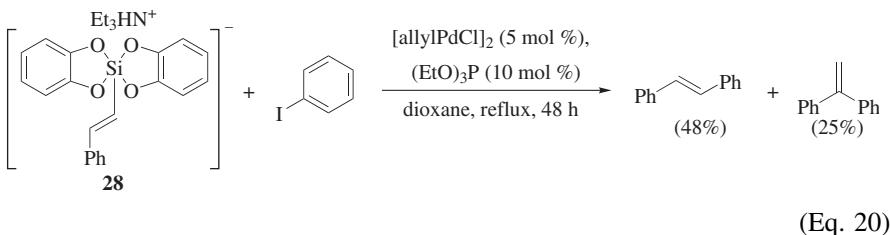


Constitutional Site Specificity. Alkenylsilanes can display the same divergence of site selectivity (*ipso* or *cine*) as is also seen in the cross-coupling of alkenylstannanes^{82–85} (Scheme 6). In general, the *ipso* pathway is dominant for most combinations of organosilyl donors and aryl/alkenyl electrophiles, but in some instances *cine* substitution can become the major pathway. Anomalous coupling products have been reported in the cross-coupling of bis(catecholato)alkenylsiliconates **28** (Eq. 20).^{86,87} The dependence of the *ipso/cine* product ratio on the electronic properties of the aryl electrophile in cross-coupling with **29**



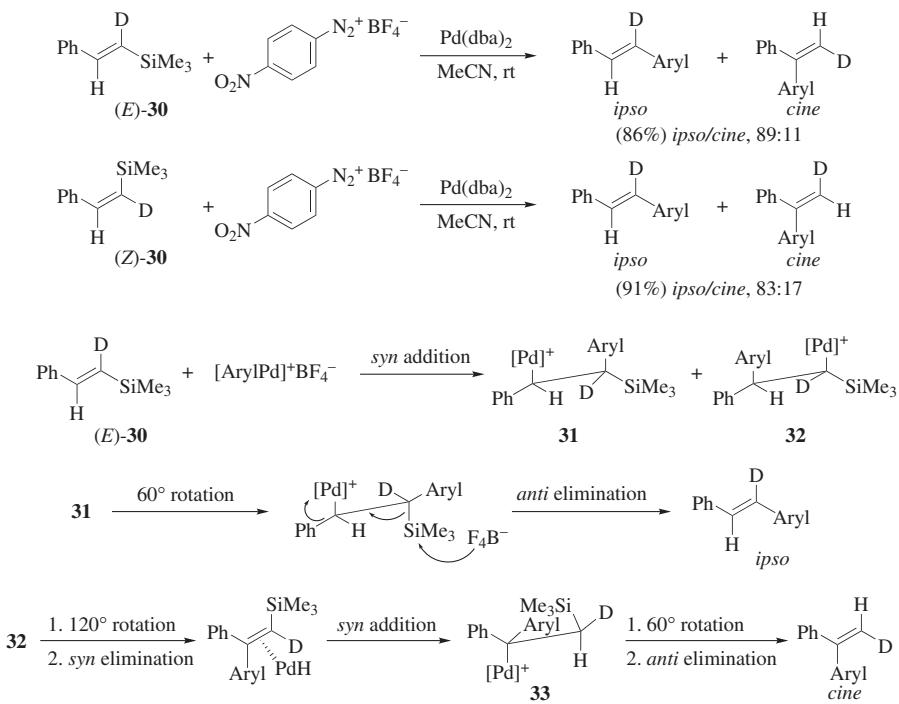
Scheme 6

provides an insight into the structural factors that influenced the mechanistic divergence (Eq. 21).^{88,89}

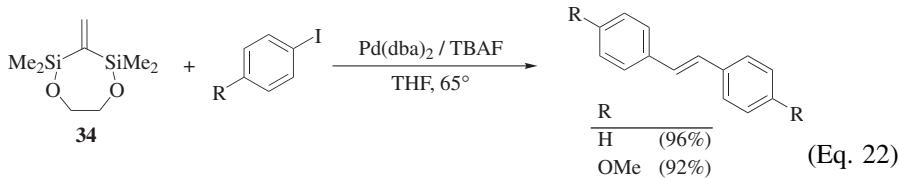


By far the most commonly encountered complications from *cine* substitution pathways occur for alkenyltrimethylsilanes^{90–92} and vinyltrimethylsilane in particular. In fact, long before the advent of modern, silicon-based, cross-coupling methods,²³ the divergent behavior of styryl- and vinyltrimethylsilanes in reactions with aryl diazonium salts in the presence of palladium(0) catalysts was demonstrated.^{93–97} These studies, employing geometrically defined and isotopically labeled 2-styryltrimethylsilanes (*E*- and (*Z*)-**30**), are interpreted in terms of a Heck-type carbopalladation process that supersedes the expected transmetalation pathway (Scheme 7). Addition of [arylPd]⁺ across the double bond produced two constitutional isomers, **31** and **32**. Adduct **31** can proceed directly to the *ipso* product by an *anti* elimination of Me₃SiF and Pd(0). Adduct **32** is proposed to undergo a *syn* β-hydride elimination, followed by a *syn* readdition, to form **33**, which then suffers an *anti* elimination of Me₃SiF and Pd(0) to form the *cine* product. The pathway for reaction of (*Z*)-**30** is similar, but interestingly, the final step to form the *ipso* product must proceed via a *syn* elimination process to explain the formation of the same geometrical isomer from both precursors. Subsequent studies have sought to refine the mechanistic details for reactions of other coupling partners, but the basic concepts remain the same.^{98–103}

A particularly dramatic and preparatively useful example of the *cine* rearrangement process involves the double cross-coupling of geminal (bis)silyl ether **34**, which under standard conditions affords the *trans*-stilbenes in excellent yield (Eq. 22).¹⁰⁴ This discovery has also been applied to the synthesis of (*E*)-poly-(arylenevinylene)s by the use of dihaloarene electrophiles.



Scheme 7



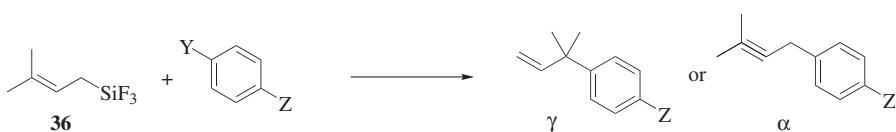
Allylsilanes

Constitutional Site Selectivity. Allylsilanes are among the most useful organosilicon reagents because of their enhanced reactivity toward a wide range of electrophiles including palladium(II) compounds.^{105–107} Accordingly, the catalytic, electrophilic substitution of allylic silanes with organopalladium species should be facile. For simple allylsilanes, no stereochemical or constitutional selectivity issues are extant,^{70,108} but allylic silanes bearing substituents on the terminal carbon can have both. For this type of cross-coupling process, allylic trifluorosilanes exhibit high reactivity and selectivity. Both (*E*)-2-butenyl- (**35**) and prenyltrifluorosilane (**36**) react with aryl iodides and triflates to afford substitution products with exclusive γ -site selectivity under activation by TBAF and (Ph₃P)₄Pd or TASF and Pd(OAc)₂/dppb, respectively (Eqs. 23a, 23b).¹⁰⁹ The site selectivity of this transformation displays a strong dependence on the ligand such

that with TBAF and (dppp)PdCl₂ the α -substitution product is formed.¹¹⁰



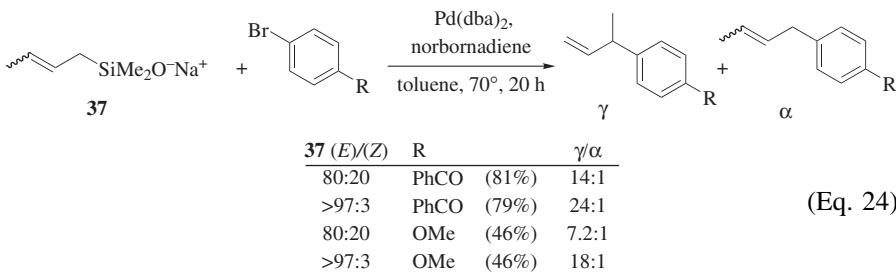
Y	Conditions	γ/α	$(E)/(Z)$
I	(Ph ₃ P) ₄ Pd, TBAF, THF, 100°, 19 h	(95%)	100:0
Br	(Ph ₂ P(CH ₂) ₃ PPh ₂)PdCl ₂ , TBAF, THF, 120°, 12 h	(92%)	0:100
OTf	(Ph ₂ P(CH ₂) ₄ PPh ₂)PdCl ₂ , TASF, THF, 100°, 12 h	(92%)	0:100



Y	Z	Conditions	γ/α
I	Ac	(Ph ₃ P) ₄ Pd, TBAF, THF, 100°, 19 h	(70%)
OTf	CO ₂ Me	(Ph ₂ P(CH ₂) ₃ PPh ₂)PdCl ₂ , TBAF, THF, 120°, 48 h	(80%)

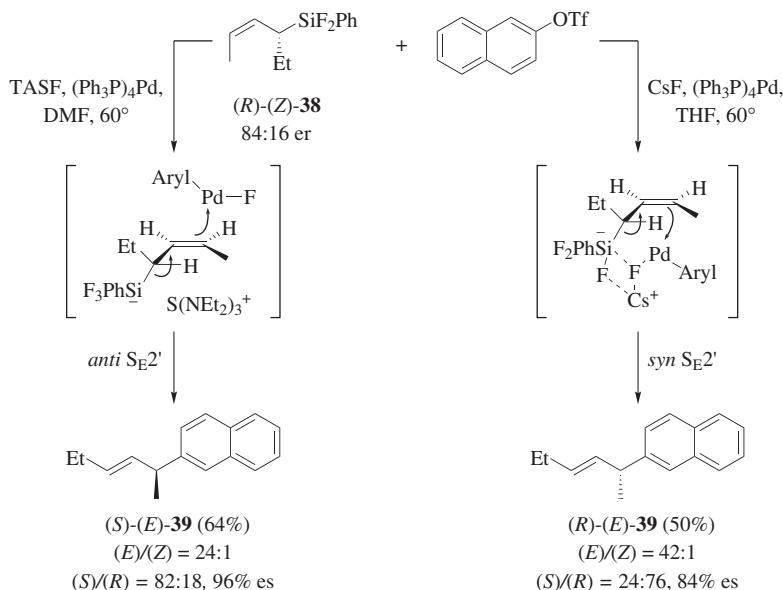
A series of substituted cyclohexenyl and cyclopentenyl benzoates have been studied for the site and stereoselectivity in palladium-catalyzed substitution reactions, including the use of TBAT as a phenylating reagent. The modest selectivities observed are rationalized on the basis of steric effects.¹¹¹

The sodium salt of 2-butenyldimethylsilanol (37) also performs well in this process and like the trifluorosilanes also displays a strong dependence of the site selectivity on the ligand.¹⁰⁸ In general, high γ -site selectivities are obtained with catalysts bearing π -acidic ligands such as dba. Norbornadiene assists in catalyst turnover. The scope with respect to the aromatic bromides is broad and the γ -site selectivity is generally higher than 10:1. Interestingly, the use of pure (*E*)-37 leads to a noticeable improvement in the γ -site selectivity (Eq. 24). The role of π -acidic ligands and double bond geometry are interpreted in terms of a kinetically controlled, γ -selective transmetalation followed by direct reductive elimination to form the branched product (see mechanistic discussion in “Stereospecificity” below).



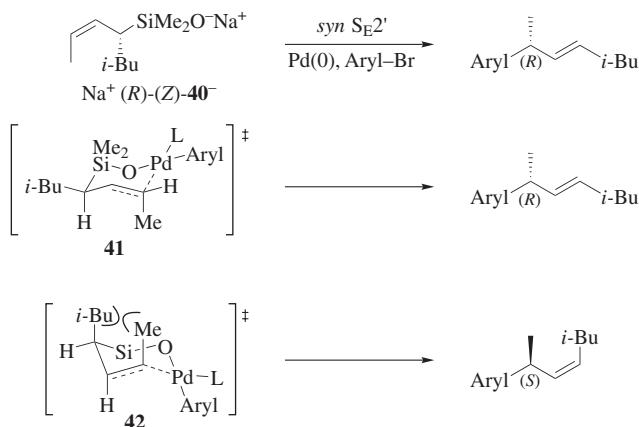
Stereospecificity. In γ -site-selective cross-coupling reactions of unsymmetrically substituted allylic silanes, a new stereogenic center is created. With the aid of enantiomerically enriched and configurationally defined allylic trifluorosilanes and dimethylsilanolates, the stereochemical course of the $S_E 2'$ process^{112,113} has been elucidated. Enantiomerically enriched allylic difluorosilane (*R*)-(Z)-**38**¹¹⁴ reacts with 2-naphthyl triflate with high γ -site selectivity, but divergent stereospecificity depending on the fluoride source and solvent polarity. With TBAF in DMF, the reaction proceeds in an overall *anti* $S_E 2'$ sense (to (*S*)-(E)-**39**) whereas with CsF in THF, an overall *syn* $S_E 2'$ process (to (*R*)-(E)-**39**) is observed (Scheme 8, es = ee (product)/ee (educt) $\times 100$).¹¹⁵ These results are explained by the operation of an open transition structure for the reaction with TASF and a closed one involving a Pd–F–Si interaction for reaction with CsF.

A similar study revealed a strong and consistent stereochemical correlation for the cross-coupling of enantiomerically enriched allylic dimethylsilanolate $\text{Na}^+ (R)$ -(Z)-**40**.¹¹⁶ In the presence of $[\text{allylPdCl}]_2$ and 4,4'-{(trifluoromethyl)dibenzylideneacetone, a wide range of aryl bromides undergo highly γ -site selective cross-coupling with perfect *syn* $S_E 2'$ stereospecificity (Scheme 9). These results are interpreted in terms of an intramolecular transmetalation via a chair-like, transition structure. In structure **41**, the Si–O–Pd linkage controls the delivery of the palladium electrophile to the γ -terminus of the allylic silane. The palladium is tricoordinate and the alkene takes up the fourth coordination site in the square-planar complex. The pseudo-equatorial orientation of the isobutyl group assures high selectivity in the formation of an (*E*) double bond in the product. In addition, the allylic methyl group is positioned orthogonal to the ligand plane



Scheme 8

of palladium to avoid unfavorable steric interactions. An alternative transition state structure (**42**) that also involves an intramolecular delivery of the palladium moiety suffers from severe 1,3-diaxial steric strain between the isobutyl and allylic methyl groups.



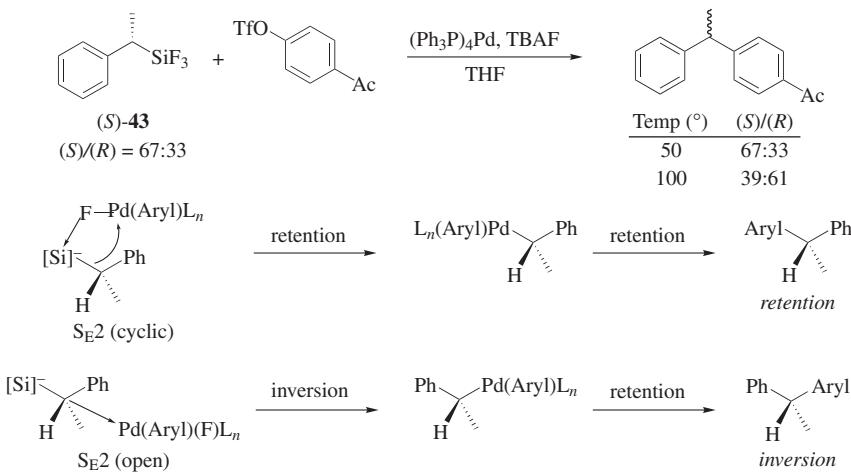
Scheme 9

Benzylsilanes

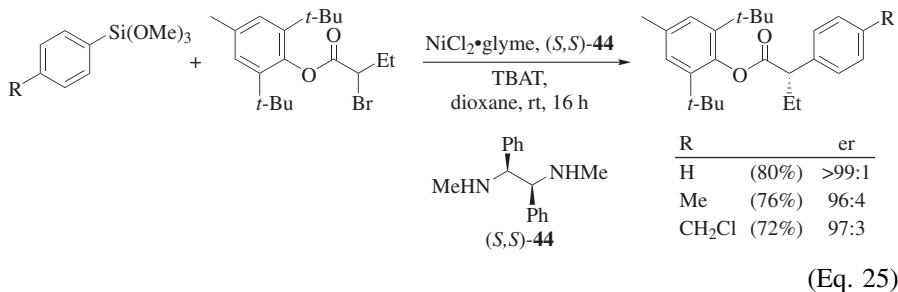
Stereospecificity. The stereochemical course of transmetalation for configurationally defined sp^3 -hybridized organosilanes has been studied by the use of enantiomerically enriched benzyltrifluorosilane (*S*)-**43** (Scheme 10).¹¹⁷ The cross-coupling of (*S*)-**43** with 4-acetylphenyl triflate in the presence of TBAF and $(Ph_3P)_4Pd$ showed an unexpected dependence on temperature and solvent composition. Thus, at low temperature (55°) nearly perfect retention of configuration was observed. As the reaction temperature was increased, the specificity decreased and ultimately changed to inversion with 65% specificity at 100° . These results are interpreted in terms of two competing pathways: a cyclic $SE2$ transition structure involving an Si–F–Pd bridge that leads to retention, and an open $SE2$ pathway that leads to inversion, the latter being favored as temperature increases.

Enantioselectivity with Aryl- and Alkenylsilanes

The foregoing examples involve the stereochemical consequences of reactions at the silicon-containing moiety in a cross-coupling process. However, silanes also participate in an important transformation in which new stereogenic centers are created by cross-coupling with alkyl halides. Specifically, these nickel-catalyzed reactions involve the combination of aryl- and alkenylsiliconates with racemic α -bromo esters in the presence of a chiral ligand, (*S,S*)-**44**, and a fluoride source (TBAT) to provide the α -aryl carboxylic esters in high yields and enantioselectivities (Eq. 25).¹¹⁸ The stereoconvergence suggests the intermediacy of a configurationally labile organonickel intermediate whose configuration is controlled by the chiral ligand.



Scheme 10



SCOPE AND LIMITATIONS

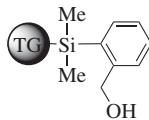
The diversity of silicon-based reagents that undergo successful cross-coupling is enormous and each has its unique advantages and disadvantages. A complete listing of the types of silicon groupings that have been employed in cross-coupling reactions is shown in Figure 3. Thus, this chapter has been organized with such practical considerations in mind. The “Scope and Limitations” section presents the characteristic strengths and weaknesses of each of the main families of organosilyl donors following the hierarchy shown in Figure 3 (which also constitute the section headings). Within each silafunctional group, the description of the coupling reactions will follow the type of transferable group (TG in Scheme 1) in the order aryl, heteroaryl, alkenyl, alkynyl, allyl, etc. On the other hand, the Tables are organized according to the structure of the transferable group in the order indicated in addition to the organic electrophile. We have presented the field in two complementary frameworks, so that one can learn the salient features of each organosilyl group and find a coupling combination of interest. To avoid confusion in the following presentation, the suffix - silanes will be employed to designate the silafunctional family and the suffix - TGs will be employed to designate the organic group transferred from the silyl moiety.

A. Triorganosilanes

1. Trialkylsilanes

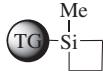


2. Hydroxymethylphenylsilanes

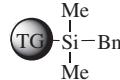
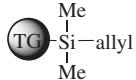


3. Alkylsilanes Containing a Labile Group

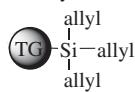
a. Silacyclobutanes



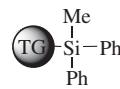
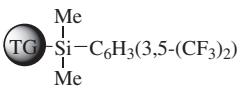
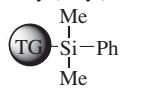
b. Allyl- and Benzylidemethylsilanes



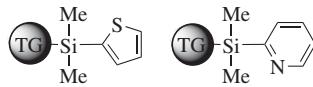
c. Triallylsilanes



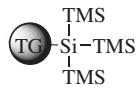
d. Aryl(alkyl)silanes



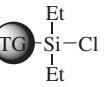
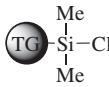
e. Heteroarylsilanes



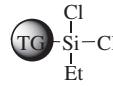
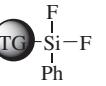
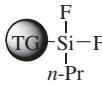
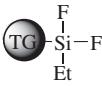
f. Hydridosilanes



B. Monohalosilanes



C. Dihalosilanes



D. Trihalosilanes

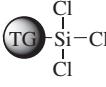
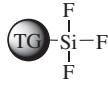
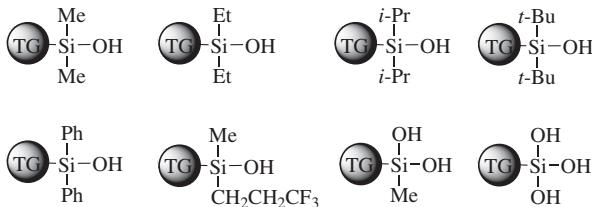
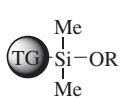


Figure 3. Hierarchy of organosilyl groups used in cross-coupling reactions.

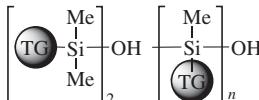
E. Silanols, Silanediols, and Silanetriols



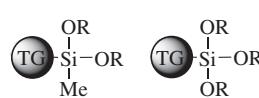
F. Silyl Ethers



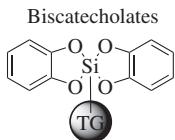
G. Di- and Polysiloxanes



H. Di- and Trialkoxysilanes



I. Siliconates



Biscatecholates

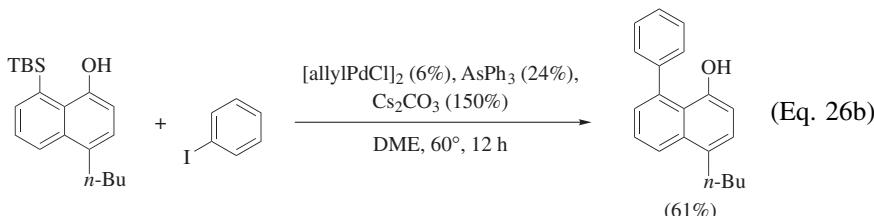
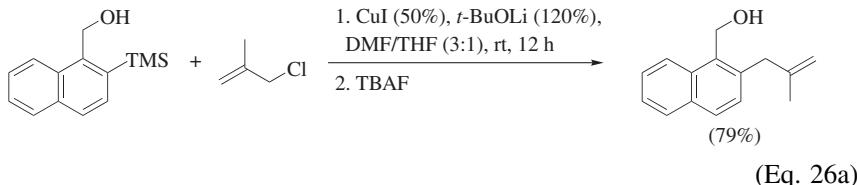
**Figure 3.** (Continued).**Cross-Coupling of Triorganosilanes****Trialkylsilanes**

This category contains silicon moieties bearing only carbon or hydrogen substituents. In some reactions the carbon substituents remain attached to silicon, and in other reactions the substituents are cleaved under the reaction conditions to heterosubstituted silanes.

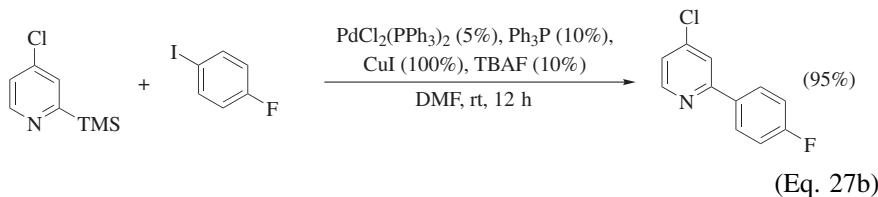
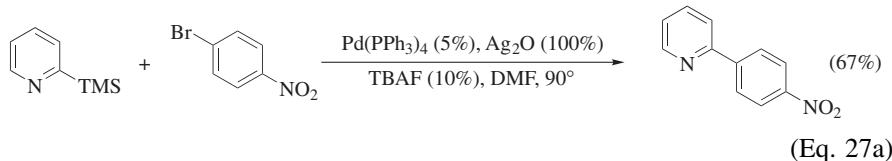
Trimethyl- and *tert*-Butyldimethylsilanes. Despite the fact that these aliphatic organosilane derivatives are the least activated toward formation of the requisite hypercoordinate 10-Si-5 species for rapid transmetalation,^{17,20} the number of examples of their cross-coupling reactions is legion. Three different strategies have been developed to activate the triorganosilyl moieties toward transmetalation depending on the nature of the transferable group (TG). For aryl- and alkenyl-TGs, intramolecular activation by an oxyanionic group is commonly employed, whereas for heteroaryl- and simple alkenyl-TGs, activation by an added reagent, usually a fluoride source, is most common. Alkynylsilanes are generally sufficiently reactive that nucleophilic additives are not needed. However, for all of these families of TGs, a copper(I) salt is usually added either in a catalytic or stoichiometric amount. The use of a copper(I) salt implies that the transmetalation step does not take place readily to palladium(II) sources, but rather requires the intermediacy of an organocupper species.

Aryl- and Heteroaryl-TGs. To activate a trialkylsilyl group toward transmetalation, the oxyanionic group is always located in a proximal position, three carbons removed (Eqs. 26a, 26b). In the first example, copper(I) *tert*-butoxide serves as the base and transmetalating agent; allyl and benzyl halides are common

electrophiles in this process.¹¹⁹ In the second example, a copper(I) salt is not needed, but the temperature is higher for the normal cross-coupling to an aromatic electrophile.¹²⁰ The failure of the corresponding methyl ethers to couple supports the need for an oxyanionic activator.



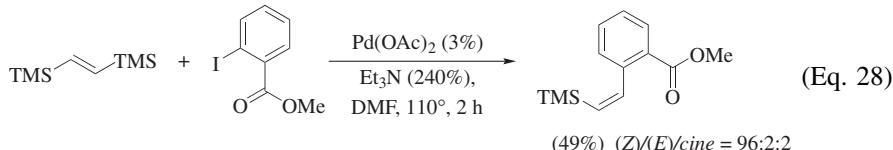
Although the cross-coupling of 2-pyridyl donor groups is considered to be a major challenge,¹²¹ a wide range of 2- and 3-trimethylsilylpyridines undergo cross-coupling with aromatic bromides and iodides under mild conditions (Eqs. 27a, 27b). Two sets of conditions are available: (1) the use of silver oxide and TBAF as the activator, which requires heating at 90°,¹²² or, (2) the use of copper iodide and TBAF, which promotes reactions at room temperature.¹²³



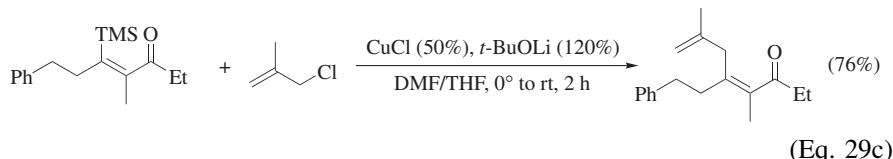
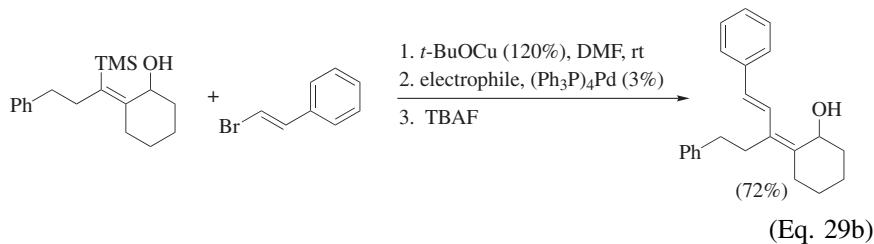
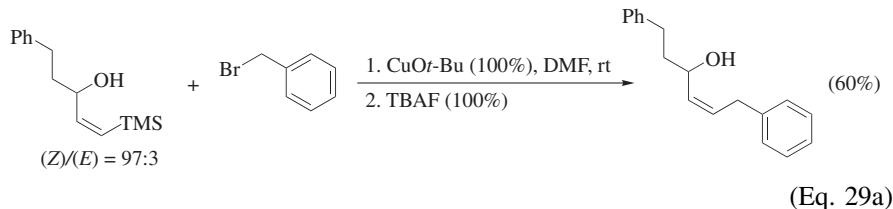
Alkenyl-TGs. Alkenyltrimethylsilanes can engage in cross-coupling using both external (fluoride) and internal (oxyanion) activation. Donation of a simple vinyl-, 1,3-butadienyl-, or (*E*)-styryl-TG can be accomplished under fairly mild conditions with TASF as the activator. Both aryl and alkenyl iodides are the typical electrophiles, and the couplings are stereospecific.^{23,89,124} With aryl diazonium salts as the electrophiles, a significant amount of the *cine* rearrangement product is formed (c.f. Scheme 7).⁹¹

(*E*)-1,2-Bis(trimethylsilyl)ethene can undergo single substitution to afford styrylsilanes without the need for anionic activators, albeit at 110° in DMF

(Eq. 28).¹⁰¹ Remarkably, the products are predominantly of the (*Z*)-styryl configuration arising from a *syn* carbopalladation and *syn* silyl depalladation. Additionally, (*E,E*)-1,4-bis(trimethylsilyl)butadiene and (*E,E,E*)-1,6-bis(trimethylsilyl)hexatriene can undergo monosubstitution to provide polyenes and styrenes with iodides and diazonium salts.^{90,91,124,125} However, these reactions involve an initial electrophilic substitution of the TMS group with BCl_3 . Thus, the cross-coupling process does not rigorously involve the TMS group and will not be discussed further.

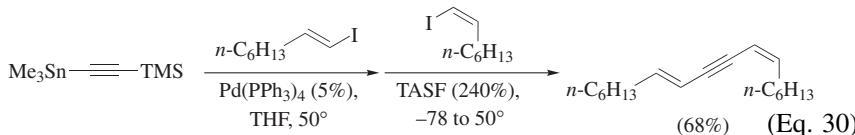


Oxyanion-assisted cross-coupling of alkenyl-TGs universally employs a *cis* disposition of the TMS group with an alkoxide three atoms removed. In all cases a stoichiometric amount of preformed copper(I) *tert*-butoxide is employed to generate the copper alkoxide that effects the transmetalation. For allylic and benzylic electrophiles, no palladium is needed for the cross-coupling, whereas $(\text{Ph}_3\text{P})_4\text{Pd}$ is added for alkenyl and aryl electrophiles (Eqs. 29a–29c).^{126–128} This strategy was put to good use to generate a trisubstituted alkene by TBS group transfer and methylation in a synthesis of dolabelide D.¹²⁹ An interesting modification of this transformation employs a copper enolate derived from 3-trimethylsilyl enones.¹³⁰

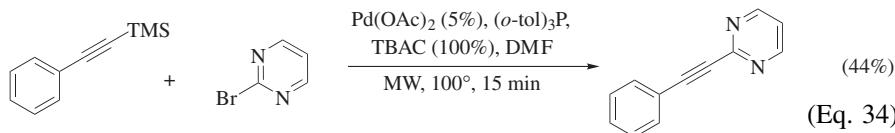
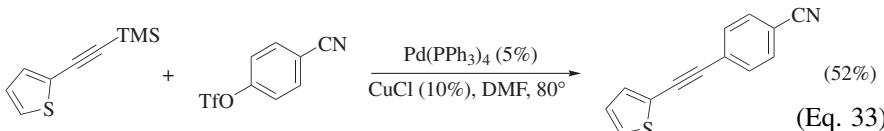
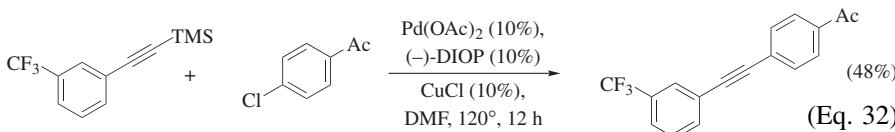
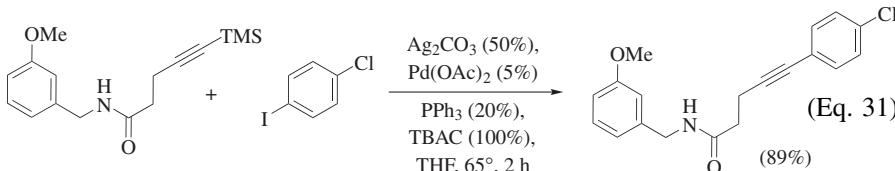


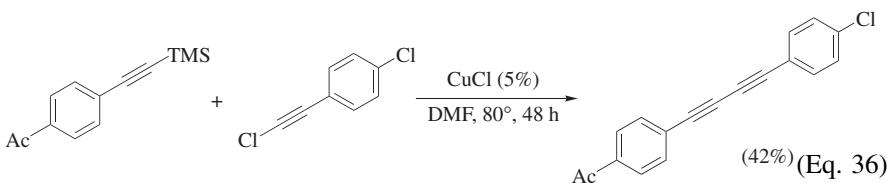
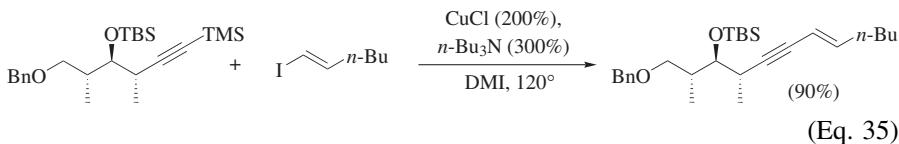
Alkynyl-TGs. By a wide margin, the cross-coupling of alkynyltrimethylsilanes represents the largest application of simple trialkylsilanes as organometallic

donors. Trimethylsilyl ethyne is used to prepare unsymmetrical tolanes¹³¹ whereas bis(trimethylsilyl)ethyne couples to form symmetrical tolanes.^{132,133} Moreover, the differential reactivity of tin and silicon has been used to good advantage for the construction of unsymmetrical enynes and dienynes with trimethylsilyl ethynyltrimethylstannane (Eq. 30).¹³⁴

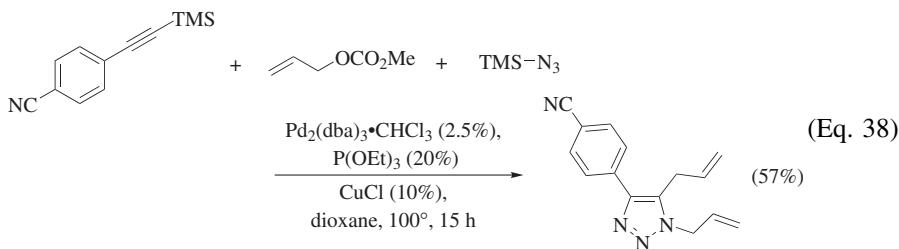
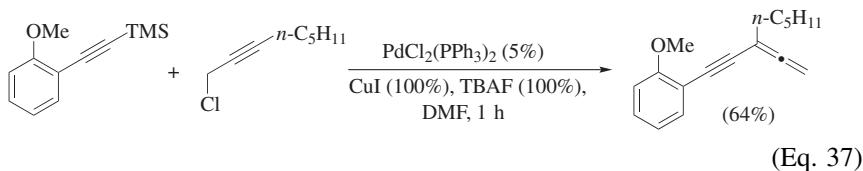


The “silyl Sonogashira” coupling process of trimethylsilyl alkynes has been extensively implemented with a wide variety of electrophiles. The large majority of these reactions employ a copper(I) or silver(I) additive but only a few require a fluoride source. Unlike the original Sonogashira reaction,^{135,136} the silyl variant does not require a base to effect the formation of the alkynyl-copper species. If a copper-free process is desired, then a fluoride source is added. The number of different recipes for the silyl Sonogashira reaction matches the number of different electrophiles employed. Thus, aryl iodides,^{133,137–139} bromides,¹⁴⁰ chlorides,¹⁴¹ and triflates;^{131,133} alkynyl iodides,¹³⁹ bromides²³ and triflates;^{131,142,143} and alkynyl chlorides^{133,144} all use different conditions (Eqs. 31–36).



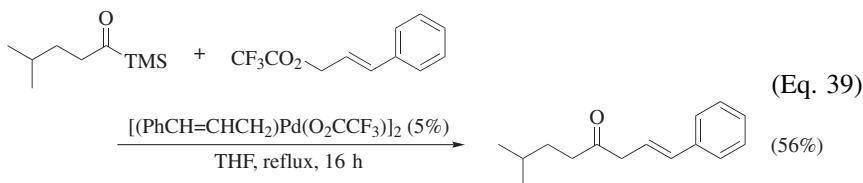


Propargyl chlorides undergo clean S_N2' cross-coupling to afford allenynes (Eq. 37),¹⁴⁵ and allyl carbonates are used in a three-component coupling process to produce diallylated triazoles (Eq. 38).¹⁴⁶ Mechanistically, the cross-coupling may take place on a copper triazole rather than a copper acetylide, but no definitive studies are on record.



The silyl Sonogashira process is also employed for the synthesis of ethynylene-arylene-ethynylene-thiophene polymers by the use of bis(trimethylsilyl)alkynyl arenes and bisaryl triflates.¹⁴⁷

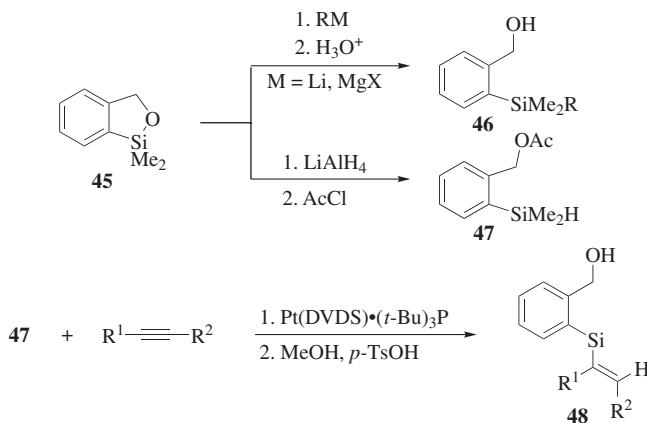
Acyl-TGs. One of the most unique examples of a silicon-based cross-coupling is the use of acyl silanes in combination with allylic and benzylic trifluoroacetates (Eq. 39).¹⁴⁸ A palladium(II) cinnamyl trifluoroacetate precatalyst shows the highest activity; phosphines inhibit the reaction and fluoride sources lower the yield.



2-Hydroxymethylphenyldimethylsilanes

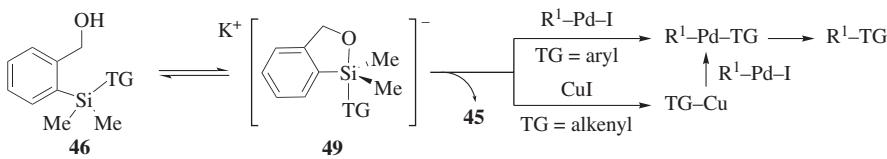
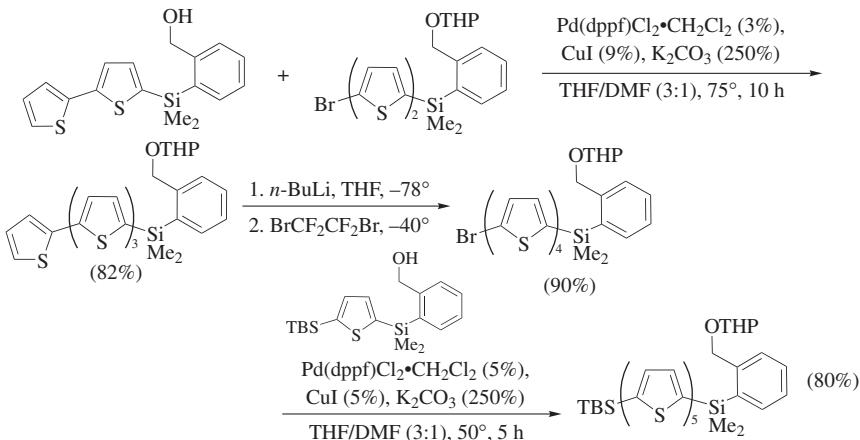
The recognition that intramolecular activation is effective in promoting cross-coupling of simple trialkylsilanes together with a continuing interest in stable and readily available coupling precursors led to the development of a “universal donor” derived from 2-hydroxymethylphenyldimethylsilanes.^{149–152} The critical carrier of the various transferable groups is siloxane **45**, which is prepared on a large scale from 2-bromobenzyl alcohol. Introduction of aryl, heteroaryl, and some alkenyl TGs (**46**) is accomplished by reaction of **45** with the corresponding organolithium or -magnesium reagents (Scheme 11). Alternatively, introduction of stereodefined alkenyl TGs (**48**) is accomplished by hydrosilylation of alkynes with hydridosilane **47**, which is prepared by reduction of **45** followed by acylation of the liberated alcohol.

The intramolecular activation by the pendant hydroxymethyl group requires a base such as K_2CO_3 , usually in DMSO or blends of DMSO with THF or water. The putative intermediate **49** is believed to exist in a unique trigonal bipyramidal geometry that places the TG in an apical position. In this way, the TG group is transferred preferentially over an equatorial phenyl group. In the cross-coupling of aryl and heteroarylsilanes, copper(I) iodide is added, which might intervene to form an organocopper species prior to transmetalation to the organopalladium intermediate (Scheme 12). The siloxane **45** is a by-product of the cross-coupling and can be recovered in good yield and reused if desired.

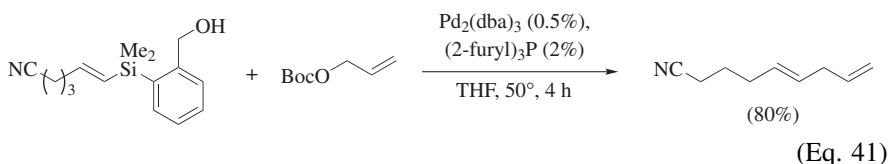
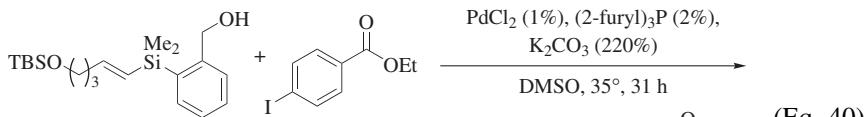


Scheme 11

Aryl- and Heteroaryl-TGs. Aryl groups bearing methyl, fluoro, or diphenylamino substituents undergo cross-coupling with aromatic bromides and iodides as well as with heteroaromatic bromides. Copper(I) iodide is used as a co-catalyst along with $PdCl_2$ or $[allylPdCl]_2$. An iterative cross-coupling procedure has been developed for the synthesis of oligoarenes and oligothiophenes that employs a THP-protected activator that is resistant to the basic cross-coupling conditions and that can be revealed by mild hydrolysis (Scheme 13).¹⁴⁹

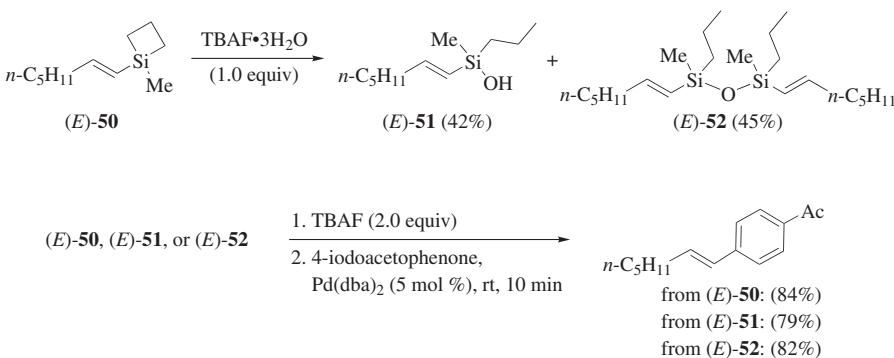
**Scheme 12****Scheme 13**

Alkenyl-TGs. The vast majority of examples in this family employ alkenyl TGs ranging from simple vinyl groups to *(E)*-alkenyl groups bearing chloro, hydroxy, silyloxy, acetoxy, cyano, carbomethoxy, or phthalimido functional groups.^{150,151} Aryl and heteroaryl iodides are the usual coupling partners, and the reactions are stereospecific. The compatibility of the TBS protecting group illustrates the advantage compared with fluoride activation (Eq. 40). Allylic carbonates participate in the cross-coupling to produce 1,4-dienes without the need for a base activator because the *tert*-butoxide generated in the formation of the π -allylpalladium intermediate serves that role (Eq. 41).¹⁵²



Alkylsilanes Containing One or More Labile Groups

Silacyclobutanes. The original motivation for investigating this somewhat esoteric family of silicon derivatives is founded on the concept of “strain release Lewis acidity”^{153–156} as a mechanism for facilitating the ability of tetraorganosilanes to achieve the requisite pentacoordinate state that is believed to be required for rapid transmetalation. Although alkenylsilacyclobutanes undergo highly efficient cross-coupling under fluoride activation, subsequent mechanistic studies revealed that the silacyclobutane ring is spontaneously cleaved on treatment with TBAF•3H₂O to a propylmethylsilanol and its corresponding disiloxanes that are the actual coupling partners. All three of these silane derivatives ((E)-**50**, (E)-**51**, and (E)-**52**) afford the cross-coupling product with equal competency (Scheme 14).⁷⁵ This discovery stimulated the investigation of organosilans and silanlates, which are now among the most versatile silicon-based coupling agents available.



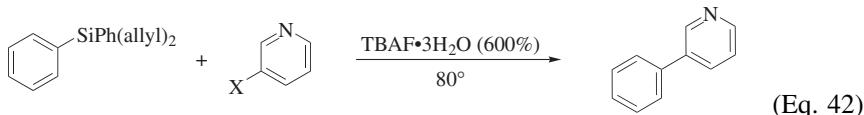
Scheme 14

Alkenyl-TGs. Simple vinyl- and 2-propenylsilacyclobutanes undergo smooth cross-coupling with a variety of aryl iodides under much milder conditions than their trimethylsilyl counterparts. No ligands are necessary in conjunction with Pd(dba)₂ and 2–3 equiv of TBAF are used to effect complete conversion in minutes at room temperature.⁴⁰ Both (E)- and (Z)-**50** bearing a pentyl substituent cross-couple readily with aryl and alkenyl iodides in very high stereospecificity and with only trace amounts of the *cine* rearrangement product. Aryl(methyl)silacyclobutanes are not sufficiently activated to undergo cross-coupling, but the arylchlorosilacyclobutane derivatives are; they will be described with other halosilanes.

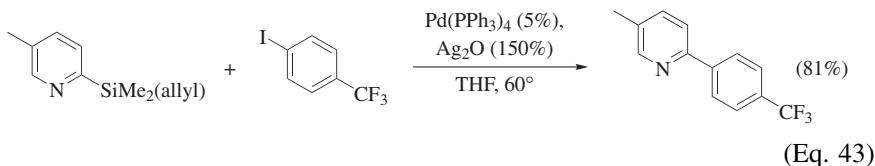
Allyl- and Benzylsilanes. These silane derivatives also serve as silanol surrogates under activation by TBAF (although they were not recognized as such at the time of their development).

Aryl- and Heteroaryl-TGs. To enable the transfer of an aryl group, either two allyl groups⁵¹ or three aryl groups⁴⁷ are needed. Only phenyl groups have served

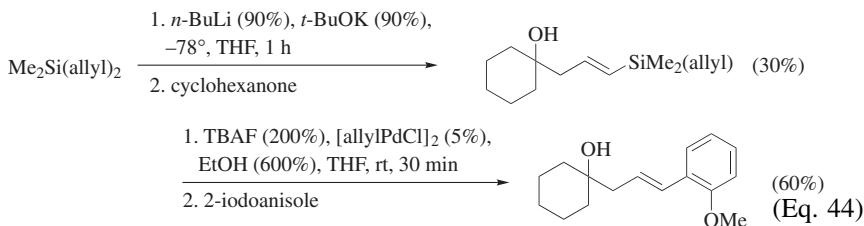
as the transferable group thus far with aromatic bromides and chlorides (Eq. 42). A 2-pyridyl group requires only a single allyl group to transfer under activation by silver(I) oxide to aryl iodides (Eq. 43).⁵¹



X	Pd Source	Ligand	Solvent	Time (h)	Yield (%)
Cl	[allylPdCl] ₂ (2.5%)	XPhos (10%)	THF/H ₂ O (25:1)	7	(95%)
Br	PdCl ₂ (5%)	PCy ₃ (10%)	DMSO/H ₂ O (15:1)	12	(96%)

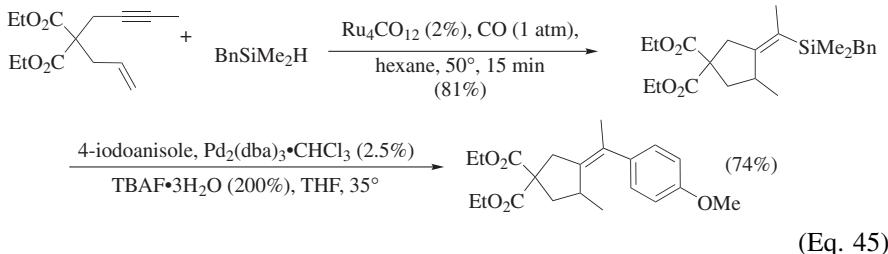


Alkenyl-TGs. Both allyl (or methallyl) and benzylsilanes serve as effective surrogates for silanols for the transfer of alkenyl groups. All of the allylsilanes are prepared by the addition of lithiated diallyl- or dimethallylsilanes to aldehydes or ketones. The resulting alkenylallylsilanes undergo facile cross-coupling with aryl iodides in the presence of TBAF (Eq. 44).¹⁵⁷

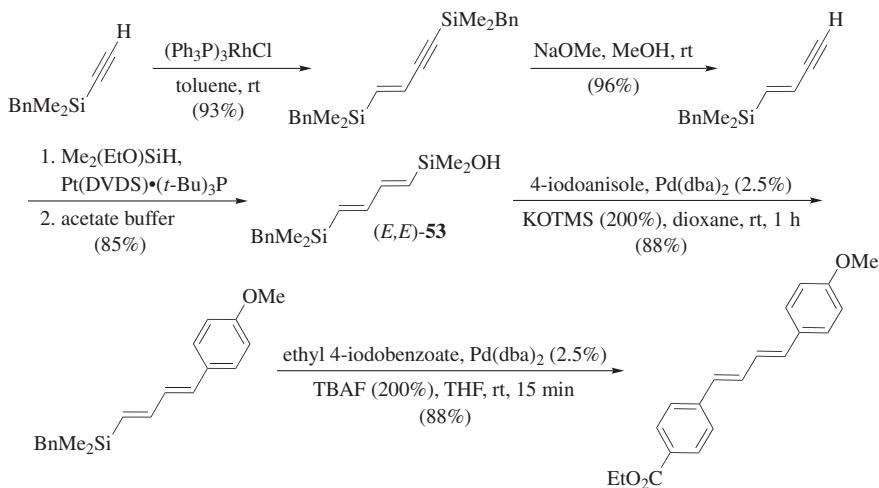


Benzylsilanes are much more versatile and have found application in sequential processes¹⁵⁸ that involve the introduction of the benzylsilane moiety by a number of different reactions, followed by a fluoride-promoted cross-coupling with aryl or alkenyl iodides. Transformations that have been employed to introduce the benzylsilane unit in a stereoselective fashion include hydrosilylation,^{43,159} alkynylsilane dimerization,⁴⁴ silylcarbocyclization,⁴⁵ and silyl alkyne Alder-ene reaction.⁴³ The utility of benzylsilanes derives from their chemical stability and robustness as silanol surrogates for the transfer of stereodefined alkenyl groups. For example, benzyldimethylsilane effects a silylcarbocyclization under rhodium catalysis to create *exo* alkylidene silanes with perfect control of double bond

geometry. Fluoride-promoted cross-coupling proceeds in good yield with preservation of the double bond configuration to produce a tetrasubstituted *exo* alkylidene unit of defined geometry (Eq. 45).⁴⁵

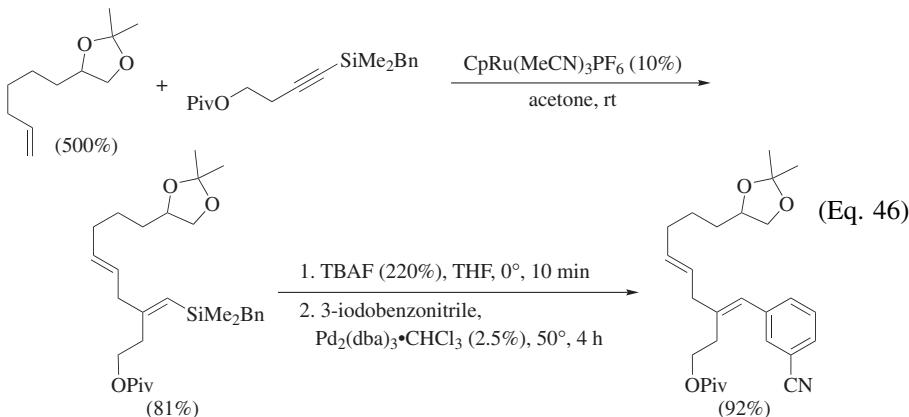


The chemical stability and resistance of the benzyldimethylsilane unit to activation by mild Brønsted bases allows for the implementation of a bifunctional reagent that contains two different silyl groups capable of independent activation for cross-coupling. 1,3-Butadienyl-1,4-(bis)silane (*E,E*)-**53** (prepared by a three-step sequence) combines the potential for selective cross-coupling of the dimethylsilanol unit under activation by KOTMS, followed by cross-coupling of the benzyldimethylsilyl moiety under fluoride activation (Scheme 15).⁴⁴

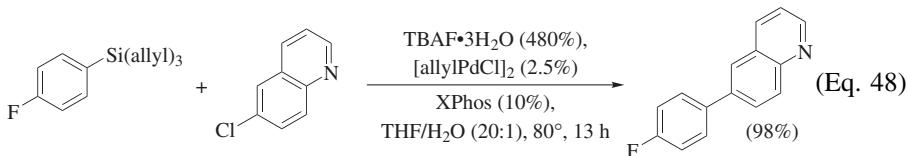
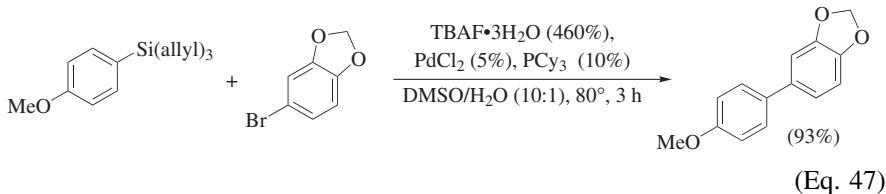


Scheme 15

Benzyldimethylsilanes are also easily incorporated into geometrically defined alkenes via an Alder-ene reaction with silylalkynes. Both the Alder-ene process and the subsequent fluoride-promoted cross-coupling can accommodate ester, ketone, carbonate, acetal, and cyano functional groups (Eq. 46).⁴³

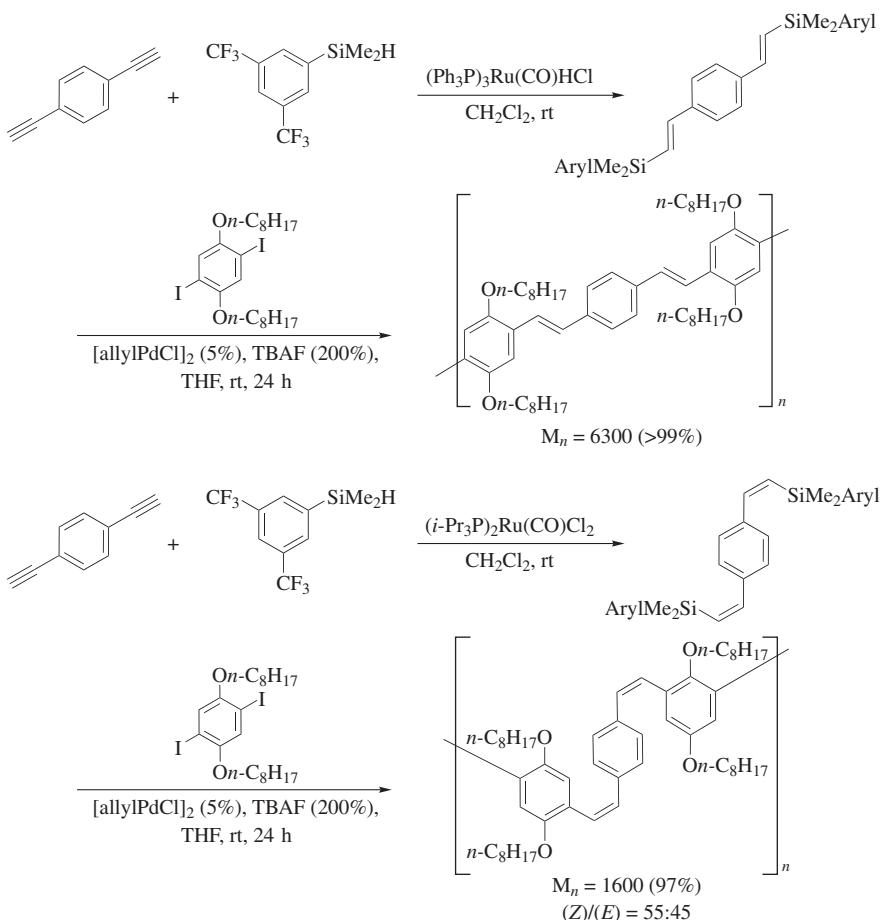


Triallylsilanes. As was noted above, a stable precursor for efficient cross-coupling of aromatic transferable groups requires at least two labile groups on the silicon moiety. However, diallylsilanes present an ambiguity as to which of the remaining two groups will be transferred. Thus, the development of aryltriallylsilanes represents the logical extension of this concept.^{46,47,160} Aryltriallylsilanes are prepared by the exhaustive allylation of aryltrichlorosilanes (prepared from the corresponding arylmagnesium halide and silicon tetrachloride) with allylmagnesium bromide. These silanes are resistant to the action of aqueous potassium hydroxide and potassium carbonate and undergo slow decomposition in aqueous HCl. However, they are also readily activated to cross-coupling in the presence of 4–5 equiv of TBAF in aqueous DMSO or aqueous THF. The scope of coupling partner is particularly broad in that aromatic iodides, bromides, and chlorides and heteroaromatic bromides and chlorides participate with assistance of the appropriate ligand, namely Cy₃P for bromides and XPhos¹⁶¹ for chlorides (Eqs. 47, 48).



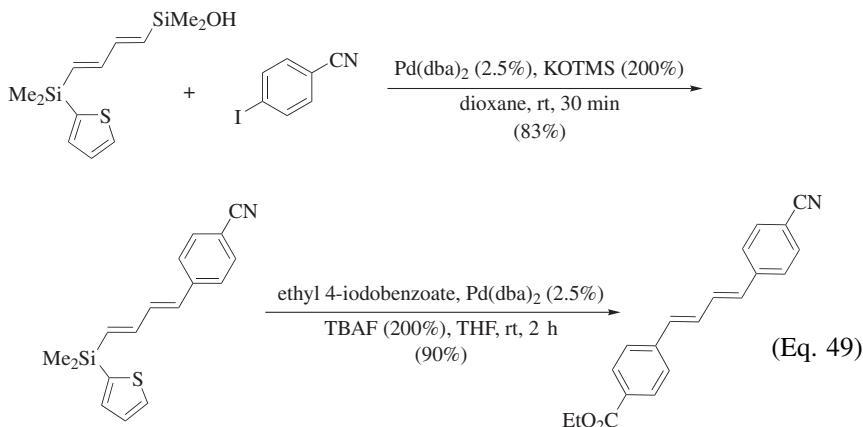
Arylalkylsilanes. *Alkenyl-TGs.* Because of the ambiguity of which substituent will be transferred, arylalkylsilanes have been used exclusively to activate alkenyl group transfers under both fluoride and alkoxide activation. The simple

phenyldimethylsilyl group can facilitate the coupling of alkenes with aryl and heteroaryl iodides in the presence of TBAF.¹⁶² Alternatively, the phenyl group can be cleaved in a separate step (with KOTMS and 18-crown-6) to the corresponding dimethylsilanol that undergoes coupling.⁴² An early report of a *cine* substitution under these conditions has been corrected.⁴¹ Under appropriate conditions, a diphenylmethylsilyl group can selectively transfer a 1-fluorovinyl moiety (instead of one of the phenyl groups) to aryl iodides in good yield.^{163,164} Finally, the synthesis of stereodefined (*E*)- and (*Z*)-(polyphenylenevinylene)s can be achieved by the *syn* or *anti* selective hydrosilylation of 1,4-diethynylbenzene with 3,5-bis(trifluoromethyl)phenyldimethylsilane using different ruthenium catalysts. The fluoride-promoted cross-coupling of the (*E*)- and (*Z*)-styrylsilanes affords isomeric polymers (Scheme 16).^{165–167}

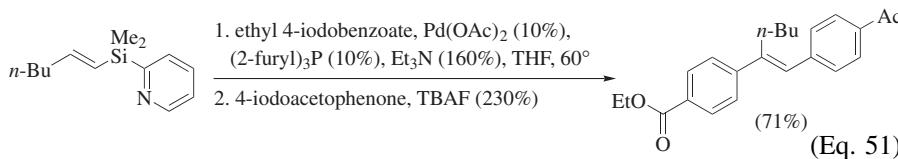
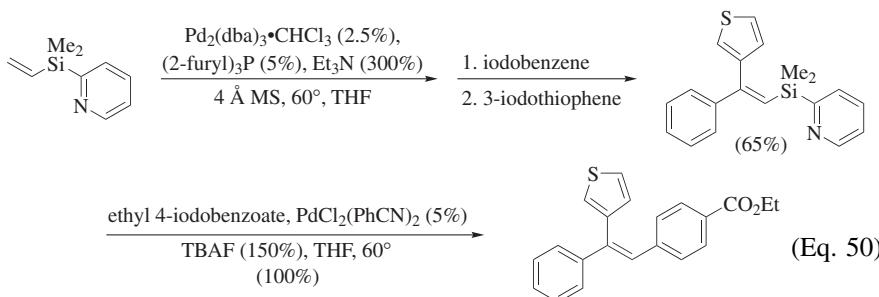
**Scheme 16**

Heteroarylsilanes. The primary motivation for the development of this class of silafunctional groups is to provide easily handled silanes bearing a range of labile groups that can be removed under different conditions. Two heteroaryl groups, 2-pyridyl and 2-thienyl, have been extensively investigated in the context of alkenyl group transfers. A single example of a bis(2-furyl)silane has been reported for the transfer of an aryl group.¹⁶⁸

Alkenyl-TGs. 2-Thienyldimethylsilyl groups are introduced onto alkenes by hydrosilylation with 2-thienyldimethylsilane. Both *syn* and *anti* hydrosilylation is achievable with judicious choice of catalyst.⁴⁹ The cross-coupling conditions are mild and no ligands are needed as the only coupling partners are aromatic iodides. 2-Thienyldimethylsilanes have found application in the synthesis of poly-4-phenylenevinylenes of different double bond configurations.¹⁶⁵ In addition, this activating group has served as a more labile silanol surrogate for two-directional functionalization of butadienes in cases where the benzylidemethylsilane leads to undesirable benzyl group migration instead of cross-coupling (Eq. 49).⁴⁴



The 2-pyridyldimethylsilyl group has been introduced and extensively developed for the modular construction of polysubstituted alkenes.⁵² The 2-pyridyl moiety provides two important features: (1) a powerful directing group for the selective introduction of carbon substituents onto alkynes or alkenes attached to the silicon atom, and (2) a labile function that is readily converted into a silanol for efficient cross-coupling. To date, only alkenyl TGs have been employed with this donor group. The directing ability of the 2-pyridyl group is illustrated in the elaboration of geometrically defined, polysubstituted alkenylsilanes by the sequential application of carbomagnesation or the Mizoroki-Heck reaction. This sequence can be carried out as individual steps (Eq. 50) or in a one-pot process (Eq. 51).^{169,170}



Through the agency of various combinations of directed Mizoroki-Heck coupling, protodesilylation, and cross-coupling, a wide variety of polysubstituted alkenes can be constructed in geometrically defined form from various aryl halides (Figure 4).

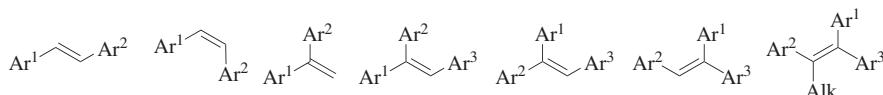
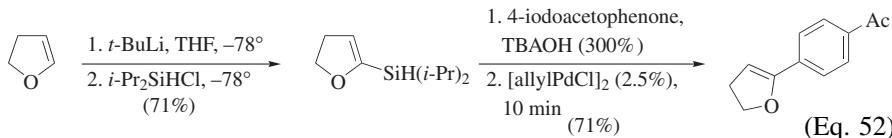


Figure 4. Permutations of products from sequential Mizoroki-Heck/cross-coupling.

Hydridosilanes. Hydridosilanes often serve as intermediates in the preparation of many chlorosilanes and silanols through a mild oxidation process. As such, their ability to serve as silanol surrogates directly in cross-coupling reactions was investigated in cases where the preparation of the silanol was problematic.¹⁷¹ Silylation of 1-lithio vinyl ethers with diisopropylchlorosilane affords the stable, isolable hydridosilanes, which are converted *in situ* by treatment with TBAF or TBAOH (tetrabutylammonium hydroxide) into the corresponding silanol. The latter then undergoes efficient cross-coupling with aromatic iodides (Eq. 52).



Cross-Coupling of Halosilanes

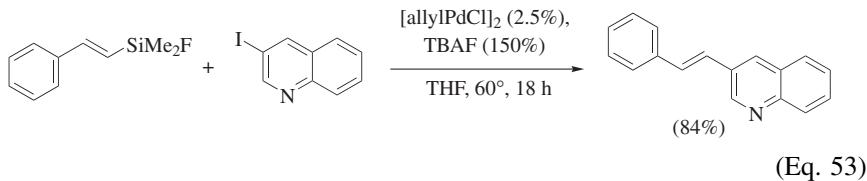
Halosilanes represent a large and highly diverse class of activating groups for silicon-based cross-coupling reactions. Early in the development of this process,

alkyl groups on triorganosilanes were systematically replaced with halogen atoms in an attempt to facilitate the formation of the hypercoordinate silicate intermediate (with added fluoride) believed to be necessary for efficient transmetalation.²⁷ Both chloro- and fluorosilanes have been studied at all levels of substitution. Because the behavior of the coupling process depends primarily on the number rather than the identity of the halogen atoms, the organization will follow increasing heteroatom substitution.

Monohalosilanes

Monofluorosilanes. This class of activating substituents was among the first silafunctional groups to be investigated for their potential in cross-coupling reactions.^{25,88,172} Fluorosilanes are readily prepared by treatment of chlorosilanes with copper(II) fluoride¹⁷³ or by protodesilylation of allylic silanes with HF.¹⁷⁴

Alkenyl-TGs. Monofluorosilanes are primarily used to activate the transfer of alkenyl groups. The reactions show good generality and excellent stereospecificity with respect to the substitution pattern on the transferable group. Aryl, heteroaryl, and alkenyl iodides serve as the electrophiles, and good stereospecificity is also seen in the electrophilic partner. All reported cross-couplings employ either TBAF or TASF as the fluoride activator (Eq. 53). A systematic study of the electronic effects of the electrophile on the constitutional site selectivity with (1-phenylethenyl)dimethylfluorosilane (**29**) was discussed above (Eq. 21).⁸⁹

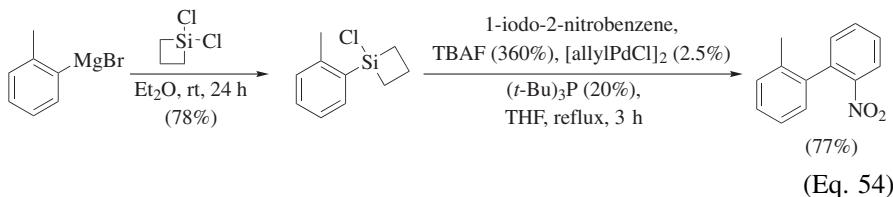


A few examples of cross-coupling of alkenyl- and aryl monofluorosilanes with allylic carbonates and epoxides have been reported,^{175,176} but these electrophiles cross-couple more effectively with difluorosilanes, which are presented in the next section.

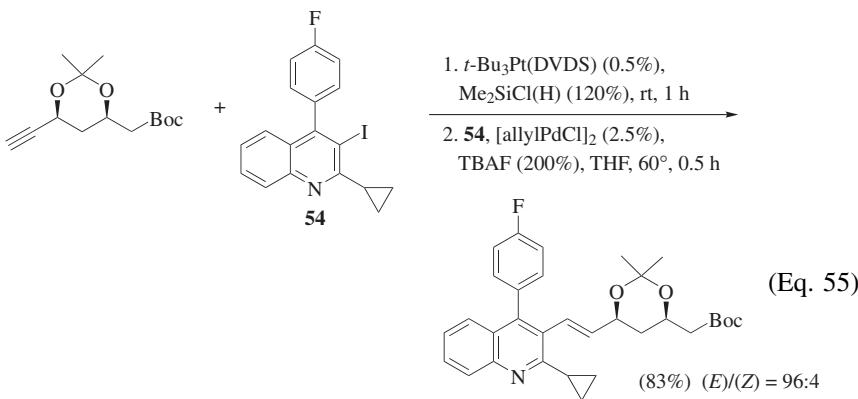
Monochlorosilanes. This class of activating group has found only limited application in cross-coupling compared with the corresponding monofluorosilanes, probably because of the greater electrophilicity and hydrolytic stability of the latter.

Aryl-TGs. The efficient transfer of aromatic groups generally requires more than one heteroatom substituent on silicon. This requirement is met by the use of chlorosilacyclobutanes, which are cleaved under the action of TBAF and provide biaryls with a range of aromatic iodides.³⁹ To suppress homocoupling, $(t\text{-Bu})_3\text{P}$ is

needed in significant amounts. The precursors are prepared by addition of the aryl-magnesium halide to commercially available dichlorosilacyclobutane (Eq. 54).



Alkenyl-TGs. Only two reports of cross-coupling of chlorodimethylsilanes as activators of alkenyl groups are on record. In one report, simple vinyl- and (*E*)-styryl reagents are coupled with iodouracil derivatives.⁸⁸ In the second, the chlorosilane is generated *in situ* by hydrosilylation of an alkyne and then is coupled with 3-idoquinoline **54** to prepare an HMG-CoA reductase inhibitor (Eq. 55).¹⁷⁷

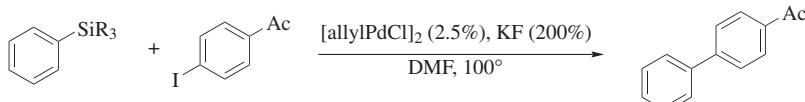


A copper-catalyzed homocoupling of monochloro- and monofluorosilanes to transfer aryl, heteroaryl, alkenyl, and alkynyl groups is on record.¹⁷⁸

Dihalosilanes

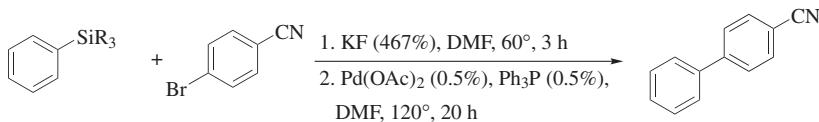
A systematic study of the structure of silafunctional donor groups clearly established the superiority of dihalosilanes to activate aromatic donor groups toward cross-coupling with aromatic halides.⁷³ By variation in the number of halogen substituents as well as the size of the spectator group, it was demonstrated that two fluorine atoms (Eq. 56, entries 3–5) and two chlorine atoms (Eq. 57, entries 2–4) provide the highest yields of biaryl products under a standard set of reaction conditions. In addition, the larger spectator group affords higher yields because the transfer of the alkyl is suppressed, or in the case of Ph₂SiCl₂ because

of statistics. However, this reagent is impractical because only one phenyl group is transferred.



Entry	SiR_3	Time (h)	
1	SiMe_3	24	(12%)
2	SiMe_2F	24	(15%)
3	SiMeF_2	12	(68%)
4	SiEtF_2	12	(71%)
5	$\text{Si}(n\text{-Pr})\text{F}_2$	12	(87%)
6	SiF_3	10	(0%)

(Eq. 56)

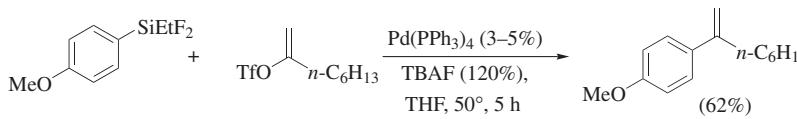


Entry	SiR_3	
1	SiMe_2Cl	(37%)
2	SiMeCl_2	(51%)
3	SiEtCl_2	(70%)
4	SiPhCl_2	(89%)
5	SiCl_3	(0%)

(Eq. 57)

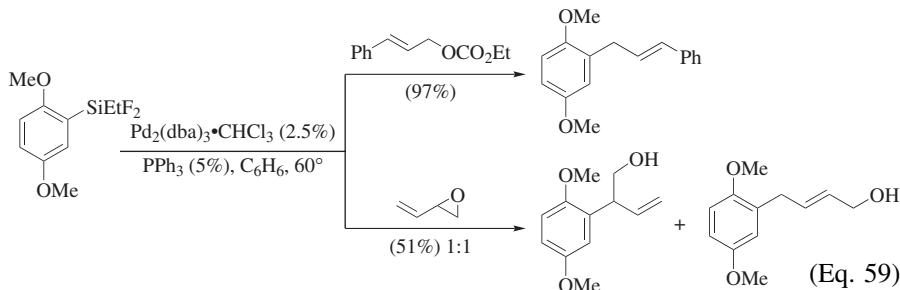
Difluorosilanes. Difluorosilanes are prepared from the corresponding dichlorosilanes by treatment with either antimony(III) fluoride or copper(II) fluoride.¹⁷⁹ The majority of the reported examples employ either ethyl- or *n*-propyldifluorosilanes. These reagents are stable in air.

Aryl- and Heteroaryl-TGs. The cross-coupling of aryldifluorosilanes with aryl iodides takes place under ligandless conditions using $[\text{allylPdCl}]_2$ as the catalyst and KF as the activator in either DMF or THF at elevated temperatures. The scope of aromatic donor groups is not large (only Me, OMe, and CF_3 substituents), but the scope of the functional groups on the electrophile is good (alcohol, ester, ketone, and aldehyde).^{73,172,179,180} Aryl and alkenyl triflates also serve as electrophiles when $(\text{Ph}_3\text{P})_4\text{Pd}$ and TBAF are used (Eq. 58).¹⁸¹

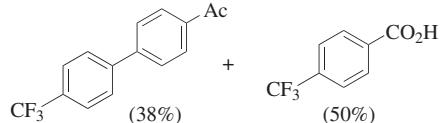
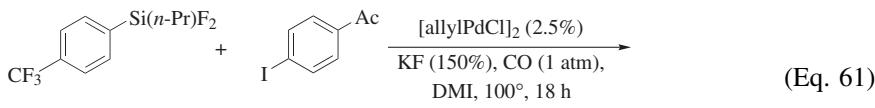
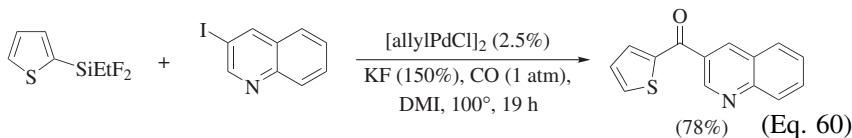


(Eq. 58)

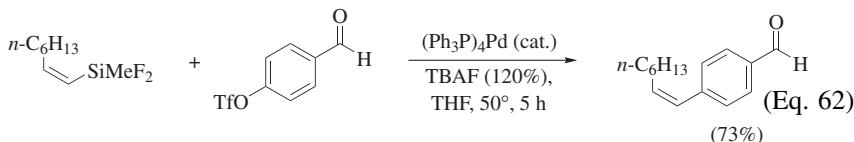
Allylic epoxides and carbonates also serve as effective electrophiles; however, the site selectivity is good only for prenyl or cinnamyl substrates (Eq. 59).¹⁷⁵



A carbonylative cross-coupling has been developed for aryl- and heteroaryldifluorosilanes (Eq. 60).¹⁷⁹ The reaction requires only 1 atm of carbon monoxide, but if the aryl donor group is not reactive (i.e. electron deficient), then byproducts such as methyl ketones (from methyl group transfer) and carboxylic acids (from interception of the acylpalladium species by fluoride followed by hydrolysis) are observed (Eq. 61).¹⁸²



Alkenyl-TGs. Most of the characteristics of the cross-coupling of aryl- and heteroaryldifluorosilanes also apply to the cross-coupling of alkenyldifluorosilanes. Reactions with aryl iodides,^{25,88} aryl and alkenyl triflates,¹⁸¹ and allylic epoxides and carbonates^{175,176} follow the same trends and in addition show high stereospecificity (Eq. 62).¹⁸¹ However, the carbonylation reactions fail, giving mixtures of direct coupling and carboxylic acids along with the desired ketones.¹⁷⁹ This problem is ameliorated by the use of alkenyltrifluorosilanes, as described in a following section.

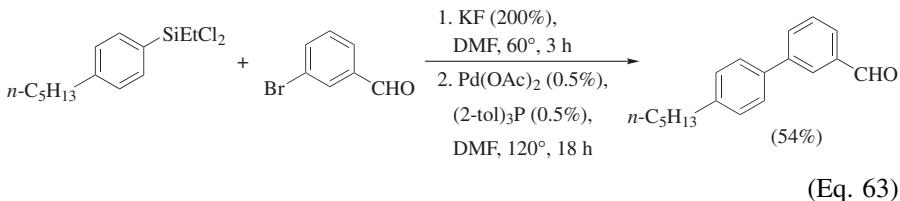


Allyl-TGs. The only examples of cross-coupling of allylic difluorosilanes have been studied in the context of asymmetric induction with chiral substrates. Both *syn* and *anti* S_E2' pathways have been identified in the cross-coupling with 1-naphthyl triflate depending on the fluoride source (Scheme 8).¹¹⁵

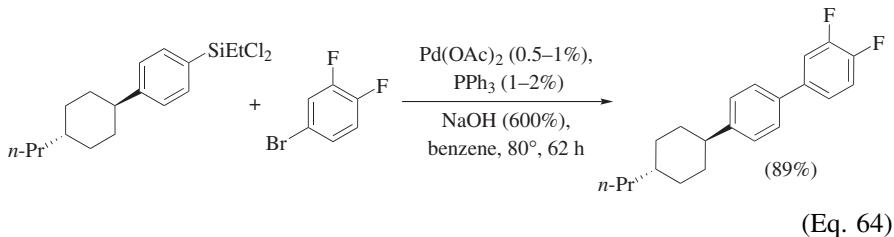
Oxidative homocoupling of aryl-, heteroaryl-, and alkenyldifluorosilanes with copper(I) chloride in DMF has been described.¹⁸³

Dichlorosilanes. Insofar as dichlorosilanes are the precursors for the preparation of difluorosilanes, the ability to use the former reagents directly would have obvious benefits. However, the conditions developed for the cross-coupling of difluorosilanes do not lead to successful cross-coupling of dichlorosilanes.¹⁸⁴ Thus, a number of new conditions have been introduced.

Aryl and Heteroaryl-TGs. Three important modifications to the reaction conditions have allowed for the cross-coupling of aryl dichlorosilanes with aromatic iodides, bromides, and chlorides. The most straightforward modification involves pretreatment of the dichlorosilane with KF in DMF at 60° for 3 h followed by addition of the palladium catalyst, a ligand if necessary, and the aryl bromide, and then heating the mixture to 120° (Eq. 63).⁷³ Although only a few different substituents have been introduced on the donor group, the functional group variation and compatibility on the electrophile is much wider (aldehyde, ketone, ester, nitrile, and nitro).

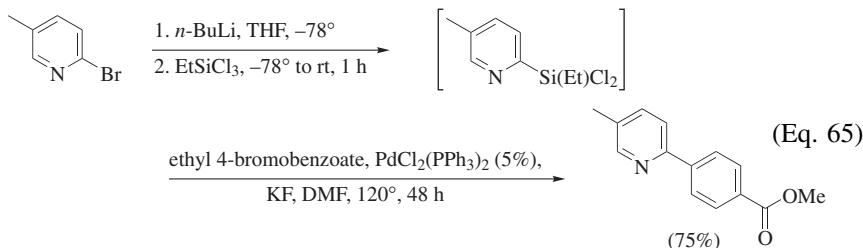


A second set of conditions applicable to both aromatic bromides and iodides involves the use of sodium hydroxide as the activator with either Pd(OAc)₂¹⁸⁵ or Pd/C¹⁸⁶ as the catalyst (Eq. 64).

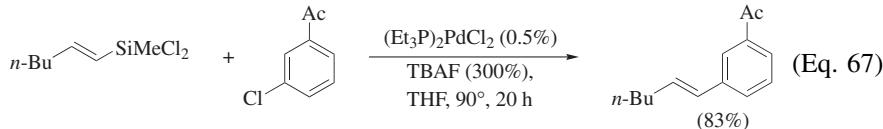
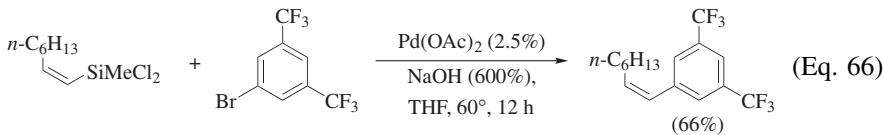


The most recent development allows the cross-coupling of aromatic chlorides.¹⁸⁷ This modification calls for the use of catalysts bearing strongly donating trialkylphosphines such as (*i*-Pr₃P)₂PdCl₂ or (dcpe)₂PdCl₂ in DMF at elevated temperature (120°) for 1–2 days.

2-Pyridyldichlorosilanes can be generated in situ and used directly for cross-coupling with a variety of aromatic bromides (Eq. 65).³⁰



Alkenyl-TGs. Alkenyldichlorosilanes undergo highly site-selective and stereo-specific cross-coupling with aromatic bromides and chlorides and an alkenyl iodide.^{185,187} Here again, two sets of conditions are available; activation with TBAF or with sodium hydroxide. Whereas no ligand is needed for the coupling with aromatic bromides with either activator, strongly donating trialkylphosphines such as those contained in $(i\text{-Pr}_3\text{P})_2\text{PdCl}_2$ or $(\text{Et}_3\text{P})_2\text{PdCl}_2$ are needed to effect cross-coupling of aromatic chlorides (Eqs. 66 and 67).



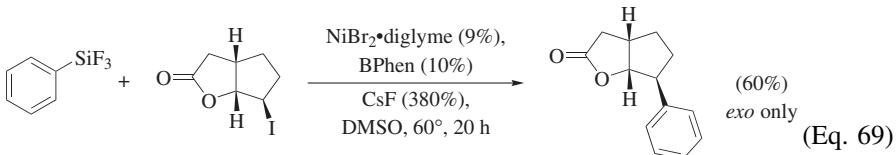
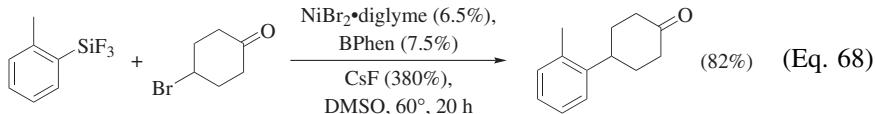
Trihalosilanes

Although the systematic studies of silafunctional groups shown in Eqs. 56 and 57 show that trihalosilanes are less reactive than the dihalosilanes under standard cross-coupling conditions, they have found utility in a number of specific applications. Only trifluorosilanes have been employed to date.

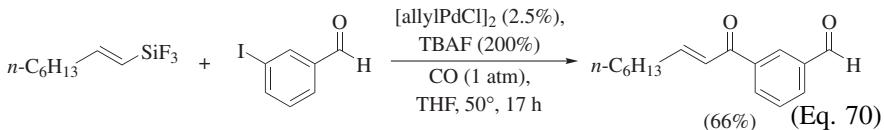
Trifluorosilanes. Trifluorosilanes are prepared from the corresponding trichlorosilanes by treatment with fluorosilicates.¹⁸⁸ These reagents are superior to antimony(III) fluoride and other metal fluorides because of their lower toxicity, cost, and milder reaction conditions.

Aryl-TGs. Aryltrifluorosilanes have found use as activated donors in nickel-catalyzed cross-coupling with aliphatic bromides.¹⁸⁹ This transformation takes place under mild conditions with cesium fluoride as the activator and with a wide range of primary and secondary bromides and iodides. Functional group compatibility on the electrophile is good (ketones, carbamates, lactones, acetals,

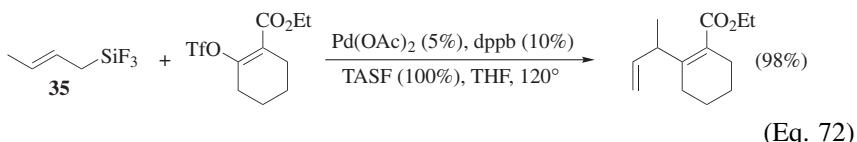
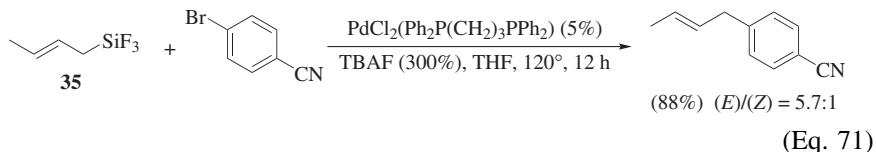
and cyano groups). The reaction is stereoconvergent (i.e. independent of halide configuration), which indicates the intermediacy of a radical or configurationally labile intermediate (Eqs. 68 and 69).¹⁸⁹



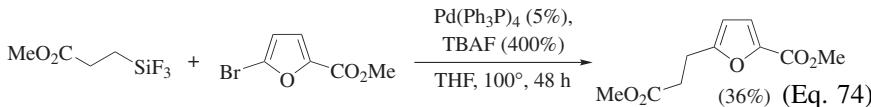
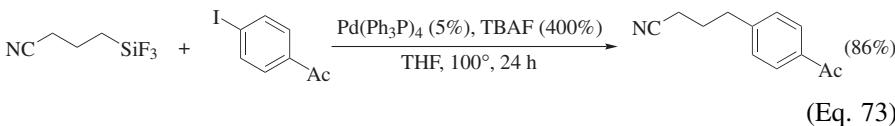
Alkenyl-TGs. The sole application of alkenyltrifluorosilanes is for carbonylative coupling with aryl and alkenyl iodides. Mono- and difluorosilanes are not sufficiently activated for this process but good yields are obtained for (*E*)-1-octenyltrifluorosilane under 1 atm of carbon monoxide (Eq. 70).¹⁷⁹ Unfortunately, the reaction is not stereospecific as (*Z*)-1-octenyltrifluorosilane gives a mixture of (*E*) and (*Z*) isomeric products. A control experiment shows that the products isomerize under the cross-coupling conditions.



Allyl-TGs. (*E*)-2-Butenyl-(35) and 3-methyl-2-but enyltrifluorosilane (36) undergo cross-coupling with aryl bromides, iodides, and triflates when activated by TBAF.¹⁰⁹ The site selectivity is dependent on the phosphine ligand (cf. Eqs. 23a, 23b) and the leaving group.¹¹⁰ In general, for aryl halides a high γ -selectivity is obtained with Ph₃P, whereas high α -selectivity is obtained with dppp (Eq. 71). Curiously however, for enol triflates, dppb gives high γ -selectivity (Eq. 72).



Alkyl-TGs. The transfer of simple alkyl groups is rare for organosilicon-based cross-coupling reactions, but alkyltrifluorosilanes are capable of this transformation together with aryl bromides, iodides, and triflates. Only primary trifluorosilanes have been used thus far, although the functional group compatibility on the alkyl donor (cyano, ester, and ketone) and electrophile (aldehyde, ketone, nitro, and ester) is good (Eqs. 73 and 74).¹⁹⁰



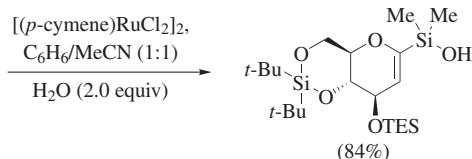
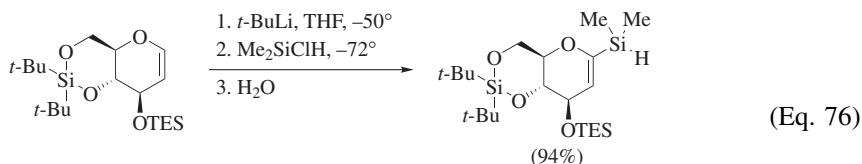
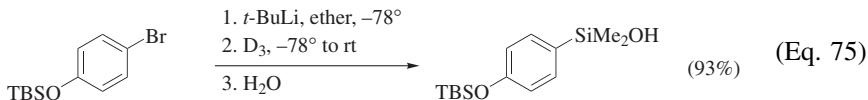
Cross-Coupling of Silanols and Silanlates

Organosilanols (and their conjugate bases) find ubiquitous application as stabilizing ligands in coordination chemistry of main group and transition metals complexes.¹⁹¹ However, prior to 2000, the only applications of silanols in organic synthesis were the use of KOTMS for the mild saponification of methyl esters¹⁹² and nitriles¹⁹³ and as an oxygen nucleophile in enantioselective allylic substitution.¹⁹⁴ In 2000, two independent reports demonstrated the utility of organosilanols as donors in cross-coupling reactions under activation by silver(I) oxide³⁷ or TBAF.³¹ The advantages of organosilanols as coupling partners are manifold in comparison to the halosilanes, including: (1) ease of synthesis, (2) stability toward oxygen and moisture, (3) ease of purification, (4) chemical stability, and (5) diversity of synthetic methods for their preparation. An additional advantage of significant synthetic importance is the ability to activate the cross-coupling of organosilanols with Brønsted bases, thus avoiding the incompatibilities associated with fluoride. Moreover, the conjugate bases of organosilanols are stable, often free-flowing powders that are “self-activating” cross-coupling partners, i.e. require no additional activators. These two variants of cross-coupling are presented separately because of the differences in substrate scope. Even those cross-coupling reactions that undoubtedly involve the silanolate salt through *in situ* generation will be presented in the “Silanols” section, only those cross-couplings that employ the preformed, isolated silanlates are included in the subsequent section.

Silanols

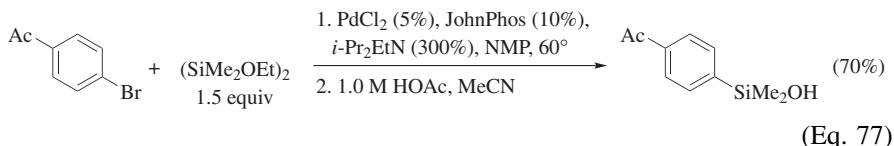
Many different methods are available for the preparation of silanols and silanol surrogates from a variety of precursors. The most common method for introduction of a silanol unit involves the reaction of an organometallic reagent (lithium or magnesium) with a silicon electrophile. The most direct process involves the reaction of the organometallic reagent with hexamethylcyclotrisiloxane (D_3) (Eq. 75).¹⁹⁵ This method works well for aryl- and alkenyllithium reagents. Less

reactive organometallic species or those unstable at higher temperatures require more reactive silicon electrophiles such as dimethyldichlorosilane or dimethylchlorosilane. Whereas the former can be converted into the corresponding silanol by mild hydrolysis (acetate buffer), the latter is converted to the silanol by oxidation with water or an alcohol under catalysis by ruthenium or iridium complexes (Eq. 76).¹⁹⁶



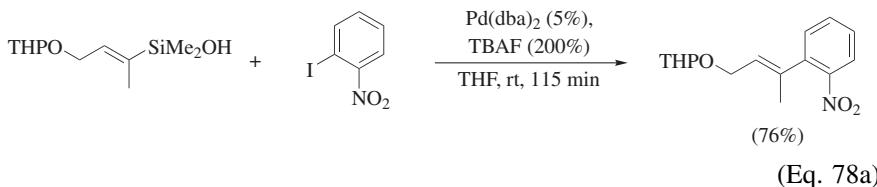
Hydrosilylation of alkynes is a powerful method for creating carbon-silicon bonds with site and stereoselectivity. For this method, silanol surrogates are needed and can be found in the many commercially available hydrosilanes bearing chloro, alkoxy, or silyloxy substituents. More robust surrogates such as benzylsilanes are also available. The steric course of the hydrosilylation is dependent on the transition-metal catalyst: (1) platinum catalysts (e.g., H_2PtCl_6 , (DVDS) $\text{Pt}\bullet(t\text{-Bu}_3\text{P})$)¹⁹⁷ react with terminal alkynes to give (*E*)-1-alkenylsilanes via a *syn* process whereas $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ promotes an *anti* addition process to afford (*Z*)-alkenylsilanes.¹⁹⁸ Remarkably, the cationic ruthenium complex $[(\text{Cp})\text{Ru}(\text{MeCN})_3]^+ \text{PF}_6^-$ reacts with terminal alkynes to afford 2-alkenylsilanes.¹⁵⁹

A palladium-catalyzed insertion method has been developed to allow the introduction of silanols on cyclic substrates wherein formation of an organometallic reagent is precluded by sensitive functionality (Eq. 77).¹⁹⁹ For effective reaction with aryl bromides, a bulky electron-rich phosphine (JohnPhos)²⁰⁰ is required. The pH of the workup is critical to suppress formation of the disiloxane.

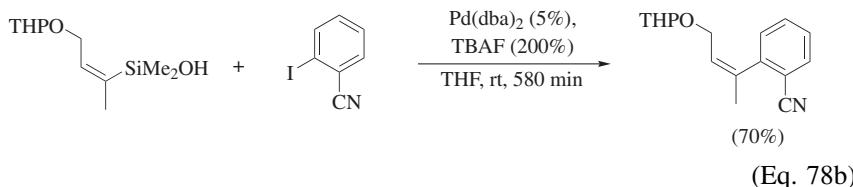


Fluoride Activation. *Aryl-TGs.* Only a simple phenyl group has been transferred under these conditions by the use of phenyldimethylsilanol in combination with a limited number of aryl iodides. A stoichiometric amount of silver(I) oxide is also used together with TBAT.²⁰¹

Alkenyl-TGs. This class represents a very large number of examples that employ acyclic and cyclic alkenylsilanes of varying substitution patterns in cross-coupling with aryl, heteroaryl, and alkenyl halides. The stereospecificity of cross-coupling of simple alkenylsilanes has been discussed previously (Eq. 7) and is further illustrated for a prenylating agent (Eqs. 78a, 78b).⁷⁹ For the iodide electrophiles, no phosphine ligand is needed and the reactions take place at room temperature with electron-deficient, electron-rich, and sterically hindered arenes. In a competition study, dimethyl-, diethyl-, diisopropyl-, and diphenylsilanols react at approximately the same rate under activation by TBAF.⁷²



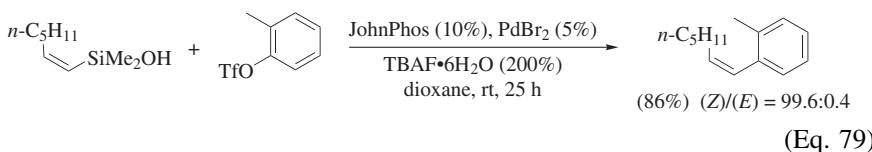
(Eq. 78a)



(Eq. 78b)

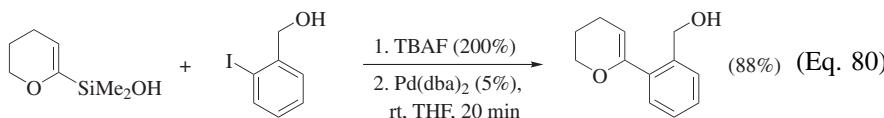
Cross-coupling reactions with alkenyl iodides and bromides proceed with high geometrical selectivity and only minor amounts of *cine* substitution products (Eq. 19).^{31,79,171} Diisopropylsilanols give slightly higher geometrical selectivities compared to dimethylsilanols.³¹

Aryl triflates can participate in cross-coupling reactions but the conditions need to be carefully adjusted. To facilitate the oxidative addition step, an electron-rich, hindered phosphine (JohnPhos) is needed and to suppress fluoride-assisted S–O bond cleavage of the triflate, the TBAF is hydrated with 6 to 8 equiv of water (Eq. 79).²⁰² For electron-deficient aryl triflates, $\text{TBAF}\cdot 30\text{H}_2\text{O}$ is needed.



(Eq. 79)

α -Alkoxyalkenylsilanols, both cyclic (pyranyl and furanyl) and acyclic, undergo ready cross-coupling with aryl iodides under the standard conditions with TBAF (Eq. 80).



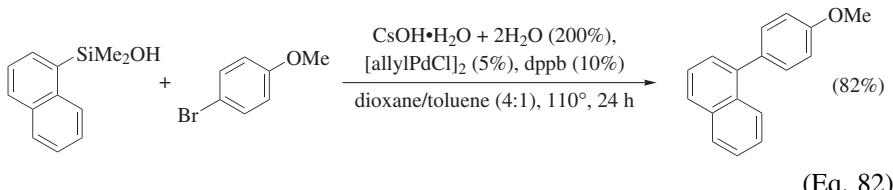
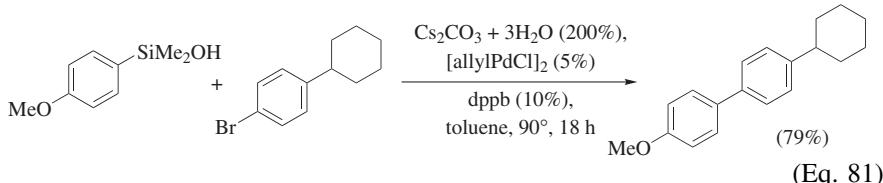
(Eq. 80)

Alkynyl-TGs. A limited set of simple alkynylsilanols undergo a “copper-free,” Sonogashira-type cross-coupling with aryl iodides using $(\text{Ph}_3\text{P})_4\text{Pd}$ and TBAF.¹³⁸ In this case, the silanol offers no advantage when compared to the scope of fluoride-promoted coupling of alkynyltrimethylsilanes (Eqs. 31–36).

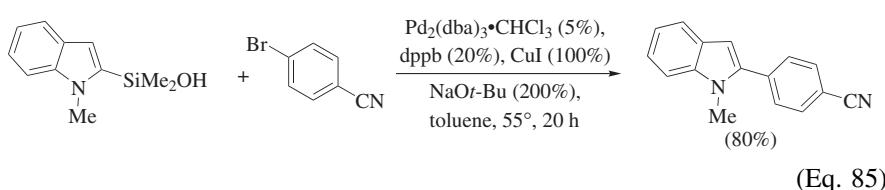
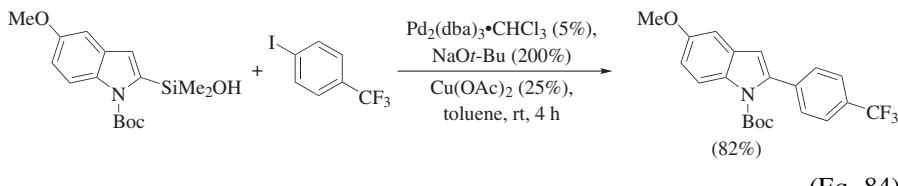
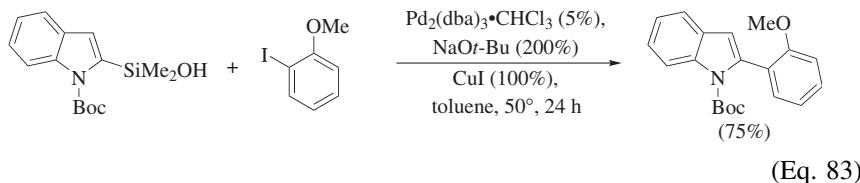
Brønsted Base Activation. For this disparate collection of cross-coupling reaction conditions, the only unifying characteristic is that the activators are all Brønsted bases. Thus, under this rubric is found activation by silver(I) oxide, potassium trimethylsilanolate, cesium carbonate, cesium hydroxide, potassium *tert*-butoxide, and sodium hydride. Undoubtedly, the corresponding silanolate is being formed to some extent and is likely the active component. However, because the parent silanol is the species employed in these processes, these conditions are described in this section.

Aryl-TGs. The first reported use of silanols in a cross-coupling reaction employed a full equivalent of silver(I) oxide as the activator in the presence of $\text{Pd}(\text{OAc})_2$ in warm THF.^{36,37,203} Phenylsilanols bearing electron-donating and withdrawing groups can be used with similarly modified aryl iodides. It is likely that silver activates the arylpalladium iodide by abstraction of an iodide to form a cationic palladium(II) species and activates the arylsilanol through formation of a hypercoordinate complex. The intermediacy of a palladium(II) silanolate was not suggested.

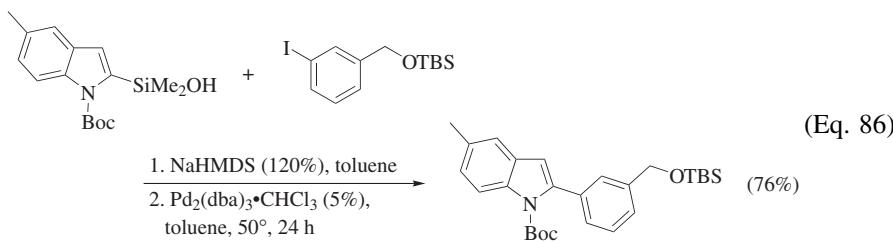
Phenylsilanols can also undergo cross-coupling in the presence of cesium bases (carbonate or hydroxide). However, the bases must carry 2–3 molecules of water of hydration to reverse the formation of inactive disiloxanes formed from the silanols under the elevated temperatures needed to effect cross-coupling with aryl iodides and bromides (90–110°).^{204,205} In addition, ligands play an important role in suppressing the formation of homocoupling products from, as well as reduction of, the electrophile (Eqs. 81, 82). The failure of disiloxanes to undergo cross-coupling under Brønsted base activation sharply contrasts with their behavior under fluoride activation, which supports the divergence of mechanism under the different reaction conditions (Schemes 4 and 5). The limited scope of arylsilanol TGs and harsh reaction conditions limit the utility of this method, which has been replaced by the use of the preformed potassium silanolate salts (*vide infra*).

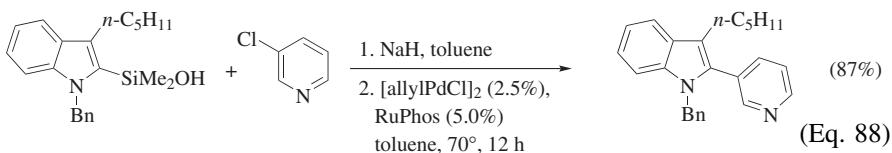
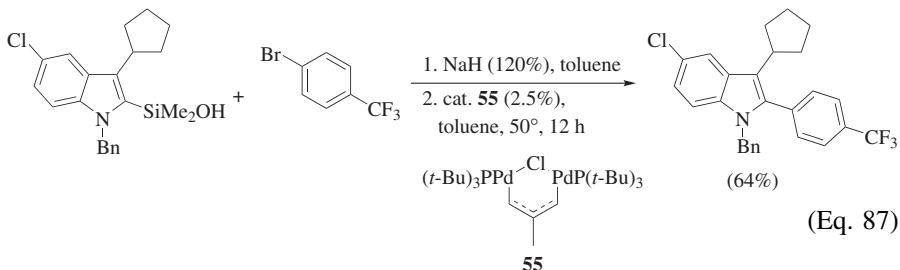


Heteroaryl-TGs. A significant number of π -excessive heteroaromatic silanols have been prepared and three different conditions for their cross-coupling reactions have been developed, two of which involve the use of the parent silanol.^{206–208} *N*-Boc- and *N*-methyl 2-indolydimethylsilanol undergo smooth cross-coupling with aryl bromides and iodides in the presence of sodium *tert*-butoxide and 1.0 equiv of copper(I) iodide to suppress protodesilylation (Eqs. 83–85). The amount of copper can be reduced to 25 mol % with activated indole derivatives.

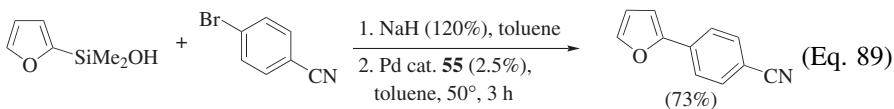


A more general protocol involves the stoichiometric deprotonation of the heteroarylsilanol with either sodium hydride or sodium hexamethyldisilazide. This modification allows a number of important advances, including the elimination of copper(I) salts to suppress protodesilylation (no protons) and the ability to cross-couple with aryl and heteroaryl bromides and chlorides (Eqs. 86–88).^{208,209} For the less reactive electrophiles, an appropriate phosphine ligand or precatalyst is needed to effect oxidative addition. SPhos,²¹⁰ RuPhos,²¹¹ and the palladium(I) dimer **55**²¹² serve in this capacity.

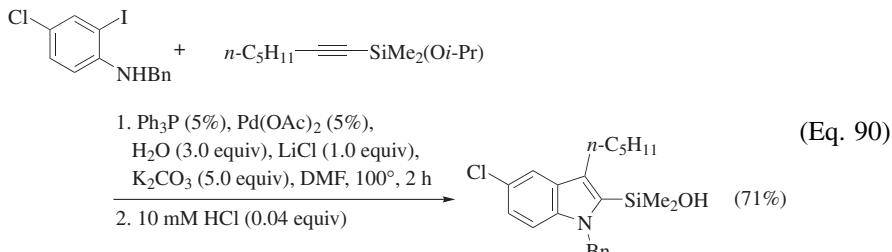




In addition, 2-furyl-, 2-thienyl-, and *N*-Boc-(2-pyrrolyl)dimethylsilanols undergo cross-coupling under these conditions with a similar scope of electrophile (Eq. 89).²⁰⁸

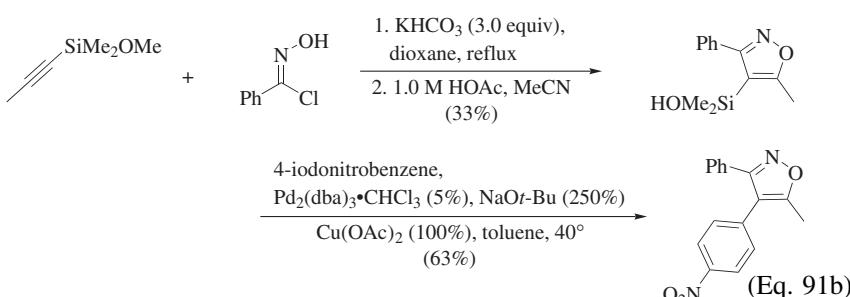
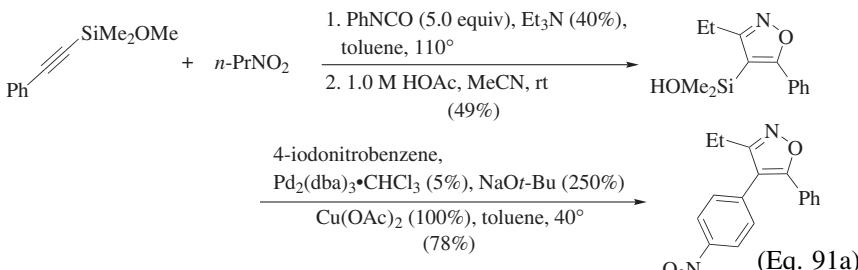


The 3-substituted-2-indolylsilanols in Eqs. 86–88 are prepared by a variant of the Larock indole synthesis that employs alkynylsilyl ethers and places the silanol group in the 2-position for coupling (Eq. 90).²⁰⁹ 2-Iodo-*N*-alkyl anilines are used as precursors with both isopropyl and *tert*-butylsilyl ethers. These silyl ethers are sufficiently robust to withstand the Larock heteroannulation conditions and can be deprotected with very mild acid hydrolysis. The sequence then allows for the controlled construction of 2,3-disubstituted indoles from anilines whereby unsymmetrical alkynes would otherwise lead to mixtures of constitutional isomers. The cross-coupling of isolated, preformed sodium silanolate salts represent the third variant, which is discussed in the next section.

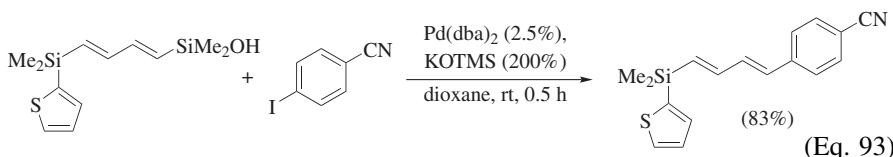
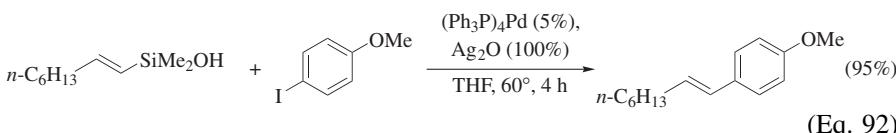


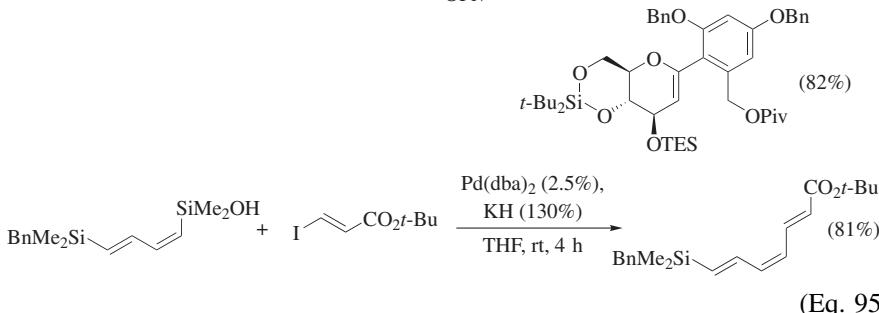
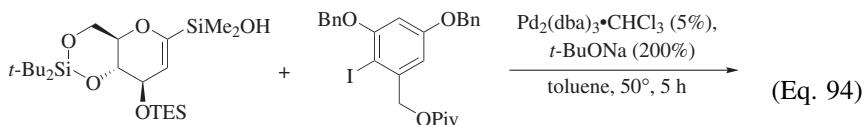
Another sequential process that first constructs a silylated heterocycle, which is then used for cross-coupling, involves the [3+2] cycloaddition of nitrile oxides with alkynylsilyl ethers (Eqs. 91a, 91b).²¹³ The nitrile oxides can be generated

under two different conditions, both sufficiently mild to allow the use of an alkynylsilyl methyl ether as the 2 π -component. The [3+2] cycloaddition reactions proceed in modest regioselectivity (ca. 4–5:1), and the minor constitutional isomers can be removed easily. The cross-coupling reactions require extensive optimization to suppress protodesilylation. As had been observed before, copper salts, this time copper(II) acetate, are used to maximize the yield of the cross-coupling product.

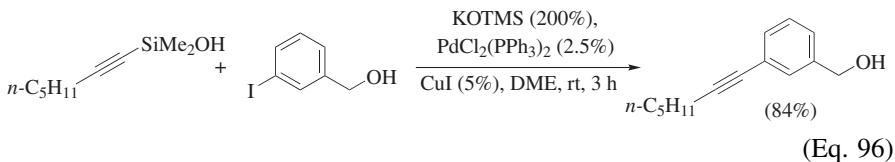


Alkenyl-TGs. Several different methods of activation have been employed for this family of organosilans including silver(I) oxide³⁷ (Eq. 92), KOTMS^{32,44} (Eq. 93), sodium *tert*-butoxide^{214,215} (Eq. 94), and potassium hydride²¹⁶ (Eq. 95). Both aromatic and olefinic iodides are active partners. Functional group compatibility is good and the reactions are stereospecific with respect to the alkenylsilanol unit. Diisopropylsilans react significantly slower (ca. 20-fold) than dimethylsilans under activation by KOTMS.





Alkynyl-TGs. As is the case with trimethylsilylalkynes, the silanol version of the Sonogashira reaction offers little advantage under activation by fluoride, but activation by KOTMS leads to a significantly more rapid transmetalation (room temperature compared to 65–120°). Copper(I) iodide is essential for clean cross-coupling, and in this report the substrates are limited to aryl iodides (Eq. 96).²¹⁷

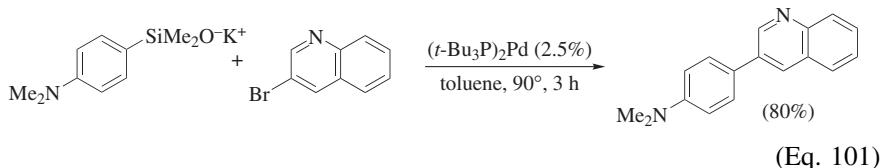
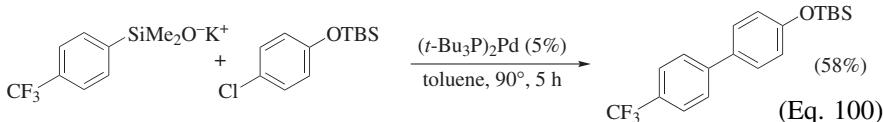
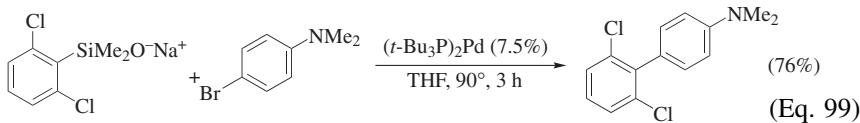
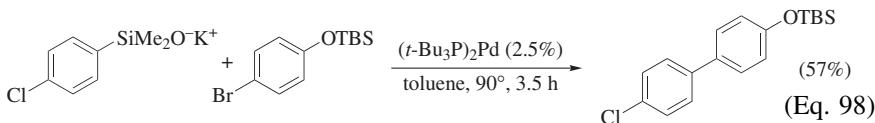
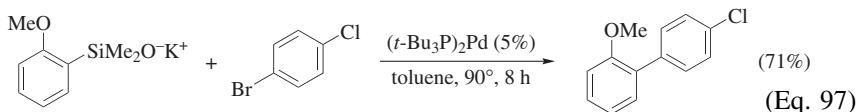


Silanolates

Although silanolate salts are certainly the reactive species in the cross-coupling reactions carried out under Brønsted base activation, these salts are always generated *in situ* from the parent silanol. Depending on the strength of the Brønsted base employed, the formation of the silanolate may or may not be quantitative. Moreover, the conjugate acid remains in the reaction mixture (except in the case of NaH and KH). The preformation and isolation of the sodium or potassium silanolates (from the corresponding hydrides) offers a number of preparative advantages. First, silanols dimerize to the corresponding disiloxanes in the presence of acids or bases, and isolating the metal salt prevents this process. Second, using the isolated preformed silanolate in the reaction not only simplifies the experimental procedure (adding one reagent as opposed to the silanol and base), but also ensures that the cross-coupling partner is always present in its active form. Moreover, a metal silanolate can be generated cleanly with a stoichiometric quantity of metal hydride, without the need for an excess of an activator. The use of an excess of the activator can be problematic in the cross-coupling reaction for several reasons. Surplus activator (i.e. KO*t*-Bu, KOTMS) can compete with silanolate for the Pd center of the arylpalladium halide. As a competitive inhibitor, the activator can form an inactive species in the cross-coupling reaction where it serves as a ligand on the Pd(II) aryl complex. This process sequesters palladium in an inactive form, and subsequently slows the cross-coupling reaction.⁷⁷

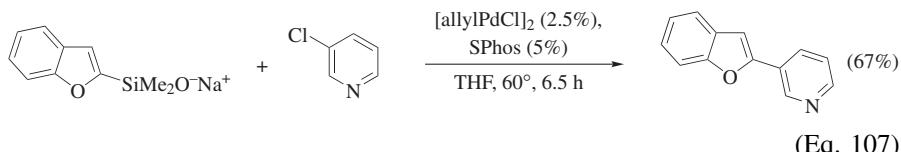
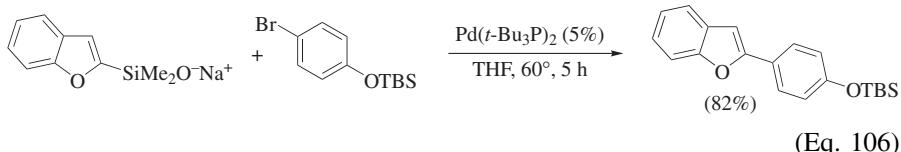
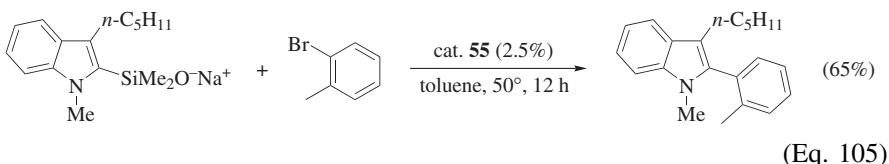
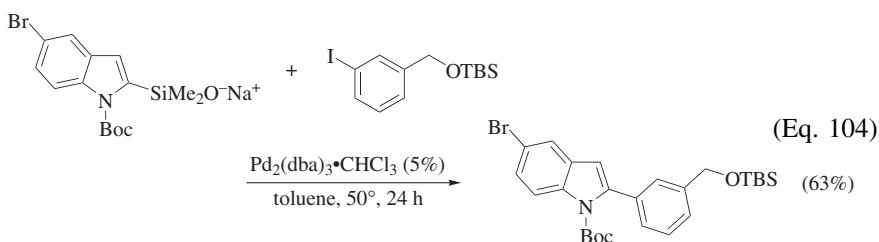
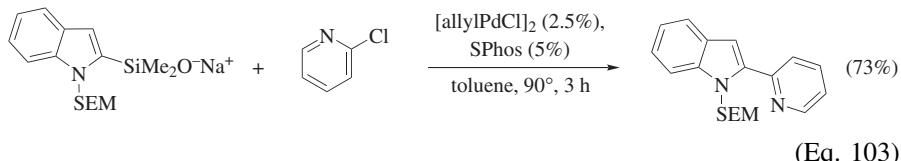
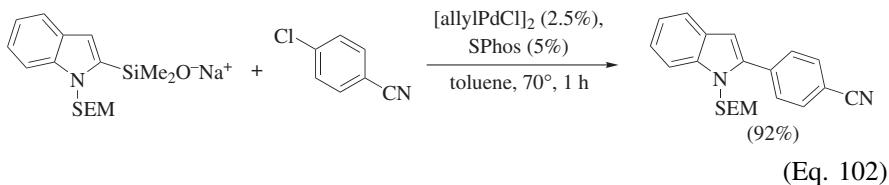
Silanolate must displace the activator to allow the Pd to reenter the catalytic cycle as the palladium silanolate. An excess of the activator can also limit functional group compatibility. For example, when NaOt-Bu is employed with substrates bearing ethyl esters, a competing transesterification reaction takes place.⁵⁴ Furthermore, excess amounts of hydride reagents give reduction products,³² and are incompatible with substrates bearing sensitive functional groups. The direct introduction of the silanolate avoids these problems and many of these salts are stable, free-flowing powders.

Aryl-TGs. The limitations encountered in the cross-coupling of arylsilanols under Brønsted base activation (Eqs. 81, 82) are substantially overcome by the use of potassium arylsilanolate salts in combination with $(t\text{-Bu}_3\text{P})_2\text{Pd}$.⁵⁴ A wide range of arylsilanlates bearing various functional groups (alkoxy, dialkylamino, trifluoromethyl, fluoro, chloro, and alkoxy carbonyl) couple effectively with aryl bromides and chlorides bearing an equally diverse set of functional groups (halo, alkoxy, silyloxy, and alkoxy carbonyl) in good yield. In addition, various heteroaromatic bromides function as cross-coupling partners (Eqs. 97–101).⁵⁴ Other ligand/catalyst combinations show more limited generality.²¹⁸

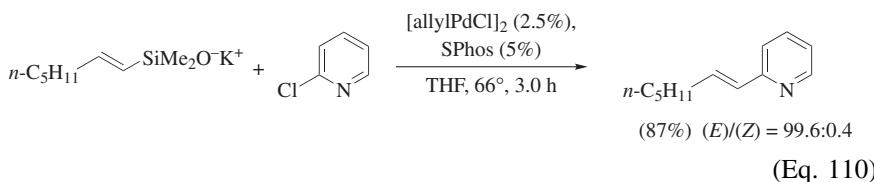
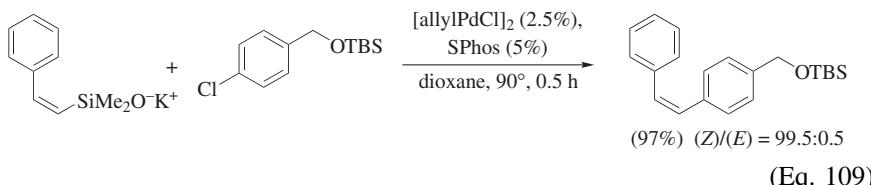
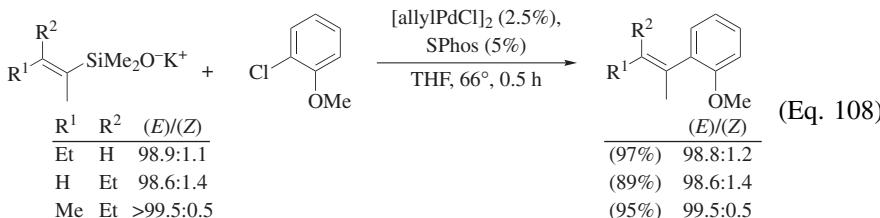


Heteroaryl-TGs. The successful cross-coupling of in situ generated sodium silanlates of π -excessive heterocyclic silanols illustrated in Eqs. 83–89 can be

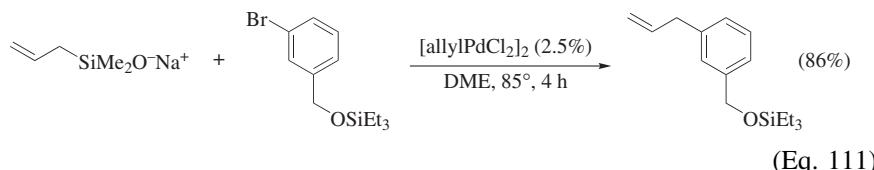
extended to other heterocycles and coupling partners by the use of preformed salts. For example, the preformed *N*-SEM-2-indolylsilanolate can engage in cross-coupling with a variety of aryl and heteroaryl bromides and chlorides whereas the 5-bromo-*N*-Boc-2-indolylsilanolate couples with iodides selectively,²⁰⁸ and *N*-Me-3-pentyl-2-indolylsilanolate (formed by a Larock annulation process)²⁰⁹ couples cleanly with a variety of aryl bromides. Moreover, a large number of 2-benzofuranyl silanolates undergo smooth coupling under similar conditions (Eqs. 102–107).⁵⁴

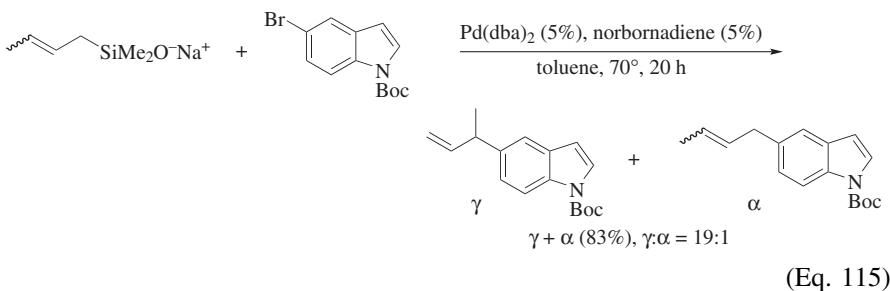
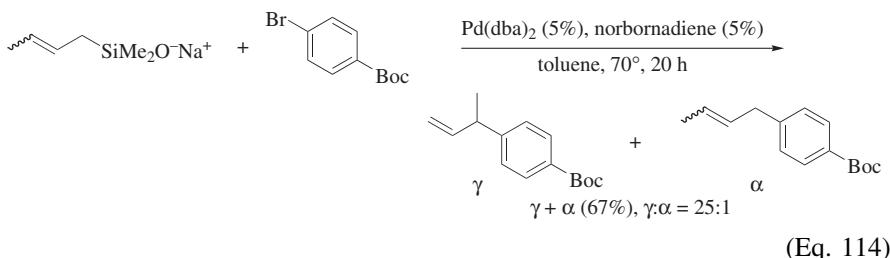
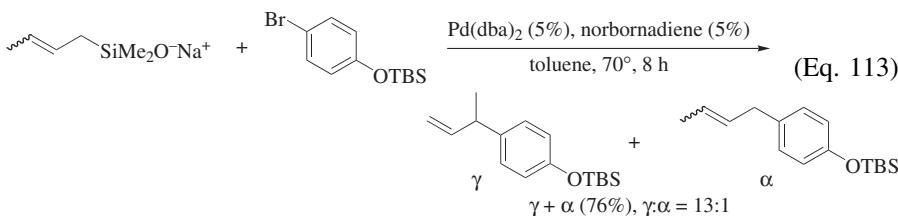
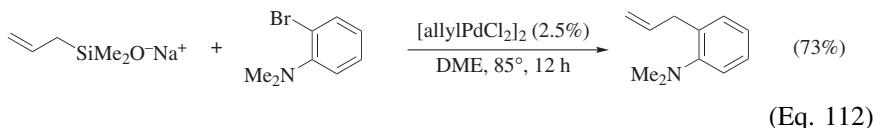


Alkenyl-TGs. Although alkenylsilanols undergo efficient cross-coupling by various methods of activation with Brønsted bases, the preformed potassium salts are highly effective in reactions with aromatic and heteroaromatic chlorides.⁸⁰ These reactions display superior generality with respect to the acceptor, extremely high stereospecificity for a number of different alkenylsilanolate substitution patterns, and overall higher yields than the couplings with the corresponding bromides or iodides (Eqs. 108–110).⁸⁰ The absence of byproducts derived from reduction or homocoupling of the electrophile accounts for the better performance of these reactions.



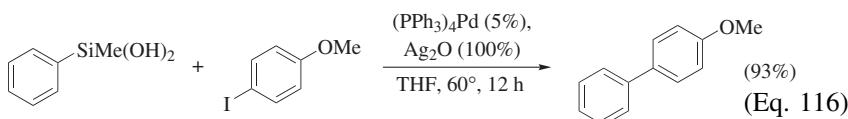
Allyl-TGs. The sodium salts of allyldimethylsilanol and 2-butenyldimethylsilanol undergo palladium-catalyzed cross-coupling with a wide variety of aryl bromides to afford allylated and crotylated arenes.¹⁰⁸ The reaction of the allyldimethylsilanolate affords good yields of the allylation products from both electron-rich and sterically hindered bromides (Eqs. 111, 112). Sodium 2-butenyldimethylsilanolate ((E)/(Z) = 80:20) affords good yields of the γ -substituted product with electron-rich and electron-poor bromides (Eqs. 113–115). The site selectivity (Eq. 24) is strongly influenced by olefinic ligands (dibenzylideneacetone and norbornadiene). Configurationally homogeneous (E)-silanlates give slightly higher γ -selectivity than the pure (Z)-silanlates.

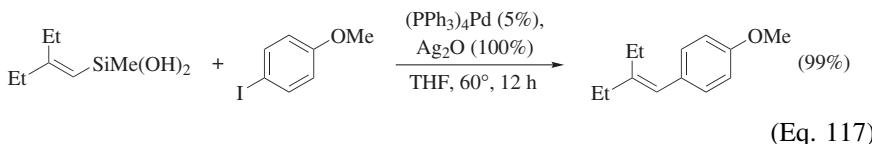




Silanediols and -Triols

Aryl- and Alkenyl-TG's. Both aromatic and olefinic silanediols and -triols can be prepared by buffered hydrolysis of the corresponding chlorides and react with aromatic iodides under standard cross-coupling conditions.³⁷ In general, silanediols react more readily than the corresponding silanols and afford comparable or higher yields (Eqs. 116 and 117). In some cases, the crude hydrolysis product can be used directly in the cross-coupling reaction without isolation of the silanediol.





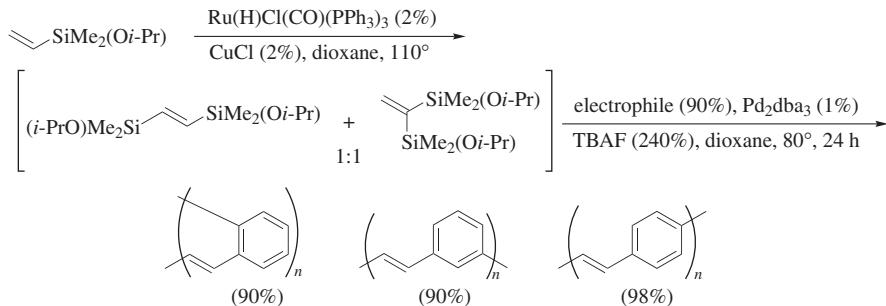
Cross-Coupling of Monoalkoxysilanes

This family of monofunctional cross-coupling precursors is distinguished by the diversity of synthetic methods that have been applied to the introduction of the silyl moiety into the substrates. These transformations allow a logical classification into reactions that create acyclic silyl ethers and cyclic silyl ethers as described below. The vast majority of cross-coupling reactions of alkoxysilanes involve alkenyl transferable groups by virtue of the methods for their construction and subsequent intended application. All cross-couplings are promoted by fluoride.

Acyclic Silyl Ethers

Three principal methods have been employed for preparing silyl ethers for cross-coupling: (1) ruthenium-catalyzed silylative coupling, (2) addition of lithioallylsilanes to carbonyl compounds, and (3) silylstannylation or hydrosilylation.

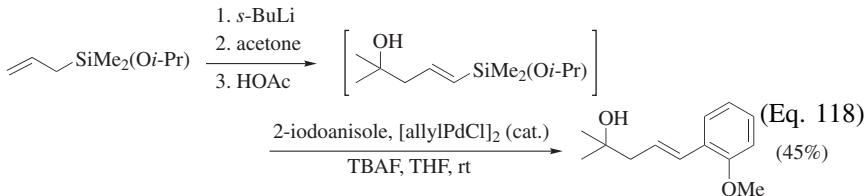
Ruthenium-Catalyzed Silylative Coupling. In a process that superficially resembles cross-metathesis, vinylsilanes undergo a mechanistically distinct cross-metathesis or dimerization with loss of ethylene to form higher alkenylsilanes or 1,2-disilylethenes.^{219–221} The specific application that involves monoalkoxysilanes is the ruthenium-catalyzed dimerization of isopropoxydimethylvinylsilane to produce a mixture of 1,1- and 1,2-disilylethenes, which are employed as a mixture for the synthesis of arenevinylene polymers (Scheme 17).¹⁰⁴ Polymers derived from 1,2-, 1,3-, and 1,4-diiodobenzene as well as 2,5-diiodothiophene have been prepared.



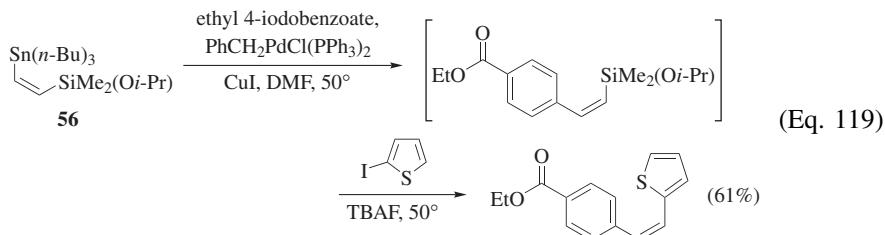
Scheme 17

Addition of Lithioallylsilane. Lithiation of isopropoxydimethylallylsilane with *s*-BuLi in THF followed by addition of the anion to aldehydes and ketones results in the exclusive formation of the γ -addition product bearing an (*E*)

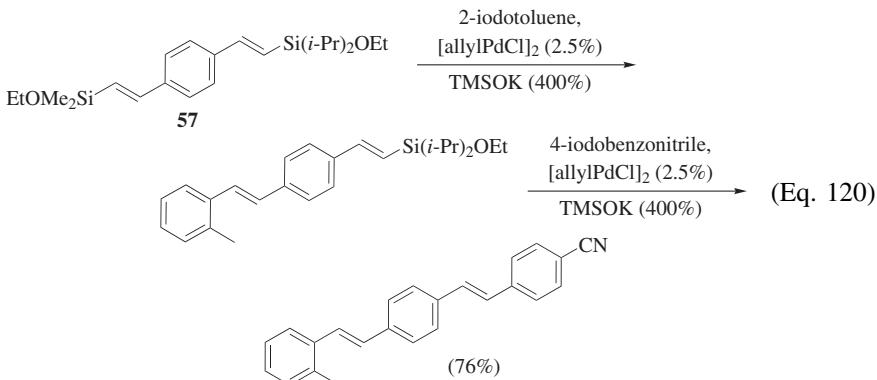
double bond. These alkenylsilanes (often not isolated) undergo fluoride-promoted cross-coupling under standard conditions with aryl iodides (Eq. 118).^{157,222} The alkoxysilane is most likely converted into a silanol under the coupling conditions.⁷⁴



Silylstannylation and Hydrosilylation. A useful linchpin reagent, **56**, is prepared by the *syn* silylstannylation of acetylene in high yield. This reagent allows for the stepwise installation of aryl residues toward the synthesis of unsymmetrical stilbenes (Eq. 119).¹²⁸



The bis(alkenylsilylether) **57** is prepared by a combination of platinum-catalyzed hydrosilylation and ruthenium-catalyzed silylative coupling (Eq. 120). Selective cross-coupling of **57** is made possible by the large difference in the reactivity of the diisopropylsilyl ether vs. the dimethylsilyl ether under activation by KOTMS.⁷²

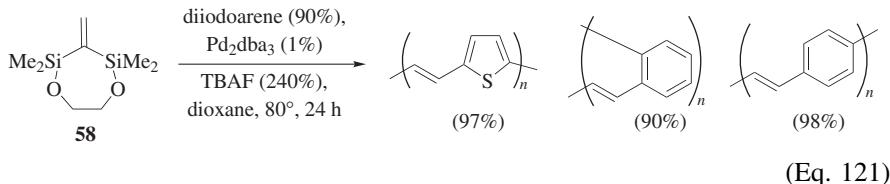


Cyclic Silyl Ethers

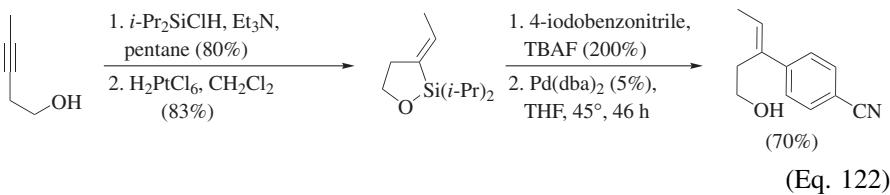
Four principal methods have been employed for preparing cyclic silyl ethers for cross-coupling: (1) ruthenium-catalyzed silylative coupling,

(2) intramolecular hydrosilylation, (3) intramolecular silylformylation, and (4) ring-closing metathesis.

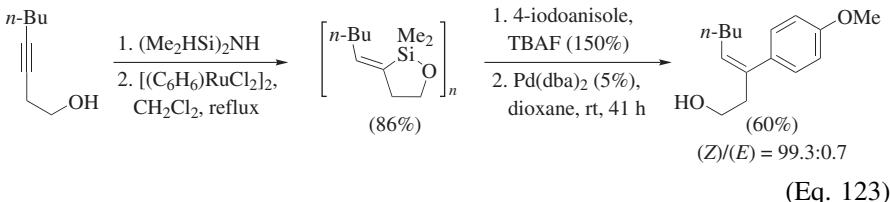
Ruthenium-Catalyzed Silylative Coupling. Cyclic (bis)silylethene **58** is prepared by ruthenium-catalyzed silylative coupling of 1,2-bis(dimethylvinylsilyloxy)-ethane. Remarkably, this reagent undergoes cross-coupling with diiodoarenes exclusively via a *cine* substitution pathway to afford poly(arenevinylene)s in high yield (Eq. 121).



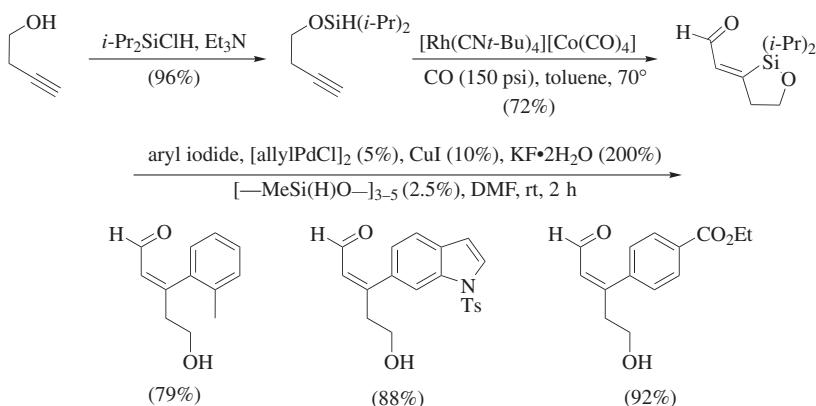
Intramolecular Hydrosilylation. Platinum-catalyzed intramolecular hydrosilylation is a powerful method for the construction of cyclic silyl ethers.²²³ Five-membered ring siloxanes can be prepared in good yield starting from stable diisopropyl silyl ethers. The use of Speier's catalyst affords the (*E*)-*exo*-alkylidene double bond with high geometrical selectivity resulting from *syn* addition. Cross-coupling with aryl iodides under standard conditions with TBAF affords geometrically defined homoallylic alcohols in good yield (Eq. 122).²²⁴ This transformation can also be run as a one-pot process starting from the homo-propargyl alcohol by in situ silylation with tetramethyldisilazane followed by the same sequence as above.²⁶ Overall yields are generally higher in the one-pot process.



Intramolecular hydrosilylation using a ruthenium catalyst affords the isomeric (*Z*)-*exo*-alkylidene siloxanes via an *anti* addition. However, because of the additional steric encumbrance, only dimethylsilyl ethers are sufficiently reactive. These ethers are difficult to isolate because of rapid oligomerization, but can be prepared in situ and used efficiently in subsequent cross-couplings (Eq. 123).¹⁹⁸



Intramolecular Silylformylation. The intramolecular hydrosilylation process can be run under an atmosphere of carbon monoxide (150 psi) to afford products of *syn* addition of a formyl group and the siloxane tether. The formyl group renders these alkenylsilanes considerably less reactive and an extensive optimization of fluoride source, palladium catalyst, solvent, and additives is required to suppress protodesilylation. Satisfactory reaction conditions for cross-coupling with a range of aromatic iodides could be identified (Scheme 18).⁸¹ The diverse functionality in these products is noteworthy.

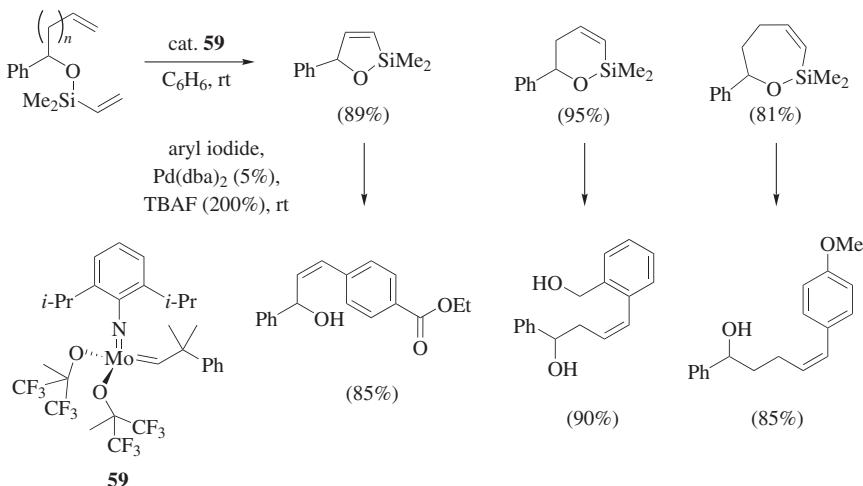


Scheme 18

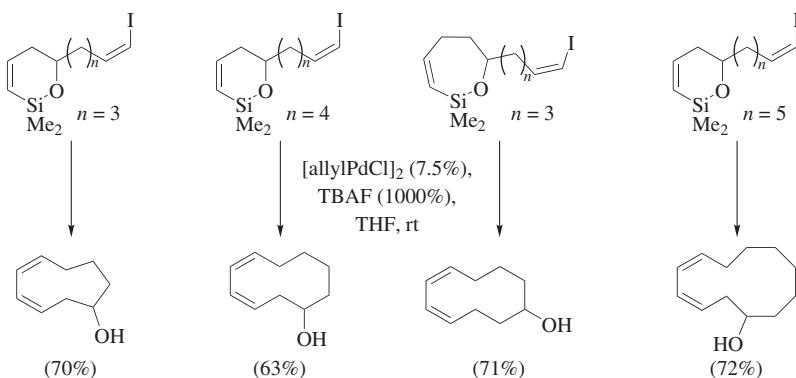
Ring-Closing Metathesis. This process is used to form cyclic siloxanes containing an endocyclic double bond as part of the alkenylsilane. Subsequent cross-coupling of the alkenylsiloxane can be performed either inter- or intramolecularly.

Tandem Ring-Closing Metathesis/Intermolecular Cross-Coupling. Whereas ring-closing metathesis with allylsilanes is facile, reaction with vinylsilanes is very sluggish, likely because of steric effects. Thus, the more reactive molybdenum-based catalysts such as **59** are required to effect the closure of vinyldimethylsilyl ethers of unsaturated alcohols (Scheme 19). Five-, six-, and seven-membered siloxane rings can be formed by this process and all three substrates undergo facile cross-coupling with aryl iodides under standard conditions with TBAF.^{225,226} The endocyclic double bond assures the stereospecific construction of (*Z*)-unsaturated alcohols.

Tandem Ring-Closing Metathesis/Intramolecular Cross-Coupling. A useful modification of the tandem process involves the attachment of the organic electrophile to the constructed siloxane. The subsequent intramolecular cross-coupling reaction affords medium-sized rings bearing a (*Z,Z*)-1,3-diene unit. Adjusting the length of the chain that links the two alkenes in the substrate allows control of the ring size and position of the hydroxy group in the product (Scheme 20). In this way, nine-, ten-, eleven- and twelve-membered rings can be prepared, although high dilution (slow addition) reaction conditions are necessary to achieve good



Scheme 19



Scheme 20

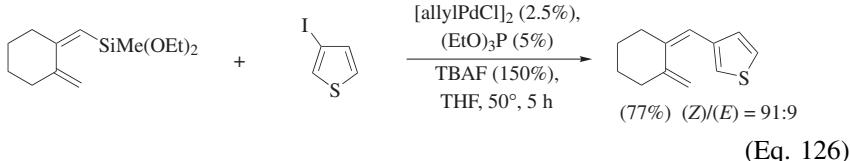
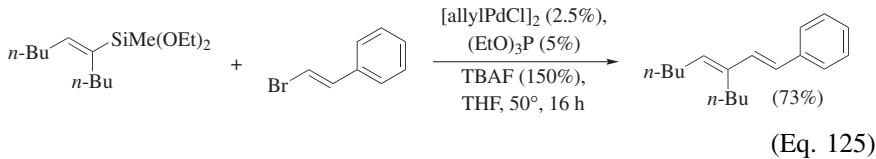
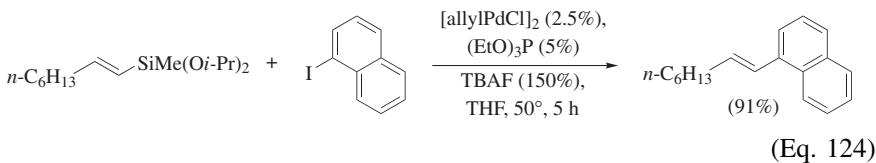
yields of monomeric products.^{226,227} Medium-ring ethers can also be prepared by this process.^{228,229}

Cross-Coupling of Di- and Trialkoxysilanes, and Silatranes

Dialkoxysilanes

Alkenyl-TGs

Only two reports describe the cross-coupling of dialkoxysilanes, both of which employ hydrosilylation of alkynes to introduce the silyl moiety. In one study, all three families, mono-, di- and trialkoxyalkenylsilanes, undergo cross-coupling under activation by TBAF and all three reacted, although the mono- and dialkoxy-silanes give higher yields. Cross-coupling with aryl iodides as well as alkenyl iodides and bromides are successful (Eqs. 124–126).^{26,230}



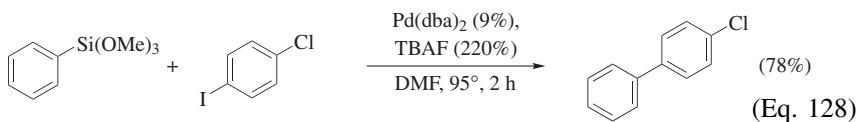
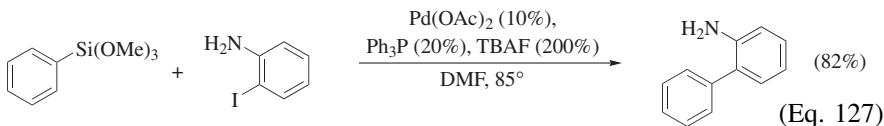
Trialkoxysilanes

This family of organosilicon donors is among the most commonly employed cross-coupling reagents. Although comparative studies of di- and trialkoxyalkenylsilanes show the former to be more reactive,²⁶ such direct comparisons are not available for the corresponding arylsilanes.²³¹ More likely, the prevailing reason for the use of trialkoxyarylsilanes is the commercial availability of a few simple derivatives that dominate the application with a wide variety of electrophiles. Accordingly, the following sections are organized according to the electrophilic partner, the leaving group, and the mode of activation. The vast majority of the donors are trimethoxy- or triethoxysilanes with a few examples of tris(2,2,2-trifluoroethoxy)silanes.⁷⁰

Aryl-TGs

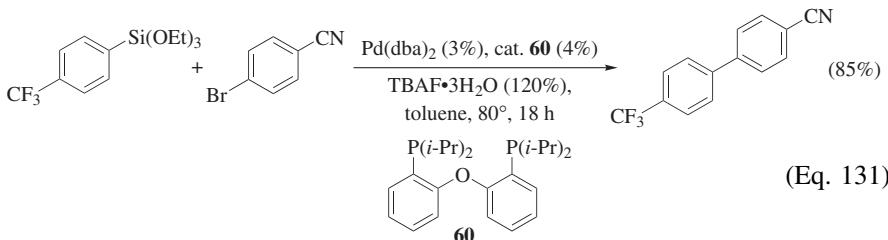
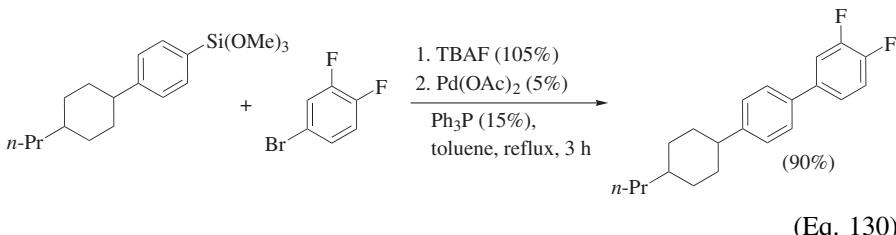
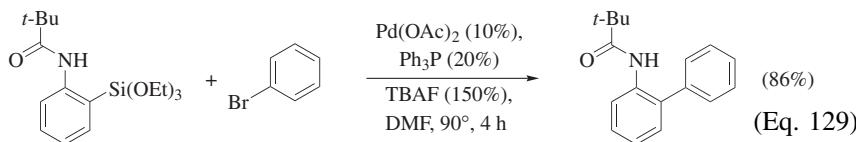
This donor family represents the largest class of coupling partners although the structural diversity of the substrates is not large, for the most part, substituted benzenes and naphthalenes.

Aryl Iodides. Fluoride Activation. Aryliodides bearing amino (alkylamino), acetamido, nitro, alkoxy, and chloro groups undergo cross-coupling under standard conditions with TBAF activation using either palladium acetate/triphenylphosphine or Pd(dba)₂ (Eqs. 127, 128).^{70,232}

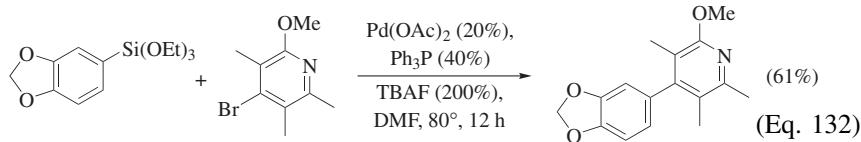


Non-Fluoride Activation. Catalysis of organic reactions by transition-metal nanoparticles has become a viable synthetic method with many practical advantages.²³³ Only a few simple examples of coupling of aryltrimethoxysilanes with aryl iodides are known but they still represent a novel technology. The catalytic system involves formation of nanoparticles from sodium chloropalladate in NaOH solution in the presence of sodium dodecylsulfate (SDS) at 100°.²³⁴

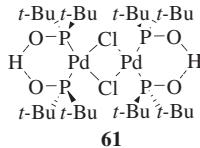
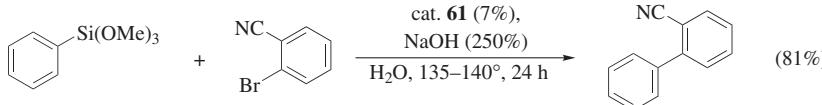
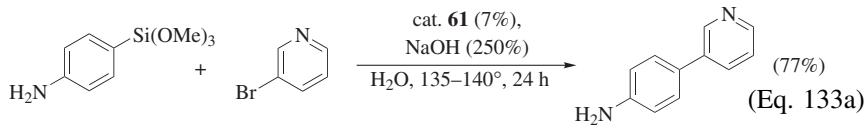
Aryl Bromides. Fluoride Activation. A much greater diversity of aryltrialkoxy silanes has been introduced for the cross-coupling with aryl bromides. The parent phenyltrimethoxysilane undergoes high yielding cross-coupling reactions with a wide variety of aromatic bromides (bearing amino, nitro, alkoxy, keto, or trifluoromethyl substituents) under the same conditions employed for aromatic iodides.^{70,232,235,236} In addition, PdCl₂ can be used as the catalyst²³⁷ and a thiourea-based ligand has also been employed.²³⁸ Functionalized aryltrialkoxy silanes bearing various *ortho* (carbamate, amide, alkoxy, methoxymethyl) and *para* substituents undergo cross-coupling under standard conditions (Eq. 129, 130).^{239,240} These partners can be prepared by directed ortho-metallation and trapping with various silicon electrophiles, whereas *para*-substituted aryltrialkoxy silanes are prepared by treatment of aryllithium reagents with Si(OEt)₄. In addition, bis(2-diisopropylphosphinophenyl) ether (**60**) provides high yields for cross-coupling of both electron-rich and electron-deficient aryltrimethoxysilanes (Eq. 131).²⁴¹



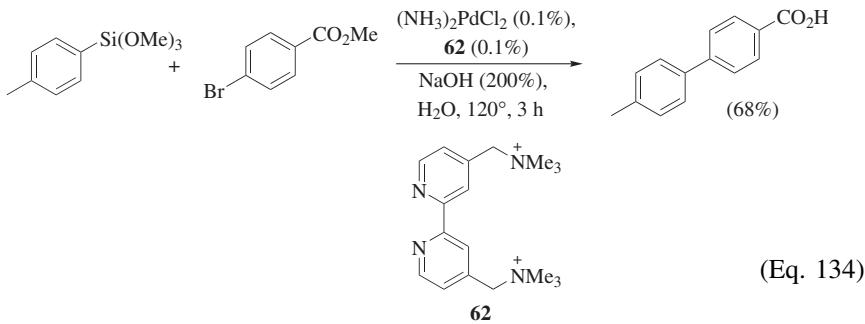
A number of heteroaromatic bromides, primarily pyridines and thiophenes, also undergo smooth cross-coupling under standard reaction conditions (Eq. 132).^{236,237,240–244}



Non-Fluoride Activation. In addition to palladium nanoparticles that have been applied in catalytic reactions with aromatic bromides to a greater extent than with aromatic iodides,²³⁴ a catalytic system has been reported based on the dimeric palladium(II) phosphinous acid complex **61** that operates in hot (140°) aqueous NaOH. A wide range of aromatic and heteroaromatic bromides undergo high-yielding cross-coupling reactions (Eqs. 133a and 134b).²⁴⁵



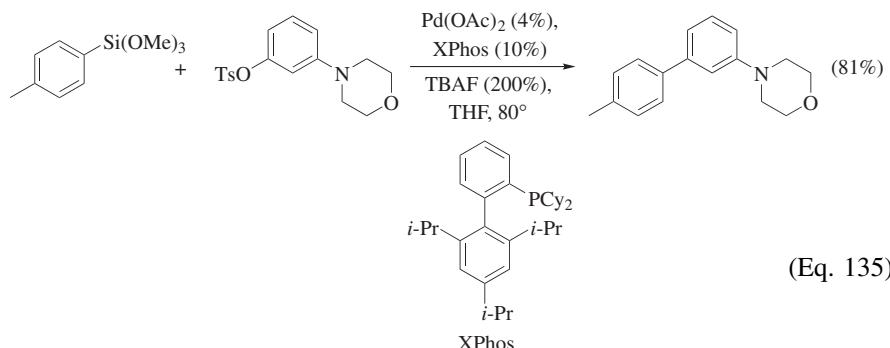
A second catalytic system has been developed that employs a water-soluble bipyridine ligand **62** in aqueous NaOH (Eq. 134).²⁴⁶ Palladium loadings are low (0.1–0.01 mol%) and the diversity of cross-coupling partners is good, but reaction conditions are far from mild.



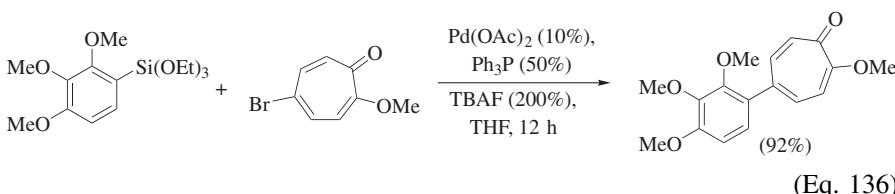
Aryl Chlorides. *Fluoride Activation.* As with all other donors, the ability to engage aromatic chlorides in cross-coupling reactions depends on the choice of ligand to facilitate oxidative addition. For phenyltrimethoxysilane as well, bulky, electron-rich phosphorus-based ligands are used such as **60**,²⁴¹ **61**,²⁴⁷ and 2-(dicyclohexylphosphino)biphenyl²³⁶ (Cyclohexyl JohnPhos) together with simple aromatic chlorides. Other than the choice of ligand, the cross-coupling reactions are unexceptional in that either palladium acetate or Pd(dba)₂ is used as the catalyst together with TBAF.

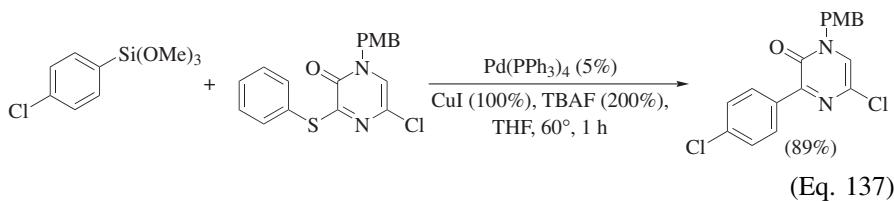
Non-Fluoride Activation. The large majority of the reported reactions for cross-coupling with aromatic and heteroaromatic chlorides employ phenyltrimethoxysilane under the same conditions described for the coupling of aromatic bromides above, namely aqueous NaOH with Pd(OAc)₂/thiourea ligand,²³⁸ (NH₃)₂PdCl₂/bipyridyl ligand **62**,²⁴⁶ or palladium complex **61**.²⁴⁵

Aryl Sulfonates. Both aryl mesylates²⁴⁸ and aryl tosylates²⁴⁹ undergo cross-coupling with aryltrimethoxysilanes under standard conditions (palladium acetate, TBAF, THF/t-BuOH) in the presence of XPhos²⁵⁰ as the critical ligand additive. The structural diversity explored in the aryl sulfonate and the aryl siliconate is modest (Eq. 135).



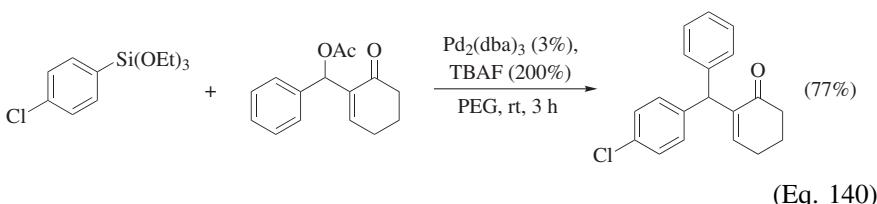
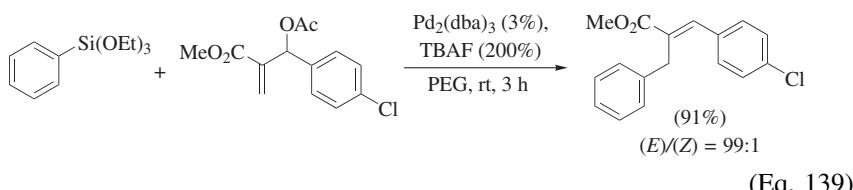
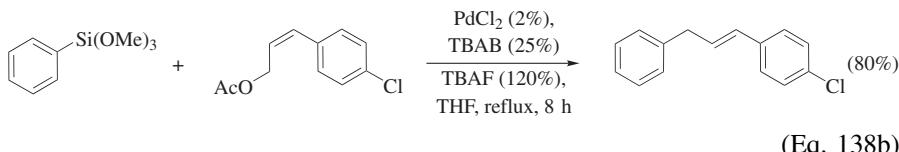
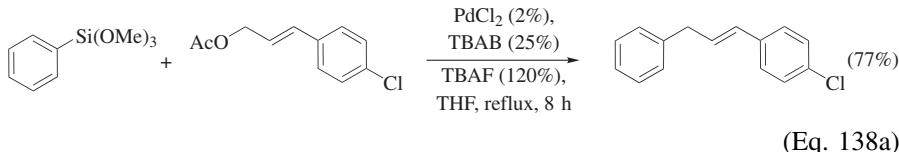
Alkenyl Electrophiles. A limited number of alkanyl bromides and thio ethers have been successfully cross-coupled with aryltrimethoxysilanes under fluoride activation. The bromides react under standard conditions (Eq. 136)²⁵¹ whereas the thio ethers (more accurately heterocyclic thio ethers) require the addition of copper(I) iodide in stoichiometric quantities to couple cleanly (Eq. 137).²⁵²



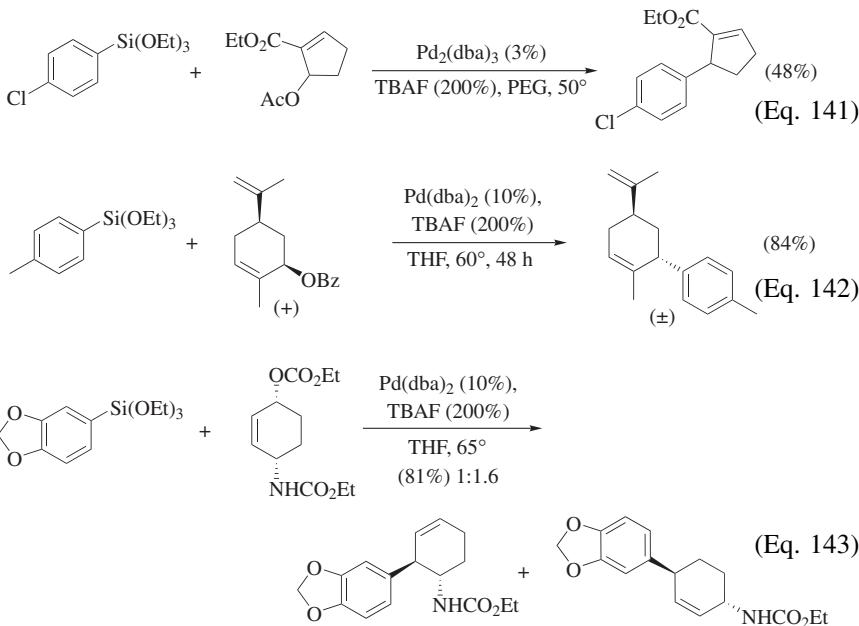


Allylic Carboxylates. Arylation of allylic benzoates and acetates can be effected by cross-coupling with aryltrimethoxysilanes under fluoride activation. The primary issues in this transformation are the site selectivity on the allyl moiety and configuration of the resulting double bond. For acyclic allylic electrophiles, both of these issues are relevant whereas for cyclic allylic electrophiles the double bond is necessarily *cis*.

Acyclic Electrophiles. Arylation of linear allylic benzoates and acetates gives rise to linear products in a stereoconvergent fashion (Eqs. 138a, 138b)^{253,254} whereas branched electrophiles afford either linear or branched products depending on the substitution pattern of the allylic group. If the terminus of the branched allylic electrophile is unsubstituted, then linear products are obtained with high (*E*)-selectivity (Eq. 139). However, branched products are formed when the alkene is contained in a ring (Eq. 140).²⁵⁵



Cyclic Electrophiles. Arylation of cyclic allylic carboxylates with equivalent substitution at the allylic termini proceeds under standard conditions in modest to good yields and with high *anti* selectivity with respect to the starting carboxylate (Eqs. 141 and 142).^{253,255} However, the site selectivity in unsymmetrically substituted electrophiles is poor (Eq. 143).²⁵³

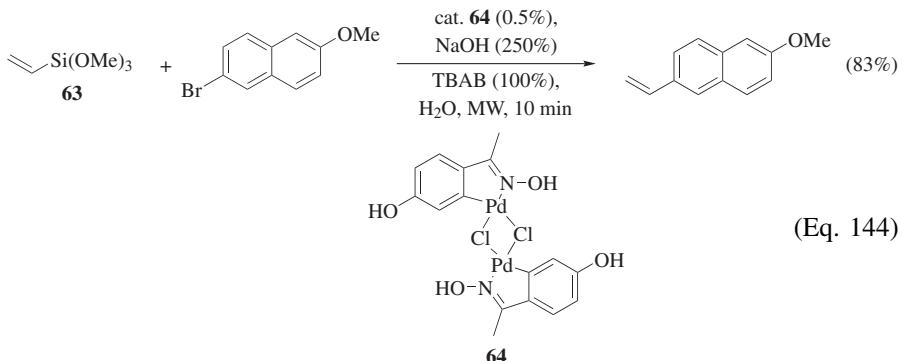


Alkyl Halides. An important recent development in asymmetric substitution of aliphatic halides involves the combination of aryltrimethoxysilanes with racemic α -bromo esters in the presence of the chiral ligand (*S,S*)-**44** and a fluoride source (TBAT) to provide the α -aryl carboxylic esters in high yields and enantioselectivities (Eq. 25).¹¹⁸ The bulky BHT ester is essential for high enantioselectivity.

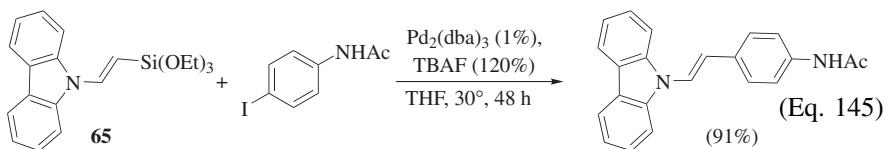
Alkenyl-TGs

The vast majority of examples of this donor group employ the parent vinyltrimethoxysilane for simple vinylation^{62,70,87} or as a linking group in the preparation of vinylenearylene polymers.²⁵⁶

Aryl Halides. Direct vinylation of aromatic bromides and chlorides with vinyltrimethoxysilane (**63**) can be accomplished in aqueous NaOH with tetra-*n*-butylammonium bromide (TBAB) and either palladium acetate or palladacycle catalyst **64** under microwave heating (Eq. 144).²⁵⁷ This method has also been employed for cross-coupling of (*E*)-styryltrimethoxysilane.

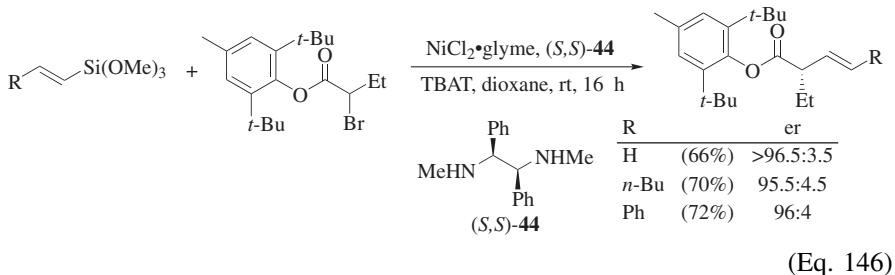


(*E*)-*N*-Styrylcarbazoles can also be prepared by cross-coupling of the silyl-alkenylcarbazole reagent **65**, which itself is prepared by a silylative coupling reaction of **63** with 9-vinylcarbazole. The cross-coupling reaction takes place under standard conditions with a variety of aryl iodides (Eq. 145).²⁵⁸



Allylic Carboxylates. Vinylation of allylic carboxylates with **63** under fluoride activation affords 1,4-dienes in a stereoconvergent fashion.²⁵⁴

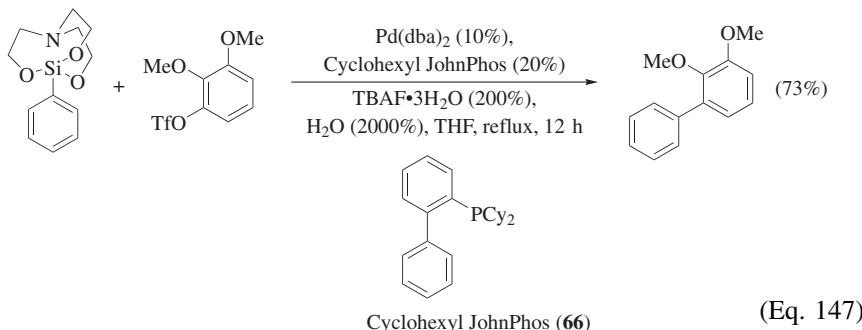
Alkyl Halides. The enantioselective coupling of racemic α -bromo esters in the presence of a chiral ligand, (*S,S*)-**44**, and a fluoride source (TBAT) can also be effected with alkenyltrimethoxysilanes in good yields and high selectivities (Eq. 146).¹¹⁸



Silatrane

Silatrane represent a unique class of trialkoxysilanes by virtue of the internal coordination of the silicon by the nitrogen atom.²⁵⁹ These reagents have been

applied to the cross-coupling of aromatic triflates with moderate success.²⁶⁰ As is the case with silanols, addition of water²⁰² is crucial to suppress the cleavage of the triflate in the presence of TBAF (Eq. 147). Oxidative addition is facilitated by the ligand Cyclohexyl JohnPhos (**66**).²⁰⁰



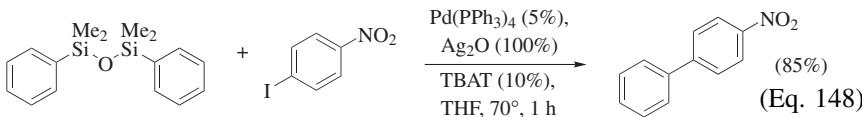
Cross-Coupling of Di- and Polysiloxanes

Disiloxanes are synthetic equivalents of silanols and polysiloxanes are synthetic equivalents of silanediols. In fact, the dimers and oligomers readily form from silanols and silanediols under acid or base catalysis. The oligomers can be engaged in cross-coupling under activation by either fluoride sources or by silanolate exchange with KOTMS.

Disiloxanes

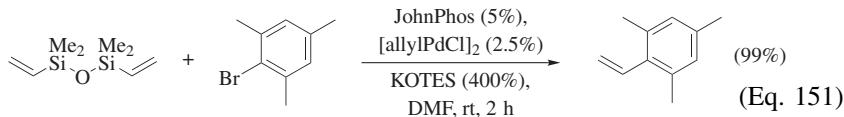
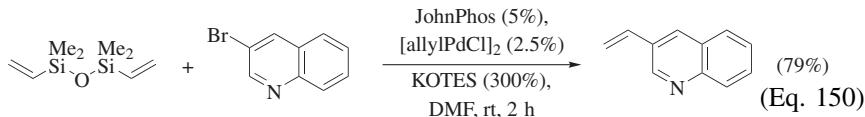
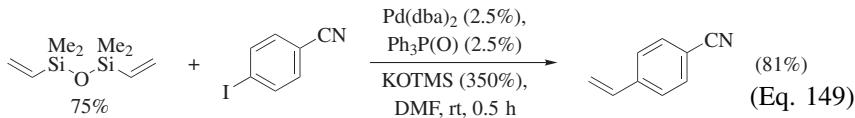
Symmetrical Disiloxanes. Although only a limited number of symmetrical disiloxanes are commercially available,²⁰¹ they can be prepared by hydrosilylation of terminal alkynes with tetramethylidisiloxane²⁶¹ or by silylative coupling with divinyltetramethylidisiloxane (DVDS).²⁵⁸

Aryl-TGs. A single report describes the cross-coupling of aryldimethyl disiloxanes with reactive aryl iodides and bromides under activation by silver oxide and TBAF or TBAT (Eq. 148).²⁰¹

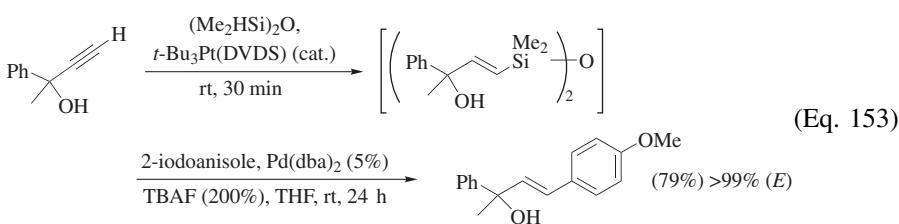
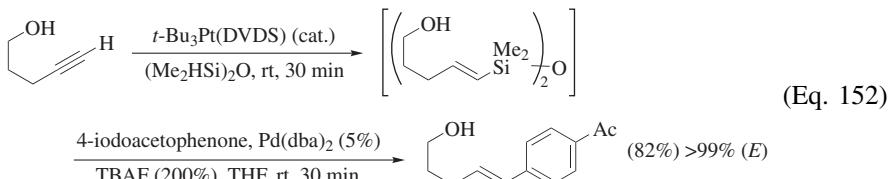


Alkenyl-TGs. For the transfer of a simple vinyl group,⁶² the commercially available and inexpensive reagent divinyltetramethylidisiloxane (DVDS) is ideal. Both vinyl groups are active and the atom economy of the reagent is high. The development of suitable conditions for vinylation with DVDS takes advantage of Design of Experiment protocols (DoE) to generate the reactive species potassium

vinyldimethylsilanolate in situ by a silanolate exchange reaction with KOTMS or potassium triethylsilylolate (KOTES).²⁶² A wide range of aromatic iodides (Eq. 149) and bromides (Eqs. 150 and 151) undergo vinylation in good yield under mild conditions. An *Organic Syntheses* procedure has been developed for the vinylation of bromides.²⁶³



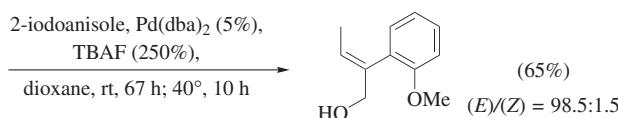
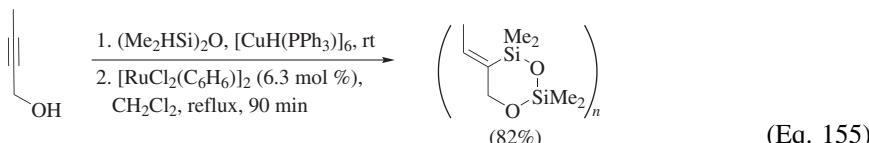
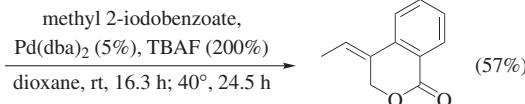
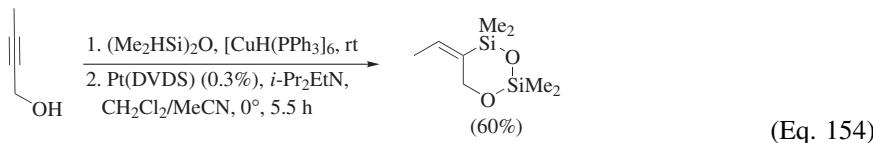
Symmetrical disiloxanes are also readily available from the highly site- and stereoselective hydrosilylation of terminal alkynes with tetramethyldisiloxane with Karstedt's catalyst.¹⁹⁷ The in situ generated disiloxanes undergo efficient cross-coupling under standard conditions ($\text{Pd}(\text{dba})_2/\text{TBAF}$) to afford the (*E*)-styrenes with high selectivity; only traces of (*Z*)-isomers and internal isomers are detected (Eqs. 152 and 153).²⁶¹ Interestingly, cross-coupling with alkenyl iodides leads to a greater proportion of the internal isomer which must arise from a *cine* substitution.



Unsymmetrical Disiloxanes. All unsymmetrical alkenyl disiloxanes used for cross-coupling are prepared by hydrosilylation of terminal alkynes with

unsymmetrical hydrosilanes. Hydrosilylation of terminal alkynes with penta-methyldisiloxane using $(\text{Ph}_3\text{P})_3\text{RuI}$ as the catalyst affords both (*E*)- and (*Z*)-alkenylsilanes depending on the reaction conditions.²³⁰ Cross-coupling under standard conditions with TBAF affords good yields of the styrenes or stilbenes, albeit with a narrow substrates scope.

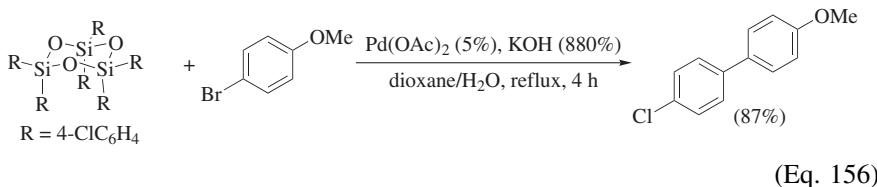
The intramolecular version of this reaction employs either platinum or ruthenium catalysts to effect the *syn* or *anti* hydrosilylation of a tethered alkene, followed by cross-coupling under standard reaction conditions to afford (*Z*)- and (*E*)-allylic alcohols, respectively (Eqs. 154 and 155).²⁶⁴



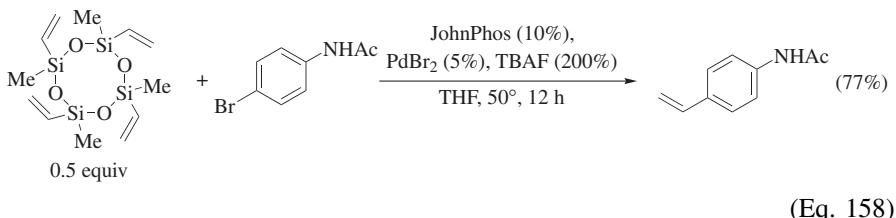
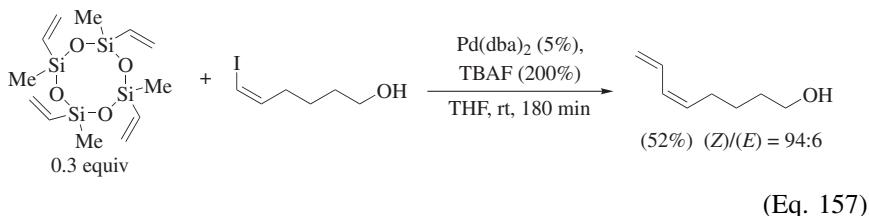
Polysiloxanes

Trimers and Tetramers. A number of discrete oligomers of aryl and vinyl-siloxanes are commercially available such as hexaphenylcyclotrisiloxane and tetramethyltetravinylcyclotetrasiloxane (D_4V). However, other aryl trisiloxanes can be prepared from aryl dichlorosilanes by hydrolysis to the silanediol and acid-catalyzed dehydration.²⁶⁵ In addition, silylative cross-coupling of D_4V with terminal alkenes affords higher homologs of the cyclic tetramers that are also competent in cross-coupling.²⁶⁶

Aryl-TGs. Three simple hexaarylcyclotrisiloxanes have been employed in cross-coupling reactions with aryl iodides, bromides, and chlorides under activation by KOH in the presence of $\text{Pd}(\text{OAc})_2$ (Eq. 156). Under these conditions, all six aryl groups are transferred.



Alkenyl-TGs. Simple vinylation of aromatic iodides and bromides is effected under mild conditions with fluoride activation using D₄V.²⁶⁷ The reagent is the least expensive of the commercially available silicon-based vinylating reagents and all four vinyl groups are transferred (0.3 equiv of D₄V).⁶² The cross-coupling of aryl and alkenyl iodides proceeds at room temperature without added ligands, whereas the coupling of aryl bromides requires 50° and a bulky phosphine ligand to facilitate oxidative addition (Eq. 157, 158). Moreover, the slower coupling of the aromatic bromides led to the formation of secondary products derived from a Heck coupling which can be suppressed by increasing the loading of D₄V to 0.5 equiv. An *Organic Syntheses*²⁶³ procedure has been developed for the coupling of a heteroaryl bromide.



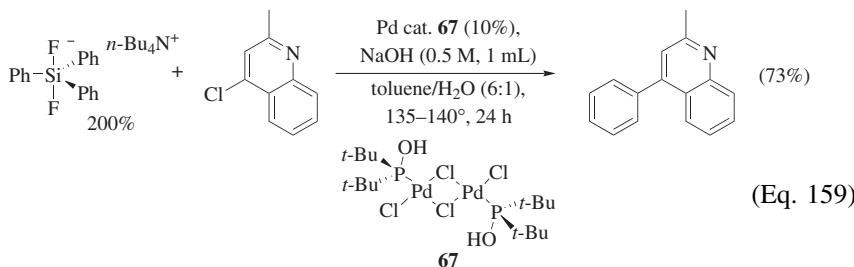
Oligomers. Two commercially available silicones have been used for the transfer of phenyl and alkenyl groups. Polyphenylmethylsilicone undergoes cross-coupling with aryl iodides under activation by silver(I) oxide and (Ph₃P)₄Pd. For the transfer of alkenyl groups, polymethylhydridosilane (PMHS) is employed in platinum-catalyzed hydrosilylation of terminal alkynes to prepare (*E*)-alkenyl-silicones that transfer the alkenyl group to aryl iodides under activation by TBAF and Pd₂(dba)₃•CHCl₃.²⁶⁸

Cross-Coupling of Siliconate Complexes

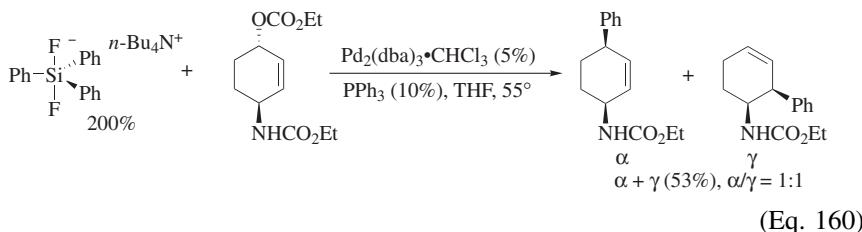
The early recognition that for effective transmetalation from silicon to palladium the silicon moiety must be anionically activated led to the introduction of a number of stable siliconate complexes for cross-coupling. Stable siliconates bearing fluorine and oxygen atoms have been prepared and are competent in cross-coupling with aryl, heteroaryl, and allyl electrophiles. Siliconates are reactive anionic complexes that have limited substrate scope and are not atom economical. Accordingly, these reagents have, for the most part, been supplanted by more easily prepared, readily available, and less sensitive reagents.

Fluorosiliconates

Difluorosiliconates. This category contains only one species, TBAT, which can transfer but a single phenyl group from the three attached to silicon.^{69,269} This inefficiency is compounded by the need to use multiple equivalents of the reagent. Other combinations of phenyl and methyl groups on a difluorosilicate have been investigated, but these give poorer yields of coupling products than TBAT.²⁷⁰ Phenylation with TBAT can be effected without additional activators in DMSO or DMF at elevated temperature or with aqueous NaOH (also at elevated temperature). Aromatic iodides, bromides, and triflates participate in the coupling and in some cases, activated chlorides as well. Heteroaromatic bromides and chlorides (pyridines, quinolines, and thiophenes) couple effectively in the presence of dimeric palladium(II) phosphinous acid complex **67**, which operates in hot (135°) aqueous NaOH (Eq. 159).



Allylic benzoates and carbonates undergo phenylation with TBAT in a net invertive displacement process; however, the site selectivity is highly substrate dependent (Eq. 160).¹¹¹



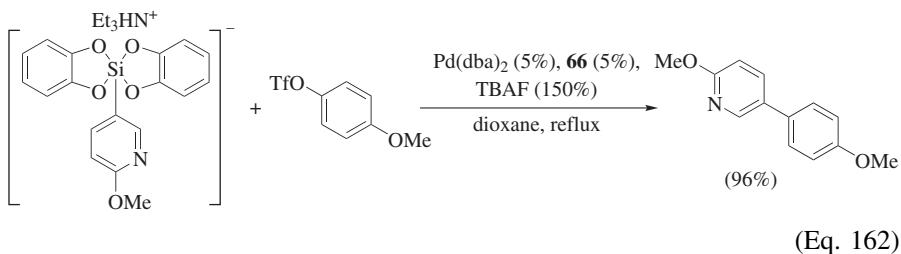
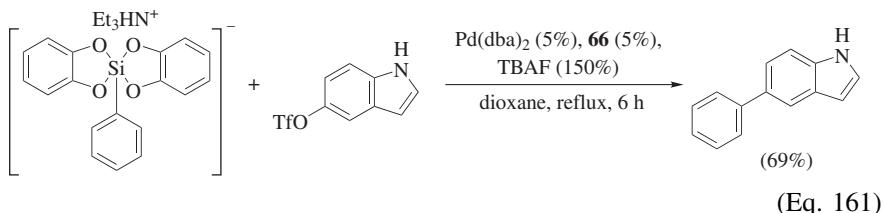
Pentafluorosiliconates. These hypercoordinate species (prepared by treatment of organotrichlorosilanes with KF)²⁷¹ were the first silicon reagents to demonstrate potential in palladium-catalyzed cross-coupling reactions.²¹ Prior studies had shown the ability of pentafluorosiliconates to undergo oxidative dimerization^{21,272,273} or carbonylation²⁷⁴ reactions to form esters. The best described cross-coupling reaction of these salts is the reaction with allylic halides, but the halide is used in 10-fold excess.²¹ Aside from providing a soluble, anhydrous source of fluoride, TASF can also deliver methyl groups to activated aromatic bromides and iodides.²⁷⁵

Catecholsiliconates

The synthesis, structure, and properties of pentacoordinate catecholsiliconates have been the subject of extensive studies.^{17–20} However, their use as reagents

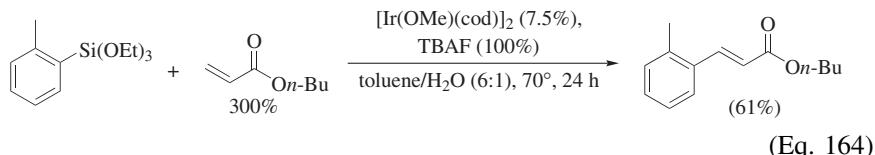
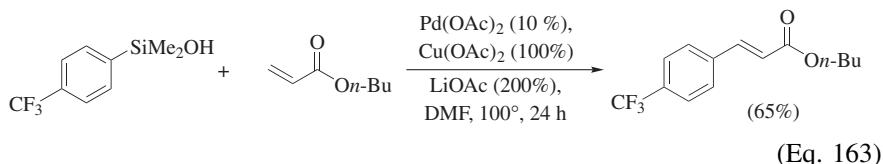
for carbon–carbon bond formation did not materialize until a 1988 report on the coupling of alkenylsiliconates with aryl iodides and triflates.^{22,87} Most of these coupling reactions involve the parent vinylsiliconate because the more substituted alkenylsiliconates give a significant amount of the *cine* substitution products (Eq. 20).

Aromatic and heteroaromatic siliconates are well suited for cross-coupling with aromatic and heteroaromatic triflates.²⁷⁶ The siliconates are easily prepared from the aromatic trialkoxysilicates by treatment with catechol and triethylamine in alcoholic solution. The reaction conditions generally employ Pd(dba)₂, ligand **66** (Eq. 147), and TBAF in refluxing THF or dioxane. Good functional-group compatibility is seen for the electrophile, but the nucleophile is limited to the availability of the arylsiliconate (Eqs. 161, 162).



Oxidative Heck Reactions

Although beyond the scope of this chapter, a number of silanols, silanediols, and siliconates undergo oxidative Heck-type reactions with activated alkenes under catalysis by palladium(II) acetate and a stoichiometric amount of copper(II) acetate^{203,277,278} (Eq. 163) or with an iridium(I) catalyst and a sacrificial alkene as the oxidizing agent (Eq. 164).²⁷⁹



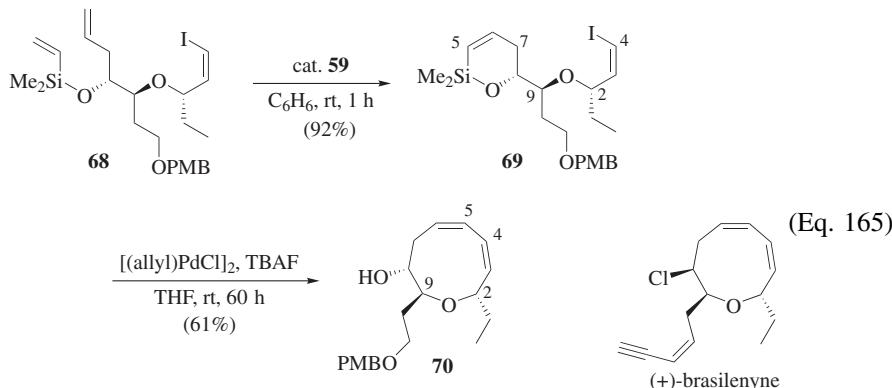
APPLICATIONS TO SYNTHESIS

Overview

The diversity of transferable groups and organo electrophiles that participate in cross-coupling reactions mediated by myriad silicon moieties is amply illustrated in the “Scope and Limitations” section. Silafunctional derivatives of alkynes, arenes, heteroarenes, alkenes, and to a limited extent alkanes can deliver the transferable group efficiently to halides and sulfonates derivatives of a similar set of organic residues. Accordingly, these methods have been featured in a number of total syntheses of natural products. The examples selected below highlight some of the unique features of silicon-based cross-coupling.

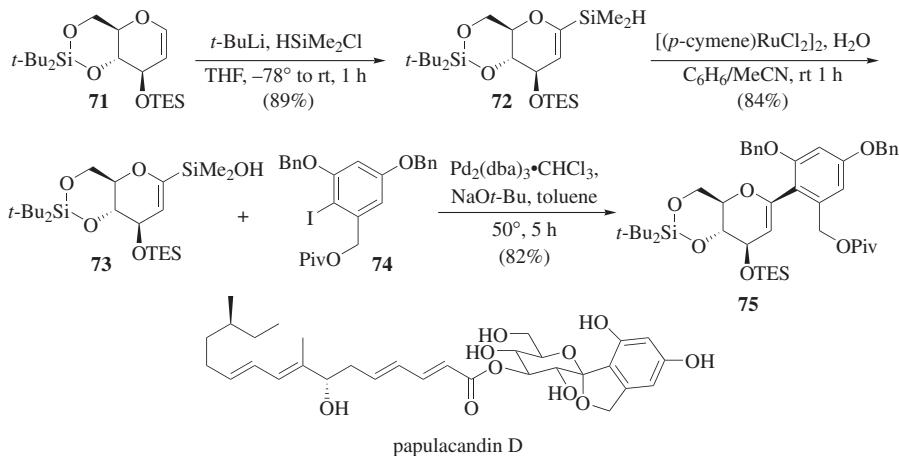
Total Synthesis of Natural Products

(+)-Brasilenyne.^{228,229,280} (+)-Brasilenyne is a marine antifeedant isolated from the digestive gland of a sea hare (*Aplysia brasiliiana*). The most prominent structural feature of brasilenyne is the nine-membered cyclic ether bearing a 1,3-*cis,cis*-diene unit. The key precursor **68**, which contains all of the carbons and the stereocenters needed for brasilenyne, is poised for a sequential ring-closing metathesis/cross-coupling reaction to install the key diene unit and construct the oxocene ring (Eq. 165). The amalgamation of the powerful ring-closing metathesis process (RCM) with a silicon-based cross-coupling reaction allows for a general synthesis of medium-sized rings containing a 1,3-*cis,cis*-diene unit (cf. Scheme 20). Silyl ether **68** is first subjected to a highly efficient RCM reaction using Schrock’s catalyst (**59**; Scheme 19) to afford six-membered cyclic alkenylsilyl ether **69**. In the subsequent cross-coupling reaction, the six-membered siloxane ring is transformed by the combination of TBAF and $[(\pi\text{-allyl})\text{PdCl}]_2$ to the nine-membered ring ether **70** through the formation of the C(4)–C(5) bond. The stereospecificity of the cross-coupling process assures the specific generation of the (Z,Z)-conjugated diene at the desired position in the nine-membered ether. The synthesis of (+)-brasilyene could then be completed by a straightforward introduction of chlorine at C(8) and elaboration of the enyne side chain following a literature precedent.



(+)-Papulacandin D.^{214,215} The papulacandins are a family of antifungal agents, isolated from the deuteromycetous fungus *Papularia sphaerosperma*, that have demonstrated potent in vitro antifungal activity against various pathogens. All of the papulacandins are amphipathic molecules composed of an aromatic moiety linked via a spirocyclic structure to a lactose moiety with two different aliphatic acyl side-chains. The simplest member of the family, papulacandin D, lacks the *O*-(6'-acyl- β -galactoside) at the O(4) position. The key strategic disconnection for the synthesis of papulacandin D requires the cross-coupling of a 2-pyranylsilanol with an aryl halide (Scheme 21). Although α -oxyalkenylsilanols are competent substrates for cross-coupling, the requirement for fluoride activation is clearly incompatible with the silyl ether protecting groups planned in the total synthesis. Therefore, fluoride-free conditions for the cross-coupling had to be developed.

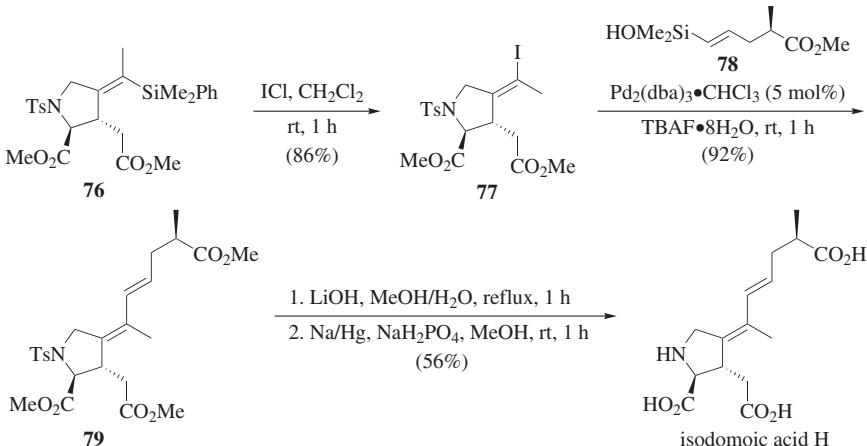
The actual synthesis requires the cross-coupling of the glycal silanol **73** with the protected iodo resorcinol derivative **74** (Scheme 21). To prepare **73**, silyl-protected glycal **71** is lithiated at C(1) followed by capture with chlorodimethylsilane. The resulting hydrosilane **72** is subjected to a ruthenium-catalyzed, oxidative hydrolysis to afford the base-sensitive silanol **73**. The key cross-coupling reaction is quite challenging because of protodesilylation of **73**, but ultimately this critical transformation could be achieved efficiently using sodium *tert*-butoxide as the Brønsted-base activator and $\text{Pd}_2(\text{dba})_3 \bullet \text{CHCl}_3$ as the catalyst to provide *C*-arylglycal **75** in good yield. Glycal **75** contains the entire carbon framework of the sugar fragment of papulacandin D.



Scheme 21

(+)-Isodomoic Acids G and H.^{281,282} Whereas the two target molecules described above are oxygenated natural products, the neuroactive marine natural products, isodomoic acids G and H, were the first alkaloids synthesized via silicon-based cross-coupling. The initial strategic connection of these targets was inspired by the sequential silylcyclization/cross-coupling reactions

(Eq. 45) involving a silicon-based donor related to **76** and a 5-iodopentenoate acceptor related to **78**. Surprisingly, after an extensive survey of conditions, none of the key cross-coupling product **79** could be detected. The failure to effect this coupling led to a reversal in the roles of the donor and the acceptor (Scheme 22).

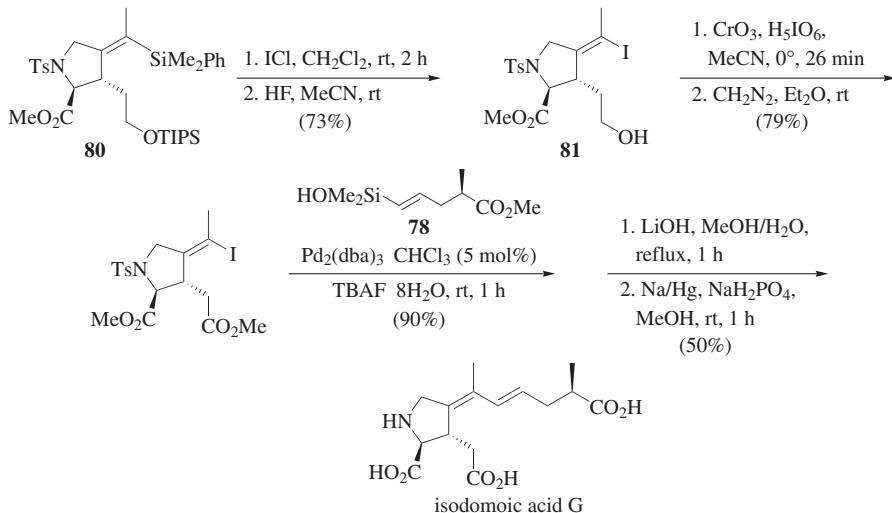


Scheme 22

Accordingly, treatment of alkenylphenyldimethylsilane **76** with iodine monochloride effects an iododesilylation that proceeds with a complete *inversion* of double bond configuration, presumably through an anchimeric participation of the neighboring carbonyl group. In the key cross-coupling reaction of **77**, the fluoride hydration level plays a critical role. When the TBAF is tri-, tetra- or hexahydrated, the conversion is modest and the reaction stalls within 2 h. However, the reaction rate improves dramatically by employing $\text{TBAF} \bullet 8\text{H}_2\text{O}$. With this activator, the coupling with silanol **78** proceeds rapidly to afford the protected isodoic acid H, **79**, in 92% yield. The synthesis is completed by the saponification of the three methyl esters of **79** using LiOH , followed by a detosylation using sodium amalgam to afford isodoic acid H.

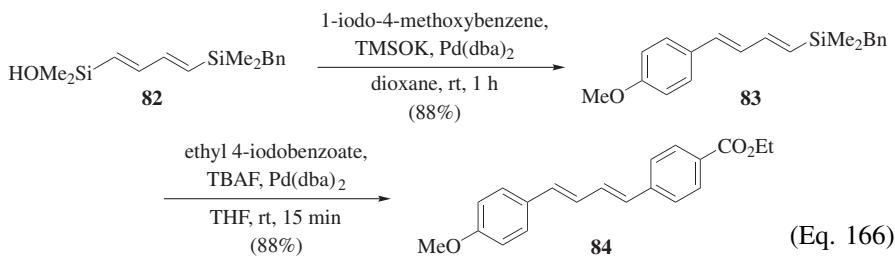
The invertive iododesilylation pathway could be suppressed by employing **80** in which the triisopropylsilyl ether prevents the anchimeric participation of the ether oxygen, thus enabling the synthesis of isodoic acid G (Scheme 23). Treatment of **80** with iodine monochloride proceeds with exclusive *retention* of double bond configuration, affording (*E*)-alkenyl iodide **81** in 73% yield. (*E*)-Alkenyl iodide **81** is subjected to the same sequence of cross-coupling with **78** and deprotection as described above, to achieve the total synthesis isodoic acid G.

(+)-RK-397.^{216,283} The silicon-based cross-coupling reaction is mechanistically unique in that two different modes of transmetalation are possible. This mechanistic duality has significant preparative utility because the different mechanistic pathways can be accessed via complementary reaction conditions. The feasibility of using both modes of activation in a single reagent is illustrated by



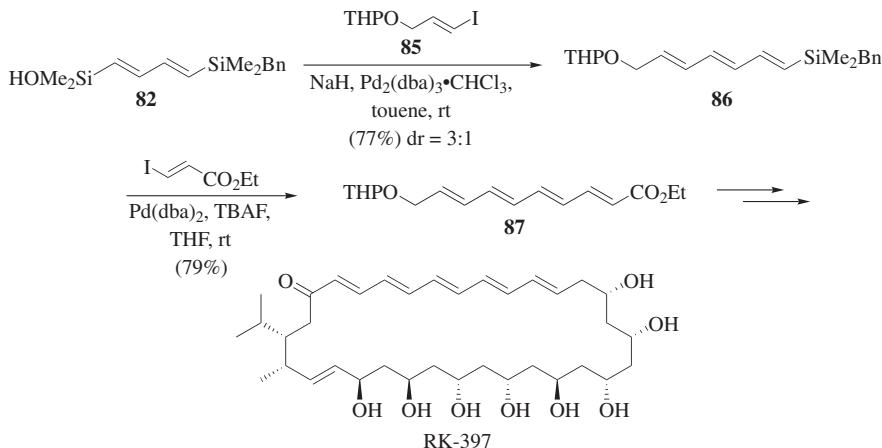
Scheme 23

sequential Brønsted base/fluoride-promoted cross-coupling reactions using the linchpin reagent (*E,E*)-[(4-benzyldimethylsilyl)-1,3-butadienyl]dimethylsilanol (**82**). This bifunctional reagent can combine with two electrophiles under complementary conditions for the construction of unsymmetrical polyenes. In the first cross-coupling reaction, **82** is treated with KOTMS in the presence of an aryl iodide and Pd(db_a)₂ to afford the (1-aryl-1,3-butadienyl)benzylsilane **83**. The benzyldimethylsilyl group is inert under these conditions. Subsequently, treatment of **83** with TBAF effects the second cross-coupling reaction which proceeds smoothly to afford the unsymmetrical 1,4-diaryl-1,3-butadiene **84** (Eq. 166).



The total synthesis of the polyene-polyol antifungal agent RK-397 aptly demonstrates the power of complementary modes of activation for silicon-based cross-coupling reaction (Scheme 24). Whereas in the above synthetic study both electrophiles are *aryl* iodides, the construction of the polyene fragment of RK-397 requires the cross-coupling reaction with two *alkenyl* iodides. This extension is challenging because alkenyl iodides are less reactive. Thus, for the cross-coupling

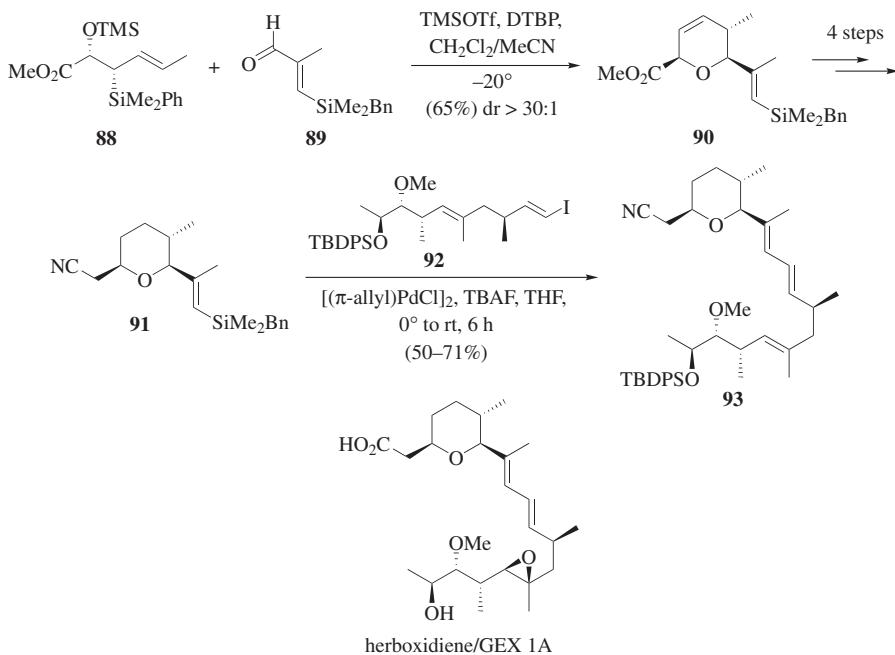
of **82** with alkenyl iodide **85**, NaH is employed instead of KOTMS as the Brønsted base promoter. The stoichiometric generation of the silanolate using a strong base such as NaH provides heightened reactivity. The resulting triene **86** is then combined with ethyl (*E*)-3-iodopropenoate under fluoride-promoted cross-coupling conditions to afford tetraene **87**. This key fragment is then incorporated into the polyol fragment, completing the total synthesis of RK-397.



Scheme 24

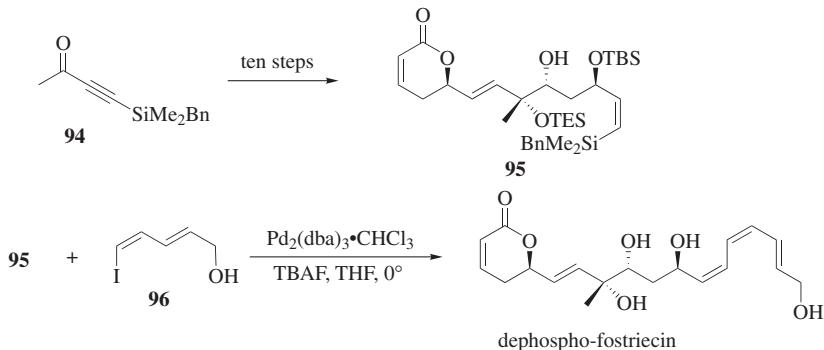
Herboxidiene/GEX IA.²⁸⁴ An important feature of silicon-based cross-coupling reactions for complex molecule synthesis is the stability of organosilicon groups to many different reaction conditions. Because of this feature, the silicon can be introduced early in the synthetic route (if the strategy calls for it) and can be carried through until the key bond-forming process is called into service. The total synthesis of the phytotoxic antitumor compound herboxidiene/GEX 1A highlights this empowering feature of silicon-based cross-coupling reactions (Scheme 25). In the early stage of the synthesis, allylsilane **88** and (*E*)-3-benzyldimethylsilylmethacrolein (**89**) are combined in a Lewis acid promoted [4 + 2] annulation reaction to prepare **90**, a dihydropyran bearing an alkenylbenzyldimethylsilyl group. This “masked” equivalent of an alkenylsilanol is carried through four steps that involve an aggressive reducing agent (lithium aluminum hydride), a basic nucleophile (4-dimethylaminopyridine), and elevated temperature (refluxing DMF), to arrive at the cross-coupling substrate **91**. Treatment of benzylsilane **91** with TBAF and [allylPdCl]₂ promotes the cross-coupling with a fourteen carbon fragment, alkenyl iodide **92**, to afford the advanced intermediate **93**, which possesses the complete carbon skeleton of herboxidiene/GEX 1A.

Dephospho-Fostriecin. An extreme example of the robustness of the benzylidemethylsilyl group to be carried through many synthetic transformations is illustrated in the formal synthesis of fostriecin, a cytotoxic phosphate ester isolated from *Streptomyces pulveraceus* (Scheme 26). The silyl moiety is introduced



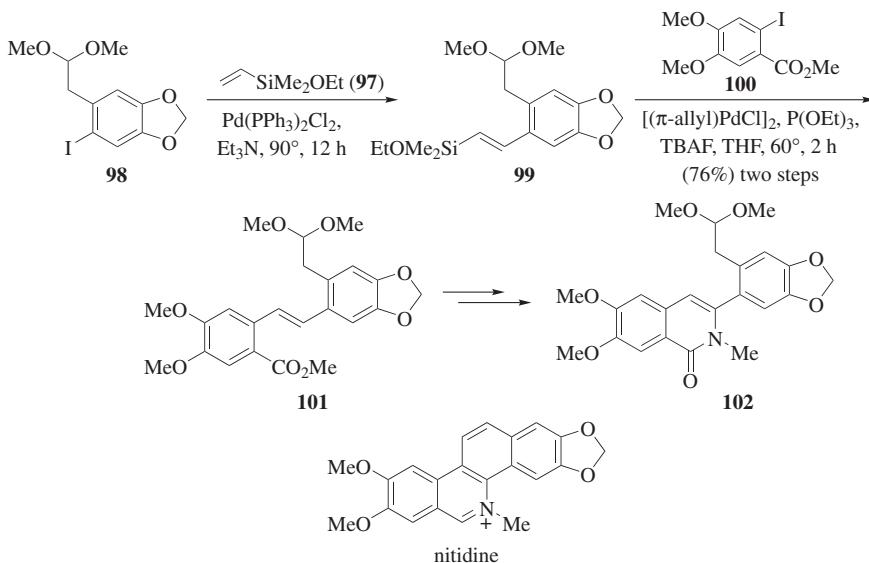
Scheme 25

very early in the synthetic route (structure **94**) and survives the next ten steps, which include aldol addition, hydrogenation, acidic hydrolysis, organomagnesiate coupling, acylation, ring-closing metathesis, and diimide reduction, to reach intermediate **95**. A fluoride-mediated cross-coupling of **95** with **96** (with concomitant deprotection) completes the synthesis of dephospho-fostriecin **97**.



Scheme 26

Nitidine.²⁸⁵ The formal total synthesis of the anti-leukemic compound nitidine employs an interesting Heck/cross-coupling reaction sequence to unite the two oxygenated benzene subunits in stilbene **101** (Scheme 27). The commercially available building block ethoxydimethylvinylsilane (**97**) serves as a linchpin reagent through an interesting Heck reaction/cross-coupling sequence, to assemble the carbon skeleton of the target molecule **102**, thus intercepting a previous synthesis of nitidine.²⁸⁶ In the first step of this sequential process, aryl iodide **98** undergoes a Heck reaction with ethoxydimethylvinylsilane catalyzed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ to afford ethoxydimethylstyrylsilane **99**. Without purification, **99** is combined with aryl iodide **100**, and the mixture is treated with TBAF in the presence of $[\pi\text{-allyl}\text{PdCl}]_2$ to afford the cross-coupling product **101** in 76% yield.



Scheme 27

COMPARISON WITH OTHER METHODS

In the year after the Nobel Prize for cross-coupling reactions (2010), the challenge of comparing the utility and impact of silicon-based cross-coupling methods to the venerable Suzuki, Stille, and Negishi reactions is daunting. Furthermore, recent analyses of reactions commonly used in the discovery and process departments of pharmaceutical companies show a high and increasing percentage of carbon-carbon bond construction through the classical cross-coupling processes.²⁸⁷ This trend is self-fulfilling as more and more sophisticated building blocks containing boronic acids or their surrogates become commercially available.

Direct comparisons among the various methods are rare and further complicated by the dozens of different organosilicon donors that are able to accomplish a given transformation. Accordingly, only generalizations will be provided here.

In terms of reaction scope, there are no major classes of cross-coupling with organosilicon donors that cannot also be done with boron, tin, or zinc. Indeed, the opposite is true for aliphatic transferable groups that can be coupled via stannanes¹⁵ or trifluoroborates,^{288,289} but not with silicon donors. In addition, carbonylative processes and reactions with acid chlorides are better effected with stannanes.^{13,14} However, an important corollary to this statement is that the comparable performance of the silicon-based processes to the tin-based processes lends a distinct advantage to silicon in view of the lower cost, lower molecular weight, and significantly lower toxicity of the starting materials, intermediates, and waste products.

These issues notwithstanding, the silicon-based cross-coupling reactions do offer important advantages for a number of significant applications: (1) vinylation to form styrenes, (2) hydrolytically or stereochemically labile boron derivatives, (3) chemical robustness in multistep synthesis, and (4) constructive introduction of silicon. First, a cost and atom-efficiency analysis of commercially available vinylating reagents shows that vinylsilicon reagents are significantly more cost-effective than either boron- or tin-based vinylating reagents.⁶² Second, the requirement for protic media in most Suzuki cross-coupling reactions often leads to undesired protiodeboronation of the precursor. This problem can be addressed by the use of anhydrous silanolate salts as is illustrated in the cases of sodium *N*-Boc 2-indolylsilanolates²⁰⁸ and 2,6-dichlorophenyltrimethylsilanolate.⁵⁴ In addition, the cross-coupling of alkenylboronic acids can be attended by loss in stereospecificity,^{210,290} again a problem obviated by the use of alkenylsilanolate salts.⁸⁰ Third, the stability of organosilicon donor moieties is amply illustrated in many total synthesis endeavors whereby conditions not likely to be tolerated by boronic acids are successfully employed. However, this advantage is now being challenged by the introduction of robust protecting groups for boronic acids.^{291,292} Finally, the myriad transformations for introduction of organosilicon donor groups that can then be combined with cross-coupling in a telescoped sequence (as illustrated in the total syntheses of brasilenyne and isodomoic acids G and H) offer unique advantages to the silicon-based cross-coupling approach.¹⁵⁸

EXPERIMENTAL CONDITIONS

Preparation of Organosilane Precursors

The evolution of silicon chemistry in organic synthesis over the past 40 years has yielded a wealth of preparatively useful methods for the introduction of organosilicon moieties into organic compounds.⁴ In addition, and partly thanks to the silicone polymer industry, a large number of inexpensive silicon-containing building blocks are commercially available. Among the most common are: SiCl₄, HSiCl₃, Me₂SiHCl, Me₂SiCl₂, (ClMe₂Si)₂, (Me₂HSi)₂O, (MeO)₃SiCl, and (Me₂SiO)₃ (D₃). In addition, an increasing number of reagents are becoming

available for direct cross-coupling including D₄V, DVDS, vinylMe₂SiCl, allylMe₂SiCl, PhSi(OMe)₃, (Ph₂SiO)₃, etc.

The construction of carbon-silicon bonds in organic substrates can be accomplished by four basic strategies: (1) addition of organometallic nucleophiles to silicon electrophiles, (2) hydrosilylation and its manifold variants, (3) silylative coupling and metathesis, and (4) insertion with silanes or disilanes. Each of these strategies is described in detail below.

Additions to Silicon Electrophiles. Organolithium and -magnesium reagents derived from all classes of transferable groups react readily with chlorosilanes but these transformations can be complicated by multiple additions to polyhalosilane precursors. Solutions to this problem include the use of a large excess of the inexpensive halosilane or the use of masking groups such as dialkylamino groups that can later be converted into chloro groups by treatment with PCl₃ or AsCl₃. Alternatively, hydridochlorosilanes offer the advantage of containing but a single nucleofuge, leaving behind a silicon hydrogen bond that can be easily converted into a halogen (Cl₂ or SO₂Cl₂) or oxygen (H₂O/[C₆H₆]RuCl₂]. Organolithium reagents are considerably more reactive than organomagnesium reagents for this purpose and the reactivity of the silicon electrophile decreases with decreasing numbers of chlorides and increasing size of the organic residues. The resulting chlorosilanes can be readily converted to fluorosilanes by treatment with copper(II) fluoride,¹⁷³ antimony(III) fluoride, or fluorosilicates.¹⁸⁸ Hexamethylcyclotrisiloxane (D₃) is one of the most useful reagents for the introduction of a dimethylsilanol unit, but it reacts only with organolithium reagents (Eq. 75).

Hydrosilylation. Hydrosilylation of alkynes is a well-established, workhorse method for introducing organosilyl functional groups with controllable site and stereoselectivity.²²³ Many hydrosilanes bearing chloro, alkoxy, silyloxy, and alkyl substituents are commercially available. For the hydrosilylation of terminal alkynes, transition-metal catalysts can selectively control the site of carbon-silicon bond formation. Thus, platinum catalysts (e.g., H₂PtCl₆, (DVDS)Pt-(t-Bu₃P))¹⁹⁷ react via a *syn* hydrosilylation process to afford (*E*)-1-alkenylsilanes, whereas [(aryl)RuCl₂]₂ promotes an *anti* hydrosilylation process to afford (*Z*)-alkenylsilanes,¹⁹⁸ and the cationic ruthenium complex [(Cp)Ru(MeCN)₃]⁺ PF₆⁻ reverses the site selectivity to afford 2-alkenylsilanes.¹⁵⁹

Hydrosilylation of alkynes (and its carbonylative cousin) can also be carried out intramolecularly to set alkene geometry for subsequent cross-coupling processes. Moreover, the various incarnations of silylcarbocyclization allow for the construction of rings as part of the hydrosilylation process.^{293,294}

Silylative Coupling and Metathesis. The construction of alkenylsilanes by silylative coupling superficially resembles cross-metathesis, but in fact is a mechanistically distinct dimerization with loss of ethylene to form higher alkenylsilanes or 1,2-disilylethenes.²¹⁹⁻²²¹ A variety of ruthenium catalysts are effective

for this transformation, the most common of which is RuHCl(CO)(PCy₃)₂/CuCl. Moreover, the process can employ a wide range of vinylsilane precursors bearing alkyl, aryl, and alkoxy groups on silicon and alkenyl coupling partners bearing aryl, alkyl, alkoxy, and amino groups on the double bond. Finally, oligomeric vinylsiloxanes can be homologated to higher alkenylsiloxanes by this method.

Cross-metathesis and ring-closing metathesis of allylic silanes²⁹⁵ and silyl ethers²⁹⁶ is an established method for introducing allylic silane moieties.²⁹⁷

Insertion with Hydrosilanes and Disilanes. Transition-metal-catalyzed insertion of aryl iodides and bromides into silicon-hydrogen bonds provides a mild method for the formation of arylsilanes that would not be compatible with organometallic addition to silicon electrophiles. However, this transformation is complicated by the reduction of the halide in different types of aromatic substrates.^{168,298–300} An alternative method that obviates the problem of reduction is the insertion with a disilane. This process allows the introduction of simple trialkylsilanes^{199,301} as well as alkoxy silanes¹⁹⁹ by appropriate choice of disilane precursor.

Experimental Variables

As with all cross-coupling reactions, many experimental variables are critical to the success of the organosilicon-based process. However, this family of coupling reactions is further complicated by the large number of different organosilicon precursors and the different modes of activation of the silanes to effect the coupling process. Given the large number of possible permutations, selecting the “best conditions” for a new transformation is a formidable challenge. [In passing, the advantages of using a Design of Experiment optimization approach cannot be overemphasized.]²⁶² The following sections provide general guidelines for the initial selection of components for all silicon-based cross-coupling reactions along with specific recommendations for special classes.

Palladium Source.³⁰² All of the common palladium sources employed for Stille and Suzuki cross-coupling reactions are also used for silicon-based cross-coupling. Nickel(II) sources have been used only with aliphatic halides and although highly useful, only NiX₂•diglyme has been employed.

Palladium(0). Although these sources obviate the need for *in situ* reduction to form an active catalytic species, they have varying degrees of oxygen sensitivity ranging from robust (Pd(db_a)₂, Pd₂(db_a)₃•CHCl₃ and their congeners) to highly air sensitive ((*t*-Bu₃P)₂Pd) and some of the more common in between (e.g., (Ph₃P)₄Pd). This category also contains *in situ* generated palladium nanoparticles. Such “ligandless” palladium catalysts have high activity, but can be plagued with low turnover number (TON) through precipitation of palladium black.

Palladium(II). These catalyst sources have the advantage of being air stable and generally less expensive than Pd(0) sources. They are available in two varieties, inorganic salts (PdCl₂, Pd(OAc)₂, (NH₃)₂PdCl₂) and ligated complexes ((Ph₃P)₂PdCl₂, (PhCN)₂PdCl₂, (dpff)PdCl₂, [allylPdCl]₂, (*t*-Bu₂POH)PdCl₂).³⁰³

The ligated complexes allow the precise stoichiometry of the ligand to be controlled. Alternatively, the use of $[\text{allylPdCl}]_2$ allows many different ligands to be introduced because the reduction of this precatalyst affords “ligandless” palladium(0).³⁰⁴

Palladium(I). This novel class of palladacycle, exemplified by compound **55** (Eq. 87),²¹² has found application in challenging cross-coupling processes with aromatic bromides and chlorides.

Ligands. Over the past decade, the development of new ligands for palladium-catalyzed transformations has revolutionized the field by extending the scope of substrates that can be effectively coupled while simultaneously lowering catalyst loading and reaction temperatures.^{305–309} Unfortunately, many of the early investigations on silicon-based cross-coupling did not benefit from these advances; only the more recent developments in the cross-coupling of trialkoxysilanes, silanols, and silanolates, and hydroxymethylphenyldimethylsilanes have incorporated the newer technologies. For the most part, the ligand choice is dictated by the electrophile and less so by the organosilicon donor. Nearly all of the ligands employed are phosphines; the advances in *N*-heterocyclic carbene ligands have not yet found their way into these coupling processes. However, olefinic ligands such as the dibenzylideneacetone family have proved useful in certain circumstances.³¹⁰

Iodides. These most reactive substrates (as well as activated bromides) can couple without added ligands, although some form of stabilization of the Pd(0) species is often needed to prevent catalyst decomposition.

Bromides, Chlorides, and Sulfonates. To facilitate oxidative addition of the organohalide to the Pd(0) species, phosphine ligands of varying electronic properties and steric bulk are needed. In many cases, a trade-off between reaction temperature and donicity of the ligand allows for weaker ligands to be employed if higher temperatures can be tolerated. Among the weaker ligands are the arylphosphines such as Ph_3P , $(2\text{-tolyl})_3\text{P}$, $(2\text{-furyl})_3\text{P}$, dppp, dppb, and dppf. The bulkier, more electron-rich phosphines such as Cy_3P and *t*- Bu_3P have enabled the cross-coupling of unreactive halides, as have the large class of biarylphosphane ligands (JohnPhos, SPhos, XPhos, RuPhos).^{306,309}

Solvents. Many different solvents have found use in silicon-based cross-coupling reactions ranging from aromatic hydrocarbons (benzene, toluene) to ethereal solvents (THF, dioxane, DME) to dipolar aprotic solvents (DMF, DMSO, DMI) to water. For the majority of examples, THF and DMF are the solvents of choice, but at higher temperatures, these solvents (and especially dioxane) can often contribute to reduction of the organohalide. Water is a special case for the reaction of hydrolytically compatible organosilicon donors, trialkoxysilanes for the most part, in the presence of alkaline activators.

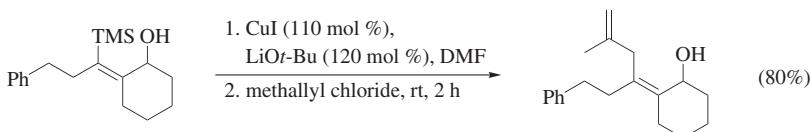
Additives. Aside from ligands for the palladium catalyst, occasionally other additives have been used to solve specific problems. For example, copper salts

have been used to suppress protodesilylation or to facilitate slow transmetalation of the organosilicon donor to the palladium(II) intermediate.^{81,208,213} Other additives have been employed to extend catalyst lifetime by stabilizing the Pd(0) nanoparticles with surfactants^{234,254} such as tetra-*n*-butylammonium salts, sodium dodecylsulfate, or triphenylphosphine oxide.²¹⁸

Fluoride Sources. A large majority of the known silicon-based cross-coupling reactions require a fluoride source to activate the silicon moiety to transmetalation. The most commonly employed sources are soluble tetralkylammonium fluorides such as TBAF•3H₂O, TMAF•4H₂O, and TEAF•2H₂O (TMAF = tetramethylammonium fluoride; TEAF = tetraethylammonium fluoride). The activity of the fluoride source is dependent on both the size of the ammonium cation as well as the hydration level. In a number of cases, Brønsted base promoted side reactions can be suppressed by increasing the hydration level with additional equivalents of water.^{54,202,281,282,311} Anhydrous sources of fluoride have also been used, including KF, CsF, and the organic soluble siliconates TBAT and TASF. Although TMAF can be made anhydrous, it is only sparingly soluble, even in DMF.³¹²

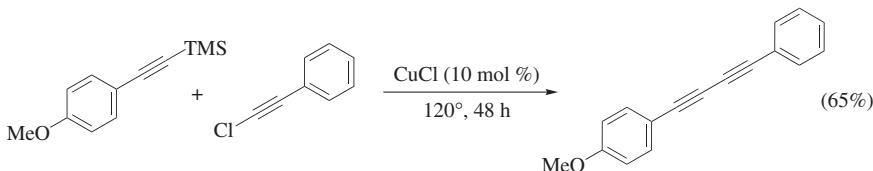
Brønsted Bases. The advent of organosilanol as viable donors in silicon-based cross-coupling, together with the discovery of a new mechanistic pathway involving the conjugate base silanolate salts, stimulated the introduction of a new class of activators. Initially, silver oxide³⁷ and silver carbonate were used, but these expensive agents can be replaced by the inexpensive and soluble alkali trimethylsilanolates.³² Moreover, the discovery that the silanolates are self-activating allowed for the stoichiometric generation of the silanolate salts either *in situ* with strong bases such as sodium or potassium *tert*-butoxide, sodium or potassium hydride, or (in special cases) sodium hexamethyldisilazide.^{55,208} Finally, many of the silanolate salts are stable, easily handled powders, and methods for the preparation and direct use of these reagents without added activators have been described.^{54,80,108,209}

EXPERIMENTAL PROCEDURES

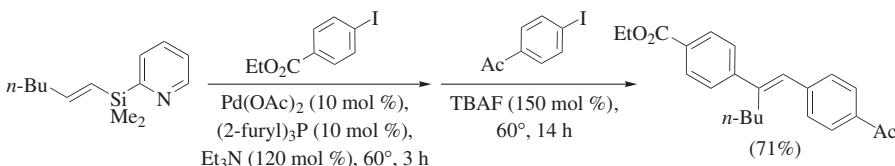


(Z)-2-(2-Methyl-6-phenylhex-1-en-4-ylidene)cyclohexanol [Hydroxyl-Assisted Allylation of an Alkenylsilane].¹²⁷ Copper(I) iodide (63 mg, 0.33 mmol) and DMF (1 mL) were placed in a flask and cooled to 0°. Lithium *tert*-butoxide (1 M in THF, 0.36 mL, 0.36 mmol) was added under argon and the

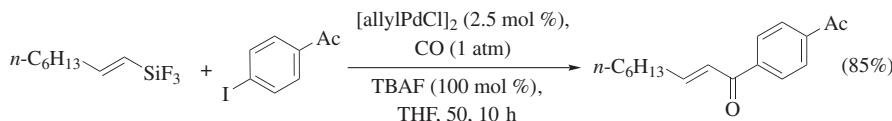
mixture was stirred for 20 min at rt. A DMF (1 mL) solution of (*Z*)-2-[3-phenyl-1-(trimethylsilyl)propan-1-ylidene]cyclohexanol (86 mg, 0.30 mmol) and a DMF (1 mL) solution of methallyl chloride (33 mg, 0.36 mmol) were successively added to the mixture. After the mixture was stirred for 2 h at rt, the reaction was quenched by addition of 3.5% aqueous NH₄OH solution. The organic materials were extracted with Et₂O, dried over Na₂SO₄, and concentrated. The residue was dissolved in THF (3 mL), and TBAF (1 M in THF, 0.3 mL, 0.3 mmol) was added to the solution. The mixture was stirred for 2 h at rt and diluted with water (15 mL). The organic materials were extracted with EtOAc, washed with 1 M HCl and water, and dried over Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by PTLC (hexane/EtOAc, 4:1) to afford the coupling product (65 mg, 80%): IR (neat) 3369, 3064, 3026, 2931, 2854, 1645, 1603, 1496, 1452, 1373, 1350, 1335, 1255, 1227, 1176, 1142, 1093, 1074, 1045, 1030, 987, 964, 889, 748, 698 cm⁻¹; ¹H NMR δ 1.09–1.20 (m, 1H), 1.32 (bs, 1H), 1.40–1.53 (m, 2H), 1.71 (s, 3H), 1.70–1.82 (m, 2H), 1.89–1.95 (m, 1H), 2.11 (dt, *J* = 13.7 Hz, *J* = 3.4 Hz, 1H), 2.25–2.37 (m, 2H), 2.45 (d, *J* = 13.7 Hz, 1H), 2.63 (t, *J* = 8.2 Hz, 2H), 2.75 (d, *J* = 15.9 Hz, 1H), 2.87 (d, *J* = 15.9 Hz, 1H), 4.68 (s, 2H), 4.77 (s, 1H), 7.16–7.20 (m, 3H), 7.24–7.28 (m, 2H); ¹³C NMR δ 20.1, 22.9, 25.1, 27.4, 33.7, 34.4, 35.2, 39.8, 66.7, 110.8, 125.8, 128.2, 128.3, 130.0, 136.8, 142.1, 144.4. Anal. Calcd for C₁₉H₂₆O: C, 84.39; H, 9.69. Found: C, 84.16; H, 10.15.



1-(4-Methoxyphenyl)-4-phenyl-1,3-butadiyne [Cross-Coupling of an Alkynylsilane with an Alkynyl Chloride].¹³³ To a solution of CuCl (2.4 mg, 0.02 mmol, 10 mol %) in DMF (1.5 mL) were added 1-chloro-2-phenylethyne (50 mg, 0.37 mmol) and [(4-methoxyphenyl)ethynyl]trimethylsilane (50 μL, 0.24 mmol) at rt. The reaction mixture was stirred for 48 h at 120°, quenched with 3 M HCl, and extracted with Et₂O (2 × 25 mL). The combined ethereal layers were washed with aqueous NaHCO₃ solution and brine and dried over MgSO₄. Filtration and evaporation provided a brown, oily residue. Column chromatography (silica gel, hexane/CH₂Cl₂, 10:1) afforded the diyne (36 mg, 65%) as a colorless solid: mp 96–97°; IR (KBr) 3076, 3056, 3035, 2216, 1599, 1506, 828 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.83 (s, 3H), 6.86 (d, *J* = 9.0 Hz, 2H), 7.30–7.58 (m, 7H); ¹³C NMR (50.3 MHz, CDCl₃) δ 55.3, 72.7, 74.2, 81.0, 81.8, 113.7, 114.2, 122.0, 128.4, 129.0, 132.4, 134.1, 160.4; HRMS (*m/z*): [M]⁺ calcd for C₁₇H₁₇O, 232.0888; found, 232.0896.

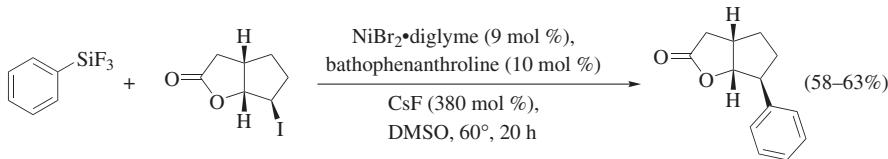


(*E*)-1-(4-Acetyl)phenyl-2-(4-ethoxycarbonyl)phenyl-1-hexene [One-Pot Sequential Heck/Hiyama Coupling Reaction of 2-Pyridylsilanes].¹⁷⁰ To a solution of $\text{Pd}(\text{OAc})_2$ (4.3 mg, 0.02 mmol, 10 mol %), tri-2-furylphosphine (5.1 mg, 0.02 mmol, 10 mol %), triethylamine (32.7 mg, 0.32 mmol), and ethyl 4-iodobenzoate (75.2 mg, 0.27 mmol) in THF (0.9 mL) was added (*E*)-dimethyl(2-pyridyl)(1-hexenyl)silane (65.7 mg, 0.30 mmol) under argon, and the reaction mixture was stirred at 60° for 3 h. After the mixture was cooled to rt, 4-iodoacetophenone (48.2 mg, 0.20 mmol) and TBAF (0.46 mmol, 1.0 M in THF) were added to the reaction mixture, and the reaction mixture was stirred at 60° for 14 h. The catalyst was removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated, and the residue was chromatographed on silica gel (hexane/EtOAc, 10:1) to afford the product (48.6 mg, 71%) as a colorless oil: IR (neat) 1105, 1271, 1603, 1684, 1717 cm^{-1} ; ^1H NMR (300 MHz) δ 0.84 (t, $J = 7.2$ Hz, 3H), 1.27–1.44 (m, 4H), 1.41 (t, $J = 7.2$ Hz, 3H), 2.63 (s, 3H), 2.73 (t, $J = 7.2$ Hz, 2H), 4.40 (q, $J = 7.2$ Hz, 2H), 6.77 (s, 1H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.53 (dm, $J = 8.4$ Hz, 2H), 7.98 (dm, $J = 8.4$ Hz, 2H), 8.06 (dm, $J = 8.7$ Hz, 2H); ^{13}C NMR (75 MHz) δ 13.8, 14.3, 22.6, 26.6, 29.9, 30.7, 60.9, 126.5, 128.4, 128.5, 128.9, 129.4, 129.7, 135.3, 142.7, 144.7, 147.1, 166.4, 197.6; HRMS–EI (*m/z*): [M]⁺ calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3$, 350.1882; found, 350.1884.

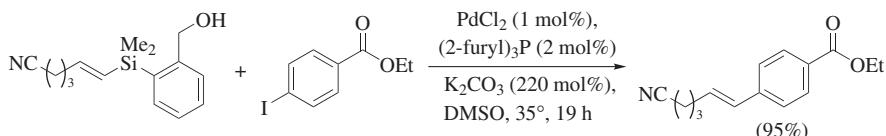


(*E*)-1-(4-Acetylphenyl)-2-nonen-1-one [Palladium-Catalyzed Carbonylative Coupling of an Alkenyltrifluorosilane with an Aryl Iodide].¹⁷⁹ To a THF (1.5 mL) solution of 1-(4-iodophenyl)ethanone (49 mg, 0.20 mmol), 1-(tri-fluoromethyl)-1-octene (59 mg, 0.30 mmol), and $[\text{allylPdCl}]_2$ (1.8 mg, 2.5 mol %) was added a THF (0.3 mL) solution of TBAF (1.0 M, 0.30 mmol) under 1 atm of carbon monoxide (balloon). After heating at 50° for 10 h, the reaction mixture was cooled to rt, and additional TBAF (0.15 mmol) was introduced. After the mixture was heated at 50° for 12 h, the solvent was removed under reduced pressure to give a crude product. Purification by silica gel column chromatography (hexane/Et₂O, 10:1) afforded 1-(4-acetylphenyl)-2-nonen-1-one (44 mg, 85%) as a colorless solid: mp 48–50°; IR (KBr) 2950, 1680, 1620, 1115, 1005, 960, 820 cm^{-1} ; ^1H NMR (90 MHz) δ 0.73–1.03 (m, 3H), 1.16–1.80 (m, 8H),

2.07–2.40 (m, 2H), 2.64 (s, 3H), 6.85 (d, $J = 17$ Hz, 1H), 6.90–7.15 (m, 1H), 8.00 (br s, 4H). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.96; H, 8.61.

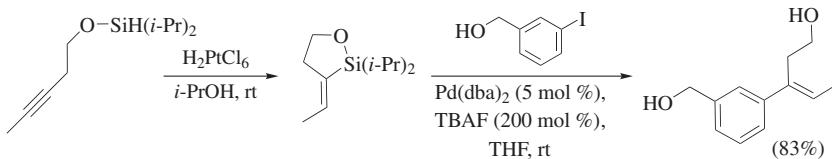


(3a*R*^{*,6*R*^{*,6a*S*^{*}})-6-Phenylhexahydrocyclopenta[*b*]furan-2-one [Nickel-Catalyzed Cross-Coupling of an Aryl trifluorosilane with a Secondary Alkyl Iodide].¹⁸⁹} $NiBr_2\bullet$ diglyme (23 mg, 0.09 mmol), bathophenanthroline (25 mg, 0.10 mmol), and CsF (574 mg, 3.8 mmol) were added to a 20-mL vial equipped with a stir bar; these compounds were weighed in air, and no special handling precautions were employed. The vial was sealed with a septum screw cap and then evacuated (vacuum pump, 0.5 mmHg) and backfilled with argon (three cycles). DMSO (14.0 mL) was added, and the greenish-yellow suspension was stirred for 10 min. Then phenyltrifluorosilane (1.5 mmol) was added. After the reaction mixture was stirred for an additional 10 min, the alkyl halide (1.0 mmol) was added, and the mixture was heated in an oil bath at 60° for 20 h, with vigorous stirring. The vial was kept sealed during heating and was not attached to an argon or nitrogen inlet. When the reaction was complete, the cooled reaction mixture was poured into Et_2O (50 mL) and filtered through a pad of silica gel, which was washed with Et_2O (3 × 40 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexanes/ $EtOAc$, 80:20) to afford the product (117–127 mg, 58–63%) as a colorless oil: R_f 0.15 (hexanes/ $EtOAc$, 80:20); IR (thin film) 2958, 1772 (br), 1495, 1452, 1164, 1036 cm⁻¹; ¹H NMR 300 MHz, $CDCl_3$) δ 1.52–1.66 (m, 1H), 1.78–1.90 (m, 1H), 2.21–2.31 (m, 2H), 2.42 (dd, $J = 18.0$ Hz, $J = 3.0$ Hz, H(3), 1H), 2.83 (dd, $J = 18.0$ Hz, $J = 10.0$ Hz, H(3), 1H), 2.93–3.05 (m, H(3a), 1H), 3.33 (ddd, $J = 10.0$ Hz, $J = 6.5$ Hz, $J = 4.0$ Hz, H(6), 1H), 4.92 (dd, $J = 7.5$ Hz, $J = 4.0$ Hz, H(6a), 1H), 7.23–7.27 (m, 3H), 7.31–7.37 (m, 2H); ¹³C NMR (75 MHz, $CDCl_3$) δ 32.0, 32.6, 35.6, 38.5, 51.9, 91.6, 126.6, 127.0, 128.6, 141.5, 177.1; HRMS–EI (m/z): [M]⁺ calcd for $C_{13}H_{14}O_2$, 202.0994; found, 202.0985.



(*E*)-6-(4-Ethoxycarbonylphenyl)-5-hexenenitrile [Brønsted Base Activated Coupling of a 2-Hydroxymethylphenylsilane].¹⁵¹ To a mixture of K_2CO_3 (304 mg, 2.2 mmol), tri(2-furyl)phosphine (4.6 mg, 20 μ mol), and $PdCl_2$ (1.8 mg, 10 μ mol) in DMSO (2.5 mL) were added the alkenylsilane (1.1 mmol)

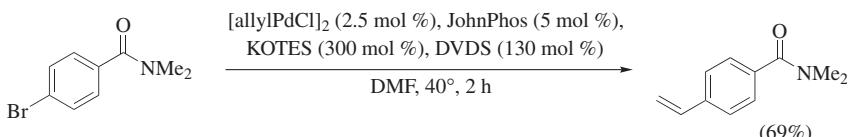
and ethyl 4-iodobenzoate (1.0 mmol) sequentially, and the resulting mixture was stirred at 35°. After 19 h, the mixture was diluted with Et₂O, washed with water and brine, and dried over anhydrous MgSO₄. Concentration in vacuo followed by flash chromatography on silica gel afforded the title product (95% yield) as a colorless oil: *R*_f 0.30 (hexanes/EtOAc, 5:1); IR (neat) 2984, 2937, 2907, 2243, 1711, 1607, 1458, 1437, 1414, 1366, 1271, 1180, 1126, 1109, 1092, 1024, 968, 955, 768, 750, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.39 (t, *J* = 7.2 Hz, 3H), 1.86 (m, 4H), 2.38–2.44 (m, 4H), 4.36 (q, *J* = 7.2 Hz, 2H), 6.22–6.31 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 2H), 7.98 (d, *J* = 6.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 14.3, 16.5, 24.8, 31.7, 60.9, 119.4, 125.9, 129.1, 129.9, 130.4, 131.2, 141.4, 166.4; EIMS (70 eV) *m/z* (%) 244 (14, M⁺ + 1), 243 (81, M⁺), 199 (15), 198 (100), 197 (16), 196 (19), 170 (12), 157 (14), 145 (15), 130 (14), 129 (43), 128 (22), 117 (57), 116 (16), 115 (40); HRMS-EI (70 eV) (*m/z*): [M]⁺ calcd for C₁₅H₁₇NO₂, 243.1259; found, 243.1259.



(E)-3-(3-Hydroxymethylphenyl)-3-penten-1-ol [Sequential Intramolecular Hydrosilylation/Cross-Coupling of a Homopropargyl Ether].²²⁴ To a solution of diisopropyl-(3-pentynyloxy)silane (10.2 g, 51.5 mmol) in 200 mL of dry CH₂Cl₂ at rt was added H₂PtCl₆·6H₂O (0.90 mL of 0.2 M solution in isopropyl alcohol, 0.18 mmol, 0.35% equiv). A vigorous exotherm was noted; the reaction mixture was cooled in a water bath, and stirring was continued for 70 min. The solvent was then evaporated in vacuo to give 10.7 g of an amber liquid. Fractional distillation of the liquid afforded the cyclic siloxane (8.50 g, 83%) as a colorless liquid: bp 57° (0.5 mm Hg); TLC *R*_f 0.74 (pentane/Et₂O, 4:1, SiO₂); GC *t*_R 5.56 min (100%) (HP-5, injector 225°, column 300°, 15 psi); IR (neat) 2941, 2865, 1643, 1463, 1053, 1022 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.01 (m, HC(8), H₃C(9), 14H), 1.77 (md, *J* = 6.6 Hz, H₃C(7), 3H), 2.47 (m, H₂C(4), 2H), 4.00 (t, *J* = 6.6 Hz, H₂C(5), 2H), 5.93 (m, HC(6), 1H); ¹³C NMR: (125.6 MHz, CDCl₃) δ 12.6 (C7), 16.8 (C8), 17.2/17.3 (C9'/C9), 32.5 (C4), 67.2 (C5), 133.5 (C6), 136.8 (C3); EIMS (70 eV) *m/z* (%): 198 (10, M⁺), 173 (15), 155 (100), 127 (60), 105 (26), 77 (45). Anal. Calcd for C₁₁H₂₂OSi: C, 66.60; H, 11.18; Si, 14.16. Found: C, 66.38; H, 11.29; Si, 14.28.

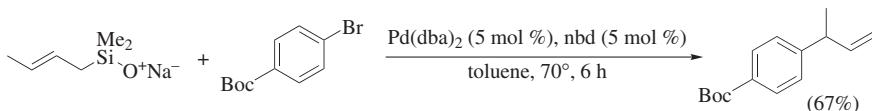
In a two-necked flask fitted with a rubber septum and gas inlet tube, the oxasilacyclopentane (248 mg, 1.25 mmol, 1.1 equiv) was dissolved in a solution of TBAF in THF (2.3 mL, 2.3 mmol, 2.0 equiv), and the mixture was stirred for 10 min at ambient temperature under nitrogen. 2-Iodobenzyl alcohol (264 mg, 1.13 mmol, 1.0 equiv) was added in three portions over 25-min intervals, and Pd(dba)₂ (32.4 mg, 0.0565 mmol, 0.050 equiv) was added following the first

portion of iodide. The mixture was stirred at rt for a total of 5 h. The crude mixture was then loaded onto 2 g of silica gel and was purified by column chromatography (SiO_2 , 31 g, pentane/ Et_2O , 9:7 to 1:1). Removal of the solvent and Kugelrohr distillation of the resulting oil afforded the title product (176 mg, 81%) as a colorless oil: bp 220° (air bath (0.08 mm Hg)); TLC R_f 0.32 (Et_2O , SiO_2); GC t_R 5.59 min (100%) (HP-5, injector 225°, detector 300°, column 270°, 15 psi); IR (CHCl_3) 3611 (s), 3012 (s), 2961 (m), 2937 (m), 2884 (m), 1603 (w), 1401 (s), 1384 (m), 1233 (m), 1016 (s), 908 (m) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.70 (br s, OH, 1H), 1.86 (d, J = 7.1 Hz, $\text{H}_3\text{C}(5)$, 3H), 2.84 (t, $\text{H}_2\text{C}(2)$, 2H), 3.64 (t, J = 6.9 Hz, $\text{H}_2\text{C}(1)$, 2H), 4.69 (s, $\text{H}_2\text{C}(7')$, 2H), 5.94 (q, J = 6.9 Hz, $\text{HC}(4)$, 1H), 7.23–7.31 (m, $\text{HC}(4')$, $\text{HC}(5')$, $\text{HC}(6')$, 3H), 7.36 (s, $\text{HC}(2')$, 1H); ^{13}C NMR (125.6 MHz, CDCl_3) δ 14.6 (C5), 33.0 (C2), 61.4 (C1), 65.6 (C7'), 125.1, 125.7, 125.8, 126.3, 128.8, 136.9, 141.2, 143.3; EIMS (70 eV) m/z (%): 192 (25, M^+), 174 (22), 156 (43), 143 (85), 129 (100), 117 (62), 103 (22), 91 (85), 77 (40). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.89; H, 8.15.

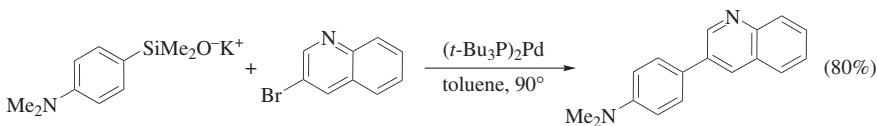


***N,N*-Dimethyl-4-ethenylbenzamide [Base-Promoted Vinylation of an Aryl Bromide with DVDS].**²⁶² To an oven-dried, 2-necked, 10-mL round-bottomed flask equipped with a magnetic stir bar, septum, and gas adapter was added allylpalladium chloride dimer (18 mg, 0.05 mmol, 0.025 equiv), and 2-(di-*tert*-butylphosphino)biphenyl (29 mg, 0.1 mmol, 0.05 equiv). The gas adapter was attached to an argon manifold, then evacuated and refilled with argon. After this evacuation/refill process was repeated two additional times, the flask was charged with DMF (2 mL) via syringe. The argon adapter was removed, and *N,N*-dimethyl-4-bromobenzamide (456 mg, 2 mmol) was quickly added as a solid, and the gas adapter was replaced. To the mixture was added DVDS (597 μL , 2.6 mmol, 1.3 equiv) neat, via syringe. The argon adapter was again removed, KOTES (1 g, 6.0 mmol, 3.0 equiv) was quickly added, and the argon adapter was replaced. An additional 2 mL of DMF was then added via syringe, and the mixture was placed in a preheated oil bath, warmed to 40°, and stirred for 2 h. After the reaction was determined to be complete by GC analysis, the mixture was cooled to rt, and then was partitioned between EtOAc (50 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (50 mL), and the organic layers were washed with water (50 mL). The organic phases were combined, dried over Na_2SO_4 , and then were filtered and concentrated in vacuo (rt, 50 mm Hg). Purification of the crude product by column chromatography (silica gel, 30 mm x 120 mm, hexane/EtOAc, 3/2) afforded the product (242 mg, 69%) as a white solid: mp 48–50°; TLC R_f 0.2 (SiO_2 , hexane/EtOAc, 3:2); IR 2930 (m), 1653 (m), 1616 (s), 1559 (w), 1517 (w), 1490 (m), 1448 (w), 1395 (s), 1265 (m),

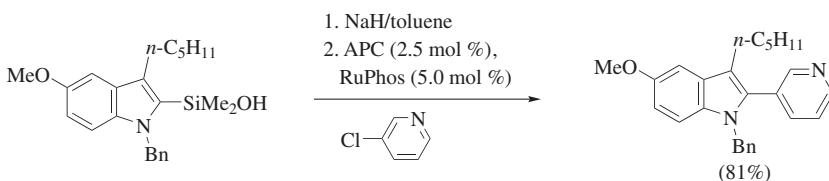
1219 (w), 1180 (w), 1083 (m), 1016 (w), 998 (w), 939 (w), 920 (w), 852 (m), 775 (w), 734 (w) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.98 (s, HC(8), 3H), 3.10 (s, HC(8), 3H), 5.30 (d, J = 10.9, H_{cis} C(1), 1H), 5.79 (d, J = 17.6, H_{trans} C(1), 1H), 6.71 (dd, J = 17.6, J = 10.9, HC(2), 1H), 7.38 (d, J = 8.3, HC(5), 2H), 7.42 (d, J = 8.3, HC(4), 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 35.6 (C8), 39.8 (C8), 115.38 (C1), 126.3 (C4), 127.7 (C5), 135.8 (C6), 136.4 (C2), 139.0 (C3), 171.62 (C7); EIMS (70 eV) m/z (%): 175 (29, M^+), 174 (25), 132 (12), 131 (100), 105 (18), 103 (28), 77 (32).



4-(1-Methyl-2-propen-1-yl)benzoic Acid, 1,1-Dimethylethyl Ester [Self-Activated Cross-Coupling of Sodium 2-Butenyltrimethylsilanolate with an Aryl Bromide].¹⁰⁸ To an oven-dried, single-neck, 5-mL round-bottomed flask containing a magnetic stir bar, equipped with a reflux condenser and an argon inlet capped with a septum, was added $\text{Pd}(\text{dba})_2$ (28.8 mg, 0.05 mmol, 0.05 equiv). The flask was then sequentially evacuated and filled with argon three times. Then *tert*-butyl 4-bromobenzoate (257 mg, 1.0 mmol) was added by syringe. Sodium 2-butenyltrimethylsilanolate (308 mg, 2.0 mmol, 2.0 equiv), pre-weighed into a 10-mL, two-necked round-bottomed flask in a drybox, was dissolved in toluene (2.0 mL), and then norbornadiene (nbd, 5.2 μL , 0.05 mmol, 0.050 equiv) was added by syringe. The solution of the silanolate and nbd in toluene was added to the aryl bromide by syringe. The reaction mixture was heated under argon to 70° in a preheated oil bath. After 6 h, the mixture was cooled to rt, filtered through silica gel (2 cm x 2 cm) in a glass-fritted filter (coarse, 2 cm x 5 cm), and the filter cake washed with Et_2O (3 \times 10 mL). The filtrate was concentrated (rt, 20 mm Hg) and the residue was purified by silica gel chromatography (20 cm x 20 mm, hexane/EtOAc, gradient 100:0 to 20:1), followed by Kugelrohr distillation, to afford the product (155 mg, 67%) as a clear, colorless oil: bp 155° (5 mmHg, ABT); TLC R_f 0.33 (hexane/EtOAc, 20:1) [silica gel, UV]; GC $\gamma-t_R$: 6.70 min, $\alpha-t_R$: 6.88 and 6.95 min (25:1 [3.2:1], $\gamma:\alpha$ [(E) or (Z)]) IR (film) 2975 (m), 2931 (m), 1718 (s), 1700 (m), 1636 (w), 1610 (m), 1578 (w), 1507 (w), 1477 (m), 1457 (m), 1413 (m), 1392 (m), 1368 (m), 1291 (s), 1256 (m), 1167 (m), 1117 (m), 1017 (m), 915 (m), 849 (m), 771 (m), 708 (m) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.37 (d, J = 7.0 Hz, HC(5), 3H), 1.59 (s, HC(11), 1H), 3.51 (ap, J = 7.0 Hz, HC(6), 1H), 5.05 (m, HC(8), 2H), 5.98 (ddd, J = 17.7 Hz, J = 9.8 Hz, J = 6.4 Hz, HC(7), 1H), 7.26 (m, HC(2), 2H), 7.93 (m, HC(3), 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 20.8 (C5), 28.5 (C11), 43.3 (C6), 81.0 (C10), 114.0 (C8), 127.4 (C2), 129.9 (C3), 130.2 (C4), 142.7 (C7), 150.6 (C1), 166.0 (C9); EIMS (70 eV) m/z (%): 232 (12, M^+), 176 (48), 159 (53), 131 (100), 117 (37), 84 (18). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68. Found: C, 77.28; H, 8.72.

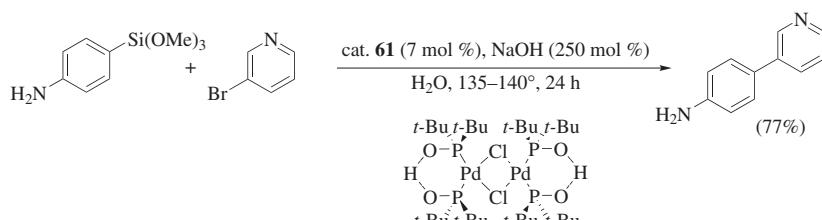


3-(4-N,N-Dimethylaminophenyl)quinoline [Self-Activated Cross-Coupling of a Potassium Dimethylarylsilanolate with an Aryl Bromide].⁵⁴ In an oven-dried, 5-mL, round-bottomed flask equipped with a magnetic stir bar, reflux condenser, and three-way argon adapter was charged $(t\text{-Bu}_3\text{P})_2\text{Pd}$ (12.8 mg, 0.025 mmol, 2.5 mol %) in a drybox. The flask was sealed away from the atmosphere and removed to a hood. Dry toluene (2 mL) was added via syringe through the three-way adapter, resulting in a colorless solution on stirring. 3-Bromoquinoline (136 mL, 1.0 mmol, 1.0 equiv) and potassium (4-dimethylaminophenyl)dimethylsilanolate (350 mg, 1.5 mmol, 1.5 equiv) were added sequentially by removal of the adapter, adding the reagents as liquid and solid, respectively, and replacing the adapter as quickly as possible. The flask was placed into a preheated 90° oil bath and stirred at 90° under a static flow of argon. After 3 h, the mixture was cooled to rt and poured onto water (10 mL). The aqueous layer was extracted with EtOAc (3×20 mL), and the organic extracts were washed with brine (15 mL) and dried (MgSO_4 , 5 g). Purification by MPLC (24 g of SiO_2 , 30 mL/min, hexane/EtOAc 9:1, 3 CV), gradient to hexane/EtOAc 3:2 (5 CV), hexane/EtOAc 3:2 (6 CV), followed by sublimation (80° , 0.1 mmHg), afforded analytically pure yellow-colored plates (198 mg, 80%): mp 127–129°; TLC R_f 0.26 (SiO_2 , hexanes/EtOAc, 3:2); IR (KBr) 2952 (w), 2849 (w), 2798 (w), 1602 (s), 1525 (s), 1355 (m), 1292 (w), 1212 (m), 1061 (w), 950 (w), 813 (s) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.03 (s, $\text{H}_3\text{C}(5')$, 6H), 6.86 (d, $J = 8.9$ Hz, $\text{HC}(3')$, 2H), 7.54 (ddd, $J_1 = 1.4$ Hz, $J_2 = 7.0$ Hz, $J_3 = 8.3$ Hz, $\text{HC}(5)$, 1H), 7.64 (d, $J = 8.9$ Hz, $\text{HC}(2')$, 2H), 7.67 (ddd, $J_1 = 1.4$ Hz, $J_2 = 7.0$ Hz, $J_3 = 8.3$ Hz, $\text{HC}(4)$, 1H), 7.84 (d, $J = 8.4$ Hz, $\text{HC}(6)$, 1H), 8.11 (d, $J = 8.4$ Hz, $\text{HC}(3)$, 1H), 8.22 (d, $J = 2.2$ Hz, $\text{HC}(7)$, 1H), 9.19 (d, $J = 2.2$ Hz, $\text{HC}(2)$, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 40.4 ($\text{C}5'$), 40.5 ($\text{C}5'$), 112.8 ($\text{C}3'$), 125.4 ($\text{C}9$), 126.7 ($\text{C}5$), 127.7 ($\text{C}6$), 128.0 ($\text{C}2'$), 128.3 ($\text{C}1$), 128.6 ($\text{C}4$), 129.1 ($\text{C}3$), 131.3 ($\text{C}7$), 133.8 ($\text{C}4'$), 146.7 ($\text{C}8$), 149.9 ($\text{C}2$), 150.4 ($\text{C}1'$); EIMS (70 eV) m/z (%): 248 (M^+ , 100), 232 (12), 218 (1), 204 (12), 176 (4), 151 (2), 124 (10), 102 (6), 88 (4); HRMS (m/z): $[\text{M}]^+$ calcd $\text{C}_{17}\text{H}_{16}\text{N}_2$, 248.1314; found, 248.1312. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_3$: C, 82.22; H, 6.49; N, 11.28. Found: C, 81.88; H, 6.46; N, 11.23.



1-Benzyl-5-methoxy-3-pentyl-2-(pyridin-3-yl)-1*H*-indole [Brønsted Base Promoted Cross-Coupling of an Indolylsilanol with an Aryl Chloride].²⁰⁹

To a flame-dried, 5-mL round-bottomed flask equipped with a stir bar was added NaH (29 mg, 1.2 mmol, 1.2 equiv) and toluene (0.4 mL) under dry argon atmosphere inside a drybox. In a separate flame-dried 5-mL conical flask was added *N*-benzyl-5-methoxy-3-pentyl-(2-indolyl)dimethylsilanol (458 mg, 1.2 mmol, 1.2 equiv) in toluene (2.0 mL); this silanol solution was added dropwise to the above suspension by glass pipette. The conical flask containing the silanol was washed with toluene (0.4 mL), and the rinse was added to the reaction mixture. The resulting mixture was stirred for 10 min whereupon 3-chloropyridine (95 mL, 1.0 mmol, 1.0 equiv), RuPhos (23 mg, 0.05 mmol, 0.05 equiv), and APC (9 mg, 0.025 mmol, 0.025 equiv) were added. The flask was sealed with a rubber septum and removed from the drybox. After being stirred at 70° for 1 h, the black, crude reaction mixture was filtered through a plug of silica gel (3 g), which was eluted with EtOAc (200 mL) to give a light-yellow solution that was concentrated under reduced pressure. The resulting yellow semi-solid was purified by silica gel column chromatography (20 × 100 mm) and eluted with hexane/EtOAc 4:1 (30 × 10-mL fractions). The combined fractions were further purified by concentration and recrystallization in boiling hexane (2 mL) to afford the product (312 mg, 81%) as light-yellow plates: mp 101–102° (hexane); TLC R_f 0.09 (SiO₂, hexane/EtOAc, 4:1) [silica gel, UV]; IR (Nujol) 3057 (w), 3026 (w), 2958 (s), 2940 (s), 2911 (s), 2857 (s), 1612 (w), 1581 (w), 1568 (w), 1543 (w), 1496 (w), 1484 (m), 1468 (s), 1453 (s), 1424 (m), 1377 (m), 1351 (m), 1223 (m), 1181 (m), 1169 (m), 1100 (w), 1043 (m), 1029 (m), 1021 (m), 832 (m), 810 (s), 718 (s) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.83 (t, *J* = 6.8 Hz, HC(5''), 3H), 1.26 (m, HC(3''), HC(4''), 4H), 1.62 (m, HC(2''), 2H), 2.66 (t, *J* = 7.6 Hz, HC(1''), 2H), 3.90 (s, HC(10), 3H), 5.16 (s, HC(1'), 2H), 6.86 (m, HC(3'), HC(6), 3H), 7.11 (m, HC(7), HC(4), 2H), 7.23 (m, HC(5'), HC(4'), 3H), 7.31 (dd, *J* = 7.8 Hz, *J* = 4.9 Hz, HC(5''), 1H), 7.56 (dt, *J* = 7.8 Hz, *J* = 2.0 Hz, HC(6''), 1H), 8.58 (d, *J* = 1.8 Hz, HC(2''), 1H), 8.61 (dd, *J* = 4.9 Hz, *J* = 1.7 Hz, HC(4''), 1H); ¹³C NMR (125.6 MHz, CDCl₃) δ 14.0 (C5''), 22.4 (C4''), 24.5 (C1''), 30.6 (C2''), 31.7 (C3''), 47.6 (C1'), 55.9 (C10), 101.4 (C4), 111.0 (C7), 112.2 (C6), 115.6 (C3), 123.1 (C5''), 125.8 (C3'), 127.2 (C5'), 128.2 (C2), 128.3 (C2'), 128.6 (C4'), 132.5 (C1'), 134.5 (C9), 137.6 (C6''), 138.1 (C8), 149.1 (C2''), 151.0 (C4''), 154.1 (C5); EIMS (70 eV) *m/z* (%): 384 (55, M⁺), 327 (100), 277 (10), 193 (7), 91 (92). Anal. Calcd for C₂₆H₂₈N₂O: C, 81.21; H, 7.34; N, 7.29. Found: C, 80.92; H, 7.42; N, 7.24.



4-(3-Pyridyl)aniline [Cross-Coupling of an Aryltrialkoxysilane with an Aryl Bromide in Aqueous NaOH].²⁴⁵ A mixture of 3-bromopyridine, (100 mg), catalyst **61** (7 mol %), and 4-aminophenyltrimethoxysilane (2 equiv) was stirred in 5 mL of 0.5 M aqueous NaOH at 135° for 24 h using a closed vessel. The reaction mixture was allowed to cool to rt, and then was quenched with water and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, and the solvents were removed under vacuum. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc/Et₃N, 100:10:1) to afford the coupling product (77%): ¹H NMR (300 MHz, CDCl₃) δ 3.75 (bs, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 7.30 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.79 (ddd, *J* = 2.2 Hz, *J* = 2.2 Hz, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 5.0 Hz, 1H), 8.77 (bs, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 115.7, 123.7, 127.8, 128.2, 133.8, 136.9, 146.9, 147.1, 147.5; EIMS (70 eV) *m/z* (%): 169 (100, M⁺-H), 142 (14, M⁺-H,-HCN), 117 (9, M⁺-HCN,-C₂H₂).

TABULAR SURVEY

The tables are organized by the structure of the transferable group attached to silicon and the structure of the electrophile. Thus, the primary rubric of the tables follows the order: arylsilanes (Table 1), heteroarylsilanes (Table 2), alkenylsilanes (Table 3), alkynylsilanes (Table 4), sp³ (i.e. alkyl) silanes (Table 5) and acylsilanes (Table 6). Table 7 contains oxidative Heck reactions for completeness. Carbons attached to the transferable group through heteroatoms are not counted. The secondary rubric (i.e. A, B, C, etc.) follows the order: aryl electrophiles, heteroaryl electrophiles, alkenyl electrophiles, alkynyl electrophiles, allyl electrophiles, and alkyl electrophiles. This organization is intentionally different from that in the “Scope and Limitations” section to allow the reader to make direct comparisons of substrate types independent of the nature of the silicon donor group. Although this organization allows the reader to identify which silicon moiety would be most suitable for a given pair of transferable group and electrophile, a hierarchy for presenting the various silicon groups had to be constructed that would be consistent across all tables. The hierarchy proceeds as follows: (1) increasing number of heteroatoms on silicon, (2) total carbon count of carbon moieties bonded to silicon, (3) atomic number of substituents on silicon, and (4) carbon count of heteroatomic substituents bonded to silicon. A graphical illustration of that hierarchy is found in Figure 5.

A series of charts precedes the tables. These charts depict catalysts, ligands, and reagents that are indicated by bold numbers in the table entries, and are arranged primarily by structural type. The reader is referred to these charts to locate the structure with which the bold numbers are associated.

The tables cover the literature through 2008.

The following abbreviations are used in the tables:

Bphen	1,10-phenanthroline
Cy ₃ P(O)	tricyclohexylphosphine oxide

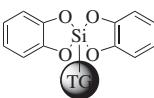
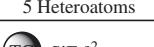
0 Heteroatoms	1 Heteroatom	2 Heteroatoms	3 Heteroatoms	4 Heteroatoms
				
				
				
				
				
				
				
				
				
				
				
				
				
				

Figure 5. Hierarchy of silicon groups for the third rubric in the tables.

dCypb	1,4-(dicyclohexylphosphino)butane
(-)-DIOP	1,1'-{[(4 <i>R</i> , 5 <i>R</i>)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis(methylene)}bis[1,1-diphenylphosphine]
DMI	1,3-dimethyl-2-imidazolidinone
DMPU	1,3-dimethyl-3,4,5,6-tetrahydro-2(1 <i>H</i>)-pyrimidinone
DVDS	divinyltetramethylsiloxane
glyme	1,2-dimethoxyethane
MW	microwave irradiation
NaHMDS	sodium bis(trimethylsilyl)amide
nbd	norbornadiene
PEG	polyethylene glycol
SCS	sodium dodecyl sulfate
TBAB	tetra- <i>n</i> -butylammonium bromide
TBAC	tetra- <i>n</i> -butylammonium chloride
TBAT	tetra- <i>n</i> -butylammonium difluorotriphenylsiliconate
TBOH	tetra- <i>n</i> -butylammonium hydroxide

CHART 1. LIGANDS USED IN TABLES

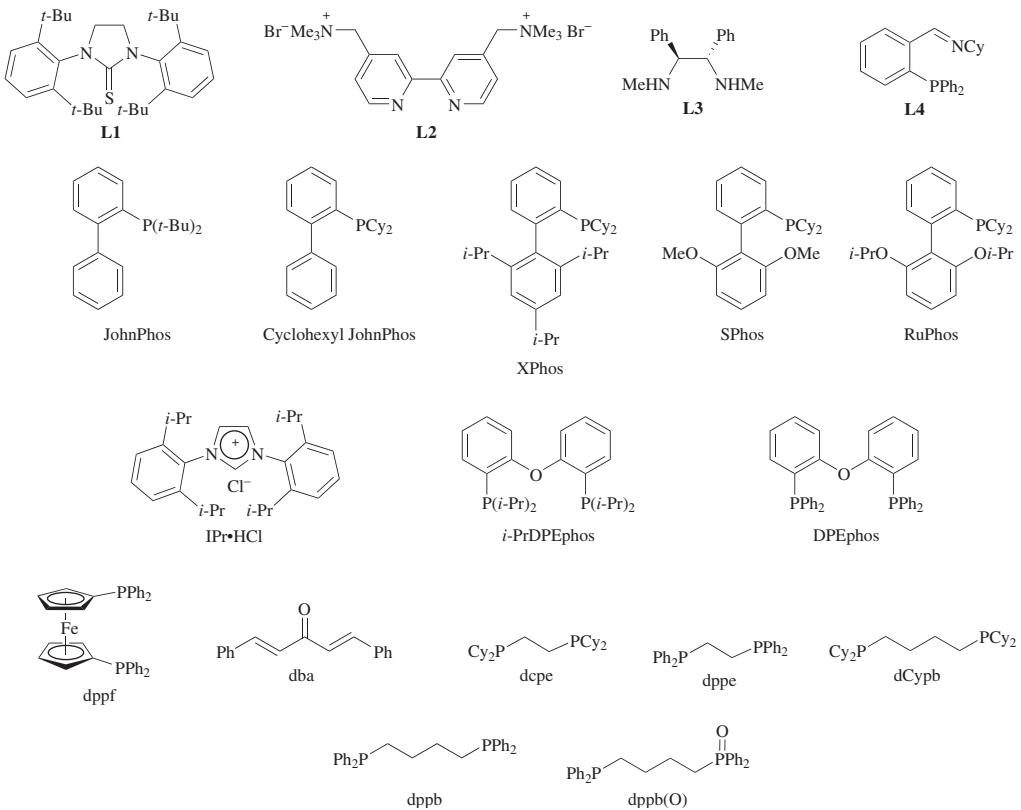


CHART 2. PALLADIUM CATALYSTS USED IN TABLES

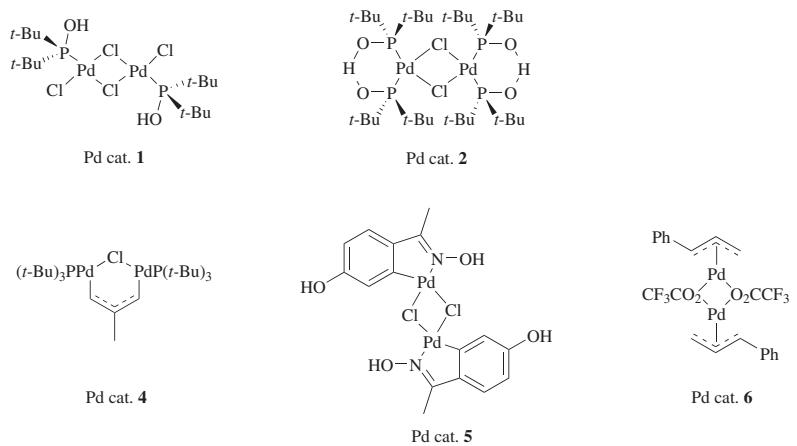


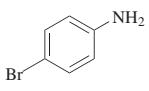
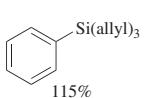
TABLE 1A. CROSS-COUPING OF ARYLSILANES WITH ARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		CuI (5%), TBAF (120%), MeCN, rt, 5 min	 (76)	178
		CuI (5%), TBAF (120%), MeCN, rt, 5 min	 (73)	178
		Pd(PPh ₃) ₄ (5%), dioxane, reflux, 60 h	 (75)	87
		Pd(dba) ₂ (10%), Cyclohexyl JohnPhos (20%), TBAF·3H ₂ O (200%), H ₂ O (2000%), THF, reflux, 12 h	 (75)	260
		PdCl ₂ (5%), TBAF·3H ₂ O (200%), toluene, 100°, 10 h	 (31)	237
		Pd(OAc) ₂ (3%), L1 (12%), TBAF·3H ₂ O (200%), acetone, 80°, 24 h	 (35)	238

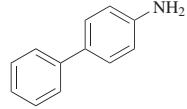
200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(96)	237
120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(96)	234
400%		Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (400%), dioxane, 80°, 4 h		(82)	238
 200%		[allylPdCl] ₂ (2.5%), DMSO, 120°, 2 h		(85)	270
200%		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h		(100)	186
200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(90)	237
120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(94)	234

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 316			Pd(OAc) ₂ (3%), L1 (12%), TBAF·3H ₂ O (200%), dioxane, 80°, 1 h 	(86) 238
		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85° 		(82) 232
		Pd(OAc) ₂ (10%), P(o-tol) ₃ (20%), TBAF (200%), DMF, 85° 		(75) 232
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90° 		(87) 248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90° 		(92) 248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80° 		(97) 249

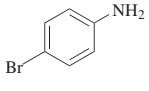
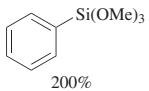


TBAF•3H₂O (460%),
PdCl₂ (5%),
PCy₃ (10%),
DMSO/H₂O (10:1), 80°, 3 h

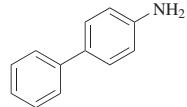


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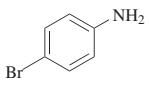
Pd(OAc)₂ (10%),
PPh₃ (20%),
TBAF (200%), DMF, 85°



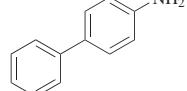
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200%

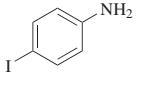
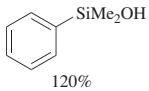


Pd(OAc)₂ (10%),
P(o-tol)₃ (20%),
TBAF (200%), DMF, 85°

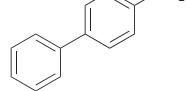


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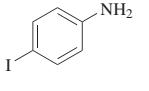
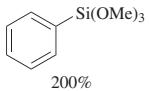


Pd(PPh₃)₄ (3%),
Ag₂O (100%),
TBAT (12%),
THF, 70°, 0.5 h

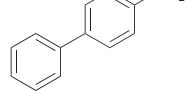


(52)

201

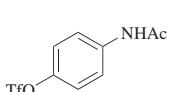
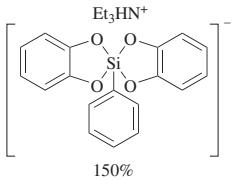


Pd(OAc)₂ (10%),
PPh₃ (20%),
TBAF (200%),
DMF, 85°

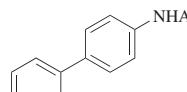


(95)

232



Pd(dba)₂ (5%),
Cyclohexyl JohnPhos (5%),
TBAF (150%), THF,
reflux, 6 h



(92)

276

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
200%		Pd(OAc) ₂ (10%), P(o-tol) ₃ (20%), TBAF (200%), DMF, 85°		(77)
200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85°		(70)
200%		Pd(OAc) ₂ (10%), P(o-tol) ₃ (20%), TBAF (200%), DMF, 85°		(72)
200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85°		(65)
200%		PdCl ₂ (5%), TBAF·3H ₂ O (200%), toluene, 100°, 10 h		(87)
200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85°		(69)

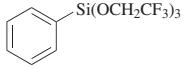
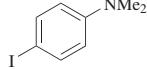
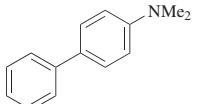
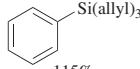
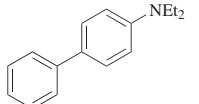
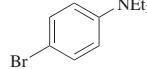
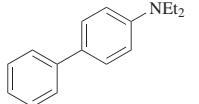
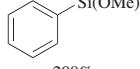
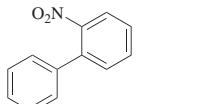
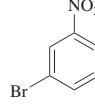
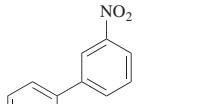
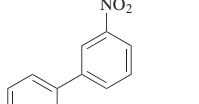
	200%					
		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85°		(85)		232
	115%	TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (20:1), 80°, 3 h		(88)		47
	110%	1. TBAF (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 5 h		(75)		46
	200%	Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 85°		(58)		232
	200%	Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (200%), dioxane, 80°, 24 h		(66)		238
	120%	Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(93)		234

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 Ph-Si(F) ₂ -Ph	 TfO	Pd(dba) ₂ (10 mol%), THF, 95°, 2.5 h	 (73)	69
 200%	 TfO	Pd(dba) ₂ (10%), TBAF·3H ₂ O (200%), PPh ₃ (20%), H ₂ O (1000%), THF, reflux, 2 h	 (50)	260
 Et ₃ HN ⁺ 150%	 TfO	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (46)	276
 Ph-Si(F) ₂ -Ph	 Cl	[allylPdCl] ₂ (2.5%), DMSO, 120°, 26 h	 (54)	270
 Si(OMe) ₃ 200%	 Cl	PdCl ₂ (5%), TBAF·3H ₂ O (200%), toluene, 100°, 10 h	 (90)	237

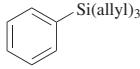
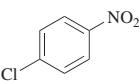
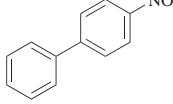
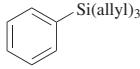
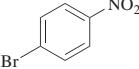
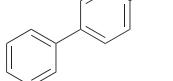
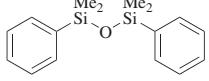
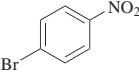
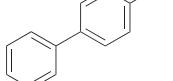
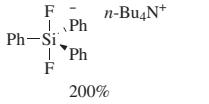
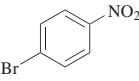
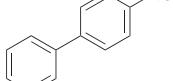
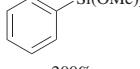
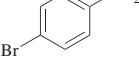
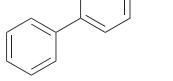
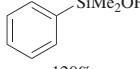
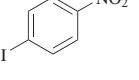
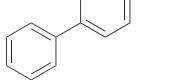
	400%		Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (400%), dioxane, 80°, 24 h		(78)	238
	115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 4 h		(87)	47
	150%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAT (10%), dioxane, 70°, 1 h		(92)	201
	200%		[allylPdCl] ₂ (2.5%), DMSO, 120°, 4 h		(77)	270
	200%		Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (200%), dioxane, 80°, 24 h		(81)	238
	120%		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70°, 0.5 h		(78)	201

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 150%	 I	Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAT (10%), THF, 70°, 1 h	 NO ₂	(85) 201
 1 mmol per unit	 I	Pd(PPh ₃) ₃ (5%), Ag ₂ O (100%), THF, 60°, 24 h	 NO ₂	(96) 268
 200%	 I	[allylPdCl] ₂ (2.5%), DMSO, 120°, 1.5 h	 NO ₂	(89) 270
 200%	 TfO	Pd(dba) ₂ (10%), Cyclohexyl JohnPhos (20%), TBAF•3H ₂ O (200%), H ₂ O (2000%), THF, reflux, 12 h	 MeO	(90) 260
 150%	 TfO	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 MeO	(95) 276

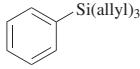
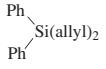
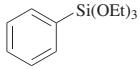
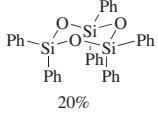
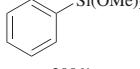
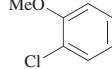
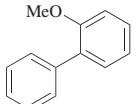
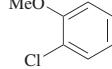
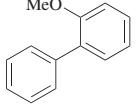
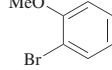
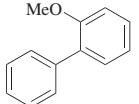
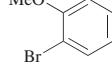
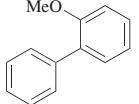
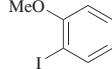
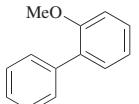
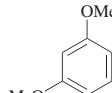
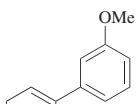
	125%				
	150%				
	120%				
	20%				
	200%				
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h		(94)	47
		TBAF•3H ₂ O (600%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (25:1), 80°, 12 h		(79)	47
		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(90)	234
		Pd(NH ₃) ₂ Cl ₂ (1%), L2 (1%), NaOH (200%), H ₂ O, 120°, 3 h		(46)	246
		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1: 1), reflux, 4 h		(87)	265
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH, 90°		(94)	248

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(97)
200%				248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(85)
200%				249
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h		(99)
125%				47
		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1) 135–140°, 24 h		(73)
200%				269
		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(87)
200%				237

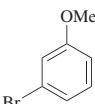
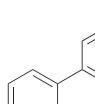
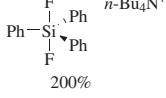
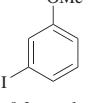
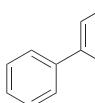
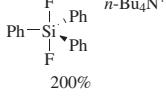
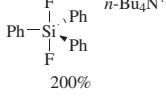
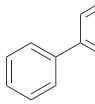
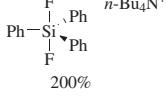
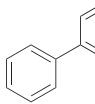
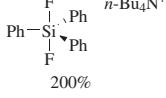
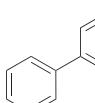
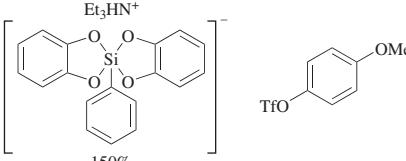
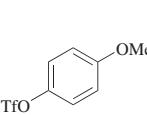
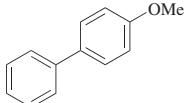
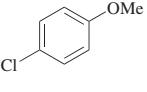
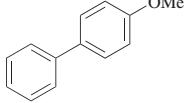
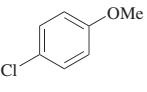
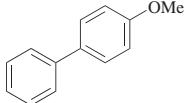
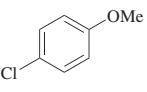
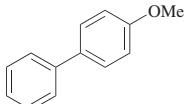
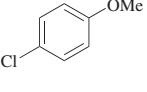
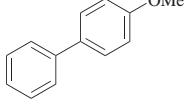
 1 mmol per unit	 120%	 (90)	234	
	 200%	 0.2 mmol	 (59)	268
	 200%	 0.2 mmol	 (87)	269
	 200%	 0.2 mmol	 (59)	186
	 200%	 0.2 mmol	 (78)	246
	 200%	 0.2 mmol	 (90)	260

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (96)	276
Ph ₂ Si(allyl) ₂ 150%		TBAF•3H ₂ O (600%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (25:1), 80°, 8 h	 (93)	47
Ph ₂ Si(allyl) ₂ 105%		TBAF•3H ₂ O (330%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (40:1), 80°, 12 h	 (86)	47
Ph ₂ Si(OMe) ₃ 200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 80°, 45 h	 (29)	236
Ph ₂ Si(OMe) ₃ 200%		Pd ₂ dba ₃ (10%), Cyclohexyl JohnPhos (15%), TBAF (200%), DMF, 87°, 27 h	 (71)	236

200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(11)	237
200%		Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (20%), dioxane, 80°, 48 h		(11)	238
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h		(92)	47
125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h		(97)	47
110%		1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (2:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%) 80°, 6 h		(100)	46
150%		TBAF•3H ₂ O (600%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (15:1), 80°, 11 h		(93)	47

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆						
	 150%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAT (10%), dioxane, 70°, 1 h		(31)	201
			Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 4 h		(91)	265
328	 200%		Pd(OAc) ₂ (5%), PPh ₃ (10%), TBAF (200%), DMF, 90°, 24 h		(87)	236
	 200%		Pd(OAc) ₂ (10%), P(o-tol) ₃ (20%), TBAF (200%), DMF, 90°, 24 h		(70)	236
	 120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(92)	234

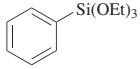
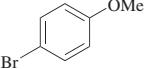
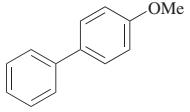
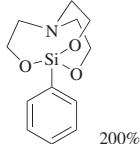
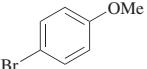
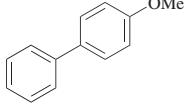
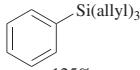
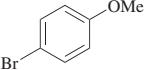
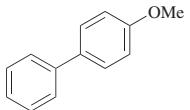
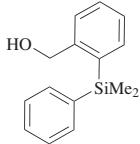
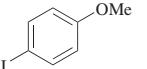
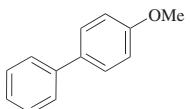
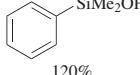
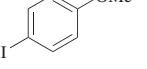
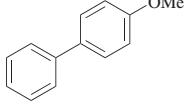
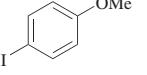
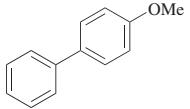
	Br		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 24 h		(78)	246
	Br		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF•3H ₂ O (200%), THF, reflux, 2 h		(73)	260
	Br		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h		(97)	47
	I		PdCl ₂ (3%), CuI (10%), L4 (4%), K ₂ CO ₃ (200%), H ₂ O (200%), DMSO, 50°, 16 h		(99)	151
	I		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(35)	37
	I		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70°, 0.5 h		(85)	201

TABLE 1A. CROSS-COUPLED OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆						
	 150%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAT (10%), THF, 70°, 1 h		(96)	201
	 120%		Pd(OAc) ₂ (5%), Ag ₂ O (100%), THF, 60°, 7 h		(51)	203
330	 120%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(93)	37
	 120%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(80)	37
	 1 mmol per unit		0.2 mmol Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 20 h		(52)	268
			Pd ₂ dba ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 20 h		(79)	268

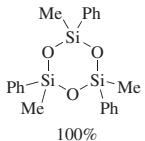
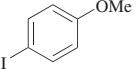
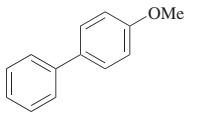
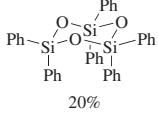
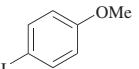
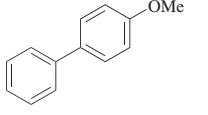
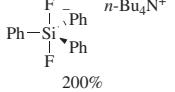
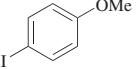
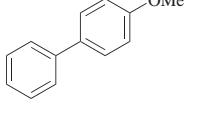
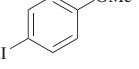
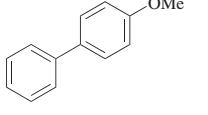
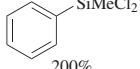
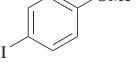
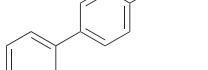
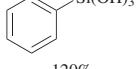
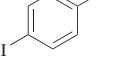
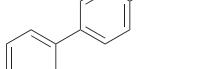
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 120 h		(39)	268
		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 4 h		(91)	265
		[allylPdCl] ₂ (10%), DMF, 95°, 19 h		(97)	69
		Pd(dba) ₂ (10%) THF, 95°, 2.5 h		(88)	69
		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h		(80)	186
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(83)	37

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

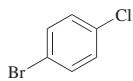
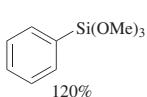
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆					
		Pd(dba) ₂ (9%), TBAF (360%), DMF, 95°, 2 h		(54)	70
250%					
		Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (20%), dioxane, 80°, 1 h		(95)	238
200%					
		Pd(dba) ₂ (9%), TBAF (190%), DMF, 95°, 2 h		(77)	70
190%					
		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF•3H ₂ O (200%), THF, reflux, 2 h		(78)	260
200%					
		[allylPdCl] ₂ (2.5–5.0%), KF (200%), DMF, 70°, 10 h		(81)	73
120–150%					
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (150%), THF/t-BuOH (1:1), 90°		(70)	248
200%				(22)	

		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (300%), THF/t-BuOH (1:1), 90°		(18)		(68)	248
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(85)			47
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(91)			47
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 2 h		(95)			47
		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 2 h		(85)			265
		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(92)			234
200%							
125%							
125%							
115%							
20%							
120%							

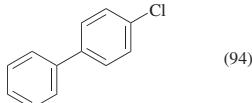
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 20%		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 9 h	 (67)	265
 20%		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 24 h	 (70)	265
 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 10 h	 (87)	47
		1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 12 h	 (93)	160
 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 12 h	 (98)	47

335

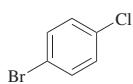


Na_2PdCl_4 (1.5%),
SDS (20%),
 NaOH (600%),
 H_2O , 100°, 5 min

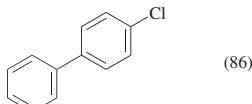


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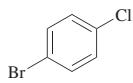
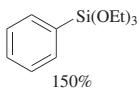
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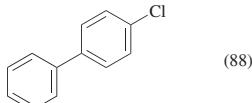
$\text{Pd}(\text{OAc})_2$ (3%), **L1** (12%),
TBAF•3H₂O (200%),
dioxane, 80°, 4 h



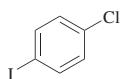
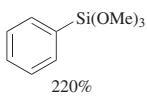
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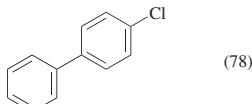
$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ (0.01%),
L2 (0.01%),
 NaOH (200%),
 H_2O , 120°, 36 h



246

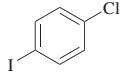


$\text{Pd}(\text{dba})_2$ (9%),
TBAF (220%),
DMF, 95°, 2 h

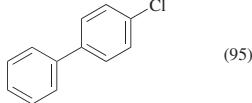


70

200%

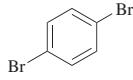


$\text{Pd}(\text{OAc})_2$ (3%), **L1** (12%),
TBAF•3H₂O (200%),
dioxane, 80°, 2 h

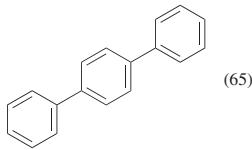


238

400%

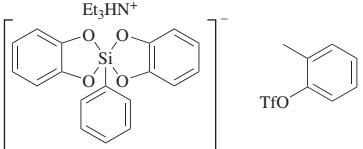
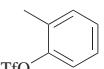
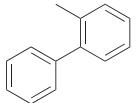
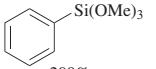
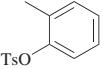
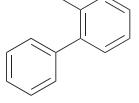
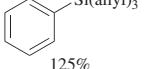
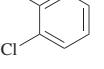
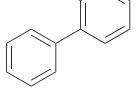
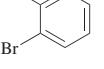
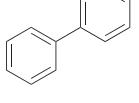
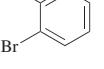
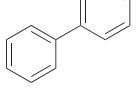


$\text{Pd}(\text{OAc})_2$ (3%), **L1** (12%),
TBAF•3H₂O (400%),
dioxane, 80°, 6 h



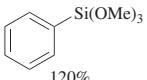
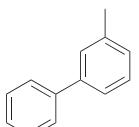
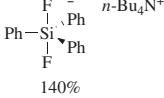
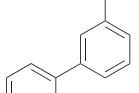
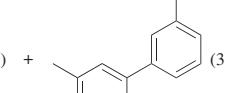
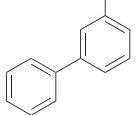
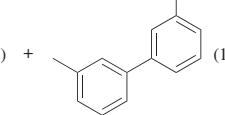
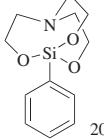
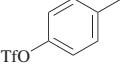
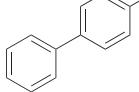
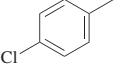
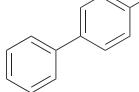
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TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (92)	276
 200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (30)	249
 125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 16 h	 (88)	47
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h	 (91)	47
150%		TBAF•3H ₂ O (600%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (15:1), 80°, 14 h	 (87)	47

		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h		(67)	269
200%					
		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(81)	237
200%					
120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(92)	234
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(84)	37
120%					
		[allylPdCl] ₂ (10%), DMF, 95°, 4 h		(93) +	(2) 69
140%					
200%		Pd(dba) ₂ (10%), THF, 95°, 5 h		(90)	69
		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(90)	237
200%					

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min	 (86)	234
		[allylPdCl] ₂ (10%), DMF, 95°, 24 h	 (97) +  (3)	69
200%		Pd(dba) ₂ (10%), THF, 95°, 26.5 h	 (68) +  (10)	69
		Pd(dba) ₂ (10%), Cyclohexyl JohnPhos (20%), TBAF•3H ₂ O (200%), H ₂ O (2000%), THF, reflux, 12 h	 (87)	260
125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h	 (98)	47

		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 110°, 18 h		(99)	241
120%					
200%		Pd ₂ dba ₃ (10%), Cyclohexyl JohnPhos (15%), TBAF (200%), DMF, 87°, 27 h		(63)	236
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/ H ₂ O (10:1), 80°, 3 h		(96)	47
115%					
200%		Pd(OAc) ₂ (3%), PPh ₃ (6%), TBAF (200%), DMF, 90°, 24 h		(77)	236
200%		Pd(OAc) ₂ (10%), P(<i>o</i> -tol) ₃ (20%), TBAF (200%), DMF, 90°, 24 h		(78)	236
200%		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(71)	245
200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(98)	237

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min	 (94)	234
200%		Pd(OAc) ₂ (3%), L1 (12%), TBAF·3H ₂ O (200%), dioxane, 80°, 4 h	 (39)	238
120%		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70°, 0.5 h	 (100)	201
120%		Pd(PPh ₃) ₄ (5 %), Ag ₂ O (1 eq), THF, 60°, 12 h	 (81)	37
200%		CuI (200%), NaOC ₆ H ₅ (200%), DMI, 130°, 12 h	 (20)	231
140%		[allylPdCl] ₂ (10%), DMF, 95°, 24 h	 (86) + (4)	69

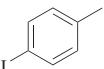
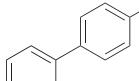
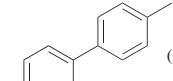
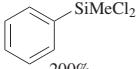
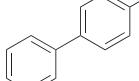
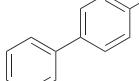
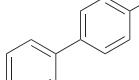
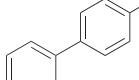
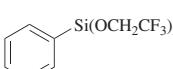
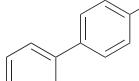
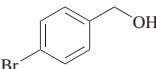
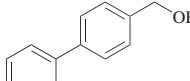
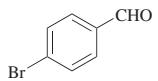
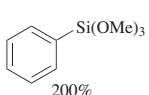
						
200%		Pd(dba) ₂ (10%), THF, 95°, 25.5 h		(64)	+ 	(17) 69
		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h		(61)		186
200%		Pd(dba) ₂ (9%), TBAF (190%), DMF, 95°, 2 h		(90)		70
		[allylPdCl] ₂ (18%), TBAF (220%), DMF, 95°, 2 h		(85)		70
220%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min		(90)		234
		Pd(dba) ₂ (9%), TBAF (200%), DMF, 95°, 2 h		(97)		70
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 4 h		(79)		47

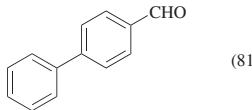
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		[allylPdCl]₂ (2.5%), DMSO, 120°, 6 h	 (90)	270
 150%		Pd(NH ₃) ₂ Cl ₂ (10%), L2 (10%), NaOH (200%), H ₂ O, 120°, 3 h	 (88)	246
 120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 5 min	 (88)	234
 150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (98)	276
 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (2:1), 80°, 2 h	 (54)	47

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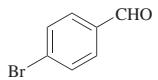


PdCl₂ (5%),
TBAF•3H₂O (200%),
toluene, 100°, 10 h

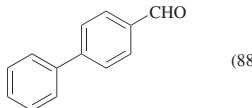


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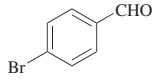
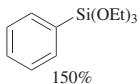
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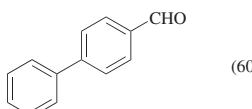
Na₂PdCl₄ (1.5%),
SDS (20%),
NaOH (600%),
H₂O, 100°, 5 min



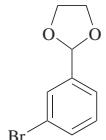
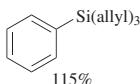
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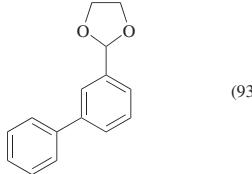
Pd(NH₃)₂Cl₂ (0.1%),
L2 (0.1%), NaOH (200%),
H₂O, 120°, 6 h



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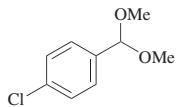


TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 3 h

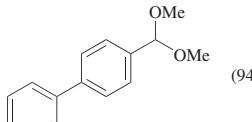


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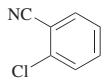
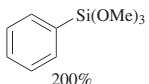
125%



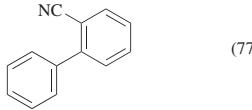
TBAF•3H₂O (500%),
[allylPdCl]₂ (2.5%),
XPhos (10%),
THF/H₂O (20:1), 80°, 12 h



47



Pd cat. **2** (7%),
TBAF (200%),
MeCN, 80°, 24 h



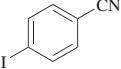
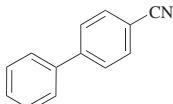
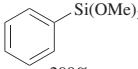
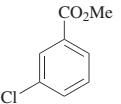
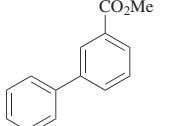
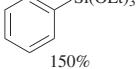
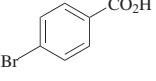
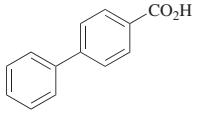
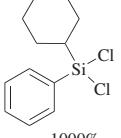
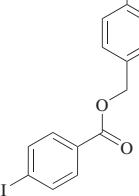
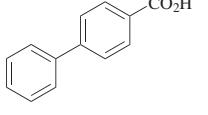
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TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 200%	 	Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h	 (77)	245
 150%	 	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (89)	276
 200%	 	Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (54)	269
 200%	 	Pd cat. 2 (7%), TBAF (200%), MeCN, 80°, 24 h	 (77)	247
 200%	 	Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h	 (81)	245

	150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(91)	276
	200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(62)	249
	125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(77)	47
150%		TBAF•3H ₂ O (600%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (25:1), 80°, 5 h		(74)	47	
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h		(69)	47	
200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(85)	237	

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		PdCl ₂ (3%), CuI (10%), L4 (4%), K ₂ CO ₃ (200%), H ₂ O (200%), DMSO, 50°, 7 h	 (97)	151
116%				
		Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h	 (80)	247
200%				
		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 6 h	 (86)	246
150%				
346				
		Wang Resin 1. Pd(PPh ₃) ₄ (5%), TBAF (1000%), THF, 80°, 48 h 2. TFA, CH ₂ Cl ₂	 (96)	184
1000%				

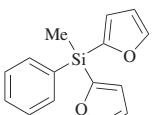
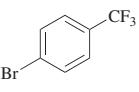
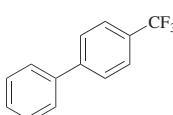
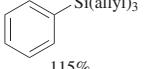
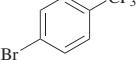
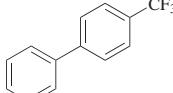
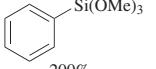
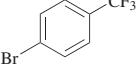
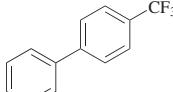
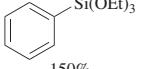
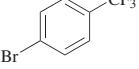
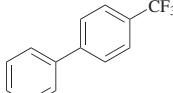
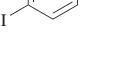
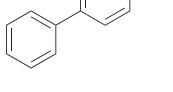
	TfO	Pd(dba) ₂ (10%), THF, 95°, 19 h		(90)	69
	TfO	Pd(dba) ₂ (10%), PPh ₃ (20%), TBAF·3H ₂ O (200%), H ₂ O (1000%), THF, reflux, 2 h		(21)	260
	TsO	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(94)	276
	Br	Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 3 h		(84)	246
	MsO	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(65)	248

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(78)
200%				248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(62)
200%				249
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(71)
125%				47
		TBAF•3H ₂ O (330%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (40:1), 80°, 5 h		(87)
105%				47
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (2:1), 80°, 3 h		(75)
115%				47

150%		TBAF•3H ₂ O (600%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (15:1), 80°, 11 h		(61)	47
125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(86)	47
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 2 h		(96)	47
200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(81)	249
125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(95)	47
120%		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 110°, 18 h		(93)	241

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆			PdCl ₂ (dpdf) (5%), TBAF (200%), dioxane/H ₂ O (8:1), 90°, 16 h	 (76)	168
	200%				
			TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h	 (95)	47
	115%				
350			PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h	 (80)	237
	200%				
			Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 3 h	 (90)	246
	150%				
			1. TBAF (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 3 h	 (97)	46

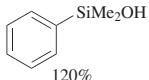
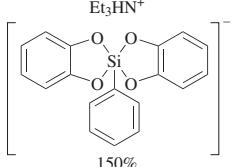
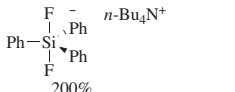
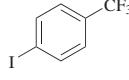
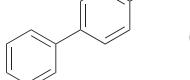
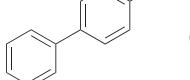
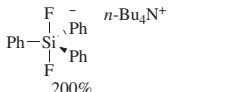
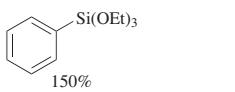
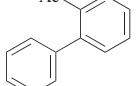
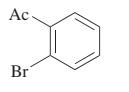
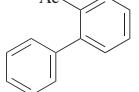
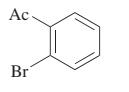
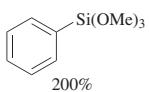
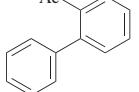
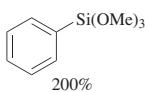
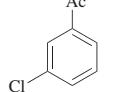
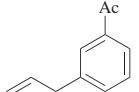
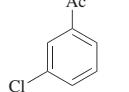
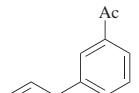
	120%			
	150%			
	200%			
		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70° 0.5 h		(86)
	(86)	201		
	276			
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(93)
	(93)	276		
		[allylPdCl] ₂ (2.5%), DMSO, 120°, 6 h		(61)
	(61)	270		
		Pd(NH ₃) ₂ Cl ₂ (1%), L2 (1%), NaOH (200%), H ₂ O, 120°, 48 h		(47)
	(47)	246		
		Pd cat. 2 (7%), TBAF (200%), MeCN/ THF (5:1), 80°, 24 h		(63)
	(63)	247		
		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(90)
	(90)	245		

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd cat. 2 (7%), TBAF (200%), MeCN/ THF (5:1), 80°, 24 h	 (71)	247
		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h	 (90)	245
		Pd(dba) ₂ (10%), THF, 95°, 18.5 h	 (73)	69
		Pd(dba) ₂ (10%), PPh ₃ (20%), TBAF•3H ₂ O (200%), H ₂ O (1000%), THF, reflux, 2 h	 (56)	260
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (96)	276

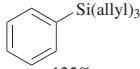
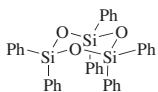
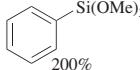
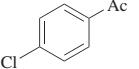
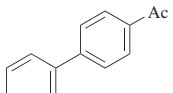
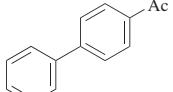
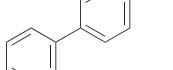
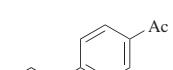
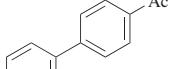
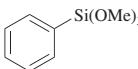
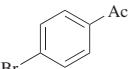
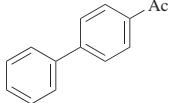
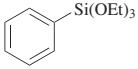
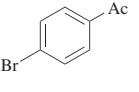
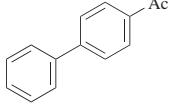
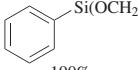
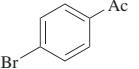
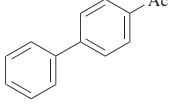
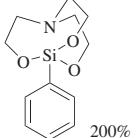
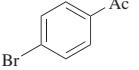
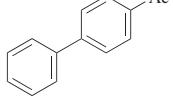
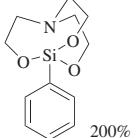
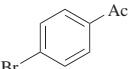
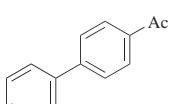
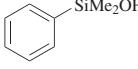
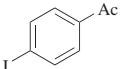
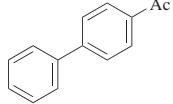
	125%				
	20%				
	200%				
					
			TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h	(69)	47
			Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 8 h	(15)	265
			Pd(OAc) ₂ (10%), P(o-tol) ₃ (20%), TBAF (200%), DMF, 80°, 45 h	(30)	236
			Pd ₂ dba ₃ (10%), Cyclohexyl JohnPhos (15%), TBAF (200%), DMF, 87°, 27 h	(47)	236
			Pd(OAc) ₂ (3%), L1 (12%), TBAF•3H ₂ O (400%), dioxane, 80°, 24 h	(77)	238
			TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 2 h	(81)	47

TABLE 1A. CROSS-COUPLED OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%	 Br	Pd(PPh ₃) ₃ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70°, 0.5 h	 (38)	201
 150%	 Br	Pd(PPh ₃) ₃ (5%), Ag ₂ O (100%), TBAT (10%), dioxane, 70°, 1 h	 (55)	201
 20%	 Br	Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 0.5 h	 (97)	265
 200%	 Br	[allylPdCl] ₂ (10%), DMF, 95°, 21 h	 (62) + (8)	69
		Pd(dba) ₂ (10%), THF, 95°, 5 h	 (90)	69

200%		[allylPdCl]₂ (2.5%), DMSO, 120°, 4 h	(85) + (—) 270
120–160%		Pd(OAc)₂ (0.5–1%), PPh₃ (1–2%), NaOH (600%), benzene, 80°, 39 h	(89) 185
200%		Pd(OAc)₂ (3%), PPh₃ (6%), TBAF (200%), DMF, 90°, 24 h	(83) 236
200%		Pd(OAc)₂ (10%), P(o-tol)₃ (20%), TBAF (200%), DMF, 90°, 24 h	(78) 236
180%		Pd(dba)₂ (9%), TBAF (180%), DMF, 95°, 2 h	(78) 70
120%		Na₂PdCl₄ (1.5%), SDS (20%), NaOH (600%), H₂O, 100°, 5 min	(95) 234
180%		Pd cat. 3 (2%), NaOH (250%), H₂O, 140°, 3 h	(80) 314

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%		Pd cat. 3 (4%), TBAF (200%), <i>o</i> -xylene, 80°, 4 h	 (57)	314
 200%		Pd(OAc) ₂ (3%), L1 (12%), TBAF·3H ₂ O (200%), dioxane, 80°, 5 h	 (86)	238
 150%		Pd(NH ₃) ₂ Cl ₂ (0.01%), L2 (0.01%), NaOH (200%), H ₂ O, 120°, 6 h	 (94)	246
 190%		Pd(dba) ₂ (9%), TBAF (190%), DMF, 95°, 2 h	 (56)	70
 200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF·3H ₂ O (200%), THF, reflux, 2 h	 (71)	260
 120%		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAT (12%), THF, 70°, 0.5 h	 (98)	201

357

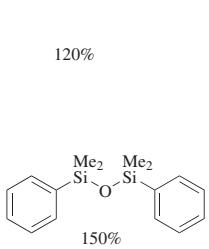
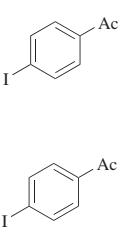
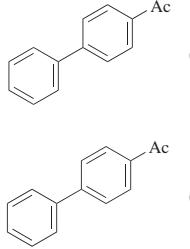
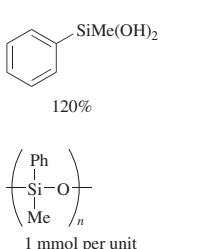
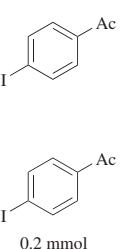
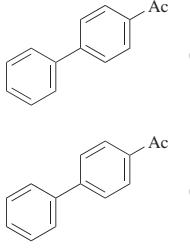
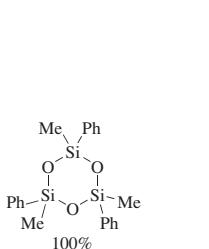
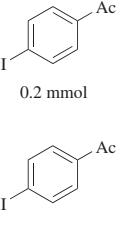
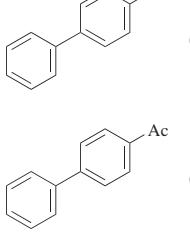
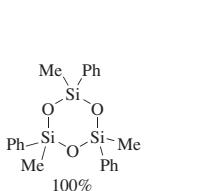
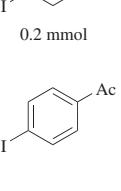
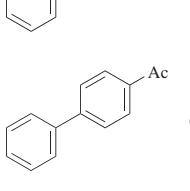
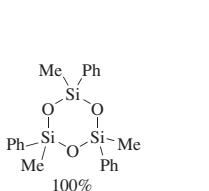
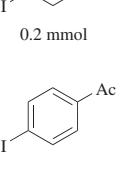
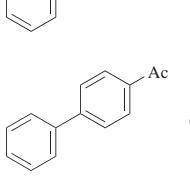
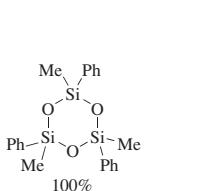
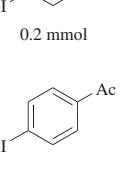
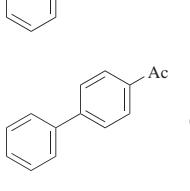
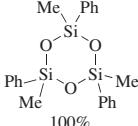
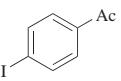
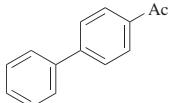
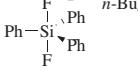
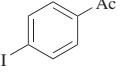
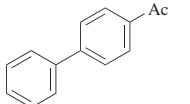
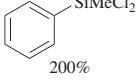
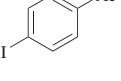
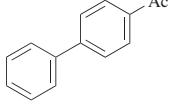
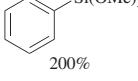
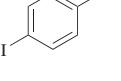
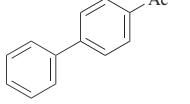
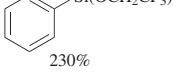
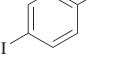
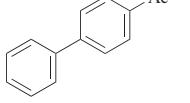
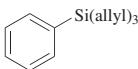
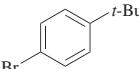
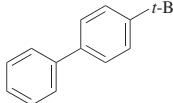
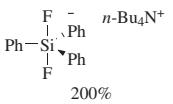
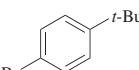
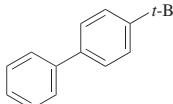
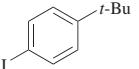
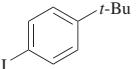
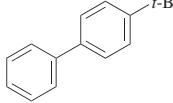
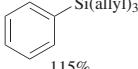
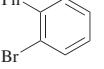
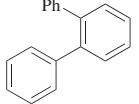
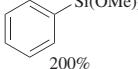
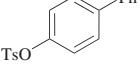
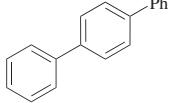
	120%		Pd(PPh ₃) ₄ (3%), Ag ₂ O (100%), TBAF (12%), THF, 70°, 0.5 h		(75)	201
	150%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAT (10%), THF, 70°, 1 h		(77)	201
	120%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(97)	37
	1 mmol per unit		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 20 h		(67)	268
	0.2 mmol		Pd ₂ dba ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 20 h		(53)	268
	100%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 24 h		(55)	268

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  100%		Pd ₂ dba ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 40 h	 (36)	268
  n-Bu ₄ N ⁺ 200%		[allylPdCl] ₂ (10%), DMF, 95°, 21 h	 (100)	69
358  200%		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h	 (81)	186
  200%		Pd(dba) ₂ (9%), TBAF (200%), DMF, 95°, 2 h	 (58)	70
  230%		Pd(dba) ₂ (9%), TBAF (230%), DMF, 95°, 2 h	 (78)	70

	Iodobenzene	Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF•3H ₂ O (200%), THF, reflux, 2 h	 (80)	313
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°	 (92)	248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH, 90°	 (96)	248
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (95)	276
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (88)	249
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (81)	249

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆					
 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 4 h	 (97)	47	
 200%		Pd cat. I (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (66)	269	
360	 200%		Pd cat. I (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (87)	269
	 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h	 (98)	46
	 200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (67)	249

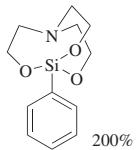
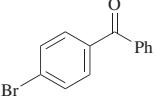
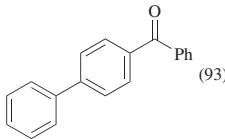
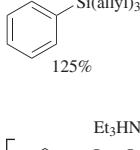
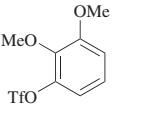
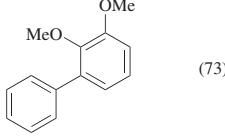
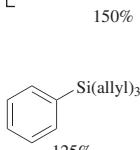
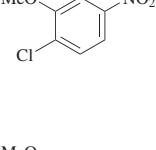
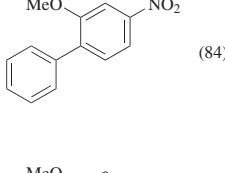
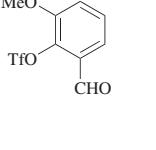
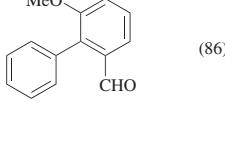
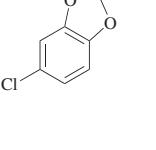
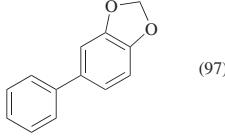
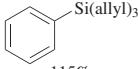
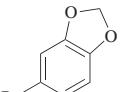
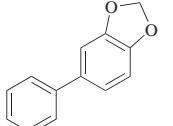
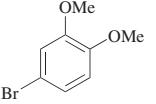
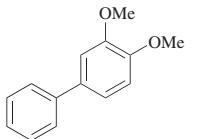
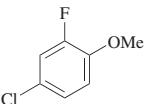
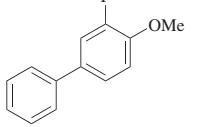
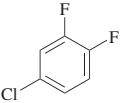
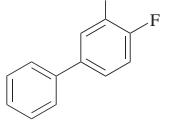
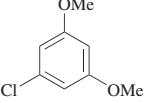
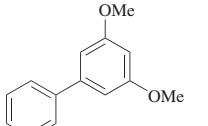
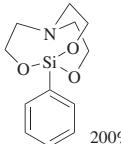
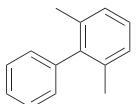
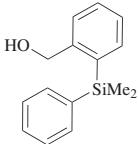
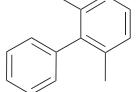
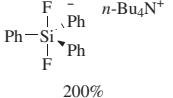
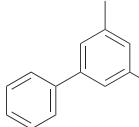
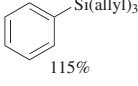
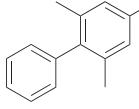
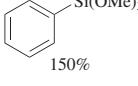
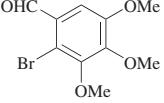
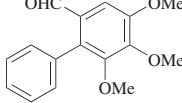
	200%		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h		(93)	237
	125%		Pd(dba) ₂ (10%), Cyclohexyl JohnPhos (20%), TBAF•3H ₂ O (200%), H ₂ O (2000%), THF, reflux, 12 h		(73)	260
	150%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(84)	47
	125%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h		(86)	276
			TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h		(97)	47

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 2 h		(96)
115%				47
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 2 h		(97)
115%				47
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(95)
125%				47
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(89)
125%				47
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 8 h		(94)
125%				47

125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h		(87)	47
150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h		(96)	276
125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h		(87)	47
150%		TBAF•3H ₂ O (600%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (25:1), 80°, 20 h		(57)	47
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 4 h		(95)	46
200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h		(85) 95% pure	236

TABLE 1A. CROSS-COUPLED OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF•3H ₂ O (200%), THF, reflux, 2 h		(65) 236
  116%		PdCl ₂ (3%), CuI (10%), L4 (4%), K ₂ CO ₃ (200%), H ₂ O (200%), DMSO, 50°, 13 h		(94) 151
  200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h		(90) 315
  115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 6 h		(92) 47
  150%		Pd(OAc) ₂ (5%), PPh ₃ (25%), TBAF (150%), THF, reflux, 18 h		(94) 235

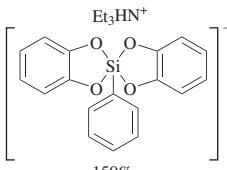
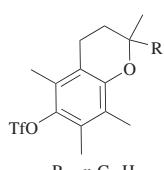
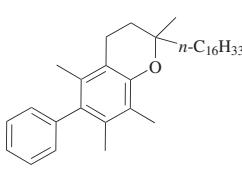
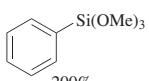
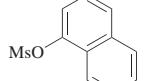
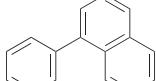
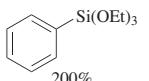
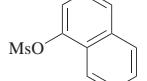
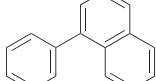
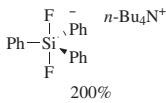
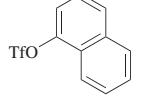
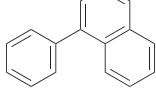
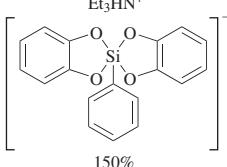
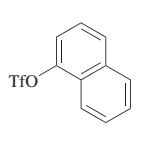
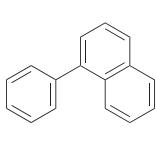
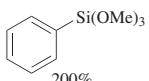
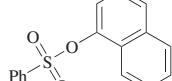
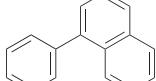
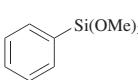
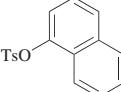
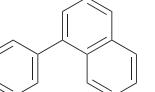
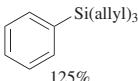
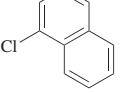
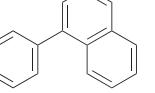
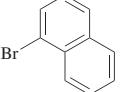
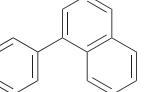
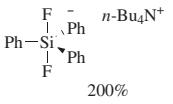
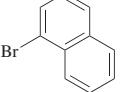
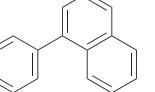
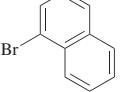
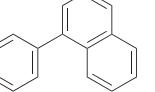
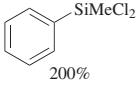
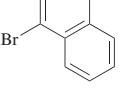
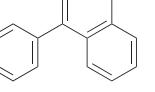
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h		(90)	276
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90°		(81)	248
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90°		(71)	248
		Pd(dba) ₂ (10%), THF, 95°, 25.5 h		(71)	69
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(86)	276
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(94)	249

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (88)	249
		TBAF·3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h	 (94)	49
115%		TBAF·3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h	 (96)	47
		Pd cat. I (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (85)	269
200%		[allylPdCl] ₂ (2.5%), DMSO, 120°, 4 h	 (66)	270
		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h	 (65)	186

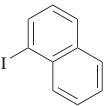
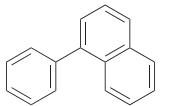
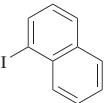
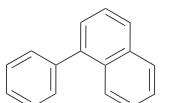
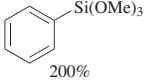
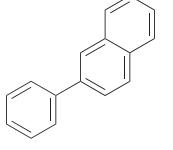
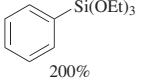
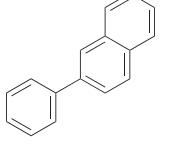
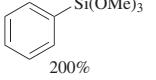
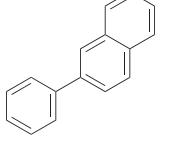
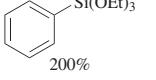
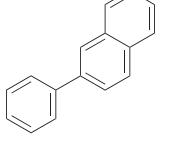
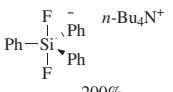
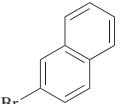
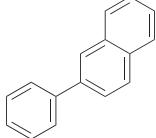
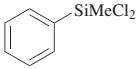
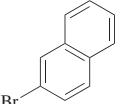
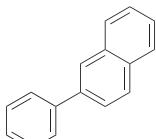
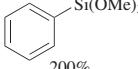
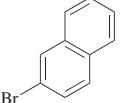
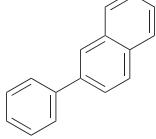
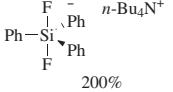
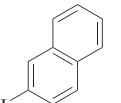
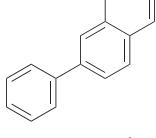
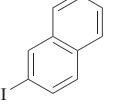
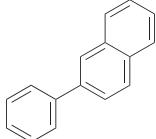
	Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h		(72)	186
	Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h		(85)	269
	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(83)	248
	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(84)	248
	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(95)	249
	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(99)	249

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (88)	269
 200%		Pd/C (5%), KOH (800%), H ₂ O, 100°, 12–36 h	 (51)	186
 200%		Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h	 (81)	247
 200%		Pd. cat 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h	 (77)	245
		[allylPdCl] ₂ (2.5%), DMSO, 120°, 1 h	 (83)	270

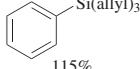
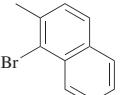
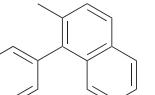
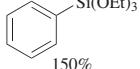
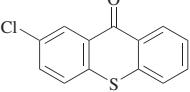
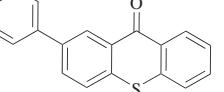
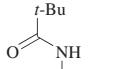
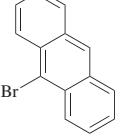
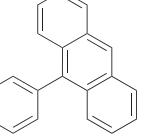
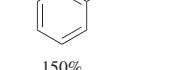
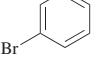
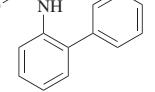
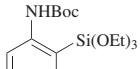
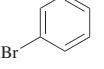
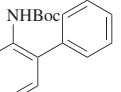
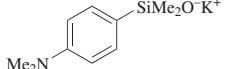
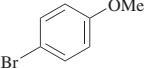
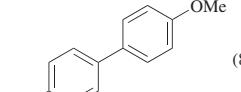
	115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 18 h		(99)	47
	125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h		(98)	47
	150%		Pd(NH ₃) ₂ Cl ₂ (1%), L2 (1%), NaOH (200%), H ₂ O, 120°, 24 h		(88)	246
	150%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (150%), DMF, 90°, 4 h		(86)	239
	150%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (150%), DMF, 90°, 4 h		(88)	239
	150%		(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h		(88)	54

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 150%		$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (2.5%), toluene, 90°, 3 h	 (73)	54
 120%		$[\text{allylPdCl}]_2$ (0.5%), CuI (3%), RuPhos (2.1%), K_2CO_3 (250%), THF/DMF (3:1), 75°, 22 h	 (93)	149
 120%		$[\text{allylPdCl}]_2$ (0.5%), CuI (3%), RuPhos (2.1%), K_2CO_3 (250%), THF/DMF (3:1), 75°, 7 h	 (88)	149

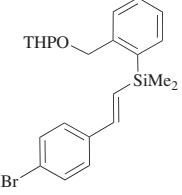
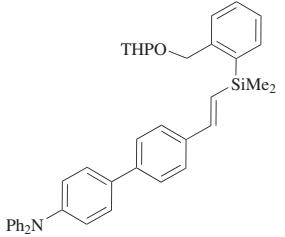
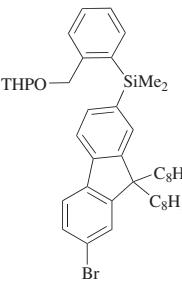
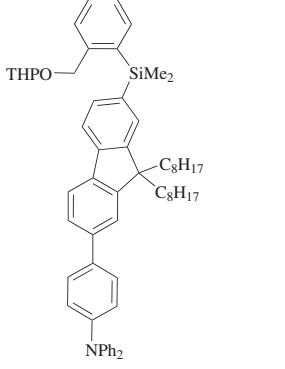
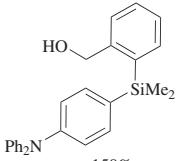
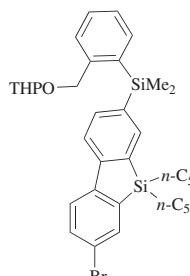
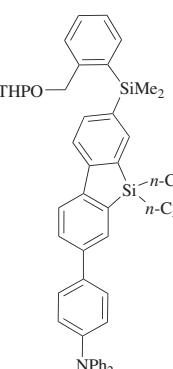
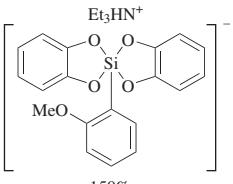
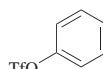
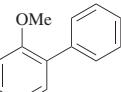
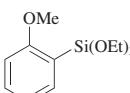
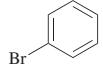
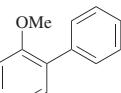
 <p>120%</p>	<p>[allylPdCl]₂ (0.5%), CuI (3%), RuPhos (2.1%), K₂CO₃ (250%), THF/DMF (3:1), 75°, 17 h</p>	 <p>(93)</p>	<p>149</p>
 <p>150%</p>	<p>[allylPdCl]₂ (0.5%), CuI (3%), RuPhos (2.1%), K₂CO₃ (250%), THF/DMF (3:1), 75°, 30 h</p>	 <p>(93)</p>	<p>149</p>

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  150%	 	[allylPdCl] ₂ (2.5%), CuI (3%), RuPhos (2.1%), K ₂ CO ₃ (250%), THF/DMF (3:1), 75°, 24 h	  (93)	149
372  150%	 	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h	  (41)	276
  150%	 	Pd(OAc) ₂ (50%), PPh ₃ (100%), TBAF (150%), DMF, 90°, 15 min	  (75)	239

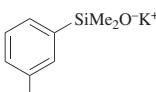
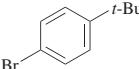
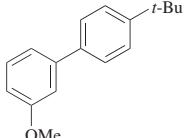
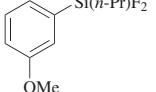
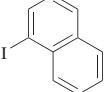
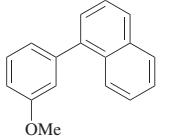
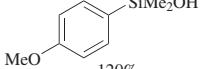
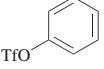
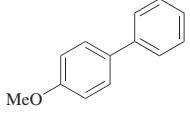
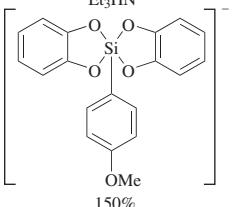
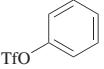
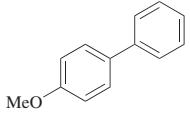
150%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (150%), DMF, 90°, 4 h		(39)	239
150%		Pd(OAc) ₂ (50%), PPh ₃ (100%), TBAF (150%), DMF, 90°, 15 min		(87)	239
150%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (150%), DMF, 90°, 4 h		(54)	239
150%		(t-Bu ₃ P) ₂ Pd (5%), toluene, 90°, 8 h		(83)	54
150%		Pd(OAc) ₂ (50%), PPh ₃ (100%), TBAF (150%), DMF, 90°, 15 min		(49)	239
150%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (150%), DMF, 90°, 4 h		(12)	239

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆					
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 8 h		(71)	54
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 6 h		(71)	54
 150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(87)	276
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 5.5 h		(80)	54
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 3 h		(78)	54

	150%								
		[allylPdCl]2 (5%), KF (200%), DMF, 100°, 15 h		(83)		73			
	120%				[allylPdCl]2 (0.5%), P(o-tol)3 (0.5%), KF (200%), DMF, 120°, 18 h		(48)		73
	150%				[allylPdCl]2 (5%), KF (200%), DMF, 70°, 15 h		(76)		73
	120%				[allylPdCl]2 (0.5%), P(o-tol)3 (0.5%), KF (200%), DMF, 120°, 18 h		(82)		73
	120%				[allylPdCl]2 (0.5%), P(o-tol)3 (0.5%), KF (200%), DMF, 120°, 18 h		(70)		73

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 3.5 h	 (82)	54
150%				
		[allylPdCl] ₂ (5%), KF (200%), DMF, 100°, 15 h	 (94)	73
150%				
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 5 h	 (1)	36
120%				
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h	 (91)	276
150%				

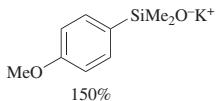
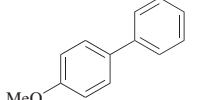
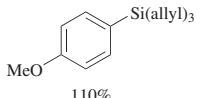
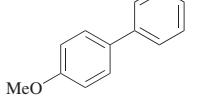
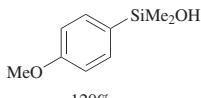
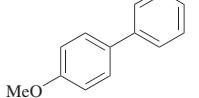
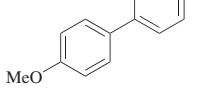
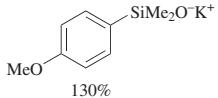
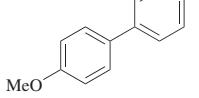
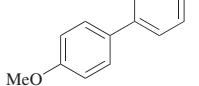
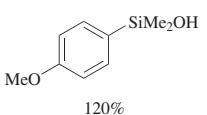
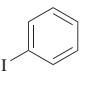
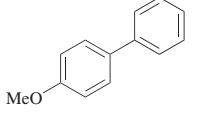
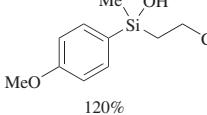
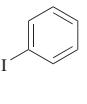
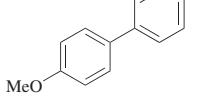
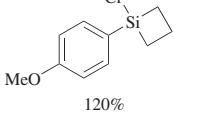
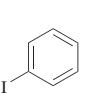
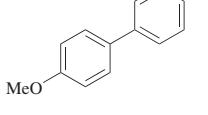
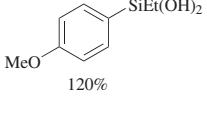
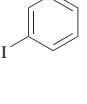
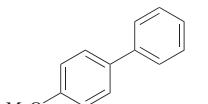
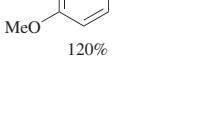
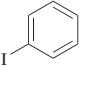
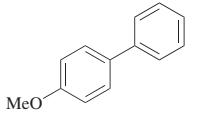
		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 5 h		(88)	54
		1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°		(96)	46
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 5 h		(2)	36
120%		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), toluene, 90°, 12 h		(85)	204
		[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 30 min		(72)	218
130%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(80)	37
120%					

TABLE 1A. CROSS-COUPLED OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (5%), Ag ₂ O (100%), THF, 60°, 7 h		(46)
120%				203
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), toluene, 90°, 8 h		(91)
120%				204
		Pd(OAc) ₂ (5%), Ag ₂ O (100%), THF, 60°, 7 h		(74)
120%				203
		TBAF (360%), [allylPdCl] ₂ (2.5%), (t-Bu) ₃ P (20%), THF, reflux, 1 h		(91)
120%				39
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(95)
120%				37

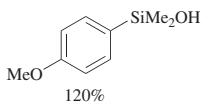
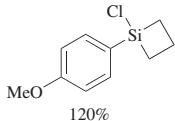
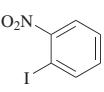
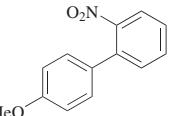
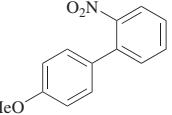
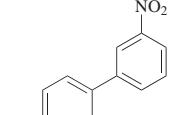
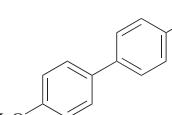
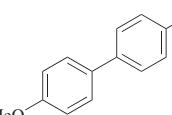
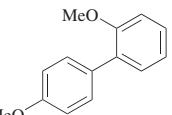
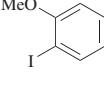
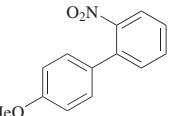
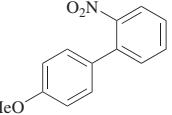
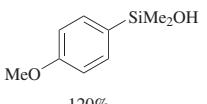
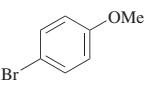
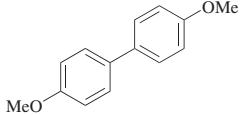
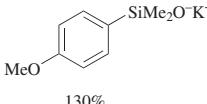
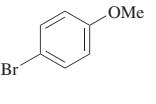
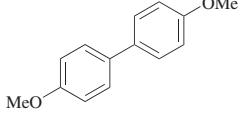
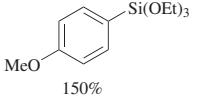
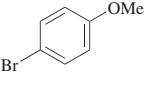
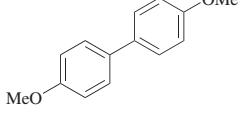
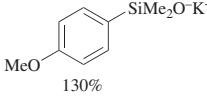
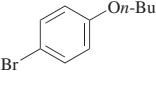
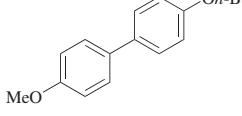
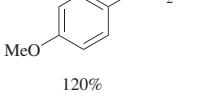
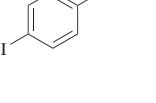
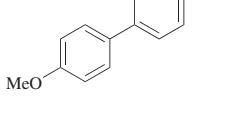
	120%				
	120%				
					
			Cs ₂ CO ₃ + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), dioxane, 90°, 24 h		(83)
					204, 205
			TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 3 h		39
			TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 3 h		39
			Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		37
			TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 1 h		39
			Cs ₂ CO ₃ + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), dioxane, 90°, 24 h		(84)
					204, 205

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), toluene, 90°, 18 h	 (92)	204
 130%		[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 1 h	 (81)	218
 150%		Pd(NH ₃) ₂ Cl ₂ (1%), L2 (1%), NaOH (200%), H ₂ O, 120°, 9 h	 (73)	246
 130%		[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 1 h	 (61)	218
 120%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h	 (55)	37

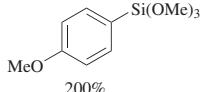
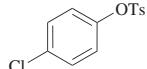
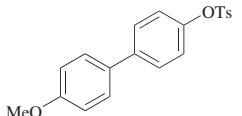
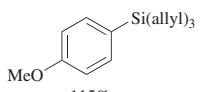
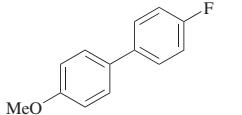
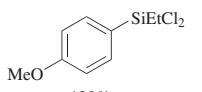
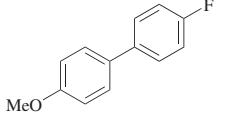
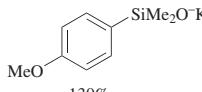
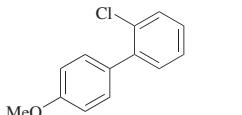
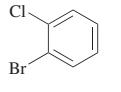
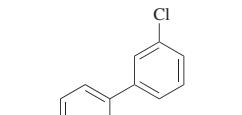
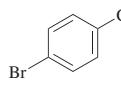
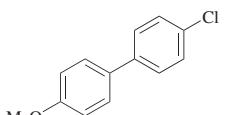
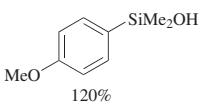
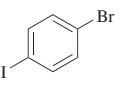
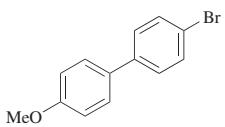
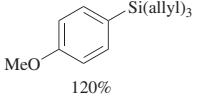
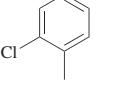
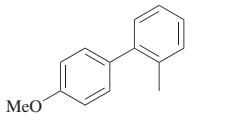
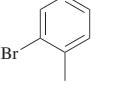
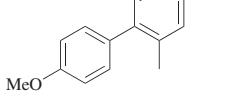
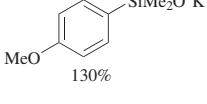
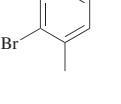
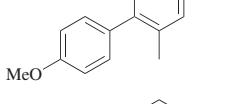
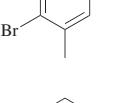
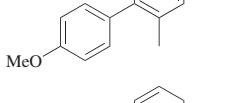
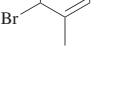
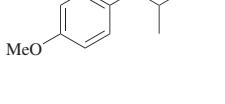
	200%				
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(70)	249
	115%			(98)	47
	120%			(91)	73
	130%			(86)	218
	130%	[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 0.5 h		(86)	218
	130%	[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 45 min		(80)	218

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
MeO-  SiMe ₂ OH 120%	I- 	Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h	 (60)	37
MeO-  Si(allyl) ₃ 120%	Cl- 	TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h	 (93)	47
110%	Br- 	1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 3 h	 (90)	46
MeO-  SiMe ₂ O ⁻ K ⁺ 130%	Br- 	[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 0.5 h	 (85)	218
150%	Br- 	(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	 (88)	54
150%	Br- 	(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	 (88)	54

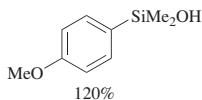
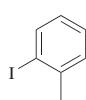
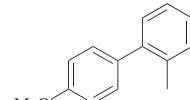
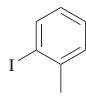
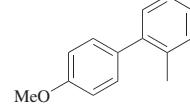
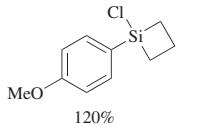
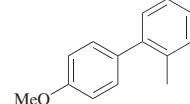
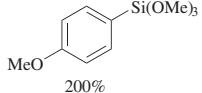
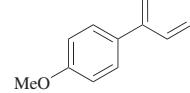
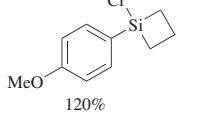
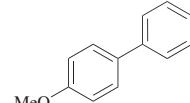
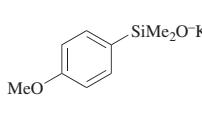
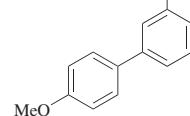
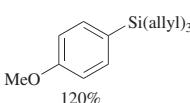
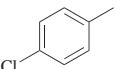
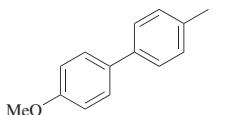
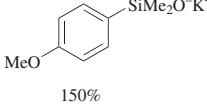
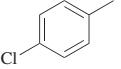
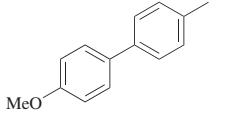
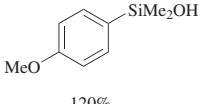
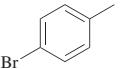
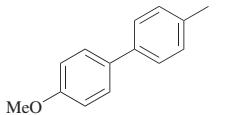
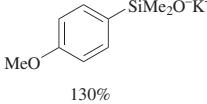
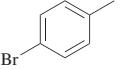
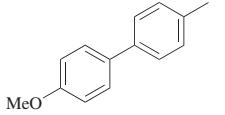
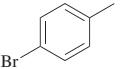
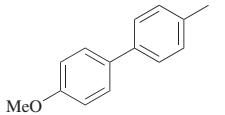
	120%					
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(69)	37	
	120%	Cs ₂ CO ₃ + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), dioxane, 90°, 24 h		(85)	204, 205	
	120%	TBAF (360%), [allylPdCl] ₂ (2.5%), (t-Bu) ₃ P (20%), THF, reflux, 3 h		(89)	39	
	200%	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(68)	249	
	120%	TBAF (360%), [allylPdCl] ₂ (2.5%), (t-Bu) ₃ P (20%), THF, reflux, 1 h		(85)	39	
	130%	[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 1 h		(67) 97% pure by GC	218	

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h	 (95)	47
 150%		(t-Bu ₃ P) ₂ Pd (5%), toluene, 90°, 7 h	 (81)	54
 120%		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), toluene, 90°, 18 h	 (90)	204
 130%		[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 35 min	 (63)	218
150%		(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	 (88)	54

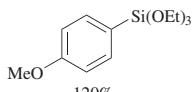
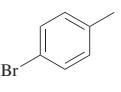
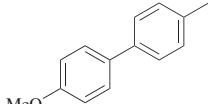
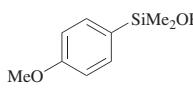
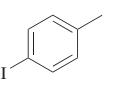
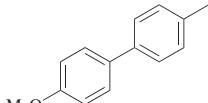
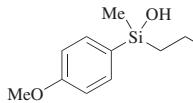
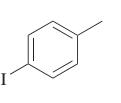
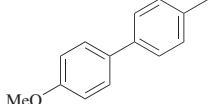
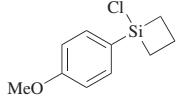
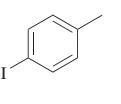
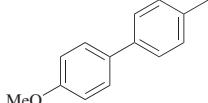
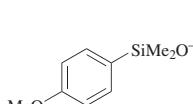
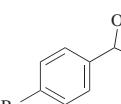
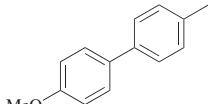
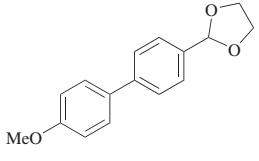
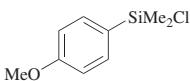
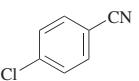
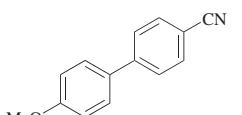
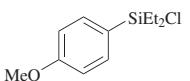
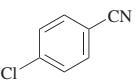
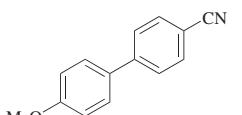
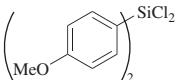
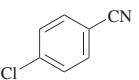
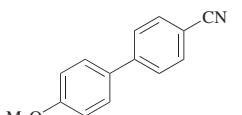
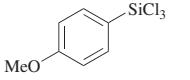
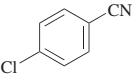
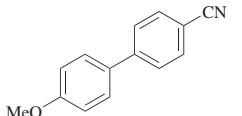
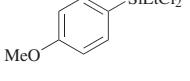
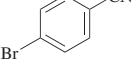
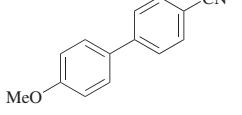
		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 80°, 18 h		(89)	241
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(75)	37
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), toluene, 90°, 6 h		(90)	204
		Pd(OAc) ₂ (5%), Ag ₂ O (100%), THF, 60°, 7 h		(68)	203
		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 1 h		(92)	39
		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 4 h		(78)	54

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	 (93)	187
120%				
		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	 (95)	187
120%				
386				
		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	 (92)	187
120%				
		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	 (73)	187
120%				
		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 (67)	73
120%				

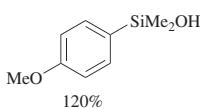
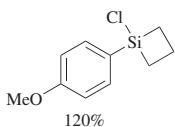
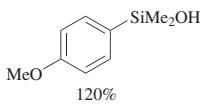
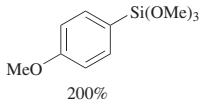
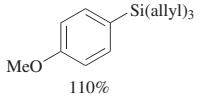
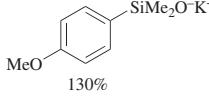
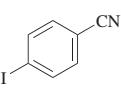
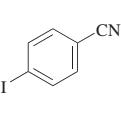
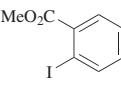
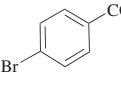
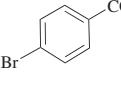
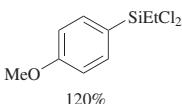
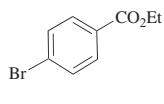
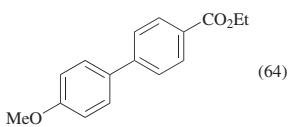
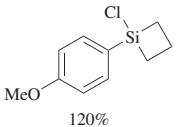
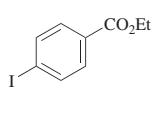
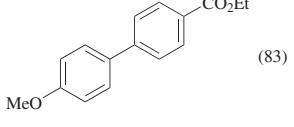
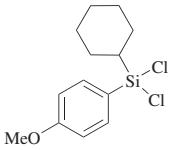
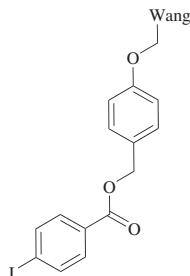
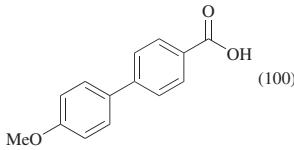
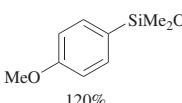
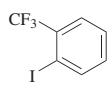
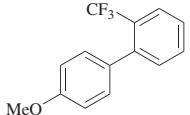
	120%			
	120%			
	120%			
	200%			
	110%			
	130%			
				
				
				
				
				
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), toluene, 90°, 6 h	(85)	204
		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 1 h	(81)	39
		Cs ₂ CO ₃ + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), dioxane, 90°, 24 h	(88)	204, 205
		Pd(OAc) ₂ (4%), Xphos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°	(50)	248
		1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 1 h	(72)	46
		[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 1 h	(82)	218

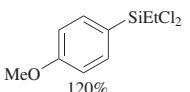
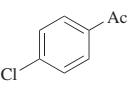
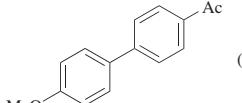
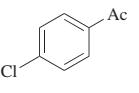
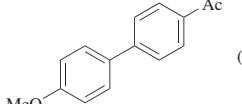
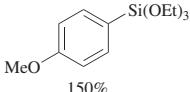
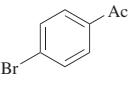
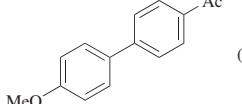
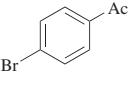
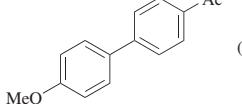
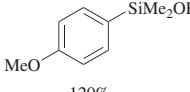
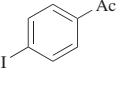
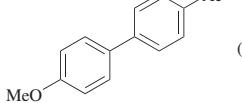
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 (64)	73
 120%		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 1 h	 (83)	39
 500%		Wang Resin 1. Pd(PPh ₃) ₄ (5%), TBAF (500%), THF, 80°, 30 h 2. TFA/CH ₂ Cl ₂ (1:3)	 (100)	184
 120%		Cs ₂ CO ₃ + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), dioxane, 90°, 24 h	 (82)	204, 205

389

	120%			
		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 3 h		(89)
	130%	[allylPdCl] ₂ (2.5%), Ph ₃ P(O) (5%), toluene, 90°, 0.5 h		(79)
	120%	Pd(OAc) ₂ (0.5%), P(o-tol) ₃ (0.5%). KF (200%), DMF, 120°, 18 h		(62)
	120%	Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), toluene, 90°, 3 h		(87)
	120%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(54)
	120%	(i-Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h		(62)

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
MeO-  120%	Cl- 	(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	MeO-  (62)	187
200%	Cl- 	(dcpe) ₂ PdCl ₂ (2%), KF (1000%), DMF, 120°, 48 h	MeO-  (97)	187
MeO-  150%	Br- 	Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 3 h	MeO-  (70)	246
150%	Br- 	Pd(NH ₃) ₂ Cl ₂ (0.01%), L2 (0.01%), NaOH (200%), H ₂ O, 120°, 9 h	MeO-  (76)	246
MeO-  120%	I- 	Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h	MeO-  (50)	37

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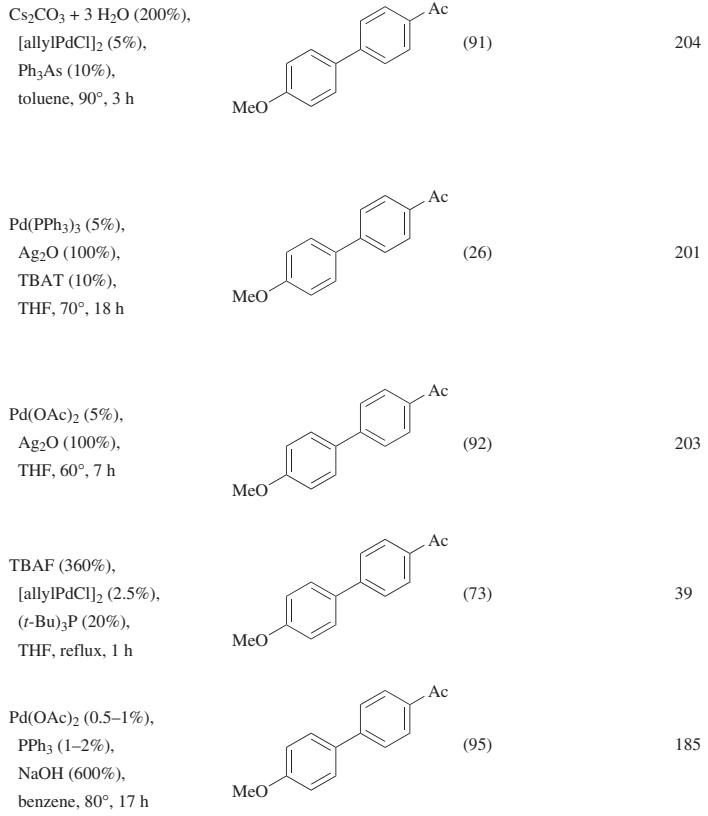
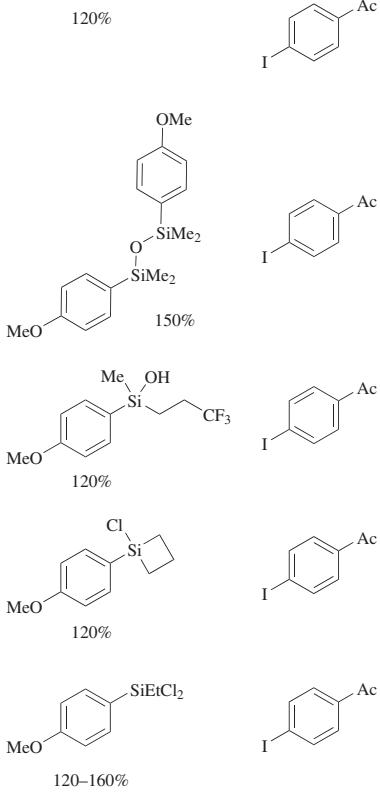
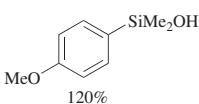
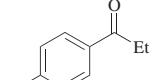
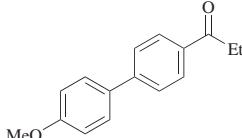
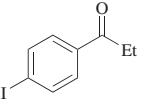
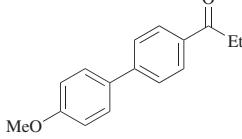
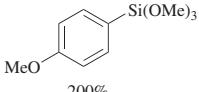
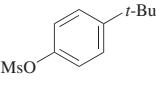
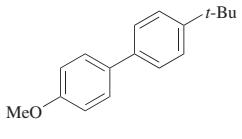
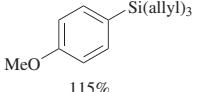
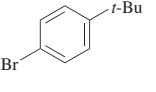
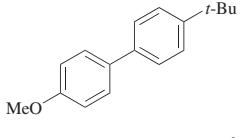
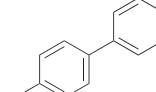
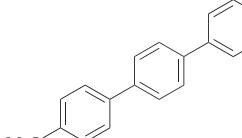


TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), toluene, 90°, 24 h		(90)
120%				204
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), Ph ₃ As (10%), toluene, 90°, 8 h		(87)
120%				204
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90°		(67)
200%				248
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 4 h		(98)
115%				47
		TBAF•3H ₂ O (400%), [allylPdCl] ₂ (2.5%), XPhos (10%), DMSO/H ₂ O (20:1), 80°, 8 h		(87)
120%				47

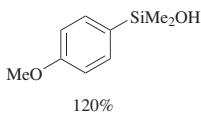
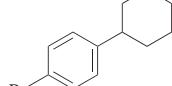
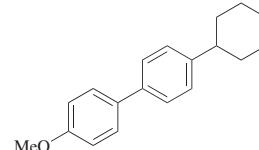
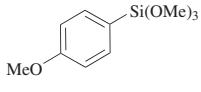
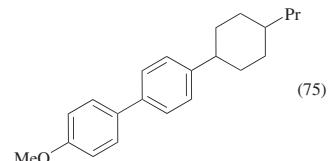
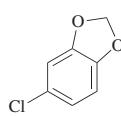
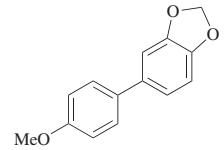
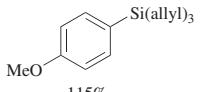
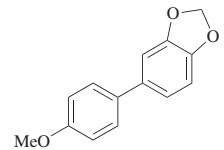
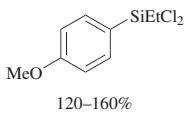
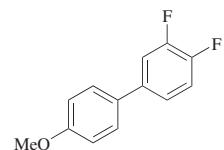
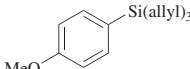
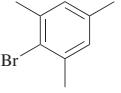
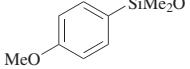
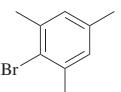
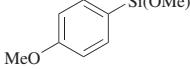
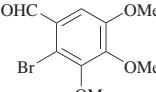
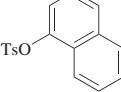
	120%			
		Cs ₂ CO ₃ + 3 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), toluene, 90°, 18 h		(79) 204
	120%	1. TBAF (105%) 2. Pd(OAc) ₂ (5%), Ph ₃ P (15%), toluene, reflux, 30 h		(75) 187
	120%	TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(94) 47
	115%	TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h		(93) 47
	120–160%	Pd(OAc) ₂ (0.5–1%), PPh ₃ (0.1–2%), NaOH (600%), THF, 60°, 14 h		(75) 185

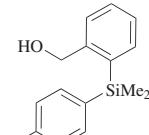
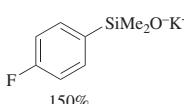
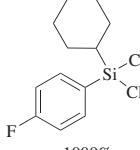
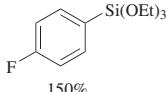
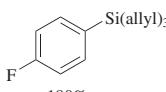
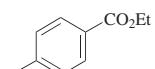
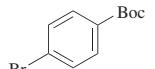
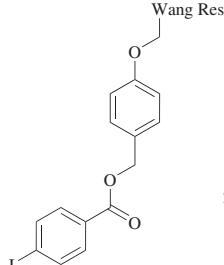
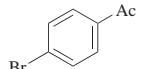
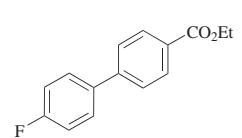
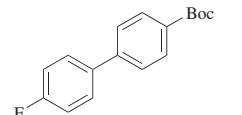
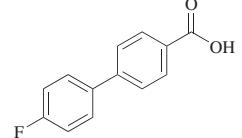
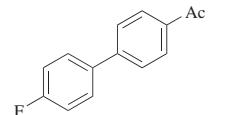
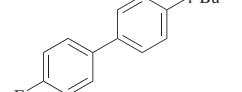
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
MeO-  -Si(allyl) ₃ 120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h	 (87)	47
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 6 h	 (97)	47
MeO-  -SiMe ₂ O ⁻ K ⁺ 150%		[allylPdCl] ₂ (2.5%), dppb(O) (5%), toluene, 90°, 1 h	 (77)	218
MeO-  -Si(OMe) ₃ 150%		Pd(OAc) ₂ (5%), PPh ₃ (25%), TBAF (150%), THF, reflux, 18 h	 (93)	235
200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (81)	249

		[allylPdCl]₂ (2.5%), Ph₃P(O) (5%), toluene, 90°, 35 min		(85)	218
		Cs₂CO₃ + 2 H₂O (200%), [allylPdCl]₂ (5%), dpbp (10%), dioxane, 90°, 24 h		(86)	204
		TBAF (360%), [allylPdCl]₂ (2.5%), (t-Bu)₃P (20%), THF, reflux, 2 h		(85)	39
		Pd(OAc)₂ (4%), XPhos (10%), TBAF (200%), THF/t-BuOH (1:1), 90°		(96)	248
		(t-Bu₃P)₂Pd (5%), toluene, 90°, 3.5 h		(62)	54
150%		(t-Bu₃P)₂Pd (5%), toluene, 90°, 3.5 h		(34)	54

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆					
			(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	(86)	54
	150%				
			Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 48 h	(28)	246
	150%				
396			(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 4 h	(81)	54
	150%				
			TBAF•3H ₂ O (480), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 11 h	(99)	47
	180%				
			TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 18 h	(69)	47
	180%				

			
	116%		
			
	150%		
			
	1000%		
			
	150%		
			
	180%		
			
			
			
			
	(91)	151	
	(70)	54	
	(91)	184	
	(68)	246	
	(88)	47	

PdCl₂ (3%), CuI (10%),
L4 (4%), K₂CO₃ (200%),
H₂O (200%),
DMSO, 50°, 3 h

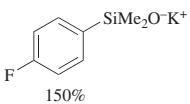
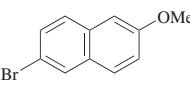
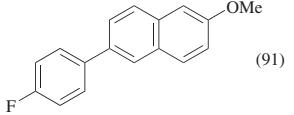
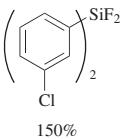
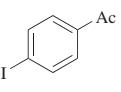
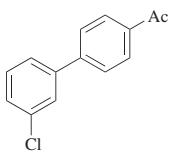
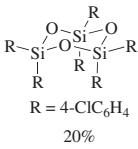
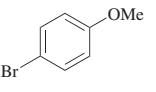
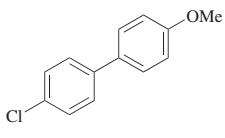
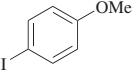
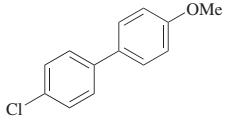
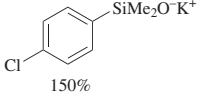
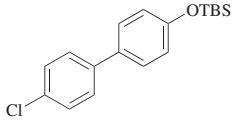
(*t*-Bu₃P)₂Pd (2.5%),
toluene, 90°, 3 h

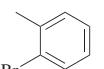
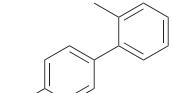
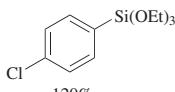
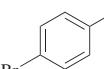
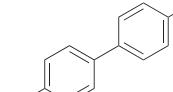
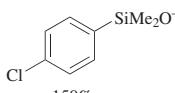
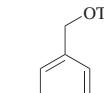
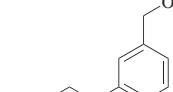
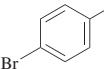
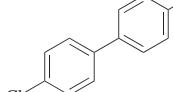
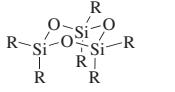
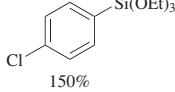
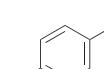
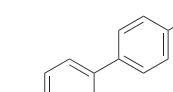
1. Pd(PPh₃)₄ (5%),
TBAF (1000%),
THF, 80°, 72 h
2. TFA, CH₂Cl₂

Pd(NH₃)₂Cl₂ (0.1%),
L2 (0.1%),
NaOH (200%),
H₂O, 120°, 6 h

TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 11 h

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 4 h	 (91)	54
 150%		[allylPdCl] ₂ (5%), KF (200%), DMF, 70°, 43 h	 (74)	73
398				
 17%		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 4 h	 (87)	265
		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 4 h	 (89)	265
	 150%	(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3.5 h	 (57)	54

	150%			(68)	54
	120%			(78)	241
	150%			(60)	54
	150%			(42)	265
 R = 4-ClC6H4	20%			(88)	246
	150%			(72)	246

$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (2.5%),
toluene, 90°, 3.5 h

Pd(dba)₂ (3%),
i-Pr-DPEphos (4%),
TBAF•3H₂O (120%),
toluene, 80°, 18 h

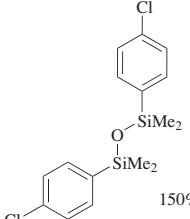
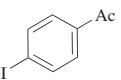
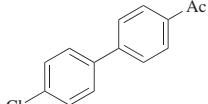
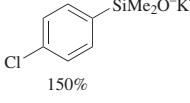
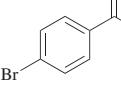
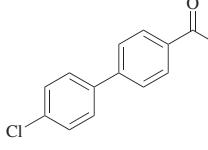
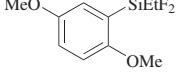
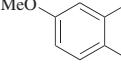
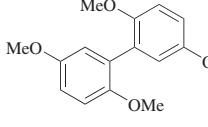
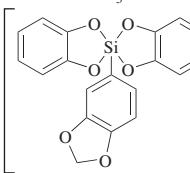
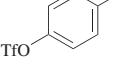
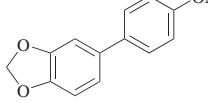
$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (5%),
toluene, 90°, 3.5 h

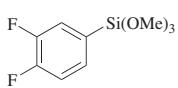
$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (5%),
toluene, 90°, 3.5 h

Pd(OAc)₂ (5%),
KOH (880%),
dioxane/H₂O,
reflux, 0.5 h

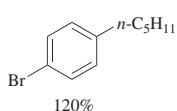
Pd(NH₃)₂Cl₂ (0.1%),
L2 (0.1%), NaOH (200%),
H₂O, 120°, 6 h

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  150%		Pd(PPh ₃) ₃ (5%), Ag ₂ O (100%), TBAT (10%), THF, 70°, 18 h		(37) 201
  150%		(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3.5 h		(56) 54
  		CuCl (100%), DMF, 60°, 24 h		(77) 183
  150%	 	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(89) 276

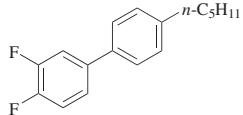
10⁴

200%



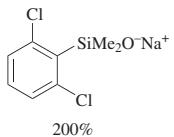
120%

1. TBAF (105%),
2. Pd(OAc)₂ (5%),
Ph₃P (15%),
toluene, reflux, 30 h

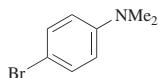


(78)

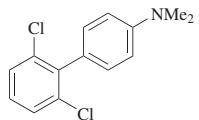
240



200%



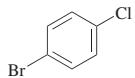
(t-Bu₃P)₂Pd (7.5%),
THF, 90°, 3 h



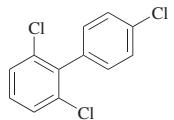
(76)

54

200%



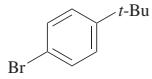
(t-Bu₃P)₂Pd (7.5%),
THF, 90°, 3 h



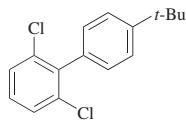
(70)

54

200%

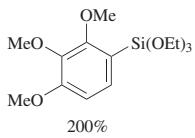


(t-Bu₃P)₂Pd (7.5%),
THF, 90°, 3 h

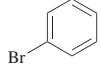


(68)

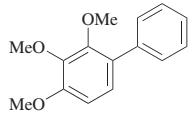
54



200%



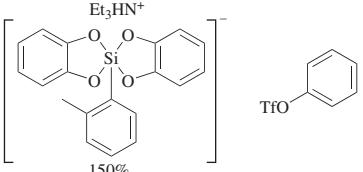
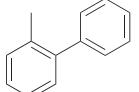
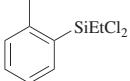
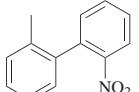
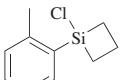
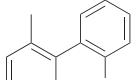
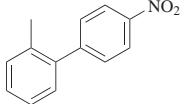
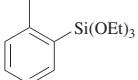
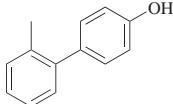
Pd(OAc)₂ (50%),
PPh₃ (100%),
TBAF (150%), THF, 1 h



(70)

251

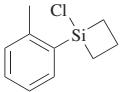
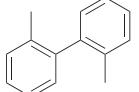
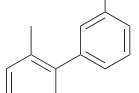
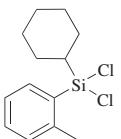
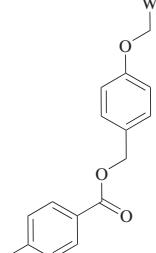
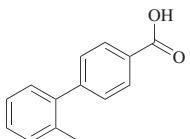
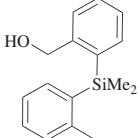
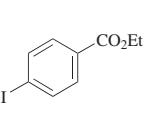
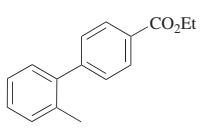
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇		TFOC ₆ H ₅	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h	 (40)	276
402		Br-C ₆ H ₄ -NO ₂	Pd(OAc) ₂ (0.5%), P(o-tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 (88)	73
		I-C ₆ H ₄ -NO ₂	TBAF (360%), [allylPdCl] ₂ (2.5%), (t-Bu) ₃ P (20%), THF, reflux, 3 h	 (77)	39
		I-C ₆ H ₄ -NO ₂	TBAF (360%), [allylPdCl] ₂ (2.5%), (t-Bu) ₃ P (20%), THF, reflux, 2 h	 (73)	39
		Br-C ₆ H ₄ -OH	Pd(NH ₃) ₂ Cl ₂ (1%), L2 (1%), NaOH (200%), H ₂ O, 120°, 24 h	 (68)	246

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		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(92)	47
		Cs ₂ CO ₃ •H ₂ O + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), dioxane/toluene (4:1), 110°, 24 h		(83)	205
		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 48 h		(31)	246
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(30)	37
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 6 h		(79)	47
		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 48 h		(44)	246

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
 120%		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 12 h	 (85)	39
120%		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 8 h	 (76)	39
Wang Resin				
 1000%		1. Pd(PPh ₃) ₄ (5%), TBAF (1000%), THF, 80°, 48 h 2. TFA, CH ₂ Cl ₂	 (93)	184
 116%		PdCl ₂ (3%), CuI (10%), L4 (4%), K ₂ CO ₃ (200%), H ₂ O (200%), DMSO, 80°, 5 h	 (81)	151

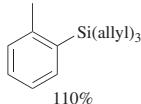
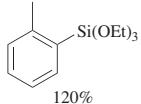
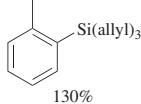
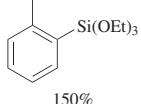
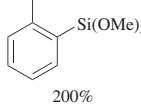
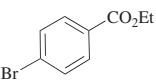
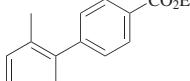
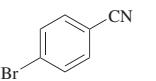
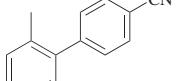
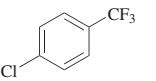
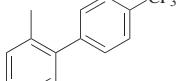
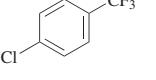
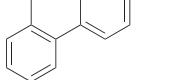
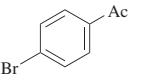
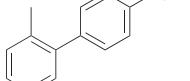
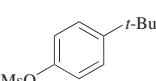
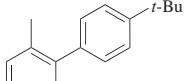
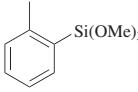
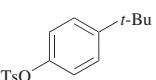
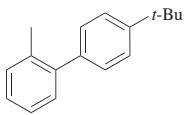
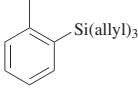
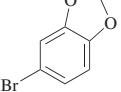
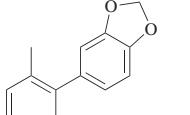
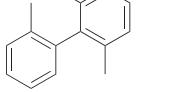
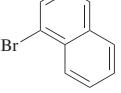
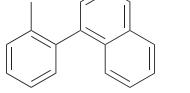
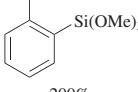
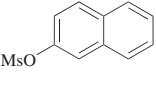
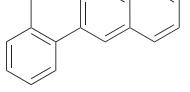
	110%					
	120%					
	130%					
	130%					
	150%					
	200%					
		1. TBAF•3H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 1 h		(57)	46	
		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3 H ₂ O (120%), toluene, 80°, 18 h		(85)	241	
		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(78)	47	
		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(78)	160	
		Pd(NH ₃) ₂ Cl ₂ (0.01%), L2 (0.01%), NaOH (200%), H ₂ O, 120°, 18 h		(89)	246	
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°		(77)	248	

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	 (53)	249
 130%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 8 h	 (92)	47
130%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h	 (66)	47
130%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 20 h	 (87)	47
 200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°	 (85)	248

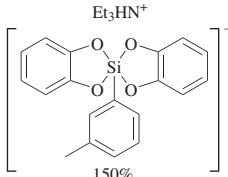
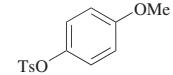
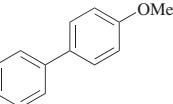
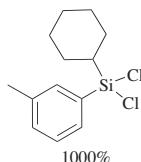
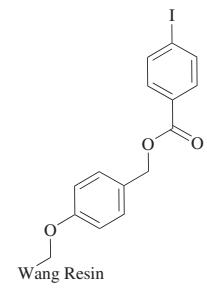
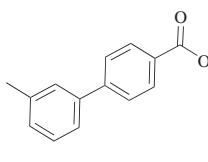
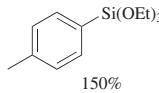
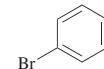
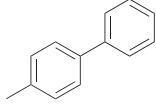
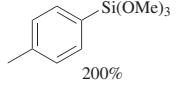
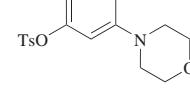
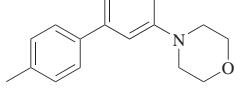
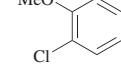
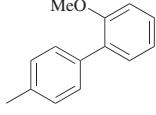
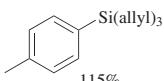
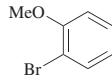
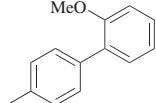
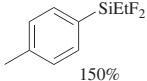
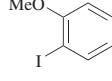
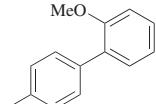
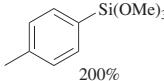
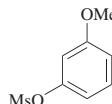
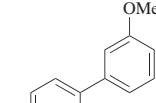
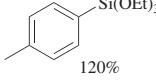
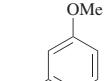
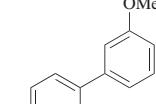
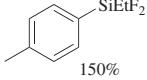
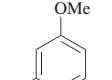
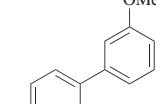
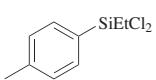
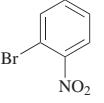
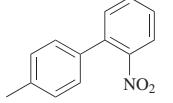
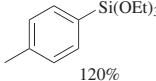
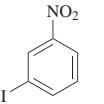
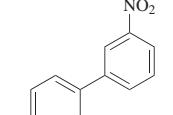
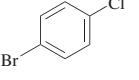
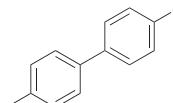
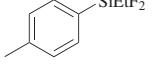
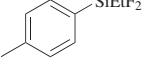
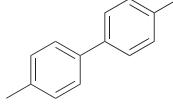
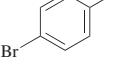
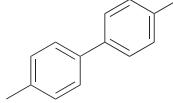
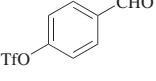
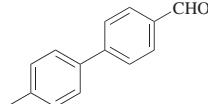
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		1. Pd(PPh ₃) ₄ (5%), TBAF (1000%), THF, 80°, 48 h 2. TFA, CH ₂ Cl ₂		(94)	184
		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 48 h		(32)	246
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°		(81)	249
120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(85)	47

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
 115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 6 h	 (80)	47
 150%		[allylPdCl] ₂ (5.0%), KF (200%), DMF, 80°, 6 h	 (45)	73
 200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°	 (96)	248
 120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 6 min	 (80)	234
 150%		[allylPdCl] ₂ (5%), KF (200%), DMF, 80°, 9 h	 (83)	73

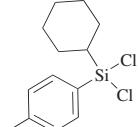
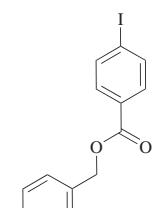
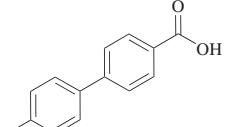
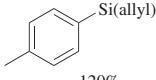
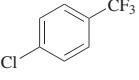
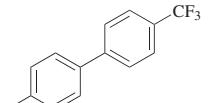
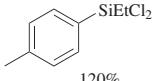
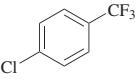
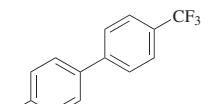
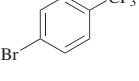
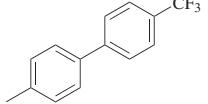
	150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(92)	276
	120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 4 h		(93)	47
	115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 6 h		(94)	47
	150%		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 80°, 18 h		(73)	241
			Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 48 h		(37)	246
			Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 12 h		(99)	37

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h		(92)
120%				73
		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 6 min		(75)
120%				234
150%		Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 24 h		(62)
				246
		CuCl (100%), DMF, 60°, 24 h		(60)
				183
120%		Na ₂ PdCl ₄ (1.5%), SDS (20%), NaOH (600%), H ₂ O, 100°, 6 min		(80)
				234
120%		Pd(PPh ₃) ₄ (3–5%), TBAF (120%), THF, 50°, 4 h		(92)
				181

	150%			
		[allylPdCl]₂ (5%), KF (200%), DMF, 100°, 15 h		(86) 73
	120–150%	[allylPdCl]₂ (2.5–5%), KF (200%), DMF, 100°, 49 h		(89) 180
	120%	Pd(OAc)₂ (0.5%), P(o-tol)₃ (0.5%), KF (200%), DMF, 120°, 18 h		(83) 73
	120%	Pd(OAc)₂ (0.5%), P(o-tol)₃ (0.5%), KF (200%), DMF, 120°, 18 h		(70) 73
	15%	[allylPdCl]₂ (5%), KF (200%), DMF, 100°, 21 h		(67) 73
	150%	Pd(NH₃)₂Cl₂ (0.1%), L2 (0.1%), NaOH (200%), H₂O, 120°, 3 h		(68) 246

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₇					
 1000%	 Wang Resin	1. Pd(PPh ₃) ₄ (5%), TBAF (1000%), THF, 80°, 48 h 2. TFA, CH ₂ Cl ₂		(94) 184	
412	 120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°		(89) 47
	 120%		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h		(68) 187
	 120%		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120, 18 h		(41) 73

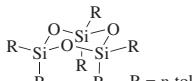
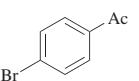
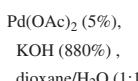
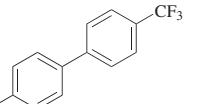
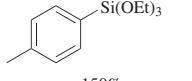
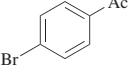
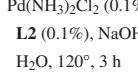
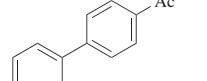
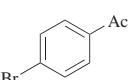
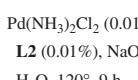
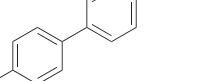
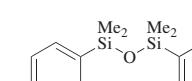
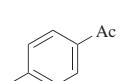
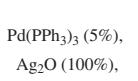
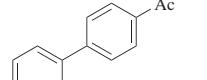
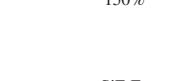
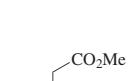
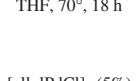
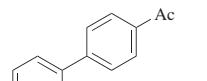
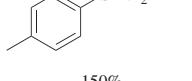
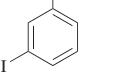
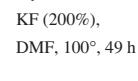
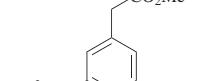
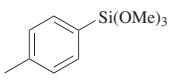
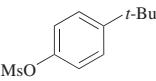
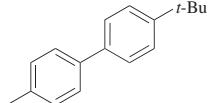
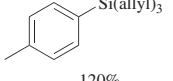
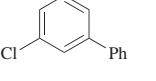
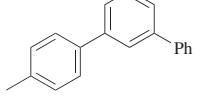
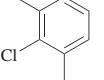
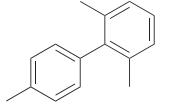
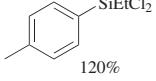
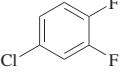
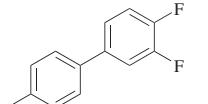
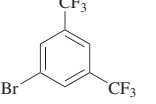
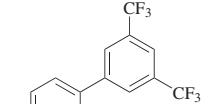
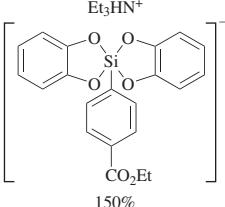
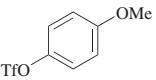
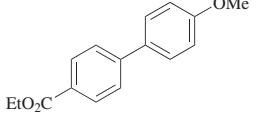
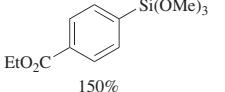
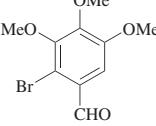
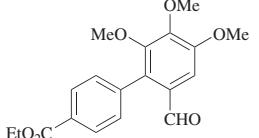
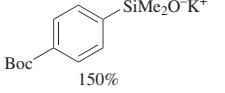
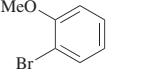
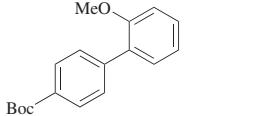
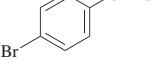
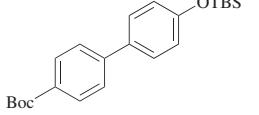
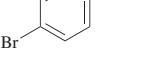
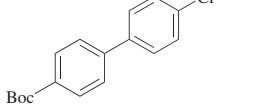
 <p>20%</p>	 <p>Br</p>	 <p>Ac</p>	<p>Pd(OAc)₂ (0.5%), P(o-tol)₃ (0.5%), KF (200%), DMF, 120, 18 h</p>	 <p>(91)</p>	<p>73</p>
 <p>150%</p>	 <p>Br</p>	 <p>Ac</p>	<p>Pd(OAc)₂ (5%), KOH (880%), dioxane/H₂O (1:1), reflux, 0.5 h</p>	 <p>(92)</p>	<p>265</p>
 <p>150%</p>	 <p>Br</p>	 <p>Ac</p>	<p>Pd(NH₃)₂Cl₂ (0.1%), L2 (0.1%), NaOH (200%), H₂O, 120°, 3 h</p>	 <p>(87)</p>	<p>246</p>
 <p>150%</p>	 <p>Br</p>	 <p>Ac</p>	<p>Pd(NH₃)₂Cl₂ (0.01%), L2 (0.01%), NaOH (200%), H₂O, 120°, 9 h</p>	 <p>(91)</p>	<p>246</p>
 <p>150%</p>	 <p>Br</p>	 <p>Ac</p>	<p>Pd(PPh₃)₃ (5%), Ag₂O (100%), TBAT (10%), THF, 70°, 18 h</p>	 <p>(59)</p>	<p>201</p>
 <p>150%</p>	 <p>I</p>	 <p>CO₂Me</p>	<p>[allylPdCl]₂ (5%), KF (200%), DMF, 100°, 49 h</p>	 <p>(89)</p>	<p>73</p>

TABLE 1A. CROSS-COUPLED OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90°	 (71)	248
200%				
		TBAF•3H ₂ O (400%), [allylPdCl] ₂ (2.5%), XPhos (10%), DMSO/H ₂ O (20:1), 80°, 8 h	 (81)	47
120%				
120%		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 9 h	 (66)	47
		(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (5%), KF (600%), DMF, 120°, 24–48 h	 (65)	187
120%				
120–160%		Pd(OAc) ₂ (0.5–1%), PPh ₃ (1–2%), NaOH (600%), THF, 60°, 39 h	 (85)	185

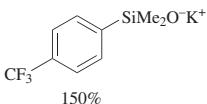
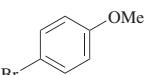
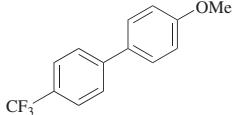
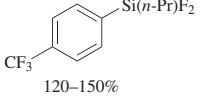
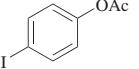
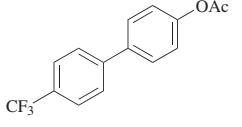
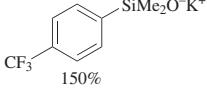
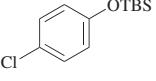
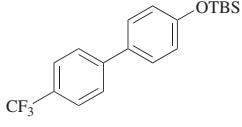
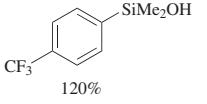
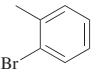
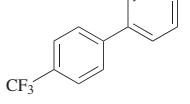
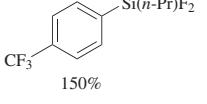
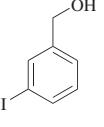
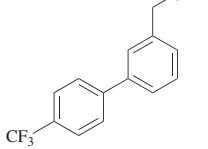
	150%			
		Pd(OAc) ₂ (5%), PPh ₃ (25%), TBAF (150%), THF, reflux, 18 h	(87)	235
	200%	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	(63)	249
	200%	Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80°	(78)	249
	150%			
		(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	(77)	54
	150%	(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	(71)	54

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		276
  150%		Pd(OAc) ₂ (5%), PPh ₃ (25%), TBAF (150%), THF, reflux, 18 h		265
  150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 7 h		54
  150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 6 h		54
  150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 6 h		54

	150%		Pd(NH3)2Cl2 (1%), L2 (1%), NaOH (200%), H2O, 120°, 6 h		(66)	244
	150%		(t-Bu3P)2Pd (5%), toluene, 90°, 5 h		(91)	54
	150%		(t-Bu3P)2Pd (5%), toluene, 90°, 5 h		(78)	54
	200%		Pd(OAc)2 (4%), XPhos (10%), TBAF (200%), THF, 80°		(85)	249
	150%		[allylPdCl]2 (5%), KF (200%), DMF, 80°, 28 h		(52)	73
	120%		Pd(PPh3)4 (5%), Ag2O (100%), THF, 60°, 36 h		(84)	37

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇	 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	 (92)	54
418	 120–150%		[allylPdCl] ₂ (2.5–5%), KF (200%), DMF, 100°, 13 h	 (47)	180
	 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 5 h	 (58)	54
	 120%		Cs ₂ CO ₃ ·H ₂ O + 2 H ₂ O (200%), [allylPdCl] ₂ (5%), dppb (10%), dioxane/toluene (4:1), 110°, 24 h	 (26)	205
	 150%		[allylPdCl] ₂ (5%), KF (200%), DMF, 100°, 19 h	 (64)	73

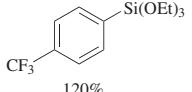
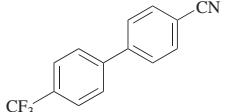
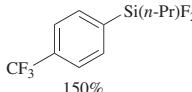
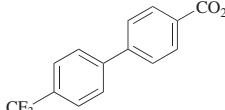
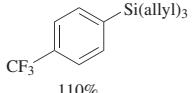
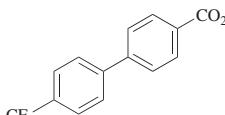
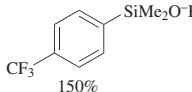
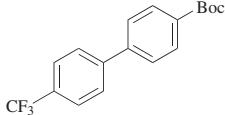
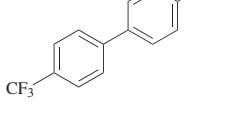
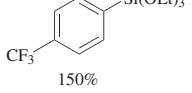
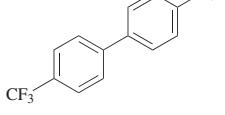
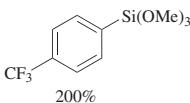
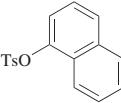
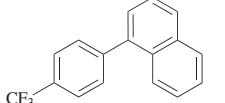
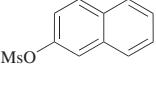
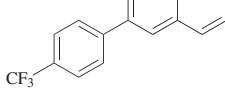
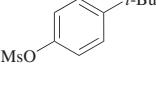
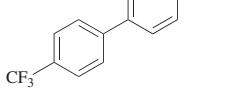
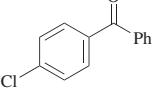
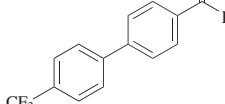
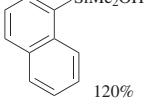
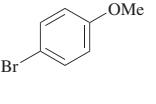
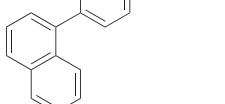
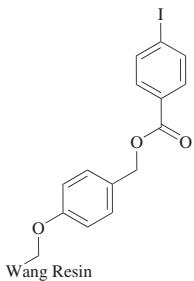
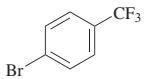
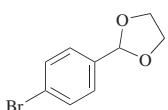
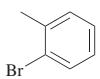
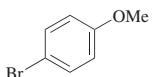
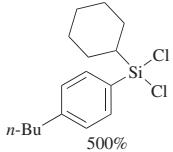
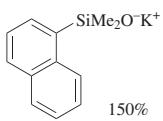
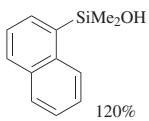
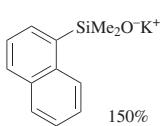
	Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 80°, 18 h		(85)	241
	[allylPdCl] ₂ (5%), KF (200%), DMF, 100°, 13 h		(47)	73
	1. TBAF•H ₂ O (440%), DMSO/H ₂ O (10:1), rt, 1 h 2. PdCl ₂ (5%), PCy ₃ (10%), 80°, 1 h		(49)	46
	(<i>t</i> -Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 5 h		(62)	54
	(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 5 h		(68)	54
	Pd(NH ₃) ₂ Cl ₂ (0.1%), L2 (0.1%), NaOH (200%), H ₂ O, 120°, 3 h		(76)	246

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

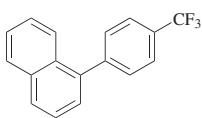
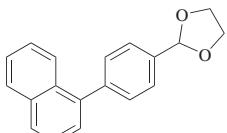
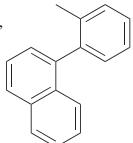
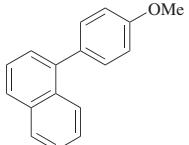
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF, 80° 	(91) 249
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90° 	(90) 248	
		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH (1:1), 90° 	(55) 248	
		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 5 h 	(58) 54	
C_{10}			$Cs_2CO_3 \cdot H_2O + 2 H_2O$ (200%), [allylPdCl] ₂ (5%), dppb (10%), dioxane/toluene (4:1), 110°, 24 h 	(82) 205

421



$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (2.5%),
toluene, 90°, 4 h

$\text{Cs}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ + 2 H₂O (200%),
 $[\text{allylPdCl}]_2$ (5%),
dppb (10%),
dioxane/toluene (4:1),
110°, 24 h



$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (5%),
toluene, 90°, 4 h

$(t\text{-Bu}_3\text{P})_2\text{Pd}$ (5%),
toluene, 90°, 5 h

(82)

54

(85)

205

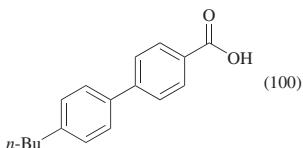
(71)

54

(81)

54

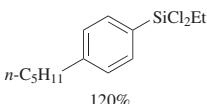
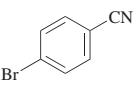
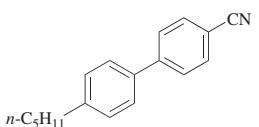
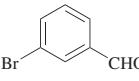
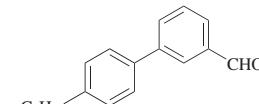
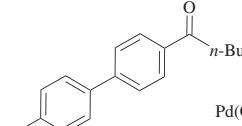
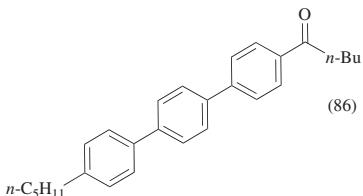
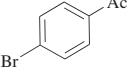
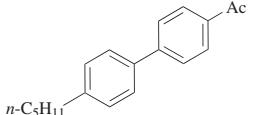
1. $\text{Pd}(\text{PPh}_3)_4$ (5%),
TBAF (500%),
THF, 80°, 30 h
2. TFA, CH_2Cl_2



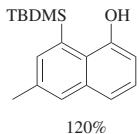
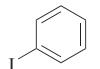
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184

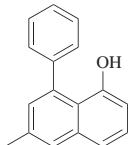
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁				
 n-C ₅ H ₁₁ -C ₆ H ₅ -SiCl ₂ Et 120%	 Br-C ₆ H ₄ -C(=N)C ₆ H ₅	Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 n-C ₅ H ₁₁ -C ₆ H ₅ -C ₆ H ₄ -C ₆ H ₄ -C(=N)C ₆ H ₅	(73)
120%	 Br-C ₆ H ₄ -C(=O)H	Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 n-C ₅ H ₁₁ -C ₆ H ₅ -C ₆ H ₄ -C ₆ H ₄ -C(=O)H	(54)
120%	 Br-C ₆ H ₄ -C(=O)n-Bu	Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 n-C ₅ H ₁₁ -C ₆ H ₅ -C ₆ H ₄ -C ₆ H ₄ -C(=O)n-Bu	(86)
120%	 Br-C ₆ H ₄ -C(=O)Ac	1. TBAF (105%), 2. Pd(OAc) ₂ (5%), Ph ₃ P (15%), toluene, reflux, 30 h	 n-C ₅ H ₁₁ -C ₆ H ₅ -C ₆ H ₄ -C ₆ H ₄ -C(=O)Ac	(84)

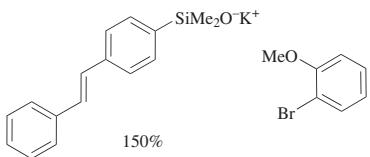
423

 C_{14} 

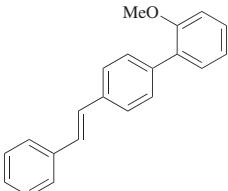
[allylPdCl]₂ (6%),
AsPh₃ (24%),
Cs₂CO₃ (150%),
DME, 60°, 2.5 h



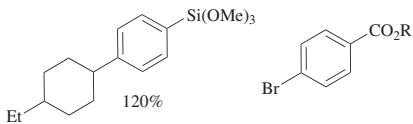
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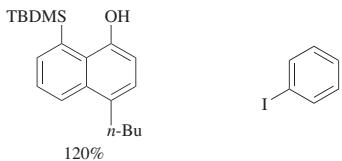
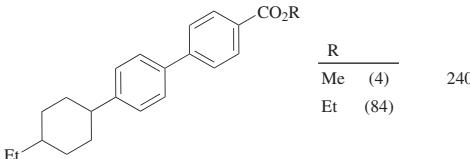
(*t*-Bu₃P)₂Pd (2.5%),
toluene, 90°, 10 h



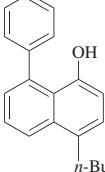
(56) 54



1. TBAF (105%),
2. Pd(OAc)₂ (5%),
Ph₃P (15%),
toluene, reflux, 30 h

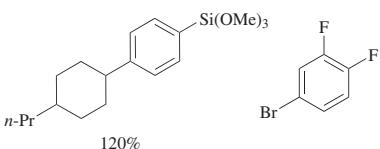
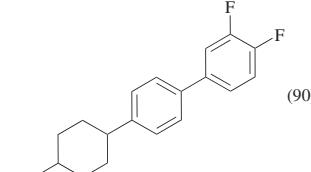
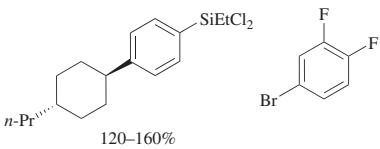
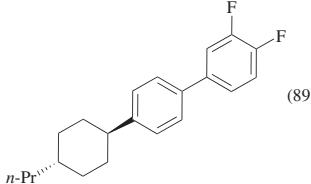
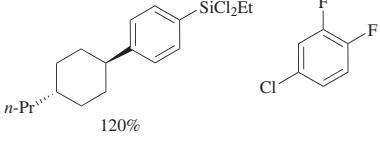
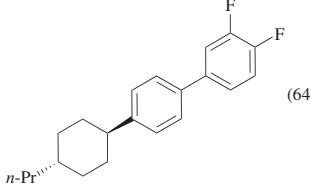


[allylPdCl]₂ (6%),
AsPh₃ (24%),
Cs₂CO₃ (150%),
DME, 60°, 12 h



(61) 120

TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅				
 120%		1. TBAF (105%), 2. Pd(OAc) ₂ (5%), Ph ₃ P (15%), toluene, reflux, 3 h	 (90)	240
 120–160%		Pd(OAc) ₂ (0.5–1%), PPh ₃ (1–2%), NaOH (600%), benzene, 80°, 62 h	 (89)	185
 120%		Pd(OAc) ₂ (0.5%), KF (600%), DMF, 150°, 20 h	 (64)	187

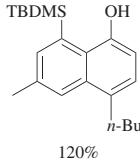
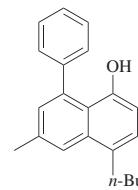
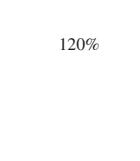
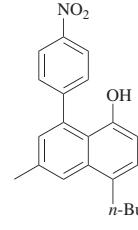
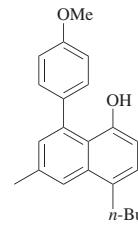
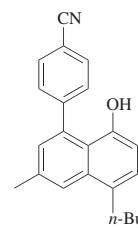
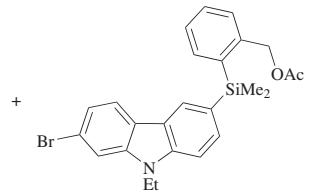
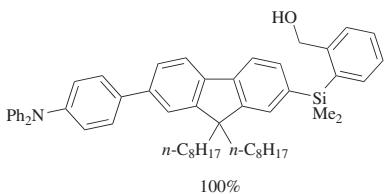
	I		[allylPdCl]₂ (6%), AsPh₃ (24%), Cs₂CO₃ (150%), DME, 60°, 2 h		(77)	120
	I		[allylPdCl]₂ (6%), AsPh₃ (24%), Cs₂CO₃ (150%), DME, 60°, 7 h		(55)	120
	I		[allylPdCl]₂ (6%), AsPh₃ (24%), Cs₂CO₃ (150%), DME, 60°, 8 h		(80)	120
	I		[allylPdCl]₂ (6%), AsPh₃ (24%), Cs₂CO₃ (150%), DME, 60°, 2 h		(81)	120

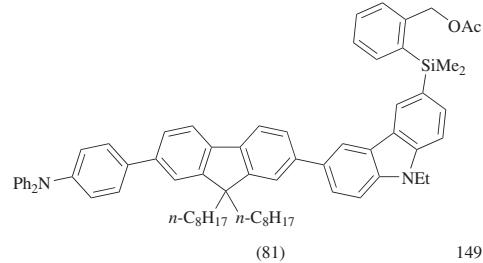
TABLE 1A. CROSS-CO尤LING OF ARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅					
426					
C ₁₇					

427

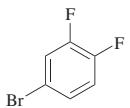
C₃₅

[allylPdCl]₂ (0.5%),
RuPhos (2%), CuI (3%),
K₂CO₃ (250%),
THF/DMF (3:1), 75°, 17 h

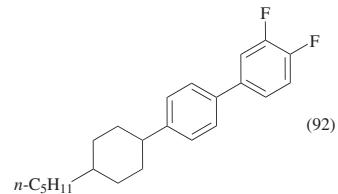


149

120%

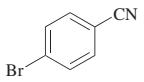


1. TBAF (105%),
2. Pd(OAc)₂ (5%),
Ph₃P (15%),
toluene, reflux, 10 h

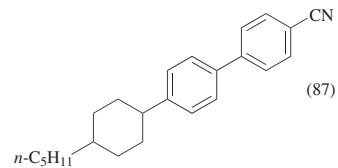


240

120%

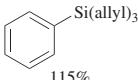
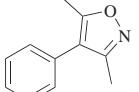
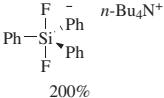
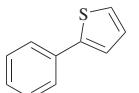
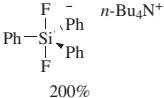
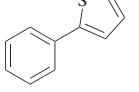
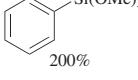
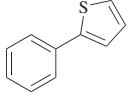
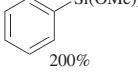
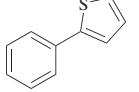


1. TBAF (105%),
2. Pd(OAc)₂ (5%),
Ph₃P (15%),
toluene, reflux, 30 h



240

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 18 h		(61)
115%				47
		1. TBAF (500%), THF/H ₂ O (20:1, 5 mL), rt, 1 h 2. [allylPdCl] ₂ (2.5%), XPhos (10%), 80°, 12 h		(93)
125%				160
		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h		(66)
200%				269
		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(44)
200%				245
		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h		(64)
200%				236

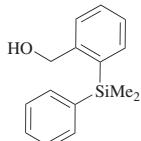
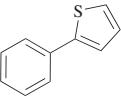
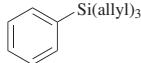
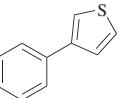
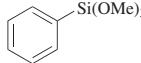
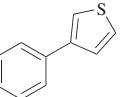
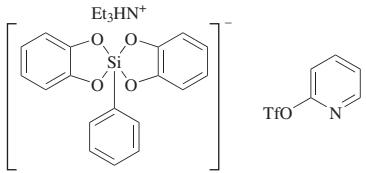
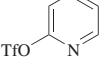
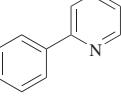
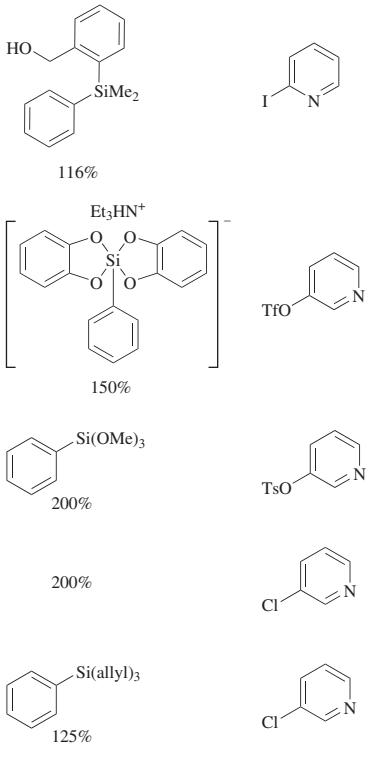
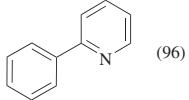
	116%		
		PdCl ₂ (3%), CuI (10%), L4 (4%), K ₂ CO ₃ (200%), H ₂ O (200%), DMSO, 50°, 13 h	(93)
			151
	125%		
		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 12 h	(94)
			47
	200%		
		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h	(70)
			236
	150%		
		PdCl ₂ (5%), TBAF•3H ₂ O (200%), toluene, 100°, 10 h	(50)
			237
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h	(73)
			276

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 20%		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O (1:1), reflux, 22 h	 (69)	265
 125%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 23 h	 (86)	47
 20%		Pd(OAc) ₂ (5%), KOH (880%), dioxane/H ₂ O, reflux, 8 h	 (70)	265
 200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h	 (76)	236
 120%		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 80°, 18 h	 (73)	241
 200%		Pd(OAc) ₂ (3%), IPr•HCl (3%), TBAF (200%), 1,4-dioxane/THF (5:2), 80°, 7 h	 (81)	244



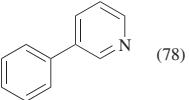
PdCl₂ (3%), CuI (10%),
L4 (4%), K₂CO₃ (200%),
H₂O (200%),
DMSO, 50°, 13 h



(96)

151

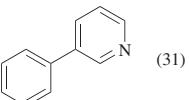
Pd(dba)₂ (5%),
Cyclohexyl JohnPhos (5%),
TBAF (150%),
dioxane, reflux, 6 h



(78)

276

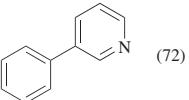
Pd(OAc)₂ (4%),
XPhos (10%),
TBAF (200%), THF, 80°



(31)

249

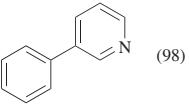
Pd cat. **2** (7%),
NaOH (250%),
H₂O, 135–140°, 24 h



(72)

245

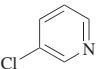
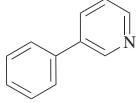
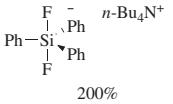
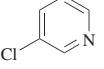
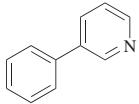
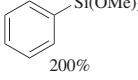
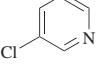
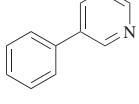
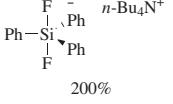
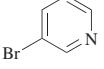
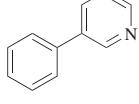
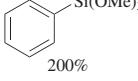
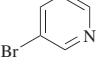
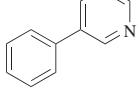
TBAF•H₂O (500%),
[allylPdCl]₂ (2.5%),
XPhos (10%),
THF/H₂O (20:1), 80°, 14 h



(98)

47

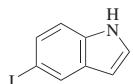
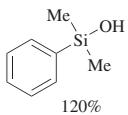
TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 150%		TBAF•3H ₂ O (600%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (25:1), 80°, 7 h	 (95)	47
 200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (56)	269
 200%		Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h	 (58)	247
 200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (92)	269
 200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h	 (62)	236

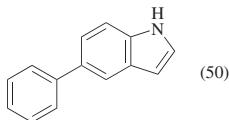
120%		Pd(dba) ₂ (3%), <i>i</i> -Pr-DPEphos (4%), TBAF•3H ₂ O (120%), toluene, 80°, 18 h		(81)	241
200%		Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h		(92)	247
200%		Pd cat. 2 (7%), TBAF (250%), H ₂ O, 135–140°, 24 h		(99)	245
150%		Pd(NH ₃) ₂ Cl ₂ (0.5%), L2 (0.5%), NaOH (200%), H ₂ O, 120°, 5 h		(67)	246
200%		Pd(OAc) ₂ (10%), PPh ₃ (20%), TBAF (200%), DMF, 90°, 24 h		(62)	236
115%		TBAF•3H ₂ O (460%), PdCl ₂ (5%), PCy ₃ (10%), DMSO/H ₂ O (10:1), 80°, 3 h		(89)	47

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

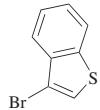
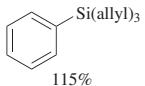
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
200%		Pd(OAc) ₂ (20%), PPh ₃ (40%), TBAF (200%), DMF, 80°, 12 h	(97)	242, 243
200%		Pd(OAc) ₂ (20%), PPh ₃ (40%), TBAF (200%), DMF, 80°, 12 h	(36)	242, 243
200%		Pd(OAc) ₂ (20%), PPh ₃ (40%), TBAF (200%), DMF/THF, 80°, 12 h	(89)	242, 243
150%		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane, reflux, 6 h	(69)	276



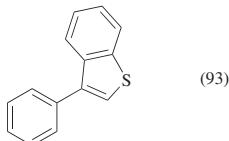
Pd(PPh₃)₃ (3%),
Ag₂O (10%),
TBAT (12%),
THF, 70°, 0.5 h



201

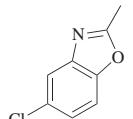


TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 5 h

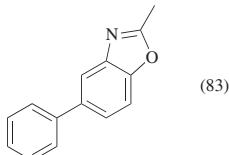


47

125%

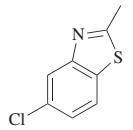


TBAF•3H₂O (500%),
[allylPdCl]₂ (2.5%),
XPhos (10%),
THF/H₂O (20:1), 80°, 14 h

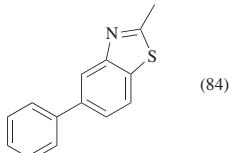


47

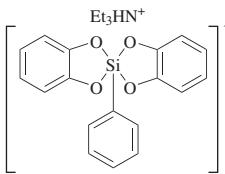
125%



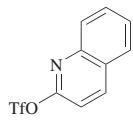
TBAF•3H₂O (500%),
[allylPdCl]₂ (2.5% eq),
XPhos (10%),
THF/H₂O (20:1), 80°, 12 h



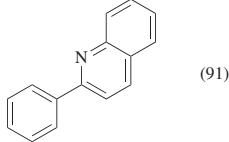
47



150%

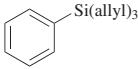
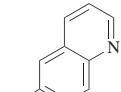
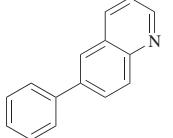
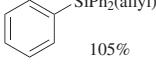
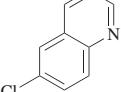
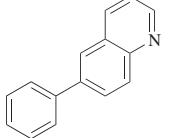
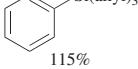
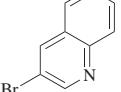
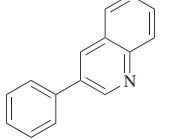
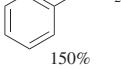
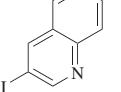
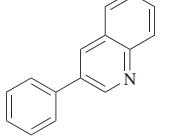
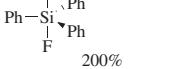
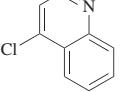
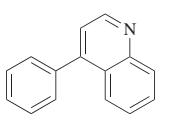


Pd(dba)₂ (5%),
Cyclohexyl JohnPhos (5%),
TBAF (150%),
THF, reflux, 6 h



276

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 125%		TBAF•3H ₂ O (500%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 14 h	 (99)	47
 105%		TBAF•3H ₂ O (330%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (40:1), 80°, 7 h	 (96)	47
 115%		TBAF•3H ₂ O (460%), [allylPdCl] ₂ (5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 2 h	 (97)	47
 150%		[allylPdCl] ₂ (2.5%), KF (200%), DMF, 100°, 12 h	 (68)	172
 200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (70)	269

	200%				
	200%	Pd cat. 2 (7%), TBAF (200%), MeCN/THF, 80°, 24 h		(88)	247
	200%	Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(88)	245
	200%	Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h		(75)	247
	200%	Pd cat. 2 (7%), TBAF (200%), MeCN/THF (5:1), 80°, 24 h		(89)	247
	200%	Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(81)	245
	200%	Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h		(73)	269

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 Ph-Si(F)(Ph) ₂ 200%		Pd cat. 1 (10%), NaOH (0.5 M, 1 mL), toluene/H ₂ O (6:1), 135–140°, 24 h	 (72)	269
 H ₂ N--Si(OMe) ₃ 200%		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h	 (77)	245
 Me ₂ N--SiMe ₂ O ⁻ K ⁺ 150%		(t-Bu ₃ P) ₂ Pd (2.5%), toluene, 90°, 3 h	 (80)	54
 Ph ₂ N--SiMe ₂ -CH ₂ CH ₂ OH 120%		[allylPdCl] ₂ (1.5%), CuI (3%), RuPhos (2.1%), K ₂ CO ₃ (250%), THF/DMF (3:1), 75°, 7 h	 (81)	149

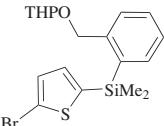
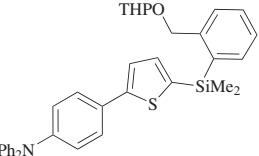
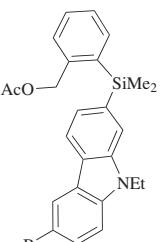
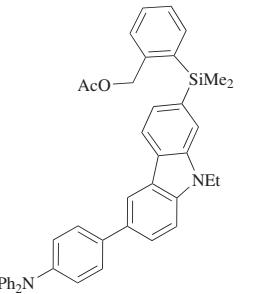
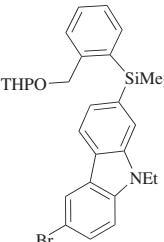
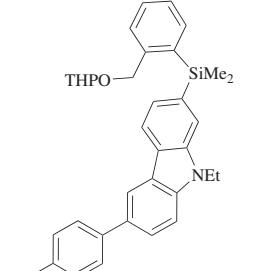
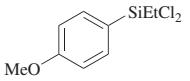
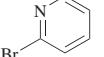
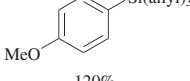
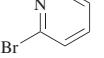
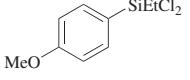
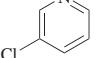
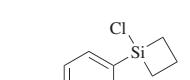
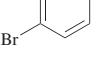
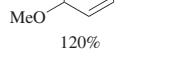
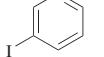
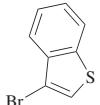
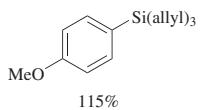
 <p>120%</p>	<p>[allylPdCl]₂ (1.5%), CuI (3%), RuPhos (2.1%), K_2CO_3 (250%), THF/DMF (3:1), 75°, 8 h</p>	 <p>(81)</p>	149
 <p>150%</p>	<p>[allylPdCl]₂ (0.5%), CuI (3%), RuPhos (2.1%), K_2CO_3 (250%), THF/DMF (3:1), 75°, 18 h</p>	 <p>(94)</p>	149
 <p>120%</p>	<p>[allylPdCl]₂ (0.5%), CuI (3%), RuPhos (2.1%), K_2CO_3 (250%), THF/DMF (3:1), 75°, 22 h</p>	 <p>(85)</p>	149

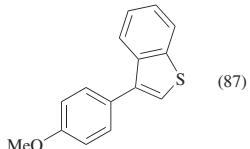
TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  120%		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (200%), DMF, 120°, 18 h	 (23) + (63)	73
120–160%  120%		Pd(OAc) ₂ (0.5–1%), PPh ₃ (1–2%), NaOH (600%), THF, 60°, 39 h	 (64) + (—)	185
440  120%		TBAF 3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 6 h	 (92)	47
120%  120%		Pd(OAc) ₂ (0.5%), P(<i>o</i> -tol) ₃ (0.5%), KF (2 eq), DMF, 120°, 18 h	 (69)	73
120%  120%		TBAF (360%), [allylPdCl] ₂ (2.5%), (<i>t</i> -Bu) ₃ P (20%), THF, reflux, 5 h	 (71)	39

†

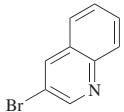


TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 5 h

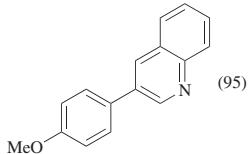


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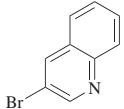
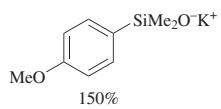
115%



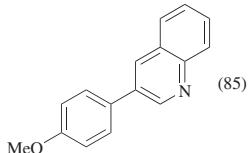
TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 4 h



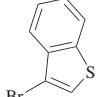
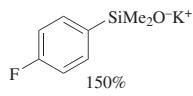
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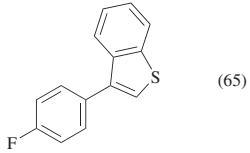
(t-Bu₃P)₂Pd (5%),
toluene, 90°, 5 h



54

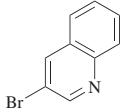


(t-Bu₃P)₂Pd (2.5%),
toluene, 90°, 5 h

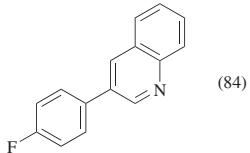


54

150%



(t-Bu₃P)₂Pd (2.5%),
toluene, 90°, 5 h

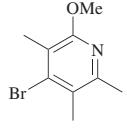
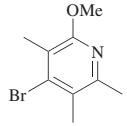
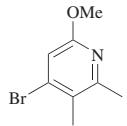
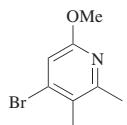
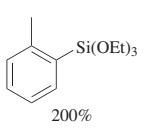
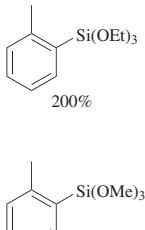
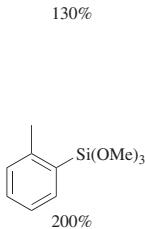


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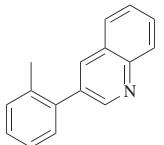
TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
<chem>C6</chem>		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 13 h		(98) 47
		(t-Bu ₃ P) ₂ Pd (5%), toluene, 90°, 3.5 h		(61) 54
		Pd(OAc) ₂ (20%), PPh ₃ (40%), TBAF (200%), DMF, 80°, 12 h		(61) 243
<chem>C7</chem>		TBAF•3H ₂ O (480%), [allylPdCl] ₂ (2.5%), XPhos (10%), THF/H ₂ O (20:1), 80°, 7 h		(87) 47

443



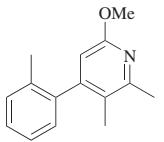
TBAF•3H₂O (460%),
PdCl₂ (5%), PCy₃ (10%),
DMSO/H₂O (10:1),
80°, 20 h



(80)

47

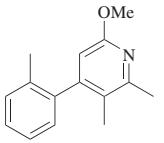
Pd(OAc)₂ (20%),
PPh₃ (40%),
TBAF (200%),
DMF, 80°, 12 h



(10)

242

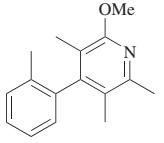
Pd(OAc)₂ (20%),
PPh₃ (40%),
TBAF (200%),
DMF, 80°, 12 h



(10)

243

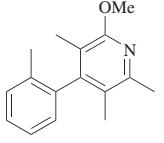
Pd(OAc)₂ (20%),
PPh₃ (40%),
TBAF (200%),
DMF 80°, 12 h



(10)

242

Pd(OAc)₂ (20%),
PPh₃ (40%),
TBAF (200%),
DMF, 80°, 12 h



(10)

243

TABLE 1B. CROSS-COUPLING OF ARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

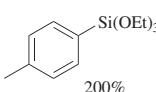
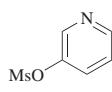
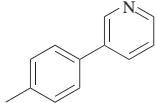
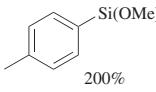
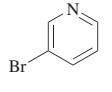
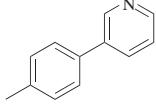
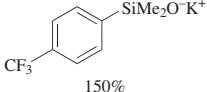
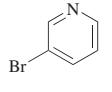
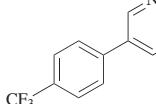
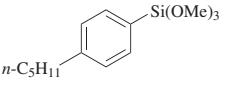
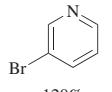
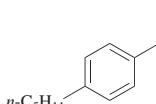
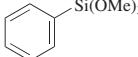
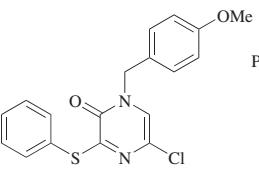
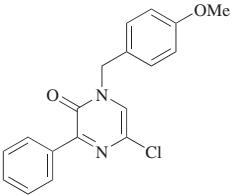
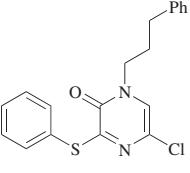
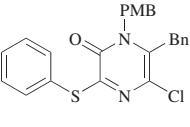
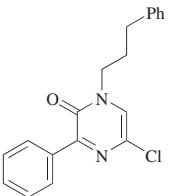
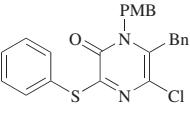
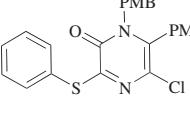
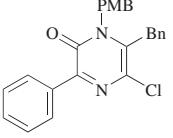
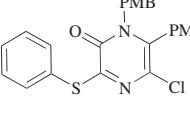
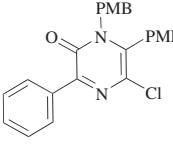
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
 200%		Pd(OAc) ₂ (4%), XPhos (10%), TBAF (200%), THF/ <i>t</i> -BuOH, 90°		(40)
 200%		Pd cat. 2 (7%), NaOH (250%), H ₂ O, 135–140°, 24 h		(92)
 150%		(<i>t</i> -Bu ₃ P) ₂ Pd (5%), toluene, 90°, 5 h		(78)
C ₁₁				
 120%		1. TBAF (105%) 2. Pd(OAc) ₂ (5%), Ph ₃ P (15%), toluene, reflux, 30 h		(72)
				240

TABLE 1C. CROSS-CO尤LING OF ARYLSILANES WITH ALKENYL ELECTROPHILES

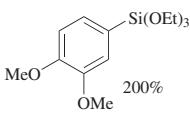
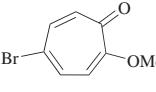
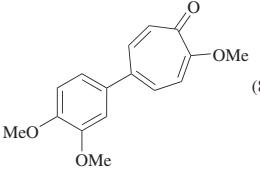
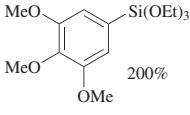
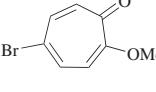
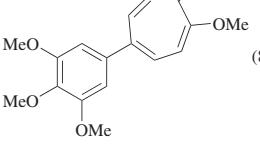
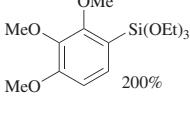
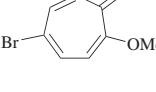
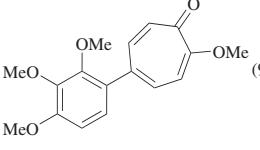
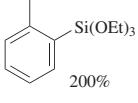
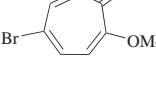
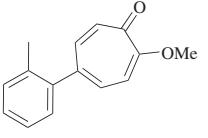
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(63)
		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (300%), LiOAc (200%), DMF, 100°, 3 h		(59)
		Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), THF, reflux, 6 h		(89)
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h		(84)
		Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1 h		(90)

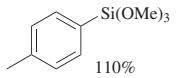
TABLE 1C. CROSS-COUPLING OF ARYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 3 h		(79) 252
110%				
		Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1 h		(89) 252
120%				
		Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1.5 h		(95) 252
130%				
		Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1.5 h		(90) 252
110%				

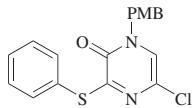
	200%		
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	(81) 251
	120%	Pd(PPh ₃) ₄ (3–5%), TBAF (120%), THF, 50°, 5 h	(62) 181
	110%	Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1 h	(98) 252
	120%	Pd(PPh ₃) ₄ (5%), CuI (100%), TBAF (200%), THF, 60°, 1 h	(89) 252
	200%	Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	(81) 251

TABLE 1C. CROSS-COUPLING OF ARYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

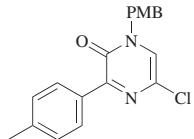
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	 (88)	251
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	 (89)	251
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	 (92)	251
C ₇				
		Pd(OAc) ₂ (10%), PPh ₃ (50%), TBAF (200%), THF, 12 h	 (81)	251



110%



Pd(PPh_3)₄ (5%),
CuI (100%), TBAF (200%),
THF, 60°, 1 h

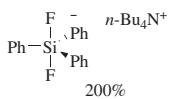


(89)

252

TABLE 1D. CROSS-CO尤LING OF ARYLSILANES WITH ALLYL ELECTROPHILES

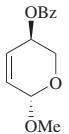
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), benzene, 40°	 I + II (68), I:II = 1:2	175
200%				
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), DMF, 60°, 19 h		175
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), benzene, 60°, 19 h		175
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), DMF, 60°, 19 h		175
200%		Pd(dba) ₂ , TBAF, DMF, 85°		70
200%		Pd(dba) ₂ (10%), TBAF (200%), THF, 50°, 14 h		253



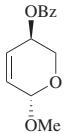
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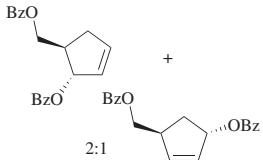
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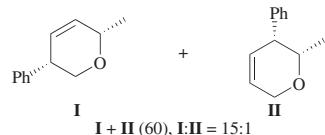
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200%

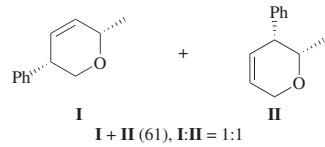


Pd(dba)₂ (10%),
TBAF (200%),
THF, 50°, 14 h



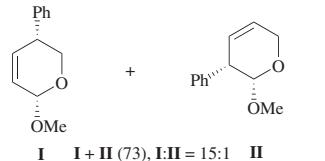
316

Pd(dba)₂ (8.5%),
dppe (8.5%),
THF, reflux, 12 h



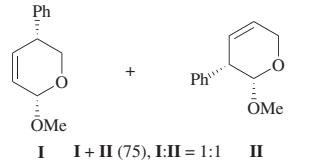
316

Pd(dba)₂ (8.5%),
dppe (8.5%),
THF, reflux, 12 h



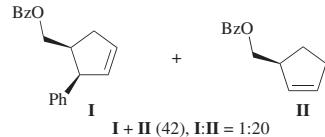
316

Pd(dba)₂ (5%),
PPh₃ (5%),
THF, reflux, 12 h



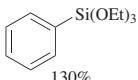
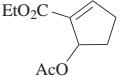
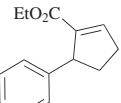
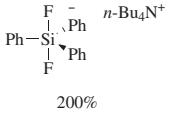
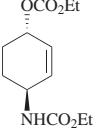
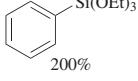
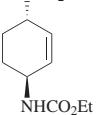
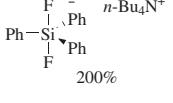
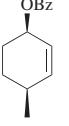
316

Pd(dba)₂ (5.4%),
PPh₃ (5.4%),
THF, reflux, 12 h



111

TABLE 1D. CROSS-CO尤LING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, 50°	 (48)	255
 200%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), PPh ₃ (10%), THF, 55°	 I + II (53), I : II = 1:1 II	111
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), PPh ₃ (10%), THF, 48 h	 I + II (51), I : II = 1:1 II	111
 200%		Pd(dba) ₂ (10%), PPh ₃ (10%), THF, 75°, 17 h	 I + II (94), I : II = 1:2	111

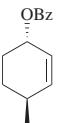
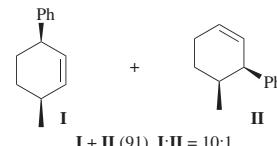
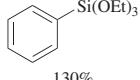
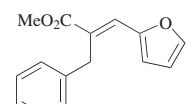
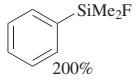
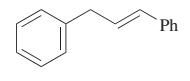
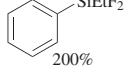
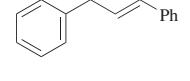
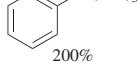
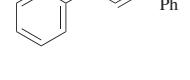
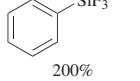
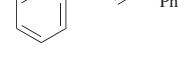
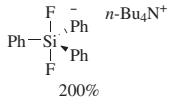
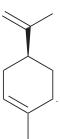
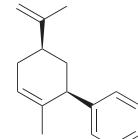
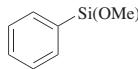
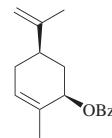
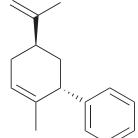
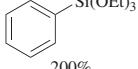
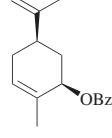
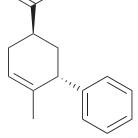
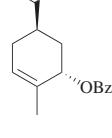
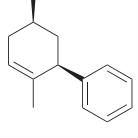
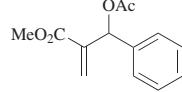
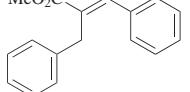
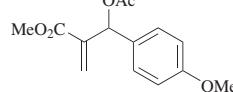
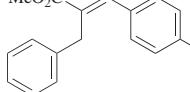
		Pd(dba) ₂ (10%), PPh ₃ (10%), THF, 75°, 17 h		111
200%				
				255
130%			(78) (E)/(Z) = 99:1	
				175
200%			(90) (E)/(Z) = 99:1	
				175
200%			(91)	
				253
200%			(95)	
				175
200%			(73)	
		Pd(dba) ₂ (5%), PPh ₃ (5%), THF, reflux, 12 h		316
200%			(60)	

TABLE 1D. CROSS-CO尤LING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(dba) ₂ , TBAF, DMF, 85°		(81) 70
		Pd(dba) ₂ (10%), TBAF (200%), THF, 50°, 14 h		(83) 253
200%		Pd(dba) ₂ (10%), TBAF (200%), THF, 54°, 14 h		(84) 253
200%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(92) (E)/(Z) = 93:7 255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(94) (E)/(Z) = 99:1 255

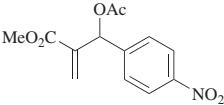
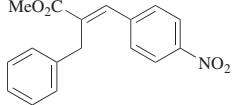
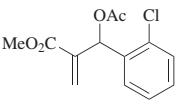
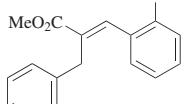
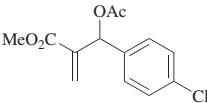
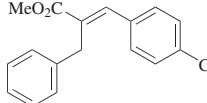
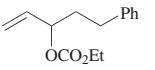
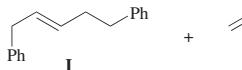
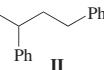
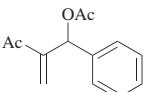
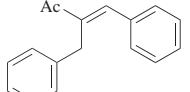
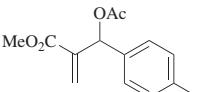
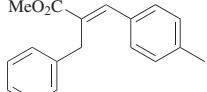
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(62) (<i>E</i>)/(<i>Z</i>) = 96:4	255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(86) (<i>E</i>)/(<i>Z</i>) = 92:8	255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(91) (<i>E</i>)/(<i>Z</i>) = 99:1	255
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), benzene, 60°, 19 h	 + 	I + II (93), I:II = 10:1	175
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 6 h		(90)	255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(89) (<i>E</i>)/(<i>Z</i>) = 95:5	255

TABLE 1D. CROSS-CO尤LING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 8 h	 (51)	255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h	 (85) (E)/(Z) = 90:10	255
456				
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 8 h	 (70)	255
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 8 h	 (61)	111
130%		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h	 (87) (E)/(Z) = 96:4	255

457

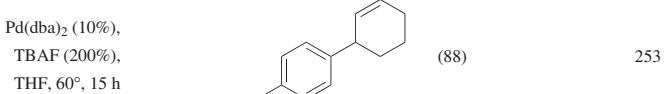
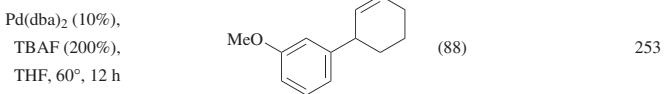
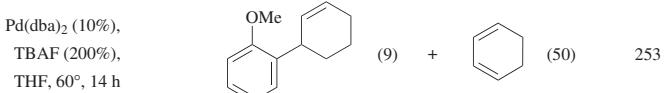
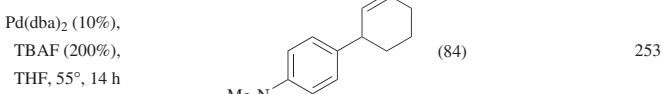
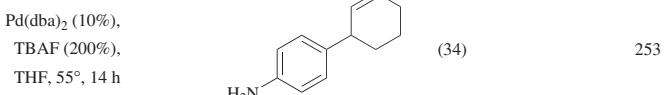
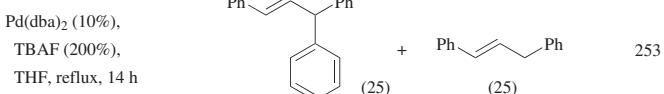
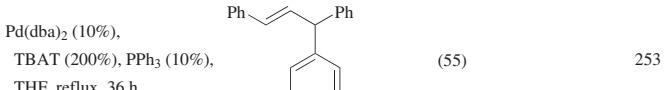
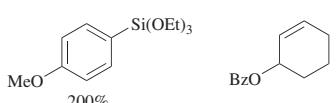
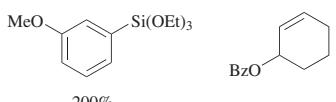
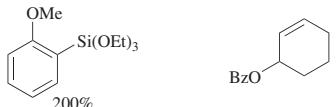
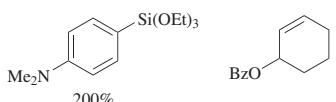
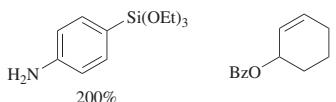
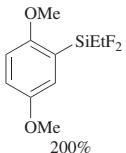
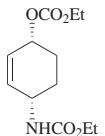
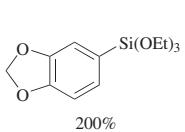
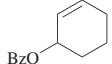
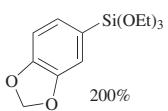


TABLE 1D. CROSS-CO尤LING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

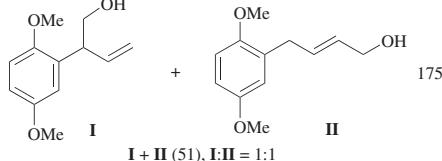
	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆						
			Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 20 h		(78)	253
			Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 12 h		(87)	253
458	200%					
			Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, 50°		(48)	255
	130%					
			Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(92) (E)/(Z) = 98:2	255
	130%					
			Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 8 h		(77)	255
	130%					



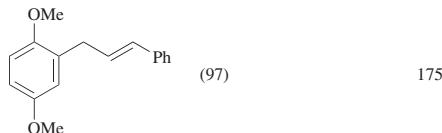
200%



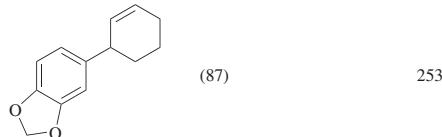
Pd₂(dba)₃•CHCl₃ (2.5%),
PPh₃ (5%),
benzene, 60°



Pd₂(dba)₃•CHCl₃ (2.5%),
PPh₃ (5%),
benzene, 60°, 19 h



Pd(dba)₂ (10%),
TBAF (200%),
THF, 60°, 14 h



Pd(dba)₂ (10%),
TBAF (200%),
THF, 65°

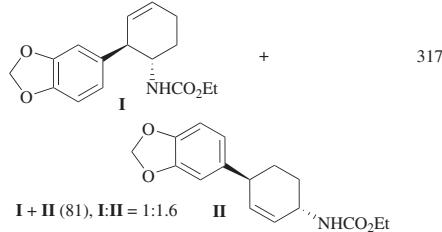
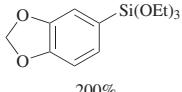
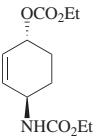
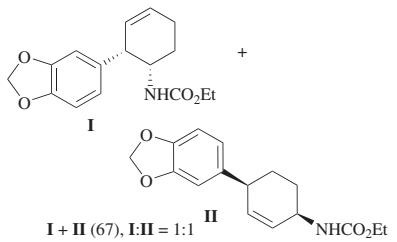
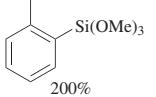
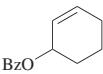
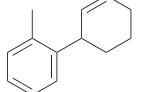
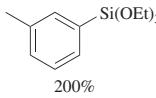
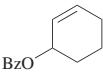
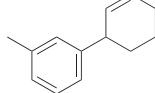
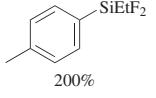
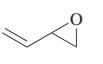
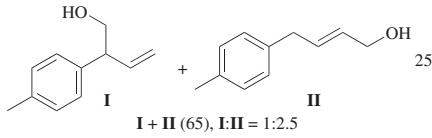


TABLE 1D. CROSS-COUPLING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, 55°, 20 h	 I + II (67), I : II = 1:1	111
200%	NHCO ₂ Et			
C ₇				
		Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 15 h	 (77)	253
200%	BzO			
		Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 10 h	 (86)	253
200%	BzO			
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), benzene, 60°	 I + II (65), I : II = 1:2.5	253
200%				

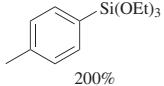
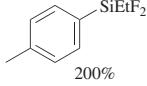
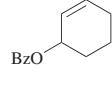
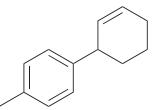
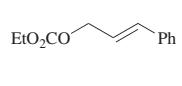
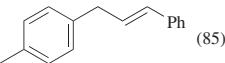
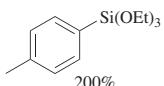
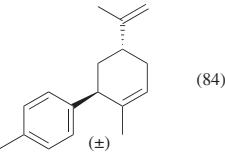
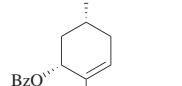
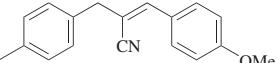
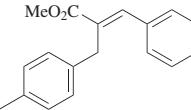
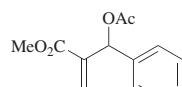
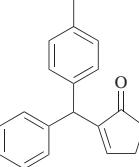
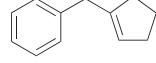
	200%			
	200%			
		Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 12 h		(87)
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), PPh ₃ (5%), benzene, 60°, 19 h		(85)
	200%	Pd(dba) ₂ (10%), TBAF (200%), THF, 60°, 48 h		(84) (±)
		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, 50°, 5 h		(54)
	130%	Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 3 h		(86) (E)/(Z) = 97:3
		Pd ₂ (dba) ₃ (3%), TBAF (200%), PEG, rt, 8 h		(53)
	130%			
				
				253
				175
				253
				255
				255
				255

TABLE 1D. CROSS-COUPLING OF ARYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
 130%		$\text{Pd}_2(\text{dba})_3$ (3%), TBAF (200%), PEG, rt, 8 h	 (66)	255
 130%		$\text{Pd}_2(\text{dba})_3$ (3%), TBAF (200%), PEG, rt, 8 h	 (61)	255

TABLE 1E. CROSS-CO尤LING OF ARYLSILANES WITH ALKYL ELECTROPHILES

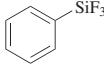
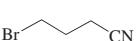
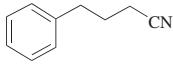
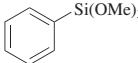
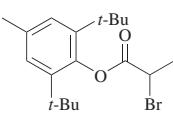
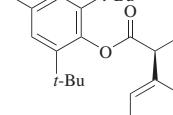
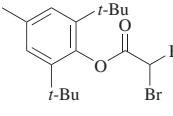
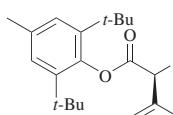
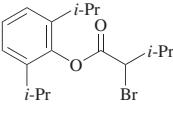
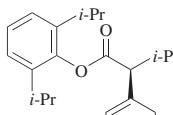
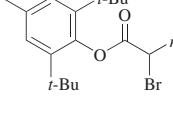
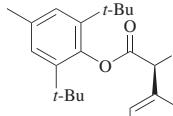
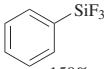
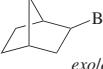
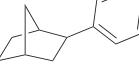
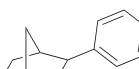
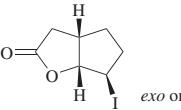
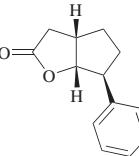
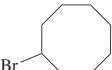
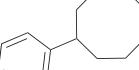
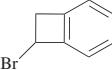
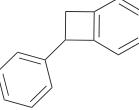
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(73) 189
150%				
		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(84) 89% ee 118
130%				
130%		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(80) 99% ee 118
130%				
130%		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(72) 75% ee 118
130%				
130%		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(76) 92% ee 118

TABLE 1E. CROSS-COUPLING OF ARYLSILANES WITH ALKYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
130%			NiCl ₂ *glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h 	(64) 93% ee 118
130%			NiCl ₂ *glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h 	(72) 84% ee 118
130%			NiCl ₂ *glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h 	(78) 80% ee 118
130%			NiCl ₂ *glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h 	(68) 99% ee 118

130%		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(70) 86% ee	118
130%		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h		(80) 92% ee	118
150%				(82)	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(60) <i>cis/trans</i> = 55:45	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(80)	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(63)	189

TABLE 1E. CROSS-COUPLING OF ARYLSILANES WITH ALKYL ELECTROPHILES(Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
150%		 <i>exo/endo</i> = 96:4	 (62) <i>exo/endo</i> = 94:6	189
150%	 <i>exo/endo</i> = 6:94	 (70) <i>exo/endo</i> = 95:5	189	
150%	 <i>exo</i> only	 (60) <i>exo</i> only	189	
150%		 (62)	189	
150%		 (80)	189	

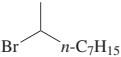
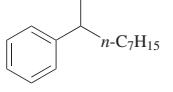
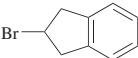
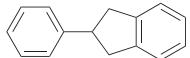
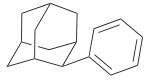
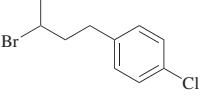
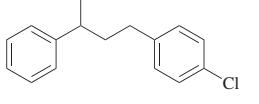
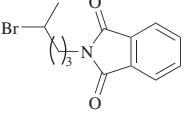
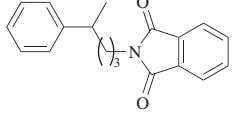
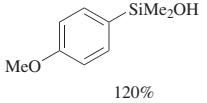
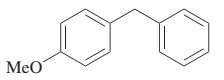
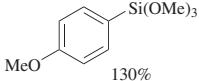
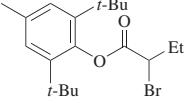
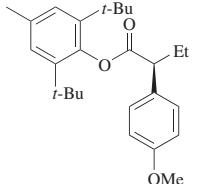
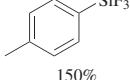
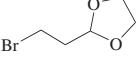
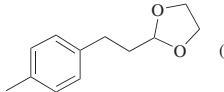
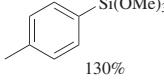
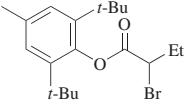
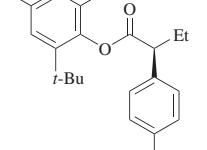
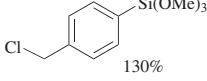
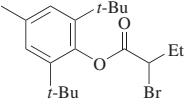
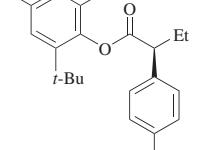
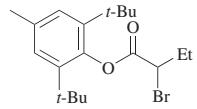
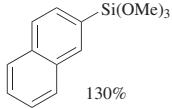
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(65)	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(71)	189
150%		NiBr ₂ •diglyme (9%), BPhen (10%), CsF (380%), DMSO, 60°, 20 h		(68)	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h		(72)	189
150%		NiBr ₂ •diglyme (6.5%), BPhen (10%), CsF (380%), DMSO, 60°, 20 h		(70)	189
120%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), THF, 60°, 36 h		(55)	37

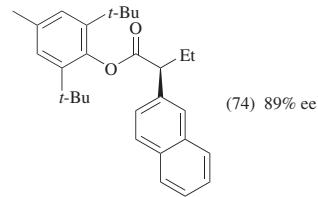
TABLE 1E. CROSS-COUPLING OF ARYLSILANES WITH ALKYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h	 (64) 87% ee	118
C ₇				
		NiBr ₂ •diglyme (6.5%), BPhen (7.5%), CsF (380%), DMSO, 60°, 20 h	 (80)	189
468				
		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h	 (76) 92% ee	118
		NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt, 16 h	 (72) 94% ee	118

C₁₀



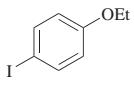
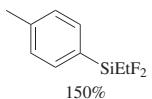
NiCl₂*glyme (10%),
L3 (12%),
TBAT (200%),
dioxane, rt, 16 h



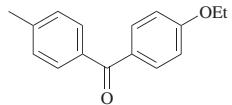
118

TABLE 1F. CARBOXYLATIVE CROSS-CO尤LING OF ARYLSILANES WITH MISCELLANEOUS ELECTROPHILES

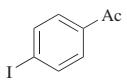
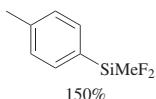
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₆					
		[allylPdCl] ₂ (2.5%), KF (110%), CO (1 atm), DMI, 100°, 5 h		(60)	179, 182
150%					
150%		[allylPdCl] ₂ (2.5%), KF (110%), CO (1 atm), DMI, 100°, 5 h		(61)	179, 182
150%					
4/70			 (52) +	(14)	179
150%					
150%			 (49) +	(23)	179
150%					
150%				(80)	179, 182
150%					
150%		[allylPdCl] ₂ (2.5%), KF (110%), CO (1 atm), DMI, 100°, 15 h		(67)	179, 182

C₇

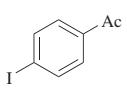
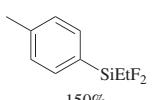
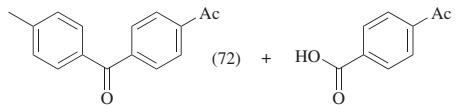
[allylPdCl]₂ (2.5%),
KF (110%), CO (1 atm),
DMI, 100°, 19 h



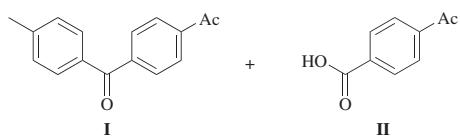
182



[allylPdCl]₂ (2.5%),
KF (165%), CO (1 atm),
DMI, 100°, 12 h



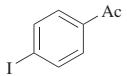
Pd cat. (2.5%), KF (*x*%),
CO (1 atm), solvent, 100°



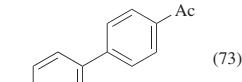
Pd cat.	<i>x</i>	Solvent	Time (h)	I	II	
[allylPdCl] ₂	165	DMF	48	(41)	(—)	179
PdCl ₂ (PPh ₃) ₂	165	DMI	12	(34)	(46)	179
Pd(PPh ₃)	165	DMI	12	(51)	(43)	179
[allylPdCl] ₂	165	DMI	12	(—)	(64)	179
[allylPdCl] ₂	110	DMI	3	(91)	(—)	179, 182

17

150%

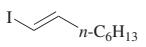


[allylPdCl]₂ (2.5%),
KF (165%), CO (1 atm),
DMI, 150°, 1 h

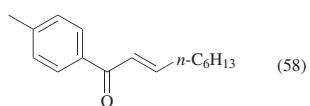


179

150%



[allylPdCl]₂ (2.5%),
KF (150%), CO (1 atm),
DMI, 50°, 25 h



179

TABLE 1F. CARBOXYLATIVE CROSS-COUPLING OF ARYLSILANES WITH MISCELLANEOUS ELECTROPHILES (*Continued*)

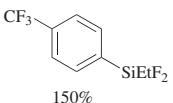
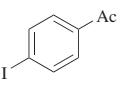
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  150%	 	[allylPdCl]2 (2.5%), KF (110%), CO (1 atm), DMI, 100°, 18 h	<p>(38) + (50)</p>	179, 182

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES

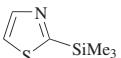
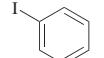
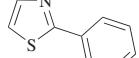
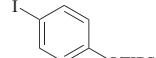
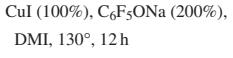
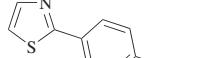
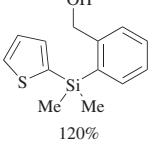
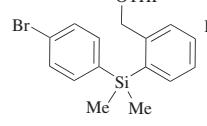
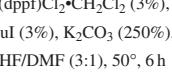
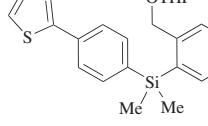
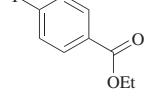
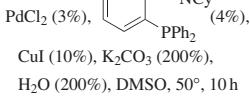
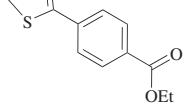
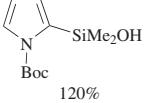
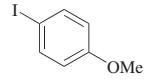
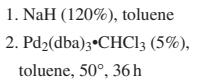
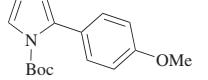
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3		 50%		(93)
	 50%		 (87)	231
C_4	 120%			 (96)
			 (93)	149
473	 120%			 (72)
				207, 208

TABLE 2A. CROSS-COUPLED HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
<chem>C3</chem>	<chem>Ic1ccccc1</chem>	<chem>CuI</chem> (100%), <chem>C6F5ONa</chem> (200%), DMI, 130°, 12 h	<chem>c1ncsc1-c2ccccc2</chem> (9)	231
	<chem>Ic1ccccc1-OTiPS</chem>	<chem>CuI</chem> (100%), <chem>C6F5ONa</chem> (200%), DMI, 130°, 12 h	<chem>c1ncsc1-c2ccccc2-OTiPS</chem> (8)	
<chem>C4</chem>	<chem>Ic1ccccc1-SiMe2OH</chem> 120%	1. <chem>NaH</chem> (120%), toluene 2. <chem>Pd2(dba)3•CHCl3</chem> (5%), toluene, rt, 3 h	<chem>c1ccccc1-N(C)(C)c2ccccc2</chem> (80)	207, 208
	<chem>Ic1ccccc1-C(=O)OEt</chem> 120%	1. <chem>NaH</chem> (120%), toluene 2. <chem>Pd2(dba)3•CHCl3</chem> (5%), toluene, rt, 3 h	<chem>c1ccccc1-N(C)(C)c2ccccc2-C(=O)OEt</chem> (76)	
<chem>474</chem>	<chem>Ic1ccccc1-SiMe2OMe</chem> 50%	<chem>CuI</chem> (100%), <chem>C6F5ONa</chem> (200%), DMI, 130°, 12 h	<chem>c1ccccc1-N(C)c2ccccc2</chem> (93)	231
	<chem>Ic1ccccc1-OMe</chem>	1. <chem>NaH</chem> (120%), toluene 2. <chem>Pd2(dba)3•CHCl3</chem> (5%), toluene, 50°, 36 h	<chem>c1ccccc1-N(C)(C)c2ccccc2-OMe</chem> (72)	
<chem>Br-C(=O)c1ccc(cc1)-OMe</chem> 120%	<chem>Br-c1ccc(cc1)-OMe</chem>	1. <chem>NaH</chem> (120%), toluene 2. <chem>Pd cat. 4</chem> (2.5%), toluene, 50°, 6 h	<chem>c1ccccc1-Oc2ccccc2</chem> (66)	207, 208

120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), furyl ₃ As (20%), toluene, 50°, 24 h		(71)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(71)	207, 208
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h		(61)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(73)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(60)	207, 208
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 1 h		R Na (79) ^a H (82)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(71)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 6 h		(69)	207, 208

TABLE 2A. CROSS-COUPING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
		Pd(dppf)Cl ₂ CH ₂ Cl ₂ (3%), CuI, K ₂ CO ₃ (250%), THF/DMF (3:1), 50°, 6 h		(96)
120%				285
		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(71)
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 80°, 24 h		(72)
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(77)
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h		(79)
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(78)
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(67)
				207, 208
				207, 208
				207, 208
				207, 208
				207, 208
				207, 208
				207, 208

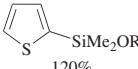
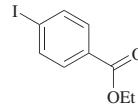
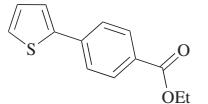
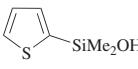
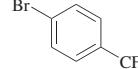
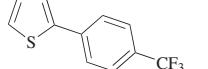
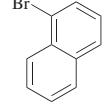
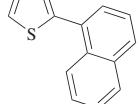
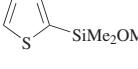
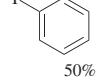
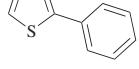
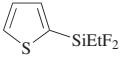
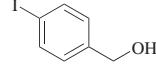
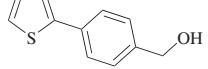
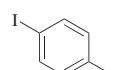
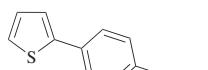
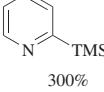
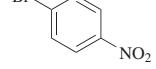
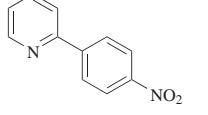
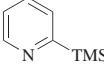
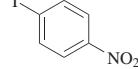
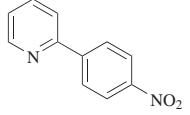
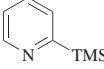
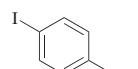
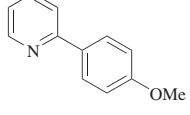
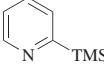
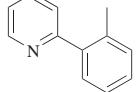
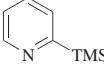
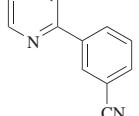
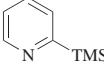
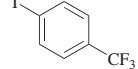
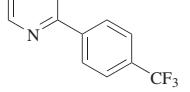
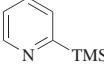
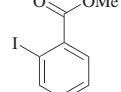
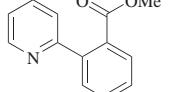
	120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 1–3 h		R Na (87) ^a H (78)	207, 208
	120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 3 h		(86)	207, 208
120%		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 7 h		(74)	207, 208	
	50%		CuI (100%), C ₆ F ₅ ONa (200%), DMI, 130°, 12 h		(75)	231
150%			[allylPdCl] ₂ (2.5%), KF (200%), DMF, 100°, 64 h		(81)	172
150%			[allylPdCl] ₂ (2.5%), KF (200%), DMF, 100°, 64 h		(96)	172
C ₅			Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(67)	122

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(75)
300%				122
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(45)
300%				122
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(21)
300%				122
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(65)
300%				122
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(50)
300%				122
		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(48)
300%				122

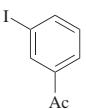
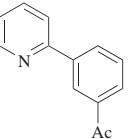
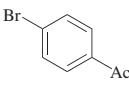
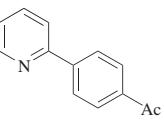
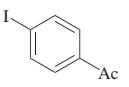
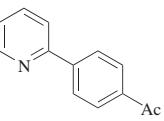
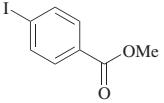
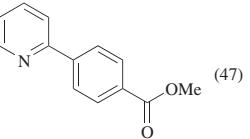
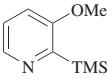
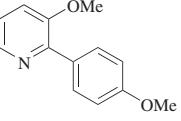
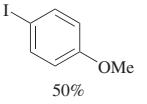
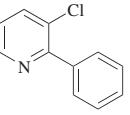
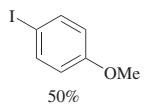
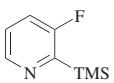
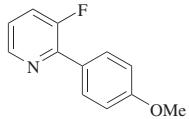
300%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(61)	122
300%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(40)	122
300%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(47)	122
300%		Pd(PPh ₃) ₄ (5%), Ag ₂ O (100%), TBAF (10%), DMF, 90°		(47)	122
		PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h		(85)	123
		PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h		(72)	123

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

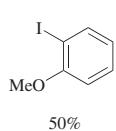
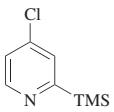
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, 120°, 12 h	(38)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(55)	123
480				
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(82)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(88)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(80)	123



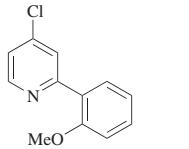
PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



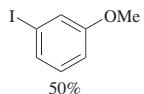
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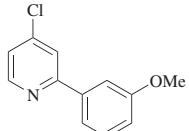
PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



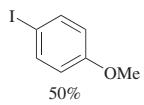
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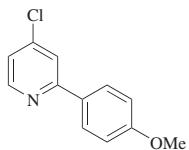
PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



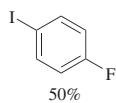
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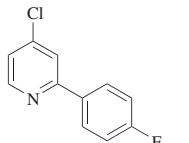
PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



123



PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



123

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(42) + (40)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(—)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(64)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(—)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, rt, 12 h	(—)	123
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (200%), DMF, 120°, 48 h	(20)	123

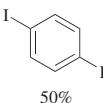
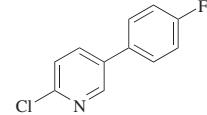
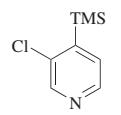
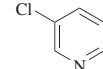
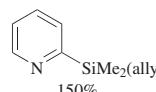
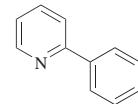
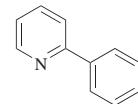
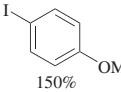
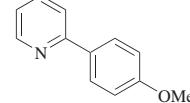
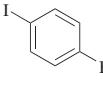
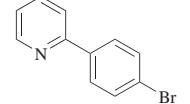
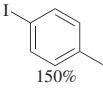
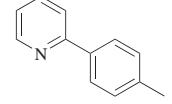
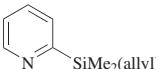
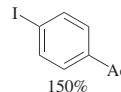
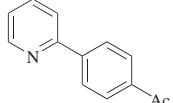
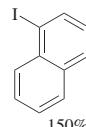
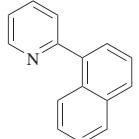
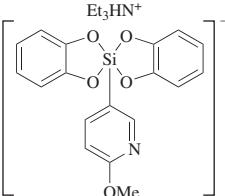
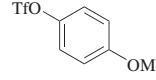
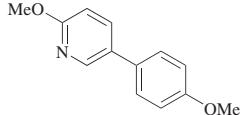
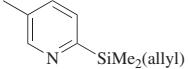
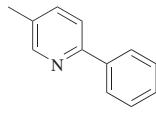
	50%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (10%), DMF, rt, 24 h		(—)	123
	150%	PdCl ₂ (PPh ₃) ₂ (5%), Ph ₃ P (10%), CuI (100%), TBAF (10%), DMF, rt, 12 h		(—)	123
	150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(60)	51
	150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(78)	51
	150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(72)	51
	150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(81)	51
	150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(93)	51

TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
	 150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(59) 51
	 150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(76) 51
484	 150%	TfO-  OMe	Pd(dba) ₂ (5%), Cyclohexyl JohnPhos (5%), TBAF (150%), dioxane	 (96) 276
C ₆		 150%	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°	 (80) 51

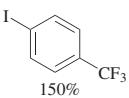
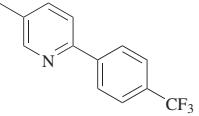
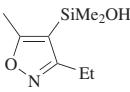
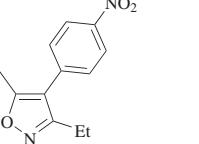
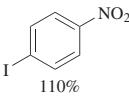
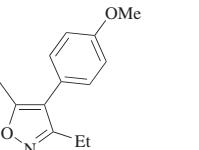
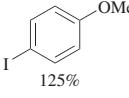
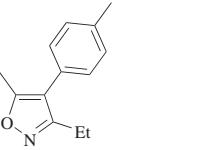
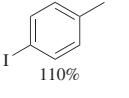
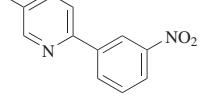
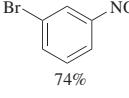
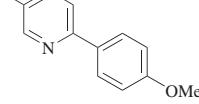
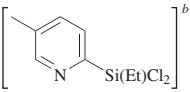
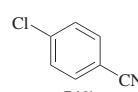
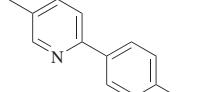
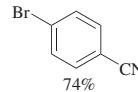
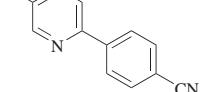
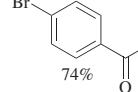
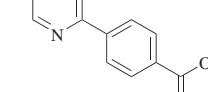
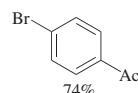
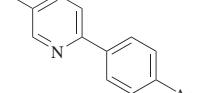
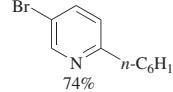
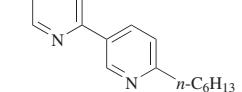
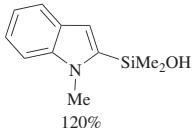
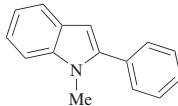
	Pd(PPh ₃) ₄ (5%), Ag ₂ O (150%), THF, 60°		(81)	51
	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOr-Bu (250%), Cu(OAc) ₂ (100%), toluene, 40°		(57)	213
	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOr-Bu (250%), Cu(OAc) ₂ (25%), toluene, 80°		(52)	213
	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOr-Bu (250%), Cu(OAc) ₂ (25%), toluene, 80°		(56)	213
	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h		(80)	30
	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h		(84)	30

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 ^b	 74%	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h	 (81)	30
	 74%	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h	 (92)	30
	 74%	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h	 (73)	30
	 74%	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 48 h	 (75)	30
	 74%	PdCl ₂ (PPh ₃) ₂ (5%), KF, DMF, 120°, 72 h	 (82)	30

C₈

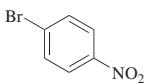
Pd₂(dba)₃•CHCl₃ (5%),
NaOt-Bu (200%), CuI (100%),
toluene, rt, 3 h



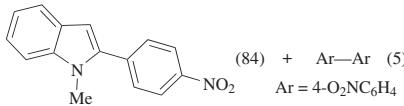
(82)

206, 208

120%



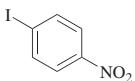
Pd₂(dba)₃•CHCl₃ (5%),
dppb (20%), CuI (100%),
NaOt-Bu (200%),
toluene, 55°, 20 h



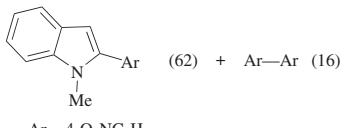
(84) + Ar—Ar (5)

206, 208

120%



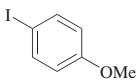
Pd₂(dba)₃•CHCl₃ (5%),
CuI (100%), NaOt-Bu (200%),
toluene, rt, 3 h



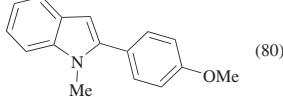
(62) + Ar—Ar (16)

206, 208

120%



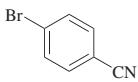
Pd₂(dba)₃•CHCl₃ (5%),
CuI (100%), NaOt-Bu (200%),
toluene, rt, 3 h



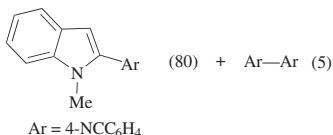
(80)

206, 208

120%



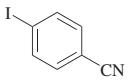
Pd₂(dba)₃•CHCl₃ (5%),
dppb (20%), CuI (100%),
NaOt-Bu (200%),
toluene, 55°, 20 h



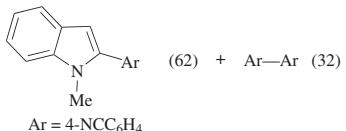
(80) + Ar—Ar (5)

206, 208

120%



Pd₂(dba)₃•CHCl₃ (5%),
CuI (100%), NaOt-Bu (200%),
toluene, rt, 3 h



(62) + Ar—Ar (32)

206, 208

TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 488			[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 70°, 3 h (94)	208
		[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 70°, 3 h (94)	 (94)	208
		Pd cat. 4 (2.5%), toluene, 50° (93)	 (93)	208
		Pd cat. 4 (2.5%), toluene, 50° (89)	 (89)	208
		[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 70°, 1 h (92)	 (92)	208
		Pd cat. 4 (2.5%), toluene, 50° (83)	 (83)	208

120%		Pd cat. 4 (2.5%), toluene, 50°		(93)	208
120%		[allylPdCl]2 (2.5%), SPhos (5%), toluene, 70°, 1 h		(92)	208
120%		[allylPdCl]2 (2.5%), SPhos (5%), toluene, 70°, 3 h		(88)	208
120%		[allylPdCl]2 (2.5%), SPhos (5%), toluene, 70°, 1 h		(93)	208
120%		Pd2(dba)3•CHCl3 (5%), NaOt-Bu (200%), CuI (100%), toluene, 40°, 12 h		(70) + Ph—Ph (12)	206, 208
120%		Pd2(dba)3•CHCl3 (5%), NaOt-Bu (200%), CuI (100%), toluene, 40°, 12 h		(72) + Ar—Ar (14) Ar = 3-O2NC6H4	206, 208
120%		Pd2(dba)3•CHCl3 (5%), NaOt-Bu (200%), CuI (100%), toluene, rt, 6 h		(84) + Ar—Ar (6) Ar = 4-O2NC6H4	206, 208

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
120%			Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaHMDS (120%), toluene, rt 	(93) 208
120%			Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, 50°, 24 h 	(75) + Ar—Ar (15) 206, 208 Ar = 2-MeOC ₆ H ₄
120%			Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, 50°, 24 h 	(72) + Ar—Ar (14) 206, 208 Ar = 4-MeOC ₆ H ₄
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 80°, 3 h 		(68) 207, 208
120%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaHMDS (120%), toluene, rt 		(62) 208
120%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, 50°, 24 h 	(73) + Ar—Ar (14) 206, 208 Ar = 2-MeC ₆ H ₄	

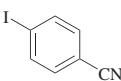
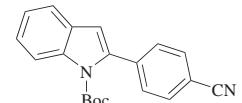
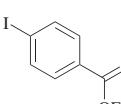
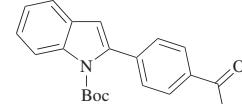
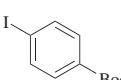
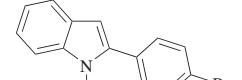
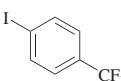
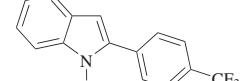
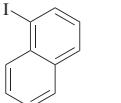
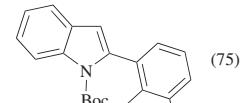
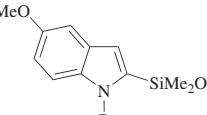
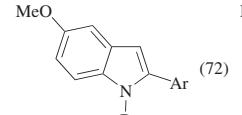
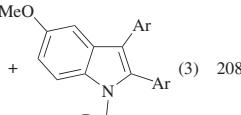
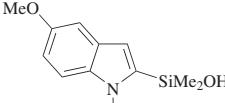
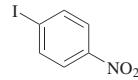
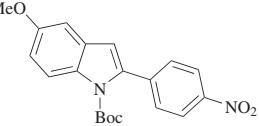
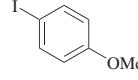
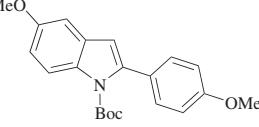
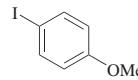
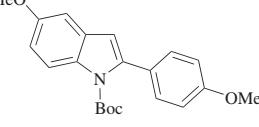
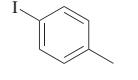
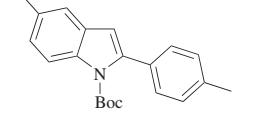
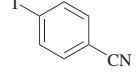
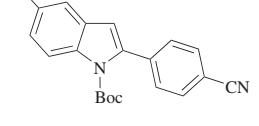
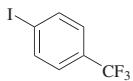
 120%	1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h	 (81)	207, 208
 120%	1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h	 (82)	207, 208
 120%	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, rt, 24 h	 (84) + Ar—Ar (trace)	206, 208 Ar = 4-BocC ₆ H ₄
 120%	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, rt, 24 h	 (84) + Ar—Ar (3)	206, 208 Ar = 4-CF ₃ C ₆ H ₄
 120%	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), CuI (100%), toluene, 60°, 24 h	 (75) + Ar—Ar (13)	206 Ar = 1-naphthyl
 120%	Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (200%), Cu(OAc) ₂ (25%), toluene, rt, 3 h	 (72) +  (3)	208 Ar = 4-O ₂ NC ₆ H ₄

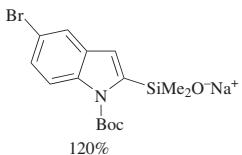
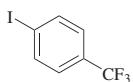
TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h	 (80)	208
120%				
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 50°, 24 h	 (52)	208
120%				
120%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaHMDS (120%), toluene, 40°, 12 h	 (82)	208
120%				
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 40°, 24 h	 (68)	208
120%				
120%		1. NaH (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h	 (77)	208

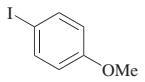
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120%



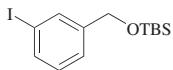
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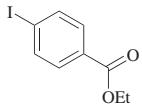
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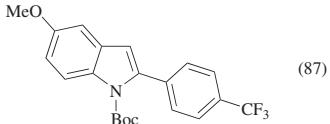
1. NaH (120%), toluene
2. Pd₂(dba)₃•CHCl₃ (5%),
toluene, rt, 3 h

Pd₂(dba)₃•CHCl₃ (5%),
NaOr-Bu (200%),
Cu(OAc)₂ (25%),
toluene, rt, 4 h

Pd₂(dba)₃•CHCl₃ (5%),
toluene, 80°, 24 h

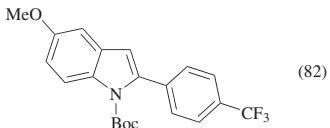
Pd₂(dba)₃•CHCl₃ (5%),
toluene, 50°, 24 h

Pd₂(dba)₃•CHCl₃ (5%),
toluene, rt, 4 h



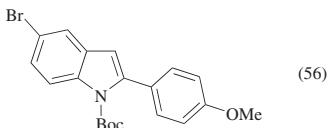
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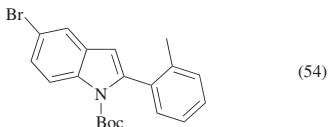
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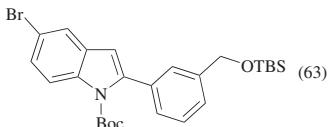
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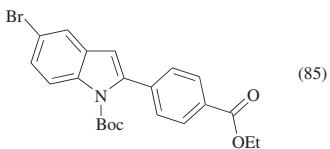
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208



(63)

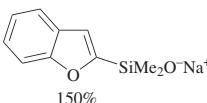
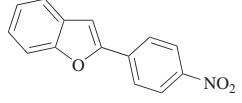
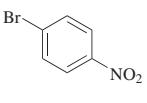
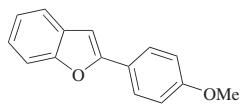
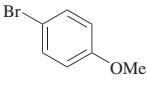
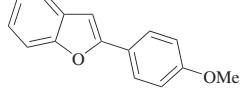
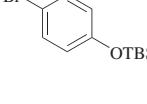
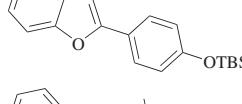
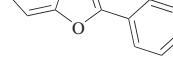
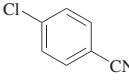
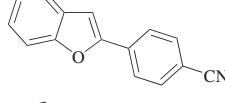
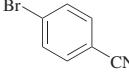
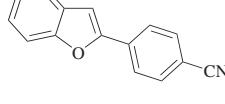
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(85)

208

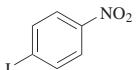
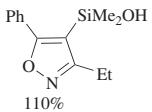
TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
150%		Pd(<i>t</i> -Bu ₃ P) ₂ (5%), THF, 60°, 8 h	 (58)	54
150%		[allylPdCl] ₂ (2.5%), SPhos (5%), THF, 60°, 3.5 h	 (77)	54
150%		Pd(<i>t</i> -Bu ₃ P) ₂ (5%), toluene, 60°, 5 h	 (82)	54
150%		Pd(<i>t</i> -Bu ₃ P) ₂ (5%), toluene, 60°, 5 h	 (99)	54
150%		Pd(<i>t</i> -Bu ₃ P) ₂ (5%), toluene, 60°, 8 h	 (95)	54
150%		[allylPdCl] ₂ (2.5%), SPhos (5%), THF, 60°, 3.5 h	 (64)	54
150%		Pd(<i>t</i> -Bu ₃ P) ₂ (5%), dioxane, 70°, 3.5 h	 (59)	54

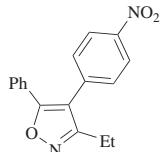
			Pd(t-Bu ₃ P) ₂ (5%), toluene, 60°, 5 h		(71)	54
	150%		[allylPdCl] ₂ (2.5%), SPhos (5%), THF, 60°, 3 h		(82)	54
	150%		[allylPdCl] ₂ (2.5%), SPhos (5%), THF, 60°, 5 h		(85)	54
C ₉			1. NaHMDS (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 50°, 3 h		(65)	208
	120%		1. NaHMDS (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, 50°, 24 h		(76)	208
	120%		1. NaHMDS (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 3 h		(82)	208

TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 120%		1. NaHMDS (120%), toluene 2. Pd ₂ (dba) ₃ •CHCl ₃ (5%), toluene, rt, 24 h	 (70)	208
C ₁₀ 110%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), Cu(OAc) ₂ (100%), toluene, 40°	 (63)	208
 110%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), dioxane, 80°	 (63)	213
 110%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), dioxane, 80°	 (75)	213

C₁₁

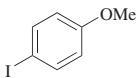
Pd₂(dba)₃•CHCl₃ (5%),
NaOt-Bu (250%),
Cu(OAc)₂ (100%),
toluene, 40°



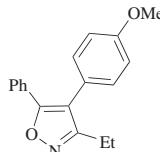
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213

110%



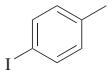
Pd₂(dba)₃•CHCl₃ (5%),
NaOt-Bu (250%),
Cu(OAc)₂ (25%),
toluene, 80°



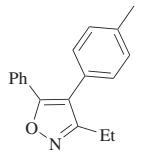
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213

110%



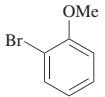
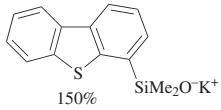
Pd₂(dba)₃•CHCl₃ (5%),
NaOt-Bu (250%),
Cu(OAc)₂ (25%),
toluene, 80°



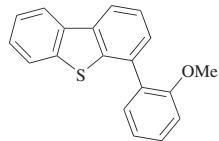
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74

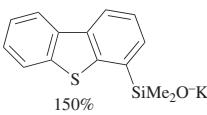
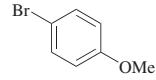
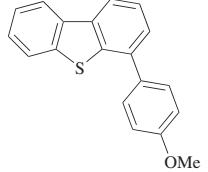
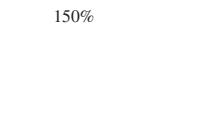
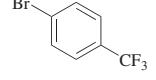
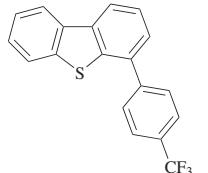
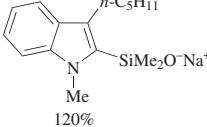
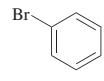
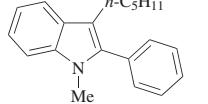
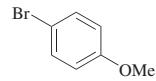
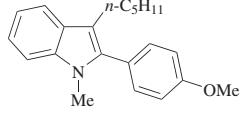
C₁₂

Pd(*t*-Bu₃P)₂ (2.5%),
toluene, 90°, 3 h

(89) (81)^c

54

TABLE 2A. CROSS-COUPLING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
<chem>C12</chem>			Pd(<i>t</i> -Bu ₃ P) ₂ (2.5%), toluene, 90°, 3 h  (96) (84) ^c	54
			Pd(<i>t</i> -Bu ₃ P) ₂ (2.5%), toluene, 90°, 3 h  (93)	54
<chem>C13</chem>			Pd cat. 4 (2.5%), toluene, 50°, 6 h  (86)	209
			Pd cat. 4 (2.5%), toluene, 50°, 2 h  (75)	209

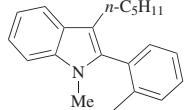
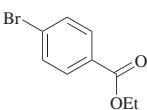
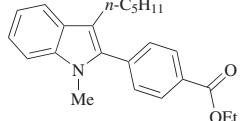
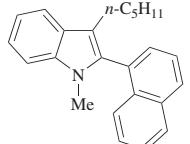
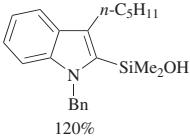
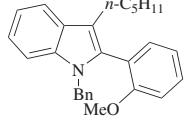
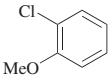
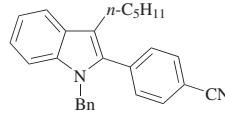
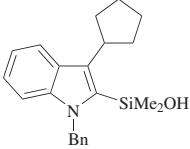
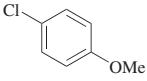
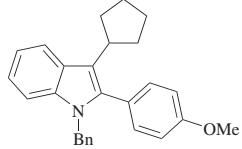
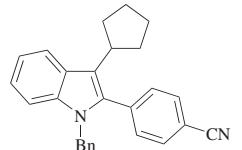
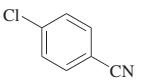
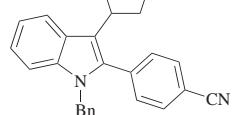
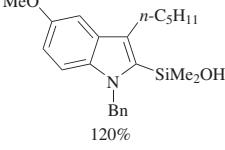
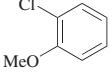
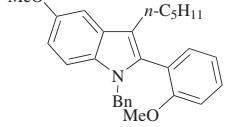
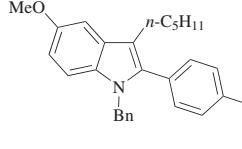
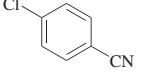
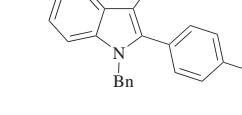
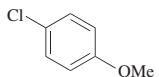
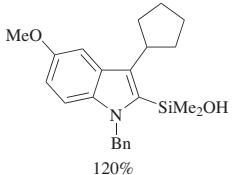
120%		Pd cat. 4 (2.5%), toluene, 50°, 12 h		(65)	209
120%		Pd cat. 4 (2.5%), toluene, 50°, 1 h		(73)	209
120%		Pd cat. 4 (2.5%), toluene, 50°, 3 h		(81)	209
120%		1. NaH (120%), toluene 2. [allylPdCl]2 (2.5%), Ru-Phos (5.0%), toluene, 70°, 12 h		(82)	209
120%		1. NaH (120%), toluene 2. [allylPdCl]2 (2.5%), SPhos (5.0%), toluene, 70°, 1 h		(82)	209

TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

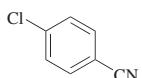
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃  120%		1. NaH (120%), toluene 2. [allylPdCl] ₂ (2.5%), RuPhos (5.0%), toluene, 90°, 12 h	 (65)	209
500  120%		1. NaH (120%), toluene 2. [allylPdCl] ₂ (2.5%), SPhos (5.0%), toluene, 70°, 1 h	 (89)	209
 120%		1. NaH (120%), toluene 2. [allylPdCl] ₂ (2.5%), RuPhos (5.0%), toluene, 70°, 24 h	 (71)	209
 120%		1. NaH (120%), toluene 2. [allylPdCl] ₂ (2.5%), SPhos (5.0%), toluene, 70°, 1 h	 (87)	209



1. NaH (120%), toluene
2. [allylPdCl]₂ (2.5%),
RuPhos (5.0%),
toluene, 90°, 12 h

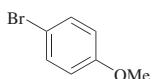
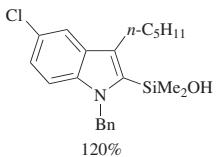
209

120%



1. NaH (120%), toluene
2. [allylPdCl]₂ (2.5%),
SPhos (5.0%),
toluene, 70°, 1 h

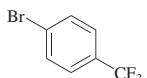
209



1. NaH (120%), toluene
2. Pd cat. **4** (2.5%),
toluene, 50°, 24 h

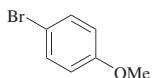
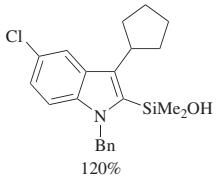
209

120%



1. NaH (120%), toluene
2. Pd cat. **4** (2.5%),
toluene, 50°, 12 h

209



1. NaH (120%), toluene
2. Pd cat. **4** (2.5%),
toluene, 50°, 12 h

209

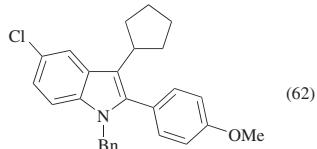
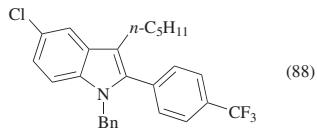
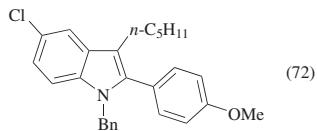
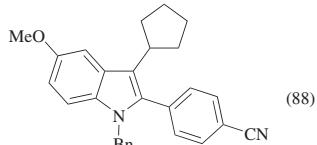
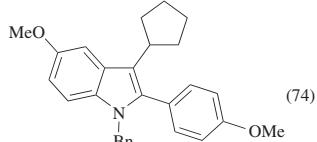
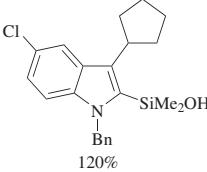
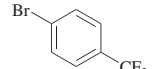
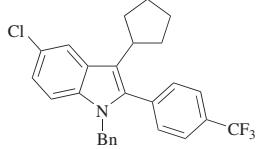
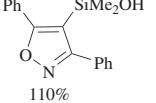
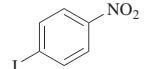
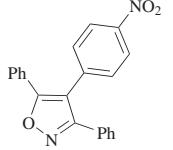
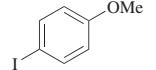
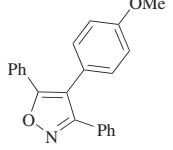
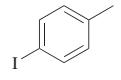
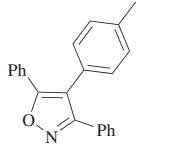


TABLE 2A. CROSS-CO尤LING OF HETEROARYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 		1. NaH (120%), toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 12 h		209
C ₁₅ 		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), dioxane, 80°		213
502 110%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), dioxane, 80°		213
110%		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOt-Bu (250%), dioxane, 80°		213

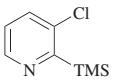
^a NaH is not needed when the sodium silanolate is used.

^b The reactive silane is generated *in situ* from 2-bromo-5-methylpyridine, *n*-BuLi, and EtSiCl₃.

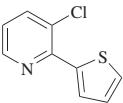
^c This value is the yield of analytically pure material.

TABLE 2B. CROSS-CO尤LING OF HETEROARYLSILANES WITH HETEROARYL ELECTROPHILES

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄	 120%		Pd(dppf)Cl ₂ •CH ₂ Cl ₂ (1%), CuI (3%), K ₂ CO ₃ (250%), THF/DMF (3:1), 75°, 6 h	 (96)	149
	 120%		Pd(dppf)Cl ₂ •CH ₂ Cl ₂ (5%), CuI (5%), K ₂ CO ₃ (250%), THF/DMF (3:1), 50°, 5 h	 (80)	149
504			CuI (5%), TBAF (120%), MeCN, rt, 5 min	 (75)	178
			CuI (5%), TBAF (120%), MeCN, rt, 5 min	 (71)	178
			CuCl (100%), DMF, 60°, air, 3 h	 (78)	183
	150%		[allylPdCl] ₂ (2.5%), KF (200%), DMF, 100°, 12 h	 (82)	172

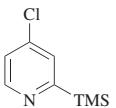
C₅

PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h

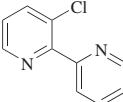


(78)

123

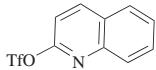
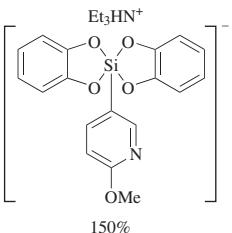


PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h

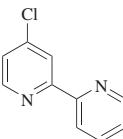


(65)

123



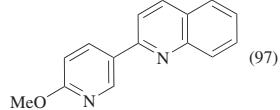
PdCl₂(PPh₃)₂ (5%), Ph₃P (10%),
CuI (100%), TBAF (200%),
DMF, rt, 12 h



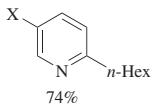
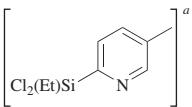
(85)

125

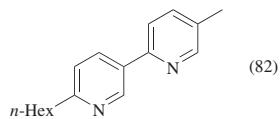
Pd(dba)₂ (5%),
Cyclohexyl JohnPhos (5%),
TBAF (150%), dioxane



276

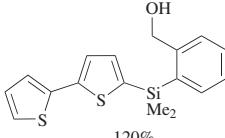
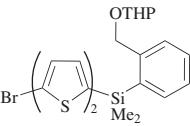
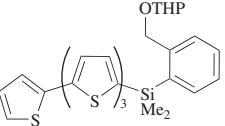
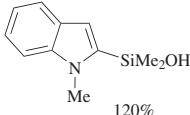
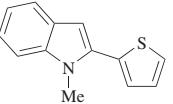
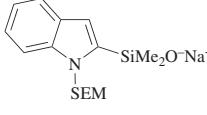
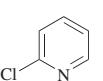
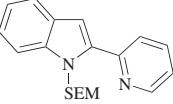
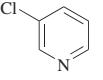
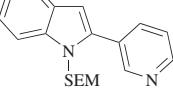
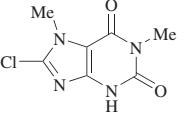
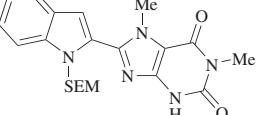
C₆

PdCl₂(PPh₃)₂ (5%),
KF, DMF, 120°, 48 h



30

TABLE 2B. CROSS-COUPLING OF HETEROARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(dppf)Cl ₂ •CH ₂ Cl ₂ (3%), CuI (9%), K ₂ CO ₃ (250%), THF/DMF (3:1), 75°, 10 h		(82) 149
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaOr-Bu (200%), CuI (100%), toluene, rt, 6 h		(73) 206, 208
		[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 90°, 3 h		(73) 208
		[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 70°, 2 h		(84) 208
120%		[allylPdCl] ₂ (2.5%), SPhos (5%), toluene, 70°, 3 h		(86) 208

705

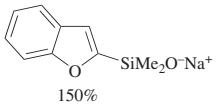
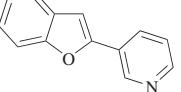
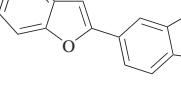
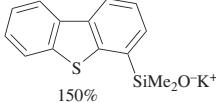
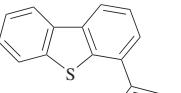
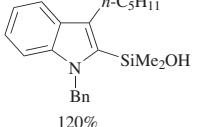
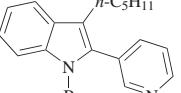
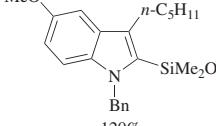
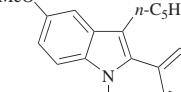
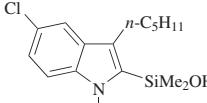
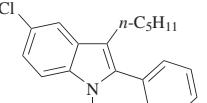
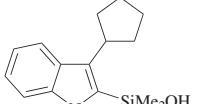
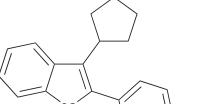
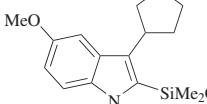
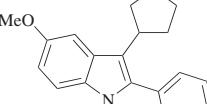
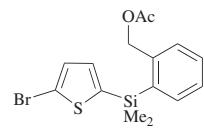
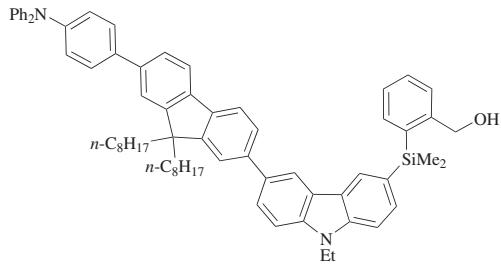
	150%		(67)	54
	150%		(91)	54
C ₁₂				
	150%		(73)	(65) ^b 54
C ₁₃				
	120%		(87)	209
	120%		(81)	209

TABLE 2B. CROSS-COUPLING OF HETEROARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃  120%		1. NaH, toluene 2. Pd cat. 4 (2.5%), toluene, 50°, 12 h	 (88)	209
508  120%		1. NaH (120%), toluene 2. [allylPdCl]₂ (2.5%), RuPhos (5.0%) toluene, 90°, 12 h	 (69)	209
 120%		1. NaH (120%), toluene 2. [allylPdCl]₂ (2.5%), RuPhos (5.0%) toluene, 90°, 12 h	 (86)	209

C₄₇

[allylPdCl]₂ (1%),
RuPhos (11%), CuI (3%),
K₂CO₃ (100%), THF/DMF (3:1),
75°, 24 h

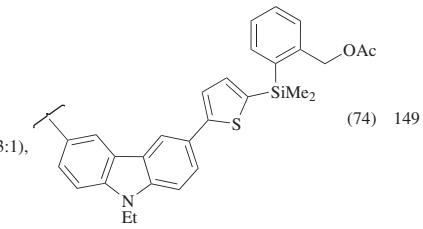


TABLE 2B. CROSS-COUPLING OF HETEROARYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

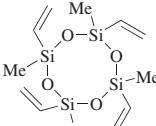
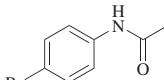
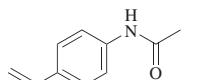
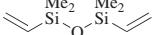
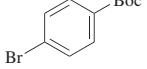
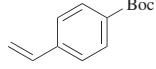
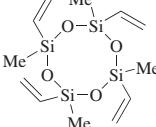
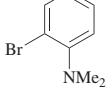
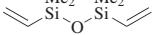
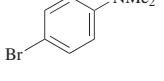
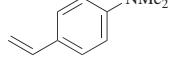
	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₁					
510			Pd(dppf)Cl ₂ •CH ₂ Cl ₂ (5%), CuI (5%), K ₂ CO ₃ (250%), THF/DMF (3:1), 75°, 24 h	(68)	149

^a The starting silane was generated *in situ* from 2-bromo-5-methylpyridine.^b This value is the yield of analytically pure material.

TABLE 2C. CROSS-CO尤LING OF HETEROARYLSILANES WITH MISCELLANEOUS ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
150%		[allylPdCl]₂ (2.5%), KF (150%), CO (1 atm), DMI, 100°, 6 h	(72)	179, 182
150%		[allylPdCl]₂ (2.5%), KF (150%), CO (1 atm), DMI, 100°, 19 h	(78)	179, 182
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), Ph ₃ P (5%), benzene, 60°, 19 h	(97)	175
200%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), Ph ₃ P (5%), benzene, 60°		175

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 50%		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 12 h	 (77)	318
 130%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (300%), DMF, 40°, 2 h	 (60)	262
 50%		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 24 h	 (78) + (10)	318
 200%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (400%), DMF, 40°, 24 h	 (70)	262

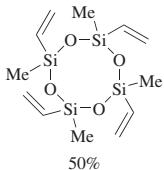
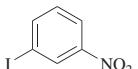
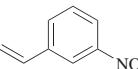
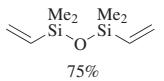
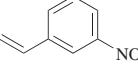
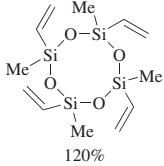
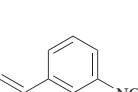
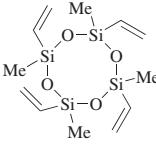
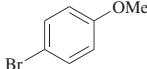
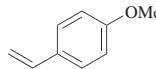
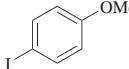
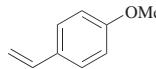
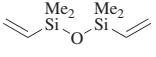
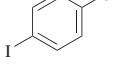
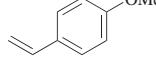
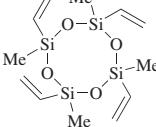
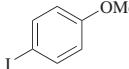
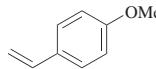
	50%		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 2 h		(85)	318
	120%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1.5 h		(86)	40
120%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h		(92)	40	
75%		Pd(dba) ₂ (2.5%), Ph ₃ P(O) (2.5%), KOTMS (350%), DMF, rt, 1 h		(76)	262	
120%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(87)	267	

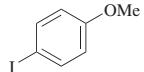
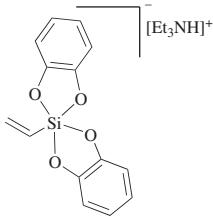
TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		Pd(PPh ₃) ₄ (5%), LiCl (300%), dioxane, reflux, 12 h	 (57)	22
		[allylPdCl] ₂ (2.5%), TASF (130%), HMPA, 50°	 (83)	23
		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h	 (90)	40
		Catechol (50%), [allylPdCl] ₂ (5%), (EtO) ₃ P (10%), Et ₃ N (50%), dioxane, reflux, 30 h	 (86)	87
		PdCl ₂ (PhCN) ₂ (5%), (EtO) ₃ P (10%), dioxane, reflux, 60 h	 (80)	22

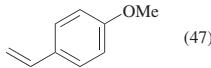
		JohnPhos (5%), [allylPdCl]2 (2.5%), KOSiEt3 (400%), DMF, 40°, 24 h		(72)		(15)	262
		Pd(dba)2 (5%), Ph3As (10%), TBAF (300%), THF, rt, 10 h		(75)			40
		Pd(dba)2 (5%), Ph3P(O) (5%), KOTMS (350%), DMF, rt, 14 h		(68)			262
		Pd(PPh3)4 (5%), LiCl (300%), dioxane, reflux, 60 h		(52)			22
		JohnPhos (5%), [allylPdCl]2 (2.5%), KOSiEt3 (400%), DMF, 35°, 4 h		(74)			262
		Pd(dba)2 (5%), Ph3P(O) (5%), KOTMS (350%), THF, reflux, 1 h		(71)			262

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

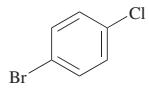
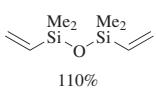
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
 50%		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 10 h	 (86)	318
 150%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (450%), THF, rt, 4 h	 (74)	40
 75%		Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), DMF, rt, 1.5 h	 (80)	262
 150%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 240 min	 (46)	267



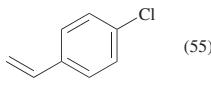
PdCl₂PhCN₂ (5%),
(EtO)₃P (10%),
dioxane, reflux, 110 h



22

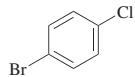


Pd(dba)₂ (5%),
Ph₃P(O) (5%),
KOTMS (350%),
THF, reflux, 3 h

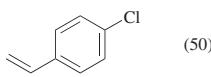


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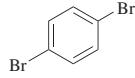
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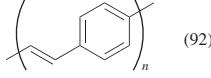
JohnPhos (5%),
KOSiEt₃ (300%),
[allylPdCl]₂ (2.5%),
DMF, 40°, 3 h



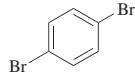
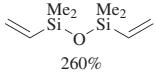
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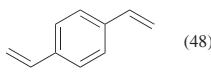
1. Ru(H)Cl(CO)(PPh₃)₃ (2%), CuCl (2%), dioxane, 110°
2. Electrophile (90%), Pd₂(dba)₃ (1%), TBAF (240%), dioxane, 80°, 24 h



104

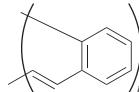
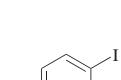
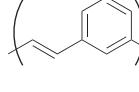
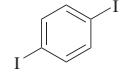
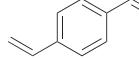
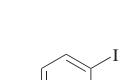
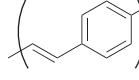


JohnPhos (5%),
[allylPdCl]₂ (2.5%),
KOSiEt₃ (600%),
DMF, 40°, 2 h



262

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		1. Ru(H)Cl(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile (90%), Pd ₂ dba ₃ (1%), TBAF (240%), dioxane, 80°, 24 h	 (90)	104
		1. Ru(H)Cl(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile (90%), Pd ₂ dba ₃ (1%), TBAF (240%), dioxane, 80°, 24 h	 (90)	104
		[allylPdCl] ₂ (2.5%), TASF (220%), HMPA, 50°	 (84)	23
		1. Ru(H)Cl(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile (90%), Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 16 h	 (98)	104

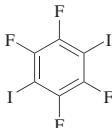
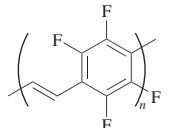
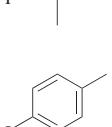
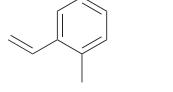
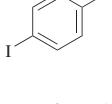
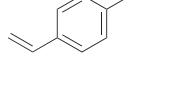
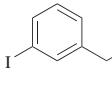
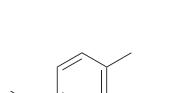
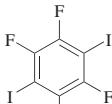
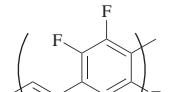
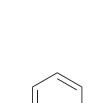
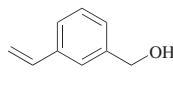
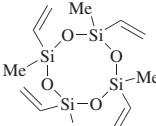
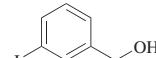
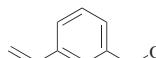
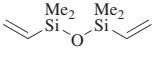
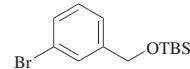
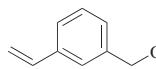
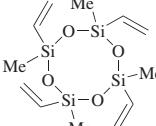
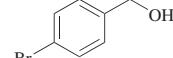
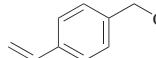
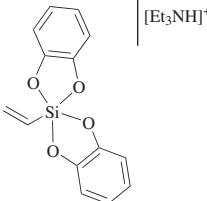
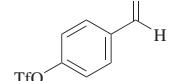
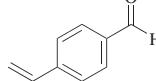
		1. Ru(H)Cl(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile (90%), Pd ₂ dba ₃ (1%), TBAF (240%), dioxane, 80°, 48 h		(43)	104
		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 16 h		(70)	40
		[allylPdCl] ₂ (2.5%), TASF (130%), HMPA, 50°		(89)	23
		TBAF, Pd(dba) ₂ (cat.) DMF, 85°		(66)	22
		PdCl ₂ (PhCN) ₂ (5%), (EtO) ₃ P (10%), dioxane, reflux, 60 h		(38)	70
		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 7.5 h		(79)	40

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂  120%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 480 min	 (59)	267
  200%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (400%), THF, 40°, 24 h	 (64)	262
520  50%		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 14 h	 (54)	318
  		Pd(PPh ₃) ₄ (5%), LiCl (300%), dioxane, reflux, 60 h	 (41)	22

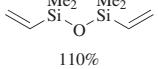
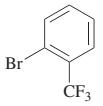
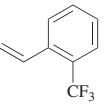
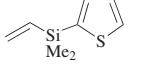
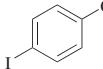
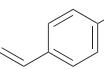
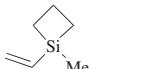
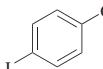
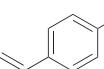
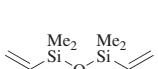
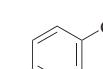
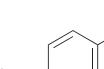
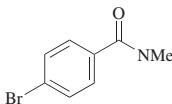
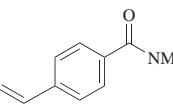
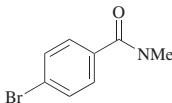
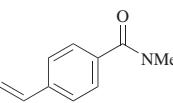
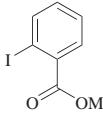
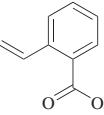
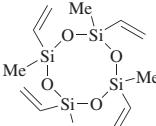
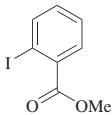
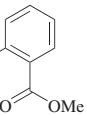
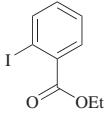
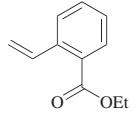
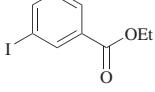
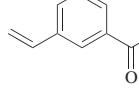
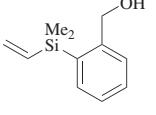
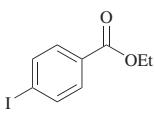
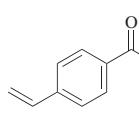
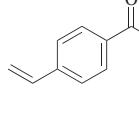
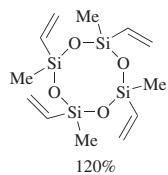
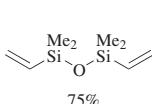
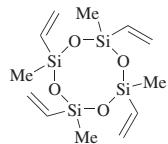
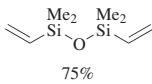
	110%		Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), THF, reflux, 3 h		(52)	262
	120%		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 0.5 h		(90)	49
	120%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h		(87)	40
	75%		Pd(dba) ₂ (2.5%), Ph ₃ P(O) (2.5%), KOTMS (350%), DMF, rt, 0.5 h		(81)	262
	130%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (300%), DMF, 40°, 2 h		(69)	262
	110%		Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), THF, reflux, 3 h		(34)	262
	120%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 14 h		(85)	40

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

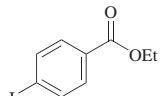
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂  120%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (200%), THF, rt, 480 min	 (83)	267
50% 		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 5 h	 (86)	318
522  120%		Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 1 h	 (90)	40
110% 		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h	 (93)	40
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 19 h	 (87)	150



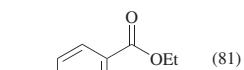
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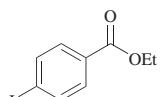
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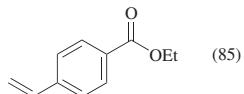
Pd(dba)₂ (2.5%),
Ph₃P(O) (2.5%),
KOTMS (350%),
DMF, rt, 0.5 h



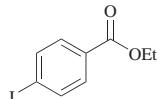
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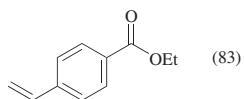
Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 10 min



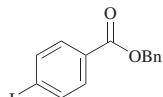
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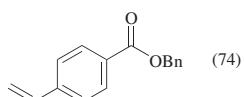
JohnPhos (10%),
PdBr₂ (5%), TBAF (200%),
THF, 50°, 5 h



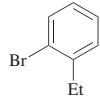
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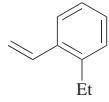
Pd(dba)₂ (5%),
Ph₃P(O) (5%),
KOTMS (350%),
DMF, rt, 1.5 h



262

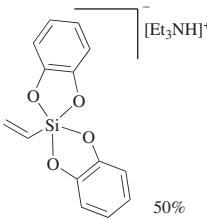
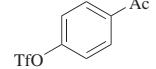
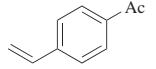
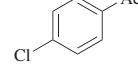
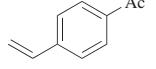
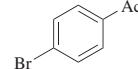
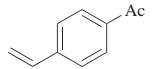
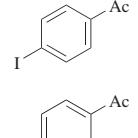
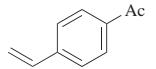
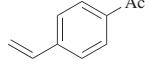


JohnPhos (10%),
PdBr₂ (5%), TBAF (200%),
THF, 50°, 17 h



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TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		(Ph ₃ P) ₄ Pd (5%), LiCl (300%), dioxane, reflux, 110 h	 (68)	87
		Pd cat. 5 (2%), NaOH (250%), TBAB (100%), H ₂ O, MW, 25 min	 (60)	257
200%		Pd cat. 5 (0.5%), NaOH (250%), TBAB (100%), H ₂ O, 120°, 20 h	 (89)	257
		[allylPdCl] ₂ (2.5%), TASF (130%), HMPA, 50°	 (86)	23
130%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h	 (85)	40
120%				

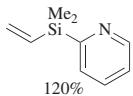
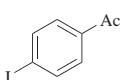
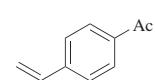
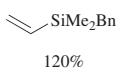
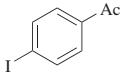
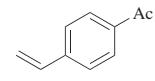
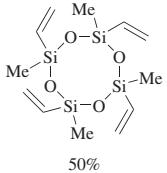
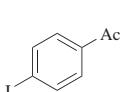
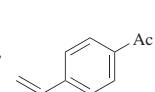
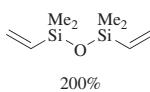
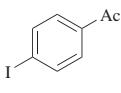
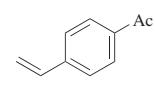
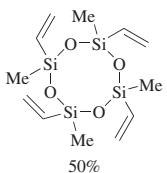
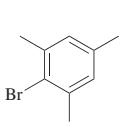
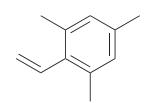
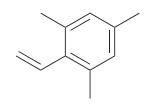
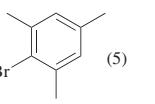
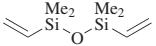
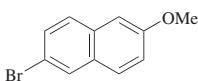
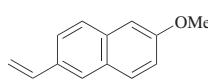
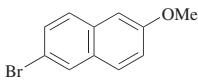
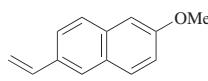
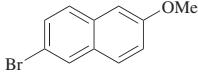
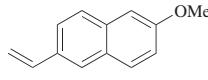
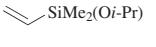
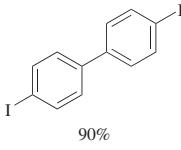
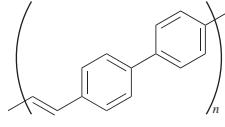
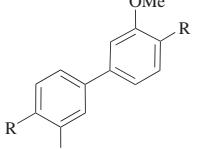
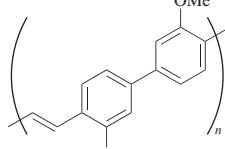
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(79)	169
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(79)	169
		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 3 h		(91)	318
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(88)	267
		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (400%), DMF, 40°, 24 h		(99)	262
		JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 48 h	 + 	(72) + (5)	318

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ 120%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 6 h	 (80)	40
 75%		Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), DMF, rt, 4 h	 (69)	262
526 50%		(Ph ₃ P) ₄ Pd (5%), LiCl (300%), dioxane, reflux, 30 h	 (59)	22, 87
 130%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (300%), DMF, rt, 12 h	 (80) + (5)	262
 200%		Pd cat. 5 (1%), NaOH (250%), TBAB (100%), H ₂ O, 120°, 24 h	 (90)	257

	130%		[allylPdCl]2 (2.5%), TASF (130%), HMPA, 50°		(98)	23
	120%		Pd(dba)2 (5%), TBAF (300%), THF, rt, 4 h		(86)	40
	75%		Pd(dba)2 (5%), Ph3P(O) (5%), KOTMS (350%), DMF, rt, 2.5 h		(80)	262
	50%		JohnPhos (10%), PdBr2 (5%), TBAF (200%), THF, 50°, 3 h		(71)	318
	120%		Pd(dba)2 (5%), TBAF (200%), THF, rt, 3 h		(64)	267
	50%		JohnPhos (10%), PdBr2 (5%), TBAF (200%), THF, 50°, 3 h		(81)	318

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂  130%		JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (300%), DMF, rt, 4 h	 (82)	262
 110%		Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), THF, reflux, 3 h	 (70)	262
 200%		Pd cat. 5 (0.5%), NaOH (250%), TBAB (100%), H ₂ O, MW, 10 min	 (83)	257
  90%		1. Ru(H)(Cl)(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile, Pd ₂ dba ₃ (1%), TBAF (240%), dioxane, 80°, 16 h	 (98)	104
  120%	 R = N ₂ BF ₄	Pd(OAc) ₂ (10%), EtOH, 80°	 (—)	256

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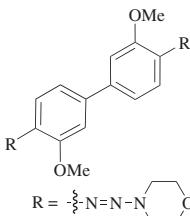
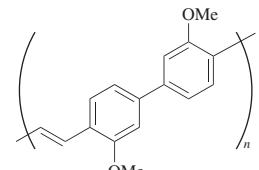
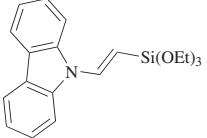
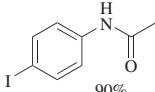
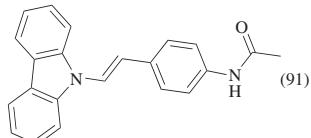
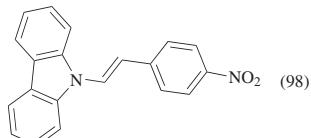
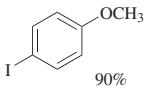
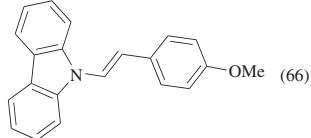
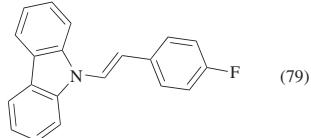
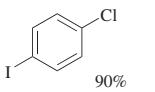
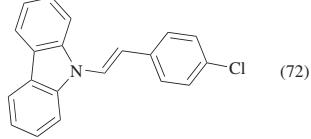
 <p>$R = -\text{N}(\text{N})=\text{N}-$</p> <p>$\text{Si}(\text{OMe})_3$ 200%</p> <p>$\text{Me}_2\text{Si}(\text{OEt})_2$ 120%</p> <p>$\text{Si}(\text{OEt})_3$ 120%</p>	<p>120%</p> <p>Pd(OAc)₂ (10%), aq. HClO₄ (400%), EtOH, 80°</p> <p>Pd(dba)₂ (5%), Ph₃P(O) (5%), KOTMS (350%), THF, reflux, 3 h</p> <p>Pd(OAc)₂ (10%), aq. HClO₄ (400%), EtOH, 80°</p>	 <p>(—)</p> <p>(61)</p> <p>(93)</p> <p>(—)</p>	<p>256</p> <p>257</p> <p>262</p> <p>256</p>

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 48 h		258
				258
530				
		Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 48 h		258
				258
		Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 48 h		258

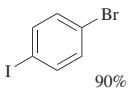
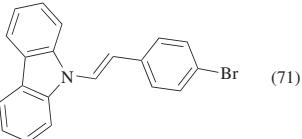
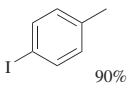
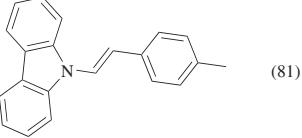
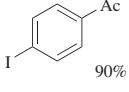
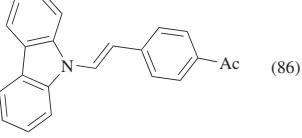
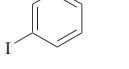
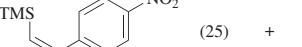
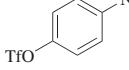
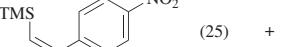
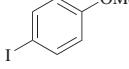
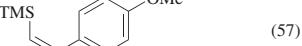
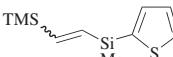
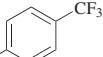
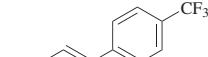
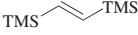
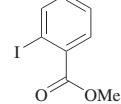
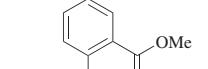
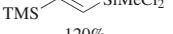
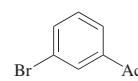
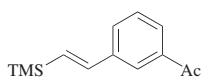
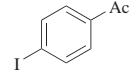
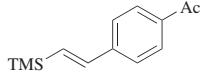
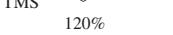
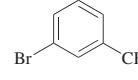
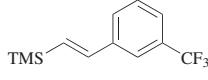
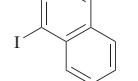
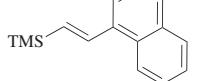
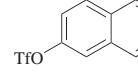
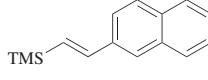
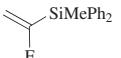
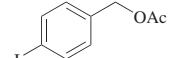
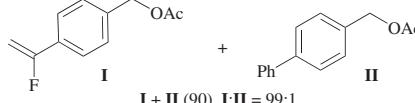
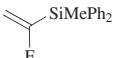
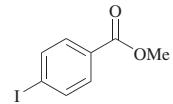
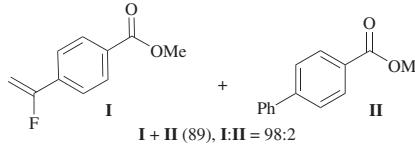
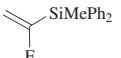
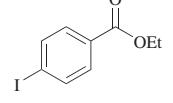
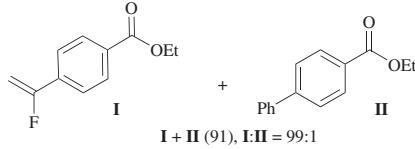
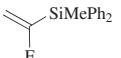
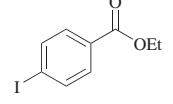
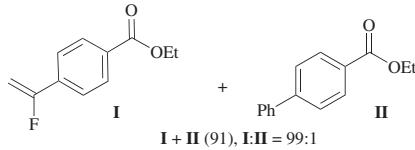
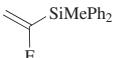
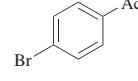
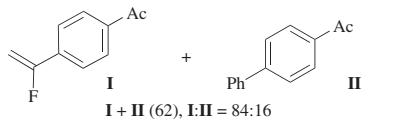
	Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 48 h		(71)	258
	Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 48 h		(81)	258
	Pd ₂ (dba) ₃ (1%), TBAF (120%), THF, 30°, 24 h		(86)	258
TMS-CH=CH-TMS	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h		(43)	101
	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h		(25)	101
	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h		(40)	101
	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h		(57)	101

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
TMS- 	I- 	Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 1 h	TMS- 	(95) (E)/(Z) = 96:4 49
TMS- 	I- 	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h	TMS- 	(49) 101
TMS- 	Br- 	Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 12 h	TMS- 	(62) 185
TMS- 	I- 	[allylPdCl] ₂ (2.5%), TASF (150%), THF, 5.5 h	TMS- 	(67) 25
TMS- 	Br- 	Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 36 h	TMS- 	(74) 185
TMS- 	I- 	Pd(OAc) ₂ (3%), Et ₃ N (240%), DMF, 110°, 2 h	TMS- 	(55) 101
TMS- 	Tfo- 	(Ph ₃ P) ₄ Pd (cat.), TBAF (120%), THF, 50°, 5 h	TMS- 	(74) 181

<chem>C=C(F)C[Si]2CCPh2C2</chem>	<chem>Ic1ccc([N+](=O)[O-]cc1)</chem>	(Ph_3P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	<chem>C=C(F)c1ccc([N+](=O)[O-]cc1)</chem> (84) 99:1 + <chem>c1ccc([N+](=O)[O-]cc1)cc1</chem> 163, 164
<chem>Ic1ccc([N+](=O)[O-]cc1)</chem>	<chem>Ic1ccc([N+](=O)[O-]cc1)</chem>	(Ph_3P) ₄ Pd (5%), CsF (230%), CuI (5%), DMI/THF, 9:1, rt	<chem>C=C(F)c1ccc([N+](=O)[O-]cc1)</chem> (84) 99:1 + <chem>c1ccc([N+](=O)[O-]cc1)cc1</chem> 164
<chem>Ic1ccc([O-]c1)cc1</chem>	<chem>Ic1ccc([O-]c1)cc1</chem>	(Ph_3P) ₄ Pd (5%), CuI (5%), CsF (230%), DMI, 50°	<chem>C=C(F)c1ccc([O-]c1)cc1</chem> I + <chem>c1ccc([O-]c1)cc1</chem> II I + II (63), I:II = 93:7 164
<chem>Ic1ccc(CC[O]c1)cc1</chem>	<chem>Ic1ccc(CC[O]c1)cc1</chem>	(Ph_3P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	<chem>C=C(F)c1ccc(CC[O]c1)cc1</chem> I + <chem>c1ccc(CC[O]c1)cc1</chem> II I + II (86), I:II = 98:2 163, 164
<chem>Ic1ccc(CC(=O)Oc1)cc1</chem>	<chem>Ic1ccc(CC(=O)Oc1)cc1</chem>	(Ph_3P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	<chem>C=C(F)c1ccc(CC(=O)Oc1)cc1</chem> I + <chem>c1ccc(CC(=O)Oc1)cc1</chem> II I + II (86), I:II = 98:2 164
			<chem>C=C(F)c1ccc(CC(=O)OAc)c1</chem> I + <chem>c1ccc(CC(=O)OAc)c1</chem> II I + II (90), I:II = 99:1 163, 164

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂  150%	I 	(Ph ₃ P) ₄ Pd (5%), CsF (230%), CuI (5%), DMI, rt	 I + II (90), I:II = 99:1	164
	I 	(Ph ₃ P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	 I + II (89), I:II = 98:2	163, 164
	I 	(Ph ₃ P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	 I + II (91), I:II = 99:1	163, 164
	I 	(Ph ₃ P) ₄ Pd (5%), CsF (230%), CuI (5%), DMI, rt	 I + II (91), I:II = 99:1	164
	I 	(Ph ₃ P) ₄ Pd (5%), CsF (1.5%), CuI (5%), DMI, rt	 I + II (62), I:II = 84:16	163

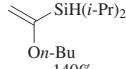
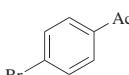
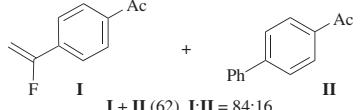
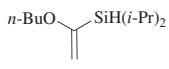
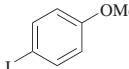
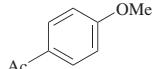
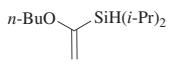
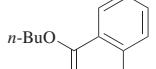
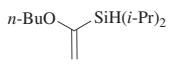
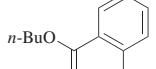
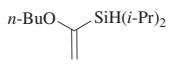
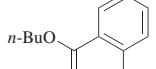
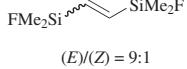
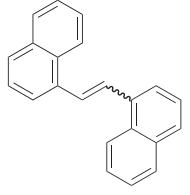
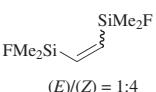
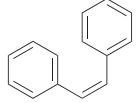
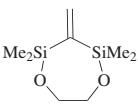
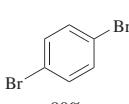
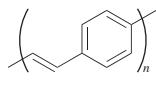
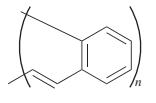
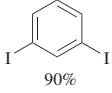
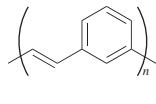
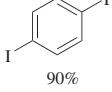
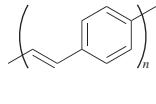
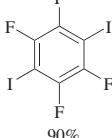
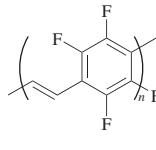
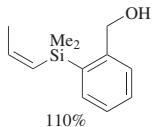
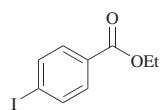
 140%		<p>(Ph₃P)₄Pd (5%), CsF (230%), CuI (10%), DMI, rt</p>	 I + II (62), I:II = 84:16	164
 140%		<p>1. TBAF (200%) 2. [allylPdCl]₂ (2.5%) 3. 1 N HCl, 10 min</p>	 (94)	171
 140%		<p>1. TBAF (200%) 2. [allylPdCl]₂ (2.5%), 30 min</p>	 (83)	171
 140%		<p>1. TBAF (200%) 2. [allylPdCl]₂ (2.5%), 15 h</p>	 (76)	171
 140%		<p>1. TBAF (200%) 2. [allylPdCl]₂ (2.5%), 10 min</p>	 (89)	171
 (E)/(Z) = 9:1	 200%	<p>[allylPdCl]₂ (2.5%), TASF (150%), THF, 24 h</p>	 (45) (E)/(Z) = 9:1	25

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
	 200%	[allylPdCl] ₂ (2.5%), TASF (150%), THF, 24 h		(43) (E)/(Z) = 1:4 25
	 90%	Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 24 h		(94) 104
	 90%	Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 24 h		(97) 104
	 90%	Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 24 h		(98) 104
	 90%	Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 16 h		(96) 104
	 90%	Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 48 h		(35) 104

C_3 

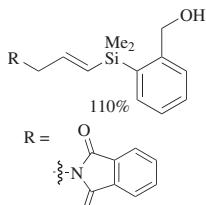
110%



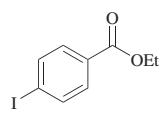
90%

PdCl_2 (1%),
 $(2\text{-furyl})_3\text{P}$ (2%),
 K_2CO_3 (220%),
 DMSO , 35° , 19 h

(91) (Z/E) = 94:6 150, 151

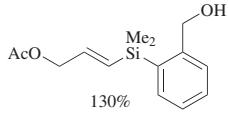


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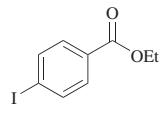


PdCl_2 (1%),
 $(2\text{-furyl})_3\text{P}$ (2%),
 K_2CO_3 (220%),
 DMSO , 35° , 24 h

(93) 150

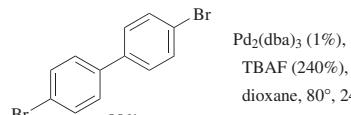


130%



PdCl_2 (1%),
 $(2\text{-furyl})_3\text{P}$ (2%),
 K_2CO_3 (220%),
 DMSO , 35° , 25 h

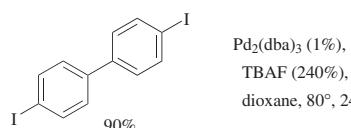
(93) 150



90%

$\text{Pd}_2(\text{dba})_3$ (1%),
 TBAF (240%),
 dioxane , 80° , 24 h

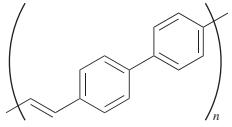
(98) 104



90%

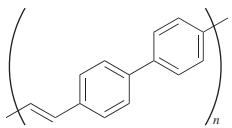
$\text{Pd}_2(\text{dba})_3$ (1%),
 TBAF (240%),
 dioxane , 80° , 24 h

(98) 104



(98)

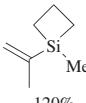
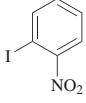
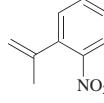
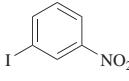
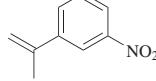
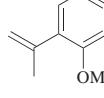
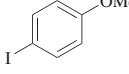
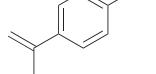
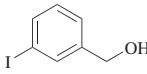
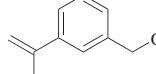
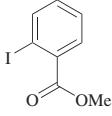
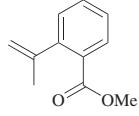
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TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃  120%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 4 h	 (79)	40
120%		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 1 h	 (84)	40
120%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 1 h	 (73)	40
120%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min	 (85)	40
120%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min	 (87)	40
120%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (300%), THF, rt, 20 h	 (78)	40

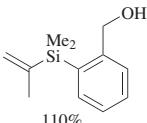
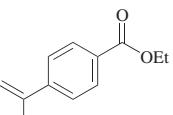
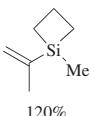
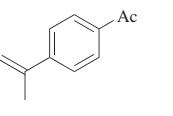
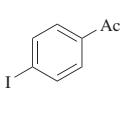
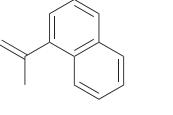
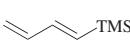
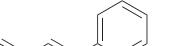
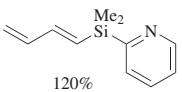
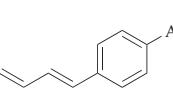
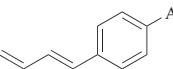
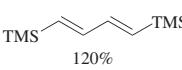
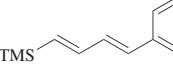
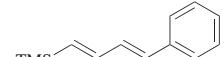
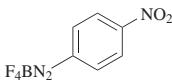
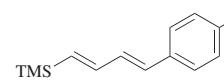
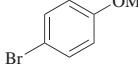
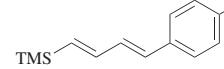
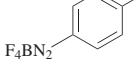
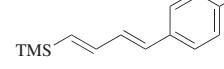
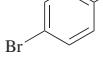
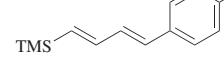
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 24 h		(96)	150, 151
		Pd(dba) ₂ (1%), TBAF (200%), THF, rt, 60 min		(89)	40
		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min		(84)	40
C ₄					
		[allylPdCl] ₂ (2.5%), TBAF (110%), THF, 60°, 21 h		(75)	89
	120%	PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(75)	169
	120%	PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(75)	169
	120%	1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h		(45)	124

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), NaOH (2 M), benzene, reflux	 (98)	125
120%		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	 (40)	124
540		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), NaOH (2 M), benzene, reflux	 (61)	125
120%		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	 (40)	125
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), NaOH (2 M), benzene, reflux	 (73)	125

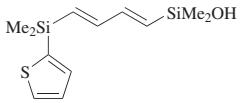
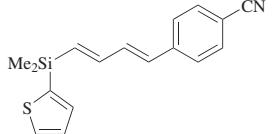
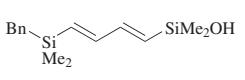
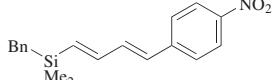
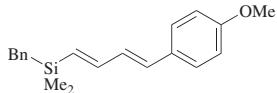
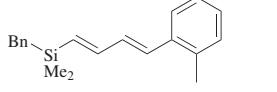
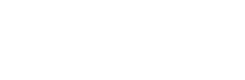
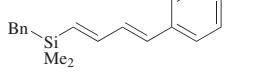
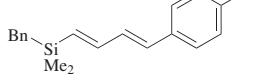
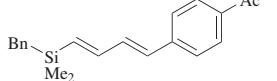
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 0.5 h		(83)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 0.5 h		(96)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 1 h		(88)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 6 h		(96)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 1 h		(85)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 0.5 h		(93)	44
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 18 h		(76)	44

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
		Pd(dba) ₂ (2.5%), KOTMS (200%), dioxane, rt, 4 h	 (91)	44
 110%		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 25 h	 (96) (Z)/(E) = 94:6	150, 151
 110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 40 min	 (91)	79
 110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 100 min	 (77)	79
 110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 115 min	 (76)	79
 110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 200 min	 (90) (E)/(Z) = 93:7	79

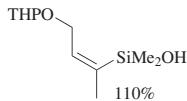
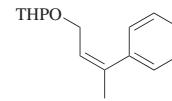
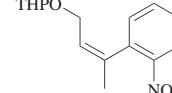
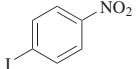
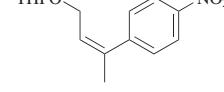
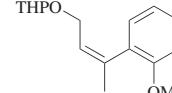
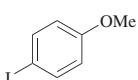
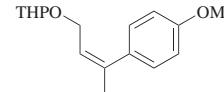
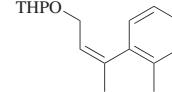
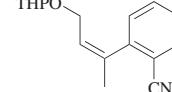
	110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 40 min		(75)	79
110%		Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (200%), THF, rt, 610 min		(77)	79	
120%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 400 min		(77)	79	
110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 600 min		(70)	79	
110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 390 min		(70)	79	
110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 90 min		(79)	79	
110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 580 min		(70)	79	

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
THPO- CH=CH-SiMe ₂ OH 120%	I-C ₆ H ₄ -CO ₂ Me	Pd(dba) ₂ (5%), Ph ₃ As (10%), TBAF (200%), THF, 35°, 48 h	THPO- CH=CH-C ₆ H ₄ -CO ₂ Me (80)	79
110%	I-C ₆ H ₄ -CO ₂ Me	Pd(dba) ₂ (5%), TBAF (200%), THF, 35°, 150 min	THPO- CH=CH-C ₆ H ₄ -CO ₂ Me (82)	79
110%	I-C ₆ H ₄ -Ac	Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 40 min	THPO- CH=CH-C ₆ H ₄ -Ac (73)	79
110%	I-C ₁₀ H ₇	Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 140 min	THPO- CH=CH-C ₁₀ H ₇ (76)	79
105%	I-C ₆ H ₅	Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 3.3 h; then 45°, 1.4 h	CH=CH-C ₆ H ₅ HO (79)	264
105%	I-C ₆ H ₄ -OMe	Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 12.9 h; then 40°, 13 h	CH=CH-C ₆ H ₄ -OMe (81)	264

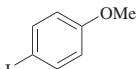
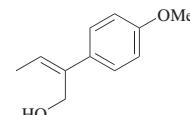
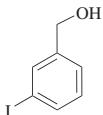
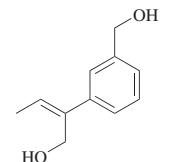
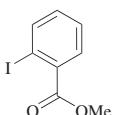
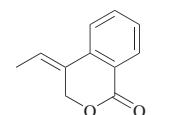
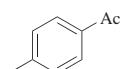
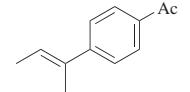
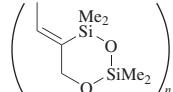
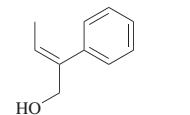
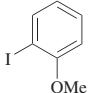
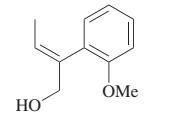
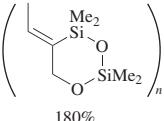
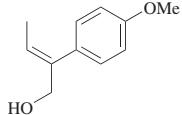
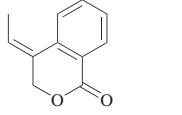
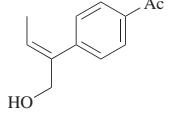
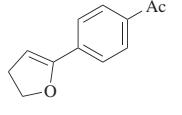
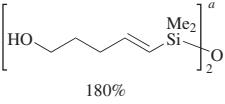
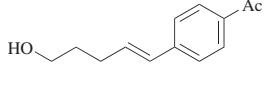
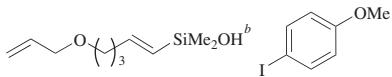
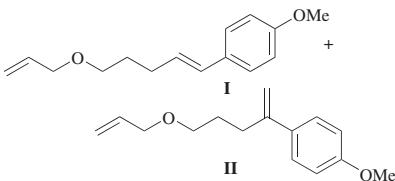
105%		Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 3.2 h; then 35°, 2 h		(71)	264
105%		Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 5.4 h; then 40°, 1.9 h		(81)	264
105%		Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 16.3 h; then 40°, 24.5 h		(57)	264
105%		Pd(dba) ₂ (5%), TBAF (200%), dioxane, rt, 10.1 h		(82)	264
180%		Pd(dba) ₂ (5%), TBAF (250%), dioxane, rt, 75 h		(57) (<i>E</i>)/(<i>Z</i>) = 97.7:2.3	264
180%		Pd(dba) ₂ (5%), TBAF (250%), dioxane, rt, 67 h; then 40°, 10 h		(65) (<i>E</i>)/(<i>Z</i>) = 98.5:1.5	264

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

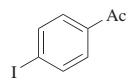
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C₄		Pd(dba) ₂ (5%), TBAF (250%), dioxane, rt, 20 h; then 40°, 3.5 h	 (57) (E)/(Z) = 97.3:2.7	264
	 (52)	Pd(dba) ₂ (11%), TBAF (200%), dioxane, rt, 23 h; then 35°, 23 h	264	
	 (64) (E)/(Z) = 98.5:1.5	Pd(dba) ₂ (5%), TBAF (250%), dioxane, rt, 22.5 h; then 40°, 10 h	264	
	 (71)	1. TBAOH (300%) 2. [allylPdCl] ₂ (2.5%), THF, rt, 10 min	171	
C₅		1. <i>t</i> -Bu ₃ Pt(DVDS) (cat.) (SiHMe ₂) ₂ O (90%), 30 min 2. Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min	 (82)	261



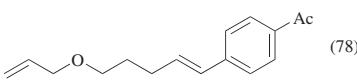
Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 10 min



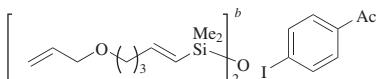
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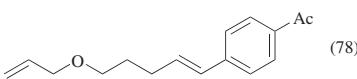
1. *t*-Bu₃Pt(DVDS) (cat.),
(SiHMe₂)₂O (98%), 30 min
2. Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 10 min



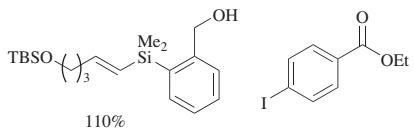
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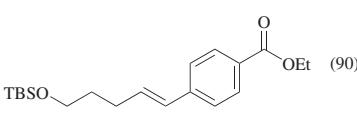
1. *t*-Bu₃Pt(DVDS) (cat.),
(SiHMe₂)₂O (98%), 30 min
2. Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 10 min



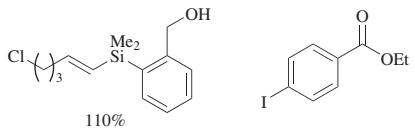
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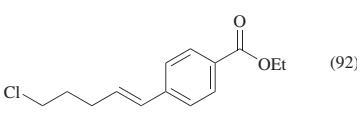
PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 31 h



150

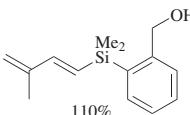
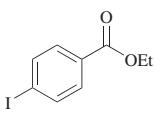
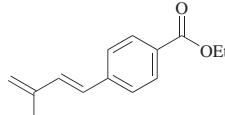
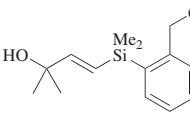
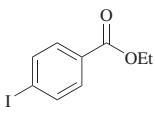
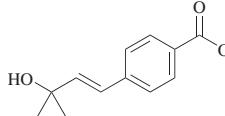
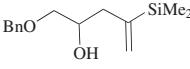
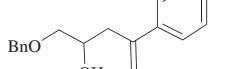
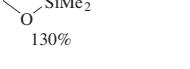
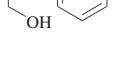


PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 50 h



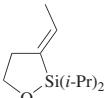
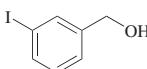
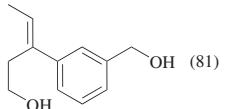
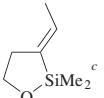
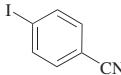
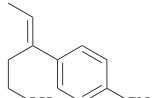
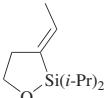
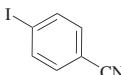
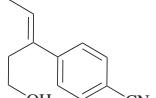
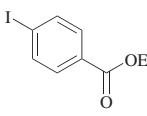
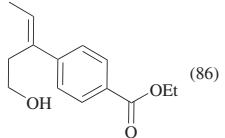
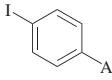
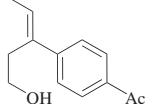
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TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅			PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 25 h		(93)
			PdCl ₂ (5%), (2-furyl) ₃ P (10%), K ₂ CO ₃ (220%), DMSO, 50°, 72 h		(92)
548			1. TBAF (220%), 10 min, THF, 0° 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), rt, 4 h		(95)
			1. TBAF (220%), 10 min, THF, 0° 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), rt, 4 h		(91)
			TBAF (220%), Pd(dba) ₂ (10%), THF, rt, 40 min		(85) (E)/(Z) = 97.2:2.8 224

		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, rt, 6.66 h		(88)	224
110%					
		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, 35°, 23 h		(56)	224
110%					
		TBAF (220%), Pd(dba) ₂ (10%), THF, 35°, 480 min		(75) (E)/(Z) = 98.3:1.7	224
130%					
		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, 35°, 10 h		(74)	224
110%					
		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, rt, 6.5 h		(72)	224
110%					
		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, rt, 6.83 h		(74)	224
110%					

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
 110%		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, rt, 6 h	 (81)	224
 130%		TBAF (220%), Pd(dba) ₂ (10%), THF, rt, 40 min	 (74) (E)/(Z) = 96.7:3.3	224
 110%		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, 45°, 46 h	 (70)	224
110%		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, 45°, 16 h	 (86)	224
110%		1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, rt, 6 h	 (70)	224

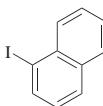
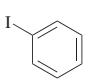
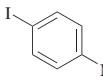
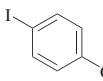
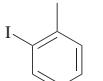
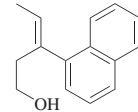
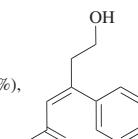
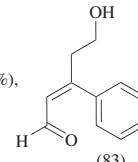
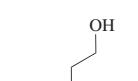
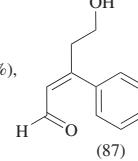
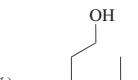
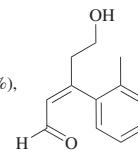
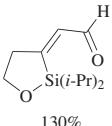
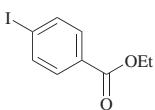
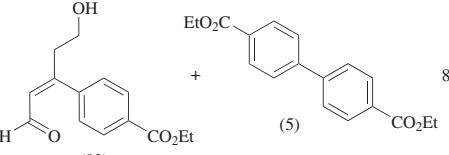
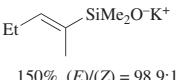
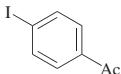
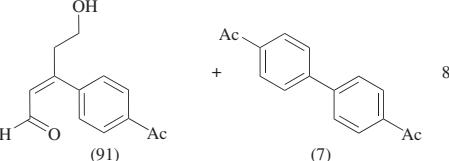
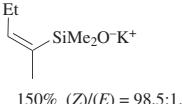
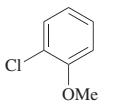
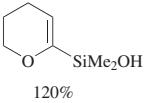
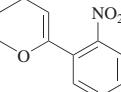
 <p>110%</p>	 <p>130%</p>	 <p>130%</p>	 <p>130%</p>	 <p>150%</p>
<p>1. TBAF (200%)</p> <p>2. Pd(dba)₂ (5%),</p> <p>THF, 35°, 8 h</p>	 <p>(76) (E)/(Z) = 96.2:3.8</p>	<p>(76)</p>	<p>[allylPdCl]₂ (5%),</p> <p>CuI (10%), KF 2H₂O (200%),</p> <p>[−MeSi(H)O−]_{3−5} (2.5%),</p> <p>DMF, rt, 2 h</p>	 <p>(93)</p>
<p>[allylPdCl]₂ (5%),</p> <p>CuI (10%), KF 2H₂O (200%),</p> <p>[−MeSi(H)O−]_{3−5} (2.5%),</p> <p>DMF, rt, 1 h</p>	 <p>(83)</p>	<p>(83)</p>	 <p>(13)</p>	<p>(13)</p>
<p>[allylPdCl]₂ (5%),</p> <p>CuI (10%), KF 2H₂O (200%),</p> <p>[−MeSi(H)O−]_{3−5} (2.5%),</p> <p>DMF, rt, 2 h</p>	 <p>(87)</p>	<p>(87)</p>	 <p>(5)</p>	<p>(5)</p>
<p>[allylPdCl]₂ (5%),</p> <p>CuI (10%), KF 2H₂O (400%),</p> <p>[−MeSi(H)O−]_{3−5} (2.5%),</p> <p>DMF, rt, 4 h</p>	 <p>(79)</p>	<p>(79)</p>		<p>81</p>

TABLE 3A. CROSS-COUPLED OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
		[allylPdCl] ₂ (5%), CuI (10%), KF 2H ₂ O (200%), [-MeSi(H)O-] ₃₋₅ (2.5%), DMF, rt, 2 h	 (92) (5)	81
130%				
		[allylPdCl] ₂ (5%), CuI (10%), KF 2H ₂ O (200%), [-MeSi(H)O-] ₃₋₅ (2.5%), DMF, rt, 2 h	 (91) (7)	81
150% (E)/(Z) = 98.9:1.1				
		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 66°, 0.5 h	 (97) (E)/(Z) = 98.8:1.2 (98)	80
150% (Z)/(E) = 98.5:1.5				
		1. TBAF (200%) 2. [allylPdCl] ₂ (2.5%), rt, THF, 10 min	 (85)	171
120%				

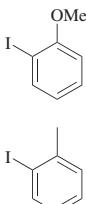
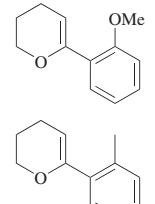
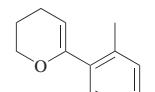
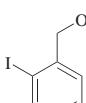
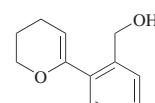
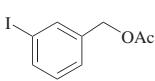
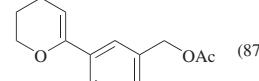
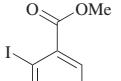
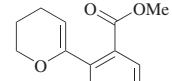
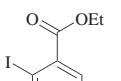
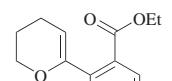
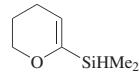
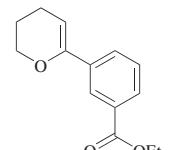
120%		1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min		(74)	171
120%		1. TBAF (200%) 2. Pd(dba)2 (5%), rt, THF, 20 min		(80)	171
120%		1. TBAF (200%) 2. Pd(dba)2 (5%), rt, THF, 20 min		(88)	171
120%		1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 20 min		(87)	171
120%		1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 4 h		(92)	171
120%		1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min		(86)	171
		1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min		(81)	171

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
<chem>C=C1OC(C=C1)SiH(i-Pr)2</chem> 120%	<chem>Ic1ccc(C(=O)OCC)cc1</chem>	1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min	<chem>C=C1OC(C=C1)c2ccc(C(=O)OCC)cc2</chem> (81)	171
	<chem>Ic1ccc(C(=O)OCC)cc1</chem>	1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min	<chem>C=C1OC(C=C1)c2ccc(C(=O)OCC)cc2</chem> (86)	
<chem>C=C1OC(C=C1)SiMe2OH</chem> 120%	<chem>Ic1ccc(C(=O)OCC)cc1</chem>	1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min	<chem>C=C1OC(C=C1)c2ccc(C(=O)OCC)cc2</chem> (86)	171
	<chem>Ic1ccc(C(=O)OCC)cc1</chem>	1. TBAF (200%) 2. [allylPdCl]2 (2.5%), rt, THF, 10 min	<chem>C=C1OC(C=C1)c2ccc(C(=O)OCC)cc2</chem> (86)	
<chem>n-BuC=C[Si](Oc1ccc(I)cc1)(Oc2ccc(I)cc2)[Et3N]^-</chem>	<chem>Ic1ccc([N+](=O)[O-]2)cc1</chem>	[allylPdCl]2 (5%), (EtO)3P (10%), dioxane, reflux, 110 h	<chem>n-BuC=Cc1ccc([N+](=O)[O-]2)cc1</chem> (64)	87
	<chem>Ic1ccc([N+](=O)[O-]2)cc1</chem>	PdCl2(PhCN)2 (5%), (EtO)3P (10%), dioxane, reflux, 40 h	<chem>n-BuC=Cc1ccc([N+](=O)[O-]2)cc1</chem> (54)	

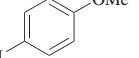
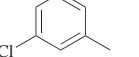
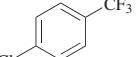
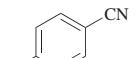
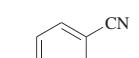
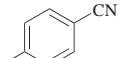
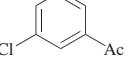
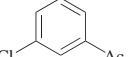
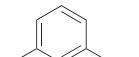
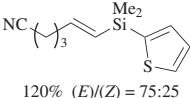
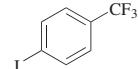
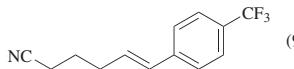
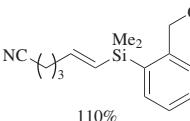
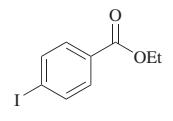
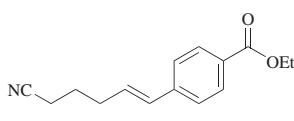
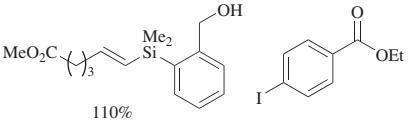
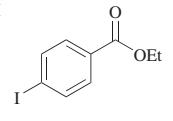
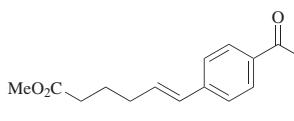
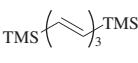
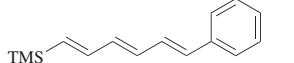
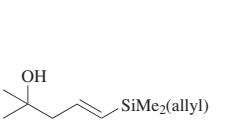
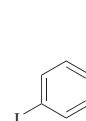
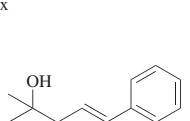
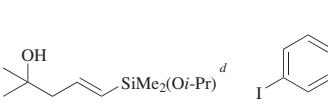
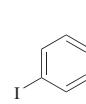
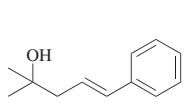
<i>n</i> -Bu <chem>C=CC[Si](C)(C)O</chem>	I 	(Ph ₃ P) ₄ P (5%), Ag ₂ O (100%), THF, 60°, 4 h	<i>n</i> -Bu <chem>C=CCc1ccc(O)c(C)c1</chem>	(79)	37
<i>n</i> -Bu <chem>C=CC[Si](C)(C)Cl</chem>	Cl 	(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (2.5%), NaOH (600%), C ₆ H ₆ , 80°, 12 h	<i>n</i> -Bu <chem>C=CCc1ccc(C)c(C)c1</chem>	(91)	185
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)O</chem>	Cl 	(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (2.5%), NaOH (600%), C ₆ H ₆ , 80°, 12 h	<i>n</i> -Bu <chem>C=CCc1ccc(C(F)(F)F)c(C)c1</chem>	(95)	185
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)O</chem>	Cl 	(Et ₃ P) ₂ PdCl ₂ (0.5%), TBAF (300%), THF, 90°, 20 h	<i>n</i> -Bu <chem>C=CCc1ccc(C#N)c(C)c1</chem>	(83)	187
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)O</chem>	Br 	Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 12 h	<i>n</i> -Bu <chem>C=CCc1ccc(C#N)c(C)c1</chem>	(80)	185
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)O</chem>	I 	(Ph ₃ P) ₄ Pd (5%), Ag ₂ O (100%), THF, 60°, 4 h	<i>n</i> -Bu <chem>C=CCc1ccc(C#N)c(C)c1</chem>	(87)	37
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)Cl</chem>	Cl 	(Et ₃ P) ₂ PdCl ₂ (0.5%), TBAF (300%), THF, 90°, 20 h	<i>n</i> -Bu <chem>C=CCc1ccc(C(=O)C)c(C)c1</chem>	(83)	187
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)Cl</chem>	Cl 	(<i>i</i> -Pr ₃ P) ₂ PdCl ₂ (2.5%), NaOH (600%), C ₆ H ₆ , 80°, 12 h	<i>n</i> -Bu <chem>C=CCc1ccc(C(=O)C)c(C)c1</chem>	(65)	185
120%	120%	120%	120%	120%	120%
<i>n</i> -Bu <chem>C=CC[Si](C)(C)Cl</chem>	Br 	Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 5 h	<i>n</i> -Bu <chem>C=CCc1ccc(C(=O)C)c(C)c1</chem>	(79)	185

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 1 h	 (90) (E)/(Z) = 81:19	49
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 19 h	 (95)	150, 151
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 18 h	 (92)	150
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), NaOH (2 M), benzene, reflux	 (45)	90, 125
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (85)	157
		Pd ₂ (dba) ₃ (cat.), TBAF, THF, rt	 (71)	222

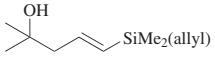
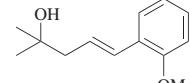
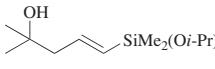
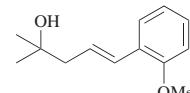
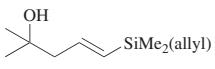
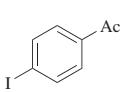
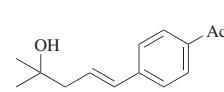
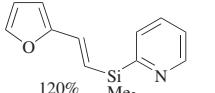
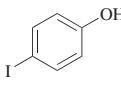
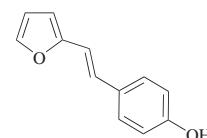
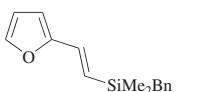
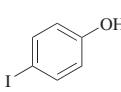
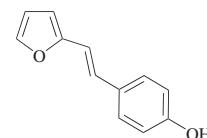
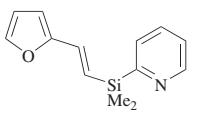
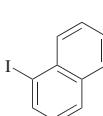
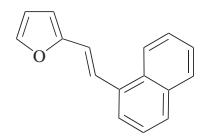
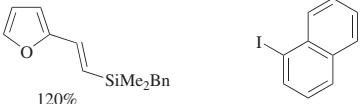
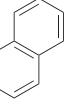
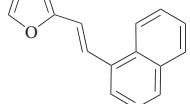
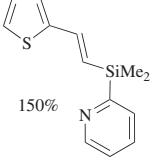
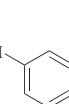
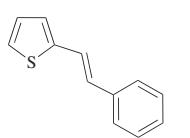
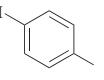
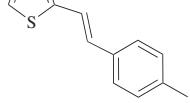
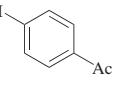
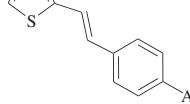
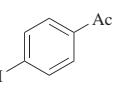
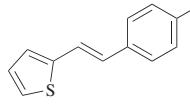
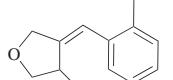
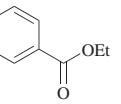
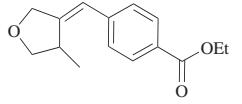
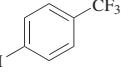
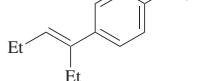
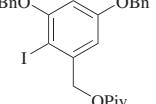
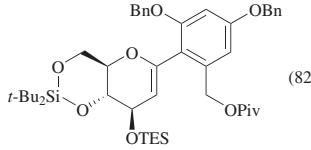
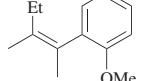
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(65)	157
		[allylPdCl] ₂ (cat.), TBAF, THF, rt		(45)	222
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(87)	157
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(73)	169
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(73)	169
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(98)	169

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
 120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(98) 169
 150%		PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°		(90) 170
558 150%		PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°		(93) 170
150%		PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°		(90) 170
150%		1. 2-Iodothiophene (130%), Pd(OAc) ₂ (10%), (2-furyl) ₃ P (10%), Et ₃ N (160%), THF, 60° 2. Electrophile, TBAF (230%)		(93) 170

		[allylPdCl]₂ (2.5%), TBAF (150%), THF, 22 h		(83)	25
		[allylPdCl]₂ (2.5%), TBAF (150%), THF, 22 h		(74)	25
		(Ph₃P)₄Pd (5%), Ag₂O (100%), THF, 60°, 18 h		(99)	37
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, rt		(90)	45
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, rt		(85)	45
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, rt		(72)	45
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, rt		(89)	45

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
110%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF•3H ₂ O (200%), THF, rt	 (77)	45
110%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF•3H ₂ O (200%), THF, rt	 (88)	45
120%		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 1 h	 (86)	49
<i>t</i> -Bu ₂ Si(O...)-O- <i>t</i> -Bu- <i>cis</i> -cyclopentane-1,2-diol		Pd ₂ (dba) ₃ •CHCl ₃ (5%), <i>t</i> -BuONa (200%), toluene, 50°, 5 h	 (82)	215
150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 66°, 0.75 h	 (95) (<i>Z</i>)/(<i>E</i>) > 99:1	80

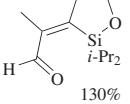
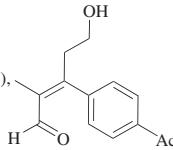
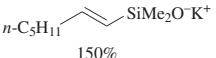
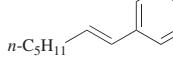
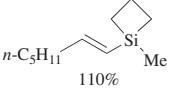
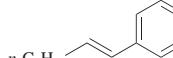
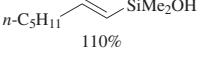
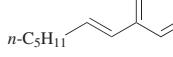
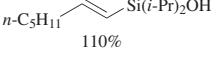
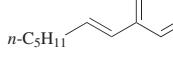
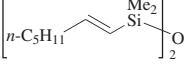
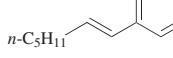
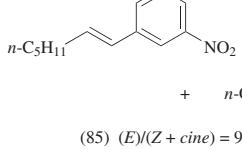
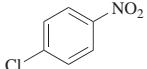
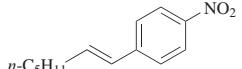
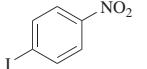
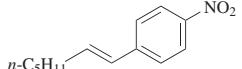
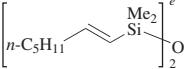
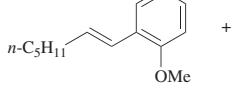
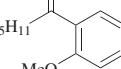
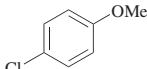
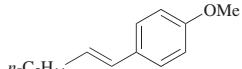
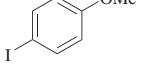
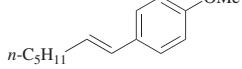
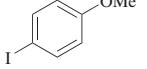
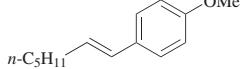
	I-	[allylPdCl]₂ (10%), CuI (20%), KF 2H₂O (200%), [-MeSi(H)O]₃-₅ (5%), DMF, rt, 7 h		(83)	81
C ₇					
	Cl	SPhos (5%), [allylPdCl]₂ (2.5%), THF, 60°, 1.5 h		(93) (E)/(Z) = 99.4:0.6	80
	I	Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min		(91) (E)/(Z) = 99.9:0.1	38
	I	Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(91) (E)/(Z) = 97.8:2.2	31
	I	Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 0.5 h		(91) (E)/(Z) = 99.3:0.7	32
	I	Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(82) (E)/(Z) = 99.2:0.8	31
130%	I	Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(85) (E)/(Z + cine) = 97.5:2.5	261

TABLE 3A. CROSS-COUPLED OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ O ⁻ K ⁺ 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 0.33 h	 (87) (E)/(Z) = 99.2:0.8	80
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ OH		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 0.25 h	 (95) (E)/(Z) = 98.5:1.5	32
 130%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 +  (82) (E)/(Z + cine) = 99.4:0.6	261
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ O ⁻ K ⁺ 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 66°, 3.5 h	 (89) (E)/(Z) = 99.6:0.4	80
<i>n</i> -C ₅ H ₁₁ CH=CHSi(Me)C ₂ H ₅ 110%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min	 (94) (E)/(Z) = 99:1	38
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ OH 110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 (95) (E)/(Z) = 97.2:2.8	31

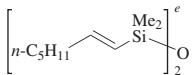
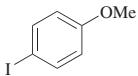
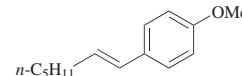
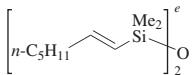
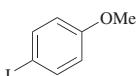
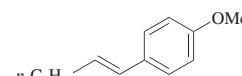
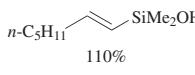
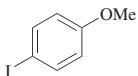
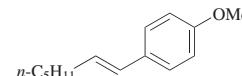
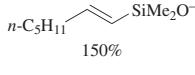
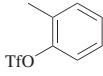
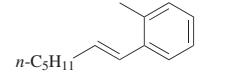
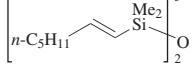
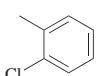
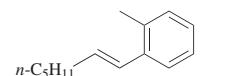
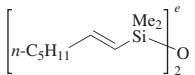
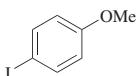
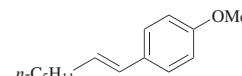
		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 1 h 1. <i>t</i> -Bu ₃ Pt(DVDS) (cat.), (SiHMe ₂) ₂ O (130–200%), 30 min 2. Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 (88) (<i>E</i>)/(<i>Z</i>) = 99.3:0.7	32
		1. <i>t</i> -Bu ₃ Pt(DVDS) (cat.), (SiHMe ₂) ₂ O, 60 min 2. Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min	 (84) (<i>E</i>)/(<i>Z</i>)/ <i>cine</i> = 96.5:1.4:2.1	261
		1. <i>t</i> -Bu ₃ Pt(DVDS) (cat.), (SiHMe ₂) ₂ O, 60 min 2. Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min	 (83)	319
		JohnPhos (10%), PdBr ₂ (5%), TBAF•6H ₂ O (200%), dioxane, rt, 16 h	 (85) (<i>E</i>)/(<i>Z</i>) = >99.9:0.1	202
		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 2 h	 (95) (<i>E</i>)/(<i>Z</i>) = 99.8:0.2	162
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 (78) (<i>E</i>)/(<i>Z</i> + <i>cine</i>) = 97.4:2.6	80, 261

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ OH		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 9 h	(80) (<i>E</i>)/(<i>Z</i>) = 99.5:0.5	32
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ O ⁺ K ⁺ 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 1.5 h	(92) (<i>E</i>)/(<i>Z</i>) = 98.8:1.2	80
150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 1 h	(91) (<i>E</i>)/(<i>Z</i>) = 99.7:0.3	80
150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 2 h	(91) (<i>E</i>)/(<i>Z</i>) = 99.2:0.8	80
		Pd(dba) ₂ (5%), PhAs (10%), TBAF (200%), THF, rt, 20 h	+	261 (88) (<i>E</i>)/(<i>Z</i> + <i>cine</i>) = 96.7:3.3
<i>n</i> -C ₅ H ₁₁ CH=CHSiMe ₂ OH		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 0.25 h	(85) (<i>E</i>)/(<i>Z</i>) = 99.8:0.2	32

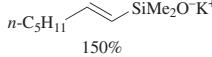
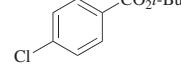
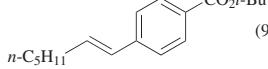
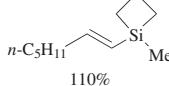
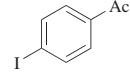
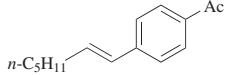
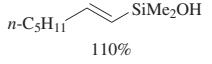
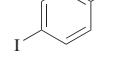
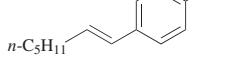
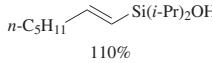
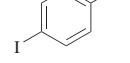
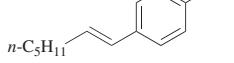
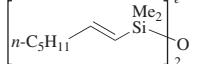
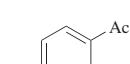
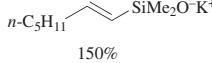
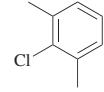
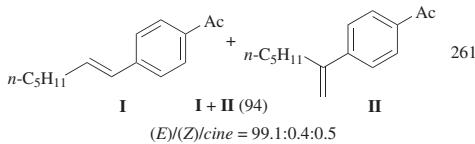
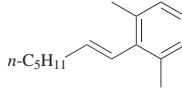
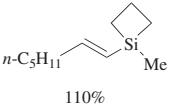
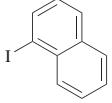
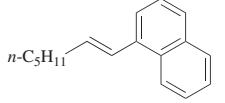
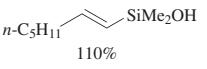
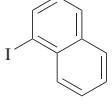
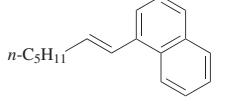
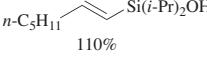
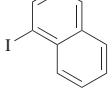
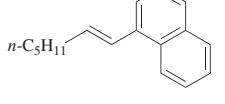
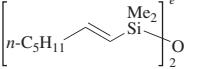
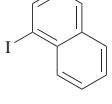
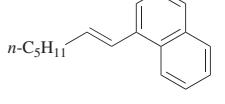
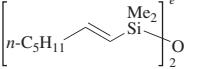
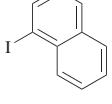
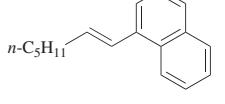
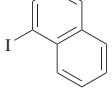
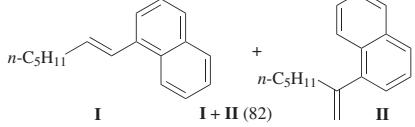
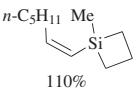
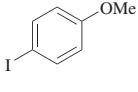
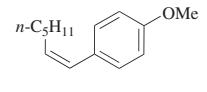
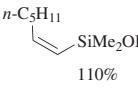
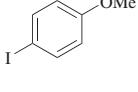
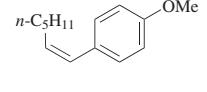
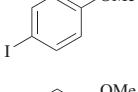
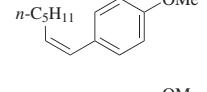
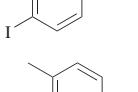
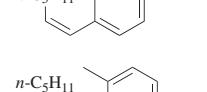
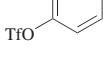
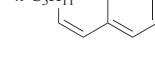
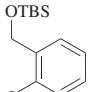
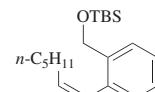
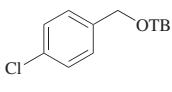
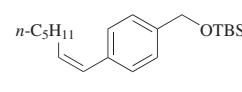
 150%		SPhos (5%), [allylPdCl]2 (2.5%), THF, 60°, 0.5 h	 (97) (E)/(Z) = 99.6:0.4	80
 110%		Pd(dba)2 (5%), TBAF (300%), THF, rt, 10 min	 (84) (E)/(Z) = 99.7:0.3	38
 110%		Pd(dba)2 (5%), TBAF (200%), THF, rt, 10 min	 (93) (E)/(Z) = 96.5:3.5	31
 110%		Pd(dba)2 (5%), KOTMS (200%), DME, rt, 9 h	 (82) (E)/(Z) = 98.8:1.2	32
 130%		Pd(dba)2 (5%), TBAF (200%), THF, rt, 10 min	 (80) (E)/(Z) = 99.5:0.5	31
 150%		1. <i>t</i> -Bu3Pt(DVDS) (cat.), (SiHMe2)2O (130–200%), 30 min 2. Pd(dba)2 (5%), TBAF (200%), THF, rt, 10 min	 I + II (94) (E)/(Z)/cine = 99.1:0.4:0.5	261
		SPhos (5%), [allylPdCl]2 (2.5%), THF, 60°, 2 h	 (95) (E)/(Z) = 99.7:0.3	80

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  110%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 30 min		(93) (<i>E</i>)/(<i>Z</i>) = 99.8:0.2 38
  110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min		(89) (<i>E</i>)/(<i>Z</i>) = 96.5:3.5 31
  110%		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 2 h		(93) (<i>E</i>)/(<i>Z</i>) = 97.9:2.1 32
  110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min		(85) (<i>E</i>)/(<i>Z</i>) = 98.4:1.6 31
  110%		Pd(dba) ₂ (5%), TBAOH (200%), THF, rt, 30 min		(78) (<i>E</i>)/(<i>Z</i>) = 99.2:0.8 31
  130%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		I + II (82) (<i>E</i>)/(<i>Z</i>)/ <i>cine</i> = 98.4:0.1:1.5 261

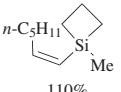
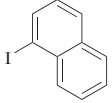
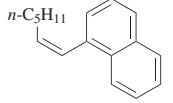
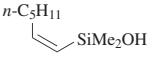
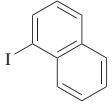
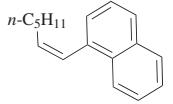
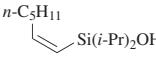
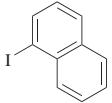
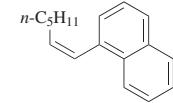
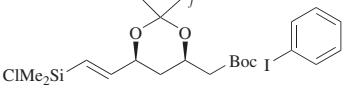
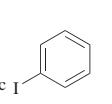
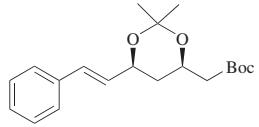
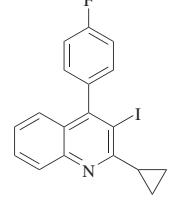
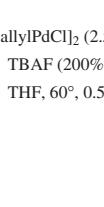
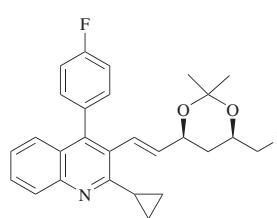
150%		SPhos (5%), [allylPdCl]2 (2.5%), THF, 60°, 0.5 h		(98) (E)/(Z) = 99.5:0.5	80
150%		SPhos (5%), [allylPdCl]2 (2.5%), THF, 60°, 1.5 h		(92) (Z)/(E) = 98.6:1.4	80
110%		Pd(dba)2 (5%), TBAF (300%), THF, rt, 10 min		(90) (E)/(Z) = 99.1:0.9	38
110%		Pd(dba)2 (5%), TBAF (200%), THF, rt, 10 min		(90) (Z)/(E) = 97.3:2.7	31
110%		Pd(dba)2 (5%), KOTMS (200%), DME, rt, 7.5		(86) (Z)/(E) = 98.2:1.8	32
110%		Pd(dba)2 (5%), TBAF (200%), THF, rt, 10 min		(81) (Z)/(E) = 99.4:0.6	31
150%		Pd(dba)2 (5%), KOTMS (200%), DME, rt, 0.25 h		(85) (Z)/(E) = 96.2:3.8	32
150%		SPhos (5%), [allylPdCl]2 (2.5%), THF, 66°, 3 h		(96) (Z)/(E) = 99.5:0.5	80

TABLE 3A. CROSS-COUPLED OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min		(90) (Z)/(E) = 97.5:2.5 38
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(94) (Z)/(E) = 97.4:2.6 31
		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 9.5 h		(91) (Z)/(E) = 98.9:1.1 32
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min		(80) 320
110%		JohnPhos (10%), PdBr ₂ (5%), TBAF•6H ₂ O (200%), dioxane, rt, 25 h		(86) (Z)/(E) = 99.6:0.4 202
		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 14.5 h		(76) (Z)/(E) = 98.0:2.0 32
150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 1.5 h		(98) (Z)/(E) = 99.6:0.4 80

		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 0.25 h		(83) (Z)/(E) = 99.3:0.7	32
		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 0.33 h		(97) (Z)/(E) = 98.8:1.2	80
150%					
		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min		(88) (Z)/(E) = 98:2	38
110%					
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(92) (Z)/(E) = 95.2:4.8	31
110%					
		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 13 h		(83) (Z)/(E) = 97.1:2.9	32
110%					
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min		(86) (Z)/(E) = 99.0:1.0	38
150%					
		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 2 h		(87) (Z)/(E) = 99.8:0.2	80
110%					
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min		(85) (Z)/(E) = 96.7:3.3	31

TABLE 3A. CROSS-COUPLED OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  110%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 30 min		(91) (Z)/(E) = 98.5:1.5 38
 		Pd(dba) ₂ (5%), KOTMS (200%), DME, rt, 9 h		(88) (Z)/(E) = 97.2:2.8 32
570 		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 30 min		(79) (Z)/(E) = 97.7:2.3 31
 		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 0.5 h		(81) (E)/(Z) = 96:4 177
 		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 0.5 h		(83) (E)/(Z) = 96:4 177

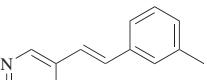
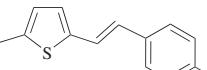
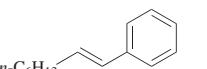
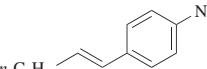
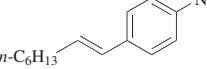
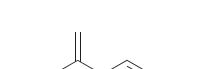
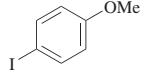
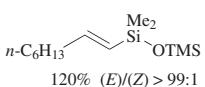
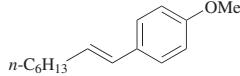
		PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°		(97)	170
		[allylPdCl] ₂ (2.5%), TBAF (150%), THF, 65°, 12 h		(57)	162
C ₈		Pd ₂ (dba) ₃ (1%), TBAF (200%), THF, 20°, 1 h		(93)	321
157		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 26 h		(99)	150, 151
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min		(81) (E)/(Z) > 99:1	230
		[allylPdCl] ₂ (5%), (EtO) ₃ P (10%), dioxane, reflux, 110 h		(51)	87

TABLE 3A. CROSS-COUPLED OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

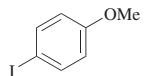
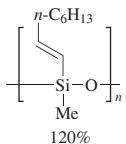
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		PdCl ₂ (PhCN) ₂ (5%), (EtO) ₃ P (10%), dioxane, reflux, 110 h		(33)
		[allylPdCl] ₂ (2.5%), TBAF (200%), CO (1 atm), THF, 50°, 17 h		(71)
		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 0.5 h		(97) (E)/(Z) = 99:1
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 40 h		(89)
		(Ph ₃ P) ₄ Pd (5%), Ag ₂ O (100%), THF, 60°, 4 h		(95)



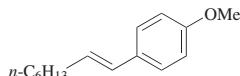
Pd₂(dba)₃•CHCl₃ (5%),
TBAF (200%),
THF, rt, 10 min



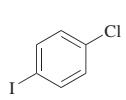
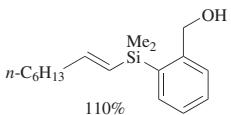
(95) (*E*)/(*Z*) > 99:1 230



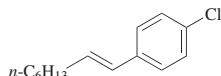
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF (120%),
THF, 60°, 1 h



(98) 268



PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 19 h

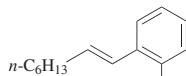


(93) 150, 151

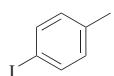
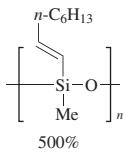
110%



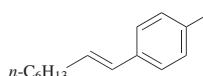
PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 47 h



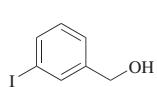
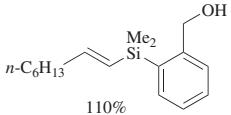
(94) 150, 151



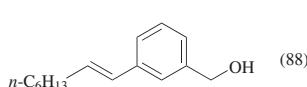
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF (120%),
THF, 60°, 1 h



(51) 268

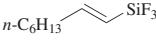
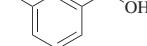
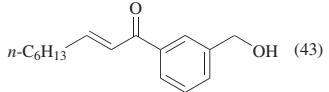
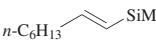
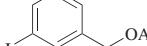
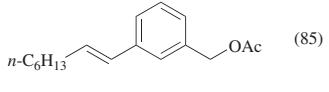
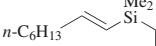
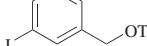
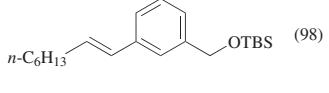
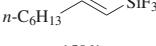
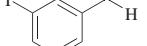
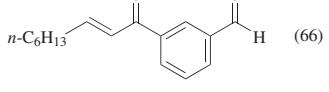
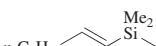
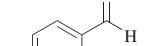
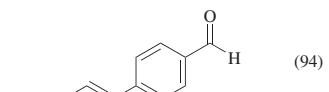
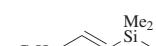
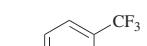
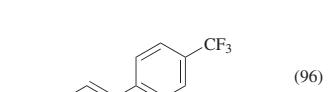


PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 47 h



(88) 150, 151

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		[allylPdCl] ₂ (2.5%), TBAF (200%), CO (1 atm), THF, 50°, 17 h	 (43)	179
		[allylPdCl] ₂ (2.5%), TASF (150%), THF, 24 h	 (85)	25
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 23 h	 (98)	150, 151
		[allylPdCl] ₂ (2.5%), TBAF (200%), CO (1 atm), THF, 50°, 17 h	 (66)	179
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 20 h	 (94)	150, 151
		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 5 h	 (96) (E)/(Z) = 97:3 49	

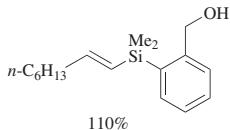
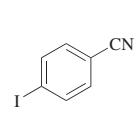
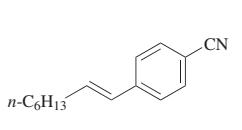
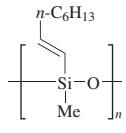
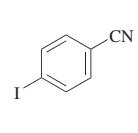
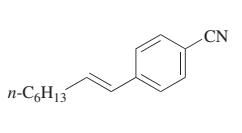
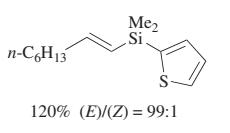
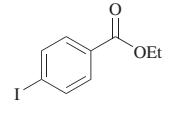
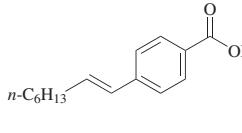
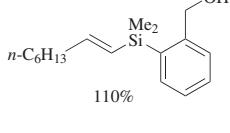
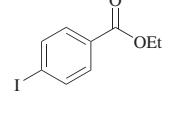
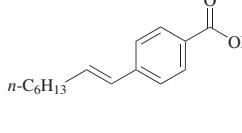
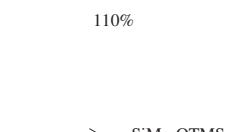
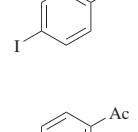
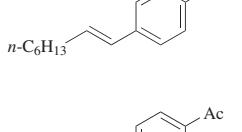
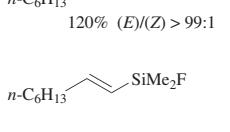
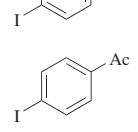
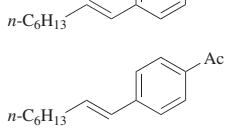
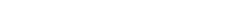
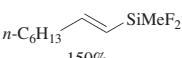
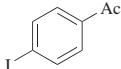
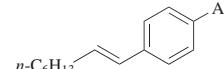
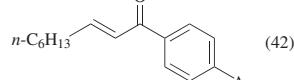
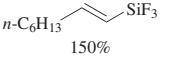
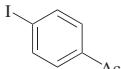
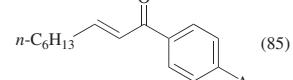
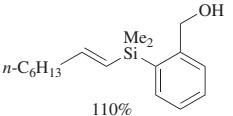
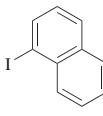
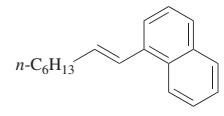
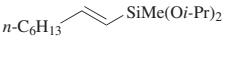
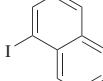
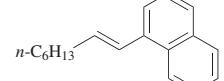
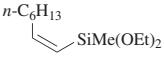
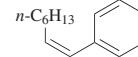
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 20 h		(93)	150, 151
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 2 h		(90)	268
		Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 0.5 h		(94) (E)/(Z) = 99:1	49
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 18 h		(96)	150, 151
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 17 h		(94)	150, 151
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min [allylPdCl] ₂ (2.5%), TASF (150%), THF, 24 h		(86) (E)/(Z) > 99:1	230
				(78)	25

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
 150%		[allylPdCl] ₂ (2.5%), TBAF (300%), CO (1 atm), THF, 50°, 12 h	 (52) +  (42)	179
 150%		[allylPdCl] ₂ (2.5%), TBAF (300%), CO (1 atm), THF, 50°, 22 h	 (85)	179
 110%		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 23 h	 (91)	150, 151
 110%		[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 5 h	 (91)	26
 120% (Z)/(E) = 97:3		[allylPdCl] ₂ (2.5%), Ph ₃ P (5%), TBAF (200%), THF, rt, 19 h		(99) (Z)/(E) > 95:5 230

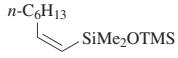
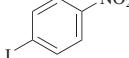
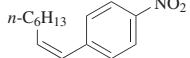
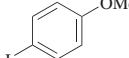
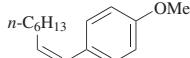
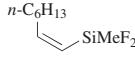
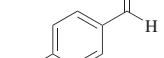
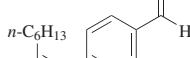
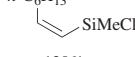
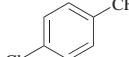
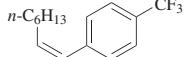
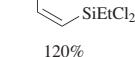
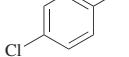
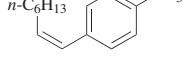
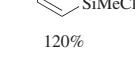
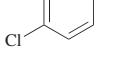
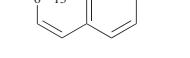
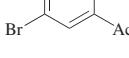
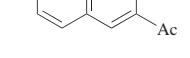
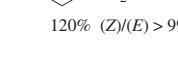
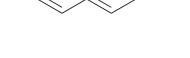
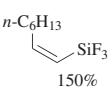
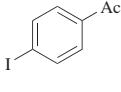
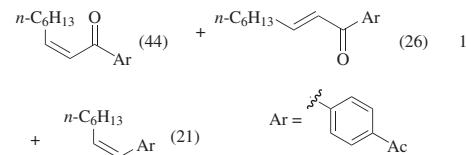
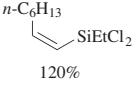
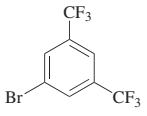
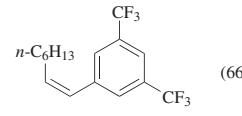
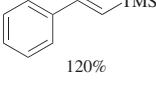
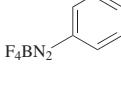
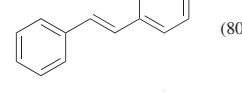
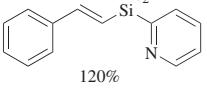
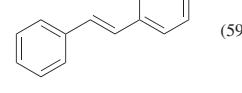
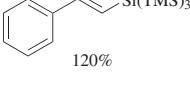
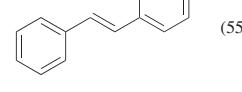
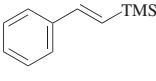
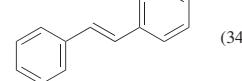
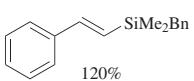
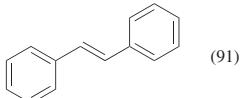
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min		(76) (Z)/(E) > 99:1	230
120% (Z)/(E) > 99:1					
120% (Z)/(E) = 94:5		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min		(82) (Z)/(E) = 94:5	230
		(Ph ₃ P) ₄ Pd (cat.), TBAF (120%), THF, 50°, 5 h		(73)	181
120%					
		(Et ₃ P) ₂ PdCl ₂ (0.5%), TBAF (300%), THF, 90°, 20 h		(58)	187
120%					
		(dppe)PdCl (2.5%), NaOH (600%), C ₆ H ₆ , 80°, 12 h		(55)	185
120%					
		(Et ₃ P) ₂ PdCl ₂ (0.5%), TBAF (300%), THF, 90°, 20 h		(91)	187
120%					
		Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 12 h		(70)	185
120%					
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min		(93) (Z)/(E) > 99:1	230
120% (Z)/(E) > 99:1					

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

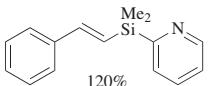
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		[allylPdCl]2 (2.5%), TBAF (200%), CO (1 atm), THF, 50°, 12 h		179
		Pd(OAc)2 (2.5%), NaOH (600%), THF, 60°, 12 h		185
		1. BCl3, CH2Cl2, 0° 2. Pd(OAc)2 (6%), dioxane, rt, 24 h		124
		PdCl2(PhCN)2 (5%), TBAF (100%), THF, 60°		169
		1. H2O2, NaOH, H2O/THF, 1 h 2. Electrophile, (Ph3P)4Pd (cat.), 40°		322
		[allylPdCl]2 (2.5%), TBAF (110%), THF, 60°, 21 h		89



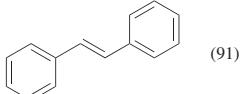
PdCl₂(PhCN)₂ (5%),
TBAF (100%),
THF, 60°



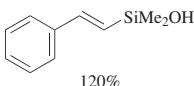
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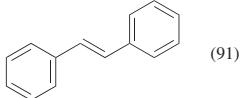
PdCl₂(PhCN)₂ (5%),
TBAF (100%),
THF, 60°



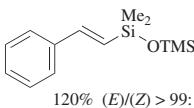
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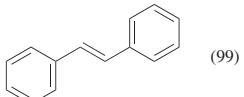
(Ph₃P)₄P (5%),
Ag₂O (100%),
THF, 60°, 7 h



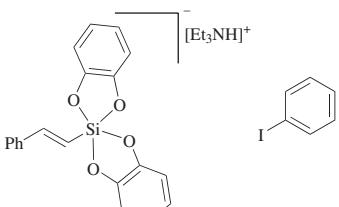
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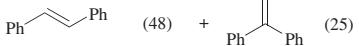
Pd₂(dba)₃•CHCl₃ (5%),
TBAF (200%),
THF, rt, 10 min



230



[allylPdCl]₂ (5%),
(EtO)₃P (10%),
dioxane, reflux, 110 h



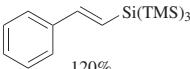
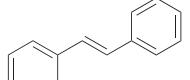
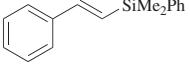
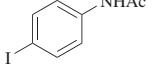
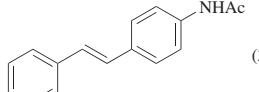
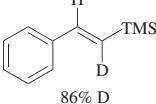
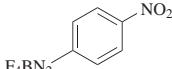
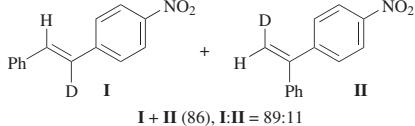
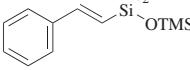
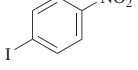
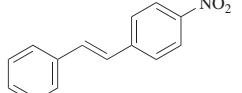
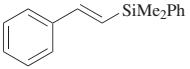
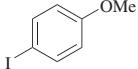
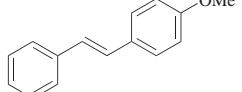
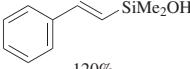
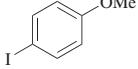
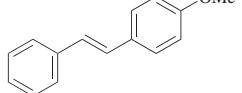
22, 87

PdCl₂(PhCN)₂ (5%),
(EtO)₃P (10%),
dioxane, reflux, 60 h



87

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
 120%		1. H ₂ O ₂ , NaOH, H ₂ O/THF, 1 h 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), 40°	 (75)	322
 120%		[allylPdCl] ₂ (2.5%), TBAF (150%), THF, 65°, 120 h	 (34)	162
 86% D		Pd(dba) ₂ (5%)	 I + II (86), I : II = 89:11	93
 120% (E)/(Z) > 99:1		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min	 (84) (E)/(Z) > 99:1	230
 120%		[allylPdCl] ₂ (2.5%), TBAF (150%), THF, 65°, 48 h	 (67)	162
 120%		(Ph ₃ P) ₄ P (5%), Ag ₂ O (100%), THF, 60°, 7 h	 (89)	203

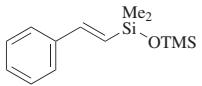
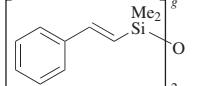
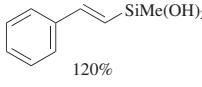
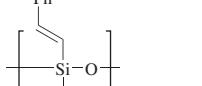
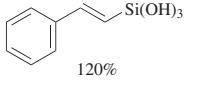
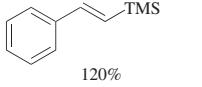
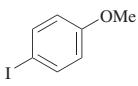
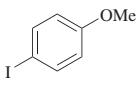
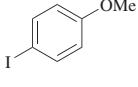
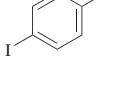
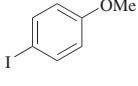
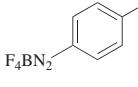
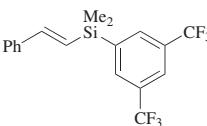
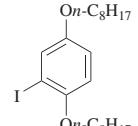
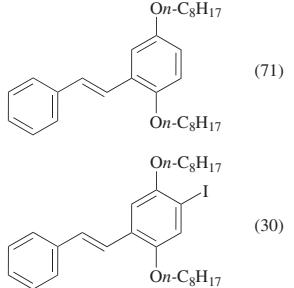
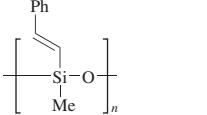
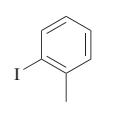
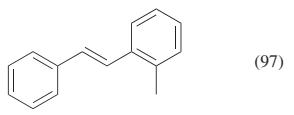
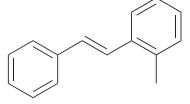
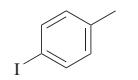
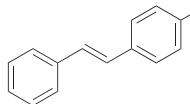
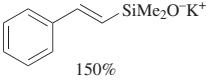
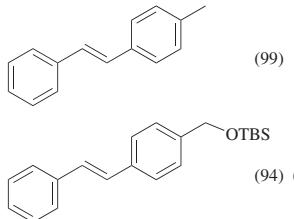
	120% (E)/(Z) > 99:1		
	150%		
	120%		
	500%		
	120%		
	120%		
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min	(90) (E)/(Z) > 99:1 230
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	(74) 261
		(Ph ₃ P) ₄ Pd (5%), Ag ₂ O (100%), THF, 60°, 12 h	(95) 37
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 1 h	(99) 268
		(Ph ₃ P) ₄ Pd (5%), Ag ₂ O (100%), THF, 60°, 4 h	(76) 37
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	(61) 124

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		[allylPdCl] ₂ (5%), TBAF•3H ₂ O (100%), THF, rt		166
		[allylPdCl] ₂ (5%), TBAF•3H ₂ O (100%), THF, rt		166
500%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 1 h		268
500%		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF (120%), THF, 60°, 1 h		268
150%		SPhos (5%), [allylPdCl] ₂ (2.5%), dioxane, 90°, 1.25 h		80

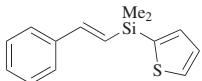
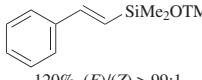
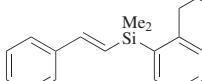
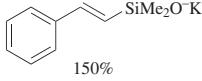
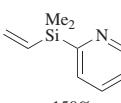
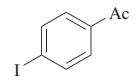
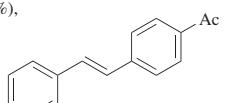
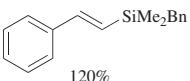
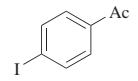
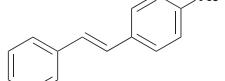
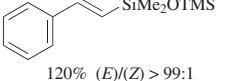
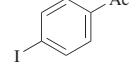
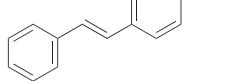
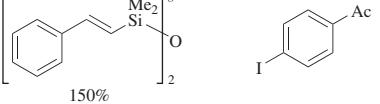
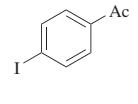
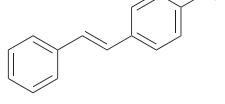
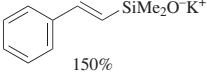
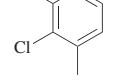
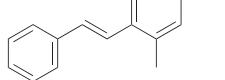
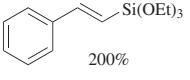
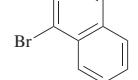
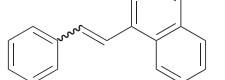
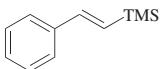
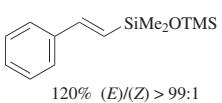
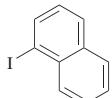
	120% (<i>E</i>)/(<i>Z</i>) = 99:1		
	120% (<i>E</i>)/(<i>Z</i>) > 99:1		
	110%	Pd(OAc) ₂ (5%), TBAF (120%), THF, rt, 1 h	(98) (<i>E</i>)/(<i>Z</i>) = 99:1 49
	150%	[allylPdCl] ₂ (2.5%), Ph ₃ P (5%), TBAF (200%), THF, rt, 22 h	(57) (<i>E</i>)/(<i>Z</i>) > 99:1 230
	150%	PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 19 h	(88) 150, 151
	150%	SPhos (5%), [allylPdCl] ₂ (2.5%), dioxane, 90°, 0.5 h	(89) (<i>E</i>)/(<i>Z</i>) = 99.9:0.1 80
	120%	PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°	(84) 170
	120%	PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°	(84) 169

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

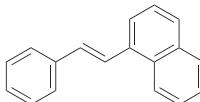
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
 150%		1. PhI (130%), Pd(OAc) ₂ (10%), (2-furyl) ₃ P (10%), Et ₃ N (160%), THF, 60° 2. Electrophile, TBAF (230%)	 (69)	170
 120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°	 (84)	169
 120% (E)/(Z) > 99:1		Pd ₂ (dba) ₃ •CHCl ₃ (5%), TBAF (200%), THF, rt, 10 min	 (85) (E)/(Z) > 99:1	230
 150%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 (89)	261
 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), dioxane, 90°, 1.25 h	 (91) (E)/(Z) = 99.7:0.3	80
 200%		Pd cat. 5 , (1%), NaOH (250%), TBAB (100%), H ₂ O, MW, 120°, 20 min	 (83) (E)/(Z) = 1.9:1	257



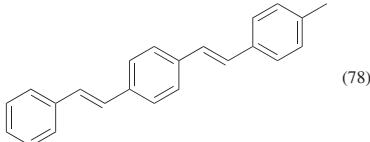
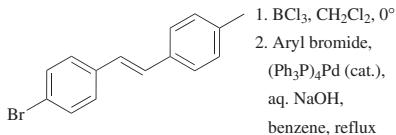
216%



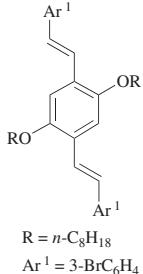
Pd₂(dba)₃•CHCl₃ (5%),
TBAF (200%),
THF, rt, 10 min

(94) (*E*)/(*Z*) > 99:1

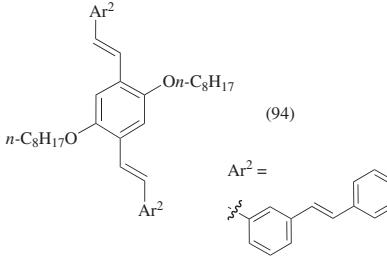
230



90

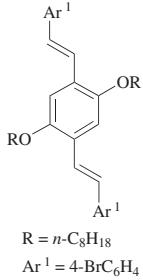


1. BCl₃, CH₂Cl₂, 0°
2. H₂O, Na₂CO₃
3. Electrophile,
(Ph₃P)₄Pd (20%),
Na₂CO₃, toluene,
MeOH, reflux



91

216%



1. BCl₃, CH₂Cl₂, 0°
2. H₂O, Na₂CO₃
3. Electrophile,
(Ph₃P)₄Pd (20%),
Na₂CO₃, toluene,
MeOH, reflux

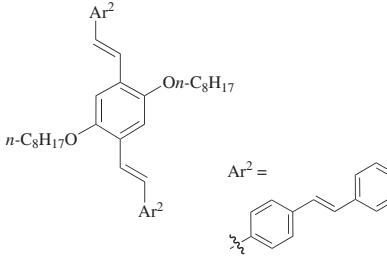
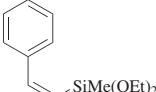
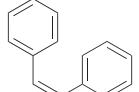
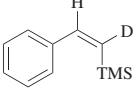
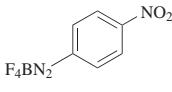
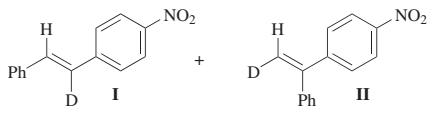
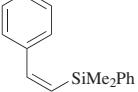
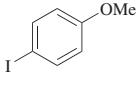
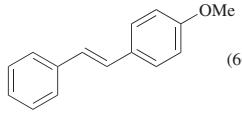
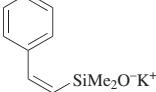
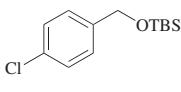
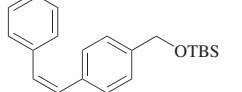
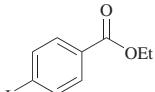
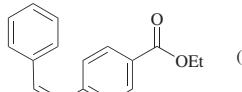
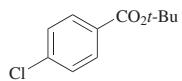
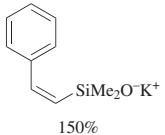
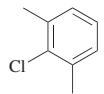
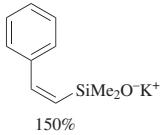
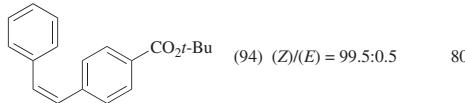


TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

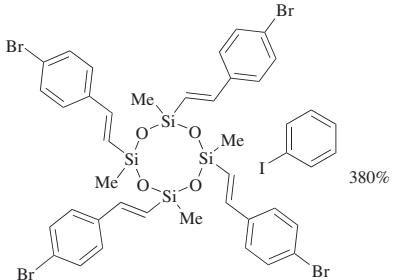
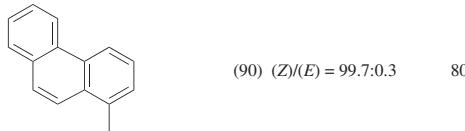
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		[allylPdCl] ₂ (2.5%), Ph ₃ P (5%), TBAF (200%), THF, 60°, 6 h	 (86) (Z)/(E) = 91:9	230
120% (Z)/(E) = 98:2				
		Pd(dba) ₂ (5%)	 I + II (91), I:II = 83:17	93
97% D				
589				
		[allylPdCl] ₂ (2.5%), TBAF (150%), THF, 65°, 48 h	 (66)	162
150%				
		SPhos (5%), [allylPdCl] ₂ (2.5%), dioxane, 90°, 1.25 h	 (97) (Z)/(E) = 99.5:0.5	80
110%				
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 35°, 11 h	 (92)	150



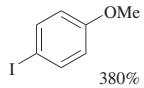
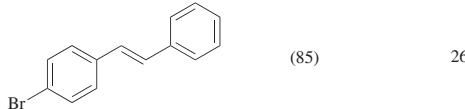
SPhos (5%),
[allylPdCl]₂ (2.5%),
dioxane, 90°, 0.5 h



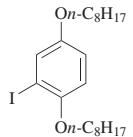
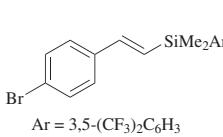
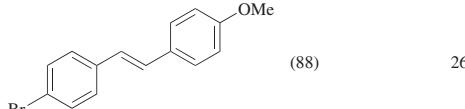
SPhos (5%),
[allylPdCl]₂ (2.5%),
dioxane, 90°, 1.25 h



Pd(dba)₂ (5%),
TBAF (800%),
THF, 65°



Pd(dba)₂ (5%),
TBAF (800%),
THF, 65°



[allylPdCl]₂ (5%),
TBAF•3H₂O (100%),
THF, rt

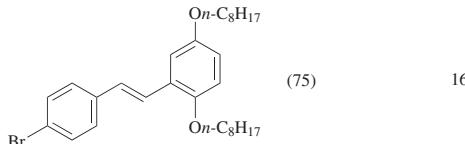
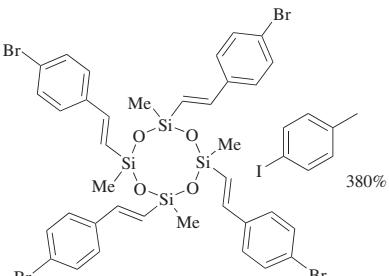
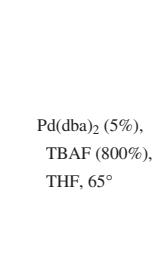
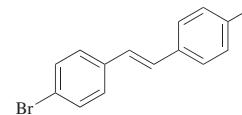
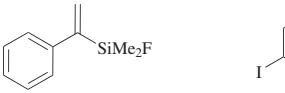
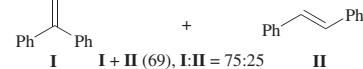
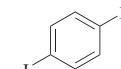
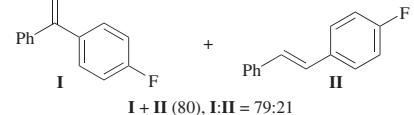
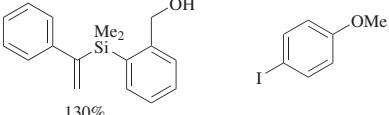
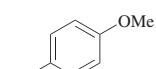
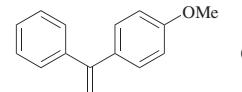
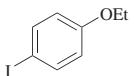
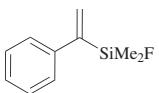
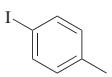
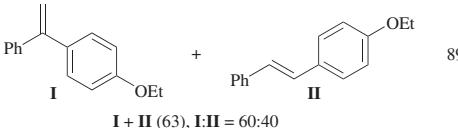


TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

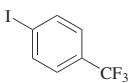
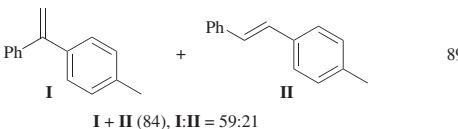
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(dba) ₂ (5%), TBAF (800%), THF, 65°	 (92)	266
		[allylPdCl] ₂ (2.5%), TBAF (110%), THF, 60°, 4 h		89
		[allylPdCl] ₂ (2.5%), TBAF (110%), THF, 60°, 4 h		89
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 50°, 12 h	 (80)	150, 151



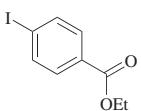
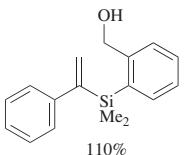
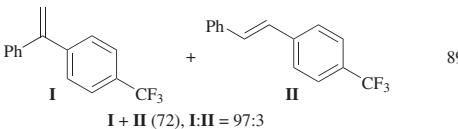
[allylPdCl]₂ (2.5%),
TBAF (110%),
THF, 60°, 20 h



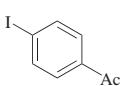
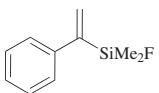
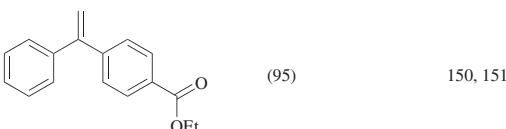
[allylPdCl]₂ (2.5%),
TBAF (110%),
THF, 60°, 14 h



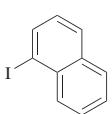
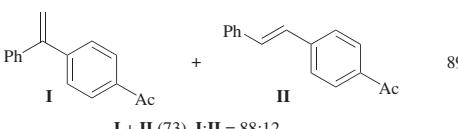
[allylPdCl]₂ (2.5%),
TBAF (110%),
THF, 60°, 24 h



PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 25 h



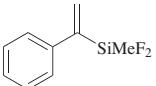
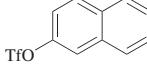
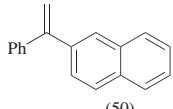
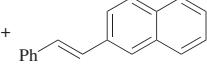
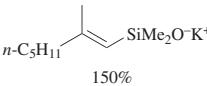
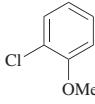
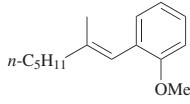
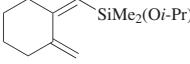
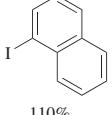
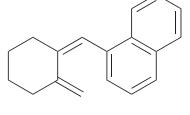
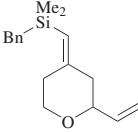
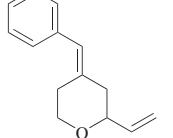
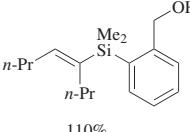
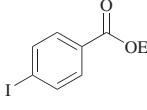
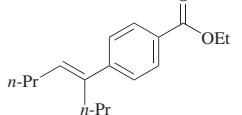
[allylPdCl]₂ (2.5%),
TBAF (110%),
THF, 60°, 20 h

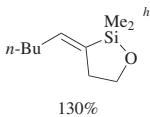


[allylPdCl]₂ (2.5%),
TBAF (110%),
THF, 60°, 21 h

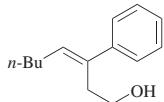


TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
 120%		(Ph ₃ P) ₄ Pd (cat.), TBAF (120%), THF, 50°, 5 h	 (50) +  (26)	181
 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 66°, 1 h	 (98) (E)/(Z) > 99:1	80
 110%		[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 7 h	 (79) (Z)/(E) = 95:5	26
 150%		Pd ₂ (dba) ₃ CHCl ₃ (2%), TBAF (200%), THF, 23°, 2.5 h	 (85)	323
 110%		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (220%), DMSO, 50°, 29 h	 (92)	150, 151

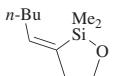


TBAF (220%),
Pd(dba)₂ (5%),
THF, rt, 90 min

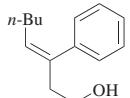


(85) (*E*)/(*Z*) = 98.3:1.7

224

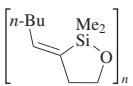


1. TBAF (150%)
2. Pd(dba)₂ (5%),
dioxane, 45°, 8.1 h

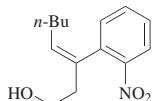


(65) (*E*)/(*Z*) = 95.3:4.7

198

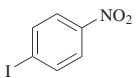


1. TBAF (150%)
2. Pd(dba)₂ (5%),
dioxane, rt, 7 h;
then 35°, 47 h

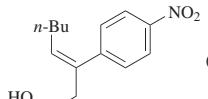


(66) (*Z*)/(*E*) = 96.2:3.8

198

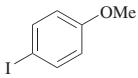


1. TBAF (150%)
2. Pd(dba)₂ (5%),
dioxane, 45°, 7.6 h

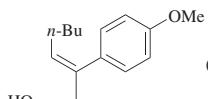


(68) (*Z*)/(*E*) = 96.4:3.6

198

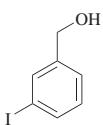


1. TBAF (150%)
2. Pd(dba)₂ (5%),
dioxane, rt, 41 h

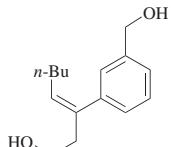


(60) (*Z*)/(*E*) = 99.3:0.7

198



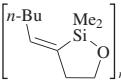
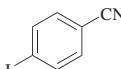
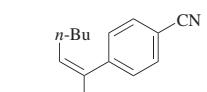
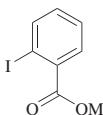
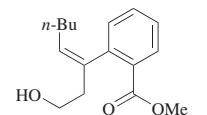
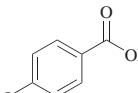
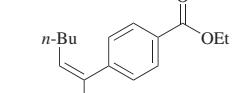
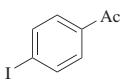
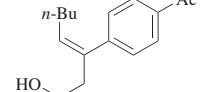
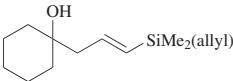
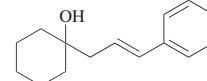
1. TBAF (150%)
2. Pd(dba)₂ (5%),
dioxane, rt, 13.5 h,
then 45°, 33 h

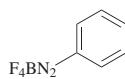
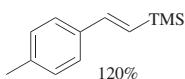
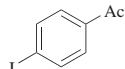
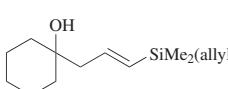
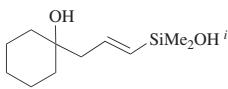
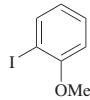
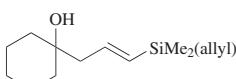
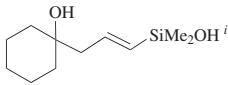


(59) (*Z*)/(*E*) = 98.4:1.6

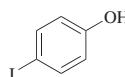
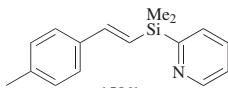
198

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		1. TBAF (150%) 2. Pd(dba) ₂ (5%), dioxane, 45°, 25.5 h	 (64)	198
		1. TBAF (150%) 2. Pd(dba) ₂ (5%), dioxane, 35°, 43 h	 (64) (Z)/(E) = 95:5	198
		1. TBAF (150%) 2. Pd(dba) ₂ (5%), dioxane, 40°, 15.5 h	 (72) (Z)/(E) = 96.5:3.5	198
		1. TBAF (150%) 2. Pd(dba) ₂ (5%), dioxane, rt, 46 h	 (66) (Z)/(E) = 97.4:2.6	198
C ₉		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (83)	157



120%



Pd₂(dba)₃ (cat.),
TBAF, electrophile,
THF, rt

1. TBAF (200%),
[allylPdCl]₂ (5%),
EtOH (600%),
THF, rt, 30 min
2. Electrophile

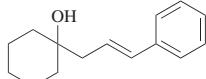
Pd₂(dba)₃ (cat.),
TBAF, electrophile,
THF, rt

1. TBAF (200%),
Pd₂(dba)₃ (5%),
EtOH (600%),
THF, rt, 30 min
2. Electrophile

1. BCl₃, CH₂Cl₂, 0°
2. Pd(OAc)₂ (6%),
dioxane, rt, 24 h

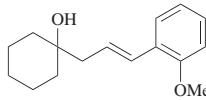
1. BCl₃, CH₂Cl₂, 0°
2. Pd(OAc)₂ (6%),
dioxane, rt, 24 h

PdCl₂(PhCN)₂ (5%),
TBAF (150%),
THF, 60°



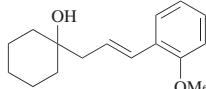
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222



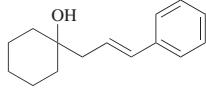
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157



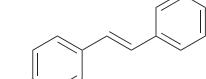
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222



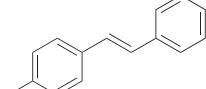
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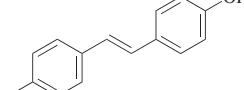
(72)

124



(58)

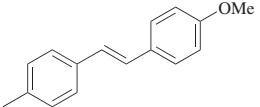
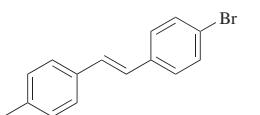
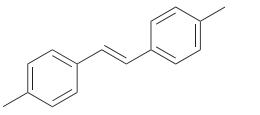
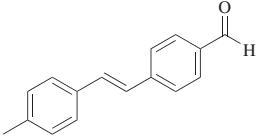
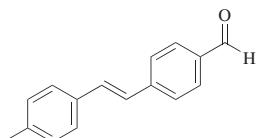
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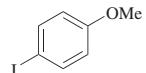
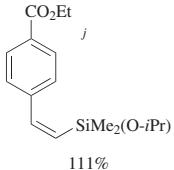


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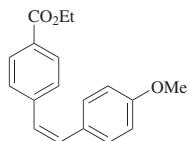
170

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉				
120%		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	(65)	124
120%		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	(60)	124
120%		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Pd(OAc) ₂ (6%), dioxane, rt, 24 h	(62)	124
150%		1. Pd(OAc) ₂ (10%), (2-furyl) ₃ P (10%), Et ₃ N (160%), THF, 60° 2. Electrophile, TBAF (230%)	(92)	170
150%		PdCl ₂ (PhCN) ₂ (5%), TBAF (150%), THF, 60°	(91)	170

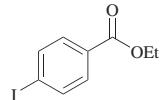
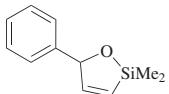


PdCl(PPh₃)(Bn) (5%),
CuI (10%), TBAF (278%),
DMF, 50°, 8 h

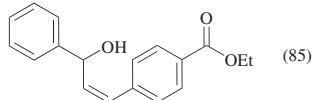


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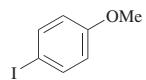
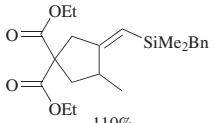
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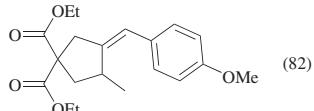
Pd(dba)₂ (3%),
TBAF (200%),
THF, rt, 30 min



225, 226



Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt

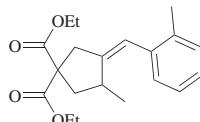


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110%



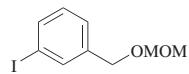
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TBAF•3H₂O (200%),
THF, rt



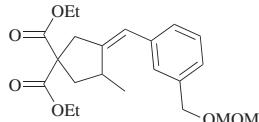
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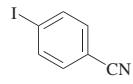
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt



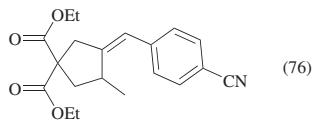
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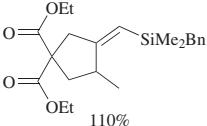
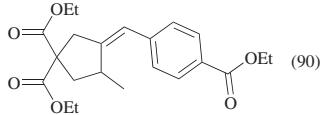
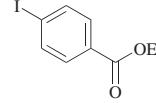
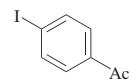
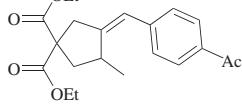
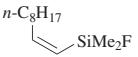
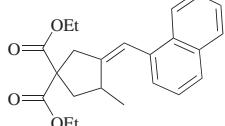
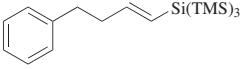
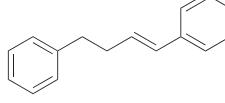
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt



(76)

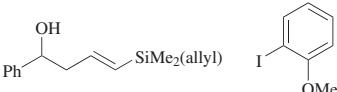
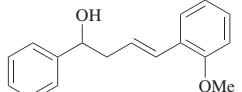
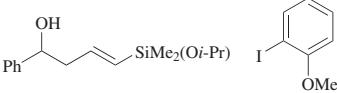
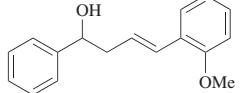
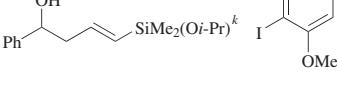
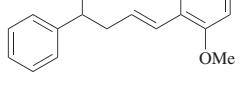
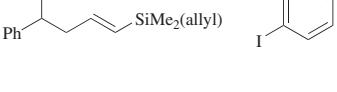
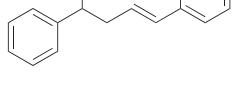
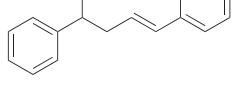
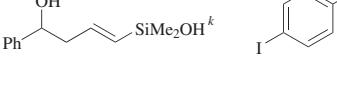
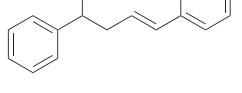
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TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF•3H ₂ O (200%), THF, rt	 (90)	45
				
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF•3H ₂ O (200%), THF, rt	 (86)	45
C ₁₀		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), TBAF•3H ₂ O (200%), THF, rt	 (85)	45
		1. H ₂ O ₂ , NaOH, H ₂ O/THF, 1 h 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), 40°	 (56)	322

		[allylPdCl]₂ (cat.), TBAF (200%), THF, 50°, 24 h		(82)	222
		1. TBAF (200%), Pd₂(dba)₃ (cat.), EtOH (600%), THF, rt, 30 min 2. Electrophile		(91)	157
		1. TBAF (200%), Pd₂(dba)₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(91)	157
		Pd₂(dba)₃ (cat.), TBAF (200%), THF, rt, 4 h		(97)	222
		Pd₂(dba)₃ (5%), TBAF (240%), electrophile (70%)		(90)	222
		1. TBAF (200%), [allylPdCl]₂ (cat.), EtOH (600%), THF, rt, 30 min 2. Electrophile		(63)	157

TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
		1. TBAF (200%), [allylPdCl] ₂ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(63) 157
		[allylPdCl] ₂ (cat.), TBAF (200%), THF, rt, 1.5 h		(93) 222
		[allylPdCl] ₂ (5%), TBAF (240%), electrophile (70%)		(65) 222
		1. TBAF (200%), Pd ₂ (dba) ₃ (cat.), EtOH (600%), THF, rt, 30 min 2. Electrophile		(78) 157
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(78) 157
		[allylPdCl] ₂ (5%), TBAF (240%), electrophile (70%)		(86) 222

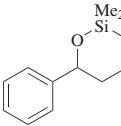
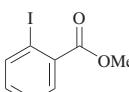
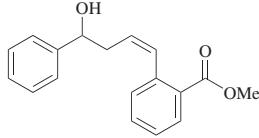
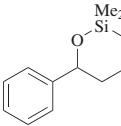
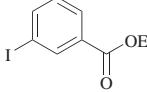
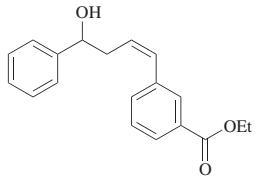
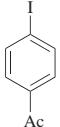
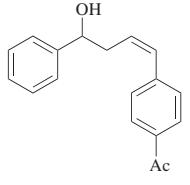
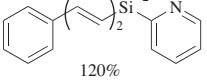
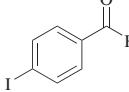
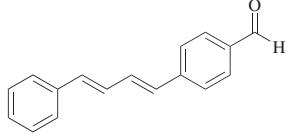
		Pd2(dba)3 (cat.), TBAF (200%), THF, rt, 4 h		(90)	222
		[allylPdCl]2 (5%), TBAF (240%), electrophile (70%)		(86)	222
		[allylPdCl]2 (cat.), TBAF (200%), THF, rt, 3 h		(99)	222
		[allylPdCl]2 (5%), TBAF (240%), electrophile (70%)		(63)	222
		[allylPdCl]2 (5%), TBAF (240%), electrophile (70%)		(56)	222
		1. TBAF (200%), Pd2(dba)3 (cat.), EtOH (600%), THF, rt, 30 min 2. Electrophile		(85)	157
		1. TBAF (200%), Pd2(dba)3 (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(85)	157

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀			Pd ₂ (dba) ₃ (5%), TBAF (240%), electrophile (70%)	 (89)	222
900			Pd ₂ (dba) ₃ (cat.), TBAF (200%), THF, rt, 3 h	 (98)	222
			Pd ₂ (dba) ₃ (5%), TBAF (240%), electrophile (70%)	 (89)	222
			1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (84)	157
			Pd ₂ (dba) ₃ (5%), TBAF (240%), electrophile (70%)	 (91)	222

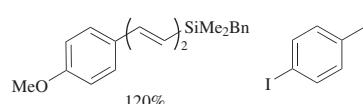
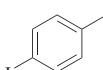
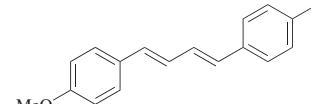
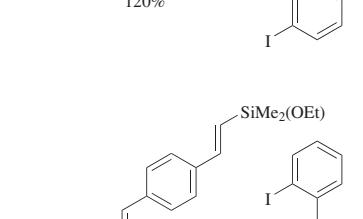
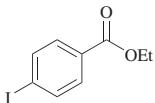
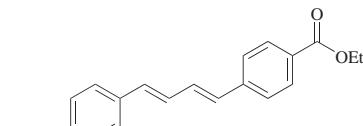
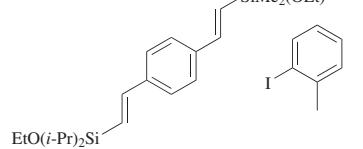
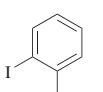
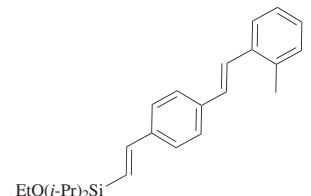
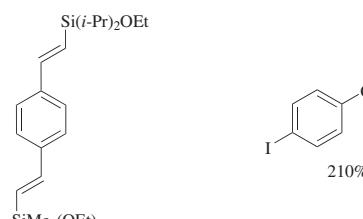
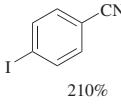
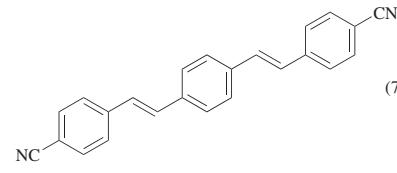
		Pd ₂ (dba) ₃ (cat.), TBAF (200%), THF, rt, 4 h		(96)	222
		Pd ₂ (dba) ₃ (5%), TBAF (240%), electrophile (70%)		(91)	222
		Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 90 min		(86)	225, 226
		Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 30 min		(92)	225, 226
		Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 30 min		(89)	225, 226
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 180 min		(90)	225, 226

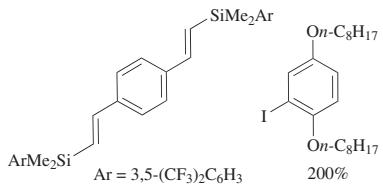
TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 180 min	 (84)	225, 226
		Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 30 min	 (93)	225, 226
602		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 10 min	 (90)	225, 226
		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°	 (89)	169

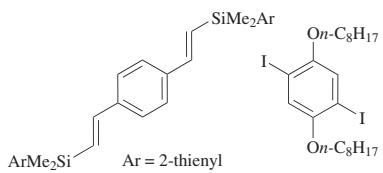
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(89)	169
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(85)	169
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(85)	169
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(73)	169
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(73)	169
	120%		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 15 min		(91)	44

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

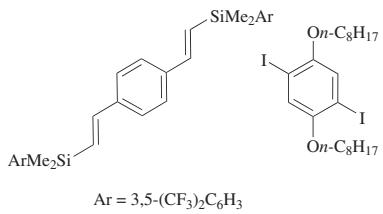
	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀					
	 120%		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 15 min		(86) 44
	 120%		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 15 min		(88) 44
604			[allylPdCl] ₂ (2.5%), KOTMS (400%), rt		(—) 72
	 210%		[allylPdCl] ₂ (2.5%), TBAF (400%), rt		(79) 45



[allylPdCl]₂ (5%),
TBAF•3H₂O (100%),
THF, rt, 24 h



[allylPdCl]₂ (5%),
TBAF (200%),
THF, rt, 24 h



[allylPdCl]₂ (5%),
TBAF (200%),
THF, rt, 24 h

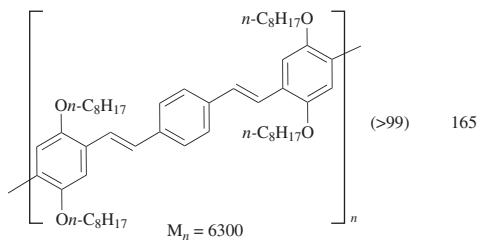
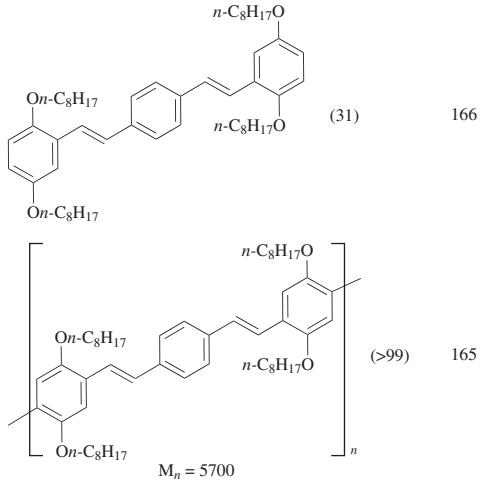
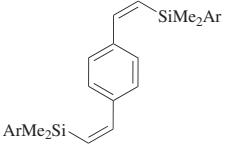
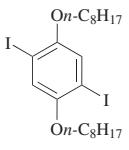
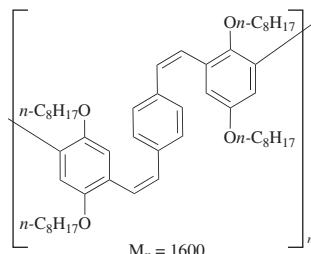
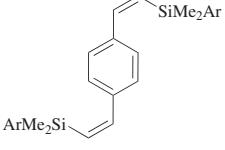
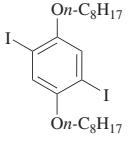
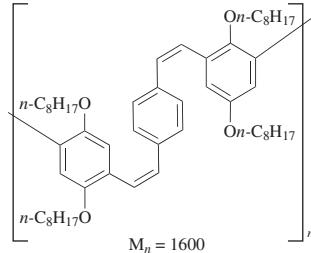
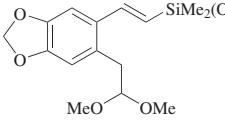
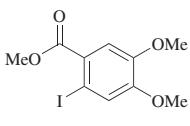
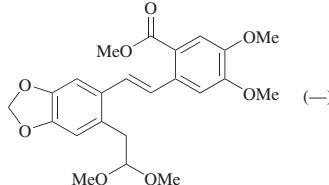


TABLE 3A. CROSS-CO尤LING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
 ArMe ₂ Si-CH=CH-SiMe ₂ Ar	 I- On-C ₈ H ₁₇ On-C ₈ H ₁₇	[allylPdCl] ₂ (5%), TBAF (200%), THF, rt, 24 h	 $\left[\text{---} \text{C}_8\text{H}_{17}\text{O} \text{---} \text{C}_6\text{H}_3(\text{On-C}_8\text{H}_{17})_2 \text{---} \text{C}_6\text{H}_3(\text{On-C}_8\text{H}_{17})_2 \text{---} \text{C}_8\text{H}_{17}\text{O} \text{---} \right]_n$ $M_n = 1600$ $(Z)/(E) = 55:45$	(97) 165
 ArMe ₂ Si-CH=CH-SiMe ₂ Ar	 I- On-C ₈ H ₁₇ On-C ₈ H ₁₇	[allylPdCl] ₂ (5%), TBAF (200%), THF, rt, 24 h	 $\left[\text{---} \text{C}_8\text{H}_{17}\text{O} \text{---} \text{C}_6\text{H}_3(\text{On-C}_8\text{H}_{17})_2 \text{---} \text{C}_6\text{H}_3(\text{On-C}_8\text{H}_{17})_2 \text{---} \text{C}_8\text{H}_{17}\text{O} \text{---} \right]_n$ $M_n = 1600$ $(Z)/(E) = 55:45$	(97) 165
				909
 MeO-CH ₂ -CH ₂ -CH=CH-SiMe ₂ (OEt)	 MeO-C(=O)- I- OMe OMe	[allylPdCl] ₂ (5%), (EtO) ₃ P (10%), TBAF (120%), THF, 60°, 2 h	 MeO-C(=O)- --- MeO-CH ₂ -CH ₂ -CH=CH- --- OMe	(—) 285

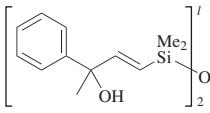
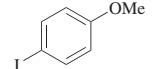
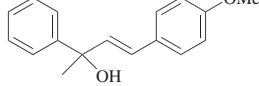
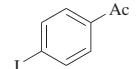
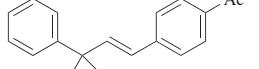
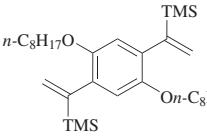
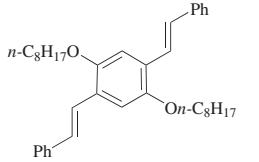
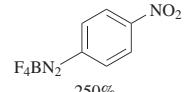
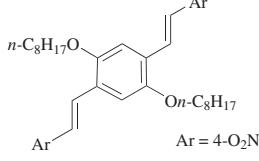
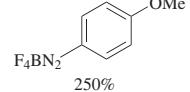
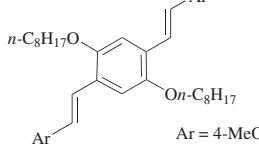
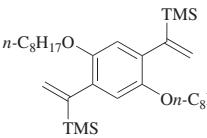
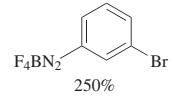
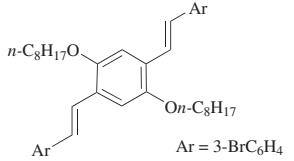
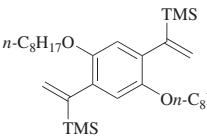
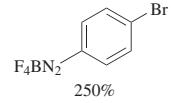
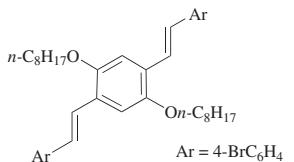
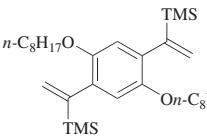
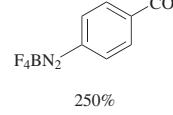
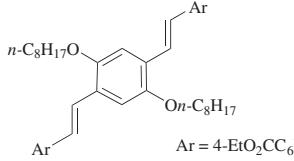
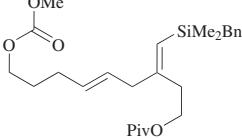
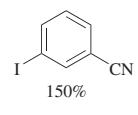
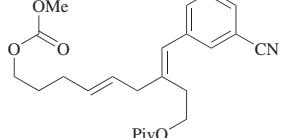
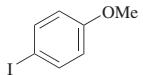
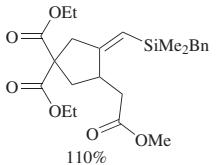
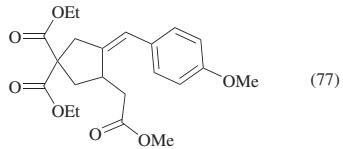
	130%		
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 24 h	 (79)
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 24 h	 (72)
	250%	Pd(dba) (25%), MeCN, rt	 (56)
	250%	Pd(dba) (25%), MeCN, rt	 (45) Ar = 4-O ₂ NC ₆ H ₄
	250%	Pd(dba) (25%), MeCN, rt	 (66) Ar = 4-MeOC ₆ H ₄
			261
			261
			91
			91
			91

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

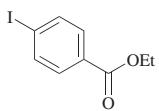
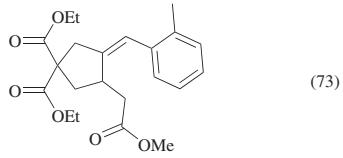
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
	 250%	Pd(dba) (25%), MeCN, rt	 (80)	91
	 250%	Pd(dba) (25%), MeCN, rt	 (65)	90, 91
	 250%	Pd(dba) (25%), MeCN, rt	 (83)	91
	 150%	1. TBAF (220%), THF, 0°, 10 min 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), 4 h	 (70)	43



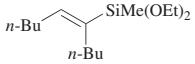
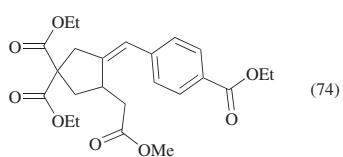
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt



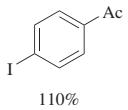
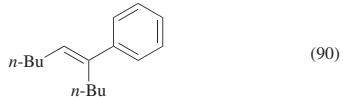
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt



Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, rt



TBAF (150%),
[allylPdCl]₂ (2.5%),
(EtO)₃P (5%),
THF, 50°, 5 h



TBAF (150%),
[allylPdCl]₂ (2.5%),
(EtO)₃P (5%),
THF, 50°, 5 h

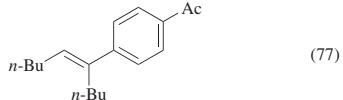
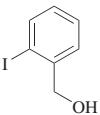
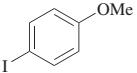
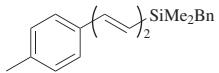
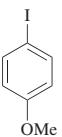
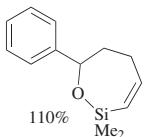
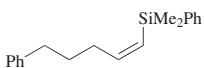


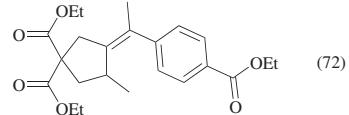
TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TBAF (150%), THF, 50°, 5 h		(96) 26
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TBAF (150%), THF, 50°		(67) 26
910				
		1. TBAF (220%), THF, 0°, 10 min 2. Pd₂(dba)₃•CHCl₃ (2.5%), 4 h		(76) 43
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, 35°		(74) 45
		Pd₂(dba)₃•CHCl₃ (2.5%), TBAF•3H₂O (200%), THF, 35°		(64) 45

19

C₁₁

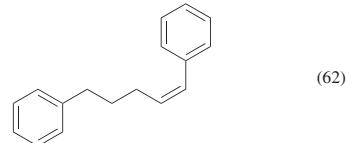
Pd₂(dba)₃•CHCl₃ (2.5%),
TBAF•3H₂O (200%),
THF, 35°



(72)

45

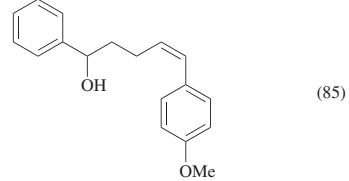
1. KOTMS (200%),
18-c-6 (200%),
THF, rt, 30 min
2. Electrophile,
Pd₂(dba)₃ (5%), 67°, 2 h



(62)

42

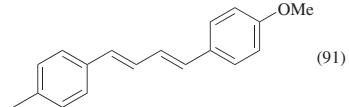
Pd(dba)₂ (3%),
TBAF (200%),
THF, rt, 30 min



(85)

225, 226

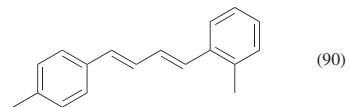
Pd(dba)₂ (2.5%),
TBAF (200%),
THF, rt, 1 h



(91)

44

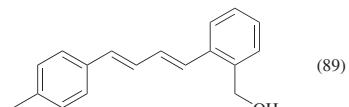
Pd(dba)₂ (2.5%),
TBAF (200%),
THF, rt, 1 h



(90)

44

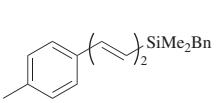
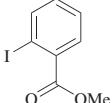
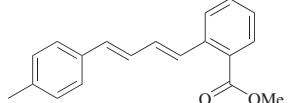
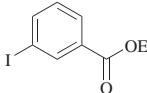
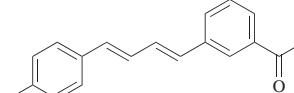
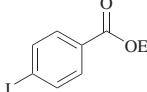
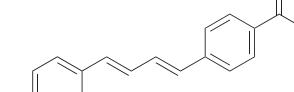
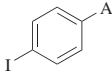
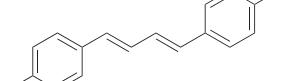
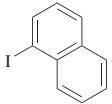
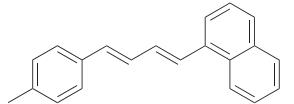
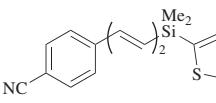
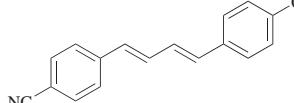
Pd(dba)₂ (2.5%),
TBAF (200%),
THF, rt, 12 h



(89)

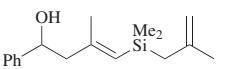
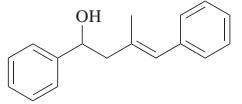
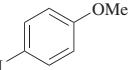
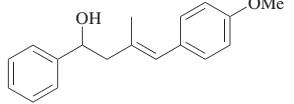
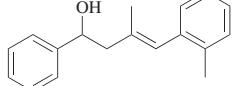
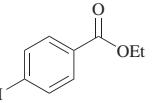
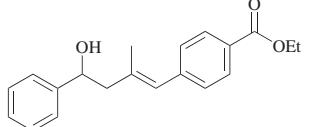
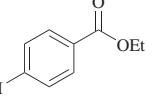
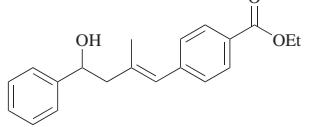
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TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁				
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 1 h	 (74)	44
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 1 h	 (90)	44
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 1 h	 (85)	44
612		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 1 h	 (90)	44
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 1 h	 (92)	44
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 2 h	 (81)	44

	Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 2 h		(89)	44
	Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 2 h		(90)	44
	1. TBAF (220%), 10 min, THF, 0° 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), rt, 4 h		(97)	43
	1. TBAF (220%), 10 min, THF, 0° 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), rt, 4 h		(89)	43
	1. KOTMS (200%), 18-c-6 (200%), THF, rt, 30 min 2. Electrophile, Pd ₂ (dba) ₃ (5%), 67°, 2 h		(86)	42
	Pd ₂ (dba) ₃ (cat.), TBAF, <i>t</i> -BuOK, 18-c-6, THF, rt, 45 min		(85) (<i>E</i>)/(<i>Z</i>) = 9:1	41
	Pd ₂ (dba) ₃ (cat.), TBAF, THF, rt, 30 min		(89) (<i>E</i>)/(<i>Z</i>) = 9:1	41

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁				
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(74) 157
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(70) 157
		1. TBAF (200%), [allylPdCl] ₂ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(11) 157
		1. TBAF (200%), Pd ₂ (dba) ₃ (cat.), EtOH (600%), THF, rt, 30 min 2. Electrophile		(82) 157
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(82) 157

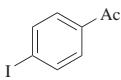
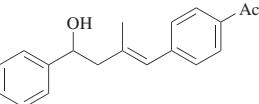
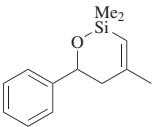
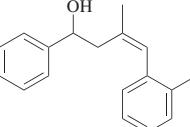
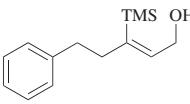
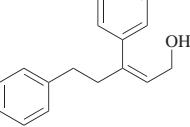
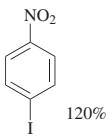
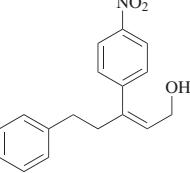
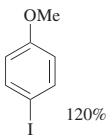
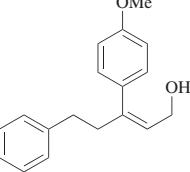
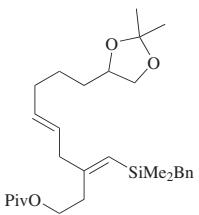
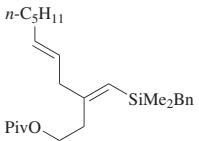
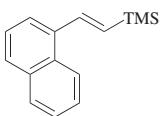
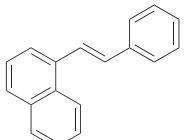
	1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile		(83)	157
	Pd(dba) ₂ (3%), TBAF (200%), THF, rt, 45 min		(83)	225, 226
	1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF		(77)	127
	1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF		(63)	127
	1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF		(66)	127

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂				
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (97)	157
		Pd ₂ (dba) ₃ (cat.), TBAF, THF, rt	 (87)	222
		1. TBAF (200%), [allylPdCl] ₂ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (63)	157
		[allylPdCl] ₂ (cat.), TBAF, THF, rt	 (71)	222
		1. TBAF (200%), Pd ₂ (dba) ₃ (5%), EtOH (600%), THF, rt, 30 min 2. Electrophile	 (85)	157



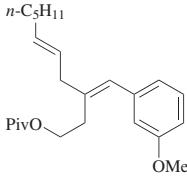
1. BCl_3 , CH_2Cl_2 , 0°
2. $\text{Pd}(\text{OAc})_2$ (6%),
dioxane, rt, 24 h



(50)

124

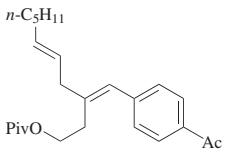
1. TBAF (220%),
 THF , 0° , 10 min
2. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2.5%),
4 h



(60)

43

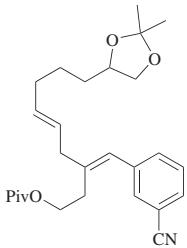
1. TBAF (220%),
 THF , 0° , 10 min
2. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2.5%),
4 h, 50°



(67)

43

1. TBAF (220%),
 THF , 0° , 10 min
2. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (2.5%),
4 h, 50°

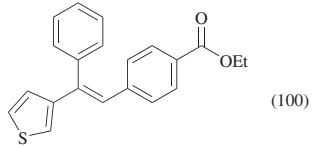
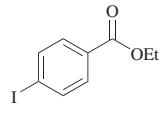
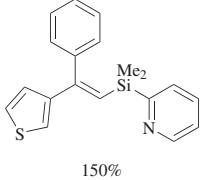


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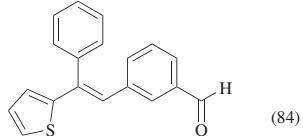
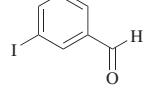
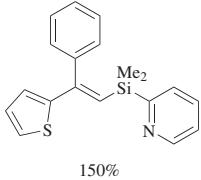
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TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

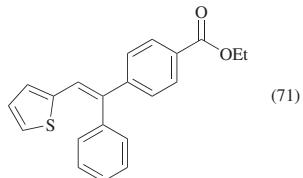
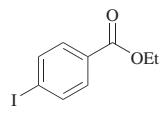
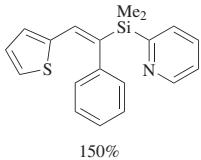
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂				
		1. KOTMS (200%), 18-c-6 (200%), THF, 67°, 30 min 2. Electrophile, $Pd_2(dba)_3$ (5%), 67°, 2 h		(76) 42
		1. KOTMS (200%), 18-c-6 (200%), THF, rt, 30 min 2. Electrophile, $Pd_2(dba)_3$ (5%), 67°, 2 h		(67) 42
		$PdCl_2(PhCN)_2$ (5%), TBAF (150%), THF, 60°		(80) 170
		$PdCl_2(PhCN)_2$ (5%), TBAF (150%), THF, 60°		(100) 170



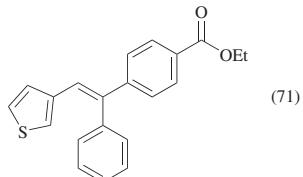
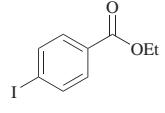
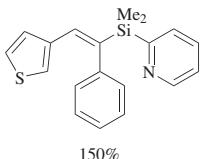
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170

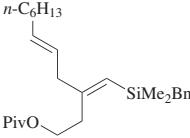
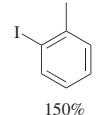
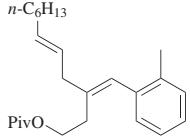
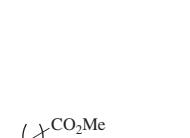
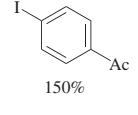
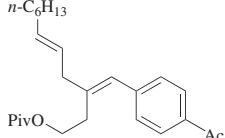
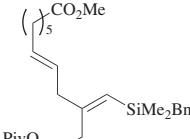
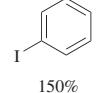
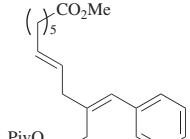
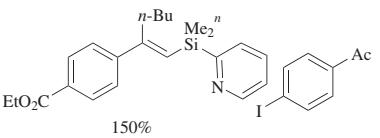
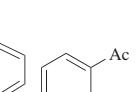
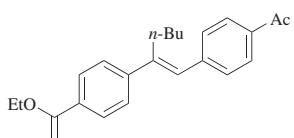


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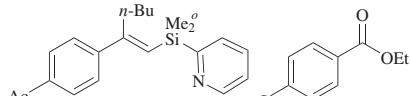


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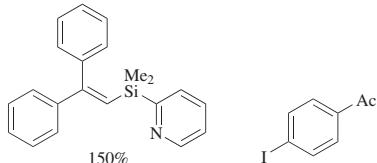
TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃				
		1. TBAF (220%), THF, 0°, 10 min 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), 4 h		(91) 43
		1. TBAF (220%), THF, 0°, 10 min 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), 4 h		(91) 43
620				
		1. TBAF (220%), THF, 0°, 10 min 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), 4 h		(88) 43
		1. Pd(OAc) ₂ (10%), (2-furyl) ₃ P (10%), Et ₃ N (160%), THF, 60° 2. Electrophile, TBAF (230%)		(71) 169, 170

C14

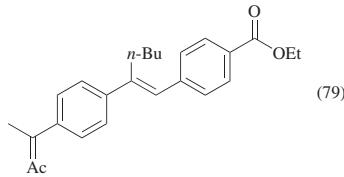


150%



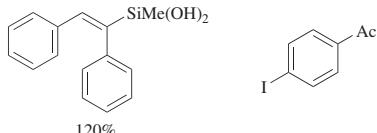
150%

1. $\text{Pd}(\text{OAc})_2$ (10%),
 $(2\text{-furyl})_3\text{P}$ (10%),
 Et_3N (160%), THF, 60°
2. Electrophile,
TBAF (230%)



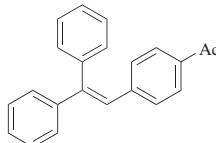
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169, 170



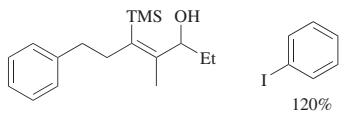
120%

$\text{PdCl}_2(\text{PhCN})_2$ (5%),
TBAF (150%),
THF, 60°



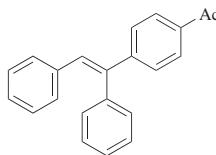
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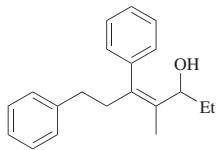
120%

1. $t\text{-BuOCu}$ (120%),
DMF, rt
2. Electrophile,
 $(\text{Ph}_3\text{P})_4\text{Pd}$ (3%), 4 h
3. TBAF



(71)

37

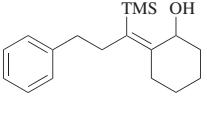
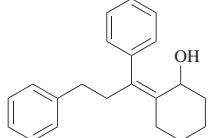
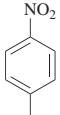
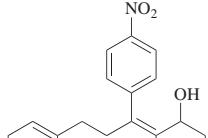
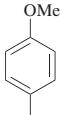
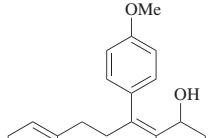
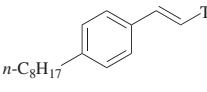
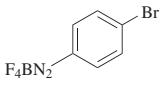
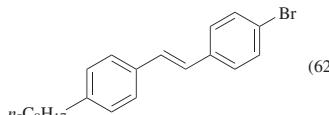


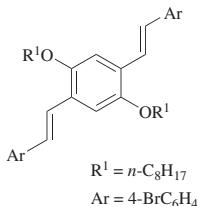
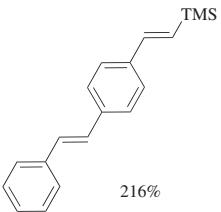
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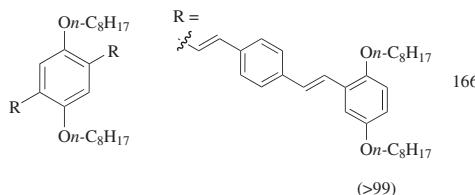
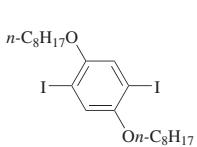
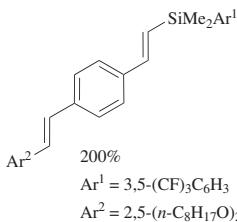
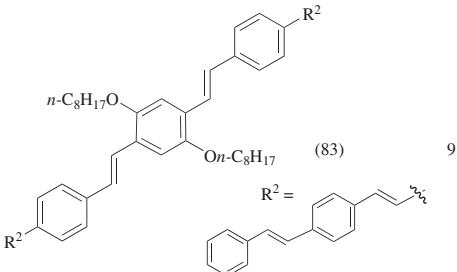
621

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

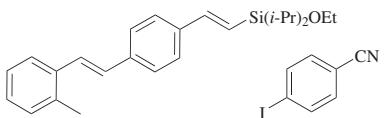
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C15				
		1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF	 (78)	127
		1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF	 (67)	127
		1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF	 (60)	127
622				
C16				
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, Pd(OAc) ₂ (7%), dioxane, 24 h	 (62)	91



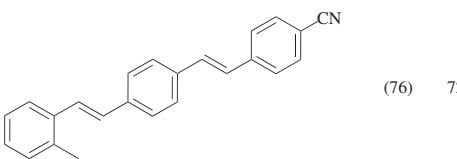
1. BCl_3 , CH_2Cl_2 , 0°
 2. H_2O , Na_2CO_3
 3. Electrophile,
 $(\text{Ph}_3\text{P})_4\text{Pd}$ (20%), Na_2CO_3 ,
 toluene, MeOH , reflux



C₁₇

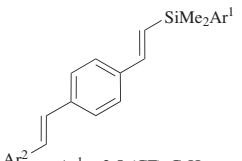
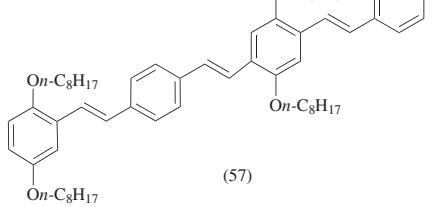
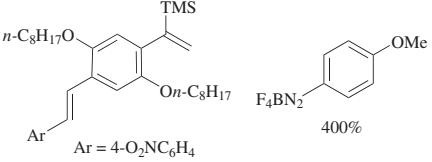
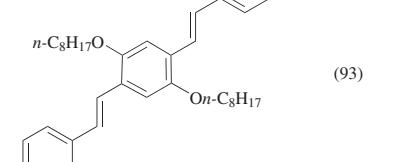
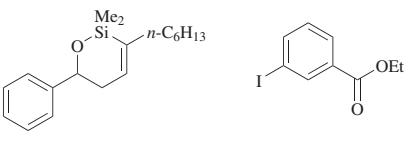
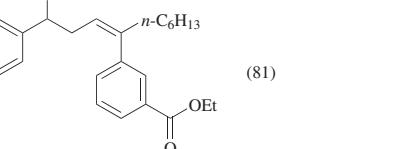


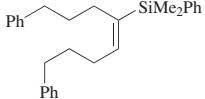
[allylPdCl]₂ (2.5%),
 TBAF (300%), rt



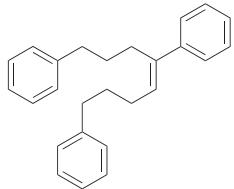
623

TABLE 3A. CROSS-COUPLING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C16				
 <p>Ar¹ = 3,5-(CF₃)₂C₆H₃ Ar² = 2,5-(<i>n</i>-C₈H₁₇O)₂C₆H₃</p>		[allylPdCl] ₂ (5%), TBAF•3H ₂ O (100%), THF, rt	 <p>(57)</p>	166
624	 <p>Ar = 4-O₂NC₆H₄ 400%</p>	Pd(dba) (6%), MeCN, rt	 <p>(93)</p>	91
		Pd(dba) ₂ (10%), TBAF (200%), THF, rt, 24 h	 <p>(81)</p>	225, 226

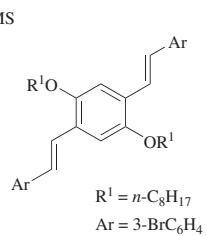
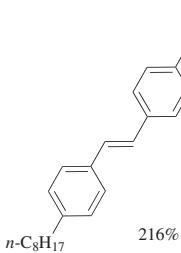
C₂₀

1. KOTMS (200%),
18-C-6 (200%),
THF, rt, 30 min
2. Electrophile,
 $Pd_2(dba)_3$ (5%), 67°, 2 h

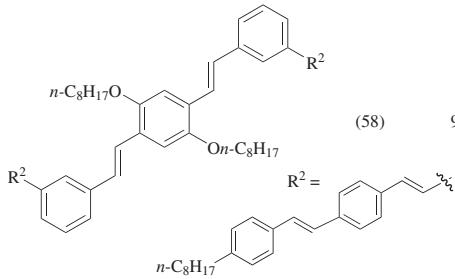


(82)

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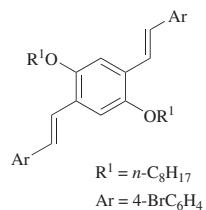
C₂₄

1. BCl_3 , CH_2Cl_2 , 0°
2. H_2O , Na_2CO_3
3. Electrophile,
 $(Ph_3P)_4Pd$ (20%), Na_2CO_3 ,
toluene, MeOH, reflux



625

216%



1. BCl_3 , CH_2Cl_2 , 0°
2. H_2O , Na_2CO_3
3. Electrophile,
 $(Ph_3P)_4Pd$ (20%), Na_2CO_3 ,
toluene, MeOH, reflux

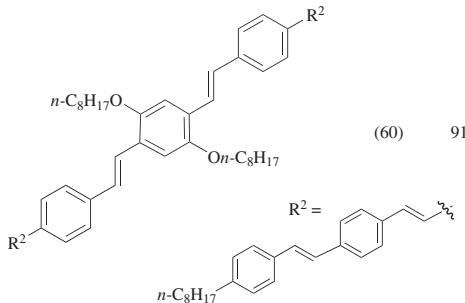


TABLE 3A. CROSS-COUPING OF ALKENYLSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
^a The starting silane was generated in situ by reaction of pent-4-yn-1-ol with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^b The starting silane was generated in situ by reaction of 5-(allyloxy)pent-1-yne with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^c The starting silane was generated in situ by treating pent-3-yn-1-ol with tetramethyldisilazane followed by catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^d The starting silane was generated in situ by the reaction of allyl(isopropoxy)dimethylsilane with <i>s</i> -BuLi (110%) and acetone (110%) at -78°.				
^e The starting silane was generated in situ by treating 1-heptyne with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^f The starting silane was generated in situ by treating <i>tert</i> -butyl 2-((4 <i>R</i> ,6 <i>S</i>)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)acetate with dimethylchlorosilane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^g The starting silane was generated in situ by treating phenylacetylene with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^h The starting silane was generated in situ by treating oct-3-yn-1-ol with tetramethyldisilazane followed by catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
ⁱ The starting silane was generated in situ by the reaction of allyl(isopropoxy)dimethylsilane with cyclohexanone at -78° in the presence of <i>s</i> -BuLi followed by quenching with acetic acid.				
^j The starting silane was generated in situ by the reaction of isopropoxy(dimethyl)[(Z)-2-(tributylstannyl)vinyllsilane with ethyl 4-iodobenzoate under palladium catalysis.				
^k The starting silane was generated in situ by the reaction of allyl(isopropoxy)dimethylsilane with benzaldehyde at -78° in the presence of <i>s</i> -BuLi followed by quenching with acetic acid.				
^l The starting silane was generated in situ by treating 2-phenylbut-3-yn-2-ol with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of <i>t</i> -Bu ₃ P-Pt(DVDS).				
^m The starting silane was generated in situ by the reaction of allyl(isopropoxy)dimethylsilane with 3-phenylpropanal at -78° in the presence of <i>s</i> -BuLi followed by quenching with acetic acid.				
ⁿ The starting silane was generated in situ by the reaction of (<i>E</i>)-(1-hexenyl)dimethyl(2-pyridyl)silane with ethyl 4-iodobenzoate, Pd(OAc) ₂ , (2-furyl) ₃ P, and Et ₃ N.				
^o The starting silane was generated in situ by the reaction of (<i>E</i>)-(1-hexenyl)dimethyl(2-pyridyl)silane with 4-iodoacetophenone, Pd(OAc) ₂ , (2-furyl) ₃ P, and Et ₃ N.				

TABLE 3B. CROSS-CO尤LING OF ALKENYLSILANES WITH HETEROARYL ELECTROPHILES

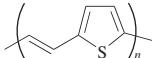
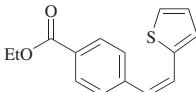
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
<chem>CC[Si]2(C)(C)OCC(O)C2</chem>	<chem>Ic1ccsc1I</chem>	1. Ru(HCl)(CO)(PPh ₃) ₃ (2%), CuCl (2%), dioxane, 110° 2. Electrophile, Pd ₂ dba ₃ (1%), TBAF (240%), dioxane, 80°, 24 h	 (90)	104
<chem>CC[Si](C)(C)OCC(C)=C</chem>	<chem>Brc1ccc2ccccc2n1</chem>	Pd(dba) ₂ (5%), Ph ₃ P(O) (5%), KOTMS (350%), THF, reflux, 3 h	<chem>CC=CC1=CC=CC2=CC=CC=CC2N=C1</chem> (91)	262
	<chem>Brc1ccc2ccccc2n1</chem>	JohnPhos (5%), [allylPdCl] ₂ (2.5%), KOSiEt ₃ (300%), DMF, rt, 2 h	<chem>CC=CC1=CC=CC2=CC=CC=CC2N=C1</chem> (79)	262
<chem>CC[Si]2(C)(C)OCC(C)=C[Si]2(C)(C)OCC(C)=C</chem>	<chem>Brc1ccc2ccccc2n1</chem>	JohnPhos (10%), PdBr ₂ (5%), TBAF (200%), THF, 50°, 3 h	<chem>CC=CC1=CC=CC2=CC=CC=CC2N=C1</chem> (89)	318
<chem>CC[SnBu3]2CC[Si]2(C)(C)OCC(O)C2</chem>	<chem>Ic1ccsc1I</chem>	1. Ethyl 4-iodobenzoate, PhCH ₂ PdCl(PPh ₃) ₂ , CuI, DMF, 50° 2. 2-Iodothiophene, TBAF, 50°	 (61)	128

TABLE 3B. CROSS-COUPLING OF ALKENYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₂			Pd ₂ (dba) ₃ (1%), TBAF (240%), dioxane, 80°, 24 h		(97)	104
C ₄			Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 300 min		(80) + (20)	79
628			Pd(dba) ₂ (6%), TBAF (200%), THF, 35°, 41 h		(66)	79
C ₅			1. TBAF (200%) 2. Pd(dba) ₂ (5%), THF, 45°, 45 h		(73)	79
			[allylPdCl] ₂ (5%), CuI (10%), KF 2H ₂ O (200%), [-MeSi(H)O-] ₃₋₅ (2.5%), DMF, rt, 3 h		(78)	81

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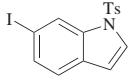
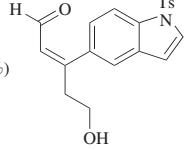
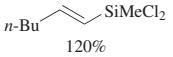
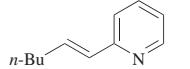
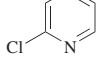
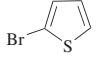
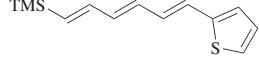
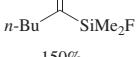
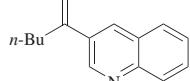
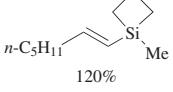
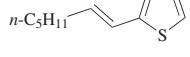
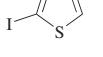
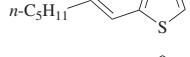
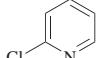
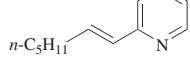
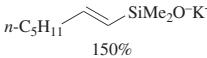
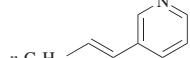
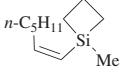
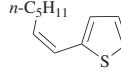
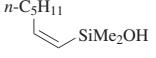
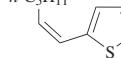
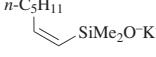
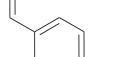
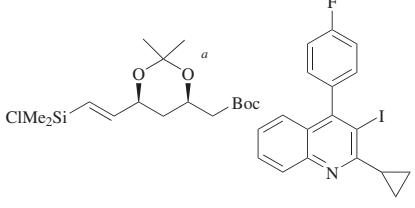
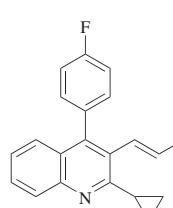
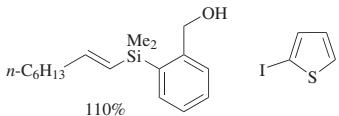
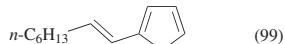
		[allylPdCl]₂ (5%), CuI (10%), KF 2H₂O (200%) [-MeSi(H)O]₃-₅ (2.5%), DMF, rt, 2 h		(88)	81
C ₆				(79)	185
		(i-Pr ₃ P) ₂ PdCl ₂ (2.5%), NaOH (600%), C ₆ H ₆ , 80°, 12 h			
		1. BCl ₃ , CH ₂ Cl ₂ , 0° 2. Electrophile, (Ph ₃ P) ₄ Pd (cat.), NaOH (2 M), benzene, reflux		(38)	125
629		[allylPdCl]₂ (2.5%), TBAF (150%), THF, 60°, 44 h		(64)	172
C ₇		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 180 min		(89) (E)/(Z) = 99.0:1.0	38
		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 180 min		(83) (E)/(Z) = 95.7:4.3	31
		SPhos (5%), [allylPdCl]₂ (2.5%), THF, 60°, 3 h		(87) (E)/(Z) = 99.6:0.4	80

TABLE 3B. CROSS-CO尤LING OF ALKENYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

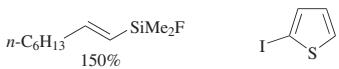
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 1.5 h	 (85) (E)/(Z) = 99.8:0.2	80
 120%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 180 min	 (85) (Z)/(E) = 97.8:2.2	38
 120%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 180 min	 (81) (Z)/(E) = 97.5:2.5	31
 150%		SPhos (5%), [allylPdCl] ₂ (2.5%), THF, 60°, 1.5 h	 (91) (Z)/(E) = 99.3:0.7	80
		1. <i>t</i> -Bu ₃ Pt(DVDS) (0.5%), Me ₂ SiCl(H) (120%), rt, 1 h 2. Electrophile, [allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 0.5 h	 (83) (E)/(Z) = 96:4	177

C₈

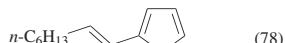
PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 23 h



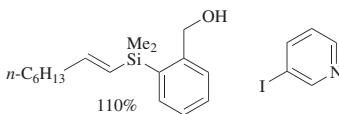
150, 151



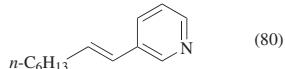
[allylPdCl]₂ (2.5%),
TBAF (150%),
THF, 60°, 12 h



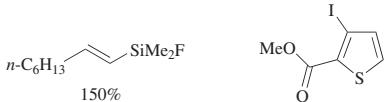
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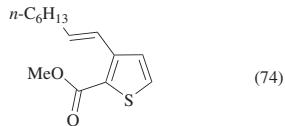
PdCl₂ (1%),
(2-furyl)₃P (2%),
K₂CO₃ (220%),
DMSO, 35°, 23 h



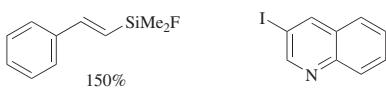
150, 151



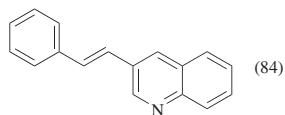
[allylPdCl]₂ (2.5%),
TBAF (150%),
THF, 60°, 36 h



172



[allylPdCl]₂ (2.5%),
TBAF (150%),
THF, 60°, 18 h

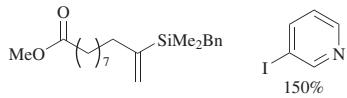


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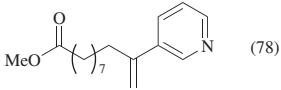
631

TABLE 3B. CROSS-COUPLED OF ALKENYLSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈			(Ph ₃ P) ₄ Pd (2.5%), TBAF (150%), Et ₃ N (100%), THF, 65°, 112 h	 (31)	162
			[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 7 h	 (77) (Z)/(E) = 91:9	26
632			Pd(dba) ₂ (5%), TBAF (1000%), 45°, 7 d	 (59)	188
C ₉			PdCl(PPh ₃)(Bn) (5%), CuI (10%), TBAF (278%), DMF, 50°, 8 h	 (61)	128
C ₁₀			[allylPdCl] ₂ (2.5%), TASF (50%), DMF, 60°, 5 h	 (62)	172



1. TBAF (220%),
THF, 0°, 10 min
2. Pd₂(dba)₃•CHCl₃ (2.5%),
50°, 4 h



^a The starting silane was generated in situ by treating *tert*-butyl 2-((4*R*,6*S*)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)acetate with dimethylchlorosilane in the presence of catalytic amounts of *t*-Bu₃P-Pt(DVDS).

^b The starting silane was generated in situ by reaction of isopropoxy(dimethyl)[(Z)-2-(tributylstannyl)vinyl]silane with ethyl 4-iodobenzoate under palladium catalysis.

TABLE 3C. CROSS-COUPLING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
		[allylPdCl] ₂ (2.5%), TBAF (400%), THF, 60°, 14 h		(82) 88
 120%		[allylPdCl] ₂ (2.5%), TBAF (300%), THF, rt, 1 h		(46) (E)/(Z) = 100:0 40
120%		[allylPdCl] ₂ (2.5%), TBAF (300%), THF, rt, 1 h		(48) (Z)/(E) = 98:2 40
 120%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 180 min		(52) (Z)/(E) = 94:6 267
		PdCl ₂ PhCN ₂ (5%), (EtO) ₃ P (10%), dioxane, reflux, 60 h		(29) 22

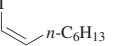
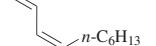
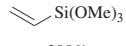
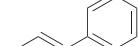
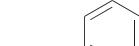
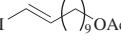
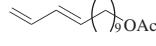
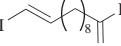
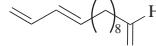
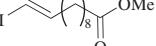
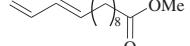
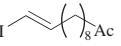
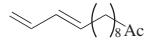
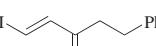
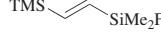
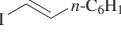
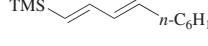
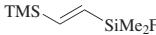
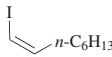
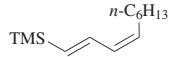
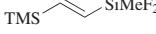
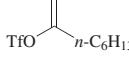
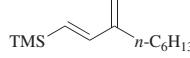
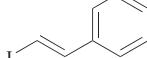
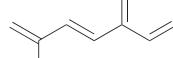
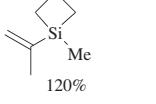
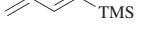
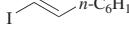
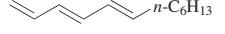
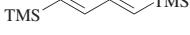
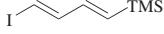
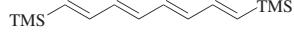
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(76)	23
		Pd cat. 5 (0.5%), NaOH (250%), TBAB (100%), H₂O, MW, 15 min		(81)	257
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(93)	23
130%		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(70)	23
130%		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(52)	23
130%		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(88)	23
130%		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(67)	23
130%		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TASF (130%), THF, 50°		(85)	23
TMS 		[allylPdCl]₂ (2.5%), TASF (150%), THF, 15 h		(70)	25

TABLE 3C. CROSS-CO尤LING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			[allylPdCl]2 (2.5%), TASF (150%), THF, 12 h 	(55) 25
			(Ph3P)4Pd (cat.), TBAF (120%), THF, 50°, 5 h 	(90) 181
			[allylPdCl]2 (2.5%), (EtO)3P (5%), TASF (130%), THF, 50° 	(181) 23
C_3			[allylPdCl]2 (2.5%), TBAF (300%), THF, rt, 12 h 	(71) (<i>E</i>)/(<i>Z</i>) = 100:0 40
C_4			[allylPdCl]2 (2.5%), (EtO)3P (5%), TASF (130%), THF, 50° 	(78) 23
			1. BCl_3 , CH_2Cl_2 , 0° 2. Na_2CO_3 (2 M) 3. Electrophile, (Ph_3P) ₄ Pd (cat.), Na_2CO_3 (2 M), MeOH, toluene, reflux 	(70) 90, 125

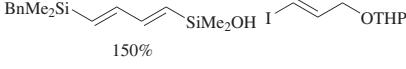
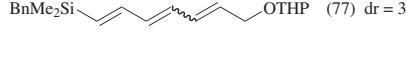
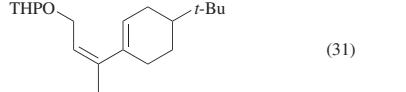
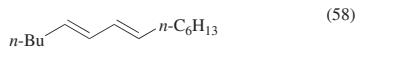
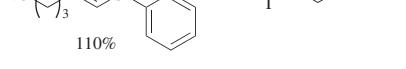
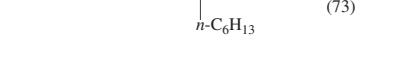
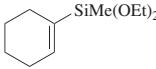
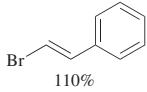
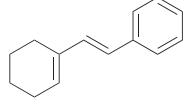
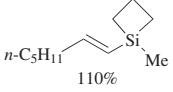
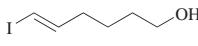
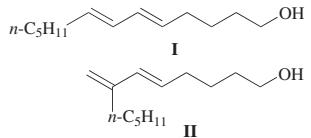
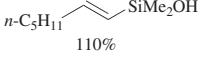
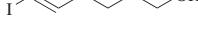
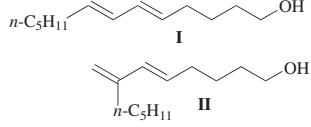
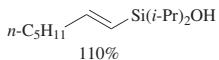
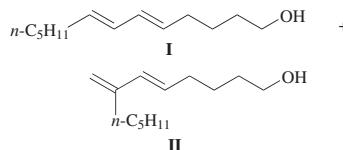
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), NaH (140%), THF, rt, 6 h		(77) dr = 3:1	216
C ₅		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 45°, 48 h		(31)	79
		1. TBAF (200%) 2. [allylPdCl] ₂ (2.5%), THF, 45°, 47 h		(45)	224
		1. TBAF (200%) 2. [allylPdCl] ₂ (2.5%), rt, THF, 2 h		(81)	171
C ₆		Pd(OAc) ₂ (2.5%), NaOH (600%), THF, 60°, 12 h		(58)	185
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (210%), L4 (5%), DMSO, 35°, 3 h		(73)	151
		PdCl ₂ (1%), (2-furyl) ₃ P (2%), K ₂ CO ₃ (210%), L4 (5%), DMSO, 35°, 3 h		(73)	151

TABLE 3C. CROSS-CO尤LING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆  110%	 110%	[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 16 h	 (63)	26
C ₇  110%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 90 min	 I + II I + II (95), I:II = 90:10 I (E,E)/(E,Z) = 98.4:1.6	38
638  110%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 90 min	 I + II I + II (95), I:II = 86:14 I (E,E)/(E,Z) = 95.8:4.2	31

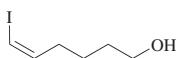
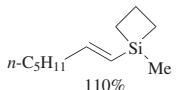
C₇

Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 90 min

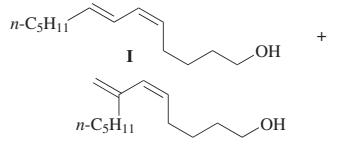


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I + II (87), I:II = 96:4
I (E,E)/(E,Z) = 97.8:2.2

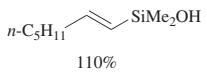


Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 90 min

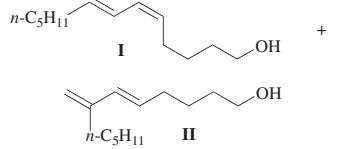


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I + II (70), I:II = 99:1
I (E,Z)/((Z,Z) + (E,E)) = 97.0:3.0

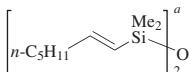


Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 90 min

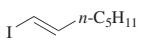


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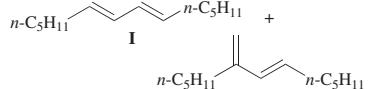
I + II (73), I:II = 99:1
I (Z,E)/(Z,Z) = 94.1:5.9



130%



Pd(dba)₂ (5%),
TBAF (200%),
THF, rt, 16 h

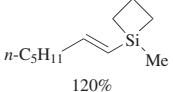
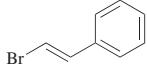
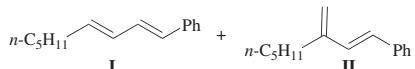
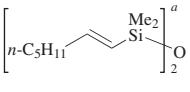
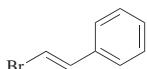
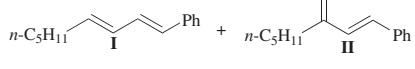
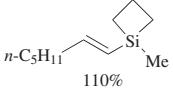
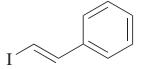
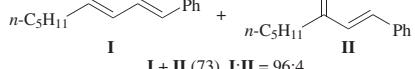
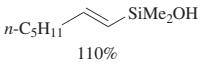
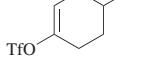
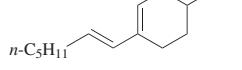
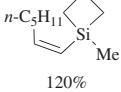
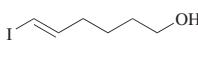
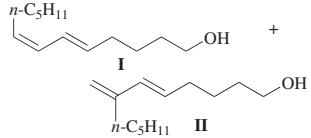


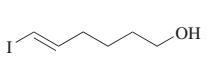
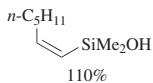
261

I + II (67) (E,E)/((E,Z) + II) = 91.4:8.6

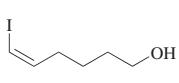
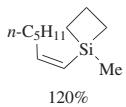
639

TABLE 3C. CROSS-CO尤LING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

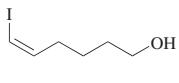
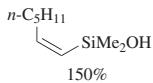
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇  120%		[allylPdCl] ₂ (2.5%), TBAF (300%), THF, rt, 60 min	 I + II (80), I : II = 98:2 I (<i>E,E</i>)/(<i>E,Z</i>) = 98.4:1.6	38
46  130%		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, rt, 14 h	 I + II (70) (<i>E,E</i>)/(<i>E,Z</i>)/ II = 92.0:3.2:4.8	261
60  110%		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min	 I + II (73), I : II = 96:4 I (<i>E,E</i>)/(<i>E,Z</i>) = 98.0:2.0	38
66  110%		JohnPhos (10%), PdBr ₂ (5%), TBAF•3H ₂ O (200%), dioxane, 50°	 (62) (<i>E</i>)/(<i>Z</i>) = 98.7:1.3	202
70  120%		Pd(dba) ₂ (5%), TBAF (200%), THF, rt, 90 min	 I + II (74), I : II = 85:15 I (<i>E,Z</i>)/(<i>(Z,Z)</i> + (<i>E,E</i>)) = 97.0:3.0	38



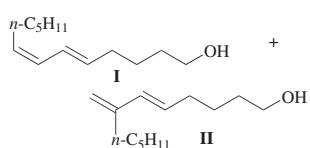
Pd(dba)₂ (5%),
 TBAF (200%),
 THF, rt, 90 min



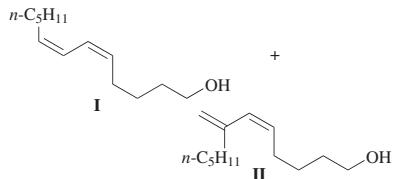
[allylPdCl]₂ (2.5%),
 TBAF (300%),
 THF, rt, 300 min



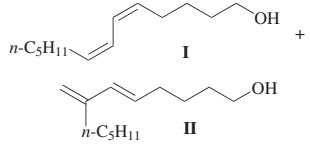
[allylPdCl]₂ (2.5%),
 TBAF (200%),
 THF, rt, 300 min



31
I + II (72), **I:II** = 91:9
 (*E,Z*)/(*(Z,Z)* + (*E,E*)) = 95.4:4.6



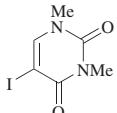
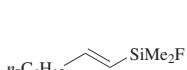
38
I + II (65), **I:II** = 99:1
I (*Z,Z*)/other isomers = 94.8:5.2



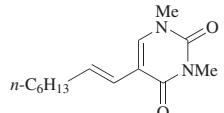
31
I + II (64), **I:II** = 99:1
I (*Z,Z*)/other isomers = 87.8:12.2

TABLE 3C. CROSS-CO尤LING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
		[allylPdCl] ₂ (2.5%), TBAF (300%), THF, rt, 300 min	 I + II (68), I:II = 93.2:6.8 I (Z,Z)/other isomers = 92.4:7.6	31
		Pd(dba) ₂ (5%), TBAF (300%), THF, rt, 10 min	 I + II (75), I:II = 98:2 I (E,Z)/(Z,Z) + (E,E) = 97.2:2.8	38
		JohnPhos (10%), PdBr ₂ (5%), TBAF•6H ₂ O (200%), dioxane, 50°, 25 h	 I	202
		Pd(dba) ₂ (cat.), TBAF	 (79) dr = 5:1	216

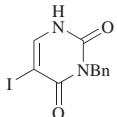
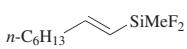


[allylPdCl]₂ (2.5%),
TBAF (200%),
THF, 60°, 14 h

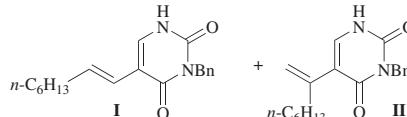


(70)

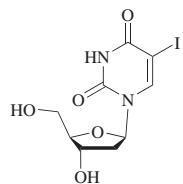
88



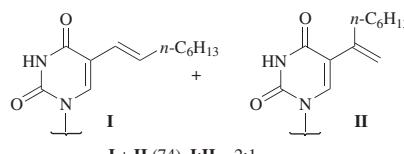
[allylPdCl]₂ (2.5%),
TBAF (200%),
THF, 60°, 44 h

**I + II (53), I:II = 2:1**

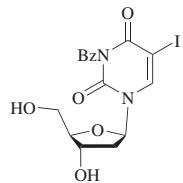
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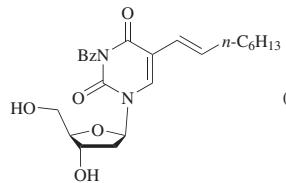
[allylPdCl]₂ (2.5%),
TBAF (200%),
DMF, 60°

**I + II (74), I:II = 2:1**

88



[allylPdCl]₂ (2.5%),
TBAF (200%),
THF, 60°

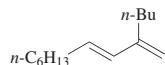


(60)

88



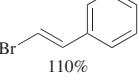
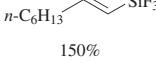
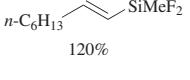
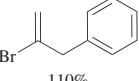
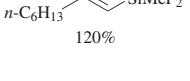
[allylPdCl]₂ (2.5%),
TASF (150%),
THF, 22 h



(69)

25

TABLE 3C. CROSS-CO尤LING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		[allylPdCl] ₂ (2.5%), TASF (150%), THF, 16 h	(83)	25
		[allylPdCl] ₂ (2.5%), TASF (150%), THF, 21 h	(89)	25
		[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 16 h	(71)	26
		[allylPdCl] ₂ (2.5%), TBAF (200%), CO (1 atm), THF, 50°, 20 h	(45)	179
		(Ph ₃ P) ₄ Pd (cat.), TBAF (120%), THF, 50°, 4 h	(82)	181
		[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TBAF (150%), THF, 50°, 12 h	(31)	26
		(Ph ₃ P) ₄ Pd (cat.), TBAF (120%), THF, 50°, 0.5 h	(99)	181

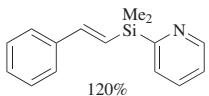
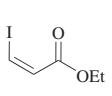
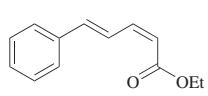
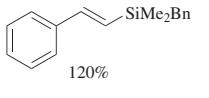
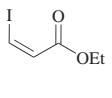
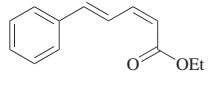
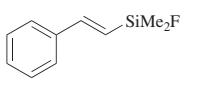
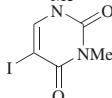
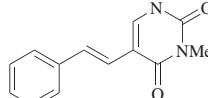
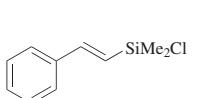
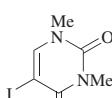
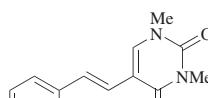
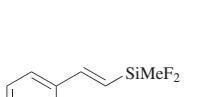
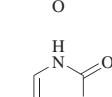
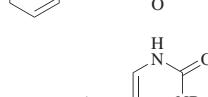
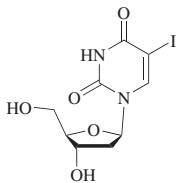
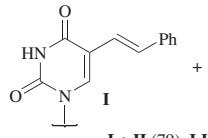
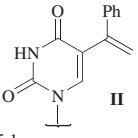
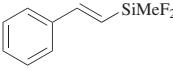
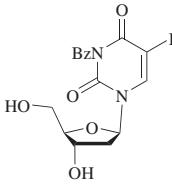
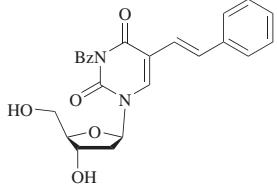
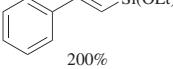
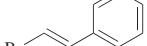
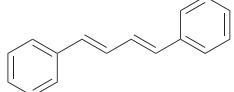
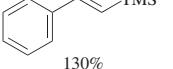
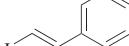
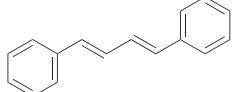
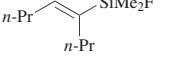
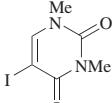
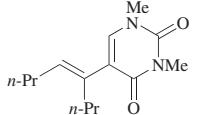
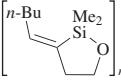
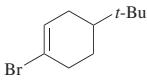
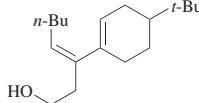
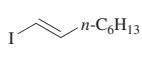
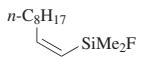
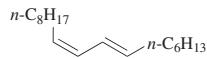
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(91)	169
	120%		PdCl ₂ (PhCN) ₂ (5%), TBAF (100%), THF, 60°		(91)	169
			[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 16 h		(69)	88
			[allylPdCl] ₂ (2.5%), TBAF (400%), THF, 60°, 14 h		(70)	88
			[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 48 h		(58)	88
		[allylPdCl] ₂ (2.5%), TBAF (200%), DMF, 60°		+ 	I + II (79), I:II = 5:1	88

TABLE 3C. CROSS-COUPLING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°	 (64)	88
 200%		Pd cat. 5 (0.5%), NaOH (250%), TBAB (100%), H ₂ O, 120° (MW), 20 min	 (81) (E)/(Z) = 2:1	257
 130%		[allylPdCl] ₂ (2.5%), (EtO) ₃ P (5%), TAASF (130%), THF, 50°	 (32)	23
		[allylPdCl] ₂ (2.5%), TBAF (200%), THF, 60°, 11 h	 (63)	88
		[allylPdCl] ₂ (3.7%), TBAF (100%), 45°, 3 d	 (32)	198

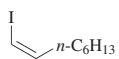
C₁₀

(Ph₃P)₄Pd (5%),
TASF (150%),
DMF, 14 h

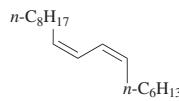


(84)

25

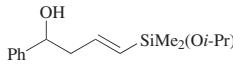


(Ph₃P)₄Pd (5%),
TASF (150%),
DMF, 19 h

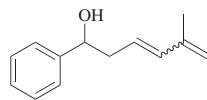


(74)

25

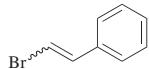


[allylPdCl]₂ (cat.),
TBAF (200%),
THF, 50°, 24 h

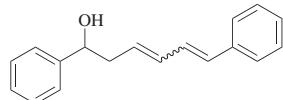


(38)

222

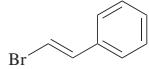
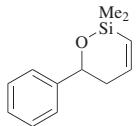


[allylPdCl]₂ (cat.),
TBAF (200%),
THF, 50°, 2 h

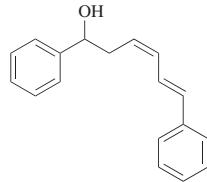


(66)

222

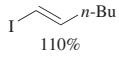
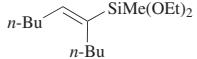


1. TBAF (200%)
2. [allylPdCl]₂ (2.5%)

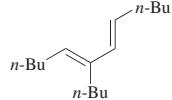


(78)

226



[allylPdCl]₂ (2.5%),
(EtO)₃P (5%),
TBAF (150%),
THF, 50°, 6 h

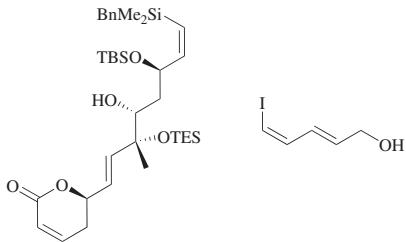


(45)

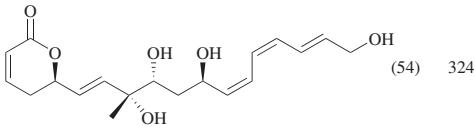
26

TABLE 3C. CROSS-COUPLING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

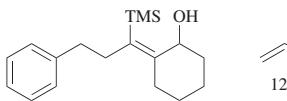
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TBAF (150%), THF, 50°, 16 h		(73) 26
		[allylPdCl]₂ (2.5%), (EtO)₃P (5%), TBAF (150%), THF, 50°		(43) 26
648	C ₁₁			
		Pd(dba) ₂ (2.5%), TBAF (200%), THF, rt, 4 h		(72) 44
		1. TBAF (220%), THF, 0°, 10 min 2. Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), rt, 4 h		(65) 43
		1. <i>t</i> -BuOCu (120%), DMF, rt 2. Electrophile, (Ph ₃ P) ₄ Pd (3%), 4 h 3. TBAF		(63) 127

C₁₄

Pd₂(dba)₃•CHCl₃ (5%),
TBAF (400%),
THF, 0° to rt

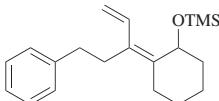


(54) 324

C₁₅

$\text{CH}_2=\text{CHBr}$
120%

1. *t*-BuOCu (120%),
DMF, rt
2. Electrophile,
(Ph₃P)₄Pd (3%)

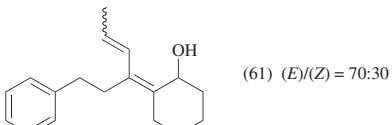


(71)

127

$\text{Br}-\text{CH}=\text{CH}_2$
120% *E/Z* = 75:25

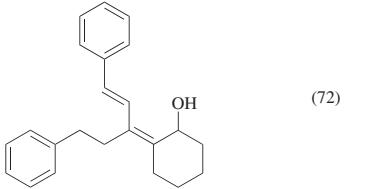
1. *t*-BuOCu (120%),
DMF, rt
2. Electrophile,
(Ph₃P)₄Pd (3%)

(61) (*E*)/(*Z*) = 70:30

127

$\text{Br}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{Ph}$
120%

1. *t*-BuOCu (120%), DMF, rt
2. Electrophile,
(Ph₃P)₄Pd (3%)
3. TBAF



(72)

127

TABLE 3C. CROSS-COUPING OF ALKENYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

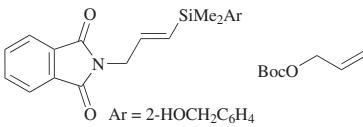
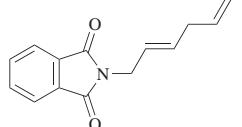
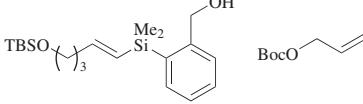
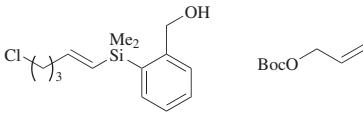
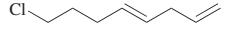
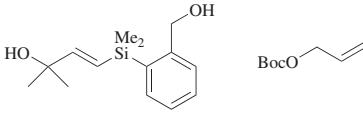
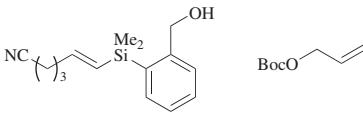
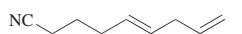
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
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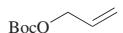
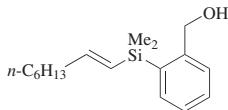
^a The starting silane was generated *in situ* by treating 1-heptyne with 1,1,3,3-tetramethyldisiloxane in the presence of catalytic amounts of *t*-Bu₃P-Pt(DVDS).

TABLE 3D. CROSS-CO尤LING OF ALKENYLSILANES WITH ALLYL ELECTROPHILES

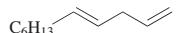
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₂					
<chem>=C[Si](OEt)3</chem>		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 7 h		(85)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 8 h		(75)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 7 h		(80)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 7 h		(80)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 8 h		(78)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 8 h		(78)	254
		PdCl ₂ (2%), TBAB (25%), TBAF (120%), THF, reflux, 8 h		(78)	254

TABLE 3D. CROSS-COUPLED OF ALKENYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₃		BocOCH=CH ₂	Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 3 h		(85)	152
C ₅		BocOCH=CH ₂	Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 2 h		(72)	152
		BocOCH=CH ₂	Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 2 h		(74)	152
		BocOCH=CH ₂	Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 4 h		(53)	152
C ₆		BocOCH=CH ₂	Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 4 h		(85)	152

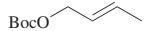
C₈

Pd₂(dba)₃ (0.5%),
(2-furyl)₃P (2%),
THF, 50°, 2 h

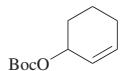
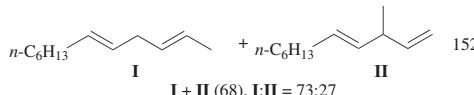


(85)

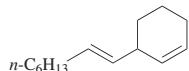
152



Pd₂(dba)₃ (0.5%),
(2-furyl)₃P (2%),
THF, 50°, 3 h

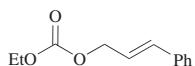


Pd₂(dba)₃ (0.5%),
(2-furyl)₃P (2%),
THF, 50°, 3 h

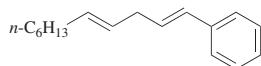


(93)

152

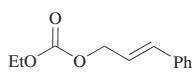


Pd(OAc)₂ (5%),
Ph₃P (5%),
DMF, 60°, 24 h

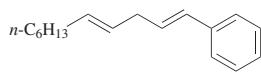


(72)

175, 176

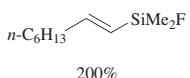


Pd(OAc)₂ (5%),
Ph₃P (5%),
DMF, 60°, 28 h



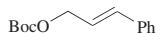
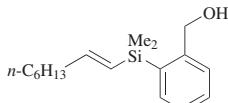
(73)

175, 176

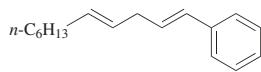


200%

200%

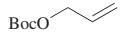
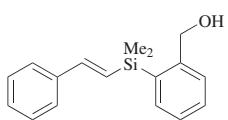


Pd₂(dba)₃ (0.5%),
(2-furyl)₃P (2%),
THF, 50°, 3 h

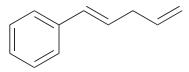


(93)

152



Pd₂(dba)₃ (0.5%),
(2-furyl)₃P (2%),
THF, 50°, 2 h

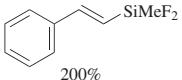
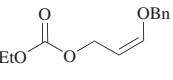
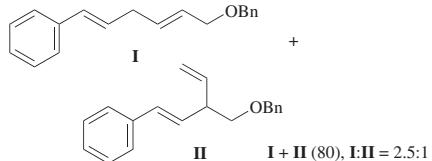
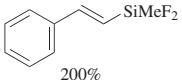
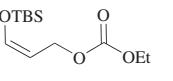
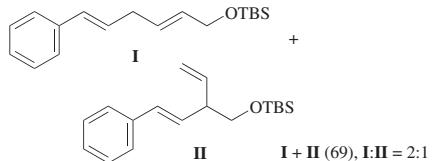
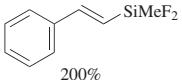
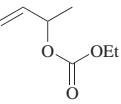
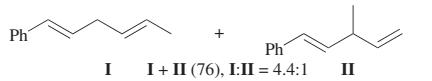
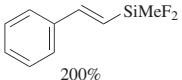
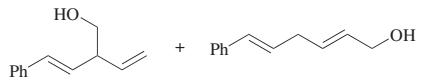
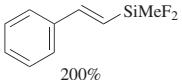
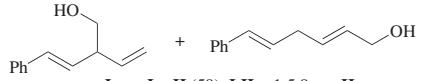


(91)

152

653

TABLE 3D. CROSS-COUPLED OF ALKENYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 		Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 90°, 1.5 h	 I + II (80), I:II = 2.5:1	175, 176
		Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 90°, 4 h	 I + II (69), I:II = 2:1	175, 176
200% 		Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 90°, 1.5 h	 I + II (76), I:II = 4.4:1	175, 176
200% 		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), (2-MePh) ₃ P (10%), benzene, 40°	 I + II (41), I:II = 1:4.8	175
200% 		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OCH ₃) ₃ CEt (10%), benzene, 40°	 I + II (59), I:II = 1:5.9	175

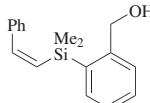
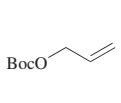
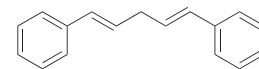
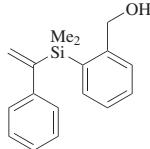
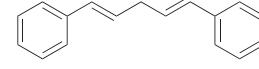
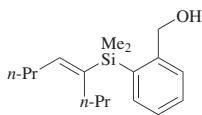
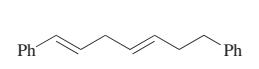
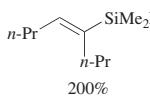
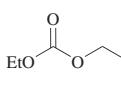
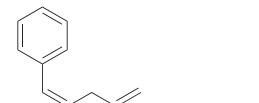
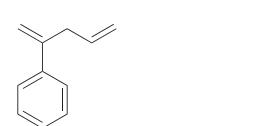
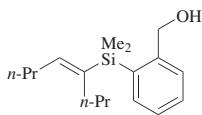
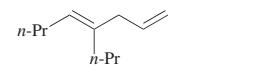
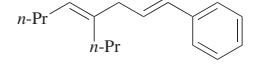
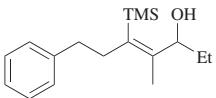
200%			Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 60°, 2 h	 (91)	175
200%			Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 60°, 1 h	 (94)	175
200%			Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 90°, 1 h	 I + II (90), I : II = 3.5:1 II	175, 176
			Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 2 h	 (92)	152
			Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 3 h	 (81)	152
			Pd ₂ (dba) ₃ (0.5%), (2-furyl) ₃ P (2%), THF, 50°, 24 h	 (78)	152
			Pd(OAc) ₂ (5%), Ph ₃ P (5%), DMF, 60°, 48 h	 (40) 31% rsm	175

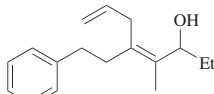
TABLE 3D. CROSS-CO尤LING OF ALKENYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
		1. CuOt-Bu (100%), DMF, rt 2. TBAF (100%)		(67)
C_{11}				
		1. t-BuOCu (120%), DMF, rt, 15 h 2. TBAF		(74)
C_{13}				
		1. t-BuOCu (120%), DMF, rt, 12 h 2. TBAF		(73)
96				
			Pd(OAc)2 (10%), THF, rt, 24 h	
$i\text{-}Bu$				
		1. t-BuOCu (120%), DMF, rt, 10 h 2. TBAF		(76)

C14



1. *t*-BuOCu (150%),
THF, rt, 14 h
2. TBAF

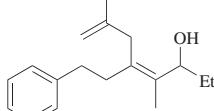


(80)

126, 127

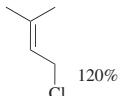


1. *t*-BuOCu (150%),
THF, rt, 21 h
2. TBAF

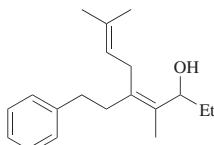


(85)

126, 127

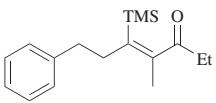


1. *t*-BuOCu (120%),
DMF, rt, 4 h
2. TBAF

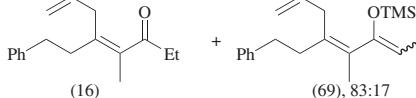


(75)

126, 127



CuCl (50%),
t-BuOLi (120%),
DMF/THF, 0° to rt, 2 h

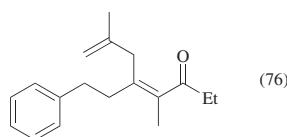


(69), 83:17

130

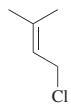


CuCl (50%),
t-BuOLi (120%),
DMF/THF, 0° to rt, 2 h

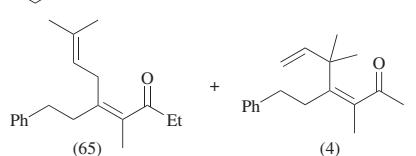


(76)

130



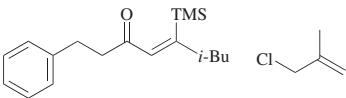
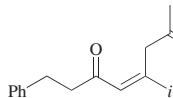
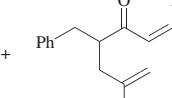
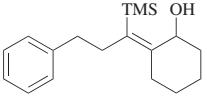
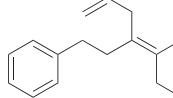
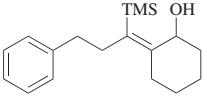
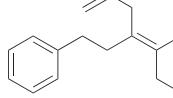
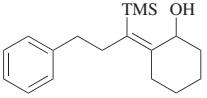
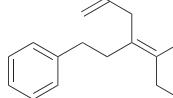
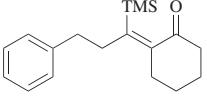
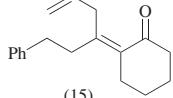
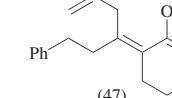
CuCl (50%),
t-heptOLi (120%),
DMF/THF, 0° to rt, 2 h



(4)

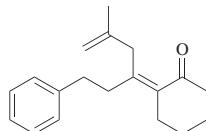
130

TABLE 3D. CROSS-CO尤LING OF ALKENYLSILANES WITH ALLYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅				
		CuCl (300%), <i>t</i> -heptOLi (300%), DMF/THF, 0° to rt, 2 h	 + 	130
	 120%	1. <i>t</i> -BuOCu (150%), THF, rt, 16 h 2. TBAF		126, 127
	 120%	1. <i>t</i> -BuOCu (150%), THF, rt, 16 h 2. TBAF		446
	 120%	1. <i>t</i> -BuOCu (150%), DMF, rt, 2 h, 2. TBAF		126, 127
		CuCl (50%), <i>t</i> -heptOLi (120%), DMF/THF, 0° to rt, 1 h	 + 	130

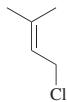


1. CuCl (50%),
t-BuOLi (120%),
DMF/THF, 0° to rt, 2 h
2. TBAF

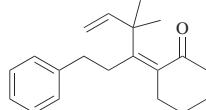


(80)

130



CuCl (50%),
t-heptOLi (120%),
DMF/THF, 0° to rt, 1 h



(63)

130

TABLE 3E. CROSS-COUPLING OF ALKENYLSILANES WITH ALKYL/BENZYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂			 (66) 93% ee	118
C ₆			 (70) 91% ee	118
C ₈			 (75)	152
			 (87)	152
			 (89)	152

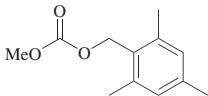
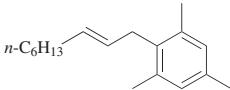
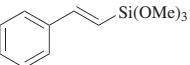
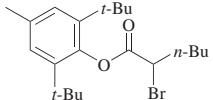
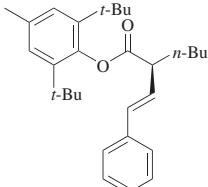
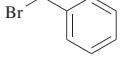
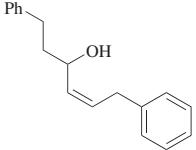
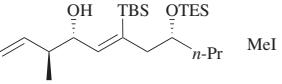
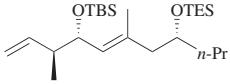
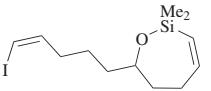
C ₈		Cp(allyl)Pd (5%), dppf (5%), THF, 80°, 10 h		(86)	152
C ₁₁				NiCl ₂ •glyme (10%), L3 (12%), TBAT (200%), dioxane, rt	(92) 72% ee 118
					
196		1. CuOr-Bu (100%), DMF, rt 2. TBAF (100%)		(60)	128
C ₁₂		1. n-BuLi, -78° 2. MeI, CuBr•Me ₂ S, DMPU, -78° to rt		(-)	129

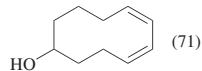
TABLE 3F. INTRAMOLECULAR CROSS-COUPLING OF ALKENYLSILANES

Silane	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈			
	[allylPdCl] ₂ (7.5%), TBAF (1000%), THF, rt, 60 h		226, 227
C ₉			
	[allylPdCl] ₂ (7.5%), TBAF (1000%), THF, rt, 45 h		226, 227
			662
	[allylPdCl] ₂ (7.5%), TBAF (1000%), THF, rt, 45 h		226, 227
	[allylPdCl] ₂ (7.5%), TBAF (1000%), THF, rt, 45 h		226, 227
C ₁₀			
	[allylPdCl] ₂ (7.5%), TBAF (1000%), THF, rt, 45 h		226, 227

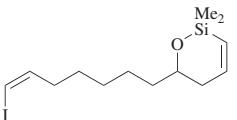


C₁₁

[allylPdCl]₂ (10%),
TBAF (1000%),
THF, rt, 60 h

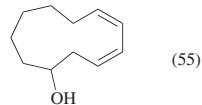


226, 227

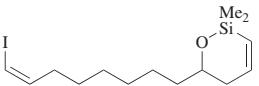


C₁₂

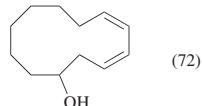
[allylPdCl]₂ (10%),
TBAF (1000%),
THF, rt, 75 h



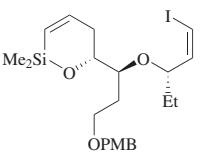
226, 227



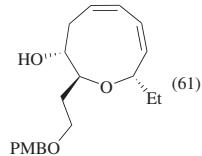
[allylPdCl]₂ (10%),
TBAF (1000%),
THF, rt, 75 h



226, 227

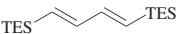
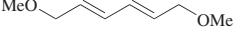
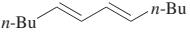
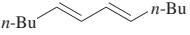
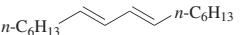
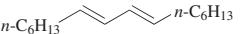
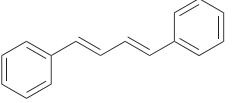
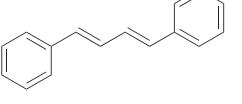


[allylPdCl]₂ (7.5%),
TBAF, rt, 60 h

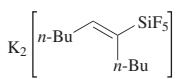


228, 229

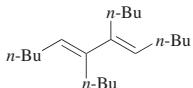
TABLE 3G. HOMODIMERIZATION OF ALKENYLSILANES

Silane	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ $\text{K}_2\left[\text{TES}-\text{CH}=\text{CH}-\text{SiF}_5\right]$	AgF (100%), MeCN, rt	 (58)	273
C ₃ $\text{K}_2\left[\text{MeO}-\text{CH}_2-\text{CH}=\text{CH}-\text{SiF}_5\right]$	aq. AgNO ₃ (110%), Et ₂ O, rt	 (51)	273
C ₆ $\text{K}_2\left[n\text{-Bu}-\text{CH}=\text{CH}-\text{SiF}_5\right]$	AgF (100%), MeCN, rt	 (63)	273
	CuCl, 200°, 20 mmHg	 (30) 96% (<i>E,E</i>)	272
C ₈ $\text{K}_2\left[n\text{-C}_6\text{H}_{13}-\text{CH}=\text{CH}-\text{SiF}_5\right]$	AgF (100%), MeCN, rt	 (74)	273
	CuCl, 250°, 3 mmHg	 (35) 95% (<i>E,E</i>)	272
	CuCl, 250°, 3 mmHg	 (64)	272
	PdCl ₂ , MeCN, 3 h	 (54)	21

C₁₀



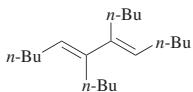
AgF (100%), MeCN, rt



(72)

273

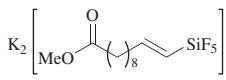
CuCl, 200°, 3 mmHg



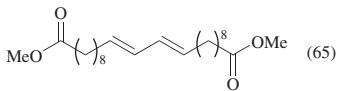
(43) (*E,E*)/other isomers = 92:8

272

C₁₁

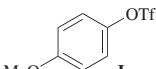
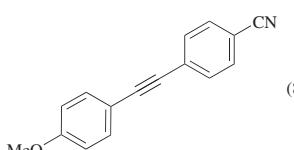
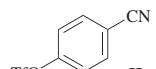
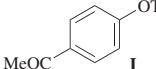
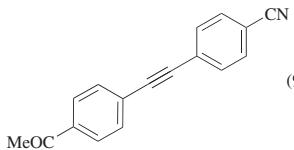
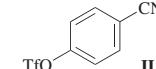
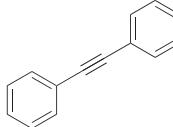
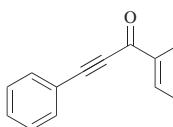
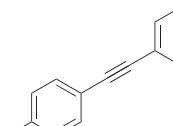


aq. AgNO₃ (110%), Et₂O, rt



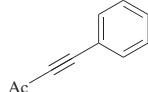
273

TABLE 4A. CROSS-COUPLING OF ALKYNYLSILANES WITH ARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ ≡—TMS	 I	1. I , Pd(PPh ₃) ₄ (10%), NEt ₃ /DMF 60°, 6 h 2. II , CuCl (10%), DMF, 80°, 12 h	 (80)	131
	 II			
TMS—≡—TMS	 I	1. I , Pd(PPh ₃) ₄ (10%), NEt ₃ /DMF 60°, 6 h 2. II , CuCl (10%), DMF, 80°, 12 h	 (94)	131
	 II			
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), MeCN, 50°, 5 h	 (77)	132
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h	 (66)	132
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), MeCN, 50°, 5 h	 (80)	132

C₄

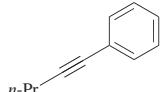
Pd₂(dba)₃•CHCl₃ (5%),
CuI (10%), MeCN,
50°, 5 h



(85) 132

C₅

Pd(PPh₃)₄ (5%),
TBAF (100%),
THF, 60°, 2 h



(95) 138

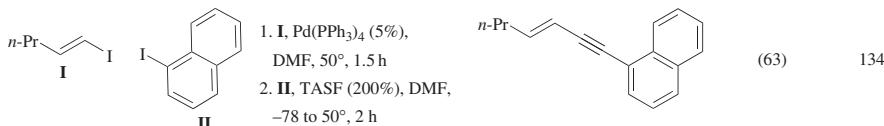
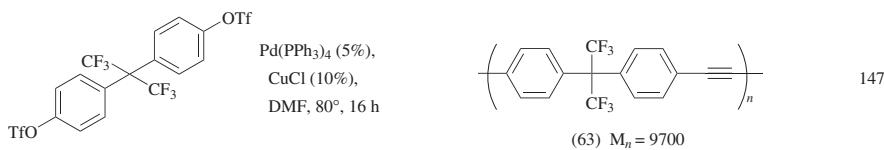
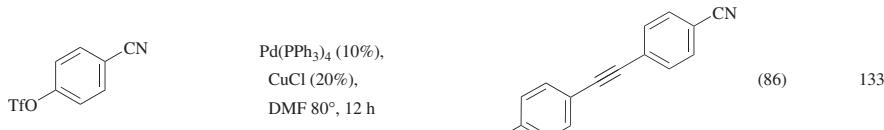
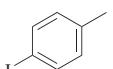
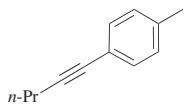
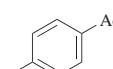
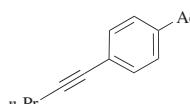
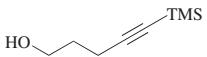
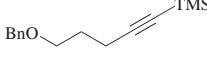
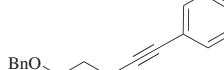
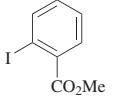
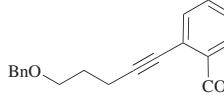
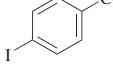


TABLE 4A. CROSS-COUPLING OF ALKYNYL SILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
<i>n</i> -Pr— \equiv —SiMe ₂ OH		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 3 h	 <i>n</i> -Pr— \equiv —C ₆ H ₄ —CH ₃	(90) 138
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 2 h	 <i>n</i> -Pr— \equiv —C ₆ H ₄ —CH(=O)Ac	(72) 138
		Pd(PPh ₃) ₄ (10%), AgCl (20%), MeOH (800%), K ₂ CO ₃ (800%), DMF, 40°, 19 h		(71) 143
		CuCl (200%), Bu ₃ N (300%), DMI, 120°		(60) 139
		CuCl (200%), Bu ₃ N (300%), DMI, 120°		(84) 139
		CuCl (200%), Bu ₃ N (300%), DMI, 120°		(88) 139

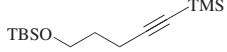
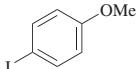
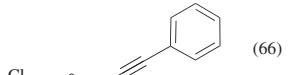
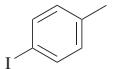
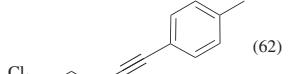
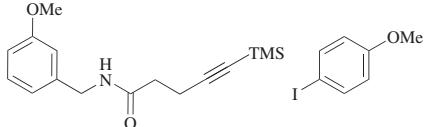
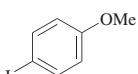
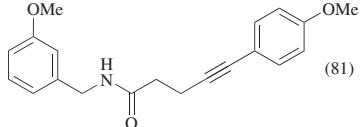
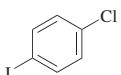
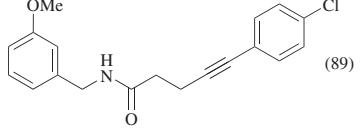
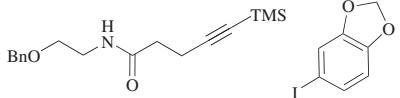
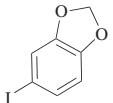
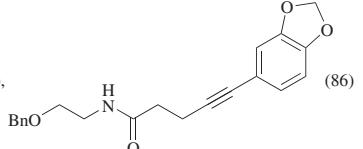
		<p>Ag₂CO₃ (50%), Pd(OAc)₂ (5%), PPh₃ (20%), TBAC (100%), THF, 65°, 2 h</p>		(84)	137
		<p>Pd(PPh₃)₄ (5%), TBAF (100%), THF, 60°, 2 h</p>		(66)	138
		<p>Pd(PPh₃)₄ (5%), TBAF (100%), THF, 60°, 2 h</p>		(62)	138
		<p>Ag₂CO₃ (50%), Pd(OAc)₂ (5%), PPh₃ (20%), TBAC (100%), THF, 65°, 2 h</p>		(81)	137
		<p>Ag₂CO₃ (50%), Pd(OAc)₂ (5%), PPh₃ (20%), TBAC (100%), THF, 65°, 2 h</p>		(89)	137
		<p>Ag₂CO₃ (50%), Pd(OAc)₂ (5%), PPh₃ (20%), TBAC (100%), THF, 65°, 2 h</p>		(86)	137

TABLE 4A. CROSS-COUPLING OF ALKYNYL SILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅				
		Ag ₂ CO ₃ (50%), Pd(OAc) ₂ (5%), PPh ₃ (20%), TBAC (100%), THF, 65°, 2 h		(82) 137
C ₆				
		Pd(PPh ₃) ₄ (10%), AgCl (20%), MeOH (400%), K ₂ CO ₃ (400%), DMF, 40°, 20 h		(99) 143
t-Bu-C≡C-TMS	Ph ₃ Sb(OAc) ₂	Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h		(80) 132
	(p-tol) ₃ Sb(OAc) ₂	Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h		(77) 132
		Pd(PPh ₃) ₄ (5%), AgCl (20%), MeOH (800%), K ₂ CO ₃ (800%), DMF, 40°		(76) 326

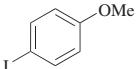
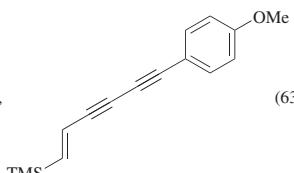
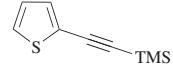
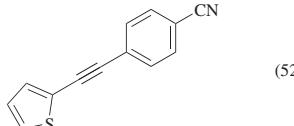
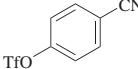
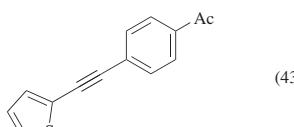
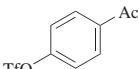
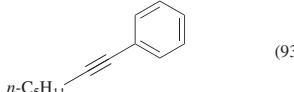
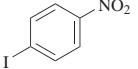
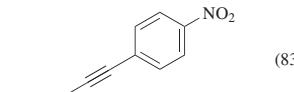
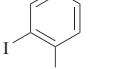
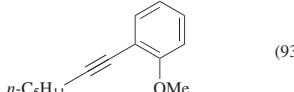
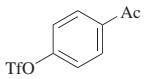
	Pd(PPh ₃) ₄ (5%), AgCl (20%), MeOH (800%), K ₂ CO ₃ (800%), DMF, 40°		(63)	326
	Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°		(52)	131, 133
	Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°		(43)	133
	KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(93)	217
	KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(83)	217
	KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 24 h		(93)	217

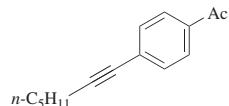
TABLE 4A. CROSS-COUPLING OF ALKYNYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇				
<i>n</i> -C ₅ H ₁₁ —≡—SiMe ₂ OH		KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(95)
		KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 24 h		(93)
		KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(87)
<i>n</i> -C ₅ H ₁₁ —≡—TMS		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 12 h		(70)
		KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(84)
		KOTMS (200%), PdCl ₂ (PPh ₃) ₂ (2.5%), CuI (5%), DME, rt, 3 h		(75)

673

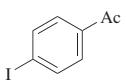


Pd(PPh₃)₄ (5%),
CuCl (10%),
DMF, 80°

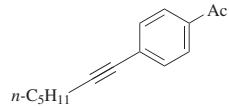


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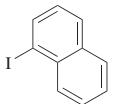


KOTMS (200%),
PdCl₂(PPh₃)₂ (2.5%),
CuI (5%),
DME, rt, 3 h

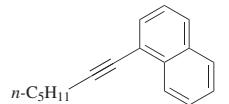


(92)

217

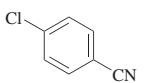
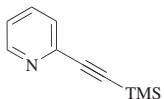


KOTMS (200%),
PdCl₂(PPh₃)₂ (2.5%),
CuI (5%),
DME, rt, 3 h

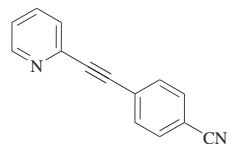


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217

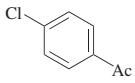


Pd(OAc)₂ (10%),
(-)-DIOP (10%),
CuCl (10%),
DMF, 120°, 48 h

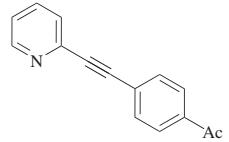


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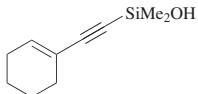


Pd(OAc)₂ (10%),
(-)-DIOP (10%),
CuCl (10%),
DMF, 120°, 48 h

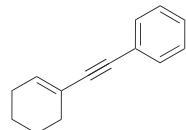


(37)

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C₈

Pd(PPh₃)₄ (5%),
TBAF (100%),
THF, 60°, 2 h

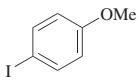


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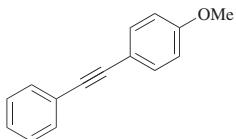
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TABLE 4A. CROSS-CO尤LING OF ALKYNYL SILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 1 h		(77)
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°, 37 h		(48) M _n = 8900 147
674				
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), MeCN, 50°, 5 h		(81)
		Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h		(62)
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 3 h		(10)
				141



Pd(OAc)₂ (5%),
PPh₃ (20%), CuCl (10%),
Ag₂CO₃ (50%),
TBAC (100%),
THF 65°, 2 h

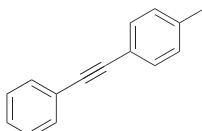


(92)

137

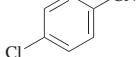
(*p*-tol)₃Sb(OAc)₂

Pd₂(dba)₃•CHCl₃ (5%),
CuI (10%),
MeCN, 50°, 5 h

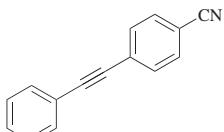


(80)

132

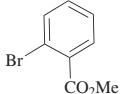


Pd(OAc)₂ (10%),
(-)-DIOP (10%),
CuCl (10%),
DMF, 120°, 6 h

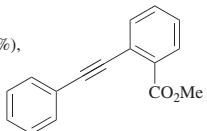


(47)

141

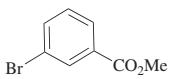


Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min

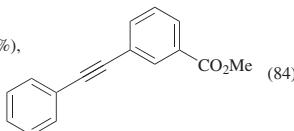


(85)

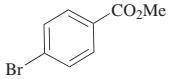
140



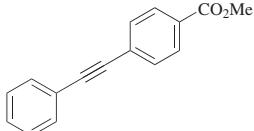
Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min



140



Pd(OAc)₂ (5%),
TBAC (100%), DMF,
MW, 100°, 15 min



(7)

140

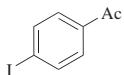
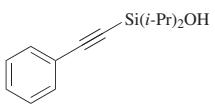
TABLE 4A. CROSS-COUPLING OF ALKYNYSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(OAc) ₂ (5%), (<i>o</i> -tol) ₃ P, TBAC (100%), DMF, MW, 100°, 15 min		(85)
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 6 h		(34)
676				
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF		(89)
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°		(97)
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 10 h		(57)

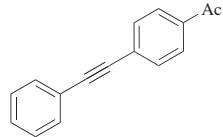
	PdCl ₂ (dppb) (5%), CuCl (10%), DMF, 120°, 12 h		(56)	133
	[allylPdCl] ₂ (2.5%), TBAF (100%), CO (30 atm), THF, 50°, 20 h		(64)	179
	Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°, 14 h		(64)	133
	Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°, 12 h		(65)	133
	[allylPdCl] ₂ (2.5%), TBAF (150%), THF, 60°, 48 h		(30)	162
	Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 2.5 h		(97)	138

TABLE 4A. CROSS-COUPLING OF ALKYNYSILANES WITH ARYL ELECTROPHILES (*Continued*)

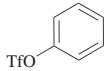
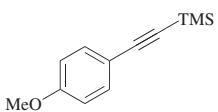
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 2 h		(73) 138
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 2.5 h		(95) 138
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 3 h		(99) 138
		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 2 h		(78) 138
678		Pd(PPh ₃) ₄ (5%), TBAF (100%), THF, 60°, 3 h		(71) 138



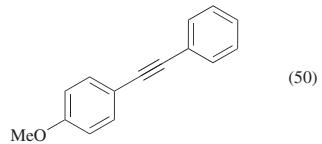
$\text{Pd}(\text{PPh}_3)_4$ (5%),
TBAF (100%),
THF, 60° , 3 h



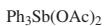
(52) 138



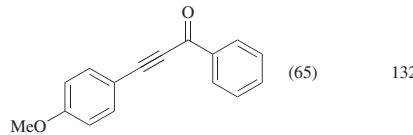
$\text{Pd}(\text{PPh}_3)_4$ (5%),
 CuCl (10%),
DMF, 80°



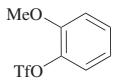
(50) 133



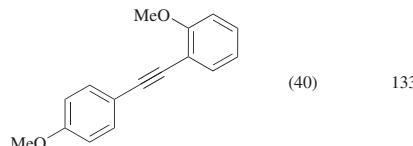
$\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (5%),
 CuI (10%), CO (1 atm),
MeCN, 50° , 5 h



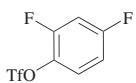
132



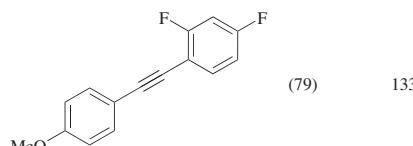
$\text{Pd}(\text{PPh}_3)_4$ (5%),
 CuCl (10%),
DMF, 80°



133



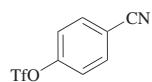
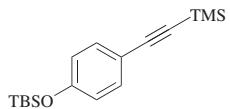
$\text{Pd}(\text{PPh}_3)_4$ (5%),
 CuCl (10%),
DMF, 80°



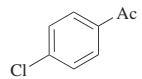
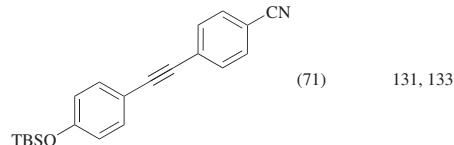
133

TABLE 4A. CROSS-COUPLING OF ALKYNYSILANES WITH ARYL ELECTROPHILES (*Continued*)

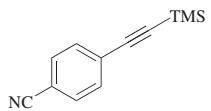
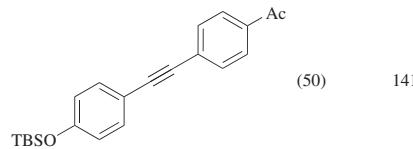
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
	(<i>p</i> -tol) ₃ Sb(OAc) ₂	Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h	 (80)	132
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°	 (51)	131, 133
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 12 h	 (71)	141
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°	 (65)	131, 133
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 12 h	 (34)	141

C₉

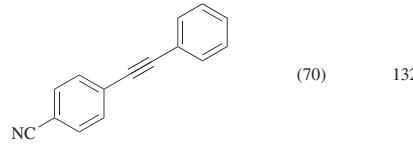
Pd(PPh₃)₄ (5%),
CuCl (10%),
DMF, 80°



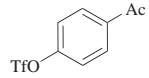
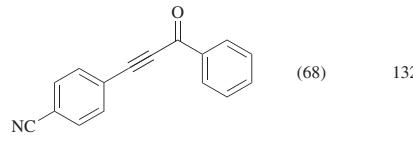
Pd(OAc)₂ (10%),
CuCl (10%),
(-)-DIOP (10 %),
DMF, 120°, 12 h



Pd₂(dba)₃•CHCl₃ (5%),
CuI (10%),
MeCN, 50°, 5 h



Pd₂(dba)₃•CHCl₃ (5%),
CuI (10%), CO (1 atm),
MeCN, 50°, 5 h



Pd(PPh₃)₄ (5%),
CuCl (10%),
DMF, 80°

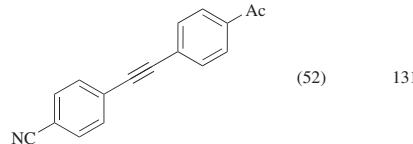
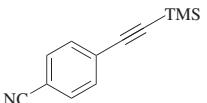
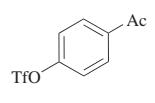
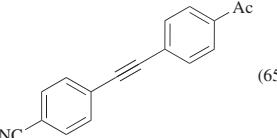
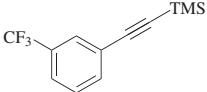
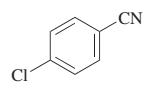
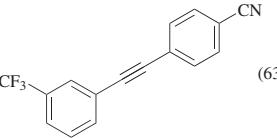
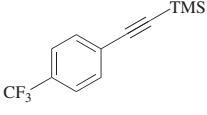
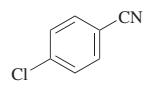
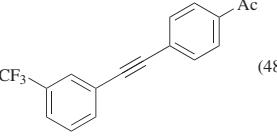
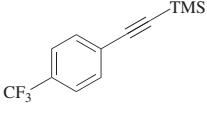
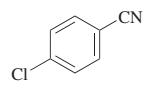
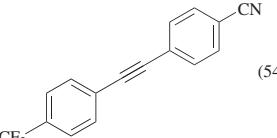


TABLE 4A. CROSS-COUPLING OF ALKYNYLSILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀				
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°	 (65)	133
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 24 h	 (63)	141
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 12 h	 (48)	141
		Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 24 h	 (54)	141

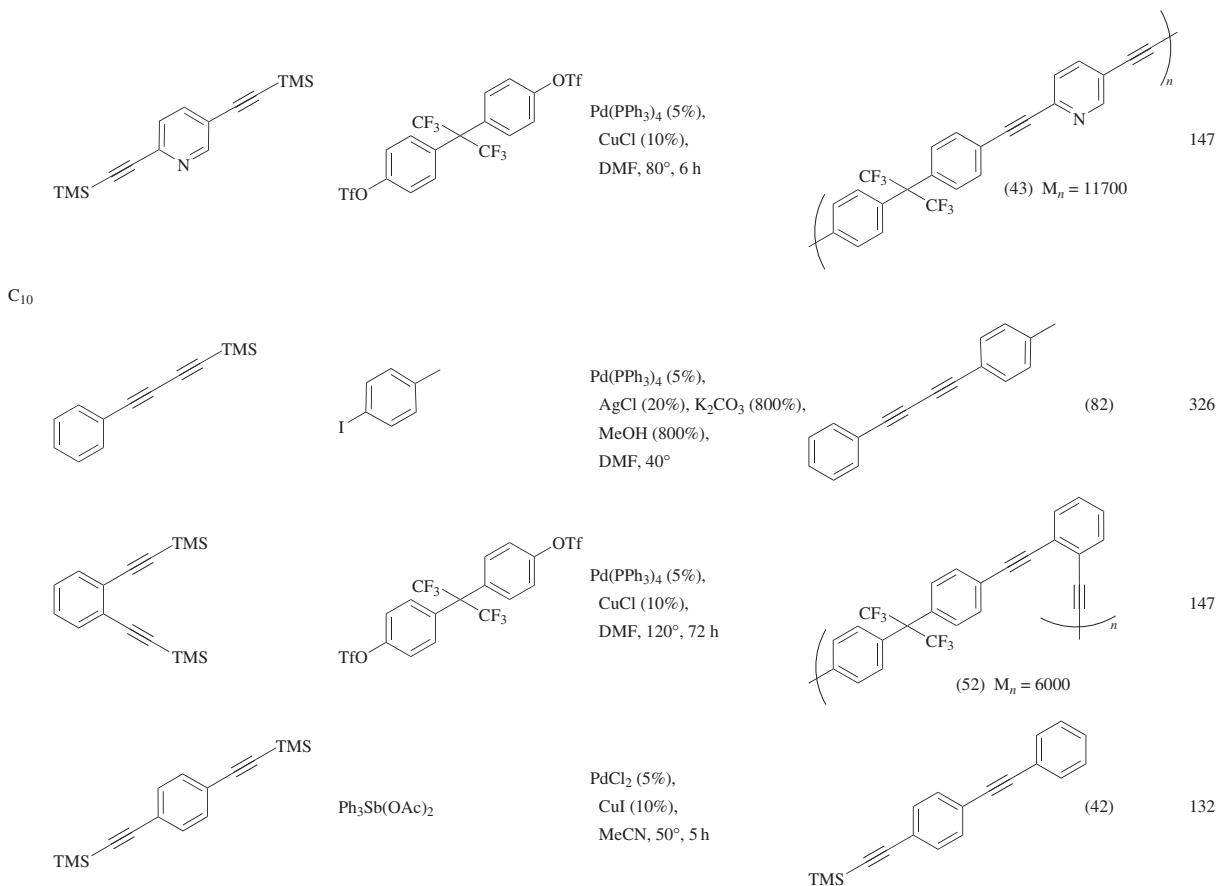
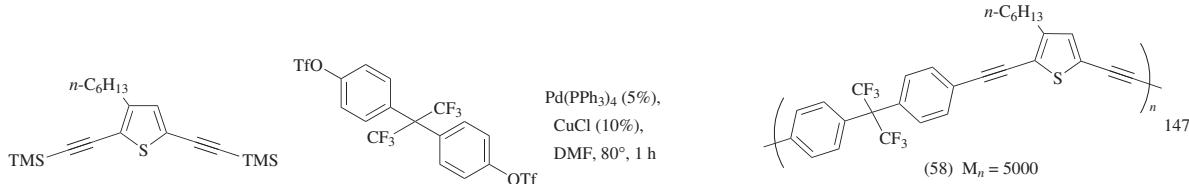


TABLE 4A. CROSS-COUPLING OF ALKYNYL SILANES WITH ARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀				
	Ph ₃ Sb(OAc) ₂	Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), CO (1 atm), MeCN, 50°, 5 h	 (58)	132
	Ph ₃ Sb(OAc) ₂	Pd ₂ (dba) ₃ •CHCl ₃ (5%), CuI (10%), MeCN, 50°, 5 h	 (75)	132
	TfO-C ₆ H ₄ -C(F ₃) ₂ -OTf	Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 80°, 5 h	 (90) M _n = 7800	147

C₁₄



C₂₂

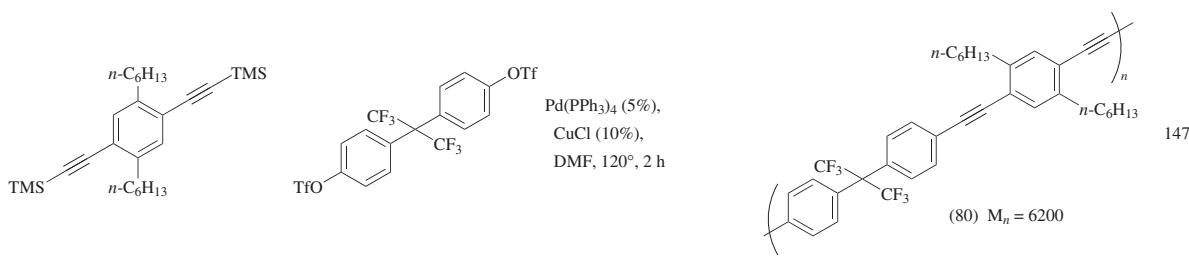
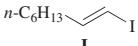
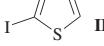
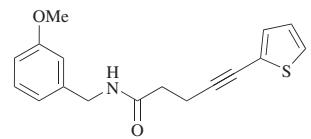
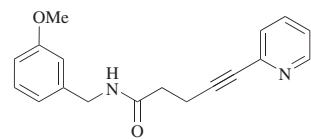
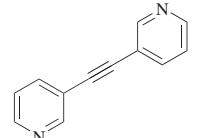
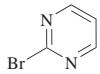
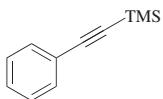
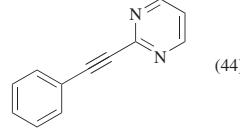


TABLE 4B. CROSS-COUPLING OF ALKYNYLSILANES WITH HETEROARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂				
Me ₃ Sn— \equiv —TMS	 I	1. I , Pd(PPh ₃) ₄ (5%), DMF 50°, 6 h		(55)
	 II	2. II , TASF (240%), -78 to 50°, 2 h		134
C ₅				
	 (89)	Pd(OAc) ₂ (5%), PPh ₃ (20%), Ag ₂ CO ₃ (50%), TBAC (100%), 65°, 2 h		137
	 (72)	PdCl ₂ (PPh ₃) ₂ (5%), Ag ₂ CO ₃ (50%), TBAC (100%), 65°, 2 h		137
C ₇				
	 (82)	Pd(OAc) ₂ (5%), (<i>o</i> -tol) ₃ P (10%), TBAC (100%), DMF, MW, 100°, 15 min		140

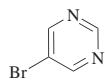
C₈

Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min

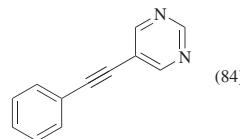


(44)

140

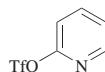


Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min

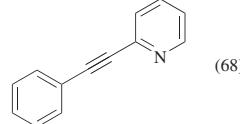


(84)

140

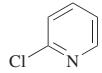


Pd(PPh₃)₄ (5%),
CuCl (10%),
DMF, 40°, 16 h

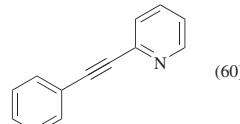


(68)

133

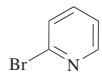


Pd(OAc)₂ (10%),
(-)-DIOP (10%), CuCl (10%),
DMF, 120°, 12 h

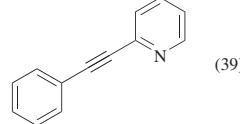


(60)

141

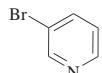


Pd(OAc)₂ (5%),
TBAC (100%), DMF,
MW, 100°, 15 min

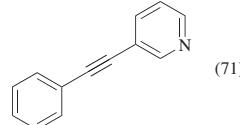


(39)

140



Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min



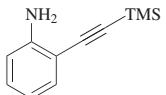
(71)

140

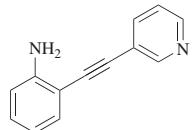
TABLE 4B. CROSS-COUPLING OF ALKYNYSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd(OAc) ₂ (5%), (<i>o</i> -tol) ₃ P (10%), TBAC (100%), DMF, MW, 100°, 15 min	 (90)	140
		Pd(OAc) ₂ (5%), TBAC (100%), DMF, MW, 100°, 15 min	 (33)	140
		Pd(OAc) ₂ (5%), (<i>o</i> -tol) ₃ P (10%), TBAC (100%), DMF, MW, 120°, 2.5 min	 (50)	140
688				
		Pd(PPh ₃) ₄ (5%), CuCl (10%), DMF, 40°, 9 h	 (62)	133
		Pd(OAc) ₂ (5%), (<i>o</i> -tol) ₃ P (10%), TBAC (100%), DMF, MW, 100°, 15 min	 (57)	140

69

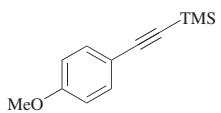
C₉

Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min

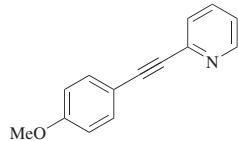


(81)

140

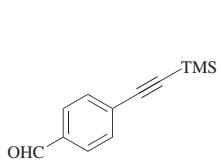


Pd(OAc)₂ (10%),
(-)-DIOP (10%), CuCl (10%),
DMF, 120°, 3 h

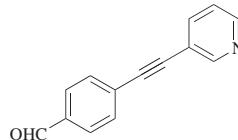


(45)

141

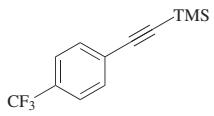


Pd(OAc)₂ (5%), (*o*-tol)₃P (10%),
TBAC (100%), DMF,
MW, 100°, 15 min

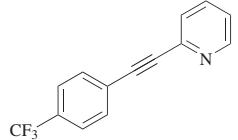


(60)

140

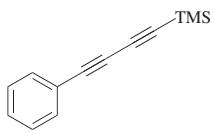


Pd(OAc)₂ (10%),
(-)-DIOP (10%), CuCl (10%),
DMF, 120°, 12 h

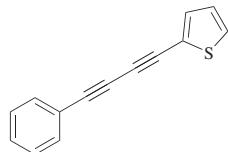


(65)

141

C₁₀

Pd(PPh₃)₄ (5%),
AgCl (20%), K₂CO₃ (800%),
MeOH (800%), DMF, 40°



(87)

326

TABLE 4B. CROSS-COUPLING OF ALKYNYSILANES WITH HETEROARYL ELECTROPHILES (*Continued*)

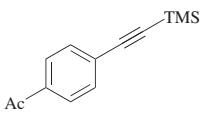
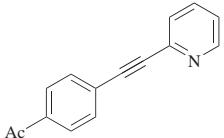
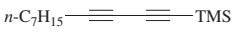
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	 	Pd(OAc) ₂ (10%), (-)-DIOP (10%), CuCl (10%), DMF, 120°, 3 h	  (36)	141
C ₁₁ 	 	Pd(PPh ₃) ₄ (5%), AgCl (20%), K ₂ CO ₃ (800%), MeOH (800%), DMF, 40°	  (76)	326

TABLE 4C. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKENYL ELECTROPHILES

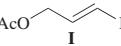
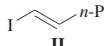
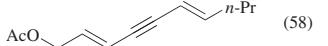
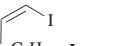
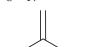
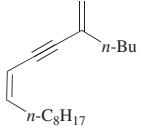
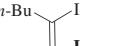
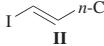
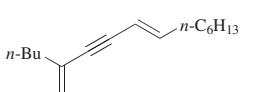
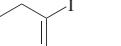
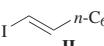
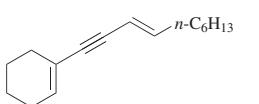
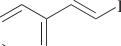
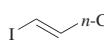
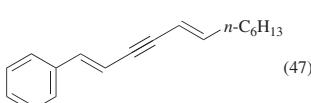
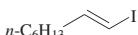
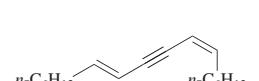
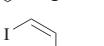
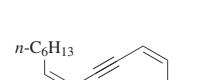
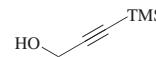
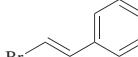
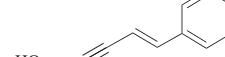
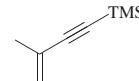
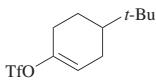
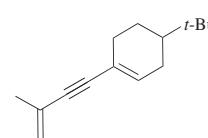
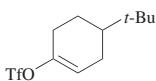
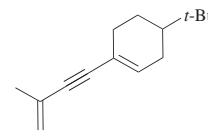
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ Me ₃ Sn— \equiv —TMS	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°	 (58)	134
 n-Bu	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°	 (85)	134
169	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°	 (80)	134
	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°	 (72)	134
	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°	 (47)	134

TABLE 4C. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₂					
<chem>Me3SnC#C[TMS]</chem>	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°		(68) 134	
	 	1. I , Pd(PPh ₃) ₄ (5%), THF, 50° 2. II , TASF (240%), -78 to 50°		(70) 134	
C ₃			[allylPdCl] ₂ (2.5%), TASF (100%), THF		(84) 23
C ₅			Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 18 h		(99) 142
		Pd(PPh ₃) ₄ (10%), AgCl (20%), K ₂ CO ₃ (400%), MeOH (400%), DMF, 15 h		(89) 143	

693

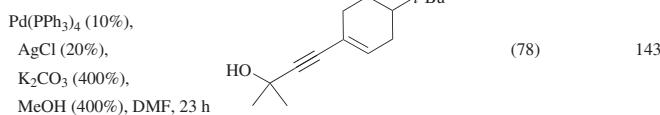
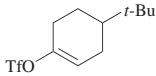
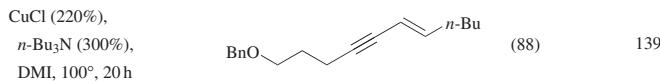
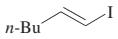
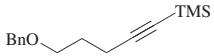
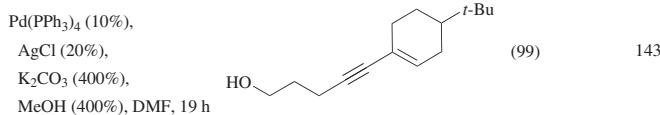
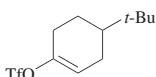
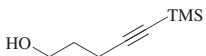
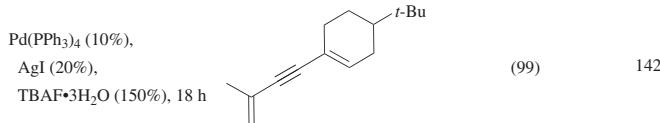
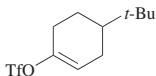
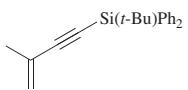
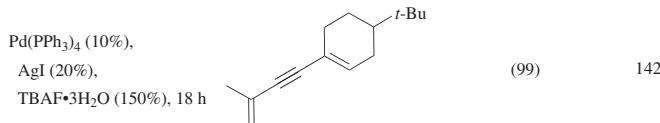
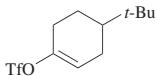
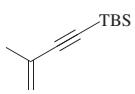


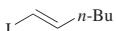
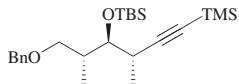
TABLE 4C. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆				
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 21 h	 (87)	142
		Pd(PPh ₃) ₄ (10%), AgCl (20%), K ₂ CO ₃ (400%), MeOH (400%), DMF, 20 h	 (99)	143
		Pd(PPh ₃) ₄ (10%), AgCl (20%), K ₂ CO ₃ (400%), MeOH (400%), DMF	 (96)	143
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 24 h	 (84)	142
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 24 h	 (75)	142
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 24 h	 (75)	142

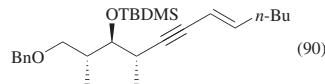
		Pd(PPh ₃) ₄ (5%), AgCl (20%), K ₂ CO ₃ (800%), MeOH (800%), DMF, 40°		(88)	326
		Pd(PPh ₃) ₄ (10%), AgCl (20%), K ₂ CO ₃ (400%), MeOH (400%), DMF, 25 h		(76)	143
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 22 h		(78)	142
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 22 h		(67)	142
		Pd(PPh ₃) ₄ (10%), AgI (20%), TBAF•3H ₂ O (150%), 22 h		(66)	142

TABLE 4C. CROSS-CO尤LING OF ALKYNYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

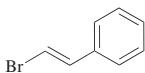
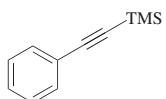
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇		[allylPdCl]2 (2.5%), TASF (100%), THF		(86) 23
		CuCl (200%), n-Bu3N (300%), DMI, 120°, 3.5 h		(70) 139
		CuCl (200%), n-Bu3N (300%), DMI, 120°, 3.5 h		(64) 139
C ₈		CuCl (200%), n-Bu3N (300%), DMI, 120°, 19 h		(94) 139
		CuCl (200%), n-Bu3N (300%), DMI, 120°, 5 h		(73) 139
		CuCl (200%), n-Bu3N (300%), DMI, 120°		(91) 139



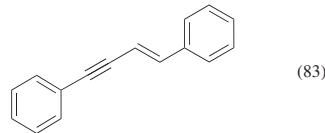
CuCl (200%),
n-Bu₃N (300%),
DMI, 120°



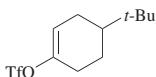
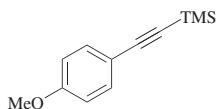
139



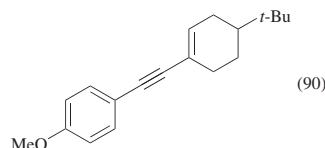
[allylPdCl]₂ (2.5%),
TASF (100%), THF



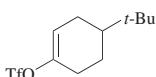
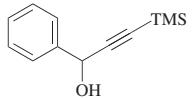
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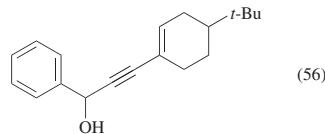
CuCl (10%),
Pd(PPh₃)₄ (5%),
DMF, 80°



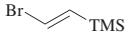
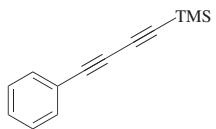
131

C₉

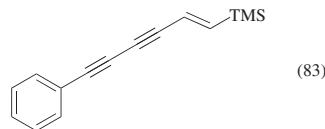
Pd(PPh₃)₄ (10%),
AgCl (20%),
K₂CO₃ (400%),
MeOH (400%), DMF, 22 h



143

C₁₀

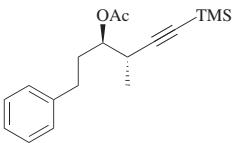
Pd(PPh₃)₄ (5%),
AgCl (20%),
K₂CO₃ (800%),
MeOH (800%), DMF, 40°



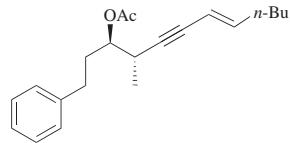
326

TABLE 4C. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKENYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁				
	I	CuCl (200%), <i>n</i> -Bu ₃ N (300%), DMI, 120°, 14 h	 (87)	139
	I <i>n</i> -C ₇ H ₁₅	CuCl (200%), <i>n</i> -Bu ₃ N (300%), DMI, 120°, 3 h	 (90)	139
	Br TMS	Pd(PPh ₃) ₄ (5%), AgCl (20%), K ₂ CO ₃ (800%), MeOH (800%), DMF, 40°	 (75)	326
C ₁₃				
	I	CuCl (200%), <i>n</i> -Bu ₃ N (300%), DMI, 120°, 16 h	 (80)	139
	I <i>n</i> -Bu	CuCl (200%), <i>n</i> -Bu ₃ N (300%), DMI, 120°, 3.5 h	 (91)	139

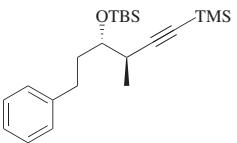


CuCl (200%),
 $n\text{-Bu}_3\text{N}$ (300%),
DMI, 120°, 3.5 h

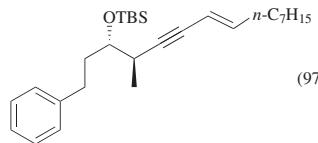


(70)

139



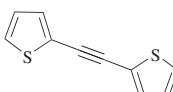
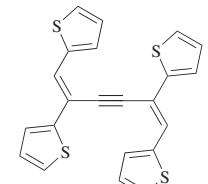
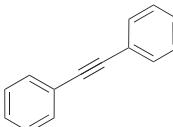
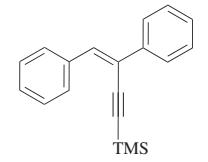
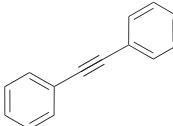
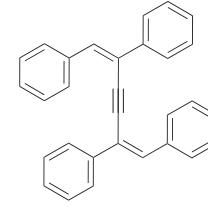
CuCl (200%),
 $n\text{-Bu}_3\text{N}$ (300%),
DMI, 120°, 4 h



(97)

139

TABLE 4D. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKYNYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂	TMS— \equiv —TMS	 1. [Rh(OH)(cod)] ₂ (5%), dCypb (5 %), 3,4,5-(MeO) ₃ C ₆ H ₂ OH (300%), <i>o</i> -xylene, reflux, 2 h 2. KF (20%), 2 h	 (60)	327
		 [Rh(OH)(cod)] ₂ (3%), dCypb (3%), PhOH (300%), <i>o</i> -xylene, 130°, 6 h	 (64)	327
		 [Rh(OH)(cod)] ₂ (5%), dCypb (5%), 3,4,5-(MeO) ₃ C ₆ H ₂ OH (300%), KF (20%), <i>o</i> -xylene, reflux, 6 h	 (69)	327

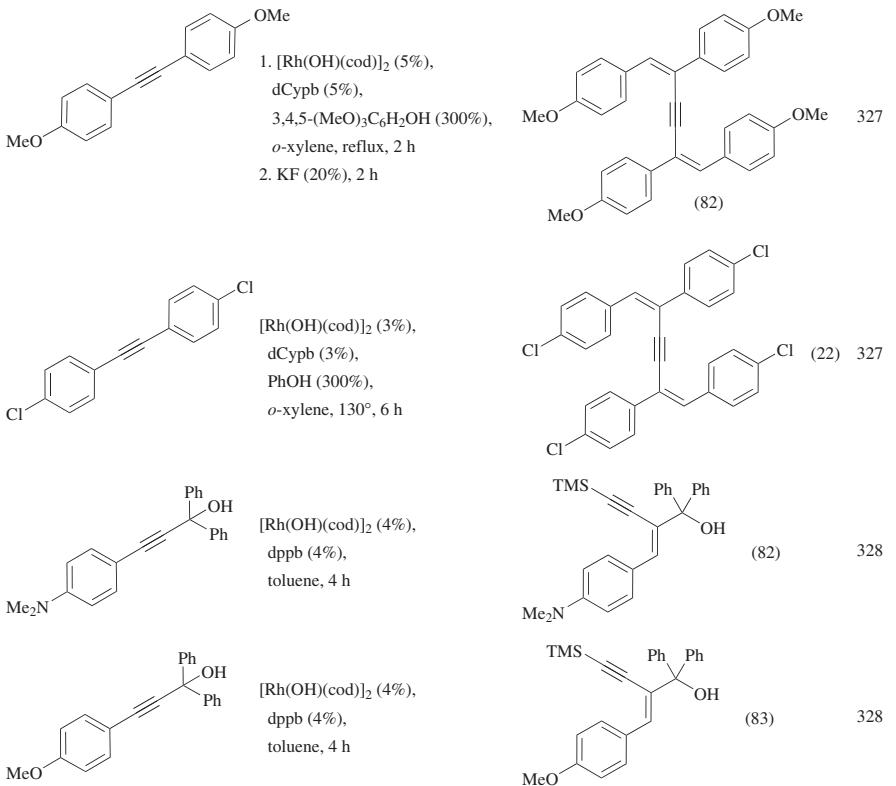
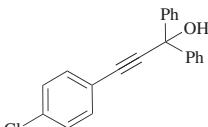
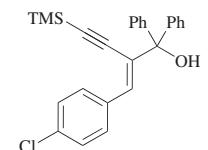
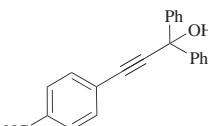
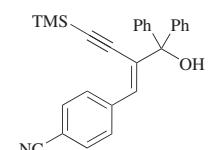
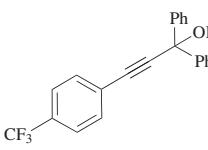
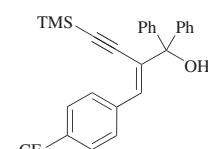
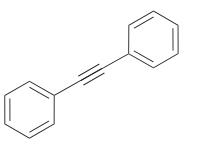
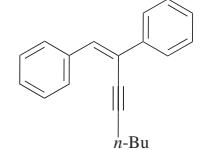
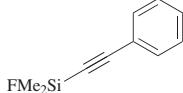
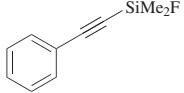


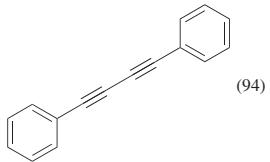
TABLE 4D. CROSS-CO尤LING OF ALKYNYL SILANES WITH ALKYNYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C_2	TMS— \equiv —TMS		[Rh(OH)(cod)] ₂ (4%), dppb (4%), toluene, 4 h	 (87)	328
		[Rh(OH)(cod)] ₂ (4%), dppb (4%), toluene, 4 h	 (57)	328	
		[Rh(OH)(cod)] ₂ (4%), dppb (4%), toluene, 4 h	 (73)	328	
C_6	$n\text{-Bu}-\equiv-\text{TMS}$		[Rh(OH)(cod)] ₂ (3%), dCypb (3%), 3,4,5-(MeO) ₃ C ₆ H ₂ OH (200%), <i>o</i> -xylene, reflux, 12 h	 (30)	327

703

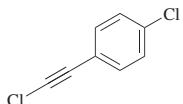
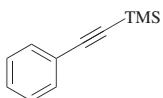


CuCl (5%),
TBAF (118%),
MeCN, rt, 5 min

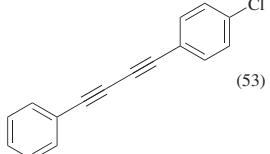


(94)

178

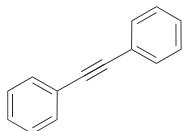
 C_8 

CuCl (10%), DMF,
80°, 48 h

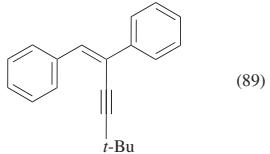


(53)

133, 144

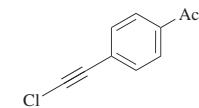


[Rh(OH)(cod)]₂ (3%),
dCypb (3%),
3,4,5-(MeO)₃C₆H₂OH (200%),
o-xylene, reflux, 12 h

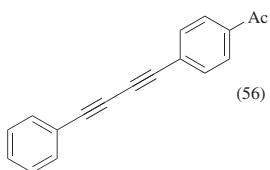


(89)

327



CuCl (10%), DMF,
80°, 48 h



(56)

133, 144

TABLE 4D. CROSS-COUPLING OF ALKYNYLSILANES WITH ALKYNYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		CuCl (5%), TBAF (118%), MeCN, rt, 5 min		(91) 178
		CuCl (5%), DMF, 80°, 48 h		(65) 133, 144
		CuCl (5%), DMF, 80°, 48 h		(54) 133, 144
		CuCl (5%), DMF, 80°, 48 h		(52) 133, 144

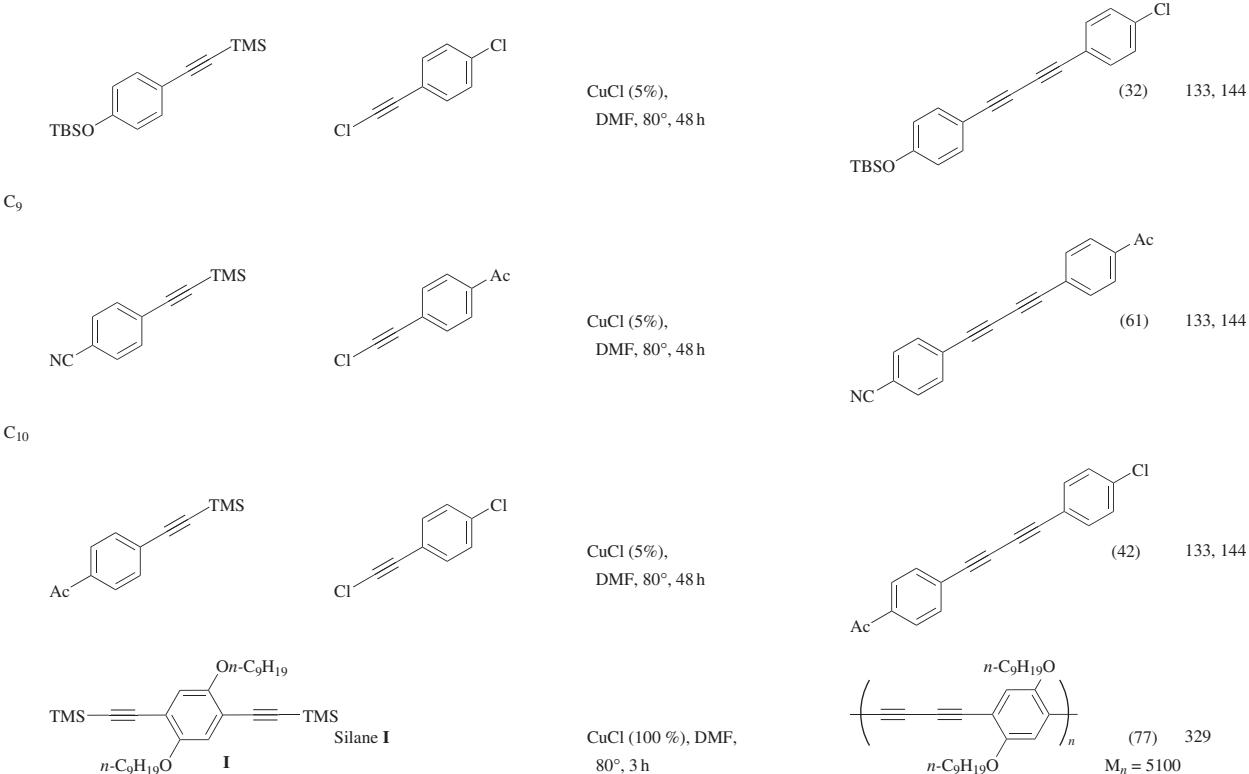


TABLE 4D. CROSS-CO尤LING OF ALKYNYL SILANES WITH ALKYNYL ELECTROPHILES (*Continued*)

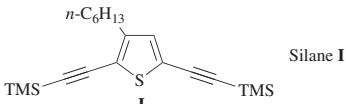
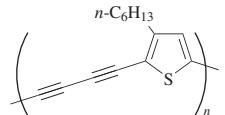
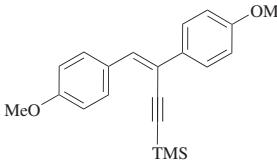
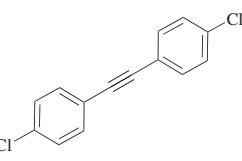
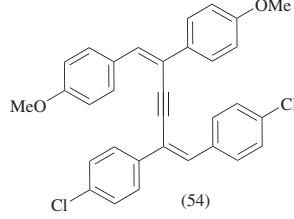
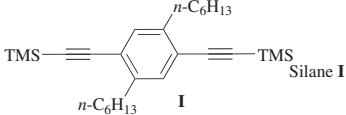
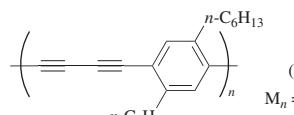
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄				
	Silane I	CuCl (100%), DMF, 60°, 4 h		(94) M _n = 4000 329
C ₁₆				
		[Rh(OH)(cod)] ₂ (5%), dCypb (5%), 3,4,5-(MeO) ₃ C ₆ H ₂ OH (300%), KF (20%), <i>o</i> -xylene, 130°, 12 h		(54) 327
C ₂₂				
	Silane I	CuCl (100 %), DMF, 80°, 36 h		(45) M _n = 7900 329

TABLE 4E. CROSS-CO尤LING OF ALKYNYL SILANES WITH ALLYL/PROPARGYL ELECTROPHILES

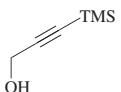
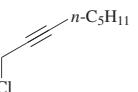
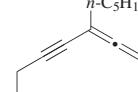
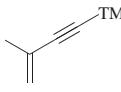
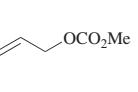
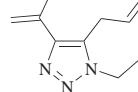
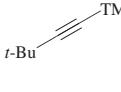
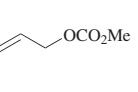
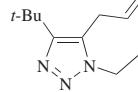
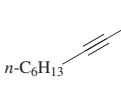
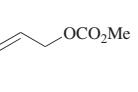
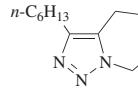
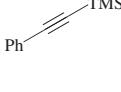
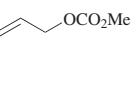
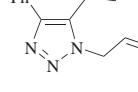
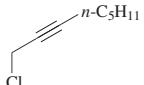
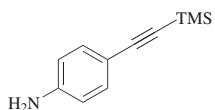
	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃			PdCl ₂ (PPh ₃) ₂ (5%), CuI (100%), TBAF (100%), DMF, 1 h	 (64)	145
C ₅			Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 5 h	 (69)	146
C ₆			Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 24 h	 (51)	146
C ₈			Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 4 h	 (63)	146
			Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 8 h	 (77)	146

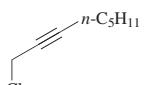
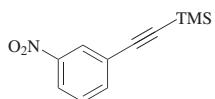
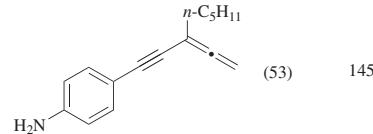
TABLE 4E. CROSS-COUPLING OF ALKYNYSILANES WITH ALLYL/PROPARGYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 150°, 2 h		(51) 146
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 150°, 2 h		(34) 146
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 120°, 2 h		(70) 146
708		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 5 h		(75) 146

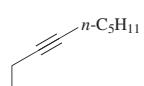
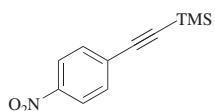
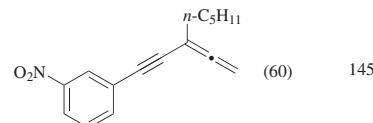
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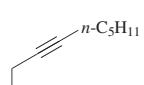
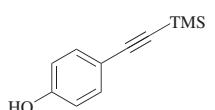
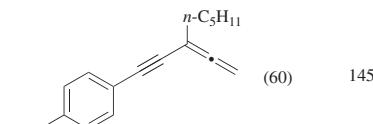
PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



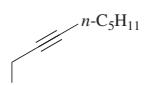
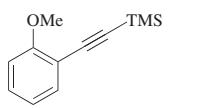
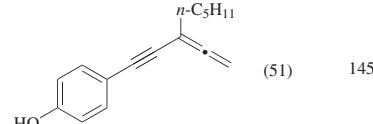
PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



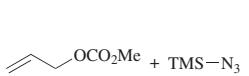
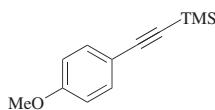
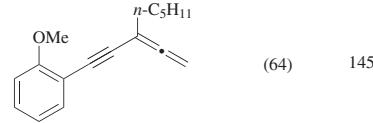
PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



Pd₂(dba)₃•CHCl₃ (2.5%),
P(OEt)₃ (20%),
CuCl (10%),
dioxane, 100°, 5 h

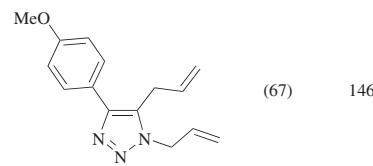
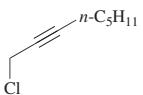
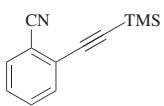
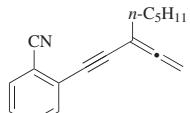


TABLE 4E. CROSS-COUPLING OF ALKYNYLSILANES WITH ALLYL/PROPARGYL ELECTROPHILES (*Continued*)

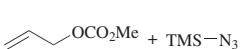
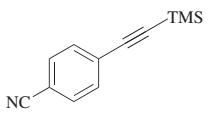
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈				
		PdCl ₂ (PPh ₃) ₂ (5%), CuI (100%), TBAF (100%), DMF, 1 h		(66) 145
		PdCl ₂ (PPh ₃) ₂ (5%), CuI (100%), TBAF (100%), DMF, 1 h		(63) 145
710				
		Pd ₂ (dba) ₃ •CHCl ₃ (2.5%), P(OEt) ₃ (20%), CuCl (10%), dioxane, 100°, 10 h		(71) 146
C ₉				
		PdCl ₂ (PPh ₃) ₂ (5%), CuI (100%), TBAF (100%), DMF, 1 h		(67) 145



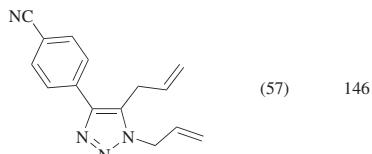
PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



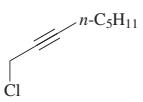
(57) 145



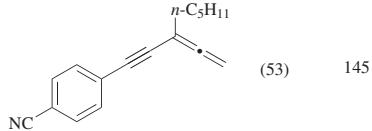
Pd₂(dba)₃•CHCl₃ (2.5%),
P(OEt)₃ (20%),
CuCl (10%),
dioxane, 100°, 15 h



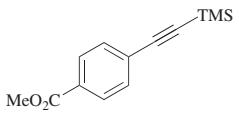
(57) 146



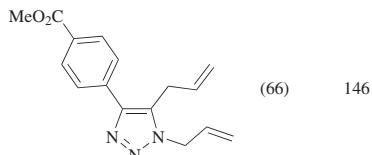
PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



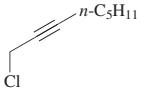
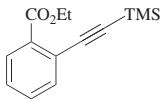
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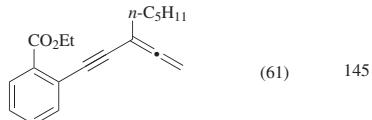
Pd₂(dba)₃•CHCl₃ (2.5%),
P(OEt)₃ (20%),
CuCl (10%),
dioxane, 100°, 13 h



(66) 146



PdCl₂(PPh₃)₂ (5%),
CuI (100%), TBAF (100%),
DMF, 1 h



(61) 145

TABLE 4E. CROSS-COUPLING OF ALKYNYLSILANES WITH ALLYL/PROPARGYL ELECTROPHILES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	n-C ₅ H ₁₁ Cl	PdCl ₂ (PPh ₃) ₂ (5%), CuI (100%), TBAF (100%), DMF, 1 h	(59)	145

TABLE 5A. CROSS-COUPLING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₁					
(Et ₂ N) ₃ S ⁺ Me ₃ SiF ₂ ⁻ 200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(86)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(67)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(84)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(17)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(82)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(59)	275
200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(13)	275

TABLE 5A. CROSS-COUPLING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁					
	(Et ₂ N) ₃ S ⁺ Me ₃ SiF ₂ ⁻ 200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(78)
	200%		[allylPdCl] ₂ (2.5%), THF, 50°, 20 h		(81)
C ₃					
714					
	250%		[allylPdCl] ₂ (2.5%), DME, 85°, 12 h		(73)
	250%		[allylPdCl] ₂ (2.5%), DME, 85°, 7 h		(84)
	250%		[allylPdCl] ₂ (2.5%), DME, 85°, 12 h		(78)
	250%		[allylPdCl] ₂ (2.5%), DME, 85°, 3 h		(80)
	222%		Pd(dba) ₂ (9%), TBAF (231%), DMF, 85°		(60)

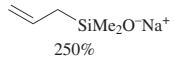
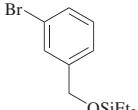
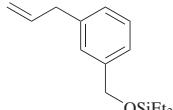
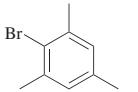
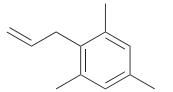
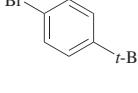
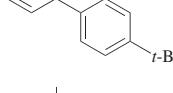
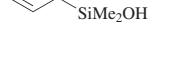
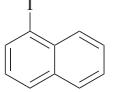
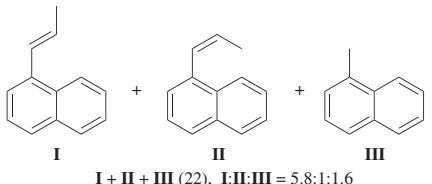
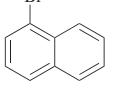
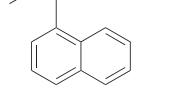
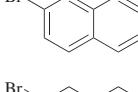
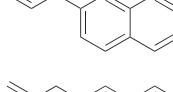
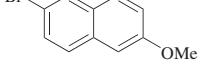
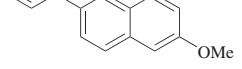
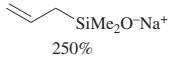
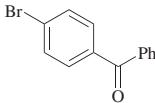
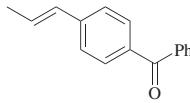
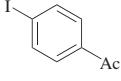
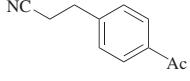
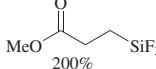
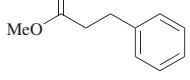
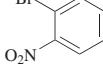
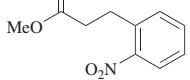
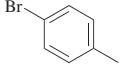
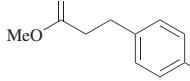
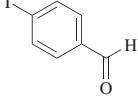
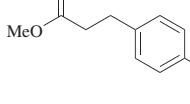
		[allylPdCl2]2 (2.5%), DME, 85°, 4 h		(86)	108
250%					
500%		[allylPdCl2]2 (2.5%), dioxane, 100°, 7 h		(80)	108
250%		[allylPdCl2]2 (2.5%), DME, 85°, 9 h		(74)	108
		[allylPdCl2]2 (2.5%), Cy3P(O) (10%), <i>t</i> -BuOK (200%), THF, 60°		I + II + III (22), I:II:III = 5.8:1:1.6	108
			I		
			II		
			III		
250%		[allylPdCl2]2 (2.5%), DME, 85°, 2 h		(85)	108
250%		[allylPdCl2]2 (2.5%), DME, 85°, 9 h		(71)	108
250%		[allylPdCl2]2 (2.5%), DME, 85°, 6 h		(95)	108

TABLE 5A. CROSS-COUPING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.	
C_3					
		[allylPdCl ₂] ₂ (2.5%), DME, 85°, 1 h		(76)	108
		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 21 h		(87)	190
		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 48 h		(75)	190
		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 10 h		(32)	190
		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 48 h		(62)	190
		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 11 h		(76)	190

		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 8 h		(77)	190
C ₄					
		Pd(PPh ₃) ₄ (5%), TBAF (150%), THF, 100°		(53)	109
		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 6 h			108
		PdCl ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 12 h		(58) (E)/(Z) = 6.5:1	110
		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 110°, 3 h			108
	I		II	III	
				I (E)/(Z)	
				80:20	
				>97:3	
				<4:96	
				II + III	
				(46)	
				18:1	
				(59)	
				II:III	
				7.2:1	
				4.0:1	

TABLE 5A. CROSS-CO尤LING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 8 h	 I + II (76), I:II = 13:1	108
200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 5 h	 I + II (67), I:II = 12:1	108
718 150%		Pd(PPh ₃) ₄ (5%), TBAF (150%), THF, 100°	 (78)	109
200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 6 h	 I + II (79), I:II = 15:1	108
200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 1.5 h	 (40) I:II = 14:1	108

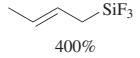
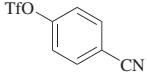
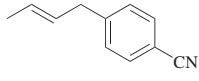
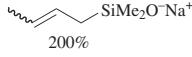
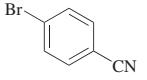
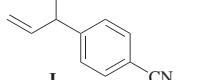
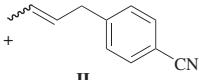
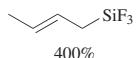
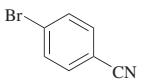
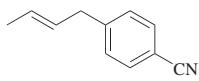
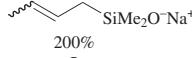
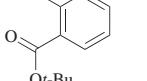
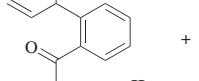
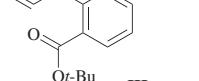
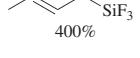
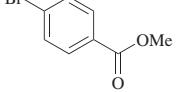
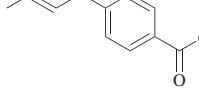
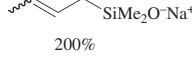
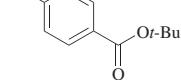
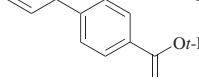
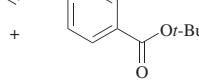
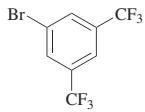
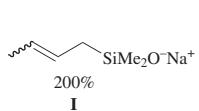
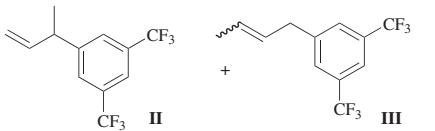
		PdCl ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 12 h		(100) (E)/(Z) = 5.7:1	110
		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 6 h	 I	 II	108
		PdCl ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 12 h		(88) (E)/(Z) = 5.7:1	110
		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 20 h	 II	 III	108
			I (E)/(Z)	II + III	
			80:20	(82)	1:2.5
			>97:3	(82)	1:2.5
			<4:96	(79)	1:2.5
					III (E)/(Z)
					8.3:1
					8.4:1
					8.4:1
		PdCl ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 12 h		(95) (E)/(Z) = 7.2:1	110
		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 20 h	 I	 II	108
			I + II (67)	I:II	
					25:1

TABLE 5A. CROSS-COUPLED OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 200%			Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 4 h 	108
150%			Pd(OAc) ₂ (5%), dppb (10%), TASF (100%), THF, 100° 	(96) 109
400%			PdCl ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 12 h 	(92) (E)/(Z) = 7.2:1 110
400%			PdCl ₂ (5%), L (5%), TBAF (300%), THF, 120° 	I I + II (85), I:II = 55:45 110
		L	I + II I:II I (E)/(Z)	
		Ph ₂ PCH ₂ PPh ₂	(85)	4.6:1
		Ph ₂ P(CH ₂) ₂ PPh ₂	(86)	8.1:1
		Ph ₂ P(CH ₂) ₃ PPh ₂	(92)	7.2:1
		Ph ₂ P(CH ₂) ₄ PPh ₂	(57)	4.3:1
		Ph ₂ P(CH ₂) ₅ PPh ₂	(77)	4.8:1
		Ph ₃ P	(97)	—
150%			Pd(PPh ₃) ₄ (5%), TBAF (150%), THF, 80° 	(95) 109

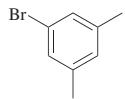


Pd(dba)₂ (5%),
norbornadiene (5%),
toluene, 70°, 3 h

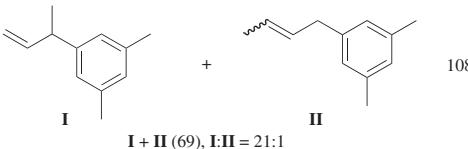
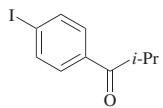
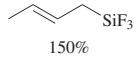


I (E)/(Z)	II + III	II:III
80:20	(62)	3.4:1
>97:3	(74)	3.6:1
<4:96	(68)	2.6:1

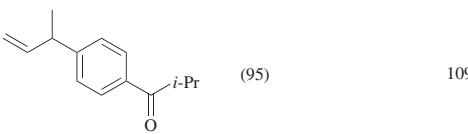
200%



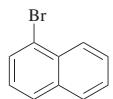
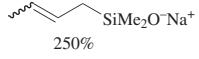
Pd(dba)₂ (5%),
norbornadiene (5%),
toluene, 70°, 6 h

**I + II (69), I:II = 21:1**

Pd(PPh₃)₄ (5%), TBAF (150%),
THF, 100°, 90 h



(95)



[allylPdCl₂]₂ (2.5%),
Ph₃PO (5%),
DME, 85°, 1 h

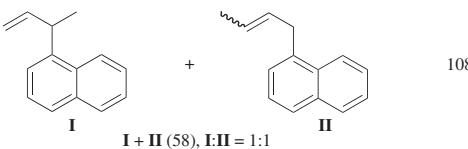
**I + II (58), I:II = 1:1**

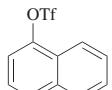
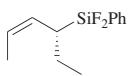
TABLE 5A. CROSS-COUPLED OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄				
200% I		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 6 h	 II + III	108
200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 6 h	 I + II (80), I:II = 25:1	108
200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 3 h	 I + II (69), I:II = 24:1	108
200% I		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 20 h	 II + III	108
			I (E)/(Z) I + II II:III	
			80:20 (50) 14:1	
			>97:3 (51) 25:1	
			<4:96 (51) 13:1	

	<chem>NCCCCSiF3</chem> 200%	<chem>Ic1ccc(C)c(I)c1</chem>	Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 24 h	<chem>CNCCCCc1ccc(C)c(I)c1</chem> (86)	190												
	<chem>CC(=O)OCCCSiF3</chem> 200%	<chem>Ic1ccc(C)c(I)c1</chem>	Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 22 h	<chem>CC(=O)OCCCCc1ccc(C)c(I)c1</chem> (45)	190												
C ₅																	
	<chem>CC(C)=CCC[Si]F3</chem> 150%	<chem>Ic1ccc(OC)c(I)c1</chem>	Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (150%), THF, 100°	<chem>CC(C)=CCCc1ccc(OC)c(I)c1</chem> (51)	109												
		<chem>Tc1ccc(C#N)c(I)c1</chem> 400%	PdCl ₂ (<i>Ph</i> ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°, 48 h	<chem>CC(C)=CCCc1ccc(C#N)c(I)c1</chem> (49)	110												
	<chem>CC(=O)OCc1ccc(I)c(I)c1</chem> 400%	<chem>Ic1ccc(OC)c(I)c1</chem>	PdCl ₂ (<i>Ph</i> ₂ P(CH ₂) ₃ PPh ₂) (5%), TBAF (300%), THF, 120°	<chem>CC(C)=CCCc1ccc(OC)c(I)c1 + CC(C)=CCCc1ccc(C(=O)OC)c(I)c1</chem> I + II	110												
	<chem>Ic1ccc(C)c(I)c1</chem> 150%			<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>OTf</td> <td>(60)</td> <td>100:0</td> </tr> <tr> <td>Br</td> <td>(38)</td> <td>1:1</td> </tr> <tr> <td>I</td> <td>(35)</td> <td>73:27</td> </tr> </tbody> </table>	R	I + II	I:II	OTf	(60)	100:0	Br	(38)	1:1	I	(35)	73:27	
R	I + II	I:II															
OTf	(60)	100:0															
Br	(38)	1:1															
I	(35)	73:27															
			Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (300%), THF, 100°	<chem>CC(C)=CCCc1ccc(C)c(I)c1</chem> (70)	109												

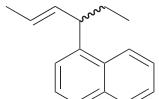
TABLE 5A. CROSS-COUPING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.									
C_5		Pd(Ph_3P) ₄ (4.3%), TASF (400%), DMF, 60°	 (39), er = 79.5:20.5, (<i>E</i>)/(<i>Z</i>) = 3.1:1	115									
C_6		Pd(Ph_3P) ₄ (5%), TASF (400%), solvent, 60°	 <table border="1" style="margin-left: auto; margin-right: auto;"><tr><th>Solvent</th><th>er</th><th>(<i>E</i>)/(<i>Z</i>)</th></tr><tr><td>THF</td><td>(64)</td><td>70.5:29.5</td></tr><tr><td>DMF</td><td>(70)</td><td>83:17</td></tr></table>	Solvent	er	(<i>E</i>)/(<i>Z</i>)	THF	(64)	70.5:29.5	DMF	(70)	83:17	115
Solvent	er	(<i>E</i>)/(<i>Z</i>)											
THF	(64)	70.5:29.5											
DMF	(70)	83:17											
724		Pd(Ph_3P) ₄ (5%), TBAF (200%), THF, 100°, 38 h	 (62)	190									
		Pd(Ph_3P) ₄ (5%), TBAF (200%), THF, 100°, 24 h	 (61)	190									
		Pd(Ph_3P) ₄ (5%), TBAF (200%), THF, 100°, 37 h	 (63)	190									
		Pd(Ph_3P) ₄ (5%), TBAF (200%), THF, 100°, 24 h	 (62)	190									

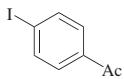
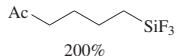
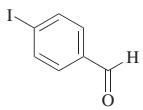
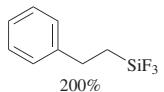
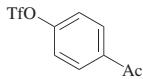
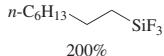


120%

Pd(Ph_3P)₄ (4.3%), F⁻ (400%),
solvent, 60°

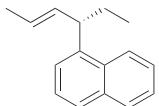


115

C₈

F ⁻	Solvent	er	(E)/(Z)
TASF	THF (50)	76.5:23.5	<i>S</i> 9.3:1
TASF	DMF (64)	81.5:18.5	<i>S</i> 24:1
CsF	THF (50)	75.5:24.5	<i>R</i> 42:2
CsF	DMF (50)	81:19	<i>S</i> 15:1
KF	THF (50)	55:45	<i>R</i> 100:0
CsF/18-crown-6	THF (38)	56.5:43.5	<i>S</i> 16:1

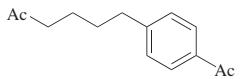
Pd(Ph_3P)₄ (4.3%), TASF (400%),
solvent, 60°



115

Solvent	er	(E)/(Z)
THF (68)	70:30	4.5:1
DMF (55)	83.5:16.5	4.3:1

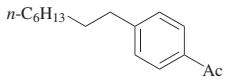
Pd(Ph_3P)₄ (5%), TBAF (400%),
THF, 100°, 18 h



(66)

190

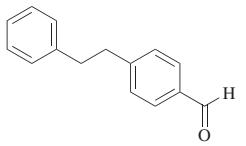
Pd(Ph_3P)₄ (5%), TBAF (200%),
THF, 50°, 2.5 h



(65)

181

Pd(Ph_3P)₄ (5%), TBAF (200%),
THF, 100°, 24 h



(61)

190

TABLE 5A. CROSS-COUPLING OF sp^3 -ORGANOSILANES WITH ARYL ELECTROPHILES (Continued)

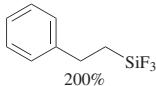
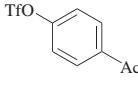
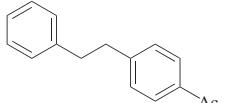
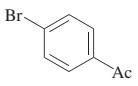
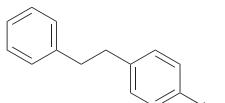
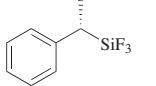
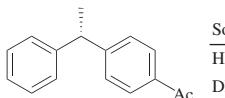
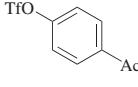
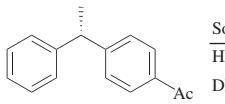
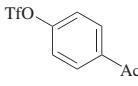
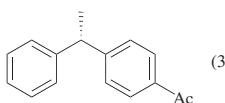
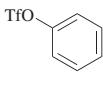
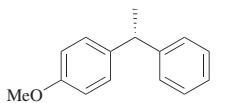
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.								
C ₈												
		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), THF, 50°, 2.5 h	 (71)	181								
200%		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), THF, 100°, 34 h	 (71)	190								
726		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), solvent, 60°		<table> <thead> <tr> <th>Solvent</th> <th>er</th> </tr> </thead> <tbody> <tr> <td>HMPA/THF (1:10)</td> <td>54:46 (<i>R</i>)</td> </tr> <tr> <td>DMF/THF (1:10)</td> <td>58:42 (<i>S</i>)</td> </tr> <tr> <td>DMSO/THF (1:10)</td> <td>58:42 (<i>S</i>)</td> </tr> </tbody> </table> 117	Solvent	er	HMPA/THF (1:10)	54:46 (<i>R</i>)	DMF/THF (1:10)	58:42 (<i>S</i>)	DMSO/THF (1:10)	58:42 (<i>S</i>)
Solvent	er											
HMPA/THF (1:10)	54:46 (<i>R</i>)											
DMF/THF (1:10)	58:42 (<i>S</i>)											
DMSO/THF (1:10)	58:42 (<i>S</i>)											
200%		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), solvent, 60°		<table> <thead> <tr> <th>Solvent</th> <th>er</th> </tr> </thead> <tbody> <tr> <td>HMPA/THF (1:10)</td> <td>54:46 (<i>R</i>)</td> </tr> <tr> <td>DMF/THF (1:10)</td> <td>58:42 (<i>S</i>)</td> </tr> <tr> <td>DMSO/THF (1:10)</td> <td>58:42 (<i>S</i>)</td> </tr> </tbody> </table> 117	Solvent	er	HMPA/THF (1:10)	54:46 (<i>R</i>)	DMF/THF (1:10)	58:42 (<i>S</i>)	DMSO/THF (1:10)	58:42 (<i>S</i>)
Solvent	er											
HMPA/THF (1:10)	54:46 (<i>R</i>)											
DMF/THF (1:10)	58:42 (<i>S</i>)											
DMSO/THF (1:10)	58:42 (<i>S</i>)											
200%		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), THF, 50°	 (31–51), er = 66:34–67:33	117								
200%		Pd(<i>Ph</i> ₃ P) ₄ (5%), TBAF (200%), THF, 60°	 (35), er = 54.5:44.5	117								

TABLE 5B. CROSS-COUPLING OF SP³-ORGANOSILANES WITH HETEROARYL ELECTROPHILES

	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁	(Et ₂ N) ₃ S ⁺ Me ₃ SiF ₂ ⁻ 150%		[allylPdCl] ₂ (2.5%), DMF, 80°, 24 h	 (79)	275
	150%		[allylPdCl] ₂ (2.5%), DMF, 80°, 24 h	 (66)	275
C ₃	MeO-C(=O)-CH ₂ -CH ₂ -SiF ₃ 200%		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 48 h	 (36)	190
	200%		Pd(Ph ₃ P) ₄ (5%), TBAF (400%), THF, 100°, 8 h	 (65)	190
C ₄	 200%		Pd(dba) ₂ (5%), norbornadiene (5%), toluene, 70°, 3.5 h	 I + II (83), I : II = 19:1	108

TABLE 5C. CROSS-COUPLING OF sp^3 -ORGANOSILANES WITH ALKENYL ELECTROPHILES

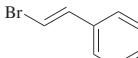
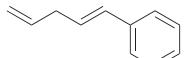
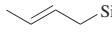
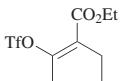
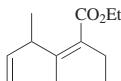
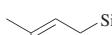
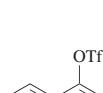
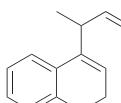
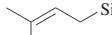
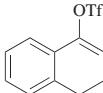
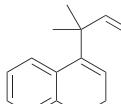
	Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃	 133%		[allylPdCl]2 (2.5%), TASF (133%), THF, rt	 (28)	23
C ₄	 150%		Pd(OAc) ₂ (5%), dppb (10%), TASF (100%), THF, 120°	 (98)	109
	 150%		Pd(OAc) ₂ (5%), dppb (10%), TASF (100%), THF, 100°	 (85)	109
C ₅	 150%		Pd(OAc) ₂ (5%), dppb (10%), TASF (100%), THF, 120°	 (83)	109

TABLE 5D. CROSS-COUPLING OF sp^3 -ORGANOSILANES WITH ALKYL ELECTROPHILES

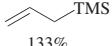
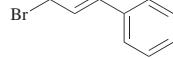
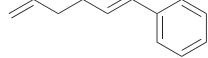
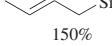
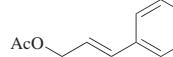
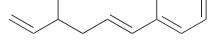
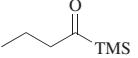
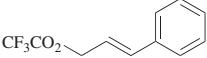
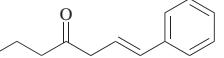
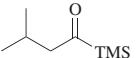
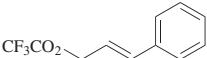
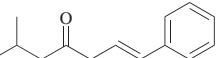
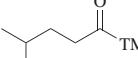
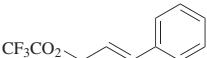
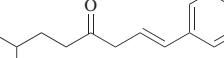
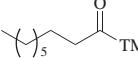
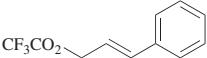
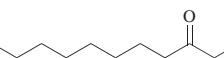
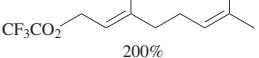
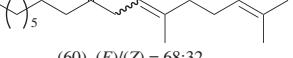
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃  133%		[allylPdCl] ₂ (5%), TASF (133%), THF, rt	 (83)	23
C ₄  150%		Pd(PPh ₃) ₄ (5%), TBAF (150%), THF, 60°	 (54)	109

TABLE 6. CROSS-CO尤LING OF ACYL ORGANOSILANES WITH ALLYL ELECTROPHILES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄		 200%	Pd cat. 6 (5%), THF, reflux, 16 h 	(55) 148
C ₅		 200%	Pd cat. 6 (5%), THF, reflux, 16 h 	(43) 148
C ₆		 200%	Pd cat. 6 (5%), THF, reflux, 16 h 	(56) 148
C ₉		 200%	Pd cat. 6 (5%), THF, reflux, 16 h 	(63) 148
	 200%	Pd cat. 6 (5%), THF, reflux, 16 h  (60), (E)/(Z) = 68:32		148

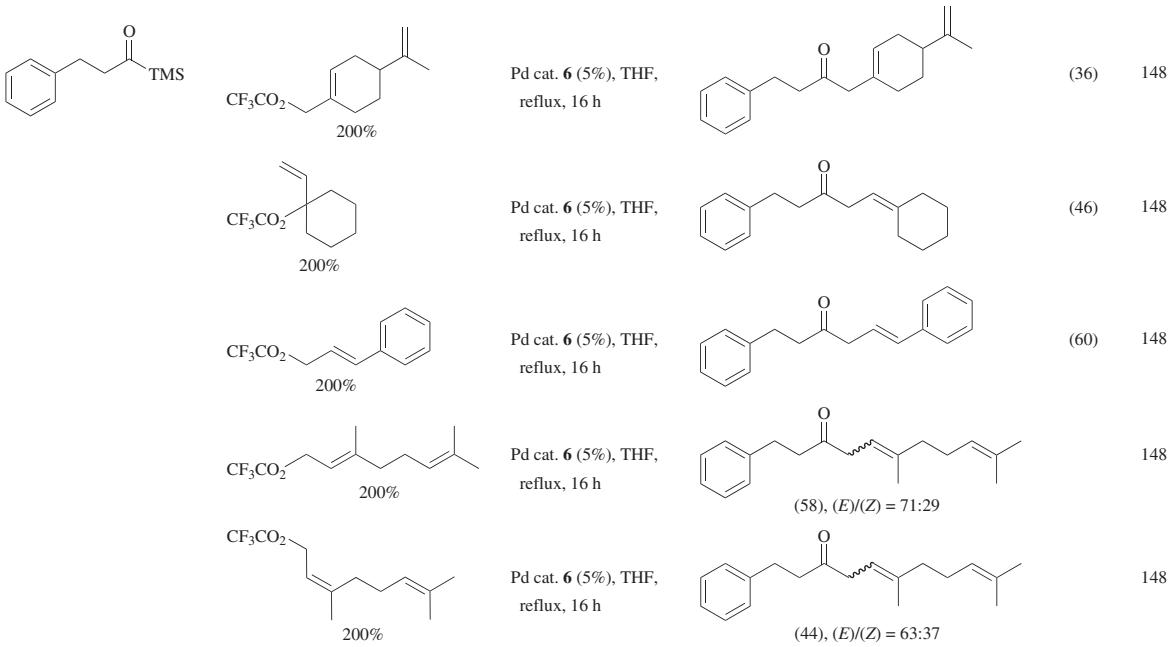
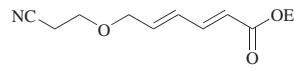
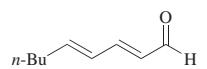
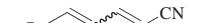
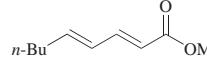
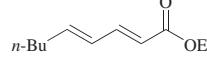
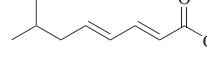
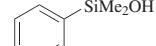
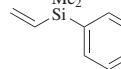
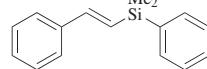


TABLE 7. OXIDATIVE HECK REACTION OF ALKENYL- AND ARYLSILANES

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ $\text{K}_2\left[\text{NC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}=\text{CH}-\text{SiF}_5\right]$ 1000%		Pd(OAc) ₂ (100%), THF, rt, 20 h	 (23)	21
C ₆ $\text{K}_2\left[n\text{-Bu}-\text{CH}=\text{CH}-\text{SiF}_5\right]$ 1000%		Pd(OAc) ₂ (100%), THF, rt, 4 h	 (20)	21
		Pd(OAc) ₂ (100%), THF, rt, 45 h	 (43)	21
		Pd(OAc) ₂ (100%), THF, rt, 47 h	 (37)	21
		Pd(OAc) ₂ (100%), THF, rt, 20 h	 (48)	21
K ₂ $\text{K}_2\left[i\text{-Bu}-\text{CH}=\text{CH}-\text{SiF}_5\right]$ 1000%		Pd(OAc) ₂ (100%), THF, rt, 20 h	 (38)	21
		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h	 (57)	277

	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(34) (<i>E</i>)/(<i>Z</i>) ~ 2:1	277
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (300%), LiOAc (200%), DMF, 100°, 3 h		(43) (<i>E</i>)/(<i>Z</i>) ~ 5:2	203
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(37)	277
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(56)	277
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (300%), LiOAc (200%), DMF, 100°, 3 h		(70)	203
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(69)	277
	100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, rt, 48 h		(57)	277

TABLE 7. OXIDATIVE HECK REACTION OF ALKENYL- AND ARYLSILANES (*Continued*)

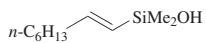
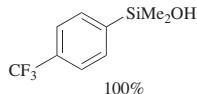
Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆		[Ir(OMe)(cod)] ₂ (3%), toluene, 120°, 24 h		(64)
				279
		[IrCl(cod)] ₂ (5%), TBAF (100%), toluene/H ₂ O (6:1), 120°, 24 h		(71) (0)
		[IrCl(cod)] ₂ (5%), TBAF (100%), toluene/H ₂ O (6:1), 70°, 24 h		(62) (3)
		[IrCl(cod)] ₂ (5%), TBAF (100%), toluene/H ₂ O (6:1), 120°, 24 h		(70) (5)
		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h		(48)
		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (300%), LiOAc (200%), DMF, 100°, 3 h		(79)
		[Ir(OMe)(cod)] ₂ (3%), toluene, 120°, 24 h		(50) (4)
				279
				203

<chem>K2[PhSiF5]</chem>		[Ir(OMe)(cod)]2 (3%), toluene/H2O (6:1), 120°, 24 h		(41)		(8)	279
		Pd(OAc)2 (100%), MeCN, reflux, 32 h		(53)		21	
		Pd(OAc)2 (10%), Cu(OAc)2 (100%), LiOAc (200%), DMF, 100°, 48 h		(55) (E)/(Z) ~ 9:1		277	
100%		Pd(OAc)2 (10%), Cu(OAc)2 (100%), LiOAc (200%), DMF, 100°, 48 h		(49)		277	
100%		Pd(OAc)2 (10%), Cu(OAc)2 (100%), LiOAc (200%), DMF, 100°, 24 h		(63)		277	
		Pd(OAc)2 (10%), Cu(OAc)2 (300%), LiOAc (200%), DMF, 100°, 3 h		(59)		203	
100%		Pd(OAc)2 (10%), Cu(OAc)2 (100%), LiOAc (200%), DMF, 100°, 24 h		(55)		277	
100%							

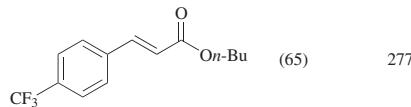
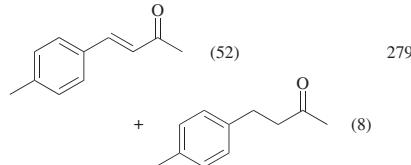
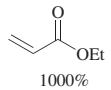
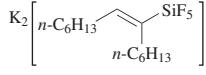
TABLE 7. OXIDATIVE HECK REACTION OF ALKENYL- AND ARYLSILANES (*Continued*)

Silane	Electrophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		 300%		[Ir(OMe)(cod)] ₂ (5%), toluene/H ₂ O (6:1), 120°, 24 h (62) 279
		 300%		[IrCl(cod)] ₂ (5%), TBAF (100%), THF/H ₂ O (6:1), 70°, 24 h (70) 279
C_7		 100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h (54) 277
		 300%		[Ir(OMe)(cod)] ₂ (7.5%), TBAF (100%), toluene/H ₂ O (6:1), 70°, 24 h (61) 279
		 100%		Pd(OAc) ₂ (10%), Cu(OAc) ₂ (100%), LiOAc (200%), DMF, 100°, 24 h (54) 277
		 300%		[Ir(OMe)(cod)] ₂ (5%), toluene/H ₂ O (6:1), 120°, 24 h (63) 279

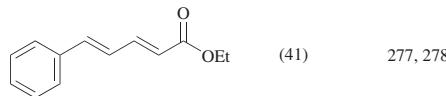
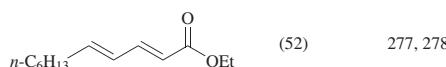
737

C₈

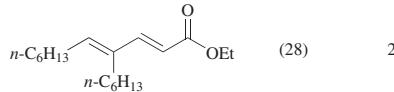
[Ir(OMe)(cod)]₂ (3%),
toluene/H₂O (6:1),
120°, 24 h

C₁₄

Pd(OAc)₂ (10%),
Cu(OAc)₂ (100%),
LiOAc (200%),
DMF, 100°, 24 h



Pd(OAc)₂ (10%),
Cu(OAc)₂ (300%),
LiOAc (200%),
DMF, 100°, 44 h



REFERENCES

- ¹ Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.
- ² Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1983.
- ³ Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, pp 541–686.
- ⁴ Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: West Sussex, 1999.
- ⁵ Katsukyo, M.; Hosomi, A. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 409–592.
- ⁶ Corriu, R.; Masse, J. *J. Chem. Soc., Chem. Commun.* **1972**, 144.
- ⁷ Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, 94, 4374.
- ⁸ Suzuki, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Great Britain, 1998, pp 49–97.
- ⁹ Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 41–123.
- ¹⁰ Suzuki, A. *Organoboranes in Organic Syntheses*; Hokkaido University Press: Sapporo, 2004.
- ¹¹ Knochel, P. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Great Britain, 1998, pp 387–419.
- ¹² Knochel, P.; Calaza, M. I.; Hupe, E. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, pp 619–670.
- ¹³ Mitchell, T. N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 125–161.
- ¹⁴ Mitchell, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Great Britain, 1998, pp 167–202.
- ¹⁵ Farina, V.; Krishnamurthy, V.; Scott, W. *Org. React.* **1997**, **50**, 1.
- ¹⁶ Pauling, L. C. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1960.
- ¹⁷ Chuit, C.; Corriu, R.; Reye, C.; Young, J. *Chem. Rev.* **1993**, 93, 1371.
- ¹⁸ Corriu, R.; Young, J. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: Great Britain, 1991, pp 1–47.
- ¹⁹ Corriu, R.; Young, J. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: Great Britain, 1991, pp 49–66.
- ²⁰ Chuit, C.; Corriu, R.; Reye, C. In *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1999, pp 147–170.
- ²¹ Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, **1**, 542.
- ²² Hosomi, A.; Kohra, S.; Tominaga, Y. *Chem. Pharm. Bull.* **1988**, **36**, 4622.
- ²³ Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, **53**, 918.
- ²⁴ Walsh, R. *Acc. Chem. Res.* **1981**, **14**, 246.
- ²⁵ Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, **54**, 268.
- ²⁶ Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, **30**, 6051.
- ²⁷ Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.
- ²⁸ Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Great Britain, 1998, pp 421–453.
- ²⁹ Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, **219**, 61.
- ³⁰ Hiyama, T. *J. Organometal. Chem.* **2002**, **653**, 58.
- ³¹ Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, **2**, 565.
- ³² Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2001**, **123**, 6439.
- ³³ Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, **35**, 835.
- ³⁴ Denmark, S. E.; Sweis, R. F. *Chem. Pharm. Bull.* **2002**, **50**, 1531.
- ³⁵ Denmark, S. E.; Ober, M. H. *Aldrichimica Acta* **2003**, **36**, 75.
- ³⁶ Hirabayashi, K.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Org. Lett.* **1999**, **1**, 299.
- ³⁷ Hirabayashi, E.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, **65**, 5342.
- ³⁸ Denmark, S. E.; Choi, J. Y. *J. Am. Chem. Soc.* **1999**, **121**, 5821.

- ³⁹ Denmark, S. E.; Wu, Z. *Org. Lett.* **1999**, *1*, 1495.
- ⁴⁰ Denmark, S. E.; Wang, Z. *Synthesis* **2000**, 999.
- ⁴¹ Anderson, J. C.; Anguille, S.; Bailey, R. *Chem. Commun.* **2002**, 2018.
- ⁴² Anderson, J. C.; Munday, R. H. *J. Org. Chem.* **2004**, *69*, 8971.
- ⁴³ Trost, B. M.; Machacek, M. R.; Ball, Z. T. *Org. Lett.* **2003**, *5*, 1895.
- ⁴⁴ Denmark, S. E.; Tymonko, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 8004.
- ⁴⁵ Denmark, S. E.; Liu, J. H. C. *J. Am. Chem. Soc.* **2007**, *129*, 3737.
- ⁴⁶ Nakao, Y.; Oda, T.; Sahoo, A. K.; Hiyama, T. *J. Organometal. Chem.* **2003**, *687*, 570.
- ⁴⁷ Sahoo, A. K.; Oda, T.; Nakao, Y.; Hiyama, T. *Adv. Synth. Catal.* **2004**, *346*, 1715.
- ⁴⁸ Hiyama, T. *Proc. Japan Acad.* **2002**, *78B*, 154.
- ⁴⁹ Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, 138.
- ⁵⁰ Itami, K.; Mitsudo, K.; Nokami, T.; Kamei, T.; Koike, T.; Yoshida, J. *J. Organometal. Chem.* **2002**, *653*, 105.
- ⁵¹ Nokami, T.; Tomida, Y.; Kamei, T.; Itami, K.; Yoshida, J. *Org. Lett.* **2006**, *8*, 729.
- ⁵² Itami, K.; Yoshida, J. *Synlett* **2006**, 157.
- ⁵³ Denmark, S. E.; Baird, J. D. *Chem. Eur. J.* **2006**, *12*, 4954.
- ⁵⁴ Denmark, S. E.; Smith, R. C.; Chang, W.-T. T.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 3104.
- ⁵⁵ Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486.
- ⁵⁶ Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471.
- ⁵⁷ Nakao, Y.; Sahoo, A. K.; Imanaka, H.; Yada, A.; Hiyama, T. *Pure Appl. Chem.* **2006**, *78*, 435.
- ⁵⁸ Spivey, A. C.; Gripton, C. J. G.; Hannah, J. P. *Curr. Org. Synth.* **2004**, *1*, 211.
- ⁵⁹ Oestreich, M.; Sempere-Culler, F.; Machotta, A. B. *Angew. Chem. Int. Ed.* **2005**, *44*, 149.
- ⁶⁰ Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 163–216.
- ⁶¹ Denmark, S. E. *J. Org. Chem.* **2009**, *74*, 2915.
- ⁶² Denmark, S. E.; Butler, C. R. *Chem. Commun.* **2009**, 20.
- ⁶³ Denmark, S. E.; Liu, J. H.-C. *Angew. Chem. Int. Ed.* **2010**, *49*, 2978.
- ⁶⁴ Echavarren, A. M.; Cardenas, D. J. In *Metal-Catalyzed Cross-Coupling Reactions*; 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 1–40.
- ⁶⁵ Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.
- ⁶⁶ Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.
- ⁶⁷ Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.
- ⁶⁸ Mateo, C.; Fernandez-Rivas, C.; Echavarren, A. M.; Cardenas, D. J. *Organometallics* **1997**, *16*, 1997.
- ⁶⁹ Mowery, M. E.; DeShong, P. J. *Org. Chem.* **1999**, *64*, 3266.
- ⁷⁰ Mowery, M. E.; Deshong, P. J. *Org. Chem.* **1999**, *64*, 1684.
- ⁷¹ Handy, C. J.; Manoso, A. S.; McElroy, W. T.; Seganish, W. M.; DeShong, P. *Tetrahedron* **2005**, *61*, 12201.
- ⁷² Denmark, S. E.; Neuville, L.; Christy, M. E. L.; Tymonko, S. A. *J. Org. Chem.* **2006**, *71*, 8500.
- ⁷³ Hatanaka, Y.; Goda, K.; Okahara, Y.; Hiyama, T. *Tetrahedron* **1994**, *50*, 8301.
- ⁷⁴ Denmark, S. E.; Sweis, R. F.; Wehrli, D. *J. Am. Chem. Soc.* **2004**, *126*, 4865.
- ⁷⁵ Denmark, S. E.; Wehrli, D.; Choi, J. Y. *Org. Lett.* **2000**, *2*, 2491.
- ⁷⁶ Sugiyama, A.; Ohnishi, Y. Y.; Nakaoka, M.; Nakao, Y.; Sato, H.; Sakaki, S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 12975.
- ⁷⁷ Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 4876.
- ⁷⁸ Denmark, S. E.; Smith, R. C. *J. Am. Chem. Soc.* **2010**, *132*, 1243.
- ⁷⁹ Denmark, S. E.; Pan, W. J. *Organomet. Chem.* **2002**, *653*, 98.
- ⁸⁰ Denmark, S. E.; Kallemeijn, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 15958.
- ⁸¹ Denmark, S. E.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 5153.
- ⁸² Kikukawa, K.; Umekawa, H.; Matsuda, T. *J. Organomet. Chem.* **1986**, *311*, C44.
- ⁸³ Farina, V.; Hossain, M. A. *Tetrahedron Lett.* **1996**, *37*, 6997.

- ⁸⁴ Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553.
- ⁸⁵ Fillion, E.; Taylor, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 12700.
- ⁸⁶ Hosomi, A.; Kohra, S.; Tominaga, Y. *Chem. Pharm. Bull.* **1988**, *36*, 4622.
- ⁸⁷ Hojo, M.; Murakami, C.; Aihara, H.; Komori, E.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Bull. Soc. Chim. France* **1995**, *132*, 499.
- ⁸⁸ Matsuhashi, H.; Hatanaka, Y.; Kuroboshi, M.; Hiyama, T. *Heterocycles* **1996**, *42*, 375.
- ⁸⁹ Hatanaka, Y.; Goda, K.; Hiyama, T. *J. Organomet. Chem.* **1994**, *465*, 97.
- ⁹⁰ Naso, F.; Babudri, F.; Farinola, G. M. *Pure Appl. Chem.* **1999**, *71*, 1485.
- ⁹¹ Babudri, F.; Farinola, G. M.; Lopez, L. C.; Martinelli, M. G.; Naso, F. *J. Org. Chem.* **2001**, *66*, 3878.
- ⁹² Ancora, R.; Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Eur. J. Org. Chem.* **2002**, 4127.
- ⁹³ Kikukawa, K.; Ikenaga, K.; Wada, F.; Matsuda, T. *Chem. Lett.* **1983**, 1337.
- ⁹⁴ Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K.; Wada, F.; Matsuda, T. *J. Organometal. Chem.* **1984**, *270*, 277.
- ⁹⁵ Kikukawa, K.; Ikenaga, K.; Wada, F.; Matsuda, T. *Tetrahedron Lett.* **1984**, *25*, 5789.
- ⁹⁶ Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Perkin Trans. I* **1986**, 1959.
- ⁹⁷ Ikenaga, K.; Matsumoto, S.; Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1988**, 873.
- ⁹⁸ Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.
- ⁹⁹ Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.
- ¹⁰⁰ Daves, G. D.; Hallberg, A. *Chem. Rev.* **1989**, *89*, 1433.
- ¹⁰¹ Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.
- ¹⁰² Albéniz, A. C.; Espinet, P.; López-Fernández, R. *Organometallics* **2006**, *25*, 5449.
- ¹⁰³ Gordillo, A.; de Jesús, E.; López-Mardomingo, C. *J. Am. Chem. Soc.* **2009**, *131*, 4584.
- ¹⁰⁴ Prukala, W.; Pawluc, P.; Posala, K.; Marciniec, B. *Synlett* **2008**, 41.
- ¹⁰⁵ Kjellgran, J.; Kritikos, M.; Szabó, K. J. *J. Organomet. Chem.* **2006**, *691*, 3640.
- ¹⁰⁶ Mascári, I.; Szabó, K. J. *Chem. Eur. J.* **2001**, *7*, 4097.
- ¹⁰⁷ Kliegman, J. M. *J. Organomet. Chem.* **1971**, *29*, 73.
- ¹⁰⁸ Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 16382.
- ¹⁰⁹ Hatanaka, Y.; Ebina, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 7075.
- ¹¹⁰ Hatanaka, Y.; Goda, K.-I.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 6511.
- ¹¹¹ Hoke, M. E.; Brescia, M. R.; Bogaczyk, S.; DeShong, P.; King, B. W.; Crimmins, M. T. *J. Org. Chem.* **2002**, *67*, 327.
- ¹¹² Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1994**, *59*, 5130.
- ¹¹³ Denmark, S. E.; Almstead, N. G. *J. Mex. Chem. Soc.* **2009**, *53*, 174.
- ¹¹⁴ Ohmura, H.; Matsuhashi, H.; Tanaka, M.; Kuroboshi, M.; Hiyama, T.; Hatanaka, Y.; Goda, K.-I. *J. Organomet. Chem.* **1995**, *499*, 167.
- ¹¹⁵ Hatanaka, Y.; Goda, K.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 1279.
- ¹¹⁶ Denmark, S. E.; Werner, N. S. *J. Am. Chem. Soc.* **2010**, *132*, 3612.
- ¹¹⁷ Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793.
- ¹¹⁸ Dai, X.; Strotman, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3302.
- ¹¹⁹ Taguchi, H.; Takami, K.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2004**, *45*, 429.
- ¹²⁰ Akai, S.; Ikawa, T.; Takayanagi, S. I.; Morikawa, Y.; Mohri, S.; Tsubakiyama, M.; Egi, M.; Wada, Y.; Kita, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 7673.
- ¹²¹ Dick, G. R.; Knapp, D. M.; Gillis, E. P.; Burke, M. D. *Org. Lett.* **2010**, *12*, 2314.
- ¹²² Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 6314.
- ¹²³ Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697.
- ¹²⁴ Babudri, F.; Farinola, G. M.; Naso, F.; Panessa, D. *J. Org. Chem.* **2000**, *65*, 1554.
- ¹²⁵ Babudri, F.; Farinola, G. M.; Fiandanese, V.; Mazzone, L.; Naso, F. *Tetrahedron* **1998**, *54*, 1085.
- ¹²⁶ Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *Org. Lett.* **2001**, *3*, 3811.
- ¹²⁷ Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *J. Org. Chem.* **2002**, *67*, 8450.
- ¹²⁸ Murakami, M.; Matsuda, T.; Itami, K.; Ashida, S.; Terayama, M. *Synthesis* **2004**, 1522.
- ¹²⁹ Park, P. K.; O'Malley, S. J.; Schmidt, D. R.; Leighton, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 2796.
- ¹³⁰ Taguchi, H.; Miyashita, H.; Tsubouchi, A.; Takeda, T. *Chem. Commun.* **2002**, 2218.

- ¹³¹ Nishihara, Y.; Ikegashira, K.; Mori, A.; Hiyama, T. *Chem. Lett.* **1997**, 1233.
- ¹³² Kang, S. K.; Ryu, H. C.; Hong, Y. T. *J. Chem. Soc., Perkin Trans. I* **2001**, 736.
- ¹³³ Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, 65, 1780.
- ¹³⁴ Hatanaka, Y.; Matsui, K.; Hiyama, T. *Tetrahedron Lett.* **1989**, 30, 2403.
- ¹³⁵ Marsden, J. A.; Haley, M. M. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 317–394.
- ¹³⁶ Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley-VCH: Great Britain, 1998, pp 203–229.
- ¹³⁷ Koseki, Y.; Omino, K.; Anzai, S.; Nagasaka, T. *Tetrahedron Lett.* **2000**, 41, 2377.
- ¹³⁸ Chang, S.; Yang, S. H.; Lee, P. H. *Tetrahedron Lett.* **2001**, 42, 4833.
- ¹³⁹ Marshall, J. A.; Chobanian, H. R.; Yanik, M. M. *Org. Lett.* **2001**, 3, 4107.
- ¹⁴⁰ Sorensen, U. S.; Pombo-Villar, E. *Tetrahedron* **2005**, 61, 2697.
- ¹⁴¹ Nishihara, Y.; Inoue, E.; Okada, Y.; Takagi, K. *Synlett* **2008**, 3041.
- ¹⁴² Halbes, U.; Bertus, P.; Pale, P. *Tetrahedron Lett.* **2001**, 42, 8641.
- ¹⁴³ Halbes, U.; Pale, P. *Tetrahedron Lett.* **2002**, 43, 2039.
- ¹⁴⁴ Nishihara, Y.; Ikegashira, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, 39, 4075.
- ¹⁴⁵ Girard, D.; Brousseau, S.; Provost, O.; Brion, J. D.; Alami, M. *Tetrahedron Lett.* **2007**, 48, 6022.
- ¹⁴⁶ Kamijo, S.; Jin, T.; Yamamoto, Y. *Tetrahedron Lett.* **2004**, 45, 689.
- ¹⁴⁷ Nishihara, Y.; Ando, J.; Kato, T.; Mori, A.; Hiyama, T. *Macromolecules* **2000**, 33, 2779.
- ¹⁴⁸ Obora, Y.; Ogawa, Y.; Imai, Y.; Kawamura, T.; Tsuji, Y. *J. Am. Chem. Soc.* **2001**, 123, 10489.
- ¹⁴⁹ Nakao, Y.; Chen, J. S.; Tanaka, M.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, 129, 11694.
- ¹⁵⁰ Nakao, Y.; Imanaka, H.; Chen, J. S.; Yada, A.; Hiyama, T. *J. Organometal. Chem.* **2007**, 692, 585.
- ¹⁵¹ Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, 127, 6952.
- ¹⁵² Nakao, Y.; Ebata, S.; Chen, J. S.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, 36, 606.
- ¹⁵³ Denmark, S. E.; Griedel, B. D. *J. Org. Chem.* **1994**, 59, 5136.
- ¹⁵⁴ Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, 116, 7026.
- ¹⁵⁵ Denmark, S. E.; Griedel, B. D.; Coe, D. M. *J. Org. Chem.* **1993**, 58, 988.
- ¹⁵⁶ Denmark, S. E.; Jacobs, R. T.; Dai-Ho, G. *Organometallics* **1990**, 9, 3015.
- ¹⁵⁷ Li, L. H.; Navasero, N. *Org. Lett.* **2006**, 8, 3733.
- ¹⁵⁸ Denmark, S. E.; Liu, J. H.-C. *Isr. J. Chem.* **2010**, 50, 577.
- ¹⁵⁹ Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, 127, 17644.
- ¹⁶⁰ Sahoo, A. K.; Nakao, Y.; Hiyama, T. *Chem. Lett.* **2004**, 33, 632.
- ¹⁶¹ Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, 125, 11818.
- ¹⁶² Rossi, R.; Carpita, A.; Messeri, T. *Gazz. Chim. Ital.* **1992**, 122, 65.
- ¹⁶³ Hanamoto, T. *J. Syn. Org. Chem. Jpn.* **2002**, 60, 1168.
- ¹⁶⁴ Hanamoto, T.; Kobayashi, T.; Kondo, M. *Synlett* **2001**, 281.
- ¹⁶⁵ Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organometal. Chem.* **2003**, 676, 49.
- ¹⁶⁶ Katayama, H.; Nagao, M.; Ozawa, F.; Ikegami, M.; Arai, T. *J. Org. Chem.* **2006**, 71, 2699.
- ¹⁶⁷ Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, 645, 192.
- ¹⁶⁸ Murata, M.; Ohara, H.; Oiwa, R.; Watanabe, S.; Masuda, Y. *Synthesis* **2006**, 1771.
- ¹⁶⁹ Itami, K.; Nokami, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, 123, 5600.
- ¹⁷⁰ Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, 123, 11577.
- ¹⁷¹ Denmark, S. E.; Neuville, L. *Org. Lett.* **2000**, 2, 3221.
- ¹⁷² Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Heterocycles* **1990**, 30, 303.
- ¹⁷³ Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, 39, 983.
- ¹⁷⁴ Tamao, K.; Ishida, N. *Tetrahedron Lett.* **1984**, 25, 4249.
- ¹⁷⁵ Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, 70, 1943.
- ¹⁷⁶ Matsuhashi, H.; Hatanaka, Y.; Kuroboshi, M.; Hiyama, T. *Tetrahedron Lett.* **1995**, 36, 1539.

- ¹⁷⁷ Hiyama, T. *Pure Appl. Chem.* **1996**, 68, 609.
¹⁷⁸ Kang, S. K.; Kim, T. H.; Pyun, S. J. *J. Chem. Soc., Perkin Trans. I* **1997**, 797.
¹⁷⁹ Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Tetrahedron* **1992**, 48, 2113.
¹⁸⁰ Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989**, 1711.
¹⁸¹ Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1990**, 31, 2719.
¹⁸² Hatanaka, Y.; Hiyama, T. *Chem. Lett.* **1989**, 2049.
¹⁸³ Nishihara, Y.; Ikegashira, K.; Toriyama, F.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, 73, 985.
¹⁸⁴ Homsi, F.; Hosoi, K.; Nozaki, K.; Hiyama, T. *J. Organometal. Chem.* **2001**, 624.
¹⁸⁵ Hagiwara, E.; Gouda, K.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1997**, 38, 439.
¹⁸⁶ Huang, T. S.; Li, C. J. *Tetrahedron Lett.* **2002**, 43, 403.
¹⁸⁷ Gouda, K.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, 61, 7232.
¹⁸⁸ Damrauer, R.; Simon, R. A.; Kanner, B. *Organometallics* **1988**, 7, 1161.
¹⁸⁹ Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, 126, 7788.
¹⁹⁰ Matsuhashi, H.; Kuroboshi, M.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1994**, 35, 6507.
¹⁹¹ Lickiss, P. *Adv. Inorg. Chem.* **1995**, 42, 147.
¹⁹² Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, 50, 5831.
¹⁹³ Merchant, K. J. *Tetrahedron Lett.* **2000**, 41, 3747.
¹⁹⁴ Lyothier, I.; Difieber, C.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2006**, 45, 6204.
¹⁹⁵ Denmark, S. E.; Butler, C. R. In *e-EROS Encyclopedia of Reagents for Organic Synthesis*, 2007.
¹⁹⁶ Lee, M.; Ko, S.; Chang, S. J. *Am. Chem. Soc.* **2000**, 122, 12011.
¹⁹⁷ Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, 6, 191.
¹⁹⁸ Denmark, S. E.; Pan, W. T. *Org. Lett.* **2002**, 4, 4163.
¹⁹⁹ Denmark, S. E.; Kalleymen, J. M. *Org. Lett.* **2003**, 5, 3483.
²⁰⁰ Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, 121, 9550.
²⁰¹ Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, 49, 3939.
²⁰² Denmark, S. E.; Sweis, R. F. *Org. Lett.* **2002**, 4, 3771.
²⁰³ Hirabayashi, K.; Kondo, T.; Toriyama, F.; Nishihara, Y.; Mori, A. *Bull. Chem. Soc. Jpn.* **2000**, 73, 749.
²⁰⁴ Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, 5, 1357.
²⁰⁵ Denmark, S. E.; Ober, M. *Adv. Synth. Catal.* **2004**, 346, 1703.
²⁰⁶ Denmark, S. E.; Baird, J. D. *Org. Lett.* **2004**, 6, 3649.
²⁰⁷ Denmark, S. E.; Baird, J. D. *Org. Lett.* **2006**, 8, 793.
²⁰⁸ Denmark, S. E.; Baird, J. D.; Regens, C. S. *J. Org. Chem.* **2008**, 73, 1440.
²⁰⁹ Denmark, S. E.; Baird, J. D. *Tetrahedron* **2009**, 65, 3120.
²¹⁰ Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, 127, 4685.
²¹¹ Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, 126, 13028.
²¹² Werner, H.; Kühn, A. *J. Organometal. Chem.* **1979**, 179, 439.
²¹³ Denmark, S. E.; Kalleymen, J. M. *J. Org. Chem.* **2005**, 70, 2839.
²¹⁴ Denmark, S. E.; Kobayashi, T.; Regens, C. S. *Tetrahedron* **2010**, 66, 4745.
²¹⁵ Denmark, S. E.; Regens, C. S.; Kobayashi, T. *J. Am. Chem. Soc.* **2007**, 129, 2774.
²¹⁶ Denmark, S. E.; Fujimori, S. *J. Am. Chem. Soc.* **2005**, 127, 8971.
²¹⁷ Denmark, S. E.; Tymonko, S. A. *J. Org. Chem.* **2003**, 68, 9151.
²¹⁸ Denmark, S. E.; Smith, R. C.; Tymonko, S. A. *Tetrahedron* **2007**, 63, 5730.
²¹⁹ Marciniec, B.; Kujawa, M.; Pietraszuk, C. *New J. Chem.* **2000**, 24, 671.
²²⁰ Marciniec, B.; Pietraszuk, C. In *Topics in Organometallic Chemistry*; Bruneau, C., Dixneuf, P. H., Eds.; Springer: Berlin, 2004; Vol. 11, pp 197–248.
²²¹ Marciniec, B. *Coord. Chem. Rev.* **2005**, 249, 2374.
²²² Li, L. H.; Navasero, N. *Org. Lett.* **2004**, 6, 3091.
²²³ Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Great Britain, 1998; Vol. 2, pp 1687–1792.
²²⁴ Denmark, S. E.; Pan, W. T. *Org. Lett.* **2001**, 3, 61.
²²⁵ Denmark, S. E.; Yang, S. M. *Org. Lett.* **2001**, 3, 1749.
²²⁶ Denmark, S. E.; Yang, S. M. *Tetrahedron* **2004**, 60, 9695.

- ²²⁷ Denmark, S. E.; Yang, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 2102.
²²⁸ Denmark, S. E.; Yang, S. M. *J. Am. Chem. Soc.* **2002**, *124*, 15196.
²²⁹ Denmark, S. E.; Yang, S. M. *J. Am. Chem. Soc.* **2004**, *126*, 12432.
²³⁰ Mori, A.; Takahisa, E.; Yamamura, Y.; Kato, T.; Mudalige, A. P.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Organometallics* **2004**, *23*, 1755.
²³¹ Ito, H.; Sensui, H.; Arimoto, K.; Miura, K.; Hosomi, A. *Chem. Lett.* **1997**, 639.
²³² DeShong, P.; Handy, C.; Mowery, M. *Pure Appl. Chem.* **2000**, *72*, 1655.
²³³ Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem. Int. Ed.* **2005**, *44*, 7852.
²³⁴ Ranu, B. C.; Dey, R.; Chattopadhyay, K. *Tetrahedron Lett.* **2008**, *49*, 3430.
²³⁵ Seganish, W. M.; DeShong, P. *Org. Lett.* **2006**, *8*, 3951.
²³⁶ Mowery, M. E.; DeShong, P. *Org. Lett.* **1999**, *1*, 2137.
²³⁷ Pan, C. D.; Liu, M. C.; Zhao, L.; Wu, H. Y.; Ding, J. C.; Cheng, J. *Catal. Commun.* **2008**, *9*, 1685.
²³⁸ Wu, Z. S.; Yang, M.; Li, H. L.; Qi, Y. X. *Synthesis* **2008**, 1415.
²³⁹ Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 6790.
²⁴⁰ Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997**, 1309.
²⁴¹ Murata, M.; Yoshida, S.; Nirei, S.; Watanabe, S.; Masuda, Y. *Synlett* **2006**, 118.
²⁴² McElroy, W. T.; DeShong, P. *Tetrahedron* **2006**, *62*, 6945.
²⁴³ McElroy, W. T.; DeShong, P. *Org. Lett.* **2003**, *5*, 4779.
²⁴⁴ Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053.
²⁴⁵ Wolf, C.; Lerebours, R. *Org. Lett.* **2004**, *6*, 1147.
²⁴⁶ Chen, S. N.; Wu, W. Y.; Tsai, F. Y. *Tetrahedron* **2008**, *64*, 8164.
²⁴⁷ Wolf, C.; Lerebours, R.; Tanzini, E. H. *Synthesis* **2003**, 2069.
²⁴⁸ Zhang, L.; Qing, J.; Yang, P. Y.; Wu, J. *Org. Lett.* **2008**, *10*, 4971.
²⁴⁹ Zhang, L.; Wu, J. *J. Am. Chem. Soc.* **2008**, *130*, 12250.
²⁵⁰ Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653.
²⁵¹ Seganish, W. M.; Handy, C. J.; DeShong, P. *J. Org. Chem.* **2005**, *70*, 8948.
²⁵² Mehta, V. P.; Sharma, A.; Van der Eycken, E. *Adv. Synth. Catal.* **2008**, *350*, 2174.
²⁵³ Correia, R.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7159.
²⁵⁴ Dey, R.; Chattopadhyay, K.; Ranu, B. C. *J. Org. Chem.* **2008**, *73*, 9461.
²⁵⁵ Kabalka, G. W.; Dong, G.; Venkataiah, B.; Chen, C. L. *J. Org. Chem.* **2005**, *70*, 9207.
²⁵⁶ Sengupta, S.; Sadhukhan, S. K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2235.
²⁵⁷ Alacid, E.; Najera, C. *Adv. Synth. Catal.* **2006**, *348*, 2085.
²⁵⁸ Prukala, W.; Marciniec, B.; Majchrzak, M.; Kubicki, M. *Tetrahedron* **2007**, *63*, 1107.
²⁵⁹ Verkade, J. G. *Coordination Chemistry Reviews* **1994**, *137*, 233.
²⁶⁰ Riggleman, S.; DeShong, P. *J. Org. Chem.* **2003**, *68*, 8106.
²⁶¹ Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073.
²⁶² Denmark, S. E.; Butler, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 3690.
²⁶³ Denmark, S. E.; Butler, C. R. *Org. Synth.* **2009**, *86*, 274.
²⁶⁴ Denmark, S. E.; Pan, W. T. *Org. Lett.* **2003**, *5*, 1119.
²⁶⁵ Endo, M.; Sakurai, T.; Ojima, S.; Katayama, T.; Unno, M.; Matsumoto, H.; Kowase, S.; Sano, H.; Kosugi, M.; Fugami, K. *Synlett* **2007**, 749.
²⁶⁶ Marciniec, B.; Wachner, J.; Pawluc, P.; Kubicki, M. *J. Mol. Catal. A: Chem.* **2007**, *265*, 25.
²⁶⁷ Denmark, S. E.; Wang, Z. *J. Organomet. Chem.* **2001**, *624*, 372.
²⁶⁸ Mori, A.; Suguro, M. *Synlett* **2001**, 845.
²⁶⁹ Lerebours, R.; Wolf, C. *Synthesis* **2005**, 2287.
²⁷⁰ Penso, M.; Albanese, D.; Landini, D.; Lupi, V. *J. Mol. Catal. A: Chem.* **2003**, *204*, 177.
²⁷¹ Tamao, K.; Yoshida, J.-I.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355.
²⁷² Yoshida, J. I.; Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, *20*, 1141.
²⁷³ Tamao, K.; Matsumoto, H.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, *20*, 1137.
²⁷⁴ Tamao, K.; Kakui, T.; Kumada, M. *Tetrahedron Lett.* **1979**, *20*, 619.
²⁷⁵ Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1988**, *29*, 97.

- ²⁷⁶ Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 1137.
- ²⁷⁷ Hirabayashi, K.; Ando, J.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1409.
- ²⁷⁸ Hirabayashi, K.; Nishihara, Y.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 7893.
- ²⁷⁹ Koike, T.; Du, X. L.; Sanada, T.; Danda, Y.; Mori, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 89.
- ²⁸⁰ Denmark, S. E.; Yang, S. M. In *Strategy and Tactics in Organic Synthesis*; Harmata, M. A., Ed.; Elsevier: Amsterdam, 2005; Vol. 6.
- ²⁸¹ Denmark, S. E.; Liu, J. H.-C.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 14188.
- ²⁸² Denmark, S. E.; Liu, J. H.-C.; Muhuhi, J. M. *J. Org. Chem.* **2011**, *76*, 201.
- ²⁸³ Denmark, S. E.; Fujimori, S. In *Strategies and Tactics in Organic Synthesis*; Harmata, M. A., Ed.; Elsevier: Amsterdam, 2008; Vol. 7.
- ²⁸⁴ Zhang, Y.; Panek, J. S. *Org. Lett.* **2007**, *9*, 3141.
- ²⁸⁵ Minami, T.; Nishimoto, A.; Hanaoka, M. *Tetrahedron Lett.* **1995**, *36*, 9505.
- ²⁸⁶ Hanaoka, M.; Yamagishi, H.; Marutani, M.; Mukai, C. *Chem. Pharm. Bull.* **1987**, *35*, 2345.
- ²⁸⁷ Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem.* **2006**, *2337*.
- ²⁸⁸ Darses, S.; Genet, J.-P. *Chem. Rev.* **2008**, *108*, 288.
- ²⁸⁹ Molander, G. A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275.
- ²⁹⁰ Navarro, O.; Marion, N.; Mei, J.; Nolan, S. P. *Chem. Eur. J.* **2006**, *12*, 5142.
- ²⁹¹ Noguchi, H.; Hojo, K.; Sugimoto, M. *J. Am. Chem. Soc.* **2007**, *129*, 758.
- ²⁹² Gillis, E. P.; Burke, M. D. *Aldrichimica Acta* **2009**, *42*, 17.
- ²⁹³ Ojima, I.; Moralee, A. C.; Vassar, V. C. *Top. Catal.* **2002**, *19*, 89.
- ²⁹⁴ Fujiwara, M.; Ojima, I. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005, pp 129–150.
- ²⁹⁵ Huber, J. D.; Perl, N. R.; Leighton, J. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 3037.
- ²⁹⁶ Evans, P. A.; Cui, J.; Gharpure, S. J.; Polosukhin, A.; Zhang, H. R. *J. Am. Chem. Soc.* **2003**, *125*, 14702.
- ²⁹⁷ Connon, S. J.; Blechert, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 1900.
- ²⁹⁸ Murata, M.; Yamasaki, H.; Uogishi, K.; Watanabe, S.; Masuda, Y. *Synthesis* **2007**, 2944.
- ²⁹⁹ Murata, M.; Ota, K.; Yamasaki, H.; Watanabe, S.; Masuda, Y. *Synlett* **2007**, 1387.
- ³⁰⁰ Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7449.
- ³⁰¹ Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895.
- ³⁰² Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.
- ³⁰³ Li, G. Y. *Angew. Chem. Int. Ed.* **2001**, *40*, 1513.
- ³⁰⁴ Denmark, S. E.; Smith, R. C. *Synlett* **2006**, *18*, 2921.
- ³⁰⁵ Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coordin. Chem. Rev.* **2004**, *248*, 2283.
- ³⁰⁶ Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338.
- ³⁰⁷ Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555.
- ³⁰⁸ Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534.
- ³⁰⁹ Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461.
- ³¹⁰ Fairlamb, I. J. S.; Kapdi, A. R.; Lee, A. F.; McGlacken, G. P.; Weissburger, F.; de Vries, A. H. M.; Schmieder-van de Vondervoort, L. *Chem. Eur. J.* **2006**, *12*, 8750.
- ³¹¹ Denmark, S. E.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 11768.
- ³¹² Christe, K.; Wilson, W.; Wilson, R.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, *112*, 7619.
- ³¹³ Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305.
- ³¹⁴ Ines, B.; SanMartin, R.; Churruca, F.; Dominguez, E.; Urtiaga, M. K.; Arriortua, M. I. *Organometallics* **2008**, *27*, 2833.
- ³¹⁵ Kjellgren, J.; Sundén, H.; Szabo, K. J. *J. Am. Chem. Soc.* **2005**, *127*, 1787.
- ³¹⁶ Brescia, M. R.; DeShong, P. *J. Org. Chem.* **1998**, *63*, 3156.
- ³¹⁷ Shukla, K. H.; Boehmler, D. J.; Bogacyzk, S.; Duvall, B. R.; Peterson, W. A.; McElroy, W. T.; DeShong, P. *Org. Lett.* **2006**, *8*, 4183.
- ³¹⁸ Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63.
- ³¹⁹ Denmark, S. E.; Wang, Z. *Org. Synth.* **2004**, *81*, 54.
- ³²⁰ Denmark, S. E.; Wang, Z. *Org. Synth.* **2004**, *81*, 42.

- ³²¹ Berthon-Gelloz, G.; Schumers, J. M.; De Bo, G.; Marko, I. E. *J. Org. Chem.* **2008**, *73*, 4190.
- ³²² Wnuk, S. F.; Garcia, P. I.; Wang, Z. Z. *Org. Lett.* **2004**, *6*, 2047.
- ³²³ Trost, B. M.; Machacek, M. R.; Faulk, B. D. *J. Am. Chem. Soc.* **2006**, *128*, 6745.
- ³²⁴ Trost, B. M.; Frederiksen, M. U.; Papillon, J. P. N.; Harrington, P. E.; Shin, S.; Shireman, B. T. *J. Am. Chem. Soc.* **2005**, *127*, 3666.
- ³²⁵ Yoshida, J. I.; Tamao, K.; Takahashi, M.; Kumada, M. *Tetrahedron Lett.* **1978**, 2161.
- ³²⁶ Fiandanese, V.; Bottalico, D.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **2003**, *44*, 9087.
- ³²⁷ Horita, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1751.
- ³²⁸ Horita, A.; Tsurugi, H.; Funayama, A.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 2231.
- ³²⁹ Nishihara, Y.; Kato, T.; Ando, J.; Mori, A.; Hiyama, T. *Chem. Lett.* **2001**, 950.

