Supporting Information

A concise approach to the tricyclic framework of longipinane- and *ent*-longipinane-type sesquiterpenoids

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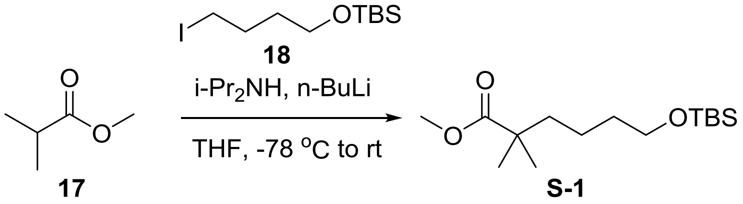
General information

Oxygen and moisture-sensitive reaction were carried out under argon atmosphere. Solvents THF and toluene were refluxed with Na, CH_2Cl_2 was refluxed with CaH_2 and freshly distilled prior to use. 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 with UV light to visualize the course of reaction. Infrared spectra were recorded on a 670 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz instrument, and chemical shifts (δ) are given in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.27), CD_3OD (4.78, 3.31); ^{13}C NMR: $CDCl_3$ (77.0), CD_3OD (49.0)]. High-resolution mass spectral (HRMS) data were recorded on a Bruker Daltonics APEXII 47e FT-ICR spectrometer using electrospray ionization (ESI). Melting points were measured on a Tech X-4 melting point apparatus and were uncorrected.

Experimental Procedures



Methyl 6-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylhexanoate (S-1): To a stirred solution of diisopropylamine (12.62 mL, 89.54 mmol) in anhydrous THF (200 mL) at 0 °C under an argon atmosphere was added *n*-BuLi (32.83 mL, 2.5 M in hexanes, 82.08 mmol) and the solution was stirred at 0 °C for 30 min. Then the freshly prepared LDA was cooled to -78 °C and a solution of **17** (8.00 g, 78.35 mmol) in anhydrous THF (50 mL) was added and then stirred for 1 h, after which iodide **18**[1] (23.45 g, 74.62 mmol) in THF (50 mL) solution was added dropwise to the reaction mixture, and the resulting solution was stirred at the same temperature for 0.5 h, the resulting solution was allowed to warm to ambient temperature and stirred for 10 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl ether (3×50). The combined organic phase was dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was chromatographed on silica-gel column with petroleum/ethyl acetate (50:1) to give the product ester **S-1** (20.67 g, 71.64 mmol, 96% yield) as a colourless oil.

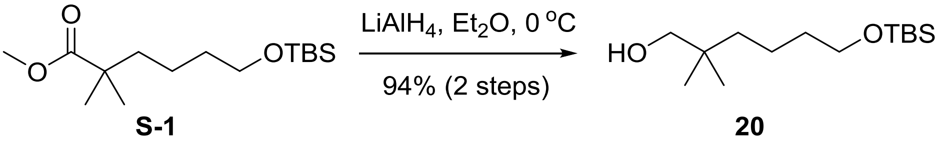
Data for **S-1**

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 1.58 – 1.42 (m, 4H), 1.34 – 1.21 (m, 2H), 1.16 (s, 6H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 62.9, 51.5, 42.3, 40.6, 33.2, 25.9, 25.1, 21.2, 18.3, -5.3.

HRMS (ESI): calcd for $C_{15}H_{32}O_3Si$ ($[M + H]^+$) 289.2193, found 289.2200.

IR (neat) ν_{max}: 2952.0, 2931.1, 2858.5, 1735.5, 1473.1, 1462.7, 1256.5, 1193.0, 1144.3, 1103.6, 836.7, 775.4 cm^{-1}.



6-((*tert*-Butyldimethylsilyl) oxy)-2, 2-dimethylhexan-1-ol (20): To the stirred solution of above ester **S-1**(20.67 g, 71.64 mmol) in Et_2O (260 mL) at 0 °C was added lithium aluminum hydride (2.86 g, 75.22 mmol) portionwise. The reaction mixture was stirred at the same temperature for 20 min. After which time TLC analysis showed full conversion, the reaction was quenched with H_2O (2.86 mL), 10 % aqueous NaOH (5.72 mL) and H_2O (8.58 mL). After stirring at room temperature for 1 h, the mixture was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether/ethyl acetate = 2:1) to afford **20** (18.27 g, 70.14 mmol, 94% overall yield for two steps) as a colorless oil.

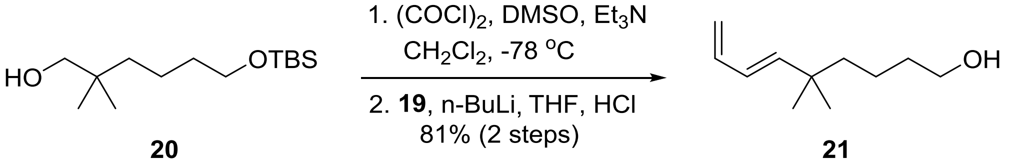
Data for **20**

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (t, *J* = 6.5 Hz, 2H), 3.24 (s, 2H), 2.06 (s, 1H), 1.50 – 1.40 (m, 2H), 1.31 – 1.14 (m, 4H), 0.85 (s, 9H), 0.81 (s, 6H), -0.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 71.70, 63.02, 38.24, 35.00, 33.53, 25.91, 23.80, 19.97, 18.28, -5.31.

HRMS (ESI): calcd for $C_{14}H_{32}O_2Si$ ($[M + H]^+$) 261.2244, found 261.2248.

IR (neat) ν_{max}: 3366.8, 2954.1, 2931.7, 2895.4, 2859.2, 1472.4, 1387.8, 1362.2, 1254.9, 1104.1, 1041.3, 836.4, 810.0, 775.4 cm^{-1}.



(*E*)-5, 5-Dimethylnona-6, 8-dien-1-ol (21): To a solution of oxalyl chloride (9.05 mL, 105.32 mmol) in dry CH_2Cl_2 (150 mL) at -78 °C was added a solution of DMSO (14.94 mL, 210.63 mmol) in dry CH_2Cl_2 (50 mL). After stirring for 30 min at -78 °C, a solution of **20** (18.29 g, 70.21 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise. The mixture was stirred at -78°C for 2 h, then Et_3N (39.40 mL, 280.84 mmol) was added and the mixture was warmed to ambient temperature. The reaction mixture was stirred at the same temperature for 0.5 h. It was diluted with H_2O (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with H_2O, brine and dried over anhydrous Na_2SO_4. After filtered and concentrated in vacuo, the crude aldehyde was obtained. This compound could be directly used in next steps without further purication.

To a stirred solution of diethyl allylphosphonate **19**[2] (18.76 g, 105.32 mmol) in dry THF (200 mL) at -78 °C was added n-BuLi (42.13 mL, 2.5 M in hexane, 105.32 mmol) dropwise under argon atmosphere. After stirring for 1 h, a solution of the crude aldehyde produced above in THF (80 mL) was added dropwise. After stirring at -78 °C for 0.5 h, the resulting solution was allowed to warm to ambient temperature and stirred for 12 h. The reaction was quenched with 6 N HCl (50 mL) at ambient temperature. After stirring for 4 h at the same temperature, careful neutralization with sodiun hydroxide aqueous solution. The resulting mixture was extracted with ether for 3 times. The combined organic layer was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel chromatography (petroleum ether/EtOAc = 5:1) to afford the desired product **21** (9.57 g, 56.87 mmol, 81% overall yield for two steps) as a colorless oil.

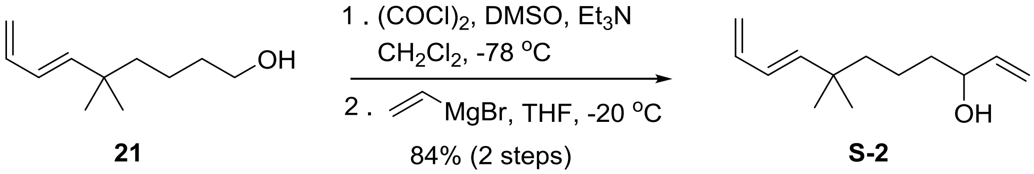
Data for **21**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.32 (dt, *J* = 17.0, 10.2 Hz, 1H), 5.96 (dd, *J* = 15.6, 10.3 Hz, 1H), 5.66 (d, *J* = 15.6 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 5.00 – 4.95 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 1.56 – 1.49 (m, 3H), 1.35 – 1.24 (m, 4H), 1.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.08, 137.69, 126.99, 114.76, 62.96, 42.93, 36.03, 33.49, 27.04, 20.90.

HRMS (ESI): calcd for $C_{11}H_{20}O$ ($[M + H]^+$) 169.1587, found 169.1590.

IR (neat) ν_{max}: 3355.1, 3087.0, 3033.0, 2957.9, 2935.8, 2865.1, 1648.3, 1602.6, 1464.7, 1460.0, 1384.0, 1363.4, 1252.0, 1053.2, 1005.3, 895.6, 776.9 cm^{-1}.



(*E*)-7,7-Dimethylundeca-1,8,10-trien-3-ol (S-2): To a solution of oxalyl chloride (7.33 mL, 85.31 mmol) in anhyd CH_2Cl_2 (120 mL) at -78 °C was added a solution of DMSO (12.10 mL, 170.61 mmol) in dry CH_2Cl_2 (40 mL). After stirring for 30 min at -78 °C, a solution of **21** (9.57 g, 56.87 mmol) in anhyd CH_2Cl_2 (40 mL) was added dropwise. The mixture was stirred at -78°C for 2 h, then Et_3N (31.91 mL, 227.48 mmol) was added and the mixture was warmed to ambient temperature. The mixture was stirred for 0.5 h at the same temperature and diluted with H_2O (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layer was washed with H_2O, brine and dried over anhydrous Na_2SO_4. After filtered and concentrated in vacuo, the crude aldehyde was obtained. This compound can be directly used in next steps without further purication.

To a solution of the above crude aldehyde in dry THF (100 mL) at -20 °C was added vinylmagnesium bromide (1.0 M solution in anhyd THF, 85.31 mL, 85.31 mmol). The mixture was allowed to warm up to ambient temperature and stirred for 4 h. After which time TLC analysis showed full conversion, the reaction was quenched with 50 mL saturated aqueous NH_4Cl. The aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give **S-2** (9.28 g, 47.77 mmol, 84% overall yield for two steps) as a colorless oil.

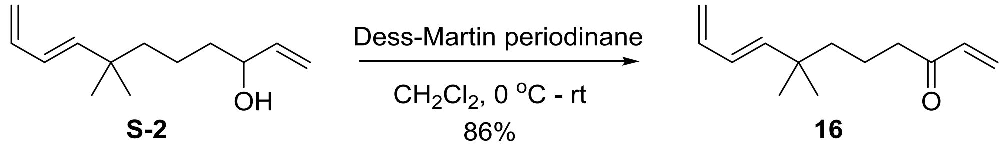
Data for **S-2**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dt, *J* = 17.0, 10.2 Hz, 1H), 5.99 – 5.93 (m, 1H), 5.85 – 5.81 (m, 1H), 5.65 (d, *J* = 15.6 Hz, 1H), 5.21 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.10 – 5.08 (m, 2H), 4.98 – 4.95 (m, 1H), 4.08 (dd, *J* = 12.9, 6.2 Hz, 1H), 1.87 (br s, 1H), 1.50 – 1.46 (m, 2H), 1.32 – 1.27 (m, 4H), 1.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.04, 141.25, 137.69, 126.95, 114.69, 114.46, 73.08, 42.97, 37.69, 36.02, 27.03, 20.45.

HRMS (ESI): calcd for $C_{13}H_{22}O$ ($[M + H]^+$) 195.1743, found 195.1747.

IR (neat) ν_{max}: 3356.0, 3084.8, 3034.9, 3016.7, 2958.9, 2939.2, 2867.1, 1647.7, 1602.6, 1460.6, 1423.7, 1383.5, 1362.9, 1285.2, 1202.1, 1109.7, 1066.8, 1004.7, 953.5, 920.6, 895.8, 658.9 cm^{-1}.



(*E*)-7,7-Dimethylundeca-1,8,10-trien-3-one (16): To a solution of **S-2** (9.28 g, 47.77 mmol) in dry CH_2Cl_2 (150 mL) at 0 °C was added Dess-Martin periodinane (24.31 g, 57.32 mmol) successively. The mixture was stirred for 4 h at ambient temperature. After which time TLC analysis showed full conversion, the reaction was quenched with a mixture of aq sat. $NaHCO_3$ and aq sat. $Na_2S_2O_3$ (1:1, 100 mL). The mixture was stirred for 30 min at ambient temperature. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 25:1) to give **16** (7.87 g, 40.95 mmol, 86% yield) as a colorless oil.

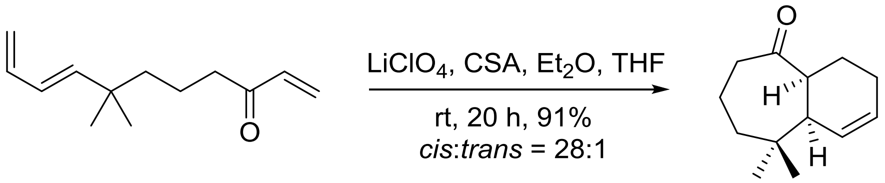
Data for **16**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 – 6.28 (m, 2H), 6.19 (d, *J* = 17.1 Hz, 1H), 5.97 (dd, *J* = 15.6, 10.3 Hz, 1H), 5.80 (dd, *J* = 10.5, 0.7 Hz, 1H), 5.64 (d, *J* = 15.6 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.59 – 1.51 (m, 2H), 1.32 – 1.28 (m, 2H), 1.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.58, 144.54, 137.52, 136.44, 127.70, 127.13, 114.79, 42.43, 40.07, 35.93, 26.91, 19.15.

HRMS (ESI): calcd for $C_{13}H_{20}O$ ($[M + H]^+$) 193.1587, found 193.1590.

IR (neat) ν_{max}: 3388.4, 3085.9, 3034.9, 3019.2, 2959.5, 2869.1, 2370.9, 1701.5, 1683.3, 1648.1, 1616.2, 1603.0, 1459.7, 1451.7, 1401.8, 1384.3, 1362.9, 1262.0, 1199.9, 1092.4, 1006.1, 959.6, 897.0, 656.7 cm^{-1}.



16 **22**

9,9-Dimethyl-3,4,4a,6,7,8,9,9a-octahydro-5H-benzo[7]annulen-5-one (22): To a solution of $LiClO_4$ (26.5 g, 250 mmol) in dry Et_2O (40 mL) and camphorsulfonic acid (104 mg, 0.45 mmol) in dry THF (1 mL), a solution of the above **16** (4.31 g, 22.42 mmol) in dry Et_2O (9 mL) was added dropwise. The mixture was stirred at ambient temperature for 20 h. It was cooled to 0 °C, and diluted with H_2O. The filtrate was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to give **22** (3.92 g, 20.40 mmol, *cis*/*trans* = 28/1, inseparable, 91% yield) as a colorless oil.

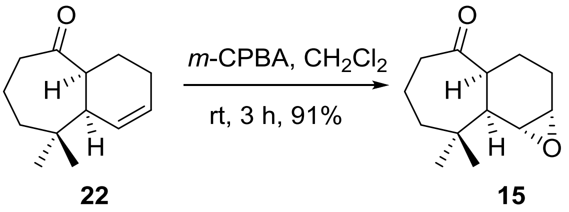
Data for **22**

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 – 5.80 (m, 2H), 2.77 – 2.75 (m, 1H), 2.65 (td, *J* = 12.9, 2.6 Hz, 1H), 2.41 – 2.37 (m, 1H), 2.26 (s, 1H), 2.09 – 1.96 (m, 2H), 1.93 – 1.82 (m, 2H), 1.76 – 1.65 (m, 2H), 1.54 – 1.43 (m, 1H), 1.35 – 1.32 (m, 1H), 1.07 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 217.93, 128.16, 127.56, 48.38, 44.94, 44.55, 38.22, 36.44, 31.00, 28.41, 25.18, 22.26, 21.70.

HRMS (ESI): calcd for $C_{13}H_{20}O$ ($[M + H]^+$) 193.1587, found 193.1592.

IR (neat) ν_{max}: 3365.8, 3027.3, 2957.4, 2927.2, 2867.3, 2841.0, 2369.0, 2346.3, 1691.8, 1474.6, 1452.6, 1438.4, 1386.9, 1366.4, 1322.0, 1291.3, 1253.1, 1204.5, 1168.4, 1133.9, 1116.0, 1018.9, 645.0, 639.7 cm^{-1}.



8,8-Dimethyldecahydro-4H-cyclohepta[3,4]benzo[1,2-b]oxiren-4-one (15): To a solution of **22** (1.85 g, 9.60 mmol) in CH_2Cl_2 (100 mL) was added *m*-CPBA (85%, 2.34 g, 11.52 mmol) at room temperature and the mixture was stirred for 3 h. After which time TLC analysis showed full conversion, the reaction was quenched with saturated $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. The residual was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to give **15** (1.82 g, 8.74 mmol, 91% yield) as a clear crystal. M.p. 84–86 °C.

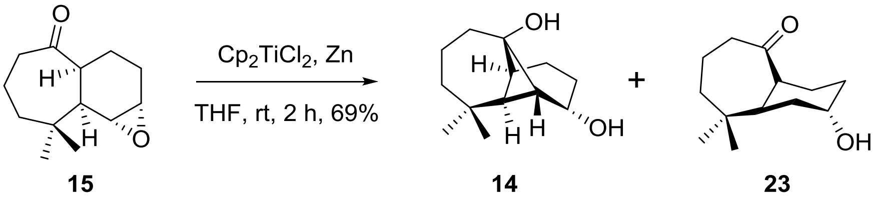
Data for **15**

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 – 3.20 (m, 2H), 2.49 – 2.34 (m, 3H), 1.96 – 1.93 (m, 1H), 1.74 – 1.68 (m, 3H), 1.64 – 1.54 (m, 3H), 1.42 (t, J = 15.4 Hz, 2H), 1.14 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 216.56, 53.15, 52.22, 45.44, 45.14, 44.67, 38.48, 35.86, 31.29, 24.95, 24.54, 21.27, 20.68.

HRMS (ESI): calcd for $C_{13}H_{20}O_2$ ($[M + H]^+$) 209.1536, found 209.1541.

IR (neat) ν_{max}: 3368.6, 2956.2, 2930.7, 2869.2, 2371.7, 2346.4, 1693.2, 1450.7, 1440.3, 1367.8, 1318.3, 1260.2, 1180.3, 1121.0, 869.5, 810.3, 779.8 cm^{-1}.



6,6-Dimethyltricyclo[5.4.0.0^{2,8}]undecane-2,9-diol (14): A mixture of Cp_2TiCl_2 (3.05 g, 12.25 mmol) and activated Zn powder (1.28 g, 19.60 mmol) in strictly deoxygenated THF (100 mL) was stirred at room temperature until the red solution turned green. To the solution of Cp_2TiCl was slowly added epoxide **15** (1.02 g, 4.90 mmol) in strictly deoxygenated THF (30 mL). The reaction was stirred for 1.5 h, the mixture was then added H_2O and ethyl ether (1:100, 100mL) and stirred for 3 h. The mixture filtered and the filtrate was evaporated under reduced pressure. The residue was purified through neutral alumina chromatography (dichloromethane/methanol, 3:1) to give **14** (712 mg, 3.39 mmol, 69%

yield) as a clear crystal (M.p. 144–146 °C) and **23** (0.29 g, 1.37 mmol, 28% yield) as a colorless oil.

Data for **14**

^{1}H NMR (400 MHz, MeOD): δ 4.32 (ddd, J = 8.4, 5.9, 2.6 Hz, 1H), 2.25 – 2.22 (m, 1H), 2.15 (t, J = 4.5 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.99 – 1.90 (m, 1H), 1.83 – 1.67 (m, 3H), 1.64 – 1.61 (m, 1H), 1.61 – 1.55 (m, 2H), 1.51 – 1.42 (m, 1H), 1.38 – 1.35 (m, 2H), 0.91 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, MeOD): δ 75.30, 71.52, 50.37, 43.94, 42.98, 41.68, 39.86, 32.76, 28.69, 28.36, 26.62, 24.97, 21.11.

HRMS (ESI): calcd for $C_{13}H_{22}O_2$ ($[M + H]^+$) 211.1693, found 211.1694.

IR (neat) ν_{max}: 3402.7, 2928.8, 2865.8, 2368.6, 1740.9, 1726.3, 1689.7, 1459.1, 1373.8, 1242.4, 1117.3, 1046.6, 1007.8, 957.6 cm^{-1}.

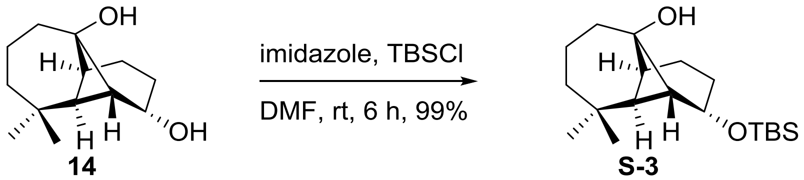
Data for **23**

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21 – 4.16 (m, 1H), 2.77 – 2.76 (m, 1H), 2.64 (ddd, J = 15.3, 6.3, 2.8 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.12 – 2.03 (m, 1H), 1.99 (dt, J = 13.1, 3.4 Hz, 1H), 1.92 – 1.78 (m, 3H), 1.70 – 1.64 (m, 3H), 1.62 – 1.51 (m, 3H), 1.43 (dt, J = 14.1, 4.1 Hz, 1H), 1.04 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 216.76, 66.06, 48.26, 45.83, 40.89, 38.11, 35.71, 31.40, 30.90, 29.32, 26.61, 24.68, 19.68.

HRMS (ESI): calcd for $C_{13}H_{22}O_2$ ($[M + H]^+$) 211.1693, found 211.1689.

IR (neat) ν_{max}: 3430.7, 2936.3, 2869.4, 2371.0, 1685.2, 1450.3, 1367.4, 1235.0, 1198.7, 1122.7, 1062.0, 972.3 cm^{-1}.



9-((*tert*-Butyldimethylsilyl)oxy)-6,6-dimethyltricyclo[5.4.0.0^{2,8}]undecan-2-ol (S-3): To a stirred solution of alcohol **14** (597 mg, 2.84 mmol) in DMF (15 mL) at room temperature was added imidazole (290 mg, 4.26 mmol) and TBSCl (557 mg, 3.69 mmol). The resulting solution was stirred at the same temperature for 6 h, when TLC analysis of the crude mixture showed full conversion. The solution was poured into 200 mL of ethyl acetate, and then washed with water (20 mL×3). The organic layer was washed with brine and dried over anhydrous Na_2SO_4, concentrated in vacuo. The residue was purified through silica chromatography (petroleum ether/ethyl acetate, 50:1) to give **S-3** (914 mg, 2.82 mmol, nearly quant.) as colorless oil.

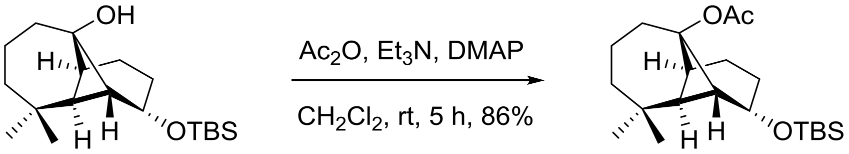
Data for **S-3**

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.37 – 4.32 (m, 1H), 2.16 (s, 2H), 2.02 (dtd, *J* = 14.4, 8.6, 2.7 Hz, 1H), 1.90– 1.76 (m, 3H), 1.72 – 1.67 (m, 1H), 1.64 (s, 1H), 1.60 – 1.48 (m, 3H), 1.35 – 1.32 (m, 2H), 1.22 (s, 1H), 0.90 (s, 3H), 0.87 (s, 9H), 0.86 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 74.84, 71.09, 50.12, 42.76, 41.77, 41.08, 38.53, 31.84, 27.93, 26.99, 25.85, 24.11, 20.03, 17.98, -4.52, -4.68.

HRMS (ESI): calcd for $C_{19}H_{36}O_2Si$ ($[M + H]^+$) 325.2557, found 325.2560.

IR (neat) ν_{max}: 3423.3, 2953.0, 2928.4, 2856.3, 2370.9, 1460.8, 1363.2, 1254.2, 1115.4, 1077.2, 1067.7, 1036.5, 1005.2, 970.1, 905.6, 858.1, 836.0, 773.5 cm^{-1}.



S-3 **S-4**

9-((*tert*-Butyldimethylsilyl)oxy)-6,6-dimethyltricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (S-4): To a stirred solution of **S-3** (914 mg, 2.82 mmol) and DMAP (172 mg, 1.41 mmol) in CH_2Cl_2 (30 mL) was added acetic anhydride (533 μL, 5.64 mmol) followed by triethylamine (1.12 mL, 8.46 mmol) at 0 °C. The resulting solution was stirred at room temperature for 5 h, when TLC analysis of the crude mixture showed full conversion. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water and brine, dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified through silica chromatography (petroleum ether/ethyl acetate = 80:1) to give **S-4** (889 mg, 2.43 mmol, 86% yield) as colorless oil.

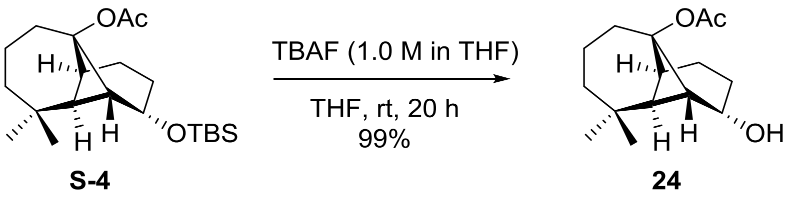
Data for **S-4**

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 – 4.16 (m, 1H), 2.46 (s, 1H), 2.41 – 2.35 (m, 1H), 2.06 – 1.88 (m, 6H), 1.85 – 1.79 (m, 1H), 1.73 – 1.64 (m, 2H), 1.56 – 1.48 (m, 3H), 1.35 (s, 1H), 1.32 (s, 1H), 0.88 (s, 3H), 0.85 (s, 9H), 0.84 (s, 3H), 0.00 (s, 3H), -0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.92, 83.12, 71.00, 49.52, 44.55, 41.73, 38.78, 35.53, 31.72, 27.97, 27.84, 27.07, 25.83, 25.34, 21.59, 19.82, 17.99, -4.70, -4.74.

HRMS (ESI): calcd for $C_{21}H_{38}O_3Si$ ($[M + Na]^+$) 389.2482, found 389.2492.

IR (neat) ν_{max}: 3446.7, 2954.1, 2930.1, 2856.6, 2374.4, 1735.2, 1463.1, 1365.9, 1240.4, 1093.5, 1080.8, 1059.6, 1037.9, 1006.3, 963.2, 855.6, 836.4, 774.5 cm^{-1}.



9-Hydroxy-6,6-dimethyltricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (24): To a stirred solution of **S-4** (889 mg, 2.43 mmol) in THF (20 mL) was added dropwise tetra-*n*-butylammonium fluoride (7.29 mL, 1.0 M in THF, 7.29 mL) at 0 °C. The resulting solution was stirred at room temperature for 20 h, when TLC analysis of the crude mixture showed full conversion. The reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water and brine, dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified through silica chromatography (petroleum ether/ethyl acetate = 10:1) to give **24** (609 mg, 2.41 mmol, nearly quant.) as colorless oil.

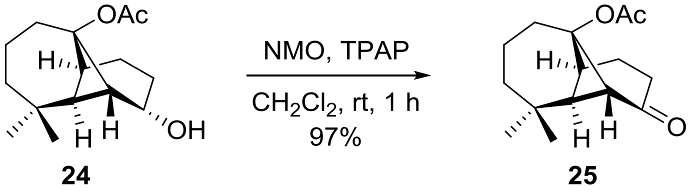
Data for **24**

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33 – 4.27 (m, 1H), 2.53 (s, 2H), 2.28 – 2.00 (m, 4H), 1.99 (s, 3H), 1.91 – 1.85 (m, 1H), 1.80 – 1.74 (m, 1H), 1.71 (s, 1H), 1.62 – 1.57 (m, 2H), 1.55 – 1.48 (m, 1H), 1.41 – 1.36 (m, 2H), 0.92 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.04, 83.11, 70.59, 49.27, 44.39, 41.89, 38.67, 35.42, 31.65, 28.02, 27.76, 25.79, 24.92, 21.55, 19.72.

HRMS (ESI): calcd for $C_{15}H_{24}O_3$ ($[M + Na]^+$) 275.1618, found 275.1624.

IR (neat) ν_{max}: 3407.6, 2952.0, 2868.4, 2365.7, 1732.5, 1466.0, 1459.3, 1367.2, 1240.9, 1094.5, 1052.8, 1014.3, 958.7, 944.4 cm^{-1}.



6,6-Dimethyl-9-oxotricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (25): Compound **24** (609 mg, 2.41 mmol) was dissolved in CH_2Cl_2 (30 mL), NMO (1.13 g, 9.64 mmol) and TPAP (127 mg, 0.36 mmol) was added at room temperature. The resulting reaction mixture was stirred at room temperature for 1 h.

After which time TLC analysis showed full conversion, the mixture was then filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 50:1) to give the ketone **25** (585 mg, 2.34 mmol, 97% yield) as a clear crystal. M.p. 70–72 °C.

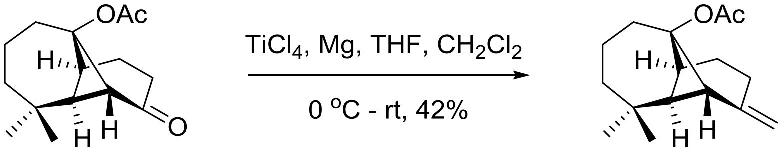
Data for **25**

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 3.08 (d, *J* = 5.1 Hz, 1H), 2.86 (s, 1H), 2.52 – 2.43 (m, 1H), 2.32 – 2.21 (m, 2H), 2.15 – 1.74 (m, 6H), 1.67 – 1.49 (m, 3H), 1.38 (dt, *J* = 23.4, 13.9 Hz, 2H), 0.88 (s, 3H), 0.83 (s, 3H).

^{13}**C NMR** (100 MHz, $CDCl_3$): δ 210.75, 169.20, 81.72, 58.67, 46.93, 41.66, 38.24, 34.96, 32.57, 32.33, 27.56, 27.37, 22.03, 21.27, 19.28.

HRMS (ESI): calcd for $C_{15}H_{22}O_3$ ($[M + Na]^+$) 273.1461, found 273.1464.

IR (neat) ν_{max}: 3414.9, 2954.9, 2868.7, 1734.5, 1717.7, 1465.5, 1368.6, 1233.6, 1088.9, 1067.5, 1011.0, 983.7 cm^{-1}.



25 **26**

6,6-Dimethyl-9-methylenetricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (26): To a 0 ºC suspension consisting of Mg (156 mg, 6.48 mmol), $TiCl_4$ (1.62 mL, 1.0 M in methylene chloride, 1.62 mmol), and CH_2Cl_2 (4 mL) was added over a 2-min period a solution of ketone **25** (203 mg, 0.81 mmol) in CH_2Cl_2 (3 mL) and THF (2 mL). After being stirred for 30 min at 0 ºC, the resulting green-black mixture was stirred for an additional 20 min at room temperature. The reaction mixture was recooled to 0 ºC. Saturated potassium carbonate solution (10 mL) was added and the mixture was diluted with ether (20 mL). The organic layer was separated, dried, evaporadted, and purified by chromatography on silica chromatography (petroleum ether/ethyl acetate = 80:1) to give **26** (84 mg, 0.34 mmol, 42% yield) as colorless oil.

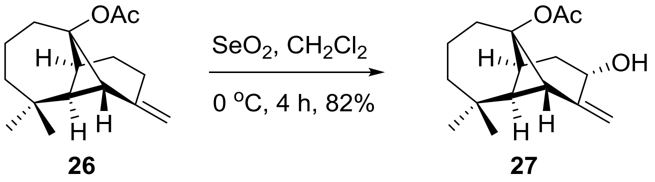
Data for **26**

^{1}**H NMR** (400 MHz, $CDCl_3$): δ 4.66 – 4.61 (m, 2H), 3.12 (d, *J* = 5.7 Hz, 1H), 2.58 – 2.54 (m, 1H), 2.53 – 2.45 (m, 1H), 2.36 – 2.28 (m, 1H), 2.25 – 2.18 (m, 1H), 2.06 – 1.98 (m, 1H), 1.94 (s, 3H), 1.88 – 1.78 (m, 1H), 1.68 – 1.55 (m, 3H), 1.49 (s, 1H), 1.41 – 1.39 (m, 2H), 0.90 (d, *J* = 3.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.36, 151.11, 107.64, 82.95, 52.71, 50.26, 41.56, 38.74, 35.15, 32.31, 28.05, 27.83, 25.38, 23.36, 21.77, 19.70.

HRMS (ESI): calcd for $C_{16}H_{24}O_2$ ($[M + Na]^+$) 271.1669, found 271.1675.

IR (neat) ν_{max}: 3448.2, 3073.6, 2952.2, 2904.4, 2867.3, 1735.5, 1644.3, 1458.1, 1366.1, 1248.1, 1234.5, 1090.7, 1072.1, 1009.8, 878.8, 738.0 cm^{-1}.



10-Hydroxy-6,6-dimethyl-9-methylenetricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (27): To a solution of **26** (30 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) and H_2O (0.1 mL) at 0 °C was added SeO_2 (53 mg, 0.48 mmol) portionwise. The resulting solution was stirred at the same temperature for 4 h, after which time TLC analysis showed full conversion, the reaction quenched by addition of brine, the water phase was extracted with 50 mL CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica-gel column with petroleum/EtOAc (50:1) to afford **27** (26 mg, 0.10 mmol，82% yield) as colorless oil.

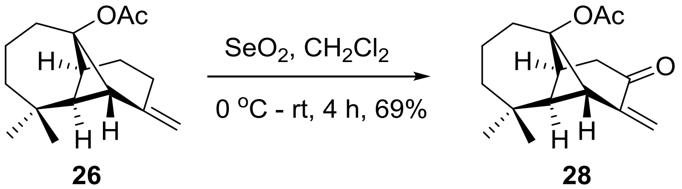
Data for **27**

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05 (s, 1H), 4.92 (s, 1H), 4.47 (d, J = 7.8 Hz, 1H), 3.19 (d, J = 5.9 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.55 – 2.47 (m, 1H), 2.24 – 2.18 (m , 1H), 1.98 – 1.93 (m, 1H), 1.92 (s, 3H), 1.80 (dt, J = 14.1 Hz, 1H), 1.71 (s, 1H), 1.66 (s, 1H), 1.65 – 1.58 (m, 2H), 1.42 – 1.39 (m, 2H), 0.91 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.24, 155.68, 111.21, 82.49, 66.67, 51.87, 51.39, 41.37, 38.61, 37.57, 34.82, 32.35, 27.94, 27.69, 21.68, 19.66.

HRMS (ESI): calcd for $C_{16}H_{24}O_3$ ($[M + Na]^+$) 287.1618, found 287.1622.

IR (neat) ν_{max}: 3390.4, 2955.6, 2922.0, 2850.4, 2372.9, 2346.1, 1735.3, 1726.3, 1459.8, 1260.0, 1232.1, 1114.7, 1072.6, 1027.2, 788.2, 739.7 cm^{-1}.



6, 6-Dimethyl-9-methylene-10-oxotricyclo[5.4.0.0^{2,8}]undecan-2-yl acetate (28): To a solution of **26**

(32 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added SeO_2 (57 mg, 0.52 mmol) portionwise. The resulting solution was stirred at room temperature for 4 h, after which time TLC analysis showed full conversion, the reaction quenched by addition of brine the water phase was extracted with 150 mL CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica-gel column with petroleum/EtOAc (70:1) to afford **28** (24 mg, 0.09 mmol, 69% yield) as a clear crystal. M.p. 86–88 °C.

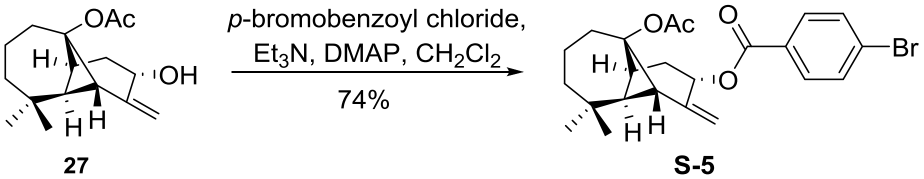
Data for **28**

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (d, *J* = 1.4 Hz, 1H), 5.09 (d, *J* = 1.3 Hz, 1H), 3.43 (d, *J* = 6.6 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.56 – 2.45 (m, 1H), 2.35 – 2.27 (m, 1H), 2.01 – 1.92 (m, 1H), 1.86 (s, 3H), 1.70 – 1.63 (m, 2H), 1.51 (s, 1H), 1.47 (dd, *J* = 10.1, 3.6 Hz, 2H), 0.94 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.35, 169.33, 147.56, 118.48, 81.93, 54.73, 49.35, 43.12, 39.69, 38.56, 34.49, 32.66, 27.74, 27.52, 21.27, 19.38.

HRMS (ESI): calcd for $C_{16}H_{22}O_3$ ($[M + Na]^+$) 285.1461, found 285.1466.

IR (neat) ν_{max}: 3404.5, 2954.5, 2869.0, 1738.2, 1709.9, 1630.9, 1466.7, 1457.9, 1369.3, 1286.9, 1231.8, 1109.2, 1087.5, 1054.1, 937.1 cm^{-1}.



27

S-5

2-Acetoxy-6,6-dimethyl-9-methylenetricyclo[5.4.0.0^{2,8}]undecan-10-yl 4-bromobenzoate (S-5): To a stirred solution of **27** (80 mg, 0.3 mmol) and DMAP (37 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) was added *p*-bromobenzoyl chloride (132 mg, 0.6 mmol) followed by triethylamine (126 μL, 0.9 mmol) at 0 ºC. The resulting solution was stirred at room temperature for 3 h, when TLC analysis of the crude mixture showed full conversion. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with water and brine, dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified through silica chromatography (petroleum ether/ethyl acetate = 100:1) to give **S-5** (99 mg, 0.22 mmol, 74% yield) as colorless oil.

Data for **S-5**

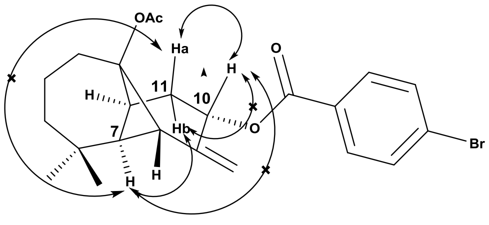
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 5.79 (d, J = 7.7Hz, 1H), 5.03 (d, J = 24.7 Hz, 2H), 3.27 (d, *J* = 5.8 Hz, 1H), 2.74 (ddd, J = 14.4, 9.0, 2.8 Hz, 1H), 2.65 – 2.60 (m, 1H), 2.29 – 2.24 (m, 1H), 2.00 (s, 3H), 1.98 – 1.93 (m, 1H), 1.87 (dt, J = 14.6, 2.8 Hz, 1H), 1.71 (s, 1H), 1.65 – 1.63 (m, 2H), 1.44 (d, J = 7.1 Hz, 2H), 0.95 (d, J = 12.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.26, 165.50, 149.47, 131.64, 131.06, 129.38, 127.97, 113.77, 82.29, 69.24, 51.84, 51.44, 40.91, 38.50, 35.60, 34.62, 32.32, 28.03, 27.80, 21.73, 19.56.

HRMS (ESI): calcd for $C_{23}H_{27}BrO_4$ ($[M + Na]^+$) 469.0985, found 469.0989.

IR (neat) ν_{max}: 3414.4, 3084.7, 2953.5, 2904.7, 2867.1, 1735.2, 1717.3, 1649.7, 1590.0, 1483.9, 1455.4, 1397.7, 1367.0, 1267.3, 1244.4, 1230.9, 1173.2, 1113.8, 1102.1, 1090.0, 1068.7, 1012.3, 916.1, 847.6, 757.3, 733.6 cm^{-1}.

NOESY spectrum (600 MHz) of **S-5** in $CDCl_3$.



S-5

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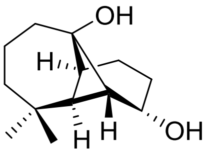
(1) (a) Y. S. Cheng, W. Y. Yu, Y. F. Xu, R. G. Salomon, *J. Nat. Prod.*, 2017, **80**, 488−498. (b) K. Q. Huynh, C. A. Seizert, T. J. Ozumerzifon, P. A. Allegretti, E. M. Ferreira, *Org. Lett*., 2017, **19**, 294−297.

(2) (a) S. M. Jing, V. Balasanthiran, V. Pagar, J. C. Gallucci, T. V. RajanBabu, *J. Am. Chem. Soc.*, 2017, **139**, 18034–18043. (b) G. Zhao, M. He, H. Li, S. Duan, Z. Yuan, X. Xie, X. She, *Chem. Commun*., 2015, **51**, 17321−17323.



14

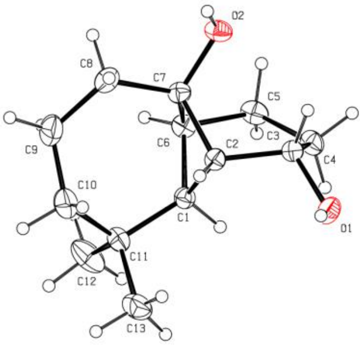


Figure S1

Figure S1: X-ray crystallographic structure of compound **14** (CCDC 1847732).

Crystal data and structure refinement for compound ***14***

Identification code	hem_052
Empirical formula	$C_{13}H_{22}O_2$
Formula weight	210.31
Temperature/K	295.38(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.8513(6)
b/Å	8.0917(4)
c/Å	24.6768(12)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2366.4(2)

Z	8
ρ_{calc}g/cm^3	1.181
μ/mm^{-1}	0.077
F(000)	928.0
Crystal size/mm^3	0.17 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.44 to 52.04
Index ranges	$-6 \leqslant h \leqslant 14$, $-9 \leqslant k \leqslant 8$, $-30 \leqslant l \leqslant 14$
Reflections collected	5202
Independent reflections	2321 [R_{int} = 0.0362, R_{sigma} = 0.0567]
Data/restraints/parameters	2321/0/140
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0642, wR_2 = 0.1520
Final R indexes [all data]	R_1 = 0.0908, wR_2 = 0.1749
Largest diff. peak/hole / e Å^{-3}	0.62/-0.24

Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å2×10^3) for hem_052. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U (eq)
O1	1754.0(14)	1870(2)	2583.5(8)	43.4(5)
O2	-1465.0(15)	112(2)	2928.9(7)	39.2(5)
C1	616.6(19)	1570(3)	3761.0(9)	30.3(6)
C2	132.8(18)	2014(3)	3195.7(9)	28.3(5)
C3	740.0(19)	1041(3)	2755.4(9)	31.3(6)
C7	-963.3(19)	1067(3)	3354.0(9)	31.2(6)
C11	543(2)	2864(3)	4215.0(10)	39.5(6)
C6	-204(2)	68(3)	3742.0(10)	33.6(6)
C5	369(2)	-1339(3)	3432.5(10)	38.6(6)
C4	1101(2)	-663(3)	2964.1(10)	37.7(6)

C8	-1878(2)	2089(4)	3628.3(11)	42.8(7)
C10	-589(3)	3826(4)	4214.0(13)	59.4(9)
C13	1455(3)	4170(4)	4112.8(13)	58.6(9)
C9	-1634(3)	2840(5)	4173.4(13)	60.7(9)
C12	760(3)	2045(4)	4753.2(11)	68.9(11)

Anisotropic Displacement Parameters (Å^2×10^3) for hem_052. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U11	U22	U33	U23	U13	U12
O1	37.2(10)	42.4(11)	50.7(11)	2.2(9)	12.5(8)	0.4(9)
O2	36.5(10)	34.2(10)	47.0(10)	-1.9(8)	-12.6(8)	0.2(8)
C1	30.1(12)	29.4(13)	31.4(12)	-1.1(10)	0.2(10)	1.9(11)
C2	29.8(11)	22.8(11)	32.4(11)	2.0(10)	1.2(10)	2.7(10)
C3	30.1(11)	32.4(13)	31.3(12)	-0.7(10)	-0.2(10)	-1.4(11)
C7	29.4(12)	29.7(13)	34.6(12)	1.6(10)	-2.6(10)	1.1(11)
C11	44.6(15)	36.8(14)	36.9(14)	-8.4(11)	0.8(12)	0.0(13)
C6	38.7(13)	29.7(13)	32.4(12)	4.8(11)	-1.5(11)	-1.0(11)
C5	44.4(14)	25.3(12)	45.9(14)	2.3(11)	-10.7(12)	3.1(12)
C4	39.3(13)	32.0(14)	41.8(13)	-6.4(11)	-6.2(12)	10.6(12)
C8	31.7(13)	48.3(17)	48.4(15)	1.3(13)	3.4(11)	2.3(13)
C10	57.1(19)	61(2)	60.5(19)	-22.4(16)	6.1(15)	7.4(17)
C13	68(2)	47.3(18)	60.7(19)	-14.1(15)	0.7(16)	-16.5(17)
C9	46.4(16)	77(2)	58.7(19)	-16.9(17)	8.9(15)	13.5(17)
C12	107(3)	62(2)	37.9(16)	-4.9(15)	-17.1(18)	-6(2)

Bond Lengths for hem_052.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.440(3)	C7	C8	1.522(3)
O2	C7	1.432(3)	C11	C10	1.551(4)

C1	C2	1.550(3)	C11	C13	1.533(4)
C1	C11	1.536(3)	C11	C12	1.507(4)
C1	C6	1.558(3)	C6	C5	1.530(3)
C2	C3	1.523(3)	C5	C4	1.545(4)
C2	C7	1.558(3)	C8	C9	1.504(4)
C3	C4	1.533(3)	C10	C9	1.476(4)
C7	C6	1.542(3)			

Bond Angles for hem_052.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	85.56(17)	C1	C11	C10	113.0(2)
C11	C1	C2	118.5(2)	C13	C11	C1	108.0(2)
C11	C1	C6	121.2(2)	C13	C11	C10	105.3(2)
C1	C2	C7	88.21(17)	C12	C11	C1	109.4(2)
C3	C2	C1	110.33(18)	C12	C11	C10	111.7(3)
C3	C2	C7	108.56(18)	C12	C11	C13	109.2(2)
O1	C3	C2	111.33(19)	C7	C6	C1	88.52(17)
O1	C3	C4	106.54(19)	C5	C6	C1	108.5(2)
C2	C3	C4	110.94(19)	C5	C6	C7	109.82(19)
O2	C7	C2	115.35(19)	C6	C5	C4	111.1(2)
O2	C7	C6	114.47(19)	C3	C4	C5	114.4(2)
O2	C7	C8	108.86(19)	C9	C8	C7	118.7(2)
C6	C7	C2	85.82(17)	C9	C10	C11	117.0(3)
C8	C7	C2	115.9(2)	C10	C9	C8	116.1(3)
C8	C7	C6	115.1(2)				

Torsion Angles for hem_052.

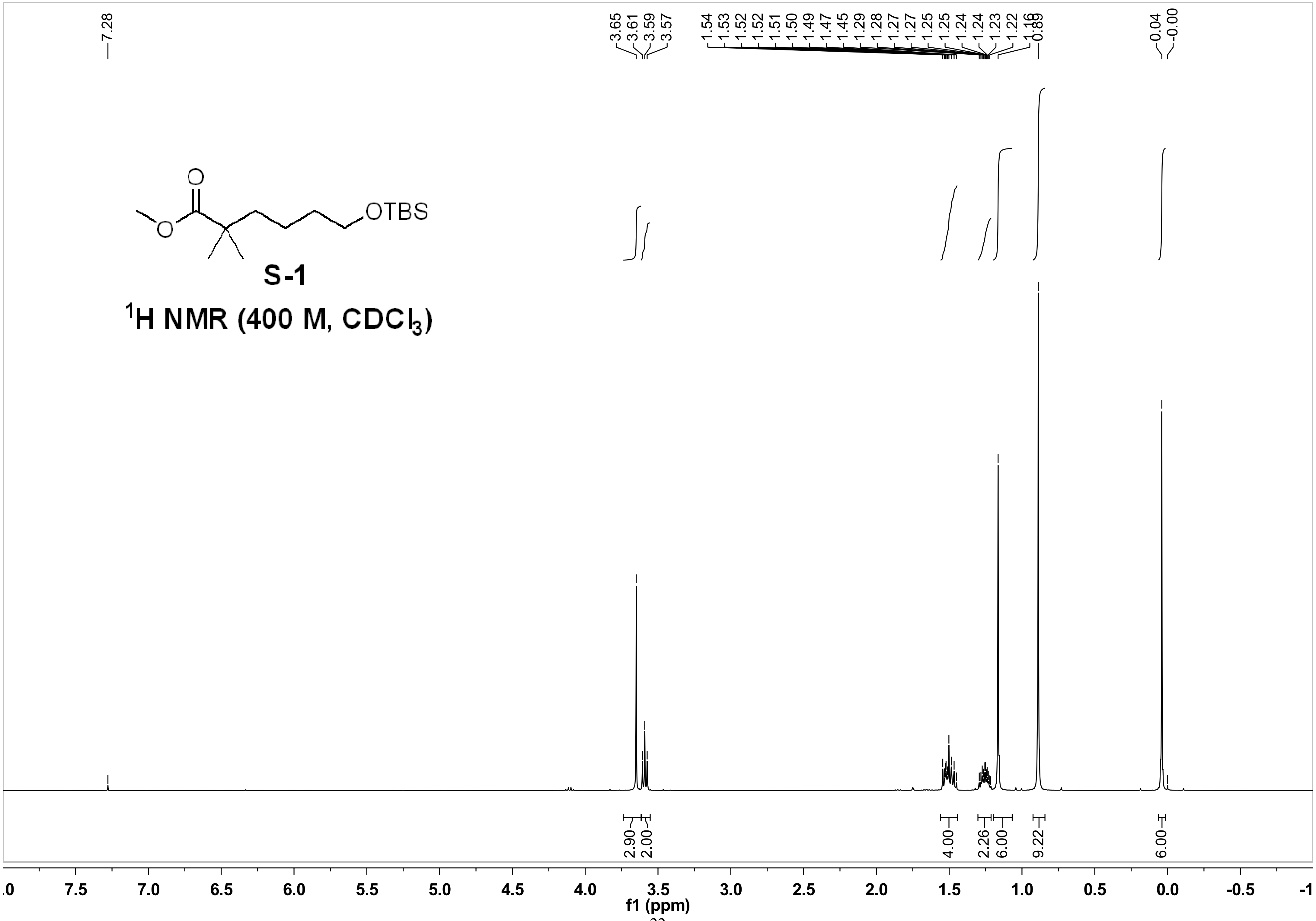
A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C4	C5	147.5(2)	C3	C2	C7	C8	-159.0(2)
O2	C7	C6	C1	141.61(19)	C7	C2	C3	O1	178.96(18)

O2	C7	C6	C5	32.4(3)	C7	C2	C3	C4	-62.6(2)
O2	C7	C8	C9	163.9(3)	C7	C6	C5	C4	59.6(3)
C1	C2	C3	O1	-85.9(2)	C7	C8	C9	C10	52.0(4)
C1	C2	C3	C4	32.5(3)	C11	C1	C2	C3	153.0(2)
C1	C2	C7	O2	-140.9(2)	C11	C1	C2	C7	-97.9(2)
C1	C2	C7	C6	-25.74(17)	C11	C1	C6	C7	95.1(2)
C1	C2	C7	C8	90.2(2)	C11	C1	C6	C5	-154.5(2)
C1	C11	C10	C9	48.1(4)	C11	C10	C9	C8	-72.9(4)
C1	C6	C5	C4	-35.7(3)	C6	C1	C2	C3	-83.67(19)
C2	C1	C11	C10	39.6(3)	C6	C1	C2	C7	25.48(16)
C2	C1	C11	C13	-76.5(3)	C6	C1	C11	C10	-63.5(3)
C2	C1	C11	C12	164.7(2)	C6	C1	C11	C13	-179.6(2)
C2	C1	C6	C7	-25.76(16)	C6	C1	C11	C12	61.7(3)
C2	C1	C6	C5	84.68(19)	C6	C7	C8	C9	33.9(3)
C2	C3	C4	C5	26.1(3)	C6	C5	C4	C3	-24.4(3)
C2	C7	C6	C1	25.61(16)	C8	C7	C6	C1	-91.1(2)
C2	C7	C6	C5	-83.6(2)	C8	C7	C6	C5	159.7(2)
C2	C7	C8	C9	-64.0(3)	C13	C11	C10	C9	165.8(3)
C3	C2	C7	O2	-30.0(3)	C12	C11	C10	C9	-75.8(3)
C3	C2	C7	C6	85.12(19)					

Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for hem_052.

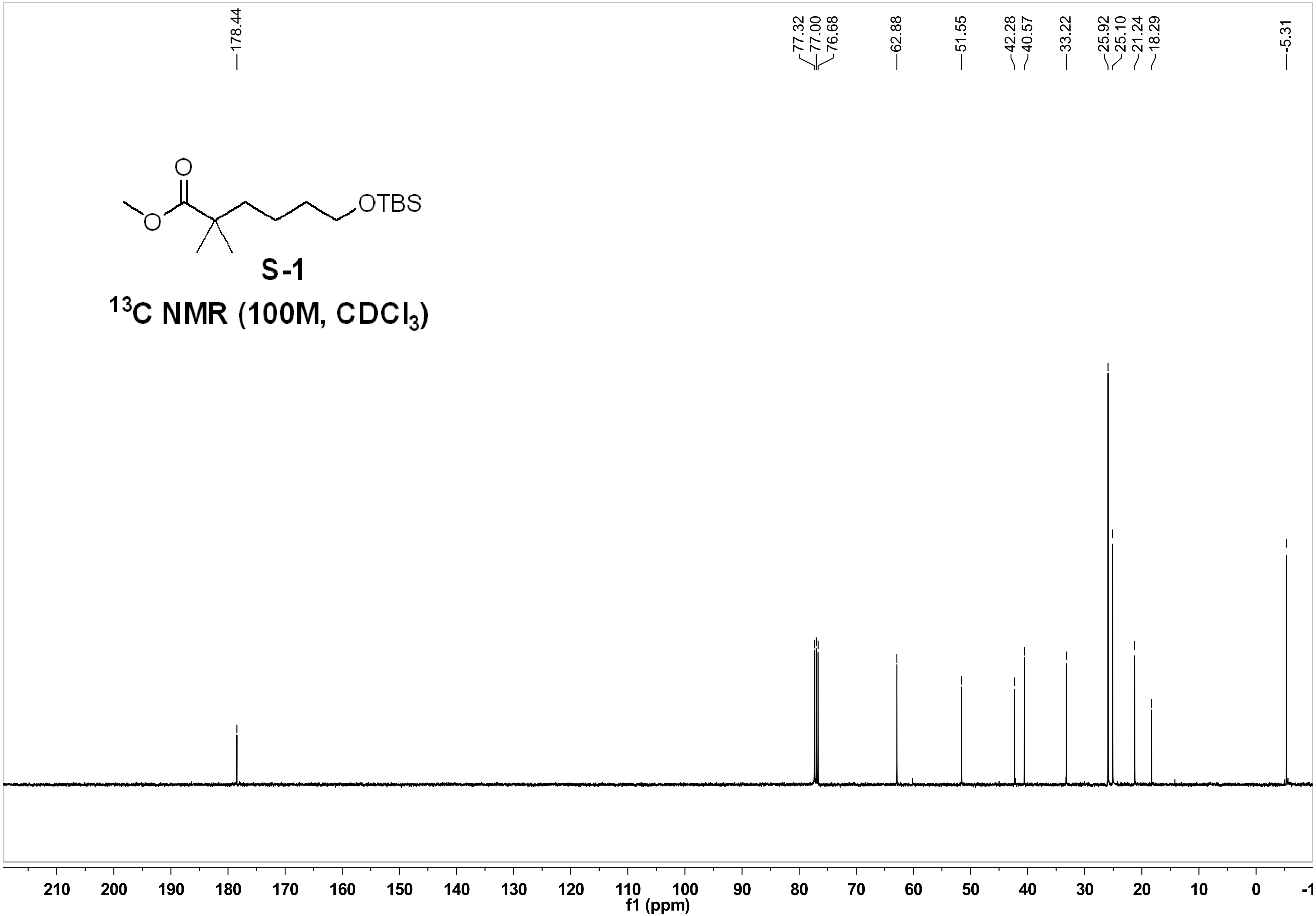
Atom	x	y	z	U(eq)
H1	1592	2775	2456	65
H2	-1962	656	2782	59
H1A	1397	1185	3724	36
H2A	38	3197	3124	34
H3	236	903	2444	38
H6	-549	-240	4089	40
H5A	-201	-2076	3287	46

H5B	840	-1968	3679	46
H4A	1878	-597	3086	45
H4B	1075	-1442	2665	45
H8A	-2079	2981	3384	51
H8B	-2539	1393	3667	51
H10A	-628	4473	4544	71
H10B	-576	4597	3913	71
H13A	2187	3676	4152	88
H13B	1374	5052	4370	88
H13C	1375	4601	3752	88
H9A	-2265	3542	4272	73
H9B	-1595	1956	4438	73
H12A	166	1272	4829	103
H12B	784	2868	5033	103
H12C	1469	1471	4740	103



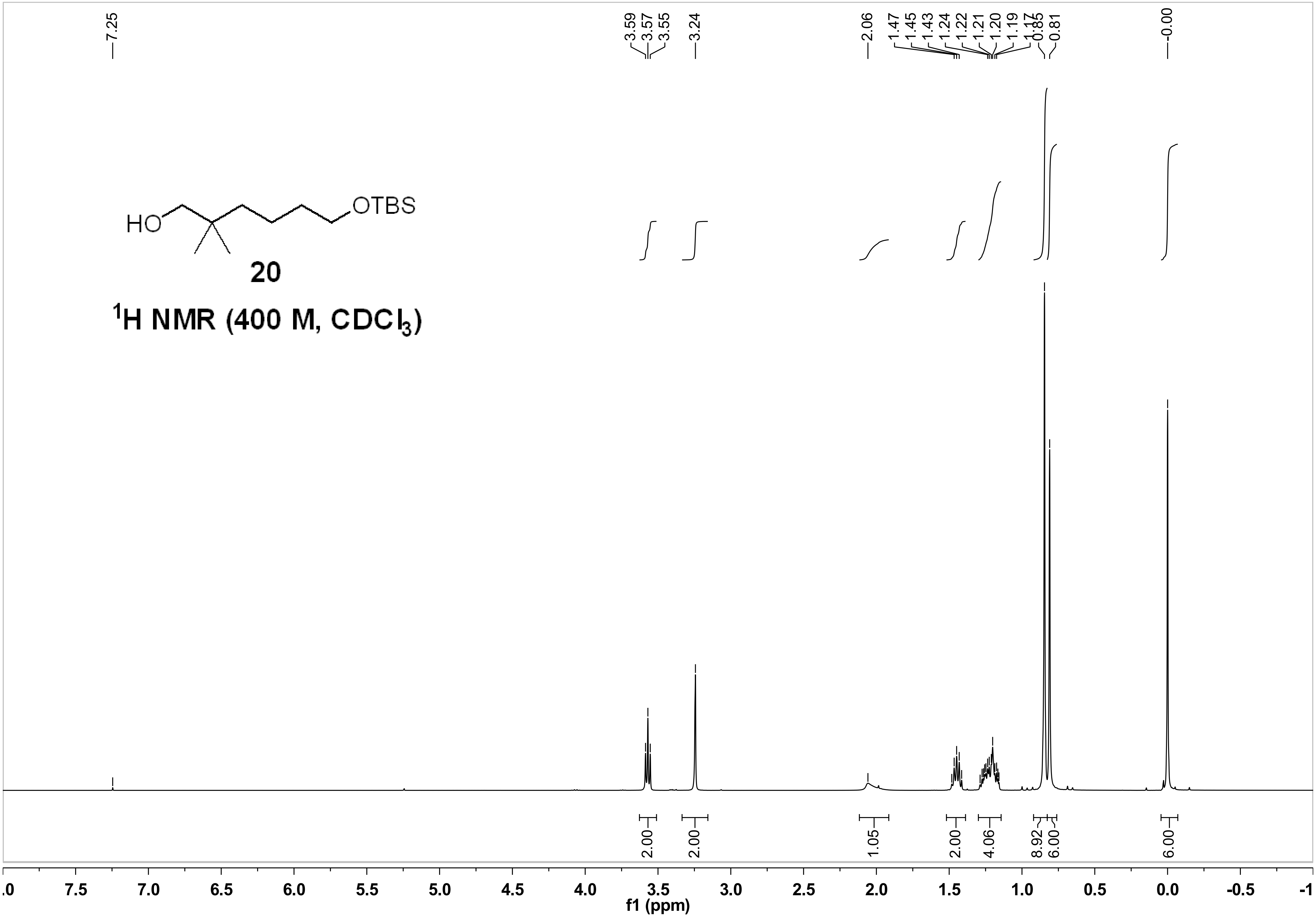
S-1

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



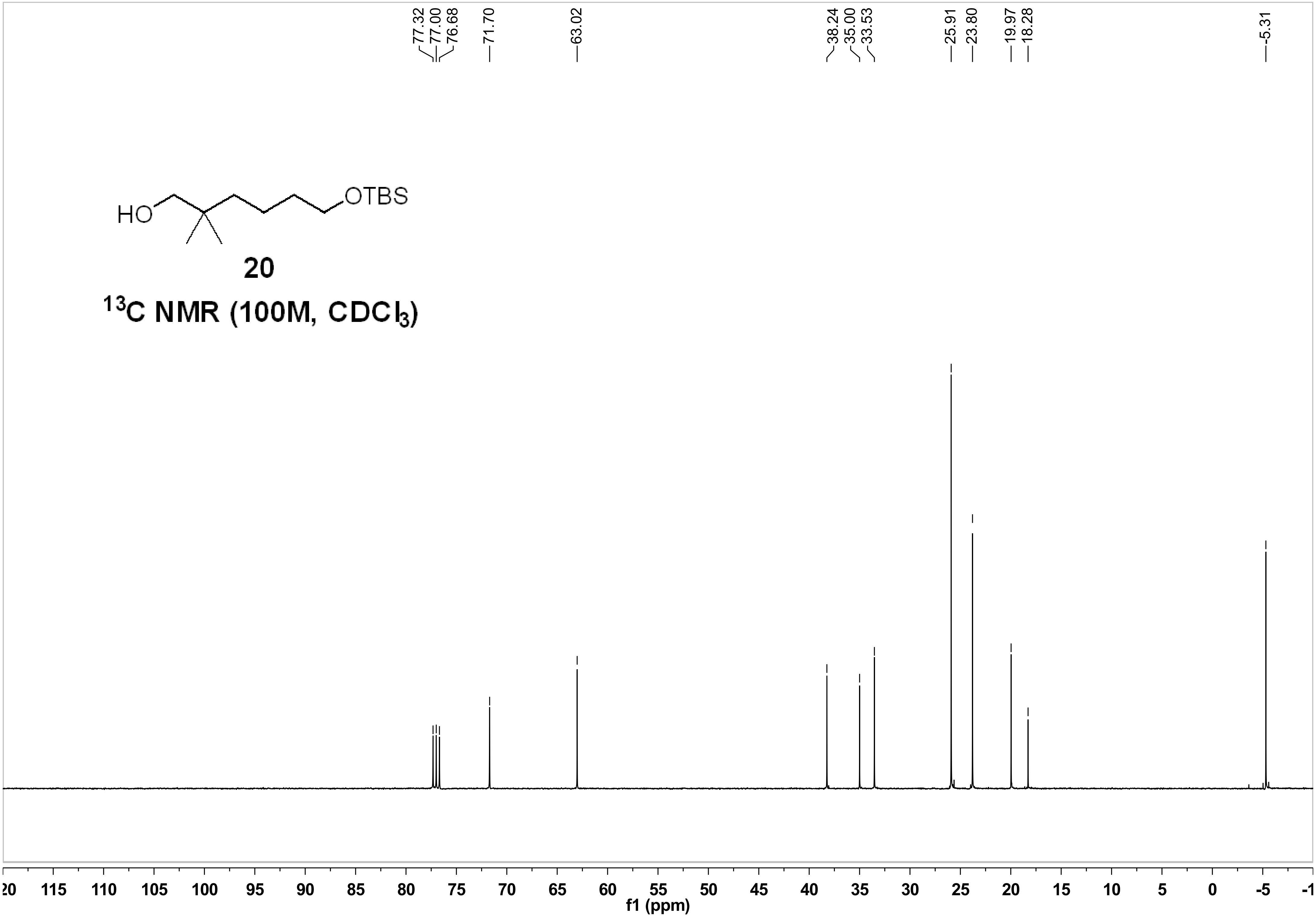
S-1

^{13}C NMR (100M, CDCl$_3$)



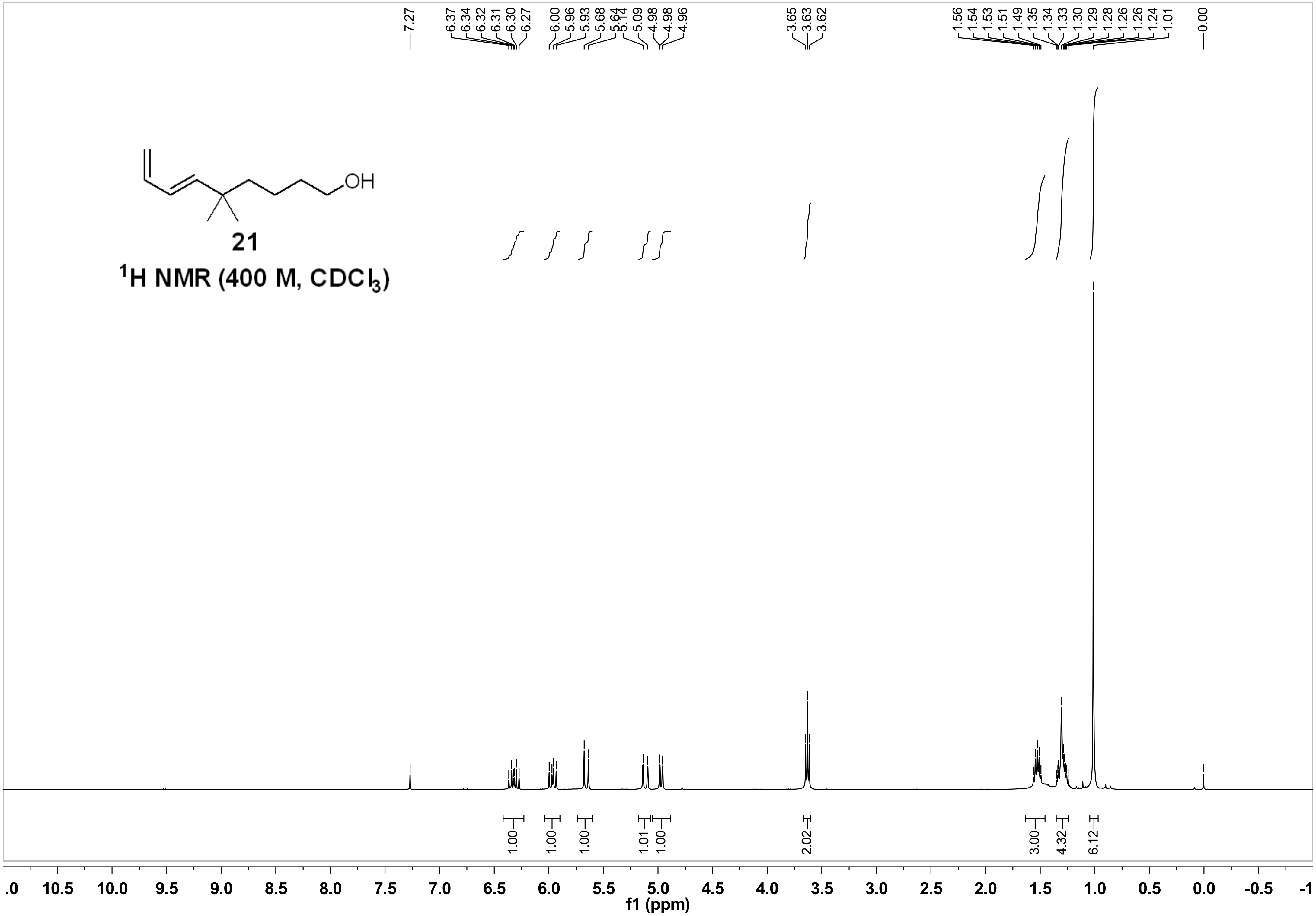
20

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



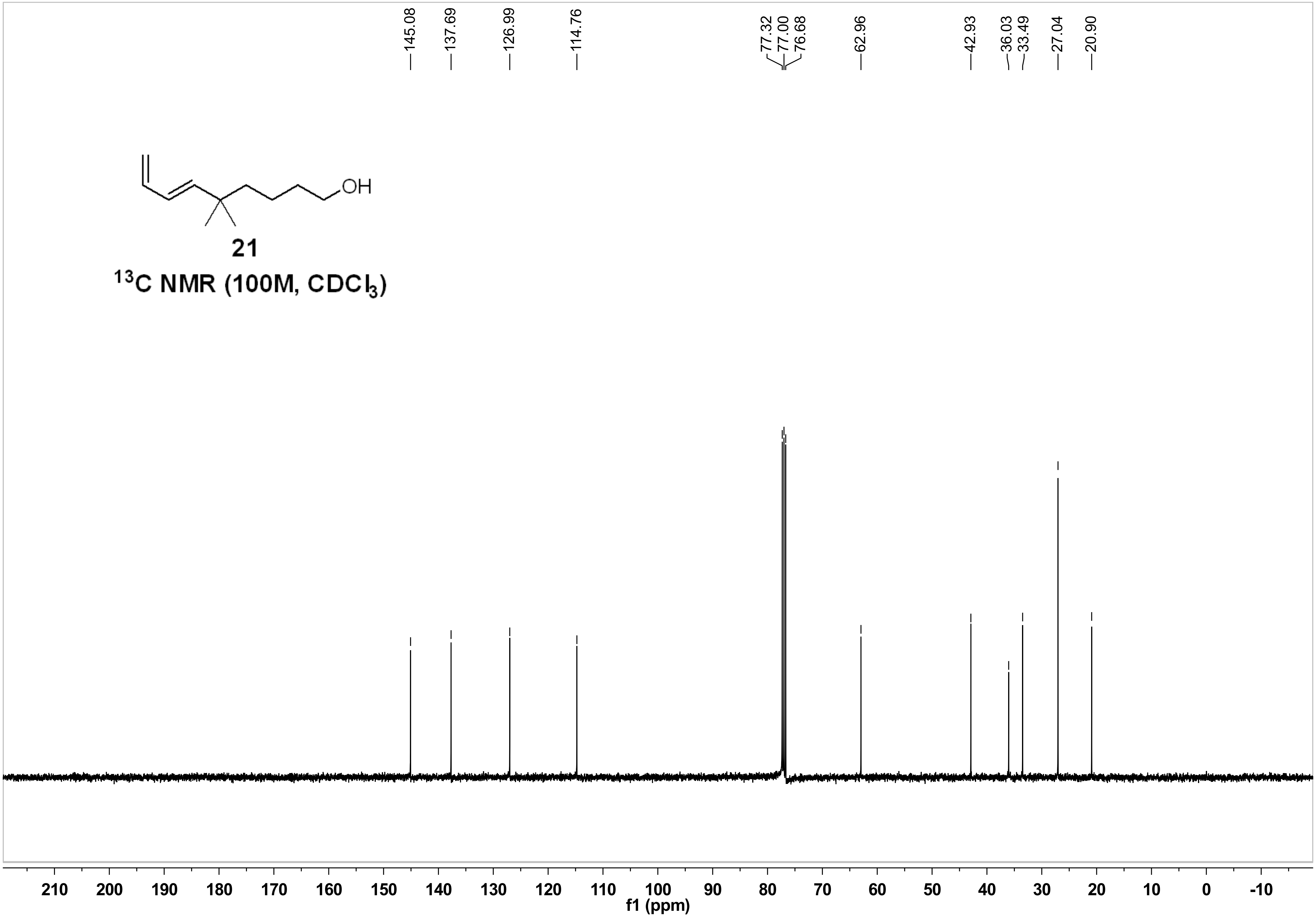
20

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



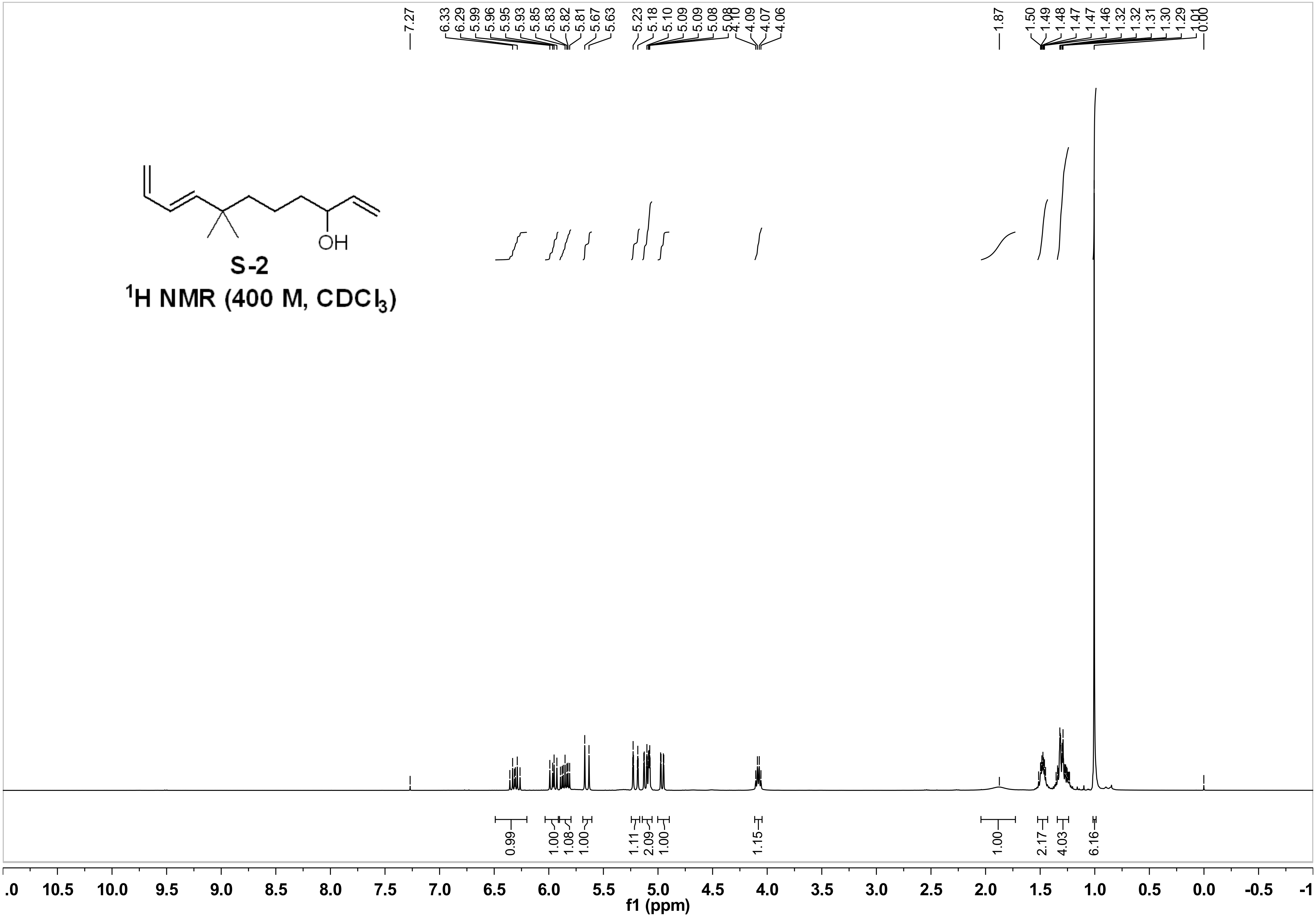
21

^{1}H NMR (400 M, CDCl$_3$)

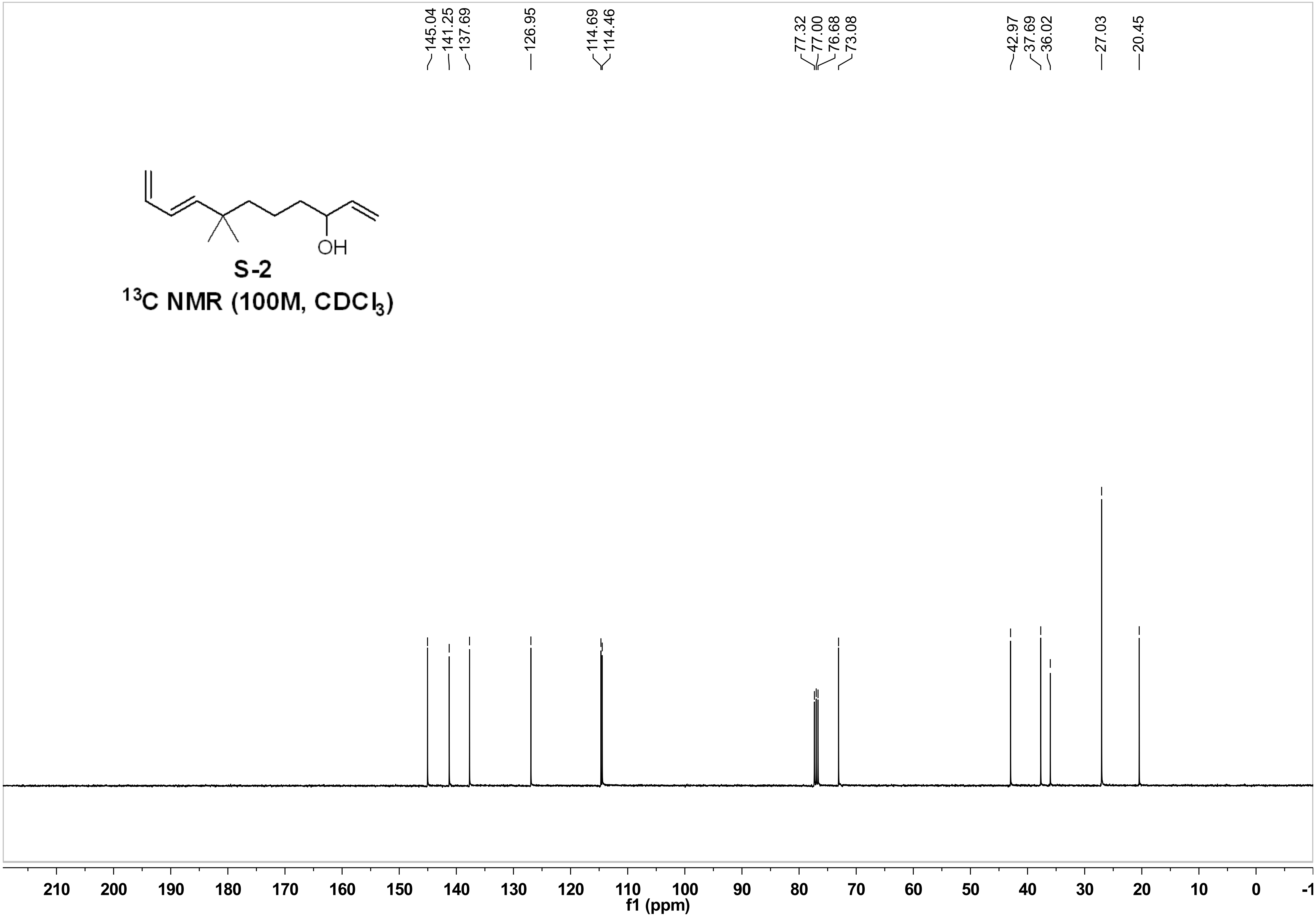


21

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

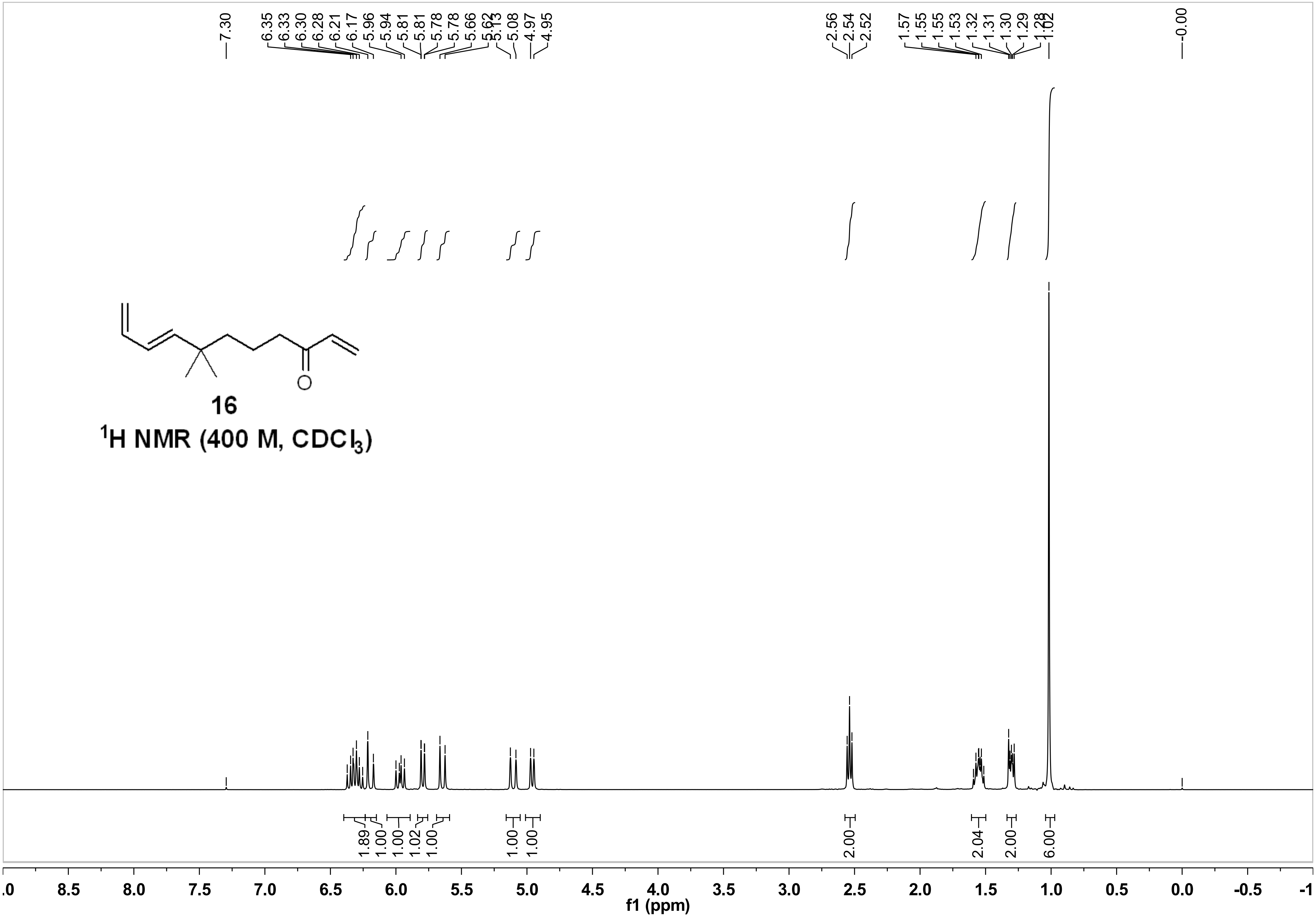

S-2

^{1}H NMR (400 M, CDCl$_3$)

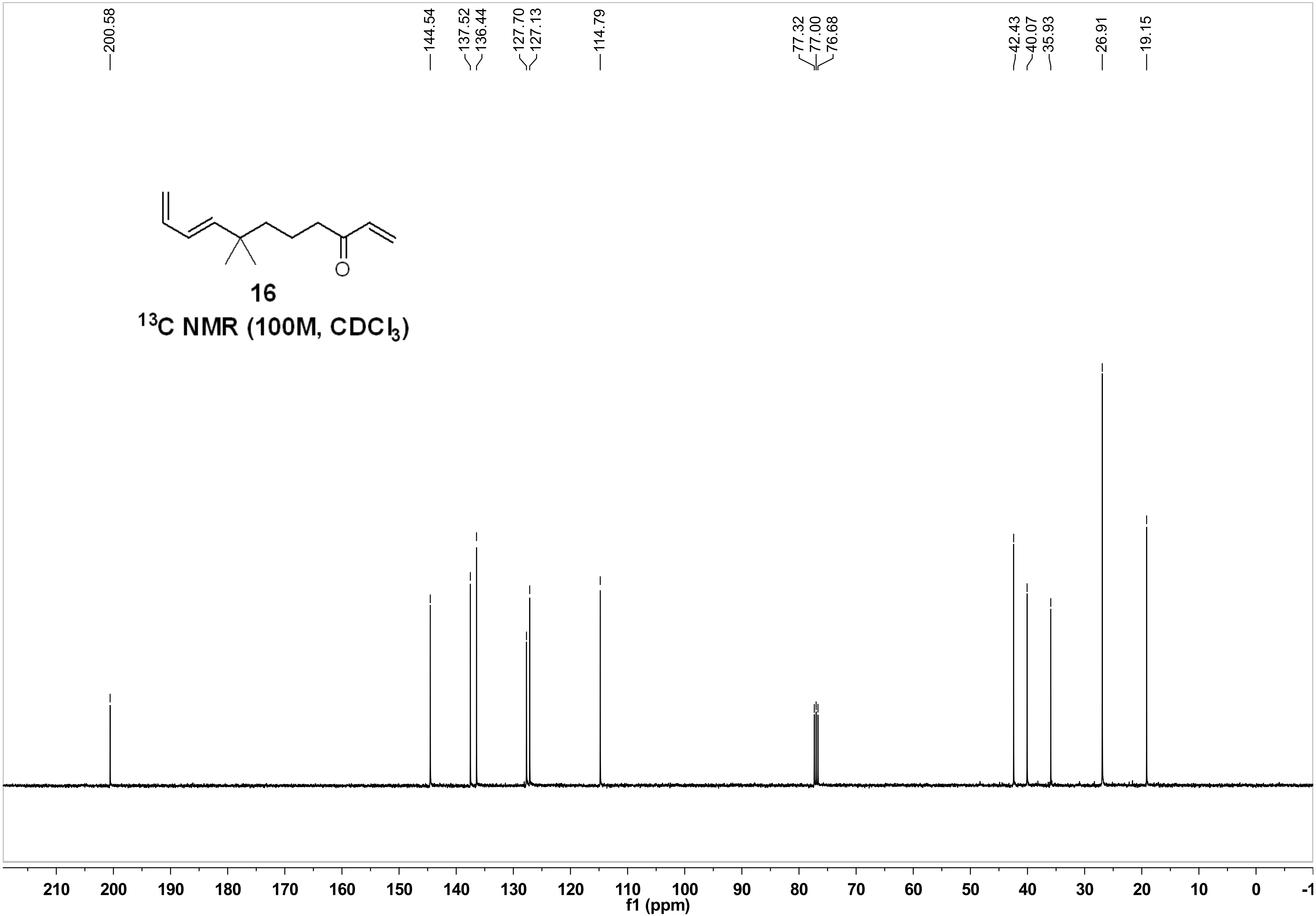


S-2

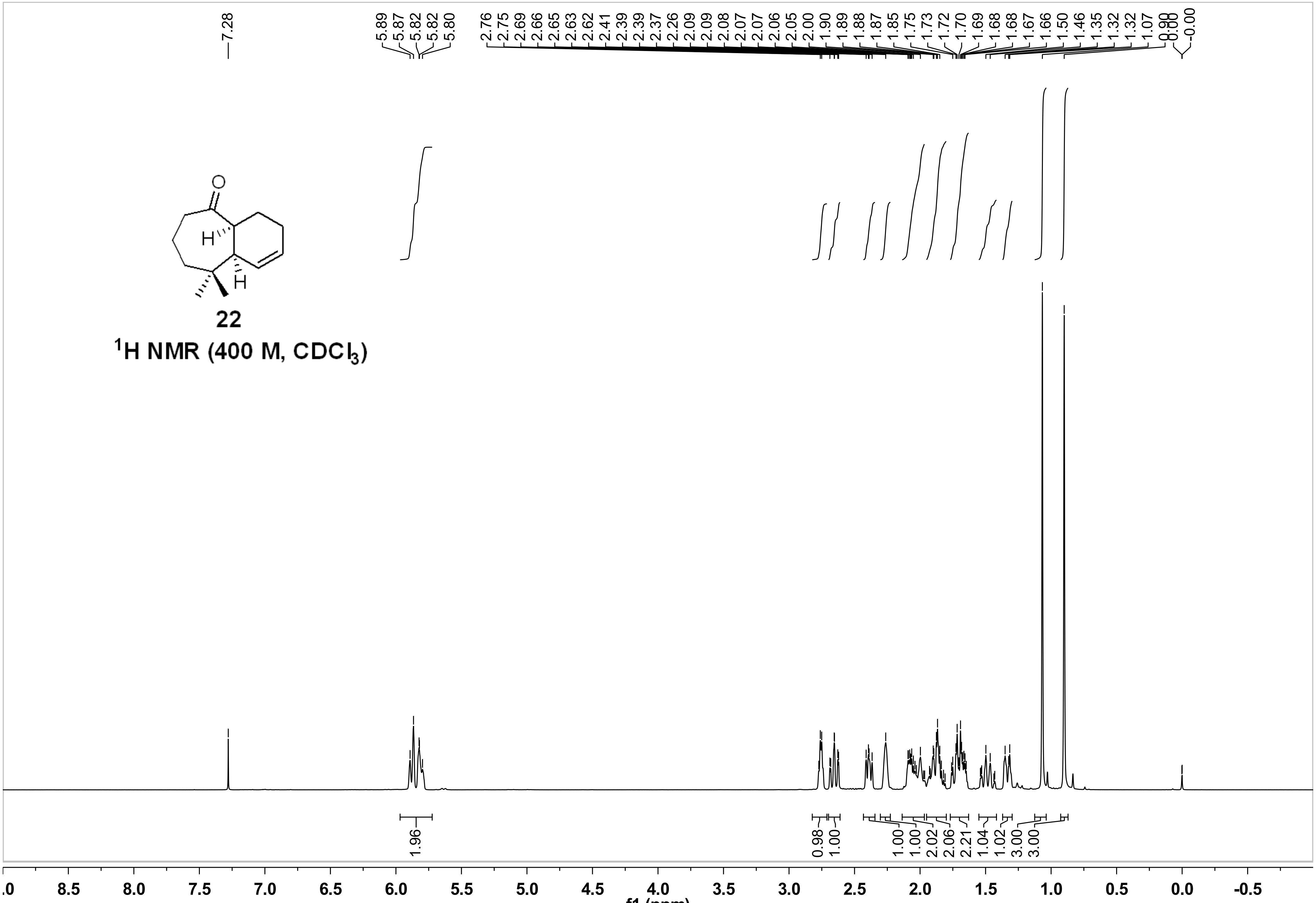
^{13}C NMR (100M, $CDCl_3$)


16

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

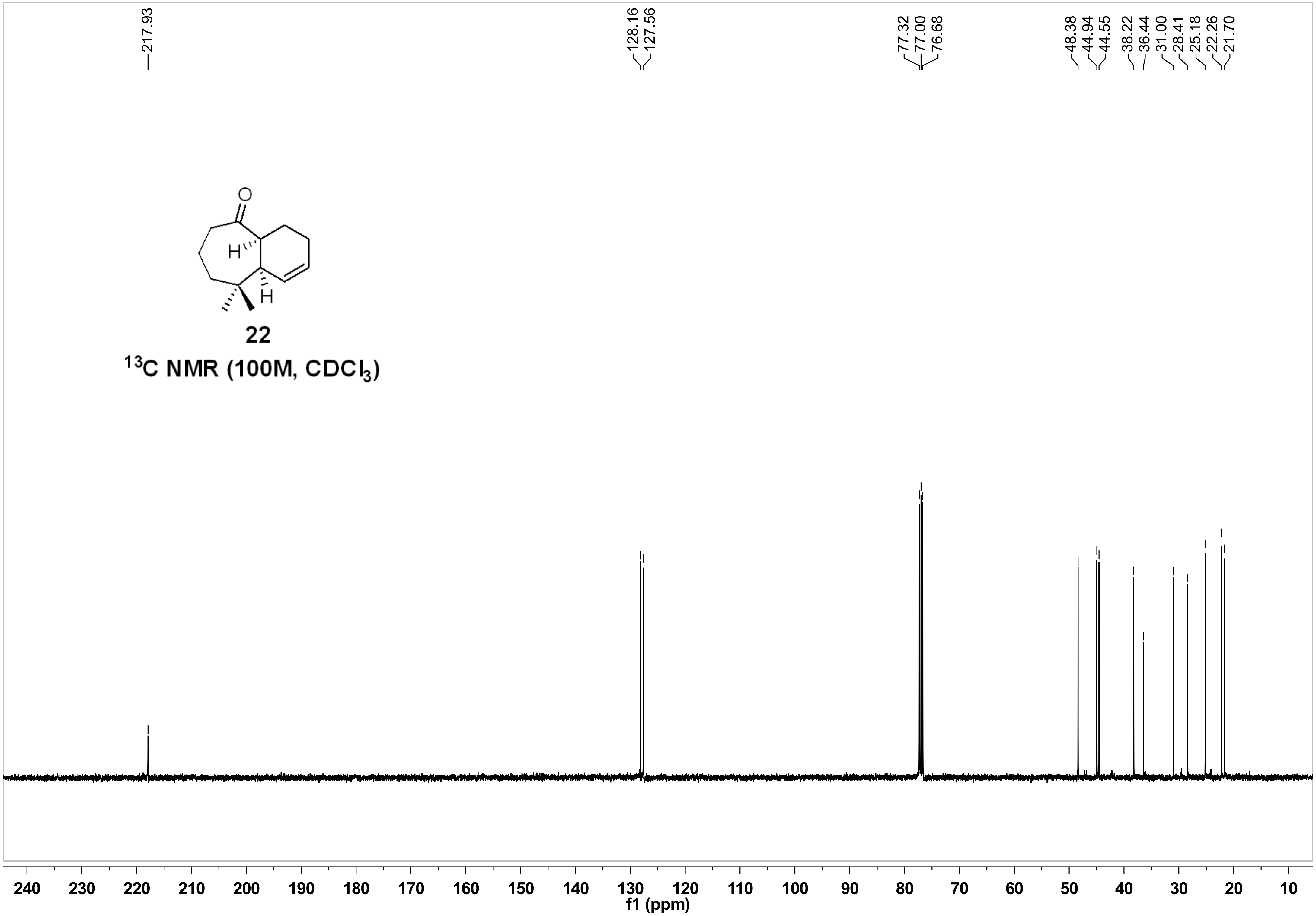

16

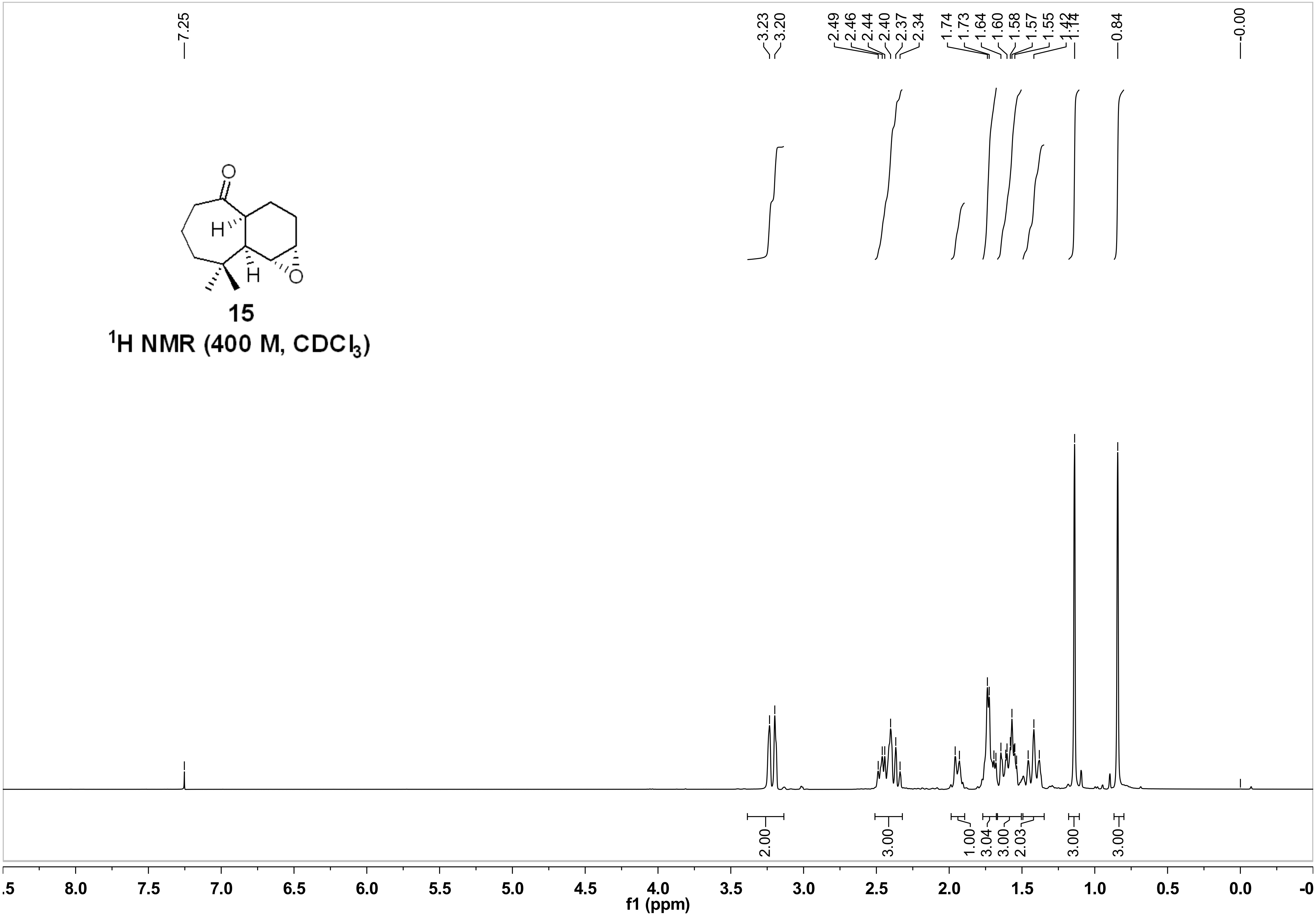
^{13}C NMR (100M, CDCl$_3$)



22

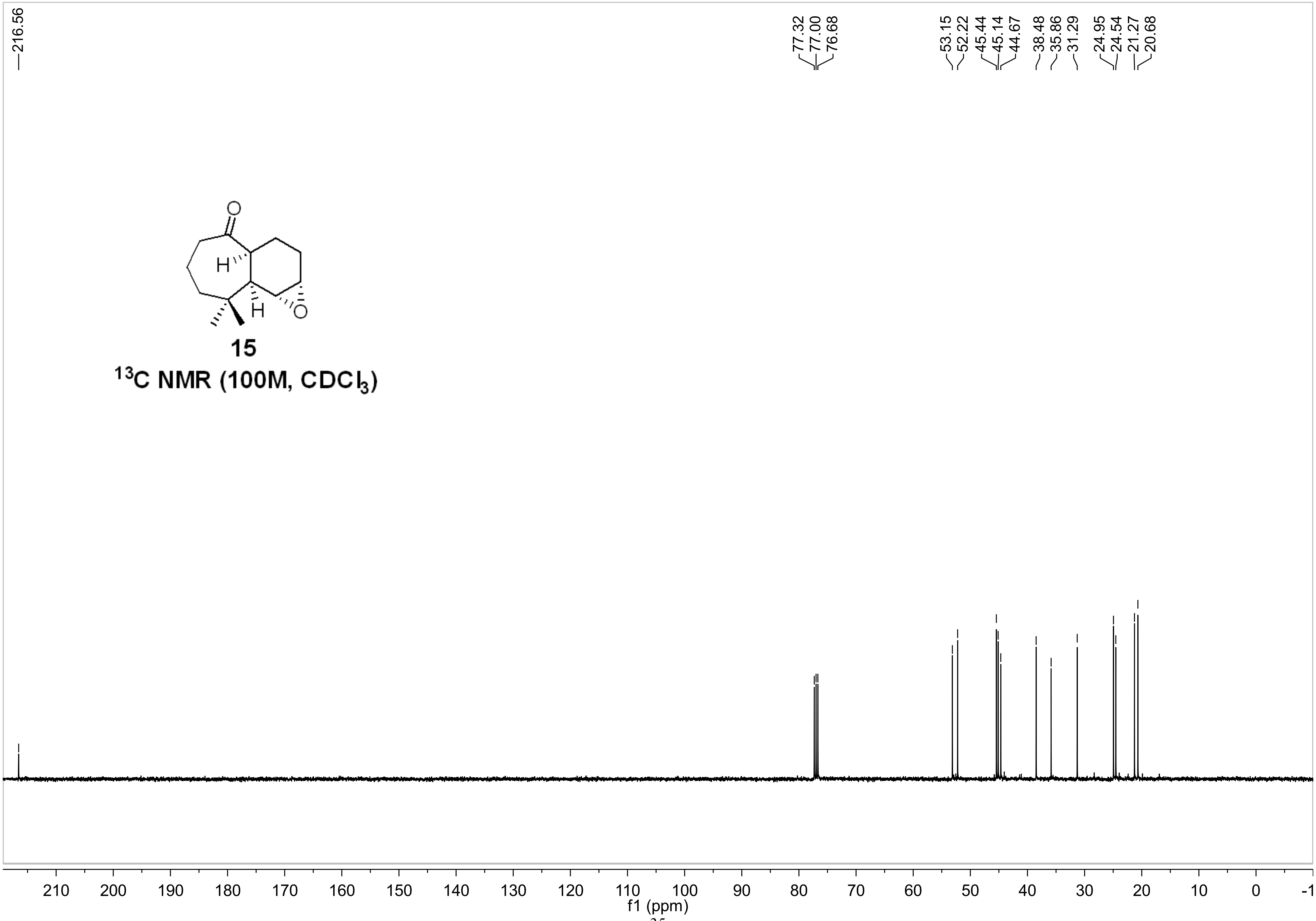
^{1}H NMR (400 M, CDCl$_3$)


217.93
128.16
127.56
77.32
77.00
76.68
48.38
44.94
44.55
38.22
36.44
31.00
28.41
25.18
22.26
21.70
O
H
H
22
^{13}C NMR (100M, CDCl$_3$)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

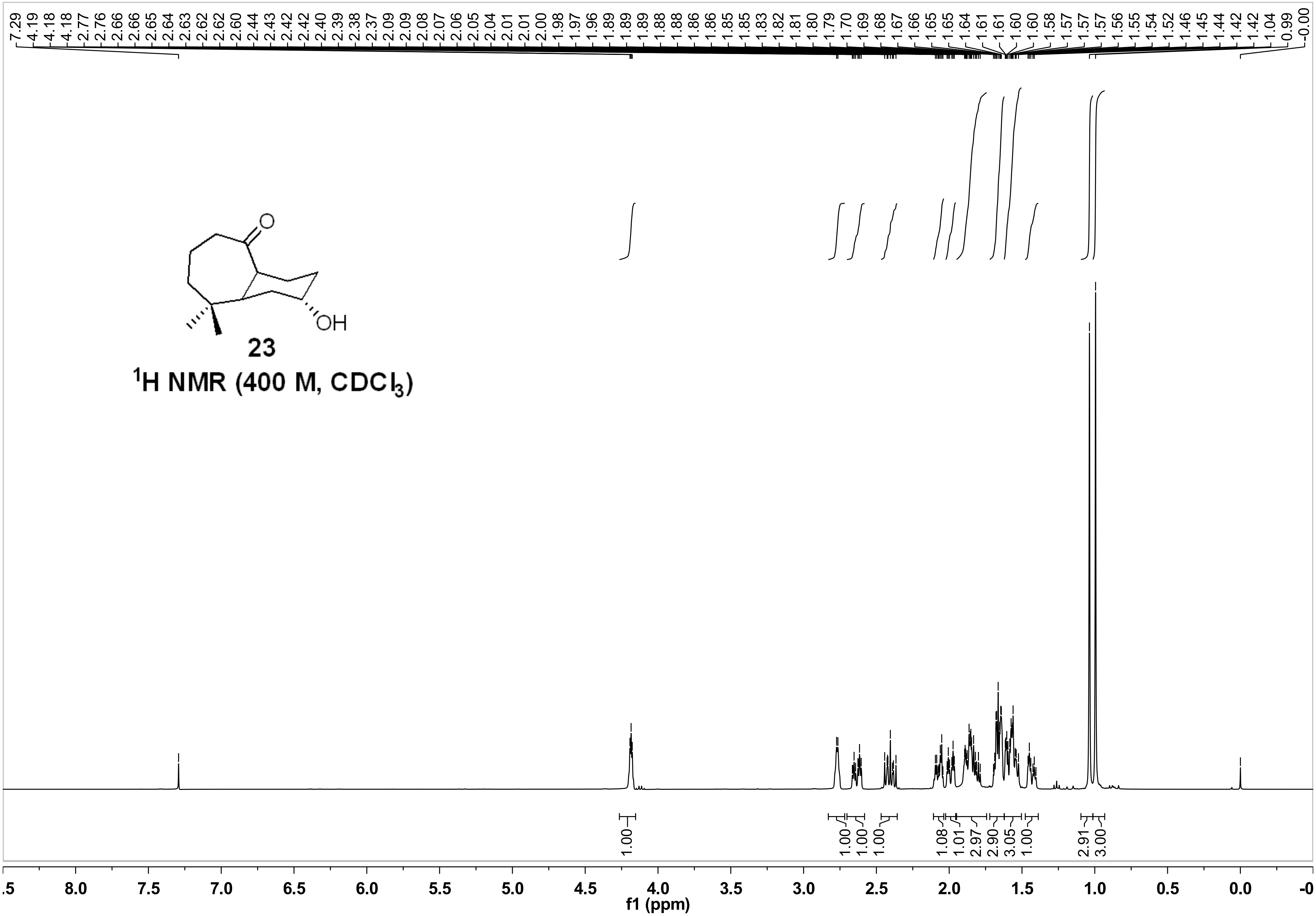


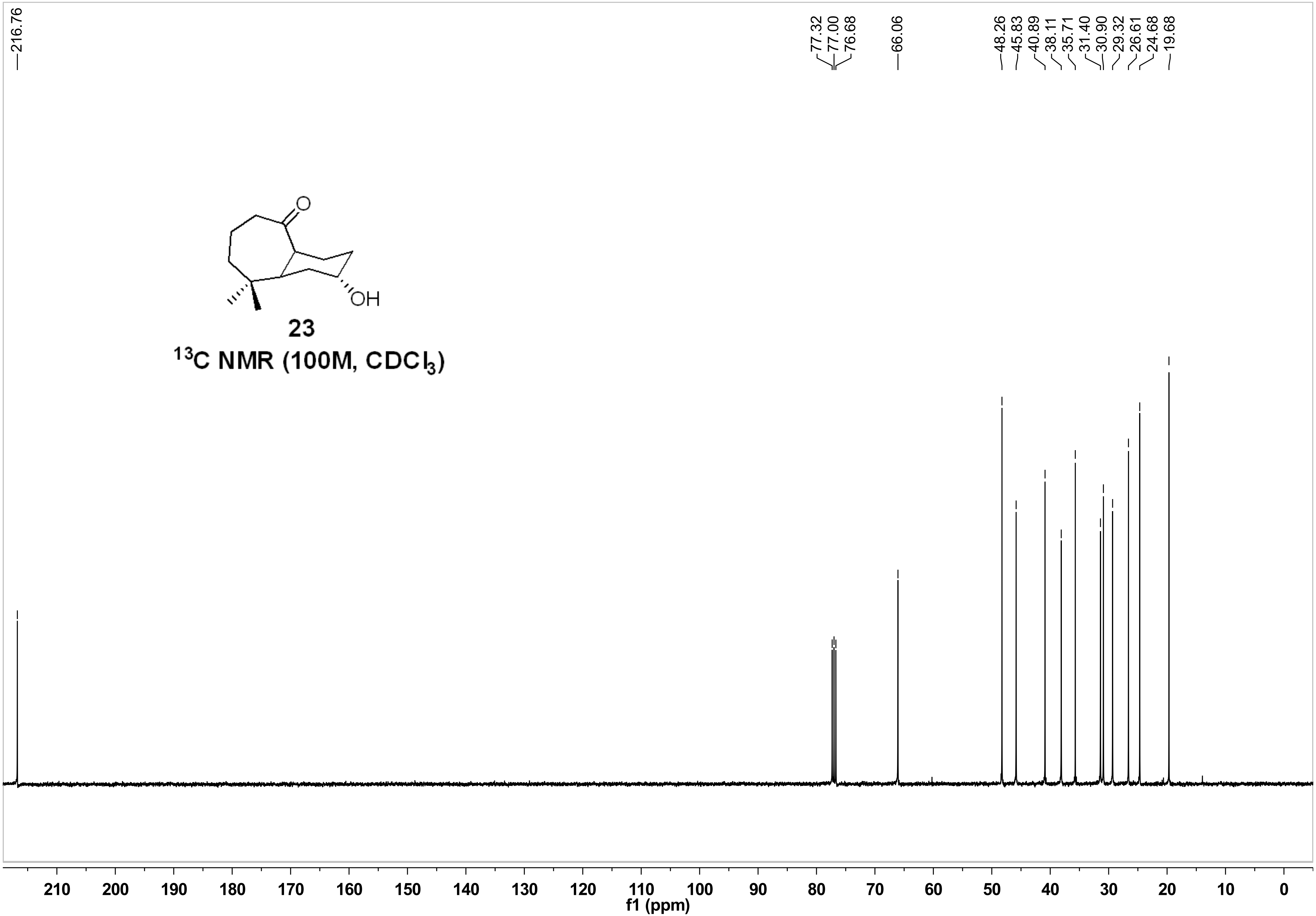
15

^{1}H NMR (400 M, CDCl$_3$)


15

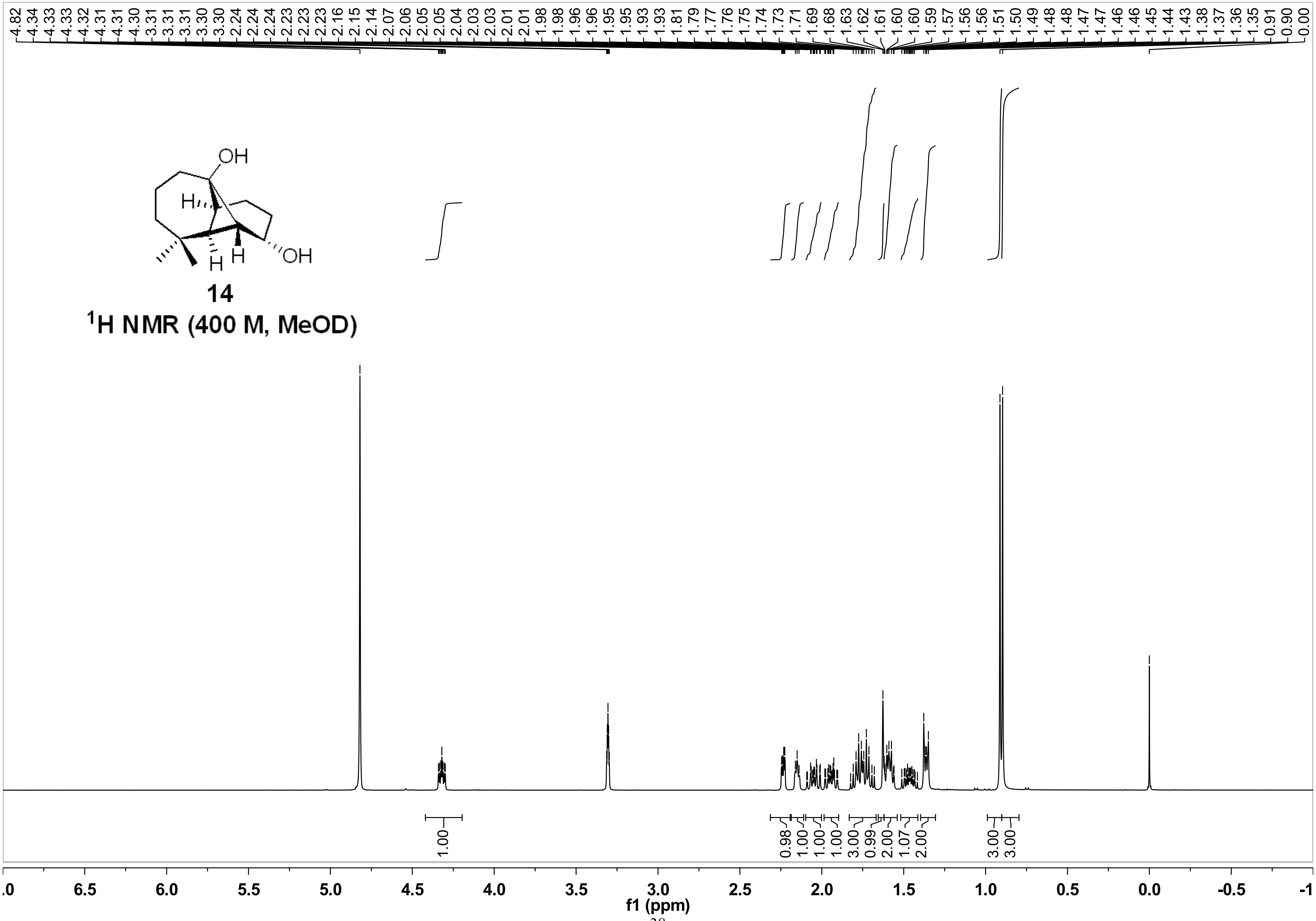
^{13}C NMR (100M, $CDCl_3$)


7.29
4.19
4.18
4.18
2.77
2.76
2.66
2.66
2.65
2.64
2.63
2.62
2.62
2.60
2.44
2.43
2.42
2.42
2.40
2.39
2.38
2.37
2.09
2.09
2.08
2.07
2.06
2.05
2.04
2.01
2.01
2.00
1.98
1.97
1.96
1.89
1.89
1.88
1.88
1.86
1.86
1.85
1.85
1.83
1.82
1.81
1.80
1.79
1.70
1.69
1.68
1.67
1.66
1.65
1.65
1.64
1.61
1.61
1.60
1.60
1.58
1.57
1.57
1.57
1.56
1.55
1.54
1.52
1.46
1.45
1.44
1.42
1.42
1.04
0.99
0.00
O
OH
23
^{1}H NMR (400 M, CDCl$_3$)
1.00
1.00
1.00
1.00
1.08
1.01
2.97
2.90
3.05
1.00
2.91
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



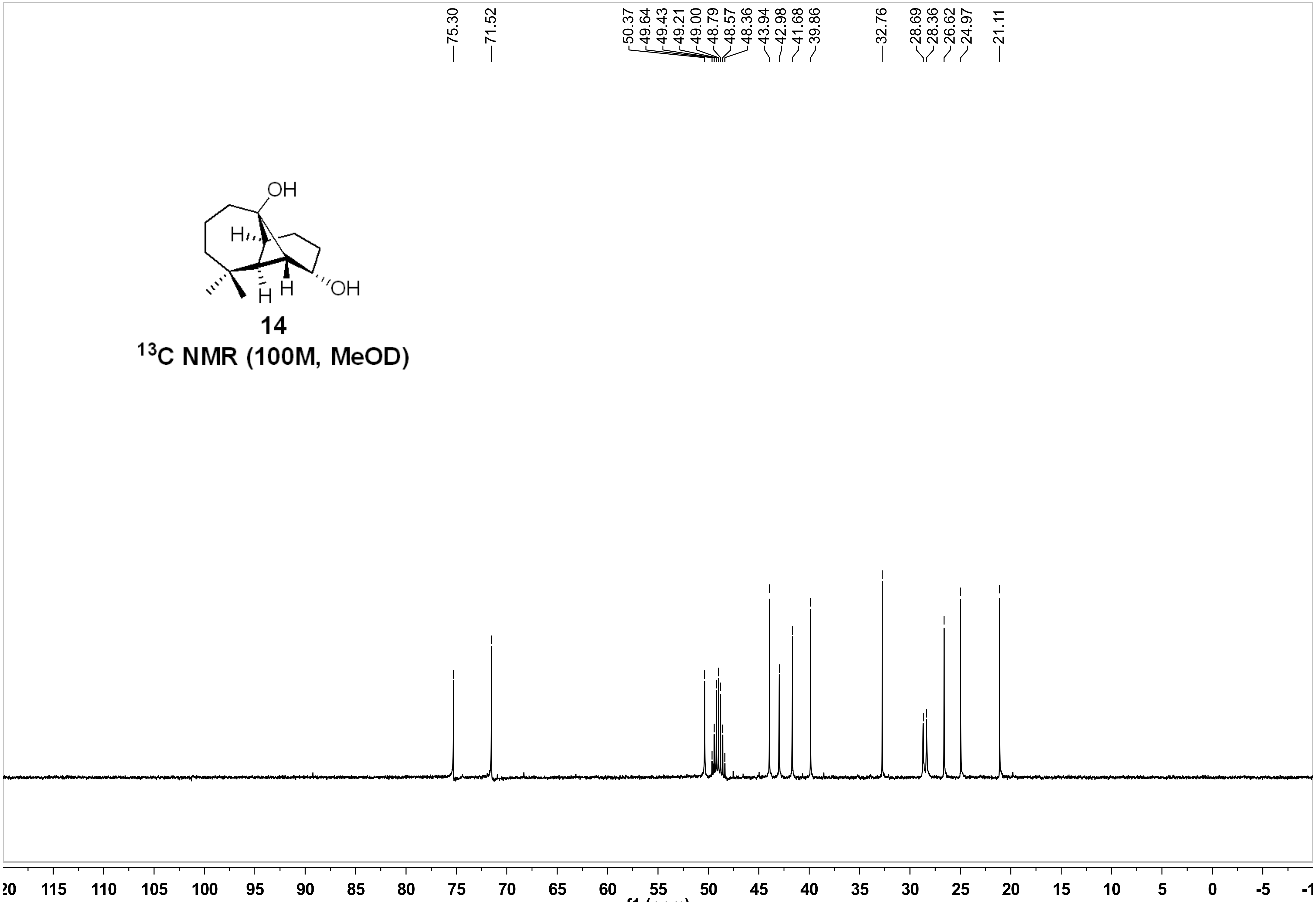
23

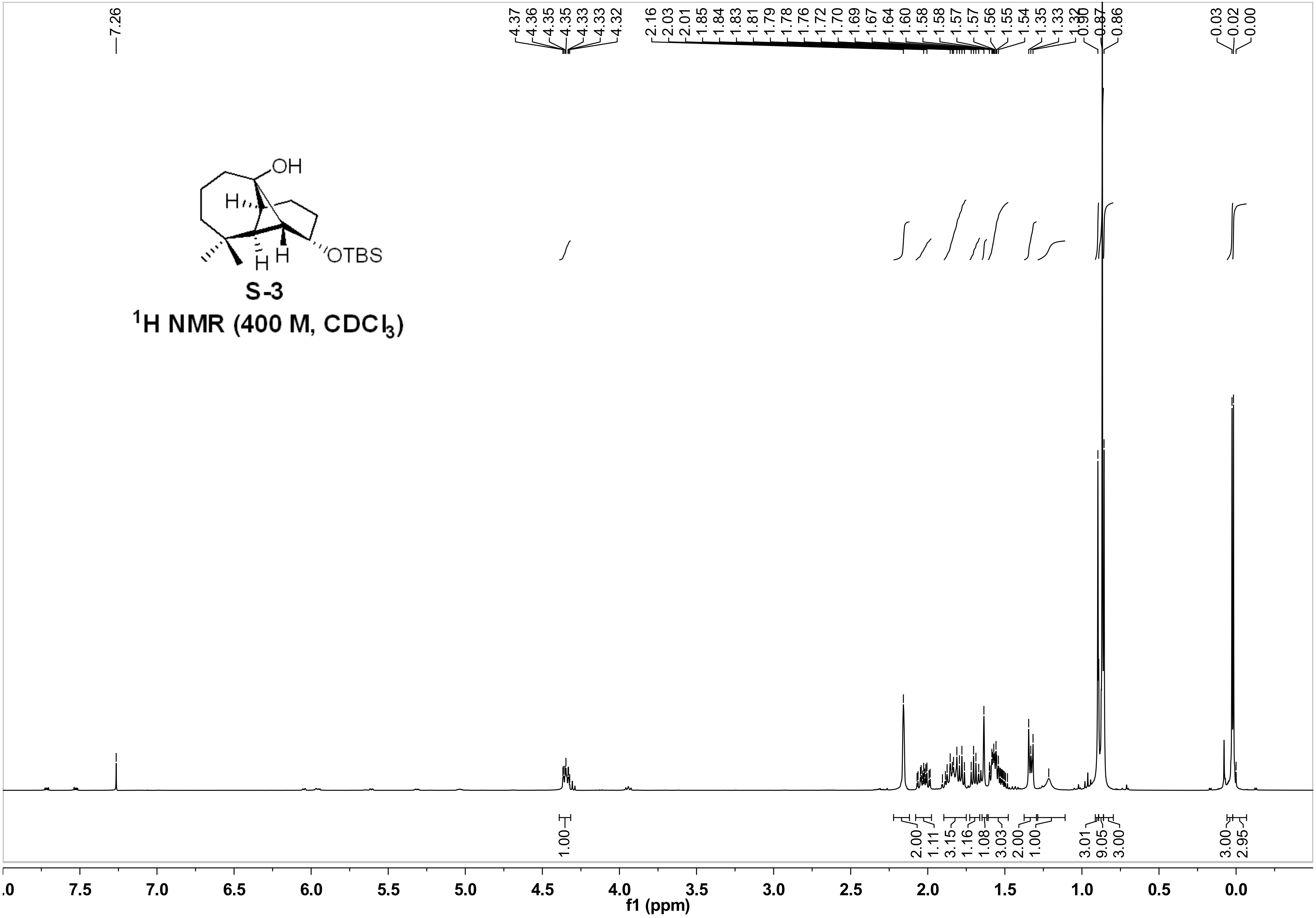
^{13}C NMR (100M, CDCl$_3$)



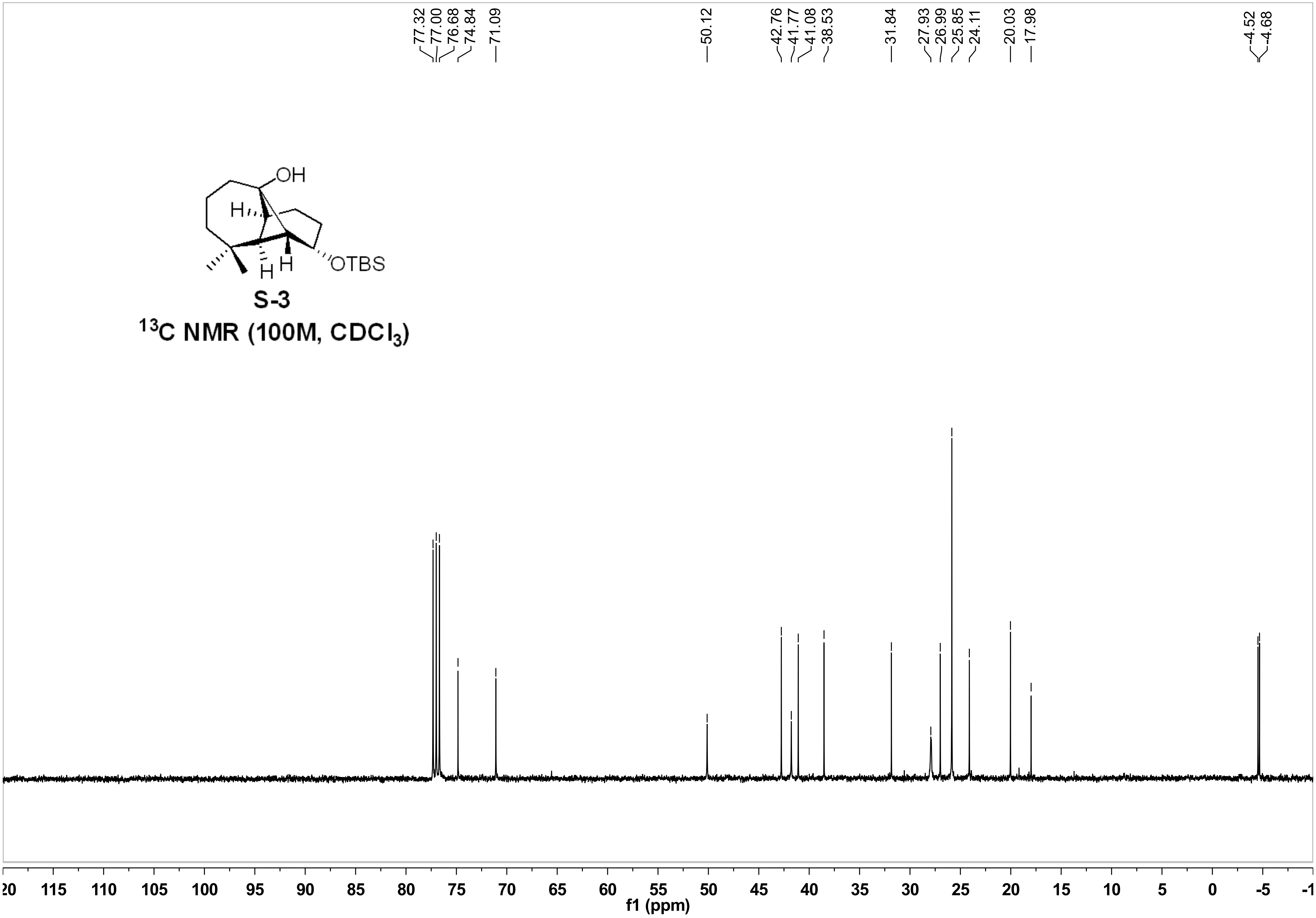
14

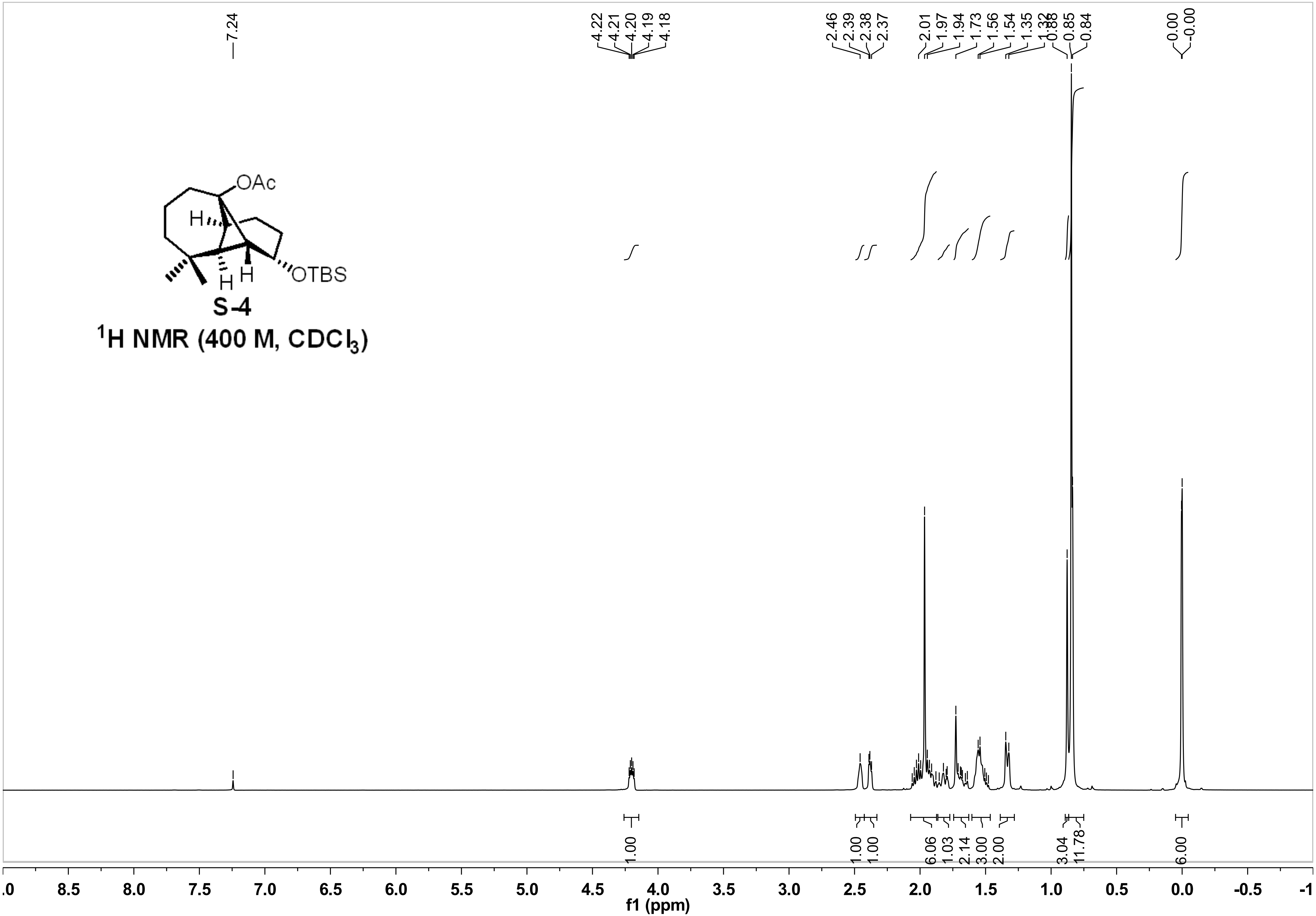
^{1}H NMR (400 M, MeOD)


75.30
71.52
50.37
49.64
49.43
49.21
49.00
48.79
48.57
48.36
43.94
42.98
41.68
39.86
32.76
28.69
28.36
26.62
24.97
21.11
OH
H
H
H
OH
14
^{13}C NMR (100M, MeOD)
20
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-1
f1 (ppm)



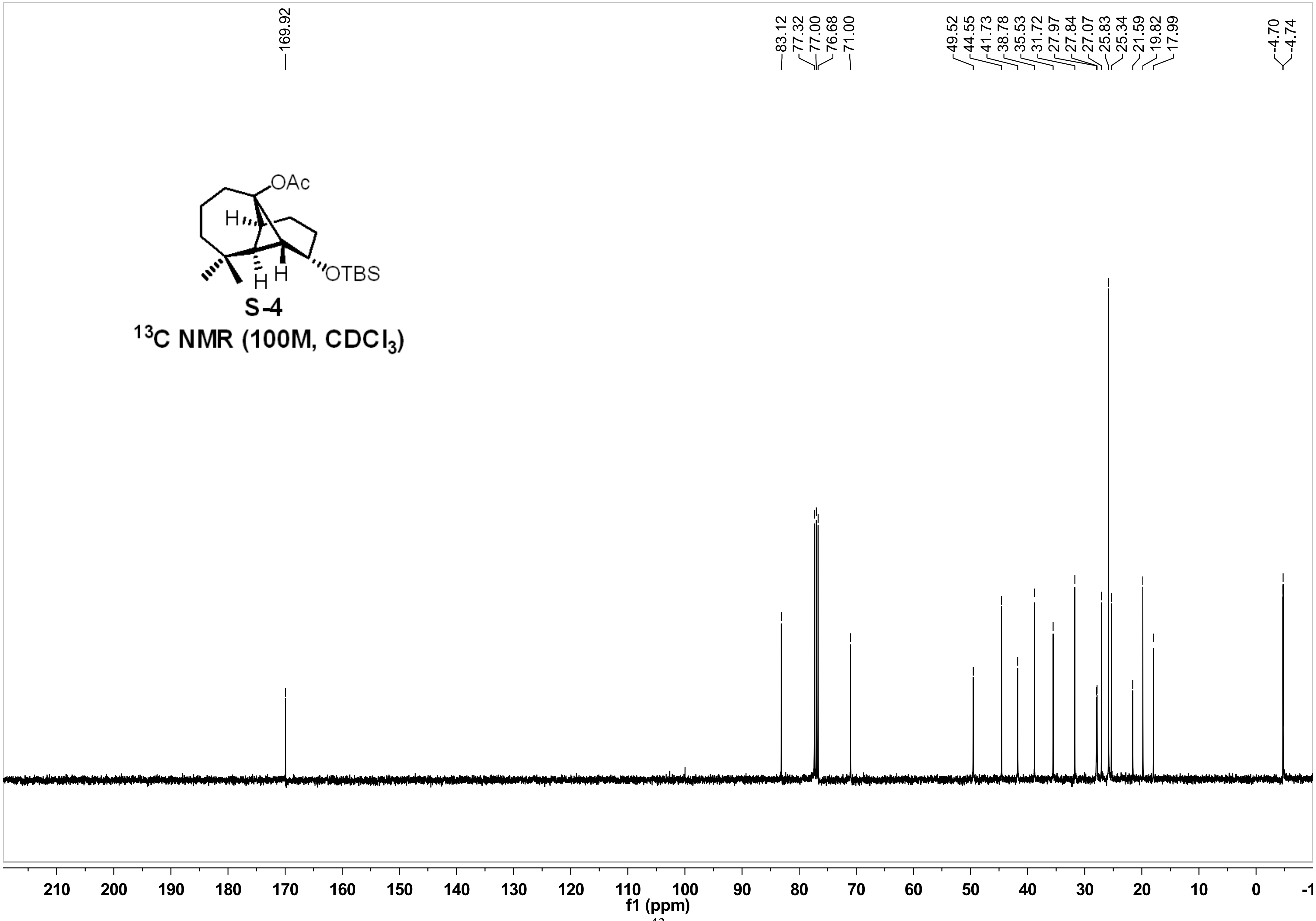
S-3
^{1}H NMR (400 M, CDCl$_3$)
OH
H
H
H
OTBS
7.26
4.37
4.36
4.35
4.35
4.33
4.33
4.32
2.16
2.03
2.01
1.85
1.84
1.83
1.81
1.79
1.78
1.76
1.72
1.70
1.69
1.67
1.64
1.60
1.58
1.58
1.57
1.57
1.56
1.55
1.54
1.35
1.33
1.32
0.90
0.87
0.86
0.03
0.02
0.00
1.00
2.00
1.11
3.15
1.16
1.08
3.03
2.00
1.00
3.01
9.05
3.00
3.00
2.95
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


77.32
77.00
76.68
74.84
71.09
50.12
42.76
41.77
41.08
38.53
31.84
27.93
26.99
25.85
24.11
20.03
17.98
-4.52
-4.68
OH
H
H
H
OTBS
S-3
^{13}C NMR (100M, CDCl$_3$)
20
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-1
f1 (ppm)



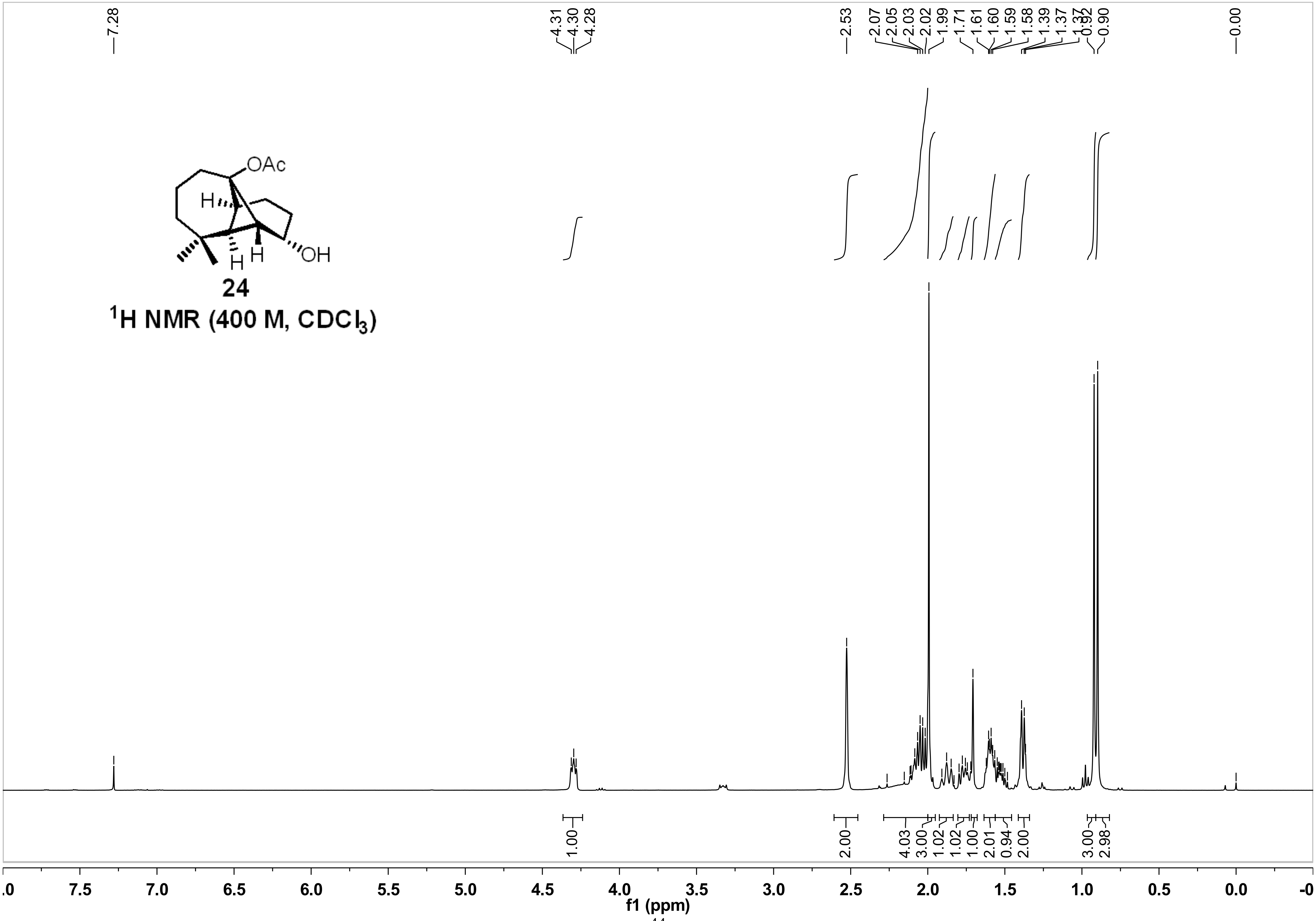
S-4

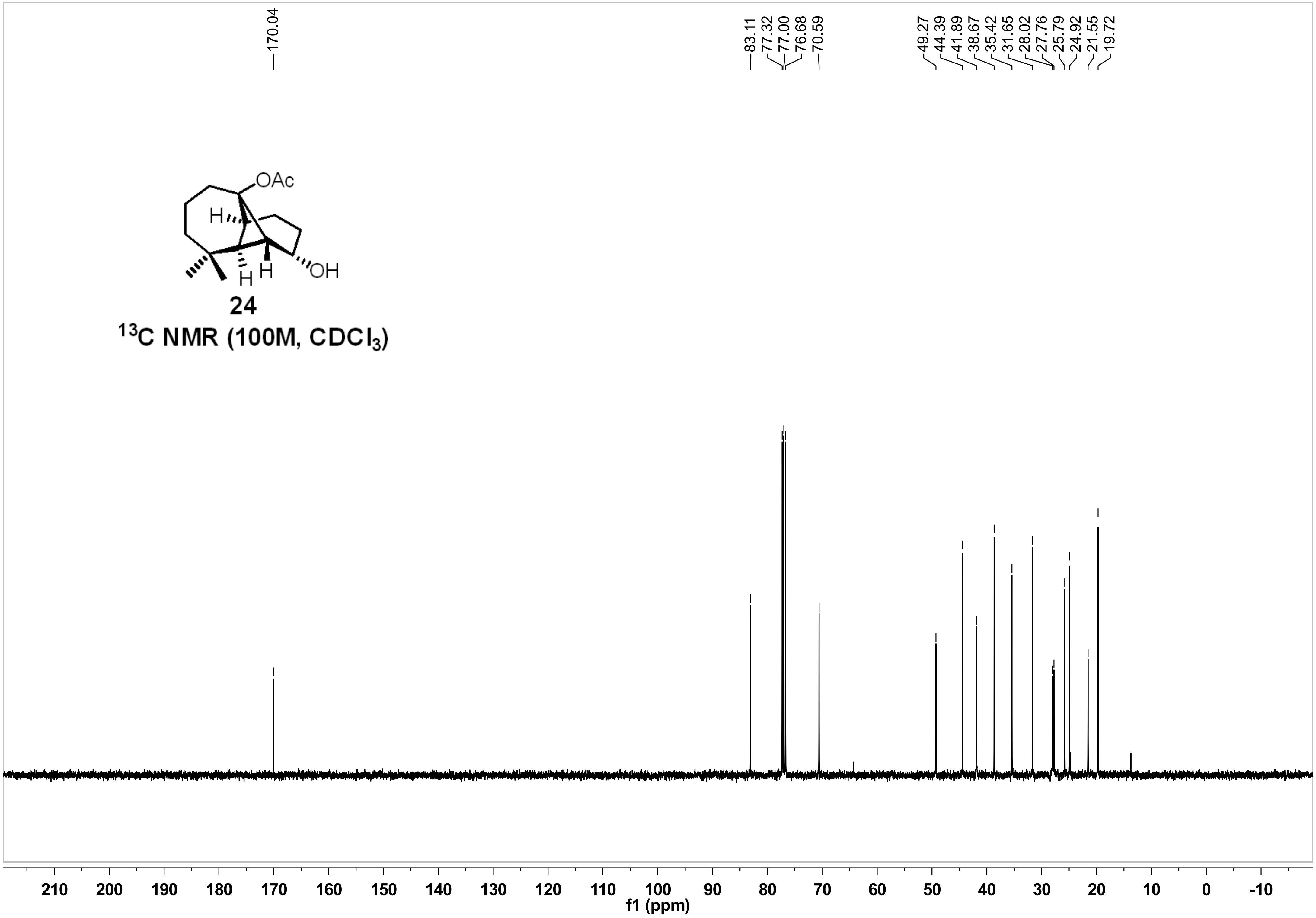
^{1}H NMR (400 M, $CDCl_3$)



S-4

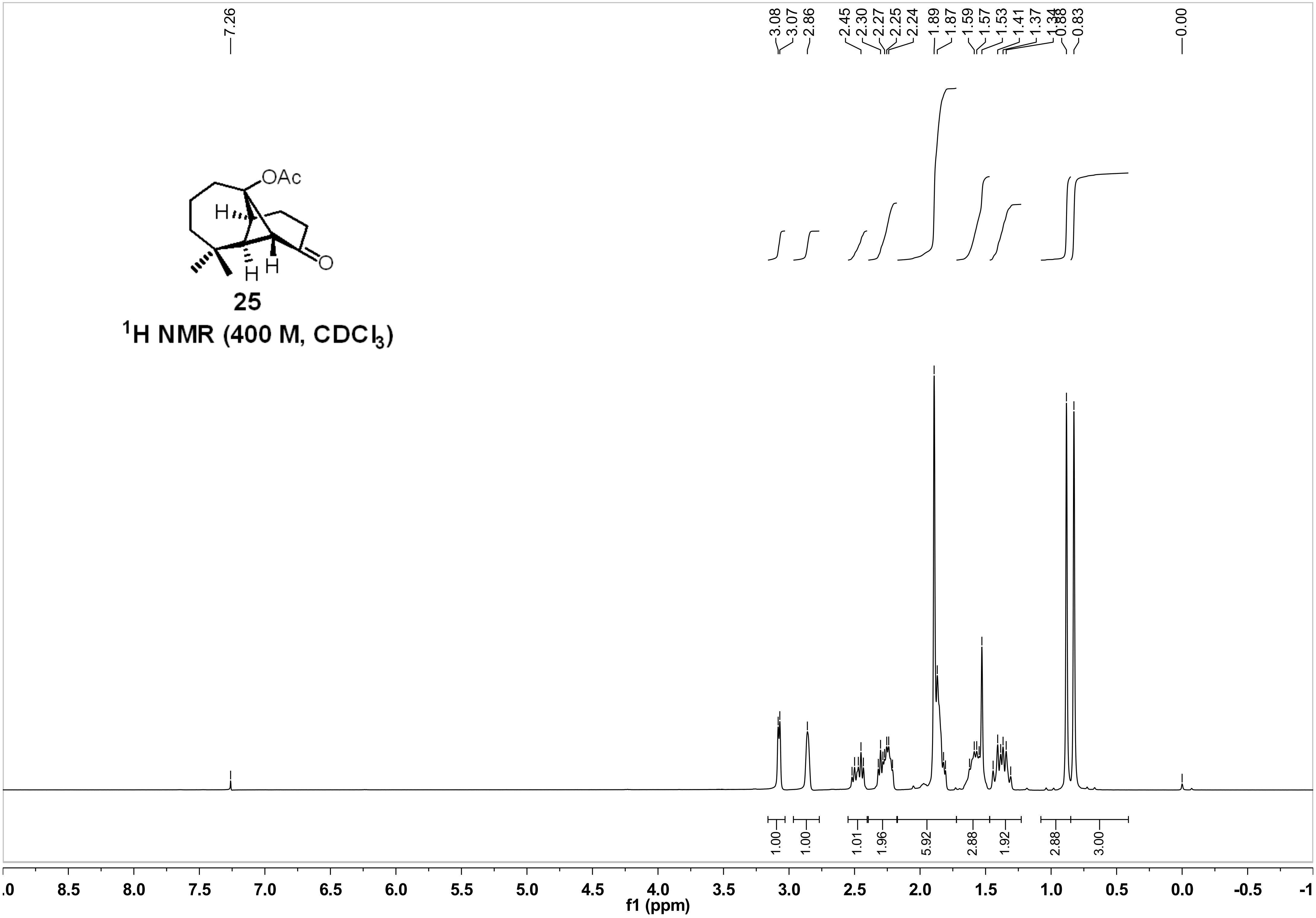
^{13}C NMR (100M, CDCl$_3$)


7.28
4.31
4.30
4.28
2.53
2.07
2.05
2.03
2.02
1.99
1.71
1.61
1.60
1.59
1.58
1.39
1.37
1.37
0.92
0.90
0.00
OAc
H
H
H
OH
24
^{1}H NMR (400 M, CDCl$_3$)
1.00
2.00
4.03
3.00
1.02
1.02
1.00
2.01
0.94
2.00
3.00
2.98
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



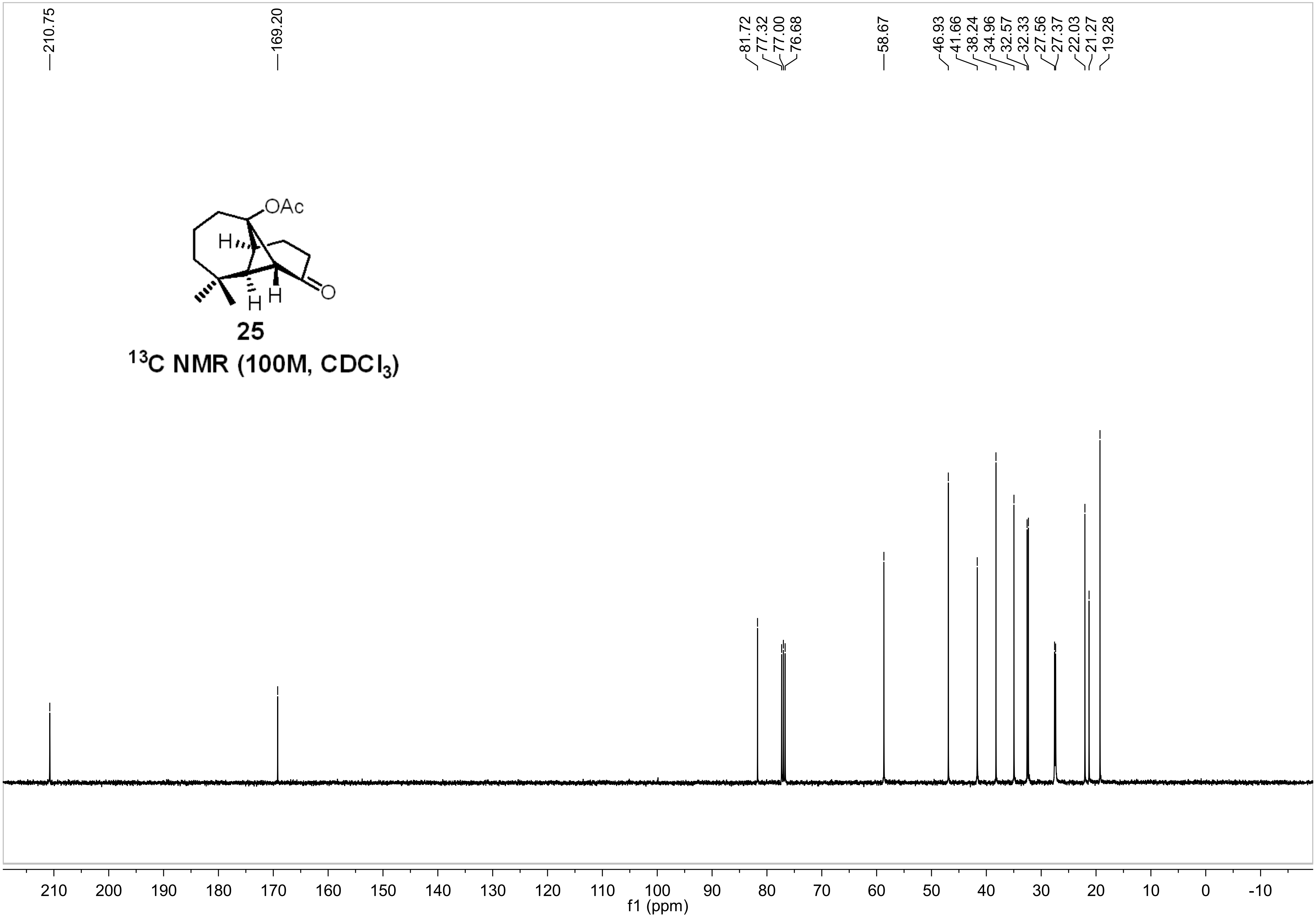
24

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



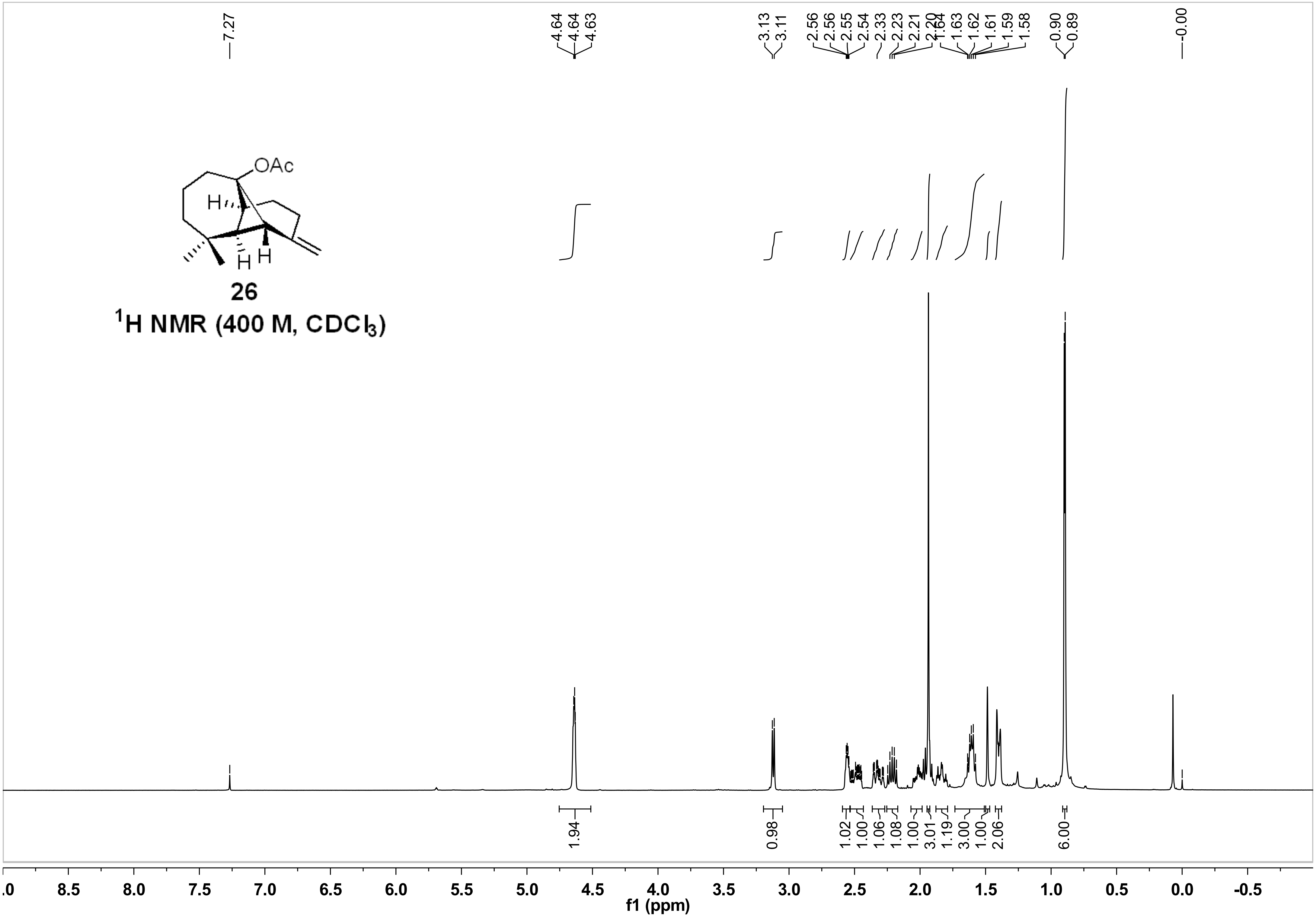
25

^{1}H NMR (400 M, CDCl$_3$)



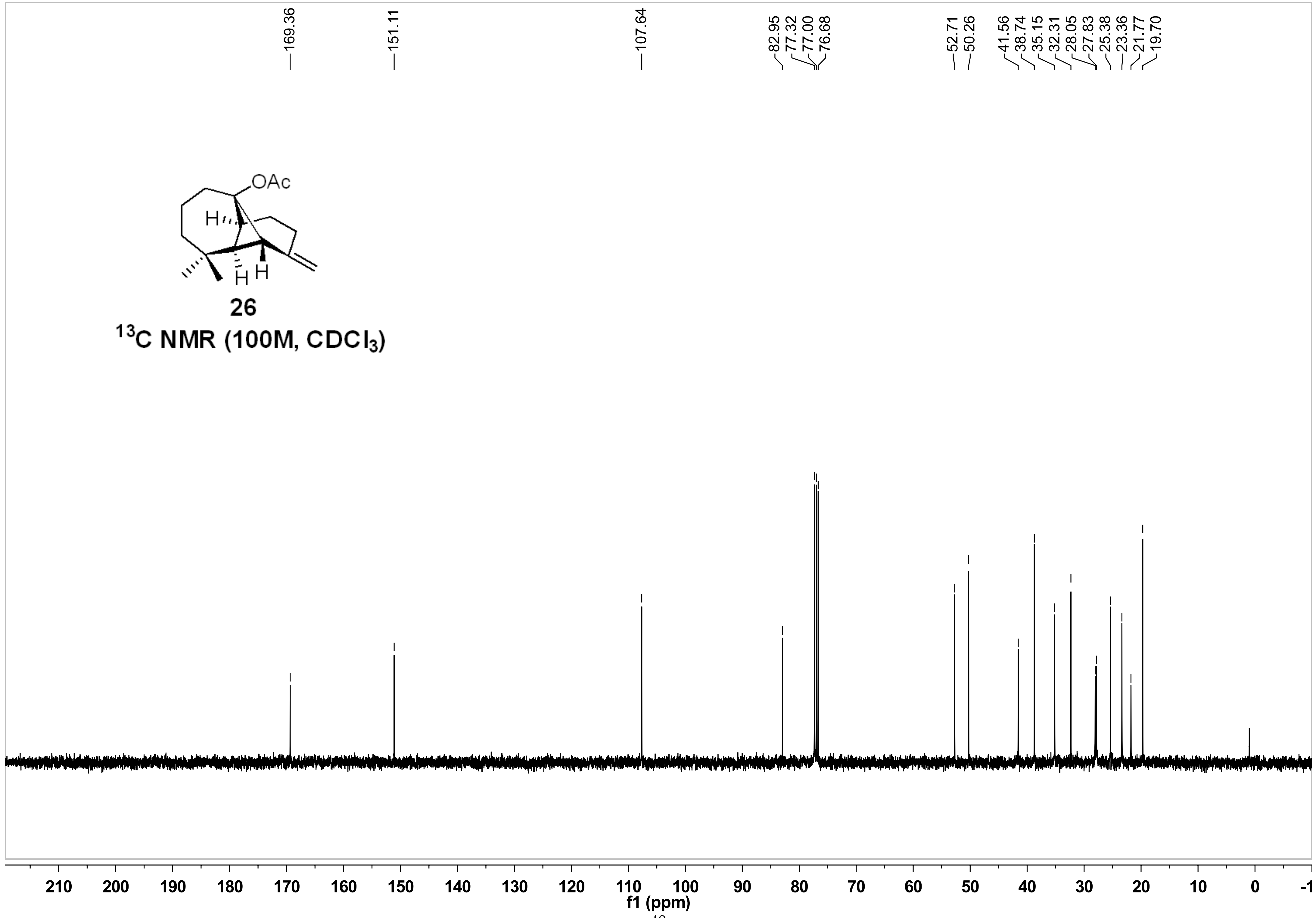
25

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



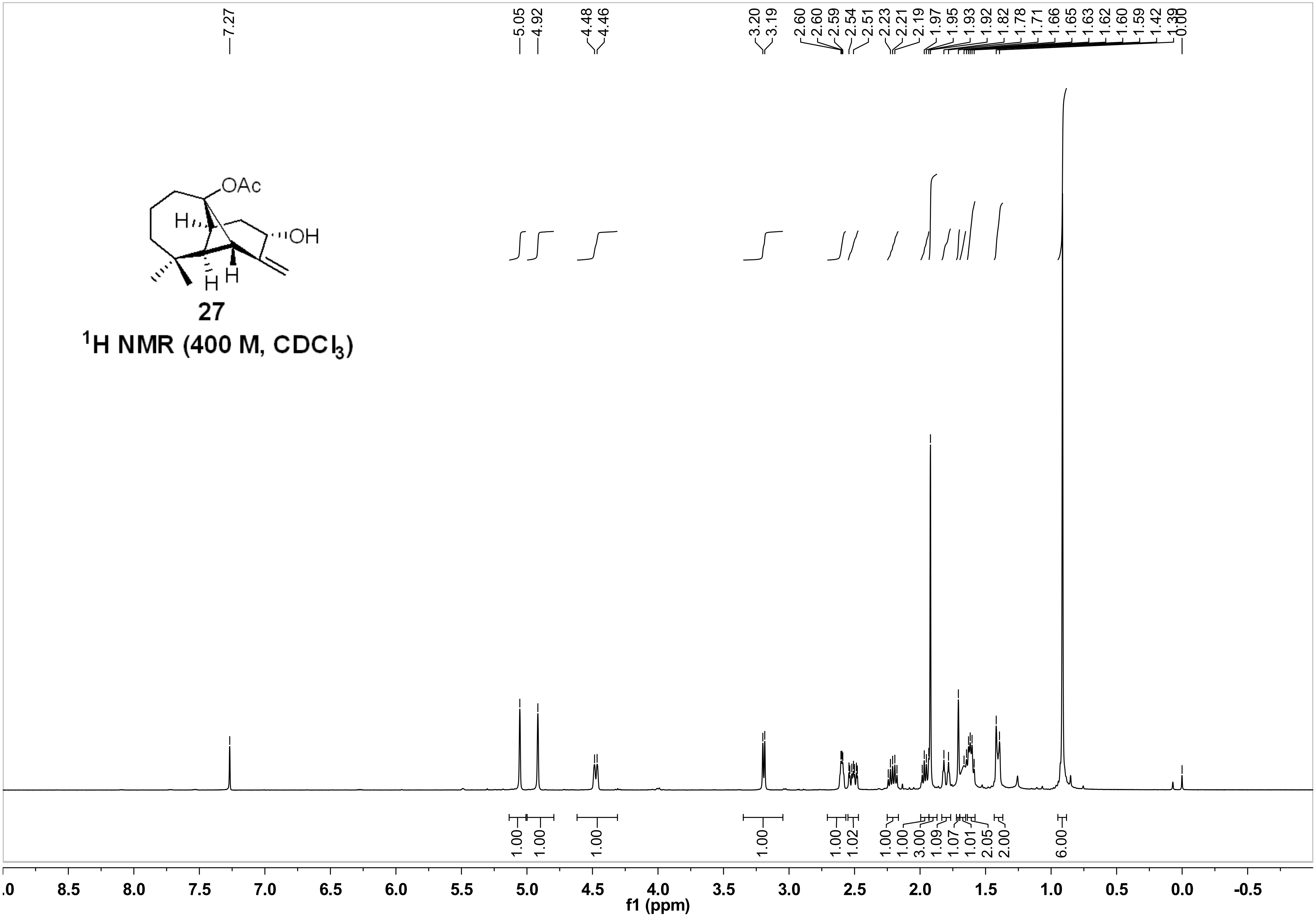
26

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



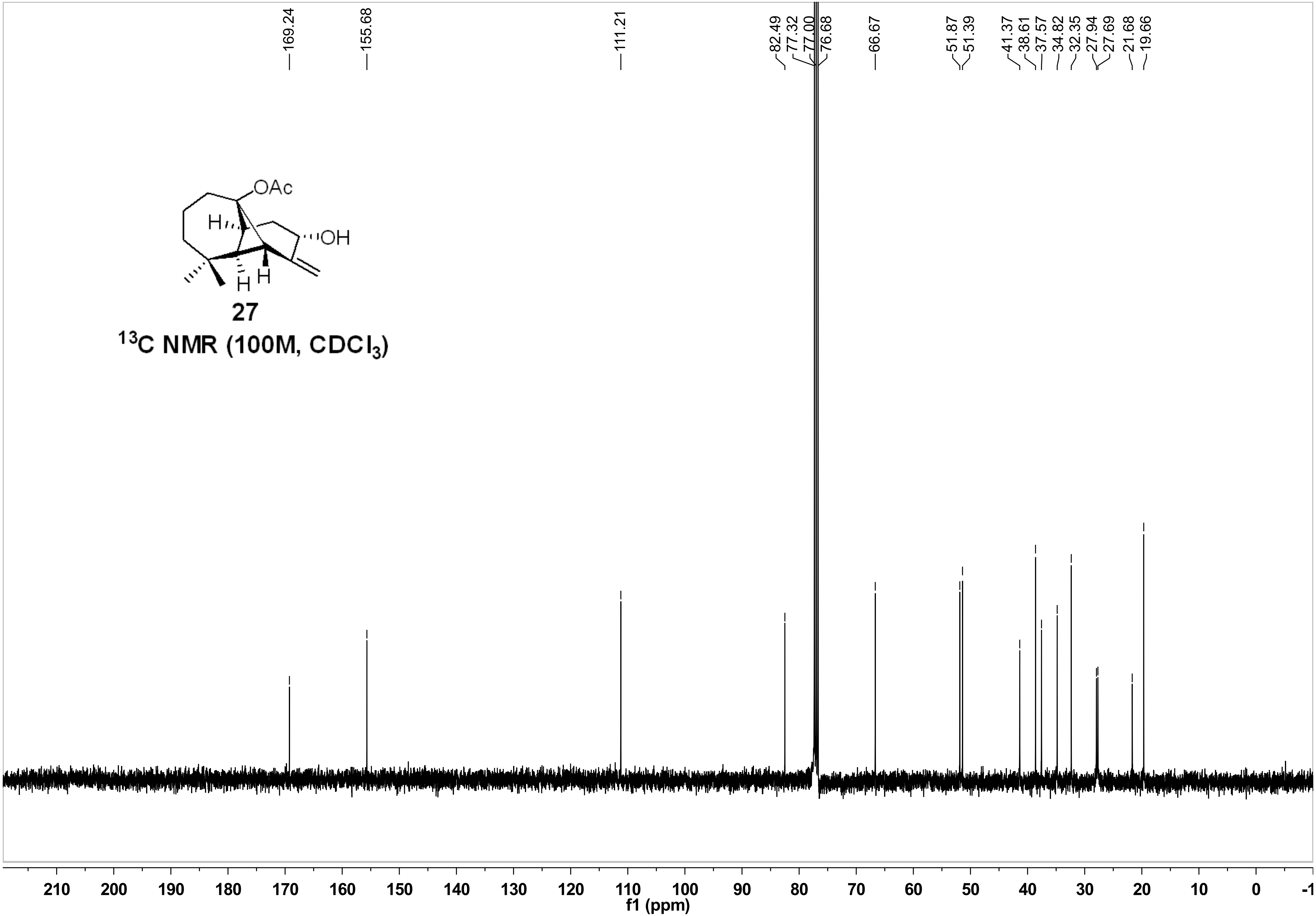
26

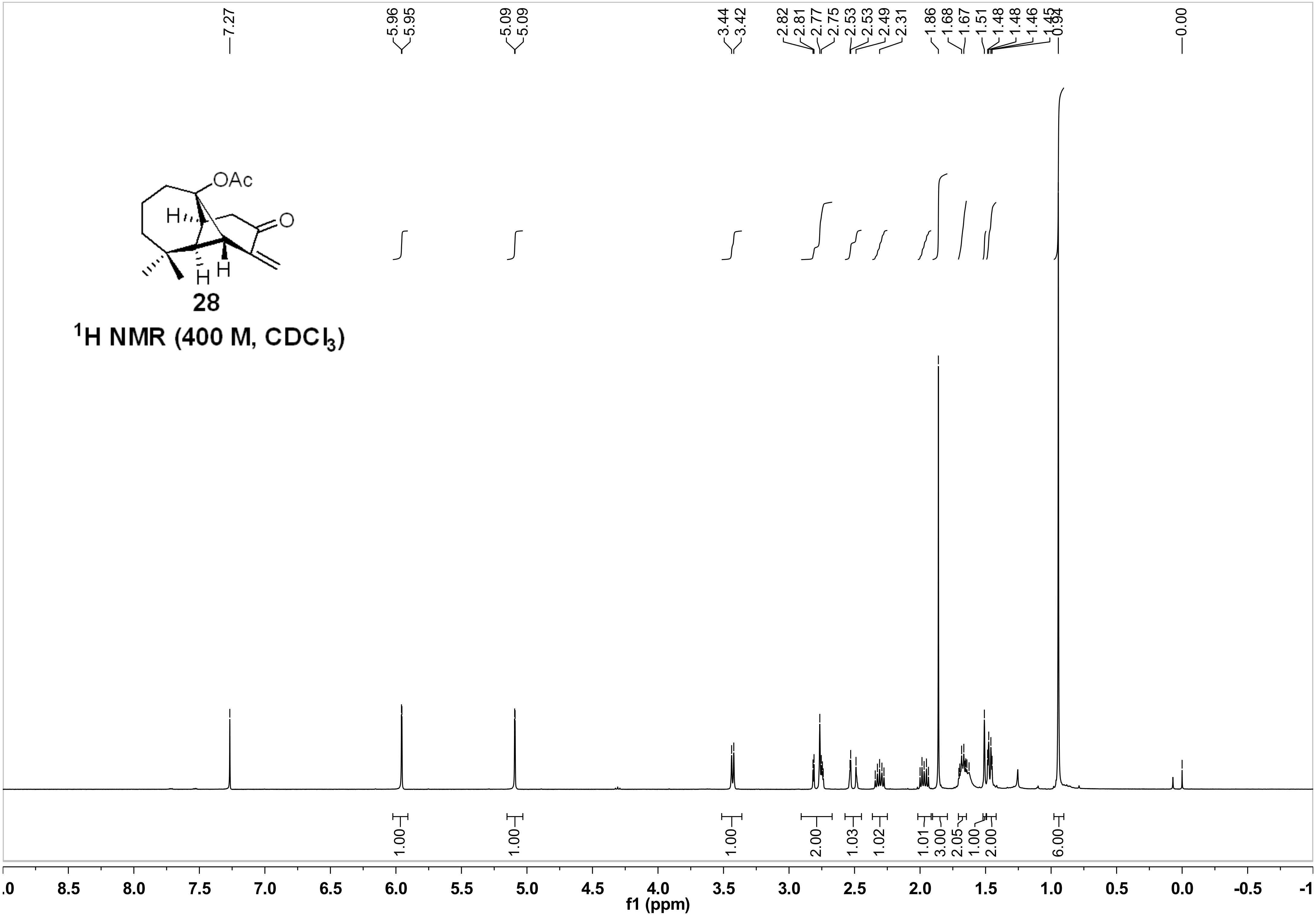
^{13}C NMR (100M, $CDCl_3$)

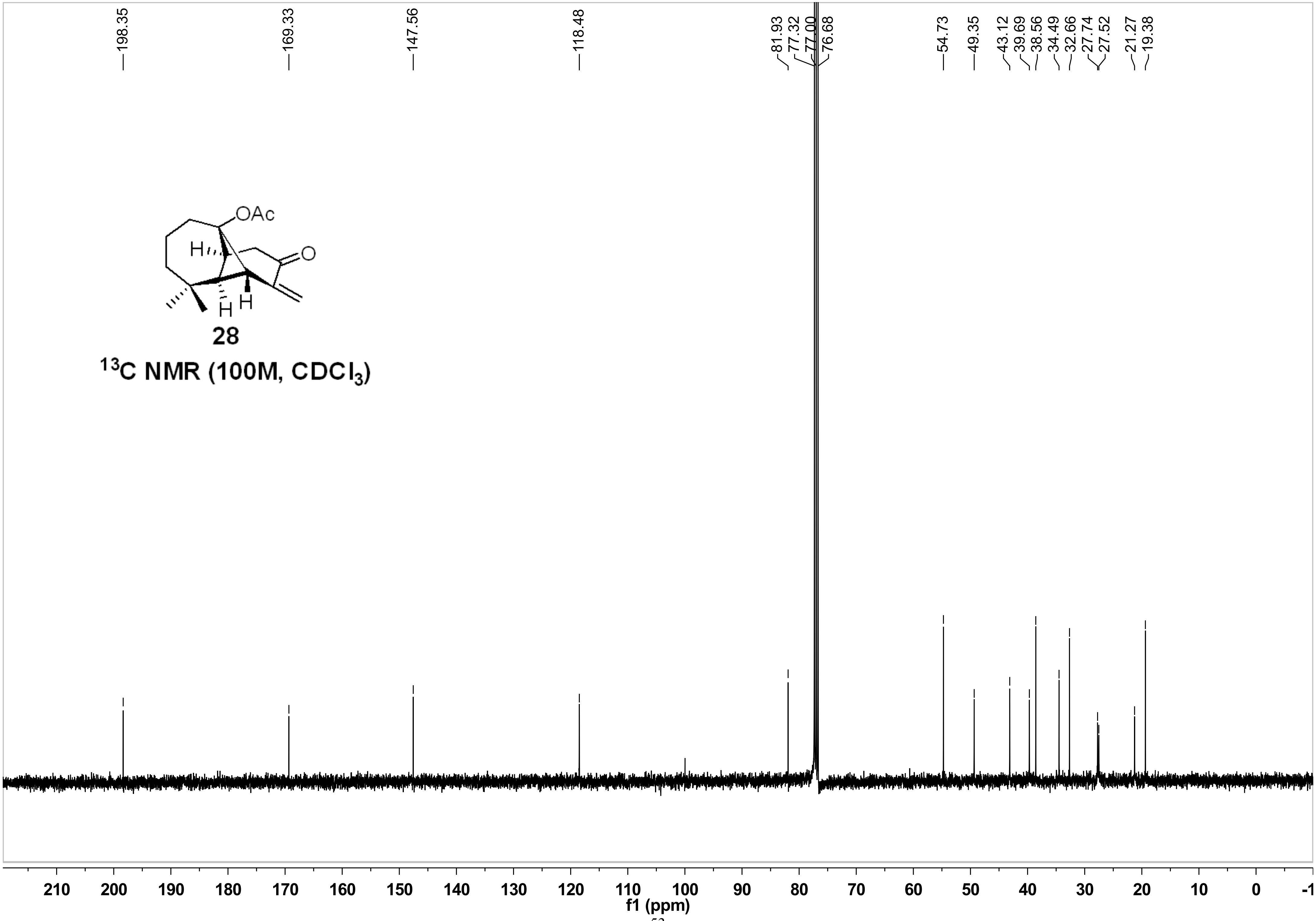


27

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

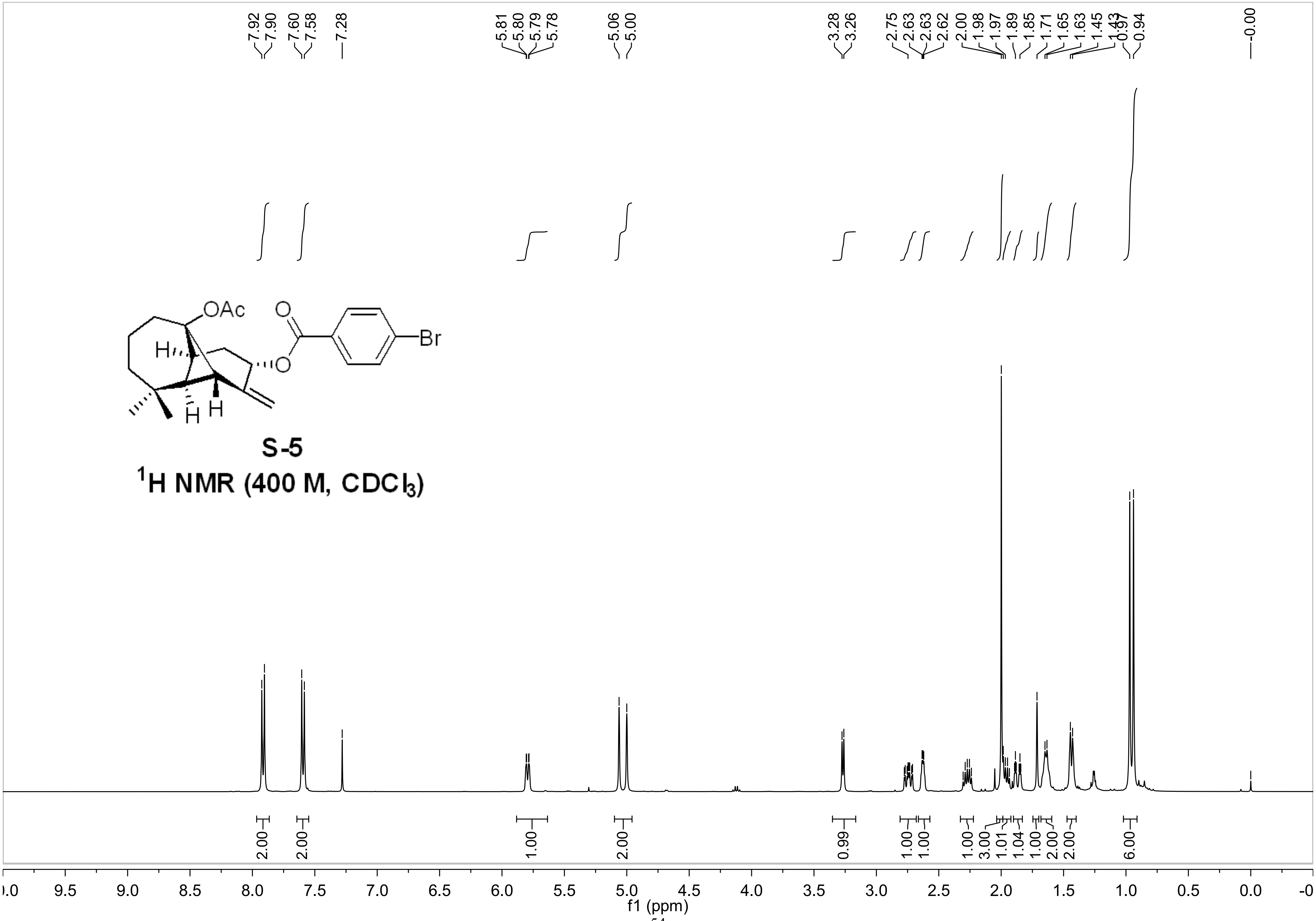

169.24
155.68
111.21
82.49
77.32
77.00
76.68
66.67
51.87
51.39
41.37
38.61
37.57
34.82
32.35
27.94
27.69
21.68
19.66
OAc
H
OH
H
H
27
^{13}C NMR (100M, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.27
5.96
5.95
5.09
5.09
3.44
3.42
2.82
2.81
2.77
2.75
2.53
2.53
2.49
2.31
1.86
1.68
1.67
1.51
1.48
1.48
1.46
1.45
0.94
0.00
OAc
H
O
H
H
28
^{1}H NMR (400 M, CDCl$_3$)
1.00
1.00
1.00
2.00
1.03
1.02
1.01
3.00
2.05
1.00
2.00
6.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



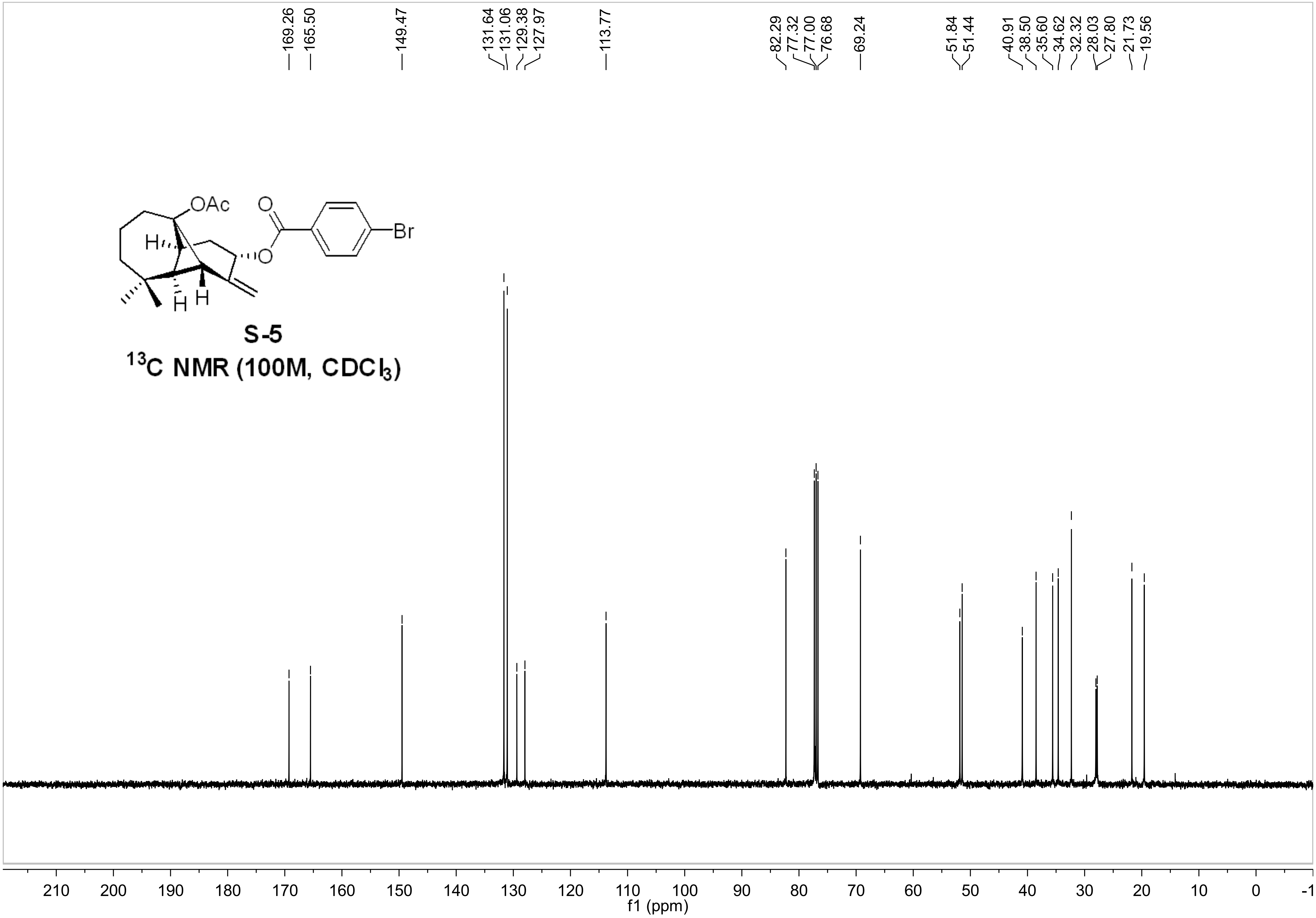
28

^{13}C NMR (100M, CDCl$_3$)



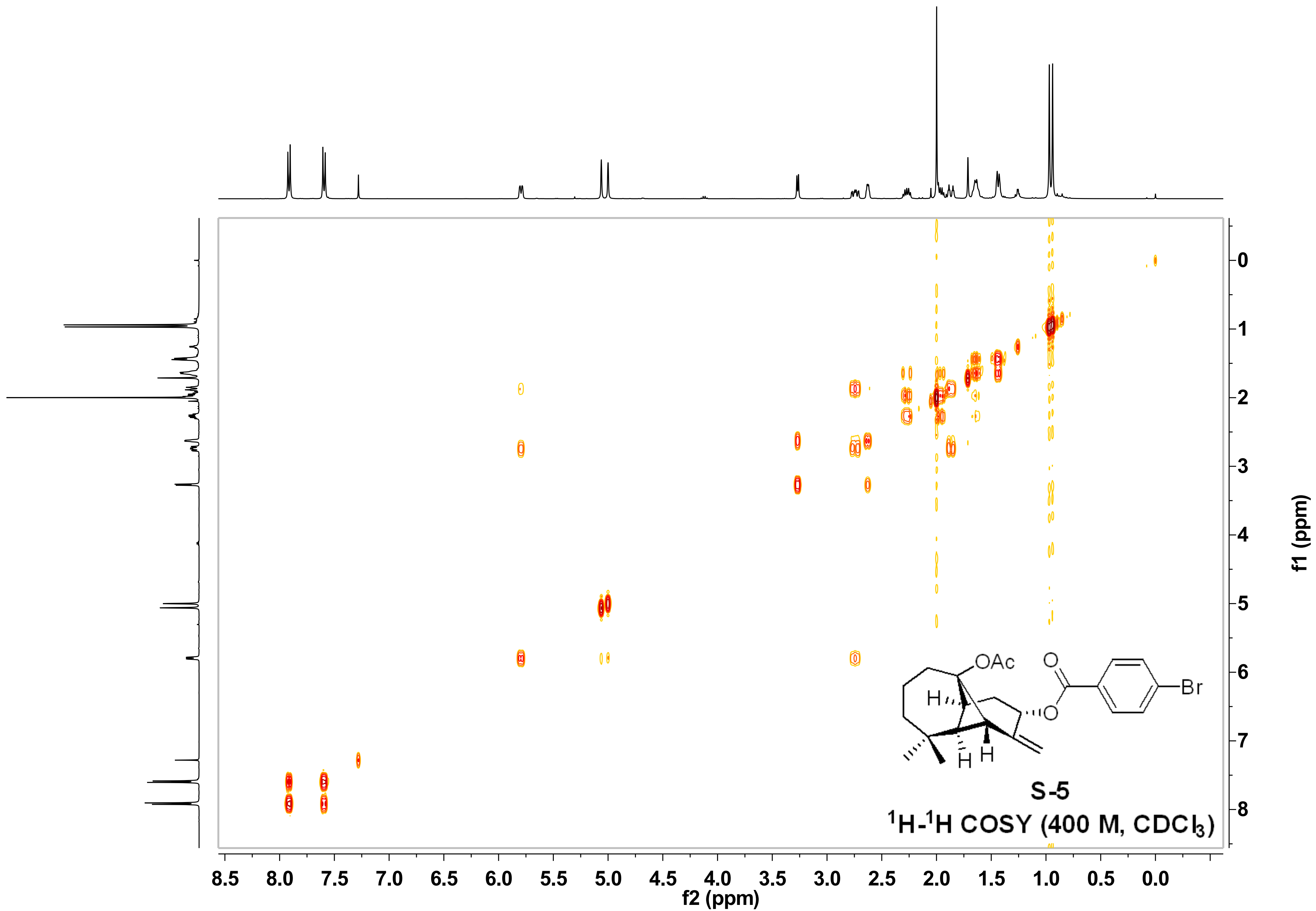
S-5

^{1}H NMR (400 M, CDCl$_3$)



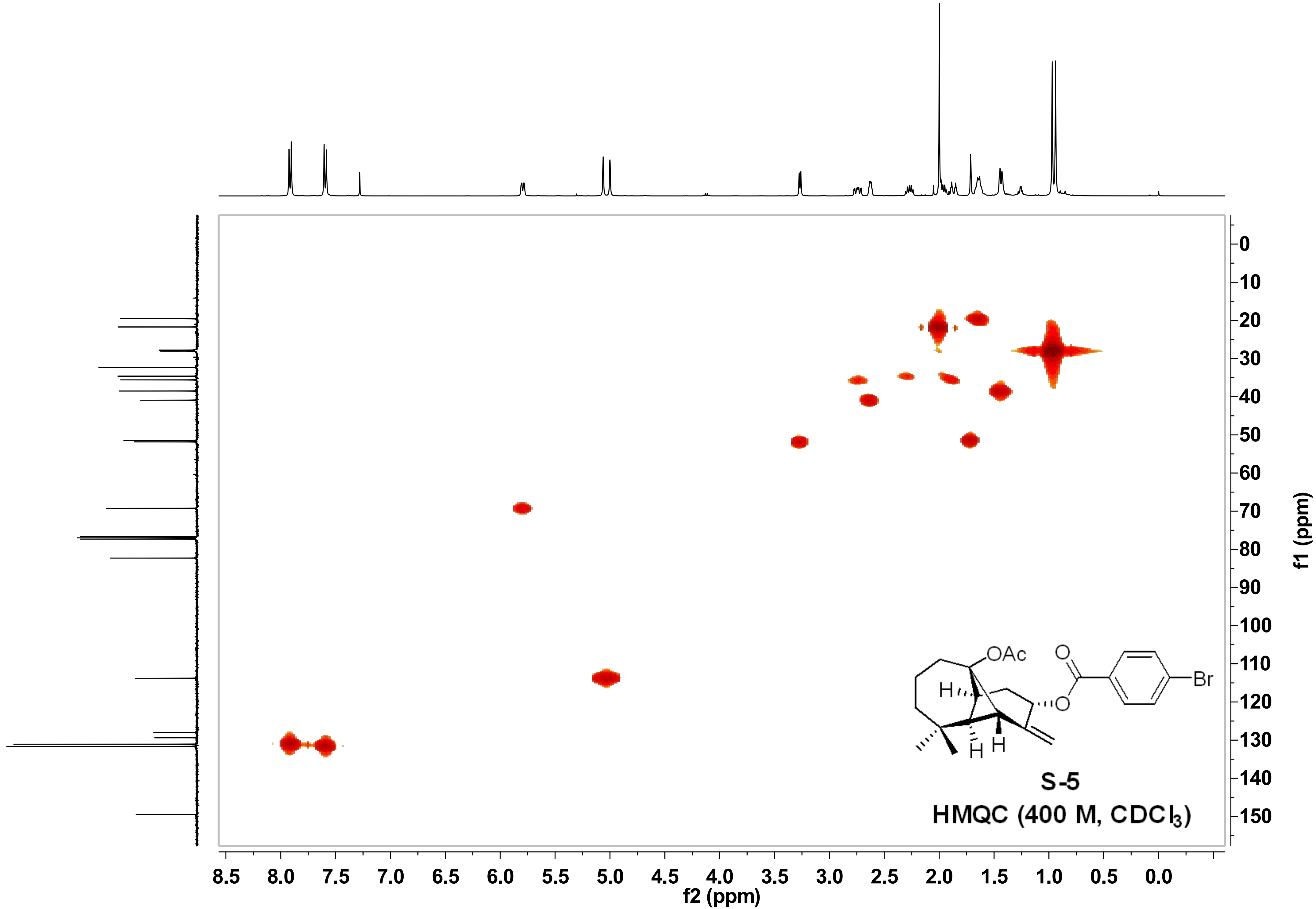
S-5

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



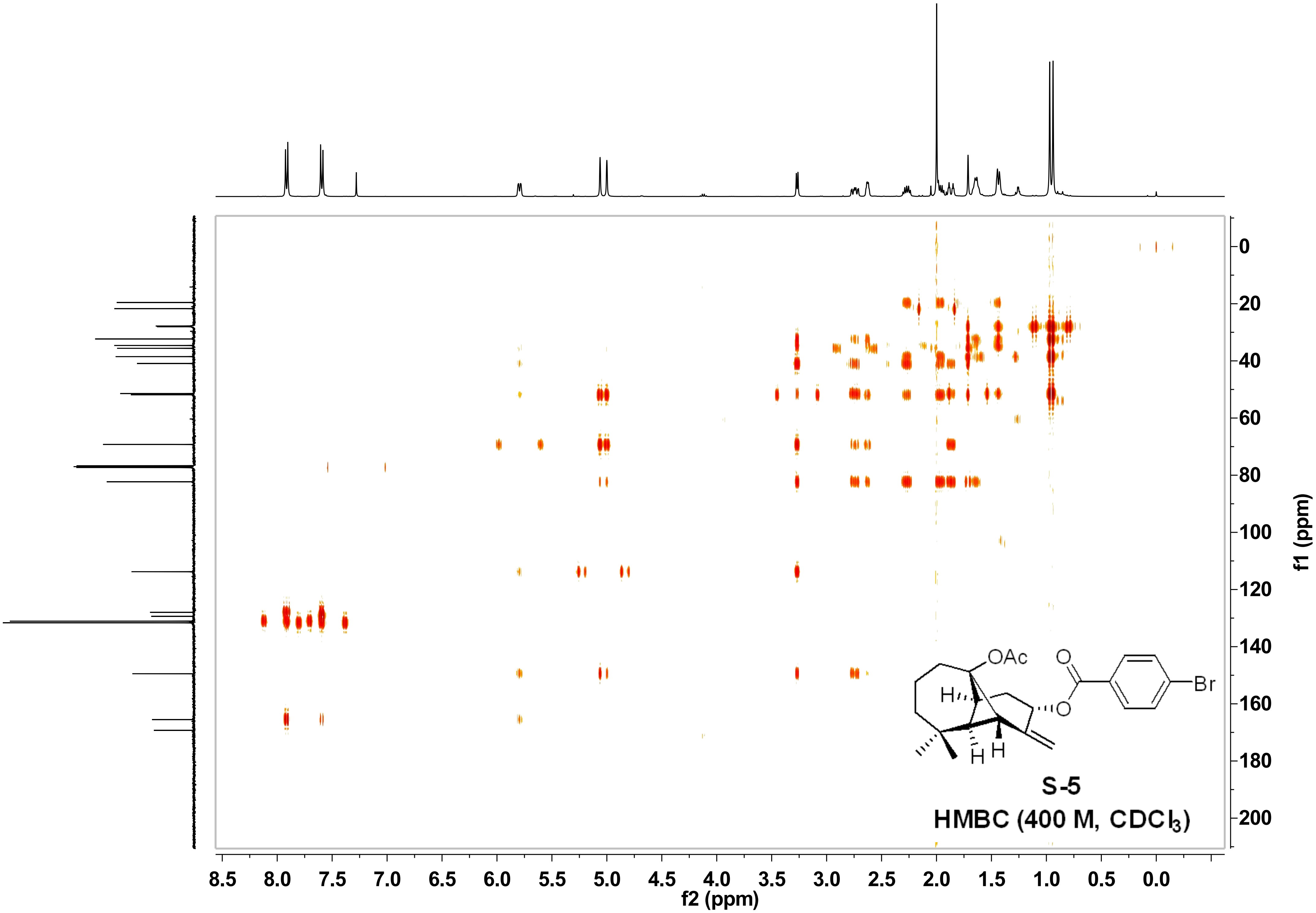
S-5

^{1}H-^{1}H COSY (400 M, CDCl$_3$)

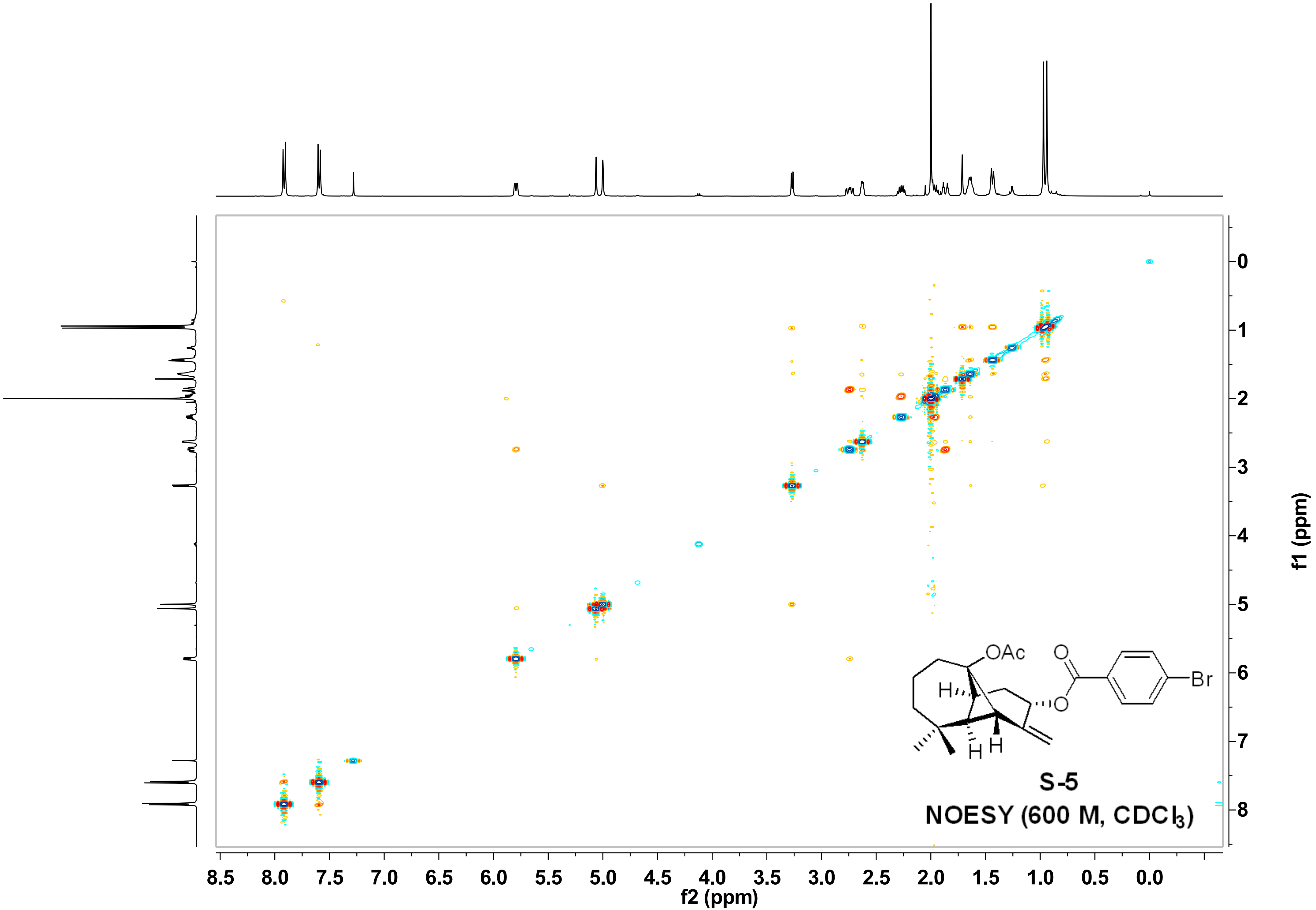


S-5

HMQC (400 M, $CDCl_3$)



OAc
O
O
Br
H
H
H
S-5
HMBC (400 M, CDCl$_3$)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)



S-5

NOESY (600 M, CDCl$_3$)