Synthesis of β-Hydroxy Ketones and Vinyl Silanes from Homopropargylic Alcohols via Intramolecular Hydrosilation

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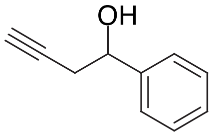
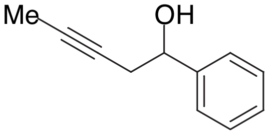
Supporting Information:

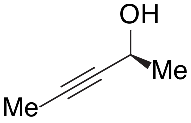
General. Unless otherwise stated all reactions were performed in flame dried glassware under an atmosphere of nitrogen or argon. Anhydrous THF, diethyl ether, and dichloromethane were purified by pressure filtration through activated alumina. All other solvents were dried according to known procedures with the exception of anhydrous MeOH which was used as received. 1,1,3,3-tetramethyldisilazane (TMDS) was obtained from Gelest and used as recieved. All proton and carbon NMR spectra were acquired in $CDCl_3$ at 300 MHz and 75 MHz respectively unless otherwise stated. All aqueous solutions used in the workup procedures were saturated unless otherwise stated. All IR spectra were acquired as a thin film on NaCl plates unless otherwise stated. Melting and boiling points are uncorrected. Bulb to bulb distillation temperatures refer to the temperature of the bath. Concentration *in vacuo* refers to high vacuum (0.005-0.1 mm Hg). Concentration refers to rotory evaporation with a water aspirator (*ca* 100-20 mm Hg).



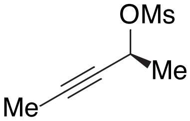
1-Phenyl-3-butyn-1-ol (2c). To a solution of allenylmagnesium bromide, generated from magnesium (1.00 g, 40 mg-atoms), mercuric chloride (100 mg), and propargyl bromide (3.00 mL, 20 mmol), in ether (50 mL), was added benzaldehyde (1.96 g,18 mmol). After 30 min, the reaction was quenched with NH_4Cl (100 mL), extracted with ether (200 mL), washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Bulb to bulb distillation (0.05 mm Hg, 85ºC) afforded 2.60 g (98%) of alcohol as a colorless liquid. Spectral characteristics matched those previously reported.[1]



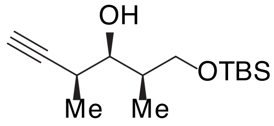
1-Phenyl-3-pentyn-1-ol (2d). To a solution of 1-phenyl-3-butyn-1-ol (6.9 g, 47.5 mmol), imidazole (6.47 g, 95.0 mmol), in DMF (40 mL) was added TMSCl (6.70 mL, 53 mmol)) at 0 ºC. After 15 min the mixture was warmed to rt for 2 h, diluted with ether (100 mL) and filtered. The solution was washed with $NaHCO_3$, brine, dried over Na_2SO_4, concentrated and used without purification. To a -78 ºC solution of LDA (75 mmol) in THF (100 mL) was added the alkyne dropwise over 10 min. After 5 min, HMPA (25 mL, 150 mmol) was added followed by iodomethane (14 mL, 200 mmol), and the mixture was warmed to rt for 4 h. The reaction was quenched with 10% HCl and was vigoursly stirred for 2 h. Solid NaCl was then added and the mixture was extracted with ether (100 mL), washed with $NaHCO_3$, brine, dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (20% EtOAc/hexanes) afforded 5.46 g (72%) of alcohol as a colorless oil. Spectral characteristics matched those previously reported.[2]



(*S*)-3-Pentyn-2-ol. To a solution of (*S*)-3-butyn-2-ol[3] (3.00 g, 43.0 mmol), DMF (40 mL) and imidazole (3.60 g, 53.0 mmol) was added TBSCl (6.70 g, 43.5 mmol). The solution was stirred overnight, diluted with ether (100 mL) and filtered. The filtrate was washed six times with brine (50 mL). The combined aqueous extracts were back extracted with ether (100 mL) and rewashed with fresh brine (50 mL). The combined organic extracts were dried over $MgSO_4$ and carefully concentrated without heat due to the volatility of the compound to afford 8.02 g (101%) of alkyne as a yellow oil . The crude alkyne was redissolved in THF (40 mL) and cooled to -78ºC. A solution of BuLi (2.5 M in hexanes, 20 mL, 50 mmol) was added dropwise over 15 min. Upon completion of the addition the yellow solution was warmed to rt for 30 min. then recooled to -78 ºC, and iodomethane (10 mL, 150 mmol) was added dropwise over 10 min. The resulting solution was allowed to warm to rt slowly overnight. After 15 h the mixture was quenched with NH_4Cl (100 mL) and extracted with ether (200 mL). The organic extracts were washed with brine, dried over $MgSO_4$, and carefully concentrated to afford 8.9 g (104%) of a yellow oil. The resulting residue was redissolved in MeOH (20 mL) and *p*-TsOH (1.00 g, 5.8 mmol) was added. After 18 h the volatile components were distilled without heat directly into a -78 °C trap *in vacuo*. The resulting colorless solution was fractionally distilled (20 mm Hg, bp 50 °C) to afford 3.12 g (85%) of alcohol as a colorless liquid. The purity of the alcohol was determined to be *ca* 75% by GC and NMR analysis, the remaining material being residue from the TBS protecting group for a corrected yield of 65%. The impurities did not affect subsequent reactions. Spectral characteristics matched those previously reported.[4]

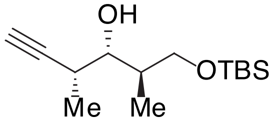


(*S*)-3-Pentyne-2-ol Methanesulfonate (1b). To a -78 °C solution of (*S*)-3-pentyn-2-ol (3.12 g, *ca* 28 mmol) in CH_2Cl_2 (300 mL) was added methanesulfonyl chloride (6.85 g, 60 mmol) followed by Et_3N (14 mL, 100 mmol). After 1 h, the cooling bath was removed and the mixture allowed to warm to 0 °C, then quenched with $NaHCO_3$ (200 mL) and warmed to rt The mixture was extracted with ether (300 mL), washed with brine (200 mL), dried over $MgSO_4$, and concentrated to afford 4.98 g, (110%) of mesylate as a light yellow oil contaminated with TBS residue which was used without further purification. Spectral characteristics matched those previously reported.[5]

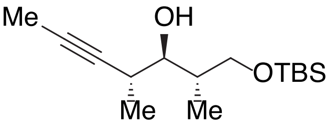


(2*R*,3*R*,4*S*)-1-(*tert*-Butyldimethylsilyloxy)-2,4,-dimethyl-5-hexyn-3-ol (6). To a solution of (*M*)-allenyl stannane (3.25 g, 10.0 mmol), CH_2Cl_2 (50 mL), and (2*R*)-3-(*tert*-butyldimethylsilyloxy)-2-methylpropanal (2.02 g, 10.0 mmol) at -78 °C was added $BF_3{\bullet}OEt_2$ (3.70 mL, 30.0 mmol) dropwise over 2 min. After 30 min the reaction was rapidly quenched by pouring it into a stirred $NaHCO_3$ solution (100 mL). After warming to rt the mixture was extracted with ether (200 mL), dried over $MgSO_4$, concentrated, and purified by chromatography on silica gel (5% ether/hexanes-10% EtOAc/hexanes) followed by bulb to bulb distillation (0.025 mm Hg, 75-

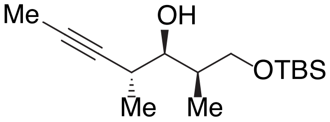
85 ºC) affording 2.35 g (90%) of alcohol as a colorless oil. R_f = 0.66 (20% EtOAc/hexanes); $[\alpha]_D$ -1.62 (c 1.36, $CHCl_3$); IR 3492, 3309, 2942, 2854 cm^{-1}; ^{1}H NMR d 0.07 (s, 6H), 0.89 (s, 9H), 0.98 (d, *J*=6.9 Hz, 3H), 1.28 (d, *J*=6.9 Hz, 3H), 2.04 (d, *J*=2.7 Hz, 1H), 2.14 (m, 1H), 2.50 (m, 1H), 3.52 (s, 1H), 3.68 (dd, *J*=9.9, 3.6 Hz, 2H), 3.85 (dd, *J*=9.9, 3.0 Hz, 1H); ^{13}C NMR d -5.7, 9.3, 17.6, 18.1, 25.8, 30.1, 36.2, 69.4, 69.8, 78.3, 86.3; Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.32; H, 10.90.



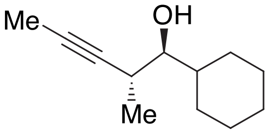
(2*R*,3*S*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4,-dimethyl-5-hexyn-3-ol (8). To a solution of (*P*)-allenyl stannane (220 mg, 0.64 mmol), CH_2Cl_2 (5 mL), and (2*R*)-3-(*tert*-butyldimethylsilyloxy)-2-methylpropanal (100 mg, 0.494 mmol) at -78 ºC was added Me_2AlCl (1.0 M in hexanes, 1.20 mL, 1.20 mmol) over 10 s. After 30 min the reaction was rapidly quenched by pouring it into a stirred NH_4Cl solution (20 mL) and diluting with ether. After warming to rt the mixture was extracted with ether (50 mL), dried over $MgSO_4$, concentrated, and purified by chromatography on silica gel (5% ether/hexanes-10% EtOAc/hexanes) followed by bulb to bulb distillation (0.025 mm Hg, 75-85 ºC) affording 83 mg (65%) of alcohol as a colorless oil. R_f = 0.66 (20% EtOAc/hexanes); IR 3492, 3309, 2942, 2854 cm^{-1}; ^{1}H NMR d 0.06 (s, 6H), 0.88 (s, 9H), 1.00 (d, J=7.2 Hz, 3H), 1.26 (d, J=6.9 Hz, 3H), 2.02 (m, 1H), 2.06 (d, J=2.4, 1H), 2.57 (m, 1H), 3.41 (br, 1H), 3.59 (d, J=5.1 Hz, 1H), 3.62 (d, J=4.8 Hz, 1H), 3.95 (dd, J= 3.6, 9.9 Hz, 1H); ^{13}C NMR d -5.7, 14.7, 16.2, 18.1, 25.7, 30.8, 35.9, 66.7, 69.6, 78.9, 86.9.



(2*S*,3*R*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-5-heptyn-3-ol (12b). To a -78 ºC solution of $Pd(OAc)_2$ (96 mg, 0.43 mmol), in THF (80 mL), was added triphenylphosphine (113 mg, 0.43 mmol). After the phosphine had dissolved a solution of mesylate **1b** (75% purity, 2.42 g, *ca* 11.20 mmol) in THF (5 mL) was added followed by (*S)*-aldehyde (1.75 g, 8.6 mmol), and finally diethylzinc (1.0 M in hexanes, 25.0 mL, 25.0 mmol). The solution was warmed to -20 ºC overnight, quenched with NH_4Cl, extracted with ether (300 mL), and washed with NaHCO$_3$ and brine. Charcoal (1 g), Celite 545, and MgSO$_4$, were added to the extracts and stirred for 30 min followed by filtration and concentration. Purification by chromatography on silica gel (5% EtOAc/hexanes) afforded a yellow oil. Bulb to bulb distillation (85-95 °C, 0.05 mm Hg) afforded 1.65 g (70%) of alcohol as a colorless oil. R$_f$ = 0.66 (20% EtOAc/hexanes); [α]$_D$ +9.7 (c 0.75, CHCl$_3$); IR 3501, 2925, 2864 cm^{-1}; ^{1}H NMR δ 0.07 (s, 6H), 0.82 (d, *J*=6.9 Hz, 3H), 0.89 (s, 9H), 1.22 (d, *J*=6.9 Hz, 3H), 1.80 (d, *J*=2.4 Hz, 3H), 1.95 (m, 1H), 2.61 (m, 1H), 3.26 (dd, *J*=2.7, 8.1 Hz, 1H), 3.61 (dd, *J*=7.5, 9.9 Hz, 1H), 3.71 (dd, *J*=4.5, 9.9 Hz, 1H); ^{13}C NMR δ -5.6, 3.6, 10.3, 13.5, 18.3, 25.9, 30.4, 38.8, 67.1, 68.1, 78.8, 79.5; Anal. Calcd for C$_{15}$H$_{30}$O$_2$Si: C, 66.61; H, 11.18. Found: C, 66.31; H, 10.98.

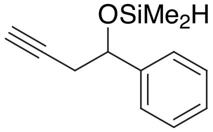


(2*R*,3*R*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-5-heptyn-3-ol (10b). The same scale, procedure, and workup described for the *anti,anti* alcohol was followed with the enantiomeric aldehyde to afford 1.75 g (74%) of alcohol as a colorless oil. R$_f$ = 0.66 (20% EtOAc/hexanes); [α]$_D$ -1.0 (c 1.3, CHCl$_3$); IR 3510, 2959, 2854 cm^{-1}; ^{1}H NMR *d* 0.04 (s, 6H), 0.88 (s, 9H), 0.91 (d, *J*=7.2 Hz, 3H), 1.11 (d, *J*=7.2 Hz, 3H), 1.75 (m, 1H), 1.80 (d, *J*=2.4 Hz, 3H), 2.58 (m, 1H), 3.47 (dd, *J*=3.6, 6.6 Hz, 1H), 3.63 (m, 2H); ^{13}C NMR δ -5.5, 3.6, 10.3, 17.9, 18.2, 25.8, 30.7, 37.6, 65.2, 67.1, 76.2, 80.7; Anal. Calcd for C$_{15}$H$_{30}$O$_2$Si: C, 66.61; H, 11.18. Found: C, 66.74; H, 11.36.



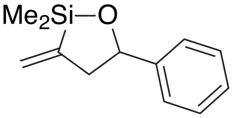
***anti*-1-Cyclohexyl-2-methyl-3-pentyn-1-ol (2b).** The general procedure and workup described for homopropargylic alcohol # was followed with racemic mesylate. To a solution of Pd(OAc)$_2$ (40 mg, 0.18 mmol) in THF (60 mL), at -78 °C was added PPh$_3$ (47 mg, 0.18 mmol), mesylate (2.19 g, 13.4 mmol), cyclohexanecarboxaldehyde (1.00 g, 8.9 mmol), and Et$_2$Zn (1.0 M in hexanes, 25 mL, 25.0 mmol). After 20 h at -20 °C, workup and purification by chromatography on silica gel, then bulb to bulb distillation (0.05 mm Hg, 100 °C) afforded 1.18 g (73%) of alcohol as a colorless oil. R$_f$ = 0.65 (20% EtOAc/hexanes); IR 3449, 2925, 2855 cm^{-1}; ^{1}H

NMR δ 0.97-1.96 (m, 11H), 1.18 (d, J=7.2 Hz, 3 H), 1.81 (d, J=2.4 Hz, 3H), 2.67 (m, 1H), 2.99 (dd, J=4.2, 7.2 Hz, 1H).

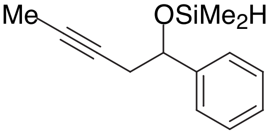


General Procedure for Alcohol Silylation:

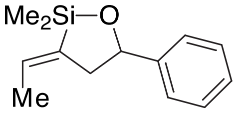
1-(Hydrodimethylsilyloxy)-1-phenyl-3-butyne (3c). A dry flask was charged with alcohol **2c** (2.60 g, 18 mmol), and 1,1,3,3-tetramethyldisilazane (TMDS) (2.25 mL, 13 mmol) at rt. After 1 min the evolution of ammonia was evident. Once the initial exothermic reaction slowed the mixture was heated to 60 ºC for 2 h, then cooled to rt and the excess silazane was removed *in vacuo* to afford a colorless oil which was used without further purification. ^{1}H NMR δ 0.13 (d, J=3.0 Hz, 3H), 0.22 (d, J=3.0 Hz, 3H), 1.96 (t, J=2.7 Hz, 1H), 2.51-2.69 (m, 2H), 4.63 (septet, J=3.0 Hz, 1H), 4.81 (t, J=6.0 Hz, 1H), 7.26-7.39 (m, 5H).

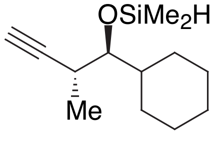


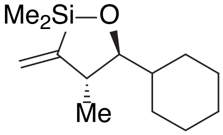
General Procedure for Hydrosilation: 2,2-Dimethyl-3-methylene-5-phenyl-1-oxa-2-silacyclopentane (4c). The residue from the previous step was diluted with toluene (6 mL) and H_2PtCl_6 (7.3 mg, 0.018 mmol) was added at rt. The mixture was gradually heated to 70 ^{0}C and after 1 h was cooled to rt. Concentration and bulb to bulb distillation (0.05 mm Hg, 100 ºC) afforded 2.9 g (80%) of siloxane as a colorless oil. Spectral characteristics matched those previously reported.[6]

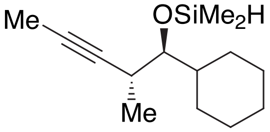


1-Phenyl-1-(hydrodimethylsilyloxy)-3-pentyne (3d). The foregoing general procedure was employed with alcohol **2d** (5.46 g, 30 mmol), and TMDS (3.53 mL, 20 mmol). After heating for 2 h to ensure complete reaction the excess silazane was removed *in vacuo* and the colorless oil was used without further purification. ^{1}H NMR δ 0.14 (d, J=3.0 Hz, 3H), 0.21 (d, J=3.0 Hz, 3H), 1.76 (t, J=2.4 Hz, 3H), 2.43-2.64 (m, 2H), 4.65 (sept. J=2.7 Hz, 1H), 4.77 (dd, J=5.7 Hz, 7.2 Hz, 1H), 7.24-7.40 (m, 5H).

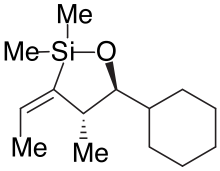

(*E*)-2,2,3-Trimethyl-3-methylene-5-phenyl-1-oxa-2-silacyclopentane (4d). To the residual oil was added toluene (7.00 mL) and H_2PtCl_6 (12.2 mg, 0.030 mmol). **(Caution: *Stirring was initiated and after a 10 s induction period a highly exothermic reaction with rapid and violent evolution of gas occured.*)** Analysis of the crude mixture after 2 min by NMR indicated complete consumption of the starting material. The olive green mixture was concentrated, and bulb to bulb distilled (0.05 mm Hg, 110 ºC) affording 5.12 g (79%) of siloxane as a colorless oil. ^{1}H NMR 0.34 (s, 3H), 0.37 (s, 3H), 1.73 (d, *J*=6.6 Hz, 3H), 2.31 (m, 1H), 2.98 (dd, *J*=5.2, 14.1 Hz, 1H), 5.02 (dd, *J*=5.2, 9.4 Hz, 1H), 5.91 (m, 1H), 7.20-7.40 (m, 5H).


***anti*-1-Cyclohexyl-1-(hydrodimethylsilyloxy)-2-methyl-3-butyne (3a).** The general procedure was employed with alcohol **2a**[7] (1.0 g, 6.06 mmol) and TMDS (0.73 mL, 4.2 mmol). After heating at 60 ºC for two h the excess silazane was removed *in vacuo* and the resulting oil used without further purification. IR 2960, 2881, 2200 cm^{-1}; ^{1}H NMR δ 0.23 (app. t, *J*=3.3 Hz, 6H), 1.18 (d, *J*=7.2 Hz, 3H), 0.85-1.92 (m, 11H), 2.05 (d, *J*=2.7 Hz, 1H), 2.70 (m, 1H), 3.20 (dd, *J*=3.9, 6.9 Hz, 1H), 4.70 (septet, *J*=2.7 Hz, 1H)

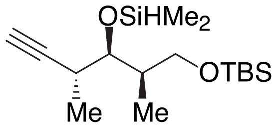

***anti*-2,2,4-Trimethyl-3-methylene-5-cyclohexyl-1-oxa-2-silacyclopentane (4a).** The foregoing residue was diluted with toluene (6 mL) and H_2PtCl_6 (4 mg, 0.01 mmol) was added. The mixture was gradually heated to 70 ºC for 1 h. Concentration and bulb to bulb distillation(0.05 mm Hg, 85 ºC) afforded 1.15 g (92%) of siloxane as a colorless oil. ^{1}H NMR δ 0.20 (s, 3H), 0.24 (s, 3H), 1.03 (d, *J*=6.9 Hz, 3H), 0.90-1.90 (m, 11H), 2.49 (m, 1H), 3.36 (dd, *J*=4.2, 6.3 Hz, 1H), 5.41 (t, *J*=2.4 Hz, 1H), 5.63 (t, *J*=2.4 Hz, 1H).



***anti*-1-Cyclohexyl-1-(hydrodimethylsilyoxy)-2-methyl-3-pentyne (3b).** The general procedure was employed with alcohol **2b** (600 mg, 3.33 mmol) and TMDS (0.40 mL, 2.33 mmol). After heating at 60 ºC for two h the excess silazane was removed *in vacuo* and the resulting oil used without further purification. ^{1}H NMR δ 0.23 (apparent t, *J*=3.0 Hz, 6H), 0.90-1.90 (m, 11H), 1.11 (d, *J*=6.9Hz, 3H), 1.79 (d, *J*=2.4 Hz, 3H), 2.63 (m, 1H), 3.17 (dd, *J*=5.4, 6.3 Hz, 1H), 4.70 (septet, *J*=3.0 Hz, 1H).

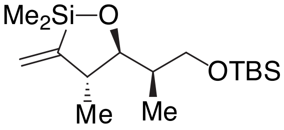


(*E*) *anti*-2,2,3,4-Tetramethyl-3-methylene-5-cyclohexyl-1-oxa-2-silacyclopentane (4b). The above residual oil was dissolved in toluene (4 mL), H_2PtCl_6 (*ca* 1.0 mg, 0.002 mmol) was added and the mixture was heated to 70 ºC for 3 h. Concentration and bulb to bulb distillation (0.05 mm Hg, 90 ºC) afforded 714 mg (90%) of siloxane as a colorless oil. IR 2952, 2855 cm^{-1}; ^{1}H NMR δ 0.19 (s, 3H), 0.21 (s, 3H), 0.89-1.23 (m, 6H), 1.04 (d, *J*=7.2 Hz, 3H), 1.62-1.88 (m, 5H), 1.73 (d, *J*=6.6 Hz, 3H), 2.76 (q, *J*=7.2 Hz, 1H), 3.52 (d, *J*=7.5 Hz, 1H), 5.82 (qd, *J*=6.6, 1.8 Hz, 1H); ^{13}C NMR d 0.4, 1.4, 15.8, 21.1, 26.1, 26.6, 28.6, 29.7, 38.6, 44.1, 89.5, 132.0, 146.1.

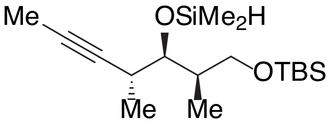


(2*R*,3*R*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-hexyne (11a). The general procedure was employed with alcohol **10a**[8] (428 mg, 1.65 mmol), and TMDS (0.58 mL, 3.30 mmol). The mixture was heated to 90 ºC overnight. After 14 h the bath was cooled to 40 ºC and excess silazane was removed *in vacuo* (*ca* 0.01 mm Hg, 3 h) to afford a light yellow oil which was used without purification. IR 3309, 2968, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.23 (d, *J*=2.7 Hz, 3H), 0.25 (d, *J*=2.7 Hz, 3H), 0.85 (d,

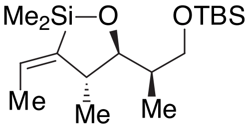
J=7.0 Hz, 3H), 0.90 (s, 9H), 1.15 (d, J=7.0 Hz, 3H), 1.85 (m, 1H), 2.05 (d, J=2.4 Hz, 1H), 2.67 (m, 1H), 3.48 (d, J=6.3 Hz, 2H), 3.68 (dd, J=4.5 Hz, 6.6 Hz, 1H), 4.72 (sept, J=2.7Hz, 1H).



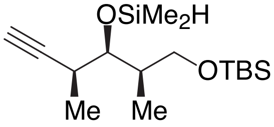
Cyclic Siloxane (11a'). The above residue was dissolved in THF (3.5 mL), and H_2PtCl_6 (0.056 M in THF, 60 μL, 0.0044 mmol) was added. The mixture was heated to 55 °C and monitored by IR (2121 cm^{-1}, Si-H). After 6 h the reaction was judged complete by the disapperance of the Si-H stretch in the IR spectrum. The light yellow mixture was cooled to rt, diluted with ether, and filtered through Celite 545. Concentration afforded 490 mg (93%) of vinyl siloxane as a light yellow oil which was used without purification. IR 2968, 2855 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.20 (d, J=3.6 Hz, 6H), 0.82 (d, J=6.6 Hz, 3H), 0.88 (s, 9H), 1.00 (d, J=6.6 Hz, 3H), 1.78 (m, 1H), 2.41 (m, 1H), 3.49 (dd, J=6.3 Hz, 9.9 Hz, 1H), 3.62 (m, 2H), 5.42 (t, J=2.7 Hz, 1H), 5.61 (t, J=2.7 Hz, 1H); ^{13}C NMR δ = -5.4, -0.5 , -0.2, 9.3, 14.7, 18.3, 25.9, 38.7, 42.0, 66.2, 82.4, 119.6, 156.2.



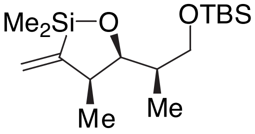
(2*R*,3*R*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-heptyne (11b). The general procedure was employed with alcohol **10b** (520 mg, 1.89 mmol), and TMDS (0.66 mL, 3.79 mmol) at 90 °C overnight, affording after concentration a light yellow oil which was used directly. IR 2960, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.22 (d, J=3.0 Hz, 3H), 0.24 (d, J=3.0 Hz, 3H), 0.82 (d, J=6.9 Hz, 3H), 0.89 (s, 9H), 1.07 (d, J=6.9 Hz, 3H), 1.78 (d, J=2.4 Hz, 3H), 1.86 (m, 1H), 2.58 (m, 1H), 3.49 (m, 2H), 3.63 (m, 1H), 4.72 (septet, J=3.0 Hz, 1H).



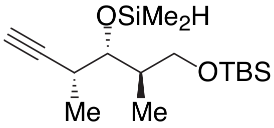
Cyclic Siloxane (11b'). The general procedure was employed with the residue from the previous step in THF (4 mL) and H_2PtCl_6 (0.056 M in THF, 60 μL, 0.0044 mmol). The reaction was heated to 55 °C for 4 h, cooled, filtered and concentrated affording a yellow oil which was used without further purification. IR 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.03 (s, 6H), 0.19 (s, 3H), 0.20 (s, 3H), 0.84 (d, *J*=6.9 Hz, 3H), 0.88 (s, 9H), 1.05 (d, *J*=7.2 Hz, 3H), 1.55 (m, 1H), 1.72 (d, *J*=6.6 Hz, 3H), 2.75 (q, *J*=7.2 Hz, 1H), 3.40 (dd, *J*=6.0, 9.9 Hz, 1H), 3.54 (dd, *J*=5.4, 9.9 Hz, 1H), 3.81 (dd, *J*=1.8, 6.0 Hz, 1H), 5.80 (qd, *J*=6.6, 2.1 Hz, 1H); ^{13}C NMR δ -4.9, 0.5, 1.8, 12.5, 16.3, 26.3, 39.9, 42.5, 66.5, 86.2, 132.3, 146.6.



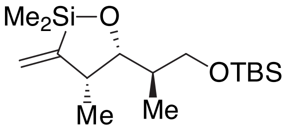
(2*R*,3*R*,4*S*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-hexyne (7). The general procedure was employed with alcohol **6** (350 mg, 1.35 mmol), and TMDS (0.47 mL, 2.69 mmol) affording after concentration a light yellow oil which was used without purification. IR 3309, 2968, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.05 (d, *J*=2.4 Hz, 6H), 0.23 (d, *J*=2.7 Hz, 6H), 0.79 (d, *J*=6.6 Hz, 3H), 0.89 (s, 9H), 1.20 (d, *J*=6.9 Hz, 3H), 2.05 (d, *J*=2.4 Hz, 1H), 2.16 (m, 1H), 2.55 (m, 1H), 3.42 (m, 2H), 3.75 (dd, *J*=8.7, 2.4 Hz, 1H), 4.68 (septet, *J*=2.7 Hz, 1H).



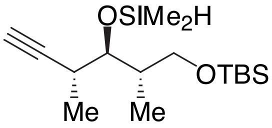
Siloxane (7'). The general procedure was employed with the residue from the previous step in THF (2.7 mL) and H_2PtCl_6 (0.056 M in THF, 48 μL, 0.0027 mmol). The mixture was heated to 50 °C for 3.5 h, cooled, filtered and concentrated affording a yellow oil which was used without purification. IR 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.19 (s, 3H), 0.29 (s, 3H), 0.89 (m, 12H), 0.99 (d, *J*=7.2 Hz, 3H), 1.74 (m, 1H), 2.66 (m, 1H), 3.37 (dd, *J*=6.3, 9.9 Hz, 1H), 3.54 (dd, *J*=5.4, 9.9 Hz, 1H), 3.85 (dd, *J*=5.4, 6.3 Hz, 1H), 5.33 (t, *J*=2.1 Hz, 1H), 5.61 (t, *J*=2.1 Hz, 1H); ^{13}C NMR -5.4, -0.2, 13.3, 14.5, 18.3, 25.9, 38.3, 44.4, 65.8, 80.6, 119.4, 157.1.



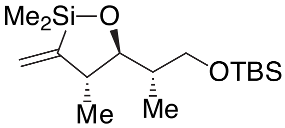
(2*R*,3*S*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-hexyne (9). The general procedure was employed with alcohol **8** (140mg, 0.54 mmol), and TMDS (0.20 mL, 1.08 mmol) affording after concentration a light yellow oil which was used directly. IR 3309, 2968, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.22 (d, *J*=2.7 Hz, 3H), 0.23 (d, *J*=2.7 Hz, 3H), 0.90 (s, 12H), 1.14 (d, *J*=6.6 Hz, 3H), 1.95 (m, 1H), 2.05 (d, *J*=2.7 Hz, 1H), 2.69 (m, 1H), 3.48 (dd, *J*=6.6, 9.9 Hz, 1H), 3.62 (t, *J*=5.7 Hz, 1H), 3.68 (dd, *J*=4.5, 9.9 Hz, 1H), 4.72 (septet, *J*=2.7 Hz, 1H).



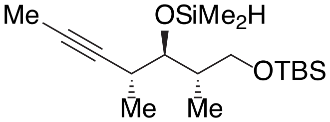
Siloxane (9'). The general procedure was employed with the residue from the previous step in THF (1.2 mL) and H$_2$PtCl$_6$ (0.056 M in THF, 19 μL, 0.001 mmol). The mixture was heated to 50 ºC for 5 h, cooled, filtered, and concentrated affording a yellow oil which was used without further purification. IR 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.03 (s, 6H), 0.17 (s, 3H), 0.27 (s, 3H), 0.88 (s, 12H), 0.92 (d, *J*=6.9 Hz, 3H), 1.67 (m, 1H), 2.52 (m, 1H), 3.59-3.69 (m, 2H), 3.72 (dd, *J*=3.0, 9.3 Hz, 1H), 5.33 (dd, *J*=1.2, 2.4 Hz, 1H), 5.68 (dd, *J*=0.9, 2.7 Hz, 1H); ^{13}C NMR d -5.5, -5.3, -0.8, 0.4, 13.1, 15.2, 18.4, 25.9, 38.2, 44.7, 65.2, 79.6, 120.7



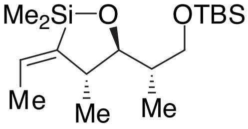
(2*S*,3*R*,4*R*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-hexyne (13a). The general procedure was employed with alcohol **12a** (130 mg, 0.50 mmol), and TMDS (0.20 mL, 1.08 mmol) affording after concentration a light yellow oil which was used directly. IR 3318, 2960, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.24 (d, *J*=2.7 Hz, 3H), 0.25 (d, *J*=2.7 Hz, 3H), 0.89 (s, 9H), 0.92 (d, *J*=6.9 Hz, 3H), 1.22 (d, *J*=6.9 Hz, 3H), 1.93 (m, 1H), 2.79 (m, 1H), 3.45 (dd, *J*=3.3, 8.1 Hz, 1H), 3.59 (m, 2H), 4.69 (septet, *J*=2.7 Hz, 1H).



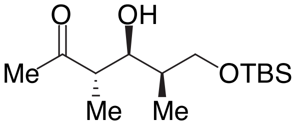
Siloxane (13a'). The general procedure was employed with the residue from the previous step in THF (1 mL), and H_2PtCl_6 (0.056 M in THF, 18 μL, 0.0010 mmol). After 4 h at 55 ºC the mixture was filtered, concentrated and used without purification. IR 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.03 (s, 6H), 0.22 (s, 3H), 0.24 (s, 3H), 0.88 (s, 9H), 0.94 (d, *J*=6.9 Hz, 3H), 1.06 (d, *J*=7.0 Hz, 3H), 1.85 (m, 1H), 2.59 (m, 1H), 3.39 (dd, *J*=7.2, 9.9 Hz, 1H), 3.48 (apparent t, *J*=5.7 Hz, 1H), 3.78 (dd, *J*=5.4, 9.9 Hz, 1H), 5.40 (t, *J*=2.4 Hz, 1H), 5.63 (t, *J*=2.4 Hz, 1H).



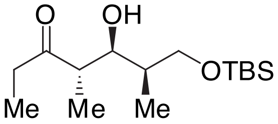
(2*S*,3*R*,4*R*)-1-(tert-Butylydimethylsilyloxy)-2,4-dimethyl-3-(hydrodimethylsilyloxy)-5-heptyne (13b). The general procedure was employed with alcohol **12b** (274 mg, 1.01 mmol), and TMDS (0.35 mL, 2.00 mmol) affording after concentration a light yellow oil which was used directly. IR 2960, 2855, 2121 cm^{-1}; ^{1}H NMR δ 0.04 (s, 6H), 0.23 (d, *J*=2.4 Hz, 6H), 0.90 (s, 9H), 0.92 (d, *J*=7.2 Hz, 3H), 1.15 (d, *J*=6.9 Hz, 3H), 1.78 (d, *J*=2.4 Hz, 3H), 1.92 (m, 1H), 2.65 (m, 1H), 3.39 (dd, *J*=3.9, 7.5 Hz, 1H), 3.60 (m, 2H), 4.70 (septet, *J*=2.4 Hz, 1H).



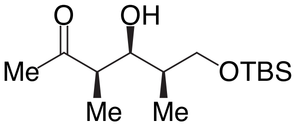
Siloxane (13b'). The general procedure was employed with the residue from the previous step in THF (2 mL), and H_2PtCl_6 (0.056 M in THF, 35 μΛ, 0.0020 mmol). After 7 h at 55 ºC the mixture was filtered, concentrated, and used without purification. IR 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.02 (s, 6H), 0.20 (s, 3H), 0.22 (s, 3H), 0.87 (s, 12H), 1.05 (d, *J*=7.2 Hz, 3H), 1.53 (m, 1H), 1.73 (d, *J*=6.3 Hz, 3H), 2.80 (q, *J*=7.2 Hz, 1H), 3.35 (dd, *J*=8.1, 9.6 Hz, 1H), 3.64 (d, *J*=8.1 Hz, 1H), 3.76 (dd, *J*=4.5 Hz, 9.6 Hz, 1H), 5.83 (qd, *J*=6.3, 1.5 Hz, 1H); ^{13}C NMR δ -5.3, 0.5, 1.4, 13.7, 15.8, 18.3, 21.0, 25.9, 38.5, 42.2, 65.3, 87.1, 132.4, 145.7.



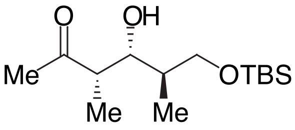
General Oxidation Procedure: (3*S*,4*S*,5*R*)-3,5-dimethyl-6-(*tert*-butyldimethylsilyloxy)-4-hydroxy-2-hexanone (16a). To a solution of siloxane **11a'** (50 mg, 0.15 mmol) in THF/MeOH (1:1, 2 mL) was added $KHCO_3$ (47 mg, 0.47 mmol), KF (9.0 mg, 0.15 mmol) and H_2O_2 (30% in H_20, 1.0 mL, *ca* 8.8 mmol). After 6 h the reaction was judged complete by TLC analysis and excess peroxide was quenched by addition of solid $Na_2S_2O_3$ (**Caution:** ***exothermic, induction period***). The mixture was diluted with brine (10 mL), and extracted with ether (50 mL), dried over $MgSO_4$, tested for peroxides, then concentrated and purified by chromatography on silica gel (10% EtOAc/hexanes) affording 32 mg (70%) of ketone as a colorless oil. R_f = 0.33 (20% EtOAc/hexanes); $[\alpha]_D$ +1.0 (c=2.0, $CHCl_3$); IR 3493, 2960, 2855, 1710 cm^{-1}; ^1H NMR δ 0.06 (s, 6H), 0.88 (s, 9H), 0.93 (d, *J*=6.9 Hz, 3H), 0.98 (d, *J*=7.2 Hz, 3H), 1.71 (m, 1H), 2.22 (s, 3H), 2.70 (dq, *J*=6.9 Hz, 9.3 Hz, 1H), 3.22 (br, 1H), 3.66 (dd, *J*=4.5 Hz, 9.9 Hz, 1H), 3.76 (dd, *J*=3.6 Hz, 9.6 Hz, 1H); ^{13}C NMR δ -5.6, 9.2, 13.3, 18.2, 25.8, 29.8, 35.6, 49.9, 68.6, 76.0, 213.3; Anal Calcd for $C_{14}H_{30}O_3Si$: C, 61.26; H, 11.02. Found: C, 61.19; H, 11.09.



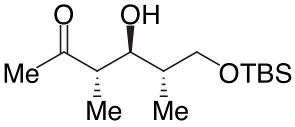
(4*S*,5*S*,6*R*)-4,6-dimethyl-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-3-heptanone (16b). The general procedure was employed with siloxane **11b'** (630 mg, 1.89 mmol), THF/MeOH (1:1, 8 mL), $KHCO_3$ (600 mg, 6.00 mmol), KF (111 mg, 1.90 mmol) and 30% H_2O_2 (8 mL, *ca* 70 mmol). After 3 h, the reaction was worked up as previously described and purified by chromatography on silica gel (5% to 20% EtOAc/hexanes) affording 372 mg (68%) of ketone as a colorless oil. R_f = 0.50 (20% EtOAc/hexanes); $[\alpha]_D$ +11.8 (c 1.0, $CHCl_3$); IR 3501, 2960, 2864, 1710 cm^{-1}; ^1H NMR δ 0.05 (s, 6H), 0.87 (s, 9H), 0.95 (t, *J*=7.2 Hz, 6H), 1.04 (d, *J*=7.2 Hz, 3H), 1.70 (m, 1H), 2.51 (q, *J*=7.2 Hz, 2H), 2.66 (dq, *J*=7.2, 9.3 Hz, 1H), 3.21 (br, 1H), 3.65 (dd, *J*=4.8, 9.9 Hz, 1H), 3.75 (dd, *J*=3.9, 9.9 Hz, 1H), 3.97 (dd, *J*=1.8, 9.3 Hz, 1H); ^{13}C NMR δ -5.6, 7.4, 9.2, 13.6, 18.2, 25.8, 35.6, 36.2, 48.8, 68.6, 76.2, 215.8; Anal Calcd for $C_{15}H_{32}O_3Si$: C, 62.45; H, 11.18. Found: C, 62.73; H, 11.28.



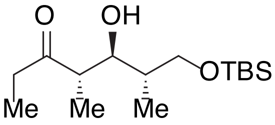
(3*R*,4*S*,5*R*)-3,5-Dimethyl-6-(*tert*-butyldimethylsilyloxy)-4-hydroxy-2-hexanone (14). The general procedure was employed with siloxane **7'** (425 mg, 1.33 mmol), THF/MeOH (1:1, 6 mL), $KHCO_3$ (400 mg, 4.05 mmol), KF (80 mg, 1.35 mmol) and 30% H_2O_2 (6 mL, *ca* 53 mmol). After 5 h, the mixture was worked up as previously described and purified by chromatography on silica gel (5% to 20% EtOAc/hexanes) affording 255 mg (70%) of ketone as a light yellow oil. After failing combustion analysis the compound was further purified by bulb to bulb distillation (0.01 mm Hg, 135 °C) affording a colorless oil. R_f = 0.30 (20% EtOAc/hexanes); $[\alpha]_D$ +7.9 (c=1.0, $CHCl_3$); IR 3493, 2960, 2855, 1710 cm^{-1}; ^1H NMR δ 0.05 (s, 6H), 0.88 (s, 9H), 0.95 (d, *J*=7.2 Hz, 3H), 1.18 (d, *J*=6.9 Hz, 3H), 1.62 (m, 1H), 2.15 (s, 3H), 2.72 (m, 1H), 3.20 (br, 1H), 3.55 (dd, *J*=4.5, 10.2 Hz, 1H), 3.71 (dd, *J*=3.3, 10.2 Hz, 1H), 3.93 (dd, *J*=3.9, 6.9 Hz, 1H); ^{13}C NMR δ -5.7, 11.1, 12.6, 18.1, 25.7, 29.0, 36.9, 50.2, 68.0, 74.6, 212.7. The second distilled sample also failed to give a satifactory combustion analysis. In both samples the carbon content was low by *ca* 0.5%



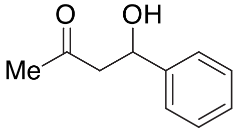
(3*S*,4*R*,5*R*)-3,5-Dimethyl-6-(*tert*-butyldimethylsilyloxy)-4-hydroxy-2-hexanone (15). The general procedure was employed with siloxane **9'** (172 mg, 0.54 mmol), THF/MeOH (1:1, 2 mL), $KHCO_3$ (160 mg, 1.60 mmol), KF (30 mg, 0.52 mmol) and H_2O_2 (2 mL, *ca* 18 mmol). After 5 h, the mixture was worked up as previously described and purified by chromatography on silica gel (5% to 20% EtOAc/hexanes) affording 102 mg (69%) of ketone as a light yellow oil. R_f = 0.33 (20% EtOAc/hexanes); $[\alpha]_D$ -8.6 (c=1.0, $CHCl_3$); IR 3484, 2960, 2855, 1710 cm^{-1}; ^1H NMR δ 0.06 (s, 6H), 0.82 (d, *J*=6.9 Hz, 3H), 0.88 (s, 9H), 1.12 (d, *J*=7.2 Hz, 3H), 1.74 (m, 1H), 2.20 (s, 3H), 2.57 (m, 1H), 3.61 (dd, *J*=7.2, 10.2 Hz, 1H), 3.74 (dd, *J*=3.9, 10.2 Hz, 1H), 3.87 (br, 1H), 3.89 (dt, *J*=8.4, 2.4 Hz, 1H). ^{13}C NMR δ -5.6, 8.8, 13.3, 18.1, 25.8, 28.4, 37.2, 49.8, 68.1, 75.9, 212.3; Anal Calcd for $C_{14}H_{30}O_3Si$: C, 61.26; H, 11.02. Found: C, 60.99; H, 11.05.



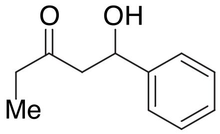
(3*S*,4*S*,5*S*)-3,5-Dimethyl-6-(*tert*-butyldimethylsilyloxy)-4-hydroxy-2-hexanone (17a). The general procedure was employed with siloxane **13a'** (160 mg, 0.50 mmol), THF/MeOH (1:1, 2 mL), $KHCO_3$ (150 mg, 1.60 mmol), KF (29 mg, 0.50 mmol) and H_2O_2 (2 mL, *ca* 18 mmol). After 3 h, the reaction was worked up as previously described and purified by chromatography on silica gel (5% to 20% EtOAc/hexanes) affording 100 mg (72%) of ketone as a colorless oil. After failing combustion analysis the compound was further purified by bulb to bulb distillation (0.010 mm Hg, 135 °C) affording a colorless oil. R_f=0.32 (20% EtOAc/hexanes); $[\alpha]_D$ +4.6 (c=3.7, $CHCl_3$); IR 3484, 2960, 2855, 1710 cm^{-1}; ^1H NMR δ 0.04 (s, 6H), 0.88 (s, 9H), 0.96 (d, *J*=6.9 Hz, 3H), 1.10 (d, *J*=7.2 Hz, 3H), 1.77 (m, 1H), 2.19 (s, 3H), 2.79 (m, 1H), 3.60 (dd, *J*=5.4, 10.2 Hz, 2H), 3.75 (dd, *J*=4.2, 9.9 Hz, 2H); ^{13}C NMR δ -5.7, -5.6, 13.8, 14.7, 18.1, 25.8, 29.5, 36.5, 50.7, 66.2, 78.2, 213.3. The second distilled sample also failed to give a satifactory combustion analysis. In both samples the carbon content was low by *ca* 0.7-0.8%



(4S,5S,6S)-4,6-Dimethyl-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-3-heptanone (17b). The general procedure was employed with siloxane **13b'** (325 mg, 0.98 mmol), THF/MeOH (1:1, 4 mL), $KHCO_3$ (300 mg, 3.00 mmol), KF (58 mg, 1.00 mmol) and H_2O_2 (4 mL, *ca* 36 mmol). After 3 h, the reaction was worked up as previously described and purified by chromatography on silica gel (5% to 20% EtOAc/hexanes) affording 202 mg (70%) of ketone as a colorless oil. R_f= 0.50 (20% EtOAc/hexanes); $[\alpha]_D$ +11.1 (c 1.0, $CHCl_3$); IR 3493, 2968, 2855, 1719 cm^{-1}; ^1H NMR δ 0.07 (s, 6H), 0.88 (s, 9H), 1.00 (apparent dd, *J*=7.2, 7.2 Hz, 6H), 1.08 (d, *J*=6.9 Hz, 3H), 1.75 (m, 1H), 2.53 (m, 2H), 2.83 (m, 1H), 3.57-3.68 (m, 2H), 3.62 (dd, *J*=4.8, 10.2 Hz, 1H), 3.75 (dd, *J*=4.2, 10.2 Hz, 1H); ^{13}C NMR δ -5.6, 7.4, 14.1, 14.8, 18.1, 25.8, 35.8, 36.5, 49.5, 68.8, 78.1, 215.9. Anal Calcd for $C_{15}H_{32}O_3Si$: C, 62.45; H, 11.18. Found: C, 62.33; H, 11.18.

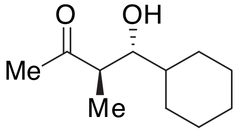


4-Phenyl-4-hydroxy-2-butanone (5c) The general procedure was employed with siloxane **4c** (204 mg, 1.0 mmol), THF/MeOH (1:1, 2 mL), KF (180 mg, 3.0 mmol), $KHCO_3$ (300 mg, 3.0 mmol) and H_2O_2 (2 mL, *ca* 17.6 mmol). After 2 h the reaction was worked up and purified by chromatography on silica gel (10% EtOAc/hexanes) affording140 mg (87%) of ketone as a colorless oil. Spectral characteristics matched those previously reported.[9]

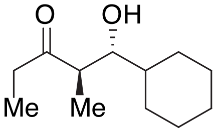


5-Phenyl-5-hydroxy-3-pentanone (5d). The general procedure was employed with siloxane **4d** (220 mg, 1.0 mmol), THF/MeOH (1:1, 2 mL), KF (180 mg, 3.0 mmol), $KHCO_3$ (300 mg, 3.0 mmol) and H_2O_2 (2 mL, *ca* 17.6 mmol). After 2 h the reaction was worked up and purified by chromatography on silica gel (10% EtOAc/hexanes) affording140 mg (87%) of ketone as a colorless oil. Spectral characteristics matched those previously reported.[10]

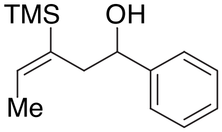
Oxidation of (*E*)-5-Phenyl-3-(benzyldimethylsily)-2-penten-5-ol (18e) to Ketone (5d). To a solution of the vinylsilane **18e** (100 mg, 0.32 mmol) in THF (1mL) was added TBAF (1.0 M in THF, 0.320 mL, 0.32 mmol). After 1 h starting material was not present by TLC analysis and H_2O_2 (30%, 2 mL, *ca* 17.6 mmol), MeOH (1 mL), and $KHCO_3$ (100 mg, 1.00 mmol) were added. After 2 h the reaction was worked up and purified affording 48 mg (84%) of ketone.



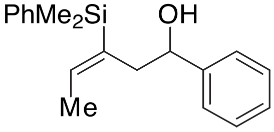
***anti* -4-Cyclohexyl-4-hydroxy-3-methyl-2-butanone (5a)** The general procedure was employed with siloxane **4a** (223 mg, 1.00 mmol), THF/MeOH (1:1, 4 mL), $KHCO_3$ (300 mg, 3.00 mmol), KF (160 mg, 3.00 mmol) and H_2O_2 (4 mL, *ca* 36 mmol). After 3 h, the reaction was worked up as previously described and purified by chromatography on silica gel affording 154 mg (85%) of ketone as a colorless oil. Spectral characteristics matched those previously reported.[7]



***anti* -5-Cyclohexyl-5-hydroxy-4-methyl-3-pentanone (5b).** The general procedure was employed with siloxane **4b** (238 mg, 1.00 mmol), THF/MeOH (1:1, 4 mL), $KHCO_3$ (300 mg, 3.00 mmol), KF (160 mg, 3.00 mmol) and H_2O_2 (4 mL, *ca* 36 mmol). After 3.5 h, the reaction was worked up as previously described and purified by chromatography on silica gel affording 160 mg (82%) of ketone as a colorless oil. Spectral characteristics matched those previously reported.[7]

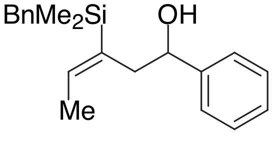


(*E*)-5-Phenyl-3-trimethylsilyl-2-penten-5-ol (18c). To a 0 °C solution of siloxane **4d** (600 mg, 2.75 mmol), in ether (10 mL), was added MeLi (1.4 M in pentane, 4.30 mL, 6.00 mmol). The colorless solution was warmed to rt for 1 h then cautiously quenched by dropwise addition of NH_4Cl (15 mL). The mixture was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (5% EtOAc/hexanes) afforded 440 mg (69%) of silane as a colorless oil. IR 3449, 3073, 2916 cm^{-1}; ^{1}H NMR δ 0.12 (s, 9H), 1.68 (d, *J*=6.6 Hz, 3H), 2.01 (br, 1H), 2.45 (dd, *J*=4.2, 13.2 Hz, 1H), 2.69 (dd, *J*=9.6, 13.2 Hz, 1H), 4.68 (dd, *J*=4.2, 9.6 Hz, 1H), 6.11 (q, *J*=6.6 Hz, 3H), 7.20-7.50 (m, 5H).

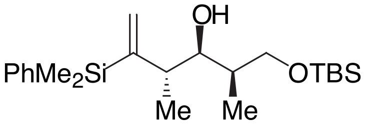


(*E*)-5-Phenyl-3-phenyldimethylsilyl-2-penten-5-ol (18d). To a 0 °C solution of siloxane **4d** (600 mg, 2.75 mmol), in ether (10 mL), was added PhMgBr (3.0 M in Et_2O, 2.00 mL, 6.00 mmol). The colorless solution was warmed to rt for 1 h then cautiously quenched by dropwise addition of NH_4Cl (15 mL). The mixture was extracted with ether (50 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (5% EtOAc/hexanes) afforded 535 mg (66%) of silane as a colorless oil. $R_f = 0.45$ (20%

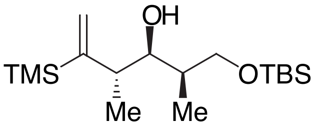
EtOAc/hexanes); IR 3449, 3073, 2916 cm^{-1}; ^{1}H NMR δ 0.41 (s, 6H), 1.72 (d, *J*=6.6 Hz, 3H), 1.83 (br, 1H), 2.41 (dd, *J*=3.6, 12.9 Hz, 1H), 2.65 (dd, *J*=9.9, 12.9 Hz, 1H), 4.46 (dd, *J*=3.9, 9.3 Hz, 1H), 6.19 (q, *J*=6.6 Hz, 1H), 7.20-7.60 (m, 10H).



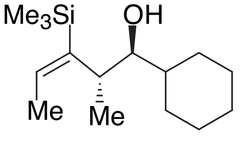
(E)-5-Phenyl-3-(benzyldimethylsily)-2-penten-5-ol (18e). To an ice cooled solution of benzylmagnesium chloride (1.0 M in Et_2O, 10 mL, 10.0 mmol) was added dropwise siloxane **4d** (1.0 g, 4.5 mmol), in ether (1 mL). After 10 min the cooling bath was removed and the mixture stirred at rt. for 2 h. Standard work up and purification by chromatography on silica gel (5% EtOAc/hexanes) afforded 1.11 g (80%) of silane as a colorless oil. R_f = 0.58 (20% EtOAc/hexanes); IR 3423, 3021, 2925 cm^{-1}; ^{1}H NMR δ 0.10 (s, 3H), 0.12 (s, 3H), 1.71 (d, *J*=6.6 Hz, 3H), 1.99 (br, 1H), 2.19 (s, 2H), 2.44 (dd, *J*=4.5, 13.2 Hz, 1H), 2.68 (dd, *J*=9.6, 13.2 Hz, 1H), 4.62 (dd, *J*=4.5, 9.6 Hz, 1H), 6.09 (q, *J*=6.6 Hz, 1H), 7.01-7.39 (m, 5H); ^{13}C NMR δ -3.1, -2.9, 15.0, 25.9, 39.8, 73.5, 124.0, 125.6, 127.4, 128.0, 128.2, 128.3, 136.3, 140.0, 140.2, 144.4.



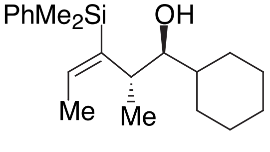
(2*R*,3*S*,4*S*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-5-(phenyldimethylsilyl)-5-hexen-3-ol. To a solution of siloxane (50 mg, 0.15 mmol), in ether (1 mL) was added phenylmagnesium bromide (3.0 M in ether, 0.10 mL, 0.30 mmol). After 1.5 h at rt the mixture was quenched with NH_4Cl (1 mL), extracted with ether (3 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (1% EtOAc/hexanes) afforded 55 mg (89%) of vinylsilane as a colorless oil. R_f = 0.77 (20% EtOAc/hexanes), $[\alpha]_D$ +2.4 (c 3.0, $CHCl_3$); IR 3510, 2960, 2855 cm^{-1}; ^{1}H NMR δ 0.05 (s, 6H), 0.4 (s, 6H), 0.84 (apparent t, *J*=5.4 Hz, 6H), 0.90 (s, 9H), 1.76 (m, 1H), 2.05 (br, 1H), 2.48 (m, 1H), 3.60 (m, 2H), 3.72 (d, *J*=9.9 Hz, 1H), 5.57 (d, *J*=2.4 Hz, 1H), 5.85 (d, *J*=2.4 Hz, 1H), 7.34 (m, 3H), 7.54 (m, 2H); ^{13}C NMR δ -5.4, -2.2, 8.5, 18.2, 25.9, 35.4, 43.4, 67.7, 74.7, 127.3, 127.7, 128.9, 133.9, 138.5, 154.5.



(2*R*,3*S*,4*S*)-1-(*tert*-Butyldimethylsilyloxy)-2,4-dimethyl-5-(trimethylsilyl)-5-hexen-3-ol. To a solution of siloxane (50 mg, 0.15 mmol), in ether (1 mL) was added methyllithium (1.4 M in ether, 0.20 mL, 0.28 mmol). After 1.5 h at rt the mixture was quenched with NH_4Cl (1 mL), extracted with ether (3 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (1% EtOAc/hexanes) afforded 40 mg (77%) of vinylsilane as a colorless oil. $R_f = 0.84$ (20% EtOAc/hexanes); $[\alpha]_D$ +1.1 (c 4.0, $CHCl_3$); IR 3528, 2960, 2864 cm^{-1}; ^1H NMR δ 0.06 (s, 6H), 0.13 (s, 9H), 0.87 (d, *J*=7.0 Hz, 3H), 0.89 (s, 9H), 0.92 (d, *J*=6.9 Hz, 3H), 1.84 (m, 1H), 2.09 (br, 1H), 2.46 (m, 1H), 3.65 (m, 2H), 3.78 (d, *J*=9.9 Hz, 1H), 5.52 (d, *J*=2.4 Hz, 1H), 5.74 (d, *J*=2.4 Hz, 1H); ^{13}C NMR δ -5.4, -0.7, 8.5,18.2, 18.3, 25.9, 36.4, 43.6, 67.6, 74.4, 125.5, 156.2; Anal Calcd for $C_{17}H_{38}O_2Si_2$: C, 61.75; H, 11.58. Found: C, 61.59; H, 11.51.



(*E*),*anti*-1-Cyclohexyl-2-methyl-3-(trimethylsilyl)-3-penten-1-ol (18a). To a solution of siloxane **4b** (50 mg, 0.21 mmol), in ether (1 mL) was added methyllithium (1.4 M in ether, 0.30 mL, 0.42 mmol). After 1.5 h at rt the mixture was quenched with NH_4Cl (1 mL), extracted with ether (3 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (1% EtOAc/hexanes) afforded 52 mg (98%) of vinylsilane as a colorless oil**.** $R_f = 0.88$ (20% EtOAc/hexanes); IR 3571, 2925, 2846 cm^{-1}; ^1H NMR δ 0.11 (s, 9H), 0.98 (d, *J*=6.9 Hz, 3H), 1.10-1.90 (m, 11H), 1.73 (d, *J*=6.9 Hz, 3H), 2.97 (m, 1H), 3.32 (d, *J*=9.9 Hz, 1H), 6.08 (q, *J*=6.6 Hz, 1H); ^{13}C NMR δ 0.8, 16.7, 24.2, 26.5, 27.0, 31.5, 38.1, 39.4, 77.5, 138.4, 144.6



(*E*),*anti* -1-Cyclohexyl-2-methyl-3-(phenyldimethylsilyl)-3-penten-1-ol (18b). To a solution of siloxane **4b** (50 mg, 0.21 mmol), in ether (1 mL) was added phenylmagnesium bromide (3.0 M in ether, 0.14 mL, 0.42 mmol). After 2 h at rt the mixture was quenched with NH_4Cl (1 mL), extracted with ether (3 mL), dried over $MgSO_4$, and concentrated. Purification by chromatography on silica gel (1% EtOAc/hexanes) afforded 60 mg (91%) of vinylsilane as a colorless oil**.** R_f = 0.80 (20% EtOAc/hexanes); IR 3571, 2933, 2855 cm^{-1}; ^{1}H NMR δ 0.43 (s, 6H), 0.89 (d, *J*=6.9 Hz, 3H), 1.10-1.90 (m, 11H), 1.77 (d, *J*=6.9 Hz, 3H), 2.97 (m, 1H), 3.23 (d, *J*=9.6 Hz, 1H), 6.13 (q, *J*=6.6 Hz, 1H), 7.33 (m, 3H), 7.51 (m, 2H); ^{13}C NMR δ -0.7, 16.9, 24.2, 26.4, 26.6, 26.9, 31.3, 38.2, 39.3, 77.5, 127.7, 128.8, 133.8, 140.2, 143.1.

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