Annual Reports B Dynamic Article Links

Cite this: *Annu. Rep. Prog. Chem., Sect. B*, 2011, **107**, 68–90

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Heteroatom methods

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DOI: 10.1039/c1oc90010b

The report deals with some advances in organo-oxygen, -nitrogen, -boron and -silicon chemistry from 2010.

1. Introduction

This article focuses on advances in organo-oxygen, -nitrogen, -boron and -silicon chemistry over the past year, particularly with regard to the use of catalytic methodology, both metal-catalysed and organocatalytic. Of particular interest last year were the advances in oxa-Michael chemistry, aza-Michael and aza-Diels-Alder reactions, the conjugate addition of organoboron species, and borylation reactions, and two particular highlights are the development of catalytic direct amide formation from the dehydrogenative reaction of primary alcohols with amines and the diborylation of unsaturated ketones using phosphine catalysis (see sections 3.1 and 4.2 respectively).

1.1 Review articles

"Carbo- and heterocyclization of oxygen- and nitrogen-containing electrophiles by platinum, gold, silver and copper species."[1]

"Pd-catalysed oxidative coupling with organometallic reagents *via* C–H activation."[2]

"Rearrangement of *β*-amino alcohols *via* aziridiniums: a review."[3]

"Aziridinyl anions: Generation, reactivity, and use in modern synthetic chemistry."[4]

N,*N*-Dialkylhydrazones in organic synthesis. From simple *N*,*N*-dimethylhydrazones to supported chiral auxilliaries."[5]

"Ynamides: A modern functional group for the new Millenium."[6]

"Recent advances in transition metal-catalyzed *N*-atom transfer reactions of azides."[7]

"Direct amination of aryl halides with ammonia."[8]

"Asymmetric 1,3-dipolar cycloadditions of acrylamides."[9]

"Boronic acids and esters in the Petasis-borono Mannich multicomponent reaction."[10]

A new context for palladium mediated B-addition reaction: an open door to consecutive functionalization."[11]

"C–H activation for the construction of C-B bonds."[12]

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"A synthetic double punch: Suzuki-Miyaura cross-coupling mates with C–H functionalization."[13]

"Expanding the limits of organoboron chemistry: Synthesis of functionalized arylboronates."[14]

"Enantioselective conjugate borylation."[15]

"The thermal and boron-catalysed direct amide formation reactions: mechanistically understudied yet important processes."[16]

"Silylative coupling of olefins with vinylsilanes in the synthesis of π-conjugated double bond systems."[17]

"Iron-catalysed hydrosilylation reactions."[18]

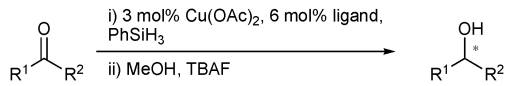
"Silicon-based cross-coupling reactions in the total synthesis of natural products."[19]

"Recent advances in the use of temporary silicon tethers in metal-mediated reactions."[20]

2. Organooxygen chemistry

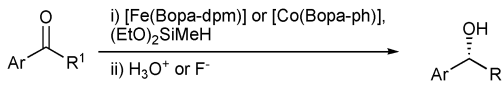
2.1 Hydrosilylation of ketones

The reduction of ketones using silanes under metal-catalysed conditions has seen some interesting results in the past year. Use of copper catalysts allowed the enantioselective reduction of a wide range of ketones, with the use of chiral binaphthophosphepine ligands allowing the reaction to proceed with high enantioselectivity in many cases.[21] (Scheme 1)



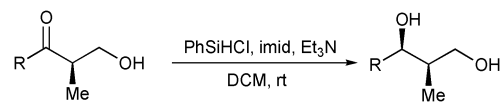
Scheme 1

A similar reduction was performed using chiral bis(oxazolinylphenyl)amine ligands in combination with either iron(II) or cobalt(II) catalysts. This method, when applied to enones, led to 1,4-reduction with variable selectivity for one enantiomer at the 4-position.[22] (Scheme 2)



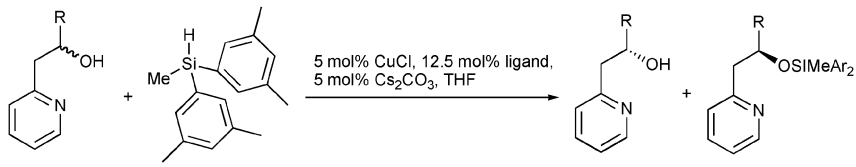
Scheme 2

Diastereoselective hydrosilylation of ketones by diphenylchlorosilane has also been reported in ketones possessing an α-chiral centre. Substrates had to possess a β-hydroxyl group which reacted to give the silyl ether prior to reduction. Diastereoselectivity was predictable, based on a cyclic transition state model. In addition, a range of non-diastereoselective reductions were also perfomed.[23] (Scheme 3)



Scheme 3

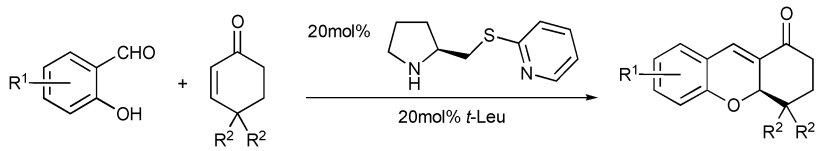
Another method to access chiral alcohols using silicon chemistry was reported. Use of a chiral copper(I) catalyst allowed the selective silylation of two enantiomers in their reaction with a silane reagent. Substrate scope was somewhat limited with the alcohol requiring a β-2-pyridyl function, however, the efficiency of the kinetic resolution was high.[24] (Scheme 4)



Scheme 4

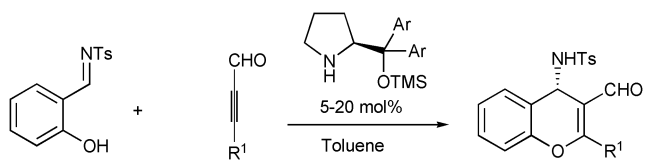
2.2 Oxa-Michael reactions

Oxa-Michael additions have been used this year in both inter- and intra-molecular reactions. Dealing with intermolecular reactions first, an oxa-Michael followed by a Mannich reaction was used in the organocatalytic cyclisation of salicylic aldehydes with cyclohexenones. The reaction proceeded in high yield for a range of different substrates and enantioselectivity was generally high.[25] (Scheme 5)



Scheme 5

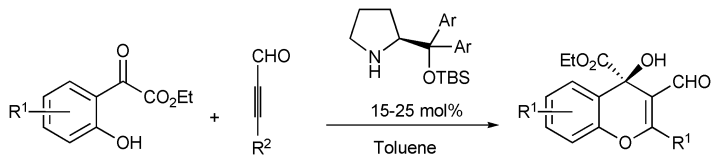
A similar cyclisation was used in the asymmetric synthesis of 4-amino-4*H*-chromenes, again using an organocatalytic approach. In this case, the use of an *N*-tosyl imine gave the desired amino group with impressive enantioselectivity and high yields.[26] (Scheme 6)



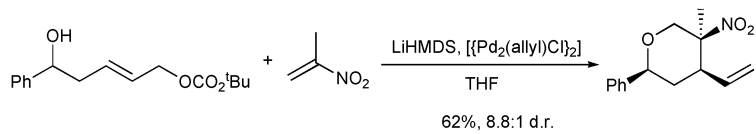
Scheme 6

Similarly, chiral 4-hydroxy-chromenes were produced using an analogous method and demonstrated high enantiocontrol of the forming quaternary centre. Yields were high and the method tolerated a range of aryl and alkyl substituents at the 2-position.[27] (Scheme 7)

Another tandem reaction initiated by an oxa-Michael process allowed the formation of substituted tetrahydropyrans through the use of a second, intramolecular Tsuji-Trost reaction. This method allowed a number of different substitution patterns



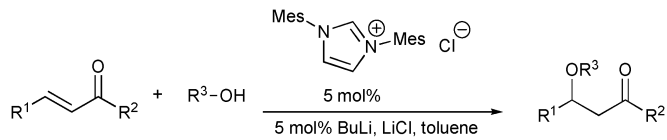
Scheme 7



Scheme 8

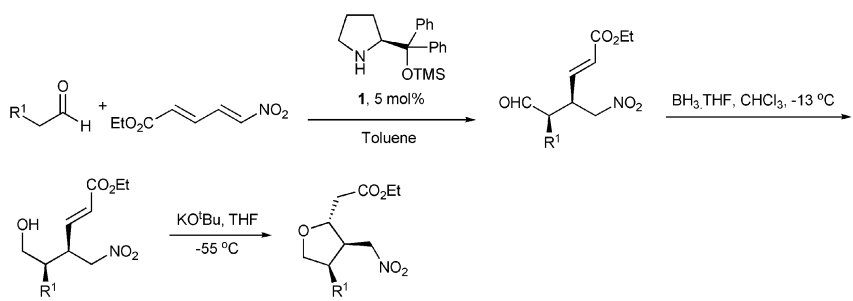
to be produced in good yields and with moderate to good diastereoselectivity.[28] (Scheme 8)

N-Heterocyclic carbene catalysis has been used in the addition of primary and secondary alcohols to acyclic enones. Yields were high for a range of different alcohols, and the method represents an interesting alternative for the synthesis of 1,3-dioxygenated alkanes.[29] (Scheme 9)



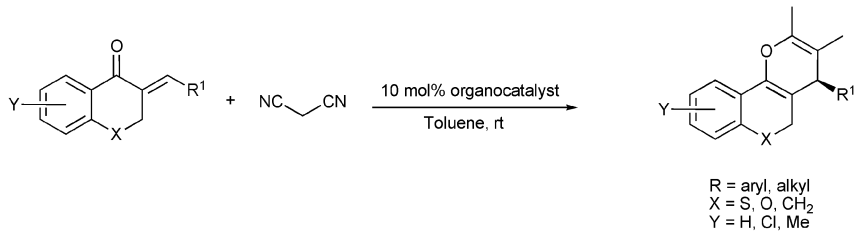
Scheme 9

An intramolecular oxa-Michael reaction was employed in the synthesis of a number of trisubstituted tetrahydrofurans. Following a nitro-Michael/reduction sequence, addition of potassium *tert*-butoxide gave the cyclised product in good yield and with high diastereoselectivity. The initial nitro-Michael reaction could be performed with high enantio- and diastereo-selectvity through the use of pyrrolidine-based organocatalyst **1** making this an efficient method for the preparation of chiral functionalised tetrahydrofurans.[30] (Scheme 10)



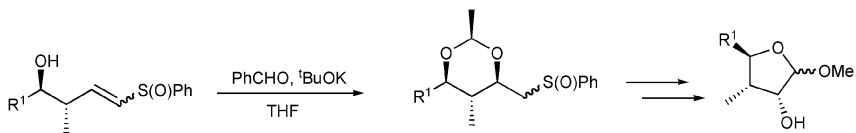
Scheme 10

A Michael-oxa-Michael sequence was also used in the synthesis of a range of pyranochromenes, again employing an organocatalyst in order to achieve asymmetric induction. The reaction tolerated a range of aryl and alkyl groups possessing different functional groups and gave high yields and enantioselectivities.[31] (Scheme 11)



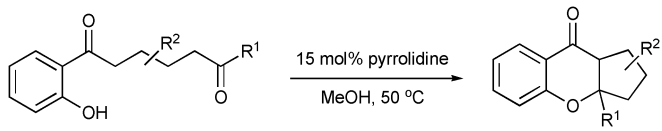
Scheme 11

Another cyclisation using an intramolecular oxa-Michael addition employed an initial hemiacetal formation of an adjacent chiral alcohol to direct the incoming oxa-nucleophile to the vinyl sulfoxide. This approach gave good yields and extremely high diastereoselectivity. A subsequent Pummerer rearrangement led to the products' conversion to a range of substituted methyl furanosides.[32] (Scheme 12)



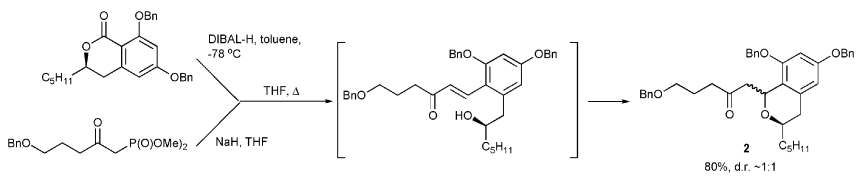
Scheme 12

An oxa-Michael reaction was combined with an organocatalytic aldol reaction to produce substituted chromanones with high diastereoselectivity. Unfortunately, the reversibility of the reaction did not permit the induction of chirality through the use of an asymmetric catalyst.[33] (Scheme 13)



Scheme 13

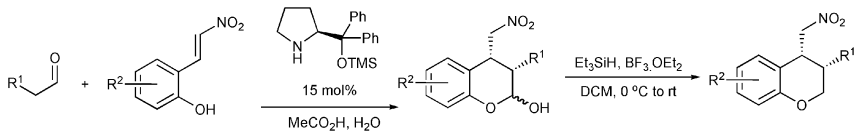
Finally, an oxa-Michael reaction was used in a cyclisation *en route* to the core of berkelic acid, the reaction following a Horner-Wadsworth-Emmons reaction to give cyclic ether **2**, albeit as a mixture of diastereoisomers.[34] (Scheme 14)



Scheme 14

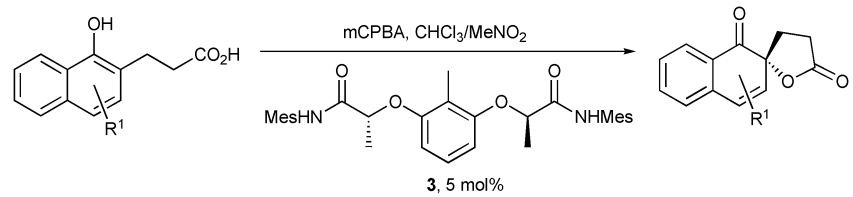
2.3 Miscellaneous organooxygen chemistry

The combination of an organocatalytic nitro-Michael addition and hemiacetal formation provided a route to 2-hydroxy chromans, which could be dehydroxylated using triethylsilane to give the chroman derivative. The enantioselectivity was extremely high, and yields and diastereoselectivities were also generally impressive.[35] (Scheme 15)



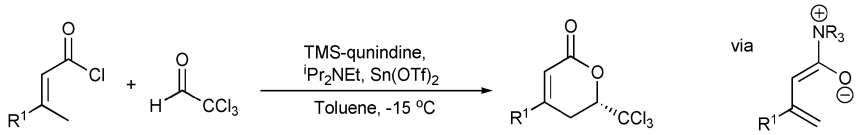
Scheme 15

The enantioselectivity of the Kita oxidative spirolactonisation has been improved by the development of more efficient precatalysts. Screening a number of iodoresorcinol-derived species revealed precatalyst **3**, which gave good to high yields and high enantioselectivity for a number of substrates, although those possessing methoxy substituents were found to be problematic.[36] (Scheme 16)



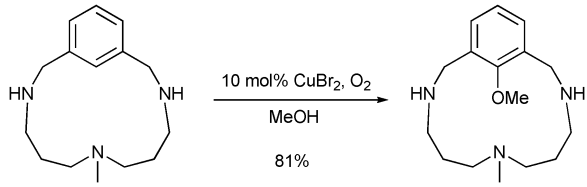
Scheme 16

A catalytic asymmetric hetero-Diels-Alder reaction was reported, involving the addition of zwitterionic dienolate intermediates to trichloroacetaldehyde. Both yields and enantioselectivities were moderate to high for a number of different substrates, and it was shown that the trichloromethyl group could be efficiently derivatised. In addition, new conditions were developed to allow the reaction of other, less reactive aldehydes.[37] (Scheme 17)



Scheme 17

Finally, the reported copper(II)-catalysed aryl ether formation by oxidation of aryl C–H bonds is worth reporting. Although apparently limited to a substrate possessing three nitrogen atoms acting as ligands, the selective oxidation of one C–H bond is interesting and the study provides mechanistic insights into the process.[38] (Scheme 18)

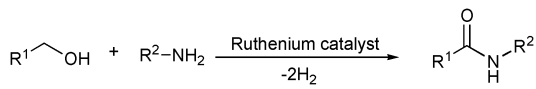


Scheme 18

3. Organonitrogen chemistry

3.1 Amide formation and other reactions

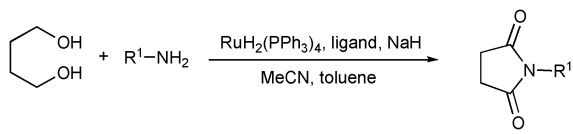
Perhaps the most exciting work in this area involves the reaction of alcohols and amines under ruthenium catalysis. In all cases no oxidant was required, the reaction proceeding by evolution of dihydrogen. It is interesting to note that in two cases, replacement of the alcohol with an aldehyde did not lead to significant amide formation, apparently owing a requirement for the alcohol to ligate the ruthenium catalyst prior to oxidation. Nevertheless, high yields were obtained for a range of alcohols and amines in both cases.[39,40] (Scheme 19)



Scheme 19

It has been shown that amide formation from aldehydes and alcohols is possible under similar conditions. Hong *et al*. developed a system capable of forming amides from both alcohols and aldehydes, yields being generally good, although some competing imine formation was seen in the case of some aldehydes.[41]

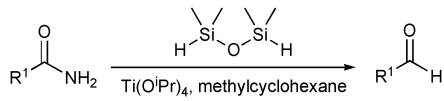
The same methodology has been applied to the synthesis of cyclic imides from diols. Once again, the reaction proceeds through evolution of dihydrogen, giving the imides in moderate to good yields.[42] (Scheme 20)



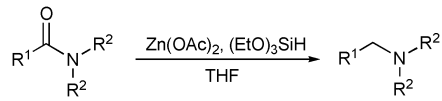
Scheme 20

Another method for direct amide bond formation is the direct reaction of acids and amines using, for example, boronic acid catalysis. A computational study on the use of such catalysts proposed that such reactions proceeded *via* a monoacyl boronate, this being formed in a fast equilibrium process, and that this species reacts with the amine to form a tetrahedral intermediate, the collapse of which is rate-determining. Observations of accelerated catalysis using *ortho*-haloboronic acids were explained by means of stabilising hydrogen bonding effects in the transition state of the rate determining step.[43]

Other work on amides has involved their reduction: two silicon-based methods have been reported, one being selective for the formation of the aldehyde,[44] the other for the formation of the amine.[45] Both methods are mild and high yielding, making them useful methods for what can be a difficult transformation. (Schemes 21 and 22)

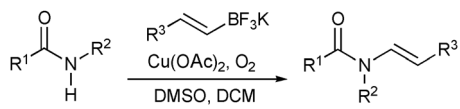


Scheme 21



Scheme 22

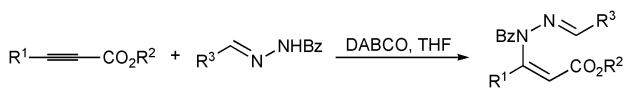
Derivatisation of primary and secondary amides to enamides has also been the subject of recent research, with the use of copper(II) catalysis giving efficient reaction between such species and vinyl trifluoroborates.[46] (Scheme 23)



Scheme 23

3.2 Aza-Michael reactions

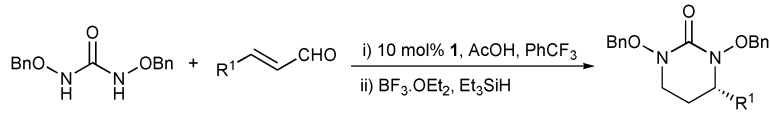
The aza-Michael reaction has received considerable attention in the last year, both with the development of new methodology and its use in synthetic applications. Hydrazones have been added to activated alkynes in good yields through the use of tertiary amine catalysts. Reactions gave enamines in moderate to excellent yields and were generally *Z*-selective.[47] (Scheme 24)



Scheme 24

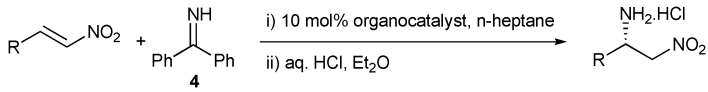
Anilines have been added to methyl vinyl ketone simply by performing them 'on-water', *i.e.* reaction occurs in the heterogeneous emulsion at the water-organic interface. Yields were somewhat variable depending on the substituents on the aniline, however, the reaction clearly constitutes a green method for performing such reactions. The method was also found to work with *N*-acryloyl-2,5-dimethylpyrrole, which provides greater synthetic scope for further derivatisation.[48]

The aza-Michael reaction of ureas has been combined with subsequent hemiaminal formation and dehydroxylation in the synthesis of chiral pyrimidinones. Use of pyrrolidine organocatalyst **1** generally gave high asymmetric induction and excellent yields.[49] (Scheme 25)



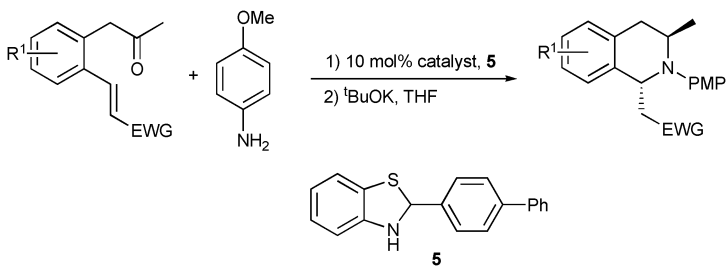
Scheme 25

The formal aza-Michael addition of ammonia to nitroalkenes has been realised through the use of benzophenone imine **4** and a thiourea-based organocatalyst. Yields and e.e.s were high, and the benzophenone protecting group was easily removed by hydrolysis following the addition reaction.[50] (Scheme 26)



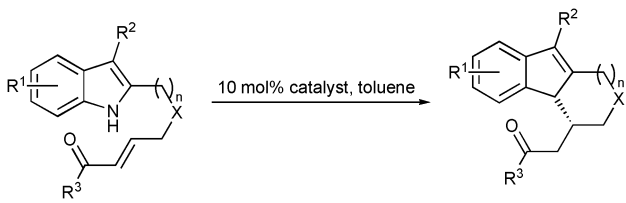
Scheme 26

An intramolecular aza-Michael reaction was used as the final cyclisation step to give a number of tetrahydroisoquinolines. A reductive amination, using benzothiazole **6** as a reducing agent, installed the required amine which was then cyclised under basic conditions.[51] (Scheme 27)



Scheme 27

An intramolecular aza-Michael involving indole derivatives has also been reported. In this case, having installed the required olefin through a cross-metathesis reaction, use of a chiral phosphoric acid catalyst gave high yields and enantioselectivity. The selectivity for *N*- as opposed to *C*3-alkylation appeared to be due to the reversibility of the two reactions and thus thermodynamic control.[52] (Scheme 28)

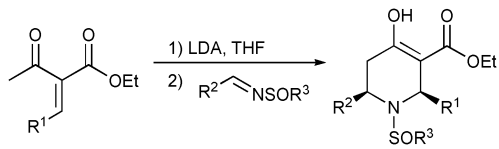


Scheme 28

Addition of fluorinated nucleophiles to sulfinyl imines has been used to generate a nitrogen nucleophile for a tandem aza-Michael reaction. Tetrabutylammonium

triphenyldifluorosilicate was used to generate the initial nucleophile from the corresponding trimethylsilane, and the use of a chiral sulfinyl imine gave very high diastereoselectivity in most cases.[53]

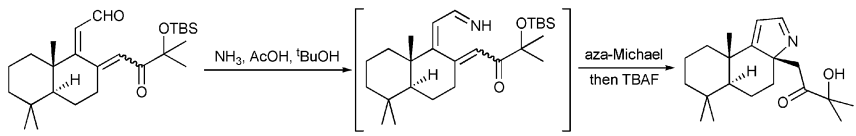
Another example of an aza-Michael as part of a tandem reaction is seen in a one-pot synthesis of piperidines. Following an initial imino-aldol reaction, an aza-Michael reaction cyclised the ring. The reactions proceeded in moderate yields with a chiral sulfinyl imine giving excellent levels of asymmetric induction.[54] (Scheme 29)



Scheme 29

The palladium-catalysed conversion of spirocyclopropanes also appeared to proceed by an intramolecular aza-Michael reaction; following palladium-mediated opening of the cyclopropane ring and *β*-hydride elimination to furnish the enone, an aza-Michael reaction gave the palladium enolate which underwent a second *β*-hydride elimination to give the observed product.[55]

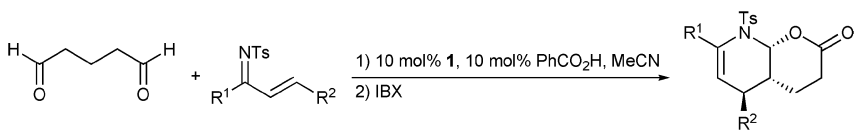
Aza-Michael reactions have also been used recently in total synthesis. A 'biomimetic' cyclisation was one of the final steps in the synthesis of chamobtusin A (Scheme 30),[56] whilst an asymmetric approach to lentiginosine utilised a double aza-Michael reaction.[57]



Scheme 30

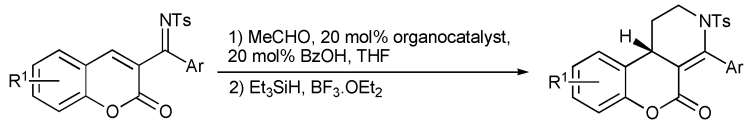
3.3 Aza-Diels-Alder reactions

A number of asymmetric, organocatalytic aza-Diels-Alder reactions were reported, including an example involving the use of organocatalyst **1** in the reactions of *N*-tosyl-1-aza-1,3-butadienes with aldehydes. Following a Diels-Alder reaction with the aldehyde, hemiacetal formation and oxidation afforded the fused lactones. Enantioselectivities were routinely high and yields were moderate.[58] (Scheme 31)



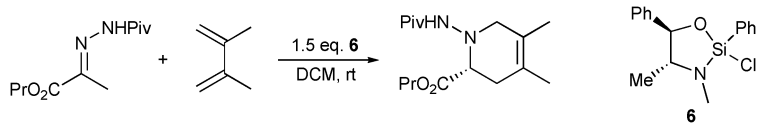
Scheme 31

Another example of organocatalysis in an aza-Diels-Alder reaction was seen in the use of *N*-tosyl-imino-coumarins. As in the preceding example, reaction of the *N*-tosyl imine with an aldehyde provided the hemiaminal as the product, though in this case a silane reduction was employed to yield the amine.[59] (Scheme 32)



Scheme 32

The use of super stoichiometric chlorosilanes such as **6** as promoters of formal aza-Diels-Alder reactions received attention with the discovery that they could be used in the asymmetric reaction of acylhydrazones with non-Danishefsky-type dienes. A number of examples were reported with high yields and generally high e.e.s and the reaction is thought to proceed *via* a Mannich-Michael manifold activated by the silicon Lewis-acid. Furthermore, it was shown that the N–N bond could be efficiently cleaved to give the corresponding amine.[60] (Scheme 33)

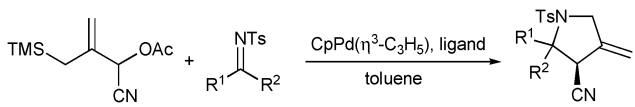


Scheme 33

The aforementioned chlorosilane promoter was also shown to be of use in reactions of acylhydrazones with Danishefsky's diene. Again, yields and e.e.s were good and the N–N bond could be reductively cleaved.[61]

Two metal-catalysed asymmetric aza-Diels-Alder reactions are also worth mentioning: use of ytterbium(III) triflate allowed the efficient reaction of Brassard's diene with a number of imines,[62] whilst use of scandium(III) triflate led to the reaction of similar imines with cyclopentadiene.[63]

One [3 + 2] reaction is also worth noting: the palladium-catalysed reaction of allylsilanes with *N*-tosyl imines allowed the construction of substituted pyrrolidines in good yield, generally high diastereocontrol and high e.e.[64] (Scheme 34)

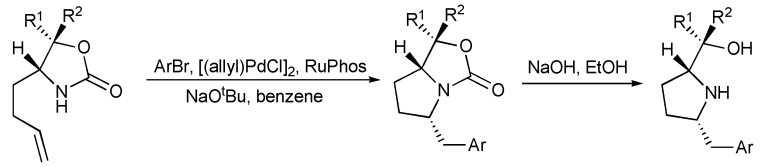


Scheme 34

3.4 Miscellaneous organonitrogen chemistry

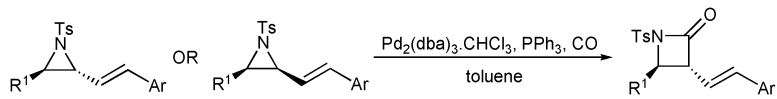
Several other examples of novel organonitrogen chemistry which do not fall into the previous categories are worthy of note. Another palladium-catalysed synthesis of pyrrolidines, this time employing a carboamination reaction, showed some impressive results. Reactions gave good yields and high diastereoselectivity, and it was shown that the resulting cyclic carbamate could be efficiently ring-opened to give the aminol.[65] (Scheme 35)

The iterative use of an aza-Claisen rearrangement allowed the synthesis of fluvirucinine A_2 in by an efficient route with high stereocontrol.[66]



Scheme 35

A method for the synthesis of *trans*-β-lactams from *N*-tosyl-aziridines has been developed. The geometry of the product was *trans* regardless of the geometry of the aziridine, which was explained by a palladium-mediated isomerisation followed by faster formation of the *trans*-product.[67] (Scheme 36)



Scheme 36

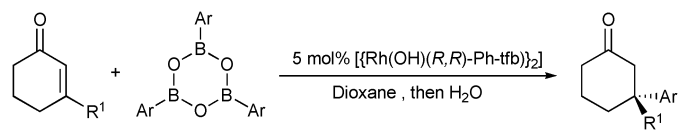
An asymmetric synthesis of *trans*-aziridines was developed, using sulphonamides as chiral auxiliaries. The reactions gave moderate to good yields and high diastereocontrol and *trans*-selectivity.[68] (Scheme 37)

Scheme 37

4. Organoboron chemistry

4.1 Conjugate addition of organoboron species

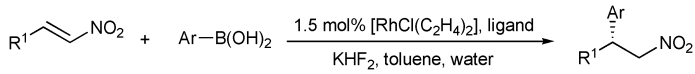
The conjugate addition of aryl boronic acids and boroxines to β,β-disubstituted α,β-unsaturated ketones has been demonstrated. When using boroxines for the addition reaction, the use of a rhodium catalyst and chiral ligand gave the formation of quaternary centres in good yields and high e.e.s for both cyclic and acyclic substrates.[69] Interestingly, the addition of boronic acids employed a palladium(II) catalyst, and the use of chiral ligands was not reported.[70] (Scheme 38)



Scheme 38

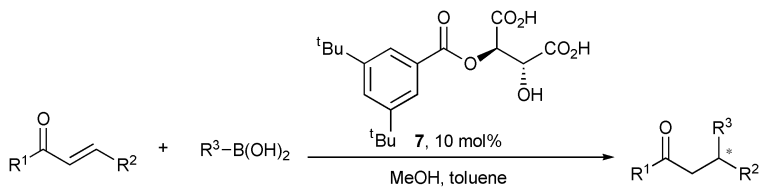
Asymmetric addition of organoboronic acids to nitroalkenes to form chiral tertiary centres with moderate to high e.e. has been reported. The reaction

apparently proceeds with the initial formation of the organotrifluoroborate through the addition of potassium hydrogen difluoride to the reaction.[71] (Scheme 39)



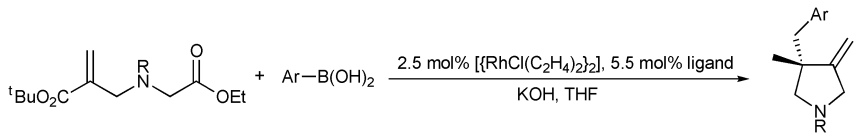
Scheme 39

The formation of chiral tertiary centres though the addition of boronic acids to acyclic enones has been performed using an organocatalyst. Tartaric acid derivative **7** gave generally good yields and moderate to good yields with a range of substrates.[72] (Scheme 40)



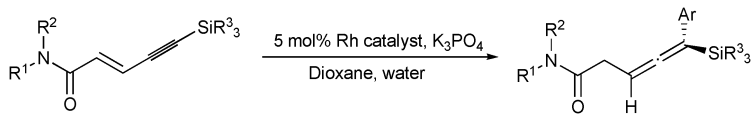
Scheme 40

The rhodium-catalysed conjugate addition of aryl boronic acids has been used as part of a tandem reaction, with the subsequent intramolecular Dieckmann reaction of the resulting rhodium enolate giving access to the pyrrolidine ring system. Use of asymmetric ligands led to high levels of asymmetric induction.[73] (Scheme 41)



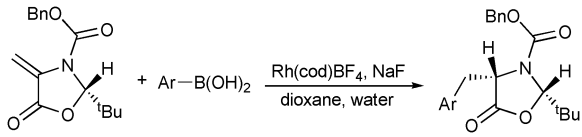
Scheme 41

Rhodium catalysis was also used in the 1,6-addition of arylboronic acids to enynamides to give allene products. Substrates possessed a terminal silyl group, which was retained in the product, and use of a norbornadiene-derived ligand gave very high e.e.s.[74] (Scheme 42)



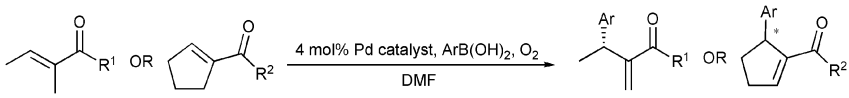
Scheme 42

Other uses of the conjugate addition of boron reagents include the use of rhodium catalysis in the synthesis of enantiopure dehydroamino acid derivatives,[75] and the asymmetric addition of silyl groups to a range of enones.[76] (Scheme 43)



Scheme 43

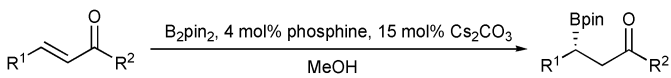
The reaction of boronic acids with enones under metal catalysis can also be used to generate chiral centres with the retention of a double bond: a palladium-catalysed oxidative Heck reaction using dioxygen as oxidant gave moderate yields but high e.e.s for a range of substrates.[77] (Scheme 44)



Scheme 44

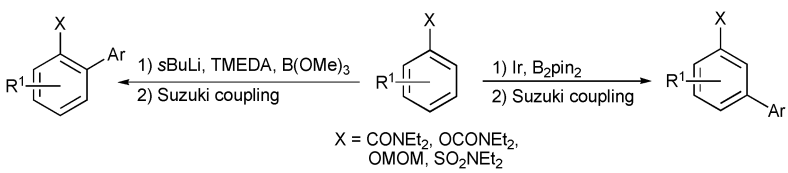
4.2 Borylation reactions

Following on from the previous section, there have been several reports employing conjugate addition reactions to introduce boron functionality into a molecule. Reaction of enones with B_2pin_2 has been shown to be catalysed by phosphines, with the use of chiral phosphines giving varying, and in some cases high, e.e.s.[78] The reaction has also been shown to be copper-catalysed, and use of copper with chiral ligands was shown to give high levels of enantioselectivity in formation of quaternary centres.[79,80] This methodology was applied only to acyclic systems which somewhat limits the scope, although it was demonstrated that α,β-unsaturated nitriles undergo the same reaction.[79] (Scheme 45)



Scheme 45

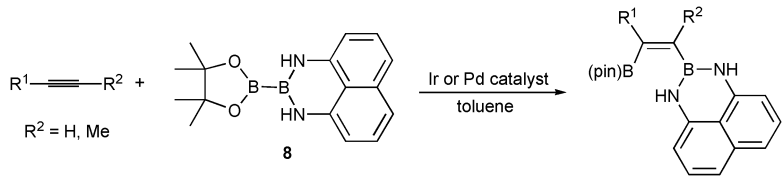
Another interesting paper examined aryl borylation using two different methods, namely iridium catalysed C–H activation and directed metalation. The two methods were shown to be complementary, metalation giving *ortho*-borylation and C–H activation giving *meta*-borylation, the products of which were subjected to Suzuki couplings with aryl bromides.[81] (Scheme 46)



Scheme 46

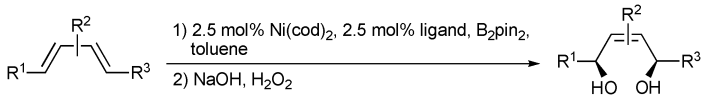
The borylation of aryl and benzyl bromides using B_2pin_2 and a palladacycle catalyst has been shown to be proceed efficiently under mild conditions and tolerated a wide range of functional groups.[82]

Regioselective diboration of alkynes has been shown to be possible through the use of diboron species **8**. Terminal and methyl-substituted internal alkynes were employed to give generally very high selectivity using either platinum or iridium catalysis.[83] (Scheme 47)



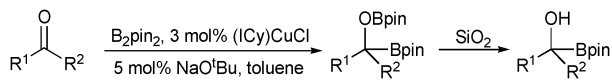
Scheme 47

Diboration of dienes was demonstrated by using a nickel catalyst, and the resulting diboronate species were oxidised to selectively give the *syn*-1,4-diols.[84] (Scheme 48)



Scheme 48

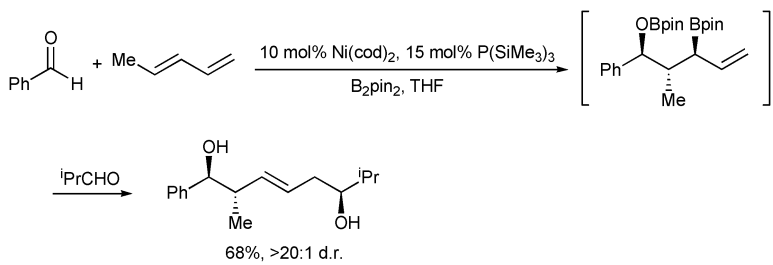
The preparation of α-hydroxy boronate esters was realised by the copper-catalysed diboration of ketones and deprotection of the resulting borate species using silica. The use of α-substituted ketones gave the formation of the expected alcohols with high diastereoselectivity.[85] (Scheme 49)



Scheme 49

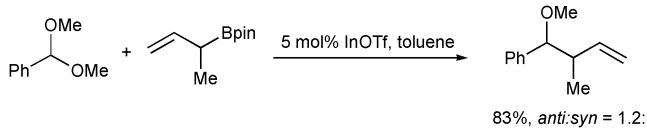
4.3 Allylboron chemistry

Borylation of dienes to yield an allyl boronate followed by reaction with an aldehyde has been employed in the synthesis of *syn*-1,3-diols. Further, addition of a second aldehyde to trap the second allyl boronate intermediate gave a *syn*-1,6-diol in good yield and with high diastereoselectivity.[86] (Scheme 50)



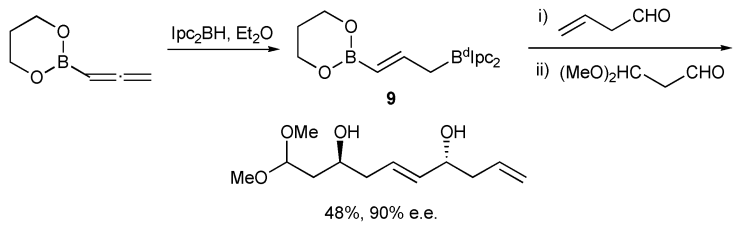
Scheme 50

Reaction of dimethyl acetals with allyl boronates gave unusual α-selectivity when using an indium catalyst. Such regioselectivity was shown to be opposite to that of the Hosomi-Sakurai reaction of organosilanes which occurred under the same conditions, making the two methods complementary.[87] (Scheme 51)



Scheme 51

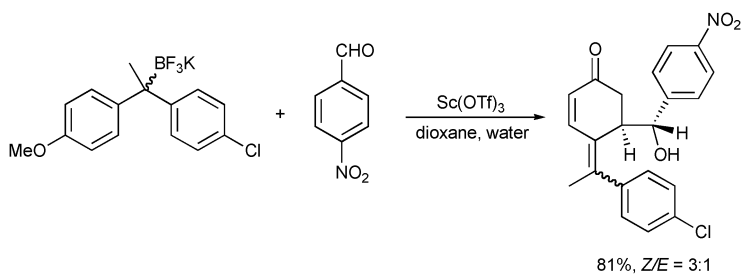
The hydroboration of allenyl boronate led to intermediate **9** which was used in a one-pot double allylboration with two different aldehydes to give an *anti*-1,5-diol. Further derivitisation led to an efficient synthesis of (+)-strictifolione.[88] (Scheme 52)



Scheme 52

The reaction of allyl boronates with nitrosobenzene has been employed in the synthesis of allyl alcohols. The reaction could be performed in the same pot as the preceding hydroboration reaction and gave complementary regioselectivity to that seen for peroxide oxidation.[89]

Although not normally regarded as allyl boron reagents, benzyl boron species were shown to participate in similar reactions with concurrent loss of aromaticity. A 4-methoxy substituent on the aryl ring was required for this reaction to occur, and the product could be cyclised though a 1,6-conjugate addition by changing the Lewis acid catalyst.[90] (Scheme 53)

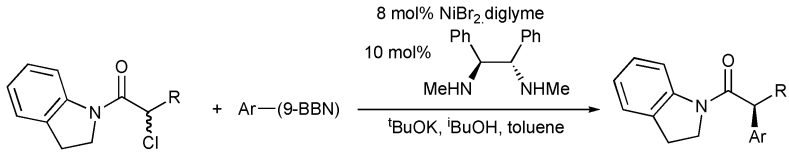


Scheme 53

4.4 Suzuki-Miyaura couplings

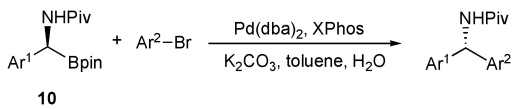
It would be difficult to devote a section to organoboron chemistry without mentioning metal-catalysed cross-coupling reactions. Perhaps the most interesting

work in this area in the past year has involved the asymmetric reaction of alkyl compounds. Asymmetric ligands and nickel catalysts allowed the coupling of racemic α-halo amides with aryl boranes to with high selectivity for one enantiomer. The selectivity was shown to be independent of which enantiomer of amide was used.[91] (Scheme 54)



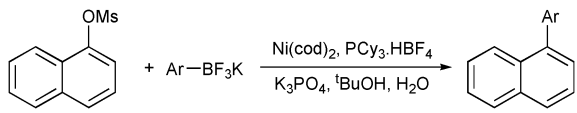
Scheme 54

Suzuki-Miyaura couplings of alkyl boronate esters of type **10** with aryl bromides were shown to proceed with complete inversion of the chiral centre, the selectivity being explained by an intramolecular coordination of boron by the amide oxygen.[92] Similarly, use of alkyl trifluoroborates showed complete inversion of stereochemistry during Suzuki couplings with aryl chlorides.[93] (Scheme 55)



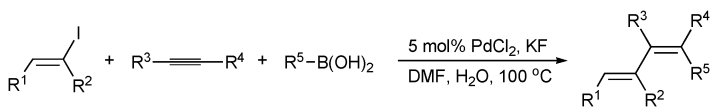
Scheme 55

Other work on cross-couplings of organoboron species led to the development of conditions for efficiently performing all alkyl cross-couplings by using a nickel catalyst,[94] the ability to use aryl mesylates in Suzuki-Miyaura couplings[95] and different conditions for the coupling of alkyl chlorides *versus* bromides and iodides with trifluoroborates.[96] (Scheme 56)



Scheme 56

Finally, aryl boronic acids found use in palladium-catalysed three-component reactions leading to highly substituted 1,3-dienes. An impressive number of examples were reported and yields were generally high, although selectivity between different regioisomers was somewhat variable.[97] (Scheme 57)

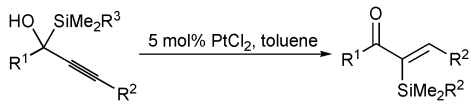


Scheme 57

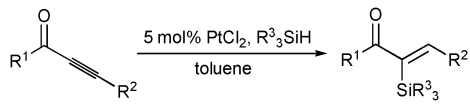
5. Organosilicon chemistry

5.1 Vinylsilanes

Methodology has been developed for the selective synthesis of *E*- or *Z*-α-silyl enones; platinum-catalysed rearrangement of α-hydroxypropargylsilanes gave *Z*-isomers, whilst platinum-catalysed hydrosilylation of ynones gave *E*-isomers. In both cases yields were high and selectivity was generally good.[98] (Schemes 58 and 59)

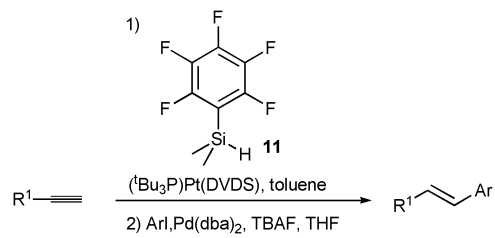


Scheme 58



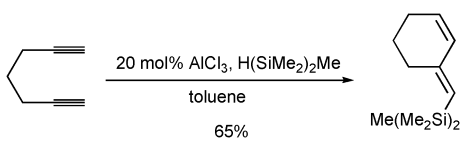
Scheme 59

Platinum-catalysed hydrosilylation of alkynes was also employed using fluorinated silane **11**. The resulting *E*-vinylsilanes were found to undergo efficient Hiyama coupling with aryl iodides. The paper also reported a method for the synthesis of *Z*-vinylsilanes starting from alkynes involving nucleophilic addition to the chlorosilane and subsequent reduction.[99] (Scheme 60)



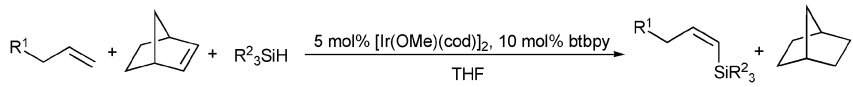
Scheme 60

Aluminium-catalysed hydrosilylation of diynes was reported, the final product depending on the silane used and with cyclisation as shown in Scheme 61 being possible.[100]



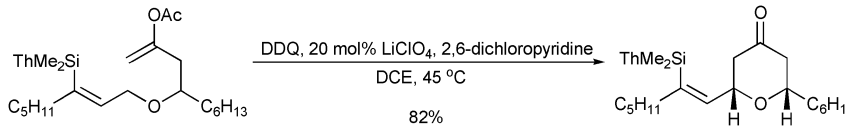
Scheme 61

Synthesis of vinylsilanes from simple alkenes was reported. Use of an iridium catalyst and norbornene as an oxidant was shown to tolerate a wide range of functionalities in the olefin and gave good *Z*-selectivity.[101] (Scheme 62)



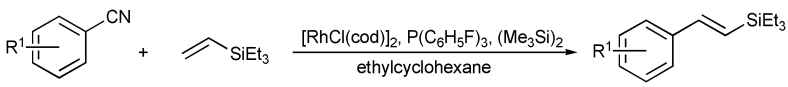
Scheme 62

Vinylsilanes were substrates in an interesting oxidative cyclisation reaction. Silyl-substituted allyl ethers reacted to give tetrahydropyran structures, with both *E*- and *Z*-silanes being reactive.[102] (Scheme 63)



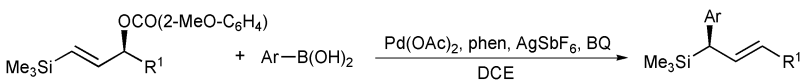
Scheme 63

Rhodium catalysis allowed Heck-Mizoroki-type couplings of vinylsilanes with aryl cyanides. The correct choice of conditions was critical in minimising side reactions, however, once optimised a range of substrates were shown to react with generally good yields.[103] (Scheme 64)



Scheme 64

Vinylsilanes were employed in the palladium-catalysed synthesis of chiral allylsilanes in which phenylboronic acid reacted with silyl-substituted allyl esters. The reaction of the resulting allylsilane with *iso*butyraldehyde was shown to proceed with a high level of retention of chirality.[104] (Scheme 65)

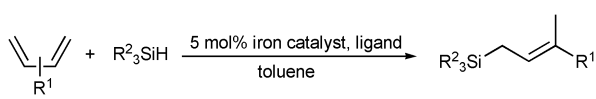


Scheme 65

Vinylsilanes were also employed in an intramolecular Hiyama coupling in the synthesis of macrolactones. The outcome of the reactions was found to be influenced by both solvent choice and the hydration level of the TBAF used in the reaction. Nevertheless, the reaction provided an efficient route to such compounds.[105]

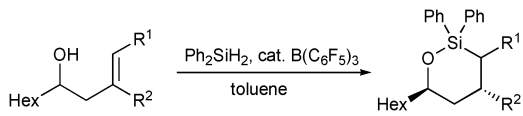
5.2 Other organosilicon chemistry

Catalytic hydrosilylation of alkenes saw a useful advance with the development of an iron catalyst, low loadings of which allowed the regio- and stereo-selective hydrosilylation of dienes. Both selectivities were extremely high and yields were routinely good.[106] (Scheme 66)



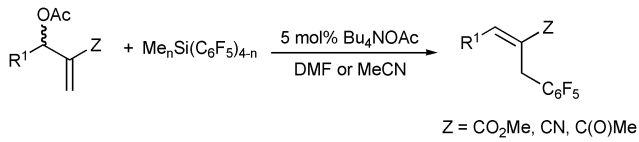
Scheme 66

Hydrosilylation also featured as part of a tandem reaction which effected the overall hydration of hydroxyl-containing alkenes. A triarylborane catalyst was employed which gave variable stereoselectivity and yields.[107] (Scheme 67)



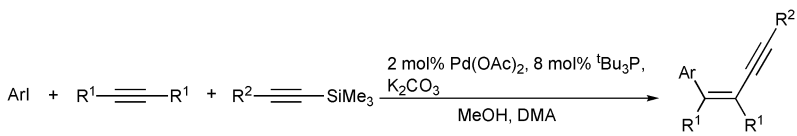
Scheme 67

Fluorinated silanes were shown to react with acetylated Baylis-Hilman adducts to give the addition of a perfluorophenyl group with concurrent loss of acetate. A range of adducts were shown to be reactive and the reaction was generally highly *E*-selective and required only catalytic tetrabutylammonium acetate in order to proceed.[108] (Scheme 68)



Scheme 68

Finally, the palladium-catalysed coupling of alkynyl silanes with internal alkynes and aryl iodides was shown to lead to the formation of enynes. The reaction gave good stereoselectivity, together with some regioselectivity when applied to non-symmetric internal alkynes.[109] (Scheme 69)



Scheme 69

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