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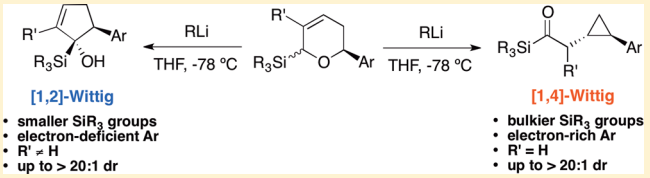
Stereoconvergent [1,2]- and [1,4]-Wittig Rearrangements of 2-Silyl-6-aryl-5,6-dihydropyrans: A Tale of Steric vs Electronic Regiocontrol of Divergent Pathways

Luis M. Mori-Quiroz and Robert E. Maleczka, Jr.*

Department of Chemistry, Michigan State University, 578 South Shaw Lane, East Lansing, Michigan 48824, United States

Supporting Information

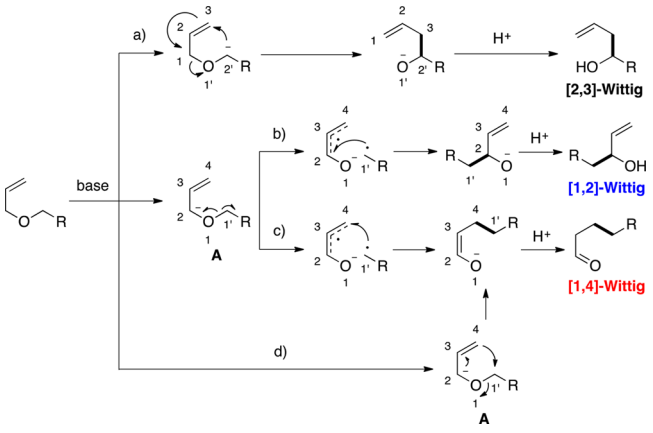
ABSTRACT: The regiodivergent ring contraction of diastereomeric 2-silyl-5,6-dihydro-6-aryl-(2*H*)-pyrans via [1,2]- and [1,4]-Wittig rearrangements to the corresponding α-silylcyclopentenols or (α-cyclopropyl)acylsilanes favor the [1,4]-pathway by *ortho* and *para* directing groups in the aromatic appendage and/or by sterically demanding silyl groups. The [1,2]-pathway is dominant with *meta* directing or electron-poor aromatic moieties. Exclusive [1,2]-Wittig rearrangements are observed when olefin substituents *proximal* to the silyl are present. *cis* and *trans* diastereomers exhibit different reactivities, but converge to a single [1,2]- or [1,4]-Wittig product with high diastereoselectivity and yield.



INTRODUCTION

Since their discovery more than 70 years ago,[1] Wittig rearrangements have evolved into powerful tools for the isomerization of α-metalated ethers into alkoxides. Wittig rearrangements can proceed through a concerted, orbital-symmetry-allowed [2,3]-sigmatropic shift (Scheme 1, route a),[2,3]

Scheme 1. Possible Wittig Rearrangement Pathways of an Allylic Ether



or a stepwise [1,2]-migration involving a radical/radical anion pair (route b).[4] Arguably, the [2,3]-Wittig rearrangement pathway has enjoyed more attention from both mechanistic and synthetic perspectives, resulting in an impressive display of applications such as the stereoselective assembly of adjacent chiral centers, the transfer of chirality, and the formation of olefins with specific geometries.[2,3] Although some of these features are also characteristics of the [1,2]-Wittig rearrangement, a narrower range of substrates are capable of efficient [1,2]-migration, perhaps a reflection of the requisite radical-stabilizing groups (i.e., R in Scheme 1) for facile C−O bond homolysis. Another complication is the inherent "problem" of regioselectivity that arises in (alkoxyallyl)metal species (**A** in Scheme 1), where the [1,4]-migration competes with the [1,2]-shift, leading to mixtures of products.[5,6] Relative to the [2,3]- and [1,2]-shifts, [1,4]-Wittig rearrangements (routes c and d) are unique in their ability to generate stereodefined enolates[7−9] (rather than alkyl alkoxides). In addition, [1,4]-Wittig rearrangements have the potential to transfer chirality and stereoselectively form adjacent chiral centers. Although there is some evidence supporting a stepwise mechanism for the [1,4]-pathway (route c),[9,10] a concerted process is allowed by orbital symmetry (route d) and might be operative in some instances. As such, the underlying factors that govern regiocontrol in favor of either the [1,4]- or [1,2]-pathway remain unclear.[8,11−13] In general, the [1,4]-shift is favored at lower temperatures, while the nature of the base and base counterion can affect the product distribution. However, the [1,4]:[1,2]-selectivity seems to be mostly substrate-dependent, and few studies have attempted to uncover features within a substrate type that can drive the rearrangement down one path over the other.[9,14]

Although the ring contractions of macrocyclic ethers by means of Wittig rearrangements via [1,2]- and [2,3]-pathways have been documented in the work of Marshall[15−17] and Takahashi,[18−22] the behavior of smaller cyclic ethers is limited to only a few examples explored in the course of mechanistic studies.[8,23−27] Although certain dihydrothiopyrans have been shown to isomerize to the corresponding cyclopropyl thioenolates under basic conditions at low temperatures,[28−33] we

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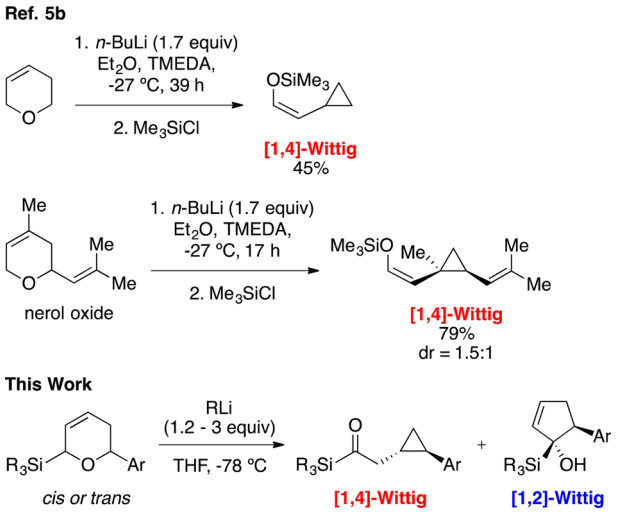
are aware of only two [1,4]-Wittig rearrangements of cyclic allylic ethers. Reported by Rautenstrauch in 1972, these examples involve the isomerization of dihydropyran and nerol oxide to the corresponding α-cyclopropylacetaldehydes (Scheme 2).[8] Surprisingly, these rearrangements did not receive

Scheme 2. Wittig Rearrangements of Dihydropyrans



further attention despite being complementary to Simmons–Smith-type reactions,[34−36] transition-metal-catalyzed diazoalkyl decomposition/olefin insertions,[37−42] and intramolecular cyclizations,[43−46] cycloisomerizations,[47−50] or stepwise cyclopropanation reactions.[51]

In this paper we demonstrate that the regioselection in favor of the [1,4]- or [1,2]-pathway within the context of the Wittig rearrangements of diastereomeric 2-silyl-6-aryl-5,6-dihydro-(2*H*)-pyrans (Scheme 2) is dependent on both electronic and steric factors. Thus, through electronic "tuning" at the aromatic appendage, judicious choice of the silyl group, or selecting certain olefin substitution patterns, allows one to maneuver these ring contractions toward α-silylcyclopentenols (via [1.2]-Wittig) or (α-cyclopropyl)acylsilanes (via [1,4]-Wittig), with excellent diastereoselectivities and in a stereoconvergent fashion.

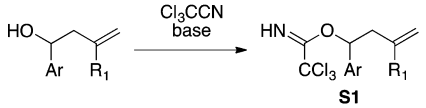
RESULTS AND DISCUSSION

Synthesis of 2-Silyl-5,6-dihydro-6-aryl-(2*H*)-pyrans and Precursors. Benzylic trichloroacetimidates **S1** were prepared by addition of homoallylic alcohols to trichloroacetonitrile under basic conditions (Scheme 3). α-Hydroxysilanes **S2** were prepared by retro-Brook rearrangement of in situ generated *O*-silylated allylic alcohols. The preparation of *O*-trimethylsilyl α-hydroxysilanes **S2-f** and **S2-g** involved trapping of the corresponding alkoxides with (TMS)Cl prior to aqueous workup (Scheme 3).

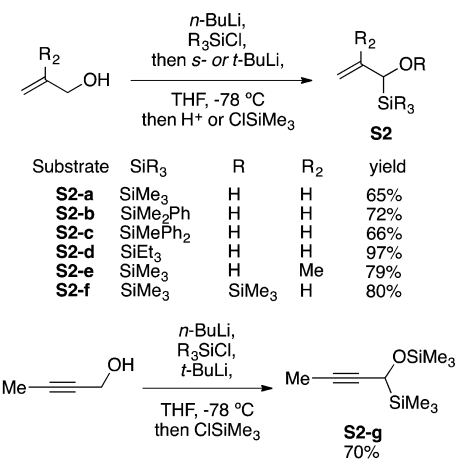
Lewis acid-catalyzed etherification of α-hydroxysilanes **S2** with benzylic trichloroacetimidates **S1** provided diastereomeric dienes **S3** that were submitted to ring-closing metathesis to afford cyclic ethers **1** and **2** (Scheme 4). Without exception, diastereomeric producs **1** (*trans*) and **2** (*cis*) were completely separated by column chromatography, although in some cases these could be prepared from diastereomerically pure precursors *syn*- or *anti*-**S3**. The alternative preparation of some dienes **S3** is shown in Scheme 5. Compounds **S3-j** and **S3-x** were synthesized by a three-component condensation of allyltrimethylsilane, a benzaldehyde derivative and *O*-trimethylsilyl α-hydroxysilane **S2-f** or **S2-g**, whereas dienes **S3-k** were prepared by Suzuki cross-coupling of precursors **S3-cc** with phenylboronic acid (Scheme 5).

Behavior of Model Substrates. Our group recently reported the highly selective [1,4]-Wittig rearrangement of allyl benzyl ether bearing a trimethylsilyl group at the α-allylic position.[13,52] Given the ability of the silyl group to (1) allow a selective deprotonation[53−56] step and (2) suppress the competitive [1,2]-pathway, we envisioned that diastereomeric cyclic ethers **1a**/**2a** (*trans* and *cis*, respectively) would be suitable substrates for Wittig rearrangements (Scheme 6). Indeed, under optimized conditions[57] (THF, −78 °C), the *trans* diastereomer **1a** underwent fast and selective allylic deprotonation by *n*-butyllithium and rearrangement within 5 min to give a mixture of the *trans* [1,4]-Wittig (α-cyclopropyl)acylsilanes **3a** and *cis* [1,2]-Wittig α-silylcyclopentenol **4a** in good overall yield (82%), albeit with modest selectivity (~2.4:1) in favor of the [1,4]-product. Remarkably, the diastereoselectivity of both [1,4]- and [1,2]-products was excellent. On the other hand, *cis* diastereomer **2a** was significantly less reactive and required excess *s*-butyllithium for complete conversion in 3 h. To our surprise, the same major diastereomers for both the corresponding [1,4]-shift (**3a**) and [1,2]-shift (**4a**) were obtained in

Scheme 3. Synthesis of Precursors S1 and S2



Substrate	Ar	R_1	yield
S1-b	2-$MeOC_6H_4$	H	78%
S1-c	3-$MeOC_6H_4$	H	85%
S1-d	4-$MeOC_6H_4$	H	65%
S1-e	2-MeC_6H_4	H	61%
S1-f	3-MeC_6H_4	H	80%
S1-g	4-MeC_6H_4	H	90%
S1-h	4-FC_6H_4	H	82%
S1-i	4-ClC_6H_4	H	76%
S1-l	2-naphthyl	H	95%
S1-t	2-PrC_6H_4	H	81%
S1-z	4-MeC_6H_4	Me	43%
S1-aa	2-thiophenyl	H	95%
S1-bb	2-furyl	H	42%
S1-cc	4-BrC_6H_4	H	86%



Substrate	SiR_3	R	R_2	yield
S2-a	$SiMe_3$	H	H	65%
S2-b	$SiMe_2Ph$	H	H	72%
S2-c	$SiMePh_2$	H	H	66%
S2-d	$SiEt_3$	H	H	97%
S2-e	$SiMe_3$	H	Me	79%
S2-f	$SiMe_3$	$SiMe_3$	H	80%

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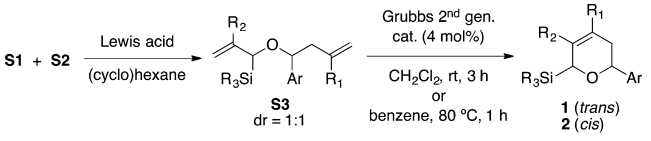
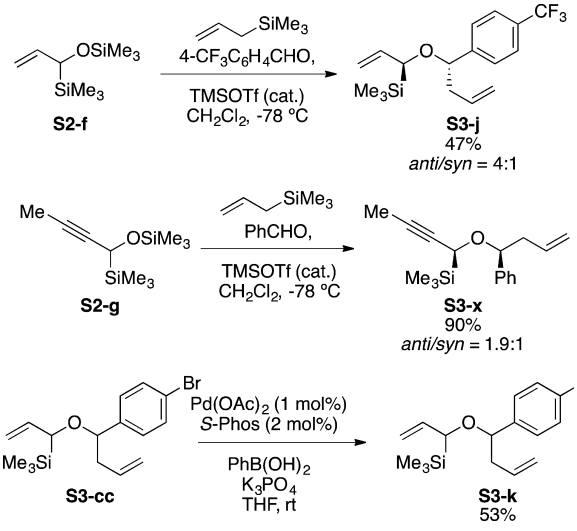
Scheme 4. Synthesis of Dienes S3 and Silyl Cyclic Ethers 1 and 2



	Ar	SiR_3	R_1	R_2	yield **S3**	**1** / **2**	yield **1** / yield **2** [a]
S3-a	C_6H_5	$SiMe_3$	H	H	62%	**1a** / **2a**	92% / 97%
S3-b	2-$MeOC_6H_4$	$SiMe_3$	H	H	77%	**1b** / **2b**	(93%)
S3-c	3-$MeOC_6H_4$	$SiMe_3$	H	H	60%	**1c** / **2c**	86% / 92%
S3-d	4-$MeOC_6H_4$	$SiMe_3$	H	H	60%	**1d** / **2d**	90% / 91%
S3-e	2-MeC_6H_4	$SiMe_3$	H	H	73%	**1e** / **2e**	(92%)
S3-f	3-MeC_6H_4	$SiMe_3$	H	H	56%	**1f** / **2f**	(78%)
S3-g	4-MeC_6H_4	$SiMe_3$	H	H	75%	**1g** / **2g**	(96%)
S3-h	4-FC_6H_4	$SiMe_3$	H	H	39%	**1h** / **2h**	88% / 93%
S3-i	4-ClC_6H_4	$SiMe_3$	H	H	54%	**1i** / **2i**	(91%)
S3-l	2-naphthyl	$SiMe_3$	H	H	48%	**1l** / **2l**	90% / 93%
S3-m	C_6H_5	$SiMe_2Ph$	H	H	58%	**1m** / **2m**	89% / 91%
S3-n	C_6H_5	$SiMePh_2$	H	H	83%	**1n** / **2n**	(61%)
S3-o	C_6H_5	$SiEt_3$	H	H	70%	**1o** / **2o**	84% / 95%
S3-p	3-$MeOC_6H_4$	$SiMe_2Ph$	H	H	71%	**1p** / **2p**	86% / 87%
S3-q	4-ClC_6H_4	$SiMe_2Ph$	H	H	91%	**1q**	92% / -
S3-r	4-ClC_6H_4	SiEt	H	H	67%	**1r**	83% / -
S3-s	2-naphthyl	$SiEt_3$	H	H	45%	**1r** / **2r**	94% / 79%
S3-t	2-PrC_6H_4	$SiMe_3$	H	H	24%	**1t** / **2t**	85% / 75%
S3-u	C_6H_5	$SiMe_3$	H	Me	44%	**1u** / **2u**	(90%)
S3-v	4-$MeOC_6H_4$	$SiMe_3$	H	Me	83%	**1v** / **2v**	72% / 86%
S3-w	4-MeC_6H_4	$SiMe_3$	H	Me	61%	**1w** / **2w**	(98%)
S3-y	C_6H_5	$SiMe_3$	Me	H	61%	**1y** / **2y**	63% / 67%
S3-z	4-MeC_6H_4	$SiMe_3$	Me	H	65%	**1z** / **2z**	82% / 60%
S3-aa	2-thiophenyl	$SiMe_3$	H	H	60%	**1aa** / **2aa**	(93%)
S3-bb	2-furyl	$SiMe_3$	H	H	49%	**1bb** / **2bb**	82% / 87%
S3-cc	4-BrC_6H_4	$SiMe_3$	H	H	37%	-	-
						1j / **2j**	(92%)
						1k / **2k**	(63%)
						1x / **2x**	62% / 49%

[a]Values in parentheses refer to the yield of a mixture of diastereomers **1** and **2** prepared from the corresponding mixture of *syn*/*anti* precursors **S3**. See the Experimental Section for diastereomeric ratios.

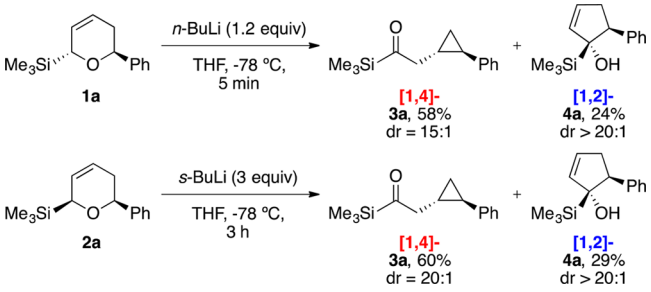
Scheme 5. Alternative Synthesis of Dienes S3



virtually the same [1,4]:[1,2] regioisomeric ratio (~2:1) observed for the *trans* isomer and in good overall yield.

The full stereoconvergence in the [1,2]- and [1,4]-Wittig rearrangements of *trans* (**1a**) and *cis* (**2a**) diastereomers is of significant importance because, in particular for the [1,2]-Wittig pathway, it challenges the known stereochemical outcome of this manifold.[4] However, this apparent conflict can be rationalized by invoking the intermediacy of a common intermediate, and we have gathered supporting evidence of such species (vide infra) that accounts for the observed stereoconvergence and the similar product ratios obtained from the isomerization of each diastereomer.

Scheme 6. [1,2]- and [1,4]-Wittig Rearrangements of Model 2-Silyldihydropyrans 1a and 2a under Optimized Conditions



Electronic Effects. Our study continued with the evaluation of the electronic effects on the aromatic appendage (Table 1). Such modifications to pyrans **1a** and **2a** were expected to directly impact the ability of the benzylic carbon to migrate through a [1,4]- or [1,2]-mode. Nonetheless, the same reactivity trend was observed for these compounds: *trans* diastereomers **1b**–**l** (entries 1–11) underwent complete rearrangement within 10 min, whereas *cis* diastereomers **2b**–**l** (entries 12–22) required at least 3 h for complete conversion.

A second trend was clearly observed in the *trans* diastereomers series: Electron-donating groups located at the *ortho* and *para* positions increased the [1,4]-selectivity (entries 3, 4, and 6), with the *p*-methoxy-substituted compound **1d** giving exclusive [1,4]-selectivity. *o*-Methoxy substrate **1b** (entry 1) is an exception that might be attributed to coordination of oxygen lone pairs to the lithium cation during rearrangement, leading to a slight decrease in [1,4]:[1,2]-selectivity relative to that of the unsubstituted analogue **1a**. The inductively electron-withdrawing methoxy group located at the *meta* position (entry 2) led to an evident decrease in [1,4]:[1,2]-selectivity, providing the [1,2]-Wittig product in slight excess over the [1,4]-product. The weakly electron-donating methyl group located at the *meta* position (entry 5) led to a negligible effect in product distribution relative to that of the model substrate **1a**. The fine balance between resonance and inductive effects was even more evident in halogenated compounds (entries 7 and 8): *p*-Fluoro-substituted compound **1h** afforded a 6:1 [1,4]:[1,2]-selectivity, whereas *p*-chloro-substituted compound **1i** gave the reverse regioselection ([1,4]:[1,2] = 1:1.5). On the opposite side of the spectrum, a *p*-trifluoromethyl group at the phenyl ring led to exclusive formation of the [1,2]-Wittig product (entry 9), whereas a *p*-biphenyl and 2-naphthyl groups directly attached to the migrating carbon also afforded high selectivity in favor of the [1,2]-shift (entries 10 and 11). In all pertinent cases, the [1,2]-Wittig product was obtained as a single diastereomer, whereas the [1,4]-product was formed with high diastereoselection (>15:1).

Evaluation of *cis* diastereomers (entries 12–22, Table 1) confirmed the stereoconvergence of the [1,4]- and [1,2]-Wittig rearrangements. Both [1,4]- and [1,2]-pathways proceeded with diastereoselectivity similar to that of their *trans* counterparts, and the same electronic effects in product distribution were observed in most cases. The sluggishness of *cis* diastereomers to undergo allylic deprotonation had a detrimental effect on the overall yield due to competitive reactions such as *ortho* metalation (entries 14 and 18), lithium–halogen exchange (entry 19), and presumably competitive benzylic deprotonation (entry 20). Competitive *ortho* metalation, in particular, seems to retard rearrangement significantly, as suggested by deuterium quenching experiments.[S8]

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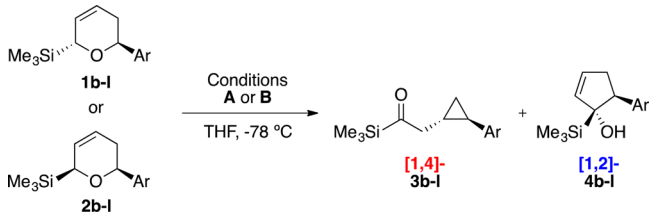
Table 1. Electronic Effects on the [1,2]:[1,4]-Product Distribution



entry	substrate	Ar	conditions[a]	[1,4] yield[b] (%)	[1,4] dr[c]	[1,2] yield[b,d] (%)	[1,4]:[1,2] ratio
1	**1b**	2-MeOC$_6$H$_4$	A	56	15:1	37	1.5:1.0
2	**1c**	3-MeOC$_6$H$_4$	A	33	17:1	44	1.0:1.3
3	**1d**	4-MeOC$_6$H$_4$	A	65	15:1		>98.5:1.0
4	**1e**	2-MeC$_6$H$_4$	A	80	20:1	15	5.3:1.0
5	**1f**	3-MeC$_6$H$_4$	A	59	20:1	30	2.0:1.0
6	**1g**	4-MeC$_6$H$_4$	A	86	20:1	7	12.3:1.0
7	**1h**	4-FC$_6$H$_4$	A	66	20:1	11	6.0:1.0
8[e]	**1i**	4-ClC$_6$H$_4$	A	28	15:1	65	1.0:2.3
9	**1j**	4-CF$_3$C$_6$H$_4$	A	trace		80	<1.0:98.5
10	**1k**	4-PhC$_6$H$_4$	A	4	nd	59	1.0:14.8
11	**1l**	2-Naph	A	3	nd	96	1.0:32.0
12	**2b**	2-MeOC$_6$H$_4$	B	50	15:1	34	1.5:1.0
13	**2c**	3-MeOC$_6$H$_4$	B	33	18:1	25	1.3:1.0
14[f]	**2d**	4-MeOC$_6$H$_4$	B	52	8:1		>98.5:1.0
15	**2e**	2-MeC$_6$H$_4$	B	69	20:1	12	5.8:1.0
16	**2f**	3-MeC$_6$H$_4$	B	51	20:1	20	2.6:1.0
17	**2g**	4-MeC$_6$H$_4$	B	73	20:1	7	10.4:1.0
18[g]	**2h**	4-FC$_6$H$_4$	B	25	10:1	3	8.3:1.0
19[h]	**2i**	4-ClC$_6$H$_4$	B	nd	nd	nd	
20[h]	**2j**	4-CF$_3$C$_6$H$_4$	B	nd		12	>1.0:98.5
21	**2k**	4-PhC$_6$H$_4$	B	7	7:1	75	1.0:10.7
22[i]	**2l**	2-Naph	B	<4	nd	59	1.0:14.8

[a]Conditions: (A) *n*-BuLi (1.2 equiv), 10 min; (B) *s*-BuLi (3 equiv), 3 h. [b]Isolated yields. [c]Determined by ^{1}H NMR of isolated material. [d]dr > 20:1 in all cases. [e]A 1.1 equiv amount of *n*-BuLi. [f]At −78 °C, 6 h, then rt, 20 h. [g]Total of 58% recovered **2h** and isomeric enol cyclic ether. [h]Complex mixture. [i]Time 6 h.

We conducted a Hammett plot analysis for *para*-substituted compounds (X = MeO, Me, F, Cl, and CF$_3$) in the *trans* series (Table 1, entries 3 and 6−9) because these diastereomers underwent clean rearrangement relative to their *cis* counterparts. Since the [1,2]-Wittig rearrangement is believed to follow a stepwise mechanism and assuming the [1,4]-shift proceeds by an analogous homolytic process, both would be dependent on the extent of radical stabilization at the migrating center. Therefore, we initially attempted to correlate $\sigma^{\bullet}$ scales vs $\log(k_X/k_0)$ (where k_X = [1,2]:[1,4] ratio derived from *para*-substituted compounds and k_0 = [1,2]:[1,4] ratio from **1a**); however, severe deviations from linearity were obtained. On the other hand, good correlation of our data with σ and σ^+ parameters was obtained ($R^2 > 0.96$) (Figure 1). This suggests that spin delocalization of a presumed benzylic radical is not as important as the polar effects induced by the *para* substituents in the transition state of C−O bond cleavage, which is likely the rate-determining step.[59] A buildup of negative charge at the benzylic migrating carbon appears to favor the [1,2]-migration, whereas any increasingly positive character of this position favors the [1,4]-shift. The large ρ values (3.10 and 4.37) indicate a high sensitivity to the nature of the substituent X, and a balance between resonance and inductive effects seems to play an important role in determining the [1,4]:[1,2]-selectivity. We cautiously interpret these observations as supporting evidence for a stepwise mechanism for both [1,2]- and [1,4]-pathways, in which a relatively slow C−O bond homolysis is followed by rapid intramolecular recombination of the diradical anion, leading to the observed products.

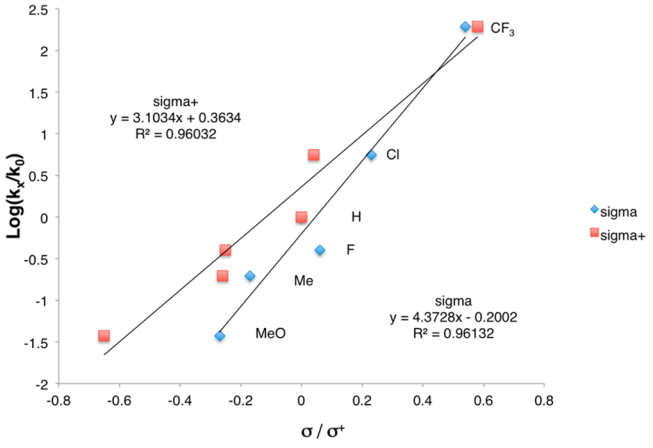


Figure 1. Hammett plots of $\log(k_X/k_0)$ vs σ and σ^+.

Discarding a Background Isomerization Pathway. We were cognizant of the possibility that the [1,2]-Wittig alkoxide and [1,4]-Wittig enolate (that is, the primary rearrangement products) might equilibrate prior to workup, giving a false "electronic effect". In fact, α-cyclopropyl ketones bearing anion-stabilizing groups attached to the ring are known to undergo ring expansion to their cyclopentenol isomers under basic

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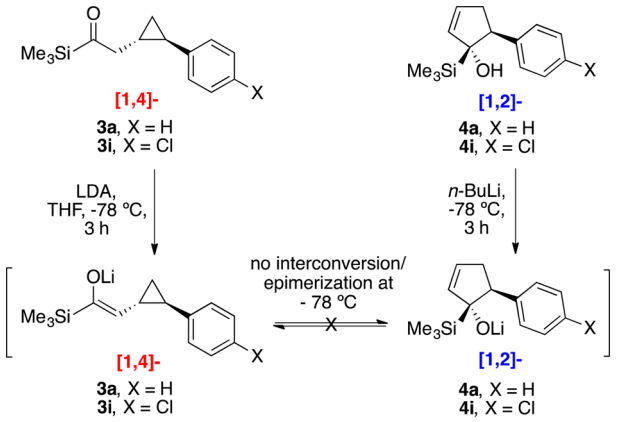
conditions,[60] whereas some cyclopropyl thioenolates isomerize to the corresponding cyclopentenyl thiolates.[32,33] However, independent subjection of selected products to the reaction conditions A or B (Table 1) did not lead to any [1,2]/[1,4]-interconversion (or vice versa) (Scheme 7). In line with this

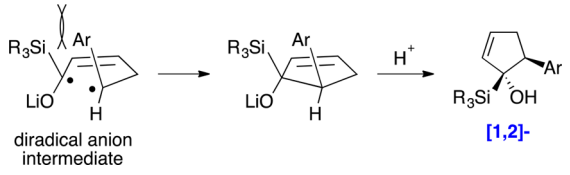
Scheme 7. Isomerization of the [1,4]-Enolate to the [1,2]-Alkoxide (and Vice Versa) Was Not Observed



observation, the diastereoselectivity in both [1,4]- and [1,2]-ring contractions is defined during rearrangement, as little or no change in diastereomeric ratio was observed in these control experiments. In fact, only upon warming the reaction mixture of certain [1,2]-products (alkoxides) for prolonged periods was epimerization ever observed. Thus, we have established that the observed product ratios are a true consequence of electronic effects and a secondary equilibration pathway is not operative at −78 °C.[61]

Stereoelectronic Effects of the Silyl Group. We next looked to tackle the modest [1,4]:[1,2]-selectivity obtained in most cases, as well as the adverse [1,4]-selectivity in electron-deficient substrates. A closer inspection of the [1,2]-Wittig product reveals two adjacent stereocenters in which the bulkier groups (Ph and $SiMe_3$) are in a *cis* relationship. Since the [1,2]-Wittig pathway proceeds via a radical/radical anion intermediate (Scheme 8),[4] we rationalized that increasing the steric

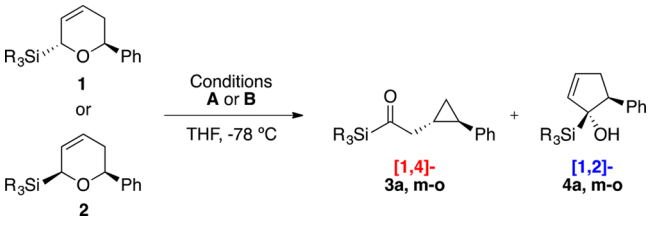
Scheme 8. Diradical Anion Species Leading to Alkoxide Products by Intramolecular Recombination ([1,2]-Product)



demand of the silyl (SiR_3) group would inhibit recombination via the [1,2]-pathway, indirectly stimulating the [1,4]-migration.

Gratifyingly, our hypothesis was right, and a gradual increase in the steric demand of the silyl group consistently led to greater [1,4]:[1,2]-product ratios (Table 2). In the *trans* series, changing a $SiMe_3$ group to a $SiMe_2Ph$ group increased the selectivity from 2.4:1 to ∼10:1 (entries 1 and 2), and the even larger $SiMePh_2$ group facilitated exclusive [1,4]-Wittig rearrangement in excellent yield (entry 3). We believe the improved regioselectivity is primarily dominated by the sterics of the silyl group with little electronic contribution. Indeed,

Table 2. Effect of the Silyl Group on the [1,2]:[1,4]-Selectivity[a]



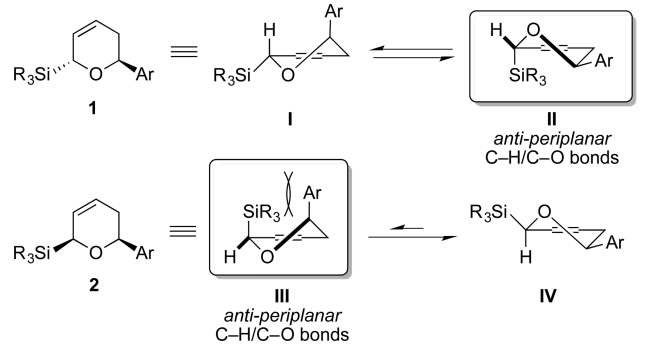
entry	substrate	SiR_3	[1,4] yield[b] (%)	[1,4] dr[c]	[1,2] yield[b,d] (%)	[1,4]:[1,2] ratio
1	**1a**	$SiMe_3$	58	15:1	24	2.4:1.0
2	**1m**	$SiMe_2Ph$	69	20:1	7	9.9:1.0
3	**1n**	$SiMePh_2$	79	20:1		>98.5:1.0
4	**1o**	$SiEt_3$	93	20:1	5	18.6:1.0
5	**2a**	$SiMe_3$	60	20:1	29	2.1:1.0
6	**2m**	$SiMe_2Ph$	74	20:1	7	10.6:1.0
7[e]	**2n**	$SiMePh_2$	51	20:1		>98.5:1.0
8[f]	**2o**	$SiEt_3$	71	10:1	4	17.8:1.0

[a]Conditions: (A) *n*-BuLi (1.2 equiv), 10 min; (B) *s*-BuLi (3 equiv), 3 h. [b]Isolated yields. [c]Determined by ^{1}H NMR of isolated material. [d]dr > 20:1 in all cases. [e]Total of 16% recovered **2n**. [f]At −78 to 0 °C, 6 h.

increasing the bulkiness of the silyl group only with alkyl groups ($SiEt_3$, entry 4) also led to excellent [1,4]:[1,2]-selectivity.

The corresponding *cis* diastereomers afforded virtually the same product ratios with excellent diastereoselectivities. However, the more sterically demanding silyl groups were deleterious for the reactivity of these isomers. Given that the reactivity of *trans* isomers was minimally affected, the severe loss of reactivity in *cis* diastereomers suggests bulkier silyl groups shift the conformational equilibrium to the less reactive conformation. The relevant conformers for both *trans* and *cis* diastereomers involve half-chair arrangements and are depicted in Scheme 9. Although the system in discussion involves a

Scheme 9. Conformational Analysis for the *trans* (1) and *cis* (2) Diastereomers Relevant for the Deprotonation Step



dihydropyran structure, we believe it is reasonable to use *A* values (derived from the cyclohexane system) to estimate conformational ratios since the overall trend should remain. Accordingly, in the case of *trans* diastereomer **1**, conformers **I** and **II** are expected to exist in approximately a 1:2.5 ratio, with a small predominance of conformer **II** on the basis of the conformational *A* values for trimethylsilyl and phenyl groups in cyclohexane (2.5 and 2.9, respectively).[62,63]

As we have previously suggested in the case of α-silyl acyclic ethers,[14] we believe the optimum conformation for allylic

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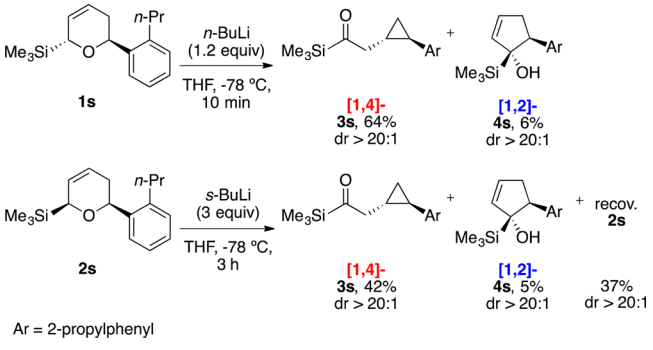
deprotonation requires an antiperiplanar arrangement of the allylic C−H and benzylic C−O bonds,[64,65] which presumably heightens the acidity of the allylic C−H bond.[66] In addition, the resulting pseudoequatorial carbanion is expected to be more stable than the axial one, as suggested by theoretical[67,68] and experimental[26,69−73] studies. Conformer **II**, in which the aryl ring is orientated pseudoequatorially and the silyl group pseudoaxially, meets this requirement. Although an increase in the steric demand of the silyl group is expected to shift the conformational equilibrium to the less reactive conformer **I**, the extent of this perturbation is expected to be modest given the larger Si−C bond length (1.89 Å vs 1.54 Å for C−C bonds) and the absence of severe steric interactions of the pseudoaxial silyl group in conformer **II**. On the other hand, *cis* diastereomers **2** are intrinsically "locked" in conformation **IV** in which both aryl and silyl groups are oriented in pseudoequatorial positions. The required conformation for deprotonation (conformation **III**) presents a severe steric clash between these bulky groups, which is expected to get worse as the silyl group becomes more sterically demanding.

Because the conformational equilibrium was also expected to be dependent on the steric demand of the aryl group, we reasoned that installing a large *ortho* substituent would lead to an increase in the population of conformers **II** and **IV** (for the *trans*-**1** and *cis*-**2** diastereomers, respectively), leading to a further increase of reactivity of the *trans* diastereomer (**1**) and a decrease in the reactivity of the *cis* diastereomer (**2**). Consistent with this hypothesis is the observation that placement of a propyl group at the *ortho* position of the phenyl ring did not influence the reactivity of **1s** (full conversion in <10 min as observed with **1a**), whereas **2s** reacted more slowly than the unsubstituted **2a** (only 63% conversion in 3 h vs full conversion in the case of **2a**) (Scheme 10).

Scheme 10. Effect of Increasing Steric Demand at the *ortho* Position of the Aromatic Ring



Of interest is the observation that the effect of increasing the steric demand of the aryl group on product distribution is equivalent to what was observed by changing the size of the silyl group. In the *trans* series the [1,4]:[1,2] ratio gradually increased from 2.4:1 for the unsubstituted substrate **1a** to 5.3:1 for *o*-methyl analogue **1e** and to 11:1 for *o*-propyl analogue **1s**. A similar increase in [1,4]:[1,2]-selectivity is observed in corresponding *cis* diasteromers **2a** (2:1), **2e** (5.8:1), and **2s** (8.4:1). This is supportive of our initial hypothesis and the determining role of sterics in the product distribution.

Outcome of Antagonistic Electronic and Steric Properties. We also evaluated the competition between *opposite* steric and electronic effects as per the above discussion. For this purpose, we chose substrates that were electronically biased toward the [1,2]-Wittig rearrangement and studied the effect of silyl groups larger than $SiMe_3$, which were expected to shift the selectivity in favor of the [1,4]-pathway (Table 3). *trans* and *cis* diastereomers **1p** and **2p** bearing an *m*-methoxy group at the phenyl ring and the bulky $SiMe_2Ph$ underwent rearrangement with higher [1,4]:[1,2]-selectivity (3.9:1 and 3.5:1, respectively, entries 2 and 3) relative to the $SiMe_3$ counterpart **1c** (∼1:1.3, entry 1). Following this trend, in the *trans*-substituted (*p*-chlorophenyl)dihydropyran series, the [1,4]:[1,2]-selectivity was gradually reversed from 1:2.3 with the $SiMe_3$ analogue **1i** (entry 4) to ∼1:1 for the bulkier $SiMe_2Ph$ group in **1q** (entry 5) and to 2.8:1 for the $SiEt_3$ derivative **1r** (entry 6). The *trans*-2-naphthyl-substituted dihydropyrans bearing a $SiMe_3$ (**1l**) and $SiEt_3$ (**1s**) afforded ∼1:32 and ∼1:5 [1,4]:[1,2]-selectivities (entries 7 and 8), respectively. Analysis of the crystal structure of [1,2]-Wittig product **4s** (Figure 2) bearing the 2-naphthyl and $SiEt_3$ groups in a *cis* relationship suggests a significant steric clash between these groups exists and thus the [1,4]:[1,2]-selectivity is higher for **1s** vs **1l**.

The opposite diastereomer **2s** afforded a 5:1 [1,4]:[1,2]-selectivity (entry 9). The opposite regioselectivity obtained from diastereomers **1s** and **2s** is a consequence of the higher temperature and prolonged reaction time for the rearrangement of **2s**. One possible explanation is that under these reaction conditions the initially formed [1,2]-Wittig alkoxide isomerizes to the corresponding [1,4]-enolate. However, we also speculate that competitive arene metalation leads to an electron-rich species that following allylic deprotonation rearranges preferentially via the [1,4]-Wittig pathway. Although no evidence of the intermediacy of such species was gathered in this specific case, we have determined that doubly lithiated species (heteroaryl/allylic dianion) rearrange with remarkably different selectivies relative to the monolithiated species (see below).

Effect of Olefin Substitution. The effect of olefin substitution was studied next. Alkyl or alkenyl substitution *proximal* to the silyl group veered the selectivity exclusively to the [1,2]-Wittig rearrangement. Cyclopentenols were obtained in good yields and excellent diastereoselectivity; however, a noticeable decrease in reactivity was observed in both *trans* and *cis* diastereomeric ethers, and longer reaction times were required for complete conversion (Table 4).[74] We attempted to shift the selectivity in favor of the [1,4]-pathway by electronic modification of the aromatic ring (introducing *para* electron-donating groups), but only the [1,2]-products were obtained, and no cyclopropyl compounds were observed in these cases.

In contrast to the previous examples, alkyl olefin substitution *distal* to the silyl group provided low [1,4]:[1,2]-product selectivity, but with good overall yields (Table 5). The diastereoselectivity of the [1,2]-shift remained high as in previous examples, but that of the [1,4]-product, bearing an all-carbon quaternary center, was modest. The lower [1,4]:[1,2]-selectivity with respect to that of unsubstituted analogues (Scheme 6) suggests the methyl substitution slightly hinders the [1,4]-shift due to steric reasons.

The exclusive [1,2]-selectivity observed in substrates having olefin substitution *proximal* to the silyl group (but not when *distal*) can be attributed to an unfavorable steric interaction between the olefin substituent and the silyl group. We conjecture that this leads to partial localization of the allyl anion (prior to rearrangement)[75,76] or of the putative diradical anion intermediate in a stepwise scenario (Scheme 8), leading to a structural distortion that completely inhibits the [1,4]-Wittig migration.

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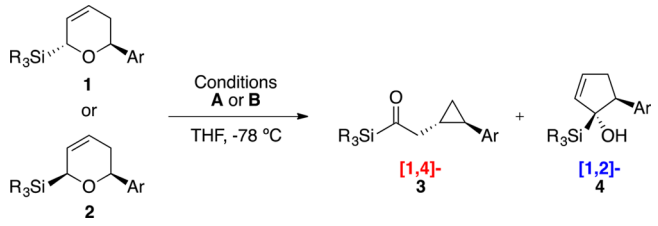
Table 3. Competition between Electronic and Steric Effects[a]



entry	substrate	SiR_3	Ar	[1,4] yield[b,c] (%)	[1,2] yield[b,c] (%)	[1,4]:[1,2] ratio
1	**1c**	$SiMe_3$	3-$MeOC_6H_4$	33	44	1.0:1.3
2	**1p**	$SiMe_2Ph$	3-$MeOC_6H_4$	67	17	3.9:1.0
3[d]	**2p**	$SiMe_2Ph$	3-$MeOC_6H_4$	49	14	3.5:1.0
4	**1i**	$SiMe_3$	4-ClC_6H_4	28	65	1.0:2.3
5	**1q**	$SiMe_2Ph$	4-ClC_6H_4	47	44	1.1:1.0
6	**1r**	$SiEt_3$	4-ClC_6H_4	64	23	2.8:1.0
7	**1l**	$SiMe_3$	2-Naph	3	96	1.0:32.0
8	**1s**	$SiEt_3$	2-Naph	16	75	1.0:4.7
9[e]	**2s**	$SiEt_3$	2-Naph	45	9	5.0:1.0

[a]Conditions: (A) *n*-BuLi (1.2 equiv), 10 min; (B) *s*-BuLi (3 equiv), 3 h. [b]Isolated yields. [c]See the Experimental Section for the dr of the products. [d]Time 6 h, 20% recovered **2p** and isomeric cyclic enol ether. [e]At −78 to 0 °C, 6 h.

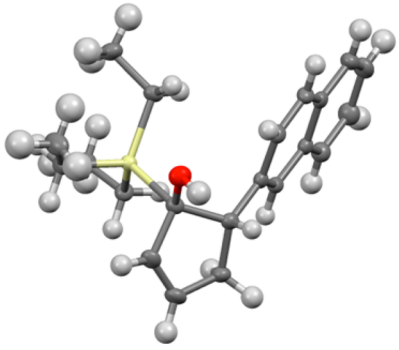
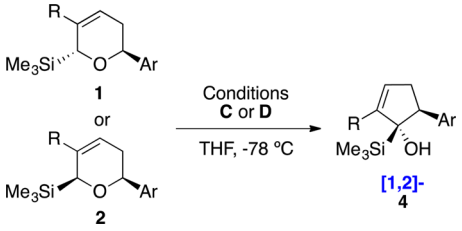


Figure 2. Crystal structure of [1,2]-Wittig product **4s**.

Table 4. Olefin Substitution Proximal to the Silyl Group[a]



entry	substrate	R	Ar	time (h)	yield of 4[b] (%)
1	**1u**	Me	Ph	0.5	85
2	**1v**	Me	4-$MeOC_6H_4$	0.5	72
3	**1w**	Me	4-MeC_6H_4	0.5	91
4[c]	**1x**	isopropenyl	Ph	1.5	75
5	**2u**	Me	Ph	7	79
6	**2v**	Me	4-$MeOC_6H_4$	7	26
7	**2w**	Me	4-MeC_6H_4	6	75
8[d]	**2x**	isopropenyl	Ph	20	12

[a]Conditions: (C) (**1u**−**x**) *n*-BuLi (1.2 equiv), 30 min; (D) (**2u**−**x**) *s*-BuLi (3 equiv), 6−7 h. [b]Isolated yields. [c]Total of 13% recovered **1x**. [d]Total of 51% recovered **2x**.

[1,4]-Wittig Selectivity of Dianionic Species. We have found that the [1,4]:[1,2]-selectivity in certain heteroaryl-substituted substrates diverged markedly when proceeding through the usual allylic monoanion or through a dianionic species generated by initial deprotonation at the heteroaryl ring followed by allylic deprotonation. Diastereomeric 2-thiophene-yl (**1aa**/**2aa**) and 2-furyl (**1bb**/**2bb**) cyclic ethers were subjected to our standard reaction conditions for *cis* and *trans* diastereomers (Scheme 11). The *trans* isomers **1aa** and **1bb** underwent complete rearrangement within 10 min with significantly different [1,4]:[1,2]-selectivities, revealing a high electronic dependence. The *trans*-2-thiophene-yl-substituted compound **1aa** afforded a 3:1 [1,4]:[1,2]-product ratio in 97% overall yield, whereas the analogous *trans*-2-furyl-substituted compound **1bb** rearranged exclusively via the [1,2]-pathway to give cyclopentenol **4bb** in 81% yield. On the contrary, the corresponding *cis* diasteromers **2aa** (2-thiophene-yl) and **2bb** (2-furyl) underwent exclusive [1,4]-Wittig rearrangements to give (cyclopropyl)acylsilanes **3aa** and **3bb** (>20:1 selectivity) in 84% and 48% yields (based on recovered starting material (brsm)), respectively, both with low diastereoselectivity.

The unexpected exclusive [1,4]-Wittig selectivity in the rearrangement of both *cis* diastereomers **2aa** and **2bb** suggested that competitive deprotonation at the heteroaryl system was taking place. Indeed, deuterium-trapping experiments demonstrated the intermediacy of a dianionic species formed by deprotonation at the 5-position of both thiophene-yl and furyl rings and at the allylic position. Additional control experiments discarded the potential isomerization of the [1,2]-alkoxide to the [1,4]-enolate within the reaction time (3 h) at −78 °C. For instance, both [1,4]-enolate and [1,2]-alkoxide products were generated in 10 min from the rearrangement of *trans*-2-thiophene-yl-substituted isomer **1aa**, and the reaction mixture was kept at −78 °C for an additional 3 h. Both [1,4]- and [1,2]-Wittig products **3aa** and **4aa** were isolated in a combined 81% overall yield and in a 5:1 ratio. That is, the [1,4]:[1,2]-selectivity was not significantly modified, and [1,4]/[1.2]-equilibration does not take place to a significant extent. Although this product ratio is slightly higher than that observed when the reaction was stopped after 10 min, the lower yield of the reaction suggests some product decomposition took place during the extended time, thereby influencing the measured product distribution.

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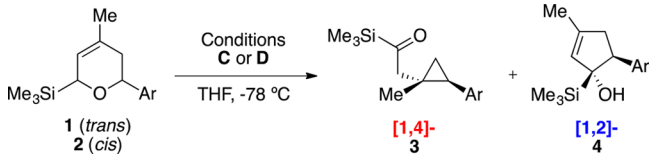
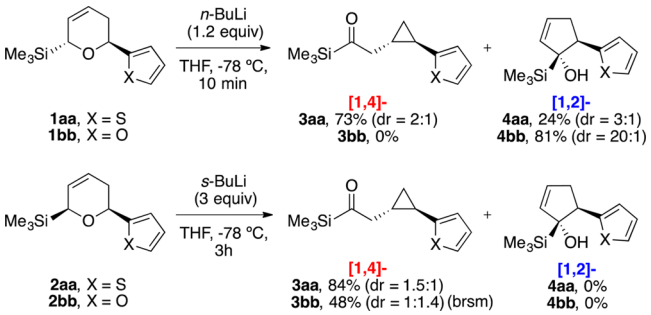
Table 5. Olefin Substitution Distal to the Silyl Group[a]



entry	substrate	Ar	[1,4] yield[b] (%)	dr	[1,2] yield[b] (%)	dr	[1,4]:[1,2] ratio
1	**1y**	Ph	44	7:1	38	20:1	1.2:1.0
2	**1z**	4-MeC_6H_4	44	9:1	43	20:1	1.0:1.0
3	**2y**	Ph	42	6:1	32	12:1	1.3:1.0
4	**2z**	4-MeC_6H_4	45	5:1	30	20:1	1.5:1.0

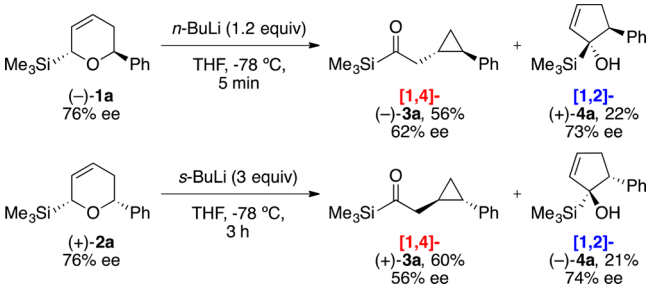
[a]Conditions (C) (**1y**, **1z**) *n*-BuLi (1.2 equiv), 15 min; (D) (**2y**, **2z**): *s*-BuLi (3 equiv), 6 h. [b]Isolated yields.

Scheme 11. Rearrangements of Heteroaromatic Substrates



Stereochemical Course of the [1,4]- and [1,2]-Wittig Rearrangements. To ascertain the origin of stereoconvergence, we first studied the rearrangement of enantiomerically enriched substrates (−)-**1a** and (+)-**2a** (both in 76% ee) (Scheme 12). Although the [1,2]-Wittig shift is known to occur

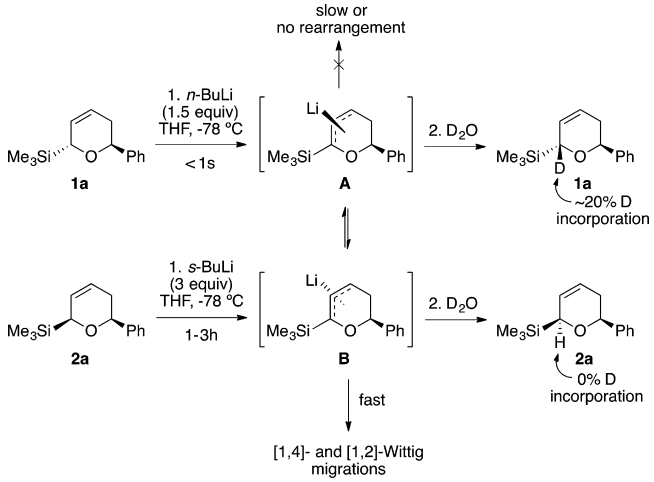
Scheme 12. Stereochemical Course of the [1,4]- and [1,2]-Wittig Rearrangements of (−)-1a and (+)-2a



with high retention of stereochemistry at the migrating carbon, in both acyclic[4] and cyclic[26] ethers, the stereochemical course of the competing [1,4]-Wittig pathway has only been studied in one acyclic instance.[10] As expected, [1,2]-Wittig rearrangement of (−)-**1a** and (+)-**2a** proceeded with very high retention of stereochemistry at the benzylic carbon to give enantiomeric cyclopentenols (+)-**4a** and (−)-**4a** in 73% and 74% ee, respectively. Importantly, the [1,4]-Wittig shift of (−)-**1a** and (+)-**2a** also occurred with retention of stereochemistry at the migrating center to give enantiomeric (α-cyclopropyl)-acylsilanes (−)-**3a** and (+)-**3a** in 62% and 56% ee, respectively.

In separate experiments, we attempted to trap allylic carbanions **A** and **B** generated by deprotonation of **1a** and **2a**, respectively (Scheme 13). Quenching the reaction of **1a** with D_2O immediately after *n*-BuLi addition (t < 1s) led to deuterium incorporation (20%) at the allylic position without

Scheme 13. Deuterium Trapping Experiments and Proposed Origin of Stereoconvergence



epimerization (dr > 20:1). On the other hand, attempts to trap the allylic anion **B** derived from **2a** with D_2O were unsuccessful, suggesting such species undergoes immediate rearrangement. On the basis of these results, we speculate the fleeting carbanion **B** is the actual species undergoing rearrangement, which implies the allylic carbanion **A**, generated from **1a** (which can be trapped with D_2O), has to isomerize[77] to species **B**. This is consistent with the fact that the chiral information at the silicon-bearing center (the allylic stereocenter) is destroyed during both [1,2]- and [1,4]-Wittig rearrangements and the absolute configurations of both products are determined exclusively by the configurations of the migrating carbon.

It is important to note that the rearrangement of species **B** is in accord with the "normal" stereochemical course at the lithium-bearing carbon in the [1,2]-Wittig pathway (assuming a localized character of (α-silylallyl)lithium **B**) involving inversion of stereochemistry. Lastly, the observation that the stereochemical course of the [1,4]-Wittig rearrangement in these cyclic systems mirrors that of the competing [1,2]-migration strongly suggests both pathways involve the same stepwise mechanism.

■ CONCLUSIONS

In summary, we have developed a method to access (α-cyclopropyl)acylsilanes and α-silylcyclopentenol structures with high diastereoselectivities and overall high efficiency via [1,4]- and [1,2]-Wittig rearrangements of 2-silyl-6-aryldihydropyrans. The regioselective allylic deprotonations that trigger

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these rearrangements are made possible by the silyl appendage. *trans*/*cis* diastereomers show markedly different reactivities toward the deprotonation step, which we have rationalized on the basis of the expected acidities of equilibrating conformers. We have shown that the [1,4]:[1,2]-selectivity is governed by both electronic and steric characteristics of the reacting cyclic ethers. The [1,4]-Wittig pathway is favored by increasing the electron density at the migrating carbon and also by increasing the steric demand of the silyl group. On the other hand, electron-deficient migrating centers favor the [1,2]-pathway, and olefin substitution at the olefin *proximal* to the silyl group leads to exclusive [1,2]-migration. The role of the silyl group in determining the [1,4]:[1,2]-selectivity seems to be predominantly steric; however, electronic modification at the silyl group substituents has not been explored in this study. Stereochemical experiments demonstrate both [1,4]- and [1,2]-Wittig rearrangements of dihydropyrans proceed with high retention of stereochemistry at the migrating center. Deuterium-trapping experiments support the intermediacy of a common intermediate, which is responsible for the observed stereoconvergence of both isomerization pathways. Taken together, our results make it reasonable to conclude that the primary mechanism of the [1,4]-Wittig migration in these cyclic ethers involves a stepwise process analogous to the [1,2]-pathway. Further studies to expand the scope of these transformations are under way.

EXPERIMENTAL SECTION

Unless otherwise noted all reactions were run under a positive atmosphere of nitrogen in oven-dried or flame-dried round-bottom flasks or disposable drum vials capped with rubber septa. Solvents were removed by rotary evaporation at temperatures lower than 45 °C. Column chromatography was run on 230−400 mesh silica gel. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl; dichloromethane, benzene, diisopropylamine, triethylamine, and trimethylsilyl chloride were distilled from calcium hydride. Hexane and cyclohexane were used as received. Triethylsilyl chloride, dimethylphenylsilyl chloride, and diphenylmethylsilyl chloride were used as received. Methyllithium (1.4 M in diethyl ether), *n*-butyllithum (1.6 M in hexanes), and *sec*-butyllithium (1.4 M in cyclohexane) were titrated with diphenylacetic acid (average of three runs). ^{1}H NMR spectra were collected on 500 and 600 MHz instruments using $CDCl_3$ as the solvent, which was referenced at 7.24 ppm (residual chloroform proton), and ^{13}C NMR spectra were collected in $CDCl_3$ at 126 or 151 MHz and referenced at 77 ppm. High-resolution mass spectrometry (HRMS) analysis was performed on TOF instruments. Optical rotations were measured at a wavelength of 589 nm (sodium D line) in chloroform. Enantiomeric excess was determined by HPLC analysis. Melting points are not corrected. The crystal structures of **4s** and **7** were deposited in the Cambridge Crystallographic Data Centre and allocated deposition numbers CCDC 1027999 and 1028000.

General Methods. *Preparation of Trichloroacetimidates* ***S1****: General Procedure A.* To a solution of the corresponding homoallylic alcohol (∼110 mmol) in diethyl ether (12 mL) was added slowly sodium hydride (0.15 equiv, dispersion in mineral oil, 60% (w/w)). The mixture was stirred vigorously for 5 min and then cooled in an ice bath. Trichloroacetonitrile (1 equiv) was then added dropwise, within 5 min approximately. The ice bath was removed after 15 min and the mixture stirred for about 1 h at room temperature and then concentrated by rotary evaporation. A solution of dry methanol (0.15 equiv) in pentane (12 mL) was added to precipitate salts. The solids were filtered through a plug a Celite and rinsed with pentane. The filtrate was concentrated by rotary evaporation, and the crude product could be used without further purification in the next step. However, in all cases the crude product was partially purified by silica gel column chromatography (typically 5% EtOAc in hexanes) buffered with ∼1% triethylamine.

Preparation of Trichloroacetimidates ***S1****: General Procedure B.* To a solution of the corresponding homoallylic alcohol (16 mmol) in dichloromethane (80 mL) was added DBU (0.18 equiv). The solution was cooled at 0 °C, and trichloroacetonitrile (1.4 equiv) was added. The reaction was followed by TLC (typically 5% EtOAc in hexanes) using triethylamine-prewashed plates. After completion of the reaction (typically 3−4 h), the reaction mixture was concentrated by rotary evaporation, and the residue was partially purified by silica gel column chromatography (typically 5% EtOAc in hexanes) buffered with ∼1% triethylamine.

Preparation of α-Hydroxysilanes ***S2****: General Procedure C.* A solution of the corresponding allylic alcohol in THF was cooled at −78 °C, and *n*-butyllithium (1.6 M in hexanes) was added dropwise over 5 min. After 30 min the corresponding chlorosilane was added dropwise via syringe. After the resulting solution was stirred for 1 h, *sec*-butyllithium or *tert*-butyllithium (see below for details) was added dropwise over 45−60 min, and then the reaction was kept at the indicated temperature.

Preparation of Diastereomeric Diene ***S3****: General Procedure D.* To a solution of α-silyl allylic alcohol **S2** (4 mmol, 1 equiv) in hexane (22 mL) was added the desired trichloroacetimidate **S1** (1.5−1.9 equiv). The solution was cooled at 0 °C and 0.1 equiv of (TMS)OTf in hexane was added dropwise. The reaction was warmed at room temperature and monitored by TLC. Typically, formation of a thick suspension indicated the end of the reaction. The solid was filtered through a plug of Celite and rinsed with hexanes (∼50 mL). The filtrate was extracted with $NaHCO_3$(satd) (3 × 20 mL), H_2O (2 × 20 mL), and brine (20 mL) and dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography.

Alternative Synthesis of Diastereomeric Acyclic Ethers ***S3****: General Procedure E.* To a solution of *O*-trimethylsilyl α-(trimethylsilyl)allylic alcohol (10 mmol) in dichloromethane (50 mL) were added allyltrimethylsilane (1.1 equiv) and the desired benzaldehyde derivative (1.1 equiv). The solution was cooled at −78 °C, and (TMS)OTf (0.2 equiv) was added dropwise. The reaction was followed by TLC and usually required between 1 and 4 h. The reaction was quenched by adding $NaHCO_3$(satd) (20 mL). The aqueous phase was washed with dichloromethane (2 × 30 mL). Combined organic extracts were washed with $NaHCO_3$(satd) (2 × 20 mL), H_2O (20 mL), and brine (20 mL) and dried over $MgSO_4$. After filtration and concentration, the residue was purified by column chromatography.

Synthesis of Cyclic Ethers ***1*** *and/or* ***2****: General Procedure F.* To a solution of bisallylic ether **S3** (0.96 mmol) in dichloromethane (10 mL) was added second-generation Grubbs catalyst, and the mixture was stirred at room temperature under nitrogen. After 3 h the solution was concentrated by rotary evaporation and the residue purified by column chromatography.

Synthesis of Cyclic Ethers ***1*** *and/or* ***2****: General Procedure G.* A round-bottom flask was charged with bisallylic ether **S3** (0.96 mmol), which was dissolved in benzene (0.05−0.07 M). Second-generation Grubbs catalyst was added, and a condenser was attached to the flask. The system was flushed with nitrogen and then heated in an oil bath at 80 °C for 1 h. The reaction mixture was then cooled at room temperature and concentrated and the product purified by column chromatography. *Important note*: All 2-silyl-6-aryl-5,6-dihydropyrans **1** and **2** are air sensitive and upon isolation undergo autoxidation (observable by ^{1}H NMR within 1 h after isolation), which is minimized when the compound is diluted (<0.05 M). For this reason, freshly purified dihydropyrans **1** and **2** were immediately submitted to the Wittig rearrangement conditions (general procedure H).

Wittig Rearrangements of 2-Silyl-6-aryl-5,6-dihydropyrans: General Procedure H. Freshly prepared and purified 2-silyl-6-aryldihydropyran **1** or **2** was dissolved in THF under nitrogen (concentration 0.08 M, unless otherwise noted) and the solution cooled at −78 °C (dry ice/acetone bath), *n*-butyllithium (1.2 equiv, 1.6 M in hexanes, conditions A and C) or *sec*-butyllithium (3.0 equiv, 1.4 M in cyclohexane, conditions B and D) was added *dropwise* (1 drop/s) to give a colored solution. After the indicated time (10−30 min for *trans*

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diastereomers **1** or 3−7 h for *cis* diastereomers **2**), the reaction was quenched by adding NH_4Cl(satd) and diluted with H_2O and diethyl ether. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with NH_4Cl(satd), H_2O, and brine. The solution was dried over magnesium sulfate, filtered, quickly concentrated in a rotovap at room temperature (no effort was made to remove all THF to minimize the time the crude reaction was concentrated), and *immediately* loaded into a buffered column (packed with ∼1% triethylamine). Elution with 5% and 10% EtOAc in hexanes afforded the acylsilane and cyclopentenol products, respectively.

Preparation of Starting Materials, Precursors, and Products. Synthesis of Trichloroacetimidates S1. *Preparation of 1-(2-Methoxyphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-b**).* Applying general procedure A to 1-(2-methoxyphenyl)but-3-en-1-ol (13 g, 73.4 mmol, 1 equiv), sodium hydride (0.44 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (10.6, 73.4 mmol, 1 equiv), and diethyl ether (24 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 18.4 g (78%) of compound **S1-b** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1 H), 7.42 (dd, J = 1.2, 7.8 Hz, 1 H), 7.24 (m, 1 H), 6.94 (t, J = 7.8 Hz, 1 H), 6.87 (d, J = 7.8 Hz, 1 H), 6.28 (t, J = 6.6 Hz, 1 H), 5.84 (m, 1 H), 5.08 (dd, J = 1.8, 16.8 Hz, 1 H), 5.03 (d, J = 10.2 Hz, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 155.9, 133.6, 128.7, 128.4, 125.9, 120.6, 117.6, 110.4, 91.8, 75.0, 55.5, 39.6; IR (film) 3344, 3070, 2955, 1664, 1300, 1076, 794 cm^{-1}.

*Preparation of 1-(3-Methoxyphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-c**).* Applying general procedure A to 1-(3-methoxyphenyl)but-3-en-1-ol (13 g, 72.9 mmol, 1 equiv), sodium hydride (0.29 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (10.5 g, 72.9 mmol, 1 equiv), and diethyl ether (24 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 19.88 g (85%) of compound **S1-c** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.27 (t, J = 8.0 Hz, 1 H), 6.97 (m, 2 H), 6.83 (dd, J = 2.5, 8.0 Hz, 1 H), 5.86 (m, 1 H), 5.81 (m, 1 H), 5.13 (m, 1 H), 5.08 (m, 1 H), 3.79 (s, 3 H), 2.78 (m, 1 H), 2.64 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 159.6, 141.3, 133.0, 129.4, 118.4, 118.1, 113.3, 111.6, 91.7, 79.9, 55.1, 41.0; IR (film) 3341, 3070, 2936, 1664, 1290, 1078, 796 cm^{-1}.

*Preparation of 1-(4-Methoxyphenyl)but-3-en-1-yl 2,2,2-Yrichloroacetimidate (**S1-d**).* Applying general procedure A to 1-(4-methoxyphenyl)but-3-en-1-ol (10.7 g, 60 mmol, 1 equiv), sodium hydride (0.36 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (8.7 g, 60 mmol, 1 equiv), and diethyl ether (20 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 12.6 g (65%) of **S1-d** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1 H), 7.33 (m, 2 H), 6.87 (m, 2 H), 5.83 (m, 1 H), 5.77 (m, 1 H), 5.11 (m, 1 H), 5.06 (m, 1 H), 3.79 (s, 3 H), 2.79 (m, 1 H), 2.61 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 159.3, 133.2, 131.6, 127.7 (2 C), 118.1, 113.7 (2 C), 91.8, 79.9, 55.2, 40.9; IR (film) 3340, 3065, 2930, 1664, 1295, 1076, 796 cm^{-1}.

*Preparation of 1-(2-Methylphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-e**).* Applying general procedure A to 1-(2-methylphenyl)but-3-en-1-ol (4.5 g, 27.74 mmol, 1 equiv), sodium hydride (0.166 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (4 g, 27.74 mmol, 1 equiv), and diethyl ether (10 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 7.29 g (61%) of compound **S1-e** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.25 (t, J = 8.0 Hz, 1 H), 7.21 (m, 2 H), 7.12 (d, J = 8.0 Hz, 1 H), 5.86 (dd, J = 5.0, 7.5 Hz, 1 H), 5.83 (m, 1 H), 5.13 (dq, J = 1.5, 17.0 Hz, 1 H), 5.09 (m, 1 H), 2.78 (m, 1 H), 2.62 (m, 1 H), 2.36 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 139.6, 137.9, 133.2, 128.7, 128.3, 126.8, 123.1, 118.1, 91.7, 80.2, 41.1, 21.5; IR (film) 3418, 1653, 1305, 1085 cm^{-1}.

*Preparation of 1-(3-Methylphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-f**).* Applying general procedure A to 1-(3-methylphenyl)but-3-en-1-ol (4.22 g, 26 mmol, 1 equiv), sodium hydride (0.156 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (3.75 g, 26 mmol, 1 equiv), and diethyl ether (15 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 6.37 g (80%) of compound **S1-f** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 7.44 (m, 1 H), 7.20−7.13 (m, 3 H), 6.04 (dd, J = 5.0, 8.0 Hz, 1 H), 5.82 (ddt, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.12 (dq, J = 1.5, 17.0 Hz, 1 H), 5.07 (m, 1 H), 2.74 (m, 1 H), 2.57 (m, 1 H), 2.42 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 138.2, 135.0, 133.3, 130.2, 127.8, 126.2, 125.5, 118.0, 91.7, 77.1, 40.3, 19.2; IR (film) 3344, 3078, 2980, 1662, 1311, 1078, 796 cm^{-1}.

*Preparation of 1-(4-Methylphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-g**).* Applying general procedure A to 1-(4-methylphenyl)but-3-en-1-ol (6.5 g, 40.07 mmol, 1 equiv), sodium hydride (0.24 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (5.79 g, 40.1 mmol, 1 equiv), and diethyl ether (14 mL) afforded after column chromatography (4% EtOAc in hexanes, column buffered with Et_3N) 11.08 g (90%) of compound **S1-g** as a semisolid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 5.84 (dd, J = 5.0, 7.5 Hz, 1 H), 5.80 (ddt, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.11 (dq, J = 1.5, 17.5 Hz, 1 H), 5.07 (m, 1 H), 2.77 (m, 1 H), 2.61 (m, 1 H), 2.33 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 137.7, 136.6, 133.2, 129.1 (2 C), 126.2 (2 C), 118.1, 91.7, 80.1, 41.0, 21.2; IR (film) 3335, 3060, 1662, 1310, 1060 cm^{-1}.

*Preparation of 1-(4-Fluorophenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-h**).* Applying general procedure B to 1-(4-fluorophenyl)-3-en-1-ol (4.07 g, 24.49 mmol, 1 equiv), trichloroacetonitrile (5.3 g, 36.74 mmol, 1 equiv), and DBU (810 mg, 5.31 mmol, 0.18 equiv) in CH_2Cl_2 (150 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 6.25 g (82%) of compound **S1-h** as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.36 (m, 2 H), 7.02 (m, 2 H), 5.84 (dd, J = 5.4, 7.8 Hz, 1 H), 5.76 (ddt, J = 7.2, 10.2, 17.4, 1 H), 5.11−5.06 (m, 2 H), 2.76 (m, 1 H), 2.60 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (J = 246.4 Hz), 161.4, 135.3 (d, J = 3.2 Hz), 132.7, 128.1 (d, J = 8.5 Hz, 2 C), 118.4 (d, J = 3.2 Hz), 115.3 (d, J = 21.1 Hz, 2 C), 91.6, 79.4 (d, J = 1.7 Hz), 40.9; IR (film) 3343, 3083, 2982, 1664, 1512, 1230, 1076, 796 cm^{-1}.

*Preparation of 1-(4-Chlorophenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-i**).* Applying general procedure A to 1-(4-chlorophenyl)but-3-en-1-ol (11 g, 60.22 mmol, 1 equiv), sodium hydride (0.36 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (8.7 g, 60.22 mmol, 1 equiv), and diethyl ether (21 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 14.97 g (76%) of compound **S1-i** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.32 (s, 4 H), 5.83 (dd, J = 5.5, 7.5 Hz, 1 H), 5.77 (m, 1 H), 5.11−5.06 (m, 2 H), 2.75 (m, 1 H), 2.60 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 138.1, 133.8, 132.6, 128.6 (2 C), 127.7 (2 C), 118.6, 91.5, 79.4, 40.8; IR (film) 3343, 3081, 2928, 1664, 1294, 1078, 796 cm^{-1}.

*Preparation of 1-(Naphthalen-2-yl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-l**).* Applying general procedure B to 1-(naphthalen-2-yl)-3-en-1-ol (4.63 g, 23.3 mmol, 1 equiv), trichloroacetonitrile (5.05 g, 34.95 mmol, 1 equiv), and DBU (640 mg, 4.19 mmol, 0.18 equiv) in CH_2Cl_2 (350 mL) afforded after column chromatography (8% EtOAc in hexanes, column buffered with Et_3N) 7.62 g (95%) of compound **S1-l** as a cream-colored solid: mp 42−43 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.83 (m, 4 H), 7.53 (dd, J = 1.8, 9.0 Hz, 1 H), 7.47 (m, 2 H), 6.05 (m, 1 H), 5.83 (m, 1 H), 5.13 (m, 1 H), 5.08 (m, 1 H), 2.88 (m, 1 H), 2.71 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 137.0, 133.1, 133.06, 133.01, 128.3, 128.1, 127.7, 126.2, 126.1, 125.5, 124.0, 118.3, 91.7, 80.3, 40.9; IR (film) 3341, 3059, 1664, 1304, 1076, 794 cm^{-1}.

*Preparation of 1-(2-Propylphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-t**).* Applying general procedure B to 1-(2-propylphenyl)-3-en-1-ol (1.5 g, 7.88 mmol, 1 equiv), trichloroacetonitrile (1.7 g, 11.82 mmol, 1 equiv), and DBU (240 mg, 1.58 mmol, 0.2 equiv) in CH_2Cl_2 (40 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 2.15 g (81%) of compound **S1-t** as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.47 (m, 1 H), 7.21 (m, 2 H), 7.16 (m, 1 H), 6.10 (dd, J = 4.5, 9.0 Hz, 1 H), 5.87 (ddt, J = 7.5, 10.5, 17.5 Hz, 1 H), 5.14 (dq, J = 1.5, 17.0 Hz, 1 H), 5.08 (m, 1 H), 2.75 (m, 2 H), 2.67 (m, 1 H), 2.54 (m, 1 H), 1.77−1.62 (m, 2 H), 1.00 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 139.5, 137.8, 133.6, 129.3, 127.8, 126.1, 125.7, 117.9,

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91.7, 76.9, 41.1, 34.6, 24.0, 14.2; IR (film) 3346, 3078, 2961, 1664, 1309, 1076, 794 cm^{-1}.

*Preparation of 3-Methyl-1-(4-methylphenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-z**).* Applying general procedure A to 3-methyl-1-(*p*-tolyl)but-3-en-1-ol (4 g, 22.64 mmol, 1 equiv), sodium hydride (0.136 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (3.27 g, 42 mmol, 1 equiv), and diethyl ether 8.5 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 3.1 g (43%) of compound **S1-z** as a white solid: mp 59−60 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 5.95 (dd, J = 5.0, 9.0 Hz, 1 H), 4.81 (m, 1 H), 4.76 (m, 1 H), 2.77 (dd, A of ABX system, J = 9.0, 14.5 Hz, 1 H), 2.48 (dd, B of ABX system, J = 5.0, 14.5 Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 140.9, 137.7, 137.1, 129.1 (2 C), 126.2 (2 C), 113.7, 91.7, 79.2, 45.1, 22.8, 21.2; IR (film) 3343, 3070, 2924, 1660, 1304, 1080, 794 cm^{-1}.

*Preparation of 1-(Thiophene-2-yl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-aa**).* Applying general procedure B to 1-(thiophene-2-yl)but-3-en-1-ol (2.5 g, 16.21 mmol, 1 equiv), trichloroacetonitrile (3.51 g, 24.31 mmol, 1 equiv), and DBU (0.44 g, 2.92 mmol, 0.18 equiv) in CH_2Cl_2 (100 mL) afforded after column chromatography (7% EtOAc in hexanes, column buffered with Et_3N) 4.1 g (95%) of compound **S1-aa** as a yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.26 (dd, J = 1.5, 5.5 Hz, 1 H), 7.10 (m, 1 H), 6.96 (dd, J = 3.5, 5.0 Hz, 1 H), 6.20 (dd, J = 6.0, 7.5 Hz, 1 H), 5.81 (ddt, J = 6.5, 10.0, 17.0 Hz, 1 H), 5.16 (dq, J = 1.5, 17.5 Hz, 1 H), 5.10 (m, 1 H), 2.88 (m, 1 H), 2.75 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 141.9, 132.6, 126.4, 126.0, 125.4, 118.6, 91.5, 75.6, 40.7; IR (film) 3341, 3078, 2943, 1662, 1290, 1072, 794 cm^{-1}.

*Preparation of 1-(Furan-2-yl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-bb**).* Applying general procedure B to 1-(furan-2-yl)but-3-en-1-ol (2.53 g, 18.31 mmol, 1 equiv), trichloroacetonitrile (3.97 g, 27.47 mmol, 1 equiv), and DBU (0.5 g, 3.3 mmol, 0.18 equiv) in CH_2Cl_2 (170 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 2.17 g (42%) of compound **S1-bb** as a yellow oil: ^1H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1 H), 7.39 (dd, J = 1.0, 2.0 Hz, 1 H), 6.39 (d, J = 3.0 Hz, 1 H), 6.33 (dd, J = 2.0, 3.0 Hz, 1 H), 6.00 (t, J = 6.5 Hz, 1 H), 5.77 (ddt, J = 7.0, 10.5, 17.0 Hz, 1 H), 5.15 (dq, J = 1.5, 17.5 Hz, 1 H), 5.08 (m, 1 H), 2.90−2.78 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 151.5, 142.6, 132.5, 118.4, 110.2, 108.9, 91.5, 73.0, 36.9; IR (film) 3343, 3080, 2926, 1662, 1300, 1076, 796 cm^{-1}.

*Preparation of 1-(4-Bromophenyl)but-3-en-1-yl 2,2,2-Trichloroacetimidate (**S1-cc**).* Applying general procedure A to 1-(4-bromophenyl)but-3-en-1-ol (9.54 g, 42 mmol, 1 equiv), sodium hydride (0.25 g, 60% (w/w) oil dispersion, 0.15 equiv), trichloroacetonitrile (6.06 g, 42 mmol, 1 equiv), and diethyl ether (14 mL) afforded after column chromatography (5% EtOAc in hexanes, column buffered with Et_3N) 13.4 g (86%) of **S1-cc** as a yellow solid: mp 37−38 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 7.48 (m, 2 H), 7.27 (m, 2 H), 5.83 (dd, J = 5.5, 7.5 Hz, 1 H), 5.77 (ddt, J = 6.5, 10.0, 17.0 Hz, 1 H), 5.13−5.07 (m, 2 H), 2.76 (m, 1 H), 2.61 (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 138.6, 132.5, 131.5 (2 C), 128.0 (2 C), 121.9, 118.6, 91.5, 79.3, 40.7; IR (film) 3343, 3081, 2934, 1664, 1294, 1072, 794 cm^{-1}.

Synthesis of α-Silyl Allylic Alcohols S2. *Preparation of 1-(Trimethylsilyl)prop-2-en-1-ol (**S2-a**).*[78] A solution of allyl alcohol (2.73 g, 47.06 mmol) in THF (117 mL) was cooled to −78 °C. *n*-BuLi (1.61 M in hexanes, 31.57 mL, 50.83 mmol) was added dropwise and the mixture stirred for 1 h. Then freshly distilled (TMS)Cl (5.97 mL, 47.06 mmol) was added slowly from a syringe. After 1.5 h *t*-BuLi (1.66 M in pentane, 34.02 mL, 63.98 mmol) was added dropwise and the reaction stirred for an additional 1.5 h. The reaction was quenched by the addition of aqueous NH_4Cl and diluted with Et_2O, and the mixture was warmed to room temperature. After the layers were separated, the aqueous phase was washed with Et_2O (3 × 50 mL). Then all the organic phases were combined, washed with H_2O (4 × 25 mL) and brine (3 × 17 mL), and dried over Na_2SO_4 overnight. Filtration and concentration furnished the crude product **S2-a** (65%) as a yellow THF solution (90.1% pure), which was used in the next step without further purification: ^1H NMR (500 MHz, $CDCl_3$) δ 6.73 (ddd, J = 5.5, 11.0, 17.0 Hz, 1 H), 5.77 (dt, J = 2.0, 17.0 Hz, 1 H), 5.69 (dt, J = 2.0, 11.0 Hz, 1 H), 4.72 (m, 1 H) 0.76 (s, 9 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 140.1, 109.6, 69.3, −4.05; IR (neat) 3430, 2959, 1634, 1250 cm^{-1}. **S2-a** is a known compound and has spectral data in accord with the reported data.[78]

*Preparation of 1-(Dimethylphenylsilyl)prop-2-en-1-ol (**S2-b**).*[79,80] Applying general procedure C to allyl alcohol (3 g, 51.65 mmol, 1 equiv) in THF (130 mL) at −78 °C, *n*-BuLi (1.6 M in hexanes, 35 mL, 55.78 mmol, 1.08 equiv), phenyldimethylsilyl chloride (9.52 g, 55.78 mmol, 1.08 equiv), and *t*-BuLi (1.7 M in pentane, 36.5 mL, 62 mmol, 1.2 equiv) afforded 7.15 g (72%) of **S2-b** as a colorless oil after column chromatography: ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (m, 2 H), 7.36 (m, 3 H), 5.98 (ddd, J = 5.5, 11.0, 17.5 Hz, 1 H), 5.06 (dt, J = 1.5, 17.0 Hz, 1 H), 4.98 (dt, J = 1.5, 11.0 Hz, 1 H), 4.20 (m, 1 H), 0.33 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 136.0, 134.2 (2 C), 129.5, 127.9 (2 C), 110.1, 68.5, −5.8, −6.1; IR (film) 3426, 3071, 2959, 1427, 1250, 1115, 835 cm^{-1}. **S2-b** is a known compound and has spectral data in accord with the reported data.[79,80]

*Preparation of 1-(Methydiphenylsilyl)prop-2-en-1-ol (**S2-c**).* Applying general procedure C to allyl alcohol (2 g, 34.48 mmol, 1 equiv) in THF (85 mL), *n*-BuLi (22 mL, 34.48 mmol, 1.0 equiv), methyldiphenylsilyl chloride (8.03 g, 34.48 mmol, 1.0 equiv), and *t*-BuLi (24 mL, 41.4 mmol, 1.2 equiv) afforded 5.77 g (66%) of **S2-c** as colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 4 H), 7.43−7.35 (m, 6 H), 6.04 (ddd, J = 5.5, 11.0, 17.5 Hz, 1 H), 5.12 (dt, J = 2.0, 17.0 Hz, 1 H), 5.02 (dt, J = 2.0, 11.0 Hz, 1 H), 4.59 (m, 1 H), 1.43 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 135.1 (2 C), 135.0 (2 C), 134.4, 134.1, 129.7, 129.68, 127.93 (2 C), 129.1 (2 C), 110.8, 67.6, −7.1; IR (film) 3431, 3071, 3041, 3964, 1427, 1115, 904, 790 cm^{-1}.

*Preparation of 1-(Triethylsilyl)prop-2-en-1-ol (**S2-d**).*[81] Applying general procedure C to allyl alcohol (2 g, 34.5 mmol, 1 equiv) in THF (70 mL), *n*-BuLi (23.7 mL, 37.9 mmol, 1.1 equiv), triethylsilyl chloride (5.7 g, 37.9 mmol, 1.1 equiv), and *s*-BuLi (30 mL, 41.4 mmol, 1.2 equiv) afforded 5.75 g (97%) of **S2-d** as colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 6.05 (ddd, J = 5.0, 10.5, 16.0 Hz, 1 H), 5.07 (dd, J = 1.5, 17.0 Hz, 1 H), 4.96 (dd, J = 1.5, 10.5 Hz, 1 H), 4.16 (m, 1 H), 0.97 (t, J = 8.0 Hz, 9 H), 0.60 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 109.0, 67.4, 7.4, 1.6; IR (film) 3402, 2955, 1458, 1097 cm^{-1}. **S2-d** is a known compound and has spectral data in accord with the reported data.[81]

*Preparation of 2-Methyl-1-(trimethylsilyl)prop-2-en-1-ol (**S2-e**).*[78] Compound **S2-e** was prepared by a slight modification of general procedure C according to the literature.[78] To a solution of methallyl alcohol (4 g, 55.5 mmol, 1 equiv) in THF (100 mL) at −78 °C was added dropwise *n*-BuLi (38 mL, 61 mmol, 1.1 equiv). After 1 h trimethylsilyl chloride (7 mL, 55.5 mmol, 1 equiv) was added and the mixture stirred for an additional 1 h at −78 °C. Then *t*-BuLi (42 mL, 72 mmol, 1.3 equiv) was added dropwise over a period of 45 min and the temperature raised to −35 °C for 6 h. The reaction was quenched by adding a solution of acetic acid (4.1 mL, 72 mmol, 1.3 equiv) in THF (10 mL) and removal of the cold bath. After 15 min the reaction was diluted with $NaHCO_3$(satd) and pentane (300 mL). The organic phase was washed with H_2O (3 × 50 mL) and brine (50 mL) and dried over Na_2SO_4. After filtration the residue was carefully concentrated to give 79% **S2-e** as a THF solution (ca. 76%, w/w): ^1H NMR (600 MHz, $CDCl_3$) δ 4.77 (m, 1 H), 4.74 (m, 1 H), 3.85 (s, 1 H), 1.68 (m, 3 H), 1.37 (s, 1 H), 0.05 (s, 9 H).

*Preparation of Trimethyl((1-(trimethylsilyl)allyl)oxy)silane (**S2-f**).* Compound **S2-f** was prepared by a slight modification of general procedure C prior to workup. Following application of general procedure C to allyl alcohol (1 g, 17.24 mmol, 1 equiv) in THF (45 mL) at −78 °C, *n*-BuLi (1.6 M in hexanes, 11.6 mL, 18.62 mmol, 1.08 equiv), trimethylsilyl chloride (2.2 mL, 17.24 mmol, 1 equiv), and *t*-BuLi (1.7 M in pentane, 12.2 mL, 20.69 mmol, 1.2 equiv) (added dropwise over ∼50 min and stirred at −78 °C for 2.5 h), the reaction was slowly treated (5 min) with trimethylsilyl chloride (5.47 mL, 43.1 mmol, 2.5 equiv) and the mixture stirred at −78 °C for 1 h and at room temperature for 1 h. The reaction was cooled at −78 °C and quenched

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with $NaHCO_3$(satd) (50 mL) and the mixture diluted immediately with Et_2O (100 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. Filtration and evaporation of solvent gave the crude product (80%), which was almost pure and was used in the next step without further purification. Analytically pure (colorless oil) **S2-f** was obtained by column chromatography on buffered silica gel: ^{1}H NMR (300 MHz, $CDCl_3$) δ (5.87 (ddd, J = 5.0, 10.5, 17.0 Hz, 1 H), 5.01 (dd, J = 2.0, 17.0 Hz, 1 H), 4.88 (dd, J = 2.0, 10.5 Hz, 1 H), 3.93 (dd J^3 = 2.0, 5.0 Hz, 1 H), 0.067 (s, 9 H), −0.027 (s, 9 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 139.4, 109.5, 69.2, 0.08, −4.1; IR (neat) 2959, 2901, 2818, 1250, 1020, 841 cm^{-1}.

*Preparation of Trimethyl((1-(trimethylsilyl)but-2-yn-1-yl)oxy)-silane (**S2-g**).* Compound **S2-g** was prepared by a slight modification of general procedure C prior to workup. Following general procedure C, to 2-butyn-1-ol (3 g, 42.8 mmol, 1 equiv) in THF (150 mL) at −78 °C was slowly added *n*-BuLi (1.6 M in hexanes, 31 mL, 46.2 mmol, 1.08 equiv). After 30 min trimethylsilyl chloride (5 g, 46.2 mmol, 1.08 equiv) was added and the mixture stirred at the same temperature for 1 h. Then *t*-BuLi (1.7 M in pentane, 31 mL, 51.3 mmol, 1.2 equiv) was added dropwise over ∼1 h, and the yellow mixture was stirred at −78 °C for 3 h. Trimethylsilyl chloride (6.93 g, 64.2 mmol, 1.5 equiv) was added slowly (5 min) and the mixture stirred at −78 °C for 1 h and at room temperature for 1 h. The reaction was cooled at −78 °C and quenched with $NaHCO_3$(satd) (50 mL) and the mixture immediately diluted with Et_2O (100 mL). The aqueous phase was extracted with Et_2O (3 × 50 mL). Combined organic extracts were washed with brine and dried over $MgSO_4$. Column chromatography (2% EtOAc in hexanes) afforded 6.4 g (70%) of **S2-g** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (q, J = 2.5 Hz, 1 H), 1.83 (d, J = 2.5 Hz, 3 H), 0.11 (s, 9 H), 0.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 82.4, 79.4, 56.5, 3.9, 0.0, −4.2.

Synthesis of α-Silyl Allylic Ethers S3. *syn/anti-(1-((1-(2-Methoxyphenyl)but-3-en-1-yl)oxy)allyl)trimethylsilane (**S3-b**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (2.78 g, 54.7% (w/w) in THF, 1 mmol), trichloroacetimidate **S1-b** (6.7 g, 20.73 mmol, 1.8 equiv), and (TMS)OTf (trace) in cyclohexane (64 mL) afforded after column chromatography (10% CH_2Cl_2 in hexanes) 2.58 g (77%) of *syn/anti*-**S3-b** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti*-**S3-b** = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 1.5, 8.0 Hz, 1 H), 7.34 (dd, J = 1.5, 7.5 Hz, 1 H), 7.18 (m, 2 H), 6.94 (t, J = 7.5 Hz, 1 H), 6.92 (t, J = 7.5 Hz, 1 H), 6.82 (dd, J = 1.0, 8.5 Hz, 1 H), 6.79 (dd, J = 1.0, 8.0 Hz, 1 H), 5.87 (ddt, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.77 (m, 2 H), 5.65 (ddd, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.01−4.87 (m, 8 H), 4.80 (m, 2 H), 3.79 (dt, J = 1.5, 7.5 Hz, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.44 (dt, J = 1.0, 7.5 Hz, 1 H), 2.47−2.35 (m, 4 H), 0.04 (s, 9 H), −0.01 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 155.7, 138.02, 137.98, 135.9, 135.4, 132.3, 131.0, 127.8, 127.5, 127.4, 127.3, 120.4, 120.2, 116.2, 115.9, 112.7, 111.7, 110.3, 109.9, 75.6, 74.4, 73.2, 72.5, 55.4, 55.3, 41.9, 39.9, −3.7, −3.9; IR (film) 3076, 2957, 2835, 1489, 1244, 841 cm^{-1}; HRMS (EI) m/z 290.1700 [(M^+), calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*syn/anti-(1-((1-(3-Methoxyphenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-c**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.83 g, 54.7% (w/w) in THF, 7.68 mmol), trichloroacetimidate **S1-c** (4.46 g, 13.8 mmol, 1.8 equiv), and (TMS)OTf (97 μL, 0.538 mmol, 0.07 equiv) in cyclohexane (43 mL) afforded after column chromatography (15% CH_2Cl_2 in hexanes) 1.34 g (60%) of *syn/anti*-**S3-c** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti*-**S3-c** = 1:0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, J = 8.0 Hz, 0.4 H), 7.19 (t, J = 8.0 Hz, 1 H), 6.88 (m, 1 H), 6.85 (m, 1 H), 6.80 (m, 1.2 H), 6.75 (ddd, J = 1.0, 2.5, 8.0 Hz, 1 H), 5.80 (m, 0.4 H), 5.71 (m, 1.4 H), 5.67 (ddd, J = 2.0, 10.5, 17.0 Hz, 1 H), 5.03−4.95 (m, 3.6 H), 4.92 (dt, J = 1.5, 17.0 Hz, 1 H), 4.83 (dt, J = 1.5, 11.0 Hz, 1 H), 4.40 (dd, J = 6.0, 8.0 Hz, 0.4 H), 4.34 (t, J = 6.0 Hz, 1 H), 3.79 (s, 1.2 H), 3.78 (s, 3 H), 3.77 (dt, J = 1.5, 7.0 Hz, 1 H), 3.44 (dt, J = 1.5, 7.5 Hz, 0.4 H), 2.48 (m, 1.4 H), 2.41 (m, 1 H), 2.32 (m, 0.4 H), 0.04 (s, 9 H), −0.02 (s, 3.6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 159.3, 145.3, 144.3, 137.8, 137.5, 135.4, 134.8, 129.0, 128.8, 119.8, 119.0, 116.8, 116.4, 113.0, 112.9, 112.3 (2 C), 112.1, 111.9, 80.8, 79.1, 75.7, 72.9, 55.14, 55.12, 43.0, 41.6, −3.7, −3.9; IR (film) 3076, 2957, 1248, 1047, 841 cm^{-1}; HRMS (EI) m/z 290.1685 [(M^+), calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*syn/anti-(1-((1-(4-Methoxyphenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-d**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (2 g, 15.35 mmol), trichloroacetimidate **S1-d** (9.9 g, 30.7 mmol, 2 equiv), and (TMS)OTf (194 μL, 1.07 mmol, 0.07 equiv) in cyclohexane (85 mL) afforded after column chromatography (15% CH_2Cl_2 in hexanes) 4.35 g (60%) of *syn/anti*-**S3-d** (1:1) as a colorless oil. Spectroscopic data for *syn*-**S3-d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 8.5 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 5.74−5.62 (m, 2 H), 4.96 (m, 2 H), 4.92 (dt, J = 2.0, 17.0 Hz, 1 H), 4.82 (dt, J = 1.5, 10.0 Hz, 1 H), 4.30 (t, J = 6.0 Hz, 1 H), 3.78 (s, 3 H), 3.76 (dt, J = 1.5, 7.0 Hz, 1 H), 2.49 (m, 1 H), 2.39 (m, 1 H), 0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 138.0, 135.7, 135.0, 127.7 (2 C), 116.7, 113 (2 C), 111.6, 80.7, 75.5, 55.2, 41.5, −3.7; IR (film) 3076, 2957, 1514, 1248, 1039, 841 cm^{-1}; HRMS (EI) m/z 290.1688 [(M^+), calcd for $C_{17}H_{26}O_2Si$, 290.1702]. Spectroscopic data for *anti*-**S3-d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, J = 8.5 Hz, 2 H), 6.84 (d, J = 8.0 Hz, 2 H), 5.82−5.68 (m, 2 H), 4.97 (m, 4 H), 4.36 (t, J = 7.0 Hz, 1 H), 3.79 (s, 3 H), 3.39 (dt, J = 1.0, 7.0 Hz, 1 H), 2.51 (m, 1 H), 2.31 (m, 1 H), −0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 137.7, 135.6, 134.5, 128.5, 116.2, 113.5, 112.7, 78.7, 72.5, 55.2, 43.0, −4.0; IR (film) 3076, 2957, 1514, 1258, 1039, 841 cm^{-1}; HRMS (EI) m/z 290.1695 [(M^+), calcd for $C_{17}H_{26}O_2Si$, 290.1702].

*syn/anti-(1-((1-(2-Methylphenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-e**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.17 g, 85.5% (w/w) in Et_2O, 8.98 mmol), trichloroacetimidate **S1-e** (3.85 g, 12.57 mmol, 1.4 equiv), and (TMS)OTf (40 μL, 0.225 mmol, 0.025 equiv) in cyclohexane (45 mL) afforded after column chromatography (hexanes) 1.81 g (73%) of *syn/anti*-**S3-e** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti* **S3-e** = 1.0:0.5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 1.0, 7.5 Hz, 1 H), 7.38 (dd, J = 1.5, 7.5 Hz, 0.5 H), 7.23 (m, 4.5 H), 5.86 (ddt, J = 7.0, 10.0, 17.0 Hz, 0.5 H), 5.79 (m, 1.5 H), 5.63 (ddd, J = 7.5, 10.5, 18.0 Hz, 1 H), 5.06−4.96 (m, 4 H), 4.91 (ddd, J = 1.5, 2.0, 17.5 Hz, 1 H), 4.81 (ddd, J = 1.5, 2.0, 10.0 Hz, 1 H), 4.77 (dd, J = 5.0, 8.0 Hz, 0.5 H), 4.56 (dd, J = 5.5, 6.5 Hz, 1 H), 3.79 (dt, J = 1.0, 7.5 Hz, 1 H), 3.39 (dt, J = 1.5, 8.0 Hz, 0.5 H), 2.52−2.44 (m, 1.5 H), 2.41−2.29 (m, 1.5 H), 2.28 (s, 4.5 H), 0.07 (s, 9 H), 0.01 (s, 4.5 H); ^{13}C NMR (151 MHz, $CDCl_3$) (*syn*-**S3-e**, major) δ 142.1, 138.06, 135.1, 134.0, 129.8, 126.7, 126.57, 125.7, 116.7, 111.8, 78.2, 75.0, 41.1, 19.3, −3.7; (*anti* **S3-e**, minor) δ 140.7, 138.1, 135.9, 135.6, 129.9, 126.8, 126.60, 125.9, 116.3, 113.1, 76.6, 73.0, 42.3, 19.1, −3.9; IR (film) 3077, 2957, 1247, 1060, 842 cm^{-1}; HRMS (EI) m/z 274.1753 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*syn/anti-(1-((1-(3-Methylphenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-f**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.17 g, 85.5% (w/w) in Et_2O, 8.98 mmol), trichloroacetimidate **S1-f** (3.85 g, 12.57 mmol, 1.4 equiv), and (TMS)OTf (162 μL, 0.898 mmol, 0.1 equiv) in cyclohexane (45 mL) afforded after column chromatography (hexanes) 1.38 g (56%) of *syn/anti*-**S3-f** (1:1) as a colorless oil. Spectroscopic data for *syn*-**S3-f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 8.0 Hz, 1 H), 7.08 (m, 2 H), 7.02 (d, J = 7.5 Hz, 1 H), 5.72 (ddt, J = 7.0, 10.0, 17.5 Hz, 1 H), 5.67 (ddd, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.01−4.93 (m, 2 H), 4.91 (dt, J = 2.0, 17 Hz, 1 H), 4.83 (ddd, J = 1.5, 2.0, 10.5 Hz, 1 H), 4.33 (t, J = 6.0 Hz, 1 H), 3.79 (dt, J = 1.5, 7.0 Hz, 1 H), 2.50 (m, 1 H), 2.40 (m, 1 H), 2.33 (s, 3 H), 0.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 137.9, 137.3, 135.0, 127.7, 127.6, 127.3, 123.7, 116.7, 111.8, 104.7, 81.0, 75.6, 41.6, 21.5, −3.7; IR (film) 3079, 2958, 1247, 910, 845 cm^{-1}; HRMS (EI) m/z 274.1750 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for *anti*-**S3-f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, J = 7.5 Hz, 1 H), 7.06 (m, 2 H), 7.02 (d, J = 8.0 Hz, 1 H), 5.81 (ddt J = 7.0, 10.0, 17.0 Hz, 1 H), 5.73 (ddd, J = 7, 10.5, 17.0 Hz, 1 H), 5.01 (m, 1 H), 4.97 (m, 1 H), 4.39 (dd, J = 5.5, 8.0 Hz, 1 H), 3.42 (dt, J = 1.0, 7.9 Hz, 1 H), 2.51 (m, 1H), 2.34 (s, 3 H), 2.31 (m 1 H), −0.02 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 137.63, 137.62, 135.6, 128.0, 127.96, 127.95, 124.4, 116.2, 112.7, 79.2, 72.8, 43.1, 21.4, −3.9;

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IR (film) 3079, 2959, 1247, 911, 842 cm^{-1}; HRMS (EI) *m/z* 274.1741 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*syn/anti-(1-((1-(4-Methylphenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-g**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (2.78 g, 54% (w/w) in Et_2O, 11.52 mmol, 1 equiv), trichloroacetimidate **S1-g** (6 g, 19.58 mmol, 1.7 equiv), and (TMS)OTf (trace, <0.02 equiv) in hexane (64 mL) afforded after column chromatography (hexanes) 2.38 g (75%) of *syn/anti*-**S3-g** (1:1) as a colorless oil. Spectroscopic data for *syn* **S3-g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz, 2 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 5.72 (m, 1 H), 5.67 (m, 1 H), 5.01−4.90 (m, 3 H), 4.83 (m, 1 H), 4.34 (t, *J* = 6.0 Hz, 1 H), 3.78 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.51 (m, 1 H), 2.41 (m, 1 H), 2.32 (s, 3 H), 0.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.5, 137.9, 136.4, 135.0, 128.6 (2C), 126.5 (2C), 116.7, 111.7, 80.8, 75.5, 41.5, 21.1, −3.7; IR (film) 3070, 2959, 1514, 1248, 1062, 910, 841 cm^{-1}; HRMS (EI) *m/z* 274.1749 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for *anti*-**S3-g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 4 H), 5.81 (m, 1 H), 5.74 (m, 1 H), 5.04−4.95 (m, 4 H), 4.40 (dd, *J* = 6.0, 7.5 Hz, 1 H), 3.43 (dt, *J* = 1.0, 7.5 Hz, 1 H), 2.53 (m, 1 H), 2.34 (s, 3 H), 2.33 (m, 1 H), −0.01 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 137.7, 136.9, 135.6, 128.8 (2 C), 127.3 (2 C), 116.2, 112.8, 79.0, 72.7, 43.1, 21.2, −4.0; IR (film) 3076, 2957, 1514, 1248, 1057, 910, 841 cm^{-1}; HRMS (EI) *m/z* 274.1753 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*syn/anti-(1-((1-(4-Fluorophenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-h**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.26 g, 69.9% (w/w) in THF, 6.73 mmol, 1 equiv), trichloroacetimidate **S1-h** (2.9 g, 9.43 mmol, 1.4 equiv), and (TMS)OTf (121 μL, 0.673 mmol, 0.1 equiv) in hexane (37 mL) afforded after column chromatography (hexanes) a total of 724 mg (39%) of *syn/anti*-**S3-h** (1:1) as a colorless oil. Diastereomers were partially separated. Spectroscopic data for *syn*-**S3-h**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 6.0, 9.0 Hz, 2 H), 6.96 (t, *J* = 9.0 Hz, 2 H), 5.65 (m, 2 H), 4.96 (m, 2 H), 4.87 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.83 (dt, *J* = 1.5, 10.5 Hz, 1 H), 4.33 (t, *J* = 6.0 Hz, 1 H), 3.77 (dt, *J* = 1.5, 7.0 Hz, 1 H), 2.48 (m, 1 H), 2.38 (m, 1 H), 0.03 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.1 Hz), 139.2 (d, *J* = 3.2 Hz), 137.7, 134.5, 128.1 (d, *J* = 7.9 Hz, 2 C), 117.1, 114.6 (d, *J* = 21.7 Hz, 2 C), 111.9, 80.4, 75.8, 41.4, −3.8; IR (film) 3078, 2959, 1518, 1224, 839 cm^{-1}; HRMS (EI) *m/z* 278.1505 [(M^+), calcd for $C_{16}H_{23}OSiF$, 278.1502]. Spectroscopic data for *anti*-**S3-h**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.5, 8.0 Hz, 2 H), 6.99 (t, *J* = 8.5 Hz, 2 H), 5.73 (m, 2 H), 5.02−4.94 (m, 4 H), 4.39 (t, *J* = 6.5 Hz, 1 H), 3.36 (d, *J* = 7.5 Hz, 1 H), 2.50 (m, 1 H), 2.31 (m, 1 H), −0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.3 Hz), 138.1 (d, *J* = 3.2 Hz), 137.4, 135.1, 128.8 (d, *J* = 7.9 Hz, 2 C), 116.6, 114.9 (d, *J* = 21.3 Hz, 2 C), 113.0, 78.6, 73.0, 43.0, −4.0; IR (film) 3078, 2959, 1518, 1224, 835 cm^{-1}; HRMS (EI) *m/z* 278.1492 [(M^+), calcd for $C_{16}H_{23}OSiF$, 278.1502].

*syn/anti-(1-((1-(4-Chlorophenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-i**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (5.5 g, solution 36.2% (w/w) in THF, 15.35 mmol, 1 equiv), trichloroacetimidate **S1-i** (10 g, 30.7 mmol, 2 equiv), and (TMS)OTf (190 μL, 1.07 mmol, 0.07 equiv) in cyclohexane (85 mL) afforded after column chromatography (hexanes) 1.425 g (54%) of *syn/anti*-**S3-i** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti* **S3-i** = 0.7:1.0); ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 3.4 H), 7.24 (m, 2 H), 7.18 (m, 1.4 H), 5.82−5.62 (m, 3.4 H), 5.04 (m, 0.7 H), 5.02−4.96 (m, 4.1 H), 4.90 (dt, *J* = 1.5, 17.0 Hz, 1 H), 4.85 (dt, *J* = 1.5, 11.0 Hz, 1 H), 4.42 (dd, *J* = 6.0, 7.0 Hz, 0.7 H), 4.36 (t, *J* = 6.0 Hz, 1 H), 3.80 (dt, *J* = 1.5, 7.0 Hz, 1 H), 3.39 (m, 0.7 H), 2.55−2.30 (m, 3.4 H), 0.06 (s, 9 H), −0.01 (s, 7.3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 140.9, 137.7, 137.3, 134.9, 134.7, 134.3, 133.0, 132.5, 128.7 (2 C), 128.3 (2 C), 128.2, 128.0 (2 C), 127.9 (2 C), 127.4, 117.2, 116.8, 113.1, 112.1, 80.3, 78.6, 75.9, 73.1, 42.9, 41.3, −3.8, −4.0; IR (film) 3078, 2957, 1491, 1248, 1089, 841 cm^{-1}; HRMS (EI) *m/z* 294.1218 [(M^+), calcd for $C_{16}H_{23}OSiCl$, 294.1207].

*syn/anti-(1-((1-(4-(Trifluoromethyl)phenyl)but-3-en-1-yl)oxy)-allyl)trimethylsilane (**S3-j**).* Applying general procedure E to alcohol **S2-f** (1 g, 4.95 mmol, 1 equiv), 4-(trifluoromethyl)benzaldehyde (862 mg, 4.95 mmol, 1 equiv), allyltrimethylsilane (625 mg, 4.95 mmol, 1 equiv), and (TMS)OTf (180 μL, 0.989 mmol, 0.2 equiv) in CH_2Cl_2 (50 mL) for 30 min at −78 °C afforded after workup and column chromatography (10% CH_2Cl_2 in hexanes) 765 mg of a mixture of *anti/syn*-**S3-j** (4:1) as a colorless oil: mixture of diastereomers (*anti*:*syn*-**S3-j** = 0.8:0.2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1.6 H), 7.56 (d, *J* = 7.8 Hz, 0.4 H), 7.42 (d, *J* = 8.4 Hz, 0.4 H), 7.37 (d, *J* = 7.8 Hz, 1.6 H), 5.83−5.73 (m, 1.6 H), 5.71−5.64 (m, 0.4 H), 5.07 (m, 0.8 H), 5.03−4.98 (m, 2.8 H), 4.92 (dt, *J* = 1.8, 17.4 Hz, 0.2 H), 4.86 (dt, *J* = 1.8, 10.8 Hz, 0.2 H), 4.53 (dd, *J* = 6.6, 7.8 Hz, 0.8 H), 4.47 (t, *J* = 6.0 Hz, 0.2 H), 3.84 (dt, *J* = 1.8, 7.2 Hz, 0.2 H), 3.40 (d, *J* = 7.8 Hz, 0.8 H), 2.53 (m, 1 H), 2.46 (m, 0.2 H), 2.36 (m, 0.8 H), 0.09 (s, 1.8 H), 0.02 (s, 7.2 H); ^{13}C NMR (151 MHz, $CDCl_3$) (*anti*) δ 146.7, 137.2, 134.6, 129.6 (q, *J* = 32.3 Hz), 127.6 (2 C), 125.1 (q, *J* = 3.78 Hz, 2 C), 124.3 (q, *J* = 272.0 Hz), 117.0, 113.4, 78.7, 73.5, 42.9, −4.0; (*syn*) δ 147.7, 137.5, 134.0, 129.1 (q, *J* = 32.1 Hz), 126.8 (2 C), 124.9 (q, *J* = 3.6 Hz, 2 C), CF_3 carbon could not be located, 117.5, 112.4, 80.3, 76.2, 41.3, −3.8; IR (film) 3080, 2959, 1325, 1128, 841 cm^{-1}; HRMS (EI) *m/z* 328.1457 [(M^+), calcd for $C_{17}H_{23}OSiF_3$, 328.1470].

*syn/anti-(1-((1-([1,1′-Biphenyl]-4-yl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-k**).* To a solution of *syn/anti*-**S3-z** (1:1, 342 mg, 1.01 mmol, 1 equiv) in THF (2.2 mL) was added S-Phos (4.2 mg, 0.02 mmol, 0.02 equiv), phenylboronic acid (184 mg, 1.512 mmol, 1.5 equiv), and $K_3PO_4{\cdot}2H_2O$ (500 mg, 2.016 mmol, 2 equiv). The mixture was degassed with three freeze−pump−thaw cycles, and then $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 0.01 equiv) was added at room temperature. The mixture was stirred at room temperature under a nitrogen atmosphere and the reaction monitored by TLC (hexanes). After 9 h the reaction was concentrated and the residue subjected to column chromatography (10% CH_2Cl_2 in hexanes) to afford a total of 327 mg (53%) of *syn/anti*-**S3-k** (1:1). Diastereomers were partially separated. Spectroscopic data for *syn*-**S3-k**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.33 (tt, *J* = 1.2, 7.2 Hz, 1 H), 5.77 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.72 (ddd, *J* = 7.2. 10.8, 18.0 Hz, 1 H), 5.04−4.98 (m, 2 H), 4.96 (dt, *J* = 1.8, 16.8 Hz, 1 H), 4.87 (dt, *J* = 1.8, 10.8 Hz, 1 H), 4.45 (t, *J* = 6.0 Hz, 1 H), 3.85 (dt, *J* = 1.2, 7.2 Hz, 1 H), 2.57 (m, 1 H), 2.49 (m, 1 H), 0.09 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 141.1, 139.7, 137.9, 134.8, 128.7 (2 C), 127.04, 127.02 (2 C), 126.97 (2 C), 126.6 (2 C), 116.9, 112.0, 80.6, 75.7, 41.4, −3.7; IR (film) 3077, 2957, 1250, 840 cm^{-1}; HRMS (EI) *m/z* 336.1923 [(M^+), calcd for $C_{22}H_{28}OSi$, 336.1909]. Spectroscopic data for *anti*-**S3-k**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.33 (m, 3 H), 5.85 (ddt, *J* = 7.2, 10.2, 17.4 Hz, 1 H), 5.77 (ddd, *J* = 7.8, 10.8, 18.0 Hz, 1 H), 5.07−5.00 (m, 4 H), 4.50 (dd, *J* = 5.4, 7.8 Hz, 1 H), 3.49 (d, *J* = 7.2 Hz, 1 H), 2.58 (m, 1 H), 2.40 (m, 1 H), 0.01 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 140.9, 140.2, 137.6, 135.4, 128.7 (2 C), 127.7 (2 C), 127.2, 127.0 (2 C), 126.8 (2 C), 116.5, 112.9, 78.9, 72.9, 43.1, −3.9; IR (film) 3077, 2957, 1247, 840 cm^{-1}; HRMS (EI) *m/z* 336.1920 [(M^+), calcd for $C_{22}H_{28}OSi$, 336.1909].

*syn/anti-(1-((1-(Naphthalen-2-yl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-l**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.07 g, 44% (w/w) in THF, 5.72 mmol, 1 equiv), trichloroacetimidate **S1-l** (2.74 g, 8 mmol, 1.4 equiv), and (TMS)OTf (47 μL, 0.259 mmol, 0.05 equiv) in hexane (32 mL) afforded after column chromatography (10% CH_2Cl_2 in hexanes) a total of 852 mg (48%) of *syn/anti*-**S3-l** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-l** were separable by column chromatography. Spectroscopic data for *syn*-**S3-l**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 2 H), 7.78 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.72 (s, 1 H), 7.45 (m, 3 H), 5.80−5.63 (m, 2 H), 5.02−4.96 (m, 2 H), 4.92 (dq, *J* = 2.0, 15.0 Hz, 1 H), 4.81 (dq, *J* = 1.5, 10.5 Hz, 1 H), 4.53 (m, 1 H), 3.59 (dq, *J* = 1.5, 7.0 Hz, 1 H), 2.61 (m, 1 H), 2.51 (m, 1 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 137.9, 134.8, 133.1, 132.8, 127.9, 127.6, 127.5, 125.8, 125.4, 125.3, 125.0, 116.9, 111.9, 81.3, 75.9, 41.5, −3.7; IR (film) 3060, 2959, 2825, 1241, 860, 841 cm^{-1}; HRMS (EI) *m/z* 310.1753 [(M^+), calcd for $C_{20}H_{26}OSi$, 310.1753]. Spectroscopic data for *anti*-**S3-l**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 3 H), 7.65 (s, 1 H), 7.44 (m, 3 H), 5.86−5.72 (m, 2 H), 5.06−4.96 (m, 4 H), 4.59 (dd, *J* = 6.0,

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7.5 Hz, 1 H), 3.44 (m, 1 H), 2.62 (m, 1 H), 2.43 (m, 1 H), −0.02 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.5, 135.3, 133.1, 133.0, 128.0, 127.8, 127.7, 126.5, 125.9, 125.6, 125.1, 116.5, 112.9, 79.3, 72.9, 42.8, −4.0; IR (film) 3057, 2959, 2831, 1246, 859, 841 cm^{-1}; HRMS (EI) m/z 310.1745 [(M^+), calcd for $C_{20}H_{26}OSi$, 310.1753].

*syn/anti-Dimethylphenyl(1-((1-phenylbut-3-en-1-yl)oxy)allyl)-silane (**S3-m**).* Applying general procedure D to **S2-b** (256 mg, 1.331 mmol, 1 equiv), the trichloroacetimidate of 1-phenylbut-3-en-1-ol (662 mg, 2.26 mmol, 1.7 equiv), and (TMS)OTf (24 μL, 0.133 mmol, 0.1 equiv) in hexane (7 mL) afforded after column chromatography (hexanes) a total of 250 mg (58%) of *syn/anti*-**S3-m** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-m** were separable by column chromatography. Spectroscopic data for *syn*-**S3-m**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.35 (m, 3 H), 7.26 (m, 2 H), 7.21 (m, 3 H), 5.65−5.55 (m, 2 H), 4.91−4.87 (m, 3 H), 4.81 (m, 1 H), 4.28 (t, J = 6.0 Hz, 1 H), 3.98 (dt, J = 1.8, 7.2 Hz, 1 H) 2.45 (m, 1 H), 2.35 (m, 1 H), 0.36 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 137.4, 137.0, 134.7, 134.3 (2 C), 129.2, 127.8 (2 C), 127.6 (2 C), 126.9, 126.6 (2 C), 81.1, 75.2, 41.5, −5.2, −5.5; IR (film) 3071, 2961, 1427, 1248, 1115, 837 cm^{-1}; HRMS (EI) m/z 322.1751 [(M^+), calcd for $C_{21}H_{26}OSi$, 322.1753]. Spectroscopic data for *anti*-**S3-m**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (m, 2 H), 7.36 (m, 1 H), 7.32 (m, 2 H), 7.21 (m, 3 H), 7.06 (m, 2 H), 5.78 (ddt, J = 7.2, 10.2, 17.4 Hz, 1 H), 5.69 (ddd, J = 7.2, 10.8, 17.4 Hz, 1 H), 5.02−4.93 (m, 4 H), 4.43 (dd, J = 5.4, 7.8 Hz, 1 H), 3.60 (d, J = 7.8 Hz, 1 H), 2.50 (quintet, A of ABX system, J = 7.2 Hz, 1 H), 2.32 (quintet, B of ABX system, J = 7.2 Hz, 1 H), 0.28 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 137.1, 136.8, 135.4, 134.4 (2 C), 129.0, 128.0 (2 C), 127.4 (2 C), 127.30 (2 C), 127.26, 79.2, 72.5, 43.0, −5.3, −6.0; IR (film) 3071, 2961, 1427, 1248, 1115, 837 cm^{-1}; HRMS (EI) m/z 322.1753 [(M^+), calcd for $C_{21}H_{26}OSi$, 322.1753].

*syn/anti-Methyldiphenyl(1-((1-phenylbut-3-en-1-yl)oxy)allyl)-silane (**S3-n**).* Applying general procedure D to **S2-c** (2.17 g, 8.53 mmol, 1 equiv), the trichloroacetimidate of 1-phenylbut-3-en-1-ol (5 g, 17.07 mmol, 2 equiv), and (TMS)OTf (230 μL, 1.28 mmol, 0.15 equiv) in cyclohexane (41 mL) afforded after column chromatography (10% CH_2Cl_2 in hexanes) 2.7 g (83%) of *syn/anti*-**S3-n** (1:1) as a colorless oil. Spectroscopic data for *syn*-**S3-n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 2 H), 7.59 (m, 2 H), 7.39−7.33 (m, 5 H), 7.27 (m, 3 H), 7.22 (m, 3 H), 5.67 (ddd, J = 7.0, 10.5, 17.5 Hz, 1 H), 5.47 (m, 1 H), 4.93 (dt, J = 2.0, 17.5 Hz, 1 H), 4.85−4.81 (m, 3 H), 4.31 (dt, J = 1.5, 7.0 Hz, 1 H), 4.27 (t, J = 7.0 Hz, 1 H), 2.44 (m, 1 H), 2.31 (m, 1 H), 0.59 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 137.1, 135.4 (2 C), 135.2 (2 C), 134.8, 134.6, 129.4, 129.3, 127.8 (2 C), 127.7 (2 C), 127.6 (2 C), 127.0, 126.7, 81.4, 74.7, 41.5, −6.5; IR (film) 3071, 2975, 1429, 1115, 734 cm^{-1}; HRMS (EI) m/z 384.1901 [(M^+), calcd for $C_{26}H_{28}OSi$, 384.1909]. Spectroscopic data for *anti*-**S3-n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.49 (m, 2 H), 7.40 (m, 1 H), 7.37−7.29 (m, 5 H), 7.19 (m, 3 H), 6.97 (m, 2 H), 5.84−5.73 (m, 2 H), 5.05−4.97 (m, 4 H), 4.50 (dd, J = 5.5, 7.5 Hz, 1 H), 3.93 (dt, J = 1.5, 8.0 Hz, 1 H), 2.53 (m, 1 H), 2.35 (m, 1 H), 0.53 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 136.7, 135.5 (2 C), 135.4, 135.3 (2 C), 135.2, 129.4, 129.2, 128.0 (2 C), 127.54 (2 C), 127.52 (2 C), 127.46 (2 C), 127.3, 116.5, 114.8, 79.2, 72.1, 42.9, −6.6; IR (film) 3071, 3976, 1429, 1115, 724 cm^{-1}; HRMS (EI) m/z 384.1889 [(M^+), calcd for $C_{26}H_{28}OSi$, 384.1909].

*syn/anti-Triethyl(1-((1-phenylbut-3-en-1-yl)oxy)allyl)silane (**S3-o**).* Applying general procedure D to **S2-d** (583 mg, 3.38 mmol, 1 equiv), the trichloroacetimidate of 1-phenylbut-3-en-1-ol (1.48 g, 5.07 mmol, 1.5 equiv), and (TMS)OTf (31 μL, 0.169 mmol, 0.05 equiv) in hexane (19 mL) afforded after column chromatography (hexanes) a total of 720 mg (70%) of *syn/anti*-**S3-o** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-o** were separable by column chromatography. Spectroscopic data for *syn*-**S3-o**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.20 (m, 1 H), 5.68 (m, 2 H), 4.98−4.88 (m, 3 H), 4.80 (dd, J = 1.0, 10.0 Hz, 1 H), 4.35 (t, J = 6.0 Hz, 1 H), 3.98 (dd, J = 1.5, 7.5 Hz, 1 H), 2.52 (m, 1 H), 2.42 (m, 1 H), 0.98 (t, J = 8.0 Hz, 9 H), 0.62 (dq, J = 1.5, 7.5 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 138.3, 134.8, 127.8 (2 C), 126.8, 126.6 (2 C), 116.8, 111.8, 80.9, 74.3, 41.3, 7.5, 1.8; IR (film) 3078, 2953, 1454, 1014, 910 cm^{-1}; HRMS (EI) m/z 302.2063 [(M^+), calcd for $C_{19}H_{30}OSi$, 302.2066]. Spectroscopic data for *anti*-**S3-o**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.24 (m, 3 H), 5.78 (m, 2 H), 5.02−4.95 (m, 4 H), 4.41 (dd, J = 5.4, 7.8 Hz, 1 H), 3.55 (dt, J = 1.2, 7.8 Hz, 1 H), 2.52 (m, 1 H), 2.34 (m, 1 H), 0.88 (t, J = 7.8 Hz, 9 H), 0.54 (dq, J = 2.4, 7.8 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 138.0, 135.5, 128.1 (2 C), 127.43 (2 C), 127.37, 116.3, 112.8, 79.0, 71.5, 42.9, 7.3, 1.6; IR (film) 3064, 2953, 1450, 1011, 910 cm^{-1}; HRMS (EI) m/z 302.2065 [(M^+), calcd for $C_{19}H_{30}OSi$, 302.2066].

*syn/anti-(1-((1-(3-Methoxyphenyl)but-3-en-1-yl)oxy)allyl)-dimethylphenylsilane (**S3-p**).* Applying general procedure D to **S2-b** (1 g, 5.2 mmol, 1 equiv), trichloroacetimidate **S1-c** (2.68 g, 8.32 mmol, 1.6 equiv), and (TMS)OTf (94 μL, 0.52 mmol, 0.1 equiv) in hexane (29 mL) afforded after column chromatography (15% CH_2Cl_2 in hexanes) a total of 1.298 g (71%) of *syn/anti*-**S3-p** (1:1). Diastereomers were partially separated and obtained as colorless oils. Spectroscopic data for *syn*-**S3-p**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2 H), 7.36 (m, 3 H), 7.19 (t, J = 7.8 Hz, 1 H), 6.85 (d, J = 0.6 Hz, 1 H), 6.81 (dd, J = 0.6, 7.2 Hz, 1 H), 6.76 (ddd, J = 0.6, 2.4, 7.8 Hz, 1 H), 5.70−5.59 (m, 2 H), 4.94 (m, 3 H), 4.86 (dt, J = 10.8 Hz, 1 H), 4.29 (t, J = 6.0 Hz, 1 H), 4.00 (dt, J = 1.2, 7.8 Hz, 1 H), 3.78 (s, 3 H), 2.46 (m, 1 H), 2.37 (m, 1 H), 0.39 (s, 3 H), 0.35 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 145.0, 137.4, 136.9, 134.7, 134.3 (2 C), 129.2, 128.8, 127.6 (2 C), 119.0, 116.8, 112.5, 112.4, 111.9, 81.0, 75.2, 55.1, 41.6, −5.2, −5.6; IR (film) 3071, 2958, 1254, 1046, 837 cm^{-1}; HRMS (EI) m/z 352.1855 [(M^+), calcd for $C_{22}H_{28}O_2Si$, 352.1859]. Spectroscopic data for *anti*-**S3-p**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.33 (m, 3 H), 7.14 (t, J = 7.8 Hz, 1 H), 6.76 (ddd, J = 0.6, 2.4, 7.8 Hz, 1 H), 6.68 (m, 2 H), 5.80 (ddt, J = 7.2, 10.2, 17.4 Hz, 1 H), 5.69 (ddd, J = 7.2, 10.2, 18.0 Hz, 1 H), 5.03−4.94 (m, 4 H), 4.43 (dd, J = 5.4, 7.8 Hz, 1 H), 3.69 (s, 3 H), 3.66 (dt, J = 1.2, 7.2 Hz, 1 H), 2.51 (m, 1 H), 2.33 (m, 1 H), 0.29 (s, 3 H), 0.27 (s, 3 H).). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 143.8, 137.1, 136.8, 135.4, 134.4 (2 C), 129.04, 129.03, 127.4 (2 C), 119.8, 116.4, 113.7, 113.2, 112.2, 79.1, 72.5, 43.0, −5.3, −5.8; IR (film) 3071, 2958, 1254, 1046, 837 cm^{-1}; HRMS (EI) m/z 352.1859 [(M^+), calcd for $C_{22}H_{28}O_2Si$, 352.1859].

*syn/anti-(1-((1-(4-Chlorophenyl)but-3-en-1-yl)oxy)allyl)-dimethylphenylsilane (**S3-q**).* Applying general procedure D to **S2-b** (1 g, 5.2 mmol, 1 equiv), trichloroacetimidate **S1-i** (2.72 g, 8.32 mmol, 1.6 equiv), and (TMS)OTf (94 μL, 0.52 mmol, 0.1 equiv) in hexane (29 mL) afforded after column chromatography (hexanes and 10% CH_2Cl_2 in hexanes) a total of 1.686 g (91%) of *syn/anti*-**S3-q** (1:1). Diastereomers were partially separated and obtained as colorless oils. Spectroscopic data for *syn*-**S3-q**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2 H), 7.40−7.36 (m, 3 H), 7.25 (m, 2 H), 7.18 (m, 2 H), 5.67−5.55 (m, 2 H), 4.95−4.85 (m, 4 H), 4.29 (t, J = 6.0 Hz, 1 H), 4.00 (dt, J = 1.2, 5.4 Hz, 1 H), 2.45 (m, 1 H), 2.35 (m, 1 H), 0.39 (s, 3 H), 0.35 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 137.2, 136.7, 134.3 (2 C), 134.2, 132.5, 129.2, 128.0 (2 C), 127.9 (2 C), 127.6 (2 C), 117.2, 112.6, 80.4, 75.4, 41.3, −5.3, −5.7; IR (film) 3072, 2961, 1490, 1114, 913, 836 cm^{-1}; HRMS (EI) m/z 356.1352 [(M^+), calcd for $C_{21}H_{25}OSiCl$, 356.1363]. Spectroscopic data for *anti*-**S3-q**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (m, 2 H), 7.39 (tt, J = 1.8, 7.8 Hz, 1 H), 7.34 (t, J = 7.2 Hz, 2 H), 7.17 (m, 2 H), 6.95 (m, 2 H), 5.76 (m, 1 H), 5.71 (ddd, J = 7.2, 10.2, 17.4 Hz, 1 H), 5.03 (dt, J = 1.8, 10.8 Hz, 1 H), 5.01−4.96 (m, 3 H), 4.42 (dd, J = 6.0, 7.8 Hz, 1 H), 3.56 (d, J = 7.8 Hz, 1 H), 2.48 (m, 1 H), 2.30 (m, 1 H), 0.31 (s, 3 H), 0.26 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 136.8, 136.6, 134.8, 134.4 (2 C), 132.9, 129.1, 128.6 (2 C), 128.2 (2 C), 127.5 (2 C), 116.8, 113.7, 78.5, 72.7, 42.9, 31.6, 22.7, 14.1, −5.3, −6.3; IR (film) 3076, 2961, 1489, 1093, 911, 830 cm^{-1}; HRMS (EI) m/z 356.1355 [(M^+), calcd for $C_{21}H_{25}OSiCl$, 356.1363].

*syn-(1-((1-(4-Chlorophenyl)but-3-en-1-yl)oxy)allyl)triethylsilane (**S3-r**).* Applying general procedure D to **S2-d** (0.73 g, 4.23 mmol, 1 equiv), trichloroacetimidate **S1-i** (1.8 g, 5.5 mmol, 1.3 equiv), and (TMS)OTf (76 μL, 0.24 mmol, 0.1 equiv) in hexane (24 mL) afforded after column chromatography (hexanes and 10% CH_2Cl_2 in hexanes) a total of 0.96 g (ca. 67%) of impure *syn/anti*-**S3-r** (1:1). Only compound *syn*-**S3-q** was purified by subsequent column chromatography: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (m, 2 H), 7.19 (m, 2 H), 5.64

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(m, 2 H), 4.96−4.93 (m, 2 H), 4.88 (dt, J = 1.8, 17.4 Hz, 1 H), 4.81 (dt, J = 1.8, 10.8, 1 H), 4.32 (t, J = 6.0 Hz, 1 H), 3.96 (dt, J = 1.2, 7.8 Hz, 1 H), 2.48 (m, 1 H), 2.37 (m, 1 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.61 (dq, J = 3.0, 7.8 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 138.1, 134.2, 132.4, 127.9 (2 C), 117.2, 112.0, 80.3, 74.6, 41.2, 7.4, 1.7; IR (film) 3033, 2957, 1491, 833 cm^{-1}; HRMS (EI) m/z 336.1663 [(M^+), calcd for $C_{19}H_{29}OSiCl$, 336.1676].

*syn/anti-Triethyl(1-((1-(naphthalen-2-yl)but-3-en-1-yl)oxy)allyl)-silane (**S3-s**).* Applying general procedure D to **S2-d** (860 mg, 5 mmol, 1 equiv), trichloroacetimidate **S1-l** (2.4 g, 7 mmol, 1.4 equiv), and (TMS)OTf (22.5 μL, 0.125 mmol, 0.025 equiv) in hexane (28 mL) afforded after column chromatography (hexanes and 10% CH_2Cl_2 in hexanes) a total of 793 mg (45%) of *syn/anti*-**S3-s** (1:1). Diastereomers were partially separated and obtained as colorless oils. Spectroscopic data for *syn*-**S3-s**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (m, 2 H), 7.81 (d, J = 8.5 Hz, 1 H), 7.74 (s, 1 H), 7.47 (m, 3 H), 5.74 (m, 2 H), 5.04−4.95 (m, 3 H), 4.82 (m, 1 H), 4.55 (d, J = 6.0 Hz, 1 H), 4.08 (dt, J = 1.0, 7.0 Hz, 1 H), 2.65 (m, 1 H), 2.54 (m, 1 H), 1.05 (t, J = 8.0 Hz, 9 H), 0.69 (dq, J = 2.0, 8.0 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 138.3, 134.7, 133.1, 132.7, 127.9, 127.7, 127.5, 125.7, 125.4, 125.3, 125.0, 116.9, 111.9, 81.2, 74.6, 41.4, 7.5, 1.8; IR (film) 3057, 2953, 2878, 1414, 1018, 910, 817 cm^{-1}; HRMS (EI) m/z 352.2210 [(M^+), calcd for $C_{23}H_{32}OSi$, 352.2222]. Spectroscopic data for *anti*-**S3-s**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (m, 3 H), 7.63 (s, 1 H), 7.46−7.41 (m, 3 H), 5.79 (m, 2 H), 5.04−4.94 (m, 4 H), 4.59 (dd, J = 6.0, 8.0 Hz, 1 H), 3.58 (d, J = 8.0 Hz, 1 H), 2.60 (m, 1 H), 2.41 (m, 1 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.55 (dq, J = 4.0, 8.0 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.7, 138.0, 135.4, 133.1, 133.09, 128.0, 127.8, 127.7, 126.6, 125.9, 125.6, 125.1, 116.5, 112.9, 79.1, 71.6, 42.9, 7.4, 1.6; IR (film) 3059, 2953, 2876, 1458, 1020, 910 cm^{-1}; HRMS (EI) m/z 352.2222 [(M^+), calcd for $C_{23}H_{32}OSi$, 352.2222].

*syn/anti-Trimethyl(1-((1-(2-propylphenyl)but-3-en-1-yl)oxy)allyl)-silane (**S3-t**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (380 mg, 69.6% (w/w) in THF, 2.03 mmol, 1 equiv), trichloroacetimidate **S1-t** (679 mg, 2.03 mmol, 1 equiv), and (TMS)OTf (37 μL, 0.2 mmol, 0.1 equiv) in hexane (11 mL) afforded after column chromatography (hexanes) a total of 144.5 mg (24%) of *syn/anti*-**S3-t** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-t** were separable by column chromatography. Spectroscopic data for *syn*-**S3-t**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 1 H), 7.15 (m, 2 H), 7.07 (m, 1 H), 5.80 (ddt, J = 7.0, 10.0, 17.0 Hz, 1 H), 5.61 (ddd, J = 7.5, 10.5, 17.5 Hz, 1 H), 5.03−4.97 (m, 2 H), 4.87 (dt, J = 2.0, 17.5 Hz, 1 H), 4.79 (ddd, J = 1.5, 2.0, 10.5 Hz, 1 H), 4.58 (dd, J = 5.0, 7.5 Hz, 1 H), 3.78 (dt, J = 1.5, 7.5 Hz, 1 H), 2.53 (m, 2 H), 2.46 (m, 1 H), 2.36 (m, 1 H), 1.59 (m, 2 H), 0.96 (t, J = 7.5 Hz, 3 H), 0.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 138.5, 138.1, 135.4, 128.8, 126.9, 126.6, 125.6, 116.6, 111.8, 77.9, 76.6, 42.1, 34.5, 24.2, 14.2, −3.8; IR (film) 3074, 2959, 1248, 841 cm^{-1}; HRMS (EI) m/z 302.2078 [(M^+), calcd for $C_{19}H_{30}OSi$, 302.2066]. Spectroscopic data for *anti*-**S3-t**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 1.5, 7.5 Hz, 1 H), 7.18 (m, 2 H), 7.10 (m, 1 H), 5.92 (m, 1 H), 5.76 (ddd, J = 7.5, 11.0, 17.5 Hz, 1 H), 5.06−4.96 (m, 4 H), 4.78 (dd, J = 4.5, 9.0 Hz, 1 H), 3.39 (dt, J = 1.0, 7.0 Hz, 1 H), 2.53 (m, 2 H), 2.47 (m, 1 H), 2.28 (m, 1 H), 1.55 (m, 2 H), 0.95 (t, J = 7.0 Hz, 3 H), 0.00 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 140.4, 138.1, 135.9, 129.1, 126.8, 126.7, 126.0, 116.1, 112.8, 74.4 72.8, 43.2, 34.5, 24.6, 14.2, −4.0; IR (film) 3076, 2959, 1248, 841 cm^{-1}; HRMS (EI) m/z 302.2080 [(M^+), calcd for $C_{19}H_{30}OSi$, 302.2066].

*syn/anti-Trimethyl(2-methyl-1-((1-phenylbut-3-en-1-yl)oxy)allyl)-silane (**S3-u**).* Applying general procedure D to **S2-e** (2.6 g, 76.9% (w/w) in THF, 13.86 mmol, 1 equiv), the trichloroacetimidate of 1-phenylbut-3-en-1-ol (7.3 g, 24.95 mmol, 1.8 equiv), and (TMS)OTf (0.25 mL, 1.386 mmol, 0.1 equiv) in hexane (70 mL) afforded after column chromatography (hexanes) a total of 1.67 g (44%) of *syn/anti*-**S3-u** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti*-**S3-u** = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.19 (m, 10 H), 5.81 (ddt, J = 7.0, 10.5, 17.0 Hz, 1 H), 5.67 (ddt, J = 7.0, 10.5, 17.0 Hz, 1 H), 5.00−4.93 (m, 3 H), 4.80 (m, 1 H), 4.66 (m, 2 H), 4.32 (t, J = 6.0 Hz, 1 H), 4.28 (dd, J = 6.0, 8.0 Hz, 1 H), 3.77 (s, 1 H), 3.31 (s, 1 H), 2.52 (m, 2 H), 2.48 (m, 1 H), 2.34 (m, 1 H), 1.63 (m, 3 H), 1.51 (m, 3 H), 0.07 (s, 9 H), −0.02 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 144.4, 143.4, 142.3, 135.5, 134.6, 128.1 (2 C), 127.8 (2 C), 127.5 (2 C), 127.4, 126.8, 126.6 (2 C), 116.9, 116.4, 109.9, 109.5, 80.0, 79.0, 77.8, 75.4, 43.0, 40.5, 20.4, 20.3, −3.0, −3.2; IR (film) 3072, 2959, 1248, 1060, 839 cm^{-1}; HRMS (EI) m/z 274.1753 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*syn/anti-(1-((1-(4-Methoxyphenyl)but-3-en-1-yl)oxy)-2-methylallyl)trimethylsilane (**S3-v**).* Applying general procedure D to **S2-e** (660 mg, 79% (w/w) in THF, 3.6 mmol, 1 equiv), trichloroacetimidate **S1-d** (1.86 g, 5.77 mmol, 1.6 equiv), and (TMS)OTf (0.32 μL, 0.18 mmol, 0.05 equiv) in hexane (20 mL) afforded after column chromatography (15% and 20% CH_2Cl_2 in hexanes) a total of 918 mg (83%) of *syn/anti*-**S3-v** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-v** were separable by column chromatography. Spectroscopic data for *syn*-**S3-v**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2 H), 6.81 (m, 2 H), 5.66 (ddt, J = 7.2, 10.2, 17.4 Hz, 1 H), 4.98−4.93 (m, 2 H), 4.67 (m, 1 H), 4.65 (m, 1 H), 4.27 (t, J = 6.6 Hz, 1 H), 3.78 (s, 3 H), 3.75 (s, 1 H), 2.52 (m, 1 H), 2.43 (m, 1 H), 0.06 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 145.1, 135.5, 134.8, 127.7 (2 C), 116.8, 113.1 (2 C), 109.3, 79.8, 77.7, 55.1, 40.5, 20.3, −2.9; IR (film) 3033, 2950, 1238, 840 cm^{-1}; HRMS (EI) m/z 304.1853 [(M^+), calcd for $C_{18}H_{28}O_2Si$, 304.1859]. Spectroscopic data for *anti*-**S3-v**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 2 H), 5.78 (ddt, J = 6.6, 9.6, 16.8 Hz, 1 H), 4.99−4.94 (m, 2 H), 4.80 (s, 1 H), 4.66 (s, 1 H), 4.23 (t, J = 7.2 Hz, 1 H), 3.80 (s, 3 H), 3.30 (s, 1 H), 2.53 (m, 1 H), 2.33 (m, 1 H), −0.02 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.9, 144.5, 135.6, 134.3, 128.7 (2 C), 116.3, 113.4 (2 C), 109.8, 78.5, 75.0, 55.1, 43.0, 20.4, −3.2; IR (film) 3074, 2955, 1247, 824 cm^{-1}; HRMS (EI) m/z 304.1859 [(M^+), calcd for $C_{18}H_{28}O_2Si$, 304.1859].

*syn/anti-Trimethyl(2-methyl-1-((1-(4-methylphenyl)but-3-en-1-yl)oxy)allyl)silane (**S3-w**).* Applying general procedure D to **S2-e** (380 mg, 79% (w/w) in THF, 2.083 mmol, 1 equiv), trichloroacetimidate **S1-g** (1.02 g, 3.33 mmol, 1.6 equiv), and (TMS)OTf (19 μL, 0.104 mmol, 0.05 equiv) in hexane (12 mL) afforded after column chromatography (2% CH_2Cl_2 in hexanes) a total of 390 mg (61%) of *syn/anti*-**S3-w** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti*-**S3-w** = 1.4:1.0); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 2.8 H), 7.13 (s, 4 H), 7.09 (d, J = 7.8 Hz, 2.8 H), 5.81 (ddt, J = 7.2, 10.2, 17.4 Hz, 1 H), 5.68 (ddt, J = 6.6, 9.6, 16.8 Hz, 1.4 H), 5.01−4.94 (m, 4.8 H), 4.81 (m, 1 H), 4.69 (m, 1 H), 4.67 (m, 2.8 H), 4.31 (t, J = 5.4 Hz, 1.4 H), 4.27 (t, J = 6.6 Hz, 1 H), 3.78 (s, 1.4 H), 3.33 (s, 1 H), 2.53 (m, 2.4 H), 2.46 (m, 1.4 H), 2.35 (s, 3 H), 2.34 (heavily overlapped, m, 1 H), 2.33 (s, 4.2 H), 1.64 (d, J = 0.6 Hz, 3 H), 1.53 (d, J = 0.6 Hz, 4.2 H), 0.07 (s, 12.6 H), −0.08 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) (*syn*-**S3-v**, major) δ 145.0, 140.4, 136.2, 134.8, 128.5 (2C), 126.5 (2C), 116.8, 109.4, 79.8, 77.6, 40.5, 21.1, 20.3, −3.0; (*anti*-**S3-w**, minor) δ 144.4, 139.3, 136.9, 135.7, 128.8 (2 C), 127.5 (2 C), 116.3, 109.8, 78.8, 75.2, 43.1, 21.2, 20.4, −3.2; IR (film) 3075, 2957, 1247, 840 cm^{-1}; HRMS (EI) m/z 288.1895 [(M^+), calcd for $C_{18}H_{28}OSi$, 288.1909].

*syn/anti-Trimethyl(1-((1-phenylbut-3-en-1-yl)oxy)but-2-yn-1-yl)-silane (**S3-x**).* Applying general procedure E to compound **S2-g** (1 g, 4.66 mmol, 1 equiv), benzaldehyde (544 mg, 5.13 mmol, 1.1 equiv), allyltrimethylsilane (586 mg, 5.13 mmol, 1.1 equiv), and (TMS)OTf (170 μL, 0.932 mmol, 0.2 equiv) in CH_2Cl_2 (47 mL) for 1 h at −78 °C afforded after workup and column chromatography (1% EtOAc in hexanes) 1.08 g (90%) of a mixture of *anti*/*syn*-**S3-x** (1.6:1) as a yellow oil. Compounds *anti*- and *syn*-**S3-x** were partially separated by column chromatography. Spectroscopic data for *syn*-**S3-x**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.28 (m, 4 H), 7.21 (tt, J = 1.5, 7 Hz, 1 H), 5.72 (dddd, J = 7, 10, 14, 17 Hz, 1 H), 4.98 (m, 2 H), 4.56 (t, J = 6 Hz, 1 H), 3.86 (q, J = 2.5 Hz, 1 H), 2.57−2.44 (m, 2 H), 1.70 (d, J = 3 Hz, 3 H), 0.12 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 134.6, 127.8, 126.9, 126.7, 116.9, 83.4, 81.1, 77.6, 62.3, 40.7, 3.7, −3.7; IR (neat) 3072, 3030, 2959, 2363, 2335, 1641, 1452, 1248, 1057, 843 cm^{-1}; HRMS (EI) m/z 272.1594 [(M^+), calcd for $C_{17}H_{24}OSi$, 272.1596]. Spectroscopic data for *anti*-**S3-x**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.25 (m, 3 H), 5.75 (dddd, J = 7, 10.5, 14, 17.5 Hz, 1 H), 5.01−4.93 (m, 2 H), 4.67

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(t, J = 7 Hz, 1 H), 3.45 (q, J = 2.5 Hz, 1 H), 2.54 (m, 1 H), 2. 36 (m, 1 H), 1.87 (d, J = 2.5 Hz, 3 H), 0.05 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 135.2, 128.1, 127.4, 127.3, 116.2, 82.8, 79.8, 77.3, 60.3, 42.6, 3.9, −4; IR (neat) 3076, 2959, 2361, 2336, 1653, 1539, 1456, 1248, 844 cm^{-1}; HRMS (EI) m/z 272.1590 [(M^+), calcd for $C_{17}H_{24}OSi$, 272.1596].

*syn/anti-Trimethyl(1-((3-methyl-1-phenylbut-3-en-1-yl)oxy)allyl)-silane (**S3-y**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.5 g, 44% (w/w) in THF, 5.07 mmol, 1 equiv), the trichloroacetimidate of 3-methyl-1-phenylbut-3-en-1-ol (2.49 g, 8.11 mmol, 1.6 equiv), and (TMS)OTf (47 μL, 0.5 mmol, 0.1 equiv) in hexane (28 mL) afforded after column chromatography (2% CH_2Cl_2 in hexanes) a total of 847 mg (61%) of *syn/anti*-**S3-y** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-y** were separable by column chromatography. Spectroscopic data for *syn*-**S3-y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 4 H), 7.19 (m, 1 H), 5.62 (ddd, J = 7.0, 10.5, 17.0 Hz, 1 H), 4.88 (m, 1 H), 4.79 (m, 1 H), 4.70 (m, 1 H), 4.60 (m, 1 H), 4.41 (t, J = 6.5 Hz, 1 H), 3.76 (dt, J = 1.5, 7.0 Hz, 1 H), 2.52 (dd, A of ABX system, J = 7.0, 14.0 Hz, 1 H), 2.26 (dd, B of ABX system, J = 6.5, 14.0 Hz, 1 H), 1.67 (s, 3 H), 0.02 (s, 9 H); IR (film) 3065, 2957, 1245, 841 cm^{-1}; HRMS (EI) m/z 274.1741 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for *anti*-**S3-y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2 H), 7.28 (m, 3 H), 5.76 (ddd, J = 7.5, 10.5, 17.5 Hz, 1 H), 5.06 (dq, J = 1.0, 10.0 Hz, 1 H), 4.99 (dt, J = 1.5, 17.5 Hz, 1 H), 4.75 (m, 1 H), 4.67 (m, 1 H), 4.55 (dd, J = 6.0, 8.0 Hz, 1 H), 3.42 (dt, J = 1.0, 7.5 Hz, 1 H), 2.52 (dd, A of ABX system, J = 8.0, 13.5 Hz, 1 H), 2.29 (dd, B of ABX system, J = 5.0, 13.5 Hz, 1 H), 1.76 (s, 3 H), 0.00 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.8, 137.5, 128.0 (2 C), 127.3 (2 C), 127.27, 113.0, 112.6, 78.7, 72.8, 47.0, 23.3, −4.0; IR (film) 3076, 2959, 1247, 840 cm^{-1}; HRMS (EI) m/z 274.1745 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*syn/anti-Trimethyl(1-((3-methyl-1-(4-methylphenyl)but-3-en-1-yl)oxy)allyl)silane (**S3-z**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (0.97 g, 85.5% (w/w) in THF, 6.35 mmol, 1 equiv), trichloroacetimidate **S1-z** (2.85 g, 8.89 mmol, 1.4 equiv), and (TMS)OTf (57 μL, 0.317 mmol, 0.05 equiv) in hexane (35 mL) afforded after column chromatography (5% and 30% CH_2Cl_2 in hexanes) a total of 1.2 g (65%) of *syn/anti*-**S3-z** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-z** were separable by column chromatography. Spectroscopic data for *syn*-**S3-z**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, J = 7.0 Hz, 2 H), 7.07 (d, J = 7.5 Hz, 2 H), 5.64 (dddd, J = 1.0, 7.0, 10.5, 17.0 Hz, 1 H), 4.90 (dq, J = 1.5, 17.0 Hz, 1 H), 4. 80 (m, 1 H), 4.70 (m, 1 H), 4.61 (m, 1 H), 4.39 (t, J = 7.0 Hz, 1 H), 3.75 (dt, J = 1.5, 7.0 Hz, 1 H), 2.51 (dd, A of ABX system, J = 7.0, 14.0 Hz, 1 H), 2.31 (s, 3 H), 2.25 (dd, B of ABX system, J = 6.5, 13.5 Hz, 1 H), 1.67 (d, J = 1.0 Hz, 3 H), 0.02 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 141.0, 138.2, 136.4, 128.5 (2 C), 126.6 (2 C), 113.0, 111.6, 80.5, 76.0, 46.1, 23.1, 21.1, −3.7; IR (film) 3079, 2961, 1248, 1060, 841 cm^{-1}; HRMS (EI) m/z 288.1900 [(M^+), calcd for $C_{18}H_{28}OSi$, 288.1909]. Spectroscopic data for *anti*-**S3-z**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 4 H), 5.72 (ddd, J = 8.0, 11.0, 17.5 Hz, 1 H), 5.00 (ddd, J = 1.0, 2.0, 10.5 Hz, 1 H), 4.95 (ddd, J = 1.0, 2.0, 17.0 Hz, 1 H), 4.71 (m, 1 H), 4.64 (m, 1 H), 4.49 (dd, J = 5.0, 8.0 Hz, 1 H), 3.39 (dt, J = 1.0, 7.5 Hz, 1 H), 2.46 (dd, A of ABX system, J = 9.0, 13.5 Hz, 1 H), 2.33 (s, 3 H), 2.23 (dd, B of ABX system, J = 5.5, 14.0 Hz, 1 H), 1.72 (m, 3 H), −0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.7, 137.6, 136.8, 128.8 (2 C), 127.2 (2 C), 112.9, 112.5, 78.4, 72.6, 47.0, 23.3, 21.2, −4.0; IR (film) 3076, 2961, 1248, 1053, 841 cm^{-1}; HRMS (EI) m/z 288.1909 [(M^+), calcd for $C_{18}H_{28}OSi$, 288.1909].

*syn/anti-Trimethyl(1-((1-(thiophene-2-yl)but-3-en-1-yl)oxy)allyl)-silane (**S3-aa**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (1.03 g, 77.4% (w/w) in THF, 6.14 mmol, 1 equiv), trichloroacetimidate **S1-aa** (2.75 g, 9.21 mmol, 1.5 equiv), and (TMS)OTf (55.5 μL, 0.307 mmol, 0.05 equiv) in hexane (34 mL) afforded after column chromatography (hexanes) a total of 982 mg (60%) of *syn/anti*-**S3-aa** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-aa** were separable by column chromatography. Spectroscopic data for *syn*-**S3-aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, J = 1.0, 5.0 Hz, 1 H), 6.91 (dd, J = 3.0, 5.0 Hz, 1 H), 6.86 (m, 1 H), 5.80−5.70 (m, 2 H), 5.07−4.96 (m, 3 H), 4.89 (dt, J = 1.5, 10.5 Hz, 1 H), 4.64 (t, J = 6.0 Hz, 1 H), 3.83 (dt, J = 1.5, 7.0 Hz, 1 H), 2.63−2.50 (m, 2 H), 0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 137.5, 134.3, 126.1, 124.0, 123.6, 117.3, 112.3, 76.5, 75.7, 41.4, −3.86; IR (neat) 3076, 2957, 1248, 1062, 912, 841 cm^{-1}; HRMS (EI) m/z 266.1148 [(M^+), calcd for $C_{14}H_{22}OSiS$, 266.1161]. Spectroscopic data for *anti*-**S3-aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.92 (dd, J = 3.5, 5.0 Hz, 1 H), 6.87 (m, 1 H), 5.79 (dddd, J = 7.0, 10.0, 14.0, 17.0 Hz, 1 H), 5.71 (ddd, J = 7.5, 10.5, 17.5 Hz, 1 H), 5.04 (m, 1 H), 5.01 (m 2 H), 4.98 (m, 1 H), 4.69 (t, J = 7.0 Hz, 1 H), 3.56 (dt, J = 1.5, 7.5 Hz, 1 H), 2.61 (m, 1 H), 2.45 (m, 1 H) −0.03 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 137.4, 134.9, 126.0, 125.5, 124.8, 116.8, 113.1, 74.7, 72.8, 43.4, −4.0; IR (neat) 3076, 2957, 1248, 914, 843 cm^{-1}; HRMS (EI) m/z 266.1153 [(M^+), calcd for $C_{14}H_{22}OSiS$, 266.1161].

*syn/anti-(1-((1-(Furan-2-yl)but-3-en-1-yl)oxy)allyl)trimethylsilane (**S3-bb**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (990 mg, 77.4% (w/w) in THF, 5.9 mmol, 1 equiv), trichloroacetimidate **S1-bb** (2.17 g, 7.67 mmol, 1.3 equiv), and (TMS)OTf (27 μL, 0.147 mmol, 0.025 equiv) in hexane (33 mL) afforded after column chromatography (hexanes) a total of 720 mg (49%) of *syn/anti*-**S3-bb** (1:1) as a colorless oil. Compounds *syn*- and *anti*-**S3-bb** were separable by column chromatography. Spectroscopic data for *syn*-**S3-bb**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 1H), 6.27 (ddd, J = 0.5, 2.0, 3.0 Hz, 1 H), 6.19 (m, 1 H), 5.75 (dddd, J = 7.0, 10.5, 14.0, 17.5 Hz, 1 H), 5.69 (ddd, J = 7.0, 10.5, 17.0 Hz, 1 H), 5.04 (ddt, J = 1.5, 2.0, 17.0 Hz, 1 H), 4.99 (m, 1 H), 4.92 (ddd, J = 1.5, 2.0, 17.5 Hz, 1 H), 4.83 (ddd, J = 1.0, 2.0, 11.0 Hz, 1 H), 4.33 (t, J = 6.5 Hz, 1 H), 3.73 (dt, J = 1.5, 7.0 Hz, 1 H), 2.64−2.52 (m, 2 H), 0.01 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 141.4, 137.6, 134.5, 117.0, 111.4, 109.9, 107.2, 76.0, 75.1, 38.0, −3.89; IR (neat) 3078, 2959, 1248, 841 cm^{-1}; HRMS (EI) m/z 250.1381 [(M^+), calcd for $C_{14}H_{22}O_2Si$, 250.1389]. Spectroscopic data for *anti*-**S3-bb**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 1 H), 6.29 (dd, J = 2.0, 3.0 Hz, 1 H), 6.17 (dd, J = 1.0, 3.5 Hz, 1 H), 5.75 (m, 2 H), 5.05−4.95 (m, 4 H), 4.40 (t, J = 7.0 Hz, 1 H), 3.51 (dt, J = 1.5, 7.0 Hz, 1 H), 2.60 (m, 1 H), 2.52 (m, 1 H), −0.07 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 141.9, 137.3, 134.7, 116.7, 112.4, 109.7, 108.0, 73.1, 72.7, 39.4, −4.2; IR (neat) 3078, 2957, 1248, 841 cm^{-1}; HRMS (EI) m/z 250.1379 [(M^+), calcd for $C_{14}H_{22}O_2Si$, 250.1389].

*syn/anti-(1-((1-(4-Bromophenyl)but-3-en-1-yl)oxy)allyl)-trimethylsilane (**S3-cc**).* Applying general procedure D to α-(trimethylsilyl)allyl alcohol (2.3 g, solution 44% (w/w) in THF, 11.51 mmol, 1 equiv), trichloroacetimidate **S1-cc** (6.8 g, 18.4 mmol, 1.6 equiv), and (TMS)OTf (208 μL, 1.151 mmol, 0.1 equiv) in hexane (64 mL) afforded after column chromatography (hexanes) 1.425 g (37%) of *syn/anti*-**S3-cc** (1:1) as a colorless oil: mixture of diastereomers (*syn*:*anti*-**S3-cc** = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.39 (m, 2 H), 7.14 (m, 2 H), 7.10 (m, 2 H), 5.76−5.59 (m, 4 H), 5.01−4.93 (m, 6 H), 4.87 (dt, J = 1.8, 16.8 Hz, 1 H), 4.83 (dt, J = 1.8, 10.8 Hz, 1 H), 4.38 (dd, J = 6.0, 7.8 Hz, 1 H), 4.32 (t, J = 6.0 Hz, 1 H), 3.77 (dt, J = 1.8, 7.2 Hz, 1 H), 3.35 (dt, J = 1.1, 7.8 Hz, 1 H), 2.49 (m, 2 H), 2.40 (m, 1 H), 2.35 (m, 1 H), 0.03 (s, 9 H), −0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 141.5, 137.6, 137.3, 134.8, 134.2, 131.3 (2 C), 131.0 (2 C), 129.1 (2 C), 128.3 (2 C), 121.1, 120.6, 117.3, 116.8, 113.1, 112.1, 80.3, 78.6, 76.0, 73.1, 42.8, 41.3, −3.8, −4.0; IR (film) 3078, 2957, 1487, 1246, 1070, 1010, 841 cm^{-1}; HRMS (EI) m/z 338.0712 [(M^+), calcd for $C_{16}H_{23}OSiBr$, 338.0702].

Synthesis of Cyclic Ethers 1 and 2. *trans-Trimethyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**1a**).*[14] Applying general procedure F to *syn*-**S3-a** (184 mg, 0.707 mmol) and Grubbs second-generation catalyst (24 mg, 0.028 mmol, 0.04 equiv) in CH_2Cl_2 for 3 h followed by column chromatography (30% CH_2Cl_2 in hexanes) afforded 151 mg (92%) of **1a** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.24 (m, 5 H), 5.83−5.76 (m, 2 H), 4.72 (t, J = 5.5 Hz, 1 H), 4.01 (m, 1 H), 2.41−2.38 (m, 2 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 128.5 (2C), 128.4, 127.5, 126.9 (2C), 120.3, 72.6, 70.4, 30.4, −2.7; HRMS (CI) m/z 261.1664 [($M + H)^+$, calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of **1a** was confirmed on the basis of negative NOESY signals between protons at 4.72 and 4.01 ppm.

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*cis-Trimethyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**2a**).*[14] Following general procedure F, to *anti*-**S3-a** (167 mg, 0.641 mmol) in CH_2Cl_2 (10 mL, ~0.7 M) was added Grubbs second-generation catalyst (21.4 mg, 0.025 mmol, 0.04 equiv), and the solution was stirred under nitrogen at room temperature for 3 h. The reaction mixture was concentrated and purified by column chromatography (10% CH_2Cl_2 in hexanes) to afford 144 mg (97%) of **2a** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.22 (m, 5 H), 5.82−5.78 (m, 2 H), 4.38 (dd, J = 3.5, 10 Hz, 1 H), 4.17−4.15 (m, 1 H), 2.26−2.12 (m, 2 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 128.10 (2C), 128.06, 126.9, 125.6 (2C), 121.1, 75.3, 71.6, 34.2, −4.0; HRMS (CI) m/z 261.1681 [(M + H)$^+$, calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of **2a** was assigned on the basis of positive NOESY signals between protons at 4.15 and 2.26−2.12 ppm.

*trans-(6-(2-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1b**) and cis-(6-(2-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (**2b**).* Applying general procedure F to *syn*/*anti*-**S3-b** (2:1 ratio, 280 mg, 0.964 mmol, 1 equiv) and second-generation Grubbs catalyst (33 mg, 0.039 mmol, 0.04 equiv) in CH_2Cl_2 (10 mL) for 3 h afforded after column chromatography (25% CH_2Cl_2 in hexanes and 7% EtOAc in hexanes) 153 mg (62%) of **1b** and 82 mg (31%) of **2b** as colorless oils. Spectroscopic data for **1b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (dd, J = 1.8, 7.8 Hz, 1 H), 7.23 (t, J = 8.4 Hz, 1 H), 6.95 (tt, J = 0.6, 7.2 Hz, 1 H), 6.85, (d, J = 8.4 Hz, 1 H), 5.82 (m, 2 H), 5.02 (dd, J = 4.2, 8.4 Hz, 1 H), 4.14 (m, 1 H), 3.81 (s, 3 H), 2.29 (m, 2 H), 0.09 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 131.0, 128.2, 127.8, 127.0, 120.9, 120.6, 110.3, 72.3, 67.0, 55.3, 30.7, −2.7; IR (film) 1493, 1248, 1049, 839 cm^{-1}; HRMS (EI) m/z 262.1388 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389]. Spectroscopic data for **2b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, J = 1.8, 7.8 Hz, 1 H), 7.21 (dt, J = 1.8, 7.8 Hz, 1 H), 6.98 (dt, J = 1.2, 7.8 Hz, 1 H), 6.83 (d, J = 1.2, 7.8 Hz, 1 H), 5.80 (m, 2 H), 4.72 (dd, J = 2.4, 10.2 Hz, 1 H), 4.16 (m, 1 H), 3.80 (s, 3 H), 2.35 (m, 1 H), 1.98 (m, 1 H), 0.10 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 132.7, 127.7, 127.6, 126.1, 121.7, 120.8, 109.9, 71.4, 70.0, 55.3, 32.9, −3.9; IR (film) 1493, 1248, 1049, 841 cm^{-1}; HRMS (EI) m/z 262.1382 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*trans-(6-(3-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1c**).* Applying general procedure F to *syn*-**S3-c** (95.9 mg, 0.33 mmol, 1 equiv) and second-generation Grubbs catalyst (9.8 mg, 0.012 mmol, 0.035 equiv) in CH_2Cl_2 (3.5 mL) for 3 h afforded after column chromatography (35% CH_2Cl_2 in hexanes) 74 mg (86%) of **1c** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.94 (m, 2 H), 6.79 (m, 1 H), 5.79 (m, 2 H), 4.69 (t, J = 5.5 Hz, 1 H), 4.03 (m, 1 H), 3.79 (s, 3 H), 2.39 (m, 2 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 143.9, 129.2, 128.1, 120.0, 118.9, 112.6, 112.3, 72.3, 70.2, 55.2, 30.3, −2.9; IR (film) 1248, 1051, 841 cm^{-1}; HRMS (EI) m/z 262.1400 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*cis-(6-(3-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**2c**).* Applying general procedure F to *anti*-**S3-c** (109 mg, 0.375 mmol, 1 equiv) and second-generation Grubbs catalyst (17.7 mg, 0.021 mmol, 0.04 equiv) in CH_2Cl_2 (5.5 mL) for 3 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 91 mg (92%) of **2c** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, J = 8.0 Hz, 1 H), 6.92 (m, 2 H), 6.78 (ddd, J = 0.5, 2.5, 8.0 Hz, 1 H), 5.79 (m, 2 H), 4.37 (dd, J = 3.0, 10.0 Hz, 1 H), 4.15 (m, 1 H), 3.79 (s, 3 H), 2.23 (m, 1 H), 2.15 (m, 1 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 145.8, 129.1, 128.0, 121.1, 118.0, 112.2, 111.4, 75.2, 71.6, 55.1, 34.1, −4.0; IR (film) 1248, 1049, 841 cm^{-1}; HRMS (EI) m/z 262.1394 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*trans-(6-(4-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1d**).* Applying general procedure F to *syn*-**S3-d** (155 mg, 0.534 mmol, 1 equiv) and second-generation Grubbs catalyst (14 mg, 0.016 mmol, 0.03 equiv) in CH_2Cl_2 (6 mL) for 3 h afforded after column chromatography (35% CH_2Cl_2 in hexanes) 126 mg (90%) of **1d** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 9.0 Hz, 2 H), 6.87 (d, J = 9.0 Hz, 1 H), 5.80 (m, 2 H), 4.70 (t, J = 5.0 Hz, 1 H), 3.98 (m, 1 H), 3.79 (s, 3 H), 2.40 (m, 2 H), 0.10 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 134.2, 128.1, 127.9, 120.0, 113.6, 71.9, 69.6, 55.2, 30.0, −3.0; IR (film) 1513, 1248, 1038, 840 cm^{-1}; HRMS (EI) m/z 262.1403 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*cis-(6-(4-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**2d**).* Applying general procedure F to *anti*-**S3-d** (149 mg, 0.513 mmol, 1 equiv) and second-generation Grubbs catalyst (17.4 mg, 0.021 mmol, 0.04 equiv) in CH_2Cl_2 (6 mL) for 3 h afforded after column chromatography (25% CH_2Cl_2 in hexanes) 122 mg (91%) of **2d** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2 H), 6.87 (m, 2 H), 5.79 (m, 2 H), 4.34 (dd, J = 4.0, 9.0 Hz, 1 H), 4.16 (m, 1 H), 3.79 (s, 3 H), 2.18 (m, 2 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 136.3, 128.1, 126.9, 121.2, 113.5, 75.0, 71.7, 55.2, 34.1, −4.0; IR (film) 1248, 1072, 1039, 841 cm^{-1}; HRMS (EI) m/z 262.1390 [(M$^+$), calcd for $C_{15}H_{22}O_2Si$, 262.1389].

*trans-Trimethyl(6-(2-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1e**) and cis-Trimethyl(6-(2-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2e**).* Applying general procedure F to *syn*/*anti*-**S3-e** (2:1 ratio, 234 mg, 0.8526 mmol, 1 equiv) and second-generation Grubbs catalyst (29 mg, 0.034 mmol, 0.04 equiv) in CH_2Cl_2 (9 mL) for 3 h afforded after column chromatography (15% CH_2Cl_2 in hexanes and 5% EtOAc in hexanes) 114 mg (62%) of **1e** and 79 mg (30%) of **2e** as colorless oils. Spectroscopic data for **1e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 1 H), 7.19 (m, 3 H), 5.90 (m, 1 H), 5.82 (dq, J = 2.0, 10.0 Hz, 1 H), 4.99 (t, J = 5.0 Hz, 1 H), 3.82 (quintet, J = 3.0 Hz, 1 H), 2.54−2.46 (m, 1 H), 2.42 (s, 3 H), 2.40−2.34 (m, 2 H), 0.11 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 136.3, 130.3, 128.2, 127.2, 126.6, 125.5, 120.4, 69.7 (d, J = 5.8 Hz), 68.5 (d, J = 3.2 Hz), 29.5, 19.4 (d, J = 1.4 Hz,), −3.3; IR (film) 3028, 2955, 1247, 1052, 840 cm^{-1}; HRMS (EI) m/z 246.1444 [(M$^+$), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **2e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.5 Hz, 1 H), 7.23 (t, J = 7.5 Hz, 1 H), 7.17 (dt, J = 1.5, 7.5 Hz, 1 H), 7.13 (d, J = 7.0 Hz, 1 H), 5.84 (m, 2 H), 4.56 (dd, J = 4.5, 8.5 Hz, 1 H), 4.20 (m, 1 H), 2.35 (s, 3 H), 2.22 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 134.6, 130.0, 128.0, 126.8, 126.1, 125.6, 121.5, 73.1 (d, J = 3.9 Hz, 1 H), 71.8, 32.4, 19.2, −3.9; IR (film) 3027, 2957, 1247, 1072, 843 cm^{-1}; HRMS (EI) m/z 246.1436 [(M$^+$), calcd for $C_{15}H_{22}OSi$, 246.1440].

*trans-Trimethyl(6-(3-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1f**) and cis-Trimethyl(6-(3-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2f**).* Applying general procedure F to *syn*/*anti*-**S3-f** (~2:1 ratio, 228 mg, 0.8307 mmol, 1 equiv) and second-generation Grubbs catalyst (24.8 mg, 0.029 mmol, 0.035 equiv) in CH_2Cl_2 (9 mL) for 3 h afforded after column chromatography (15% CH_2Cl_2 in hexanes and 5% EtOAc in hexanes) 120 mg (59%) of **1f** and 60 mg (29%) of **2f** as colorless oils. Spectroscopic data for **1f**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (t, J = 7.8 Hz, 1 H), 7.19 (m, 2 H), 7.09 (d, J = 7.8 Hz, 1 H), 5.81 (m, 2 H), 4.69 (t, J = 6.0 Hz, 1 H), 4.07 (m, 1 H), 2.39 (m, 2 H), 2.36 (s, 3 H), 0.12 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 137.8, 128.09, 128.06, 128.0, 127.2, 123.6, 120.1, 72.5, 70.4, 30.5, 21.5, −2.9; IR (film) 3028, 2917, 1247, 1055, 840 cm^{-1}; HRMS (EI) m/z 246.1440 [(M$^+$), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **2f**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, J = 7.8 Hz, 1 H), 7.18 (m, 2 H), 7.06 (d, J = 7.8 Hz, 1 H), 5.83 (m, 2 H), 4.38 (dd, J = 3.0, 9.6 Hz, 1 H), 4.19 (m, 1 H), 2.37 (s, 3 H), 2.27−2.17 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 128.1 (2 C), 127.7, 126.4, 122.7, 121.2, 75.5, 71.6, 34.1, 21.5, −3.9; IR (film) 3028, 2917, 1247, 1074, 873 cm^{-1}; HRMS (EI) m/z 246.1436 [(M$^+$), calcd for $C_{15}H_{22}OSi$, 246.1440].

*trans-Trimethyl(6-(4-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1g**) and cis-Trimethyl(6-(4-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2g**).* Applying general procedure F to *syn*/*anti*-**S3-g** (~1.15:1 ratio, 228.8 mg, 0.834 mmol, 1 equiv) and second-generation Grubbs catalyst (28.3 mg, 0.033 mmol, 0.04 equiv) in CH_2Cl_2 (9 mL) for 3 h afforded after column chromatography (10% CH_2Cl_2 in hexanes and 6% EtOAc in hexanes) 108 mg (53%) of **1g** and 88 mg (43%) of **2g** as colorless oils. Spectroscopic data for **1g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 7.5 Hz, 2 H), 7.14 (d, J = 8 Hz, 2 H), 5.83−5.76 (m, 2 H), 4.71 (t, J = 5.5 Hz, 1 H), 4.00 (m, 1 H), 2.39 (m, 2 H), 2.33 (s, 3 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz,

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$CDCl_3$) δ 139.1, 136.8, 128.9 (2 C), 128.1, 126.6 (2 C), 120.1, 72.2, 69.8, 30.1, 21.1, −2.9; IR (film) 3028, 2955, 1248, 1053, 841 cm^{-1}; HRMS (EI) m/z 246.1452 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **2g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 2 H), 5.82−5.77 (m, 2 H), 4.36 (dd, J = 4.0, 9.5 Hz, 1 H), 4.15 (m, 1 H), 2.33 (s, 3 H), 2.24−2.13 (m, 2 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 136.5, 128.8 (2 C), 128.1, 125.6 (2 C), 121.2, 75.3, 71.6, 34.1, 21.1, −4.0; IR (film) 3028, 2957, 1248, 1072, 858, 841 cm^{-1}; HRMS (EI) m/z 246.1440 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440].

*trans-(6-(4-Fluorophenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1h**).* Applying general procedure F to *syn*-**S3-h** (95 mg, 0.341 mmol, 1 equiv) and second-generation Grubbs catalyst (11.6 mg, 0.014 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) for 3 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 75.2 mg (88%) of **1h** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, J = 5.5, 9.0 Hz, 2 H), 7.01 (t, J = 9.0 Hz, 2 H), 5.79 (m, 2 H), 4.70 (t, J = 5.5 Hz, 1 H), 3.98 (m, 1 H), 2.44−2.32 (m, 2 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (d, J = 247.1 Hz), 137.7 (d, J = 3.0 Hz), 128.3 (d, J = 8.0 Hz, 2 C), 128.2, 119.8, 114.9 (d, J = 21.2 Hz, 2 C), 71.6, 69.8, 30.1, −3.0; IR (film) 3030, 2957, 2899, 1510, 1248, 1055, 841 cm^{-1}; HRMS (EI) m/z 250.1177 [(M^+), calcd for $C_{14}H_{19}OSiF$, 250.1189].

*cis-(6-(4-Fluorophenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**2h**).* Applying general procedure G to *anti*-**S3-h** (93 mg, 0.334 mmol, 1 equiv) and second-generation Grubbs catalyst (11.3 mg, 0.013 mmol, 0.04 equiv) in benzene (4.2 mL) for 1 h at 80 °C afforded after column chromatography (10% CH_2Cl_2 in hexanes) 77.5 mg (93%) of **2h** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.00 (m, 2 H), 5.80 (m, 2 H), 4.37 (dd, J = 3.5,10.0 Hz, 1 H), 4.17 (m, 1 H), 2.21 (m, 1 H), 2.13 (m, 1 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, J = 244.9 Hz), 139.8 (d, J = 3.5 Hz), 128.1, 127.2 (d, J = 7.9 Hz, 2 C), 121.0, 114.9 (d, J = 21.2 Hz, 2 C), 74.8, 71.7, 34.2, −4.0; IR (film) 3030, 2959, 2775, 1512, 1248, 839 cm^{-1}; HRMS (EI) m/z 250.1183 [(M^+), calcd for $C_{14}H_{19}OSiF$, 250.1189].

*trans-(6-(4-Chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1i**) and cis-(6-(4-Chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (**2i**).* Applying general procedure F to *syn/anti*-**S3-i** (~1:1.4 ratio, 210 mg, 0.746 mmol, 1 equiv) and second-generation Grubbs catalyst (25.3 mg, 0.03 mmol, 0.04 equiv) in CH_2Cl_2 (8 mL) for 3 h afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 75.5 mg (38%) of **1i** and 105.6 mg (53%) of **2i** as colorless oils. Spectroscopic data for **1i**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 4 H), 5.78 (m, 2 H), 4.71 (dd, J = 5.0, 10.0 Hz, 1 H), 3.97 (m, 1 H), 2.42 (m, 1 H), 2.34 (m, 1 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 132.9, 128.3 (2 C), 128.2, 128.0 (2 C), 119.7, 71.6, 69.7, 30.0, −3.0; IR (film) 3030, 2956, 1492, 1248, 1090, 1055, 1015, 841 cm^{-1}; HRMS (EI) m/z 266.0890 [(M^+), calcd for $C_{14}H_{19}OSiCl$, 266.0894]. Spectroscopic data for **2i**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 4 H), 5.81 (m, 2 H), 4.37 (dd, J = 3.5, 10.0 Hz, 1 H), 4.17 (m, 1 H), 2.22 (m, 1 H), 2.12 (m, 1 H), 0.10 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 132.6, 128.2 (2 C), 128.1, 127.0 (2 C), 120.9, 74.7, 71.7, 34.0, −4.0; IR (film) 3030, 2957, 2896, 1490, 1248, 1088, 1073, 1014, 841 cm^{-1}; HRMS (EI) m/z 266.0883 [(M^+), calcd for $C_{14}H_{19}OSiCl$, 266.0894].

*trans-Trimethyl(6-(4-(trifluoromethyl)phenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**1j**) and cis-Trimethyl(6-(4-(trifluoromethyl)-phenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2j**).* Applying general procedure F to *syn/anti*-**S3-j** (~1:4.1 ratio, 296 mg, 0.904 mmol, 1 equiv) and second-generation Grubbs catalyst (31 mg, 0.036 mmol, 0.04 equiv) in CH_2Cl_2 (9.5 mL) for 3 h afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 50 mg (18%) of **1j** and 201 mg (74%) of **2j** as colorless oils. Spectroscopic data for **1j**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 5.80 (m, 2 H), 4.77 (t, J = 5.0 Hz, 1 H), 4.01 (m, 1 H), 2.46 (m, 1 H), 2.36 (m, 1 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 129.4 (q, J = 32.1 Hz), 128.3, 126.8 (2 C), 125.1 (q, J = 3.9 Hz, 2 C), 124.3 (q, J = 270.8 Hz), 119.6, 71.7, 70.0, 30.1, −3.1; IR (neat) 1325, 1250, 1126, 1068, 839 cm^{-1}; HRMS (EI) m/z 300.1151 [(M^+), calcd for $C_{15}H_{19}OSiF_3$, 300.1157]. Spectroscopic data for **2j**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.0 Hz, 1 H), 5.87−5.79 (m, 2 H), 4.46 (dd, J = 3.0, 10.0 Hz, 1 H), 4.19 (m, 1 H), 2.27 (m, 1 H), 2.14 (m, 1 H), 0.12 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 129.2 (q, J = 38.4 Hz), 128.1, 125.9 (2 C), 125.1 (q, J = 4.7 Hz, 2 C), 124.3 (q, J = 324.3 Hz), 120.7, 74.9, 71.7, 34.0, −4.1; IR (neat) 1325, 1250, 1165, 1126, 1068, 841 cm^{-1}; HRMS (EI) m/z 300.1157 [(M^+), calcd for $C_{15}H_{19}OSiF_3$, 300.1157].

*trans-(6-([1,1′-Biphenyl]-4-yl)-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**1k**) cis-(6-([1,1′-Biphenyl]-4-yl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane and (**2k**).* Applying general procedure F to *syn/anti*-**S3-k** (~2:1 ratio, 161 mg, 0.478 mmol, 1 equiv) and second-generation Grubbs catalyst (16.2 mg, 0.0191 mmol, 0.04 equiv) in CH_2Cl_2 (5 mL) for 3 h afforded after column chromatography (15% and 35% CH_2Cl_2 in hexanes) 24.6 mg (17%) of **1k** and 67 mg (46%) of **2k** as colorless oils. Spectroscopic data for **1k**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 4 H), 7.44 (m, 4 H), 7.33 (m, 1 H), 5.83 (m, 2 H), 4.79 (t, J = 6.0 Hz, 1 H), 4.06 (m, 1 H), 2.45 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 141.0, 140.1, 128.7 (2 C), 128.2, 127.1, 127.08 (2 C), 127.05 (2 C), 126.97 (2 C), 120.0, 72.1, 70.0, 30.2, −2.9; IR (film) 3028, 2955, 1248, 1070, 841 cm^{-1}; HRMS (EI) m/z 308.1584 [(M^+), calcd for $C_{20}H_{24}OSi$, 308.1596]. Spectroscopic data for **2k**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (m, 4 H), 7.44 (m, 4 H), 7.43 (m, 1 H), 5.85 (m, 2 H), 4.47 (dd, J = 3.5, 10.0 Hz, 1 H), 4.22 (s, 1 H), 2.33−2.20 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 141.1, 139.9, 128.7 (2 C), 128.1, 127.1 (3 C), 126.9 (2 C), 126.1 (2 C), 121.1, 75.2, 71.7, 34.1, −4.0; IR (film) 3030, 2957, 1246, 1070, 841 cm^{-1}; HRMS (EI) m/z 308.1594 [(M^+), calcd for $C_{20}H_{24}OSi$, 308.1596].

*trans-Trimethyl(6-(naphthalen-2-yl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1l**).* Applying general procedure G to *syn*-**S3-l** (102 mg, 0.328 mmol, 1 equiv) and second-generation Grubbs catalyst (11.2 mg, 0.013 mmol, 0.04 equiv) in benzene (4.1 mL) for 1 h at 80 °C afforded after column chromatography (40% CH_2Cl_2 in hexanes) 83.4 mg (90%) of **1l** as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.54 (dd, J = 1.8, 8.4 Hz, 1 H), 7.45 (m, 2 H), 5.87 (m, 1 H), 5.81 (m, 1 H), 4.91 (t, J = 6.0 Hz, 1 H), 4.04 (quintet, J = 3.0 Hz, 1 H), 2.52 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 133.2, 132.8, 128.2, 128.0, 127.9, 127.6, 125.9, 125.7, 125.2, 125.1, 120.0, 72.5, 69.9, 30.2, −3.0; IR (film) 3028, 2955, 2897, 1248, 841 cm^{-1}; HRMS (EI) m/z 282.1436 [(M^+), calcd for $C_{18}H_{22}OSi$, 282.1440].

*cis-Trimethyl(6-(naphthalen-2-yl)-5,6-dihydro-2H-pyran-2-yl)-silane (**2l**).* Applying general procedure G to *anti*-**S3-l** (110 mg, 0.3543 mmol, 1 equiv) and second-generation Grubbs catalyst (12 mg, 0.014 mmol, 0.04 equiv) in benzene (4.4 mL) for 1 h at 80 °C afforded after column chromatography (10% CH_2Cl_2 in hexanes) 93 mg (93%) of **2l** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.48 (dd, J = 1.5, 8.5 Hz, 1 H), 7.44 (m, 2 H), 5.84 (m, 2 H), 4.56 (dd, J = 3.5, 9.5 Hz, 1 H), 4.23 (m, 1 H), 2.34−2.22 (m, 2 H), 0.12 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 133.3, 132.8, 128.1, 127.9, 127.8, 127.6, 125.8, 125.5, 124.3, 124.1, 121.1, 75.5, 71.7, 34.0, −4.0; IR (film) 3028, 2957, 2772, 1246, 1072, 841 cm^{-1}; HRMS (EI) m/z 267.1217 [($M - CH_3$)$^+$, calcd for $C_{17}H_{19}OSi$, 267.1205].

*trans-Dimethylphenyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**1m**).* Applying general procedure F to *syn/anti*-**S3-m** (~13:1 ratio, 99 mg, 0.307 mmol, 1 equiv) and second-generation Grubbs catalyst (10 mg, 0.0123 mmol, 0.04 equiv) in CH_2Cl_2 (3.5 mL) at room temperature afforded after column chromatography (10% and 30% CH_2Cl_2 in hexanes) 80.4 mg (89%) of **1m** and 2.5 mg (3%) of **2m** as colorless oils. Spectroscopic data for **1m**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2 H), 7.39−7.32 (m, 7 H), 7.26 (m, 1 H), 5.84−5.77 (m, 2 H), 4.65 (dd, J = 5.0, 6.5 Hz, 1 H), 4.29 (m, 1 H), 2.42−2.31 (m, 2 H) 0.43 (s, 3 H), 0.40 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 136.9, 134.1, 129.3, 128.2, 127.8, 127.2, 126.6, 120.5, 72.3, 69.8, 30.2, −4.4, −4.6; IR (film) 3071, 2960, 1113, 724 cm^{-1}; HRMS (EI) m/z 294.1436 [(M^+), calcd for $C_{19}H_{22}OSi$, 294.1440].

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*cis-Dimethylphenyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**2m**).* Applying general procedure F to *anti*-**S3-m** (119.8 mg, 0.3714 mmol, 1 equiv) and second-generation Grubbs catalyst (12.6 mg, 0.0148 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature afforded after column chromatography (20% CH_2Cl_2 in hexanes) 99 mg (91%) of **2m** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 2 H), 7.43−7.38 (m, 7 H), 7.31 (t, J = 7 Hz, 1 H), 5.84 (m, 2 H), 4.48 (m, 2 H), 2.33−2.19 (m, 2 H), 0.47 (s, 3 H), 0.45 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 136.7, 134.2, 129.2, 128.1, 127.8, 127.7, 127.0, 125.6, 121.5, 75.5, 71.3, 34.0, −5.1, −5.9; IR (film) 3071, 2959, 1428, 1115, 724 cm^{-1}; HRMS (EI) m/z 294.1440 [(M^+), calcd for $C_{19}H_{22}OSi$, 294.1440].

*trans-Methyldiphenyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**1n**) and cis-Methyldiphenyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)-silane (**2n**).* Applying general procedure G to *syn*/*anti*-**S3-n** (∼1:1.7 ratio, 312 mg, 0.811 mmol, 1 equiv) and second-generation Grubbs catalyst (27.5 mg, 0.032 mmol, 0.04 equiv) in benzene (11.6 mL) at room temperature afforded after column chromatography (20% and 30% CH_2Cl_2 in hexanes) 75 mg (26%) of **1n** and 101 mg (35%) of **2n** as colorless oils. Spectroscopic data for **1n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.59 (m, 2 H), 7.49−7.23 (m, 11 H), 5.87−5.80 (m 2 H), 4.63 (m, 2 H), 2.43−2.32 (m, 2 H), 0.66 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 135.3, 135.13 (2 C), 135.08 (2 C), 134.97, 129.5, 129.4, 128.1 (2 C), 127.9 (2 C), 127.8 (2 C), 127.7, 127.2, 126.7 (2 C), 121.1, 72.1, 68.5, 29.7, −5.5; IR (film) 3071, 2975, 1111, 724 cm^{-1}; HRMS (EI) m/z 356.1579 [(M^+), calcd for $C_{24}H_{24}OSi$, 356.1596]. Spectroscopic data for **2n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 4 H), 7.41−7.30 (m, 10 H), 7.24 (m, 1 H), 5.80 (m, 2 H), 4.76 (m, 1 H), 4.49 (dd, J = 3.0, 10.0 Hz, 1 H), 2.26 (m, 1 H), 2.19 (m, 1 H), 0.64 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 135.22 (2 C), 135.16, 135.1 (2 C), 134.8, 129.5, 129.4, 128.1 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6, 126.9, 125.6 (2 C), 122.1, 75.8, 70.9, 33.9, −6.4; IR (film) 3069, 2963, 1427, 788, 696 cm^{-1}; HRMS (EI) m/z 356.1587 [(M^+), calcd for $C_{24}H_{24}OSi$, 356.1596].

*trans-Triethyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**1o**).* Applying general procedure F to *syn*-**S3-o** (73.5 mg, 0.243 mmol, 1 equiv) and second-generation Grubbs catalyst (8.3 mg, 0.01 mmol, 0.04 equiv) in CH_2Cl_2 (3 mL) at room temperature afforded after column chromatography (25% CH_2Cl_2 in hexanes) 55.9 mg (84%) of **1o** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 7.2 Hz, 2 H), 7.32 (t, J = 7.2 Hz, 2 H), 7.24 (m, 1 H), 5.76 (m, 2 H), 4.74 (t, J = 5.4 Hz, 1 H), 4.14 (m, 1 H), 2.44 (m, 1 H), 2.39 (m, 1 H), 0.97 (t, J = 7.8 Hz, 9 H), 0.64 (q, J = 7.8 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 128.9, 128.1 (2 C), 127.1, 126.6 (2 C), 119.4, 72.3, 67.7, 30.0, 7.5, 2.6; IR (film) 3030, 2955, 1454, 1072 cm^{-1}; HRMS (EI) m/z 274.1737 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*cis-Triethyl(6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**2o**).* Applying general procedure G to *anti*-**S3-o** (102 mg, 0.337 mmol, 1 equiv) and second-generation Grubbs catalyst (11.4 mg, 0.013 mmol, 0.04 equiv) in benzene (4.8 mL) at 80 °C for 1 h afforded after column chromatography (10% CH_2Cl_2 in hexanes) 88 mg (95%) of **2o** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4 H), 7.24 (m, 1 H), 5.84 (m, 1 H), 5.76 (m, 1 H), 4.39 (dd, J = 3.5, 9.5 Hz, 1 H), 4.33 (m, 1 H), 2.28−2.16 (m, 2 H), 1.01 (t, J = 8.0 Hz, 9 H), 0.68 (q, J = 8.0 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 128.7, 128.1 (2 C), 126.9, 125.6 (2 C), 120.7, 75.7, 70.2, 34.1, 7.5, 1.9; IR (film) 3028, 2953, 1454, 1072 cm^{-1}; HRMS (EI) m/z 274.1746 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*trans-(6-(3-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-dimethylphenylsilane (**1p**).* Applying general procedure F to *syn*-**S3-p** (174 mg, 0.4936 mmol, 1 equiv) and second-generation Grubbs catalyst (17 mg, 0.0197 mmol, 0.04 equiv) in CH_2Cl_2 (5 mL) at room temperature for 3 h afforded after column chromatography (40% CH_2Cl_2 in hexanes) 137.4 mg (86%) of **1p** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, 2 H), 7.39−7.34 (m, 3 H), 7.24 (t, J = 8.4 Hz, 1 H), 6.89 (m, 2 H), 6.80 (m, 1 H), 5.83−5.77 (m, 2 H), 4.62 (t, J = 5.4 Hz, 1 H), 4.30 (m, 1 H), 3.79 (s, 3 H), 2.40−2.31 (m, 2 H), 0.42 (s, 3 H), 0.39 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 143.7, 136.9, 134.1 (2 C), 129.3, 129.1, 127.8 (2 C), 127.7, 120.5, 118.9, 112.7, 112.2, 72.2, 69.9, 55.1, 30.2, −4.4, −4.6; IR (film) 3071, 2954, 1492, 1244, 814 cm^{-1}; HRMS (EI) m/z 324.1536 [(M^+), calcd for $C_{20}H_{24}O_2Si$, 324.1546].

*cis-(6-(3-Methoxyphenyl)-5,6-dihydro-2H-pyran-2-yl)-dimethylphenylsilane (**2p**).* Applying general procedure G to *anti*-**S3-p** (95 mg, 0.269 mmol, 1 equiv) and second-generation Grubbs catalyst (9.2 mg, 0.011 mmol, 0.04 equiv) in benzene (3.8 mL) at 80 °C for 1 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 75.4 mg (87%) of **2p** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (m, 2 H), 7.37 (m, 3 H), 7.26 (t, J = 7.8 Hz, 1 H), 6.96 (m, 1 H), 6.94 (dd, J = 0.6, 7.2 Hz, 1 H), 6.81 (ddd, J = 1.2, 3.0, 8.4 Hz, 1 H), 5.79 (m, 2 H), 4.42 (m, 2 H), 3.82 (s, 3 H), 2.25 (m, 1 H), 2.16 (m, 1 H), 0.41 (s, 3 H), 0.39 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 145.6, 136.7, 134.2 (2 C), 129.2, 129.1, 127.7, 127.6 (2 C), 121.5, 118.0, 112.4, 111.2, 75.3, 71.3, 55.1, 33.9, −5.2, −5.9; IR (film) 3070, 2959, 1494, 1249, 815 cm^{-1}; HRMS (EI) m/z 324.1546 [(M^+), calcd for $C_{20}H_{24}O_2Si$, 324.1546].

*trans-(6-(4-Chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)-dimethylphenylsilane (**1q**).* Applying general procedure G to *syn*-**S3-q** (128 mg, 0.359 mmol, 1 equiv) and second-generation Grubbs catalyst (12.2 mg, 0.014 mmol, 0.04 equiv) in benzene (5.1 mL) at 80 °C for 1 h afforded after column chromatography (25% CH_2Cl_2 in hexanes) 109 mg (92%) of **1q** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.39−7.33 (m, 3 H), 7.27 (m, 2 H), 7.21 (m, 2 H), 5.80−5.75 (m, 2 H), 4.58 (t, J = 5.4 Hz, 1 H), 4.22 (m, 1 H), 2.35−2.27 (m, 2 H), 0.39 (s, 3 H), 0.37 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 136.7, 134.1 (2 C), 132.9, 129.3, 128.3 (2 C), 128.0 (2 C), 127.9, 127.8 (2 C), 120.3, 71.5, 69.6, 30.0, −4.4, −4.7; IR (film) 3068, 2957, 1490, 1249, 809 cm^{-1}; HRMS (EI) m/z 328.1035 [(M^+), calcd for $C_{19}H_{21}OSiCl$, 328.1050].

*trans-(6-(4-Chlorophenyl)-5,6-dihydro-2H-pyran-2-yl)-triethylsilane (**1r**).* Applying general procedure G to *syn*-**S3-r** (94.6 mg, 0.281 mmol, 1 equiv) and second-generation Grubbs catalyst (9.5 mg, 0.012 mmol, 0.04 equiv) in benzene (4 mL) at 80 °C for 1 h afforded after column chromatography (25% CH_2Cl_2 in hexanes) 71.9 mg (83%) of **1r** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 4 H), 5.75 (m, 2 H), 4.71 (t, J = 5.4 Hz, 1 H), 4.09 (m, 1 H), 2.44 (m, 1 H), 2.32 (m, 1 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.62 (q, J = 7.8 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 132.8, 129.0, 128.3 (2 C), 128.0 (2 C), 119.1, 71.6, 67.4, 29.8, 7.4, 2.5; IR (film) 3030, 2953, 2878, 1493, 1014, 819, 715 cm^{-1}; HRMS (EI) m/z 308.1349 [(M^+), calcd for $C_{17}H_{25}OSiCl$, 308.1363].

*trans-Triethyl(6-(naphthalen-2-yl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1s**).* Applying general procedure G to *syn*-**S3-s** (99.5 mg, 0.282 mmol, 1 equiv) and second-generation Grubbs catalyst (9.6 mg, 0.0113 mmol, 0.04 equiv) in benzene (4 mL) at 80 °C for 1 h afforded after column chromatography (25% CH_2Cl_2 in hexanes) 85.7 mg (94%) of **1s** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (m, 4 H), 7.57 (dd, J = 1.5, 8.5 Hz, 1 H), 7.49 (m, 2 H), 5.85 (m, 2 H), 4.96 (t, J = 5.0 Hz, 1 H), 4.20 (m, 1 H), 2.63−2.52 (m, 2 H), 1.03 (t, J = 8.0 Hz, 9 H), 0.70 (dq, J = 1.5, 8.0 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 133.2, 132.7, 129.0, 128.1, 127.8, 127.6, 125.8, 125.6, 125.3, 125.1, 119.4, 72.4, 67.6, 29.9, 7.5, 2.6; IR (film) 3055, 2953, 2874, 1458, 1018, 817, 719 cm^{-1}; HRMS (EI) m/z 324.1902 [(M^+), calcd for $C_{21}H_{28}OSi$, 324.1909].

*cis-Triethyl(6-(naphthalen-2-yl)-5,6-dihydro-2H-pyran-2-yl)silane (**2s**).* Applying general procedure G to *anti*-**S3-s** (102.2 mg, 0.29 mmol, 1 equiv) and second-generation Grubbs catalyst (9.8 mg, 0.0116 mmol, 0.04 equiv) in benzene (4.1 mL) at 80 °C for 1 h afforded after column chromatography (10% CH_2Cl_2 in hexanes) 74.8 mg (79%) of **2s** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 4 H), 7.49 (dd, J = 1.0, 8.0 Hz, 1 H), 7.44 (m, 2 H), 5.88 (m, 1 H), 5.81 (m, 1 H), 4.55 (dd, J = 4.5, 9.5 Hz, 1 H), 4.39 (m, 1 H), 2.31 (m, 2 H), 1.04 (t, J = 8.0 Hz, 9 H), 0.70 (dq, J = 1.5, 8.0 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 133.3, 132.7, 128.7, 128.0, 127.8, 127.6, 125.8, 125.5, 124.3, 124.1, 120.7, 75.9, 70.3, 34.0, 7.5, 1.9; IR (film) 3028, 2951, 2874, 1458, 1072, 815, 715 cm^{-1}; HRMS (EI) m/z 324.1894 [(M^+), calcd for $C_{21}H_{28}OSi$, 324.1909].

*trans-Trimethyl(6-(2-propylphenyl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1t**).* Applying general procedure G to *syn*-**S3-t** (36 mg, 0.119 mmol, 1 equiv) and second-generation Grubbs catalyst (4 mg,

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0.0048 mmol, 0.04 equiv) in benzene (2.4 mL) at 80 °C for 1 h afforded after column chromatography (25% CH_2Cl_2 in hexanes) 27.9 mg (85%) of **1t** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 1 H), 7.17 (m, 3 H), 5.86 (dq, J = 3.5, 10.0 Hz, 1 H), 5.81 (m, 1 H), 4.97 (t, J = 5.5 Hz, 1 H), 3.90 (quintet, J = 3.0 Hz, 1 H), 2.72−2.60 (m, 2 H), 2.42−2.31 (m, 2 H), 1.61 (m, 2 H), 0.98 (t, J = 7.0 Hz, 3 H), 0.07 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 139.3, 129.2, 128.1, 127.2, 126.9, 125.6, 120.5, 69.4, 69.1, 34.6, 30.7, 24.9, 14.3, −3.1; IR (film) 3028, 2959, 2872, 1248. 839 cm^{-1}; HRMS (EI) m/z 274.1755 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*cis-Trimethyl(6-(2-propylphenyl)-5,6-dihydro-2H-pyran-2-yl)-silane (**2t**).* Applying general procedure G to *anti*-**S3-t** (57 mg, 0.188 mmol, 1 equiv) and second-generation Grubbs catalyst (6.4 mg, 0.0075 mmol, 0.04 equiv) in benzene (3.8 mL) at 80 °C for 1 h afforded after column chromatography (12% CH_2Cl_2 in hexanes) 38.6 mg (75%) of **2t** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 2.0, 7.0 Hz, 1 H), 7.20 (m, 2 H), 7.15 (m, 1 H), 5.83 (m, 2 H), 4.58 (dd, J = 3.0, 10.0 Hz, 1 H), 4.18 (m, 1 H), 2.62 (m, 2 H), 2.25 (m, 1 H), 2.17 (m, 1 H), 1.63 (m, 2 H), 0.99 (t, J = 7.0 Hz, 3 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.3, 128.9, 128.0, 126.9, 126.1, 126.0, 121.6, 72.7, 71.9, 34.5, 33.4, 24.6, 14.3, −3.9; IR (film) 3028, 2959, 2872, 1248, 841 cm^{-1}; HRMS (EI) m/z 274.1740 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*trans-Trimethyl(3-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-yl)-silane (**1u**) and cis-Trimethyl(3-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-yl)silane (**2u**).* Applying general procedure F to *syn*/*anti*-**S3-u** (∼1:1 ratio, 309 mg, 1.126 mmol, 1 equiv) and second-generation Grubbs catalyst (38 mg, 0.045 mmol, 0.04 equiv) in CH_2Cl_2 (13 mL) at room temperature for 3 h afforded after column chromatography (10% and 25% CH_2Cl_2 in hexanes) 159 mg (57%) of **1u** and 100 mg of **2u** (36%) as colorless oils. Spectroscopic data for **1u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.30 (m, 4 H), 7.24 (tt, J = 1.5, 6.5 Hz, 1 H), 5.47 (m, 1 H), 4.54 (dd, J = 5.0, 7.5 Hz, 1 H), 4.01 (d, J = 1.0 Hz, 1 H), 2.33−2.29 (m, 2, H), 1.68 (m, 3 H), 0.18 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 135.4, 128.2 (2 C), 127.1, 126.0 (2 C), 115.8, 75.0, 72.9, 32.1, 20.4, −1.4; IR (film) 3029, 2957, 1250, 839 cm^{-1}; HRMS (EI) m/z 246.1440 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **2u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 4 H), 7.22 (m, 1 H), 5.51 (m, 1 H), 4.29 (dd, J = 3.0, 8.5 Hz, 1 H), 4.05 (m, 1 H), 2.20 (m, 1 H), 2.10 (m, 1 H), 1.66 (m, 3 H), 0.13 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 135.3, 128.1 (2 C), 126.8, 125.6 (2 C), 117.0, 75.0, 74.4, 34.2, 20.0, −2.6; IR (film) 3030, 2957, 1248, 839 cm^{-1}; HRMS (EI) m/z 246.1432 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440].

*trans-(6-(4-Methoxyphenyl)-3-methyl-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (**1v**).* Applying general procedure F to *syn*-**S3-v** (94.6 mg, 0.311 mmol, 1 equiv) and second-generation Grubbs catalyst (10.6 mg, 0.0124 mmol, 0.04 equiv) in CH_2Cl_2 (3.5 mL) at room temperature for 3 h afforded after column chromatography (60% CH_2Cl_2 in hexanes) 61.5 mg (72%) of **1v** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2 H), 6.87 (m, 2 H), 5.47 (m, 1 H), 4.49 (dd, J = 4.5, 9.0 Hz, 1 H), 3.99 (m, 1 H), 3.78 (s, 3 H), 2.37−2.24 (m, 2 H), 1.64 (m, 3 H), 0.15 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 135.3, 134.9, 127.3 (2 C), 115.9, 113.6 (2 C), 74.9, 72.5, 55.2, 32.0, 20.4, −1.4; IR (film) 2959, 1248, 838 cm^{-1}; HRMS (EI) m/z 276.1549 [(M^+), calcd for $C_{16}H_{24}O_2Si$, 276.1546].

*cis-(6-(4-Methoxyphenyl)-3-methyl-5,6-dihydro-2H-pyran-2-yl)-trimethylsilane (**2v**).* Applying general procedure F to *anti*-**S3-v** (116.9 mg, 0.3839 mmol, 1 equiv) and second-generation Grubbs catalyst (13 mg, 0.0154 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature for 3 h afforded after column chromatography (35% CH_2Cl_2 in hexanes) 91 mg (86%) of **2v** as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 6.85 (m, 2 H), 5.49 (m, 1 H), 4.23 (dd, J = 3.0, 10.8 Hz, 1 H), 4.04 (m, 1 H), 3.78 (s, 3 H), 2.16 (m, 1 H), 2.07 (m, 1 H), 1.65 (d, J = 1.2 Hz, 3 H), 0.11 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 136.3, 135.3, 126.8 (2 C), 117.1, 113.5 (2 C), 74.6, 74.4, 55.2, 34.2, 20.0, −2.6; IR (film) 2964, 1248, 839 cm^{-1}; HRMS (EI) m/z 276.1551 [(M^+), calcd for $C_{16}H_{24}O_2Si$, 276.1546].

*trans-Trimethyl(3-methyl-6-(4-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**1w**) and cis-Trimethyl(3-methyl-6-(4-methyl-phenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2w**).* Applying general procedure G to *syn*/*anti*-**S3-w** (∼1.5:1 ratio, 159 mg, 0.551 mmol, 1 equiv) and second-generation Grubbs catalyst (17.6 mg, 0.021 mmol, 0.04 equiv) in benzene (7 mL) at 80 °C for 1 h afforded after column chromatography (15% and 35% CH_2Cl_2 in hexanes) 86 mg (60%) of **1w** and 55 mg (38%) of **2w** as colorless oils. Spectroscopic data for **1w**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2 H), 7.14 (d, J = 7.8 Hz, 2 H), 5.49 (m, 1 H), 4.52 (dd, J = 4.2, 9.0 Hz, 1 H), 4.02 m, 1 H), 2.34 (s, 3 H), 2.31 (m, 2 H), 1.65 (m, 3 H), 0.16 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 136.7, 135.3, 128.9 (2 C), 125.9 (2 C), 115.9, 74.9, 72.8, 32.2, 21.1, 20.4, −1.4; IR (film) 3026, 2959, 1250, 839 cm^{-1}; HRMS (EI) m/z 260.1583 [(M^+), calcd for $C_{16}H_{24}OSi$, 260.1596]. Spectroscopic data for **2w**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, J = 7.8 Hz, 2 H), 7.14 (d, J = 7.8 Hz, 2 H), 5.52 (m, 1 H), 4,28 (dd, J = 3.0, 4.2 Hz, 1 H), 4.07 (m, 1 H), 2.34 (s, 3 H), 2.21 (m, 1 H), 2.12 (m, 1 H), 1.68 (m, 3 H), 0.15 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 136.4, 135.3, 128.7 (2 C), 125.6 (2 C), 117.1, 74.8, 74.3, 34.2, 21.1, 20.0, −2.6; IR (film) 3028, 2963, 1248, 843 cm^{-1}; HRMS (EI) m/z 260.1590 [(M^+), calcd for $C_{16}H_{24}OSi$, 260.1596].

*trans-Trimethyl(6-phenyl-3-(prop-1-en-2-yl)-5,6-dihydro-2H-pyran-2-yl)silane (**1x**).* Applying general procedure F to *syn*-**S3-x** (201 mg, 0.738 mmol, 1 equiv) and second-generation Grubbs catalyst (25 mg, 0.03 mmol, 0.04 equiv) in CH_2Cl_2 (8 mL) at room temperature for 12 h afforded after column chromatography (4% EtOAc in hexanes) 125 mg (62%) of **1x** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4 H), 7.25 (tt, J = 1.5, 7 Hz, 1 H), 5.83 (m, 1 H), 4.92 (s, 1 H), 4.82 (s, 1 H), 4.65 (q, J = 2.0 Hz, 1 H), 4.56 (dd, J = 6.0, 8.5 Hz, 1 H), 2.42 (m, 2 H), 1.89 (t, J = 0.5, Hz, 3 H), 0.10 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 141.5, 140.5, 128.3 (2 C), 127.3, 125.8 (2 C), 117.8, 112.3, 72.8, 71.8, 32.7, 21.4, −0.8; IR (neat) 3089, 3031, 2955, 2895, 1450, 1248, 1028, 839 cm^{-1}; HRMS (EI) m/z 272.1590 [(M^+), calcd for $C_{17}H_{24}OSi$, 272.1596].

*cis-Trimethyl(6-phenyl-3-(prop-1-en-2-yl)-5,6-dihydro-2H-pyran-2-yl)silane (**2x**).* Applying general procedure F to *anti*-**S3-x** (291.7 mg, 1.07 mmol, 1 equiv) and second-generation Grubbs catalyst (74.4 mg added in two portions, 0.0154 mmol, 0.07 equiv) in CH_2Cl_2 (11 mL) at room temperature for 27 h afforded after column chromatography (4% EtOAc in hexanes) 141.8 mg (49%) of **2x** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 7.24 (tt, J = 1.5, 7.0 Hz, 1 H), 5.88 (dt, J = 1.5, 7.5 Hz, 1 H), 4.85 (s, 2 H), 4.63 (t, J = 2,0 Hz, 1 H), 4.28 (dd, J = 3.0, 10.0 Hz, 1 H), 2.32 (ddt, J = 3.0, 7.0, 17.0 Hz, 1 H), 2.19 (dddd, J = 2.5, 4.0, 12.5, 16.5 Hz, 1 H), 1.90 (s, 3 H), 0.09 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 142.7, 140.7, 128.1 (2 C), 127.0, 125.7 (2 C), 118.5, 111.5, 74.3, 71.5, 34.7, 21.7, −2.3; IR (neat) 3088, 3030, 2953, 2895, 1452, 1246, 1028, 841 cm^{-1}; HRMS (EI) m/z 272.1586 [(M^+), calcd for $C_{17}H_{24}OSi$, 272.1596].

*trans-Trimethyl(4-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-yl)-silane (**1y**).* Applying general procedure G to *syn*-**S3-y** (102 mg, 0.3716 mmol, 1 equiv) and second-generation Grubbs catalyst (12.6 mg, 0.015 mmol, 0.04 equiv) in benzene (10 mL) at 80 °C for 1.5 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 58 mg (63%) of **1y** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4 H), 7.26 (tt, J = 2.0, 7.5 Hz, 1 H), 5.47 (m, 1 H), 4.73 (t, J = 5.5 Hz, 1 H), 3.95 (m, 1 H), 2.29 (m, 2 H), 1.78 (m, 3 H), 0.08 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 128.2, 127.5, 127.2, 126.6, 121.2, 72.5, 69.5, 34.8, 23.4, −2.9; IR (film) 3030, 2959, 1248, 1099, 841 cm^{-1}; HRMS (EI) m/z 246.1433 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440].

*cis-Trimethyl(4-methyl-6-phenyl-5,6-dihydro-2H-pyran-2-yl)-silane (**2y**).* Applying general procedure G to *anti*-**S3-y** (104.2 mg, 0.3796 mmol, 1 equiv) and second-generation Grubbs catalyst (13 mg, 0.0152 mmol, 0.04 equiv) in benzene (5.4 mL) at 80 °C for 2 h afforded after column chromatography (10% CH_2Cl_2 in hexanes) 62 mg (67%) of **2y** as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, J = 7.5 Hz, 2 H), 7.31 (t, J = 7.5 Hz, 2 H), 7.23 (tt, J = 1.5, 7.0 Hz, 1 H), 5.47 (d, J = 1.0 Hz, 1 H), 4.38 (dd, J = 3.5, 10.0 Hz, 1 H), 4.08 (m, 1 H), 2.15−2.02 (m, 2 H), 1.73 (s, 3 H), 0.06 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 128.8, 128.1, 126.9, 125.6, 121,

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75.7, 71.2, 38.9, 23.2, 3.97; IR (film) 3035, 2958, 1248, 1099, 840 cm^{-1}; HRMS (EI) *m/z* 246.1430 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440].

*trans-Trimethyl(4-methyl-6-(4-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**1z**).* Applying general procedure G to *syn*-**S3-z** (148.7 mg, 0.515 mmol, 1 equiv) and second-generation Grubbs catalyst (17.5 mg, 0.0206 mmol, 0.04 equiv) in benzene (10.5 mL) at 80 °C for 1.5 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 110 mg (82%) of **1z** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 7.5 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 2 H), 5.44 (m, 1 H), 4.69 (t, J = 5.5 Hz, 1 H), 3.92 (quintet, J = 2.5 Hz, 1 H), 2.33 (s, 3 H), 2.27 (m, 2 H), 1.77 (m, 3 H), 0.06 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 136.8, 128.9 (2 C), 127.6, 126.6 (2 C), 121.2, 72.4, 69.3, 34.7, 23.5, 21.1, −3.0; IR (film) 3025, 2959, 2855, 1248, 841 cm^{-1}; HRMS (EI) *m/z* 260.1583 [(M^+), calcd for $C_{16}H_{24}OSi$, 260.1596].

*cis-Trimethyl(4-methyl-6-(4-methylphenyl)-5,6-dihydro-2H-pyran-2-yl)silane (**2z**).* Applying general procedure G to *anti*-**S3-z** (122 mg, 0.4229 mmol, 1 equiv) and second-generation Grubbs catalyst (14.4 mg, 0.0169 mmol, 0.04 equiv) in benzene (8.5 mL) at 80 °C for 1.5 h afforded after column chromatography (10% CH_2Cl_2 in hexanes) 66 mg (60%) of **2z** as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, J = 7.8 Hz, 2 H), 7.13 (d, J = 7.8 Hz, 2 H), 5.46 (d, J = 1.8, Hz, 1 H), 4.34 (dd, J = 3.0, 10.2 Hz, 1 H), 4.07 (m, 1 H), 2.33 (s, 3 H), 2.11 (m, 1 H), 2.02 (dt, J = 3.0, 16.8 Hz, 1 H), 1.73 (m, 3 H), 0.06 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 136.5, 128.80, 128.78 (2 C), 125.6 (2 C), 121.0, 75.6, 71.2, 38.9, 23.2, 21.1, −3.9; IR (film) 3019, 2959, 2766, 1246, 1101, 841 cm^{-1}; HRMS (EI) *m/z* 260.1602 [(M^+), calcd for $C_{16}H_{24}OSi$, 260.1596].

*trans-Trimethyl(6-(thiophene-2-yl)-5,6-dihydro-2H-pyran-2-yl)-silane (**1aa**) and cis-Trimethyl(6-(thiophene-2-yl)-5,6-dihydro-2H-pyran-2-yl)silane (**2aa**).* Applying general procedure F to *syn/anti*-**S3-aa** (~2:1 ratio, 95 mg, 0.357 mmol, 1 equiv) and second-generation Grubbs catalyst (12 mg, 0.0143 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) at room temperature for 3 h afforded after column chromatography (10% and 20% CH_2Cl_2 in hexanes) 53 mg (62%) of **1aa** and 27 mg (31%) of **2aa** as colorless oils. Spectroscopic data for **1aa**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, J = 1.8, 5.4 Hz, 1 H), 6.96 (m, 1 H), 6.95 (dd, J = 3.6, 5.4 Hz, 1 H), 5.77 (m, 2 H), 5.05 (t, J = 4.8 Hz, 1 H), 4.00 (m, 1 H), 2.58 (m, 1 H), 2.42 (m, 1 H), 0.08 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 128.3, 126.3, 124.7, 124.5, 119.3, 68.5, 68.1, 30.2, −3.3; IR (neat) 3031, 2957, 1248, 1051, 841 cm^{-1}; HRMS (EI) *m/z* 238.0840 [(M^+), calcd for $C_{12}H_{18}OSiS$, 238.0848]. Spectroscopic data for **2aa**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, J = 1.8, 5.4 Hz, 1 H), 6.95 (dd, J = 3.6, 4.8 Hz, 1 H), 6.92 (m, 1 H), 5.81−5.74 (m, 2 H), 4.64 (t, J = 6.0 Hz, 1 H), 4.18 (m, 1 H), 2.33 (m, 2 H), 0.07 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 128.1, 126.2, 124.1, 122.4, 120.4, 71.96, 71.94, 33.9, −4.1; IR (neat) 3030, 2957, 1248, 1070, 843 cm^{-1}; HRMS (EI) *m/z* 238.0824 [(M^+), calcd for $C_{12}H_{18}OSSi$, 238.0848].

*trans-(6-(Furan-2-yl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (**1bb**).* Applying general procedure F to *syn*-**S3-bb** (45.5 mg, 0.1817 mmol, 1 equiv) and second-generation Grubbs catalyst (6.1 mg, 0.007 mmol, 0.04 equiv) in CH_2Cl_2 (2 mL) at room temperature for 3 h afforded after column chromatography (30% CH_2Cl_2 in hexanes) 33 mg (82%) of **1bb** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1 H), 6.31 (dd, J = 2.0, 3.0 Hz, 1 H), 6.26 (m, 1 H), 5.76 (m, 2 H), 4.86 (t, J = 5.0 Hz, 1 H), 3.86 (m, 1 H), 2.49−2.37 (m, 2 H), 0.07 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 141.9, 128.1, 119.2, 109.9, 107.1, 68.1, 66.4, 27.7, −3.4; IR (neat) 3030, 2955, 1248, 1057, 1012, 841 cm^{-1}; HRMS (EI) *m/z* 222.1081 [(M^+), calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*cis-(6-(Furan-2-yl)-5,6-dihydro-2H-pyran-2-yl)trimethylsilane (**2bb**).* Applying general procedure G to *anti*-**S3-bb** (108 mg, 0.431 mmol, 1 equiv) and second-generation Grubbs catalyst (14.6 mg, 0.017 mmol, 0.04 equiv) in benzene (6 mL) at 80 °C for 1 h afforded after column chromatography (20% CH_2Cl_2 in hexanes) 83 mg (87%) of **2bb** as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1 H), 6.32 (dd, J = 2.0, 3.0 Hz, 1 H), 6.23 (m, 1 H), 5.77 (m, 2 H), 4.42 (dd, J = 3.0, 5.5 Hz, 1 H), 4.14 (m, 1 H), 2.43 (m, 1 H), 2.21 (m, 1 H), 0.04 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 141.7, 128.1, 120.6, 110.0, 105.8, 71.7, 69.6, 29.8, −4.1; IR (film) 3030, 2959, 2776, 1248, 843 cm^{-1}; HRMS (EI) *m/z* 222.1080 [(M^+), calcd for $C_{12}H_{18}O_2Si$, 222.1076].

Wittig Rearrangements of Cyclic Ethers 1 and 2. *2-(2-Phenylcyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3a**) and 5-Phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4a**).* Applying general procedure H to **2a** (67.2 mg, 0.289 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.65 mL, 3 equiv) at −78 °C for 3 h afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 40.4 mg (60%) of **3a** (dr > 20:1) and 19.2 mg (29%) of **4a** (dr > 20:1) as colorless oils. Spectroscopic data for **3a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.06−7.27 (m, 5 H), 2.68 (dd, J = 6.3, 16.8 Hz, 2 H), 1.65 (dt, J = 5.1, 9.3 Hz, 1 H), 1.31 (m, 1 H), 1 (m, 1 H), 0.76 (m, 1 H), 0.2 (s, 9 H); ^{13}C NMR (62.8 MHz, $CDCl_3$) δ 247.2, 142.8, 129.1, 128.2, 125.9, 125.5, 53.1, 22.7, 16.7, 15.7, −3.1; IR (film) 3028, 2959, 1711, 1643, 1604, 1496, 1250, 846 cm^{-1}; HRMS (ESI) *m/z* 233.1362 [($M + H)^+$, calcd for $C_{14}H_{21}OSi$, 233.1362]. Spectroscopic data for **4a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.19−7.31 (m, 3 H), 7.38 (m, 2 H), 5.98 (dddd, J = 1.8, 2.7, 4.8, 5.7 Hz, 1 H), 5.76 (dddd, J = 1.5, 2.1, 3.6, 5.7 Hz, 1 H), 3.43 (dd, J = 8.4, 10.5 Hz, 1 H), 2.57−2.79 (m, 2 H), 1.48 (s, 1 H), −0.31 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 137.3, 130.6, 128.5, 128.17, 126.7, 84.4, 60, 35.4, −3.5; IR (neat) 3441, 3059, 2955, 2928, 2856, 1496, 1452, 1246 cm^{-1}; HRMS (ES) *m/z* 215.1244 [($M - OH)^+$, calcd for $C_{14}H_{19}Si$, 215.1256].

*2-(2-(2-Methoxyphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3b**) and 5-(2-Methoxyphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4b**).* Applying general procedure H to **2b** (76 mg, 0.2896 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.62 mL, 3 equiv) at −78 °C for 3 h afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 35.5 mg (47%) of **3b** (dr = 18:1) as a colorless oil and 29.6 mg (39%) of **4b** (dr > 20:1) as a white solid. Spectroscopic data for **3b**: ^1H NMR (600 MHz, $CDCl_3$) δ 6.92 (ddd, J = 2.4, 7.2, 8.4 Hz, 1 H), 6.66 (m, 2 H), 6.62 (d, J = 8.4 Hz, 1 H), 2.84 (dd, A of ABX system, J = 6.0, 16.8 Hz, 1 H), 2.53 (dd, B of ABX system, J = 7.2, 16.8 Hz, 1 H), 1.91 (dt, J = 4.8, 8.4 Hz, 1 H), 1.30 (m, 1 H), 0.91 (dt, J = 5.4, 8.4 Hz, 1 H), 0.72 (dt, J = 5.4, 9.0 Hz, 1 H), 0.19 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.6, 158.0, 130.9, 126.4, 125.2, 120.5, 110.1, 55.4, 53.3, 16.7, 15.3, 14.7, −3.2; IR (film) 2955, 1645, 1248, 1047, 843 cm^{-1}; HRMS (ESI) 263.1464 [($M + H)^+$, calcd for $C_{15}H_{23}O_2Si$, 263.1467]. Spectroscopic and melting point data for **4b**: mp 46−47 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, J = 1.8, 7.8 Hz, 1 H), 7.23 (m, 1 H), 6.97 (dt, J = 0.6, 7.8 Hz, 1 H), 6.88 (dd, J = 1.2, 8.4 Hz, 1 H), 5.90 (m, 1 H), 5.74 (m, 1 H), 3.87 (s, 1 H, OMe), 3.87 (m, 1 H, overlapped with OMe), 3.84 (s, 1 H), 2.83 (m, A of ABX system, 1 H), 2.54 (dddd, B of ABX system, J = 1.2, 3.0, 8.4, 15.6 Hz, 1 H), −0.31 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 136.9, 129.2, 128.7, 127.9, 127.7, 121.1, 110.6, 84.0, 55.6, 52.7, 35.3, −3.9; HRMS (ESI) 245.1357 [($M - OH)^+$, calcd for $C_{15}H_{21}OSi$, 245.1362].

*2-(2-(3-Methoxyphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3c**) and 5-(3-Methoxyphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4c**).* Applying general procedure H to **1c** (70.4 mg, 0.268 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.2 mL, 1.2 equiv) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 22.9 mg (33%) of **3c** (dr = 17:1) and 31.1 mg (44%) of **4c** (dr > 20:1) as colorless oils. Spectroscopic data for **3c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, J = 8.0 Hz, 1 H), 6.66 (m, 2 H), 6.60 (m, 1 H), 2.74 (dd, A of ABX system, J = 6.5, 17.0 Hz, 1 H), 2.57 (dd, B of ABX system, J = 7.0, 17.0 Hz, 1 H), 1.62 (dt, J = 5.0, 8.5 Hz, 1 H), 1.31 (m, 1 H), 0.97 (dt, J = 5.0, 8.5 Hz, 1 H), 0.74 (dt, J = 5.5, 9.0 Hz, 1 H), 0.19 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 159.7, 144.6, 129.2, 118.4, 111.7, 110.9, 55.1, 53.1, 22.8, 16.8, 15.8, −3.2; IR (film) 2957, 1645, 1250, 1157, 1047, 844 cm^{-1}; HRMS (ESI) 263.1467 [($M + H)^+$, calcd for $C_{15}H_{23}O_2Si$, 263.1467]. Spectroscopic data for **4c**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, J = 7.5 Hz, 1 H), 6.97 (m, 2 H), 6.77 (m, 1 H), 5.96 (m, 1 H), 5.76 (m, 1 H), 3.41 (dd, J = 8.0 10.0 Hz, 1 H), 2.70 (m, 1 H), 2.62 (m, 1 H), 1.24 (s, 1 H), −0.3 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 142.1, 137.2, 130.5, 129.1, 120.9, 114.4, 112.0, 84.3, 60.0, 55.2,

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35.4, −3.4; IR (film) 3452, 3055, 2952, 1246, 839 cm^{-1}; HRMS (ESI) 245.1360 [$(M - OH)^+$, calcd for $C_{15}H_{21}OSi$, 245.1362].

*2-(2-(4-Methoxyphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3d**).* Applying general procedure H to **1d** (82 mg, 0.312 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.23 mL, 1.2 equiv) at −78 °C for 10 min afforded after workup and column chromatography (5% and EtOAc in hexanes) 53.2 mg (65%) of **3d** (dr = 15:1) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, J = 8.5 Hz, 2 H), 6.77 (d, J = 8.5 Hz, 2 H), 2.70 (dd, A of ABX system, J = 6.5, 17.0 Hz, 1 H), 2.60 (dd, B of ABX system, J = 7.0, 17.0 Hz, 1 H), 1.59 (dt, J = 4.5, 9.0 Hz, 1 H), 1.22 (m, 1 H), 0.89 (dt, J = 5.0, 8.5 Hz, 1 H), 0.68 (dt, J = 5.0, 8.5 Hz, 1 H), 0.18 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.7, 157.7, 134.8, 127.1 (2 C), 113.8 (2 C), 55.3, 53.2, 22.0, 16.1, 15.0, −3.1; IR (film) 2958, 1644, 843 cm^{-1}; HRMS (ESI) m/z 263.1466 [$(M + H)^+$, calcd for $C_{15}H_{23}O_2Si$, 263.1467].

*2-(2-(2-Methylphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3e**) and 5-(2-Methylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4e**).* Applying general procedure H to **1e** (109 mg, 0.442 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.33 mL, 1.2 equiv) in THF (5.5 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 86.6 mg (80%) of **3e** (dr > 20:1) and 16.3 mg (15%) of **4e** (dr > 20:1) as colorless oils. Spectroscopic data for **3e**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.13−7.04 (m, 4 H), 2.84 (dd, A of ABX system, J = 6.0, 16.8 Hz, 1 H), 2.63 (dd, B of ABX system, J = 7.2, 16.8 Hz, 1 H), 2.37 (s, 3 H), 1.64 (dt, J = 5.4, 10.2 Hz, 1 H), 1.34 (m, 1 H), 0.92 (dt, J = 5.4, 9.0 Hz, 1 H), 0.74 (dt, J = 4.8, 8.4 Hz, 1 H), 0.22 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.3, 140.2, 137.5, 129.5, 125.8, 125.74, 125.73, 53.2, 20.9, 19.7, 14.5, 13.6, −3.2; IR (film) 3065, 2958, 1643, 1249, 847 cm^{-1}; HRMS (EI) m/z 246.1432 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **4e**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 1 H), 7.16−7.09 (m, 3 H), 6.00 (ddd, J = 2.0, 2.5, 5.5 Hz, 1 H), 5.72 (ddd, J = 1.5, 2.5, 6.0 Hz, 1 H), 3.76 (t, J = 9.0 Hz, 1 H), 2.77 (ddt, A of ABX system, J = 2.5, 9.5, 16.5 Hz, 1 H), 2.71 (dddd, B of ABX system, J = 1.5, 2.5, 8.5, 16.5 Hz, 1 H), 2.49 (s, 3 H), 1.40 (s, 1 H), −0.28 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 138.2, 136.5, 131.3, 130.7, 127.2, 126.4, 125.4, 86.2, 55.0, 38.1, 21.0, −3.4; IR (film) 3440, 3060, 2958, 1247, 839 cm^{-1}; HRMS (ESI) 229.1411 [$(M - OH)^+$, calcd for $C_{15}H_{21}Si$, 229.1413].

*2-(2-(3-Methylphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3f**) and 5-(3-Methylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4f**).* Applying general procedure H to **1f** (91.4 mg, 0.371 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.28 mL, 1.2 equiv) in THF (4.6 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 53.5 mg (59%) of **3f** (dr > 20:1) and 27.6 mg (30%) of **4f** (dr > 20:1) as colorless oils. Spectroscopic data for **3f**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, J = 7.2 Hz, 1 H), 6.94 (d, J = 7.2 Hz, 1 H), 6.88 (s, 1 H), 6.86 (d, J = 7.8 Hz, 1 H), 2.75 (dd, A of ABX system, J = 6.0, 16.8 Hz, 1 H), 2.58 (dd, B of ABX system, J = 7.2, 16.8 Hz, 1 H), 2.30 (s, 3 H), 1.61 (dt, J = 4.8, 9.0 Hz, 1 H), 1.30 (m, 1 H), 0.97 (dt, J = 5.4, 8.4 Hz, 1 H), 0.73 (dt, J = 5.4, 8.4 Hz, 1 H), 0.19 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.2, 142.7, 137.8, 128.1, 126.6, 126.3, 122.9, 53.1, 22.6, 21.4, 16.6, 15.7, −3.2; IR (film) 3066, 2958, 1643, 1249, 844 cm^{-1}; HRMS (EI) m/z 246.1434 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **4f**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.12 (m, 1 H), 7.17 (m, 2 H), 7.04 (m, 1 H), 5.98 (ddd, J = 1.8, 2.4, 5.4 Hz, 1 H), 5.75 (ddd, J = 1.8, 2.4, 6.0 Hz, 1 H), 3.40 (ddt, J = 7.8, 10.2 Hz, 1 H), 2.72 (ddt, A of ABX system, J = 2.4, 10.8, 16.2 Hz, 1 H), 2.62 (dddd, J = 1.8, 3.0, 8.4, 16.2 Hz, 1 H), 2.33 (s, 3 H), 1.48 (s, 1 H), −0.30 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 137.6, 137.2, 130.6, 129.4, 128.0, 127.4, 125.3, 84.4, 59.9, 35.4, 21.4, −3.5; IR (film) 3440, 2957, 1490, 1247, 838 cm^{-1}; HRMS (ESI) 229.1401 [$(M - OH)^+$, calcd for $C_{15}H_{21}Si$, 229.1413].

*2-(2-(4-Methylphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3g**) and 5-(4-Methylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4g**).* Applying general procedure H to **1g** (70.6 mg, 0.2865 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.21 mL, 1.2 equiv) in THF (3.6 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 60.3 mg (86%) of **3g** (dr > 20:1) and 4.9 mg (7%) of **4g** (dr > 20:1) as colorless oils. Spectroscopic data for **3g**: mixture of tautomers (keto/enol = 1:0.06); ^1H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, J = 7.5 Hz, 2.12 H), 6.97 (d, J = 8.0 Hz, 2.12 H), 4.52 (d, J = 7.0 Hz, 0.06 H), 4.40 (s, 0.06 H), 2.74 (dd, A of ABX system, J = 6.0, 16.0 Hz, 1 H), 2.58 (dd, B of ABX system, J = 7.0, 17.0 Hz, 1 H), 1.84 (m, 0.06 H), 1.68 (m, 0.06 H), 1.61 (dt, J = 5.0, 9.0 Hz, 1 H), 1.27 (m, 1 H), 1.19 (m, 0.06 H), 0.99 (m, 0.06 H), 0.93 (dt, J = 5.0, 8.5 Hz, 1 H), 0.72 (dt, J = 5.5, 8.5 Hz, 1 H), 0.19 (s, 9 H), 0.12 (s, 0.55 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.3, 139.7, 135.0, 128.9 (2C), 125.9 (2C), 53.2, 22.4, 20.9, 16.5, 15.4, −3.2; IR (film) 3060, 2958, 1643, 1248, 844 cm^{-1}; HRMS (EI) m/z 246.1442 [(M^+), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **4g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 7.5 Hz, 2 H), 5.97 (m, 1 H), 5.75 (ddd, J = 1.5, 2.0, 6.0 Hz, 1 H), 3.39 (dd, J = 8.0, 10.5 Hz, 1 H), 2.70 (m, 1 H), 2.59 (m, 1 H), 2.32 (s, 3 H), −0.30 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 136.2, 130.6, 128.8 (2 C), 128.3 (2 C), 84.4, 59.7, 35.5, 21.0, −3.4; IR (film) 3443, 2957, 1491, 1247, 839 cm^{-1}; HRMS (ESI) 229.1407 [$(M - OH)^+$, calcd for $C_{15}H_{21}Si$, 229.1413].

*2-(2-(4-Fluorophenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3h**) and 5-(4-Fluorophenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4h**).* Applying general procedure H to **1h** (60.3 mg, 0.24 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.18 mL, 1.2 equiv) in THF (3 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% EtOAc in hexanes) 39.5 mg (66%) of **3h** (dr > 20:1) and 6.7 mg (11%) of **4h** (dr > 20:1) as colorless oils. Spectroscopic data for **3h**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (m, 2 H), 6.90 (m, 2 H), 2.67 (m, 2 H), 1.60 (dt, J = 4.5, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.90 (dt, J = 5.0, 8.5 Hz, 1 H), 0.72 (dt, J = 5.0, 8.5 Hz, 1 H), 0.18 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 161.1 (d, J = 243.4 Hz), 138.3 (d, J = 3.2 Hz), 127.5 (d, J = 7.7 Hz, 2 C), 114.9 (d, J = 21.3 Hz, 2 C), 53.0, 22.1, 16.3, 15.2, −3.2; IR (film) 3071, 2959, 1645, 1512, 1250, 844 cm^{-1}; HRMS (EI) m/z 250.1181 [(M^+), calcd for $C_{14}H_{19}OSiF$, 250.1189]. Spectroscopic data for **4h**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 2 H), 6.98 (m, 2 H), 5.97 (ddd, J = 2.0, 3.0, 5.5 Hz, 1 H), 5.75 (ddd, J = 1.5, 2.5, 6.0 Hz, 1 H), 3.40 (t, J = 8.5 Hz, 1 H), 2.70−2.59 (m, 2 H), −0.30 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, J = 245.7 Hz), 137.4, 136.2, 130.5, 129.8 (d, J = 7.8 Hz, 2 C), 114.8 (d, J = 20.8 Hz, 2 C), 84.2, 59.2, 35.6, −3.4; IR (film) 3431, 3059, 2922, 1510, 839 cm^{-1}; HRMS (EI) m/z 232.1085 [$(M - H_2O)^+$, calcd for $C_{14}H_{17}SiF$, 232.1084].

*trans-2-(2-(4-Chlorophenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3i**) and cis-5-(4-Chlorophenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4i**).* Applying general procedure H to **1i** (93 mg, 0.349 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.24 mL, 1.1 equiv) in THF (4.4 mL) at −78 °C for 5 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 26 mg (28%) of **3i** (dr = 15:1) and 60.4 mg (65%) of **4i** (dr > 20:1) as colorless oils. Spectroscopic data for **3i**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 2 H), 6.99 (d, J = 9.0 Hz, 2 H), 2.66 (d, J = 7.0 Hz, 2 H), 1.59 (dt, J = 5.0, 9.0 Hz, 1 H), 1.25 (m, 1 H), 0.92 (dt, J = 5.0, 8.5 Hz, 1 H), 0.74 (dt, J = 5.5, 8.5 Hz, 1 H), 0.18 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.0, 141.4, 131.1, 128.3 (2 C), 127.4 (2 C), 53.0, 22.2, 16.7, 15.5, −3.2; IR (film) 3072, 2960, 1645, 1496, 1250, 846 cm^{-1}; HRMS (EI) m/z 266.0891 [(M^+), calcd for $C_{14}H_{19}SiOCl$, 266.0894]. Spectroscopic data for **4i**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2 H), 7.24 (m, 2 H), 5.96 (ddd, J = 2.0, 2.5, 5.5 Hz, 1 H), 5.74 (ddd, J = 1.0, 2.0, 5.5 Hz, 1 H), 3.38 (dd, J = 8.0, 10.0 Hz, 1 H), 2.66 (ddt, A of ABX system, J = 2.0, 10.0, 16.0 Hz, 1 H), 2.60 (dddd, B of ABX system, J = 1.5, 3.0, 8.0, 16.0 Hz, 1 H), 1.50 (s, 1 H), −0.30 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 137.4, 132.4, 130.4, 129.8 (2 C), 128.2 (2 C), 84.2, 59.3, 35.3, 3.4; IR (film) 3443, 3054, 2957, 1491, 1247, 838 cm^{-1}; HRMS (ESI) m/z 249.0867 [$(M - OH)^+$, calcd for $C_{14}H_{18}SiCl$, 249.0866].

*cis-5-(4-(Trifluoromethyl)phenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4j**).* Applying general procedure H to **1j** (42 mg, 0.1378 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.13 mL, 1.5 equiv) in THF 1.5 mL) at −78 °C for 30 min afforded after workup and column chromatography (10% and 15% EtOAc in hexanes) 38 mg (90%) of **4j** (dr > 20:1) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$) δ 7.53

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(m, 4 H), 5.99 (ddd, J = 1.8, 3.0, 6.0 Hz, 1 H), 5.77 (ddd, J = 1.2, 2.4, 6.0 Hz, 1 H), 3.48 (dd, J = 7.8, 9.6 Hz, 1 H), 2.73 (ddt, A of ABX system, J = 2.4, 10.8, 16.2 Hz, 1 H), 2.65 (dddd, B of ABX system, J = 1.2, 3.0, 7.8, 15.6 Hz, 1 H), 1.53 (s, 1 H), −0.31 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 137.4, 130.3, 129.0 (q, J = 32.3 Hz), 128.8 (2 C), 124.9 (q, J = 3.8 Hz, 2 C), 124.3 (q, J = 272.6 Hz), 84.2, 59.7, 35.2, −3.5; IR (neat) 3441, 1327, 1248, 1165, 1126, 1070, 843 cm^{-1}; HRMS (ESI) m/z 283.1138 [(M − OH)$^+$, calcd for $C_{15}H_{18}SiF_3$, 283.1130].

*trans-2-(2-([1,1′-Biphenyl]-4-yl)cyclopropyl)-1-(trimethylsilyl)-ethan-1-one (**3k**) and cis-5-([1,1′-Biphenyl]-4-yl)-1-(trimethylsilyl)-cyclopent-2-en-1-ol (**4k**).* Applying general procedure H to **2k** (66.8 mg, 0.2165 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.46 mL, 3 equiv) in THF (2.4 mL) at −78 °C for 3 h afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 3.5 mg (5%) of **3k** (dr = 7:1) as colorless oil and 50.4 mg (75%) of **4k** (dr > 20:1) as a white solid. Spectroscopic data for **3k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (m, 2 H), 7.46 (m, 2 H), 7.40 (m, 2 H), 7.30 (m, 1 H), 7.13 (m, 2 H), 2.76 (dd, A of ABX system, J = 6.0, 16.5 Hz, 1 H), 2.62 (dd, B of ABX system, J = 7.0, 17.0 Hz, 1 H), 1.68 (dt, J = 5.0, 9.0 Hz, 1 H), 1.35 (m, 1 H), 1.01 (dt, J = 5.5, 8.5 Hz, 1 H), 0.78 (dt, J = 5.5, 8.5 Hz, 1 H), 0.20 (s, 9 H). Spectroscopic and melting point data for **4k**: mp 75−76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (m, 2 H), 7.56 (m, 2 H), 7.48 (m, 2 H), 7.43 (m, 2 H), 7.33 (m, 1 H), 6.01 (ddd, J = 1.5, 2.5, 5.5 Hz, 1 H), 5.80 (ddd, J = 1.5, 2.5, 6.0 Hz, 1 H), 3.49 (dd, J = 8.0, 10.0 Hz, 1 H), 2.78 (ddt, A of ABX system, J = 2.0, 10.0, 16.0 Hz, 1 H), 2.68 (dddd, B of ABX system, J = 1.0, 3.0, 8.0, 16.0 Hz, 1 H), 1.56 (s, 1 H), −0.25 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 139.6, 137.3, 130.5, 128.9 (2 C), 128.7 (2 C), 127.1, 126.9 (2 C), 126.7 (2 C), 84.5, 59.7, 35.4, −3.4 (one aromatic carbon could not be located); IR (film) 3442, 3060, 2955, 1246, 839 cm^{-1}; HRMS (EI) m/z 290.1481 [(M − H_2O)$^+$, calcd for $C_{20}H_{22}Si$, 290.1491].

*trans-2-(2-(Naphthalen-2-yl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3l**) and cis-5-(Naphthalen-2-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4l**).* Applying general procedure H to **1l** (83.4 mg, 0.295 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.22 mL, 1.2 equiv) in THF (3.7 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 2.6 mg (3%) of **3l** (dr > 20:1) as a colorless oil and 79.9 mg (96%) of **4l** (dr > 20:1) as a white solid. Spectroscopic data for **3l**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (m, 3 H), 7.51 (s, 1 H), 7.41 (t, J = 7.8 Hz, 1 H), 7.36 (t, J = 7.8 Hz, 1 H), 7.20 (d, J = 8.4 Hz, 1 H), 2.77 (dd, A of ABX system, J = 6.0, 17.0 Hz, 1 H), 2.67 (dd, B of ABX system, J = 6.6, 16.8 Hz, 1 H), 1.80 (m, 1 H), 1.42 (m, 1 H), 1.09 (dt, J = 4.8, 8.4 Hz, 1 H), 0.82 (m, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.2, 140.3, 133.5, 131.9, 127.9, 127.6, 127.3, 125.9, 125.0, 124.9, 124.0, 53.2, 23.0, 16.8, 15.7, −3.1, −3.5; IR (film) 3053, 2957, 1645, 1250, 844 cm^{-1}; HRMS (EI) m/z 282.1429 [(M$^+$), calcd for $C_{18}H_{22}OSi$, 282.1440]. Spectroscopic and melting point data for **4l**: mp 58−60 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 3 H), 7.77 (d, J = 9.0 Hz, 1 H), 7.60 (dd, J = 1.8, 8.4 Hz, 1 H), 7.44 (m, 2 H), 6.04 (ddd, J = 2.4, 3.0, 6.0 Hz, 1 H), 5.82 (dq, J = 1.2, 6.0 Hz, 1 H), 3.61 (dd, J = 8.4, 10.8 Hz, 1 H), 2.89 (ddt, A of ABX system, J = 1.8, 10.8, 16.2 Hz, 1 H), 2.73 (dddd, B of ABX system, J = 1.2, 2.4, 7.8, 15.6 Hz, 1 H), 1.60 (s, 1 H), −0.31 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.2, 137.5, 133.3, 132.5, 130.5, 128.0, 127.7, 127.6, 127.5, 126.1, 125.9, 125.4, 84.4, 60.1, 35.5, −3.3; IR (film) 3437, 3055, 2957, 2855, 1246, 839 cm^{-1}; HRMS (EI) m/z 264.1326 [(M − H_2O)$^+$, calcd for $C_{18}H_{20}Si$, 264.1334].

*trans-1-(Dimethylphenylsilyl)-2-(2-phenylcyclopropyl)ethan-1-one (**3m**) and cis-1-(Dimethylphenylsilyl)-5-phenylcyclopent-2-en-1-ol (**4m**).* Applying general procedure H to **1m** (80.4 mg, 0.273 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.26 mL, 1.5 equiv) in THF (2.9 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 55 mg (69%) of **3m** (dr > 20:1) as a colorless oil and 6 mg (~6%) of **4m** (dr > 20:1) contaminated with desilylated **3m** as a colorless oil. Spectroscopic data for **3m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2 H), 7.42−7.36 (m, 3 H), 7.21 (m, 2 H), 7.11 (m, 1 H), 7.00 (m, 2 H), 2.70 (dd, A of ABX system, J = 6.5, 17.0 Hz, 1 H), 2.57 (dd, B of ABX system, J = 7.0, 16.5 Hz, 1 H), 1.54 (dt, J = 4.5, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.87 (dt, J = 5.5, 9.0 Hz, 1 H), 0.64 (dt, J = 5.5, 9.0 Hz, 1 H), 0.49 (s, 3 H), 0.48 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 245.2, 142.7, 134.3, 134.0 (2 C), 129.9, 128.17 (2 C), 128.16 (2 C), 125.8 (2 C), 125.4, 53.3, 22.6, 16.7, 15.6, −4.79, −4.82; IR (film) 3089, 2987, 1642, 1423, 1113, 698 cm^{-1}; HRMS (EI) m/z 294.1440 [(M$^+$), calcd for $C_{19}H_{22}OSi$, 294.1440]. Spectroscopic data for a mixture of **4m** and desilylated **3m** (1:0.33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (m, 0.33 H), 7.30 (m, 2.66 H), 7.26−7.20 (m, 8 H), 7.14 (m, 0.33 H), 7.07 (m, 0.66 H), 5.98 (m, 1 H), 5.70 (m, 1 H), 3.44 (t, J = 9.0 Hz, 1 H), 2.59−2.48 (m, 2.33 H), 2.43 (m, 0.33 H), 1.75 (m, 0.33 H), 1.55 (s, 1 H), 1.32 (m, 1 H), 1.06 (m, 0.33 H), 0.87 (m, 0.33 H), 0.00 (s, 3 H), −0.11 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 137.3, 134.5 (3 C), 131.0, 128.9, 128.7 (2 C), 128.0 (2 C), 127.3 (2 C), 126.8, 125.9, 84.2, 59.8, 35.4, −4.9, −5.4; HRMS (ESI) m/z 277.1402 [(M − OH)$^+$, calcd for $C_{19}H_{21}Si$, 277.1413].

*trans-1-(Methyldiphenylsilyl)-2-(2-phenylcyclopropyl)ethan-1-one (**3n**).* Applying general procedure H to **1n** (70 mg, 0.196 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.15 mL, 1.2 equiv) in THF (2.5 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% EtOAc in hexanes) 48.6 mg (70%) of **3n** (dr = 20:1) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 4 H), 7.43 (m, 2 H), 7.37 (m, 4 H), 7.20 (t, J = 7.5 Hz, 2 H), 7.11 (tt, J = 1.5, 7.5 Hz, 1 H), 6.98 (m, 2 H), 2.77 (dd, A of ABX system, J = 6.0, 17.5 Hz, 1 H), 2.66 (dd, B of ABX system, J = 7.0, 17.0 Hz, 1 H), 1.52 (m, 1 H), 1.26 (m, 1 H), 0.88 (m, 1 H), 0.74 (s, 3 H), 0.63 (dt, J = 5.5, 9.0 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 243.6, 142.8, 135.0 (4 C), 132.61, 132.59, 130.1 (2 C), 128.22 (4 C), 128.18 (2 C), 125.9 (2 C), 125.4, 54.1, 22.6, 16.7, 15.6, −5.3; IR (film) 3089, 2990, 1643, 1429, 1113, 698 cm^{-1}; HRMS (EI) m/z 356.1605 [(M$^+$), calcd for $C_{24}H_{24}OSi$, 356.1596].

*trans-2-(2-Phenylcyclopropyl)-1-(triethylsilyl)ethan-1-one (**3o**) and cis-5-Phenyl-1-(triethylsilyl)cyclopent-2-en-1-ol (**4o**).* Applying general procedure H to **1o** (91.4 mg, 0.333 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.25 mL, 1.5 equiv) in THF (4.2 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 85.2 mg (93%) of **3o** (dr > 20:1) and 4 mg (~5%) of **4o** (dr > 20:1) as colorless oils. Spectroscopic data for **3o**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (m, 2 H), 7.12 (m, 1 H), 7.06 (m, 2 H), 2.73 (dd, A of ABX system, J = 6.6, 17.4 Hz, 1 H), 2.56 (dd, B of ABX system, J = 7.2, 16.8 Hz, 1 H), 1.62 (dt, J = 4.8, 9.0 Hz, 1 H), 1.33 (m, 1 H), 0.96 (m, heavily overlapped, 1 H), 0.96 (t, J = 7.8 Hz, 9 H), 0.73 (m, heavily overlapped, 1 H), 0.73 (q, J = 7.8 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 247.0, 142.9, 128.2 (2 C), 125.9 (2 C), 125.4, 54.8, 22.6, 16.5, 15.7, −7.2, −2.1; IR (film) 3033, 2952, 1644, 1011, 730 cm^{-1}; HRMS (EI) m/z 274.1753 [(M)$^+$, calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for **4o**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 2 H), 7.28 (t, J = 7.8 Hz, 2 H), 7.23 (m, 1 H), 5.95 (m, 1 H), 5.83 (m, 1 H), 3.40 (t, J = 8.4 Hz, 1 H), 2.74 (m, 1 H), 2.64 (m, 1 H), 1.41 (s, 1 H), 0.81 (t, J = 7.8 Hz, 9 H), 0.27 (dq, J = 4.8, 7.8 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 138.1, 130.5, 128.5 (2 C), 128.1 (2 C), 126.8, 85.9, 60.6, 35.6, 7.8, 2.2; IR (film) 3465, 2951, 2878, 1012, 729 cm−^{1}; HRMS (EI) m/z 256.1641 [(M − H_2O)$^+$, calcd for $C_{17}H_{24}Si$, 256.1647].

*trans-2-(2-(3-Methoxyphenyl)cyclopropyl)-1-(methyldiphenylsilyl)ethan-1-one (**3p**) and cis-1-(Dimethyl(phenyl)-silyl)-5-(3-methoxyphenyl)cyclopent-2-en-1-ol (**4p**).* Applying general procedure H to **1p** (75.4 mg, 0.232 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.2 equiv) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 41.3 mg (44%) of **3p** (dr = 17:1) and 14.3 mg (20%) of **4p** (dr > 20:1). Spectroscopic data for **3p**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.42−7.34 (m, 3 H), 7.12 (t, J = 7.8 Hz, 1 H), 6.66 (dd, J = 3.0, 7.8 Hz, 1 H), 6.58 (d, J = 7.2 Hz, 1 H), 6.52 (t, J = 2.4 Hz, 1 H), 3.75 (s, 3 H), 2.69 (dd, A of ABX system, J = 6.0, 16.8 Hz, 1 H), 2.53 (dd, B of ABX system, J = 7.2, 17.4 Hz, 1 H), 1.51 (dt, J = 4.8, 9.0 Hz, 1 H), 1.22 (m, 1 H), 0.86 (dt, J = 5.4, 8.4 Hz, 1 H), 0.62 (dt, J = 5.4, 8.4 Hz, 1 H), 0.48 (s, 3 H), 0.47 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 245.2, 159.6, 144.5, 134.3, 134.0 (2 C), 129.9, 129.2, 128.2 (2 C), 118.3, 111.5, 110.9, 55.1, 53.2, 22.7, 16.8, 15.8, −4.80, −4.83; IR (film) 2957,

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1645, 844 cm^{-1}; HRMS (EI) m/z 324.1546 [(M^+), calcd for $C_{20}H_{24}O_2Si$, 324.1546]. Spectroscopic data for **4p**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 3 H), 7.23 (m, 2 H), 7.14 (t, J = 7.8 Hz, 1 H), 6.87 (m, 1 H), 6.79 (s, 1 H), 6.75 (dd, J = 2.4, 8.4 Hz, 1 H), 5.97 (m, 1 H), 5.71 (m, 1 H), 3.70 (s, 3 H), 3.42 (dd, J = 8.4, 10.2 Hz, 1 H), 2.58−2.48 (m, 2 H), 1.59 (s, 1 H), 0.05 (s, 3 H), −0.05 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 141.6, 137.3, 137.0, 134.5 (2 C), 131.0, 128.92, 128.89, 127.3 (2 C), 121.0, 114.5, 112.3, 84.1, 59.7, 55.1, 35.4, −4.9, −5.2; IR (film) 3440, 3030, 2957, 1250, 819 cm^{-1}; HRMS (EI) m/z 306.1436 [($M - H_2O$)$^+$, calcd for $C_{20}H_{22}OSi$, 306.1440].

*trans-2-(2-(4-Chlorophenyl)cyclopropyl)-1-(methyldiphenylsilyl)-ethan-1-one (**3q**) and cis-5-(4-Chlorophenyl)-1-(dimethyl(phenyl)-silyl)cyclopent-2-en-1-ol (**4q**).* Applying general procedure H to **1q** (83 mg, 0.2524 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.1 equiv) at −78 °C for 5 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 38.4 mg (47%) of **3q** (dr > 20:1) and 36.1 mg (44%) of **4q** (dr > 20:1). Spectroscopic data for **3q**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.51 (m, 2 H), 7.41 (m, 1 H), 7.36 (m, 2 H), 7.15 (m, 2 H), 6.90 (m, 2 H), 2.61 (m, 2 H), 1.48 (dt, J = 4.8, 9.0 Hz, 1 H), 1.16 (m, 1 H), 0.82 (dt, J = 5.4, 9.0 Hz, 1 H), 0.63 (dt, J = 5.4, 9.0 Hz, 1 H), 0.48 (s, 3 H), 0.47 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 245.1, 141.3, 134.3, 134.0 (2C), 131.0, 129.9, 128.23 (2C), 128.20 (2 C), 127.3 (2 C), 53.1, 22.1, 16.8, 15.5, −4.8, −4.9; IR (film) 3030, 2958, 1641, 1490, 1012, 823, 734 cm^{-1}; HRMS (EI) m/z 328.1049 [(M^+), calcd for $C_{19}H_{21}OSiCl$, 328.1050]. Spectroscopic data for **4q**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (m, 1 H), 7.27 (m, 2 H), 7.23 (m, 2 H), 7.15 (m, 4 H), 5.98 (ddd, J = 1.8, 3.0, 6.0 Hz, 1 H), 5.73 (ddd, J = 1.2, 2.4, 6.0 Hz, 1 H), 3.39 (dd, J = 7.2, 10.2 Hz, 1 H), 2.55 (dddd, A of ABX system, J = 1.2, 3.0, 7.8, 15.6 Hz, 1 H), 2.45 (ddt, B of ABX system, J = 2.4, 10.2, 18.0 Hz, 1 H), 1.56 (s, 1 H), 0.04 (s, 3 H), −0.03 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 137.4, 136.5, 134.3 (2 C), 132.4, 131.0, 129.9 (2 C), 129.0, 128.0 (2 C), 127.4 (2 C), 84.2, 59.0, 35.3, −4.8, −5.2; IR (film) 3440, 2950, 1246, 820 cm^{-1}; HRMS (EI) m/z 310.0946 [($M - H_2O$)$^+$, calcd for $C_{19}H_{19}SiCl$, 310.0945].

*trans-2-(2-(4-Chlorophenyl)cyclopropyl)-1-(triethylsilyl)ethan-1-one (**3r**) and cis-5-(4-Chlorophenyl)-1-(triethylsilyl)cyclopent-2-en-1-ol (**4r**).* Applying general procedure H to **1r** (69.5 mg, 0.225 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.15 mL, 1.1 equiv) in THF (2.8 mL) at −78 °C for 5 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 43.7 mg (63%) of **3r** (dr > 20:1) and 15.7 mg (23%) of **4r** (dr > 20:1). Spectroscopic data for **3r**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (m, 2 H), 7.00 (m, 2 H), 2.68−2.60 (m, 2 H), 1.57(dt, J = 5.6, 9.0 Hz, 1 H), 1.27 (m, 1 H), 0.95 (t, J = 7.8 Hz, 9 H), 0.92 (m, 1 H, overlapped), 0.73 (m, 1 H, heavily overlapped), 0.72 (q, J = 7.8 Hz, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 246.9, 141.4, 131.0, 128.3 (2 C), 127.4 (2 C), 54.7, 22.2, 16.5, 15.5, 7.2, 2.1; IR (film) 2955, 2878, 1641, 1495, 1012, 823, 734 cm^{-1}; HRMS (EI) m/z 308.1357 [(M^+), calcd for $C_{17}H_{25}OSiCl$, 308.1363]. Spectroscopic data for **4r**: ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 2 H), 7.24 (m, 2 H), 5.94 (m, 1 H), 5.82 (ddd, J = 1.2, 2.4, 6.0 Hz, 1 H), 3.35 (t, J = 8.4 Hz, 1 H), 2.69−2.60 (m, 2 H), 0.82 (t, J = 7.8 Hz, 9 H), 0.28 (m, 6 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 138.2, 132.3, 130.4, 129.8 (2 C), 128.1 (2 C), 85.7, 59.9, 35.6, 7.8, 2.3; IR (film) 3439, 3053, 2953, 2878, 1493, 1093, 1014, 825, 717 cm^{-1}; HRMS (EI) m/z 290.1249 [($M - H_2O$)$^+$, calcd for $C_{17}H_{23}SiCl$, 290.1258].

*trans-2-(2-(Naphthalen-2-yl)cyclopropyl)-1-(triethylsilyl)ethan-1-one (**3s**) and cis-5-(Naphthalen-2-yl)-1-(triethylsilyl)cyclopent-2-en-1-ol (**4s**).* Applying general procedure H to **2s** (133.5 mg, 0.411 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 1.5 mL, 5 equiv) at −78 °C, and then at 0 °C for 6 h, afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 58.8 mg (45%) of **3s** (dr = 3.2:1) and 11.8 mg (9%) of **4s** (dr > 20:1) as colorless oils. Spectroscopic data for **3s** (major diastereomer (*trans*)): ^1H NMR (500 MHz, $CDCl_3$) δ 7.76−7.70 (m, 3 H), 7.51 (s, 1 H), 7.43−7.34 (m, 2 H), 7.20 (dd, J = 2.0, 8.5 Hz, 1 H), 2.77 (dd, A of ABX system, J = 6.0, 17.0 Hz, 1 H), 2.62 (dd, B of ABX system, J = 7.0, 17.4 Hz, 1 H), 1.79 (quintet, J = 4.5 Hz, 1 H), 1.44 (m, 1 H), 1.10 (m, 1 H, 0.96 (t, J = 7.5 Hz, 9 H), 0.81 (m, 1 H), 0.74 (q, J = 7.5 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.1, 140.4, 135.5, 131.9, 127.8, 127.5, 127.3, 125.9, 125.0, 124.9, 124.0, 54.8, 22.9, 16.5, 15.7, 7.3, 2.1; IR (film) 3055, 2955, 2876, 1639, 1018, 910, 740 cm^{-1}; HRMS (EI) m/z 324.1901 [(M)$^+$, calcd for $C_{21}H_{28}OSi$, 324.1909]. Spectroscopic data for **4s**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (m, 3 H), 7.76 (d, J = 8.5 Hz, 1 H), 7.61 (dd, J = 1.0, 8.5 Hz, 1 H), 7.44 (m, 2 H), 6.00 (m, 1 H), 5.88 (m, 1 H), 3.57 (m, 1 H), 2.87 (m, 1 H), 2.73 (m, 1 H), 0.77 (t, J = 8.0 Hz, 9 H), 0.26 (dq, J = 1.5, 8.0 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 138.3, 133.3, 132.5, 130.5, 127.9, 127.7, 127.6, 127.4, 126.2, 125.8, 125.3, 85.9, 60.7, 35.8, 7.8, 2.3; IR (film) 3053, 2951, 2876, 1458, 1012, 819, 727 cm^{-1}; HRMS (ESI) m/z 307.1869 [(M − OH)$^+$, calcd for $C_{21}H_{27}Si$, 307.1882].

*trans-2-(2-(2-Propylphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3t**) and cis-5-(2-Propylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4t**).* Applying general procedure H to **1t** (26.6 mg, 0.097 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 73 μL, 1.2 equiv) in THF (1.2 mL) at −78 °C for 10 min afforded after workup and column chromatography (5% EtOAc in hexanes) 15.4 mg (64%) of **3t** (dr > 20:1) and 3 mg (6%) of **4t** (dr > 20:1) as colorless oils. Spectroscopic data for **3t**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 3 H), 7.01 (m, 1 H), 2.86 (dd, A of ABX system, J = 5.5, 16.5 Hz, 1 H), 2.69 (m, 2 H), 2.57 (dd, B of ABX system, J = 7.5, 17.0 Hz, 1 H), 1.68 (dt, J = 5.0, 9.0 Hz, 1 H), 1.62 (m, 2 H), 1.34 (m, 1 H), 0.98 (t, J = 7.0 Hz, 3 H), 0.92 (dt, J = 5.0, 8.5 Hz, 1 H), 0.74 (dt, J = 5.5, 8.5 Hz, 1 H), 0.20 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.3, 141.7, 139.8, 128.7, 125.9, 125.7, 125.6, 53.3, 35.2, 23.8, 20.3, 14.9, 14.3, 14.2, −3.2; IR (film) 3064, 2959, 2872, 1645, 1250, 844 cm^{-1}; HRMS (EI) m/z 274.1739 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753]. Spectroscopic data for **4t**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 1 H), 7.16−7.10 (m, 3 H), 6.02 (dt, J = 2.5, 5.5 Hz, 1 H), 5.74 (dt, J = 2.0, 6.0 Hz, 1 H), 3.81 (t, J = 8.5 Hz, 1 H), 3.11 (ddd, J = 6.5, 8.5, 14.0 Hz, 1 H), 2.80−2.69 (m, 2 H), 2.54 (ddd, J = 7.0, 9.5, 14.0 Hz, 1 H), 1.58 (m, 2 H), 0.96 (t, J = 7.0 Hz, 3 H), −0.28 (s, 9 H); IR (film) 3444, 3058, 2957, 1490, 1246, 838 cm^{-1}; HRMS (EI) m/z 274.1739 [(M^+), calcd for $C_{17}H_{26}OSi$, 274.1753].

*cis-2-Methyl-5-phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4u**).* Applying general procedure H to **2u** (200 mg, 0.81 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 1.8 mL, 3 equiv) at −78 °C for 7 h afforded after workup and column chromatography (10% EtOAc in hexanes) 157.7 mg (79%) of **4u** (dr = 20:1) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.27 (m, 2 H), 7.22 (m, 1 H), 5.64 (m, 1 H), 3.41 (m, 1 H), 2.63 (m, 1 H), 2.43 (m, 1 H), 1.76 (m, 3 H), 1.40 (s, 1 H), −0.30 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 140.9, 128.7 (2 C), 128.1 (2 C), 126.8, 124.8, 84.8, 61.8, 32.9, 14.6, −2.2; IR (film) 3440, 2957, 1243, 838 cm^{-1}; HRMS (ESI) m/z 229.1401 [(M − OH)$^+$, calcd for $C_{15}H_{21}Si$, 229.1413].

*5-(4-Methoxyphenyl)-2-methyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4v**).* Applying general procedure H to **1v** (61.5 mg, 0.2225 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.2 equiv) at −78 °C for 35 min afforded after workup and column chromatography (10% EtOAc in hexanes) 44 mg (72%) of **4v** (dr = 20:1) as a white solid: mp 96−97 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2 H), 6.82 (m, 2 H), 5.62 (m, 1 H), 3.78 (s, 3 H), 3.34 (dd, J = 7.5, 10.5 Hz, 1 H), 2.58 (m, 1 H), 2.41 (m, 1 H), 1.75 (dt, J = 1.5, 3.0 Hz, 3 H), 1.37 (s, 1 H), −0.29 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 145.6, 132.9, 129.5 (2 C), 124.8, 113.5 (2 C), 84.8, 61.0, 55.2, 33.1, 14.6, −2.1; IR (film) 3435, 2952, 1240, 838 cm^{-1}; HRMS (ESI) m/z 259.1507 [(M − OH)$^+$, calcd for $C_{16}H_{23}OSi$, 259.1518].

*cis-2-Methyl-5-(4-methylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4w**).* Applying general procedure H to **1w** (66.6 mg, 0.2557 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.19 mL, 1.2 equiv) at −78 °C for 15 min afforded after workup and column chromatography (10% EtOAc in hexanes) 60.2 mg (91%) of **4w** (dr = 20:1) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 5.63 (quintet, J = 1.5 Hz, 1 H), 3.36 (dd, J = 8.0, 11.0 Hz, 1 H), 2.61 (m, 1 H), 2.41 (m, 1 H), 2.32 (s, 3 H), 1.76 (m, 3 H), 1.37 (s, 1 H), −0.30 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 137.7, 136.2, 128.8 (2 C), 128.5 (2 C), 124.8, 84.8, 61.4, 33.0, 21.0, 14.6, −2.2; IR (film) 3434, 2953, 1246, 830 cm^{-1}; HRMS (ESI) m/z 243.1568 [(M − OH)$^+$, calcd for $C_{16}H_{23}Si$, 243.1569].

*cis-5-Phenyl-2-(prop-1-en-2-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4x**).* Applying general procedure H to **1x** (120 mg, 0.445 mmol,

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1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.56 mL, 2 equiv) at −78 °C for 1.5 h afforded after workup and column chromatography (4% EtOAc in hexanes) 16.3 mg (13%) of unreacted **1x** and 90 mg (75%) of **4x** (dr = 20:1) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 2 H), 7.30 (m, 2 H), 7.24 (tt, J = 1.5, 7.0 Hz, 1 H), 5.96 (dd, J = 2.5, 3.5 Hz, 1 H), 5.63 (d, J = 1.0 Hz, 1 H), 4.98 (s, 1 H), 3.53 (dd, J = 8.0, 12.0 Hz, 1 H), 2.71 (dd, J = 11.5, 16.5 Hz, 1 H), 2.49 (ddd, J = 3.5, 7.5, 16.5 Hz, 1 H), 1.94 (s, 3 H), 1.67 (s, 1 H), 0.32 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 140.1, 139.0, 128.7 (2 C), 128.1 (2 C), 126.9, 115.1, 85.2, 62.2, 31.7, 23.1, −1.7; IR (film) 3443, 3029, 2956, 1242, 833 cm^{-1}; HRMS (ESI) m/z 255.1562 [(M − OH)$^+$, calcd for $C_{17}H_{23}Si$, 255.1569].

*trans-2-(1-Methyl-2-phenylcyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3y**) and cis-3-Methyl-5-phenyl-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4y**).* Applying general procedure H to **1y** (51.3 mg, 0.208 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.16 mL, 1.2 equiv) at −78 °C for 30 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 22.5 mg (44%) of **3y** (dr = 7:1) and 19.6 mg (38%) of **4y** (dr = 20:1) as colorless oils. Spectroscopic data for **3y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4 H), 7.16 (m, 1 H), 2.91 (d, J = 17.5 Hz, 1 H), 2.52 (d, J = 17.5 Hz, 1 H), 1.89 (dd, J = 6.5, 8.5 Hz, 1 H), 0.81 (m, 2 H), 0.73 (s, 3 H), 0.20 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 247.9, 139.5, 129.4, 128.9, 127.9, 125.8, 58.6, 28.2, 18.8, 18.5, 17.1, −3.3; IR (film) 3061, 2959, 1647, 1250, 844 cm^{-1}; HRMS (EI) m/z 246.1436 [(M$^+$), calcd for $C_{15}H_{22}OSi$, 246.1440]. Spectroscopic data for **4y**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 2 H), 7.28 (m, 2 H), 7.21 (m, 1 H), 5.38 (m, 1 H), 3.47 (dd, J = 8.0, 10.0 Hz, 1 H), 2.68 (m, 1 H), 2.51 (dd, J = 8.0, 15.5 Hz, 1 H), 1.84 (m, 3 H), 1.42 (s, 1 H), −0.33 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 140.8, 130.7, 128.4 (2C), 128.1 (2C), 126.7, 84.4, 60.4, 39.6, 17.2, −3.3; IR (film) 3437, 3034, 2912, 1244, 837, 758 cm^{-1}; HRMS (ESI) m/z 229.1413 [(M − OH)$^+$, calcd for $C_{15}H_{21}Si$, 229.1412].

*trans-2-(1-Methyl-2-(4-methylphenyl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3z**) and cis-3-Methyl-5-(4-methylphenyl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4z**).* Applying general procedure H to **1z** (50.3 mg, 0.193 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.145 mL, 1.2 equiv) at −78 °C for 15 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 21.8 mg (44%) of **3z** (dr = 9:1) and 21.5 mg (43%) of **4z** (dr = 20:1) as colorless oils. Spectroscopic data for **3z**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, J = 7.8 Hz, 2 H), 7.07 (d, J = 7.8 Hz, 2 H), 2.88 (d, J = 17.4 Hz, 1 H), 2.52 (d, J = 16.8 Hz, 1 H), 2.30 (s, 3 H), 1.85 (t, J = 7.2 Hz, 1 H), 0.76 (m, 2 H), 0.72 (s, 3 H), 0.20 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 248.0, 136.3, 135.2, 129.3 (2C), 128.6 (2C), 58.7, 27.8, 21.0, 18.8, 18.3, 17.0, −3.2; IR (film) 3051, 2957, 2868, 1647, 1250, 844 cm^{-1}; HRMS (EI) m/z 260.1599 [(M$^+$), calcd for $C_{16}H_{24}OSi$, 260.1596]. Spectroscopic data for **4z**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, J = 7.8 Hz, 2 H), 7.08 (d, J = 7.8 Hz, 2 H), 5.37 (s, 1 H), 3.42 (t, J = 8.4 Hz, 1 H), 2.65 (dd, A of ABX system, J = 9.8, 15.0 Hz, 1 H), 2.49 (dd, B of ABX system, J = 7.2, 15.6 Hz, 1 H), 2.31 (s, 3 H), 1.83 (s, 3 H), 1.40 (s, 1 H), −0.32 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 137.7, 136.1, 130.6, 128.8 (2C), 128.3 (2C), 84.5, 60.0, 39.7, 21.0, 17.2, −3.3; IR (film) 3434, 3020, 2961, 2853, 1244, 837 cm^{-1}; HRMS (EI) m/z 242.1502 [(M − H_2O)$^+$, calcd for $C_{16}H_{22}Si$, 242.1491].

*trans-2-(2-(Thiophene-2-yl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3aa**) and cis-5-(Thiophene-2-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4aa**).* Applying general procedure H to **1aa** (108 mg, 0.453 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.34 mL, 1.2 equiv) at −78 °C for 10 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 78.8 mg (73%) of **3aa** (dr = 2.1:1) and 25.9 mg (24%) of **4aa** (dr = 3.2:1) as colorless oils. Spectroscopic data for **3aa**: mixture of diastereomers (1.0:0.6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J = 1.0, 5.0 Hz, 0.6 H), 7.01 (dd, J = 1.0, 5.5 Hz, 1 H), 6.87 (dd, J = 3.0, 5.0 Hz, 0.6 H), 6.85 (dd, J = 3.5, 5.0 Hz, 1 H), 6.75 (m, 1 H), 6.67 (dt, J = 1.0, 3.5 Hz, 0.6 H), 2.71 (dd, A of ABX system, J = 6.0, 16.5 Hz, 1 H), 2.60 (dd, B of ABX system, J = 7.0, 17.5 Hz, 1 H), 2.45 (dd, C of CDX system, J = 8.0, 18.5 Hz, 0.6 H), 2.39 (dd, D of CDX system, J = 6.0, 18.5 Hz, 0.6 H), 2.23 (m, 0.6 H), 1.81 (m, 1 H), 1.48 (m, 0.6 H), 1.33 (m, 1 H), 1.17 (dt, J = 5.5, 8.5 Hz, 0.6 H), 0.99 (dt, J = 5.0, 8.5 Hz, 1 H), 0.77 (dt, J = 5.0, 8.5 Hz, 1 H), 0.63 (q, J = 5.5 Hz, 0.6 H), 0.19 (s, 9 H), 0.04 (s, 5.4 H); ^{13}C NMR (126 MHz, $CDCl_3$) (major diastereomer) δ 246.9, 147.2, 126.7, 122.8, 122.1, 52.7, 17.9, 17.5, 16.4, −3.2; (minor diastereomer) δ 247.5, 143.5, 126.6, 125.5, 123.4, 47.6, 14.9, 13.2, 11.9, −3.4; IR (film) 3071, 2959, 1645, 1250, 846 cm^{-1}; HRMS (ESI) m/z 239.0922 [(M + H)$^+$, calcd for $C_{12}H_{19}OSiS$, 239.0926]. Spectroscopic data for **4aa**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (dd, J = 2.0, 6.5 Hz, 1 H), 6.07 (m, 1 H), 5.83 (ddd, J = 3.5, 8.5, 12.0 Hz, 1 H), 5.66 (ddd, J = 1.0, 3.0, 6.5 Hz, 1 H), 5.42 (dd, J = 3.0, 7.0 Hz, 1 H), 4.40 (m, 1 H), 2.81 (m, 1 H), 2.46 (quintet, J = 3.5 Hz, 1 H), 1.59 (s, 1 H), 0.15 (s, 9 H); ^{13}C NMR (600 MHz, $CDCl_3$) δ 140.8, 131.8, 129.1, 126.3, 123.1, 122.7, 67.8, 57.2, 26.4, −2.3; IR (film) 3418, 3017, 2955, 1246, 839 cm^{-1}; HRMS (ESI) m/z 221.0821 [(M − OH)$^+$, calcd for $C_{12}H_{17}SiS$, 221.0820].

*cis-5-(Furan-2-yl)-1-(trimethylsilyl)cyclopent-2-en-1-ol (**4bb**).* Applying general procedure H to **1bb** (93.8 mg, 0.422 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.29 mL, 1.2 equiv) at −78 °C for 10 min afforded after workup and column chromatography (10% EtOAc in hexanes) 76 mg (81%) of **4bb** (dr = 20:1) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (dd, J = 2.0, 3.0 Hz, 1 H), 5.84 (dddd, J = 0.5, 3.5, 7.5, 12.0 Hz, 1 H), 5.63 (ddd, J = 0.5, 3.0, 12.0 Hz, 1 H), 5.46 (m, 1 H), 5.15 (m, 1 H), 4.11 (m, 1 H), 2.82 (d of quintets, A of ABX system, J = 3.5, 20.0 Hz, 1 H), 2.50 (dt, B of ABX system, J = 7.5, 20.0 Hz, 1 H), 0.13 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 145.3, 132.1, 131.1, 103.8. 100.4, 64.9, 50.3, 24.5, −2.6; IR (film) 3499, 3013, 2955, 1246, 1151, 839 cm^{-1}; HRMS (EI) m/z 222.1068 [(M$^+$), calcd for $C_{12}H_{18}O_2Si$, 222.1076].

*2-(2-(Furan-2-yl)cyclopropyl)-1-(trimethylsilyl)ethan-1-one (**3bb**).* Applying general procedure H to **2bb** (56.6 mg, 0.255 mmol, 1 equiv) and *sec*-butyllithium (1.6 M in cyclohexane, 0.55 mL, 3 equiv) at −78 °C for 3.5 h afforded after workup and column chromatography (5% EtOAc in hexanes) 21.2 mg (37%) of **3bb** (dr = 1:0.7) as a colorless oil and 12.9 (23%) of unreacted **2bb** (single diastereomer): mixture of diastereomers (1:0.7); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 7.20 (m, 0.7 H), 6.24 (m, 1 H), 6.22 (m, 0.7 H), 5.94 (m, 1 H), 5.92 (m, 1 0.7 H), 2.70 (dd, A of ABX system, J = 6.6, 17.4 Hz, 0.7 H), 2.54 (dd, B of ABX system, J = 7.2, 16.8 Hz, 0.7 H), 2.50 (dd, C of CDX system, J = 7.2, 18.0 Hz, 1 H), 2.39 (dd, D of CDX system, J = 6.0, 18.0 Hz, 1 H), 2.05 (dt, J = 6.0, 9.0 Hz, 1 H), 1.64 (dt, J = 4.8, 8.0 Hz, 0.7 H), 1.43 (m, 1 H), 1.38 (m, 0.7 H), 1.10 (dt, J = 4.8, 8.4 Hz, 1 H), 1.03 (dt, J = 4.8, 9.0 Hz, 0.7 H), 0.66 (m, 1.7 H), 0.18 (s, 6.3 H), 0.08 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) (major diastereomer) δ 247.3, 154.4, 141.0, 110.1, 106.5, 47.7, 13.3, 12.6, 10.1, −3.2; (minor diastereomer) δ 246.9, 156.2, 140.4, 110.2, 103.6, 52.5, 15.8, 14.5, 13.3, −3.1; IR (film) 2961, 1645, 1250, 844 cm^{-1}; HRMS (EI) m/z 222.1086 [(M$^+$), calcd for $C_{12}H_{18}O_2Si$, 222.1076].

Preparation of Optically Active Substrates (−)-1a and (+)-2a. *Enzymatic Kinetic Resolution of (±)-α-(Trimethylsilyl)allyl Alcohol **S2-a**.*[82] A high-pressure glass tube was charged with racemic α-(trimethylsilyl)allyl alcohol **S2-a** (2.4 g, 18.43 mmol, 1 equiv), vinyl acetate (2.4 g, 27.65 mmol, 1.5 equiv), and pentane (10 mL). Powdered 4 Å molecular sieves (1.4 g) and lipase *Candida antarctica* (15 mg/mmol of alcohol) were added. The tube was sealed and heated in an oil bath at 40 °C. After 34 h the reaction was cooled at room temperature, filtered through a plug of Celite, and rinsed with pentane, and the filtrate was carefully concentrated. Column chromatography (5%, 10% and 15% Et_2O in pentane) afforded 1.06 g (34%) of (*S*)-1-(trimethylsilyl)allyl acetate (ee not determined) and 786 mg (31%) of (*R*)-**S2-a** ([α]$_D$ = −6.1 (*c* = 1, $CHCl_3$, 76% ee)). The enantiomeric excess (ee) was determined by HPLC (OJ column, hexanes, 0.6 mL/min, 10 °C).

*Preparation of (+)-syn-**S3-a** and (+)-anti-**S3-a** by Etherification of (R)-1-(Trimethylsilyl)prop-2-en-1-ol (**S2-a**).* Applying general procedure D to **S2-a** (76% ee, 180 mg, 1.382 mmol, 1 equiv), the trichloroacetimidate of 1-phenylbut-3-en-1-ol (606 mg, 2.07 mmol, 1.5 equiv), and (TMS)OTf (25 μL, 0.138 mmol, 0.1 equiv) in hexane (8 mL) afforded after column chromatography (7% CH_2Cl_2 in hexanes) a total of 222.5 (62%) of (+)-*syn*-**S3a**/(+)-*anti*-**S3-a** distributed in three fractions: 79.2 mg of (+)-*anti* **S3-a** ([α]$_D$ = +112 (*c* = 0.96, $CHCl_3$)),

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87.3 mg of (+)-*syn*-**S3-a** ($[\alpha]_D$ = +2 (*c* = 0.92, $CHCl_3$)), and 56 mg of a mixture of (+)-*syn*-**S3a**/(+)-*anti*-**S3-a** as a colorless oil. The enantiomeric excess of both diastereomers could not be determined by chiral HPLC or GC.

*Preparation of (−)-**1a** and (+)-**2a** by Ring-Closing Metathesis of (+)-syn-**S3-a** and (+)-anti-**S3-a**.* Applying general procedure F to (+)-*syn*-**S3a**/(+)-*anti*-**S3-a** (~1.7:1 ratio, 90 mg, 0.346 mmol, 1 equiv) and second-generation Grubbs catalyst (11.7 mg, 0.0138 mmol, 0.04 equiv) in CH_2Cl_2 (4 mL) for 3 h afforded after column chromatography (10% and 30% CH_2Cl_2 in hexanes) 42.9 mg (53%) of (−)-**1a** ($[\alpha]_D$ = −93.3 (*c* = 1.28, $CHCl_3$, ee not determined)) and 25 mg (31%) of (+)-**2a** ($[\alpha]_D$ = +66.2 (*c* = 0.72, $CHCl_3$, 76% ee)) as colorless oils. The enantiomeric excess of (+)-**2a** was determined by HPLC (OJ column, hexanes, 0.4 mL/min, 10 °C, t_R(minor) = 14.9 min, t_R(major) = 17.6 min). The enantiomeric excess of (−)-**1a** could not be obtained by HPLC but was inferred to be 76% ee on the basis of that of (+)-**2a**.

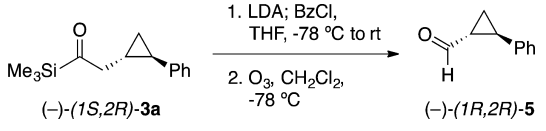
Wittig Rearrangements of (−)-1a and (+)-2a. *Preparation of (−)-**3a** and (+)-**4a** from (−)-**1a**.* Applying general procedure H to (−)-**1a** (ca. 76% ee, 42.9 mg, 0.1846 mmol, 1 equiv) and *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 1.5 equiv) in THF (2.3 mL) at −78 °C for 5 min afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 24.1 mg (56%) of (−)-**3a** (dr = 20:1) in 62% ee ($[\alpha]_D$ = −25.6 (*c* = 0.83, $CHCl_3$)) and 9.6 mg (22%) of (+)-**4a** (dr > 20:1) in 73% ee ($[\alpha]_D$ = +73.4 (*c* = 0.96, $CHCl_3$)). Chiral HPLC conditions for (−)-**3a**: OJ column, hexanes, 0.7 mL/min, 20 °C, t_R(major) = 12.7 min, t_R(minor) = 25.8 min. Chiral HPLC conditions for (+)-**4a**: OJ column, 0.5% *i*-PrOH/hexanes, 0.4 mL/min, 20 °C, t_R(minor) = 22.8 min, t_R(major) = 25.0 min.

*Preparation of (+)-**3a** and (−)-**4a** from (+)-**2a**.* Applying general procedure H to (+)-**2a** (76% ee, 25 mg, 0.1076 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in cyclohexane, 0.23 mL, 3 equiv) in THF (1.4 mL) at −78 °C for 3 h afforded after workup and column chromatography (5% and 10% EtOAc in hexanes) 15 mg (56%) of (+)-**3a** (dr = 20:1) in 56% ee ($[\alpha]_D$ = +27 (*c* = 0.79, $CHCl_3$)) and 5.2 mg (21%) of (−)-**4a** (dr > 20:1) in 74% ee ($[\alpha]_D$ = −52.7 (*c* = 0.48, $CHCl_3$)).

Assignment of Relative and Absolutive Stereochemistries of Precursors S3, Cyclic Ethers, and Wittig Rearrangement Products. The relative stereochemistries of cyclic ethers **1** (*trans*) and **2** (*cis*) were assigned by comparison with the ^{1}H NMR spectra of compounds **1a** and **2a**, whose relative stereochemistries have been determined by NOE studies. The relative stereochemistries of precursors **S3** (*syn*/*anti*) were assigned on the basis of the assignment of the corresponding cyclic ethers **1** and **2**. The relative and absolute stereochemistries of [1,4]-Wittig product (−)-**3a** were assigned by derivatization to the known aldehyde (−)-**5a**. The relative and absolute stereochemistries of [1,2]-Wittig product (+)-**4a** were determined by X-ray crystallographic analysis of its 3,5-dinitrobenzoate derivative (−)-**7**. The relative stereochemistries of all other [1,4]- and [1,2]-Wittig products were assigned by comparison of their ^{1}H NMR spectra with those of compounds **3a** and **4a**, respectively. Further support for the relative stereochemistries of [1,2]-Wittig products was obtained by X-ray crystallographic analysis of compound **4s**.

*Preparation of Compound (−)-**5**.* Compound (−)-**3a** was derivatized to the known aldehyde (−)-**5** (Scheme 14).[83−86] Enolate

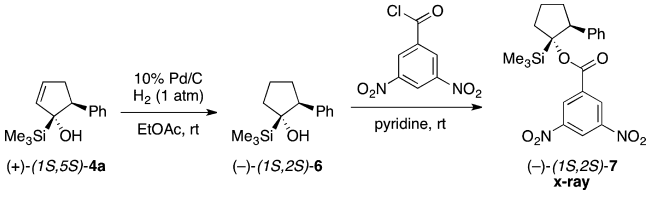
Scheme 14. Determination of the Absolute Stereochemistry of Compound (−)-3a



formation/benzoylation: To a solution of freshly distilled diisopropylamine (41 μL, 0.29 mmol, 1.3 equiv) in THF (1 mL) at −78 °C was added *n*-butyllithium (1.6 M in hexanes, 0.17 mL, 0.266 mmol, 1.2 equiv) slowly. After 10 min the reaction was warmed to 0 °C for 15 min and cooled to −78 °C. Compound (−)-**3a** (62% ee, 51.5 mg, 0.222 mmol, 1 equiv) in THF (2 mL) was added via syringe quickly to give a yellow solution. After 1 h benzoyl chloride (52 μL, 0.444 mmol, 2 equiv) was added, and the temperature kept at −78 °C for 30 min and then raised to room temperature. The reaction was quenched by adding $NaHCO_3$(satd) and diluted with diethyl ether. The aqueous phase was extracted with diethyl ether (3 × 5 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (5% EtOAc in hexanes) afforded 40 mg (54%) of enol benzoate as an oil. Ozonolysis: A solution of the benzoate (19 mg, 0.056 mmol, 1 equiv) in CH_2Cl_2 was cooled at −78 °C. Bubbling of ozone was applied for 15 min (a slightly blue color persisted), and then dimethyl sulfide (0.1 mL, excess) was added. After an additional 15 min, the cold bath was removed and the solvent was removed by rotary evaporation. Column chromatography (15% EtOAc in hexanes) afforded 4.2 mg (56%) of the known compound (−)-(1*R*,2*R*)-**5**[83−86] as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (d, *J* = 5.0 Hz, 1 H), 7.28 (m, 2 H), 7.21 (m, 1 H), 7.08 (m, 2 H), 2.61 (m, 1 H), 2.16 (m, 1 H), 1.17 (dt, *J* = 5.5, 10.0 Hz, 1 H), 1.52 (ddd, *J* = 5.0, 7.0, 8.5 Hz, 1 H); $[\alpha]_D$ = −183.4 (*c* = 0.46, $CHCl_3$) (lit.[83,84] $[\alpha]_D$ = −378 (*c* = 0.374, $CHCl_3$)).

*Preparation of Compound (−)-**6**.* To a solution of (+)-**4a** (72% ee, 15 mg, 0.065 mmol) in EtOAc (1 mL) was added 10% Pd/C (~3 mg) (Scheme 15). The system was closed with a septum, evacuated, and

Scheme 15. Determination of the Absolute Stereochemistry of Compound (+)-4a



filled with H_2. A H_2 balloon was attached and the mixture vigorously stirred for 30 min. Then the reaction mixture was filtered though a short plug of silica and concentrated. Column chromatography (HPLC conditions: OJ column, 0.5% *i*-PrOH/hexanes, 0.4 mL/min, 20 °C) afforded 15 mg (100%) of (−)-**6** as a colorless oil: $[\alpha]_D$ = −13.5° (*c* = 1, $CHCl_3$, 72% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2 H), 7.17 (m, 3 H), 3.20 (dd, *J* = 5.0, 8.0 Hz, 1 H), 2.36 (m, 1 H), 2.05 (m, 2 H), 1.92 (m, 2 H), 1.72 (m, 1 H), −0.31 (s, 9 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 128.4 (2 C), 128.2 (2 C), 126.4, 80.1, 57.9, 36.1, 31.1, 22.5, −3.2; IR (film) 3430, 2951 cm^{-1}; HRMS (ESI) *m*/*z* 217.1413 [$(M - OH)^+$, calcd for $C_{14}H_{21}Si$, 217.1404].

*Preparation of Compound (−)-(1S,2S)-**7**.* To a solution of (−)-**6** (15 mg, 0.064 mmol, 1 equiv) in pyridine (2 mL) was added 3,5-dinitrobenzoyl chloride (74.5 mg, 0.323 mmol, 5 equiv), and the mixture was vigorously stirred for ~36 h. The reaction was quenched with water (2 mL) and diluted with diethyl ether. The aqueous phase was extracted with diethyl ether (3 × 3 mL). Combined organic extracts were washed with 0.1 M HCl (2 mL) and brine, dried over $MgSO_4$, and concentrated. Column chromatography (4% EtOAc in hexanes) followed by recrystallization from hexanes/CH_2Cl_2 afforded 10.6 mg (39%) of (−)-**7** as white crystals suitable for X-ray analysis and 4.4 mg (29%) of unreacted alcohol. The absolute stereochemistry was determined as 1*S*,2*S*. Characterization data for (−)-(1*S*,2*S*)-**7**: $[\alpha]_D$ = −87 (*c* = 1.06, $CHCl_3$); mp 137 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (t, *J* = 2.0 Hz, 1 H), 9.10 (d, *J* = 2.0 Hz, 1 H), 7.32−7.22 (m, 5 H), 4.05 (dd, *J* = 5.5, 7.0 Hz, 1 H), 2.35 (m, 1 H), 2.29−2.19 (m, 2 H), 2.18−2.09 (m, 2 H), 1.93 (m, 1 H), −0.19. ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 148.7, 142.2, 135.2, 129.2, 129.1, 128.3, 127.1, 122.1, 96.2, 53.4, 35.5, 32.1, 23.7, −0.8; IR (film) 3029, 2955, 1720, 1625, 910 cm^{-1}; HRMS (EI) *m*/*z* 428.1404 [$(M)^+$, calcd for $C_{21}H_{24}N_2O_6Si$, 428.1404].

Deuterium-Trapping Experiments. *Preparation of Compounds d-**2d**, d_2-**1d**, d-**3d**, d_2-**8**, and d-**9**.* Applying general procedure H to **2d** (96 mg, 0.366 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in

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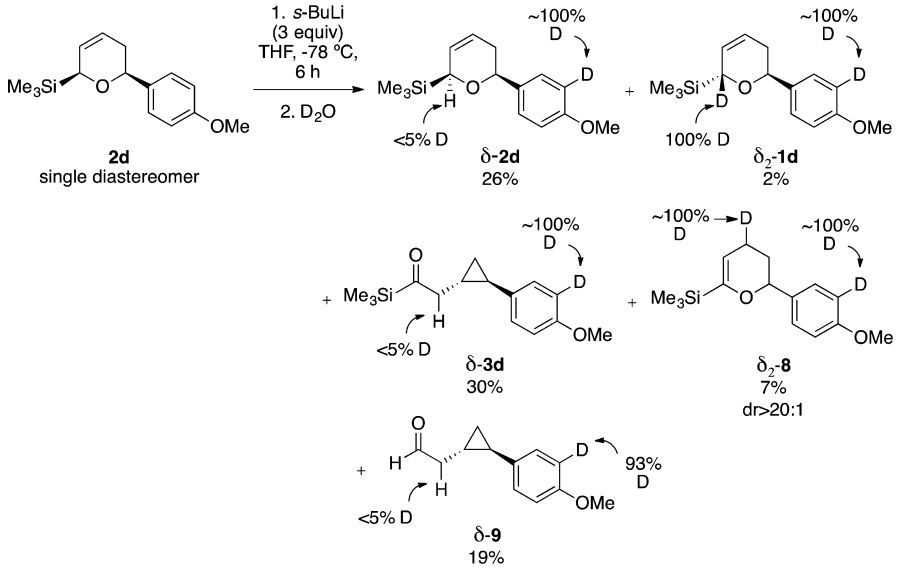
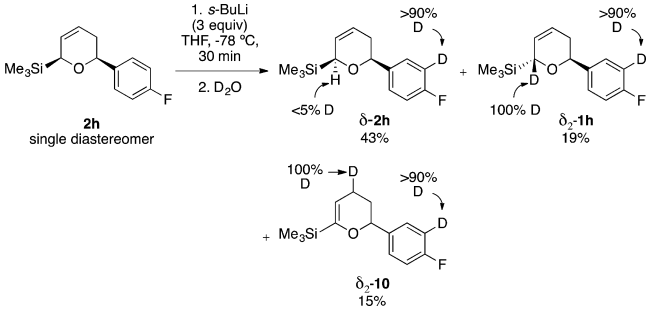
Scheme 16. Competitive *ortho* Metalation vs Allylic Deprotonation of Compound 2d



hexanes, 0.78 mL, 3 equiv) in THF (4 mL) at −78 °C for 6 h afforded after quenching with D_2O (1 mL), regular workup, and column chromatography (30% CH_2Cl_2 in hexanes, then 5% and 10% EtOAc in hexanes) 25.2 mg (26%) of *d*-**2d**, 2.2 mg (2%) of d_2-**1d**, 28 mg (30%) of *d*-**3d**, 6.9 mg (7%) of d_2-**8**, and 13.2 mg (19%) of *d*-**9** (dr > 20:1) as colorless oils (Scheme 16). Spectroscopic data for d_2-**8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 2 H), 6.87 (m, 1 H), 5.02 (m, 1 H), 4.70 (dd, J = 2.5, 10.0 Hz, 1 H), 3.79 (s, 3 H), 2.18 (m, 1 H), 2.00 (dddd, J = 1.0, 2.5, 6.5, 13.5, Hz, 1 H), 1.80 (dt, J = 10.0, 13.0 Hz, 1 H), −0.10 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 135.5, 126.9 (2 C), 126.8 (2 C), 113.6, 109.7, 75.8, 55.3, 30.2, 20.9 (t, J = 20.2 Hz), −2.4. Spectroscopic data for *d*-**9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (t, J = 2.0 Hz, 1 H), 7.01 (m, 2 H), 6.79 (d, J = 9.0 Hz, ~1 H), 3.76 (s, 3 H), 2.50 (ddd, A of ABX system, J = 2.0, 7.0, 17.5 Hz, 1 H), 2.43 (ddd, B of ABX system, J = 2.0, 7.5, 17.5 Hz, 1 H), 1.71 (dt, J = 5.0, 9.0 Hz, 1 H), 1.23 (m, 1 H), 0.98 (dt, J = 5.5, 8.5 Hz, 1 H), 0.80 (dt, J = 5.0, 8.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 157.8, 127.1, 127.0, 113.9, 55.3, 48.2, 21.9, 15.5, 14.6.

*Preparation of Compounds d-**2h**, d_2-**1h**, and d_2-**10**.* Applying general procedure H to **2h** (52.9 mg, 0.211 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in hexanes, 0.45 mL, 3 equiv) in THF (2.6 mL) at −78 °C for 0.5 h afforded after quenching with D_2O (1 mL), regular workup, and column chromatography (3% EtOAc in hexanes) 22.7 mg (43%) of *d*-**2h**, 10 mg (19%) of d_2-**1h**, and 7.9 mg (15%) of d_2-**10** as colorless oils (Scheme 17). Spectroscopic data for d_2-**10**: ^{1}H NMR

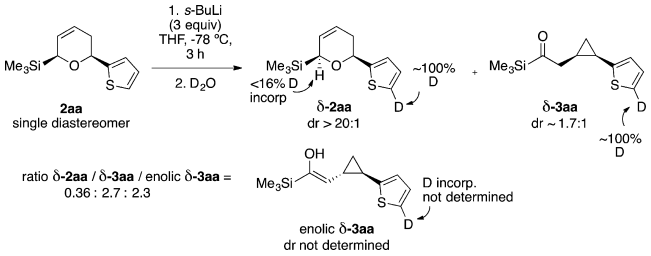
Scheme 17. Competitive *ortho* Metalation vs Allylic Deprotonation of 2h



(500 MHz, $CDCl_3$) δ 7.31 (m, 2 H), 7.03 (m, 1 H), 5.06 (m, 1 H), 4.75 (dd, J = 2.5, 10.0 Hz, 1 H), 2.20 (m, 1 H), 2.03 (m, 1 H), 1.81 (dt, J = 10.0, 13.5 Hz, 1 H), 0.13 (s, 9 H).

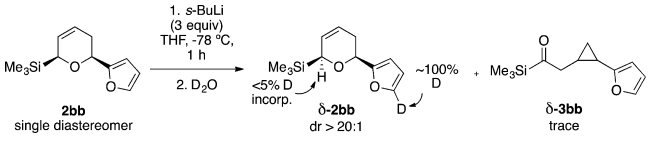
*Observation of Compounds d-**2aa**, d-**3aa**, and Enolic **3aa**.* Applying general procedure H to **2aa** (16.8 mg, 0.07 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in hexanes, 0.15 mL, 3 equiv) in THF (0.9 mL) at −78 °C for 3 h and quenching with D_2O afforded following regular workup a mixture of *d*-**2aa** (dr > 20:1), *d*-**3aa** (dr ≈ 1.7:1), and enolic **3aa** (dr not determined) in a 0.36:2.7:2.3 ratio, as determined from the crude mixture by ^{1}H NMR (Scheme 18).

Scheme 18. Competitive Thiophene Metalation vs Allylic Deprotonation of 2aa



*Observation of Compounds d-**2bb** and d-**3bb**.* Applying general procedure H to **2bb** (9.8 mg, 0.044 mmol, 1 equiv) and *sec*-butyllithium (1.4 M in hexanes, 94 μL, 3 equiv) in THF (0.6 mL) at −78 °C for 1 h and quenching with D_2O afforded following regular workup mostly *d*-**2bb** (dr > 20:1) and traces of *d*-**3aa** (dr not determined), as determined from the crude mixture by ^{1}H NMR (Scheme 19). Complete

Scheme 19. Competitive Furan Metallation vs Allylic Deprotonation of 2bb



deuterium incorporation at the 5-position of the furyl group in *d*-**2bb** is observed. Deuterium incorporation into *d*-**3aa** was not determined due to overlap with other signals.

Trapping of Intermediate Allylic Anion (Species A in Scheme 10). Following general procedure H, to **1a** (73 mg, 0.314 mmol, 1 equiv) in THF (4 mL) was added *n*-butyllithium (1.4 M in hexanes, 0.78 mL, 3 equiv) quickly at −78 °C, and immediately (<1 s) D_2O was added quickly via syringe. After regular workup the crude reaction was

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analyzed by ^{1}H NMR. Compounds *d*-**1a**, enolic **3aa**, **4a**, and **11** were present in a 1.0:0.33:0.17:0.11 ratio.

Control Experiments To Discard [1,2]/[1,4]-Interconversion. Evidence for Keto−Enol Equilibration of (Cyclopropyl)acylsilanes. In the early stage of this study involving the rearrangement of diastereomers **1a** and **2a**, we were unable to obtain reproducible isolated yields of both [1,4] (**3a**) and [1,2] (**4a**) products. The ratios of **3a** and **4a** in the crude ^{1}H NMR varied in each experiment, and the determination of the diastereomeric ratio of **3a** was complicated by the presence of additional signals in the cyclopropyl region (1.8−0.6 ppm). In addition, the integration of these signals correlated well with a doublet around 4.52 ppm (J = 7.5 Hz) and a singlet around 4.35 ppm. We later found that subjecting the reaction mixture to column chromatography immediately after workup (avoiding additional manipulation of the crude for ^{1}H NMR analysis) provided compounds **3a** and **4a** reproducibly; however, we could not isolate the additional cyclopropyl compound. Additional spectral data (^{13}C NMR, DEPT, COSY, and IR) from the crude reaction mixture strongly suggest that this species is actually the enolic form of **3a**.

Following general procedure H, to **1a** (65 mg, 0.28 mmol, 1 equiv) in THF (3 mL) at −78 °C was added *n*-butyllithium (0.27 mL, 0.42 mmol, 1.5 equiv) dropwise. After 20 min the reaction was quenched with NH_4Cl(satd) and diluted with water and Et_2O. The aqueous phase was extracted with diethyl ether three times. Combined organic extracts were washed with NH_4Cl(satd), H_2O, and brine. The solution was dried over magnesium sulfate, filtered, and quickly concentrated in a rotovap at room temperature. An aliquot of the crude reaction mixture was dissolved in $CDCl_3$ and immediately analyzed by ^{1}H NMR and IR. The IR spectrum showed a large broad band at 3435 cm^{-1} (OH from enolic **3a** and **4a**) and a small band at 1635 cm^{-1} (C=O from keto **3a**). The ^{1}H NMR spectrum shows a mixture of keto **3a**/enolic **3a**/alcohol **4a** present in a 0.29:1.0:0.64 ratio. Addition of D_2O led to disappearance of the singlet at 4.35 ppm, which has been assigned tentatively to the enol OH proton of enolic **3a**. The ^{13}C NMR spectrum of the crude reaction mixture (different run, same conditions) shows peaks at 158 and 104 ppm, attributable to the polarized enol C−C double bond. This assignment is consistent with the results of a DEPT experiment and also with the COSY 2D spectrum showing coupling of the enolic C−H bond with the cyclopropyl CH methine.

Interestingly, after column chromatography the (cyclopropyl)acylsilanes were isolated as a single tautomer (keto form). In the case of **3a**, the tautomeric mixture could be regenerated by enolization of keto **3a** with LDA, followed by regular workup. Notice that in the ^{1}H NMR spectrum of the crude reaction mixture there is no evidence of cyclopentenol **4a**, ruling out isomerization of the lithium enolate ([1,4]-product) to the corresponding alkoxide ([1,2]-product). Similar results were obtained from **3i**. Analogously, deprotonation of the [1,2]-Wittig products **4a** and **4i** with *n*-butyllithium (1.1−1.5 equiv) at −78 °C for 3 h followed by regular workup gave only **4a** and **4i**, without a trace of the corresponding cyclopropyl products.

■ ASSOCIATED CONTENT

Supporting Information

Optimization results, X-ray crystallographic data, ^{1}H NMR and ^{13}C NMR spectra of new compounds, and description of the control experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: maleczka@chemistry.msu.edu.

Notes

The authors declare no competing financial interest.

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