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Silylene oxonium ylides: di-*tert*-butylsilylene insertion into C–O bonds

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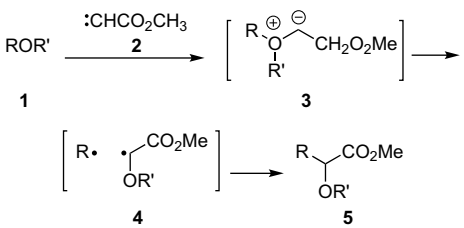
ABSTRACT

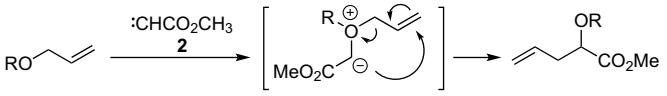
Allylic ethers undergo insertions of silylenes into C–O bonds to form allylic silanes. Silylene insertion into C–O acetal bonds was also observed. Formation of silylene ylide intermediates led to [1,2]-Stevens rearrangement products as well as [2,3]-sigmatropic products depending upon the steric environment of the starting allylic ether.

1. Introduction

Oxonium ylides are characterized by their instability and high reactivity. Common oxonium carbene ylide reactions involve [1,2]-Stevens rearrangements[1] (Scheme 1) and [2,3]-sigmatropic rearrangements (Scheme 2) to form synthetically useful products.[2–11] Analogous oxonium silylene ylides have also been observed.[12–15] Allylic ethers subjected to photolytically generated silylenes most often formed silacyclopropane intermediates instead of oxonium ylides.[14] For reactions that are thought to proceed through oxonium silylene ylide intermediates, [2,3]-sigmatropic products were observed instead of [1,2]-Stevens rearrangement products. Previously, we reported preliminary results of a metal-catalyzed silylene insertion into allylic ethers yielding formal [1,2]-Stevens rearrangement products.[16] In this paper, we expand upon the method wherein metal-catalyzed silylene transfer to allylic ethers produces allylic silanes by way of silylene insertion. A mechanism for the insertion of silylene into a C–O bond is postulated whereby the allylic silanes are thought to be generated through a diradical intermediate, creating formal [1,2]-Stevens rearrangement or [2,3]-sigmatropic rearrangement products.



Scheme 1.

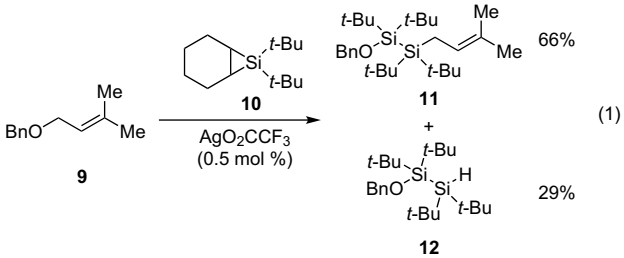


Scheme 2.

2. Results and discussion

2.1. Substrate scope

Insertion into allylic C–O bonds was first observed upon treatment of benzyl-protected allylic alcohols with a silylene source. When allylic ether **9** was treated with cyclohexene silacyclopropane (**10**) and silver trifluoroacetate, allylic disilane **11** was formed in 66% yield (Eq. 1). A disilyl hydride by-product (**12**) was also observed in 29% yield.



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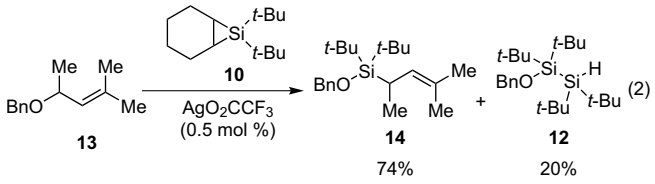
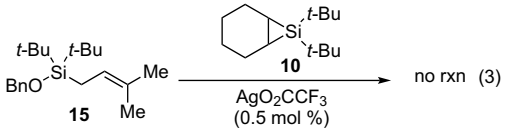
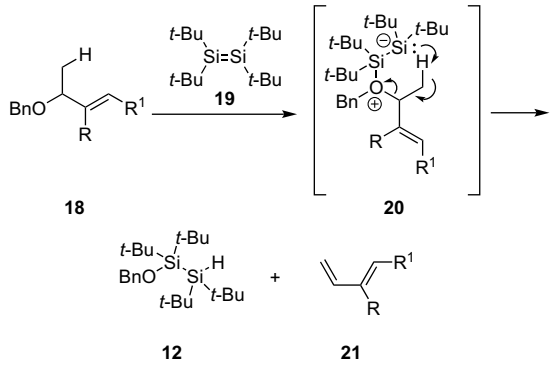
Insertion of a single silicon unit into the allylic C–O bond was observed when the allylic ether contained substitution at the α-position. Allylic ether **13** provided allylic silane **14** in 74% yield and disilyl hydride by-product **12** in 20% yield (Eq. 2). The observation that a single silicon unit had inserted into allylic ether **13** suggests that steric effects contribute to the outcome of insertions of silylenes into allylic C–O bonds.



A control experiment provided evidence that in the formation of allylic disilanes, the two silicon units are inserted simultaneously. Allylic silane **15**, bearing a single silicon unit, was subjected to the reaction conditions (Eq. 3). After 12 h of monitoring by ^{1}H NMR spectroscopy, starting material was observed unchanged. A lack of insertion of a second silylene group suggests that both silicon units are inserted concurrently, instead of sequentially.

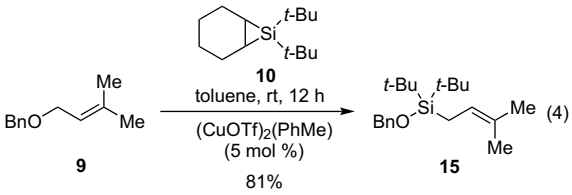


Attempts were made to optimize the silylene insertion reaction to reduce the formation of disilyl by-product **12**. When the insertion reaction conditions employed a silver salt as the catalyst, disilyl hydride by-product **12** was observed in 20–40% yield for various silylene insertion reactions. Efforts to separate the disilyl by-product from the desired allylic silanes were problematic due to the similar polarity of the two compounds. Because large amounts of by-product **12** were observed with several protecting groups and different substitution patterns at the α-position of the allylic ether, formation of the disilane by-product **12** appeared to be independent of electronic and steric factors. A mechanism for generation of disilane **12**, illustrated in Scheme 3, could be envisioned from tetra-*tert*-butyldisilene **19** forming by way of dimerization of free silylene.[17,18] Coordination of the disilene to the oxygen atom of **18** to form disilyl ylide intermediate **20** and subsequent elimination of diene **21** would provide disilane **12**. Small vinyl peaks identified in the ^{1}H NMR spectra of di-*tert*-butylsilylene insertion reaction mixtures were speculated to be characteristic of diene by-products such as **21**.

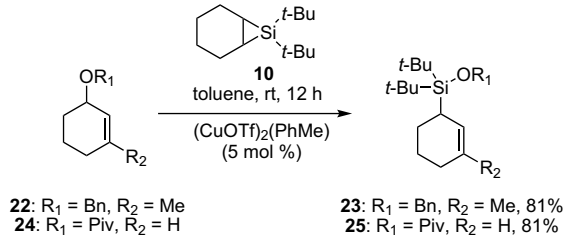


Scheme 3.

A catalyst screen was conducted in hopes of suppressing the formation of disilyl by-product **12**. Treatment of allylic ether **9** with cyclohexene silacyclopropane (**10**) and copper(I) triflate led to allylic silane **15** in 81% yield (Eq. 4). Disilyl by-product **12** was not observed. Copper-mediated silylene insertion reactions required longer reaction times but provided cleaner products in better yields than silver-mediated reactions.

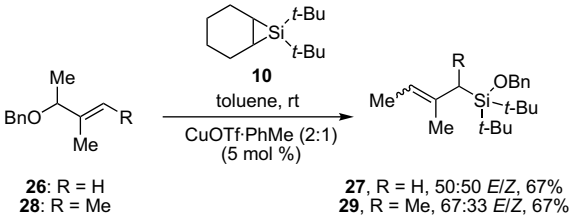


Under the optimized conditions, cyclic allylic ethers were also shown to undergo silylene insertion. Trisubstituted cyclic allylic ether **22** was treated to the reaction conditions to provide allylic silane **23** in 81% yield (Scheme 4). Pivaloate **24** underwent silylene insertion as well (Scheme 4).



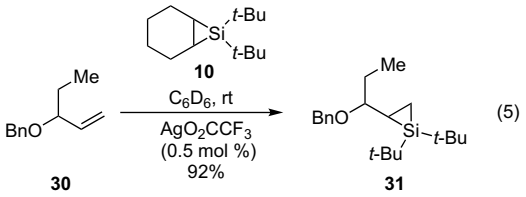
Scheme 4.

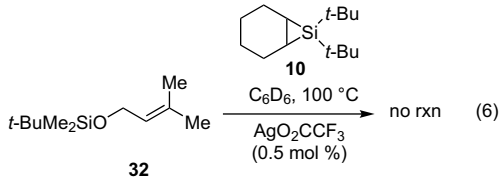
Unhindered alkenes undergo silylene transfer to form isomeric mixtures of products. Geminally disubstituted allylic ether **26** provided allylic silane **27** as a 50:50 *E*/*Z* isomeric mixture. Transposition of the double bond suggests that terminal alkenes undergo silylene insertion by way of a formal [2,3]-sigmatropic reaction, not a direct insertion. Treatment of allylic ether **28** to the reaction conditions led to an inseparable 67:33 *E*/*Z* isomeric mixture of allylic silane product **29** (Scheme 5). Partial isomerization of the alkene bond suggests that allylic ether **28** underwent both allylic transposition and direct insertion.



Scheme 5.

Various allylic ethers were treated to the reaction conditions, but not all underwent silylene insertion. Monosubstituted alkene **30** formed silacyclopropane **31** as the sole product of di-*tert*-butylsilylene transfer, suggesting that silacyclopropanes are not intermediates along the reaction pathway to C–O insertion products (Eq. 5). Silyl ether protecting groups did not undergo C–O insertion (Eq. 6). This experiment suggests that the initial complexation of the silylene unit to the allylic oxygen to form the oxonium silylene ylide is important in the insertion reaction, and that this step is sensitive to steric effects.





Silylene insertion was expanded beyond allylic substrates to other varieties of C–O bonds. Benzylic C–O bonds underwent double silylene insertion when subjected to reaction conditions (Eq 7). The higher temperatures and longer reaction times demonstrate that the benzylic C–O bond is less favorable toward silylene insertion than an allylic C–O bond. This rate difference does not follow the C–O bond dissociation energies, where insertion into a benzylic C–O bond would appear to be more favorable than an allylic C–O bond.[19] Acetals were also found to undergo silylene insertion. Benzaldehyde dimethyl acetal (**35**) inserted one silylene unit into a benzylic C–O bond to form benzylic silane **36** in 60% yield. Insertion of a silylene unit into propionaldehyde diethyl acetal **37** demonstrated that unsaturation was not necessary for the insertion reaction to proceed (Table 1). Insertion into an acetal C–O bond lacking unsaturation in the carbon backbone suggests that C–O bonds that form stabilized radicals upon homolysis may be generally susceptible to silylene insertion.

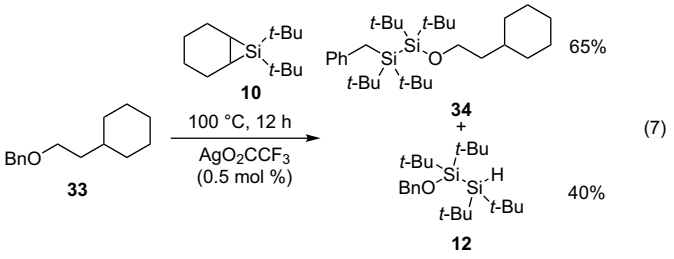
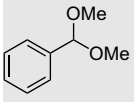
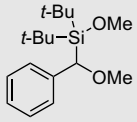
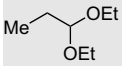
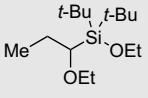


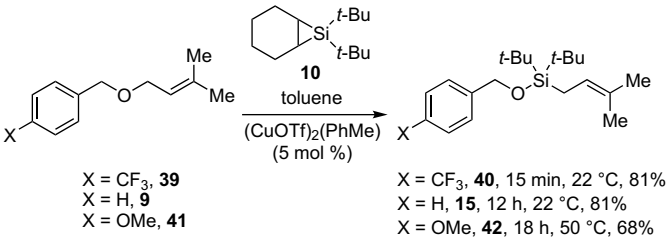
Table 1

Acetal	Product	Yield[a]
 **35**	 **36**	60%
 **37**	 **38**	50%

[a] General procedure: 1.0 equiv acetal and 1.2 equiv **10** were added to 0.5 mol % AgO_2CCF_3 in 0.7 mL of C_6D_6 at 25 °C.

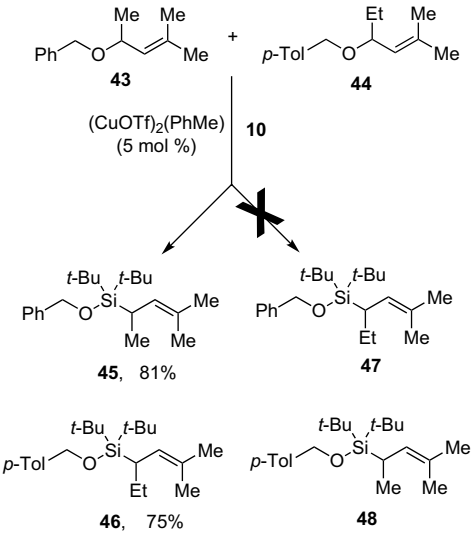
2.2. Mechanistic experiments

Alteration of the electronic properties of the starting allylic ethers influenced the rate of silylene insertion. Electron-poor (trifluoromethyl)benzyl ether **39** and electron-rich methoxybenzyl ether **41** were subjected to reaction conditions and the rates of the reaction were compared to the reaction rate for benzylic ether **9** (Scheme 6). Electron-withdrawing groups at the *para*-position on the aryl protecting group led to an increase in the rate of silylene insertion. The substrate with an electron-donating group residing in the same position did not go to completion without heating.



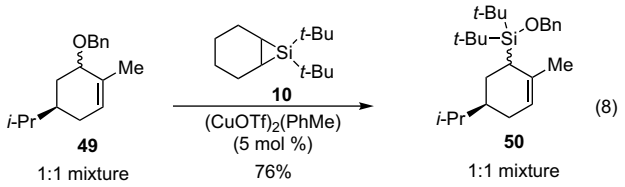
Scheme 6.

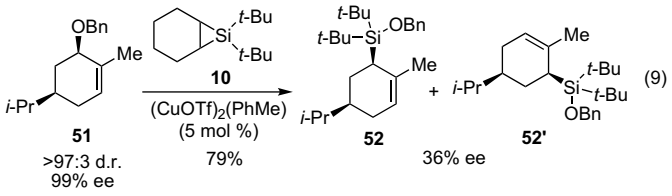
A crossover experiment provided further insight into the reaction mechanism of silylene insertion. Treatment of benzyl-protected allylic ether **43** and *p*-xylyl-protected allylic ether **44** to reaction conditions could have provided four possible allylic silane products (Scheme 7). Upon isolation of the products, only two allylic silanes (**45** and **46**) were observed. The lack of formation of crossover products **47** and **48** in the reaction suggests that once the oxonium silylene ylide is formed, insertion occurs either concertedly or through a closely associated ion or radical pair.



Scheme 7.

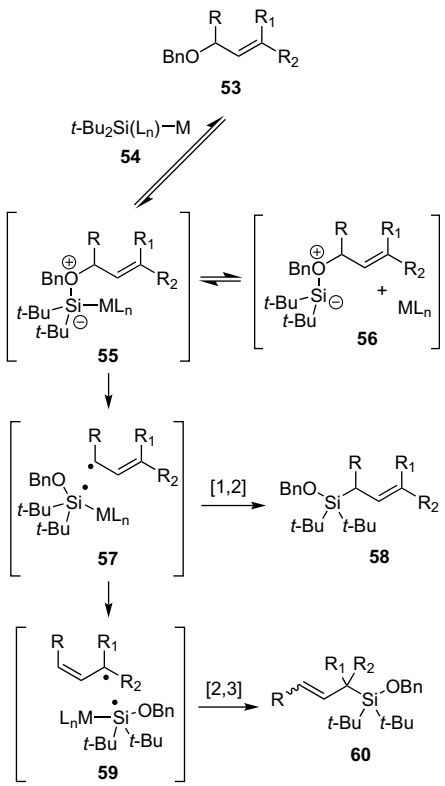
Reactions of diastereomeric cyclic allylic ethers illuminated the stereochemistry of silylene insertion. A 1:1 stereoisomeric mixture of cyclic allylic ether **49** was treated to the reaction conditions to yield a 1:1 mixture of allylic silane **50** (Eq. 8). When the cis isomer of the allylic ether (**51**) underwent silylene insertion, only the cis diastereomer of the product was formed, but erosion of enantioselectivity was observed (Eq. 9). Through X-ray crystallography and analysis of chiral esters, allylic silanes **52** and **52′** were shown to conserve facial selectivity.[16] The loss of enantioselectivity can be





explained by the production of allylic silane **52′** being formed concurrently with allylic silane **52**. Retention of facial selectivity appears to be consistent with a [1,2]-Stevens rearrangement pathway[20–22] with some allylic transposition[23] occurring.

A mechanism that is consistent with our mechanistic experiments is proposed in Scheme 8. In a reversible first step, the nucleophilic oxygen atom attacks the electrophilic metal silylenoid complex[24] to form ylide **55** or **56**. Correlation to the analogous carbene systems suggests that silylene ylide **56** is in a dynamic equilibrium with metal-associated ylide **55**.[6] The carbon–oxygen bond is then broken and a closely dissociated radical pair (or ion pair) is formed. The diradical intermediate **57** can then recombine to provide formal [1,2]-Stevens rearrangement products or [2,3]-sigmatropic rearrangement products depending upon the steric congestion of the carbon–carbon double bond.[20–23] When the terminal end of the allylic ether is not hindered, the formal [2,3]-sigmatropic rearrangement occurs to provide allylic silane transposition products, whereas when this pathway is blocked, formal [1,2]-Stevens products are observed (Scheme 8). Migration of the silylene unit occurs on the same face and consequently conserves diastereoselectivity.



Scheme 8.

3. Conclusion

Silylene insertion into allylic ethers was observed. Both silver and copper catalysts promoted the reaction, although silver salts led to formation of a disilyl hydride by-product. Acetal C–O bonds also underwent silylene insertion. Allylic ethers containing sterically hindered double bonds led to formal [1,2]-Stevens rearrangement products, while [2,3]-sigmatropic rearrangement products were observed for less bulky alkenes.

4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature using Bruker DRX 400, DRX 500, or DRX 600 spectrometer, as indicated. The data are reported as follows: chemical shift in parts per million from an internal tetramethylsilane standard on the δ scale, multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constants (Hz), and integration. Due to difficulties with purification for certain products, only characteristic peaks are listed in tabulated ^{1}H NMR spectroscopic data. High resolution mass spectra were acquired on a VG analytical 7070E or Fisions Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM reagents silica gel (SiO_2) 60 (230–400). Silacyclopropanes were stored and manipulated in an Innovative Technologies nitrogen-atmosphere dry box. All reactions were performed under an atmosphere of nitrogen or argon in glassware that had been flame-dried under a stream of nitrogen or under vacuum. Solvents were distilled or filtered through alumina before use. Sodium hydride and potassium hydride were used dry and weighed in a nitrogen-atmosphere dry box. Cyclohexene silacyclopropane (**10**) was constructed by known methods.[25,26] Additional experiments were reported previously.[16]

*4.1.1. Disilyl hydride **12***

To a Schlenck flask were added allylic ether **9** (0.088 g, 0.50 mmol), silacyclopropane **10** (0.235 g, 1.05 mmol), AgO_2CCF_3 (0.001 g, 0.005 mmol), and 3 mL of toluene. The brown solution was then placed under an Ar atmosphere and allowed to stir for 3 h, at which point the mixture was concentrated in vacuo. The resultant yellow oil was purified by flash chromatography (hexanes) to afford **12** (0.057 g, 29%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.41 (m, 5H), 5.08 (s, 2H), 3.72 (s, 1H), 1.24 (s, 18H), 1.21 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 128.1, 126.9, 126.8, 67.2, 31.4, 29.1, 24.0, 20.8; IR (thin film) 3030, 2856, 2073, 1362, 1070, 815 cm^{-1}; HRMS (GC–MS) *m*/*z* calcd for $C_{23}H_{44}NaOSi_2$ $(M+Na)^+$ 415.2828, found 415.2830. Anal. Calcd for $C_{23}H_{44}OSi_2$: C, 70.33; H, 11.29. Found: C, 70.77; H, 11.65.

*4.1.2. Representative procedure for the synthesis of aryl-protected allylic alcohols (allylic ether **22**)*

To a 0 °C solution of NaH (0.808 g, 33.7 mmol) in 86 mL of THF was added BnBr (2.92 mL, 24.6 mmol), followed by addition of 3-methyl-2-cyclohexen-1-ol (2.91 g, 25.9 mmol) dropwise. The reaction mixture was warmed to ambient temperature and

maintained for 12 h. The solution was diluted with 30 mL of H_2O. The layers were separated and the aqueous layer was extracted with hexanes (3×30 mL). The combined organic layers were washed with 30 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated in vacuo. The resultant yellow oil was purified by flash chromatography (98:2 hexanes/EtOAc) to afford **22** (2.78 g, 52%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.39 (m, 5H), 5.58–5.59 (m, 1H), 4.61 (d, J=12.0, 1H), 4.55 (d, J=12.0, 1H), 3.95–3.97 (m, 1H), 1.72–1.97 (m, 5H), 1.71 (s, 3H), 1.25–1.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 139.1, 128.4, 127.7, 127.4, 122.2, 72.7, 70.1, 30.3, 28.0, 23.8, 19.4. ^{1}H and ^{13}C NMR spectroscopic data matched those previously reported.[27]

4.1.3. Representative procedure for the synthesis of allylic silanes (allylic silane **23**)

To a Schlenck flask were added allylic ether **22** (0.202 g, 1.00 mmol), silacyclopropane **10** (0.270 g, 1.20 mmol), CuOTf·PhMe (0.026 g, 0.050 mmol, 2:1 complex), and 7 mL of toluene. The brown solution was then placed under an Ar atmosphere and allowed to stir for 12 h, at which point the mixture was concentrated in vacuo. The resultant yellow oil was purified by flash chromatography (hexanes) to afford **23** (0.278 g, 81%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.40 (m, 5H), 5.54–5.55 (m, 1H), 4.97–4.98 (m, 2H), 2.16–2.17 (m, 1H), 1.84–1.97 (m, 4H), 1.66–1.75 (m, 1H), 1.64 (s, 3H), 1.40–1.45 (m, 1H), 1.10 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 131.9, 128.4, 126.7, 125.8, 122.4, 66.0, 30.2, 29.3, 29.1, 24.5, 24.4, 22.8, 22.7; IR (thin film) 2931, 2856, 1454, 1082, 910, 735 cm^{-1}; HRMS (APCI) m/z calcd for $C_{22}H_{36}NaOSi$ $(M+Na)^+$ 367.2433, found 367.2437.

4.1.4. Allylic ether **28**

The representative procedure for the synthesis of aryl-protected allylic alcohols was followed using *trans*-3-methyl-3-penten-2-ol (0.642 g, 6.40 mmol), NaH (0.200 g, 8.32 mmol), BnBr (0.72 mL, 6.1 mmol), and 22 mL of dry THF for 12 h. Purification by flash chromatography (95:5 hexanes/EtOAc) afforded **28** (0.730 g, 63%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19–7.35 (m, 5H), 5.46 (q, J=6.0, 1H), 4.44 (d, J=11.9, 1H), 4.24 (d, J=11.9, 1H), 3.86 (q, J=6.5, 1H), 1.66 (d, J=6.5, 3H), 1.62 (s, 3H), 1.26 (d, J=6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 136.6, 128.4, 127.8, 127.4, 122.0, 80.6, 69.6, 20.3, 13.2, 10.2; IR (thin film) 2977, 2861, 1454, 1204, 1093, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{18}NaO$ $(M+Na)^+$ 213.1255, found 213.1255. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.62; H, 9.39.

4.1.5. Allylic silane **29**

The representative procedure for the synthesis of allylic silanes was followed using allylic ether **28** (0.190 g, 1.00 mmol), silacyclopropane **10** (0.337 g, 1.50 mmol), CuOTf·PhMe (0.026 g, 0.050 mmol, 2:1 complex), and 6.7 mL of toluene for 12 h. Purification by flash chromatography (99:1 hexanes/EtOAc) afforded an inseparable 67:33 *E*/*Z* isomeric mixture of **29** (0.222 g, 67%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.35 (m, 12.5H), 5.24–5.26 (m, 1.5H), 5.10–5.11 (m, 1H), 4.96–4.98 (m, 5H), 2.65–2.67 (m, 1H), 2.10–2.12 (1.5H), 1.81 (s, 3H), 1.67 (s, 4.5H), 1.62–1.63 (m, 3H), 1.56–1.58 (m, 4.5H), 1.31–1.33 (m, 4.5H), 1.26–1.28 (m, 3H), 1.12 (br s, 45H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 141.5, 140.1, 139.9, 128.14, 128.13, 126.63, 126.62, 125.61, 125.58, 117.7, 116.8, 66.0, 65.7, 30.6, 29.8, 29.2, 29.1, 28.8, 23.6, 23.3, 23.0, 22.9, 22.8, 22.5, 18.0, 16.4, 16.3, 13.4, 13.7; IR (thin film) 2966, 2858, 1473, 1376, 1113, 821 cm^{-1}; HRMS (APCI) m/z calcd for $C_{21}H_{36}NaOSi$ $(M+Na)^+$ 355.2433, found 355.2440. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 76.08; H, 11.08.

4.1.6. Benzylic silane **36**

To a J. Young NMR tube were added benzaldehyde dimethyl acetal (**35**) (19 μL, 0.125 mmol), silacyclopropane **10** (0.034 g, 0.150 mmol), AgO_2CCF_3 (0.001 g, 0.005 mmol), and 0.7 mL of benzene-d_6. The reaction mixture was kept at ambient temperature for 3.5 h. The reaction mixture was filtered through Celite with CH_2Cl_2 and concentrated in vacuo. The resultant yellow oil was purified by flash chromatography (hexanes) to afford **36** (0.022 g, 60%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.34 (m, 4H), 7.13–7.15 (m, 1H), 4.33 (s, 1H), 3.48 (s, 3H), 3.31 (s, 3H), 1.10 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 128.2, 126.3, 125.6, 78.7, 58.9, 53.0, 28.6, 28.4, 22.4, 21.8; IR (thin film) 2936, 2858, 1599, 1493, 1474, 1109 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{30}NaO_2Si$ $(M+Na)^+$ 317.1913, found 317.1922.

4.1.7. Alkyl silane **38**

To a J. Young NMR tube were added propionaldehyde diethyl acetal (**37**) (20 μL, 0.125 mmol), silacyclopropane **10** (0.034 g, 0.150 mmol), AgO_2OCF_3 (0.001 g, 0.005 mmol), and 0.7 mL of benzene-d_6. The reaction mixture was kept at ambient temperature for 20 min. The reaction mixture was filtered through Celite with CH_2Cl_2 and concentrated in vacuo. The resultant yellow oil was purified by flash chromatography (hexanes) to afford **38** (0.017 g, 50%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92–3.80 (dq, J=9.9, 6.9, 1H and dq, J=9.9, 6.9, 1H), 3.71 (dq, J=8.6, 7.0, 1H), 3.32 (dq, J=8.6, 7.0, 1H), 3.13 (dd, J=7.5, 5.6, 1H), 1.78–1.79 (m, 2H), 1.10–1.22 (t, J=6.9, 3H and t, J=7.0, 3H), 1.01–1.09 (s, 9H; s, 9H; and t, J=7.4, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 75.9, 67.9, 60.1, 28.9, 28.7, 26.0, 21.9, 21.5, 18.9, 16.2, 13.8; IR (thin film) 2974, 2859, 1474, 1117, 1086, 823 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{34}NaO_2Si$ $(M+Na)^+$ 297.2226, found 297.2232.

4.1.8. Allylic ether **39**

The representative procedure for the synthesis of aryl-protected allylic alcohols was followed using 3-methyl-2-butene-1-ol (1.02 mL, 10.0 mmol), 4-(trifluoromethyl)benzyl bromide (2.27 g, 9.5 mmol), NaH (0.312 g, 13.0 mmol), and 33 mL of THF for 12 h. Purification by flash chromatography (98:2 hexanes/EtOAc) afforded **39** (2.12 g, 87%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J=8.5, 2H), 7.47 (d, J=8.6, 2H), 5.39–5.42 (m, 1H), 4.55 (s, 2H), 4.02 (d, J=6.9, 2H), 1.77 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 137.8, 129.7 (q, J=31), 127.7, 126.5 (q, J=293), 125.3 (q, J=3.8), 120.7, 71.2, 67.0, 25.9, 18.1; IR (thin film) 2975, 2860, 1420, 1326, 1066, 823 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}F_3H_{15}NaO$ $(M+Na)^+$ 267.0973, found 267.0977. Anal. Calcd for $C_{13}H_{15}OF_3$: C, 63.93; H, 6.19. Found: C, 63.97; H, 6.22.

4.1.9. Allylic silane **40**

The representative procedure for the synthesis of allylic silanes was followed using allylic ether **39** (0.244 g, 1.00 mmol), silacyclopropane **10** (0.337 g, 1.50 mmol), CuOTf·PhMe (0.026 g, 0.050 mmol, 2:1 complex), and 6.7 mL of toluene for 12 h. Purification by flash chromatography (99:1 hexanes/EtOAc) afforded **40** (0.313 g, 81%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J=8.4, 2H), 7.46 (d, J=8.5, 2H), 5.32–5.33 (m, 1H), 4.96 (s, 2H), 1.72 (d, J=8.2, 2H), 1.65 (s, 3H), 1.62 (s, 3H), 1.07 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 129.2, 129.0 (q, J=35), 125.8, 124.4 (q, J=249), 125.1 (q, J=3.8), 120.1, 65.5, 28.3, 25.9, 21.6, 17.7, 12.2; IR (thin film) 2933, 2859, 1325, 1127, 1067, 824 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}F_3H_{33}NaOSi$ $(M+Na)^+$ 409.2151, found 409.2155. Anal. Calcd for $C_{21}H_{33}OSiF_3$: C, 65.25; H, 8.60. Found: C, 65.52; H, 8.83.

4.1.10. Allylic ether **41**

The representative procedure for the synthesis of aryl-protected allylic alcohols was followed using 3-methyl-2-buten-1-ol (0.50 mL, 5.00 mmol), *p*-methoxybenzyl chloride (0.68 mL, 5.00 mmol), NaH (0.360 g, 15.0 mmol), and 17 mL of THF for 12 h. Purification by flash chromatography (95:5 hexanes/EtOAc) afforded **41** (0.990 g, 96%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.28 (d, J=8.6, 2H), 6.89 (d, J=8.7, 2H), 5.39–5.41 (m, 1H), 4.44 (s, 2H), 3.98 (d, J=7.0, 2H), 3.81 (s, 3H), 1.76 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 137.2, 130.7, 129.5, 121.2, 113.8, 71.8, 66.3, 55.3, 25.9, 18.1. ^{1}H and ^{13}C NMR spectroscopic data matched those previously reported.[28]

4.1.11. Allylic silane **42**

The representative procedure for the synthesis of allylic silanes was followed using allylic ether **41** (0.206 g, 1.00 mmol), silacyclopropane **10** (0.337 g, 1.50 mmol), CuOTf·PhMe (0.026 g, 0.050 mmol, 2:1 complex), and 6.7 mL of toluene for 12 h. Purification by flash chromatography (99:1 hexanes/EtOAc) afforded **42** (0.237 g, 68%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J=8.7, 2H), 6.88 (d, J=8.7, 2H), 5.34–5.36 (m, 1H), 4.83 (s, 2H), 3.82 (s, 3H), 1.66 (d, J=1.1, 2H), 1.62 (s, 3H), 1.55 (s, 3H), 1.05 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 134.0, 128.8, 127.1, 120.4, 113.6, 65.7, 55.3, 28.3, 25.9, 21.6, 17.7, 12.3; IR (thin film) 2933, 2859, 1325, 1127, 1067, 824 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_2SiNa$ $(M+Na)^+$ 371.2382, found 371.2389.

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