Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photoinduced CO-releasing molecule (photoCORM) as in situ CO surrogate for palladium-catalysed aminocarbonylation

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Table of content

I. General information

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (equipped with ATR accessory, Pike) spectrophotometer. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded at room temperature at 400 or 300, 377, and 100 or 75 MHz respectively, on a Bruker AVANCE 400 spectrometer or on a Bruker AVANCE 300 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatography (TLC) was performed on Merck silica gel 60 F 254 and revealed with a UV lamp (λ = 254 nm) and $KMnO_4$ or vanillin staining. Flash Column Chromatography was conducted on silica Geduran® Si 60 Å (40 – 63 µm). High resolution mass spectrometry was performed a LTQ Orbitrap XL (Thermo Fisher Scientific) instrument equipped with an electrospray ion source in the positive mode. Reactions under argon were performed using standard Schlenk techniques. Brown glassware was employed for the formation of light-sensitive compounds. Manganese pentacarbonyl bromide ($[Mn(CO)_5Br]$) was purchased from Strem chemicals. Sodium 8-hydroxyquinolinate ligand was synthesized as described by Marshall.[1] Solvents were freshly distilled before use, according to standard procedures.

II. General procedures

Synthesis of complex 1.

This synthesis is a modification from our previous published protocol:[2]

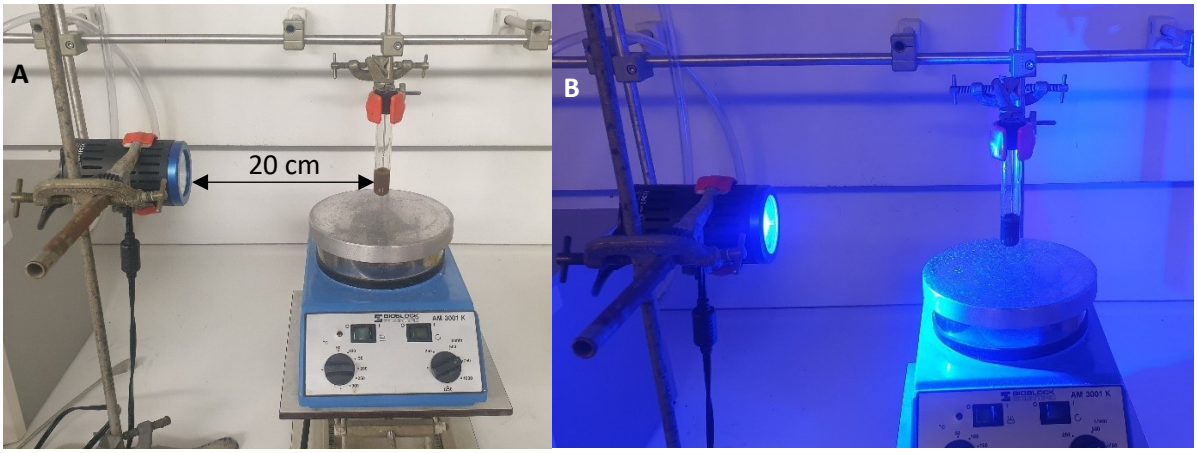
In a 100 mL brown round bottom flask was added sodium 8-hydroxiquinolinate (1 equiv., 5 mmol, 840 mg) and $Mn(CO)_5Br$ (1 equiv., 5 mmol, 1.375 g). Tetrahydrofuran (50 mL) was added, followed by 1-methyl imidazole (1 equiv., 5 mmol, 400 µL). The reaction mixture was stirred for 12h at room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 98/2) to afford the complex **1** (1.7 g, 92%) as a yellow powder.

General procedure for the aminocarbonylation reaction

In a screw tube was successively added the aryl iodide **2** (1 equiv., 0.5 mmol), TEMPO (0.5 equiv., 0.25 mmol, 39 mg), complex **1** (0.5 equiv., 0.25 mmol, 91 mg), $PdCl_2(PPh_3)_2$ (5 mol %, 0.025 mmol, 17 mg), amine **3** (2 equiv., 1 mmol) and DBU (2 equiv., 1 mmol, 150 µL). Acetonitrile (2 mL) was added and the tube was screwed. The reaction mixture was irradiated with blue LEDs under stirring for 18h at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and partitioned with a 1 M aqueous solution of hydrochloric acid (25 mL). The mixture was put under vigorous stirring until two clear phases were obtained. The organic layer was washed with 1 M HCl (25 mL), water (25 mL), brine

(25 mL) dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the expected amide **4**.

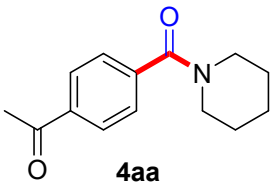
Set up for photo-reactions



A. Picture before irradiation. The distance between the tube and the LED source is 20 cm. **B.** Picture during irradiation.

Light source: Kessil Lamp. Wavelength: 450 nm. Power: 3 mW/cm^2 (1.13 10^{-8} einstein/s) at 20 cm distance between light source and reactor.

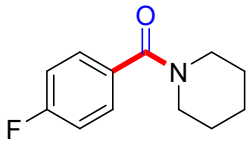
III. Compound Characterization



4aa

Following the general procedure with 4'-iodoacetophenone **2a** (0.5 mmol, 123 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 20/80) to afford **4aa** as a white powder (100 mg, 86%). The spectroscopic data are in agreement with those reported in the literature.[3]

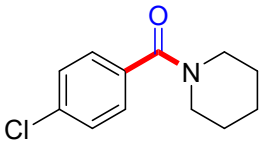
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 3.68 (bs, 2H), 3.26 (bs, 2H), 2.58 (s, 3H), 1.73 – 1.41 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 169.1, 141.0, 137.6, 128.5, 127.0, 48.7, 43.1, 26.7, 26.5, 25.6, 24.5.



4ba

Following the general procedure with 4-fluoroiodobenzene **2b** (0.5 mmol, 58 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ba** as a yellow oil (96 mg, 93%). The spectroscopic data are in agreement with those reported in the literature.[4]

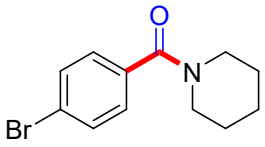
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 3.65 (s, 2H), 3.32 (s, 2H), 1.86 – 1.41 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 163.2 (d, *J* = 249.1 Hz), 132.5 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 8.4 Hz), 115.5 (d, *J* = 21.7 Hz), 48.9, 43.3, 26.5, 25.7, 24.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.97.



4ca

Following the general procedure with 1-chloro-4-iodobenzene **2c** (0.5 mmol, 120 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ca** as a brown solid (90 mg, 80%). The spectroscopic data are in agreement with those reported in the literature.[4]

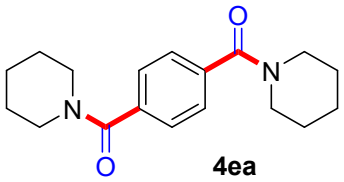
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.29 (m, 4H), 3.67 (s, 2H), 3.31 (s, 2H), 1.81 – 1.41 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 135.4, 134.9, 128.7, 128.4, 48.9, 43.3, 26.6, 25.7, 24.6.



4da

Following the general procedure with 1-bromo-4-iodobenzene **2d** (0.5 mmol, 142 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4da** as a yellow powder (102 mg, 76%). The spectroscopic data are in agreement with those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.68 (bs, 2H), 3.32 (bs, 2H), 1.97 – 1.43 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 135.4, 131.8, 128.7, 123.7, 48.9, 43.4, 26.6, 25.7, 24.7.

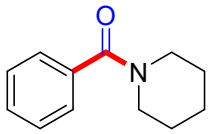


4ea

Following the general procedure with 1,4-diiodobenzene **2e** (0.5 mmol, 165 mg) and piperidine **3a** (2 mmol, 200 µL). The crude product was purified by flash column chromatography (cyclohexane/ ethyl acetate, 20/80) to afford **4ea** as a orange solid (80 mg, 53%). The spectroscopic data are in agreement with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 4H), 3.70 (br, 4H), 3.31 (br, 4H), 1.67 (br, 8H), 1.49 (br, 4H).

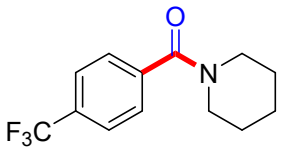
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 137.6, 132.0, 128.7, 128.6, 127.0, 48.8, 43.2, 26.6, 25.7, 24.6.



4fa

Following the general procedure with iodobenzene **2f** (0.5 mmol, 56 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4fa** as a colourless solid (77 mg, 81%). The spectroscopic data are in agreement with those reported in the literature.[4]

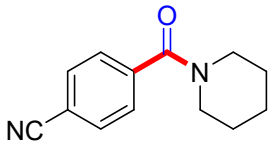
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 5H), 3.70 (br, 2H), 3.34 (br, 2H), 1.80 – 1.60 (br, 4H), 1.52 (br, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.4, 136.7, 129.5, 128.5, 126.9, 48.9, 43.2, 26.7, 25.8, 24.7.



4ga

Following the general procedure with 4-iodobenzotrifluoride **2g** (0.5 mmol, 74 µL mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ga** as a pale yellow solid (98 mg, 76%). The spectroscopic data are in agreement with those reported in the literature.[5]

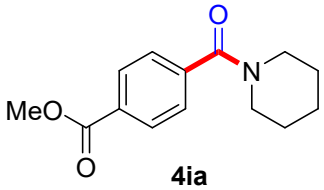
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 3.72 (bs, 2H), 3.29 (bs, 2H), 1.60 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 140.2, 131.48 (q, J = 32.7 Hz), 127.3, 125.7 (q, J = 3.8 Hz), 123.9 (q, J = 272.3 Hz), 48.8, 43.3, 26.7, 25.7, 24.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.81.



4ha

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 40/60) to afford **4ha** as a yellow powder (95 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.[5]

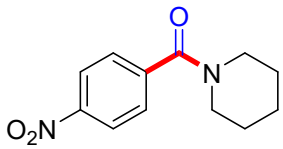
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 3.71 (bs, 2H), 3.27 (bs, 2H), 1.69 (bs, 4H), 1.51 (bs, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 141.0, 132.5, 127.6, 118.3, 113.3, 48.8, 43.3, 26.6, 25.6, 24.5.



4ia

Following the general procedure with methyl 4-iodobenzoate **2i** (0.5 mmol, 131 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ia** as a beige powder (85 mg, 68%). The spectroscopic data are in agreement with those reported in the literature.[5]

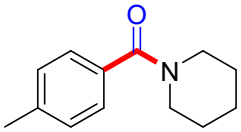
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 3.71 (bs, 2H), 3.28 (bs, 2H), 1.68 (bs, 4H), 1.50 (bs, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 166.6, 141.0, 131.0, 129.9, 126.9, 52.4, 48.8, 43.2, 26.6, 25.7, 24.6.



4ja

Following the general procedure with 1-iodo-4-nitrobenzene **2j** (0.5 mmol, 124 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 30/70) to afford **4ja** as a yellow solid (89 mg, 76%). The spectroscopic data are in agreement with those reported in the literature.[5]

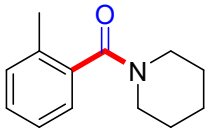
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 3.73 (s, 2H), 3.28 (s, 2H), 1.87 – 1.45 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 148.4, 142.9, 127.9, 124.0, 48.8, 43.3, 26.7, 25.6, 24.6.



4ka

Following the general procedure with 4-iodotoluene **2k** (0.5 mmol, 109 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ka** as a reddish solid (60 mg, 60%). The spectroscopic data are in agreement with those reported in the literature.[4]

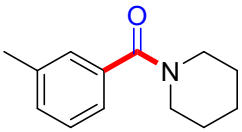
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.67 (br, 2H), 3.37 (br, 2H), 2.36 (s, 3H), 1.70 – 1.65 (br, 4H), 1.57 (br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 139.5, 133.7, 129.1, 127.0, 48.9, 43.3, 26.6, 25.8, 24.8, 21.5.



4la

Following the general procedure with 2-iodotoluene **2l** (0.5 mmol, 64 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4la** as an orange powder (40 mg, 39%). The spectroscopic data are in agreement with those reported in the literature.[5]

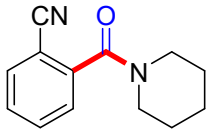
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 1H), 7.22 – 7.11 (m, 3H), 3.74 (m, 2H), 3.17 (m, 2H), 2.30 (s, 3H), 1.73 – 1.59 (m, 4H), 1.54 – 1.39 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 136.9, 134.1, 130.4, 128.7, 126.0, 125.7, 48.0, 42.5, 26.7, 25.9, 24.7, 19.1.



4ma

Following the general procedure with 3-iodotoluene **2m** (0.5 mmol, 64 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4ma** as an orange oil (64 mg, 60%). The spectroscopic data are in agreement with those reported in the literature.[5]

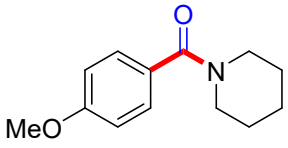
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 1H), 7.20 – 7.11 (m, 3H), 3.68 (br, 2H), 3.32 (br, 2H), 2.35 (s, 3H), 1.65 (br, 4H), 1.49 (br, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 138.3, 136.6, 130.1, 128.3, 127.5, 123.7, 48.8, 43.1, 26.6, 24.7, 21.5.



4na

Following the general procedure with 2-iodobenzonitrile **2n** (0.5 mmol, 114 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 40/60) to afford **4na** as a brown powder (60 mg, 56%). The spectroscopic data are in agreement with those reported in the literature.[7]

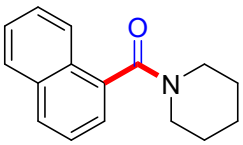
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.54 – 7.46 (m, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 3.77 (t, *J* = 5.0 Hz, 2H), 3.24 (t, *J* = 5.5 Hz, 2H), 1.93 – 1.49 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 140.9, 133.2, 133.1, 129.4, 127.4, 117.0, 110.0, 48.5, 43.2, 26.5, 25.5, 24.5.



4oa

Following the general procedure with 4-iodoanisole **2o** (0.5 mmol, 117 mg) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 30/70) to afford **4oa** as a yellow oil (78 mg, 71%). The spectroscopic data are in agreement with those reported in the literature.[5]

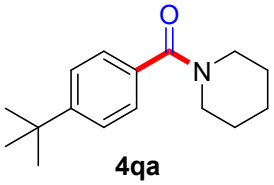
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.71 – 3.34 (m, 4H), 1.71 – 1.45 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.35, 160.55, 128.89, 128.65, 113.67, 55.37, 48.98, 43.46, 26.29, 24.70.



4pa

Following the general procedure with 1-iodonaphthalene **2p** (0.5 mmol, 73 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4pa** as a brown powder (105 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.[8]

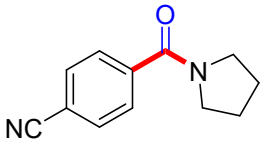
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.72 (m, 3H), 7.66 – 7.31 (m, 4H), 4.02 – 3.62 (m, 2H), 3.48 – 3.01 (m, 2H), 2.02 – 1.54 (m, 4H), 1.46 – 1.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 135.0, 133.6, 129.7, 128.9, 128.4, 126.9, 126.5, 125.3, 125.0, 123.5, 48.4, 42.8, 26.8, 26.0, 24.7.



4qa

Following the general procedure with 4-*tert*-butyliodobenzene **2q** (0.5 mmol, 89 µL) and piperidine **3a** (1 mmol, 99 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 60/40) to afford **4qa** as a yellow solid (86 mg, 70%). The spectroscopic data are in agreement with those reported in the literature.[5]

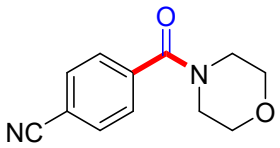
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 3.70 (bs, 2H), 3.38 (bs, 2H), 1.80 – 1.48 (m, 6H), 1.32 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 152.6, 133.7, 126.8, 125.4, 48.9, 43.2, 34.9, 31.3, 26.7, 25.8, 24.8.



4hb

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and pyrrolidine **3b** (1 mmol, 84 µL). The crude product was purified by flash column chromatography (cyclohexane/ ethyl acetate, 34/66) to afford **4hb** as a brownish solid (70 mg, 70%). The spectroscopic data are in agreement with those reported in the literature.[9]

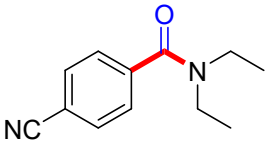
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.54 (d, *J* = 8.3 Hz, 2H), 3.60 (t, *J* = 6.9 Hz, 2H), 3.33 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.75 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 141.3, 132.2, 127.7, 118.1, 113.4, 49.3, 46.3, 26.3, 24.3.



4hc

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and morpholine **3c** (1 mmol, 87 µL). The crude product was purified by flash column chromatography (cyclohexane/ ethyl acetate, 50/50) to afford **4hc** as a brown powder (54 mg, 50%). The spectroscopic data are in agreement with those reported in the literature.[10]

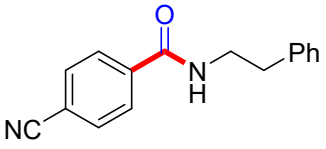
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 3.77 (s, 4H), 3.68 – 3.52 (m, 2H), 3.37 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 139.7, 132.5, 127.8, 118.0, 113.7, 66.7.



4hd

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and *N*,*N*-diethylamine **3d** (1 mmol, 103 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4hd** as a brown powder (70 mg, 69%). The spectroscopic data are in agreement with those reported in the literature.[11]

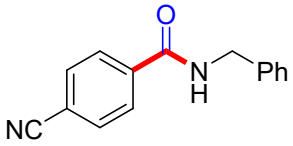
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 3.55 (bs, 2H), 3.20 (bs, 2H), 1.36 – 1.03 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.3, 141.7, 132.5, 127.2, 118.3, 113.2, 43.4, 39.6, 14.3, 13.0.



4hf

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and phenethylamine **3f** (1 mmol, 126 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 34/66) to afford **4hf** as a yellow powder (80 mg, 64%). The spectroscopic data are in agreement with those reported in the literature.[12]

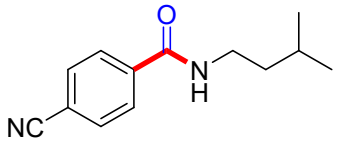
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.20 (m, 5H), 6.27 (s, 1H), 3.75 (q, *J* = 6.9 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 138.7, 138.6, 132.6, 128.9, 128.9, 127.7, 126.9, 118.1, 115.1, 41.4, 35.6.



4hg

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and benzylamine **3g** (1 mmol, 109 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4hg** as a yellow powder (75 mg, 63%). The spectroscopic data are in agreement with those reported in the literature.[12]

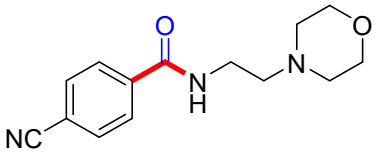
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.64 (s, 1H), 4.63 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 138.4, 137.7, 132.6, 129.0, 128.1, 128.0, 127.8, 118.1, 115.2, 44.5.



4hh

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and isopentylamine **3h** (1 mmol, 116 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4hh** as a yellow solid (50 mg, 46%).

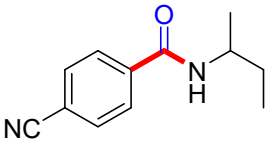
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 6.39 (s, 1H), 3.52 – 3.36 (m, 2H),1.73 – 1.57 (m, 1H), 1.54 – 1.43 (m, 2H), 0.94 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 138.9, 132.5, 127.7, 118.1, 114.9, 38.8, 38.5, 26.0, 22.5. **IR**: ν(CN) 2230, ν(CO) 1636 cm^{-1} **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}N_2OH$ 217.1335. Found 217.1335.



4hi

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and 4-(2-aminoethyl)morpholine **3i** (1 mmol, 131 µL) but the work-up was performed with a 1M solution of KOH instead of 1M HCl. The crude product was purified by flash column chromatography (CH_2Cl_2/ MeOH, 98/2) to afford **4hi** as a yellow solid (80 mg, 62%).

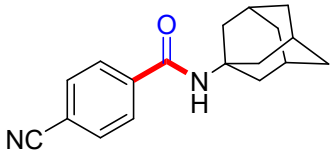
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 6.86 (s, 1H), 3.85 – 3.63 (m, 4H), 3.66 – 3.45 (m, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.56 – 2.51 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 138.6, 132.6, 127.8, 118.2, 115.2, 67.1, 56.8, 53.4, 36.3. **IR:** ν(CN) 2235; ν(CO) 1639 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_3O_2H$ 260.1394. Found 260.1394.



4hj

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and *sec*-butylamine **3j** (1 mmol, 101 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4hj** as a beige powder (86 mg, 85%). The spectroscopic data are in agreement with those reported in the literature.

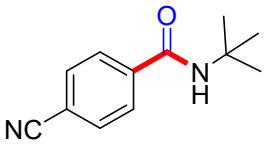
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 4.12 (dq, *J* = 8.4, 6.6 Hz, 1H), 1.59 (p, *J* = 7.3 Hz, 2H), 1.24 (d, *J* = 6.6 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3, 139.1, 132.5, 127.7, 118.2, 115.0, 47.7, 29.8, 20.5, 10.5. **IR:** ν(CN) 2235; ν(CO) 1634 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{14}N_2OH$ 203.1179. Found 203.1179.



4hk

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and adamantylamine **3k** (1 mmol, 151 mg). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 50/50) to afford **4hk** as a white powder (61 mg, 44%). The spectroscopic data are in agreement with those reported in the literature. 2229, 1640.

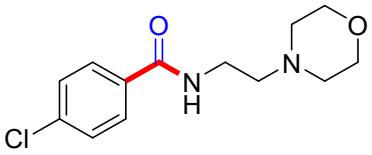
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 5.82 (s, 1H), 2.19 – 2.06 (m, 9H), 1.77 – 1.66 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 140.1, 132.5, 127.6, 118.2, 114.7, 53.0, 41.7, 36.4, 29.6. **IR:** ν(CN) 2229; ν(CO) 1640 cm^{-1}. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{20}N_2OH$ 281.1648. Found 281.1648.



4hl

Following the general procedure with 4-iodobenzonitrile **2h** (0.5 mmol, 114 mg) and *tert*-butylamine **3l** (1 mmol, 105 µL). The crude product was purified by flash column chromatography (cyclohexane/ diethyl ether, 60/40) to afford **4hl** as a yellow solid (30 mg, 30%). The spectroscopic data are in agreement with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 5.97 (s, 1H), 1.47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 140.0, 132.5, 127.6, 118.2, 114.8, 52.3, 28.9.



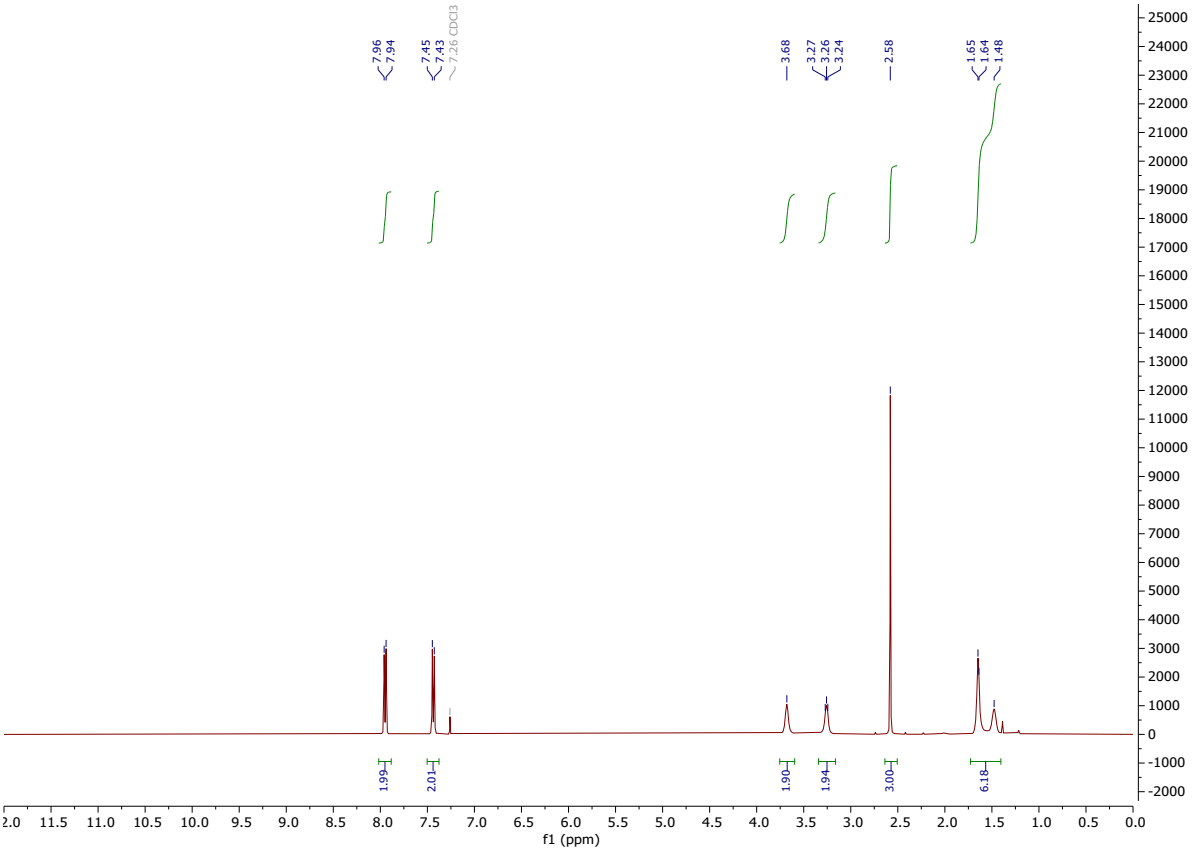
Moclobemide

Following the general procedure with 4-chlorobenzene **2c** (0.5 mmol, 120 mg) and 4-(2-aminoethyl)morpholine **3i** (1 mmol, 131 µL) but the work-up was performed with a 1M solution of KOH instead of 1M HCl. The crude product was purified by flash column chromatography (CH_2Cl_2/ MeOH, 97/3) to afford **Moclobemide** as a yellow solid (107 mg, 79%). The spectroscopic data are in agreement with those reported in the literature.[14]

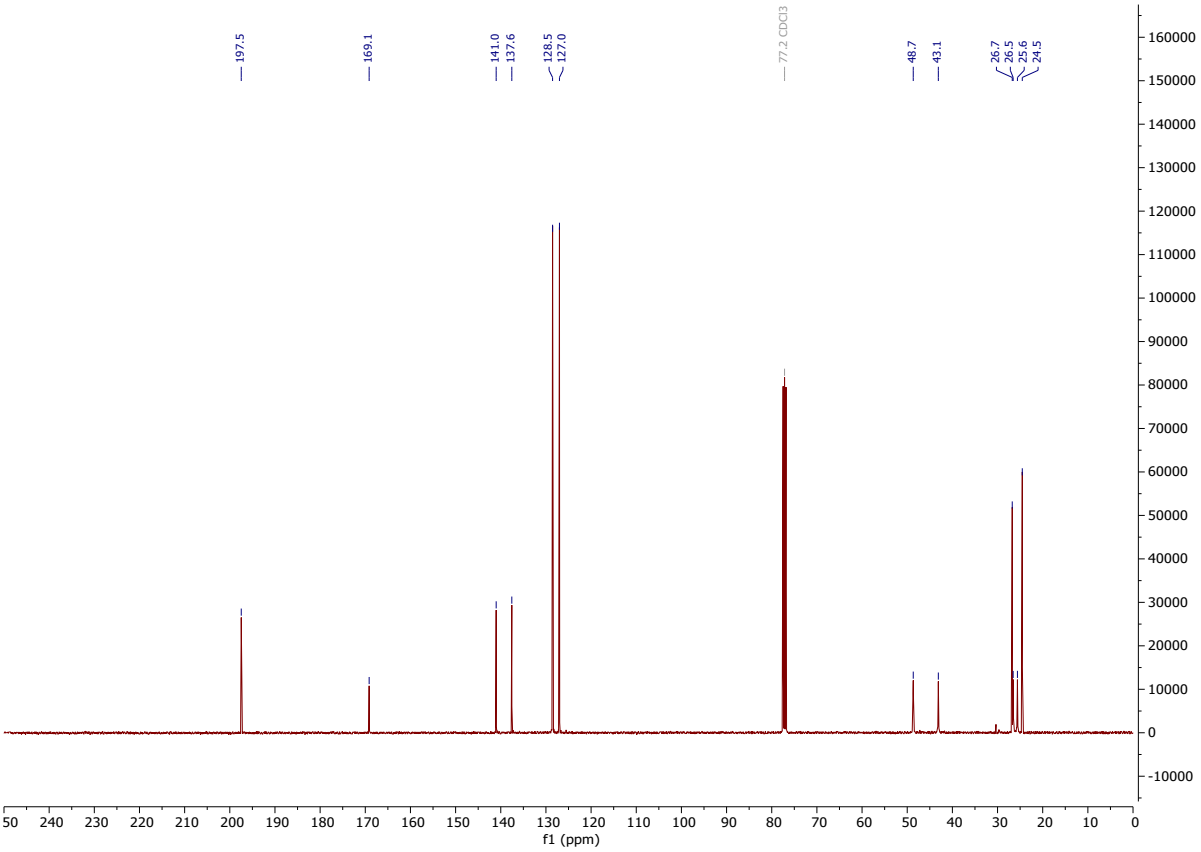
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.78 (s, 1H), 3.92 – 3.73 (m, 4H), 3.61 – 3.46 (m, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 2.56 – 2.42 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 137.6, 133.0, 128.8, 128.4, 67.0, 56.8, 53.3, 36.1.

IV. NMR spectra

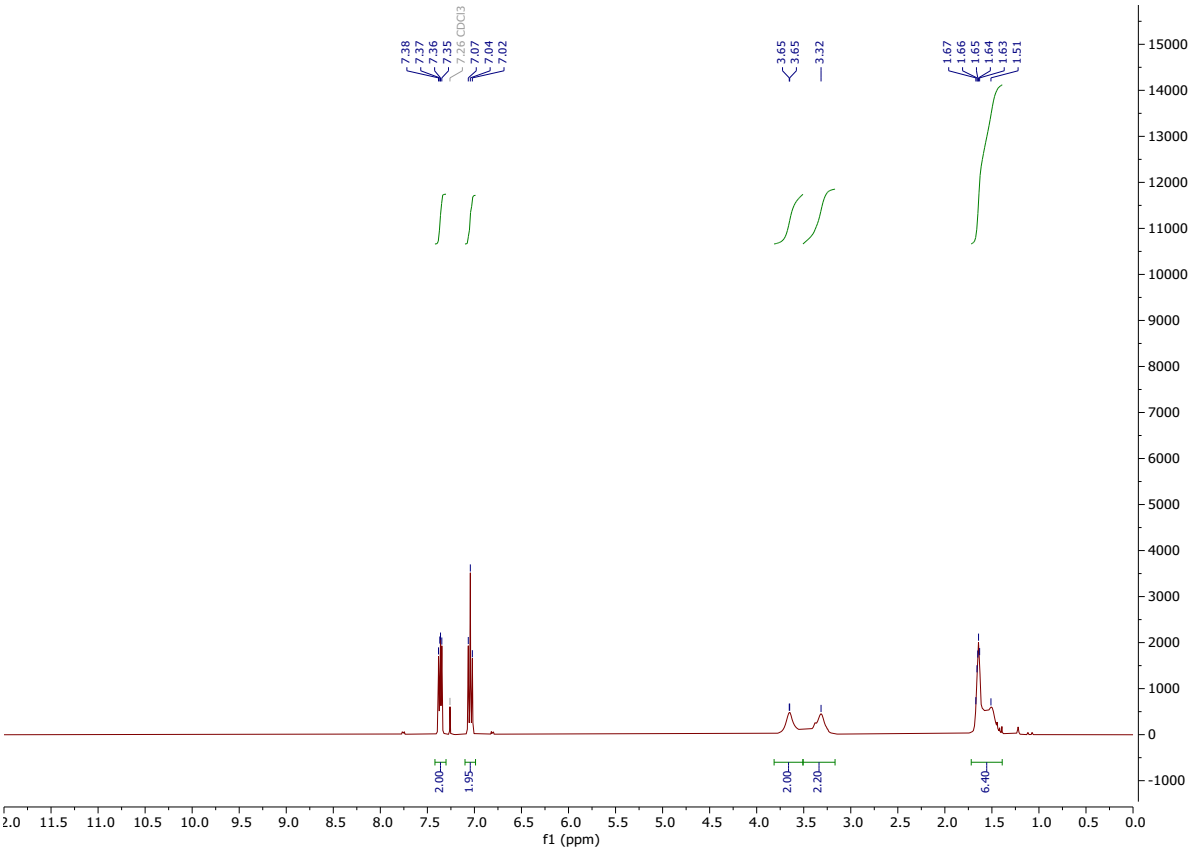
^{1}H NMR spectrum of **4aa**



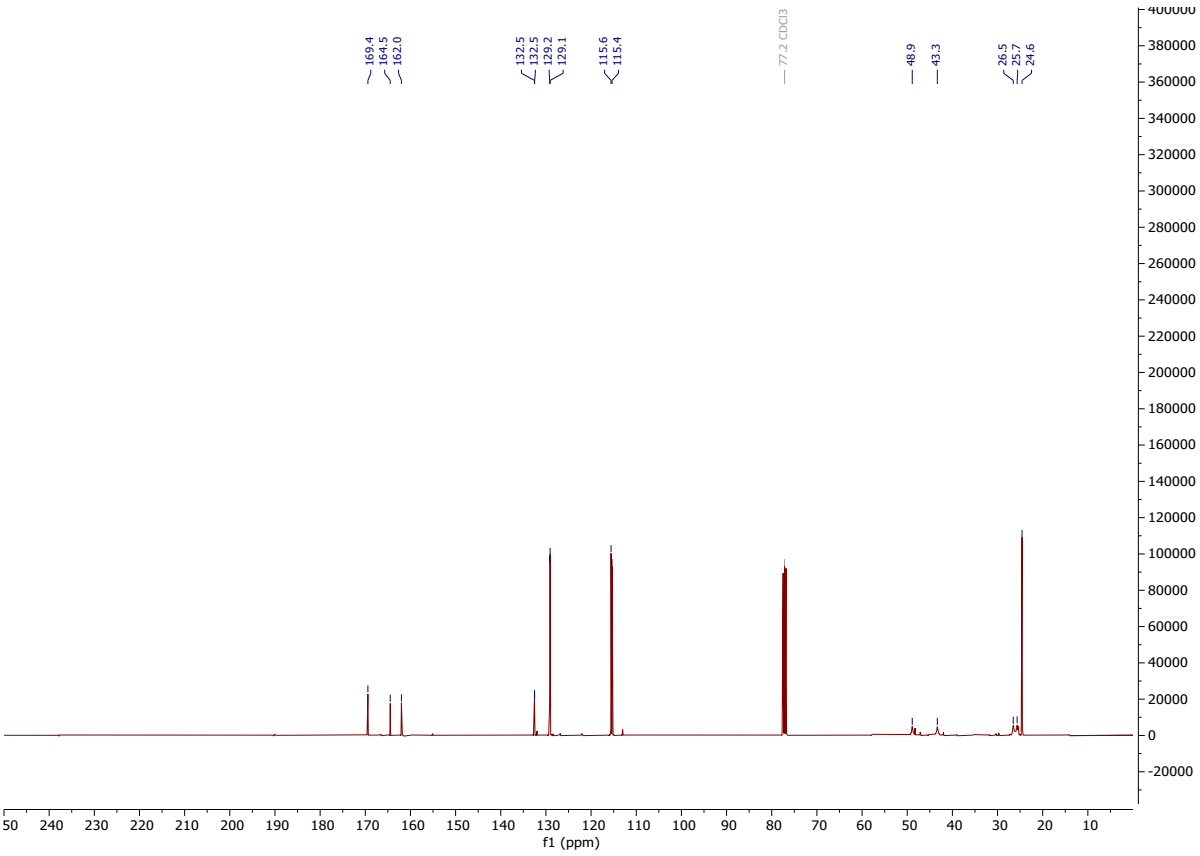
^{13}C NMR spectrum of **4aa**



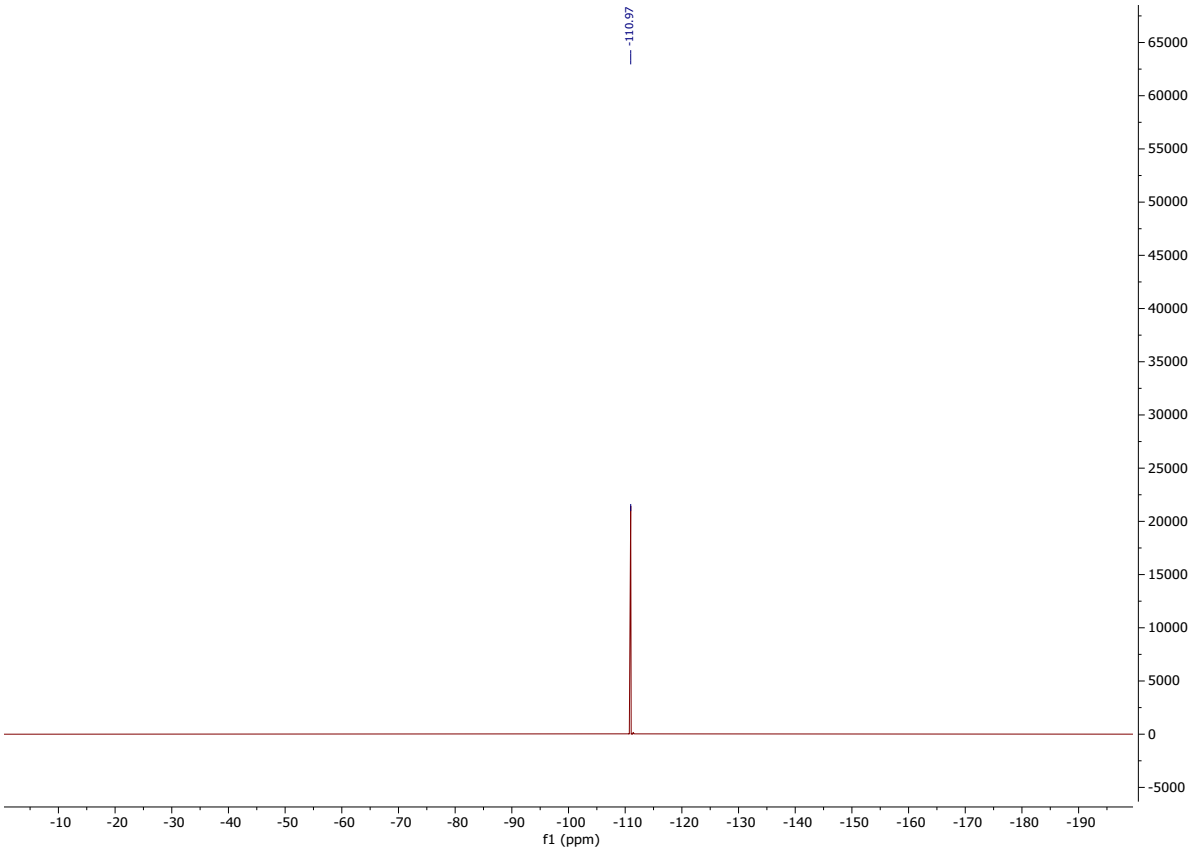
^{1}H NMR spectrum of **4ba**



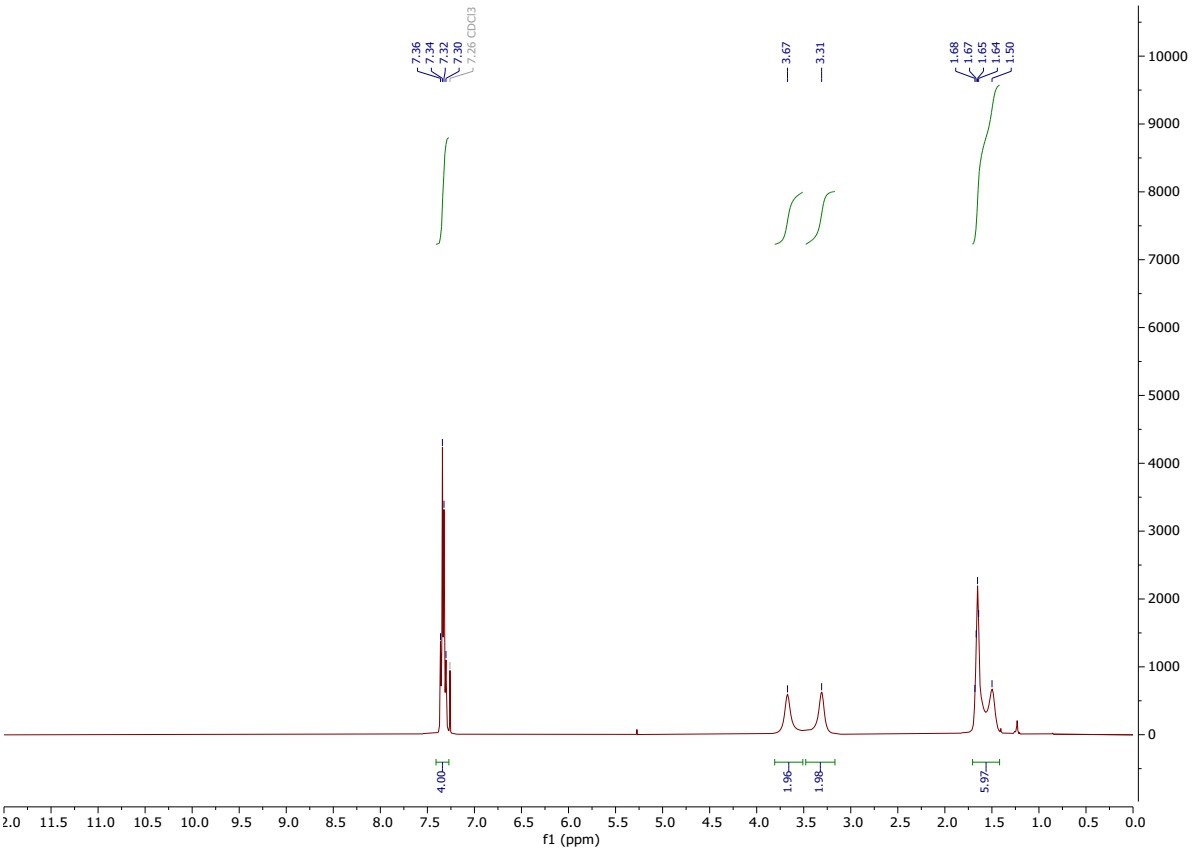
^{13}C NMR spectrum of **4ba**



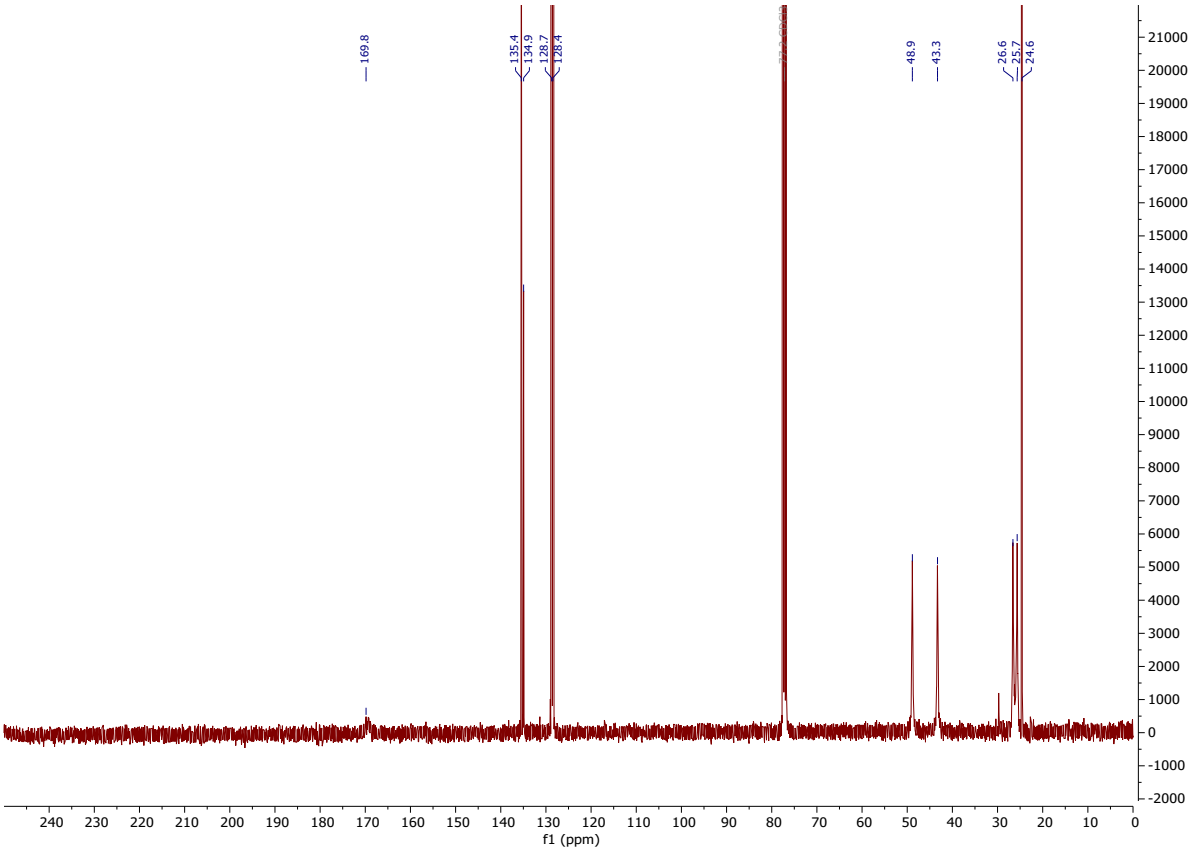
^{19}F NMR spectrum of **4ba**



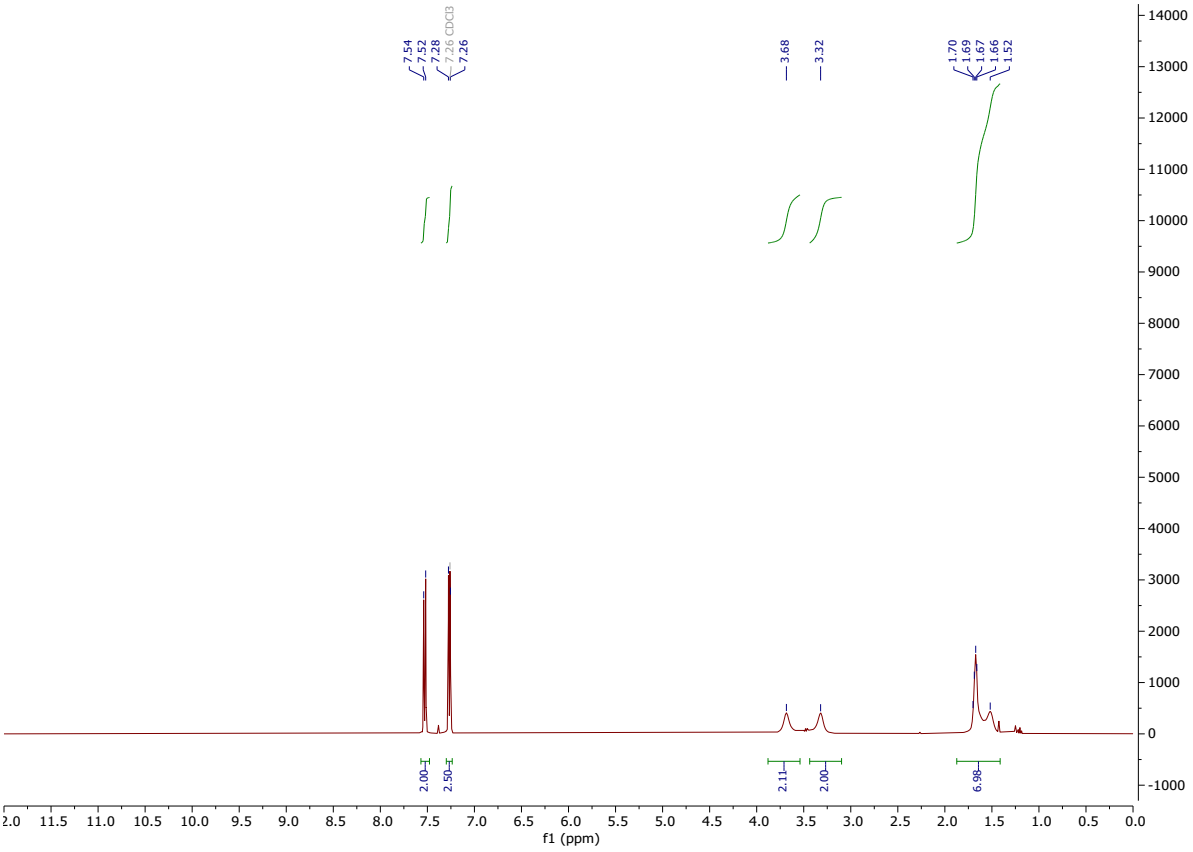
^{1}H NMR spectrum of **4ca**



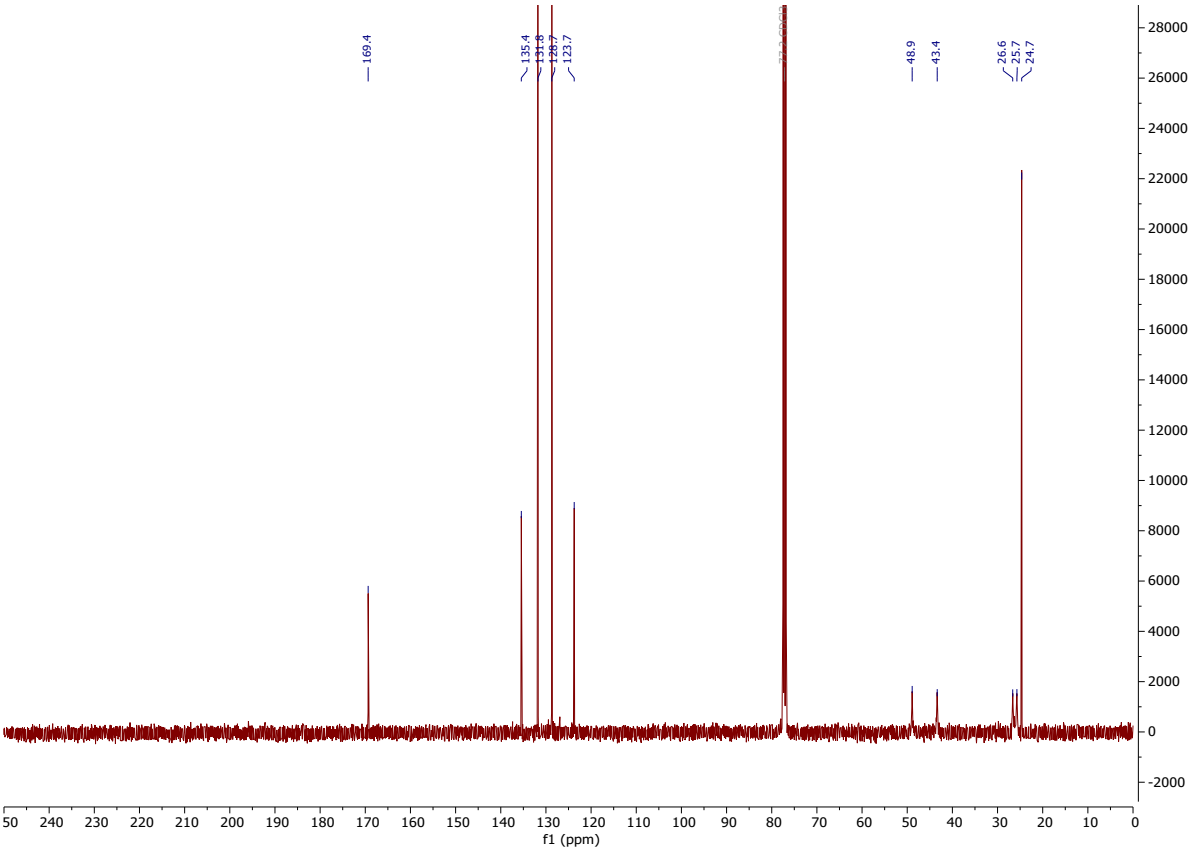
^{13}C NMR spectrum of **4ca**



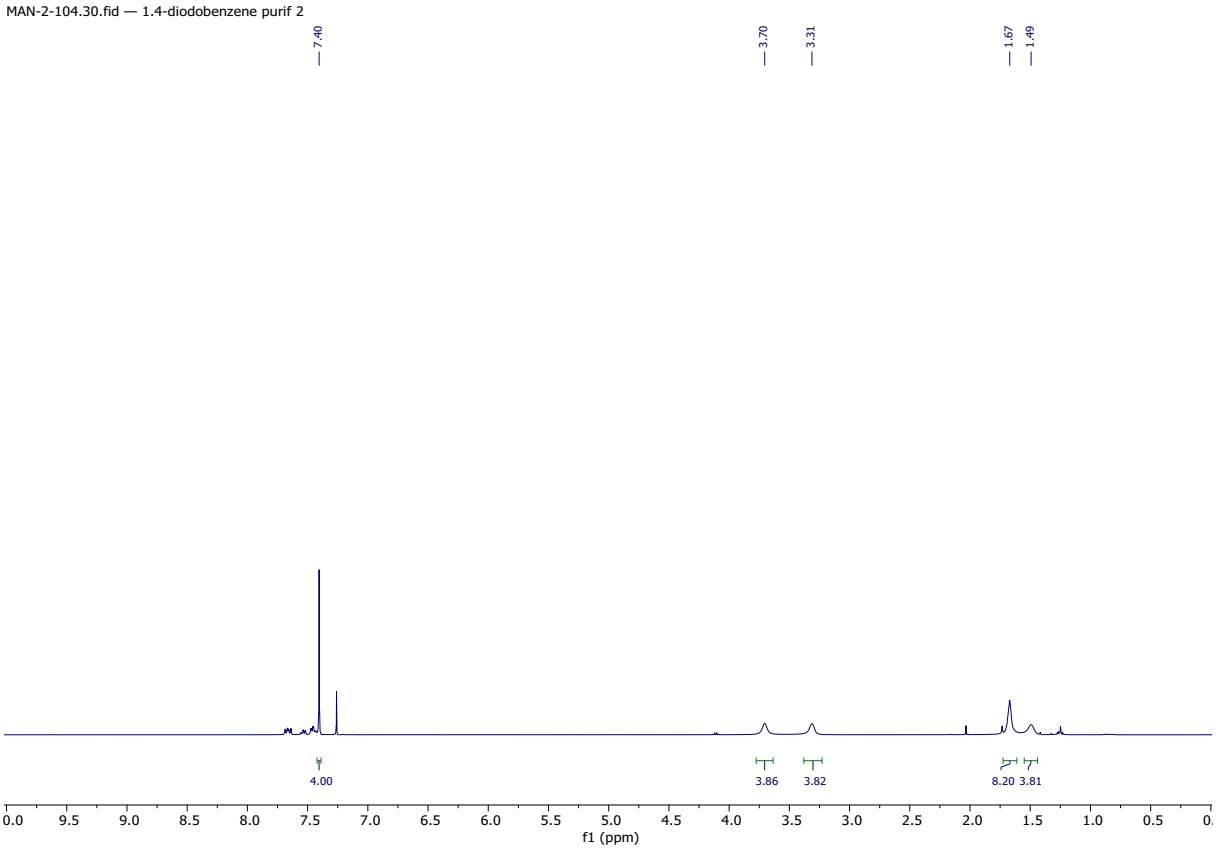
^{1}H NMR spectrum of **4da**



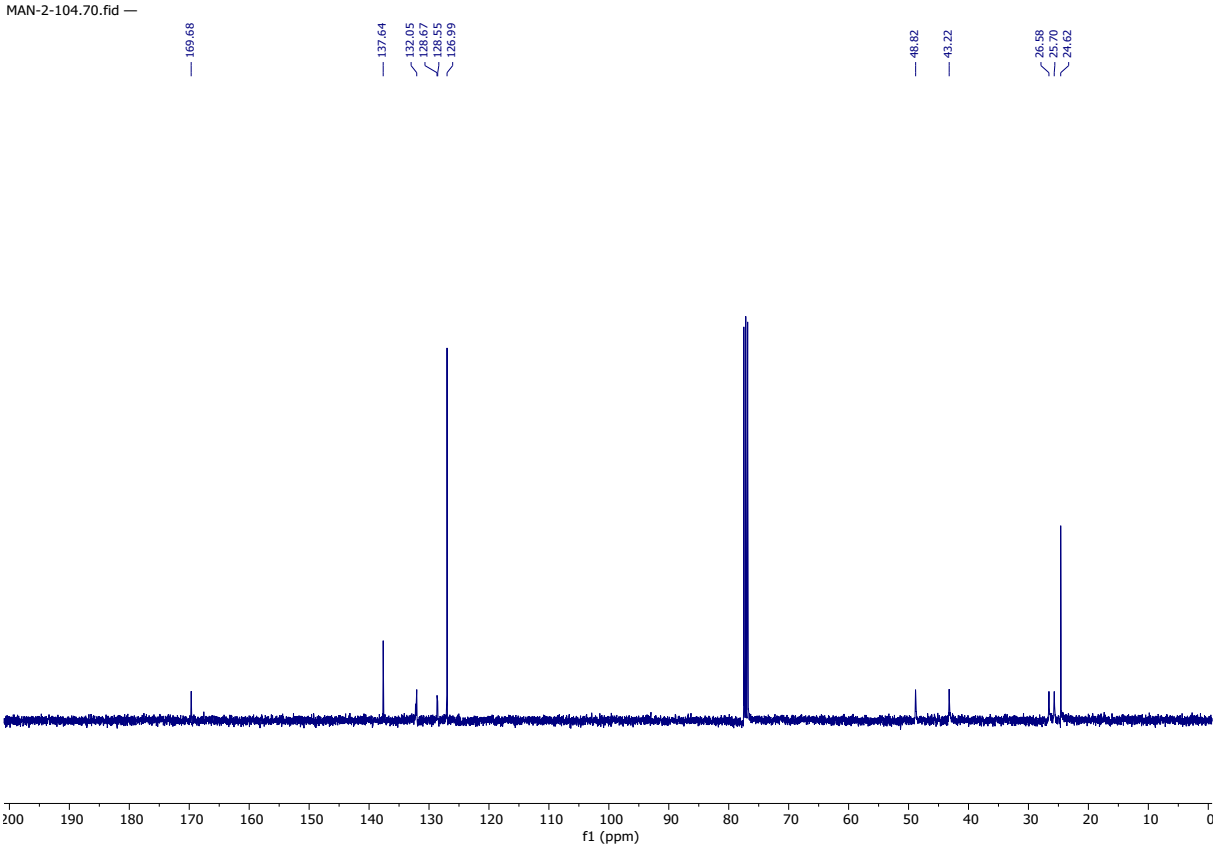
^{13}C NMR spectrum of **4da**



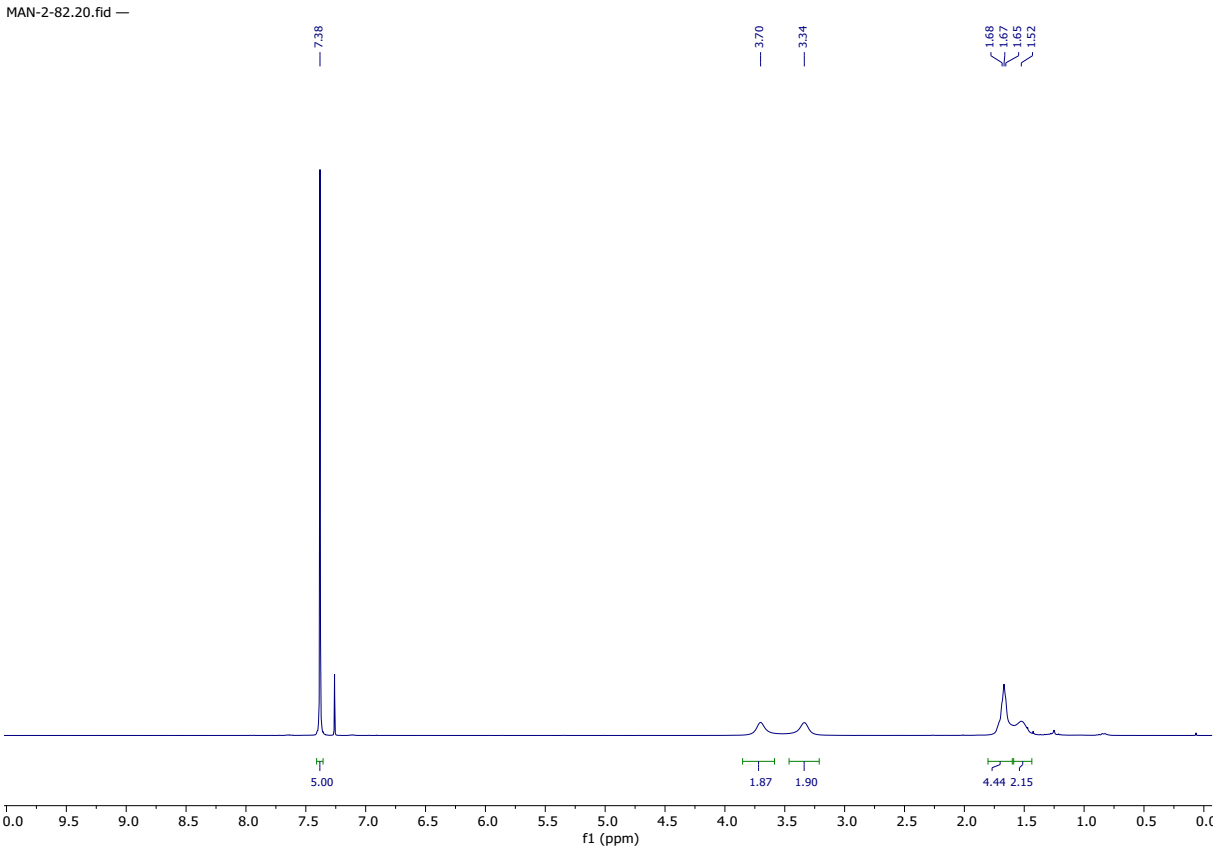
^{1}H NMR spectrum of **4ea**



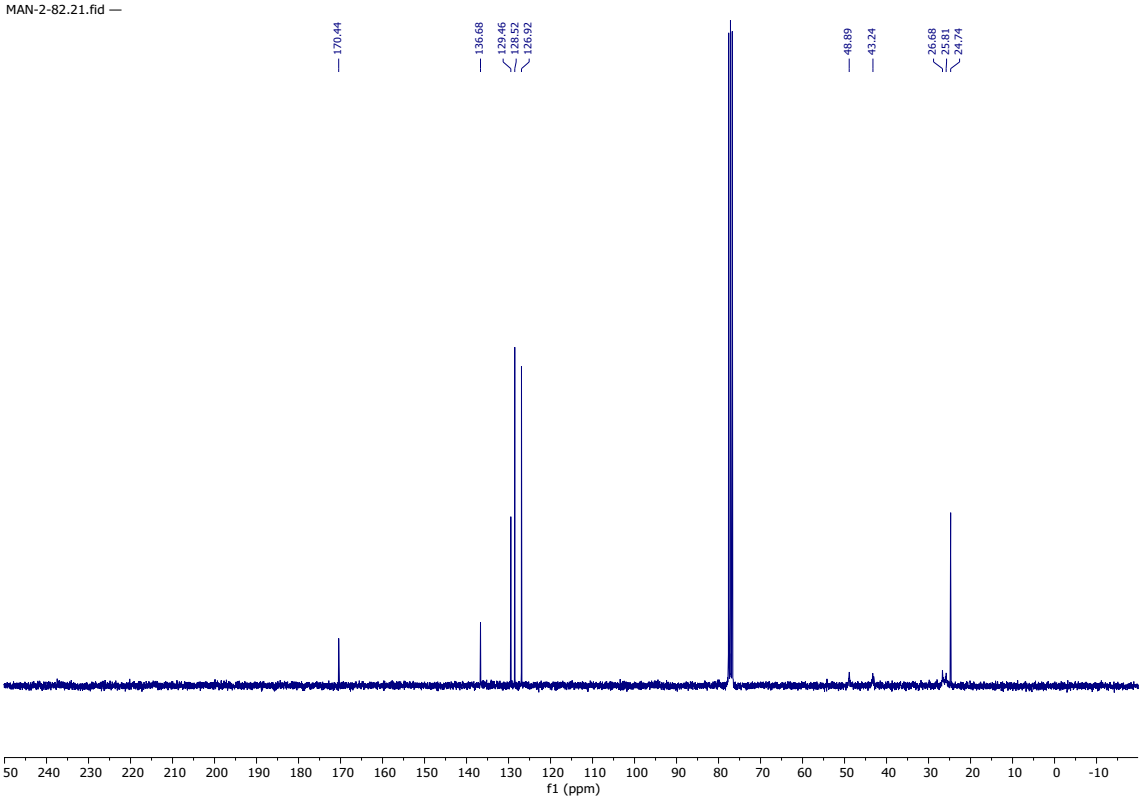
^{13}C NMR spectrum of **4ea**



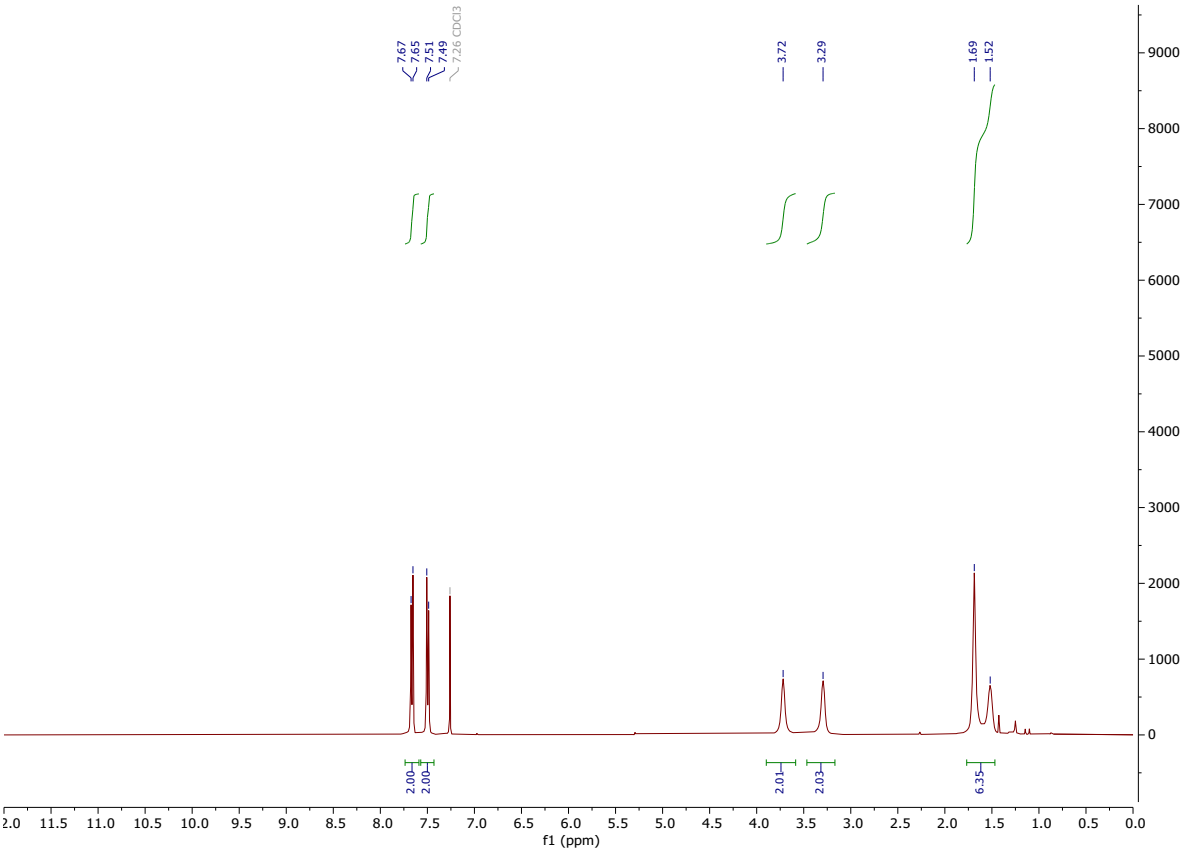
^{1}H NMR spectrum of **4fa**



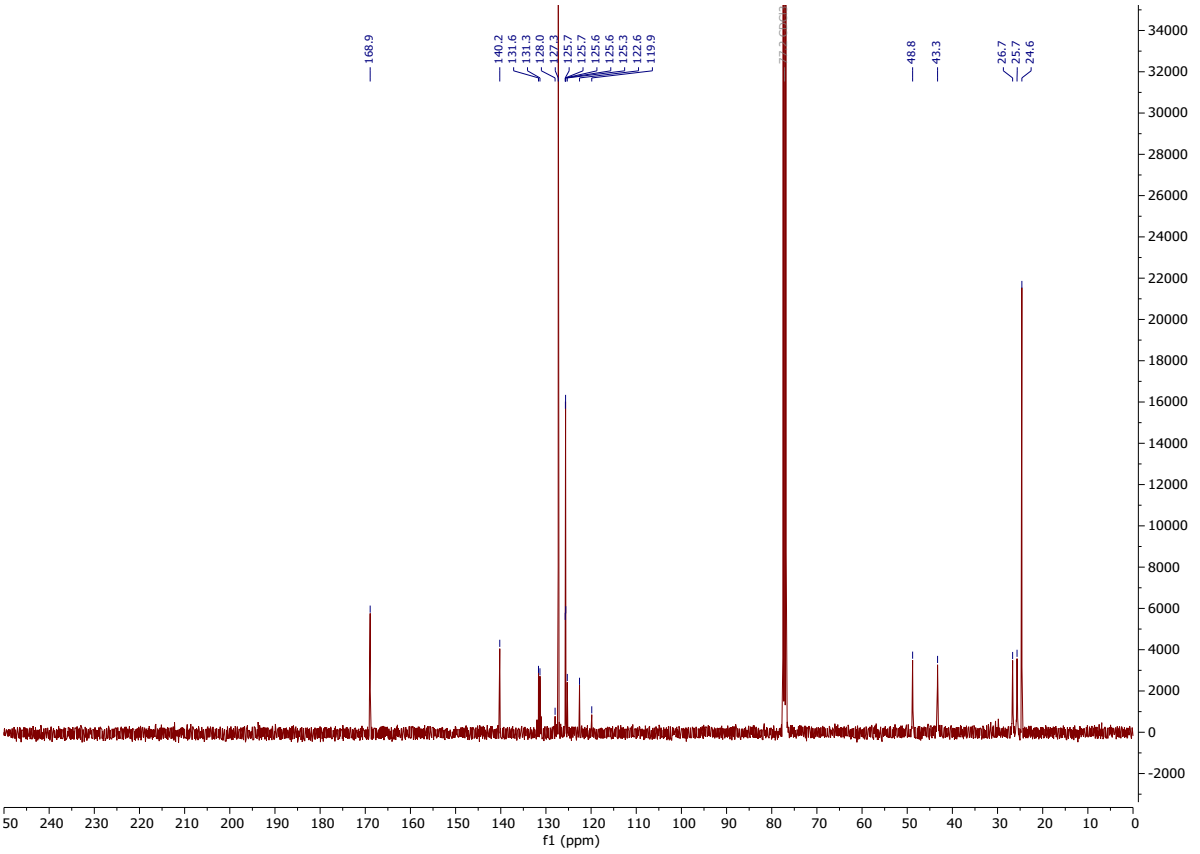
^{13}C NMR spectrum of **4fa**



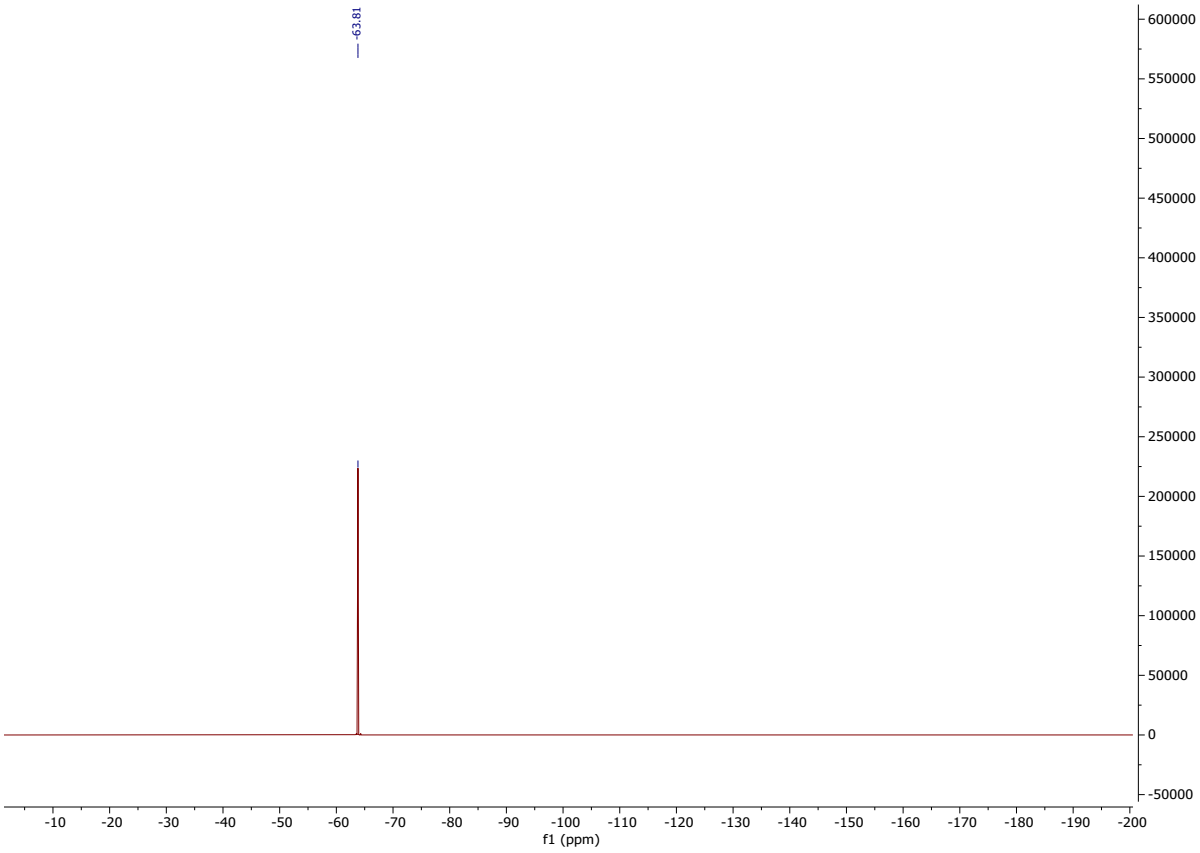
^{1}H NMR spectrum of **4ga**



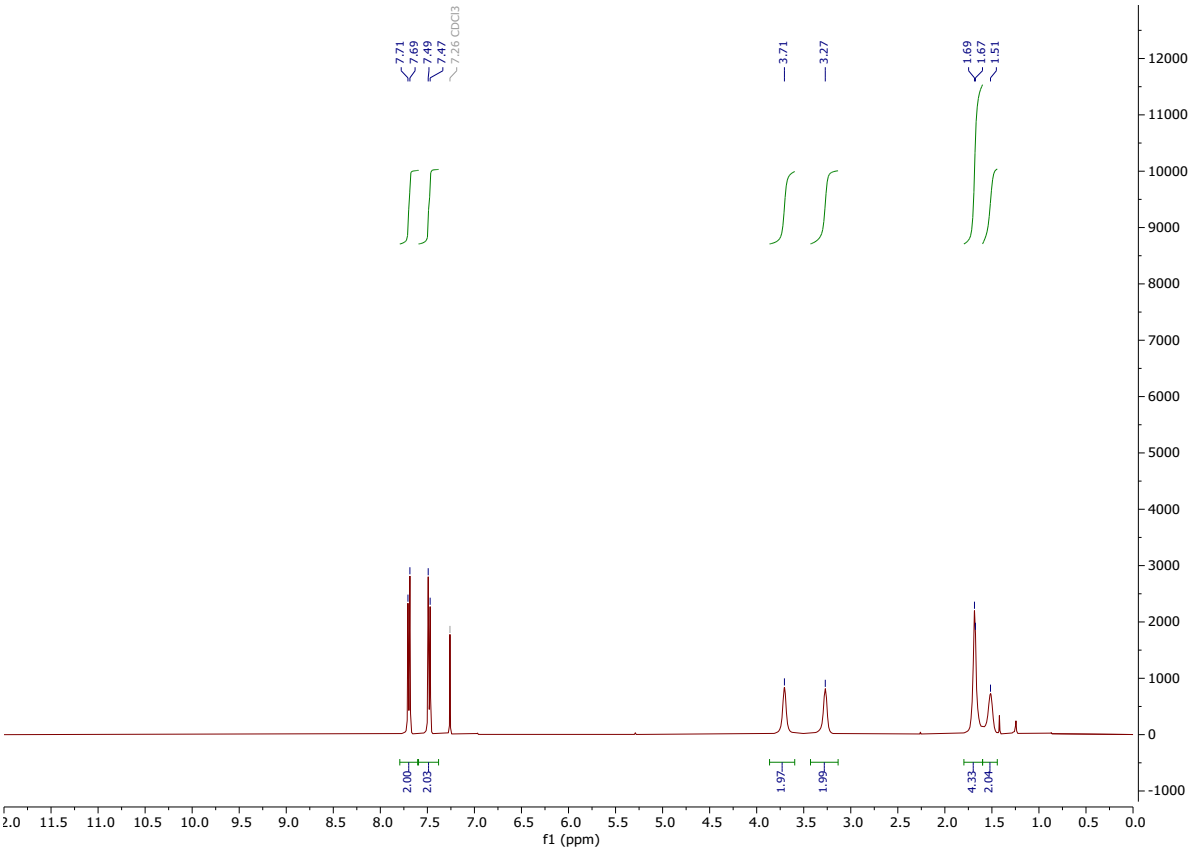
^{13}C NMR spectrum of **4ga**



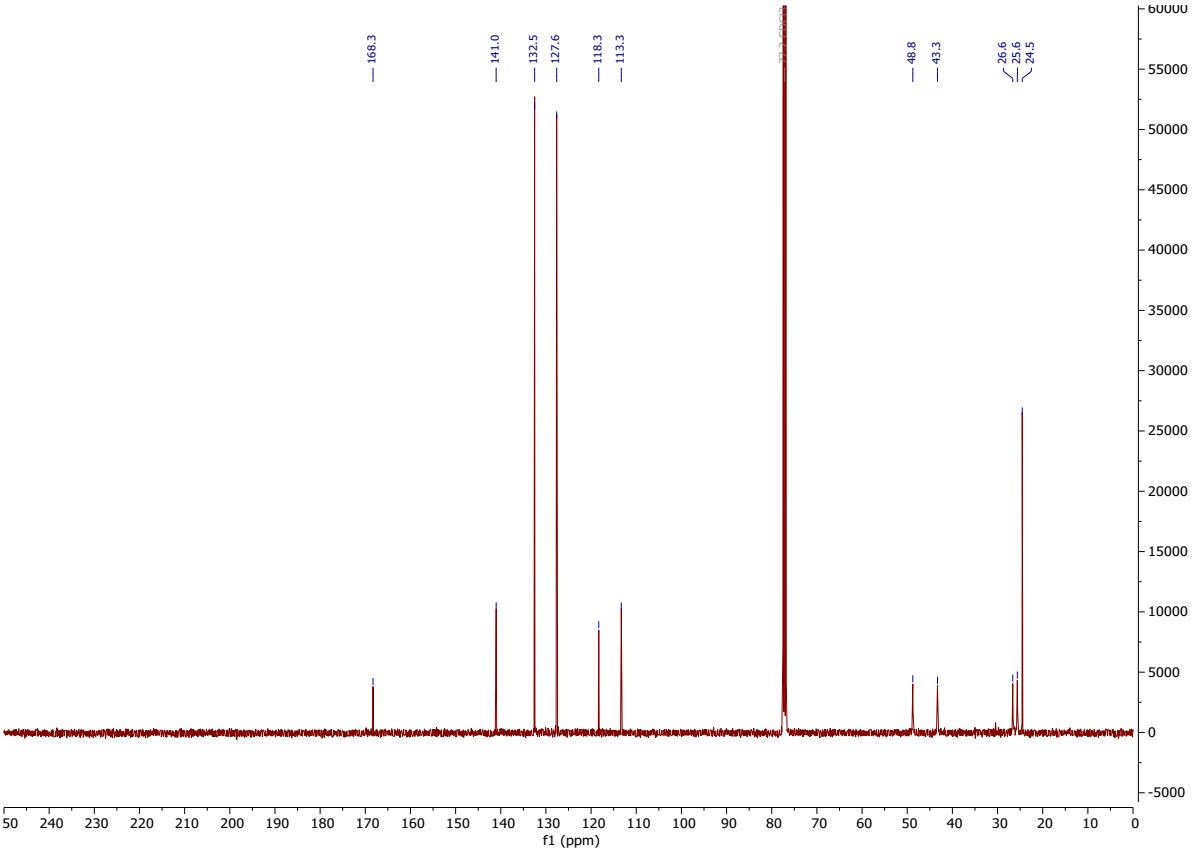
^{19}F NMR spectrum of **4ga**



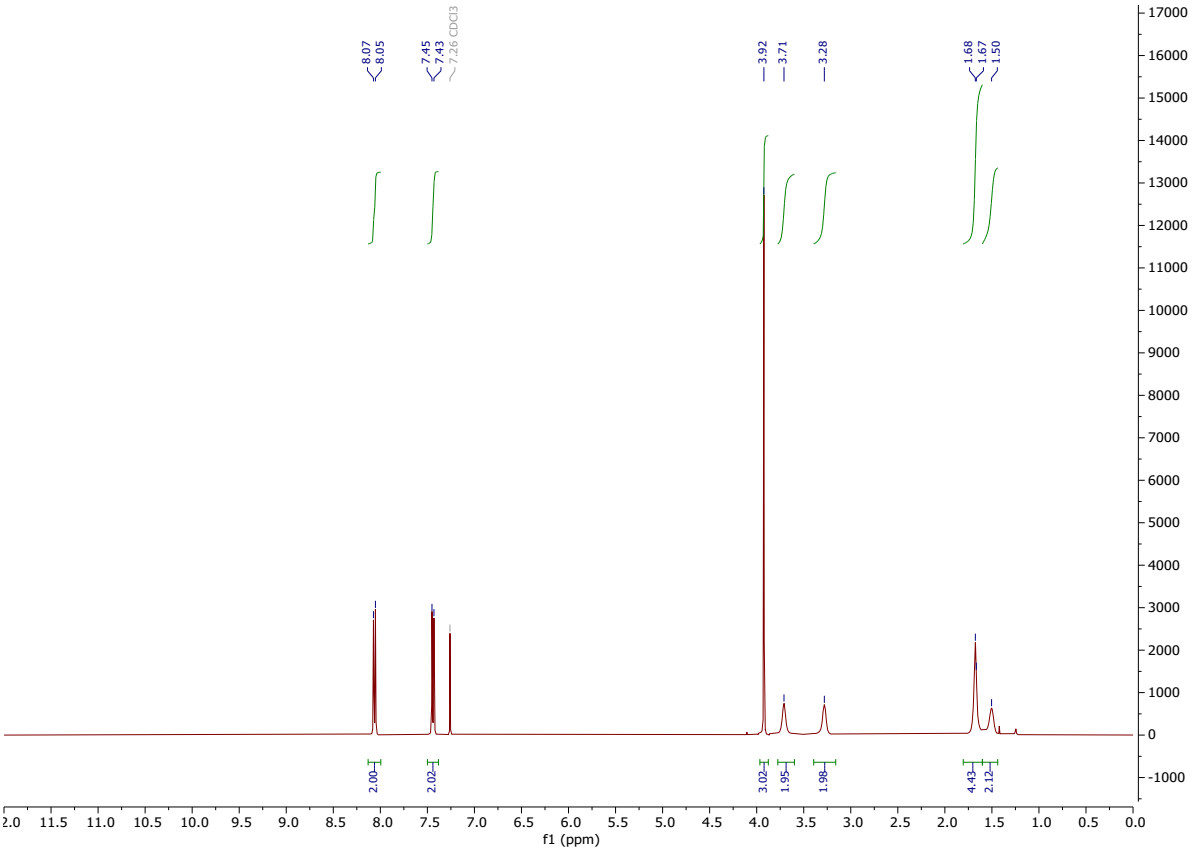
^{1}H NMR spectrum of **4ha**



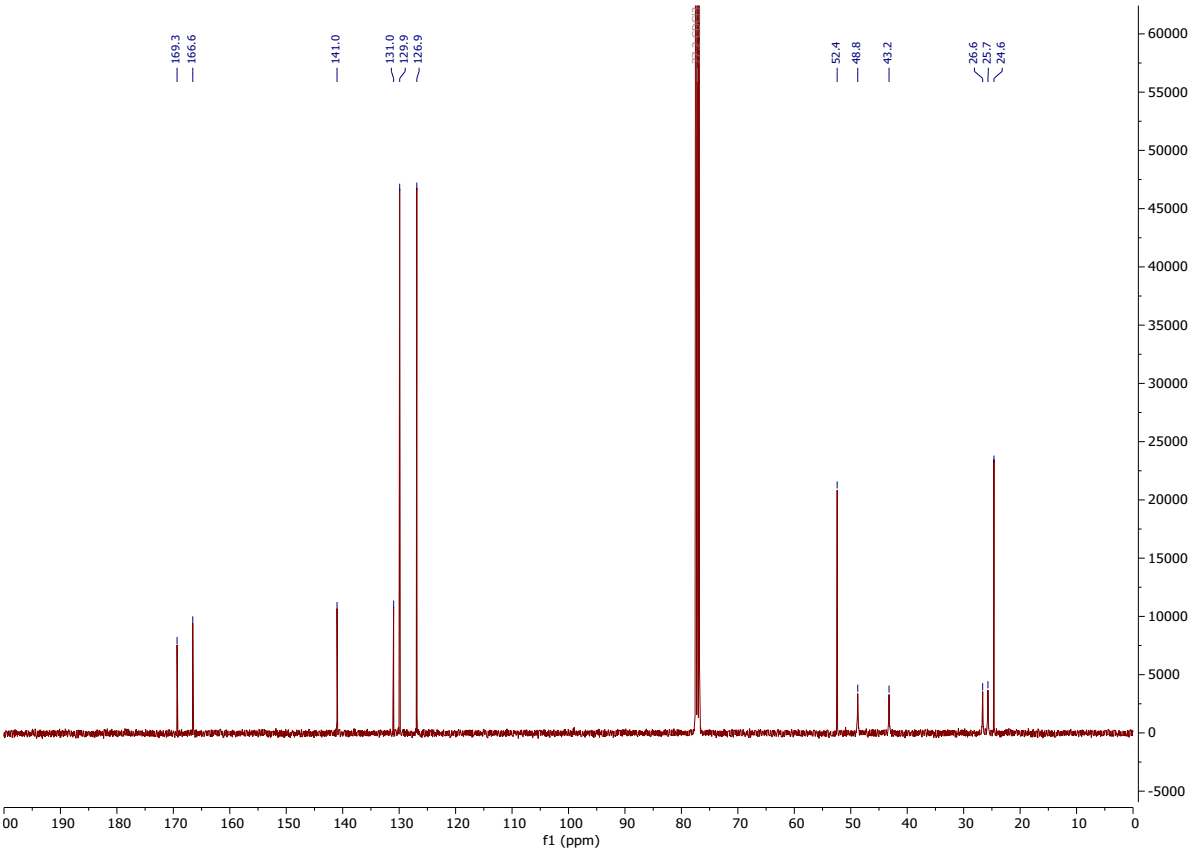
^{13}C NMR spectrum of **4ha**



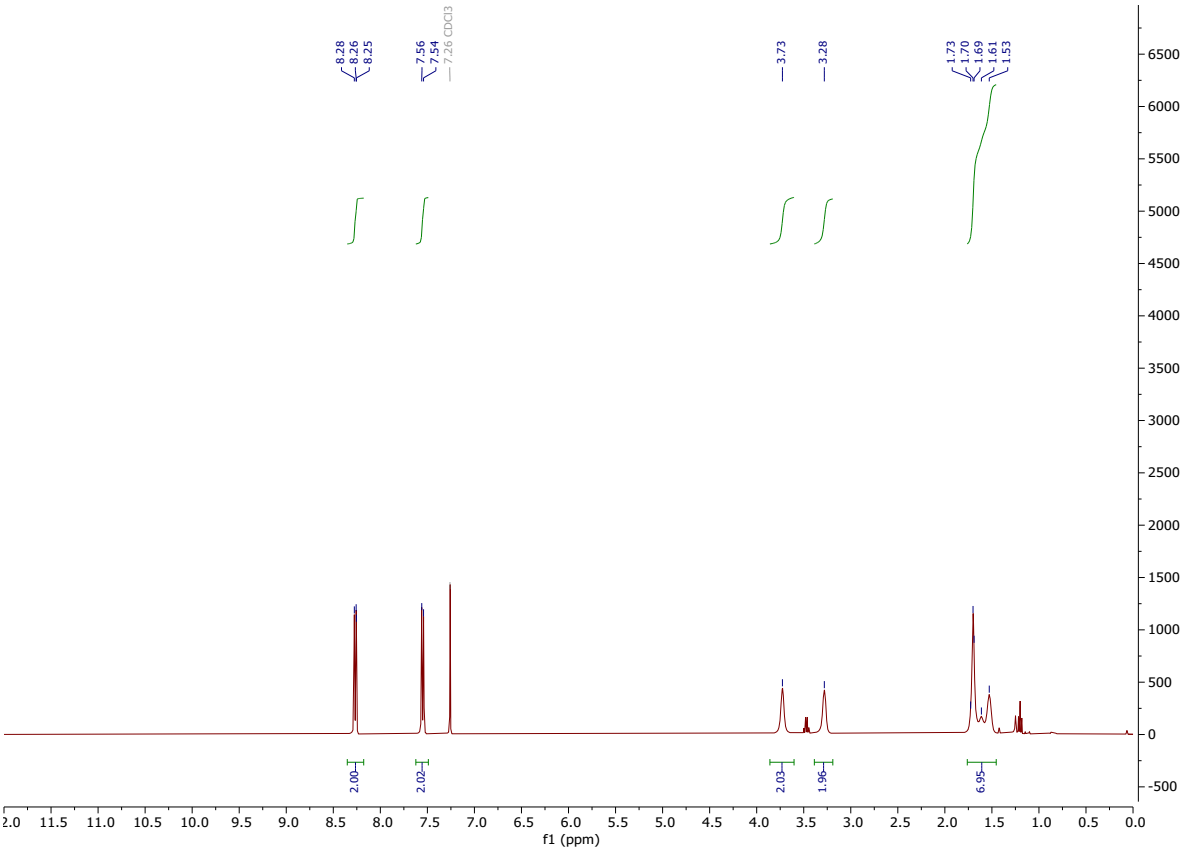
^{1}H spectrum for **4ia**



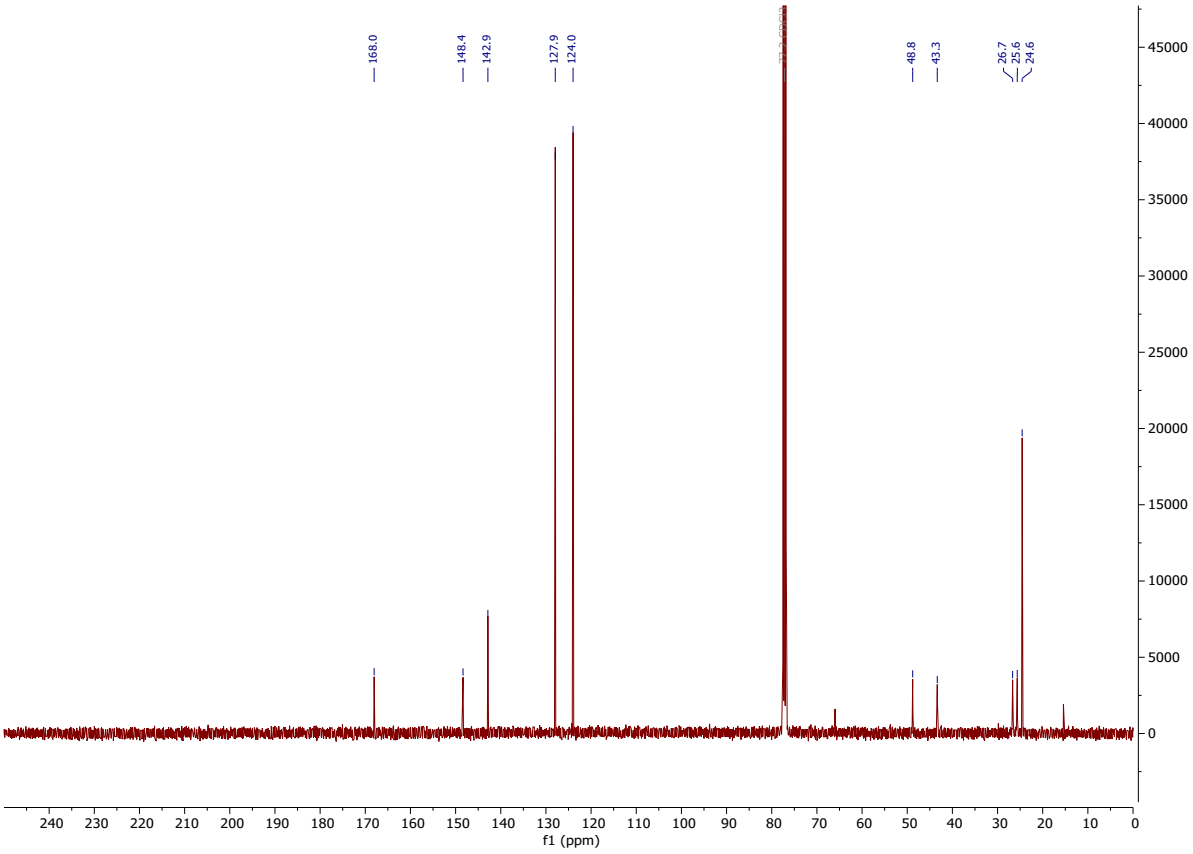
^{13}C spectrum for **4ia**



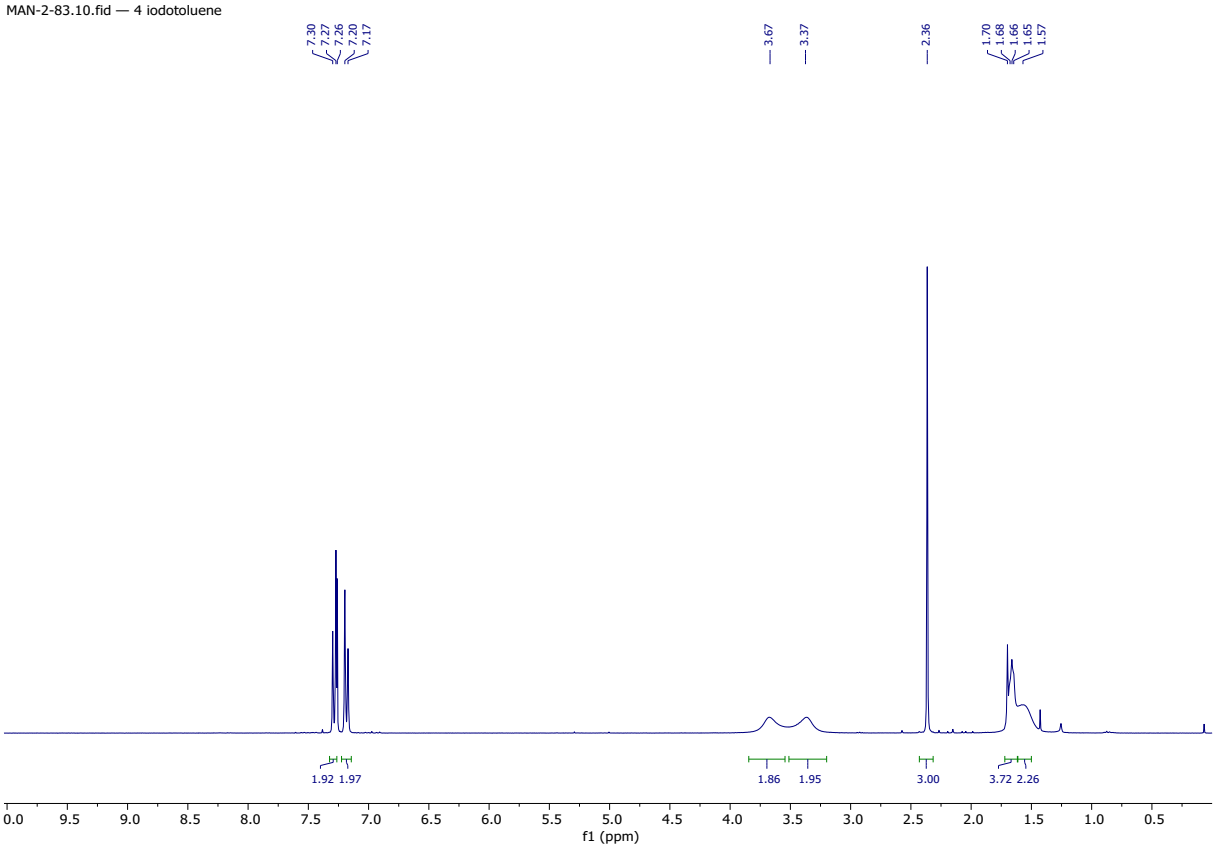
^{1}H NMR spectrum of **4ja**



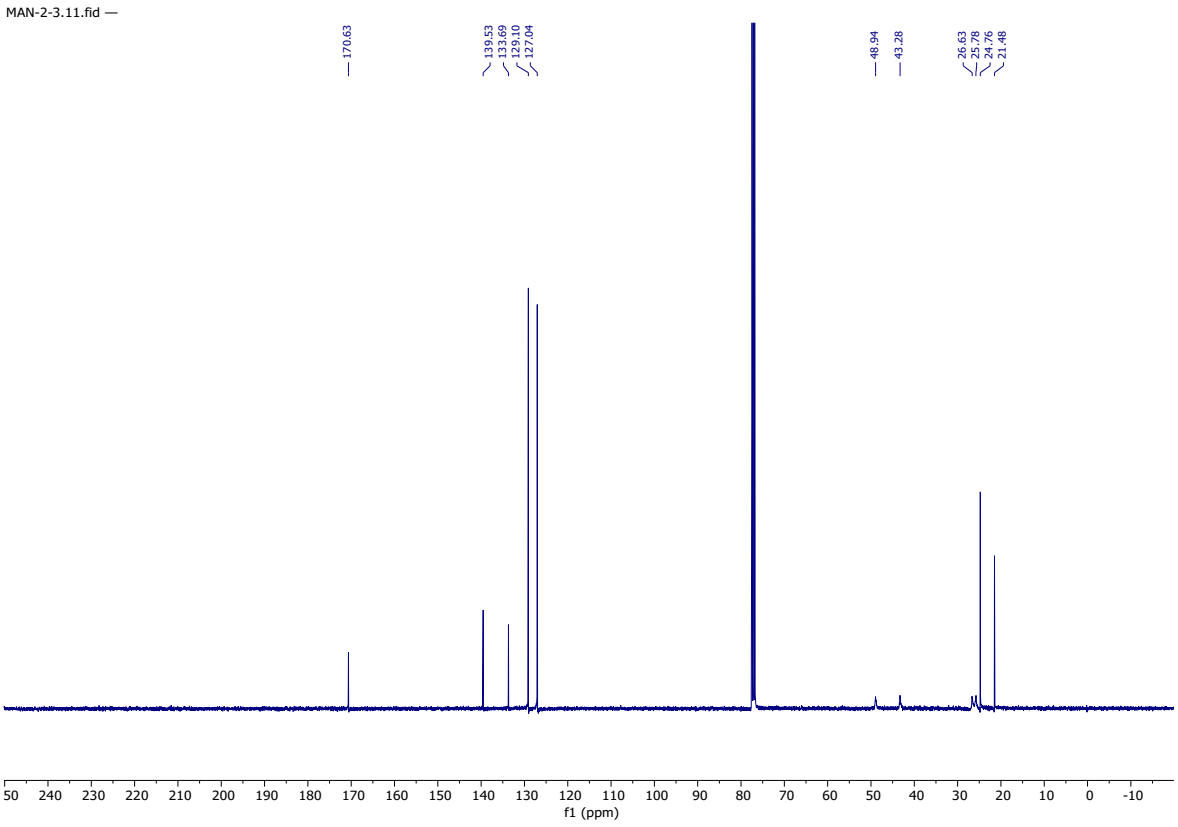
^{13}C NMR spectrum of **4ja**



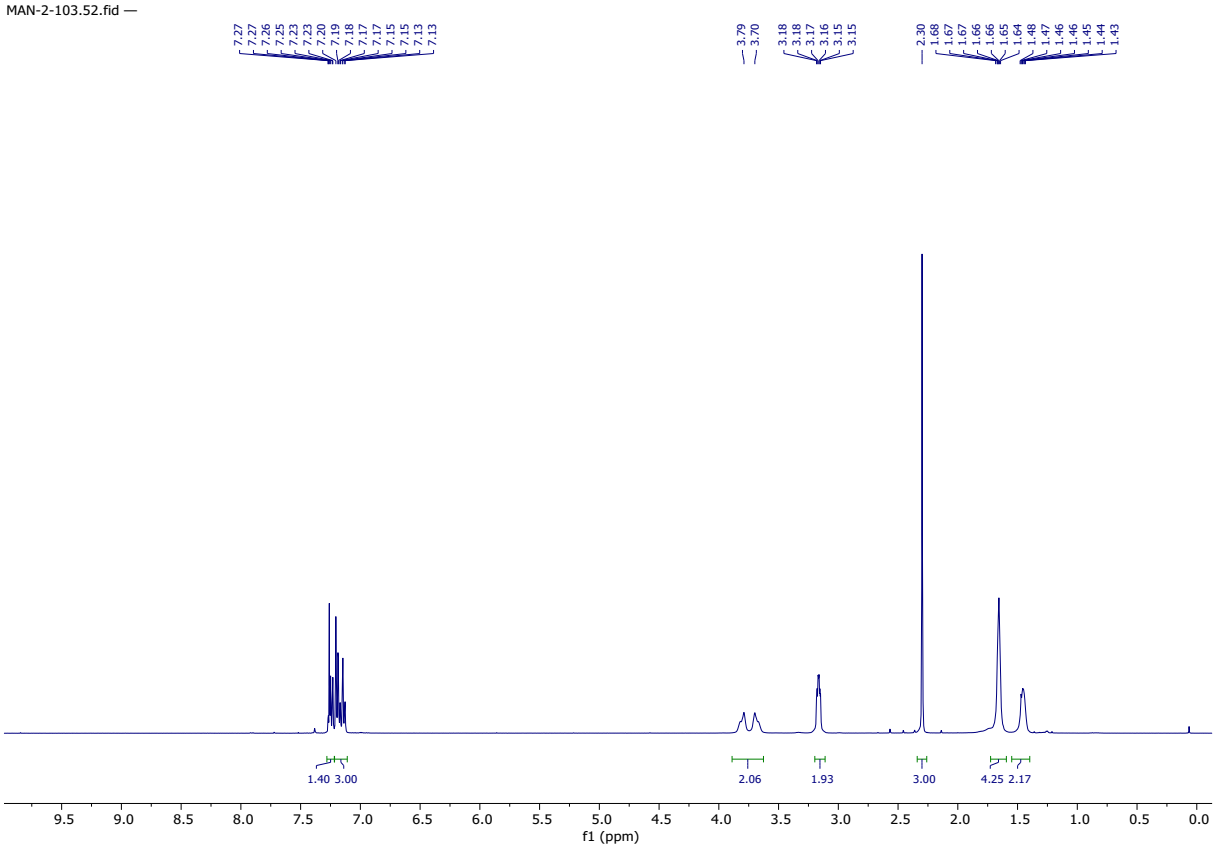
^{1}H NMR spectrum of **4ka**



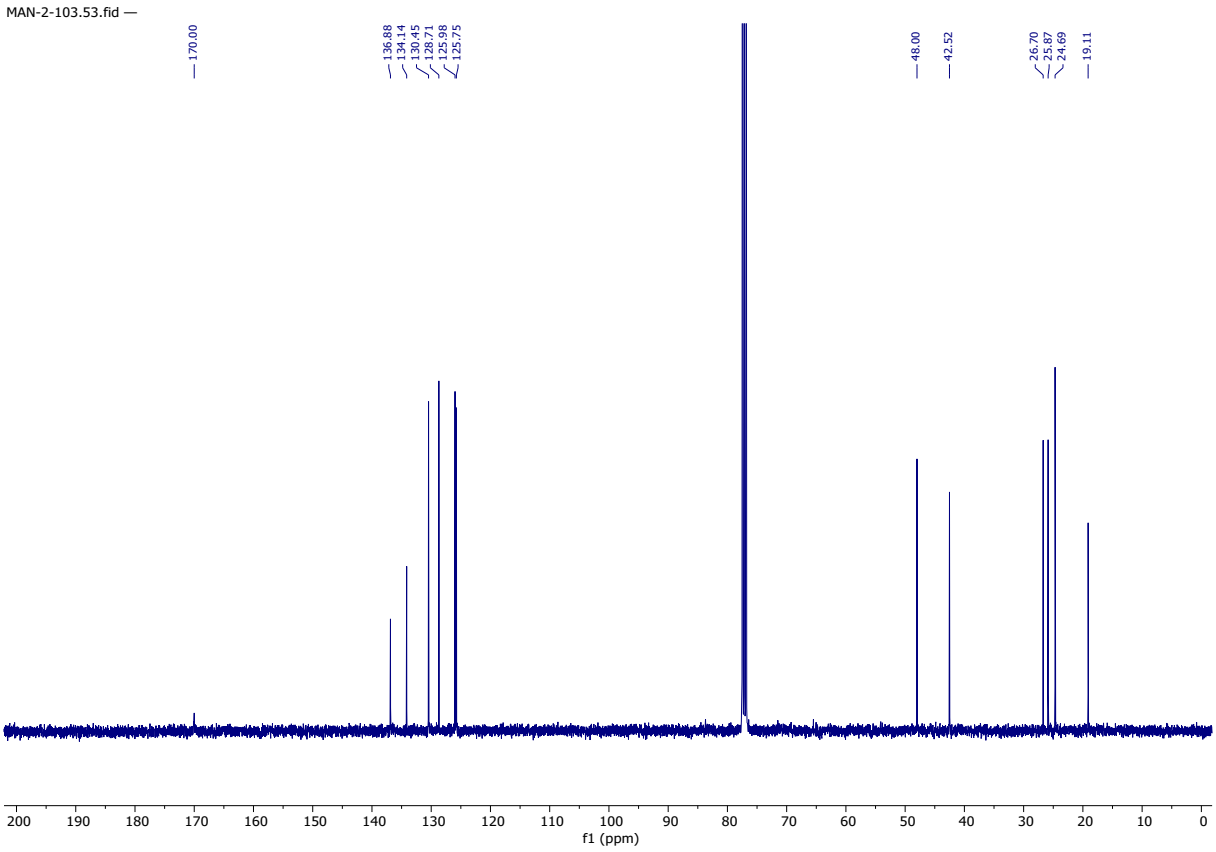
^{13}C NMR spectrum of **4ka**



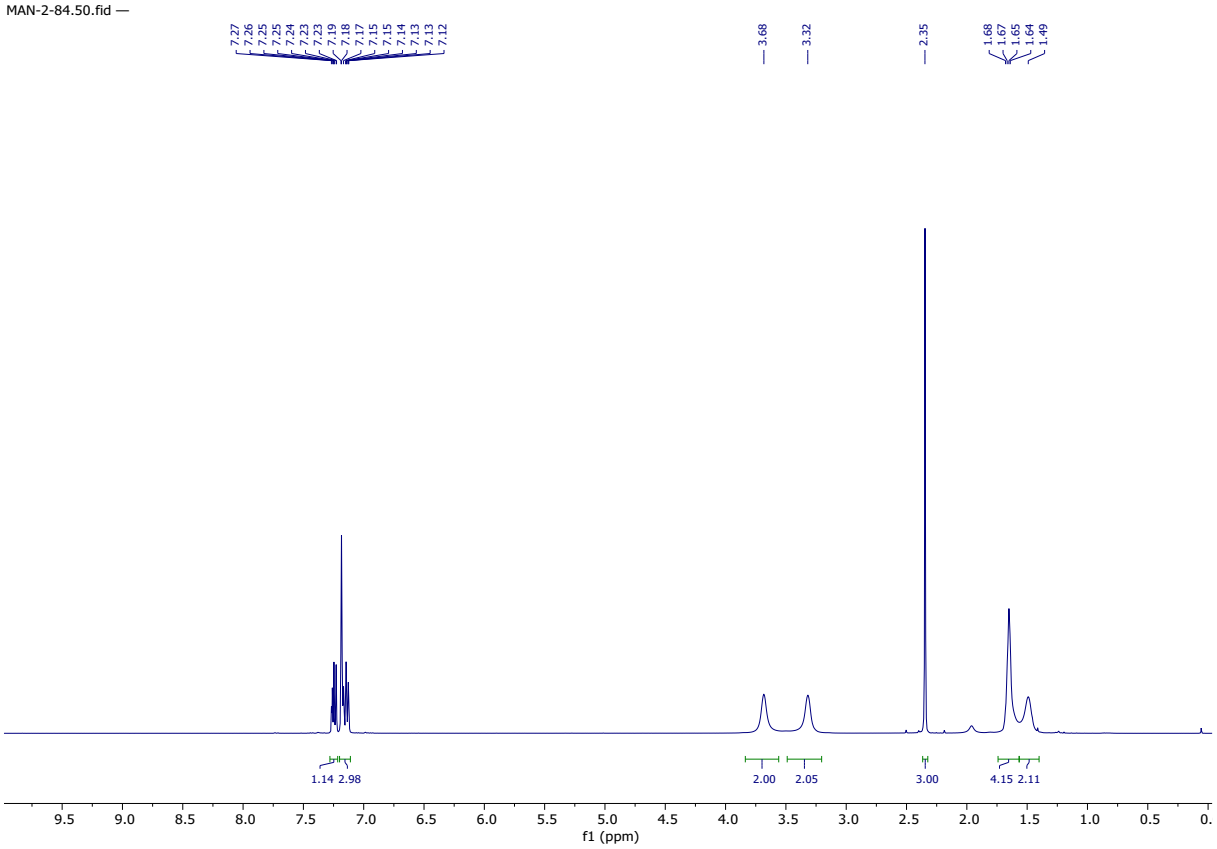
^{1}H NMR spectrum of **4la**



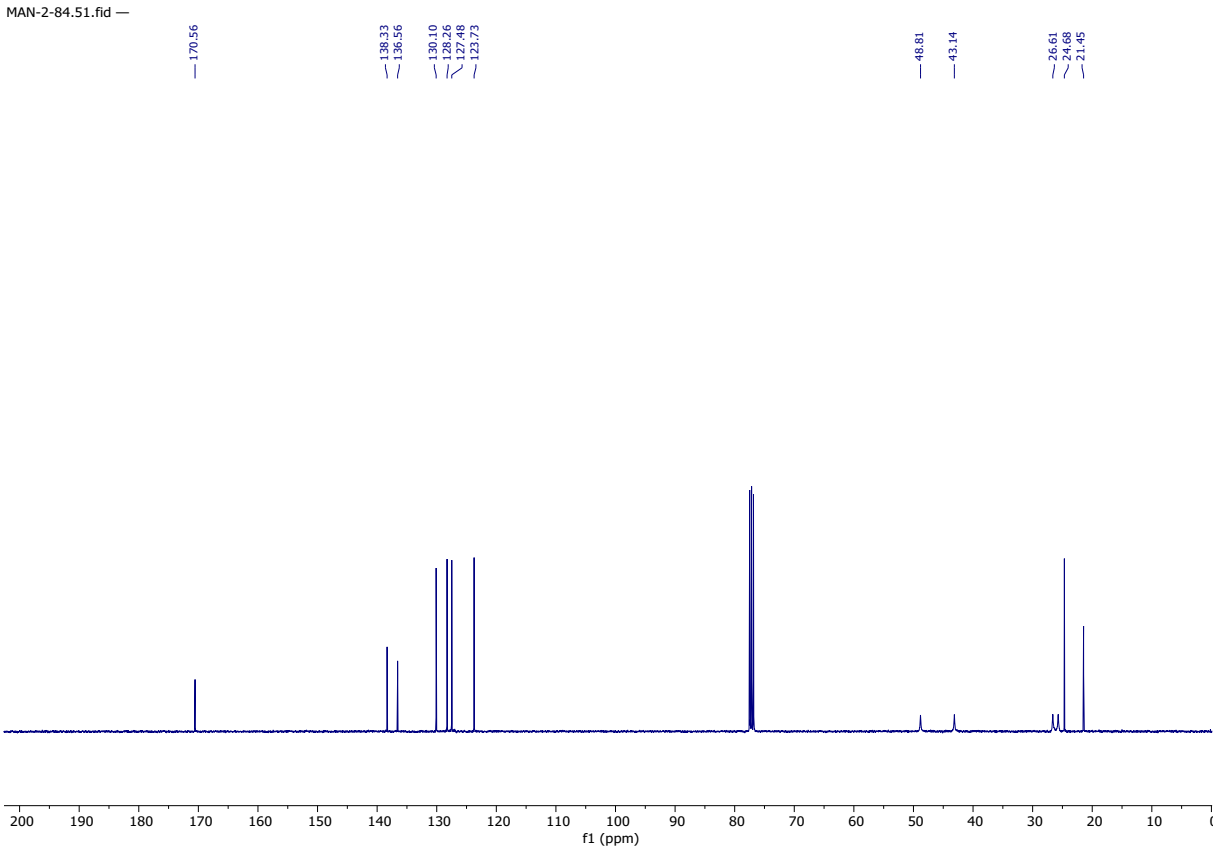
^{13}C NMR spectrum of **4la**



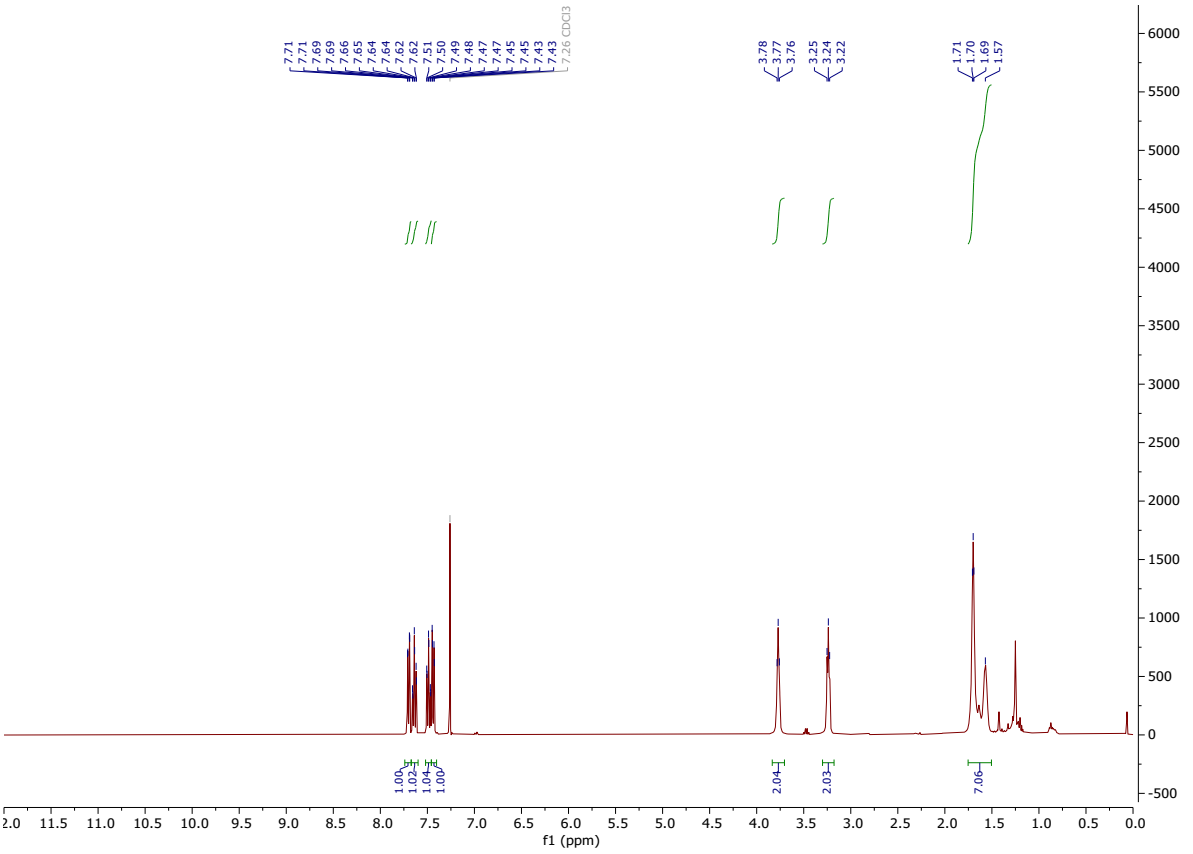
^{1}H NMR spectrum of **4ma**



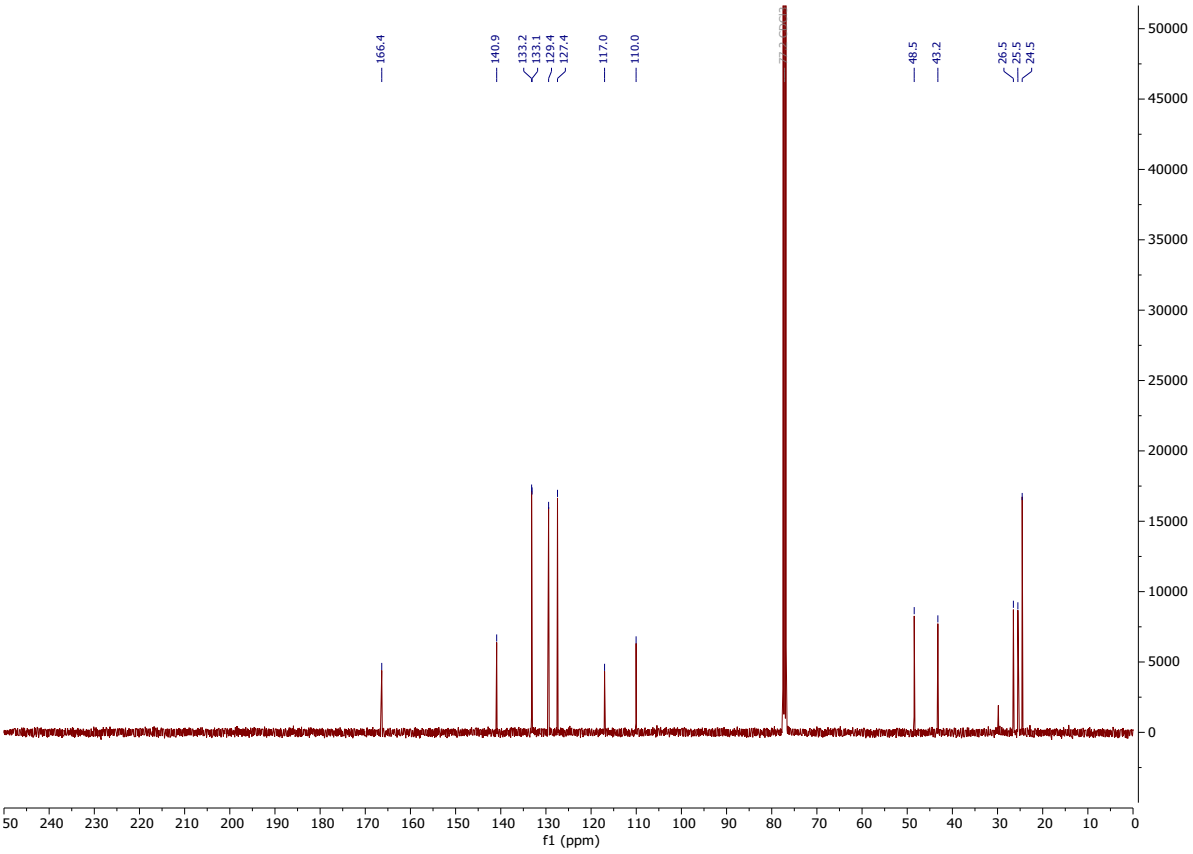
^{13}C NMR spectrum of **4ma**



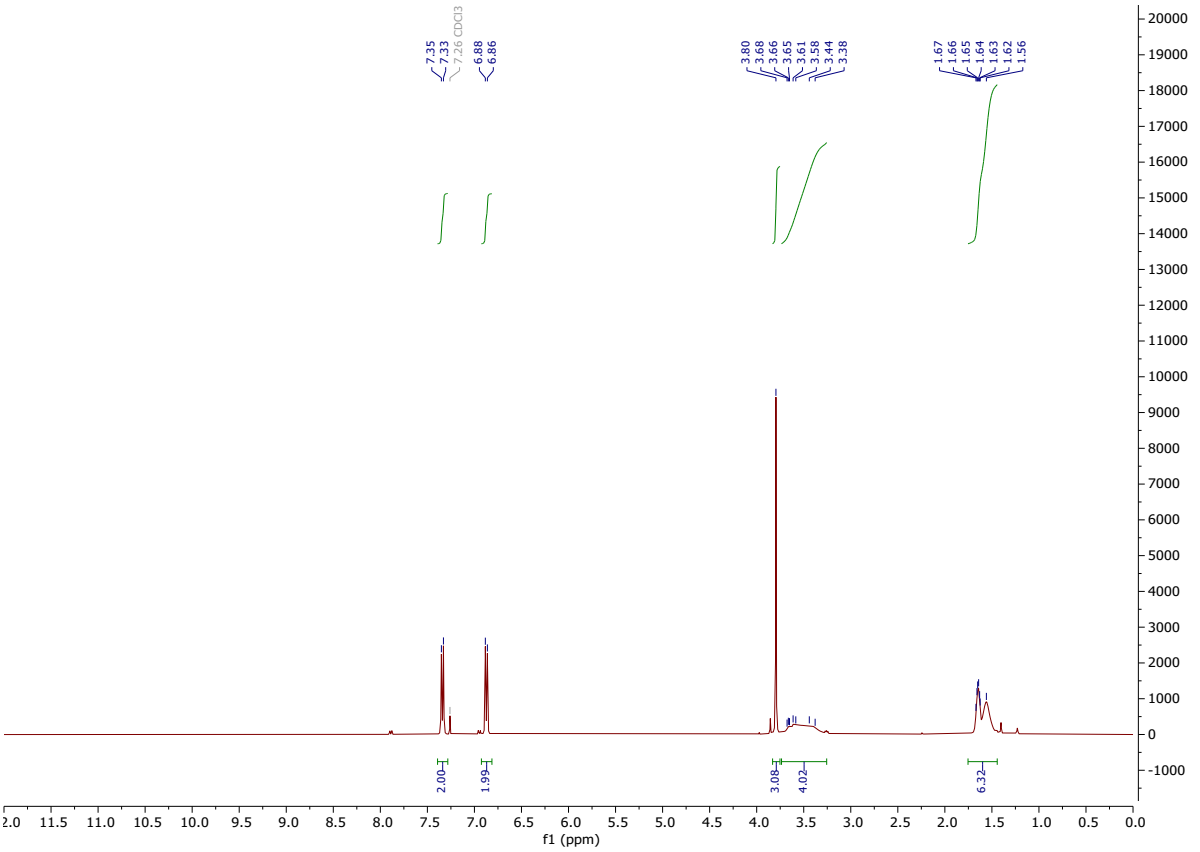
^{1}H NMR spectrum of **4na**



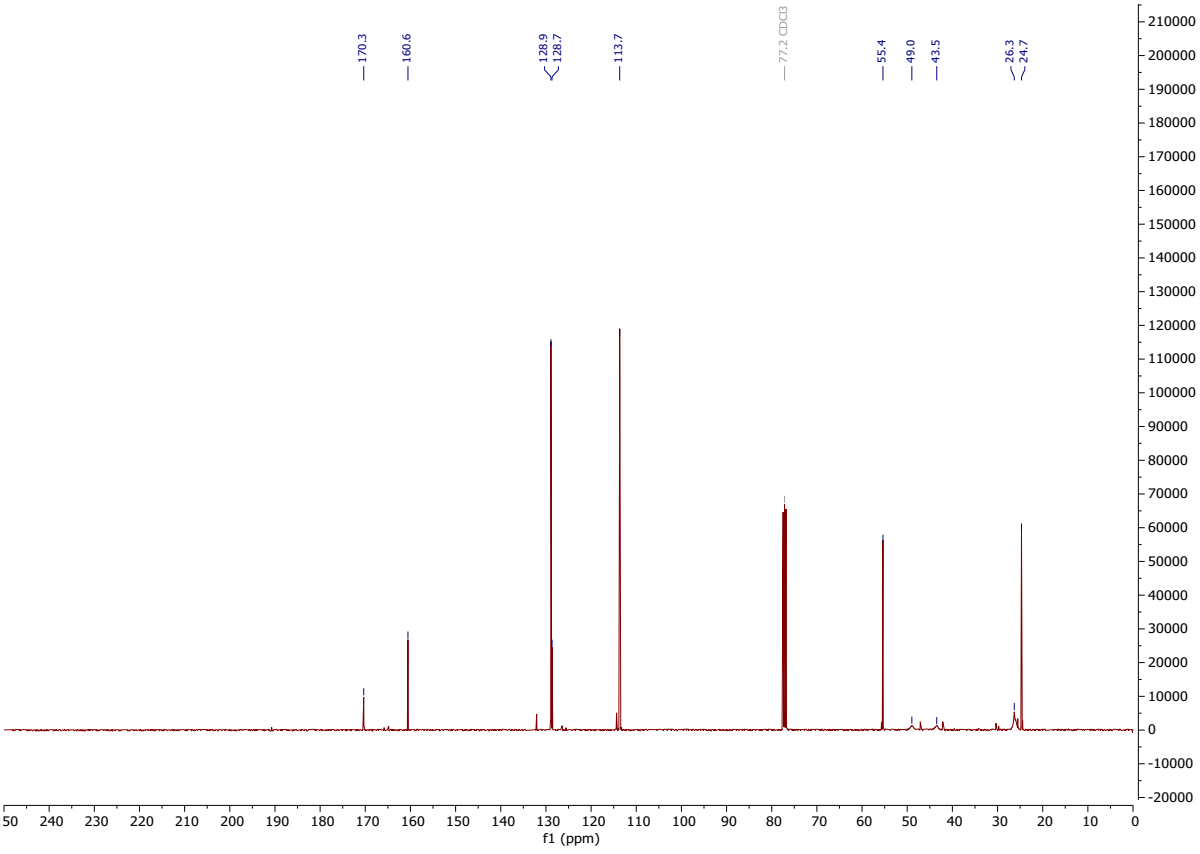
^{13}C NMR spectrum of **4na**



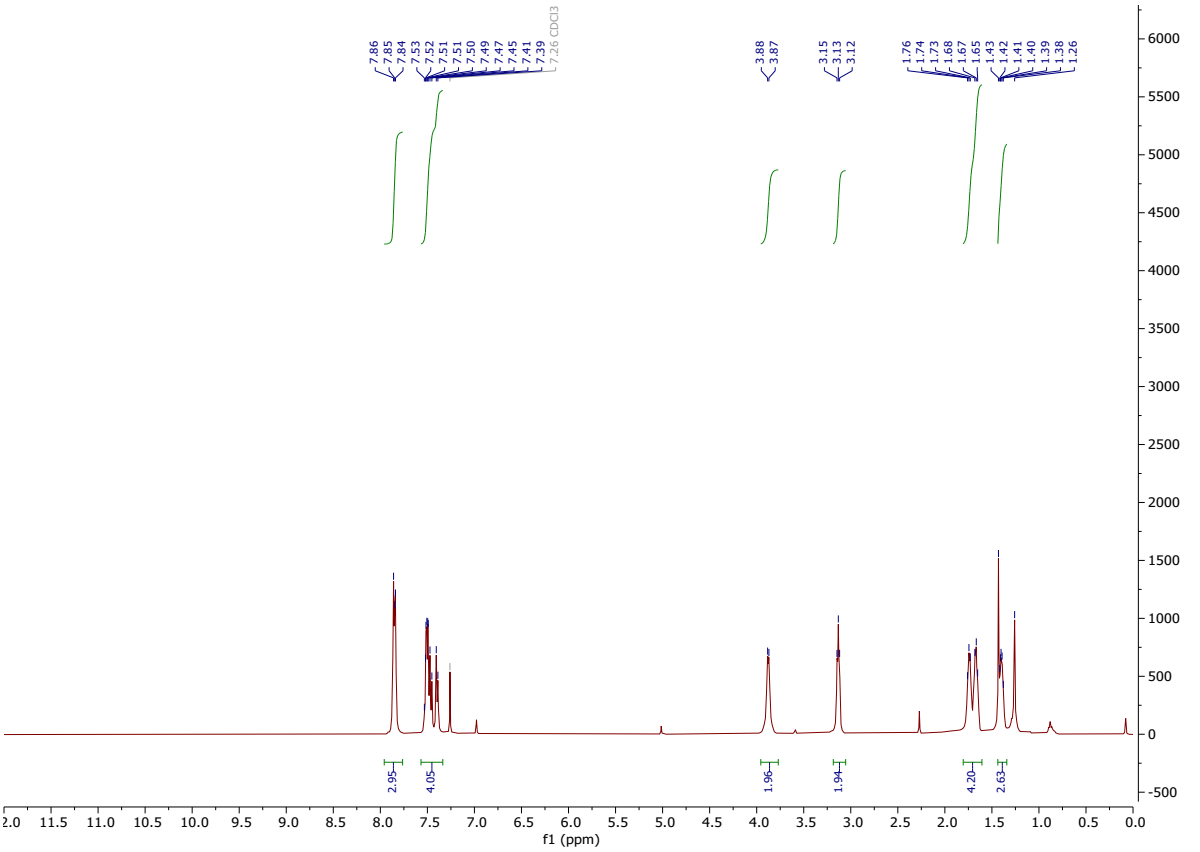
^{1}H NMR spectrum of **4oa**



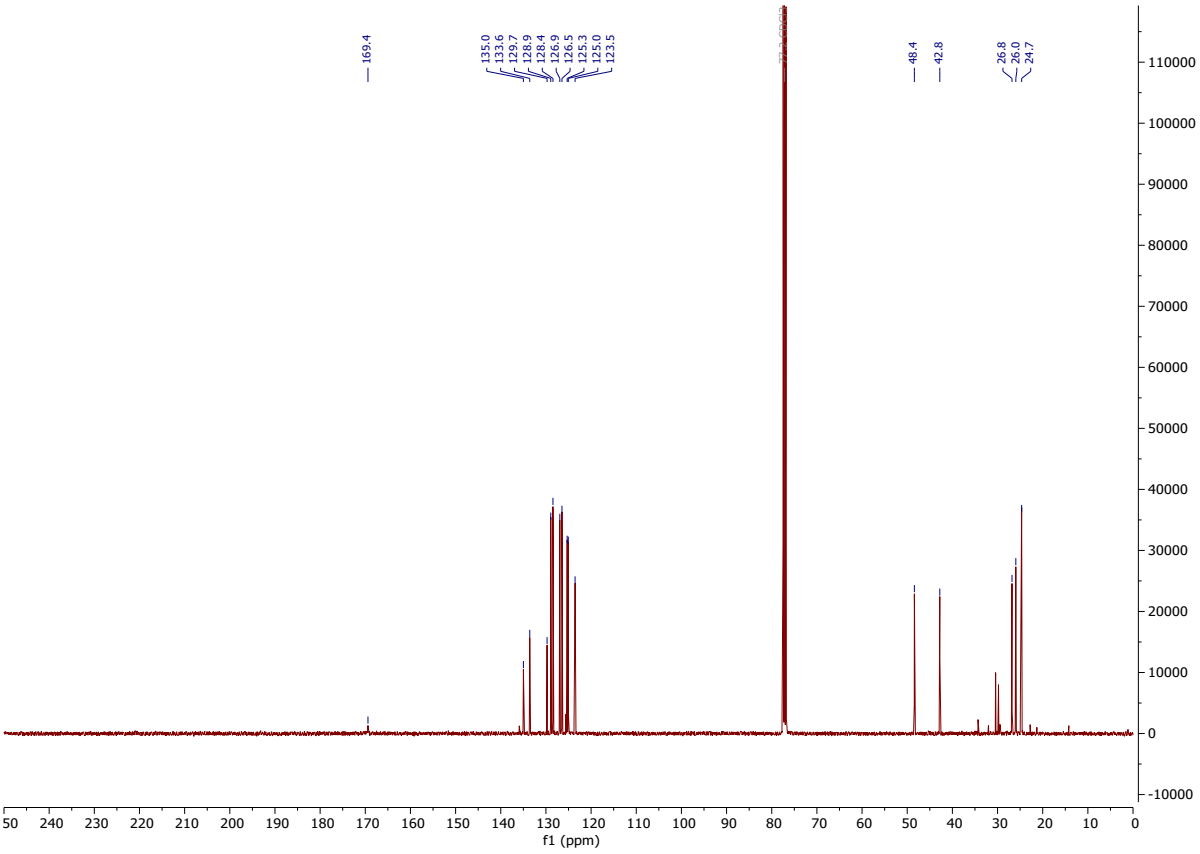
^{13}C NMR spectrum of **4oa**



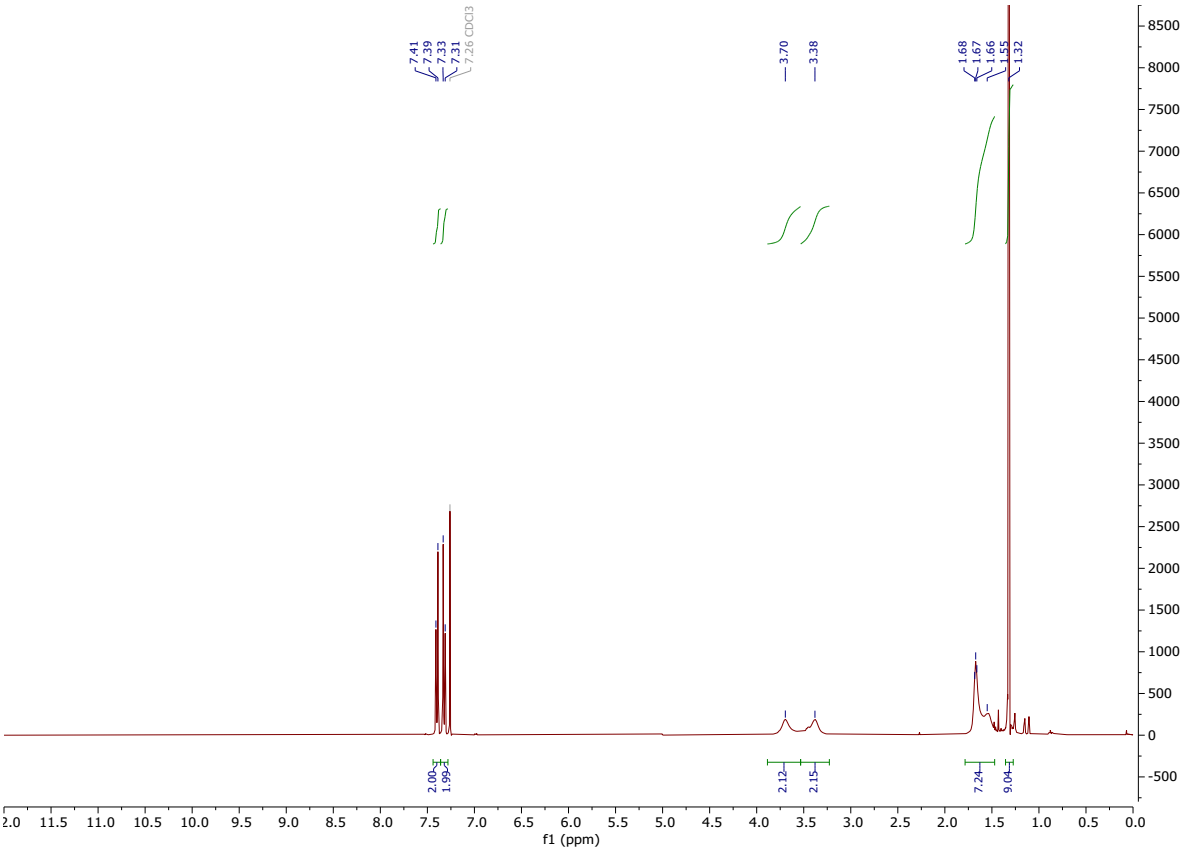
^{1}H NMR spectrum of **4pa**



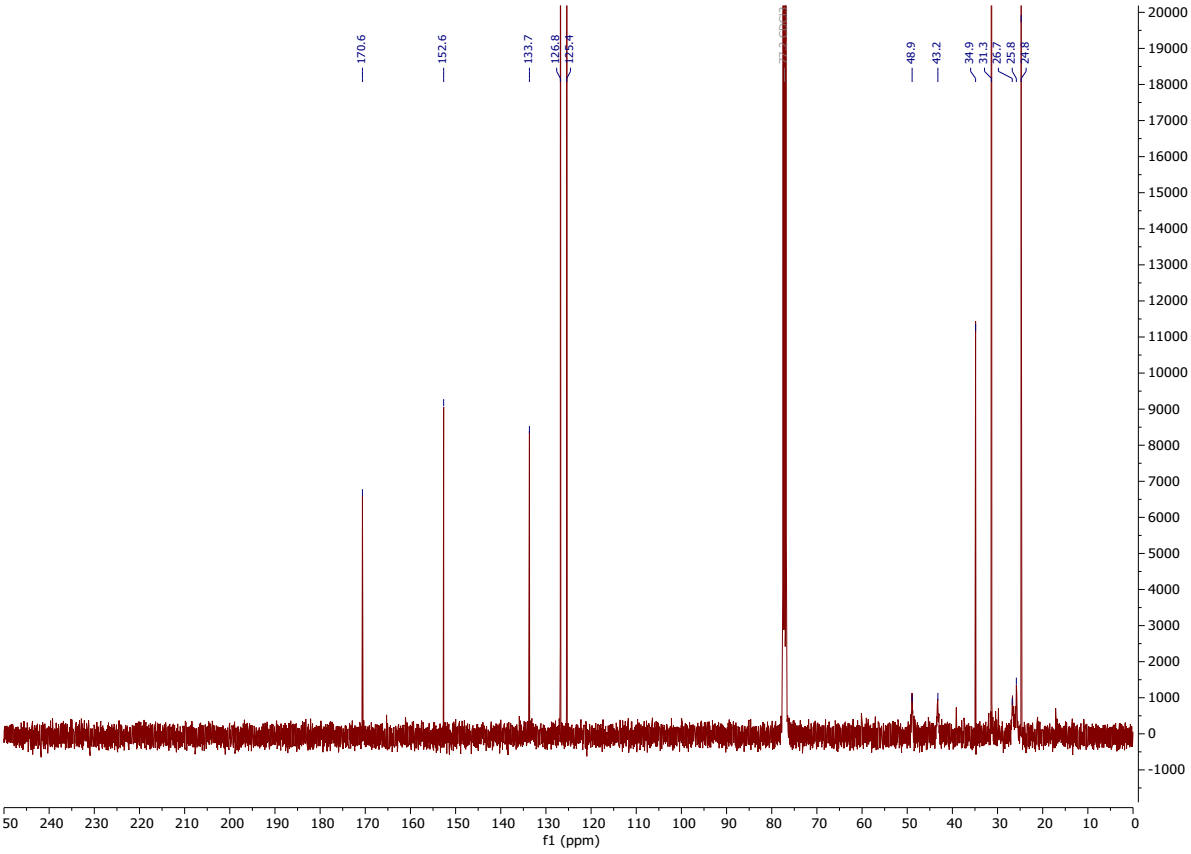
^{13}C NMR spectrum of **4pa**



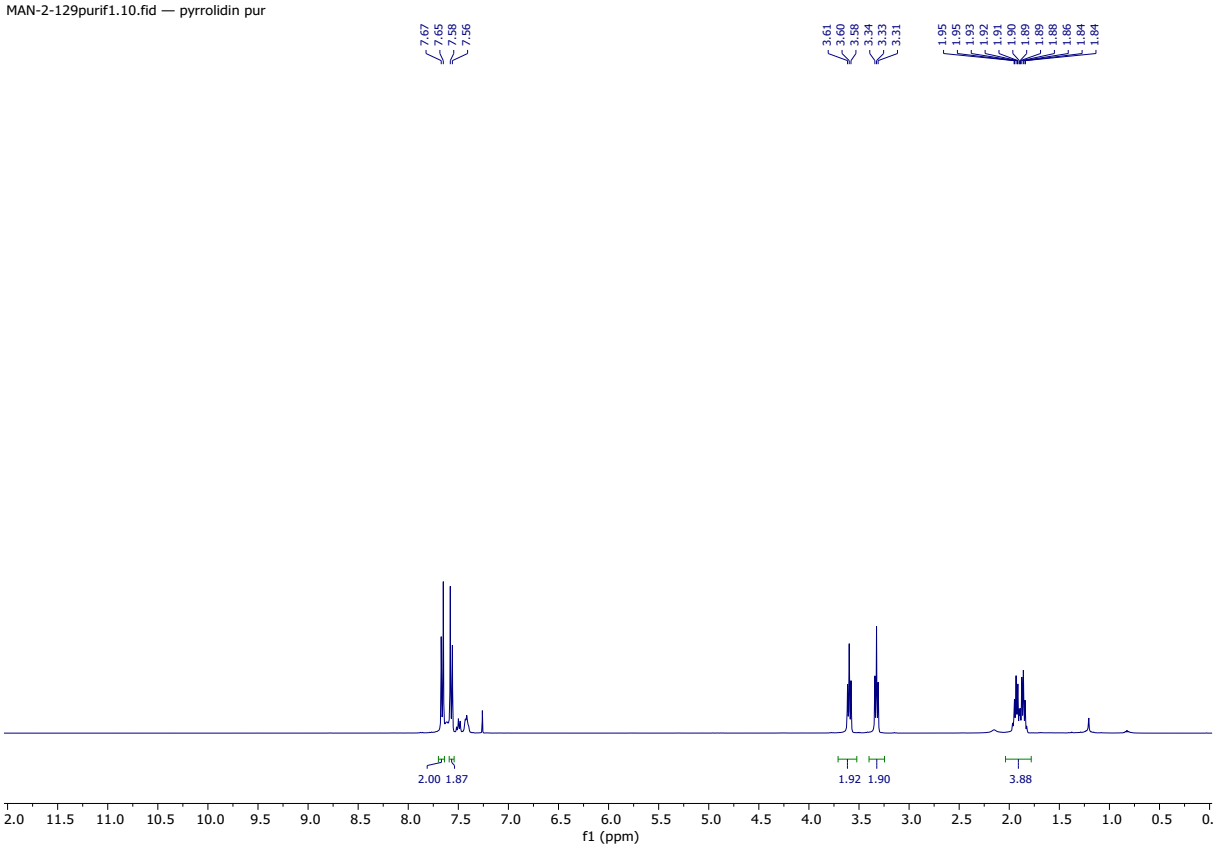
^{1}H NMR spectrum of **4qa**



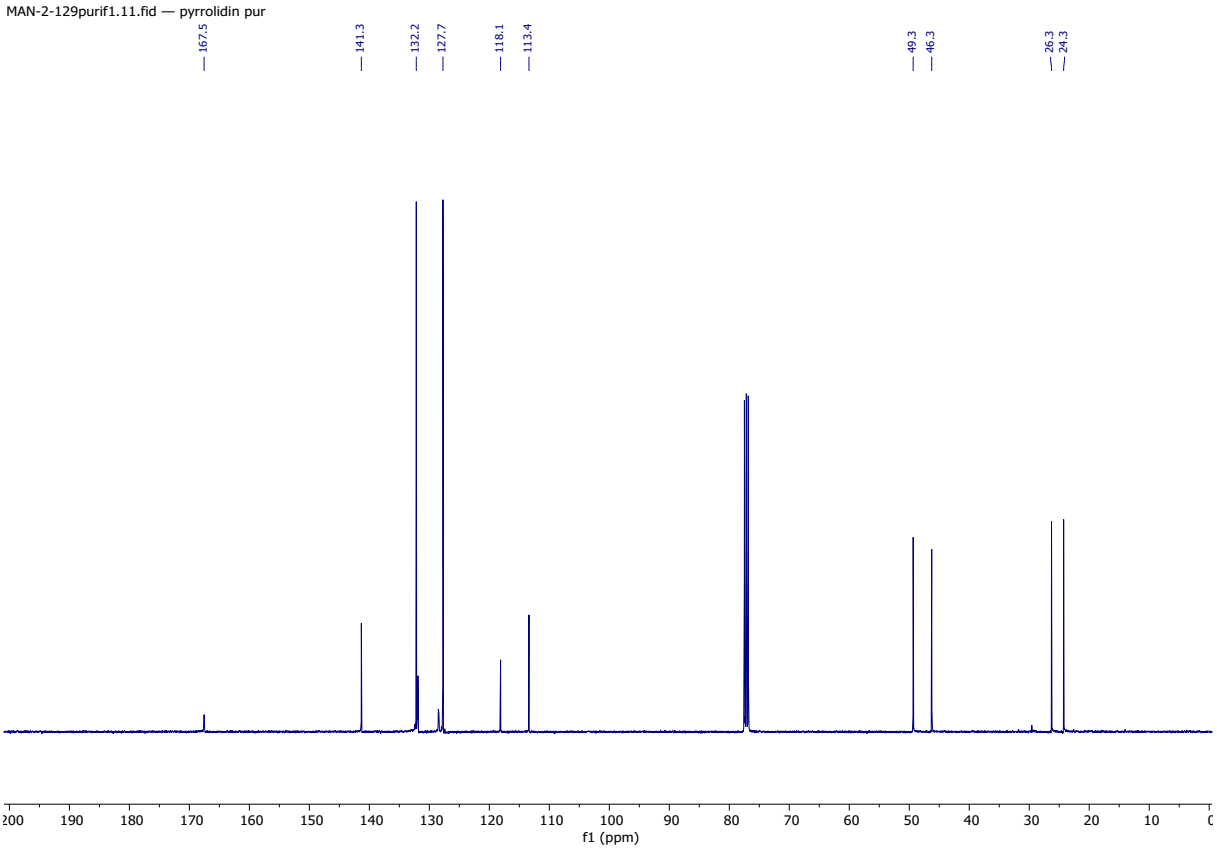
^{13}C NMR spectrum of **4qa**



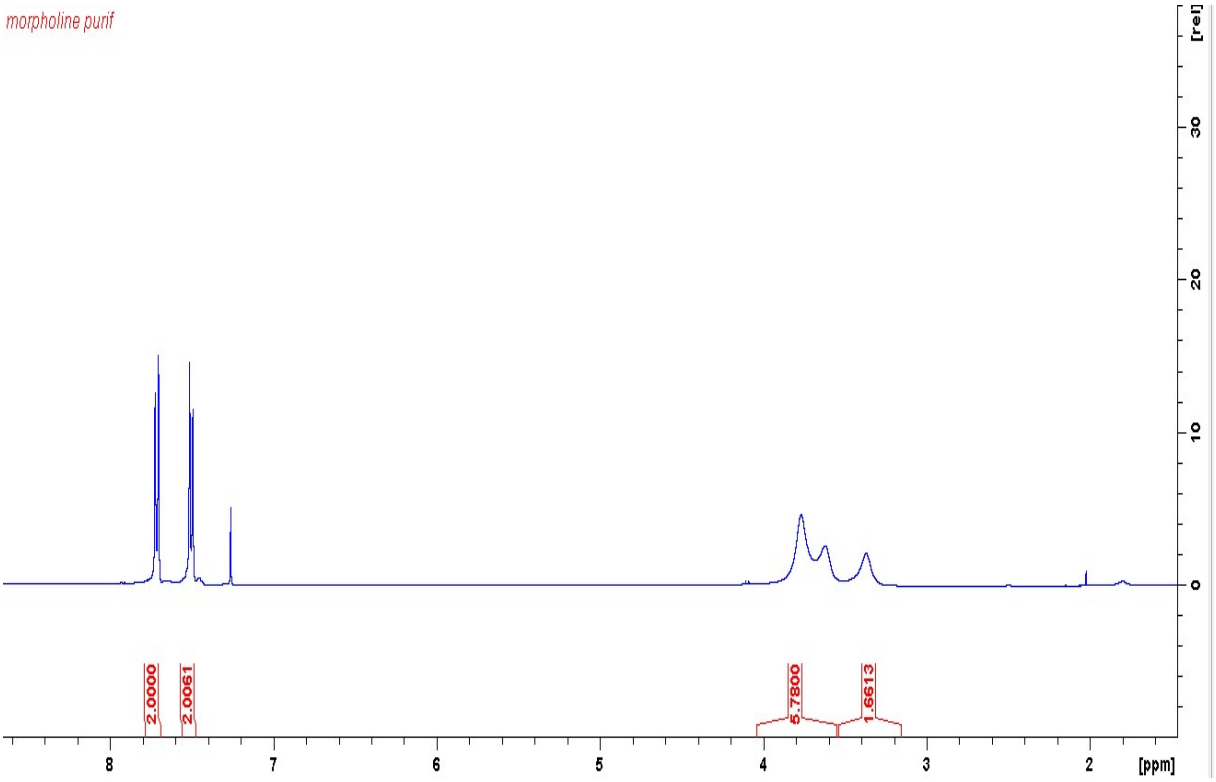
^{1}H **NMR** spectrum of **4hb**



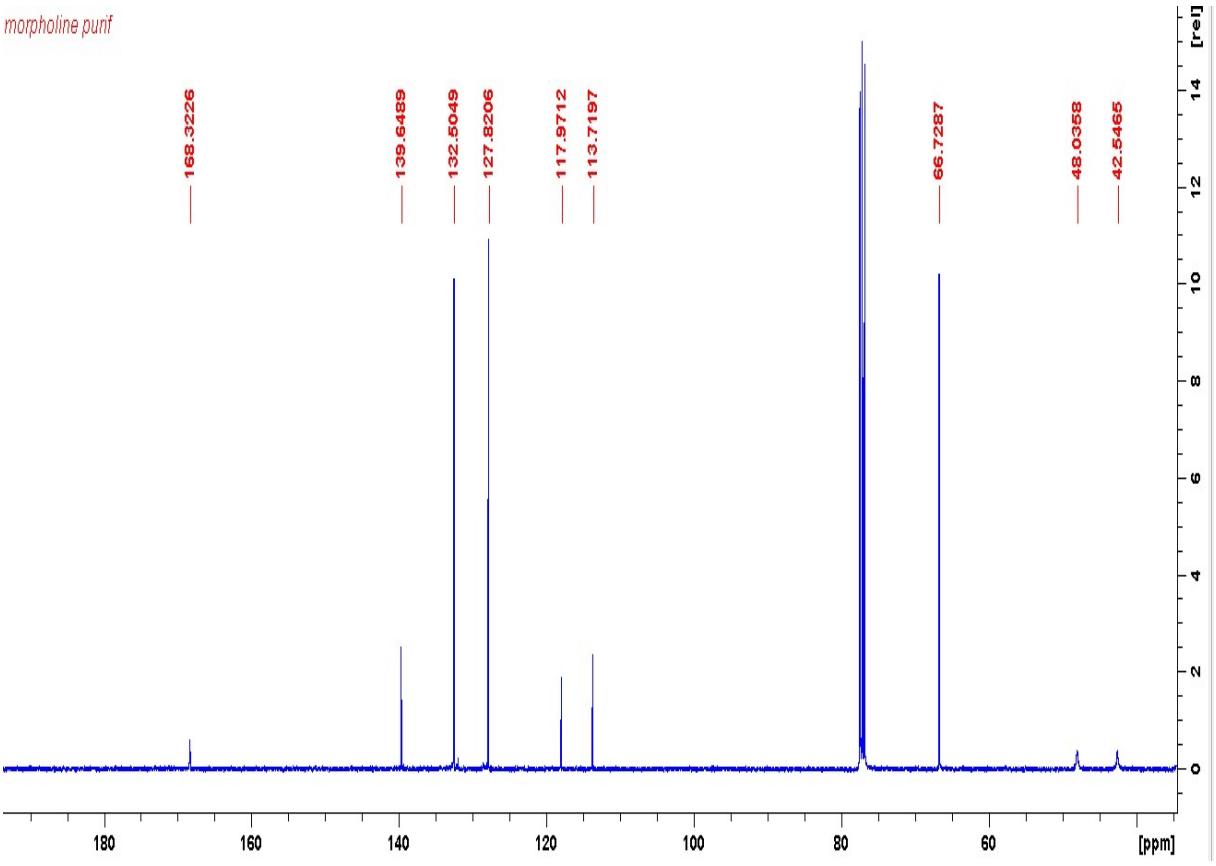
^{13}C **NMR** spectrum of **4hb**



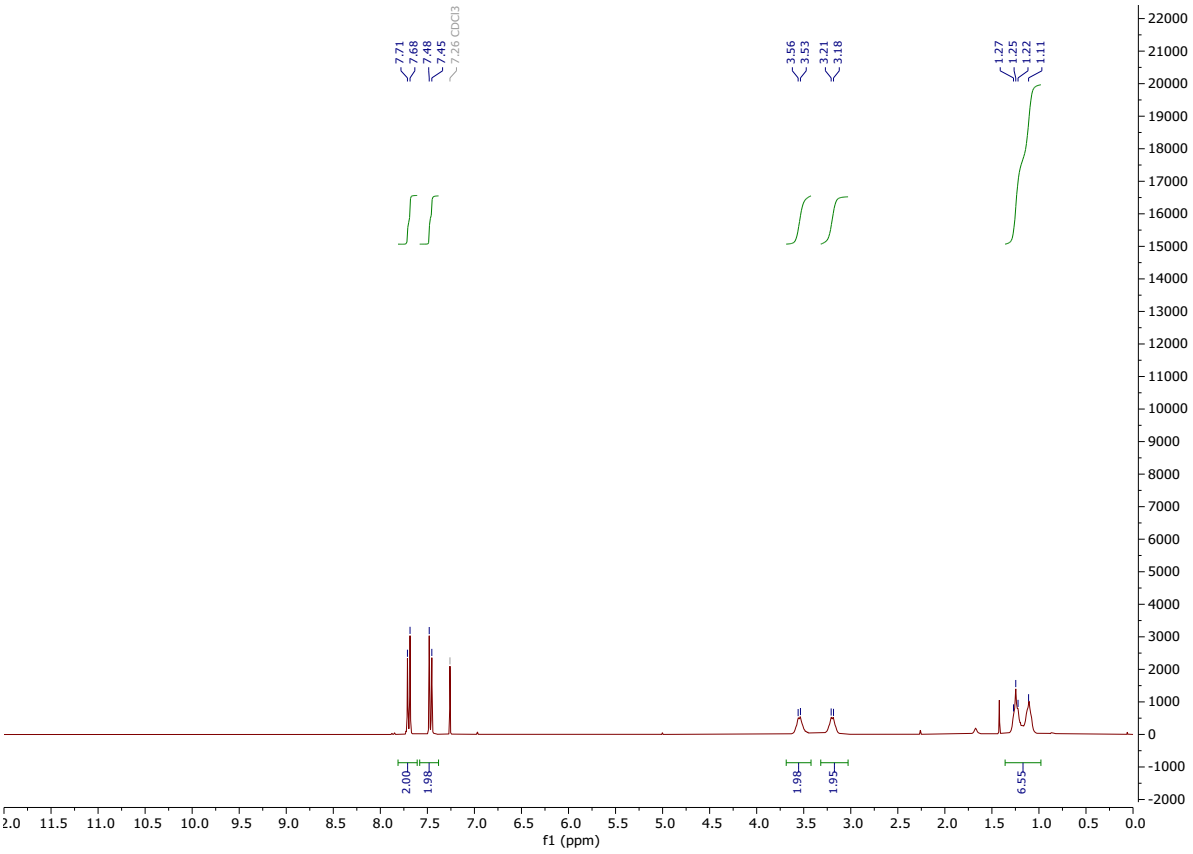
^{1}H NMR spectrum of **4hc**



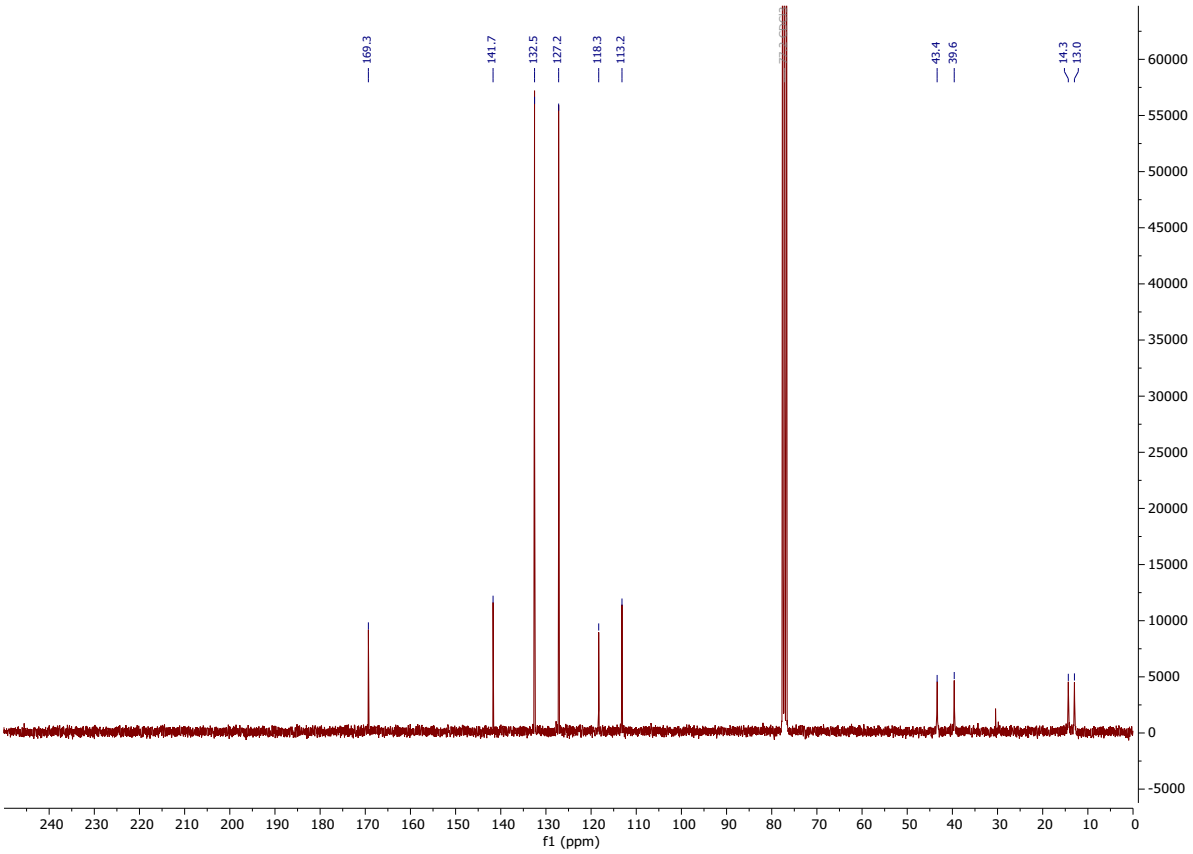
^{13}C NMR spectrum of **4hc**



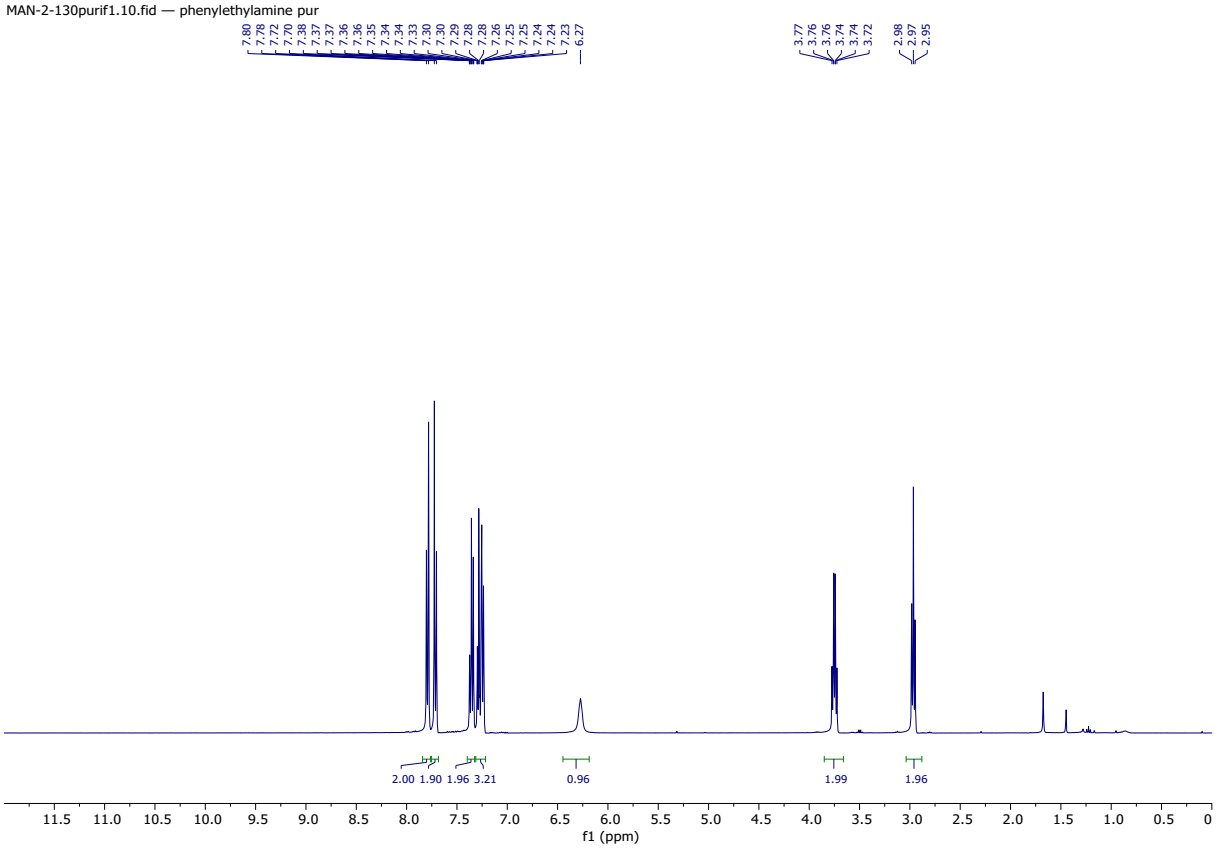
^{1}H NMR spectrum of **4hd**



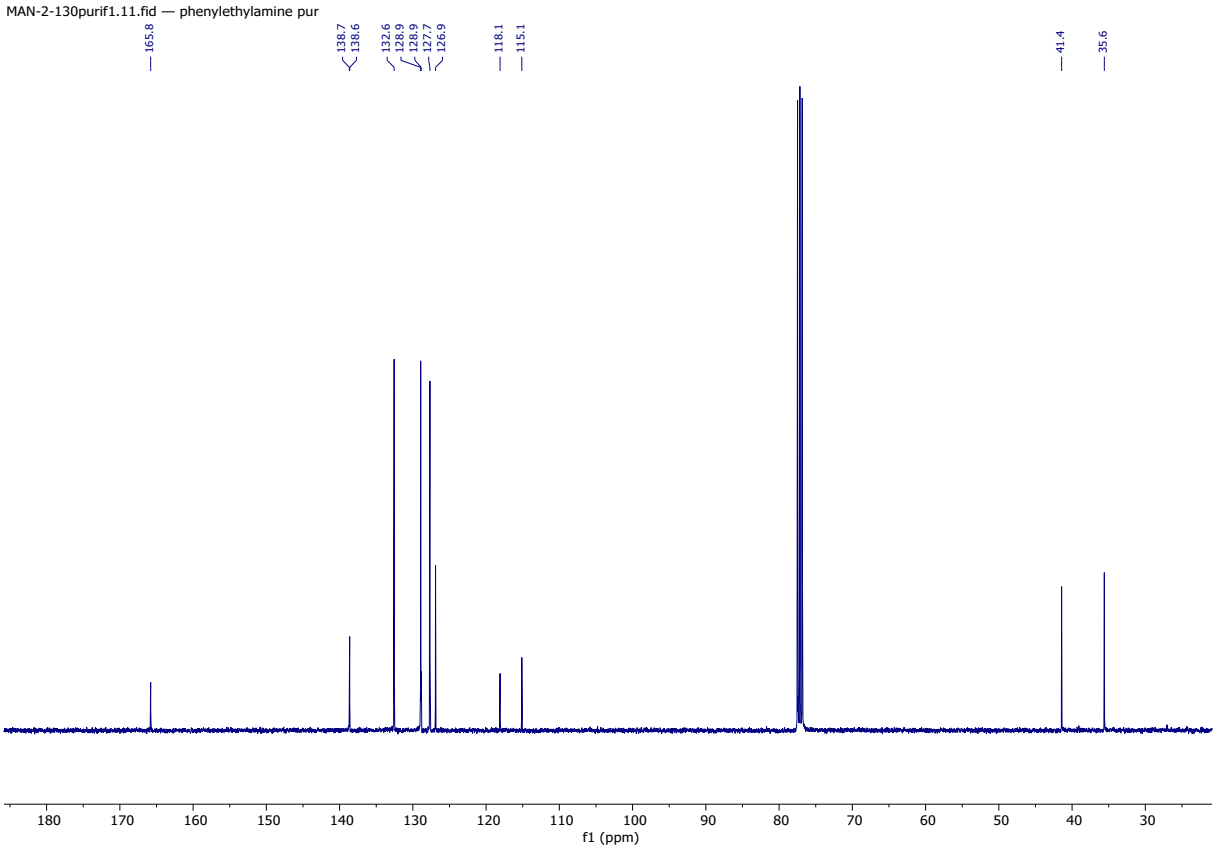
^{13}C NMR spectrum of **4hd**



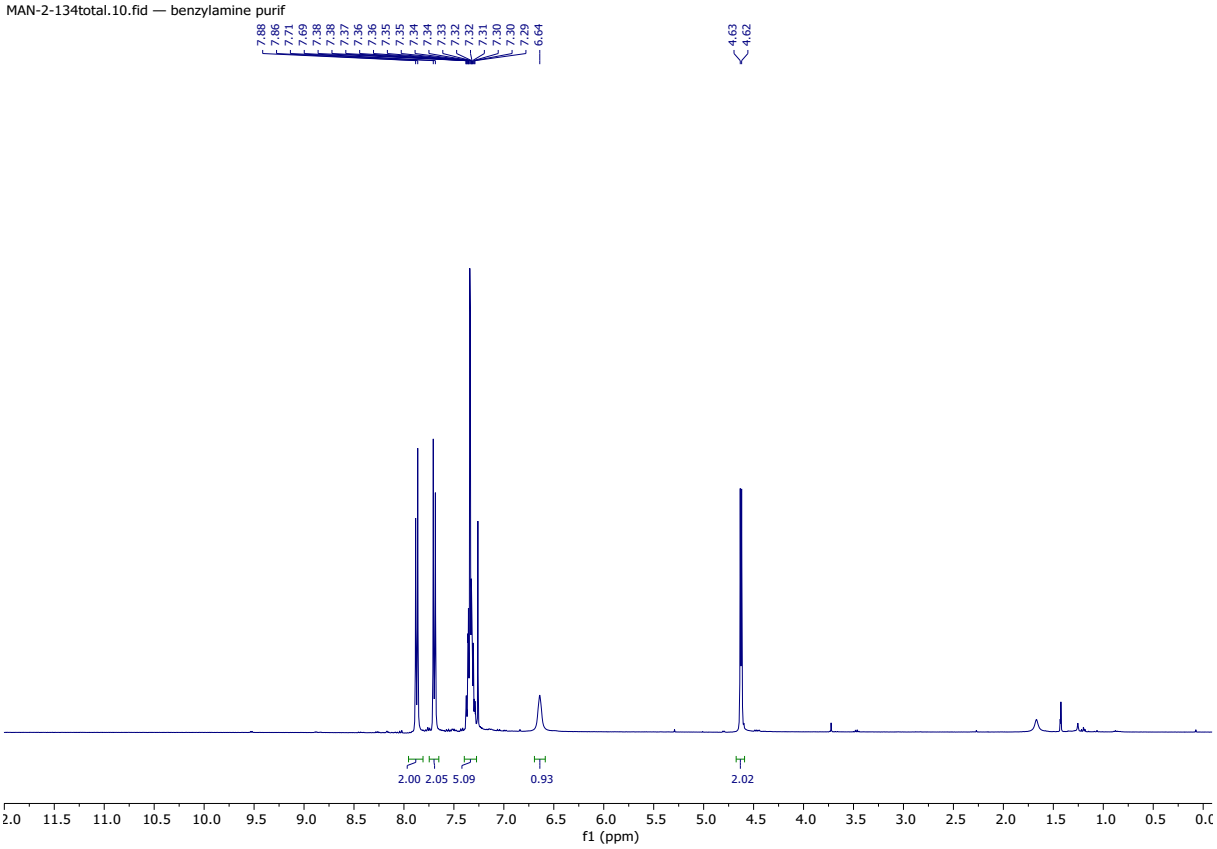
^{1}H **NMR** spectrum of **4hf**



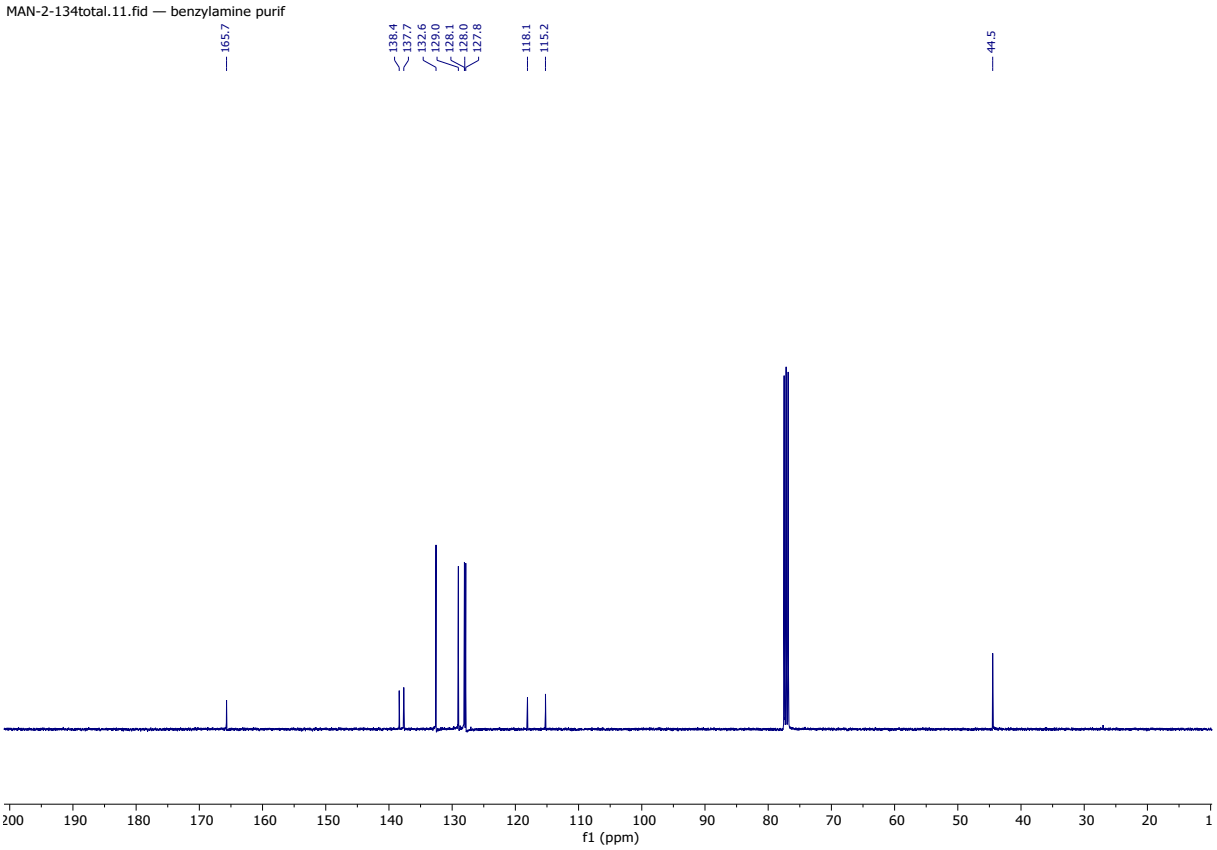
^{13}C **NMR** spectrum of **4hf**



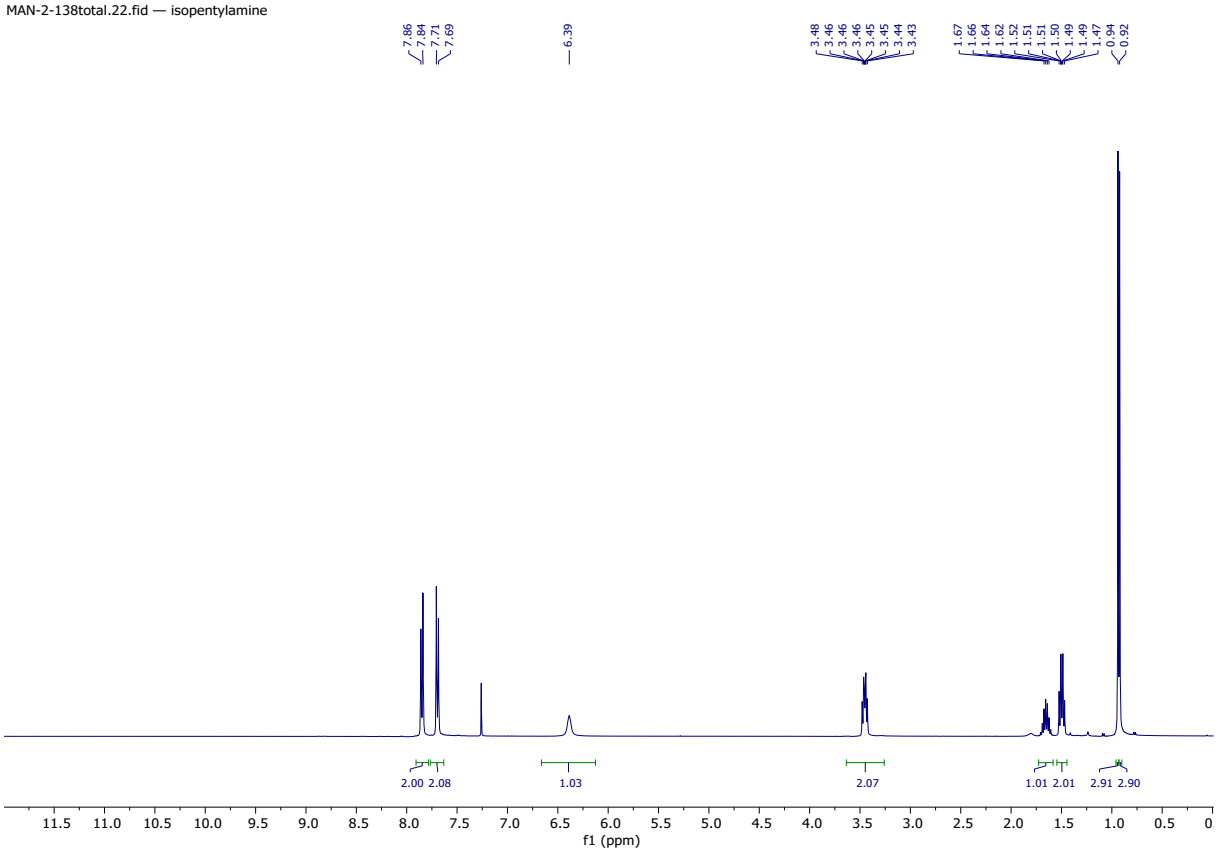
^{1}H **NMR** spectrum of **4hg**



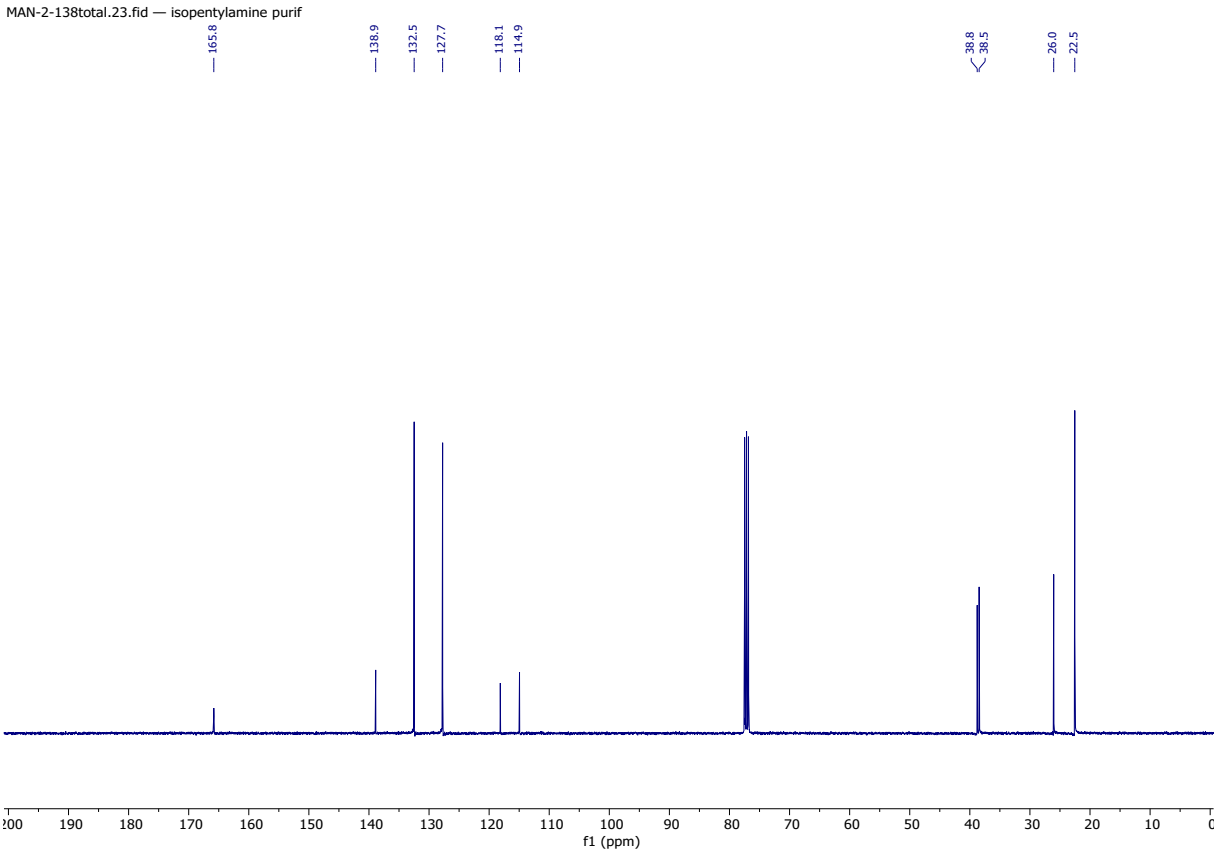
^{13}C **NMR** spectrum of **4hg**



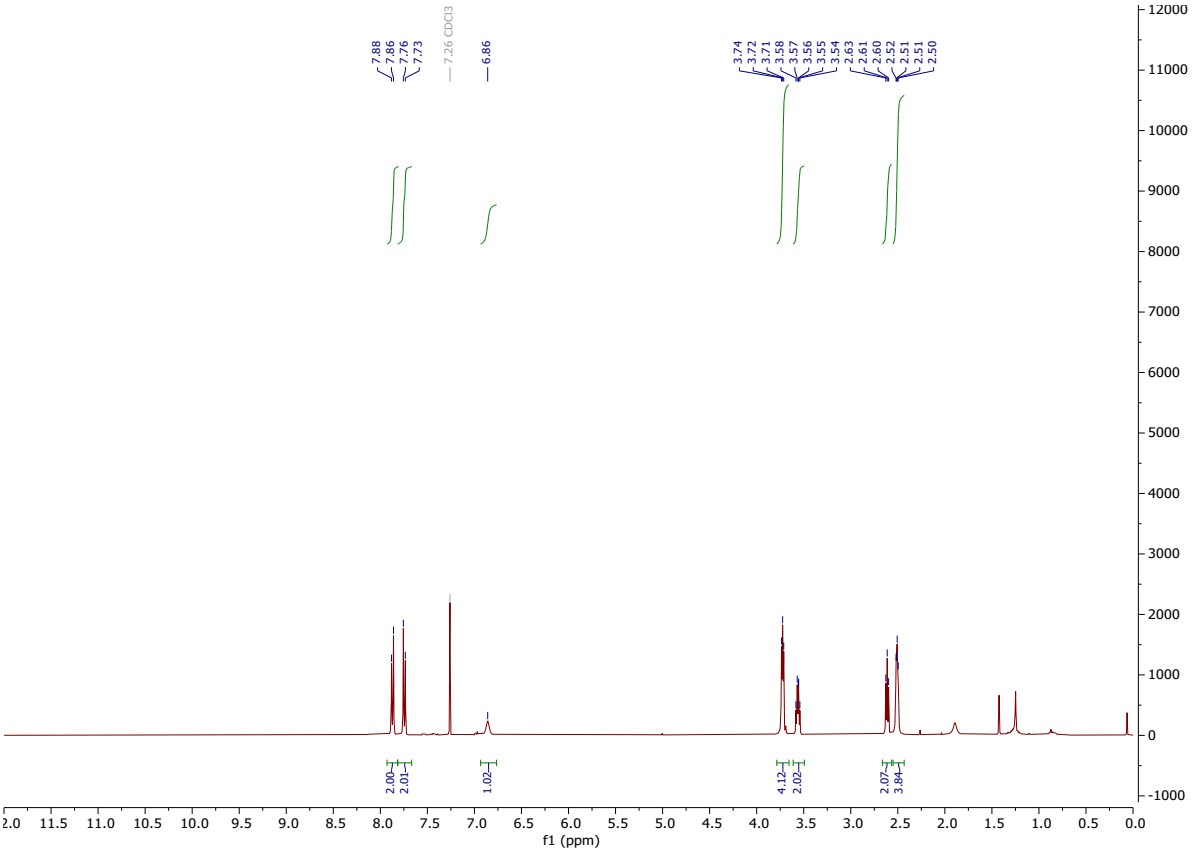
^{1}H **NMR** spectrum of **4hh**



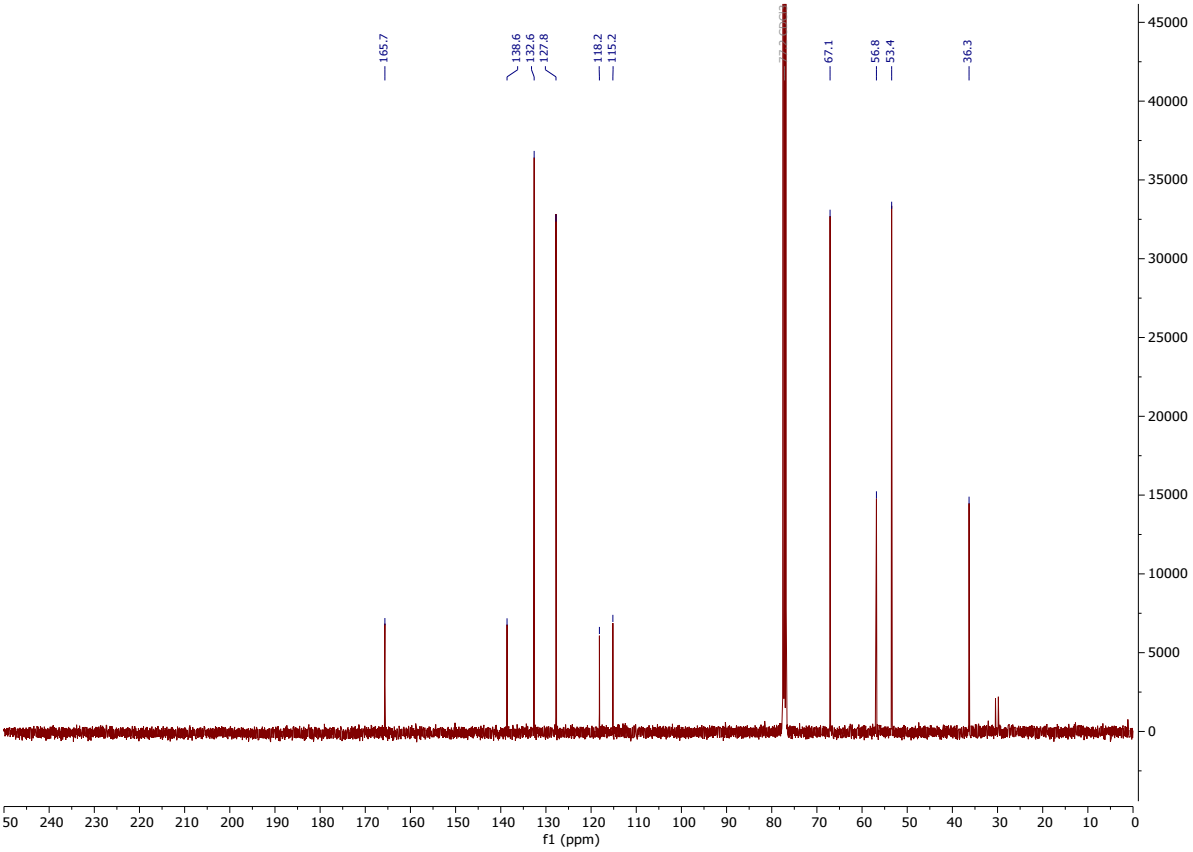
^{13}C **NMR** spectrum of **4hh**



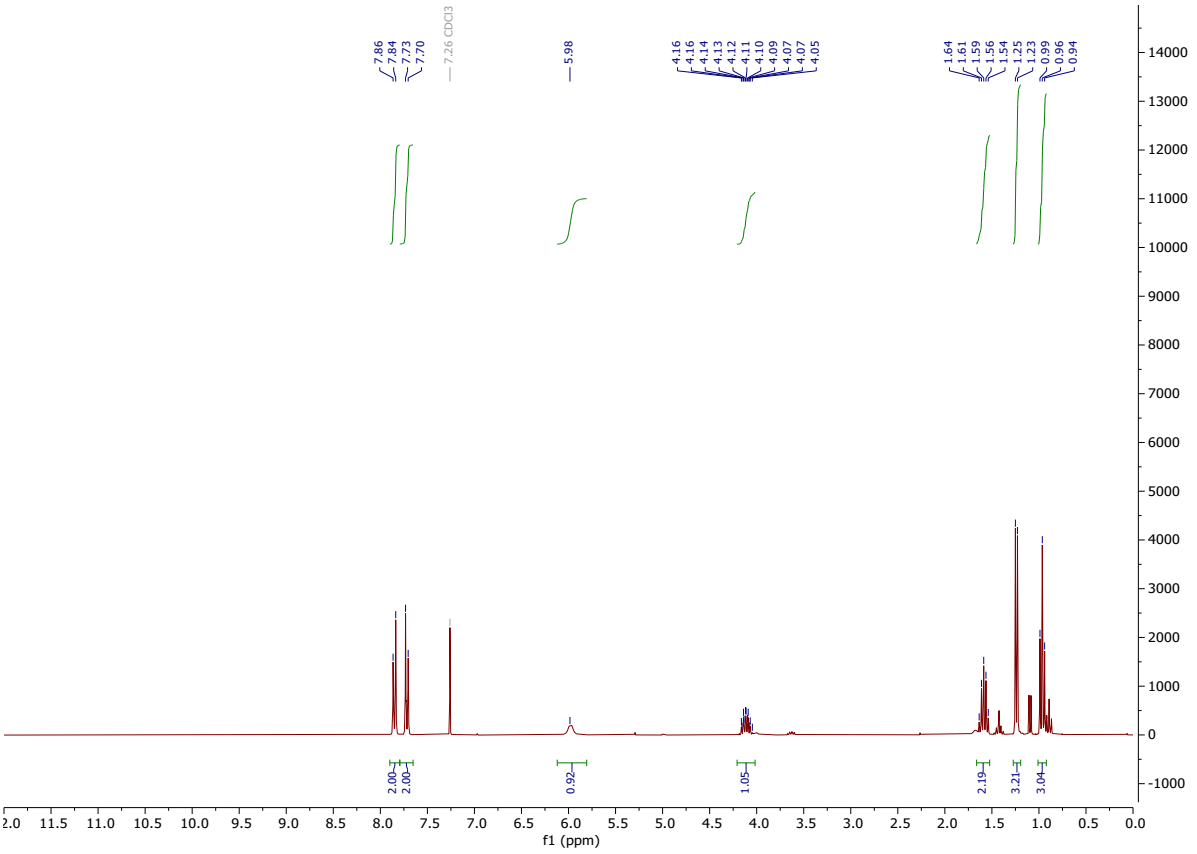
^{1}H NMR spectrum of **4hi**



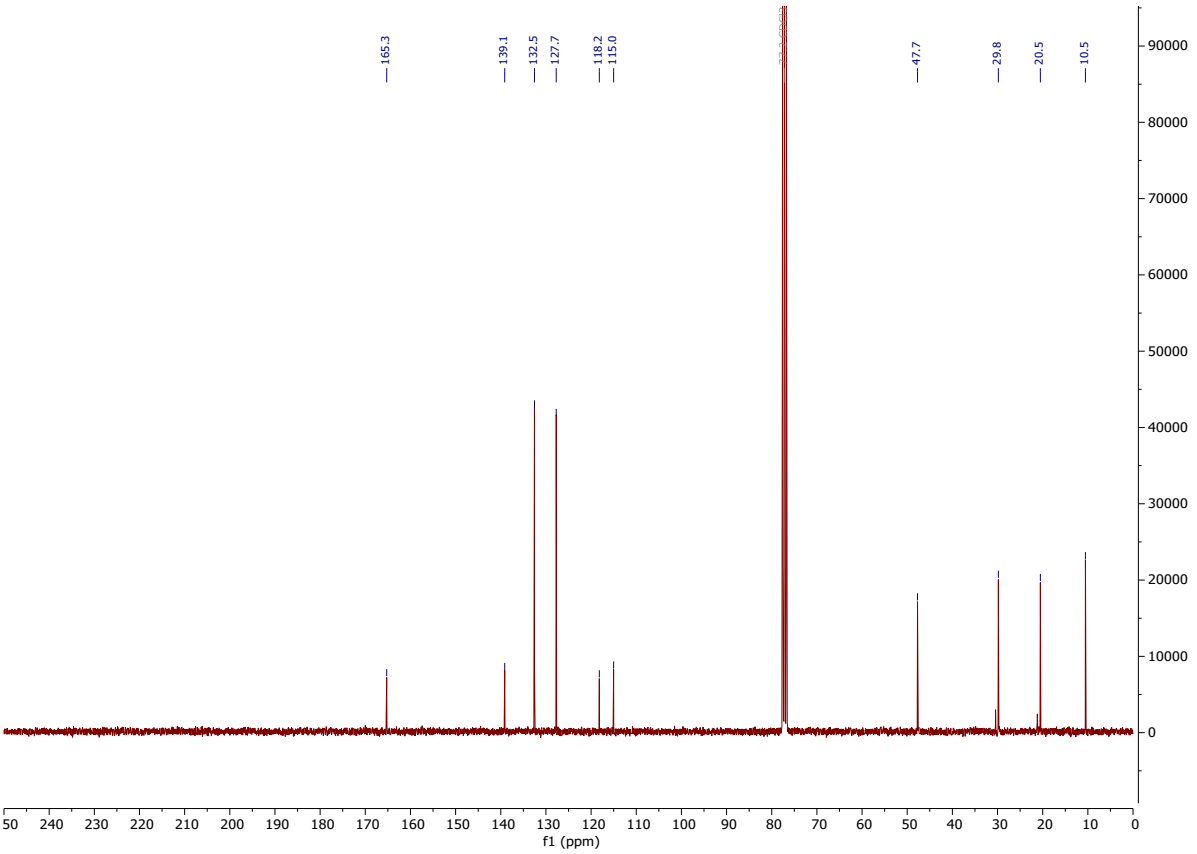
^{13}C NMR spectrum of **4hi**



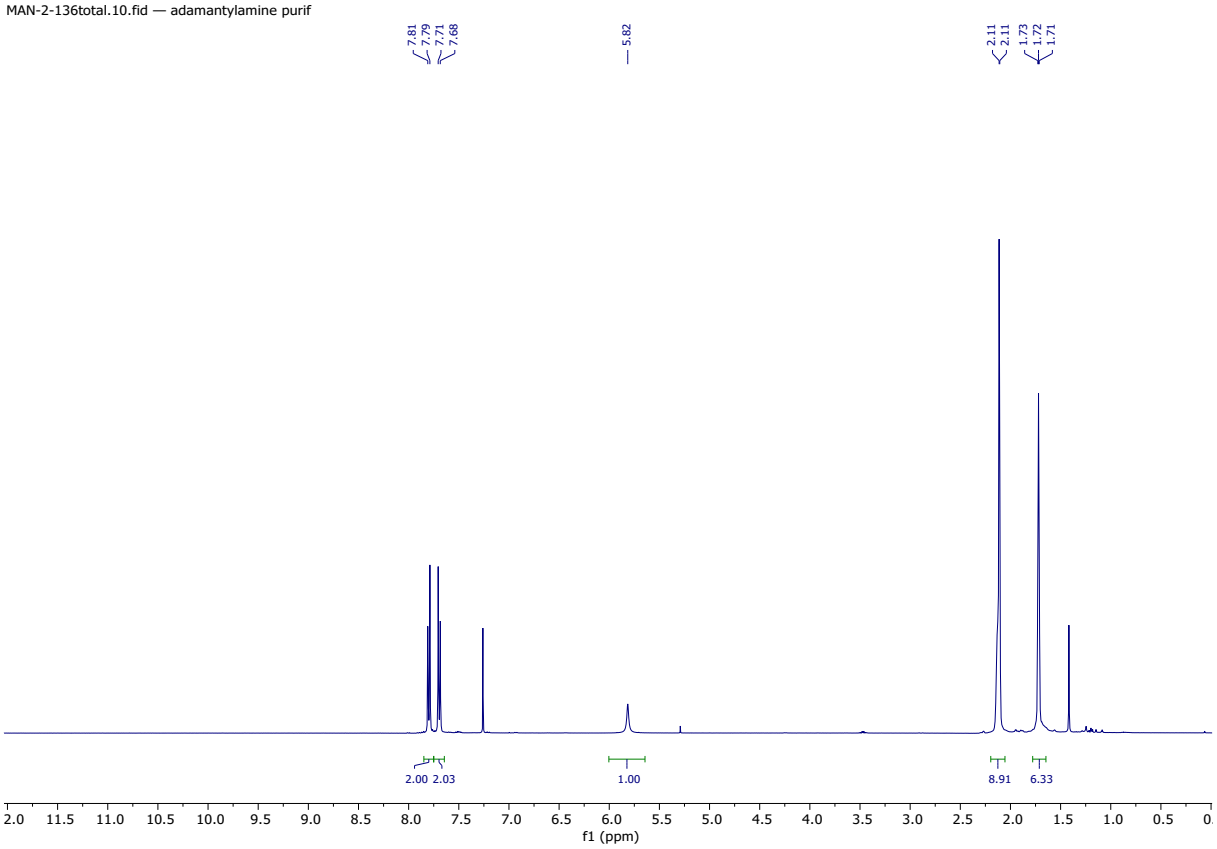
^{1}H NMR spectrum of **4hj**



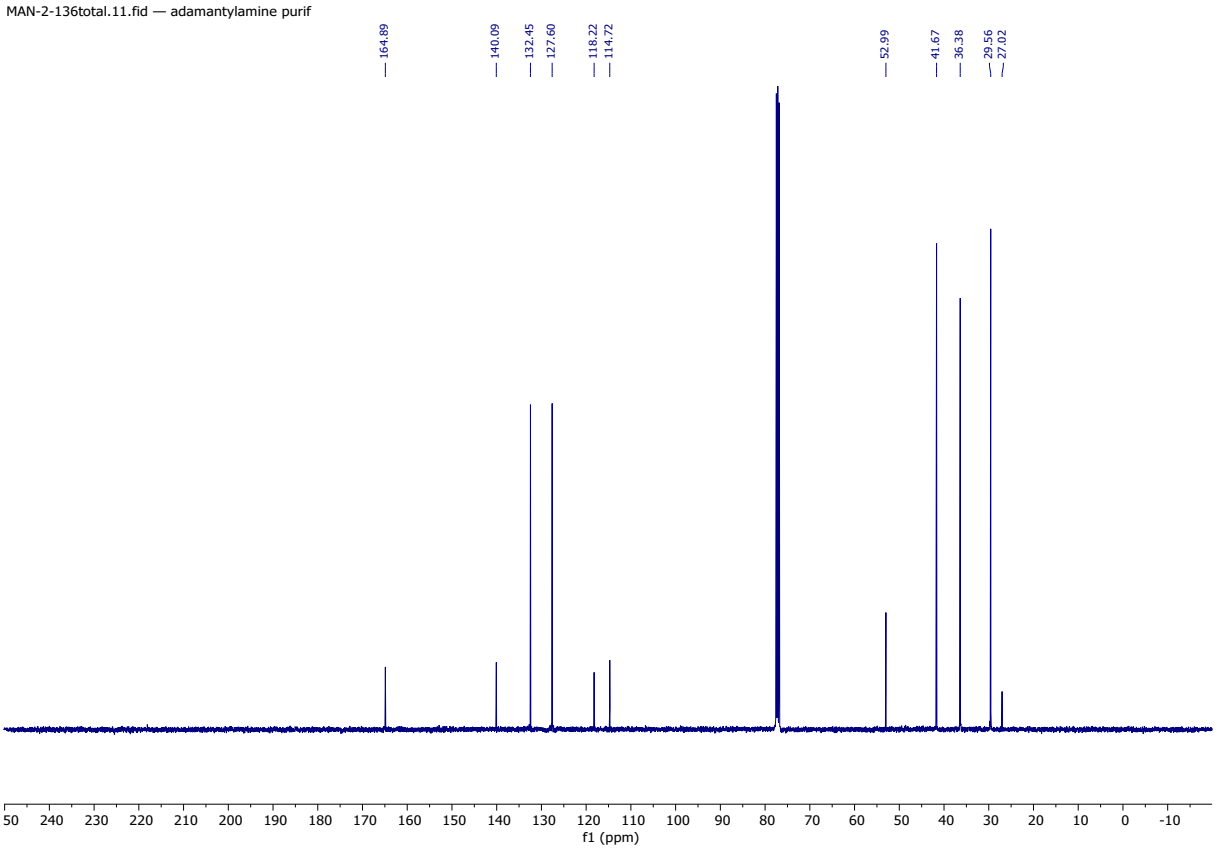
^{13}C NMR spectrum of **4hj**



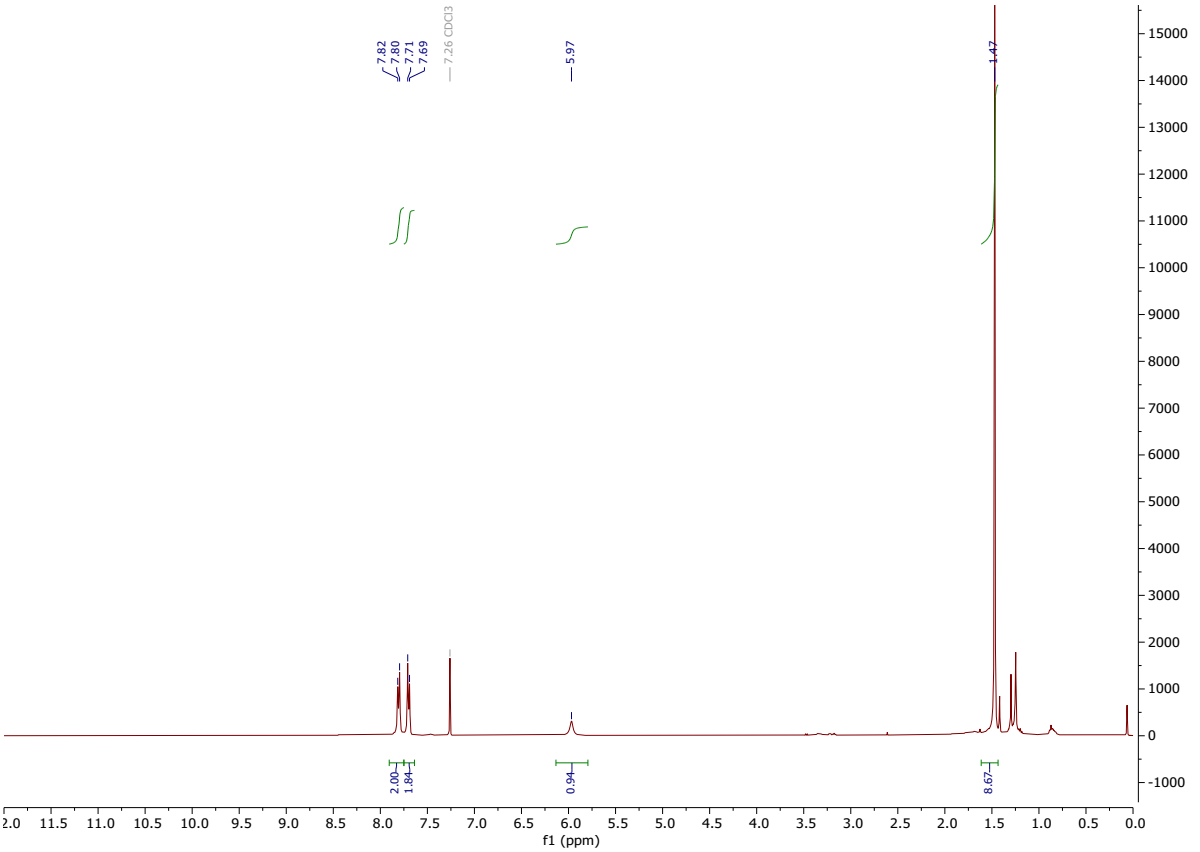
^{1}H **NMR** spectrum of **4hk**



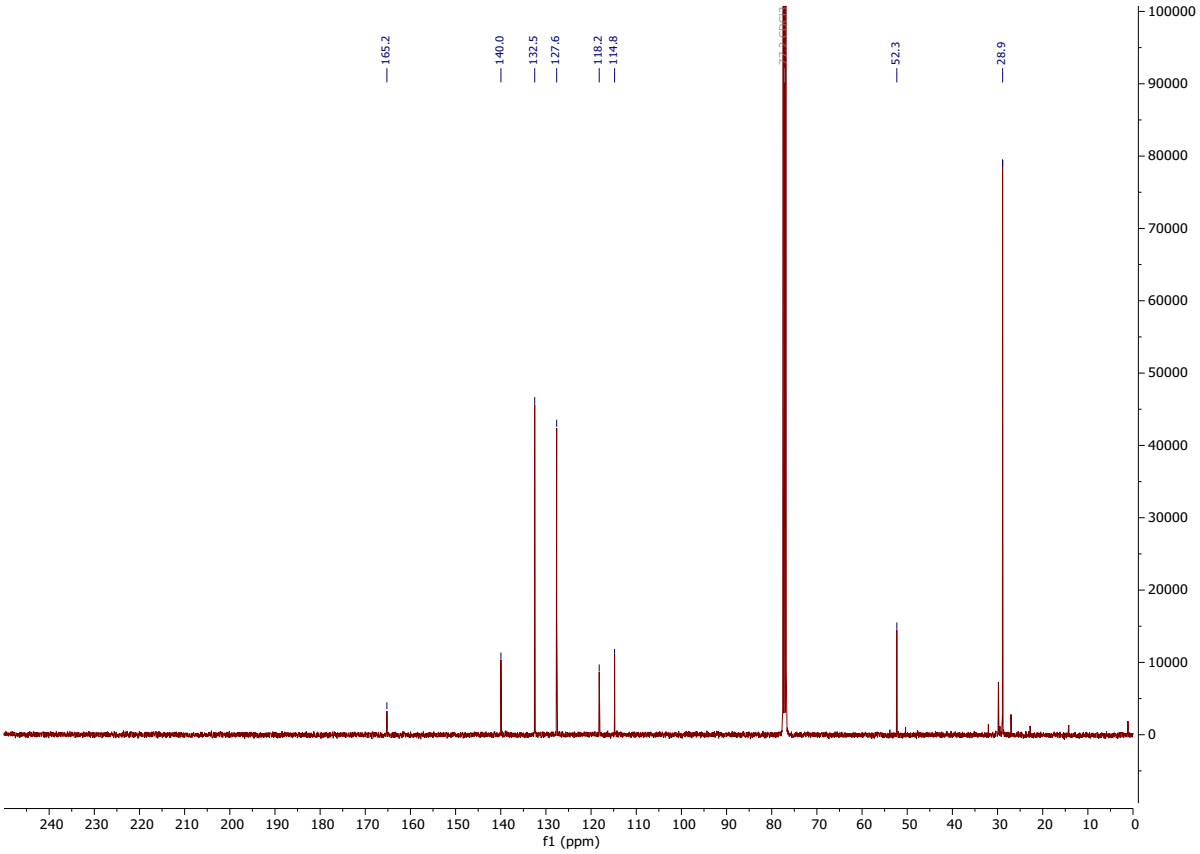
^{13}C **NMR** spectrum of **4hk**



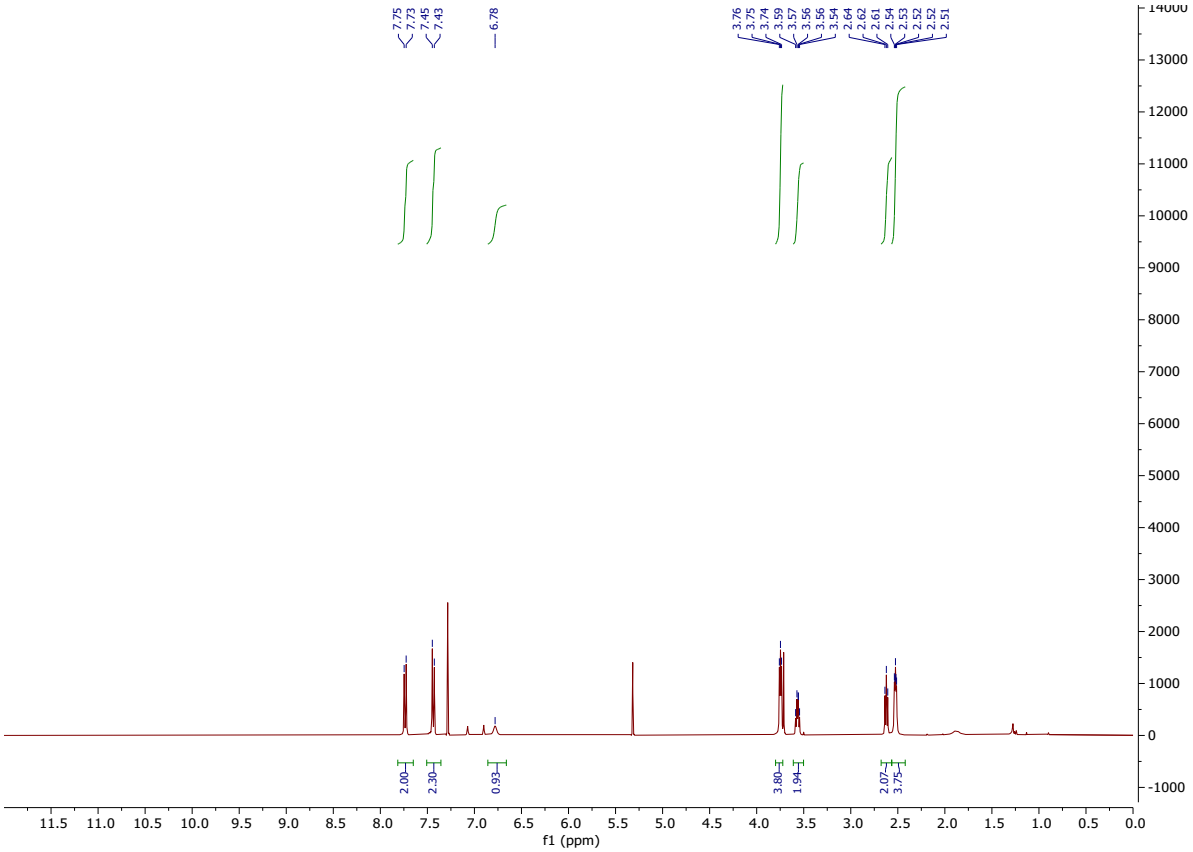
^{1}H NMR spectrum of **4hl**



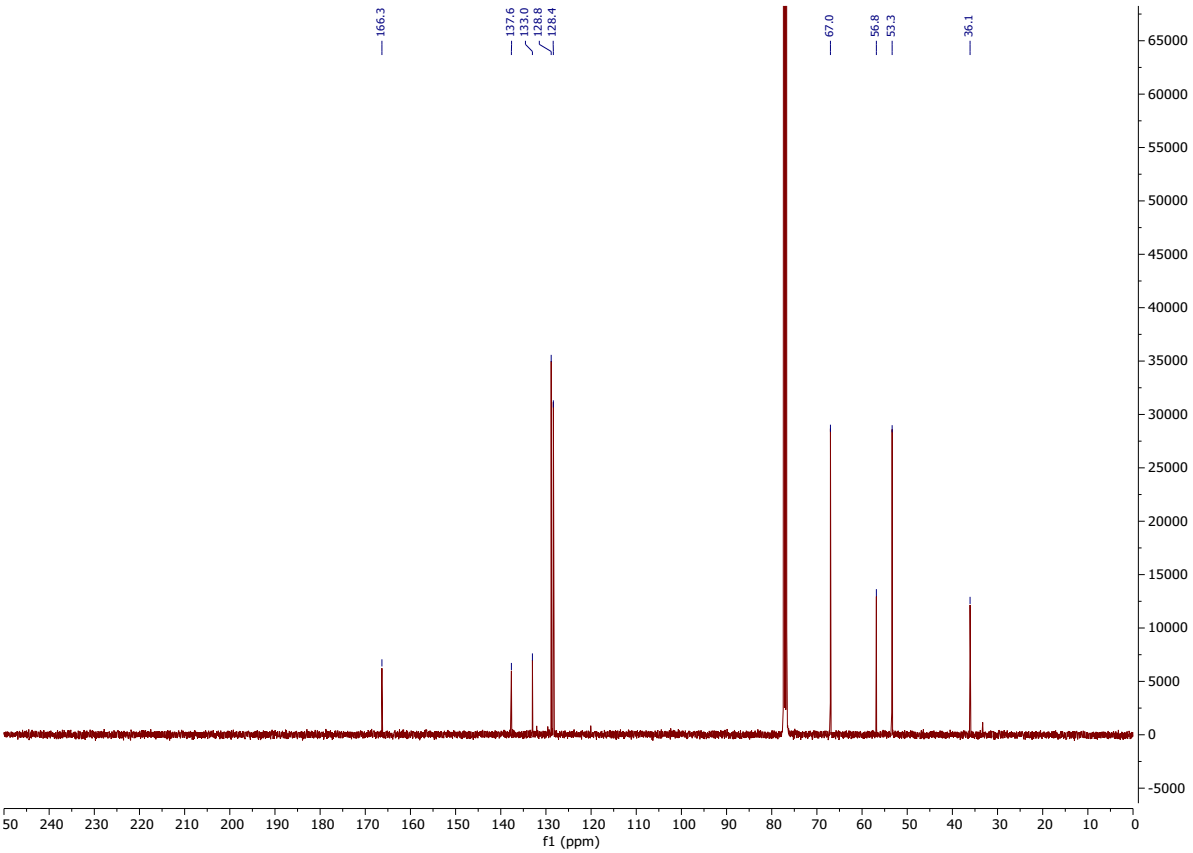
^{13}C NMR spectrum of **4hl**



^{1}H NMR spectrum of **Moclobemide**



^{13}C NMR spectrum of **Moclobemide**



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