Supplementary Material (ESI) for Chemical Communications

Mukaiyama Aldol Addition to α-Chlorosubstituted Aldehydes. Origin of the Unexpected *Syn* Selectivity

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Supporting Information

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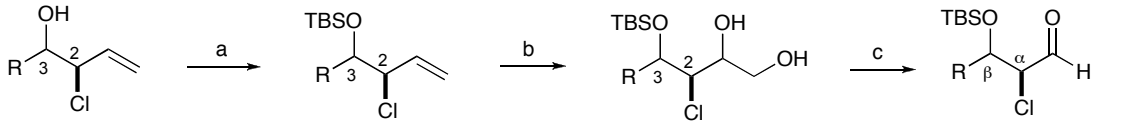
General Methods

Air and moisture sensitive reactions were carried out in flame-dried, septum-capped flask under an atmospheric pressure of nitrogen. All liquid reagents were transferred via oven-dried syringes. DMF, CH_2Cl_2, THF and Et_2O were dried using a glass-contour solvent dispensing system. Et_3N, DIPEA were distilled from CaH_2. Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates; the plates were visualized with UV light and a solution of phosphomolybdic acid in ethanol (5wt%). Flash chromatography was performed using SDS silica gel 60 (35-63 μm). Melting points where measured with a Stuart Scientific SMP3 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 MHz (100 MHz) or 500 MHz (125 MHz) on a Bruker Avance 400 or a Bruker Avance DMX 500 instrument in $CDCl_3$, using the residual peak of $CHCl_3$ (^1H NMR δ = 7.26 ppm) and the peak of $CDCl_3$ (^{13}C NMR δ = 77.0 ppm) as internal standards. Chemical shifts are reported in the δ-scale with multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, sept=septet and m=multiplet), coupling constants (Hz) and integration. IR-spectra were recorded on an ATI Mattson Infinity Series FTIR and only the strongest/structurally most important peaks (ν_{max}, cm^{-1}) are listed.

Synthesis of Aldehydes 1-9

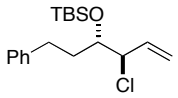
Scheme 1. Synthesis of aldehydes **1**-**2**.



26, 2,3-*anti*, R= CH_2CH_2Ph **28**, 2,3-*anti*, R= CH_2CH_2Ph **30**, 2,3-*anti*, R= CH_2CH_2Ph **1**, α,β-*anti*, R= CH_2CH_2Ph
27, 2,3-*syn*, R= CH_2CH_2Ph **29**, 2,3-*syn*, R= CH_2CH_2Ph **31**, 2,3-*syn*, R= CH_2CH_2Ph **2**, α,β-*syn*, R= CH_2CH_2Ph

a) TBDMSOTf, 2,6-lutidine, CH_2Cl_2, 64-89%. b) OsO_4, NMO, MeCN:THF:H_2O, rt, 81-98%. c) $NaIO_4$, THF:H_2O, rt, 94% (cleavage of **31**) or $Pb(OAc)_4$, CH_2Cl_2, 0 °C – rt, 98% (cleavage of **30**).

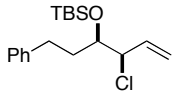
((3*R,4*S**)-4-Chloro-1-phenylhex-5-en-3-yloxy)(tert-butyl)dimethylsilane (28)**



To a stirred solution of *anti*-α-halohydrine **26** (110 mg, 522 μmol) in CH_2Cl_2 (5 mL) was added dropwise TBDMSOTf (126 μL, 548 μmol) and 2,6-lutidine (91 μL, 783 μmol) at -78 °C. The reaction mixture was allowed to reach rt and stirred over night. The reaction was quenched by addition of H_2O (7.5 mL) and the

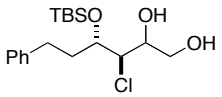
aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with H_2O (2 × 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromotagraphy (pentane) of the residue gave **28** (151 mg, 89%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (m, 5H) 5.95 (ddd, *J* = 17.1, 10.1, 8.8Hz, 1H) 5.29 (d, *J* = 17.0Hz, 1H) 5.22 (d, *J* = 10.1Hz, 1H) 4.35 (dd, *J* = 8.6, 4.2Hz, 1H) 3.90 (dd, *J* = 10.7, 4.8Hz, 1H) 2.73 (ddd, *J* = 13.3, 11.3, 5.6Hz, 1H) 2.61 (ddd, *J* = 13.5, 11.4, 5.3Hz, 1H) 1.96 (tdd, *J* = 13.8, 11.5, 5.8Hz, 1H) 1.79 (m, 1H) 0.93 (s, 9H) 0.10 (d, *J* = 9.1Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.9, 135.2, 128.4, 128.2, 125.9, 118.5, 75.1, 65.7, 36.1, 31.2, 25.9, 18.2, -4.2, -4.3; IR (film) ν_{max} = 1252, 1118, 842 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{29}ClOSi$ (M+Li): 331.1831, found: 331.1830.

((3*R,4*R**)-4-Chloro-1-phenylhex-5-en-3-yloxy)(tert-butyl)dimethylsilane (29)**



Prepared from alcohol **27** as described for **28** to afford **29** (208 mg, 64%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (m, 5H) 5.97 (ddd, *J* = 17.2, 10.2, 7.8Hz, 1H) 5.35 (td, *J* = 17.1, 1.1Hz, 1H) 5.24 (d, *J* = 10.3Hz, 1H) 4.39 (dd, *J* = 7.7, 4.9Hz, 1H) 3.88 (td, *J* = 7.4, 4.5Hz, 1H) 2.72 (ddd, *J* = 13.6, 11.7, 5.3Hz, 1H) 2.61 (ddd, *J* = 13.4, 11.5, 5.4Hz, 1H) 2.04 (m, 1H) 1.73 (m, 1H) 0.93 (s, 9H) 0.11 (d, *J* = 2.5Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.0, 134.6, 128.4, 128.3, 125.9, 118.3, 75.1, 65.3, 34.6, 31.6, 25.9, 18.1, -4.3, -4.4; IR (film) ν_{max} = 1255, 1106, 837 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{29}ClOSi$ (M+Na): 347.1568, found: 347.1571.

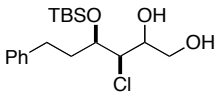
((3*R,4*S**)-4-Chloro-1-phenylhex-3-yloxy-)(tert-butyl)dimethylsilane-4,5-diol (30)**



To a stirred solution of **28** (10.2 mg, 31.4 μmol) in MeCN:H_2O:THF (2:2:1, 2.5 mL) was added NMO (5.0 mg, 41 μmol) and OsO_4 (3.1 μmol, 20 mg/mL in MeCN). The resultant solution was stirred at rt over night and quenched by addition of sodium sulfite (0.3 g) in H_2O (1 mL). After an additional 30 minutes, the aqueous phase was extracted with Et_2O (3 × 5 mL), and the combined organic phases were washed with H_2O (2 × 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford **30** (11 mg, 98%) as a yellow solid: mp 53.0-54.0 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (m, 5H) 4.16 (dd, *J* = 10.3, 5.4Hz, 1H) 4.07 (dd, *J* = 7.6, 4.5Hz, 1H) 3.94 (ddd, *J* = 7.7, 5.2, 3.6Hz, 1H) 3.88 (dd, *J* = 11.4, 3.5Hz, 1H) 3.76 (dd, *J* = 11.4, 5.2Hz, 1H) 3.48 (q, *J* = 7.0Hz, 1H) 2.75 (ddd, *J* = 13.6, 11.1, 5.9Hz, 1H) 2.67 (ddd, *J* = 13.7, 11.1, 5.4Hz, 1H) 2.25 (b, 1H) 2.08 (tdd, *J* = 14.0, 11.5, 5.9Hz, 1H) 1.96 (m, 1H) 0.95 (s, 9H) 0.15 (d, *J* = 10.5Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.4, 128.4, 128.3, 126.0, 75.2, 72.8, 63.6, 63.4, 36.4, 31.0,

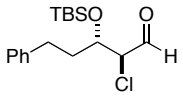
25.8, 18.1, -4.4, -4.5; IR (film) ν_{max} =3384(br), 1256, 1094, 1064, 838, 777 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{31}ClO_3Si$ (M+Na): 381.1623, found: 381.1623.

((3*R,4*R**)-4-Chloro-1-phenylhex-3-yloxy-)(tert-butyl)dimethylsilane-4,5-diol (31)**



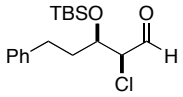
Prepared from olefin **29** as described for **30** to afford **31** (150 mg, 81%) as a yellow solid: mp 53-54.9 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (m, 5H) 4.15 (td, *J* = 8.4, 3.5Hz, 1H) 4.02 (dd, *J* = 9.7, 2.9Hz, 1H) 3.93 (m, 1H) 3.84 (m, 2H) 3.77 (m, 1H) 2.80 (ddd, *J* = 13.4, 11.5, 5.1Hz, 1H) 2.60 (m, 1H) 2.25 (m, 1H) 1.96 (dd, *J* = 7.7, 5.1Hz, 1H) 1.90 (m, 1H) 0.94 (s, 9H) 0.16 (d, *J* = 8.3Hz, 6H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.3, 128.5, 128.3, 126.1, 74.6, 72.5, 63.8, 59.3, 33.4, 32.5, 25.8, 18.0, -4.4, -4.5; IR (film) ν_{max} = 3414(br), 1254, 1076, 1042, 837, 777 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{31}ClO_3Si$ (M+H): 359.1804, found: 359.1805**.**

((3*R,4*S**)-4-Chloro-1-phenylhex-5-al-3-yloxy)(tert-butyl)dimethylsilane (1)**



To a stirred solution of **30** (103 mg, 287 μmol) in CH_2Cl_2 (2 mL) was added dropwise $Pb(OAc)_4$ (165 mg, 373 μmol) in CH_2Cl_2 (1.5 mL) at 0 °C. Precipitants started to form and the mixture was allowed to reach rt and stirred for 1 h. The reaction mixture was poured onto $NaHCO_3$ (aq, satd, 5 mL), diluted with Et_2O (3 mL) and the organic phase was washed repeatedly with $NaHCO_3$ (aq, satd) until the organic phase became colorless. Concentrated under reduced pressure gave **1** (57 mg, 60%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.48 (d, *J* = 3.5Hz, 1H) 7.24 (m, 5H) 4.18 (dd, *J* = 10.6, 5.3Hz, 1H) 4.14 (dd, *J* = 5.0, 3.5Hz, 1H) 2.69 (dd, *J* = 9.4, 7.2Hz, 2H) 2.06 (m, 1H) 1.90 (m, 1H) 0.91 (s, 9H) 0.11 (d, *J* = 1.9Hz, 6H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.8, 141.1, 128.5, 128.2, 126.1, 73.5, 65.2, 36.0, 30.7, 25.7, 15.2, -4.3, -4.6; IR (film) ν_{max} = 1731, 1254, 1116, 837, 778 cm^{-1}.

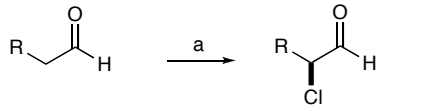
((3*R,4*R**)-4-Chloro-1-phenylhex-5-al-3-yloxy)(tert-butyl)dimethylsilane (2)**



To a stirred solution of **31** (50 mg, 139 μmol) in THF:H_2O (4:1, 1 mL) was added $NaIO_4$ (45 mg, 209 μmol) and the mixture was stirred at rt for 40 minutes before CH_2Cl_2 (1 mL) and H_2O (1 mL) was added.

The resultant solution was stirred until two phases occurred. Extrelut NT3® workup afforded **2** (43 mg, 94%) as a clear oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.60 (d, J = 2.1Hz, 1H) 7.25 (m, 5H) 4.24 (m, 2H) 2.64 (m, 2H) 2.16 (m, 1H) 1.84 (tdd, J = 13.9, 10.4, 6.2Hz, 1H) 0.89 (s, 9H) 0.07 (d, J = 19.1Hz, 6H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.6, 140.9, 128.6, 128.2, 126.2, 72.6, 67.1, 35.7, 31.6, 25.7, 18.0, -4.2, -4.7; IR (film) ν_{max} = 1733, 1255, 1112, 837, 777 cm^{-1}.

Scheme 2. Synthesis of aldehydes **6**-**7**.

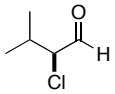


32, R= *i*-Pr
33, R= CH_2CH_2Ph

6, R= *i*-Pr
7, R= CH_2CH_2Ph

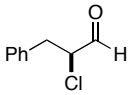
Reagents and conditions: a) NCS, L-Proline, CH_2Cl_2, 0 °C - rt, 58-60%

2-Chloro-3-methylbutanal (6)



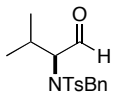
To a stirred solution of isovaleraldehyde **32** (150 mg, 1.74 mmol) in CH_2Cl_2 (7 mL) was added L-proline (40 mg, 348 μmol) and NCS (302 mg, 2.26 mmol) at 0 °C. The resultant mixture was stirred at 0 °C for 1h, allowed to reach rt and stirred for additional 1.5 h. The reaction was quenched by addition of pentane (10 mL), filtered through a short plug of celite, the organic phase was washed (H_2O, 2x15 mL), dried ($MgSO_4$) and concentrated to afford **6** (125 mg, 60%) as a clear oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.49 (d, J = 2.9Hz, 1H) 4.02 (dd, J = 5.5, 2.9Hz, 1H) 2.34 (m, 1H) 1.06 (d, J = 6.80 Hz, 3H), 1.03 (d, J = 6.67 Hz, 3H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.0, 70.4, 30.8, 19.4, 17.6.

2-Chloro-3-phenylpropanal (7).



Prepared from hydrocinnamaldehyde **33** as described for **6** to afford **7** (807 mg, 53%) as a clear oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.57 (d, J = 2.2 Hz, 1H), 7.38-7.24 (m, 5H), 4.41 (ddd, J = 8.1, 5.7, 2.1 Hz, 1H), 3.41 (dd, J = 14.5, 5.7 Hz, 1H), 3.11 (dd, J = 14.5, 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.40, 135.34, 129.40, 128.65, 127.33, 63.90, 38.28.

2-(*N*-Benzyl-*N*-tosylamino)-3-methylbutanal (9)

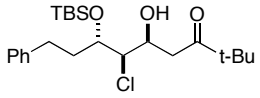


^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.30 (s, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.31-7.20 (m, 7H), 4.44 (d, J = 15.4 Hz, 1H), 4.36 (d, J = 15.4 Hz, 1H), 3.76 (d, J = 10.3 Hz, 1H), 2.41 (s, 3H), 2.19-2.07 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.70 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 198.3, 143.7, 137.5, 136.1, 129.7, 129.0, 128.2, 127.4, 71.3, 50.3, 27.0, 21.5, 20.2, 20.1; IR (film) ν_{max} = 2920, 1730, 1160 cm^{-1}; HRMS (FAB+) calcd for $C_{19}H_{23}NO_3S$ (M+Na): 368.1291, found: 368.1289.

Mukaiyama Aldol Reaction, Aldehydes 1-2, 6-7, 9

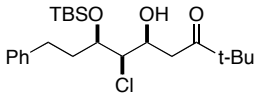
The experimental procedure for Mukaiyama aldol reaction of aldehyde **1** will be representive for all aldehydes **1**-**2**, **6**-**7**, **9**.

(5*S,6*S**,7*R**)-6-Chloro-5-yloxy-((tert-butyl)dimethylsilane)-7-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (4)**



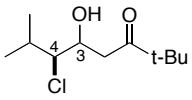
To a stirred solution of **1** (12.4 mg, 37.9 μmol) in CH_2Cl_2 (1 mL) was added $BF_3{\cdot}OEt_2$ (14 μL, 114 μmol) at -60 °C. After 5 minutes was added **3a** (16 μL, 76 μmol) and the resultant solution was stirred at -60 °C for 18 h. The reaction was quenched by addition of H_2O (5 mL) and allowed to reach rt. The aqueous phase was extracted with CH_2Cl_2 (3 × 7 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford **4** (16 mg, 99%, *dr* 95:5) as a colorless oil: Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (m, 5H) 4.56 (ddt, J = 6.3, 2.7, 1.2 Hz, 1H) 4.04 (dd, J = 11.0, 5.4 Hz, 1H) 3.90 (dd, J = 5.5. 1.2 Hz, 1H) 3.40 (d, J = 2.8 Hz, 1H) 2.76 (dd, J = 6.2, 5.7 Hz, 2H) 2.66 (ddd, J = 13.5, 11.3, 5.1 Hz, 1H) 2.55 (ddd, J = 13.5, 11.1, 6.0 Hz, 1H) 1.95 (m, 2H) 1.05 (s, 9H) 0.81 (s, 9H) 0.14 (d, J = 20.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.3, 141.5, 129.3, 128.4, 128.3, 125.9, 74.8, 65.7, 65.4, 44.3, 41.4, 36.7, 30.3, 26.2, 25.8, 18.0, -4.5, -4.7; IR (film) ν_{max} =3436(br), 1702, 1644, 1255, 1095, 837, 777 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 427.2430, found: 427.2428**.**

(5S*,6S*,7R*)-6-Chloro-5-yloxy-((tert-butyl)dimethylsilane)-7-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (**5**)



Prepared from aldehyde **2** as described for **4** to afford **5** (24 mg, 94%, *dr* 91:9) as a colorless oil. Major isomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (m, 5H) 4.41 (m, 1H) 4.01 (dd, *J* = 4.7, 2.7Hz, 1H) 3.14 (d, *J* = 4.1Hz, 1H) 2.85 (m, 2H) 2.67 (m, 2H) 2.14 (s, 1H) 1.91 (m, 1H) 1.16 (s, 9H) 0.93 (s, 9H) 0.12 (d, *J* = 2.6Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 215.2, 141.5, 128.5, 128.3, 126.0, 74.8, 68.2, 68.1, 44.4, 41.4, 35.7, 31.2, 26.4, 26.2, 25.8, 18.1, -4.1, -4.4; IR (film) ν_{max} = 3488, 1703, 1255, 1095, 1072, 837, 778 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 427.2430, found: 427.2431.

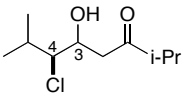
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one** (**10a, 10b**)



10a 3,4-*syn*
10b 3,4-*anti*

Prepared from aldehyde **6** as described for **4** to afford **10a** and **10b** (34 mg, 99%, *dr* 86:14) as a colorless oil. The diastereomers was separated by flash chromatography (Pentane:EtOAc 12:1). Major isomer **10a**, white solid mp 40-45 °C: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.37 (ddd, *J* = 7.5, 4.5, 2.9 Hz, 1H), 3.68 (dd, *J* = 7.6, 2.9 Hz, 1H), 2.89 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.76 (dd, *J* = 17.8, 4.6 Hz, 1H), 2.68 (s, 1H), 2.14 (qd, *J* = 13.4, 6.7, 6.7, 6.7 Hz, 1H), 1.15 (s, 1H), 1.08 (t, *J* = 6.9, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 215.6, 74.3, 68.0, 44.4, 41.9, 32.4, 26.2, 20.3, 19.9; IR (film) ν_{max} = 3491, 2962, 1701, 737 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}ClO_2$ (M+H): 221.1308, found: 221.1303; Minor isomer **10b**, colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.05 (dt, *J* = 8.6, 8.5, 2.4 Hz, 1H), 3.78 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.72-3.55 (sbr, 1H), 3.08 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.78 (dd, *J* = 18.0, 8.1 Hz, 1H), 2.41 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 1H), 1.18-1.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 218.3, 71.3, 69.4, 44.6, 40.0, 29.0, 26.2, 20.7, 15.6; IR (film) ν_{max} = 3479, 2966, 1689, 725 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}ClO_2$ (M+H): 221.1308, found: 221.1303.

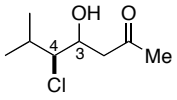
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,7-dimethyloctan-3-one** (**11a, 11b**)



11a 3,4-*syn*
11b 3,4-*anti*

Prepared from aldehyde **6** as described for **4** to afford **11a** and **11b** (112 mg, 83%, *dr* 35:65) as a colorless oil. The diastereomers was separated by flash chromotagraphy (Pentane:EtOAc 8:1). Minor isomer **11a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.37 (td, *J* = 7.5, 3.7, 3.7 Hz, 1H), 3.68 (dd, *J* = 7.3, 3.1 Hz, 1H), 2.86 (dd, *J* = 17.5, 7.9 Hz, 1H), 2.71 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.67 (s br, 1H), 2.61 (m, 1H), 2.19-2.08 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 6H), 1.07 (dd, *J* = 6.5, 5.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 214.1, 74.4, 68.0, 45.2, 41.5, 32.3, 20.4, 19.7, 17.99, 17.95; IR (film) ν_{max} = 3479, 2970, 1709, 741 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{19}ClO_2$ (M+H): 207.1146, found: 207.1147; Major isomer **11b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.05 (dt, *J* = 8.5, 8.5, 2.3 Hz, 1H), 3.74 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.51 (s br, 1H), 3.01 (dd, *J* = 17.9, 2.5 Hz, 1H), 2.73 (dd, *J* = 18.0, 8.2 Hz, 1H), 2.61 (m, 1H), 2.42-2.31 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 1H), 1.10 (d, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 214.1, 74.4, 68.0, 45.2, 41.5, 32.3, 20.4, 19.7, 17.99, 17.96; IR (film) ν_{max} = 3475, 2970, 1704, 733 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{19}ClO_2$ (M+H): 207.1146, found: 207.1149.

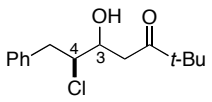
(5*S,6*S**/5*R**,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one (12a, 12b)**



12a 3,4-*syn*
12b 3,4-*anti*

Prepared from aldehyde **6** as described for **4** to afford **12a** and **12b** (136 mg, 94%, *dr* 40:60) as a colorless oil. The diastereomers was separated by flash chromotagraphy (Pentane:EtOAc 6:1). Minor isomer **12a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.36 (m, 1H), 3.67 (dd, *J* = 7.1, 3.4 Hz, 1H), 2.85 (dd, *J* = 17.3, 8.2 Hz, 1H), 2.67 (dd, *J* = 17.3, 4.1 Hz, 1H), 2.62 (s br, 1H), 2.21 (s, 3H), 2.13 (qd, *J* = 13.5, 6.7, 6.7, 6.7 Hz, 1H), 1.07 (dd, *J* = 6.7, 3.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 207.9, 74.3, 68.0, 48.4, 32.2, 30.9, 20.4, 19.5; IR (film) ν_{max} = 3456, 2966, 1712, 737 cm^{-1}; HRMS (FAB+) calcd for $C_8H_{15}ClO_2$ (M+Na): 201.0653, found: 201.0653; Major isomer **12b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.10 (dt, *J* = 8.6, 8.6, 2.5 Hz, 1H), 3.75 (dd, *J* = 8.6, 3.7 Hz, 1H), 3.36 (s br, 1H), 3.01 (dd, *J* = 18.0, 2.4 Hz, 1H), 2.72 (dd, *J* = 18.0, 8.5 Hz, 1H), 2.35 (dtd, *J* = 13.4, 6.7, 6.7, 3.7 Hz, 1H), 2.21 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ; IR (film) ν_{max} = 3448, 2966, 1708, 733 cm^{-1}; HRMS (FAB+) calcd for $C_8H_{15}ClO_2$ (M+Na): 201.0653, found: 201.0651.

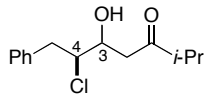
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (13a, 13b)**



13a 3,4-*syn*
13b 3,4-*anti*

Prepared from aldehyde **7** as described for **4** to afford **13a** and **13b** (575 mg, 99%, *dr* 78:22) as a colorless oil. The diastereomers was separated by flash chromotagraphy (Heptane:EtOAc 5:1→3:1). Major isomer **13a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (m, 5H), 4.22 (ddd, J = 8.3, 3.9, 2.2 Hz, 1H), 4.16 (ddd, J = 8.6, 6.6, 2.2 Hz, 1H), 3.32 (dd, J = 14.0, 6.6 Hz, 1H), 3.12 (dd, J = 14.0, 8.2 Hz, 1H), 3.03 (s br, 1H), 2.92 (dd, J = 17.9, 8.3 Hz, 1H), 2.81 (dd, J = 17.9, 4.0 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 216.0, 137.6, 129.3, 128.5, 126.8, 68.2, 66.8, 44.4, 41.0, 40.8, 26.2; IR (film) ν_{max} = 3479, 2970, 1701, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{21}ClO_2$ (M+H): 269.1303, found: 269.1304; Minor isomer **13b**, white solid, mp xx-xx °C: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.22 (m, 5H), 4.12 (ddd, J = 8.6, 7.2, 3.9 Hz, 1H), 4.07 (t, J = 7.5, 7.5 Hz, 1H), 3.69 (s br, 1H), 3.37 (dd, J = 14.4, 3.8 Hz, 1H), 3.03-2.93 (m, 2H), 2.85 (dd, J = 18.0, 8.0 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 217.5, 137.3, 129.6, 128.3, 126.8, 70.8, 65.5, 44.6, 40.1, 39.2, 26.2; IR (film) ν_{max} = 2475, 2970, 1701, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{21}ClO_2$ (M+H): 269.1303, found: 269.1305.

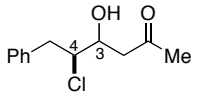
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2-methyl-7-phenylheptan-3-one** (**14a, 14b**)



14a 3,4-*syn*
14b 3,4-*anti*

Prepared from aldehyde **7** as described for **4** to afford **14a** and **14b** (163 mg, 97%, *dr* 29:71) as a colorless oil. The diastereomers was separated by flash chromotagraphy (Heptane:EtOAc 5:1). Minor isomer **14a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 4.22 (ddd, J = 8.5, 3.8, 2.4 Hz, 1H), 4.13 (ddd, J = 6.7, 8.1, 2.4 Hz, 1H), 3.31 (dd, J = 14.0, 6.7 Hz, 1H), 3.10 (dd, J = 14.0, 8.1 Hz, 1H), 2.90 (dd, J = 17.8, 8.5, Hz 1H), 2.75 (dd, J = 17.8, 3.8 Hz, 1H), 2.61 (hept, J = 6.9 Hz, 1H), 1.12 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 214.56, 137.55, 129.32, 128.53, 126.87, 68.06, 66.83, 44.33, 41.45, 40.83, 17.96, 17.95; IR (film) ν_{max} = 3467, 2970, 1705, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{14}H_{19}ClO_2$ (M+H): 255.1146, found: 255.1147; Major isomer **14b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 3H), 4.12 – 4.05 (m, 2H), 3.59 (br s, 1H), 3.34 (dd, J = 14.4, 3.3 Hz, 1H), 2.99 – 2.91 (m, 2H), 2.82 (dd, J = 17.8, 7.9 Hz, 1H), 2.62 (hept, J = 6.9 Hz, 1H), 1.12 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 214.56, 137.55, 129.32, 128.53, 126.87, 68.06, 66.83, 44.33, 41.45, 40.83, 17.96, 17.95; IR (film) ν_{max} = 3479, 2970, 1709, 1466, 1045 cm^{-1}; HRMS (FAB+) calcd for $C_{14}H_{19}ClO_2$ (M+H): 255.1146, found: 255.1145.

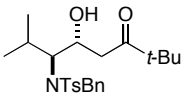
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (15a, 15b)**



15a 3,4-*syn*
15b 3,4-*anti*

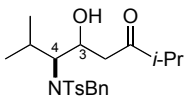
Prepared from aldehyde **7** as described for **4** to afford **15a** and **15b** (354 mg, 51%, *dr* 66:34) as a colorless oil. The following ratios were used: aldehyde 2 equiv., $BF_3{\cdot}OEt_2$ 2 equiv., enolsilane 1 equiv. The diastereomers was separated by preparative HPLC (Hexanes 99.5%, 2-propanol 0.5%). Major isomer **15b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 4.14 – 4.08 (m, 2H), 3.42 (br s, 1H), 3.32 (dd, J = 14.4, 3.3 Hz, 1H), 2.98 – 2.92 (m, 2H), 2.81 (dd, J = 17.9, 8.1 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 209.44, 137.22, 129.51, 128.39, 126.85, 70.37, 65.50, 45.85, 40.05, 30.88.; IR (film) ν_{max} = 3440, 2931, 1701, 1408, 698 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{15}ClO_2$ (M+H): 227.0833, found: 227.0834; Minor isomer **15a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 4.24 – 4.19 (ddd, J = 8.7, 3.6, 2.3 Hz, 1H), 4.11 (ddd, J = 8.0, 6.8, 2.3 Hz, 1H), 3.29 (dd, J = 14.0, 6.8 Hz, 1H), 3.09 (dd, J = 14.0, 8.0 Hz, 1H), 2.90 (dd, J = 17.8, 8.7 Hz, 1H), 2.71 (dd, J = 17.8, 3.6 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 208.38, 137.48, 129.32, 128.57, 126.92, 67.89, 66.75, 47.61, 40.80, 30.71; IR (film) ν_{max} = 3448, 2912, 1712, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{15}ClO_2$ (M+H): 227.0833, found: 227.0833.

(5*R,6*S**)-6-(*N*-Benzyl-*N*-tosylamino)-5-hydroxy-2,2,7-trimethyloctan-3-one (19b)**[1]



Prepared from aldehyde **9** as described for **4** to afford **19b** (90 mg, 85%, *dr* >2:98) as a colorless oil. Major isomer **19b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.35-7.21 (m, 5H), 4.61 (d, *J* = 15.4 Hz, 1H), 4.36 (d, *J* = 15.4 Hz, 1H), 4.01 (m, 1H), 3.43 (m, 1H), 3.26 (d, *J* = 2.2 Hz, 1H), 2.53 (m, 2H), 2.42 (s, 3H), 1.91 (m, 1H), 1.04 (s, 9H), 0.74 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 217.5, 143.2, 138.2, 137.6, 129.6, 129.1, 128.4, 127.7, 127.3, 69.2, 44.2, 41.7, 29.3, 26.3, 22.3, 21.5, 20.2; IR (neat) ν_{max} = 3400, 2970, 1690, 1160 cm^{-1}; HRMS (FAB+) calcd for $C_{25}H_{36}NO_4S$ (M+H): 446.2365, found: 446.2359.

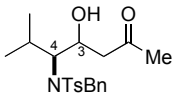
(5R*,6S*)-6-(*N*-Benzyl-*N*-tosylamino)-5-hydroxy-2,7-dimethyloctan-3-one (20a, 20b)



20a, 3,4-*syn*
20b, 3,4-*anti*

Prepared from aldehyde **9** as described for **4** to afford **20a** and **20b** (140 mg, 94%, *dr* 7:93) as a colorless oil. The diastereomers was separated by flash chromotagraphy (Heptane:EtOAc 6:1); Major isomer **20b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 8.2 HZ, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.34 – 7.24 (m, 5H), 4.63 (d, J = 15.4 Hz, 1H), 4.33 (d, J = 15.4 Hz, 1H), 3.99 (unresolved m, 1H), 3.43 (unresolved m, 1H), 3.27 (br s, J = 2.1 Hz, 1H), 2.55 – 2.35 (m, 6H), 1.96 – 1.77 (unresolved m, 1H), 1.03 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 215.81, 143.21, 138.03, 137.54, 129.52, 129.02, 128.33, 127.59, 127.19, 69.12, 66.99 (br), 48.91 (br), 44.87, 41.02, 29.17, 22.19, 21.39, 20.00, 17.86, 17.81; IR (film) ν_{max} = 3521(br), 2970, 1705, 1335, 1157 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 432.2203, found: 432.2205.

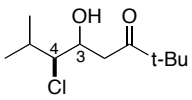
(4*R,5*S**)-5-(*N*-Benzyl-*N*-tosylamino)-4-hydroxy-6-methylheptan-2-one** (**21a, 21b**)



21a, 3,4-*syn*
21b, 3,4-*anti*

Prepared from aldehyde **9** as described for **4** to afford **21a** and **21b** (47.3 mg, 60%, *dr* 22:78) as a colorless oil. The following ratios were used: aldehyde 2 equiv., $BF_3{\cdot}OEt_2$ 2 equiv., enolsilane 1 equiv. The diastereomers was separated by flash chromotagraphy (Heptane:EtOAc 8:1 → 4:1). Major isomer **21b**: ^{1}H NMR ($CDCl_3$, 400 MHz, 55 °C) δ 7.70 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.0 Hz, 2H), 7.36 – 7.24 (m, 5H), 4.64 (d, J = 15.5 Hz, 1H), 4.32 (d, J = 15.5 Hz, 1H), 4.04 (unresolved m, 1H), 3.44 (dd, J = 6.2, 6.2 Hz 1H), 3.09 (br s, 1H), 2.63 – 2.46 (m, 2H), 2.44 (s, 3H), 2.01 (s, 3H), 1.99 – 1.87 (m, 1H), 1.04 (d, J = 6.7 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 45 °C) δ 209.56, 143.29, 138.36, 137.60, 129.56, 129.18, 128.46, 127.78, 127.41, 69.52, 67.22 (br), 49.33 (br), 48.04, 30.33, 29.37, 22.30, 21.40, 20.03; IR (film) ν_{max} = 3618(br), 2962, 1709, 1334, 1157 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 404.1890, found: 404.1890.

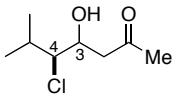
(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one** (**10a, 10b**)



10a 3,4-*syn*
10b 3,4-*anti*

To a a solution of Ph_3CBF_4 (657 mg, 1.99 mmol) in CH_2Cl_2 (17 ml) at -60 °C was added **6** (80 mg, 0.66 mmol) and the solution stirred for 15 min followed by addition of **3a** (229 mg, 1.33 mmol). The resultant mixture stirred for 18 h and then quenched by addition of H_2O (17 ml) and allowed to reach rt. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The mixture was purified by flash chromatography (Pentane:EtOAc 12:1) to afford **10a** and **10b** (117 mg, 80%, *dr* 84:16) as a colorless oil.

(5*S,6*S**/5*R**,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one** (**12a, 12b**)

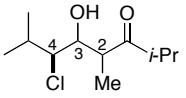


12a 3,4-*syn*
12b 3,4-*anti*

Prepared from aldehyde **6** as described for **10.** The mixture was purified by flash chromotagraphy (Pentane:EtOAc 6:1) to afford **12a** and **12b** (99 mg, 83%, *dr* 37:63) as colorless oils.

Boron enolate addition, Aldehyde 6

(4*R*,5*S*/4*S*,5*R*)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (**24a, 24b**)

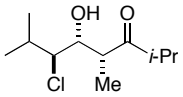


24a 2,3-*anti*, 3,4-*syn*
24b 2,3-*anti*, 3,4-*anti*

To a stirred solution of 2-methyl-3-pentanone (41 μL, 332 μmol) in Et_2O (0.6 mL) was added $(cHex)_2BCl$ (349 μL, 1M in Hexane) and Et_3N (51 μL, 365 μmol) at 0 °C. The solution turned white and was stirred for 1h before it was cooled down to -78 °C and **6** (40 mg, 332 μmol) dissolved in Et_2O (0.4 mL) was added dropwise. The resultant mixture was stirred at -78 °C for 2 h, allowed to warm up to 0 °C and after 10 minutes quenched by sequential addition of phosphate buffer pH 7 (1.5 mL), MeOH (1.5 mL) and H_2O_2 (1.5 mL). The mixture was stirred for additional 30 minutes at rt and diluted with buffer (5 mL) and CH_2Cl_2 (5 mL). The aqueous phase was extracted (CH_2Cl_2, 3 × 5 mL), the combined organic phases was washed (1:1 NaS_2O_3, 20wt%, aq. and $NaHCO_3$, satd., aq.), dried (Na_2SO_4) and concentrated to afford **24a** and **24b** (30 mg, 50%, *dr* 13:87) as a colorless oil. The diastereomers was separated by flash chromotagraphy (pentane:EtOAc 16:1). Minor isomer **24a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67 (dd, J = 8.6, 1.7 Hz, 1H), 4.03 (d, J = 7.9, 1H), 3.06 (m, 1H), 2.74 (sept, J = 6.9 Hz, 1H), 2.11 (m, 1H), 1.08 (m, 9H), 1.01 (m, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 218.1, 73.1, 71.8, 48.6, 41.1, 32.7, 20.8, 20.1, 18.0, 17.9, 13.9; IR (film) ν_{max} = cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{21}ClO_2$ (M+H): 221.1303, found: 221.1302; Major isomer **24b**:

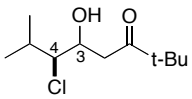
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.99 (s, 1H), 3.64 (dd, J = 10.1, 2.3 Hz, 1H), 3.52 (d, J = 10.2 Hz, 1H), 3.46 (dq, J = 7.4, 2.8 Hz, 1H), 2.77 (sept, J = 6.9 Hz, 1H), 2.54 (dsept, J = 6.7, 2.32 Hz, 1H), 1.32 (d, J =7.35 Hz, 3H), 1.14 (d, J = 7.0 Hz, 3H), 1.10 (d, J = 6.82 Hz, 3H), 1.01 (d, J = 6.85 Hz, 3H), 0.92 (d, J = 6.58 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 223.1, 76.3, 70.8, 43.3, 40.9, 28.8, 20.9, 18.1, 17.6, 15.7, 14.5; IR (film) ν_{max} = 3413(br), 1641, 1065, 1025, 742 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{21}ClO_2$ (M+H): 221.1303, found: 221.1302.

(4*R,5*R**,6*S**)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (25b)**



To 2-methyl-3-pentanone (41 μL, 332 μmol) in Et_2O (0.6 mL) at 0 °C was added 9-BBNOTf (730 μL, 0.5 M in Hexane) and DIPEA (69 μL, 398 μmol). The solution turned yellow and was allowed to reach rt and stirred for 1h before it was cooled down to -78 °C and **6** (40 mg, 332 μmol) dissolved in Et_2O (0.7 mL) was added dropwise. The resultant mixture was stirred at -78 °C for 2 h, allowed to warm up to 0 °C and after 10 minutes quenched by sequential addition of phosphate buffer pH 7 (1.5 mL), MeOH (1.5 mL) and H_2O_2 (1.5 mL). The mixture was stirred for additional 30 minutes at rt. Diluted with buffer (5 mL) and CH_2Cl_2 (5 mL). The aqueous phase was extracted (CH_2Cl_2, 3 × 5 mL), the combined organic phases was washed (1:1 NaS_2O_3, 20wt%, aq. and $NaHCO_3$ satd., aq.), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (pentane:EtOAc 16:1) to afford **25b** (61 mg, 99%, *dr* 94:6) as a colorless oil. Major isomer **25b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.93 (td, J = 10.1, 1.7, 1.7 Hz, 1H), 3.77 (dd, J = 10.1, 2.2 Hz, 1H), 3.61 (d, J = 1.9 Hz, 1H), 3.35 (dq, J = 7.3, 7.3, 7.3, 1.5 Hz, 1H), 2.82 (sept., J = 6.9, 6.9, 6.9, 6.9, 6.9, 6.9 Hz, 1H), 2.46 (dtd, J = 13.4, 6.7, 6.7, 2.2 Hz, 1H), 1.38-1.10 (m, 9H), 1.04 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 221.3, 71.1, 67.8, 43.9, 40.0, 28.1, 20.9, 18.7, 17.8, 14.5, 8.6; IR (film) ν_{max} = 3451(br), 1681, 1090, 1017, 735 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{21}ClO_2$ (M+H): 221.1303, found: 221.1301.

(5*S,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one (10a, 10b)**



10a 3,4-*syn*
10b 3,4-*anti*

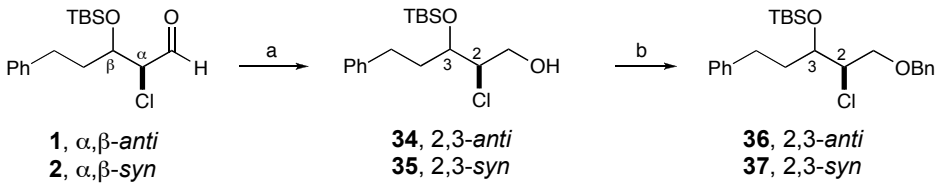
To a stirred solution of 3,3-dimethyl-2-butanone (258 μL, 2.07 mmol) in Et_2O (10.3 mL) was added $(cHex)_2BCl$ (2.18 mL, 1M in Hexane) and Et_3N (317 μL, 2.28 mmol) at 0 °C. The solution turned white and

was stirred for 1h before it was cooled down to -78 °C and **6** (250 mg, 2.07 mmol) dissolved in Et_2O (1 mL) was added dropwise. The resultant mixture was stirred at -78 °C for 2 h, allowed to warm up to 0 °C and after 10 minutes quenched by sequential addition of phosphate buffer pH 7 (6 mL), MeOH (6 mL) and H_2O_2 (6 mL). The mixture was stirred for additional 30 minutes at rt and diluted with buffer (20 mL) and CH_2Cl_2 (20 mL). The aqueous phase was extracted (CH_2Cl_2, 3 × 15 mL), the combined organic phases was washed (1:1 NaS_2O_3, 20wt%, aq. and $NaHCO_3$, satd., aq.), dried (Na_2SO_4) and concentrated to afford **10a** and **10b** (283 mg, 62%, *dr* 15:85) as a colorless oil. The diastereomers was separated by flash chromotagraphy (pentane:EtOAc 12:1).

Stereochemical determination of aldehyde 1 and 2

The relative stereochemistry of **1** and **2** was determined by analyzing the coupling constants of **40** and **41**, realized by reduction followed by protection of the primary alcohol, deprotection of the TBS-group and an epoxide formation.

Scheme 3. Reduction of aldehyde **1** and **2** followed by a benzylation.



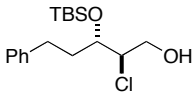
1, α,β-*anti*
2, α,β-*syn*

34, 2,3-*anti*
35, 2,3-*syn*

36, 2,3-*anti*
37, 2,3-*syn*

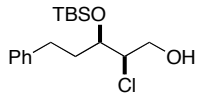
Reagents and conditions: a) $NaBH_4$, MeOH, rt, 79-89%; b) $Cl_3C(=NH)COBn$, TfOH, rt, 88-95%

(2*S,3*S**)-3-(*tert*-Butyl)dimethylsilyloxy-2-chloro-5-phenylpentan-1-ol (34)**



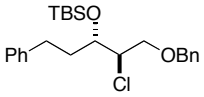
To a solution of aldehyde **1** (67 mg, 0.21 mmol) in MeOH (2 mL) was added $NaBH_4$ (10 mg, 0.26 mmol) and the reaction mixture was stirred at rt for 10 min. The reaction was quenched by addition of H_2O (8 mL), the aqueous phase was extracted (EtOAc, 4x15 mL), the combined organic phases dried ($MgSO_4$) and concentrated to afford **34** in 79% yield (53 mg, 0.16 mmol) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.33 (m, 2H), 7.29-7.22 (m, 3H), 4.12-4.07 (m, 1H), 4.01-3.90 (m, 1H), 2.77 (ddd, J = 9.48, 7.71, 4.35 Hz, 2H), 2.29 (t, J = 6.1, 6.1 Hz, 1H), 2.21-2.12 (m, 1H), 1.99-1.89 (m, 1H), 1.00 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 141.8, 128.5, 128.3, 126.0, 73.3, 65.0, 64.0, 36.3, 30.2, 25.8, 18.1, -4.4, -4.7; IR (film) ν_{max} = 2954, 2931, 2858, 1456, 1253, 1076, 779 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{30}ClO_2Si$ (M+Na): 351.1518, found: 351.15173.

(2*S*,3R)-3-(*tert*-Butyl)dimethylsilyloxy-2-chloro-5-phenylpentan-1-ol** (**35**)



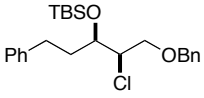
Prepared from aldehyde **2** as described for **34** to afford **35** (574 mg, 89%) as a slightly yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32-7.26 (m, 2H), 7.22-7.16 (m, 3H), 4.06 (ddd, *J* = 7.4, 4.8, 3.8 Hz, 1H), 3.99-3.95 (m, 1H), 3.94 (dd, *J* = 11.8, 4.9 Hz, 1H), 3.79 (dd, *J* = 11.8, 7.4 Hz, 1H), 2.75-2.67 (m, 1H), 2.60 (ddd, *J* = 13.6, 11.0, 5.5 Hz, 1H), 2.18-2.10 (m, 1H), 1.81-1.72 (m, 1H), 0.92 (s, 9H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 171.1, 141.5, 128.4, 128.2, 126.0, 73.2, 65.2, 63.9, 60.4, 34.4, 32.1, 25.8, 21.0, 14.2, -4.4, -4.5; IR (film) ν_{max} = 3406, 3027, 2931, 2858, 1457, 1254, 1088, 779 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{30}ClO_2Si$ (M+H): 329.1704, found: 329.1699.

(2*R*,3S)-1-(Benzyloxy)-2-chloro-3-(*tert*-butyl)dimethylsilyloxy5-phenylpentan** (**36**)



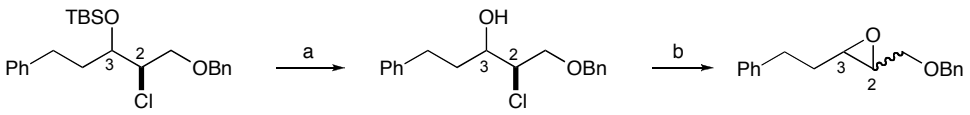
To a solution of **34** (54 mg, 0.16 mmol) in cHex:CH_2Cl_2 (2 mL:2:1) was added benzyl-2,2,2-trichloroacetimidate (61 μL, 0.33 mmol) and triflic acid (1.5 μL, 16 μmol) and the resultant mixture was stirred for 3.5 h at rt. The reaction was quenched by addition of $NaHCO_3$ (aq., satd., 3 mL) and the aqueous phase extracted (CH_2Cl_2, 3x10 mL). The combined organic phases was dried ($MgSO_4$) and concentrated in vacuo. The resultant residue was purified on flash chromatography (pentane:EtOAc 20:1) to afford **36** as a colorless oil which directly taken to the next step.

(2*R*,3R)-1-(Benzyloxy)-2-chloro-3-(*tert*-butyl)dimethylsilyloxy5-phenylpentan** (**37**)



Prepared from **35** as described for **36** to afford **37** as a colorless oil which was directly taken to the next step.

Scheme 4. Deprotection of the TBS-group followed by epoxide formation.



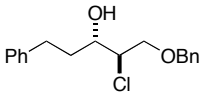
36, 2,3-*anti*
37, 2,3-*syn*

38, 2,3-*anti*
39, 2,3-*syn*

40, 2,3-*trans*
41, 2,3-*cis*

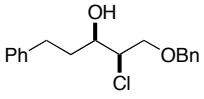
Reagents and conditions: a) TBAF, THF, rt, 64-77%, b) K_2CO_3, MeOH, rt, 33-66%

(2*R,3*S**)-1-(Benzyloxy)-2-chloro-5-phenylpentan-3-ol** (**38**)



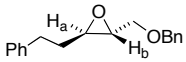
To a solution of **36** (56 mg, 0.132 mmol) in THF (2 mL) was added TBAF (50 mg, 0.159 mmol) at rt and the resultant mixture was stirred for 1h. The reaction was quenched by addition of H_2O (5 mL), the aqueous phase was extracted (Et_2O, 3x12 mL) and the combined organic phases was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified on flash chromatography (Pentane:EtOAc 20:1) to afford **38** (31 mg, 73%, two steps) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.27 (m, 2H), 7.19 (dd, *J* = 7.3, 5.1 Hz, 3H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 11.5, 3.2 Hz, 1H), 3.48 (q, *J* = 7.0, 7.0, 7.0 Hz, 1H), 3.43 (dd, *J* = 11.4, 5.6 Hz, 1H), 2.91 (td, *J* = 5.5, 2.7, 2.7 Hz, 1H), 2.86 (dt, *J* = 5.7, 5.7, 2.2 Hz, 1H), 2.81 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.74 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.88 (dt, *J* = 7.7, 7.7, 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 141.12, 137.95, 128.44, 128.40, 128.38, 127.72, 127.72, 126.05, 73.26, 70.28, 57.22, 55.41, 33.47, 32.17; IR (film) ν_{max} = 3417(br), 2923, 1454, 1099, 698 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{22}ClO_2$ (M+H): 305.1308, found: 305.1300.

(2*R,3*R**)-1-(Benzyloxy)-2-chloro-5-phenylpentan-3-ol** (**39**)



Prepared from **37** as described for **36** to afford **39** (277 mg, 56%, two steps) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28-7.15 (m, 7H), 7.09 (m, *J* = 9.8, 3.9 Hz, 3H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.96 (ddd, *J* = 6.6, 5.5, 2.6 Hz, 1H), 3.83 (dd, *J* = 4.9, 3.3 Hz, 1H), 3.71 (dd, *J* = 10.1, 6.6 Hz, 1H), 3.64 (dd, *J* = 10.1, 5.5 Hz, 1H), 2.73 (ddd, *J* = 14.8, 9.7, 5.4 Hz, 1H), 2.60 (ddd, *J* = 13.8, 9.5, 7.0 Hz, 1H), 1.90-1.81 (m, 2H), 1.74 (dddd, J = 13.9, 9.7, 7.0, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 141.47, 137.40, 128.49, 128.42, 128.42, 127.93, 127.74, 125.95, 73.55, 71.67, 70.56, 63.92, 36.07, 31.81; IR (film) ν_{max} = 3440, 3028, 2924, 2862, 1454, 1103, 698 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{22}ClO_2$ (M+H): 305.1308, found: 305.1302.

(2*R*,3R)-2-((Benzyloxy)methyl)-3-phenethyloxirane (40)**



$^3J_{Ha-Hb}$= 2.2

To a solution of **38** (15 mg, 49 μmol) in MeOH (0.5 mL) was added K_2CO_3 (2 mg, 120 μmol) at rt and the resultant mixture was stirred o.n. The reaction was diluted by addition of EtOAc (2 mL), the organic phase was washed with NaCl (aq., satd., 2 mL), NH_4Cl (aq., satd., 2 mL) and with NaCl (aq., satd., 2 mL). The organic phases was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by Flash chromatography (Pentane:EtOAc 20:1) to afford **40** (4.4 mg, 16 μmol) in 33% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.26 (m, 1H), 7.20 (dd, J = 7.3, 5.3 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 3.66 (dd, J = 11.4, 3.2 Hz, 1H), 3.43 (dd, J = 11.4, 5.6 Hz, 1H), 2.93-2.90 (m, 1H), 2.87 (dt, J = 5.7, 5.7, 2.2 Hz, 1H), 2.81 (dd, J = 14.2, 7.1 Hz, 1H), 2.73 (td, J = 13.8, 8.1, 8.1 Hz, 1H), 1.88 (dt, J = 7.8, 7.8, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 141.1, 137.9, 128.6, 128.43, 128.40, 128.37, 127.7, 126.0, 73.2, 70.3, 57.2, 55.4, 33.5, 32.2; IR (film) ν_{max} = 3027, 2927, 2850, 1454, 1107, 744 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{20}O_2$ (M+Na): 291.1356, found: 291.1355.

(2*S*,3R)-2-((Benzyloxy)methyl)-3-phenethyloxirane (41)**

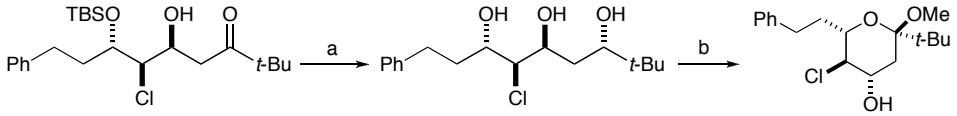
$^3J_{Ha-Hb}$= 4.4

Prepared from **39** as described for **40** to afford **41** (63 mg, 66%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (m, 1H), 7.11 (ddd, J = 6.9, 6.1, 2.4 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.42 (d, J = 11.8 Hz, 1H), 3.43 (dq, J = 11.1, 11.1, 11.1, 5.4 Hz, 1H), 3.11 (td, J = 6.2, 4.5, 4.5 Hz, 1H), 2.95 (ddd, J = 7.0, 5.7, 4.4 Hz, 1H), 2.77 (ddd, J = 14.7, 9.1, 5.9 Hz, 1H), 2.66 (ddd, J = 13.8, 8.8, 7.5 Hz, 1H), 1.82-1.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 141.0, 137.8, 128.44, 128.39, 128.36, 127.8, 127.7, 126.1, 73.3, 68.2, 55.5, 55.4, 32.7, 29.9; IR (film) ν_{max} = 3028, 2924, 2862, 1496, 1454, 1095, 744 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{20}O_2$ (M+Na): 291.1356, found: 291.1355.

Stereochemical determination of Mukaiyama aldol product 4 and 5

The relative stereochemistry of **4** was determined by analyzing the coupling constants of **43**, realized by desilylation followed by an acetal formation (Scheme 5).

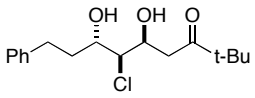
Scheme 5. Stereochemical determination of **4**.



4 **42** **43**

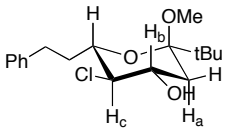
Reagents and conditions: a) TBAF, THF, 0 °C – rt; b) $CH(OMe)_3$, PPTS, MeOH, rt, 34% over two steps

(5*S,6*R**,7*R**)-6-Chloro-5,7-dihydroxy-2,2-dimethyl-9-phenylnonan-3-one (42)**



To a solution of **4** (9.2 mg, 21.5 μmol) in THF (1 mL) was added TBAF (8.2 mg, 25.8 μmol) at 0 °C. The reaction mixture was allowed to reach rt and stirred for 3 h before CH_2Cl_2 (1 mL) and H_2O (1 mL) was added. Extrelut NT3® workup afforded **56** (8.6 mg), which was used directly in the next step.

(4*R,5*S**,6*S**)-2-tert-Butyl-5-chloro-tetrahydro-2-methoxy-6-phenethyl-2H-pyran-4-ol (43)**

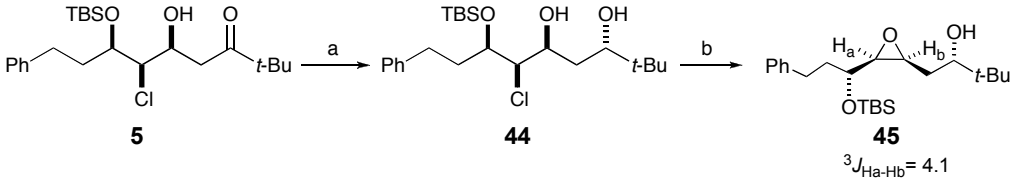


$^3J_{Ha\text{-}Hb}$ = 11.1 (ax-ax)
$^3J_{Hb\text{-}Hc}$ = 10.0 (ax-ax)

To a solution of **42** (4 mg) in MeOH (1 mL) was added $CH(OMe)_3$ (25.8 mg, 242 μmol) and PPTS (0.3 mg, 1.2 μmol) at rt. The reaction mixture was stirred at rt over night and quenched by addition of H_2O (1 mL) and CH_2Cl_2 (1 mL). Extrelut NT3® workup afforded **43** (2 mg, 34% over two steps) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (m, 5H) 3.96 (m, 1H) 3.57 (m, 1H) 3.43 (t, J = 9.8Hz, 1H) 3.30 (s, 3H) 2.94 (ddd, J = 13.9, 11.0, 5.0Hz, 1H) 2.70 (ddd, J = 13.8, 10.7, 6.1Hz, 1H) 2.43 (d, J = 2.7Hz, 1H) 2.33 (m, 1H) 2.22 (dd, J = 13.1, 5.0Hz, 1H) 1.87 (m, 1H) 1.67 (dd, J = 13.1, 11.1Hz, 1H) 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 128.5, 128.43, 128.41, 126.0, 94.4, 71.8, 64.5, 53.4, 33.5, 30.7, 29.7, 27.9, 22.3, 14.1.

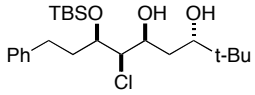
The relative stereochemistry of **5** was determined by analyzing the coupling constants of epoxide **45**, realized by a 1,3-reduction followed by an epoxide formation (Scheme 6).

Scheme 6. Stereochemical determination of **5**.



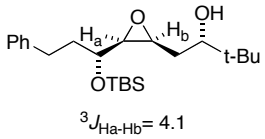
Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH (1:1), 0 °C, 67%; b) K_2CO_3, EtOH, 70 °C, 39%.

(3*S,5*S**,6*R**,7*R**)-6-Chloro-7-yloxy-((tert-butyl)dimethylsilane-2,2-dimethyl-9-phenylnonane-3,5-diol** (**44**)



To a solution of **5** (16 mg, 38 μmol) in MeCN:AcOH (1:1, 1 mL) was added $Me_4NBH(OAc)_3$ (50 mg, 191 μmol) at 0 °C. The reaction mixture was stirred for 30 minutes followed by Extrelut NT3® workup. Flash chromatography (pentane:EtOAc 8:1) of the residue gave **44** (11 mg, 67%) which was used directly in the next step.

(*S)-1-((2*S**,3*R**)-3-((*R**)-1-Yloxy-((tert-butyl)dimethylsilane)-3-phenylpropyl)oxiran-2-yl)-3,3-dimethylbutan-2-ol** (**45**).



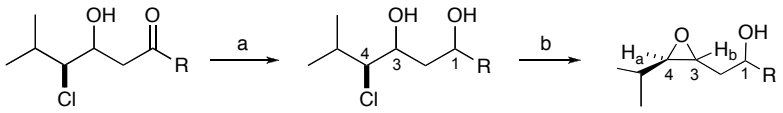
To a solution of diol **44** (10 mg, 23 μmol) in EtOH (1 mL) was added K_2CO_3 (7 mg, 46 μmol) and the reaction mixture was warmed up to 70 °C and stirred over night and quenched by addition of H_2O (5 mL). The aqueous was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure to give **45** (3.5 mg, 39%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.17 (m, 5H) 3.46 (m, 2H) 3.24 (dt, J = 8.8, 3.4Hz, 1H) 2.94 (dd, J = 7.8, 4.1Hz, 1H) 2.76 (ddd, J = 14.2, 10.2, 6.1Hz, 1H) 2.68 (m, 2H) 1.90 (m, 1H) 1.66 (m, 1H) 1.38 (ddd, J = 14.2, 9.0, 1.6Hz, 1H) 0.85 (s, 9H) 0.84 (s, 9H) -0.01 (d, J = 11.1Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.12, 128.42, 128.31, 125.73, 68.64, 59.92, 55.20, 37.64, 34.88, 30.78, 30.05, 25.83, 25.51, 18.12, -4.04, -4.20; IR (film) ν_{max}

=3445(br), 2955, 2929, 1255, 1103, 836 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{40}O_3Si$ (M+Na): 415.2644, found: 415.2639**.**

Stereochemical determination of Mukaiyama aldol products 10-15

The relative stereochemistry of **10** - **12** was determined by analyzing the coupling constants of epoxide **49** - **51**, and by NOESY measurements of epoxide **55** – **57**, which were realized by a 1,3-reduction followed by an epoxide formation (Scheme 7).

Scheme 7. Stereochemical determination of **10** - **12**

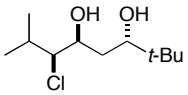


1,3-*anti* 1,3-*anti*

10a, 3,4-*syn*, R= *t*-Bu	**46a**, 3,4-*syn*, R= *t*-Bu	**49a**, 3,4-*cis*, R= *t*-Bu
10b, 3,4-*anti*, R= *t*-Bu	**46b**, 3,4-*anti*, R= *t*-Bu	**49b**, 3,4-*trans,* R= *t*-Bu
11a, 3,4-*syn*, R= *i*-Pr	**47a**, 3,4-*syn*, R= *i*-Pr	**50a**, 3,4-*cis*, R= *i*-Pr
11b, 3,4-*anti*, R= *i*-Pr	**47b**, 3,4-*anti*, R= *i*-Pr	**50b**, 3,4-*trans*, R= *i*-Pr
12a, 3,4-*syn*, R= Me	**48a**, 3,4-*syn*, R= Me	**51a**, 3,4-*cis*, R= Me
12b, 3,4-*anti*, R= Me	**48b**, 3,4-*anti*, R= Me	**51b**, 3,4-*trans*, R= Me

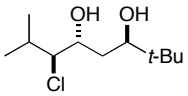
Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH (1:1), -30 °C, 73-99%; b) K_2CO_3, EtOH, 70 °C, 85-99%.

(3*S,5*S**,6*S**)-6-Chloro-2,2,7-trimethyloctane-3,5-diol** (**46a**)



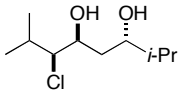
To a solution of $Me_4NBH(OAc)_3$ (216 mg, 0.82 mmol) in MeCN (0.7 ml) and AcOH (0.7 ml) at -30 °C was added a solution of **10a** (36 mg, 0.16 mmol) in MeCN (0.2 ml) and the resultant solution stirred for 18 h. The reaction was quenched by addition of 0.5 N aqeous sodium potassium tartrate (2.5 ml) and stirred vigorously for 20 min at rt. The mixture was diluted with CH_2Cl_2 (6.5 ml) and washed with saturated aqueous $NaHCO_3$ (10 ml). The aqueous phase was extracted with CH_2Cl_2 (3x10 ml) and the combined organic phases washed with saturated aqueous $NaHCO_3$ (10 ml). The aqueous phase was extracted with CH_2Cl_2 (3x10 ml) and the combined organic phases dried (Na_2SO_4), filtered and concentrated to to afford **46a** (26 mg, 73%) as a white solid mp: 128.5-130.3 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.09 (ddd, J = 8.8, 5.1, 2.9 Hz, 1H), 3.83 (t, J = 5.3, 5.3 Hz, 1H), 3.57 (dd, J = 10.8, 1.2 Hz, 1H), 2.17 (s, 1H), 2.16-2.06 (m, 1H), 1.91 (s br, 2H), 1.71 (ddd, J = 14.2, 9.1, 1.8 Hz, 1H), 1.49 (ddd, J = 14.0, 10.8, 2.9 Hz, 1H), 1.34-1.23 (m, 1H), 1.07 (d, J = 6.7 Hz, 3H), 1.05-1.01 (m, 3H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 77.1, 75.7, 70.0, 53.4, 36.1, 34.7, 31.7, 25.6, 20.9, 17.9; IR (film) ν_{max} = 3367(br), 2962, 1065, 1007 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{23}ClO_2$ (M+H): 223.1465, found: 223.1461.

(3*R,5*R**,6*S**)-6-Chloro-2,2,7-trimethyloctane-3,5-diol** (**46b**)



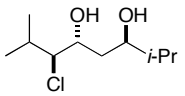
Prepared from **10b** as described for **4ab** to afford **46b** (84 mg, 92%) as a white solid mp: 122.5-124.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.35 (ddd, J = 8.1, 4.0, 3.5 Hz, 1H), 3.66 (dd, J = 7.2, 3.4 Hz, 1H), 2.84 (dd, J = 17.3, 8.2 Hz, 1H), 2.67 (dd, J = 17.3, 4.1 Hz, 1H), 2.47 (s br, 1H), 2.20 (s, 3H), 2.17-2.06 (m, 1H), 1.07 (d, J = 3.3 Hz, 3H), 1.05 (d, J = 3.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 76.4, 70.5, 34.8, 32.8, 29.9, 25.4, 20.7, 17.0; IR (film) ν_{max} = 3429(br), 2962, 1466, 1045 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{23}ClO_2$ (M+H): 223.1465, found: 223.1460.

(3*S,5*S**,6*S**)-6-Chloro-2,7-dimethyloctane-3,5-diol** (**47a**)



Prepared from **11a** as described for **46a** to afford **47a** (24 mg, 99%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.16-4.03 (m, 1H), 2.11 (qd, J = 12.2, 6.6, 6.6, 6.6 Hz, 1H), 3.81 (t, J = 5.4, 5.4 Hz, 1H), 3.67 (ddd, J = 9.5, 5.8, 2.3 Hz, 1H), 1.73-1.66 (m, 2H), 1.59 (ddd, J = 14.3, 9.7, 3.0 Hz, 1H), 1.07 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 73.2, 69.9, 38.1, 33.9, 31.5, 20.9, 18.6, 17.8, 17.7; IR (neat) ν_{max} = 3367(br), 2926, 1392, 1049 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{21}ClO_2$ (M+H): 209.1303, found: 209.1302.

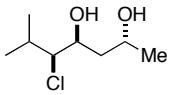
(3*R,5*R**,6*S**)-6-Chloro-2,7-dimethyloctane-3,5-diol** (**47b**)



Prepared from **11b** as described for **46a** to afford **47b** (108 mg, 95%) as a white solid mp: 94.3-97.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ; 4.09-3.98 (m, 1H), 3.86 (dd, J = 7.5, 4.6 Hz, 1H), 3.74 (dd, J = 12.0, 6.2 Hz, 1H), 2.58-2.35 (m, 2H), 2.35-2.26 (m, 1H), 1.83-1.80 (m, 2H), 1.71 (sext.d, J = 13.3, 6.6, 6.6, 6.6, 6.6, 6.6 Hz, 1H), 1.04 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 74.2, 73.0, 70.2, 35.4, 34.0, 29.7, 20.7, 18.5, 17.8, 17.0; IR (film)

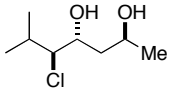
ν_{max} = 3379(br), 2970, 1030, 733 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{21}ClO_2$ (M+H): 209.1303, found: 209.1301.

(2*R,4*S**,5*S**)-5-Chloro-6-methylheptane-2,4-diol** (**48a**)



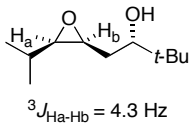
Prepared from **12a** as described for **46a** to afford **48a** (38 mg, 84%) as a white solid mp: 86.5-88.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.10 (dddd, *J* = 12.5, 9.3, 5.8, 2.9 Hz, 1H), 3.77 (t, *J* = 5.4, 5.4 Hz, 1H), 2.46 (s br, 1H), 2.16-2.03 (m, 1H), 1.72 (ddd, *J* = 14.3, 9.5, 2.8 Hz, 1H), 1.57 (ddd, *J* = 14.3, 8.9, 3.0 Hz, 1H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 69.7, 64.7, 42.6, 31.4, 23.7, 20.9, 17.6; IR (film) ν_{max} = 3367(br), 2966, 733 cm^{-1}; HRMS (FAB+) calcd for $C_8H_{17}ClO_2$ (M+H): 181.0990, found: 181.0989.

(2*S,4*R**,5*S**)-5-Chloro-6-methylheptane-2,4-diol** (**48b**)



Prepared from **12b** as described for **46a** to afford **48b** (94 mg, 91%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.23 (dqd, *J* = 12.5, 6.3, 6.3, 6.3, 3.5 Hz, 1H), 4.04 (dt, *J* = 7.5, 7.5, 3.1 Hz, 1H), 3.84 (dd, *J* = 7.3, 4.9 Hz, 1H), 2.41 (s, 1H), 2.27 (dtd, *J* = 13.3, 6.7, 6.7, 5.0 Hz, 1H), 1.86-1.74 (m, 1H), 1.27 (d, *J* = 6.3 Hz, 1H), 1.02 (t, *J* = 7.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 73.1, 70.0, 65.6, 40.0, 29.8, 23.9, 20.6, 17.1; IR (film) ν_{max} = 3367(br), 2966, 1462, 1072, 733 cm^{-1}; HRMS (FAB+) calcd for $C_8H_{17}ClO_2$ (M+H): 181.0990, found: 181.0988.

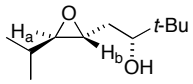
(*S)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)-3,3-dimethylbutan-2-ol** (**49a**)



Prepared from **46a** as described for **45** to afford **49a** (16 mg, 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.52 (ddd, *J* = 10.6, 4.2, 2.0 Hz, 1H), 3.23 (td, *J* = 8.0, 4.1, 4.1 Hz, 1H), 2.66 (dd, *J* = 9.3, 4.3 Hz, 1H), 1.76 (s, 1H), 1.64 (ddd, *J* = 14.4, 10.6, 3.9 Hz, 1H), 1.53 (ddd, *J* = 14.3, 7.9, 2.1 Hz, 1H), 1.48-1.38 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ

77.4, 63.5, 55.9, 34.9, 29.5, 27.4, 25.5, 20.3, 18.4; IR (film) ν_{max} = 3452(br), 2962, 1470, 1072, 876 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}O_2$ (M+H): 187.1698, found: 187.1694.

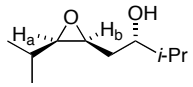
(*R)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)-3,3-dimethylbutan-2-ol** (**49b**)



$^3J_{Ha\text{-}Hb}$ = 2.3 Hz

Prepared from **46b** as described for **45** to afford **49b** (59 mg, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.43 (d, *J* = 10.5 Hz, 1H), 2.99 (ddd, *J* = 6.4, 4.2, 2.4 Hz, 1H), 2.61 (dd, *J* = 7.0, 2.3 Hz, 1H), 2.07 (s, 1H), 1.74 (s br, 1H), 1.68 (ddd, *J* = 14.7, 10.7, 4.2 Hz, 1H), 1.60 (ddd, *J* = 14.3, 6.2, 2.0 Hz, 1H), 1.57-1.46 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 76.7, 64.4, 56.5, 34.6, 33.3, 30.6, 25.5, 19.0, 18.3; IR (film) ν_{max} = 3467(br), 2958, 1466, 1076, 894 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}O_2$ (M+H): 187.1698, found: 187.1693.

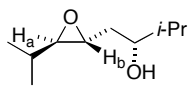
(*S)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)-3-methylbutan-2-ol** (**50a**)



$^3J_{Ha\text{-}Hb}$ = 4.3 Hz

Prepared from **47a** as described for **45** to afford **50a** (13 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.63 (unresolved m, 1H), 3.20 (ddd, *J* = 8.2, 4.3, 4.0 Hz, 1H), 2.64 (dd, J = 9.4, 4.3 Hz 1H), 1.80-1.68 (m, 3H), 1.52 (ddd, *J* = 14.5, 8.3, 3.2 Hz, 1H), 1.48-1.41 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.82 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ; IR (film) ν_{max} = 3444(br), 2962, 1466, 1045, 1011 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{20}ClO_2$ (M+H): 173.1536, found: 173.1534.

(*R)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)-3-methylbutan-2-ol** (**50b**)

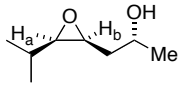


$^3J_{Ha\text{-}Hb}$ = 2.4 Hz

Prepared from **47b** as described for **45** to afford **50b** (20 mg, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.55 (dtd, *J* = 8.2, 5.1, 5.1, 2.9 Hz, 1H), 2.97 (ddd, *J* = 6.4, 4.3, 2.4 Hz, 1H), 2.61 (dd, *J* = 7.0, 2.4 Hz, 1H), 2.04 (d, *J* = 4.3 Hz, 1H), 1.78 (ddd, *J* = 14.1, 9.7, 4.3 Hz, 1H), 1.73-1.63 (m, 1H), 1.60 (ddd, *J* =

14.5, 6.2, 2.7 Hz, 1H), 1.56-1.46 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 74.0, 64.1, 56.0, 35.6, 33.8, 30.6, 19.0, 18.6, 18.3, 17.4; IR (film) ν_{max} = 3448(br), 2962, 1465 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{20}ClO_2$ (M+H):173.1536, found: 173.1535.

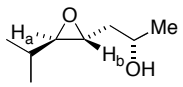
(*R)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)propan-2-ol (51a)**



$^3J_{Ha\text{-}Hb}$ = 4.3 Hz

Prepared from **48a** as described for **45** to afford **51a** (16 mg, 85%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.06 (qd, *J* = 12.4, 6.3, 6.3, 6.2 Hz, 1H), 3.15 (ddd, *J* = 8.2, 4.3, 4.0 Hz, 1H), 2.62 (dd, *J* = 9.4, 4.3 Hz, 1H), 1.82 (ddd, *J* = 14.3, 7.8, 3.6 Hz, 1H), 1.52 (ddd, *J* = 14.3, 8.4, 4.5 Hz, 1H), 1.48-1.41 (m, 1H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 66.53, 62.70, 54.75, 36.69, 23.93, 20.28, 20.28, 18.40; IR (film) ν_{max} = 3429(br), 2966, 1462, 1134 cm^{-1}; HRMS (FAB+) calcd for $C_8H_{16}O_2$ (M+Na): 167.1043, found: 167.1041.

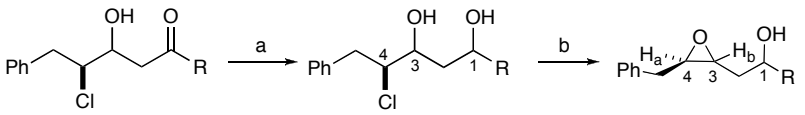
(*S)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)propan-2-ol (51b)**



$^3J_{Ha\text{-}Hb}$ = 2.4 Hz

Prepared from **48b** as described for **45** to afford **51b** (28 mg, 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.00 (dqd, *J* = 12.5, 6.3, 6.3, 6.3, 3.9 Hz, 1H), 2.94 (ddd, *J* = 6.3, 4.3, 2.4 Hz, 1H), 2.61 (dd, *J* = 7.0, 2.4 Hz, 1H), 1.84 (ddd, *J* = 14.4, 8.5, 4.2 Hz, 1H), 1.63 (ddd, *J* = 14.5, 6.1, 3.7 Hz, 1H), 1.56-1.47 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 65.6, 63.6, 55.5, 40.2, 30.5, 23.6, 19.0, 18.3; IR (film) ν_{max} 3433(br), 2966, 1462, 1134 = cm^{-1}; HRMS (FAB+) calcd for $C_8H_{16}O_2$ (M+H): 145.1223, found: 145.1222.

Scheme 8. Stereochemical determination of **13** - **15**.

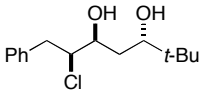


1,3-*anti* 1,3-*anti*

13a, 3,4-*syn*, R= *t*-Bu	**52a**, 3,4-*syn*, R= *t*-Bu	**55a**, 3,4-*cis*, R= *t*-Bu
13b, 3,4-*anti*, R= *t*-Bu	**52b**, 3,4-*anti*, R= *t*-Bu	**55b**, 3,4-*trans*, R= *t*-Bu
14a, 3,4-*syn*, R= *i*-Pr	**53a**, 3,4-*syn*, R= *i*-Pr	**56a**, 3,4-*cis*, R= *i*-Pr
14b, 3,4-*anti*, R= *i*-Pr	**53b**, 3,4-*anti*, R= *i*-Pr	**56b**, 3,4-*trans*, R= *i*-Pr
15a, 3,4-*syn*, R= Me	**54a**, 3,4-*syn*, R= Me	**57a**, 3,4-*cis*, R= Me
15b, 3,4-*anti*, R= Me	**54b**, 3,4-*anti*, R= Me	**57b**, 3,4-*trans*, R= Me

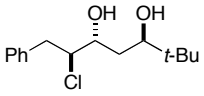
Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH (1:1), -30 °C, 90-99%; b) K_2CO_3, EtOH, 70 °C, 87-95%.

(2*S,3*S**,5*S**)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol** (**52a**)



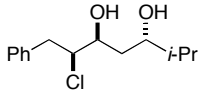
Prepared from **13a** as described for **46a** to afford **52a** (136 mg, 99%) as a white solid mp: 116.5-120.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.30 (m, 2H), 7.25 (m, 3H), 4.25-4.13 (m, 1H), 4.01 (td, J = 9.5, 2.8, 2.8 Hz, 1H), 3.56 (dd, J = 10.8, 1.8 Hz, 1H), 3.25 (dd, J = 14.1, 6.3 Hz, 1H), 3.10 (dd, J = 14.1, 8.4 Hz, 1H), 1.82 (ddd, J = 14.3, 9.5, 1.8 Hz, 2H), 1.47 (ddd, J = 14.0, 10.8, 2.9 Hz, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.6, 129.3, 128.5, 126.8, 75.7, 70.0, 69.8, 41.6, 36.8, 34.7, 25.6; IR (film) ν_{max} = 3433(br), 3332(br), 2962, 1072, 752 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{23}ClO_2$ (M+H): 271.1459, found: 271.1459.

(2*S,3*R**,5*R**)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol** (**52b**)



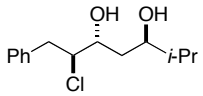
Prepared from **13b** as described for **46a** to afford **52b** (54 mg, 94 %) as a white solid: mp 132.7-134.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.27 (m, 2H), 7.25 (m, 3H), 4.20 (ddd, J = 9.6, 5. 9, 3.8 Hz, 1H), 4.14-3.95 (m, 1H), 3.62 (dd, J = 10.9, 1.8 Hz, 1H), 3.33 (dd, J = 14.4, 3.8 Hz, 1H), 2.92 (dd, J = 14.4, 9.5 Hz, 1H), 1.89 (ddd, J = 14.4, 7.6, 1.8 Hz, 1H), 1.65 (ddd, J = 14.2, 10.9, 2.9 Hz, 1H), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.9, 129.4, 128.3, 126.7, 76.4, 72.3, 67.5, 40.0, 34.9, 33.0, 25.4; IR (film) ν_{max} = 3425(br), 3302(br), 2966, 1053, 1011, 710 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{23}ClO_2$ (M+H): 271.1459, found: 271.1461.

(2*S*,3S*,5S)-2-Chloro-6-methyl-1-phenylheptane-3,5-diol (53a)**



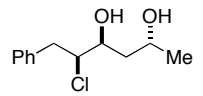
Prepared from **14a** as described for **46a** to afford **53a** (38 mg, 90%) as a white solid: mp 112.9-114.4 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (m, 2H), 7.28-7.22 (m, 3H), 3.68 (ddd, *J* = 9.6, 5.7, 2.3 Hz, 1H), 3.26 (dd, *J* = 14.1, 6.1 Hz, 1H), 3.09 (dd, *J* = 14.1, 8.5 Hz, 1H), 4.17 (ddd, *J* = 8.7, 6.1, 2.9 Hz, 1H), 4.04 (td, *J* = 9.7, 2.8, 2.8 Hz, 1H), 1.82 (ddd, *J* = 14.4, 9.7, 2.4 Hz, 1H), 1.68 (qd, *J* = 13.4, 6.7, 6.7, 6.7 Hz, 1H), 1.59 (ddd, *J* = 14.4, 9.7, 2.8 Hz, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.6, 129.3, 128.51, 126.9, 73.3, 69.8, 69.5, 41.3, 38.7, 33.9, 18.6, 17.6; IR (film) ν_{max} = 3356(br), 2958, 1076, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{14}H_{21}ClO_2$ (M+H): 257.1303, found: 257.1302.

(2*S*,3R*,5R)-2-Chloro-6-methyl-1-phenylheptane-3,5-diol (53b)**



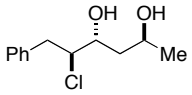
Prepared from **14b** as described for **46a** to afford **53b** (18 mg, 93%) as a white solid: mp 87.6-89.9 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 4.20 (ddd, J = 9.5, 5.7, 3.9 Hz, 1H), 4.05 (ddd, J = 8.3, 5.7, 2.8 Hz, 1H), 3.74 (ddd, J = 9.5, 5.7, 3.8 Hz, 1H), 3.32 (dd, J = 14.4, 3.8 Hz, 1H), 2.94 (dd, J = 14.4, 9.5 Hz, 1H), 1.88 (ddd, J = 14.5, 8.2, 2.5 Hz, 1H), 1.81 – 1.67 (m, 2H), 0.97 (d, J = 6.7 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.84, 129.40, 128.37, 126.74, 74.04, 72.02, 67.64, 39.87, 35.39, 33.98, 18.51, 17.69; IR (film) ν_{max} = 3375, 2958, 1454, 1052, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{14}H_{21}ClO_2$ (M+H): 257.1303, found: 257.1300.

(2*R*,4S*,5S)-5-Chloro-6-phenylhexane-2,4-diol (54a)**



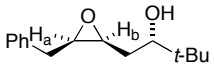
Prepared from **15a** as described for **46a** to afford **54a** (19 mg, 97%) as a white solid: mp 88.5-91.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (m, 2H), 7.28-7.23 (m, 3H), 4.18-4.10 (m, 2H), 4.03 (ddd, *J* = 9.8, 2.9, 2.9 Hz, 1H), 3.25 (dd, *J* = 14.1, 6.1 Hz, 1H), 3.08 (dd, *J* = 14.1, 8.4 Hz, 1H), 1.87 (ddd, *J* = 14.3, 9.8, 3.0 Hz, 1H), 1.59 (ddd, *J* = 14.4, 8.6, 2.9 Hz, 1H), 1.25 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.6, 129.3, 128.5, 126.9, 69.6, 69.2, 65.0, 43.0, 41.2, 23.7; IR (neat) ν_{max} = 3329(br), 2962, 1049, 698 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{17}ClO_2$ (M+Na): 251.0809, found: 251.0809.

(2*S*,4R*,5S)-5-Chloro-6-phenylhexane-2,4-diol (54b)**



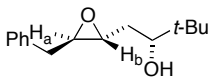
Prepared from **15b** as described for **46a** to afford **54b** (14 mg, 95%) as a white solid: mp 88.5-90.9 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (m, 2H), 7.28-7.24 (m, 3H), 4.27-4.16 (m, 2H), 4.06 (ddd, *J* = 8.3, 5.4, 2.6 Hz, 1H), 3.28 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.95 (dd, *J* = 14.4, 9.4 Hz, 1H), 1.90 (ddd, *J* = 14.5, 8.7, 2.9 Hz, 1H), 1.76 (ddd, *J* = 14.5, 8.6, 2.7 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.7, 129.4, 128.4, 126.8, 71.6, 67.7, 65.5, 39.9, 39.8, 23.9; IR (film) ν_{max} = 3379(br), 2967, 1454, 1068, 702 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{15}ClO_2$ (M+H): 229.0990, found: 229.0990.

(S*)-1-((2S*,3R*)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (55a)



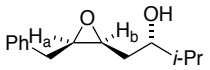
Prepared from **52a** as described for **45** to afford **55a** (65 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.28 (m, 2H), 7.23 (m, 3H), 3.32-3.21 (m, 2H), 2.92 (dd, J = 14.9, 6.4, 1H), 2.86 (dd, J = 14.9, 5.9, 1H), 1.81 (br s, 1H), 1.72-1.68 (m, 2H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.9, 128.7, 128.6, 126.5, 77.4, 57.9, 55.7, 34.5, 29.7, 25.5; IR (film) ν_{max} = 3452(br), 2962, 1076, 1010 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{22}O_2$ (M+H): 235.1693, found: 235.1692.

(R*)-1-((2R*,3R*)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (55b)



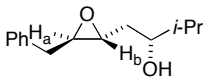
Prepared from **52b** as described for **45** to afford **55b** (19 mg, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.29 (m, 2H), 7.24 (m, 3H), 3.50-3.37 (unresolved m, 1H), 3.10-3.04 (m, 2H), 2.92 (dd, J = 14.5, 5.5 Hz, 1H), 2.85 (dd, J = 14.5, 5.2 Hz, 1H), 1.89 (d, *J* = 3.66 Hz, 1H), 1.72 (ddd, *J* = 14.38, 10.77, 3.89 Hz, 1H), 1.61 (ddd, *J* = 14.29, 6.03, 1.88 Hz, 1H), 1.04-0.71 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.3, 128.9, 128.5, 126.6, 76.7, 59.0, 57.4, 38.5, 34.6, 33.1, 25.5; IR (film) ν_{max} = 3467(br), 2958, 1080, 1007 cm^{-1}; HRMS (FAB+) calcd for $C_{15}H_{22}O_2$ (M+H): 235.1693, found: 235.1692.

(R*)-1-((2S*,3R*)-3-Benzyloxiran-2-yl)propan-2-ol (56a)



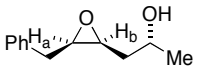
Prepared from **53a** as described for **45** to afford **56a** (19 mg, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46-7.30 (m, 2H), 7.30-7.22 (m, 3H), 3.71-3.65 (m, 1H), 3.29-3.22 (m, 2H), 2.92 (dd, J = 14.9, 6.3 Hz, 1H), 2.85 (dd, J = 14.9, 5.7 Hz, 1H), 1.85 (ddd, J = 14.3, 9.3, 4.1 Hz, 1H), 1.80-1.74 (m, 1H), 1.71 (ddd, J = 14.4, 7.6, 3.2 Hz, 1H), 1.66 (d, J = 5.3 Hz, 1H), 0.97 (dd, J = 6.8, 1.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.81, 128.76, 128.63, 126.58, 74.71, 57.47, 55.06, 34.50, 33.91, 32.21, 18.74, 17.15; IR (film) ν_{max} = 3444(br), 2962, 1454 cm^{-1}; HRMS (FAB+) calcd for $C_{14}H_{20}O_2$ (M+Na): 243.1356, found: 243.1355.

(*S)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (56b)**



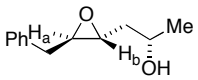
Prepared from **53b** as described for **45** to afford **56b** (65 mg, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 3.58 – 3.52 (unresolved m, 1H), 3.10 – 3.02 (m, 2H), 2.93 (dd, J = 14.5, 5.7 Hz, 1H), 2.84 (dd, J = 14.5, 5.4 Hz, 1H), 1.91 (br s, 1H), 1.80 (ddd, J = 14.1, 9.8, 4.2 Hz, 1H), 1.71 – 1.57 (m, 2H), 0.91 (d, J = 6.9 Hz, 2H), 0.90 (d, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.8 MHz*)* δ 137.23, 128.91, 128.56, 126.64, 73.88, 58.71, 56.88, 38.44, 35.35, 33.72, 18.51, 17.33.; IR (film) ν_{max} = 3444(br), 2962, 1458 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 221.1536, found: 221.1536.

(*R)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (57a)**



Prepared from **54a** as described for **45** to afford **57a** (6 mg, 87%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 4.16 – 4.07 (m, 1H), 3.26 – 3.19 (m, 2H), 2.93 (dd, J = 14.9, 6.1, 1H), 2.83 (dd, J = 14.9, 5.5, 1H), 1.91 (ddd, J = 13.8, 8.0, 3.6, 1H), 1.74 – 1.67 (m, 1H), 1.63 (d, J = 5.0, 1H), 1.33 (d, J = 6.2, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 137.72, 128.76, 128.65, 126.61, 66.44, 57.09, 54.51, 36.96, 34.47, 23.99; IR (film) ν_{max} = 3421(br), 2970, 1454 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{39}ClO_3Si$ (M+Na): 215.1043, found: 215.1042.

(*S)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (57b)**



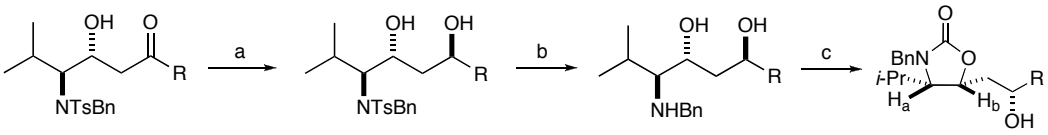
$^3J_{Ha-Hb}$ = 2.3 Hz

Prepared from **54b** as described for **45** to afford **57b** (7 mg, 95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.29 (m, 2H), 7.27-7.22 (m, 3H), 4.05-3.89 (unresolved m, 1H), 3.06 (ddd, J = 5.6, 5.6, 2.3 Hz, 1H), 2.99 (ddd, J = 6.4, 4.3, 2.3 Hz, 1H), 2.93 (dd, J = 14.5, 5.7 Hz, 1H), 2.83 (dd, J = 14.5, 5.5 Hz, 1H), 1.95 (s, 1H), 1.83 (ddd, J = 14.4, 8.6, 4.3 Hz, 1H), 1.63 (ddd, J = 14.5, 6.1, 3.6 Hz, 1H), 1.21 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ; 137.1, 128.9, 128.6, 126.7, 65.5, 58.3, 56.4, 40.0, 38.4, 23.6; IR (film) ν_{max} = 3421(br), 2970, 1454 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+H): 193.1223, found: 193.1224.

Stereochemical determination of Mukaiyama aldol product 29, 30 and 33.

The relative stereochemistry of **19b**, **20b** and **21b** was determined by analyzing the coupling constants of oxazolidinones **60b**, **69b** and **70b** (Scheme 9).

Scheme 9. Stereochemical determination of **19b**, **20b** and **21b**.



19b, R= *t*-Bu
20b, R= *i*-Pr
21b, R= Me

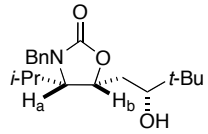
58b, R= *t*-Bu
65b, R= *i*-Pr
66b, R= Me

59b, R= *t*-Bu
67b, R= *i*-Pr
68b, R= Me

60b, R= *t*-Bu
69b, R= *i*-Pr
70b, R= Me

Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH, -30 °C; b) $Na^+C_{10}H_8^-$, THF, -78 °C (deprotection of **58b**), SmI_2, Pyrrolidine, H_2O, THF, RT (deprotection of **65b** and **66b**), 60-94%; c) Triphosgene, DIPEA, CH_2Cl_2, rt, 82% over three steps (**60b**), 94-95% (**69b** and **70b**).

(4*S,5*R**)-3-Benzyl-5-((*R**)-2-hydroxy-3,3-dimethylbutyl)-4-isopropyloxazolidin-2-one (60b)**

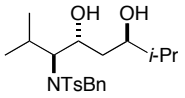


$^3J_{Ha-Hb}$ =

To a stirred solution of **19b** (19 mg, 63 μmol) in MeCN:AcOH (1:1, 2mL) was added $Me_4NBH(OAc)_3$ (83 mg, 315 μmol) at 0 °C. The resultant mixture was stirred for 30 min, diluted with H_2O (10 mL) The aqueous phase was extracted with Et_2O (2 × 15 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (pentane:EtOAc 5:1) of the residue

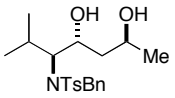
yielded the diol **58b** (26 mg) as a single diastereomer. To the diol in THF (2 mL) was added $Na^+C_{10}H_8^-$ in DME dropwise at -78 °C until the black color persisted and the solution was stirred for additional 30 min and quenched by addition of EtOH (1 mL) and H_2O (5 mL). The aqueous phase was extracted with Et_2O (2 × 15 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (pentane:EtOAc 2:1 + 1% NH_3) of the residue to afford the desired amine **59b** (9 mg) as a white solid. To the amine (7 mg, 24 μmol) in CH_2Cl_2 (1 mL) was added triphosgene (11 mg, 36 μmol) and DIEA (9 μL, 50 μmol). The resultant solution was stirred at rt over night. Extrelut NT3® workup and flash chromatography (pentane:EtOAc 10:1) to afford **60b** (7.5 mg, 82% over three steps) as a colorless oil.

***N*-Benzyl-*N*-((3*S**,4*R**,6*R**)-4,6-dihydroxy-2,7-dimethyloctan-3-yl)-4-methylbenzenesulfonamide (65b)**



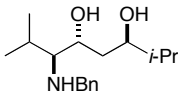
Prepared from **20b** as described for **46a** to afford **65b** (76 mg, 87%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 6.9 Hz, 2H), 7.35 – 7.27 (m, 5H), 4.58 – 4.27 (m, 2H), 4.04 (unresolved m, 1H), 3.48 – 3.14 (m, 2H), 2.43 (s, 3H), 2.41 – 2.34 (m, 1H), 2.05 (unresolved m, 1H), 1.79 (br s, 1H), 1.53 – 1.40 (m, 2H), 0.99 (d, J = 6.6 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H), 0.60 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 143.28, 138.03, 137.42, 129.57, 128.97, 128.54, 127.78, 127.31, 73.57, 71.50(br), 69.55(br), 50.20(br), 38.45, 33.46, 28.51, 21.71, 21.46, 20.51, 18.54, 17.69.; IR (film) ν_{max} = 3460(br), 2966, 1331, 1153 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+H): 432.2203, found: 432.2205.

***N*-Benzyl-*N*-((3*S**,4*R**,6*S**)-4,6-dihydroxy-2-methylheptan-3-yl)-4-methylbenzenesulfonamide (66b)**



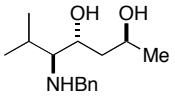
Prepared from **21b** as described for **46a** to afford **66b** (31 mg, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz, 45 °C) δ 7.70 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 6.8 Hz, 2H), 7.36 – 7.27 (m, 5H), 4.42 (unresolved m, 2H), 4.05 (unresolved m, 1H), 3.87 (unresolved m, 1H), 3.17 (unresolved m, 1H), 2.43 (s, 3H), 2.04 (unresolved m, 2H), 1.60 (ddd, J = 14.0, 11.1, 2.8 Hz, 1H), 1.01 (d, J = 6.4, 3H), 0.98 (d, J = 6.6, 3H), 0.59 (d, J = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz, 45 °C) δ 143.26, 138.49, 137.47, 129.59, 129.18, 128.61, 127.90, 127.41, 72.05(br), 70.08(br), 65.76, 43.06, 30.78, 28.61, 22.90, 21.83, 21.43, 20.62; IR (film) ν_{max} = 3502(br), 2962, 1331, 1153 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+H): 406.2047, found: 406.2047.

(3*R,5*R**,6*S**)-6-(Benzylamino)-2,7-dimethyloctane-3,5-diol (67b)**



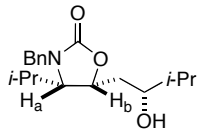
Prepared according to published procedure[2]. To a 0.13 M solution of SmI_2 (4.46 ml, 0.58 mmol) in THF, was added **65b** (25.3 mg, 58 μmol) in THF (0.5 ml), followed by pyrrolidine (82.5 mg, 1.16 mmol) and H_2O (31.4 mg, 1.74 mmol). The reaction mixture was diluted with Et_2O and washed with an aqueous solution of sodium potassium tartrate and potassium carbonate (10% w/w each), and the aqueous phase extracted with Et_2O. The combined organic phases was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield **67b** (9.7 mg, 60%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.96 (ddd, J = 8.7, 4.4, 4.4 Hz 1H), 3.90 (d, J = 12.6 Hz, 1H), 3.83 (d, J = 12.6 Hz, 1H), 3.66 – 3.60 (m, 1H), 3.30 (br s, 1H), 2.45 – 2.41 (m, 1H), 1.89 (dh, J = 13.5, 6.8 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.58 – 1.48 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 140.21, 128.55, 128.31, 127.27, 74.06, 68.25, 67.00, 54.31, 35.53, 33.81, 29.65, 20.66, 18.92, 18.86, 17.97; IR (film) ν_{max} = 3371(br), 2958, 1466 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+Na): 302.2091, found: 302.2089.

(2*S*,4R*,5S)-5-(Benzylamino)-6-methylheptane-2,4-diol (68b)**



Prepared according to published procedure[3]. To a 0.13 M solution of SmI_2 (2.18 ml, 0.28 mmol) in THF, was added **66b** (11.5 mg, 28 μmol) in THF (0.5 ml), followed by pyrrolidine (40.4 mg, 0.57 mmol) and H_2O (15.4 mg, 0.85 mmol). The reaction was stirred for 15 min was then diluted with Et_2O and washed with an aqueous solution of sodium potassium tartrate and potassium carbonate (10% w/w each), and the aqueous phase extracted with Et_2O. The combined organic phases was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield **68b** (7 mg, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 – 7.26 (m, 5H), 4.12 (dqd, J = 12.8, 6.3, 3.1, 1H), 3.99 (ddd, J = 9.9, 4.8, 2.7, 1H), 3.91 (d, J = 12.7, 1H), 3.83 (d, J = 12.7, 1H), 2.43 (dd, J = 6.3, 5.0, 1H), 1.79-1.92 (m, 1H), 1.65 – 1.58 (m, 1H), 1.47 (ddd, J = 14.1, 7.9, 2.7, 1H), 1.25 (d, J = 6.3, 3H), 1.04 (d, J = 6.8, 3H), 0.95 (d, J = 6.8, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 140.14, 128.57, 128.28, 127.31, 67.98, 66.93, 65.62, 54.28, 39.70, 29.75, 23.49, 20.58, 19.08; IR (film) ν_{max} = 3356(br), 2962, 1454 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+Na): 274.1778, found 274.1778.

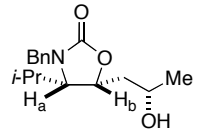
(4S*,5R*)-3-Benzyl-5-((*R)-2-hydroxy-3-methylbutyl)-4-isopropyloxazolidin-2-one (69b)**



$^3J_{Ha\text{-}Hb}$ = 7.5 Hz

Prepared from **67b** as described for **60b** to afford **69b** (7 mg, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.27 (m, 5H), 5.08 (d, J = 15.4, 1H), 4.74 (ddd, J = 10.5, 7.5, 2.7, 1H), 4.06 (d, J = 15.4, 1H), 3.71 (unresolved m, 1H), 3.41 (dd, J = 7.5, 2.1, 1H), 2.08 – 1.94 (m, 1H), 1.92 – 1.82 (m, 1H), 1.74 – 1.57 (m, 2H), 1.03 (dd, J = 14.0, 7.1, 6H), 0.93 (dd, J = 6.8, 3.4, 6H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 158.67, 136.24, 128.80, 127.83, 76.37, 72.78, 61.34, 47.59, 34.09, 33.34, 28.49, 21.30, 18.53, 17.15, 17.01; ^{13}C NMR (Acetone, 125.8 MHz) δ 158.80, 137.95, 129.25, 128.21, 128.05, 77.06, 72.31, 62.18, 47.75, 34.78, 34.13, 28.91, 21.32, 18.70, 17.28, 17.09; IR (film) ν_{max} = 3440(br), 2958, 2924, 1732, 1434 cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+Na): 328.1883, found: 328.1885.

(4*S,5*R**)-3-Benzyl-5-((*S**)-2-hydroxypropyl)-4-isopropyloxazolidin-2-one (70b)**



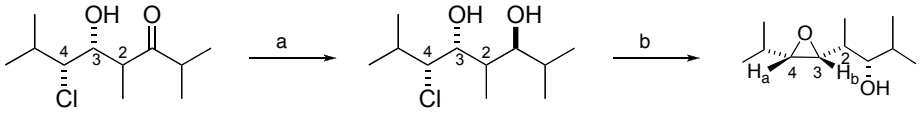
$^3J_{Ha\text{-}Hb}$ = 7.5 Hz

Prepared from **68b** as described for **60b** to afford **70b** (6 mg, 95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 – 7.26 (m, 5H), 5.07 (d, J = 15.4, 1H), 4.72 (ddd, J = 10.5, 7.5, 2.6, 1H), 4.15 – 4.08 (m, 1H), 3.41 (dd, J = 7.5, 2.1, 1H), 2.05 – 1.94 (m, 1H), 1.90 (ddd, J = 13.9, 10.5, 2.6, 1H), 1.64 (ddd, J = 14.2, 9.7, 2.6, 1H), 1.27 (d, J = 6.2, 3H), 1.04 (d, J = 7.3, 3H), 1.01 (d, J = 6.9, 3H); ^{13}C NMR (Acetone, 125.8 MHz) δ 158.78, 137.92, 129.17, 128.19, 128.04, 76.76, 64.13, 62.08, 47.73, 39.11, 28.87, 24.55, 21.29, 17.17; IR (film) ν_{max} = cm^{-1}; HRMS (FAB+) calcd for $C_{12}H_{16}O_2$ (M+Na): 300.1570, found: 300.1571.

Stereochemical determination of Mukaiyama aldol product 24a, 24b and 25b

The relative stereochemistry of **24a**, **24b** and **25b** was determined by analyzing the coupling constants of epoxide **62a**, **62b** and **64b**.

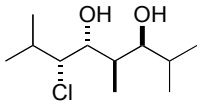
Scheme 10. Stereochemical determination of **24a**.



24a, 2,3-*anti* **61a**, 2,3-*anti* **62a**, 2,3-*anti*

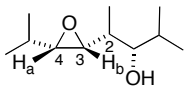
Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH (1:1), - 30 ^oC, 84%; b) K_2CO_3, EtOH, 70 °C, 92%.

(3*S,5*R**,6*R**)-6-Chloro-2,4,7-trimethyloctane-3,5-diol (61a)**



Prepared from **24a** as described for **46a** to afford **61a** (36 mg, 84%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 3.99 (dd, J = 5.4 Hz, 5.4 Hz, 1H), 3.79 (dd, J = 5.5 Hz, 5.5 Hz, 1H), 3.49 (dd, J = 9.5 Hz, 1.3 Hz, 1H), 2.47 (br s, 1H), 2.29 (br s, 1H), 2.15 – 2.02 (m, 1H), 1.93 (dqd, J = 7.0 Hz, 6.9 Hz, 1.7 Hz, 1H), 1.78 – 1.65 (m, 1H), 1.06 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H), 1.04 (d, J = 6.5 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 76.27, 75.52, 74.57, 37.07, 31.60, 31.16, 20.79, 20.01, 18.92, 18.32, 9.80; IR (film) ν_{max} = cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{23}ClO_2$ (M+H): 223.1459, found: 223.1457.

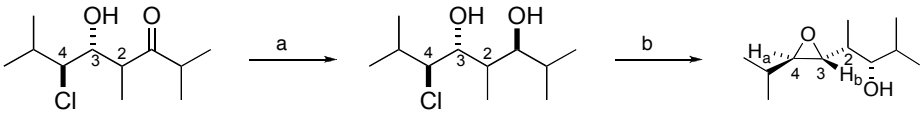
(*S)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (62a)**



$^3J_{Ha-Hb}$ = 4.2 Hz

Prepared from **61a** as described for **45** to afford **62a** (28 mg, 92%) as a colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 3.41 (unresolved m, 1H), 2.95 (dd, J = 9.4 Hz, 4.2 Hz, 1H), 2.66 (dd, J = 9.4 Hz, 4.2 Hz, 1H), 1.87 – 1.79 (m, 1H), 1.61 – 1.52 (m, 1H), 1.51 – 1.40 (m, 1H), 1.10 (d, J = 6.6 Hz, 3H), 1.01 – 0.97 (m, 9H), 0.89 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 78.37, 63.37, 60.09, 34.18, 30.98, 27.05, 20.38, 19.35, 19.02, 18.42, 10.55; IR (film) ν_{max} = 3448(br), 2962, 1466, 1385, 984 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}O_2$ (M+H): 187.1693, found: 187.1693.

Scheme 11. Stereochemical determination of **24b** and **25b**.



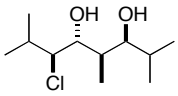
24b, 2,3-*anti*
25b, 2,3-*syn*

61b, 2,3-*anti*
63b, 2,3-*syn*

62b, 2,3-*anti*
64b, 2,3-*syn*

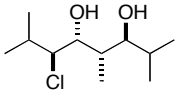
Reagents and conditions: a) $Me_4NBH(OAc)_3$, MeCN:AcOH (1:1), -30 ^oC, 26-65%; b) K_2CO_3, EtOH, rt, 97-99%.

(2*S*,3S*,5S)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (61b)**



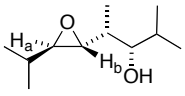
Prepared from **24b** as described for **46a** to afford **61b** (2.8 mg, 26%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.94 (dd, J = 10.2 Hz, 2.0 Hz, 1H), 3.72 (br s, 1H), 3.64 – 3.59 (m, 2H), 2.57 (dhept, J = 6.5 Hz, 2.0 Hz, 1H), 2.41 – 2.34 (m, 1H), 1.92 (br s, 1H), 1.79 – 1.68 (m, 1H), 1.08 (d, J = 7.0 Hz, 3H), 1.07 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 6.5, Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 77.81, 77.34, 69.71, 33.44, 31.67, 28.58, 21.17, 19.39, 18.60, 14.73, 10.39; IR (film) ν_{max} = 3314(br), 2966, 1462, 1068, 752 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{23}ClO_2$ (M+Na): 245.1279, found: 245.1271.

(2*S*,3R*,5R)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (63b)**



Prepared from **25b** as described for **46a** to afford **63b** (6.7 mg, 65%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.01 (d, *J* = 10.2 Hz, 1H), 3.79 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.41 (s, 1H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.44-2.35 (m, 1H), 2.29 (ddq, *J* = 7.1, 7.1, 7.1, 3.4, 1.5 Hz, 1H), 2.02 (s, 1H), 1.94-1.83 (m, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 83.3, 71.3, 68.9, 34.4, 31.0, 28.0, 21.1, 19.1, 19.0, 14.5, 10.7; IR (film) ν_{max} = 3398(br), 2965, 1462, 1077, 747 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{23}ClO_2$ (M+Na): 245.1279, found: 245.1273.

(*S)-1-((2*S*,3R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (62b)**

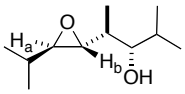


$^3J_{Ha\text{-}Hb}$= 2.3

Prepared from **61b** as described for **45** to afford **62b** (2.5 mg, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.35 (dd, J = 7.3 Hz, 4.0, Hz 1H), 2.75 (dd, J = 7.2 Hz, 2.3 Hz, 1H), 2.57 (dd, J = 7.2 Hz, 2.3 Hz, 1H), 1.85 – 1.69 (m, 2H), 1.59 – 1.44 (m, 2H), 1.03 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 7.1 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 0.96 (d, J = 6.9 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 77.98,

63.64, 60.86, 37.90, 30.97, 30.67, 19.28, 19.13, 18.37, 10.34; IR (film) ν_{max} = 3467(br), 2958, 1466, 1384, 980, 899 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}O_2$ (M+Na): 209.1512, found: 209.1507.

(*R)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol** (**64b**)

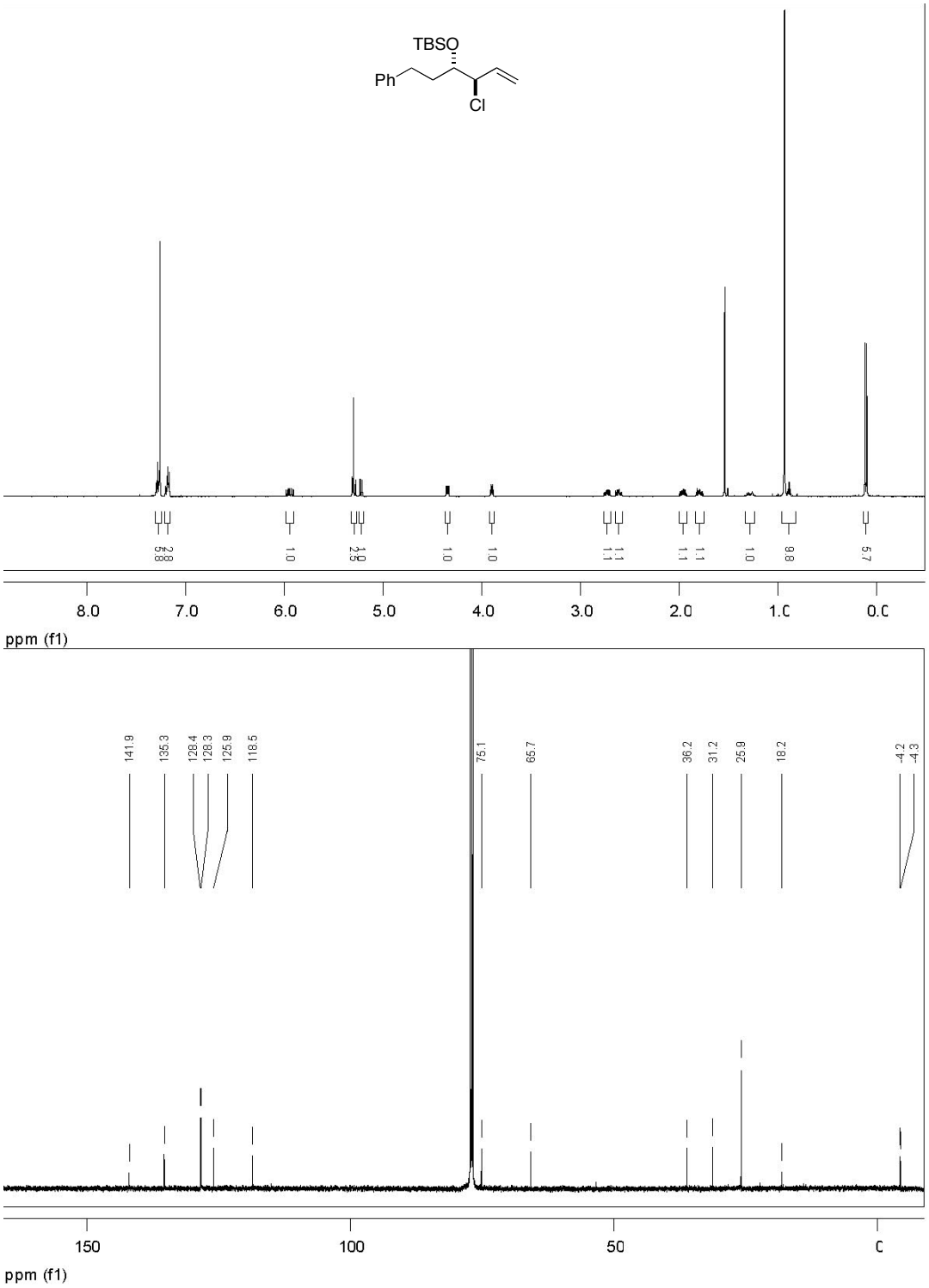


$^3J_{Ha-Hb}$= 2.5

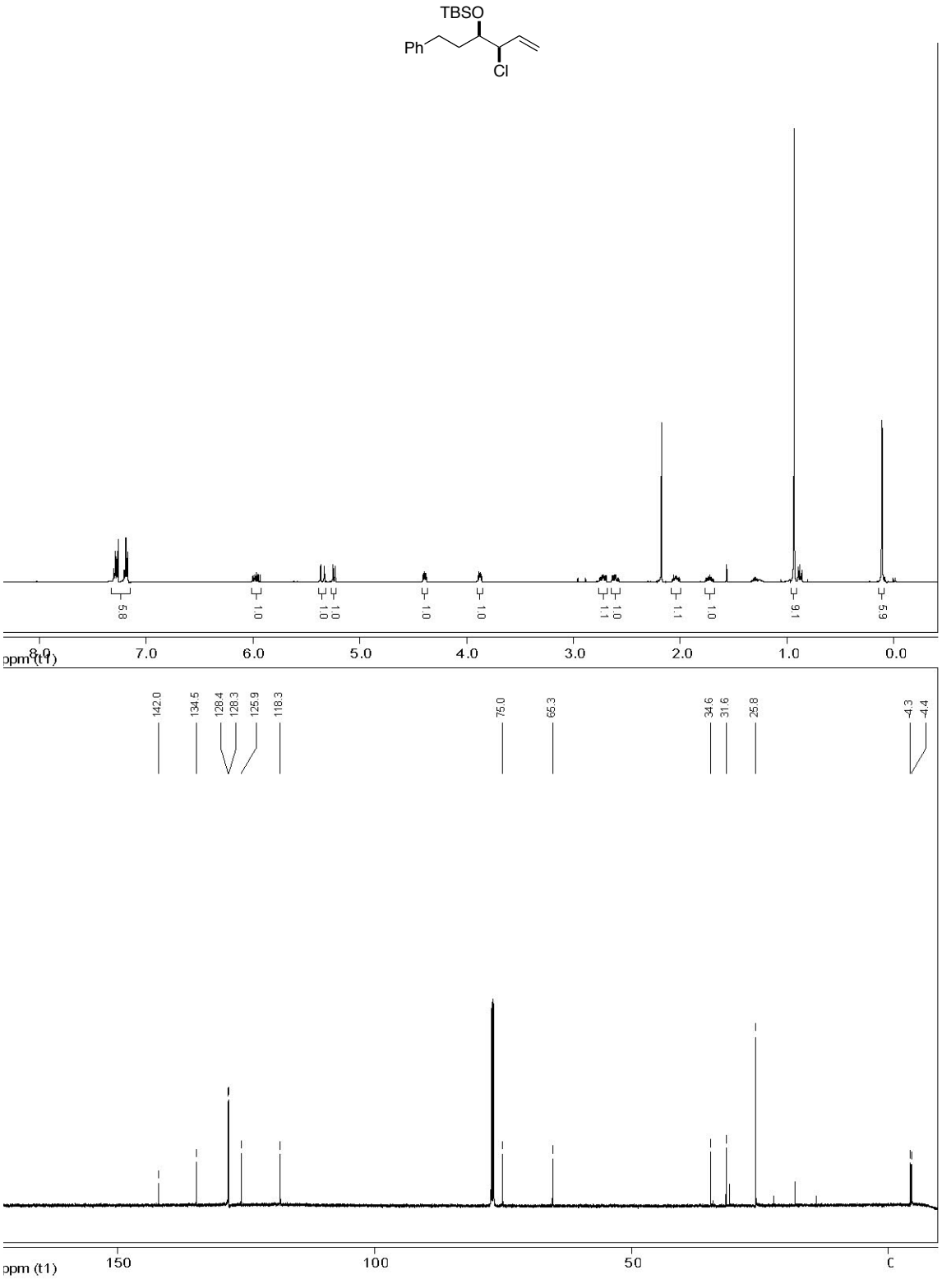
Prepared from **63b** as described for **45** to afford **64b** (4.5 mg, 97%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ; 3.22 (td, *J* = 8.2, 4.2, 4.2 Hz, 1H), 2.77 (dd, *J* = 6.7, 2.4 Hz, 1H), 2.67 (dd, *J* = 7.2, 2.4 Hz, 1H), 2.00 (d, *J* = 4.4 Hz, 1H), 1.80 (dtd, *J* = 13.6, 6.8, 6.8, 4.5 Hz, 1H), 1.70-1.62 (m, 1H), 1.47 (dt, *J* = 13.7, 13.7, 6.9 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 78.4, 63.7, 61.1, 37.7, 30.8, 30.0, 20.0, 19.1, 18.3, 15.3, 13.8; IR (film) ν_{max} = 3487(br), 2962, 1466, 994, 891 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{22}O_2$ (M+Na): 209.1512, found: 209.1506.

^{1}H and ^{13}C NMR Spectra

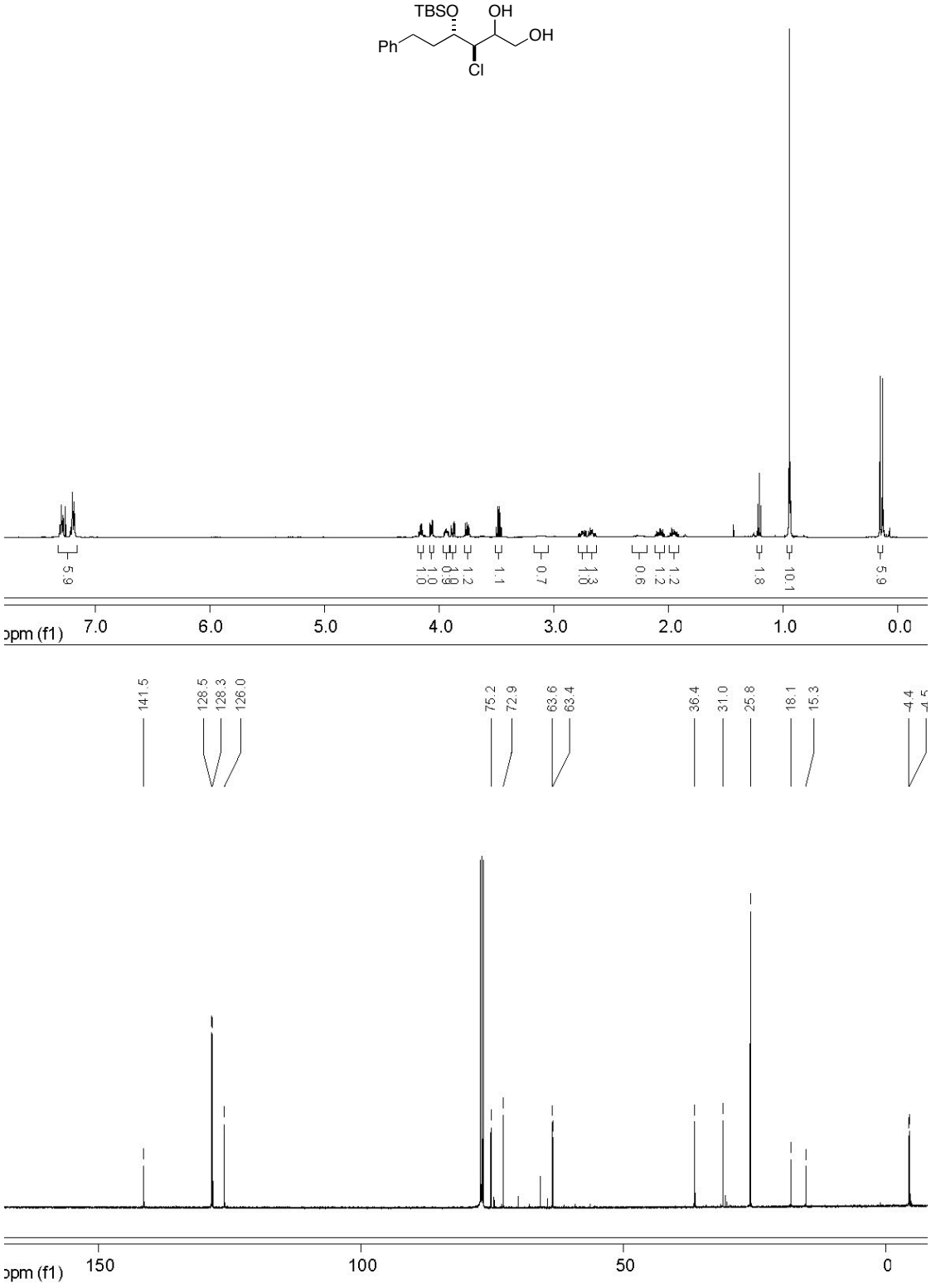
((3*R,4*S**)-4-Chloro-1-phenylhex-5-en-3-yloxy)(tert-butyl)dimethylsilane (28)**



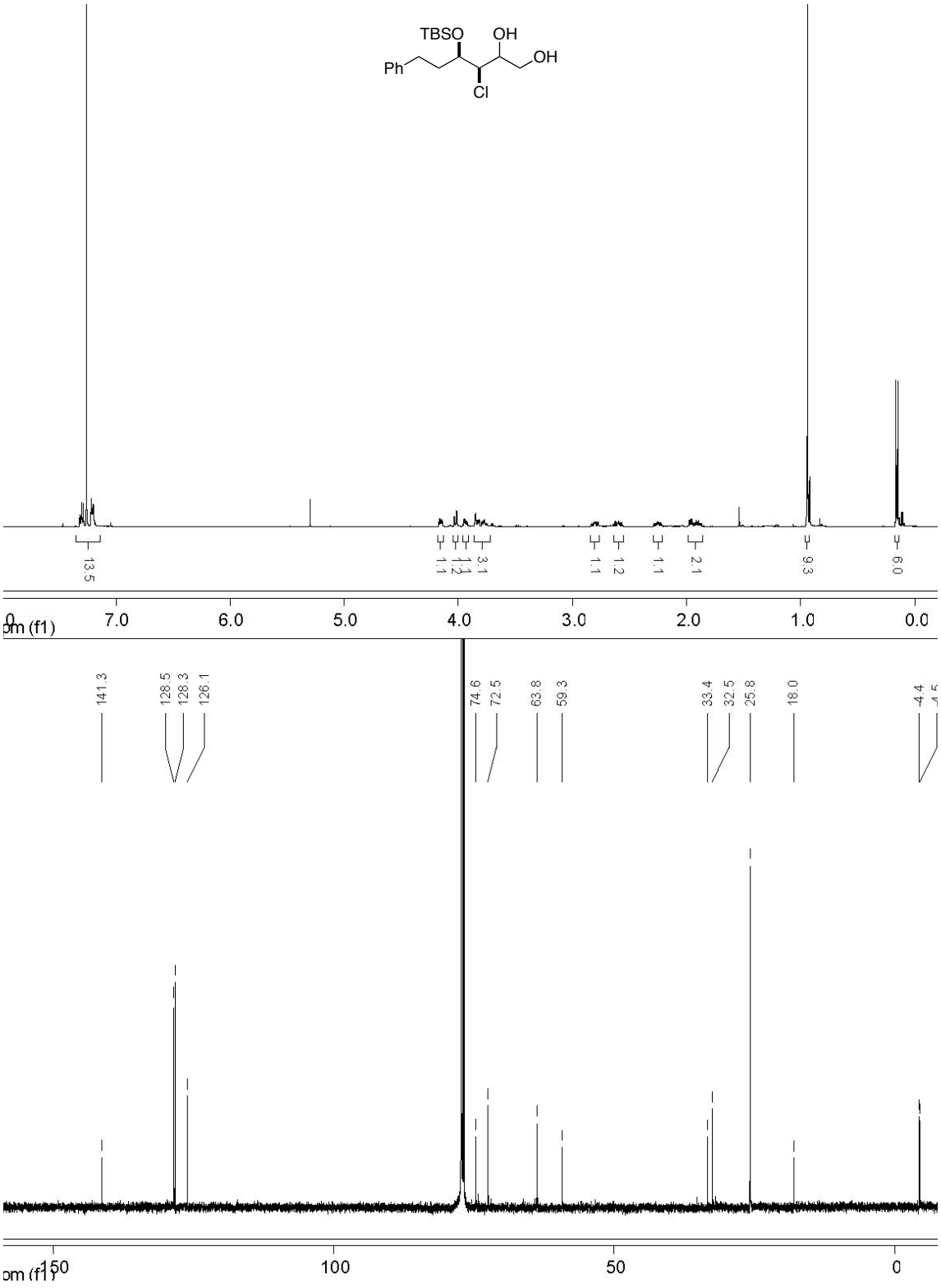
((3*R,4*R**)-4-Chloro-1-phenylhex-5-en-3-yloxy)(tert-butyl)dimethylsilane (29)**



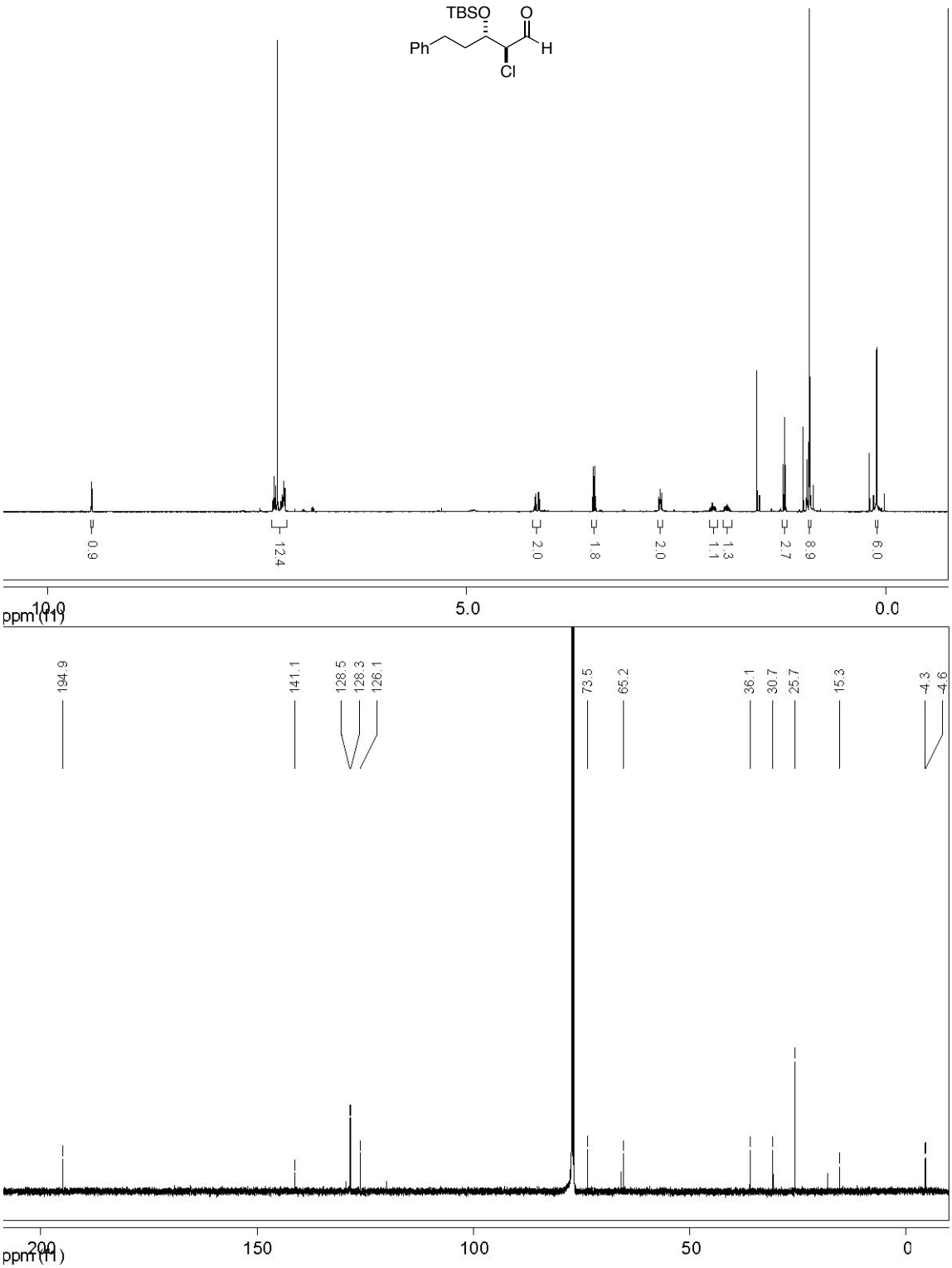
((3*R,4*S**)-4-Chloro-1-phenylhex-3-yloxy-)(tert-butyl)dimethylsilane-4,5-diol (30)**



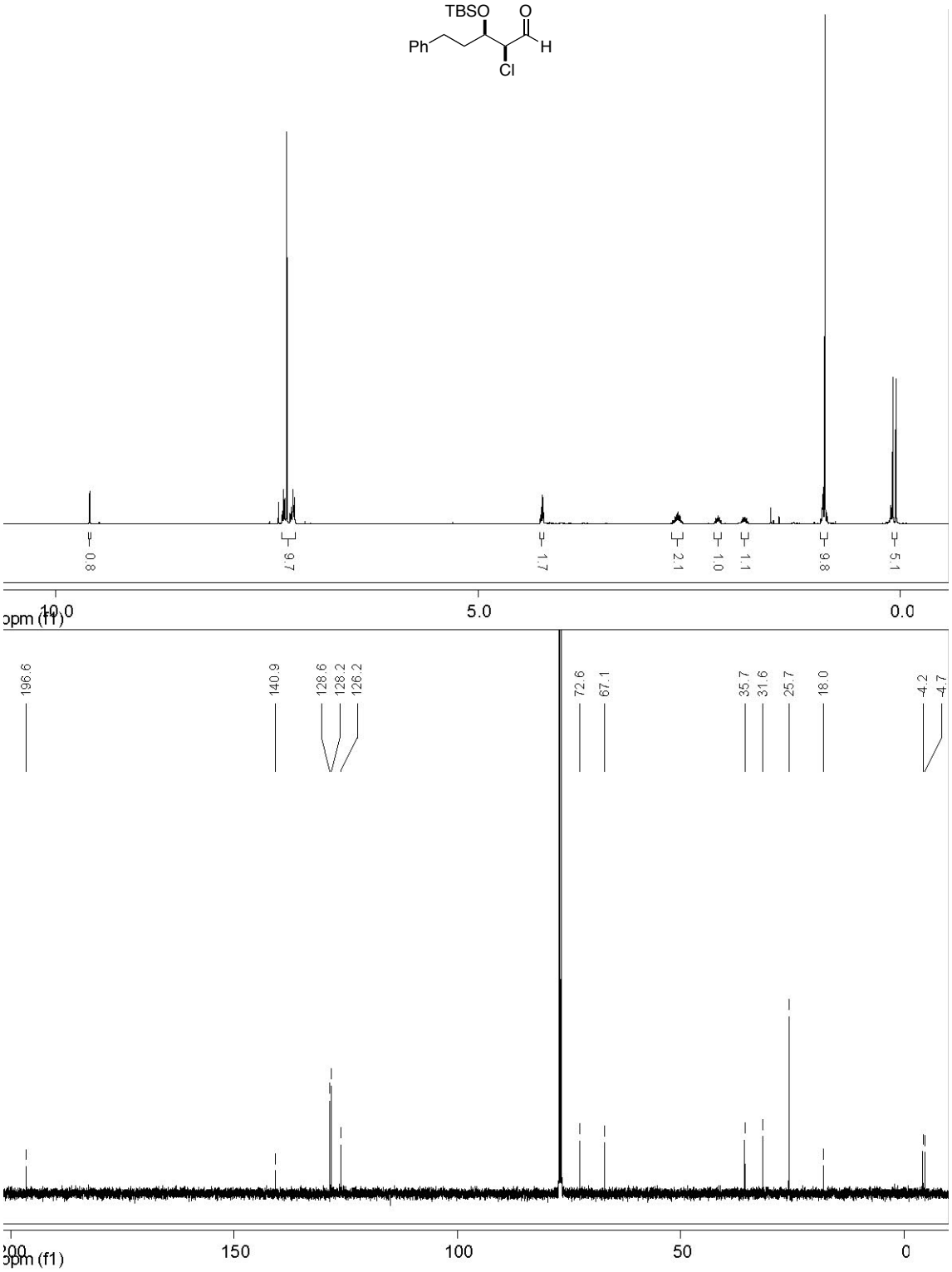
((3*R,4*R**)-4-Chloro-1-phenylhex-3-yloxy-)(tert-butyl)dimethylsilane-4,5-diol (31)**



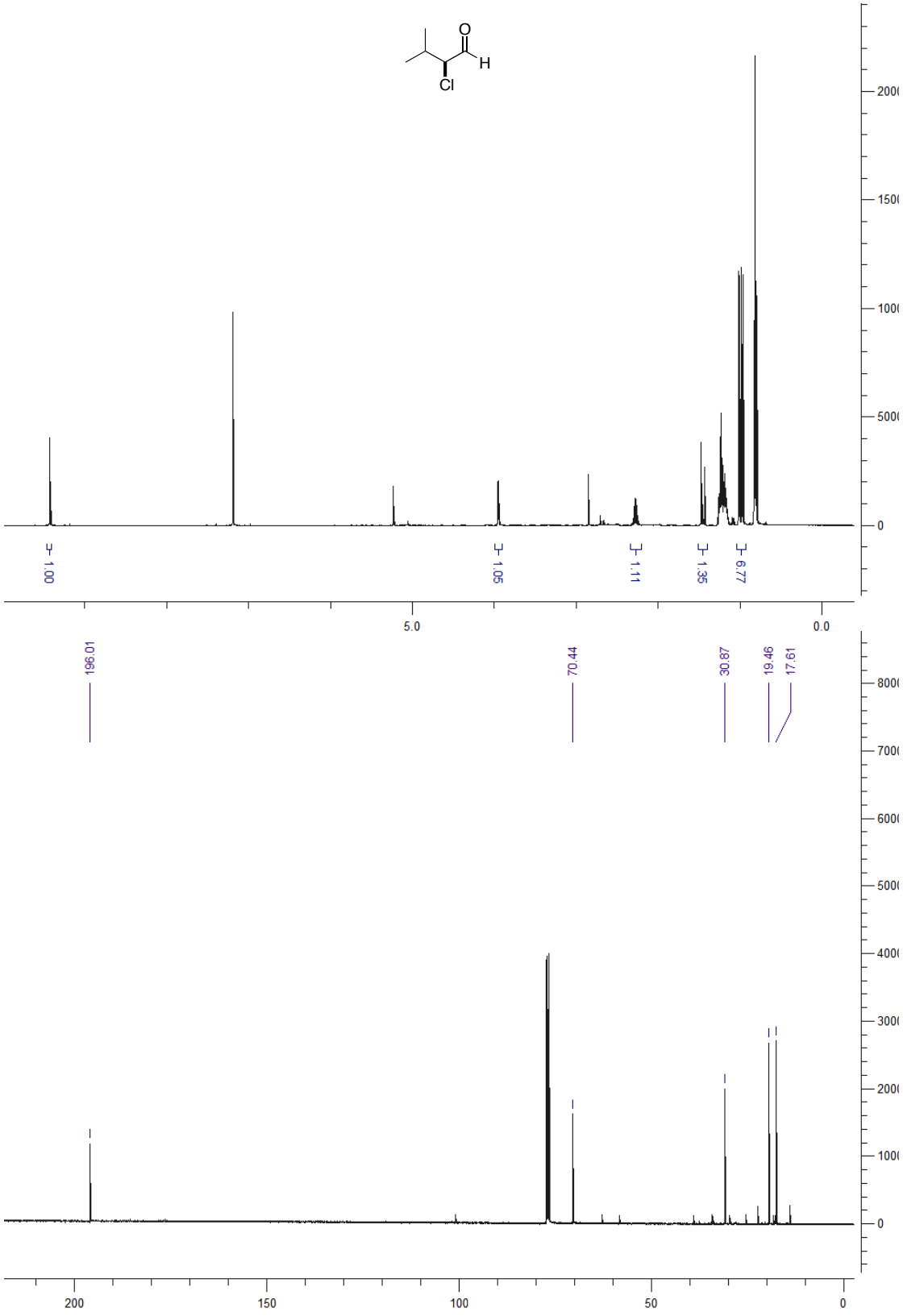
((3*R,4*S**)-4-Chloro-1-phenylhex-5-al-3-yloxy)(tert-butyl)dimethylsilane (1)**



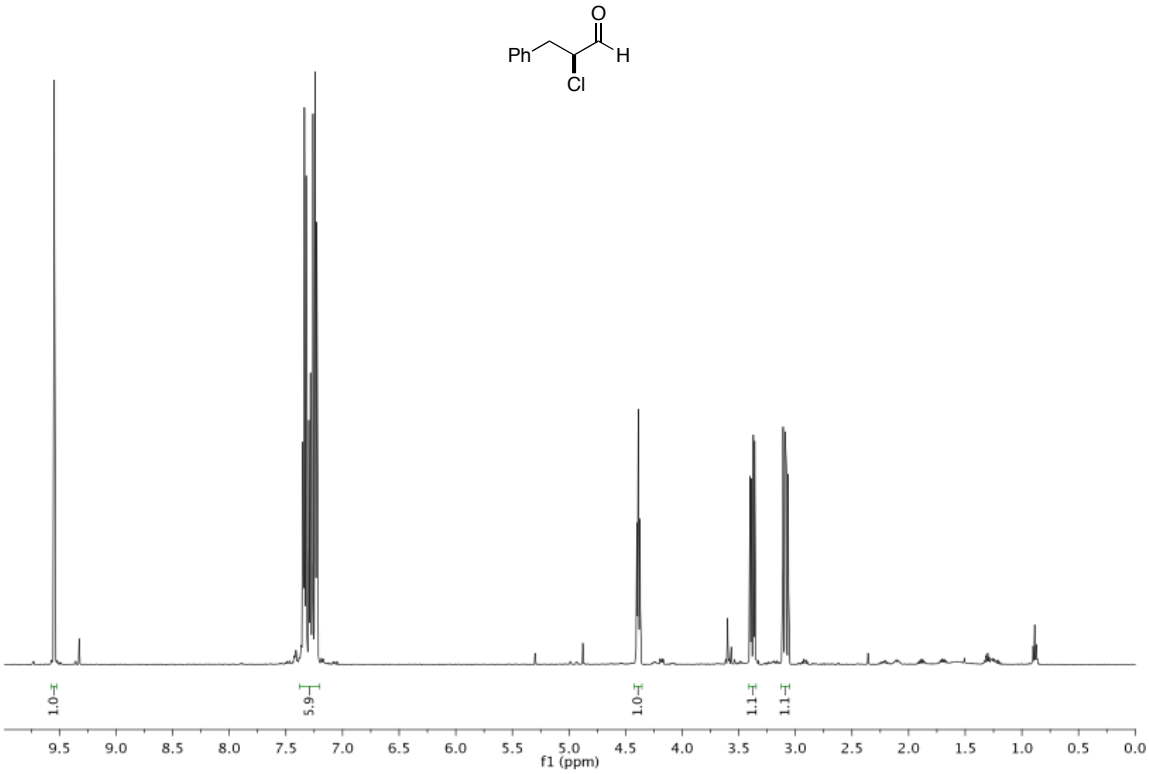
((3*R,4*R**)-4-Chloro-1-phenylhex-5-al-3-yloxy)(tert-butyl)dimethylsilane (2)**

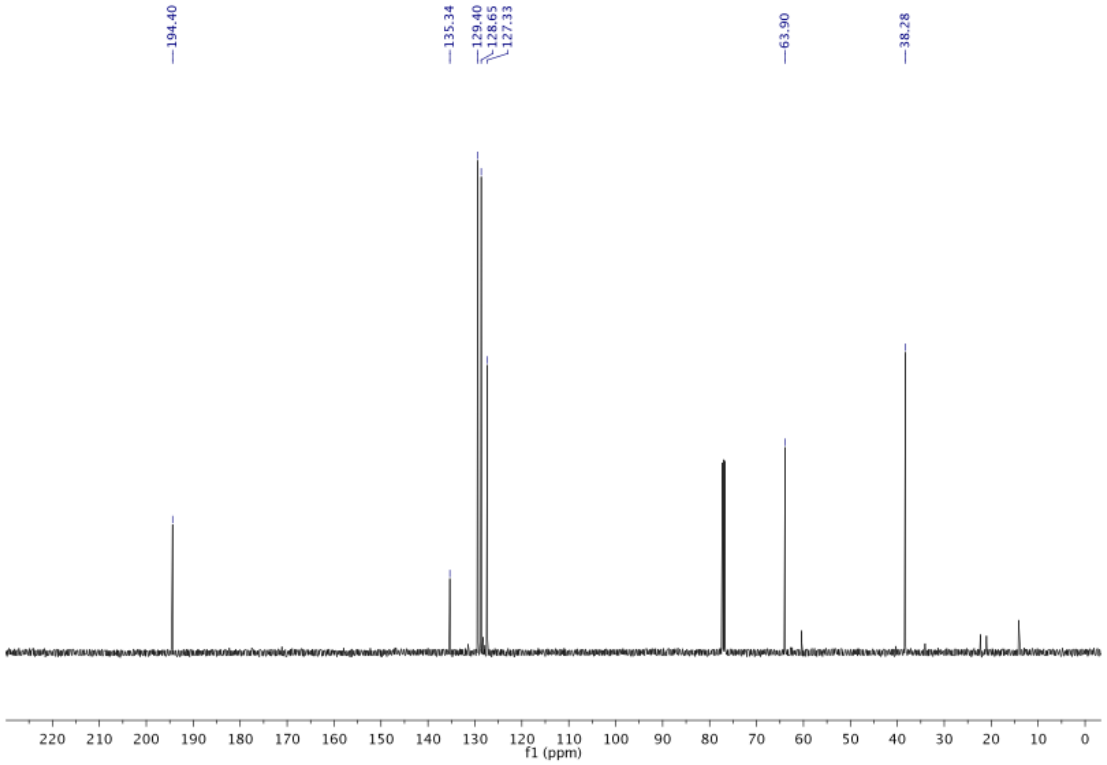


2-Chloro-3-methylbutanal (6)

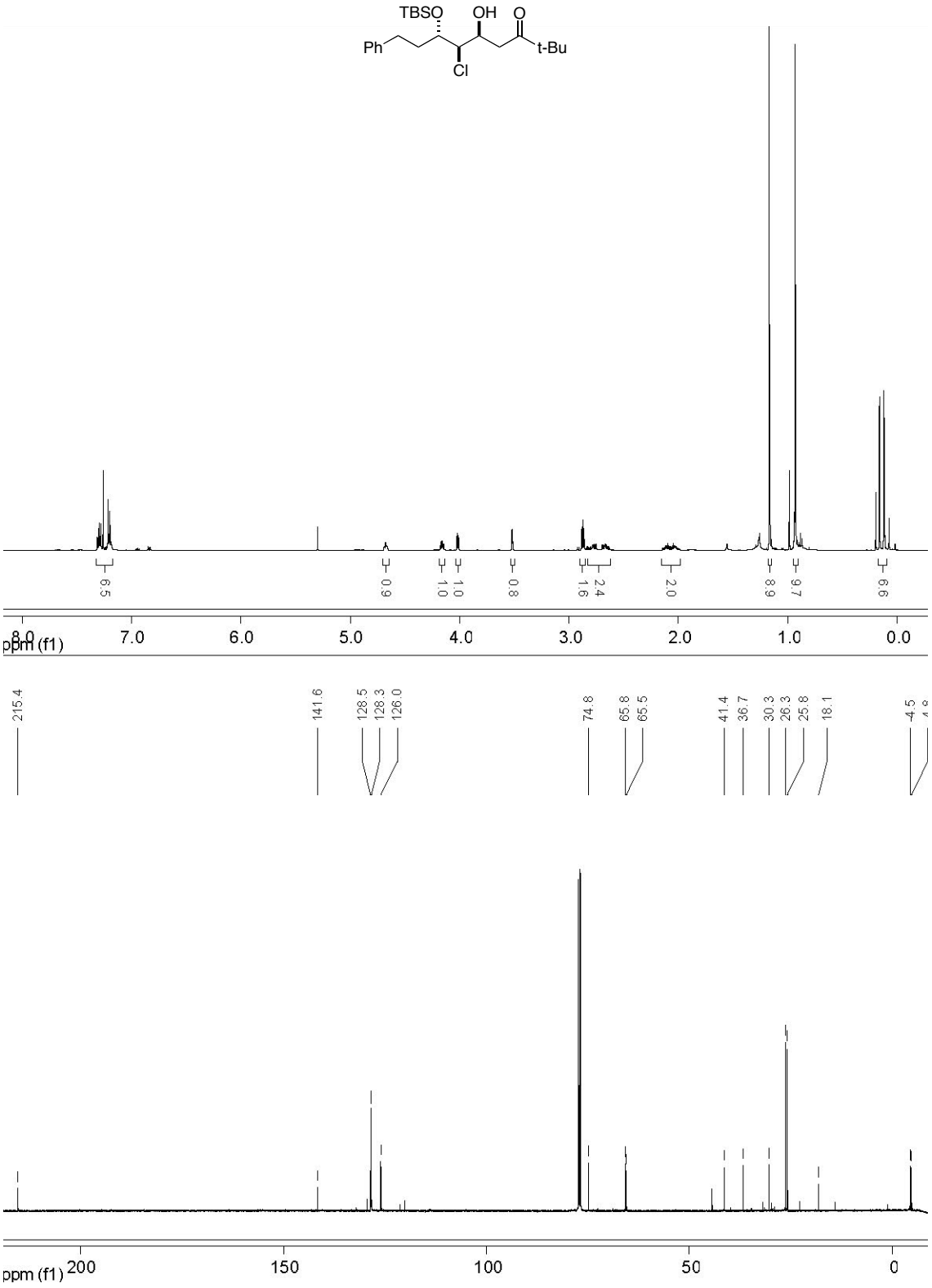


2-Chloro-3-phenylpropanal (7).

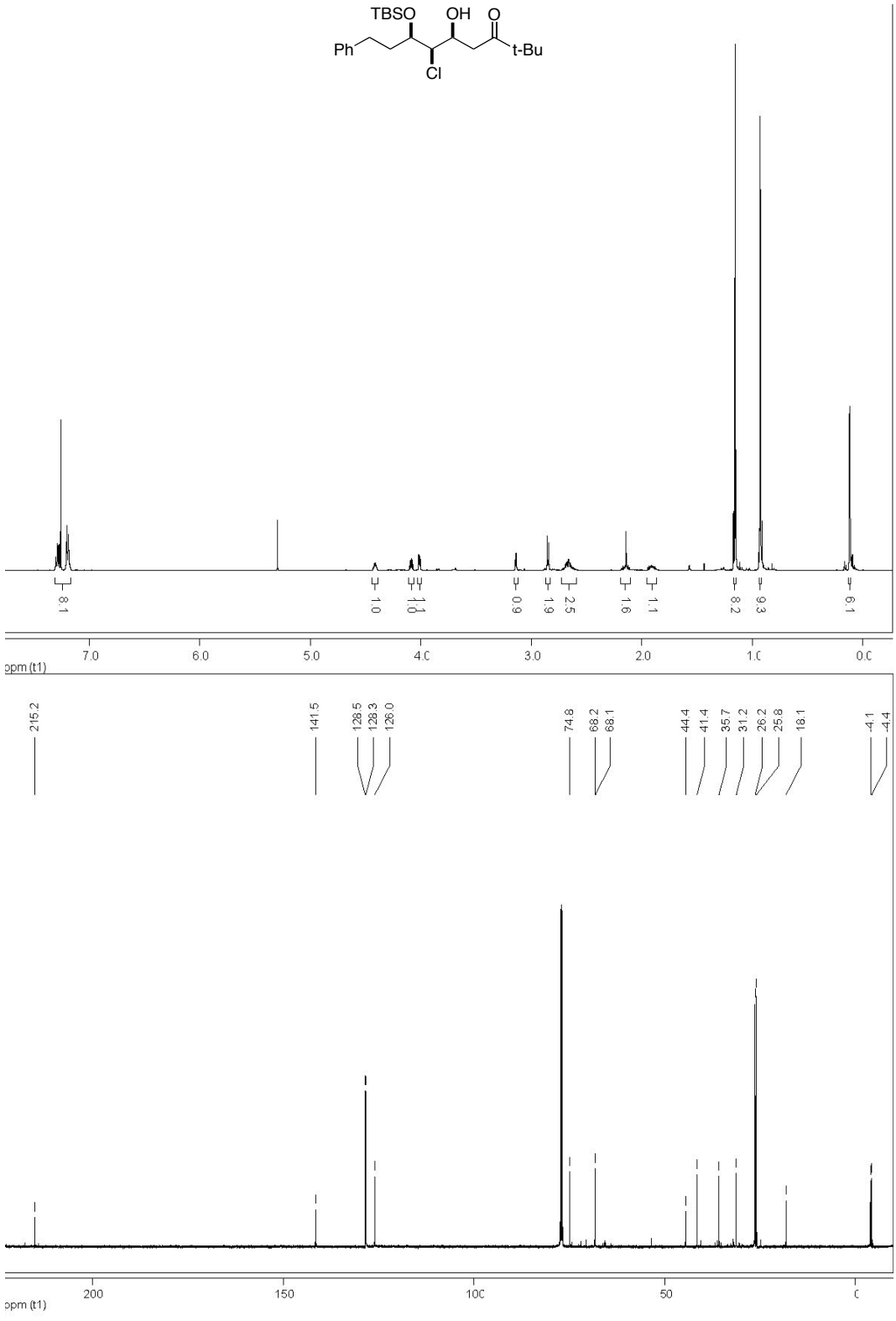




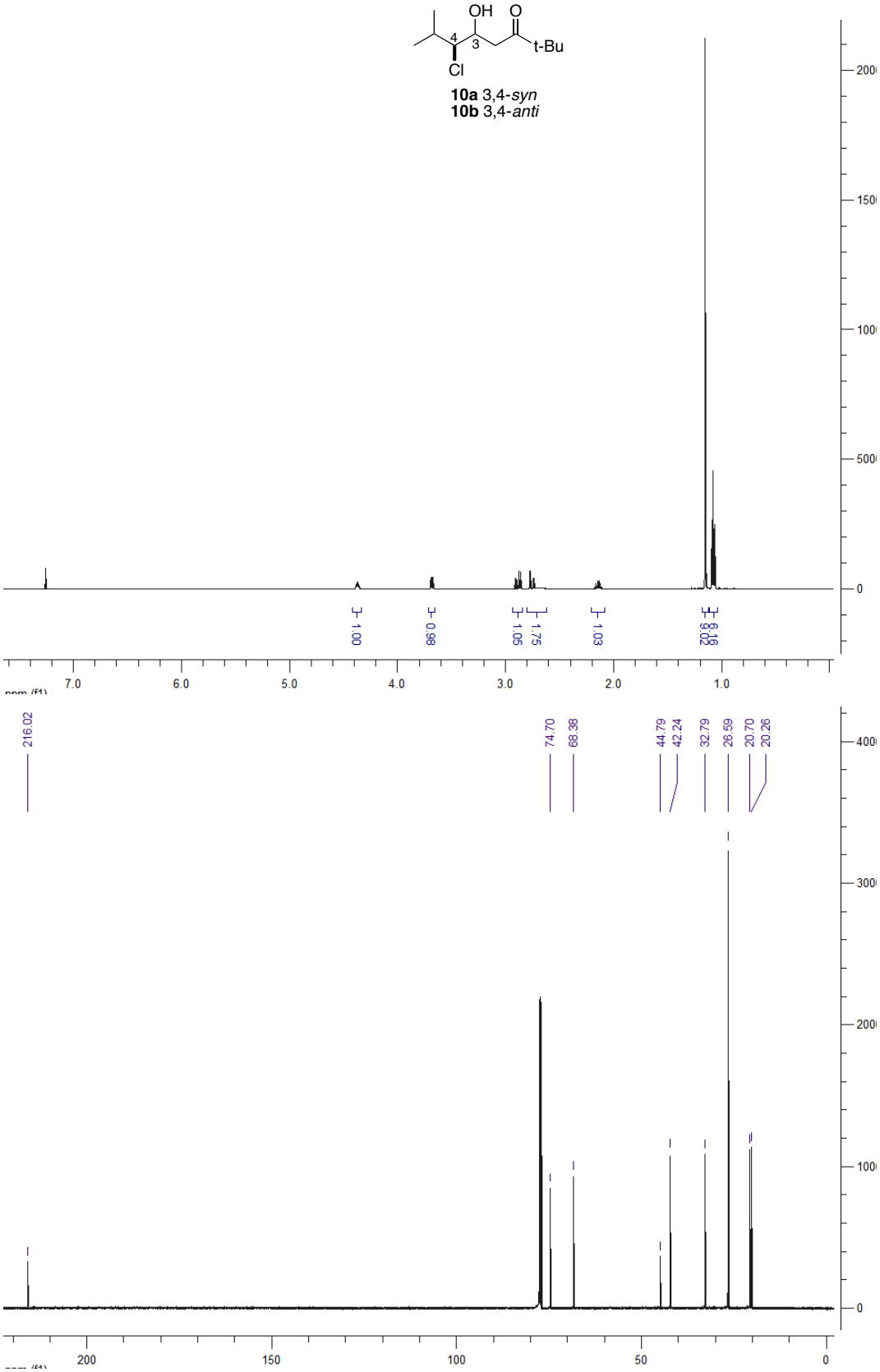
(5*S,6*S**,7*R**)-6-Chloro-5-yloxy-((tert-butyl)dimethylsilane)-7-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (4)**



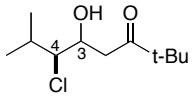
(5*S,6*S**,7*R**)-6-Chloro-5-yloxy-((tert-butyl)dimethylsilane)-7-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (5)**



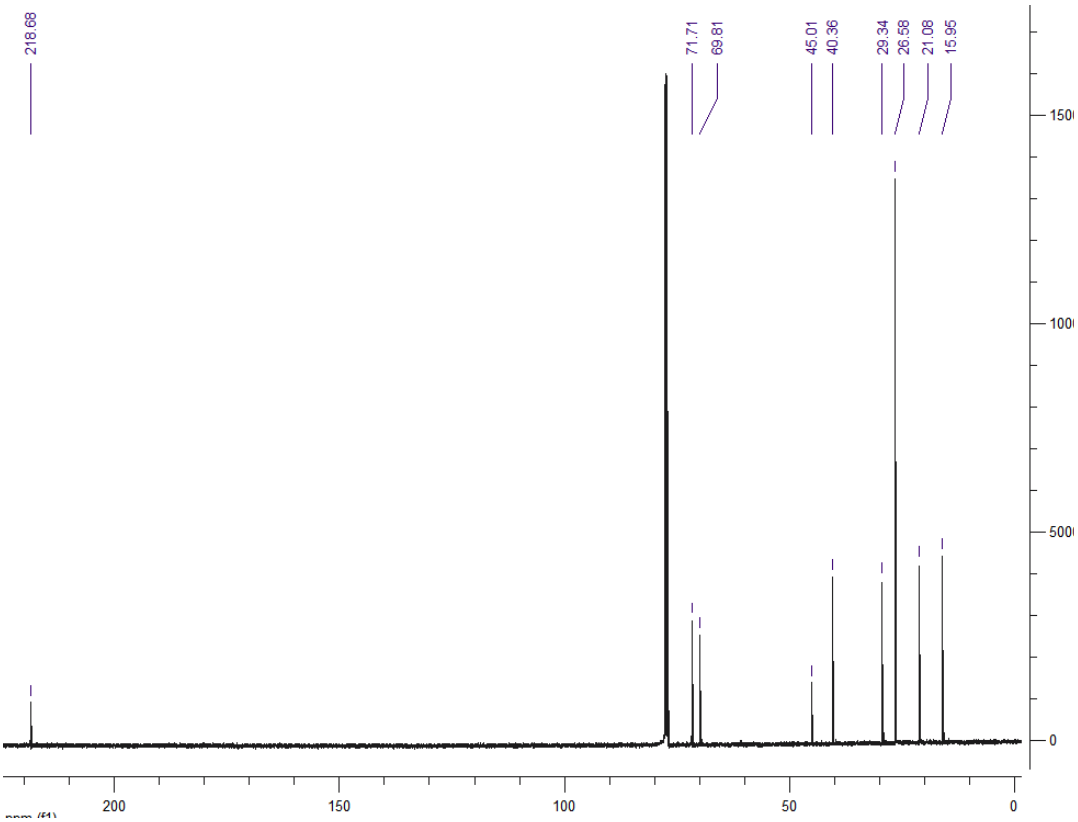
(5*S,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one (10a)**



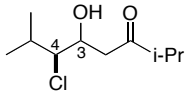
(5*R,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one (10b)**



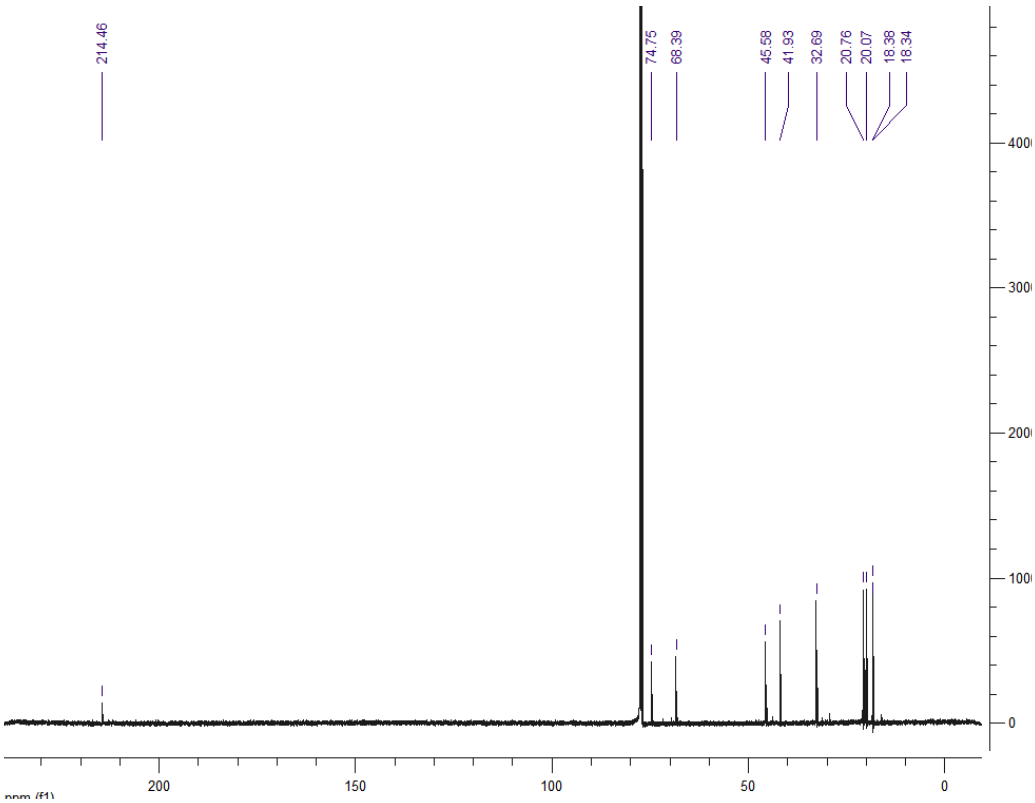
10a 3,4-*syn*
10b 3,4-*anti*



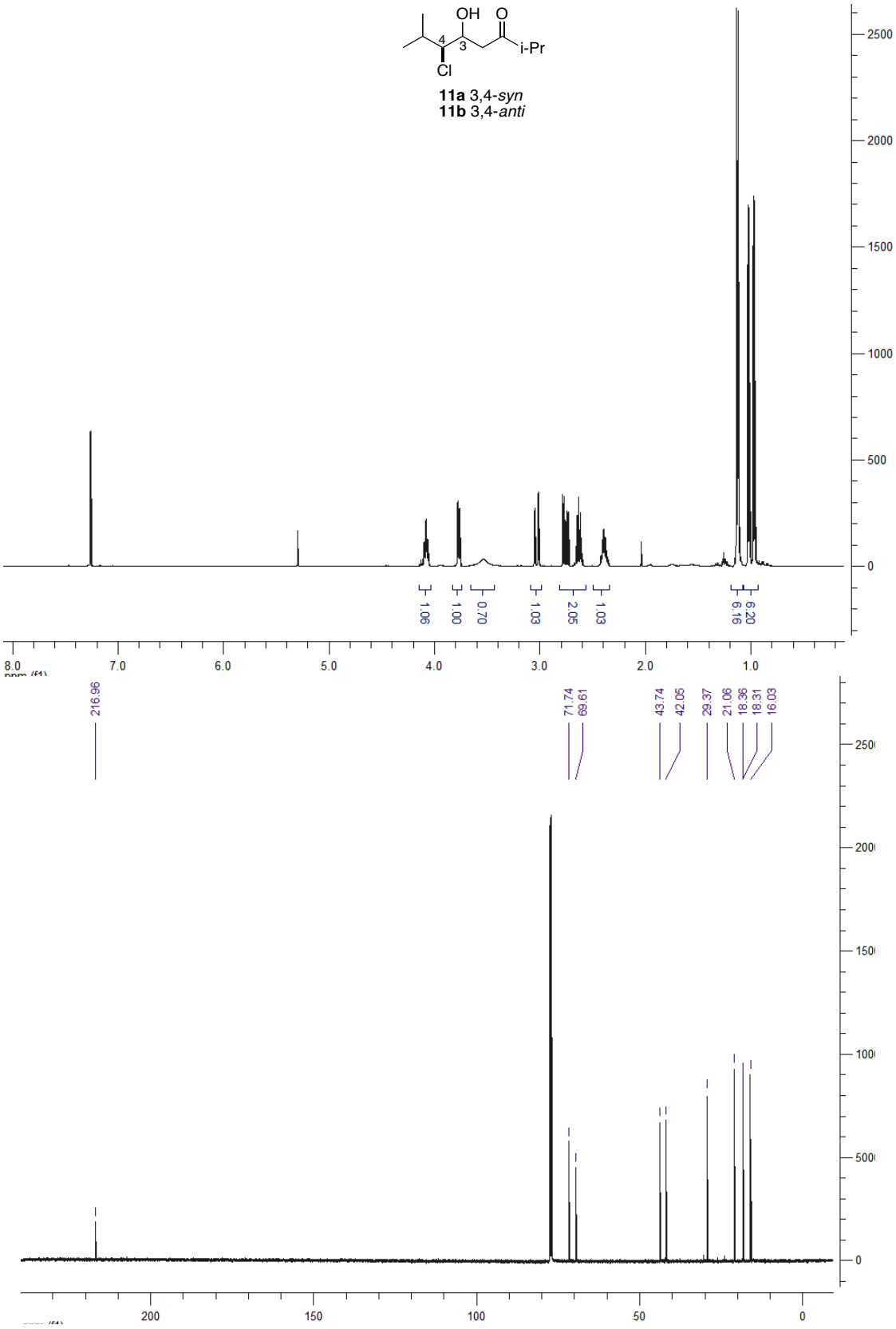
(5*S,6*S**)-6-Chloro-5-hydroxy-2,7-dimethyloctan-3-one (11a)**



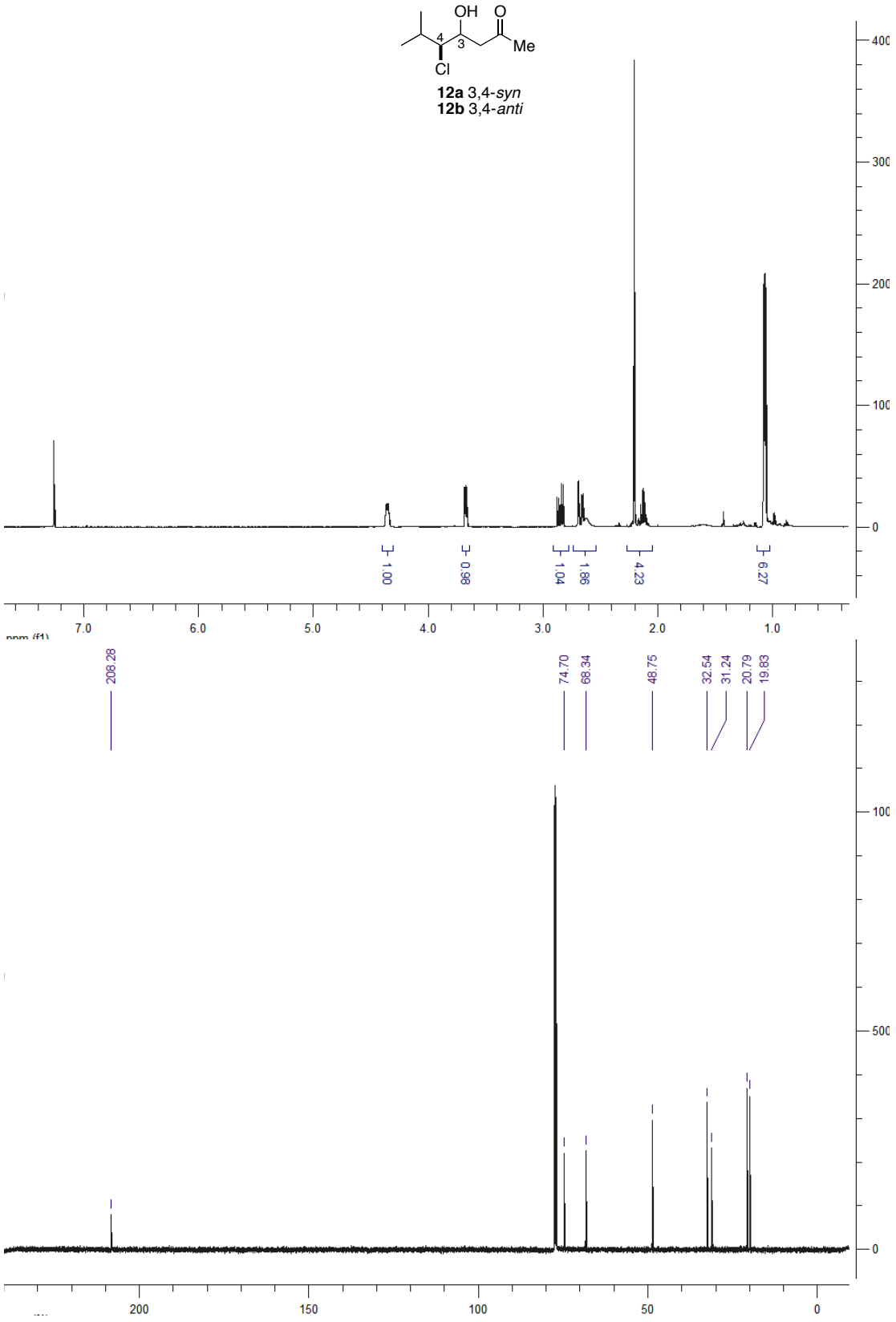
11a 3,4-*syn*
11b 3,4-*anti*



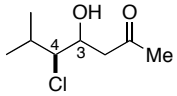
(5*R,6*S**)-6-Chloro-5-hydroxy-2,7-dimethyloctan-3-one (11b)**



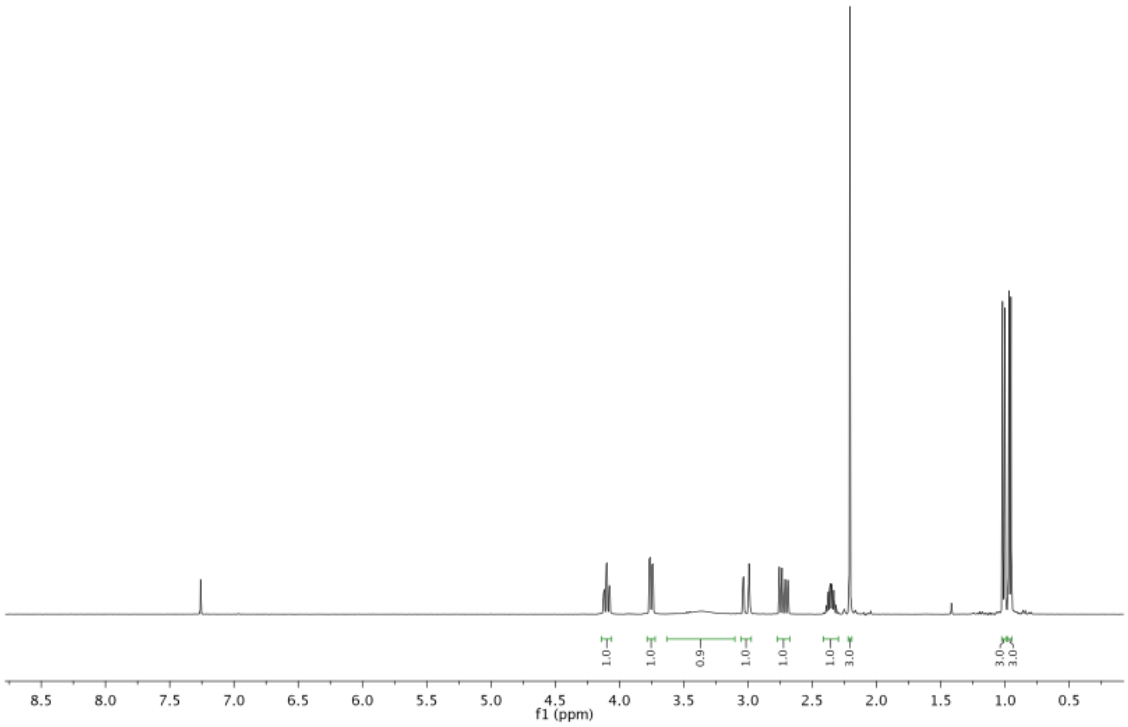
(5*S,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one (12a)**

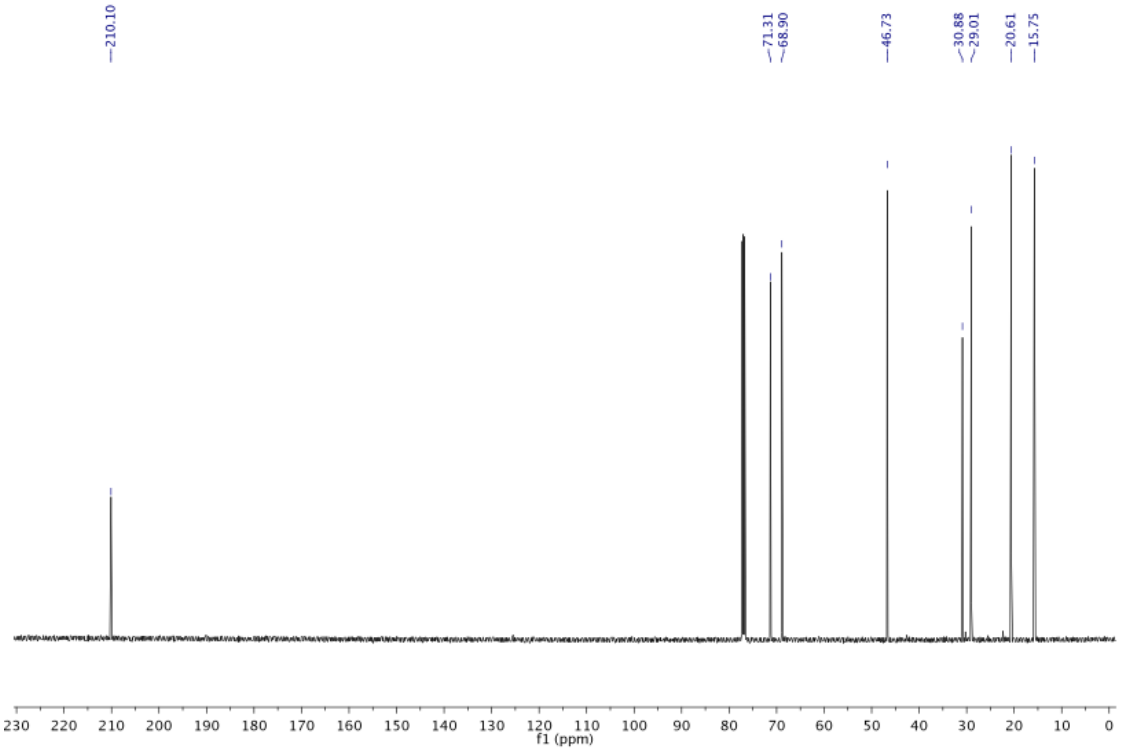


(5*R,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one (12b)**

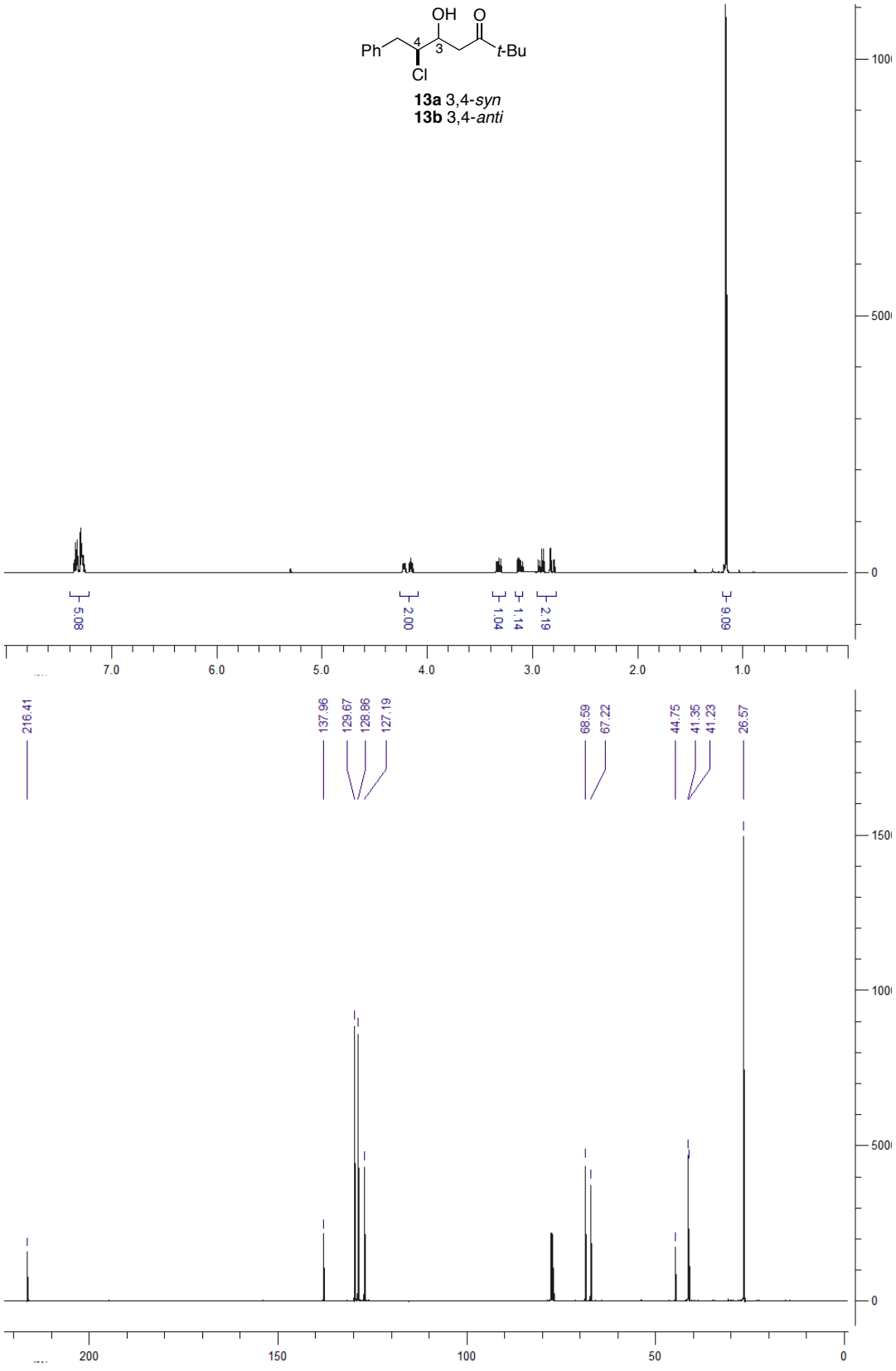


12a 3,4-*syn*
12b 3,4-*anti*

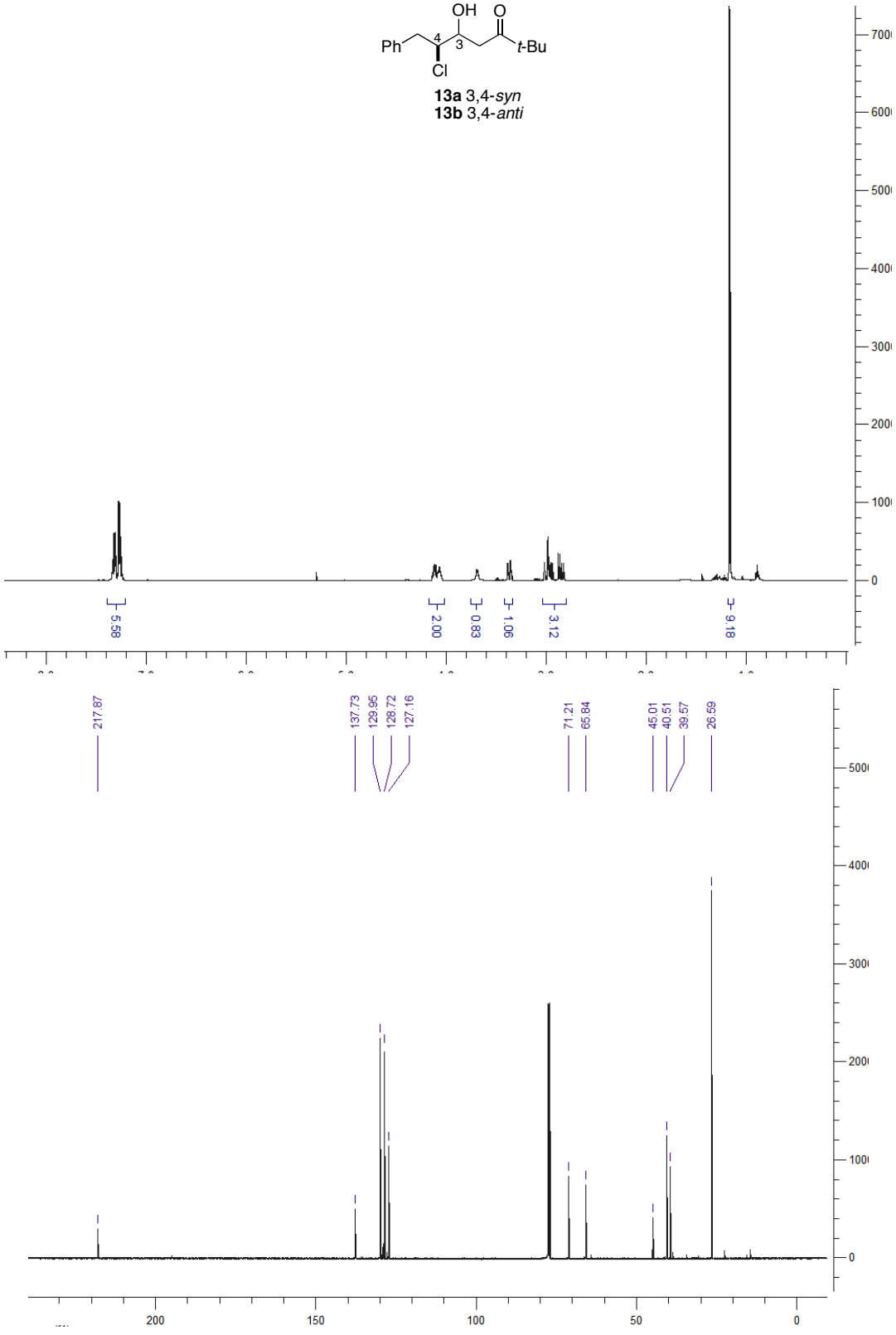




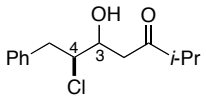
(5*S,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (13a)**



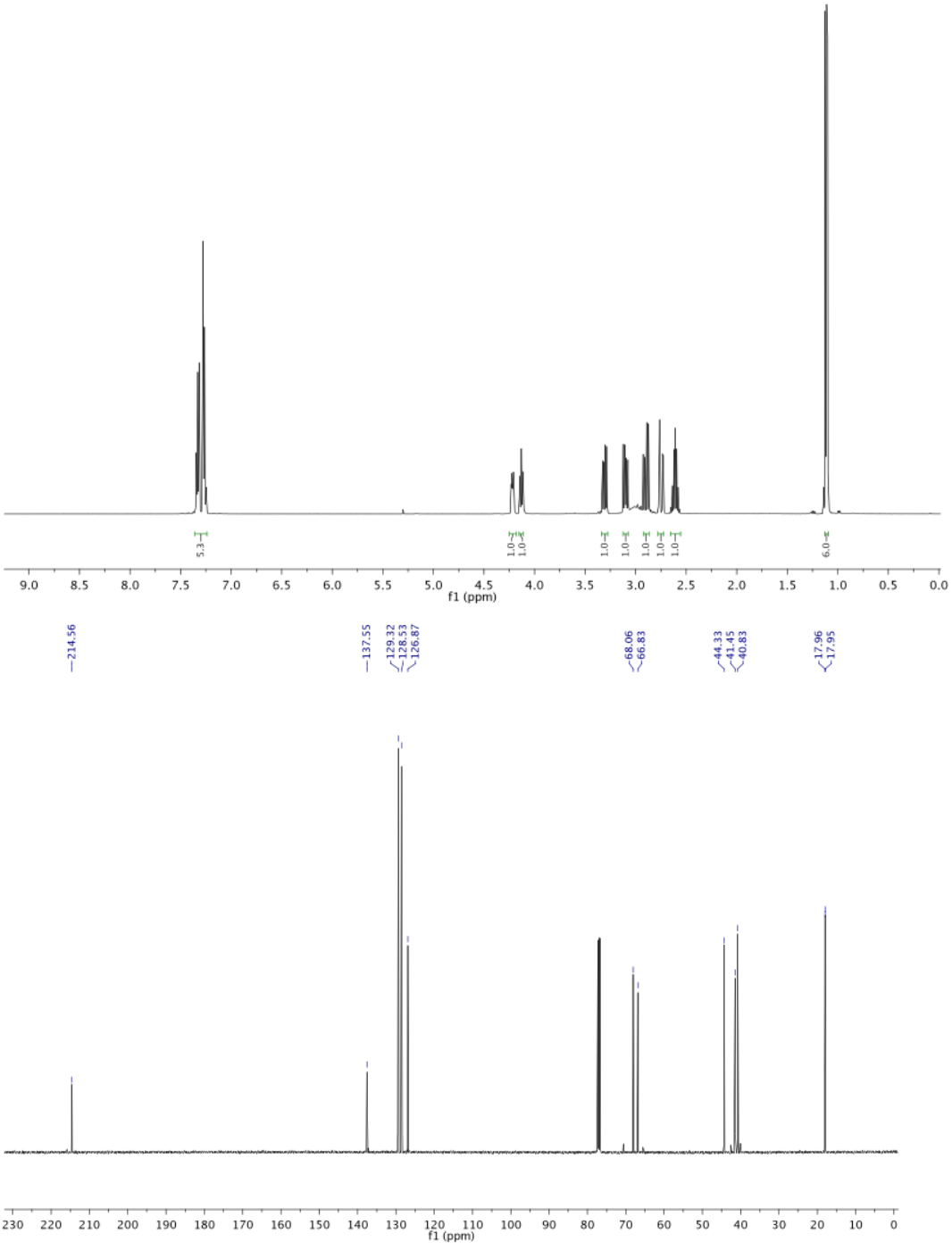
(5*R,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (13b)**



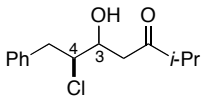
(5*S,6*S**)-6-Chloro-5-hydroxy-2-methyl-7-phenylheptan-3-one (14a)**



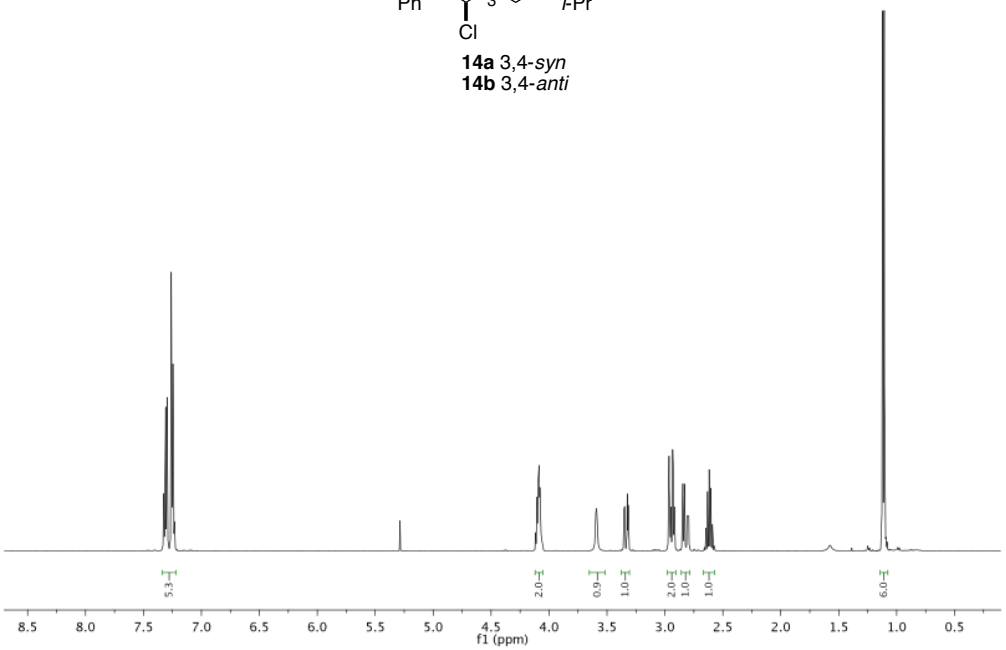
14a 3,4-*syn*
14b 3,4-*anti*

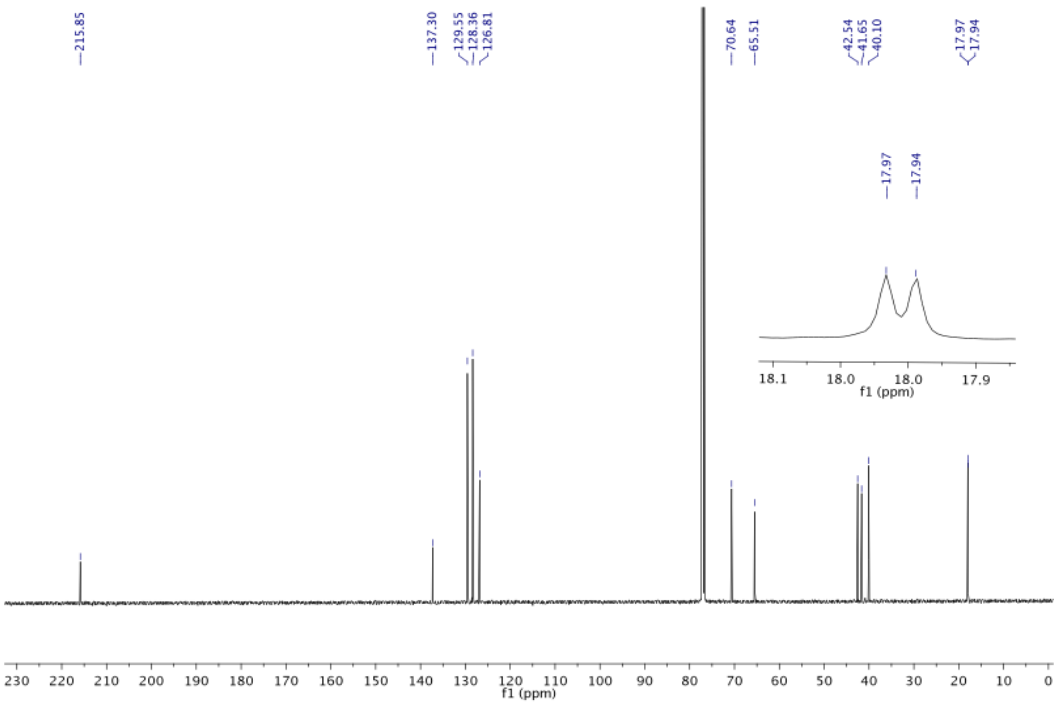


(5*R,6*S**)-6-Chloro-5-hydroxy-2-methyl-7-phenylheptan-3-one (14b)**

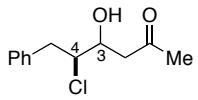


14a 3,4-*syn*
14b 3,4-*anti*

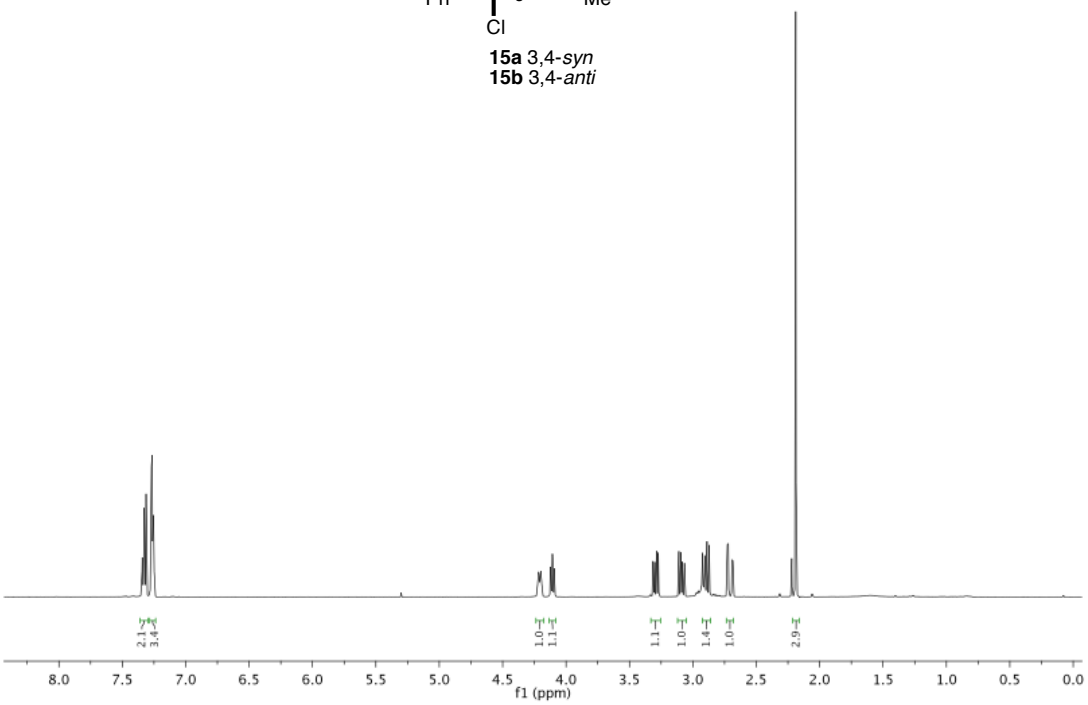


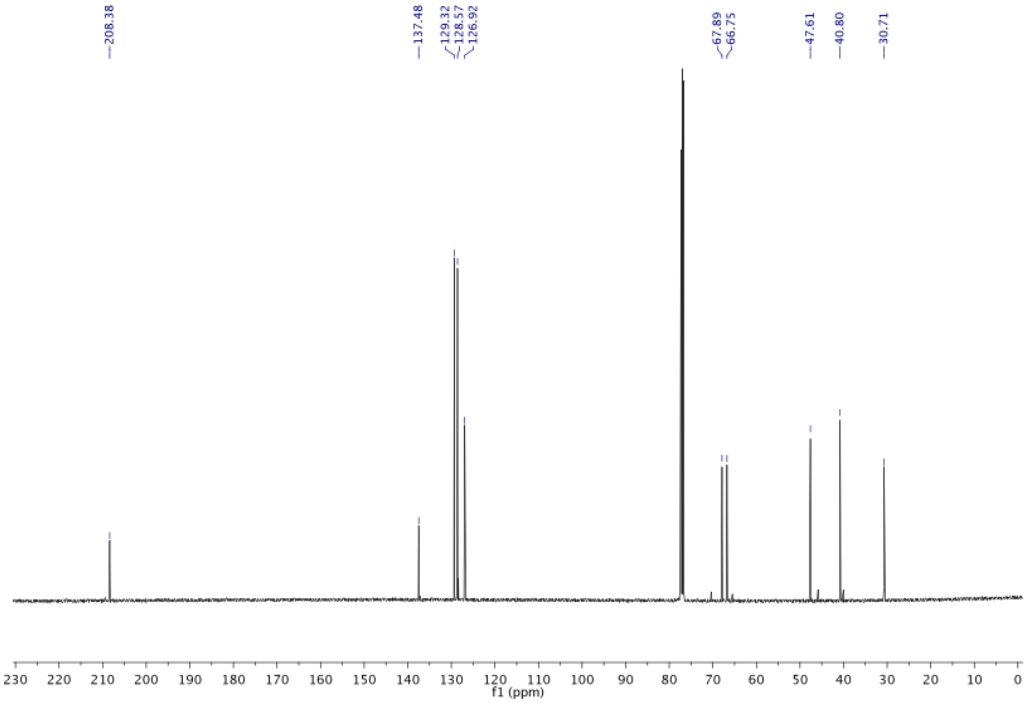


(5*S,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (15a)**

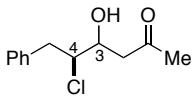


15a 3,4-*syn*
15b 3,4-*anti*

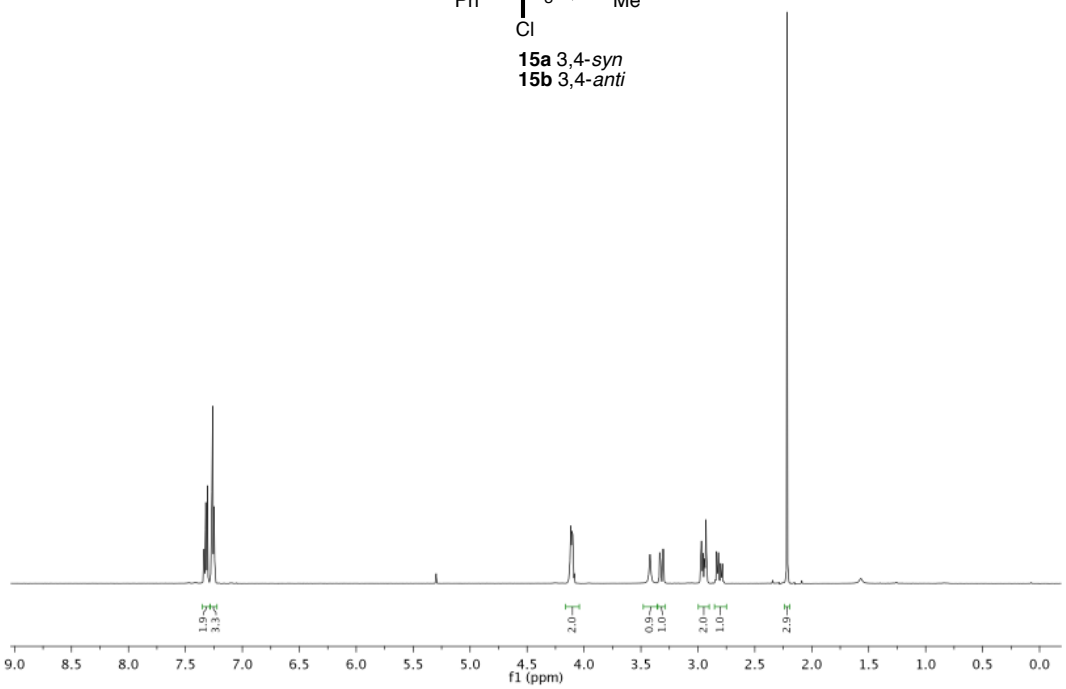


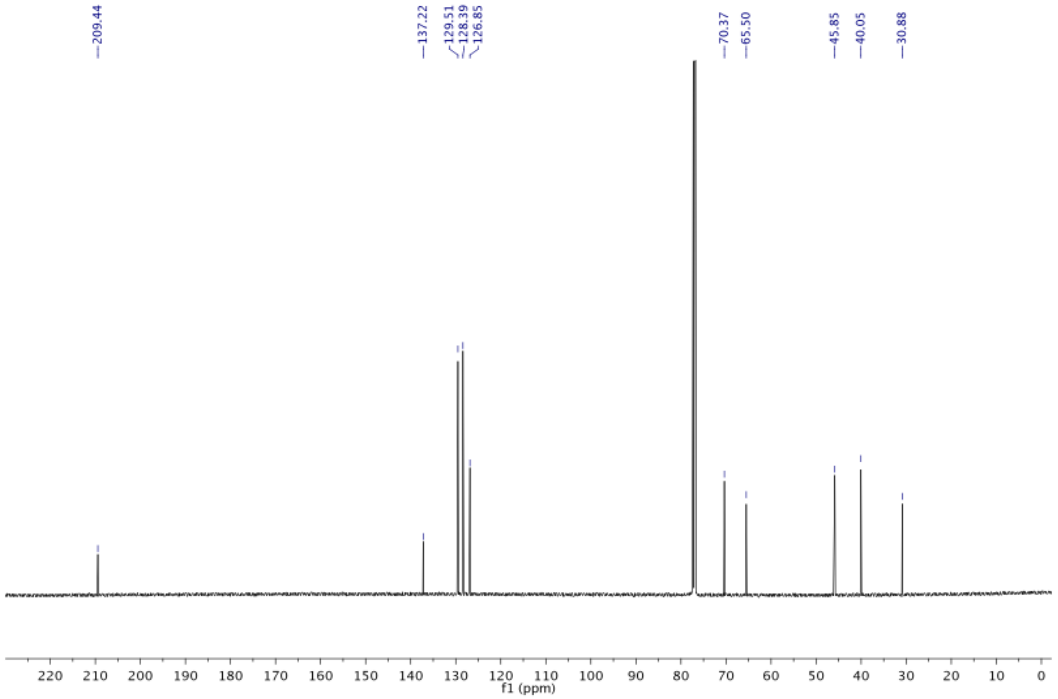


(5*R,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (15b)**

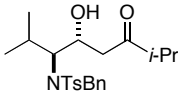


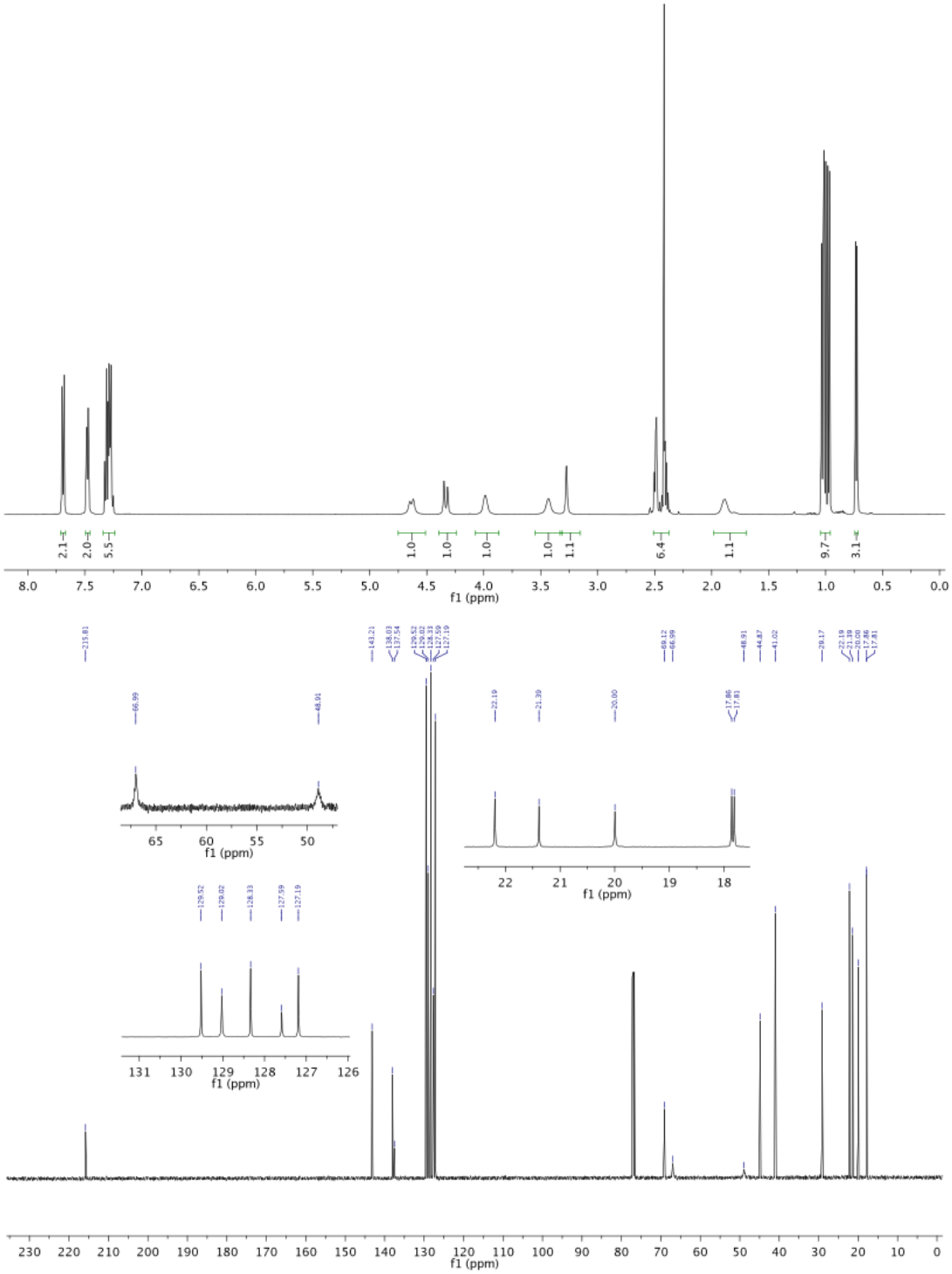
15a 3,4-*syn*
15b 3,4-*anti*



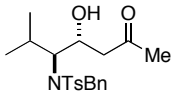


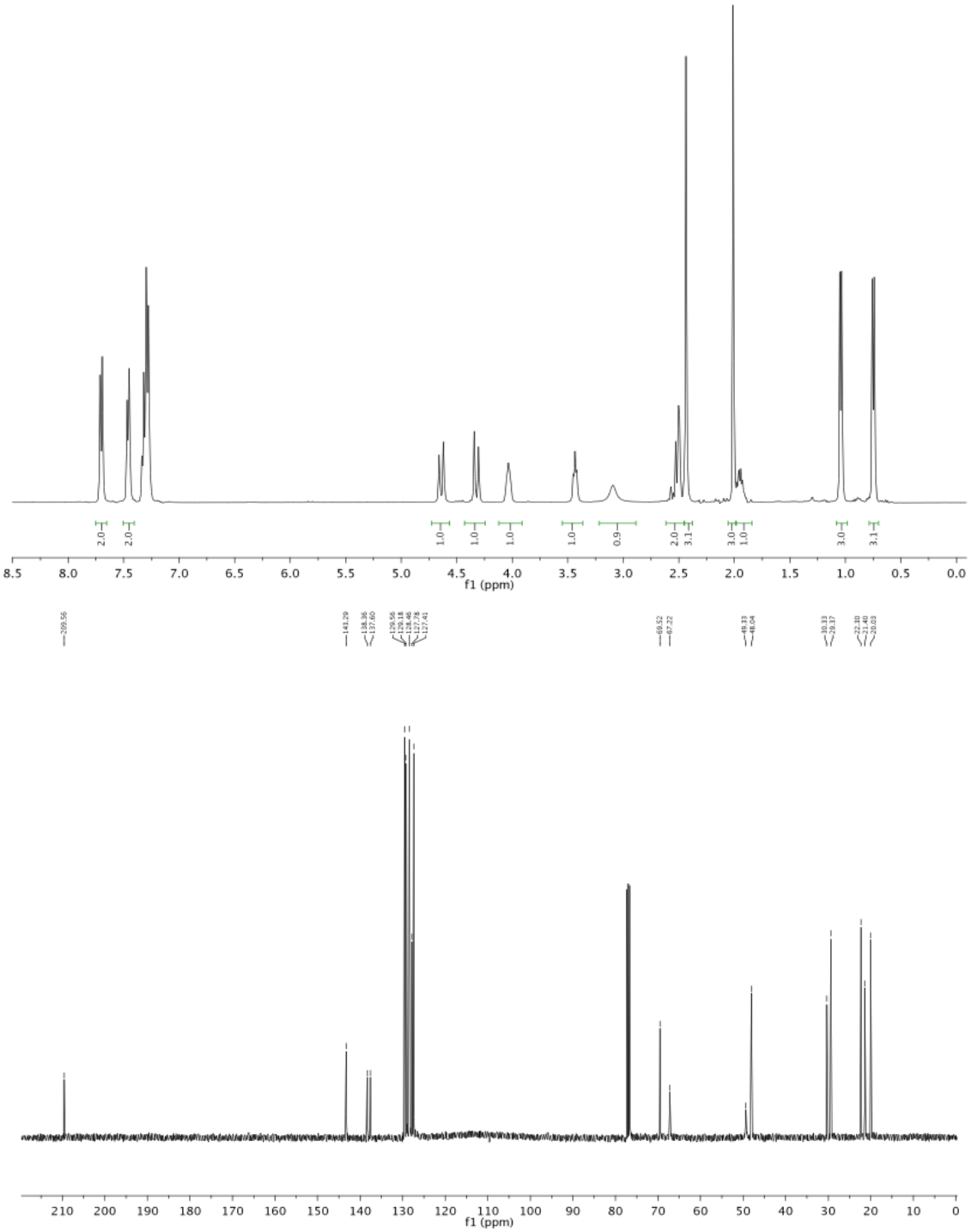
(5*R,6*S**)-6-(*N*-Benzyl-*N*-tosylamino)-5-hydroxy-2,7-dimethyloctan-3-one (20b)**



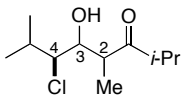


(4*R,5*S**)-5-(*N*-Benzyl-*N*-tosylamino)-4-hydroxy-6-methylheptan-2-one (21b)**

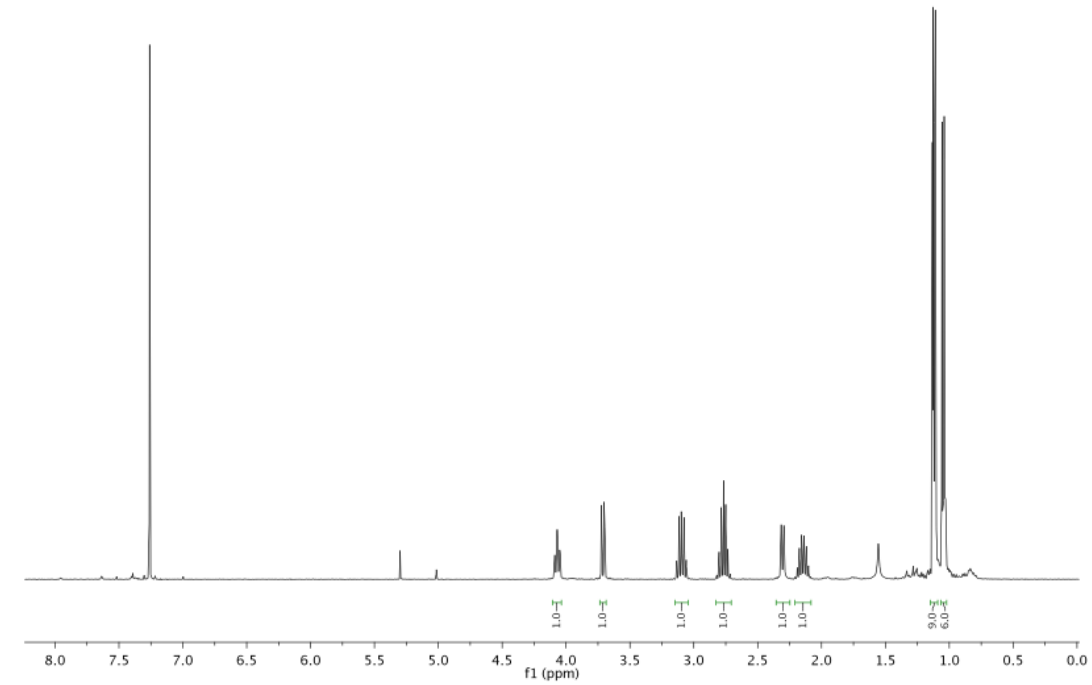


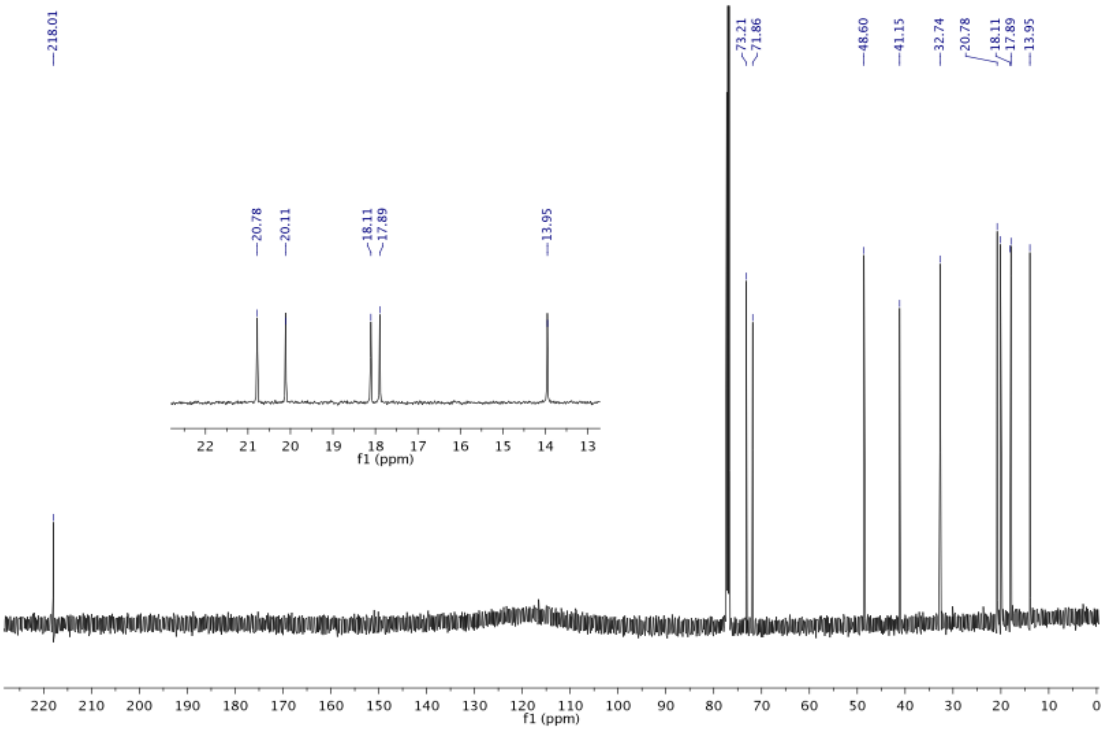


(4*R,5*S**)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (24a)**

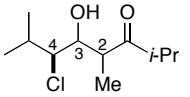


24a 2,3-*anti*, 3,4-*syn*
24b 2,3-*anti*, 3,4-*anti*

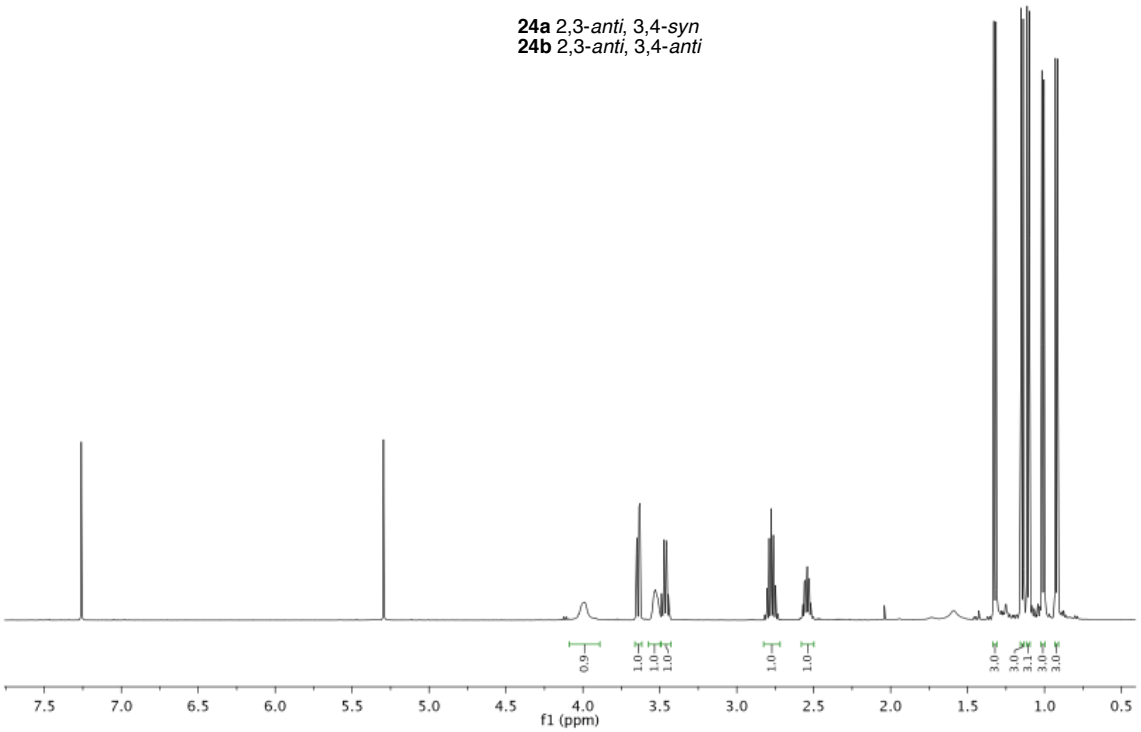


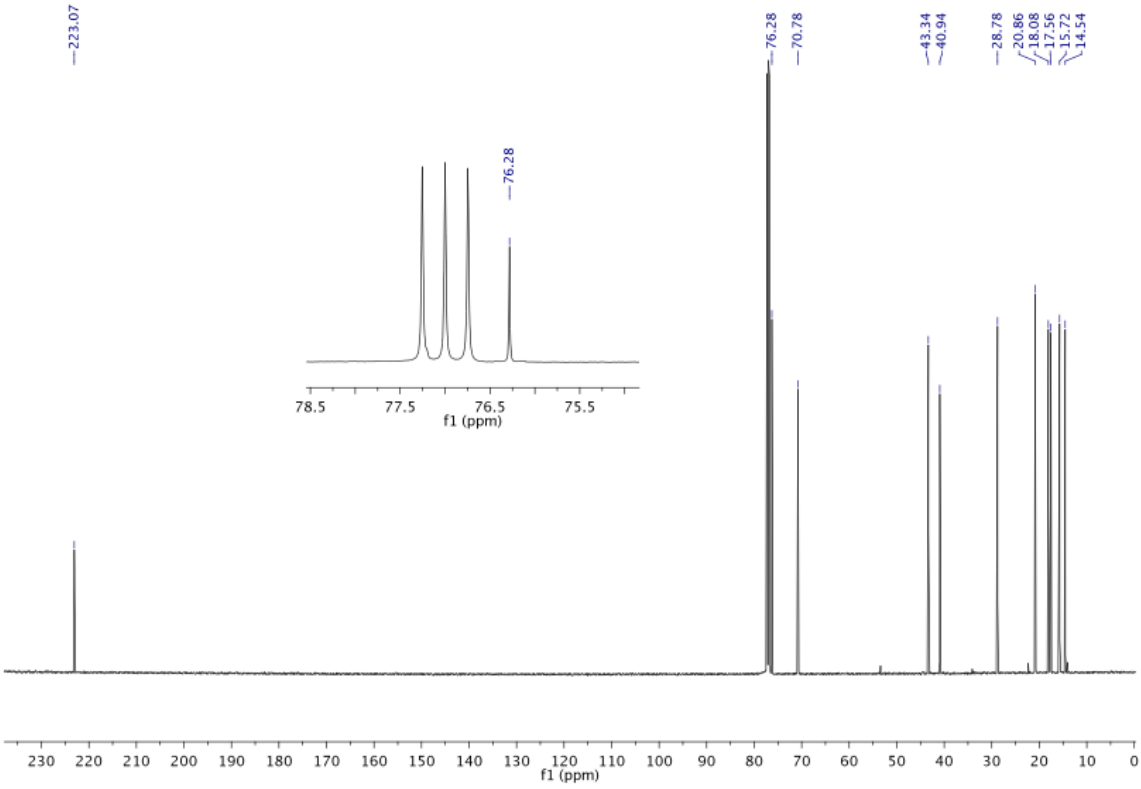


(4*S*,5R)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (24b)**

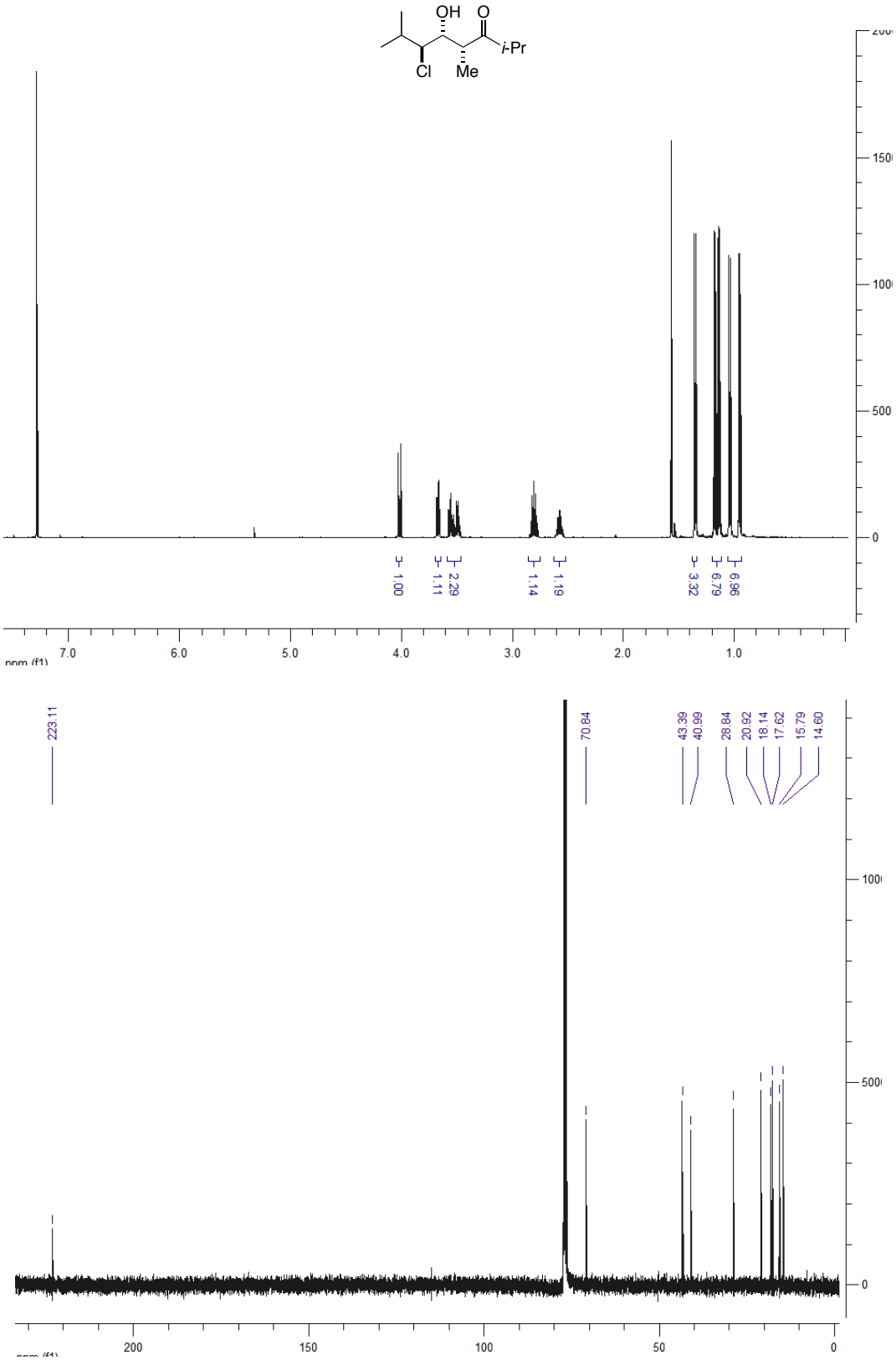


24a 2,3-*anti*, 3,4-*syn*
24b 2,3-*anti*, 3,4-*anti*

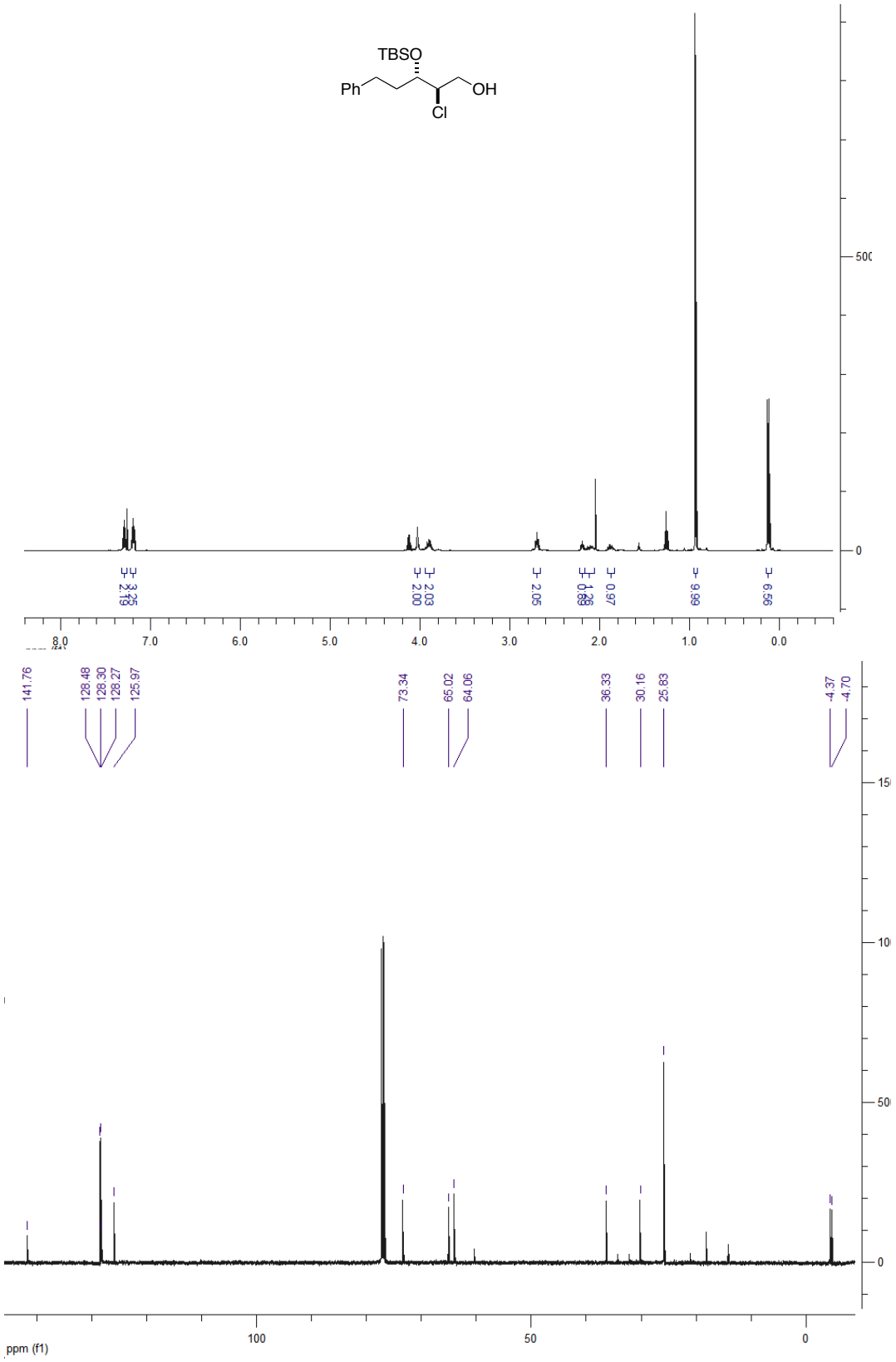




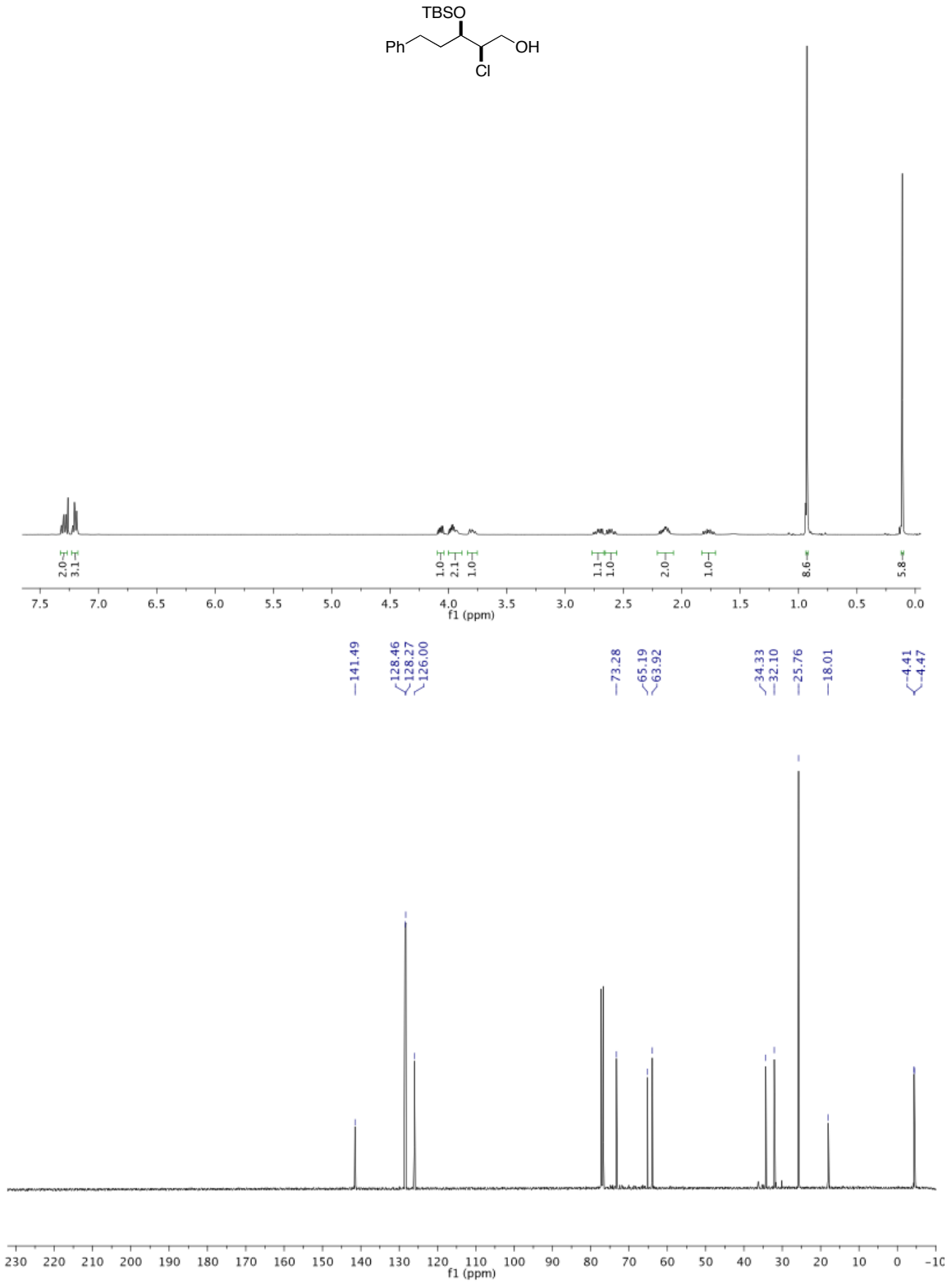
(4*R,5*R**,6*S**)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (25b)**



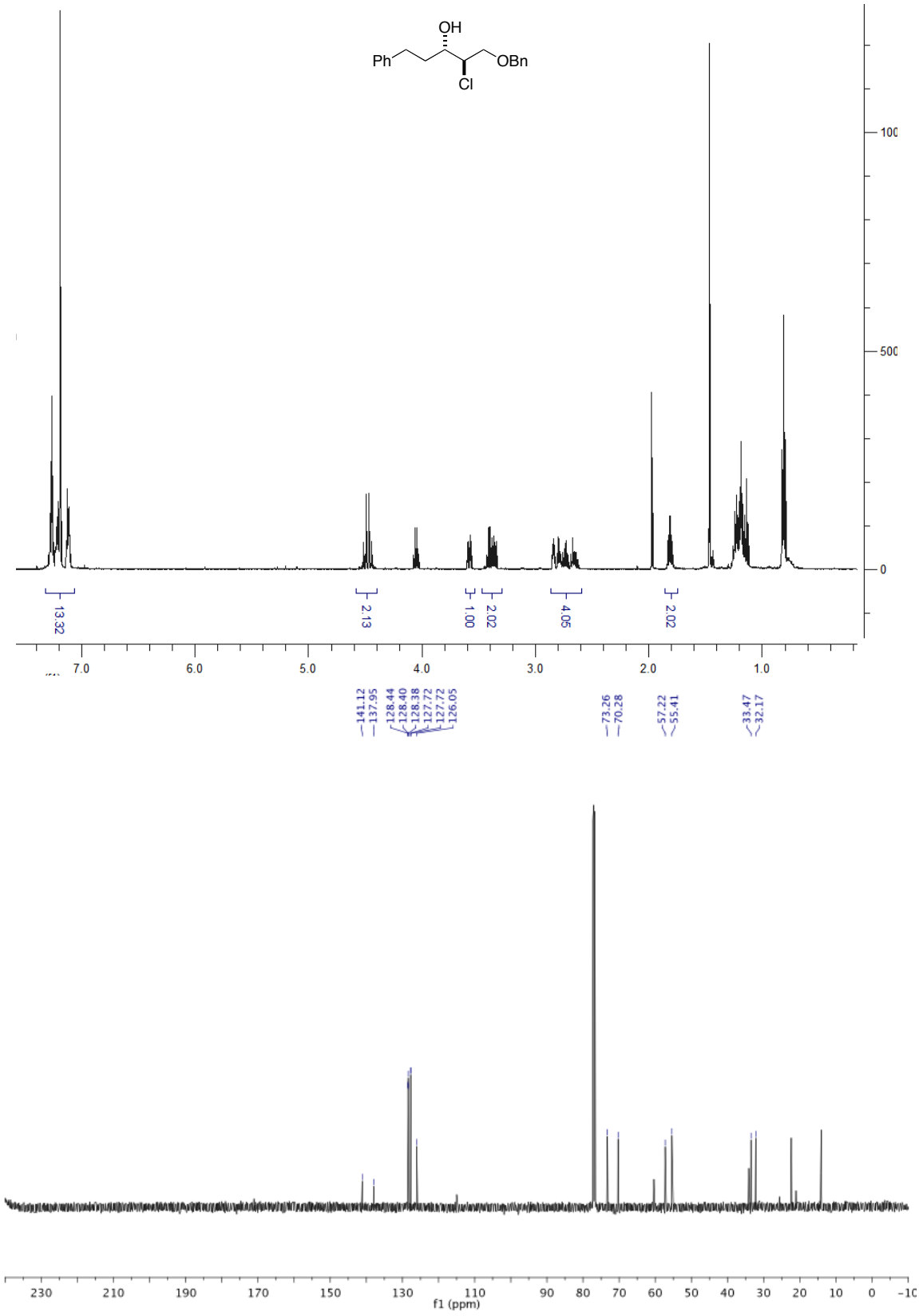
(2*S,3*S**)-3-(*tert*-Butyl)dimethylsilyloxy-2-chloro-5-phenylpentan-1-ol (34)**



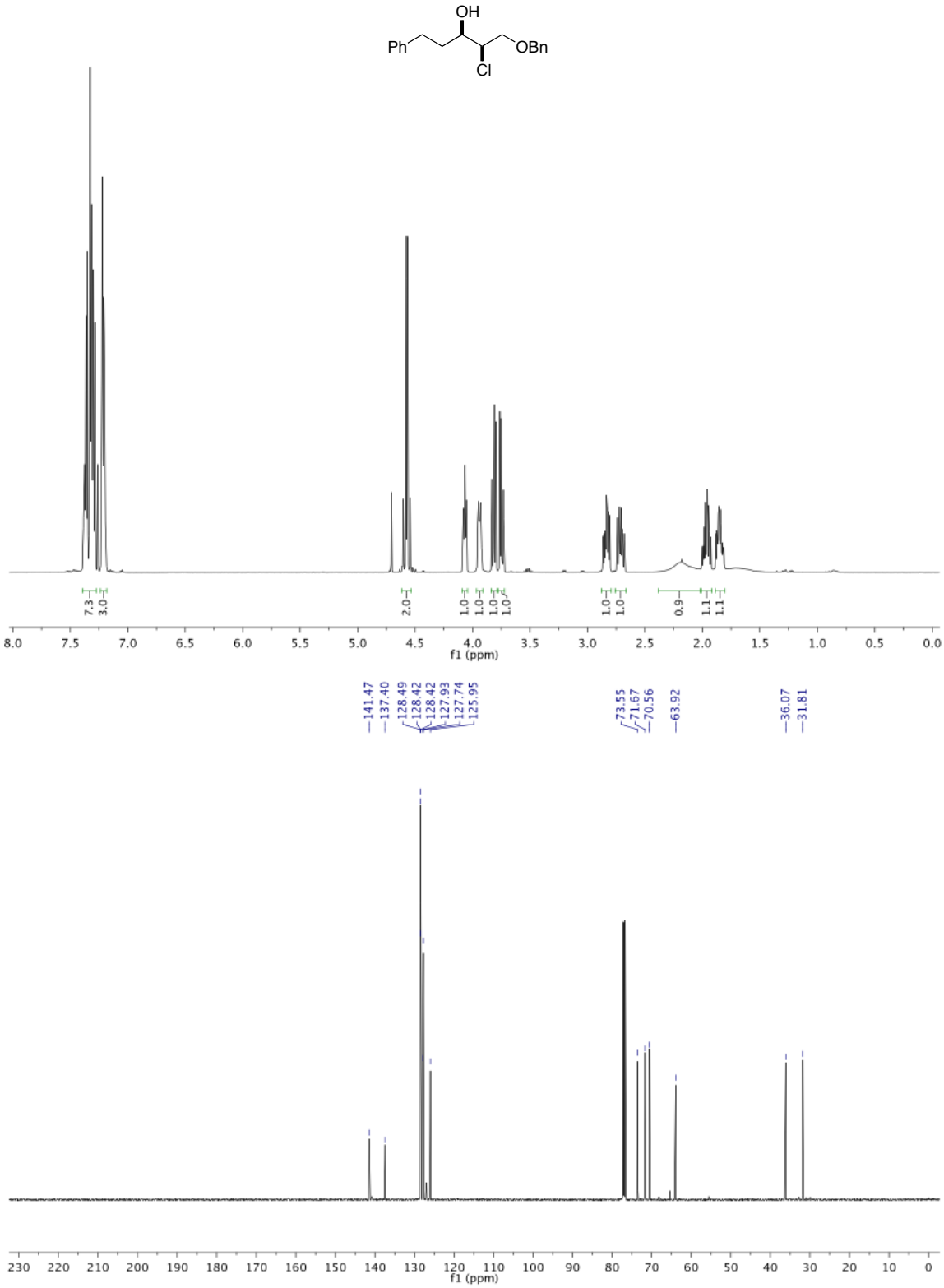
(2*S*,3R)-3-(*tert*-Butyl)dimethylsilyloxy-2-chloro-5-phenylpentan-1-ol (35)**



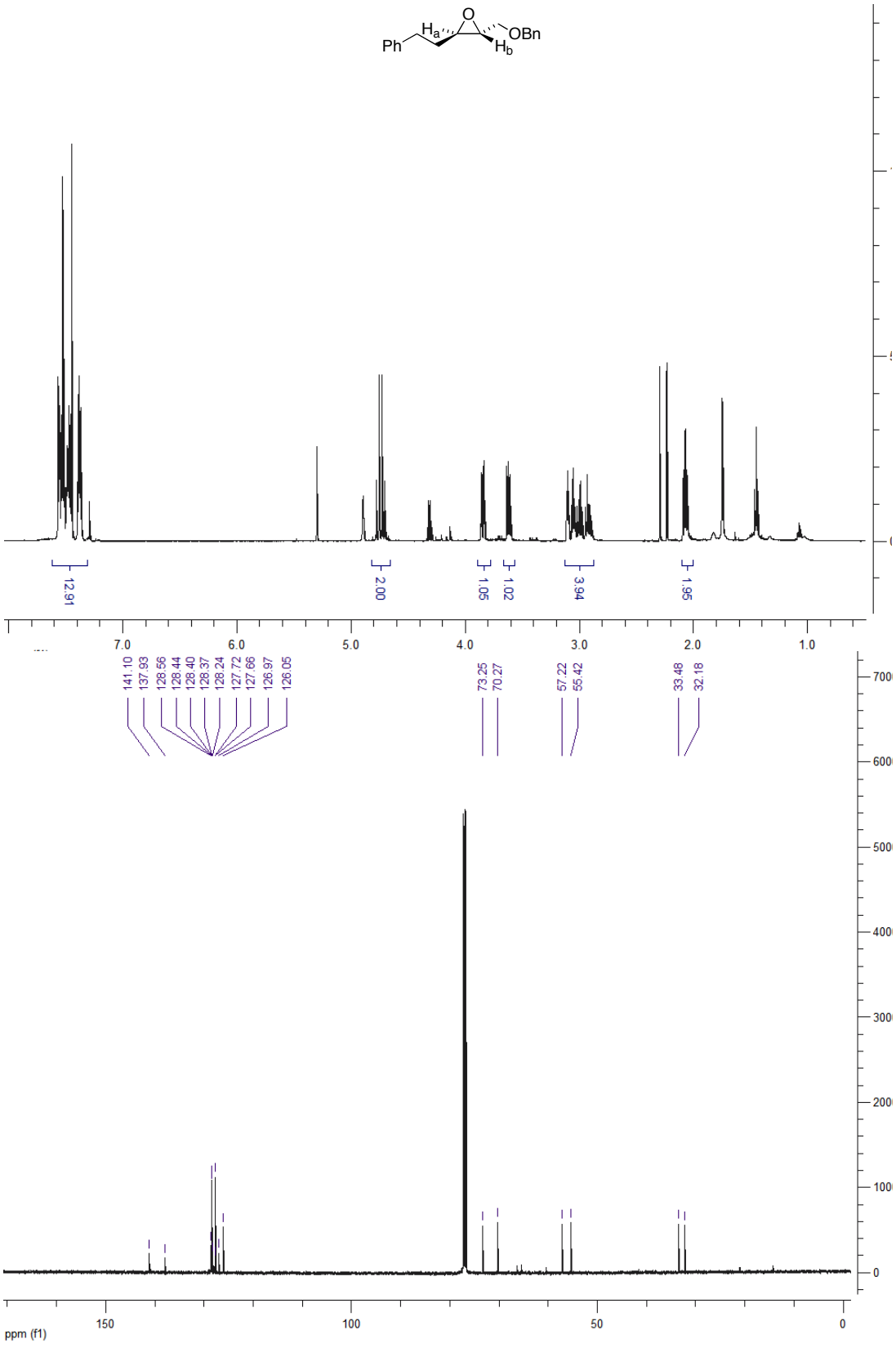
(2*R,3*S**)-1-(Benzyloxy)-2-chloro-5-phenylpentan-3-ol (38)**



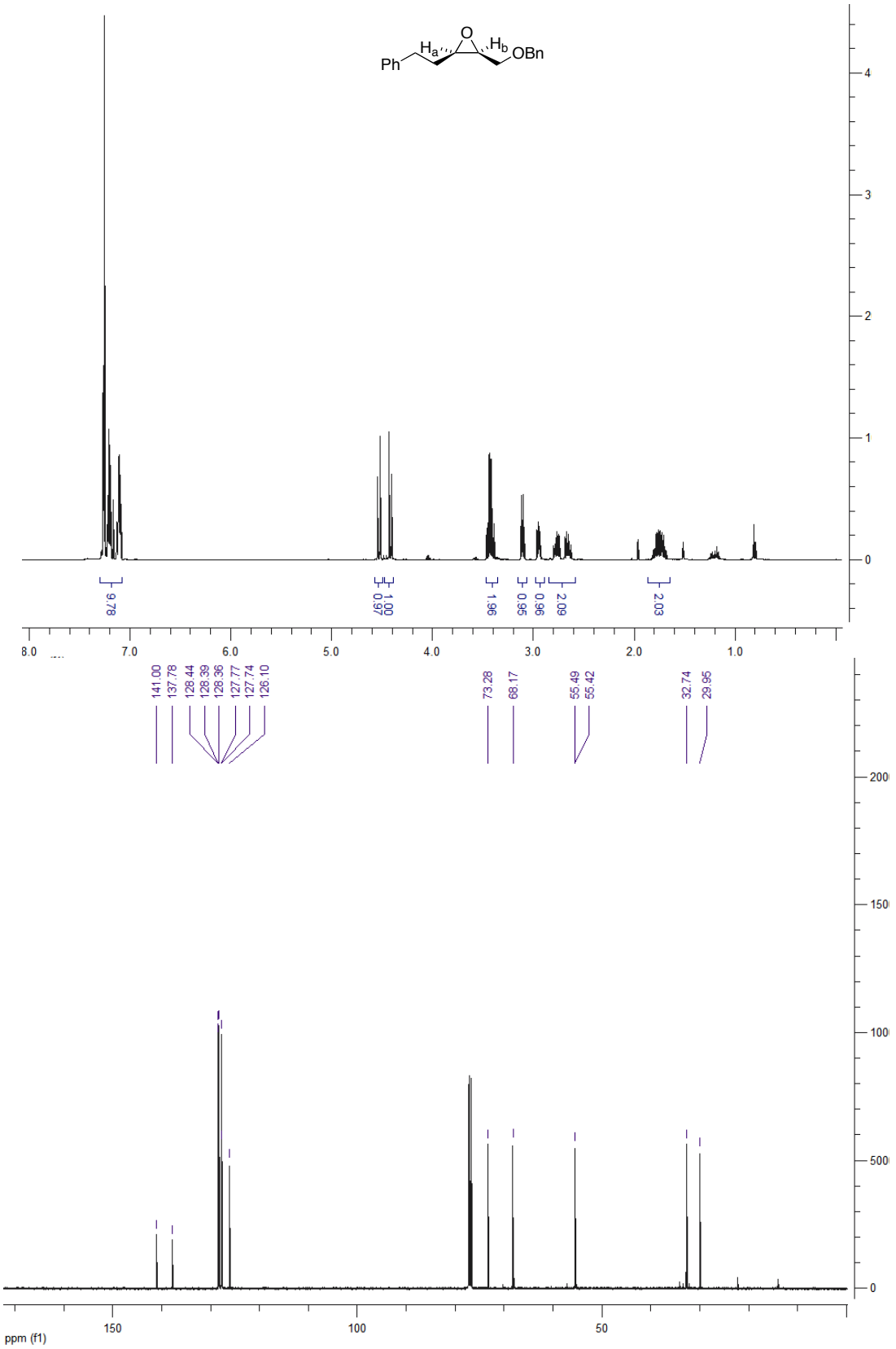
(2*R,3*R**)-1-(Benzyloxy)-2-chloro-5-phenylpentan-3-ol (39)**



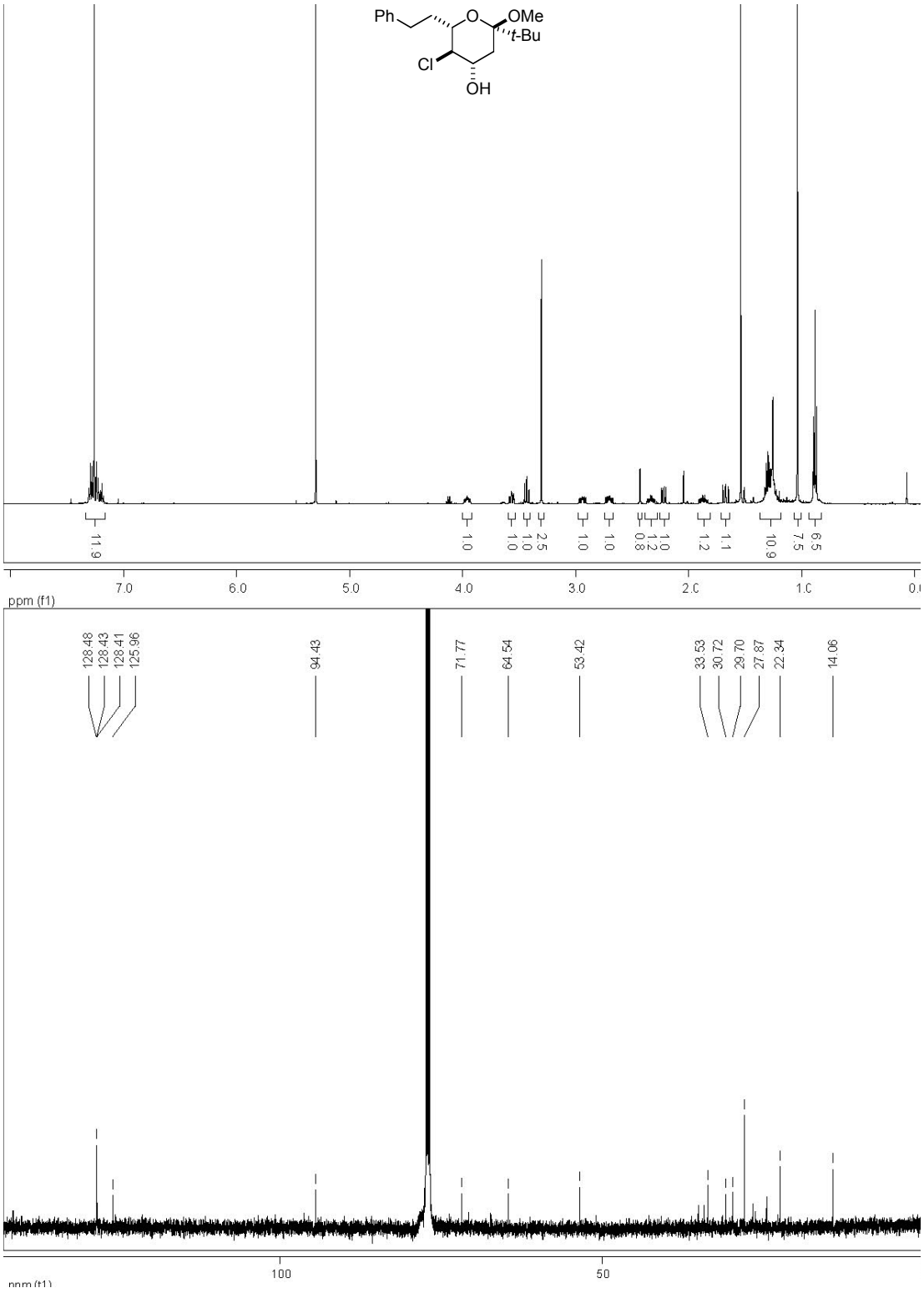
(2*R,3*R**)-2-((Benzyloxy)methyl)-3-phenethyloxirane (40)**



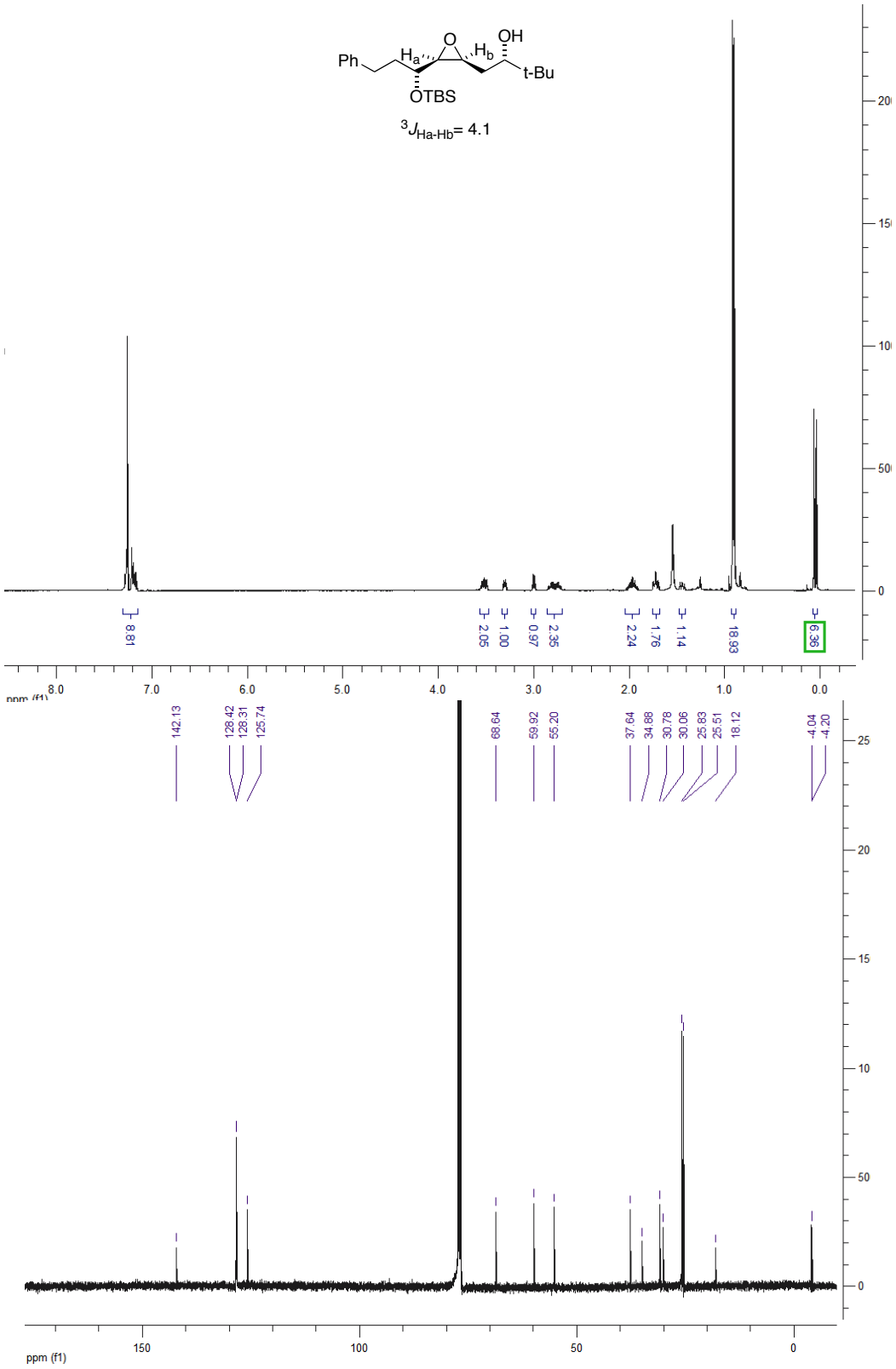
(2*S*,3R)-2-((Benzyloxy)methyl)-3-phenethyloxirane (41)**



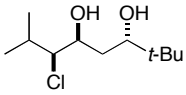
(2*S,4*S**,5*R**,6*S**)-2-*tert*-Butyl-5-chloro-tetrahydro-2-methoxy-6-phenethyl-2H-pyran-4-ol (43)**

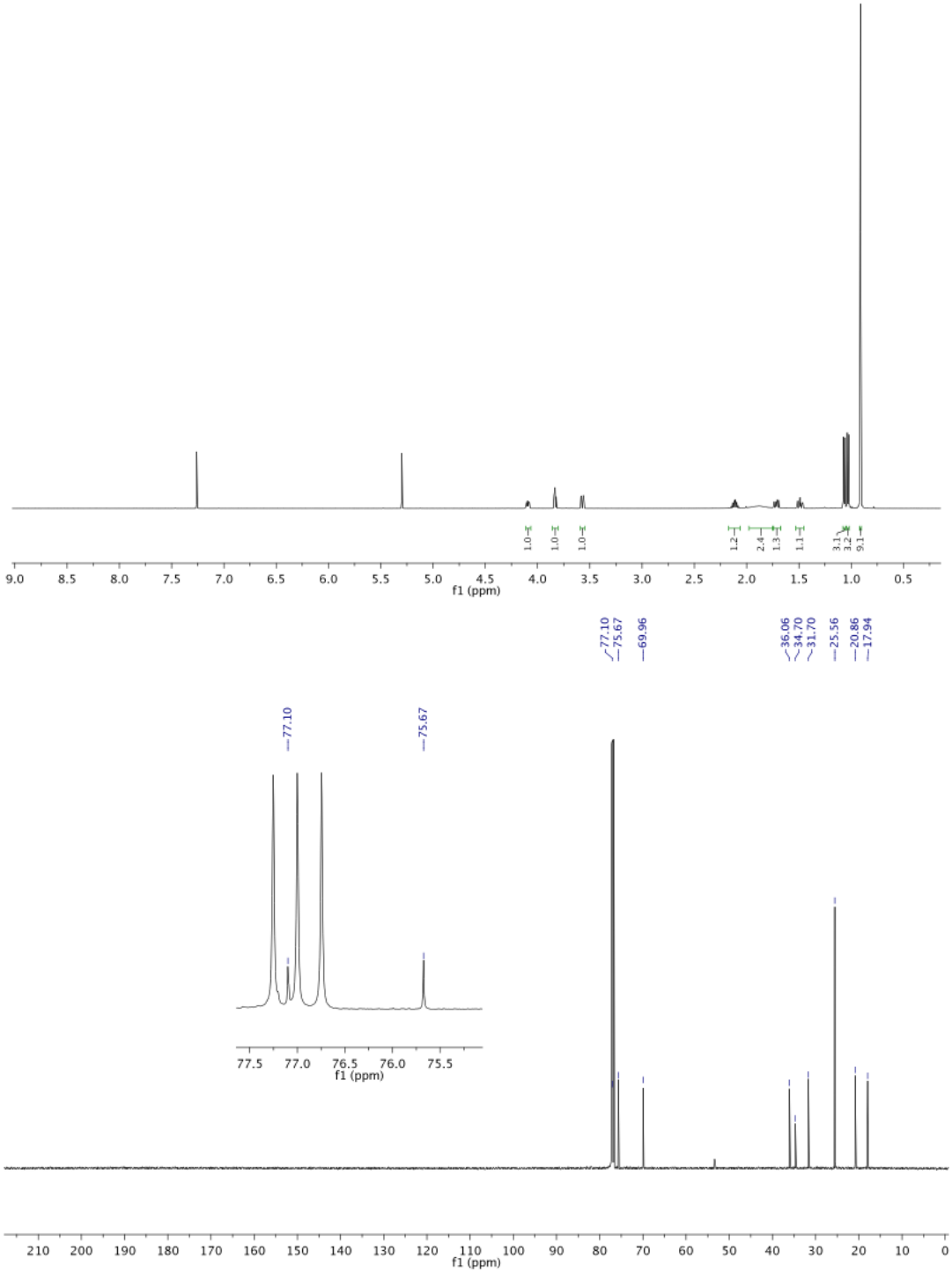


(*R)-1-((2*S**,3*R**)-3-((*R**)-1-((*tert*-Butyl)dimethylsilyloxy)-3-phenylpropyl)oxiran-2-yl)-3,3-dimethylbutan-2-ol (45)**

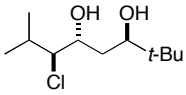


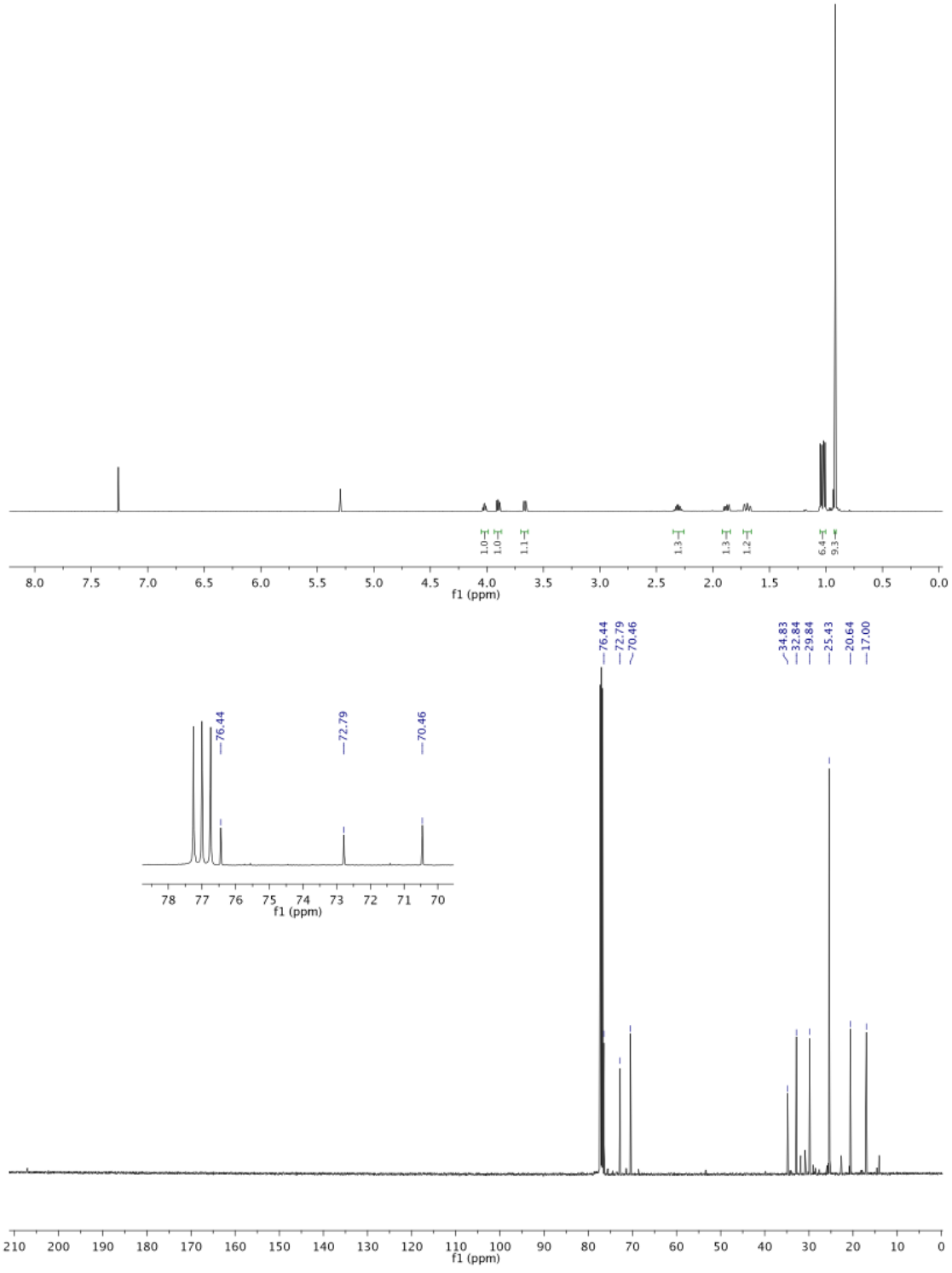
(3*S,5*S**,6*S**)-6-Chloro-2,2,7-trimethyloctane-3,5-diol (46a)**



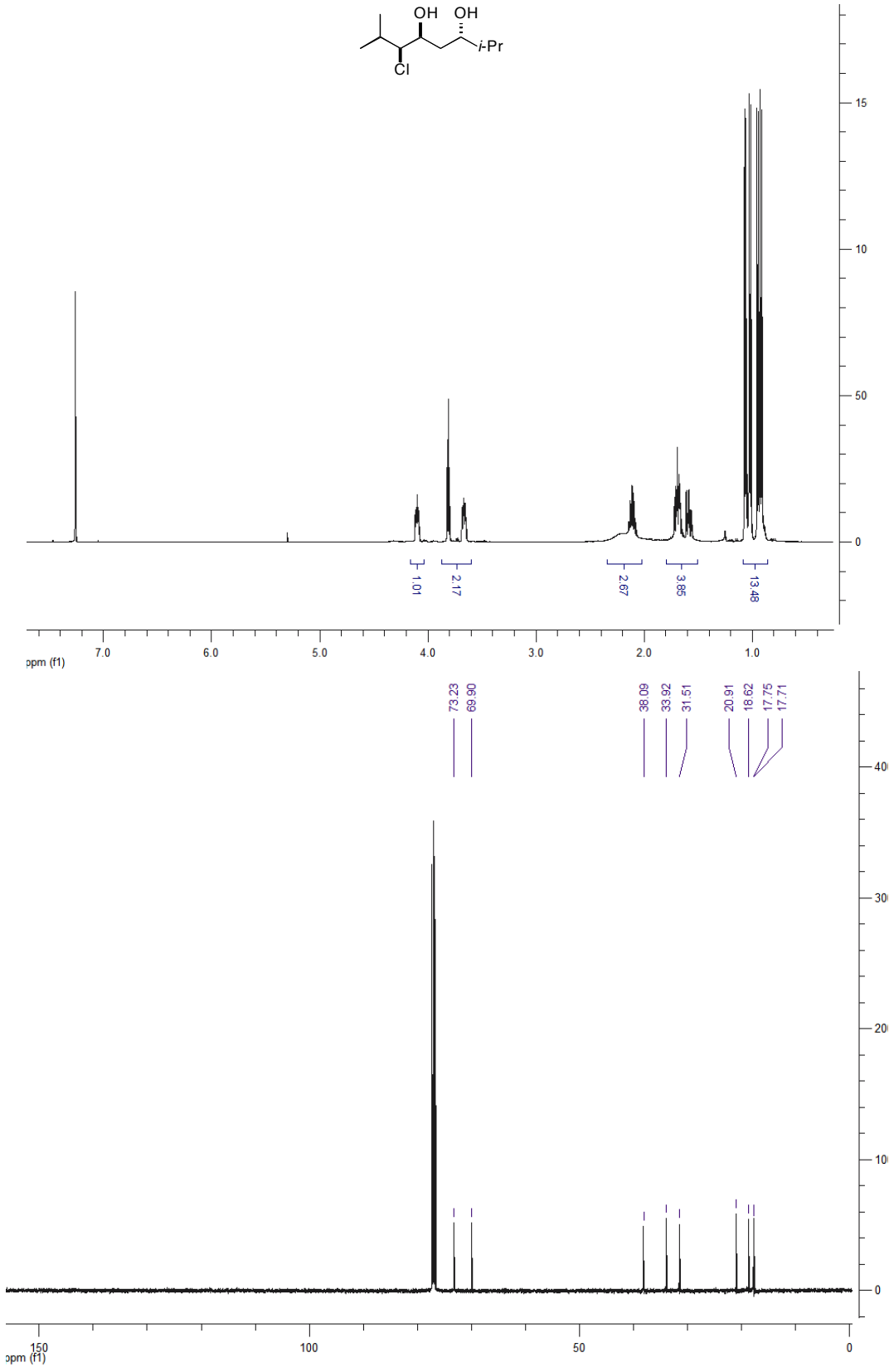


(3*R,5*R**,6*S**)-6-Chloro-2,2,7-trimethyloctane-3,5-diol (46b)**

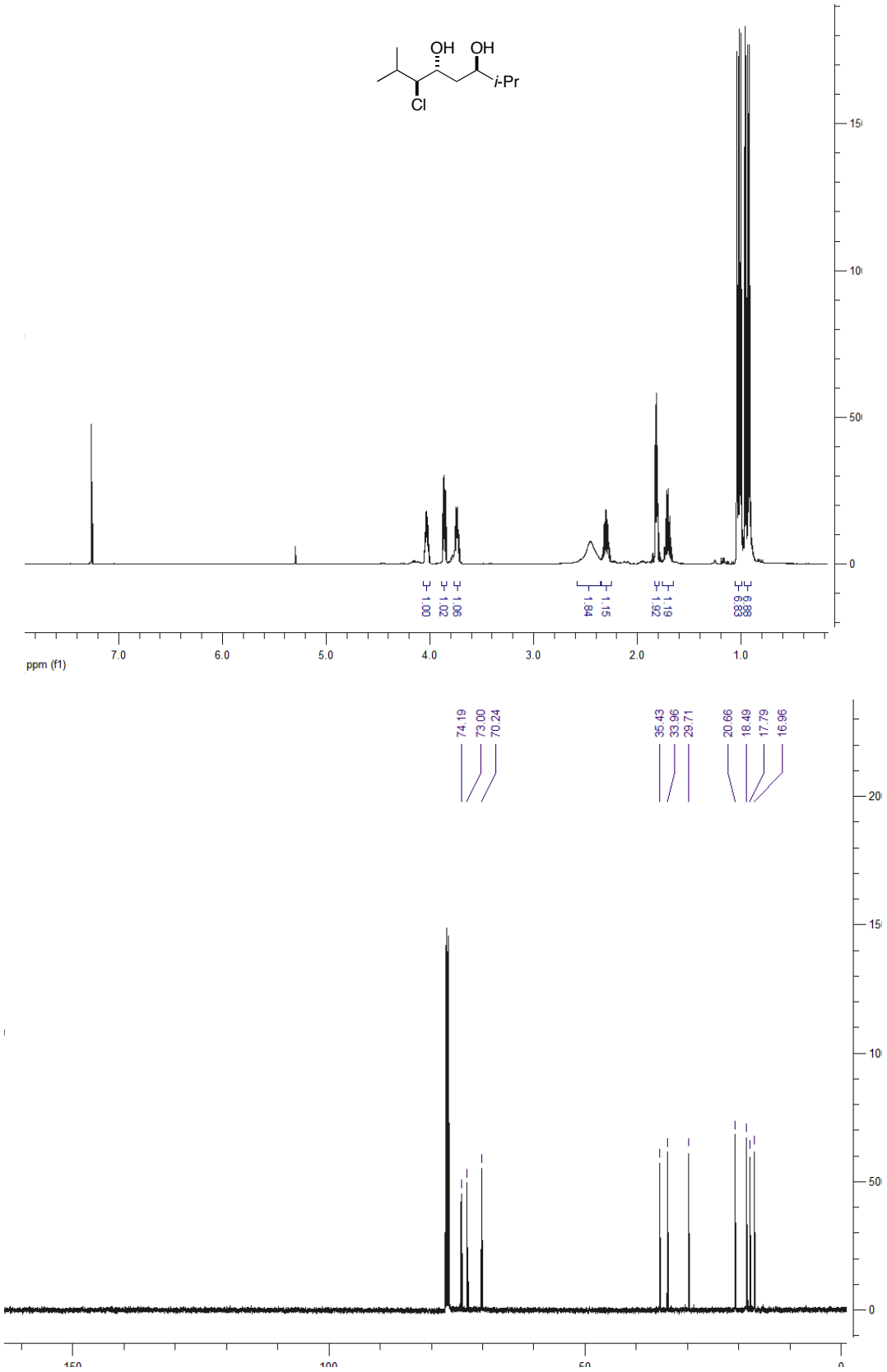




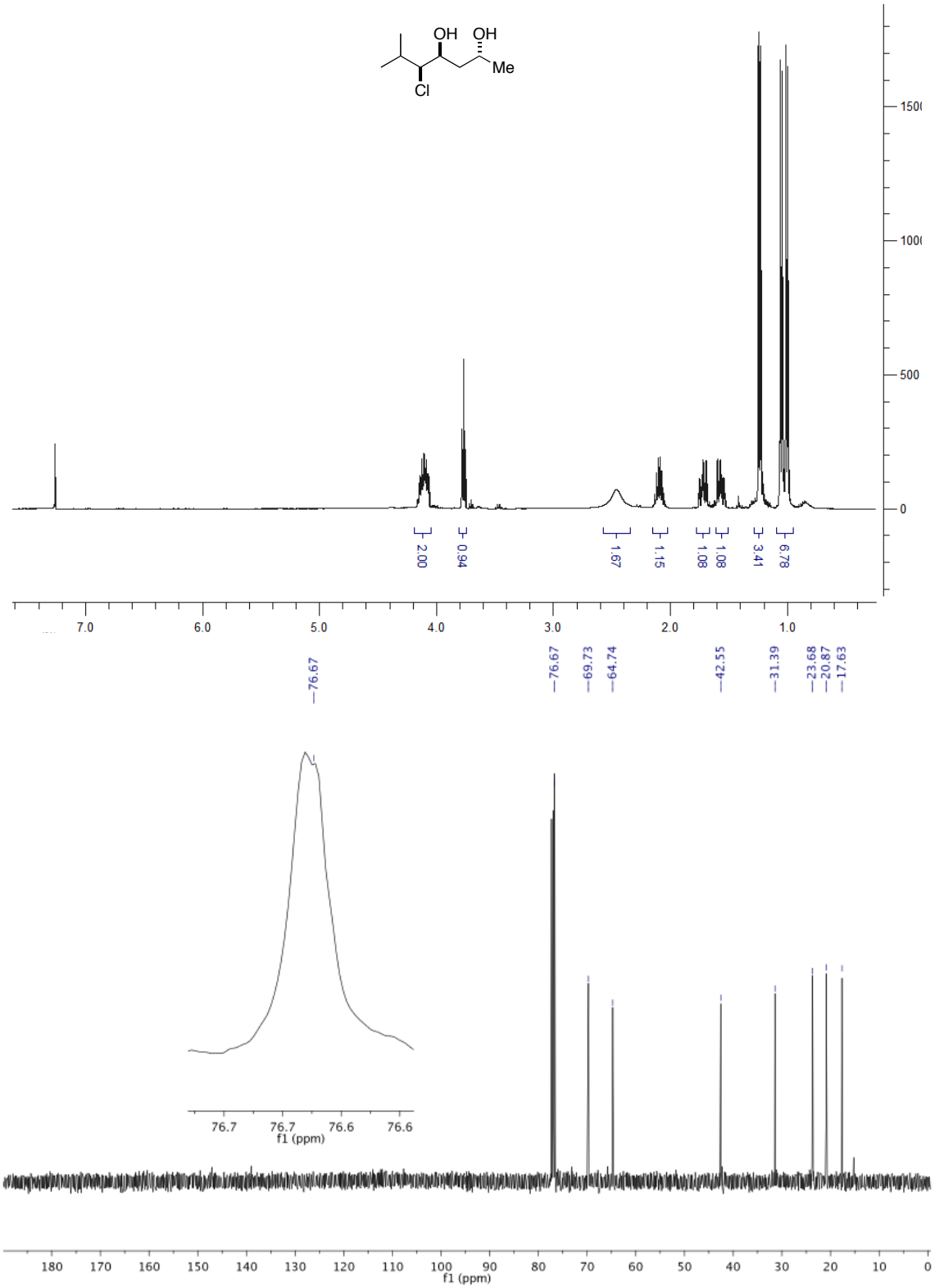
(3*S,5*S**,6*S**)-6-Chloro-2,7-dimethyloctane-3,5-diol (47a)**



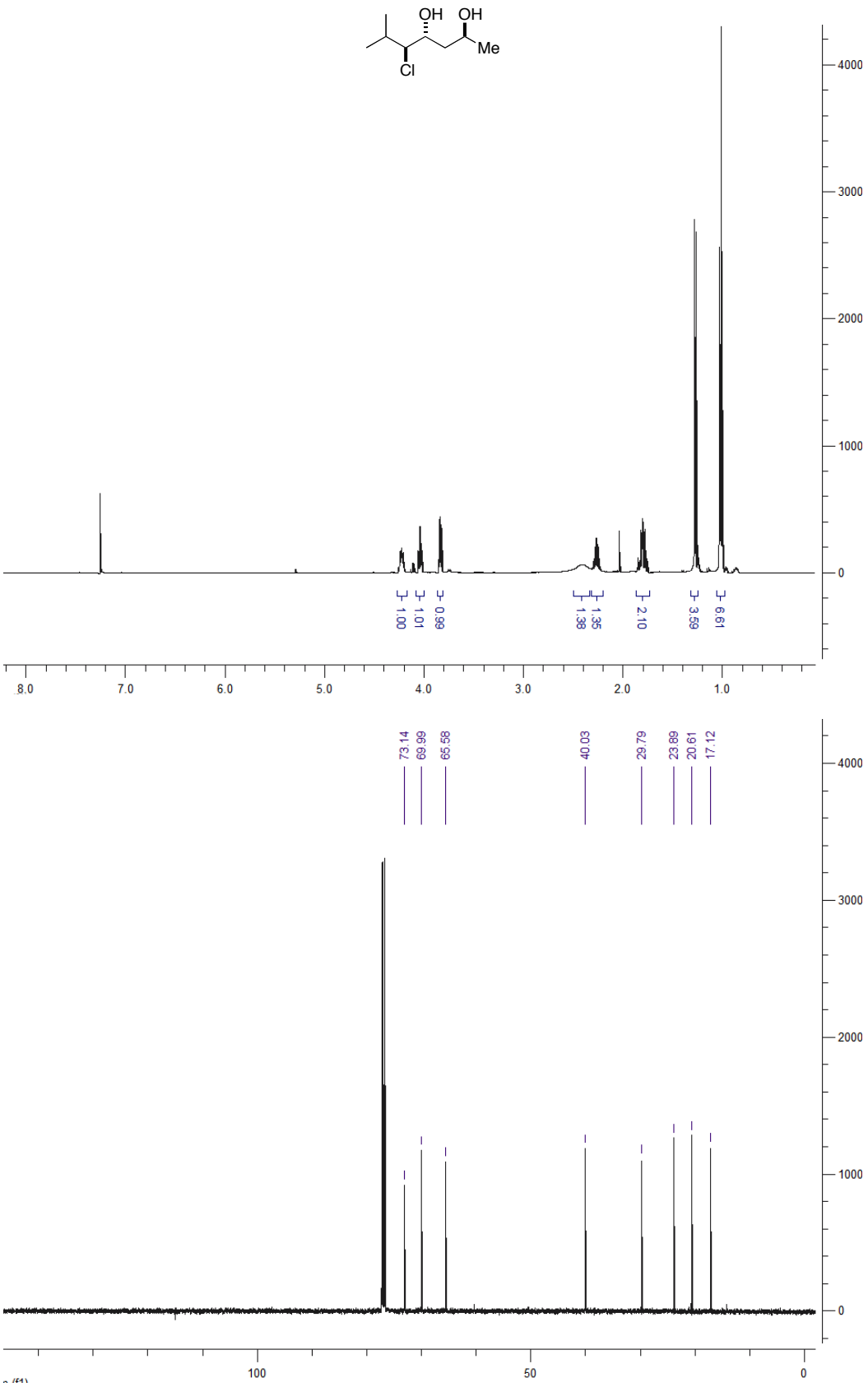
(3*R,5*R**,6*S**)-6-Chloro-2,7-dimethyloctane-3,5-diol (47b)**



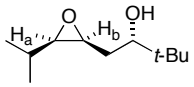
(2*R*,4S*,5S)-5-Chloro-6-methylheptane-2,4-diol (48a)**



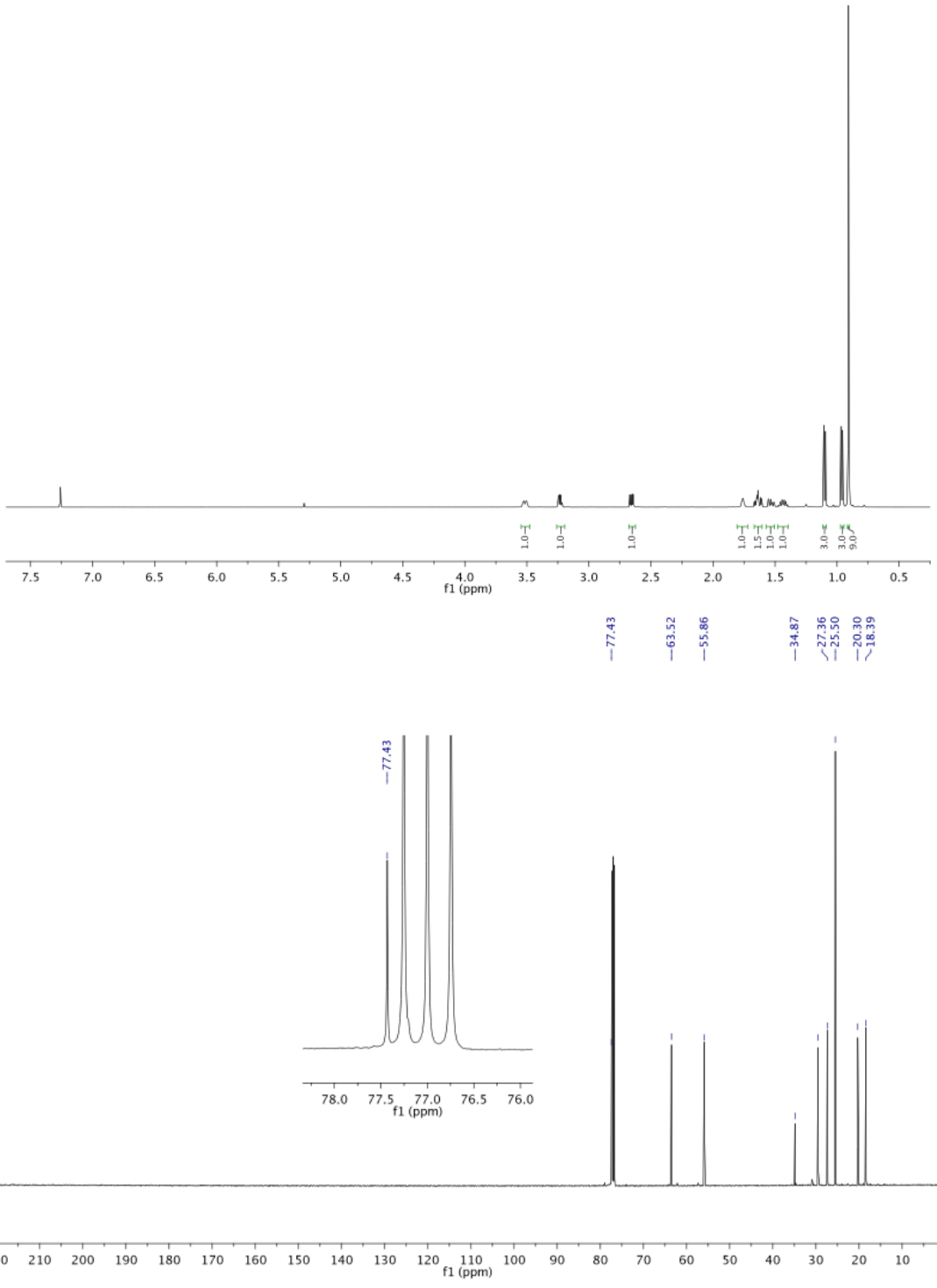
(2*S,4*R**,5*S**)-5-Chloro-6-methylheptane-2,4-diol (48b)**



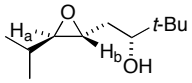
(*S)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)-3,3-dimethylbutan-2-ol (49a)**



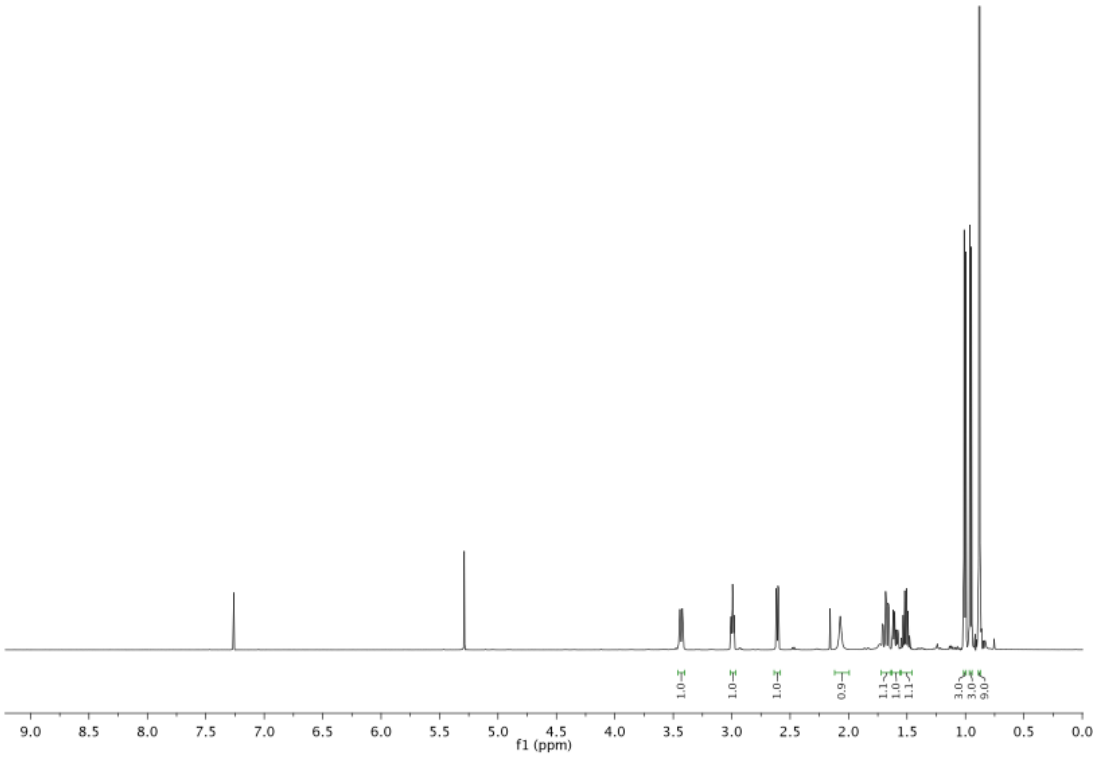
$^3J_{Ha\text{-}Hb}$ = 4.3 Hz

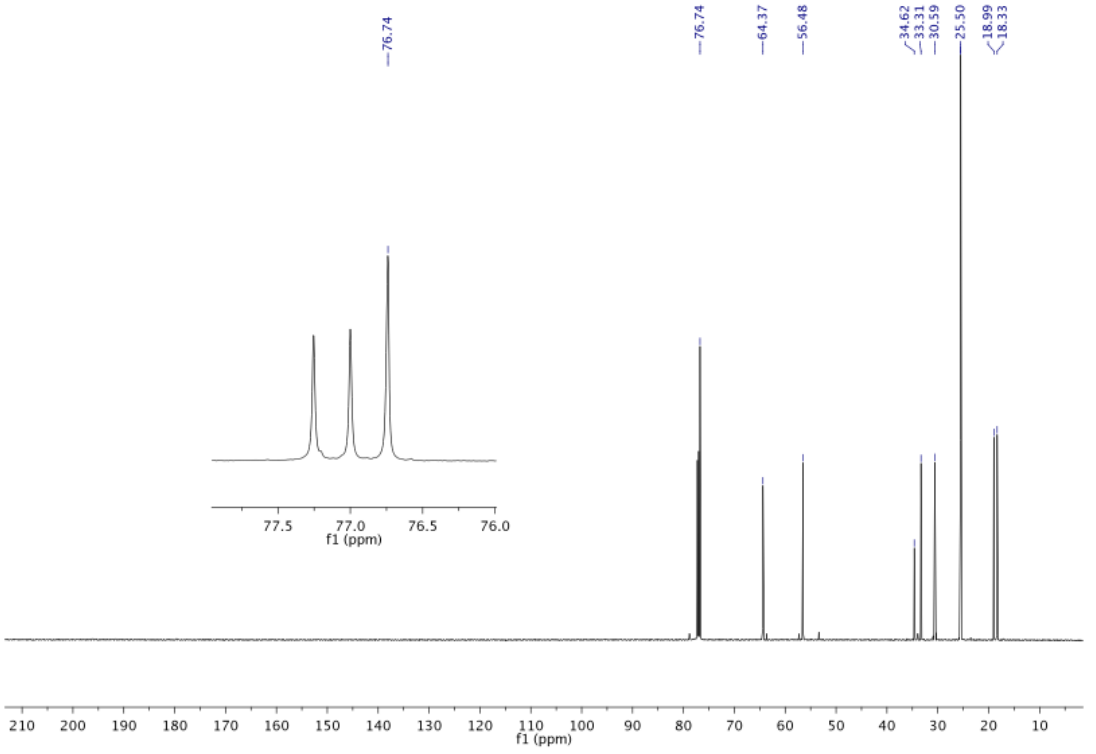


(*R)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)-3,3-dimethylbutan-2-ol (49b)**

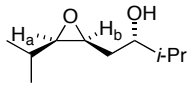


$^{3}J_{Ha\text{-}Hb}$ = 2.3 Hz

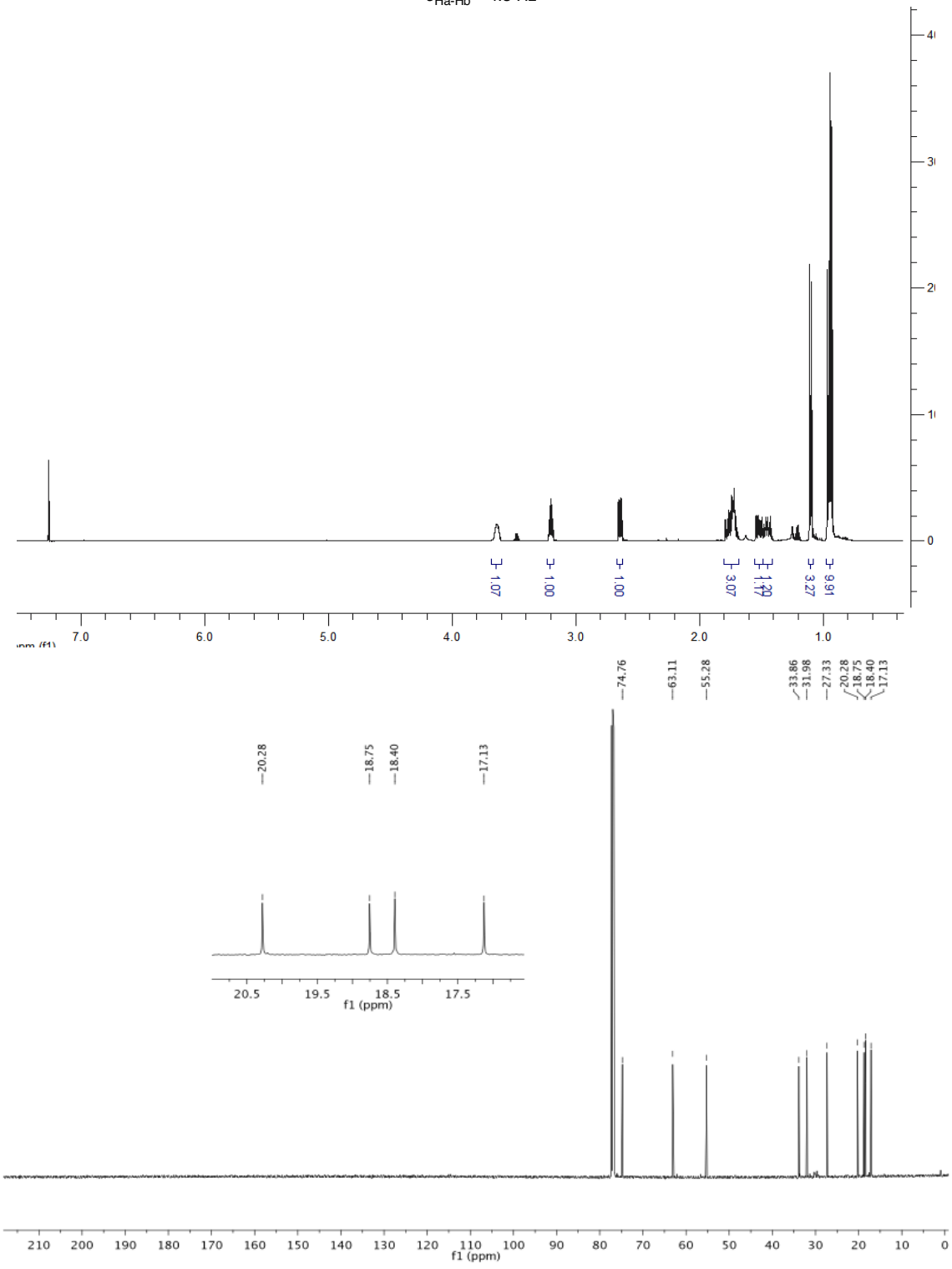




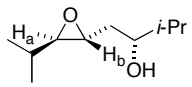
(*S)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)-3-methylbutan-2-ol (50a)**



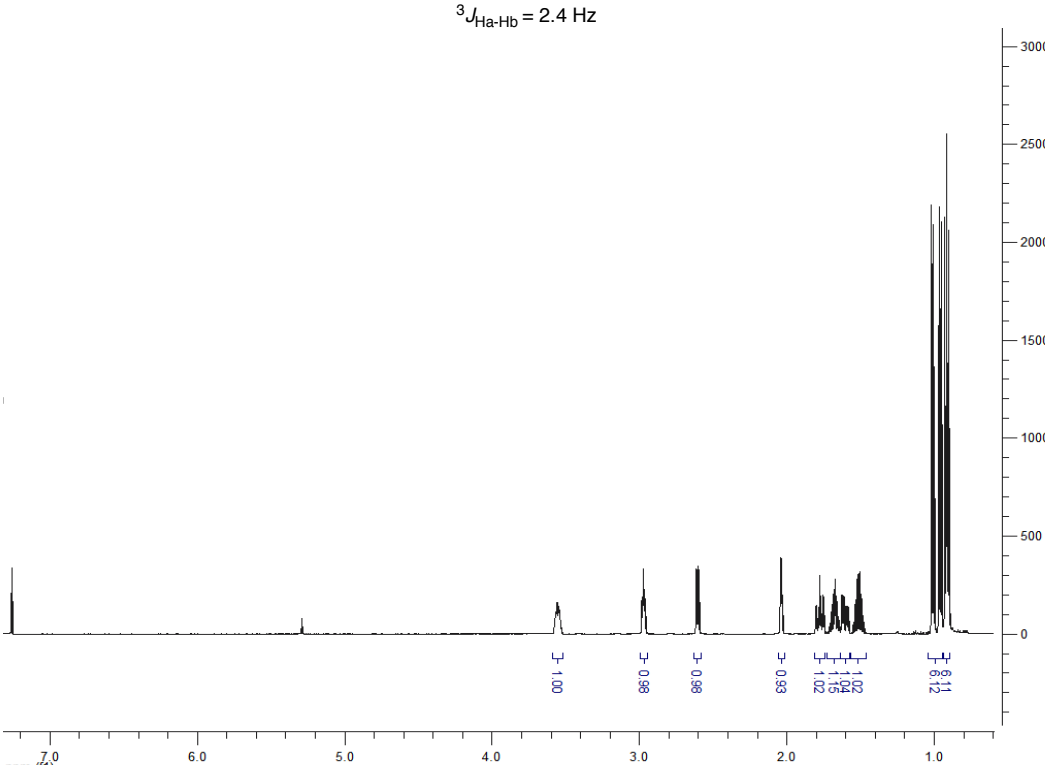
$^3J_{Ha\text{-}Hb}$ = 4.3 Hz

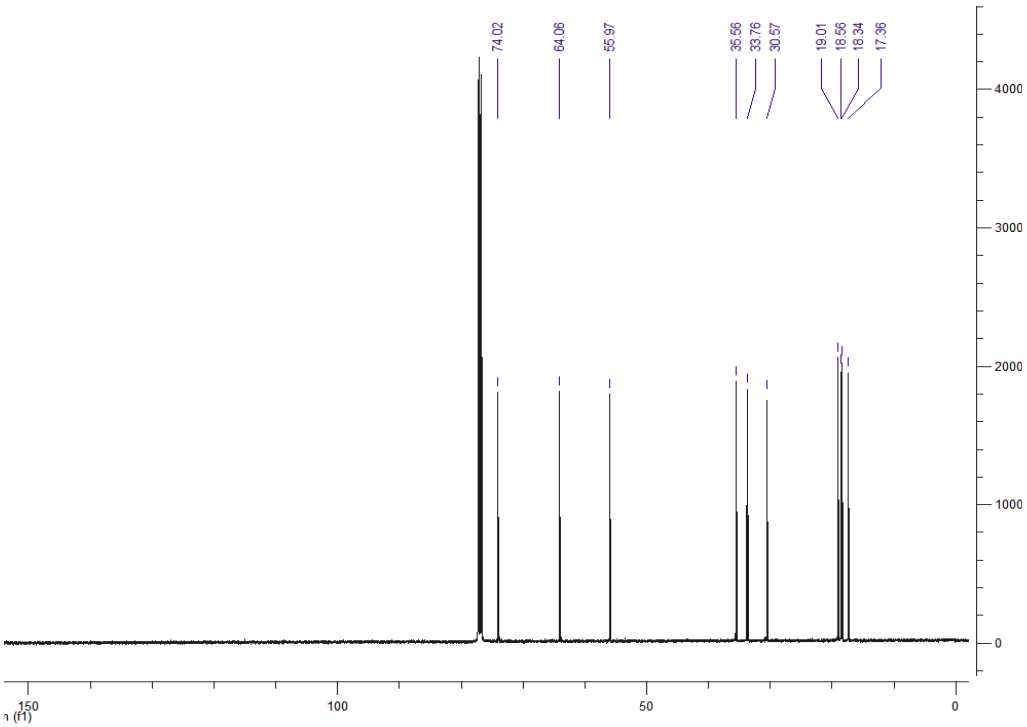


(*R)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)-3-methylbutan-2-ol (50b)**

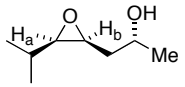


$^{3}J_{Ha\text{-}Hb}$ = 2.4 Hz

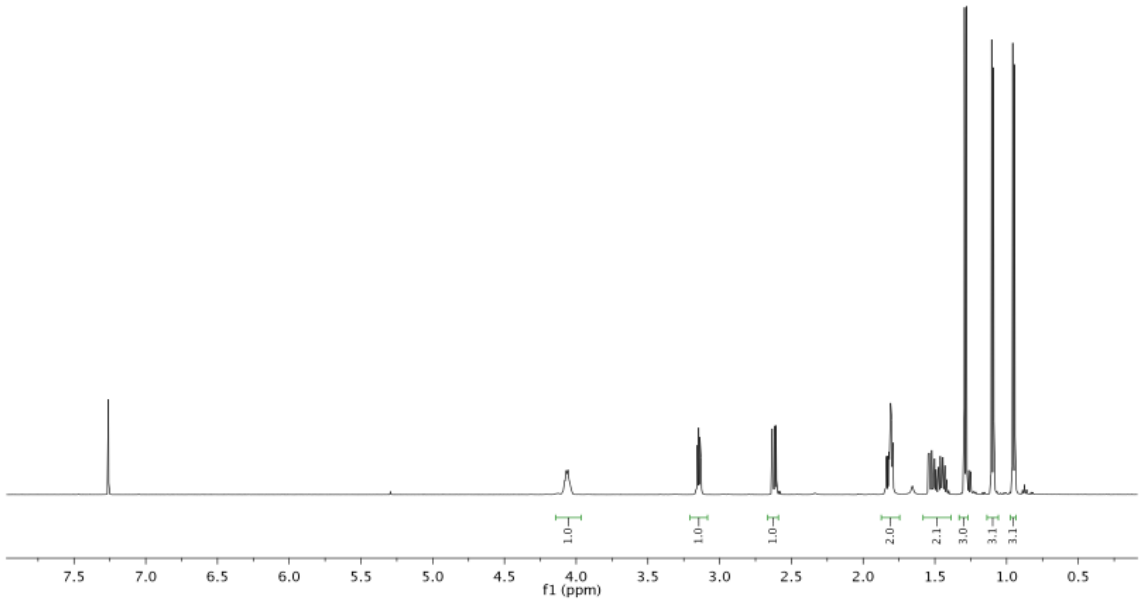


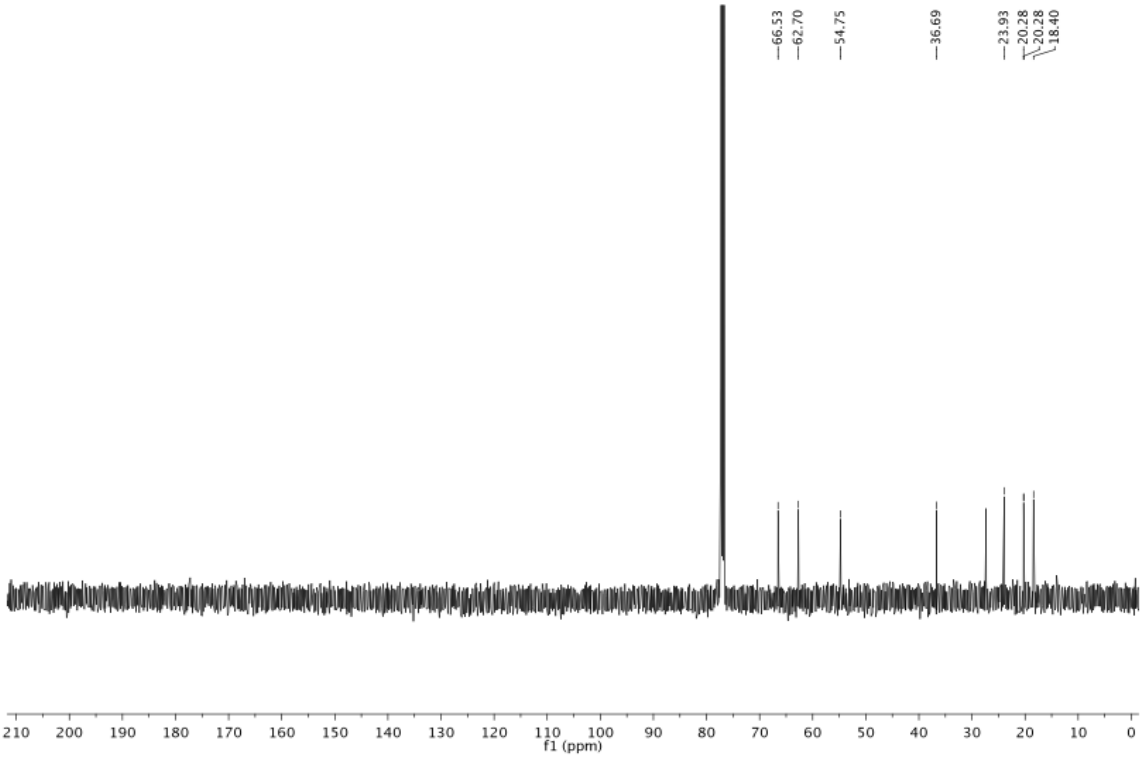


(*R)-1-((2*S**,3*R**)-3-Isopropyloxiran-2-yl)propan-2-ol (51a)**

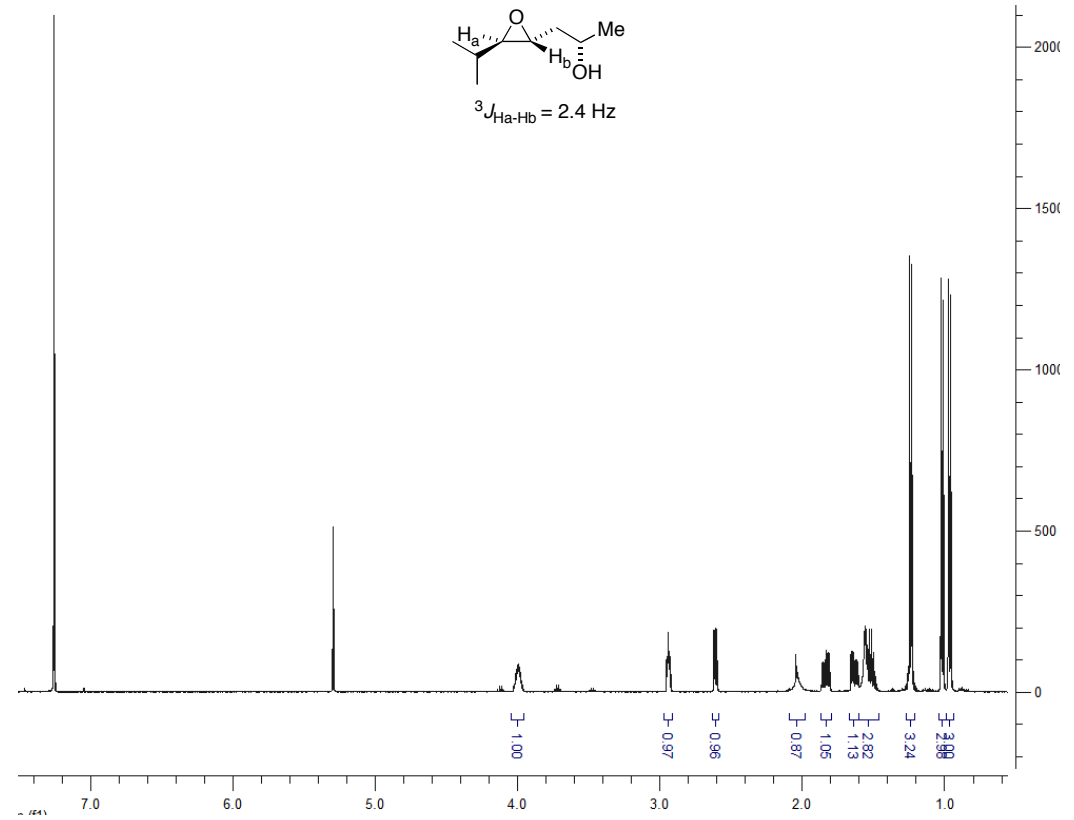


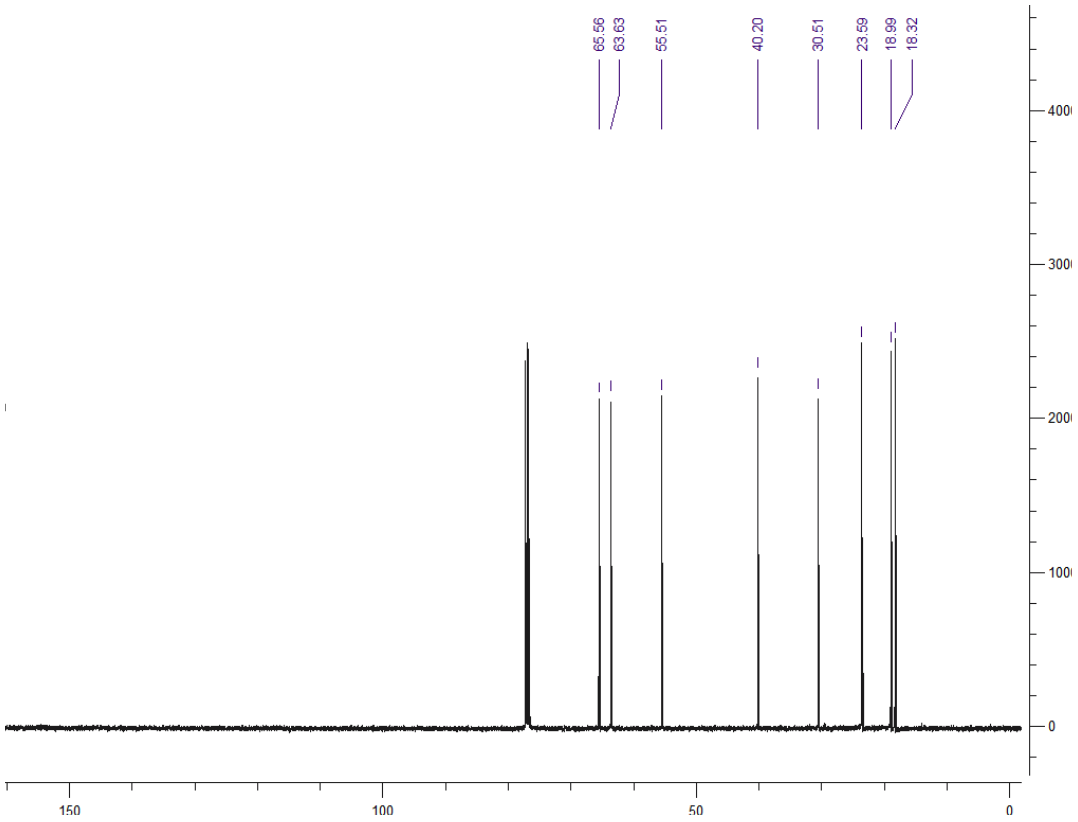
$^{3}J_{Ha\text{-}Hb}$ = 4.3 Hz



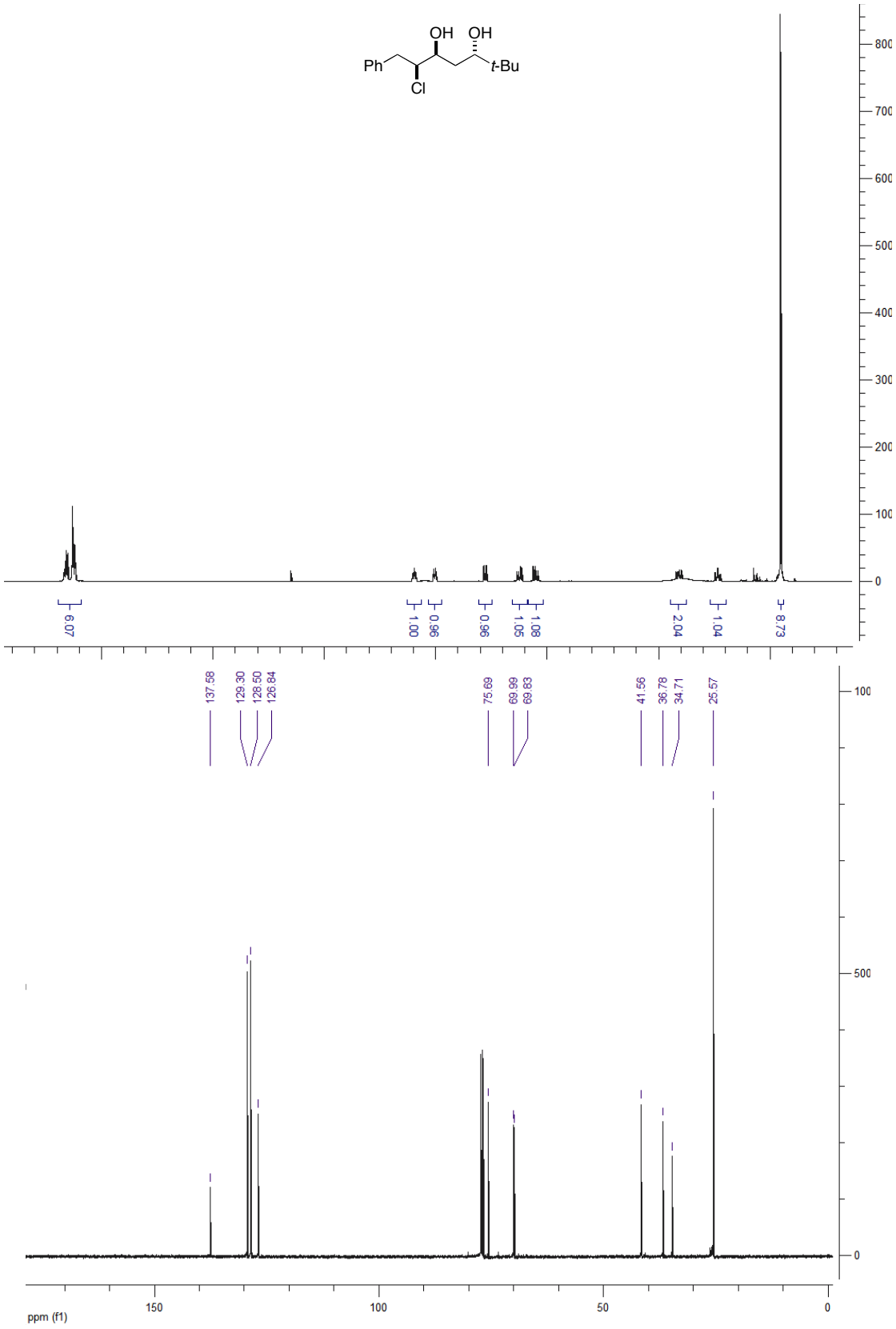


(*S)-1-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)propan-2-ol (51b)**

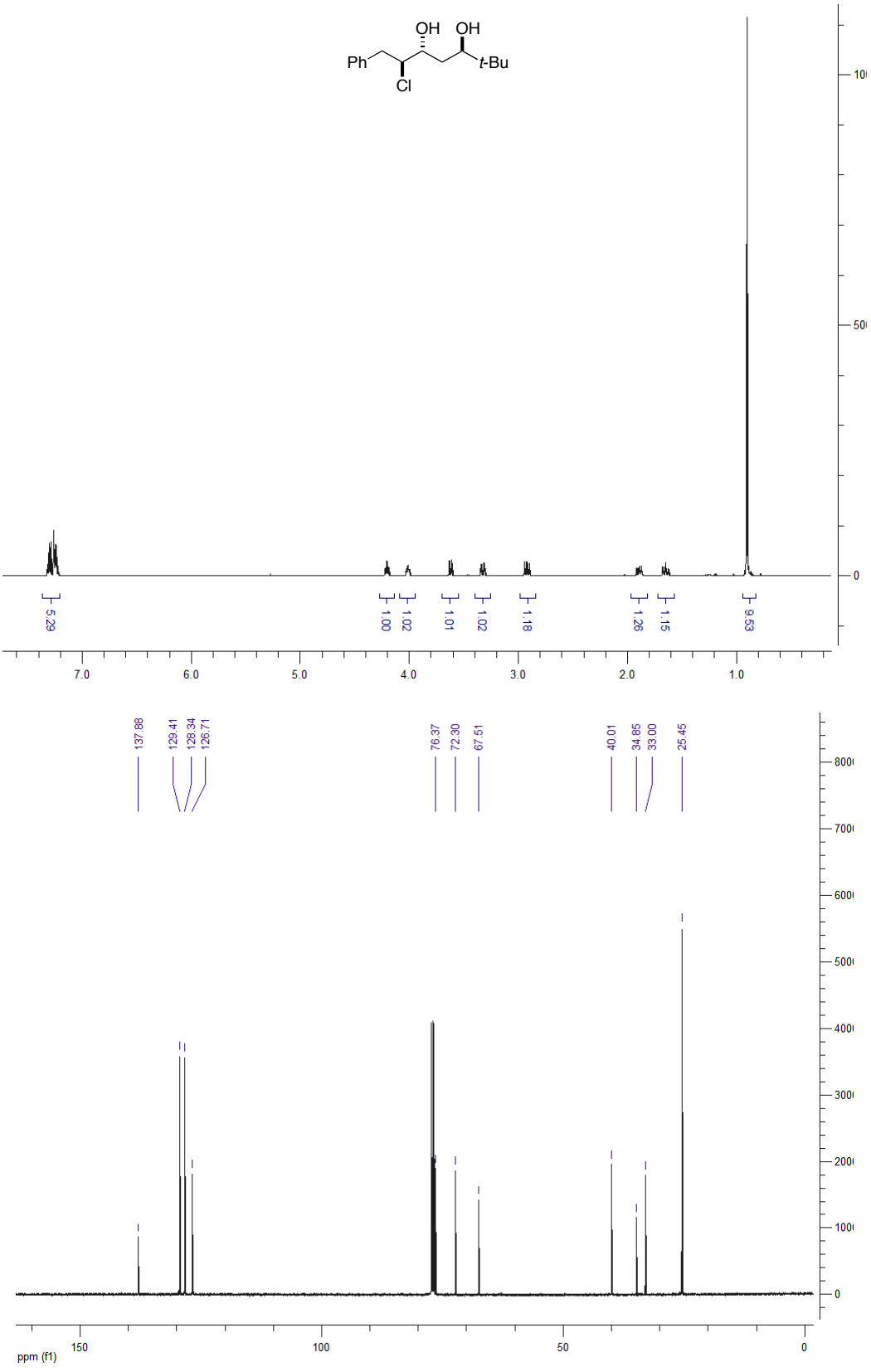




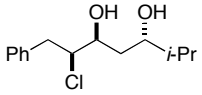
(2*S,3*S**,5*S**)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (52a)**

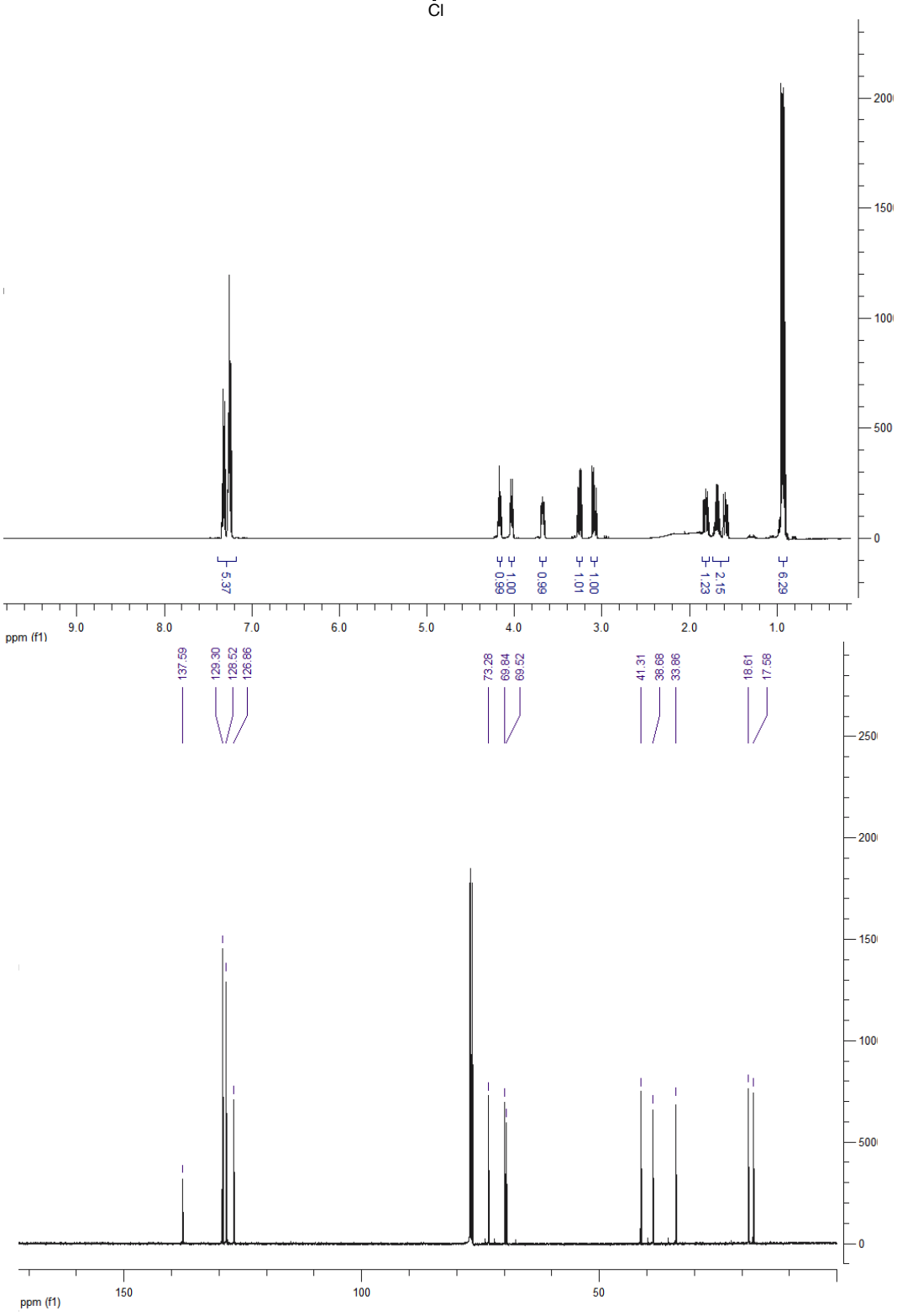


(2*S*,3R*,5R)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (52b)**

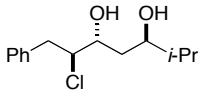


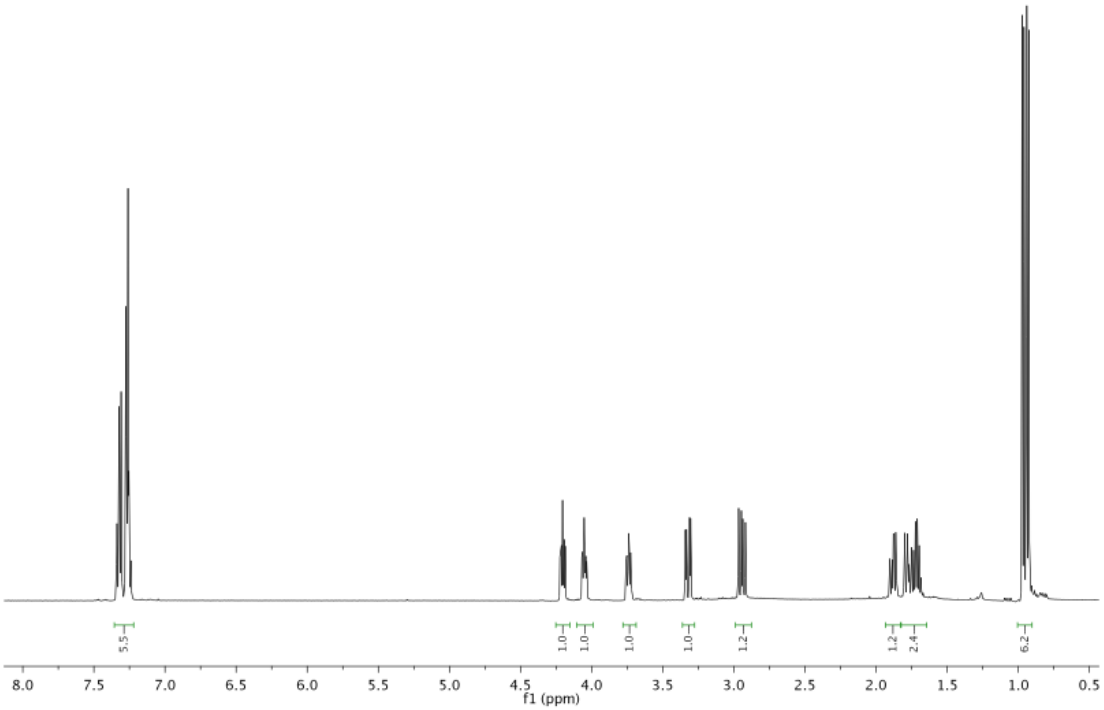
(2*S,3*S**,5*S**)-2-Chloro-6-methyl-1-phenylheptane-3,5-diol (53a)**

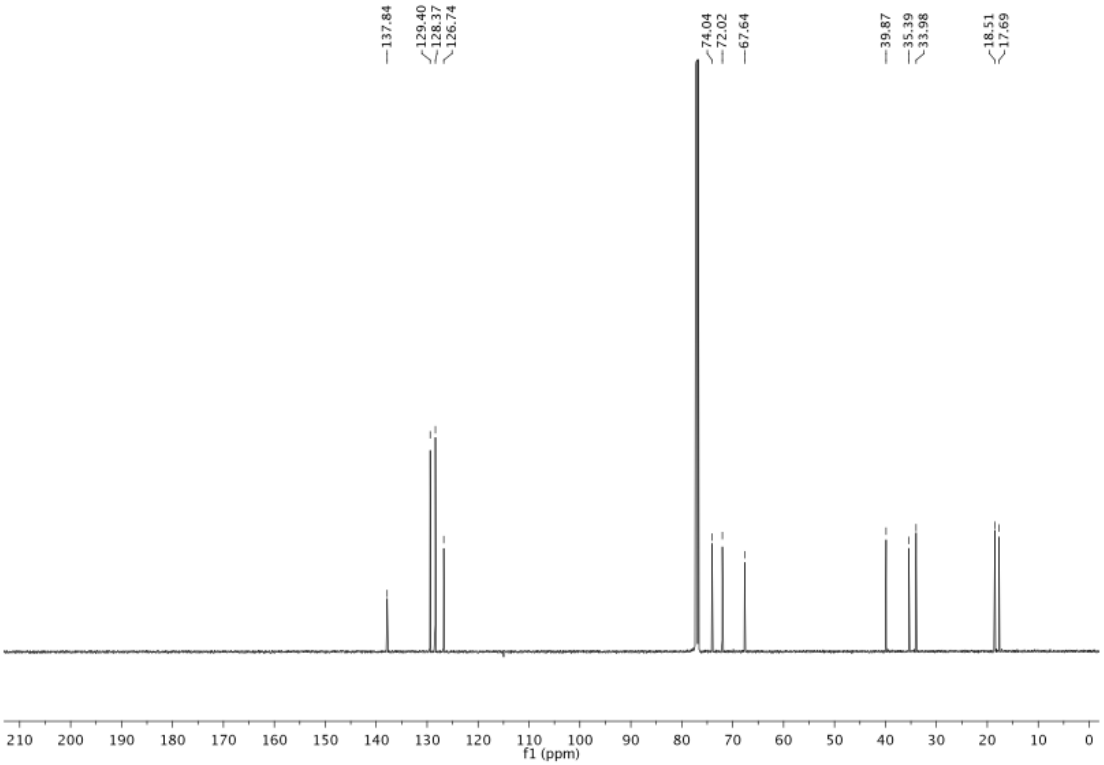




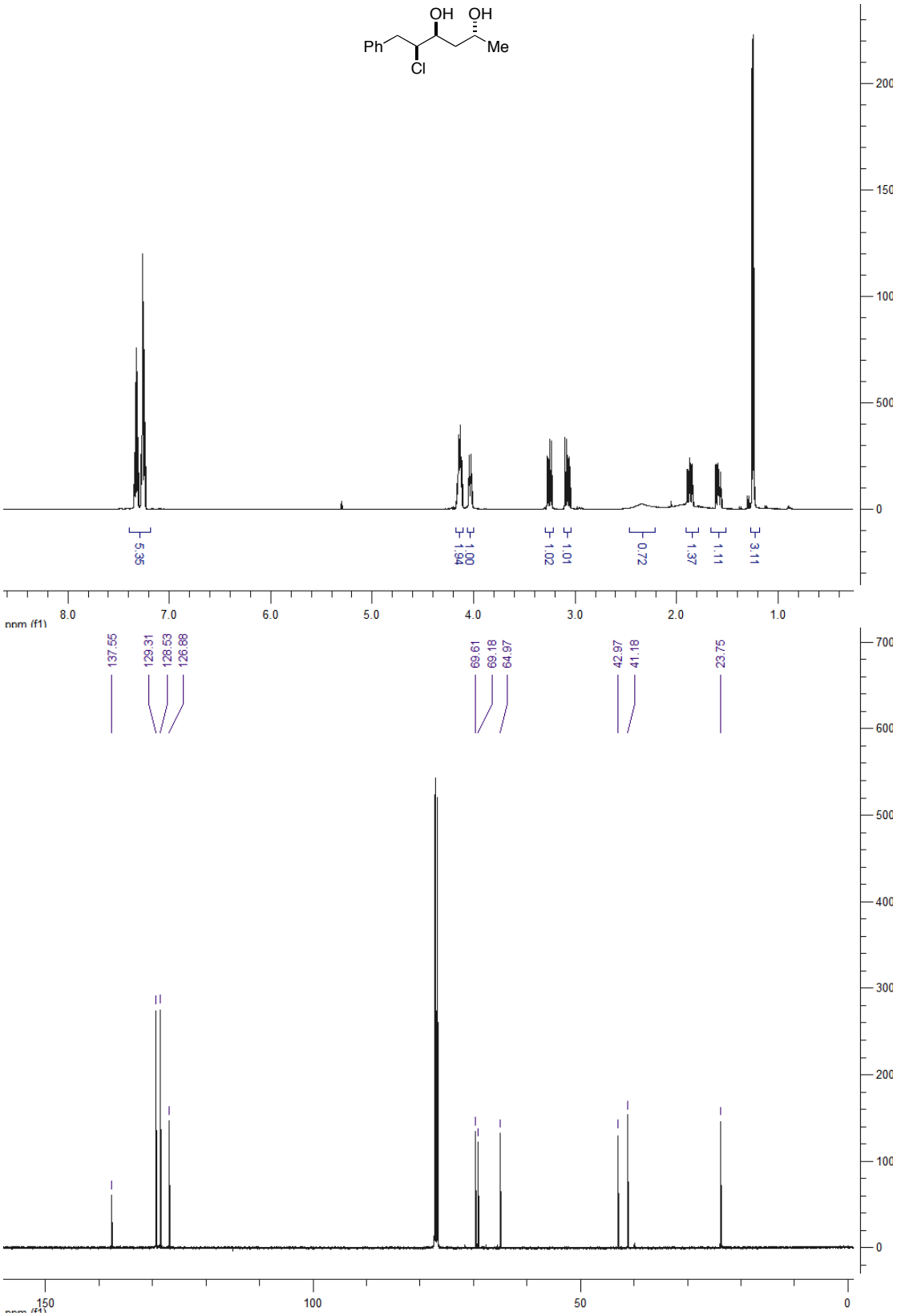
(2*S*,3R*,5R)-2-Chloro-6-methyl-1-phenylheptane-3,5-diol (53b)**



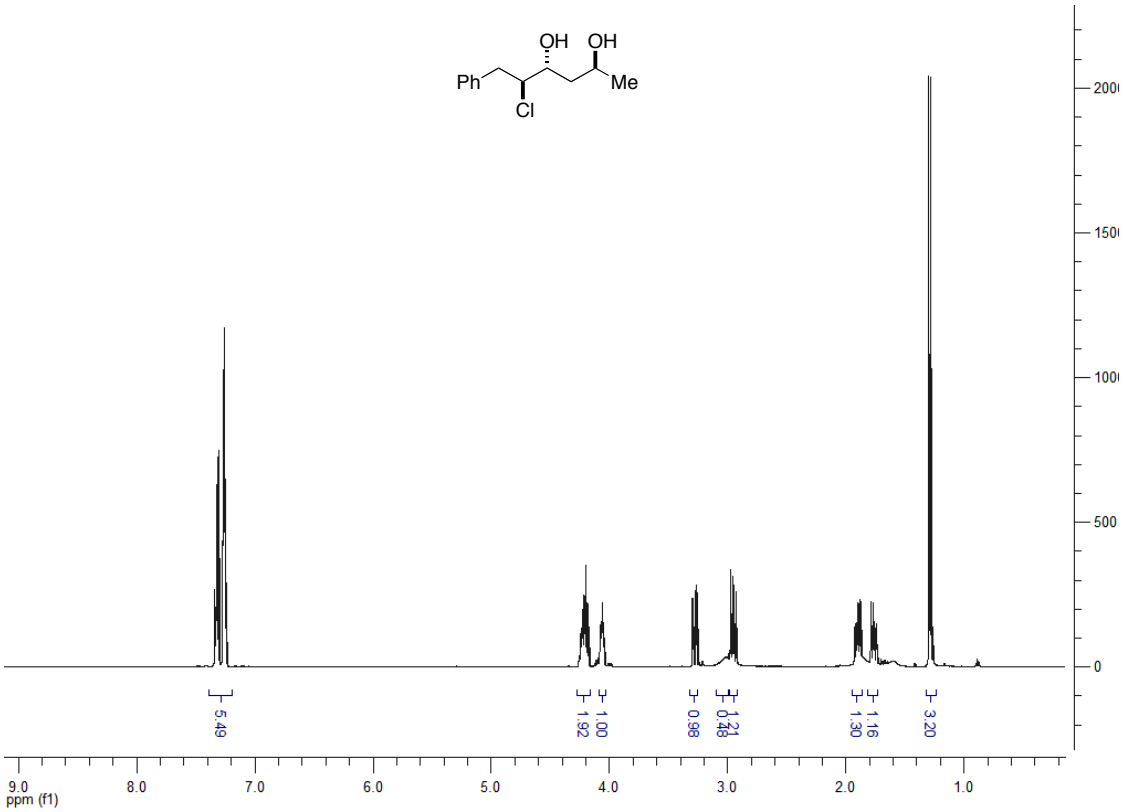


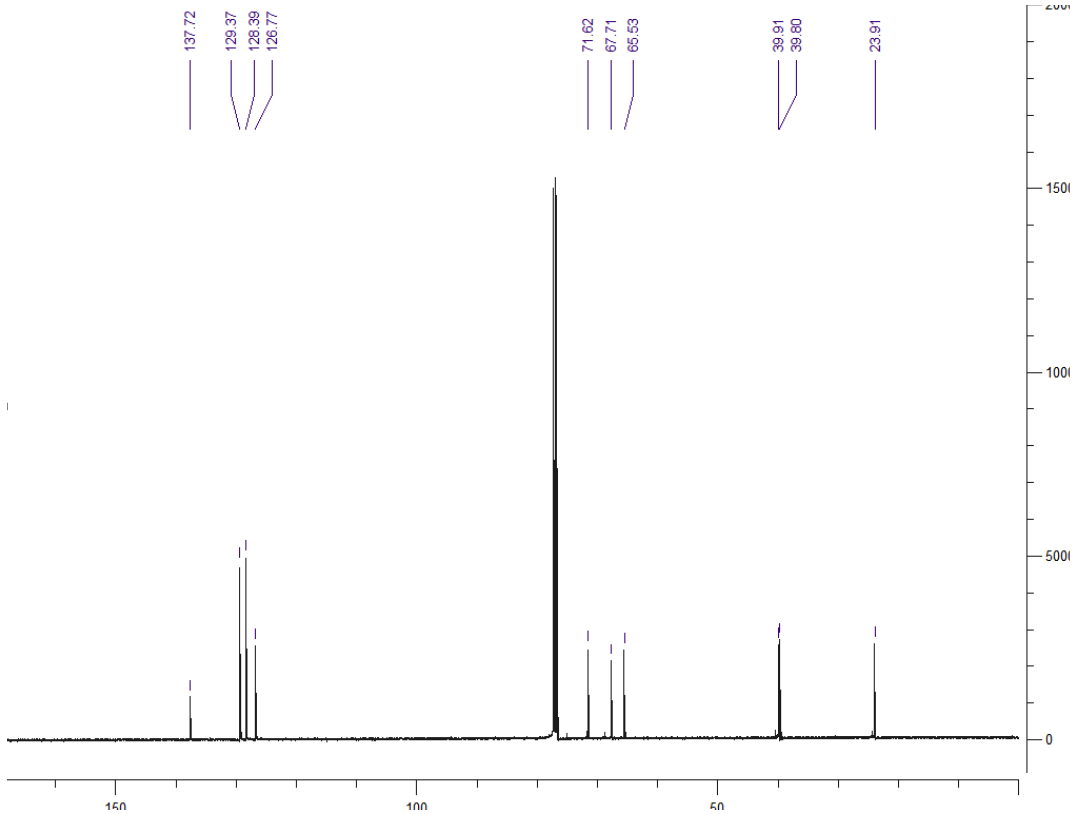


(2*R,4*S**,5*S**)-5-Chloro-6-phenylhexane-2,4-diol (54a)**

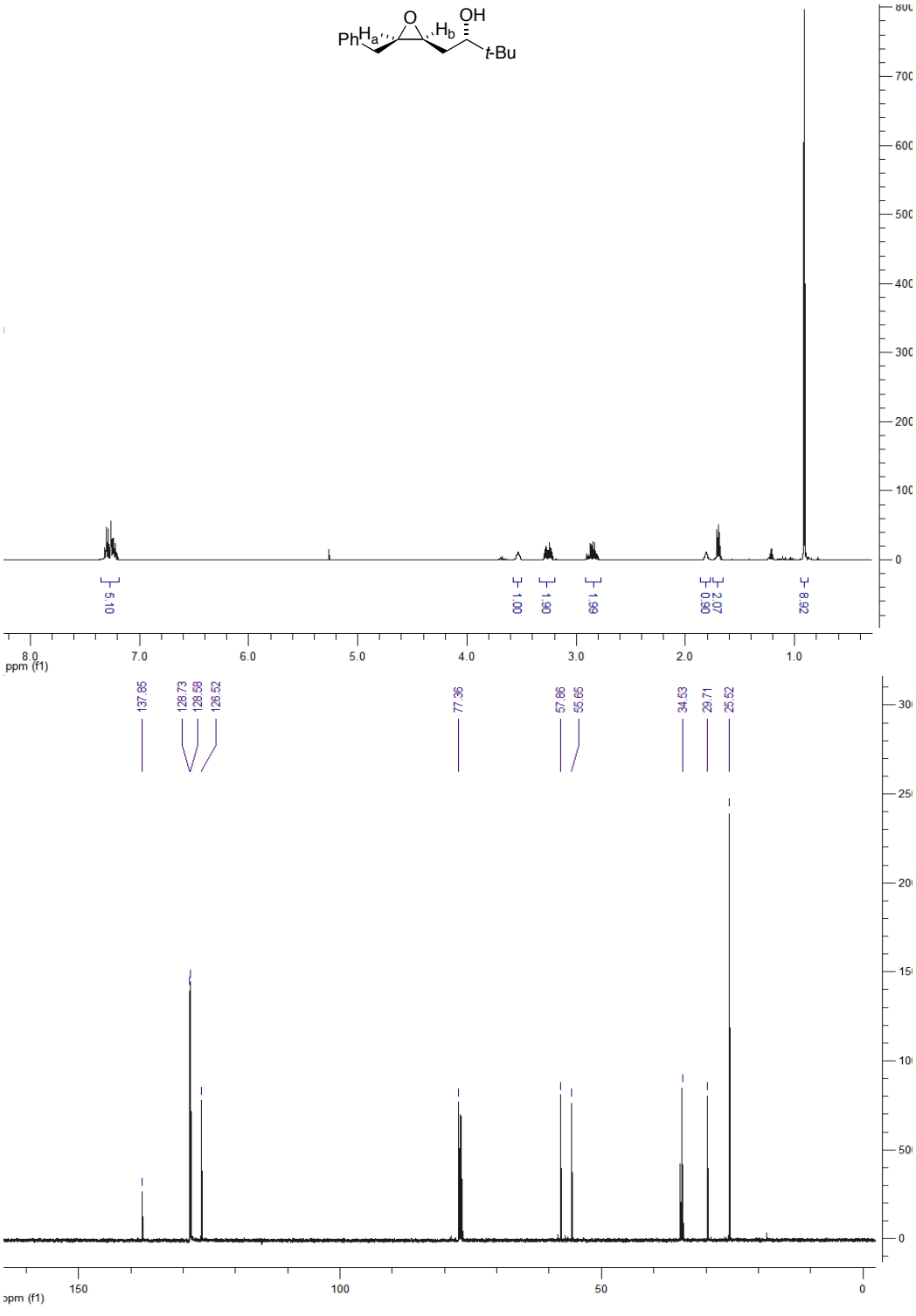


(2*S*,4R*,5S)-5-Chloro-6-phenylhexane-2,4-diol (54b)**

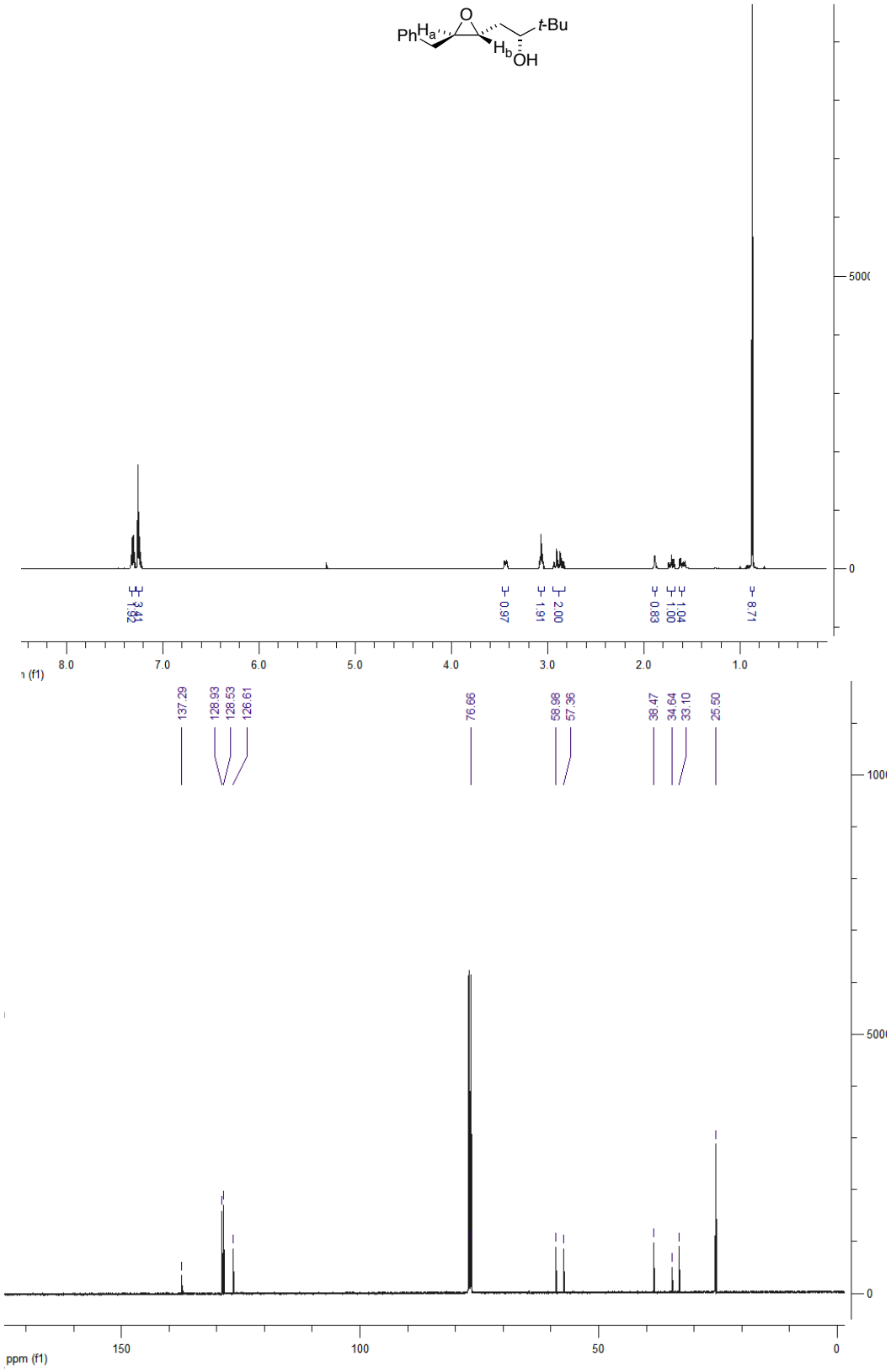




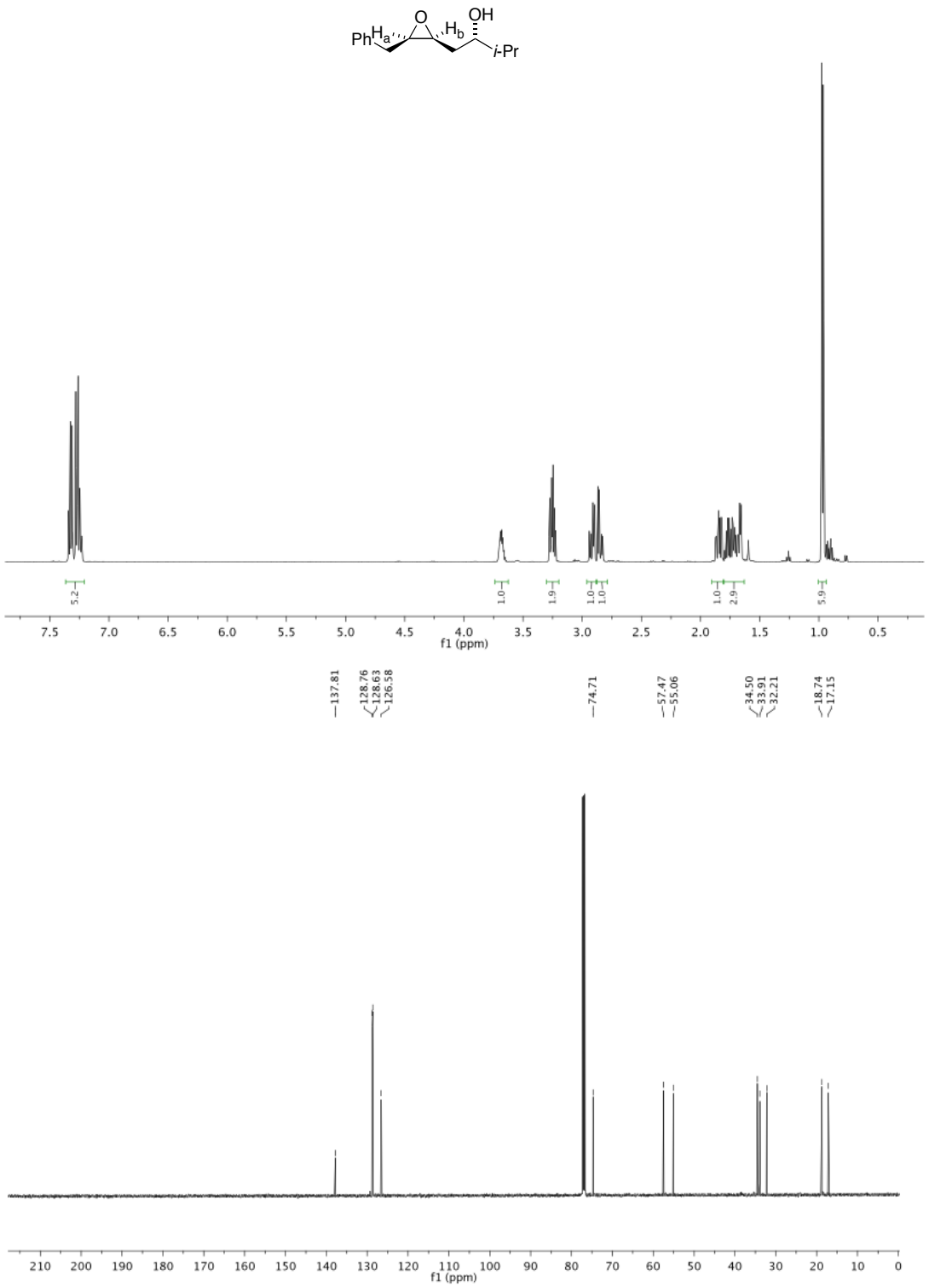
(*S)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (55a)**



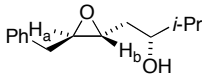
(*R)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (55b)**

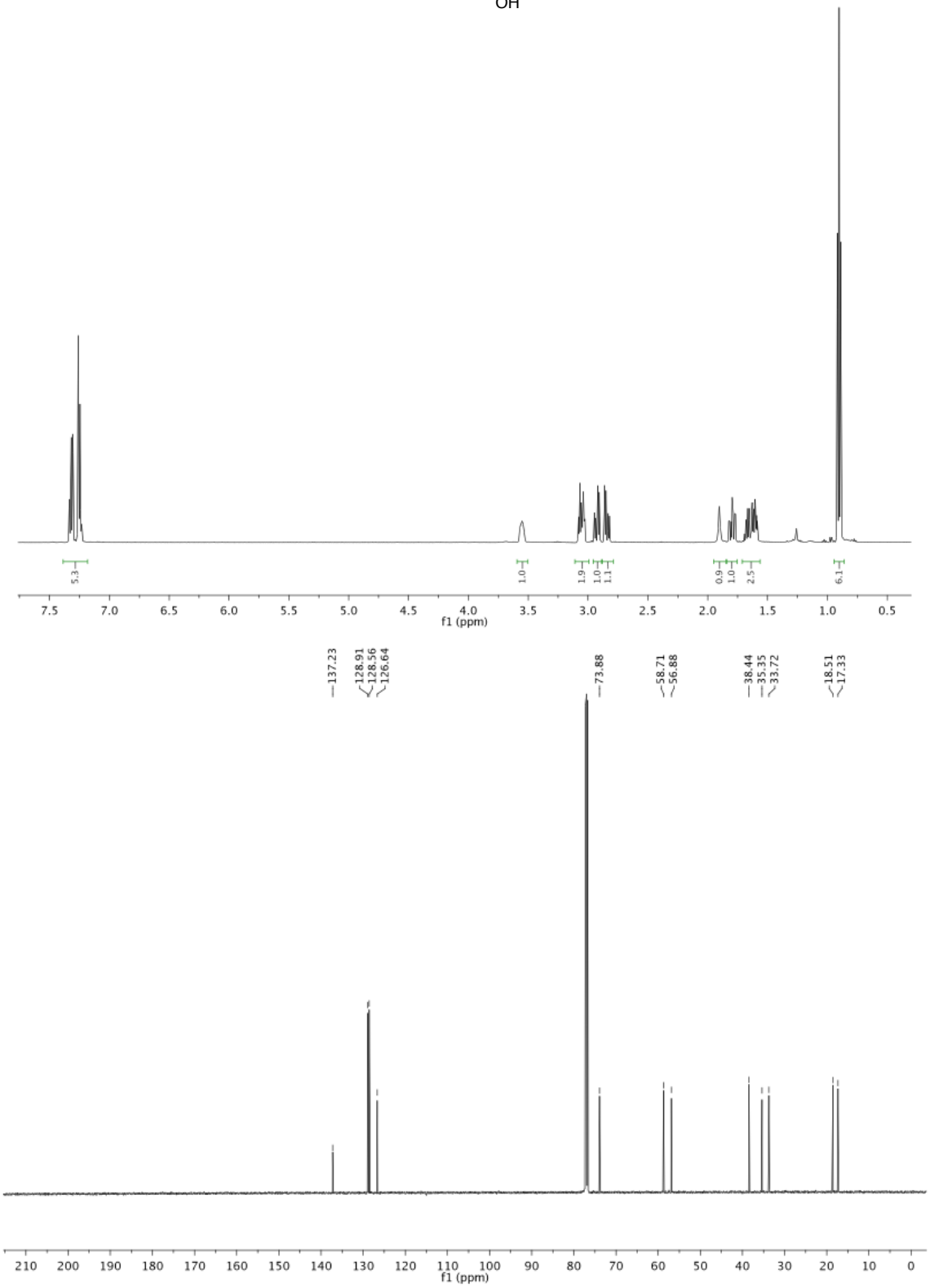


(*R)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (56a)**

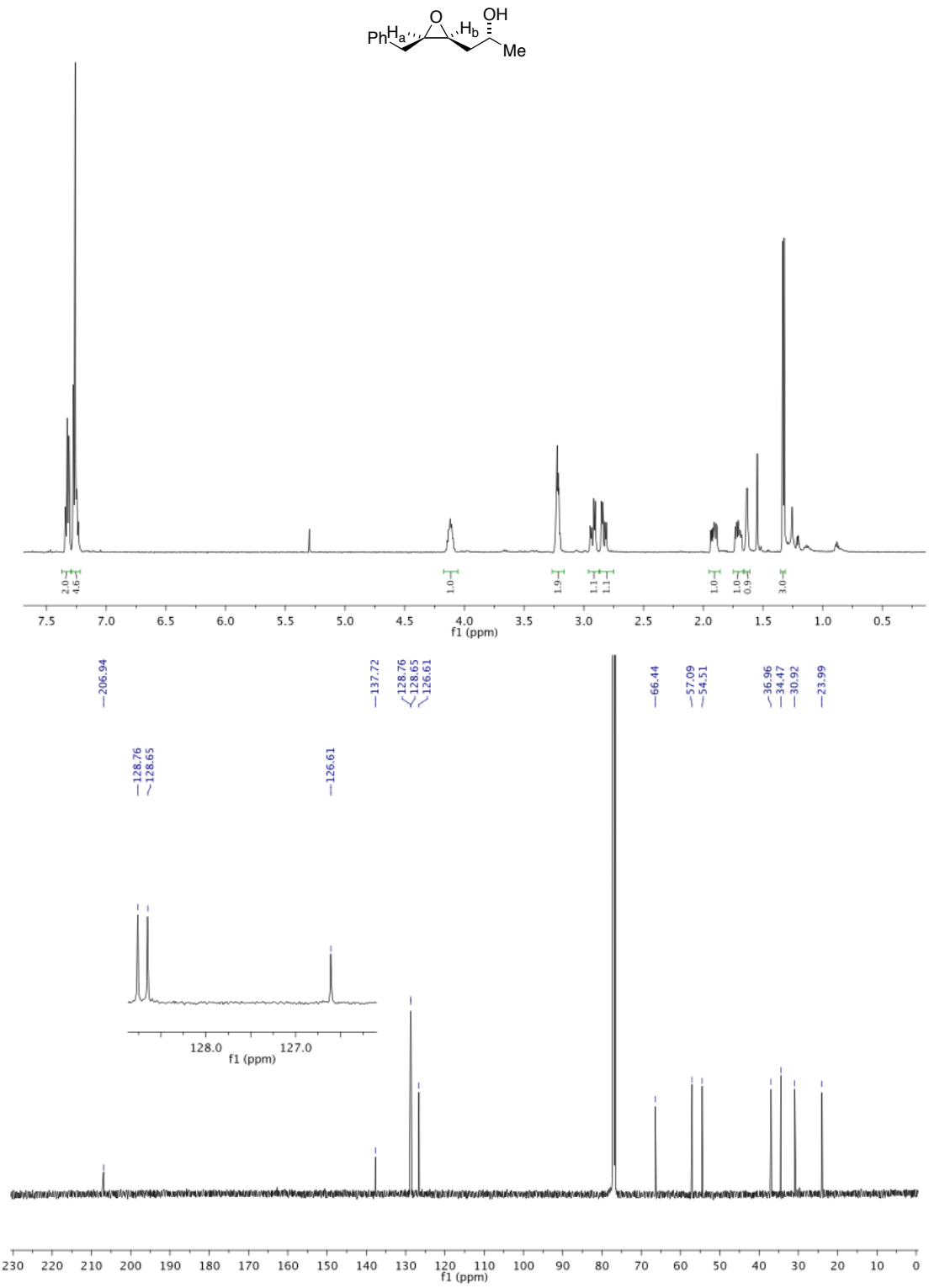


(*S)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (56b)**

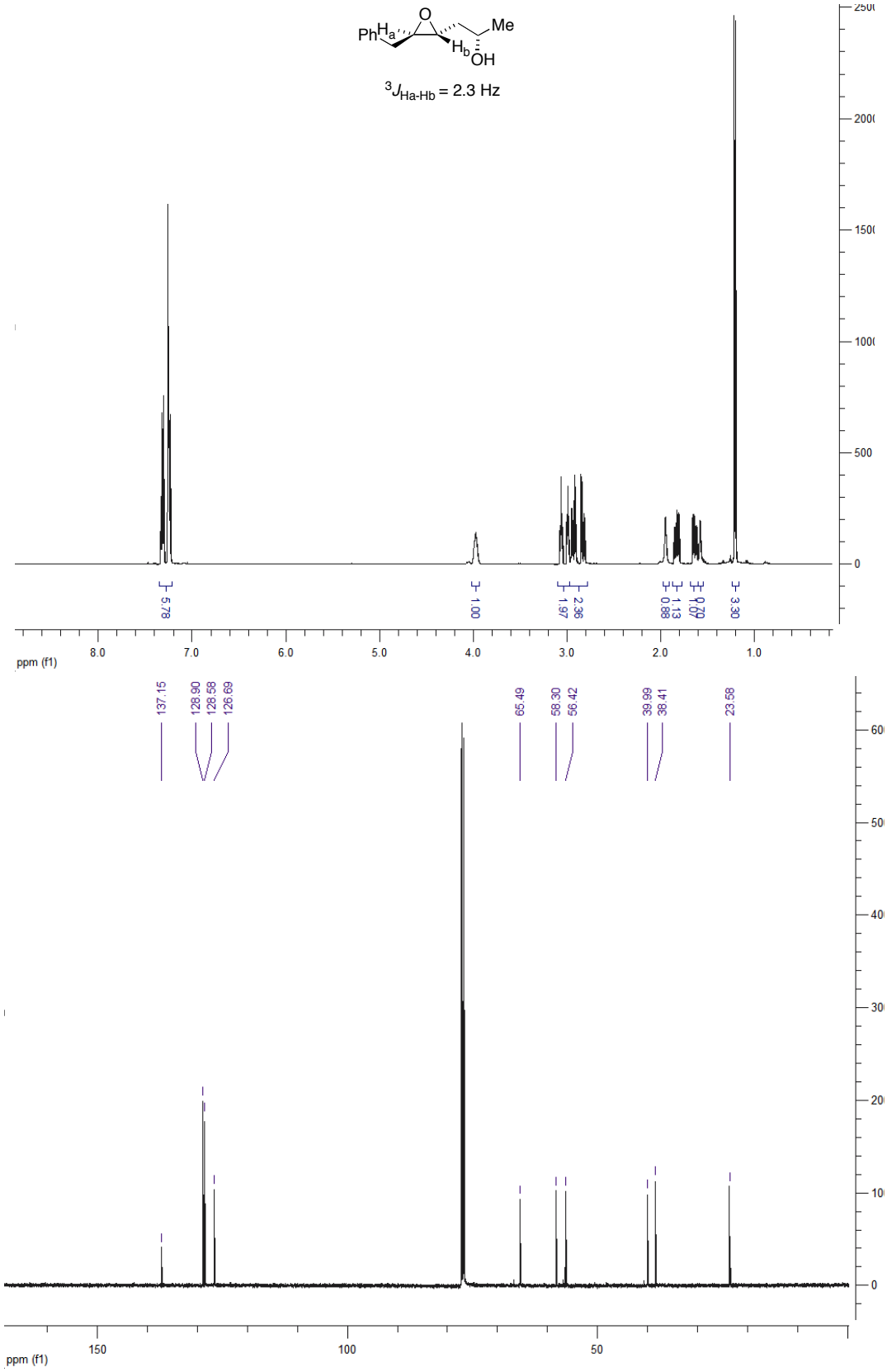




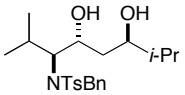
(*R)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (57a)**

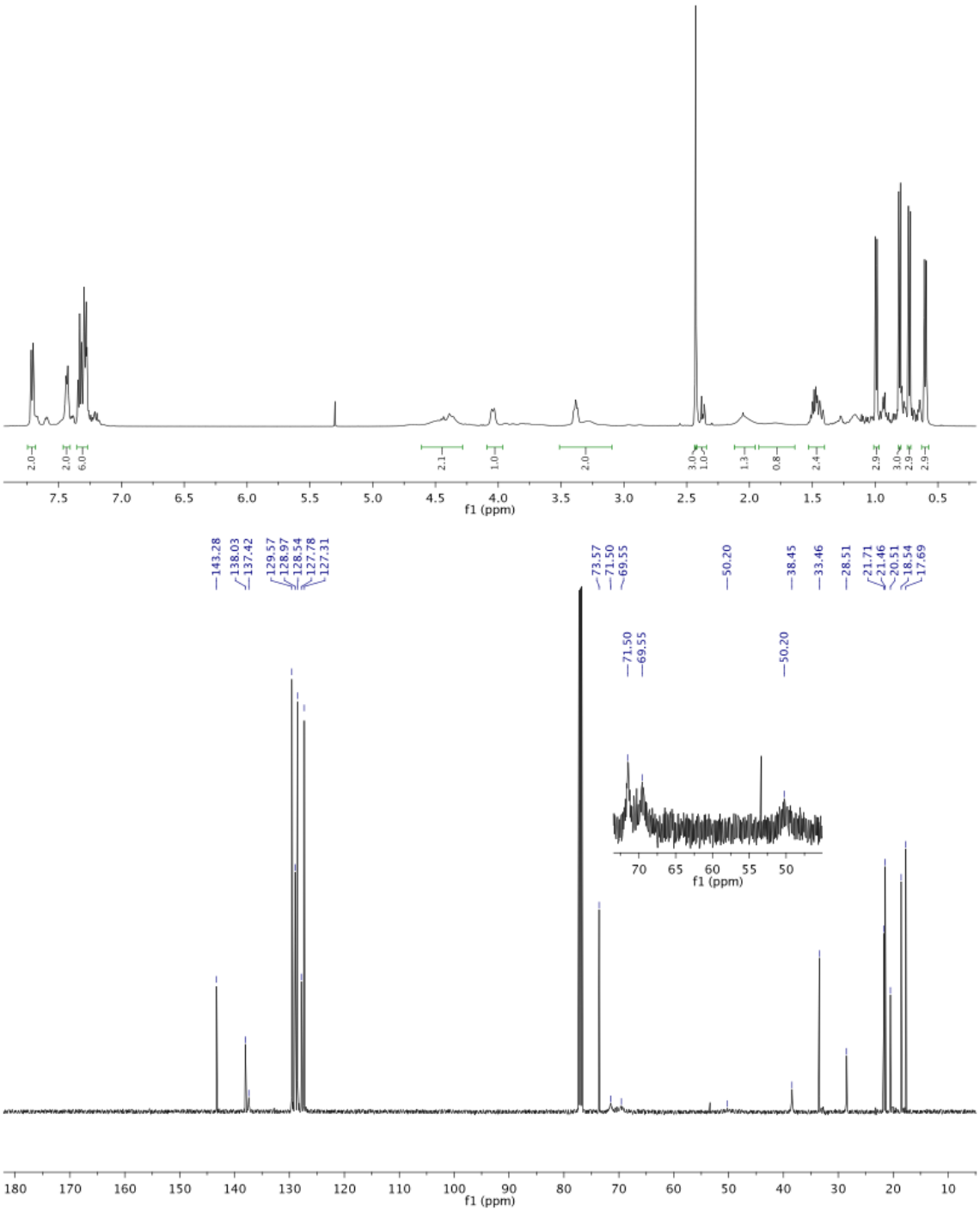


(*S)-1-((2*R**,3*R**)-3-Benzyloxiran-2-yl)propan-2-ol (57b)**

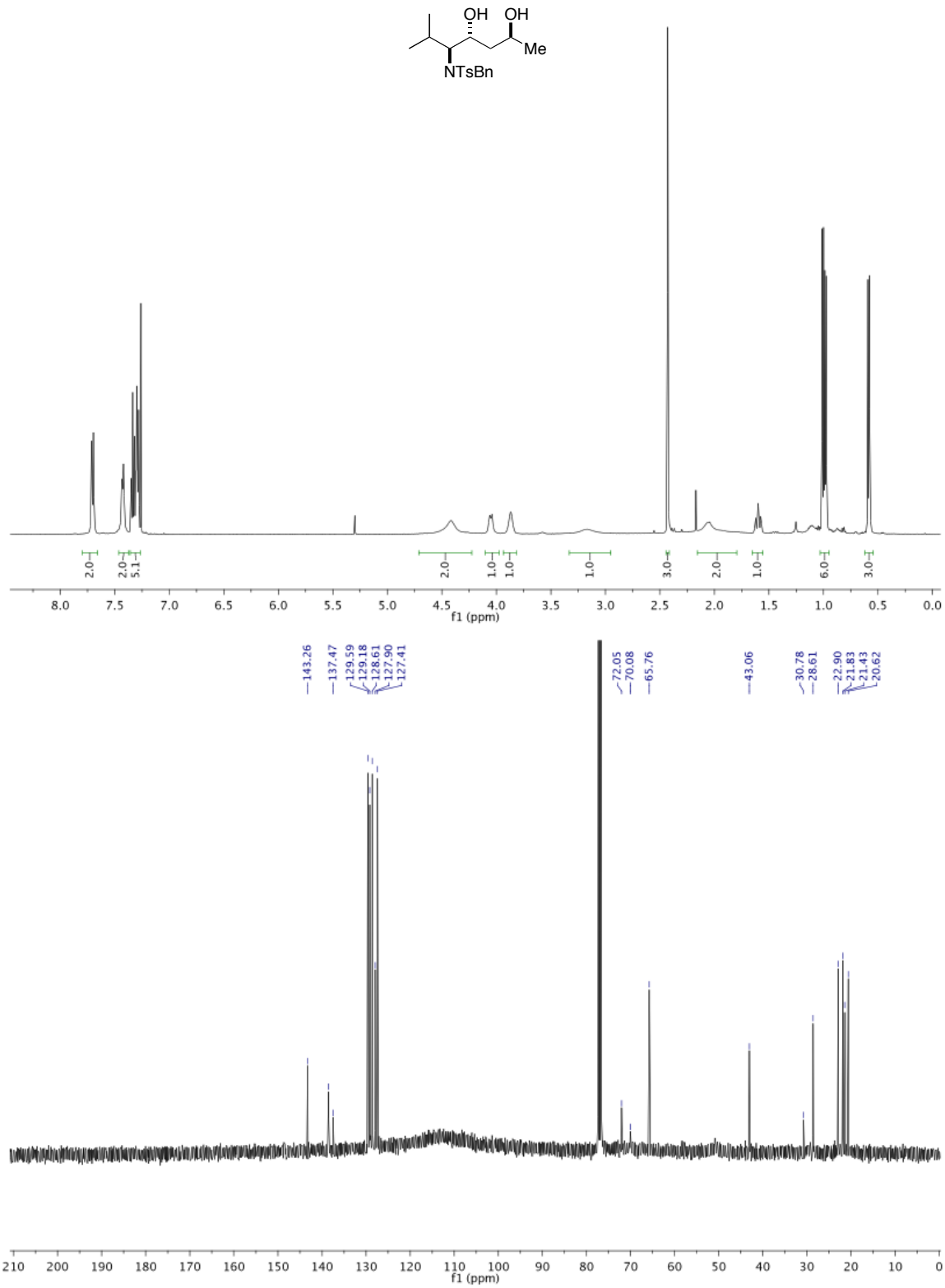


_N_-Benzyl-_N_-((3_S_*,4_R_*,6_R_*)-4,6-dihydroxy-2,7-dimethyloctan-3-yl)-4-methylbenzenesulfonamide (65b)

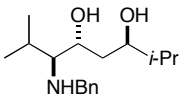


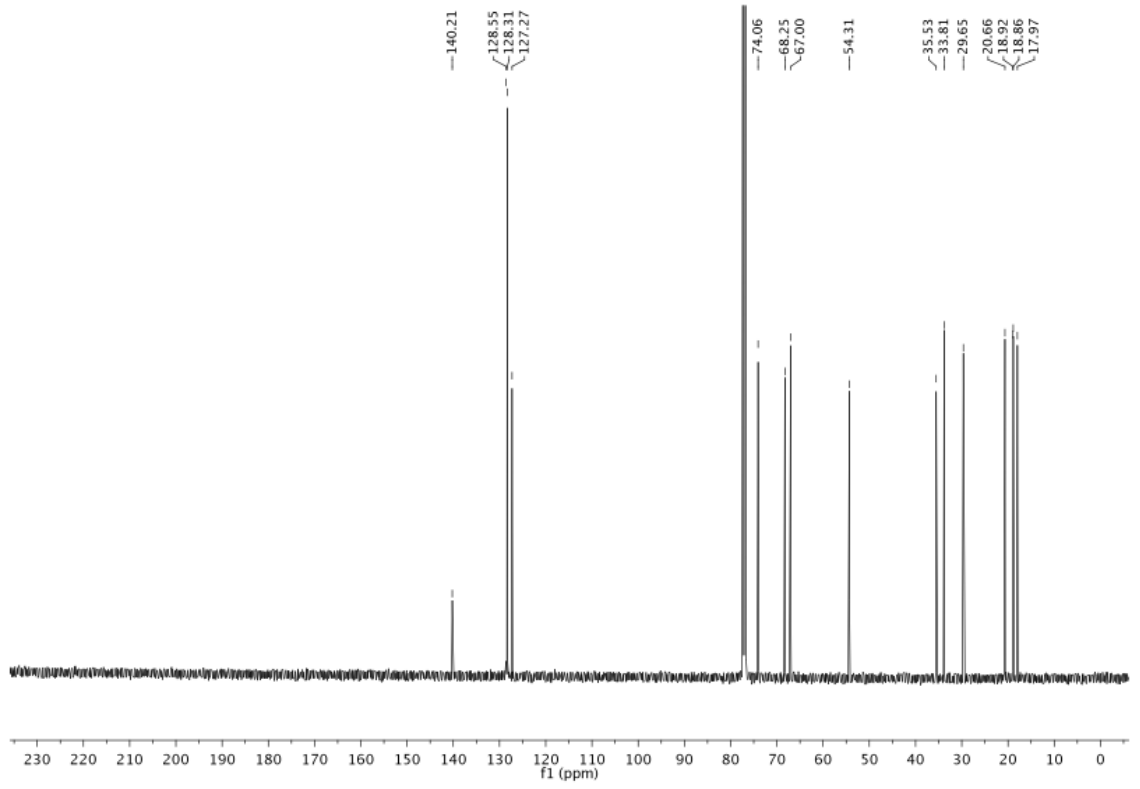


_N_-Benzyl-_N_-((3_S_*,4_R_*,6_S_*)-4,6-dihydroxy-2-methylheptan-3-yl)-4-methylbenzenesulfonamide (66b)

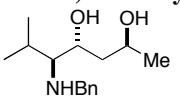


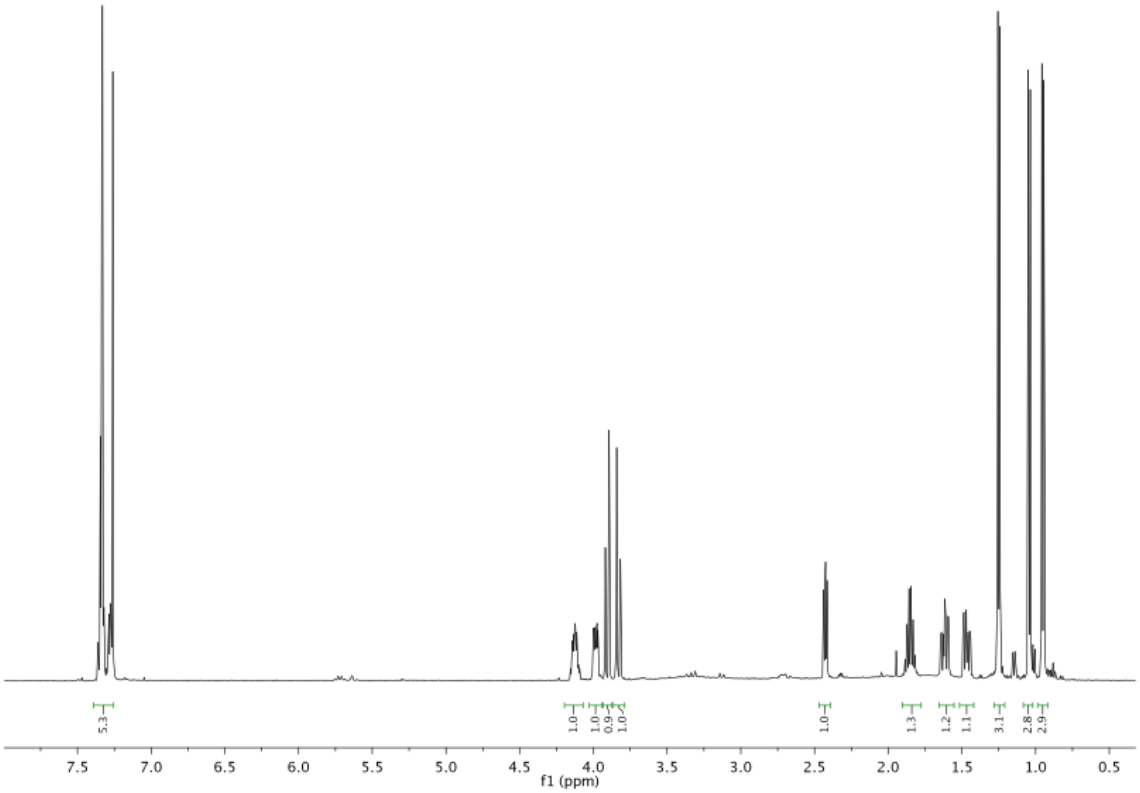
(3*R,5*R**,6*S**)-6-(Benzylamino)-2,7-dimethyloctane-3,5-diol (67b)**

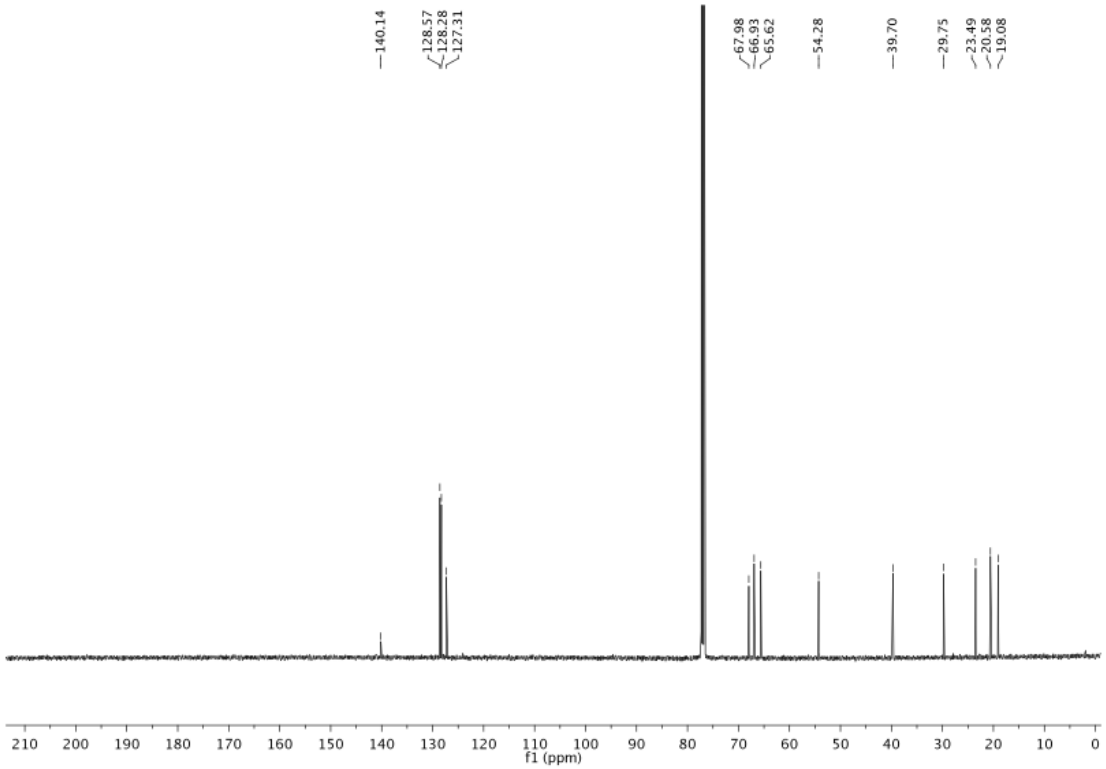




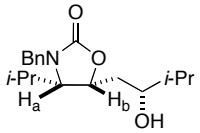
(2*S,4*R**,5*S**)-5-(Benzylamino)-6-methylheptane-2,4-diol (68b)**



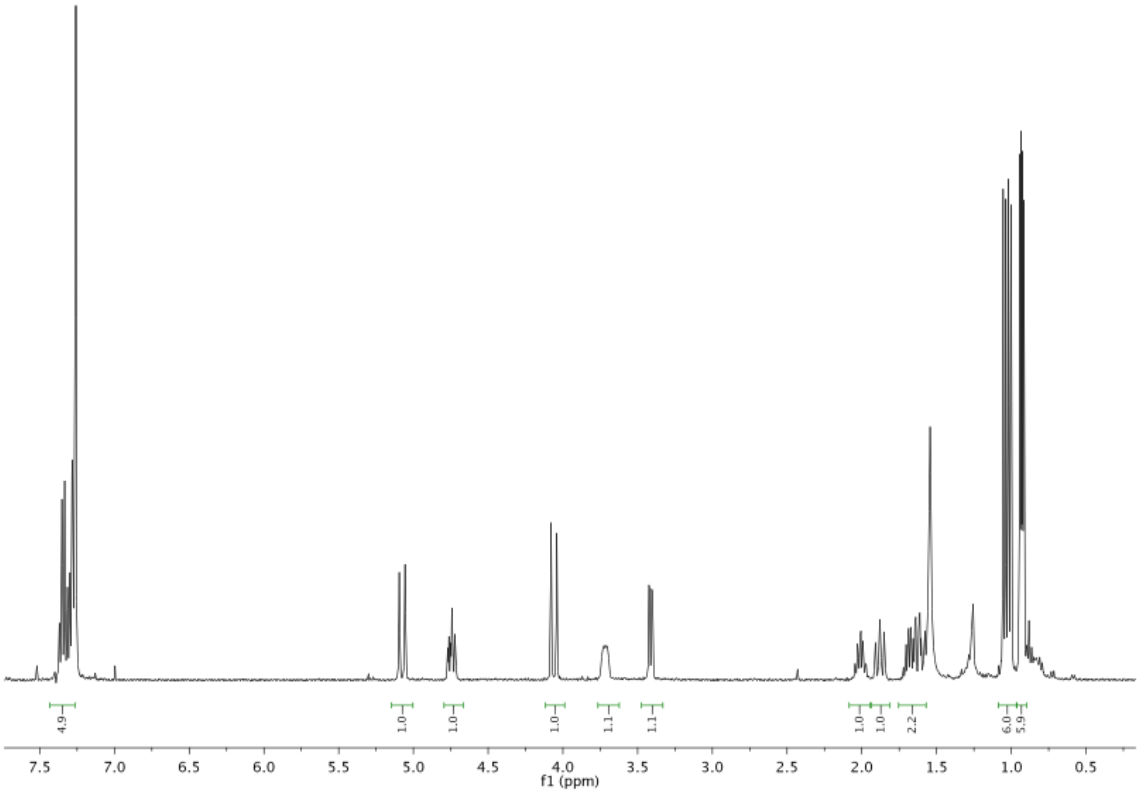


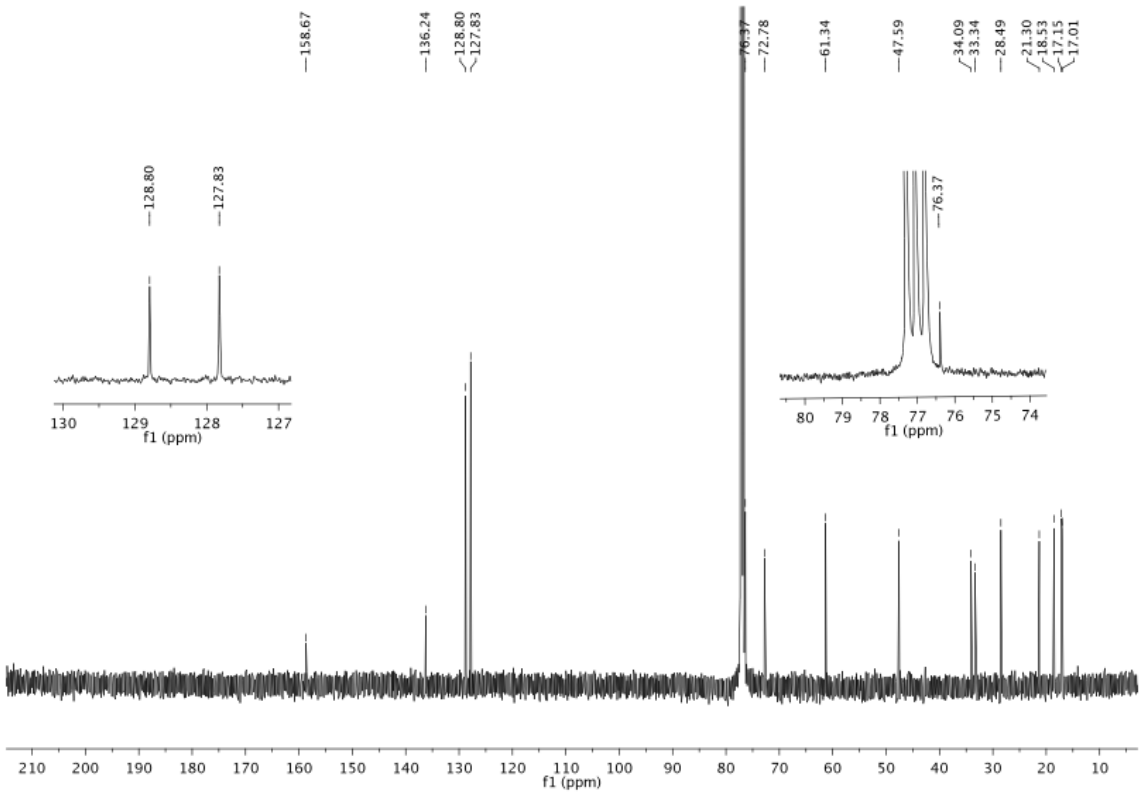


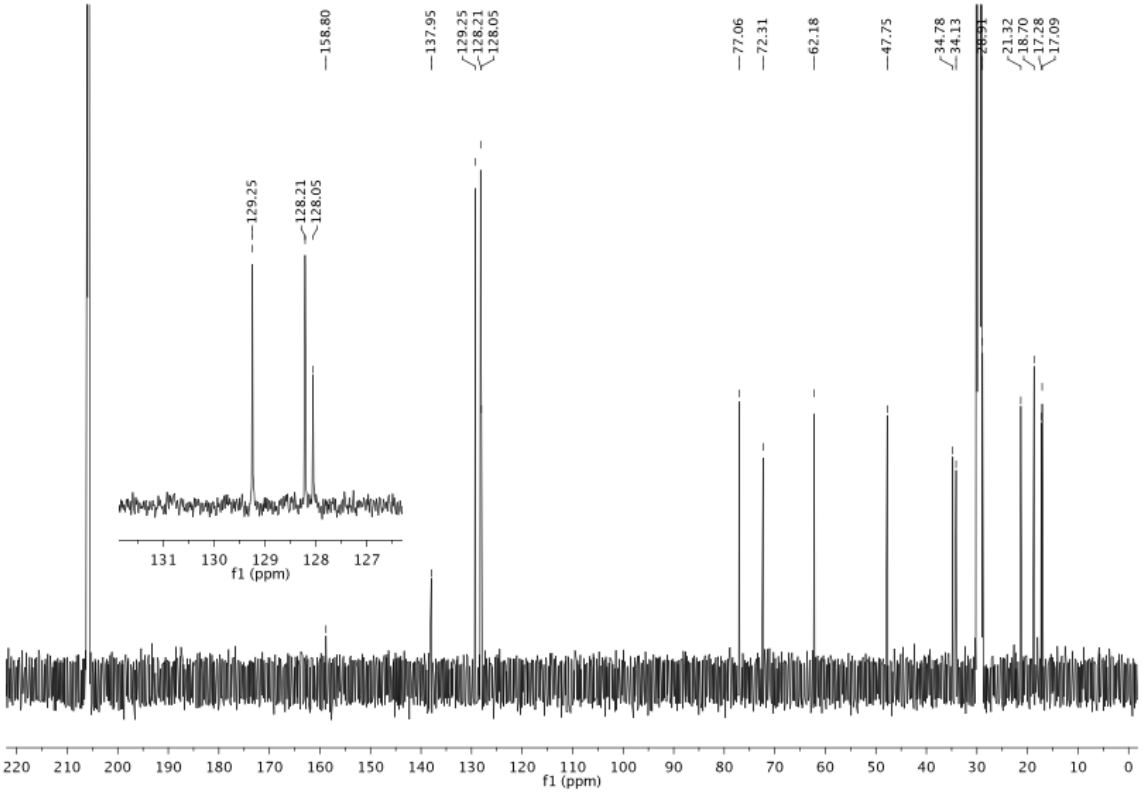
(4*S*,5R)-3-Benzyl-5-((*R*)-2-hydroxy-3-methylbutyl)-4-isopropyloxazolidin-2-one (69b)**



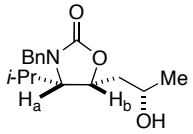
$^{3}J_{Ha\text{-}Hb}$ = 7.5 Hz



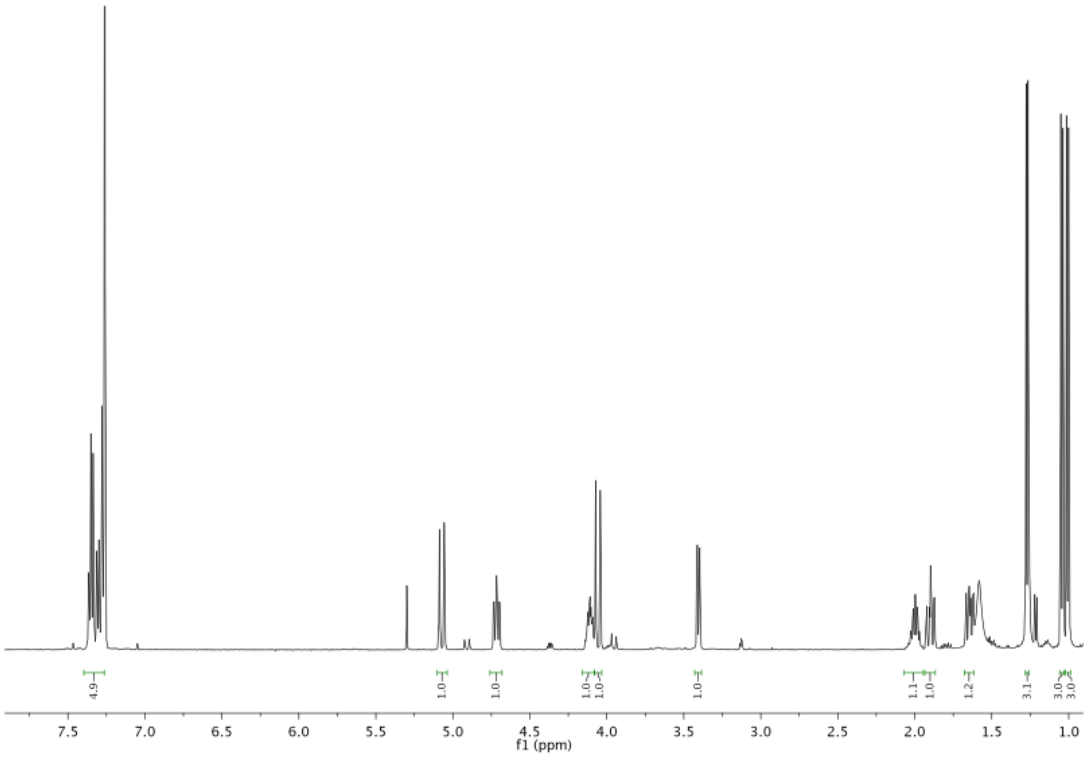

158.67
136.24
128.80
127.83
76.37
72.78
61.34
47.59
34.09
33.34
28.49
21.30
18.53
17.15
17.01
128.80
127.83
76.37
f1 (ppm)
f1 (ppm)
f1 (ppm)

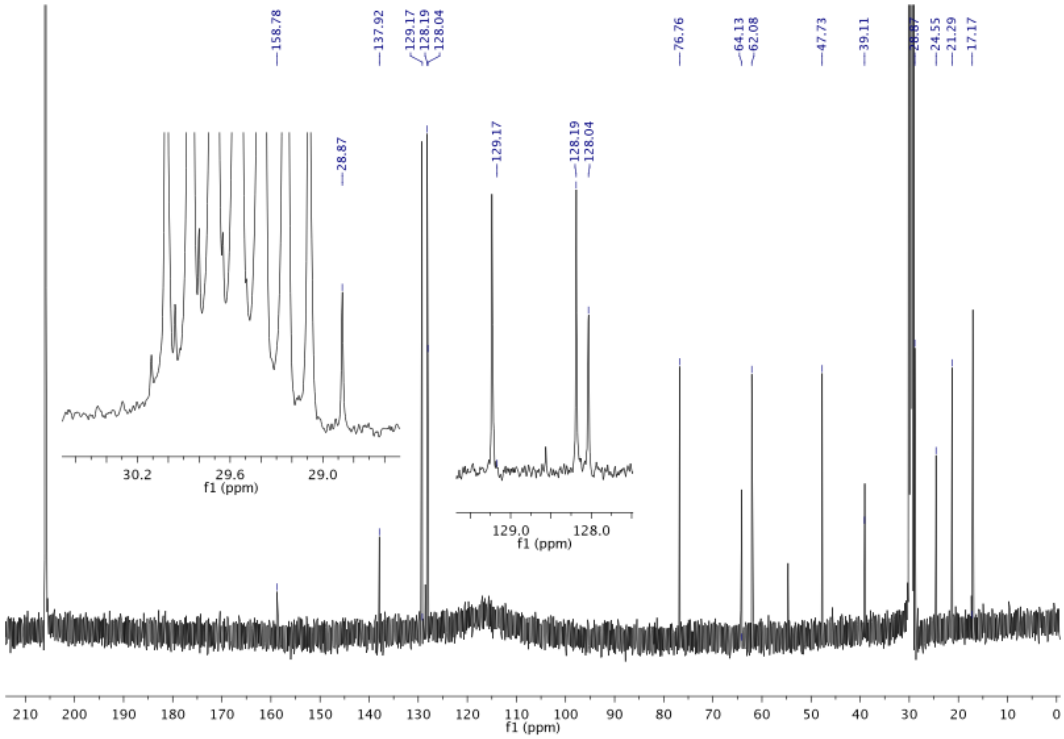

158.80
137.95
129.25
128.21
128.05
77.06
72.31
62.18
47.75
34.78
34.13
28.91
21.32
18.70
17.28
17.09
129.25
128.21
128.05
f1 (ppm)
f1 (ppm)

(4*S,5*R**)-3-Benzyl-5-((*S*)-2-hydroxypropyl)-4-isopropyloxazolidin-2-one (70b)**

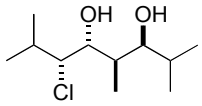


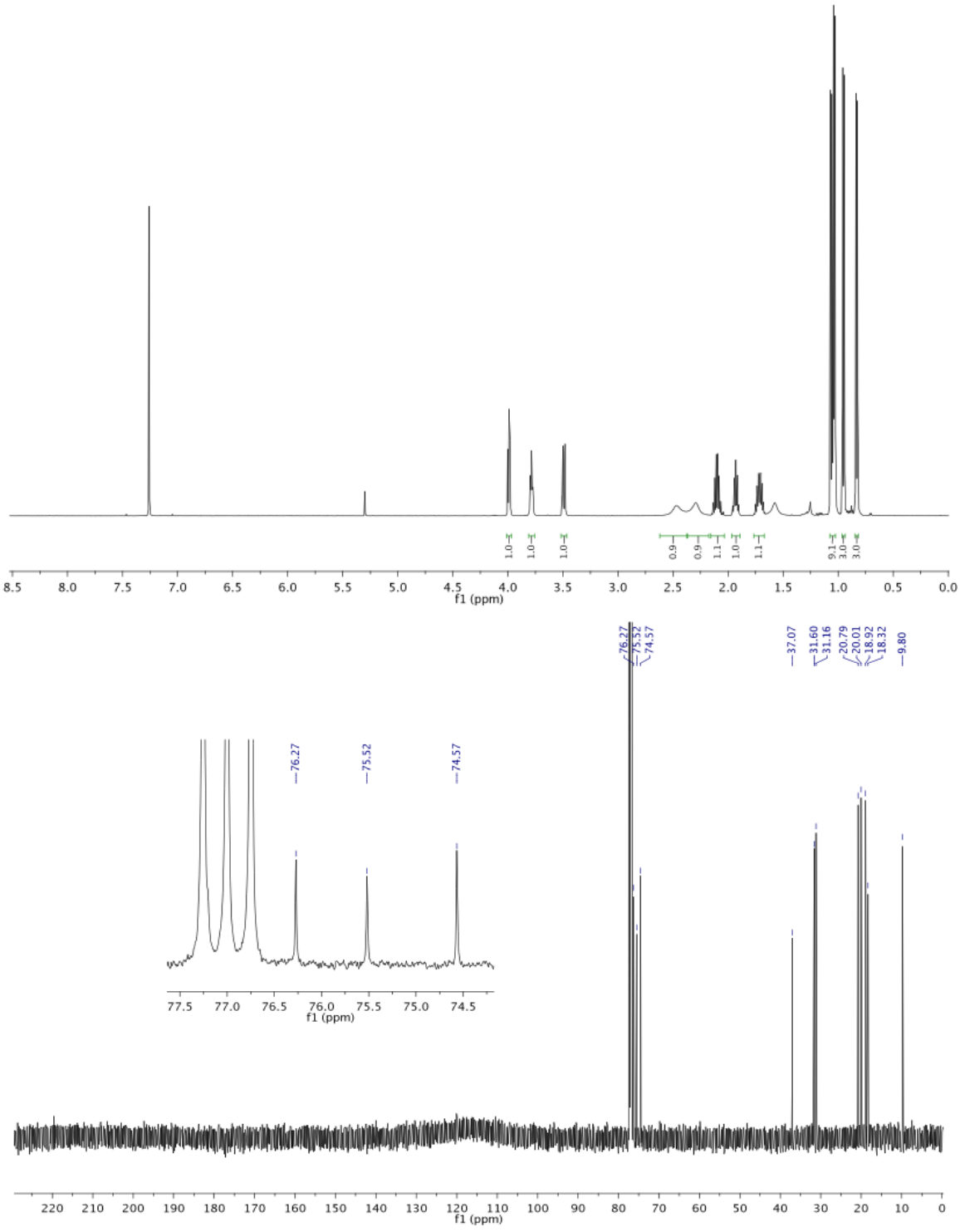
$^{3}J_{Ha\text{-}Hb}$ = 7.5 Hz



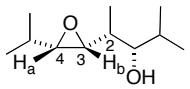


(3*S,5*R**,6*R**)-6-Chloro-2,4,7-trimethyloctane-3,5-diol (61a)**

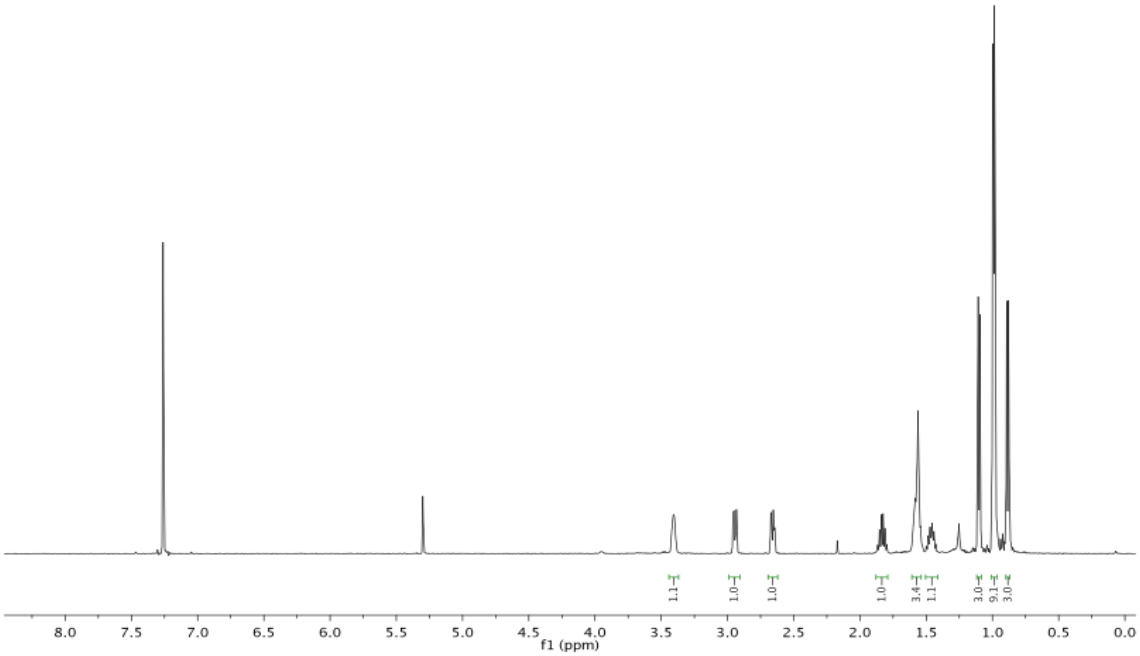


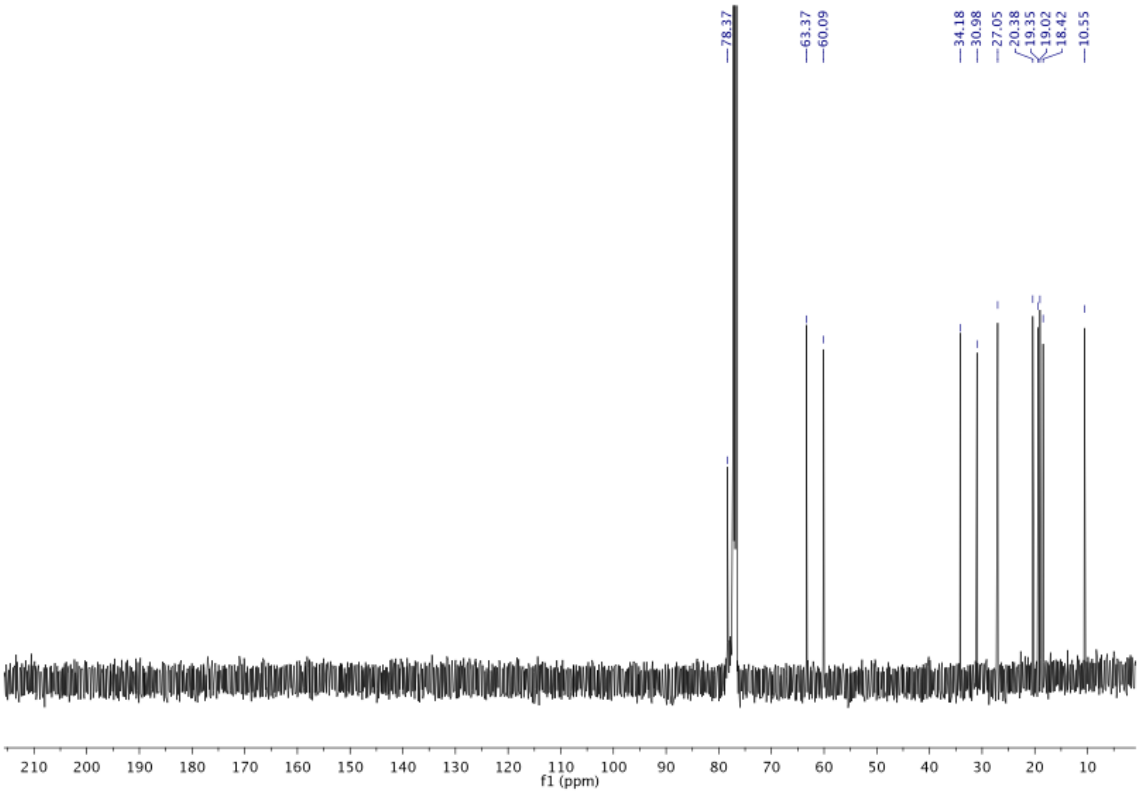


(*S)-1-((2*S**,3*R**)-3-Benzyloxiran-2-yl)-3,3-dimethylbutan-2-ol (62a)**

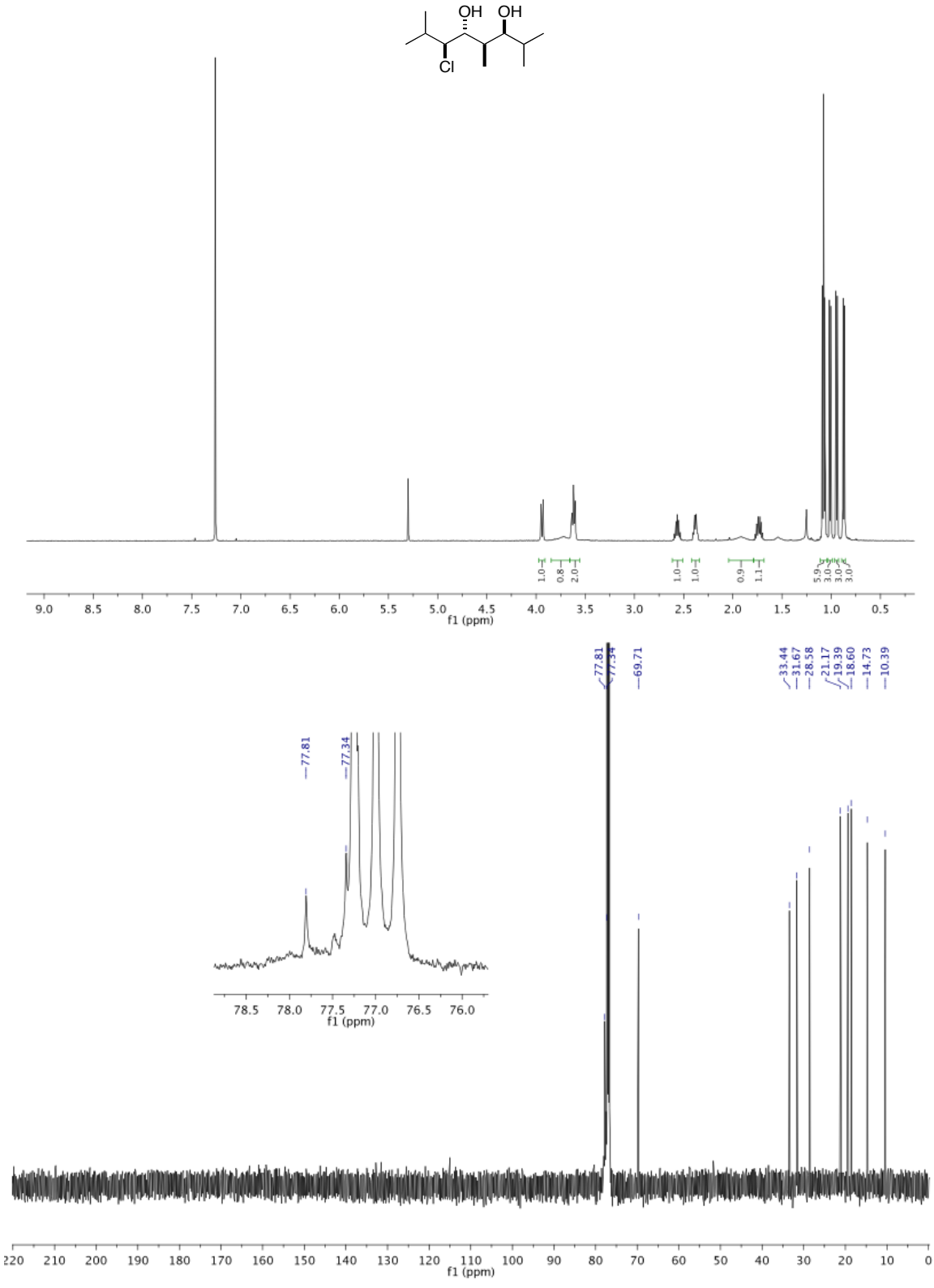


$^{3}J_{Ha\text{-}Hb}$ = 4.2 Hz

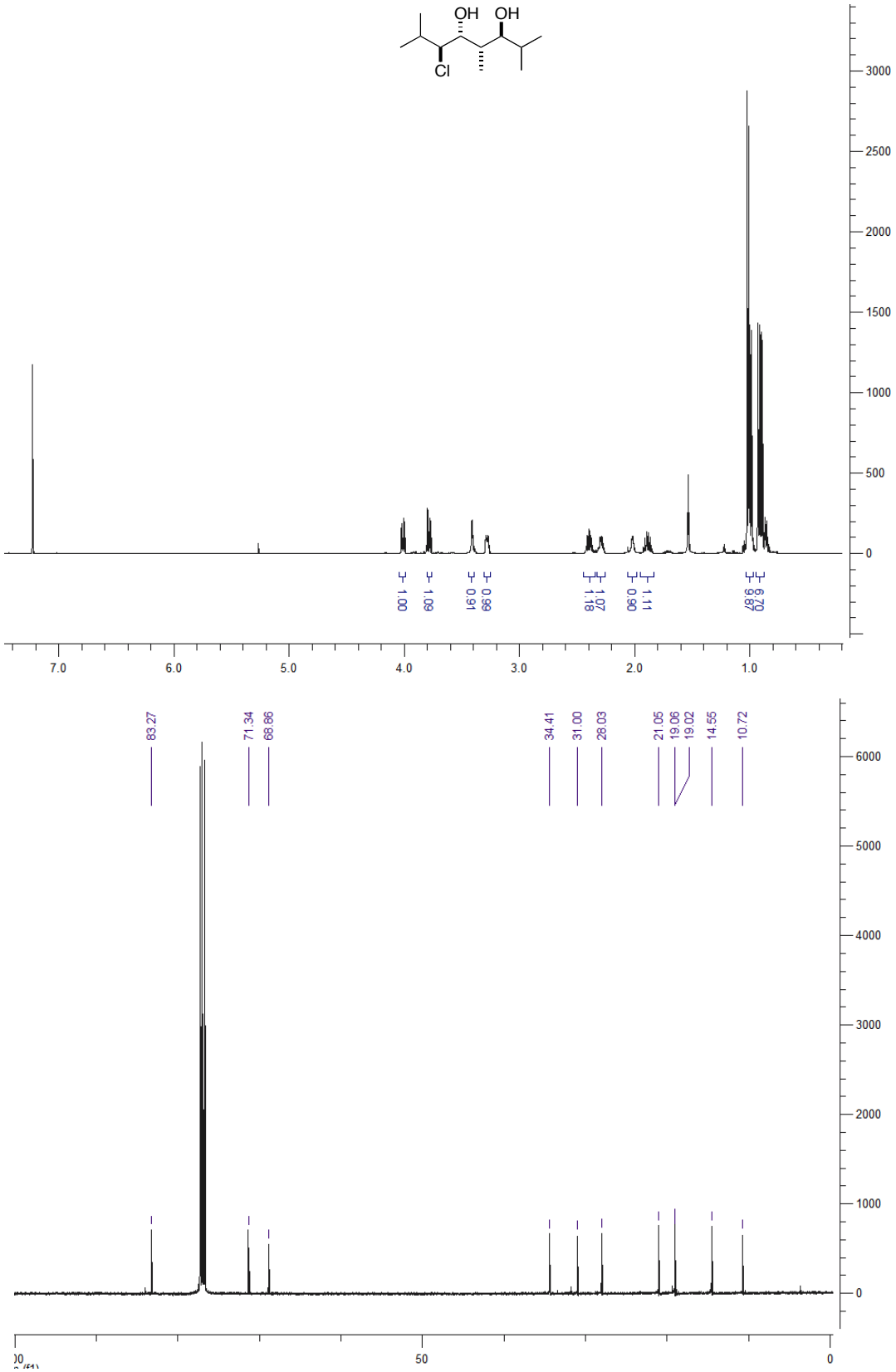




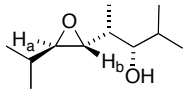
(2*S,3*S**,5*S**)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (61b)**



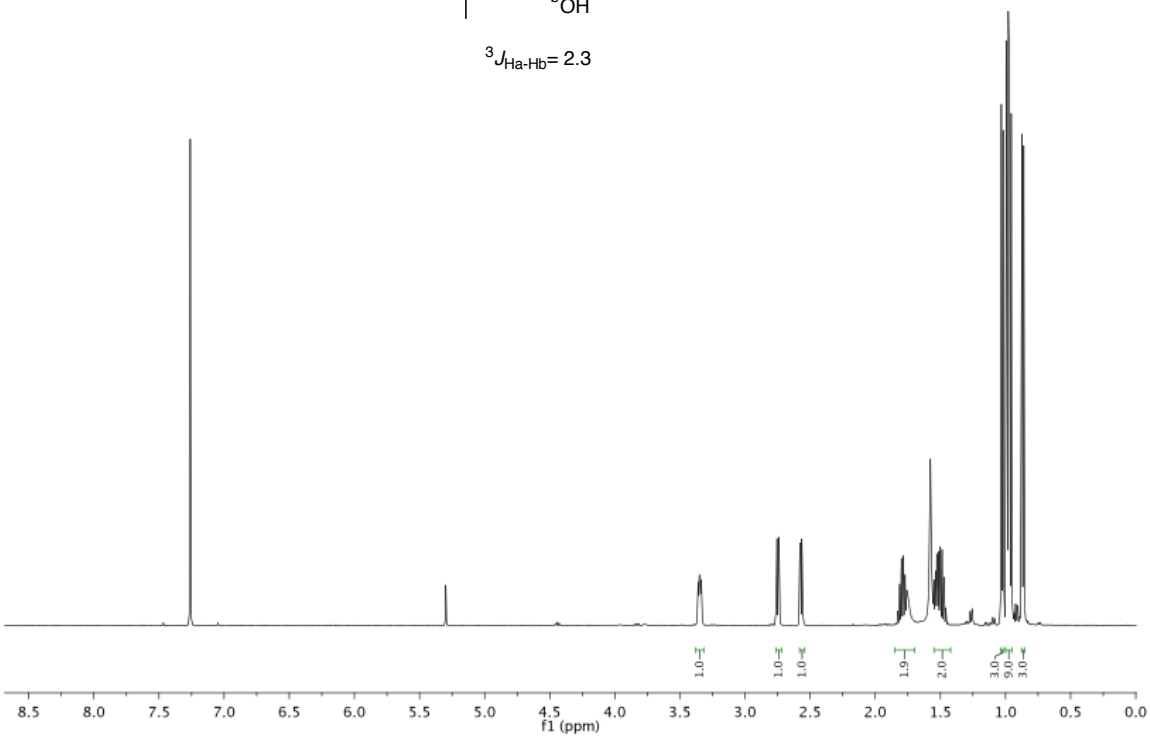
(2*S*,3R*,5R)-2-Chloro-6,6-dimethyl-1-phenylheptane-3,5-diol (63b)**

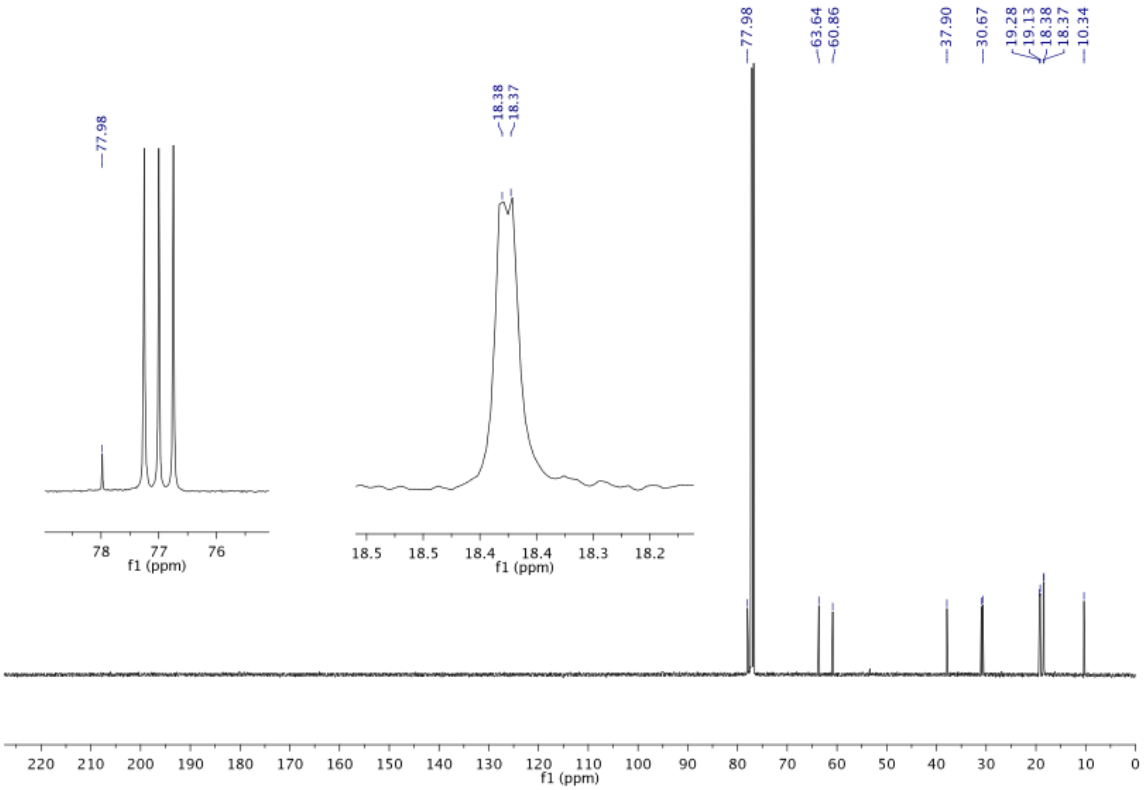


(2*R,3*S**)-2-((2*R**,3*R**)-3-Isopropyloxiran-2-yl)-4-methylpentan-3-ol (62b)**

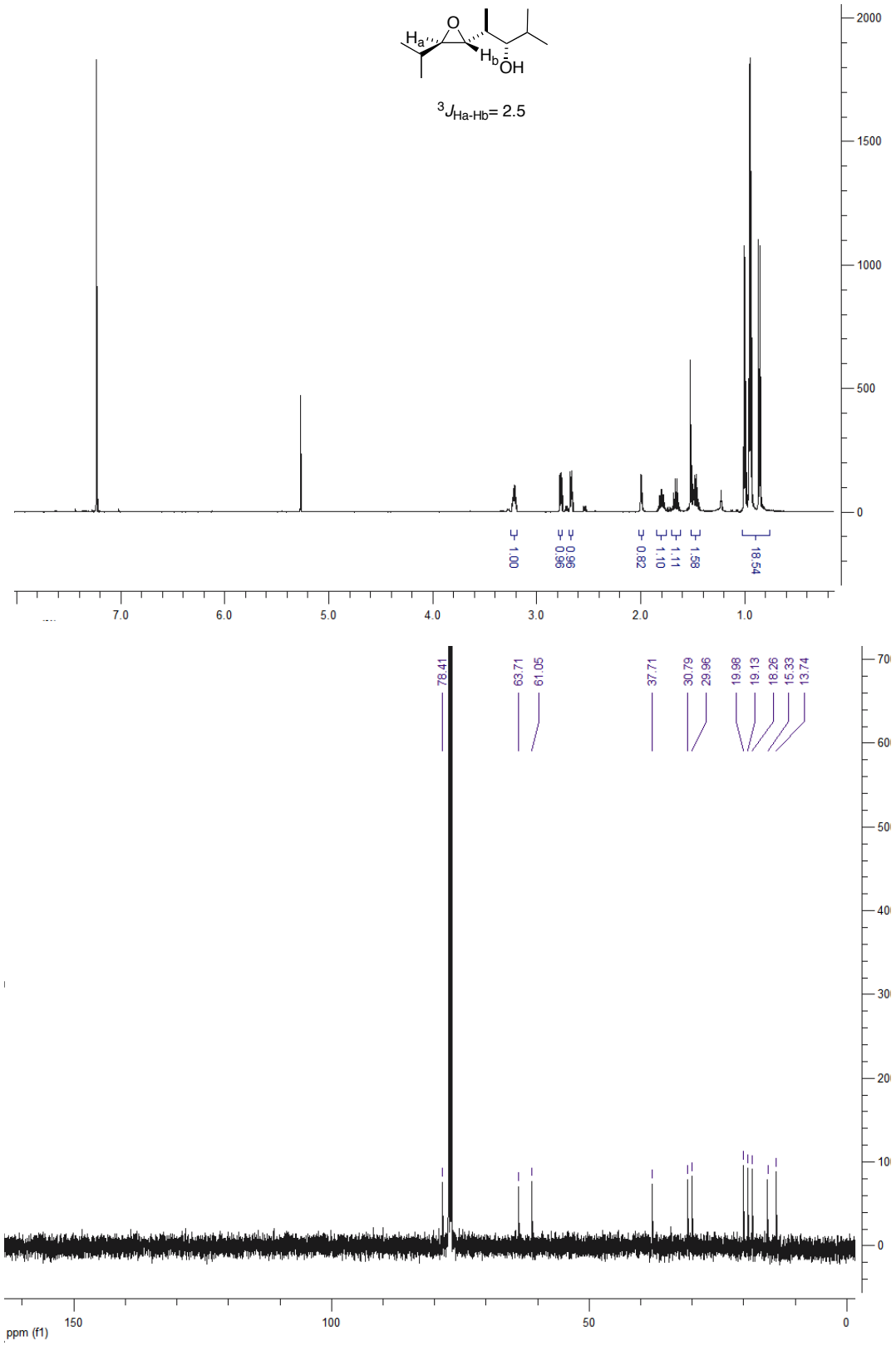


$^{3}J_{Ha\text{-}Hb}$= 2.3





(2*S*,3S)-2-((2*R*,3R**)-3-Isopropyloxiran-2-yl)-4-methylpentan-3-ol (64b)**



[1] P. Restorp, P. Somfai, *Org. Lett.*, **2005**, *7*, 893-895
[2] T. Ankner, G. Hilmersson, *Org. Lett.* **2009**, *11*, 503-506

[3] T. Ankner, G. Hilmersson, *Org. Lett.* **2009**, *11*, 503-506