Supplementary Information

A Novel Oxidative Cyclisation onto Vinyl Silanes

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General methods

^{1}H NMR and ^{13}C NMR spectra were recorded either on a 400 MHz or a 500 MHz spectrometer in $CDCl_3$, DMSO-d_6, acetone-d_6 or MeOH-d_4 and referenced to residual solvent peaks or to $SiMe_4$ as an internal standard. Chemical shifts are quoted in ppm (parts per million) with signal splittings recorded as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), apparent (app.) and broad singlet (br. s). Coupling constants, *J*, are measured in Hz. ^{1}H and ^{13}C NMR spectra were recorded at room temperature unless otherwise stated. Flash column chromatography was performed using silica gel 60 (0.033-0.070mm, BDH). TLC analyses were performed on Merck Kiesegel 60 F_{254} 0.25 mm precoated plates. Petrol refers to petroleum ether in the boiling range 40-60 °C. Product spots were visualised under UV light (λ_{max} = 254 nm) and/or by staining with potassium permanganate or vanillin solutions. Reagents obtained from Acros, Aldrich, Avocado, Fluka and Lancaster fine chemicals suppliers were used directly as supplied. All anhydrous reactions were carried out in flame-dried glassware and under an inert atmosphere of argon. All solvents were distilled and properly dried, when necessary, prior to use.

General Procedure 1:

To a solution of diol (1 mmol) in acetonitrile (12 mL) and H_2O (8 mL) was added pyridine *N*-oxide (2 mmol), citric acid (0.75 mmol), potassium osmate dihydrate (0.01 mmol) and the metal trifluoromethansulfonate (0.5 mmol). The resulting solution was warmed to 60 °C and the mixture left to stir until all starting material had reacted. Na_2SO_3 (5 mg) and H_2O (10 mL) were added and the reaction was cooled to room temperature. The mixture was extracted with EtOAc (3 × 50 mL) and the combined organic layers were washed with 2 M HCl (20 mL), 3 M NaOH (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified as specified.

General Procedure 2:

To a solution of the alkene (1 mmol) and 4-methyl morpholine *N*-oxide (2 mmol) in H_2O/THF/^{t}BuOH (1:10:8, 10 mL) was added osmium tetroxide (5.0 mol%) and the resulting

solution was stirred for 16 h at room temperature. Na_2SO_3 (200 mg) was added and the mixture was stirred for 30 min after which H_2O (40 mL) was added and the mixture extracted with EtOAc (3 × 40 mL). The combined organics were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product which was purified as specified.

General Procedure 3:

To a mixture of the aldehyde (1 mmol), freshly purified Bestmann-Ohira reagent (1.2 mmol) and K_2CO_3 (2 mmol) was added MeOH (15 mL) and the reaction was stirred for 5 h at room temperature. Et_2O (40 mL) was added and the solution washed with H_2O (50 mL), 5% w/w aqueous $NaHCO_3$ (50 mL) and a further portion of H_2O (50 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product which was purified as specified.

General Procedure 4:

The alkyne (1 mmol) and the silane (1.2 mmol) were dissolved in CH_2Cl_2 (2 mL) and the solution was cooled to 0 °C and degassed with argon for 15 min. Pentamethylcyclopentadienyltris(acetonitrile) ruthenium (II) hexafluorophosphate (2 mol%) was added and the solution was warmed to room temperature and stirred for 16 h at this temperature. The solvent was removed *in vacuo* to give the crude product which was purified as specified.

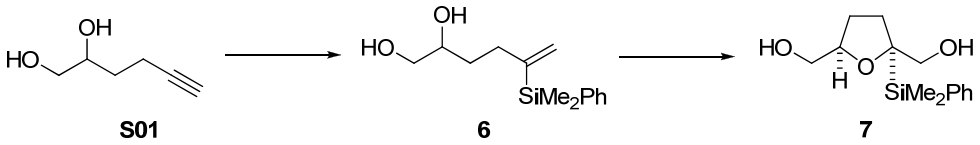
General Procedure 5:

To a solution of silylated-THF (1 mmol) in THF (5 mL) and DMF (1 mL) at 0 °C was added sodium hydride (4.0 mmol, 60% dispersion in mineral oil). The resultant mixture was stirred at 0 °C for 30 min before tetrabutylammonium iodide (0.1 mmol) and benzyl bromide (4.0 mmol) were added. The resulting solution was allowed to warm to room temperature and stirred for 20 h before a saturated solution of brine (15 mL) was added. The mixture was stirred or 30 min before being extracted with EtOAc (3 × 30 mL) and the combined organic

layers washed with H_2O (30 mL), brine (30 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product which was purified as specified.

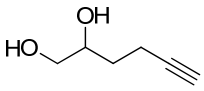
General Procedure 6:

To a solution of benzyl-protected THF (1 mmol) in THF (10 mL) at 40 °C was added tetrabutylammonium fluoride (4.0 mL, 2.0 mmol, 0.5 M solution in THF) *via* syringe pump addition over 30 min. The resultant mixture was stirred at 40 °C for a further 30 min before MeOH (2.0 mL), potassium bicarbonate (3 mmol) and urea-hydrogen peroxide (5 mmol) were added. After stirring at 40 °C for 1 h, a saturated solution of sodium thiosulfate (15 mL) was added. The mixture was extracted with EtOAc (3 × 30 mL) and the combined organic layers washed with brine (30 mL), dried over Na_2SO_4, filtered and the solvent removed in vacuo to give the crude product which was purified as specified.



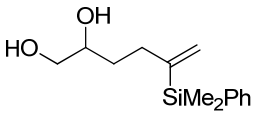
S01 **6** **7**

(±)-Hex-5-yne-1,2-diol, S01



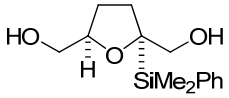
Pent-4-enal (841 mg, 10.0 mmol) was subjected to General Procedure 2. The crude aldehyde was then subjected to General Procedure 3. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 1:1, then EtOAc], gave diol **S01** as a pale yellow oil (753 mg, 66% over two steps). **^{1}H NMR** (400 MHz, MeOH-d_4) δ_H: 3.75-3.69 (1H, m), 3.51-3.43 (2H, m), 2.38-2.24 (2H, m), 2.22 (1H, s), 1.77-1.68 (1H, m), 1.61-1.52 (1H, m); **^{13}C NMR** (100 MHz, MeOH-d_4) δ_C: 83.7, 70.9, 68.6, 66.2, 32.5, 14.5.

(±)-5-(Dimethyl(phenyl)silyl)hex-5-ene-1,2-diol, 6



Diol **S01** (161 mg, 1.41 mmol) was subjected to General Procedure 4 with dimethylphenylsilane (231 mg, 1.70 mmol). Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 3:1 then 1:1], gave vinyl silane **6** as an oil (305 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.56-7.50 (2H, m), 7.40-7.32 (3H, m), 5.72 (1H, m), 5.46 (1H, m), 3.62-3.56 (1H, m), 3.50 (1H, dd, J = 11.0, 2.2), 3.32 (1H, dd, J = 11.0, 7.7), 2.40 (1H, br. s), 2.36 (1H, br. s), 2.33-2.25 (1H, m), 2.20-2.12 (1H, m), 1.49-1.43 (2H, m), 0.40 (3H, s), 0.39 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 149.7, 138.1, 133.9, 129.1, 127.8, 126.3, 71.8, 66.6, 32.0, 31.7, −3.0, −3.1; **IR** υ_{max} (thin film)/cm^{-1} 3316br., 2955, 1463, 1416, 1369, 1255, 1119, 1084, 1006, 835, 736; **HRMS** (ES^+, *m/z*): Calculated 273.1281 ($C_{14}H_{22}NaO_2Si$); Found 273.1280.

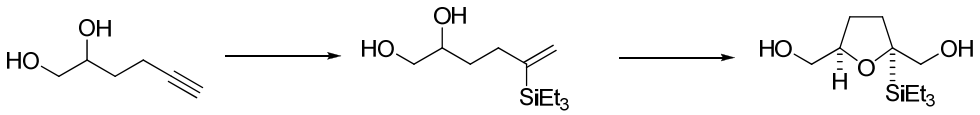
(±)-((2*R*,5*R*)-2-(Dimethyl(phenyl)silyl)tetrahydrofuran-2,5-diyl)dimethanol, 7



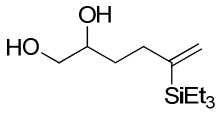
Method A: Vinyl silane **6** (180 mg, 0.718 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (2.5 mol%) at 60 °C for 16 h. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 3:1 then 1:1], gave THF **7** as prisms (183 mg, 96%).

Method B: To a stirred solution of vinyl silane **6** (46.0 mg, 0.184 mmol), pyridine-*N*-oxide (34.9 mg, 0.367 mmol) and citric acid (26.5 mg, 0.138 mmol) in acetone/TFA/H_2O (9:5:1, 14 mL) was added potassium osmate dihydrate (3.4 mg, 5 mol%) and the solution stirred for 16 h at room temperature. Na_2SO_3 (100 mg) and saturated aqueous $NaHCO_3$ (20 mL) were added, the mixture was extracted with EtOAc (3 × 25 mL) and the combined organic layers were dried over Na_2SO_4, filtered and the solvent removed *in vacuo* to give the crude product which was purified by flash column chromatography, [SiO_2, petrol/EtOAc, 3:1 then 1:1], to give THF **7** as prisms (29 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.58 (2H, dd, *J* = 7.0, 1.7), 7.41-7.33 (3H, m), 3.91-3.86 (1H, m), 3.85 (1H, dd, *J* = 11.4, 4.6), 3.79 (1H, d, *J* = 11.6), 3.52 (1H, dd, *J* = 11.4, 3.6), 3.47 (1H, d, *J* = 11.6), 2.87 (2 H, br. s), 1.99-1.87 (3H, m), 1.72-1.62 (1H, m), 0.38 (3H, s), 0.37 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 136.6, 134.4, 129.3, 127.8, 81.1, 80.6, 66.1, 64.6, 30.4, 28.1, −5.1, −5.2; **IR** (KBr disc)/cm^{-1} 3346br., 3048, 2960, 1428, 1260, 1108, 1027, 816, 776; **HRMS** (ES^+, *m/z*): Calculated 289.1230 ($C_{14}H_{22}NaO_3Si$); Found 289.1232. Data obtained for **7** were identical from both methods.

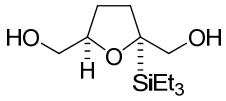


(±)-5-(Triethylsilyl)hex-5-ene-1,2-diol, 8

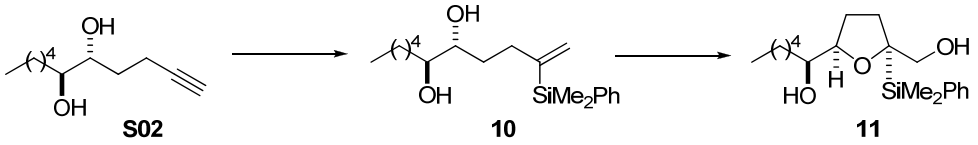


Diol **S01** (82.1 mg, 0.719 mmol) was subjected to General Procedure 4 with triethylsilane (100 mg, 0.861 mmol). Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 4:1 then 1:1], gave vinyl silane **8** as an oil (146 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 5.66 (1H, m), 5.33-5.32 (1H, m), 3.75-3.69 (1H, m), 3.66 (1H, dd, *J* = 11.0, 2.4), 3.46 (1H, dd, *J* = 11.0, 7.7), 2.69 (2H, br. s), 2.31-2.24 (1H, m), 2.17-2.09 (1H, m), 1.61-1.51 (2H, m), 0.92 (9H, t, *J* = 7.9), 0.61 (6H, q, *J* = 7.9); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 148.4, 125.5, 72.2, 66.8, 32.1, 31.9, 7.4, 2.9; **IR** (thin film)/cm^{-1} 3361br., 2953, 2875, 1458, 1417, 1237, 1047, 922, 736; **HRMS** (ES^+, *m/z*): Calculated 253.1594 ($C_{12}H_{26}NaO_2Si$); Found 253.1595.

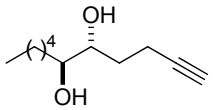
(±)-((2*R*,5*R*)-2-(Triethylsilyl)tetrahydrofuran-2,5-diyl)dimethanol, 9



Vinyl silane **8** (84.0 mg, 0.365 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (5.0 mol%) at 60 °C for 16 h. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 4:1 then 1:1], gave THF **9** as an oil (83.0 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 4.02-3.97 (1H, m), 3.90 (1H, dd, *J* = 11.5, 2.6), 3.82 (1H, d, *J* = 11.5), 3.59 (1H, dd, *J* = 11.5, 3.2), 3.45 (1H, d, *J* = 11.5), 3.17 (2H, br. s), 2.10-1.97 (3H, m), 1.87-1.78 (1H, m), 0.98 (9H, t, *J* = 7.9), 0.63 (6H, q, *J* = 7.9); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 81.8, 80.7, 68.7, 64.4, 31.2, 28.1, 7.7, 2.0; **IR** (thin film)/cm^{-1} 3356br., 2954, 1460, 1417, 1240, 1021, 932, 910, 863, 814, 751; **HRMS** (ES^+, *m/z*): Calculated 269.1543 ($C_{12}H_{26}NaO_3Si$); Found 269.1541.

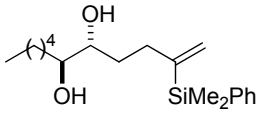


(±)-(5*R*,6*S*)-Undec-1-yne-5,6-diol, S02



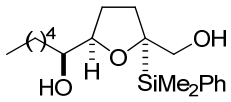
(*Z*)-Dec-4-enal (771 mg, 5.00 mmol) was subjected to General Procedure 2 to give the crude aldehyde which was then treated with General Procedure 3. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1 then 4:1], gave diol **S02** as prisms (581 mg, 63% over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 3.75 (1H, ddd, *J* = 8.5, 4.3, 3.7), 3.65 (1H, ddd, *J* = 8.0, 4.6, 3.7), 2.44-2.30 (4H, m), 1.99 (1H, t, *J* = 2.7), 1.72-1.62 (2H, m), 1.55-1.25 (8H, m), 0.89 (3H, t, *J* = 6.7); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 84.2, 74.7, 73.4, 69.0, 31.8, 31.6, 29.5, 25.6, 22.6, 15.2, 14.1; **IR** (KBr disc)/cm^{-1} 3307br., 2958, 2931, 2859, 1468, 1442, 1337, 1124, 1068, 1037, 867; **HRMS** (ES^+, *m/z*): Calculated 207.1356 ($C_{11}H_{20}NaO_2$); Found 207.1360; **m.p.** 75-76 °C.

(±)-(5*R*,6*S*)-2-(Dimethyl(phenyl)silyl)undec-1-ene-5,6-diol, 10

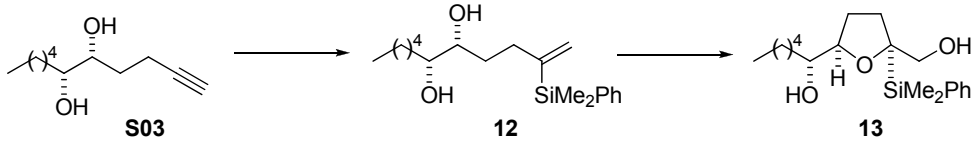


Diol **S02** (300 mg, 1.63 mmol) was subjected to General Procedure 4 with dimethylphenylsilane (266 mg, 1.96 mmol). Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 19:1 then 9:1 then 4:1], gave vinyl silane **10** as an oil (480 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.55-7.51 (2H, m), 7.38-7.34 (3H, m), 5.74 (1H, s), 5.47 (1H, s), 3.50-3.46 (2H, m), 2.37 (1H, ddd, *J* = 15.0, 7.5, 7.2), 2.15 (1H, ddd, *J* = 15.0, 8.0, 7.2), 1.85 (2H, br. s), 1.49-1.23 (10H, m), 0.91 (3H, t, *J* = 6.6), 0.40 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.0, 138.2, 133.9, 129.1, 127.8, 126.2, 74.6, 74.2, 32.2, 31.9, 31.2, 30.1, 25.7, 22.6, 14.1, −3.0, −3.1; **IR** (thin film)/cm^{-1} 3386br., 2955, 2933, 2859, 1428, 1249, 1112, 1059, 926, 833, 818, 776, 732, 700; **HRMS** (ES^+, *m/z*): Calculated 343.2064 ($C_{19}H_{32}NaO_2Si$); Found 343.2054.

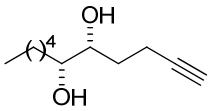
(±)-(*S*)-1-((2*R*,5*R*)-5-(Dimethyl(phenyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol 11



Vinyl silane **10** (289 mg, 0.903 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (2.5 mol%) at 60 °C for 16 h. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1 then 3:1], gave THF **11** as an oil (277 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.59-7.56 (2H, m), 7.41-7.33 (3H, m), 3.94-3.90 (1H, m), 3.81 (1H, d, *J* = 11.5), 3.74-3.70 (1H, m), 3.46 (1H, d, *J* = 11.5), 3.03 (2H, br. s), 2.03-1.91 (3H, m), 1.62-1.54 (1H, m), 1.52-1.22 (8H, m), 0.89 (3H, t, *J* = 6.9), 0.36 (3H, s), 0.36 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 136.6, 134.4, 129.3, 127.8, 84.0, 80.2, 72.4, 68.0, 33.6, 31.8, 30.4, 25.7, 25.3, 22.6, 14.1, −5.2, −5.3; **IR** (thin film)/cm^{-1} 3356br., 2931, 2861, 1428, 1249, 1110, 1056, 810, 735, 701; **HRMS** (ES^+, *m/z*): Calculated 359.2013 ($C_{19}H_{32}NaO_3Si$); Found 359.2004.

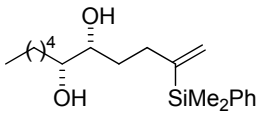


(±)-(5*R*,6*R*)-Undec-1-yne-5,6-diol, S03



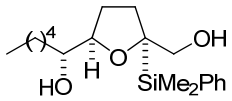
(*E*)-Dec-4-enal (771 mg, 5.00 mmol) was subjected to General Procedure 2 to give the crude aldehyde which was then treated with General Procedure 3. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1 then 4:1], gave diol **S03** as an oil (640 mg, 70% over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 3.56 (1H, ddd, *J* = 9.0, 5.0, 4.1), 3.42 (1H, ddd, *J* = 9.0, 5.0, 3.8), 2.63 (2H, br. s), 2.38-2.33 (2H, m), 1.98 (1H, t, *J* = 2.7), 1.76-1.61 (2H, m), 1.53-1.23 (8H, m), 0.89 (3H, t, *J* = 6.8); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 84.1, 74.4, 73.1, 68.9, 33.5, 32.3, 31.9, 25.3, 22.6, 14.9, 14.1; **IR** (thin film)/cm^{-1} 3311br., 2960, 2859, 2118, 1435, 1379, 1262, 1132, 1066, 941, 633; **HRMS** (ES^+, *m/z*): Calculated 207.1356 ($C_{11}H_{20}NaO_2$); Found 207.1359.

(±)-(5*S*,6*S*)-2-(Dimethyl(phenyl)silyl)undec-1-ene-5,6-diol, 12

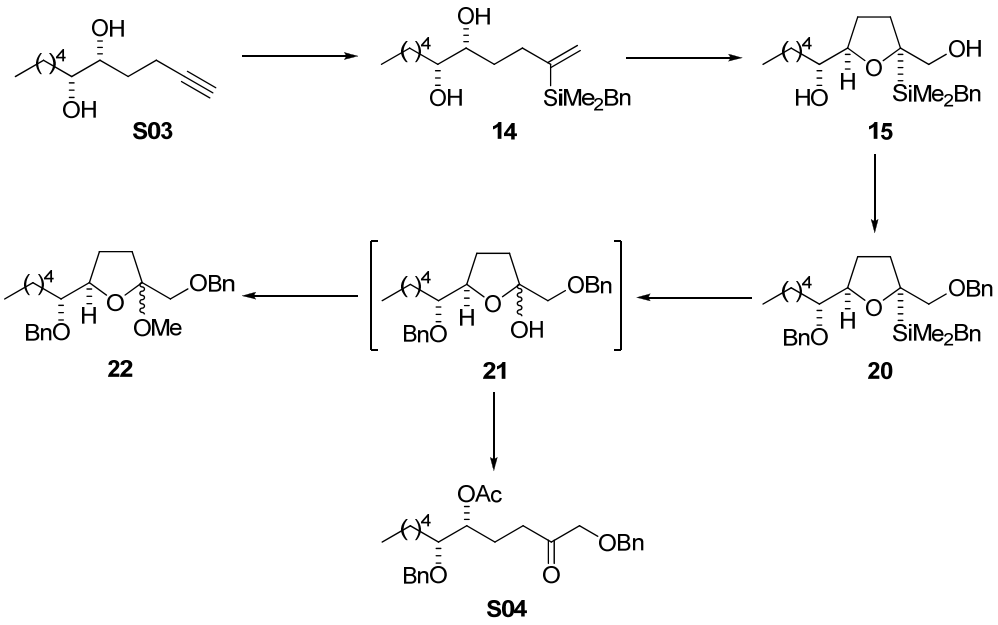


Diol **S03** (288 mg, 1.56 mmol) was subjected to General Procedure 4 with dimethylphenylsilane (255 mg, 1.87 mmol). Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 19:1 then 9:1 then 4:1], gave vinyl silane **12** as an oil (434 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.55-7.51 (2H, m), 7.37 (2H, d, *J* = 2.1), 7.35 (1H, d, *J* = 1.5), 5.73 (1H, ddd, *J* = 2.7, 1.5, 1.3), 5.47 (1H, d, *J* = 2.7), 3.32-3.26 (2H, m), 2.38-2.30 (1H, m), 2.23-2.15 (1H, m), 2.00 (2H, br. s), 1.57-1.22 (10H, m), 0.91 (3H, t, *J* = 7.0), 0.40 (3H, s), 0.40 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.0, 138.2, 133.9, 129.1, 127.8, 126.2, 74.5, 74.0, 33.5, 32.7, 31.9, 31.9, 25.3, 22.6, 14.1, −2.9, −3.1; **IR** (thin film)/cm^{-1} 3384br., 2955, 2932, 1428, 1249, 1112, 1066, 926, 833, 818, 732, 700; **HRMS** (ES^+, *m/z*): Calculated 343.2064 ($C_{19}H_{32}NaO_2Si$); Found 343.2059.

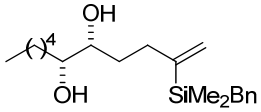
(±)-(*R*)-1-((2*R*,5*R*)-5-(dimethyl(phenyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol 13



Vinyl silane **12** (381 mg, 1.19 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (2.5 mol%) at 60 °C for 16 h. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1 then 3:1], gave THF **13** as an oil (354 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.60-7.56 (2H, m), 7.41-7.33 (3H, m), 3.72 (1H, d, *J* = 11.5), 3.61 (1H, ddd, *J* = 10.9, 6.2, 4.8), 3.48-3.42 (2H, m), 2.57 (2H, br. s), 2.20-1.89 (2H, m), 1.86-1.76 (1H, m), 1.72-1.65 (1H, m), 1.56-1.25 (8H, m), 0.91 (3H, t, *J* = 7.0), 0.40 (3H, s), 0.40 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 136.7, 134.4, 129.3, 127.8, 83.6, 80.4, 74.2, 68.2, 34.5, 31.9, 30.4, 29.2, 25.4, 22.7, 14.1, −5.0, −5.1; **IR** (thin film)/cm^{-1} 3356br., 3069, 2956, 1462, 1428, 1249, 1192, 1055, 810, 775, 736, 701; **HRMS** (ES^+, *m/z*): Calculated 359.2013 ($C_{19}H_{32}NaO_3Si$); Found 359.2008.

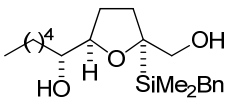


(±)-(5*S*,6*S*)-2-(Dimethyl(benzyl)silyl)undec-1-ene-5,6-diol, 14



Diol **S03** (200 mg, 1.09 mmol) was subjected to General Procedure 4 with benzyldimethylsilane (196 mg, 1.30 mmol). Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 19:1 then 9:1 then 4:1], gave vinyl silane **14** as an oil (294 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.28-7.18 (2H, m), 7.11-6.98 (3H, m), 5.67-5.64 (1H, m), 5.39-5.35 (1H, m), 3.44-3.37 (2H, m), 2.30 (1H, ddd, J = 14.8, 10.0, 5.4), 2.18 (2H, s), 2.17-2.10 (1H, m), 1.90 (2H, br. s), 1.65-1.25 (10H, m), 0.95-0.87 (3H, m), 0.08 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.2, 139.9, 128.3, 128.1, 125.3, 124.0, 74.5, 74.2, 33.6, 32.7, 31.9, 31.9, 25.5, 25.4, 22.6, 14.1, −3.4; **IR** (thin film)/cm^{-1} 3384br., 3024, 2931, 1493, 1452, 1248, 1057, 831; **HRMS** (ES$^+$, *m/z*): Calculated 357.2220 ($C_{20}H_{34}NaO_2Si$); Found 357.2220.

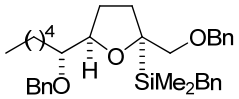
(±)-(*R*)-1-((2*R*,5*R*)-5-(dimethyl(benzyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol 15



Vinyl silane **14** (200 mg, 0.60 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (2.5 mol%) at 60 °C for 16 h. Purification by flash column chromatography,

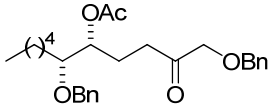
[SiO_2, petrol/EtOAc, 9:1 then 3:1], gave THF **15** as an oil (176 mg, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.26-7.18 (2H, m), 7.13-7.00 (3H, m), 3.79-3.71 (2H, m), 3.52-3.42 (2H, m), 3.17 (2H, br. s), 2.24-2.14 (2H, m), 1.96-1.82 (4H, m), 1.59-1.26 (8H, m), 0.91 (3H, t, *J* = 6.6), 0.02 (3H, s), 0.01 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 139.6, 128.3, 128.2, 124.1, 83.8, 80.2, 74.3, 68.1, 34.5, 31.9, 30.4, 29.4, 25.5, 23.3, 22.7, 14.1, −5.4, −5.4; **IR** (thin film)/cm^{-1} 3357 br., 2930, 1493, 1452, 1247, 1206, 1056, 818; **HRMS** (ES^+, *m/z*): Calculated 373.2169 ($C_{20}H_{34}NaO_3Si$); Found 373.2162.

(±)-Benzyl((2*R*,5*R*)-5-((*R*)-1-(benzyloxy)hexyl)-2-(benzyloxymethyl)tetrahydrofuran-2-yl)dimethylsilane, 20



THF **15** (450 mg, 1.29 mmol) was subjected to General Procedure 5. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1], gave THF **20** as an oil (501 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.30-7.01 (10H, m), 7.22 (2H, app. t, *J* = 7.4), 7.09 (1H, t, *J* = 7.2), 7.04 (2H, d, *J* = 7.6), 4.88 (1H, d, *J* = 11.6), 4.66 (1H, d, *J* = 11.6), 4.48 (2H, s), 3.94-3.86 (1H, m), 3.47 (1H, d, *J* = 9.2), 3.45 (1H, d, *J* = 9.2), 3.39-3.32 (1H, m), 2.25 (2H, d, *J* = 1.6), 2.05-1.95 (1H, m), 1.90-1.80 (2H, m), 1.76-1.65 (1H, m), 1.60-1.21 (8H, m), 0.91 (3H, t, *J* = 7.2), 0.05 (3H, s), 0.04 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 140.3, 139.6, 138.7, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 127.4, 84.6, 82.6, 78.2, 76.1, 73.5, 73.1, 32.0, 31.8, 30.8, 28.7, 25.4, 23.4, 22.7, 14.2, −5.4, −5.5; **IR** (thin film)/cm^{-1} 2954, 2930, 2859, 1494, 1453, 1071, 1027, 818, 735; **HRMS** (ES^+, *m/z*): Calculated 553.3108 ($C_{34}H_{46}NaO_3Si$); Found 553.3108.

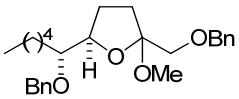
(±)-(5*R*,6*R*)-1,6-Bis(benzyloxy)-2-oxoundecan-5-yl acetate, S04



Benzylated THF **20** (150 mg, 0.28 mmol) was subjected to General Procedure 6. The resulting crude product was dissolved in pyridine (2 mL) and acetic anhydride (2 mL) and stirred at room temperature for 16 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, petrol/Et_2O, 4:1], gave ketone **S04** as an oil (91 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.39-7.25 (10H, m), 5.03 (1H, dt, *J* = 9.2, 4.2), 4.60

(2H, s), 4.58 (2H, s), 4.03 (2H, s), 3.42 (1H, dt, *J* = 8.0, 4.2), 2.46 (2H, t, *J* = 7.2), 2.04 (3H, s), 2.03-1.95 (1H, m), 1.91-1.80 (1H, m), 1.59-1.20 (8H, m), 0.88 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 207.8, 170.9, 138.4, 137.2, 128.5, 128.4, 128.0, 128.0, 127.9, 127.7, 79.2, 74.9, 73.4, 73.4, 72.4, 35.1, 31.9, 29.8, 25.3, 23.3, 22.6, 21.1, 14.1; **IR** (thin film)/cm^{-1} 2926, 1736, 1453, 1374, 1239, 1070; **HRMS** (ES^+, *m/z*): Calculated 463.2455 ($C_{27}H_{36}NaO_5$); Found 463.2456.

(±)-(5*R*)-5-((*R*)-1-(Benzyloxy)hexyl)-2-(benzyloxymethyl)-2-methoxytetrahydrofuran, 23

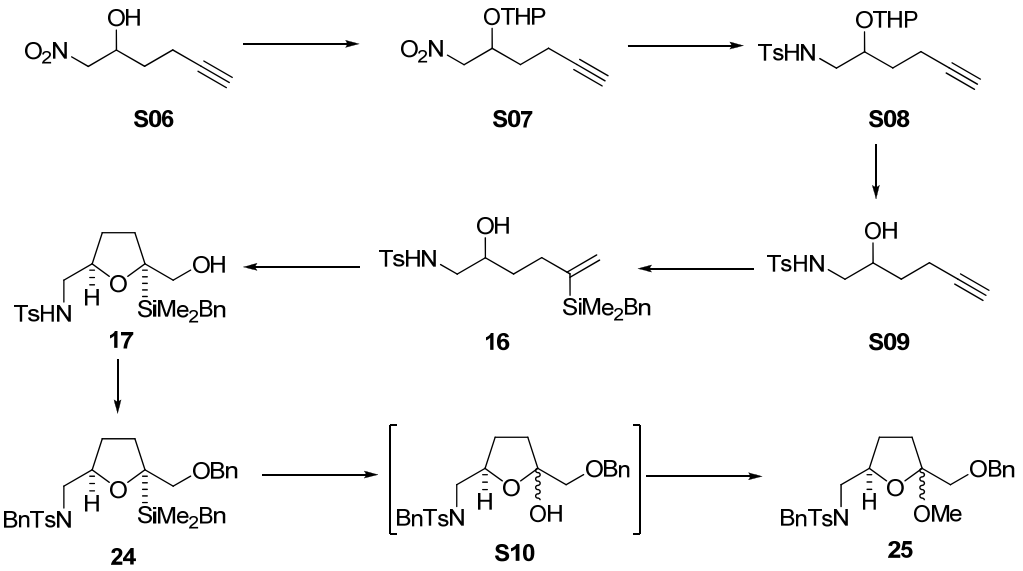


Benzylated THF **20** (76 mg, 0.14 mmol) was subjected to General Procedure 6. The resulting crude product was purified by flash column chromatography, [SiO_2, petrol/EtOAc, 4:1], to afford lactol **21** as an oil (42 mg, 74%), as a complex mixture of isomers.

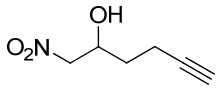
Lactol **21** (37 mg, 88 μmol) was dissolved in MeOH (1 mL) and CH_2Cl_2 (1 mL) under argon before pyridinium para-toluene sulfonate (4 mg, 18 μmol) was added. The resultant mixture was stirred at room temperature for 5 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 17:3], furnished lactol methyl ether **23** as an oil, and a (60:40) mixture of diastereomers (30 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: (diastereomeric 60:40) 7.33-7.15 (10H, m), 4.75 (0.4H, d, *J* = 11.6), 4.65 (0.6H, d, *J* = 11.6), 4.75-4.47 (3H, m), 4.16-4.09 (0.6H, m), 4.07-3.99 (0.4H, m), 3.66-3.58 (1H, m), 3.33-3.23 (2H, m), 3.19 (3H, s), 2.04-1.51 (4H, m), 1.44-1.10 (8H, m), 0.84-0.76 (3H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: (diastereomeric 60:40) 139.3, 139.2, 138.3(2), 128.4(2), 128.3(2), 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.4, 127.4, 108.2, 108.0, 84.6, 82.5, 81.8, 81.2, 73.5, 73.5, 72.9, 72.8, 70.7, 70.3, 49.0, 49.0, 34.7, 34.1, 32.1, 32.0, 31.1, 30.7, 27.5, 27.0, 25.4, 25.1, 22.7(2), 14.1(2); **IR** (thin film)/cm^{-1} 2930, 2860, 1722, 1496, 1545, 1097, 1028, 736; **HRMS** (ES^+, *m/z*): Calculated 435.2506 ($C_{26}H_{36}NaO_4$); Found 435.2490.

Protodesilylated **22**; **^{1}H NMR** (400 MHz, CD_3Cl) δ_H: 7.37-7.23 (10H, m), 4.75 (1H, d, *J* = 11.6), 4.62-4.56 (3H, m), 4.17-4.10 (1H, m), 4.05-3.98 (1H, m), 3.51 (2H, qd, *J* = 9.8, 5.2), 3.39-3.33 (1H, m), 1.96-1.82 (2H, m), 1.76-1.62 (2H, m), 1.51-1.15 (8H, m), 0.87 (3H, t, *J* = 7.0); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 139.3, 138.5, 128.3, 128.2, 128.0, 127.6, 127.5, 127.4, 82.4, 81.5, 78.4, 73.4, 73.0, 72.8, 32.0, 30.9, 28.2, 27.4, 25.4, 22.7, 14.1; **IR** (thin film)/cm^{-1}

3030, 2929, 1494, 1097, 734; **HRMS** (ES^+, *m/z*): Calculated 405.2400 ($C_{25}H_{34}NaO_3$); Found 405.2399.

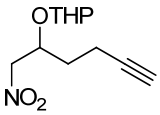


1-Nitrohex-5-yn-2-ol, S06



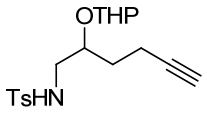
To a solution of 4-pentynal (2.0g, 24.4 mmol) in *tert*-butanol (24 mL) and tetrahydrofuran (24 mL) at 0 °C was added nitromethane (3.96 mL, 73.0 mmol) and potassium *tert*-butoxide (0.54 g, 4.8 mmol). The resulting solution was warmed to room temperature for 1.5 h before H_2O (20 mL) was added. The resultant mixture was extracted with EtOAc (3 × 40 mL), and the combined organics washed with brine (60 mL), dried over Na_2SO_4, filtered, and the solvent removed *in vacuo*. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 9:1 then 8:2], gave alkyne **S06** as an oil (3.2 g, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 4.56-4.40 (3H, m), 3.05 (1H, d, J = 5.2), 2.44-2.38 (2H, m), 2.05 (1H, t, J = 2.6), 1.76-1.69 (2H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 82.9, 80.4, 69.9, 67.4, 32.0, 14.5; **IR** (thin film)/cm^{-1} 3531 br., 3418 br., 3293, 2928, 1555, 1385, 1100, 894; **HRMS** (ES^+, *m/z*): Calculated 144.0655 ($C_6H_{10}NO_3$); Found 144.0670.

2-(1-Nitrohex-5-yn-2-yloxy)tetrahydro-2H-pyran, S07



To a solution of alkyne **S06** (1.8 g, 12.6 mmol) in CH_2Cl_2 (90 mL) under argon was added 2,3-dihydropyran (1.6 g, 18.9 mmol) and pyridinium para-toluene sulfonate (0.3 g, 1.3 mmol). The resulting mixture was stirred at room temperature for 16 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 9:1], gave alkyne **S07** as an oil and a (1:1) mixture of diastereoisomers (2.4 g, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: (diastereomeric 1:1) 4.73-4.65 (1.5H, m), 4.57-4.43 (2.5H, m), 3.92-3.78 (1H, m), 3.55-3.45 (1H, m), 2.44-2.30 (2H, m), 2.03-1.45 (9H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: (diastereomeric 1:1) 99.8, 99.6, 83.2, 82.7, 79.4, 78.4, 73.6, 73.5, 69.7, 69.4, 63.3, 63.0, 32.0, 30.9, 30.8, 30.7, 25.2, 25.2, 19.8, 19.7, 14.5, 14.3; **IR** (thin film)/cm^{-1} 3295, 2945, 1557, 1384, 1130, 1076, 1034, 989; **HRMS** (ES^+, *m/z*): Calculated 250.1050 ($C_{11}H_{17}NNaO_4$); Found 250.1049.

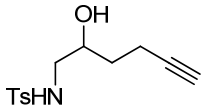
4-Methyl-*N*-(2-(tetrahydro-2H-pyran-2-yloxy)hex-5-ynyl)benzenesulfonamide, S08



A 3-neck flask fitted with a dropping funnel and reflux condenser containing a solution of alkyne **S07** (800 mg, 3.52 mmol) in Et_2O (10 mL) was heated at reflux. A solution of lithium aluminium hydride (8.80 mL, 8.80 mmol, 1.0 M solution in Et_2O), was added slowly over 1 h. The reaction was cooled to room temperature and stirred for 16 h before a saturated solution of Na_2SO_4 (3 mL) was added dropwise. The resulting mixture was filtered through a pad of Celite®, and washed with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The resultant oil was dissolved in CH_2Cl_2 (35 mL) before dimethylaminopyridine (860 mg, 7.04 mmol) and p-toluenesulfonyl chloride (738 mg, 3.87 mmol) were added. The resultant mixture was stirred at room temperature for 16 h before H_2O (20 mL) was added. The reaction mixture was extracted with Et_2O (4 × 50 mL) and the combined organics washed with brine (50 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 9:1 then 7:3], gave amine **S08** as an oil and a 1:1 mixture of diastereomers

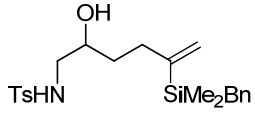
(500 mg, 40% over 2 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: (diastereomeric 1:1) 7.76-7.71 (2H, m), 7.33-7.27 (2H, m), 7.26 (1H, s), 6.15 (0.5H, dd, *J* = 8.0, 2.2), 4.72 (0.5H, t, *J* = 6.0), 4.51-4.48 (0.5H, m), 4.38 (0.5H, dd, *J* = 7.6, 2.4), 4.00-3.94 (0.5H, m), 3.89-3.81 (1H, m), 3.74-3.67 (0.5H, m), 3.52-3.42 (1H, m), 3.18-3.08 (1H, m), 2.96-2.89 (0.5H, m), 2.84-2.77 (0.5H, m), 2.43 (1.5H, s), 2.42 (1.5H, s), 2.28-2.18 (2H, m), 1.93-1.90 (1H, m), 1.87-1.72 (2H, m), 1.71-1.37 (6H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: (diastereomeric 1:1) 143.5, 143.1, 137.2, 136.8, 129.8, 129.6, 127.2, 127.1, 102.0, 97.8, 83.6, 83.1, 77.9, 73.6, 69.2, 68.8, 65.3, 63.4, 47.6, 45.2, 31.9, 31.6, 31.3, 30.9, 25.2, 25.0, 21.5, 21.4, 14.7, 14.5; **IR** (thin film)/cm^{-1} 3284 br., 2942, 1441, 1329, 1160, 1025; **HRMS** (ES^+, *m/z*): Calculated 374.1397 ($C_{18}H_{25}NNaO_4S$); Found 374.1395.

_N_-(2-Hydroxyhex-5-ynyl)-4-methylbenzenesulfonamide, S09



To a solution of amine **S08** (500 mg, 1.42 mmol) in ethanol (9 mL) at 55 °C was added pyridinium para-toluene sulfonate (36 mg, 0.14 mmol). The resulting mixture was stirred for 7 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 7:3], gave hydroxy-amine **S09** as an oil (351 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.68 (2H, d, *J* = 8.2), 7.24 (2H, d, *J* = 8.2), 5.27 (1H, br. s), 3.84-3.77 (1H, m), 3.04-2.96 (1H, m), 2.83-2.73 (1H, m), 2.61 (1H. br. s), 2.36 (3H, s), 2.22 (2H, td, *J* = 7.0, 2.8), 1.89 (1H, t, *J* = 2.8), 1.55 (2H, q, *J* = 7.0); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 143.6, 136.6, 129.8, 127.1, 83.5, 69.3, 69.3, 48.6, 32.8, 21.5, 14.7; **IR** (thin film)/cm^{-1} 3501 br., 3289 br., 2925, 1598, 1433, 1323, 1158, 1090; **HRMS** (ES^+, *m/z*): Calculated 290.0821 ($C_{13}H_{17}NNaO_3S$); Found 290.0821.

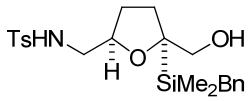
N-(5-(benzyldimethylsilyl)-2-hydroxyhex-5-enyl)-4-methylbenzenesulfonamide, 16



Hydroxy-amine **S09** (305 mg, 1.14 mmol) was subjected to General Procedure 4. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 1:9], gave vinyl silane **16** as an oil (341 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.71 (2H, d, *J* = 8.0), 7.26 (2H, d, *J* = 8.0),

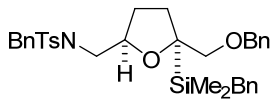
7.16-7.11 (2H, m), 7.04-6.97 (1H, m), 6.94-6.91 (2H, m), 5.54-5.51 (1H, m), 5.29-5.26 (1H, m), 5.05-4.99 (1H, br. m), 3.64-3.52 (1H, m), 2.99 (1H, ddd, *J* = 13.2, 7.2, 3.2), 2.72 (1H, ddd, *J* = 12.8, 8.0, 4.8), 2.38 (3H, s), 2.16-1.94 (5H, m), 1.45-1.37 (2H, m), 0.00 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 149.6, 143.6, 139.9, 136.7, 129.8, 128.3, 128.2, 125.6, 124.1, 70.2, 70.2, 48.7, 33.6, 31.5, 25.6, 21.6, −3.5; **IR** (thin film)/cm^{-1} 3491 br., 3284 br., 2954, 1599, 1493, 1353, 1159, 831; **HRMS** (ES^+, *m/z*): Calculated 440.1686 ($C_{22}H_{31}NNaO_3SSi$); Found 440.1684.

(±)-*N*-(((2*R*,5*R*)-5-(Benzyldimethylsilyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide, 17



Vinyl silane **16** (165 mg, 0.40 mmol) was subject to General Procedure 1 with potassium osmate dihydrate (2.5 mol%) at 60 °C for 24 h. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 1:4], gave THF **17** as an oil (152 mg, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.78 (2H, d, *J* = 8.0), 7.33 (2H, d, *J* = 8.0), 7.27-7.20 (2H, m), 7.14-7.07 (1H, m), 7.03-6.98 (2H, m), 3.97-3.90 (1H, m), 3.69 (1H, d, *J* = 11.2), 3.40 (1H, d, *J* = 11.4), 3.25 (1H, dd, *J* = 12.8, 3.6), 3.00 (1H, dd, *J* = 12.8, 5.6), 2.44 (3H, s), 2.15 (2H, d, *J* = 2.8), 1.95-1.76 (4H, m), 0.02-−0.03 (6H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 143.3, 139.4, 137.1, 129.7, 128.3, 128.3, 127.1, 124.3, 80.8, 78.7, 67.7, 47.1, 30.1, 29.5, 23.2, 21.5, −5.4; **IR** (thin film)/cm^{-1} 3484 br., 3286 br., 2956, 1599, 1451, 1324, 1159, 1058, 815; **HRMS** (ES^+, *m/z*): Calculated 456.1635 ($C_{22}H_{31}NNaO_4SSi$); Found 456.1632.

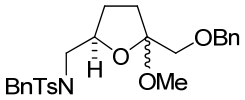
(±)-*N*-Benzyl-*N*-(((2*R*,5*R*)-5-(benzyldimethylsilyl)-5-(benzyloxymethyl)tetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide, 24



THF **17** (120 mg, 0.28 mmol) was subjected to General Procedure 5. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 9:1], gave benzylated THF **24** as an oil (130 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.85 (2H, d, *J* = 8.2), 7.47-7.35 (12H, m), 7.33-7.27 (2H, m), 7.20-7.15 (1H, m), 7.07-7.02 (2H, m), 4.61 (2H, d, *J* = 4.4), 4.51 (2H, s), 3.93-3.84 (1H, m), 3.64 (1H, dd, *J* = 14.8, 4.0), 3.40 (2H, app. q, *J* = 9.2), 3.15 (1H, dd, *J* = 14.8,

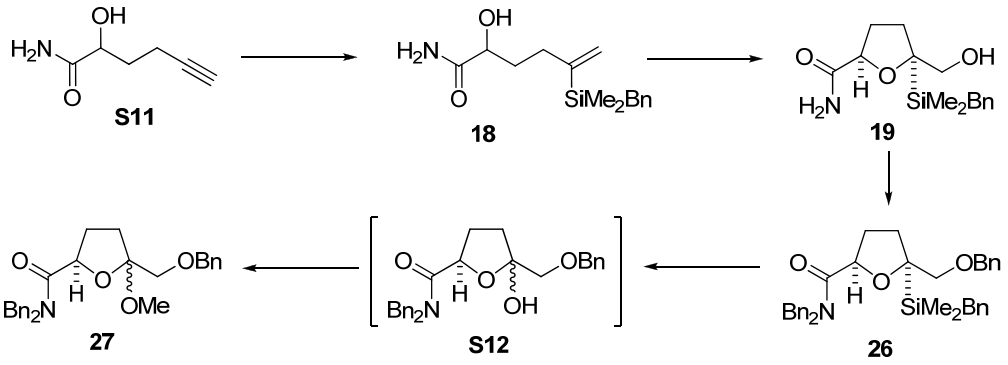
7.6), 2.50 (3H, s), 2.16 (2H, d, J = 4.4), 1.98-1.92 (1H, m), 1.89-1.75 (2H, m), 1.68-1.60 (1H, m), 0.00 (3H, s), −0.02 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 143.1, 139.9, 138.4, 137.9, 136.7, 129.6, 128.6, 128.4, 128.3, 128.3, 128.1, 127.6, 127.5, 127.5, 127.2, 124.0, 79.4, 79.3, 76.0, 73.5, 52.1, 51.9, 30.5, 30.4, 23.2, 21.5, −5.6, −5.6; **IR** (thin film)/cm^{-1} 2957, 2869, 1599, 1453, 1342, 1158, 1023, 937; **HRMS** (ES^+, *m/z*): Calculated 636.2574 ($C_{36}H_{43}NNaO_4SSi$); Found 636.2572.

(±)-(*R*)-*N*-Benzyl-*N*-((5-(benzyloxymethyl)-5-methoxytetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide, 25

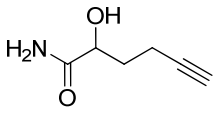


Benzylated-THF **24** (47 mg, 77 μmol) was subjected to General Procedure 6. The resulting crude product was purified by flash column chromatography, [SiO_2, petrol/EtOAc, 4:1], to afford lactol **S10** as an oil (28 mg, 76%), as a complex mixture of isomers.

Lactol **S10** (18 mg, 37 μmol) was dissolved in MeOH (1 mL) and CH_2Cl_2 (1 mL) under argon before pyridinium para-toluene sulfonate (2 mg, 8 μmol) was added. The resultant mixture was stirred at room temperature for 2 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 17:3], furnished lactol methyl ether **25** as an oil, and a (60:40) mixture of diastereomers (16 mg, 86%). **^{1}H NMR** (500 MHz, DMSO-d_6) δ_H: (diastereomeric 60:40) 7.75 (0.8H, d, J = 8.5), 7.72 (1.2H, d, J = 10.5), 7.43-7.37 (2H, m), 7.36-7.21 (10H, m), 4.47 (1.2H, d, J = 4.0), 4.44 (0.8H, d, J = 4.0), 4.38-4.35 (2H, m), 3.96-3.88 (1H, m), 3.49-3.43 (1H, m), 3.28-3.19 (2H, m), 3.11 (0.4H, dd, J = 14.5, 7.0), 3.03-2.96 (1.8H, m), 2.90 (1.8H, s), 2.41-2.37 (3H, m), 1.90-1.82 (1H, m), 1.82-1.65 (2H, m), 1.56-1.39 (1H, m); **^{13}C NMR** (125 MHz, DMSO-d_6) δ_C: (diastereomeric 60:40) 138.3, 138.3, 137.0, 137.0, 136.6, 136.4, 129.8, 129.8, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 127.4, 127.4, 127.0, 127.0, 108.2, 108.2, 78.3, 77.0, 72.4, 72.4, 70.4, 70.1, 52.8, 52.0, 52.0, 51.7, 48.3, 48.2, 33.1, 32.5, 28.3, 27.6, 21.0; **IR** (thin film)/cm^{-1} 3385 br., 2924, 1599, 1454, 1339, 1159, 1090; **HRMS** (ES^+, *m/z*): Calculated 518.1972 ($C_{28}H_{33}NNaO_5S$); Found 518.1973.

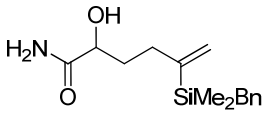


2-Hydroxyhex-5-ynamide, S11



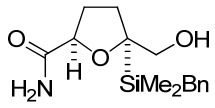
To a solution of 4-pentynal (1.0g, 12.2 mmol) in CH_2Cl_2 (60 mL) was added triethylamine (2.04 mL, 14.6 mmol). The resulting solution was cooled to 0 °C before trimethylsilyl cyanide (1.52 mL, 12.18 mmol) was added dropwise over a period of 5 min. The resulting mixture was warmed to room temperature and stirred for 4 h before H_2O (30 mL) was added. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organics were carefully washed with 2 M HCl (50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was dissolved in DMSO (1.5 mL) and cooled to 0 °C before potassium carbonate (0.33g, 2.38 mmol) and hydrogen peroxide (1.62 g, 16.7 mmol, 33% in H_2O) were added. The resulting mixture was warmed to room temperature (where a large exotherm ensued) and stirred for 30 min. The resulting suspension was diluted with H_2O (3 mL) and filtered. The solid was washed with EtOAc, before the aqueous layer was extracted with EtOAc (5 × 30 mL), and the combined organics washed with a saturated sodium thiosulfate solution (30 mL), brine (30 mL), dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The resulting crude solid was washed with Et_2O (2 mL) to remove less polar impurities and dried *in vacuo* to afford hydroxy amide **S11** as prisms (850 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.05 (1H, br. s), 6.55 (1H, br. s), 4.76 (1H, br. s), 4.09 (1H, dd, J = 8.4, 3.2), 2.36-2.30 (2H, m), 2.07-1.96 (2H, m), 1.79-1.70 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 176.3, 83.9, 70.4, 69.6, 34.3, 14.5; **IR** (KBr disc)/cm^{-1} 3284, 2544, 2379, 1671, 1608, 1400, 1290, 1095, 1062, 934, 762; **HRMS** (ES^+, *m/z*): Calculated 150.0525 ($C_6H_9NNaO_2$); Found 150.0523; **M.P.** 103 °C.

5-(Benzyldimethylsilyl)-2-hydroxyhex-5-enamide, 18



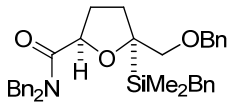
Hydroxy-amide **S11** (650 mg, 5.1 mmol) was subject to General Procedure 4. Purification by flash column chromatography, [SiO_2, petrol/acetone, 7:3], gave vinyl silane **18** as an oil (756 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.21 (2H, t, *J* = 7.4), 7.11-7.05 (1H, m), 7.00 (2H, d, *J* = 7.4), 6.43 (1H, br. s), 5.87 (1H, br. s), 5.67-5.65 (1H, m), 5.40-5.37 (1H, m), 4.14-4.08 (1H, m), 2.95 (1H, d, *J* = 5.2), 2.27-2.21 (2H, m), 2.18 (2H, s), 2.00-1.90 (1H, m), 1.79-1.67 (1H, m), 0.08 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 176.7, 149.6, 139.9, 128.3, 128.1, 125.8, 124.1, 71.7, 33.8, 31.0, 25.5, −3.4, −3.5; **IR** (thin film)/cm^{-1} 3027, 2934, 1687, 1335, 1295, 1145, 936, 837; **HRMS** (ES$^+$, *m/z*): Calculated 300.1390 ($C_{15}H_{23}NNaO_2Si$); Found 300.1390.

(±)-(2*R*,5*R*)-5-(Benzyldimethylsilyl)-5-(hydroxymethyl)tetrahydrofuran-2-carboxamide, 19



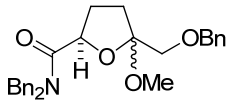
Vinyl silane **18** (120 mg, 0.43 mmol) was subjected to General Procedure 1 with potassium osmate dihydrate (5 mol%) at 60 °C for 32 h. Purification by flash column chromatography, [SiO_2, petrol/acetone, 1:1], gave THF **19** as an oil (103 mg, 81%). **^{1}H NMR** (400 MHz, MeOH-d_4) δ_H: 7.19-7.13 (2H, m), 7.05-6.97 (3H, m), 4.23-4.17 (1H, m), 3.67 (1H, d, *J* = 11.8), 3.52 (1H, d, *J* = 11.8), 2.29-2.15 (1H, m), 2.20 (2H, d, *J* = 4.4), 2.04-1.90 (3H, m), 0.00 (6H, d, *J* = 4.4); **^{13}C NMR** (100 MHz, DMSO-d_6) δ_C: 175.7, 139.6, 128.1, 128.1, 123.9, 82.1, 79.4, 65.7, 31.1, 29.2, 22.7, −5.3, −5.4; **IR** (KBr disc)/cm^{-1} 3267, 2501, 2358, 1648, 1450, 1246, 1203, 1155, 1067, 808; **HRMS** (ES$^+$, *m/z*): Calculated 316.1339 ($C_{15}H_{23}NNaO_3Si$); Found 316.1339; **M.P.** 134 °C.

(±)-(2*R*,5*R*)-*N*,*N*-Dibenzyl-5-(benzyldimethylsilyl)-5-(benzyloxymethyl)tetrahydrofuran-2-carboxamide, 26



THF **19** (45 mg, 0.15 mmol) was subject to General Procedure 5. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 17:3], gave benzylated-THF **26** as an oil (57 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.46-7.27 (15H, m), 7.24-7.18 (2H, m), 7.12-7.06 (1H, m), 7.00-6.96 (2H, m), 4.78-4.53 (7H, m), 3.62 (1H, d, *J* = 9.2), 3.57 (1H, d, *J* = 9.2), 2.71-2.60 (1H, m), 2.21 (2H, s), 2.19-2.14 (1H, m), 2.13-2.04 (1H, m), 1.96 (1H, ddd, *J* = 12.0, 10.0, 7.8), 0.01 (3H, s), 0.00 (3H, s); **^{13}C NMR** (100 MHz, acetone-d_6) δ_C: 171.6, 140.0, 138.5, 137.2, 137.0, 128.7, 128.6, 128.3, 128.3, 128.3, 128.1, 127.8, 127.5, 127.5, 127.3, 127.2, 123.9, 80.4, 77.9, 75.7, 73.6, 49.7, 47.9, 31.2, 28.5, 23.4, −5.3, −5.3; **IR** (thin film)/cm^{-1} 2956, 1651, 1451, 1245, 1096, 820; **HRMS** (ES$^+$, *m/z*): Calculated 586.2748 ($C_{36}H_{41}NNaO_3Si$); Found 586.2747.

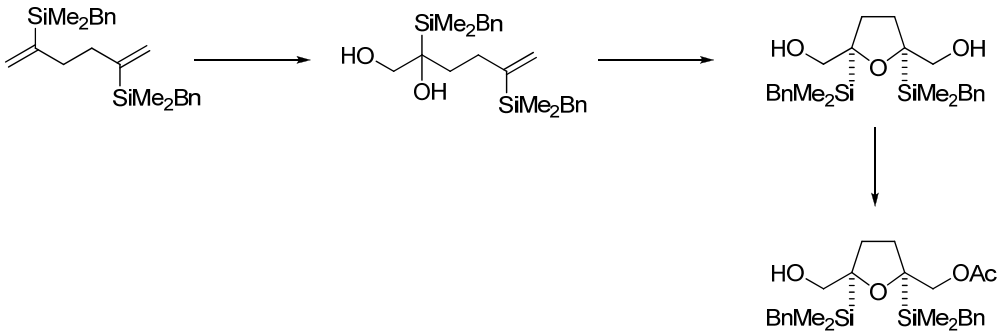
(±)-(*R*)-*N*,*N*-dibenzyl-5-(benzyloxymethyl)-5-methoxytetrahydrofuran-2-carboxamide, 27



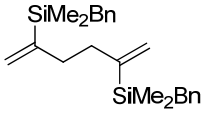
Benzylated-THF **26** (50 mg, 89 μmol) was subjected to General Procedure 6. The resulting crude product was purified by flash column chromatography, [SiO_2, petrol/EtOAc, 4:1], to afford lactol **S12** as an oil (27 mg, 71%), as a complex mixture of isomers.

Lactol **S12** (15 mg, 35 μmol) was dissolved in MeOH (1 mL) and CH_2Cl_2 (1 mL) under argon before pyridinium para-toluene sulfonate (2 mg, 8 μmol) was added. The resultant mixture was stirred at room temperature for 2 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, petrol/EtOAc, 17:3], furnished lactol methyl ether **27** as an oil, and a (60:40) mixture of diastereomers (13 mg, 84%). **^{1}H NMR** (500 MHz, DMSO-d_6) δ_H: (diastereomeric 1:1) 7.39-7.14 (15H, m), 4.91-4.87 (0.6H, m), 4.80-4.71 (0.8H, m), 4.65-4.37 (5.2H, m), 4.31-4.26 (0.4H, m), 3.64 (0.6H, d, *J* = 10.5), 3.56 (0.4H, d, *J* = 10.5), 3.44 (0.6H, d, *J* = 10.5), 3.40 (0.4H, d, *J* = 10.5), 3.17 (1.2H, s), 3.08 (1.8H, s), 2.36-2.28 (0.4H, m), 2.20-1.96 (3H, m), 1.93-1.86 (0.6H, m); **^{13}C NMR** (125 MHz, DMSO-d_6) δ_C: (diastereomeric 1:1) 170.2, 170.2, 138.3, 138.2, 137.3, 137.2, 137.1, 137.0,

128.7, 128.6, 128.4, 128.2, 128.2, 127.5, 127.5, 127.4, 127.3, 127.3, 127.1, 126.9, 126.8, 109.1, 108.8, 76.7, 75.6, 72.5, 72.4, 70.7, 70.0, 49.5, 49.3, 48.7, 48.7, 47.8, 47.8, 33.4, 33.0, 27.4, 27.3; **IR** (thin film)/cm^{-1} 2922, 1656, 1452, 1157, 1075; **HRMS** (ES^+, *m/z*): Calculated 468.2145 ($C_{28}H_{31}NNaO_4$); Found 468.2143.

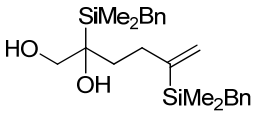


Hexa-1,5-diene-2,5-diylbis(benzyldimethylsilane), S13



1,5-Hexadiyne (200 mg, 2.56 mmol) was subjected to General Procedure 4. Purification by flash column chromatography, [SiO_2, petrol/Et_2O, 99:1], furnished vinyl silane **S13** as an oil (704 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.27-7.21 (4H, m), 7.14-7.07 (2H, m), 7.05-7.01 (4H, m), 5.67-5.65 (2H, m), 5.39-5.36 (2H, m), 2.25-2.15 (8H, m), 0.10 (12H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.3, 139.9, 128.3, 128.2, 125.1, 124.1, 35.4, 25.6, -3.5; **IR** (thin film)/cm^{-1} 3024, 2956, 1600, 1493, 1249, 1206, 1154, 1056, 832; **HRMS** (ES^+, *m/z*): Calculated 401.2091 ($C_{24}H_{34}NaSi_2$); Found 401.2090.

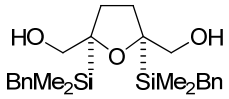
2,5-Bis(benzyldimethylsilyl)hex-5-ene-1,2-diol, 28



Vinyl silane **S13** (250 mg, 0.66 mmol) was subjected to General Procedure 2. Purification by flash column chromatography, [SiO_2, petrol/Et_2O, 3:2], furnished diol **28** as an oil (101 mg, 37%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.27-7.18 (4H, m), 7.14-7.00 (6H, m), 5.66-5.63 (1H, m), 5.39-5.35 (1H, m), 3.72 (1H, d, *J* = 11.0), 3.60 (1H, d, *J* = 11.0), 2.24 (2H, s), 2.18 (2H, s), 2.15-2.07 (2H, m), 1.74-1.59 (4H, m), 0.10 (6H, s), 0.05 (3H, s), 0.04 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 150.4, 139.9, 139.6, 128.4, 128.3, 128.3, 128.3, 125.4, 124.3, 124.1,

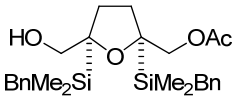
70.0, 67.6, 35.4, 29.9, 25.8, 23.5, −3.4, −4.8, −4.9; **IR** (thin film)/cm^{-1} 3418 br., 2956, 1600, 1493, 1249, 1057, 833; **HRMS** (ES^+, *m/z*): Calculated 435.2146 ($C_{24}H_{36}NaO_2Si_2$); Found 435.2146.

(±)-((2*R*,5*S*)-2,5-bis(benzyldimethylsilyl)tetrahydrofuran-2,5-diyl)dimethanol, 29



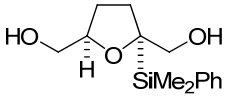
Vinyl silane **28** (72 mg, 0.17 mmol) was subject to General Procedure 1 with potassium osmate dihydrate (7.5 mol%) at 60 °C for 24 h. Purification by flash column chromatography, [SiO_2, hexanes/EtOAc, 1:4], gave THF **29** as an oil (38 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.26-7.20 (4H, m), 7.13-7.03 (6H, m), 3.73 (2H, d, *J* = 11.4), 3.59 (2H, d, *J* = 11.4), 2.94 (2H, br. s), 2.29 (4H, s), 1.89-1.80 (4H, m), 0.07 (6H, s), 0.04 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 139.7, 128.4, 128.2, 124.2, 81.1, 68.9, 31.3, 23.8, −4.6, −4.7; **IR** (thin film)/cm^{-1} 3375 br., 3023, 2956, 1600, 1493, 1247, 1044, 818; **HRMS** (ES^+, *m/z*): Calculated 451.2095 ($C_{24}H_{36}NaO_3Si_2$); Found 451.2096.

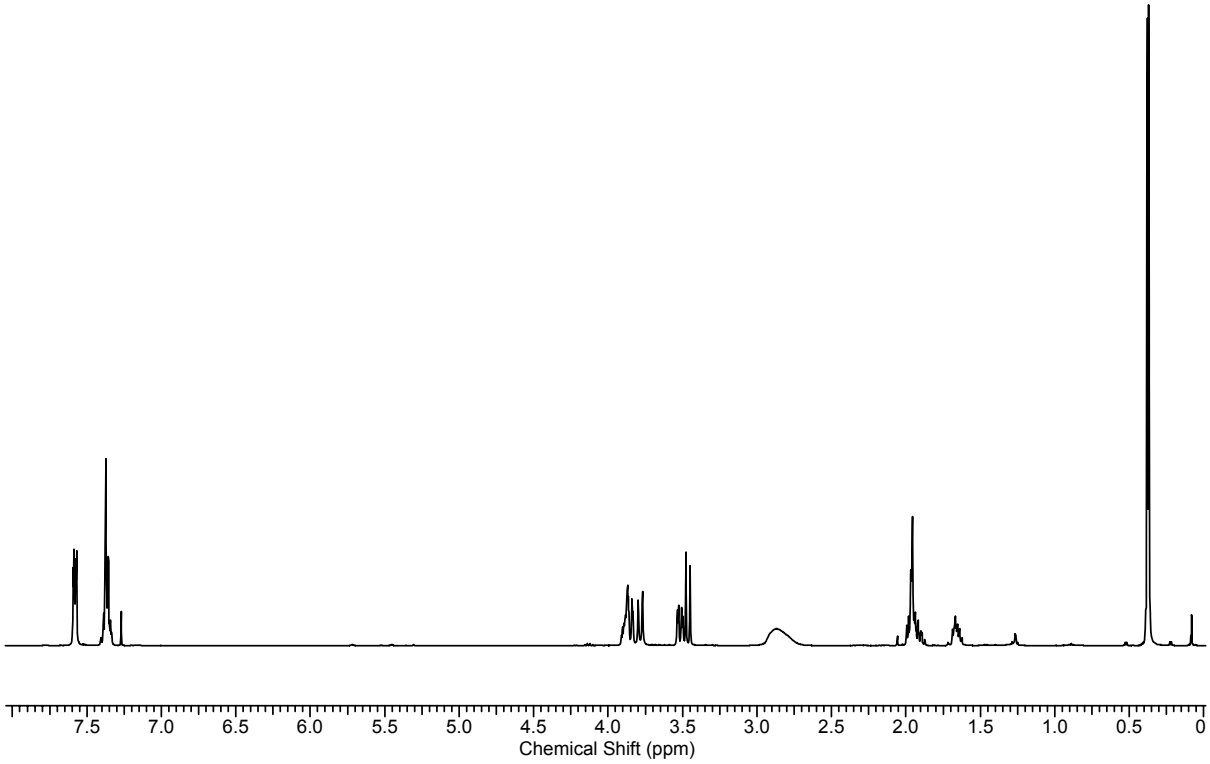
(±)-((2R,5S)-2,5-bis(benzyldimethylsilyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)methyl acetate, S14

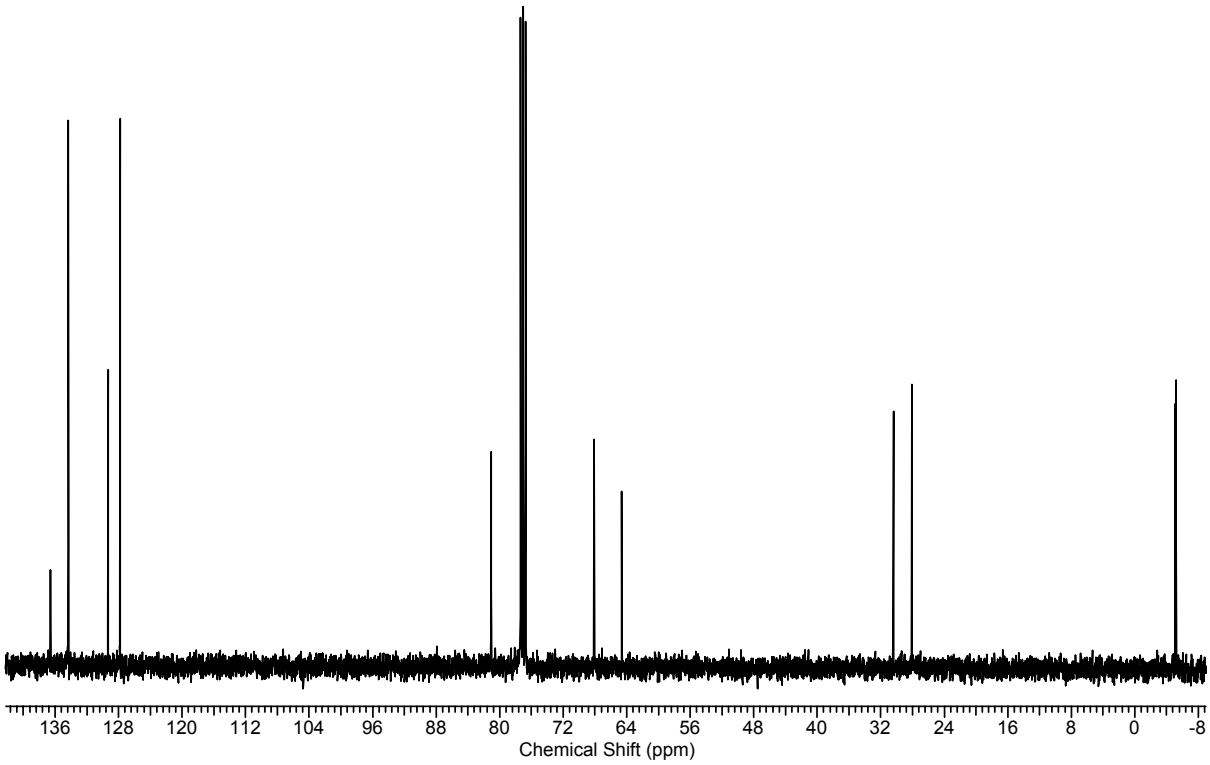


A solution of THF **29** (70 mg, 0.16 mmol) in pyridine (2 mL) and acetic anhydride (2 mL) and stirred at room temperature for 16 h before the solvent was removed *in vacuo*. Purification by flash column chromatography, [SiO_2, petrol/Et_2O, 4:1], gave mono-acetate **S14** as an oil (39 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H: 7.28-7.18 (4H, m), 7.14-7.01 (6H, m), 4.46 (1H, d, *J* = 12.0), 4.00 (1H, d, *J* = 12.0), 3.16 (2H, s), 2.30-2.22 (4H, m), 2.15 (3H, s), 1.94-1.67 (4H, m), 0.08-0.01 (12H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ_C: 171.3, 139.9, 139.4, 128.4, 128.3, 128.3, 128.2, 124.3, 124.1, 81.5, 79.0, 70.9, 68.4, 31.4, 31.7, 23.9, 23.6, 21.2, −4.6, −4.6, −4.7, −5.0; **IR** (thin film)/cm^{-1} 3502 br., 3024, 2956, 1740, 1600, 1493, 1246, 1053, 819; **HRMS** (ES^+, *m/z*): Calculated 493.2201 ($C_{26}H_{38}NaO_4Si_2$); Found 493.2205.

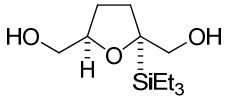
(±)-((2*R*,5*R*)-2-(Dimethyl(phenyl)silyl)tetrahydrofuran-2,5-diyl)dimethanol, 7

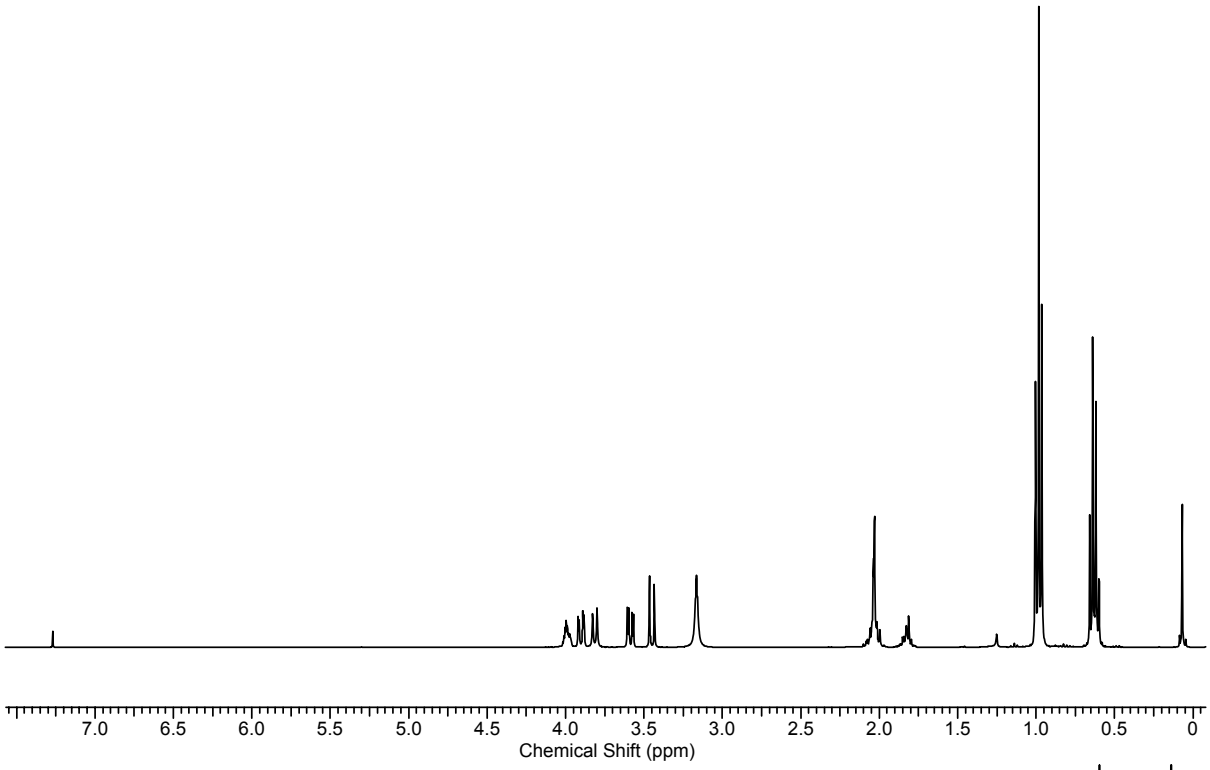


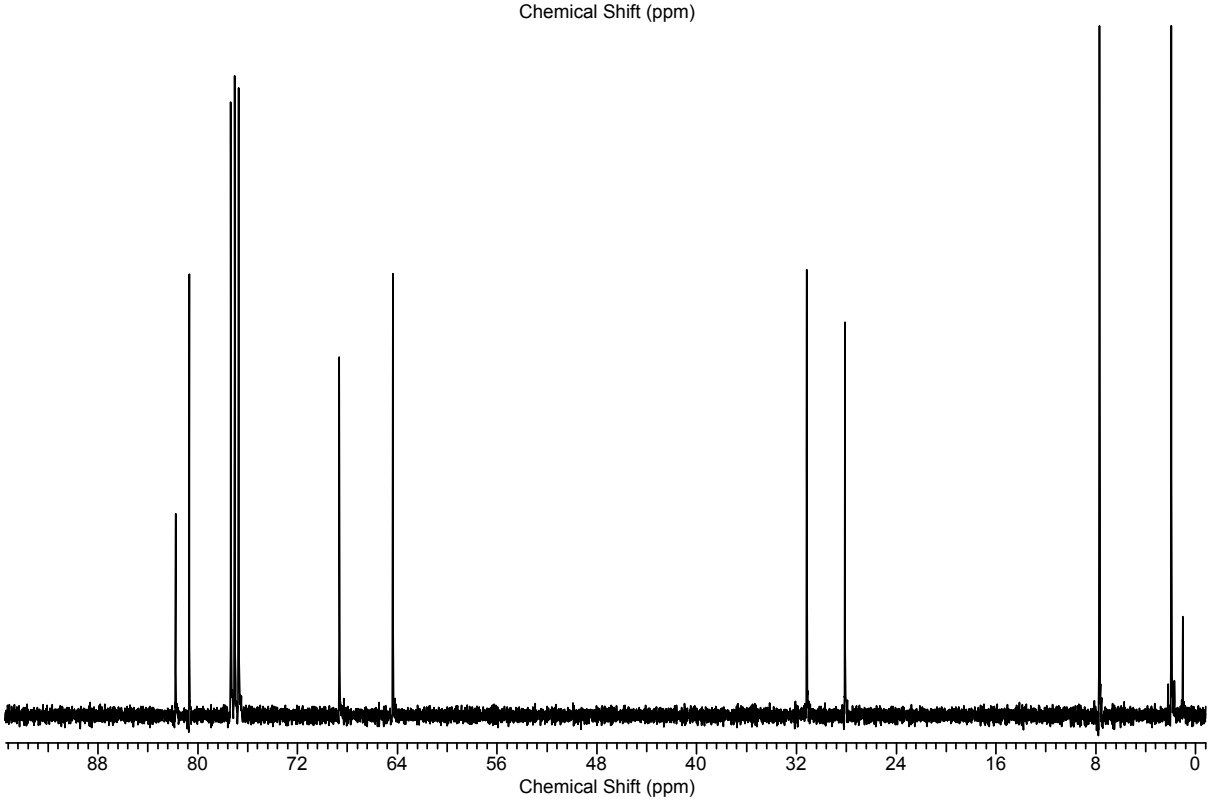




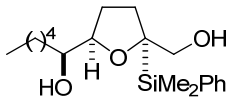
(±)-((2*R*,5*R*)-2-(Triethylsilyl)tetrahydrofuran-2,5-diyl)dimethanol, 9

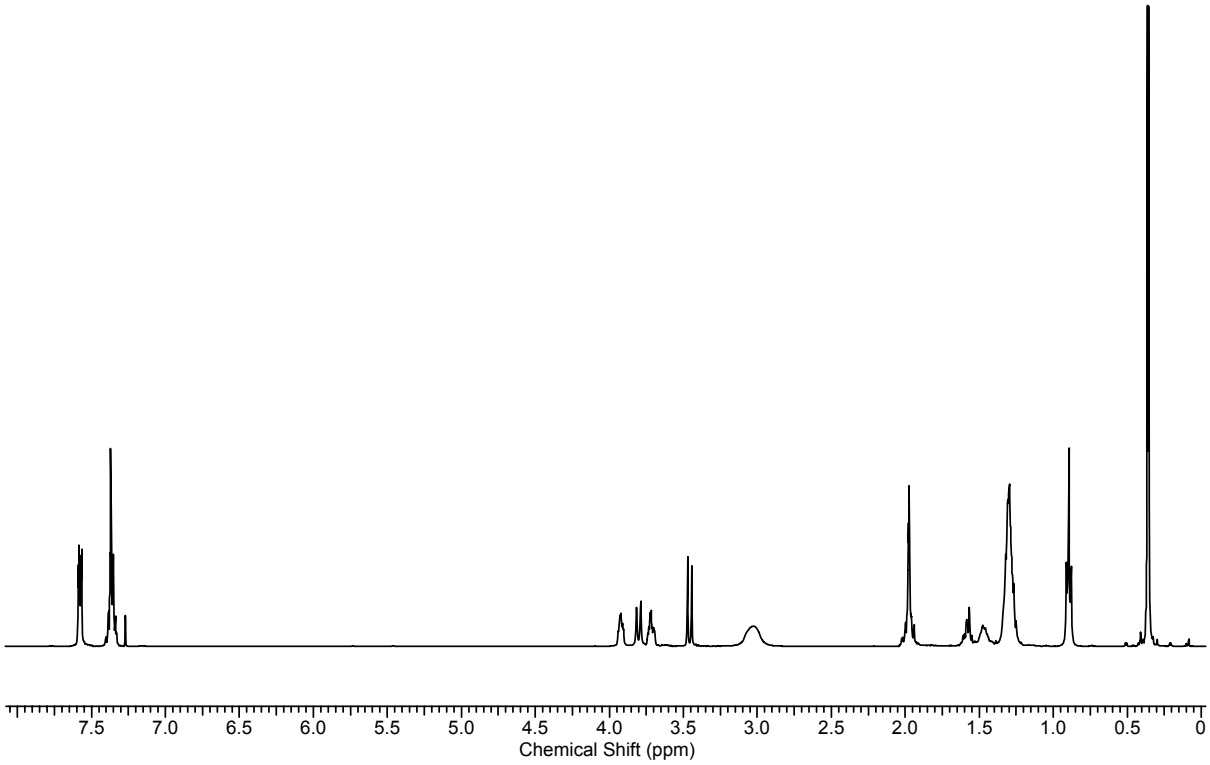


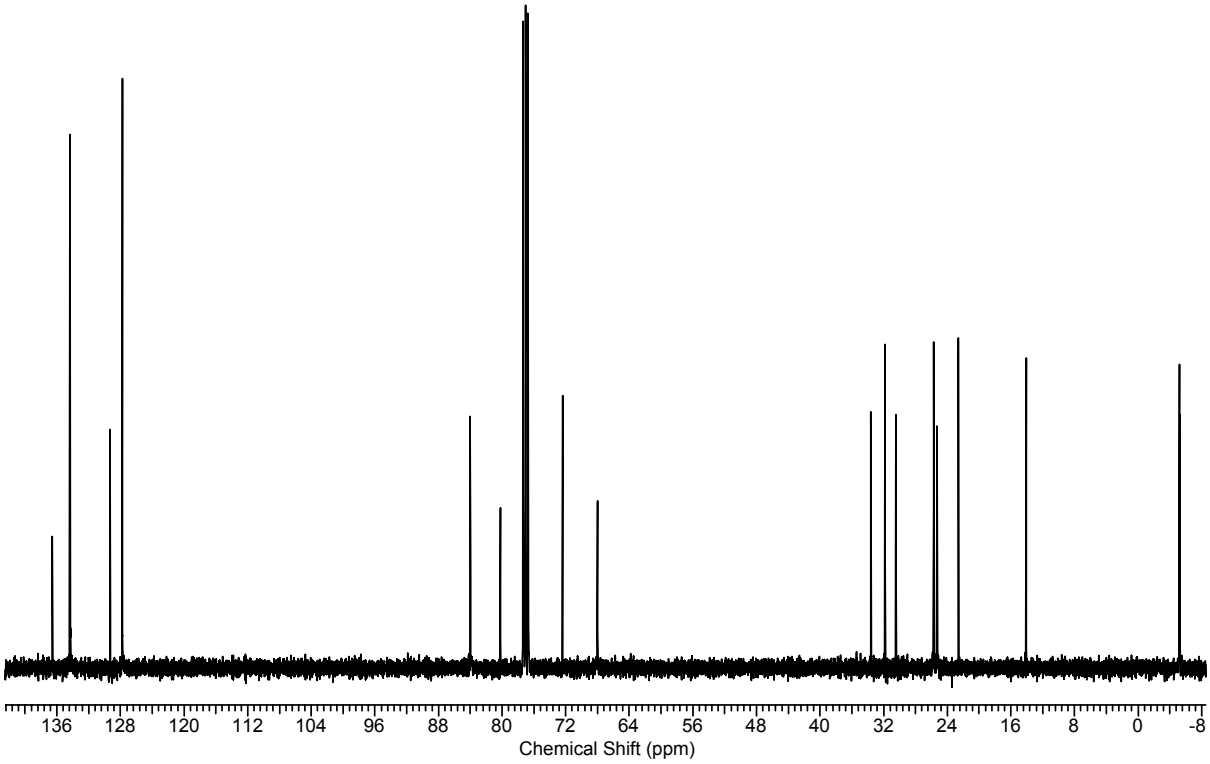




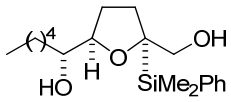
(±)-(*S*)-1-((2*R*,5*R*)-5-(Dimethyl(phenyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol, 11

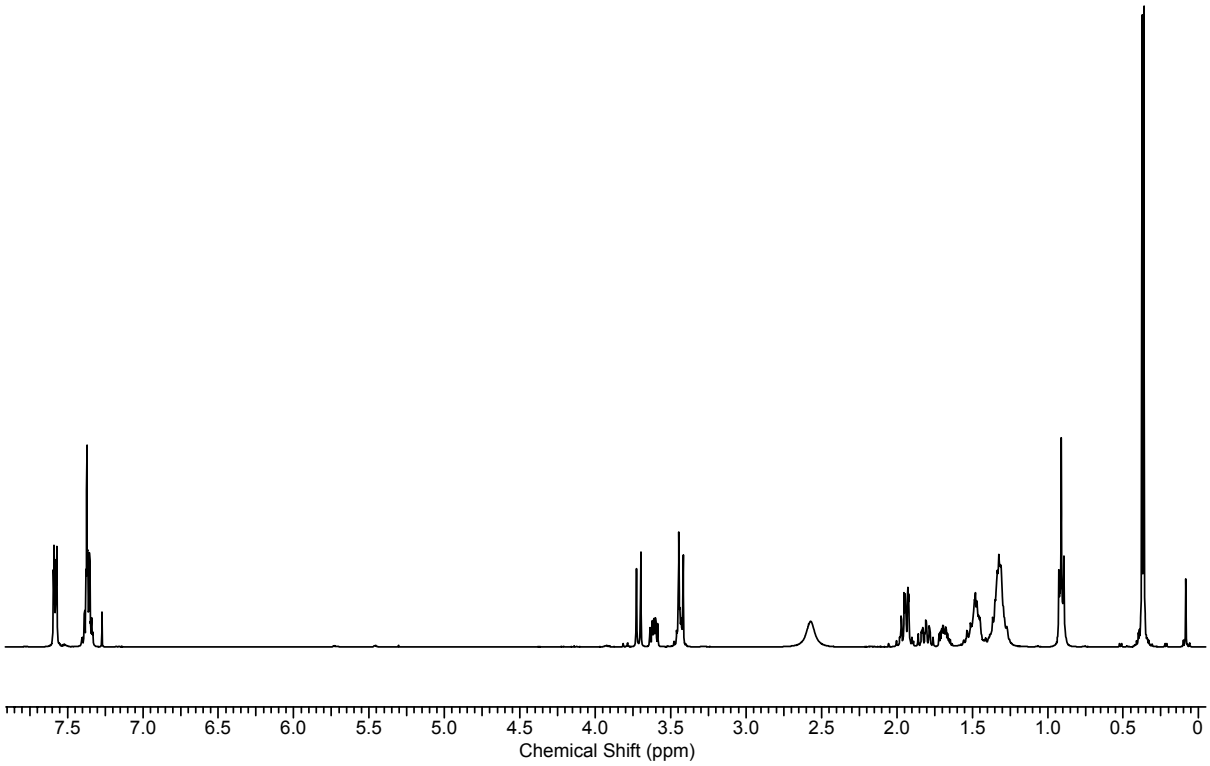


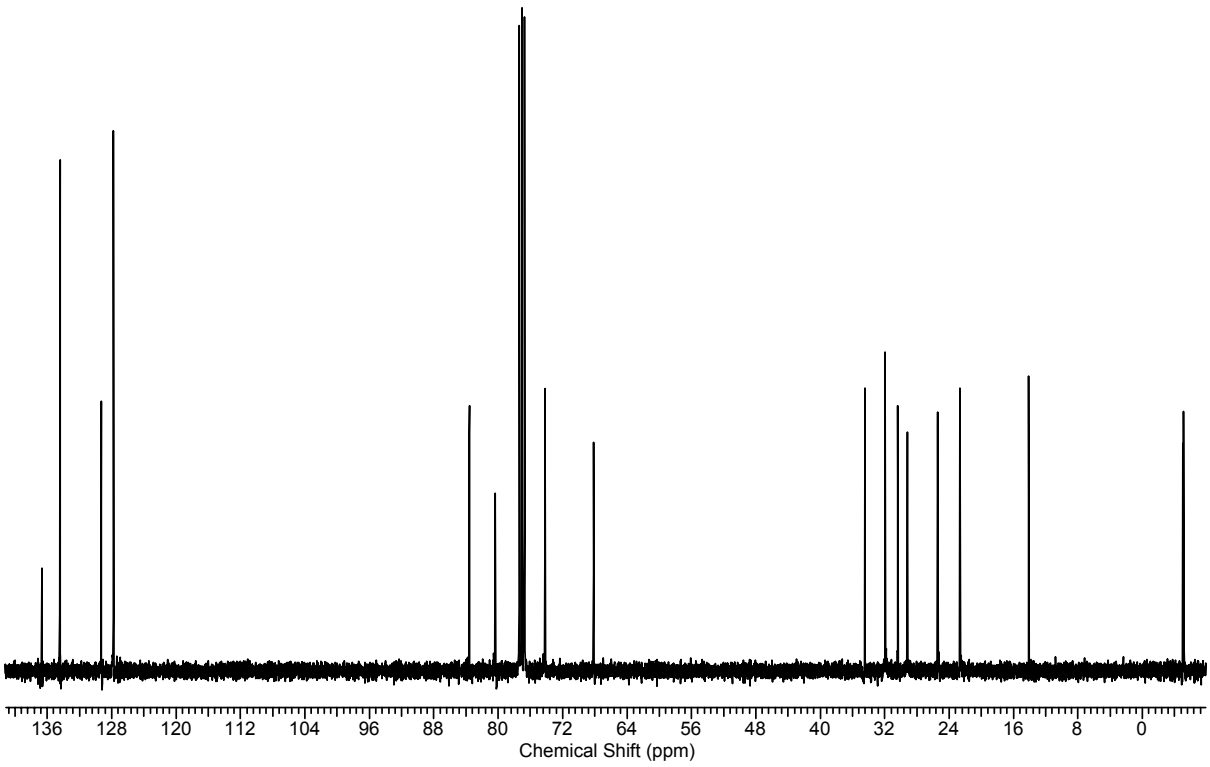




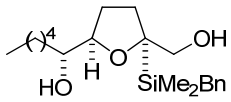
(±)-(*R*)-1-((2*R*,5*R*)-5-(dimethyl(phenyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol 13

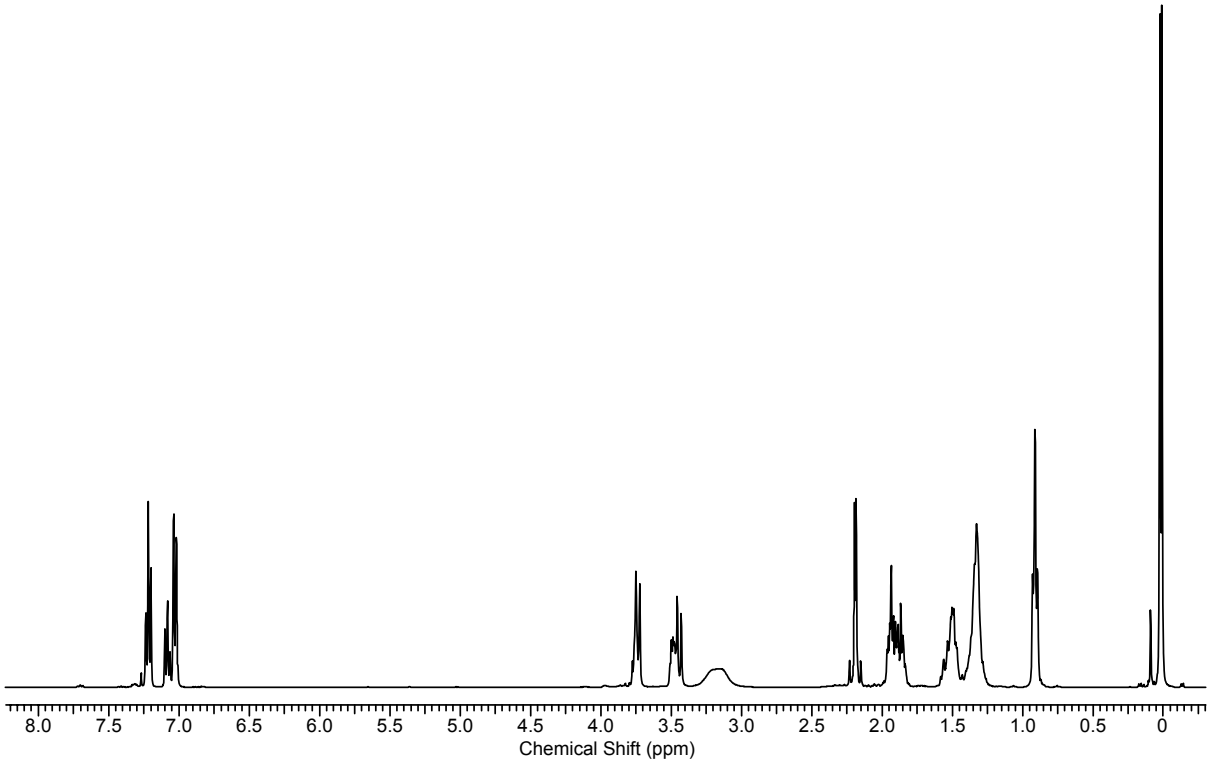


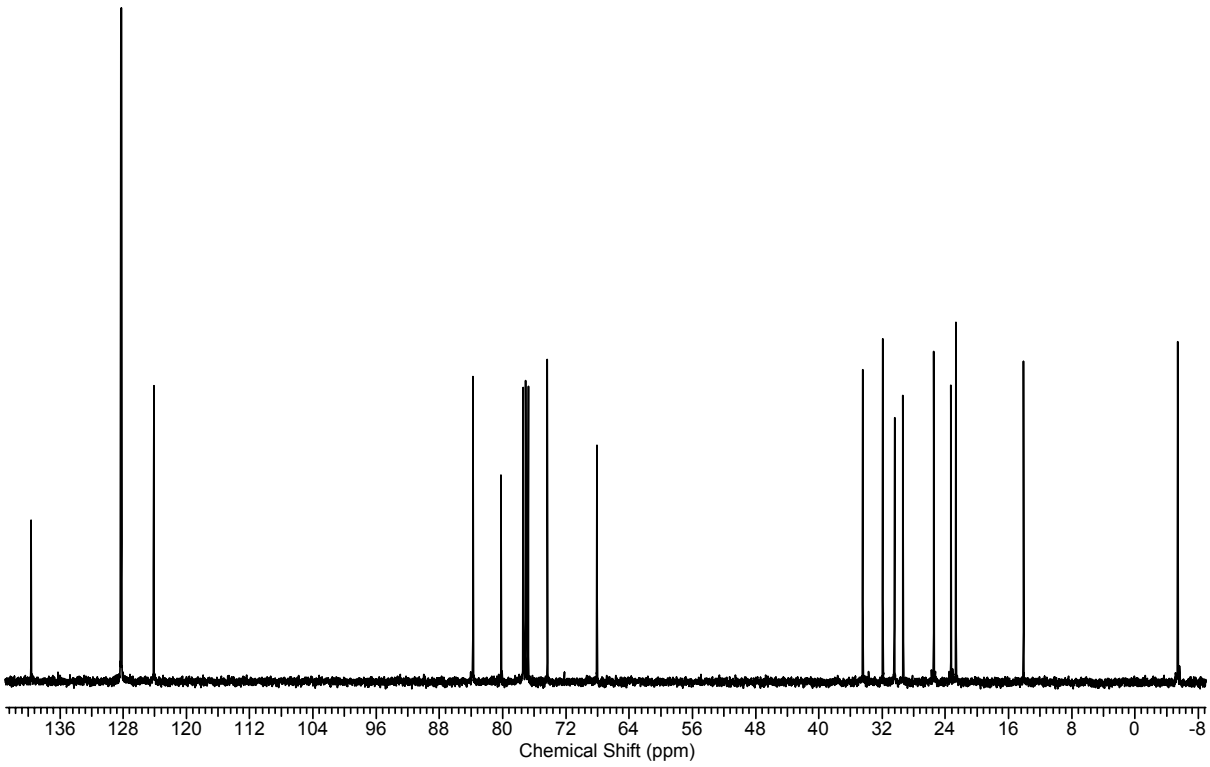




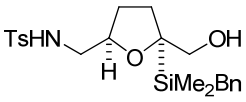
(±)-(*R*)-1-((2*R*,5*R*)-5-(dimethyl(benzyl)silyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)hexan-1-ol 15

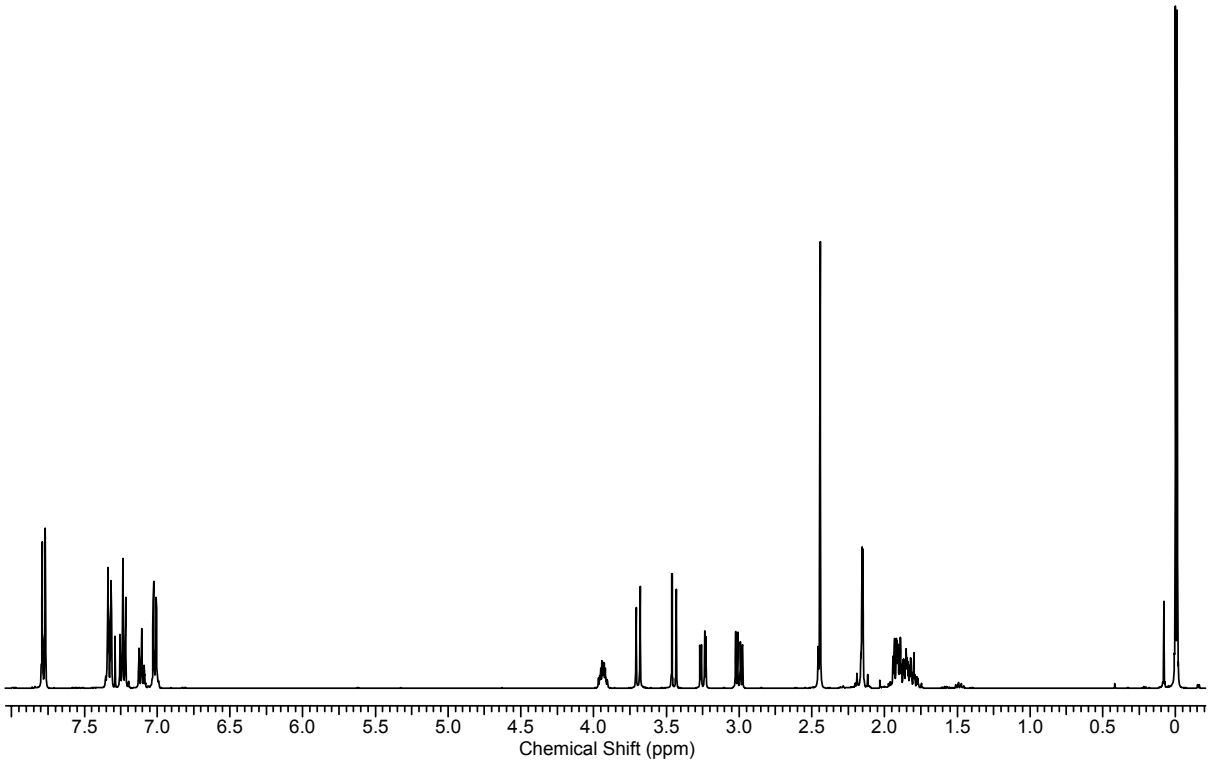


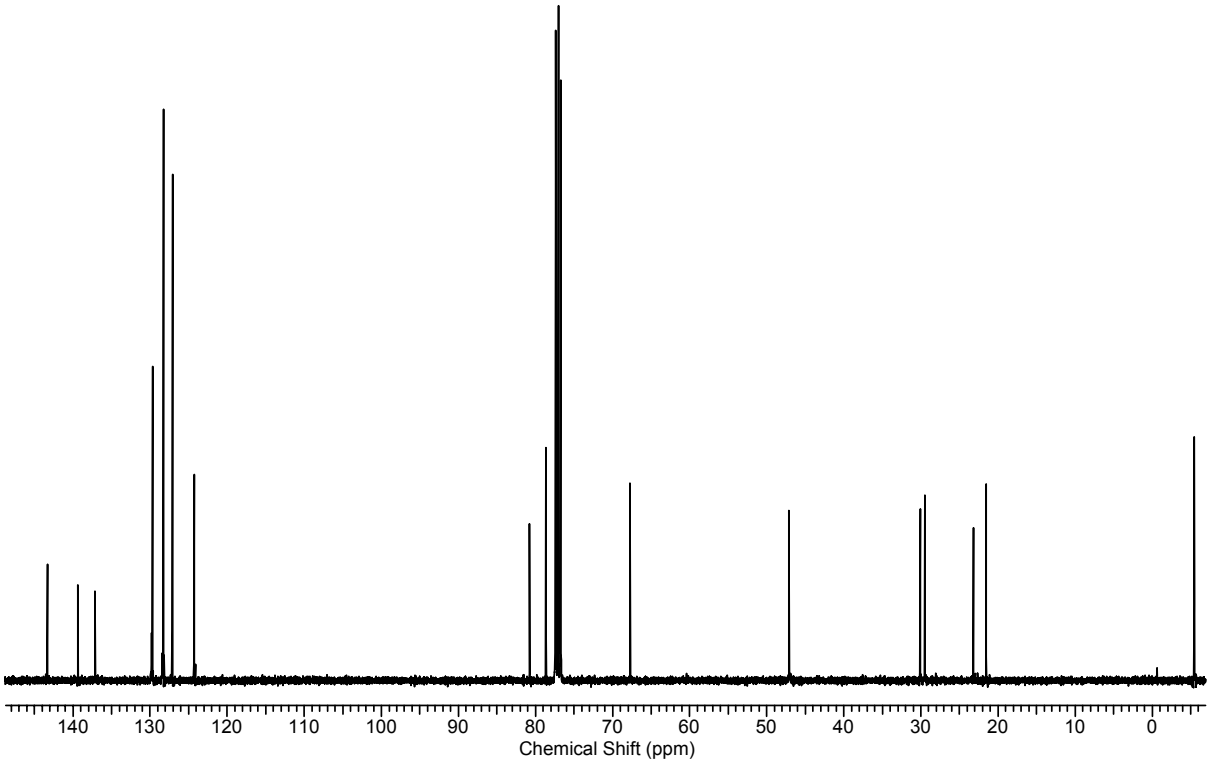




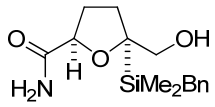
(±)-*N*-(((2*R*,5*R*)-5-(Benzyldimethylsilyl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide, 17

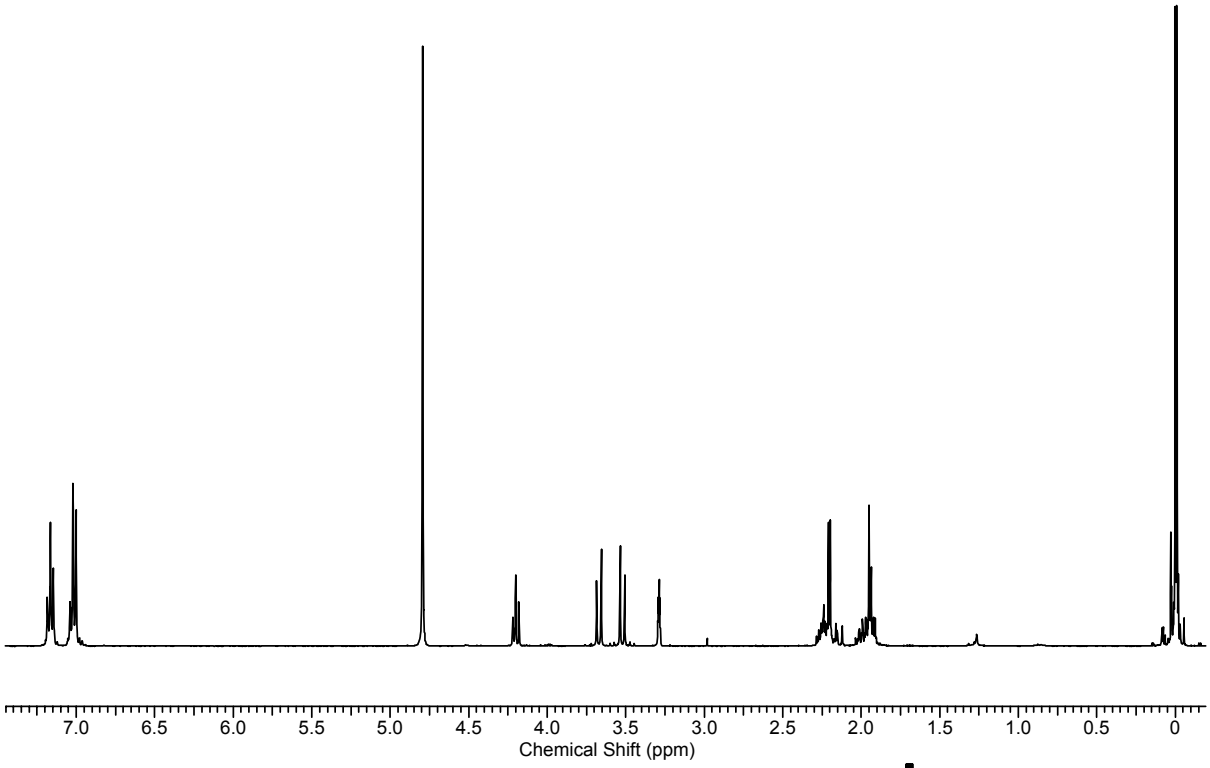


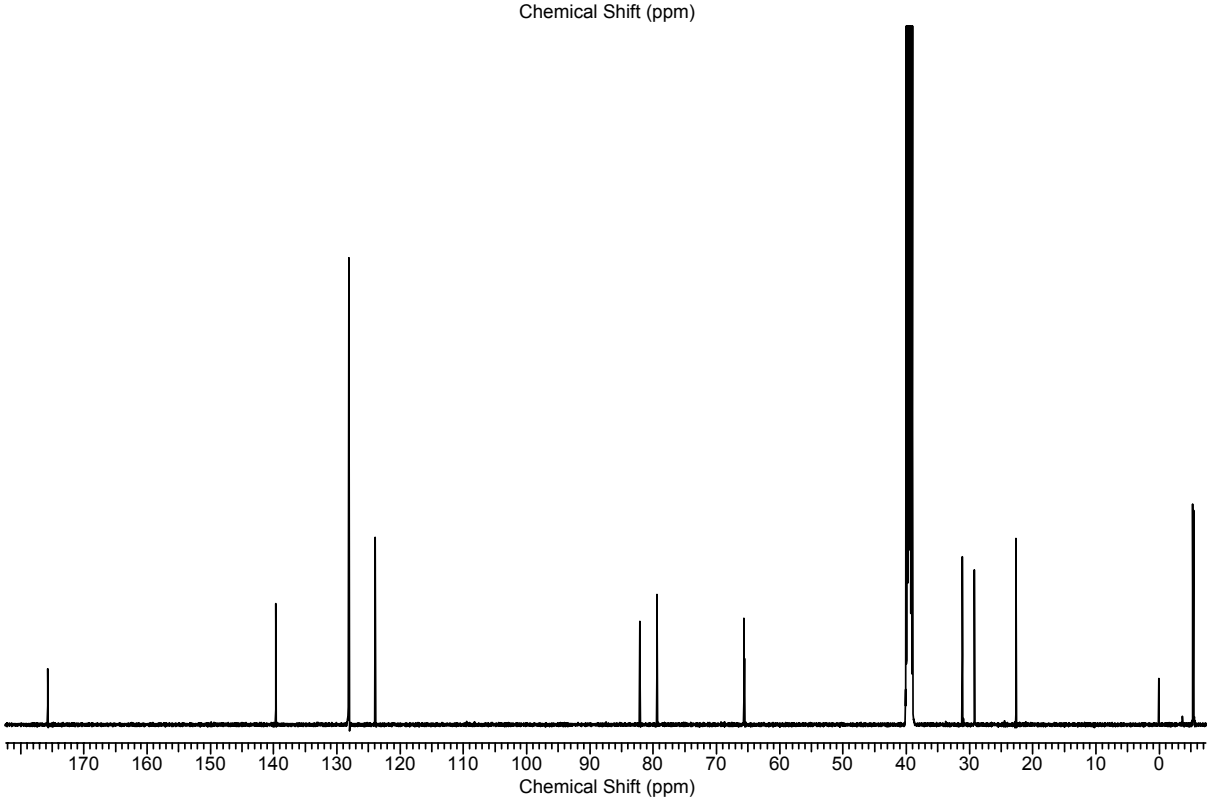




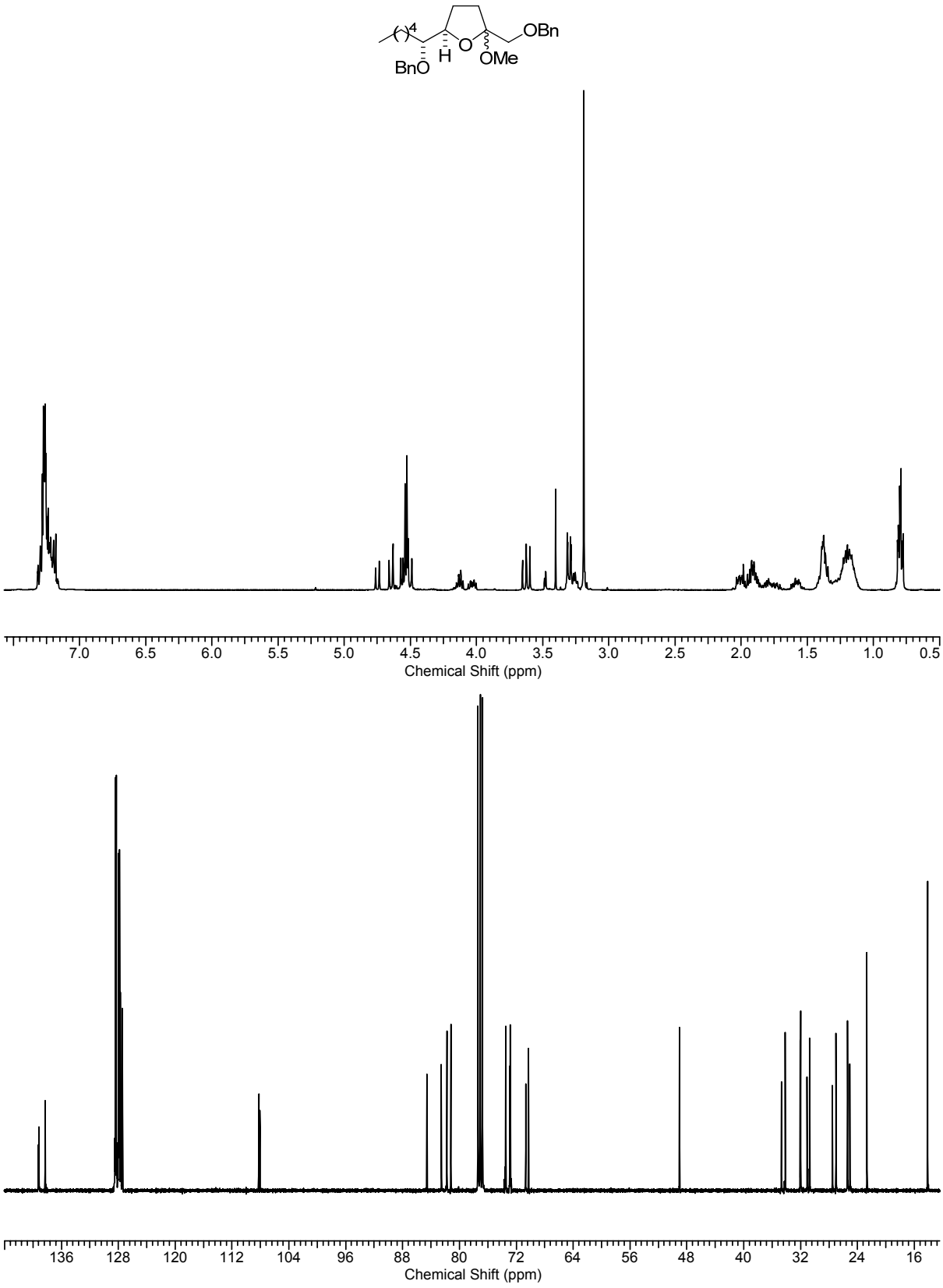
(±)-(2*R*,5*R*)-5-(Benzyldimethylsilyl)-5-(hydroxymethyl)tetrahydrofuran-2-carboxamide, 19



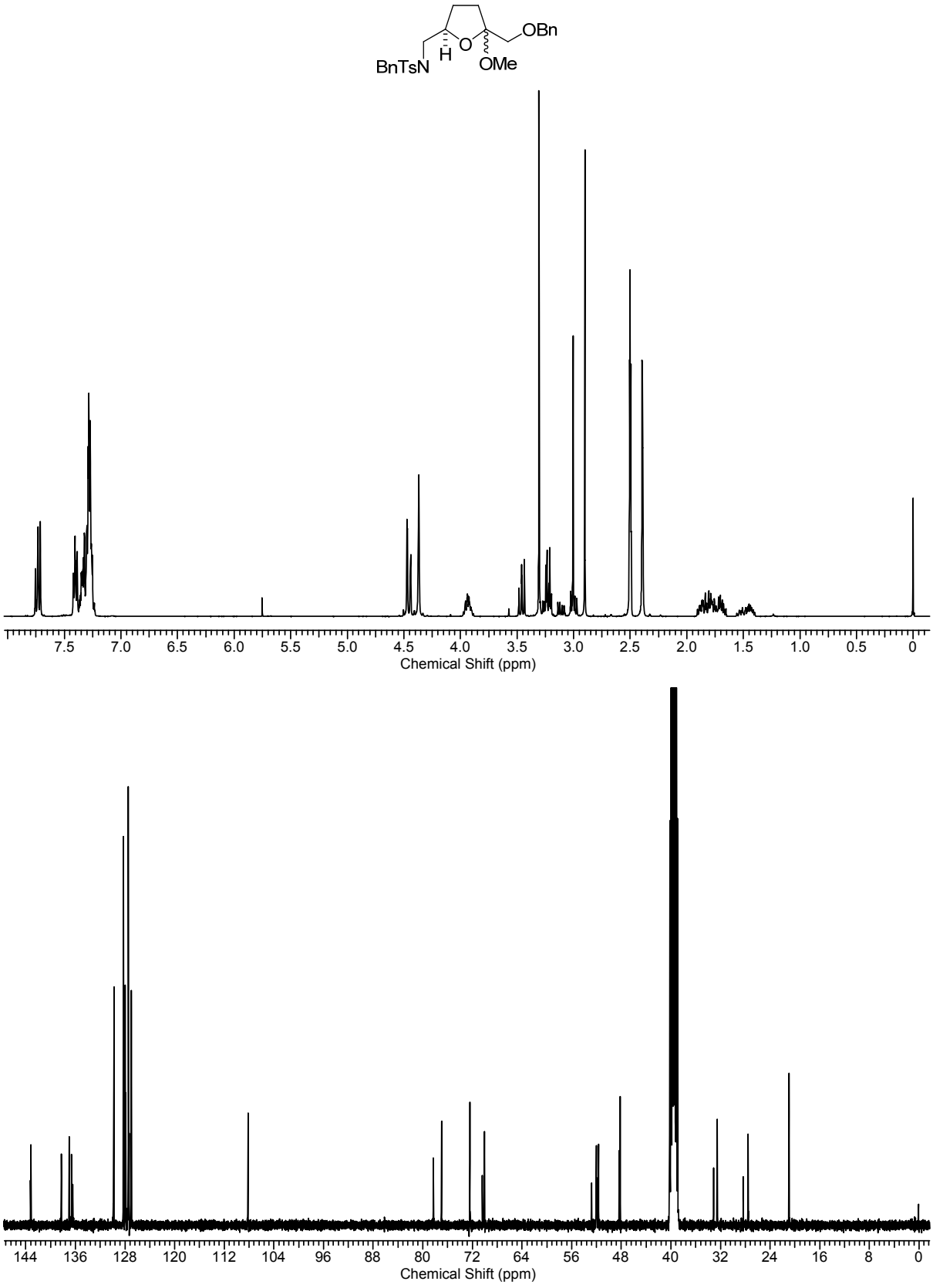




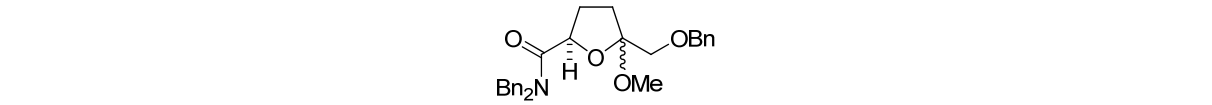
(±)-(5*R*)-5-((*R*)-1-(Benzyloxy)hexyl)-2-(benzyloxymethyl)-2-methoxytetrahydrofuran, 23

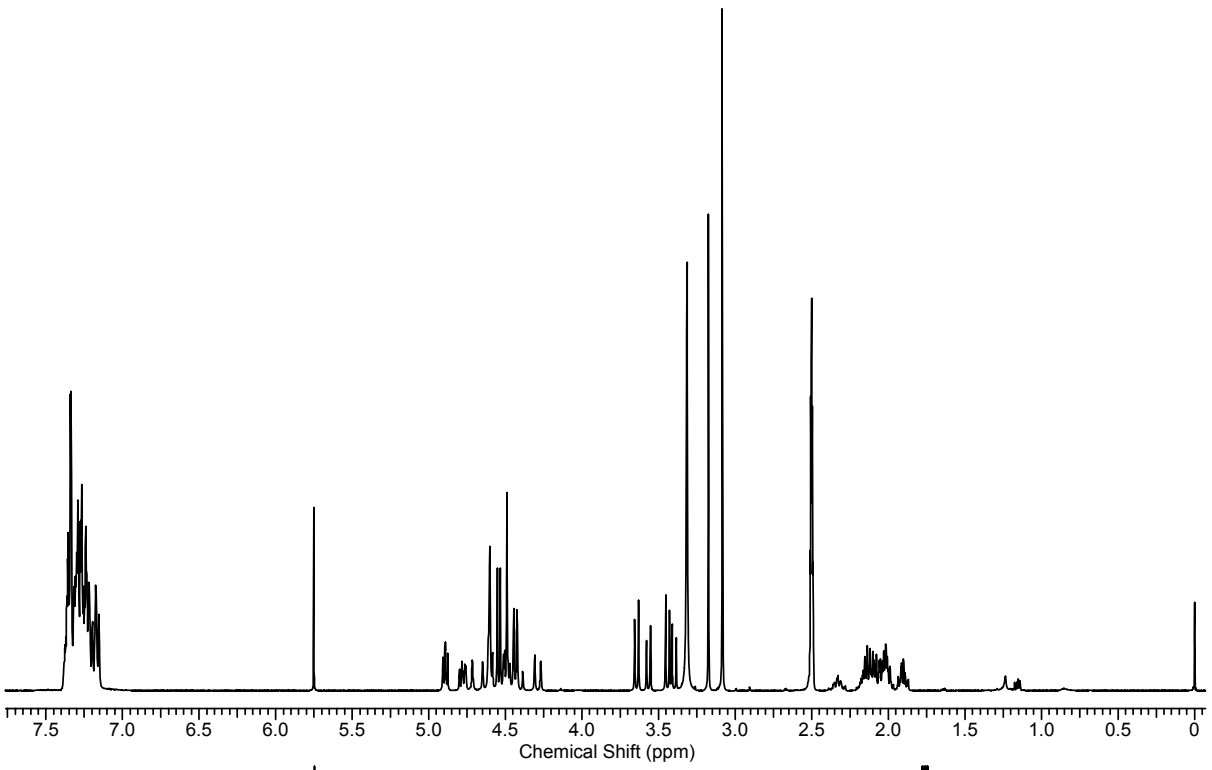


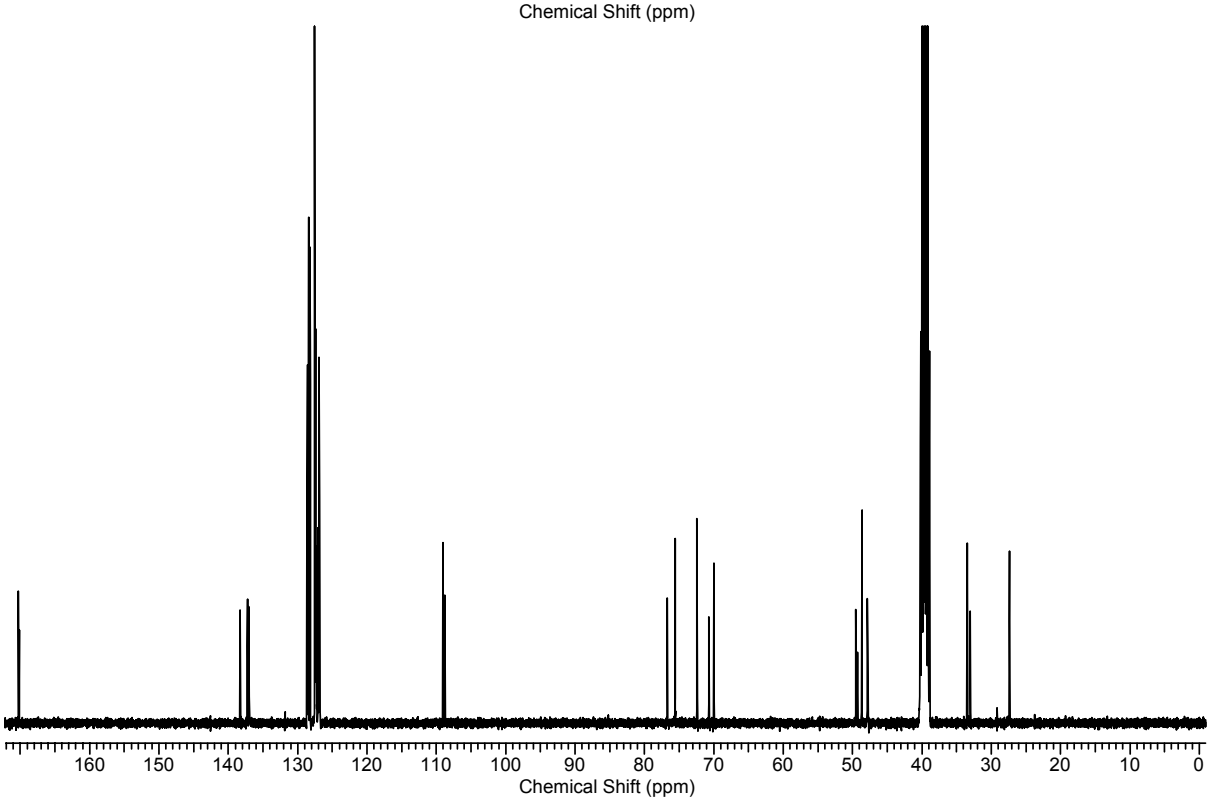
(±)-(*R*)-*N*-Benzyl-*N*-((5-(benzyloxymethyl)-5-methoxytetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide, 25



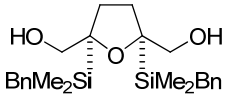
(±)-(*R*)-*N*,*N*-dibenzyl-5-(benzyloxymethyl)-5-methoxytetrahydrofuran-2-carboxamide, 27

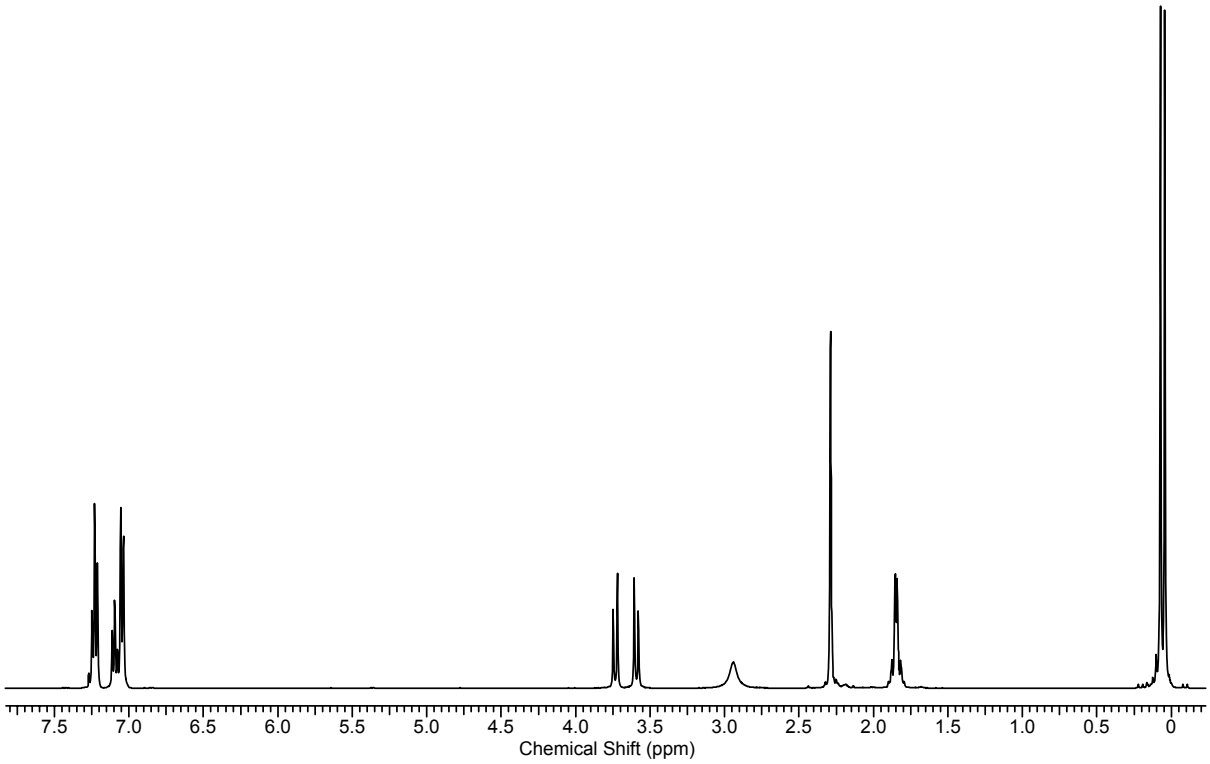


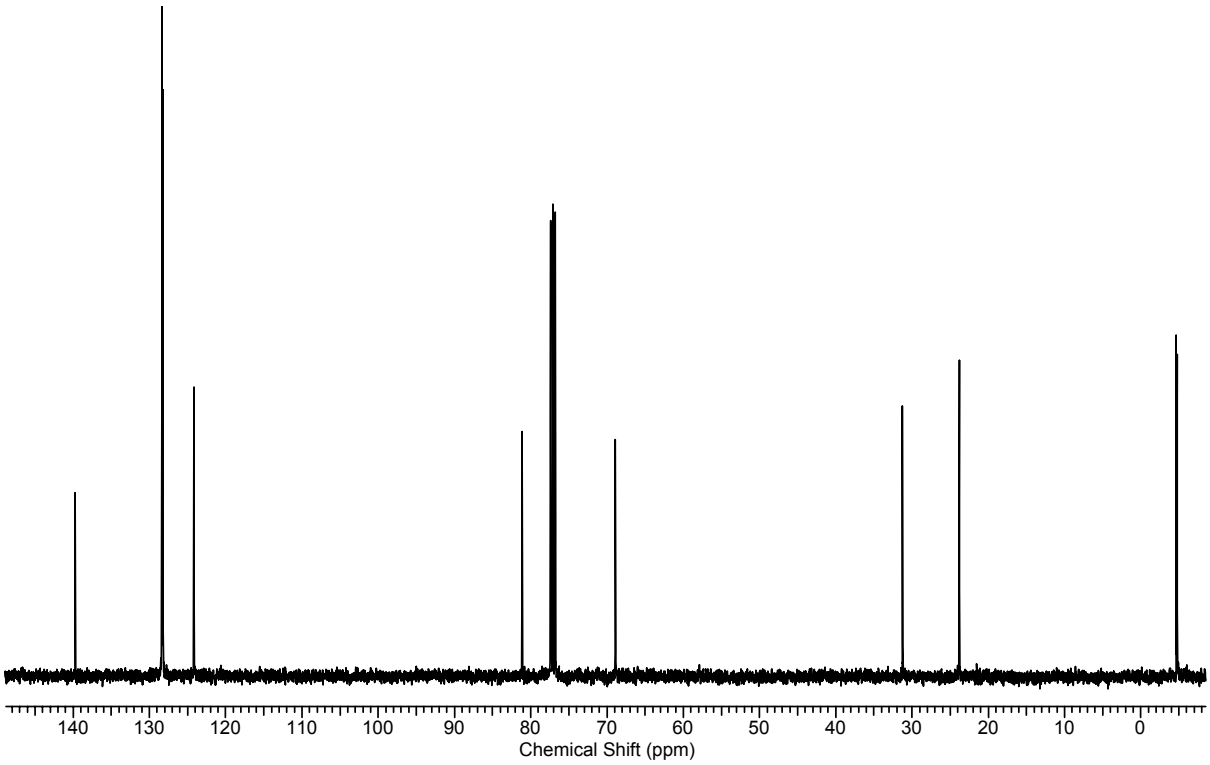




(±)-((2*R*,5*S*)-2,5-bis(benzyldimethylsilyl)tetrahydrofuran-2,5-diyl)dimethanol, 29







Single-crystal X-ray diffraction report for compound 7 (Datablock: 0320309)

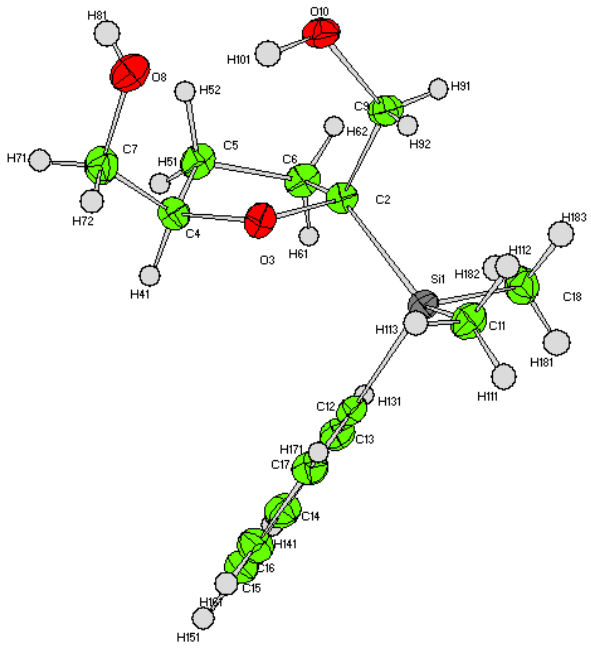


Figure 1: *Crystal structure of THF* **7**

Crystals of **7** were grown from CH_2Cl_2. A single crystal having dimensions approximately ***0.10 × 0.20 × 0.50 mm*** was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer (graphite-monochromated Mo K_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[60]

Examination of the systematic absences of the intensity data showed the space group to be ***P 1 2/c 1***. The structure was solved in this space group using the direct-methods program SIR92,[61] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program suite.[62] Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms, and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give ***R = 0.0342, wR = 0.0827***.

Attached is a thermal ellipsoid plot (CAMERON) at 50 % probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

Crystal identification	CCK 0320309
Chemical formula	C_{14} H_{22} O_3 Si_1
Formula weight	266.41
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 1 2/c 1
a (Å)	6.4912(1)
b (Å)	15.0650(2)
C (Å)	14.4629(2)
α (°)	90
β (°)	92.6057(5)
γ (°)	90
Cell volume (Å^3)	1412.86(3)
Z	4
Calculated density (Mg/m^3)	1.252
Absorption coefficient (mm^{-1})	0.09
F_{000}	576
Crystal size (mm)	0.10 × 0.20 × 0.50
Description of crystal	Colourless prism
Absorption correction	Multi-scan
Transmission coefficients (min, max)	0.85, 0.98
θ range for data collection (°)	5.10≤ θ ≤ 27.49
Index ranges	−8 ≤ h ≤ 8, −19≤ k ≤ 19, −18≤ l ≤ 18
Reflections measured	28648
Unique reflections	6414
R_{int}	0.023
Observed reflections (I > -3σ(I))	28648
Refinement method	Full-matrix least-squares on Fsqd
Parameters refined	164
Weighting scheme	Modified Sheldrick
Goodness of fit	0.9556
R	0.0342
wR	0.0827
Residual electron density (min, max) (eÅ^{-3})	−0.35, 0.36

Table 1: *Crystal structure and refinement details*

Atom	x	y	z	U_{equiv}
Si(1)	0.87193(5)	0.17013(2)	0.53944(2)	0.0186
C(2)	0.75617(19)	0.28597(8)	0.52284(9)	0.0191
O(3)	0.61726(14)	0.28187(6)	0.44033(6)	0.022
C(4)	0.6728(2)	0.34615(9)	0.37215(9)	0.0239
C(5)	0.8232(2)	0.41047(9)	0.42068(10)	0.0245
C(6)	0.9192(2)	0.35655(9)	0.50105(10)	0.0226
C(7)	0.4752(2)	0.38789(10)	0.33202(10)	0.0293
O(8)	0.36169(15)	0.43171(7)	0.40102(7)	0.0295
C(9)	0.6221(2)	0.31282(9)	0.60185(10)	0.0243
O(10)	0.51543(15)	0.39516(7)	0.58486(7)	0.0284
C(11)	0.6663(2)	0.08931(9)	0.56662(10)	0.0265
C(12)	0.98877(19)	0.13860(8)	0.42778(9)	0.0202
C(13)	1.1879(2)	0.16640(9)	0.40651(10)	0.0231
C(14)	1.2718(2)	0.14461(9)	0.32286(10)	0.0263
C(15)	1.1599(2)	0.09408(10)	0.25829(10)	0.028
C(16)	0.9638(2)	0.06512(10)	0.27774(10)	0.0283
C(17)	0.8794(2)	0.08735(9)	0.36139(10)	0.0243
C(18)	1.0739(2)	0.17535(10)	0.63545(10)	0.028

Table 2: *Atomic coordinates and equivalent isotropic thermal parameters ($Å^2$) of non-hydrogen atoms*

Atom	x	y	z	U_{iso}
H(41)	0.738	0.3155	0.3214	0.0288
H(52)	0.7474	0.4621	0.4446	0.0293
H(51)	0.9289	0.4316	0.3792	0.0299
H(62)	0.9516	0.3927	0.5561	0.0277
H(61)	1.0474	0.3283	0.4807	0.0281
H(71)	0.5079	0.4308	0.283	0.0344
H(72)	0.3848	0.3407	0.305	0.0347
H(91)	0.7096	0.32	0.6589	0.0285
H(92)	0.5215	0.2652	0.6116	0.0294
H(112)	0.6118	0.1033	0.6265	0.0405
H(111)	0.7242	0.0303	0.5695	0.0406
H(113)	0.5566	0.0917	0.5195	0.0399
H(131)	1.2668	0.2007	0.4511	0.0267
H(141)	1.407	0.1639	0.3098	0.0321
H(151)	1.2187	0.0793	0.2012	0.034
H(161)	0.8874	0.03	0.2331	0.0346
H(171)	0.7446	0.0674	0.3749	0.0295
H(182)	1.1669	0.2227	0.6246	0.0431
H(183)	1.0127	0.1857	0.6934	0.0433
H(181)	1.1506	0.1202	0.6381	0.0437
H(101)	0.4658	0.3941	0.5293	0.0426
H(81)	0.3975	0.4852	0.4023	0.0452

Table 3: *Atomic coordinates and isotropic thermal parameters ($Å^2$) of hydrogen atoms*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.01773(18)	0.01735(19)	0.02068(19)	0.00017(14)	0.00043(13)	−0.00005(14)
C(2)	0.0174(6)	0.0188(6)	0.0212(6)	−0.0006(5)	0.0006(5)	−0.0019(5)
O(3)	0.0211(5)	0.0198(5)	0.0248(5)	0.0020(4)	−0.0032(4)	−0.0028(4)
C(4)	0.0276(7)	0.0243(7)	0.0202(6)	0.0008(5)	0.0040(5)	0.0016(6)
C(5)	0.0222(6)	0.0220(7)	0.0298(7)	0.0045(6)	0.0059(6)	−0.0017(5)
C(6)	0.0191(6)	0.0200(7)	0.0286(7)	0.0005(5)	0.0012(5)	−0.0028(5)
C(7)	0.0329(8)	0.0287(8)	0.0258(7)	0.0008(6)	−0.0051(6)	0.0011(6)
O(8)	0.0239(5)	0.0269(5)	0.0377(6)	0.0019(4)	0.0011(4)	0.0023(4)
C(9)	0.0267(7)	0.0204(7)	0.0264(7)	0.0007(5)	0.0063(5)	0.0023(5)
O(10)	0.0314(5)	0.0250(5)	0.0293(5)	−0.0008(4)	0.0084(4)	0.0085(4)
C(11)	0.0262(7)	0.0215(7)	0.0319(8)	0.0035(6)	0.0025(6)	−0.0020(6)
C(12)	0.0203(6)	0.0166(6)	0.0235(7)	0.0013(5)	−0.0007(5)	0.0030(5)
C(13)	0.0209(6)	0.0201(6)	0.0282(7)	−0.0010(5)	0.0000(5)	−0.0001(5)
C(14)	0.0245(7)	0.0240(7)	0.0308(8)	0.0026(6)	0.0062(6)	0.0019(5)
C(15)	0.0350(8)	0.0263(7)	0.0231(7)	0.0015(6)	0.0054(6)	0.0056(6)
C(16)	0.0318(8)	0.0280(8)	0.0248(7)	−0.0044(6)	−0.0030(6)	0.0017(6)
C(17)	0.0209(6)	0.0240(7)	0.0278(7)	−0.0020(6)	0.0000(5)	0.0003(5)
C(18)	0.0264(7)	0.0318(8)	0.0256(7)	0.0002(6)	−0.0028(6)	0.0008(6)

Table 4: *Anisotropic thermal parameters ($Å^2$)*

Si(1)-C(2)	1.9108(13)	C(7) – O(8)	1.4288(18)
Si(1)- C(11)	1.8619(14)	O(8) – H(81)	0.838
Si(1)- C(12)	1.8762(14)	C(9) – O(10)	1.4364(16)
Si(1)- C(18)	1.8674(14)	O(10)- H(101)	0.852
C(2) – O(3)	1.4639(15)	C(12)- C(13)	1.4058(18)
C(2) – C(6)	1.5428(17)	C(12)- C(17)	1.4001(19)
C(2) – C(9)	1.5221(18)	C(13)- C(14)	1.3886(19)
O(3) – C(4)	1.4395(16)	C(14)- C(15)	1.385(2)
C(4) – C(5)	1.5240(19)	C(15)- C(16)	1.386(2)
C(4) – C(7)	1.5196(19)	C(16)- C(17)	1.392(2)
C(5) – C(6)	1.5276(19)		

Table 5: *Bond lengths (Å) (Excluding C-H bonds)*

C(2)- Si(1)- C(11)	110.01(6)	O(3) – C(4) – C(7)	107.87(11)
C(2)- Si(1)- C(12)	107.17(6)	C(5) – C(4) – C(7)	115.12(12)
C(11)-Si(1)- C(12)	109.75(6)	C(4) – C(5) – C(6)	104.06(11)
C(2)- Si(1) – C(18)	108.28(6)	C(2) – C(6) – C(5)	105.19(10)
C(11) -Si(1) - C(18)	110.88(7)	C(4) – C(7) – O(8)	112.18(11)
C(12) – Si(1) – C(18)	110.68(6)	C(2) – C(9) – O(10)	112.87(11)
Si(1) - C(2) - O(3)	106.74(8)	Si(1) – C(12) – C(13)	121.64(10)
Si(1) – C(2) - C(6)	112.68(9)	Si(1) – C(12) – C(17)	121.18(10)
O(3) – C(2) – C(6)	105.39(10)	C(13) – C(12) – C(17)	117.18(12)
Si(1) – C(2) – C(9)	112.54(9)	C(12) – C(13) – C(14)	121.41(13)
O(3) – C(2) – C(9)	105.74(10)	C(13) – C(14) – C(15)	120.20(13)
C(6) – C(2) – C(9)	113.02(11)	C(14) – C(15) – C(16)	119.63(13)
C(2) – O(3) – C(4)	111.47(9)	C(15) – C(16) – C(17)	120.14(13)
O(3) – C(4) – C(5)	106.70(10)	C(12) – C(17) – C(16)	121.43(13)

Table 6: *Bond angles (°) (Excluding H atoms)*