Supporting Information

Rapid Construction of the 6/6/5 tricyclic framework via a tandem radical cyclization reaction and its application to synthesis of 5-*epi*-7-deoxy-Isoabietenin A

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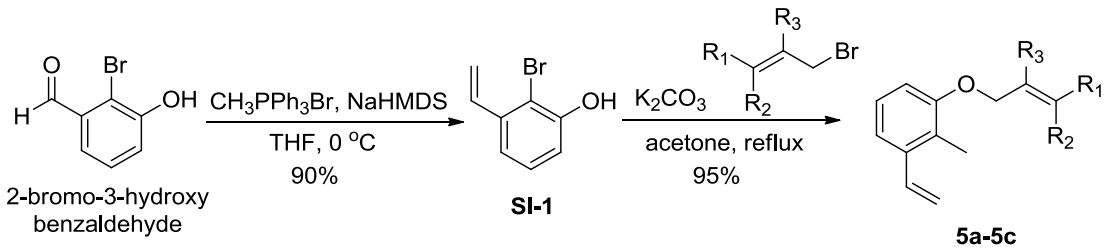
General information

All commercially available reagents were used without further purification unless otherwise noted.Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates. Melting points were measured on a digital Koffer apparatus and are uncorrected. NMR spectra were recorded on a400 MHz (^{1}H, 400 MHz; ^{13}C, 100 MHz) or 600 MHz (^{1}H, 600 MHz; ^{13}C, 150 MHz) spectrometer at 298 K.The chemical shifts (δ) are reported in ppm with referenceto internal residual solvent [^{1}H NMR, $CDCl_3$ (7.26), d_6-DMSO (2.54); ^{13}C NMR,$CDCl_3$ (77.0), d_6-DMSO (40.0)]. Coupling constants (*J*)are reported in Hz. High-resolution mass spectra (HRMS) were recorded on a FT-ICR spectrometer using electrospray ionization (ESI). Infrared spectra were recorded on a 670 FT-IR spectrometer.

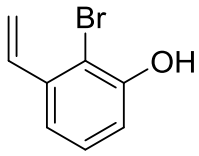
Procedure for Preparation of precursor 5a-5g

Method A



5a-**5c** were prepared according to the method A.

Synthesis of **5a** is representative.



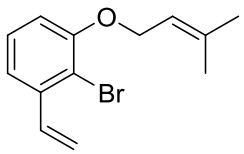
SI-1

To a suspension of methyltriphenylphosphonium bromide (11.8 g, 33.0 mmol) in dried THF (100 mL) at 0 °C under Ar was added NaHMDS (2 M in THF, 16.5 mL, 33.0 mmol) and the reaction mixture was stirred at 25 °C for 1 h. The suspension was cooled to 0 °C and a solution of 2-bromo-3-hydroxybenzaldehyde (3.02 g, 15.0 mmol) in dried THF (10 mL) was added dropwise. The reaction mixture was warmed to 25

^{o}C and stirred for 2 h. The reaction was quenched by the saturated aqueous NH_4Cl solution. The mixture was extracted with EA (3 × 50 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 20/1) to give pure **SI-1** (2.69 g, 90% yield) as a white solid. R_f = 0.48 (hexane/EtOAc = 5:1); m.p. 43-44 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.90 – 6.79 (m, 2H), 5.64 (s, 1H), 5.57 (d, *J* = 17.3 Hz, 1H), 5.24 ppm (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.2, 138.1, 135.4, 128.2, 118.6, 117.2, 114.8, 111.8 ppm; HRMS (ESI): *m/z* calcd for C_8H_8BrO $[M + H]^+$ 198.9759, found 198.9758; IR (neat) ν_{max} 3495, 1573, 1463, 1437, 1408, 1287,1262, 1191, 1021, 920, 789 cm^{-1}.

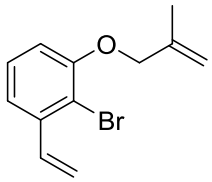
5a

To a solution of **SI-1** (1.55 g, 7.80 mmol) and potassium carbononate (2.16 g, 15.6 mmol) in acetone (50 mL) was added allyl bromide (0.80 mL, 9.4 mmol). The resulting mixture was then stirred at reflux for 10 h. After filtration through celite and washed with ethyl acetate, the solution was removed under reduced pressure and the residue was chromatographed on silica gel (hexane/EA = 100:1) to afford pure **5a** (1.8 g, 95%) as a colorless oil. R_f = 0.55 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 – 7.09 (m, 3H), 6.79 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.13 – 6.00 (m, 1H), 5.68 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.49 (ddd, *J* = 17.2, 3.1, 1.5 Hz, 1H), 5.36 (dd, *J* = 11.0, 0.9 Hz, 1H), 5.30 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.63 – 4.56 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.0, 139.2, 136.1, 132.6, 127.6, 119.1, 117.6, 116.9, 113.8, 112.3, 69.8 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}BrO$ $[M + H]^+$ 239.0066, found 239.0069; IR (neat) ν_{max} 3086, 2921, 1563, 1466, 1290, 1268, 1027, 784 cm^{-1}.



5b

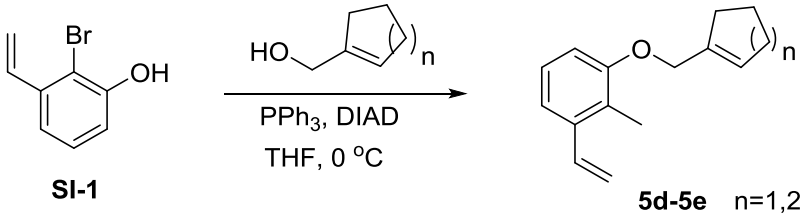
5b was prepared according to the method A. R_f = 0.60 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.07 (m, 3H), 6.80 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.67 (d, *J* = 17.4 Hz, 1H), 5.50 (t, *J* = 6.5 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 1.78 (s, 3H), 1.74 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.35, 139.12, 137.98, 136.19, 127.57, 119.41, 118.85, 116.70, 113.90, 112.45, 66.29, 25.76, 18.28 ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}BrO$ $[M + H]^+$ 267.0379, found 267.0381; IR (neat) ν_{max} 2974, 2928, 2731, 1674, 1562, 1461, 1381, 1254, 1024, 917,783 cm^{-1}.



5c

5c was prepared according to the method A. R_f = 0.70 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.05 (m, 3H), 6.78 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.69 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.36 (dd, *J* = 11.0, 1.0 Hz, 1H), 5.17 (s, 1H), 5.01 (d, *J* = 1.1 Hz, 1H), 4.49 (s, 2H), 1.86 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.09, 140.24, 139.19, 136.12, 127.60, 118.99, 116.83, 113.78, 112.83, 112.13, 72.61, 19.36 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{14}BrO$ $[M + H]^+$ 253.0223, found 253.0225; IR (neat) ν_{max} 3081, 2976, 2917, 1563, 1466, 1290, 1266, 1078, 1030, 907, 784 cm^{-1}.

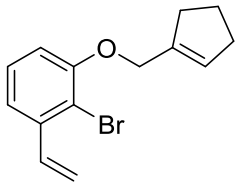
method B.



SI-1 **5d-5e** n=1,2

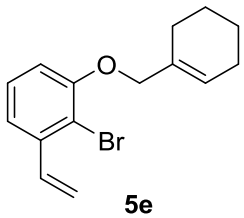
5d-**5e** were prepared according to the method B.

Synthesis of **5a** is representative.



5d

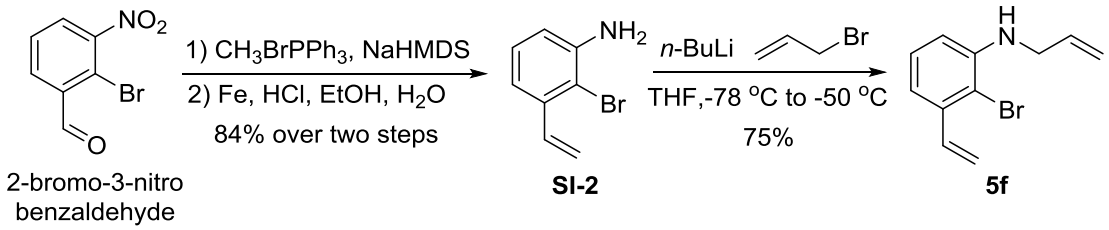
A solution of phenol **SI-1** (715 mg, 3.60 mmol), alcohol (388 mg, 3.96 mmol) and PPh_3 (1.4 g, 5.4 mmol) was stirred in dried THF (40 mL) at 0 ^oC under Ar. To this mixture was added dropwise diisopropyl azodiformate (1.07 mL, 5.40 mmol) in THF (5 mL) over a period of 10 min, and the resulting pale yellow solution was stirred at 0 ^oC for 8 h. The solvent was evaporated under reduced pressure and the resulting oil purified by flash column chromatography (silicagel, hexane/EA = 100/1) to give pure compound **5d** (682 mg, 68.0% yield) as a colorless oil. R_f = 0.63 (hexane/EtOAc = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.29 – 7.04 (m, 3H), 6.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.84 – 5.76 (m, 1H), 5.68 (dd, *J* = 17.4, 1.0 Hz, 1H), 5.35 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.63 (s, 2H), 2.49 – 2.33 (m, 4H), 1.94 ppm (tt, *J* = 10.7, 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.26, 139.44, 139.10, 136.14, 128.06, 127.57, 118.85, 116.75, 113.80, 112.11, 68.32, 32.77, 32.45, 23.19 ppm; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}BrO$ $[M + H]^+$ 279.0379, found 279.0378; IR (neat) ν_{max} 2949, 2847, 1562, 1465, 1400, 1268, 1031, 916, 783, 724 cm^{-1}.



5e

5e were prepared according to the method B. R_f = 0.70 (hexane/EtOAc = 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.24 – 7.05 (m, 3H), 6.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.85 (s, 1H), 5.67 (d, *J* = 17.4 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 4.42 (s, 2H), 2.17 – 1.99 (m, 4H), 1.76 – 1.55 ppm (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.35, 139.06, 136.17, 133.22, 127.55, 125.37, 118.80, 116.68, 113.90, 112.37, 73.70, 25.62, 24.95, 22.37, 22.26 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{18}BrO$ $[M + H]^+$ 293.0536, found 293.0534; IR (neat) ν_{max} 2925, 2855, 2360, 1561, 1465, 1265, 1028, 918, 783 cm^{-1}.

Synthesis of **5f**.



2-bromo-3-nitro benzaldehyde

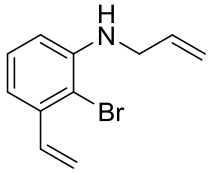
SI-2

5f

SI-2

To a suspension of methyltriphenylphosphonium bromide (1.63 g, 4.56 mmol) in dried THF (20 mL) at 0 ^{o}C under Ar was added NaHMDS(2M in THF, 2.39 mL, 4.78 mmol)and the reaction mixture was stirred at 25 ^{o}C for 1 h. The suspension was cooled to 0 ^{o}C and a solution of 2-bromo-3-nitrobenzaldehyde (1.00 g, 4.35 mmol) in dried THF (5 mL) was added dropwise. The reaction mixture was warmed to 25 ^{o}C and stirred for 2 h. The reaction was quenched by the saturated aqueous NH_4Cl solution. The mixture was extracted with EA(3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silicagel, hexane/EA =100/1) to give nitrobenzene (942 mg, 95% yield) as a colorless oil.

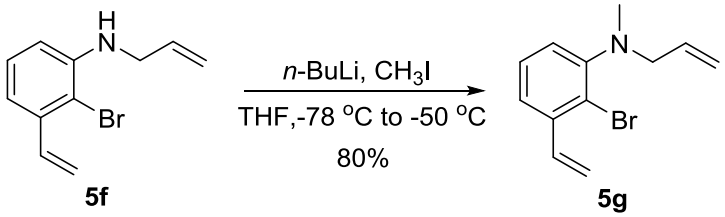
Fe powder (1.84 g, 33.0 mmol), H_2O (3.3 mL), and concd HCl (55 mg) were added to a solution of nitrobenzene (0.75 g, 3.3 mmol) in EtOH (22 mL). The mixture was heated to reflux ang stirred vigorously for 90 min. The mixture was cooled to 25 oC, EtOAc (100 mL) was added, the resulting mixture was dried with Na_2SO_4 and filtered, and the solvent was evaporated to give aniline **SI-2** (575 mg, 88%) as a colorless oil. R_f = 0.18 (hexane/EtOAc = 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 = (dd, *J* = 17.6, 10.4 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 5.65 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H), 4.13 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.31, 138.35, 136.41, 127.64, 116.53, 116.43, 114.64, 110.70 ppm; HRMS (ESI): *m/z* calcd for C_8H_9BrN $[M + H]^+$ 197.9913, found 197.9911; IR (neat) ν_{max} 3469, 3378, 1610, 1466, 1405, 1017, 918, 785 cm^{-1}.



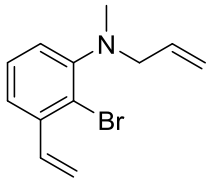
5f

To a solution of aniline (475 mg, 2.40 mmol) in THF (15 mL) was added *n*-BuLi (2.5 M in hexane, 0.96 mL, 2.4 mmol) under Ar at -78 ^{o}C. The resulting solution was allowed to stir at -78 ^{o}C for 0.5 h. Allylbromide was then added at -78 oC and the reaction mixture was allowed to stir at -50 ^{o}C for 16 h. Water was then added to quench the reaction. The mixture was extracted with Et_2O(3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silicagel, hexane/EA =100/1) to giveaniline(428 mg, 75% yield) as a colorless oil. R_f = 0.68 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 – 7.01 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.94 (ddt, *J* = 17.0, 10.3, 5.1 Hz, 1H), 5.65 (d, *J* = 17.3 Hz, 1H), 5.28 (dd, *J* = 23.9, 6.2 Hz, 2H), 5.18 (dd, *J* = 10.3, 0.9 Hz, 1H), 4.62 (s, 1H), 3.82 ppm (t, *J* = 5.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.85, 138.09, 136.73, 134.58, 127.78, 116.45, 116.33, 115.20, 111.12, 110.53, 46.37 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}BrN$ $[M + H]^+$ 238.0226, found 238.0227; IR (neat) ν_{max} 3413, 3083, 2924, 1588, 1568, 1496, 1468, 1317, 1014, 917 cm^{-1}.

Synthesis of **5g**.



5f **5g**

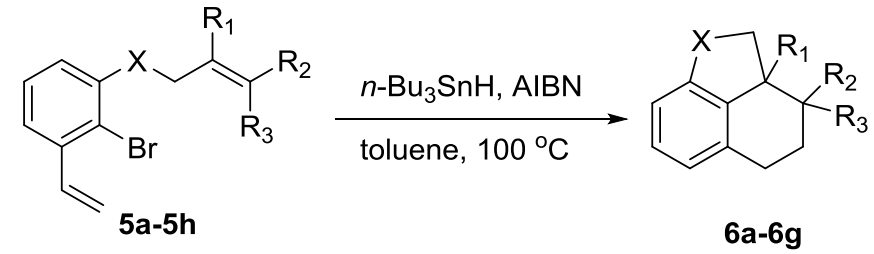


5g

To a solution of (0.20g, 0.84 mmol) in THF (15 mL) was added *n*-BuLi (2.5 M in hexane, 0.34 mL, 0.84 mmol) under Ar at -78 ^{o}C. The resulting solution was allowed to stir at -78 ^{o}C for 0.5 h. CH_3I (0.060 mL, 0.84 mmol) was then added at -78 ^{o}C and the reaction mixture was allowed to stir at -50 ^{o}C for 16 h. Water was then added to quench the reaction. The mixture was extracted with Et_2O(3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silicagel, hexane/EA =100/1) to give aniline **5g** (169 mg, 80% yield) as a colorless oil. R_f = 0.62 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (ddd, *J* = 28.4, 15.1, 8.2 Hz, 3H), 7.00 (dd, *J* = 7.0, 2.4 Hz, 1H), 5.94 (ddt, *J* = 22.8, 10.2, 6.2 Hz, 1H), 5.63 (d, *J* = 17.4 Hz, 1H), 5.25 (ddd, *J* = 27.0, 26.3, 10.5 Hz, 3H), 3.58 (d, *J* = 6.2 Hz, 2H), 2.72 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.51, 139.51, 137.13, 135.07, 127.35, 121.73, 121.64, 121.07, 117.65, 116.51, 59.69, 40.60 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}BrN$ $[M + H]^+$ 252.0382, found 252.0383; IR (neat) ν_{max} 3075, 2925, 2849, 2793, 1562, 1463, 1394, 1237, 1021, 987, 917, 796, 728 cm^{-1}.

Synthesis of 6a-6h

General Procedure for radical cascade annulation. (**method C**)



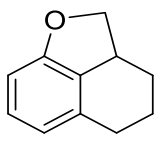
5a-5h

X=O, NH, NCH_3

6a-6g

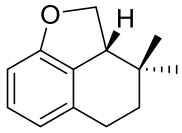
6a-**6g** were prepared according to the method C.

Synthesis of **6a** is representative.



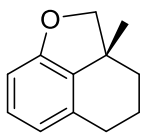
6a

To a stirred solution of **5a** (100 mg, 0.418 mmol) in degassed toluene (10 mL) at 100 ^{o}C under Ar was added dropwise a solution of *n*-Bu_3SnH (0.14 mL, 0.50 mmol) and AIBN (27 mg, 0.17 mmol) in degassed toluene (5 mL) over 2 h. The reaction was stirred at 100 ^{o}C for additional 2 h and then concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, hexane/EA = 200/1) to give **SI-3** (42 mg, 63% yield) as a colorless oil. R_f = 0.42 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.78 (t, *J* = 8.3 Hz, 1H), 3.97 (dd, *J* = 12.2, 8.3 Hz, 1H), 3.38 – 3.26 (m, 1H), 2.83 (dd, *J* = 17.5, 6.9 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.19 – 2.06 (m, 2H), 1.82 – 1.69 (m, 1H), 1.38 – 1.29 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.8, 134.7, 129.1, 128.0, 119.6, 106.2, 79.5, 38.8, 26.2, 25.3, 23.1 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}O$ $[M + H]^+$ 161.0961, found 161.0959; IR (neat) ν_{max} 2930, 1605, 1451, 1234, 1053, 931, 765 cm^{-1}.



6b

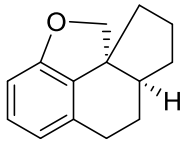
6b was prepared according to the method C. R_f = 0.48 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 1H), 4.11 (dd, *J* = 12.5, 8.4 Hz, 1H), 3.31 – 3.19 (m, 1H), 2.88 – 2.75 (m, 1H), 2.66 (dd, *J* = 18.1, 9.2 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.09 (s, 3H), 0.75 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.13, 133.94, 127.79, 127.48, 119.17, 106.04, 75.22, 48.51, 38.61, 31.56, 30.15, 24.26, 18.97 ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O$ $[M + H]^+$ 189.1273, found 189.1275; IR (neat) ν_{max} 2922, 2853, 1504, 1453, 1355, 1238, 1110, 1020, 924, 771 cm^{-1}.



6c

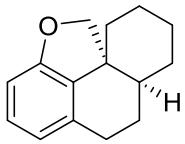
6c was prepared according to the method C. R_f = 0.57 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, MeOD) δ = 6.94 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.47

(d, *J* = 7.8 Hz, 1H), 4.36 (d, *J* = 8.0 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 2.85 – 2.70 (m, 1H), 2.61 – 2.47 (m, 1H), 2.02 (ddd, *J* = 9.9, 7.2, 3.4 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.54 – 1.41 (m, 1H), 1.21 ppm (s, 3H); ^{13}C NMR (101 MHz, MeOD) δ = 157.73, 133.52, 132.64, 127.10, 118.90, 105.30, 86.02, 39.01, 31.21, 23.57, 22.85, 18.56 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O$ $[M + H]^+$ 175.1117, found 175.1116; IR (neat) ν_{max} 2924, 2867, 1604, 1450, 1238, 1031, 929, 763, 740 cm^{-1}.



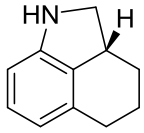
6d

6d was prepared according to the method C. R_f = 0.52 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.52 (dd, *J* = 7.8, 3.9 Hz, 2H), 2.21 – 2.02 (m, 3H), 1.82 – 1.70 (m, 2H), 1.56 – 1.39 (m, 3H), 1.30 – 1.21 ppm (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.48, 137.33, 132.34, 127.36, 118.93, 106.78, 86.77, 50.04, 40.63, 40.00, 32.35, 31.15, 24.71, 24.15 ppm; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O$ $[M + H]^+$ 201.1274, found 201.1273; IR (neat) ν_{max} 2935, 2860, 1625, 1504, 1467, 1225, 1059, 1024, 932, 778, 743 cm^{-1}.



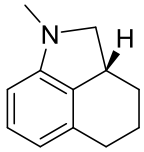
6e

6e was prepared according to the method C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (t, *J* = 7.7 Hz, 1H), 6.66 (dd, *J* = 7.6, 0.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 0.6 Hz, 1H), 4.72 (d, *J* = 8.1 Hz, 1H), 3.96 (d, *J* = 8.1 Hz, 1H), 2.93 (dd, *J* = 17.6, 7.8 Hz, 1H), 2.69 (ddd, *J* = 17.8, 10.2, 8.0 Hz, 1H), 2.36 – 2.16 (m, 1H), 1.81 (d, *J* = 12.5 Hz, 1H), 1.74 – 1.60 (m, 4H), 1.60 – 1.43 ppm (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.62, 134.25, 133.83, 127.88, 119.50, 106.33, 83.50, 43.28, 36.38, 29.80, 29.01, 25.60, 23.86, 22.98, 19.69 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{19}O$ $[M + H]^+$ 215.1430, found 215.1430; IR (neat) ν_{max} 2925, 2862, 1603, 1448, 1237, 936, 760, 735 cm^{-1}.



6f

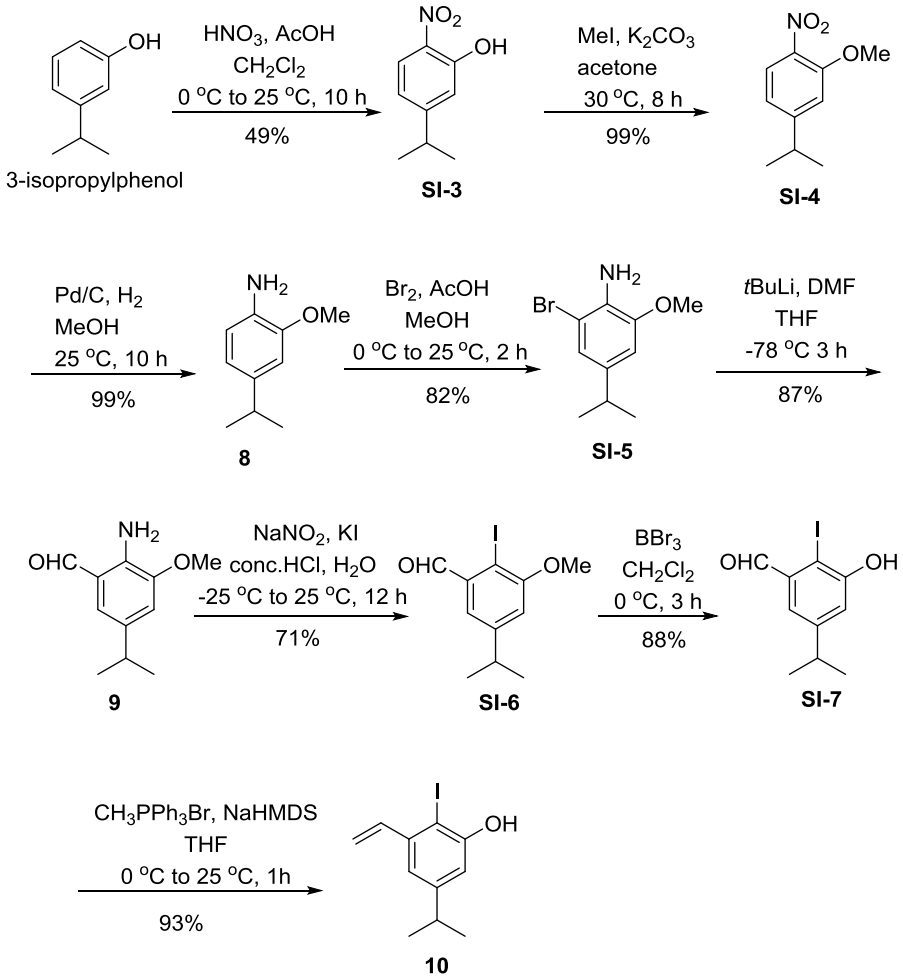
6f was prepared according to the method C. R_f = 0.34 (hexane/EtOAc = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.96 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 3.77 – 3.55 (m, 2H), 3.16 – 3.01 (m, 2H), 2.79 (dd, *J* = 17.3, 6.7 Hz, 1H), 2.71 – 2.57 (m, 1H), 2.10 (dddd, *J* = 7.9, 6.2, 5.8, 2.8 Hz, 2H), 1.88 – 1.69 (m, 1H), 1.37 ppm (ddd, *J* = 15.8, 9.9, 6.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.55, 134.03, 130.92, 127.40, 117.87, 106.16, 56.33, 38.93, 26.90, 25.80, 23.48 ppm; HRMS (ESI): *m/z* calcd for $C_{11}H_{14}N$ $[M + H]^+$ 160.1121, found 160.1118; IR (neat) ν_{max} 3371, 2925, 2863, 1603, 1454, 1247, 1140, 766, 736 cm^{-1}.



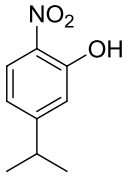
6g

6g was prepared according to the method C. R_f = 0.29 (hexane/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03 (t, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 7.6 Hz, 1H), 3.62 (t, *J* = 7.8 Hz, 1H), 3.04 (dt, *J* = 11.5, 5.7 Hz, 1H), 2.77 (d, *J* = 5.8 Hz, 1H), 2.72 (s, 3H), 2.62 (dd, *J* = 12.4, 8.0 Hz, 2H), 2.18 – 2.02 (m, 2H), 1.82 – 1.68 (m, 1H), 1.39 – 1.25 ppm (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.75, 133.42, 131.86, 127.62, 117.50, 104.36, 64.96, 37.96, 36.81, 26.71, 25.75, 23.23 ppm; HRMS (ESI): *m/z* calcd for $C_{12}H_{16}N$ $[M + H]^+$ 174.1477, found 174.1279; IR (neat) ν_{max} 2927, 2852, 2795, 1622, 1597, 1479, 1449, 1260, 1141, 958, 763, 732 cm^{-1}.

Synthesis of Precursors 16 and 18



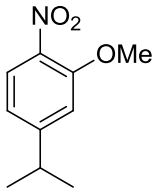
Scheme 2. Synthesis of phenol **10.** NaHMDS = sodium hexamethyldisilazide.



SI-3

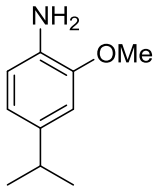
To a solution of 3-isopropylphenol (6.81 g, 50.0 mmol) in CH_2Cl_2 (170 mL) and AcOH (21 mL), was dropwise added HNO_3 (3.62 mL, 52.5 mmol) in AcOH (17 mL) at 0 °C and stirred for 2 h. The solution was then stirred at 25 °C for additional 10 h. After neutralizing with saturated $NaHCO_3$ aqueous solution, the mixture was

extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 200/1) to give 5-isopropyl-2-nitrophenol **SI-3** (4.44 g, 49% yield) as a yellow oil. R_f = 0.56 (hexane/EA = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.00 (d, *J* = 8.8, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.92 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 155.3, 131.7, 125.0, 119.1, 117.0, 77.3, 77.0, 76.7, 34.4, 23.1; HRMS (ESI): *m/z* calcd for $C_9H_{12}NO_3$ $[M + H]^+$ 182.0811, found 182.0812; IR (neat) ν_{max} 3233, 2966, 2932, 2873, 1624, 1585, 1533, 1442, 1270, 1233, 1182, 1048, 950, 876, 761, 680, 463 cm^{-1}.



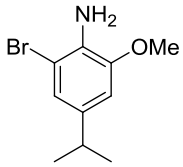
SI-4

To a solution of 5-isopropyl-2-nitrophenol **SI-3** (3.04 g, 16.8 mmol) in acetone, was added K_2CO_3 (4.64 g, 33.6 mmol) and MeI (5.3 mL, 84 mmol). The solution was then stirred at 30 ^{o}C for 8 h. After removal of the solvent *in vacuo*, the resultant residue was taken up in water and the aqueous mixture was extracted with EA (3 × 50 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 100/1) to give nitrobenzene **SI-4** (3.27 g, 99% yield) as a light yellow oil. R_f = 0.33 (hexane/EA = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 1.3 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 2.92 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.2, 137.2, 125.8, 118.1, 111.4, 56.2, 34.4, 23.4; HRMS (ESI): *m/z* calcd for $C_{10}H_{13}NO_3K$ $[M + K]^+$ 234.0527, found 234.0526; IR (neat) ν_{max} 2964, 2872, 1606, 1516, 1463, 1417, 1352, 1281, 1255, 1184, 1026, 931, 866, 830, 758, 711, 653, 462 cm^{-1}.



8

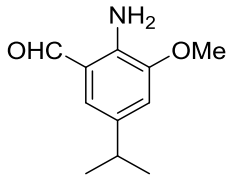
To a solution of nitrobenzene **SI-4** (2.89 g, 14.8 mmol) in methanol (30 mL) was added 10% Pd/C (800 mg). The reaction vessel was evacuated and back-filled with hydrogen (1 atm). The reaction mixture was stirred under hydrogen overnight, then filtered through Celite and concentrated *in vacuo* to give 4-isopropyl-2-methoxyaniline **8** (2.44 g, 99% yield) as a red solid. R_f = 0.34 (hexane/EA = 5/1); mp: 47–48 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82–6.67 (m, 3H), 3.92 (s, 3H), 3.75 (s, 2H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 139.3, 133.7, 118.2, 114.8, 108.8, 55.2, 33.6, 24.12; HRMS (ESI): *m/z* calcd for $C_{10}H_{16}NO$ $[M + H]^+$ 166.1226, found 166.1223; IR (neat) ν_{max} 3411, 3307, 3012, 2956, 2924, 1837, 1587, 1521, 1464, 1425, 1359, 1282, 1242, 1174, 1130, 1095, 1028, 921, 850, 814, 743, 638, 541 cm^{-1}.



SI-5

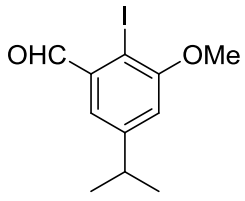
To a sloution of 4-isopropyl-2-methoxyaniline **8** (2.02 g, 12.2 mmol) in methanol (20 mL) was added slowly a solution of bromine (0.63 mL, 12 mmol) in AcOH (6 mL) at 0 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 2 h. The reaction was quenched by an aqueous solution of $Na_2S_2O_3$. The mixture was concentrated to remove the solvent. The residue was dissolved in a saturated aqueous solution of $NaHCO_3$ and extracted with EA (3 × 50 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 100/1) to give aniline **SI-5** (2.44 g, 82% yield) as a red oil. R_f = 0.44 (hexane/EA = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 1.6 Hz, 1H), 6.62 (d, *J* = 1.5 Hz, 1H), 4.08 (s, 2H), 3.87 (s, 3H), 2.80 (hept, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 147.4, 139.3, 132.4, 121.6, 108.5, 107.8, 55.7, 33.6, 24.1; HRMS (ESI): *m/z* calcd for $C_{10}H_{15}NOBr$ $[M + H]^+$ 244.0332, found 244.0329; IR (neat) ν_{max} 3475, 3378, 2958, 2868, 1617, 1574, 1462, 1419, 1283, 1224, 1174, 1137, 1043, 939, 845, 745, 640 cm^{-1}.



9

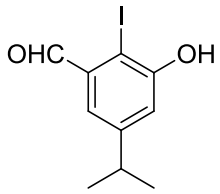
To a solution of aniline **SI-5** (0.949 g, 3.89 mmol) in dried THF was dropwise added *t*-BuLi (1.3 M in pentane, 9.6 mL, 12 mmol) at -78 °C under Ar. The reaction mixture was allowed to stir at -78 °C for 1 h. To this mixture was added DMF (0.90 mL, 12 mmol) slowly. The solution was then stirred at -78 °C for 2 h. The reaction was quenched by the saturated aqueous solution of NH_4Cl. The mixture was extracted with EA (3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 100/1) to give 2-amino-5-isopropyl-3-methoxybenzaldehyde **9** (657 mg, 87% yield) as a yellow oil. R_f = 0.40 (hexane/EA = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 6.95 (d, *J* = 1.1 Hz, 1H), 6.78 (d, *J* = 1.3 Hz, 1H), 6.25 (s, 2H), 3.88 (s, 3H), 2.84 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 146.6, 139.1, 135.7, 122.8, 117.8, 112.9, 55.6, 33.3, 23.9; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}NO_2$ $[M + H]^+$ 194.1176, found 194.1179; IR (neat) ν_{max} 3490, 3360, 2958, 2868, 2733, 1660, 1554, 1477, 1399, 1304, 1273, 1230, 1179, 1139, 1055, 951, 861, 733, 642 cm^{-1}.



SI-6

To a solution of 2-amino-5-isopropyl-3-methoxybenzaldehyde **9** (464 mg, 2.40 mmol) in concentrated HCl (13 mL) was added dropwise a solution of $NaNO_2$ (199 mg, 2.88

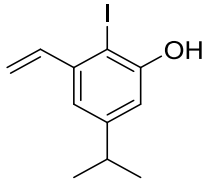
mmol) in water (10 mL) at -25 °C. The mixture was stirred at this temperature for 1.5 h. A solution of KI (4.00 g, 24.0 mmol) in water (15 mL) was added dropwise and the reaction mixture was stirred for 1 h at -25 °C and 10 h at 25 °C. The dark red-brown mixture was extracted with EA (3 × 20 mL). The organic layers were combined, washed sequently with 10% NaOH, water, 5% $NaHSO_3$, water and brine, dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 100/1) to give pure benzaldehyde **SI-6** (452 mg, 62% yield) as a yellow solid. R_f = 0.48 (hexane/EA = 10/1); mp: 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (d, *J* = 1.3 Hz, 1H), 7.38 (s, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 3.94 (s, 3H), 2.93 (hept, *J* = 6.9 Hz, 1H), 1.26 (dd, *J* = 6.9, 0.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 158.2, 151.0, 136.2, 120.2, 114.8, 90.6, 56.7, 33.9, 23.6; HRMS (ESI): *m/z* calcd for $C_{11}H_{14}IO_2$ $[M + H]^+$ 305.0033, found 305.0030; IR (neat) ν_{max} 2961, 2866, 2741, 1692, 1585, 1454, 1415, 1384, 1310, 1288, 1275, 1180, 1068, 1011, 922, 861, 713, 646, 514 cm^{-1}.



SI-7

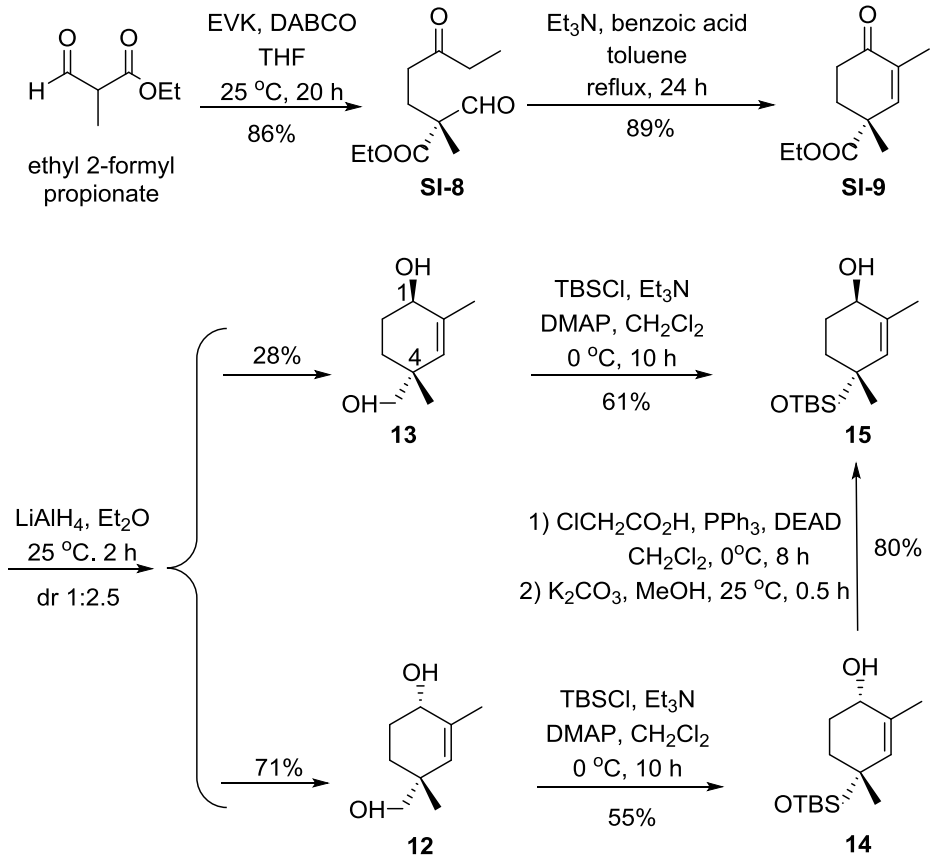
To a solution of benzaldehyde **SI-6** (242 mg, 0.800 mmol) in dried CH_2Cl_2 (10 mL) was added dropwise a solution of BBr_3 (409 mg, 2.00 mmol) in dried CH_2Cl_2 (2 mL) at 0 °C under Ar. The reaction was monitored by TLC. The reaction was quenched by water at 0 °C once the reaction was completed. The yield would decrease if the reaction was not quenched timely. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 20/1) to give compound **SI-7** (204mg, 88% yield) as a white solid. R_f = 0.60 (hexane/EA = 3/1); mp: 174–176 °C; ^{1}H NMR (400 MHz, d_6-DMSO) δ 10.57 (s, 1H), 9.88 (s, 1H), 7.71–7.70 (m, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 3.36 (hept, *J* = 6.9 Hz, 1H), 1.67 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 205.9, 167.6, 161.3, 147.1, 129.9, 129.0, 97.5, 43.8, 33.5;

HRMS (ESI): *m/z* calcd for $C_{10}H_{13}NO_3Na$ $[M + Na]^+$ 312.9696, found 312.9695; IR (neat) ν_{max} 3439, 2930, 2858, 2719, 1731, 1472, 1437, 1388, 1362, 1256, 1216, 1131, 1105, 1006, 837, 779, 669 cm^{-1}.

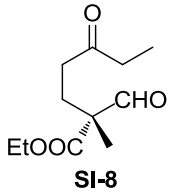


10

To a suspension of methyltriphenylphosphonium bromide (317 mg, 0.890 mmol) in dried THF (15 mL) at 0 ^oC under Ar was added NaHMDS (2 M in THF, 0.44 mL, 0.89 mmol) and the reaction mixture was stirred at 25 ^oC for 1 h. The suspension was cooled to 0 ^oC and a solution of compound **SI-7** (117 mg, 0.400 mmol) in dried THF (5 mL) was added dropwise. The reaction mixture was warmed to 25 ^oC and stirred for 2 h. The reaction was quenched by the saturated aqueous NH_4Cl solution. The mixture was extracted with EA (3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 20/1) to give pure phenol **10** (107 mg, 93% yield) as a white solid. R_f = 0.77 (hexane/EA = 3/1); mp: 52–53 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 1.8 Hz, 1H), 6.93–6.81 (m, 2H), 5.65 (dd, *J* = 17.2, 0.9 Hz, 1H), 5.48 (s, 1H), 5.33 (dd, *J* = 10.9, 0.9 Hz, 1H), 2.87 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 150.8, 141.4, 140.6, 117.3, 117.0, 112.0, 88.2, 33.7, 23.7; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}OKI$ $[M + K]^+$ 326.9643, found 326.9659; IR (neat) ν_{max} 3475, 3086, 2960, 2925, 2869, 1567, 1465, 1422, 1311, 1278, 1258, 1179, 1090, 1009, 982, 917, 860, 678, 544 cm^{-1}.

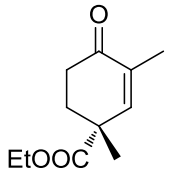


Scheme 3. Synthesis of secondary alcohol **15**. EVK = ethyl vinyl ketone, DABCO = 1,4-diazabicyclooctane, TBSCl = tert-butyldimethylsily chloride, DMAP = 4-dimethylaminopyridine, DEAD = diethyl azodiformate.



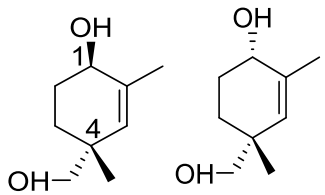
DBACO (6.03 g, 53.8 mmol) and ethyl vinyl ketone (4.2 mL, 42 mmol) were added to a stirred solution of ethyl 2-formylpropionate (5.00 g, 38.4 mmol) in THF (50 mL) at 25 °C. The resulting mixture was stirred at 25 °C for 20 h. The mixture was cooled to 0 °C. Then, 3 M HCl (50 mL) was added and the mixture was stirred at 0 °C for 10 min. The mixture was extacted with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo* to provide ethyl 2-formyl-2-methyl-5-oxoheptanoate **SI-8** (7.05 g, 86% yield) as a colorless crude oil. R_f = 0.49 (hexane/EA = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.51–2.31 (m, 4H), 2.11 (dd, *J* = 9.7, 5.8 Hz, 1H), 2.07–2.01 (m, 1H), 1.33–1.23 (m, 6H), 1.03 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 199.0, 171.9, 61.5, 56.5, 36.8, 35.9, 27.3, 17.3, 14.0, 7.7; HRMS (ESI): *m/z* calcd for $C_{11}H_{18}O_4Na$ $[M + Na]^+$ 237.1097, found 237.1095; IR (neat) ν_{max} 3486, 2981, 2940, 2734, 1716, 1461, 1375, 1297, 1246, 1182, 1112, 1021, 963, 906, 860, 794 cm^{-1}.



SI-9

To a solution of compound **SI-8** (7.05 g, 33.0 mmol) in dried toluene was added Et_3N (3.7 mL, 26 mmol) and benzoic acid (4.42 g, 36.2 mmol). The resulting mixture was stirred at reflux for 24 h with azeotropic removal of water using a Dean-Stark trap. After cooling to room temperature, the saturated aqueous NH_4Cl solution was added. The mixture was extacted with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, PE/EA = 10/1) to give unsaturated ketone **SI-9** (5.78 g, 89% yield) as a colorless oil. R_f = 0.41 (hexane/EA = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 4.17–4.04 (m, 2H), 2.53–2.31 (m, 3H), 1.93–1.81 (m, 1H), 1.73 (s, 3H), 1.34 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 174.4, 146.8, 134.6, 61.1, 43.9, 34.5, 32.6, 25.0, 15.9, 14.0; HRMS (ESI): *m/z* calcd for $C_{11}H_{17}O_3$ $[M + H]^+$ 197.1172, found 197.1180; IR (neat) ν_{max} 2979, 2933, 2874, 1731, 1682, 1450, 1364, 1268, 1239, 1176, 1130, 1107, 1025, 886, 860, 768, 728 cm^{-1}.

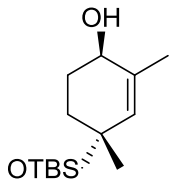


13 **12**

A solution of unsaturated ketone **SI-9** (1.97 g, 10.0 mmol) in dried Et_2O (10 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (417 mg, 11.0 mmol) in dried Et_2O (30 mL). The reaction mixture kept gently reflux by controlling the dropping speed. The solution was then stirred at 25 ^{o}C for 2 h. To the mixture was added slowly H_2O

(0.2 mL), 10% NaOH (0.4 mL) and H_2O (0.6 mL) at 0 ^oC. The mixture was stirred at 25 ^oC for additional 1 h. The mixture was filtered through a pad of silica gel, and washed with Et_2O. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 6/1) to give pure *trans*-diol **13** (435 mg, 28% yield) as a colorless oil and *cis*-diol **12** (1.11 g, 71% yield) as a colorless oil. *trans*-diol **13**. R_f = 0.46 (hexane/EA = 1/1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1H), 3.86 (d, *J* = 5.7 Hz, 1H), 3.22 (d, *J* = 10.6 Hz, 1H), 3.15 (d, *J* = 10.7 Hz, 1H), 3.10 (s, 2H), 1.86–1.76 (m, 1H), 1.67 (s, 3H), 1.61–1.47 (m, 2H), 1.32 (dd, *J* = 11.3, 8.2 Hz, 1H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 130.7, 70.0, 68.4, 37.3, 28.8, 27.7, 24.0, 20.2; HRMS (ESI): *m/z* calcd for $C_9H_{16}O_2Na$ $[M + Na]^+$ 179.1043, found 179.1040; IR (neat) ν_{max} 3332, 2936, 2865, 1450, 1375, 1280, 1192, 1137, 1048, 1019, 986, 915, 868, 733, 645 cm^{-1}.

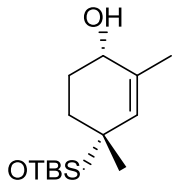
cis-diol **12**. R_f = 0.35 (hexane/EA = 1/1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (s, 1H), 4.04 (s, 2H), 3.76 (s, 1H), 3.29 (d, *J* = 10.4 Hz, 1H), 3.20 (d, *J* = 10.4 Hz, 1H), 1.82–1.64 (m, 6H), 1.12–1.05 (m, 1H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 131.5, 70.8, 67.3, 37.3, 28.3, 25.6, 22.8, 21.1; HRMS (ESI): *m/z* calcd for $C_9H_{16}O_2Na$ $[M + Na]^+$ 179.1043, found 179.1040; IR (neat) ν_{max} 3335, 2934, 2866, 1448, 1375, 1280, 1145, 1072, 986, 913, 870, 734, 646,544 cm^{-1}.



15

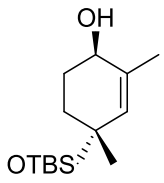
To a stirred solution of *trans*-diol **13** (309 mg, 1.98 mmol) and DMAP (24 mg, 0.20 mmol) in CH_2Cl_2 (15 mL) was added *t*-butyldimethylchlorosilane (312 mg, 2.08 mmol) followed by triethylamine (1.5 mL, 10 mmol) at 0 ^oC. After the solution was stirred at 0 ^oC for 10 h, ethyl acetate was added and the mixture was washed with H_2O and brine, then dried over anhydrous Na_2SO_4 and filtered. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 10/1) to give *trans*-alcohol **15** (325 mg, 61% yield) as a colorless oil. R_f = 0.63 (hexane/EA = 3/1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 3.93 (t, *J* =

5.1 Hz, 1H), 3.26 (d, *J* = 9.5 Hz, 1H), 3.20 (d, *J* = 9.5 Hz, 1H), 1.92–1.82 (m, 1H), 1.75 (s, 3H), 1.71–1.53 (m, 3H), 1.40–1.30 (m, 1H), 0.95 (s, 3H), 0.87 (s, 9H), 0.00 (d, *J* = 1.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 131.9, 69.9, 68.9, 37.5, 29.0, 27.6, 25.9, 24.5, 20.4, 18.3, -5.5; HRMS (ESI): *m/z* calcd for $C_{15}H_{30}O_2NaSi$ [M + Na]$^+$ 293.1907, found 293.1903; IR (neat) ν_{max} 3356, 2929, 2856. 1638, 1470, 1385, 1361, 1254, 1093, 1025, 1004, 850, 836, 774, 735, 669 cm^{-1}.



14

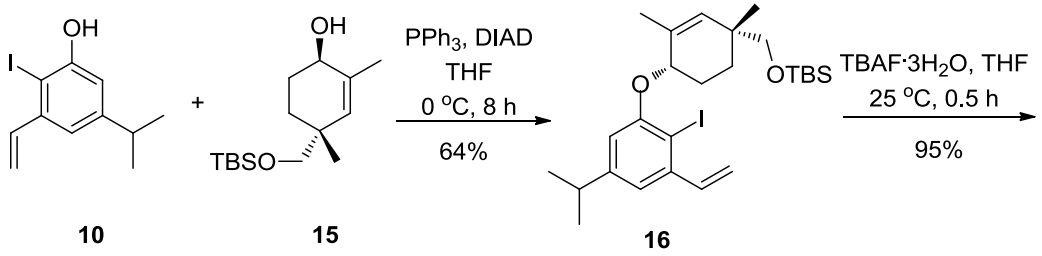
To a stirred solution of *cis*-diol **12** (931 mg, 5.96 mmol) and DMAP (73 mg, 0.60 mmol) in CH_2Cl_2 (30 mL) was added *t*-butyldimethylchlorosilane (941 mg, 6.26 mmol) followed by triethylamine (4.4 mL, 32 mmol) at 0 ^{o}C. After the solution was stirred at 0 ^{o}C for 10 h, EA was added and the mixture was washed with H_2O and brine, then dried over anhydrous Na_2SO_4 and filtered. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 10/1) to give *cis*-alcohol **14** (883 mg, 55% yield) as a colorless oil. R_f = 0.69 (hexane/EA = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 3.91 (t, *J* = 4.3 Hz, 1H), 3.32(d, *J* = 9.4 Hz, 1H), 3.24 (d, *J* = 9.4 Hz, 1H), 1.87–1.63 (m, 6H), 1.55 (s, 1H), 1.29–1.17 (m, 1H), 0.92–0.86 (m, 12H), 0.01 (d, *J* = 0.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 131.9, 71.0, 68.5, 37.5, 28.6, 26.6, 25.9, 23.2, 20.8, 18.3, -5.5; HRMS (ESI): *m/z* calcd for $C_{15}H_{30}O_2NaSi$ [M + Na]$^+$ 293.1907, found 293.1904; IR (neat) ν_{max} 3354, 2955, 2857, 1638, 1471, 1387, 1361, 1254, 1093, 1050, 1009, 982, 837, 775, 736, 669 cm^{-1}.



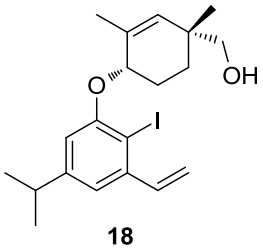
15

To a stirred solution of *cis*-alcohol **14** (661 mg, 2.44 mmol), PPh_3 (1.15 g, 4.40 mmol) and $ClCH_2COOH$ (416 mg, 4.40 mmol) in dried CH_2Cl_2 (20 mL) was added DEAD

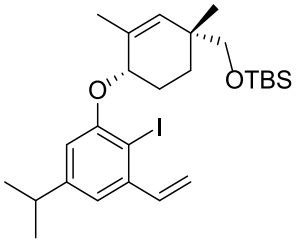
(0.70 mL, 4.4 mmol) dropwise and the resulting pale yellow solution was stirred at 0 ^{o}C for 8 h. The reaction mixture was concentrated and the residue was purified by flash chromatography to give a mixture of chloroacetate contaminated with trace amounts of triphenylphosphine oxide. The chloroacetate was hydrolyzed using K_2CO_3 (331 mg, 2.40 mmol) in MeOH (10 mL), The MeOH was evaporated and CH_2Cl_2 and water was added to the residue. The mixture was extacted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 10/1) to give *trans*-alcohol **15** (528 mg, 80% yield) as a colorless oil.



10 **15** **16**



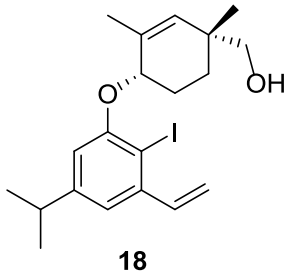
18



16

A solution of phenol **10** (161 mg, 0.595 mmol), *trans*-alcohol **15** (189 mg, 0.655 mmol) and PPh_3 (234 mg, 0.893 mmol) was stirred in dried THF (15 mL) at 0 ^{o}C under Ar. To this mixture was added dropwise diisopropyl azodiformate (181 mg, 0.893 mmol) in THF (2 mL) over a period of 10 min, and the resulting pale yellow solution was stirred at 0 ^{o}C for 8 h. The solvent was evaporated under reduced pressure and the resulting oil purified by flash column chromatography (silica gel,

hexane/EA = 100/1) to give pure compound **16** (206 mg, 64% yield) as a colorless oil. R_f = 0.76 (hexane/EA = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–6.93 (m, 2H), 6.65 (d, *J* = 1.6 Hz, 1H), 5.60 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.46 (s, 1H), 5.28 (dd, *J* = 10.9, 1.1 Hz, 1H), 4.60 (t, *J* = 4.1 Hz, 1H), 3.41 (d, *J* = 9.4 Hz, 1H), 3.34 (d, *J* = 9.4 Hz, 1H), 2.94–2.80 (m, 1H), 1.96–1.72 (m, 6H), 1.27 (m, 7H), 0.96 (s, 3H), 0.90 (s, 9H), 0.04 (d, *J* = 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 150.0, 142.6, 141.6, 133.5, 132.3, 117.1, 116.3, 111.0, 90.7, 76.4, 71.2, 37.5, 34.1, 27.8, 26.0, 24.6, 23.9, 23.1, 21.3, 18.4, -5.4; HRMS (ESI): *m/z* calcd for $C_{26}H_{41}O_2NaSiI$ $[M + Na]^+$ 563.1813, found 563.1804; IR (neat) ν_{max} 2956, 2928, 2855, 1561, 1462, 1421, 1385, 1361, 1287, 1256, 1184, 1093, 1014, 914, 837, 775, 669 cm^{-1}.

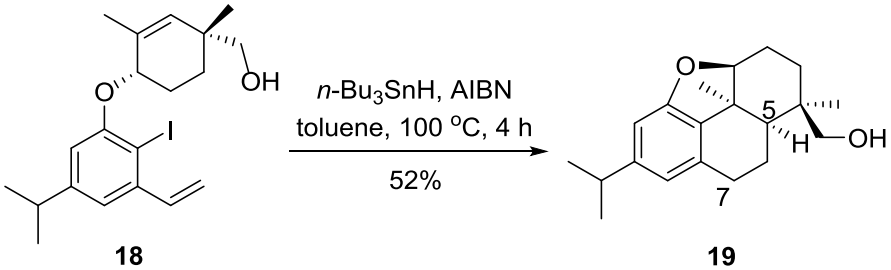


18

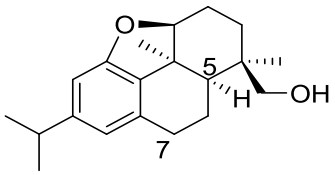
To a solution of compound **16** (187 mg, 0.346 mmol) in THF (10 mL) was added TBAF $3H_2O$ (546 mg, 1.73 mmol) in THF (4 mL), the reaction was stirred at 25 ^{o}C for 0.5 h, and then quenched with a saturated aqueous solution of NH_4Cl and further diluted with H_2O. The reaction mixture was extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexane/EA = 10/1) to give alcohol **18** (142 mg, 95% yield) as a colorless oil. R_f = 0.58 (hexane/EA = 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–6.92 (m, 2H), 6.66 (s, 1H), 5.60 (d, *J* = 17.2 Hz, 1H), 5.42 (s, 1H), 5.28 (d, *J* = 11.0 Hz, 1H), 4.60 (t, *J* = 3.6 Hz, 1H), 3.48 (d, *J* = 10.5 Hz, 1H), 3.40 (d, *J* = 10.5 Hz, 1H), 2.96–2.81 (m, 1H), 2.02–1.92 (m, 2H), 1.91–1.79 (m, 4H), 1.62 (s, 1H), 1.32–1.21 (m, 7H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 150.0, 142.6, 141.5, 134.3, 132.8, 117.3, 116.4, 111.0, 90.8, 75.5, 71.5, 37.8, 34.1, 26.7, 24.4, 23.9, 22.8, 21.6; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}O_2NaI$ $[M + Na]^+$ 449.0948, found 449.0943; IR (neat) ν_{max} 3370, 2958, 2930, 2866, 1561, 1460, 1421, 1383, 1330, 1287,

1263, 1183, 1146, 1090, 1036, 1015, 913, 848, 734, 671 cm^{-1}.

Synthesis of 5-*epi*-7-*deoxy*-Isoabietenin A

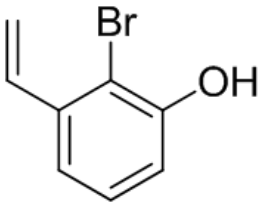


18 **19**



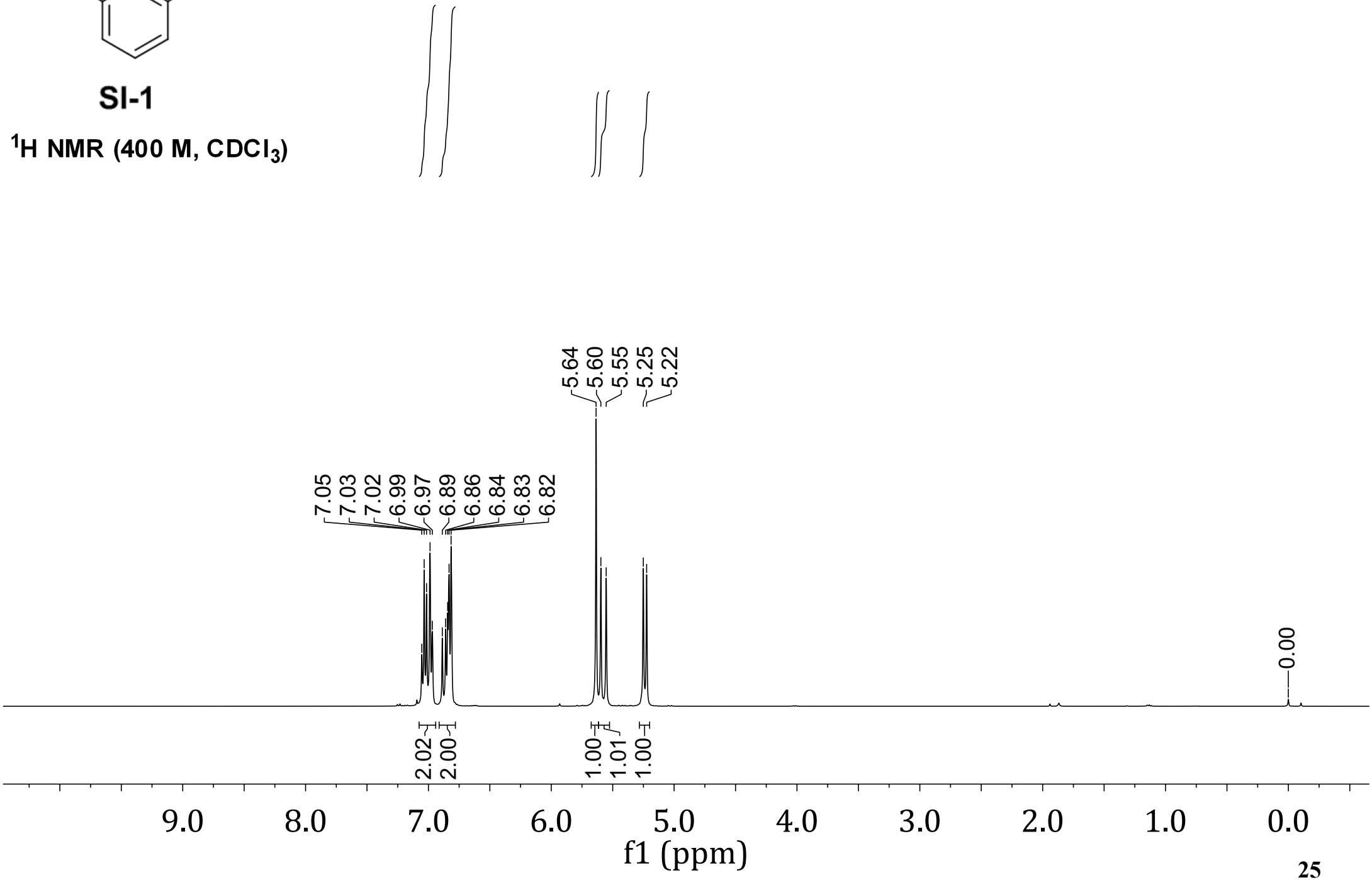
19

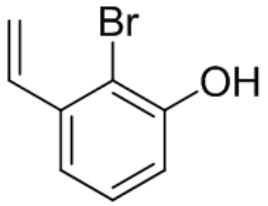
To a stirred solution of alcohol **18** (89 mg, 0.21 mmol) in degassed toluene (10 mL) at 100 °C under Ar was added dropwise a solution of *n*-Bu_3SnH (73 mg, 0.25 mmol) and AIBN (7 mg, 0.04 mmol) in degassed toluene (5 mL) over 2 h. The reaction was stirred at 100 °C for additional 2 h and then concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, hexane/EA = 25/1) to give 5-*epi*-7-*deoxy*-isoabietenin A **19** (33 mg, 52% yield) as a colorless oil. R_f = 0.58 (hexane/EA = 3/1); ^{1}H NMR (400 MHz, CDCl3) δ 6.48 (s, 2H), 4.55 (dd, *J* = 10.0, 7.4 Hz, 1H), 3.23 (s, 2H), 2.84–2.75 (m, 2H), 2.59–2.45 (m, 1H), 2.24–2.11 (m, 1H), 2.03 (dd, *J* = 15.3, 8.2 Hz, 1H), 1.85 (ddd, *J* = 10.3, 6.9, 2.9 Hz, 1H), 1.75 (ddd, *J* = 18.1, 7.0, 2.9 Hz, 2H), 1.42 (d, *J* = 2.6 Hz, 1H), 1.33–1.24 (m, 4H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.05 (s, 3H), 0.89 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 149.6, 133.4, 129.4, 117.4, 105.6, 92.0, 63.8, 47.1, 40.5, 38.4, 34.4, 29.8, 29.6, 26.0, 24.3, 24.23, 24.15, 19.2; HRMS (ESI): *m/z* calcd for $C_{20}H_{29}O_2$ $[M + H]^+$ 301.2162, found 301.2159; IR (neat) ν_{max} 3421, 2956, 2931, 2870, 1720, 1622, 1588, 1482, 1460, 1429, 1382, 1362, 1260, 1157, 1062, 1026, 1010, 993, 948, 907, 848, 734, 660, 606 cm^{-1}.



SI-1

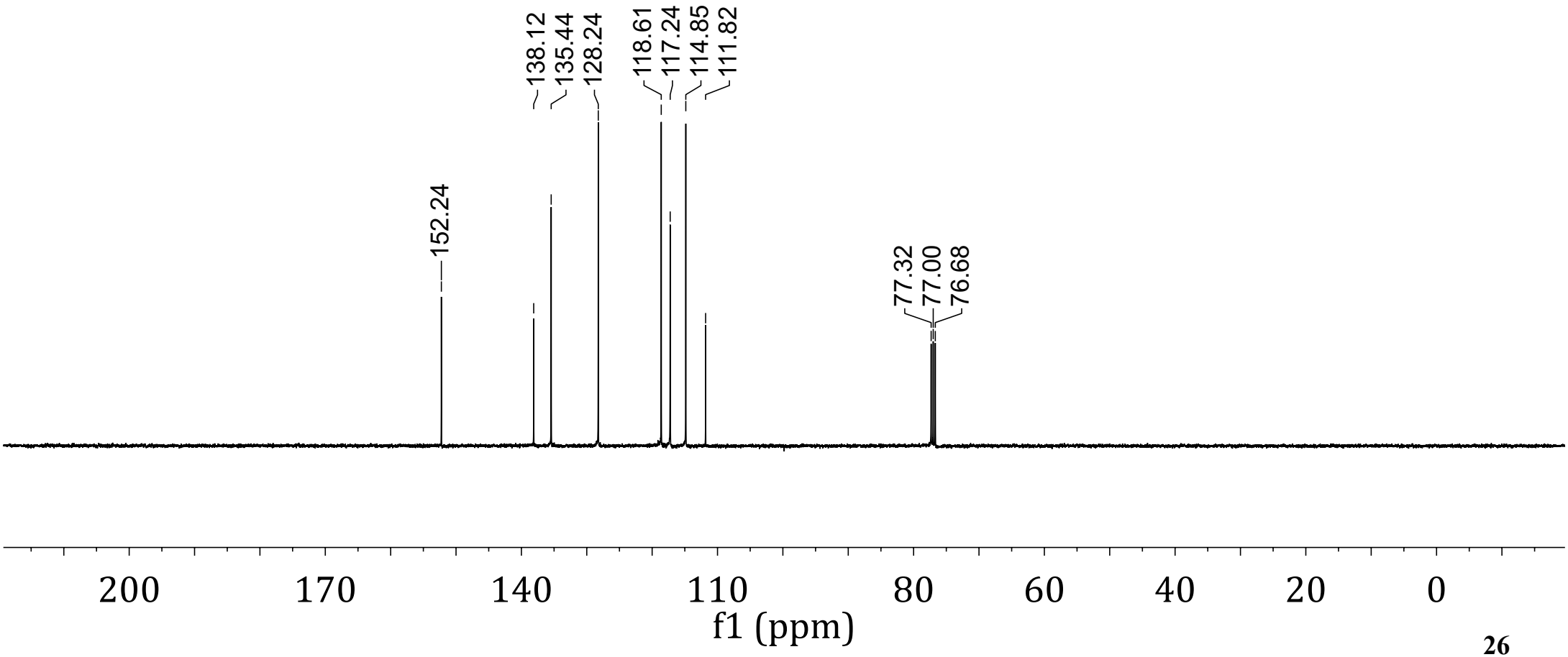
^{1}H NMR (400 M, $CDCl_3$)

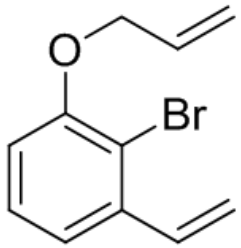




SI-1

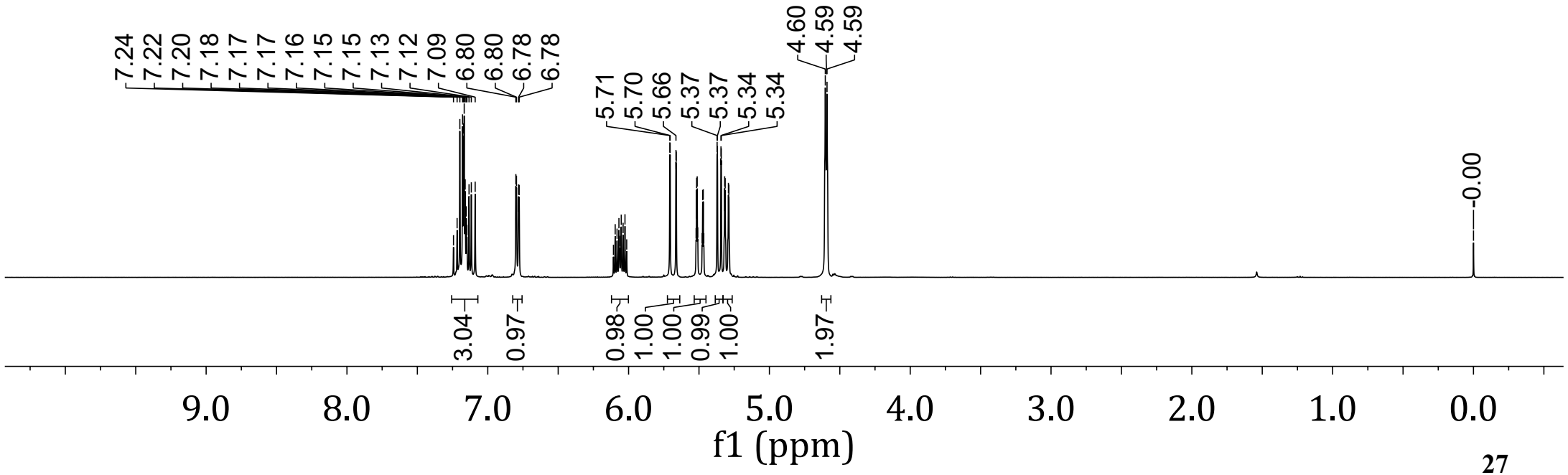
^{13}C NMR (100 M, $CDCl_3$)

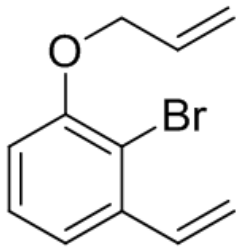




5a

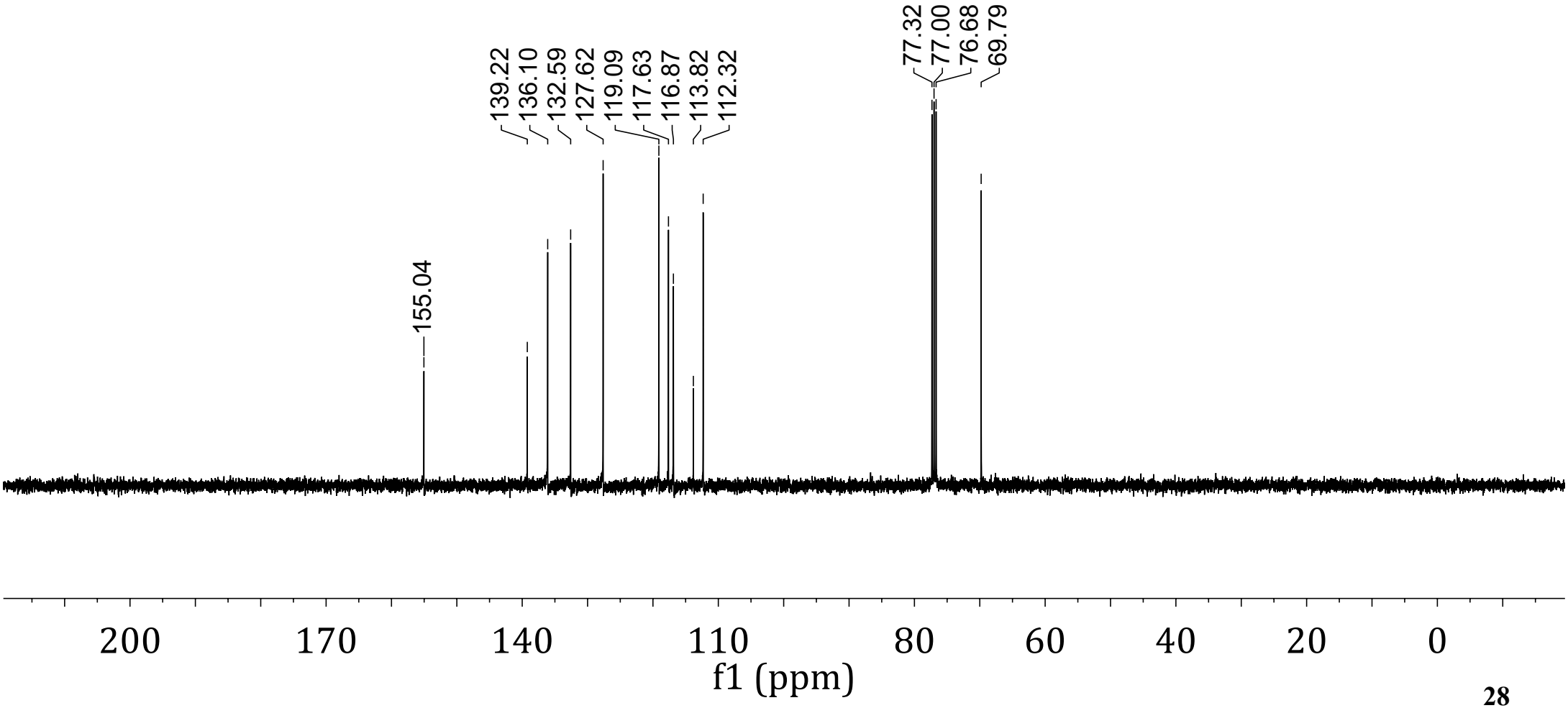
^{1}H NMR (400 M, $CDCl_3$)

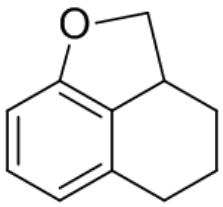




5a

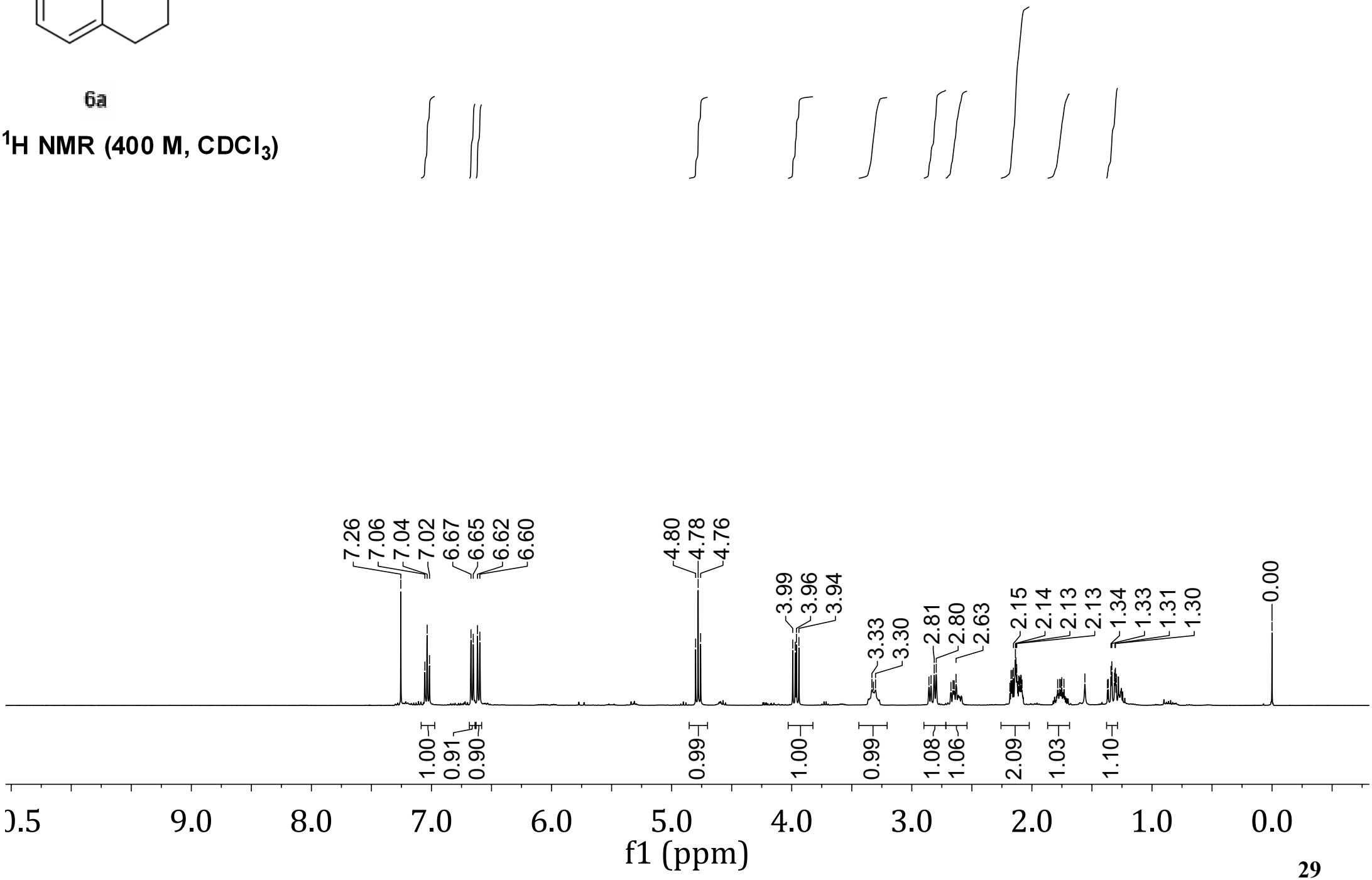
^{13}C NMR (100 M, $CDCl_3$)

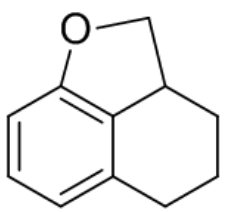




6a

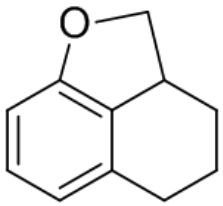
^{1}H NMR (400 M, $CDCl_3$)





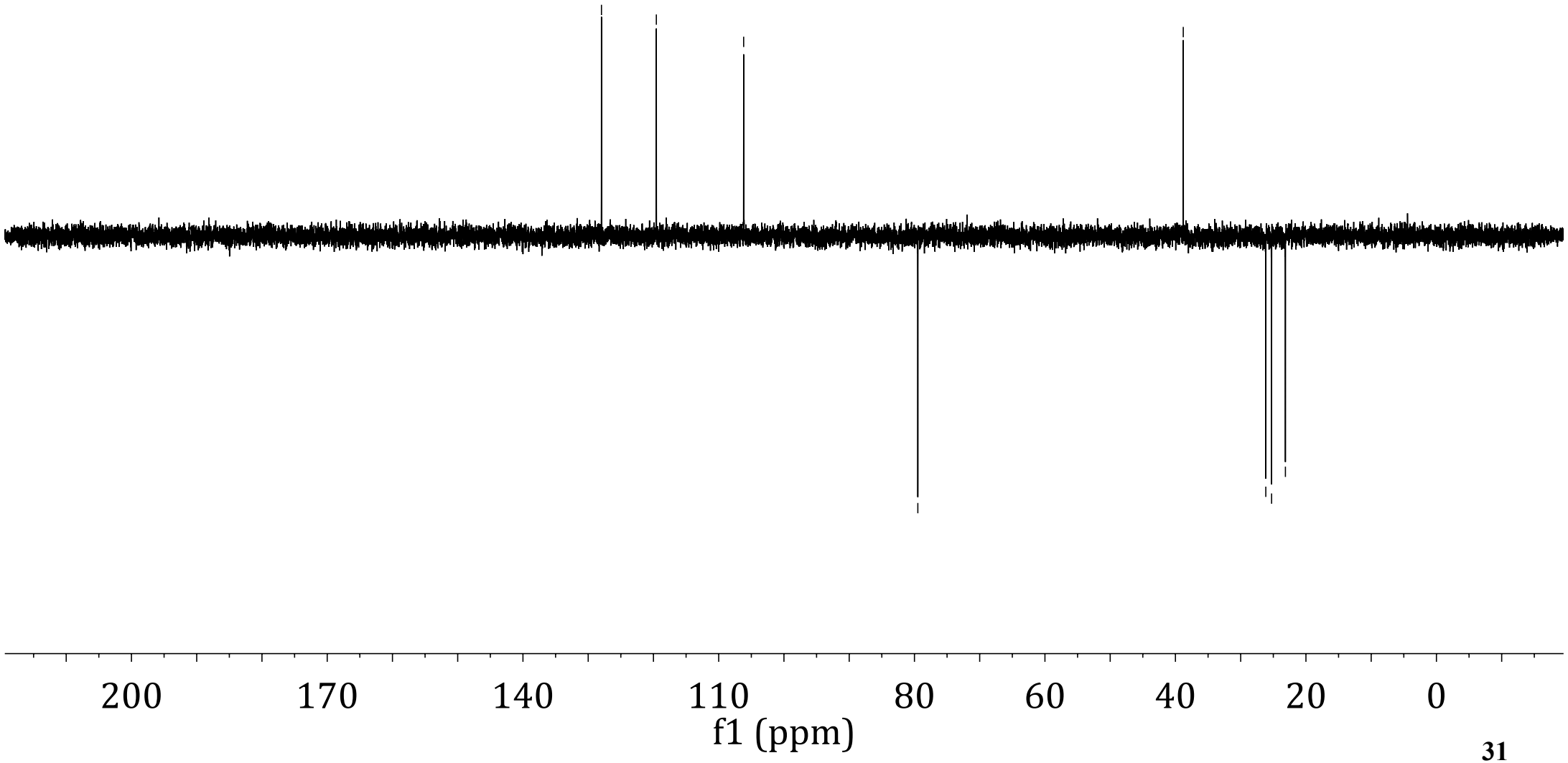
6a

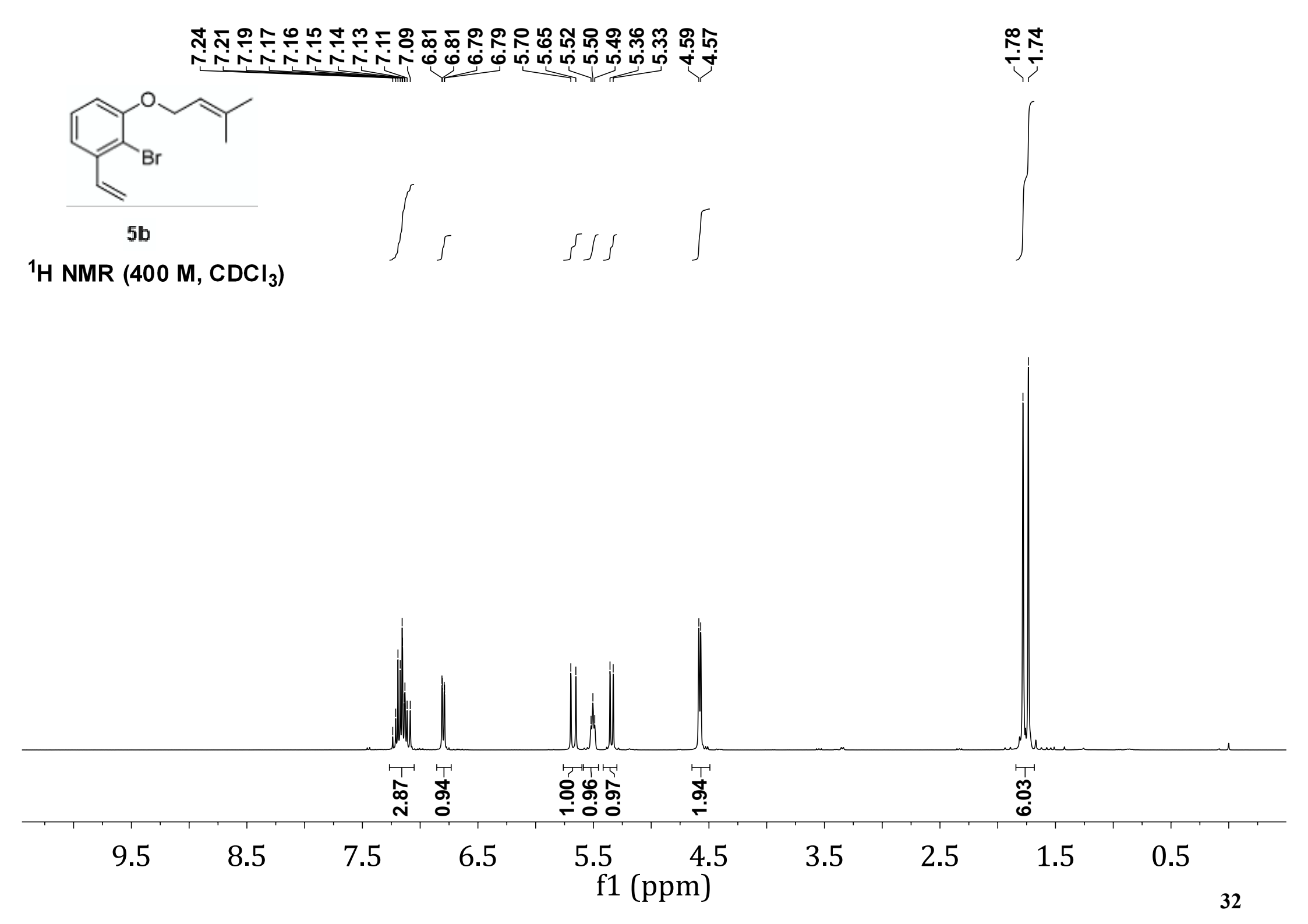
^{13}C NMR (100 M, $CDCl_3$)

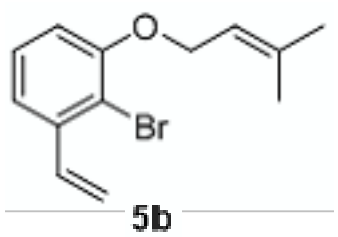


6a

DEPT-135 NMR (100M, $CDCl_3$)



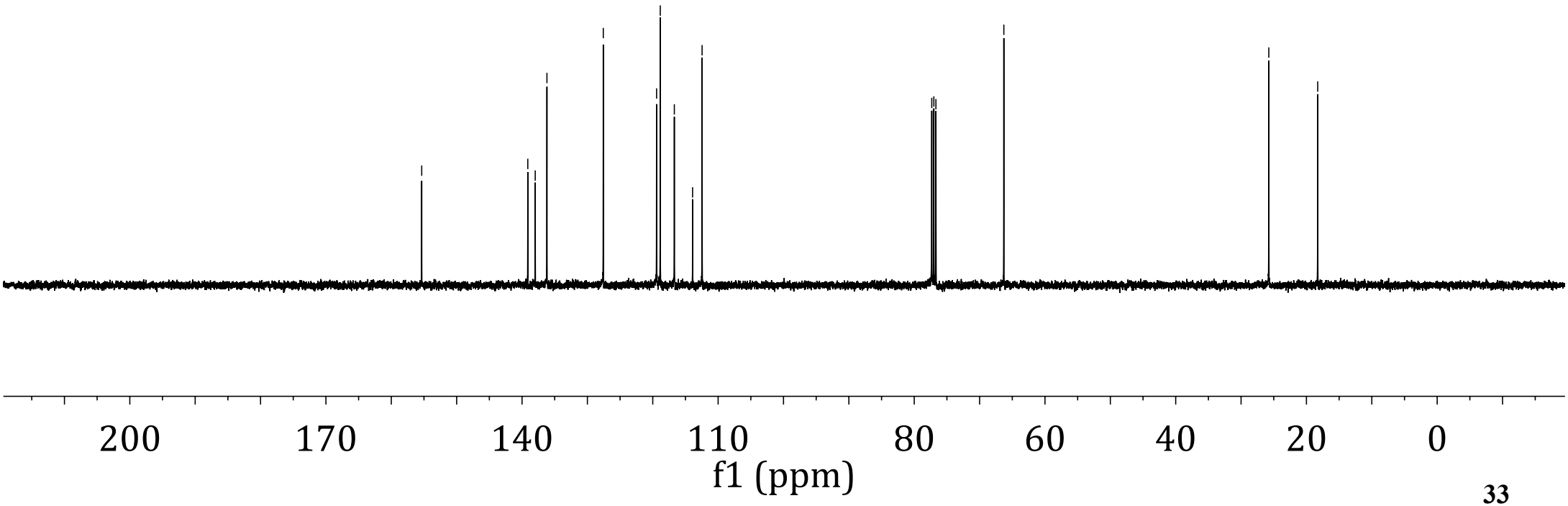

7.24
7.21
7.19
7.17
7.16
7.15
7.14
7.13
7.11
7.09
6.81
6.81
6.79
6.79
5.70
5.65
5.52
5.50
5.49
5.36
5.33
4.59
4.57
1.78
1.74
O
Br
5b
1H NMR (400 M, CDCl3)
2.87
0.94
1.00
0.96
0.97
1.94
6.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

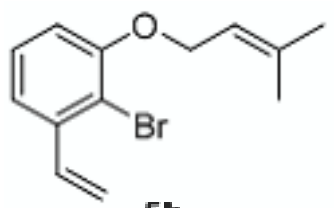


5b

155.35
139.12
137.98
136.19
127.57
119.41
118.85
116.70
113.90
112.45
77.32
77.00
76.68
66.29
25.76
18.28

^{13}C NMR (100 M, $CDCl_3$)





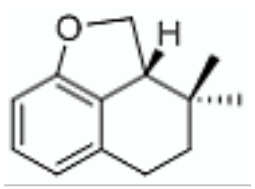
5b

136.19
127.57
119.42
118.85
116.70
112.45
66.29
25.76
18.28

DEPT-135 NMR (100M, $CDCl_3$)

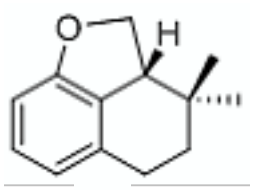
200 170 140 110 80 60 40 20 0

f1 (ppm)



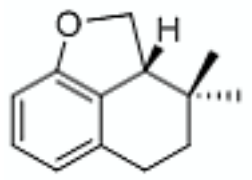
6b

^{1}H NMR (400 M, $CDCl_3$)



6b

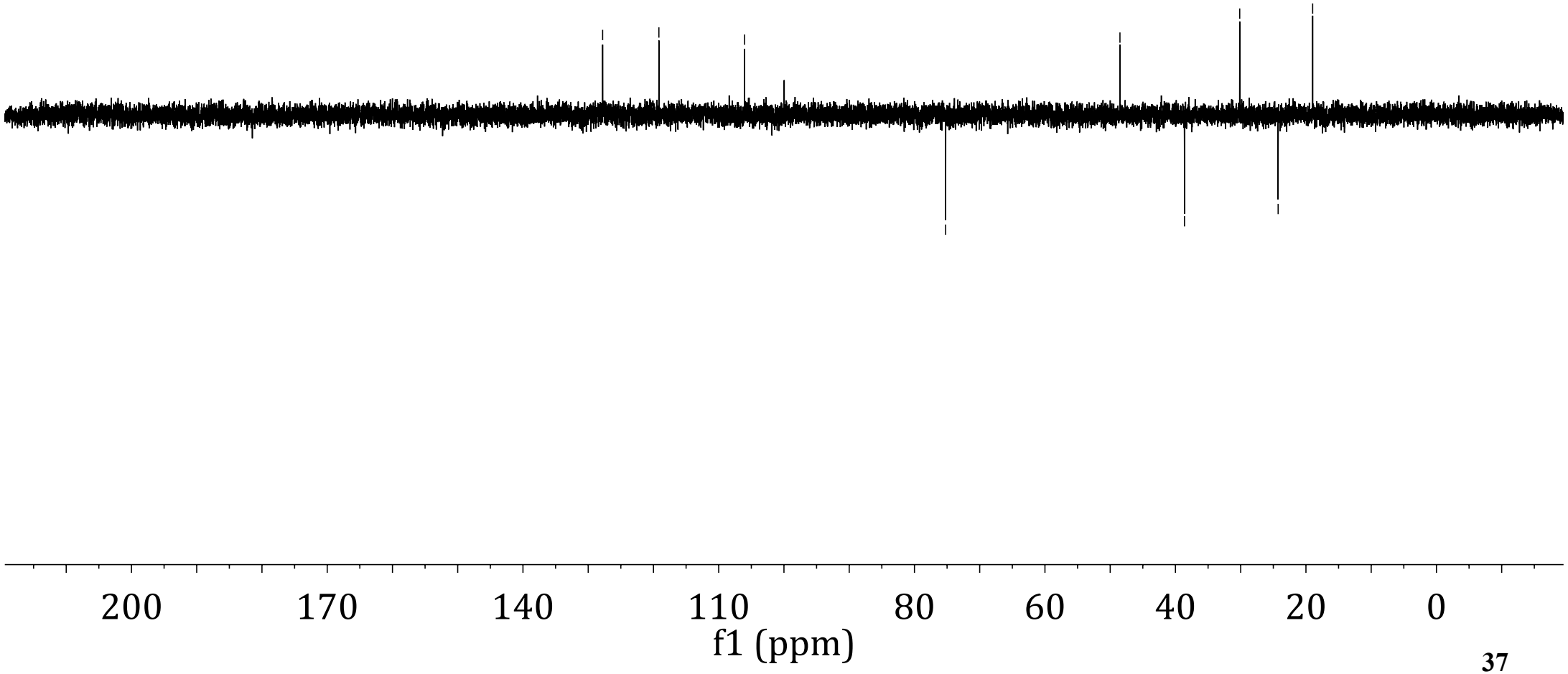
^{13}C NMR (100 M, $CDCl_3$)

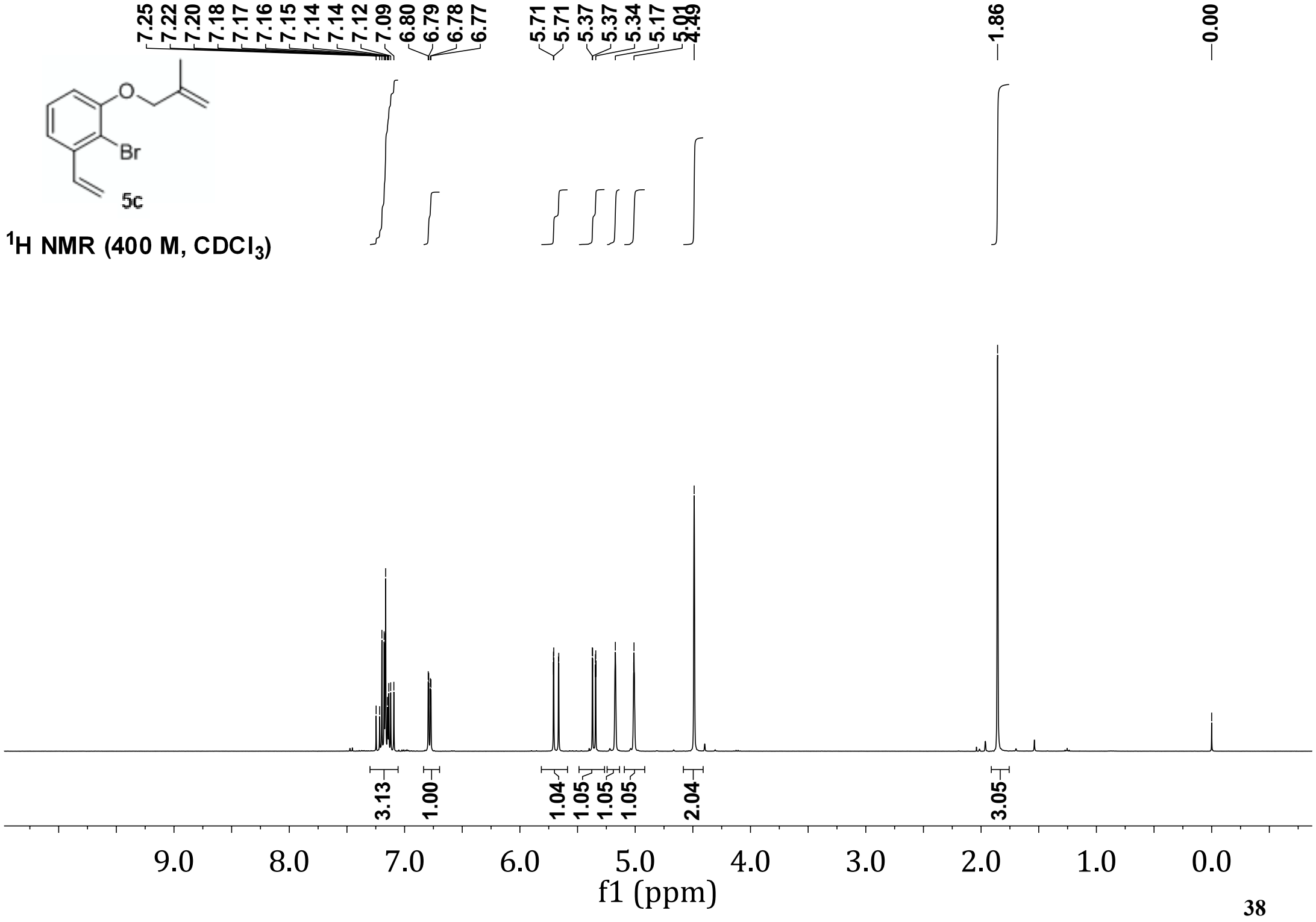


6b

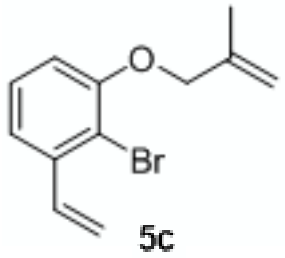
127.79
119.17
106.04
75.22
48.50
38.61
30.15
24.26
18.97

DEPT-135 NMR (100M, $CDCl_3$)





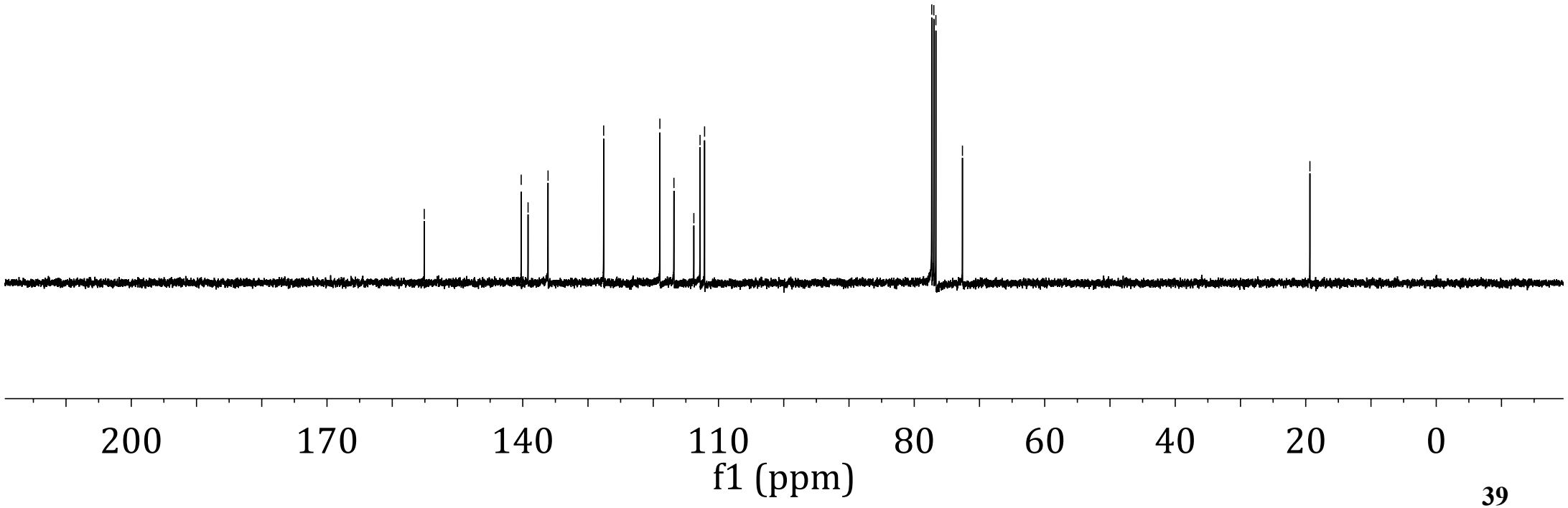
^{1}H NMR (400 M, $CDCl_3$)



5c

155.09
140.24
139.19
136.12
127.60
118.99
116.83
113.78
112.83
112.13
77.32
77.00
76.68
72.61
19.36

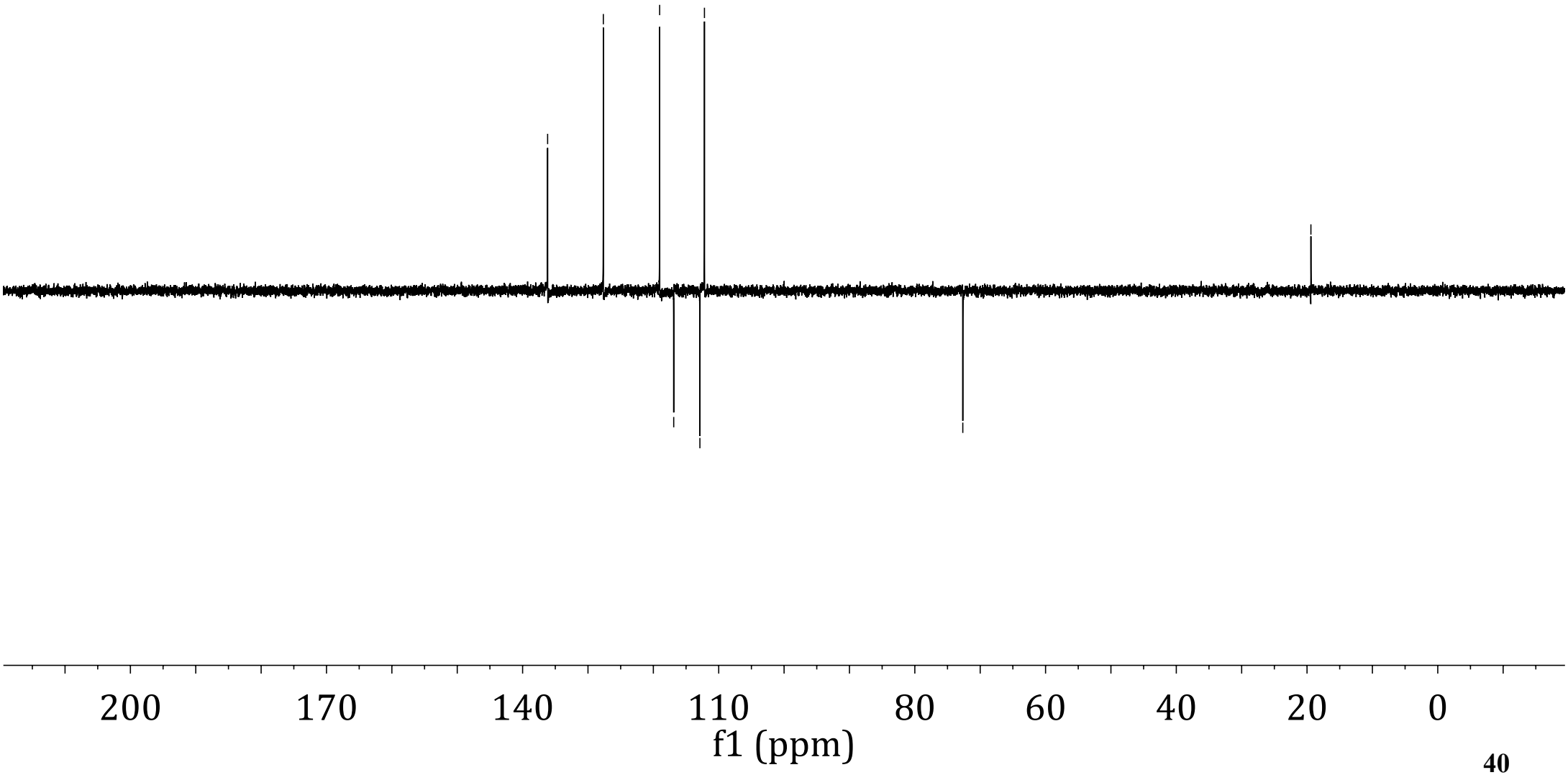
^{13}C NMR (100 M, $CDCl_3$)

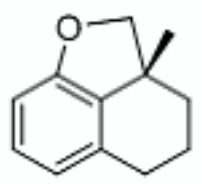


5c

136.17
127.65
119.04
116.88
112.88
112.18
72.66
19.41

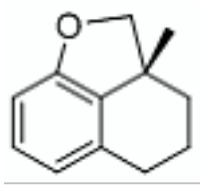
DEPT-135 NMR (100M, $CDCl_3$)





6c

^{1}H NMR (400 M, $CDCl_3$)



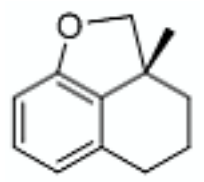
6c

^{13}C NMR (100 M, $CDCl_3$)

157.73
133.52
132.64
127.10
118.90
105.30
86.02
47.79
47.58
47.36
47.15
46.94
46.72
46.51
39.01
31.21
23.57
22.85
18.56

200 170 140 110 80 60 40 20 0

f1 (ppm)



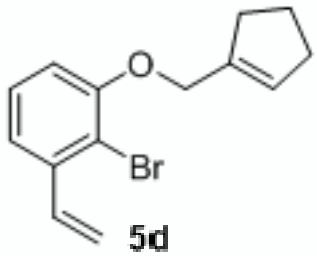
6c

127.10
118.90
105.30
86.02
31.21
23.57
22.85
18.56

DEPT-135 NMR (100M, $CDCl_3$)

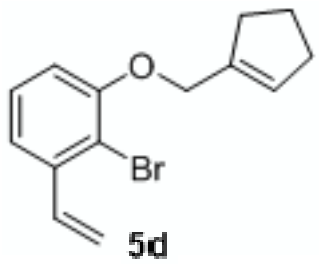
200 170 140 110 80 60 40 20 0

f1 (ppm)



5d

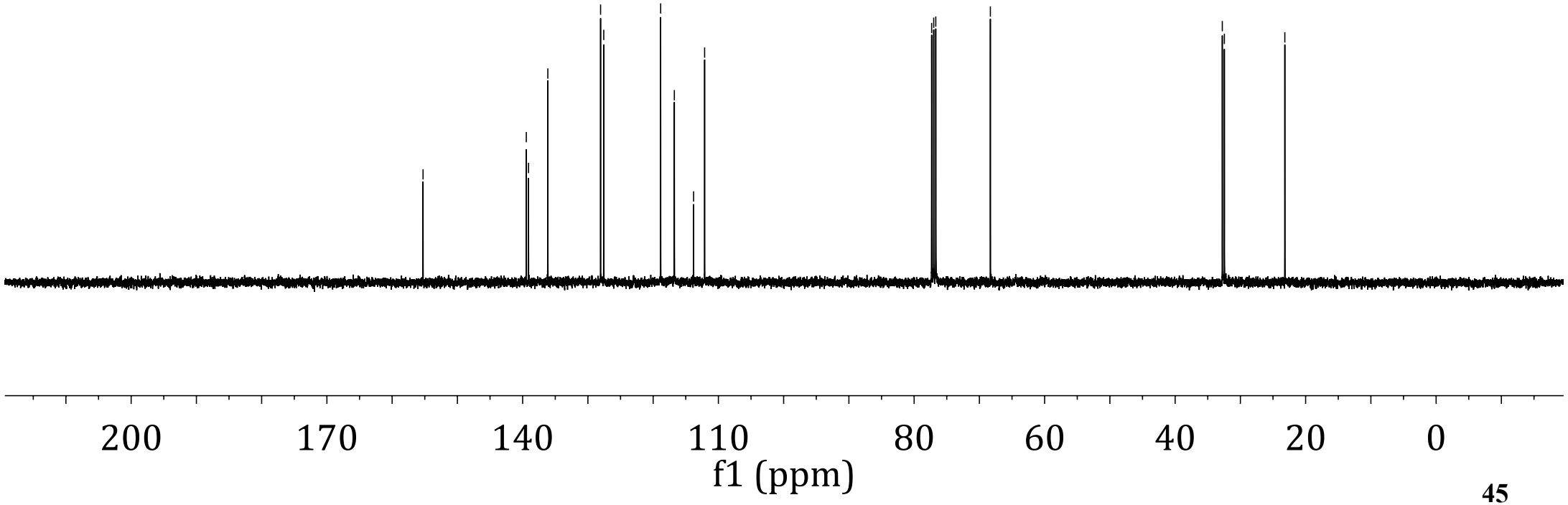
^{1}H NMR (400 M, $CDCl_3$)

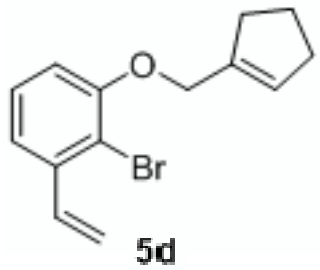


5d

155.26
139.44
139.10
136.14
128.06
127.57
118.85
116.75
113.80
112.11
77.32
77.00
76.68
68.32
32.77
32.45
23.19

^{13}C NMR (100 M, $CDCl_3$)

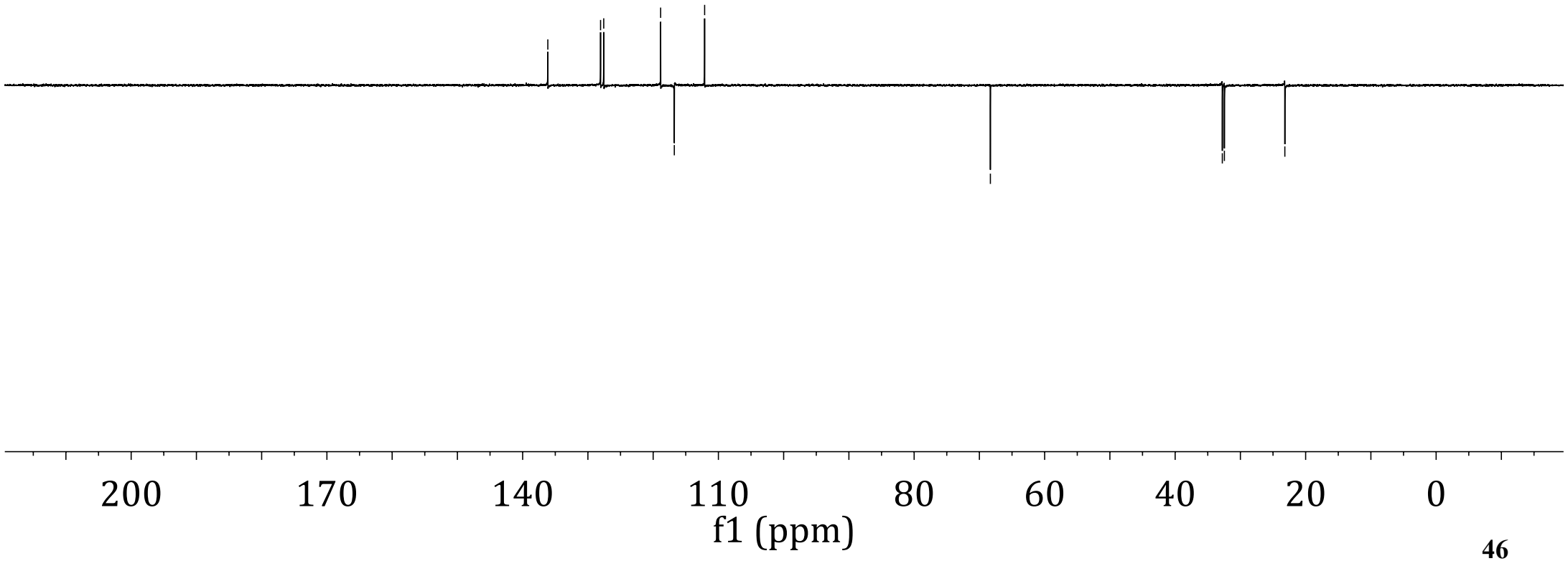


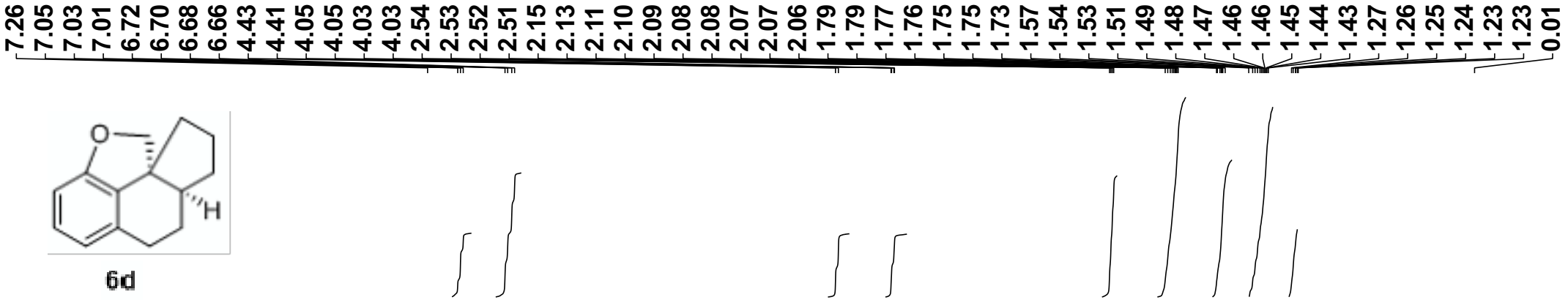


5d

136.14
128.06
127.57
118.85
116.76
112.11
68.32
32.77
32.45
23.19

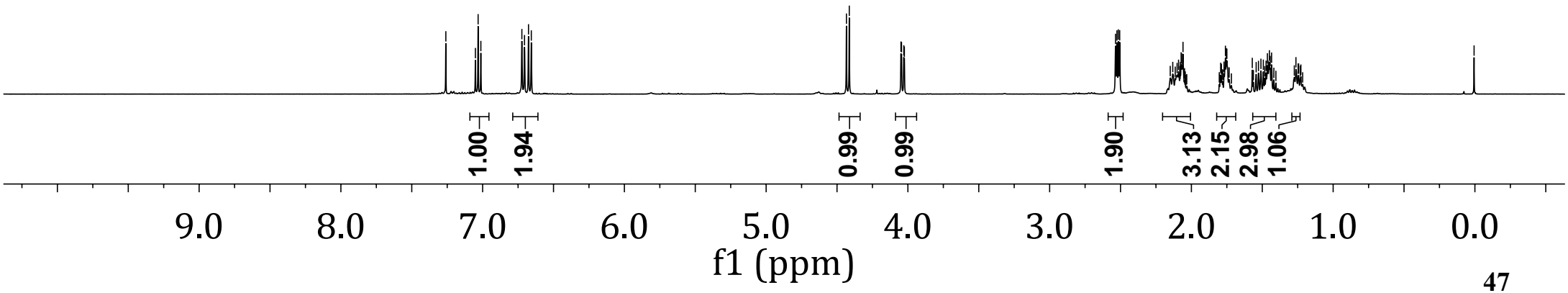
DEPT-135 NMR (100M, $CDCl_3$)

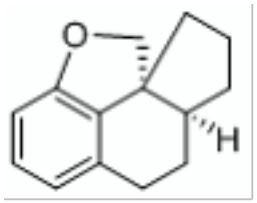




6d

^{1}H NMR (400 M, $CDCl_3$)





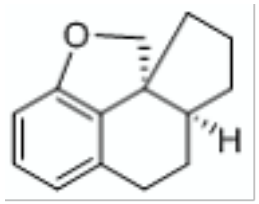
6d

^{13}C NMR (100 M, $CDCl_3$)

158.48
137.33
132.34
127.36
118.93
106.78
86.77
77.32
77.00
76.68
50.04
40.63
40.00
32.35
31.15
24.71
24.15

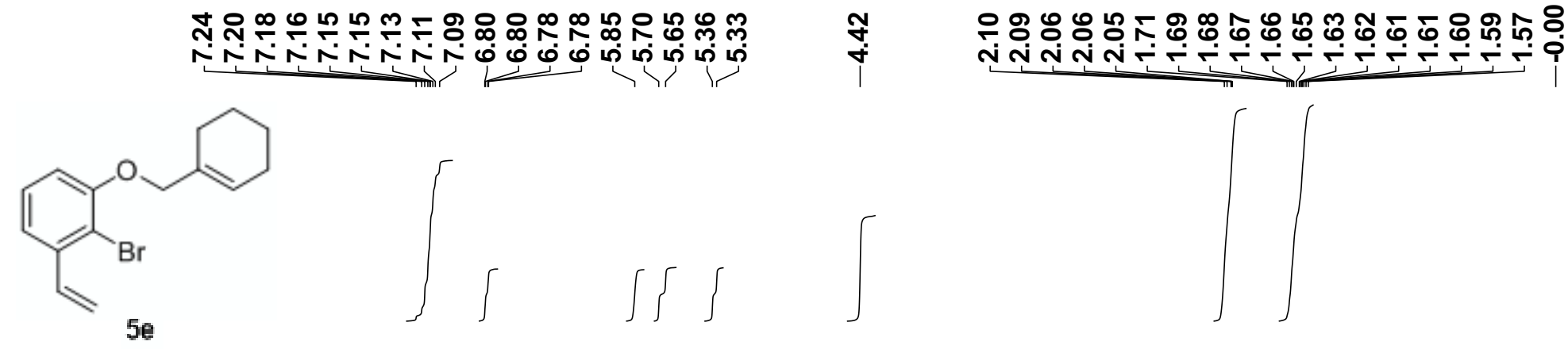
200 170 140 110 80 60 40 20 0

f1 (ppm)



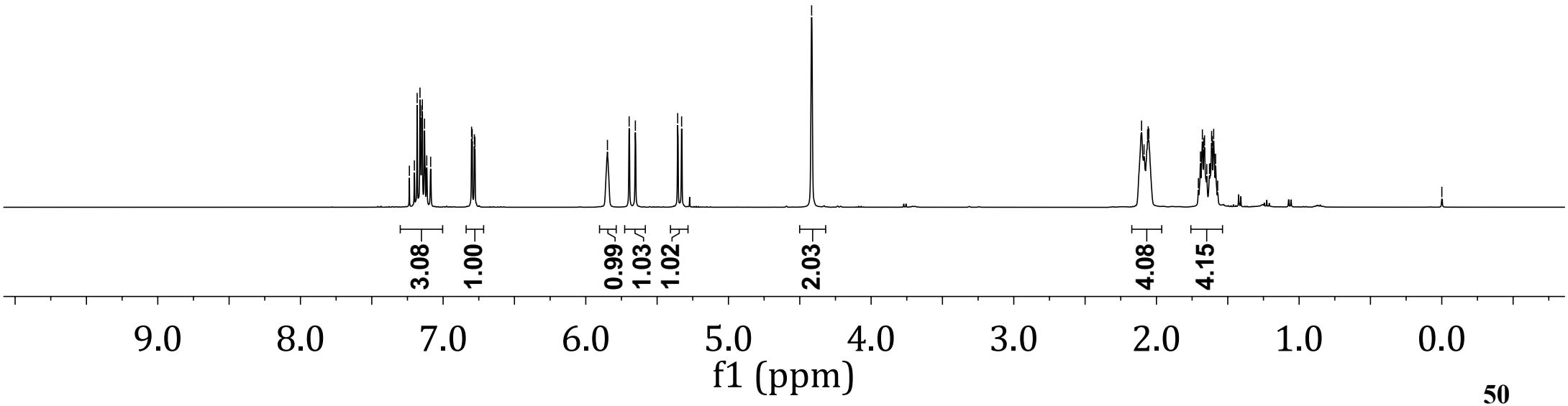
6d

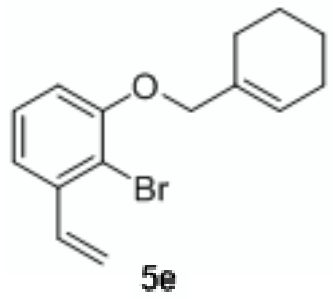
DEPT-135 NMR (100M, $CDCl_3$)



5e

^{1}H NMR (400 M, $CDCl_3$)

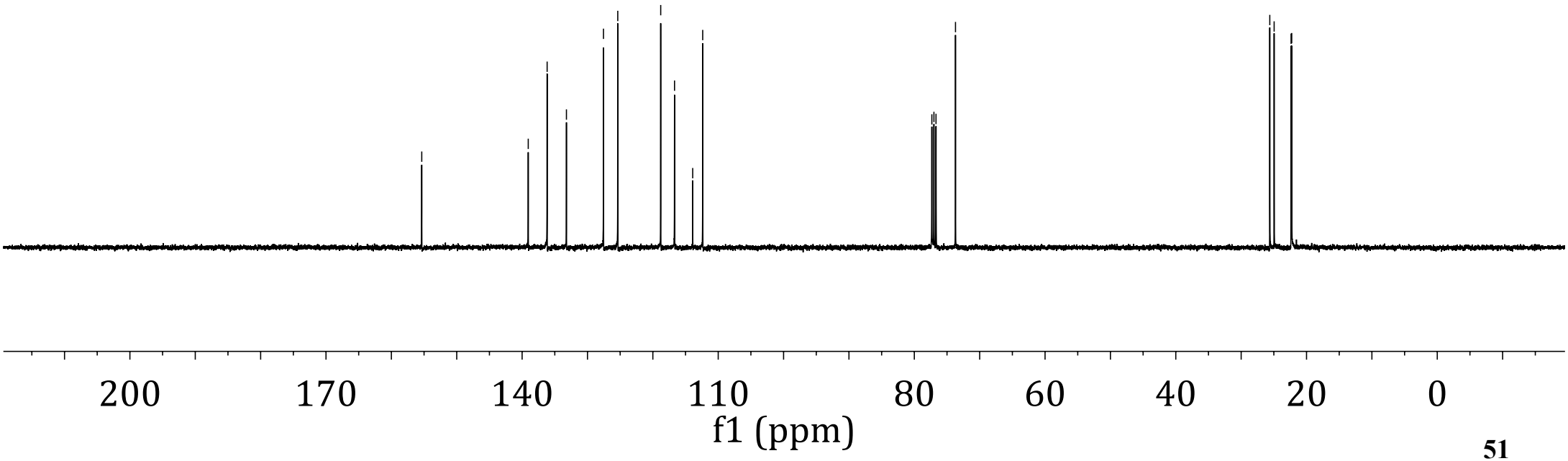


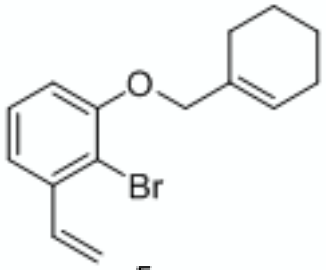


5e

155.35
139.06
136.17
133.22
127.55
125.37
118.80
116.68
113.90
112.37
77.32
77.00
76.68
73.70
25.62
24.95
22.37
22.26

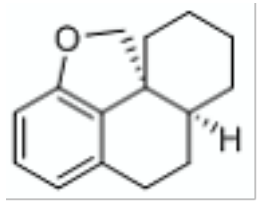
^{13}C NMR (100 M, $CDCl_3$)





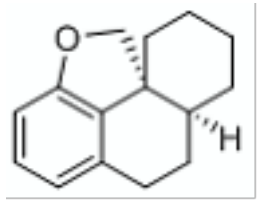
5e

DEPT-135 NMR (100M, $CDCl_3$)



6e

^{1}H NMR (400 M, $CDCl_3$)



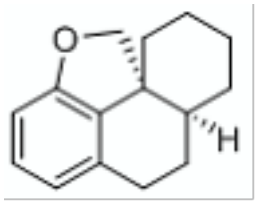
6e

^{13}C NMR (100 M, $CDCl_3$)

158.62
134.25
133.83
127.88
119.50
106.33
83.50
77.32
77.00
76.68
43.28
36.38
29.80
29.01
25.60
23.86
22.98
19.69

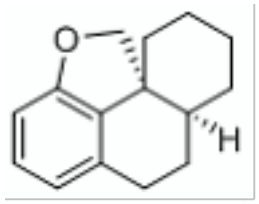
200 170 140 110 80 60 40 20 0

f1 (ppm)



6e

DEPT-135 NMR (100M, $CDCl_3$)



6e

Sample Name:
zhanghao-F65
Data Collected on:
Agilent-NMR-inova600
Archive directory:

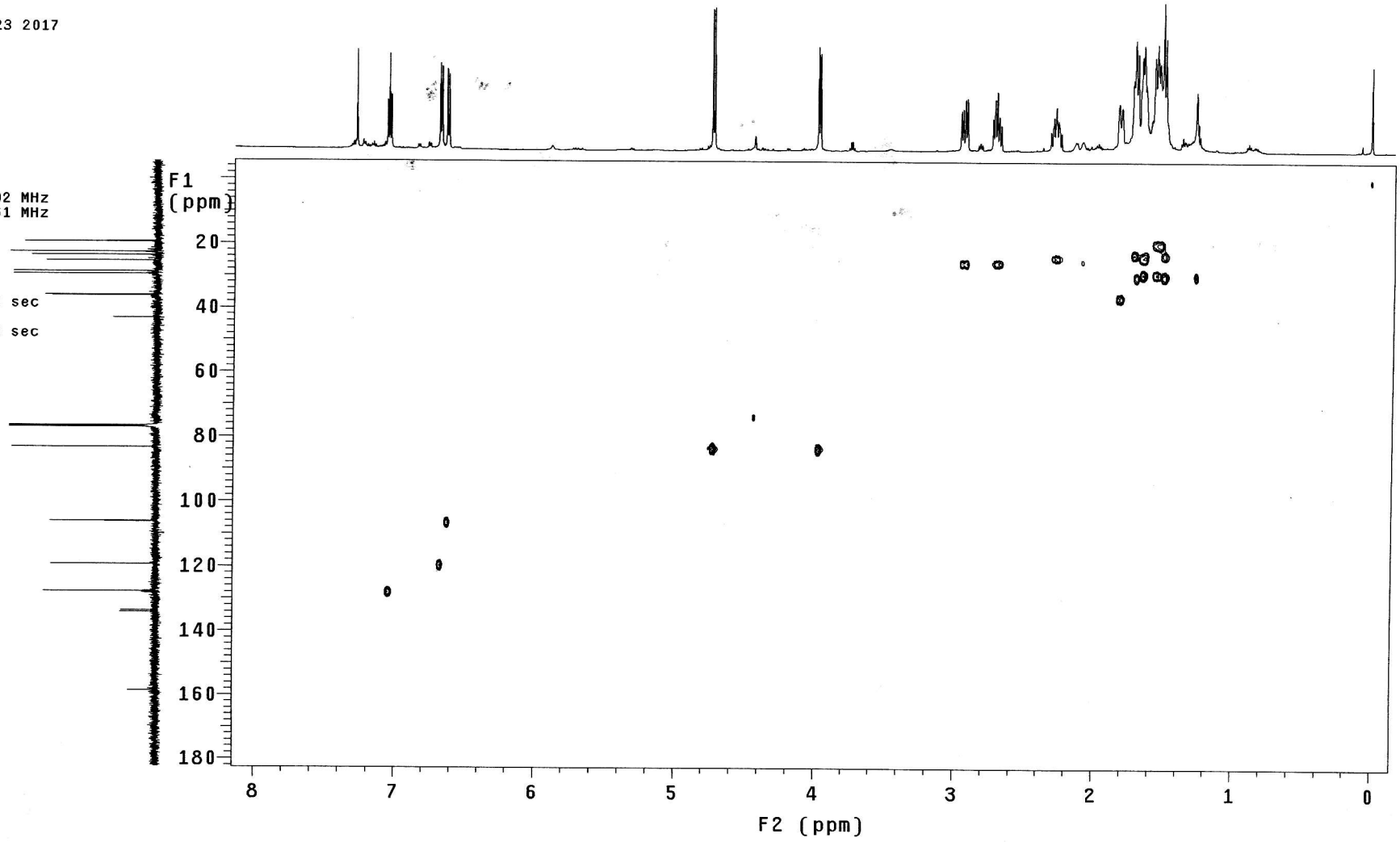
Sample directory:

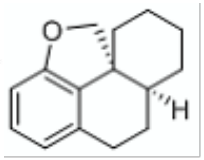
FidFile: gHSQCAD

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Mar 23 2017

Temp. 25.0 C / 298.1 K
Operator: liusq

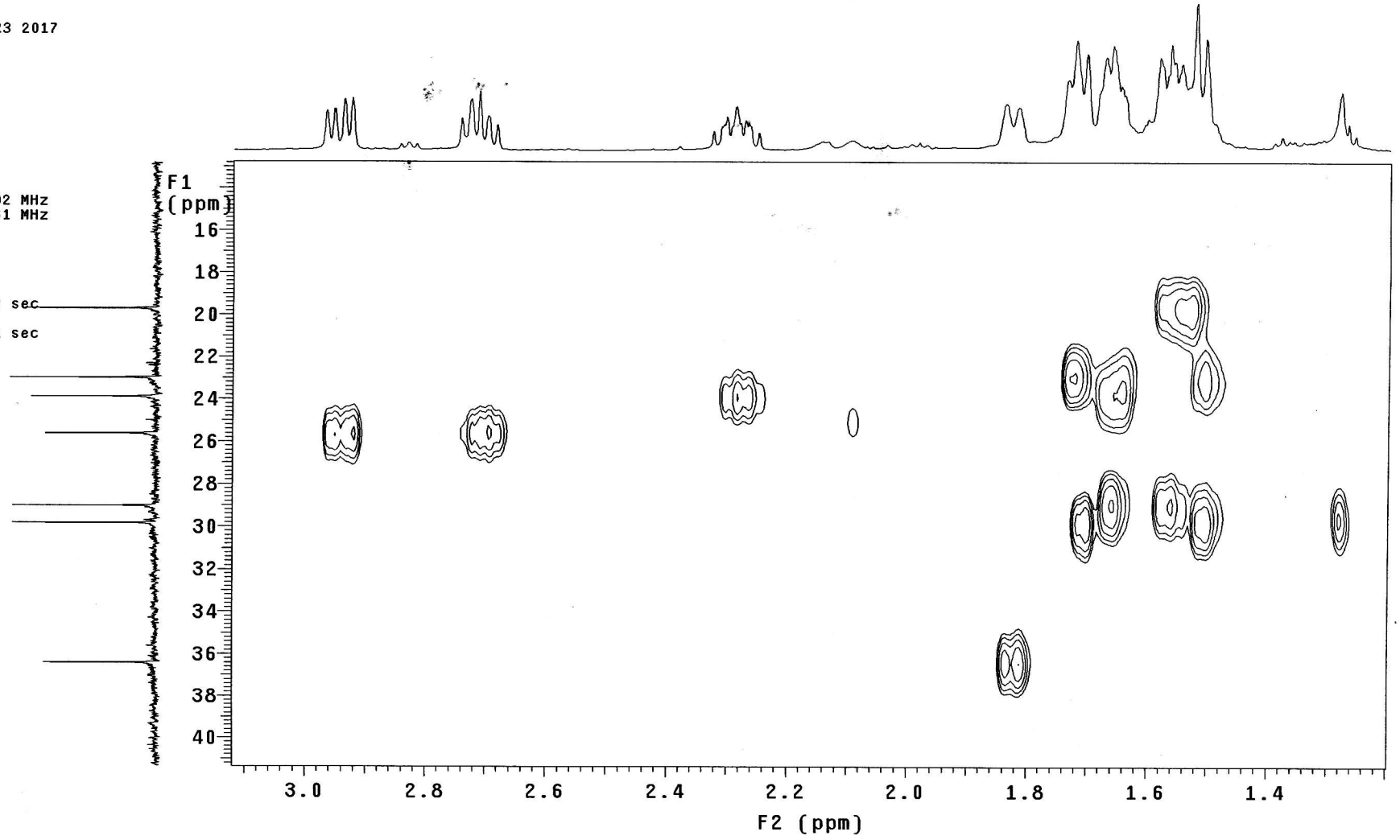
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5622.7 Hz
2D Width 33181.3 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 599.8441802 MHz
DECOUPLE C13, 150.8460261 MHz
Power 40 dB
on during acquisition
off during delay
W40_SW modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.002 sec
FT size 4096 x 2048
Total time 1 hr, 23 min

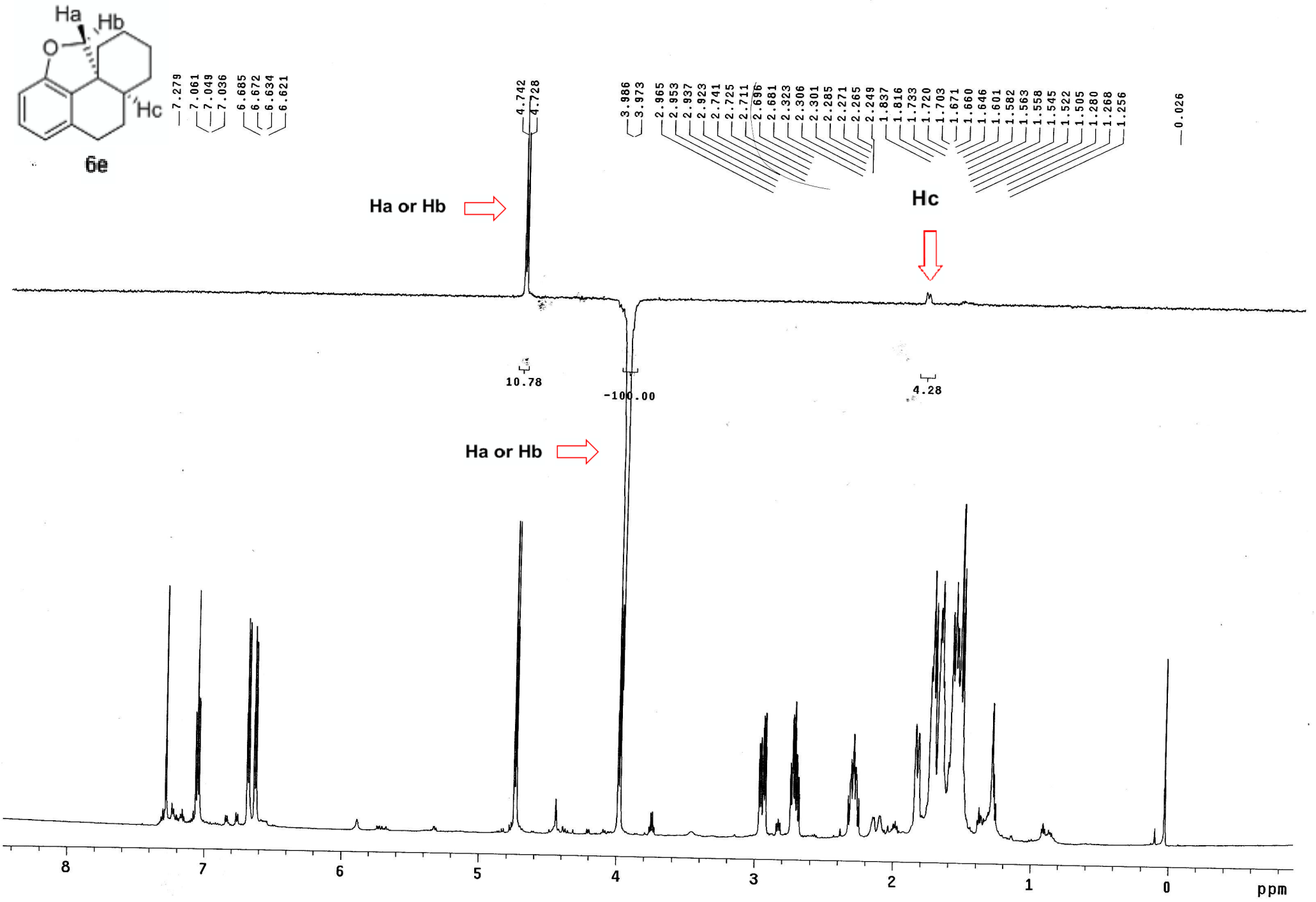


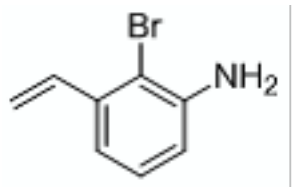


6e

```
Sample Name:
  zhanghao-F65
Data Collected on:
  Agilent-NMR-inova600
Archive directory:

Sample directory:

FidFile: gHSQCAD

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Mar 23 2017

Temp. 25.0 C / 298.1 K
Operator: liusq

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width    5622.7 Hz
2D Width 33181.3 Hz
16 repetitions
2 x 128 increments
OBSERVE   H1, 599.8441802 MHz
DECOUPLE C13, 150.8460261 MHz
Power 40 dB
on during acquisition
off during delay
W40_SW modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.002 sec
FT size 4096 x 2048
Total time 1 hr, 23 min
```

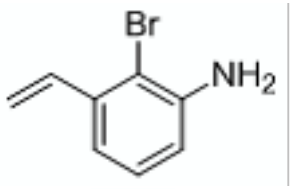



Ha
Hb
O
Hc
6e
7.279
7.061
7.049
7.036
6.685
6.672
6.634
6.621
4.742
4.728
3.986
3.973
2.965
2.953
2.937
2.923
2.741
2.725
2.711
2.696
2.681
2.323
2.306
2.301
2.285
2.271
2.265
2.249
1.837
1.816
1.733
1.720
1.703
1.671
1.660
1.646
1.601
1.582
1.563
1.558
1.545
1.522
1.505
1.280
1.268
1.256
0.026
Ha or Hb
Hc
10.78
-100.00
4.28
Ha or Hb
8
7
6
5
4
3
2
1
0
ppm



SI-2

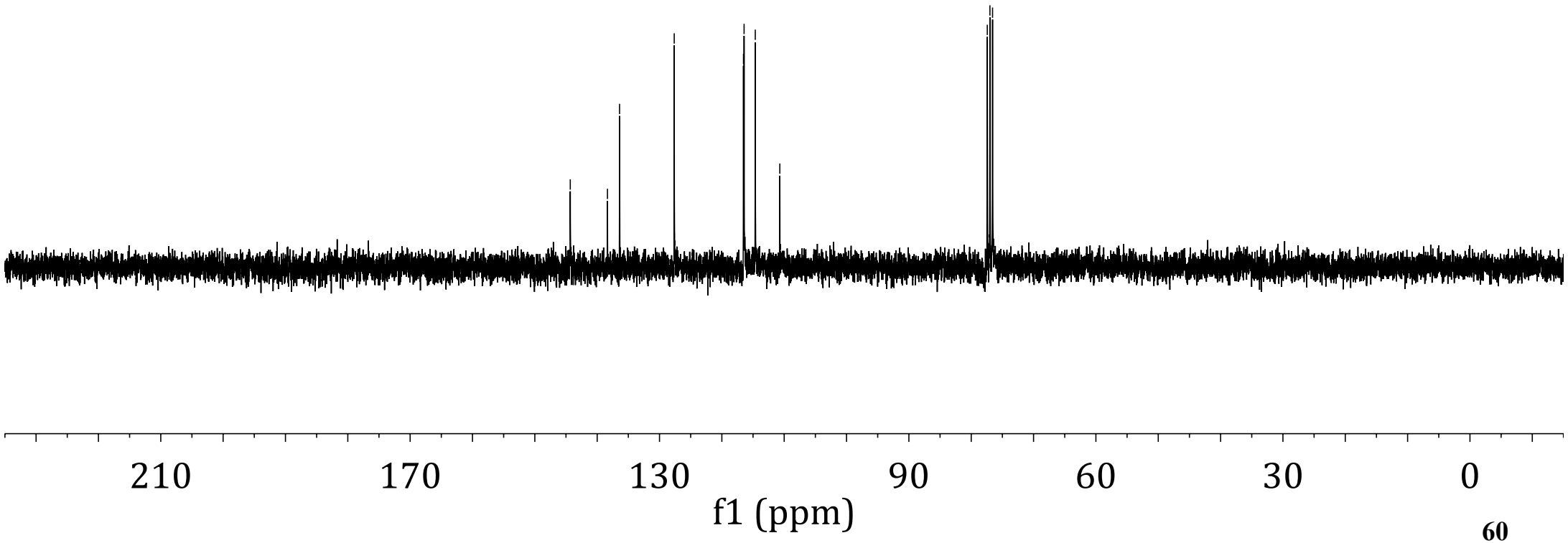
^{1}H NMR (400 M, $CDCl_3$)

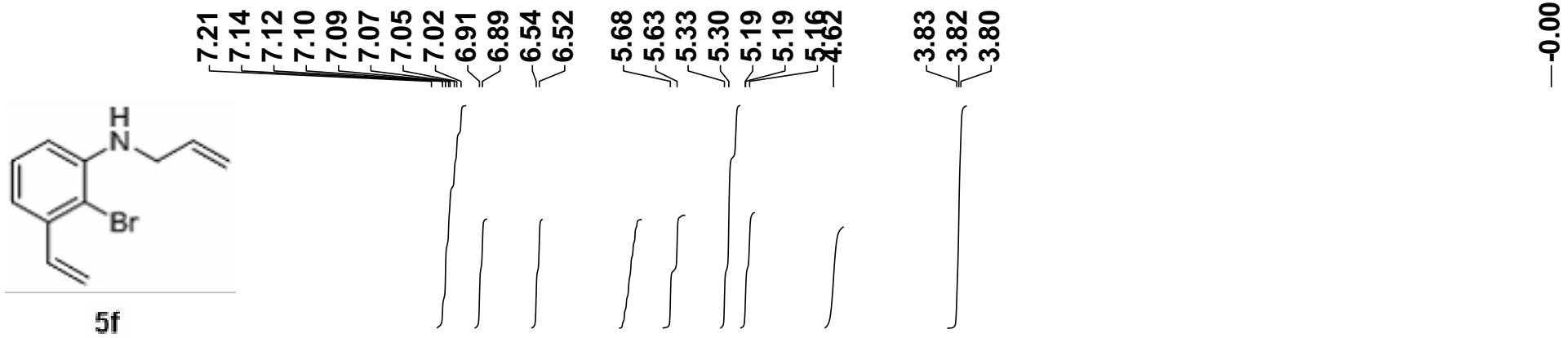


SI-2

144.31
138.35
136.41
127.64
116.53
116.43
114.64
110.70
77.42
77.00
76.58

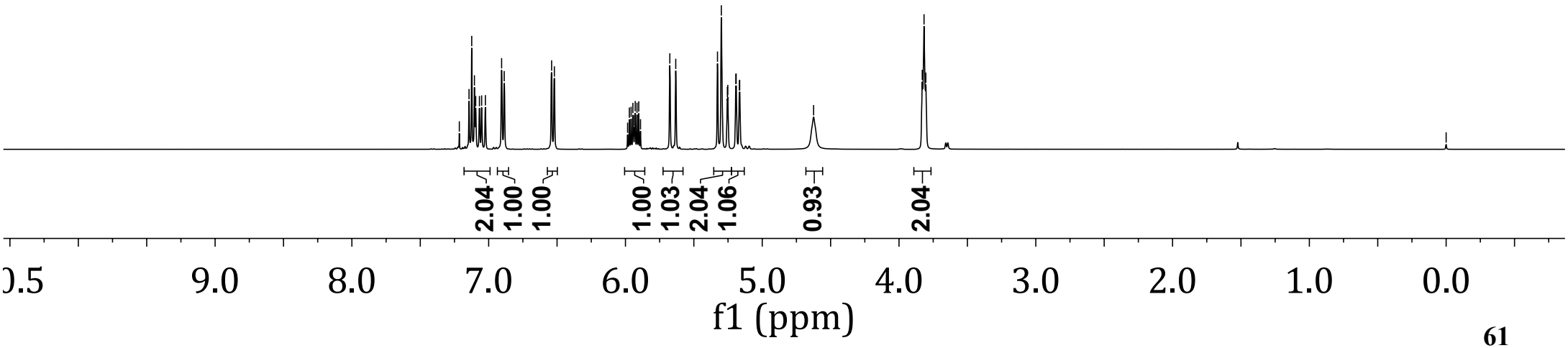
^{13}C NMR (100 M, $CDCl_3$)

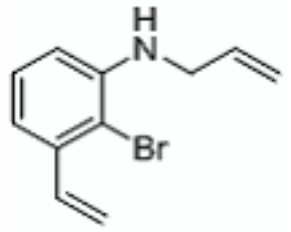




5f

^{1}H NMR (400 M, $CDCl_3$)

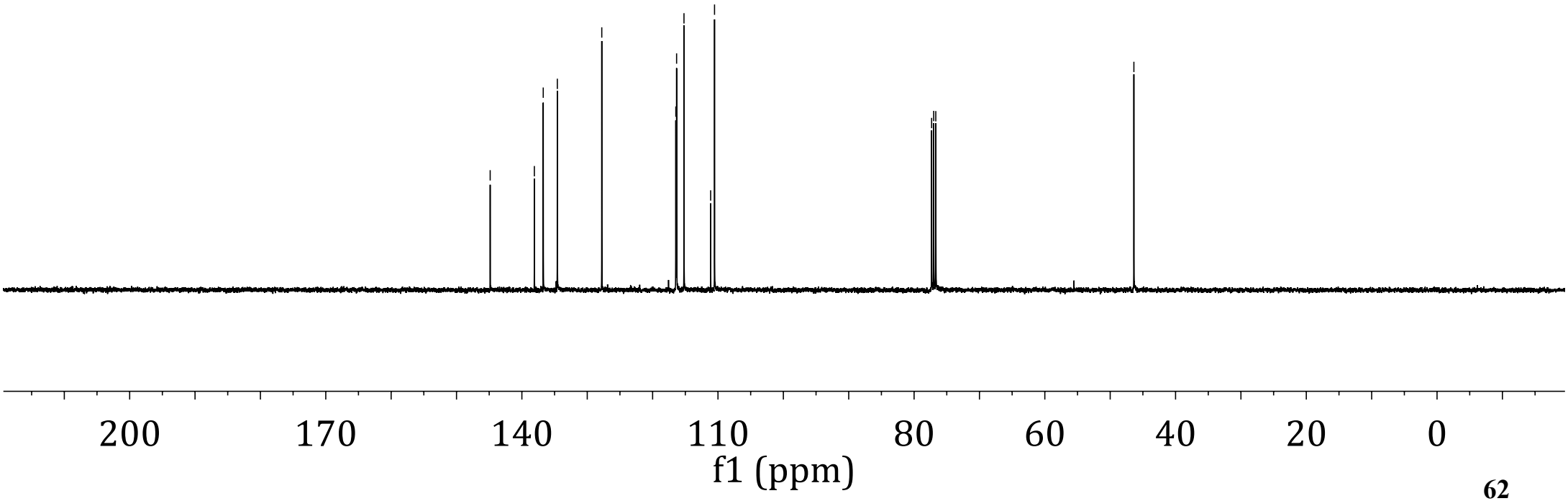


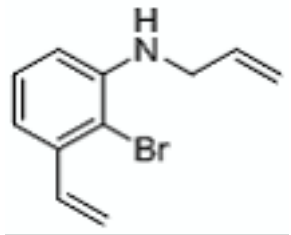


5f

144.85
138.09
136.73
134.58
127.78
116.45
116.33
115.20
111.12
110.53
77.32
77.00
76.68
46.37

^{13}C NMR (100 M, $CDCl_3$)

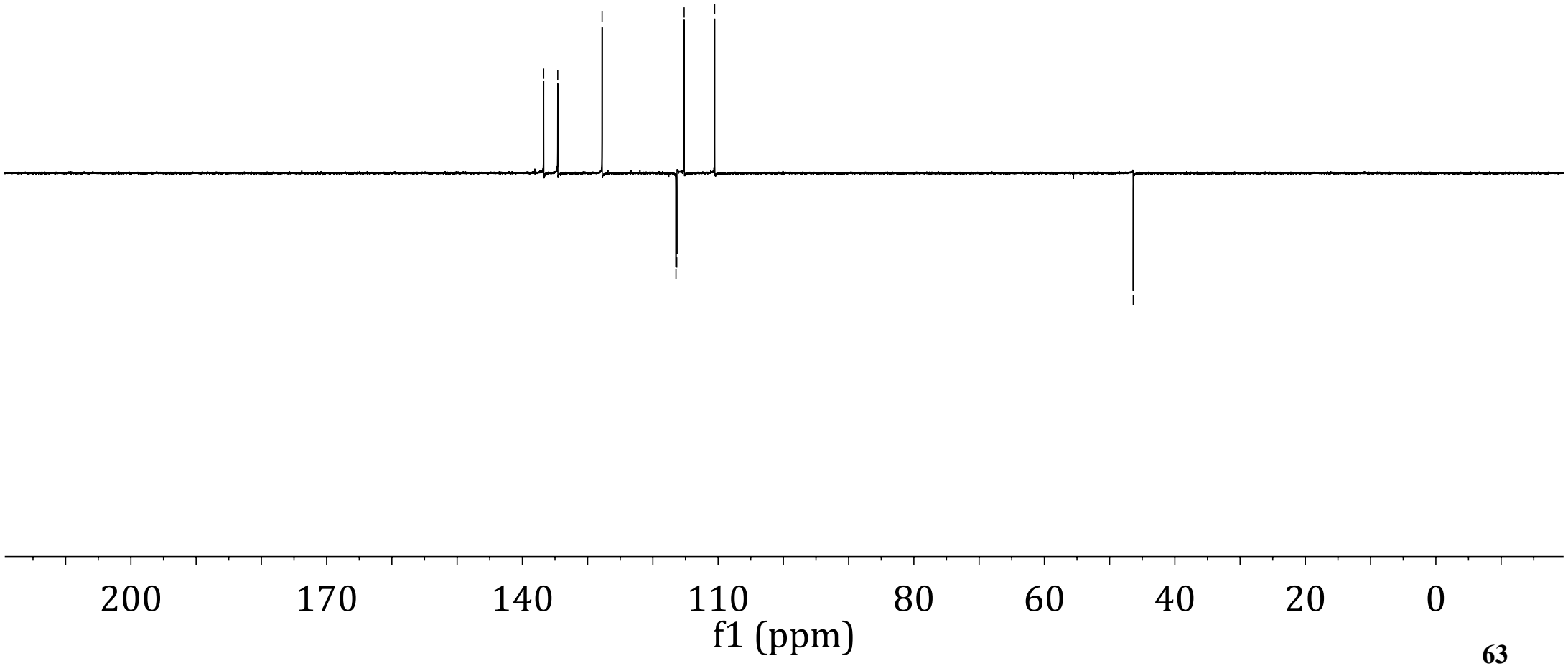


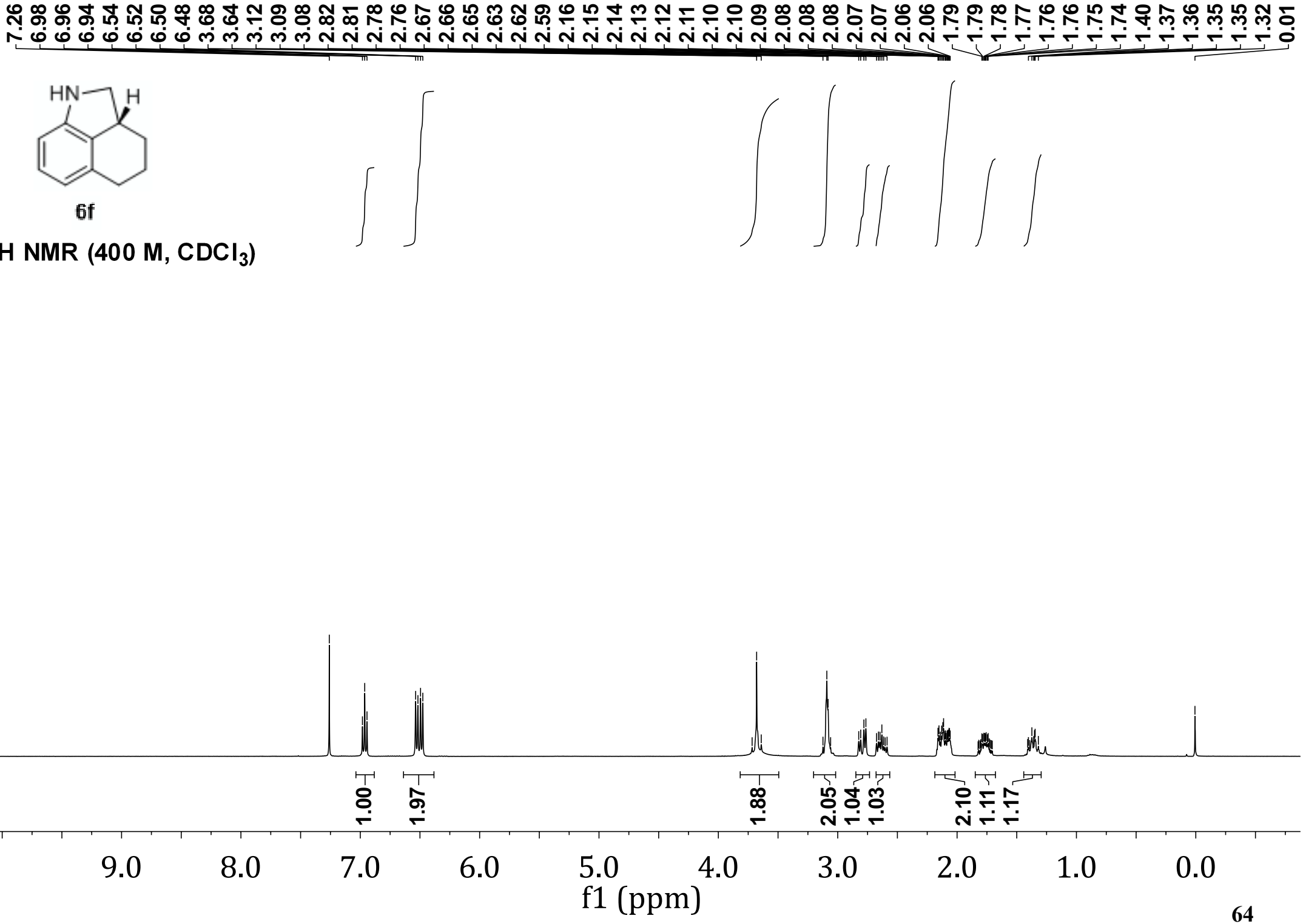


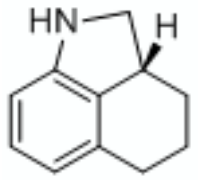
5f

136.74
134.58
127.78
116.46
116.33
115.20
110.53
46.37

DEPT-135 NMR (100M, $CDCl_3$)




7.26 6.98 6.96 6.94 6.54 6.52 6.50 6.48 3.68 3.64 3.12 3.09 3.08 2.82 2.81 2.78 2.76 2.67 2.66 2.65 2.63 2.62 2.59 2.16 2.15 2.14 2.13 2.12 2.11 2.10 2.10 2.09 2.08 2.08 2.08 2.07 2.07 2.06 2.06 1.79 1.79 1.78 1.77 1.76 1.76 1.75 1.74 1.40 1.37 1.36 1.35 1.35 1.32 0.01
HN
H
6f
1H NMR (400 M, CDCl3)
1.00
1.97
1.88
2.05
1.04
1.03
2.10
1.11
1.17
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



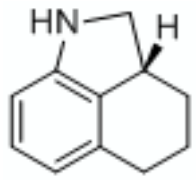
6f

^{13}C NMR (100 M, $CDCl_3$)

150.55
134.03
130.92
127.40
117.87
106.16
77.32
77.00
76.68
56.33
38.93
26.90
25.80
23.48

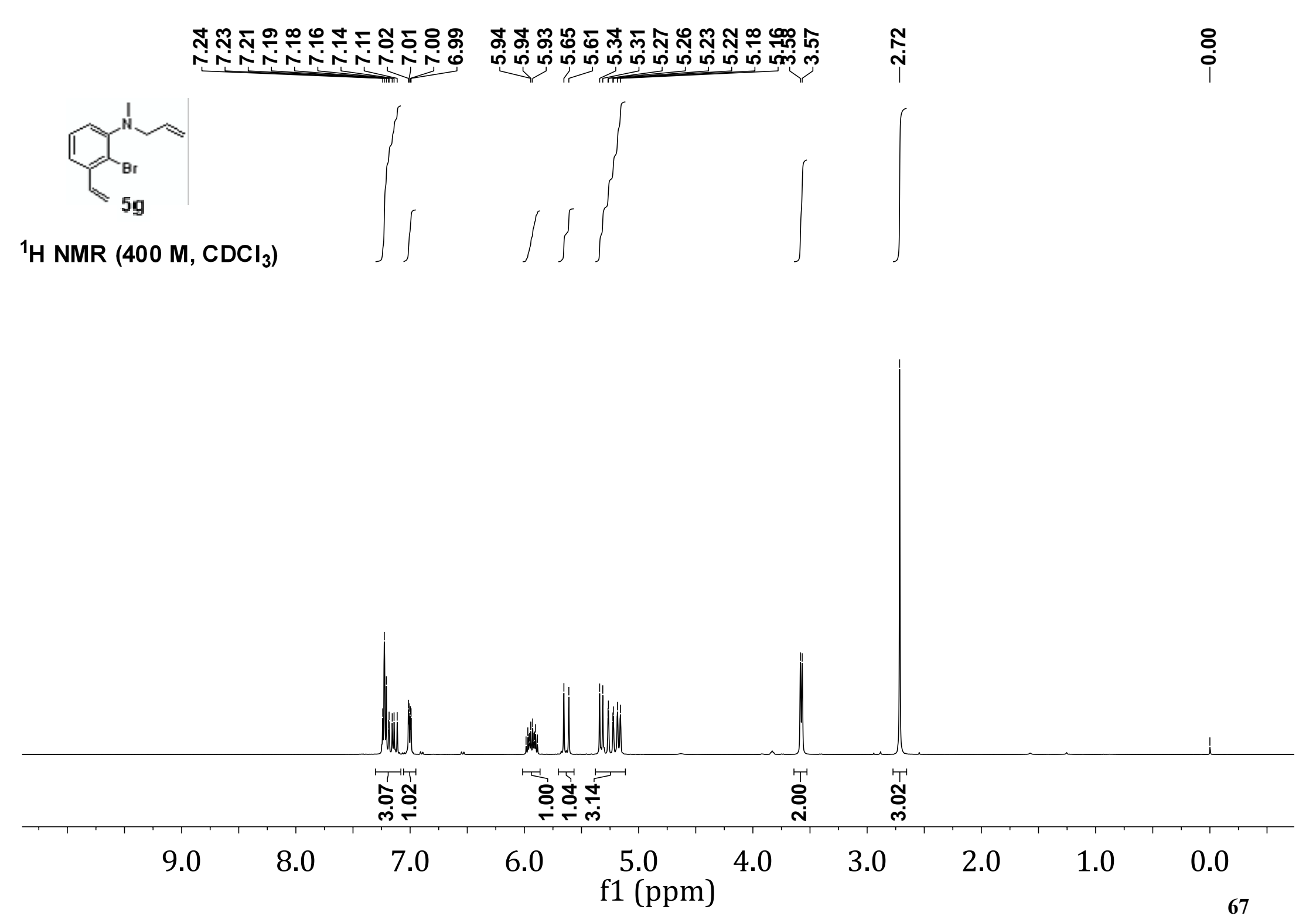
200 170 140 110 80 60 40 20 0

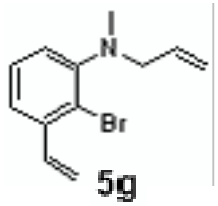
f1 (ppm)



6f

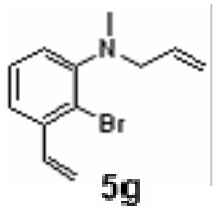
DEPT-135 NMR (100M, $CDCl_3$)


7.24
7.23
7.21
7.19
7.18
7.16
7.14
7.11
7.02
7.01
7.00
6.99
5.94
5.94
5.93
5.65
5.61
5.34
5.31
5.27
5.26
5.23
5.22
5.18
5.16
3.58
3.57
2.72
0.00
Br
5g
1H NMR (400 M, CDCl3)
3.07
1.02
1.00
1.04
3.14
2.00
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



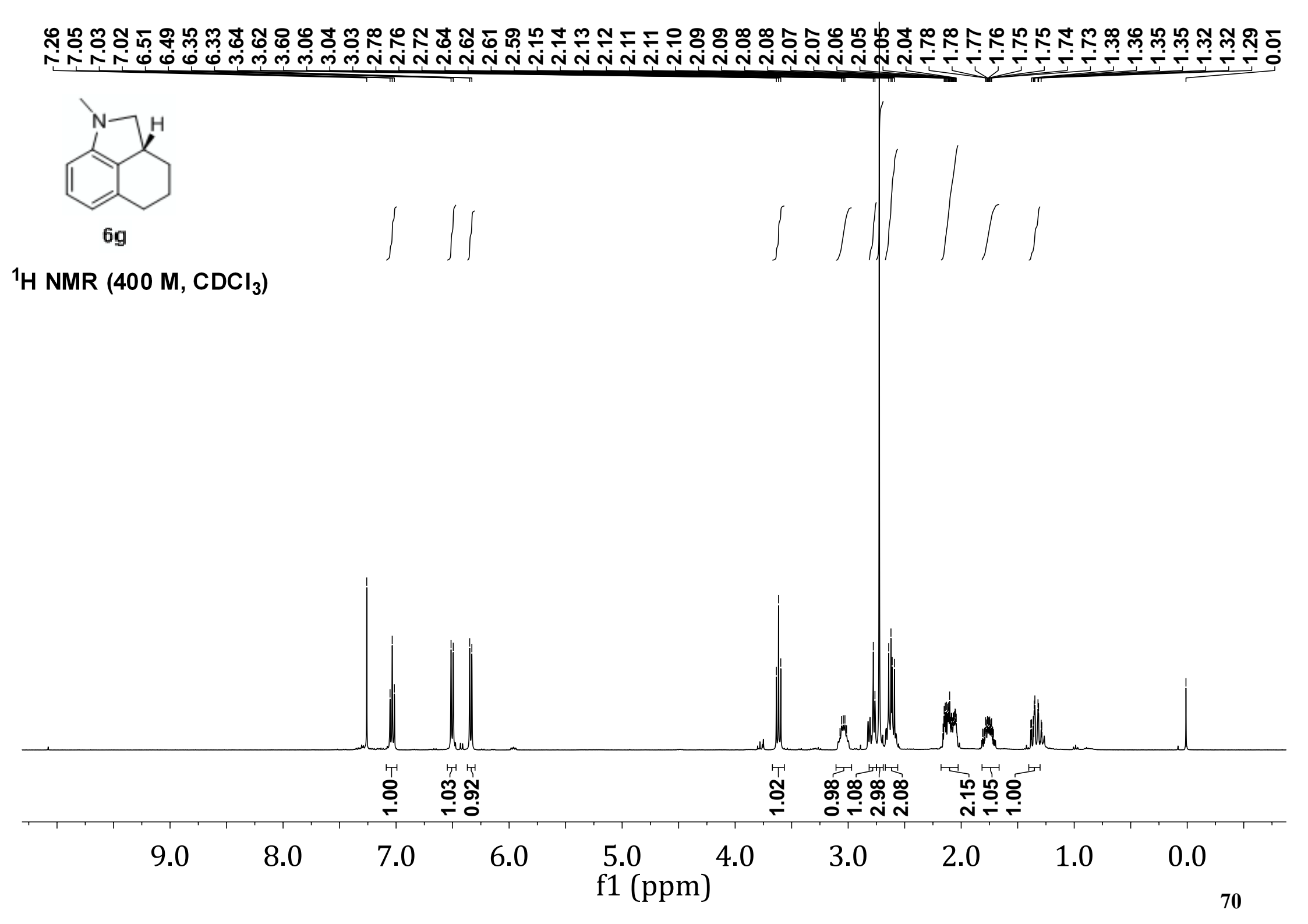
5g

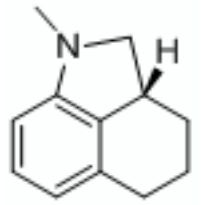
^{13}C NMR (100 M, $CDCl_3$)



5g

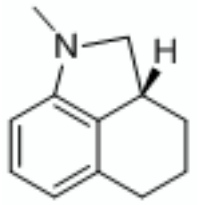
DEPT-135 NMR (100M, $CDCl_3$)


7.26 7.05 7.03 7.02 6.51 6.49 6.35 6.33 3.64 3.62 3.60 3.06 3.04 3.03 2.78 2.76 2.72 2.64 2.62 2.61 2.59 2.15 2.14 2.13 2.12 2.11 2.11 2.10 2.09 2.09 2.08 2.08 2.07 2.07 2.06 2.05 2.05 2.04 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.38 1.36 1.35 1.35 1.32 1.32 1.29 0.01
N
H
6g
1H NMR (400 M, CDCl3)
1.00 1.03 0.92 1.02 0.98 1.08 2.98 2.08 2.15 1.05 1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



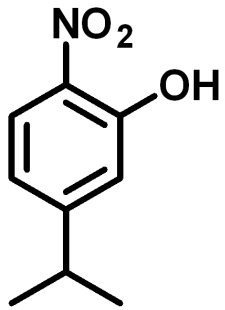
6g

^{13}C NMR (100 M, $CDCl_3$)



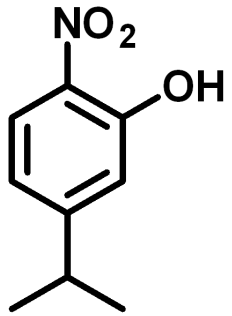
6g

DEPT-135 NMR (100M, $CDCl_3$)



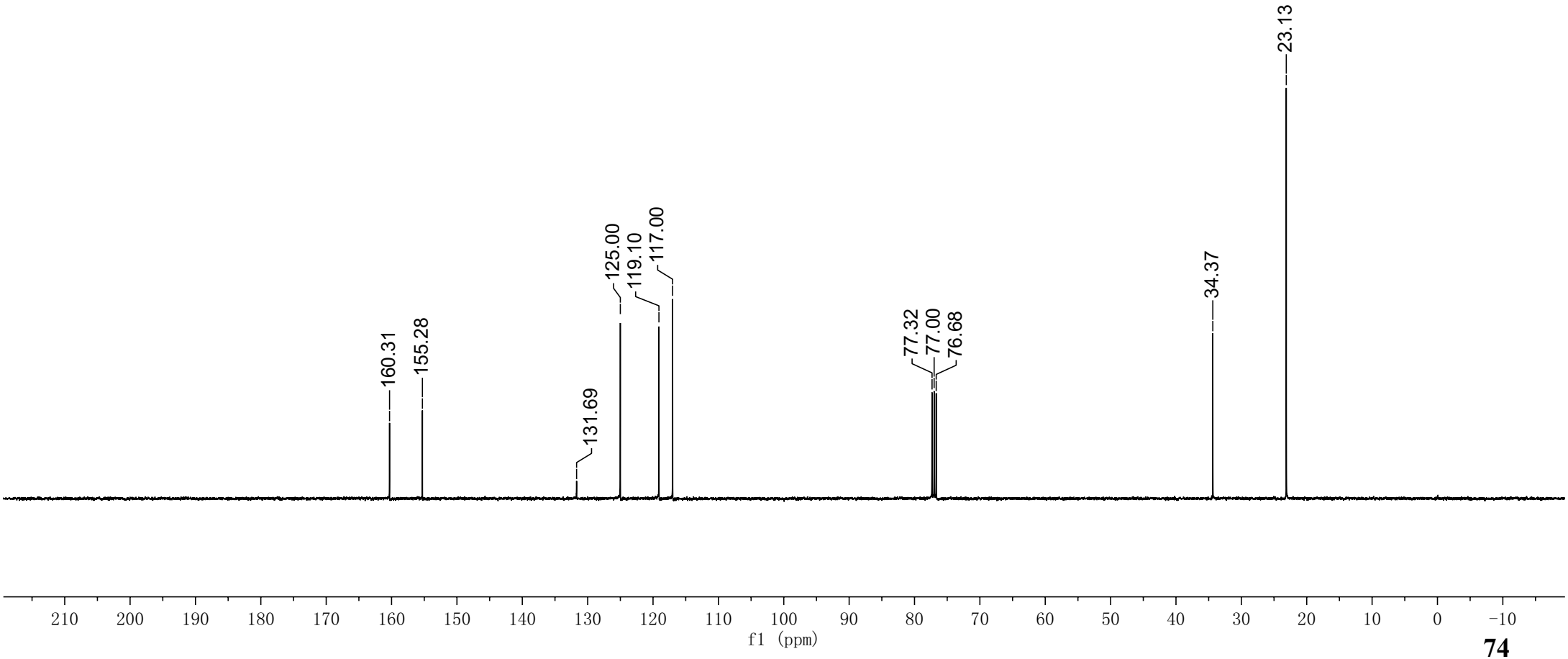
SI-3

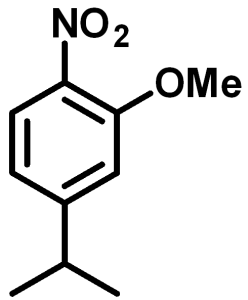
^{1}H NMR (400 M, $CDCl_3$)



SI-3

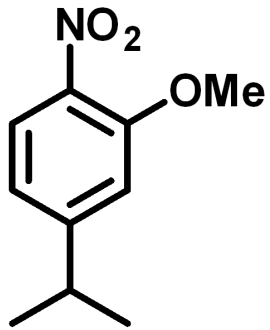
^{13}C NMR (100 M, $CDCl_3$)





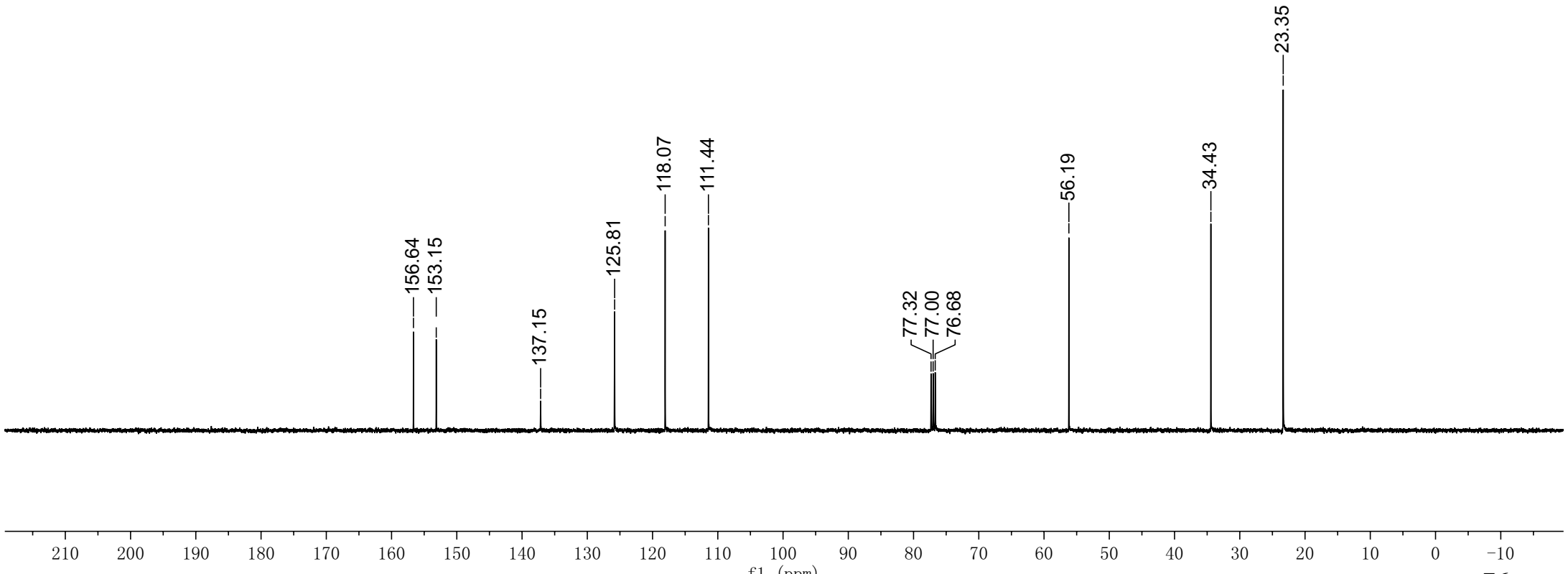
SI-4

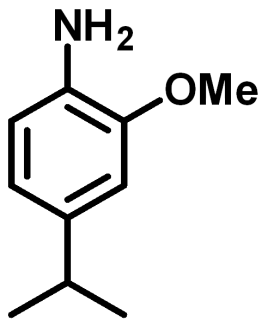
^{1}H NMR (400 M, $CDCl_3$)



SI-4

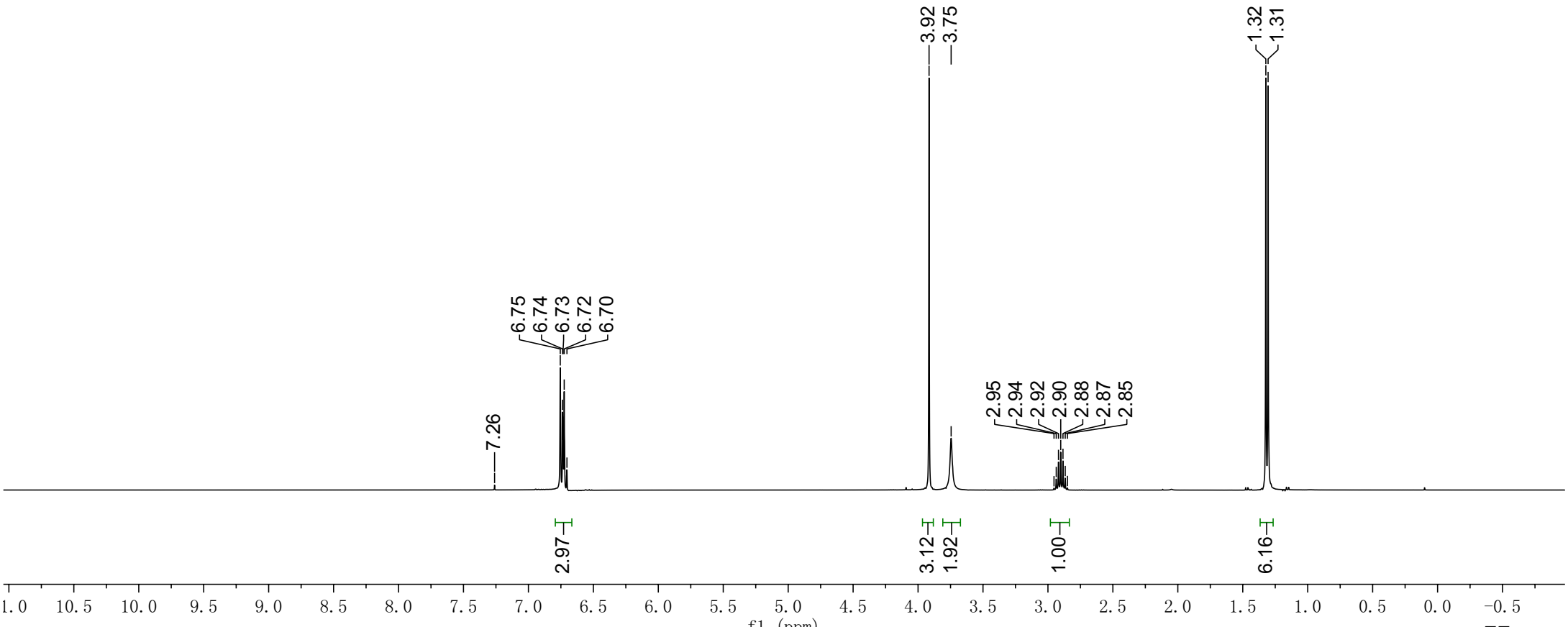
^{13}C NMR (100 M, $CDCl_3$)

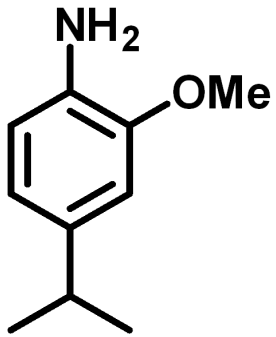




8

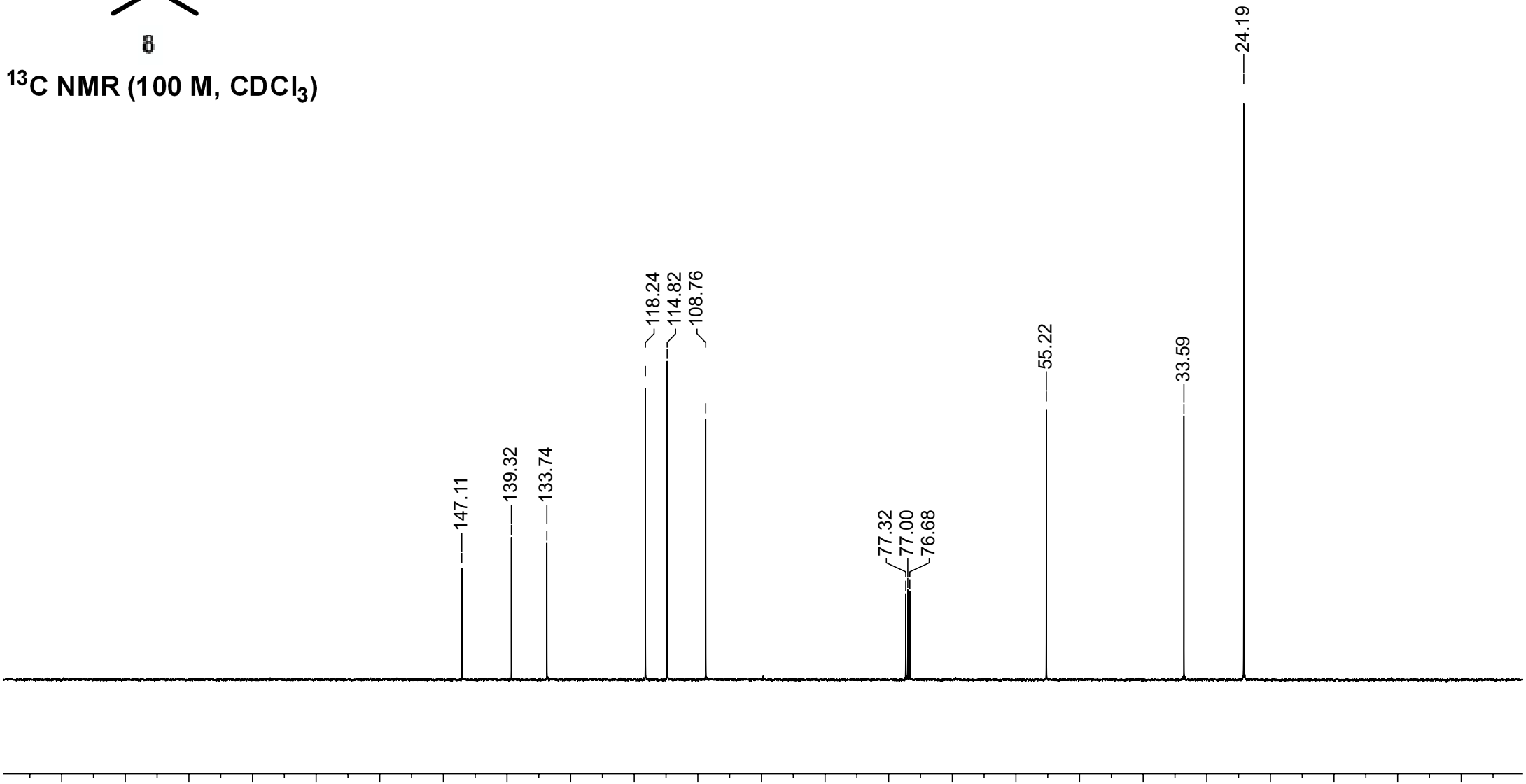
^{1}H NMR (400 M, $CDCl_3$)

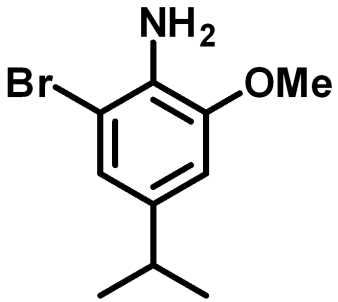




8

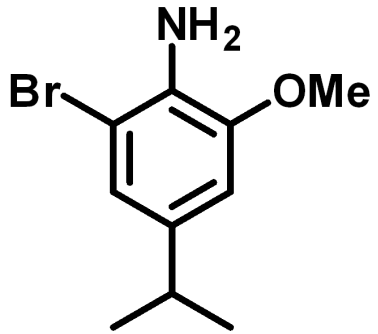
^{13}C NMR (100 M, $CDCl_3$)





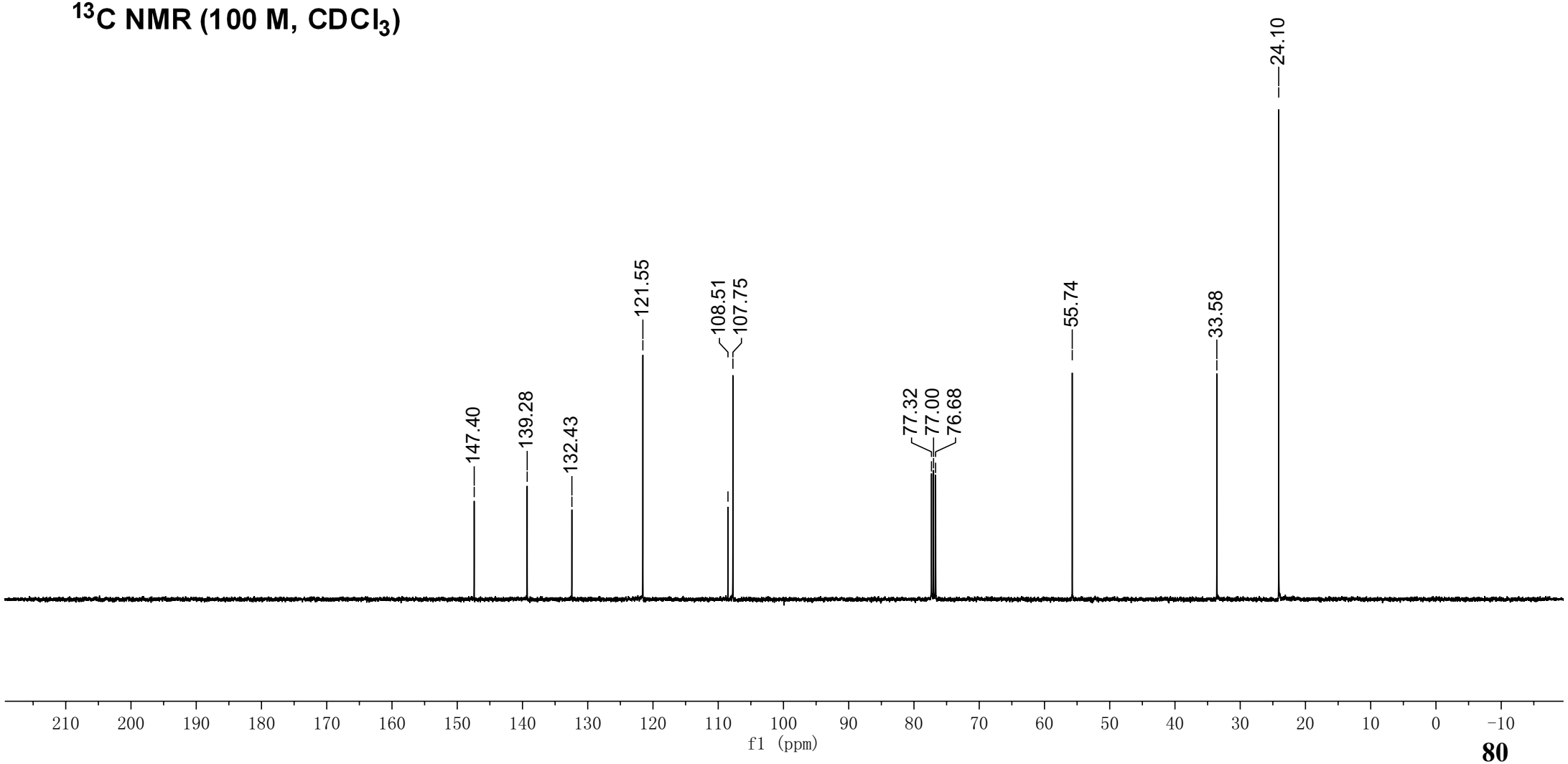
SI-5

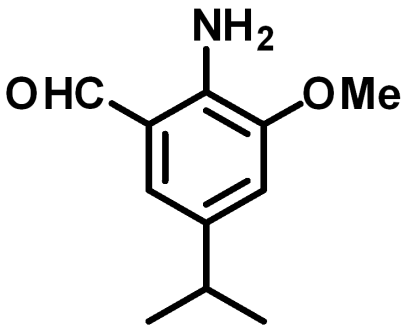
^{1}H NMR (400 M, $CDCl_3$)



SI-5

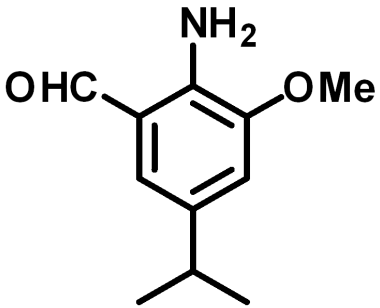
^{13}C NMR (100 M, $CDCl_3$)





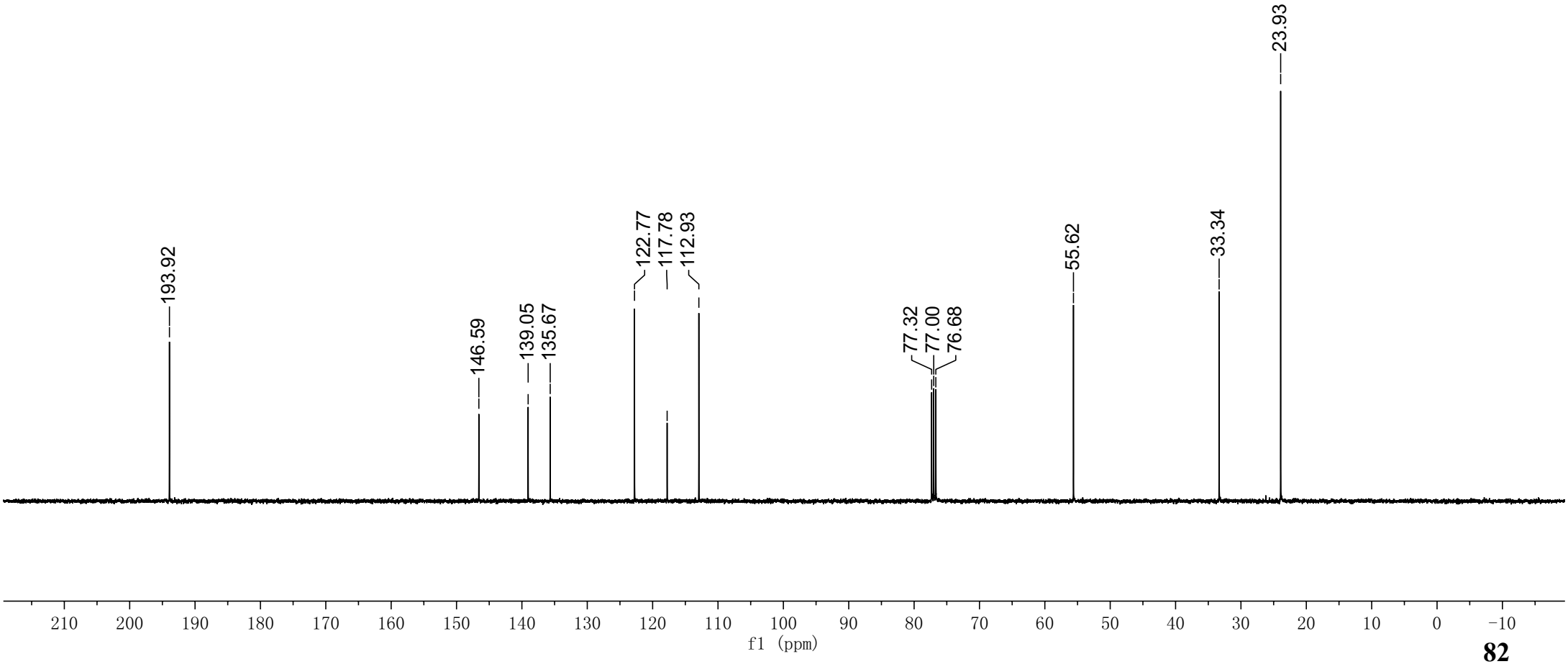
9

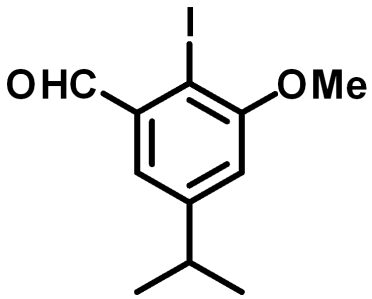
^{1}H NMR (400 M, $CDCl_3$)



9

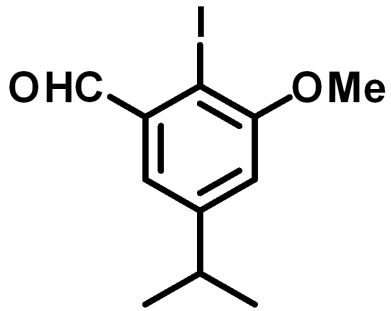
^{13}C NMR (100 M, $CDCl_3$)





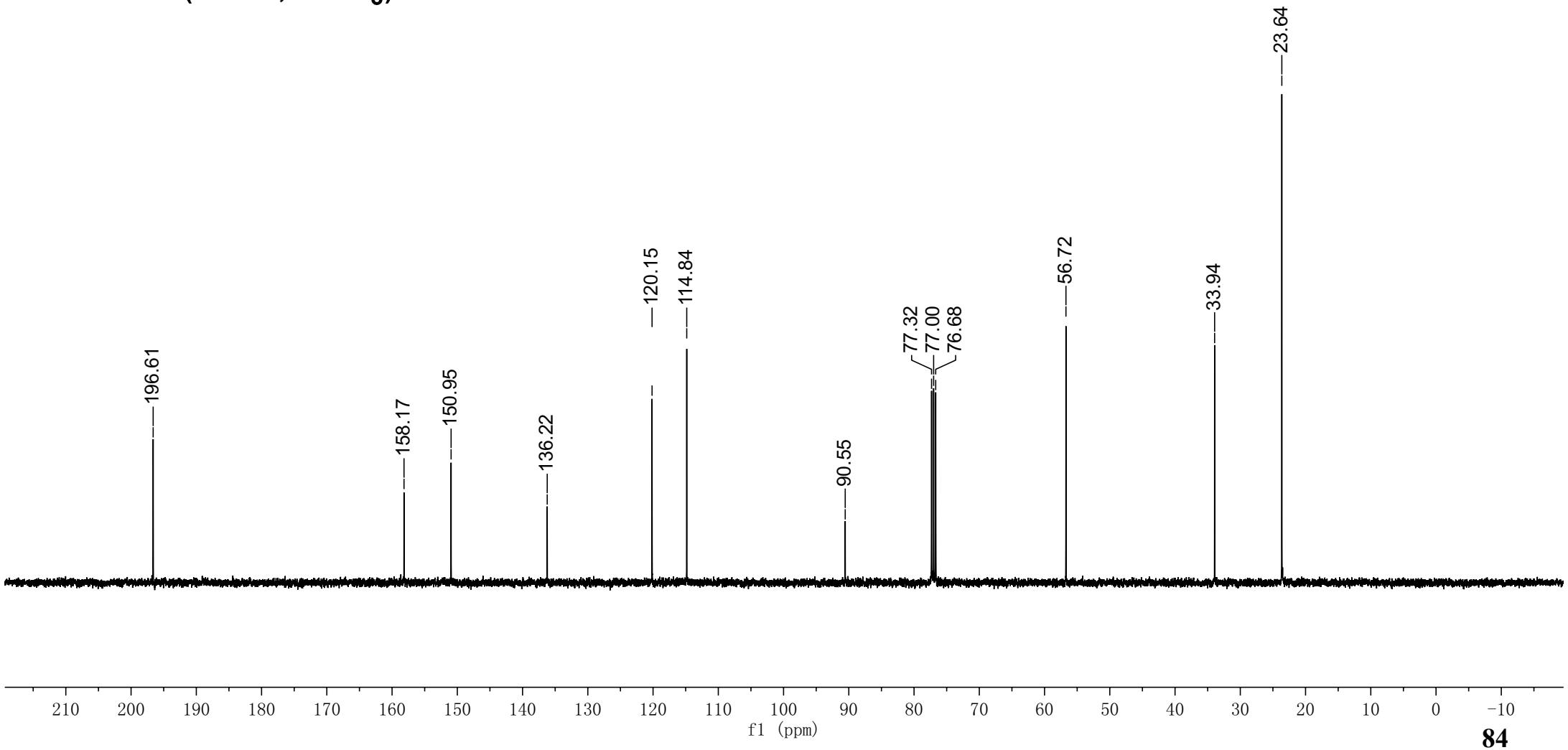
SI-6

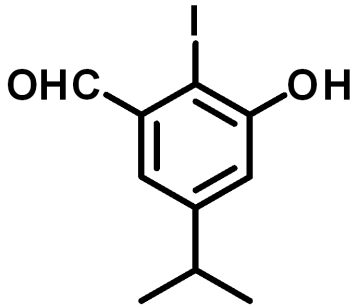
^{1}H NMR (400 M, $CDCl_3$)



SI-6

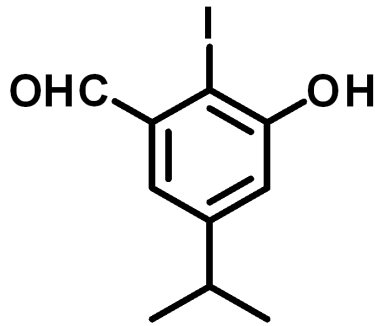
^{13}C NMR (100 M, $CDCl_3$)





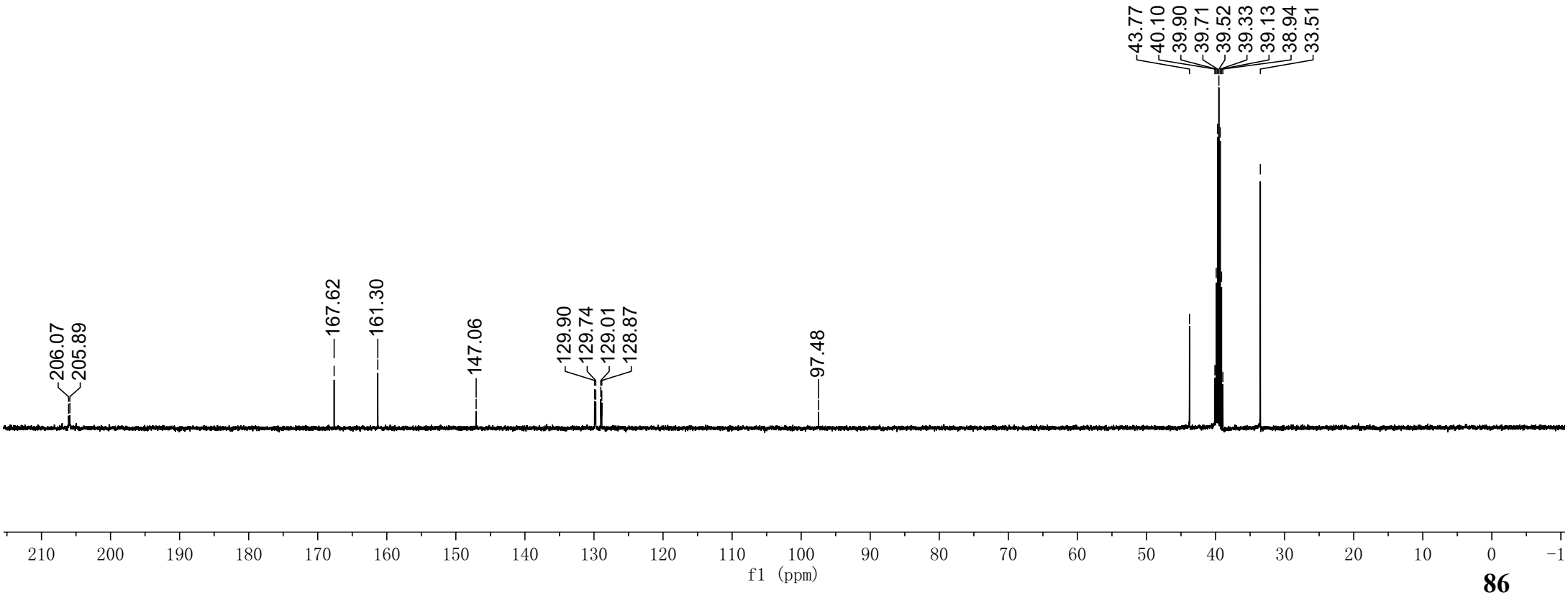
SI-7

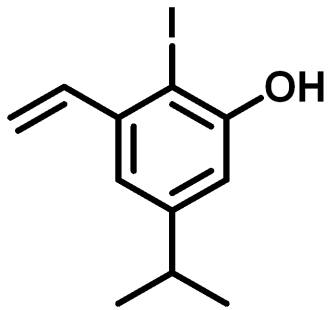
^{1}H NMR (400 M, d^6-DMSO)



SI-7

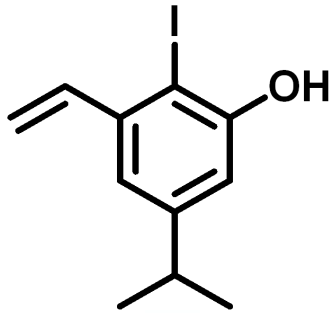
^{13}C NMR (100 M, d^{6}-DMSO)





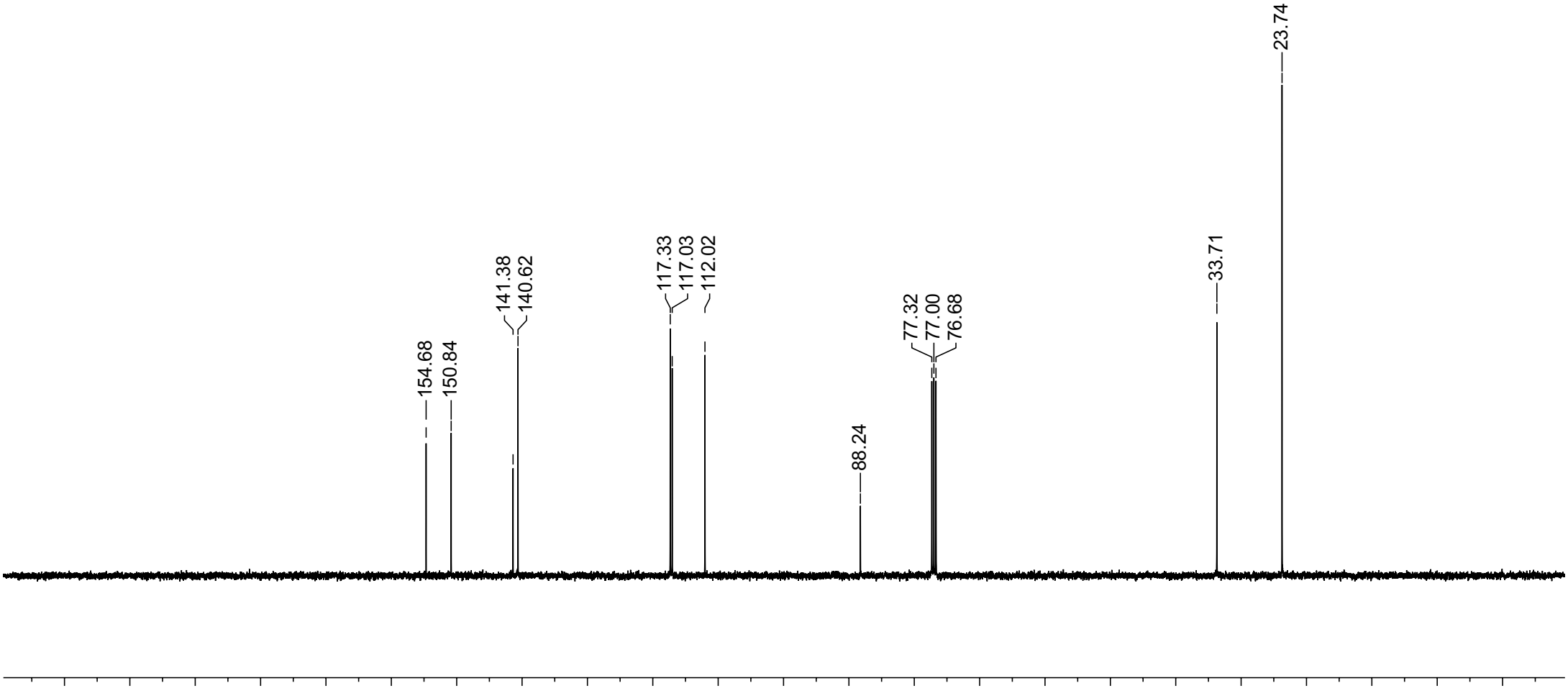
10

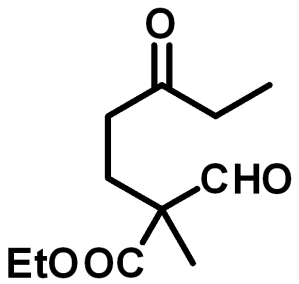
^{1}H NMR (400 M, $CDCl_3$)



10

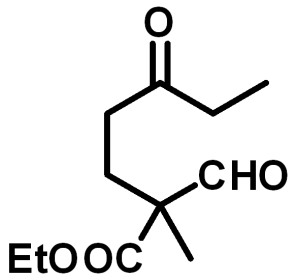
^{13}C NMR (100 M, $CDCl_3$)





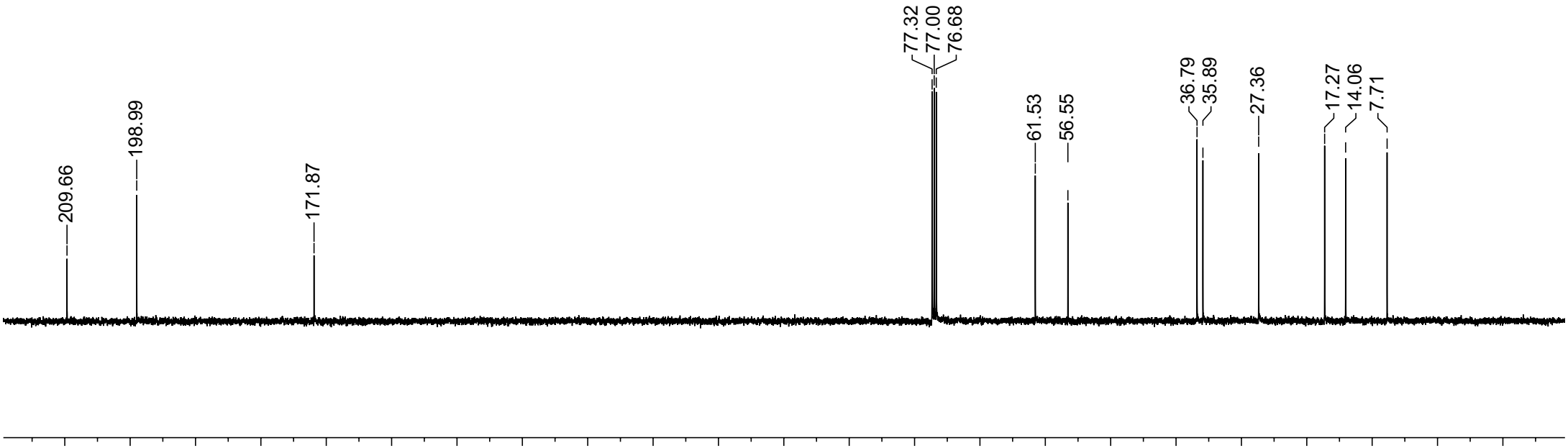
SI-8

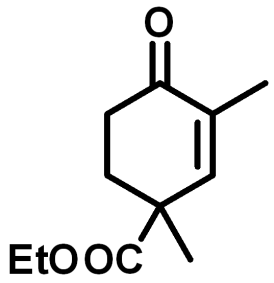
^{1}H NMR (400 M, $CDCl_3$)



SI-8

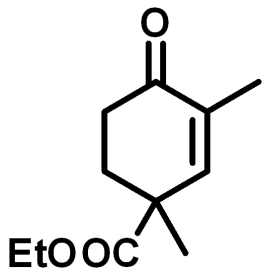
^{13}C NMR (100 M, $CDCl_3$)





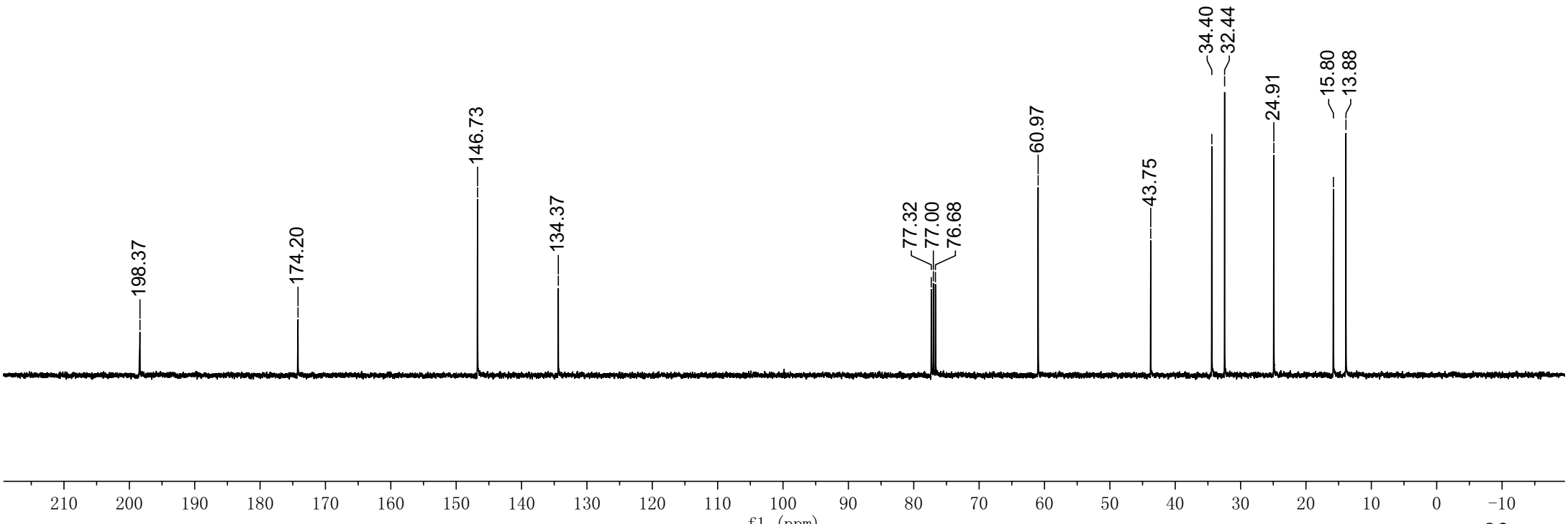
SI-9

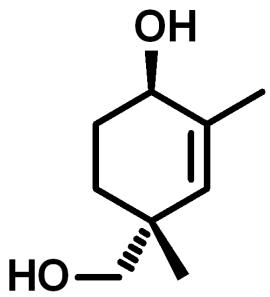
^{1}H NMR (400 M, $CDCl_3$)



SI-9

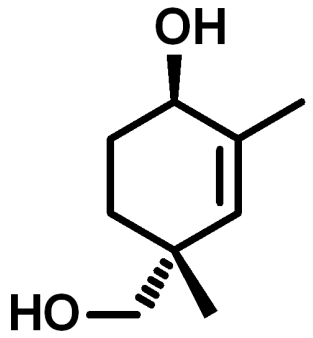
^{13}C NMR (100 M, $CDCl_3$)





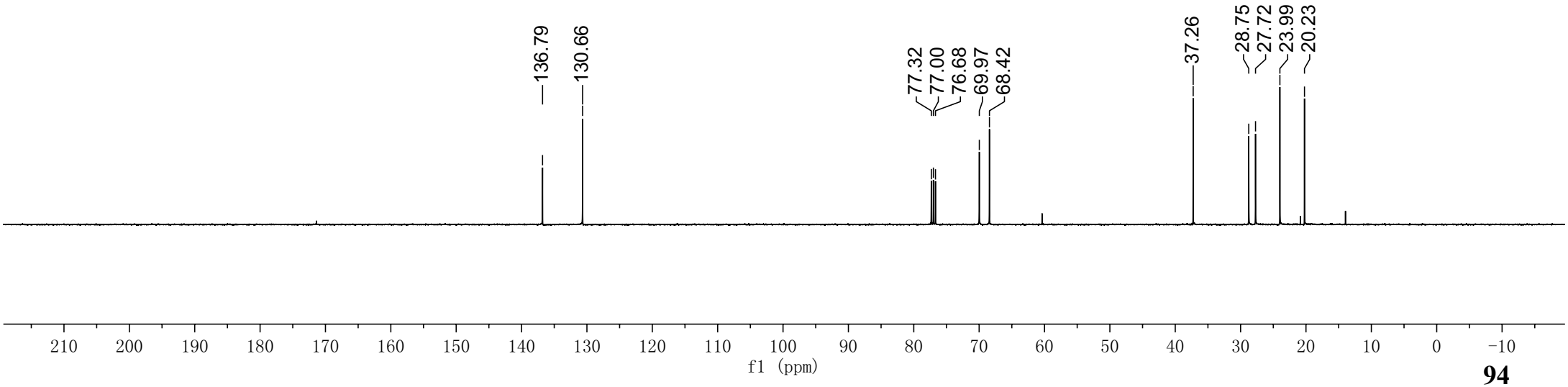
13

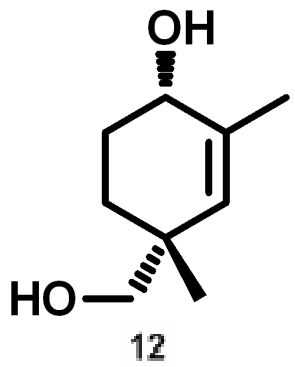
^{1}H NMR (400 M, $CDCl_3$)



13

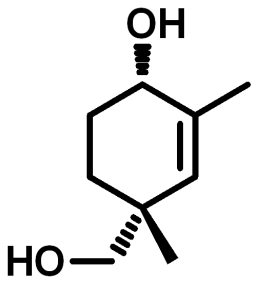
^{13}C NMR (100 M, $CDCl_3$)





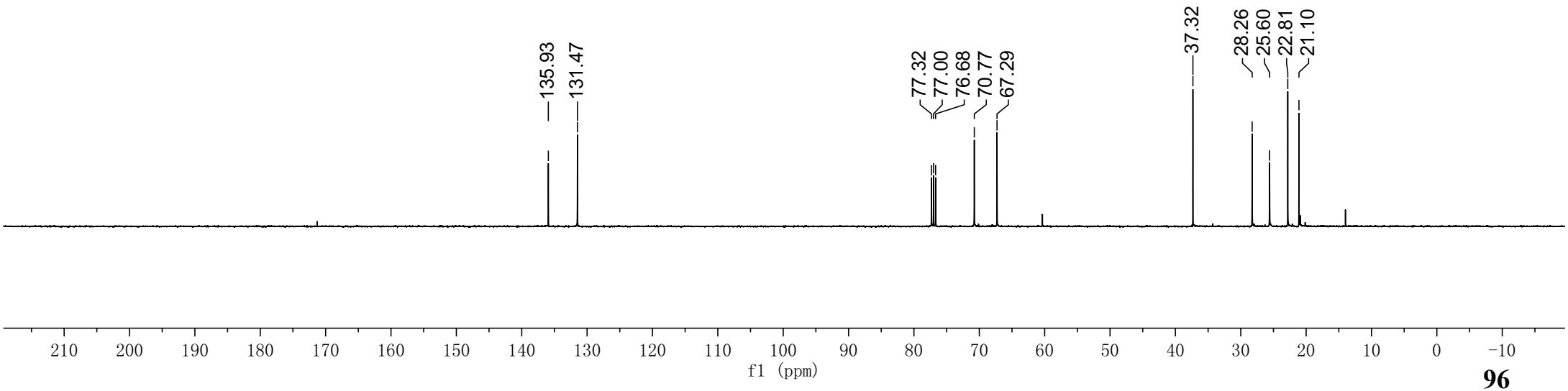
12

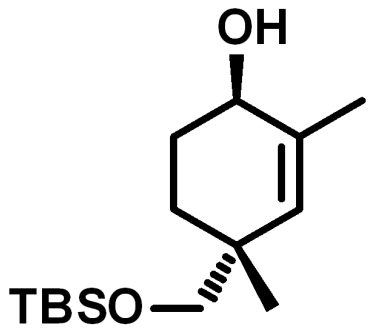
^{1}H NMR (400 M, $CDCl_3$)



12

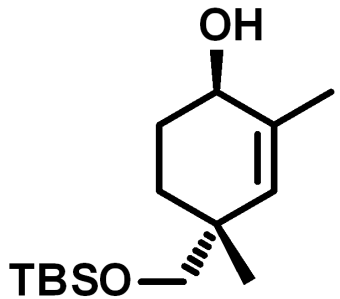
^{13}C NMR (100 M, $CDCl_3$)





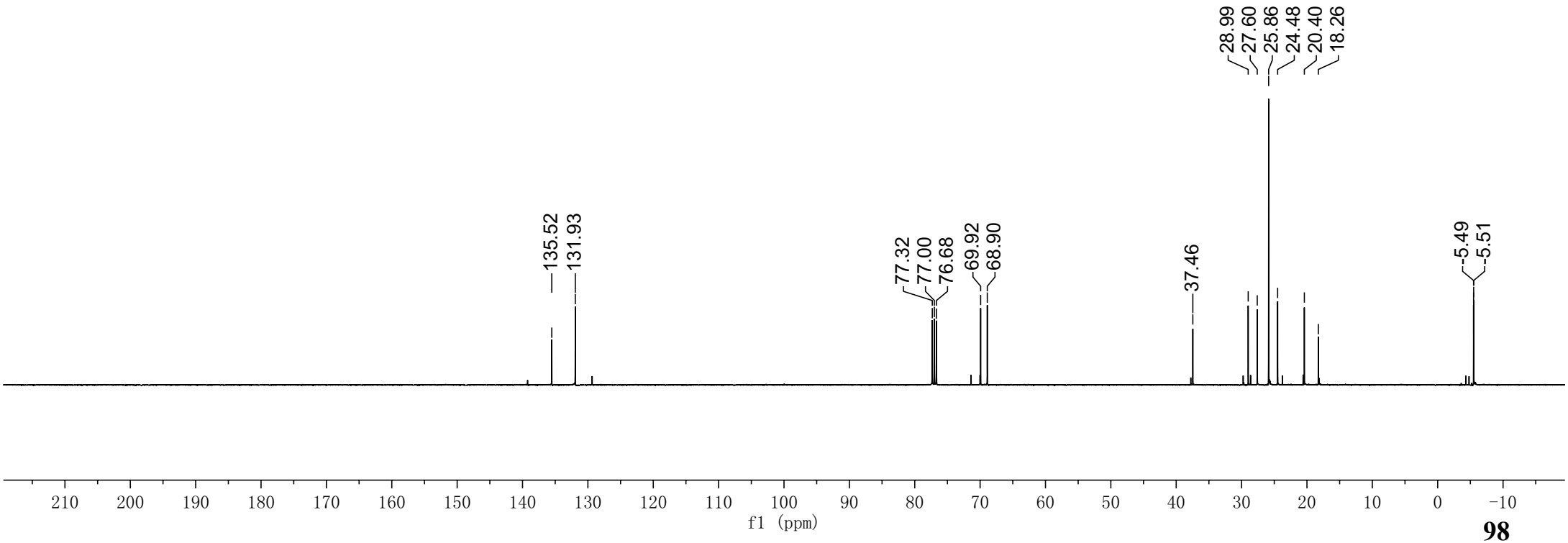
15

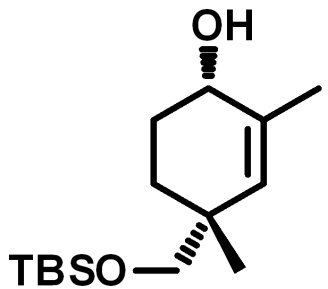
^{1}H NMR (400 M, $CDCl_3$)



15

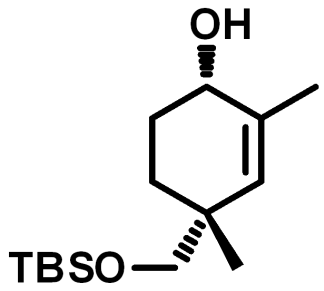
^{13}C NMR (100 M, $CDCl_3$)





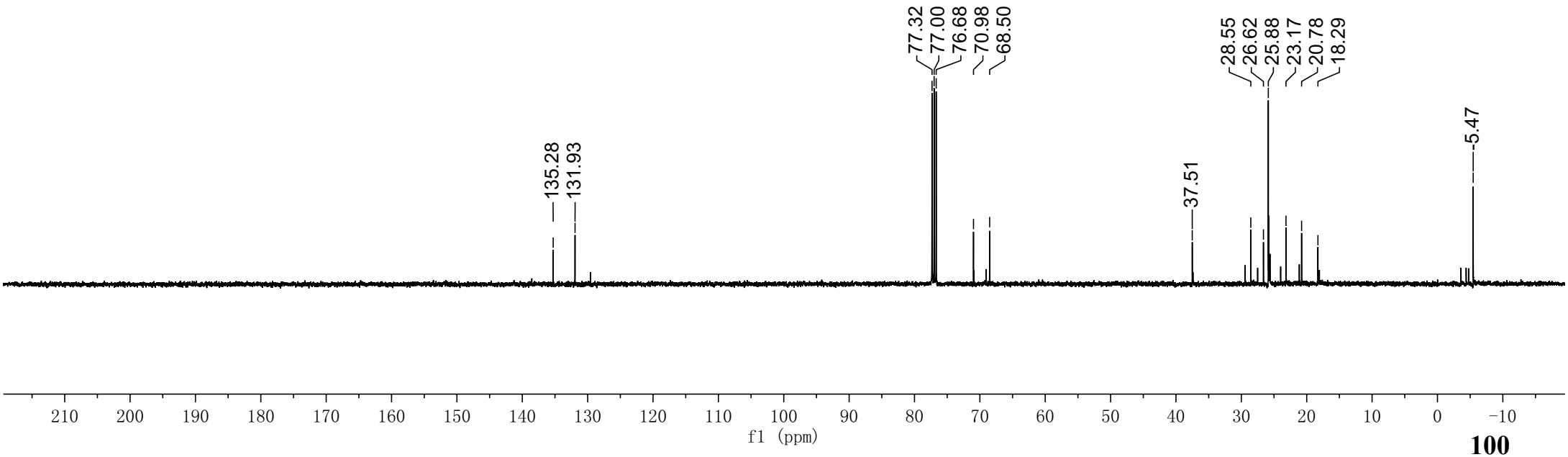
14

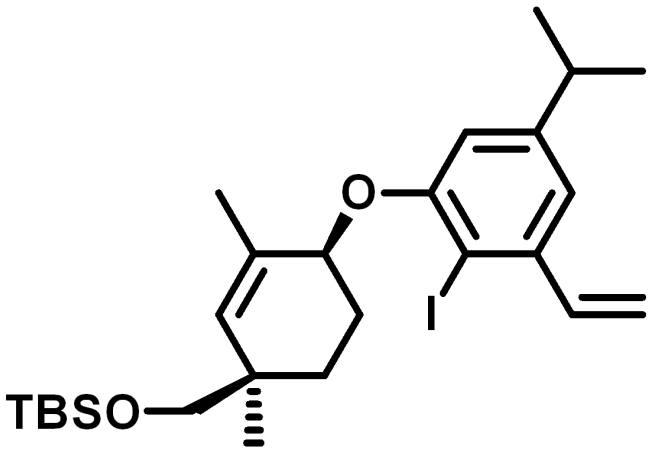
^{1}H NMR (400 M, $CDCl_3$)



14

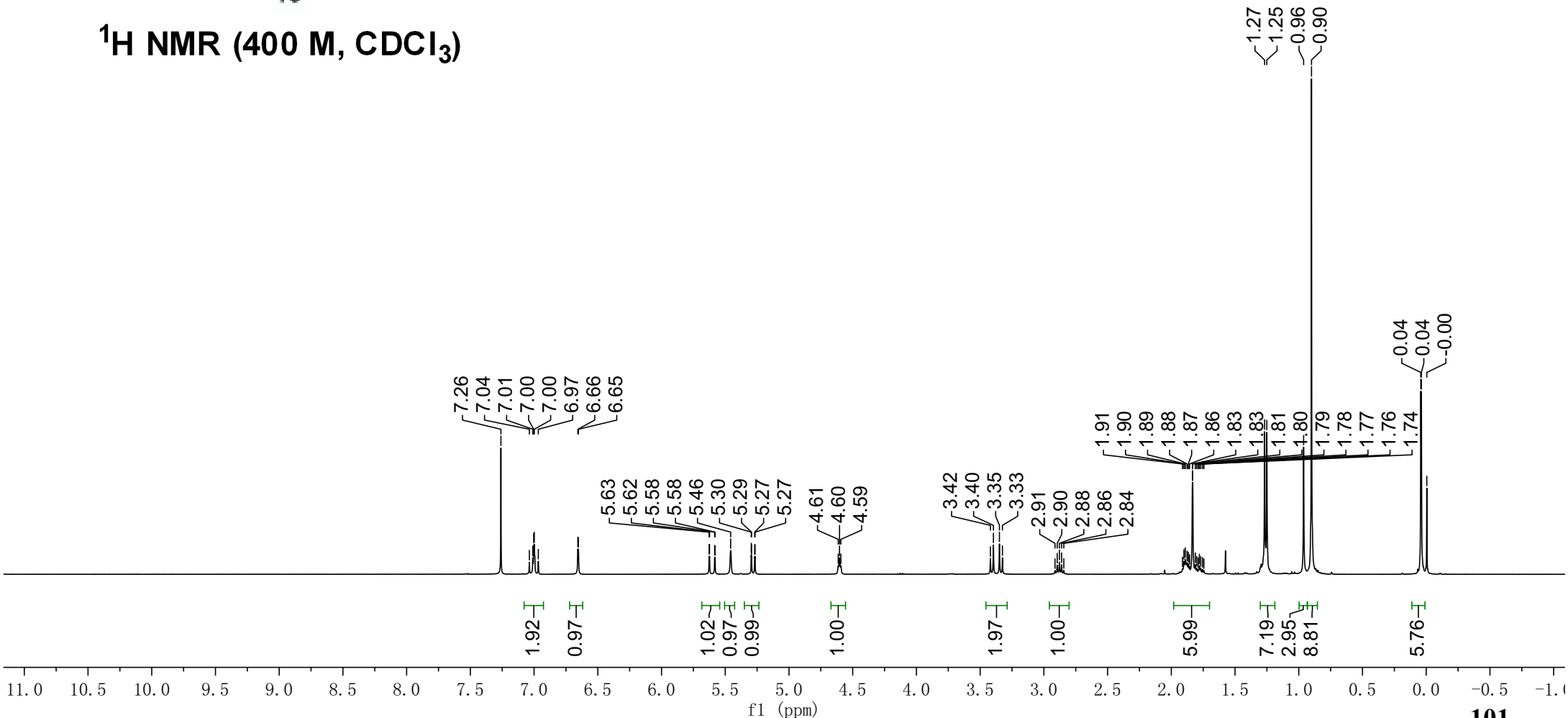
^{13}C NMR (100 M, $CDCl_3$)

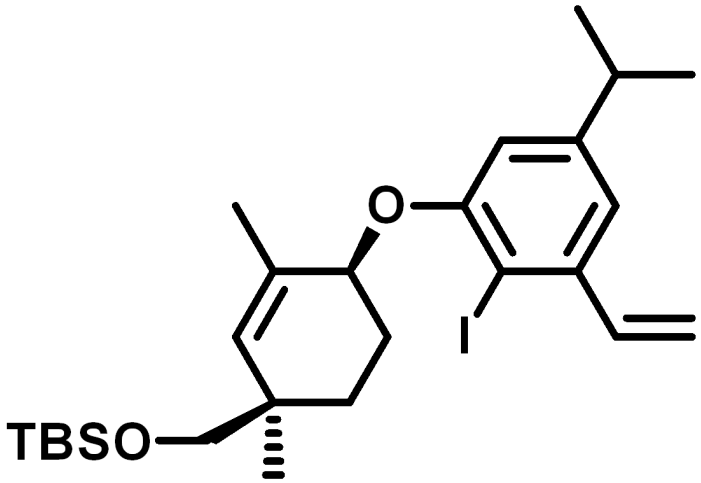




16

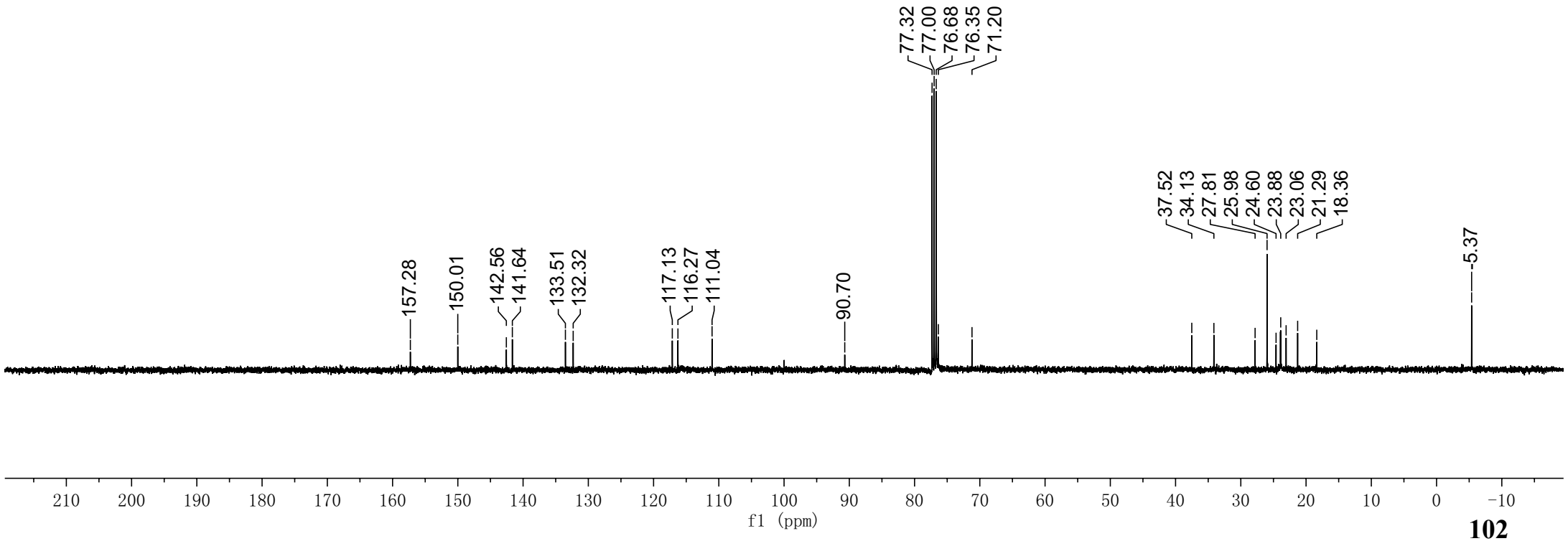
^{1}H NMR (400 M, $CDCl_3$)

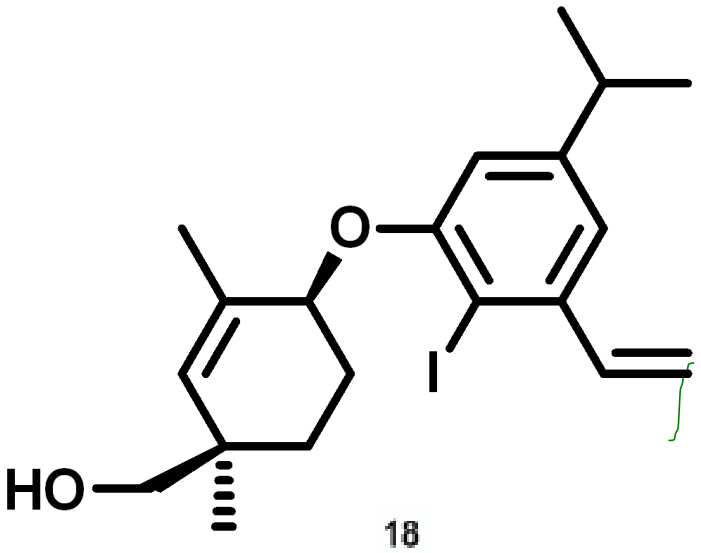




16

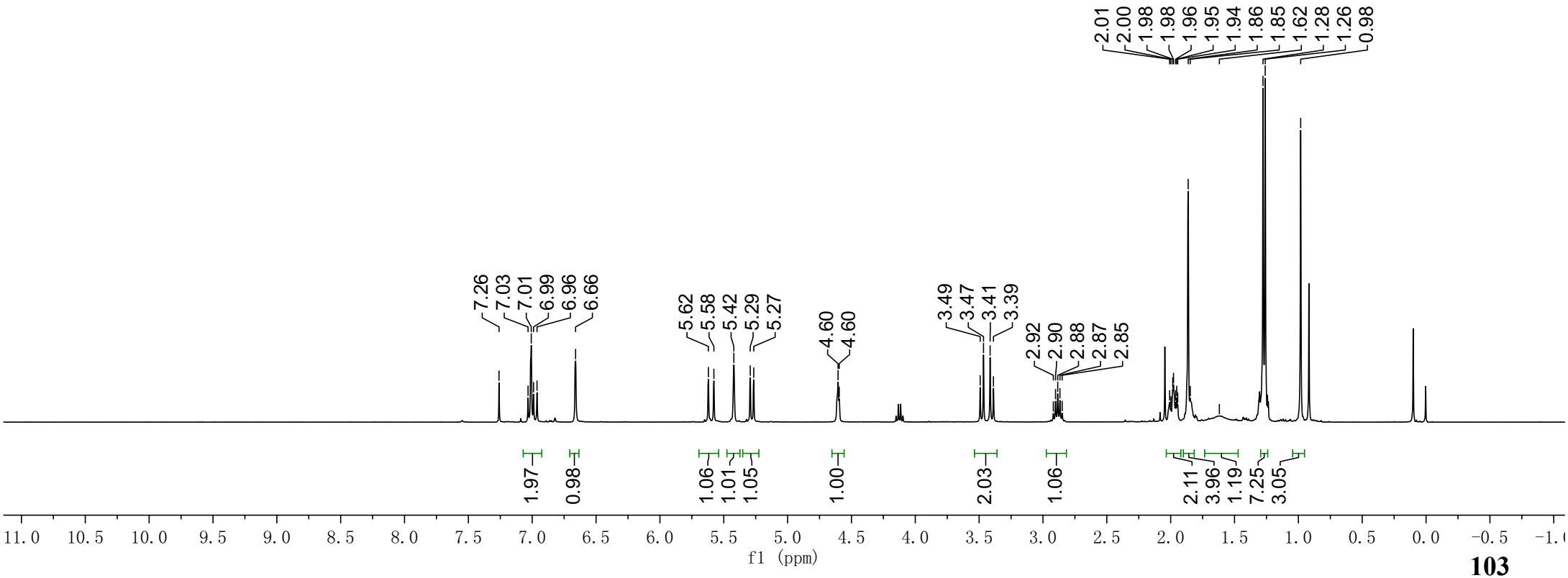
^{13}C NMR (100 M, $CDCl_3$)

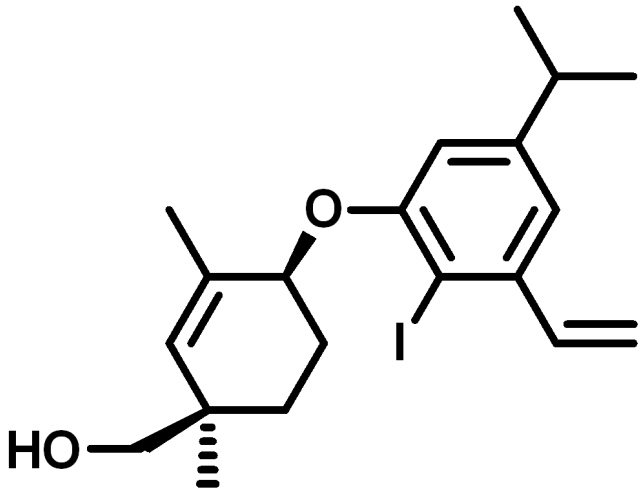




18

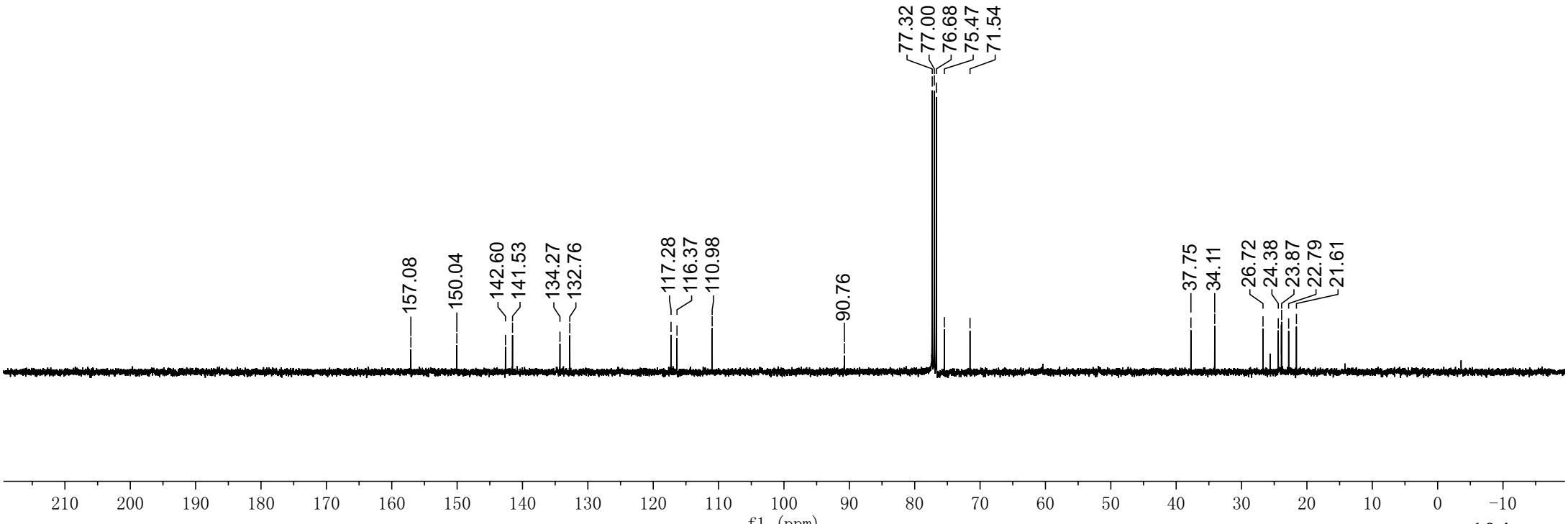
^{1}H NMR (400 M, $CDCl_3$)

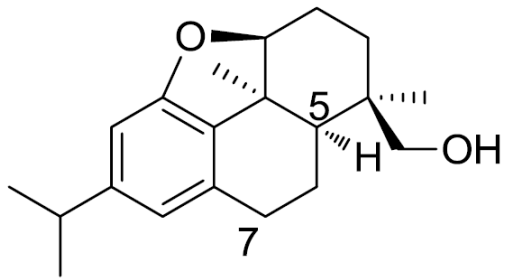




18

^{13}C NMR (100 M, $CDCl_3$)

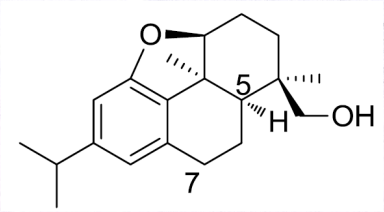




19

5-*epi*-7-*deoxy*-Isoabietenin A

^{1}H NMR (400 M, $CDCl_3$)



19

156.681
149.579
133.393
129.350
117.382
105.635
92.019
77.999
77.214
77.000
76.786
63.788
47.106
40.493
38.441
34.429
29.753
29.593
26.023
24.307
24.230
24.146
19.226
-0.011

5-*epi*-7-*deoxy*-Isoabietenin A

^{13}C NMR (150 M, $CDCl_3$)