6.1 Experimental section

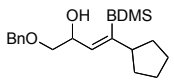
All reactions were performed under argon atmosphere unless otherwise indicated. Acetone was distilled from Drierite. Ether and methylene chloride (CH_2Cl_2) were purified on an alumina column solvent purification system, and tetrahydrofuran (THF) was distilled from sodium benzophenone ketal. TBAF was 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). With respect to purification, "eluent" or "eluting" imply that discrete fractions were taken and only those containing the desired compound were collected. "Washing" implies that all filtrate was collected in a single flask and was retained. A "silica gel plug" is a layer of silica in a sintered glass funnel, with fractions collected eluting by vacuum filtration. 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. Experimental procedures are organized by compound number, not by synthetic order. Aldehyde **23** was prepared according to the published procedure.[1] DMDO was prepared as previously described and was stored as a solution in acetone in a Schlenk flask at –20 °C for periods of up to a month.[2]

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

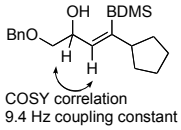


The general procedure for the synthesis of vinylsilane **11** was followed employing the alkyne (98 mg, 0.402 mmol), BDMS-H (83 μL, 0.156 mmol), acetone (0.48 mL), and complex **1** (6.1 mg, 0.012 mmol) to afford the product (153 mg, 97%) as a 9:1 mixture of regioisomers. Chromatography eluent: 10:1 pet. ether: acetone.

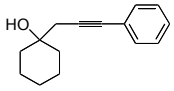
Data for major isomer (contaminated with α-silyl olefin regioisomers):
^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H), 7.19 (t, J = 7.5 Hz, 2H), 7.06 (m, 1H), 6.99 (d, J = 7.7 Hz, 2H), 5.95 (dd, J = 9.4, 1.1 Hz, 1H), 4.53 (m, 2H), 4.43 (m, 1H), 3.30 (m, 2H), 2.45 (m, 1H), 2.18-2.24 (m, 3H), 1.22-1.67 (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, $CDCl_3$).



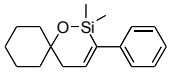
1-(3-Phenyl-2-propynyl)-cyclohexanol, 4



Iodobenzene (0.62 mL, 5.43 mmol) and 1-propargyl-cyclohexanol[3] (500 mg, 3.62 mmol) were taken up in DMF (7 mL) under Ar at 0 °C. Diisopropylamine (1.01 mL, 7.24 mmol) was added, followed by tandem addition of solid CuI (103 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (209 mg, 0.18 mmol). The mixture was allowed to warm to rt and stirred for 2 h. The mixture was then poured into aq. $KHSO_4$ (20 mL, 0.5M) and extracted with ether (3 x 15 mL). The organic extracts were washed with sat. aq. sodium bicarbonate (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was first purified on a silica gel column (eluent 10:1 pet. ether: ether), then re-purified on another silica column (eluent 20:1 pet. ether: acetone) to provide 550 mg (71%) of the desired coupling product as a clear, colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 2H), 7.27-7.32 (m, 3H), 2.58 (s, 2H), 1.84 (s, 1H), 1.27-1.75 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6, 128.2, 127.9, 123.4, 85.9, 83.7, 70.8, 36.9, 33.9, 25.6, 22.2. IR (thin film) 3440 (br, OH), 3059 (w), 2933 (s), 2858, 1490, 1443, 1151, 756, 692 cm^{-1}. Anal. Calc. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.89; H, 8.61.

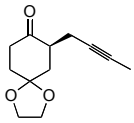
2,2-Dimethyl-3-phenyl-1-oxa-2-sila-spiro[5.5]undec-3-ene, 5



The general procedure given for the synthesis of cyclic vinylsilane **44** was employed with the alkyne (43 mg, 0.16 mmol), 1,1,3,3-tetramethyldisilazane (85 μL, 0.48 mmol), CH_2Cl_2 (0.70 mL), and complex **1** (5.0 mg, 0.0099 mmol) to afford the product (52 mg, 95%). The silylation step of this procedure was performed at 60 °C. Filtration through florisil and washing with ether provided spectroscopically homogeneous material without additional purification.

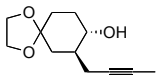
R_f 0.54 (20:1 pet. ether: ether). ^{1}H NMR (400 MHz, C_6D_6) δ 7.03-7.22 (m, 5H), 6.53 (t, J = 5.0 Hz, 1H), 2.13 (d, J = 5.0 Hz, 2H), 1.71-1.85 (m, 4H), 1.52 (m, 1H), 1.35 (m, 2H), 1.10-1.26 (m, 3H), 0.29 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ 143.3, 141.5, 140.2, 128.8, 126.7, 126.5, 73.4, 41.5, 38.5, 26.4, 22.3, 1.3. IR (thin film) 3026 (w), 2933, 2859, 1596, 1491, 1444, 1251, 1010 cm^{-1}. Anal. calc. for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88; Found: C, 74.76; H, 8.93.

(±)-(3S,4R)-3-(2-Butynyl)-4-hydroxycyclohexanone ethylene ketal, 6



Butyllithium (22.5 mL, 36.0 mmol, 1.6 M soln in hexanes) was added dropwise under Ar to a solution of diisopropylamine (6.3 mL, 45.0 mmol) in THF (100 mL) at –78 °C. The solution was warmed to 0 °C over 1 h, and then re-cooled to –78 °C, at which time 1,4-cyclohexadione monoethylene ketal (5.62 g, 36.0 mmol) was added via cannula as a solution in THF (15 mL). After stirring for 30 min at –78 °C, HMPA (1 eq.) and 1-bromo-2-butyne (2.64 g, 30.0 mmol) were added and the mixture allowed to warm to rt over 16 h. The mixture was quenched by addition of water (80 mL). The volatile components were removed *in vacuo*, and the mixture was extracted with ether (3 x 40 mL). The ether extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude alkylation product was purified on silica gel (eluent 10:1, then 4:1 pet. ether: EtOAc) to give 3.85 g (61%) of the desired 2-(2-butynyl)-1,4-cyclohexanedione 4-monoethylene ketal as a colorless oil.

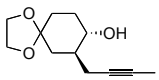
R_f 0.27 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00-4.11 (m, 4H), 2.76 (m, 1H), 2.63 (dd, J = 14.1, 6.5 Hz, 1H), 2.51 (m, 1H), 2.16-2.43 (m, 3H), 1.82-2.10 (m, 3H), 1.76 (t, J = 2.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7, 107.3, 77.1, 76.2, 64.7, 64.6, 45.6, 39.6, 38.0, 34.4, 18.7, 3.5. IR (thin film) 2957, 2886, 1715 (s), 1438, 1307, 1121, 1044, 929 cm^{-1}. Anal. calc. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; Found: C, 69.44; H, 7.80.



2-(2-Butynyl)-1,4-cyclohexanedione 4-monoethylene ketal (1.16 g, 5.57 mmol) was taken up in ether (25 mL) under Ar at 0 °C. $LiAlH_4$ (148 mg, 3.90 mmol) was added to this solution in three portions. After 10 min, the reaction was quenched by dropwise addition of water. Aq. KOH (40 mL, 1.0 M) was then added and the mixture extracted with ether (3 x 30 mL). The ether extracts were washed with sat. aq. NH_4Cl (40 mL) and brine (40 mL), then dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (80:20:1 pet. ether: EtOAc: MeOH) gave 464 mg (40%) of the desired alcohol as a single epimer together with significant impure fractions (c.a. 50%) contaminated with an unknown impurity.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 4H), 3.48 (m, 1H), 2.30 (m, 2H), 1.90-2.00 (m, 2H), 1.77 (t, J = 2.5 Hz, 3H), 1.47-1.81 (m, 6H). IR (thin film) 3420 (br OH), 2944, 1446 (w), 1359 (w), 1139, 1085 (s), 1032 (s), 927 cm^{-1}. Anal. calc. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63; Found: C, 68.38; H, 8.68.

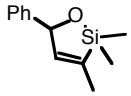
6,6,7-Trimethyl-3,4,4a,6,9,9a-hexahydro-1H-5-oxa-6-sila-benzocyclohepten-2-one 2-ethylene ketal, 7.



The general procedure given for the synthesis of cyclic vinylsilane **44** was employed with the alkyne (105 mg, 0.50 mmol), 1,1,3,3-tetramethyldisilazane (260 μL, 1.5 mmol), CH_2Cl_2 (1.0 mL), and complex **1** (7.5 mg, 0.015 mmol) to afford the product (105 mg, 78%). Chromatography on florisil, eluent: 10:1 pet. ether: ether.

R_f 0.48 (4:1 pet. ether: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (m, 1H), 3.43-3.57 (m, 5H), 1.88-2.28 (m, 5H), 1.71 (s, 3H), 1.33-1.68 (m, 4H), 1.32 (s, 3H), 0.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.2, 108.6, 78.8, 64.33, 64.28, 43.1, 42.0, 37.0, 33.7, 33.1, 22.3, 0.85, -1.1. IR (thin film) 2946 (s), 1622 (w), 1145, 1250, 1148 (s), 1119 (s), 1078 (s), 932, 825, 779 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{14}H_{24}O_3Si$: 268.1495; found: 268.1496.

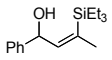
2,2,3-trimethyl-5-phenyl-2,5-dihydro-[1,2]oxasilole, 9-β



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 **1** (3.8 mg, 0.008 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 **1** (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, 10

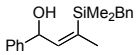


To a solution of 1-phenyl-2-butyn-1-ol (50 mg, 0.34 mmol) and triethylsilane (52 mg, 0.44 mol) in CH_2Cl_2 (0.7 mL) is added **1** (1.7 mg, 0.003 mmol) at 0º C. The solution is allowed to warm to rt and stirred for 1h. Additional triethylsilane (40 mg, 0.34 mol) and **1** (5.1 mg, 0.01 mmol) are added 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 (86.4 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.

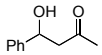
General procedure for hydrosilylation of propagylic alcohols: *(±)-(Z)*-3-(benzyldimethylsilyl)-1-phenyl-2-buten-1-ol, 11



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 at 0 °C [Cp*Ru(MeCN)$_3$]PF$_6$ (**3.1**) (35 mg, 0.069 mmol). 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.

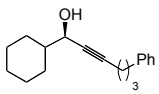
4-hydroxy-4-phenyl-butan-2-one, 14



Following the general procedure for one-pot hydrosilylation and oxidative desilylation given for **22**, employing alkyne **8** (42 mg, 0.29 mmol), BDMS-H (131 mg, 0.87 mmol), complex **1** (7.4 mg, 0.015 mmol) in CH_2Cl_2 (0.6 ml) at –30 ºC and TBAF (0.87 ml, 0.87 mmol) and $KHCO_3$ (261 mg, 2.61 mmol) and aq. H_2O_2 (1.6 ml, 16 mmol, 30% soln) in THF (1.0 mL) and MeOH (1.0 mL) provided the product hydroxyl ketone (42 mg, 88 %). Chromatography eluent: 4:1 pet. ether: EtOAc. Spectral data matched that given in the literature.[5,6]

R_f: 0.34 (2:1 P.E.: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.36 (m, 5H), 5.16 (dt, *J* = 8.5, 3.3, 1H), 3.26 (d, *J* = 3.3, 1H), 2.78-2.95 (m, 2H), 2.20 (s, 3H). IR (thin film) 3430 (br), 3031, 2923, 1711 (s), 1361, 1164, 1062, 755, 701 cm^{-1}. mp = 30-32 ºC (Lit.[6] mp = 32-36 °C).

(*R*)-1-cyclohexyl-6-phenyl-hex-2-yn-1-ol, 28



Cyclohexanecarbaldehyde (300 mg, 2.67 mmol) and 4-phenyl-1-pentyne (462 mg, 3.2 mmol) are treated as in the preparation of **31** with Zn(OTf)$_2$ (194 mg, 0.53 mmol), (+)-*N*-methylephedrine (105 mg, 0.59 mmol) and NEt_3 (135 mg, 1.34 mmol) in toluene (2.7 ml) to afford product (*R*)-1-cyclohexyl-6-

phenyl-2-hexyn-1-ol (616 mg, 90 %, 85 % ee) after purification on silica gel column (eluent: 6:1 pet. ether: EtOAc).

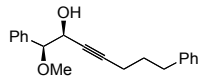
R_f: 0.43 (4:1 P.E.: EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.32 (m, 5H), 4.16 (s, 1H), 2.73 (t, J = 7.3 Hz, 2H), 2.25 (td, J = 7.1, 2.0 Hz, 2H), 1.68-1.89 (m, 8H), 1.49-1.60 (m, 1H), 1.02-1.34 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 128.4, 128.3, 125.8, 85.6, 80.7, 67.3, 44.3, 34.8, 30.3, 28.6, 28.0, 26.4, 25.9, 18.1. IR (thin film) 3375 (br), 2926 (s), 2853 (s), 1496, 1451, 1081, 1010, 746, 699 cm^{-1}. $[\alpha]^{25}_D$ +4.7º (c 1.0 in $CHCl_3$). Enantiomeric excess determined by HPLC [Chiralcel® OD column, eluting with 95:5 heptane/iPrOH, 0.9 mL/min, 254 nm: (S)-enantiomer t_R 10.7 min, (R)-enantiomer t_R 13.2 min].

(±)-Methoxyphenylacetaldehyde, 21

2-methoxy-2-phenylethanol (454 mg, 2.98 mmol) was taken up in CH_2Cl_2 (15 mL) and sat. aq. sodium bicarbonate (3 drops). Dess-Martin periodinane (1.52 g, 3.58 mmol) was added at rt under air. After stirring for 2 h, additional sat. aq. sodium bicarbonate (30 mL) was added together with sat. aq. sodium thiosulfate (15 mL) and ether (30 mL). The mixture was stirred for 10 min, then extracted. The aqueous layer was further extracted with additional ether (25 mL), and the combined organic extracts washed with sat. aq. sodium bicarbonate (20 mL) and brine (20 mL), and then dried over $MgSO_4$. Purification by Kugelrohr distillation (1.0 mmHg, chamber 130 °C) of the crude product gave 274 mg (60%) of aldehyde of sufficient purity for subsequent reactions. Spectral data matched that given in the literature.[9]

^{1}H NMR (300 MHz, C_6D_6) δ 9.37 (d, J = 1.9 Hz, 1H), 7.03-7.19 (m, 5H), 4.14 (d, J = 1.9 Hz, 1H), 2.98 (s, 3H).

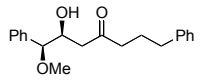
(±)-(1S,2S)-1-methoxy-1,7-diphenyl-3-heptyn-2-ol, 22



To an ether (3 mL) solution of 5-phenyl-1-pentyne (518 mg, 3.60 mmol) under Ar at 0 °C was added dropwise *n*-butyllithium (2.42 mL, 3.60 mmol, 1.48 M in hexanes). The solution was then warmed to 0 °C and allowed to stir for 20 min prior to re-cooling to –78 °C. A solution of $ZnBr_2$ (908 mg, 3.96 mmol) in ether (2.0 mL) was then added via cannula, followed after 5 min by methoxyphenylacetaldehyde (**26**) (270 mg, 1.80 mmol), also via cannula as a solution in ether (2 mL). The reaction mixture was allowed to warm to rt over 14 hr. The reaction was quenched with aq. HCl (20 mL, 0.5 M). Volatile organic species were removed under reduced pressure, and the mixture was extracted with ether (3 x 20 mL). The ether extracts were washed with sat. aq. $NaHCO_3$ (15 mL) and brine (15 mL), and then dried over $MgSO_4$. Following solvent removal under reduced pressure, purification on silica gel (eluent 85:15:1 pet. ether: EtOAc: MeOH) gave 399 mg (75%) of the desired alcohol as a 91:9 mixture of diastereomers favoring the syn product.

Data for major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.39 (m, 8H), 7.09 (d, *J* = 7.1 Hz, 2H), 4.45 (m, 1H), 4.17 (d, *J* = 7.9 Hz, 1H), 3.31 (s, 3H), 2.89 (d, *J* = 3.1 Hz, 1H), 2.55 (td, *J* = 7.6, 2.5 Hz, 2H), 2.13 (tt, *J* = 7.0, 2.0 Hz, 2H), 1.71 (tt, *J* = 7.3, 7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 137.3, 128.5, 128.4, 128.3, 128.2, 127.9, 125.8, 87.12, 87.07, 77.7, 67.0, 57.1, 34.5, 29.8, 18.0. IR (thin film) 3442 (br, OH), 3028 (w), 2936, 2234 (w), 1495, 1454, 1103 (s), 700 (s) cm^{-1}. This compound is further characterized after conversion to ketone **28**.

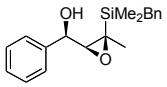
(±)-(1S,2S)- 2-hydroxy-1-methoxy-1,7-diphenyl-5-heptanone, 23



Following the general procedure for one-pot hydrosilylation and oxidative desilylation given for **28**, employing alkyne (60 mg, 0.20 mmol, 91:9 mixture of diastereomers), BDMS-H (35 μL, 0.24 mmol), complex **1** (2.0 mg, 0.0040 mmol) in acetone (0.4 ml) and TBAF (0.24 ml, 0.24 mmol, 1.0 M in THF), $KHCO_3$ (75 mg, 0.75 mmol) and aq. H_2O_2 (0.3 ml, 30% soln) in THF (0.5 mL) and MeOH (0.5 mL) provided 48 mg (78%) of pure cis derivative after separation of the minor diastereomer. Chromatography eluent: 80:20:1, then 70:30:1 pet. ether: EtOAc: MeOH.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.39 (m, 7H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 4.21 (m, 1H), 4.05 (d, *J* = 7.3 Hz, 1H), 3.25 (s, 3H), 3.11 (br OH, 1H), 2.57 (d, *J* = 7.5 Hz, 2H), 2.45 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.27 (dd, *J* = 16.4, 3.2 Hz, 1H), 1.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 141.5, 137.7, 128.6, 128.40, 128.39, 128.3, 127.6, 125.9, 86.7, 71.5, 56.9, 45.0, 42.8, 34.9, 24.8. IR (thin film) 3486 (br, OH), 3027 (w), 2932, 1712 (s), 1454, 1109, 701 (s) cm^{-1}. m.p. 51-54 °C. Anal. calc. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; Found: C, 76.71; H, 7.90.

(±)-(R)-[(2S,3R)-3-(Benzyldimethylsilyl)-3-methyloxiranyl]-phenylmethanol, 15

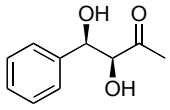


(±)-(*Z*)-3-(Benzyldimethylsilyl)-1-phenyl-2-buten-1-ol (**11**) (650 mg, 2.19 mmol, 14:1 *Z:E* mixture) was taken up in CH_2Cl_2 (20 mL), and treated with *m*-CPBA (662 mg, 3.07 mmol assuming 80% purity). After 14 hr at 0 °C, sat. aq. sodium bicarbonate (10 mL), and solid $Na_2S_2O_3$ (c.a. 2 g) was added. The mixture was extracted with ether (3 x 30 mL), and the organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. Silica gel chromatography (eluent: 100:10:1 pet. ether: EtOAc: methanol) afforded 615 mg (90%) the desired epoxy-alcohol as a single isomer.

R_f: 0.28 (80:20:1 pet.ether: EtOAc: methanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.43 (m, 5H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.09 (m, 1H), 6.95 (d, *J* = 7.1 Hz, 2H), 4.55 (d, *J* = 8.3 Hz, 1H), 3.12 (d, *J* = 8.3 Hz, 1H), 2.21 (s, 2H), 1.25 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 138.7, 128.7, 128.34, 128.29, 126.6, 124.5, 72.7, 69.9, 56.8, 24.2, 23.1, -3.5, -3.7. IR (thin film) 3432 (br, OH),

3026 (w), 2959, 1600 (w), 1494, 1452, 1251, 838, 699 cm^{-1}. This compound is further characterized after conversion to ketone **17**.

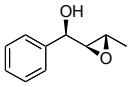
(±)-(*3S,4R*)-3,4-Dihydroxy-4-phenyl-butan-2-one, 17



(±)-(*R*)-[(*2S,3R*)-3-(Benzyldimethylsilyl)-3-methyloxiranyl]-phenylmethanol (**29**) mg, 0.19 mmol) was taken up in THF (0.6 mL) under Ar at 0 °C. TBAF (0.19 mL, 0.19 mmol, 1.0M in THF) was added dropwise, and after 5 min, methanol (0.60 mL) and $KHCO_3$ (60 mg, 0.60 mmol) were added, followed by 30% aq. H_2O_2 (0.20 mL). The mixture was then allowed to warm to rt, and after 14 hr, sat. aq. sodium bicarbonate (3 mL) was added, and the mixture extracted with ether (3 x 10 mL). The organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purification on a silica gel column (eluent: 4:1 then 1:1 pet. ether: EtOAc) afforded 25.1 mg (74%) of the desired diol as a viscous gum. Spectral data matched that given in the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.41 (m, 5H), 4.99 (m, 1H), 4.37 (m, 1H), 3.67 (d, *J* = 4.4 Hz, 1H), 2.79 (d, *J* = 6.1 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 139.9, 128.6, 128.2, 126.3, 80.6, 74.1, 26.3. IR (thin film) 3427 (br, OH), 2916 (w), 1713 (s), 1358, 1054 cm^{-1}.

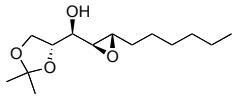
(±)-(R)-((2S,3S)-3-Methyloxiranyl)-phenylmethanol , 16



(±)-(*R*)-[(*2S,3R*)-3-(Benzyldimethylsilyl)-3-methyloxiranyl]-phenylmethanol (**15**) g, 0.202 mmol) was taken up in DMF at 0 °C under air. The solution was treated with TBAF (0.40 mL, 0.40 mmol, 1.0M in THF. After warming to rt over 30 min, the solution was quenched by addition of sat. aq. sodium bicarbonate (30 mL). The mixture was extracted with ether (3 x 10 mL). The organic layers were washed with brine (10 mL), dried of $MgSO_4$, and concentrated under reduced pressure. The crude material was applied to a silica gel column (eluent: 85:15 pet. ether: EtOAc) to give 31 mg (98%) of the desired epoxy alcohol. Stereochemistry was established by comparison to the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.41 (m, 5H), 4.49 (dd, *J* = 4.8, 4.8 Hz, 1H), 3.13 (qd, *J* = 5.3, 2.3 Hz, 1H), 2.95 (dd, *J* = 5.5, 2.3 Hz, 1H), 2.65 (d, *J* = 4.6 Hz, 1H), 1.31 (d, *J* = 5.3 Hz, 3H). IR (thin film) 2441 (br, OH), 2986, 1494 (w), 1453, 991, 871, 741, 701 cm^{-1}

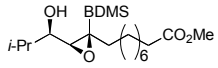
(R)-((R)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-((2S,3S)-3-hexyl-oxiranyl)-methanol, 26



Following the desilylation procedure given for the preparation of (±)-(*R*)-((*2S,3S*)-3-Methyloxiranyl)-phenylmethanol (**16**), the silyl-epoxide **25** (42 mg, 0.103 mmol) lost silicon on exposure to TBAF (0.23 mL, 2.2 eq.) to afford the desired epoxy alcohol (26.0 mg, 97%) as an inseparable 9:1 mixture of relative epimers at C2 carried through from the initial alkyne addition. Purification on silica gel column (eluent: 1:1 pet. ether: ether).

Data for major isomer:
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (dd, *J* = 8.2, 6.2 Hz, 1H), 4.06 (m, 1H), 3.99 (dd, *J* = 8.2, 5.2 Hz, 1H), 3.56 (dd, *J* = 7.2, 3.1 Hz, 1H), 2.98 (m, 2H), 2.20 (br, 1H), 1.57 (m, 2H), 1.43 (s, 3H), 1.36 (s, 3H), 1.25-1.46 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.4, 76.6, 70.7, 66.7, 58.4, 56.3, 31.7, 31.5, 29.0, 26.7, 25.8, 25.2, 22.5, 14.0. IR (thin film) 3445 (br, OH), 2931, 1456, 1380, 1258, 1217, 1069, 852 cm^{-1}. $[\alpha]^{26}_D$ –19.1° (c 0.8, CH_2Cl_2). HRMS—EI (m/z): $[M-CH_3]^+$ calcd for $C_{13}H_{23}O_4$: 243.1596; found: 243.1595.

***(±)-4-[(2R,3S)-2-(*Benzyldimethylsilyl)-3-((R)-1-hydroxy-2-methyl-propyl)-oxiranyl]-nonanoic acid methyl ester, 34**

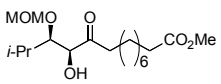


(±)-Methyl 12-hydroxy-13-methyl-10-tetradecynoate (117 mg, 0.436 mmol) and BDMS-H (90 μL, 0.52 mmol) were taken up in acetone (0.9 mL) and treated with complex **1** (6.6 mg, 0.013 mmol) at 0 °C. After allowing the solution to warm to rt over 30 min, the reaction was filtered through a short plug of silica (ca. 3 cm, eluent: 10:1 pet. ether: EtOAc) to afford crude vinylsilane. The material (169 mg, 93%) was contaminated with c.a. 15% α-silyl regioisomers and was taken directly into the epoxidation.

The crude vinylsilane (46 mg, 0.11 mmol) was taken up in CH_2Cl_2 (1.1 mL), and treated with *m*-CPBA (54 mg, 0.22 mmol based on 70% purity). After 14 hr at 0 °C, sat. aq. sodium bicarbonate (2 mL), and solid $Na_2S_2O_3$ (c.a. 0.1 g) was added. The mixture was extracted with ether (3 x 10 mL), and the organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. Silica gel chromatography (20:1, then 10:1 pet. ether: acetone) afforded 41 mg (86%, 80% for two steps) of the desired epoxy-alcohol as a single isomer.

^{1}H NMR (400 MHz, C_6D_6) δ 7.08-7.14 (m, 2H), 6.95-7.00 (m, 3H), 3.32 (s, 3H), 3.23 (m, 1H), 2.86 (d, *J* = 7.9 Hz, 1H), 2.24 (d, *J* = 13.8 Hz, 1H), 2.17 (d, *J* = 13.8 Hz, 1H), 2.06-2.10 (m, 3H), 1.88 (m, 1H), 1.73 (m, 1H), 1.52 (m, 2H), 1.11-1.24 (m, 11H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.04 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ 173.3, 139.4, 128.8, 128.6, 124.8, 74.5, 66.9, 58.8, 50.9, 37.8, 34.0, 32.8, 30.2, 29.6, 29.5, 29.3, 25.9, 25.2, 24.9, 19.4, 17.4, -2.9, -3.0. IR (thin film) 3491, 2931, 2856, 1740, 1251, 828, 700 cm^{-1}. This compound is further characterized after conversion to the MOM ether following.

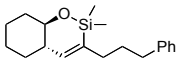
(±)-(6S,7R)-6-Hydroxy-7-methoxymethoxy-8-methyl-5-oxo-tetradecanoic acid methyl ester, 36



Following the general procedure given for the synthesis of (±)-(3S,4R)-3,4-dihydroxy-4-phenyl-butan-2-one, employing the MOM-protected alcohol **35** (34.0 mg, 0.0734 mmol), TBAF (0.073 mL, 0.073 mmol, 1.0 M in THF), $KHCO_3$ (20 mg, 0.20 mmol), aq. H_2O_2 (0.3 mL), THF (0.7 mL) and MeOH (0.7 mL) afforded the desired hydroxy ketone (13.7 mg, 54%) as a clear oil. Chromatography eluent: 100:10:1, then 80:20:1 pet. ether: EtOAc: MeOH.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (d, *J* = 7.0 Hz, 1H), 4.56 (d, *J* = 7.0 Hz, 1H), 4.19 (d, *J* = 6.4 Hz, 1H), 3.66 (s, 3H), 3.56 (m, 2H), 3.25 (s, 3H), 2.71 (m, 1H), 2.48 (m, 1H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.06 (m, 1H), 1.25-1.36 (m, 12 H), 0.11 (d, *J* = 6.8 Hz, 3H), 0.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 174.3, 97.4, 84.3, 56.1, 51.5, 38.5, 34.1, 30.4, 29.2, 29.1, 29.0, 24.9, 23.4, 19.2, 19.0. IR (thin film) 3476 (br, OH), 2931, 1739, 1714, 1035 cm^{-1}. MS—EI (m/z): $[M+H]^+$ calcd for $C_{18}H_{35}O_6$: 347.2; found: 347.4. HRMS—EI (m/z): $[M-OCH_3]^+$ calcd for $C_{17}H_{31}O_5$: 315.2171; found: 315.2171.

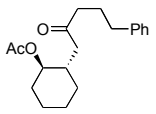
(±)-(1R,2S)-(2,2-Dimethyl-3-(3-phenyl-propyl)-4a,5,6,7,8,8a-hexahydro-2H-benzo[e][1,2]oxasiline, 39



A round-bottomed flask [Note: it is important to use a rather large flask to allow removal of the excess silane under vacuum without bumping] was charged with (±)-(*1S,2S*)-2-(5-phenyl-1-propynyl)-cyclohexanol (123 μL, 0.50 mmol) under Ar at rt. To the neat alcohol was added 1,1,3,3-tetramethyldisilazane (270 μL, 1.5 mmol) and the flask heated to 50 °C for 2 h. Next, the flask was cooled to ambient temperature and placed under vacuum (c.a. 1 mmHg) for 45 min to remove the excess silazane. An Ar atmosphere was then re-introduced and the residue taken up in CH_2Cl_2 (1.0 mL). The flask was cooled to 0 °C and solid $[Cp^*Ru(MeCN)_3]PF_6$ (2.5 mg, 0.005 mmol) was added to the solution. The flask was allowed to warm to rt, and after 15 min, the solution was diluted with ether (5 mL) and filtered through a short plug of florisil, washing with additional ether (15 mL). The volatile components were then removed under reduced pressure and the resulting residue purified on a florisil column (eluent 30:1 pet. ether: ether) to afford 130 mg (85%) of the desired silacycle as a colorless oil. NMR analysis of all products (including cross-coupling product) shown indicated complete isomeric purity. A conservative estimate of ≥ 97:3 isomeric purity for all products is in line with the uncertainty in NMR measurements.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, J = 7.6, 7.6 Hz, 2H), 7.15-7.19 (m, 3H), 6.03 (s, 1H), 3.38 (ddd, J = 10.0, 10.0, 3.9 Hz, 1H), 2.59 (t, J = 7.7 Hz, 2H), 2.10 (t, J = 7.3 Hz, 2H), 1.96 (m, 2H), 1.65-1.80 (m, 5H), 1.00-1.42 (m, 4H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 142.5, 138.5, 128.4, 128.3, 125.7, 76.0, 44.7, 35.7, 35.0, 34.7, 32.0, 31.2, 25.8, 25.0, -0.7. IR (thin film) 3027 (w), 2930 (s), 2855, 1603 (w), 1496 (w), 1449, 1248, 1064, 948, 882, 828, 785 cm^{-1}. Anal. calc. for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39; Found: C, 75.82; H, 9.30.

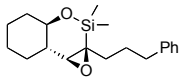
(±)-(*1R,2S*)-1-acetyloxy-2-(2-oxo-5-phenylpentyl)cyclohexane, 40



The vinyl silacycle **39** (125 mg, 0.416 mmol) was taken up in DMF (4 mL) under air at rt. Solid KHF_2 (98 mg, 1.25 mmol) was added, followed by acetic anhydride (1.2 mL) and 30% aq. H_2O_2 (1 mL). After stirring for 14 hr at rt, sat. aq. $NaHCO_3$ (40 mL) was added and the mixture stirred for 10 min until bubbling ceased. The mixture was extracted with EtOAc (3 x 15 mL) and the organic extracts washed with brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude alcohol was then taken up in CH_2Cl_2 (2 mL) and treated with pyridine (134 μL, 1.66 mmol). After cooling to 0 °C, acetyl chloride (59 μL, 0.83 mmol) was then added and the reaction mixture allowed to stir for 15 minutes. Sat. aq. Na_2SO_4 (15 mL) is then added, and the mixture extracted with EtOAc (3 x 15 mL). The extracts were washed with 0.5 M HCl (10 mL), sat. aq. Na_2SO_4 (10 mL), and brine (10 mL), then dried over Na_2SO_4, and concentrated in vacuo. The crude product was then purified on silica gel (20:1, then 10:1 pet. ether: EtOAc) which provided 78 mg (62%) of the desired acetoxy ketone as a colorless oil.

R_f 0.44 (80:20:1 pet. ether: EtOAc: MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.30 (m, 2H), 7.16-7.21 (m, 3H), 4.43 (ddd, *J* = 10.3, 10.3, 4.4 Hz, 1H), 2.61 (t, *J* = 6.6 Hz, 2H), 2.48 (dd, *J* = 16.2, 4.4 Hz, 1H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.16 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.06 (m, 1H), 1.99 (s, 3H), 1.98 (m, 1H), 1.89 (m, 2H), 1.80 (m, 1H), 1.74 (m, 1H), 1.57-1.64 (m, 2H), 1.20-1.35 (m, 3H), 0.99 (dddd, *J* = 12.2, 12.2, 12.2, 2.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.9, 170.8, 141.6, 128.44, 128.38, 126.0, 76.5, 46.2, 42.5, 38.2, 35.1, 31.8, 31.3, 25.2, 25.0, 24.5, 21.2. IR (thin film) 2935, 2859, 1732 (s), 1732 (s), 1713 (s), 1452, 1372, 1242 (s), 1030 cm^{-1}. Anal. calc. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67; Found: C, 75.29; H, 8.53.

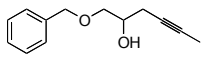
Silyl epoxide, 41



The vinyl silacycle (**39**) (25 mg, 0.173 mmol) was taken up in DCM under Ar at 0 °C. Solid *m*CPBA (18 mg, 0.173 mmol). After 3 hr, no vinylsilane remained and the mixture was diluted with pet. ether (5 mL), and filtered through a pad of celite, washing with additional pet. ether (10 mL). The volatile components were removed under reduced pressure. NMR analysis of the crude reaction mixture demonstrated clean conversion to a single epoxide product. The crude product was purified on preparative TLC (eluent 10:1 pet. ether: EtOAc) to give 8 mg (31%) of the major epoxide product. The stereochemistry is assumed by conformational analysis and analogy to **58**. Coupling constant and nOe analysis was not instructive.

R_f 0.40 (10:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.16-7.20 (m, 3H), 3.41 (ddd, *J* = 10.0, 10.0, 4.4 Hz, 1H), 2.80 (s, 1H), 2.68 (m, 1H), 2.56 (m, 1H), 1.60-1.89 (m, 8H), 1.16-1.34 (m, 5H), 0.26 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 128.35, 128.32, 125.8, 69.5, 64.2, 56.3, 43.7, 36.1, 35.4, 34.9, 29.3, 28.3, 25.8, 24.8, -1.9, -2.1. IR (thin film) 3027, 2931, 2858, 1496, 1452, 1403, 1252, 1071, 951, 789 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{19}H_{28}O_2Si$: 316.1858; found: 316.1847.

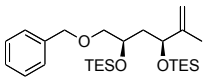
(±)-1-Benzyloxy-hex-4-yn-2-ol, 43



According to the procedure of Prieto[12] a round-bottom flask was charged with toluene (200 mL) and cooled under N_2 to 0 °C. Then, butyllithium (38 mL, 1.6 M solution in THF, 61 mmol) was added. Propyne gas was bubbled through the reaction mixture and the reaction color turned from first yellow to milky white once an excess of propyne had been introduced. After this, diethylaluminum chloride (7.25 mL, 58 mmol) was added via a syringe and the solution was stirred at 0 °C for 4.5 h. To this solution was added benzyl glycidyl ether (4.64 mL, 30 mmol) and the reaction was stirred for 10.5 h at 0 °C. Then at this temperature aq. 5 % H_2SO_4 (61 mL) was added dropwise. The aqueous phase was extracted with pet ether (1 _ 20 mL), diethyl ether (1 _ 20 mL) and the organics dried over $MgSO_4$. Purification by silica gel column (4:1 pet. ether: EtOAc) afforded 6.1 g (quant.) of the title compound, whose data matched that of the known compound.[12]

R_f: 0.26 (4:1 pet. ether: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) _ 7.27-7.38 (m, 5H), 4.57 (s, 2H), 3.92 (m, 1H), 3.59 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.48 (dd, *J* = 9.2, 6.8 Hz, 1H), 2.48 (d, *J* = 4.4 Hz, 1H), 2.39 (m, 2H), 1.78 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 137.9, 128.4, 127.73, 127.70, 78.1, 74.6, 73.4, 73.0, 69.1, 23.8, 3.5. IR (thin film) 3448 (br, OH), 2919, 2861, 1454, 1113, 738, 699 cm^{-1}.

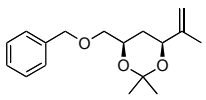
(±)-(2R,4S)-(5-Methyl-2,4-bis-triethylsilanyloxy-hex-5-enyloxymethyl)-benzene, 47



This procedure was adapted from the literature.[13] A flask was charged with Cp_2TiMe_2 (86 mg, 0.412 mmol) under Ar in the dark at rt. The TES-protected dihydroxyketone **46** (70 mg, 0.150 mmol) was added via syringe as a solution in THF (0.8 mL) and then stirred overnight at 60 °C. The reaction was stopped by adding diethyl ether (5 mL) and filtering through silica gel. Purification by silica gel column (40:1 pet. ether: diethyl ether) afforded the desired olefin (58 mg) in 84 % yield.

R_f: 0.56 (10:1 pet. ether: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) _ 7.25-7.33 (m, 5H), 4.86 (m, 1H), 4.77 (m, 1H), 4.54 (d, *J* = 12.4, 1H), 4.50 (d, *J* = 12.4 Hz, 1H), 4.20 (t, *J* = 6.8, 1H), 3.83-3.8 9 (m, 1H), 3.35-3.45 (m, 2H), 1.60-1.81 (m, 5H), 0.90-0.97 (m, 18H), 0.52-0.63 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 147.6, 138.6, 128.3, 127.7, 127.5, 111.5, 74.9, 73.8, 73.3, 69.9, 41.5, 16.8, 7.01, 6.95, 5.23, 5.19, 4.97, 4.88. IR (thin film) 2954, 2877, 2360, 1456, 1095, 1006, 728 cm^{-1}.

(±)-(3S,5R)-4-Benzyloxymethyl-6-isopropenyl-2,2-dimethyl-[1,3]dioxane, 48



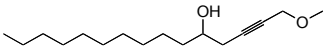
A solution of the olefin **47** (58 mg, 0.125 mmol) in THF (1.2 mL) was treated with TBAF (0.46 mL, 0.81 M soln in THF, 0.374 mmol) under Ar at 0 °C. After warming to rt for 2 h the reaction was quenched

with sat. $NaHCO_3$ (2 mL). Extraction with diethyl ether (3 _ 2 mL), washing the organics with brine (2 mL) and drying over $MgSO_4$ afforded the crude dihydroxy compound (63 mg) which was taken directly on.

The crude dihydroxy compound (63 mg, assume 0.125 mmol), PPTS (7 mg, 0.027 mmol) and CH_2Cl_2 (2.7 ml) was treated with 2-methoxypropene (130 μL, 1.333 mmol) under Ar at 0 °C. After stirring for 2 h the reaction was quenched by adding saturated $NaHCO_3$ (2 mL). Extraction with diethyl ether (3 _ 2 mL), washing the organics with brine (2 mL) and drying over $MgSO_4$ afforded the crude acetonide which was purified by silica gel column (15:1 pet ether: diethyl ether). The major diastereomer was obtained as a colourless oil (16 mg, 46 %) and its stereochemistry established by ^{13}C NMR (see main text).[14]

R_f: 0.57 (4:1 pet. ether: EtOAc). ^1H NMR (400 MHz, $CDCl_3$) _ 7.26-7.35 (m, 5H), 5.00 (m, 1H), 4.85 (m, 1H), 4.61 (d, *J* = 12.4, 1H), 4.55 (d, *J* = 12.4, 1H), 4.28 (dd, *J* = 11.6, 2.0 Hz, 1H), 4.14 (m, 1H), 3.53 (dd, *J* = 9.6, 5.6, 1H), 3.39 (dd, *J* = 10.0, 5.2, 1H), 1.74 (s, 3H), 1.62 (t, *J* = 13.2, 2.8, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.38 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 145.3, 138.3, 128.5, 127.9, 127.7, 111.1, 98.9, 73.7, 73.6, 72.1, 68.6, 32.7, 30.2, 19.8, 18.4. IR (thin film) 2988, 2921, 2853, 1454, 1380, 1201, 1102, 698 cm^{-1}. ESI-MS calcd for $C_{17}H_{24}O_3$: 276.2 $(M)^+$; Found: 299.2 $(M+Na)^+$.

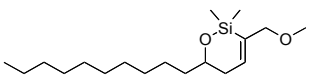
(±)-1-Methoxy-pentadec-2-yn-5-ol, 50



A round-bottom flask was charged with toluene (181 mL) and cooled under N_2 to 0 °C. Then, butyllithium (22 mL, 2.45 M solution in THF, 54 mmol) was added. Methyl propargyl ether (4.58 mL, 54 mmol) was added, followed by diethylaluminum chloride (6.46 mL, 52 mmol) and the solution was stirred at 0 °C for 4 h. To this solution was added epoxydodecane (5.92 mL, 27 mmol) and the reaction was stirred overnight at 0 °C. Then at this temperature aq. 5 % H_2SO_4 (55 mL) was added dropwise. The aqueous phase was extracted with diethyl ether (3 _ 20 mL) and the organic layers dried over $MgSO_4$. Concentration in vacuo and purification by silica gel column (4:1 pet ether: diethyl ether) afforded 1.36 g (20 %) of the title compound.

R_f: 0.49 (4:1 pet. ether: diethyl ether). ^1H NMR (500 MHz, $CDCl_3$) _ 4.10 (t, *J* = 2.1 Hz, 2H), 3.71-3.77 (m, 1H), 3.37 (s, 3H), 2.48 (ddt, *J* = 16.6, 4.5, 2.1 Hz, 1H), 2.36 (ddt, *J* = 16.6, 6.8, 2.1 Hz, 1H), 1.88 (d, *J* = 5.0 Hz, 1H), 1.51-1.55 (m, 2H), 1.25-1.46 (m, 16H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 83.3, 78.4, 76.8, 70.1, 60.2, 57.6, 36.3, 31.9, 29.6, 29.6, 29.6, 29.4, 27.7, 25.6, 22.7, 14.2. IR (thin film) 3418, 2920, 2854, 2231, 1466, 1356, 1188, 1097, 907, 722 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{16}H_{30}O_2$: 254.2246; found: 254.2246.

(±)-6-Decyl-3-methoxymethyl-2,2-dimethyl-5,6-dihydro-2H-[1,2]oxasiline, 51

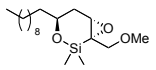


A round-bottomed flask was charged with 1-methoxy-pentadec-2-yn-5-ol **50** (300 mg, 1.180 mmol) under Ar at rt. To the neat alcohol was added 1,1,3,3-tetramethyldisilazane (1.05 mL, 5.896 mmol) and the flask heated to 50 °C over 14 h. Next, the flask was cooled to ambient temperature and placed under

vacuum (ca. 1 mmHg) for 1 h to remove the volatile species. An Ar atmosphere was then re-introduced and the residue taken up in CH_2Cl_2 (3.0 mL). The flask was cooled to 0 °C and solid $[Cp^*Ru(MeCN)_3]PF_6$ **1** (11.9 mg, 0.024 mmol) was added to the solution. The flask was allowed to warm to rt, and after 2 h, the solution was diluted with diethyl ether (10 mL) and filtered through a short plug of florisil, washing with additional diethyl ether (10 mL). After concentration under reduced pressure the cyclic siloxane was obtained as a colorless oil (361 mg, 98 %). The cyclic siloxane thus obtained was >95% homogeneous as judged by ^{1}H NMR without additional purification.

R_f: 0.43 (10:1 pet. ether: diethyl ether). ^{1}H NMR (500 MHz, C_6D_6) _ 6.37 (m, 1H), 3.92 (m, 2H), 3.86 (m, 1H), 3.09 (s, 3H), 2.07-2.14 (m, 1H), 1.87-1.92 (m, 1H), 1.56-1.69 (m, 2H), 1.28-1.44 (m, 16H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.39 (s, 3H), 0.37 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) _ 140.4, 138.4, 77.1, 71.4, 57.5, 38.3, 36.1, 32.3, 30.1, 30.0 (2), 29.9, 29.7, 25.9, 23.0, 14.3, -0.4 (2H). IR (thin film) 2924, 2855, 1615, 1467, 1248, 1106, 958, 830, 681 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{18}H_{36}O_2Si$: 312.2485; found: 312.2489.

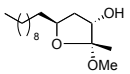
(±)-4-Decyl-1-methoxymethyl-2,2-dimethyl-3,7-dioxa-2-sila-bicyclo[4.1.0]heptane, 52



To a solution of the cyclic siloxane **51** (100 mg, 0.320 mmol) was added DMDO (9.6 mL, 0.1 M soln in acetone, 0.96 mmol) under Ar at –35 °C via cannula. After stirring over 14 h at –35 °C the reaction was quenched with dimethylsulfide (298 mg, 4.800 mmol). After warming up to rt and drying over $MgSO_4$ the mixture was concentrated under reduced pressure which afforded the crude epoxide (115 mg, 109 %) as a colorless oil contaminated with traces of aromatic impurities, which was used directly in subsequent reactions.

R_f: 0.30 (10:1 pet. ether: diethyl ether). ^{1}H NMR (500 MHz, C_6D_6) _ 3.91 (m, 1H), 3.67 (d, *J* = 11.4 Hz, 1H), 3.11 (s, 3H), 2.79 (s, 1H), 2.77 (d, *J* = 11.9 Hz, 1H), 1.75 (d, *J* = 14.8 Hz, 1H), 1.45-1.57 (m, 3H), 1.28-1.38 (m, 16 H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.50 (s, 3H), 0.37 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) _ 78.1, 66.3, 58.6, 54.7, 38.1, 34.6, 32.3, 30.09, 30.06 (2), 29.9, 29.7, 25.8, 25.7, 23.0, 14.3, -1.8, -1.9. IR (thin film) 3438, 2916, 2854, 1716, 1694, 1467, 1250, 1103, 1031, 883, 794 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{18}H_{36}O_3Si$: 328.2434; found: 328.2432.

(±)-5-Decyl-2-methoxy-2-methoxymethyl-tetrahydro-furan-3-ol, 54

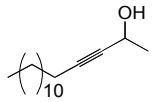


A mixture of 4-decyl-1-methoxymethyl-2,2-dimethyl-3,7-dioxa-2-sila-bicyclo[4.1.0]heptane (**52**) (13 mg, 0.036 mmol) and hydrogen peroxide (20 µL, 0.400 mmol, 35 % soln in water) in DMF (0.4 mL) was treated with TBAF (119 µL, 0.119 mmol, 1.0 M soln in THF) under Ar at rt. The reaction was then heated to 40 °C over night and was then diluted with EtOAc (2 mL) and aq. $Na_2S_2O_3$ (2 mL, 0.1 M soln). Extraction with EtOAc (3 _ 2 mL) and drying over $MgSO_4$ afforded a crude oil (15 mg) which was used directly in the next reaction.

The crude diol (7.5 mg, ~0.020 mmol) was dissolved in methanol (0.4 mL) and a few crystals CSA (~0.5 mg) were added. After stirring for 3 h at rt the reaction was filtered through celite and concentrated under vacuum. The resulting oil was purified on a silica gel column (2.5:1, pet. ether: diethyl ether) which afforded the ketal (3.6 mg) in 66 % yield over 3 steps as a single diastereomer.

R_f: 0.33 (1:2 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) _ 4.37 (dddd, *J* = 12.8, 6.4, 6.3, 6.3, 1H), 4.24 (dd, *J* = 3.9, 3.9 Hz, 1H), 3.65 (dd, *J* = 33.2, 10.4 Hz, 2H), 3.43 (s, 3H), 3.25 (s, 3H), 2.73 (d, *J* = 3.3 Hz, 1H), 1.99 (dd, *J* = 13.2, 6.1 Hz, 1H), 1.91 (ddd, *J* = 13.5, 9.7, 5.1 Hz, 1H), 1.62-1.68 (m, 1H), 1.49-1.19 (m, 17H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 108.4, 81.0, 77.9, 69.5, 59.6, 48.5, 38.7, 37.1, 32.0, 30.4, 29.8, 29.7 (2), 29.4, 26.2, 22.8, 14.2. IR (thin film) 3458, 2924, 2854, 2361, 1464, 1261, 1201, 1111, 944, 875, 804 cm^{-1}. HRMS—EI (m/z): $[M - H_3O]^+$ calcd for $C_{16}H_{31}O_3$: 271.2273; found: 271.2254.

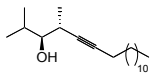
3-Hexadecyn-2-ol, 55



Ethylmagnesium bromide (43 mL, 1.0 M soln in THF, 43.2 mmol) was added slowly to a solution of 1-tetradecine (7.0 g, 36 mmol) in THF (72 mL) under Ar at 0 °C. After warming to rt for 2 h the flask was cooled down to 0 °C again and the mixture was treated with acetaldehyde (6.1 mL, 108 mmol) and stirred for 30 min. Then, the reaction was quenched with sat. aq. NH_4Cl (20 mL) and water (10 mL). The aqueous layer was extracted with diethyl ether (3 _ 20 mL), the organics were washed with brine (10 mL), sat. $NaHCO_3$-solution (10 mL) and dried over $MgSO_4$. The resulting oil was purified on a silica gel column (4:1, pet. ether: diethyl ether) which afforded the propargylic alcohol (7.8 g) in 91 % yield.

R_f: 0.47 (4:1 pet. ether: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) _ 4.45-4.52 (m, 1H), 2.16 (td, *J* = 7.1, 2.0 Hz, 2H), 1.75 (d, *J* = 5.2 Hz, 1H), 1.43-1.50 (m, 2H), 1.40 (d, *J* = 6.5 Hz. 3H), 1.18-1.37 (m, 16H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 84.8, 82.2, 58.6, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 28.8, 28.6, 24.7, 22.7, 18.6, 14.1. IR (thin film) 3343 (br, OH), 2925, 1460 (w), 1077 (w) cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{16}H_{30}O$: 238.2297; found: 238.2287.

(±)-2,4-Dimethyl-octadec-5-yn-3-ol, 56

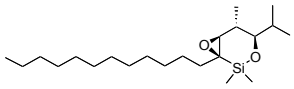


Following the procedure of Marshall,[15] triphenylphosphine (76 mg, 0.29 mmol) was added to a solution of $Pd(OAc)_2$ (65 mg, 0.29 mmol) under Ar at –78 °C. After the phosphine had dissolved, mesylate **79** (2.2 g, 6.95 mmol) was added followed by isobutyraldehyde (530 μL, 5.79 mmol) and finally diethylzinc (17 mL, 1.0 M soln in hexanes, 17 mmol). After warming to –25 °C overnight, the reaction was quenched with sat. NH_4Cl (30 mL) and extracted with ether (3 _ 15 mL). The organic layers were washed

with sat. aq. $NaHCO_3$ (10 mL), brine (10 mL) and dried over $MgSO_4$. Purification on silica gel column (20:1 then 10:1 pet. ether: diethyl ether) followed by Kugelrohr distillation (bp = 200 °C, 0.4 torr) gave the homopropargylic alcohol (1.08 g) in 63 % yield.

R_f: 0.53 (4:1 pet. ether: diethyl ether). ^1H NMR (400 MHz, $CDCl_3$) _ 2.97 (m, 1H), 2.62-2.69 (m, 1H), 2.14 (td, *J* = 7.1, 2.2 Hz, 2H), 1.70-1.80 (m, 1H), 1.67 (d, *J* = 6.4 Hz, 1H), 1.42-1.49 (m, 2H), 1.24-1.35 (m, 16H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 83.7, 80.4, 79.8, 32.2, 32.0, 30.7, 29.76, 29.73, 29.70, 29.64, 29.45, 29.21, 29.14, 28.95, 22.78, 19.7, 18.80, 18.78, 17.8, 14.2. IR (thin film) 3569, 2958, 2927, 2855, 1466, 1369, 1062, 1006 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{20}H_{38}O$: 294.2923; found: 294.2915.

(±)-1-Dodecyl-4-isopropyl-2,2,5-trimethyl-3,7-dioxa-2-sila-bicyclo[4.1.0]heptane, 58

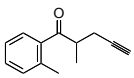


A round-bottomed flask was charged with (±)-2,4-dimethyl-octadec-5-yn-3-ol (**56**) (200 mg, 0.680 mmol) under Ar at rt. To the neat alcohol was added 1,1,3,3-tetramethyldisilazane (0.5 mL, 2.856 mmol) and the flask was heated to 80 °C overnight. The flask was cooled to ambient temperature and placed under vacuum (c.a. 1 mmHg) for 45 min to remove the volatile species. An Ar atmosphere was then re-introduced and the residue taken up in CH_2Cl_2 (1.7 mL). The flask was cooled to 0 °C and solid $[Cp^*Ru(MeCN)_3]PF_6$ **1** (17.1 mg, 0.034 mmol) was added to the solution. The flask was allowed to warm to rt, and after 2 h, the solution was diluted with ether (10 mL) and filtered through a short plug of florisil, washing with additional ether (15 mL). After concentration under reduced pressure, the crude cyclic siloxane was obtained as a colorless oil (223 mg, 97 %).

To a solution of the cyclic siloxane (233 mg, 0.680 mmol) in acetone (1 mL) was added DMDO (20 mL, 0.1 M soln in acetone, 2.04 mmol) under Ar at –78 °C via cannula. After stirringover night at –35 °C the TLC showed complete conversion. At that temperature the reaction was quenched with dimethylsulfide (634 mg, 10.20 mmol). After warming up to rt and drying over $MgSO_4$, the mixture was concentrated under reduced pressure which afforded the crude epoxide as a single diastereomer (228 mg) and colorless oil in 91 % yield over 2 steps.

R_f: 0.69 (10:1 pet. ether: diethyl ether). ^1H NMR (500 MHz, C_6D_6) _ 3.47 (dd, *J* = 10.0, 2.0 Hz,1H), 2.75 (s, 1H), 1.84-1.90 (m, 1H), 1.76-1.81(m, 1H), 1.54-1.66 (m, 2H), 1.15-1.41 (m, 20H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 7.4 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.35 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 74.6, 66.1, 56.3, 36.2, 35.3, 32.3, 30.3, 30.1 (2), 30.0 (2), 29.9, 29.7, 29.1, 27.1, 23.0, 20.6, 15.2, 14.3, 13.5, -1.8, -2.2. IR (thin film) 2926, 2855, 1714, 1462, 1255, 1034, 878, 789 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{22}H_{44}O_2Si$: 368.3111; found: 368.3100.

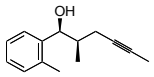
2-Methyl-1-o-tolyl-pent-4-yn-1-one, 60



Diisopropyl amine (1.23 mL, 8.77 mmol) was dissolved in THF (67 mL) under Ar at –78 °C. Butyllithium (3.1 mL, 2.4 M soln in THF, 7.42 mmol) was added via syringe and the resulting mixture was allowed to warm to 0 °C. After stirring for 15 min the reaction was recooled to –78 °C and 1-*o*-tolyl-1-propanone (**80**) (1.0 g, 6.75 mmol) was added to the LDA solution. Then, the reaction was stirred for further 30 min at this temperature, treated with propargyl bromide (0.83 mL, 80% in toluene, 7.42 mmol) and HMPA (1.17 mL, 6.75 mmol) and was allowed to warm to rt overnight. Sat. aq. NH_4Cl (30 mL) was added and the mixture extracted with ether (3 × 20 mL). The organic layers were dried over $MgSO_4$. Solvent removal in vacuo and purification on a silica gel column (eluent 20:1, pet. ether: diethyl ether) gave 486 mg (39%, contaminated with 20% starting material) of the ketone as a colorless oil.

R_f: 0.45 (10:1 pet. ether: diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$) _ 7.55-7.58 (m, 1H), 7.34-7.38 (m, 1H), 7.24-7.28 (m, 1H), 3.49 (h, *J* = 7.0, 1H), 2.62 (ddd, J = 16.9, 6.1, 2.6 Hz, 1H), 2.45 (s, 3H), 2.37 (ddd, *J* = 16.6, 7.3, 2.5 Hz, 1H), 1.99 (t, *J* = 2.7 Hz. 1H), 1.25 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 206.4, 138.0, 137.8, 131.8, 131.1, 127.7, 125.6, 82.2, 69.8, 43.3, 22.0, 20.8, 16.6. IR (thin film) 3293, 2972, 2932, 2359, 1687, 1456, 1379, 1233, 973, 742 cm^{-1}.

2-Methyl-1-o-tolyl-hex-4-yn-1-ol, 61a

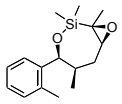


A solution of 2-methyl-1-o-tolyl-pent-4-yn-1-triethylsilyl-ether (**81**) (0.100 g, 0.331 mmol) in THF was cooled under Ar to –78 °C. Then, butyllithium (0.66 mL, 2.5 M soln in hexanes, 1.653 mmol) was introduced and the reaction flask was allowed to warm to –30 °C. After stirring for 30 min at this temperature, methyl iodide (0.103 mL, 1.653 mmol) was added at –78 °C and the reaction was allowed to warm to rt over 12 h. After quenching with water (4 mL), the aq. layer was extracted with diethyl ether (3 _ 4 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude alkyne (110 mg) was used directly in the next reaction.

The crude protected alcohol (110 mg, assume 0.331 mmol) was taken up in a mixture of acetic acid, water and THF (4 mL, 7:2.5:2.5) and heated to 40 °C over 14 h. Quenching with sat. aq. $NaHCO_3$ (5 mL), extraction with EtOAc (3 _ 5 mL) and drying over $MgSO_4$ afforded after concentration under reduced pressure a crude oil, which was purified by silica gel column (eluent 10:1, pet. ether: diethyl ether). The benzyl alcohol was obtained as a colorless oil (30 mg) in 45% yield.

Data for mixture of diastereomeres 5:1. R_f: 0.25 (10:1 pet. ether: diethyl ether). ^{1}H NMR (500 MHz, $CDCl_3$) _ 7.46 (d, *J* = 7.5 Hz, 1H), 7.22 (td, *J* = 7.4, 1.2 Hz, 1H), 7.15 (m, 2H), 5.08 (t, *J* = 4.0 Hz, 0.86H), 4.81 (dd, *J* = 7.9, 3.8 Hz, 0.14H), 2.34 (s, 3H), 2.26 (ddq, *J* = 16.5, 7.3, 2.5 Hz, 1H), 2.12 (ddq, *J* =16.5, 5.2, 2.5 Hz, 1H), 1.95 (m, 1H), 1.86 (d, *J* = 3.5 Hz, 1H) 1.81 (t, *J* = 2.6 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 141.6, 134.6, 130.4, 127.0, 126.0, 125.9, 77.7, 77.2, 72.5, 38.2, 23.8, 19.1, 13.4, 3.5. IR (thin film) 3426, 2964, 2919, 1462, 1381, 1977, 989, 750 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{14}H_{18}O$: 202.1358; found: 202.1368.

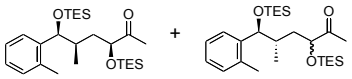
1,2,2,5-Tetramethyl-4-o-tolyl-3,8-dioxa-2-sila-bicyclo[5.1.0]octane, 62a



To a solution of the 5:1 mixture of siloxanes **82** (100 mg, 0.384 mmol) was added DMDO (20 mL, 0.1 M soln in acetone, 1.92 mmol) under Ar at –78 °C via cannula. After stirring over 2 d at –78 °C, the reaction was quenched with dimethyl sulfide (0.423 mL, 5.760 mmol). After warming to rt and drying over $MgSO_4$, the mixture was concentrated under reduced pressure which afforded the crude epoxide (117 mg, 110 %) as a colorless oil.

Data for mixture of diastereomers 4:1. R_f: 0.41 (10:1 pet. ether: diethyl ether). ^{1}H NMR (400 MHz, C_6D_6) _ 7.78 (d, *J* = 7.5 Hz, 1H), 6.98-7.21 (m, 3H), 5.22 (d, *J* = 2.7 Hz, 0.2H), 5.14 (d, *J* = 3.1 Hz, 0.8H), 2.77 (dd, *J* = 7.6, 4.2 Hz, 0.2H), 2.68 (dd, *J* = 8.1, 4.1 Hz, 0.8H), 2.07 (s, 3H), 2.00 (m, 1H), 1.90 (m, 1H), 1.54 (m, 1H), 1.16 (s, 3H), 0.68 (d, *J* = 6.9 Hz, 1H), 0.39 (s, 3H), 0.01 (s, 3H).

3,6-Bis-triethylsilanyloxy-5-methyl-6-o-tolyl-hexan-2-one, 63a and 63b

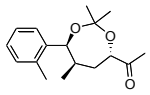


A mixture of the crude epoxide **62a** (30 mg, assume 0.109 mmol), $KHCO_3$ (108 mg, 1.085 mmol), KF (31.5 mg, 0.543 mmol) and methanol/THF (1.1 mL, 1:1 mixture) was treated with hydrogen peroxide (0.2 mL, 4.36 mmol) under Ar at 0 °C. After stirring for 15 h, the reaction was diluted with aq. NaS_2O_3 (2 mL, 0.1 M soln) and the aq. layer was extracted with EtOAc (3 _ 2 mL). Drying over $MgSO_4$ afforded a crude oil (36 mg) which was used directly in the next reaction

The crude diol (36 mg, assume 0.109 mmol) and imidazole (59 mg, 0.872 mmol) were dissolved in CH_2Cl_2 (1.1 mL) under Ar at 0 °C. Then Et_3SiCl (91 μL, 0.545 mmol) was added via syringe at 0 °C. After warming to rt, the mixture was stirred for additional 2 h. The reaction was quenched with H_2O (4 mL) and diluted with diethyl ether (5 mL). The aq. layer was extracted with diethyl ether (3 _ 3 mL), the organic layers were washed with brine (3 mL) and dried over $MgSO_4$. The resulting oil was purified on a silica gel column (30:1 pet. ether: diethyl ether) which afforded the protected product (35 mg) in 69 % yield over 2 steps as a 4:1 mixture of diastereomers.

Data for a 5:1 mixture of diastereomers:
R_f: 0.55 (2:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) _ 7.40 (d, *J* = 7.3 Hz, 0.22H), 7.36 (d, *J* = 7.3 Hz, 0.78H), 7.06-7.17 (m, 3H), 4.72 (d, *J* = 3.8 Hz, 0.22H), 4.63 (d, *J* = 4.5 Hz, 0.78H), 4.04 (dd, *J* = 9.8, 3.2 Hz, 0.22H), 3.97 (dd, *J* = 9.3, 5.0 Hz, 0.78H), 2.27 (s, 3H), 1.98 (s, 3H), 1.47-1.68 (m, 3H), 0.82-0.94 (m, 20H), 0.43-0.59 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 212.1, 211.6, 142.2 (2), 134.0, 130.0, 127.4, 126.7 (2), 126.6, 125.6, 125.4, 77.7, 77.5, 39.7, 39.2, 36.4, 35.4, 24.8, 24.7, 24.0, 19.4, 19.3, 16.7, 14.6, 6.8, 5.1, 4.9, 4.8 (2), 4.7. IR (thin film) 2956, 2878, 1716, 1462, 1240, 1079, 1007, 844, 727 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{26}H_{48}O_3Si_2$: 464.3142; found: 464.3131

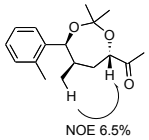
1-(2,2,6-Trimethyl-7-o-tolyl-[1,3]dioxepan-4-yl)-ethanone, 64



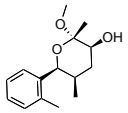
The TES protected diol **63a** and **63b** (8 mg, 0.017 mmol) was taken up in CH_2Cl_2 (0.17 mL) under Ar at –78 °C. Acetone (5 μL, 0.069 mmol) followed by TMS-OTf (0.8 μL, 1.0 M soln in CH_2Cl_2, 0.0009 mmol) were added. After stirring for 1 h at –78 °C, the reaction was quenched with NEt_3 (10 μL) and filtered through a short plug of florisil. Concentration under reduced pressure afforded a crude oil which was purified on silica gel chromatography (20:1 pet. ether: diethyl ether). The 7-membered ring acetonide (3.0 mg) was obtained in 63% yield, as a 5:1 mixture of diastereomers.

Data for mixture of diastereomers 5:1. R_f: 0.29 (10:1 pet. ether: diethyl ether). ^{1}H NMR (400 MHz, C_6D_6) _ 7.92 (d, *J* = 7.7 Hz, 0.16H), 7.64 (d, *J* = 7.8 Hz, 0.84H), 6.96-7.20 (m, 3H), 5.10 (s, 0.84H), 4.72 (d, *J* = 2.3 Hz, 0.16H), 4.20 (dd, *J* = 11.2, 1.2 Hz, 0.84H), 3.62 (dd, *J* = 3.7, 2.1 Hz, 0.16H), 2.04 (s, 3H), 2.00 (s, 3H), 1.96 (ddd, *J* = 14.1, 1.9, 1.5 Hz, 1H), 1.80-1.84 (m, 1H), 1.64-1.71 (m, 1H), 1.38 (s, 0.48H), 1.35 (s, 0.48H), 1.22 (s, 2.52H), 1.18 (s, 2.52H), 1.09 (d, *J* = 7.1 Hz, 0.48H) 0.81 (d, *J* = 6.6 Hz, 2.52H). IR (thin film) 2923, 1721, 1382, 1218, 1058, 750 cm^{-1}. HRMS—ES (m/z): $[M + Na]^+$ calcd for $C_{17}H_{24}O_3Na$: 299.1623; found: 299.1615.

Observed nOe correlations of major isomer:



2-Methoxy-2,5-dimethyl-6-o-tolyl-tetrahydro-pyran-3-ol, 65

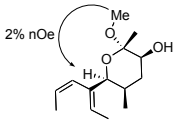


UHP (85 mg, 0.904 mmol) was added to a solution of the crude epoxide **63** (50 mg, assume 0.181 mmol) in THF (1.8 mL) under Ar at 0 °C. The reaction was allowed to warm to rt and treated with TBAF (543 μL, 1.0 M soln in THF, 0.543 mmol) dropwise via syringe pump over 6 h. After stirring for 20 h at rt the reaction was quenched by diluting with EtOAc (5 mL) and aq. $Na_2S_2O_3$ (5 mL, 0.1 M soln). Extraction with EtOAc (3 _ 5 mL) and drying over $MgSO_4$ afforded a crude oil (122 mg) which was used directly in the next reaction.

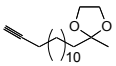
The crude diol (122 mg, assume 0.181 mmol) was dissolved in methanol (3.6 mL) at rt and a few crystals CSA (~0.5 mg) were added. After stirring for 3 h, the reaction mixture was filtered through a short plug of celite and concentrated under reduced pressure. The resulting oil was purified on a silica gel column (40:1 pet ether: acetone) which afforded the ketal (11.9 mg) in 29 % yield over 3 steps, followed by 11.4 mg (28%) of a second isomer which readily decomposed upon standing.

R_f: 0.63 (2:1 pet. ether: EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) _ 7.56 (d, *J* = 7.7 Hz, 1H), 7.11-7.23 (m, 3H), 5.05 (d, *J* = 3.2 Hz, 1H), 3.60 (ddd, *J* = 6.4, 3.5, 3.4, 1H), 3.21 (s, 3H), 2.43 (ddd, *J* = 14.2, 5.7, 3.8 Hz, 1H), 2.28 (s, 3H), 2.02 (m, 1H), 1.75 (dt, *J* = 14.3, 2.7 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 1H), 1.46 (s, 3H), 0.84

(d, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) _ 139.3, 133.6, 129.9, 126.8, 126.6, 125.6, 101.5, 77.3, 70.1, 69.9, 48.0, 33.8, 28.2, 19.3, 16.0. IR (thin film) 3478, 2932, 1462, 1381, 1233, 1135, 1058, 979, 862, 750 cm^{-1}. HRMS—EI (m/z): $[M - OCH_3]^+$ calcd for $C_{14}H_{19}O_2$: 219.1385; found: 219.1359.
Observed nOe correlations:



15-Hexadecyn-2-one ethylene ketal, 73



Potassium hydride (2.54 g, 19.0 mmol, 30% in mineral oil) was washed with hexanes (2 × 5 mL) under Ar at rt. 1,3-Diaminopropane (35 mL) was then added, and the flask heated gently with a heat gun until the mixture began to foam (ca. 2 min). The mixture was stirred for 1 hr, and hexadecyn-2-ol (0.905 g, 3.80 mmol) was added via cannula as a solution in THF (4.0 mL). After stirring 24 h, the mixture was poured into sat. aq. NH_4Cl (80 mL) under an atmosphere of Ar to prevent fires. Water (50 mL) was added, and the contents extracted with EtOAc (3 × 30 mL). The organic layers were washed with aq. HCl (40 mL, 1M soln), sodium bicarbonate (40 mL), and brine (30 mL), then dried over Na_2SO_4. The solvents were removed under reduced pressure, and the residue purified on a silica gel plug (ca. 6 cm, eluent 4:1 pet. ether: ether) to afford 787 mg (87%) of the desired terminal alkyne **55** free of any isomeric material.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (m, 1H), 2.18 (td, J = 7.1, 2.6 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.27-1.56 (m, 23H), 1.19 (d, J = 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 84.8, 68.2, 68.0, 39.3, 29.62, 29.60, 29.57, 29.47, 29.1, 28.7, 28.5, 25.8, 23.5, 18.4. IR (thin film) 3339 (br, OH), 3313 (w), 2926, 2854, 1466 cm^{-1}. m.p. 37-40 °C. Anal. Calc. for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.77; H, 12.80.

The alkyne **55** mg, 1.93 mmol) was dissolved in CH_2Cl_2 (6.0 mL) under air at 0 °C and treated sequentially with aq. sodium bicarbonate (3.0 mL, 0.5 soln), potassium bromide (23 mg, 0.19 mmol), and TEMPO (3.0 mg, 0.019 mmol). Aq. NaOCl (4.3 mL, 0.67 commercial bleach soln) was then added dropwise and the mixture stirred at 0 °C for 2 h. Sat. aq. sodium bicarbonate (30 mL) was then added, and the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The organic layers were dried over Na_2SO_4 and the solvents remove in vacuo to give the crude ketone product, which was taken up in benzene (10 mL) under Ar in a Dean-Stark apparatus. Ethylene glycol (2.1 mL, 19.3 mmol) was then added, followed by *p*-toluenesulfonic acid (18 mg, 0.096 mmol). The solution was heated to reflux for 16 h, at which time the flask was cooled to rt and treated with sat. aq. sodium bicarbonate (55 mL). The mixture was extracted with ether (2 × 30 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrate in vacuo. Purification of the resulting residue on a silica gel column (40:1 pet. ether:acetone) provided 528 mg (98%) of the desired ketal as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91-3.96 (m, 4H), 2.18 (td, J = 7.1, 2.4 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 1.24-1.64 (m, 22H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.2, 84.8, 68.0, 64.6, 39.2, 29.9, 29.59, 29.55, 29.48, 29.1, 28.7, 28.5, 24.1, 23.7, 18.4. IR (thin film) 3312, 2927, 2119 (w), 1466, 1376, 1220,

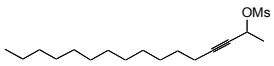
1062 cm^{-1}. MS—ES+ (m/z): $[M + H]^+$ calcd for $C_{18}H_{32}O_2$: 281.3; found: 280.9. Anal. Calc. for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.86; H, 11.72.

(*R*)-(*S*)-1-Oxiranyl-ethanol, 75

4 Å molecular sieves (ca. 10 g) were flame-dried under vacuum, then placed under an Ar atmosphere at –20 °C and treated sequentially with CH_2Cl_2 (100 mL), freshly distilled (-)-DIPT (0.60 mL, 2.8 mmol), freshly distilled Ti(O*i*-Pr)$_4$ (0.69 mL, 2.3 mmol), and anhydrous *tert*-butylhydroperoxide (8.6 mL, 47.0 mmol, 5.5 M soln in hydrocarbons) which had been pre-dried over 4 Å mlcl sieves (ca. 3 g) before delivering to the reaction vessel via cannula. After 30 min, 1-buten-2-ol (4.07 mL, 47.0 mmol) was added dropwise via cannula as a solution in CH_2Cl_2 (10 mL). The mixture was stirred at –20 °C for 54 h until chiral GC analysis of reaction aliquots showed ca. 47% conversion. At this time the reaction was quenched by addition of dimethylsulfide (4 mL), and warmed to rt. Wet acetone (75 mL, 9:1 acetone: water mix) was then added, and the mixture stirred for 1 h. The mixture was then filtered through celite with slight positive pressure, dried over $MgSO_4$, and the volatile organic species removed by distillation through a packed column. Purification on a silica gel column (eluent: 2:1, then 1:1 pet. ether: ether) followed by distillative solvent removal at ambient pressure afforded first 1.52 g (45%) of recovered allylic alcohol, followed by 1.80 g (43%) of the slower-eluting epoxy alcohol.[17,18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (m, 1H), 3.03 (m, 1H), 2.81 (dd, *J* = 5.0, 2.8 Hz, 1H), 2.74 (dd, *J* = 5.0, 4.0 Hz, 1H), 1.77 (d, *J* = 2.6 Hz, 1H), 1.27 (d, *J* = 6.5 Hz, 3H). IR (thin film) 3312, 2927, 2119 (w), 1466, 1376, 1220, 1062 cm^{-1}. $[\alpha]_D^{28}$ –21.8 (c 1.2, MeOH). Lit.[18] $[\alpha]_D$ –17.9 (c 1.16, MeOH).

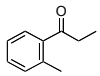
(±)-Methanesulfonic acid 1-methyl-2-pentadecynyl ester, 79



Hexadec-3-yn-2-ol (3.0 g, 12.58 mmol) and NEt_3 (2.1 mL, 15.10 mmol) were taken up in CH_2Cl_2 (125 mL) at –70 °C. At this temperature mesyl chloride (1.07 mL, 13.84 mmol) was added and the reaction was allowed warm up to 0 °C for 1 h. After washing with H_2O (3 _ 20 mL), drying the organic layer over $MgSO_4$ the mixture was concentrated under reduced pressure which afforded the crude protected alcohol (4.32 g) in quantitative yield.

R_f: 0.53 (4:1 pet. ether: EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) _ 5.28 (qt, *J* = 6.7, 2.0 Hz, 1H), 3.10 (s, 3H), 2.23 (td, *J* = 7.2, 2.0 Hz, 2H), 1.61 (d, *J* = 6.7 Hz, 3H), 1.47-1.54 (m, 2H), 1.21-1.39 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) _ 89.6, 76.9, 69.2, 39.2, 32.00, 29.73, 29.71, 29.68, 29.57, 29.43, 29.14, 28.93, 28.33, 23.1, 22.8, 18.7, 14.2. IR (thin film) 2925, 2855, 2247, 1467, 1361, 1180, 1053, 969 cm^{-1}.

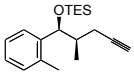
1-o-Tolyl-propan-1-one, 80



Toluic acid (5 g, 36.7 mmol) was dissolved in CH_2Cl_2 (70 mL) under Ar at rt. Then, oxalyl chloride (6.4 mL, 73.4 mmol) was added via a syringe followed by DMF (3 drops). After the reaction stopped bubbling (20 min) the solvent was removed under reduced pressure. The residue was taken up in THF (150 mL), and according to the procedure of Marchese[19] $Fe(acac)_3$ (0.39 g, 1.1 mmol) was added followed by ethylmagnesium chloride (34.9 mL, 1.0 M soln in THF, 34.9 mmol) under Ar at rt. After 20 min the reaction was quenched with aq. HCl (50 mL, 10 % in water) and extracted with diethyl ether (3 _ 30 mL), washed with $NaHCO_3$ solution (1 _ 30 mL) and water (1 _ 30 mL). After drying over $MgSO_4$ and concentration under vacuo, kugelrohr distillation (bp = 110 °C, 0.1 mmHg) afforded the ketone in 75% yield (4.1 g). Spectral data matched that previously reported.[20]

R_f: 0.38 (10:1 pet. ether: diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$) _ 7.62 (dd, *J* = 7.2,1.7 Hz, 1H), 7.35 (td, *J* = 7.2, 1.4 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 2.91 (q, *J* = 7.2 Hz, 2H), 2.49 (s, 3H), 1.19 (t, *J* = 7.3 Hz, 3H). IR (thin film) 2978, 2938, 1694, 1456, 1218, 950, 752 cm^{-1}.

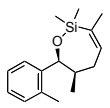
2-Methyl-1-o-tolyl-pent-4-yn-1-triethylsilyl-ether, 81



Following the procedure of Yamamoto,[21] a round bottom flask was charged with 2-methyl-1-o-tolyl-pent-4-yn-1-one (**80**) (0.200 g, 1.074 mmol), triethylsilane (0.172 mL, 1.074 mmol) and toluene (3.3 mL) under Ar at -30 °C. Then *tris*-pentafluorophenyl borane (0.430 mL, 0.05 M soln in toluene, 0.021 mmol) was added and the reaction was allowed to warm to rt overnight. After filtering through a short plug of florisil , concentration under reduced pressure silica gel column (100:1, pet. ether: diethyl ether) afforded 225 mg (69%, contaminated with 20% O-triethylsilyl-1-o-tolyl-1-propanol) of the title compound. The The diastereoselectivity ranged from 6:1 and 20:1 from run to run for unknown reasons. Spectral data matched that previously reported.[21]

Data for major diastereomer:
R_f: 0.83 (10:1 pet. ether: diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$) _ 7.42 (d, *J* = 7.4 Hz, 1H), 7.06-7.29 (m, 3H), 5.07 (d, *J* = 3.9 Hz, 1H), 2.32 (s, 3H), 2.26-2.31 (m, 1H), 2.10 (ddd, *J* = 16.6, 6.2, 2.7, 1H), 2.02 (t, *J* = 2.7 Hz, 1H), 1.87 (m, 1H), 0.85-0.94 (m, 12H), 0.48-0.54 (m, 6H). IR (thin film) 3312, 2957, 2879, 1461, 1239, 1077, 1007, 837, 746 cm^{-1}.

2,2,3,6-Tetramethyl-7-o-tolyl-2,5,6,7-tetrahydro-[1,2]oxasilepine, 82



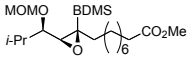
A round-bottomed flask was charged with the 5:1 mixture of diastereomers **61a** and **61b** (200 mg, 0.989 mmol) under Ar at rt. To the neat alcohol was added 1,1,3,3-tetramethyldisilazane (1.23 mL, 6.921

mmol) and the flask heated to 50 °C for 2 h. Next, the flask was cooled to ambient temperature and placed under vacuum (c.a. 1 mmHg) for 45 min to remove the volatile species. An Ar atmosphere was then re-introduced and the residue taken up in CH_2Cl_2 (2.5 mL). The flask was cooled to 0 °C and solid $[Cp^*Ru(MeCN)_3]PF_6$ **1** (24.9 mg, 0.049 mmol) was added to the solution. The reaction was allowed to warm to rt, and after 2 h, the solution was diluted with ether (10 mL) and filtered through a short plug of florisil, washing with additional ether (10 mL). After concentration under reduced pressure, the cyclic siloxane was obtained as a colorless oil (265 mg, quant., 5:1 mixture of diastereomers).

Data for a 5:1 mixture of diastereomers:

R_f: 0.65 (10:1 pet. ether: diethyl ether). ^{1}H NMR (500 MHz, C_6D_6) _ 7.90 (d, J = 7.7 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.99-7.22 (m, 2H), 6.21 (m, 1H), 5.33 (d, J = 3.4 Hz, 0.86H), 4.70 (d, J = 9.9 Hz, 0.14H), 2.34 (m, 1H), 2.12 (m, 1H), 2.06 (s, 3H), 1.99 (m, 1H), 1.74 (d, J = 1.1 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H), 0.34 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) _ 142.0, 138.9, 138.8, 133.0, 130.2, 128.3, 127.4, 126.7, 126.0, 73.2, 36.0, 22.5, 19.2, 14.5, -1.7, -1.9. IR (thin film) 3065, 2958, 1607, 1456, 1379, 1251, 1071, 1012, 931, 779, 675 cm^{-1}. HRMS—EI (m/z): $[M]^+$ calcd for $C_{16}H_{24}OSi$: 260.1596; found: 260.1610. Anal. calc. for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29; Found: C, 74.02; H, 9.50.

(±)-4-[(2S,3S)-2-(Benzyldimethylsilyl)-3-(1-methoxymethoxy-2-methyl-propyl)-oxiranyl]-tetradecanoic acid methyl ester, 35



Alcohol **34** (4.8 mg, 0.011 mmol) was taken up in CH_2Cl_2 (0.10 mL) at 0 °C and treated sequentially with diisopropyl ethyl amine (58 μL, 0.33 mmol) and chloromethyl methyl ether (0.17 μL, 0.22 mmol). After warming to rt and stirring 18 hr, the reaction was directly concentrated and applied to a short silica gel column (eluent: 10:1 pet. ether: ether) to afford the desired MOM-ether as a clear oil (5.4 mg, 100%). Alternatively, this compound could be produced by epoxidation of the *O*-protected vinylsilane, which was sluggish and afforded only moderate selectivity.

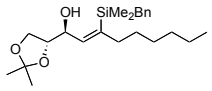
R_f: 0.45 (4:1 pet.ether: EtOAc). ^{1}H NMR (400 MHz, C_6D_6) δ 7.11-7.15 (m, 2H), 6.99 (m, 3H), 5.33 (d, J = 6.6 Hz, 1H), 4.62 (d, J = 6.6 Hz, 1H), 3.58 (dd, J = 90, 3.5 Hz, 1H), 3.35 (s, 3H), 3.26 (s, 3H), 3.12 (d, J = 9.0 Hz, 1H), 2.33 (d, J = 13.9 Hz, 1H), 2.25 (d, J = 13.9 Hz, 1H), 2.11 (t, J = 7.3 Hz, 2H), 1.82 (m, 1H), 1.74 (m, 1H), 1.55 (m, 2H), 1.23-1.35 (m, 11H), 1.13 (d, J = 7.0 Hz, 3H), 1.06 (d, J = 7.0 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ 173.2, 139.3, 128.7, 128.6, 124.7, 95.6, 78.1, 66.4, 55.4, 54.9, 50., 37.2, 34.0, 31.7, 30.1, 29.53, 29.47, 29.3, 25.8, 25.1, 24.8, 20.4, 16.8, -2.9, -3.1. IR (thin film) 2928 (s), 1742 (s), 1464, 1251, 1157, 1033, 828 cm^{-1}. MS—EI (m/z): $[M+H]^+$ calcd for $C_{27}H_{46}O_5Si$: 479.3; found: 479.4.

2-(1-Azido-ethyl)-oxirane, 84

$Zn(N_3)_2$•$6H_2O$ was prepared according to the previously published procedure.[22] Triphenylphosphine (2.38 g, 9.08 mmol) and the epoxy alcohol (0.400 g, 4.54 mmol) were taken up in benzene (9.0 mL) at 0 °C and treated sequentially with diisopropyl azodicarboxylate (1.79 mL, 9.08 mmol) and $Zn(NO_3)_2$•$6H_2O$ (1.82 g, 5.90 mmol). The flask was warmed to rt, and after 5 h, additional triphenylphosphine (1.19 g, 4.54 mmol), diisopropyl azodicarboxylate (0.90 mL, 4.54 mmol), and $Zn(NO_3)_2$•$6H_2O$ (0.84 g, 2.72 mmol) were added and stirring continued for an additional 2 h. The mixture was diluted with pet. ether (70 mL) and washed with aq. methanol (2 × 4 mL, 60% soln). The organic layers were dried over $MgSO_4$ and distilled to a volume of ca. 5 mL, which purified on a silica gel column (eluent 10:1, then 4:1 pet. ether: ether) and distilled to 1.51 g (34 wt% assuming 100% yield, yields were determined after the subsequent step) which solution was used as a stock solution for subsequent reactions. (Pure azide could be obtained in low yield for purposes of spectroscopic identification.)

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.33 (dq, J = 6.6, 6.6 Hz, 1H), 3.03 (m, 1H), 2.82 (dd, J = 4.7, 4.2 Hz, 1H), 2.68 (dd, J = 4.7, 2.4 Hz, 1H), 1.33 (d, J = 6.8 Hz, 3H). IR (thin film) 2984, 2119 (s), 1726, 1379, 1248 (s), 910, 865 cm^{-1}.

(Z)-(S)-3-(Benzyldimethylsilyl)-1-((R)-2,2-dimethyl-[1,3]dioxolan-4-yl)-non-2-en-1-ol, 24



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 **11** was followed employing the alkyne (62 mg, 0.258 mmol), BDMS-H (54 μL, 0.31 mmol), acetone (0.6 mL), and complex **1** (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 (98.3 mg, 98%). The major regioisomer could be isolated clean of the of the α-silyl regioisomers through careful (repeated) chromatography, but this was much more easily performed after epoxidation (see Chapter 6). The chromatography eluent was 20:1 then 10:1 pet. ether: acetone.

Data for major β-silyl olefin regioisomer (contaminated with c.a. 10% inseparable α–alcohol diastereomer). Full characterization was performed after oxidation (see Chapter 6):
^{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 **32**.

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