Supporting Information

Direct Alkylation of Heteroaryls using Potassium Alkyl- and Alkoxymethyltrifluoroborates

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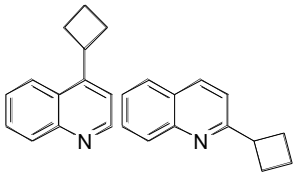
Contents

General Considerations: Acetic acid, trifluoroacetic acid and manganese(III) acetate were used as received. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.39, 125.75, and 470.55 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to external BF_3•OEt_2 (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *m* = multiplet, *br* = broad), coupling constant *J* (Hz) and integration. Analytical thin layer chromatography (TLC) was performed on silica gel (60F-254) plates (0.25 mm) precoated with a fluorescent indicator, and preparative plate purifications were performed on silica gel plates (500 μm) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 40-63 μm silica gel. Visualization was effected with ultraviolet light or iodine on silica. High-resolution mass spectra were measured under electrospray ionization (ESI).

General procedure for preparing compounds:

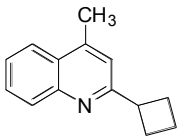
The potassium organotrifluoroborate (1 mmol, 1 equiv) and the heteroaryl (1 mmol, 1 equiv) were dissolved in a 1 : 1 mixture of acetic acid : water (13 mL), and trifluoroacetic acid (1 mmol, 1 equiv) was added. The resulting mixture was stirred at room temperature until complete dissolution then manganese(III) acetate (2.5 mmol, 2.5 equiv) was added in one portion. The mixture was stirred at 50 °C for 18 h. After cooling to room temperature, the mixture was slowly added to a saturated aq solution of Na_2CO_3 (50 mL). The aqueous layer then was extracted with EtOAc (3x20mL). The organic layers were washed with water (2x20 mL) then dried ($MgSO_4$), filtered, and evaporated under vacuum. The residue was purified by flash or preparative plate chromatography.



The alkylation of quinoline was performed according to the standard procedure, starting from cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), quinoline (129.1 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid :

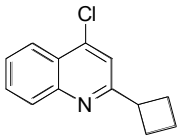
water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 96/4), both regioisomers **2aa** and **2ab** were isolated as a yellow oil (ratio 7/3, 80.8 mg, 44%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (m, 2H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.74 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.68–7.62 (m, 3H), 7.47-7.43 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 0.9 Hz, 1H), 4.14–4.07 (m, 1H), 3.87 (m, 1H), 2.56–2.42 (m, 6H), 2.35-2.27 (m, 2H), 2.22-2.08 (m, 2H), 2.00-1.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 164.8, 151.1, 147.9, 147.8, 136.2, 129.7, 129.3, 129.1, 128.8, 127.5, 126.8, 127.5, 126.8, 125.7, 125.6, 125.2, 123.9, 119.6, 116.0, 43.0, 42.8, 37.4, 28.8, 28.,3, 18.7, 18.4; IR (neat) ν = 2976, 1599, 1503, 828, 760 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}N^+$ [(MH^+)] 183.1126; found: 183.1128.



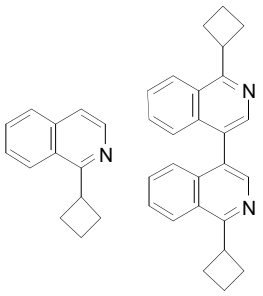
The synthesis of 2-cyclobutyl-4-methylquinoline[1] **2b** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 89/11), 2-cyclobutyl-4-methylquinoline **2b** was isolated as a yellow oil (129.2 g, 65%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.91 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.66 (m, 1H), 7.48 (m, 1H), 3.83 (m, 1H), 3.86 (s, 3H), 3.46–2.42 (m, 4H), 2.17–2.07 (m, 2H), 1.99–1.92 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7, 147.7, 144.1, 129.6, 129.0, 126.9, 125.4, 123.6, 123.6, 120.3, 42.7, 28.3 (2C), 18.8, 18.4; IR (neat) ν = 2971, 1603, 1176, 862, 756 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}N^+$ [(MH^+)] 198.1283; found: 198.1281.



The synthesis of 4-chloro-2-cyclobutylquinoline **2c** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-chloroquinoline (165.3 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 89/11), 4-chloro-2-cyclobutylquinoline **2c** was isolated as a colorless oil (121.7 mg, 56%).

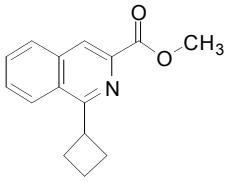
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.71 (m, 1H), 7.55 (m, 1H), 3.82 (m, 1H), 2.47–2.42 (m, 4H), 2.16–2.07 (m, 1H), 1.99–1.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 148.7, 142.6, 130.3, 129.7, 126.7, 125.0, 124.0, 119.8, 42.6, 28.3, 18.3; IR (neat) ν = 2976, 1588, 1493, 838, 757 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}NCl^+$ [(MH^+)] 218.0737; found: 218.0730.



The alkylation of isoquinoline was performed according to the standard procedure, starting from cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), isoquinoline (129.2 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water(13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 15/1), **2da** was isolated as a yellow oil (98.9 mg, 54%) and **2db** as a pale yellow solid (61.9 mg, 17%).

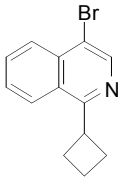
2da: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.7 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 5.7 Hz, 1H), 4.39–4.29 (m, 1H), 2.69–2.57 (m, 2H), 2.48 (q, *J* = 8.7 Hz, 2H), 2.17 (m, 1H), 1.96 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 142.1, 136.4, 129.9, 127.6, 127.04, 126.6, 125.5, 119.3, 39.6, 28.0, 18.9; IR (neat) ν = 2937, 1561, 1300, 821, 746 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}N^+$ [(MH^+)] 184.1126; found: 184.1124.

2db: mp 154–156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.40 –4.35 (m, 2H), 2.69–2.55 (m, 4H), 2.49–2.42 (m, 4H), 2.14 (m, 2H), 1.90 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 143.3, 136.4, 130.4, 127.4, 127.3, 126.3, 126.3, 125.9, 40.0, 28.3, 28.1, 19.0; IR (neat) ν = 2936, 1257, 1027, 797, 763 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}N_2^+$ [(MH^+)] 365.2018; found: 365.2016



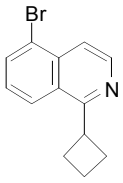
The synthesis of methyl-1-cyclobutylisoquinoline-3-carboxylate[2] **2e** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), methyl-isoquinoline-3-carboxylate (187.2 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 70/30), methyl-1-cyclobutylisoquinoline-3-carboxylate **2e** was isolated as a white solid (142.3 mg, 59%).

mp 81–83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.71–7.63 (m, 2H), 4.40–4.31 (m, 1H), 4.02 (s, 3H), 2.70 (m, 2H), 2.51 (q, *J* = 8.8 Hz, 2H), 2.17 (m, 1H), 1.94 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 164.2, 140.6, 136.0, 130.6, 129.3, 129.1, 128.0, 125.6, 122.9, 52.9, 39.7, 27.6, 18.6; IR (neat) ν = 2952, 1712, 1313, 1240, 1208, 755 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}NO_2^+$ [(MH^+)] 242.1181; found: 242.1180.



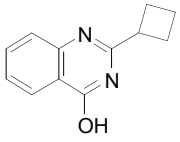
The synthesis of 4-bromo-1-cyclobutylisoquinoline **2f** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-bromo-isoquinoline (208.05 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 10/1), 4-bromo-1-cyclobutylisoquinoline **2f** was isolated as a pale yellow solid (159.9 mg, 61%).

mp 52–54 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 4.22–4.14 (m, 1H), 2.52–2.43 (m, 2H), 2.40–2.32 (m, 2H), 2.06 (m, 1H), 1.86 (t, *J* = 9.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 143.7, 134.9, 131.1, 127.9, 127.8, 126.9, 125.7, 117.9, 39.4, 27.9, 18.8; ; IR (neat) ν = 2967, 1554, 1253, 985, 763 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}BrN^+$ [(MH^+)] = 262.0231; found: 262.0236.



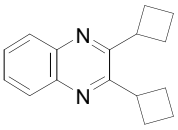
The synthesis of 5-bromo-1-cyclobutylisoquinoline **2g** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 5-bromo-isoquinoline (208.05 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 10/1), 5-bromo-1-cyclobutylisoquinoline **2g** was isolated as a pale yellow solid (167.7 mg, 64%).

mp 41–43 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 6.0 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 4.39–4.25 (m, 1H), 2.65–2.56 (m, 2H), 2.51–2.44 (m, 2H), 2.16 (m, 1H), 1.94 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 143.4, 135.5, 133.7, 127.7, 127.3, 125.1, 122.6, 118.1, 39.7, 28.0, 18.8; IR (neat) ν = 2982, 1485, 1288, 815, 752 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{13}BrN^{+}$ [(MH^{+})] = 262.0231; found: 262.0233.



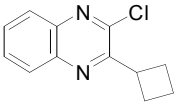
The synthesis of 4-hydroxy-3-cyclobutylquinazoline[3] **2h** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-hydroxy-quinazoline (146.15 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 80/20), 4-hydroxy-3-cyclobutylquinazoline **2h** was isolated as an off white solid (118.1 mg, 59%).

mp 229–231 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.31–8.25 (m, 1H), 7.80–7.70 (m, 2H), 7.50–7.43 (m, 1H), 3.66–3.56 (m, 1H), 2.62–2.49 (m, 2H), 2.49–2.38 (m, 2H), 2.22–2.07 (m, 1H), 2.07–1.95 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 158.8, 149.8, 135.0, 127.7, 126.6, 126.6, 121.0, 39.6, 26.8, 18.5; IR (neat) ν = 2973, 1681, 1610, 1469, 768 cm^{-1}; HRMS (ESI)) calcd for $C_{12}H_{13}N_2O^{+}$ [(MH^{+})] 201.1028; found: 201.1028.



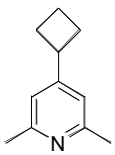
The synthesis of 2,3-dicyclobutylquinoxaline **2i** was performed starting from potassium cyclobutyltrifluoroborate (405.0 mg, 3.5 mmol), quinoxaline (146.2 mg, 1.0 mmol) and manganese(III) acetate (1340.5 mg, 5.0 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 15/1), 2,3-dicyclobutylquinoxaline **2i** was isolated as a pale yellow solid (140.6 mg, 59%).

mp 75–77 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13–7.99 (m, 2H), 7.65 (m, 2H), 3.88 (m, 2H), 2.58 (m, 2H), 2.38 (m, 2H), 2.20–2.08 (m, 2H), 1.96 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 140.8, 128.6, 128.4, 77.3, 77.0, 76.7, 38.8, 26.9, 18.0; IR (neat) ν = 2942, 1483, 1282, 1142, 761 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{19}N_2^+$ [(MH^+)] 239.1548; found: 239.1540.



The synthesis of 3-chloro-1-cyclobutylquinoxaline **2j** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 3-chloroquinoxaline (164.59 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 19.5/0.5), 3-chloro-1-cyclobutylquinoxaline **2j** was isolated as a white solid (133.4 mg, 61%).

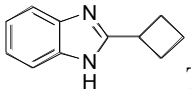
mp 51–53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.08 (m, 1H), 7.98 (m, 1H), 7.78–7.68 (m, 2H), 4.18–4.07 (m, 1H), 2.62–2.44 (m, 4H), 2.16 (m, 1H), 1.96 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 147.8, 141.2, 141.1, 130.2, 130.1, 129.1, 128.4, 39.8, 26.9, 18.2; IR (neat) ν = 2980, 1272, 1060, 993, 764 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{12}ClN_2^+$ [(MH^+)] 219.0689; found: 219.0686.



The synthesis of 4-cyclobutyl-2, 6-dimethylpyridine **2k** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), lutidine (92 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel,

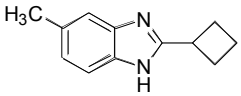
hexanes/EtOAc 99/1), 4-cyclobutyl-2,6-dimethylpyridine **2k** was isolated as a yellow oil (58.8 mg, 34%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, 2H), 3.44 (m, 1H), 2.33–2.30 (m, 2H), 2.49 (s, 2H), 2.13–2.00 (m, 6H), 1.89–1.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6 (2C), 155.6, 118.4 (2C), 39.4, 29.7 (2C), 24.6 (2C), 18.5; IR (neat) ν = 2960, 1781, 1605, 1190, 644 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{16}N^+$ [(MH^+)] 162.1283; found: 163.1278.



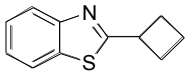
The synthesis of 2-cyclobutyl-1H-benzo[*d*]imidazole **2l** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), benzimidazole (118.1 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 55/45), 2-cyclobutyl-1H-benzo[*d*]imidazole **2l** was isolated as a white solid (104.6 mg, 60%).

mp 204–206 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 2H), 7.21 (dd, *J* = 2.9 Hz, 2H), 3.80 (m, 1H), 2.59–2.49 (m, 2H), 2.46–2.39 (m, 2H), 2.10 (m, 1H), 2.00–1.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1 (2C), 122.3 (4C), 34.3, 28.2 (2C), 18.9; IR (neat) ν = 2980, 1456, 1420, 1274, 748 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}N_2^+$ [(MH^+)] 173.1079; found: 173.1074.

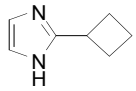


The synthesis of 2-cyclobutyl-5-methyl-1H-benzo[*d*]imidazole **2m** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 5-methylbenzimidazole (134.9 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 65/35), 2-cyclobutyl-5-methyl-1H-benzo[*d*]imidazole **2m** was isolated as a white solid (112.1 mg, 60%).

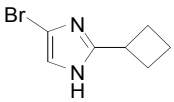
mp 145–147 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.61 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.36 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 3.85 (m, 1H), 3.88–3.81 (m, 2H), 2.61 (s, 3H), 2.59–2.53 (m, 2H), 2.09–2.01 (m, 1H), 1.93–1.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 138.6, 137.2, 131.9, 123.6, 114.7, 114.3, 34.4, 28.3 (2C), 21.7, 18.8; IR (neat) ν = 2977, 1445, 1321, 1277, 802 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{15}N_2^+$ [(MH^+)] 187.1235; found: 187.1240.

 The synthesis of 2-cyclobutylbenzo[*d*]thiazole **2n** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), benzothiazole (135.2 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 98/2), 2-cyclobutylbenzo[*d*]thiazole **2n** was isolated as a yellow oil (101.5 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 4.0 Hz, 1H), 7.42 (t, *J* = 4.0 Hz, 1H), 7.31 (t, *J* = 4.0 Hz, 1H), 3.94 (m, 1H), 2.52–2.45 (m, 4H), (m, 1H), 2.04–1.97 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.0, 153.5, 135.0, 135.9, 134.6, 122.6, 121.6, 39.1, 29.7 (2C), 18.6; IR (neat) ν = 2981, 1517, 1436, 757, 729 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}NS^+$ [(MH^+)] 190.0690; found: 190.0689.

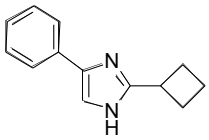
 The synthesis of 2-cyclobutyl-1H-imidazole **2o** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), imidazole (68.08 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, CH_2Cl_2/MeOH 86/14), 2-cyclobutyl-1H-imidazole **2o** was isolated as a white solid (83.9 mg, 31%).

mp 102–104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.25 (s, 1H), 6.98 (s, 2H), 3.74–3.57 (m, 1H), 2.48–2.25 (m, 4H), 1.99 (m, 1H), 1.86 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 121.4, 34.0, 28.2, 18.8; IR (neat) ν = 2979, 1566, 1437, 1095, 757 cm^{-1}; HRMS (ESI) calcd for $C_7H_{10}N_2$ [(M)] 122.0844; found: 122.0836.

 The synthesis of 4-bromo-2-cyclobutyl-1H-imidazole **2p** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-bromoimidazole (169.1 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash

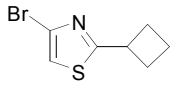
chromatography (silica gel, hexanes/EtOAc 50/50 + 2% Et_3N), 4-bromo-2-cyclobutyl-1H-imidazole **2p** was isolated as a white solid (83.9 mg, 42%).

mp 151–153 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 1H), 3.60 (m, 1H), 2.38–2.26 (m, 4H), 2.03–1.95 (m, 1H), 1.87–1.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 115.3, 113.1, 33.9, 28.5 (2C), 18.5; IR (neat) ν = 2987, 1563, 1410, 1182, 1110, 756.4 cm^{-1}; HRMS (ESI) calcd for $C_7H_{10}BrN_2^+$ [(MH^+)] 201.0027; found: 201.0024.



The synthesis of 2-cyclobutyl-4-phenyl-1H-imidazole **2q** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-phenylimidazole (147.1 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 50/50 + 2% Et_3N), 2-cyclobutyl-4-phenyl-1H-imidazole **2q** was isolated as a white solid (73.8 mg, 34%).

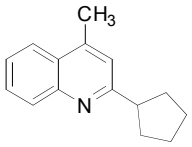
mp >260 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.4 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.21 (m, 2H), 3.62 (m, 1H), 2.40–2.30 (m, 4H), 2.06–1.97 (m, 1H), 1.92–1.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 128.8 (2C), 126.8 (2C), 124.9 (2C), 34.0, 28.5 (2C), 18.6; IR (neat) ν = 2842, 1426, 1385, 1239, 1089, 754, 696 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{15}N_2^+$ [(MH^+)] 199.1235; found: 199.1234.



The synthesis of 4-bromo-2-cyclobutylthiazole **2r** was performed according to the standard procedure, starting from potassium cyclobutyltrifluoroborate (162.0 mg, 1.0 mmol), 4-bromothiazole (92 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 99/1), 4-bromo-2-cyclobutylthiazole **2r** was isolated as a yellow oil (23.4 mg, 11%).

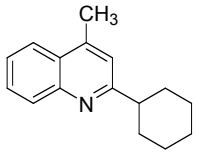
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 3.65–3.54 (m, 1H), 2.40–2.23 (m, 4H), 2.07–1.92 (m, 1H), 1.90–1.79 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 115.5, 34.0, 28.7, 18.7; IR (neat)

ν = 2952, 1603, 1248, 1109, 859, 836, 756 cm^{-1}; HRMS (ESI) calcd for $C_7H_9BrNS^+$ [(MH^+)] 217.9639; found: 217.9646.



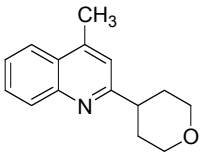
The synthesis of 2-cyclopentyl-4-methylquinoline[4] **3a** was performed according to the standard procedure, starting from potassium cyclopentyltrifluoroborate (176.03 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 95/5), 2-cyclopentyl-4-methylquinoline **3a** was isolated as a slightly yellow oil (158.5 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 3.38 – 3.29 (m, 1H), 2.63 (s, 3H), 2.17 (m 2H), 1.87 (m, 4H), 1.74 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.7, 147.4, 143.9, 129.3, 128.7, 126.8, 125.2, 123.3, 120.5, 48.6, 33.4, 25.9, 18.6; IR (neat) ν = 2950, 1603, 1448, 862, 757 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}N^+$ [(MH^+)] 212.1439; found: 212.1438



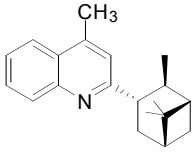
The synthesis of 2-cyclohexyl-4-methylquinoline[5] **3b** was performed according to the standard procedure, starting from potassium cyclohexyltrifluoroborate (171.1 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 97/3), 2-cyclohexyl-4-methylquinoline **3b** was isolated as a colorless oil (168.0 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 3.0 Hz, 1H), 7.90 (d, *J* = 3.1 Hz, 1H), 7.64 (td, *J* = 3.1, 2.8 Hz, 1H), 7.48 (td, *J* = 3.5, 2.7 Hz, 1H), 7.15 (s, 1H), 2.87 (tt, *J* = 12.0, 3.4 Hz, 1H), 2.64 (s, 3H), 2.01 (dd, *J* = 13.6, 1.7 Hz, 2H), 1.88 (dt, *J* = 13.2, 3.2 Hz, 2H), 1.80–1.76 (m, 1H), 1.62 (m, 2H), 1.46 (m, 2H), 1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 147.7, 144.2, 129.5, 128.9, 127.1, 125.4, 123.6, 120.3, 47.6, 32.9 (2C), 26.6 (2C), 26.2, 18.8; IR (neat) ν = 2925, 1604, 1448, 860, 757 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}N^+$ [(MH^+)] 226.1596; found: 226.1594.



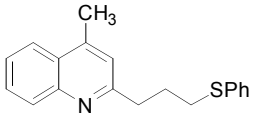
The synthesis of 4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinoline **3c** was performed according to the standard procedure, starting from potassium tetrahydro-2H-pyran-4-yl trifluoroborate (171.1 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 97/3), 4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinoline **3c** was isolated as a white solid (109.8 mg, 48%).

mp 107–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.67 (m, 1H), 7.50 (m, 1H), 7.16 (s, 1H), 4.12 (dd, *J* = 11.4, 3.9 Hz, 2H), 3.59 (m, 2H), 3.11 (m 1H), 2.68 (s, 1H), 2.01 (m 3H), 1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 147.8, 144.7, 129.7, 129.2, 127.2, 125.8, 123.7, 120.0, 68.3, 44.5, 32.4, 19.0; IR (neat) ν = 2946, 2837, 2360, 1602, 1126, 776 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}NO^{+}$ [(MH^{+})] 228.1388; found: 228.1386.



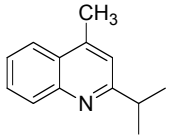
The synthesis of 4-methyl-2-((1*S*,2*S*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)quinoline **3d** was performed according to the standard procedure, starting from potassium ((1*S*,2*R*,3*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)trifluoroborate (171.1 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 97/3), 4-methyl-2-((1*S*,2*S*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)quinoline **3d** was isolated as a colorless oil (112.1 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.67 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 1H), 3.41-3.36 (m, 1H), 3.70 (s, 3H), 2.53–2.48 (m, 2H), 2.42–2.38 (m, 1H), 2.10–2.06 (m, 3H), 1.93 (t, *J* = 4.8 Hz, 1H), 1.36 (d, *J* = 9.7 Hz, 1H), 1.30 (s, 3H), 1.21 (s, 3H), 1.08 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 147.5, 144.2, 129.7, 128.9, 126.8, 125.4, 123.6, 121.5, 48.0, 47.2, 43.6, 41.8, 39.3, 35.3, 24.3, 28.5, 23.0, 21.4, 18.9; IR (neat) ν = 2901, 1602, 1450, 966, 756 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{26}N^{+}$ [(MH^{+})] 280.2065; found: 280.2066; $[\alpha]_D$ = +18.10 (c=0.02 in CH_2Cl_2).



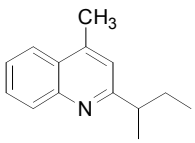
The synthesis of 2-(3-(phenylthio)propyl)-4-methylquinoline **3e** was performed according to the standard procedure, starting from 3-(phenylthio)propyl trifluoroborate (258.15 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 20/1), 2-(3-(phenylthio)propyl)-4-methylquinoline **3e** was isolated as a slightly yellowish oil (73.4 mg, 25%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.1 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.18–7.13 (m, 1H), 7.10 (s, 1H), 3.07 (t, *J* = 7.5 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.65 (s, 3H), 2.24–2.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.1, 147. 7, 144.3, 136.5, 129.3, 129.0, 129.0, 128. 8, 126.8, 125.7, 125.5, 123.5, 122.0, 37.7, 33.0, 29.0, 18.6; IR (neat) ν = 2918, 1602, 758, 739, 691 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NS^+$ [(MH^+)] 294.1316; found: 294.1307.



The synthesis of 2-isopropyl-4-methylquinoline[6] **3f** was performed according to the standard procedure, starting from isopropyltrifluoroborate (150.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 97/3), 2-isopropyl-4-methylquinoline **3f** was isolated as a colorless oil (128.5 mg, 69%).

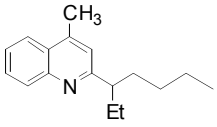
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.92 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.66 (td, *J* = 7.0, 1.5 Hz, 1H), 7.48 (td, *J* = 7.0, 1.5 Hz, 1H), 7.16 (s, 1H), 3.22 (m, 1H), 2.66 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ1 67.4, 147.6, 144.4, 129.6, 129.0, 127.1, 125.4, 123.6, 119.8, 37.3, 22.6 (2C), 18.8; IR (neat) ν = 2962, 1604, 1449, 1089, 757 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{16}N^+$ [(MH^+)] 186.1283; found: 186.1283.



The synthesis of 2-*sec*-butyl-4-methylquinoline[7] **3g** was performed according to the standard procedure, starting from *sec*-butyltrifluoroborate (164.0 mg, 1.0 mmol), lepidine

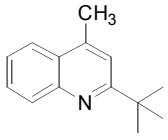
(143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 95/5), 2-*sec*-butyl-4-methylquinoline **3g** was isolated as a slightly yellow oil (128.5 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–8.04 (m, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 2.96 (m, 1H), 2.67 (s, 3H), 1.90–1.80 (m, 1H), 1.71 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.6, 147.6, 144.0, 129.5, 128.8, 126.9, 125.3, 123.5, 120.1, 44.5, 29.9, 20.3, 18.8, 12.2; IR (neat) ν = 2961, 1603, 1449, 874, 757 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{18}N^+$ [(MH^+)] 200.1439; found: 200.1443.



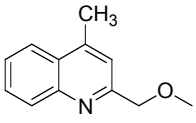
The synthesis of 2-(heptan-3-yl)-4-methylquinoline **3h** was performed according to the standard procedure, starting from potassium heptan-3-yltrifluoroborate (206.1 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 97/3), 2-(heptan-3-yl)-4-methylquinoline **3h** was isolated as a yellow oil (163.1 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.66 (m, 1H), 7.49 (m, 1H), 7.10 (s, 1H), 2.81 (m, 1H), 2.67 (s, 3H), 1.81–1.72 (m, 4H) 1.37–1.27 (m, 3H), 1.41–1.09 (m, 1H), 0.85–0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 147.8, 144.0, 129.7, 128.9, 127.1, 125.4, 123.7, 120.8, 50.7, 35.3, 30.0, 28.7, 23.0, 19.0, 14.1, 12.4; IR (neat) ν = 2957, 2871, 1602, 1448, 755 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}N^+$ [(MH^+)] 242.1909; found: 242.1908.



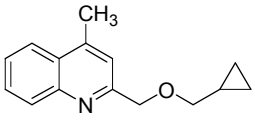
The synthesis of 2-*tert*-butyl-4-methylquinoline[6] **3i** was performed according to the standard procedure, starting from *tert*-butyltrifluoroborate (164.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 95/5), 2-tert-butyl-4-methylquinoline **3i** was isolated as a slightly yellow oil (99.6 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.97–7.93 (m, 1H), 7.67 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.50 (m, 1H), 7.37 (s, 1H), 2.70 (d, *J* = 0.5 Hz, 3H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9, 147.3, 143.5, 129.9, 128.6, 126.5, 125.3, 123.3, 118.8, 37.9, 30.1, 18.9; IR (neat) ν = 2956, 1602, 1448, 862, 757 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{18}N$ [(MH^+)] 200.1439; found: 200.1436.



The synthesis of 2-(methoxymethyl)-4-methylquinoline **4a** was performed according to the standard procedure, starting from potassium (methoxymethyl)trifluoroborate (152 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 30/70), 2-(methoxymethyl)-4-methylquinoline **4a** was isolated as a colorless oil (93.0 mg, 50%).

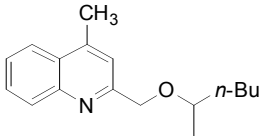
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.66 (td, *J* = 7.8, 1.3 Hz, 1H), 7.50 (td, *J* = 7.6, 1.0 Hz, 1H), 7.39 (s, 1H), 4.70 (s, 2H), 3.48 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 147.4, 145.0, 129.6, 129.3, 125.6, 123.8, 120.0, 76.1, 58.9, 18.8; IR (neat) ν = 2876, 1706, 1216, 1120, 775, 755 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}NO^+$ [(MH^+)] 188.1075; found: 188.1077.



The synthesis of 2-((cyclopropylmethoxy)methyl)-4-methylquinoline **4b** was performed according to the standard procedure, starting from potassium ((cyclopropylmethoxy)methyl)trifluoroborate (192.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 70/30), 2-((cyclopropylmethoxy)methyl)-4-methylquinoline **4b** was isolated as a colorless oil (154.5 mg, 68%).

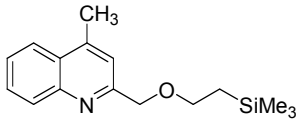
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 (td, *J* = 7.6, 1.1 Hz, 1H), 7.46 (s, 1H), 4.78 (s, 2H), 3.42 (d, *J* = 7.0 Hz, 2H), 2.69 (s, 3H), 1.19–1.11 (m, 1H), 0.57–0.54 (m, 2H), 0.24 (q, *J* = 4.7 Hz, 2H); ^{13}C NMR (125

MHz, $CDCl_3$): δ 159.2, 147.5, 145.0, 129.7, 129.3, 127.6, 126.1, 123.8, 120.2, 75.8, 74.2, 18.9, 10.7, 3.2; IR (neat) ν = 2858, 1603, 1447, 1095, 758 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}NO^+$ [(MH^+)] 228.1388; found: 228.1385.



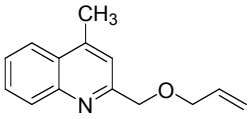
The synthesis of 2-((hexan-2-yloxy)methyl)-4-methylquinoline **4c** was performed according to the standard procedure, starting from potassium ((hexan-2-yloxy)methyl)trifluoroborate (222.1 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 70/30), 2-((hexan-2-yloxy)methyl)-4-methylquinoline **4c** was isolated as a yellowish oil (149.3 mg, 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4, 1H), 7.95–7.90 (m, 1H), 7.68–7.62 (m, 1H), 7.51–7.45 (m, 2H), 4.80 (d, *J* = 13.3 Hz, 1H), 4.71 (d, *J* = 13.3 Hz, 1H), 3.58 (m, 1H), 2.67 (d, *J* = 3.2 Hz, 3H), 1.71–1.62 (m, 1H), 1.51–1.29 (m, 5H), 1.23 (d, *J* = 6.1 Hz, 3H), 0.88 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 147.5, 144.9, 129.7, 129.4, 129.4, 127.8, 126.1, 123.9, 120.4, 76.2, 72.2, 36.6, 28.0, 23.0, 19.9, 19.1, 14.3; IR (neat) ν = 2930, 1603, 1412, 1097, 757 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}NO^+$ [(MH^+)] 258.1847; found: 258.1858.



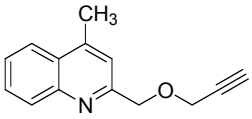
The synthesis of 4-methyl-2-((2-(trimethylsilyl)ethoxy)methyl)quinoline **4d** was performed according to the standard procedure, starting from potassium ((2-(trimethylsilyl)ethoxy)methyl)trifluoroborate (309.5 mg, 1.3 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After flash chromatography (silica gel, hexanes/EtOAc 91/9), 4-methyl-2-((2-(trimethylsilyl)ethoxy)methyl)quinoline **4d** was isolated as a yellow oil (273.5 mg, 89%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 4.14 (s, 2H), 3.51 (t, *J* = 1.1 Hz, 2H), 2.64 (s, 3H), 1.05 (t, *J* = 1.1 Hz, 2H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 147.3, 144.8, 129.5, 129.1, 127.5, 125.9, 123.7, 120.1, 73.4, 68.4, 18.8, 18.3, 1.3 (3C); IR (neat) ν = 2952, 1603, 1248, 1099, 859, 835, 756 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{24}NOSi^+$ [(MH^+)] 274.1627; found: 274.1625.



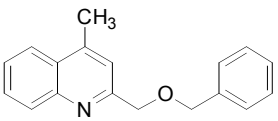
The synthesis of 2-((allyloxy)methyl)-4-methylquinoline **4e** was performed according to the standard procedure, starting from potassium ((allyloxy)methyl)trifluoroborate (178.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 50/50), 2-((allyloxy)methyl)-4-methylquinoline **4e** was isolated as a colorless oil (138.4 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.69 (td, *J* = 7.7, 1.3 Hz, 1H), 7.53 (td, *J* = 7.6, 1.0 Hz, 1H), 7.46 (s, 1H), 6.05–5.97 (m, 1H), 5.36 (dq, *J* = 17.4, 1.6 Hz, 1H), 5.24 (dq, *J* = 11.0, 1.3 Hz, 1H), 4.78 (s, 2H), 4.15 (m, 2H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 147.4, 145.0, 134.5, 129.6, 129.3, 127.6, 126.1, 123.8, 120.1, 117.6, 73.8, 72.0, 18.9; IR (neat) ν = 2847, 1602, 1447, 1094, 925, 757 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}NO^{+}$ [(MH^{+})] 214.1232; found: 214.1229.



The synthesis of 4-methyl-2-((prop-2-yn-1-yloxy)methyl)quinoline **4f** was performed according to the standard procedure, starting from potassium ((prop-2-yn-1-yloxy)methyl)trifluoroborate (176.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 50/50), 4-methyl-2-((prop-2-yn-1-yloxy)methyl)quinoline **4f** was isolated as a yellow oil (137.3 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (s, 1H), 4.84 (s, 2H), 4.31 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.8, 147.4, 145.1, 129.6, 129.3, 127.6, 126.2, 123.7, 120.2, 79.4, 75.1, 73.2, 58.2, 18.8; IR (neat) ν = 3291, 2105, 1602, 1446, 1009, 758, 636 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{14}NO^{+}$ [(MH^{+})] 212.1075; found: 212.1071.

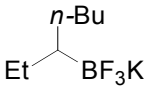


The synthesis of 2-((benzyloxy)methyl)-4-methylquinoline **4g** was performed according to the standard procedure, starting from potassium ((benzyloxy)methyl)trifluoroborate (228.0 mg, 1.0 mmol), lepidine (143 mg, 1.0 mmol) and

manganese(III) acetate (670.3 mg, 2.5 mmol) in a 1 : 1 mixture of acetic acid : water (13 mL) at 50 °C for 18 h. After preparative plate chromatography (silica gel, hexanes/EtOAc 10/1), 2-((benzyloxy)methyl)-4-methylquinoline **4g** was isolated as a colorless oil (181.7 mg, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4, 1H), 7.98 (d, *J* = 8.4, 1H), 7.73–7.68 (m, 1H), 7.54 (m, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.38 (m, 3H), 4.85 (s, 2H), 4.70 (s, 2H), 2.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 147.6, 145.3, 138.2, 130.0, 129.8, 129.5, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 127.1, 126.3, 123.9, 123.8, 120.3, 74.0, 73.2, 19.0; IR (neat) ν = 2854, 1602, 1449, 1097, 756 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO^+$ [(MH^+)] 264.1388; found: 264.1384.

Preparation of Potassium Heptan-3-yltrifluoroborate

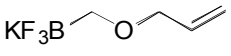


A 50 mL 2-neck flask equipped with a reflux condenser and a rubber septa was charged with Mg (0.814g, 33.5 mmol). The Mg was activated under vacuum at 50 °C for 1 h then under a flow of N_2 Et_2O (9 mL) was added. To the resulting suspension 2-bromoheptane (1.75 mL, 11.2 mmol) was slowly added and the suspension was brought to reflux. Upon completion of addition of the bromide, the resulting mixture was heated at reflux for 3 h. Into a separate flask, purged with N_2, a solution was made of trimethyl borate (1.9 mL, 16.8 mmol) in THF (45 mL) and cooled to -78 °C. To this solution, the 2-heptylmagnesium bromide suspension was added dropwise via a double ended needle. The mixture was allowed to stir for 1 h at -78 °C and then allowed to warm to rt for 1 h. To it was added saturated aqueous KHF_2 (4.5 M, 44.8 mmol) dropwise at 0 °C, and then the reaction mixture was allowed to warm to rt. After 30 min, the solution was concentrated under vacuum. The dried solids were triturated with hot acetone (3 x 50 mL) and filtered to remove inorganic salts. The resulting solution was concentrated until the trifluoroborate was minimally soluble in acetone. Et_2O (~30 mL) was added to precipitate the product. The pure compound was filtered and dried under vacuum and obtained as a white solid (230.7 mg, 10%).

^{1}H NMR (500 MHz, DMSO-*d*^{6}): δ 1.40-1.12 (m, 8H), 0.89–0.83 (m, 6H), 0.11 (*br* s, 1H); ^{13}C NMR (125 MHz, acetone-*d*^{6}): δ 32.5, 31.5, 24.5, 24.4, 14.7, 14.3; ^{11}B (128.38 MHz, DMSO): δ 2.97 (q, *J* = 51.4 Hz); ^{19}F (470.84 MHz, acetone *d*^{6}): δ -143.8; IR (neat) ν = 2925, 1459, 1075, 1043, 907 cm^{-1}; HRMS (ESI) calcd for $C_4H_{16}BOF_3^+$ [(MH^+)] 139.0542; found: 139.0537.

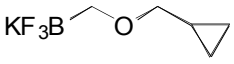
General procedure for the preparation of alkoxymethyltrifluoroborates from chloromethyltrifluoroborate

To KH (360.9 mg, 9 mmol) was added dry THF (15 mL). The alcohol was added dropwise to the suspension via syringe at 0 °C under N_2. The mixture was stirred for 15 min at 0 °C and then allowed to warm to rt for 30 min. Potassium chloromethyltrifluoroborate (469.1 mg, 3 mmol) was added to the mixture in one portion at 0 °C. The reaction mixture was stirred at 50–75 °C until ^{19}F NMR in DMSO-*d*^{6} indicated completion of the reaction after 16 h. The mixture was quenched by adding 4.5 M KHF_2 (1.33 mL, 6 mmol). The mixture was left to stir at rt for 30 min, and then suspension was concentrated and dried overnight under vacuum. The dried solids were triturated with hot acetone (80 mL) and filtered to remove inorganic salts. The resulting solution was concentrated until the trifluoroborate was minimally soluble in acetone or a mixture of acetonitrile/acetone. Et_2O (80 mL) was added to precipitate the product.



The synthesis of potassium ((allyloxy)methyl)trifluoroborate was performed according to the standard procedure, starting from chloromethyltrifluoroborate (469.1 mg, 3 mmol), allylic alcohol (615 mg, 9 mmol) and potassium hydride (360.9 mg, 9 mmol) in THF (15 mL). The desired compound was isolated as a white solid (312.4 mg, 59%).

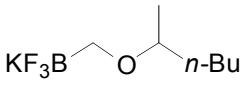
mp 171–173 °C; ^{1}H NMR (500 MHz, DMSO-*d*^{6}): δ 5.86–5.81 (m, 1H), 5.15 (d, *J* = 17.3 Hz, 1H), 5.03 (d, *J* = 9.9 Hz, 1H), 3.73 (s, 2H), 2.50 (s, 2H); ^{13}C NMR (125 MHz, DMSO-*d*^{6}): δ 137.0, 115.0, 74.1; ^{11}B (128.38 MHz, DMSO): δ 2.47 (q, *J* = 54.1 Hz, 1B); ^{19}F (470.84 MHz, DMSO): δ 141.3; IR (neat) ν = 1352, 1015, 996, 803, 734 cm$^{-1;}$ HRMS (ESI) calcd for $C_4H_7BOF_3^+$ [(MH^+)] 139.0542; found: 139.0537.



The synthesis of potassium ((cyclopropylmethoxy)methyl)trifluoroborate was performed according to the standard procedure, starting from chloromethyltrifluoroborate (469.1 mg, 3 mmol), alcohol (237 mg, 9 mmol) potassium hydride (360.9 mg, 9 mmol) in THF (15 mL). The desired compound was isolated as a white solid (441.9 mg, 77%).

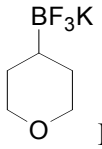
mp 185–187 °C; ^{1}H NMR (500 MHz, DMSO-*d*^{6}): δ 3.00 (d, *J* = 6.7 Hz, 2H), 2.48 (d, *J* = 5.5 Hz, 2H), 0.94–0.90 (m, 1H), 0.38 (q, *J* = 5.9 Hz, 2H), 0.07 (q, *J* = 4.8 Hz, 2H) ; ^{13}C NMR (125 MHz, DMSO *d*^{6}): δ 77.8, 10.9, 2.9 (2C); ^{11}B (128.38 MHz, DMSO): δ 2.51 (q, *J* = 37.0 Hz): ^{19}F (470.84

MHz, DMSO): δ 141.2; IR (neat) ν = 1341, 1037, 1000, 808, 732 cm^{-1}; HRMS (ESI) calcd for $C_5H_{10}BOF_3^+$ [(MH^+)] 153.0699; found: 153.0703.



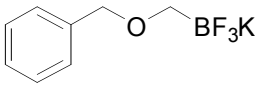
The synthesis of potassium ((hexan-2-yloxy)methyl)trifluoroborate was performed starting from chloromethyltrifluoroborate (625.5 mg, 4 mmol), alcohol (1.51 mg, 12 mmol) potassium hydride (40.1 mg, 12 mmol) in THF (20 mL). The desired compound was isolated as a white solid (665.0 mg, 25%).

mp 113–115 °C; ^{1}H NMR (500 MHz, MeOD) δ 3.28 (dd, *J* = 12.0 Hz, 6.0 Hz, 1H), 2.85 (m, 1H), 2.75 (m, 1H), 1.67 – 1.58 (m, 1H), 1.41 – 1.31 (m, 5H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.95 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, MeOD) δ 79.9, 37.8, 29.9, 24.8, 20.5, 15.3; ^{11}B NMR (128 MHz, MeOD) δ 2.32 (dd, *J* = 104.1 Hz, 51.5 Hz, 1H); ^{19}F NMR (471 MHz, MeOD) δ -141.15; IR (neat) ν = 2932, 2861, 1111, 1005, 800 $cm^{-1;}$ HRMS (ESI) calcd for $C_7H_{16}BF_3O^+$ [(MH^+)] 183.1168; found: 183.1169.



Potassium tetrahydro-2H-pyran-4-trifluoroborate (500.0 mg, 2.36 mmol) was dissolved in methanol (0.67 mL), then a 4.5 M solution of KHF_2 was added (1.57 mL, 7.07 mmol). The resulting mixture was stirred for 1 h then concentrated and dried overnight under vacuum. The dried solids were loaded into a Soxhlet extractor and extracted continuously with HPLC grade acetone (100 mL) overnight. The collected solvent was concentrated *in vacuo*. The crude solid was dissolved in a minimal amount of HPLC grade acetone (20 mL), and Et_2O (100 mL) was added, leading to precipitation of the product. The product was filtered, collected and dried overnight *in vacuo* to afford the desired pure compound as a white solid (293.8 mg, 65%).

mp >260 °C; ^{1}H NMR (400 MHz, DMSO-*d*^{6}): δ 3.74 (d, *J* = 9.8 Hz, 2H), 3.12 (m, 2H), 1.28–1.20 (m, 4H), 0.20 (br s, 1H); ^{13}C NMR (125 MHz, DMSO-*d*^{6}): δ 69.4, 28.9; ^{11}B (128.38 MHz, DMSO): δ 4.35 (q, *J* = 59.0 Hz) ^{19}F (470.84 MHz, DMSO): δ 145.0; IR (neat) ν = 2911, 2835, 1246, 1084, 986, 931 cm^{-1}; HRMS (ESI) calcd for $C_5H_9BOF_3^+$ [(MH^+)] 153.0699; found: 153.0693.



The synthesis of potassium ((benzyloxy)methyl)trifluoroborate[8] was performed starting from chloromethyltrifluoroborate (625.5 mg, 4 mmol), alcohol (1.24 mL, 12 mmol) and potassium hydride (40.1 mg, 12 mmol) in THF (20 mL). The desired compound was isolated as a white solid (822.0 mg, 30%).

mp 203–205 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35 –7.29 (m, 4H), 7.26 (m, 4.32 (s, 2H), 2.61 (d, J = 5.2 Hz, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.3, 127.8, 127.3, 126.6, 74.7; ^{11}B NMR (128 MHz, DMSO δ 3.27; ^{19}F NMR (471 MHz, DMSO) δ -141.01; IR (neat) ν = 2822, 1061, 991, 938, 732 cm^{-1}; HRMS (ESI) calcd for $C_8H_9BOF_3^+$ [(MH^+)] 189.0699; found: 189.0697.

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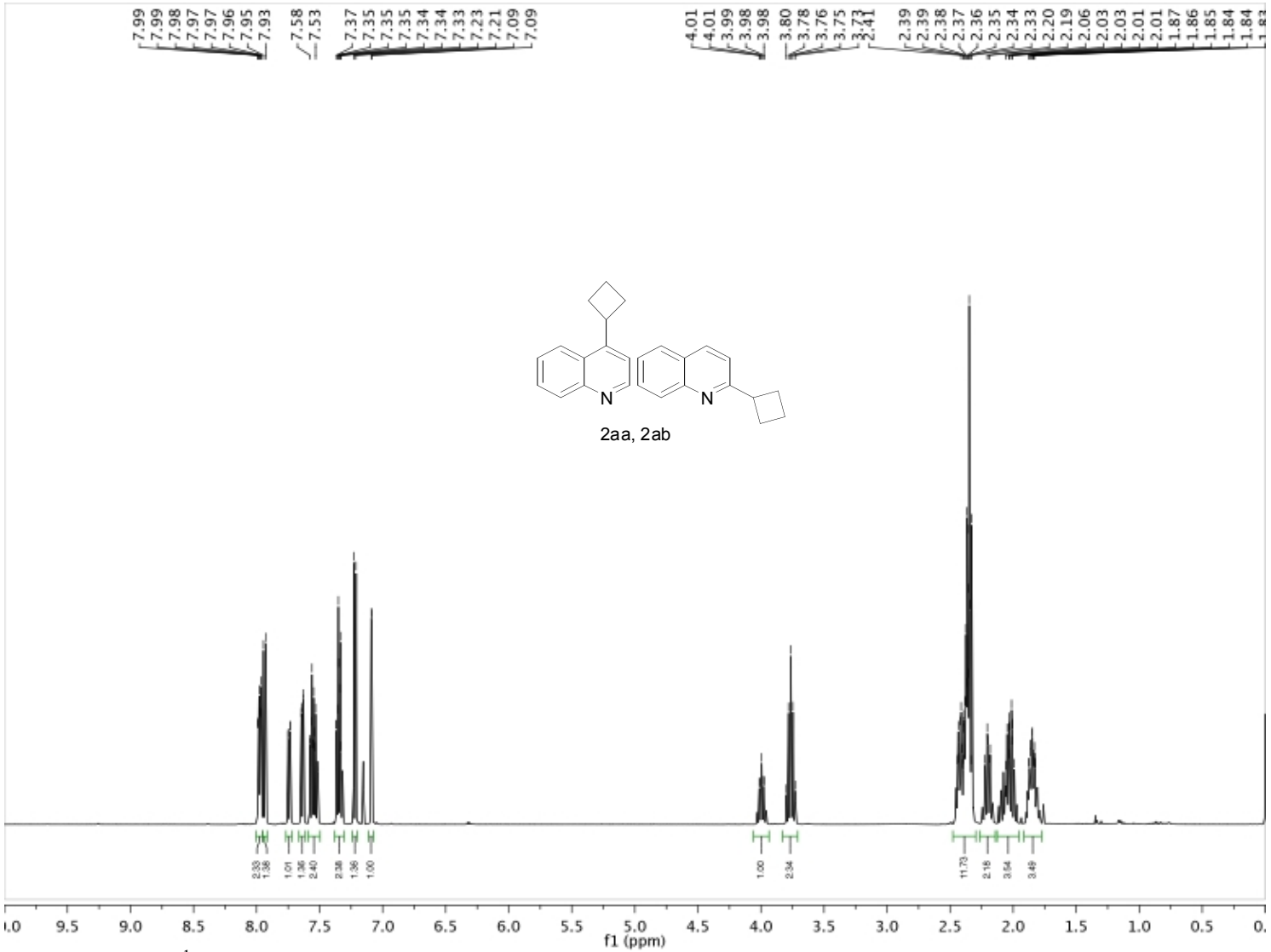
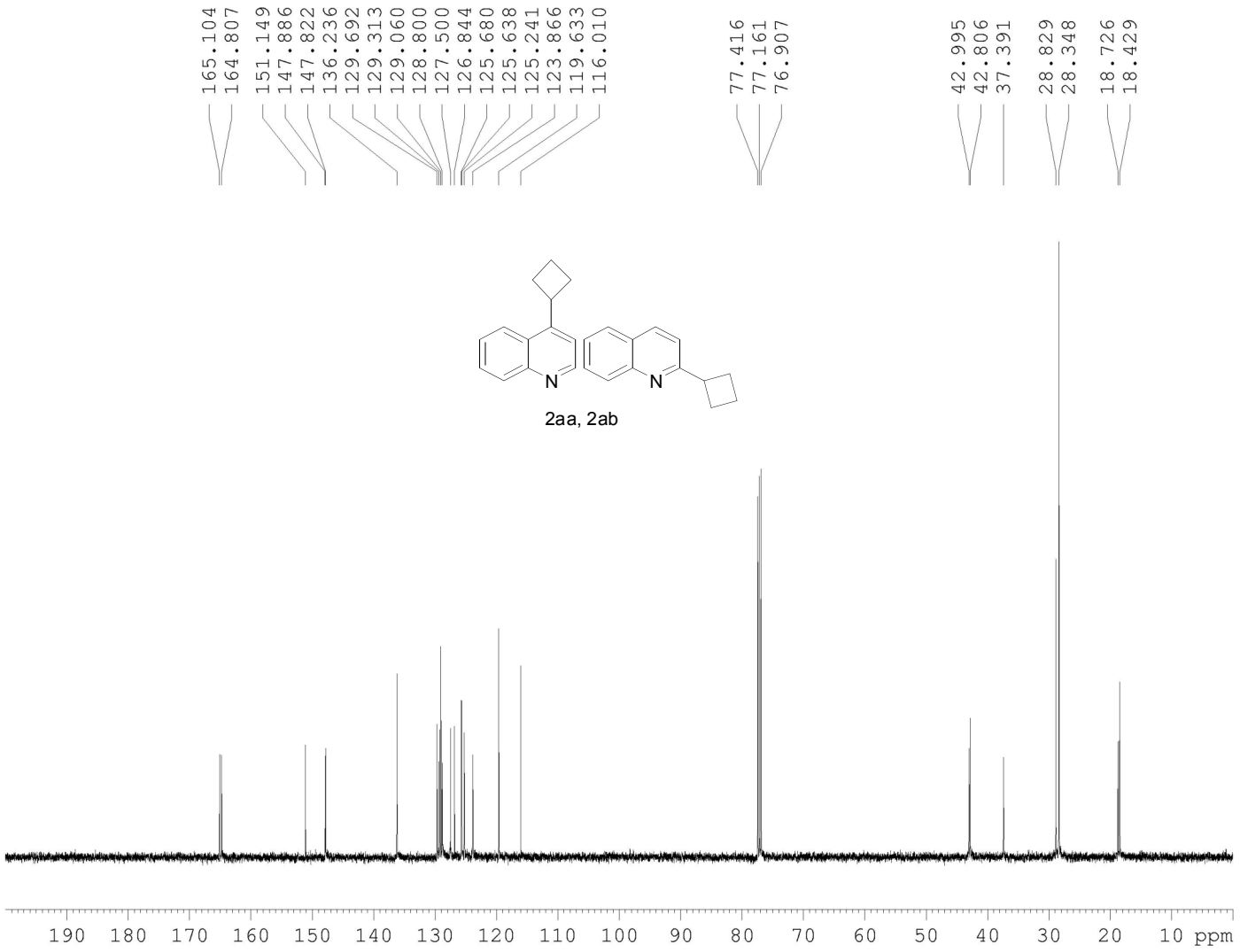
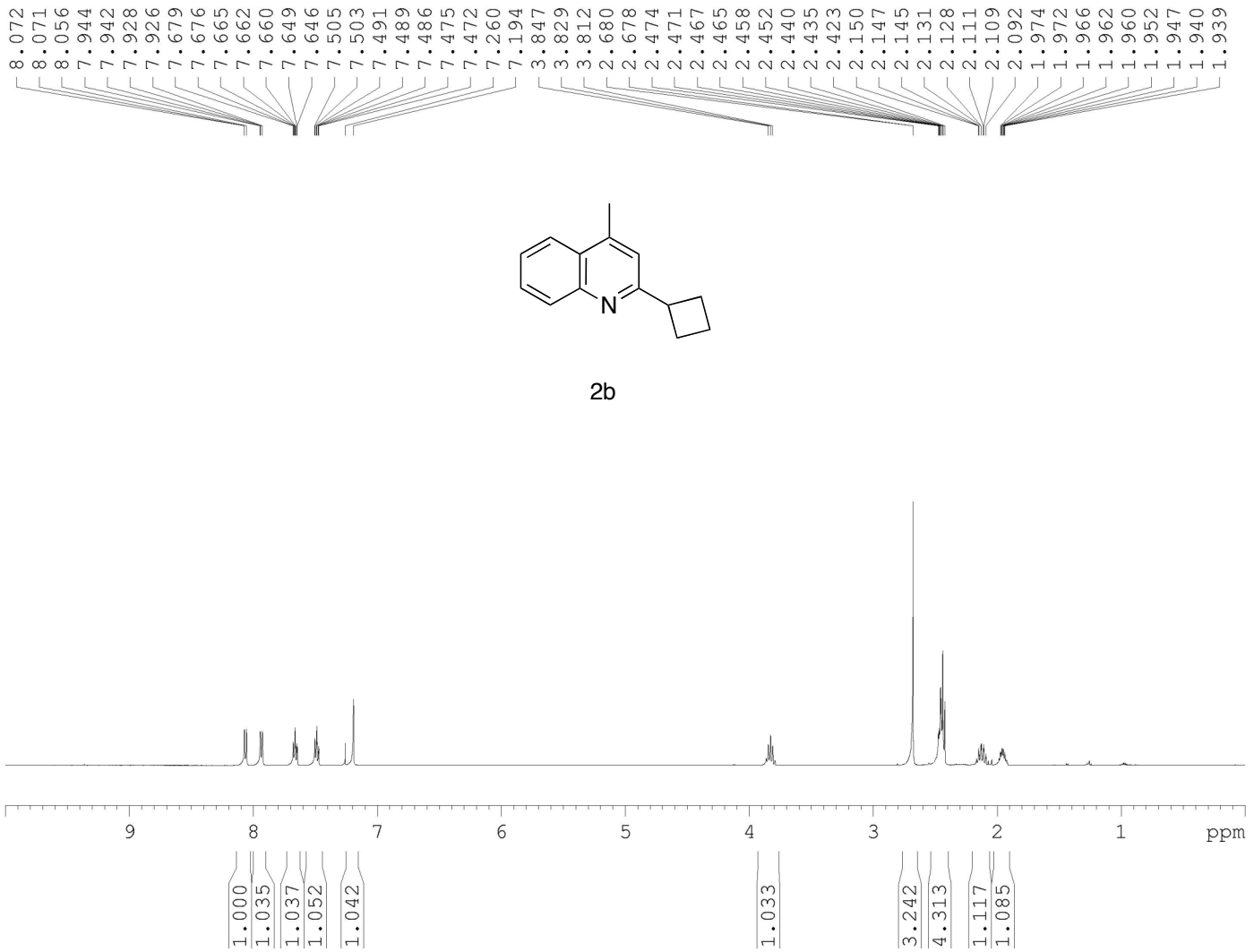


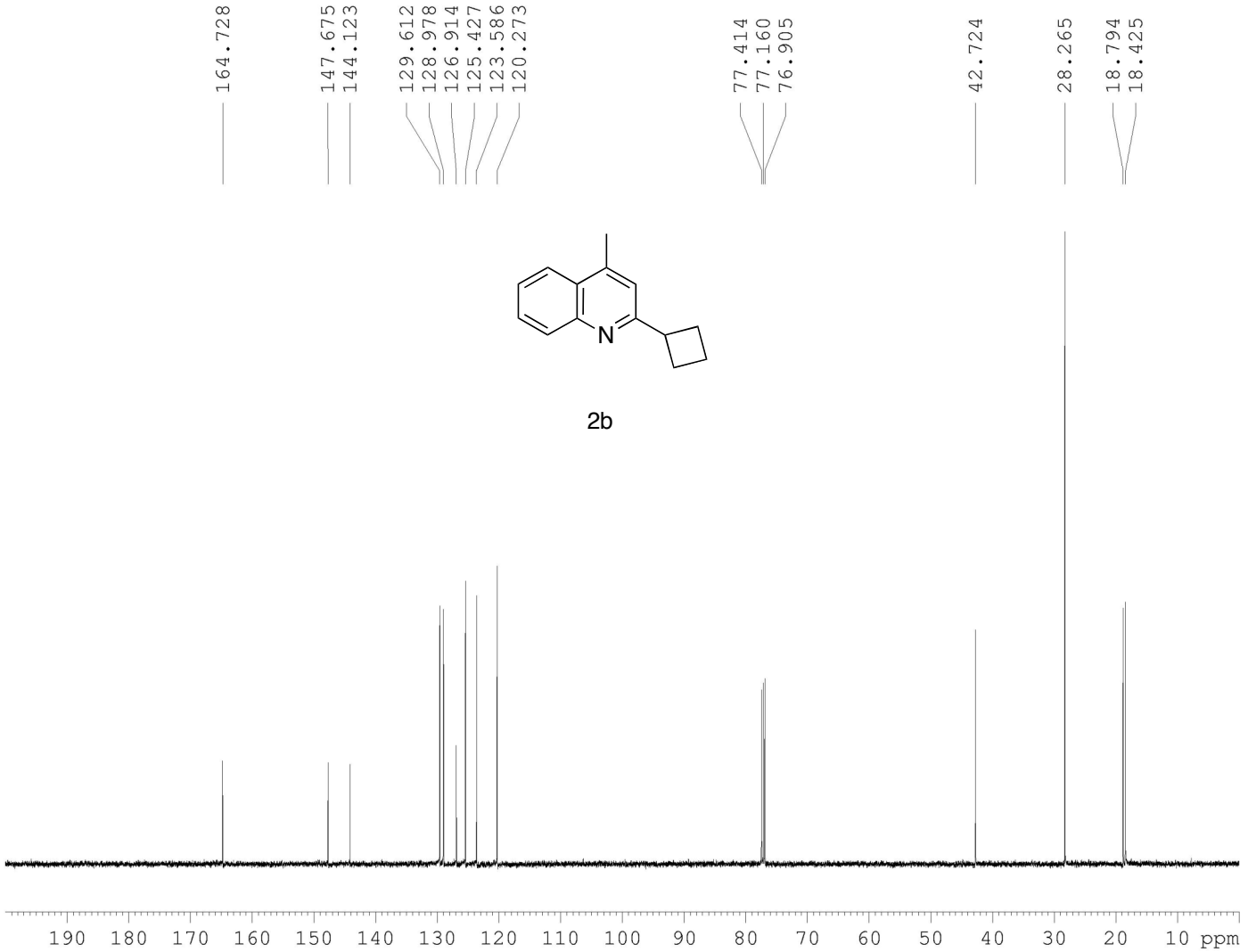
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of -2 and 4-cyclobutylquinoline **2aa** and **2a**
(Table 1, entry 1)



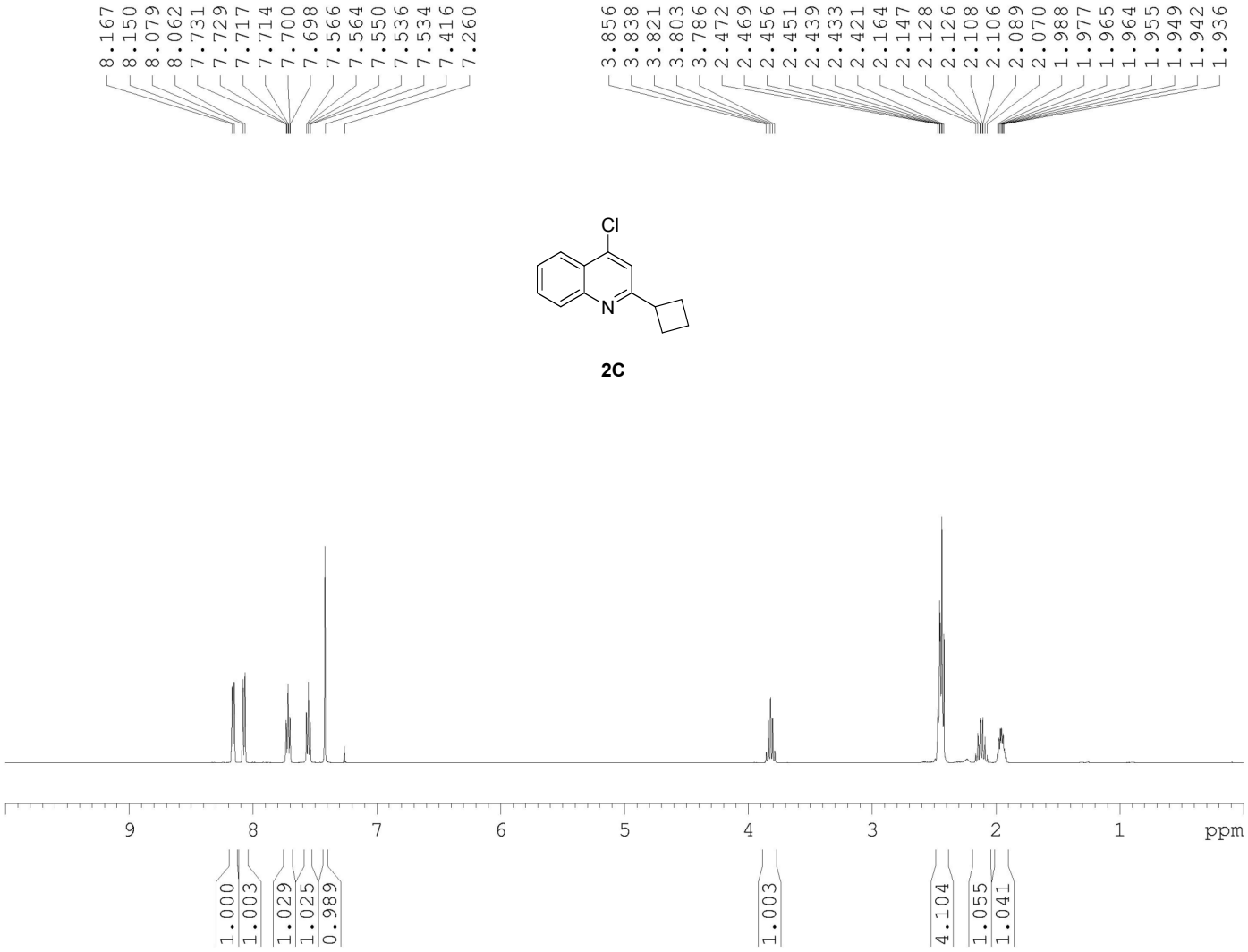
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of -2 and 4-cyclobutylquinoline **2aa** and **2ab**
(Table 1, entry 1)



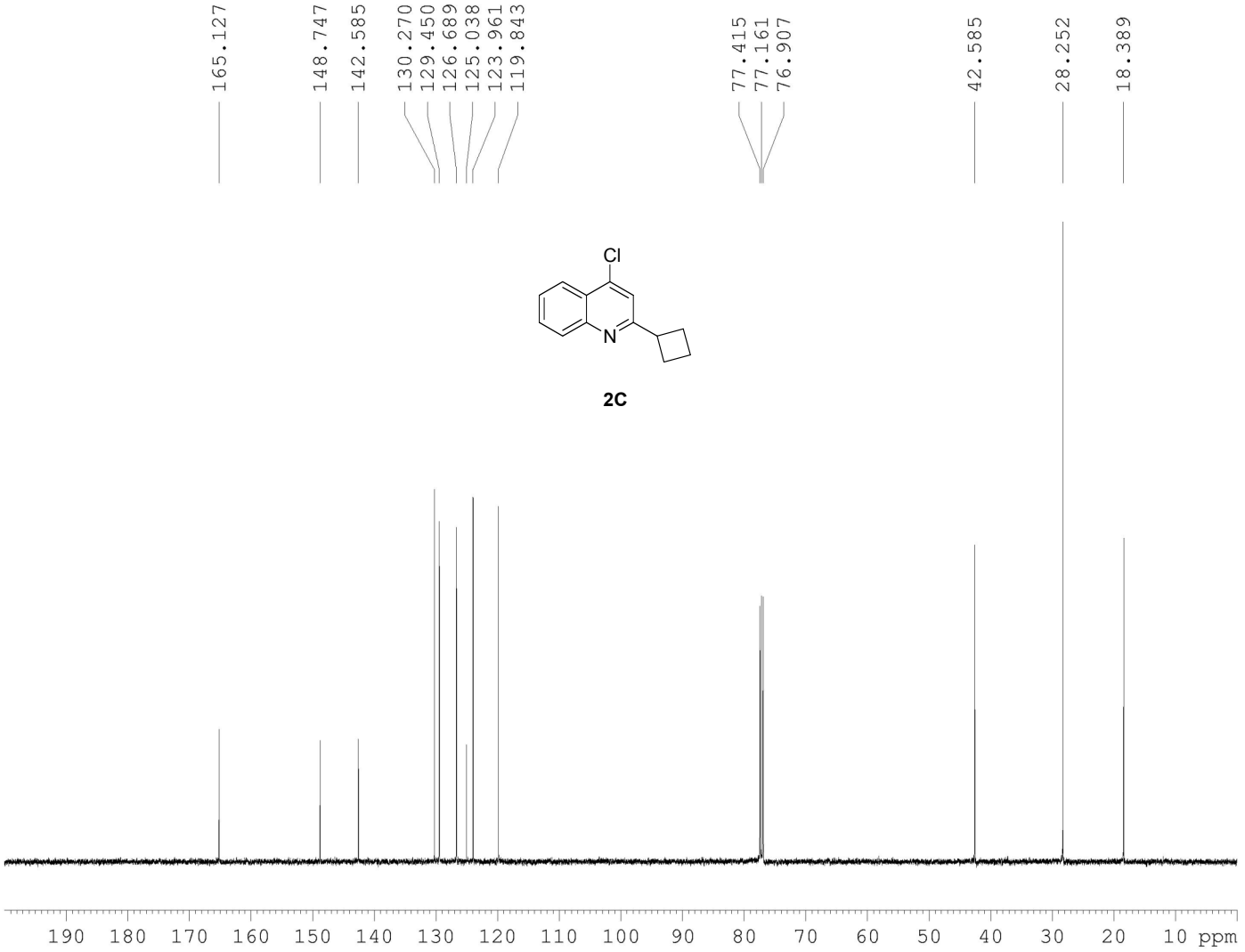
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-4-methylquinoline **2b**
(Table 1, entry 2)



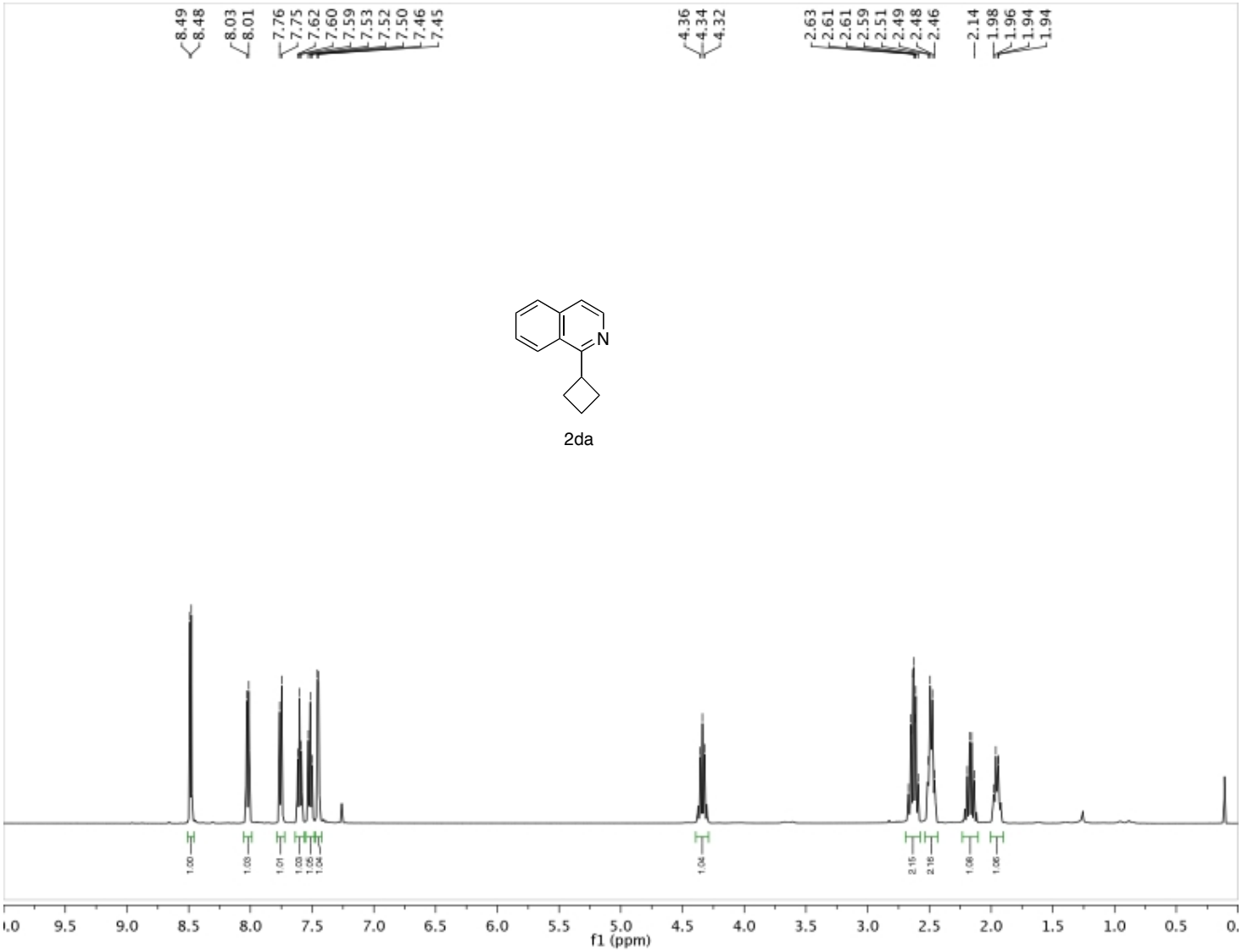
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-4-methylquinoline **2b**
(Table 1, entry 2)



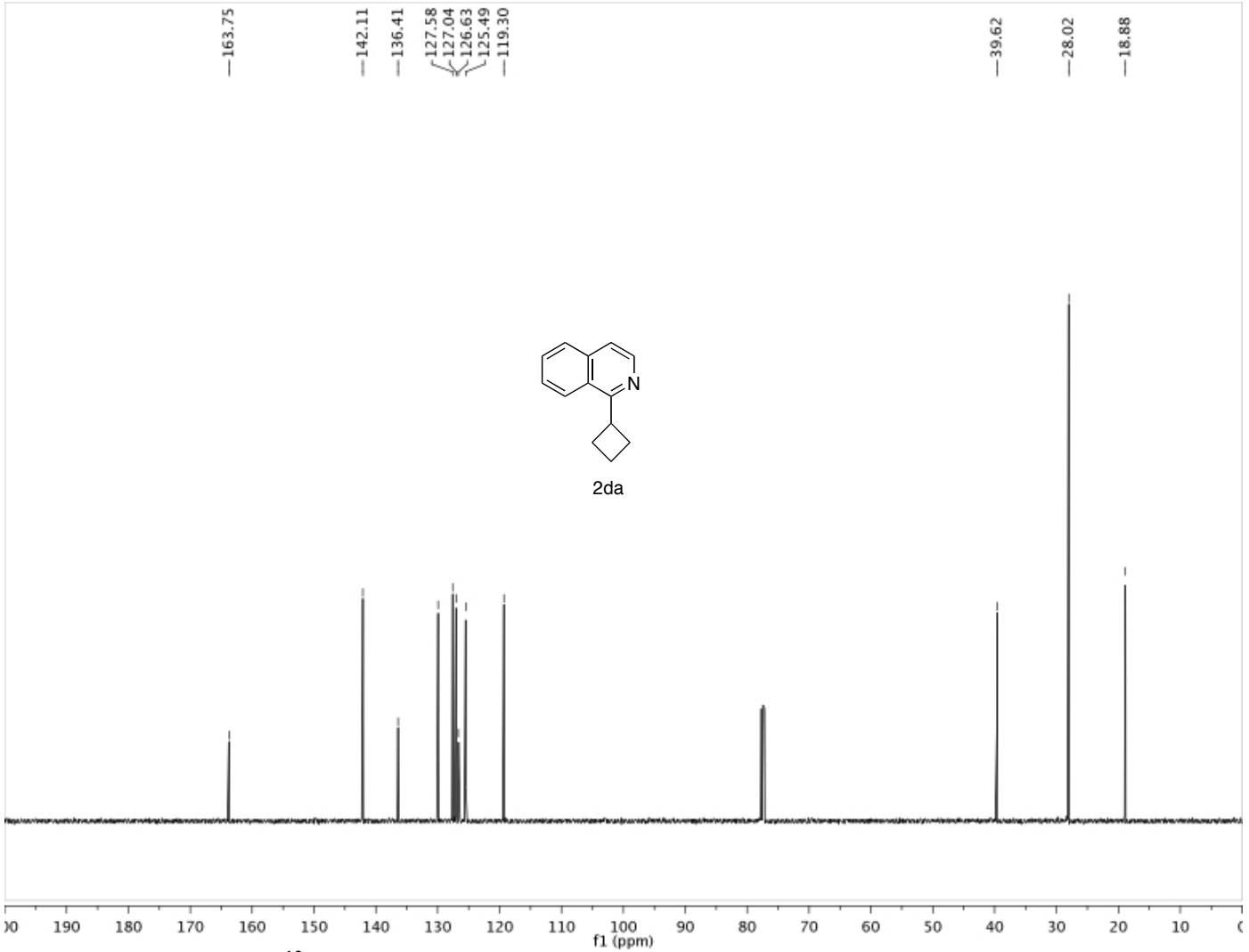
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-chloro-2-cyclobutylquinoline **2c**
(Table 1, entry 2)



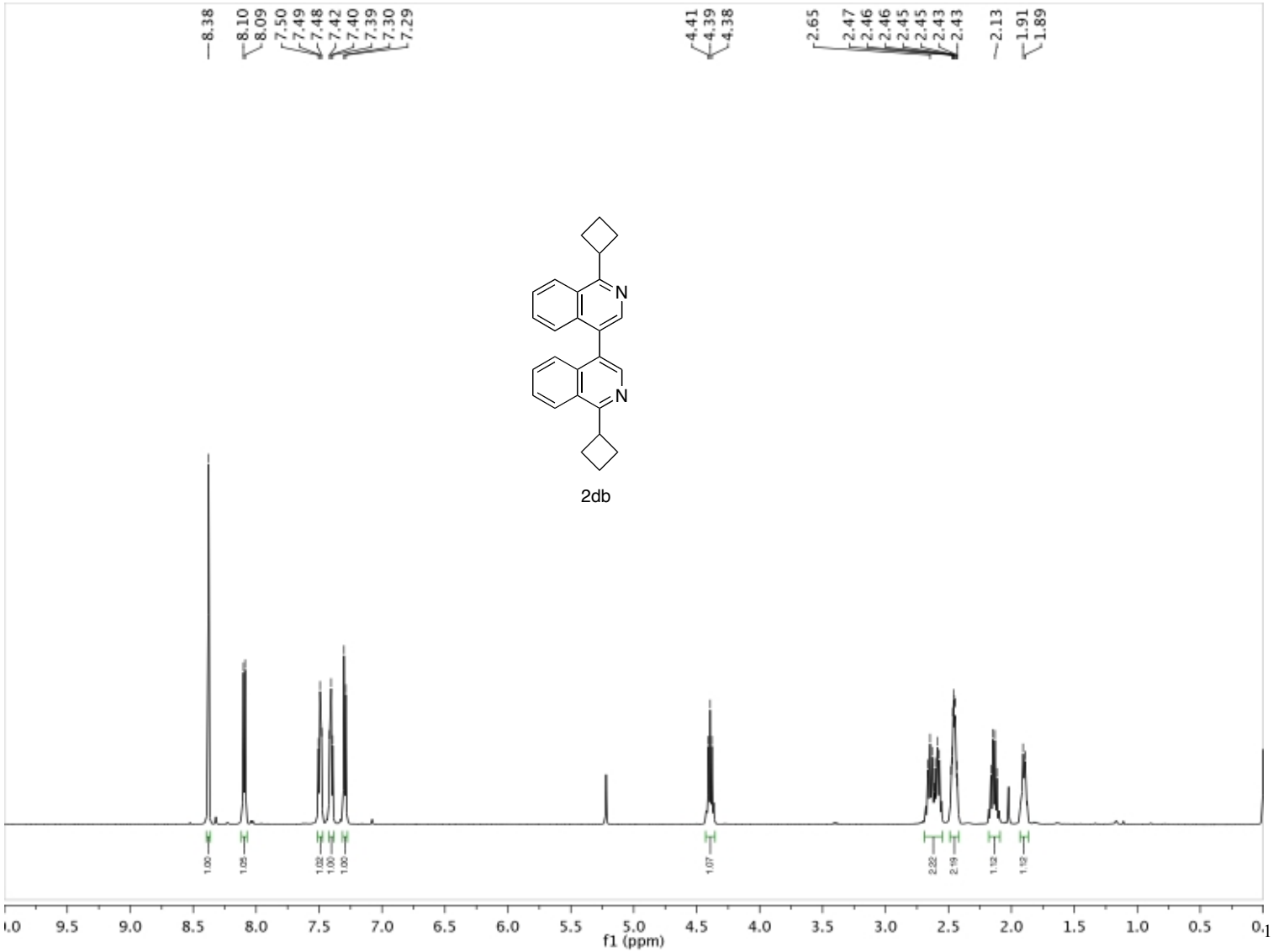
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-chloro-2-cyclobutylquinoline **2c**
(Table 1, entry 2)



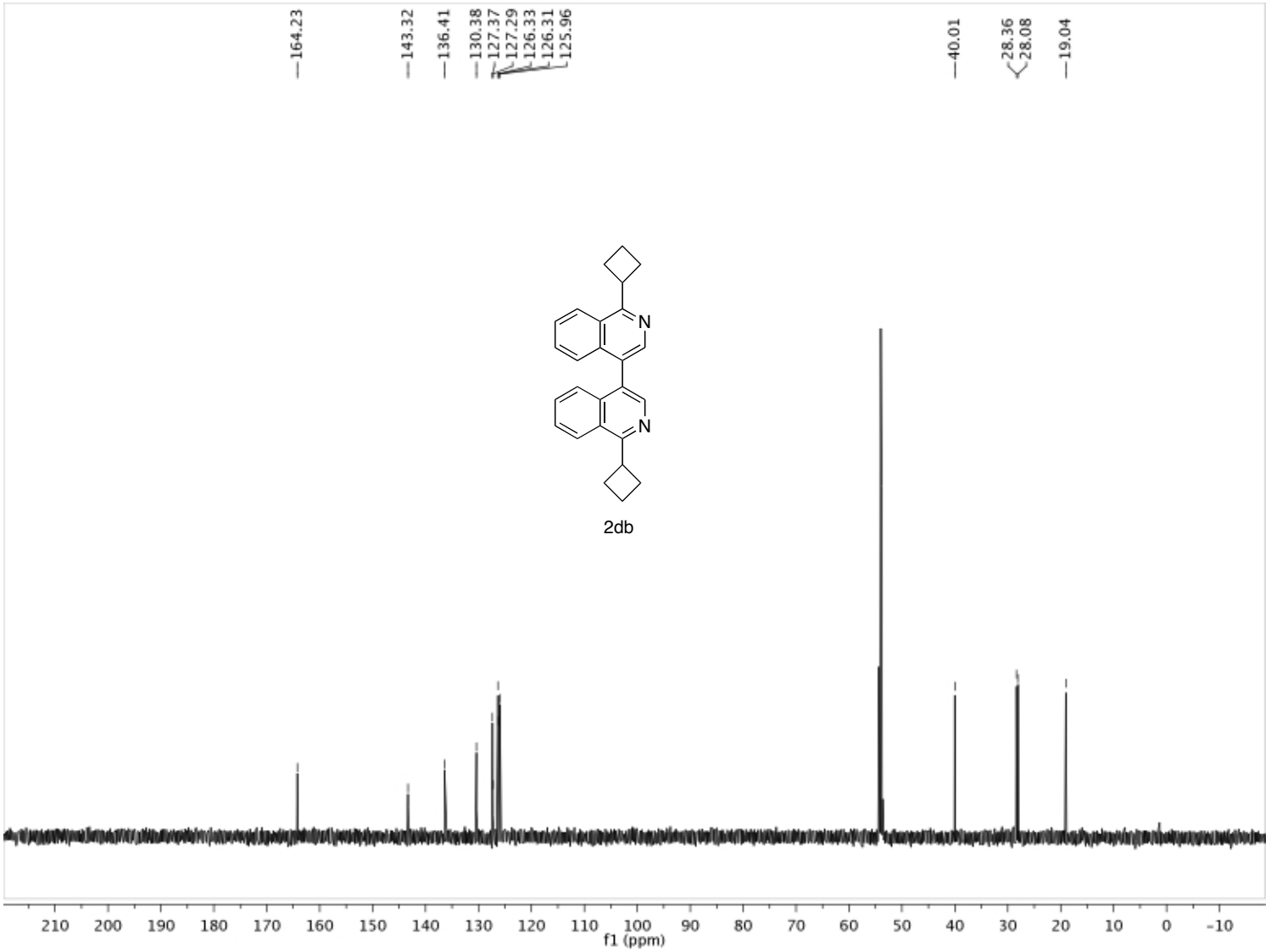
^{1}H NMR (500 MHz, $CDCl_3$) 2-cyclobutylisoquinoline **2da**
(Table 1, entry 4)



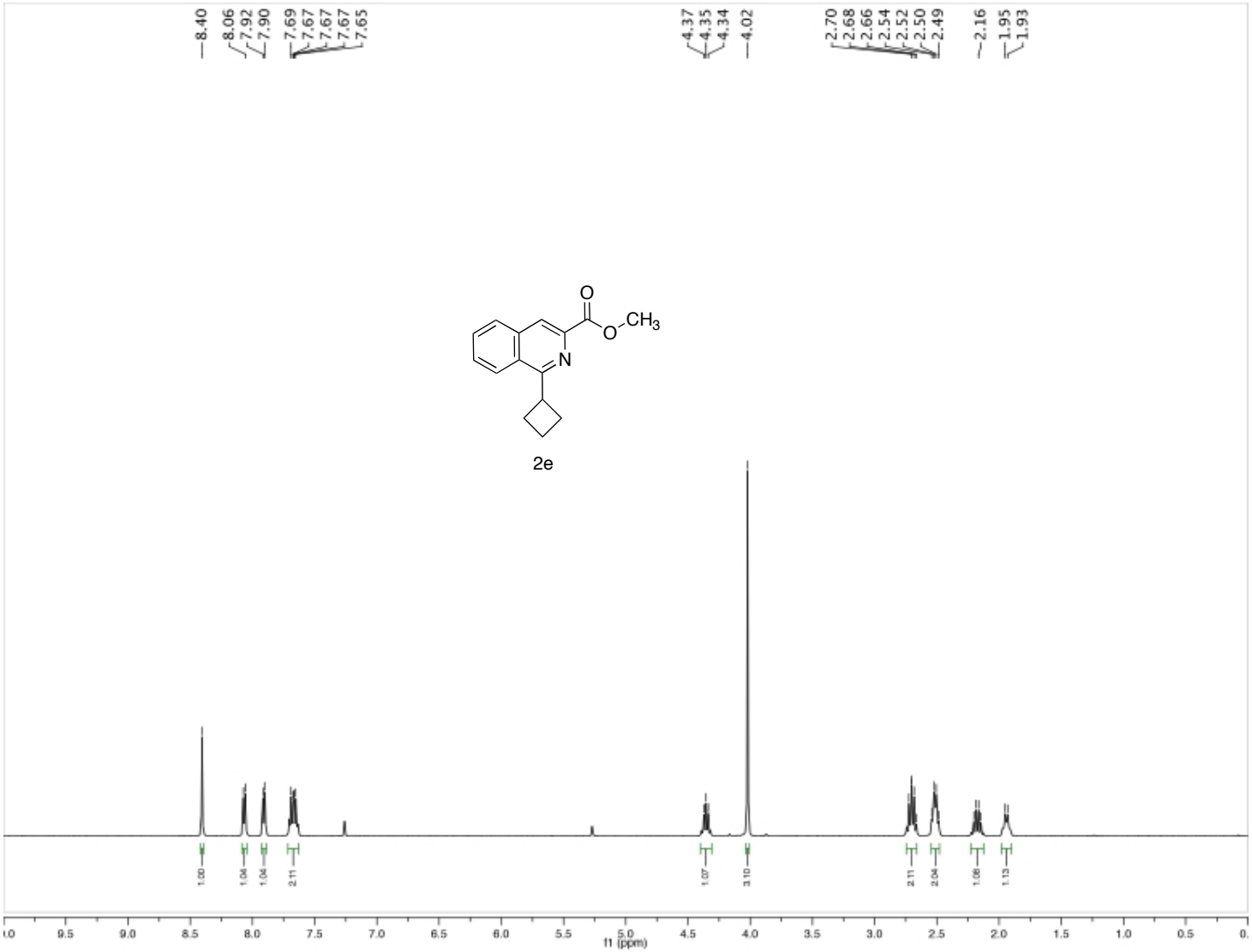
^{13}C NMR (125 MHz, $CDCl_3$) 2-cyclobutylisoquinoline **2da**
(Table 1, entry 4)



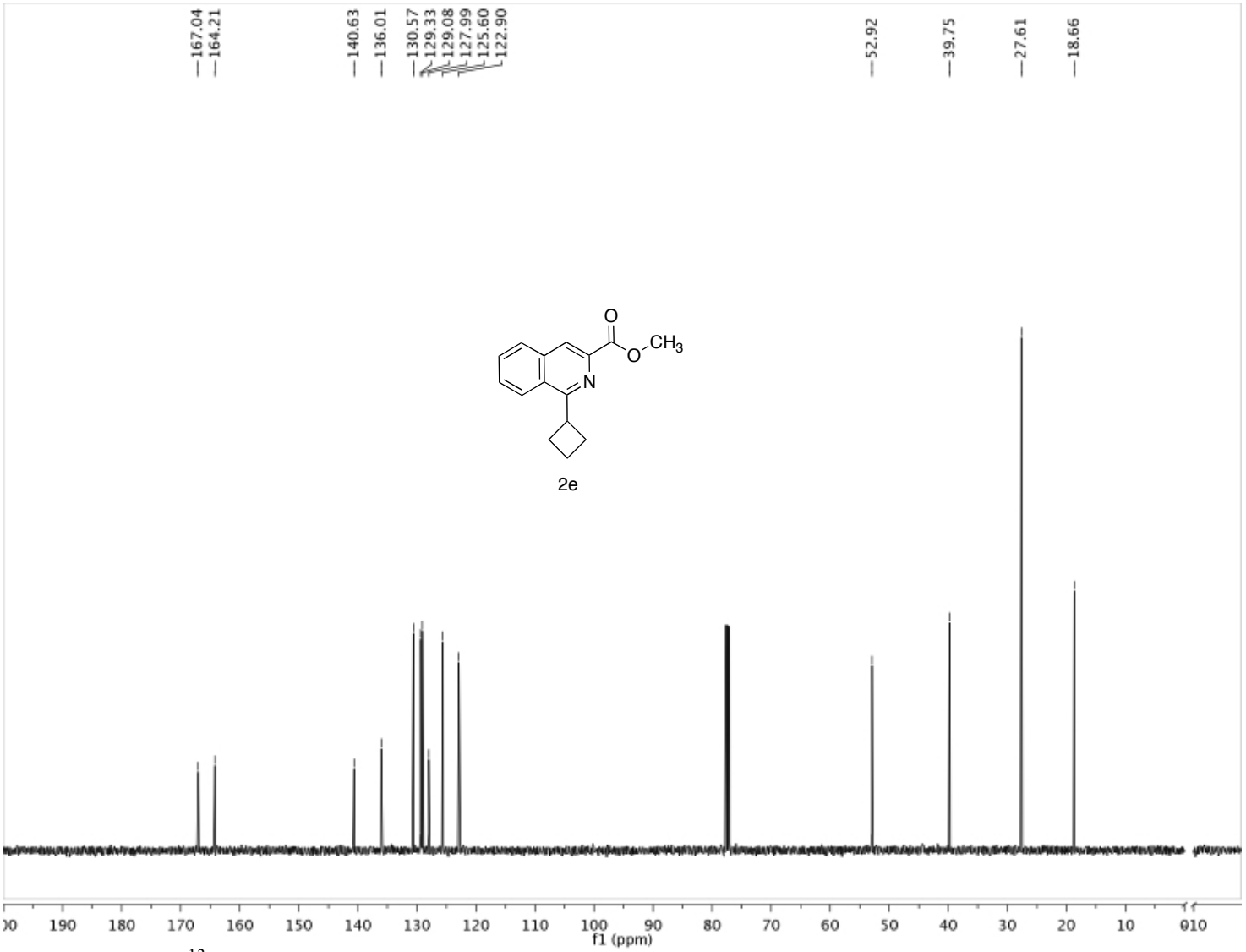
^{1}H NMR (500 MHz, $CDCl_3$) 2-cyclobutylisoquinoline **2db**
(Table 1, entry 4)



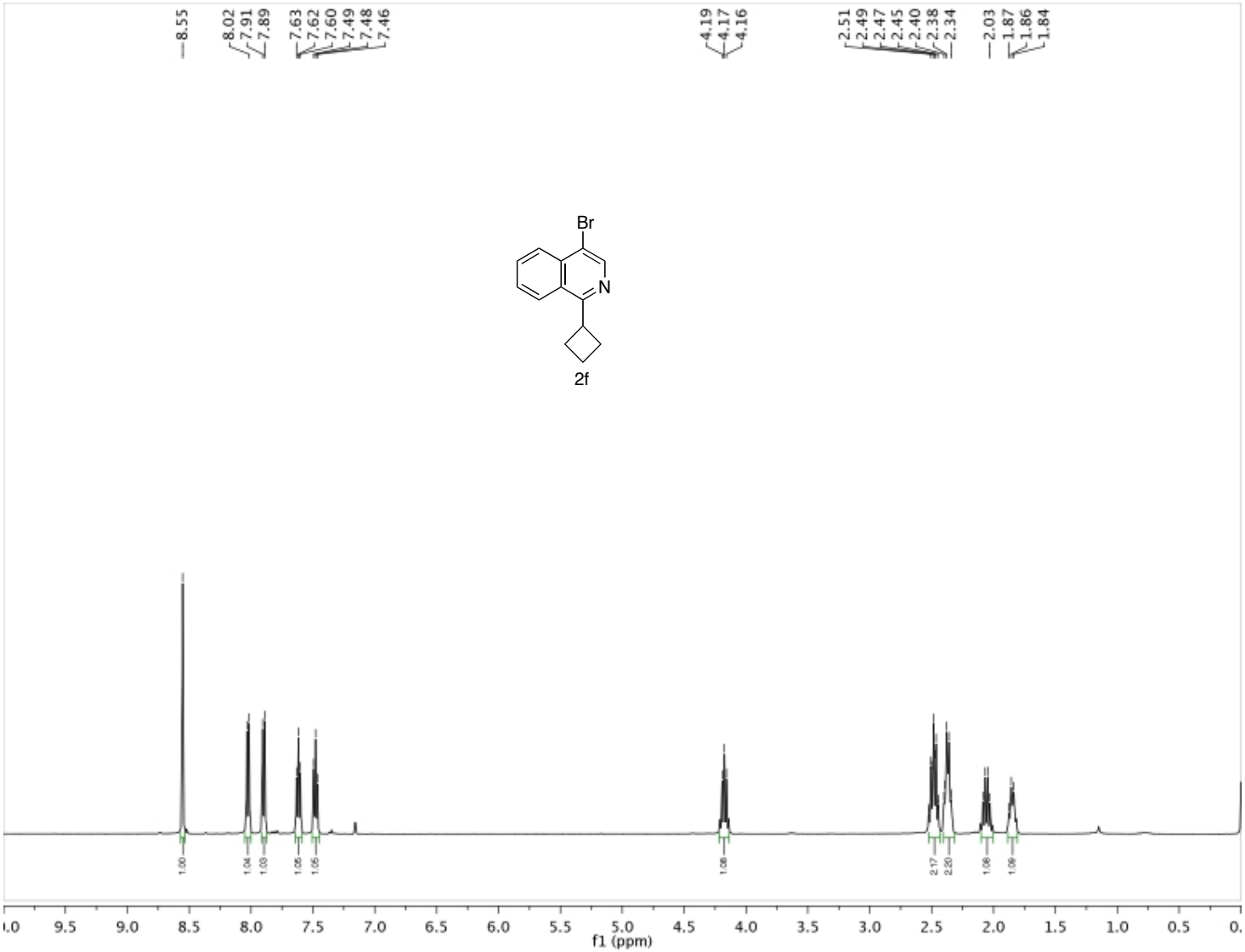
^{13}C NMR (125 MHz, $CDCl_3$) 2-cyclobutylisoquinoline **2db**
(Table 1, entry 4)



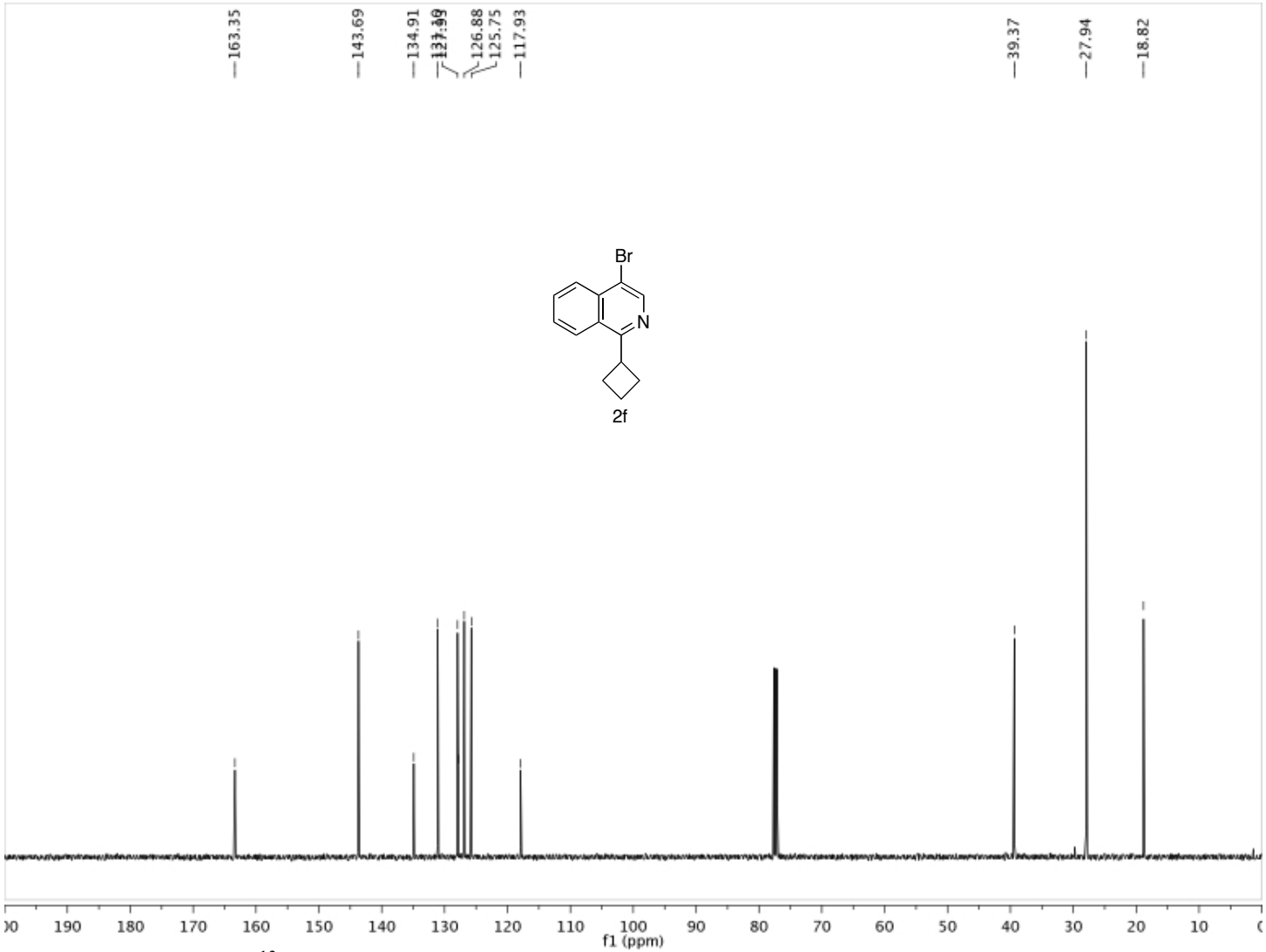
^{1}H NMR (500 MHz, $CDCl_3$) methyl-1-cyclobutylisoquinoline-3-carboxylate **2e**
(Table 1, entry 4)



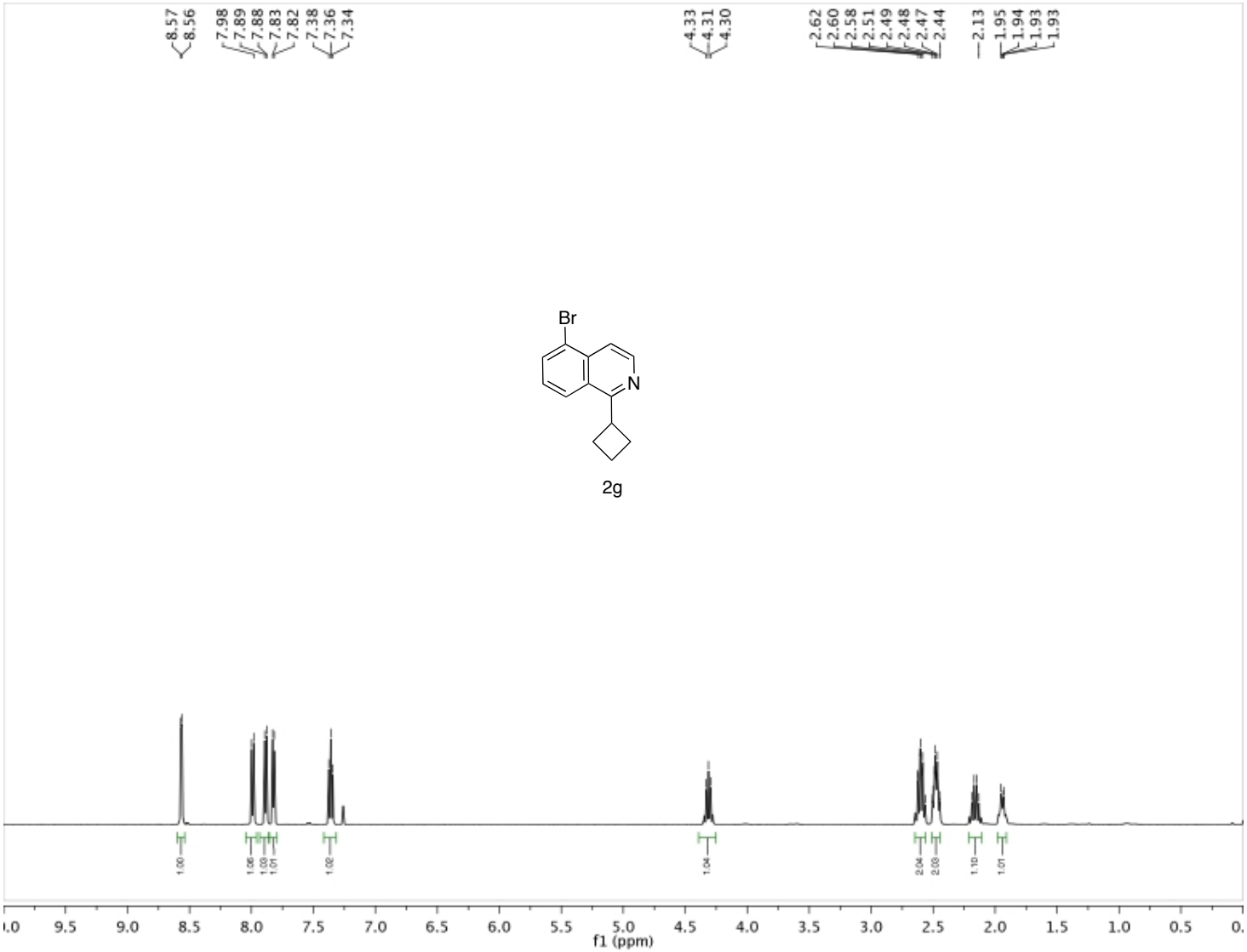
^{13}C NMR (125 MHz, $CDCl_3$) methyl-1-cyclobutylisoquinoline-3-carboxylate **2e**
(Table 1, entry 4)



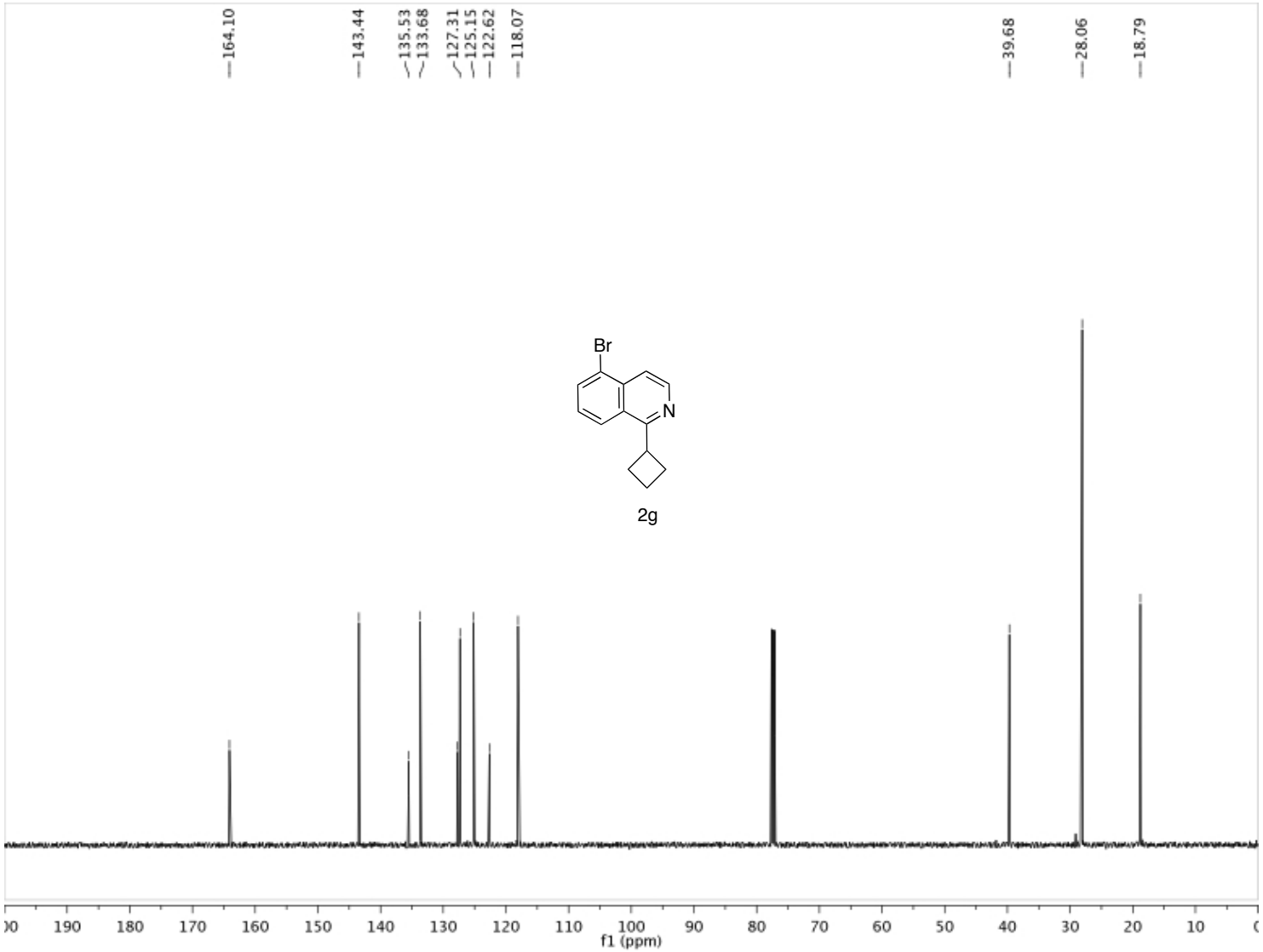
^{1}H NMR (500 MHz, $CDCl_3$) 4-bromol-1-cyclobutylisoquinoline **2f**
(Table 1, entry 4)



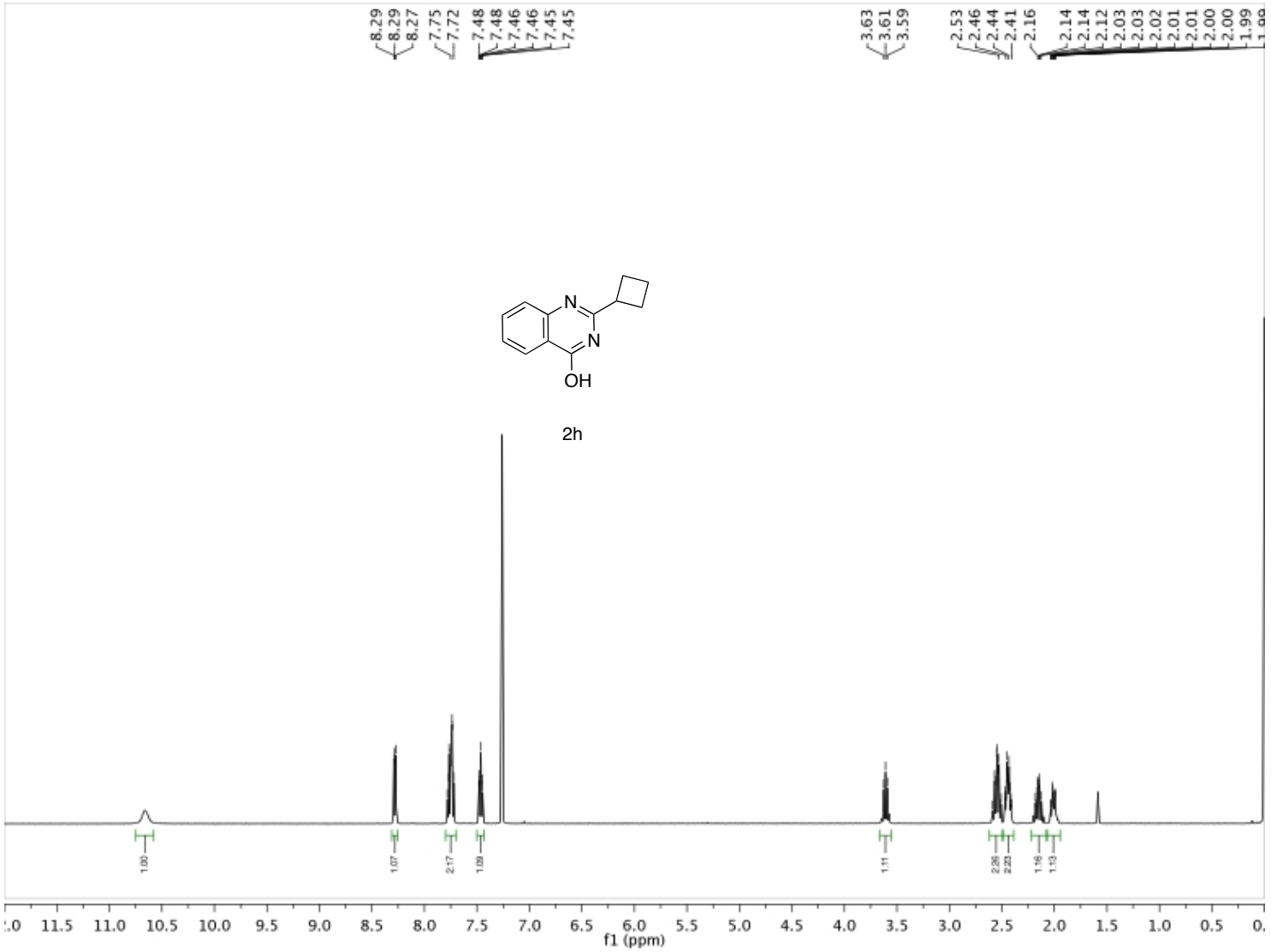
^{13}C NMR (125 MHz, $CDCl_3$) 4-bromo-1-cyclobutylisoquinoline **2f**
(Table 1, entry 4)



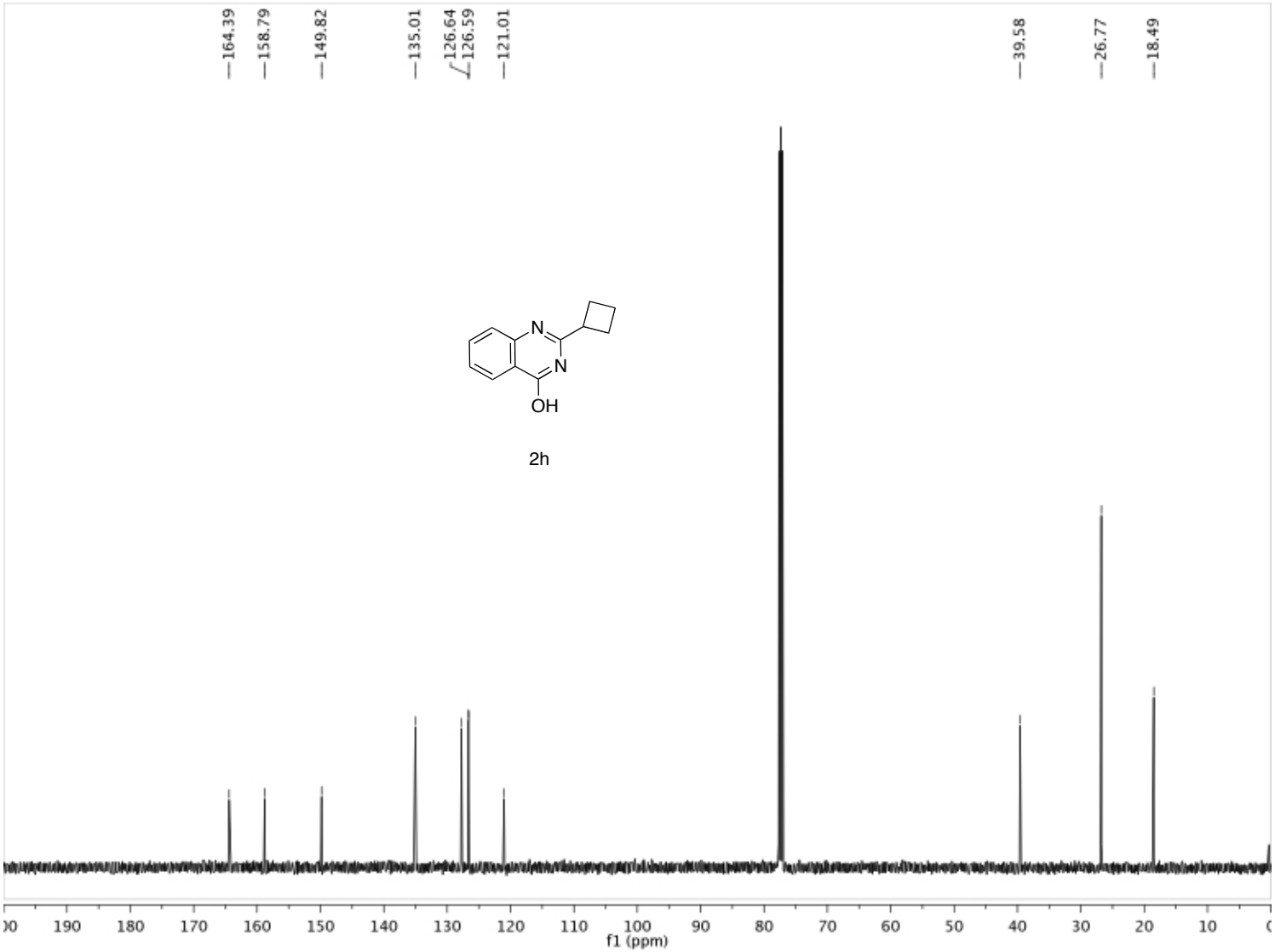
^{1}H NMR (500 MHz, $CDCl_3$) 5-bromo-1-cyclobutylisoquinoline **2g**
(Table 1, entry 4)



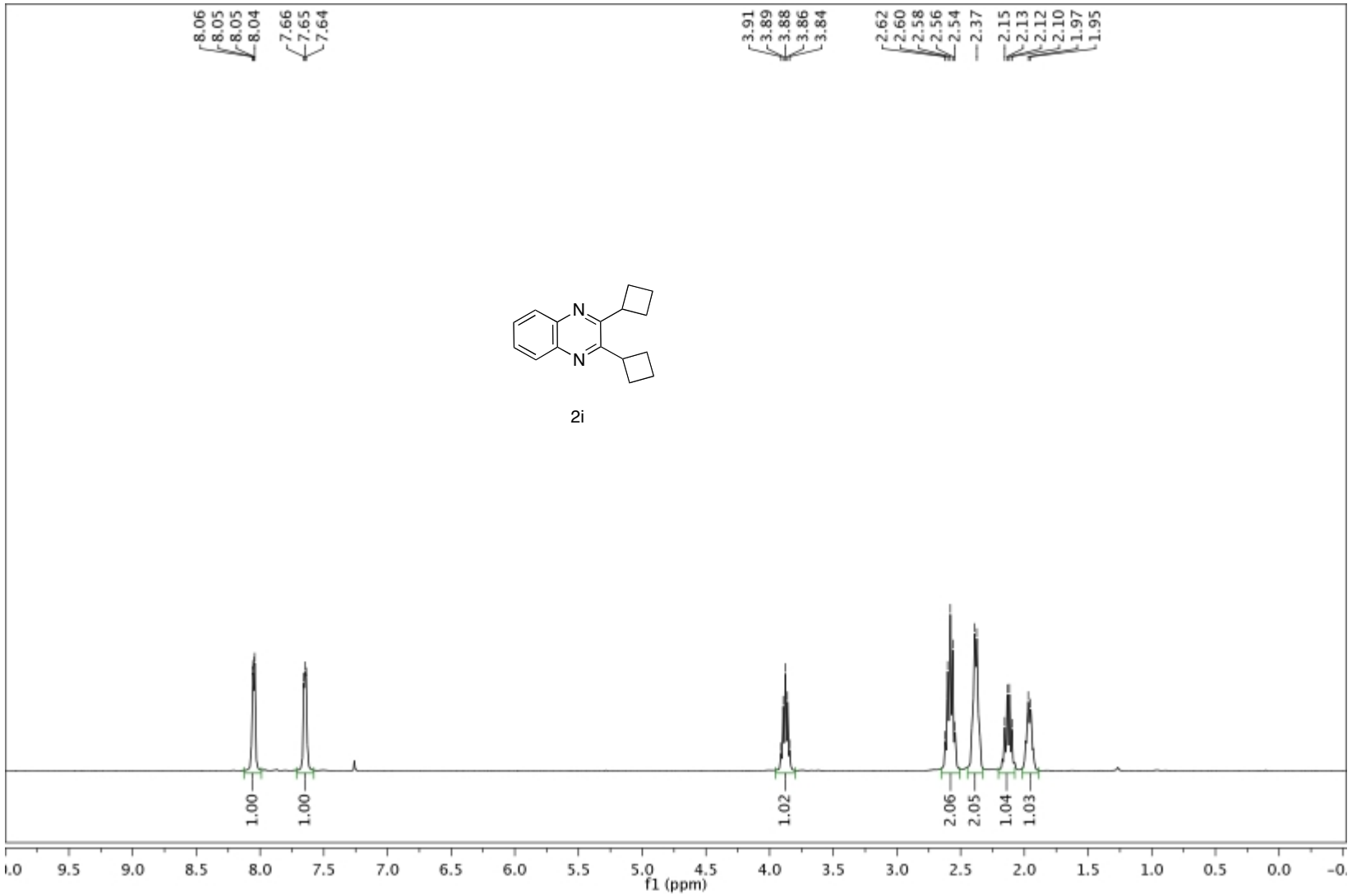
^{13}C NMR (125 MHz, $CDCl_3$) 5-bromo-1-cyclobutylisoquinoline **2g**
(Table 1, entry 4)



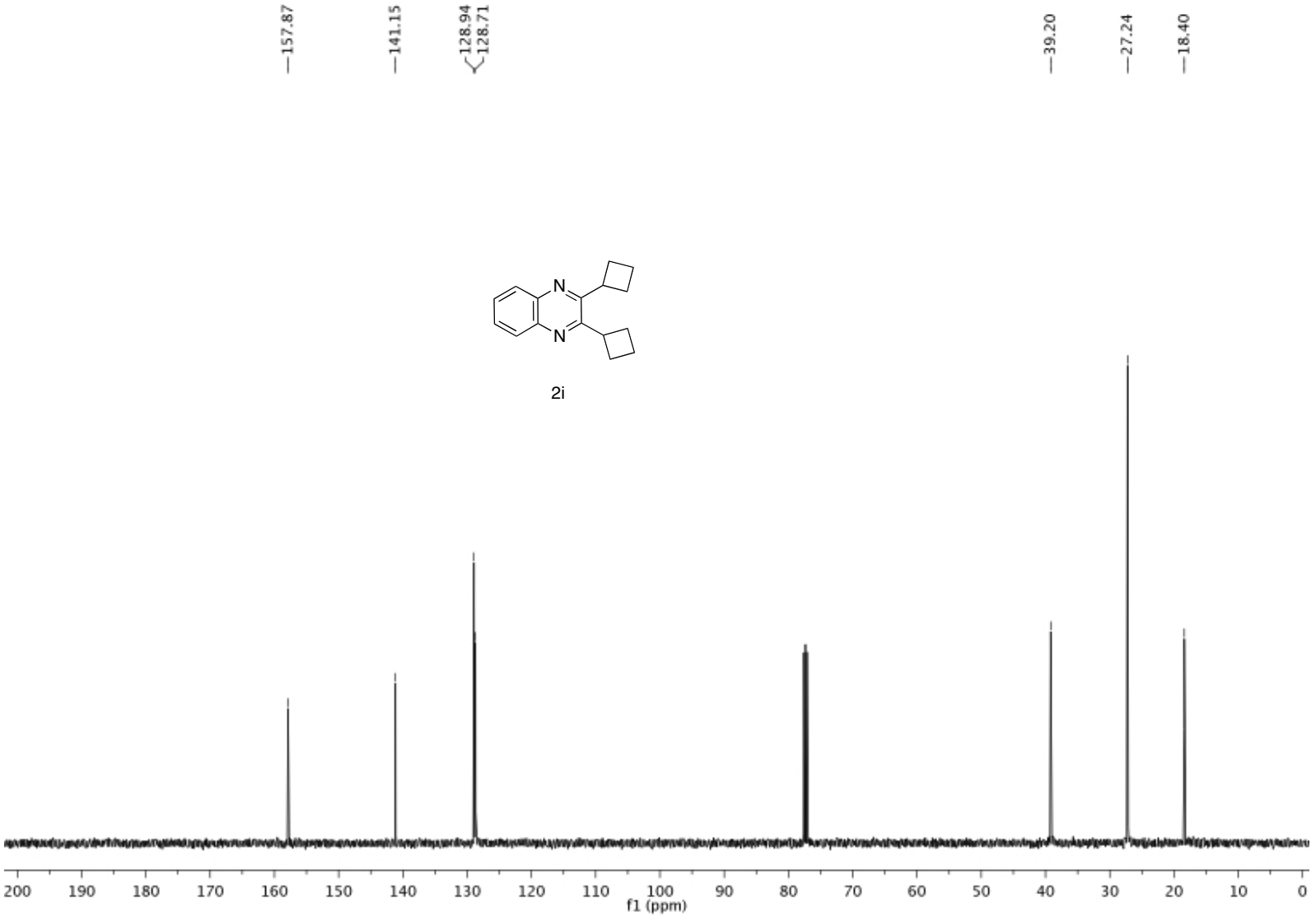
^{1}H NMR (500 MHz, $CDCl_3$) 4-hydroxy-3-cyclobutylquinazloine **2h**
(Table 1, entry 5)



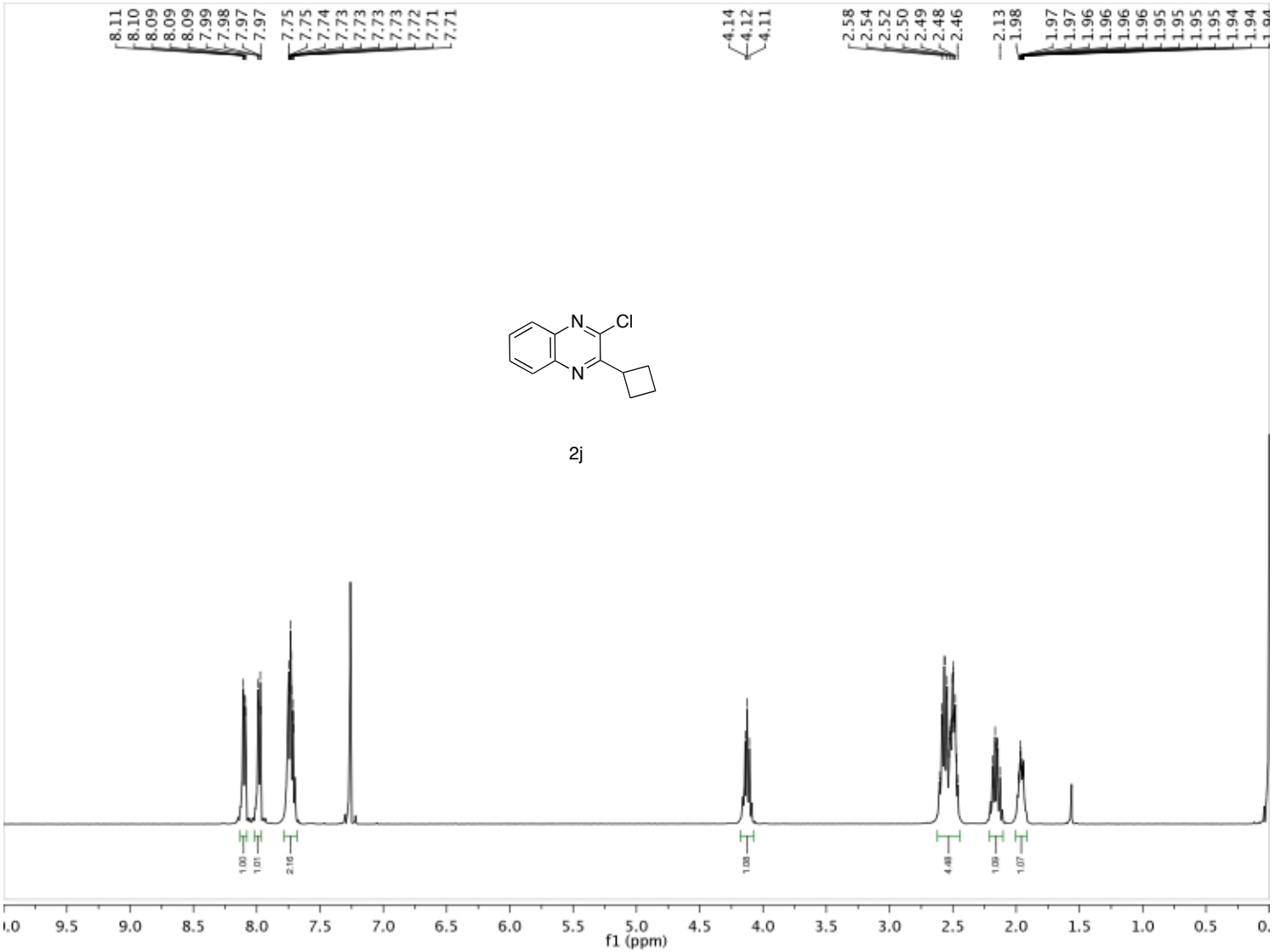
^{13}C NMR (125 MHz, $CDCl_3$) 4-hydroxy-3-cyclobutylquinazoline **2h**
(Table 1, entry 5)



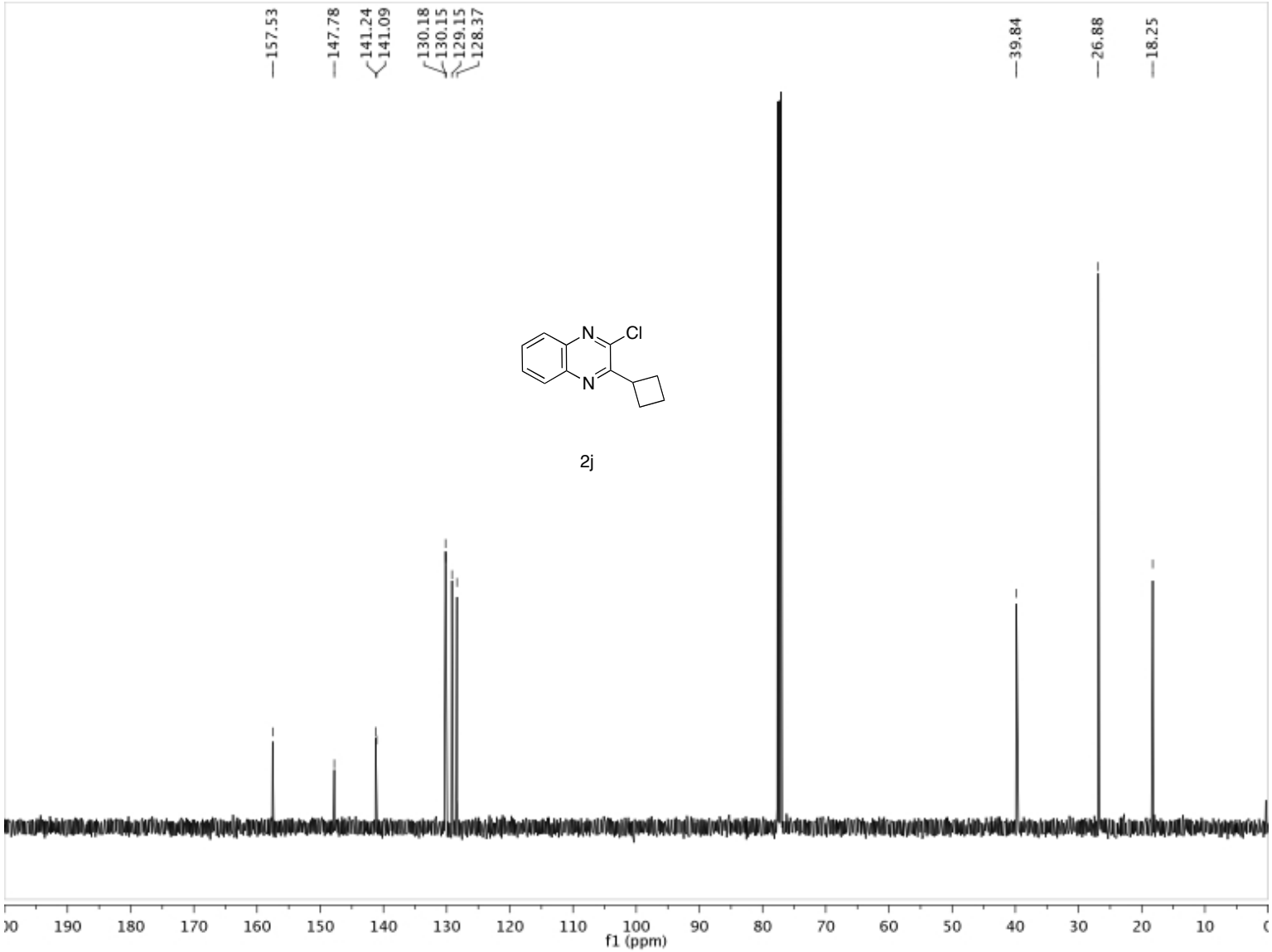
^{1}H NMR (500 MHz, $CDCl_3$) 2,3-dicyclobutylquinoxaline **2i**
(Table 1, entry 6)



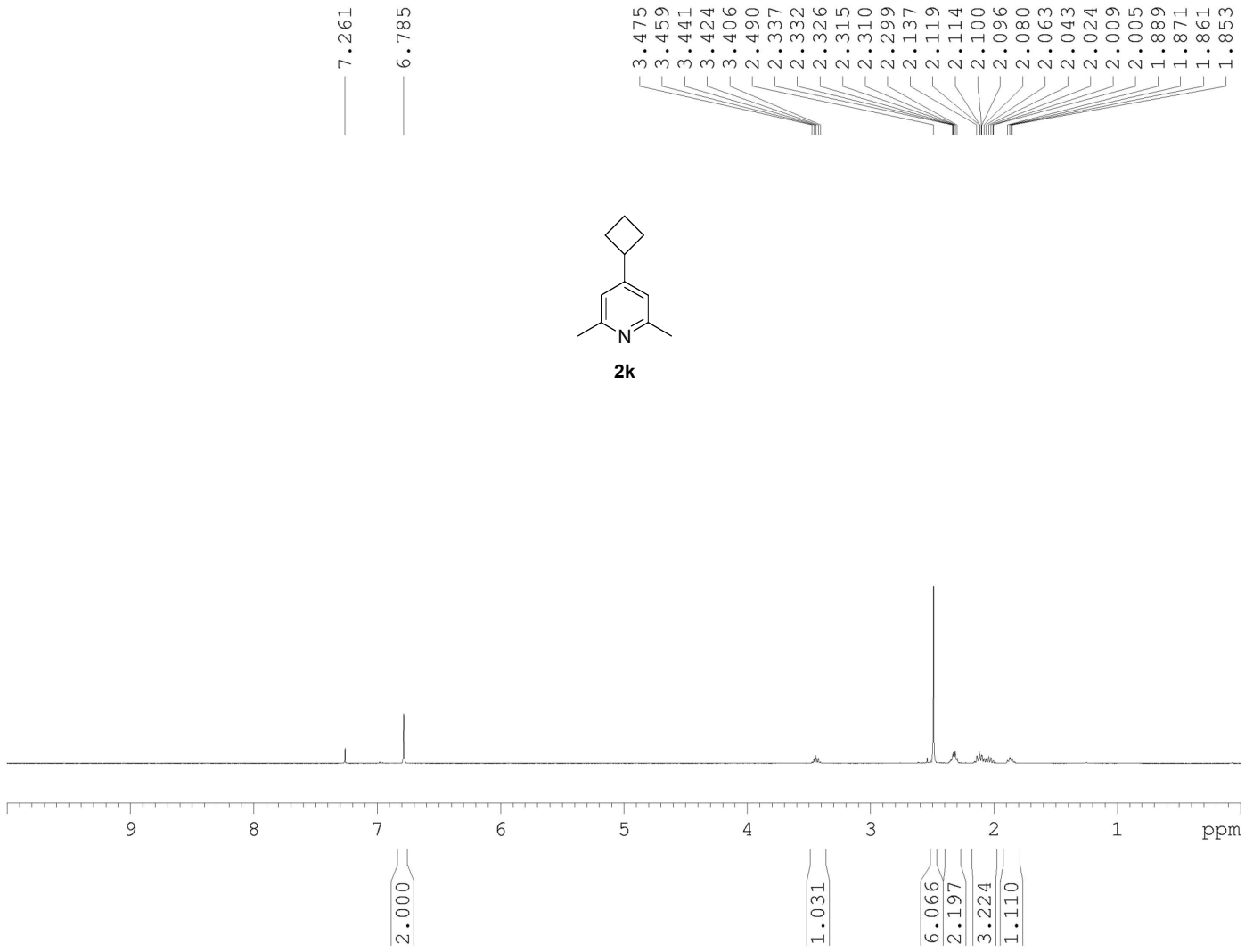
^{13}C NMR (125 MHz, $CDCl_3$) 2,3-dicyclobutylquinoxaline **2i**
(Table 1, entry 6)



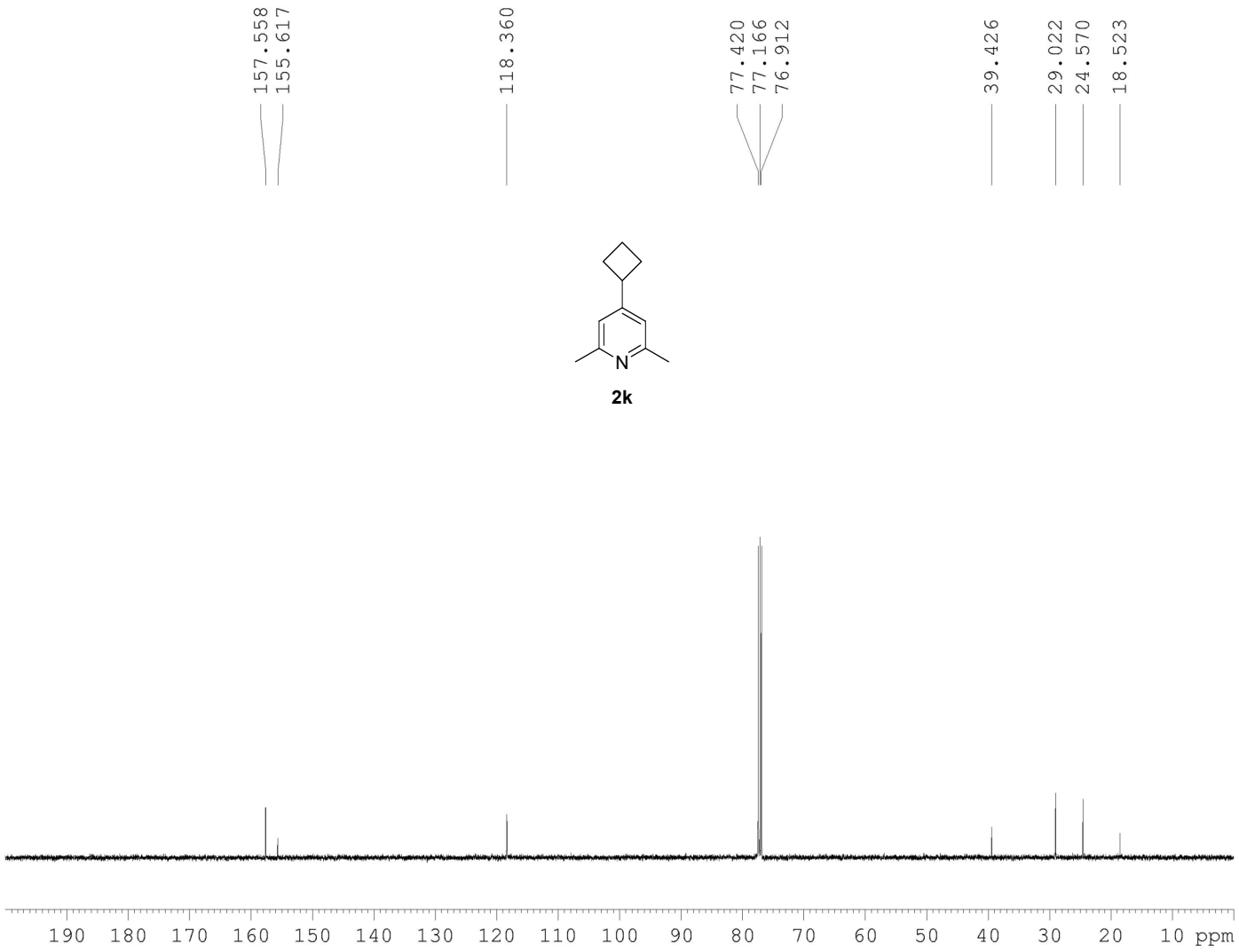
^{1}H NMR (500 MHz, $CDCl_3$) 3-chloro-1-cyclobutylquinoxaline **2j**
(Table 1, entry 7)



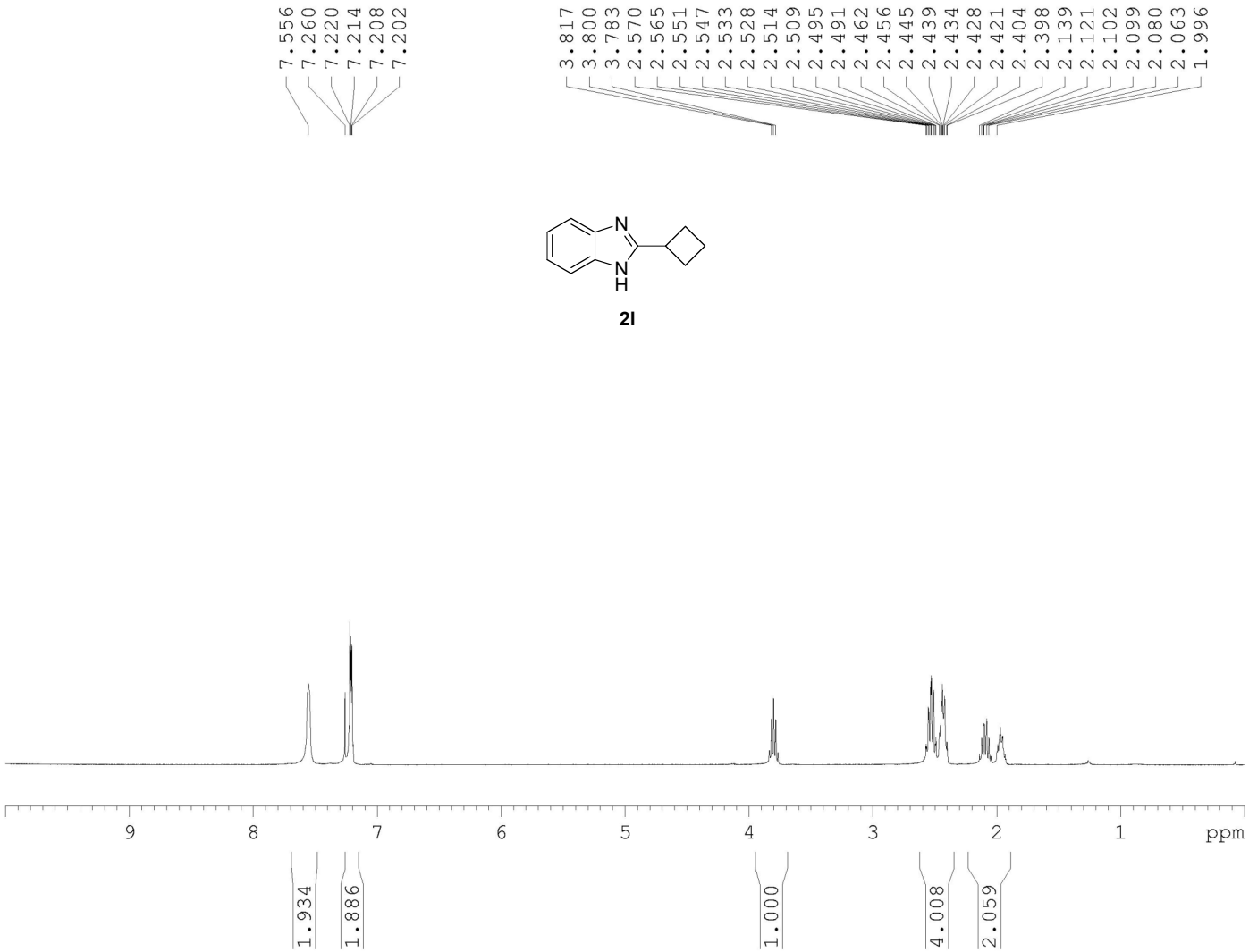
^{1}H NMR (500 MHz, $CDCl_3$) 3-chloro-1-cyclobutylquinoxaline **2j**
(Table 1, entry 7)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-cyclobutyl-2,6-dimethylpyridine **2k**
(Table 1, entry 8)

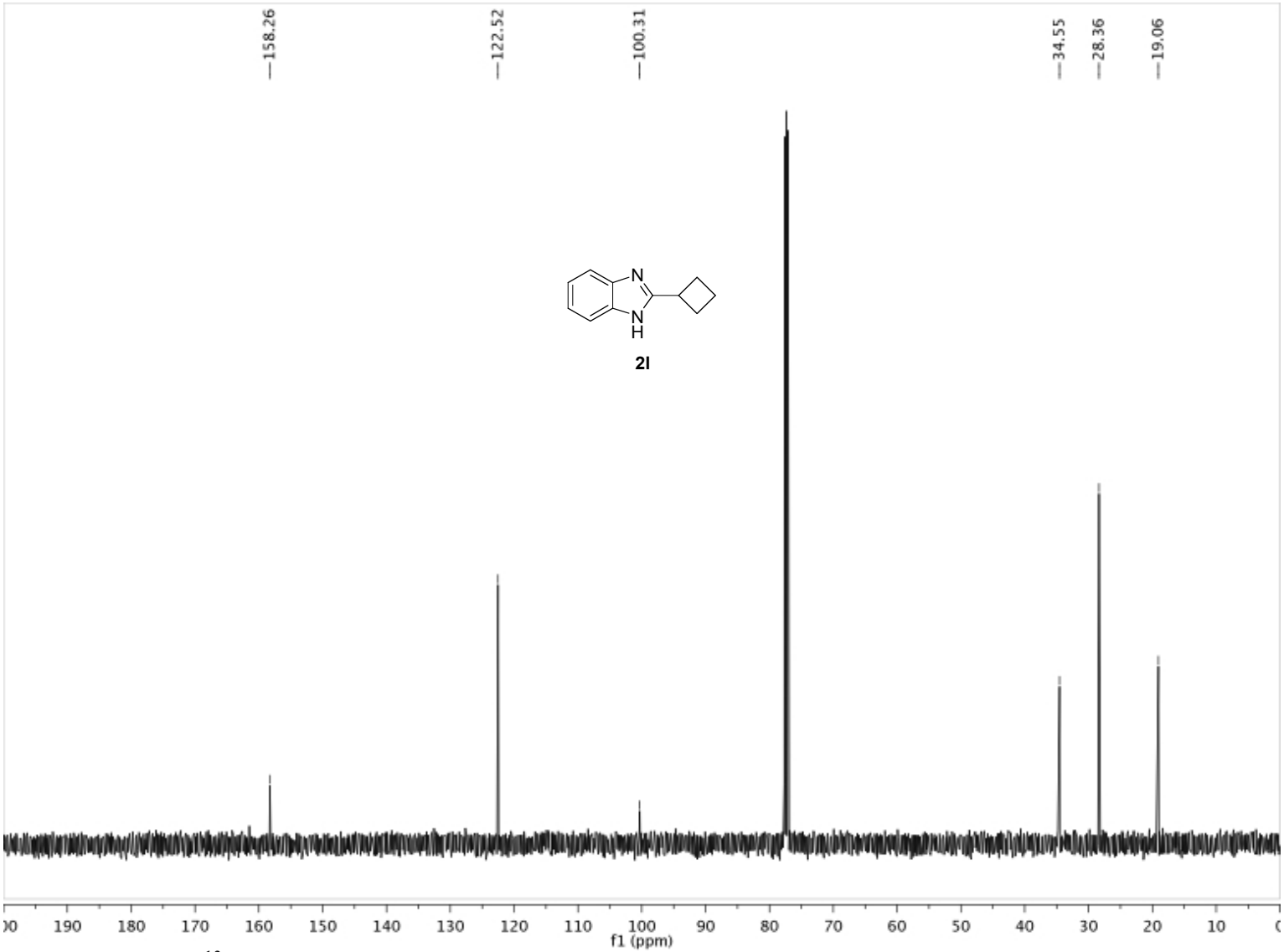


^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-cyclobutyl-2,6-dimethylpyridine **2k**
(Table 1, entry 8)

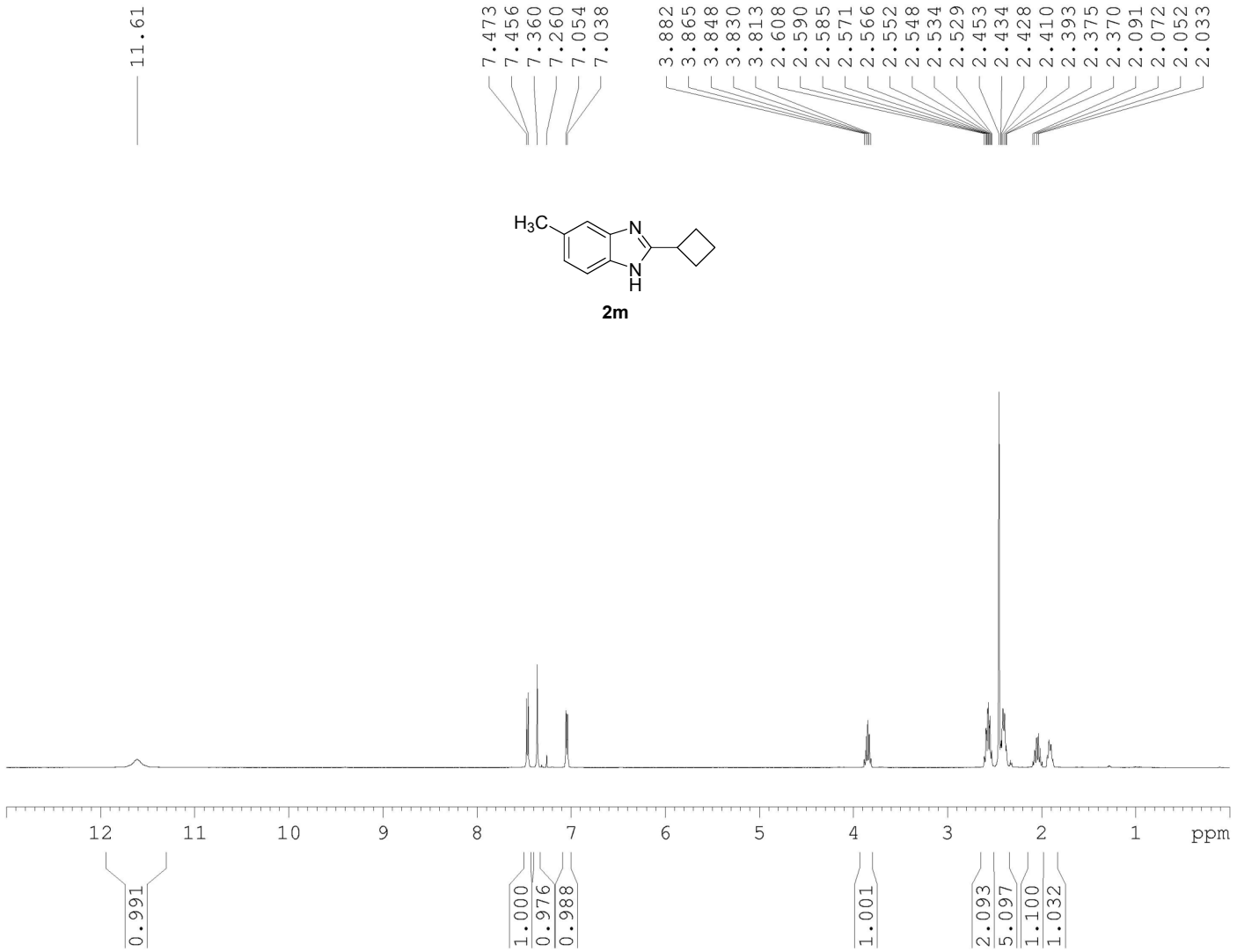


2l

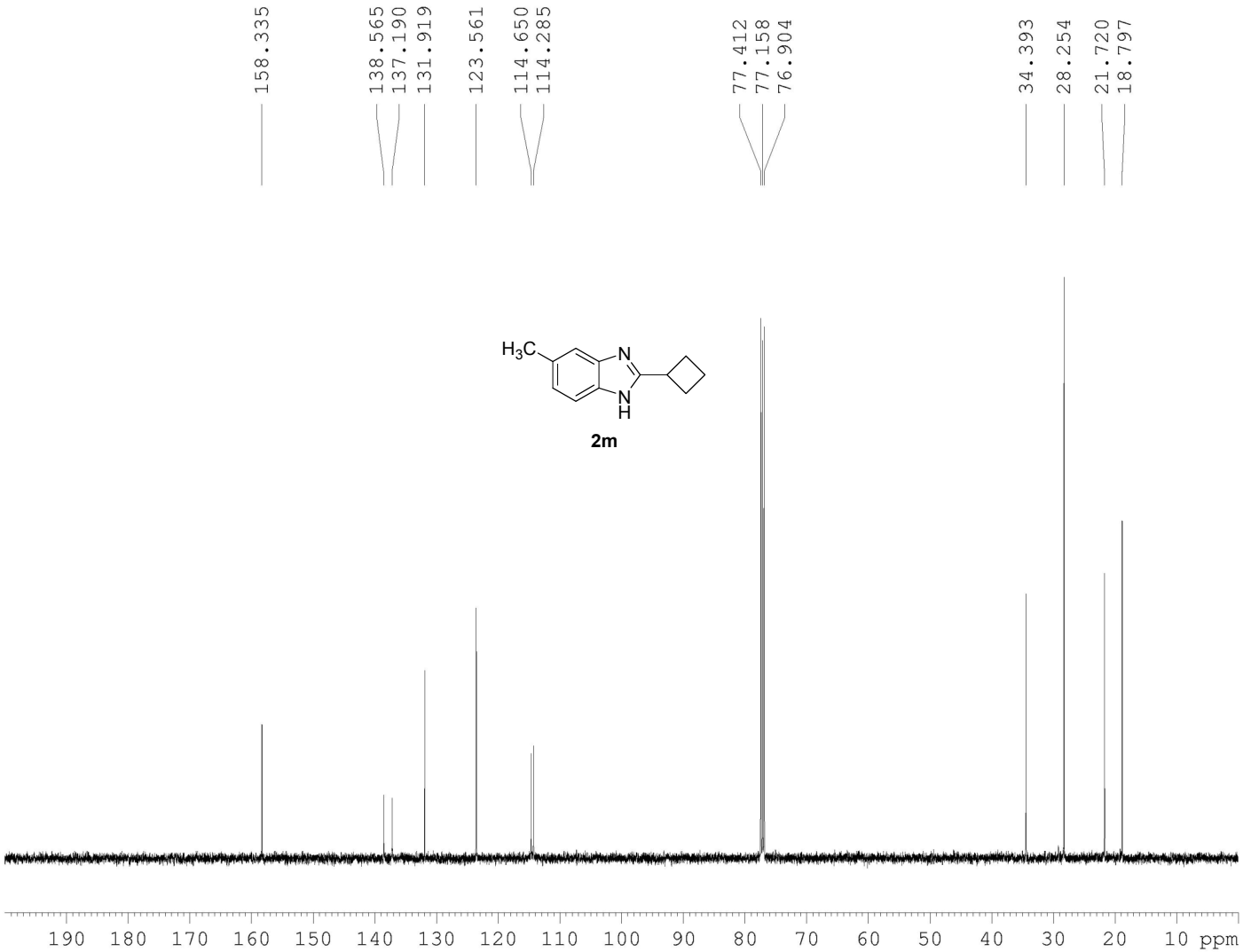
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-1H-benzo[*d*]imidazole **2l**
(Table 1, entry 9)



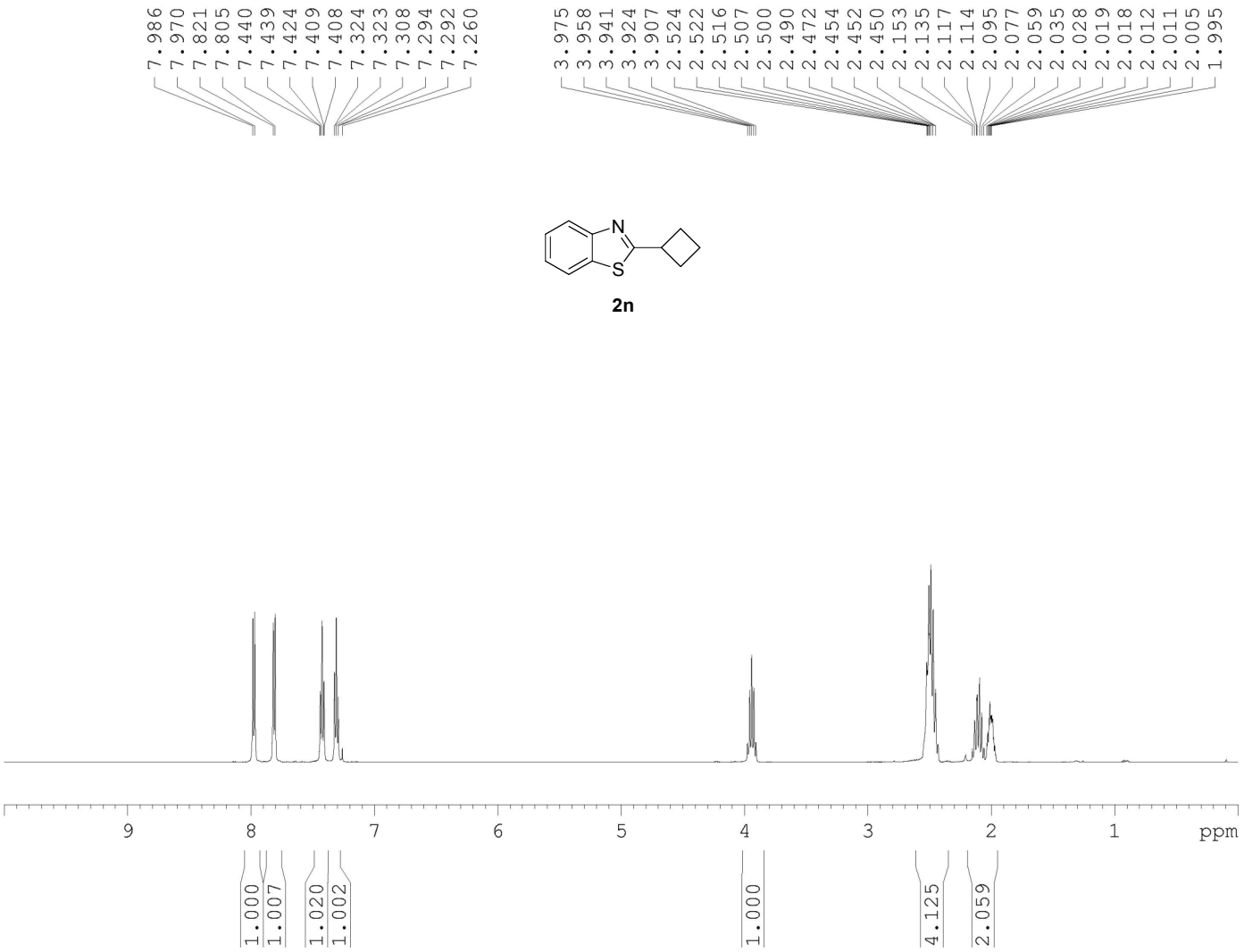
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-1H-benzo[*d*]imidazole **2l**
(Table 1, entry 9)



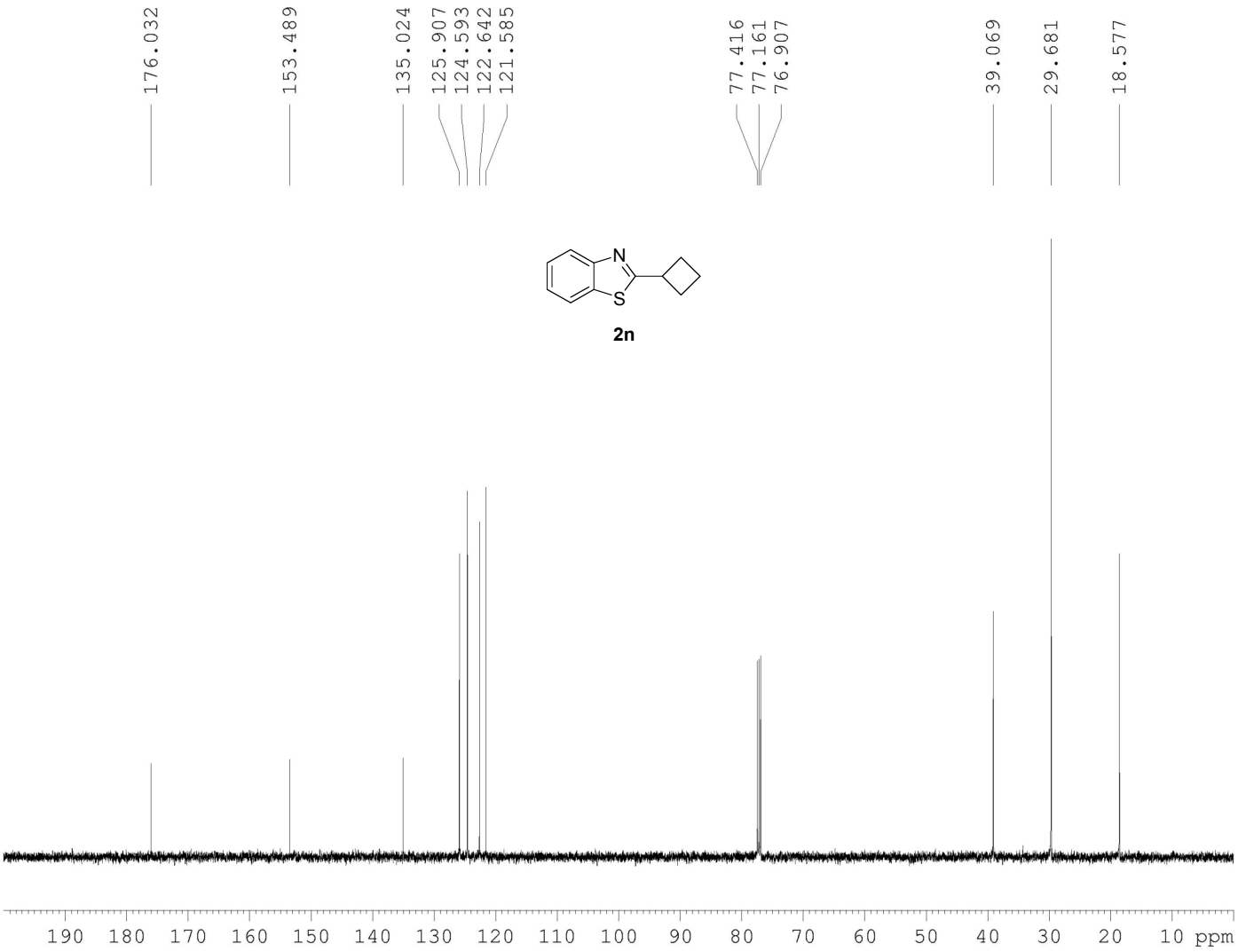
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-5-methyl-1H-benzo[*d*]imidazole **2m**
(Table 1, entry 9)



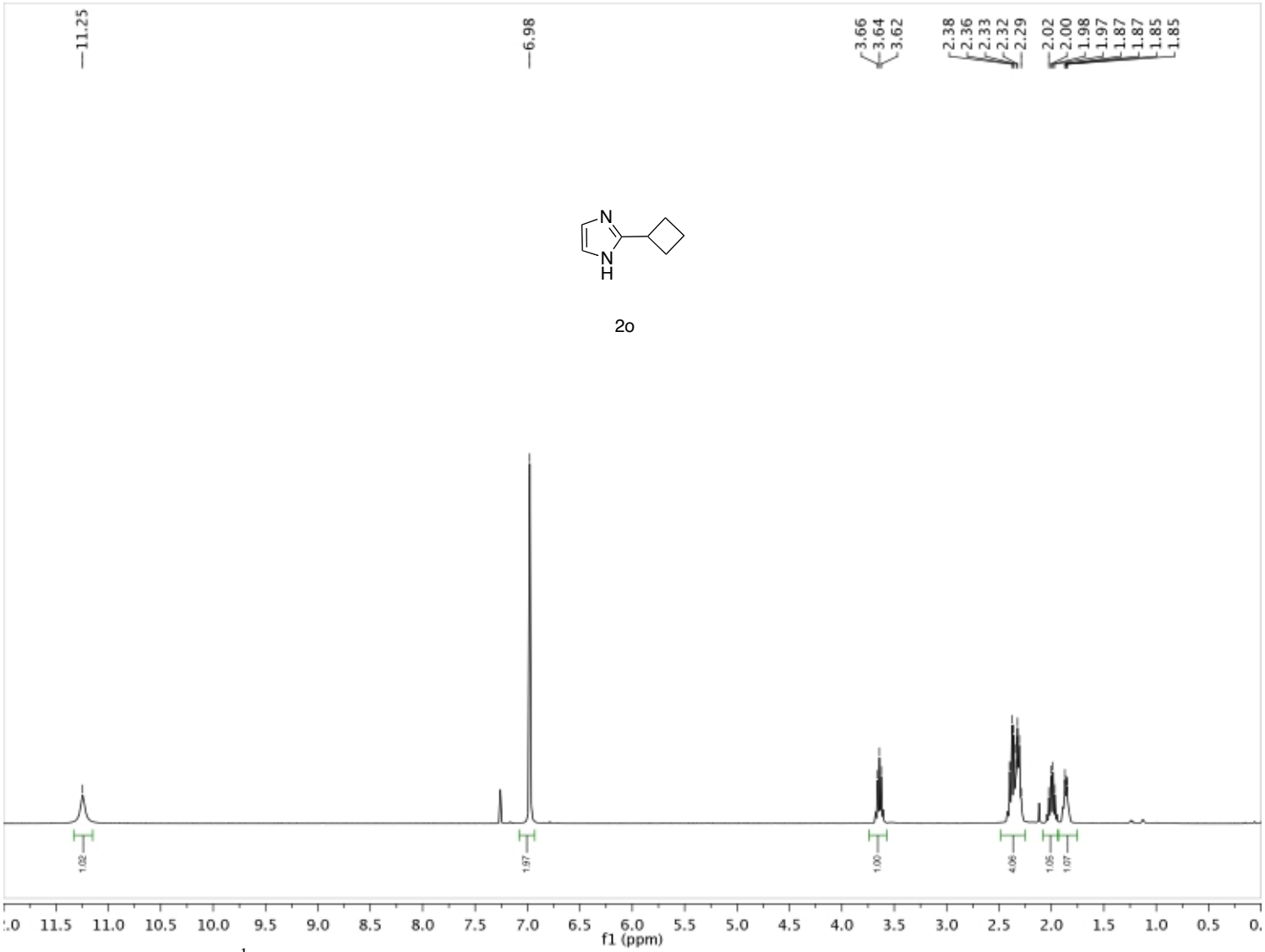
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of -2-cyclobutyl-5-methyl-1H-benzo[*d*]imidazole **2m**
(Table 1, entry 9)



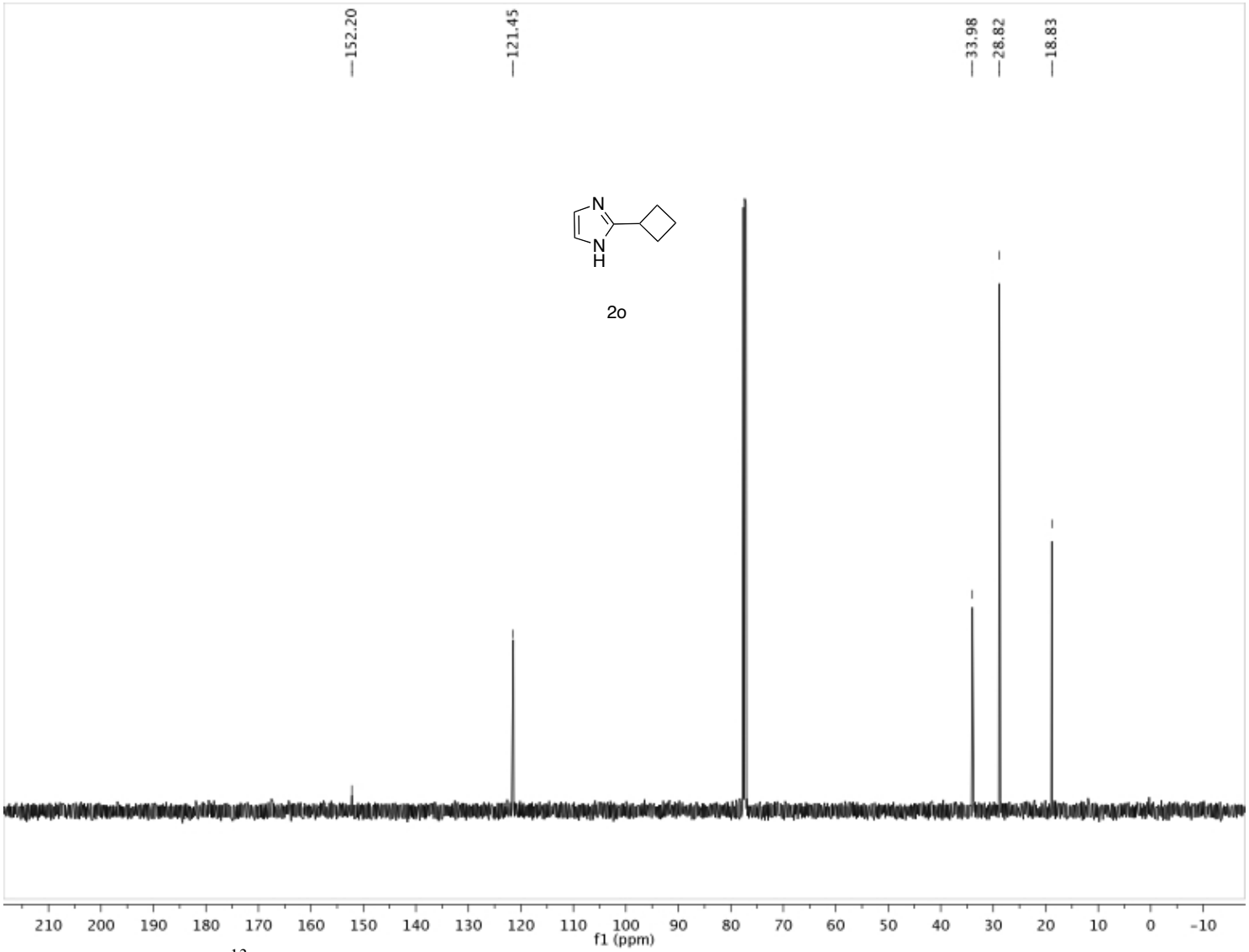
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutylbenzo[*d*]thiazole **2n**
(Table 1, entry 10)



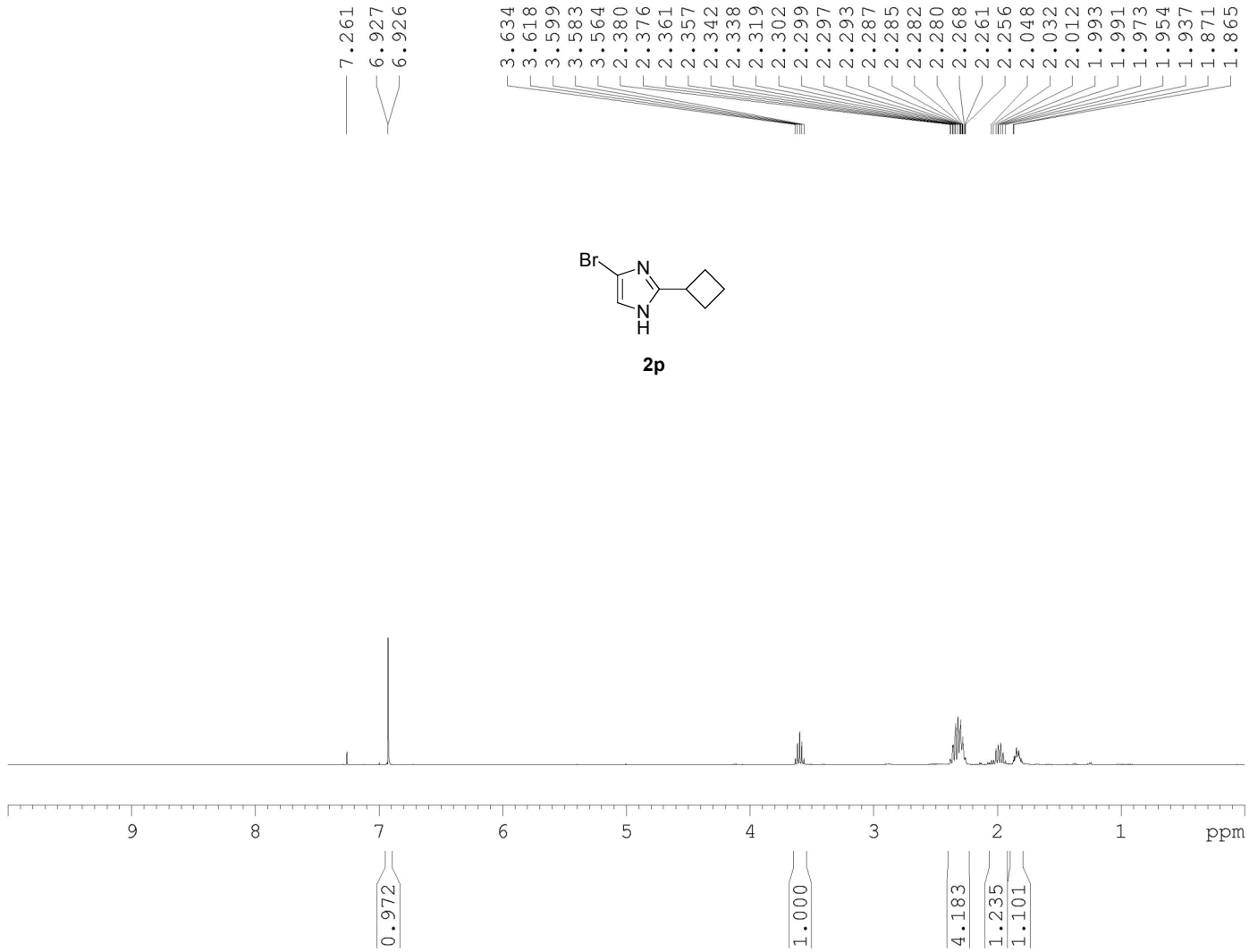
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclobutylbenzo[*d*]thiazole **2n**
(Table 1, entry 10)



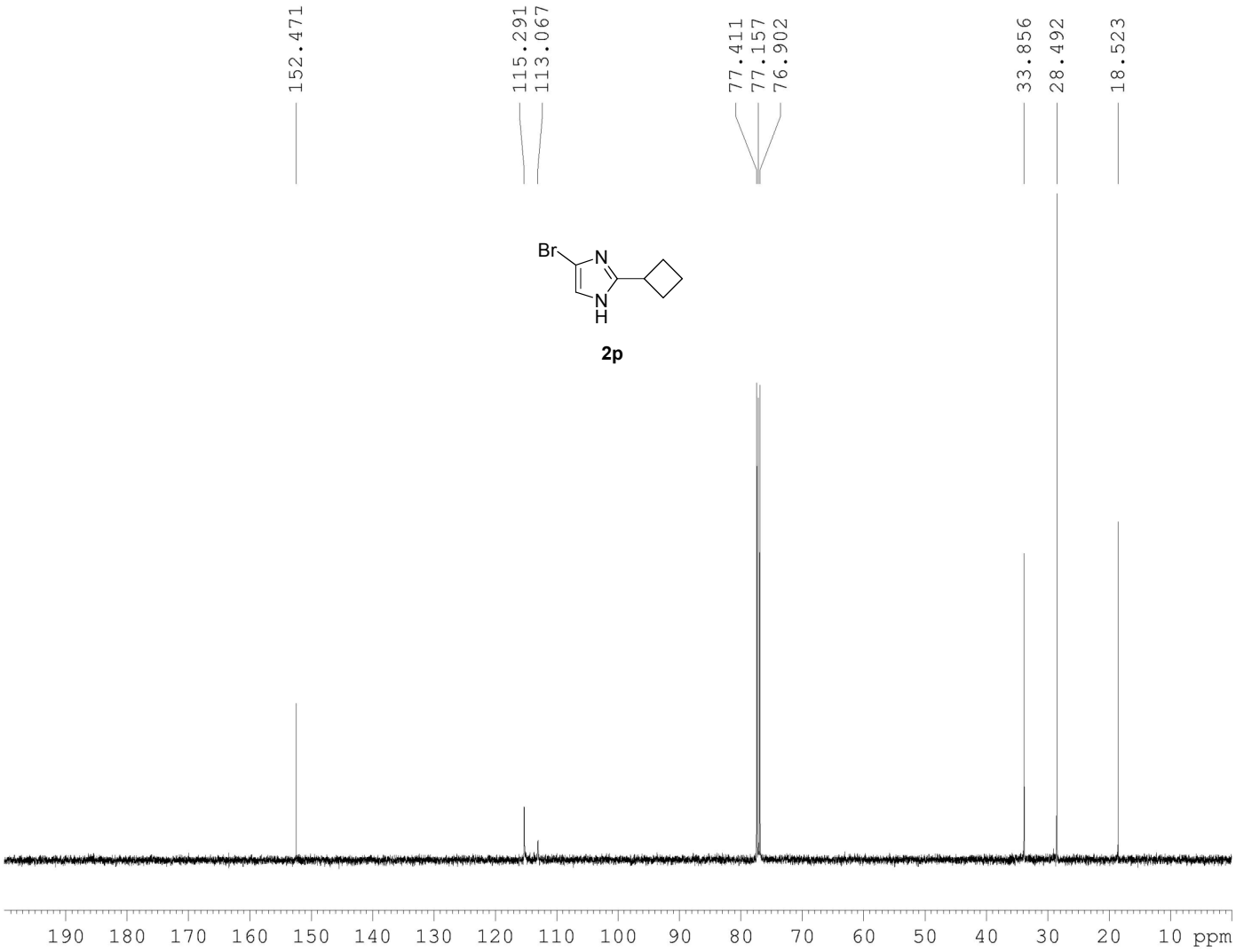
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-1H-imidazole **2o**
(Table 1, entry 11)



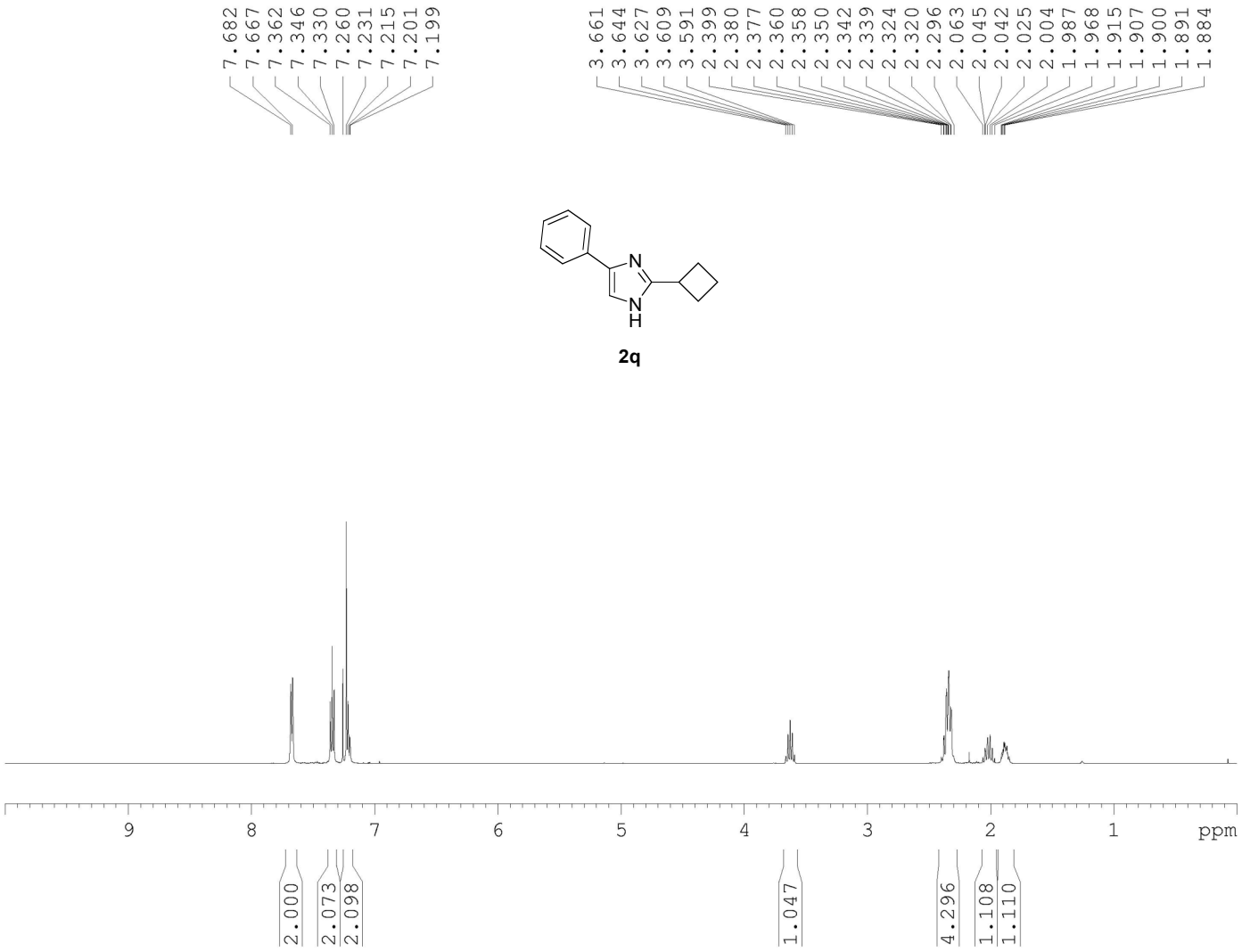
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-1H-imidazole **2o**
(Table 1, entry 11)



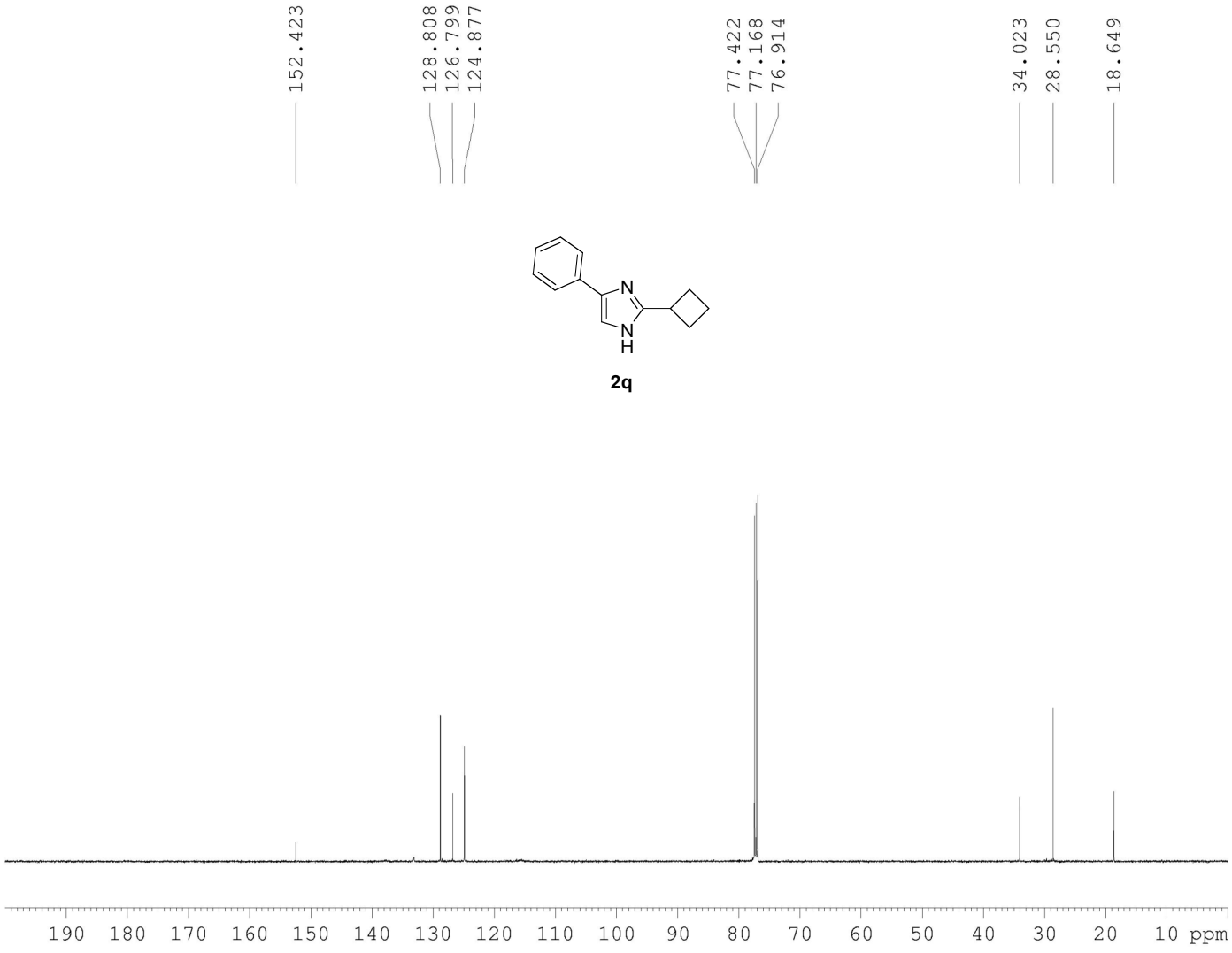
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-bromo-2-cyclobutyl-1H-imidazole **2p**
(Table 1, entry 11)



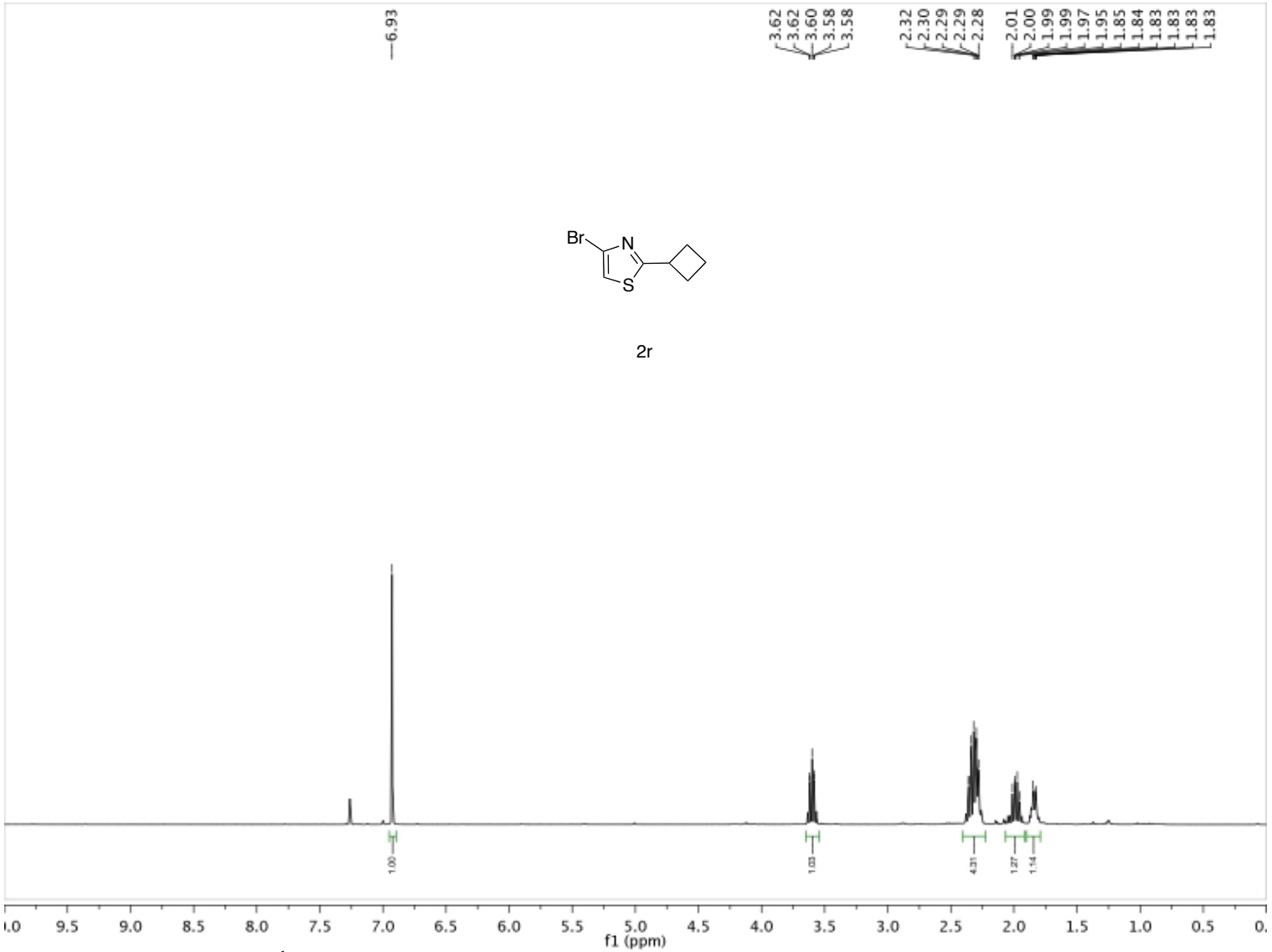
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-bromo-2-cyclobutyl-1H-imidazole 2**p**
(Table 1, entry 11)



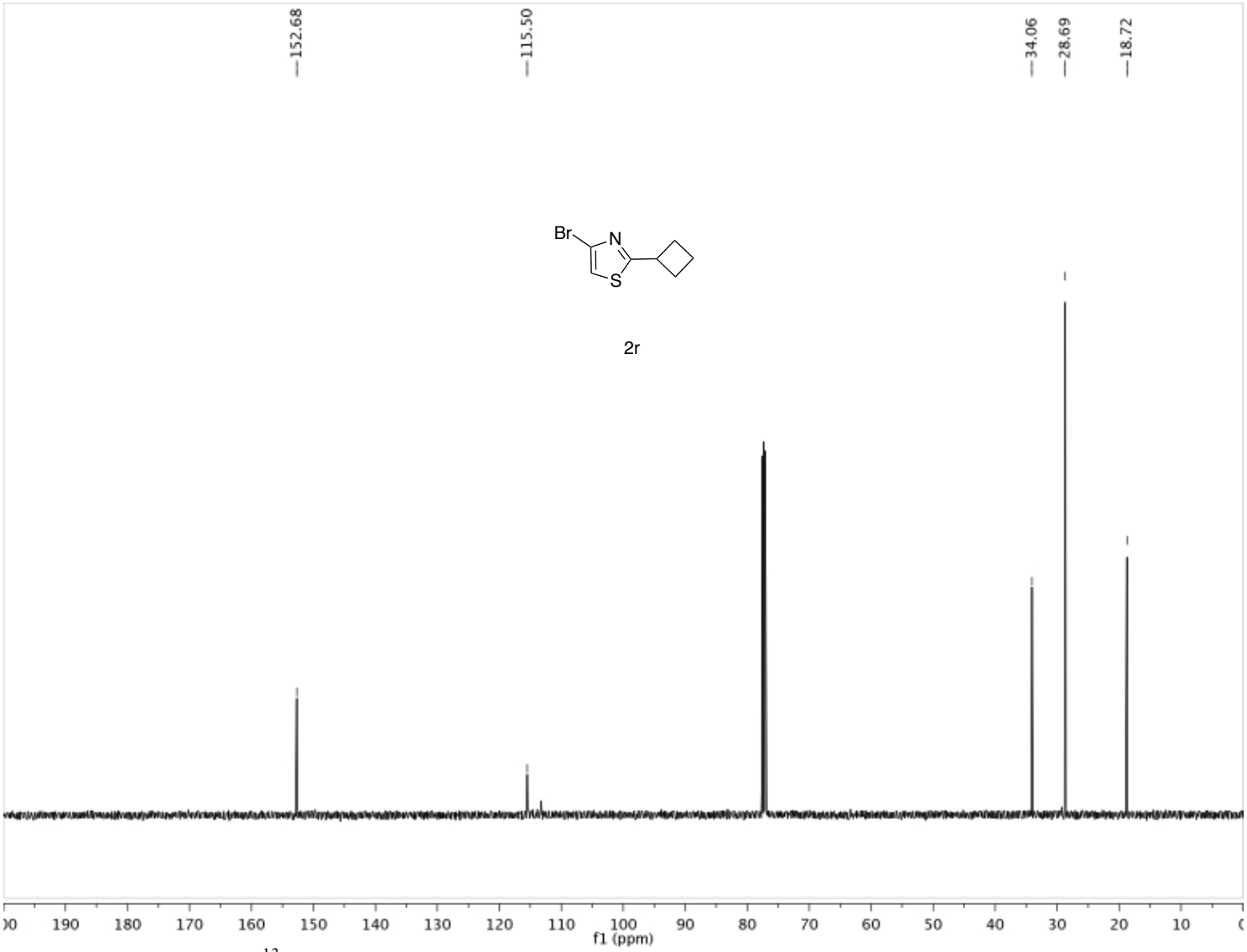
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-4-phenyl-1H-imidazole **2q**
(Table 1, entry 11)



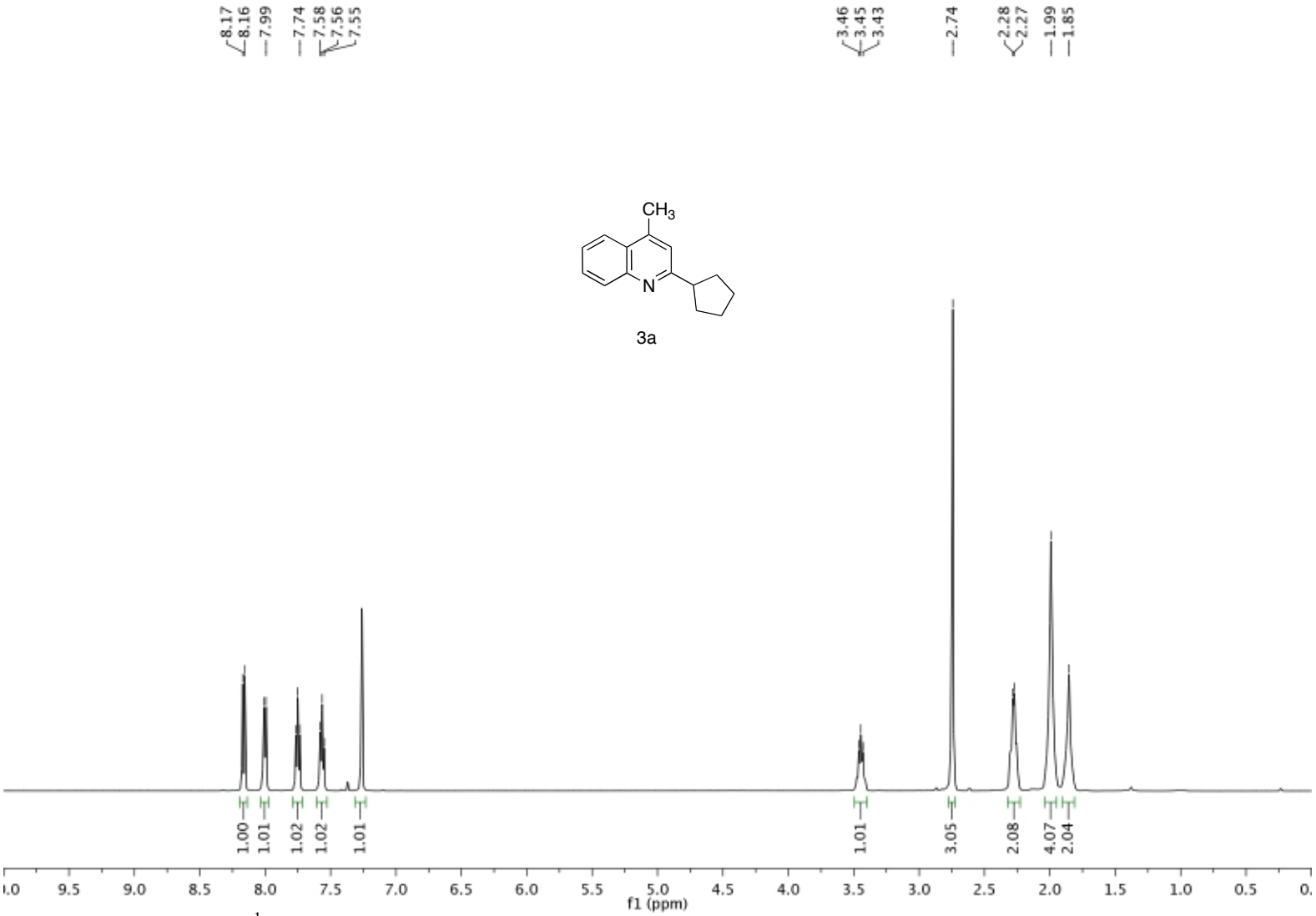
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of -2-cyclobutyl-4-phenyl-1H-imidazole **2q**
(Table 1, entry 11)



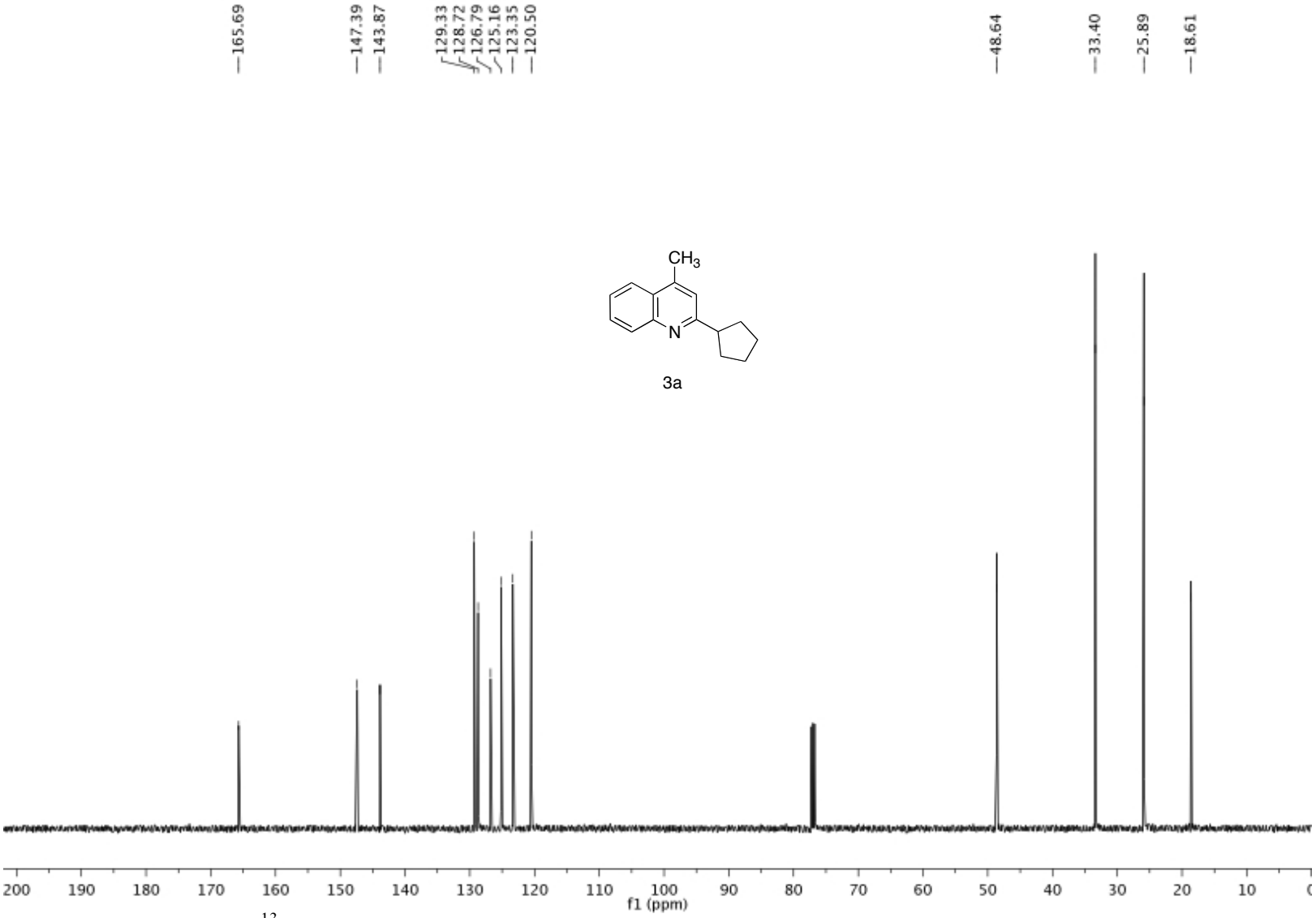
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-thiazole **2r**
(Table 1, entry 12)



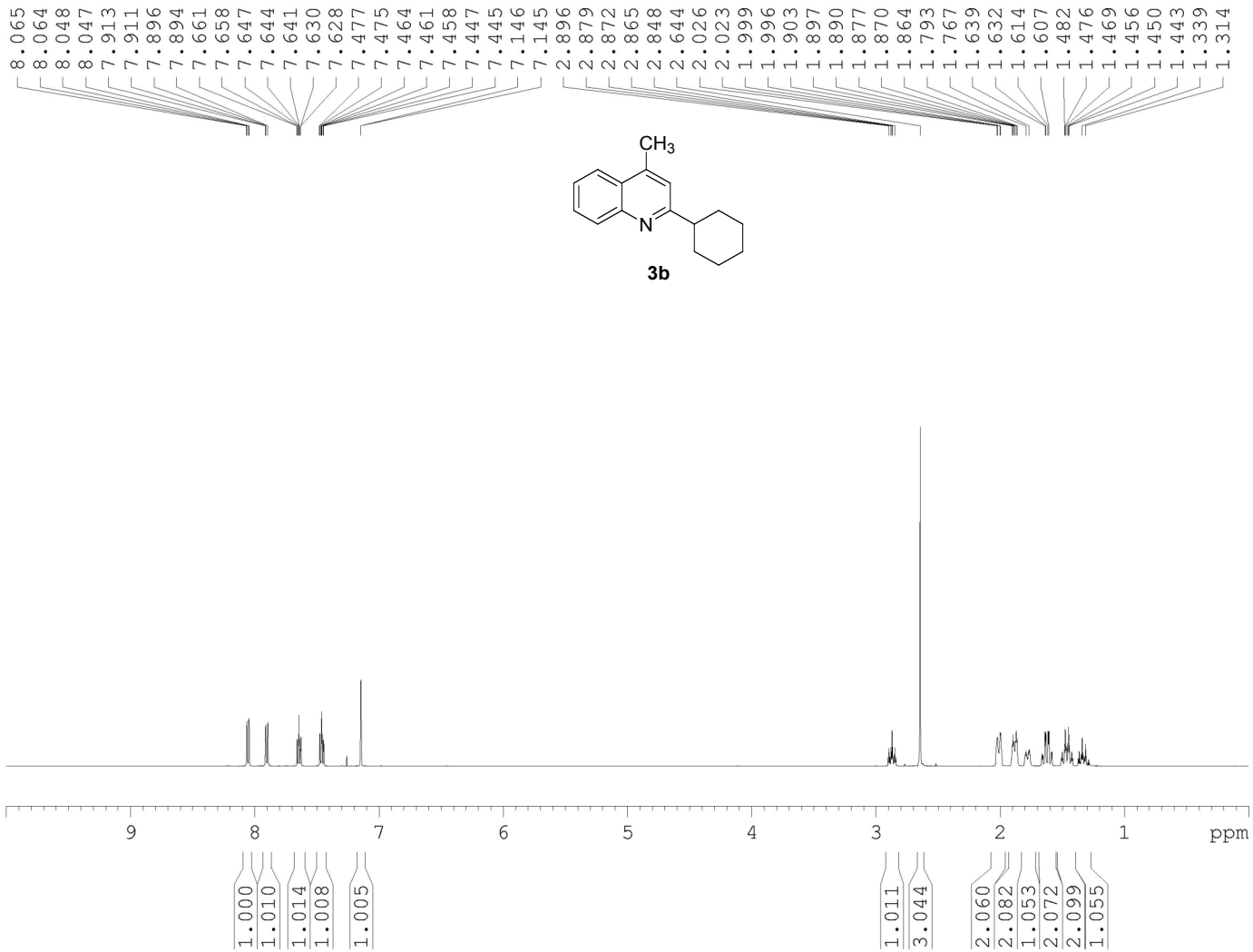
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclobutyl-thiazole **2r**
(Table 1, entry 12)



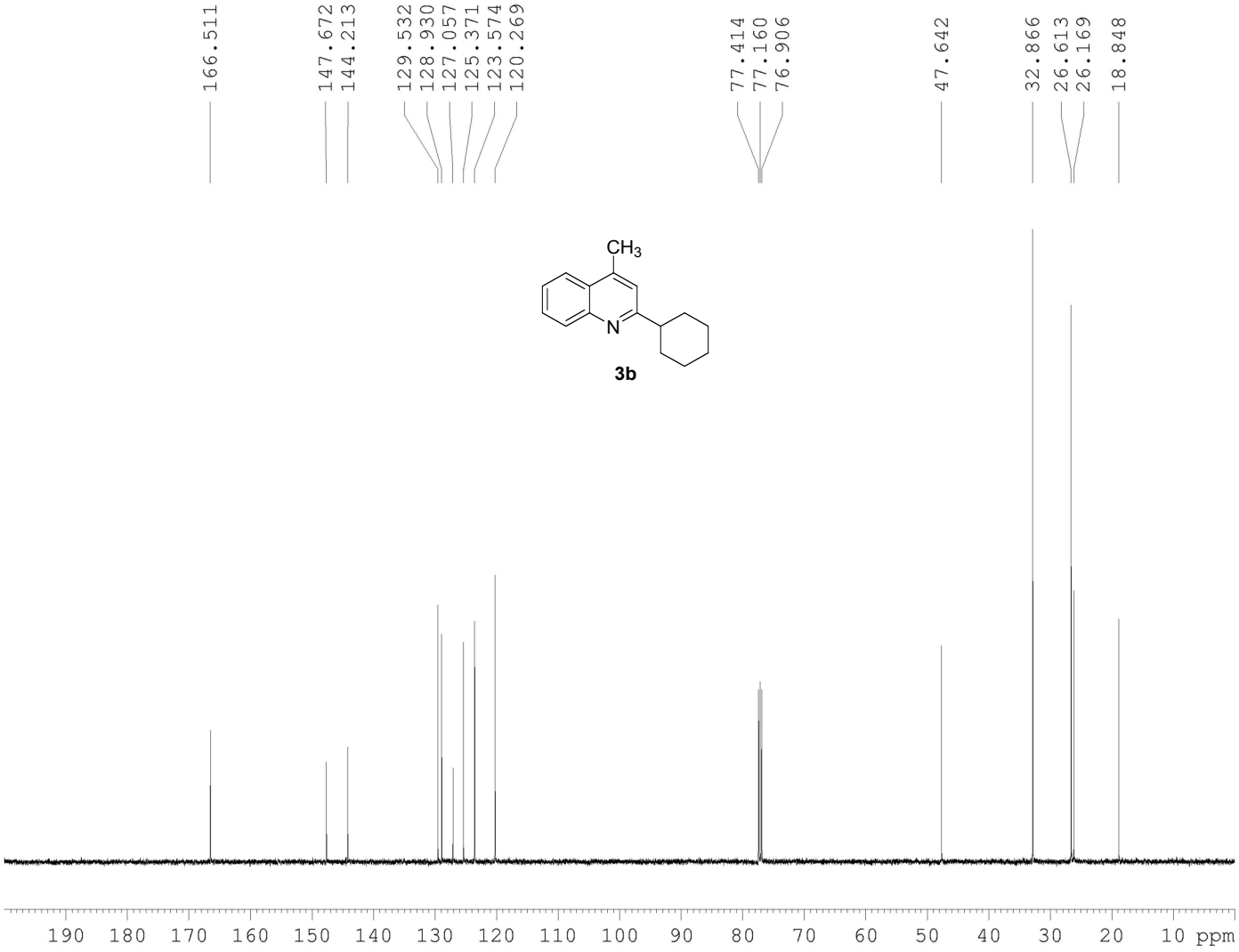
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-cyclopentyl-4-methylquinoline 3**a**
(Table 3, entry 1)



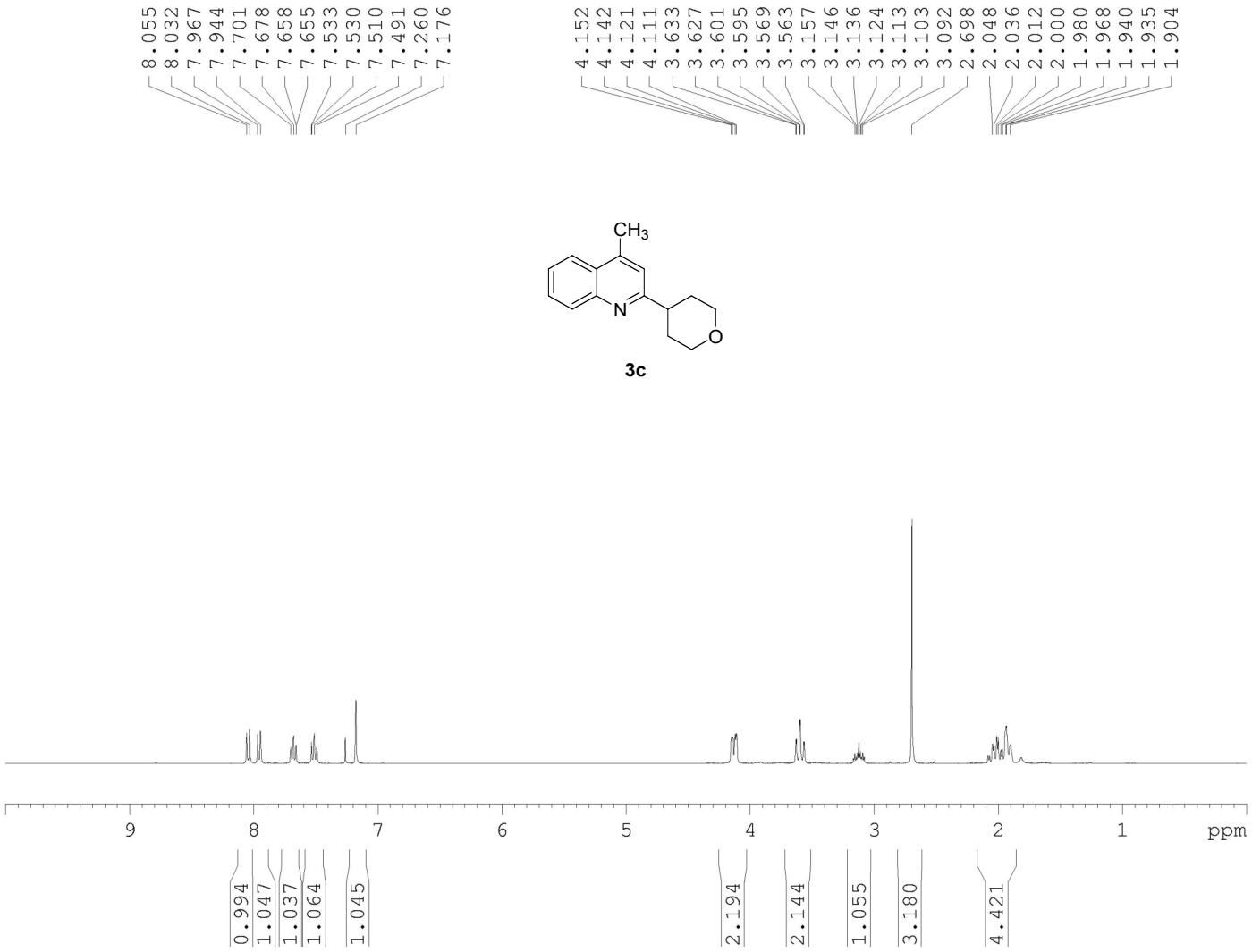
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum 2-cyclopentyl-4-methylquinoline 3**a**
(Table 3, entry 1)



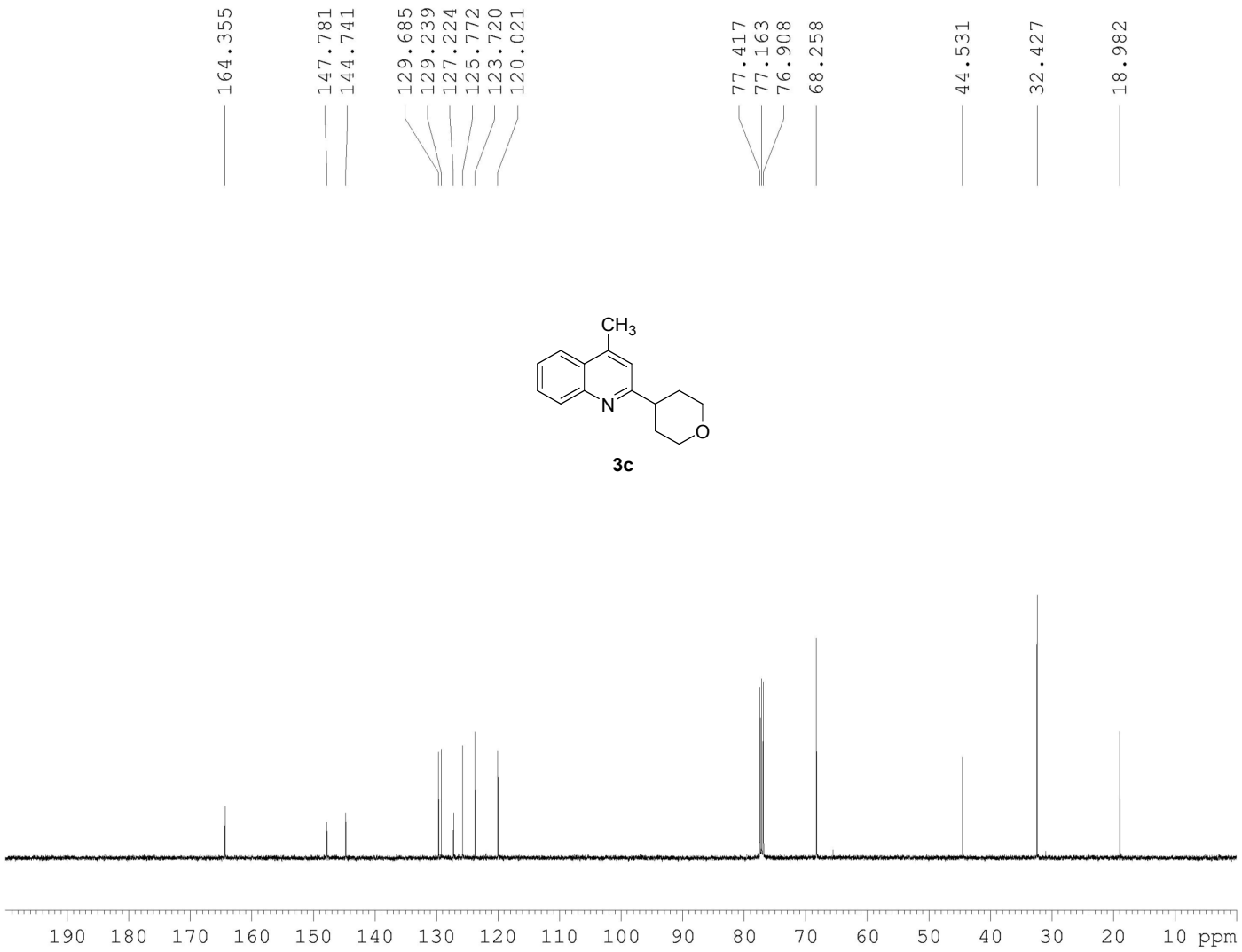
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-cyclohexyl-4-methylquinoline 3**b**
(Table 3, entry 2)



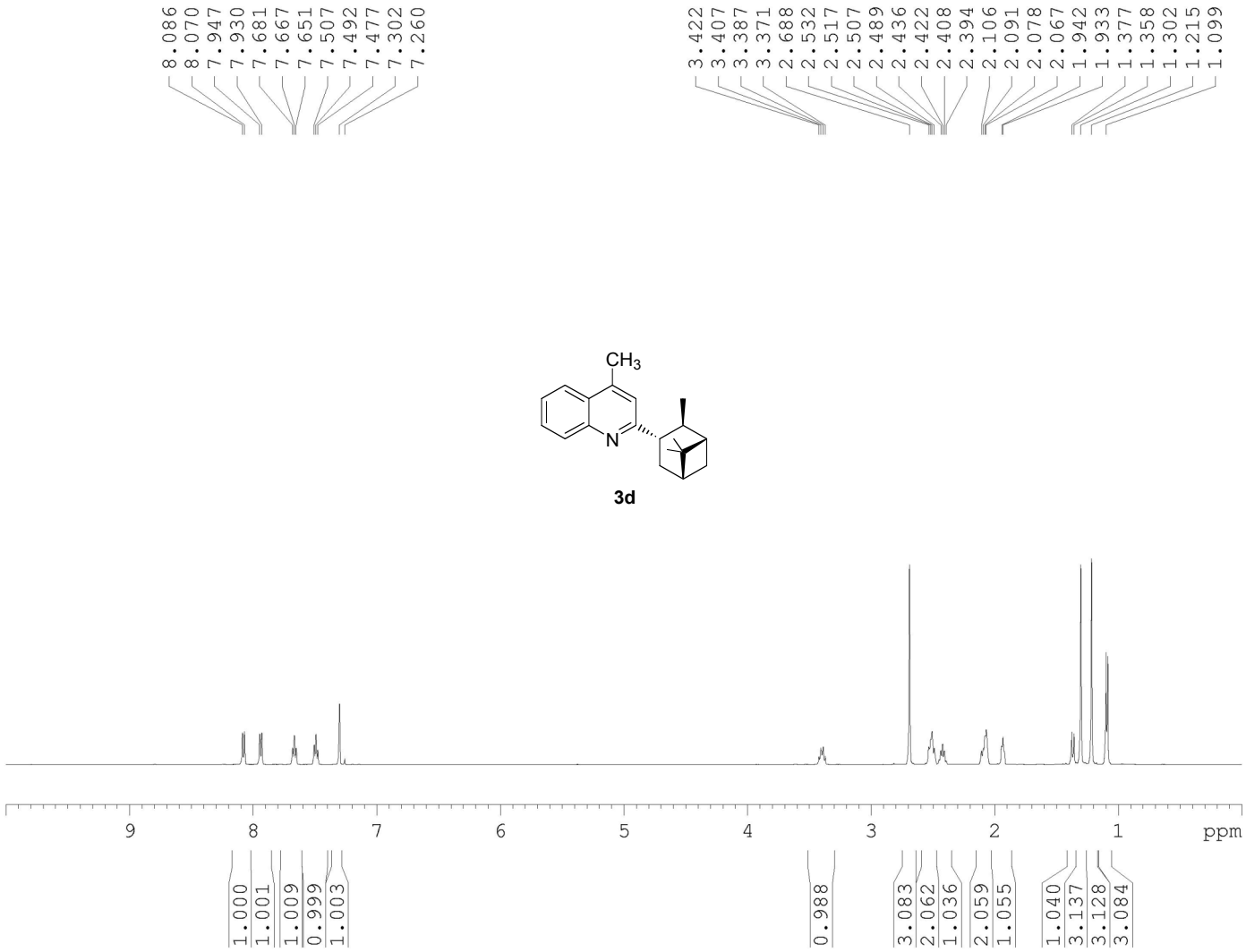
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-cyclohexyl-4-methylquinoline **3b**
(Table 3, entry 2)



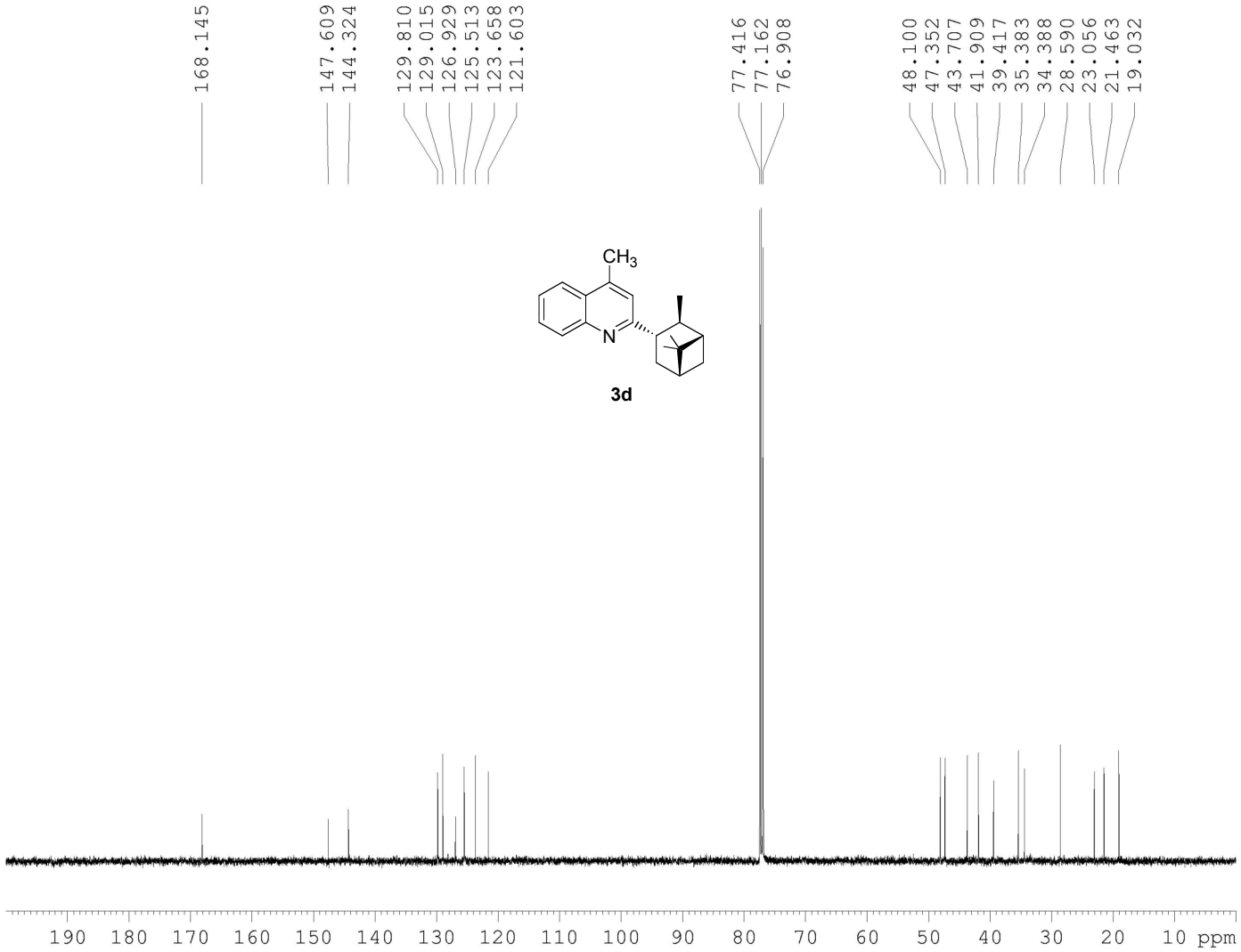
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinoline **3c**
(Table 3, entry 3)



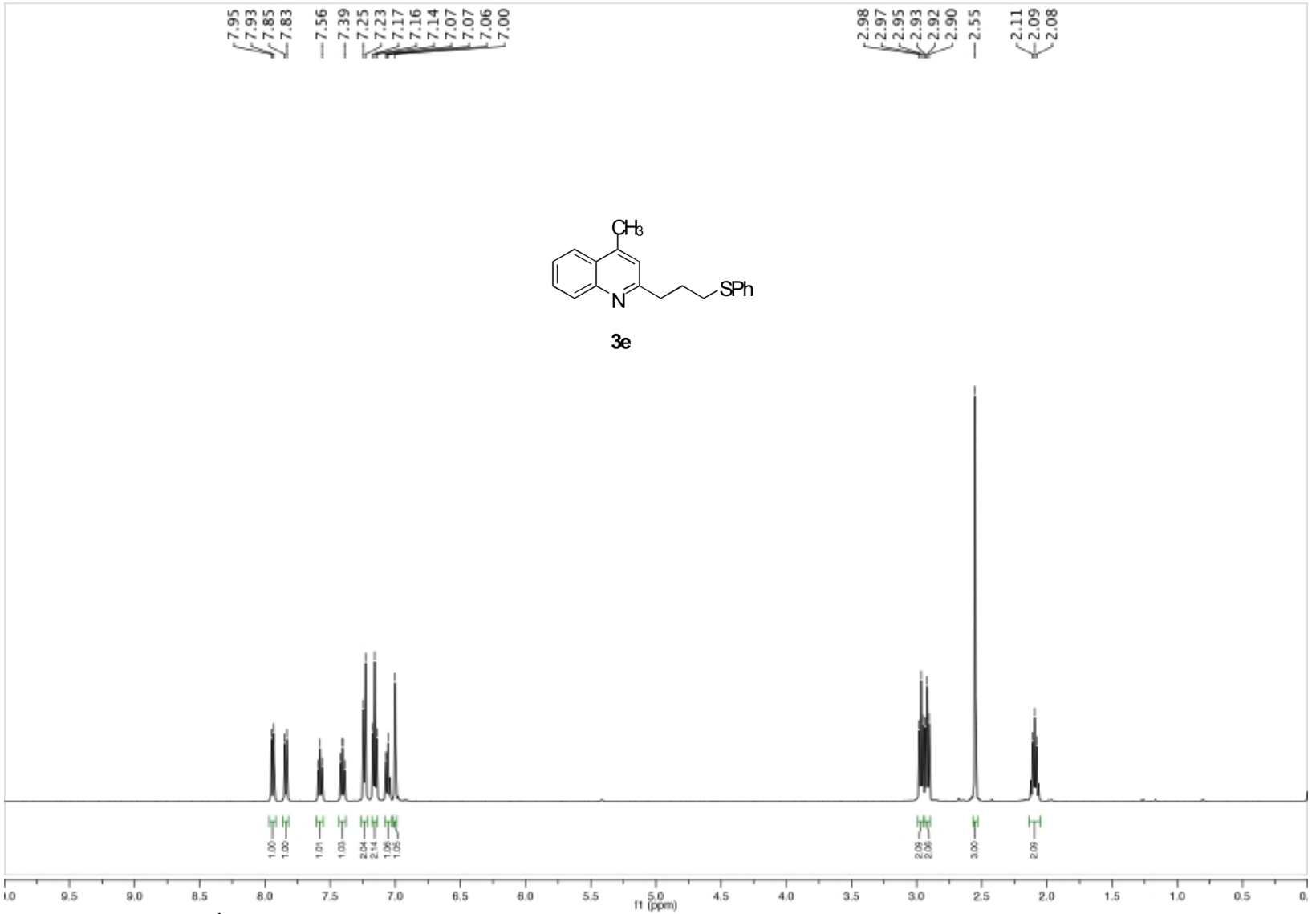
4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinoline **3c**
(Table 3, entry 3)



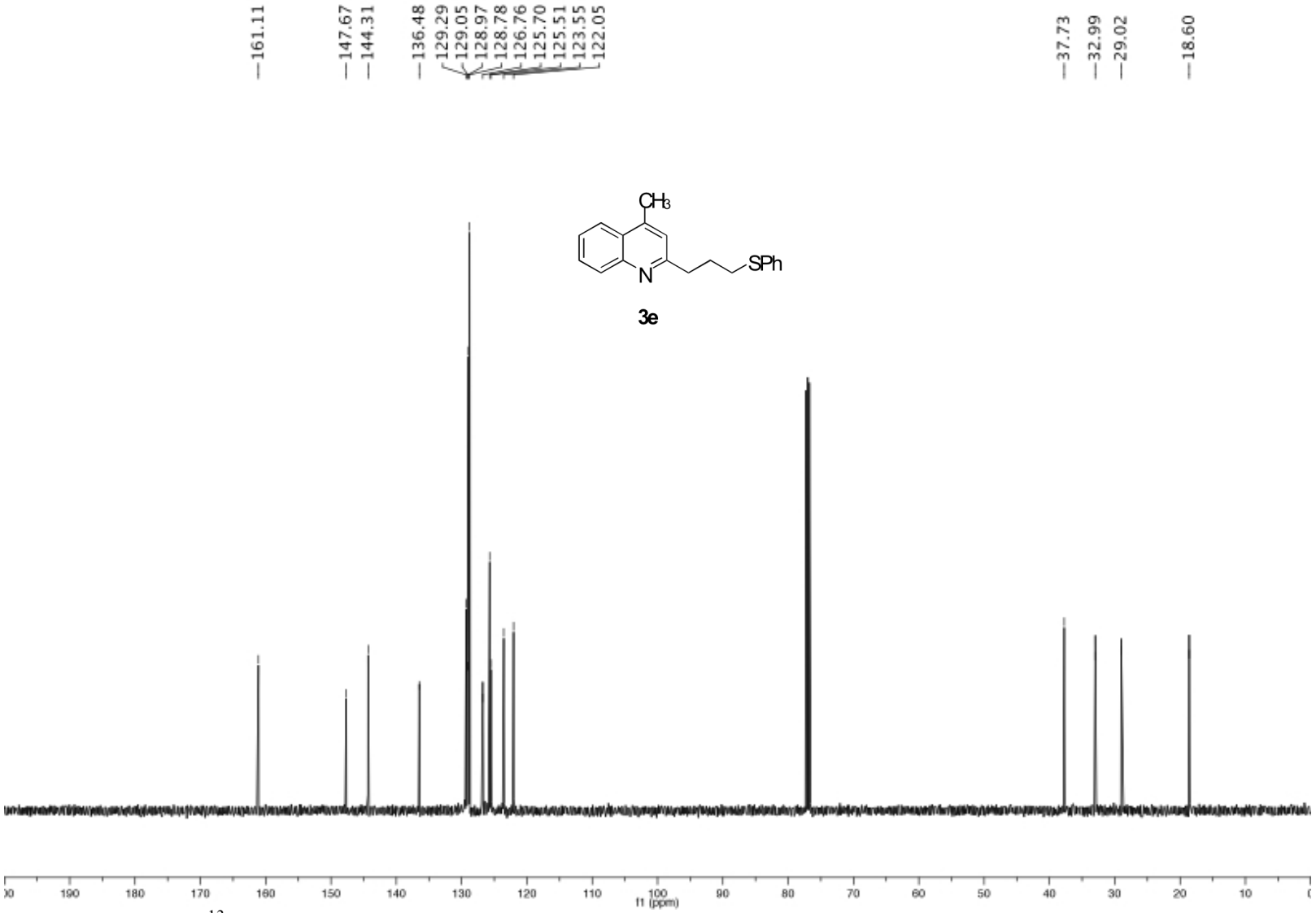
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 4-methyl-2-((1*S*,2*S*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)quinoline **3d** (Table 3, entry 4)



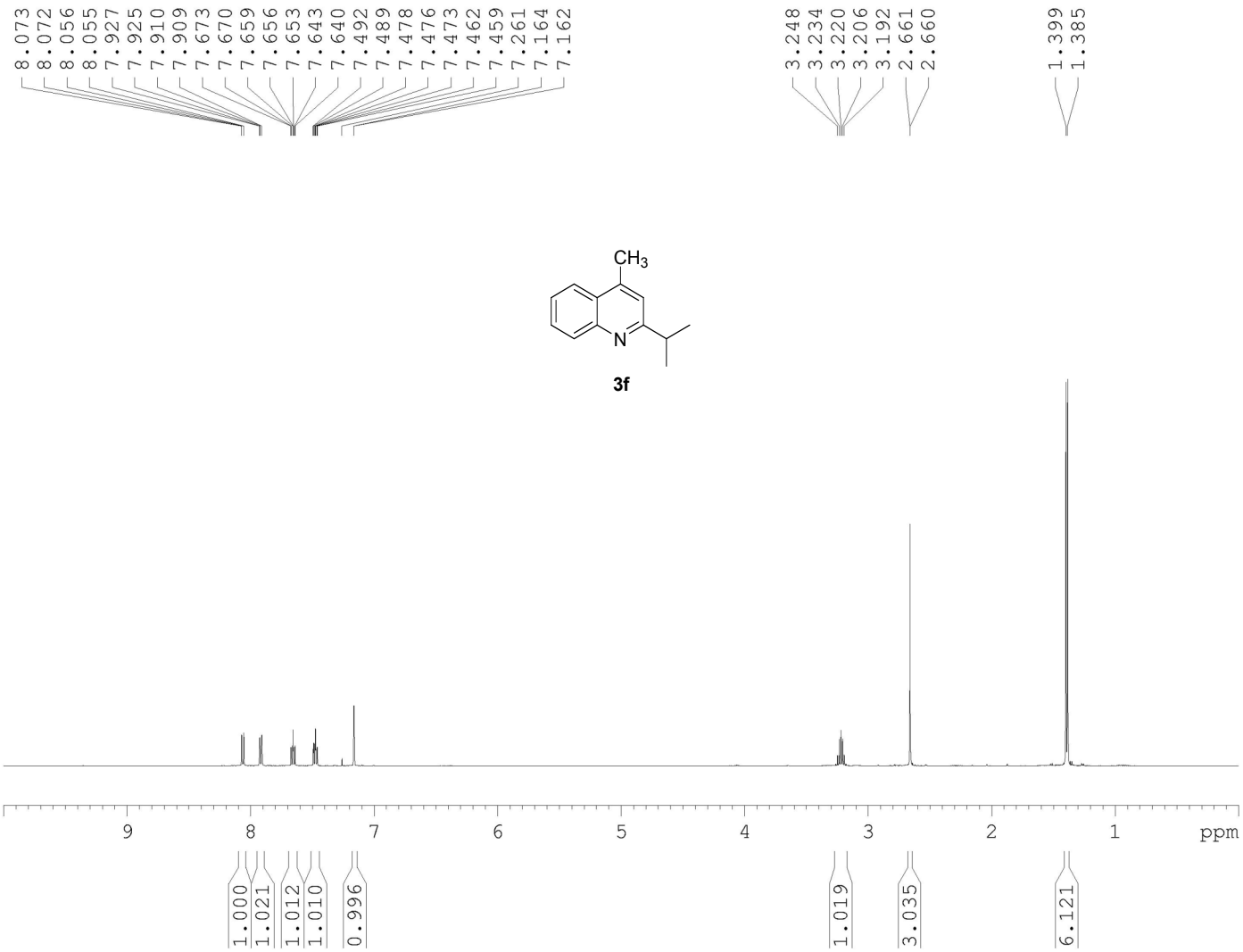
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-methyl-2-((1*S*,2*S*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)quinoline **3d** (Table 3, entry 4)



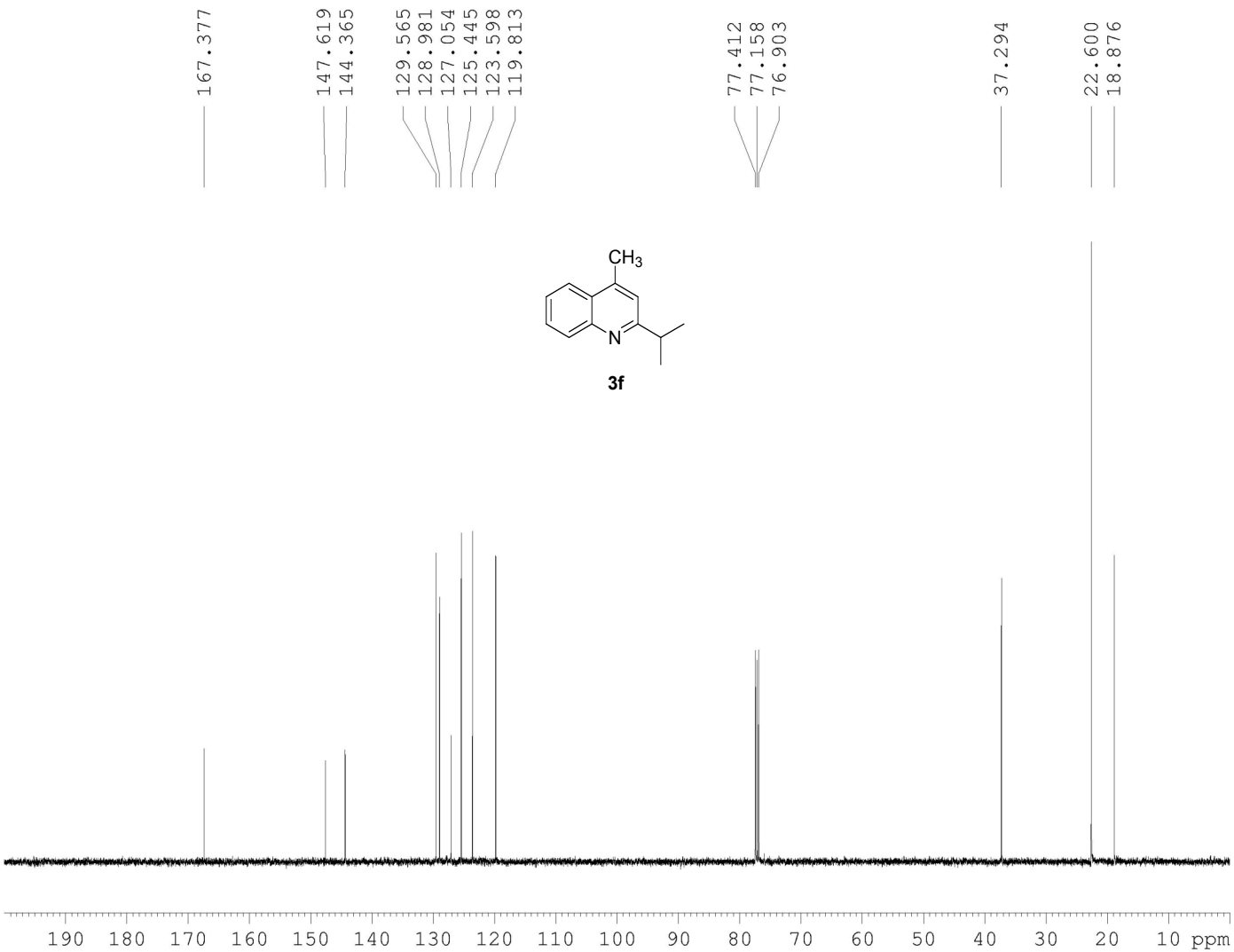
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-(3-phenylthio)propyl)-4-methylquinoline **3e**
(Table 3, entry 5)



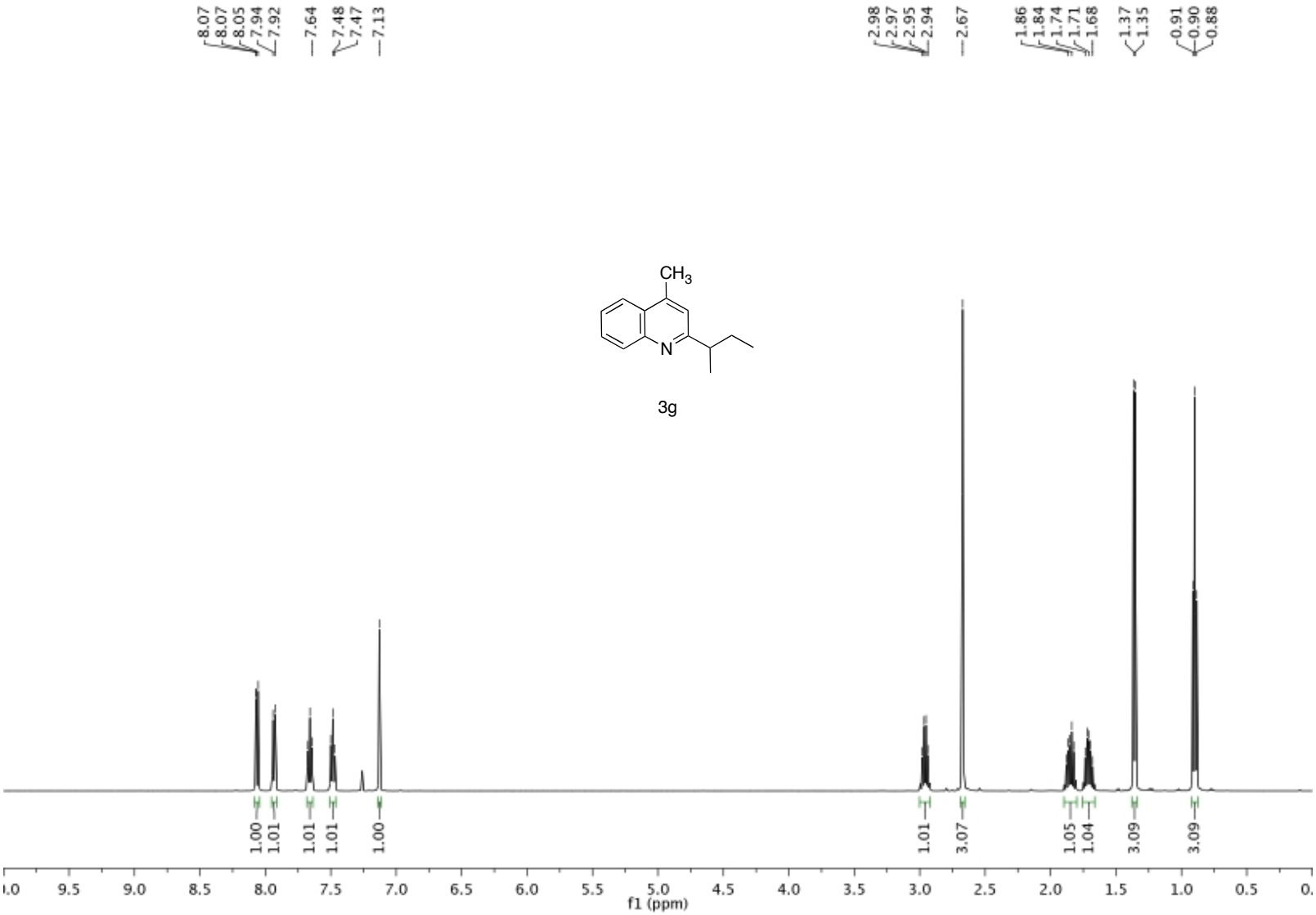
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum 2-(3-phenylthio)propyl)-4-methylquinoline **3e**
(Table 3, entry 5)



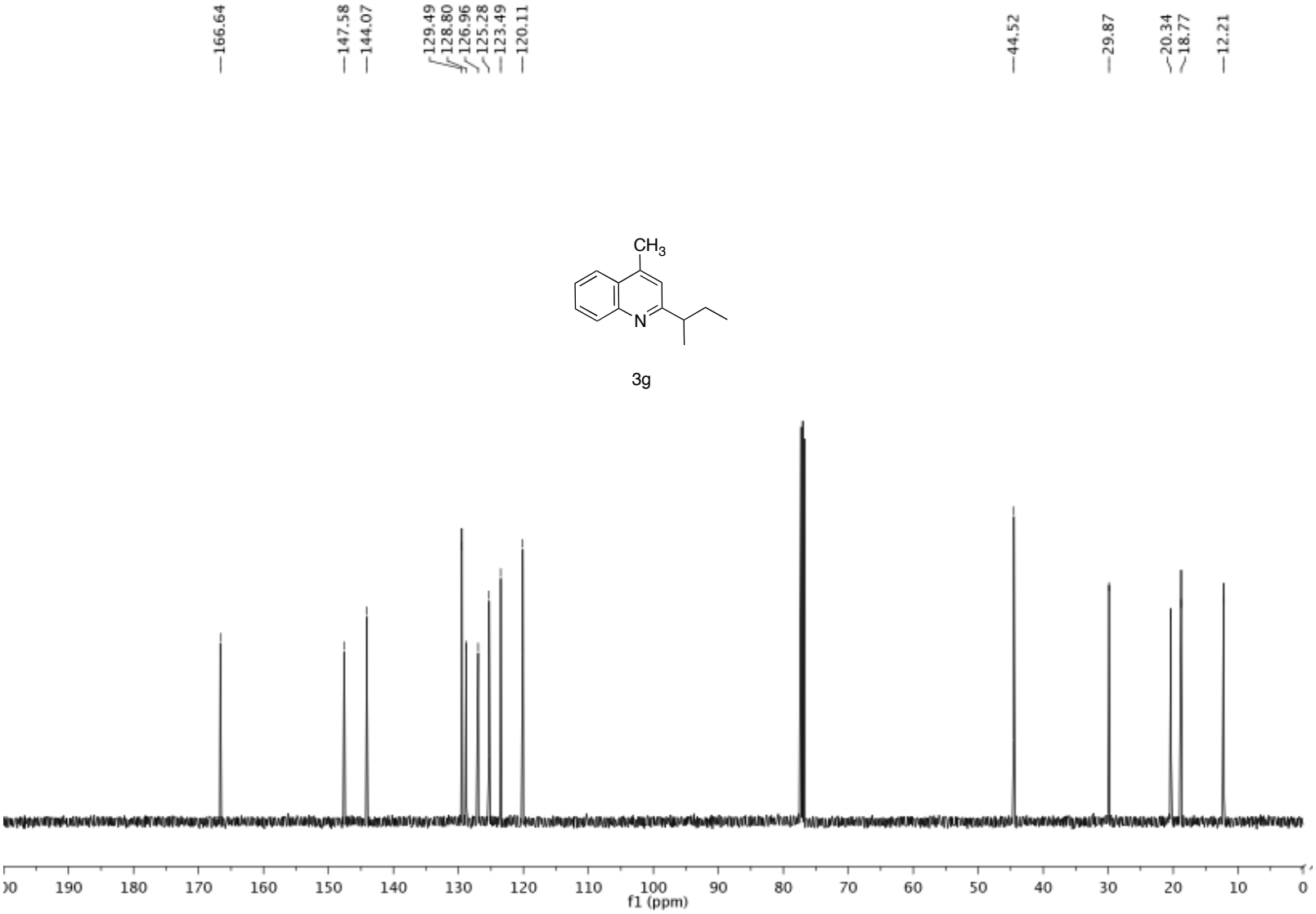
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-isopropyl-4-methylquinoline **3f**
(Table 3, entry 6)



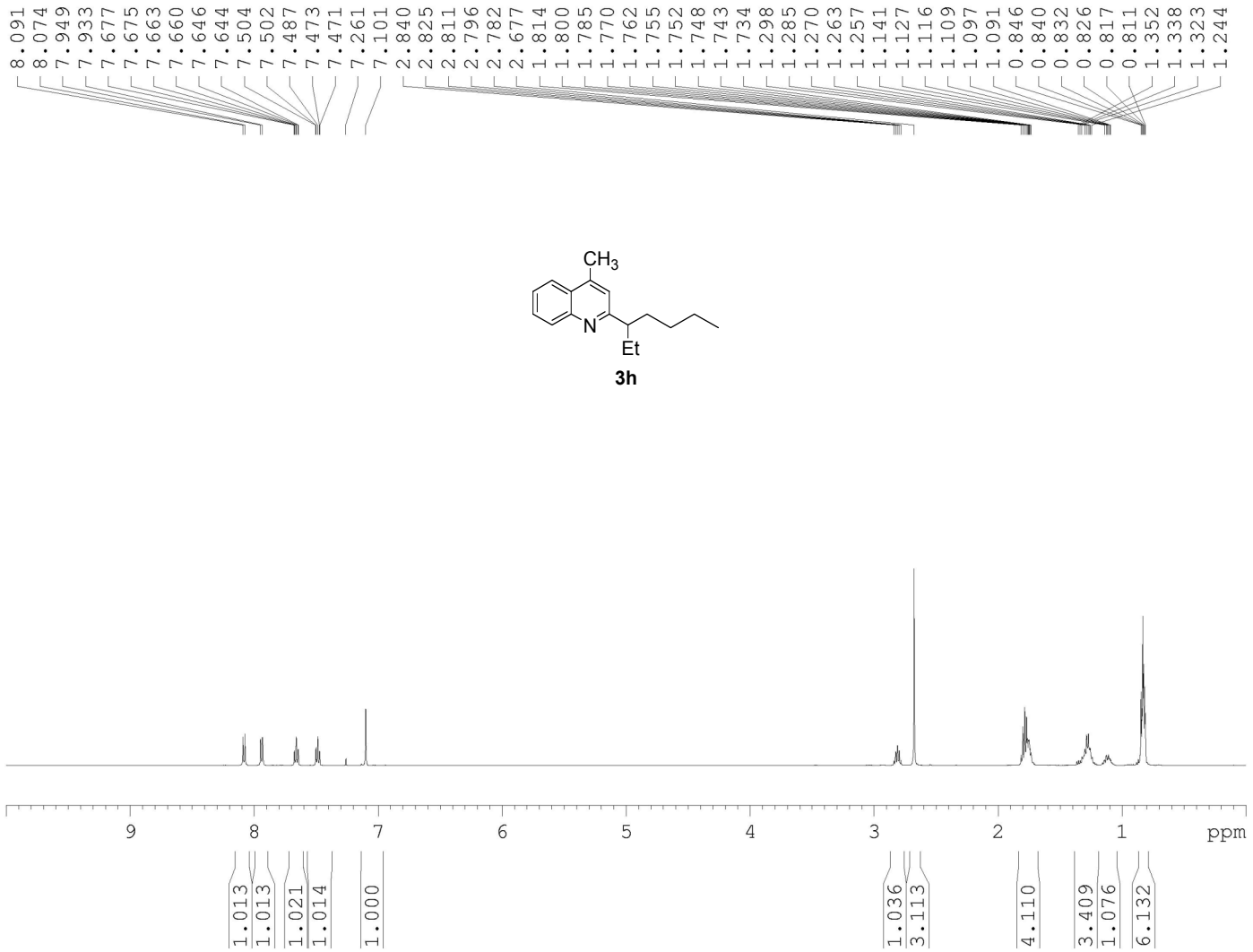
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-isopropyl-4-methylquinoline **3f**
(Table 3, entry 6)



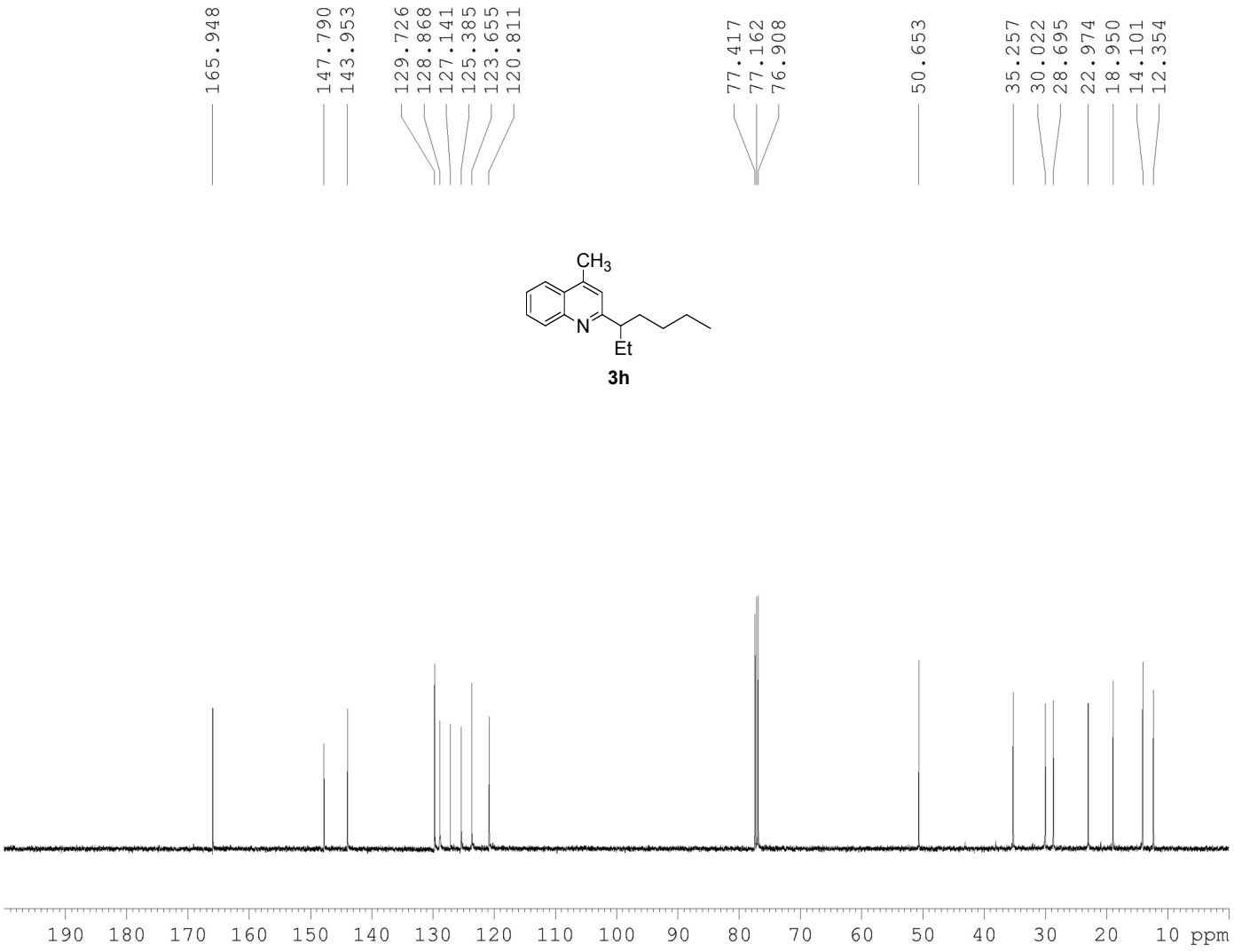
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-*sec*-butyl-4-methylquinoline **3g**
(Table 3, entry 7)



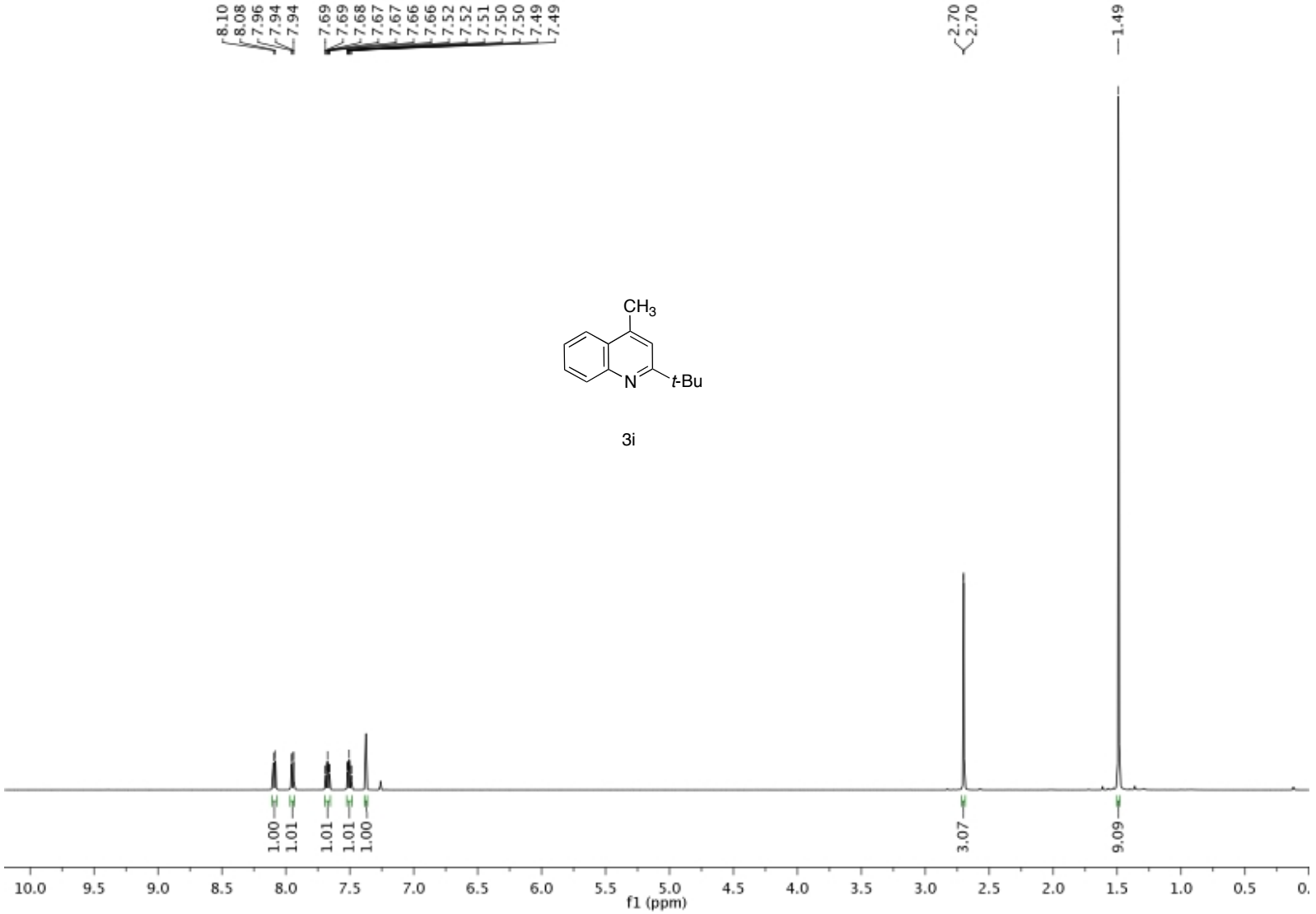
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-*sec*-butyl-4-methylquinoline **3g**
(Table 3, entry 7)



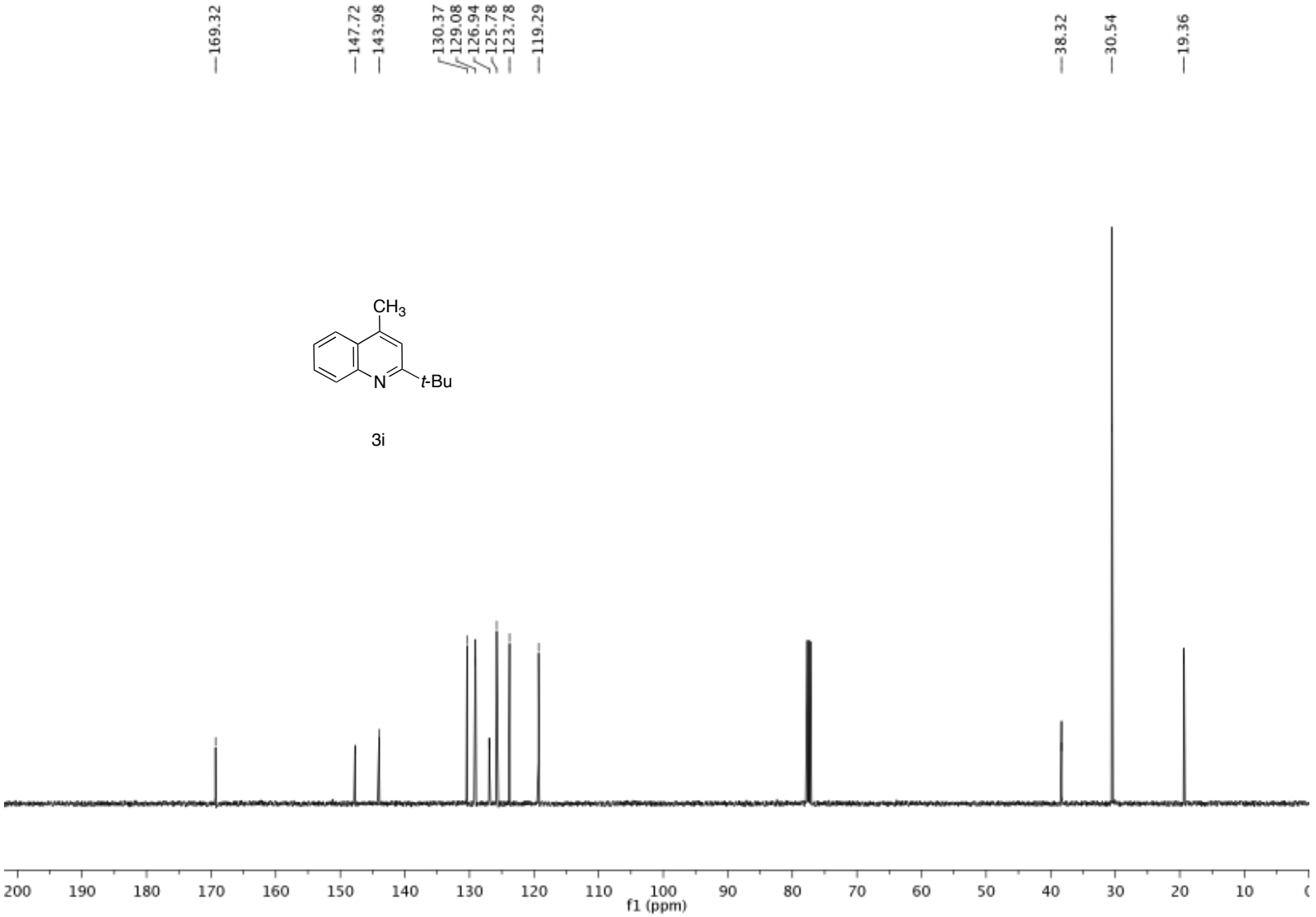
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-(heptan-3-yl)-4-methylquinoline **3h**
(Table 3, entry 8)



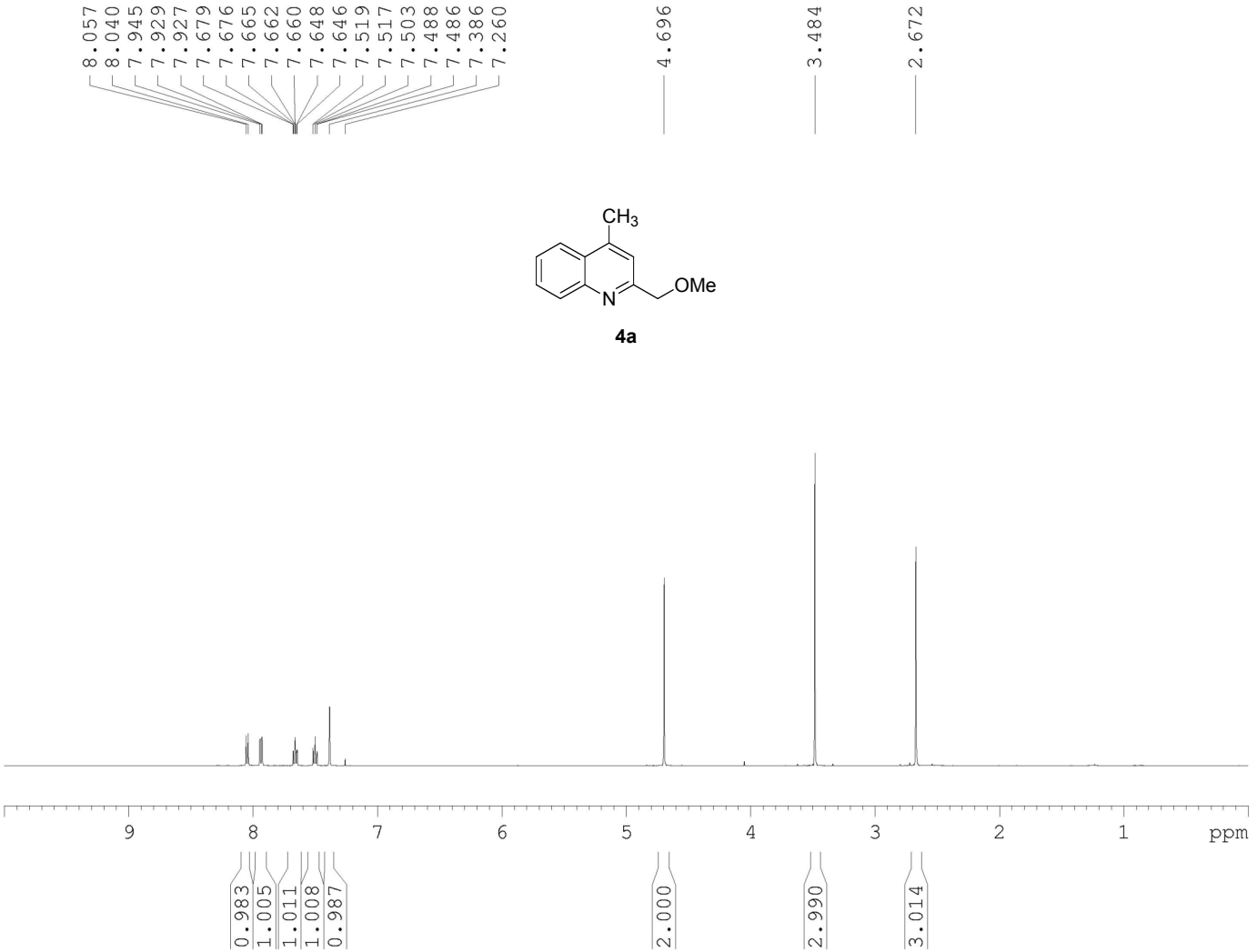
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of Spectrum 2-(heptan-3-yl)-4-methylquinoline **3h**
(Table 3, entry 8)



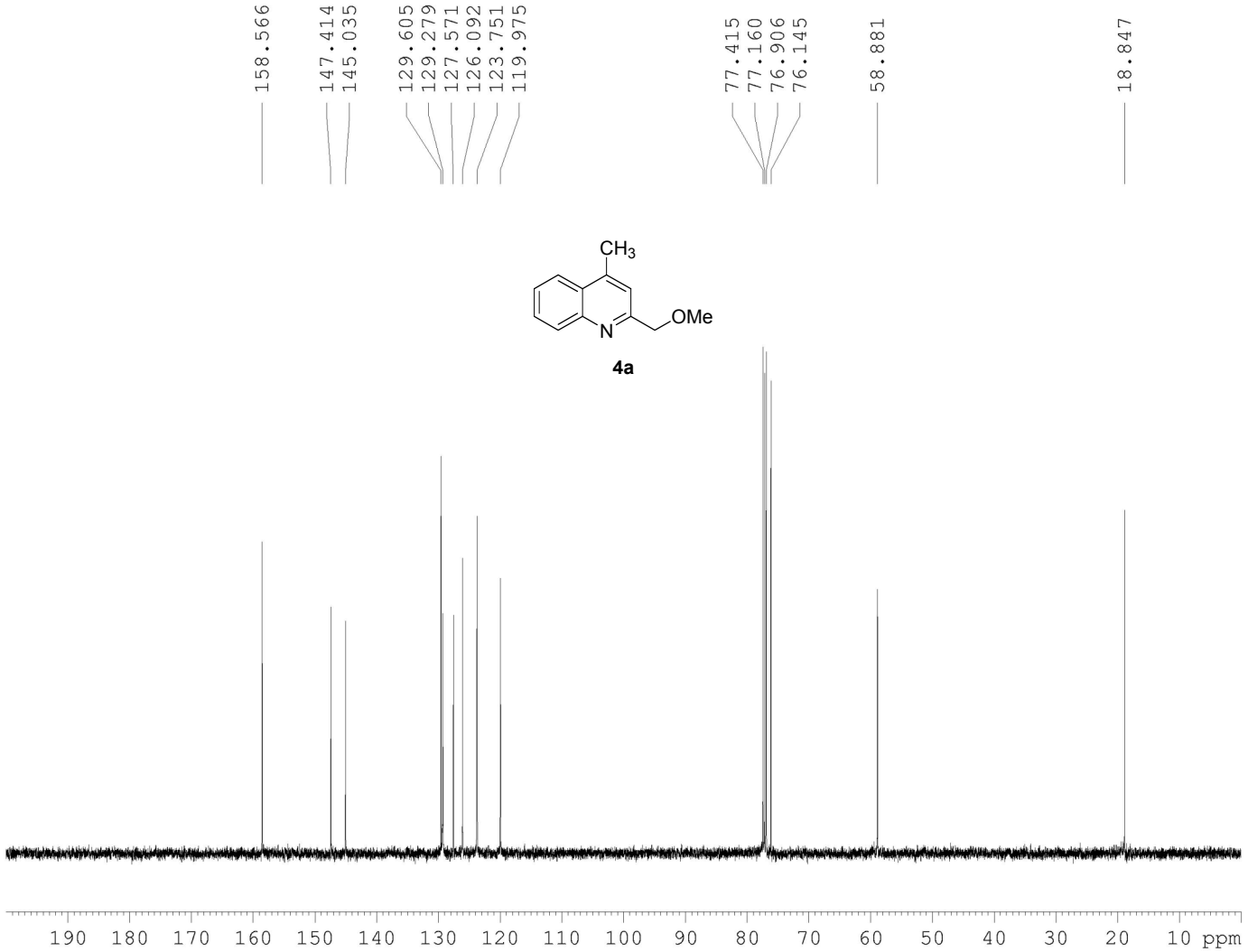
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-*tert*-butyl-4-methylquinoline **3i**
(Table 3, entry 8)



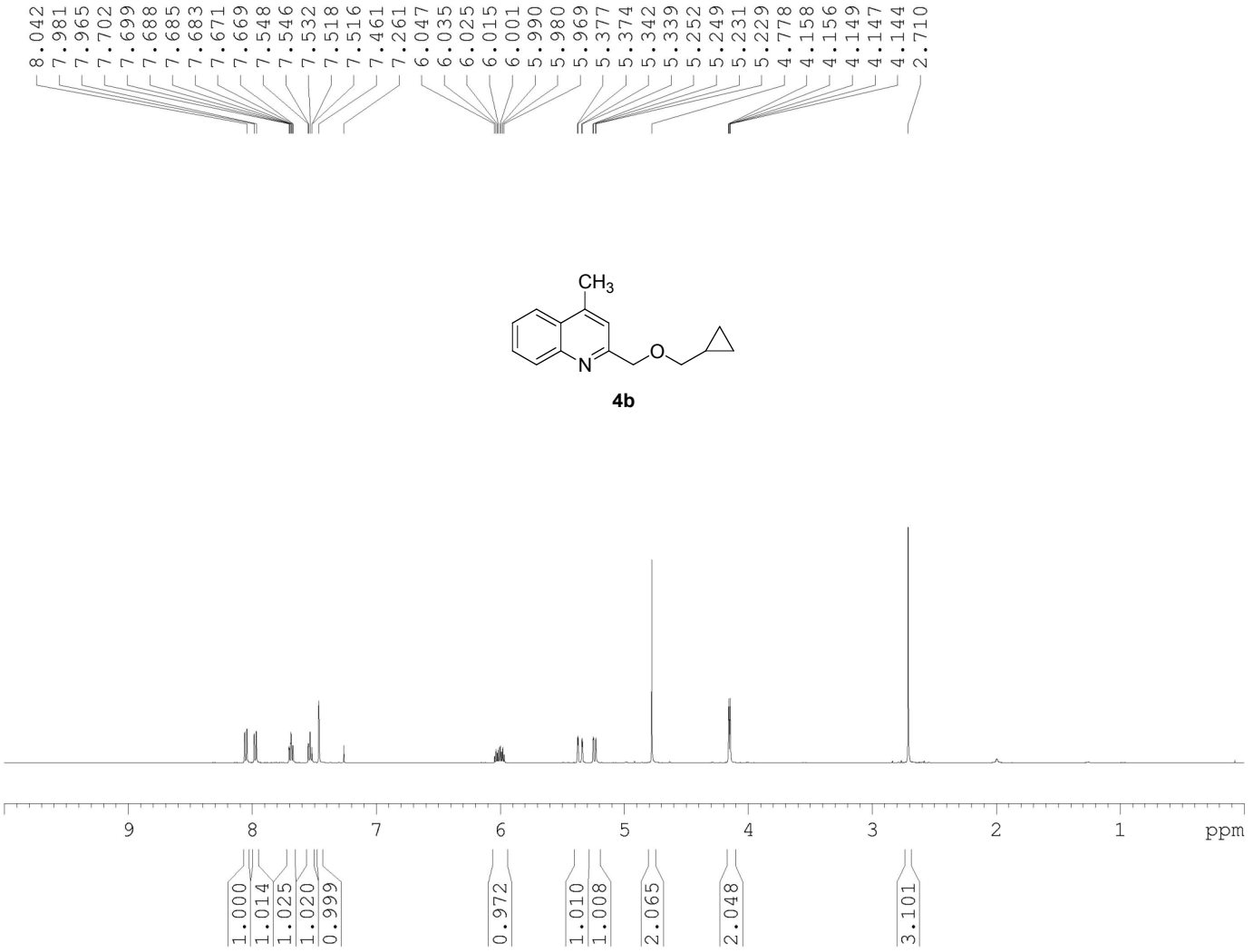
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-*tert*-butyl-4-methylquinoline **3i**
(Table 3, entry 8)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-(methoxymethyl)-4-methylquinoline **4a**
(Table 4, entry 1)

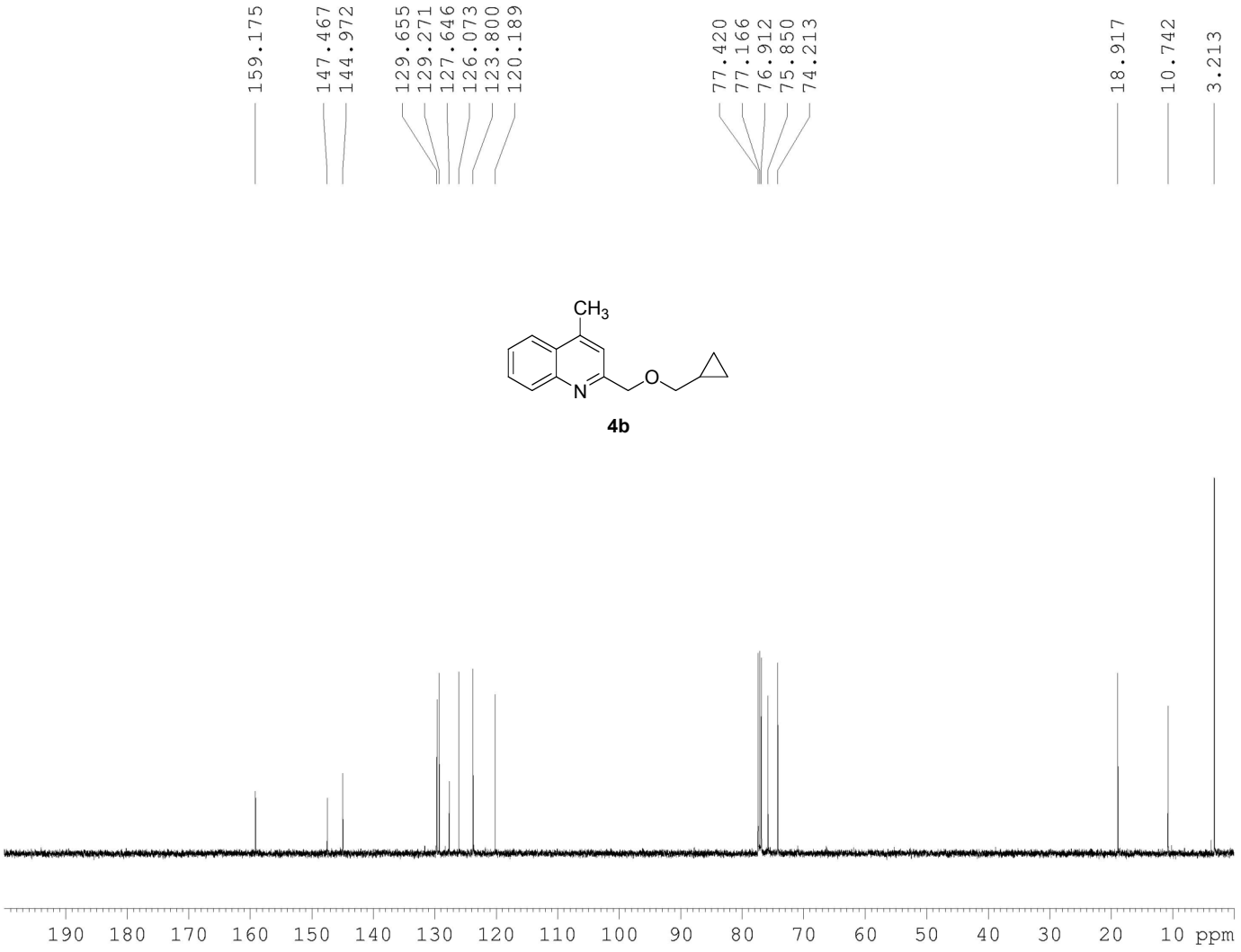


^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-(methoxymethyl)-4-methylquinoline **4a**
(Table 4, entry 1)

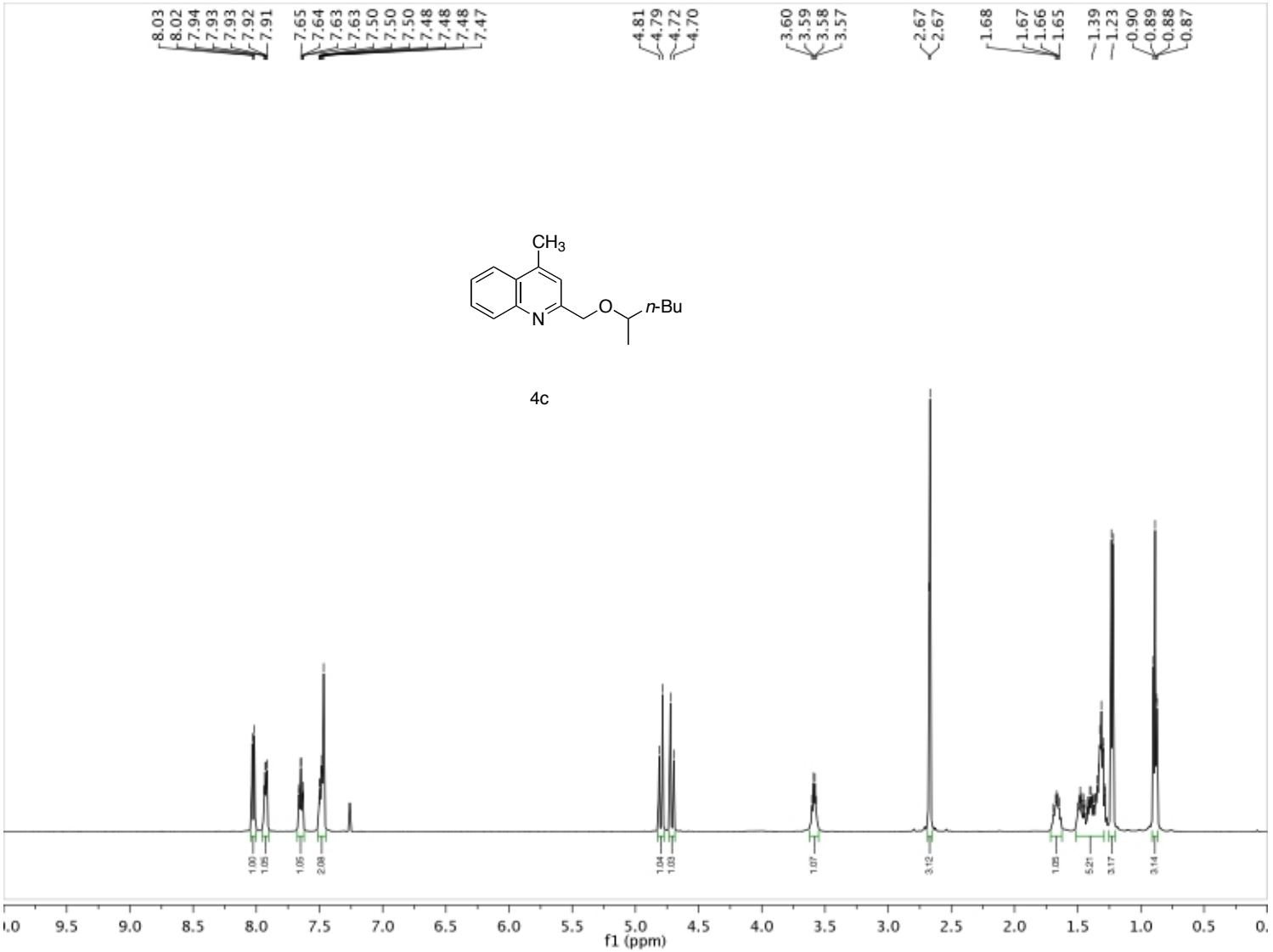


4b

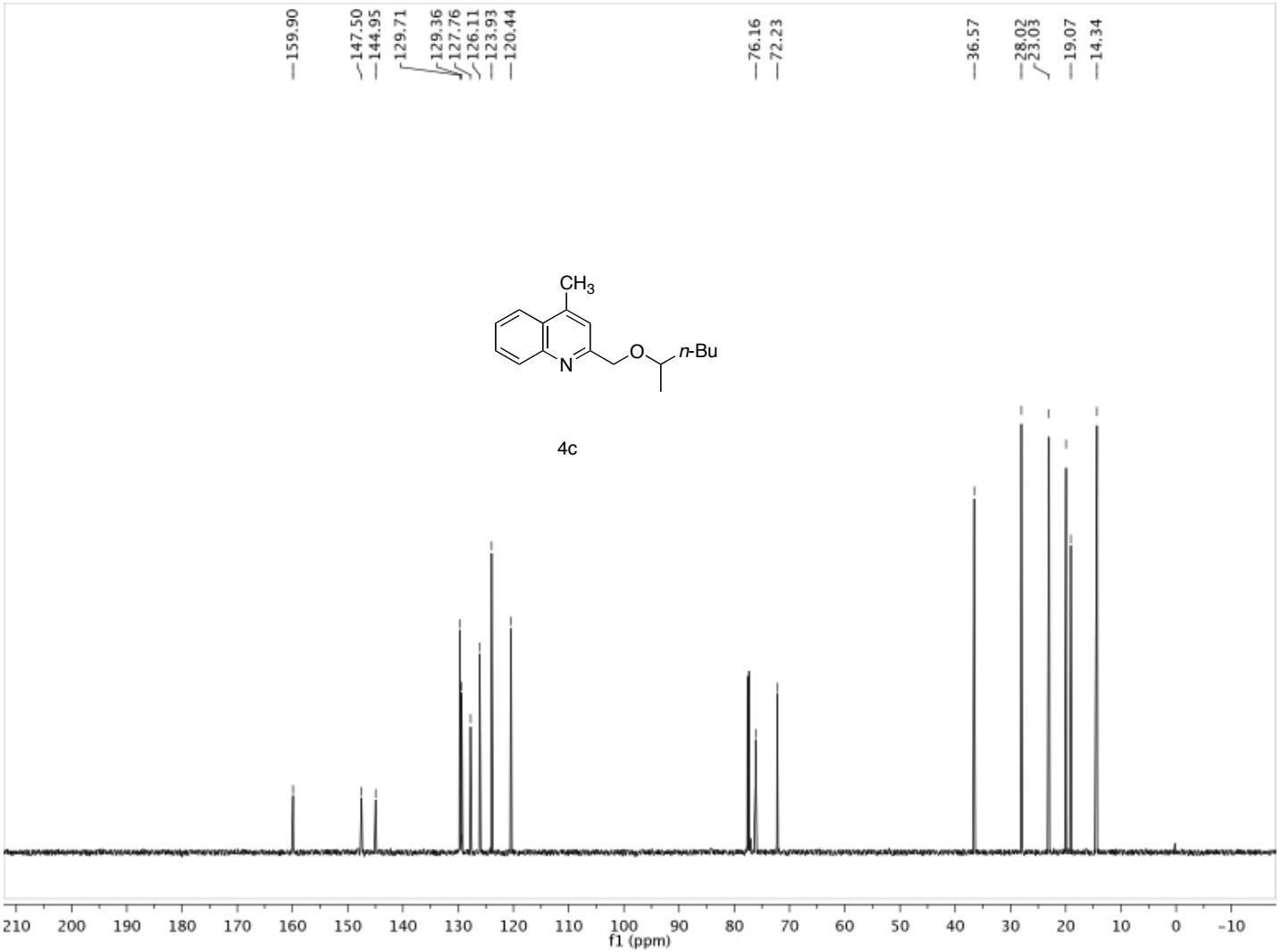
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-((cyclopropylmethoxy)methyl)-4-methylquinoline **4b**
(Table 4, entry 2)



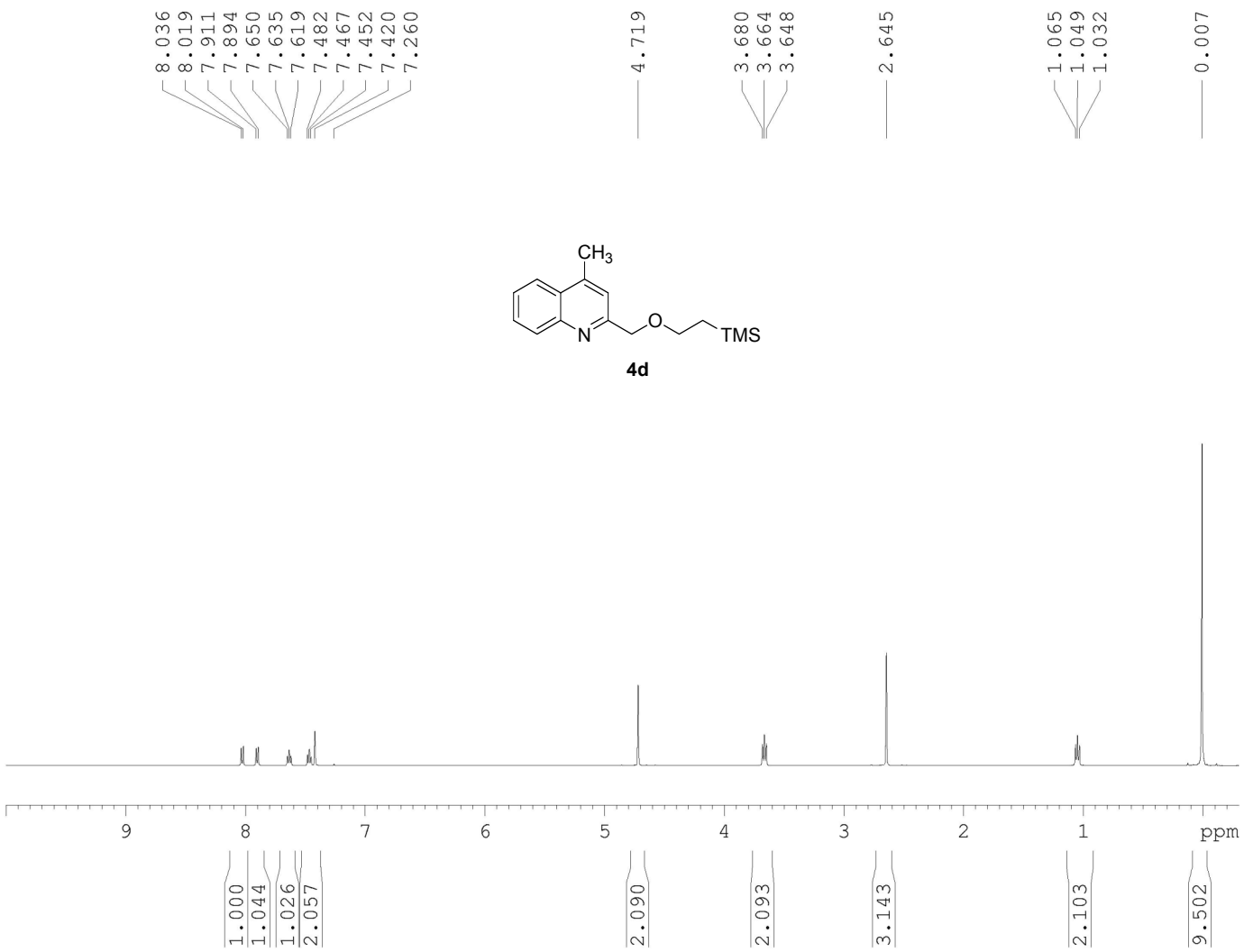
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-(heptan-3-yl)-4-methylquinoline **4b**
(Table 4, entry 2)



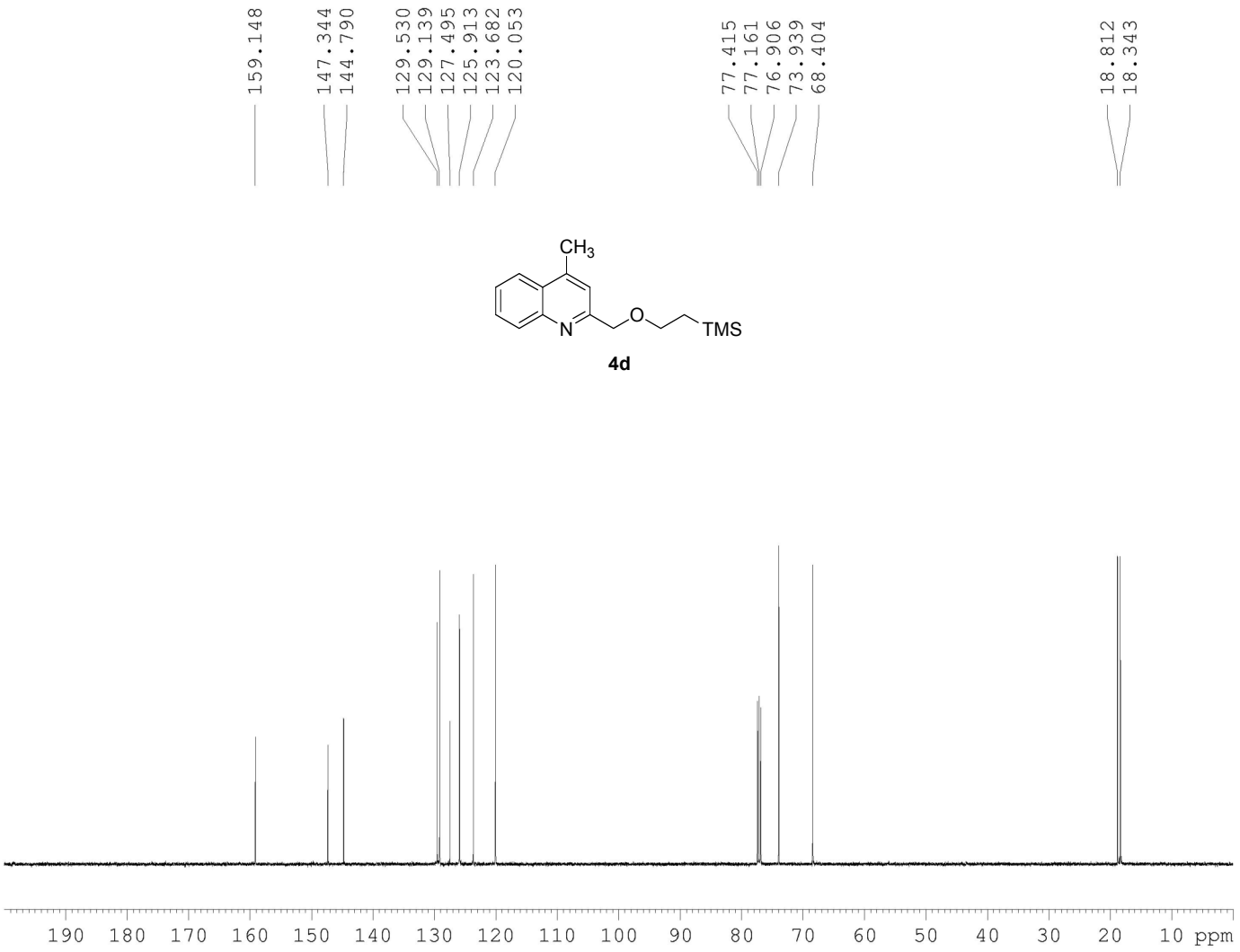
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2-((hexan-2-yloxy))methyl)-4-methylquinoline **4c**
(Table 4, entry 3)



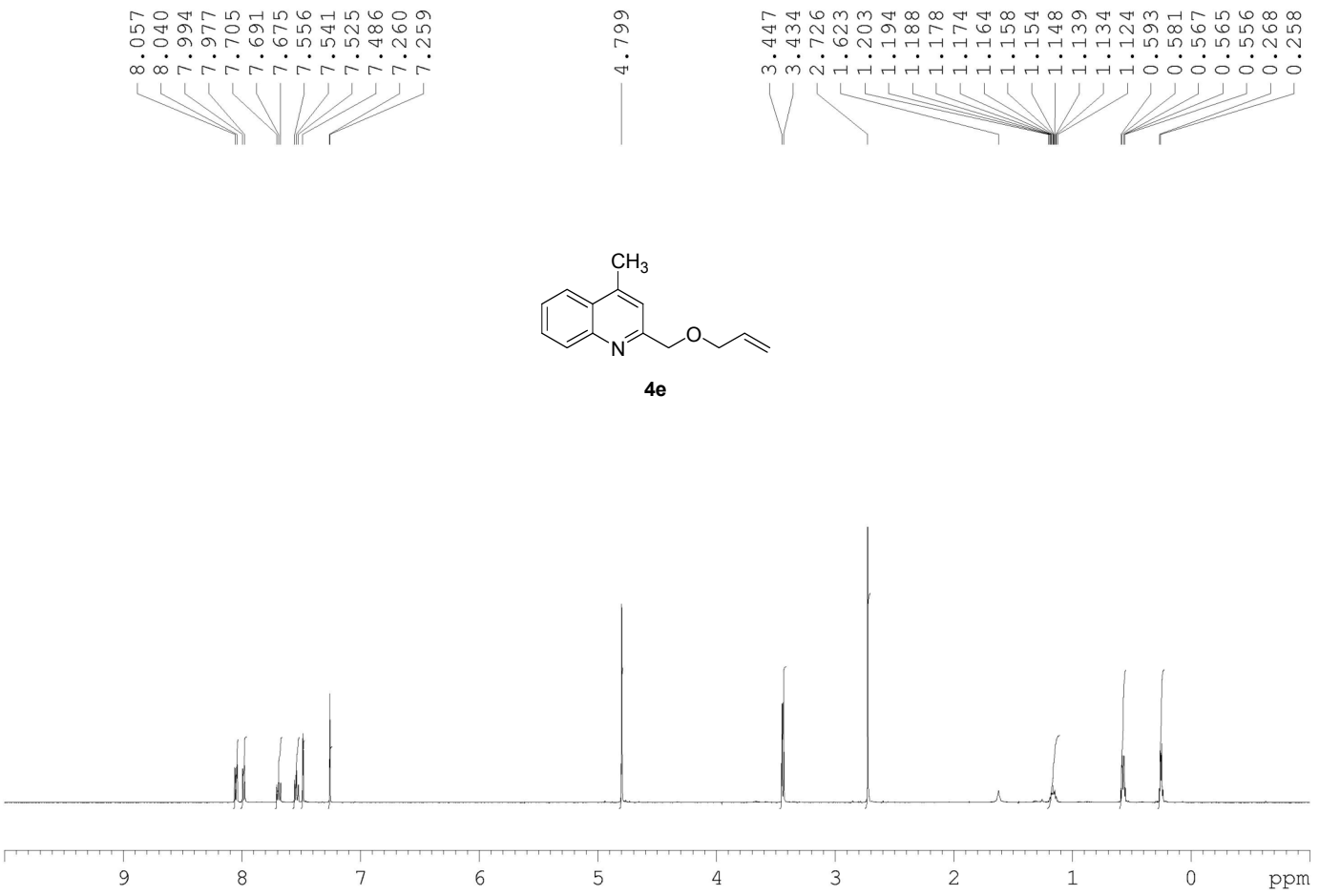
^{13}C NMR (500 MHz, $CDCl_3$) Spectrum of 2-((hexan-2-yloxy))methyl)-4-methylquinoline **4c**
(Table 4, entry 3)



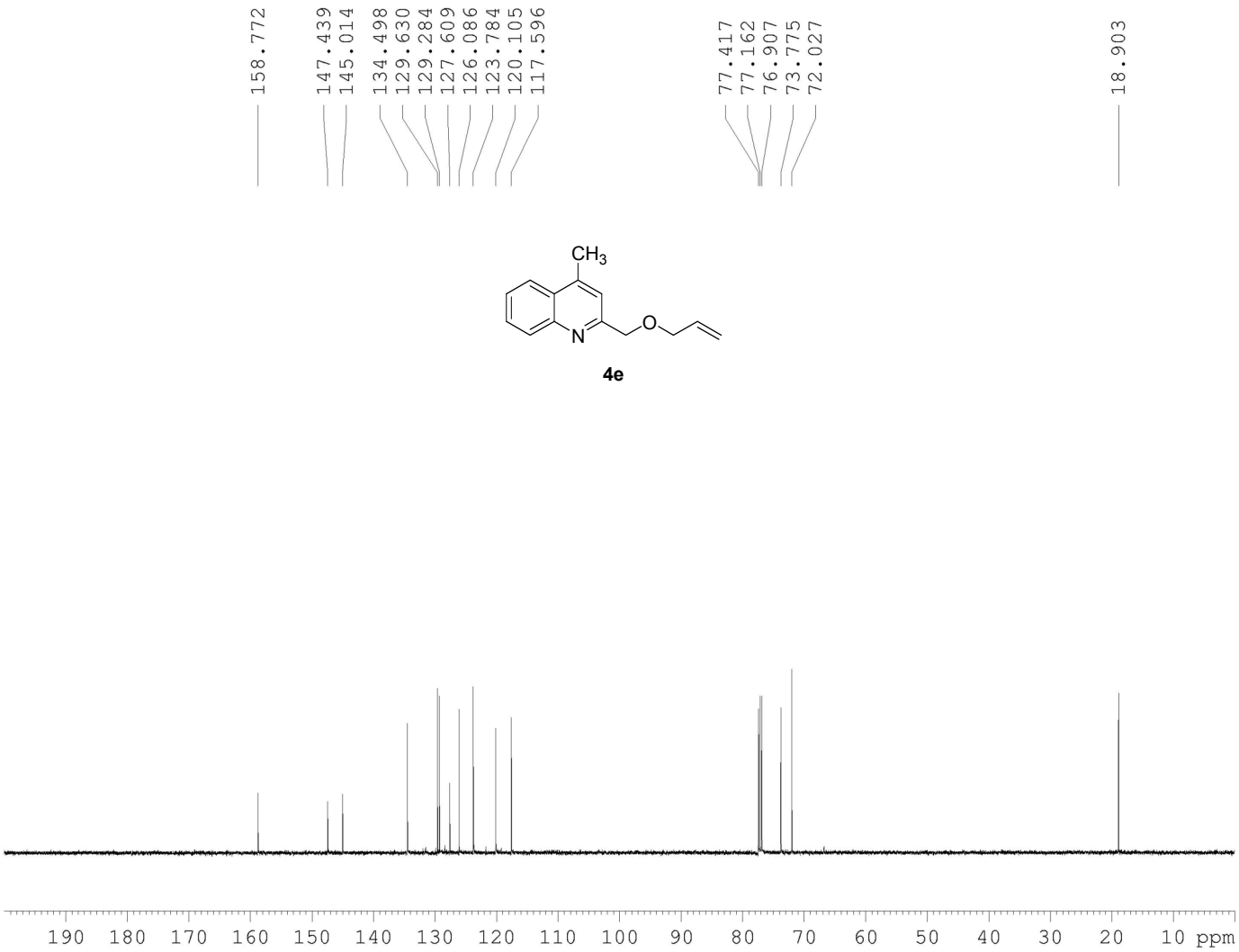
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 4-methyl-2-((2-(trimethylsilyl)ethoxy)methyl)quinoline **4d** (Table 4, entry 4)



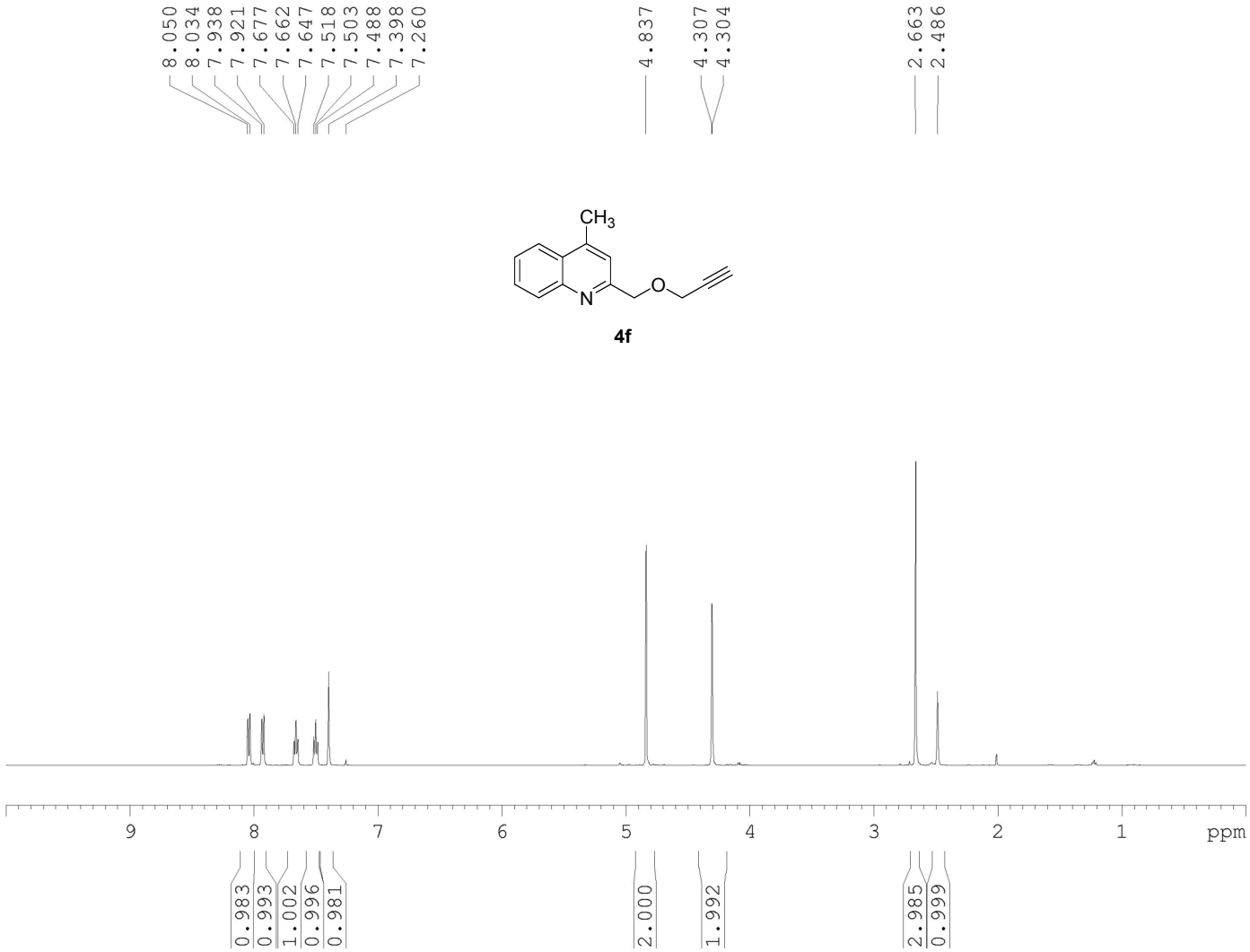
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-methyl-2-((2-(trimethylsilyl)ethoxy)methyl)quinoline **4d** (Table 4, entry 4)



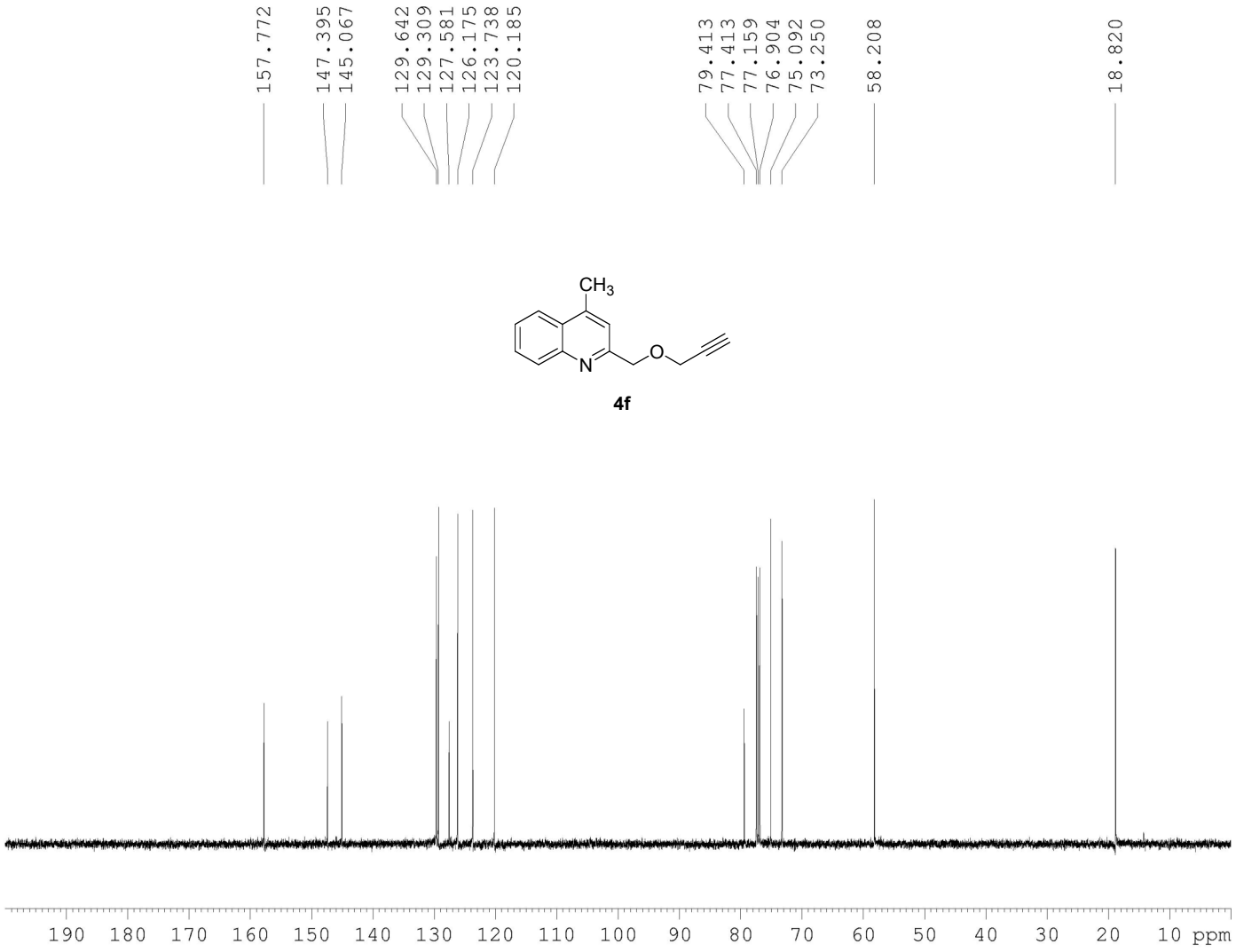
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 2-((allyloxy)methyl)-4-methylquinoline **4e**
(Table 4, entry 5)



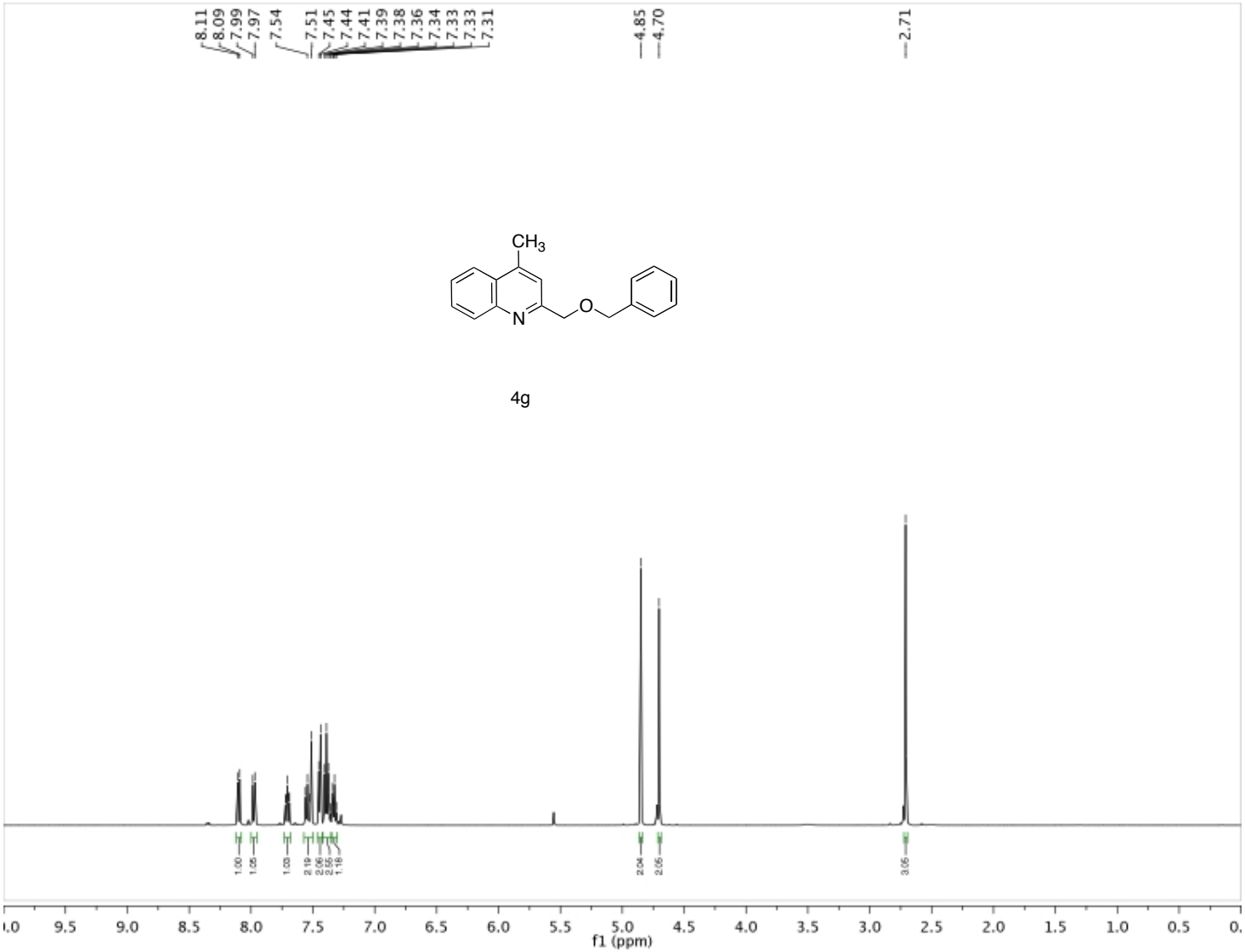
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 2-((allyloxy)methyl)-4-methylquinoline **4e**
(Table 4, entry 5)



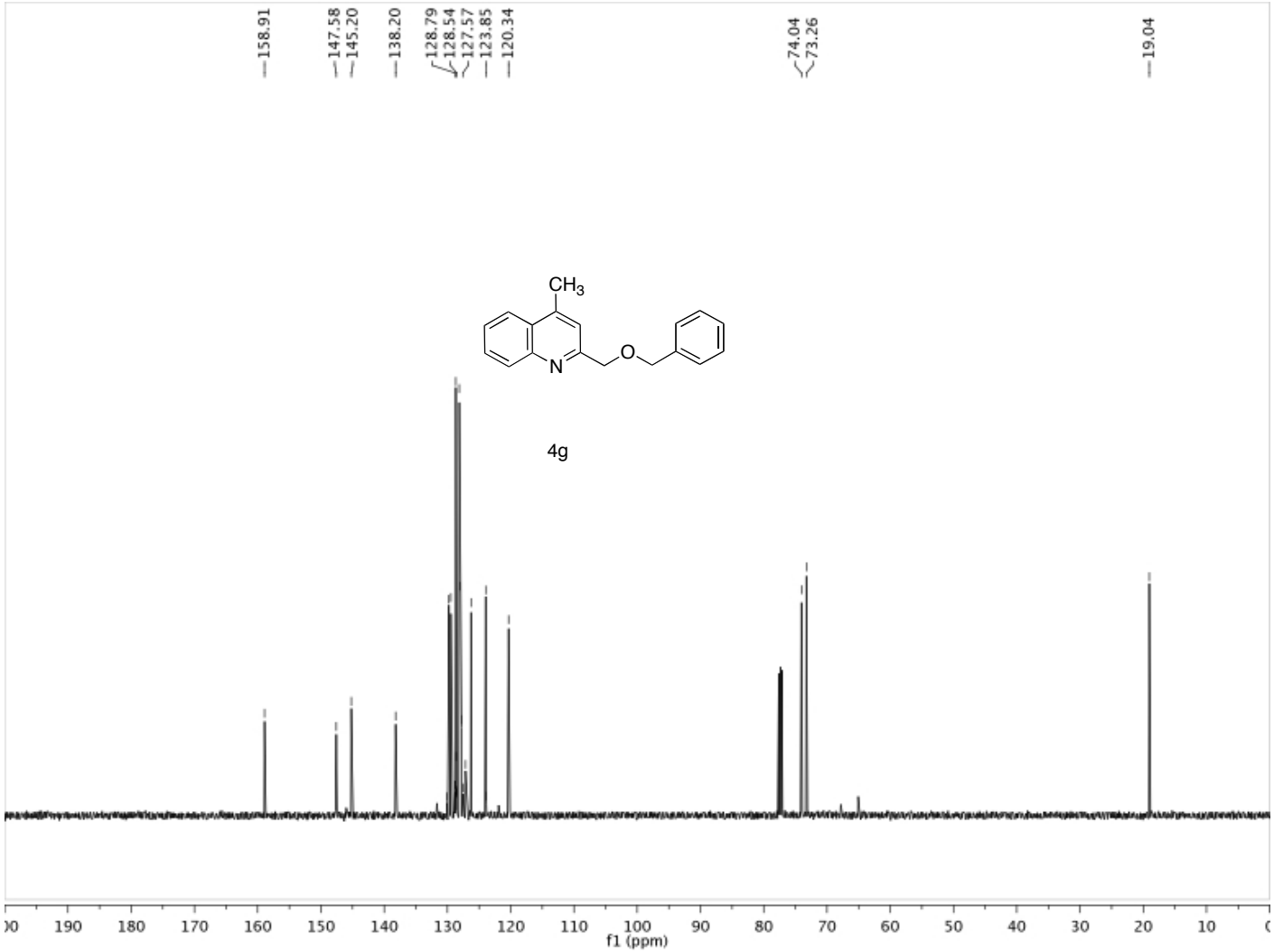
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum 4-methyl-2-((prop-2-yn-1-yloxy)methyl)quinoline **4f**
(Table 4, entry 6)



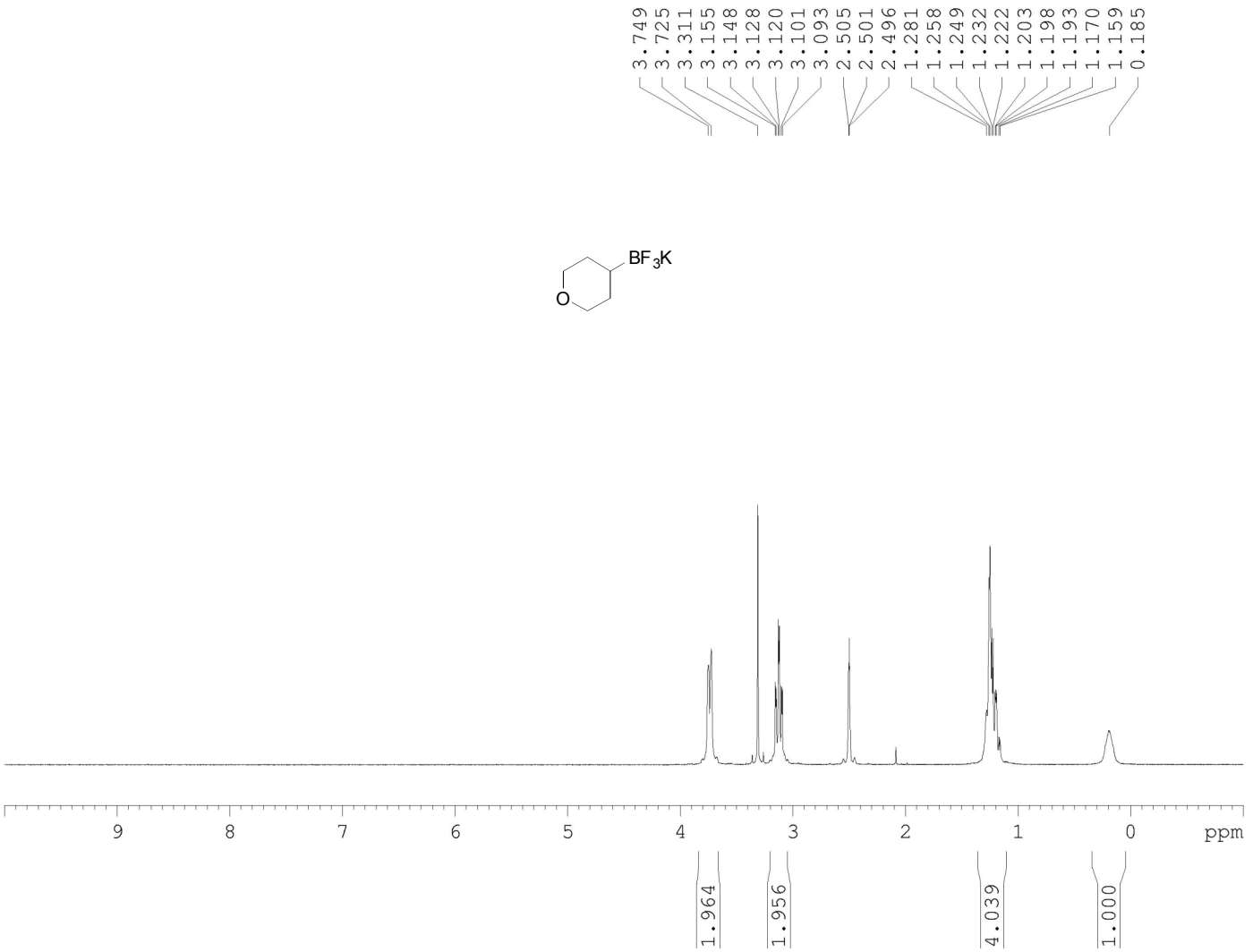
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-methyl-2-((prop-2-yn-1-yloxy)methyl)quinoline **4f**
(Table 4, entry 6)



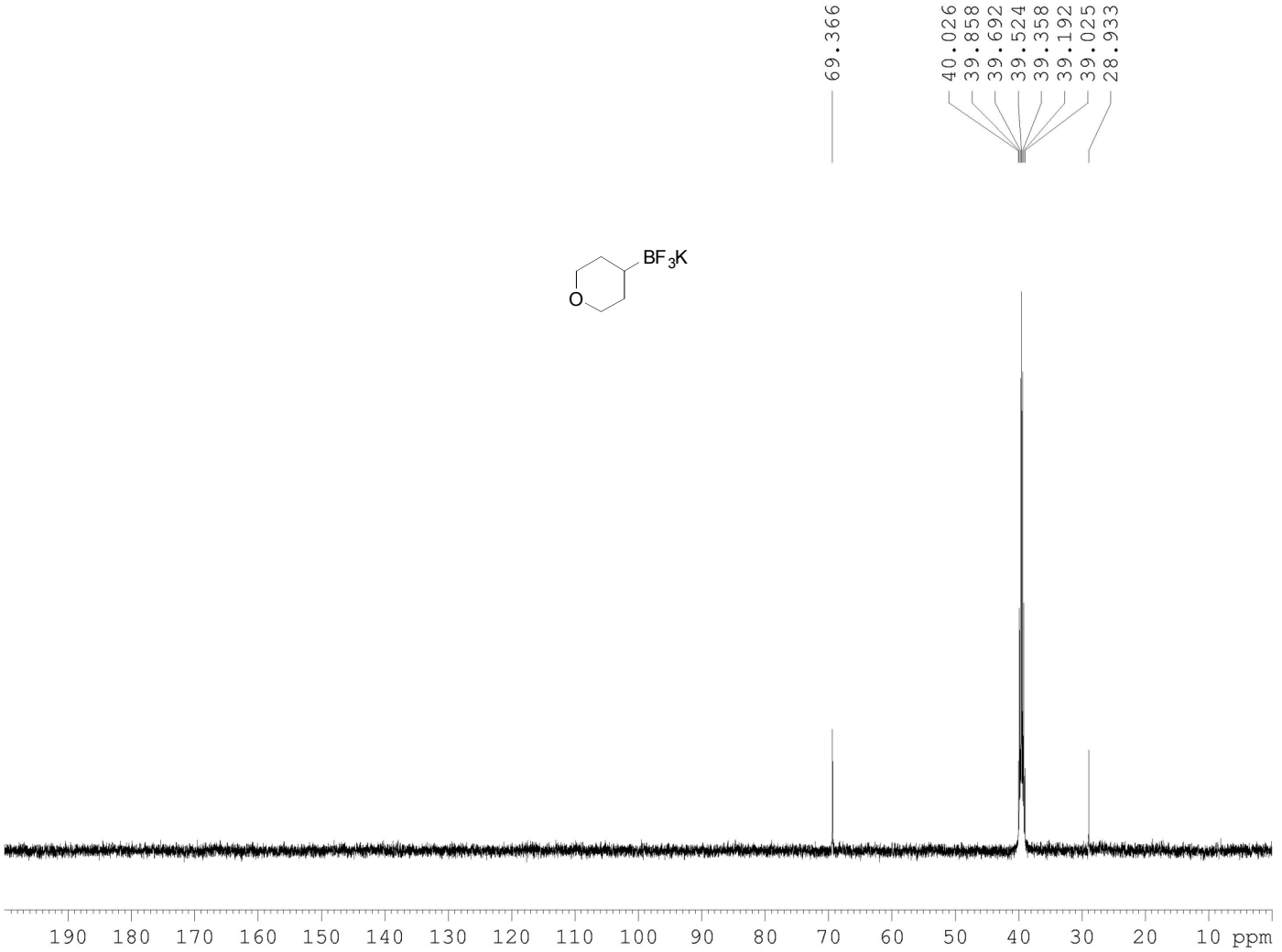
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 4-methyl-2-((benzyloxy)methyl)-4-methylquinoline **4g**
(Table 4, entry 8)



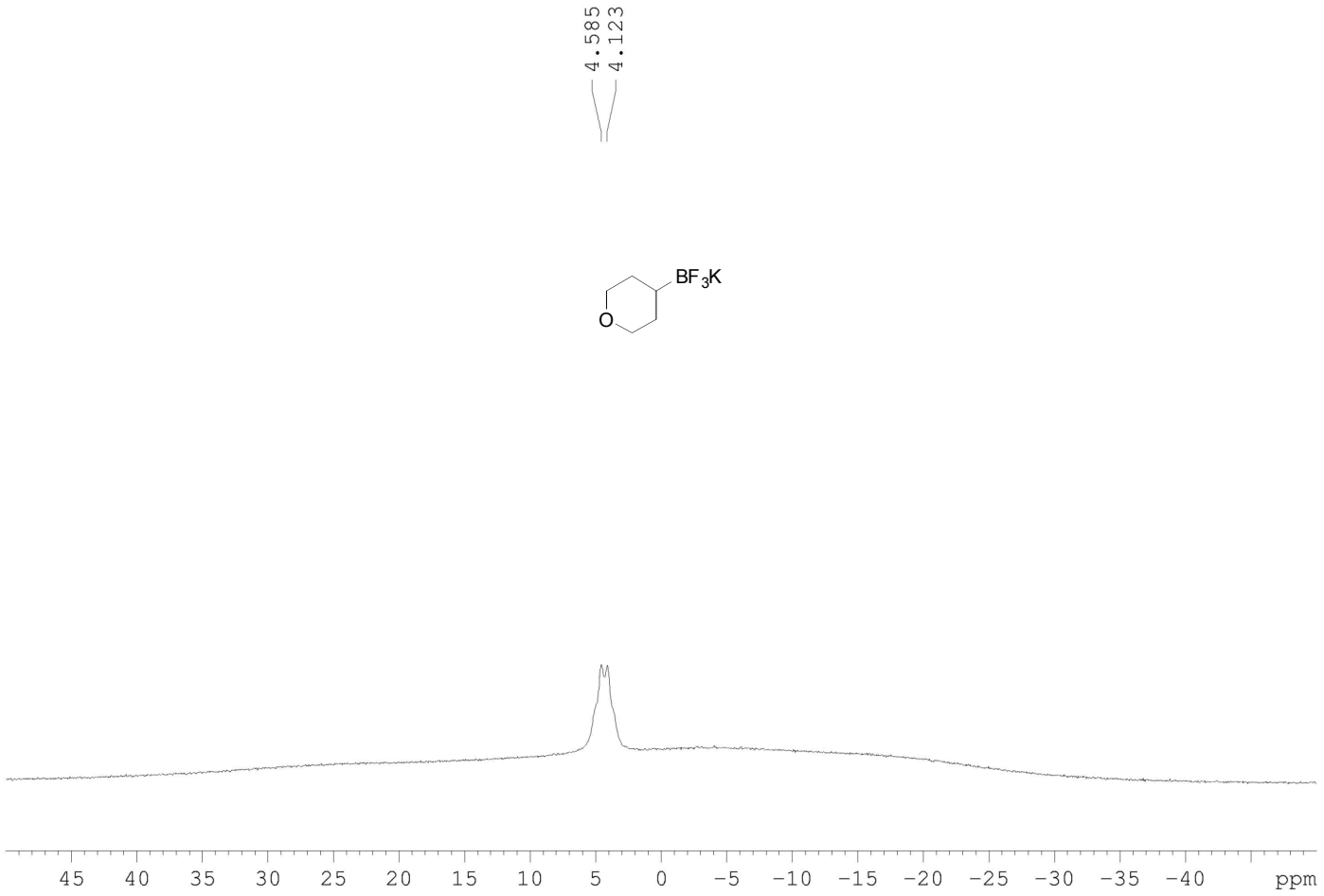
^{13}C NMR (125 MHz, $CDCl_3$) Spectrum of 4-methyl-2-((benzyloxy)methyl)-4-methylquinoline **4g** (Table 4, entry 8)



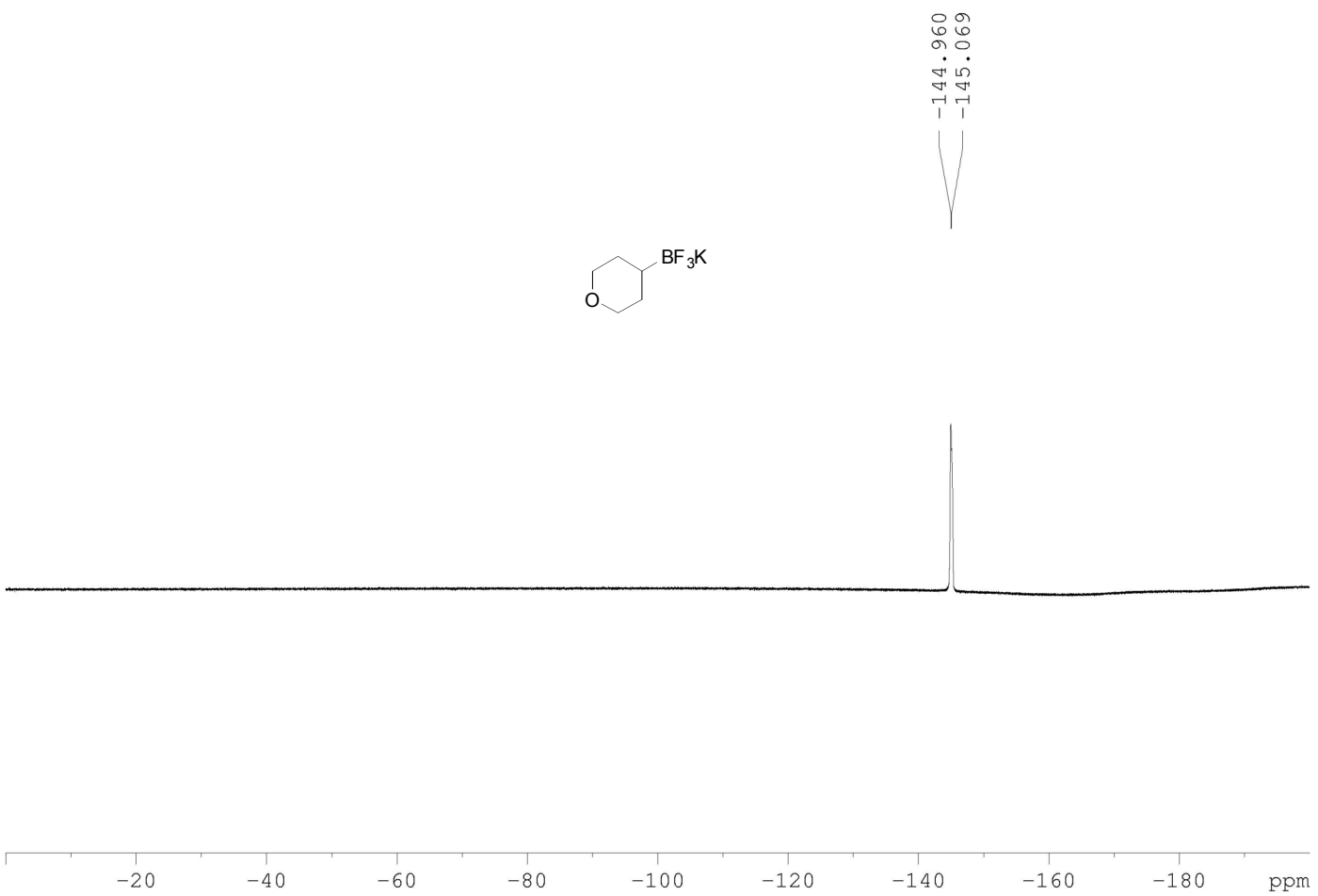
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium tetrahydro-2H-pyran-4-yl trifluoroborate



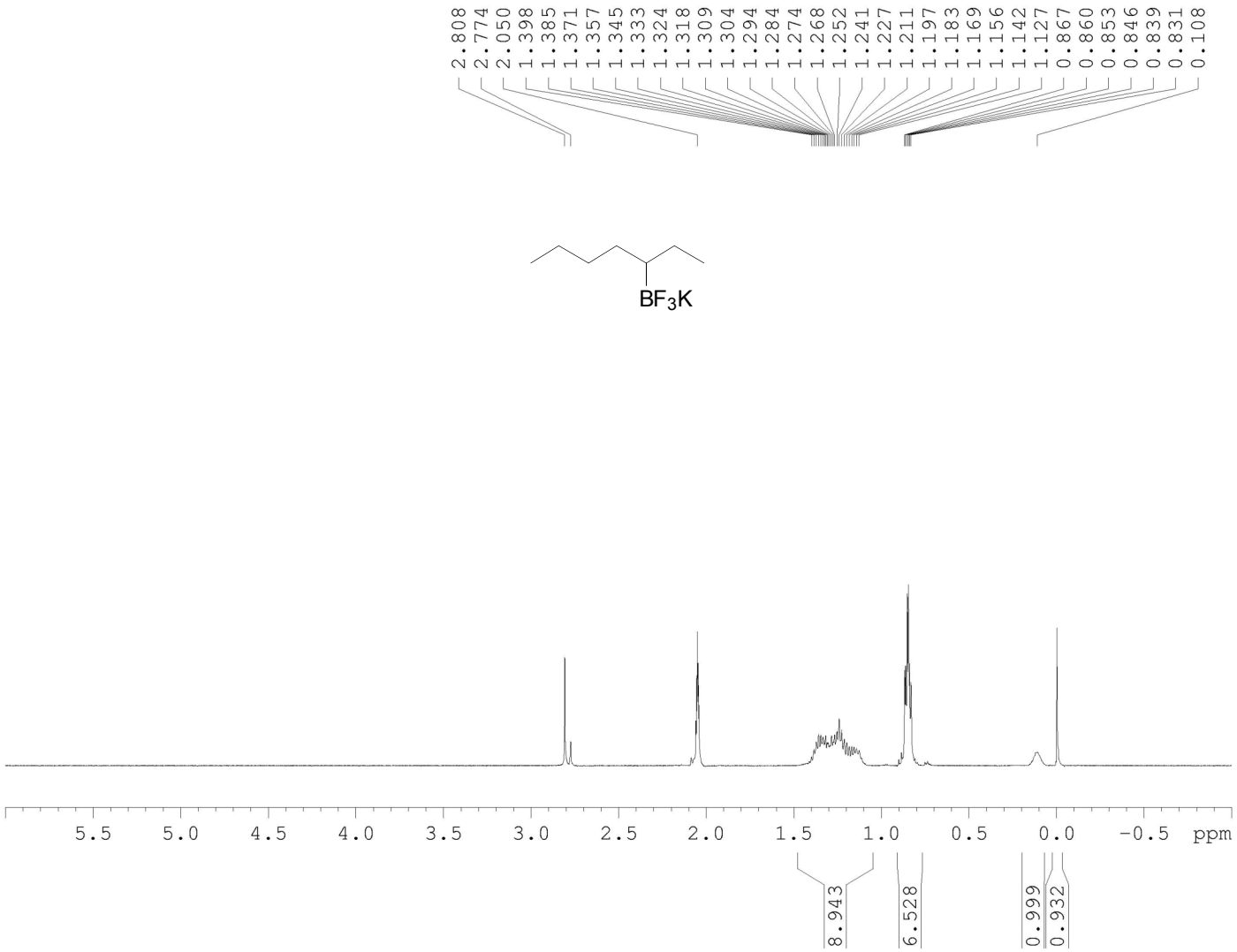
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium tetrahydro-2H-pyran-4-yl trifluoroborate



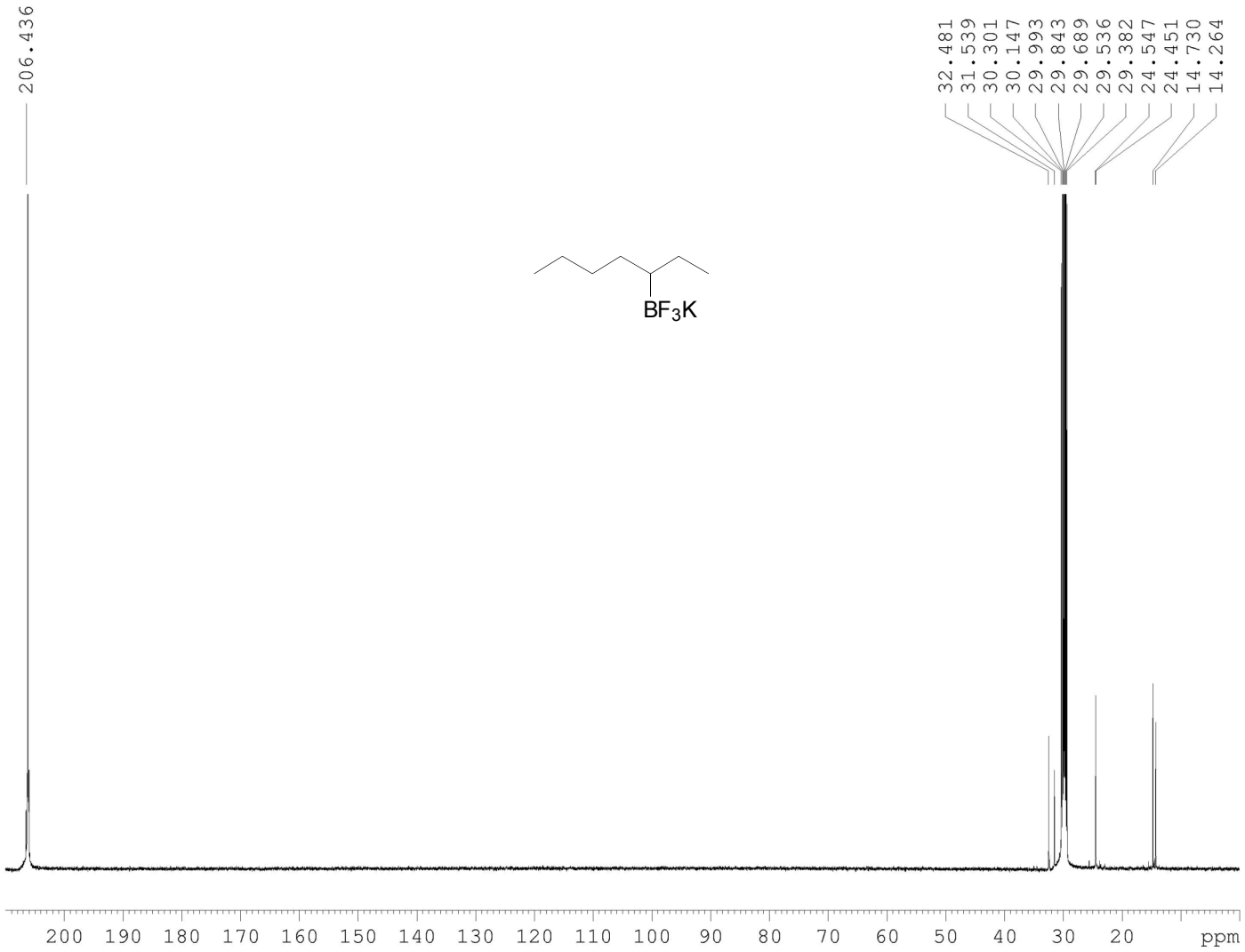
^{11}B NMR (128.38 MHz, DMSO) Spectrum of potassium tetrahydro-2H-pyran-4-yl trifluoroborate



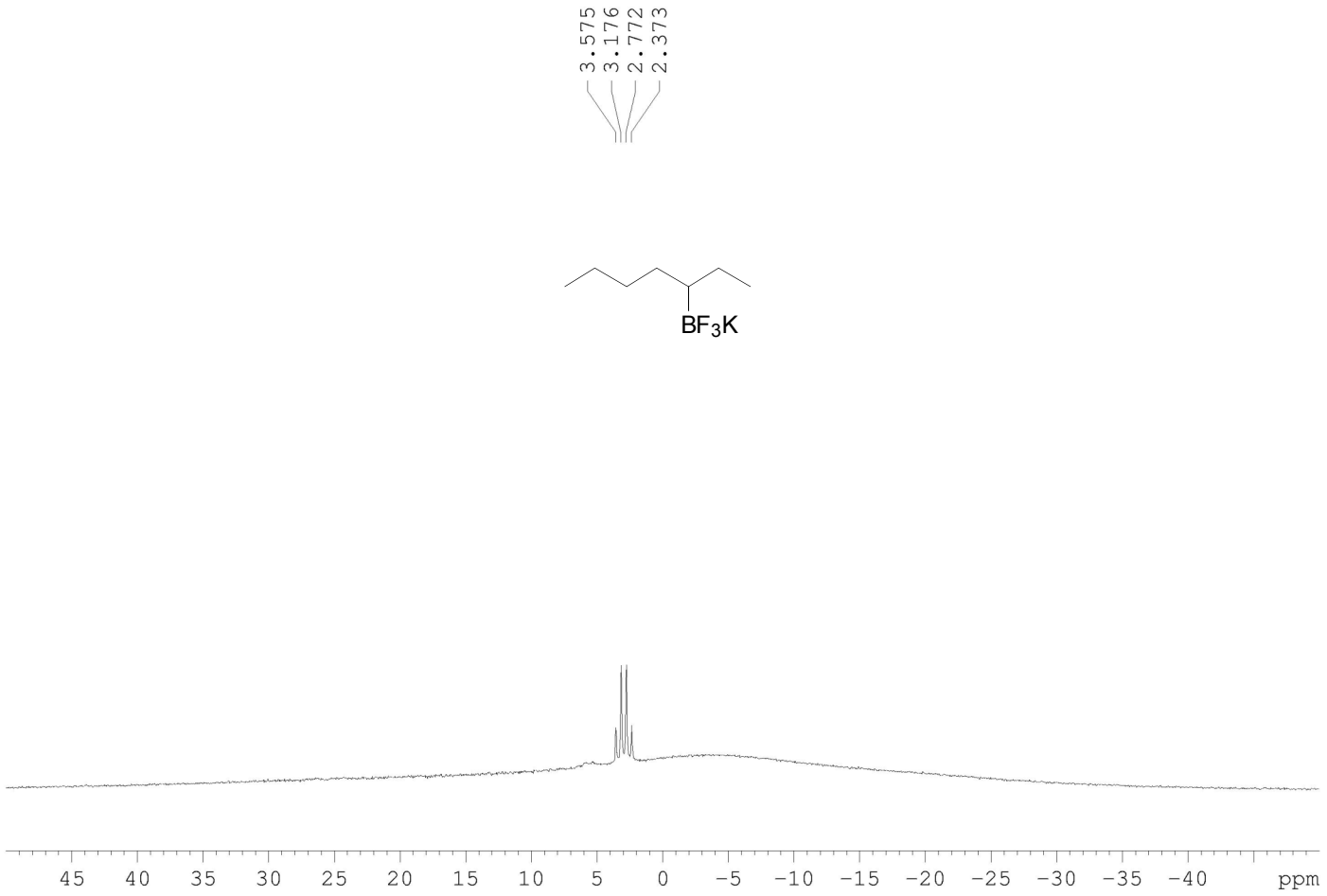
^{19}F NMR (470.84 MHz, DMSO) Spectrum of potassium tetrahydro-2H-pyran-4-yl trifluoroborate



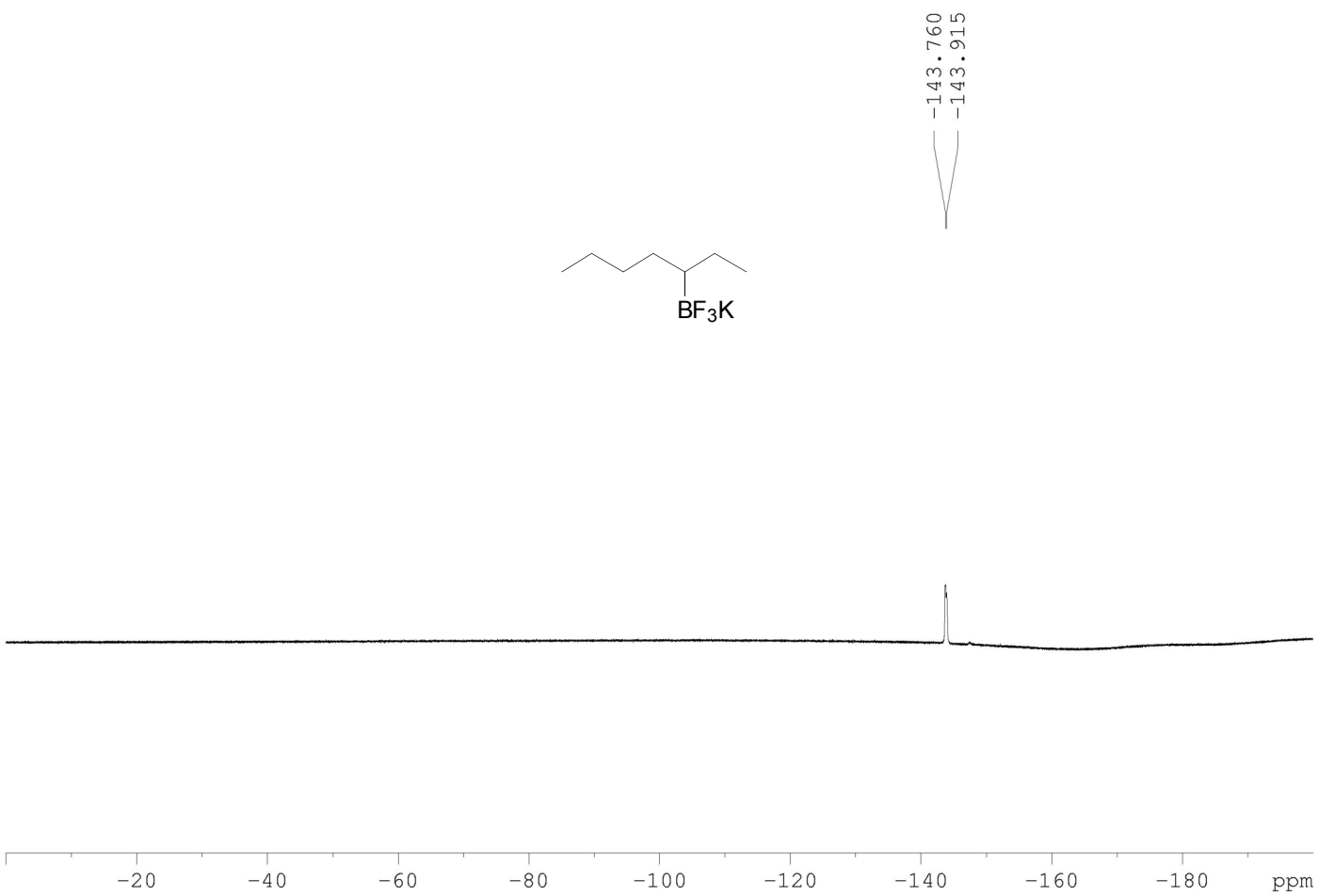
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium heptan-3-yltrifluoroborate



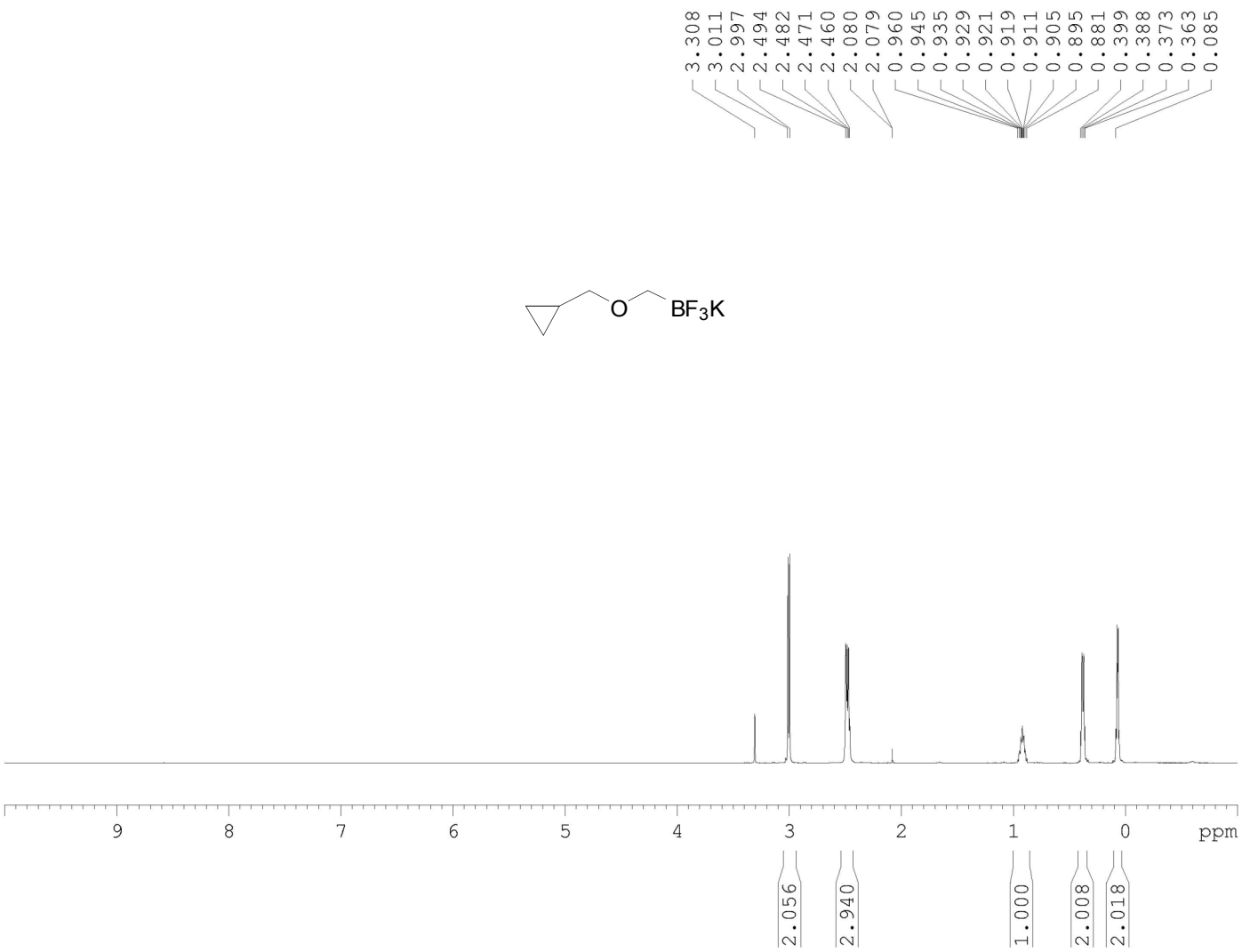
^{13}C NMR (125 MHz, acetone-d_6) Spectrum of potassium heptan-3-yltrifluoroborate



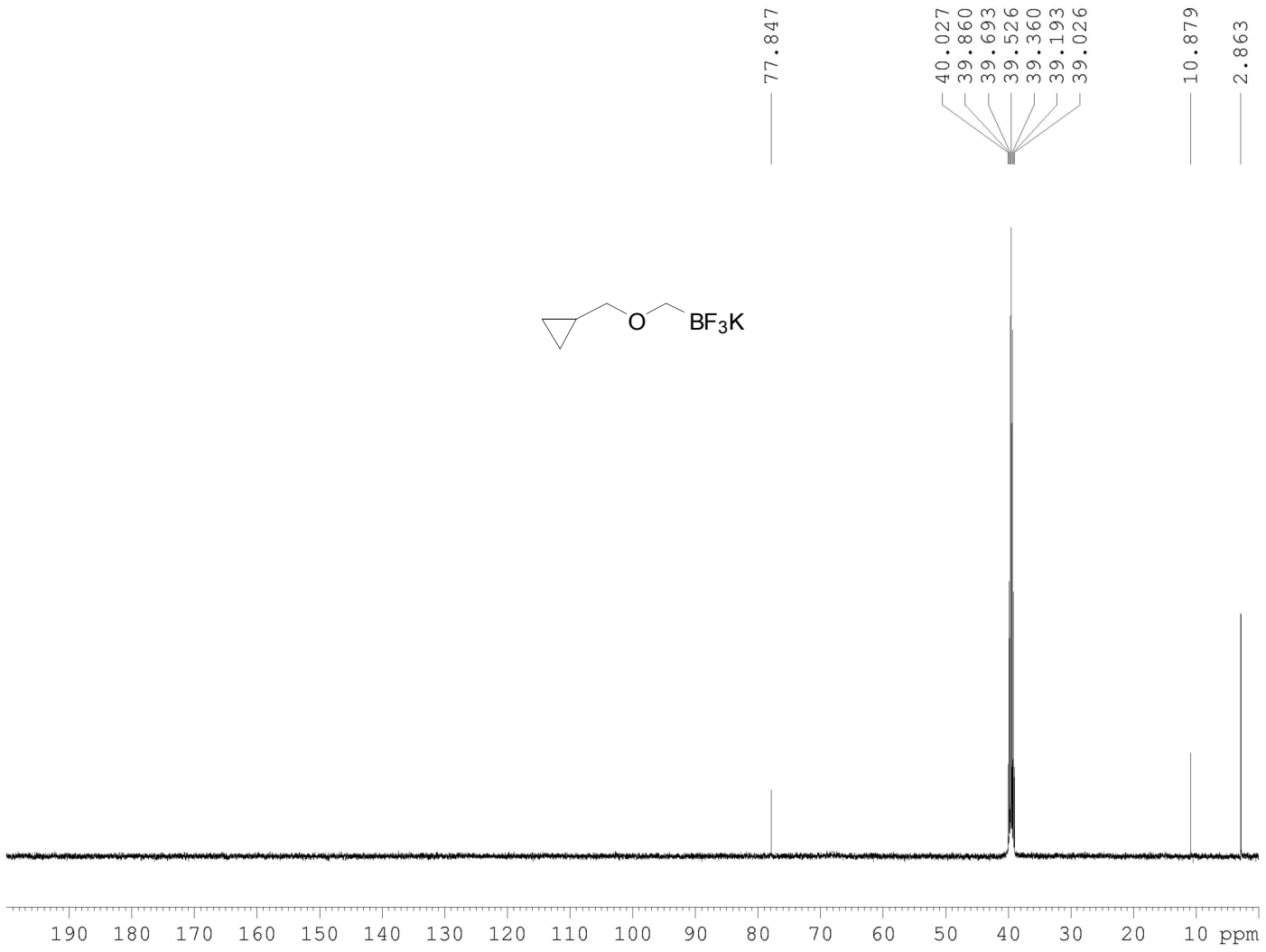
^{11}B NMR (128.38 MHz, acetone-d_6) Spectrum of potassium heptan-3-yltrifluoroborate



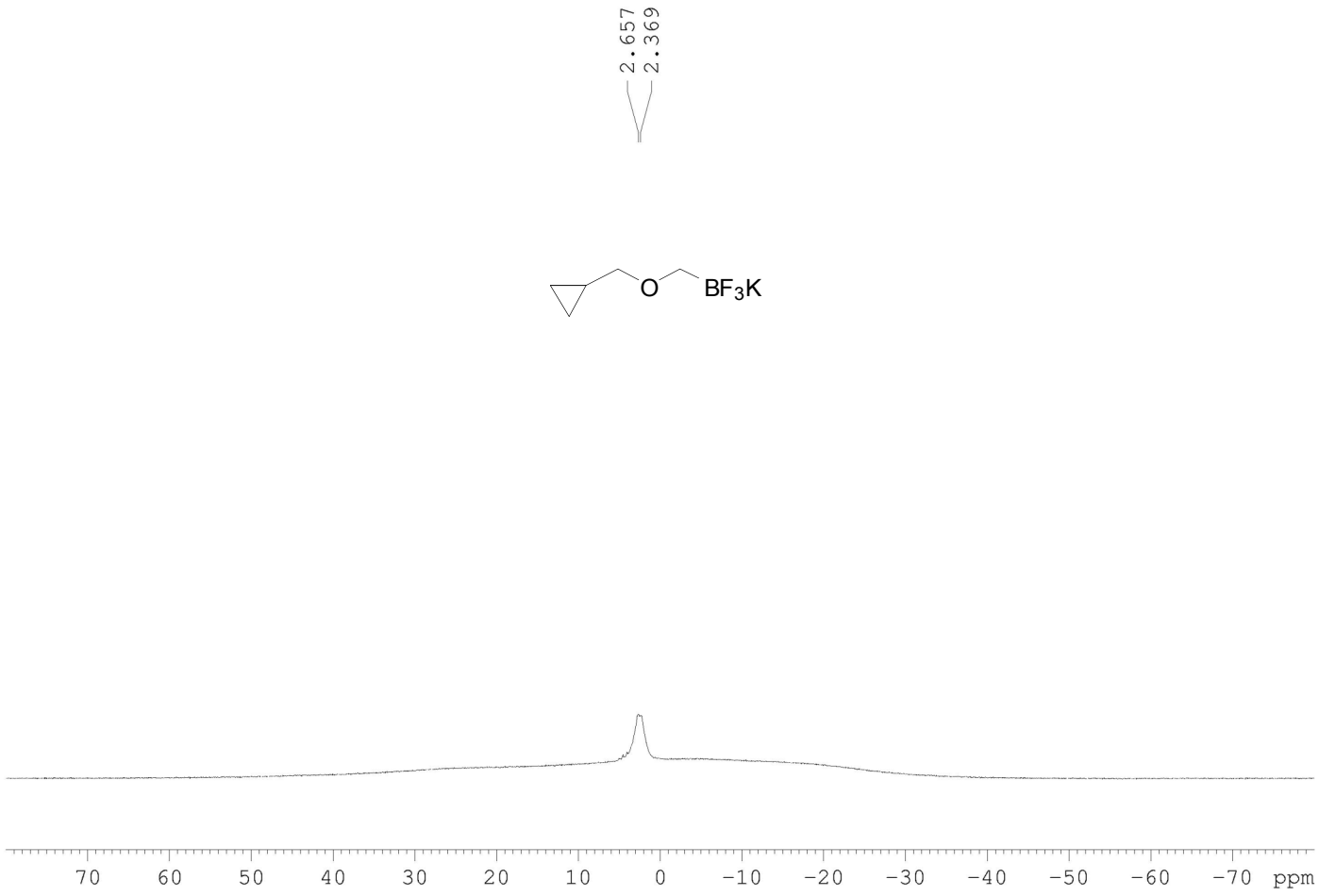
^{19}F NMR (470.84 MHz, acetone-d_6) Spectrum of potassium heptan-3-yltrifluoroborate



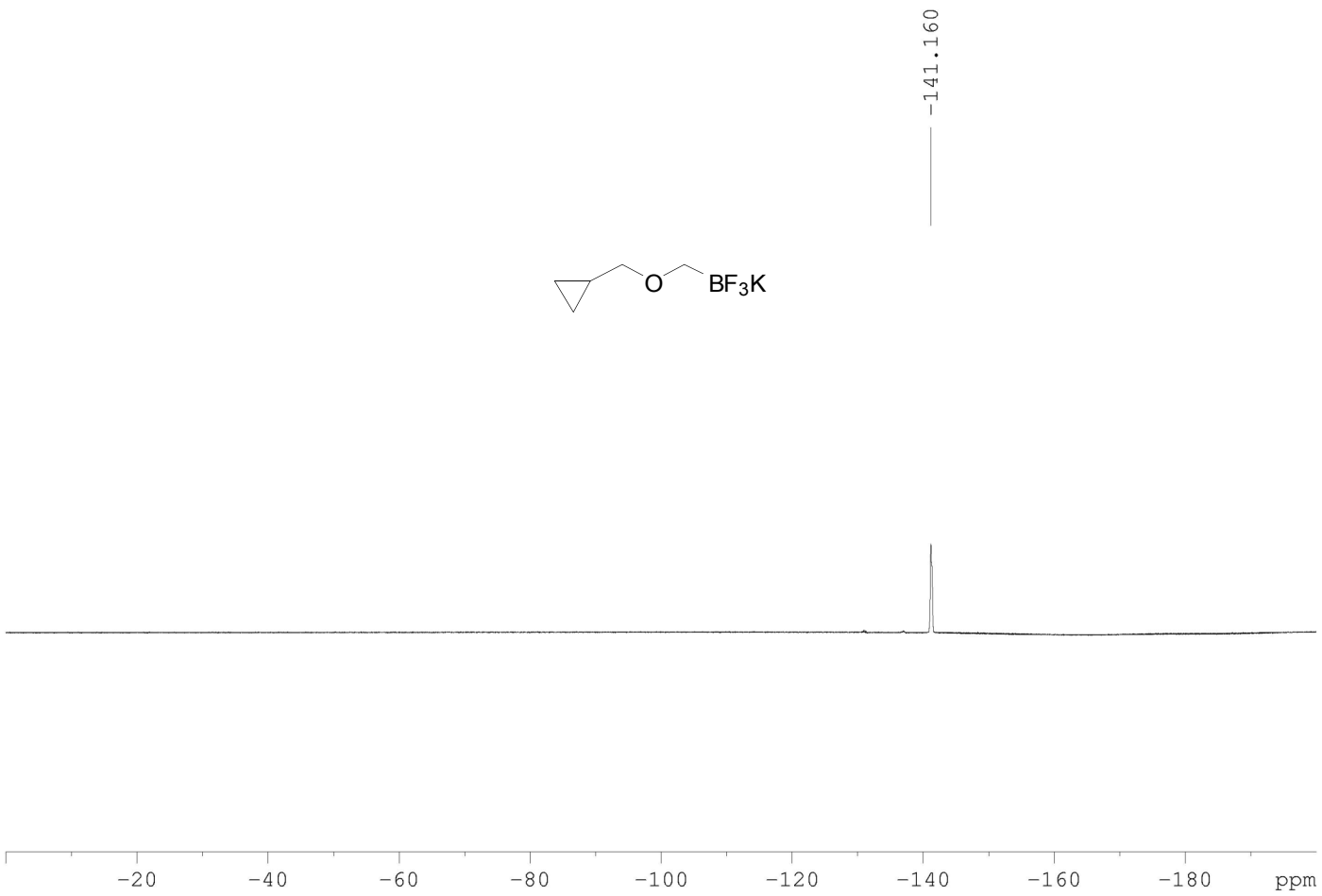
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



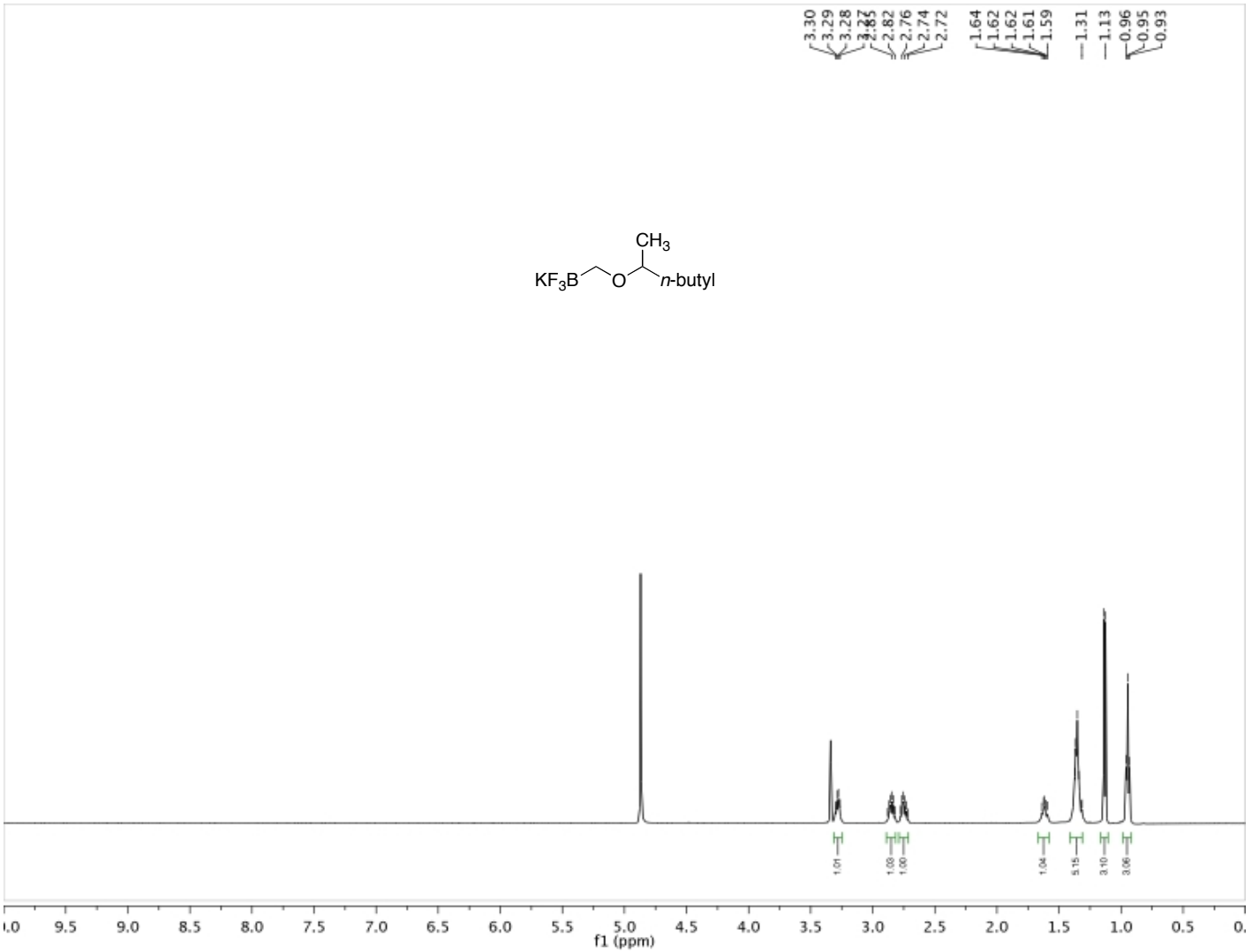
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



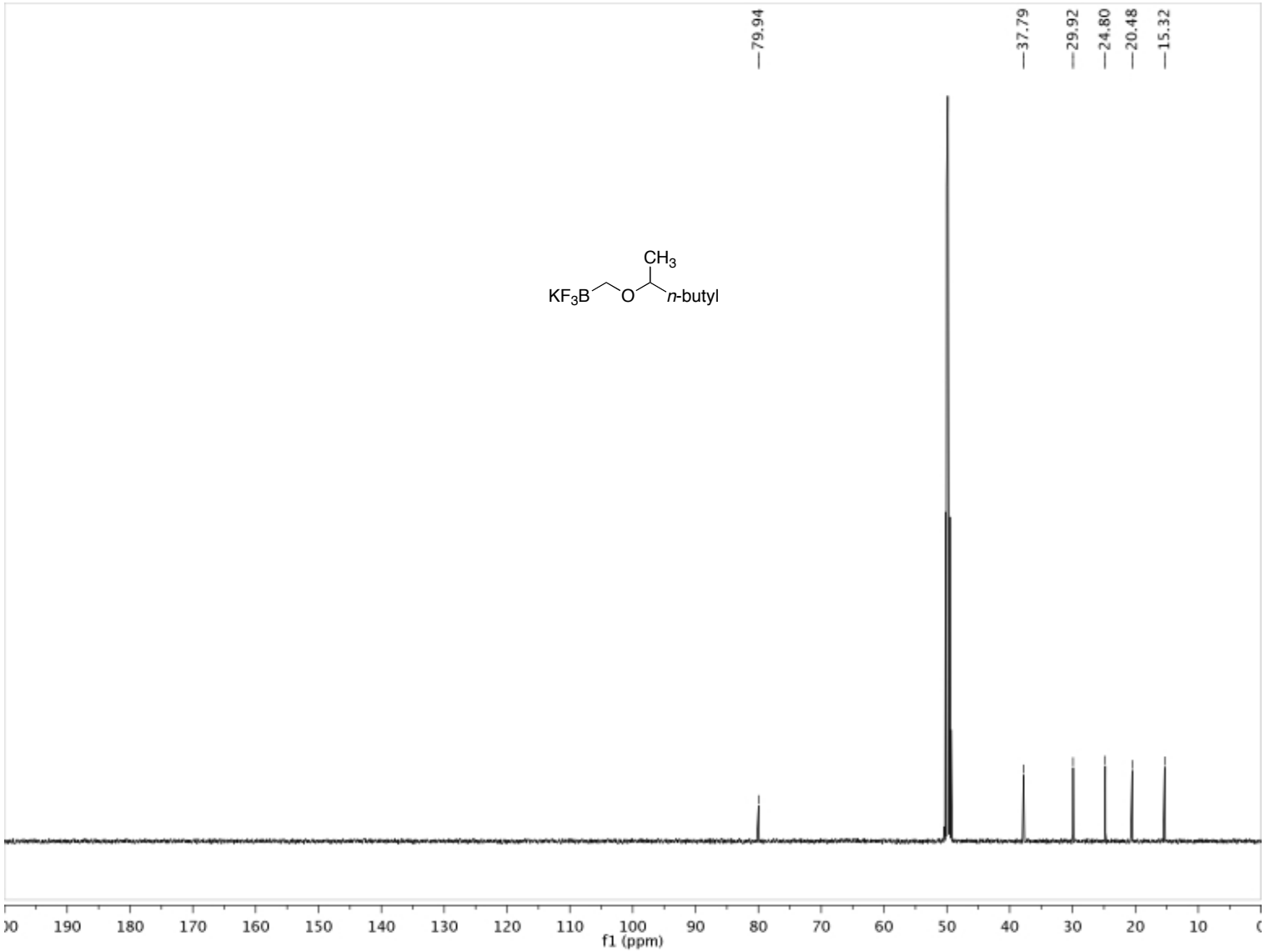
^{11}B NMR (128.38 MHz, DMSO) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



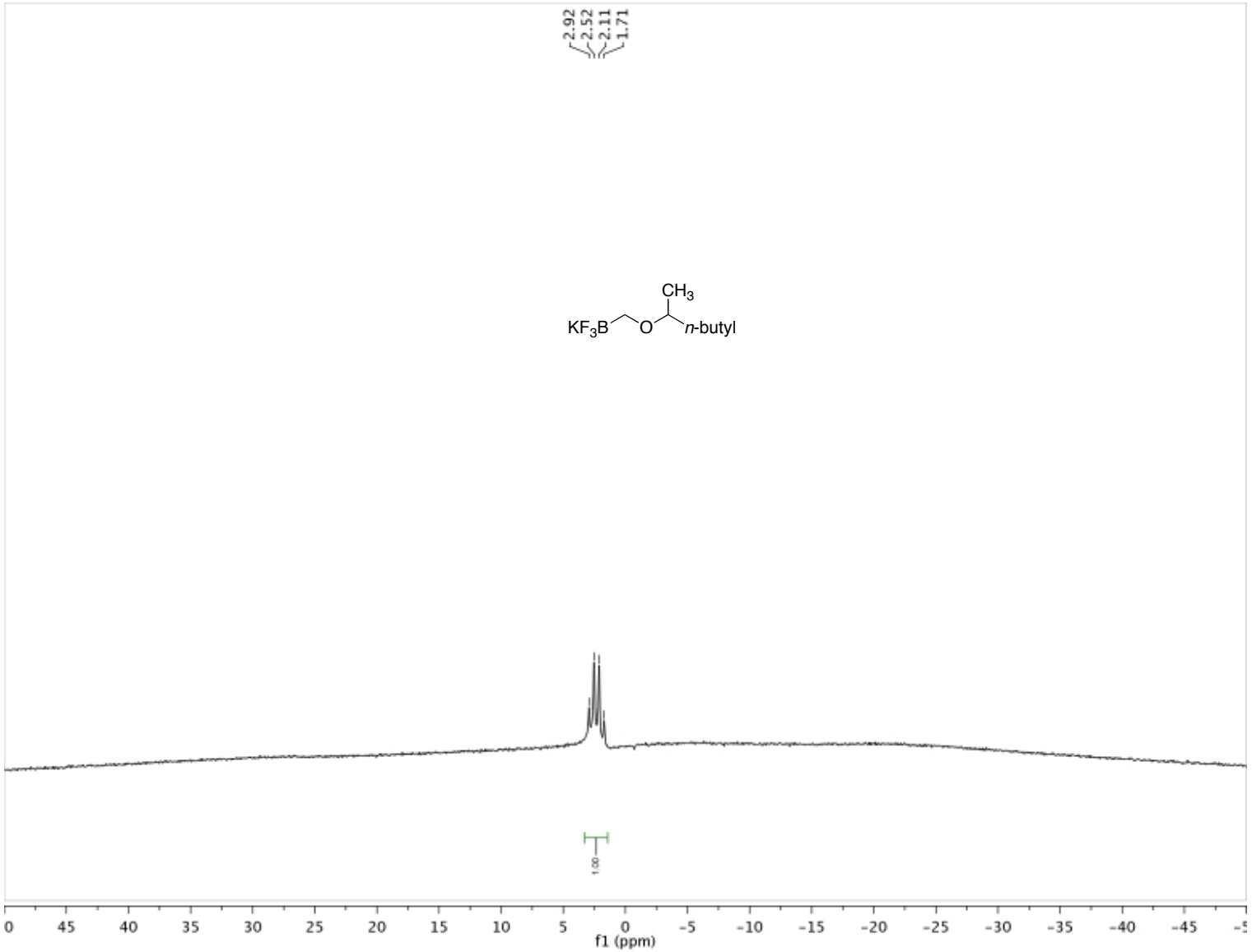
^{19}F NMR (470.84 MHz, DMSO-d_6) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



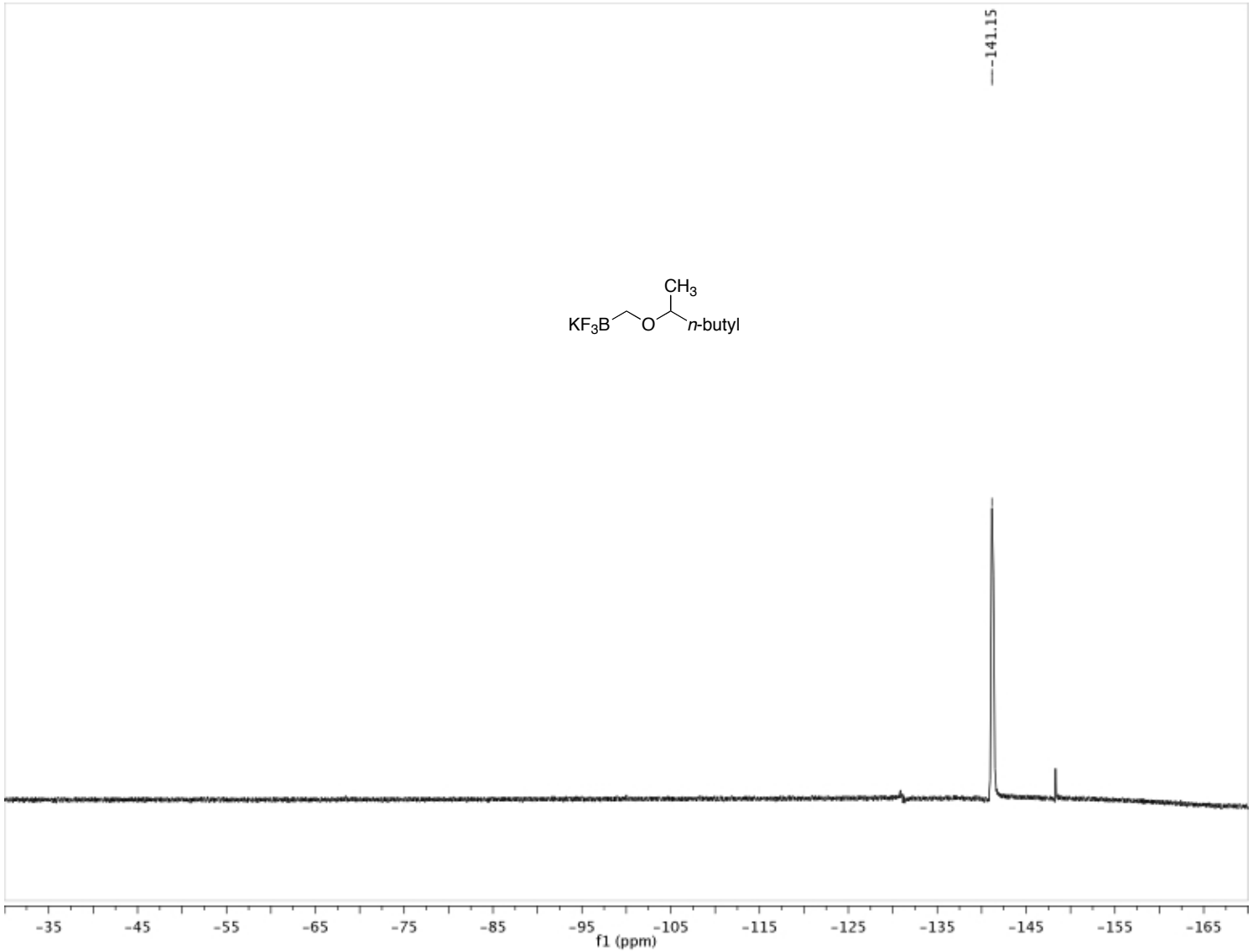
^{1}H NMR (500 MHz, MeOD) Spectrum of potassium ((hexan-2-yloxy)methyl)trifluoroborate



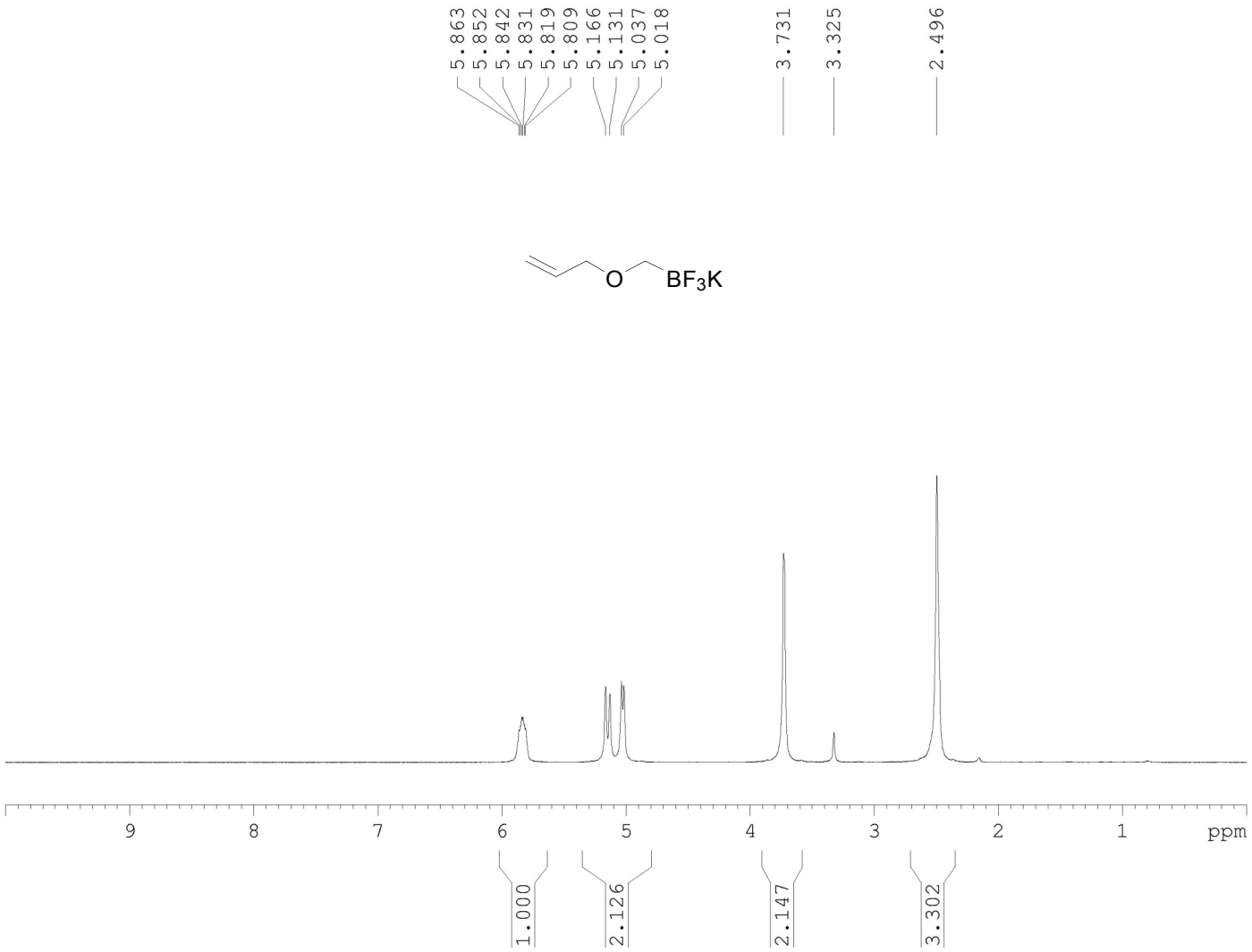
^{13}C NMR (125 MHz, MeOD) Spectrum of potassium ((hexan-2-yloxy)methyl)trifluoroborate



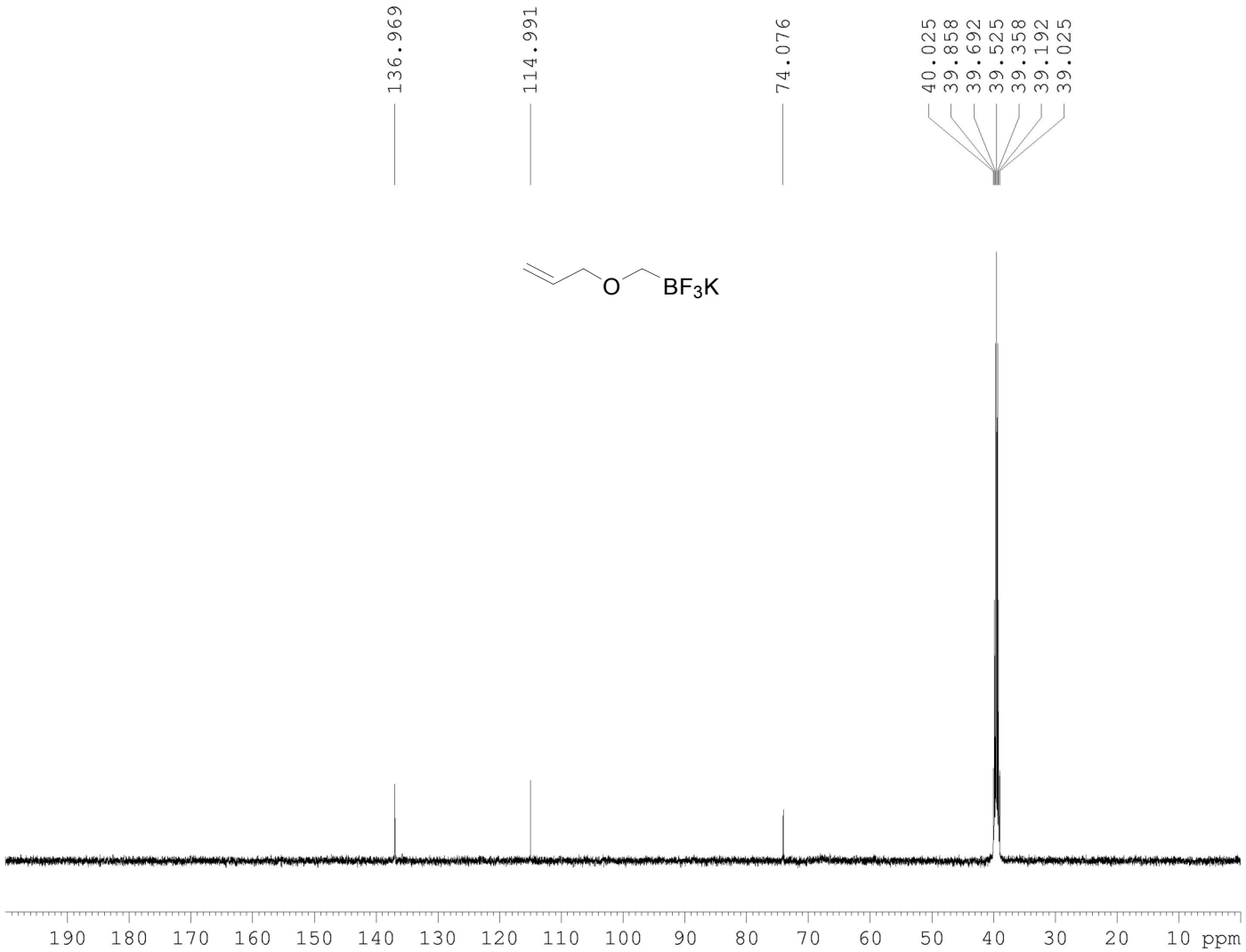
^{11}B NMR (128 MHz, MeOD) Spectrum of potassium ((hexan-2-yloxy)methyl)trifluoroborate



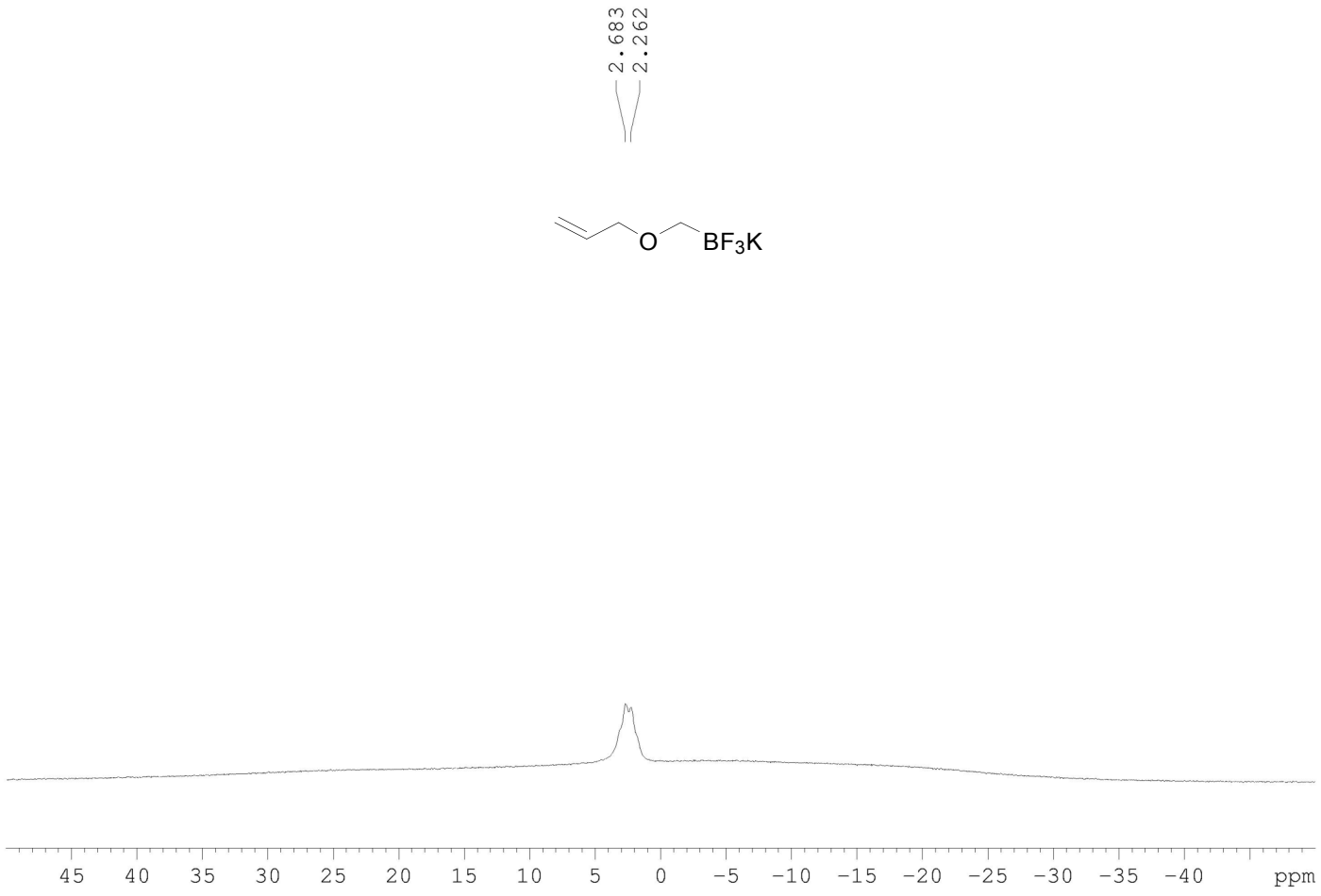
^{19}FMR (1471 MHz, MeOD) Spectrum of potassium ((hexan-2-yloxy)methyl)trifluoroborate



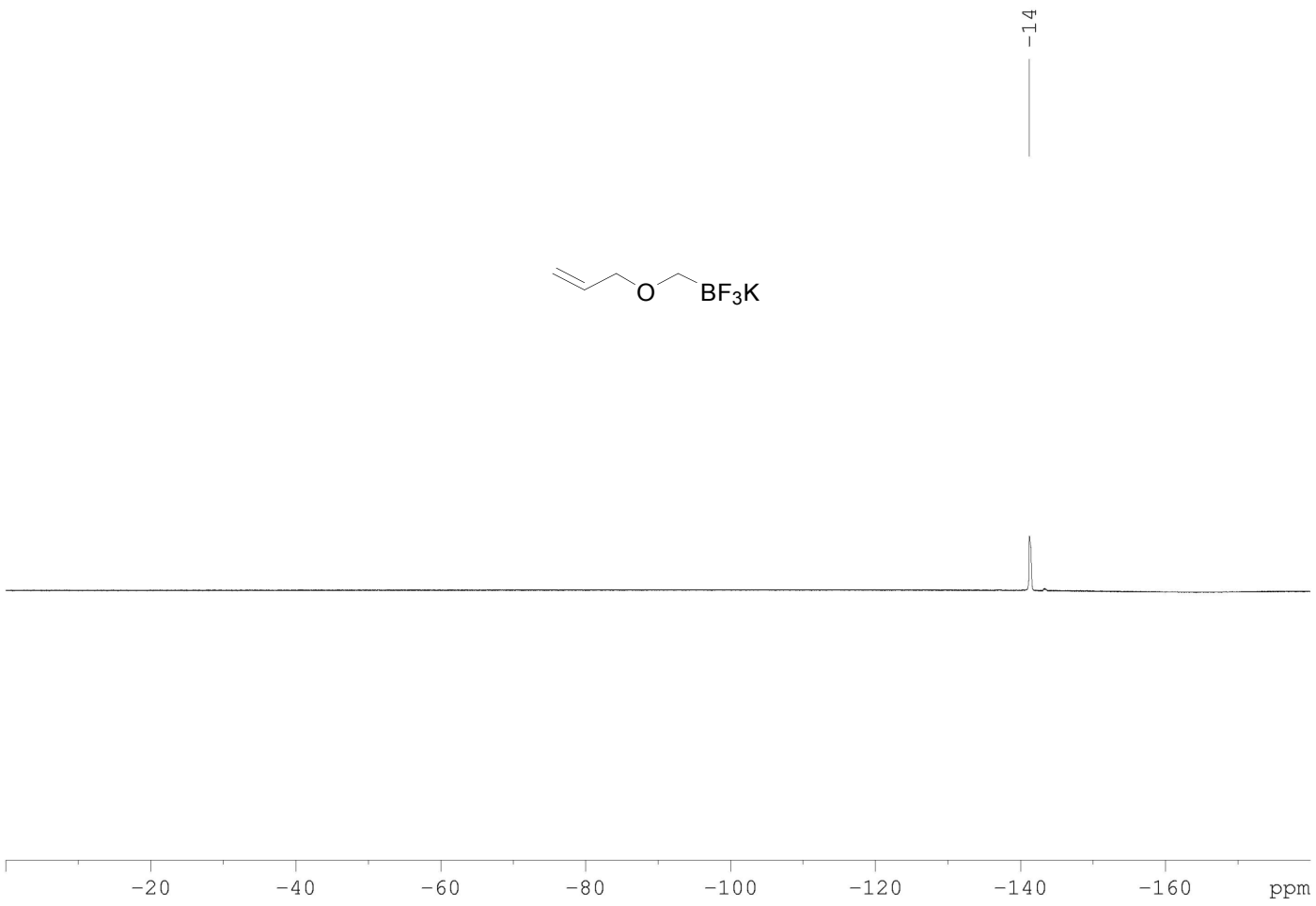
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



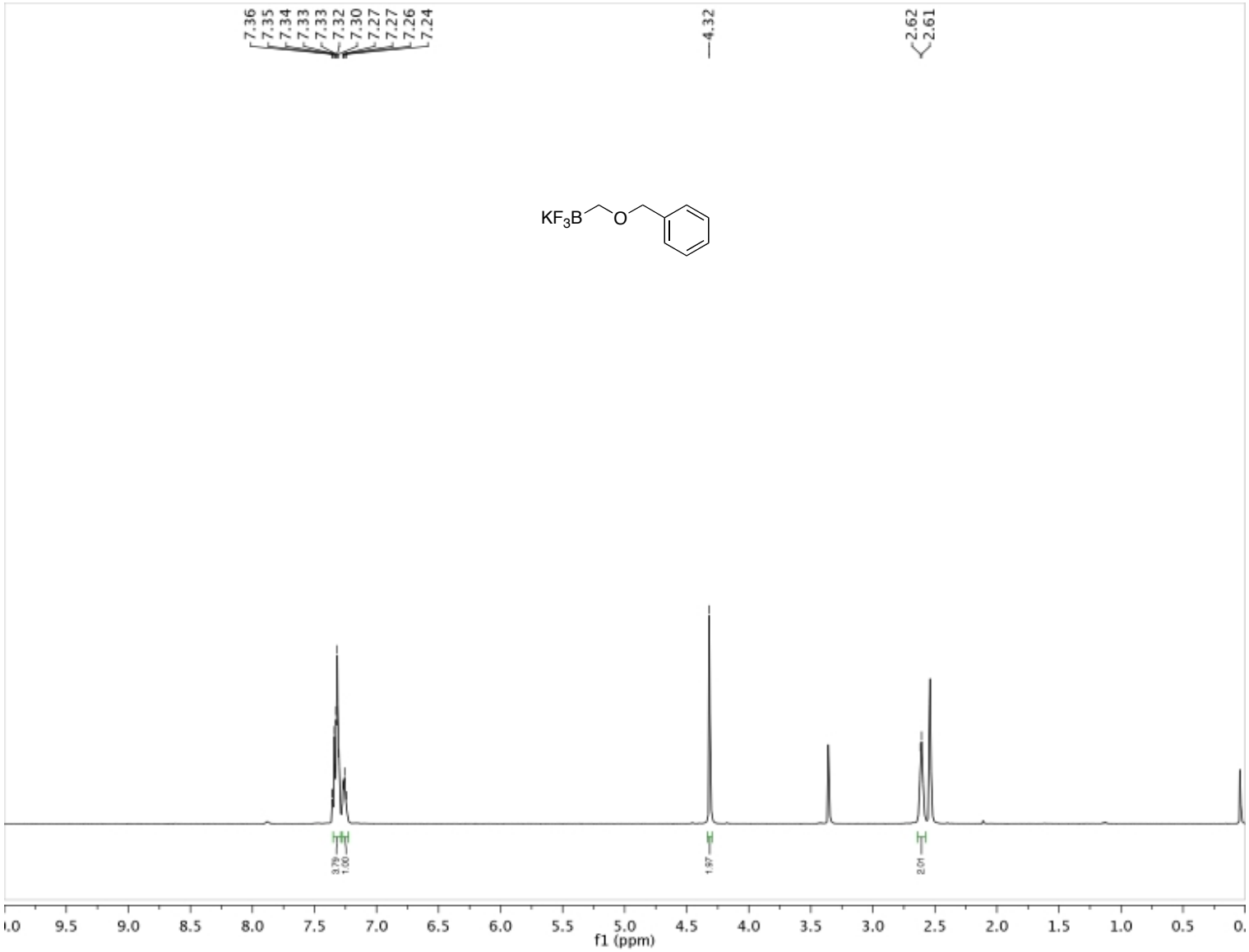
^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium potassium ((allyloxy)methyl)trifluoroborate



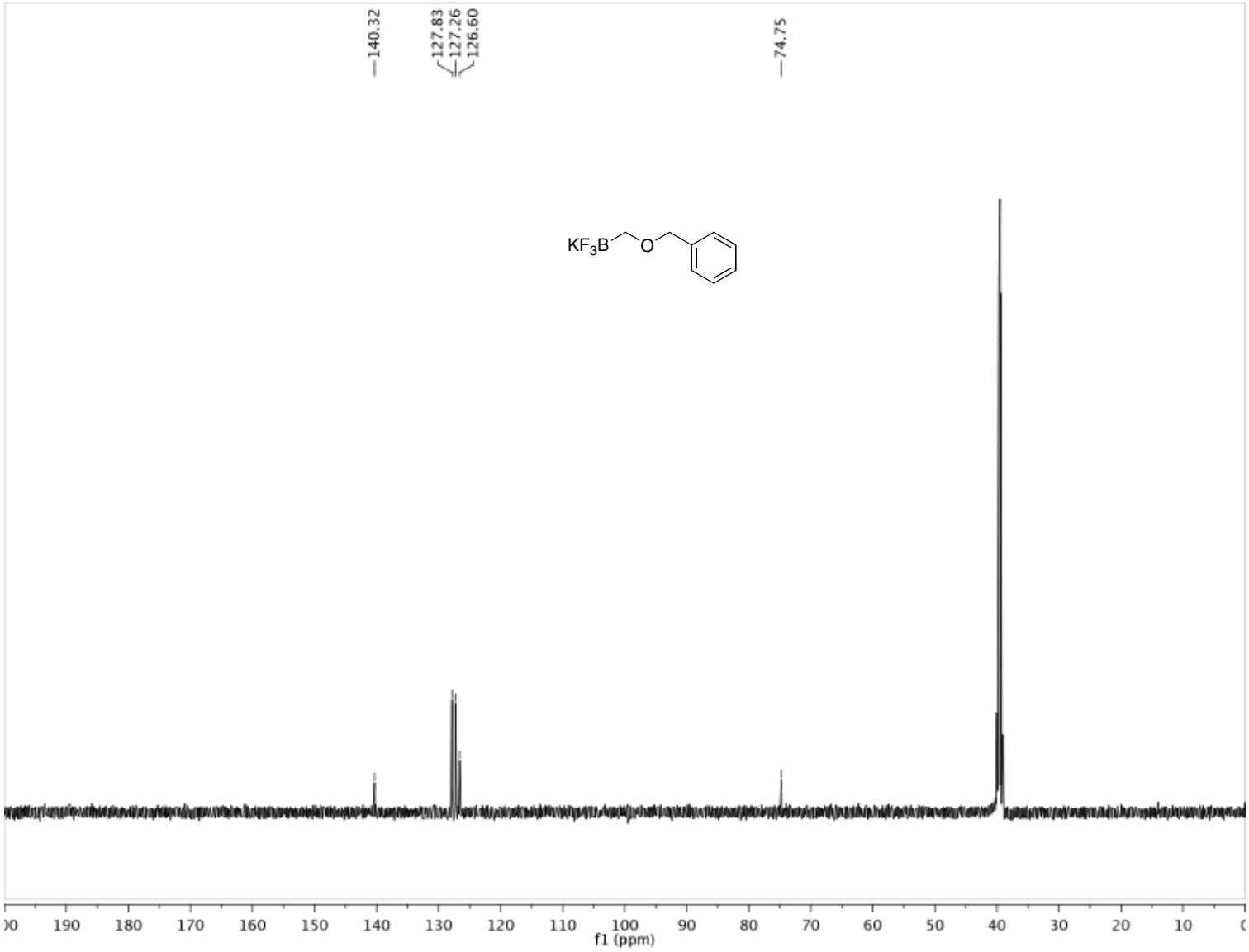
^{11}B NMR (128.38 MHz, DMSO) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



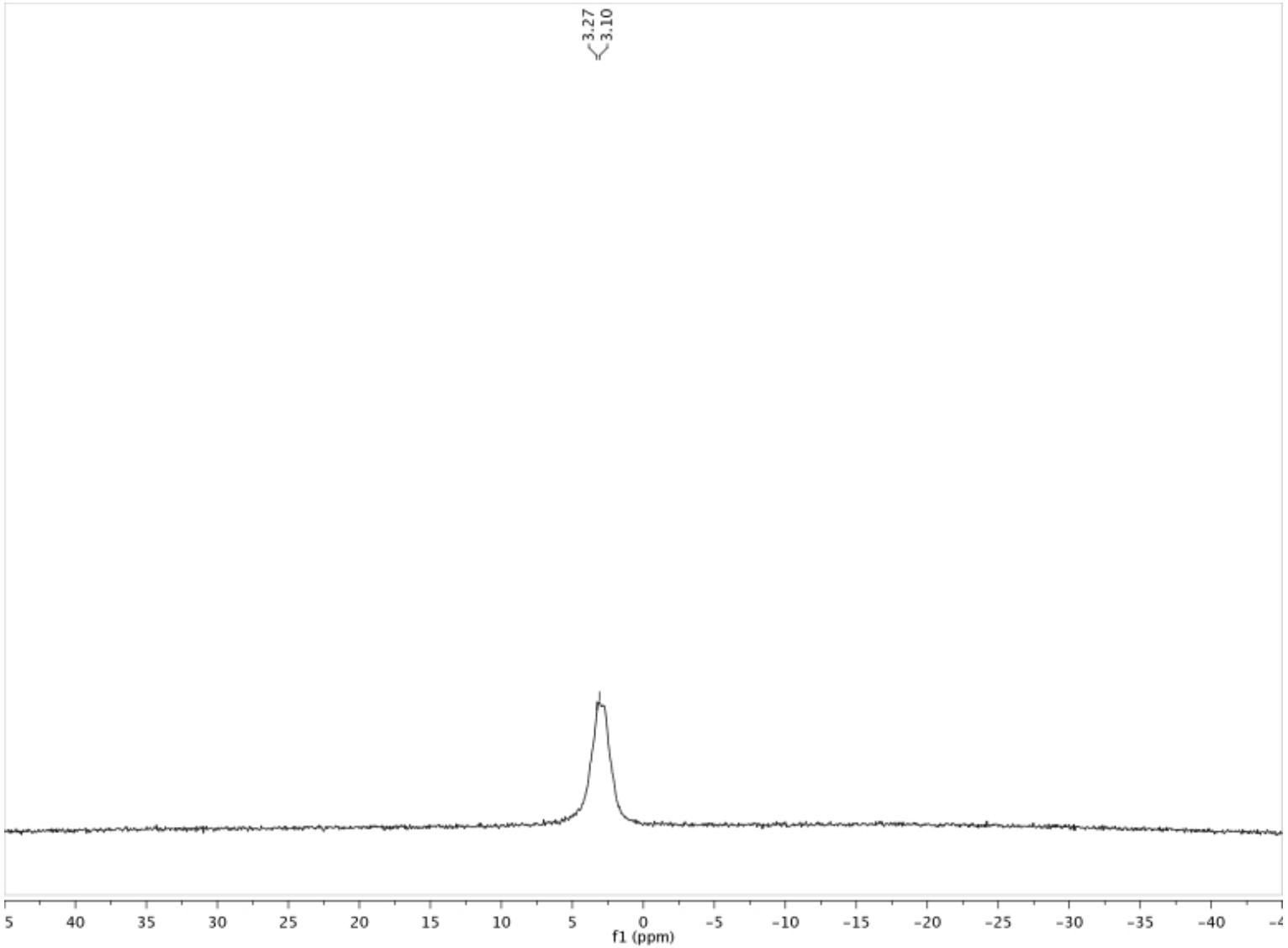
^{19}F NMR (470.84 MHz, DMSO) Spectrum of potassium ((allyloxy)methyl)trifluoroborate



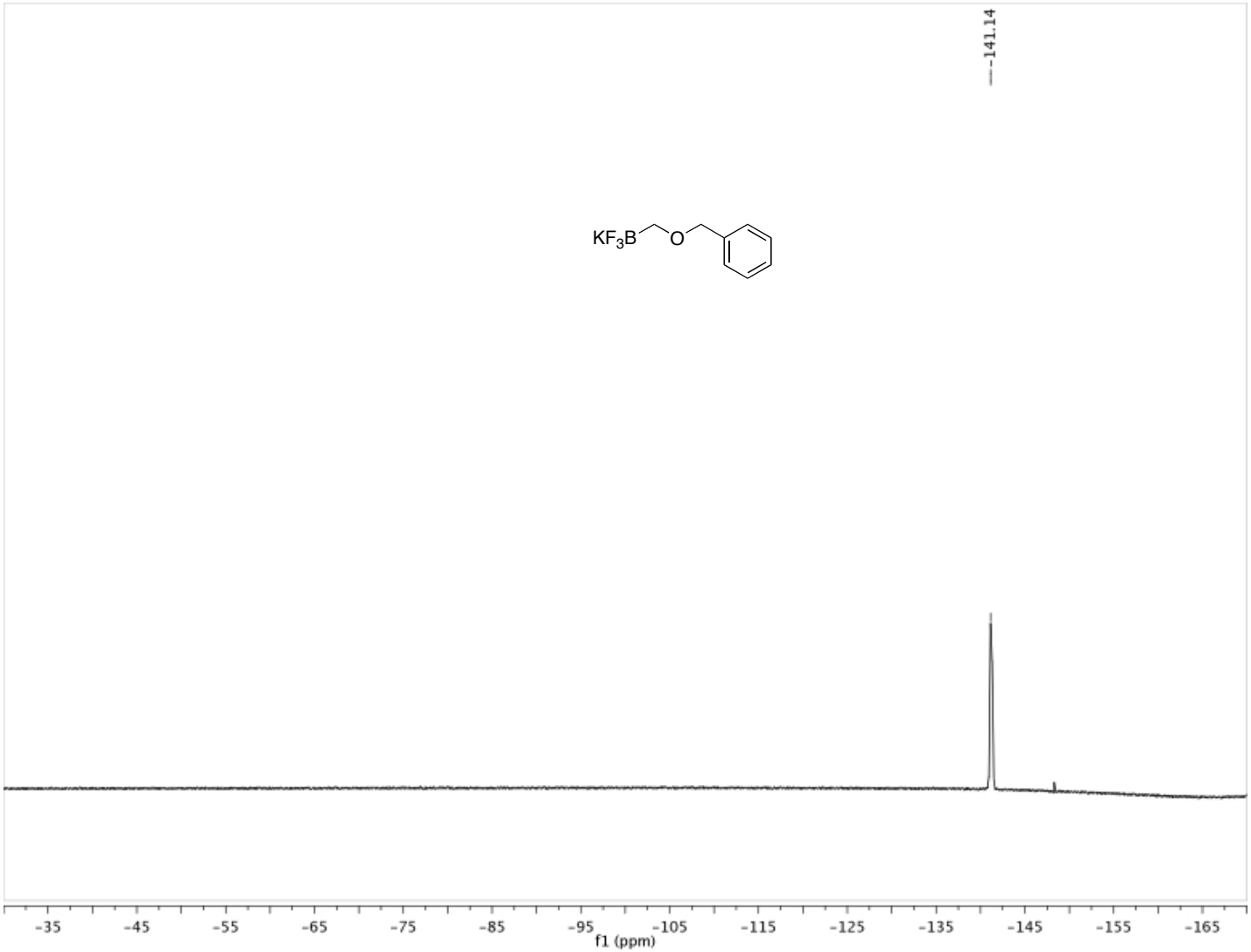
^{1}H NMR (500 MHz, DMSO-d_6) Spectrum of potassium ((benzyloxy)methyl)trifluoroborate



^{13}C NMR (125 MHz, DMSO-d_6) Spectrum of potassium ((benzyloxy)methyl)trifluoroborate



^{11}B NMR (128 MHz, DMSO) Spectrum of potassium ((benzyloxy)methyl)trifluoroborate



^{19}F NMR (471 MHz, DMSO) Spectrum of potassium ((benzyloxy)methyl)trifluoroborate