Homologation of Boronic Esters with Lithiated Epoxides for the Stereocontrolled Synthesis of 1,2 and 1,3-Diols, and 1,2,4-Triols.

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General information.

All reactions were carried out in flame dried Schlenk tubes under argon atmosphere employing standard manifold techniques. Solvents were dried by standard methods. NMR spectra were recorded on JEOL 270 MHz, JEOL 400 MHz or Eclipse 300 MHz spectrometers using tetramethylsilane as the internal standard (0.00 ppm). nOe's spectra were recorded on a VARIAN 500 MHz spectrometer. $CDCl_3$ was used as an internal standard for ^{13}C NMR spectra (77.0 ppm). CI mass spectra were obtained using a VG Platform mass spectrometer. All IR data were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. All MS were recorded on Agilent Technologies GC-MS Spectrum equipped with 6890 Series GC system, 7683 Series injector and 5973 Network Mass Selective detector. Analytical TLC was done on aluminium backed plates (1.5 x 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualised by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24} \bullet 4\ H_2O$ in 95% EtOH (w/v) followed by heating. Flash chromatography was done on silica gel (Merck Kieselgel 60). Melting points were determined with a Kofler hot stage apparatus and were not corrected. Optical rotations were obtained on a Perkin-Elmer 241MC polarimeter. Chiral HPLC separations were done on Agilent 1100 series normal phase high performance liquid chromatography units using HP Chemstation for LC or LC/MS. Daicel Chiralcel AD and OD-H (0.46 x 25 cm) were used for normal phase separations.

All chemicals were used as received from the supplier except for *tert*-butyloxirane (distilled over activated 4Å molecular sieves) and 2,2,6,6-tetramethylpiperidine (distilled over CaH_2). sBuLi was purchased as a 1.3 M solution in cyclohexane from either Fluka or Acros Chemical Compagnies. *N*,*N*,*N*,*N*-Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled over CaH_2 prior to use. Boronic pinacol ester were synthesized according to literature procedures.[1]

[1] [a] S. Morandi, E. Caselli, A. Forni, M. Buccurelli, G. Torre, F. Prati, *Tetrahedron: Asymmetry* **2005**, *16*, 2918; [b] T. J. Southwood, M. C. Curry, C. A. Hutton, *Tetrahedron* **2006**, *62*, 236.

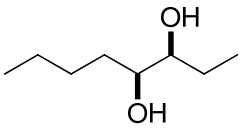
Experimental Procedures & Data

General procedure for the preparation of lithium 2,2,6,6-tetramethylpiperidide.

A 10 ml Schlenk tube was charged with 2,2,6,6-tetramethylpiperidine (1.33 ml, 0.75 M in THF). The solution was thereafter cooled to −30 °C followed by addition of *n*BuLi (0.40 ml, 2.5 M). The resulting reaction mixture was then stirred for 30 min at room temperature.

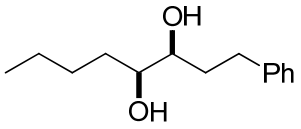
General procedure for the homologation of boronates with epoxides leading to diols.

A 10 ml Schlenk tube was charged with the corresponding epoxide (0.50 mmol) and boronate (1.00 mmol, 1.00 M in THF). The resulting solution was thereafter cooled to -30°C followed by dropwise addition of freshly prepared lithium 2,2,6,6-tetramethylpiperidide (1.00 mmol). The reaction mixture was then stirred 2 h at -30°C at which the reaction flask was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred an additional 2h at 4°C and was then diluted with H_2O (5 ml) and extracted with DCM (4 × 7 ml). The combined organic layer was dried over magnesium sulphate. The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography.

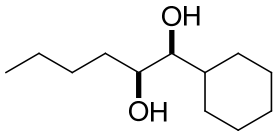


Octane-3,4-diol (3a).[2] This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 25% EtOAc/Petrol) which afforded 56 mg of a colourless oil (76%). IR ν_{max} (thin film) / cm^{-1} 3617, 2963, 2874; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.39-3.47 (m, 1H), 3.30-3.39 (m, 1H), 2.14 (br s, 2H), 1.27-1.68 (m, 8H), 0.97 (t, J = 7.4 Hz, 3H), 0.88-0.95 (m, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 76.0, 74.2, 33.4, 27.9, 26.5, 22.8, 14.1, 10.1; MS (ESI) m/z 241, 169 ($M+Na^+$); HRMS (ESI) calcd for $C_8H_{18}O_2 + Na^+$ 169.1194, found 169.1199.

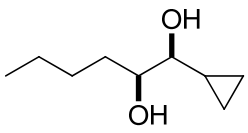
[2] All spectral data corresponded to literature values: C. Bonini, G. Righi, *Tetrahedron* **1992**, *48*, 1531.



1-Phenyloctane-3,4-diol (3b). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 25% EtOAc/Petrol) which afforded 82 mg (73%) of a colourless oil that solidified upon standing. IR ν_{max} (thin film) / cm^{-1} 3615, 3573, 2957; M.p: 50-51°C; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.14-7.32 (m, 5H), 3.37-3.48 (m, 2H), 2.85 (ddd, J = 13.9, 8.8, 6.5 Hz, 1H), 2.69 (ddd, J = 13.9, 8.9, 7.4 Hz, 1H), 2.35-2.42 (m, 1H), 2.21-2.28 (m, 1H), 1.68-1.90 (m, 2H), 1.22-1.54 (m, 6H), 0.85-0.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 142.0, 128.5, 126.0, 74.7, 73.9, 35.4, 33.4, 32.1, 27.9, 22.8, 14.1; MS (CI) m/z (%) 223 ($M+H^+$, 10), 205 (100), 187 (70), 117 (60), 91 (50); HRMS (ESI) calcd for $C_{14}H_{22}O_2 + Na^+$ 245.1506, found 245.1512.

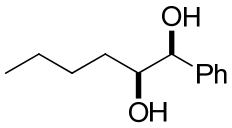


1-Cyclohexylhexane-1,2-diol (3c). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 10% EtOAc/Petrol) which afforded 83 mg of a colourless oil (83%). IR ν_{max} (thin film) / cm^{-1} 3369, 3056, 2857; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.58-3.68 (m, 1H), 3.10-3.19 (m, 1H), 2.02-2.12 (m, 2H), 1.61-1.85 (m, 5H), 1.04-1.55 (m, 12H), 0.86-0.96 (m, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 78.4, 71.4, 40.2, 33.8, 29.9, 28.0, 27.7, 26.4, 26.2, 26.1, 22.8, 14.1; MS (ESI) m/z 223 ($M+Na^+$), 217, 186, 102; HRMS (ESI) calcd for $C_{12}H_{24}O_2 + Na^+$ 223.1664, found 223.1668.

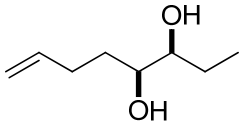


1-Cyclopropylhexane-1,2-diol (3d). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 50%

EtOAc/Petrol) which afforded 68 mg of a colourless oil (86%). IR ν_{max} (thin film) / cm^{-1} 3605, 3083, 2862; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.53-3.63 (m, 1H), 2.69 (dd, *J* = 8.7, 5.8 Hz, 1H), 2.10-2.40 (m, 2H), 1.57-1.74 (m, 1H), 1.26-1.55 (m, 5H), 0.85-1.02 (m, 4H), 0.50-0.63 (m, 2H), 0.23-0.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 79.5, 75.4, 33.2, 28.0, 22.8, 14.7, 14.1, 3.4, 2.3; MS (EI) m/z (%) 157 ($M-H^+$, 5), 141 (70), 123 (40), 85(100); MS (ESI) m/z 181 ($M+Na^+$), 149; HRMS (ESI) calcd for $C_9H_{18}O_2 + Na^+$ 181.1194, found 181.1199.



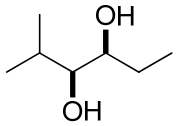
1-Phenylhexane-1,2-diol (3e).[3] This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 25% EtOAc/Petrol) which afforded 56 mg of a colourless oil (57%). IR ν_{max} (thin film) / cm^{-1} 3601, 3063, 1395; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.27-7.41 (m, 5H), 4.40 (dd, *J* = 6.8, 3.7 Hz, 1H), 3.62-3.72 (m, 1H), 2.87 (d, *J* = 3.7 Hz, 1H), 2.53 (d, *J* = 3.8 Hz, 1H), 1.17-1.52 (m, 6H), 0.80-0.89 (m, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 141.3, 128.6, 128.0, 126.9, 78.0, 76.0, 32.4, 27.9, 22.7, 14.0; MS (ESI) m/z 217 ($M+Na^+$), 106; HRMS (ESI) calcd for $C_{12}H_{18}O_2 + Na^+$ 217.1194, found 217.1199.



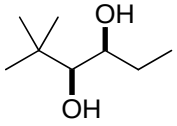
Oct-7-ene-3,4-diol (3f).[4] This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 50% EtOAc/Petrol) which afforded 34 mg of a colourless oil (47%). IR ν_{max} (thin film) / cm^{-1} 3572, 3390, 1640; ^1H NMR ($CDCl_3$, 270 MHz) δ 5.82 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.05 (dq, *J* = 17.0, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H), 3.44 (dt, *J* = 8.0, 5.1 Hz, 1H), 3.35 (ddd, *J* = 8.2, 5.1, 4.3 Hz, 1H), 2.07-2.35 (m, 4H), 1.35-1.69 (m, 4H), 0.97

[3] ^1H NMR corresponded to literature values: G. Bellucci, C. Chiappe, A. Caordoni, *Tetrahedron: Asymmetry* **1996**, *7*, 197.
[4] This compound is known in the literature but only the elemental analysis was given: R. K. Hill, *J. Am. Chem. Soc.* **1957**, *79*, 1609.

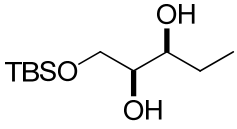
(t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 138.4, 115.1, 75.9, 73.6, 32.8, 30.0, 26.5, 10.1; MS (EI) m/z (%) 143 (M-H^+, 10), 127 (50), 109 (90), 85 (90), 57 (100); HRMS (ESI) calcd for $C_8H_{16}O_2$ + Na^+ 167.1038, found 167.1042.



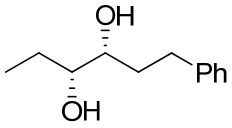
2-Methylhexane-3,4-diol (3g). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 25% EtOAc/Petrol) which afforded 43 mg of a colourless oil (65%). IR ν_{max} (thin film) / cm^{-1} 3620, 3572, 1465; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.47-3.57 (m, 1H), 3.15 (app q, J = 5.5 Hz, 1H), 2.26 (br s, 2H), 1.72-1.88 (m, 1H), 1.39-1.64 (m, 2H), 0.92-1.02 (m, 9H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 78.7, 73.4, 30.2, 26.9, 19.8, 17.1, 10.1; MS (ESI) m/z 155 (M+Na^+), 129; HRMS (ESI) calcd for $C_7H_{16}O_2$ + Na^+ 155.1039, found 155.1042.



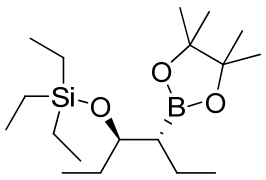
2,2-Dimethylhexane-3,4-diol (3h). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 25% EtOAc/Petrol) which afforded 28 mg of a colourless solid (38%). IR ν_{max} (thin film) / cm^{-1} 3378, 2957; M.p: 80-81 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.69 (br q, J = 6.2 Hz, 1H), 3.05 (d, J = 6.8 Hz, 1H), 2.25 (d, J = 6.8 Hz, 1H), 1.79 (d, J = 6.2 Hz, 1H), 1.43-1.68 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.93 (s, 9H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 79.4, 70.9, 35.0, 29.7, 26.3, 10.3; MS (ESI) m/z 169 (M+Na^+), 129; HRMS (ESI) calcd for $C_8H_{18}O_2$ + Na^+ 169.1195, found 169.1199.



1-(tert-Butyldimethylsilyloxy)pentane-2,3-diol (3i). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 20% EtOAc/Petrol) which afforded 64 mg of a colourless oil (54%). IR ν_{max} (thin film) / cm^{-1} 3564, 2956, 1362; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.76 (dd, J = 10.2, 3.6 Hz, 1H), 3.68 (dd, J = 10.2, 5.3 Hz, 1H), 3.59-3.45 (m, 2H), 2.72 (d, J = 4.0 Hz, 1H), 2.61 (d, J = 6.3 Hz, 1H), 1.54 (quint., J = 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 73.9, 72.6, 66.2, 26.5, 25.9, 18.3, 10.1, -5.4, -5.5; MS (ESI) m/z 257 ($M+Na^+$), 215; HRMS (ESI) calcd for $C_{11}H_{26}O_2Si + Na^+$ 257.1537, found 257.1543.

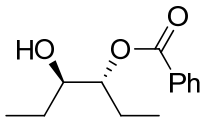


1-Phenylhexane-3,4-diol (3j). This compound was synthesised from (+)-epoxybutane according to the general procedure but was subjected to kugel-rohr distillation which afforded 134 mg (69%) of a colourless oil. IR ν_{max} (thin film) / cm^{-1} 3615, 3537, , 2965; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.15-7.32 (m, 5H), 3.41-3.50 (m, 1H), 3.32-3.41 (m, 1H), 2.85 (ddd, J = 13.8, 8.5, 6.5 Hz, 1H), 2.70 (ddd, J = 13.8, 9.1, 7.2 Hz, 1H), 2.20 (d, J = 5.2 Hz, 1H), 2.08 (d, J = 5.2 Hz, 1H), 1.70-1.90 (m, 2H), 1.35-1.65 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67 MHz) δ 142.0, 128.5, 126.0, 76.1, 73.5, 35.4, 32.1, 26.5, 10.1; MS (EI) m/z (%) 159 (30), 117 (30), 91 (100), 59 (20); HRMS (ESI) calcd for $C_{12}H_{18}O_2 + Na^+$ 217.1194, found 217.1199; $[\alpha]_D^{22}$ = +31.0 (c 1, $CHCl_3$) (e.r. = 99:1); t_R = 28.9 min (*R*,*R*-major), 32.2 min (*S*,*S*-minor) Daicel Chiralcel-AD column, 3% iPrOH in Hexane 1 mL/min.



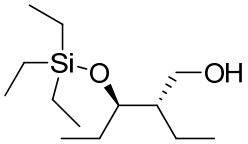
(1*R*,2*R*)-(1-Ethyl-2-triethylsiloxy)butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4). A 50 ml Schlenk tube was charged with (+)-epoxybutane (3.00 mmol) and ethyl pinacol boronic ester (6.00 mmol) in 13 mL of THF. The resulting solution was

thereafter cooled to -30°C followed by dropwise addition of freshly prepared lithium 2,2,6,6-tetramethylpiperidide (6.00 mmol). The reaction mixture was then stirred 2 h and then allowed to warm to room temperature. TES-OTf (4.50 mmol) was added and the resulting mixture was stirred at room temperature overnight. The volatiles were removed under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 1% Et_2O/Petrol) which afforded 584 mg of a colourless oil (57%). R_f 0.40 (3% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 2959, 1460, 1380; ^1H NMR (400 MHz, $CDCl_3$) δ 3.72 (td, J = 6.4, 3.3 Hz, 1H), 1.44-1.58 (m, 4H), 1.26 (s, 6H), 1.24 (s, 6H), 1.09 (ddd, J = 10.0, 4.9, 3.3 Hz, 1H), 0.98 (t, J = 7.8 Hz, 9H), 0.92 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H), 0.61 (q, J = 7.8 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 82.8, 77.0, 29.9, 25.9, 25.1, 20.9, 15.0, 11.4, 7.7, 5.9; ^{11}B NMR ($CDCl_3$, 96 MHz) δ 33.6; MS (CI) m/z (%) 341 ($M\text{-}H^+$, 10), 313 (30), 173 (90), 147 (60), 83 (100); HRMS (ESI) calcd for $C_{18}H_{39}BO_3Si + Na^+$ 365.2654, found 365.2647.



(3*R*,4*R*)-4-Hydroxyhexan-3-yl benzoate (4'). A solution of boronic ester **4** (111 mg, 0.32 mmol) in 3 mL of THF was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred at 4°C for 1h and was then diluted with H_2O (5 ml) and extracted with DCM (4 × 7 ml). The organic solvents were then removed and the crude product was purified by flash chromatography (SiO_2, 5% Et_2O/Petrol) to yield (3*R*,4*R*)-4-(triethylsilyloxy)hexan-3-ol as a colorless oil (75 mg, 99%). It was dissolved in 1 mL of DCM and diisopropylethylamine (85 µL, 0.48 mmol) and benzoyl chloride (45 µL, 0.38 mmol) were added. The mixture was stirred at room temperature for 5h. It was then poured onto water and extracted with DCM (4 x 3 mL). The combined organic layer was dried over magnesium sulfate. The organic solvents were then removed. The crude oil was dissolved in 1 mL of THF and tetrabutylammonium fluoride (151 mg, 0.48 mmol) was added. The resulting mixture was stirred at room temperature for 1h. The organic solvents were then removed and the crude product was purified by flash

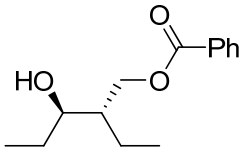
chromatography (SiO_2, 50% Et_2O/Petrol) to yield **4'** as a colorless oil (54 mg, 76%).[5] R_f 0.50 (50% Et_2O/Petrol); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 5.07 (ddd, J = 6.8, 6.0, 3.9 Hz, 1H), 3.69 (ddd, J = 8.6, 4.4, 3.9 Hz, 1H), 1.79-1.87 (m, 2H), 1.48-1.64 (m, 2H), 1.03 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 166.6, 133.2, 129.8, 128.5, 78.3, 74.0, 26.8, 23.9, 10.2, 10.0. $[\alpha]_D^{22}$ = -20.3 (c 1.07, MeOH) (e.r. = 99:1); t_R = 21.9 min (*R*,*R*-major), 24.4 min (*S*,*S*-minor) Daicel Chiralcel-AD column, 2% iPrOH in Hexane 1 mL/min.



2-ethyl-3-(triethylsilyloxy)pentan-1-ol (5). A 10 ml Schlenk tube was charged with the boronic ester **4** (40 mg, 0.12 mmol) and chloroiodomethane (17 µL, 0.23 mmol) in 0.5 mL of THF. The resulting solution was thereafter cooled to -78°C followed by dropwise addition of *n*BuLi (1.6 M in hexane, 146 µL, 0.23 mmol). The reaction mixture was stirred 30 min at -78°C and then allowed to warm to room temperature overnight. The reaction flask was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred an additional 2h at 4°C and was then diluted with H_2O (2 ml) and extracted with DCM (4 × 4 ml). The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography (SiO_2, 1% Et_2O/Petrol) to yield **5** as a colourless oil (27 mg, 90%). <u>One-pot process:</u> A 10 ml Schlenk tube was charged with (+)-epoxybutane (0.25 mmol) and ethyl pinacol boronic ester (0.50 mmol) in 500 µL of THF. The resulting solution was thereafter cooled to -30°C followed by dropwise addition of freshly prepared lithium 2,2,6,6-tetramethylpiperidide (0.50 mmol). The reaction mixture was then stirred 2 h at -30°C at which the reaction flask was allowed to warm to room temperature. TES-OTf (0.30 mmol) was added and the resulting mixture was stirred at room temperature for 2h. Chloroiodomethane (0.75 mmol) was then added and the resulting solution was thereafter cooled to -78°C followed by

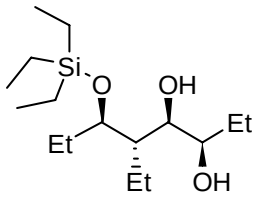
[5] All spectra data corresponded to literature values: Y. Matsumura, T. Maki, S. Murakami, O. Onomura, *J. Am. Chem. Soc*. **2003**, *125*, 2052.

dropwise addition of *n*BuLi (1.6 M in hexane, 0.75 mmol). The reaction mixture was stirred 30 min at -78°C and then allowed to warm to room temperature overnight. The reaction flask was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred an additional 30 min at 4°C and was then diluted with H_2O (2 ml) and extracted with DCM (4 × 4 ml). The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography (SiO_2, 1% Et_2O/Petrol) to yield **5** as a colourless oil (33 mg, 54%). R_f 0.50 (30% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3483, 2960, 2876;^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (dt, *J* = 11.5, 2.9 Hz, 1H), 3.77 (ddd, *J* = 7.8, 5.1, 3.2 Hz, 1H), 3.61 (ddd, *J* = 11.5, 7.6, 4.4, 1H), 3.16 (dd, *J* = 7.6, 5.1, 2.9 Hz, 1H), 1.59-1.74 (m, 3H), 1.38-1.47 (m, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.64 (q, *J* = 7.9 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 78.4, 62.3, 43.5, 28.3, 22.0, 12.1, 9.8, 7.0, 5.1; MS (ESI) m/z 269 ($M+Na^+$), 229, 215, 129; HRMS (ESI) calcd for $C_{13}H_{30}O_2Si + Na^+$ 269.1897, found 269.1907.

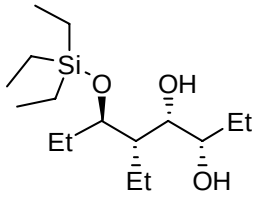


2-ethyl-3-hydroxy-pentyl benzoate (5'). 27 mg of **5** (0.11 mmol) were dissolved in 1 mL of DCM and diisopropylethylamine (22 µL, 0.16 mmol) and benzoyl chloride (15 µL, 0.13 mmol) were added. The mixture was stirred at room temperature for 5h. It was then poured onto water and extracted with DCM (4 x 3 mL). The combined organic layer was dried over magnesium sulphate. The organic solvents were then removed. The crude oil was dissolved in 1 mL of THF and tetrabutylammonium fluoride (50 mg, 0.16 mmol) was added. The resulting mixture was stirred at room temperature for 1h. The organic solvents were then removed and the crude product was purified by flash chromatography (SiO_2, 50% Et_2O/Petrol) to yield **5'** as a colorless oil (18 mg, 69%). R_f 0.50 (50% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3405, 3021, 1750;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.59 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.45 (ddd, *J* = 11.5, 4.9, 1H), 3.58-3.64 (m, 1H), 1.47-1.79 (m, 7H), 1.05 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 166.9, 133.0, 129.5, 128.4, 73.3, 64.1, 44.9,

27.5, 21.1, 11.7, 10.3; MS (EI) m/z (%) 237 ($M+H^+$, 60), 219 (90), 123 (50), 105 (40), 97 (100); HRMS (CI) calcd for $C_{14}H_{21}O_3$ ($M+H^+$) 237.1491, found 237.1489. $[\alpha]_D^{22}$ = 8.8 (c 0.91, $CHCl_3$) (e.r. = 99:1); t_R = 13.0 min (*S*,*R*-minor), 14.6 min (*R*,*S*-major) Daicel Chiralcel-OJ column, 2% iPrOH in Hexane 1 mL/min.



(3R,4R,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (6). A 10 ml Schlenk tube was charged with boronic ester **4** (102 mg, 0.30 mmol) and (+)-epoxybutane (13 μL, 0.15 mmol) in 500 μL of THF. The resulting solution was thereafter cooled to -30°C followed by dropwise addition of freshly prepared lithium 2,2,6,6-tetramethylpiperidide (0.30 mmol). The reaction mixture was then stirred 2 h at which the reaction flask was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred an additional 30 min at 4°C and was then diluted with H_2O (5 ml) and extracted with DCM (4 × 7 ml). The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography (SiO_2, 5% Et_2O/Petrol) to yield **6** as a colourless oil (16 mg, 35%). R_f 0.20 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 2962, 2937; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (br s, 1H), 3.90 (dt, *J* = 6.6, 4.4 Hz, 1H), 3.53-3.59 (m, 2H), 2.43 (br s, 1H), 1.35-1.77 (m, 7H), 1.03 (t, *J* = 7.9 Hz, 12H), 0.94 (t, *J* = 6.6 Hz, 6H), 0.70 (q, *J* = 7.9 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 77.2, 75.7, 73.6, 43.7, 29.5, 27.5, 23.1, 11.7, 10.6, 9.4, 6.8, 5.2; MS (CI) m/z (%) 305 ($M+H^+$, 10), 173 (90), 155 (100), 115 (40); HRMS (CI) calcd for $C_{16}H_{37}O_3Si$ 305.2512, found 305.2525. $[\alpha]_D^{22}$ = -16.7 (c 0.18, $CHCl_3$).

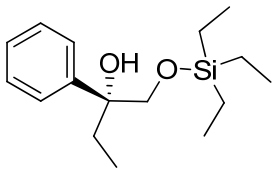


(3S,4S,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (7). A 10 ml Schlenk tube was charged with boronic ester **4** (146 mg, 0.43 mmol) and (-)-epoxybutane (18 μL, 0.21 mmol) in 500 μL of THF. The resulting solution was thereafter cooled to -30°C followed by dropwise addition of freshly prepared lithium 2,2,6,6-tetramethylpiperidide (0.43 mmol). The reaction mixture was then stirred 2 h at which the reaction flask was transferred to an ice bath and NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v) were added. The reaction mixture was stirred an additional 30 min at 4°C and was then diluted with H_2O (5 ml) and extracted with DCM (4 × 7 ml). The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography (SiO_2, 5% Et_2O/Petrol) to yield **7** as a colourless oil (29 mg, 45%). R_f 0.10 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 2963, 2957; ^1H NMR (400 MHz, $CDCl_3$) δ 3.97 (br s, 1H), 3.89 (ddd, *J* = 9.3, 5.1, 1.5 Hz, 1H), 3.81 (br d, *J* = 7.6 Hz, 1H), 3.59 (br t, *J* = 9.0 Hz, 1H), 2.92 (br s, 1H), 1.28-1.76 (m, 7H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.6 Hz, 3H), 0.66 (q, *J* = 7.8 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 76.3, 73.7, 73.5, 42.5, 28.1, 25.8, 17.8, 12.6, 10.3, 9.9, 6.9, 5.2; MS (CI) m/z (%) 305 ($M+H^+$, 20), 257 (40), 173 (90), 155 (100); HRMS (CI) calcd for $C_{16}H_{37}O_3Si$ 305.2512, found 305.2524. $[\alpha]_D^{22}$ = 23 (c 0.91, $CHCl_3$).

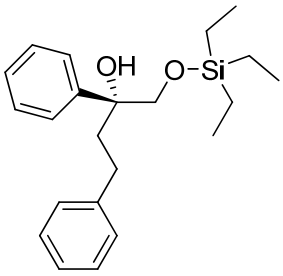
General procedure for the homologation of boronates with styrene oxide leading to compounds 9.

A 10 ml Schlenk tube was charged with (*R*)-styrene oxide (46 μL, 0.40 mmol) and TMEDA (180 μL, 1.20 mmol) in 2.75 mL of ether. The resulting solution was thereafter cooled to -115°C followed by dropwise addition of *s*BuLi (1.3 M in hexanes, 370 μL, 0.48 mmol). The resulting mixture was stirred at -115°C for 10 min. A solution of the corresponding boronic ester (0.50 mmol) in ether (1.25 mL) was then slowly added and the mixture was then stirred at -110°C for 10 min. TES-OTf (113 μL, 0.50 mmol) was added and the resulting mixture was allowed to warm to room temperature. The reaction flask was transferred to an ice bath. 3 mg of 2,6-di-tert-butyl-4-methylphenol were added, followed by a mixture of NaOH (1.0 ml, 2.0 M) and H_2O_2 (0.50 ml, >30% w/v), previously degazed under vacuum. The reaction mixture was stirred an additional 10 min at room temperature and was then diluted

with H_2O (5 ml) and extracted with ether (4 × 7 ml). The organic solvents were then removed and the crude product was subjected to silica gel flash chromatography.

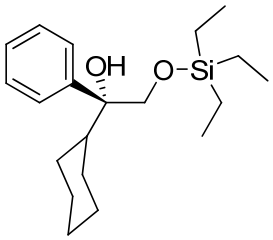


(*R*)-2-phenyl-1-(triethylsilyloxy)butan-2-ol (9a). This compound was synthesised according to the general procedure using MTBE as solvent and was purified by flash chromatography (SiO_2, 1% Et_2O/Petrol) which afforded 97 mg of a colourless oil (87%). R_f 0.60 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3553, 3062, 3029; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 8.4 Hz, 2H), 7.24-7.28 (m, 1H), 3.74 (d, J = 9.3 Hz, 1H), 3.70 (d, J = 9.3 Hz, 1H), 2.97 (s, 1H), 1.94 (dq, J = 14.9, 7.3 Hz, 1H), 1.80 (dq, J = 14.9, 7.3 Hz, 1H), 0.93 (t, J = 7.9 Hz, 9H), 0.78 (t, J = 7.3 Hz, 3H), 0.57 (q, J = 7.9 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 143.8, 128.1, 126.7, 125.6, 76.8, 70.7, 31.2, 7.8, 6.8, 4.4; MS (ESI) m/z 303 ($M+Na^+$), 245, 239, 151; HRMS (ESI) calcd for $C_{16}H_{28}O_2Si + Na^+$ 303.1745, found 303.1750; $[\alpha]_D^{22}$ = -4.5 (c 0.22, $CHCl_3$) (e.r. = 97:3); t_R = 7.0 min (*S*-minor), 7.5 min (*R*-major) Daicel Chiralcel-AD column, 0.5% iPrOH in Hexane 1 mL/min.



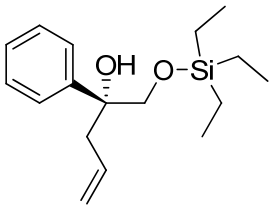
(*R*)-2,4-diphenyl-1-(triethylsilyloxy)butan-2-ol (9b). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 1% Et_2O/Petrol) which afforded 111 mg of a colourless oil (78%). R_f 0.60 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3552, 3087, 3064, 3029; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.50 (m, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.22-7.30 (m, 3H), 7.11-7.17 (m, 3H), 3.74 (d, J = 9.4 Hz, 1H), 3.68 (d, J = 9.4 Hz, 1H), 3.10 (s,

1H), 2.72 (td, *J* = 13.6, 4.2 Hz, 1H), 2.18-2.37 (m, 2H), 2.01-2.11 (m, 1H), 0.90 (t, *J* = 7.6 Hz, 9H), 0.55 (q, *J* = 7.6 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 143.4, 142.9, 128.4, 128.3, 126.9, 125.7, 125.5, 76.5, 71.0, 40.6, 29.9, 6.8, 4.4; MS (ESI) m/z 379 ($M+Na^+$), 339, 245; HRMS (ESI) calcd for $C_{22}H_{32}O_2Si + Na^+$ 379.2059, found 379.2063; $[\alpha]_D^{22}$ = -22.2 (c 0.81, $CHCl_3$) (e.r. = 95:5); t_R = 14.1 min (*S*-minor), 17.8 min (*R*-major) Daicel Chiralcel-OD-H column, 0.5% iPrOH in Hexane 0.5 mL/min.

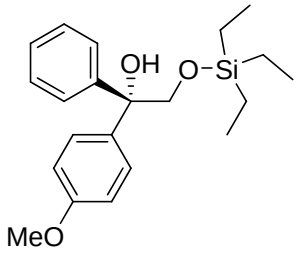


(*R*)-1-cyclohexyl-1-phenyl-2-(triethylsilyloxy)ethanol (9c). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 2% Et_2O/Petrol) which afforded 90 mg of a colourless oil (68%). R_f 0.60 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3694, 2957, 2931, 2875; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.31-7.35 (m, 2H), 7.22-7.26 (m, 1H), 3.96 (d, *J* = 9.5 Hz, 1H),, 3.88 (d, *J* = 9.5 Hz, 1H), 3.03 (s, 1H), 1.89-1.96 (m, 1H), 1.48-1.78 (m, 5H), 0.92-1.29 (m, 5H), 0.89 (t, *J* = 7.8 Hz, 9H), 0.53 (q, *J* = 7.8 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 144.1, 127.6, 126.4, 126.1, 78.1, 67.8, 45.8, 27.7, 27.1, 26.9, 26.7, 26.5, 6.7, 4.3; MS (ESI) m/z 357 ($M+Na^+$), 317, 239, 223, 151; HRMS (ESI) calcd for $C_{20}H_{34}O_2Si + Na^+$ 357.2217, found 357.2220. The stereochemistry of **9c** was determined by conversion to 1-cyclohexyl-1-phenylethane-1,2-diol (**9c'**): 59 mg of **9c** were dissolved in 1 mL of THF and tetrabutylammonium fluoride (83 mg, 0.26 mmol) was added. The resulting mixture was stirred at room temperature for 1h. The organic solvents were then removed and the crude product was purified by flash chromatography (SiO_2, 50% Et_2O/Petrol) to yield to 1-cyclohexyl-1-phenylethane-1,2-diol **9c'** as a colorless oil (38 mg, 97%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.46 (m, 4H), 7.27-7.32 (m, 1H), 4.05 (dd, *J* = 11.2, 4.2 Hz, 1H), 3.88 (dd, *J* = 11.2, 9.0 Hz, 1H), 2.63 (s, 1H), 0.99-1.90 (m, 11H); ^{13}C (100 MHz,

$CDCl_3$) δ 143.2, 128.3, 127.0, 126.3, 79.3, 69.3, 45.6, 27.3, 26.9, 26.7, 26.6, 26.4.[6] $[\alpha]_D^{22}$ = +21.1 (c 0.19, $CHCl_3$) (e.r. = 99:1); t_R = 47.2 min (*R*-major), 53.7 min (*S*-minor) Daicel Chiralcel-OD-H column, 2.5% iPrOH in Hexane 0.5 mL/min.



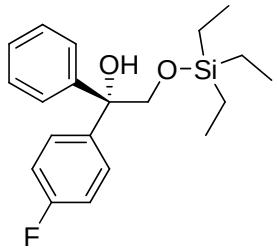
(*R*)-2-phenyl-1-(triethylsilyloxy)pent-4-en-2-ol (9d). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 1% Et_2O/Petrol) which afforded 101 mg of a colourless oil (86%). R_f 0.60 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3554, 3079, 2958, 1640; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.45 (m, 2H), 7.31-7.36 (m, 2H), 7.24-7.26 (m, 1H), 5.67 (ddt, *J* = 17.3, 10.1, 7.1 Hz, 1H), 4.99-5.09 (m, 2H), 3.75 (d, *J* = 9.5 Hz, 1H), 3.68 (d, *J* = 9.5 Hz, 1H), 2.99 (s, 1H), 2.68 (dd, J = 14.2, 7.1 Hz, 1H), 2.61 (dd, J = 14.2, 7.1 Hz, 1H),0.91 (t, *J* = 8.1 Hz, 9H), 0.56 (q, *J* = 8.1 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 143.8, 133.9, 128.1, 126.9, 125.6, 118.2, 75.9, 70.2, 43.4, 6.8, 4.4; MS (ESI) m/z 315 ($M+Na^+$), 275, 245, 239, 151; HRMS (ESI) calcd for $C_{17}H_{28}O_2Si + Na^+$ 315.1746, found 315.1750; $[\alpha]_D^{22}$ = -3.7 (c 0.27, $CHCl_3$) (e.r. = 96:4); t_R = 8.3 min (*S*-minor), 9.9 min (*R*-major) Daicel Chiralcel-OD-H column, 0.5% iPrOH in Hexane 1 mL/min.



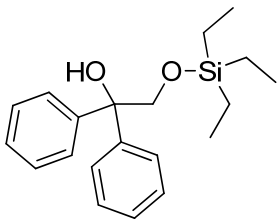
(*S*)-1-(4-methoxyphenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9e). This compound was synthesised according to the general procedure and was purified by flash

[6] All spectral data corresponded to literature values: K. P. M. Vanhessche, K. B. Sharpless, *J. Org. Chem.* **1996**, *61*, 7978.

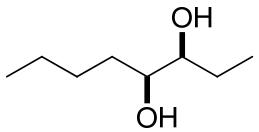
chromatography (SiO_2, 2% Et_2O/Petrol) which afforded 114 mg of a colourless oil (80%). R_f 0.50 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3540, 2958, 2913, 2877; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.1 Hz, 2H), 7.33-7.39 (m, 4H), 7.25-7.28 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.12 (s, 2H), 3.82 (s, 3H), 3.59 (s, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 158.7, 145.0, 137.0, 128.1, 128.0, 126.7, 113.5, 76.9, 69.5, 55.3, 6.8, 4.4; MS (ESI) m/z 381 ($M+Na^+$), 341, 273, 245, 151; HRMS (ESI) calcd for $C_{21}H_{30}O_2Si + Na^+$ 381.1853, found 381.1856; $[\alpha]_D^{22}$ = -4.8 (c 0.21, $CHCl_3$) (e.r. = 94:6); t_R = 18.7 min (*R*-minor), 22.1 min (*S*-major) Daicel Chiralcel-AD column, 0.5% iPrOH in Hexane 0.7 mL/min.



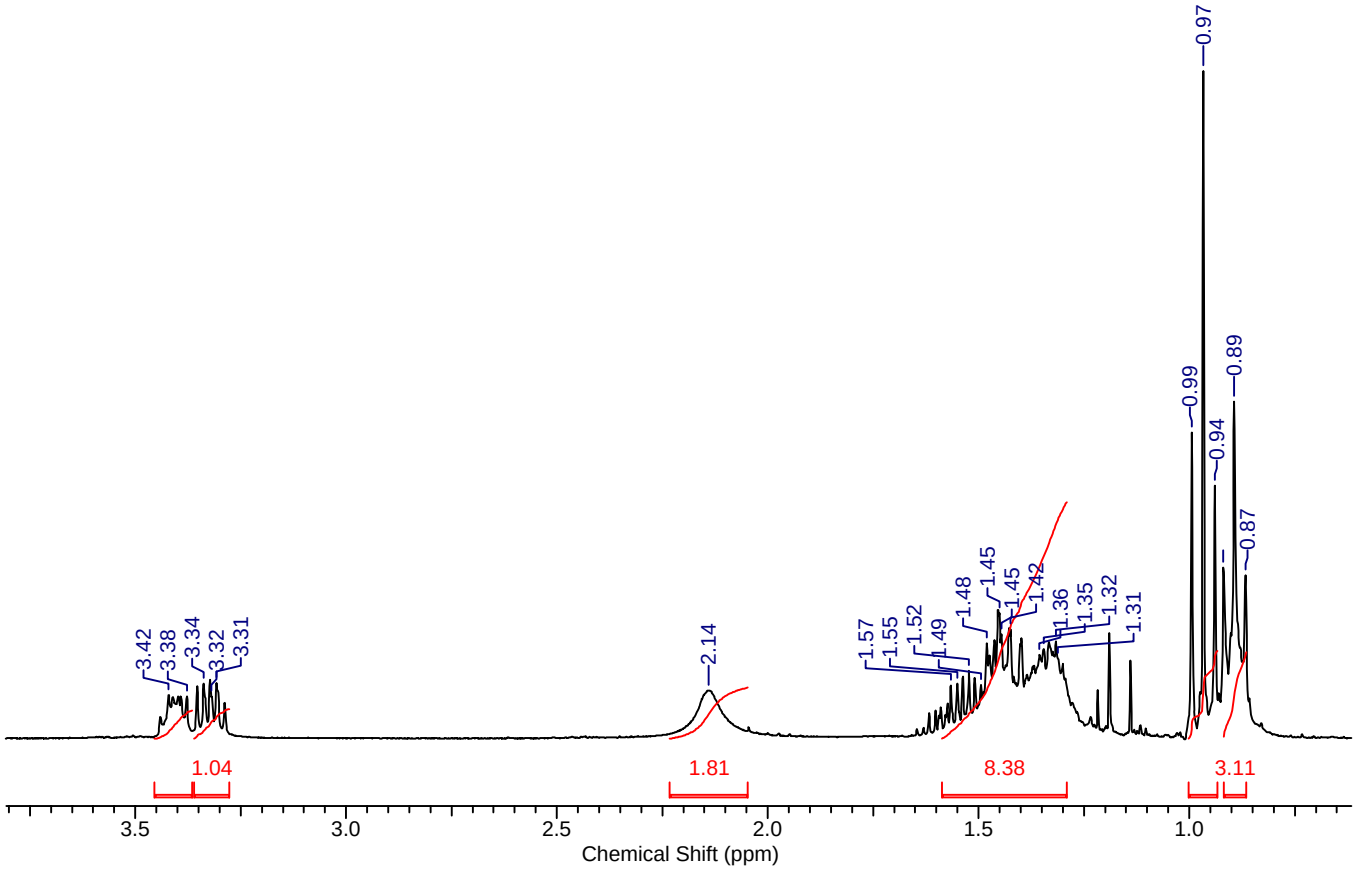
(*S*)-1-(4-fluorophenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9f). This compound was synthesised according to the general procedure (on a 0.46 mmol scale) and was purified by flash chromatography (SiO_2, 1% Et_2O/Petrol) which afforded 95 mg of a colourless oil (63%). R_f 0.50 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3691, 3547, 2959; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.21 (m, 7H), 6.98 (t, J = 8.8 Hz, 2H), 4.08 (s, 2H), 3.59 (s, 1H), 0.91 (t, *J* = 7.8 Hz, 9H), 0.58 (q, *J* = 7.8 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 144.4, 140.6, 128.6, 128.5, 128.2, 127.3, 126.6, 115.0, 114.7, 77.8, 69.3, 6.8, 4.4; MS (CI) m/z (%) 329 ((M–H_2O, 50), 201 (10), 75 (100); HRMS (CI) calcd for $C_{20}H_{26}OFSi$ (M–H_2O) 329.1737, found 329.1724; $[\alpha]_D^{22}$ = -7.8 (c 0.19, $CHCl_3$) (e.r. = 99:1); t_R = 10.8 min (*R*-minor), 13.7 min (*S*-major) Daicel Chiralcel-OD-H column, 0.5% iPrOH in Hexane 1 mL/min.

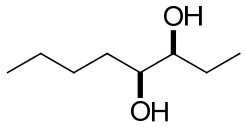


1,1-diphenyl-2-(triethylsilyloxy)ethanol (9g). This compound was synthesised according to the general procedure and was purified by flash chromatography (SiO_2, 0.5% Et_2O/Petrol) which afforded 90 mg of a colourless oil (69%). R_f 0.90 (10% Et_2O/Petrol); IR ν_{max} (thin film) / cm^{-1} 3634, 3064, 3029; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21-7.34 (m, 10H), 4.19 (br s, 3H), 0.90 (t, J = 8.1 Hz, 9H), 0.56 (q, J = 8.1 Hz, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 142.6, 128.7, 128.4, 126.4, 66.6, 53.8, 6.8, 4.5; MS (EI) m/z 336 (10), 283 (60), 117 (80), 84 (100); HRMS (ESI) calcd for $C_{20}H_{28}O_2Si + Na^+$ 351.1756, found 351.1758.

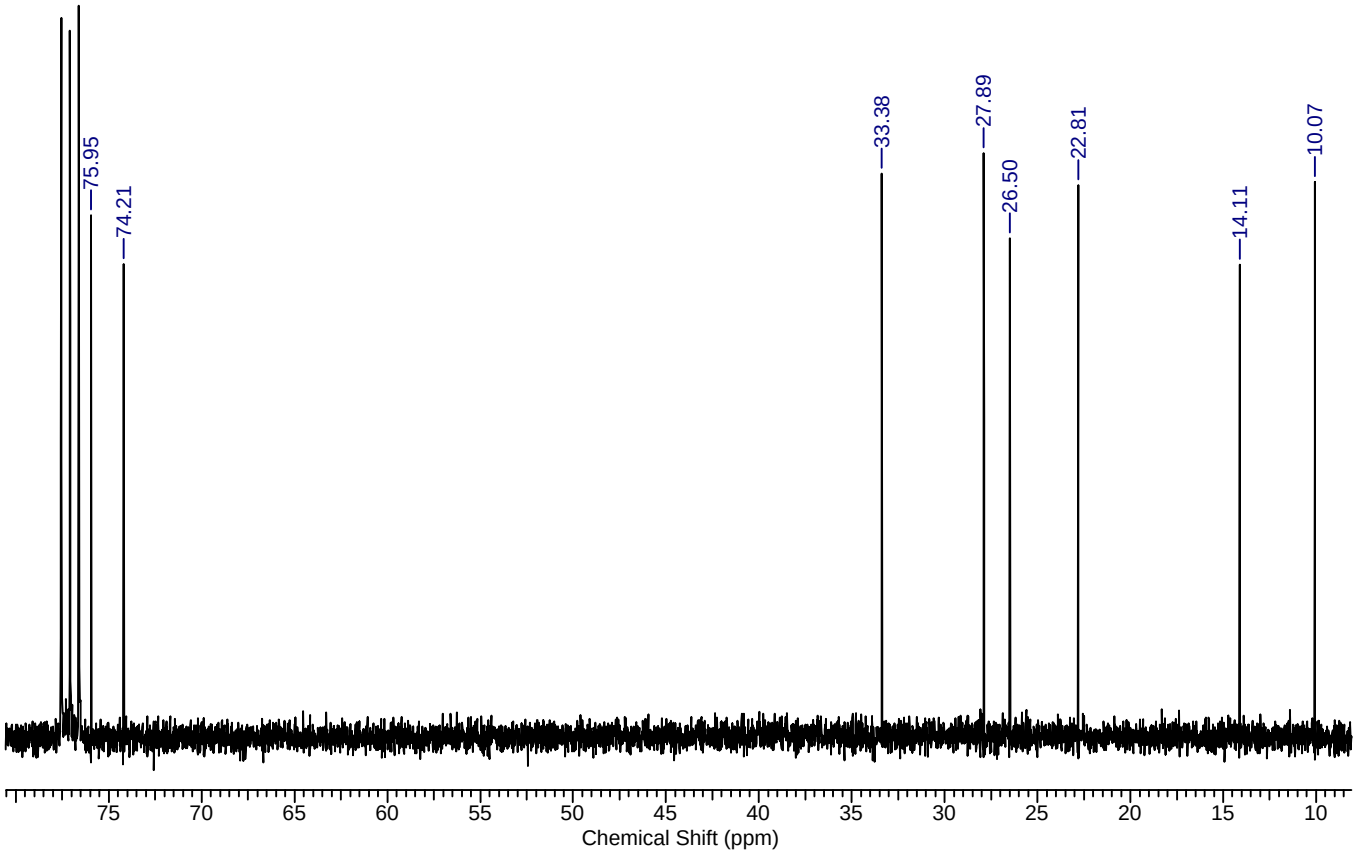


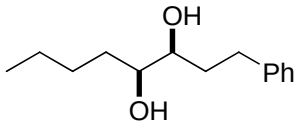
Octane-3,4-diol (3a)



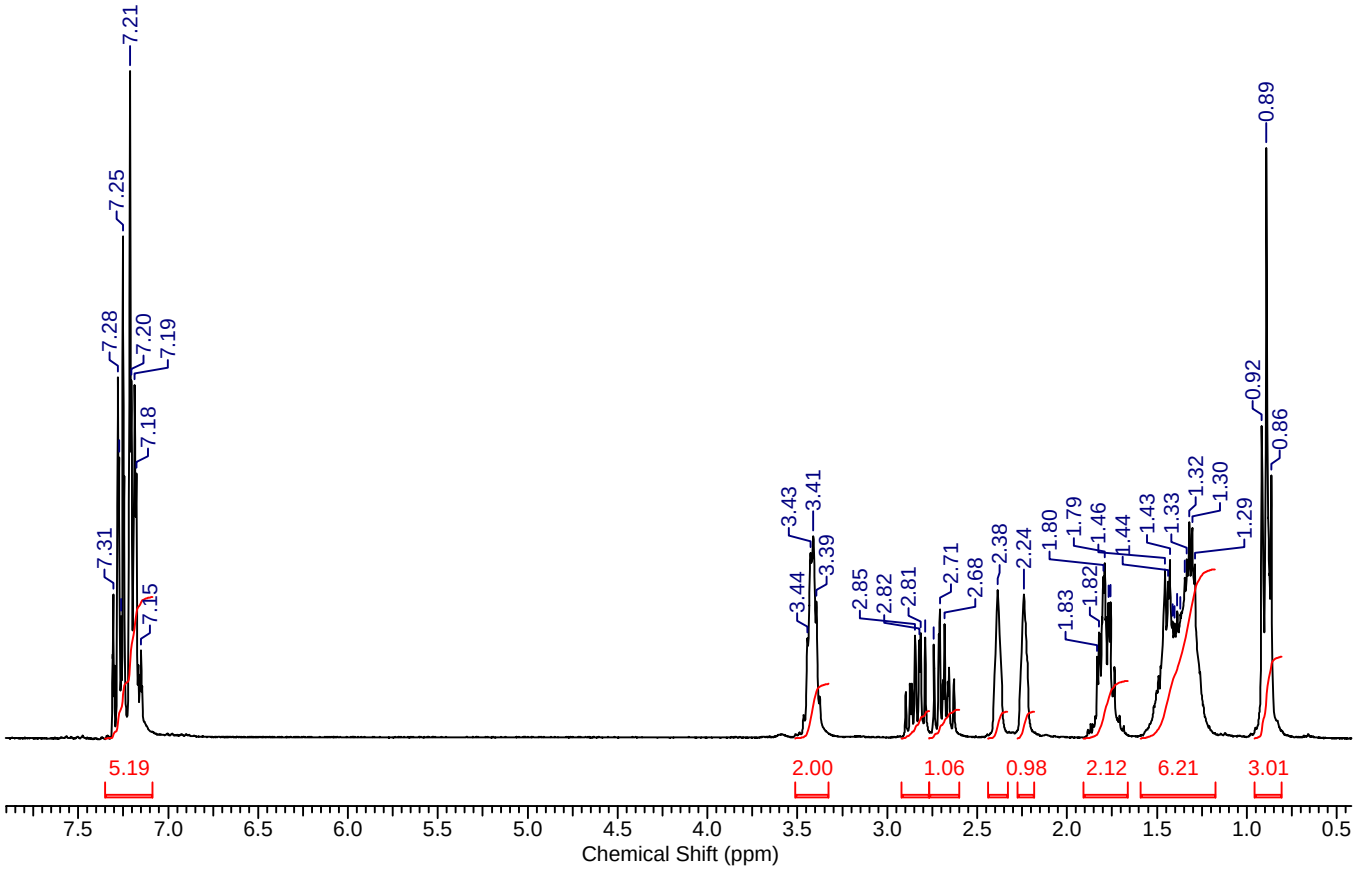


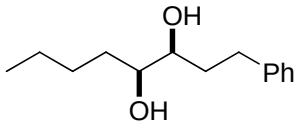
Octane-3,4-diol (3a)



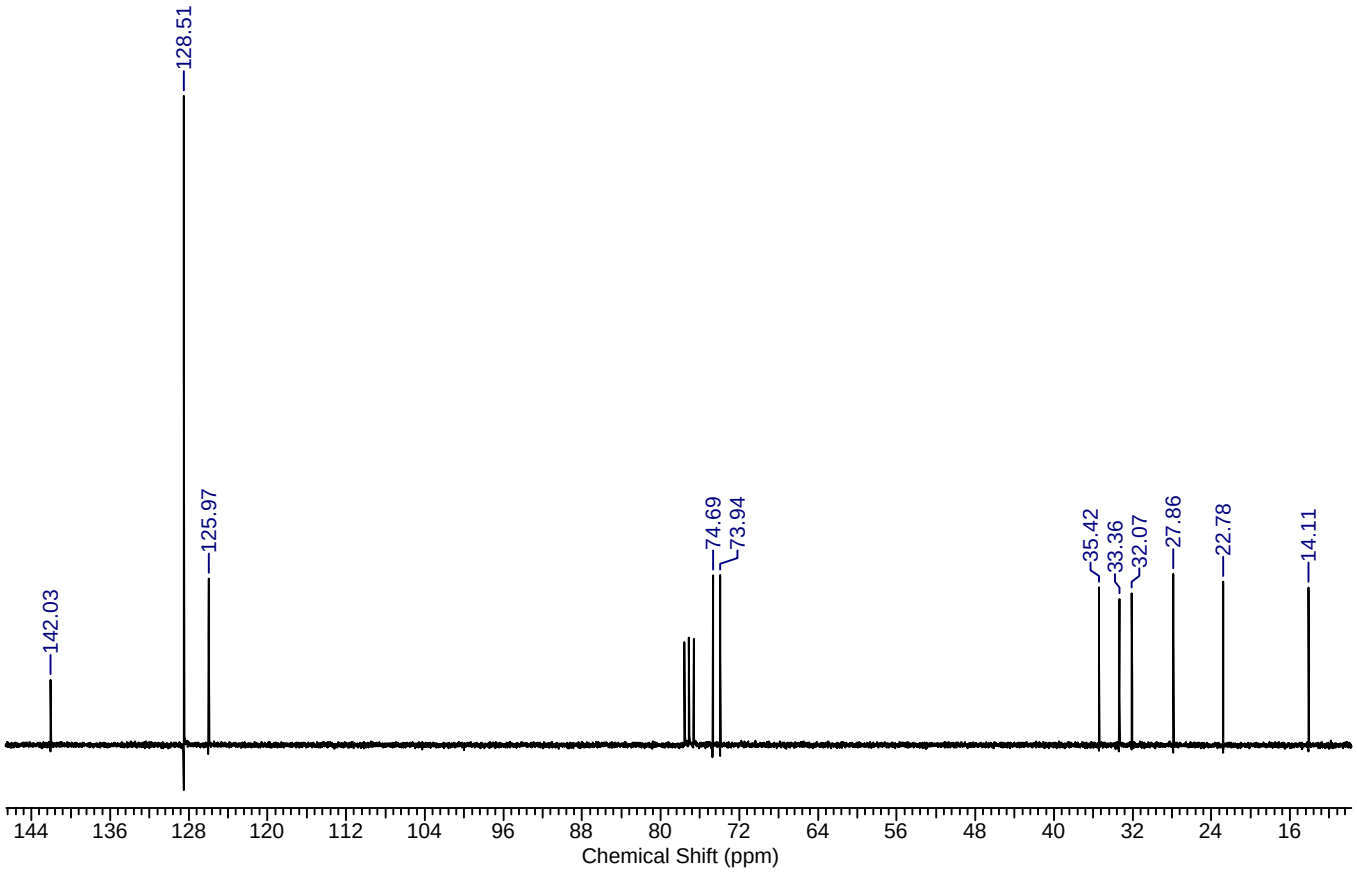


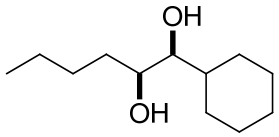
1-Phenylhexane-1,2-diol (3b)



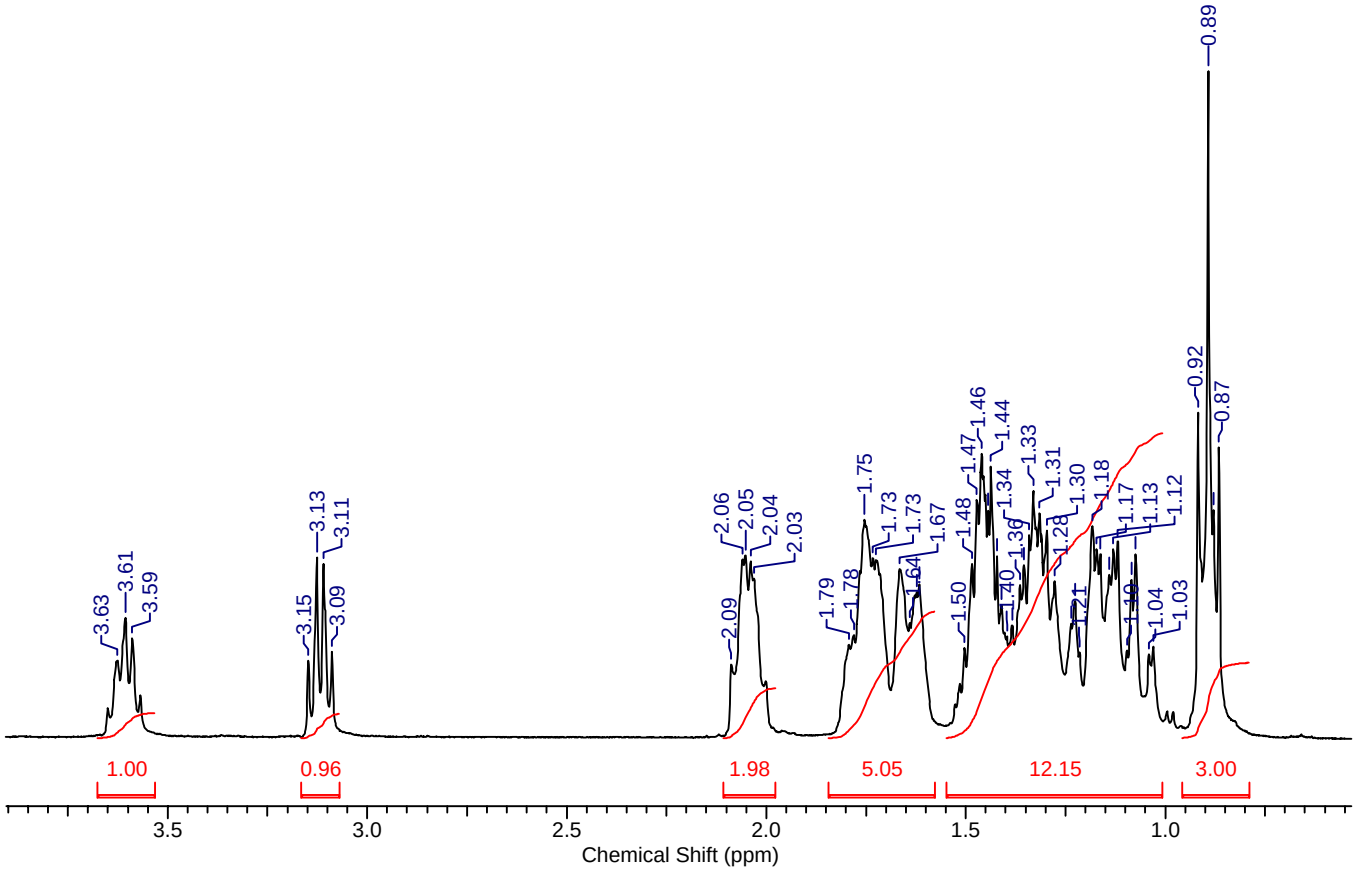


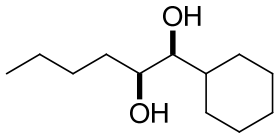
1-Phenylhexane-1,2-diol (3b)



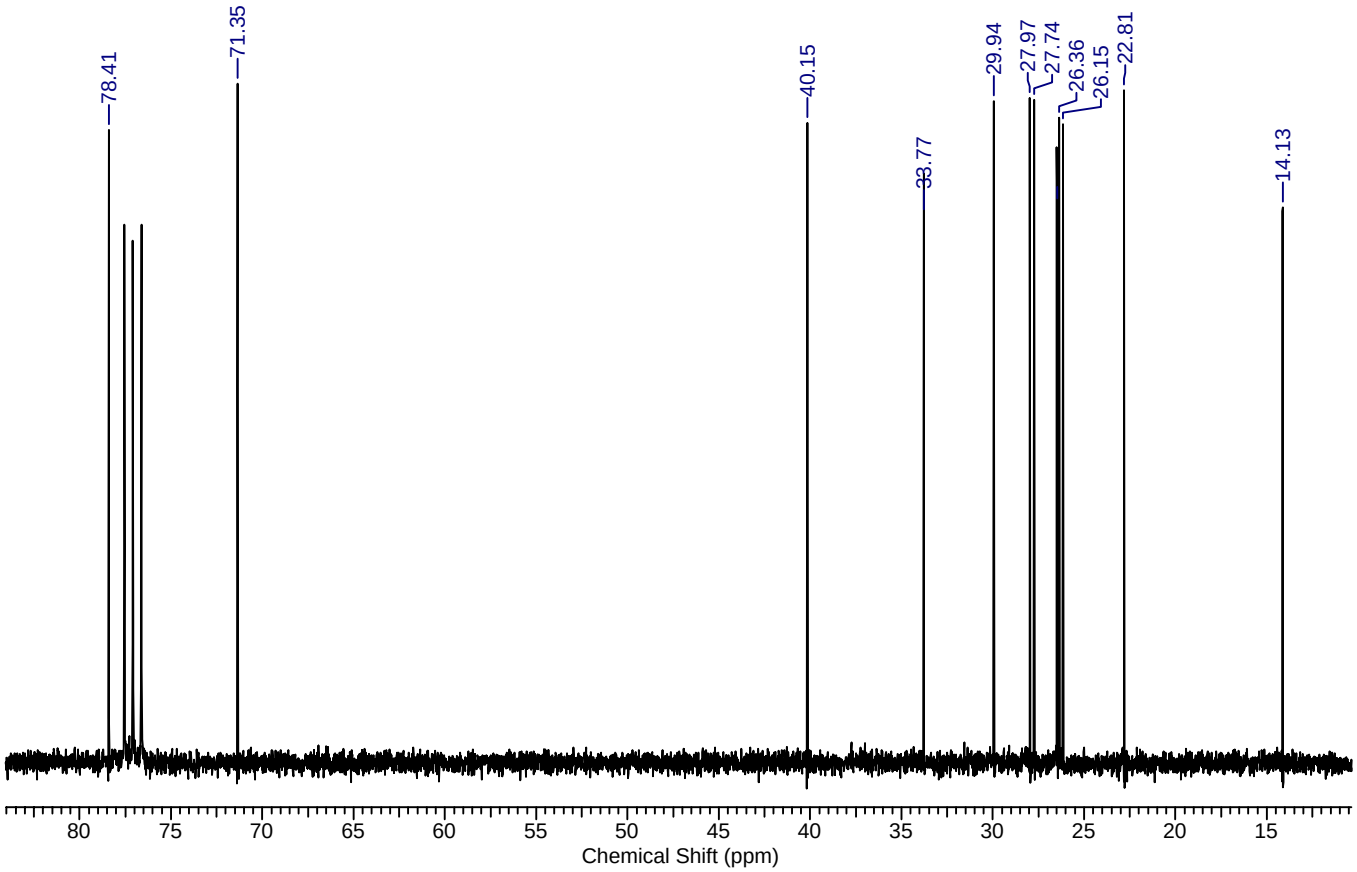


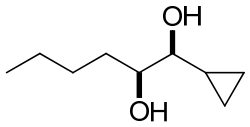
1-Cyclohexylhexane-1,2-diol (3c)



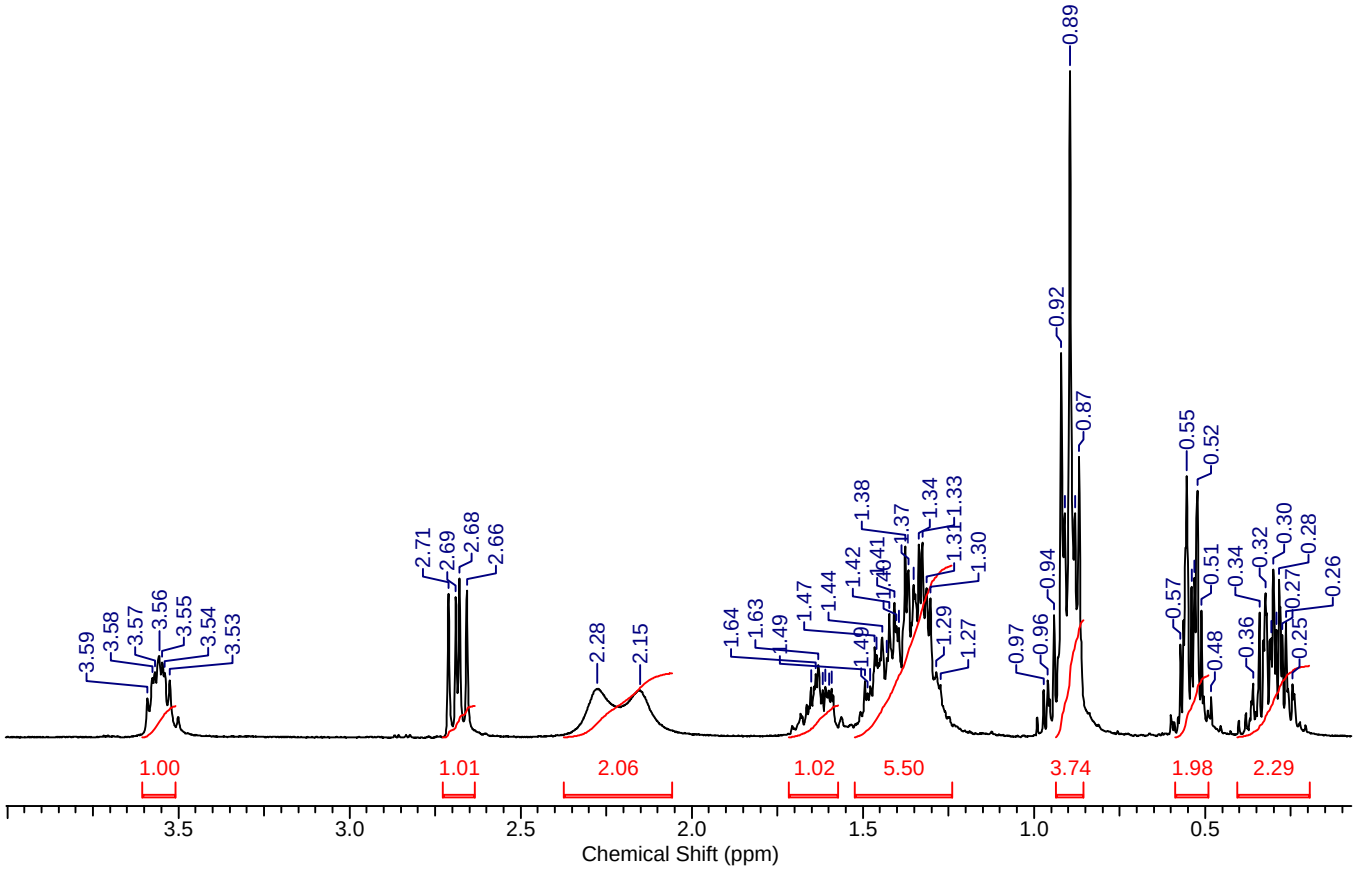


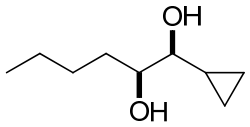
1-Cyclohexylhexane-1,2-diol (3c)



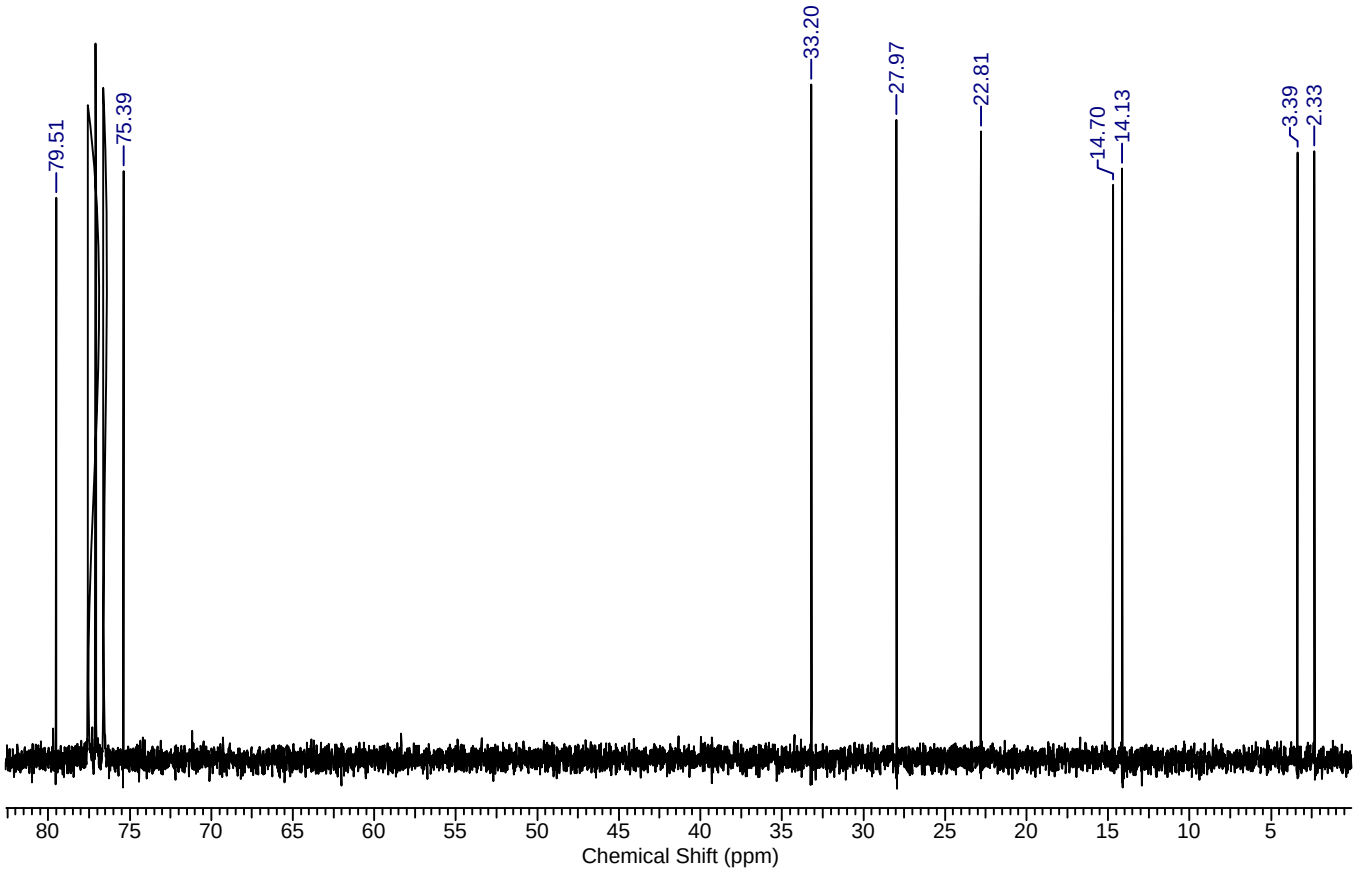


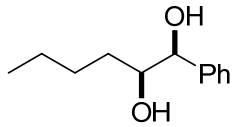
1-Cyclopropylhexane-1,2-diol (3d)



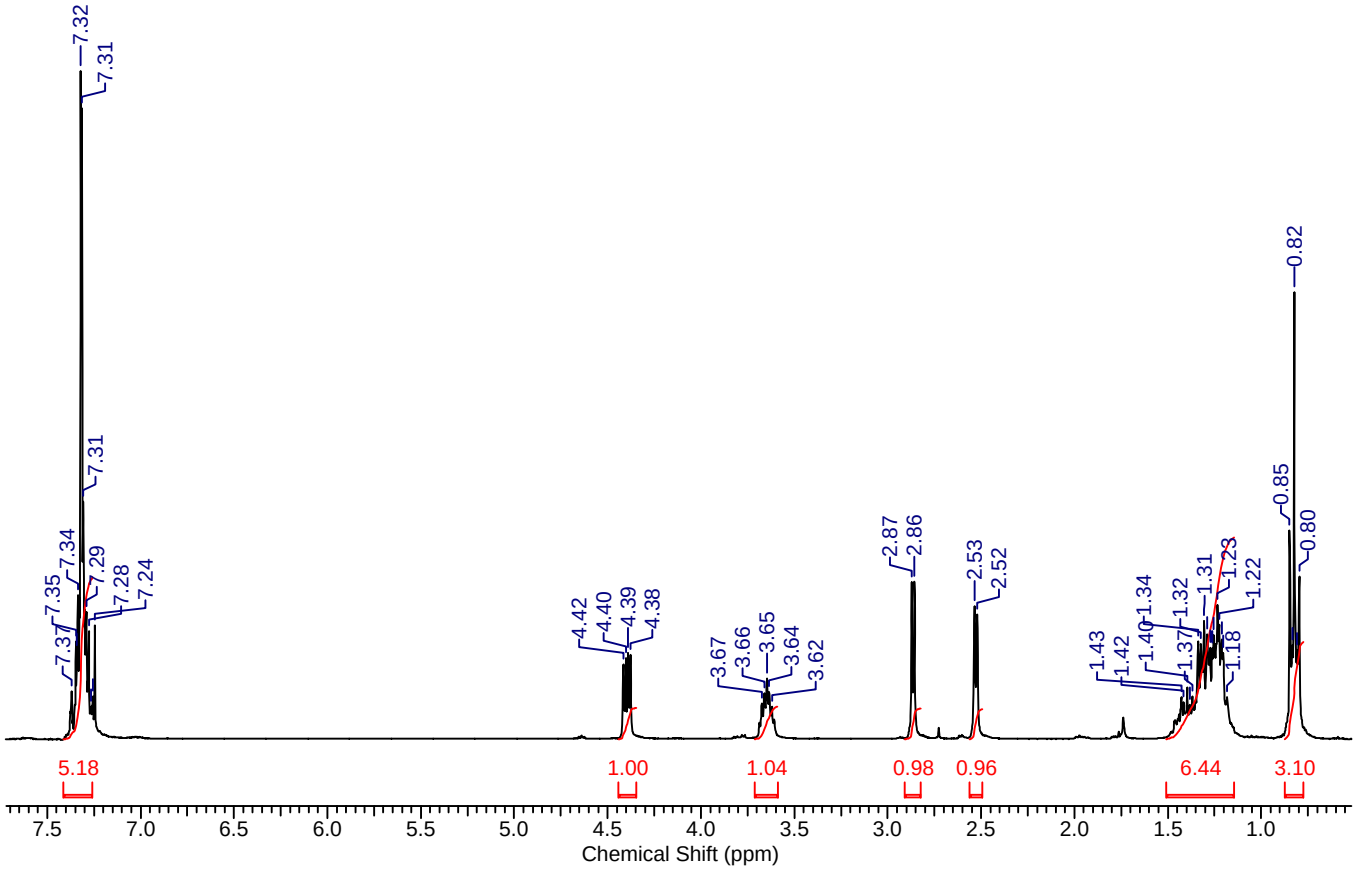


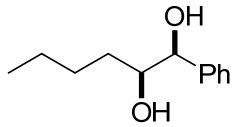
1-Cyclopropylhexane-1,2-diol (3d)



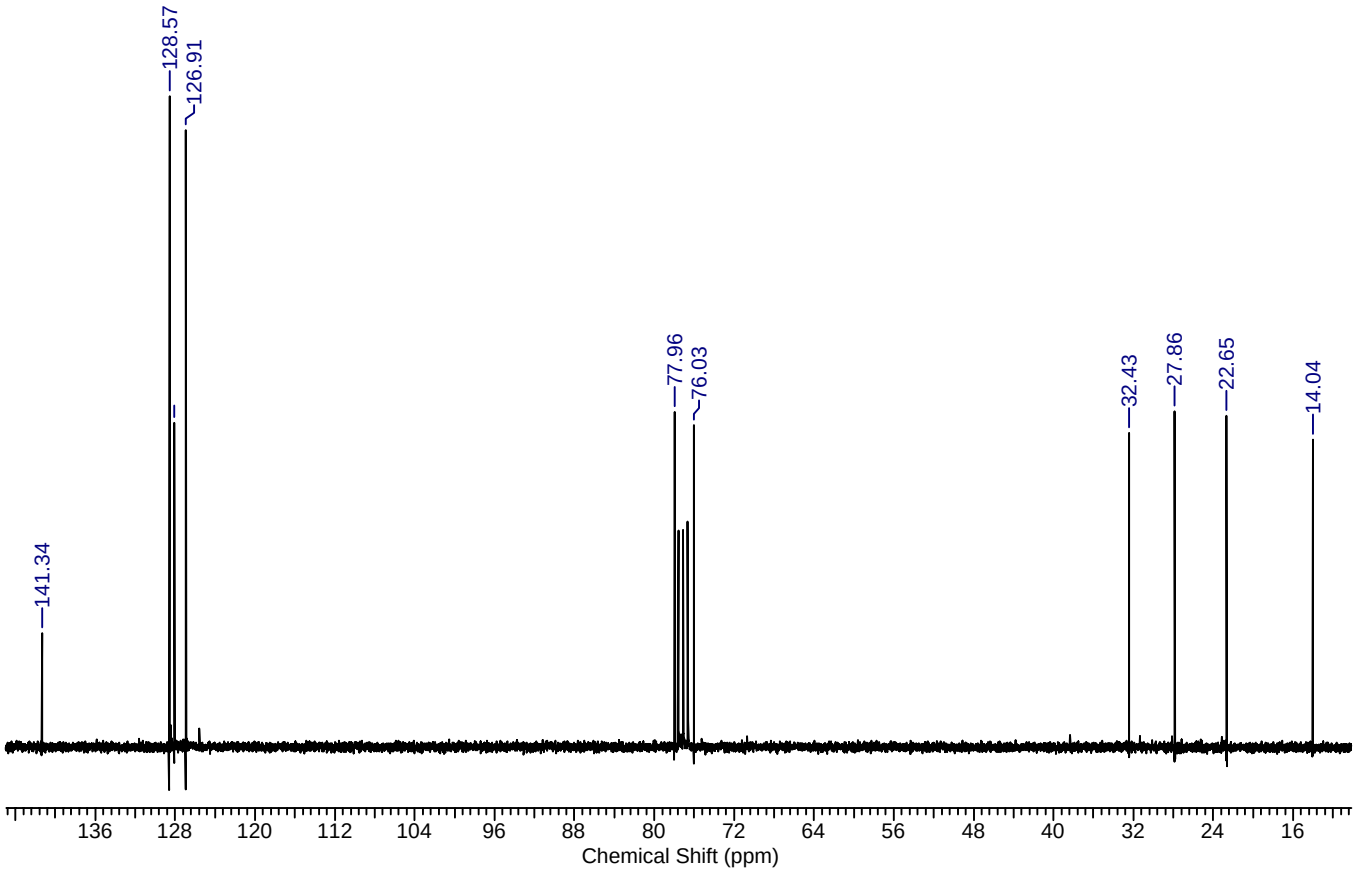


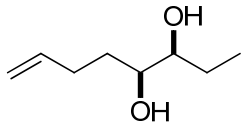
1-Phenyloctane-3,4-diol (3e)



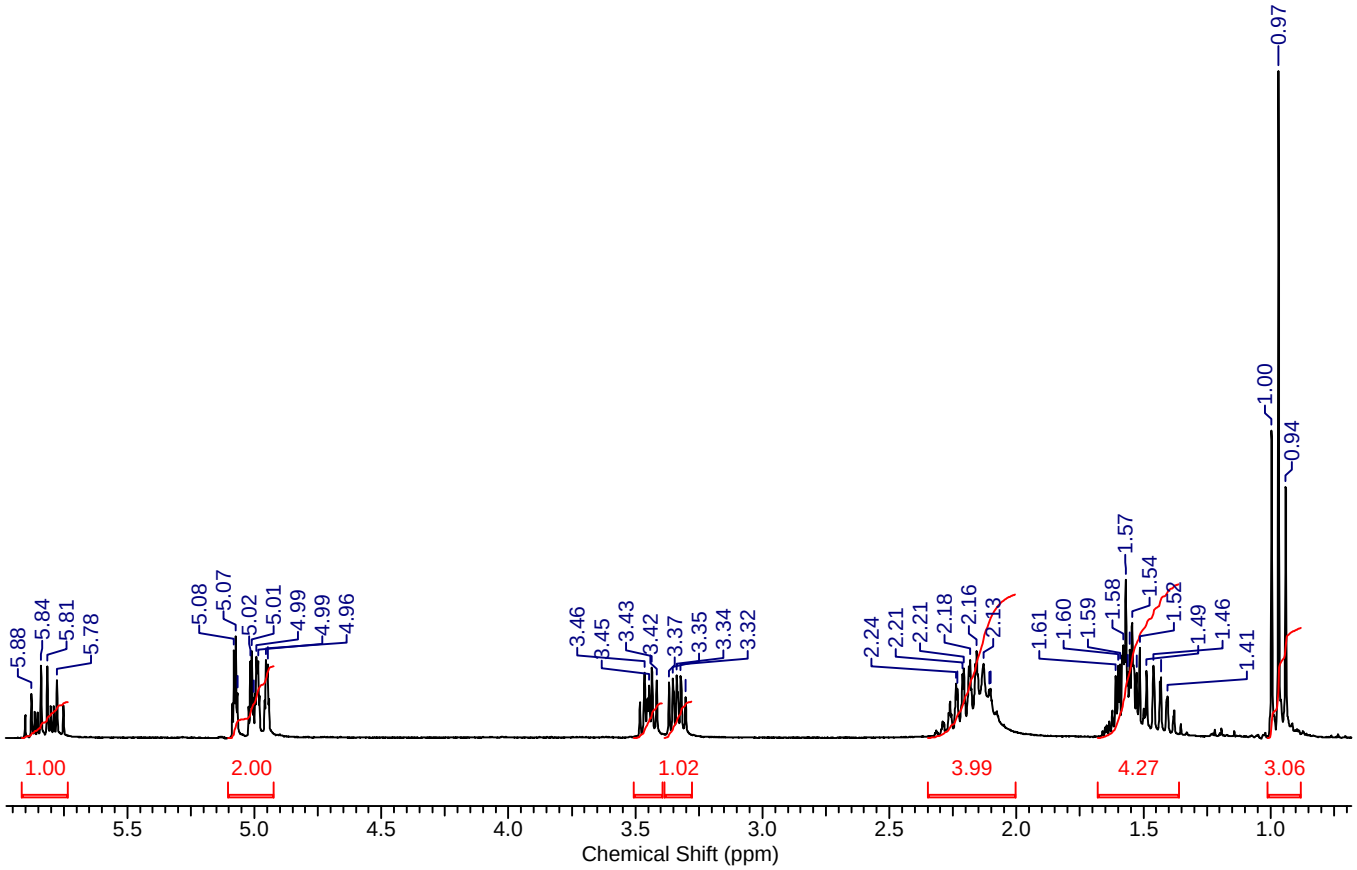


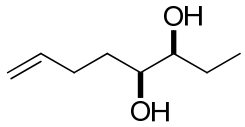
1-Phenyloctane-3,4-diol (3e)



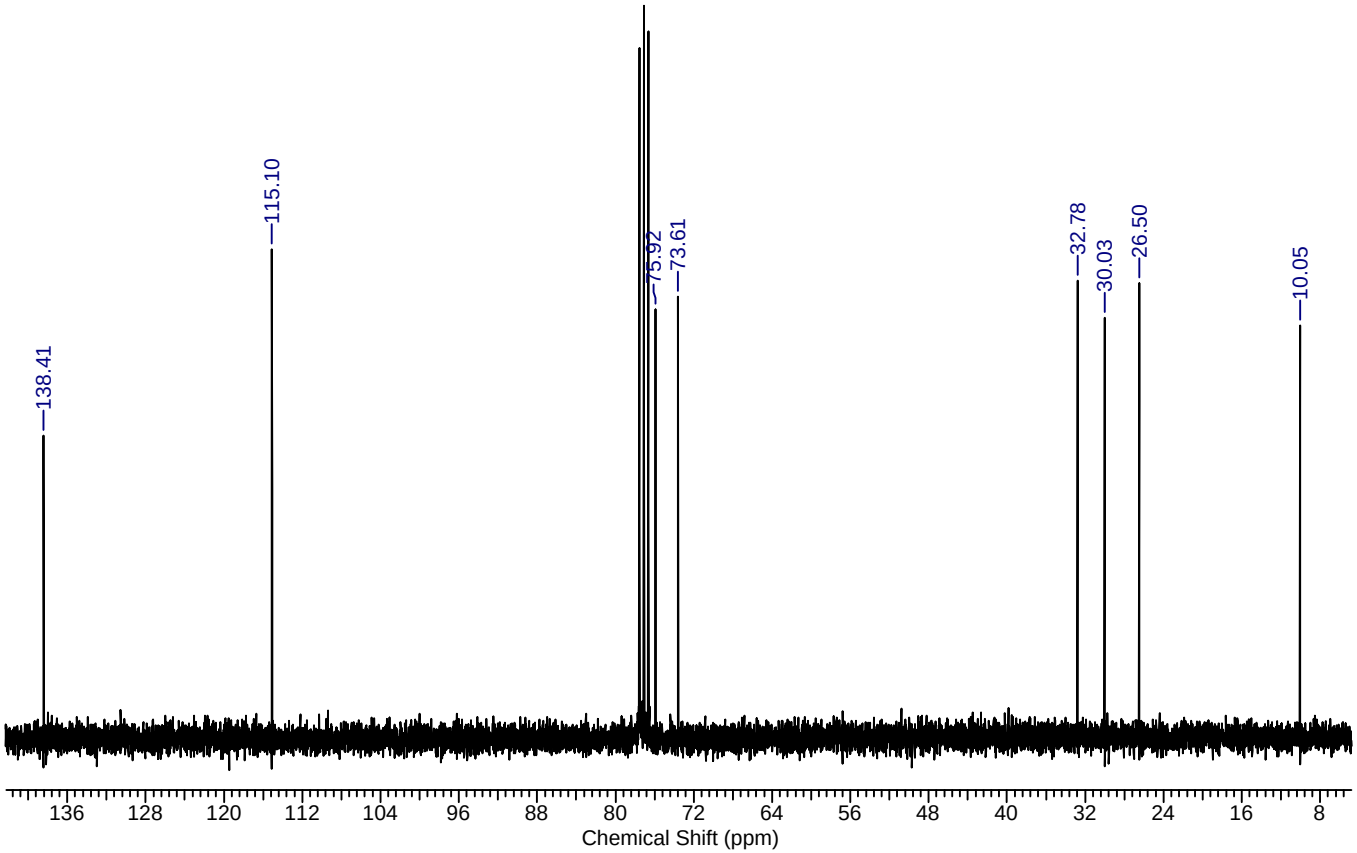


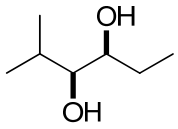
Oct-7-ene-3,4-diol (3f)



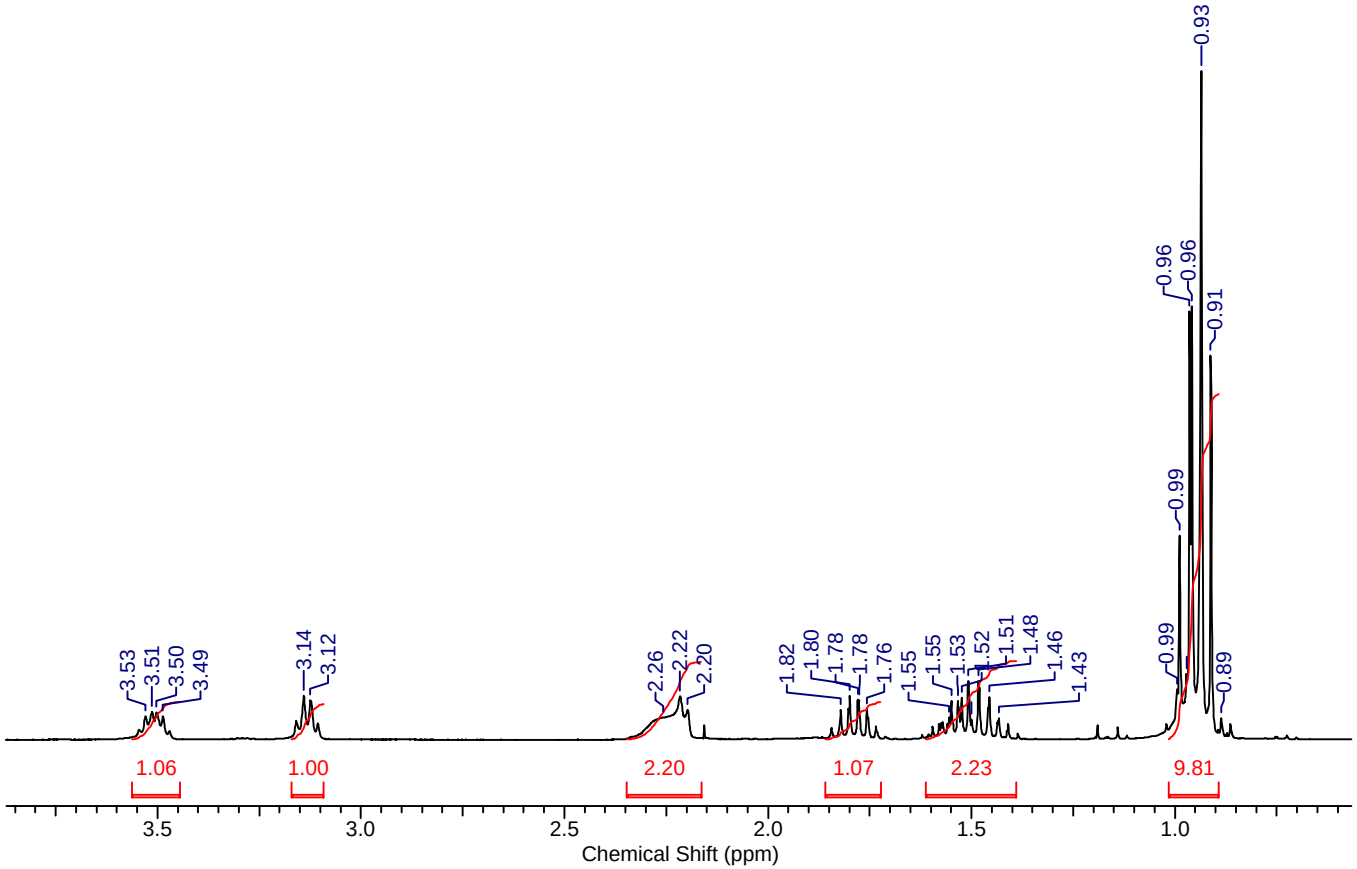


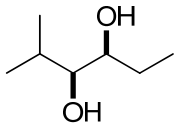
Oct-7-ene-3,4-diol (3f)



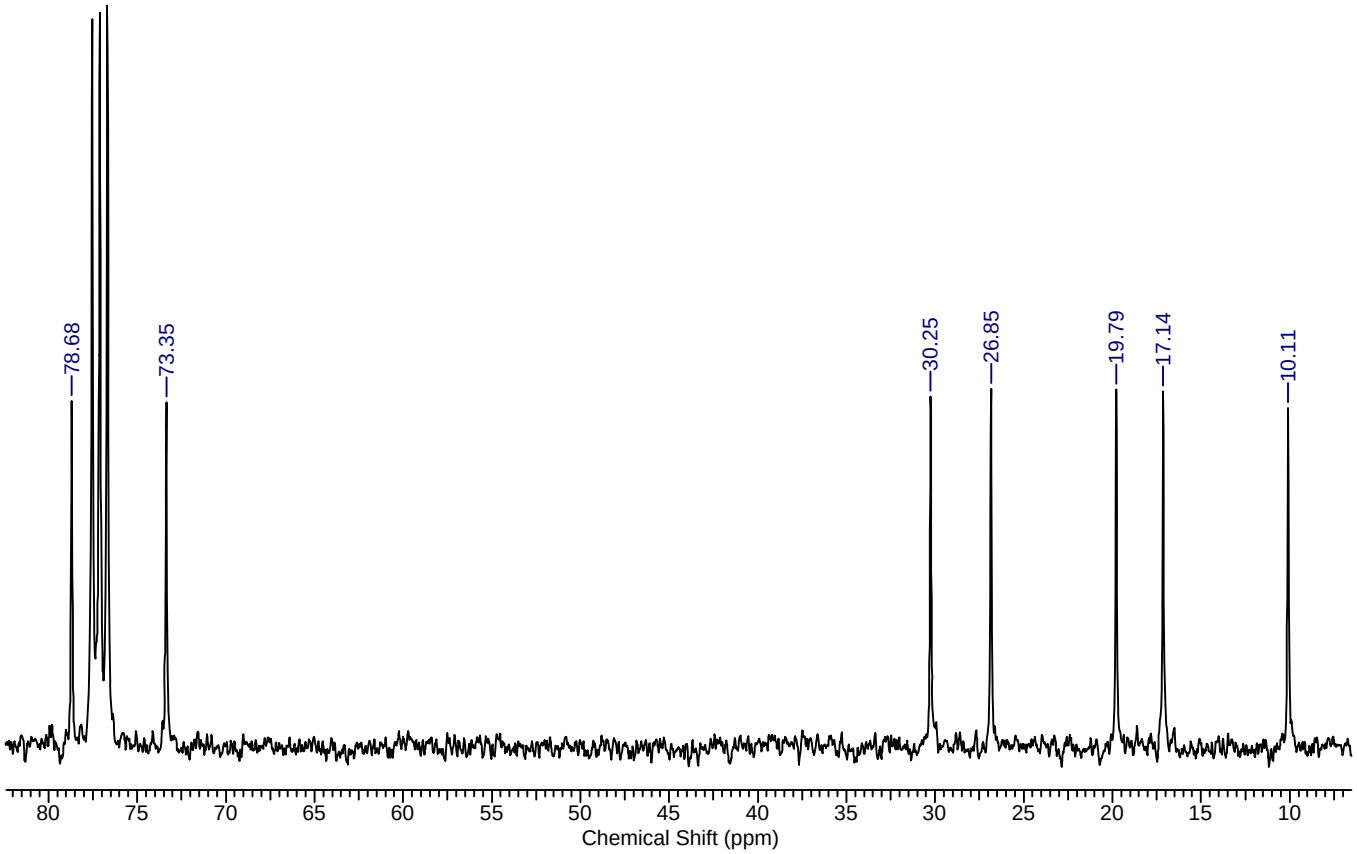


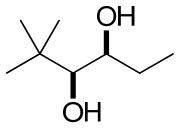
2-Methylhexane-3,4-diol (3g)



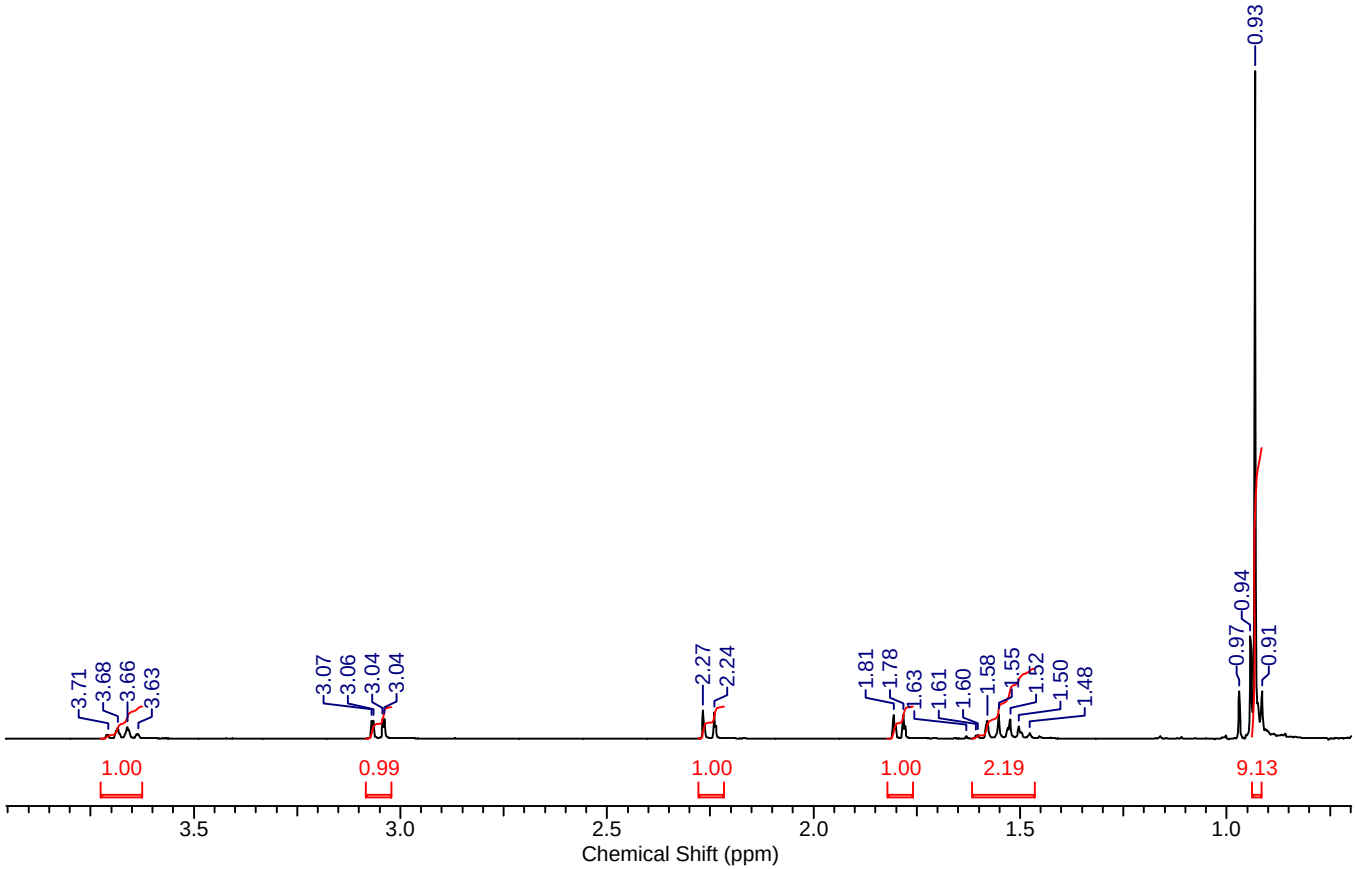


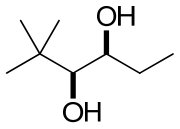
2-Methylhexane-3,4-diol (3g)



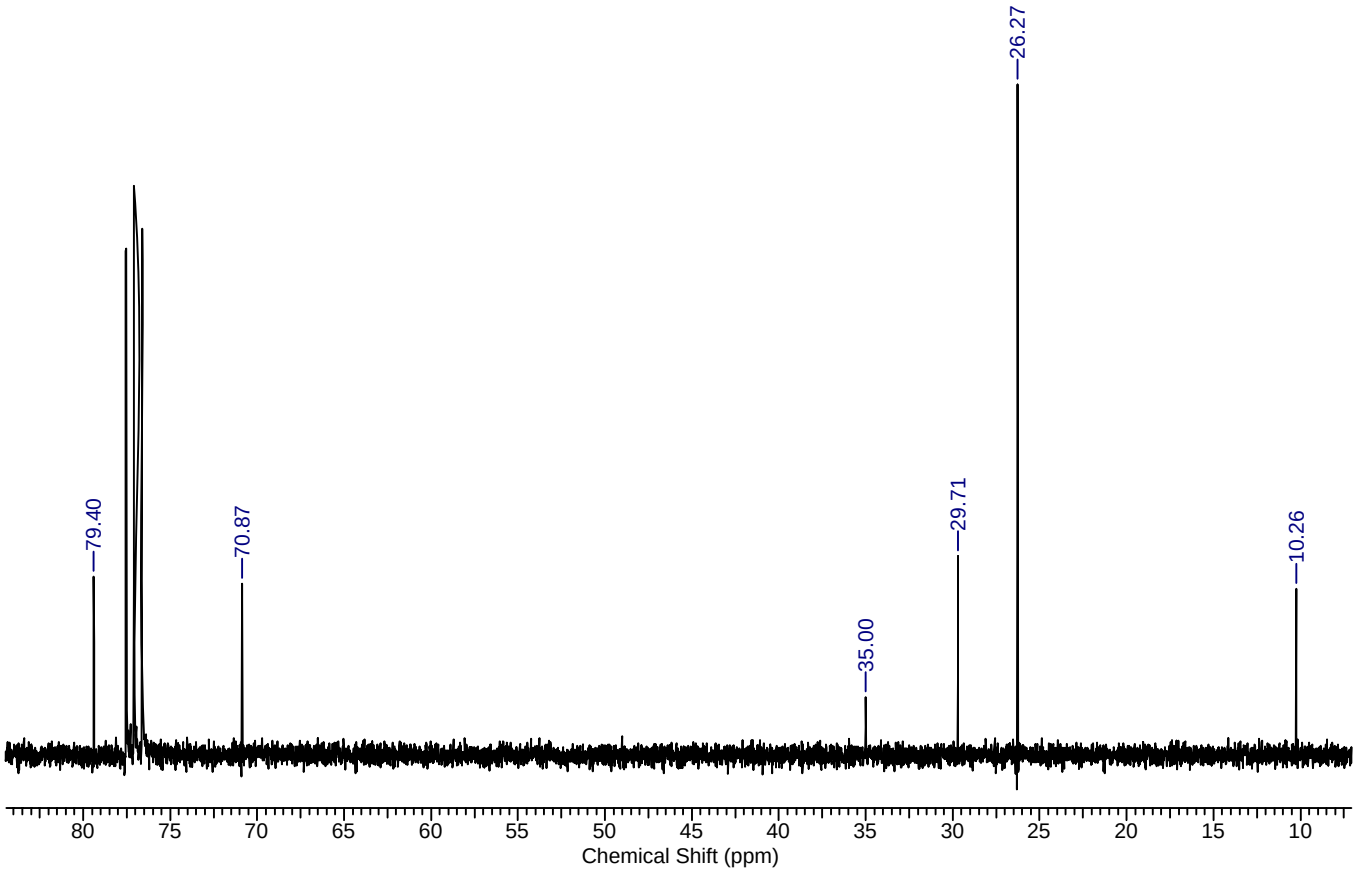


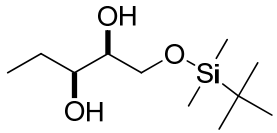
2,2-Dimethylhexane-3,4-diol (3h)



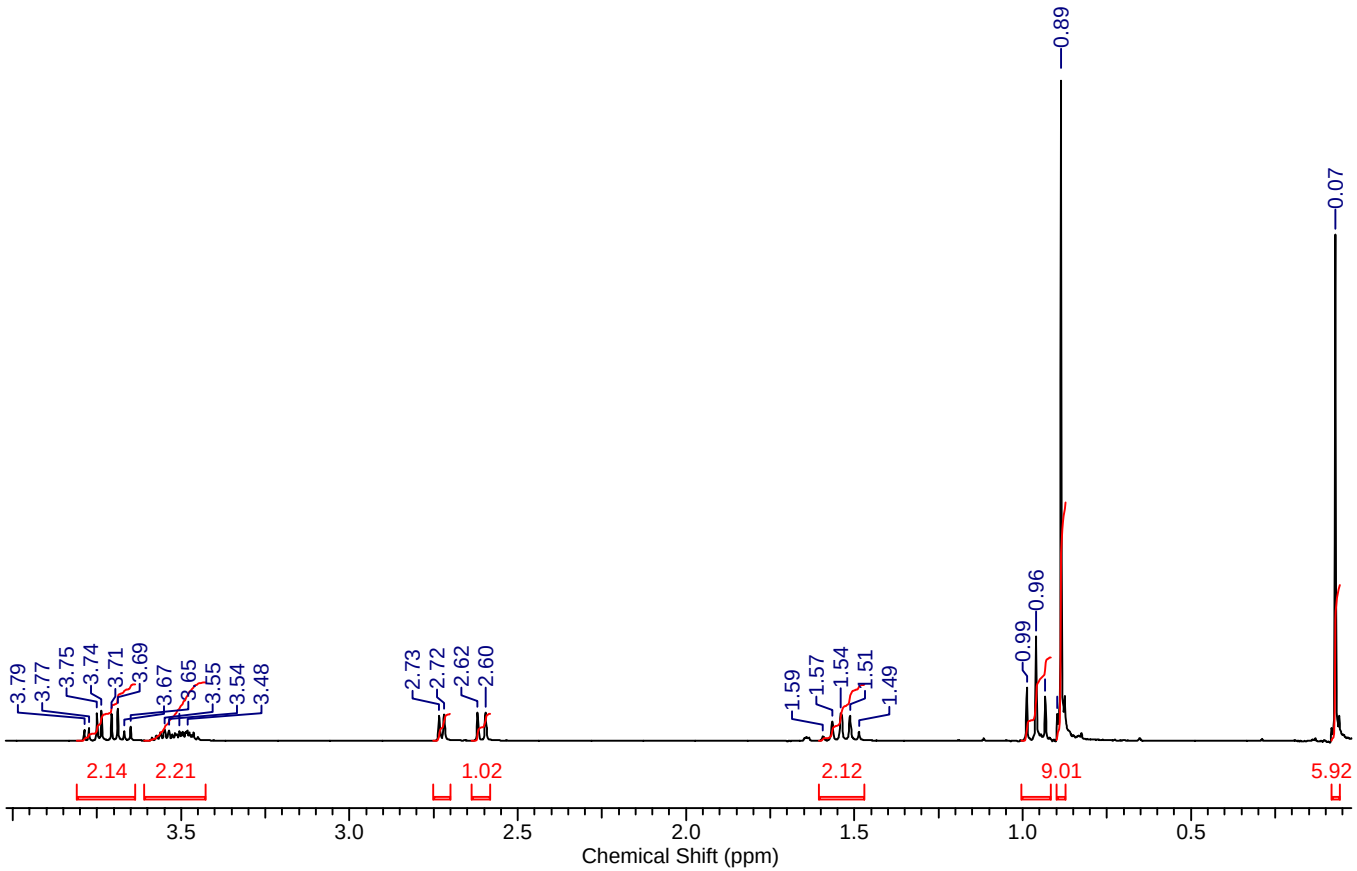


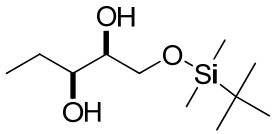
2,2-Dimethylhexane-3,4-diol (3h)



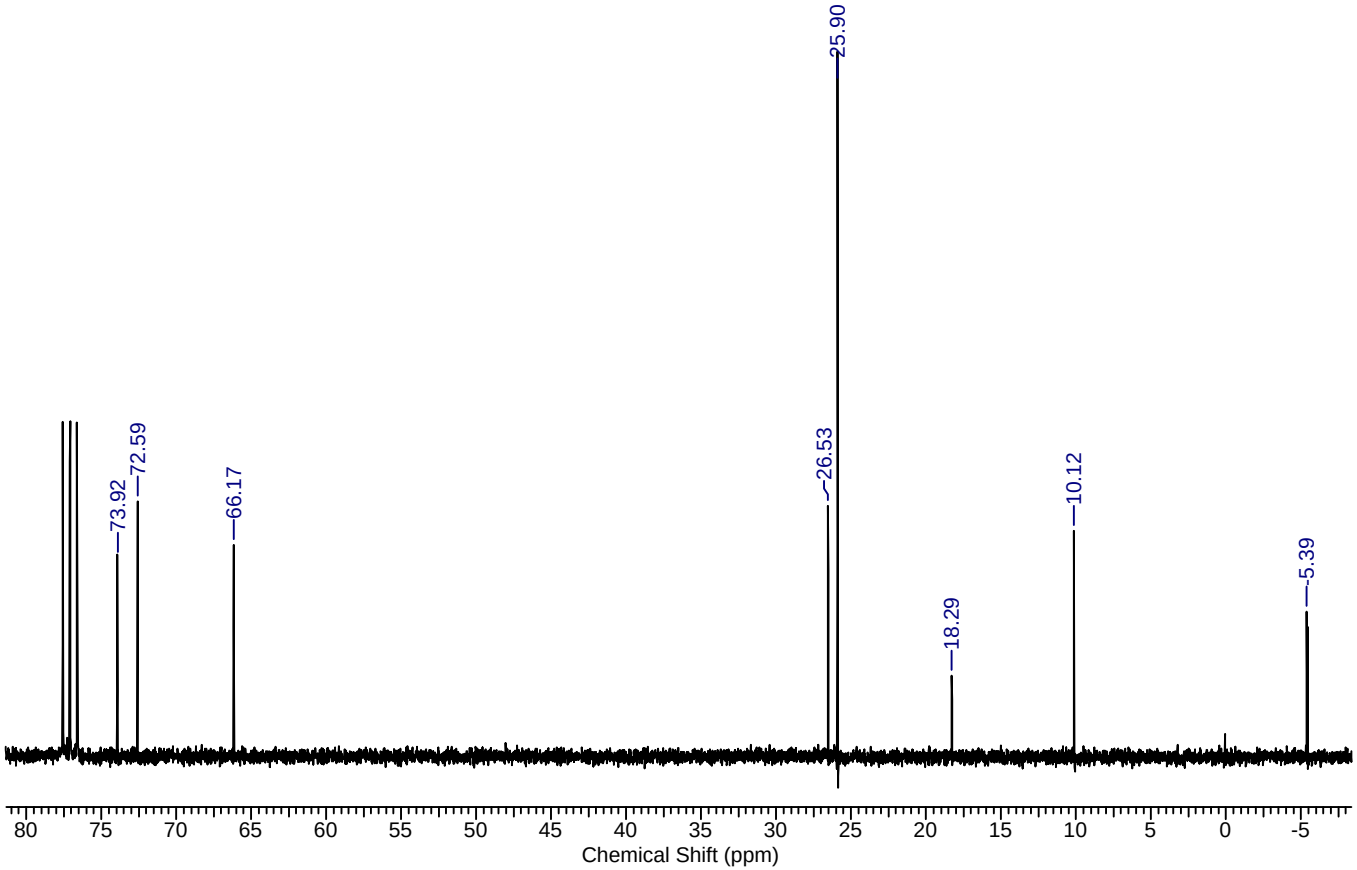


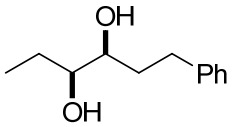
1-(tert-butyldimethylsilyloxy)pentane-2,3-diol (3i)



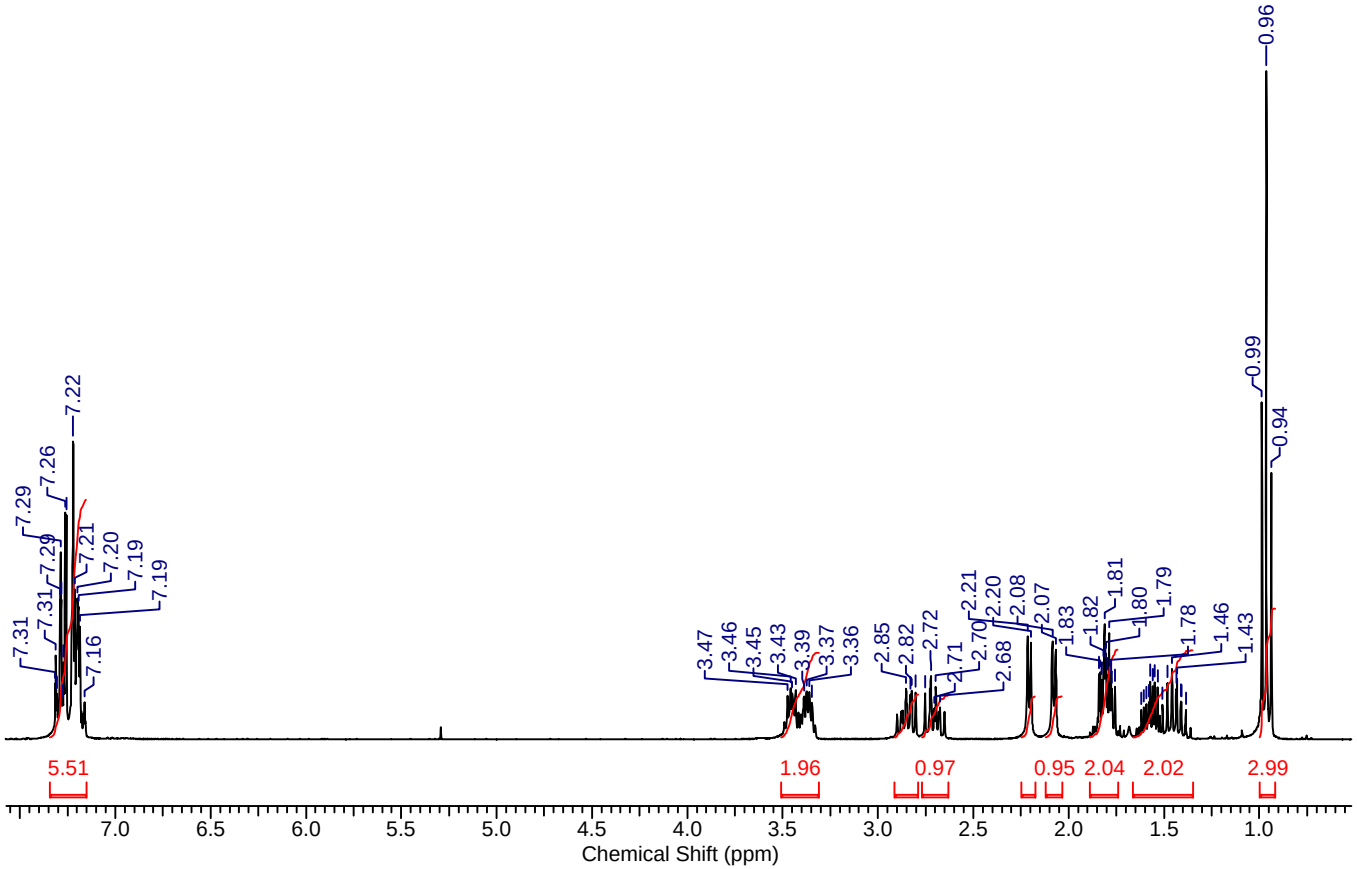


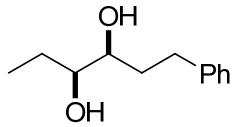
1-(tert-butyldimethylsilyloxy)pentane-2,3-diol (3i)



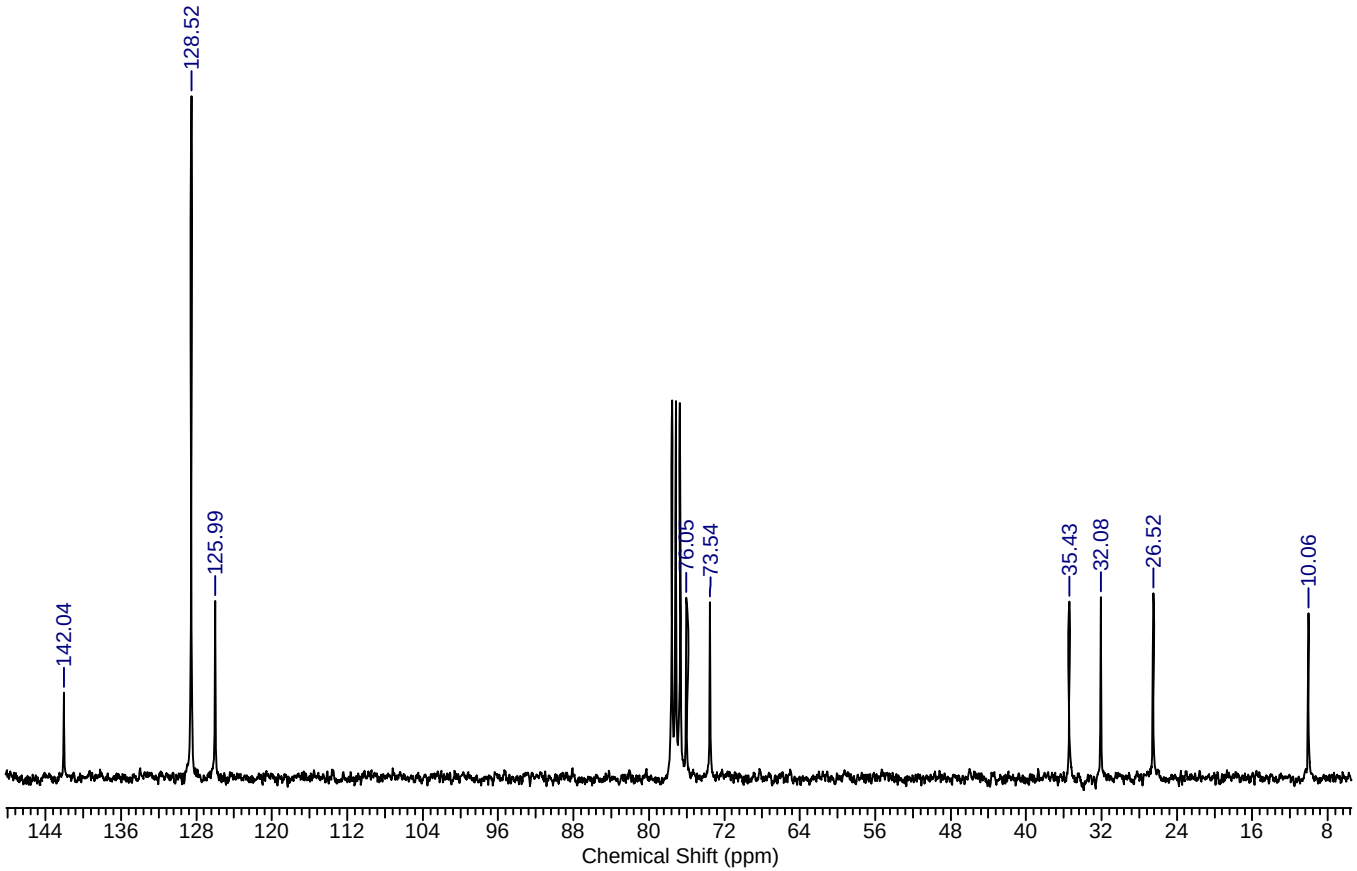


1-Phenylhexane-3,4-diol (3j)



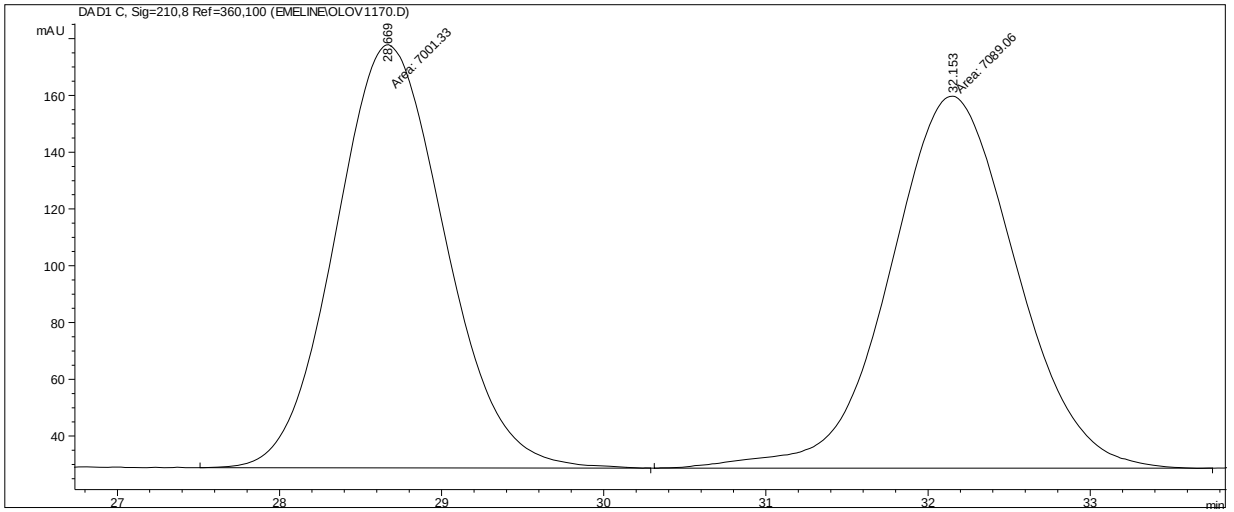


1-Phenylhexane-3,4-diol (3j)

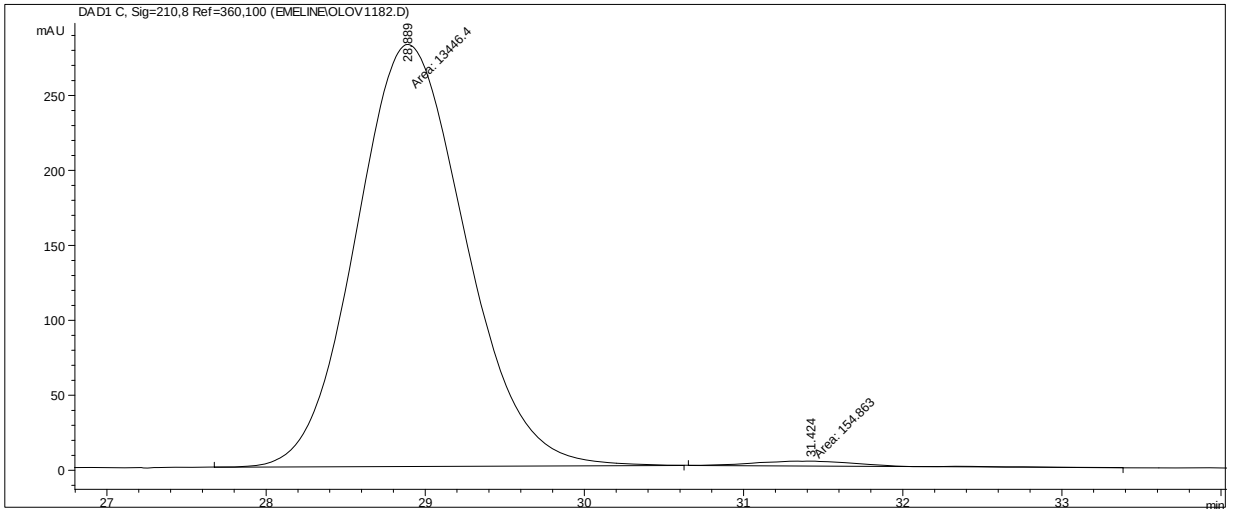


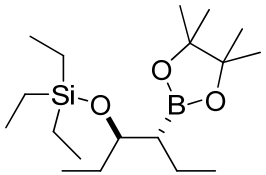
Chiral HPLC Data for diol 3j

Diol **3j** [from (±)-1,2-epoxybutane] Daicel Chiracel-AD column, 3:97 iPrOH/Hexane, 1 mL/min (210 nm)

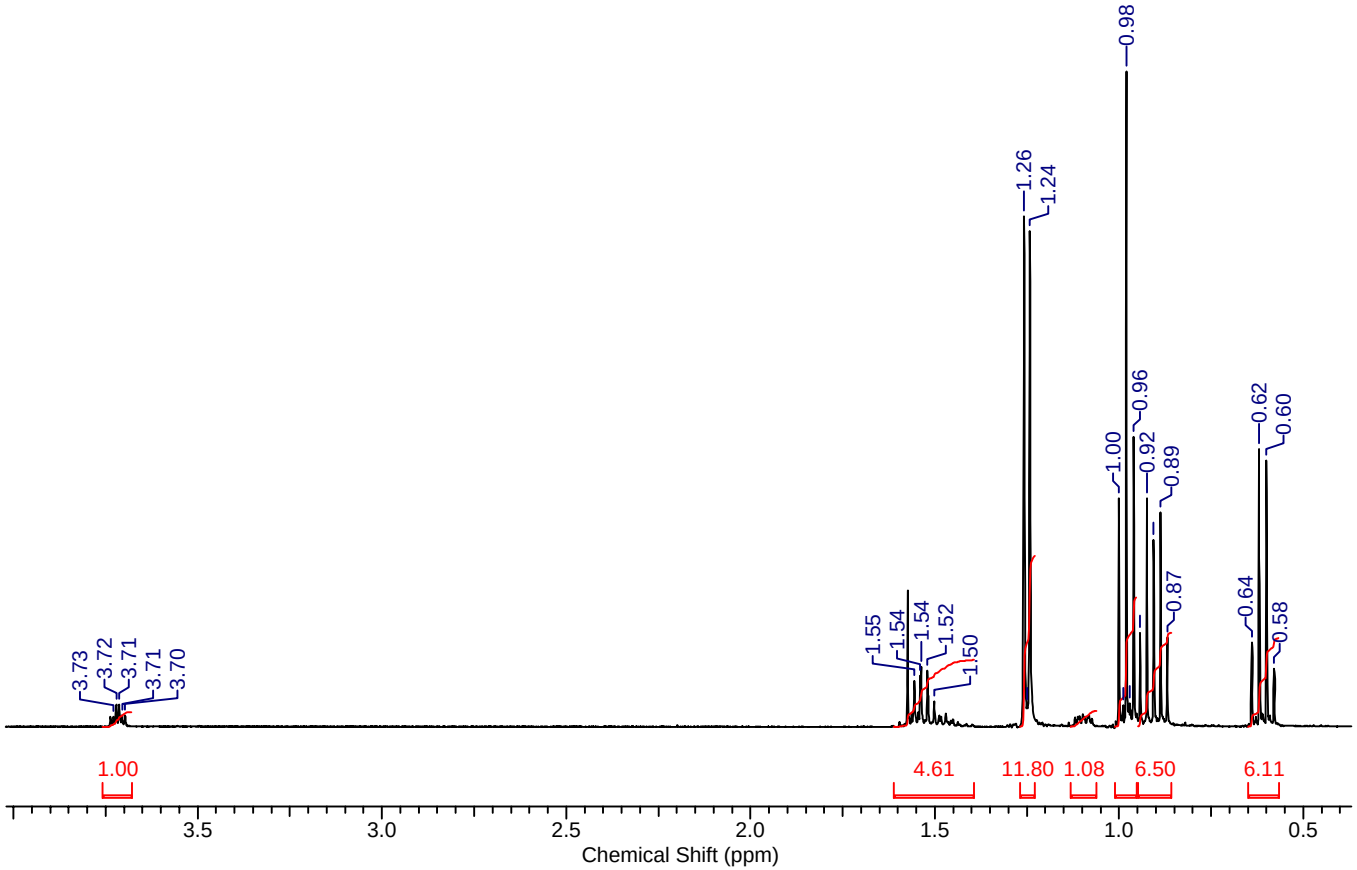


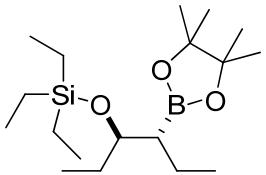
Diol **3j** [from (+)-1,2-epoxybutane] Daicel Chiracel-AD column, 3:97 iPrOH/Hexane, 1 mL/min (e.r. = 99:1) (210 nm)



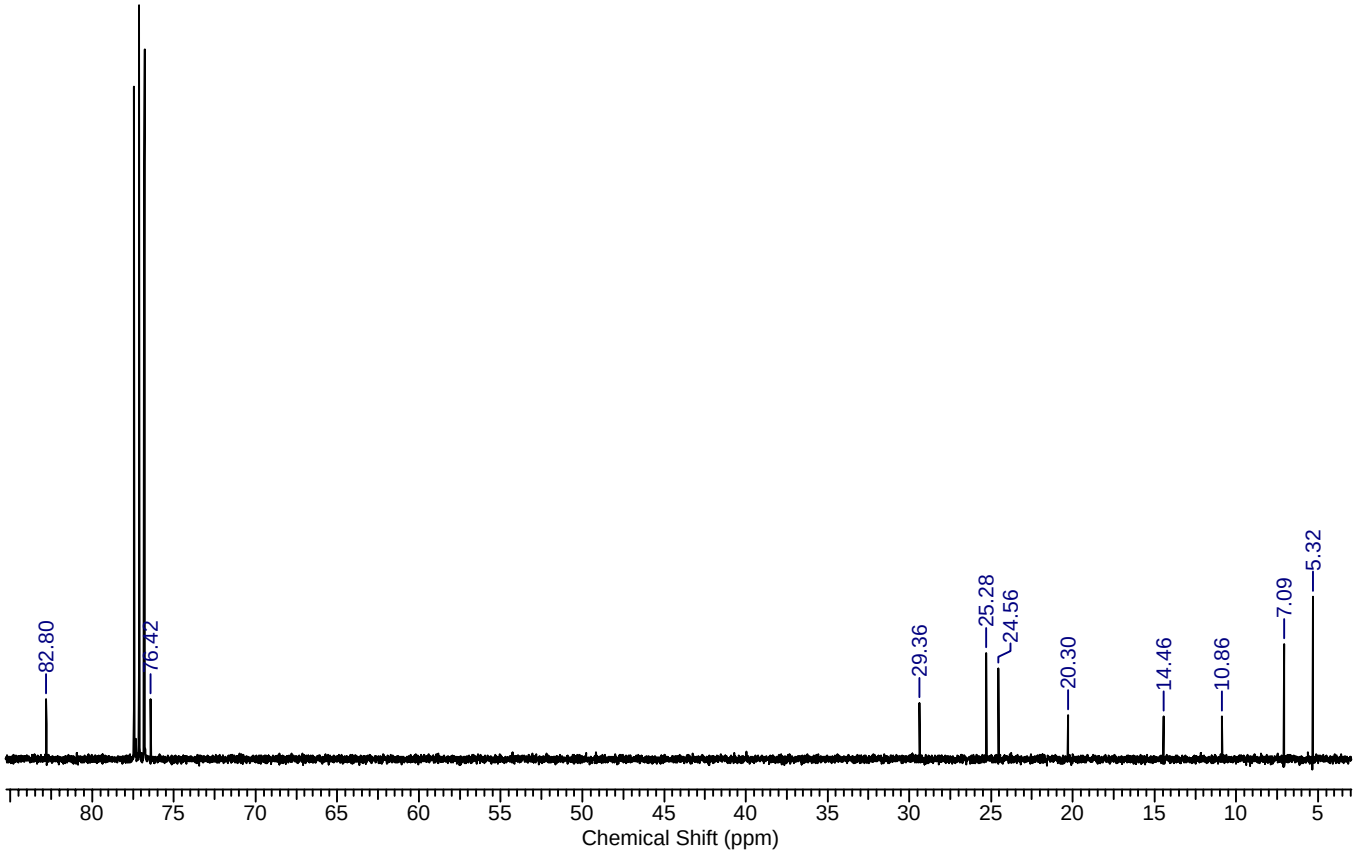


(1*R*,2*R*)-(1-Ethyl-2-triethylsiloxy)butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)



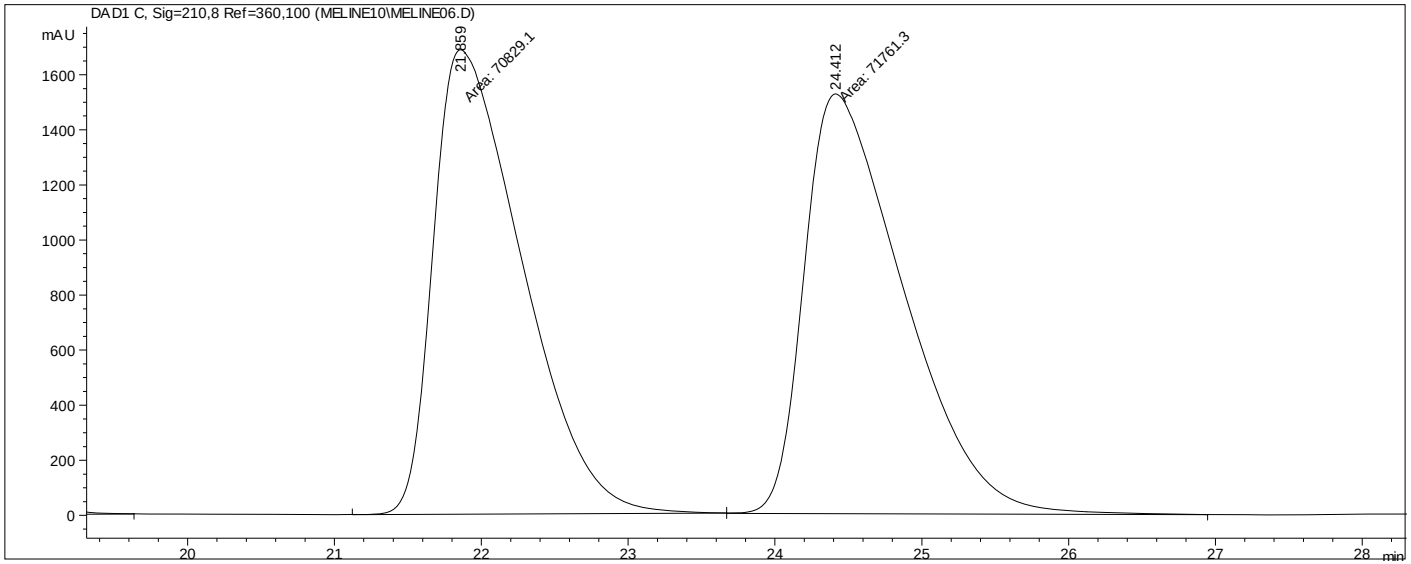


(1*R*,2*R*)-(1-Ethyl-2-triethylsiloxy)butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

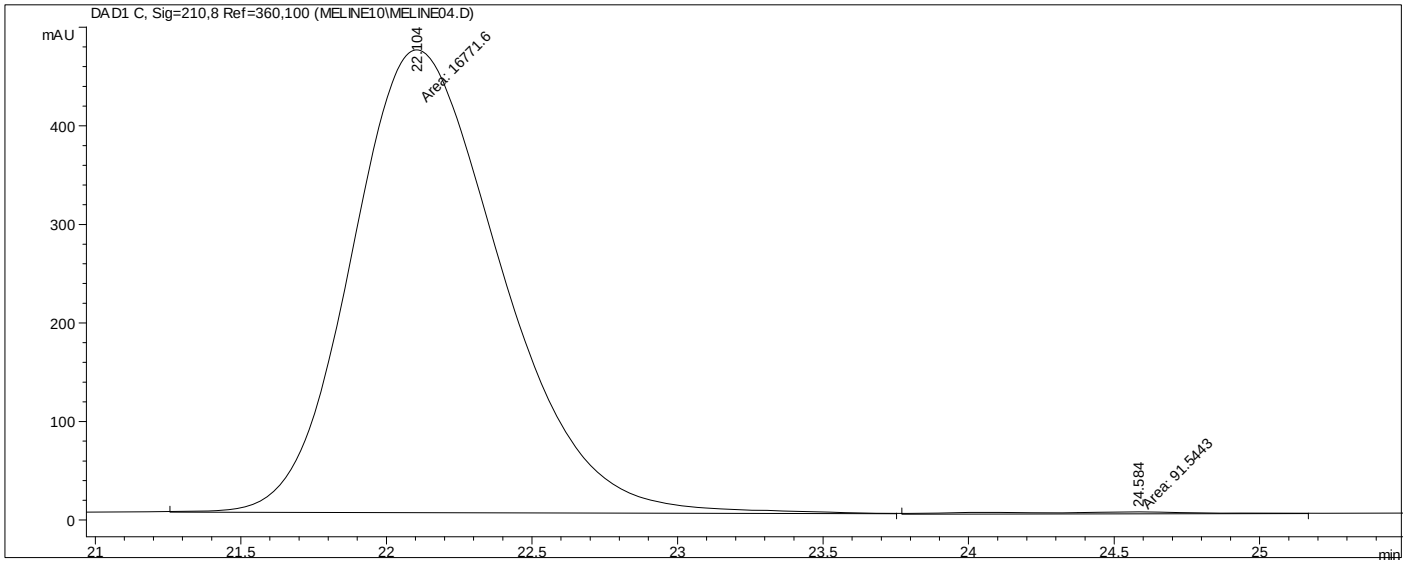


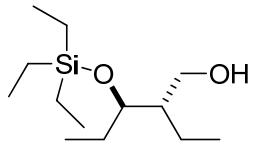
Chiral HPLC Data for 4’

4’ [from (±)-1,2-epoxybutane] Daicel Chiracel-AD column, 2:98 iPrOH/Hexane, 1 mL/min (210 nm)

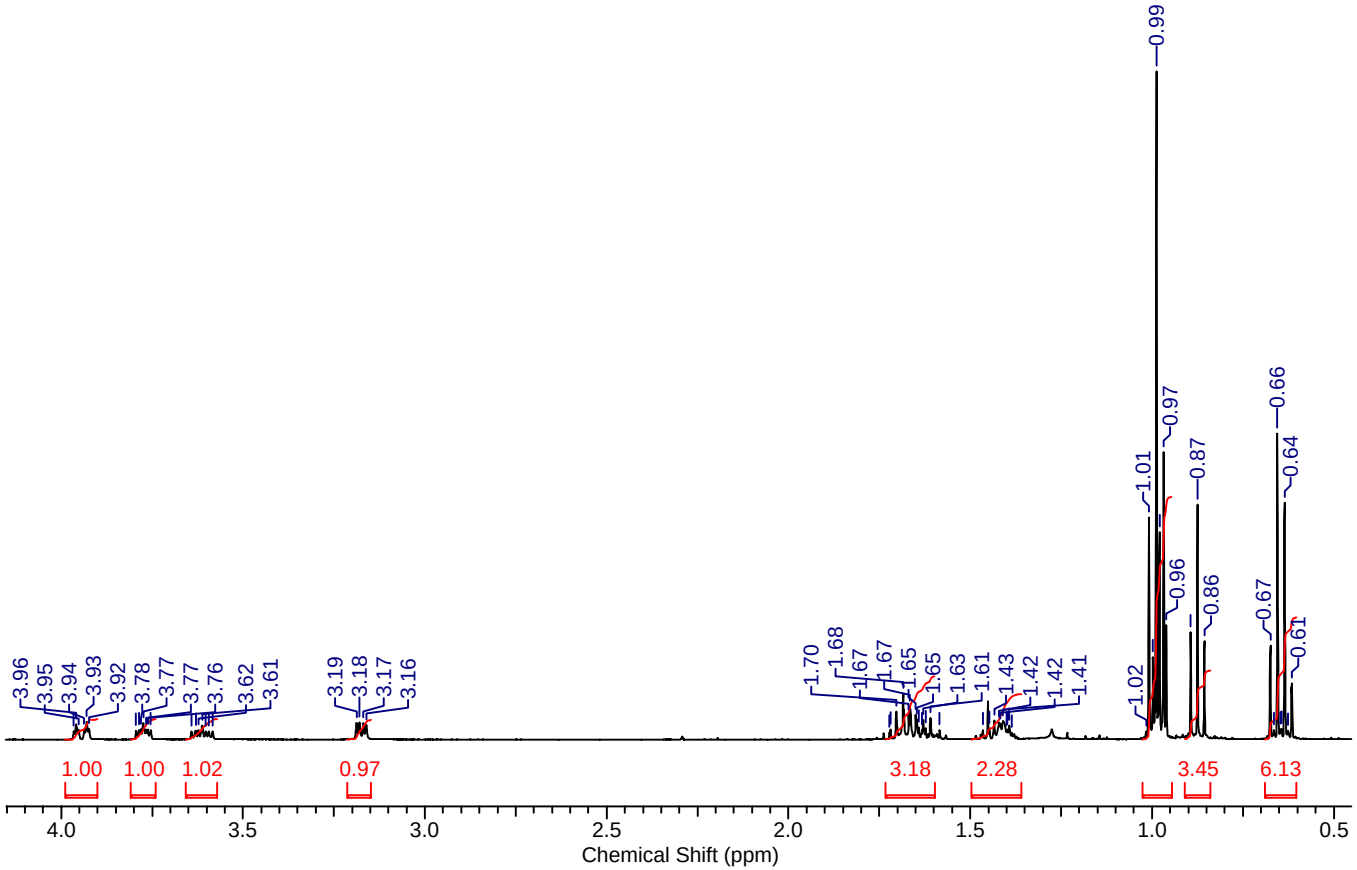


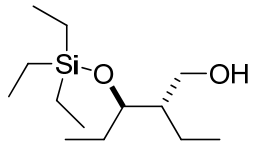
4’ [from (+)-1,2-epoxybutane] Daicel Chiracel-AD column, 2:98 iPrOH/Hexane, 1 mL/min (e.r. = 99:1) (210 nm)



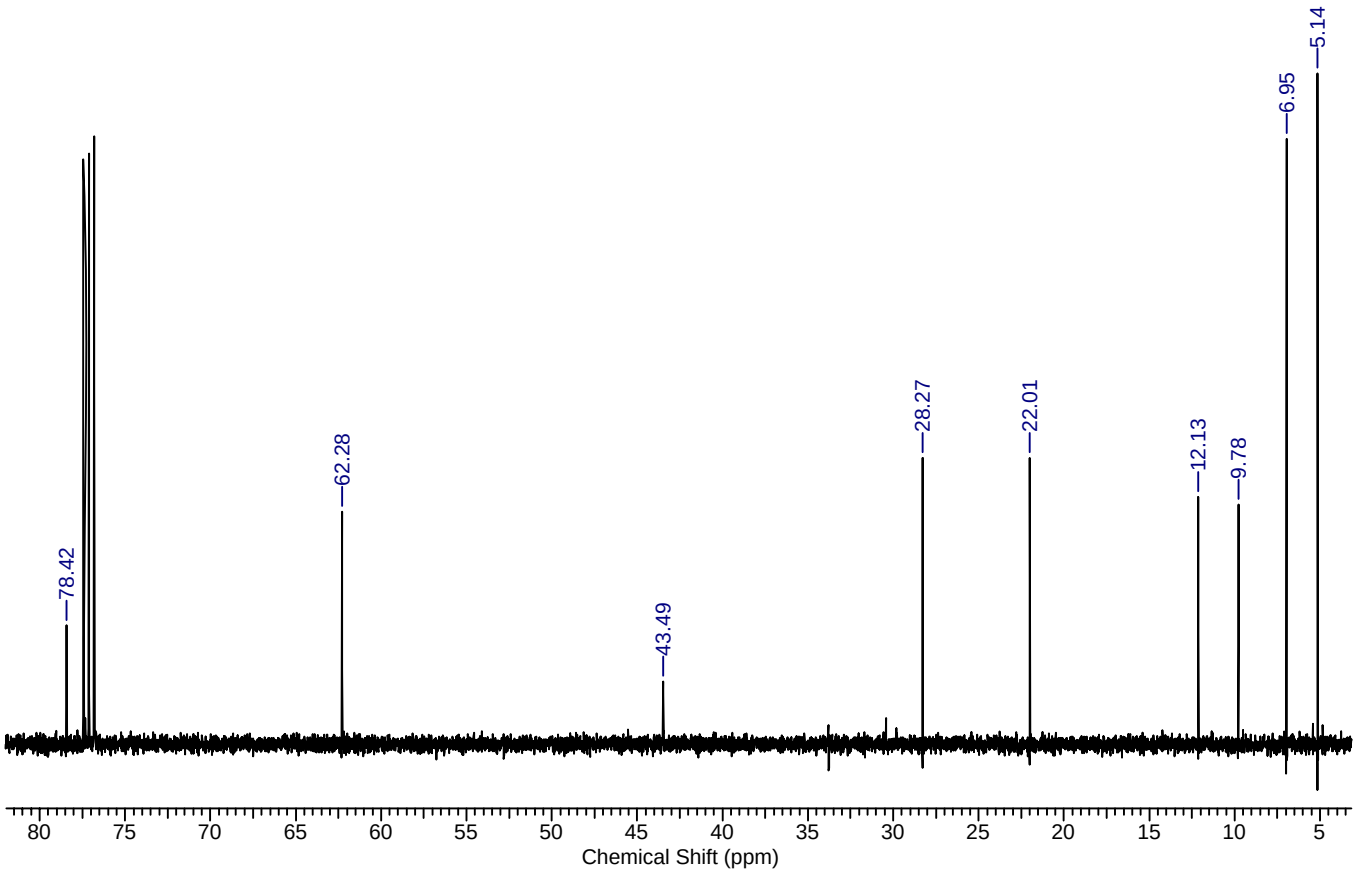


2-ethyl-3-(triethylsilyloxy)pentan-1-ol (5)



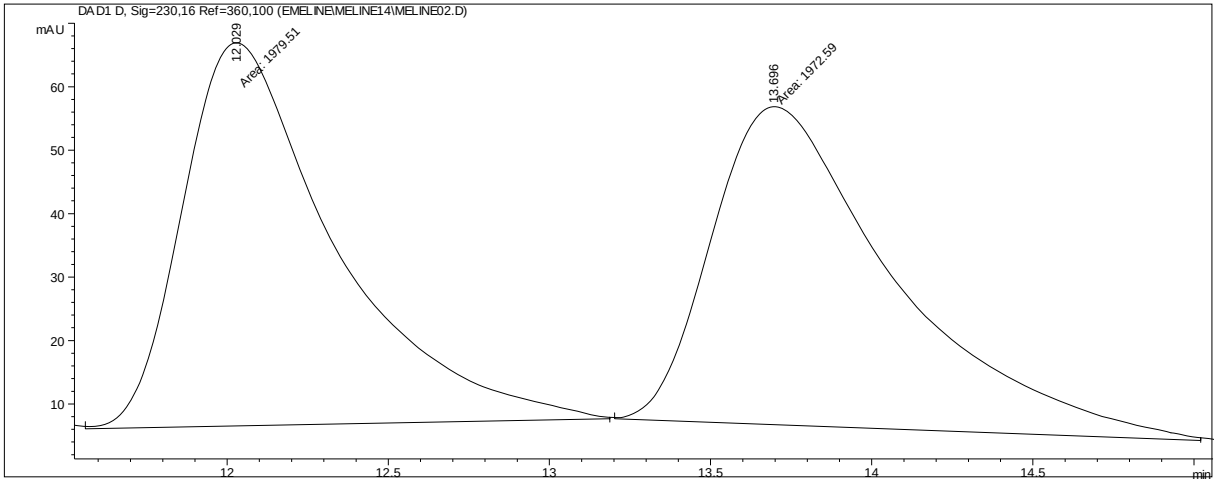


2-ethyl-3-(triethylsilyloxy)pentan-1-ol (5)

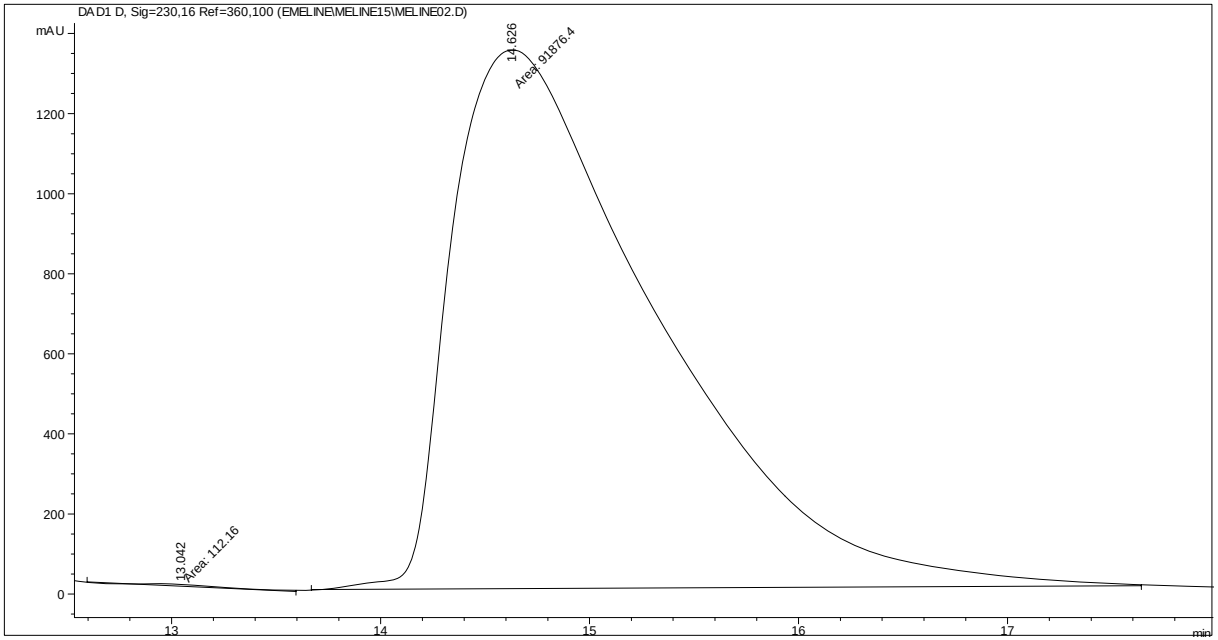


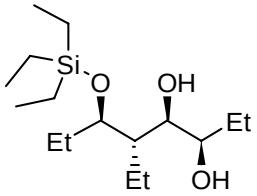
Chiral HPLC Data for 5’

5’ [from (±)-1,2-epoxybutane] Daicel Chiracel-OJ column, 2:98 iPrOH/Hexane, 1 mL/min (230 nm)

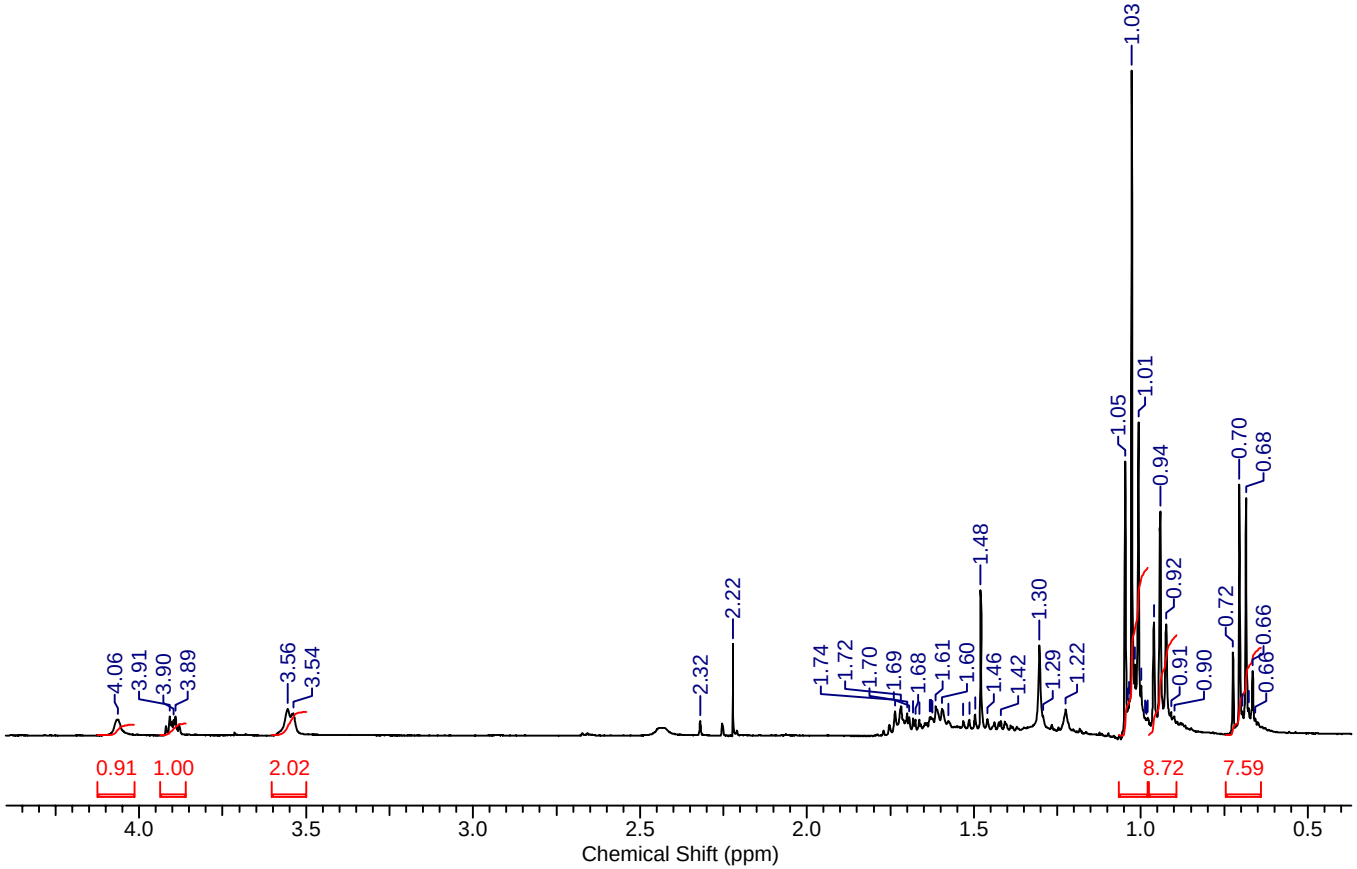


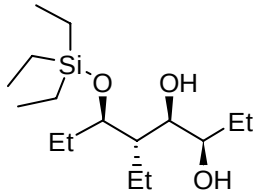
5’ [from (+)-1,2-epoxybutane] Daicel Chiracel-OJ column, 2:98 iPrOH/Hexane, 1 mL/min (e.r. = 99:1) (230 nm)



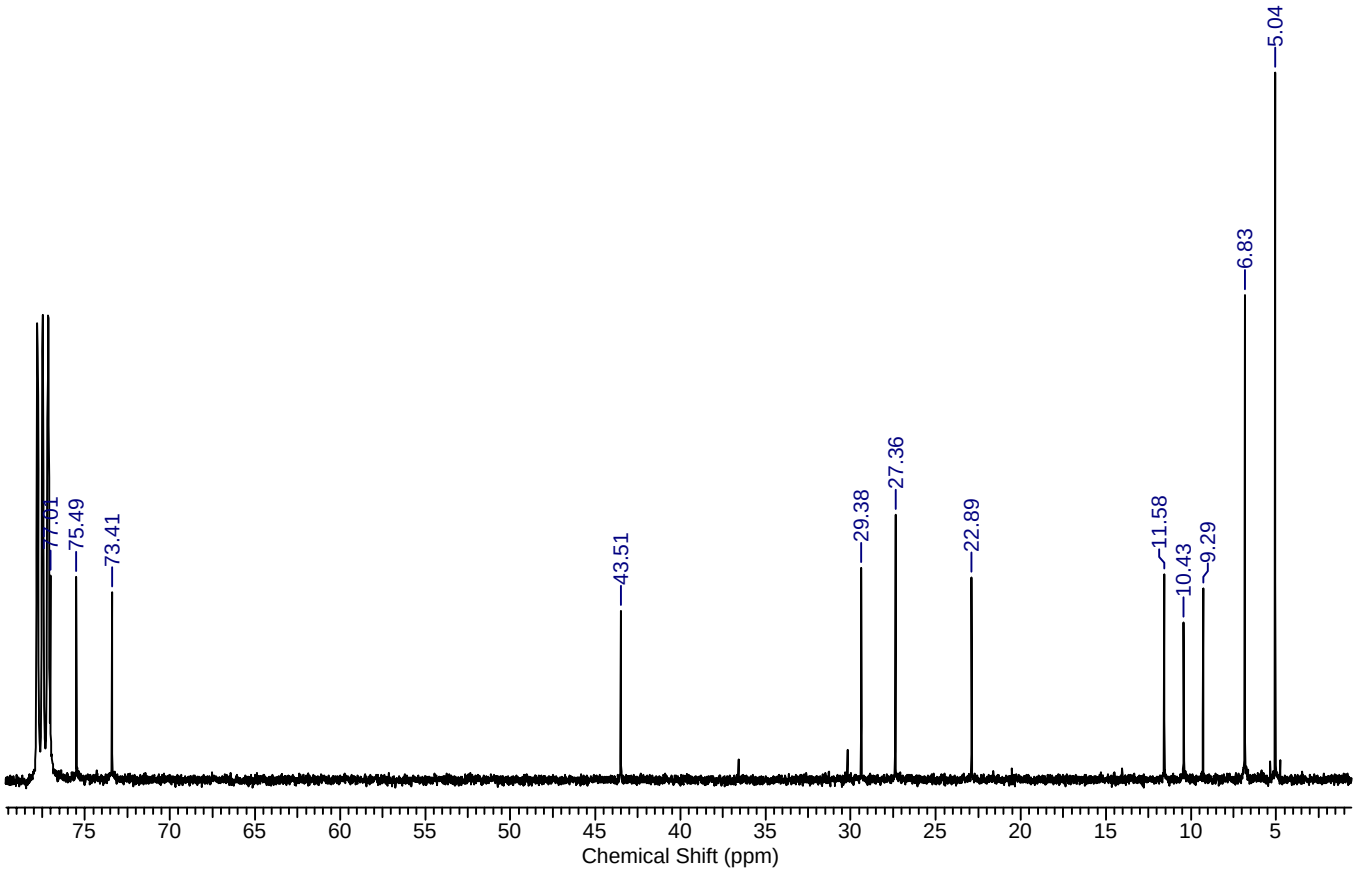


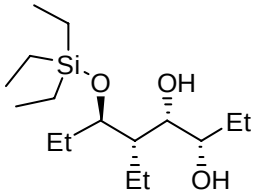
(3R,4R,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (6)



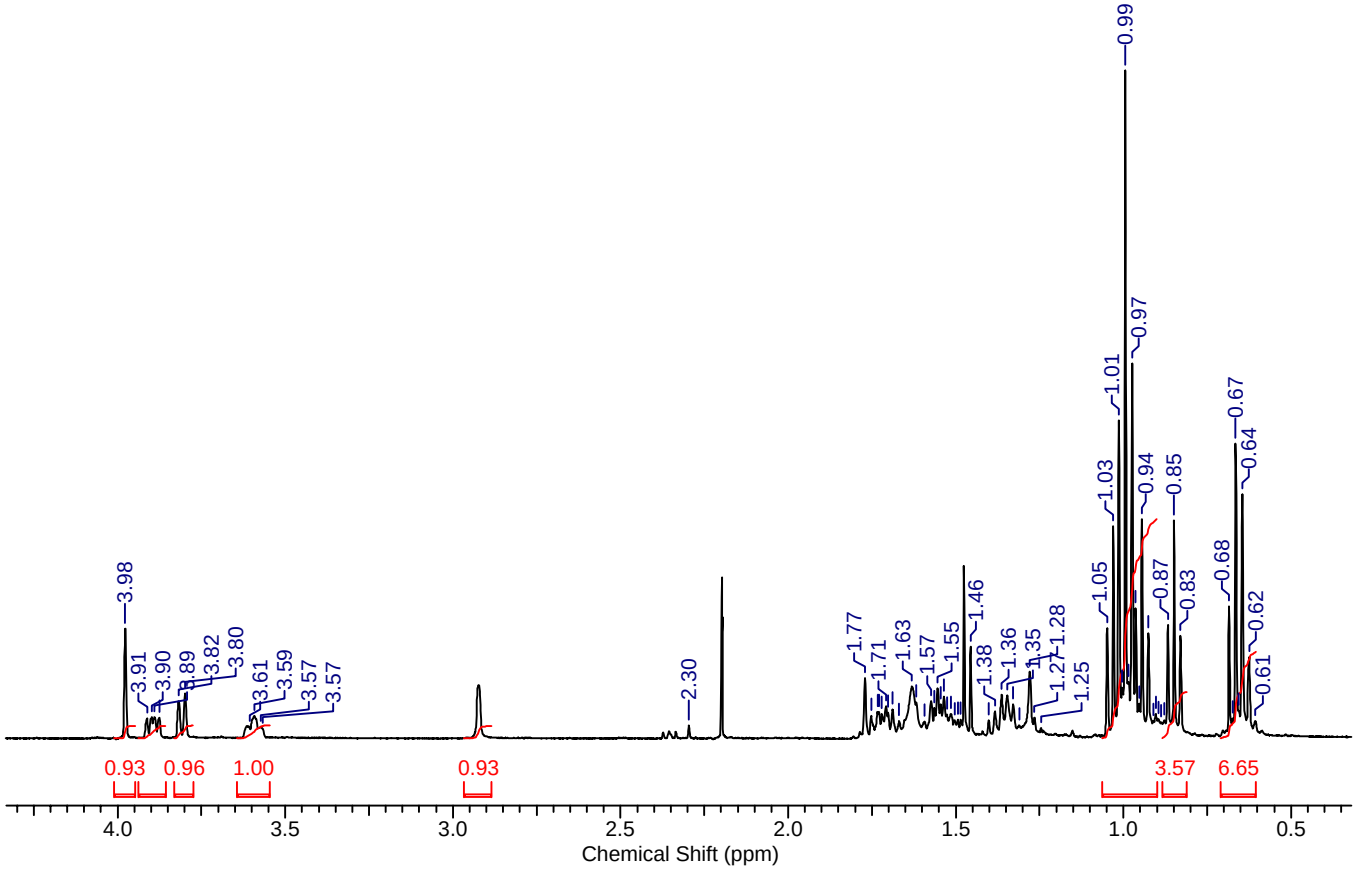


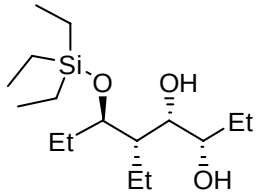
(3R,4R,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (6)



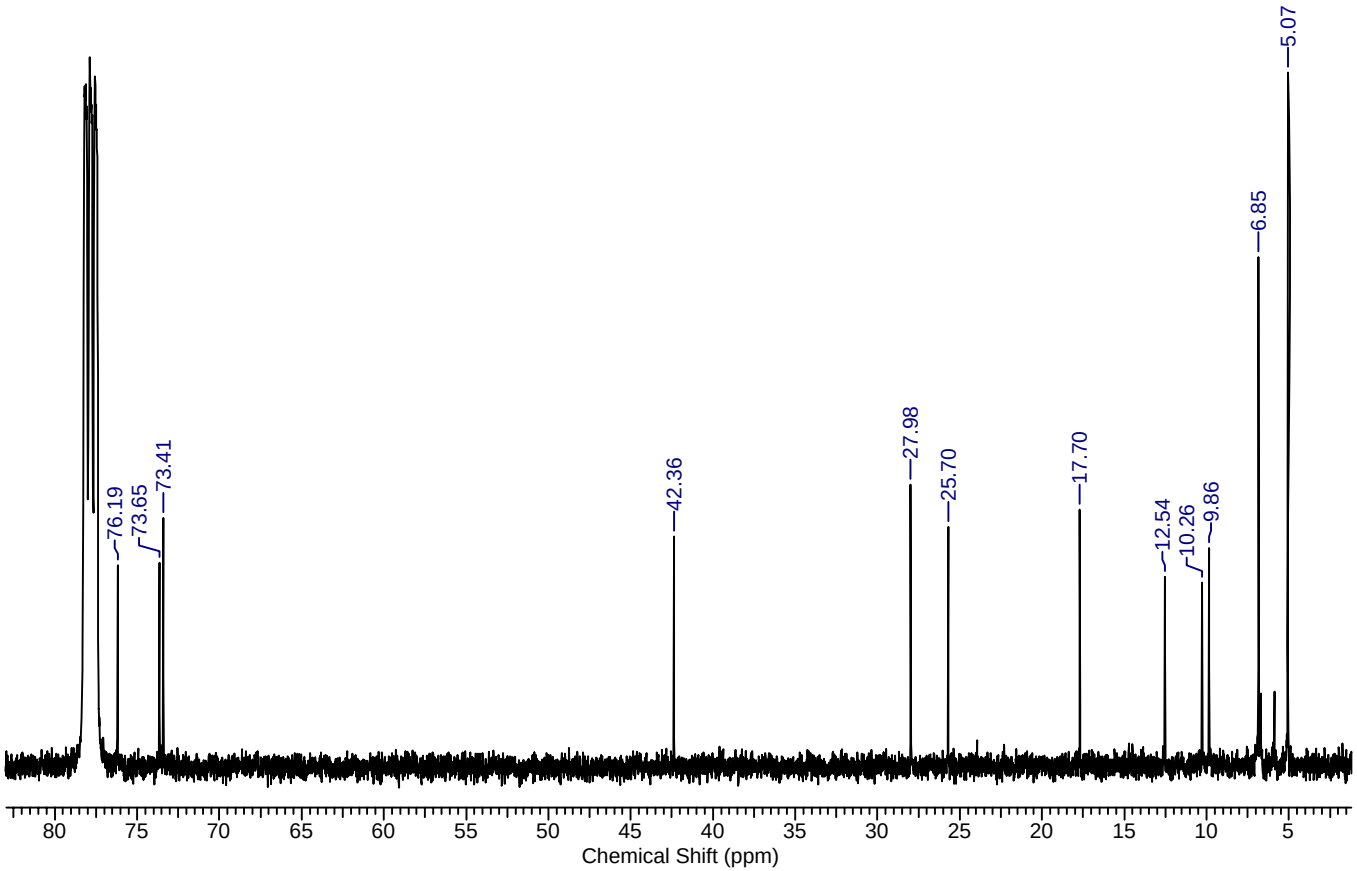


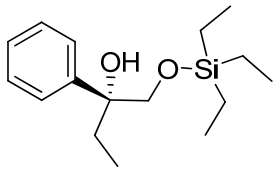
(3S,4S,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (7)



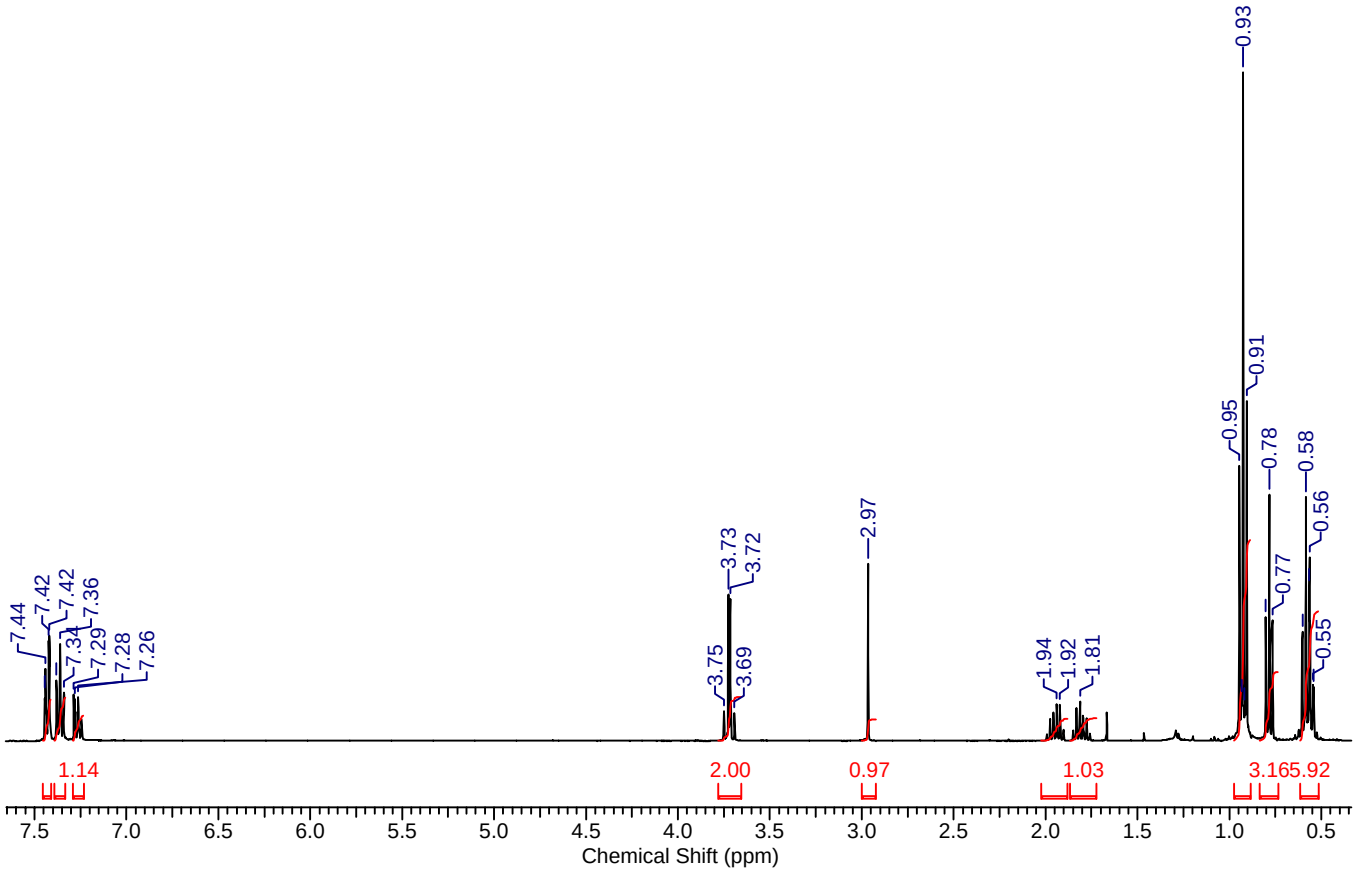


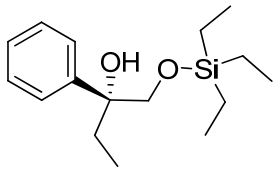
(3S,4S,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (7)



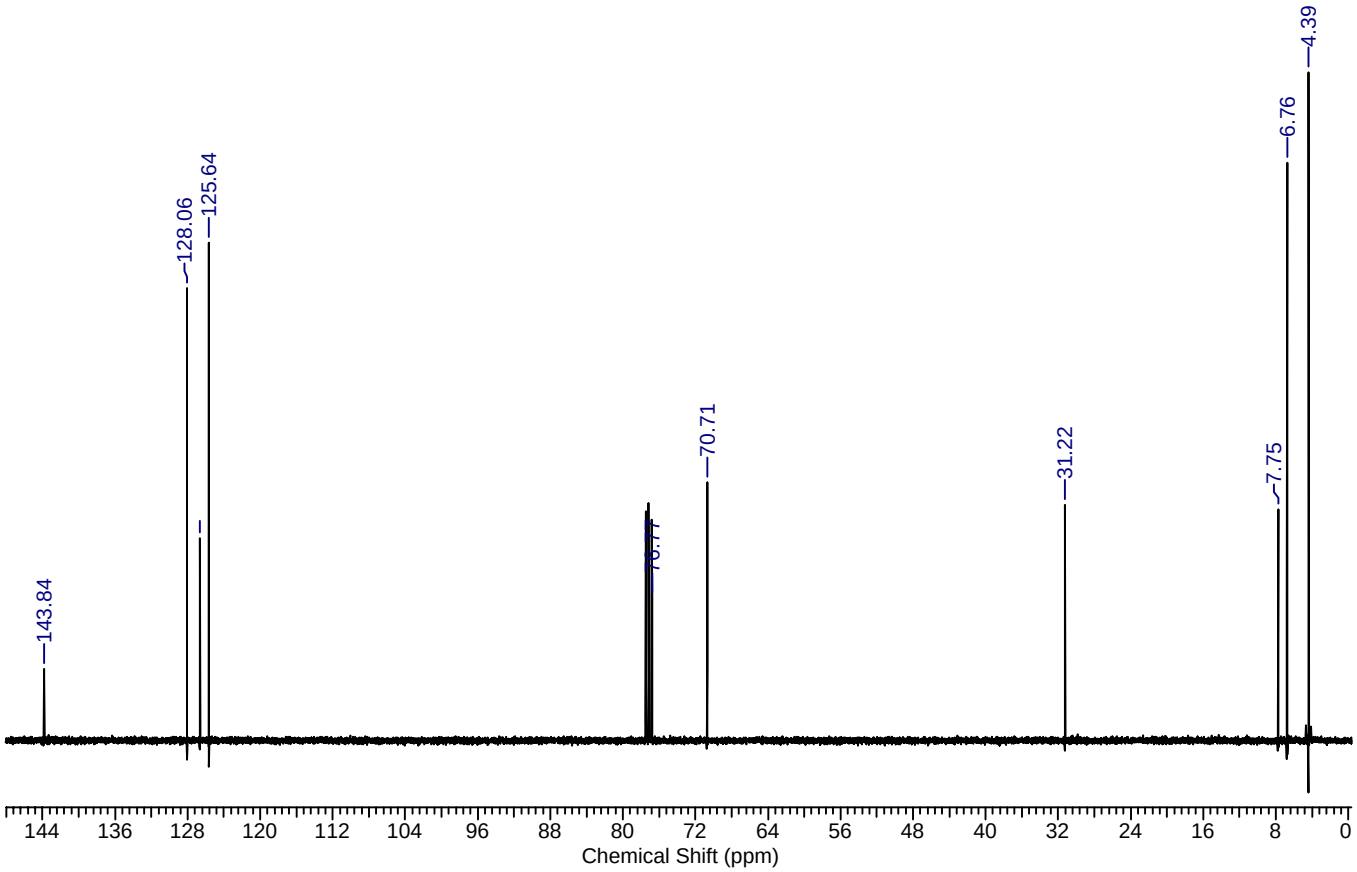


(*R*)-2-phenyl-1-(triethylsilyloxy)butan-2-ol (9a)



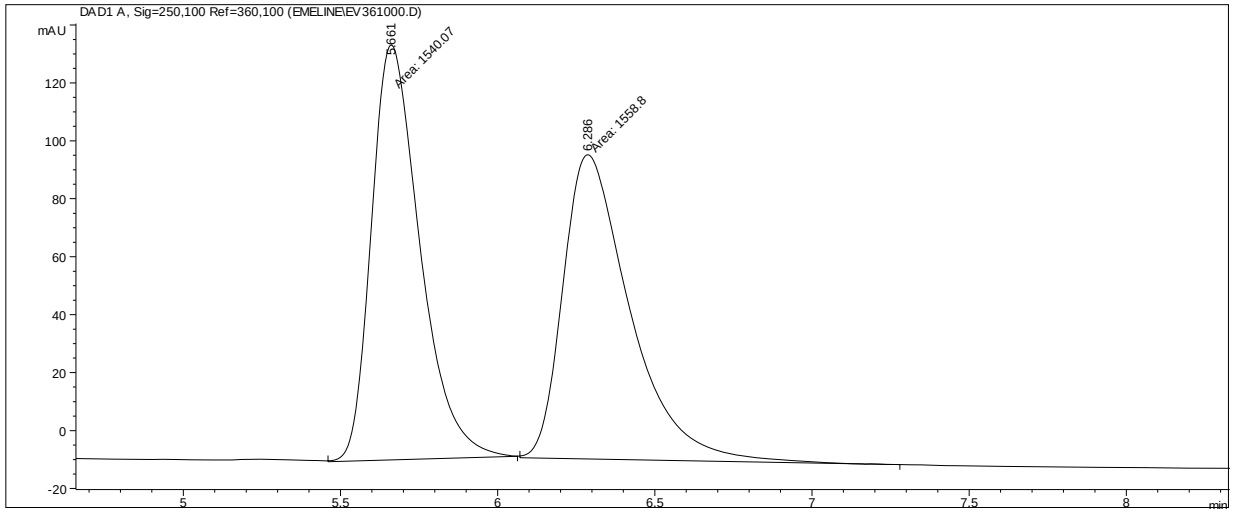


(*R*)-2-phenyl-1-(triethylsilyloxy)butan-2-ol (9a)

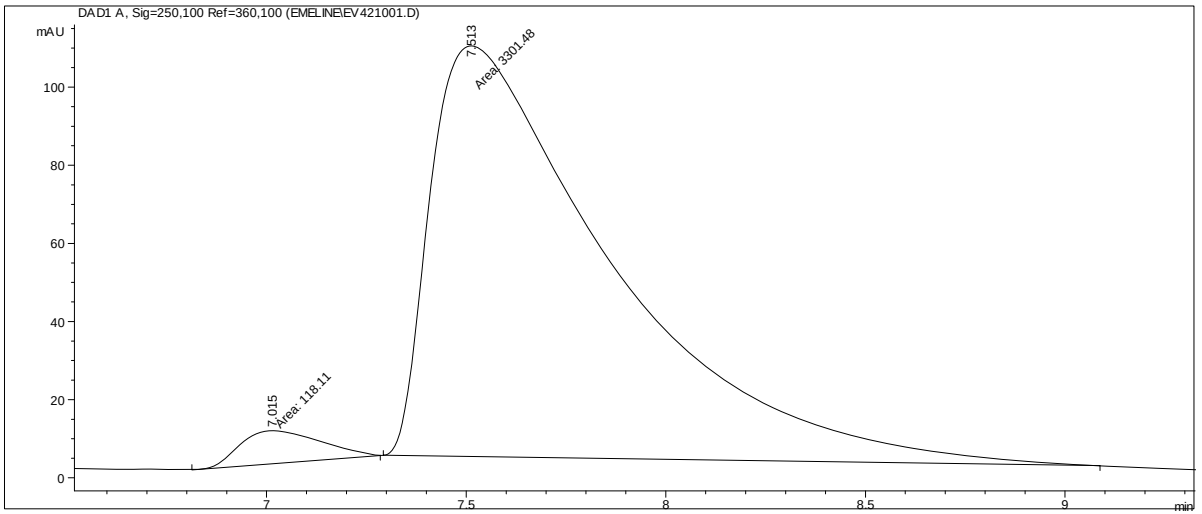


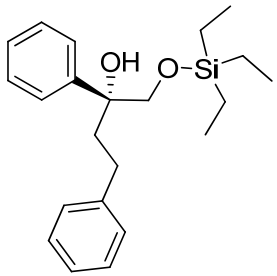
Chiral HPLC Data for 9a

9a [from (±)-styrene oxide] Daicel Chiracel-AD column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (250 nm)

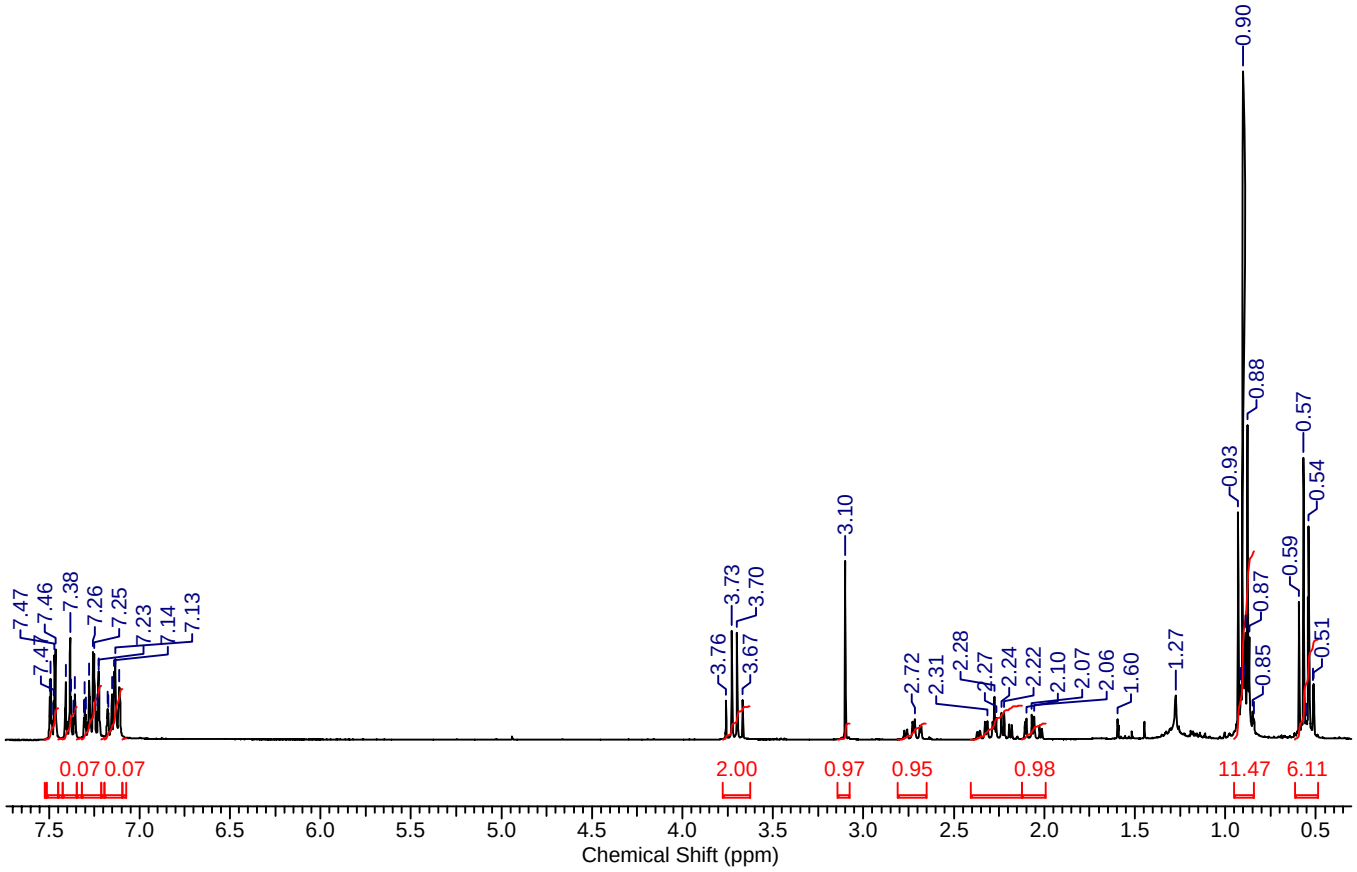


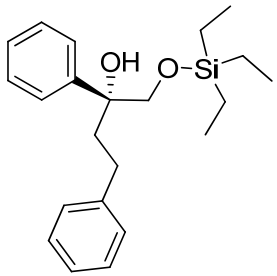
9a [from (+)-styrene oxide] Daicel Chiracel-AD column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (e.r. = 97:3) (250 nm)



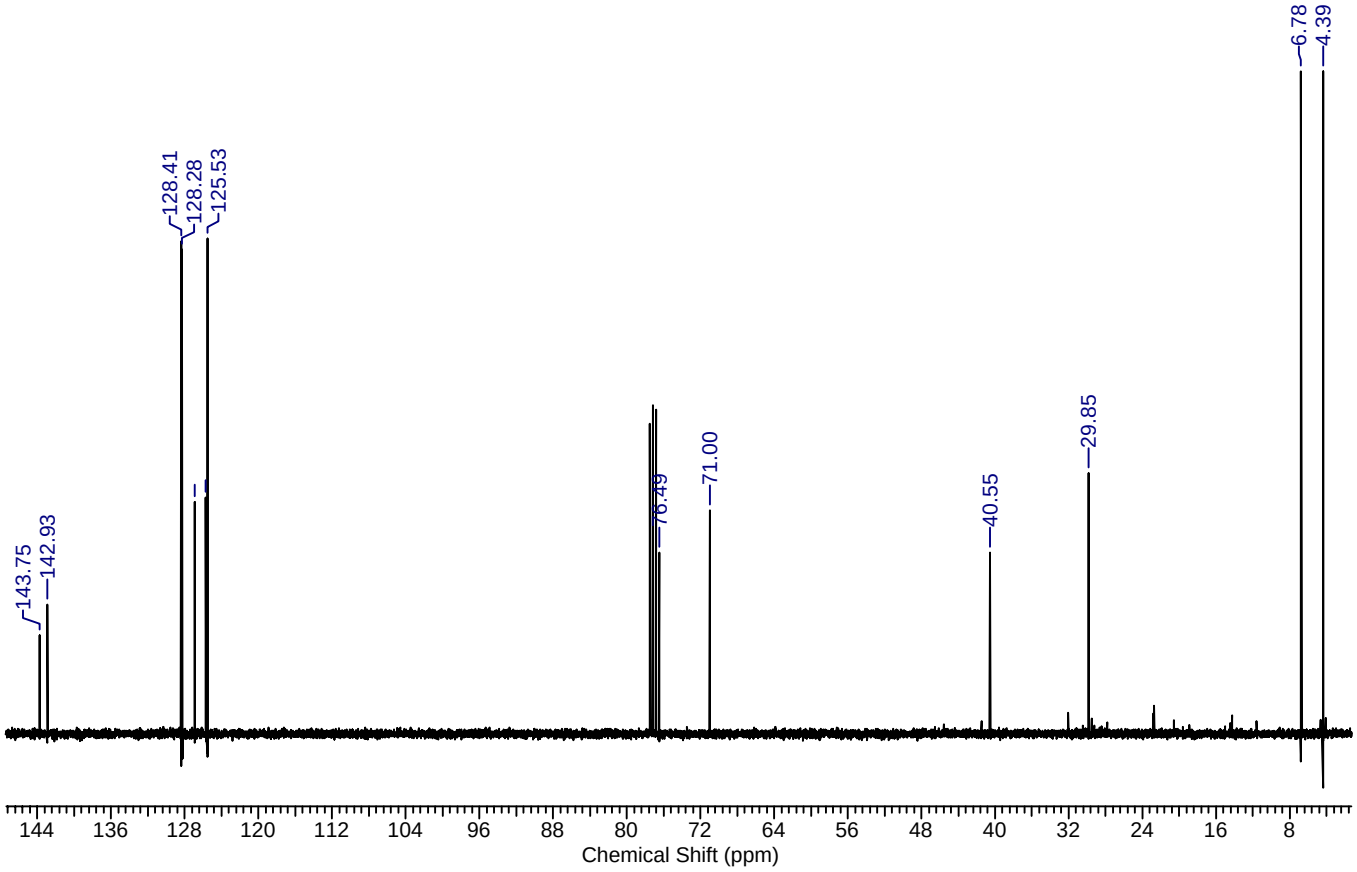


(*R*)-2,4-diphenyl-1-(triethylsilyloxy)butan-2-ol (9b)



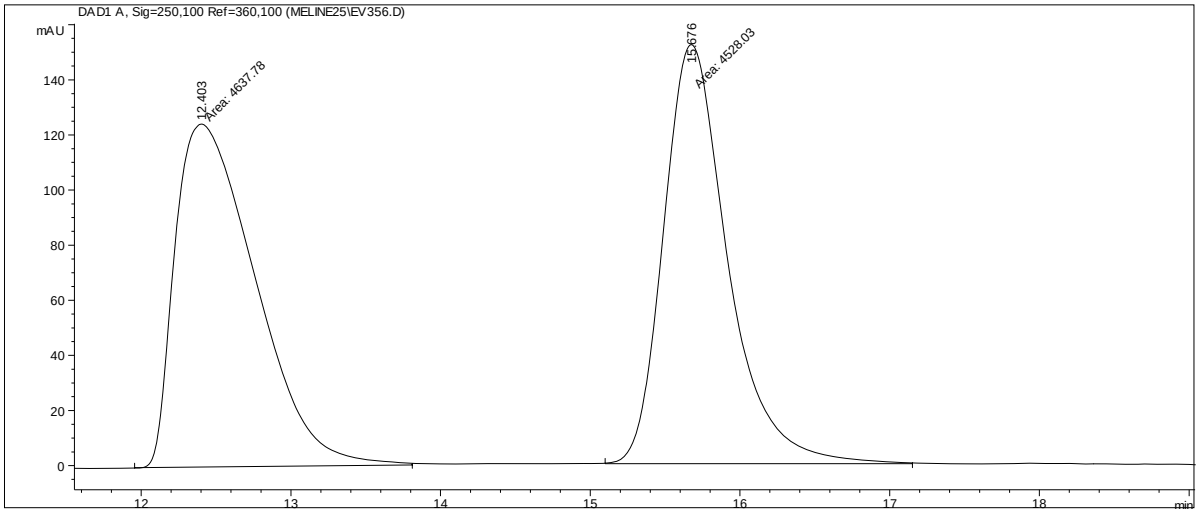


(*R*)-2,4-diphenyl-1-(triethylsilyloxy)butan-2-ol (9b)

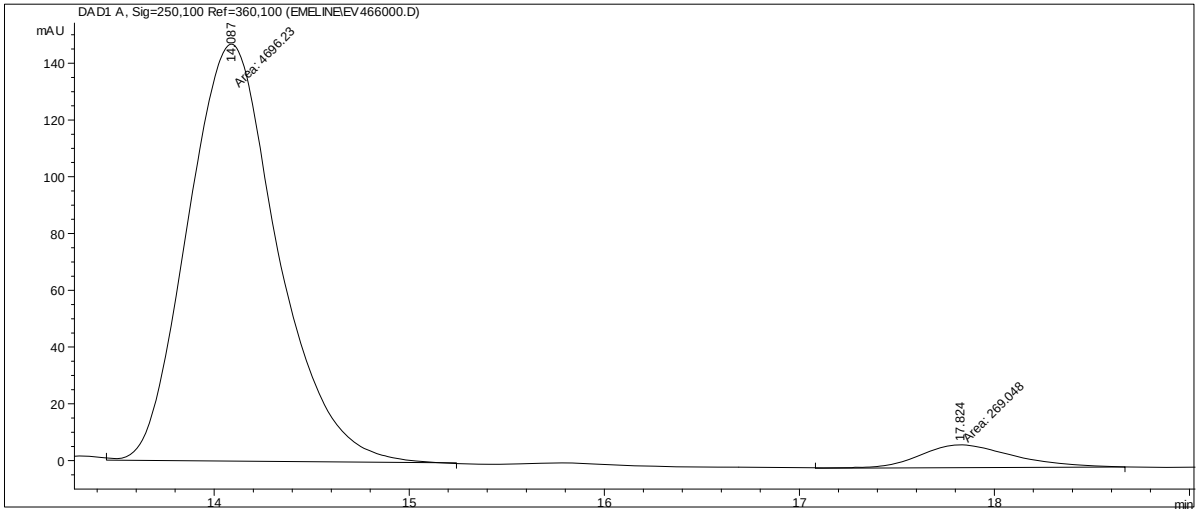


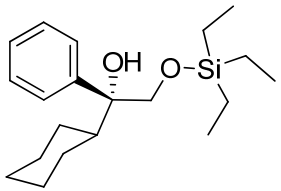
Chiral HPLC Data for 9b

9b [from (±)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 0.5 mL/min (250 nm)

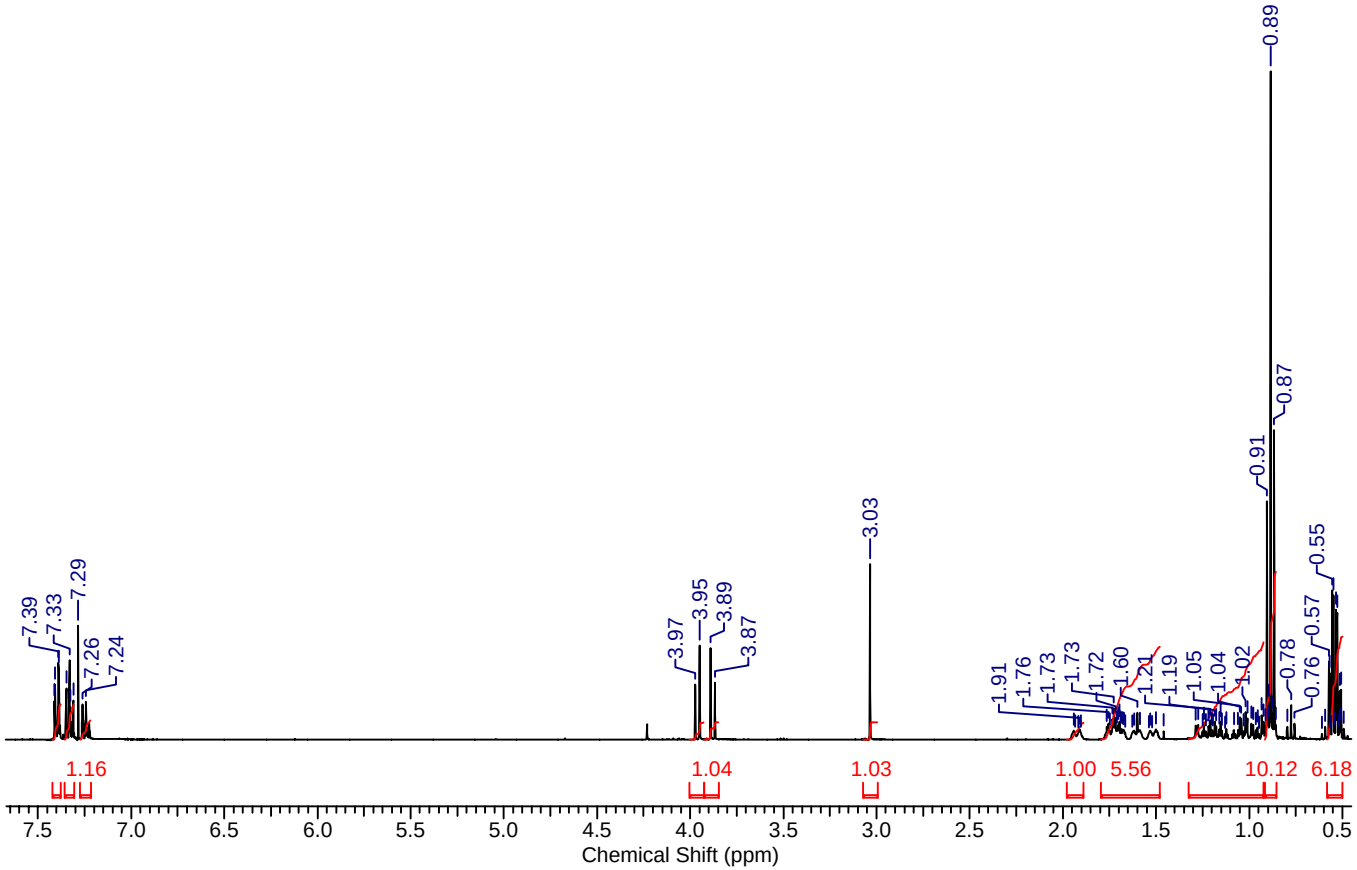


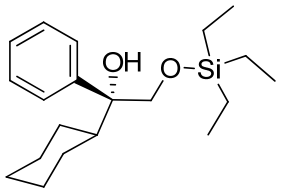
9b [from (+)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 0.5 mL/min (e.r. = 95:5) (250 nm)



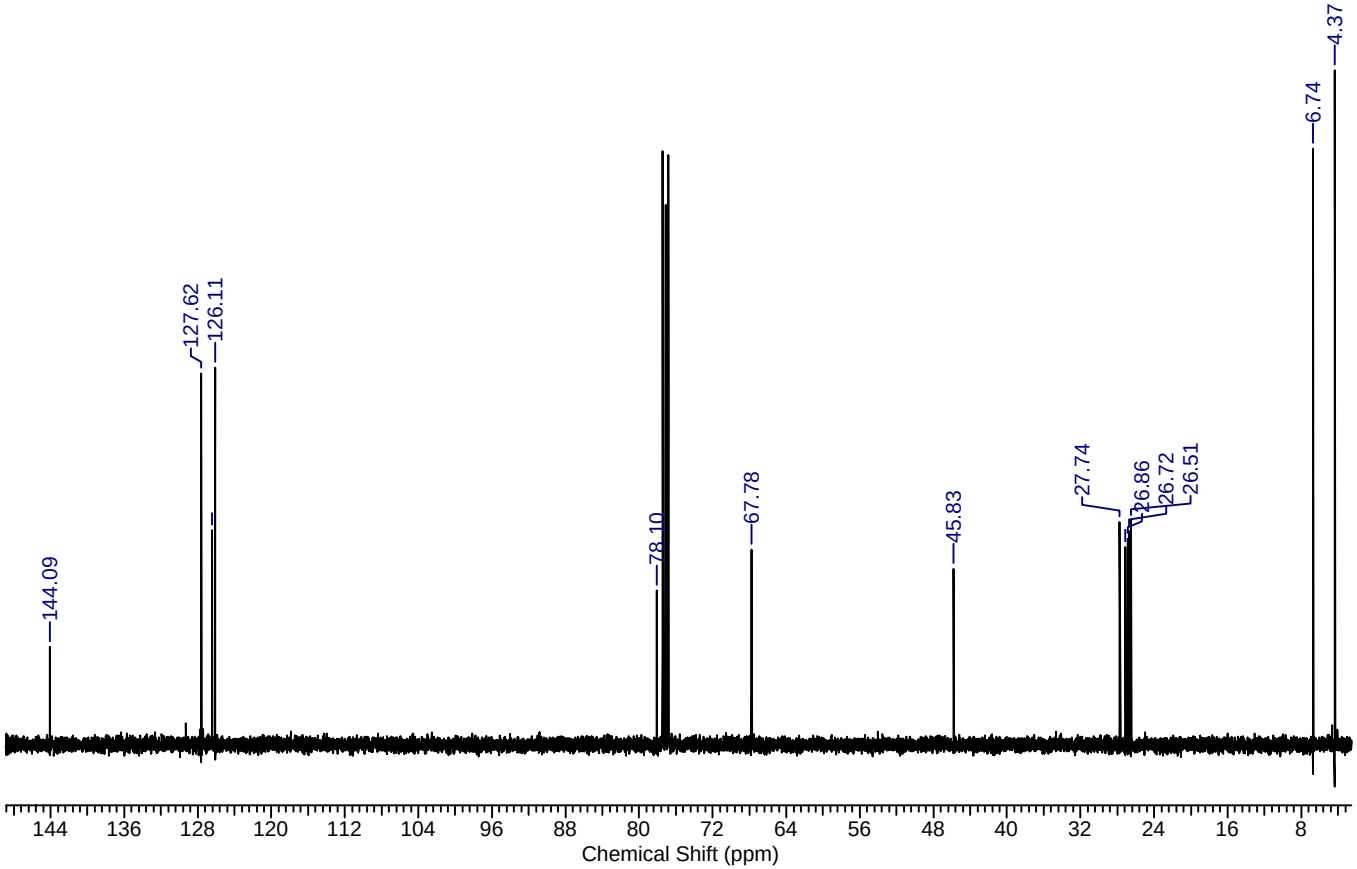


(*R*)-1-cyclohexyl-1-phenyl-2-(triethylsilyloxy)ethanol (9c)



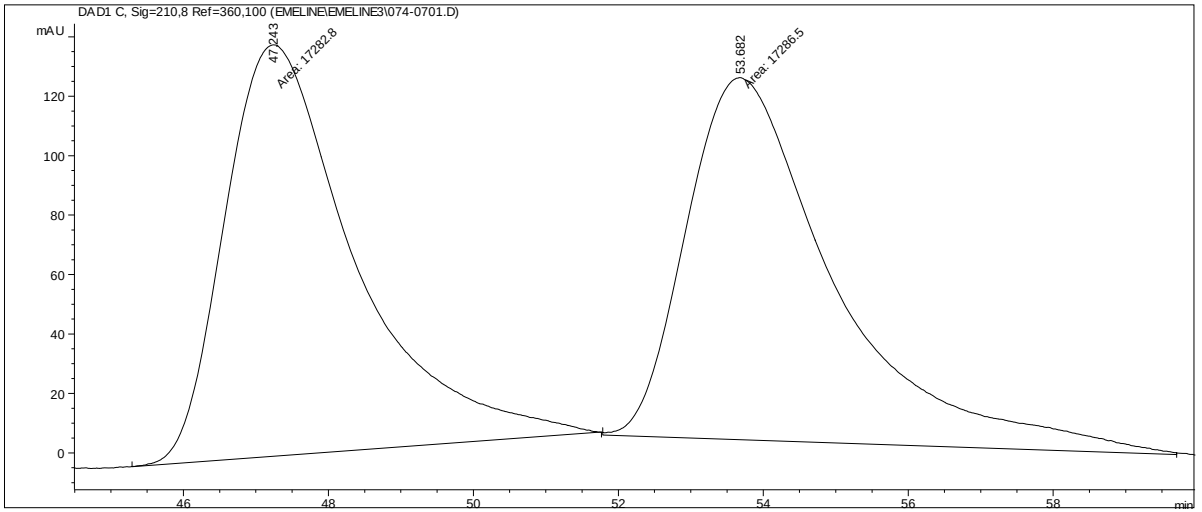


(*R*)-1-cyclohexyl-1-phenyl-2-(triethylsilyloxy)ethanol (9c)

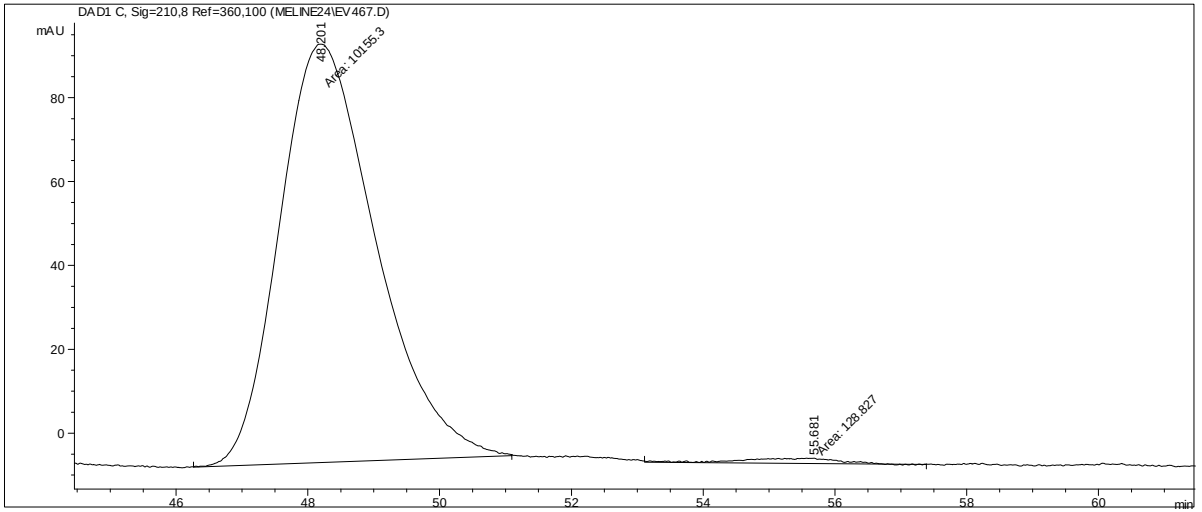


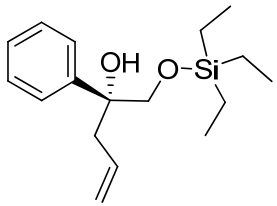
Chiral HPLC Data for 9c'

9c' [from (±)-styrene oxide] Daicel Chiracel-OD-H column, 2.5:97.5 iPrOH/Hexane, 0.5 mL/min (210 nm)

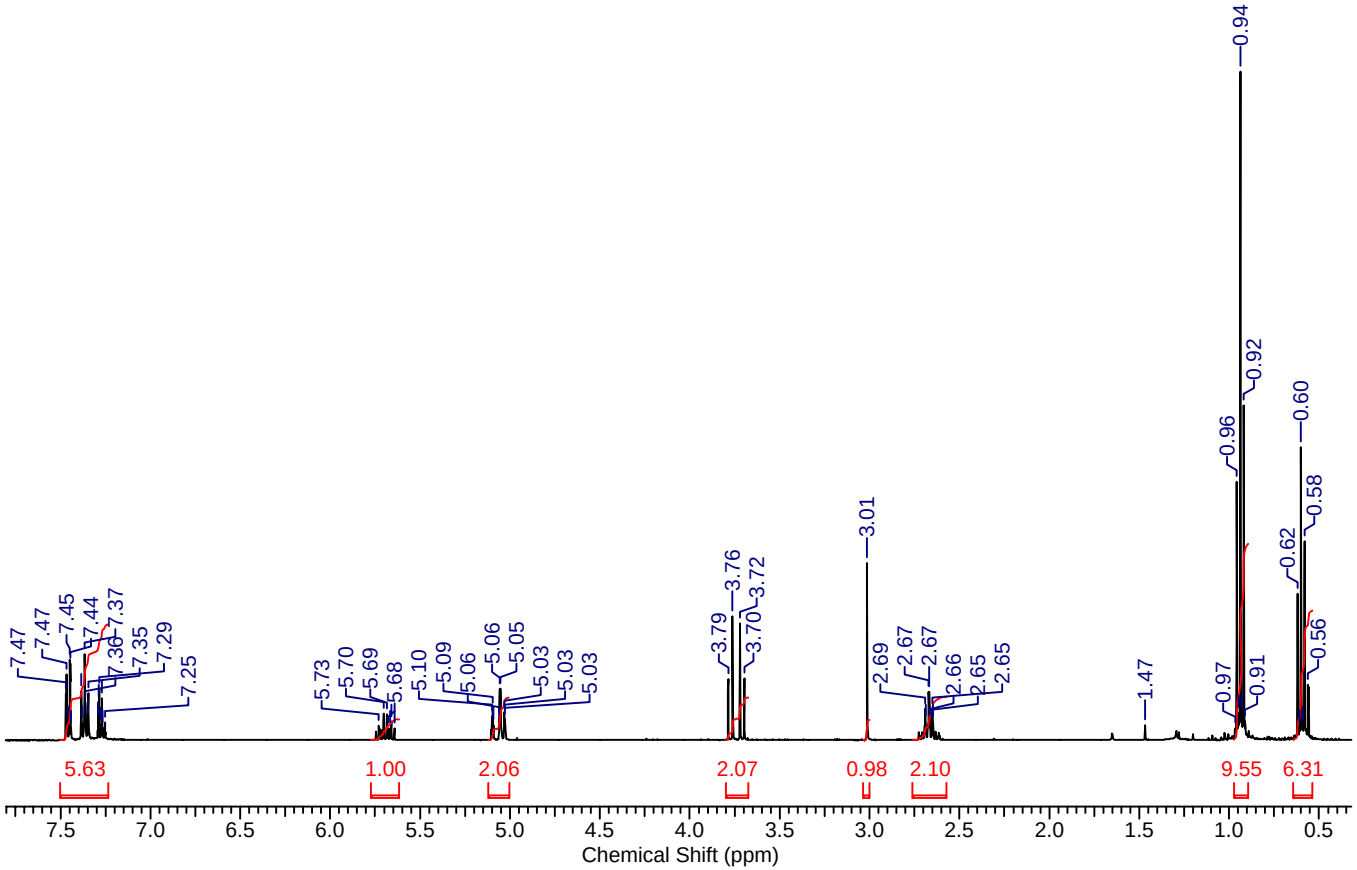


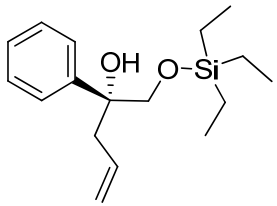
9c' [from (+)-styrene oxide] Daicel Chiracel-OD-H column, 2.5:97.5 iPrOH/Hexane, 0.5 mL/min (e.r. = 99:1) (210 nm)



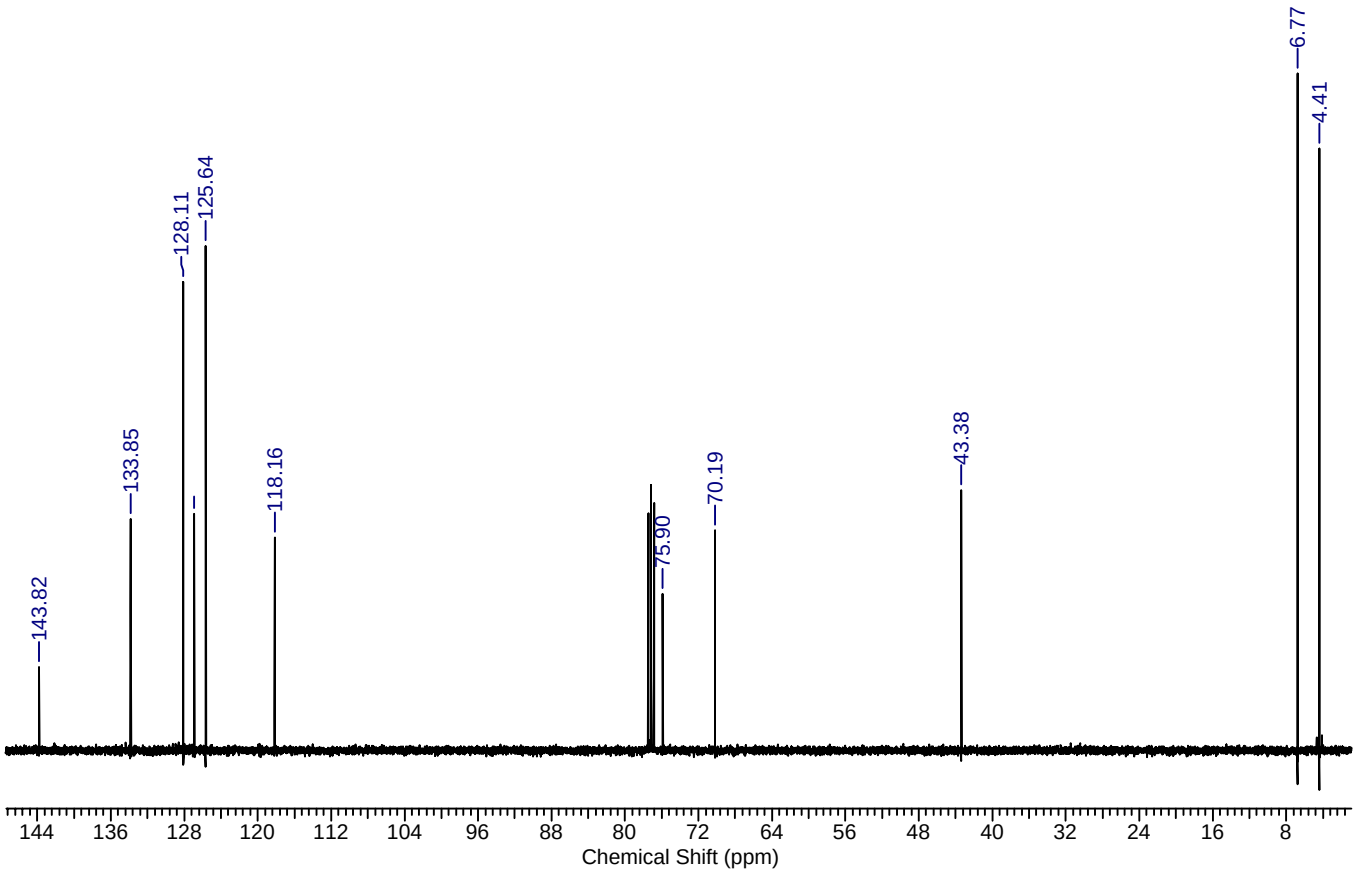


(*R*)-2-phenyl-1-(triethylsilyloxy)pent-4-en-2-ol (9d)



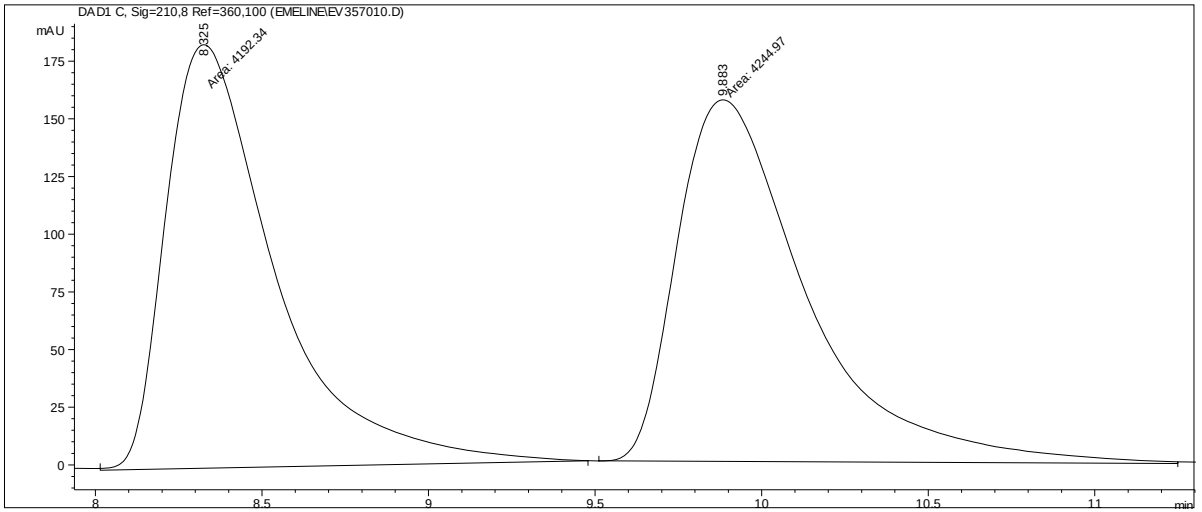


(*R*)-2-phenyl-1-(triethylsilyloxy)pent-4-en-2-ol (9d)

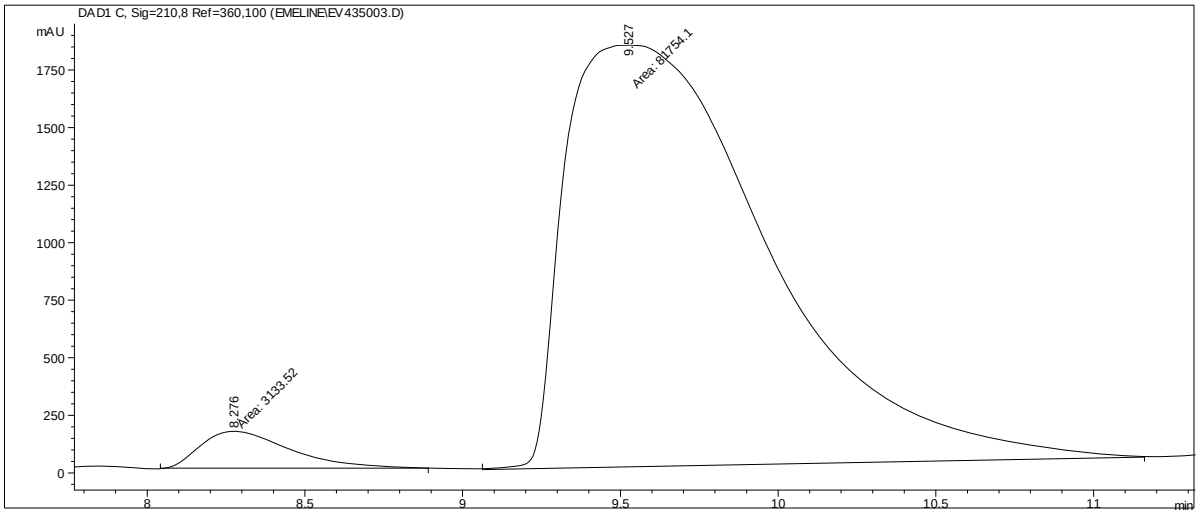


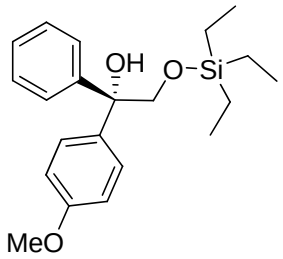
Chiral HPLC Data for 9d

9d [from (±)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (210 nm)

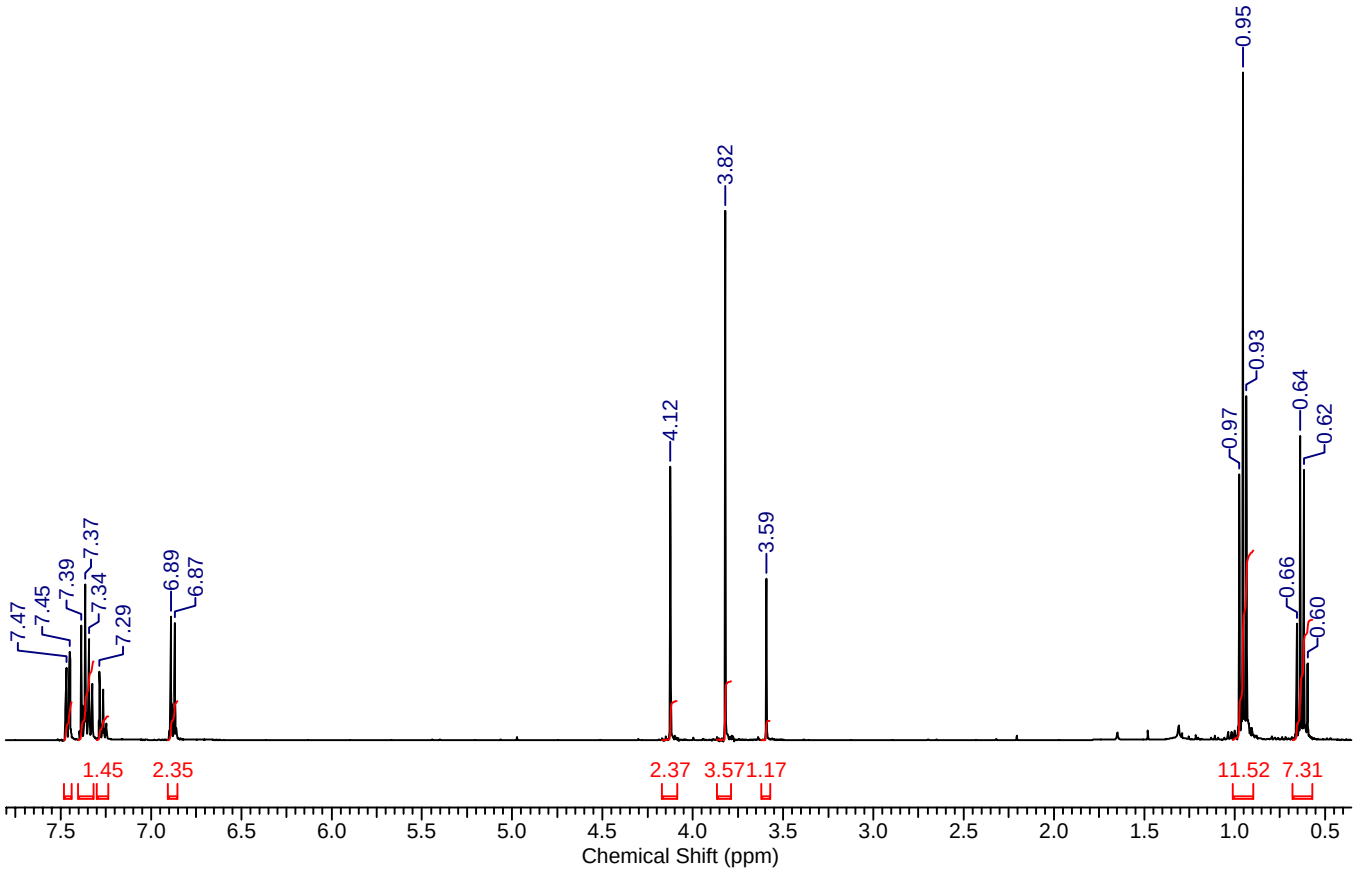


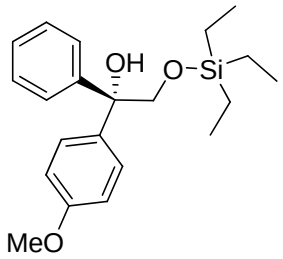
9d [from (+)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (e.r. = 96:4) (210 nm)



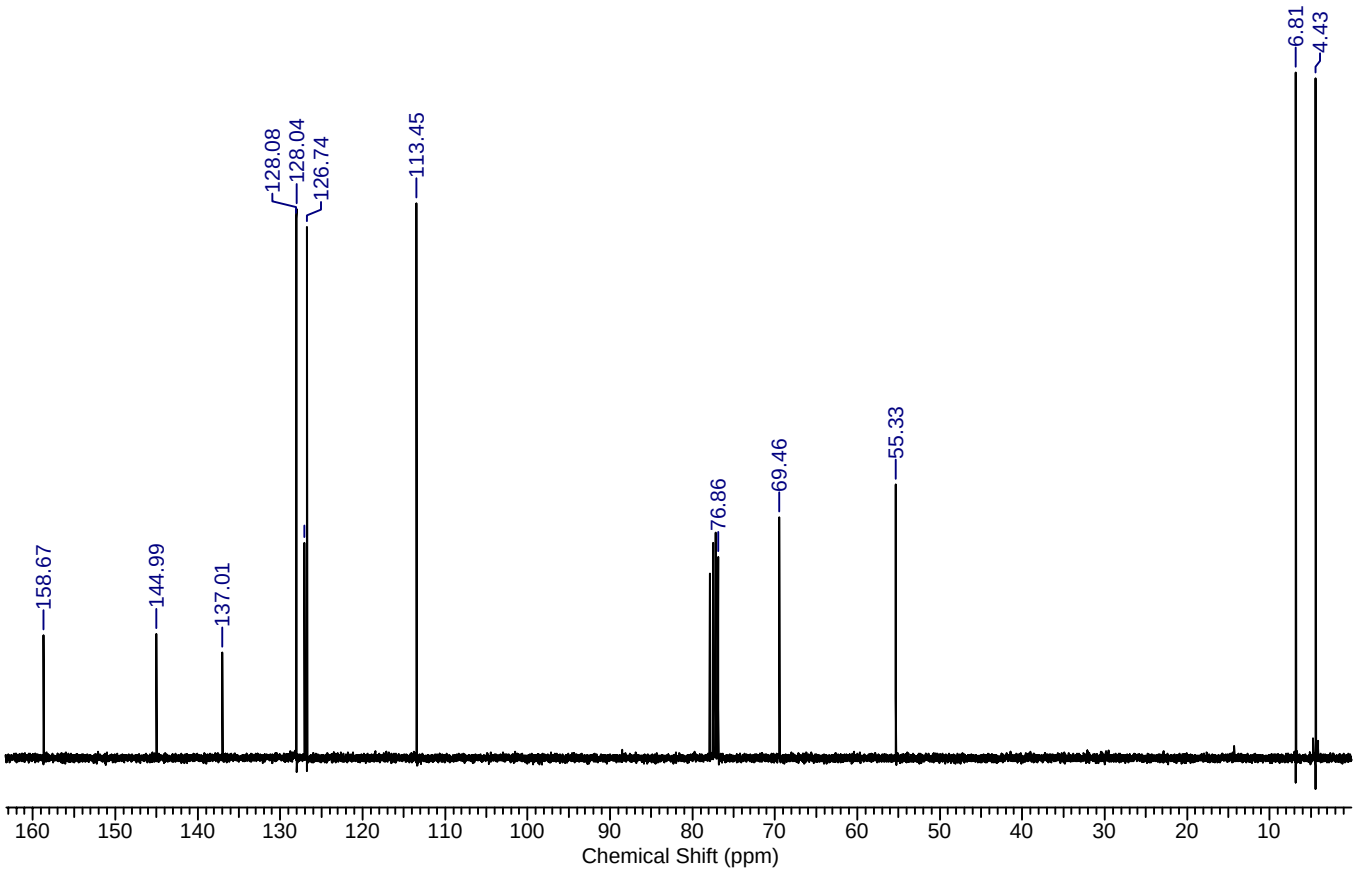


(*S*)-1-(4-methoxyphenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9e)



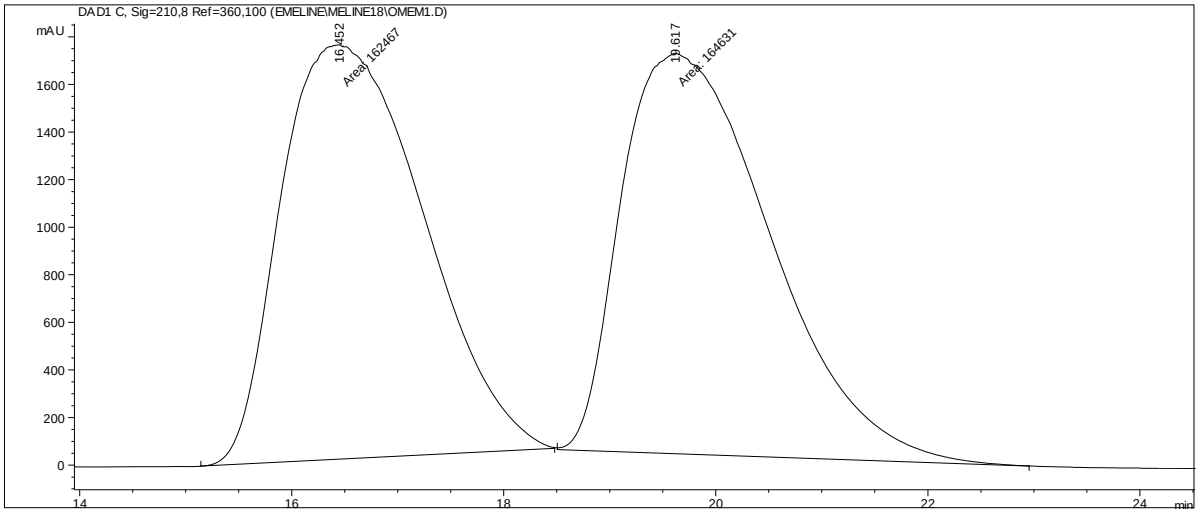


(*S*)-1-(4-methoxyphenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9e)

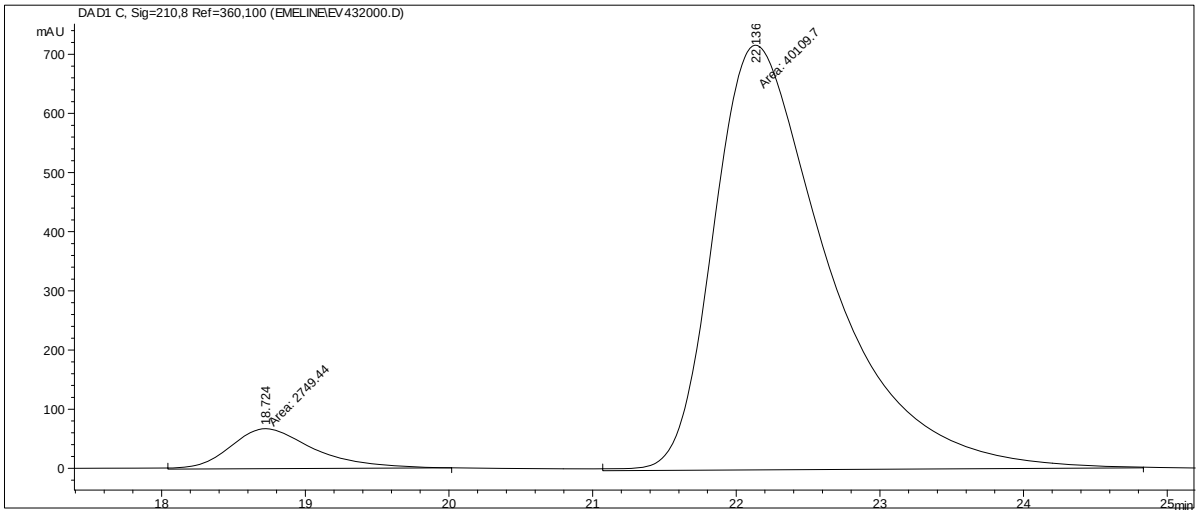


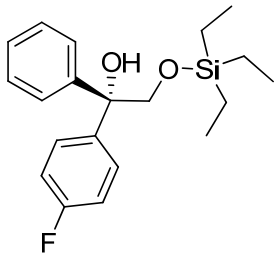
Chiral HPLC Data for 9e

9e [from (±)-styrene oxide] Daicel Chiracel-AD column, 0.5:99.5 iPrOH/Hexane, 0.7 mL/min (210 nm)

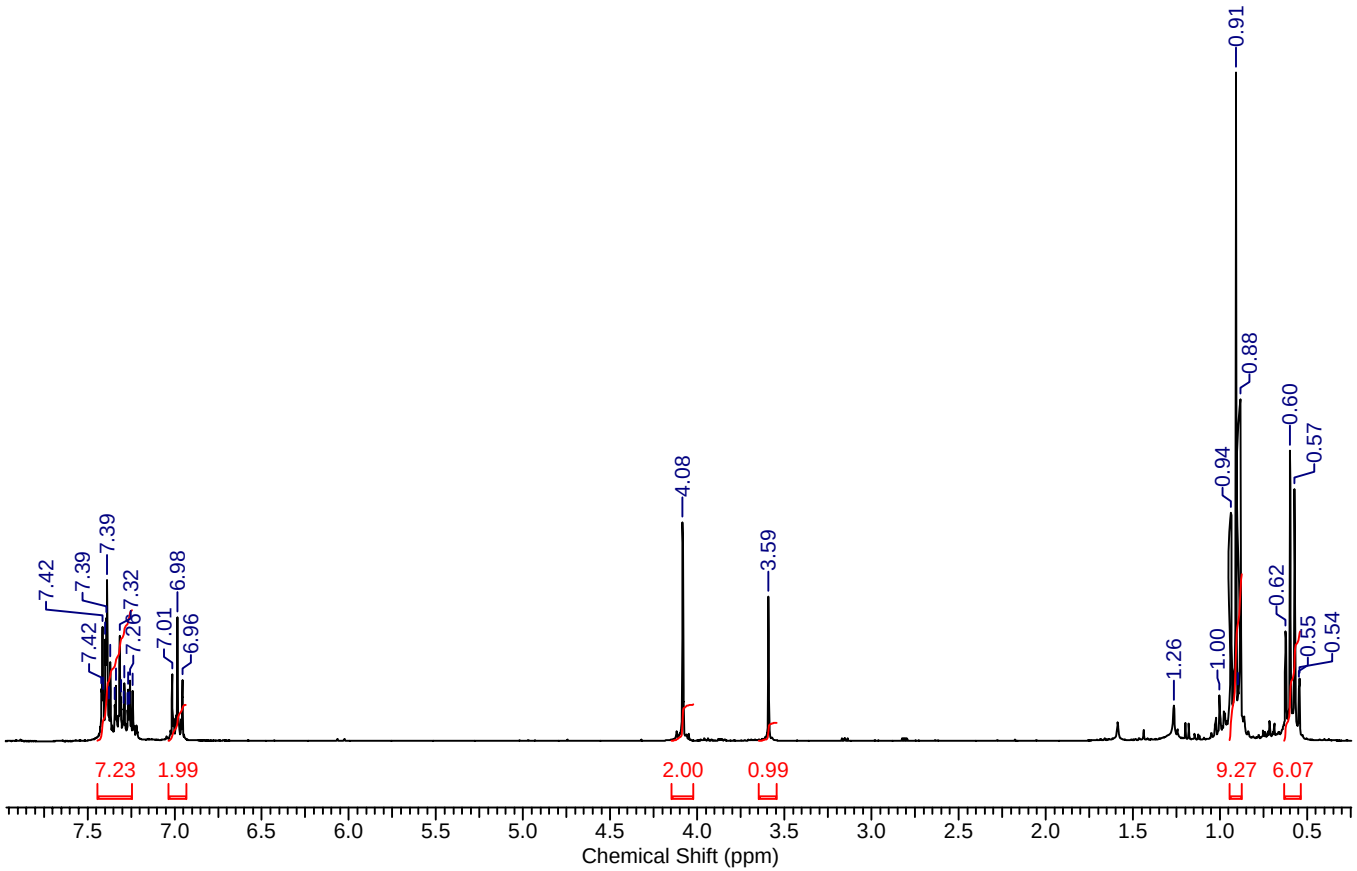


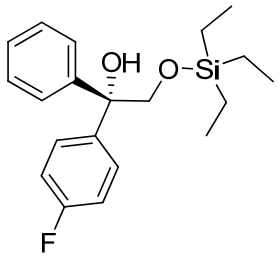
9e [from (+)-styrene oxide] Daicel Chiracel-AD column, 0.5:99.5 iPrOH/Hexane, 0.7 mL/min (e.r. = 94:6) (210 nm)



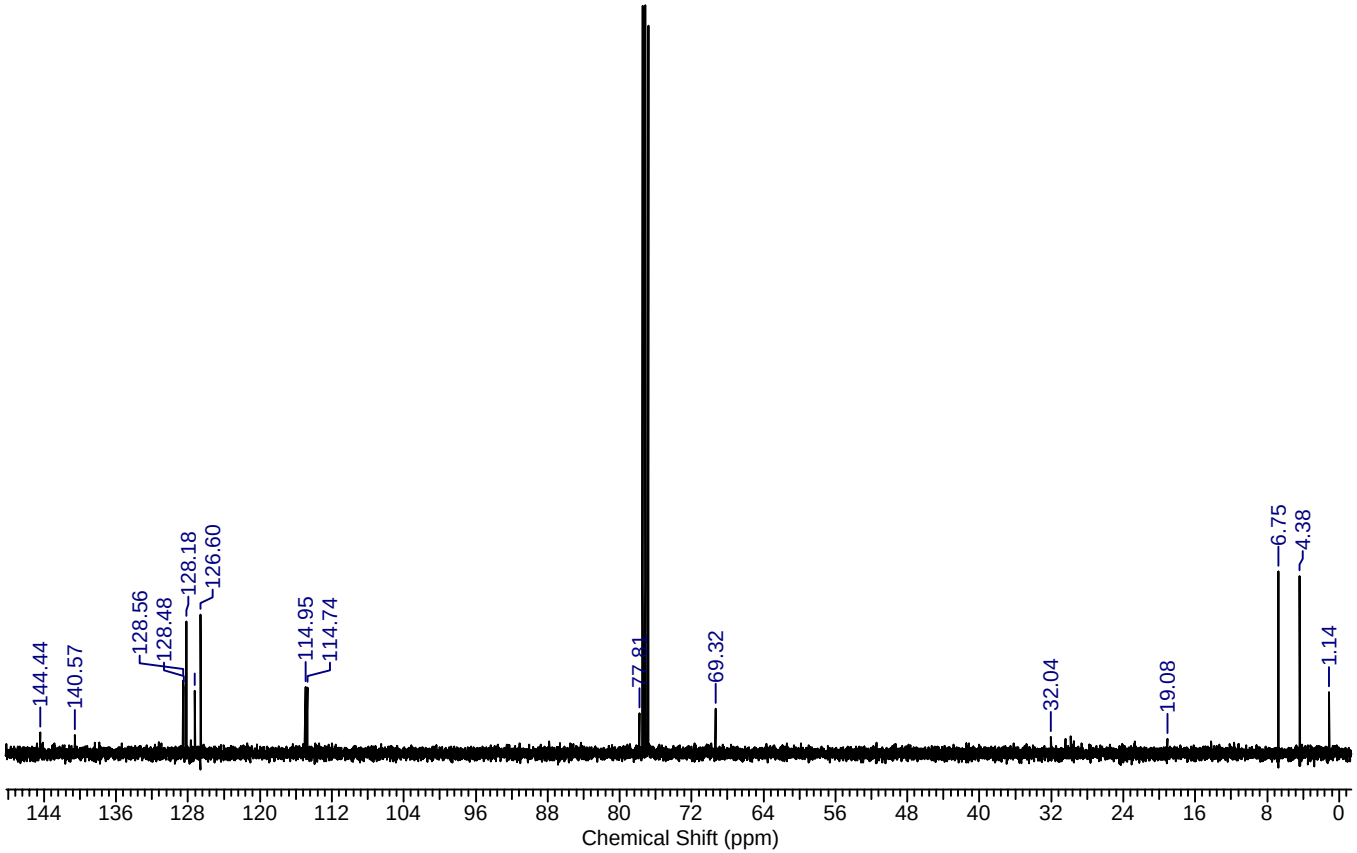


(*S*)-1-(4-fluorophenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9f)



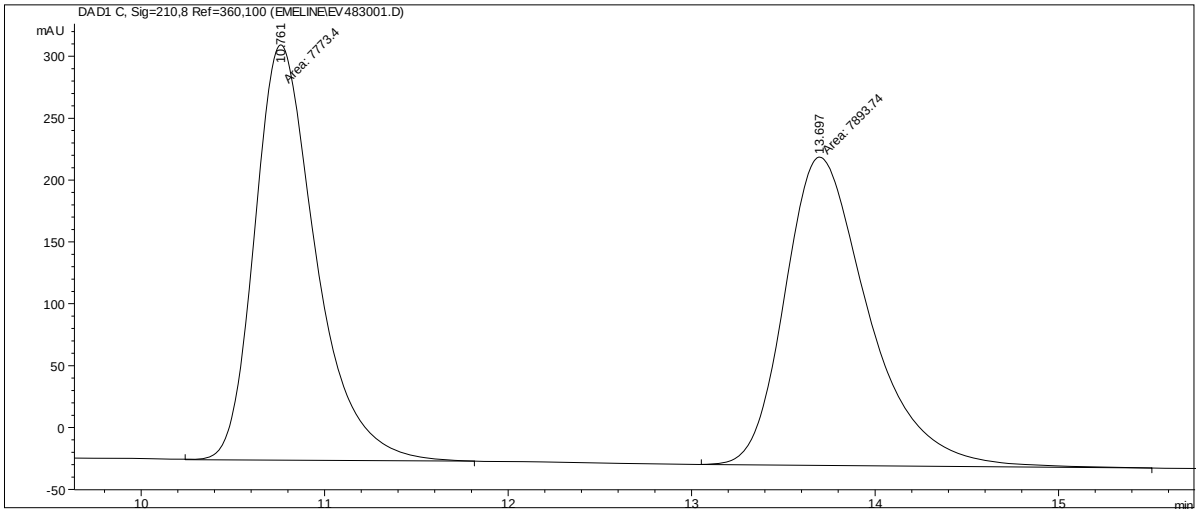


(*S*)-1-(4-fluorophenyl)-1-phenyl-2-(triethylsilyloxy)ethanol (9f)

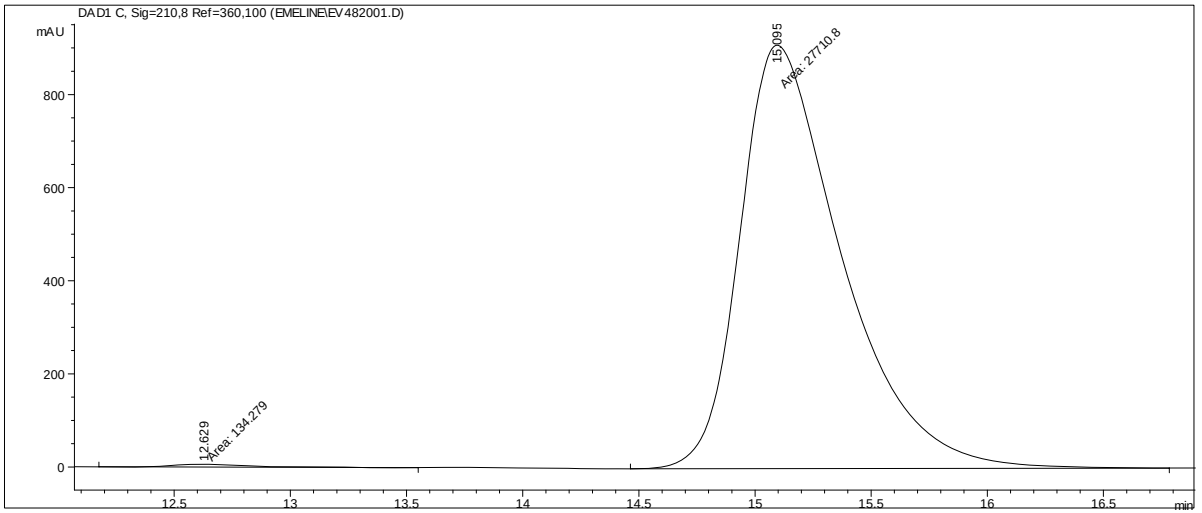


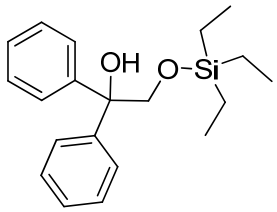
Chiral HPLC Data for 9f

9f [from (±)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (210 nm)

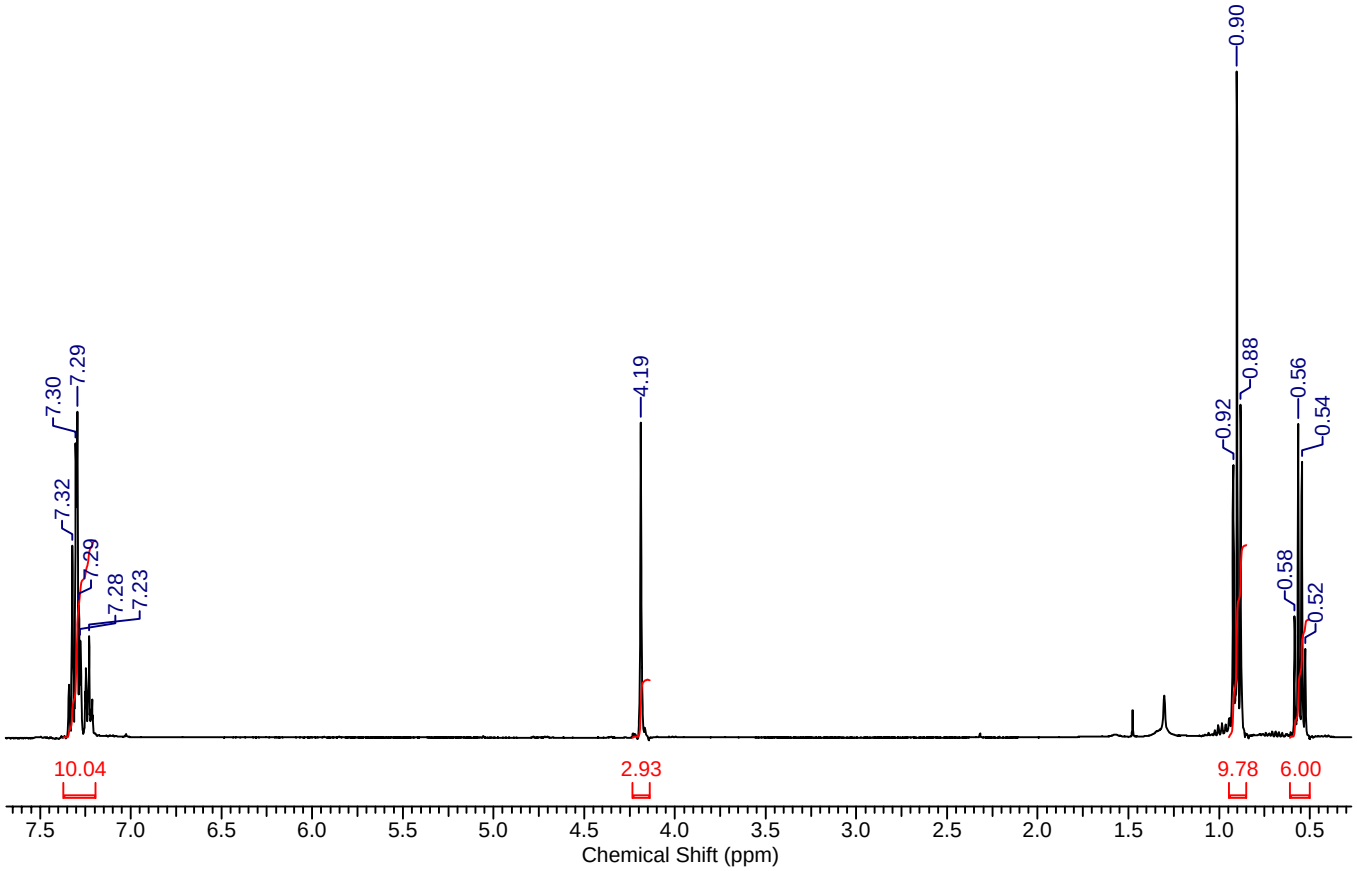


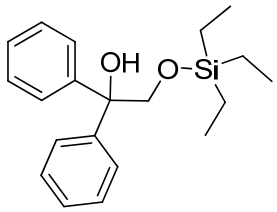
9f [from (+)-styrene oxide] Daicel Chiracel-OD-H column, 0.5:99.5 iPrOH/Hexane, 1 mL/min (e.r. = 99:1) (210 nm)



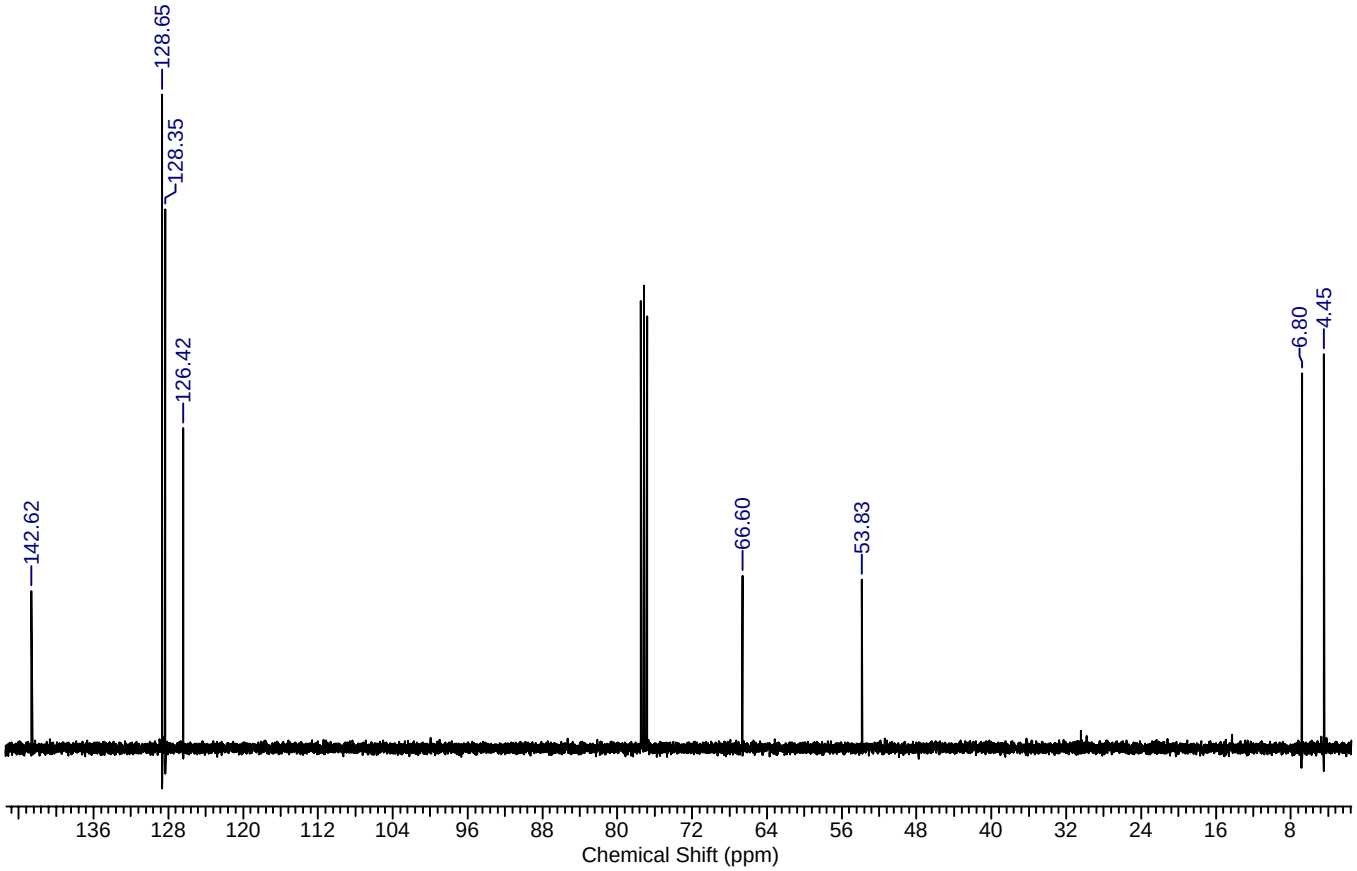


1,1-diphenyl-2-(triethylsilyloxy)ethanol (9g)

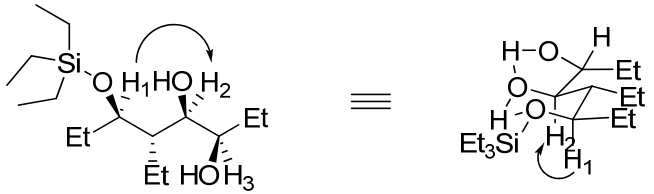




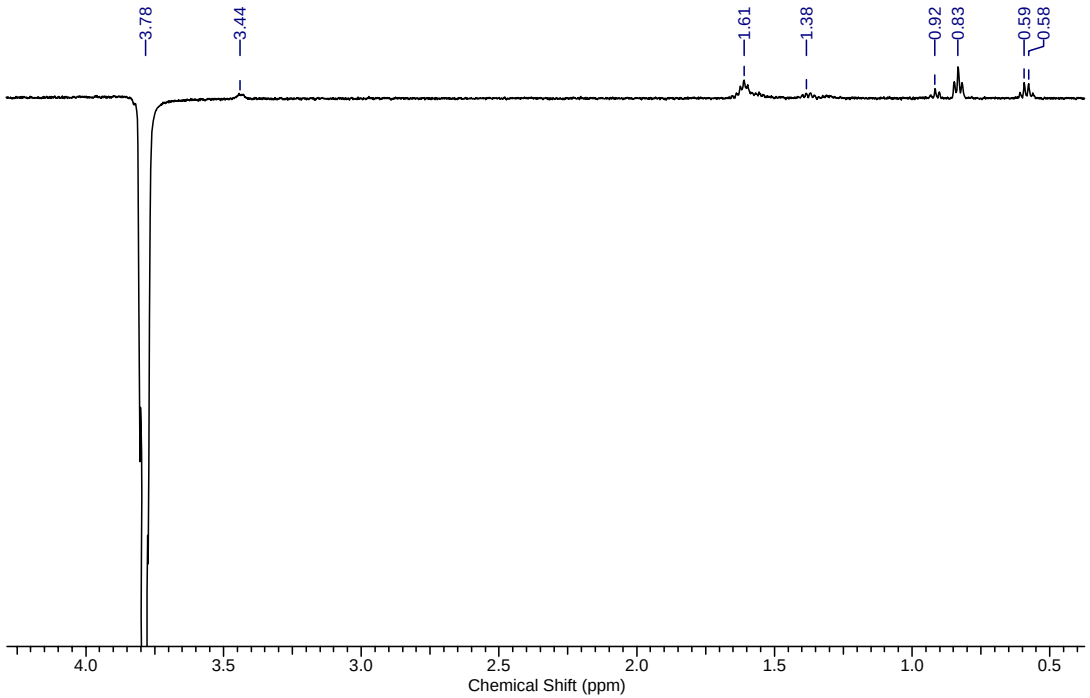
1,1-diphenyl-2-(triethylsilyloxy)ethanol (9g)



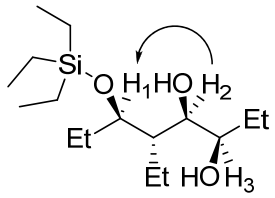
NMR experiments to give support for stereochemical assignment of **6** and **7**: nOe experiments were conducted which clearly showed that H1 and H2 were close in space in diol **6** but not in diol **7**. This arises from the preferred conformation of the diols:



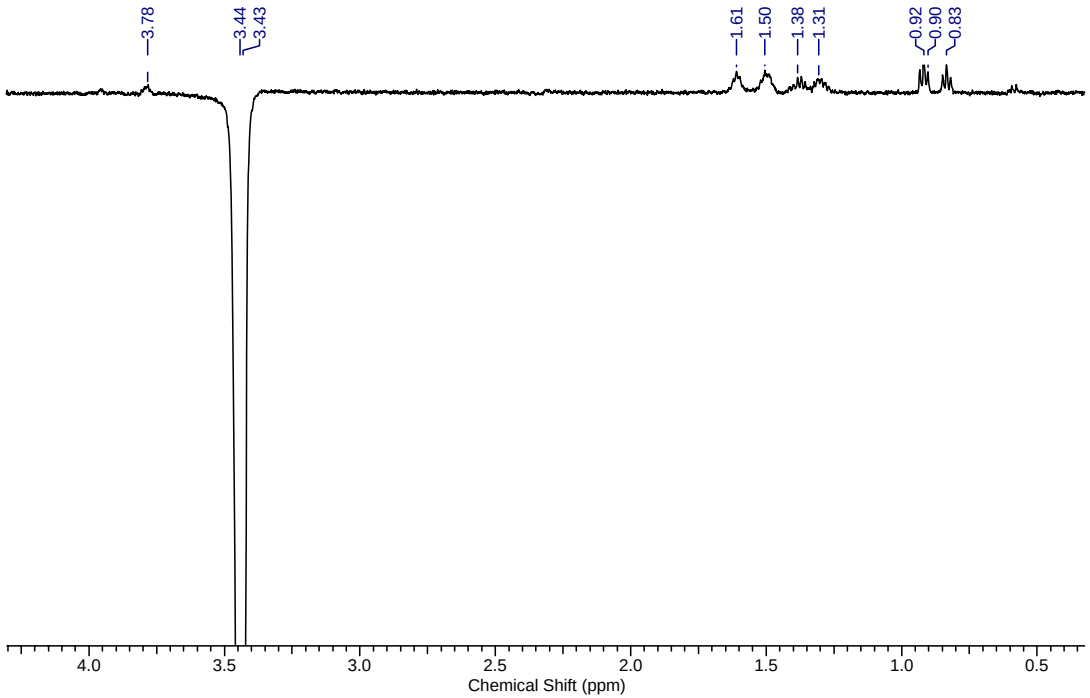
(3R,4R,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (6)



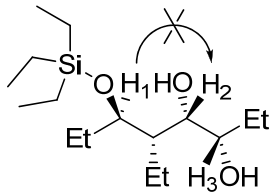
Irradiation of proton H_1 (3.78 ppm) resulted in enhancement of proton H_2 (3.44 ppm).



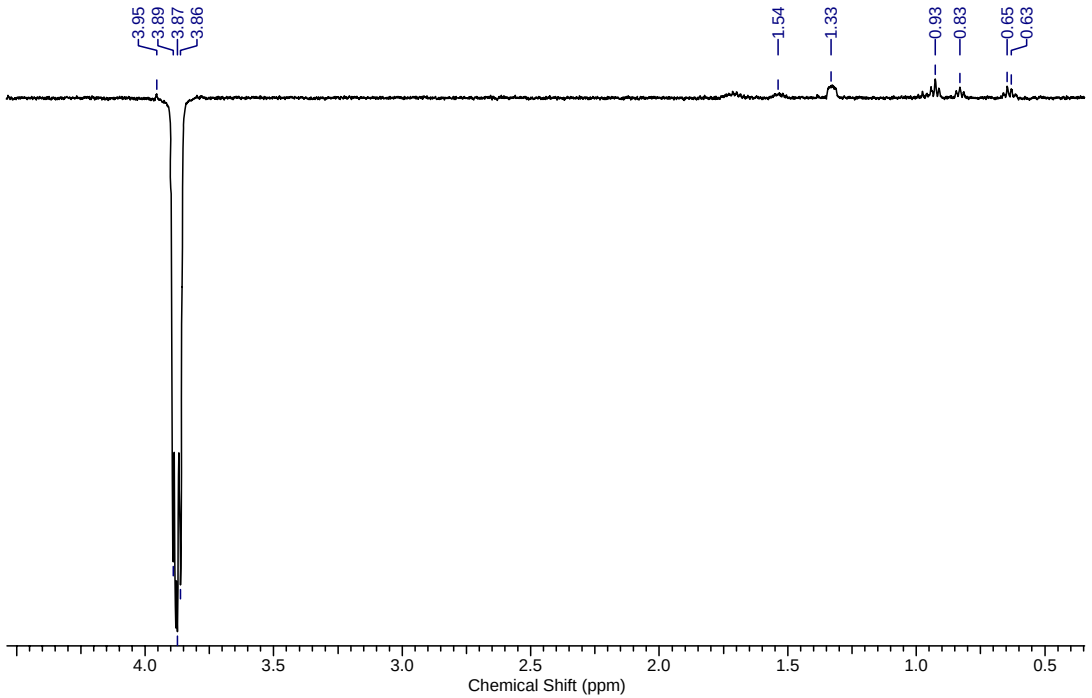
(3R,4R,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (6)



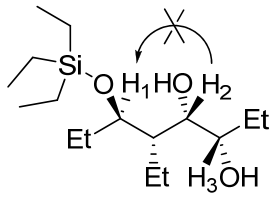
Irradiation of proton H_2 (3.44 ppm) resulted in enhancement of proton H_1 (3.78 ppm).



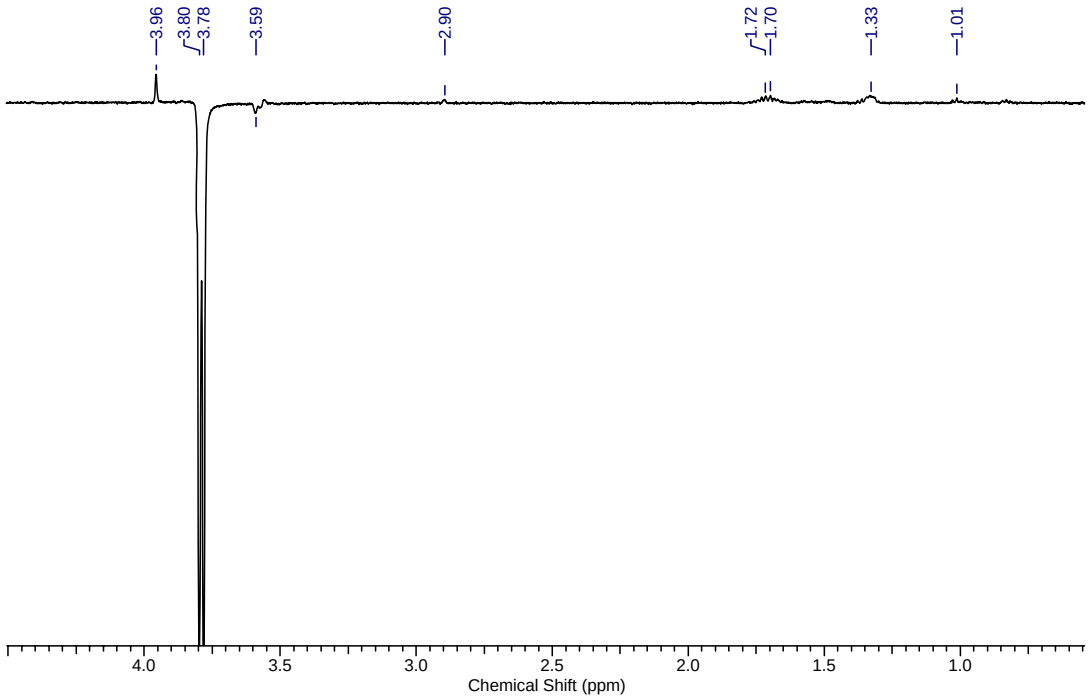
(3S,4S,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (7)



Irradiation of proton H_1 (3.87 ppm) did not result in any enhancement of proton H_2 (3.80 ppm).



(3S,4S,5S,6R)-5-ethyl-6-(triethylsilyloxy)octane-3,4-diol (7)



Irradiation of proton H_2 (3.80 ppm) resulted in enhancement of proton H_3 (3.59 ppm) but did not result in any enhancement of proton H_1 (3.87 ppm).