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Highly Stereospecific Cyclizations of Homoallylic Silanols

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Abstract

We demonstrate that di-*tert*-butylsilanols are competent nucleophiles for the intramolecular interception of palladium π-allyl species. In these reactions, allyl ethyl carbonates are the best precursors for the formation of palladium π-allyl intermediates, and $[(\text{Cinnamyl})\text{PdCl}]_2$/BINAP is superior to other Pd salt/ligand framework combinations. Our optimized protocol is compatible with a variety of silanol substrates. Importantly, the cyclization is perfectly stereospecific, proceeding via an *anti-syn* mechanism, which stands in contrast to reported analogous reactions of alcohols and phenols, known to proceed via an *anti-anti* mechanism. The alkenes in the product dioxasilinanes serve as blank slates for further functionalization.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c01170.

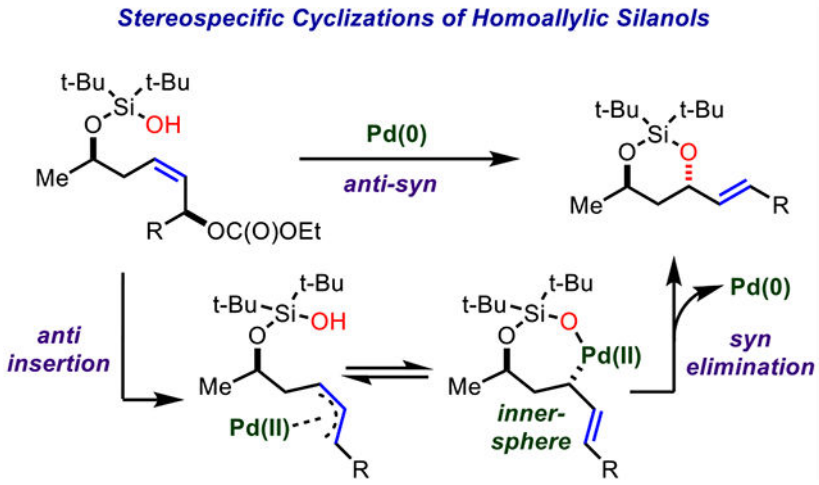
Expanded experimental procedures, reasoning for structural assignments, NMR spectra, and crystallographic information (PDF)

Accession Codes

CCDC 2164073 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.2c01170

The authors declare no competing financial interest.



The invention of highly regioselective and stereoselective methods for the installation of carbon–heteroatom linkages remains a very active area of research.[1–4] The interception of palladium π-allyl complexes with carbon nucleophiles is a well-established method for the construction of C–C bonds,[5–12] but many opportunities remain for the analogous construction of C–O bonds.[13–19] Our laboratory has a programmatic focus on the development of the di-*tert*butylsilanol auxiliary for alkene manipulation reactions.[20–25] We envisioned a new method for the construction of C–O bonds via the intramolecular interception of a palladium π-allyl species with a pendant di-*tert*-butylsilanol functional group (Scheme 1). On the basis of our previous work as well as that of others,[26–31] we expected such a reaction to be highly chemo-, regio-, and diastereoselective. This would be an important addition to the existing technology for the synthesis of complex polyhydroxylated molecules (Scheme 1).[32–38]

Before undertaking reaction optimization, we first had to develop a method that would allow for facile access to the requisite starting materials (Scheme 2). Using our laboratory's silylation procedure,[23] 3-butyn-1-ol or 4-pentyn-2-ol could be converted into the corresponding silanol. Bis-deprotonation with 2 equiv of *n*-BuLi enabled condensation with a variety of aldehydes. Reduction of the alkyne to a *cis*-alkene was effected using Lindar's catalyst under 1 atm of H_2 gas. Finally, the free alcohol was converted into an ethyl carbonate using ethyl chloroformate and pyridine. This procedure was remarkably modular, reproducible, and scalable. We have carried it out reliably on starting scales as large as 10 mmol, and all substrates shown in this account were prepared using this method.

Treating **1** with $Pd(PPh_3)_4$ and (*R*)-BINAP gave the cyclized product in 35% yield (Table 1, entry 1). When $Pd(PPh_3)_4$ was replaced with $[(Cinnamyl)PdCl]_2$, the yield increased to 62% (Table 1, entry 2). Maintaining the reaction temperature at 80 °C was crucial, as increasing it to 110 °C and decreasing it to 23 °C were both deleterious (Table 1, entry 3). The reaction performance suffered when (*R*)-BINAP was replaced with either (*R*)-DTBM-SEGPHOS (Table 1, entry 4) or Xantphos (Table 1, entry 5). Using either base (Table 1, entries 6 amd 7) or acid additives (Table 1, entries 8 and 9) was similarly deleterious.

A variety of allyl electrophiles have been used as precursors to palladium π-allyl species.[13] The ethyl carbonate and Boc moieties were chosen empirically for optimization (Table 1 and Scheme 3, entries 1 and 2). An examination of other leaving groups, including acetate (Scheme 3, entry 3), benzoate (Scheme 3, entry 4), and 2,2,2-trichloroethyl carbonate (Scheme 3, entry 5), showed that none were superior to ethyl carbonate. Thus, for exploration of the substrate scope, ethyl carbonate was retained as the leaving group.

Our optimized protocol was compatible with a variety of substrates, with both linear (Scheme 4, entry 1) and branched alkyl chains (Scheme 4, entries 1–3). Substrates with pendant cycloalkanes (Scheme 4, entries 4–7), ethers (Scheme 4, entry 1), and aromatic rings (Scheme 4, entries 1, 6, 8, and 9) all reacted well. In general, *cis*-alkene substrates were required for a productive reaction; only one *trans*-alkene substrate (Scheme 4, entry 9) cyclized as expected. In almost all of the reactions, the starting material was consumed fully, and the remaining mass balance could be attributed to a linear diene side product arising from ionization and elimination of the allylic carbonate.[39] A crystal structure of **46** (CCDC 2164073) allowed us to unambiguously establish product identity. Most substrates were designed to form six-membered dioxasilinane products, but a five-membered dioxasilolane product (Scheme 4, entry 10) could be forced to form. Yields were low, however, and the product was unstable for long-term storage, even in a freezer set to −20 °C.

With 4-pentyn-2-ol as the starting material, the aldehyde addition in Scheme 2 furnished mixtures of diastereomers. Fortunately, in all cases, these diastereomers were separable by chromatography on silica gel. We were pleased to see that the subsequent palladium-catalyzed cyclization was perfectly stereospecific. The major *syn* diastereomer reliably formed an *anti* product; the minor *anti* diastereomer formed a *syn* product (Scheme 5). Determining the stereochemistry of the linear starting materials was a considerable challenge (Scheme 6A). After various failed crystallization attempts, we globally deprotected **31** (Scheme 5; see the Supporting Information for full experimental details) and converted it into silocine **61**. On the basis of the observed NOE correlations, the stereochemistry of **61** and, by analogy, of **31** was assigned. To explain the stereospecificity of this reaction, we propose the mechanism shown in Scheme 6B. Insertion of palladium occurs *anti* to the ethyl chloroformate leaving group[40] and is followed by coordination of the silanol nucleophile (inner-sphere process).[41] Subsequent *syn* reductive elimination the furnishes product (Scheme 5). It is interesting to note that this stereoselectivity stands in contrast to related reactions where alcohols or phenols are used as nucleophiles; in these reactions, there is an overall retention of stereochemistry through an *anti-anti* mechanism.[13,18]

The product alkenyl dioxasilinanes could be further elaborated (Scheme 7). Using the second-generation Hoveyda–Grubbs catalyst, cross-metathesis of **33** with ethyl acrylate formed **62** in a 59% yield (Scheme 7A). Dihydroxylation of **48** formed tetrols **63** and **64** as a separable mixture of diastereomers (Scheme 7B).

In summary, we have demonstrated that di-*tert*-butylsilanols are competent nucleophiles for the intramolecular interception of palladium π-allyl species. In these reactions, allyl ethyl carbonates were the best precursors for the formation of palladium π-

allyl intermediates, and [(Cinnamyl)PdCl]$_2$/BINAP was superior to other Pd salt/ligand framework combinations. Our optimized protocol was compatible with a variety of silanol substrates. Importantly, the cyclization is perfectly stereospecific, proceeding via an *anti-syn* mechanism. The alkenes in the product dioxasilinanes serve as blank slates for further functionalization, and we expect this reaction to be a useful addition to the existing technology for the assembly of polyhydroxylated targets.

EXPERIMENTAL SECTION

General Considerations.

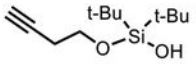
All reagents were obtained commercially unless otherwise noted. Solvents were purified by passage under 10 psi of N_2 through activated alumina columns. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer; data are reported in frequency of absorption (cm^{-1}). NMR data are recorded as chemical shift in ppm referenced internally using residual solvent peaks, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration, and coupling constant (Hz). ^{1}H NMR spectra were recorded at 400, 500, or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz. Exact mass spectra were recorded using an electrospray ion source (ESI) in either positive mode or negative mode with a time-of-flight (TOF) analyzer on a Waters LCT PremierTM mass spectrometer and are given in *m*/*z*. TLC was performed on precoated glass plates (Merck) and visualized either with a UV lamp (254 nm) or by dipping into a solution of $KMnO_4$–K_2CO_3 in water followed by heating. Flash chromatography was performed on silica gel (230–400 mesh) or Florisil (60–100 mesh).

Substrate Syntheses and Characterization of Compounds 2–5, 65, and 66.

Note: see the Supporting Information for expanded reaction schemes

Synthesis of Compounds 65 and 66.—A 100 mL round-bottom flask with a magnetic stir bar was charged with imidazole (1.36 g, 20 mmol, 2 equiv) and 80 mL of DMF. After the flask was cooled to 0 °C, di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (5.29 g, 3.9 mL, 12 mmol, 1.2 equiv) was added dropwise. Following addition, the flask was removed from the ice–water bath and the clear, colorless solution was stirred for 30 min at room temperature. Following this time, the reaction flask was cooled to 0 °C and 3-butynol or 4-pentyn-2-ol (10 mmol, 1 equiv) was added dropwise followed by the addition of one bolus of 4-dimethylaminopyridine (0.337 g, 2.75 mmol, 0.28 equiv). The reaction was warmed to room temperature over a period of 12 h. Following this time, the reaction mixture was diluted with ethyl acetate and transferred to a separatory funnel. The solution was washed once with 50 mL of **1** M HCl(aq) and then with 200 mL of H_2O and 50 mL of brine. The organic layer was collected, dried with $MgSO_4$, and concentrated under reduced pressure to yield a semisolid residue. Chromatography on silica gel (gradient of 25 to 50% DCM in Hexanes) yielded purified products.

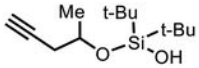
Compound 65.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl ethyl carbonate

Synthesized on a 10 mmol scale and purified using 35% to 50% CH_2Cl_2 in hexanes on silica gel (colorless oil, 1.8 g, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (t, J = 6.6 Hz, 2H), 2.44 (td, J = 6.6, 2.6 Hz, 2H), 1.99 (t, J = 2.6 Hz, 1H), 1.02 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 82.6, 69.6, 62.0, 27.5, 23.2, 20.6; IR 3480, 3300, 2940, 2870, 2350, 1730, 1470, 1130, 830, 675 cm^{-1}; HRMS (ESI) m/z [M + Na$^+$] calculated for $C_{12}H_{24}O_2SiNa^+$ 251.1438, found 251.1436.

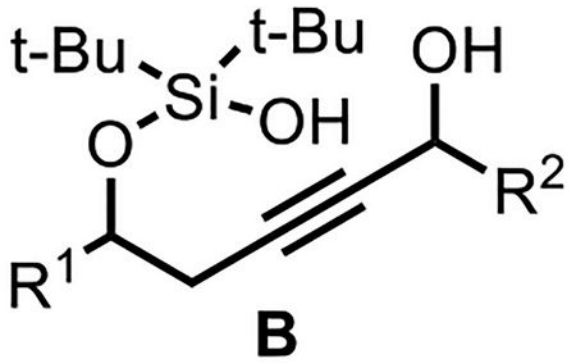
Compound 66.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl ethyl carbonate

Synthesized on a 10 mmol scale and purified using 35–50% CH_2Cl_2 in hexanes on silica gel (colorless oil, 1.07 g, 44% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28−4.23 (m, 1H), 2.39 (ddd, J = 16.6, 6.2, 2.6 Hz, 1H), 2.31 (ddd, J = 16.5, 5.8, 2.7 Hz, 1H), 2.17 (s, 1H), 2.03 (t, J = 2.7 Hz, 1H), 1.28 (d, J = 6.1 Hz, 3H), 1.02 (s, 9H), 1.01 (s, 9H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 83.0, 70.1, 67.8, 29.6, 27.6, 23.5, 20.6, 20.4; IR 3564, 3300, 2935, 2867, 2373, 1460, 1380, 1110, 1010, 835, 650 cm^{-1}; HRMS (ESI) m/z [M + H$^+$] calculated for $C_{13}H_{27}O_2Si^+$ 243.1780, found 243.1789.

General procedure for the Synthesis of Compound B.—

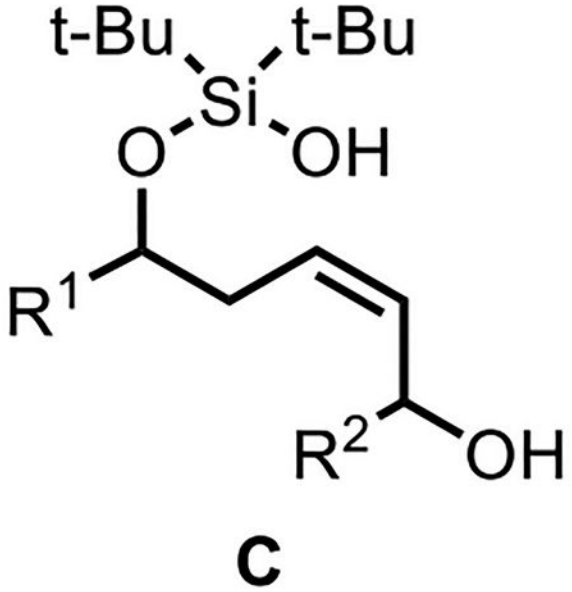


B

A 100 mL round-bottom flask with a magnetic stir bar was charged with an alkynyl silanol (3 mmol, 1 equiv) and 25 mL of dry THF. The reaction mixture was cooled to −78 °C using a dry ice–acetone bath. Then *n*-BuLi solution (2.5 M in hexanes, 6 mmol, 2.4 mL, 2 equiv) was added dropwise. The reaction flask was removed from the dry ice–acetone bath and placed in an ice–water bath. The reaction mixture was warmed to 0 °C over a period of 1.5 h. Following this time, the requisite aldehyde (6 mmol, 2 equiv) was added dropwise at 0 °C, and the reaction mixture was warmed to room temperature over a period of 12 h. The reaction mixture was quenched with careful addition of a saturated aqueous NH_4Cl solution (10 mL) and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The organic fractions were collected, dried with

$MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (gradient of 8–12% ethyl acetate in hexanes). *Note*: in the case of R^2 = H (paraformaldehyde), 4 equiv of aldehyde was used.

General procedure for the Synthesis of Compound C.—

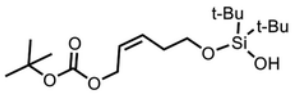


C

A 100 mL round-bottom flask with a magnetic stir bar was charged with alkynyl silanol B and MeOH (0.1 M final reaction concentration). To this were added 2 drops of quinoline and then Lindlar catalyst (10 wt %; e.g. for 100 mg of substrate, 10 mg of catalyst was added). The flask was sealed with a rubber septum, briefly evacuated, and backfilled with hydrogen gas. The reaction mixture was then stirred under 1 atm of H_2 (gas-filled balloon) for 3 h. Following this time, the reaction mixture was purged with N_2 gas, diluted with ethyl acetate, and filtered through a bed of hydrated Celite. Care was taken not to let the bed run dry during filtration. The reaction mixture was concentrated, and the resulting residue was purified by silica gel column chromatography (gradient of 10–15% ethyl acetate in hexane).

General procedure A: Synthesis of Compounds 1 and 6–32.—A 50 mL round-bottom flask with a magnetic stir bar was charged with *cis*-allylic alcohol **C** (1 mmol) and 10 mL of CH_2Cl_2 (final concentration of 0.1 M). The reaction mixture was cooled to 0 °C using an ice–water bath. Next, pyridine (158 mg, 2 mmol, 2 equiv) and DMAP (6 mg, 0.05 mmol, 0.05 equiv) were sequentially added. The reaction mixture was stirred for 5 min at 0 °C, and then ethyl chloroformate (217 mg, 2 mmol, 2 equiv) was added dropwise. The reaction mixture was warmed to room temperature over a period of 12 h. Following this time, the reaction mixture was quenched with addition of a saturated aqueous NaCl solution (brine) and transferred to a separatory funnel. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the organic fractions were collected. After drying with $MgSO_4$ and concentration *in vacuo*, the resulting residue was purified by silica gel column chromatography. Note: column conditions, scale of the reaction, isolated yields, and characterization data are associated with each compound (see below).

Synthesis of Compound 2.—

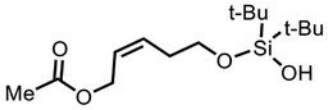


(*Z*)-*tert*-butyl (5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl) carbonate

A 50 mL round-bottom flask with a magnetic stir bar was charged with (Z)-di-*tert*-butyl((5-hydroxypent-3-en-1-yl)oxy)silanol (1 equiv, 871 mg, 3.34 mmol) and anhydrous THF (30 mL, final concentration 0.11 M). The reaction flask was cooled to 0 °C using an ice–water bath. Boc anhydride (1 equiv, 730 mg, 3.34 mmol) and 4-dimethylamino pyridine (DMAP; 0.3 equiv, 123 mg, 1 mmol) were added sequentially. The reaction mixture was warmed to room temperature over a period of 12 h. Following this period, the reaction mixture was quenched with addition of a 5% aqueous HCl solution and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate (3 × 15 mL), and the organic fractions were collected. After drying over $MgSO_4$, the organic layer was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using 2–5% ethyl acetate in hexane as eluent to give **2** (colorless oil, 845 mg, 2.34 mmol, 70% yield).

Compound 2.—Synthesized on a 3.35 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 845 mg, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83−5.52 (m, 2H), 4.64 (dd, J = 6.6, 1.0 Hz, 2H), 3.83 (t, J = 6.7 Hz, 2H), 2.46−2.28 (m, 2H), 1.48 (s, 9H), 1.01 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 132.0, 125.1, 82.3, 62.93, 63.92, 31.5, 28.0, 27.6, 20.6; IR 3562, 2934, 2860, 2358, 1741, 1473, 1370, 1290, 1164, 1101, 936, 827,645 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{18}H_{36}O_5SiNa^+$ 383.2224, found 383.2215.

Synthesis of Compound 3.—

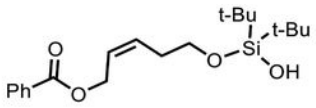


(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl acetate

A 50 mL round-bottom flask with a magnetic stir bar was charged with (*Z*)-di-*tert*-butyl((5-hydroxypent-3-en-1-yl)oxy)silanol (391 mg, 1.5 mmol, 1 equiv) and anhydrous CH_2Cl_2 (20 mL, final concentration 0.075 M). The reaction flask was cooled to 0 °C using an ice–water bath. Pyridine (242 μL, 3 mmol, 2 equiv) and DMAP (9.2 mg, 0.075 mmol, 0.05 equiv) were added sequentially. Next, Ac_2O (293 mg, 2.23 mmol, 1.5 equiv) was added dropwise. The reaction mixture was warmed to room temperature over a period of 12 h. Following this time, the reaction mixture was quenched with addition of a saturated aqueous NaCl solution (brine) and transferred to a separatory funnel. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the organic fractions were collected. After drying with $MgSO_4$ and concentration *in vacuo*, the resulting residue was purified by silica gel column chromatography using a gradient of 2–5% ethyl acetate in hexanes to give 3 (colorless oil, 220 mg, 0.727 mmol, 48% yield).

Compound 3.—Synthesized on a 1.5 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 220 mg, 48% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86−5.75 (m, 1H), 5.64−5.58 (m, 1H), 4.64 (d, J = 7.0 Hz, 2H), 3.85 (td, J = 6.6, 0.9 Hz, 2H), 2.40 (q, J = 6.8 Hz, 2H), 2.06 (s, 3H), 1.01 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.1, 132.0, 125.2, 62.9, 60.6, 31.5, 27.6, 21.2, 20.6; IR 3522, 2934, 2860, 2358, 1718, 1473, 1376, 1244, 1101, 1027, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na$^+$] calculated for $C_{15}H_{30}O_4SiNa^+$ 325.1806, found 325.1793.

Synthesis of Compound 4.—

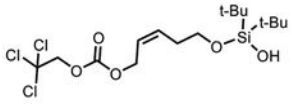


(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl benzoate

A 50 mL round-bottom flask with a magnetic stir bar was charged with (*Z*)-di-*tert*-butyl((5-hydroxypent-3-en-1-yl)oxy)silanol (400 mg, 1.54 mmol, 1 equiv) and anhydrous CH_2Cl_2 (20 mL, final concentration 0.077 M). The reaction flask was cooled to 0 °C using an ice–water bath. Pyridine (248 μL, 3.07 mmol, 2 equiv) and DMAP (9.4 mg, 0.077 mmol, 0.05 equiv) were added sequentially. Next, benzoyl chloride (260 mg, 0.215 mL, 1.85 mmol, 1.2 equiv) was added dropwise. The reaction mixture was warmed to room temperature over the next 12 h. Following this time, the reaction mixture was quenched with addition of a saturated aqueous NaCl solution (brine) and transferred to a separatory funnel. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the organic fractions were collected. After drying with $MgSO_4$ and concentration *in vacuo*, the resulting residue was purified by silica gel column chromatography using a gradient of 2–5% ethyl acetate in hexanes to give **4** (colorless oil, 303 mg, 0.831 mmol, 54% yield).

Compound 4.—Synthesized on a 1.54 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 303 mg, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.03 (m, 2H), 7.56−7.54 (m, 1H), 7.45−7.43 (m, 2H), 5.78−5.74 (m, 2H), 4.92−4.90 (m, 2H), 3.87 (t, J = 6.6 Hz, 2H), 2.46 (q, J = 6.5 Hz, 2H), 1.02 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.6, 133.0, 132.0, 130.3, 129.7, 128.4, 125.2, 62.9, 60.9, 31.5, 27.5, 20.5; IR 3522, 2934, 2860, 2358, 1701, 1473, 1358, 1270, 1101, 936, 827, 713, 645 cm^{-1}; HRMS (ESI) m/z [M + Na$^+$] calculated for $C_{20}H_{32}O_4SiNa^+$ 387.1962, found 387.1943.

Synthesis of Compound 5.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl (2,2,2-trichloroethyl) carbonate

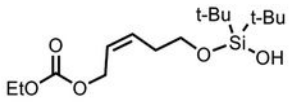
A 50 mL round-bottom flask with a magnetic stir bar was charged with (*Z*)-di-*tert*-butyl((5-hydroxypent-3-en-1-yl)oxy)silanol (391 mg, 1.5 mmol, 1 equiv) and anhydrous THF (20 mL, final concentration 0.075 M). The reaction flask was cooled to 0 °C using an ice–water bath. Pyridine (297 mg, 0.302 mL, 3.75 mmol, 2.5 equiv) was added followed by dropwise addition of 2,2,2-trichloroethyl chloroformate (382 mg, 0.248 mL, 1.8 mmol,

1.2 equiv).The reaction mixture was warmed to room temperature over the next 12 h. Following this time, the reaction mixture was quenched with addition of a saturated aqueous NH_4Cl solution and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate (3 × 15 mL), and the organic fractions were collected. After drying with $MgSO_4$ and concentration *in vacuo*, the resulting residue was purified by silica gel column chromatography using a gradient of 2–5% ethyl acetate in hexanes to give **5** (colorless oil, 285 mg, 0.654 mmol, 44% yield).

Compound 5.—Synthesized on a 1.5 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 285 mg, 44% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86−5.75 (m, 1H), 5.75−5.63 (m, 1H), 4.80 (d, J = 7.0 Hz, 2H), 4.76 (d, J = 0.9 Hz, 2H), 3.85 (td, J = 6.6, 0.9 Hz, 2H), 2.40 (q, J = 6.8 Hz, 2H), 1.01 (d, J = 0.9 Hz, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 133.4, 123.9, 94.6, 77.0, 64.9, 62.8, 31.5, 27.6, 20.6; IR 3562, 2934, 2860, 2358, 1758, 1473, 1381, 1250, 1101, 936, 822, 730 cm^{-1}; HRMS (ESI) m/z [M + Na$^+$] calculated for $C_{16}H_{29}Cl_3O_5SiNa^+$ 457.0748, found 457.0738.

Characterization of Substrates 1 and 6–32.

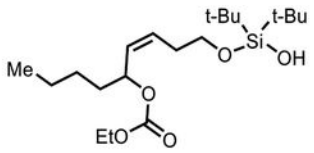
Compound 1.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 2.94 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 860 mg, 88% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dtt, J = 11.1, 7.0, 1.1 Hz, 1H), 5.68 (dtt, J = 10.9, 6.9, 1.3 Hz, 1H), 4.70 (dd, J = 6.9, 1.1 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.83 (t, J = 6.7 Hz, 2H), 2.50−2.29 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.01 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2, 132.4, 124.6, 64.0, 63.5, 62.8, 31.4, 27.4, 20.4, 14.3; IR 3530, 2934, 2860, 1724, 1473, 1376, 1270, 1101, 936, 827, 645 cm^{-1}; HRMS calculated for $C_{16}H_{32}O_5SiNa^+$ 355.1911, found 355.1896.

Compound 6.—

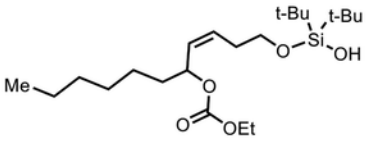


(*Z*)-1-((di-*tert*-butyl(hydroxy)silyl)oxy)non-3-en-5-yl ethyl carbonate

Synthesized using procedure A on a 0.57 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 180 mg, 81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (ddd, J = 10.1, 8.5, 6.4 Hz, 1H), 5.49−5.25 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.82 (m, 2H), 2.56 (m, 1H), 2.34 (ddtd, J = 14.2, 7.8, 6.5, 1.5 Hz, 1H), 1.83−1.64 (m, 1H), 1.63−1.43 (m, 1H), 1.41−1.18 (m, 7H), 1.02 (s, 9H), 1.00 (s, 9H), 0.89 (td, J = 5.6, 4.3, 2.6 Hz, 3H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 130.7, 129.4, 74.6, 63.9, 63.0, 34.3, 31.8, 27.5, 27.4, 27.1, 22.5, 20.6, 20.3, 14.2, 13.9; IR 3540, 2934, 1718, 1473, 1270, 1101, 1010, 942,

827, 793, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{20}H_{40}O_5SiNa^+$ 411.2543, found 411.2533.

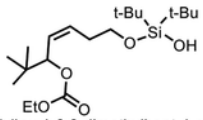
Compound 7.—



(*Z*)-1-((di-*tert*-butyl(hydroxy)silyl)oxy)undec-3-en-5-yl ethyl carbonate

Synthesized using procedure A on a 0.76 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 260 mg, 82% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (ddd, *J* = 10.1, 8.6, 6.3 Hz, 1H), 5.49−5.25 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.82 (qdd, *J* = 10.1, 7.6, 6.4 Hz, 2H), 2.65−2.43 (m, 1H), 2.33 (ddtd, *J* = 14.2, 7.8, 6.5, 1.4 Hz, 1H), 1.81−1.63 (m, 1H), 1.52 (dt, *J* = 13.9, 7.5 Hz, 1H), 1.28 (dt, *J* = 8.5, 5.7 Hz, 11H), 1.09 (s, 9H), 0.92 (m, 9H), 0.90−0.84 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 130.7, 129.4, 74.6, 63.9, 63.0, 34.6, 31.8, 31.7, 29.0, 27.5, 27.5, 24.9, 22.6, 20.6, 20.3, 14.2, 14.0; IR 3510, 2934, 2860, 1718, 1473, 1376, 1261, 1101, 1010, 936, 827, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{22}H_{44}O_5SiNa^+$ 439.2856, found 439.2828.

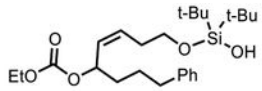
Compound 8.—



(*Z*)-7-((di-*tert*-butyl(hydroxy)silyl)oxy)-2,2-dimethylhept-4-en-3-yl ethyl carbonate

Synthesized using procedure A on a 2.5 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 740 mg, 76% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 11.1, 8.9, 5.8 Hz, 1H), 5.49 (ddt, *J* = 11.3, 9.8, 1.7 Hz, 1H), 5.15 (d, *J* = 9.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.86 (dddd, *J* = 30.8, 10.1, 7.7, 6.3 Hz, 2H), 2.76−2.55 (m, 1H), 2.33 (ddtd, *J* = 14.1, 8.1, 6.1, 1.8 Hz, 1H), 1.33 (td, *J* = 7.1, 0.6 Hz, 3H), 1.05 (s, 9H), 1.03 (s, 9H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.2, 132.1, 126.2, 81.1, 63.9, 63.0, 34.7, 31.8, 27.5, 27.4, 25.6, 20.6, 20.3, 14.3; IR 3539, 2963, 1718, 1473, 1370, 1273, 1101, 1010, 942, 827, 793, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{20}H_{40}O_5SiNa^+$ 411.2537, found 411.2533.

Compound 9.—

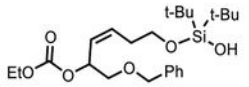


(*Z*)-8-((di-*tert*-butyl(hydroxy)silyl)oxy)-1-phenyloct-5-en-4-yl ethyl carbonate

Synthesized using procedure A on a 1.98 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless solid, 594 mg, 69% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 2H), 7.22−7.12 (m, 3H), 5.69−5.57 (m, 1H), 5.40 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.81 (m, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.60−2.49 (m, 1H), 2.39−2.24 (m, 1H), 1.85−1.50 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H).; $^{13}C\{^1H\}$ NMR

(101 MHz, $CDCl_3$) δ 154.9, 141.9, 131.0, 129.2, 128.41, 128.36, 125.9, 74.3, 63.9, 63.0, 35.6, 34.2, 31.8, 27.48, 27.46, 26.8, 20.6, 20.3, 14.2; IR 3530, 2934, 2860, 2363, 1718, 1473, 1261, 1101, 1010, 936, 827, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{25}H_{42}O_5SiNa^+$ 473.2699, found 473.2694.

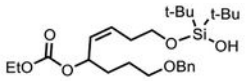
Compound 10.—



(*Z*)-1-(benzyloxy)-6-((di-*tert*-butyl(hydroxy)silyl)oxy)hex-3-en-2-yl ethyl carbonate

Synthesized using procedure A on a 0.79 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 230 mg, 64% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.27 (m, 5H), 5.77 (dddd, *J* = 11.0, 8.4, 6.7, 1.0 Hz, 1H), 5.66 (dddd, *J* = 9.2, 7.4, 3.9, 1.0 Hz, 1H), 5.48 (ddt, *J* = 10.9, 9.2, 1.5 Hz, 1H), 4.61 (d, *J* = 1.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.97−3.71 (m, 2H), 3.64 (dd, *J* = 10.8, 7.4 Hz, 1H), 3.55 (dd, *J* = 10.7, 3.9 Hz, 1H), 2.57 (dddd, *J* = 15.6, 8.5, 5.3, 1.6 Hz, 1H), 2.40 (dqd, *J* = 14.0, 6.7, 1.6 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 9H), 1.03 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, CDCl3) δ 154.8, 137.9, 132.8, 128.4, 127.8, 127.7, 125.7, 73.3, 73.2, 71.3, 64.1, 62.9, 31.9, 27.5 (2 lines), 20.6, 20.3, 14.2; IR 3528, 2934, 1747, 1473, 1370, 1281, 1101, 1010, 827, 742, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{24}H_{40}O_6SiNa^+$ 475.2492, found 475.2467.

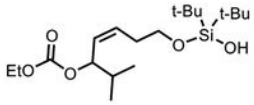
Compound 11.—



(*Z*)-1-(benzyloxy)-8-((di-*tert*-butyl(hydroxy)silyl)oxy)oct-5-en-4-yl ethyl carbonate

Synthesized using procedure A on a 0.6 mmol scale and purified using a gradient of 10% EtOAc in hexanes on silica gel (light yellow oil, 250 mg, 82%): ^1H NMR (400 MHz, chloroform-*d*) δ 7.42−7.29 (m, 5H), 5.73−5.59 (m, 1H), 5.42 (d, *J* = 7.4 Hz, 2H), 4.51 (d, *J* = 1.8 Hz, 2H), 4.18 (q, *J* = 7.2, 2H), 3.91−3.74 (m, 2H), 3.56−3.40 (m, 2H), 2.60−2.51 (m, 1H), 2.39−2.30 (m, 1H), 1.82−1.64 (m, 4H), 1.31 (t, *J* = 7.3, 3H), 1.02 (s, 9H), 1.01 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, chloroform-*d*) δ 154.8, 138.4, 130.9, 129.1, 128.3, 127.6, 127.5, 74.2, 72.9, 69.7, 63.9, 62.9, 31.7, 31.3, 27.47, 27.46, 25.3, 20.5, 20.2, 14.2. IR 3545, 2934, 2860, 2363, 1741, 1473, 1370, 1261, 1101, 1010, 942, 827, 742, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{26}H_{44}O_6SiNa^+$ 503.2799, found 503.2780.

Compound 12.—

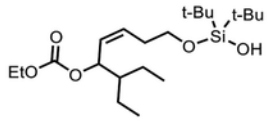


(*Z*)-7-((di-*tert*-butyl(hydroxy)silyl)oxy)-2-methylhept-4-en-3-yl ethyl carbonate

Synthesized using procedure A on a 0.9 mmol scale and purified using a gradient of 0–10% EtOAc in hexanes on silica gel (light yellow oil, 250 mg, 75% yield): ^1H NMR (400 MHz, chloroform-*d*) δ 5.71 (ddd, *J* = 11.3, 8.8, 6.1 Hz, 1H), 5.43 (ddd, *J* = 11.0, 9.7, 1.7 Hz, 1H), 5.15 (dd, *J* = 9.5, 7.1 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.83 (dddd, *J* = 16.2, 14.3, 10.0, 6.8

Hz, 2H), 2.67−2.53 (m, 1H), 2.39−2.28 (m, 1H), 1.94−1.87 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 9H), 1.01 (s, 9H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) *δ* 155.0, 131.6, 127.5, 79.0, 63.8, 63.0, 32.2, 31.8, 27.46, 27.44, 20.5, 20.2, 18.1, 17.8, 14.2; IR 3545, 2963, 2860, 1718, 1473, 1376, 1261, 1101, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{19}H_{38}O_5SiNa^+$ 397.2381, found 397.2380.

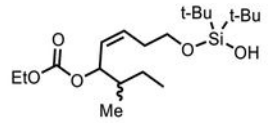
Compound 13.—



(*Z*)-8-((di-*tert*-butyl(hydroxy)silyl)oxy)-3-ethyloct-5-en-4-yl ethyl carbonate

Synthesized using procedure A on a 1.4 mmol scale and purified using a gradient of 0–10% EtOAc in hexanes on silica gel (light yellow oil, 452 mg, 76% yield): ^{1}H NMR (400 MHz, chloroform-*d*) *δ* 5.69 (ddd, *J* = 10.6, 8.9, 6.0 Hz, 1H), 5.46 (tt, *J* = 10.6, 1.5 Hz, 1H), 5.39 (dd, *J* = 9.7, 5.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.90−3.76 (m, 2H), 2.67−2.57 (m, 1H), 2.36−2.30 (m, 1H), 1.53−1.39 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.28−1.22 (m, 1H), 1.03 (s, 9H), 1.01 (s, 9H), 0.90 (td, *J* = 7.3, 5.0 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) *δ* 155.0, 131.4, 127.8, 76.0, 63.8, 63.0, 44.9, 31.8, 27.5, 27.4, 21.3, 21.2, 20.6, 20.2, 14.2, 11.2, 11.0; IR 3545, 2963, 2860, 2318, 1718, 1473, 1376, 1261, 1101, 1010, 942, 827, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{21}H_{42}O_5SiNa^+$ 425.2694, found 425.2678.

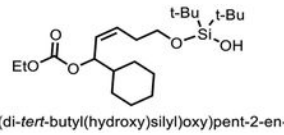
Compound 14.—



(*Z*)-8-((di-*tert*-butyl(hydroxy)silyl)oxy)-3-methyloct-5-en-4-yl ethyl carbonate

Synthesized using procedure A on a 1.8 mol scale and purified using a gradient of 0–10% EtOAc in hexanes on silica gel, inseparable ~1:1 mixture of diastereomers (light yellow oil, 510 mg, 72%): ^{1}H NMR (400 MHz, chloroform-*d*) *δ* 5.75−5.64 (m, 1H), 5.50−5.38 (m, 1H), 5.29−5.21 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.91−3.76 (m, 2H), 2.66−2.54 (m, 1H), 2.38−2.27 (m, 1H), 1.74−1.60 (m, 1H), 1.57−1.50 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20−1.07 (m, 1H), 1.03 (s, 9H), 1.01 (s, 9H), 0.97−0.88 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) *δ* 155.0, 131.6, 131.3, 127.9, 127.3, 77.9, 77.7, 63.8, 63.0, 39.0, 38.5, 31.9, 31.8, 27.46, 27.44, 25.0, 24.8, 20.6, 20.2, 14.4, 14.2, 11.4, 11.2; IR 3545, 2963, 2860, 2363, 1718, 1473, 1376, 1261, 1101, 1010, 942, 827, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M+Na^+] calculated for $C_{20}H_{40}O_5SiNa^+$ 411.2537, found 411.2520.

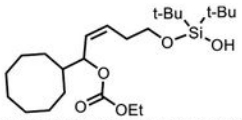
Compound 15.—



(*Z*)-1-cyclohexyl-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 1.37 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 318 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (dddd, J = 11.0, 8.8, 6.1, 0.9 Hz, 1H), 5.40 (ddt, J = 11.1, 9.6, 1.5 Hz, 1H), 5.15 (ddd, J = 9.6, 7.5, 0.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.81 (m, 2H), 2.57 (m, 1H), 2.30 (ddtd, J = 14.2, 8.0, 6.3, 1.7 Hz, 1H), 1.83 (d, J = 12.7 Hz, 1H), 1.78−1.60 (m, 4H), 1.56 (dtd, J = 11.4, 8.0, 3.7 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.26−1.11 (m, 4H), 1.05−0.97 (m, 19H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.1, 131.5, 127.9, 78.4, 63.9, 63.1, 41.8, 31.9, 28.6, 28.3, 27.49, 27.47, 26.3, 25.9, 25.7, 20.6, 20.3, 14.2; IR 3600, 2934, 2860, 1718, 1473, 1376, 1261, 1101, 947, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{22}H_{42}O_5SiNa^+$ 437.2699, found 437.2683.

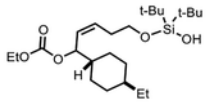
Compound 16.—



(*Z*)-1-cyclooctyl-5-((di-*tert*-butyl(hydroxy)silyl)oxy)pent-2-en-1-yl ethyl carbonate

Synthesized using procedure A on 0.963 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless oil, 350 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dddd, J = 11.1, 8.8, 6.1, 0.8 Hz, 1H), 5.41 (ddt, J = 11.1, 9.5, 1.5 Hz, 1H), 5.17 (ddd, J = 9.7, 7.2, 0.9 Hz, 1H), 4.26−4.08 (m, 2H), 3.81 (dddd, J = 25.3, 10.0, 7.8, 6.3 Hz, 2H), 2.59 (ddddd, J = 13.9, 9.0, 7.6, 6.1, 1.4 Hz, 1H), 2.32 (ddtd, J = 14.3, 8.0, 6.3, 1.7 Hz, 1H), 1.81−1.19 (m, 18H), 1.05 (s, 9H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.1, 131.6, 127.9, 78.8, 63.9, 63.1, 41.3, 31.9, 28.4, 28.1, 27.46, 27.48, 26.73, 26.67, 26.4, 25.9, 25.3, 20.6, 20.3, 14.2; IR 3510, 2929, 2860, 2363, 1718, 1473, 1261, 1101, 1010, 942, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{24}H_{46}O_5SiNa^+$ 465.3007, found 465.2990.

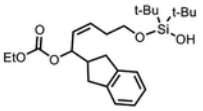
Compound 17.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)-1-((1*r*,4*r*)-4-ethylcyclohexyl)pent-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 1.43 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless solid, 516 mg, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dddd, J = 11.0, 8.8, 6.1, 0.9 Hz, 1H), 5.40 (ddt, J = 11.1, 9.6, 1.5 Hz, 1H), 5.14 (ddd, J = 9.6, 7.5, 0.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.81 (m, 2H), 2.57 (ddddd, J = 14.0, 9.0, 7.7, 6.2, 1.4 Hz, 1H), 2.30 (ddtd, J = 14.1, 7.9, 6.3, 1.7 Hz, 1H), 1.94−1.63 (m, 4H), 1.51 (dddd, J = 15.1, 11.9, 7.0, 3.4 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.24−1.13 (m, 2H), 1.13−0.94 (m, 21H), 0.93−0.76 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.1, 131.4, 127.9, 78.5, 63.9, 63.1, 41.9, 39.3, 32.2, 32.1, 31.9, 29.8, 28.6, 28.1, 27.49, 27.47, 20.6, 20.3, 14.2, 11.5; IR 3530, 2934, 2854, 2363, 1718, 1473, 1376, 1267, 1101, 1010, 936, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{24}H_{46}O_5SiNa^+$ 465.3007, found 465.2991.

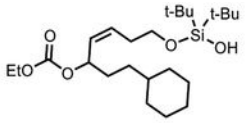
Compound 18.—



(*Z*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)-1-(2,3-dihydro-1*H*-inden-2-yl)pent-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 0.77 mmol scale and purified using 5% ethyl acetate in hexane on silica gel (colorless solid, 274 mg, 82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.07 (m, 4H), 5.74 (ddd, J = 10.6, 8.7, 6.1 Hz, 1H), 5.53−5.34 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.93−3.75 (m, 2H), 3.10 (dd, J = 15.8, 7.8 Hz, 1H), 3.01−2.91 (m, 1H), 2.86 (dd, J = 15.9, 7.8 Hz, 1H), 2.81−2.66 (m, 2H), 2.65−2.54 (m, 1H), 2.35 (ddtd, J = 14.2, 7.9, 6.4, 1.6 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.01 (s, 9H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 142.5, 142.2, 132.1, 127.9, 126.44, 126.37, 124.6, 124.4, 77.2, 64.1, 63.0, 43.5, 35.7, 35.1, 31.9, 27.49, 27.47, 20.6, 20.3, 14.2; IR 3530, 2934, 2860, 2358, 1724, 1473, 1370, 1261, 1101, 1004, 942, 827, 742, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{25}H_{40}O_5SiNa^{+}$ 471.2543, found 471.2537.

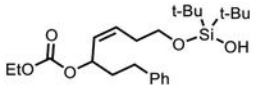
Compound 19.—



(Z)-1-cyclohexyl-7-((di-tert-butyl(hydroxy)silyl)oxy)hept-4-en-3-yl ethyl carbonate

Synthesized using procedure A on a 0.8 mmol scale and purified using a gradient of 0–10% EtOAc in hexanes on silica gel (light yellow oil, 250 mg, 66% yield). ^{1}H NMR (400 MHz, chloroform-*d*) δ 5.68−5.61 (m, 1H), 5.46−5.32 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.91−3.72 (m, 2H), 2.62−2.52 (m, 1H), 2.39−2.27 (m, 1H), 1.69−1.50 (m, 8H), 1.31 (t, J = 7.2 Hz, 3H), 1.25−1.14 (m, 6H), 1.03 (s, 9H), 1.01 (s, 9H), 0.91−0.86 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) δ 154.9, 130.7, 129.4, 74.8, 63.8, 63.0, 37.5, 33.3, 33.2, 32.4, 32.0, 31.7, 27.45, 27.44, 26.6, 26.3, 20.5, 20.2, 14.2. IR 3562, 2929, 2370, 1718, 1261, 1101, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{24}H_{46}O_5SiNa^{+}$ 465.3007, found 465.2996.

Compound 20.—



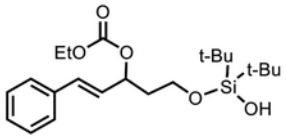
(*Z*)-7-((di-*tert*-butyl(hydroxy)silyl)oxy)-1-phenylhept-4-en-3-yl ethyl carbonate

Synthesized using procedure A on a 3.02 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 993 mg, 75% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.24 (m, 2H), 7.22−7.15 (m, 3H), 5.68 (ddd, J = 10.4, 8.6, 6.3 Hz, 1H), 5.54−5.29 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 3.81 (qdd, J = 10.0, 7.5, 6.4 Hz, 2H), 2.73−2.63 (m, 2H), 2.62−2.44 (m, 2H), 2.37−2.25 (m, 1H), 2.16−2.02 (m, 1H), 1.93−1.78 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 141.2, 131.4, 129.1, 128.6, 128.5, 126.2, 74.1, 64.1, 63.1, 36.4, 32.0, 31.5, 27.60, 27.59, 20.7, 20.4,

14.4; IR 3562, 2934, 2860, 2358, 1741, 1473, 1370, 1261, 1101, 1010, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{24}H_{40}O_5SiNa^+$ 459.2537, found 459.2534.

Note: the synthesis of this substrate was carried out using procedure A. However, the product was atypical; under the reaction conditions, we hypothesize that a rearrangement took place.

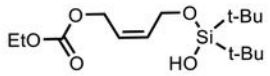
Compound 21.—



(*E*)-5-((di-*tert*-butyl(hydroxy)silyl)oxy)-1-phenylpent-1-en-3-yl acetate

Synthesized using procedure A on a 1.34 mmol scale and purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 265 mg, 48% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.36 (m, 2H), 7.32 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 2H), 7.28−7.24 (m, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 7.5 Hz, 1H), 5.54 (dddd, *J* = 8.5, 7.5, 4.9, 1.0 Hz, 1H), 4.21 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.04−3.80 (m, 2H), 2.15−2.01 (m, 1H), 2.01−1.85 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.04 (s, 9H), 1.03 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.1, 136.1, 133.1, 128.6, 128.1, 126.9, 126.7, 75.9, 64.1, 59.1, 38.0, 27.6, 27.5, 20.5, 20.4, 14.2; IR 3545, 2934, 2860, 2358, 1724, 1473, 1376, 1261, 1101, 827, 747, 645 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{22}H_{36}O_5SiNa^+$ 431.2230, found 431.2217.

Compound 22.—

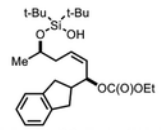


(*Z*)-4-((di-*tert*-butyl(hydroxy)silyl)oxy)but-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 5 mmol scale and purified using 3–4% ethyl acetate in hexane on silica gel (colorless oil, 965 mg, 61% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (dtt, *J* = 11.2, 6.4, 1.4 Hz, 1H), 5.55 (dtt, *J* = 11.1, 6.8, 1.5 Hz, 1H), 4.77−4.64 (m, 2H), 4.45 (dd, *J* = 6.5, 1.5 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.01 (s, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.4, 134.6, 123.6, 64.4, 63.5, 59.1, 27.5, 20.5, 14.4; IR 3545, 2934, 2860, 2358, 1730, 1473, 1267, 1090, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{15}H_{30}O_5SiNa^+$ 341.1755, found 341.1738.

Compounds 23 and 24.—Synthesized using procedure A on a 1.23 mmol scale and purified using 2.8–3.5% ethyl acetate in hexane on silica gel (1.06:1 dr, 408 mg, 72% yield).

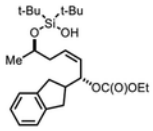
Compound 23.—



(1S*,5R*,Z)-5-((di-tert-butyl(hydroxy)silyl)oxy)-1-(2,3-dihydro-1H-inden-2-yl)hex-2-en-1-yl ethyl carbonate

Major diastereomer; colorless oil, 208 mg, 37% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.02 (m, 4H), 5.90−5.72 (m, 1H), 5.57−5.45 (m, 1H), 5.40 (dd, J = 9.6, 7.6 Hz, 1H), 4.33−4.05 (m, 3H), 3.08 (dd, J = 15.8, 7.8 Hz, 1H), 3.00−2.81 (m, 2H), 2.81−2.64 (m, 2H), 2.54−2.41 (m, 1H), 2.40−2.27 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.01 (s, 9H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 142.5, 142.2, 132.0, 127.9, 126.4, 126.3, 124.6, 124.3, 68.4, 64.0, 43.7, 37.8, 35.5, 35.0, 27.6, 27.6, 23.2, 20.4, 20.4, 14.3; IR 3562, 2934, 2860, 2358, 1718, 1473, 1376, 1261, 1010, 827 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{26}H_{42}O_5SiNa^{+}$ 485.2694, found 485.2699.

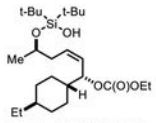
Compound 24.—



(1R*,5R*,Z)-5-((di-tert-butyl(hydroxy)silyl)oxy)-1-(2,3-dihydro-1H-inden-2-yl)hex-2-en-1-yl ethyl carbonate

Minor diastereomer; colorless oil, 200 mg, 35% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.05 (m, 4H), 5.79−5.61 (m, 1H), 5.53−5.37 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 4.02 (dddd, J = 7.9, 6.0, 4.2, 2.1 Hz, 1H), 3.18 (s, 1H), 3.09 (dd, J = 15.7, 7.7 Hz, 1H), 2.99−2.89 (m, 1H), 2.89−2.60 (m, 4H), 2.18−1.98 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (d, J = 6.0 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 142.4, 142.1, 131.9, 127.7, 126.4, 126.4, 124.6, 124.4, 77.2, 68.9, 64.2, 43.6, 38.5, 35.6, 35.1, 27.6, 27.5, 22.9, 20.7, 20.0, 14.2; IR 3608, 2934, 2854, 2358, 1718, 1473, 1376, 1261, 1004, 827 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{26}H_{42}O_5SiNa^{+}$ 485.2694, found 485.2714.

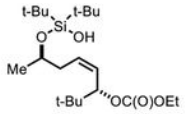
Compound 25.—



(1R*,5R*,Z)-5-((di-tert-butyl(hydroxy)silyl)oxy)-1-((1r,4R)-4-ethylcyclohexyl)hex-2-en-1-yl ethyl carbonate

Synthesized using procedure A on a 1.38 mmol scale and purified using 2.8–3.5% ethyl acetate in hexane on silica gel (colorless oil, 217 mg, 34% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72−5.57 (m, 1H), 5.39 (ddd, J = 11.1, 9.7, 1.4 Hz, 1H), 5.18 (dd, J = 9.7, 7.4 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.99 (dtd, J = 8.5, 4.1, 2.4 Hz, 1H), 3.14 (s, 1H), 2.68 (dddd, J = 13.9, 9.9, 4.1, 1.3 Hz, 1H), 2.03 (dddd, J = 14.0, 8.4, 5.8, 1.6 Hz, 1H), 1.91−1.61 (m, 4H), 1.50 (tdt, J = 11.3, 6.9, 3.3 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 6.8 Hz, 5H), 1.01 (m, 21H), 0.89−0.81 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2, 131.4, 127.8, 78.5, 69.0, 64.0, 42.0, 39.3, 38.4, 32.2, 32.1, 29.8, 28.6, 28.1, 27.6, 27.5, 22.8, 20.8, 20.0, 14.2, 11.5; IR 3545, 2929, 2854, 1724, 1467, 1376, 1270, 1084, 1010, 827, 645; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{25}H_{48}O_5SiNa^{+}$ 479.3169, found 479.3146.

Compound 26.—

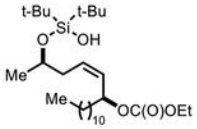


(3S*,7R*,Z)-7-((di-tert-butyl(hydroxy)silyl)oxy)-2,2-dimethyloct-4-en-3-yl ethyl carbonate

Synthesized using procedure A on a 1.94 mmol scale and purified using 5% ethyl acetate in hexane on silica gel single diastereomer (colorless oil, 200 mg, 27% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (td, J = 10.6, 5.5 Hz, 1H), 5.45 (t, J = 10.5 Hz, 1H), 5.17 (d, J = 9.8 Hz, 1H), 4.17 (q, J = 7.4 Hz, 2H), 3.98 (ddt, J = 9.1, 6.3, 3.1 Hz, 1H), 2.74 (ddd, J = 14.2, 10.3, 3.9 Hz, 1H), 2.10−1.92 (m, 1H), 1.29 (td, J = 8.1, 7.6, 2.7 Hz, 3H), 1.21 (d, J = 6.3 Hz, 3H), 1.05 (s, 9H), 1.04 (s, 9H), 0.96 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.3, 131.9, 126.1, 81.1, 69.0, 64.0, 38.4, 34.8, 27.6, 27.5, 25.5, 22.8, 20.8, 19.9, 14.2; IR 3545, 2968, 2860, 2363, 1718, 1473, 1278, 1090, 942, 827, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{21}H_{42}O_5SiNa^+$ 425.2694, found 425.2691.

Compounds 27 and 28.—Synthesized using procedure A on a 0.7 mmol scale and purified using 2.8–3.5% ethyl acetate in hexane on silica gel. Formed as a separable 1.3:1 mixture of diastereomers (colorless oil, 142 mg, 72% yield).

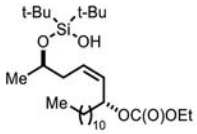
Compound 27.—



(2R*,6S*,Z)-2-((di-tert-butyl(hydroxy)silyl)oxy)heptadec-4-en-6-yl ethyl carbonate

Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (dt, J = 10.7, 7.4 Hz, 1H), 5.47−5.30 (m, 2H), 4.28−4.07 (m, 3H), 2.48−2.28 (m, 2H), 1.71 (tt, J = 9.3, 6.5 Hz, 1H), 1.52 (ddd, J = 14.4, 8.2, 5.9 Hz, 1H), 1.35−1.21 (m, 21H), 1.19 (d, J = 6.1 Hz, 3H), 1.01 (s, 9H), 0.99 (s, 9H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 130.6, 129.5, 74.6, 68.5, 63.8, 37.7, 34.8, 31.9, 29.64, 29.62, 29.50, 29.55, 29.4, 29.3, 27.57, 27.61, 25.0, 23.2, 22.7, 20.42, 20.36, 14.3, 14.1; IR 3539, 2929, 2854, 2358, 1718, 1467, 1376, 1261, 1010, 827 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{28}H_{56}O_5SiNa^+$ 523.3789, found 523.3784.

Compound 28.—



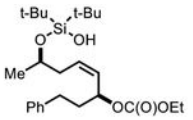
(2R*,6R*,Z)-2-((di-tert-butyl(hydroxy)silyl)oxy)heptadec-4-en-6-yl ethyl carbonate

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69−5.51 (m, 1H), 5.49−5.28 (m, 2H), 4.23−4.08 (m, 2H), 4.00 (dddd, J = 8.0, 6.0, 4.2, 2.1 Hz, 1H), 2.77−2.58 (m, 1H), 2.27 (ddd, J = 9.7, 8.6, 7.2 Hz, 1H), 2.16−1.97 (m, 1H), 1.78−1.65 (m, 1H), 1.60 (q, J = 7.4 Hz, 1H), 1.52 (q, J = 6.5 Hz, 1H), 1.29−1.22 (m, 19H), 1.21 (d, J = 6.0 Hz, 3H), 1.02 (s, 9H), 1.01 (s, 9H), 0.91−0.82 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 130.7, 129.3,

74.5, 68.9, 63.9, 38.4, 34.6, 31.9, 29.6, 29.5, 29.4, 29.32, 29.26, 29.1, 27.6, 27.5, 24.9, 22.8, 22.7, 20.7, 20.0, 14.2, 14.1; IR 3545, 2934, 2854, 2358, 1467, 1376, 1273, 1010, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{28}H_{56}O_5SiNa^+$ 523.3789, found 523.3795.

Compounds 29 and 30.—Synthesized using procedure A on a 0.872 mmol scale, formed as a separable mixture of diastereomers in a ratio of 1.3:1, and purified using 3% ethyl acetate in hexane on silica gel (colorless oil, 254 mg, 65% combined yield).

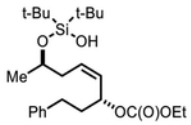
Compound 29.—



(3S*,7R*,Z)-7-((di-tert-butyl(hydroxy)silyl)oxy)-1-phenyloct-4-en-3-yl ethyl carbonate

Major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.22 (m, 2H), 7.22−7.12 (m, 3H), 5.74 (dt, *J* = 10.8, 7.4 Hz, 1H), 5.49 (ddt, *J* = 10.7, 9.1, 1.6 Hz, 1H), 5.40 (ddd, *J* = 9.4, 7.4, 5.4 Hz, 1H), 4.29−4.07 (m, 3H), 2.59−2.57 (m, 2H), 2.34 (dddd, *J* = 14.5, 12.6, 7.8, 4.5 Hz, 2H), 2.15−1.98 (m, 1H), 1.85 (ddt, *J* = 13.7, 10.2, 6.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.01 (s, 9H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 141.2, 131.0, 129.1, 128.5, 128.3, 126.0, 74.1, 68.5, 63.9, 37.7, 36.4, 31.4, 27.63, 27.59, 23.2, 20.43, 20.38, 14.3; IR 3545, 2934, 2860, 1741, 1724, 1261, 1110, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{25}H_{42}O_5SiNa^+$ 473.2694, found 473.2677.

Compound 30.—

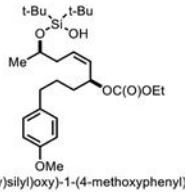


(3R*,7R*,Z)-7-((di-tert-butyl(hydroxy)silyl)oxy)-1-phenyloct-4-en-3-yl ethyl carbonate

Minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.22−7.11 (m, 3H), 5.65 (td, *J* = 9.8, 5.9 Hz, 1H), 5.51−5.35 (m, 2H), 4.26−4.10 (m, 2H), 3.99 (ddd, *J* = 8.3, 6.1, 4.2 Hz, 1H), 2.76−2.48 (m, 3H), 2.17−1.97 (m, 2H), 1.94−1.72 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.0 Hz, 3H), 1.00 (overlapping singlets, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 141.1, 131.3, 128.8, 128.5, 128.3, 126.1, 73.9, 68.8, 64.1, 38.4, 36.2, 31.3, 27.6, 27.5, 22.8, 20.7, 20.0, 14.2; IR 3545, 2934, 2860, 1724, 1267, 1010, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{25}H_{42}O_5SiNa^+$ 473.2699, found 473.2675.

Compounds 31 and 32.—Synthesized using procedure A on a 1.41 mmol scale, formed as a separable 1:1.5 mixture of diastereomers, and purified using 3% ethyl acetate in hexane on silica gel (colorless oil, 458 mg, 68% combined yield).

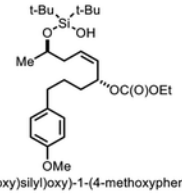
Compound 31.—



(4S*,8R*,Z)-8-((di-tert-butyl(hydroxy)silyl)oxy)-1-(4-methoxyphenyl)non-5-en-4-yl ethyl carbonate

Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.00 (m, 2H), 6.92−6.73 (m, 2H), 5.71 (dt, J = 10.0, 7.4 Hz, 1H), 5.52−5.31 (m, 2H), 4.25−4.05 (m, 3H), 3.78 (s, 3H), 2.63−2.47 (m, 2H), 2.45−2.26 (m, 2H), 1.74 (ddd, J = 10.5, 5.4, 3.0 Hz, 1H), 1.69−1.51 (m, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.19 (d, J = 6.1 Hz, 3H), 1.01 (s, 9H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 154.9, 134.0, 130.8, 129.34, 129.28, 113.8, 74.4, 68.5, 63.9, 55.3, 37.7, 34.7, 34.3, 27.62, 27.58, 27.0, 23.2, 20.43, 20.36, 14.3; IR 3545, 2934, 2860, 2358, 1741, 1513, 1256, 1010, 827 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{27}H_{46}O_6SiNa^{+}$ 517.2961, found 517.2948.

Compound 32.—



(4R*,8R*,Z)-8-((di-tert-butyl(hydroxy)silyl)oxy)-1-(4-methoxyphenyl)non-5-en-4-yl ethyl carbonate

Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.01 (m, 2H), 6.88−6.76 (m, 2H), 5.61 (td, J = 10.0, 5.9 Hz, 1H), 5.50−5.31 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 4.00 (ddd, J = 8.4, 6.1, 4.2 Hz, 1H), 3.78 (s, 3H), 2.75−2.62 (m, 1H), 2.57 (t, J = 7.4 Hz, 2H), 2.07 (dddd, J = 13.9, 8.4, 6.0, 1.4 Hz, 1H), 1.81−1.67 (m, 1H), 1.67−1.45 (m, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.20 (d, J = 6.0 Hz, 3H), 1.02 (s, 9H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 155.0, 134.0, 130.9, 129.3, 129.1, 113.8, 74.3, 68.9, 64.0, 55.3, 38.4, 34.6, 34.0, 27.6, 27.5, 27.0, 22.8, 20.7, 20.0, 14.2; IR 3545, 2934, 2860, 2358, 1718, 1513, 1261, 1010, 827 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{27}H_{46}O_6SiNa^{+}$ 517.2961, found 517.2948.

Cyclization Reaction Procedures.

General Procedure B.—[(Cinnamyl)PdCl]$_2$ (5.2 mg, 0.01 mmol, 0.05 equiv), *R*-BINAP ligand (12.5 mg, 0.02 mmol, 0.1 equiv), and a stir bar were placed in a microwave vial under a N_2 atmosphere. A 0.4 mL portion of toluene (saturated with N_2 through bubbling) was added, and the mixture was stirred for 15 min at room temperature. Over this time, the reaction mixture turned a turbid yellow-orange (Figure S1). An additional 2 mL of nitrogen-sparged toluene was added (reaction concentration 0.08 M). A silanol substrate (0.2 mmol, 1 equiv) was added to the reaction mixture. The reaction flask was sealed and then immersed in an oil bath that had been preheated to 80 °C. The reaction mixture was stirred at this temperature for 3 h. Generally, during productive reactions, the reaction mixture turned dark brown within 30 min of heating, and this color persisted throughout the reaction (Figure S1). After 3 h, the reaction flask was cooled to room temperature, and the contents were filtered through a pad of Celite using ethyl acetate. The filtrate was concentrated *in*

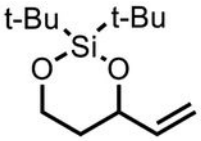
vacuo, and the resulting residue was purified by chromatography on silica gel (specific conditions are associated with each product).

Note: It is essential to maintain a N_2 atmosphere during all aspects of reaction setup and to use N_2 − sparged solvent. Care must be taken not to introduce O_2 or air into the reaction during addition of silanol substrate.

1 mmol Scale procedure.—[(Cinnamyl)PdCl]$_2$ (26 mg, 0.05 mmol, 0.05 equiv), *R*-BINAP ligand (62 mg, 0.1 mmol, 0.1 equiv), and a stir bar were placed in a nitrogen-purged 50 mL round-bottom flask. A 2.5 mL portion of toluene (saturated with N_2 through bubbling) was added, and the mixture was stirred for 15 min at room temperature. Over this time, the reaction mixture turned a turbid yellow-orange (Figure S2). An additional 10 mL of nitrogen-sparged toluene was added (reaction concentration 0.08 M). **20** (437 mg, 1 mmol, **1** equiv) was added to the reaction mixture. The reaction mixture was stirred at this temperature for 3 h. The reaction mixture turned dark brown within 30 min of heating, and this color persisted throughout the reaction (Figure S2). After 3 h, the reaction flask was cooled to room temperature, and the contents were filtered through a pad of Celite using ethyl acetate. The filtrate was concentrated *in vacuo*, and the resulting residue was purified by chromatography on silica gel to give **48** (180 mg, 0.519 mmol, 52% yield).

Characterization of Products.

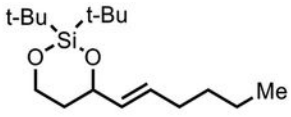
Compound 33.—



2,2-di-*tert*-butyl-4-vinyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 29 mg, 60% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, J = 17.1, 10.4, 4.6 Hz, 1H), 5.31 (dt, J = 17.1, 1.8 Hz, 1H), 5.08 (dt, J = 10.4, 1.7 Hz, 1H), 4.58 (dddt, J = 10.7, 4.4, 3.0, 1.6 Hz, 1H), 4.21−3.99 (m, 2H), 1.84 (dtd, J = 14.3, 11.0, 5.2 Hz, 1H), 1.70 (dq, J = 14.3, 2.6 Hz, 1H), 1.08 (s, 9H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.7, 113.2, 74.3, 64.1, 36.7, 27.4, 27.2, 22.7, 20.0; IR 2929, 2860, 1620, 1473, 1147, 1113, 822, 650 cm^{-1}; HRMS (ESI) m/z [M + H$^+$] calculated for $C_{13}H_{27}O_2Si^+$ 243.1780, found 243.1753.

Compound 34.—

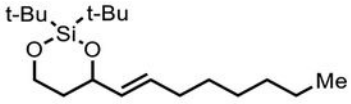


(*E*)-2,2-di-*tert*-butyl-4-(hex-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale; Purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 32.2 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68

(dtd, J = 14.9, 6.7, 1.3 Hz, 1H), 5.46 (ddt, J = 15.3, 5.7, 1.5 Hz, 1H), 4.52 (dddd, J = 11.4, 6.3, 2.6, 1.5 Hz, 1H), 4.09 (pt, J = 5.3, 2.5 Hz, 2H), 2.12−1.93 (m, 2H), 1.84 (dtd, J = 14.3, 10.8, 5.2 Hz, 1H), 1.65 (dq, J = 14.4, 2.6 Hz, 1H), 1.45−1.22 (m, 4H), 1.07 (s, 9H), 1.04 (s, 9H), 0.90 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 132.6, 130.1, 74.5, 64.0, 37.3, 31.8, 31.4, 27.4, 27.2, 22.6, 22.2, 20.0, 13.9; IR 2934, 2860, 1473, 1244, 1119, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M+Na^+] calculated for $C_{17}H_{34}O_2SiNa^+$ 321.2226, found 321.2229.

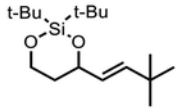
Compound 35.—



(*E*)-2,2-di-*tert*-butyl-4-(oct-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 35.9 mg, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78−5.58 (m, 1H), 5.46 (ddt, J = 15.3, 5.7, 1.4 Hz, 1H), 4.66−4.35 (m, 1H), 4.09 (pt, J = 5.3, 2.5 Hz, 2H), 2.08−1.95 (m, 2H), 1.93−1.77 (m, 1H), 1.70−1.62 (m, 1H), 1.28 (tdd, J = 7.9, 6.7, 5.7, 2.9 Hz, 8H), 1.07 (s, 9H), 1.04 (s, 9H), 0.93−0.81 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 132.6, 130.2, 74.5, 64.0, 37.3, 32.1, 31.7, 29.2, 28.8, 27.4, 27.2, 22.6, 20.0, 14.1; IR 2929, 2860, 2363, 1473, 1364, 1119, 970, 819, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{19}H_{38}O_2SiNa^+$ 349.2533, found 349.2523.

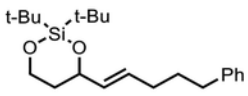
Compound 36.—



(*E*)-2,2-di-*tert*-butyl-4-(3,3-dimethylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 37 mg, 62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dd, J = 15.6, 1.4 Hz, 1H), 5.35 (dd, J = 15.6, 5.3 Hz, 1H), 4.53 (dddd, J = 10.5, 5.3, 2.9, 1.4 Hz, 1H), 4.16−4.00 (m, 2H), 1.82 (dtd, J = 14.3, 10.6, 5.2 Hz, 1H), 1.65 (dq, J = 14.3, 2.8 Hz, 1H), 1.07 (s, 9H), 1.05 (s, 9H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) 140.6, 127.5, 74.4, 63.9, 37.4, 32.5, 29.6, 27.4, 27.2, 22.6, 20.0; IR 2957, 2860, 1473, 1136, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{17}H_{34}O_2SiNa^+$ 321.2236, found 321.2205.

Compound 37.—

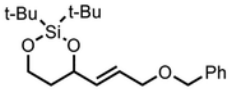


(*E*)-2,2-di-*tert*-butyl-4-(5-phenylpent-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 36.8 mg, 51% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.26 (m, 2H), 7.20 (ddt, J = 7.0, 3.0, 1.6 Hz, 3H), 5.73 (dtd, J = 14.9, 6.7, 1.3 Hz, 1H),

5.51 (ddt, J = 15.3, 5.4, 1.5 Hz, 1H), 4.69−4.44 (m, 1H), 4.21−4.04 (m, 2H), 2.64 (dd, J = 8.7, 6.8 Hz, 2H), 2.18−2.03 (m, 2H), 1.87 (dtd, J = 14.2, 10.9, 5.3 Hz, 1H), 1.75 (tt, J = 7.8, 6.5 Hz, 2H), 1.67 (dq, J = 14.3, 2.6 Hz, 1H), 1.07 (s, 9H), 1.04 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 142.5, 133.2, 129.5, 128.5, 128.3, 125.7, 74.4, 64.1, 37.3, 35.4, 31.6, 31.0, 27.5, 27.2, 22.7, 20.0; IR 2934, 2860, 2363, 1473, 1136, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{22}H_{36}O_2SiNa^+$ 383.2382, found 383.2389.

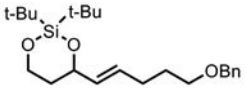
Compound 38.—



(*E*)-4-(3-(benzyloxy)prop-1-en-1-yl)-2,2-di-*tert*-butyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 40.6 mg, 56% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.24 (m, 5H), 5.88 (dtd, J = 15.4, 5.6, 1.4 Hz, 1H), 5.77 (ddt, J = 15.3, 4.6, 1.3 Hz, 1H), 4.61 (dddd, J = 10.7, 4.5, 2.7, 1.3 Hz, 1H), 4.54 (s, 2H), 4.15−4.09 (m, 2H), 4.05 (dq, J = 5.7, 1.1 Hz, 2H), 1.86 (dtd, J = 14.3, 11.0, 5.4 Hz, 1H), 1.69 (dq, J = 14.3, 2.5 Hz, 1H), 1.08 (s, 9H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 138.3, 135.7, 128.4, 127.8, 127.6, 125.4, 73.6, 72.2, 70.2, 64.1, 36.9, 27.4, 27.2, 22.7, 20.0; IR 2934, 2860, 1473, 1364, 1113, 970, 827, 742, 650 cm^{-1}; HRMS (ESI) m/z [M + H^+] calculated for $C_{21}H_{35}O_3Si^+$ 363.2355,, found 363.2316.

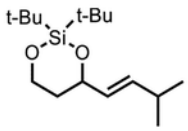
Compound 39.—



(E)-4-(5-(benzyloxy)pent-1-en-1-yl)-2,2-di-tert-butyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using a gradient of 0–2% EtOAc in hexanes on silica gel (light yellow oil, 37.6 mg, 48% yield): ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.41−7.28 (m, 5H), 5.75−5.66 (m, 1H), 5.49 (ddt, J = 15.4, 5.4, 1.6 Hz, 1H), 4.54−4.50 (m, 3H), 4.16−4.05 (m, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.15 (q, J = 7.2 Hz, 2H), 1.87−1.78 (m, 1H), 1.77−1.70 (m, 2H), 1.64 (dq, J = 14.4, 2.7 Hz, 1H), 1.05 (s, 9H) 1.01 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) δ 138.6, 133.2, 129.1, 128.3, 127.6, 127.5, 74.3, 72.8, 69.7, 64.0, 37.1, 29.2, 28.6, 27.4, 27.1, 22.6, 19.9; IR 2934, 2860, 2358, 1473, 1113, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^+] calculated for $C_{23}H_{38}O_3SiNa^+$ 413.2482, found 413.2516.

Compound 40.—

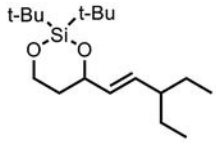


(E)-2,2-di-tert-butyl-4-(3-methylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using a gradient of 0–2% EtOAc in hexanes on silica gel (colorless oil, 28.5 mg, 50% yield): ^{1}H NMR (400 MHz,

chloroform-*d*) δ 5.66 (ddd, *J* = 15.4, 6.4, 1.4 Hz, 1H), 5.42 (ddd, *J* = 15.5, 5.5, 1.4 Hz, 1H), 4.53 (dddd, *J* = 10.3, 4.9, 2.5, 1.3 Hz, 1H), 4.17−4.05 (m, 2H), 2.35−2.26 (m, 1H), 1.90−1.80 (m, 1H), 1.66 (dd, *J* = 14.3, 2.7 Hz, 1H), 1.05 (s, 9H), 1.02 (s, 9H), 1.01 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) δ 136.8, 129.7, 74.4, 63.9, 37.3, 30.4, 27.4, 27.1, 22.5, 22.2, 19.9; IR 3563, 2860, 1473, 1364, 1119, 970, 827, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + H^+] calculated for $C_{16}H_{33}O_2Si^+$ 285.2244, found 285.2234.

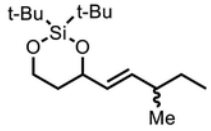
Compound 41.—



(E)-2,2-di-tert-butyl-4-(3-ethylpent-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using a gradient of 0–2% EtOAc in hexanes on silica gel (light yellow oil, 25.5 mg, 40% yield): ^{1}H NMR (400 MHz, chloroform-*d*) δ 5.49−5.36 (m, 2H), 4.56 (dt, *J* = 10.3, 3.1 Hz, 1H), 4.11 (m, 2H), 1.86 (m, 1H), 1.69 (dd, *J* = 14.3, 2.8 Hz, 1H), 1.48−1.37 (m, 2H), 1.33−1.21 (m, 3H), 1.05 (s, 9H), 1.02 (s, 9H), 0.88−0.84 (m, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) δ 133.5, 132.9, 74.1, 63.9, 45.5, 37.3, 27.5, 27.4, 27.1, 22.5, 20.0, 11.7, 11.6; IR 2963, 2860, 1473, 1124, 970, 827, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{18}H_{36}O_2SiNa^+$ 335.2377, found 335.2367.

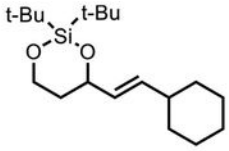
Compound 42.—



(E)-2,2-di-tert-butyl-4-(3-methylpent-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using a gradient of 0 to 2% EtOAc in hexanes on silica gel. Inseparable ~1:1 mixture of diastereomers (light yellow oil, 23.7 mg, 39% yield): ^{1}H NMR (400 MHz, chloroform-*d*) δ 5.59 (m, 1H), 5.45 (ddt, *J* = 15.4, 5.2, 1.2 Hz, 1H), 4.61−4.52 (m, 1H), 4.13 (dqt, *J* = 8.2, 5.2, 2.7 Hz, 2H), 2.10−2.02 (m, 1H), 1.93−1.81 (m, 1H), 1.73−1.66 (m, 1H), 1.39−1.29 (m, 2H), 1.07 (s, 9H), 1.04 (s, 9H), 1.01 (dd, *J* = 6.8, 3.3 Hz, 3H), 0.89 (td, *J* = 7.4, 3.9 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) δ 135.4, 131.1, 131.0, 74.3, 74.2, 63.9, 37.7, 37.6, 37.4, 37.3, 29.7, 29.6, 27.4, 27.1, 22.5, 20.0, 19.9, 19.8, 11.7, 11.6; IR 2963, 2860, 2370, 1473, 1124, 970, 827, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + H^+] calculated for $C_{17}H_{35}O_2Si^+$ 299.2406, found 299.2415.

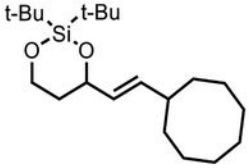
Compound 43.—



(*E*)-2,2-di-*tert*-butyl-4-(2-cyclohexylvinyl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 38.9 mg, 60% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (ddd, J = 15.5, 6.4, 1.3 Hz, 1H), 5.41 (ddd, J = 15.5, 5.5, 1.4 Hz, 1H), 4.51 (dddd, J = 10.3, 5.0, 3.1, 0.9 Hz, 1H), 4.09 (pt, J = 5.3, 2.4 Hz, 2H), 2.03−1.89 (m, 1H), 1.83 (dtd, J = 14.4, 10.7, 5.2 Hz, 1H), 1.77−1.68 (m, 4H), 1.65 (dq, J = 14.3, 2.7 Hz, 2H), 1.35−1.07 (m, 5H), 1.09 (s, 9H), 1.08 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.7, 130.2, 74.5, 64.0, 40.0, 37.3, 32.90, 32.87, 27.4, 27.2, 26.2, 26.1, 22.6, 20.0; IR 2929, 2854, 1473, 1364, 1130, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + H^{+}] calculated for $C_{19}H_{37}O_2Si^{+}$ 325.2557, found 325.2560.

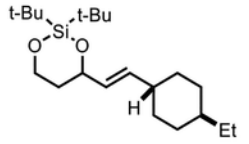
Compound 44.—



(*E*)-2,2-di-*tert*-butyl-4-(2-cyclooctylvinyl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 36.7 mg, 52% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (ddd, J = 15.4, 7.2, 1.3 Hz, 1H), 5.39 (ddd, J = 15.4, 5.5, 1.2 Hz, 1H), 4.62−4.35 (m, 1H), 4.25−3.92 (m, 2H), 2.29−2.13 (m, 1H), 1.83 (dtd, J = 14.3, 10.7, 5.2 Hz, 1H), 1.66 (tdd, J = 15.5, 4.5, 2.4 Hz, 5H), 1.60−1.33 (m, 10H), 1.07 (s, 9H), 1.04 (s, 9H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.7, 129.8, 74.5, 64.0, 40.2, 37.4, 31.9, 31.7, 27.4, 27.39, 27.44, 26.0, 25.09, 25.07, 22.6, 20.0; IR 2920, 2860, 2358, 1473, 1141, 970, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{21}H_{40}O_2SiNa^{+}$ 375.2695, found 375.2686.

Compound 45.—

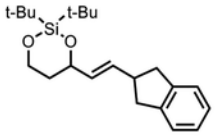


2,2-di-*tert*-butyl-4-((*E*)-2-(4-ethylcyclohexyl)vinyl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless solid, 36 mg, 51% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (ddd, J = 15.5, 6.5, 1.3 Hz, 1H), 5.41 (ddd, J = 15.4, 5.5, 1.3 Hz, 1H), 4.60−4.44 (m, 1H), 4.19−3.97 (m, 2H), 1.94−1.69 (m, 6H), 1.65 (dq, J = 14.3, 2.7 Hz, 1H), 1.29−1.14 (m, 2H), 1.13−0.96 (m, 21H), 0.96−0.80 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.7, 130.2, 74.5, 64.0, 40.4, 39.1, 37.3, 32.8, 32.82, 32.79, 30.0, 27.4, 27.2, 22.6, 20.0, 11.5; IR 2960,

2854, 2363, 1473, 1244, 1130, 970, 890, 827, 776 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{21}H_{40}O_2SiNa^+$ 375.2690, found 375.2690.

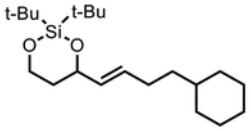
Compound 46.—



(*E*)-2,2-di-*tert*-butyl-4-(2-(2,3-dihydro-1*H*-inden-2-yl)vinyl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless solid, 35 mg, 49% yield): ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.20 (qd, *J* = 4.0, 2.7 Hz, 2H), 7.18−7.11 (m, 2H), 5.87 (ddd, *J* = 15.2, 7.1, 1.4 Hz, 1H), 5.59 (ddd, *J* = 15.3, 5.5, 0.9 Hz, 1H), 4.57 (dddd, *J* = 10.6, 5.3, 2.8, 1.3 Hz, 1H), 4.22−4.00 (m, 2H), 3.22−2.97 (m, 3H), 2.89−2.70 (m, 2H), 1.88 (dtd, *J* = 14.3, 10.7, 5.4 Hz, 1H), 1.75−1.61 (m, 1H), 1.09 (s, 9H), 1.07 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 143.15, 143.12, 133.1, 132.2, 126.2, 124.34, 124.31, 74.3, 64.0, 42.9, 39.5, 37.2, 27.5, 27.2, 22.6, 20.0; IR 2934, 2860, 2363, 1473, 1136, 970, 827, 742, 650 cm^{-1}; HRMS calculated for $C_{22}H_{34}O_2SiNa^+$ 381.2220, found 381.2223.

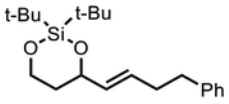
Compound 47.—



(E)-2,2-di-tert-butyl-4-(4-cyclohexylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using a gradient of 0–2% EtOAc in hexanes on silica gel (light yellow oil, 33 mg, 46% yield): ^1H NMR (400 MHz, chloroform-*d*) *δ* 5.72−5.65 (m, 1H), 5.47 (ddt, *J* = 15.3, 5.7, 1.5 Hz, 1H), 4.58−4.46 (m, 1H), 4.17−4.06 (m, 2H), 2.11−1.99 (m, 2H), 1.90−1.78 (m, 1H), 1.76−1.61 (m, 6H), 1.32−1.13 (m, 6H), 1.05 (s, 9H), 1.03 (s, 9H), 0.95−0.82 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, chloroform-*d*) *δ* 132.4, 130.4, 74.4, 64.0, 37.24, 37.22, 36.8, 33.3, 33.2, 29.4, 27.4, 27.2, 26.7, 26.4, 22.6, 19.9; IR 2923, 2854, 2358, 1470, 1124, 970, 827, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{21}H_{40}O_2SiNa^+$ 375.2690, found 375.2691.

Compound 48.—

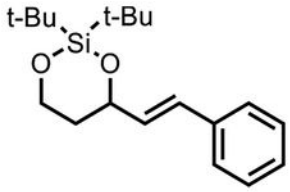


(*E*)-2,2-di-*tert*-butyl-4-(4-phenylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 37 mg, 54% yield): ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.39−7.26 (m, 2H), 7.25−7.12 (m, 3H), 5.77 (dtd, *J* = 14.9, 6.7, 1.4 Hz, 1H), 5.52 (ddt, *J* = 15.3, 5.5, 1.4 Hz, 1H), 4.55 (dddd, *J* = 11.9, 6.6, 2.6, 1.3 Hz, 1H), 4.24−3.98 (m, 2H), 2.90−2.61 (m, 2H), 2.52−2.31 (m, 2H), 1.85 (dtd, *J* = 14.4, 10.9, 5.3 Hz, 1H), 1.65 (dq, *J* =

14.3, 2.6 Hz, 1H), 1.08 (s, 9H), 1.05 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 141.9, 133.4, 128.9, 128.5, 128.3, 125.8, 74.3, 64.1, 37.2, 35.7, 34.0, 27.4, 27.2, 22.7, 20.0; IR 2934, 2869, 1473, 1364, 1101, 970, 890, 827, 747, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{21}H_{34}O_2SiNa^+$ 369.2220, found 369.2191.

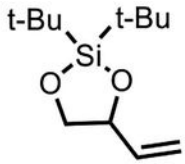
Compound 49.—



(*E*)-2,2-di-*tert*-butyl-4-styryl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel (colorless oil, 34.4 mg, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.36 (m, 2H), 7.36−7.28 (m, 2H), 7.26−7.19 (m, 1H), 6.66 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.22 (dd, *J* = 15.8, 5.1 Hz, 1H), 4.77 (dddd, *J* = 10.8, 4.7, 2.7, 1.6 Hz, 1H), 4.24−4.10 (m, 2H), 1.95 (dtd, *J* = 14.3, 11.2, 4.9 Hz, 1H), 1.78 (dq, *J* = 14.3, 2.6 Hz, 1H), 1.08 (s, 9H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$) δ 137.0, 132.3, 128.6, 128.5, 127.4, 126.5, 74.3, 64.1, 37.0, 27.5, 27.2, 22.7, 20.1; IR 2934, 2860, 2358, 1473, 1136, 970, 827, 650 cm^{-1}; HRMS (APCI) *m*/*z* [M − H] calculated for $C_{19}H_{29}O_2Si$ 317.1942, found 317.1942.

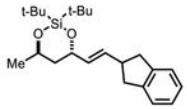
Compound 50.—



2,2-di-*tert*-butyl-4-vinyl-1,3,2-dioxasilolane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single diastereomer (colorless oil, 20 mg, 44% yield): ^{1}H NMR (400 MHz, acetone-d_6) δ 5.17−5.00 (m, 1H), 4.57 (ddt, *J* = 17.1, 2.1, 1.1 Hz, 1H), 4.35 (ddt, *J* = 10.5, 2.3, 1.1 Hz, 1H), 3.78 (dtd, *J* = 9.3, 6.1, 1.2 Hz, 1H), 3.34 (ddd, *J* = 9.2, 6.3, 0.9 Hz, 1H), 2.70 (t, *J* = 9.4 Hz, 1H), 0.26 (2 s, 18H); $^{13}C\{^{1}H\}$ NMR (101 MHz, acetone-d_6) δ 138.5, 115.8, 77.1, 70.3, 27.4, 27.3, 21.6, 21.3; IR 2934, 2860, 2358, 1650, 1473, 1050, 873, 827, 656 cm^{-1}; HRMS (APCI) *m*/*z* [M + H^+] calculated for $C_{12}H_{25}O_2Si^+$ 229.1618, found 229.1617.

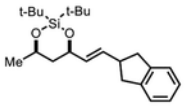
Compound 51.—



(4*S**,6*R**)-2,2-di-*tert*-butyl-4-((*E*)-2-(2,3-dihydro-1*H*-inden-2-yl)vinyl)-6-methyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *anti* diastereomer (colorless oil, 33 mg, 44% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (qd, J = 4.3, 2.1 Hz, 2H), 7.18−7.09 (m, 2H), 5.87 (ddd, J = 15.3, 7.0, 1.4 Hz, 1H), 5.66 (ddd, J = 15.2, 5.8, 0.9 Hz, 1H), 4.67 (tdd, J = 5.9, 4.2, 1.3 Hz, 1H), 4.34 (td, J = 6.3, 4.0 Hz, 1H), 3.21−3.01 (m, 3H), 2.79 (dt, J = 14.7, 7.4 Hz, 2H), 1.81 (qdd, J = 14.4, 6.1, 4.2 Hz, 2H), 1.28 (d, J = 6.3 Hz, 3H), 1.05 (s, 9H), 1.03 (s, 9H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 143.3, 143.2, 133.9, 132.2, 126.4, 126.3, 124.5, 124.4, 70.6, 66.5, 43.1, 41.7, 39.63, 39.62, 27.5, 27.4, 24.2, 21.2, 21.0; IR 2934, 2860, 2358, 1473, 1141, 982, 822, 742, 650 cm^{-1}; HRMS (APCI) m/z [M + H$^+$] calculated for $C_{23}H_{37}O_2Si^+$ 373.2557, found 373.2546.

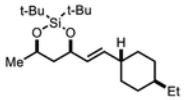
Compound 52.—



(4*R**,6*R**)-2,2-di-*tert*-butyl-4-((*E*)-2-(2,3-dihydro-1*H*-inden-2-yl)vinyl)-6-methyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *syn* diastereomer (colorless oil, 50 mg, 67% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.16 (m, 2H), 7.16−7.10 (m, 2H), 5.84 (ddd, J = 15.2, 7.1, 1.4 Hz, 1H), 5.54 (ddd, J = 15.1, 5.5, 0.9 Hz, 1H), 4.53 (dddd, J = 11.3, 5.5, 2.5, 1.3 Hz, 1H), 4.35−3.98 (m, 1H), 3.21−2.90 (m, 3H), 2.77 (ddd, J = 15.2, 7.5, 4.7 Hz, 2H), 1.63 (dt, J = 14.1, 2.4 Hz, 1H), 1.56−1.42 (m, 1H), 1.21 (d, J = 6.1 Hz, 3H), 1.04 (s, 9H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 143.29, 133.0, 132.6, 126.3 (2C), 124.5, 124.4, 74.2, 67.0, 44.6, 43.0, 39.7, 27.7, 27.5, 27.4, 25.9, 22.8, 19.8; IR 2934, 2323, 1650, 1473, 1147, 982, 827, 742, 650 cm^{-1}; HRMS (ESI) m/z [M + Na$^+$] calculated for $C_{23}H_{36}O_2SiNa^+$ 395.2377, found 395.2382.

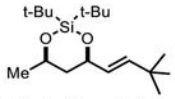
Compound 53.—



(4*R**,6*R**)-2,2-di-*tert*-butyl-4-((*E*)-2-((1*r*,4*R*)-4-ethylcyclohexyl)vinyl)-6-methyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *syn* diastereomer (colorless oil, 33 mg, 45% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (ddd, J = 15.4, 6.7, 1.3 Hz, 1H), 5.46−5.27 (m, 1H), 4.56−4.36 (m, 1H), 4.21 (ddd, J = 11.1, 6.1, 2.2 Hz, 1H), 1.94−1.82 (m, 1H), 1.76 (td, J = 11.1, 9.1, 4.5 Hz, 4H), 1.60 (dt, J = 14.1, 2.5 Hz, 1H), 1.55−1.43 (m, 1H), 1.20 (dd, J = 12.4, 6.5 Hz, 6H), 1.11−0.96 (m, 20H), 0.87 (t, J = 7.4 Hz, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.5, 130.6, 74.4, 69.9, 44.7, 40.4, 39.2, 32.98, 32.96, 32.7, 30.1, 27.6, 27.4, 24.9, 22.7, 19.8, 11.6; IR 2929, 2854, 2358, 1473, 1376, 1141, 982, 827, 650 cm^{-1}; HRMS (APCI) m/z [M + H$^+$] calculated for $C_{22}H_{43}O_2Si^+$ 367.3027, found 367.3032.

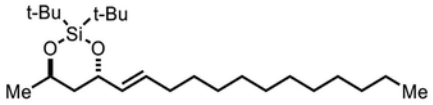
Compound 54.—



2,2-di-tert-butyl-4-((E)-3,3-dimethylbut-1-en-1-yl)-6-methyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *syn* diastereomer with relative stereochemistry assigned by NOE data (colorless oil, 38.8 mg, 62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dd, J = 15.6, 1.4 Hz, 1H), 5.31 (dd, J = 15.6, 5.4 Hz, 1H), 4.49 (dddd, J = 11.4, 5.3, 2.6, 1.4 Hz, 1H), 4.22 (dqd, J = 12.2, 6.1, 2.2 Hz, 1H), 1.60 (dt, J = 14.1, 2.4 Hz, 1H), 1.46 (dt, J = 14.1, 11.2 Hz, 1H), 1.19 (d, J = 6.1 Hz, 3H), 1.11−0.90 (m, 27H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.3, 127.8, 74.3, 69.8, 44.7, 32.5, 29.6, 27.5, 27.3, 24.8, 22.6, 19.7; IR 2934, 2860, 2358, 1473, 1364, 1147, 1096, 976, 827, 650 cm^{-1}; HRMS (APCI) m/z [M + H^{+}] calculated for $C_{18}H_{37}O_2Si^{+}$ 313.2557, found 313.2551.

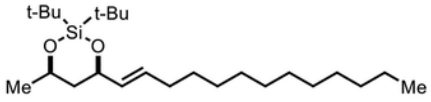
Compound 55.—



2,2-di-tert-butyl-4-methyl-6-((E)-tridec-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *anti* diastereomer, assigned on the basis of a lack of NOE enhancements and by analogy to the *syn* diastereomer (colorless oil, 40.3 mg, 49% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74−5.60 (m, 1H), 5.54 (ddt, J = 15.3, 5.9, 1.3 Hz, 1H), 4.62 (q, J = 5.7 Hz, 1H), 4.33 (td, J = 6.3, 4.0 Hz, 1H), 2.08−1.98 (m, 2H), 1.83 (ddd, J = 14.4, 6.2, 4.0 Hz, 1H), 1.74 (ddd, J = 14.4, 6.0, 4.3 Hz, 1H), 1.27 (q, J = 3.1, 2.2 Hz, 21H), 1.05−0.99 (overlapping singlets, 18H), 0.9−0.8 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.7, 130.9, 70.8, 66.6, 41.8, 32.3, 32.1, 29.9, 29.83, 29.81, 29.79, 29.7, 29.5, 29.4, 27.52, 27.46, 24.2, 22.9, 21.2, 21.0, 14.3; IR 2934, 2854, 2358, 1473, 1376, 1136, 982, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{25}H_{50}O_2SiNa^{+}$ 433.3472, found 433.3483.

Compound 56.—

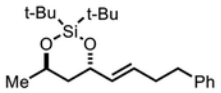


2,2-di-tert-butyl-4-methyl-6-((E)-tridec-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *syn* diastereomer, assigned on the basis of observed NOE enhancements (colorless oil, 32.9 mg, 40% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74−5.58 (m, 1H), 5.48−5.35 (m, 1H), 4.48 (dddd, J = 11.2, 5.5, 2.4, 1.2 Hz, 1H), 4.22 (ddd, J = 11.1, 6.1, 2.3 Hz, 1H), 2.02 (dddt, J = 9.9, 7.2, 6.0, 1.2 Hz, 2H), 1.64−1.57 (m, 1H), 1.47 (d, J = 14.1 Hz, 1H), 1.37−1.21 (m, 18H), 1.19 (d, J = 6.1 Hz, 3H), 1.03 (s, 9H), 0.99 (s, 9H), 0.92−0.85 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.0, 130.1, 74.4, 70.0, 44.7, 32.3, 32.1, 29.86, 29.82, 29.80, 29.78, 29.5, 29.4, 29.3, 27.7, 27.4, 25.0, 22.9, 22.8, 19.8,

14.3; IR 2934, 2854, 2358, 1467, 1376, 1147, 982, 827, 650 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{25}H_{50}O_2SiNa^+$ 433.3472, found 433.3463.

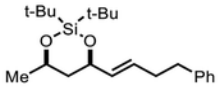
Compound 57.—



2,2-di-*tert*-butyl-4-methyl-6-((*E*)-4-phenylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *anti* diastereomer, assigned on the basis of a lack of NOE and by analogy to the *syn* diastereomer (colorless oil, 57.7 mg, 80% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 2H), 7.23−7.12 (m, 3H), 5.73 (dtd, *J* = 14.6, 6.6, 1.3 Hz, 1H), 5.56 (ddt, *J* = 15.3, 5.8, 1.4 Hz, 1H), 4.62 (q, *J* = 5.6 Hz, 1H), 4.29 (td, *J* = 6.2, 4.1 Hz, 1H), 2.78−2.64 (m, 2H), 2.44−2.30 (m, 2H), 1.79 (ddd, *J* = 14.4, 6.4, 4.1 Hz, 1H), 1.71 (ddd, *J* = 14.4, 5.8, 4.3 Hz, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.03 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.9, 133.4, 129.4, 128.5, 128.3, 125.8, 70.4, 66.5, 41.5, 35.6, 33.9, 27.4, 27.3, 24.0, 21.0, 20.9; IR 2934, 2860, 1743, 1141, 982, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + H^+] calculated for $C_{22}H_{37}O_2Si^+$ 361.2563, found 361.2580.

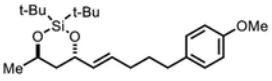
Compound 58.—



2,2-di-*tert*-butyl-4-methyl-6-((*E*)-4-phenylbut-1-en-1-yl)-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane (colorless oil, 36.8 mg, 54% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.24 (m, 2H), 7.24−7.13 (m, 3H), 5.74 (dtd, *J* = 14.9, 6.7, 1.4 Hz, 1H), 5.51−5.44 (m, 1H), 4.50 (dddd, *J* = 11.1, 5.2, 2.2, 1.1 Hz, 1H), 4.28−4.13 (m, 1H), 2.81−2.58 (m, 2H), 2.36 (dtt, *J* = 10.0, 7.7, 1.2 Hz, 2H), 1.59 (dt, *J* = 14.1, 2.4 Hz, 1H), 1.51−1.42 (m, 1H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.04 (s, 9H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.0, 133.5, 128.7, 128.5, 128.3, 125.8, 74.1, 69.9, 44.4, 35.7, 34.0, 27.5, 27.3, 24.8, 22.7, 19.7; IR 2934, 2860, 2363, 1473, 1141, 982, 827 cm^{-1}; HRMS (ESI) *m*/*z* [M + H^+] calculated for $C_{22}H_{37}O_2Si^+$ 361.2563, found 361.2560.

Compound 59.—

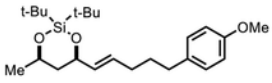


2,2-di-*tert*-butyl-4-((*E*)-5-(4-methoxyphenyl)pent-1-en-1-yl)-6-methyl-1,3,2-dioxasilinane

Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *anti* diastereomer, assigned by lack of NOE and by analogy to the *syn* diastereomer (colorless oil, 32.4 mg, 40% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.03 (m, 2H), 6.96−6.72 (m, 2H), 5.79−5.65 (m, 1H), 5.59−5.53 (m, 1H), 4.63 (q, *J* = 5.6 Hz, 1H), 4.33 (tt, *J* = 6.4, 3.4 Hz, 1H), 3.79 (d, *J* = 1.1 Hz, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.81 (d, *J* = 2.3 Hz, 1H), 1.78−1.63 (m, 3H), 1.27 (dd, *J* = 6.2,

1.0 Hz, 3H), 1.03 (s, 9H), 1.02 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7, 134.5, 133.1, 130.1, 129.3, 113.7, 70.5, 66.5, 55.3, 41.6, 34.5, 31.6, 31.1, 27.4, 27.3, 24.0, 21.1, 20.9; IR 2934, 2854, 2358, 1513, 1473, 1244, 1136, 922, 842, 650; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{24}H_{40}O_3SiNa^+$ 427.2639, found 427.2626.

Compound 60.—



2,2-di-*tert*-butyl-4-((*E*)-5-(4-methoxyphenyl)pent-1-en-1-yl)-6-methyl-1,3,2-dioxasilinane

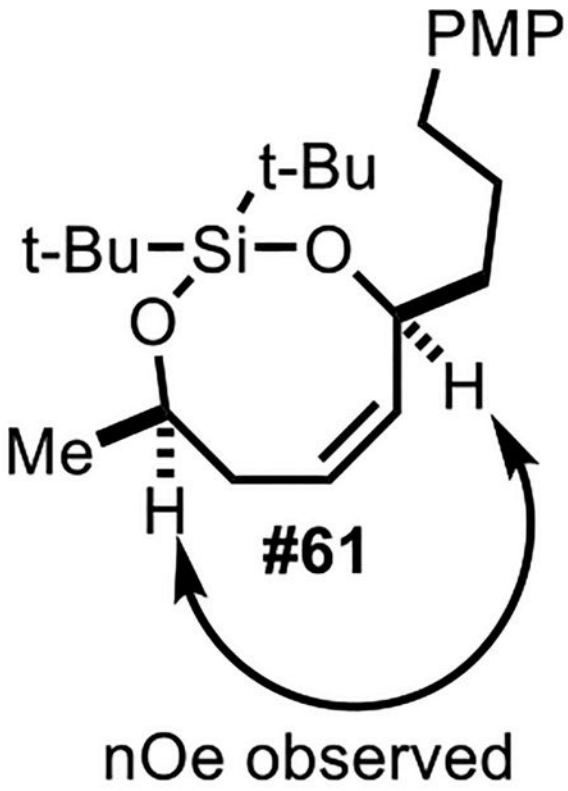
Synthesized using procedure B on a 0.2 mmol scale and purified using 1.5% ethyl acetate in hexane on silica gel; single *syn* diastereomer, relative stereochemistry assigned using NOE data (colorless oil, 56.6 mg, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2−7.0 (m, 2H), 6.9−6.8 (m, 2H), 5.7 (dtd, *J* = 14.9, 6.7, 1.3 Hz, 1H), 5.4 (ddt, *J* = 15.3, 5.5, 1.4 Hz, 1H), 4.6−4.4 (m, 1H), 4.2 (ddd, *J* = 11.1, 6.0, 2.3 Hz, 1H), 3.8 (s, 3H), 2.6 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.1 (q, *J* = 7.6 Hz, 2H), 1.7 (tt, *J* = 8.4, 6.8 Hz, 2H), 1.6−1.6 (m, 1H), 1.5 (dt, *J* = 14.0, 11.2 Hz, 1H), 1.2 (d, *J* = 6.1 Hz, 3H), 1.03 (s, 9H), 1.00 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7, 134.6, 133.3, 129.33, 129.27, 113.7, 74.2, 69.8, 55.3, 44.5, 34.5, 31.6, 31.2, 27.5, 27.3, 24.8, 22.6, 19.7; IR 2934, 2854, 2358, 1513, 1244, 1141, 976, 822 cm^{-1}; HRMS (ESI) *m*/*z* [M + Na^+] calculated for $C_{24}H_{40}O_3SiNa^+$ 427.2644, found 427.2658.

Structural Reasoning.

One challenge in this project was determining the relative stereochemistry of the linear diastereomeric starting materials (Scheme 5). Determining the relative stereochemistry was crucial to understand the mechanism of the subsequent palladium-catalyzed stereospecific cyclization. After several failed crystallization attempts of the starting silanols and ester derivatives, silocines were prepared for NOE studies.

(2*R**,6*S**,Z)-9-(4-Methoxyphenyl)non-4-ene-2,6-diol (43 mg, 0.162 mmol, 1 equiv) was dissolved in 2 mL of CH_2Cl_2 and transferred to a 10 mL round-bottom flask equipped with a magnetic stir bar, kept under a N_2 atmosphere. Freshly distilled 2,6-lutidine (75.4 μL, 0.65 mmol, 4 equiv) was added, followed by (*t*-Bu)$_2$Si(OTf)$_2$ (58.3 μL, 0.18 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 12 h and then quenched by addition of a saturated aqueous NH_4Cl solution (3 mL). After transfer to a separatory funnel, the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic fractions were collected, dried over sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by chromatography on silica gel to give **61** (colorless oil, 30 mg, 0.074 mmol, 41% yield). Note: the column was packed with a slurry of silica gel in hexanes containing 0.5% NEt_3.

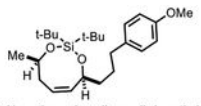
Compound 61.—



Purified using 0–1.5% ethyl acetate in hexane on silica gel; single diastereomer (colorless oil, 30 mg, 41% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.03 (m, 2H), 6.95−6.68 (m, 2H), 5.83−5.53 (m, 2H), 4.67−4.49 (m, 1H), 4.49−4.34 (m, 1H), 3.79 (s, 3H), 2.72−2.42 (m, 3H), 2.36−2.11 (m, 1H), 1.82 (m, J = 11.1, 8.2, 4.9, 1.1 Hz, 1H), 1.77−1.46 (m, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.01 (s, 9H), 0.94 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 137.2, 134.9, 129.4, 128.2, 113.8, 70.5, 69.4, 55.4, 37.9, 36.7, 35.0, 28.3, 28.0, 27.9, 23.7, 22.2, 20.2; IR 2920, 2860, 2380, 1620, 1520, 1250, 1140, 1070, 830, 744, 650 cm^{-1}; HRMS (APCI) m/z [M + H^{+}] calculated for $C_{24}H_{41}O_3Si^{+}$405.2825, found 405.2797.

(2*R**,6*R**,*Z*)-9-(4-Methoxyphenyl)non-4-ene-2,6-diol (30 mg, 0.114 mmol, 1 equiv) was dissolved in 2 mL of CH_2Cl_2 and transferred to a 10 mL round-bottom flask equipped with a magnetic stir bar, kept under a N_2 atmosphere. Freshly distilled 2,6-lutidine (53 μL, 0.45 mmol, 4 equiv) was added, followed by (t-Bu)$_2$Si(OTf)$_2$ (40.7 μL, 0.125 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 12 h and then quenched by addition of a saturated aqueous NH_4Cl solution (3 mL). After transfer to a separatory funnel, the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic fractions were collected, dried over sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by chromatography on silica gel to give **67** (colorless oil, 24 mg, 0.059 mmol, 52% yield). Note: the column was packed with a slurry of silica gel in hexanes containing 0.5% NEt_3.

Compound 67.—



(4R*,8S*,Z)-2,2-di-tert-butyl-8-(3-(4-methoxyphenyl)propyl)-4-methyl-5,8-dihydro-4H-1,3,2-dioxasilocine

Purified using 0–1.5% ethyl acetate in hexane (colorless oil, 24 mg, 35% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.04 (m, 2H), 6.90−6.73 (m, 2H), 5.73−5.56 (m, 2H), 4.56−4.38 (m, 1H), 4.17 (ddd, J = 8.0, 6.2, 2.0 Hz, 1H), 3.79 (s, 3H), 2.65−2.52 (m, 2H), 2.42−2.26 (m, 1H), 2.18 (dt, J = 13.4, 7.4 Hz, 1H), 1.84−1.70 (m, 1H), 1.70−1.48 (m, 3H), 1.21 (d, J = 6.2 Hz, 3H), 0.99 (s, 9H), 0.96 (s, 9H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 137.4, 134.9, 129.4, 127.8, 113.8, 71.4, 69.1, 55.4, 37.3, 37.1, 35.1, 28.6, 28.0, 27.9, 24.4, 21.2, 20.9; IR 2920, 2860, 2380, 1610, 1520, 1240, 1170, 1040, 830, 750, 645 cm^{-1}; HRMS (APCI) m/z [M + H^{+}] calculated for $C_{24}H_{41}O_3Si^{+}$ 405.2825, found 405.2816.

Scheme 7: procedures and Characterization.

Olefin Cross-Metathesis Reaction.—A 10 mL microwave vial was charged with **33** (49 mg, 0.2 mmol, 1 equiv), ethyl acrylate (100 mg, 1 mmol, 5 equiv), CH_2Cl_2 (4 mL, 0.05 M reaction concentration), and a magnetic stir bar. Then, the Hoveyda–Grubbs second-generation catalyst (6 mg, 0.01 mmol, 0.05 equiv) was added to the reaction mixture. The reaction vial was sealed and submerged in an oil bath preheated to 50 °C, and the reaction mixture was stirred at this temperature for 24 h. Following this time, the solvent was removed *in vacuo,* and the resulting residue was purified by chromatography on silica gel to give **62** (colorless oil, 37 mg, 0.118 mmol, 59% yield).

Compound 62.—Purified using 4% ethyl acetate in hexane on silica gel (colorless oil, 37 mg, 59% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, J = 15.3, 3.5 Hz, 1H), 6.12 (dd, J = 15.3, 2.0 Hz, 1H), 4.75 (dtd, J = 11.0, 3.1, 2.0 Hz, 1H), 4.40−3.94 (m, 4H), 1.91−1.70 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.03 (s, 9H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.9, 149.6, 119.7, 72.9, 64.3, 60.5, 36.0, 27.5, 27.3, 22.9, 20.1, 14.4; IR 2934, 2860, 2358, 1730, 1620, 1250, 1101, 930, 850, 730, 645 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{16}H_{30}O_4SiNa^{+}$ 337.1811, found 337.1838.

Dihydroxylation.—A 10 mL reaction vial was sequentially charged with $K_2OsO_4{\cdot}2H_2O$ (7.4 mg, 0.02 mmol, 0.1 equiv), NMO·H_2O (47 mg, 0.35 mmol, 1.75 equiv), 2 mL of tBuOH/H_2O (3/1 mixture), and **48** (69 mg, 0.2 mmol, 1 equiv). The reaction vial was sealed, and the reaction mixture was stirred at room temperature for 2 h. Following this time, the reaction was quenched with 2 mL of a saturated aqueous $Na_2S_2O_3$ solution and transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the organic fractions were collected and dried with $MgSO_4$. After concentration *in vacuo*, the resulting residue was purified by chromatography on silica gel to give **63** and **64** (separable 7:1 mixture of diastereomers, 59 mg combined, 0.155 mmol, 77% combined yield).

Compounds 63 and 64.—Purified using 5–15% ethyl acetate in hexane on silica gel (7:1 dr, 59 mg, 77% yield);

Compound 63.—Major diastereomer (colorless oil, 51 mg, 67% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.24−7.14 (m, 3H), 4.23−4.05 (m, 3H), 3.92 (ddd, J = 8.7, 4.6, 2.1 Hz, 1H), 3.31 (dd, J = 5.8, 2.2 Hz, 1H), 2.84 (ddd, J = 14.6, 9.3, 5.6 Hz, 1H), 2.71 (ddd, J = 13.8, 9.2, 7.0 Hz, 1H), 2.63 (s, 2H), 2.07−1.55 (m, 4H), 1.04 (s, 9H), 0.99 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 128.6, 128.5, 126.0, 76.5, 76.1, 69.7, 64.5, 35.3, 32.9, 32.1, 27.6, 27.2, 22.8, 20.0; IR 3420, 2934, 2860, 2358, 1473, 1101, 976, 822, 747, 645 cm^{-1}; HRMS (ESI) m/z [M +N a^{+}] calculated for $C_{21}H_{36}O_4SiNa^{+}$ 403.2275, found 403.2253.

Compound 64.—Minor diastereomer (colorless oil, 8 mg, 10% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.25 (m, 2H), 7.25−7.16 (m, 3H), 4.22 (ddd, J = 11.3, 3.5, 2.1 Hz, 1H), 4.13 (dq, J = 7.0, 2.4 Hz, 2H), 3.76 (ddd, J = 8.9, 4.4, 1.9 Hz, 1H), 3.25 (dd, J = 3.5, 2.0 Hz, 1H), 2.84 (ddd, J = 14.6, 9.6, 5.5 Hz, 1H), 2.71 (ddd, J = 13.8, 9.5, 6.9 Hz, 1H), 2.19 (dtd, J = 14.3, 11.0, 6.5 Hz, 1H), 2.00 (dtd, J = 14.4, 9.1, 5.4 Hz, 1H), 1.81 (dddd, J = 13.9, 9.7, 6.9, 4.4 Hz, 1H), 1.55 (dq, J = 14.4, 2.3 Hz, 1H), 1.03 (s, 9H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 128.6, 128.5, 126.0, 77.6, 75.6, 72.3, 64.2, 35.8, 32.6, 32.1, 27.5, 27.2, 22.9, 20.2; IR 3482, 2934, 2860, 2358, 1473, 1141, 1007, 970, 896, 827, 650 cm^{-1}; HRMS (ESI) m/z [M + Na^{+}] calculated for $C_{21}H_{36}O_4SiNa^{+}$ 403.2275, found 403.2269.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

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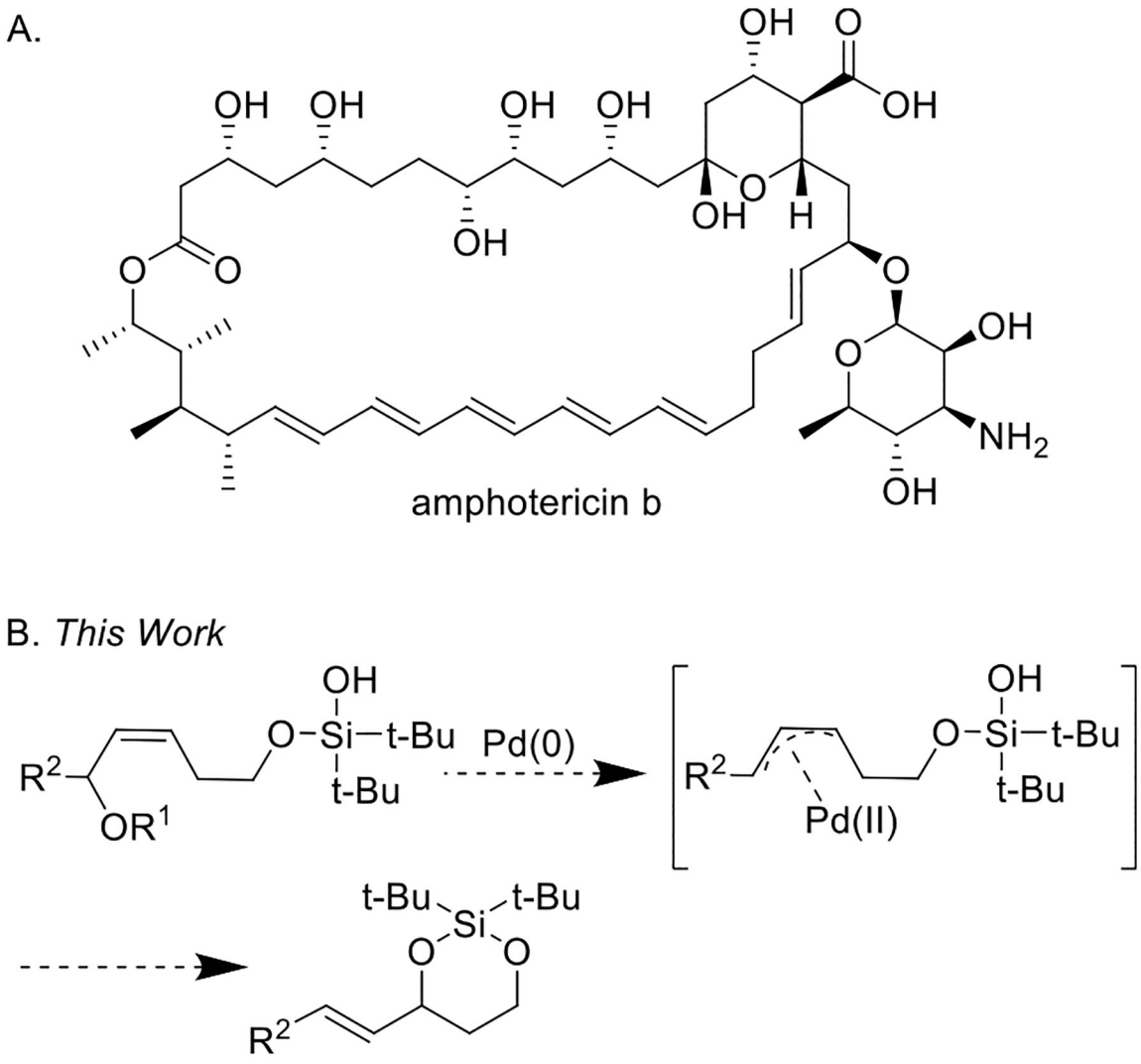
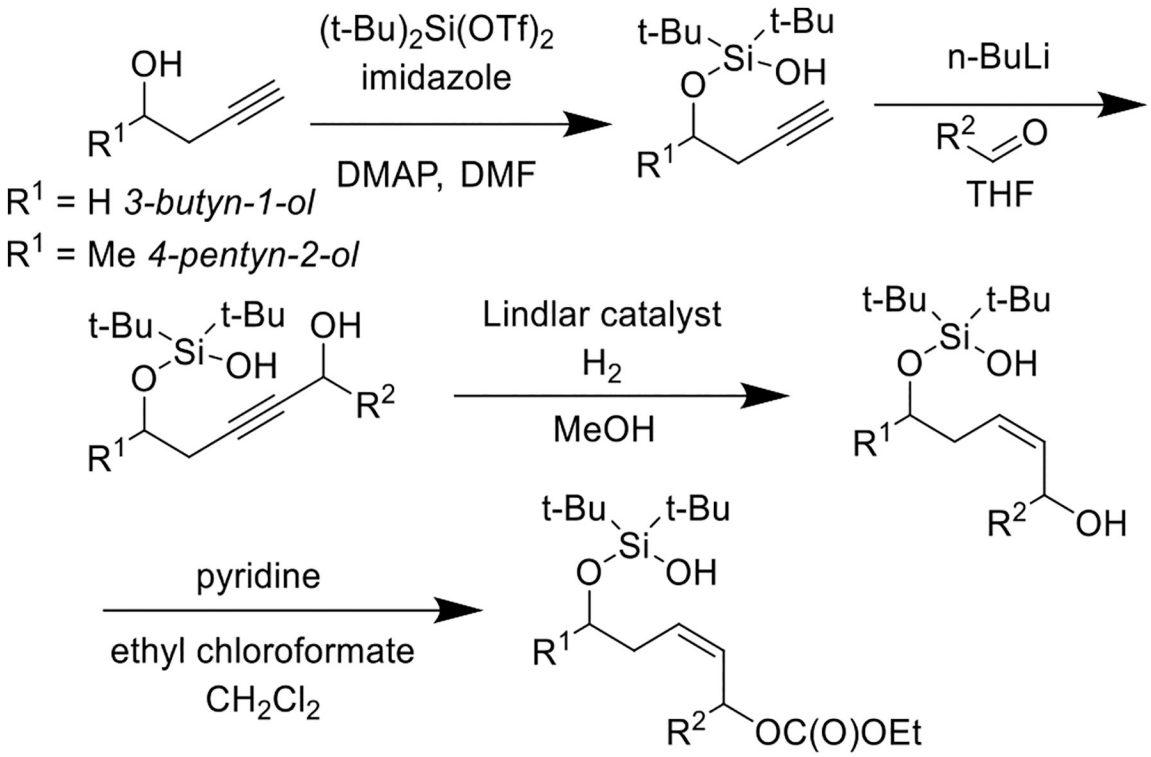
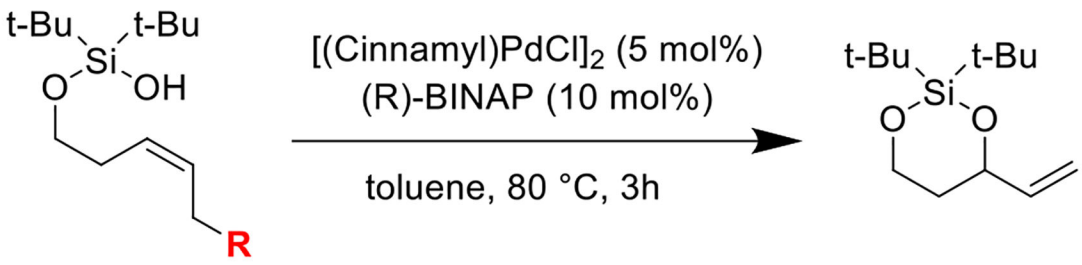


Scheme 1.

(A) Polyhydroxylated and Stereochemically Complex Biologically Active Molecules and (B) Potentially Mild and Highly Selective Method for Protected 1,3-Diol Formation

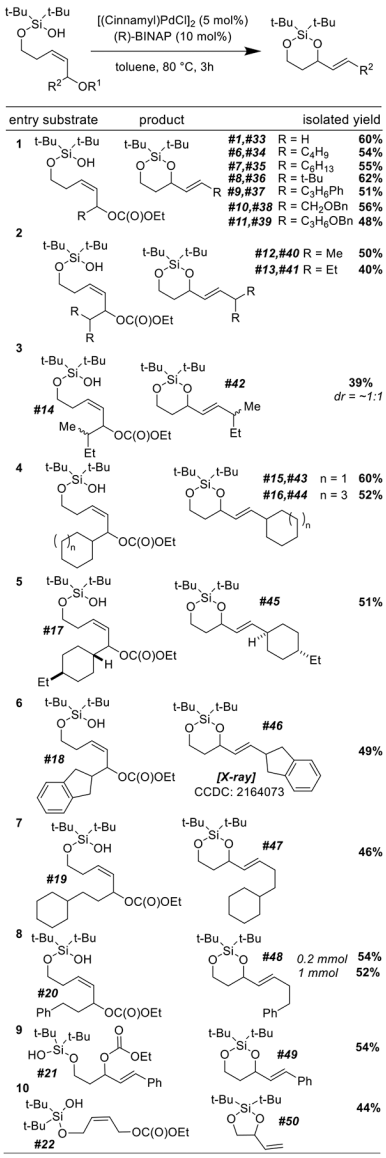


Scheme 2.
Typical Sequence for Starting Material Preparation

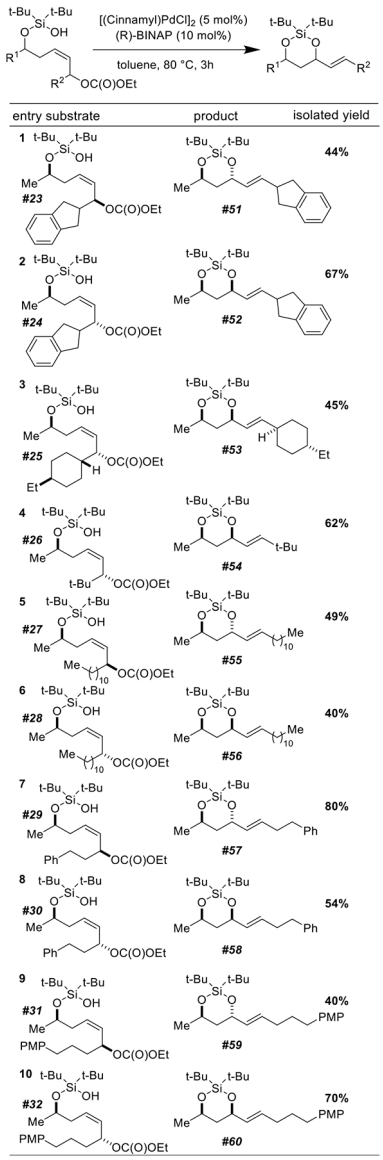


Entry	Leaving Group	Isolated Yield
1	R = OC(O)OEt	**60%**
2	R = OC(O)Ot-Bu	**43%**
3	R = OC(O)Me	**15%**
4	R = OC(O)Ph	**Trace**
5	R = $OC(O)OCH_2CCl_3$	**Trace**

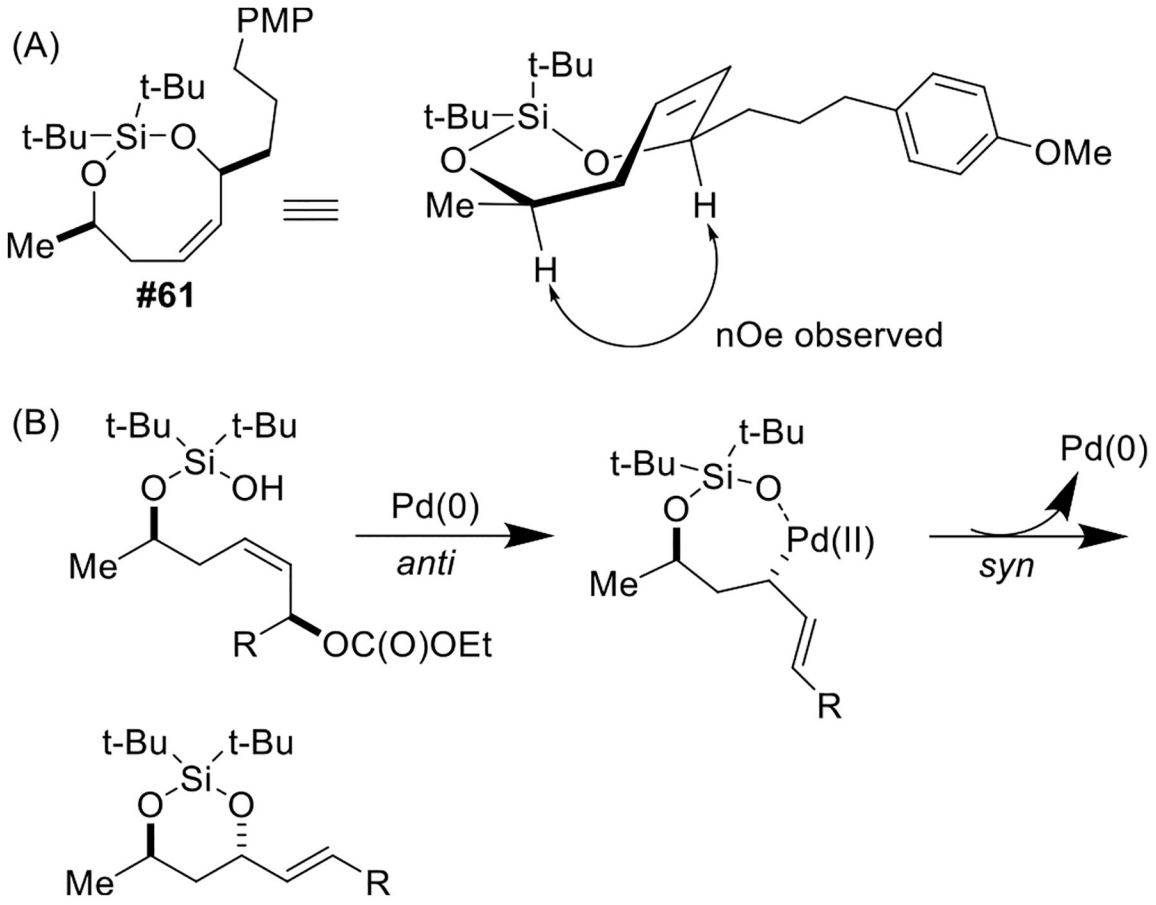
Scheme 3.
Examination of Leaving Group Effects



Scheme 4.
Substrate Scope with Primary Silanols

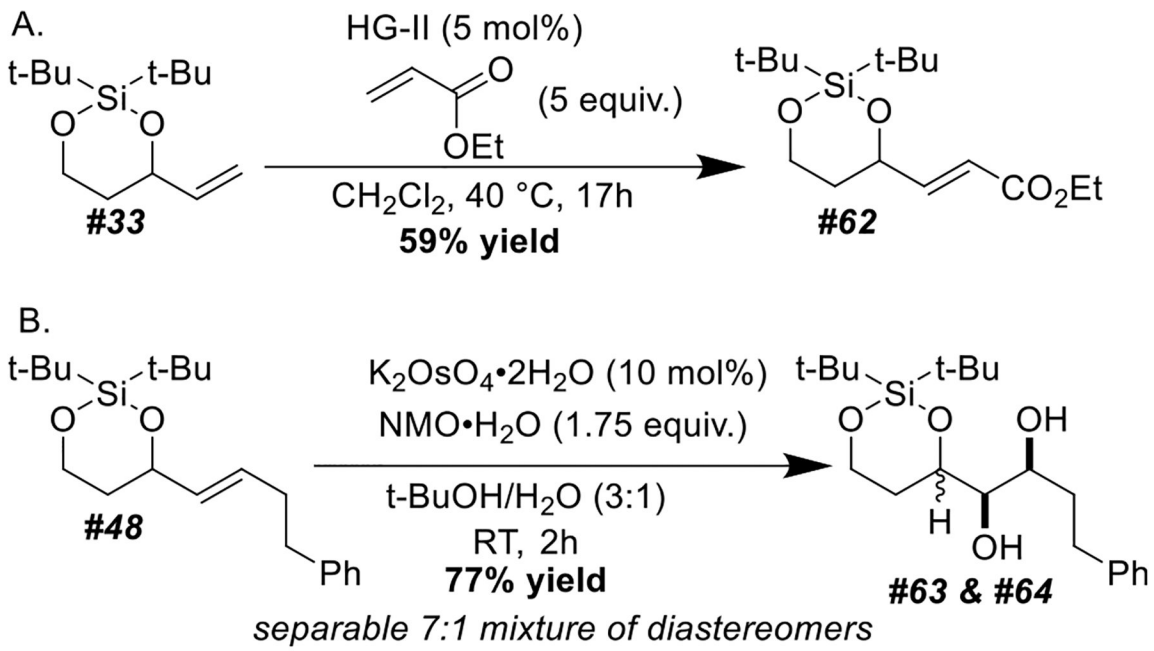


Scheme 5.
Substrate Scope with Secondary Silanols



Scheme 6.

(A) Determination of the Stereochemistry of Linear Starting Materials and (B) Mechanistic Hypothesis

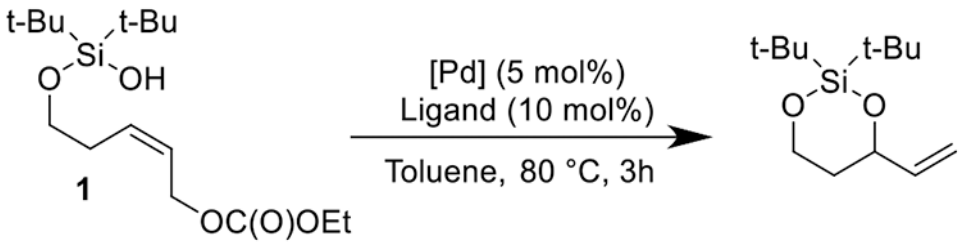


Scheme 7.

Product Alkenyl Dioxasilinanes Being Convenient Synthons for Many Transformations Including (A) Cross-Metathesis and (B) Dihydroxylation

Table 1.

Reaction Optimization



Entry	[Pd]	Additive[a]	Ligand	Yield (%)[b]
1	$Pd(PPh_3)_4$	-	(R)-BINAP[c]	35%
2	$[(Cinnamyl)PdCl]_2$	-	(R)-BINAP	62%
3	$[(Cinnamyl)PdCl]_2$	-	(R)-BINAP	28%[d] Trace[e]
4	$[(Cinnamyl)PdCl]_2$	-	(R)-DTBM-SEGPHOS	19%
5	$[(Cinnamyl)PdCl]_2$	-	Xantphos	27%
6	$[(Cinnamyl)PdCl]_2$	KO^{t}Bu	(R)-BINAP	46%
7	$[(Cinnamyl)PdCl]_2$	$NaHCO_3$	(R)-BINAP	42%
8	$[(Cinnamyl)PdCl]_2$	CH_3CO_2H	(R)-BINAP	trace
9	$[(Cinnamyl)PdCl]_2$	$PhCO_2H$	(R)-BINAP	NR

[a] 1 equiv.

[b] Performed on a 0.1 mmol scale; yields were determined by 1H NMR integration using methyl phenyl sulfone as an internal standard.

[c] Arbitrarily chosen, as no enantioselectivity was observed.

[d] At 110 °C.

[e] At room temperature. See the Supporting Information for additional conditions tested.