Supplemental Information

Full citation for ref. 46

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998.

General Experimental

All reactions were performed under argon atmosphere unless otherwise indicated. Acetone was distilled from Drierite®. Ether and methylene chloride (CH_2Cl_2) were purified on an alumina column solvent purification system, and tetrahydrofuran (THF) was distilled from sodium benzophenone ketal. TBAF was purchased from Acros as a 1.0M solution in THF. All other reagents were purchased and used as received.

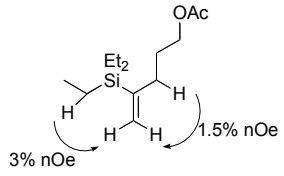
Flash chromatography was performed with EM Science silica gel (0.040-0.063 μm grade) or 200 mesh Florisil (Aldrich). Analytical thin layer chromatography was performed with 0.2-mm coated commercial silica gel plates (E. Merck, DC Plastifolien, kieselgel 60 F_{254}). Preparative thin layer chromatography was performed with 0.5-mm coated commercial silica gel plates (E. Merck, DC Plastifolien, kieselgel 60 F_{254}).

Proton and broad-band decoupled ^{13}C nuclear magnetic resonance data were acquired on a Varian GEM-300, Mercury-400 or Unity Inova-500 spectrometer as indicated. Chemical shifts are reported in ppm relative to TMS or C_6D_6 as an internal standard.

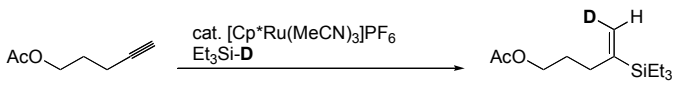
Infrared (IR) data were recorded in sodium chloride plates on PerkinElmer Paragon 500 FT-IR spectrometer. Gas chromatographic and GC-MS analyses were performed on a Hewlett-Packard 6890 Series gas chromatograph with attached HP 5973 Series mass detection. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. High resolution mass spectra (HRMS) were obtained from the Mass Spectrometry Resource, School of Pharmacy, University of California-San Francisco on a Kratos MS9 spectrometer.

Literature procedures were employed for the synthesis of ruthenium complexes **6**[1a] and **7**[1b] All compounds were judged to be pure (>95%) on the basis of ^1H NMR except where explicitly indicated otherwise.

nOe data was used to establish the identities of the olefinic protons for purposes of the labeling experiment below:



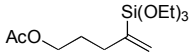
Intermolecular Hydrosilylation of Terminal Alkyne Stereochemistry: 9-*d*



8 **40**
single product isomer

5-Acetyloxy-1-pentyne (34 μL, 0.26 mmol) was taken up in CH_2Cl_2 (0.60 mL) at 0 °C under Ar. The solution was treated with $DSiEt_3$ (50 μL, 0.31 mmol, Aldrich, 97% D). The solution was next treated with solid $[Cp^*Ru(MeCN)_3]PF_6$ (2.6 mg, 0.0052 mmol) and the reaction vessel allowed to warm to rt. After 1 h, the alkyne was consumed as determined by TLC analysis, and the crude reaction mixture was concentrated and applied directly to a silica gel column (eluent 20:1 pet. ether: ether) to afford the desired selectively deuterated vinylsilane. NMR analysis indicated full deuterium incorporation at the trans position indicated in the reaction above. Isomeric purity is conservatively estimated at ≥97:3. Relevent ^{1}H NMR: (300 MHz, $CDCl_3$) δ 5.65 (s, (*E*) proton trans to silicon, 1H) 5.33 (s, (*Z*) proton cis to silicon, 1H).

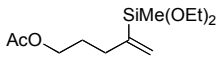
5-acetyloxy-2-(triethoxysilyl)-1-pentene, 10



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **8** (50 μL, 0.38 mmol), $(EtO)_3SiH$ (68 μL, 0.46 mmol), CH_2Cl_2 (0.70 mL), and complex **6** (2.0 mg, 0.0039 mmol) to produce the product (90 mg, 85%) as a 5:1 mixture of regioisomers. Chromatography eluent: 20:1 pet. ether: ether.

Data for major isomer:
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (dt, *J* = 3.5, 1.5 Hz, 1H), 5.67 (m, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 3.83 (q, *J* = 7.1 Hz, 6H), 2.22 (m, 2H), 2.05 (s, 3H), 1.81 (tt, *J* = 8.0, 6.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 142.5, 129.8, 64.2, 58.5, 32.2, 27.6, 21.0, 18.2. IR (thin film) 2975, 2928, 2888, 1743 (s), 1242, 1080 (s), 960, 782 cm^{-1}. Anal. calc. for $C_{13}H_{26}O_5Si$: C, 53.76; H, 9.02; Found: C, 53.66; H, 8.95.

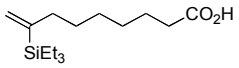
Preparation of 5-acetyloxy-2-(diethoxymethylsilyl)-1-pentene, 11



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **8** (27 μL, 0.20 mmol), $(EtO)_2MeSiH$ (38 μL, 0.24 mmol), CH_2Cl_2 (0.50 mL), and complex **7** (1.0 mg, 0.002 mmol) to afford the product (46 mg, 88%). Chromatography eluent: 20:1 pet. ether: ether.

R_f: 0.47 (10:1 pet. ether: EtOAc).^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (m, 1H), 5.60 (d, *J* = 2.7 Hz, 1H), 4.09 (t, *J* = 6.8 Hz, 2H), 3.78 (q, *J* = 7.1 Hz, 4H), 2.23 (t, *J* = 7.7 Hz, 2H), 2.01 (s, 3H), 1.82 (tt, *J* = 7.7, 6.8 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 6H), 0.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 146.3, 128.0, 64.2, 58.3, 31.7, 27.7, 21.0, 18.3, -4.7. IR (thin film) 2974, 1743 (s), 1241, 1104, 1080, 949 (w) cm^{-1}. Due to facile polymerization and/or decomposition, we were unable to obtain satisfactory HRMS or analysis of this compound.

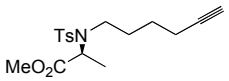
8-(Triethylsilyl)-8-nonenoic acid, 13



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **12** (68 mg, 0.44 mmol), Et_3SiH (90 μL, 0.53 mmol), CH_2Cl_2 (0.70 mL), and complex **6** (1.6 mg, 0.0044 mmol) to afford the product (106 mg, 89%). Chromatography eluent: 98:2:0.5 CH_2Cl_2: MeOH: AcOH.

R_f: 0.45 (80:20:1 pet. ether: EtOAc: AcOH).). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (m, 1H), 5.28 (d, *J* = 3.2 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.07 (t, *J* = 7.3 Hz, 2H), 1.64 (m, 2H), 1.28-1.44 (m, 6H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.1, 149.3, 125.3, 36.5, 34.3, 29.4, 29.2, 28.9, 24.9, 7.6, 3.2. IR (thin film) 3049 (w), 3000 (br, OH), 2952, 2875, 1712 (s), 1415 (w), 720 (w) cm^{-1}. Anal. calc. for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.80; H, 11.07.

(*S*)-*N*-(5-hexynyl)-*N*-(4-toluenesulfonyl)alanine methyl ester, 14



Pyridinium chlorochromate (3.52 g, 16.3 mmol) and sodium acetate (0.22 g, 2.7 mmol) was taken up in CH_2Cl_2 (40 mL) under Ar atmosphere at 0 °C. 5-Hexyn-1-ol (1.50 mL, 13.6 mmol) was added and the reaction stirred for 30 min, then warmed to room temperature and stirred an additional 1.5 h. The crude mixture was diluted with ether (100 mL) and filtered through a short plug of Florisil. Careful reduction in solvent volume under reduced pressure at 0 °C to ca. 10 mL furnished crude 5-hexynal (IR (thin film) 1723 cm^{-1}). The crude aldehyde was immediately diluted with methanol (40 mL) and treated sequentially with (*L*)-alanine methyl ester (2.08 g, 15.0 mmol) and triethylamine (2.3 mL, 20.4 mmol) under nitrogen atmosphere. 3Å mlcl sieves (ca. 2.0 g) were added to the reaction mixture. After 3 h, the mixture was cooled to 0 °C and sodium borohydride (1.00 g, 27.2 mmol) was added and the mixture was stirred for 2 h, during which time the flask was allowed to warm to rt. The mixture was quenched with aq hydrochloric acid (30 mL, 2N) and diluted with water (100 mL). The methanol solvent was removed under reduced pressure and conc. hydrochloric acid was added to bring the solution to pH = 2. The aqueous solution was washed with ether (50 mL) and treated with sat. NaOH to pH >12. The mixture thus obtained was extracted with DCM (3 x 50 mL), washed with brine (40 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Chromatography on silica gel (Eluent 20/1 then 10:1 CH_2Cl_2: NH_3-saturated methanol) followed by bulb-to-bulb distillation (0.3 torr) afforded the desired N-alkyl amino ester (1.05 g, 42%) as a clear colorless oil.

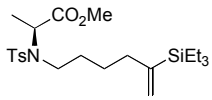
R_f: 0.40 (1:1 pet. ether : EtOAc + 2% Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.35 (q, *J* = 7.2 Hz, 1H), 2.45-2.68 (m, 2H), 2.21 (m, 2H), 1.95 (t, *J* = 2.3 Hz, 1H), 1.52-1.64 (m, 5H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 84.1, 68.3, 56.5, 51.6, 47.3, 29.1, 26.0, 19.0, 18.1. IR (thin film) 3295 (w), 2939, 1737 (s), 1435 (w), 1198, 1154 cm^{-1}. $[\alpha]^{28}_D$ –26.7° (c 1.0, $CHCl_3$). Anal. calc. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.29; H, 9.30; N, 7.50.

(*S*)-*N*-5-hexynyl-alanine methyl ester (400 mg, 2.18 mmol) was taken up in CH_2Cl_2 under Ar atmosphere at 0 °C. 2,4,6-Collidine (0.375 mL, 2.83 mmol) was added, followed by solid toluenesulfonyl chloride (500 mg, 2.26 mmol). The mixture was allowed to come to rt overnight, and after stirring a total of 18 h, the reaction was treated with Et_2NH (0.40 mL) and diluted with EtOAc (60 mL). The mixture was washed with aq $KHSO_4$ (40 mL, 0.5 M)

and brine (25 mL). After drying over Na_2SO_4, the solvent was removed in vacuo. The crude oil thus obtained was purified by silica gel chromatography (eluent 3:1 then 1:1 pet. ether: EtOAc) to obtain 481 mg (65%) of the desired *N*-tosyl amino ester as a clear, colorless oil.

R_f: 0.60 (1:1 pet. ether:EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.63 (q, *J* = 7.2 Hz, 1H), 3.55 (s, 3H), 3.20 (m, 2H), 2.42 (s, 3H), 2.19 (td, *J* = 6.9, 2.7 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.62-1.88 (m, 2H), 1.51 (tt, *J* = 6.9, 6.9 Hz, 2H), 1.41 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 143.3, 137.0, 129.4, 127.3, 83.9, 68.6, 55.0, 52.1, 45.2, 29.9, 25.7, 21.5, 18.0, 16.5. IR (thin film) 3285, 2952, 1744 (s), 1599, 1341 (s), 1154 (s) cm^{-1}. $[\alpha]^{28}_D$ –50.1° (c 1.0, $CHCl_3$). Anal. calc. for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.65; H, 6.71; N, 4.13.

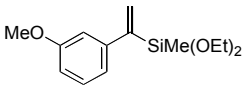
(*S*)-*N*-(5-Triethylsilyl-5-hexeneyl)-N-(toluene-4-sulfonyl)alanine methyl ester, 15



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **14** (67 mg, 0.20 mmol), Et_3SiH (38 μL, 0.24 mmol), CH_2Cl_2 (0.40 mL), and complex **6** (1.0 mg, 0.0020 mmol) to afford the product (79 mg, 88%). Chromatography eluent 5:1 pet. ether: EtOAc.

R_f: 0.57 (100:20:1 pet. ether: EtOAc: methanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.58 (d, *J* = 2.0 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 1H), 4.63 (q, *J* = 7.2 Hz, 1H), 3.54 (s, 3H), 3.24 (ddd, *J* = 15.0, 10.5, 5.4 Hz, 1H), 3.09 (ddd, *J* = 15.0, 10.5, 5.9 Hz, 1H), 2.41 (s, 3H), 2.05 (t, *J* = 7.5 Hz, 2H), 1.25-1.77 (m, 4H), 1.40 (d, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.8 Hz, 9H), 0.58 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 148.5, 143.2, 137.2, 129.4, 127.3, 125.2, 55.0, 52.0, 45.7, 35.7, 30.8, 26.1, 21.5, 16.6, 7.3, 2.9. IR (thin film) 2953 (s), 2875, 1746 (s), 1599 (w), 1462, 1344, 1153 (s), 722 cm^{-1}. $[\alpha]^{24}_D$ –39.7° (c 1.0, $CHCl_3$). HRMS—EI (m/z): [M-Et]$^+$ calcd for $C_{21}H_{34}O_4SSi$: 424.1978; found: 424.1979.

3-(1-(methyldiethoxysilyl)ethenyl)methoxybenzene, 17

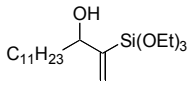


The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **16** (53 mg, 0.40 mmol), $(EtO)_2MeSiH$ (77 μL, 0.48 mmol), CH_2Cl_2 (0.80 mL), and complex **7** (2.0 mg, 0.0040 mmol) to afford the product (92 mg, 86%). Chromatography eluent: 20:1 pet. ether: ether.

R_f: 0.49 (100:10:1 pet. ether/ EtOAc/ methanol) R_f(β-silyl minor isomer) 0.43 (100:10:1 pet. ether/ EtOAc/ methanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.1, 8.1 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 9.97 (s, 1H), 6.79 (m, 1H), 6.07 (d, *J* = 3.0 Hz, 1H), 5.86 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 3.79 (q, *J* = 6.8 Hz, 4H), 1.22 (t, *J* = 6.8 Hz, 6H), 0.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 142.3, 139.2, 125.3, 124.4, 114.6, 107.6, 107.5, 53.7, 50.3,

13.5, -9.0. IR (thin film) 2064 (w), 2974, 2926, 1596, 1574, 1259, 1214, 1104 (s), 1079 (s), 951, 808 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{14}H_{22}O_3Si$: 266.1338; found: 266.1333.

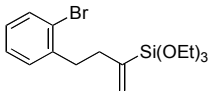
2-(Triethoxysilyl)-1-tetradecen-3-ol, 19



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **18** (105 mg, 0.50 mmol), $(EtO)_3SiH$ (111 μL, 0.60 mmol), CH_2Cl_2 (1.0 mL), and complex **7** (12.5 mg, 0.0050 mmol) to afford the product (108 mg, 58%). Chromatography on florisil, eluent 20:1 pet. ether: ether.

Data for major isomer:
^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (d, *J* = 2.1 Hz, 1H), 5.65 (d, *J* = 2.1 Hz, 1H), 4.07 (td, *J* = 7.2, 7.2 Hz, 1H), 3.85 (q, *J* = 7.0 Hz, 6H), 2.58 (d, *J* = 7.0 Hz, OH), 1.59 (m, 2H), 1.20-1.41 (m, 27H), 0.87 (*J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 128.6, 100.3, 58.7, 37.7, 31.9, 29.7, 29.6, 29.5, 29.3, 25.9, 22.7, 18.1, 14.1. IR (thin film) 3456 (br, O-H), 2926, 2855, 1103, 1081, 959, 783 cm^{-1}. HRMS—EI (m/z): $[M-Et]^+$ calcd for $C_{18}H_{37}O_4Si$: 345.2461; found: 345.2458.

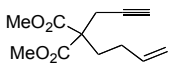
1-Bromo-2-[(3-triethoxysilyl)-3-butenyl]-benzene, 21



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne (84 mg, 0.40 mmol), $(EtO)_3SiH$ (89 μL, 0.48 mmol), CH_2Cl_2 (0.80 mL), and complex **7** (2.0 mg, 0.0040 mmol) to afford the product (137 mg, 92%) as a 13:1 mixture of regiosisomers. Chromatography eluent: 20:1 pet. ether: ether. Collection of the early fraction afforded the major isomer (121 mg, 81%) isolated pure of the minor regioisomers. Later fractions (16 mg, 11%) were mixtures of the two regioisomers.

R_f: 0.41 (10:1 pet. ether: ether). ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.21-7.26 (m, 2H), 7.04 (m, 1H), 5.80 (m, 1H), 5.70 (d, *J* = 2.9 Hz, 1H), 3.86 (q, *J* = 7.0 Hz, 6H), 2.90 (m, 2H), 2.44 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 141.5, 132.6, 130.3, 129.8, 127.4, 127.3, 124.3, 58.6, 36.0, 35.7, 18.3. IR (thin film) 2974, 1103, 1080, 961 cm^{-1}. Anal. calc. for $C_{16}H_{25}BrO_3Si$: C, 51.47; H, 6.75. Found: C, 51.55; H, 6.65.

2-But-3-enyl-2-prop-2-ynyl-malonic acid dimethyl ester, 22

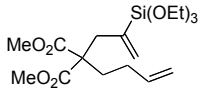


Dimethyl propargylmalonate (2.68 mL, 17.6 mmol) in DMF (16 mL) at 0 °C under N_2 was treated with sodium hydride (640 mg, 16.0 mmol, 60% dispersion in mineral oil) in several portions. After 20 min, 4-bromo-1-butene (1.63 mL, 16.0 mmol) was added to the flask, which was then allowed to warm to rt. After stirring 20 h, the mixture was diluted with sat. aq NH_4Cl (50 mL), and extracted with ether (3 x 40 mL). the organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the residue

on a silica gel column (eluent: 20:1 pet. ether: EtOAc) afforded 2.64 g (74%) of a clear, colorless oil whose data matched that reported in the literature.[2]

R_f: 0.36 (10:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (m, 1H), 5.06 (dd, *J* = 17.0, 1.3 Hz, 1H), 4.99 (dd, *J* = 10.0, 1.3 Hz, 1H), 3.75 (s, 6H), 2.85 (d, *J* = 2.7 Hz, 2H), 2.17 (m, 2H), 1.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 137.1, 115.3, 78.6, 71.4, 56.6, 52.7, 31.2, 28.3, 22.9. IR (thin film) 3293 (w), 2956, 1738 (s), 1642 (w), 1436, 1275, 1210 cm^{-1}.

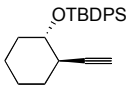
2-(2-(Triethoxysilyl)-2-propenyl)-2-(3-butenyl)malonic acid dimethyl ester, 23



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **22** (112 mg, 0.50 mmol), $(EtO)_3SiH$ (89 μL, 0.60 mmol), CH_2Cl_2 (1.0 mL), and complex **7** (10.0 mg, 0.020 mmol) to afford the product (119 mg, 61%). Chromatography eluent: 10:1, then 5:1 pet. ether: EtOAc.

R_f: 0.23 (10:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.78 (d, *J* = 2.7 Hz, 1H), 5.72 (m, 1H), 5.03 (d, *J* = 17.3 Hz, 1H), 4.95 (d, *J* = 10.0 Hz, 1H), 3.81 (q, *J* = 7.1 Hz, 6H), 3.70 (s, 6H), 2.83 (s, 2H), 1.80-2.20 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 138.5, 137.7, 134.0, 114.7, 58.6, 58.2, 52.2, 36.8, 31.0, 28.6, 18.1. IR (thin film) 2976, 2888, 1738 (s), 1435, 1168, 1102, 1080 (s), 961, 785 cm^{-1}. Anal. calc. for $C_{18}H_{32}O_7Si$: C, 55.64; H, 8.30. Found: C, 55.51; H, 8.46.

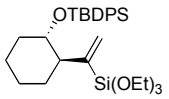
***trans*-*O*-(*tert*-Butyldiphenylsilyl)-2-ethynyl-cyclohexanol, 24**



The terminal alkyne was produced by desilylation of the TMS-alkyne, *trans*-*O*-(*tert*-butyldiphenylsilyl)-2-(2-trimethylsilyl-ethynyl)-cyclohexanol, kindly provided by Dr. Olivier Dirat (obtained by addition of lithiated TMS-acetylene (butyllithium, -78 °C) to cyclohexene oxide in the presence of $BF_3{\cdot}OEt_2$). The silyl alkyne (448 mg, 1.03 mmol) was treated with K_2CO_3 (284 mg, 2.06 mmol) in MeOH (5 mL) for 24 h. Sat. aq sodium bicarbonate (15 mL) was added, the MeOH removed under reduced pressure, and the mixture extracted with ether (2 x 30 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure, and applied to a plug of silica gel (ca. 4 cm). Elution with 10:1 pet. ether : ether provided 344 mg (92%) of the desired terminal alkyne.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.34-7.44 (m, 6H), 3.80 (ddd, *J* = 7.1, 7.1, 3.1 Hz, 1H), 2.49 (m, 1H), 2.02 (m, 1H), 2.00 (d, *J* = 2.4 Hz, 1H), 1.10-1.72 (m, 7H), 1.08 (s, 9H), 0.86 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 135.9, 134.6, 134.0, 129.53, 129.45, 127.4, 127.4, 86.8, 72.7, 69.8, 36.2, 32.3, 28.6, 27.0, 23.1, 22.2, 19.4. IR (thin film) 3309 (w), 2934, 1429, 1111 (s), 702 (s) cm^{-1}. Anal. calc. for $C_{24}H_{30}OS$: C, 79.50; H, 8.34. Found: C, 79.36; H, 8.41.

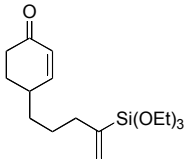
***trans*-(*tert*-Butyldiphenylsilyloxy)-2-(1-triethoxysilyl)ethenylcyclohexane, 25**



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **24** (82 mg, 0.23 mmol), $(EtO)_3SiH$ (50 μL, 0.28 mmol), CH_2Cl_2 (0.50 mL), and complex **7** (1.2 mg, 0.0023 mmol) to afford the product (104 mg, 87%) as a 20:1 mixture of regioisomers. Chromatography eluent: 10:1 pet. ether: ether. Collection of the early fractions afforded the major isomer (87 mg, 73%) isolated pure of the minor regioisomer. Later fractions (17 mg, 13%) were mixtures of the two regioisomers.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.33-7.41 (m, 6H), 5.73 (s, 2H), 3.88 (m, 1H), 3.83 (q, *J* = 7.0 Hz, 6H), 2.29 (m, 1H), 1.79 (m, 1H), 1.66 (m, 1H), 1.49 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 1.05-1.30 (m, 4H), 0.89 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 136.0, 135.9, 134.5, 129.7, 129.2, 129.1, 127.3, 127.1, 73.9, 58.4, 52.4, 36.1, 32.5, 27.0, 25.6, 24.8, 19.4, 18.2. IR (thin film) 2973, 2930, 2858, 1105, 1081, 702 cm^{-1}. Anal. calc. for $C_{30}H_{46}O_4Si_2$: C, 68.39; H, 8.80. Found: C, 68.60; H, 8.86.

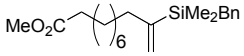
Preparation of 4-[4-(triethoxyl-silanyl)-pent-4-enyl]-cyclohex-2-enone, 27



To a solution of 4-pent-4-ynyl-cyclohex-2-enone (67 mg, 0.41 mmol) and triethoxysilane (92 μL, 0.50 mmol) in CH_2Cl_2 (0.8 mL) is added solid **7** (2.0 mg, 0.004 mmol) at 0 ºC. The solution is allowed to warm to rt and stirred for 1 h. The reaction yielded 4-[4-(triethoxyl-silanyl)-pent-4-enyl]-cyclohex-2-enone (102.5 mg, 77%) after purification on silica gel column (eluent: 85:15 pet. ether.: ether).

R_f: 0.50 (2:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (m, 1H), 5.97 (dd, *J* = 10.0, 2.0, 1H), 5.64-5.73 (m, 2H), 3.78-3.87 (m, 6H), 2.30-2.53 (m, 3H), 2.09-2.21 (m, 3H), 1.40-1.74 (m, 5H), 1.20-1.26 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 155.3, 143.3, 129.5, 128.9, 58.5, 36.9, 36.1, 36.0, 34.2, 28.6, 26.1, 18.2. IR (thin film) 2974, 2927, 1684 (s), 1390, 1167, 1103, 1080, 960, 783 cm^{-1}. Anal. Calc. for $C_{17}H_{30}O_4Si$: C, 62.54; H, 9.26. Found: C, 62.40; H, 9.12.

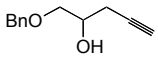
10-(Benzyldimethylsilyl)-10-undecenoic acid methyl ester, 29



Following the protocol given for the synthesis of (±)-1-benzyloxy-4-(benzyldimethylsilyl)-4-penten-2-ol (**33**) was employed. Methyl 10-undecynoate (400 mg, 2.00 mmol), BDMS-H (0.41 mL, 2.4 mmol), CH_2Cl_2 (4.0 mL), and **7** (10.0 mg, 0.020 mmol) was transformed into the desired vinylsilane (694 mg, 100%). The crude reaction mixture was filtered through florisil, washing with ether (30 mL), to provide spectroscopically homogeneous material without further purification.

R_f: 0.53 (10:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 5.59 (m, 1H), 5.29 (d, *J* = 3.0 Hz, 1H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 2H), 2.08 (t, *J* = 7.8 Hz, 2H), 1.62 (t, *J* = 7.3 Hz, 2H), 1.25-1.40 (m, 10H), 0.03 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 150.7, 140.0, 128.2, 128.5, 124.8, 123.9, 51.4, 36.1, 34.1, 29.4, 29.3, 29.2, 29.1, 28.9, 25.5, 24.9, -3.5. IR (thin film) 2928, 1742, 1248, 1206, 1171, 832 cm^{-1}. Anal. Calc. for $C_{21}H_{34}O_2Si$: C, 72.78; H, 9.89. Found: C, 72.72; H, 10.06.

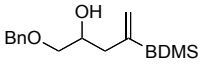
(±)-1-Benzyloxy-4-pentyn-2-ol, 30



1-Trimethylsilylpropyne (1.00 mL, 6.70 mmol) was taken up in THF (25 mL) under Ar at –20 °C. *n*-Butyllithium (4.8 mL, 6.70 mmol, 1.6 M in hexanes) was then added dropwise, and after stirring for 25 min, the flask was cooled to –78 °C and benzyloxyacetaldehyde (1.00 g, 6.70 mmol) was added dropwise. The flask was warmed to 0 °C over 30 min, and then quenched by addition of aq NH_4Cl (40 mL). After evaporative removal of THF, the mixture was extracted with EtOAc (3 x 30 mL) and the organic extracts washed with brine (20 mL) and dried over Na_2SO_4. The resulting solution was concentrated to give crude TMS-alkyne which was then taken up in methanol (20 mL) and treated with potassium carbonate (3.0 g). After stirring in air at rt for 30 min, sat. aq sodium bicarbonate (30 mL) was added. The methanol was removed under reduced pressure, and the mixture extracted with EtOAc (3 x 25 mL). The organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification on a silica gel column (eluent: 85:15:1 to 80:20:1 pet. ether: EtOAc: methanol) afforded 530 mg (42 %) of the desired terminal alkyne as a clear, colorless oil of sufficient purity (cont. with c.a. 5% unknown impurity) to carry onward. Spectral data matched that given in the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H), 4.58 (s, 2H), 3.99 (m, 1H), 3.62 (dd, *J* = 9.5, 3.9 Hz, 1H), 3.51 (dd, *J* = 9.5, 6.6 Hz, 1H), 2.45 (m, 2H), 2.03 (m, 1H). IR (thin film) 3424 (br OH), 3295 (s), 3031, 2915, 2864, 1454, 1116 (s), 739, 699 (s) cm^{-1}.

(±)-1-Benzyloxy-4-(benzyldimethylsilyl)-4-penten-2-ol, 31

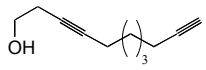


1-Benzyloxy-4-pentyn-2-ol (187 mg, 0.98 mmol) and benzyldimethylsilane (204 μL, 1.18 mmol) were taken up in CH_2Cl_2 (2.0 mL) under Ar at 0 °C. Solid $[Cp^*Ru(MeCN)_3]PF_6$ (5.0 mg, 0.0099 mmol) was added, and the flask was removed from the ice bath to allow warming to rt. After 2 h, the mixture was concentrated in vacuo and applied to a silica gel column (eluent: 10:1 to 5:1 pet. ether: EtOAc) to provide 304 mg (91%) of the desired vinysilane as an inseparable 14:1 mixture of internal: terminal regioisomers.

Data for major isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.39 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.00 (m, 2H), 5.73 (dt, *J* = 2.6, 1.4 Hz, 1H), 5.45 (d, *J* = 2.6 Hz, 1H), 4.56 (s, 3H), 3.91 (m, 1H), 3.49 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.36 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.26-2.31 (m, 3H), 2.18 (s, 2H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 139.7, 138.0, 128.6, 128.4, 128.2, 128.1, 127.8, 127.7, 124.9, 74.1, 73.4, 69.0, 40.3, 25.4, -3.4, -3.5. IR (thin film)

3453 (br, OH), 3026, 2899, 1600, 1494, 1249, 1096, 831, 698 cm^{-1}. HRMS—EI (m/z): $[M\text{-}CH_2Ph]^+$ calcd for $C_{14}H_{21}O_2Si$: 249.1311; found: 249.1319.

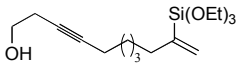
3,10-Undecadiyn-1-ol, 32



1,8-Nonadiyne (6.26 mL, 41.6 mmol) in THF (150 mL) at –78 °C was treated dropwise with butyllithium (26.3 mL, 37.8 mmol, 1.44 M in hexanes), followed by HMPA (20 mL). The mixture was warmed to –45 °C over 30 min, and ethylene oxide (28 mL, 75.6 mmol, 2.7 M soln) was added. The solution was allowed to warm to rt over 16 h. It was then quenched by addition of water (100 mL) and sat. aq sodium bicarbonate (100 mL) and the volatile organic species were removed under reduced pressure. Extraction with ether (3 x 50 mL), washing of the organic fractions with brine (40 mL), drying over $MgSO_4$, and concentration in vacuo afforded a crude residue. Purification on silica gel afforded 2.70 g (43%) of the desired mono-alcohol, followed by 1.65 g (21%) of the symmetrical *bis*-alkylation product.

R_f: 0.22 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (app. q, J = 6.1 Hz, 2H), 2.44 (m, 2H), 2.17-2.22 (m, 4H), 1.96 (t, J = 2.5 Hz, 1H), 1.85 (t, J = 6.1 Hz, 1H), 1.50-1.58 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.4, 82.3, 68.3, 61.3, 28.4, 28.0, 27.9, 23.2, 18.7, 18.3. IR (thin film) 3393 (br OH), 3298, 2939, 2116 (w), 1641 (w), 1433, 1046 cm^{-1}. Anal. calc. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.26; H, 9.66.

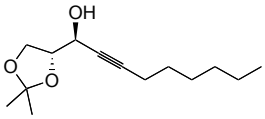
10-(Triethoxylsilyl)-10-undecen-3-yn-1-ol, 33



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **32** (66 mg, 0.40 mmol), $(EtO)_3SiH$ (77 μL, 0.42 mmol), CH_2Cl_2 (0.80 mL), and complex **7** (2.0 mg, 0.0040 mmol) to afford the product (93 mg, 71%). Chromatography on florisil, eluent: 20:1 pet. ether: EtOAc.

R_f: 0.34 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (m, 1H), 5.63 (d, J = 3.2 Hz, 1H), 3.82 (q, J = 7.0 Hz, 6H), 3.68 (td, J = 6.1, 6.1 Hz, 2H), 2.43 (m, 2H), 2.12-2.50 (m, 4H), 1.85 (t, J = 6.1 Hz, O-H), 1.32-1.56 (m, 6H), 1.23 (t, J = 7.0 Hz, 9H) . ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 129.1, 82.7, 76.3, 61.3, 58.4, 35.9, 28.9, 28.7, 28.7, 28.3, 23.2, 18.7, 18.2. IR (thin film) 3418 (br, O-H), 2975, 2930, 1080, 959 cm^{-1}. Anal. calc. for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 61.96; H, 9.72.

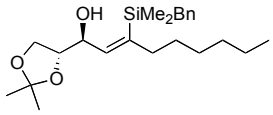
(2R,3S)-4-undecyn-1,2,3-triol 1,2-isopropylidene ketal, 36



This procedure was adapted from the method of Shimizu.[4] A solution of 1-octyne (1.59 mL, 10.8 mmol) in THF (10 mL) under Ar at –78 °C was treated with butyllithium (1.59 mL, 10.8 mmol, 1.48 M in hexanes) dropwise. After 30 min, $ClTi(O\textit{i}\text{-}Pr)_3$ (2.57 mL, 10.8 mmol) was added and the flask warmed to –60 °C. To maintain solubility, additional THF (20 mL) was added and the solution was stirred for 90 min prior to re-cooling to –78 °C. (*R*)-Glyceraldehyde isopropylidene ketal[5] (0.70 g, 5.38 mmol) was then added via syringe in one portion and the mixture stirred for 2 h prior to quenching with sat. aq NH_4Cl (20 mL) at –78 °C. Water (30 mL) was then added and the reaction extracted with ether (3 x 30 mL). The ether extracts were washed with brine (20 mL) and dried over $MgSO_4$, and the solvents were removed in vacuo. Silica gel chromatography gave 1.19 g (92 %) of the desired alcohol as a 9:1 mixture of epimeric diols favoring the trans.

Data for major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48 (m, 1H), 4.21 (ddd, *J* = 6.5, 6.5, 4.0 Hz, 1H), 4.03-4.08 (m, 2H), 2.26 (d, *J* = 4.4 Hz, 1H), 2.20 (td, *J* = 7.2, 2.1 Hz, 2H), 1.45-1.51 (m, 2H), 1.46 (s, 3H), 1.37 (s, 3H), 1.24-1.36 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.0, 87.3, 78.1, 77.0, 65.2, 62.4, 31.3, 28.5, 28.4, 26.3, 25.2, 22.5, 18.7, 14.0. IR (thin film) 3452 (br, OH), 2933, 2234 (w), 1372, 1254, 1216, 1153, 1070, 851 cm^{-1}. $[\alpha]^{26}_D$ +17.8° (c 1.0, $CHCl_3$). Anal. calc. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07; Found: C, 69.79; H, 10.15.

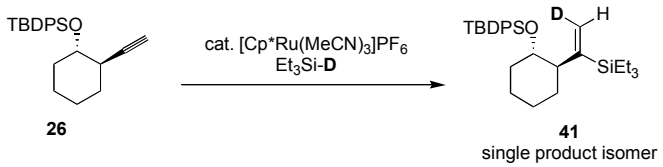
(Z)-(S)-3-(Benzyldimethylsilyl)-1-((R)-2,2-dimethyl-[1,3]dioxolan-4-yl)-non-2-en-1-ol, 37



Note: This compound was used as an inseparable 9:1 mixture of alcohol epimers at C3 and all products were isolated as such. The general procedure for the synthesis of vinylsilane **68** was followed employing the alkyne (62 mg, 0.258 mmol), BDMS-H (54 μL, 0.31 mmol), acetone (0.6 mL), and complex **7** (3.9 mg, 0.0077 mmol). The product was isolated as a 6:1 mixture of olefin regioisomers and 9:1 mixture of alcohol epimers (98 mg, 98%). The major regioisomer could be isolated free of the α-silyl regioisomers through careful (repeated) chromatography using 20:1 then 10:1 pet. ether: acetone as the eluent.

Data for major C3 epimer:
^{1}H NMR (400 MHz, C_6D_6) δ 6.95-7.13 (m, 5H), 5.95 (d, *J* = 9.3 Hz, 1H), 4.44 (ddd, *J* = 9.3, 4.5, 3.1 Hz, 1H), 3.88-4.03 (m, 3H), 2.21 (m, 2H), 2.01 (m, 2H), 1.59 (d, *J* = 3.1 Hz, 1H), 1.38 (s, 3H), 1.27 (s, 3H), 1.18-1.30 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.15 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ 144.4, 141.1, 140.0, 128.7, 128.6, 128.5, 128.3, 124.6, 109.2, 79.0, 71.0, 65.6, 38.6, 32.0, 30.5, 29.5, 27.0, 26.6, 25.4, 23.0, 14.3, -1.1, -1.5. IR (thin film) 3464 (br OH), 2928, 1601 (w), 1494, 1371, 1251, 1067, 832, 700 cm^{-1}. Additional characterization was obtained after conversion to the hydroxyl ketone **38**.

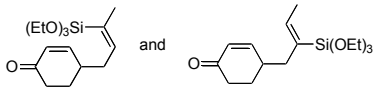
Intermolecular Hydrosilylation of Terminal Alkyne Stereochemistry: *trans*-(*tert*-butyldiphenylsilyloxy)-2-(1-triethoxysilyl)ethenylcyclohexane-*d*, 41



26 **41**
single product isomer

The terminal alkyne **26** (64 mg, 0.10 mmol) was taken up in CH_2Cl_2 (0.0.3 mL) at 0 °C under Ar. The solution was treated with $DSiEt_3$ (19 μL, 0.12 mmol, Aldrich, 97% D). The solution was next treated with solid $[Cp^*Ru(MeCN)_3]PF_6$ (2.5 mg, 0.005 mmol) and the reaction vessel allowed to warm to rt. After 1 h, the alkyne was consumed as determined by TLC analysis, and the crude reaction mixture was filtered through a plug of florisil (ca 2 cm), washing with ether (4 mL). removal of the volatile organic species and NMR analysis indicated full deuterium incorporation at a single olefinic peak (^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70). Structural assignment in this case was made by analogy to ^{1}H NMR shifts of similar vinylsilanes in this study (**9, 12, 14)**, as well as to deriviatives of 1-cyclohexyl-vinyltriethylsilane in the literature.[3] For these compounds, there is a consistent shift difference for the cis (δ 5.58 – 5.68) and trans (δ 5.28-5.37) relative to the silyl group. Isomeric purity is conservatively estimated at ≥97:3.

4-(3-Triethylsilanyl-but-2-enyl)-cyclohex-2-enone, 45

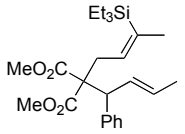


The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **44** (150 mg, 1.01 mmol), triethoxysilane (216 mg, 1.32 mmol), CH_2Cl_2 (2.0 mL), and complex **7** (5.1 mg, 0.010 mmol) to afford a 5:1 mixture of regioisomeric vinylsilanes (272 mg, 86%) after purification on silica gel column (eluent: 4:1 pet. ether: ether).

Data for 5:1 mixture of regioisomers:

R_f: 0.59 (2:1 P.E.: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88-6.92 (m, 1H), 6.26 (q, J = 7.0, 0.15 H), 6.13-6.18 (m, 0.85H), 5.94-6.00 (m, 1H), 3.82 (q, J = 7.1, 6H), 2.07-2.55 (m, 7H), 1.91 (d, J = 7.0, 0.45H), 1.84 (s, 2.55 H), 1.23 (t, J = 7.1, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 155.1, 154.8, 144.6, 143.4, 130.7, 129.0, 128.6, 58.3, 58.2, 43.9, 36.95, 36.87, 36.67, 36.23, 36.00, 28.6, 28.5, 23.7, 18.2. IR (thin film) 2974, 2927, 1682 (s), 1389.4, 1166, 1081 (br), 959, 781, 723 cm^{-1}.

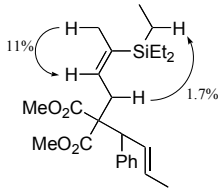
2-(1-Phenyl-but-2-enyl)-2-(3-triethylsilanyl-but-2-enyl)-malonic acid dimethyl ester, 47



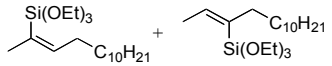
The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **46** (78.5 mg, 0.26 mmol), Et_3SiH (46 μL, 0.29 mmol), CH_2Cl_2 (0.50 mL), and complex **7** (1.1 mg, 0.0026 mmol) to afford the product (75 mg, 70%). Chromatography eluent: 30:1 pet. ether: EtOAc.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13-7.28 (m, 5H), 5.99 (ddd, *J* = 15.1, 9.0, 1.4 Hz, 1H), 5.92 (td, *J* = 6.3, 1.4 Hz, 1H), 5.51 (dq, *J* = 15.1, 6.4 Hz, 1H), 3.95 (d, *J* = 9.0 Hz, 1H), 3.69 (s, 3H), 3.64 (m, 3H), 2.56 (m, 2H), 1.70 (d, *J* = 1.5 Hz, 3H), 1.66 (d, *J* = 6.4 Hz, 3H), 0.89 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.6, 139.8, 137.3, 134.9, 129.8, 129.1, 128.4, 128.1, 127.0, 62.9, 54.5, 52.0, 51.9, 36.8, 25.3, 18.1, 7.4, 3.7. IR (thin film) 2952, 2875, 1732 (s), 1434, 1206 cm^{-1}. Anal. calc. for $C_{25}H_{38}O_4Si$: C, 69.72; H, 8.89. Found: C, 69.89; H, 8.69.

NOe data:



(Z)-2-(Triethoxysilyl)tetradecene and (Z)-3-(Triethoxysilyl)tetradecene, 49

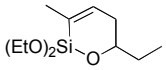


49a **49b**

The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **48** (90 mg, 0.50 mmol), $(EtO)_3SiH$ (111 μL, 0.60 mmol), CH_2Cl_2 (1.0 mL), and complex **7** (2.5 mg, 0.0050 mmol) to afford the product (172 mg, quant.) as a 2.4:1 mixture of regioisomers favoring **49a**. Filtration through florisil and washing with ether provided spectroscopically homogeneous material without additional purification.

Characterization data for a 2.4:1 mixture of 2-silyl: 3-silyl isomers:
R_f: 0.38 (10:1 pet. ether: ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (m, 0.3H), 6.18 (qt, *J* = 7.1, 1.5 Hz, 0.7H), 3.84 (q, *J* = 7.1 Hz, 4.2H), 3.83 (q, *J* = 7.0 Hz, 1.8H), 2.24 (td, *J* = 7.1, 7.1 Hz, 1.4H), 2.09 (t, *J* = 7.7 Hz, 0.6H), 1.88 (d, *J* = 7.1 Hz, 0.9H), 1.81 (s, 2.1H), 1.23-1.39 (m, 27H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 141.5, 133.6, 126.6, 58.1, 58.0, 37.8, 32.0, 31.9, 30.6, 29.9, 29.6, 29.5, 29.4, 29.3, 23.6, 22.7, 18.2, 14.1. IR (thin film) 2973, 2924, 2855, 1622 (w), 1455, 1390, 1167, 1081, 958, 780, 722 cm^{-1}. Anal. calc. for $C_{19}H_{40}O_3Si$: C, 66.22; H, 11.70; Found: C, 66.33; H, 11.73.

2,2-Diethoxy-5-ethyl-3-ethylidene-[1,2]oxasilolane, 57

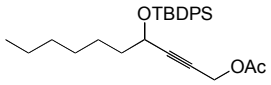


The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **56** (56 mg, 0.50 mmol), $(EtO)_3SiH$ (111 μL, 0.60 mmol), CH_2Cl_2 (1.0 mL), and complex **7** (2.5 mg, 0.0050 mmol) to afford the product (81 mg, 70%) after separation of the minor regioisomer. Chromatography eluent: 20:1 pet. ether: EtOAc.

R_f: 0.59 (10:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (m, 1H), 4.01 (m, 1H), 3.88 (td, *J* = 7.1, 2.7 Hz, 2H), 3.80 (m, 2H), 2.14 (m, 2H), 1.79 (td, *J* = 1.7, 1.7 Hz, 3H), 1.45-1.62 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 129.3, 75.2, 58.7, 58.5, 35.8, 30.5,

20.3, 18.3, 18.2, 9.9. IR (thin film) 2975, 2928, 2881, 1615 (w), 1105, 1079, 1018, 966 cm^{-1}. Anal. calc. for $C_{11}H_{22}O_3Si$: C, 57.35; H, 9.63. Found: C, 57.50; H, 9.81.

1-Acetoxy-4-(*tert*-butyldiphenylsilyloxy)-2-decyne, 58



Commercially available 1-(tetrahydropropynyloxy)-2-propyne (4.22 mL, 30.0 mmol) was dissolved in THF (30.0 mL) and the solution cooled to –78 °C. Butyllithium (20.6 mL, 33.0 mmol, 1.6 M in hexanes) was added dropwise via syringe over 10 min. Then heptaldehyde (4.61 mL, 33.0 mmol) was added and the solution was allowed to warm to room temperature and to stir for 1 h. The mixture was quenched with water (100 mL), diluted with sat. aq sodium bicarbonate (50 mL) and extracted with ether (3 x 50 mL). The combined organic extracts were washed with brine (100 mL) and dried over $MgSO_4$. Removal of the solvents under reduced pressure afforded crude 1-(tetrahydropropynyloxy)-2-decyn-4-ol (7.5 g) as a clear colorless oil. The crude alcohol (4.088 g, 16.07 mmol) was taken up in dimethylformamide (16 mL) at rt. Imidazole (1.64 g, 24.1 mmol) and *tert*-butylchlorodiphenylsilane (4.60 mL, 17.7 mmol) were added sequentially and the solution was heated to 40 °C and stirred for 18 h. The mixture was quenched with water (220 mL) and then extracted with ether (3 x 75 mL). The combined organic extracts were washed with water (75 mL), sat. aq NH_4Cl (75 mL), and brine (75 mL), then dried over $MgSO_4$. The solvents were removed in vacuo and the resulting residue (2.00 of 7.90 g) taken up in methanol (20 mL) at rt under air. Conc. HCl (1 drop) was added and the solution stirred for 2 h. The reaction was quenched with sat. aq sodium bicarbonate (80 mL), the organic solvents were removed under reduced pressure, and the mixture was extracted with ether (2 x 50 mL). The combined organic fractions were washed with brine (50 mL) and dried over $MgSO_4$. The residue was applied to a silica gel column (90:10:1, then 80:20:1 pet. ether: ether: methanol) and purified to produce 1.274 g (75% for three steps) of the desired primary propargylic alcohol. R_f 0.41 (80:20:1 pet. ether: ether: methanol).

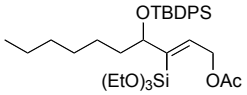
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.77 (m, 4H), 7.35-7.43 (m, 6H), 4.40 (m, 1), 4.02 (dd, J = 6.1, 1.5 Hz, 2H), 1.66 (m, 2H), 1.15-1.45 (m, 8H), 1.07 (s, 9H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.9, 134.8, 134.2, 133.6, 129.7, 129.6, 127.6, 127.3, 87.4, 83.1, 63.8, 51.0, 38.2, 31.7, 28.9, 26.9, 24.9, 22.6, 19.2. IR (thin film) 3346 (br OH), 3072, 2931, 2858, 1590, 1472, 1428, 1112, 1074, 823 cm^{-1}. HRMS (EI) calc. for $C_{26}H_{36}O_2Si$: 408.2486. Found: 351.1787 (corresponds to loss of $C_4H_9^+$, calc: 351.1780).

The primary alcohol (806 mg, 1.97 mmol) in CH_2Cl_2 (4 mL) at 0 °C was treated sequentially with triethylamine (0.750 mL, 5.38 mmol) and acetic anhydride (0.380 mL, 4.03 mmol). After stirring 15 min at rt, the mixture was diluted with ether (40 mL), filtered through a silica gel plug (ca. 3 cm), and concentrated in vacuo. Purification of the residue on a silica gel column (eluent: 10:1 pet. ether: ether) gave 814 mg (92%) of the desired primary acetate.

R_f: 0.21 (10:1 pet. ether: ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.77 (m, 4H), 7.35-7.43 (m, 6H), 4.53 (d, J = 1.5 Hz, 2H), 4.36 (m, 1H), 2.05 (s, 3H), 1.66 (m, 2H), 1.15-1.45 (m, 8H), 1.07 (s, 9H), 0.876 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 136.0, 135.8, 133.6, 133.5, 129.6, 129.5, 127.5, 127.3, 88.2, 78.6, 63.8, 52.3, 38.1,

31.7, 28.9, 26.9, 24.8, 22.6, 20.8, 19.3, 14.1. IR (thin film) 3073 (w), 2932, 1751, 1223, 1112, 702 cm^{-1}. Anal. calc. for $C_{28}H_{38}O_3Si$: C, 74.62; H, 8.50. Found: C, 74.71; H, 8.39.

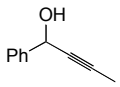
(Z)-1-Acetyloxy-4-(tert-butyldiphenylsilyloxy)-3-(triethoxysilyl)-2-decene, 59



The general procedure for the synthesis of vinylsilane **9** was followed employing the alkyne **58** (90 mg, 0.20 mmol), $(EtO)_3SiH$ (44 μL, 0.24 mmol), CH_2Cl_2 (0.4 mL), and complex **7** (4.0 mg, 0.0079 mmol) to afford the product (113 mg, 92%) as a 6.7:1 mixture of regioisomers. The chromatography eluent was 100:8 pet. ether: ether. The two regioisomers could be separated by careful chromatography with the stated conditions for characterization purposes.

Data for major isomer:
R_f: 0.32 (10:1 pet. ether: ether). ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 6.6 Hz, 2H), 7.63 (d, J = 6.6 Hz, 2H), 7.27-7.41 (m, 6H), 6.57 (t, J = 6.6 Hz, 1H), 4.80 (m, 2H), 4.46 (m, 1H), 3.68 (q, J = 7.0 Hz, 6H), 2.06 (s, 3H), 1.04-1.50 (m, 10H), 1.34 (t, J = 7.0 Hz, 9H), 1.07 (s, 9H), 0.83 (t, J = 7.1 Hz, 3H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 135.2, 134.0, 131.3, 131.2, 129.8, 129.3, 124.6, 124.5, 122.6, 122.5, 70.4, 59.1, 53.4, 32.4, 27.0, 24.4, 22.3, 19.0, 17.8, 16.2, 14.7, 13.3, 9.3. IR (thin film) 3073 (w), 2931, 2859, 1745 (s), 1231, 1105 (s), 1081 (s), 963 cm^{-1}. Anal. calc. for $C_{34}H_{54}O_6Si_2$: C, 66.40; H, 8.85. Found: C, 66.62; H, 8.63.

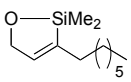
(±)-1-Phenyl-2-butyn-1-ol, 62



A commercial solution of 1-proynylmagnesium bromide (80 mL, 40 mmol, 0.5 M in THF) was treated with benzaldehyde (4.07 mL, 40 mmol) at –78 °C. The solution was allowed to warm to rt over 1 h, at which time it was quenched by addition of sat. aq NH_4Cl (100 mL). The volatile organic species were removed in vacuo, and the mixture extracted with ether (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. Distillation of the residue (b.p. 83-85, 0.3 torr) provided 6.62 g (91%) of the desired propargylic alcohol. Spectral data matched that previously reported.[6]

R_f: 0.22 (10:1 pet. ether: ether). ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.53 (m, 5H), 5.40 (m, 1H), 2.28 (d, J = 6.0 Hz, 1H), 1.89 (d, J = 1.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 128.5, 128.2, 126.5, 83.1, 79.1, 64.7, 3.7. IR (thin film) 3357 (br OH), 3032, 2919, 2230, 1453, 1136, 1002 cm^{-1}.

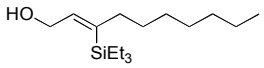
3-Heptyl-2,2-dimethyl-2,5-dihydro-[1,2]oxasilole, 64



To a solution of dec-2-yn-1-ol (100 mg, 0.65 mmol) and dimethylethoxysilane (101.4 mg, 0.97 mmol) in CH_2Cl_2 (1.4 mL) is added **7** (8.2 mg, 0.018 mmol) at 0 ºC. The solution is allowed to warm to rt, stirred for 2h, filtered through a plug of florisil, concentrated under reduced pressure and purified on florisil column (eluent: 100:1 pet. ether: ether) to afford 3-heptyl-2,2-dimethyl-2,5-dihydro-[1,2]oxasilole (39.6 mg, 29%).

R_f: 0.79 (2:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (s, 1H), 4.54 (d, J = 1.7, 2H), 2.25 (td, J = 7.8, 1.7 Hz, 2H), 0.86-1.55 (m, 13H), 0.31 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 140.9, 71.7, 31.8, 31.1, 29.8, 29.5, 29.1, 22.7, 14.1, 0.4. IR (thin film) 3319 (w), 2926 (s), 2855, 1790, 1466, 1251, 1077, 862, 828, 789 cm^{-1}. The instability of this compound did not allow us to obtain elemental analysis or high-resolution MS data.

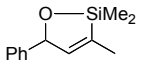
(Z)-3-(Triethylsilyl)-dec-2-en-1-ol, 65



The general procedure for the synthesis of vinylsilane **68** was followed employing the alkyne (1.00 g, 6.48 mmol), Et_3SiH (1.23 mL, 7.78 mmol), CH_2Cl_2 (13 mL), and complex **7** (33 mg, 0.065 mmol) to afford the product (1.74 g, 99%) as a 13:1 mixture of regioisomers. Chromatography eluent: 100:10:1 to 80:20:1 pet. ether: ether: methanol.

R_f: 0.65 (2:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (t, J = 7.1 Hz, 1H), 4.17 (dd, J = 6.3, 6.3 Hz, 2H), 2.04 (t, J = 6.3 Hz, 2H), 1.22-1.32 (m, 13H), 1.15 (t, J = 5.6 Hz, 1H), 0.86-0.97 (m, 9H), 0.61-0.71 (m, 6H).). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 141.0, 62.3, 38.1, 31.8, 30.5, 29.5, 29.2, 22.6, 14.1, 7.5, 4.3. IR (thin film) 3317 (br), 2926, 2874, 1463, 1004, 732 cm^{-1}. Anal. Calc. for $C_{16}H_{34}OSi$: C, 71.04; H, 12.67. Found: C, 71.21; H, 12.76.

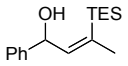
2,2,3-trimethyl-5-phenyl-2,5-dihydro-[1,2]oxasilole, 66



To a solution of 1-phenyl-2-butyn-1-ol (55 mg, 0.38 mmol) and dimethylethoxysilane (46.9 mg, 0.45 mmol) in CH_2Cl_2 (0.8 mL) was added **7** (3.8 mg, 0.0075 mmol) at 0 ºC. The solution was allowed to warm to rt and stirred for 20 min, at which time TLC analysis indicated incomplete consumption of the alkyne. Another portion of ethoxydimethylsilane (38 mg, 0.36 mmol) and **7** (1.9 mg, 0.004 mmol) at 0 ºC were added and the solution stirred at rt for 20 min. Purification on florisil column (eluent: 60:1 pet. ether: EtOAc) afforded 2,2,3-trimethyl-5-phenyl-2,5-dihydro-[1,2]oxasilole (57.5 mg, 74%).

R_f: 0.66 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.37 (m, 5H), 6.41 (s, 1H), 5.64 (s, 1H), 1.89 (t, J = 1.7, 3H), 0.36 (s, 3H), 0.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 142.8, 136.8, 127.3, 125.9, 83.5, 15.4, 0.31, -0.45. IR (thin film) 2952, 2856, 1452, 1249, 1061, 869, 781, 689 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{12}H_{16}OSi$: 203.089. Found: 203.0901.

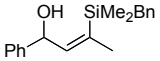
(Z)-1-Phenyl-3-(triethyl-silanyl)-but-2-en-1-ol, 67



To a solution of (±)-1-phenyl-2-butyn-1-ol (50 mg, 0.34 mmol) and triethylsilane (52 mg, 0.44 mol) in CH_2Cl_2 (0.7 mL) is added **7** (1.7 mg, 0.003 mmol) at 0º C. The solution is allowed to warm to rt and stirred for 1h. Additional triethylsilane (40 mg, 0.34 mol) and **7** (5.1 mg, 0.01 mmol) are added at 0 ºC, the mixture is stirred at rt for 1h, filtered through a plug of florisil to yield 1-phenyl-3-(triethylsilyl)-2-buten-1-ol (86 mg, 97%) after purification on silica gel column (Eluent: 10:1 pet. ether: EtOAc).

R_f: 0.74 (2:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.42 (m, 5H), 6.23 (d, J = 9.8, 1H), 5.34 (dd, J = 9.8, 2.9, 1H), 1.84 (s, 3H), 1.70 (d, J = 2.9, 1H), 0.99 (t, J = 7.7, 9H), 0.76 (q, J = 7.7, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 143.5, 137.7, 128.5, 127.4, 126.0, 72.7, 25.7, 7.5, 4.2. IR (thin film) 3332 (br), 2953 (s), 2875, 1451, 1004, 734 (s), 698 (s) cm^{-1}. Anal. Calc. for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found: C, 73.35; H, 10.02.

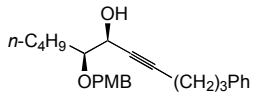
General procedure for hydrosilylation of propagylic alcohols: *(±)-(Z)*-3-(benzyldimethylsilyl)-1-phenyl-2-buten-1-ol, 68



To a solution of (±)-1-phenyl-2-butynol (500 mg, 3.42 mmol) in acetone (7.0 mL) is added benzyldimethylsilane (0.591 mL, 4.10 mmol) and $[Cp^*Ru(MeCN)_3]PF_6$ (**7**) (35 mg, 0.069 mmol) at 0 °C. The solution is allowed to warm to rt and stirred for 45 min. The crude reaction mixture was directly concentrated under reduced pressure and applied to a silica gel column (eluent: 6:1 pet. ether: ether). The minor α-silyl olefin regioisomers could be separated to afford cleanly the desired vinylsilane (920 mg, 91%).

R_f: 0.26 (4:1 pet. ether: ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05-7.39 (m, 10H), 6.19 (dd, J = 9.5, 1.6 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H), 2.30 (s, 2H), 1.85 (d, J = 1.6 Hz, 3H), 1.47 (s, 1H), 0.28 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 143.0, 139.6, 137.0, 128.36, 128.23, 128.10, 127.29, 125.9, 124.3, 72.5, 26.1, 24.9, -1.40, -1.69. IR (thin film) 3346 (br), 3026, 2952, 1600, 1493, 1451, 1250, 1003, 831, 699 (s) cm^{-1}. Anal. Calc. for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 77.10; H, 8.19.

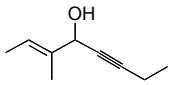
Preparation of (±)-(S,S)-7-(4-methoxy-benzyloxy)-1-phenyl-undec-4-yn-6-ol, 69



To a solution of pent-4-ynyl-benzene (50 mg, 0.34 mmol) in ether (0.3 mL) is added butyllithium (0.21 mL, 0.34 mL) at 0 ºC and stirred for 2.5 h. At –78 ºC anhydrous $ZnBr_2$ (83 mg, 0.37 mmol) in ether (0.3 mL) is added to the solution above via cannula, followed by 2-(4-methoxy-benzyloxy)-hexanal (40 mg, 0.17 mmol). The solution is stirred and allowed to warm to 0 ºC slowly over 2h. The reaction is quenched with sat. aq ammonium chloride (10 mL), extracted with ether (20 mL), washed with brine (10 mL) and dried over $MgSO_4$. The reaction yielded (±)-(*S,S*)-7-(4-methoxy-benzyloxy)-1-phenyl-undec-4-yn-6-ol (44.8 mg, 70 %) after silica gel chromatography (eluent: 10:1 to 4:1 to 2:1 pet. ether: ether).

R_f: 0.07 (4:1 pet. ether: ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.30 (m, 7H), 6.87 (d, *J* = 8.5, 2H), 4.62 (s, 3H), 4.30-4.31 (m, 1H), 3.79 (s, 3H), 3.48 (dt, *J* = 5.9, 5.4, 1H), 2.71 (t, *J* = 7.5, 2H), 2.25 (td, *J* = 7.0, 1.7, 2H), 1.84 (p, *J* = 7.0, 2H), 1.62-1.62 (m, 2H), 1.26-1.43 (m, 4H), 0.90 (t, *J* = 7.1, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 141.5, 130.3, 129.5, 128.5, 128.3, 125.9, 113.8, 86.0, 82.2, 79.4, 72.8, 64.8, 55.2, 34.8, 30.6, 30.1, 27.3, 22.8, 18.2, 14.0. IR (thin film) 3443 (br), 2932, 2859, 1613, 1514 (s), 1248 (s), 1035, 700.0 cm^{-1}. Anal. Calc. for $C_{25}H_{32}O_3$: C, 78.91; H, 8.48. Found: C, 79.17; H, 8.57.

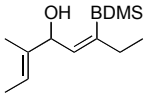
(E)-3-Methyl-oct-2-en-5-yn-4-ol, 71



Gaseous 1-butyne was condensed into a flask at –40 °C under N_2 to ca. 2.5 g of alkyne. The flask was then cooled to –78 °C and THF (50 mL) was introduced. The flask was treated with butyllithium (14.9 mL, 23.8 mmol, 1.6 M soln in hexanes). After stirring for 20 min, (*E*)-2-methyl-2-butenal (2.30 mL, 23.8 mmol) was introduced and the flask was allowed to warm to 0 °C over 20 min. The mixture was quenched with sat. aq NH_4Cl (25 mL) and extracted with ether (2 x 40 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification was achieved through Kugelrohr distillation of the resulting residue, collecting 2 fractions, to provide first 1.20 g of a mixture of compounds, including mostly the desired alcohol, followed by 1.60 g (49%) of a fraction of pure propargylic alcohol (chamber 150 °C, ca. 1 torr).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (q, *J* = 6.7 Hz, 1H), 4.74 (m, 1H), 2.25 (qd, *J* = 7.6, 2.0 Hz, 2H), 1.75 (s, 3H), 1.64 (d, *J* = 6.7 Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 122.2, 88.1, 78.8, 68.3, 13.8, 13.2, 12.4, 11.8. IR (thin film) 3384 (br OH), 2978, 1316, 996 cm^{-1}. Additional characterization was obtained after conversion to the vinylsilane **72**.

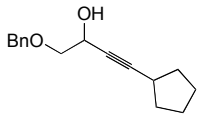
(±)(2E,5Z)-6-(Benzyldimethylsilyl)-3-methyl-octa-2,5-dien-4-ol, 72



The general procedure for the synthesis of vinylsilane **68** was followed employing the alkyne (100 mg, 0.72 mmol), BDMS-H (0.150 mL, 0.86 mmol), acetone (1.4 mL), and complex **7** (7.1 mg, 0.014 mmol), with isolation by chromatography (eluent: 20:1 pet. ether: EtOAc). The major product (100 mg, 48%) was isolated in pure form, eluting after the less polar minor α-silyl olefin regioisomers (21 mg, 10%).

Data for major isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.03 (dt, *J* = 9.6, 1.5 Hz, 1H), 5.53 (m, 1H), 4.56 (d, *J* = 9.0 Hz, 1H), 2.24 (s, 2H), 2.08 (m, 2H), 1.60-1.63 (m, 6H), 1.14 (d, *J* = 2.9 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.18 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.2, 140.1, 137.2, 128.5, 128.4, 124.5, 120.7, 75.8, 30.9, 27.0, 14.9, 13.4, 12.5, -1.0, -1.2. Anal. Calc. for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 74.74; H, 9.65. HRMS—EI (m/z): $[M]^+$ calcd for $C_{18}H_{28}OSi$: 288.1909; found: 288.1895.

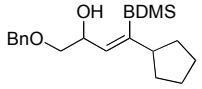
(±)-1-Benzyloxy-4-cyclopentyl-3-butyn-2-ol, 73



Cyclopentylacetylene (0.60 mL, 6.79 mmol) was taken up in THF (8 mL) at 0 °C and treated with ethylmagnesium chloride (2.73 mL, 6.79 mmol, 25 wt% soln in ether). The solution was heated to 45 °C and stirred for 30 min, at which time the flask was cooled to –78 °C and treated with benzyloxyacetaldehyde (0.90 mL, 6.41 mmol). The flask was allowed to warm to rt over 1 h and then quenched by addition of sat. aq NH_4Cl (10 mL). The volatile organic species were removed under reduced pressure, and the mixture extracted with ether (50 mL). The organic layers were washed with brine (10 mL), dried over $MgSO_4$, concentrated in vacuo, and purified on a silica gel column (eluent: 85:15 pet. ether: EtOAc) to give 1.27 g (81%) of a crude mixture of the desired propargyl alcohol together with (±)-1-benzyloxy-2-hexanol, the product of ethylmagnesium chloride addition. These were separated by distillation (b.p. 154-155 °C, ca. 1 torr) to provide 540 mg (35%) of the desired propargylic alcohol.

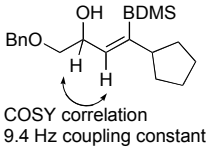
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.36 (m, 5H), 4.54-4.61 (m, 3H), 3.62 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.52 (dd, *J* = 9.8, 7.8 Hz, 1H), 2.62 (m, 1H), 2.41 (m, 1H), 1.50-1.92 (m, 8H). IR (thin film) 3426 (br OH), 2959, 2869, 2235 (w), 1453, 1109, 737, 698 cm^{-1}. Additional characterization was obtained after conversion to the vinylsilane **76**.

(±)-4-(Benzyl-dimethyl-silanyl)-1-benzyloxy-4-cyclopentyl-but-3-en-2-ol, 74

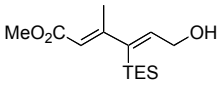


The general procedure for the synthesis of vinylsilane **68** was followed employing the alkyne (98 mg, 0.402 mmol), BDMS-H (83 μL, 0.156 mmol), acetone (0.48 mL), and complex **7** (6.1 mg, 0.012 mmol) to afford the product (153 mg, 97%) as a 9:1 mixture of regioisomers. Chromatography eluent: 10:1 pet. ether: acetone.

Data for major isomer (contaminated with α-silyl olefin regioisomers):
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.06 (m, 1H), 6.99 (d, *J* = 7.7 Hz, 2H), 5.95 (dd, *J* = 9.4, 1.1 Hz, 1H), 4.53 (m, 2H), 4.43 (m, 1H), 3.30 (m, 2H), 2.45 (m, 1H), 2.18-2.24 (m, 3H), 1.22-1.67 (m, 8H), 0.16 (s, 3H), 0.13 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.2, 140.1, 138.2, 136.8, 128.7, 128.6, 128.4, 128.1, 128.0, 124.4, 74.3, 73.5, 70.1, 45.9, 33.7, 33.1, 27.1, 25.2, 25.1, -0.7, -1.0. IR (thin film) 3450 (br, OH), 2953, 2867, 1494, 1452, 1251, 1102, 831, 698 cm^{-1}. Anal. Calc. for $C_{25}H_{34}O_2Si$: C, 76.09; H, 8.68. Found: C, 75.82; H, 8.53.
Regioisomer determined by COSY correlation (gCOSY, 500MHz, $CDCl_3$).



Methyl (2E,4Z)-6-hydroxy-3-methyl-4-(triethylsilyl)-2,4-hexadienoate, 76



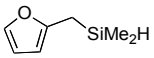
The general procedure for the synthesis of vinylsilane **68** was followed employing the alkyne **73** [7] (20 mg, 0.13 mmol), Et_3SiH (25 μL, 0.156 mmol), CH_2Cl_2 (0.3 mL), and complex **7** (3.3 mg, 0.0065 mmol) to give 22 mg (63%, 84% based on unreacted starting material as determined by ^1H NMR analysis of the crude reaction mixture) of the desired product as a single regio- and geometric isomer. Purification by preparative TLC (eluent: 50:50:1 pet. ether: EtOAc: MeOH).

^1H NMR (300 MHz, $CDCl_3$) δ 6.12 (t, J = 6.8 Hz, 1H), 5.49 (m, 1H), 4.22 (d, J = 6.8 Hz, 2H), 3.70 (s, 3H), 2.21 (d, J = 1.2 Hz, 3H), 1.48 (br OH, 1H), 0.96 (t, J = 7.8 Hz, 9H), 0.68 (q, J = 7.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 164.6, 146.7, 141.3, 114.1, 61.9, 50.9, 20.8, 7.5, 4.4. IR (thin film) 3447 (br OH), 2954, 2877, 1717, 1700, 1624, 1457, 1149 cm^{-1}. HRMS—EI (m/z): $[M-CH_3]^+$ calcd for $C_{13}H_{23}O_3Si$: 255.1416; found: 255.1409.

(*Z*)-5-(Benzyldimethylsilyl)-4-hepten-3-one, 78

Competition experiment (Scheme 5): 4-Hepyn-3-one (55 mg, 0.50 mmol), the alkynyl alcohol **97** (56 mg, 0.50 mmol), and benzyldimethylsilane (78 μL, 0.45 mmol) were taken up in acetone at 0 °C. Solid $[Cp^*Ru(MeCN)_3]PF_6$ (2.5 mg, 0.005 mmol) was added, and the flask immediately allowed to warm to rt. After stirring 25 min., the mixture was diluted with ether (5 mL) and washed through a plug of silica gel (ca. 2 cm), washing with additional ether (10 mL). Concentration in vacuo and examination of the crude reaction mixture by ^1H NMR analysis of the olefinic region showed clean conversion to three vinylsilane products, in a ration of 100: 7.5: 4 for **78**: **98a**: **98b**. The minor isomers appear as multiplets, δ 6.00 and 6.15 for **98a** and **98b**, respectively.

Dimethyl-(2-furanylmethyl)silane, 79



Furan (7.5 mL, 108 mmol) was dissolved in ether (50 mL) and cooled to -40 °C. Butyllithium (21 mL, 52.5 mmol, 2.5 M solution in hexanes) was added to the reaction slowly. After the addition was completed, the reaction was allowed to warm to rt and stirred for 3 h. The resultant lithium salt was cooled to –78 ºC for 15 min and (bromomethyl)dimethylsilyl chloride (9.8 g, 53.5 mmol) was added to the reaction. The resultant reaction mixture was allowed to stir warming up to rt overnight. The reaction was quenched with sat. aq NH_4Cl (30 mL) and the mixture was extracted with ether (2 x 100 mL). The combined organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product as a brown oil. The crude product was purified by silica gel column chromatography (eluent: pet. ether, then 5% CH_2Cl_2: pet. ether) to give 10.2 g (88%) of desired (bromomethyl)-(2-furanyl)-dimethylsilane as clear oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (m, 1H), 6.74 (m, 1H), 6.41 (m, 1H), 2.63 (s, 2H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ156.3, 147.2, 121.3, 109.5, 15.8, -4.3. IR (thin film) 3112, 2963, 1551, 1455, 1385, 1253, 1110, 1007, 901, 812, 749 cm^{-1}.

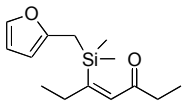
The bromomethylsilane (440 mg, 2.0 mmol) was dissolved in toluene (6 mL) and treated with 25% wt/v NaOMe/MeOH (2.37 mmol). The resultant mixture was stirred at 110 ºC for 1 h and reaction was confirmed to be complete by GC. Dilution of the reaction with ether (30 mL) and filteration through Celite afforded the crude

methoxysilane solution. The filtrate was concentrated under reduced pressure and purified by Krugelrohr distillation (chamber 200 ºC, 35 torr) to provide 220 mg (64%) of a clear, colorless oil. The crude silyl ether can be use directly in the reduction which follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.25 (m, 1 H), 6.26 (m, 1H), 5.87 (m, 1H), 3.43 (s, 3H), 2.18 (s, 2H), 0.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 140.2, 110.5, 104.2, 50.5, 17.5, -2.5. IR (thin film) 2958, 2927, 2854, 2832, 1590, 1506, 1253, 1091, 838 cm^{-1}.

The silyl ether (200 mg, 1.17 mmol) in ether (10 mL) was treated with $LiAlH_4$ (100mg, 2.63 mmol). The resultant mixture was stirred at rt for 2 h and the reaction was confirmed to be complete by GC. The reaction was cooled in an ice bath and quenched with $Na_2SO_4 \cdot 10H_2O$ (1.0 g). The mixture was filtered through Celite and washed with ether (3 x 10 mL). The solution was concentrated under reduced pressure to give the crude product. The crude product can be purified by distillation. Due to the volatile nature of the product, isolated distillation yield was only 42 mg (25%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 1H), 6.26 (m, 1H), 5.86 (m, 1H), 4.02 (m, 1H), 2.18 (d, *J*= 3.2 Hz, 2H), 0.13 (d, *J*= 0.5 Hz, 3H), 0.12 (d, *J*= 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 140.2, 110.4, 103.9, 15.5, -4.4; IR (thin film) 2960, 1590, 1505, 1255, 1144, 1065, 840 cm^{-1}.

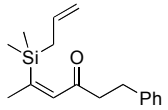
(*Z*)-(2-Furanylmethyl-dimethylsilyl)-4-hepten-3-one, 80



The general procedure given for the synthesis of **78** was employed with the alkyne (27 mg, 0.25 mmol), (2-furanylmethyl)-dimethylsilane (41.5 mg, 0.30 mmol), acetone (0.50 mL), and complex **7** (6.0 mg, 0.012 mmol) to give the product (55 mg, 89%). Chromatography eluent: 40:1 pet. ether: ether.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.59 (t, *J* = 1.5 Hz, 1H), 6.14 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.68 (dd, *J* = 3.1, 0.9 Hz, 1H), 2.44 (q, *J* = 7.3 Hz, 2H), 2.27 (s, 2H), 2.17 (qd, *J* = 7.3, 1.5 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.10 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.3, 164.9, 154.8, 139.7, 136.3, 110.3, 103.7, 36.3, 31.4, 16.7, 13.8, 8.0, -2.2. IR (thin film) 2969, 1691, 1578, 1246, 1144, 1006, 926, 832, 721 cm^{-1}.

(*Z*)-5-(Allyldimethylsilyl)-1-phenyl-4-hexen-3-one, 82

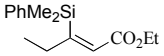


The general procedure given for the synthesis of **78** was employed with the alkyne (15 mg, 0.087 mmol), allyldimethylsilane (18 μL, 0.131 mmol), CH_2Cl_2 (0.2 mL), and complex **7** (1.6 mg, 0.0035 mmol) to give the product (16.6 mg, 70%). Chromatography eluent: 40:1 pet. ether: ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.31 (m, 5H), 6.72 (d, *J* = 1.7 Hz, 1H), 5.76 (m, 1H), 4.80-4.87 (m, 2H), 2.94 (m, 2H), 2.80 (m, 2H), 1.99 (d, *J* = 1.7 Hz, 3H), 1.77 (d, *J* = 8.3 Hz, 2H), 0.16 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 161.2, 141.2, 138.1, 135.4, 128.4, 128.3, 126.0, 112.9, 44.6, 30.0, 26.5, 22.7, -3.0. IR (thin film) 3029 (w),

2956, 1688 (s), 1580, 1440, 1254, 841, 698 cm^{-1}. HRMS—EI (m/z): $[M\text{-}C_3H_5]^+$ calcd for $C_{14}H_{19}OSi$: 231.1205; found: 231.1216.

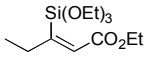
Ethyl (*Z*)-3-(dimethylphenylsilyl)-2-pentenoate, 85



The general procedure given for the synthesis of **78** was employed with alkyne (0.30 mL, 2.28 mmol), dimethylphenylsilane (0.35 mL, 2.73 mmol), acetone (5.0 mL), and complex **7** (18 mg, 0.046 mmol) to give the product (571 mg, 96%). Chromatography eluent: 15:1 pet. ether: ether.

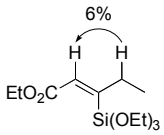
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.54 (m, 2H), 7.31-7.33 (m, 3H), 6.38 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.27 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.48 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 164.6, 139.0, 133.7, 130.3, 128.5, 127.5, 60.0, 32.0, 14.1, 13.6, -1.7. IR (thin film) 2967, 1716 (s), 1601 (w), 1247, 1198, 1112, 1041, 818, 703 cm^{-1}. HRMS—EI (m/z): $[M\text{-}CH_3]^+$ calcd for $C_{14}H_{19}O_2Si$: 247.1154; found: 247.1116.

(Z)-3-(Triethoxysilyl)-2-pentenoate ethyl ester, 86

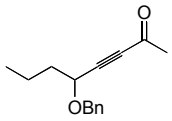


The general procedure given for the synthesis of **78** was employed with the alkyne (66 mg, 0.50 mmol), $(EtO)_3Si\text{-}H$ (111 μL, 0.60 mmol), CH_2Cl_2 (1.0 mL), and complex **7** (2.5 mg, 0.005 mmol) to afford the product (144 mg, 99%) as a 5:1 mixture of regioisomers. Filtration through florisil and washing with ether provided spectroscopically homogeneous 5:1 mixture of regioisomers without additional purification. The major β-silyl regioisomers could be obtained free of the minor α-silyl isomer by careful chromatography on silica (eluent: 20:1 pet.ether: EtOAc, Y.N.D.).

Data for pure major isomer:
R_f: 0.52 (10:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (t, *J* = 1.6 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.86 (q, *J* = 7.0 Hz, 6H), 2.36 (qd, *J* = 7.3, 1.6 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 9H), 1.07 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 156.8, 132.5, 60.3, 58.8, 31.3, 18.1, 14.2, 13.6. IR (thin film) 2976, 2929, 2887, 1726 (s), 1608, 1445, 1390, 1368, 1342, 1205, 1107 (s), 961 cm^{-1}. HRMS—EI (m/z): $[M\text{-}OEt]^+$ calcd for $C_{11}H_{21}O_4Si$: 245.1209; found: 245.1201.
NOe data:



5-Benzyloxy-3-octyn-2-one, 87

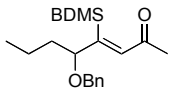


1-Hexyne-3-ol (4.00 g, 40.8 mmol) in DMF (40 mL) at 0 °C was treated with sodium hydride (1.96 g, 49.0 mmol, 40% suspension in mineral oil). After stirring 15 min, benzyl bromide (7.3 mL, 61.2 mmol) was added and the mixture was allowed to warm to rt and was stirred for 6 h. The reaction was then quenched by addition of water (200 mL), and extracted with ether (3 x 60mL). The organic extracts were washed with water (2 x 40 mL) and brine (40 mL), dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was distilled, discarding a forerun (b.p. 56-62 °C, 1 torr) before collecting 6.29 g (82%) of 3-benzyloxy-1-hexyne (b.p. 66-70 °C, 1 torr). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.36 (m, 5H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.07 (m, 1H), 2.45 (d, *J* = 2.2 Hz, 1H), 1.73 (m, 2H), 1.50 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

3-Benzyloxy-1-hexyne (1.60 g, 8.50 mmol) in ether (50 mL) under Ar at –78 °C was treated dropwise with butyllithium (5.86 mL, 8.50 mmol, 1.45M soln in hexanes). After 30 min, N,N-dimethylacetamide (1.2 eq.) was added, and the flask was placed in the cold room to warm to 5 °C over 3 h. The mixture was then poured into water (80 mL), the layers were separated, and the aqueous layer was extracted with ether (20 mL). The organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. Silica gel column purification (eluent 85:15 pet. ether: ether) gave 1.16 g (59%) of the desired ketone.

R_f: 0.30 (10:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.36 (m, 5H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.50 (d, *J* = 11.7 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 1.79 (m, 2H), 1.51 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). IR (thin film) 2963, 2210, 1727, 1682, 1220 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{150}H_{18}O_2Si$: 230.1307; found: 230.1303.

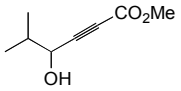
(*Z*)-4-benzyldimethylsilyl-5-benzyloxy-3-octen-2-one, 88



The general procedure given for the synthesis of **78** was employed with 0.09 mmol of alkyne (0.30 mg, 1.30 mmol), BDMS-H (0.27 mL, 1.6 mmol), acetone (2.6 mL), and complex **7** (7.0 mg, 0.013 mmol) to give the product (333 mg, 67%). Chromatography eluent: 40:1 pet. ether: EtOAc.

R_f: 0.42 (10:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.36 (m, 7H), 7.00-7.07 (m, 4H), 4.27 (d, *J* = 11.7 Hz, 1H), 3.99 (d, *J* = 11.7 Hz, 1H), 3.92 (m, 1H), 2.48 (d, *J* = 13.2 Hz, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.32 (s, 3H), 1.49 (m, 1H), 1.11-1.30 (m, 3H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.13 (s, 3H), 0.127 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 163.6, 140.3, 138.4, 135.4, 128.4, 128.3, 128.1, 127.8, 127.6, 124.1, 81.3, 70.9, 38.7, 31.2, 24.6, 19.4, 13.8, -2.2, -2.4. IR (thin film) 3027 (w), 2959, 1690 (s), 1576, 1494, 1357, 1248, 1195, 1110, 1073, 831, 699 cm^{-1}.

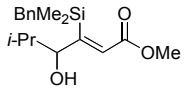
Methyl 5-methyl-4-hydroxy-2-hexynoate, 89



A stirred solution of methyl propiolate (3.0 mL, 35.9 mmol) in THF (60 mL) at –78 °C was treated with a solution of LDA (prepared from 15.8 mL, 39.5 mmol, of 2.5M butyllithium and 6.04 mL, 39.5 mmol, of diisopropylamine in 60 mL of THF) dropwise via cannula. The mixture was stirred for 20 min at –78 °C, and then treated with isobutyraldehyde (3.3 mL, 39.5 mmol). The flask was allowed to warm to 0 °C over 30 min, and was quenched by addition of sat. aq NH_4Cl (60 mL). The volatile organic species were removed under reduced pressure, and the mixture was then extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (35 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified on a silica gel column (eluent: 4:1 pet. ether: ether) to afford 3.40 g (61%) of the desired hydroxyl ester, whose spectra matched that of the known compound.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29 (dd, J = 5.9, 5.9 Hz, 1H), 3.78 (s, 3H), 1.93-2.21 (m, 2H), 1.04 (d, J = 6.6 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H).

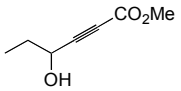
Methyl (*Z*)-4-Hydroxy-5-methyl-3-(benzyldimethylsilyl)-2-hexenoate, 90



The general procedure given for the synthesis of vinylsilane **78** was employed with the alkyne (0.50 g, 3.20 mmol), BDMS-H (0.66 mL, 3.84 mmol), acetone (6.5 mL), and complex **7** (16 mg, 0.032 mmol) to afford the product (868 mg, 88%). Isolation was by silica gel chromatography (eluent: 40:1 pet. ether: EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.06 (m, 1H), 6.60 (d, J = 1.5 Hz, 1H), 4.12 (ddd, J = 3.7, 3.7, 1.5 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 2H), 1.61 (m, 1H), 1.22 (d, J = 3.7 Hz, 1H), 0.94 (d, J = 6.9 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H), 0.18 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 165.2, 140.0, 129.2, 128.4, 128.1, 124.2, 79.0, 51.5, 31.6, 24.9, 20.5, 14.5, -2.1, -2.2. IR (thin film) 3456 (br OH), 2963, 1721 (s), 1203 (s), 831, 700 cm^{-1}. HRMS—EI (m/z): $[M-CH_3]^+$ calcd for $C_{16}H_{23}O_3Si$: 291.1416; found: 291.1411.

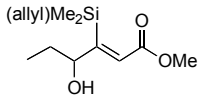
Methyl 4-hydroxy-2-hexynoate, 91



The method previously described for the synthesis of methyl 5-methyl-4-hydroxy-2-hexynoate was followed, employing methyl propiolate (4.0 mL, 47.6 mmol), butyllithium (21.0 mL, 52.3 mmol, 2.45 M soln in hexanes), diisopropylamine (8.05 mL, 57.6 mmol), THF (150 mL), and propionaldehyde (3.0 mL, 52 mmol) to produce the desired alcohol (2.50 g) in 49% yield, whose spectra matched that of the known compound.[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (m, 1H), 3.79 (s, 3H), 2.08 (m, 1H), 1.81 (m, 2H), 1.22 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H).

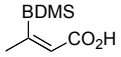
Methyl (*Z*)-4-hydroxy-3-(allyldimethylsilyl)-hex-2-enoate, 92



The general procedure given for the synthesis of **78** was employed with the alkyne (70 mg, 0.49 mmol), allyldimethylsilane (83 μL, 0.60 mmol), acetone (1.0 mL), and complex **7** (12 mg, 0.024 mmol) to afford the product (87 mg, 73%). Chromatography eluent: 15:1, then 10:1 pet. ether: EtOAc.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 1.5 Hz, 1H), 5.77 (ddt, *J* = 17.0, 10.1, 8.1 Hz, 1H), 4.83-4.88 (m, 2H), 4.35 (m, 1H), 3.74 (s, 3H), 1.78-1.85 (m, 2H), 1.65-1.72 (m, 2H), 1.31 (m, 1H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 166.0, 135.1, 127.8, 113.4, 75.6, 51.4, 30.1, 23.0, 10.1, -2.5, -2.6. IR (thin film) 3427 (br), 2952, 1723, 1630 (w), 1603 (w), 1536, 1322, 1248, 1206, 842 cm^{-1}. Anal. Calc. for $C_{13}H_{24}O_3Si$: C, 60.89; H, 9.43. Found: C, 59.57; H, 9.17. HRMS—EI (m/z): $[M\text{-allyl}]^+$ calcd for $C_9H_{17}O_3Si$: 201.0947; found: 201.0955.

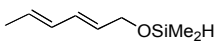
(*Z*)-3-(Benzyldimethylsilyl)-butenoic acid, 96



The general procedure given for the synthesis of **78** was employed with the alkyne (103 mg, 1.23 mmol), BDMS-H (254 μL, 1.47 mmol), acetone (2.5 mL), and complex **7** (6.0 mg, 0.012 mmol) to afford the product (270 mg, 94%). Chromatography eluent: 100:10:0.1 pet. ether: EtOAc: AcOH.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.7 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.00 (m, 2H), 6.41 (q, *J* = 1.6 Hz, 1H), 2.39 (s, 2H), 1.90 (d, *J* = 1.6 Hz, 3H), 0.15 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 165.9, 139.9, 130.3, 128.3, 128.1, 124.0, 27.1, 24.6, -2.7. IR (thin film) 3025 (br OH), 2955, 1690 (s), 1600, 1442, 1249 (s), 829, 699 cm^{-1}. Anal. Calc. for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74. Found: C, 66.51; H, 7.92.

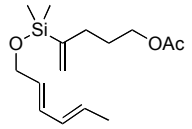
(E,E)-Dimethyl-1-hexa-2,4-dienyloxysilane, 99



Sorbol (1.028 g, 1.18 mmol) was treated with 1,1,3,3-tetramethyldisilazane (0.52 mL, 2.95 mmol) in a flask at rt. The flask was brought to 40 °C for 30 min and then cooled to rt. The excess silazane was removed under vacuum and the desired silyl ether distilled (92-94 °C at ca. 20 torr) to provide 1.10 g (67%) of the desired compound as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 14.9, 10.5 Hz, 1H), 6.05 (m, 1H), 5.59-5.75 (m, 2H), 4.63 (sep, *J* = 2.8 Hz, 1H), 4.19 (d, *J* = 5.6 Hz, 2H), (d, *J* = 6.8 Hz, 3H), 0.22 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.1, 130.8, 129.7, 128.7, 64.7, 18.1, -1.5. IR (thin film) 3022, 2961, 2856, 2114 (s), 1450, 1382, 1253, 1108, 1056, 988, 900 cm^{-1}.

Acetic acid 4-(hexa-2,4-dienyloxy-dimethyl-silanyl)-pent-4-enyl ester, 100



Path a: dienyl silane.

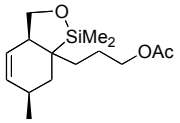
(E,E)-Dimethyl-1-hexa-2,4-dienyloxysilane (47 mg, 0.30 mmol) and 5-acetoxy-1-pentyne (33 μL, 0.25 mmol) were taken up in CH_2Cl_2 under an Ar atmosphere at 0 °C. Solid $[Cp^*Ru(MeCN)_3]PF_6$ (6.0 mg, 0.012 mmol) was added and the flask warmed to rt. After 45 min, TLC analysis indicated that some starting alkyne remained, and additional $Cp^*Ru(MeCN)_3^+PF_6^-$ (4.0 mg, 0.008 mmol) was added at 0 °C to drive the reaction to completion. After stirring an additional 1 h at rt, the solvents were removed under vacuum, and the residue purified by silica gel chromatography (eluent: 20:1 then 10:1 pet. ether : ether) to afford 38 mg (54%) of the desired silyl ether.

Path b: Chlorosilane.

5-Acetoxy-pentyne (42 μL, 0.32 mmol) was dissolved in CH_2Cl_2. Freshly distilled chlorodimethylsilane (70 μL, 0.63 mmol) was added at 0 °C, followed by solid $[Cp^*Ru(MeCN)_3]PF_6$ (1.6 mg, 0.00317 mmol). The mixture was allowed to warm to rt, where it was stirred for 1 h. Triethylamine (133 μL, 0.95 mmol) and (*E*,*E*)-2,4-hexadiene-1-ol (89 μL, 0.79 mmol) were added, followed by additional CH_2Cl_2 (2 mL) to maintain solubility. After 20 min, the mixture was diluted with benzene (10 mL) and filtered through celite. Silica gel chromatography (eluent: 20:1 then 10:1 pet. ether : ether) gave 60 mg (67%) of the desired silyl ether.

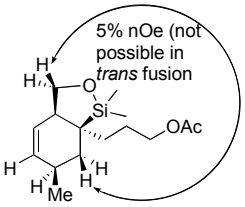
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.14 (dd, *J* = 14.8, 10.4 Hz, 1H), 6.01 (ddd, *J* = 14.8, 14.8, 1.4 Hz, 1H), 5.65 (dd, *J* = 2.0 Hz, 1H), 5.55-5.69 (m, 2H), 5.45 (d, *J* = 2.0 Hz, 1H), 4.10 (d, *J* = 5.6 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.19 (t, *J* = 7.7 Hz, 2H), 2.03 (s, 3H), 1.72-1.81 (m, 2H), 1.72 (d, *J* = 6.6 Hz, 3H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 148.9, 130.9, 130.8, 129.4, 129.1, 126.5, 64.2, 63.4, 31.5, 27.6, 21.0, 18.1, -2.1. IR (thin film) 2958, 1742 (s), 1388, 1250 (s), 1043, 989, 833 cm^{-1}.

Acetic acid 3-(1,1,6-trimethyl-3,3a,6,7-tetrahydro-benzo[c][1,2]oxasilol-7a-yl)-propyl ester, 102

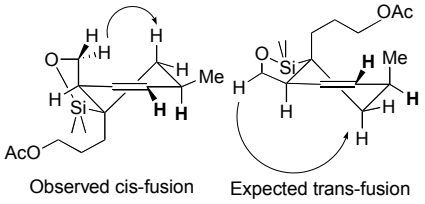


The triene **100** (37 mg, 0.13 mmol) was taken up in benzene-d_6 (4 mL) in a teflon-ringed screw-top vial and placed in a 180 °C bath for 20 h. The solution was then concentrated in vacuo and the residue applied to a silica gel column (eluent: 10:1 then 4:1 pet. ether : ether) to give the oxasilacycle product (26 mg, 70%).

R_f: 0.23 (10:1 pet. ether : EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61 (d, *J* = 10.5 Hz, 1H), 5.12 (m, 1H), 3.99-4.13 (m, 3H), 3.48 (dd, *J* = 11.0, 9.6 Hz, 1H), 2.12-2.28 (m, 2H), 2.05 (s, 3H), 1.58-1.85 (m, 3H), 1.20-1.44 (m, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.20 (s, 3H), 0.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 134.5, 123.6, 70.9, 64.8, 45.9, 29.8, 28.8, 28.5, 26.7, 25.4, 21.4, 20.9, -2.2, -2.7. IR (thin film) 2955, 2868 , 1743 (s), 1238 (s), 1040 (s), 856, 825, 783 cm^{-1}. HRMS—EI (m/z): $[M - CH_3]^+$ calcd for $C_{14}H_{23}O_3Si$: 267.1416; found: 267.1418.
Stereochemical data:

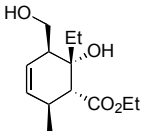


Figures to the right are likely conformations of the possible products. Arrows indicate observed nOe plausible only in the cis structure. Bold **H** indicates protons with very small (<1 Hz) coupling consistent with the perpendicular arrangement of protons in the cis structure.



Observed cis-fusion Expected trans-fusion

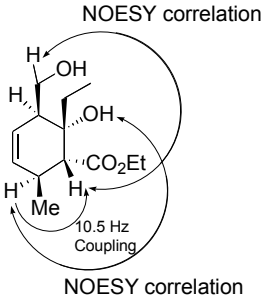
(1R,2S,5S,6S)-6-Ethyl-6-hydroxy-5-hydroxymethyl-2-methyl-cyclohex-3-enecarboxylic acid ethyl ester, 106



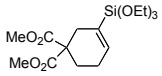
The starting triene (115 mg, 0.41 mmol) was taken up in benzene-d_6 (5.0 mL) in a screw-top vial with a Teflon seal and placed in a 180 °C bath for 36 h. The solution was then transferred to a round-bottomed flask and the solvent removed under reduced pressure. A solution of hydrogen peroxide (0.25 mL, 30% soln in water) and TBAF (1.2 mL, 1.2 mmol, 1.0 M in THF) in DMF (4.0 mL) was added to the residue and brought to 50 °C for 100 min. Sat. aq $NaHCO_3$ (25 mL) and water (20 mL) were added and the mixture was extracted with EtOAc (3 x 20 mL). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Chromatography on silica gel (eluent: 10:1 then 4:1 pet ether : ethyl acetate) provided the desired diol (63 mg, 65%) as a clear, colorless oil.

R_f: 0.57 (50:50:1 pet. ether : EtOAc : methanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (d, J = 10.0 Hz, 1H), 5.57 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.61 (s, 2H), 3.04 (m, 1H), 2.63 (m, 1H), 2.49 (d, J = 10.5 Hz, 1H), 2.30 (m, 1H), 1.64 (m, 1H), 1.39 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 1.00 (d, J = 7.1 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 134.6, 124.0, 72.8, 62.3, 60.7, 54.5, 43.5, 32.1, 30.2, 19.5, 14.3, 6.8. IR (thin film) 3446 (br, OH), 2964 (s), 1715 (s), 1456, 1375, 1260, 1181, 1029 cm^{-1}. HRMS—EI (m/z): $[M - C_2H_5]^+$ calcd for $C_{11}H_{17}O_4$: 213.1127; found: 213.1133.

Stereochemical Characterization:



4-(Triethoxysilyl)-3-cyclohexene-1,1-dicarboxylic acid dimethyl ester, 107



2-(2-(triethoxysilyl)-2-propenyl)-2-(3-butenyl)malonic acid dimethyl ester (28 mg, 0.072 mmol) was taken up in methylene chloride (3 mL) under an Ar atmosphere. Solid (1,3-bis-(2,4,6-trimethylphenyl)-2-

imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium (Grubb's 2nd generation) (1.6 mg, 0.0019 mmol) was added and the reaction stirred for 7 h. TLC analysis showed incomplete conversion, so additional catalyst (2.0 mg, 0.0024 mmol) was added the reaction stirred for an additional 16 h. The solvents were then removed in vacuo and the crude oil purified by silica gel chromatography (eluent 10:1 pet. ether: EtOAc) to afford 22.5 mg (87%) of the desired vinylsilane as a clear, colorless oil.

R_f: 0.37 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (m, 1H), 3.83 (q, J = 7.0 Hz, 6H), 3.71 (s, 6H), 2.65 (m, 2H), 2.10-2.24 (m, 4H), 1.24 (t, J = 7.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 140.2, 127.7, 58.5, 52.8, 52.5, 31.8, 27.0, 23.9, 18.3. IR (thin film) 2975, 1737 (s), 1255, 1167, 1077 (s), 959 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{16}H_{28}O_7Si$: 360.1604; found: 360.1599.

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