Supporting Information

Homogenous Nickel-Catalyzed Chemoselective Transfer Hydrogenation of Functionalized Nitroarenes with Ammonia-Borane

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1. General information

Substrates and related compounds were purchased from different companies and were used without any purification. The $NiCl_2.6H_2O$ was purchased from TCI with the product no. N0851(25 gm). Catalytic reactions were carried out in 21 mL ACE pressure tubes, which were purchased from Sigma Aldrich. NMR spectra were obtained at 25 ˚C on a Bruker AVANCE III 400 and 600 MHz NMR spectrometer using $CDCl_3$, CD_3OD, or DMSO-d_6 as a solvent. ^1H NMR spectra were recorded at 400 MHz using a 400 NMR spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet; and b, broad. ^{13}C NMR spectra were recorded at 101 MHz using a 400 NMR spectrometer. Chemical shifts are reported in delta (δ) units. The reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (TLC Silica gel 60 F254), and compounds were monitored/visualized with UV light.

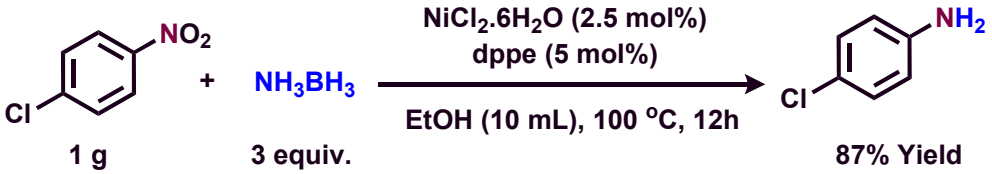
2. General Procedure for the Transfer Hydrogenation of Nitro Compound

A dried, 21 mL screw-cap pressure tube was charged with a magnetic stir bar, 2.5 mol% $NiCl_2.H_2O$ (2.97 mg), 5 mol% dppe (9.96 mg), 46.29 mg of Ammonia borane (1.5 mmol), and 0.5 mmol substrate (nitro compound). Then, ethanol (2 mL) was slowly added through the walls, and the pressure tube was tightly closed with a screw cap. Then, the pressure tube was placed in a pre-heated aluminium block, and reactions were allowed to progress for the desired time (12 h) and temperature (100 ˚C) under stirred conditions. After the completion of the reaction, the pressure tube was cooled to room temperature, and the autogenous pressure build-up in the tube was released slowly by losing the screw cap. The solid catalyst was separated from the mixture by simple filtration through filter paper and washed with ethyl acetate. After evaporating the solvent through a rotary evaporator, the obtained crude mixture was purified by using 60-120 mesh silica gel column chromatography (ethyl acetate: hexane) to obtain the pure desired product, which was further submitted for NMR analysis.

3. Gram scale synthesis of 4-Chloro aniline (1)

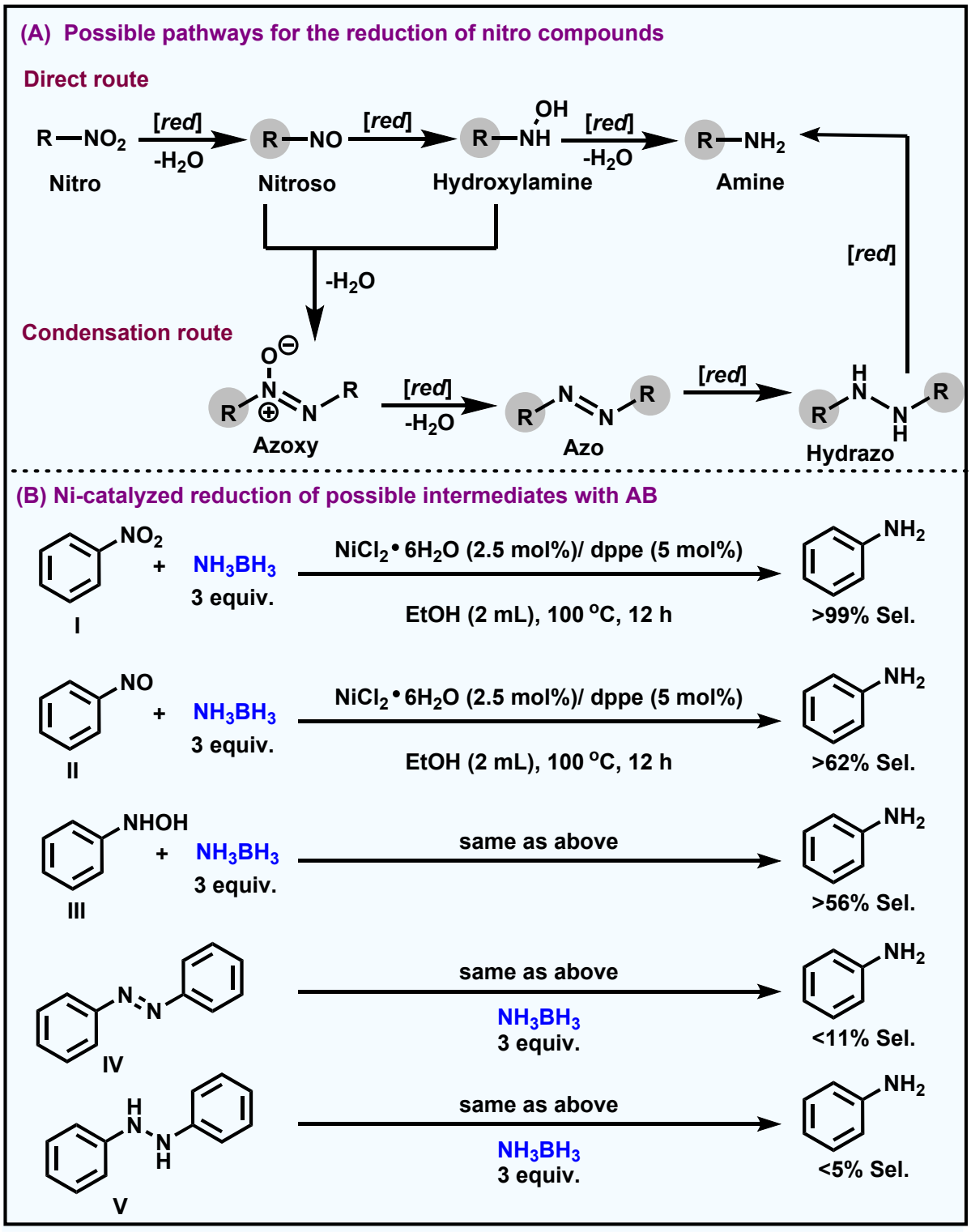
A dry, 50 mL screw-cap Ace Schlenk tube was charged with a magnetic stir bar, 2.5 mol% $NiCl_2.6H_2O$ (37.67 mg), 5 mol% dppe (126.29 mg), 19.02 mmol Ammonia borane (587.14 mg),

and 1 gm (6.34 mmol) 4-Nitrochlorobenzene. Then, ethanol (10 mL) was slowly added through the walls, and the Schlenk tube was tightly closed with a screw cap. Then, the reaction mixture containing the Schlenk tube was placed in a pre-heated aluminium block, and reactions were allowed to progress for the desired time (12 h) and temperature (100 ˚C) under stirred conditions. After the completion of the reaction, the Schlenk tube was cooled to room temperature, and the autogenous pressure build-up in the Schlenk tube was released slowly by losing the screw cap. The solid catalyst was separated from the mixture by simple filtration through filter paper and washed with ethyl acetate. After evaporating the solvent through a rotary evaporator, the obtained crude mixture was purified by using 60-120 mesh silica gel column chromatography (ethyl acetate: hexane). The 4-Chloroaniline was obtained with an 87% yield, which was further submitted for NMR analysis.



4. Safety advice

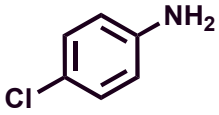
All transfer hydrogenation reactions are carried out in ACE® pressure tubes. Hydrogenation reactions with NH_3BH_3 in the presence of $NiCl_2.6H_2O$ at high temperatures are in general exothermic. Hence, appropriate safety measurements are required.



Scheme S1. (A) Mechanistic Studies; (B) Ni-catalyzed reduction of possible intermediates with AB.[a] [a]Reaction conditions: 0.5 mmol of (I) or (II) or (III) or (IV), 3 equiv. NH_3BH_3, 2.5 mol% $NiCl_2 \cdot 6H_2O$, 5 mol% dppe, 2 mL degassed ethanol, 100 °C, 12 h, and selectivity is determined with GC-MS.

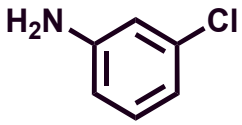
5. Spectroscopic data (^{1}H & ^{13}C)

4-Chloroaniline (1)



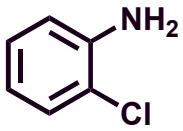
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 3.44 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.9, 129.1, 123.2, 116.3.

3-Chloroaniline (2)



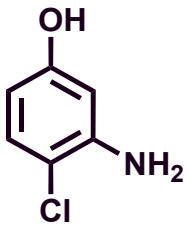
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.75 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 6.67 (t, *J* = 2.1 Hz, 1H), 6.59 – 6.51 (m, 1H), 3.63 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.8, 134.8, 130.5, 118.4, 114.9, 113.4.

2-Chloroaniline (3)



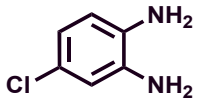
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.08 (td, *J* = 7.7, 1.4 Hz, 1H), 6.77 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.71 (td, *J* = 7.7, 1.4 Hz, 1H), 3.93 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.9, 129.5, 127.7, 119.3, 119.1, 115.9.

3-Amino-4-chlorophenol (4)



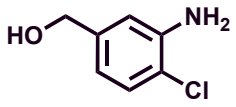
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.14 – 6.50 (m, 1H), 6.36 – 5.83 (m, 1H), 3.98 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$ & DMSO-d_6)** δ 156.8, 143.7, 129.6, 109.8, 106.7, 102.8.

4-Chlorobenzene-1,2-diamine (5)



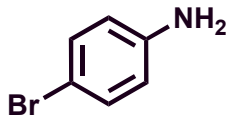
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (d, *J* = 2.2 Hz, 1H), 6.66 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 3.36 (s, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.1, 133.1, 124.8, 119.7, 117.6, 116.3.

(3-Amino-4-chlorophenyl)methanol (6)



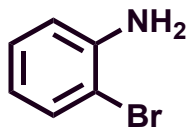
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 1H), 6.77 (s, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.56 (s, 2H), 3.96 (s, 2H), 1.87 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.9, 140.7, 129.5, 118.4, 117.5, 114.2, 64.8.

4-Bromoaniline (7)



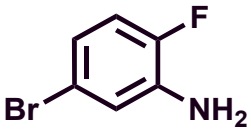
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.58 – 6.53 (m, 2H), 3.51 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.5, 132.0, 116.8, 110.2.

2-Bromoaniline (8)



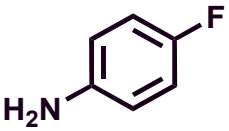
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.3, 1.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.65 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 4.09 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.2, 132.6, 128.4, 119.5, 115.9, 109.4.

5-Bromo-2-fluoroaniline (9)



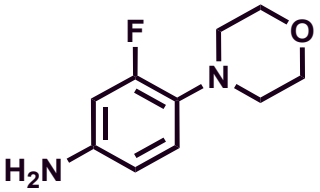
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.73 (m, 3H), 3.70 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.7 (d, $J_{C\text{-}F}$ = 230 Hz), 136.1 (d, $J_{C\text{-}F}$ = 14 Hz), 121.1 (d, $J_{C\text{-}F}$ = 6 Hz), 119.4 (d, $J_{C\text{-}F}$ = 4 Hz), 116.8 (d, $J_{C\text{-}F}$ = 3 Hz), 116.6 (d, $J_{C\text{-}F}$ = 20 Hz).

4-Fluoroaniline (10)



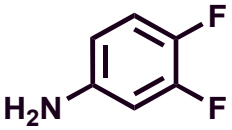
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.79 (m, 2H), 6.72 – 6.48 (m, 2H), 3.49 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.4 (d, $J_{C\text{-}F}$ = 233 Hz), 142.7 (d, $J_{C\text{-}F}$ = 2 Hz), 116.2 (d, $J_{C\text{-}F}$ = 7 Hz), 115.7 (d, $J_{C\text{-}F}$ = 23 Hz).

3-Fluoro-4-morpholinoaniline (11)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dd, J = 13.1, 5.2 Hz, 1H), 6.54 – 6.25 (m, 2H), 3.97 – 3.70 (m, 4H), 3.50 (s, 2H), 3.11 – 2.83 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.8 (d, $J_{C\text{-}F}$ = 244 Hz), 142.9 (d, $J_{C\text{-}F}$ = 10 Hz), 131.7 (d, $J_{C\text{-}F}$ = 10 Hz), 120.3 (d, $J_{C\text{-}F}$ = 4 Hz), 110.7 (d, $J_{C\text{-}F}$ = 3 Hz), 103.9 (d, $J_{C\text{-}F}$ = 23 Hz), 67.2, 51.8 (d, $J_{C\text{-}F}$ = 2 Hz).

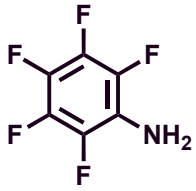
3,4-Difluoroaniline (12)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dt, J = 10.4, 8.8 Hz, 1H), 6.45 (ddd, J = 12.1, 6.7, 2.8 Hz, 1H), 6.33 (dddd, J = 8.8, 3.4, 2.9, 1.6 Hz, 1H), 3.53 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.6 (dd,

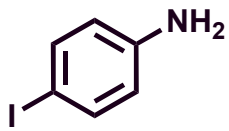
$J_{C\text{-}F}$ = 257 Hz, $J_{C\text{-}F}$ = 230Hz), 143.4 (dd, $J_{C\text{-}F}$ = 11Hz, $J_{C\text{-}F}$ = 6Hz), 143.7 (dd, $J_{C\text{-}F}$ = 248Hz, $J_{C\text{-}F}$ = 223Hz), 117.5 (dd, $J_{C\text{-}F}$ = 18Hz, $J_{C\text{-}F}$ = 18Hz), 110.3 (dd, $J_{C\text{-}F}$ = 9Hz, $J_{C\text{-}F}$ = 2Hz) 103.9 (d, $J_{C\text{-}F}$ = 20Hz)

2,3,4,5,6-Pentafluoroaniline (13)



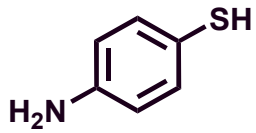
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.2, 137.8, 136.8, 135.4, 134.6, 132.2, 121.9.

4-Iodoaniline (14)



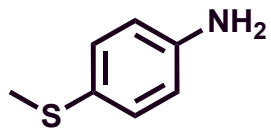
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 6.54 – 6.38 (m, 2H), 3.52 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.1, 137.9, 117.3, 79.4.

4-Aminothiophenol (15)



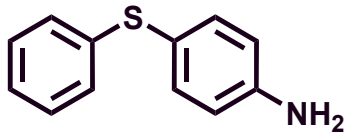
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 1H), 7.20 – 7.11 (m, 1H), 6.57 (dd, *J* = 8.0, 1.3 Hz, 2H), 3.76 (s, 2H), 3.34 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.3, 145.5, 134.0, 133.0, 125.5, 116.3, 115.9, 115.5.

4-(Methylthio)aniline (16)



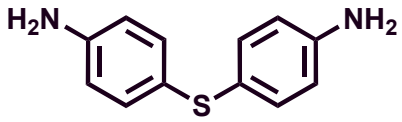
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 2H), 6.73 – 6.49 (m, 2H), 3.55 (s, 2H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.2, 131.1, 125.7, 115.8, 18.8.

4-(Phenylthio)aniline (17)



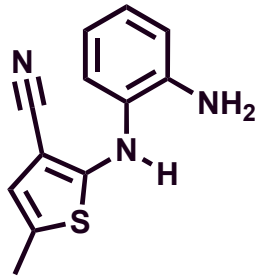
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H), 7.32 – 7.23 (m, 2H), 7.23 – 7.12 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.68 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 139.8, 136.2, 128.9, 127.3, 125.3, 120.4, 115.9.

4((4-Aminophenyl)thio)aniline (18)



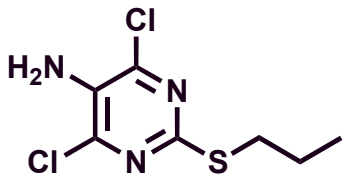
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.8 Hz, 4H), 6.59 (d, *J* = 7.9 Hz, 4H), 3.65 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8, 132.8, 124.9, 115.8.

2-((2-Aminophenyl)amino)-5-methylthiophene-3-carbonitrile (19)



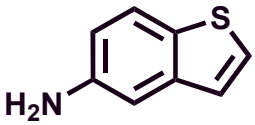
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.07 (td, *J* = 8.0, 1.3 Hz, 1H), 6.86 – 6.72 (m, 2H), 6.53 (s, 1H), 6.44 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 2H), 2.25 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.98, 141.4, 127.9, 127.7, 124.9, 122.3, 119.5, 117.0, 116.3, 86.7, 15.0.

4,6-Dichloro-2-(propylthio)pyrimidin-5-amine (20)



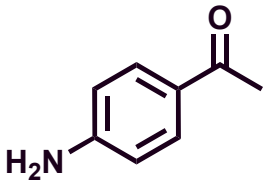
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.46 – 2.49 (m, 2H), 2.01 – 1.39 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 145.3, 131.5, 33.4, 22.4, 13.4.

5-Aminobenzothiophene (21)



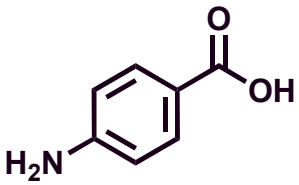
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.09 (s, 1H), 6.78 (dd, *J* = 8.4, 1.3 Hz, 1H), 3.48 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 140.9, 130.5, 127.2, 123.1, 122.9, 114.9, 108.4.

1-(4-Aminophenyl)ethan-1-one (22)



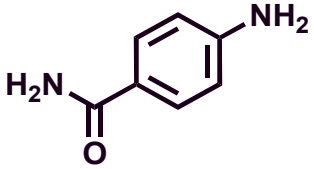
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.65 (m, 2H), 6.79 – 6.39 (m, 2H), 4.27 (s, 2H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.7, 151.4, 130.8, 127.6, 113.7, 26.1.

4-Aminobenzoicacid (23)



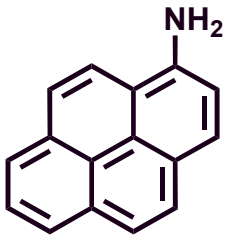
^{1}H NMR (400 MHz, MeOD) δ 7.91 – 7.61 (m, 2H), 6.78 – 6.46 (m, 2H), 4.68 (s, 3H, NH_3^+). **^{13}C NMR (101 MHz, MeOD)** δ 169.5, 152.1, 131.8, 118.6, 113.6.

4-Aminobenzamide (24)



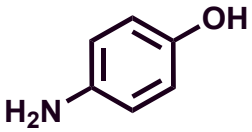
^{1}H NMR (400 MHz, MeOD) δ 9.66 – 8.82 (m, 2H), 8.65 – 7.95 (m, 2H), 6.44 (s, 4H). **^{13}C NMR (101 MHz, MeOD)** δ 171.4, 152.1, 129.1, 120.9, 113.3.

Pyrene-1-amine (25)



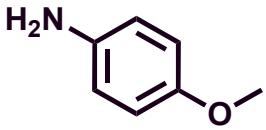
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 8.01 – 7.88 (m, 5H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 4.42 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.9, 132.3, 131.7, 127.7, 127.5, 126.1, 126.0, 125.5, 125.0, 124.3, 124.2, 123.8, 123.6, 120.2, 116.9, 114.0.

4-Aminophenol (26)



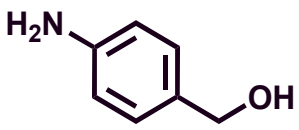
^{1}H NMR (600 MHz, DMSO) δ 8.42 (s, 1H), 6.55 – 6.43 (m, 4H), 4.37 (s, 2H). **^{13}C NMR (151 MHz, DMSO)** δ 148.8, 141.0, 116.1, 115.9.

***p*-Anisidine (27)**



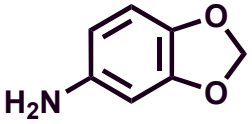
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 – 6.72 (m, 2H), 6.69 – 6.61 (m, 2H), 3.75 (s, 3H), 3.31 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 140.0, 116.5, 114.8, 55.8.

(4-Aminophenyl)methanol (28)



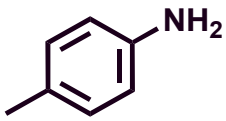
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 3.72 (s, 2H), 2.70 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.0, 131.3, 128.4, 114.7, 64.3.

3,4-(Methylenedioxy)aniline (29)



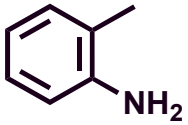
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (d, *J* = 8.2 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.11 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.84 (s, 2H), 3.50 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.2, 141.4, 140.3, 108.6, 106.9, 100.7, 98.1.

_p_-Toluidine (30)



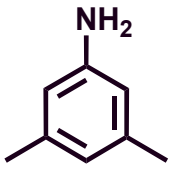
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.44 (s, 2H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.9, 129.8, 127.8, 115.3, 20.5.

_o_-Toluidine (31)



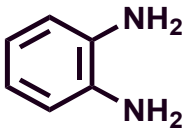
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 11.5, 4.0 Hz, 2H), 6.80 (td, *J* = 7.4, 0.6 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.56 (s, 2H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 130.5, 127.1, 122.1, 118.7, 115.0, 17.4.

3,5-Dimethylaniline (32)



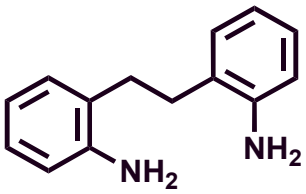
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H), 6.42 (s, 2H), 3.58 (s, 2H), 2.36 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 139.1, 120.6, 113.3, 21.5.

Benzene-1,2-diamine (34)



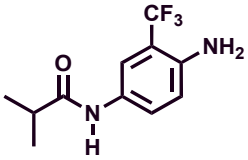
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.64 (m, 4H), 3.37 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.8, 120.3, 116.8.

2,2'-(Ethane-1,2-diyl)dianiline (35)



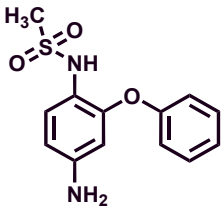
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.4 Hz, 4H), 6.77 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.37 (s, 4H), 2.82 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.3, 129.6, 127.3, 126.3, 119.1, 115.9, 31.0.

Flutamide (36)



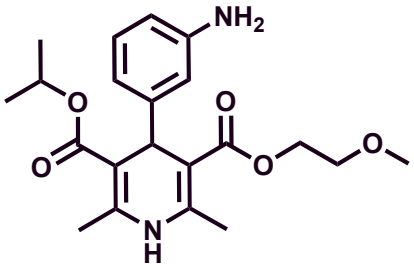
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.1 Hz, 1H), 7.47 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 4.10 (d, *J* = 24.0 Hz, 2H), 2.48 (hept, *J* = 6.9 Hz, 1H), 1.71 (s, 1H), 1.24 (t, *J* = 6.9 Hz, 7H).

Nimesulide (37)



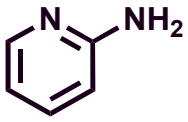
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 3H), 7.20 – 7.11 (m, 1H), 7.00 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.42 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.33 (s, 1H), 6.17 (d, *J* = 2.5 Hz, 1H), 3.67 (s, 2H), 2.92 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.8, 150.5, 146.2, 130.2, 127.2, 124.3, 118.9, 117.9, 110.6, 104.5, 38.9.

Nimodipine (38)



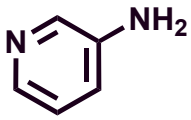
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (t, 1H), 6.67 (d, 1H), 6.66 (s, 1H), 6.48 (d, 1H), 5.93 (s, 1H), 5.04 – 4.88 (m, 2H), 4.28 – 4.15 (m, 2H), 3.61 – 3.53 (m, 2H), 3.39 (s, 3H), 3.28 (s, -NH_2 protons 2H), 2.27 (s, 6H), 1.24 (d, 3H), 1.12 (d, 3H).

2-Aminopyridine (39)



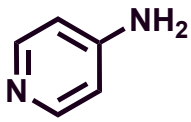
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.36 (tdd, *J* = 8.2, 1.9, 0.9 Hz, 1H), 6.69 – 6.51 (m, 1H), 6.51 – 6.36 (m, 1H), 4.61 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6, 148.0, 137.7, 113.9, 108.6.

3-Aminopyridine (40)



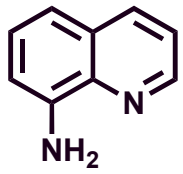
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.5 Hz, 1H), 7.95 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.09 – 6.95 (m, 1H), 6.92 (ddd, *J* = 8.2, 2.8, 1.4 Hz, 1H), 3.73 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.8, 139.6, 137.4, 123.8, 121.5.

4-Aminopyridine (41)



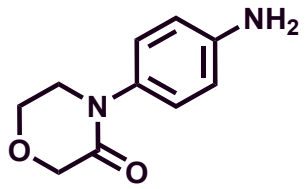
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 4.8, 1.4 Hz, 2H), 6.50 (dd, *J* = 4.7, 1.6 Hz, 2H), 4.24 (s, 2H), 2.46 (s, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 152.8, 150.2, 109.6.

Quinolin-8-amine (42)



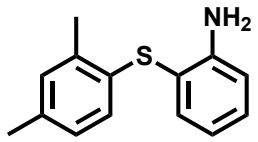
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.15 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.93 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.98 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.5, 144.0, 138.5, 136.1, 128.9, 127.4, 121.4, 116.1, 110.1.

4-(4-Aminophenyl)morpholin-3-one (43)



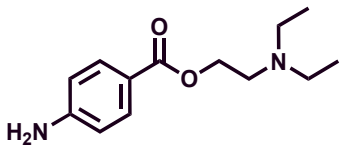
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 6.91 (m, 2H), 6.77 – 6.54 (m, 2H), 4.30 (s, 2H), 4.07 – 3.92 (m, 2H), 3.81 – 3.58 (m, 4H, CH_2 and NH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 145.8, 132.1, 126.8, 115.5, 68.6, 64.2, 50.2.

2-((2,4-dimethylphenyl)thio)aniline (44)



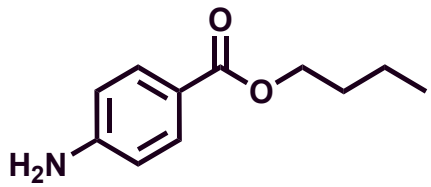
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.23 (dd, *J* = 11.4, 4.0 Hz, 1H), 7.03 (s, 1H), 6.93 – 6.82 (m, 1H), 6.84 – 6.66 (m, 3H), 4.34 – 3.12 (m, 2H), 2.42 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.4, 136.7, 135.8, 135.4, 131.8, 131.2, 130.5, 127.4, 126.6, 118.9, 115.4, 115.2, 20.8, 20.1.

Procaine (45)



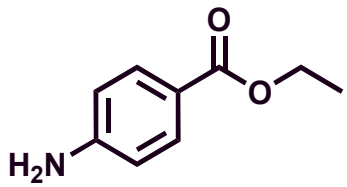
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.73 (m, 2H), 6.92 – 6.40 (m, 2H), 4.33 (t, *J* = 6.3 Hz, 2H), 4.06 (s, 2H), 2.83 (t, *J* = 6.3 Hz, 2H), 2.62 (q, *J* = 7.1 Hz, 4H), 1.06 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.7, 150.8, 131.6, 119.9, 113.8, 62.8, 51.1, 47.8, 12.1.

Butyl 4-aminobenzoate (46)



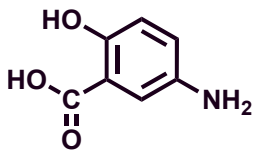
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.65 (m, 2H), 6.83 – 6.45 (m, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 4.05 (s, 2H), 1.83 – 1.60 (m, 2H), 1.45 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 150.8, 131.6, 120.0, 113.8, 64.2, 30.9, 19.3, 13.8.

Ethyl 4-aminobenzoate (47)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.65 (m, 2H), 6.98 – 6.38 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.20 – 3.89 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 150.9, 131.6, 119.9, 113.8, 60.3, 14.4.

5-Aminosalicylicacid (48)



^{1}H NMR (600 MHz, DMSO) δ 8.51 (s, NH_2, OH, COOH, 4H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR (151 MHz, DMSO)** δ 172.3, 157.3, 131.8, 125.2, 119.4, 117.6, 116.6.

Figure S1: ^{1}H NMR spectrum of 4-Chloroaniline (1).

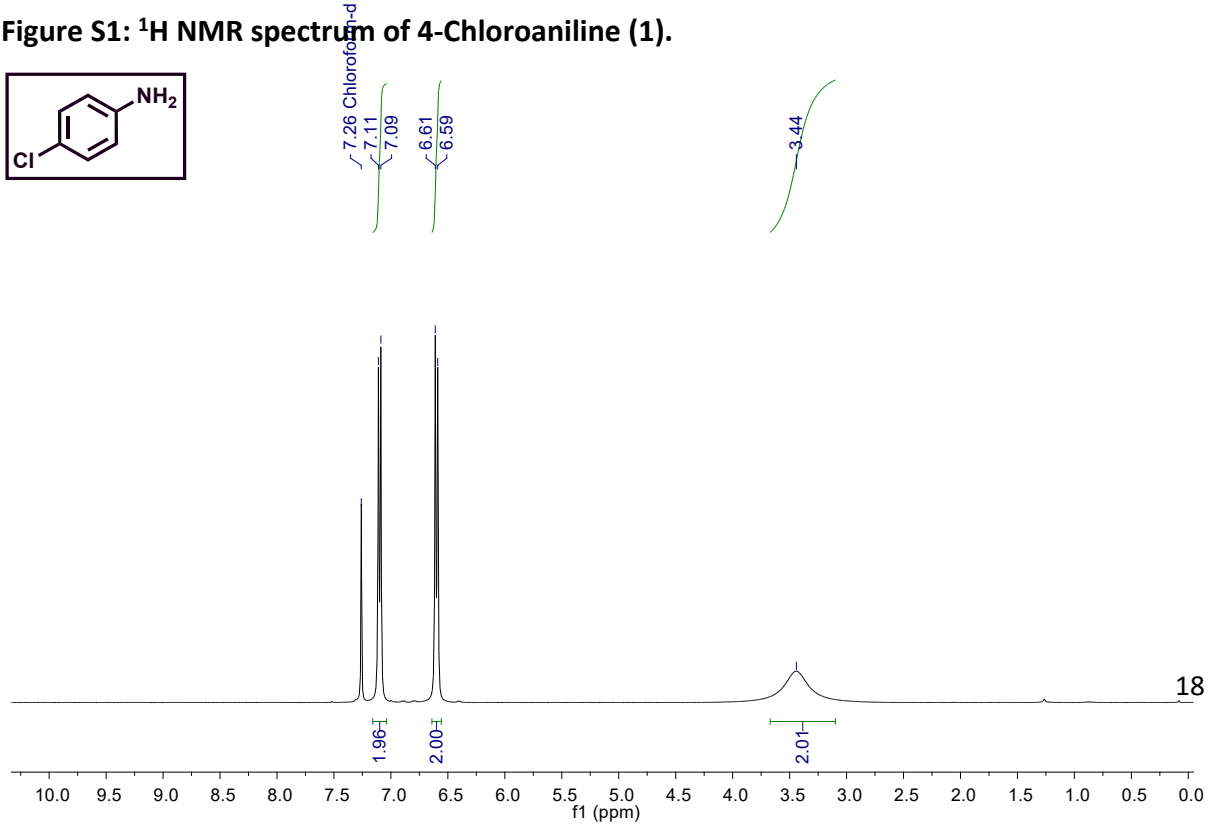


Figure S2: ^{13}C NMR spectrum of 4-Chloroaniline (1).

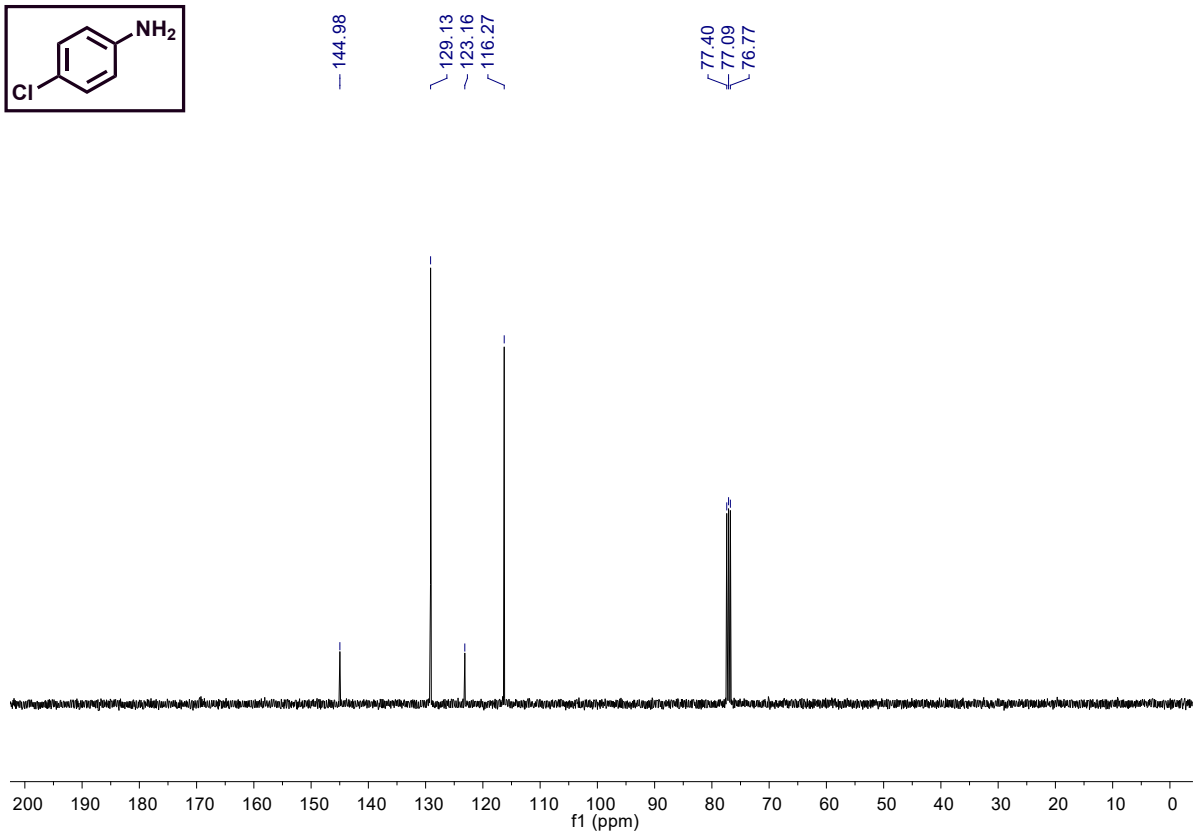


Figure S3: ^{1}H NMR spectrum of 3-Chloroaniline (2).

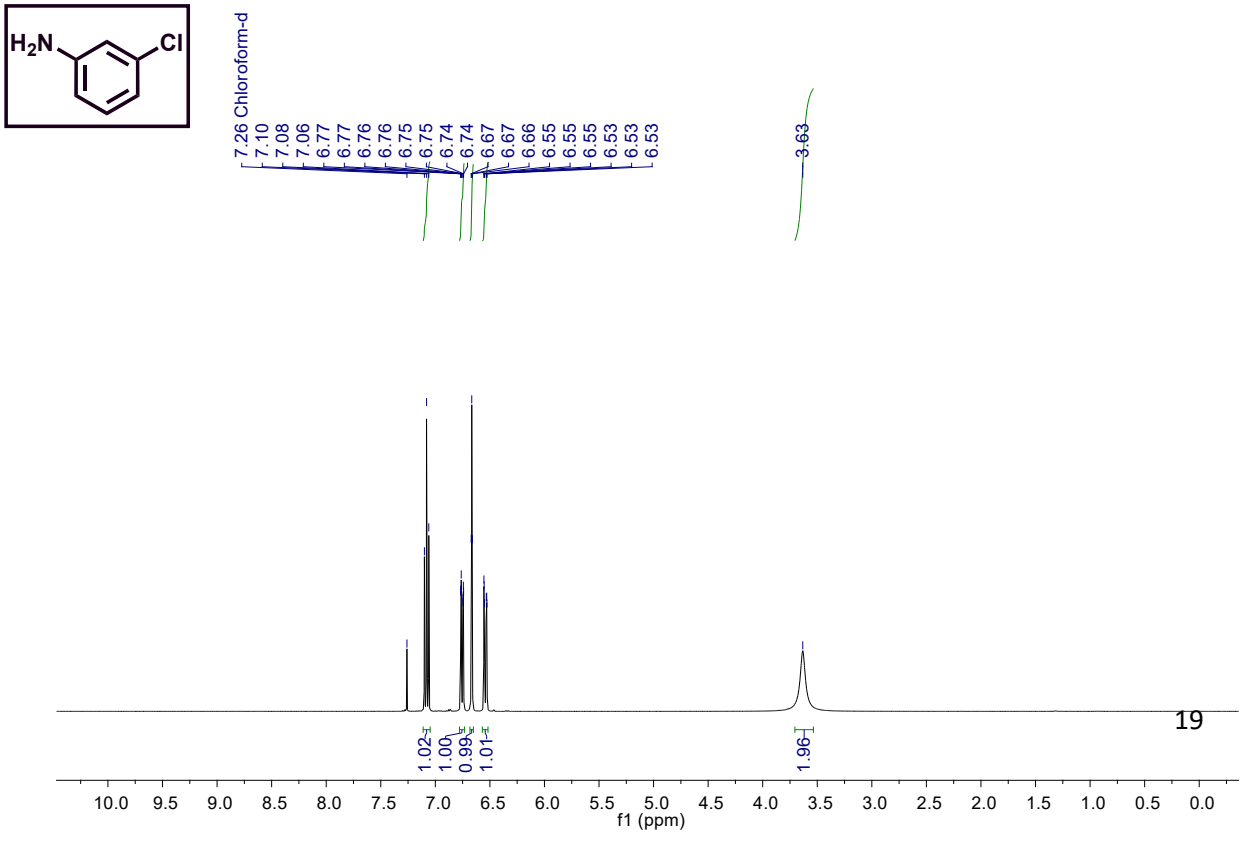


Figure S4: ^{13}CNMR spectrum of 3-Chloroaniline (2).

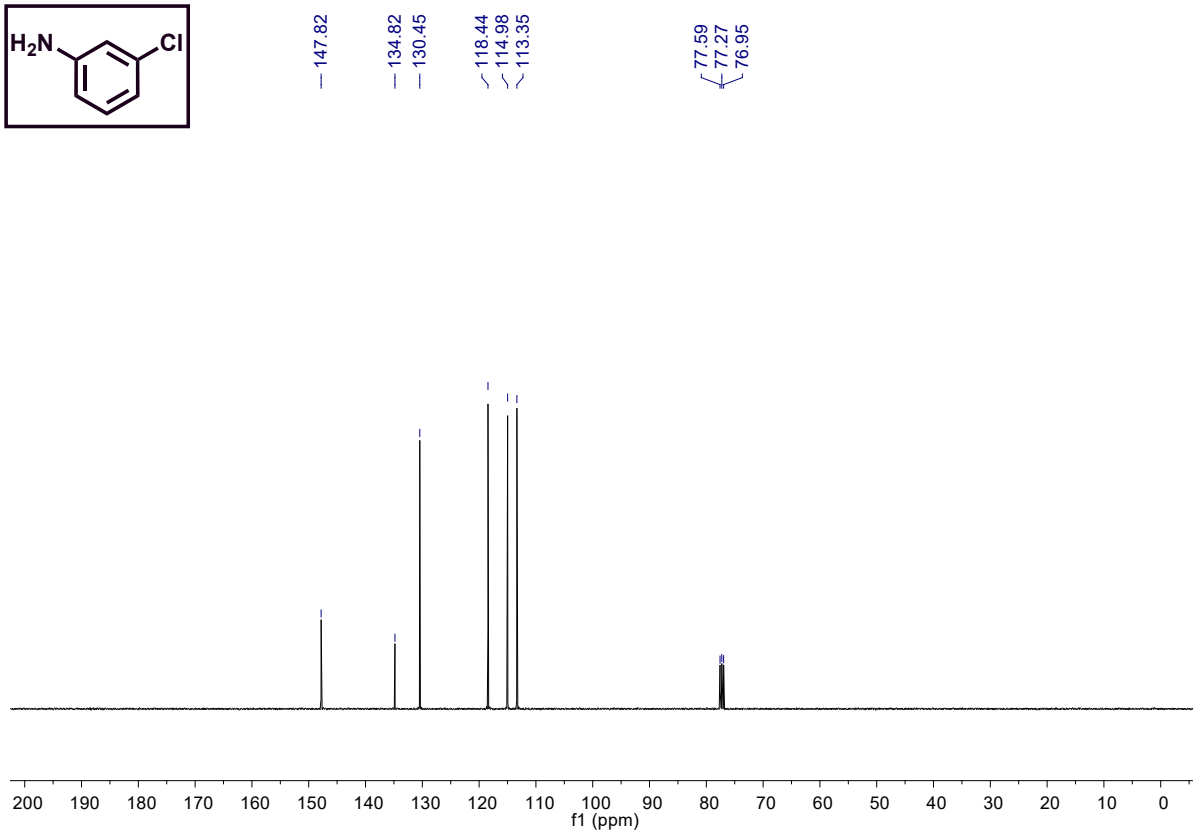


Figure S5: ^{1}H NMR spectrum of 2-Chloroaniline (3)

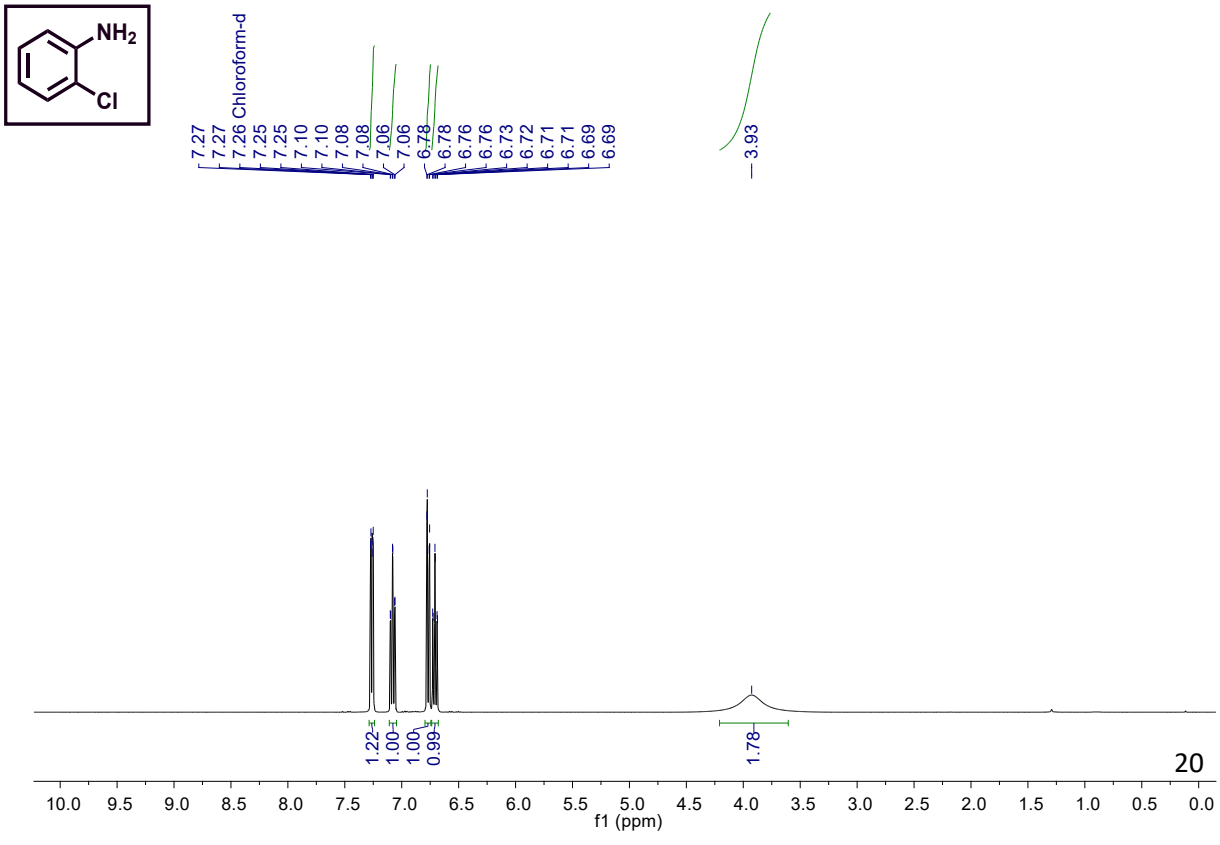


Figure S6: ^{13}C NMR spectrum of 2-Chloroaniline (3).

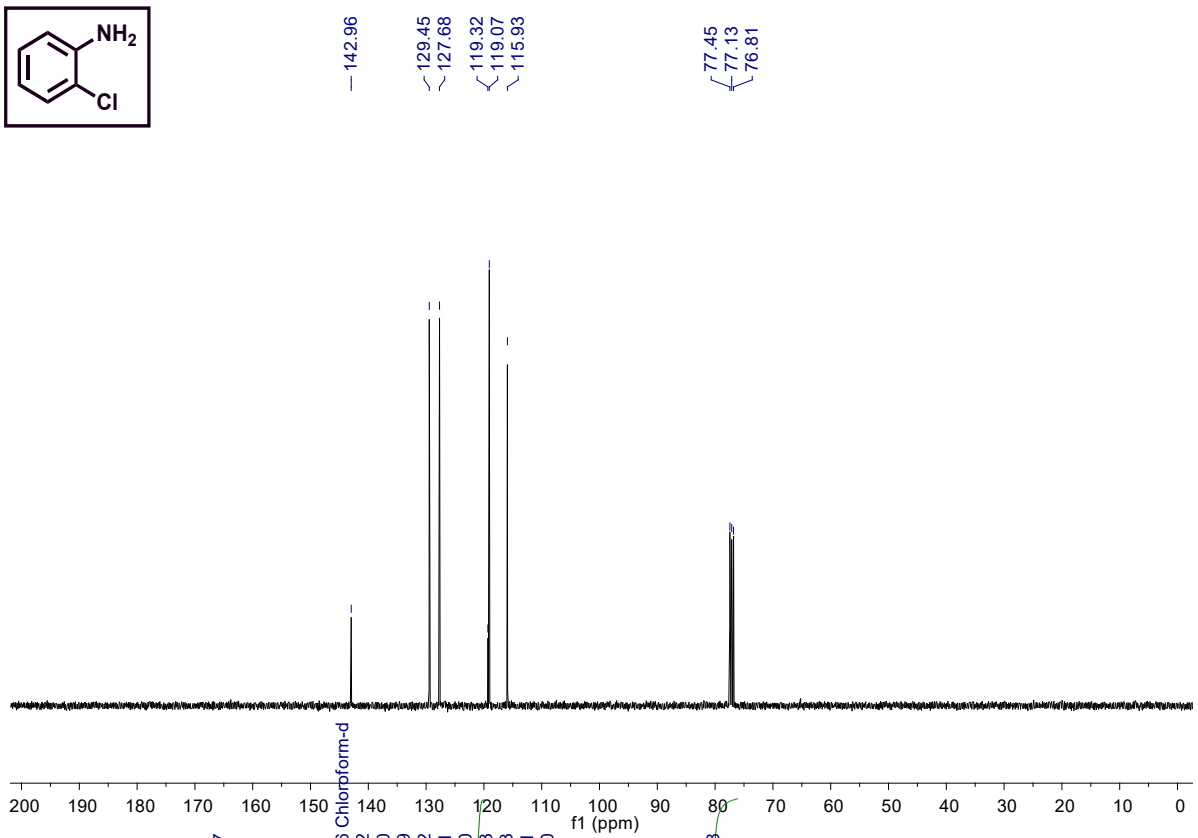


Figure S7: ^{1}H NMR spectrum of 3-Amino-4-chlorophenol (4).

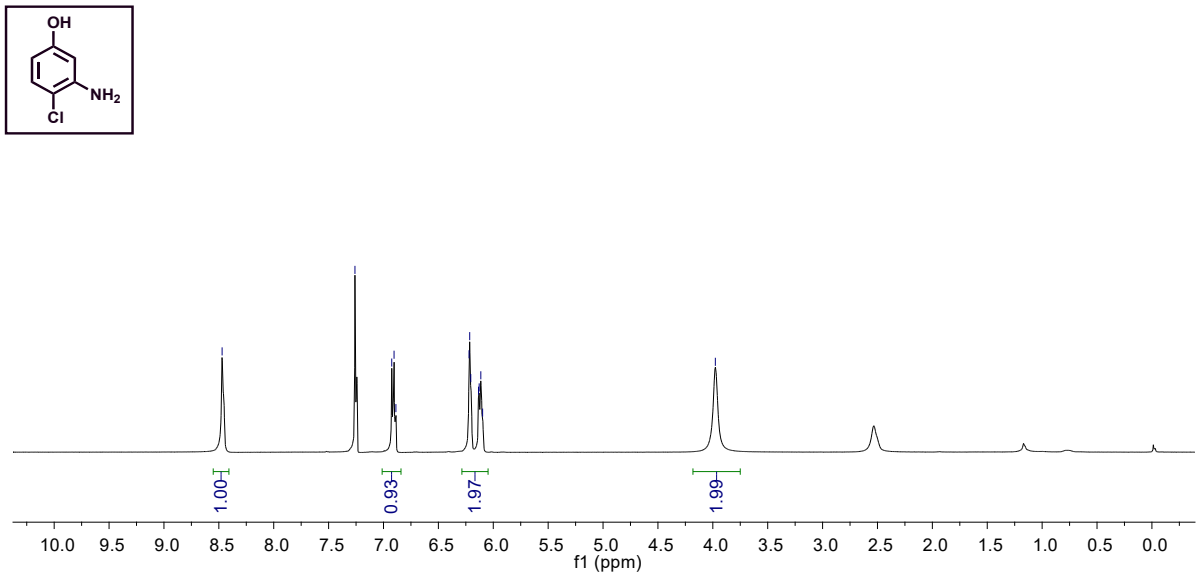


Figure S8: ^{13}C NMR spectrum of 3-Amino-4-chlorophenol (4). (101 MHz, $CDCl_3$ & DMSO-d_6)

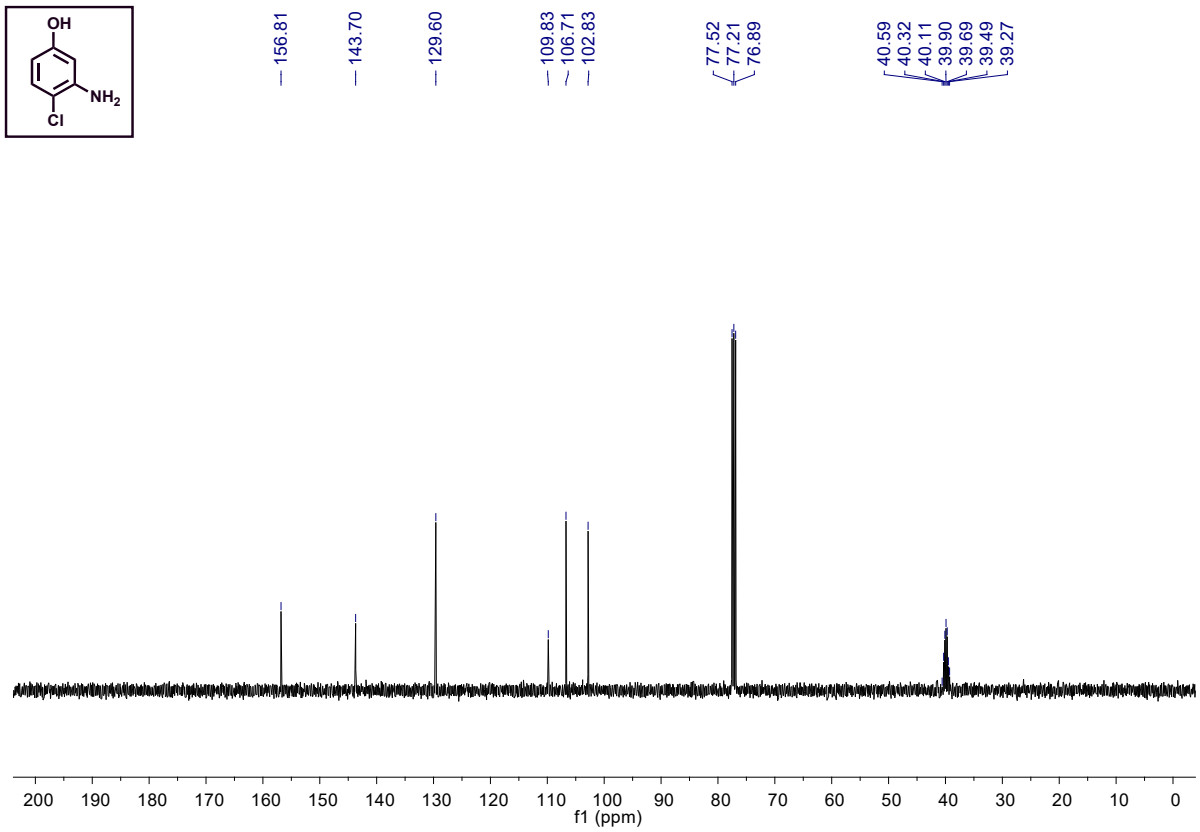


Figure S9: ^{1}H NMR spectrum of 4-Chlorobenzene-1,2-diamine (5).

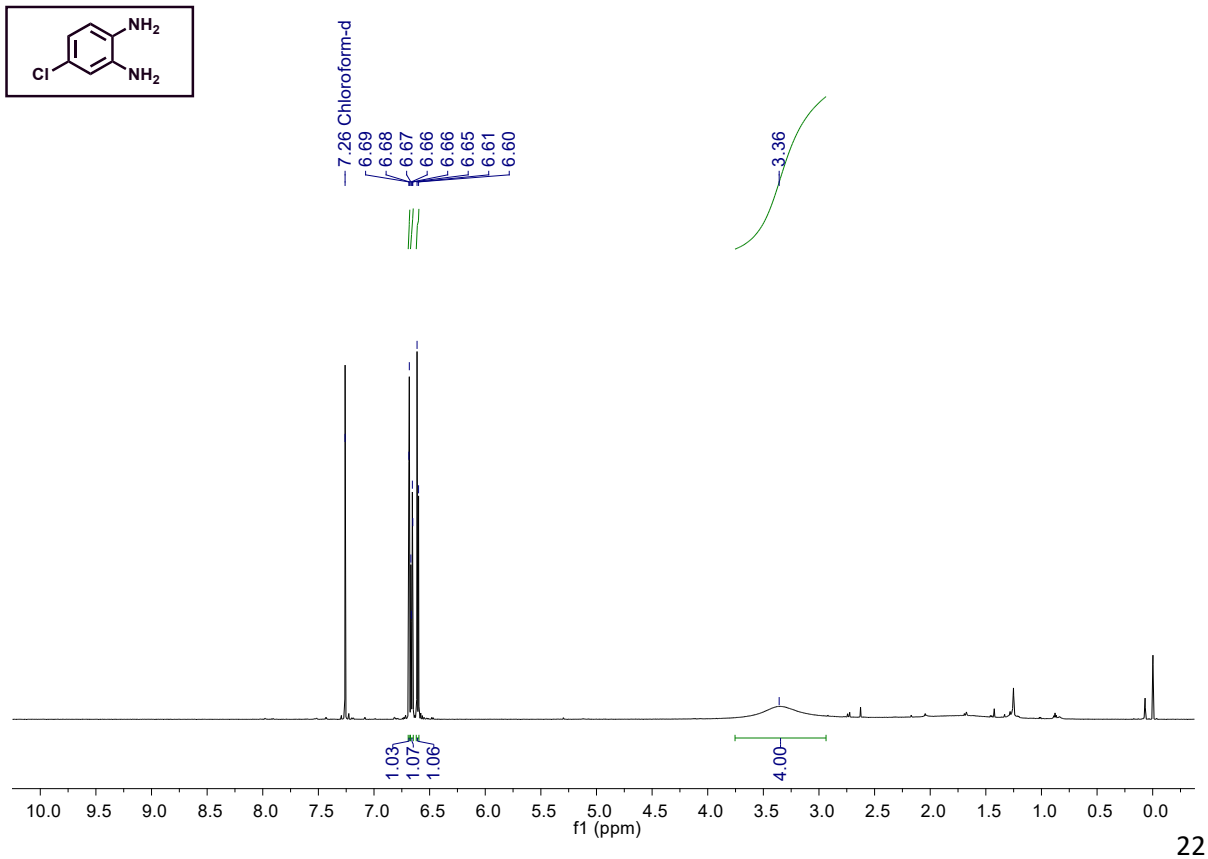


Figure S10: ^{13}C NMR spectrum of 4-Chlorobenzene-1,2-diamine (5).

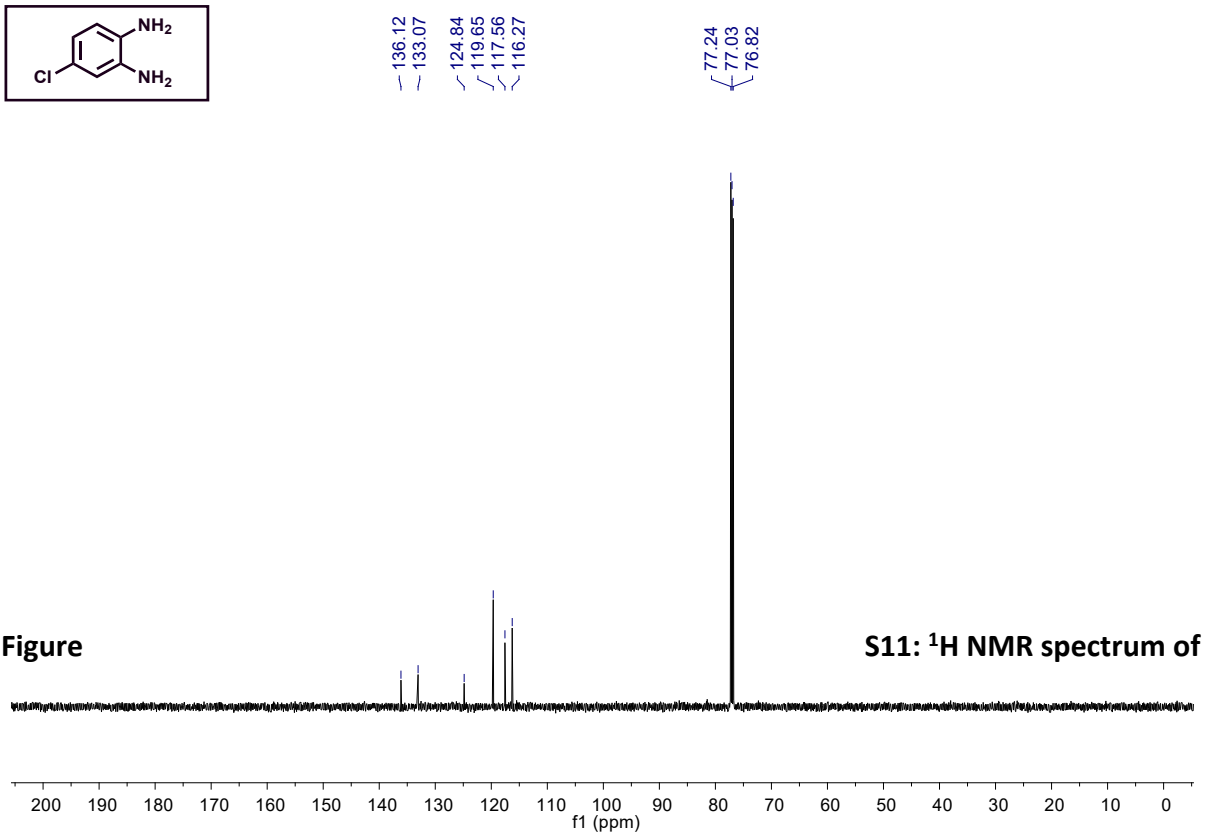


Figure S11: ^{1}H NMR spectrum of (3-Amino-4-chlorophenyl)methanol (6).

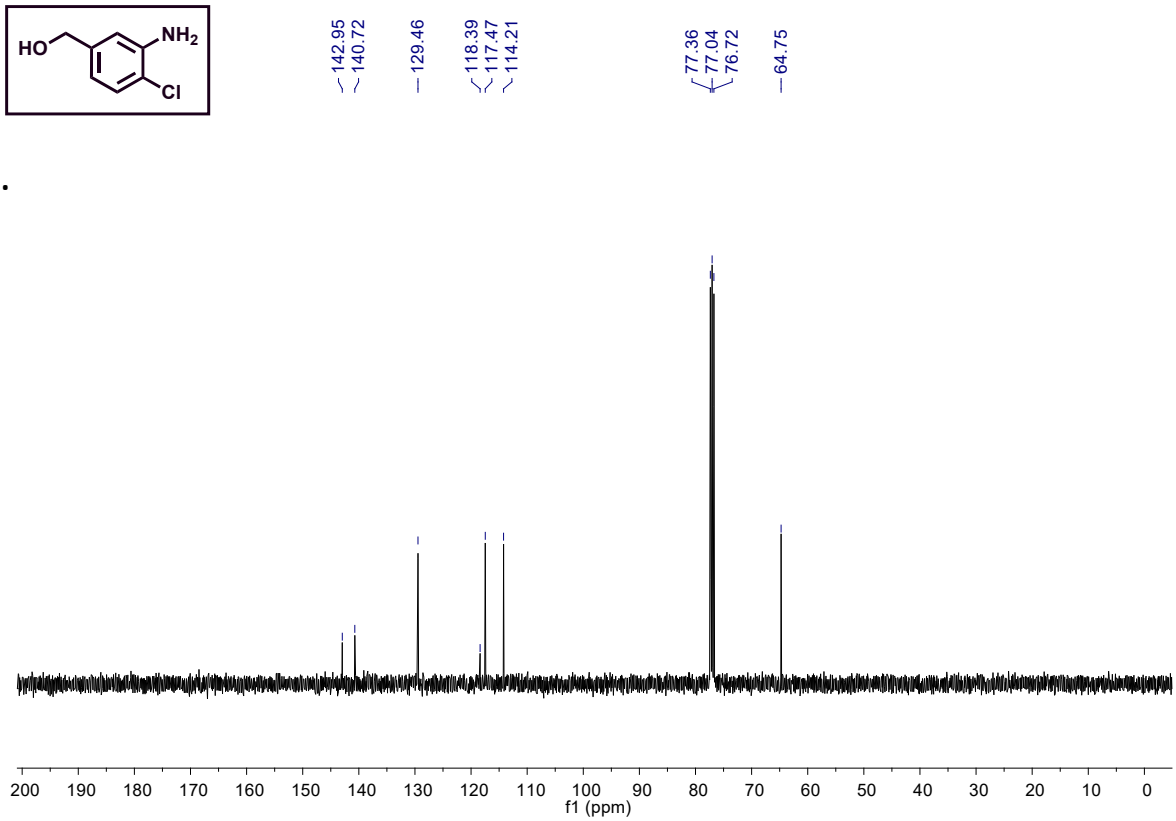


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Figure S12: ^{13}C NMR spectrum of (3-Amino-4-chlorophenyl)methanol (6).

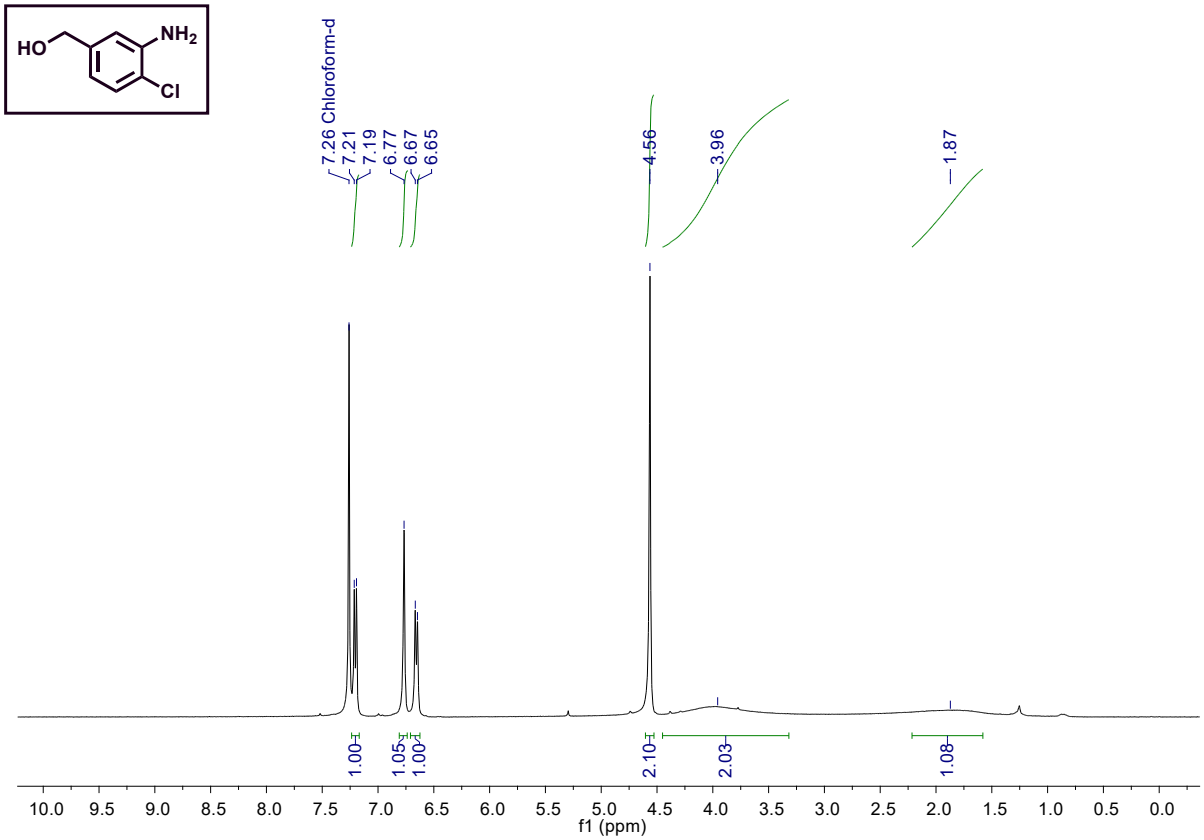

Figure S13: ^{1}H NMR spectrum of 4-Bromoaniline (7).

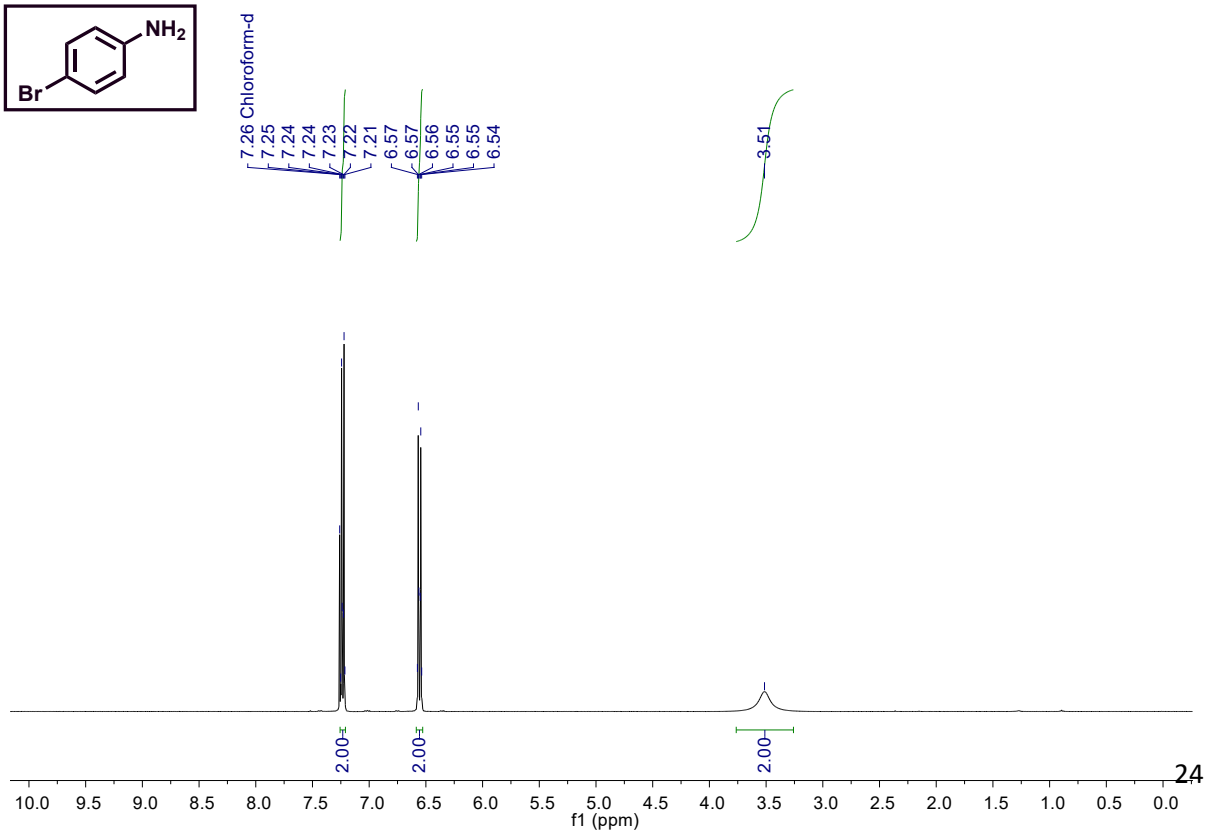

Figure S14: ^{13}C NMR spectrum of 4-Bromoaniline (7).

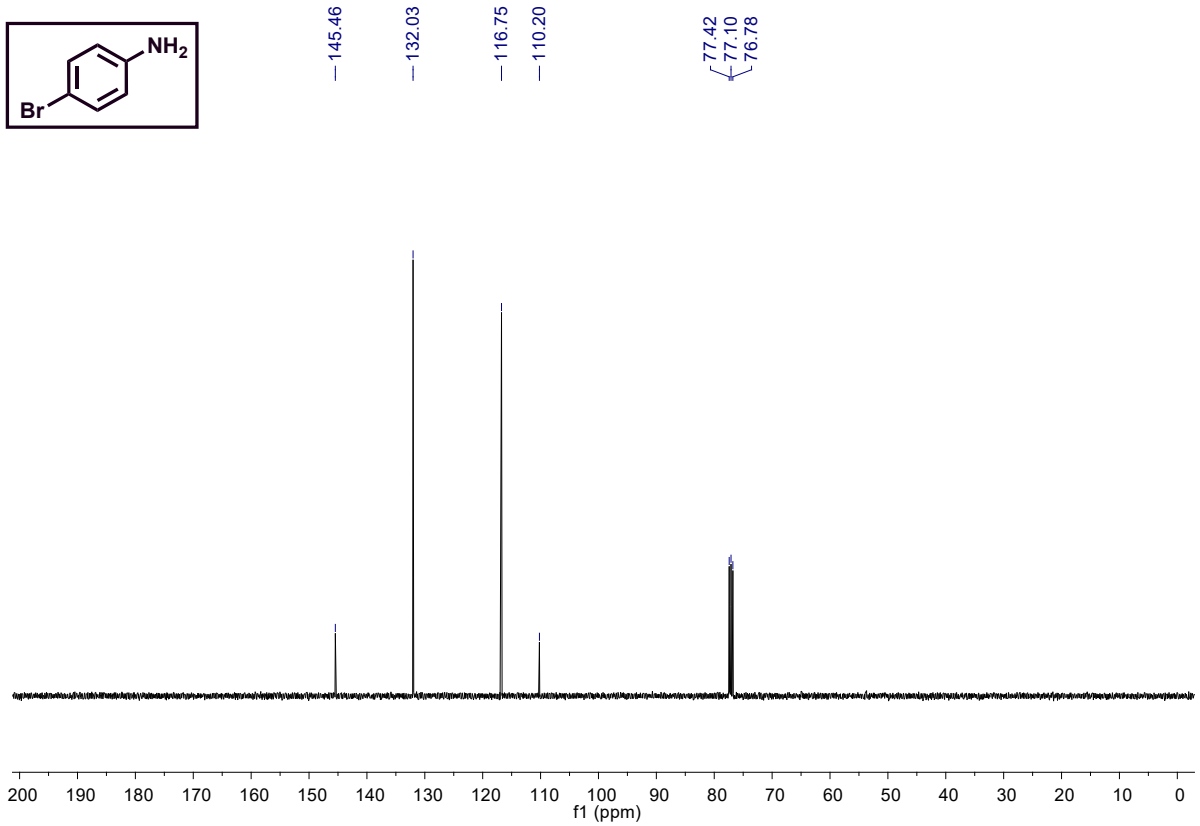

Figure S15: ^{1}H NMR spectrum of 2-Bromoaniline (8).

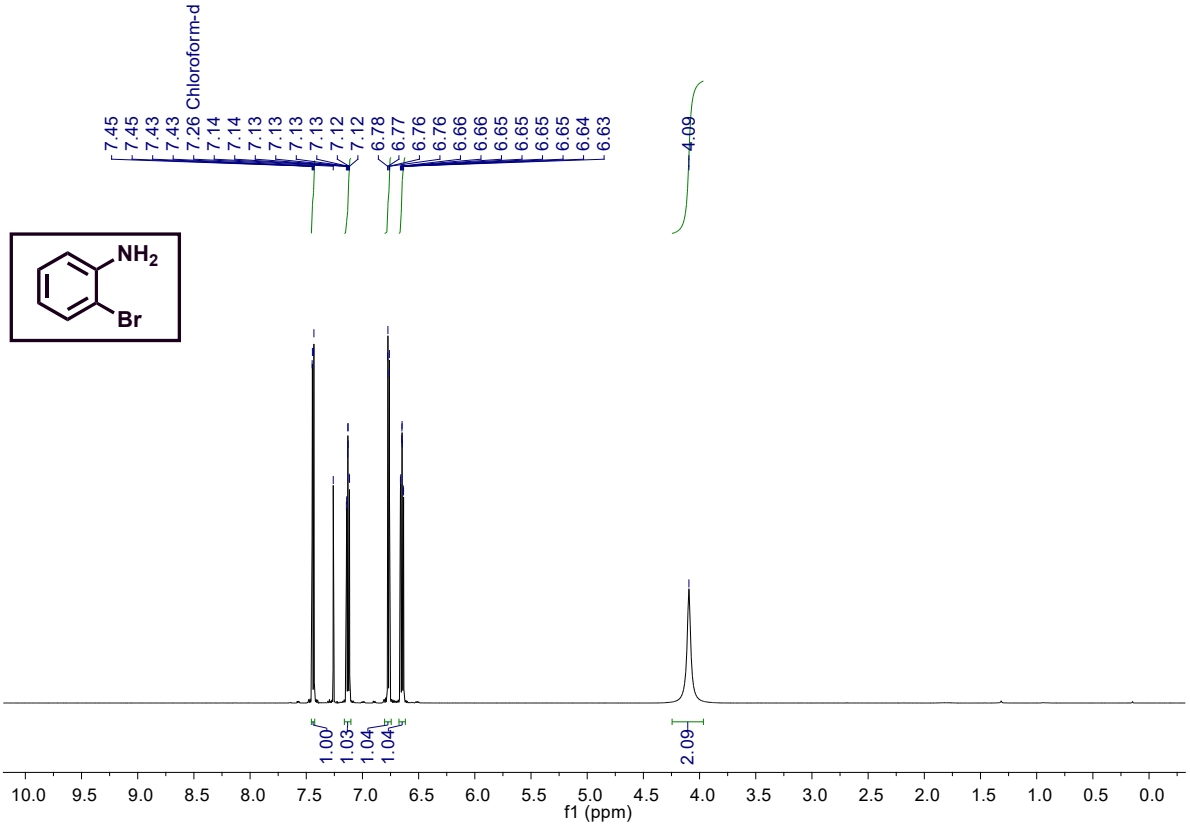

Figure S16: ^{13}C NMR spectrum of 2-Bromoaniline (8).

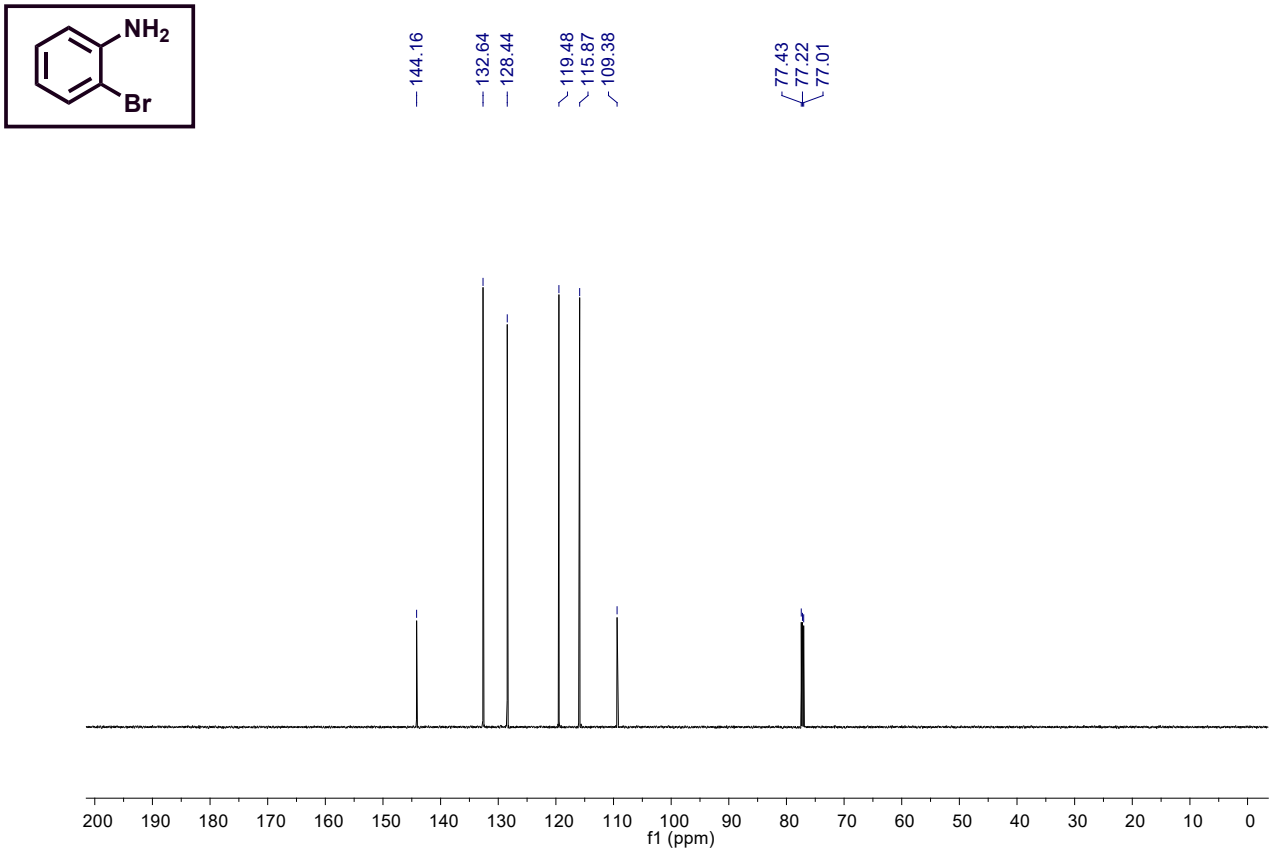

Figure S17: ^{1}H NMR spectrum of 5-Bromo-2-fluoro aniline (9).

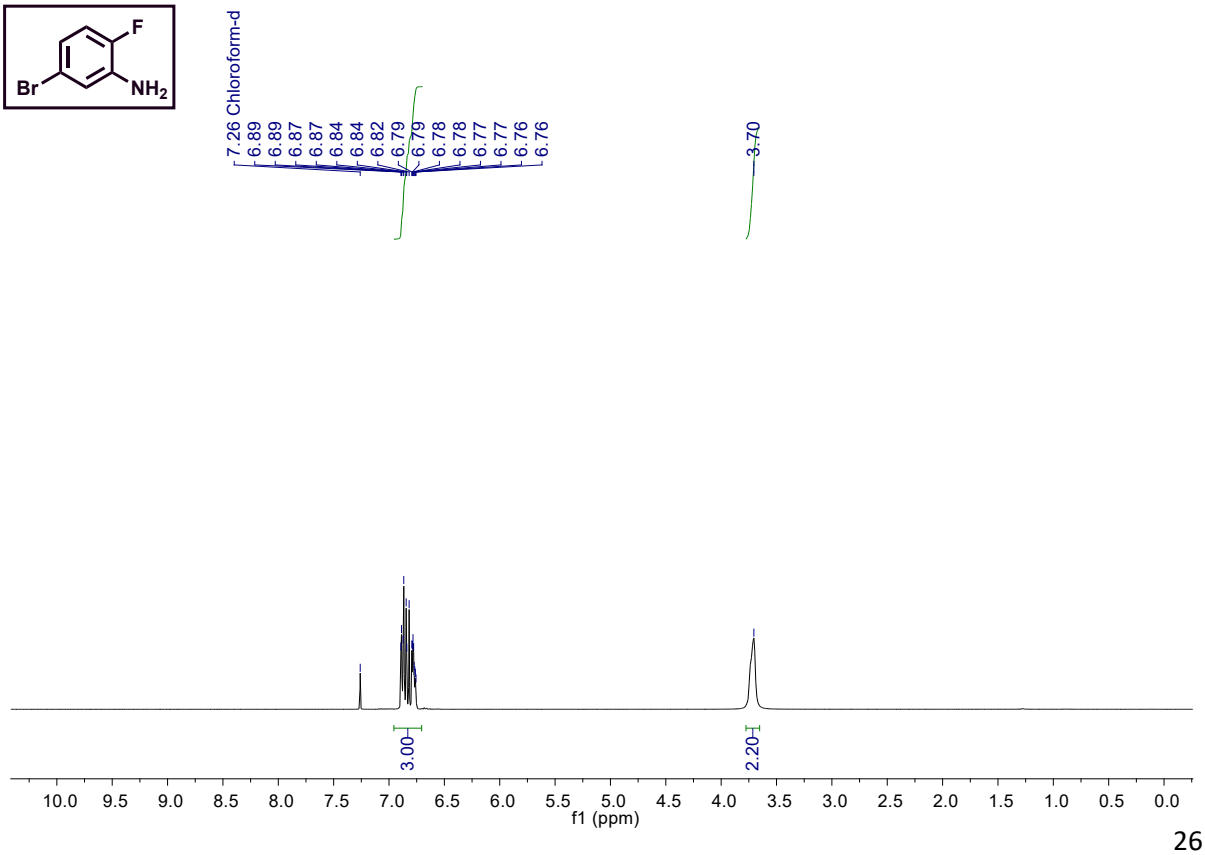

Figure S18: ^{13}C NMR spectrum of 5-Bromo-2-fluoro aniline (9).

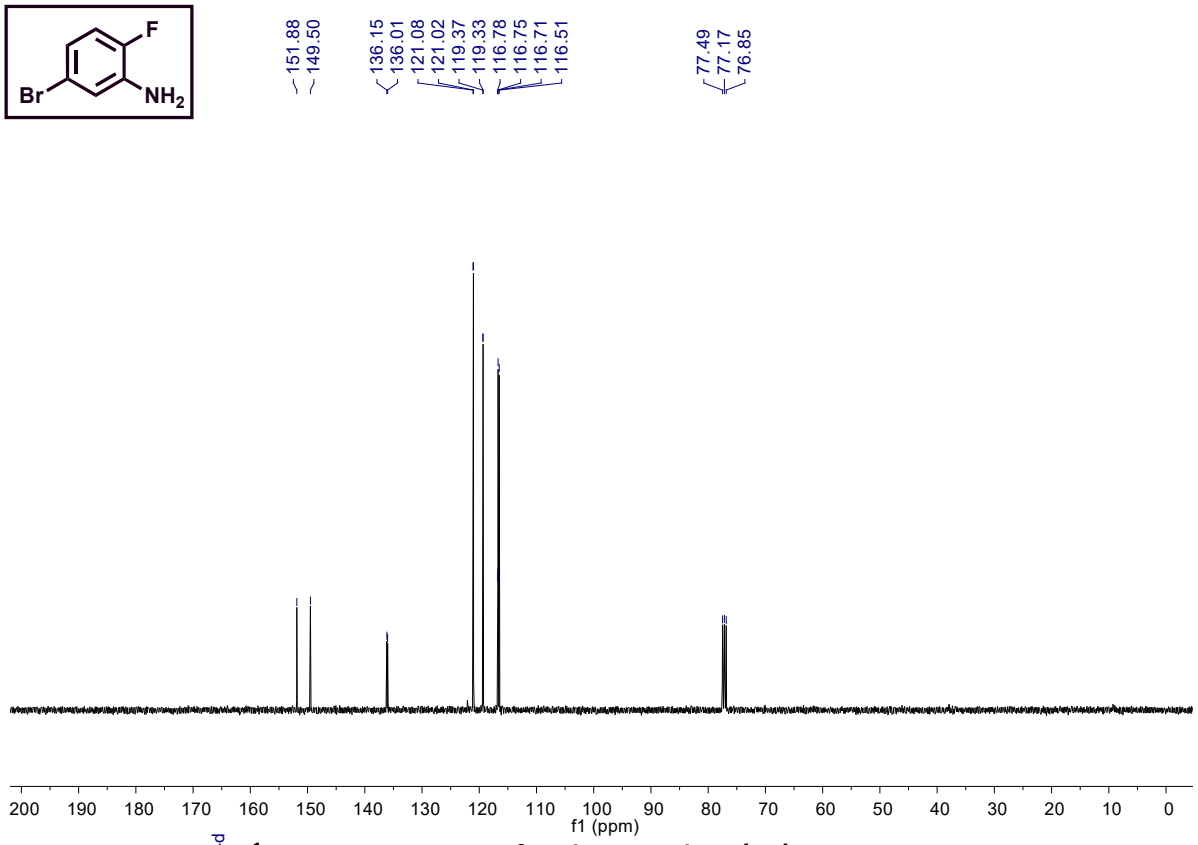

Figure S19: ^{1}H NMR spectrum of 4-Fluoroaniline (10).

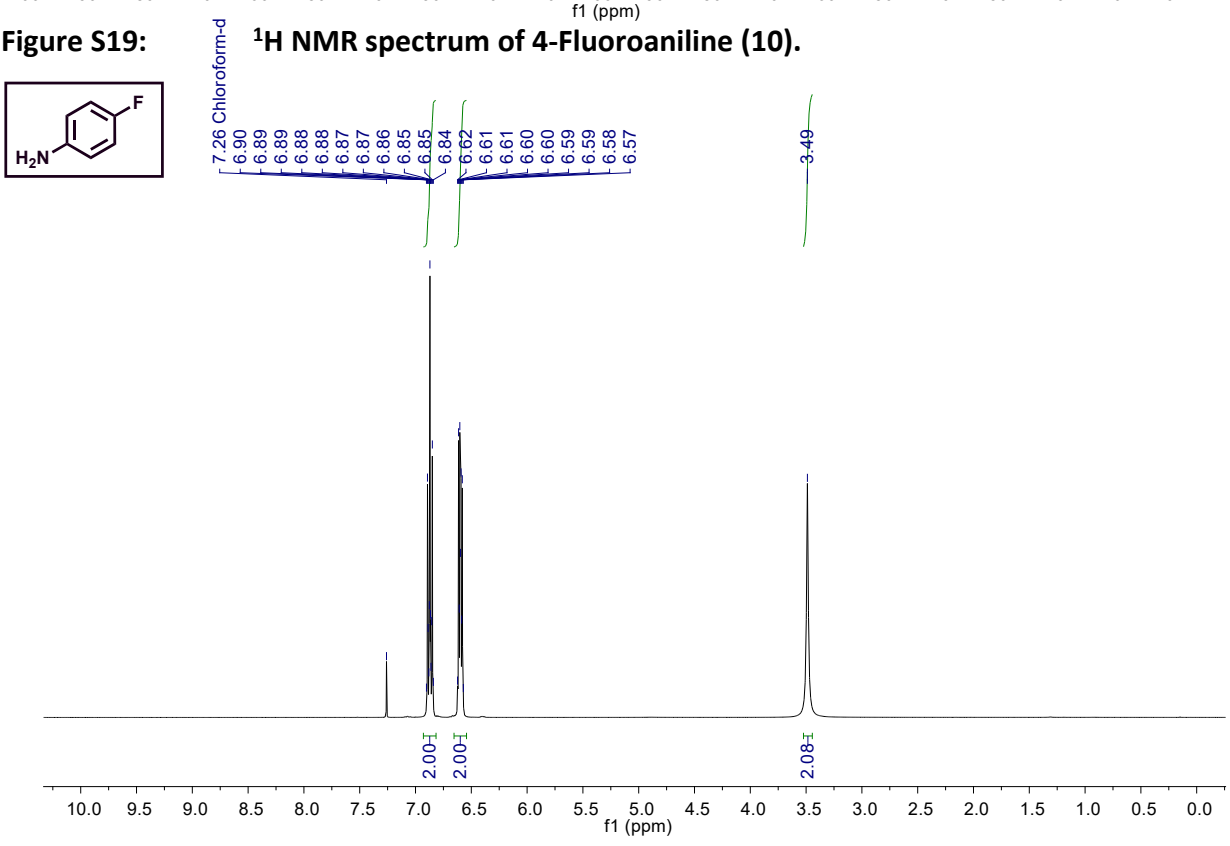

Figure S20: ^{13}C NMR spectrum of 4-Fluoroaniline (10).

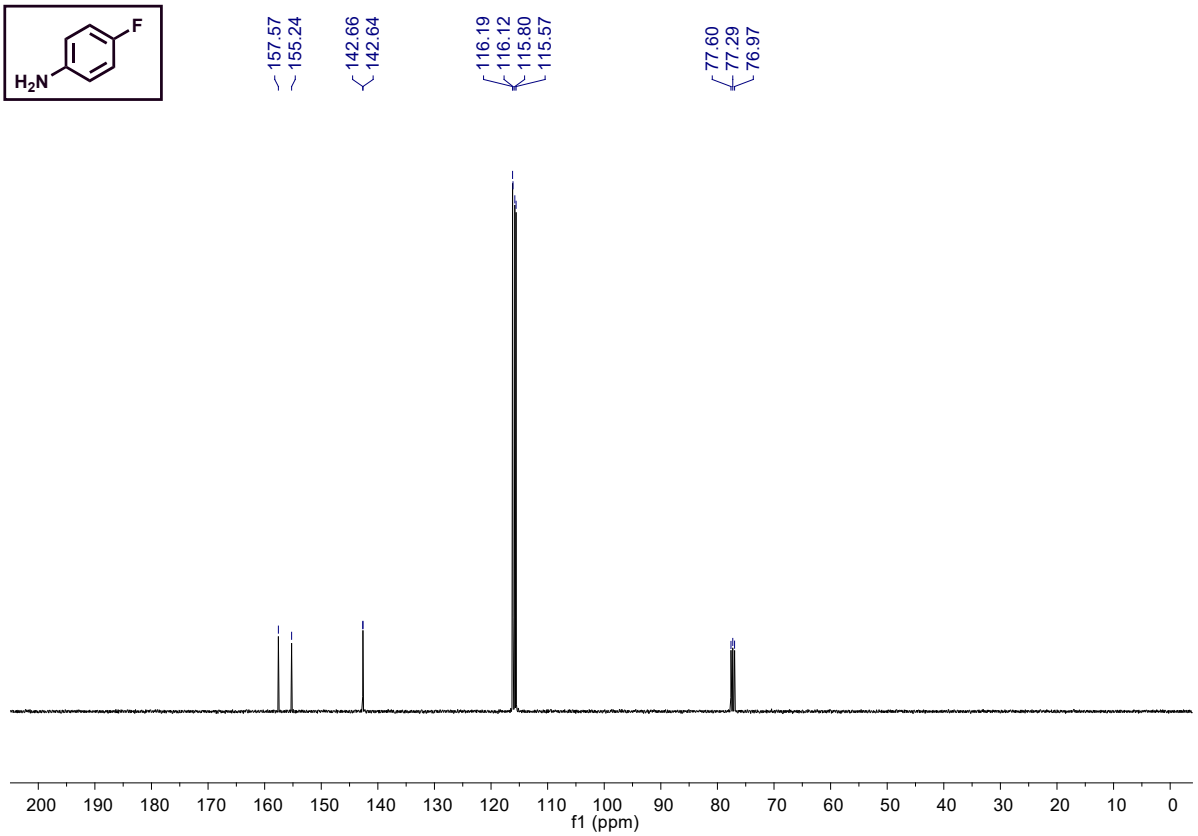

Figure S21: 1H NMR spectrum of 3-Fluoro-4-morpholinoaniline (11).

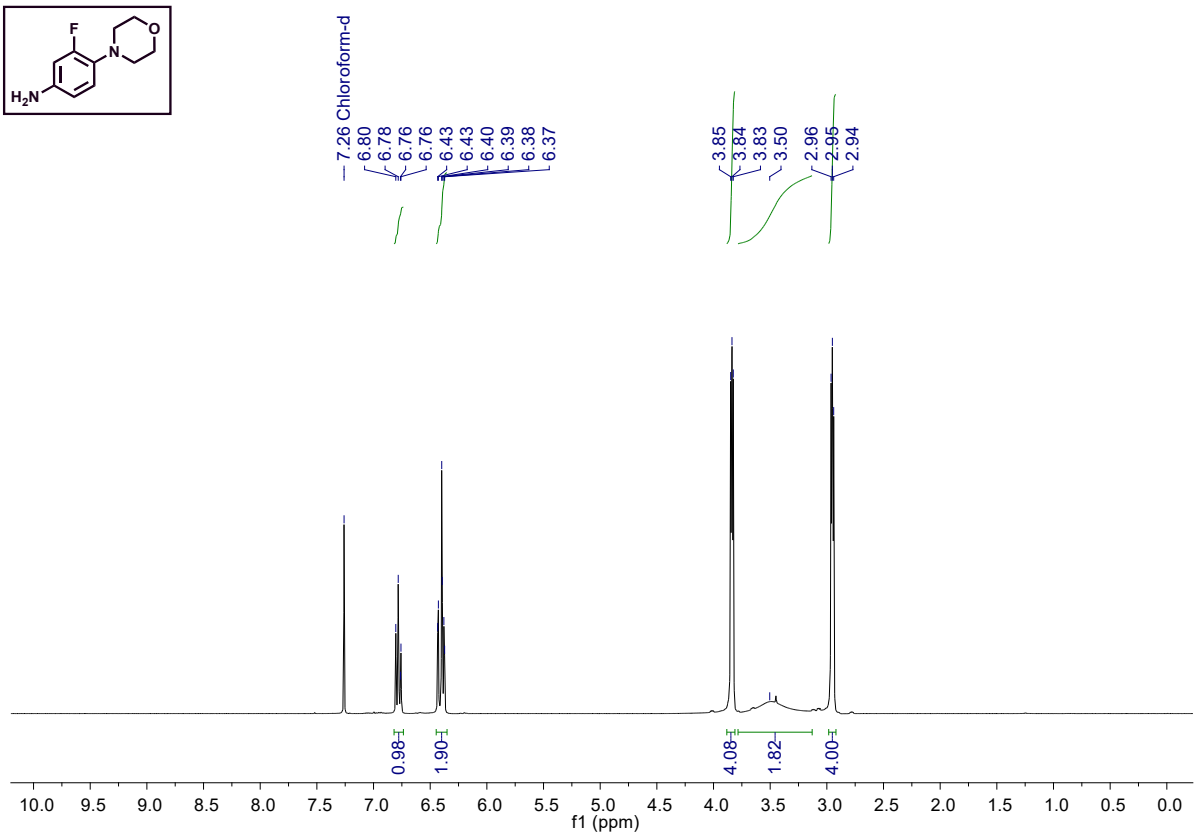

Figure S22: ^{13}C NMR spectrum of 3-Fluoro-4-morpholinoaniline (11).

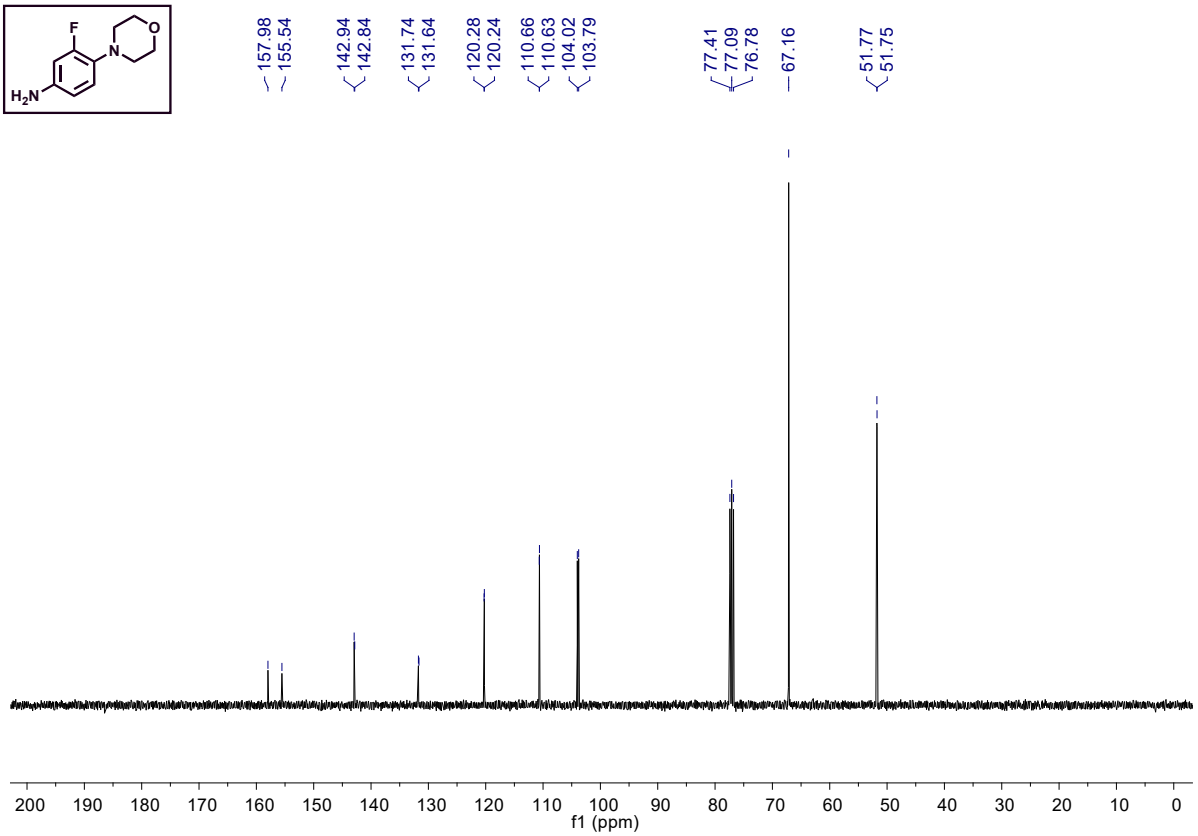

Figure S23: ^{1}H NMR spectrum of 3,4-Difluoroaniline (12).

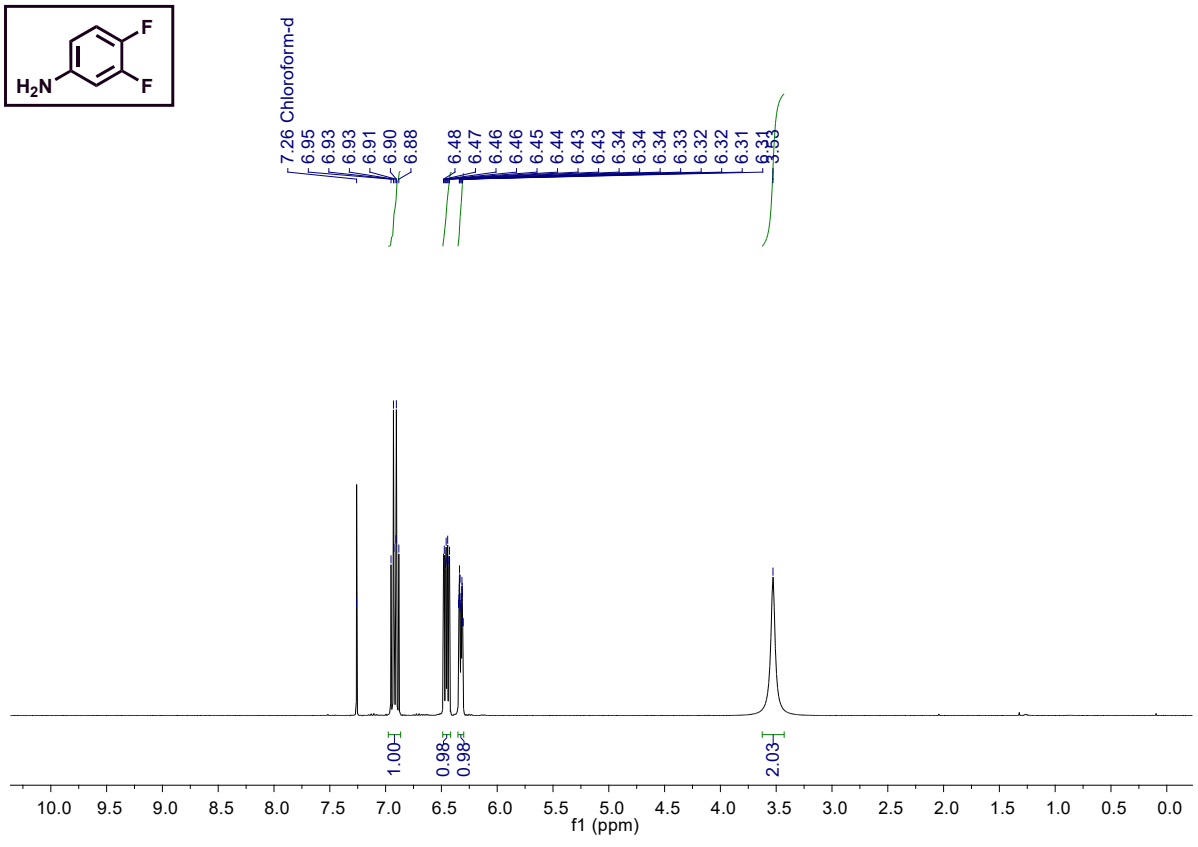

Figure S24: ^{13}C NMR spectrum of 3,4-Difluoroaniline (12).

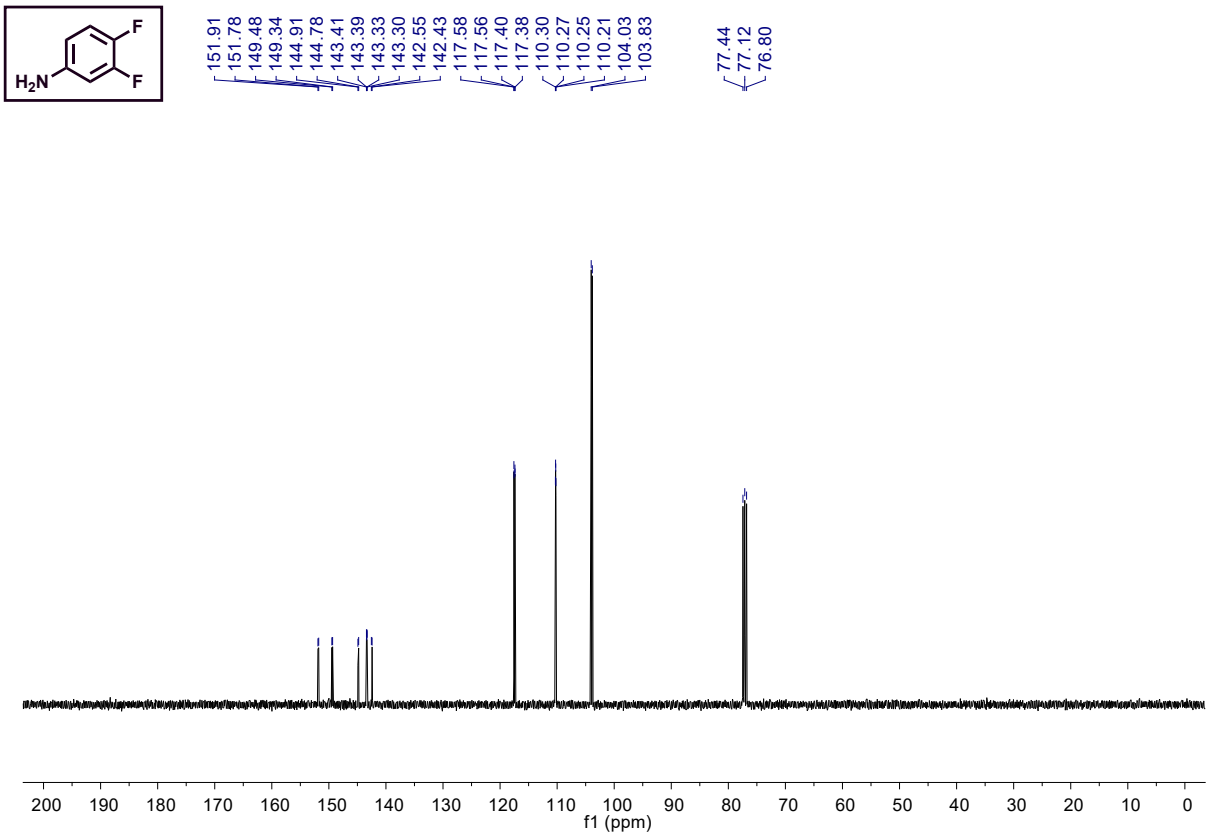

Figure S25: ^{1}H NMR spectrum of 2,3,4,5,6-Pentafluoroaniline (13)

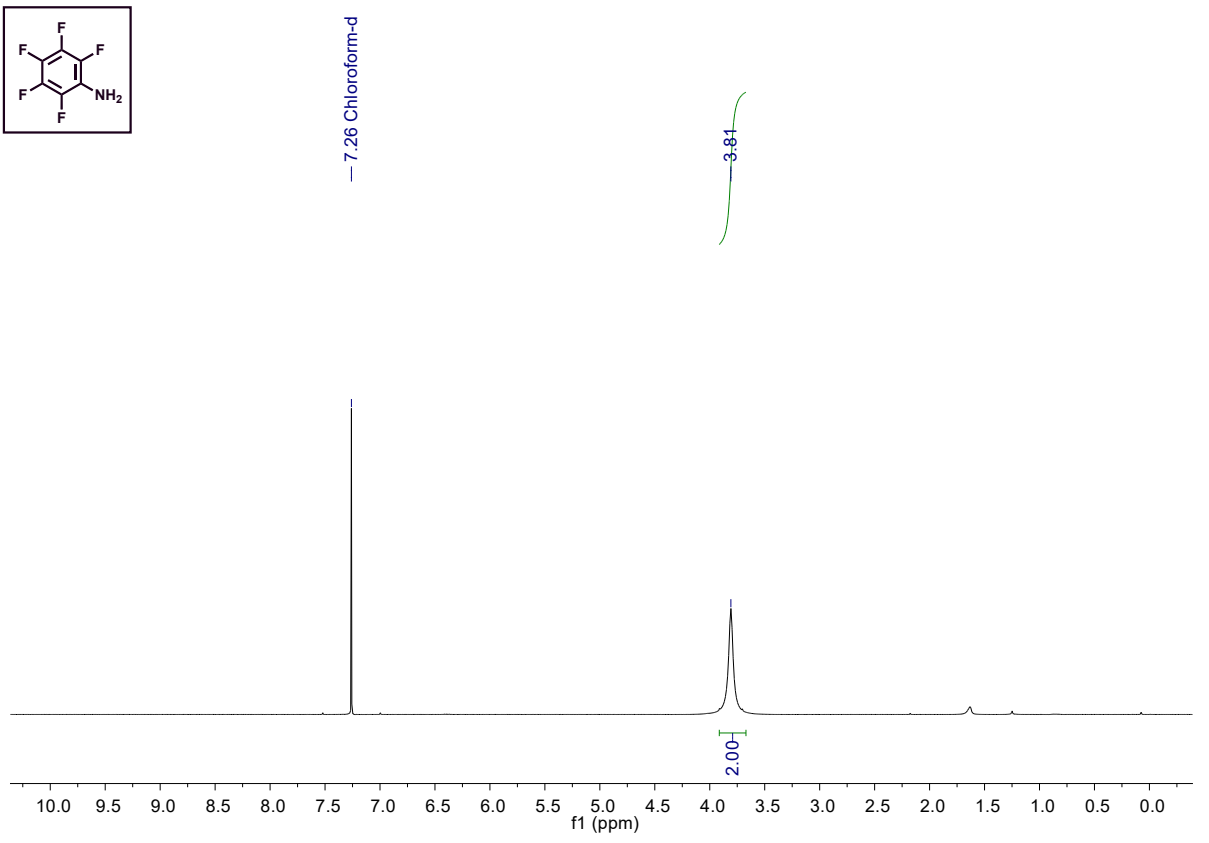

Figure S26: ^{13}C NMR spectrum of 2,3,4,5,6-Pentafluoroaniline (13).

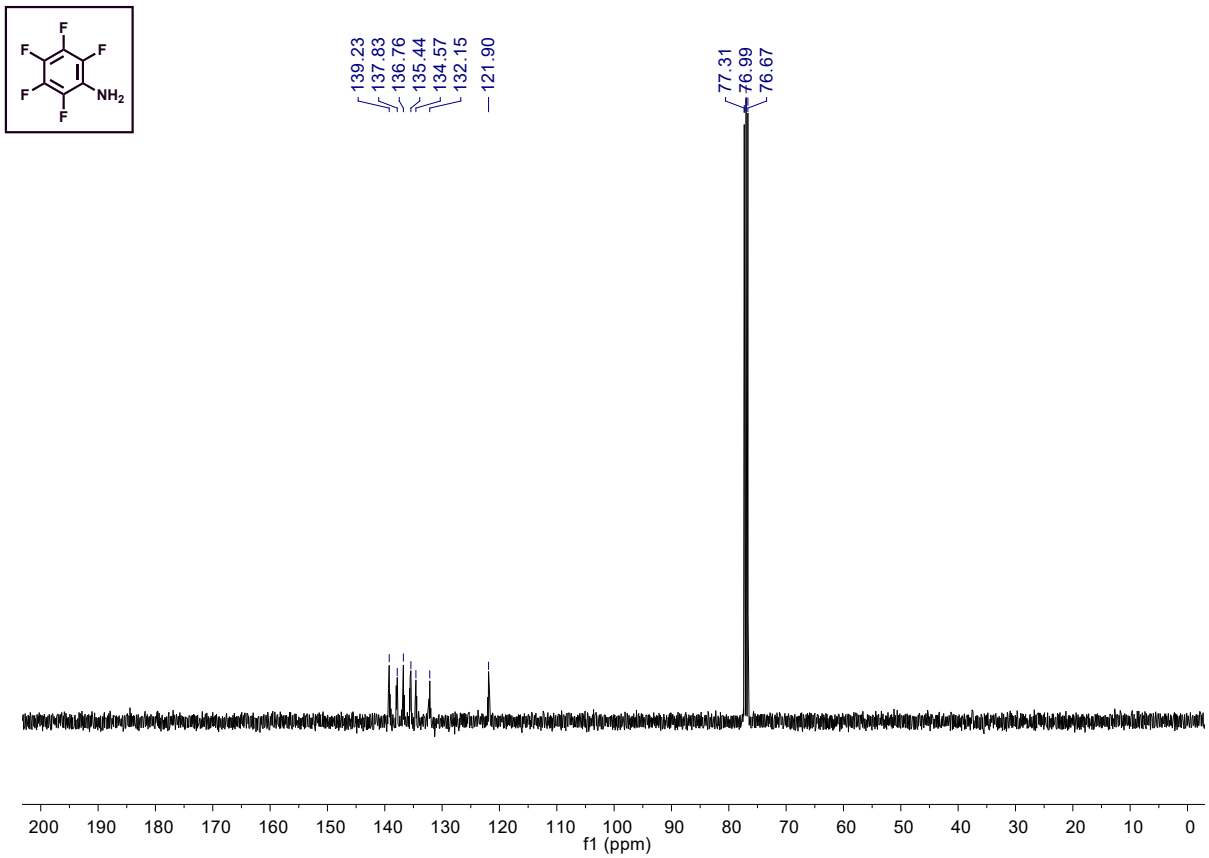

Figure S27: ^{1}H NMR spectrum of 4-Iodoaniline (14)

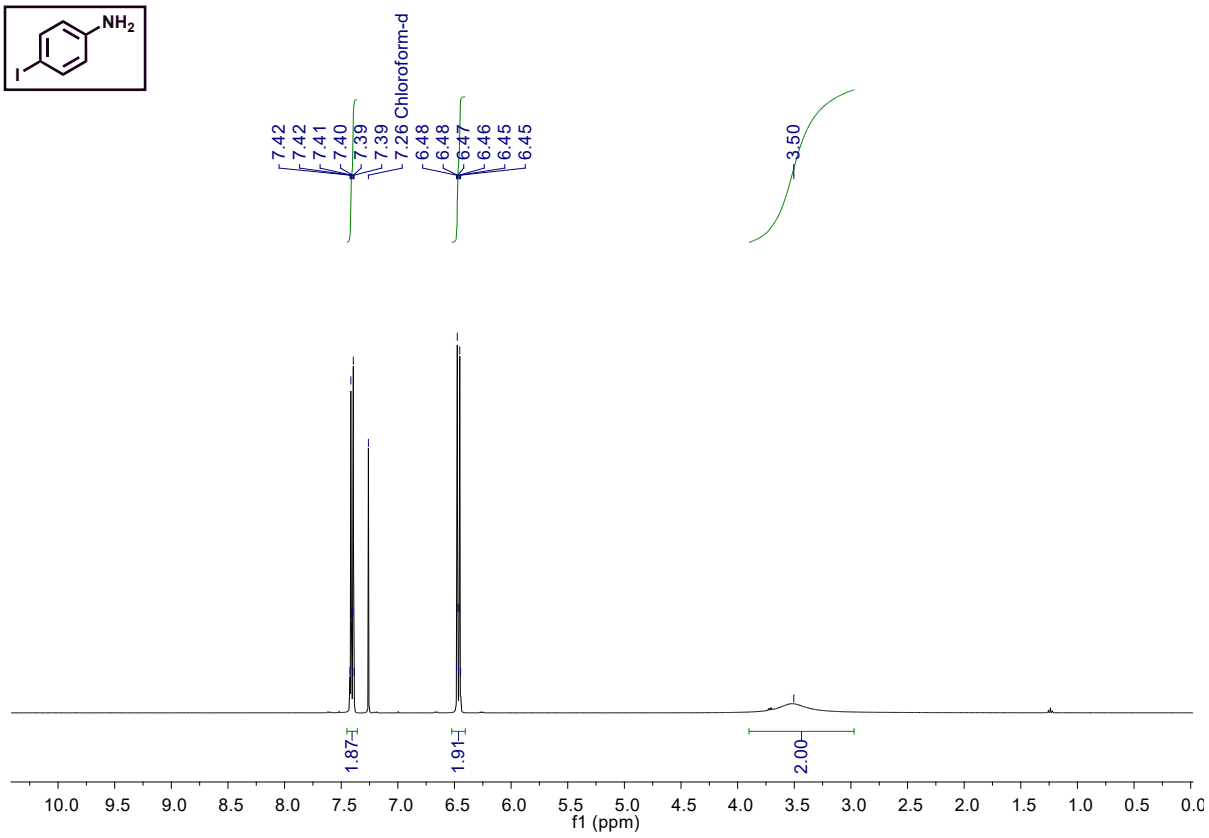

Figure S28: ^{13}C NMR spectrum of 4-Iodoaniline (14)

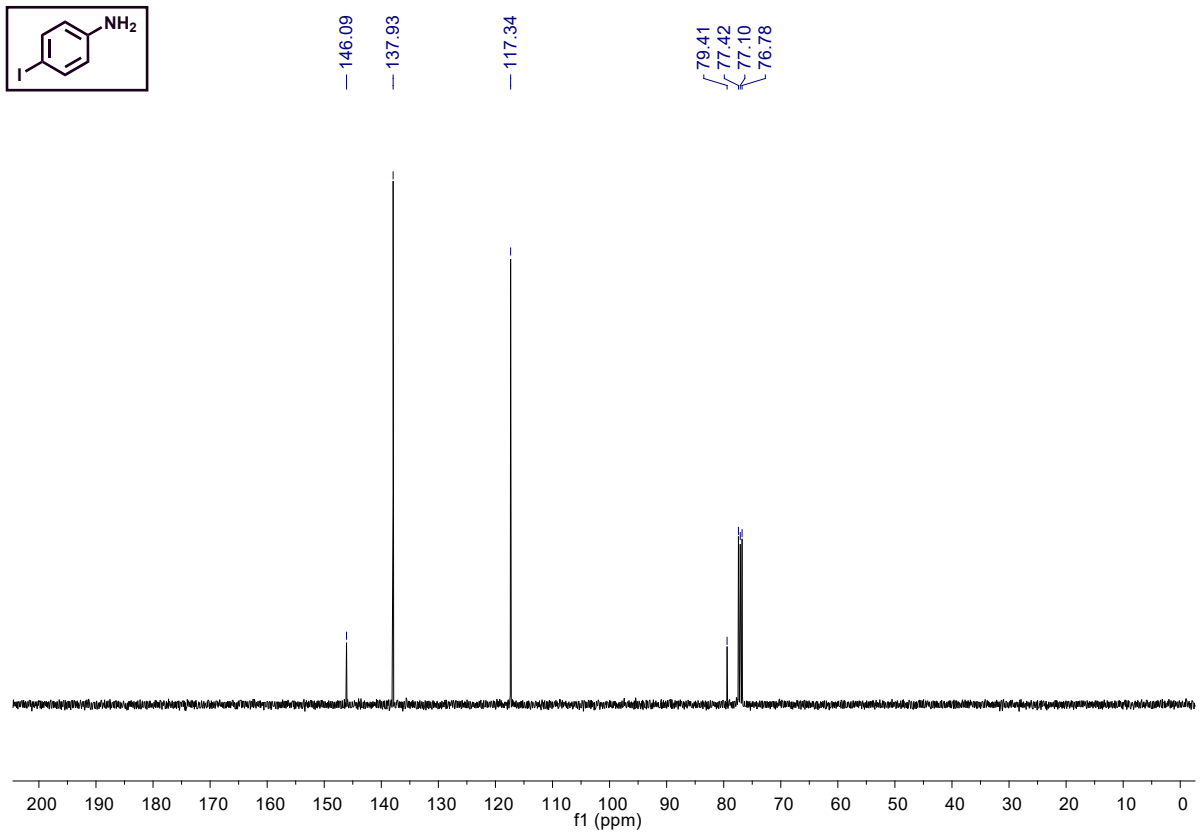

Figure S29: ^{1}H NMR spectrum of 4-Aminothiophenol (15)

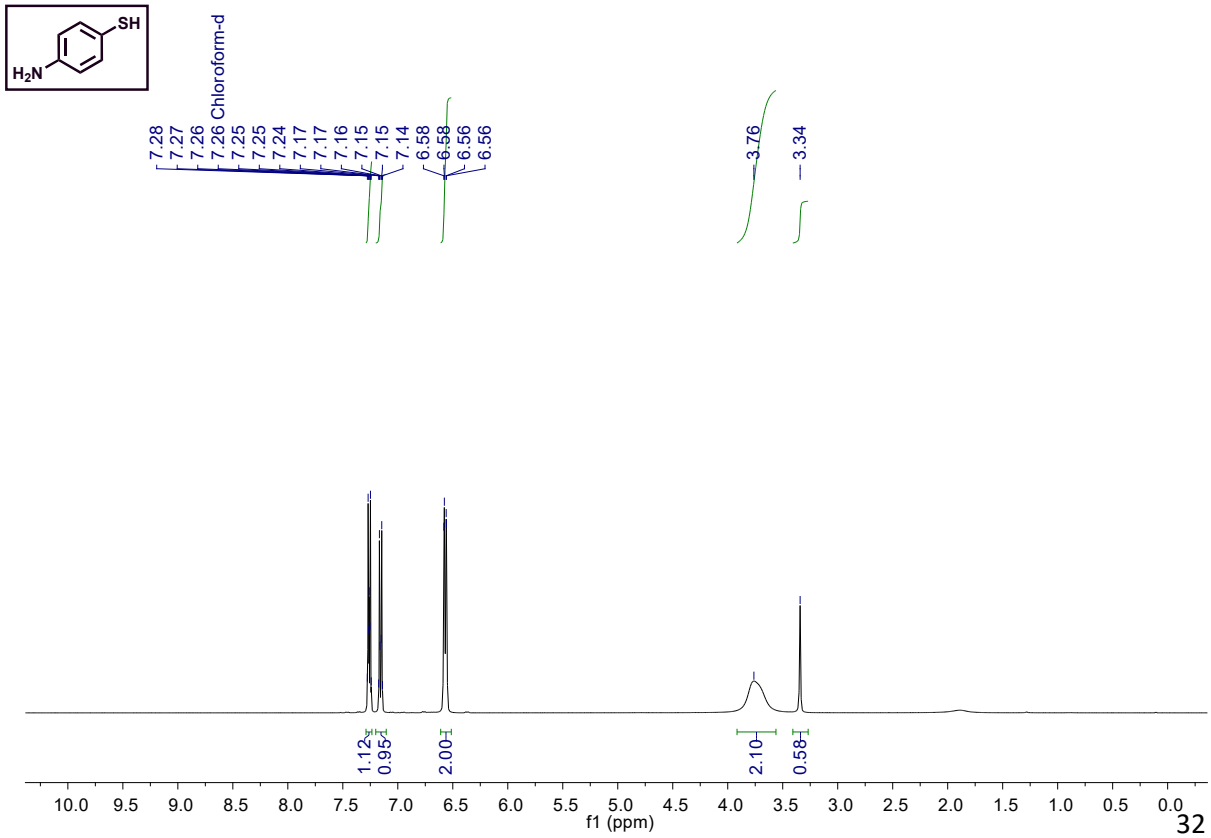

Figure S30: ^{13}C NMR spectrum of 4-Aminothiophenol (15).

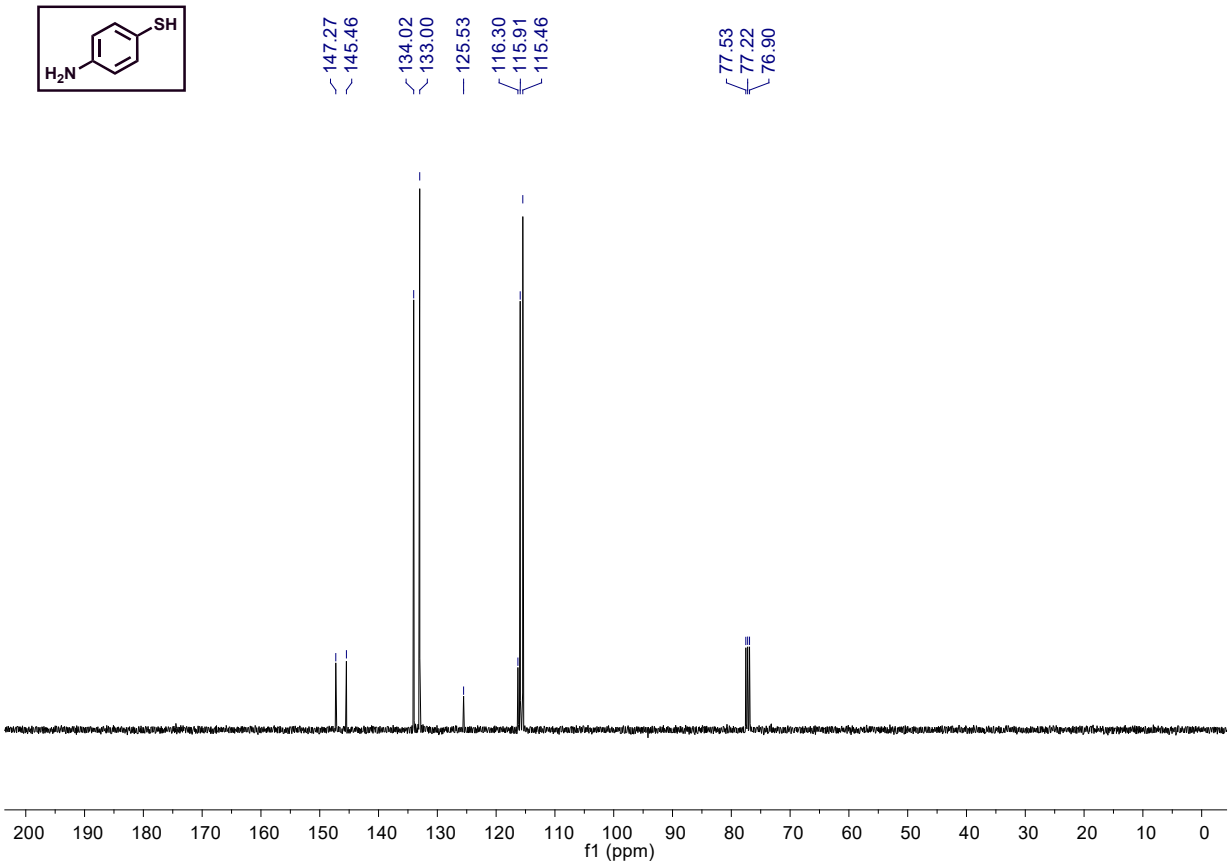

Figure S31: ^{1}H NMR spectrum of 4-(Methylthio)aniline (16)

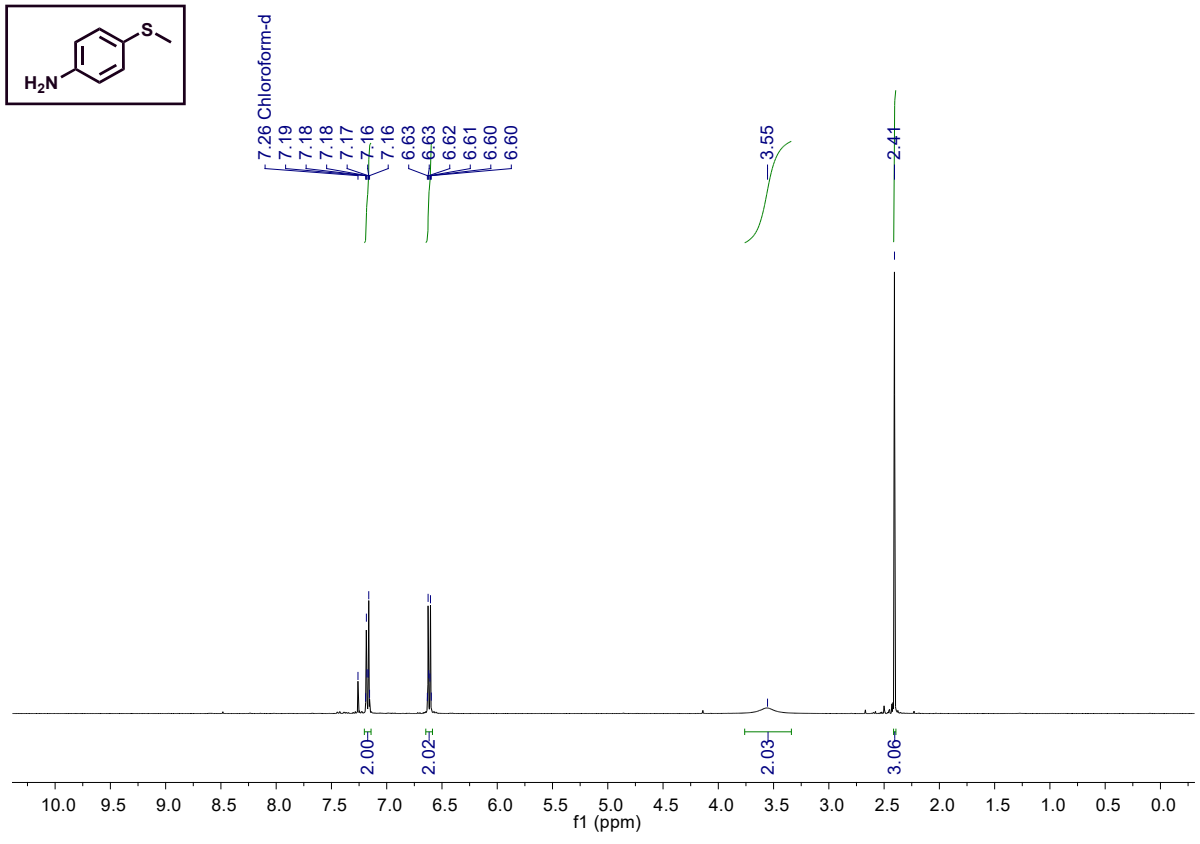

Figure S32: ^{13}C NMR spectrum of 4-(Methylthio)aniline (16)

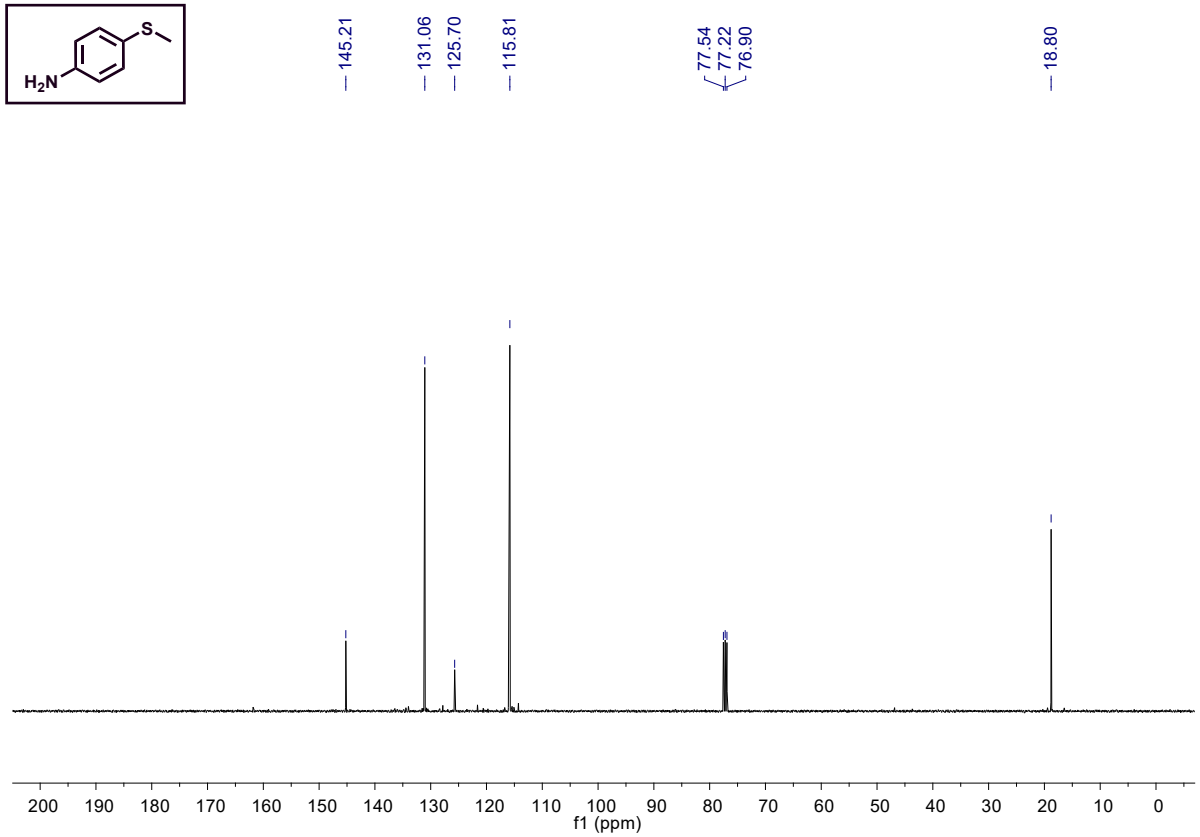

Figure S33: ^{1}H NMR spectrum of 4-(Phenylthio)aniline (17)

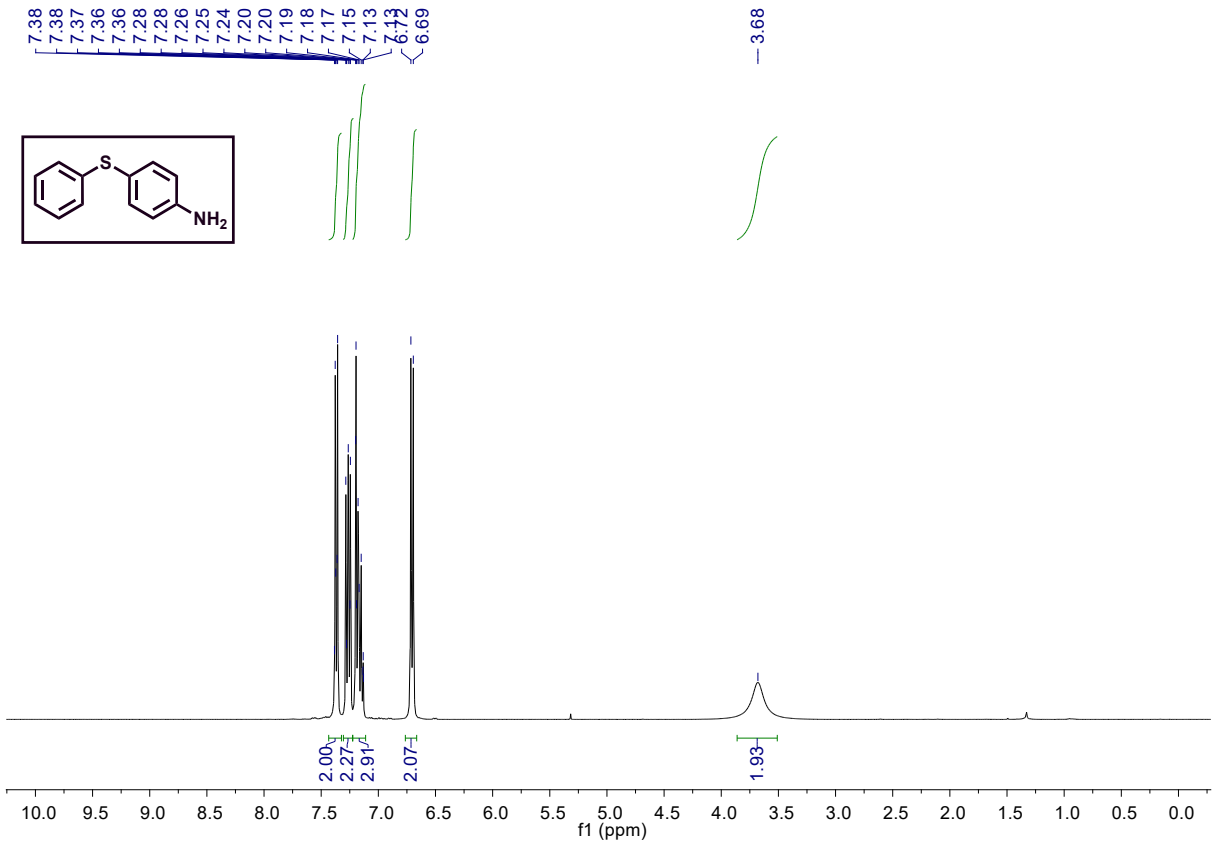

Figure S34: ^{13}C NMR spectrum of 4-(Phenylthio)aniline (17)

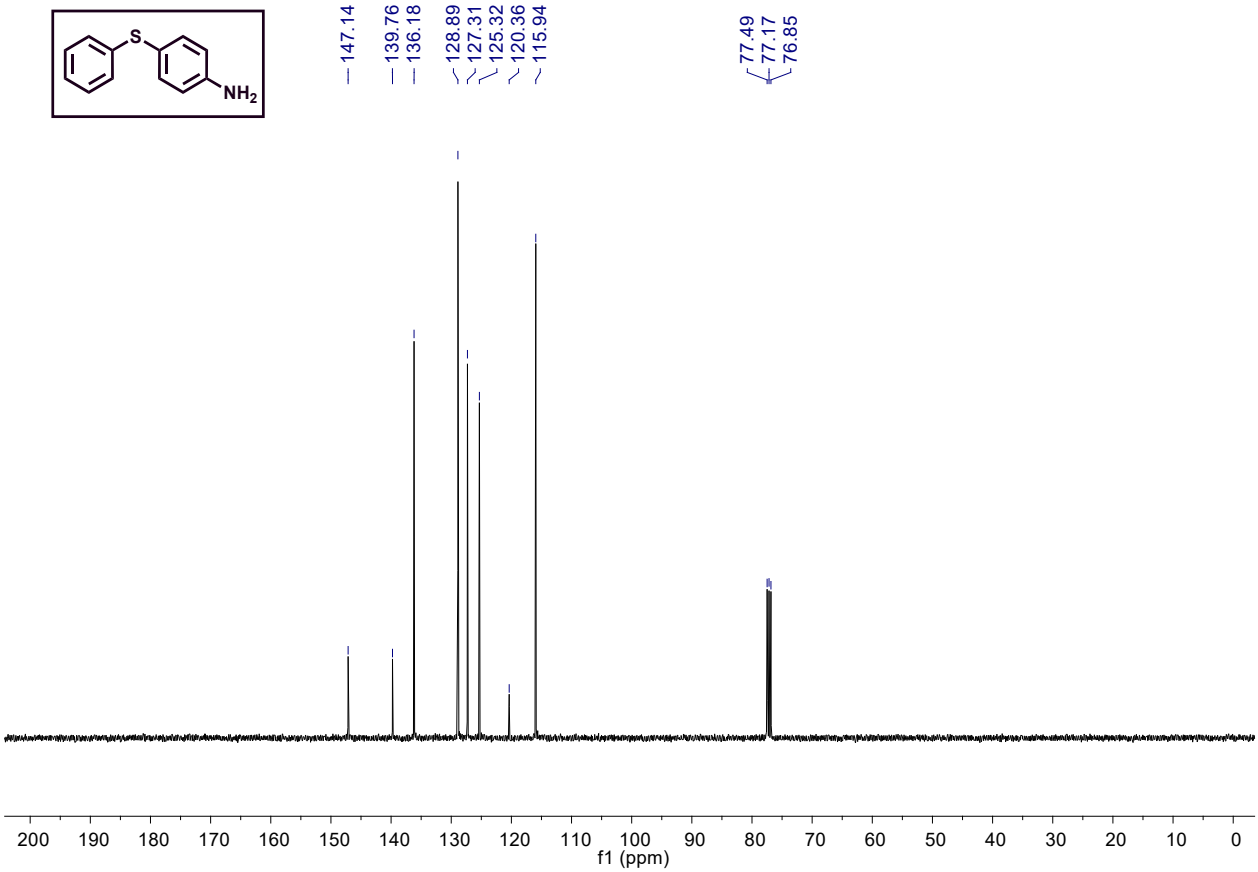

Figure S35: ^{1}H NMR spectrum of 4-(Phenylthio)aniline (18)

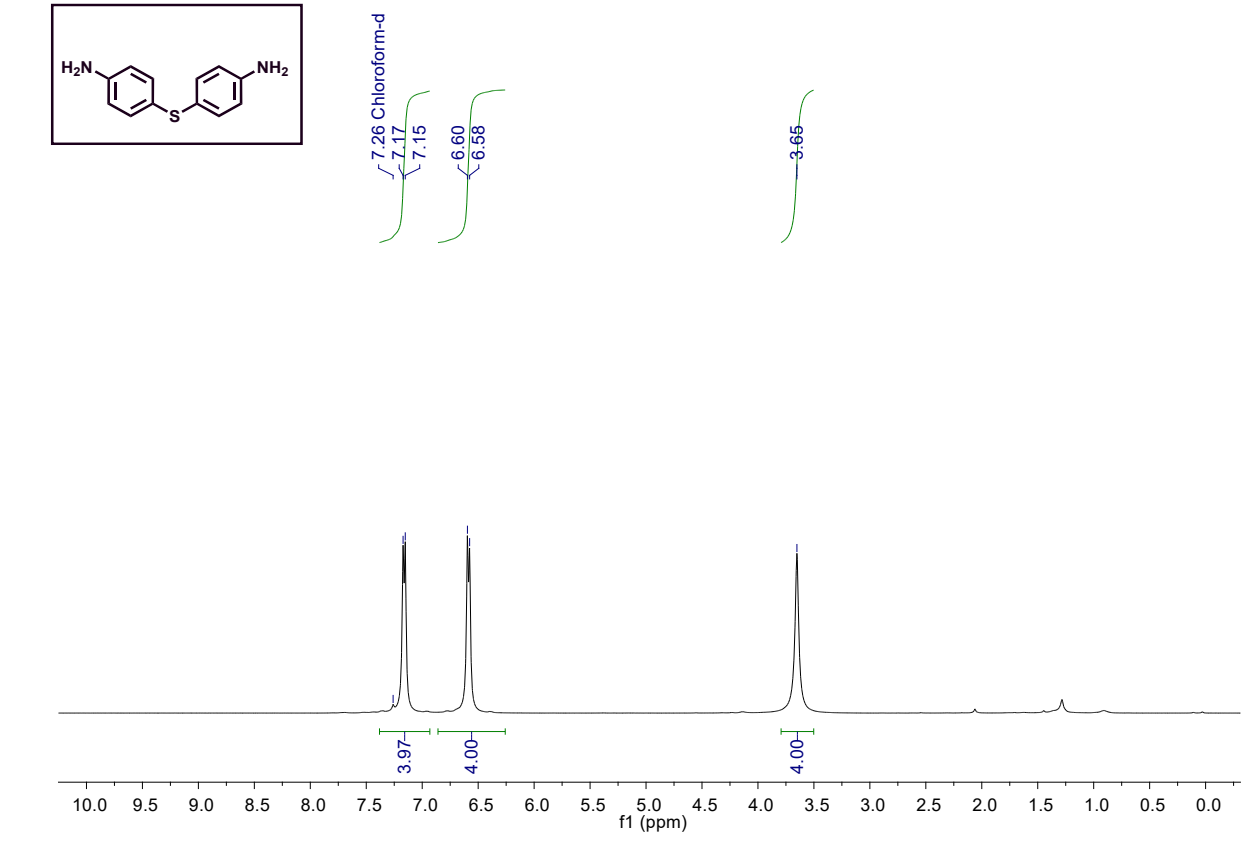

Figure S36: ^{13}C NMR spectrum of 4-(Phenylthio)aniline (18)

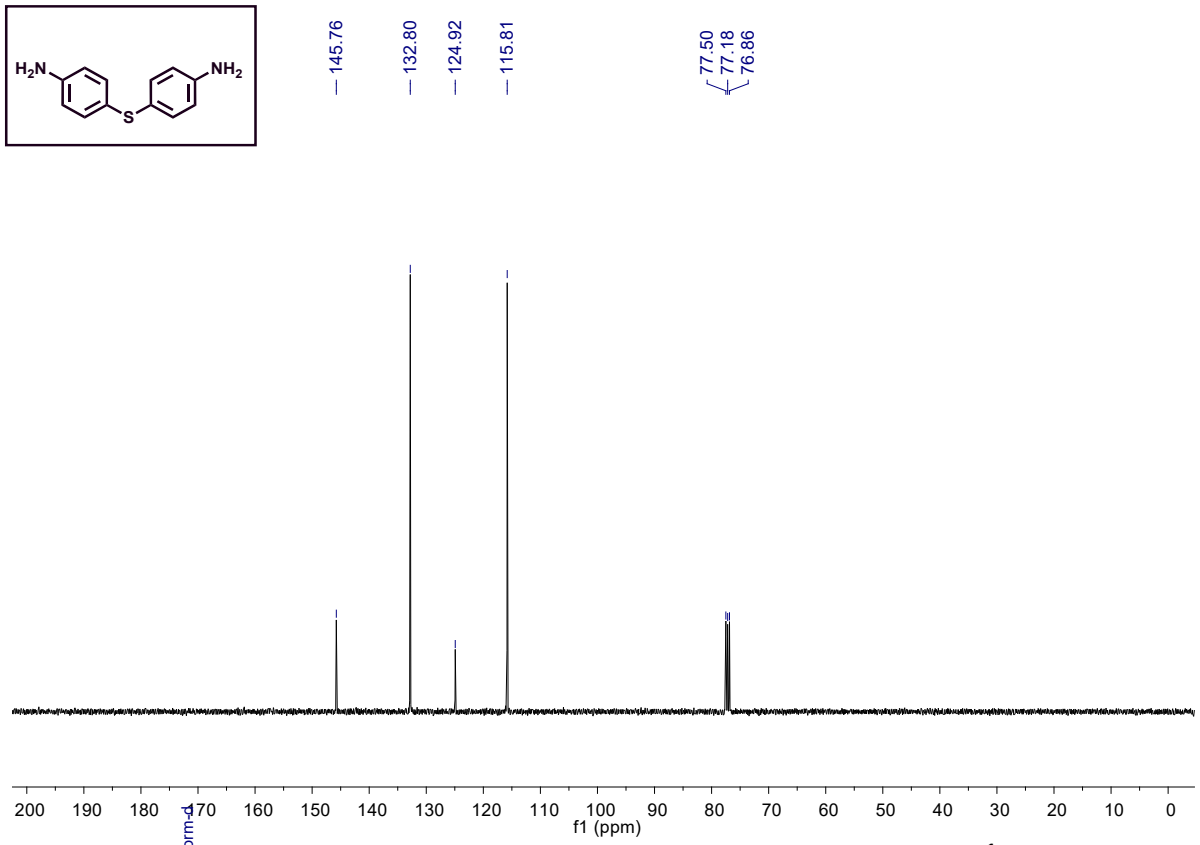

Figure S37: ^{1}H NMR spectrum of 2-((2-Aminophenyl)amino)-5-methylthiophene-3-carbonitrile (19)

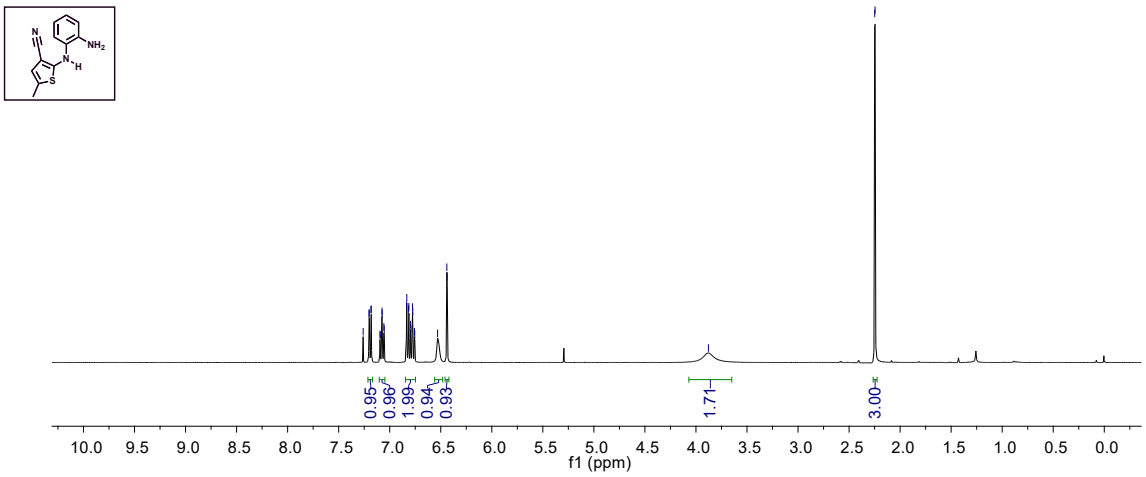

Figure S38: ^{13}C NMR spectrum of 2-((2-Aminophenyl)amino)-5-methylthiophene-3-carbonitrile (19)

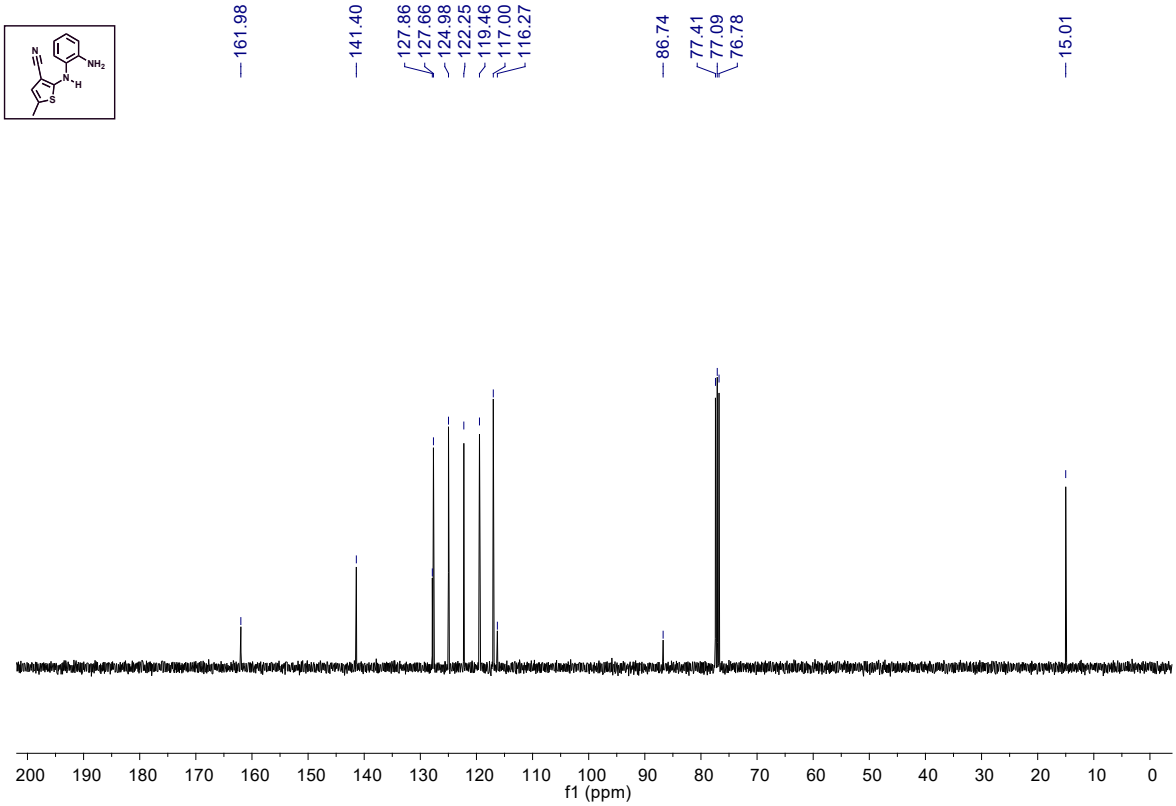

Figure S39: ^{1}H NMR spectrum of 4,6-Dichloro-2-(propylthio)pyrimidin-5-amine (20)

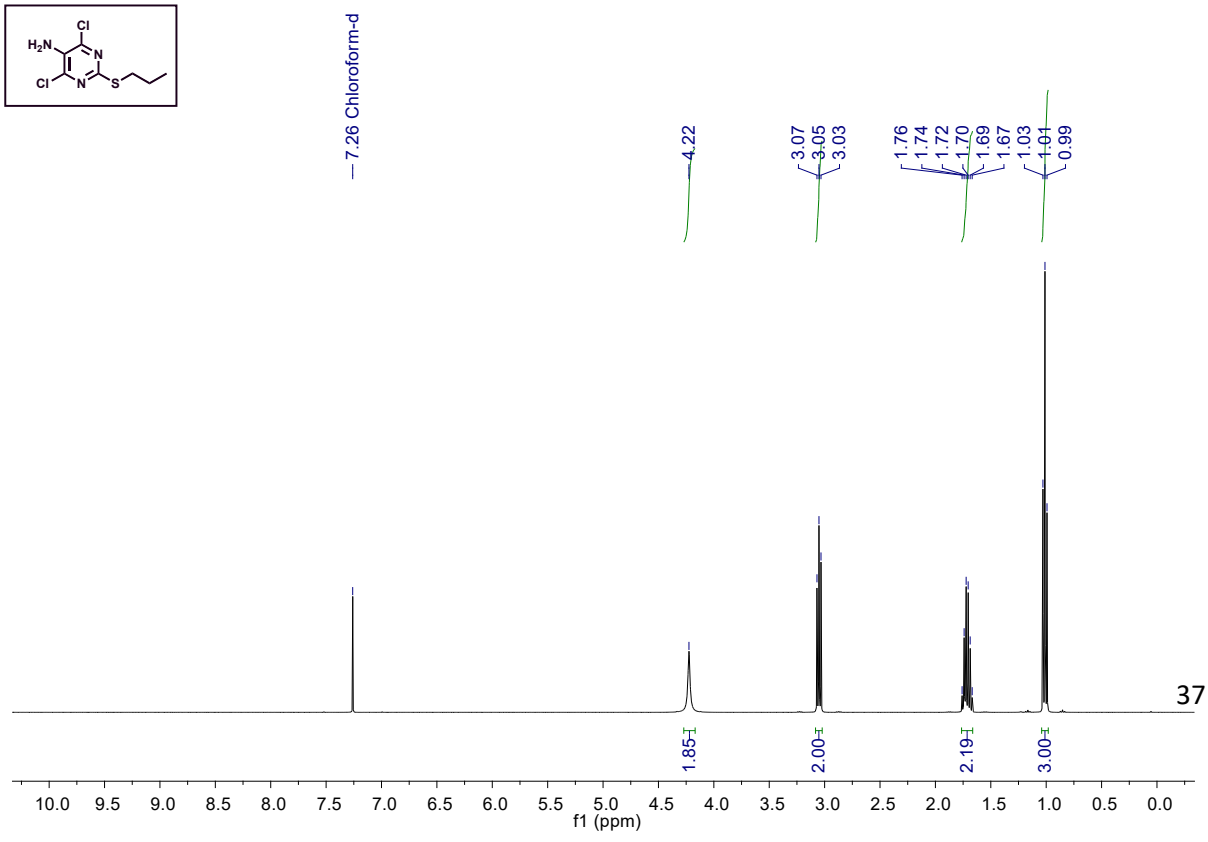

Figure S40: ^{13}C NMR spectrum of 4,6-Dichloro-2-(propylthio)pyrimidin-5-amine (20)

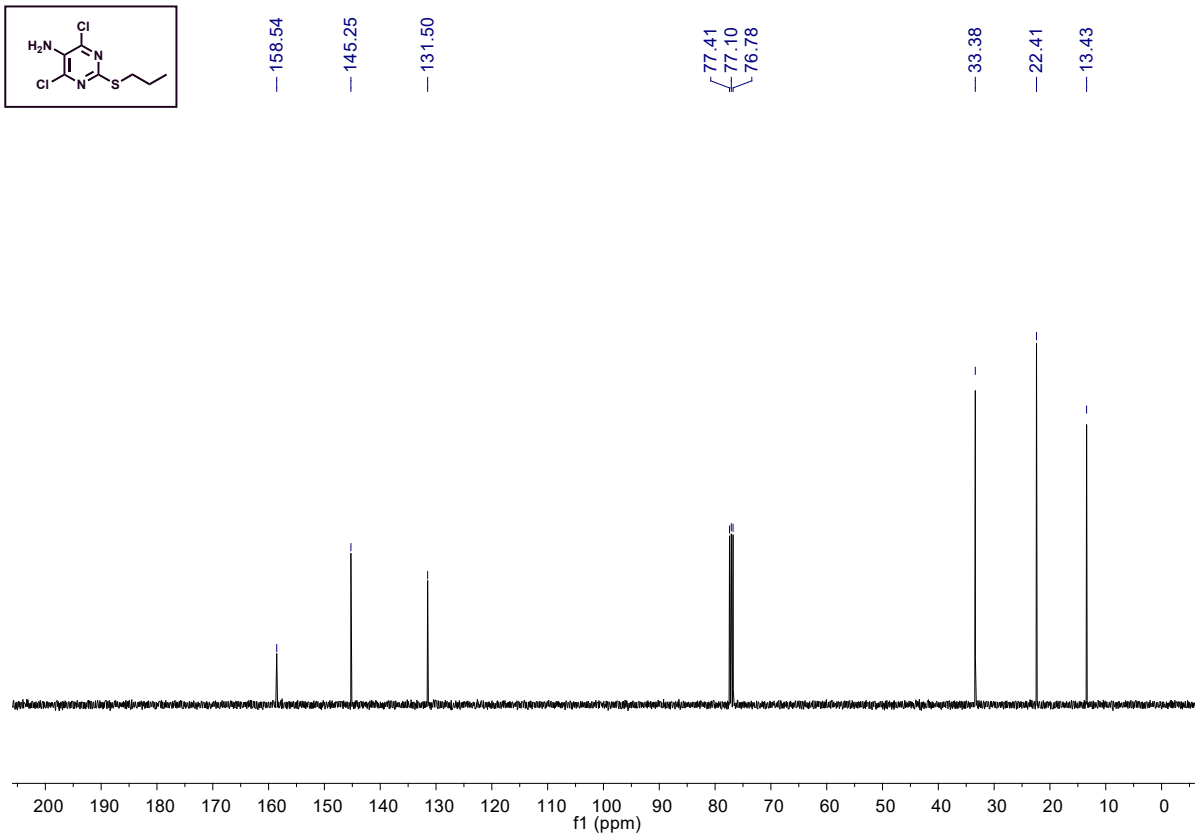

Figure S41: ^{1}H NMR spectrum of 5-Aminobenzothiophene (21)

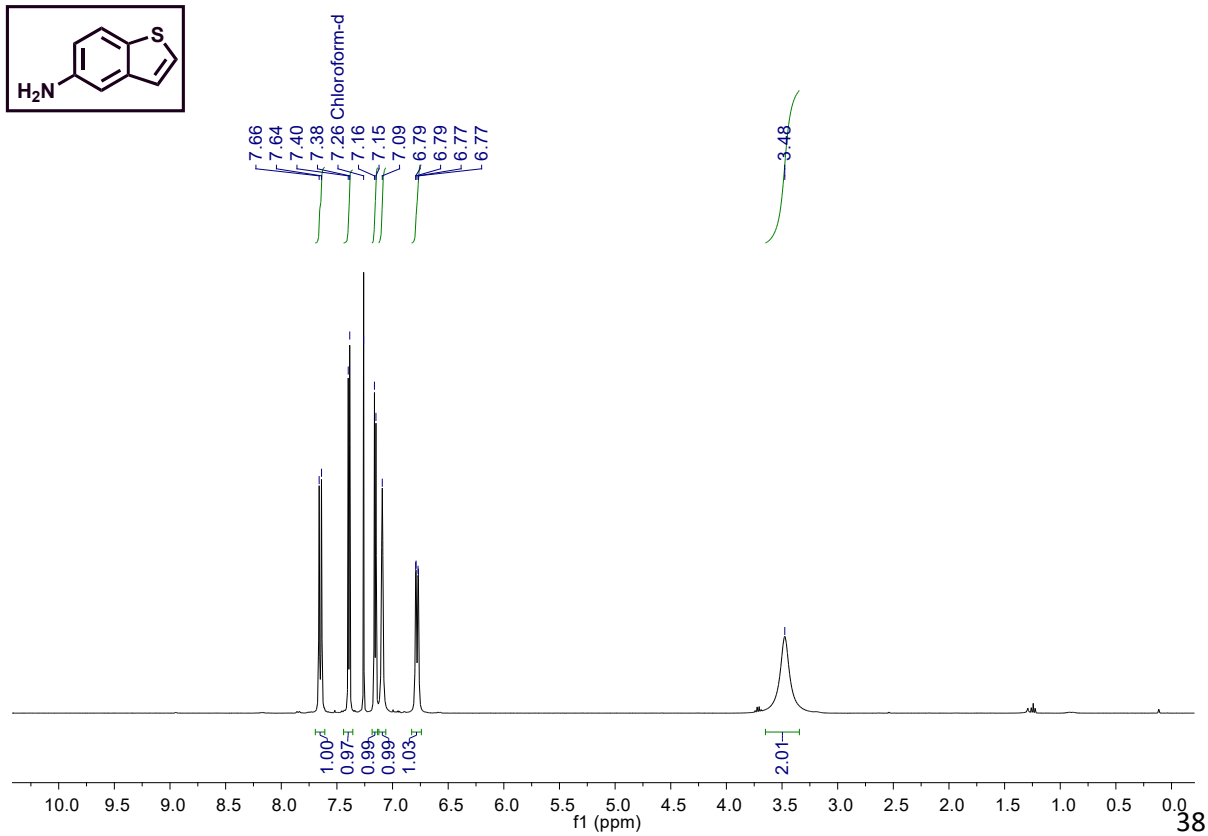

Figure S42: ^{13}C NMR spectrum of 5-Aminobenzothiophene (21)

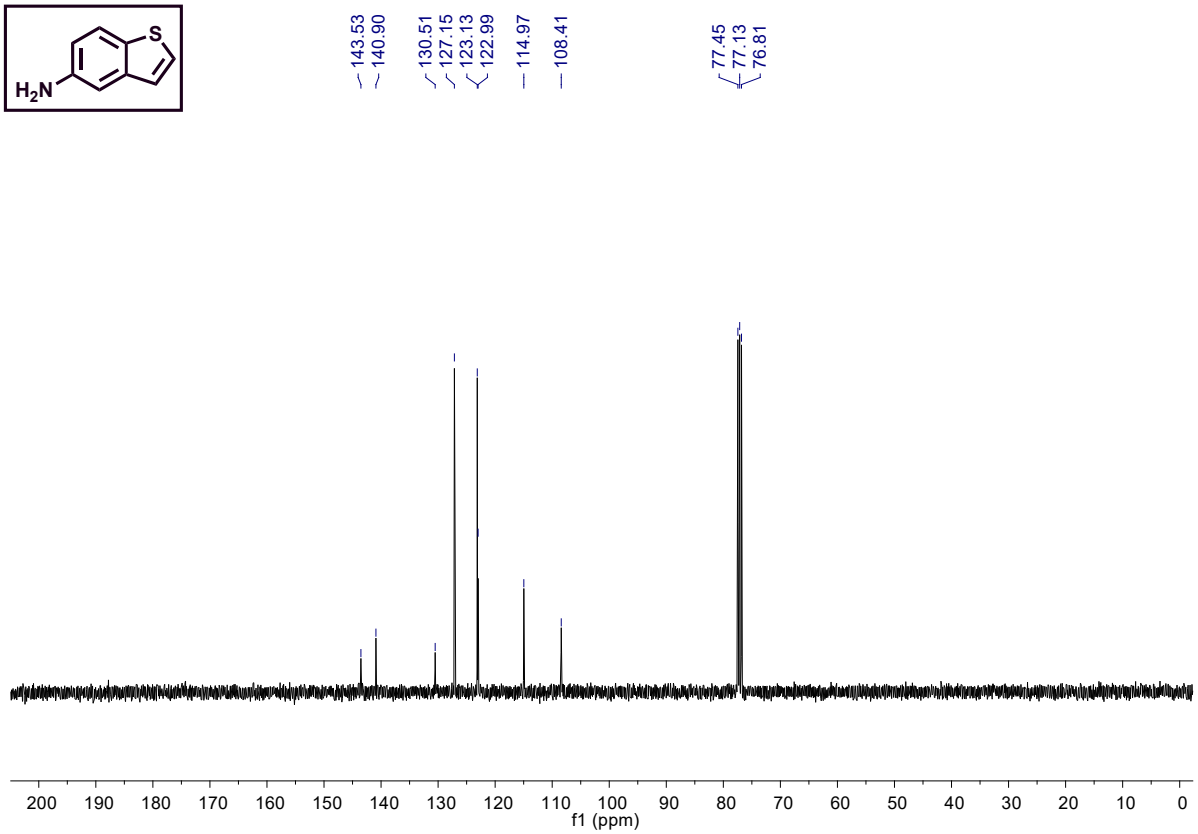

Figure S43: ^{1}H NMR spectrum of 1-(4-Aminophenyl)ethan-1-one (22)

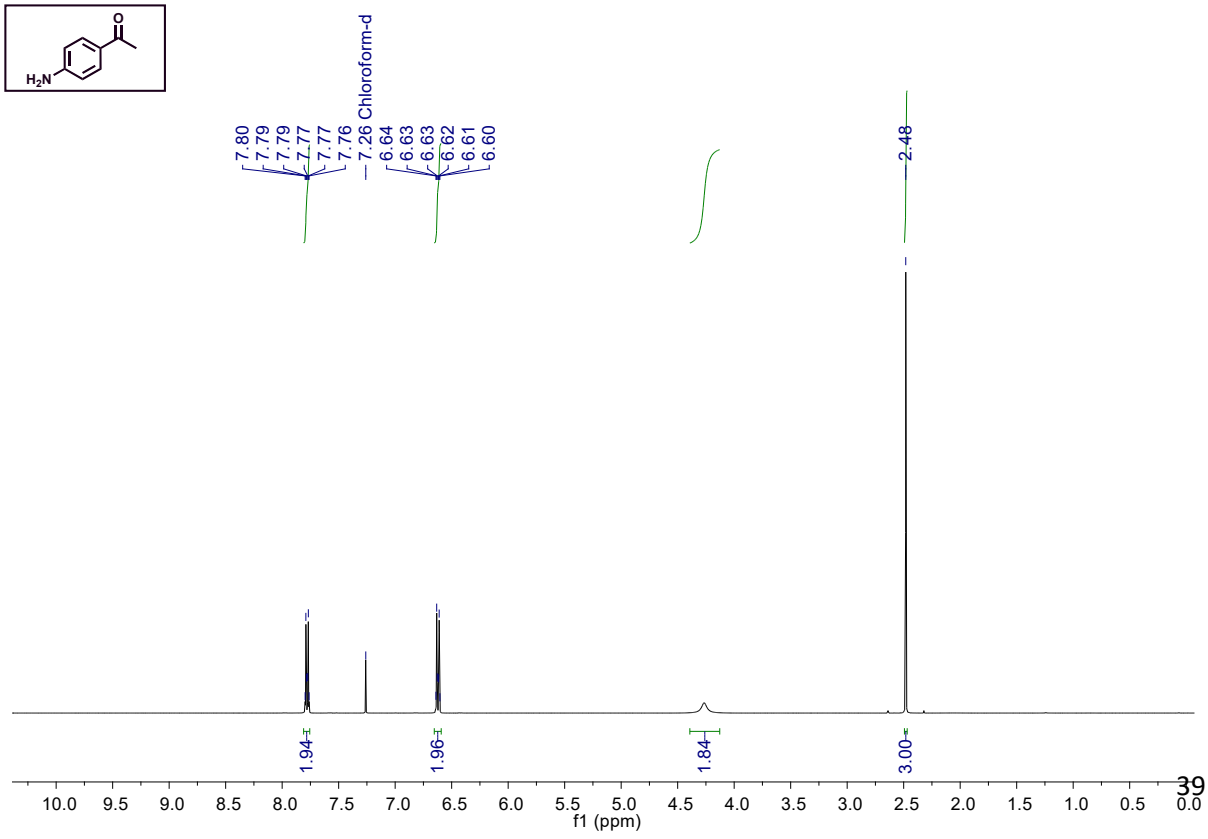

Figure S44: ^{13}C NMR spectrum of 1-(4-Aminophenyl)ethan-1-one (22)

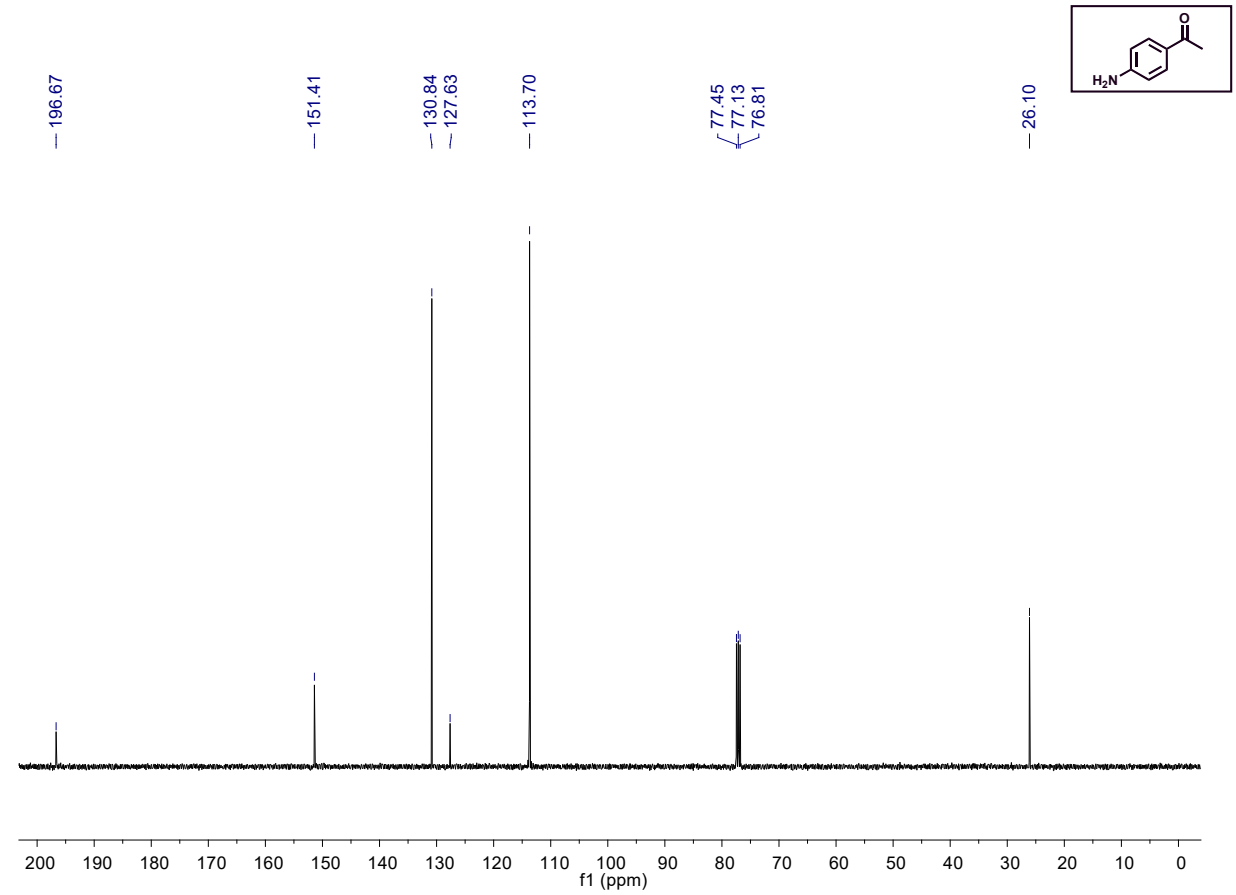

Figure S45: ^{1}H NMR spectrum of 4-Amino benzoic acid (23)

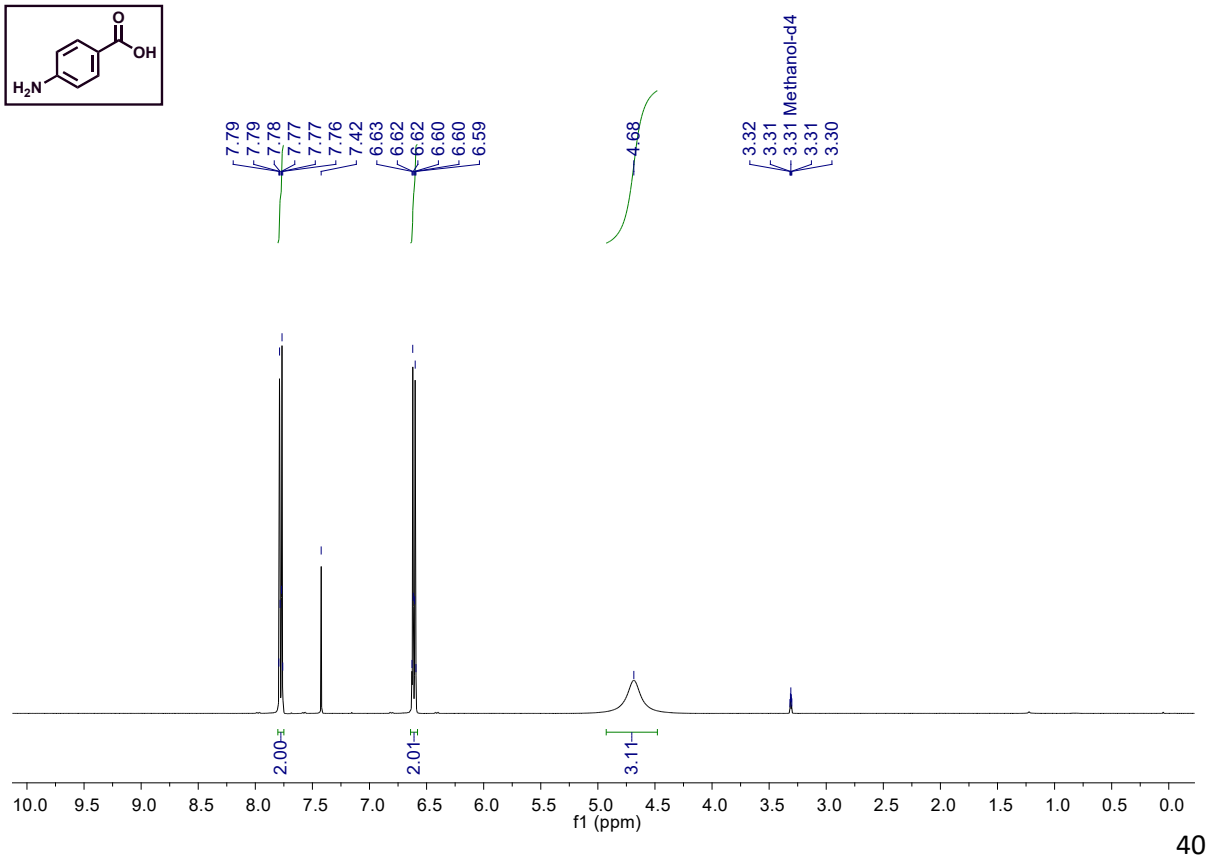

Figure S46: $^{13}C\{1H\}$ NMR spectrum of 4-Amino benzoic acid (23)

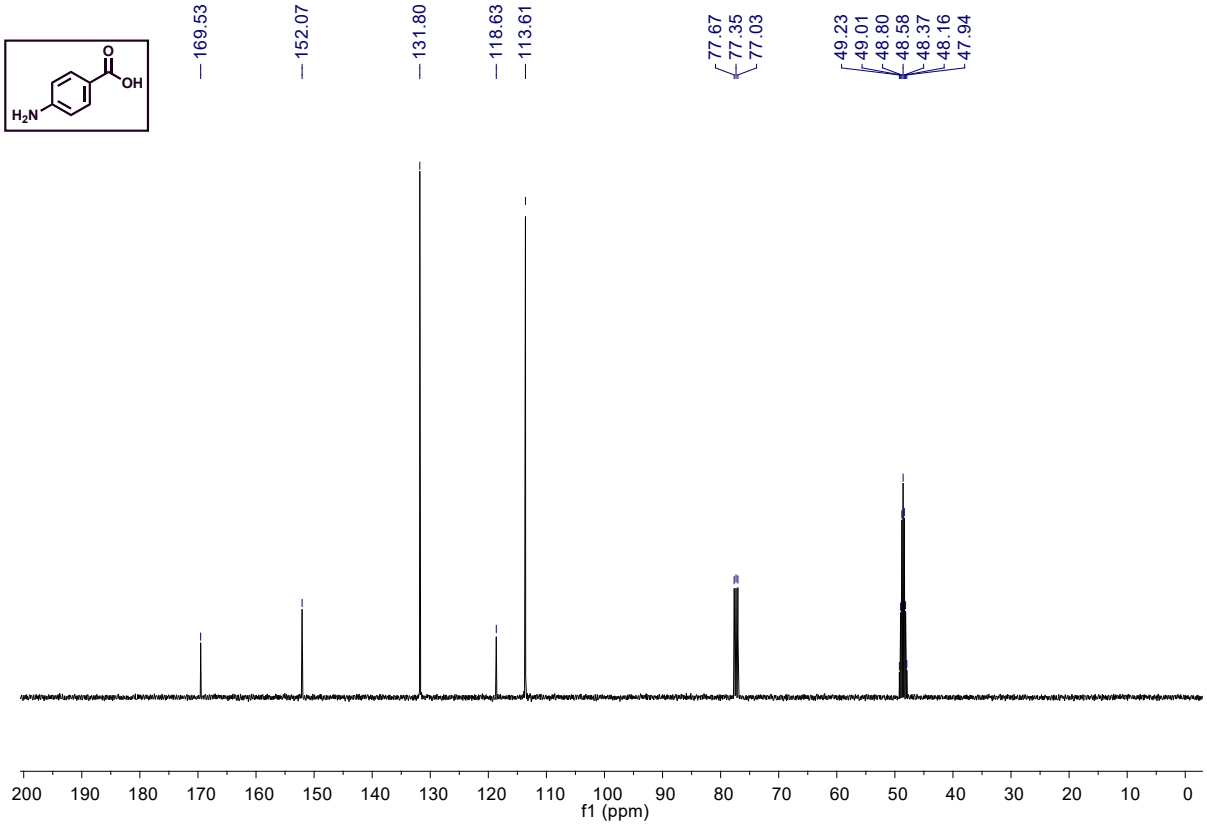

Figure S47: ^{1}H NMR spectrum of 4-Aminobenzamide (24)

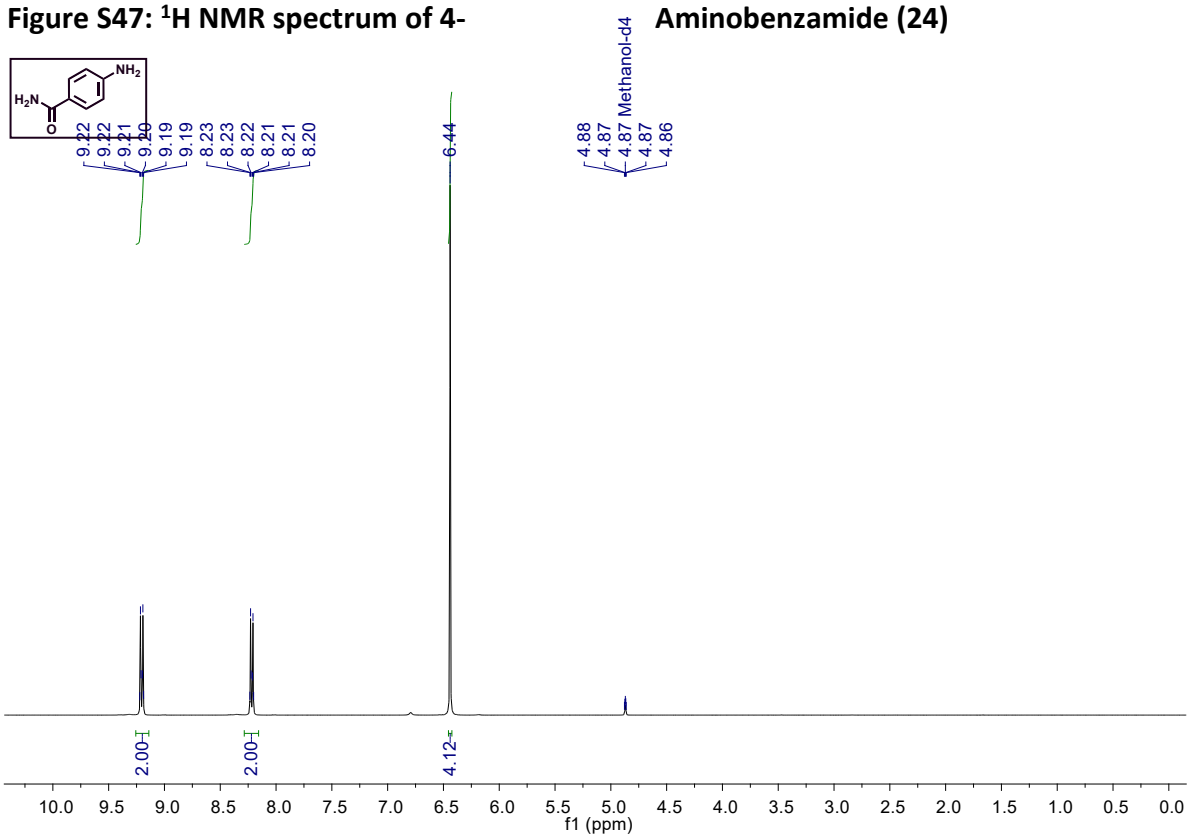

Figure S48: 13C{1H} NMR spectrum of 4-Aminobenzamide (24)

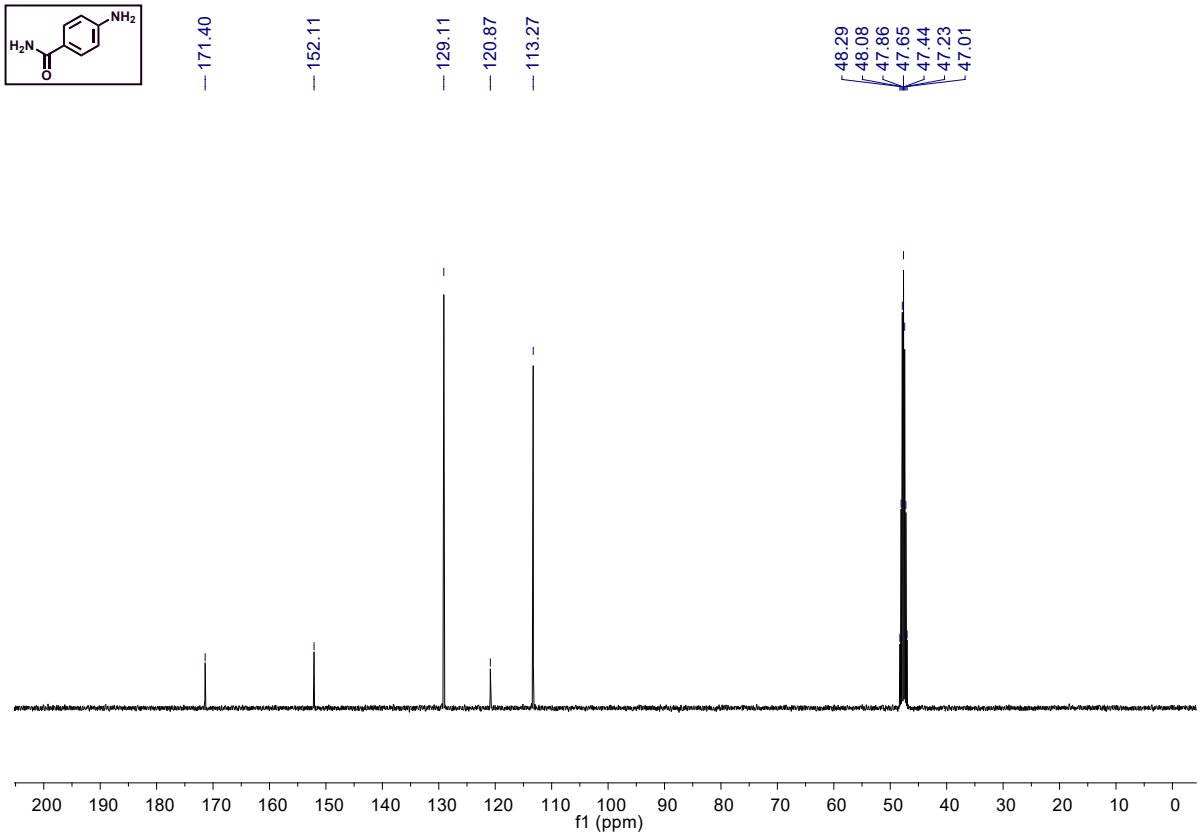

Figure S49: ^{1}H NMR spectrum of Pyrene-1-amine (25)

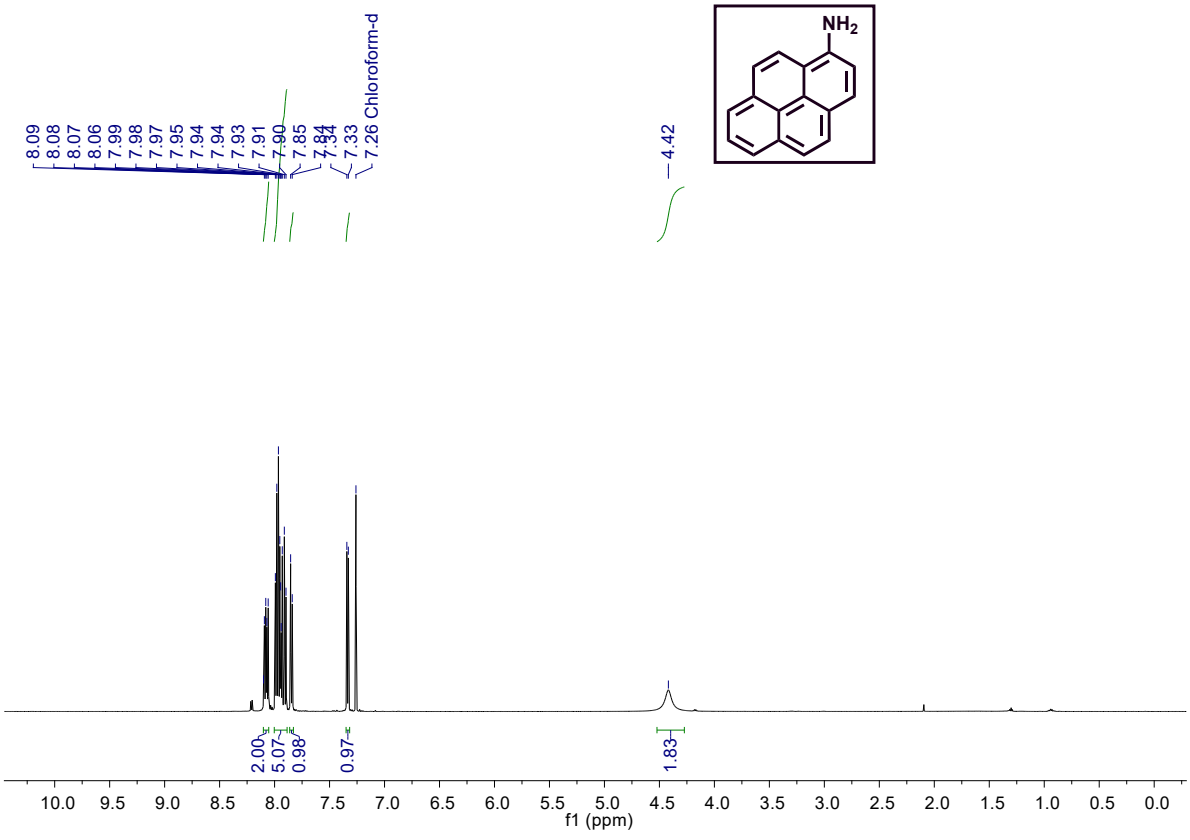

Figure S50: 13C{1H} NMR spectrum of Pyrene-1-amine (25)

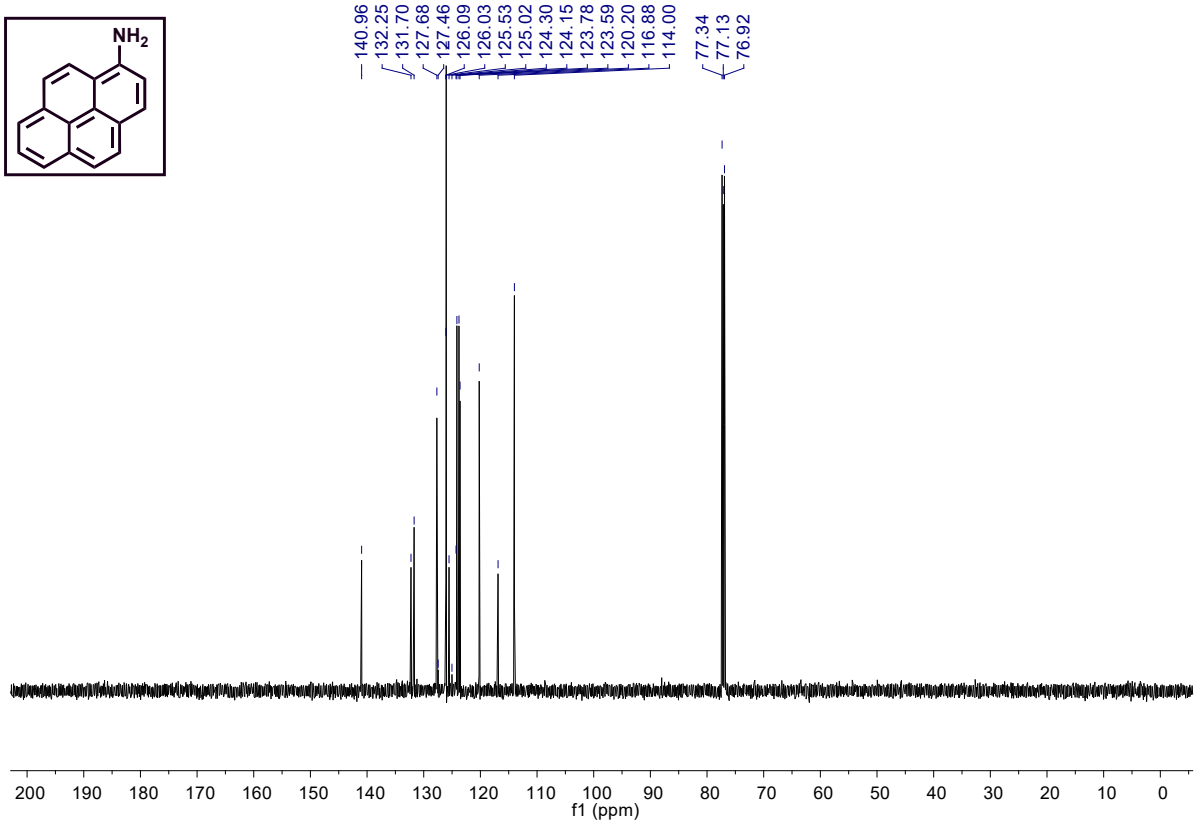

Figure S51: ^{1}H NMR spectrum of 4-Aminophenol (26)

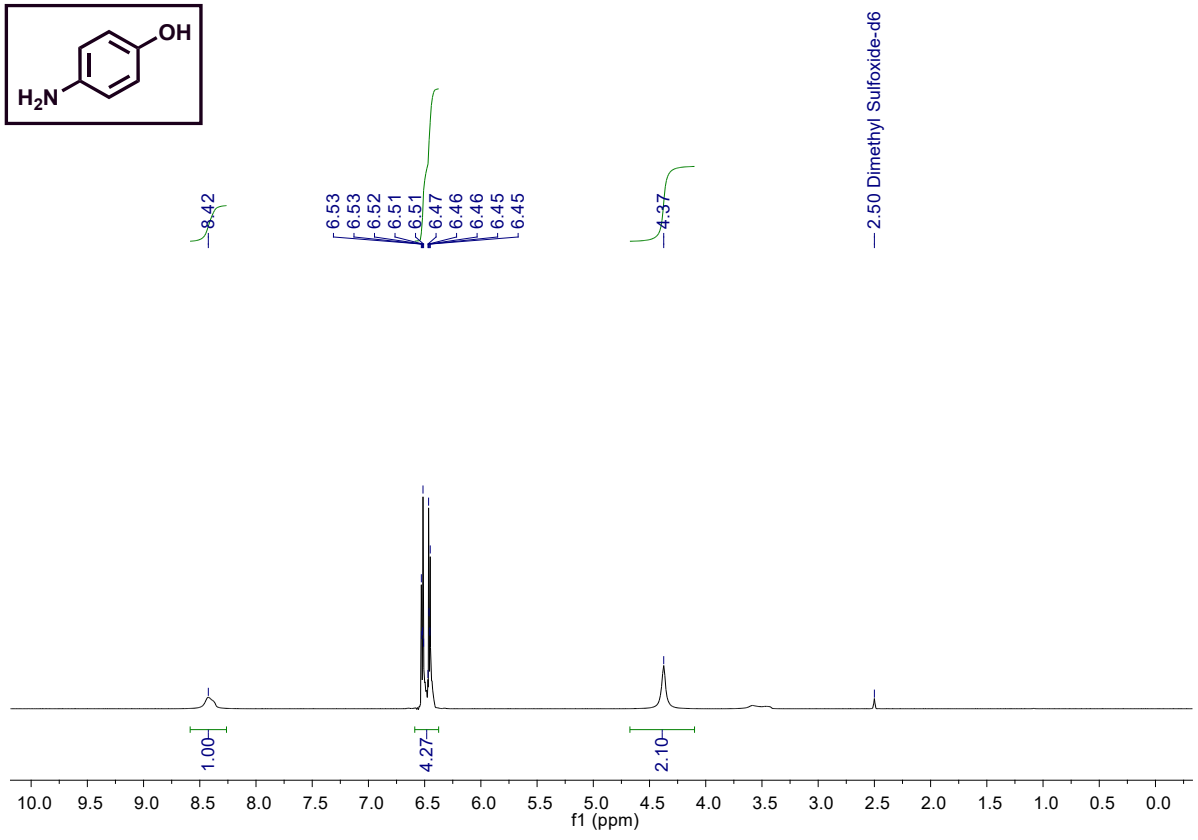

Figure S52: ^{13}C NMR spectrum of 4-Aminophenol (26)

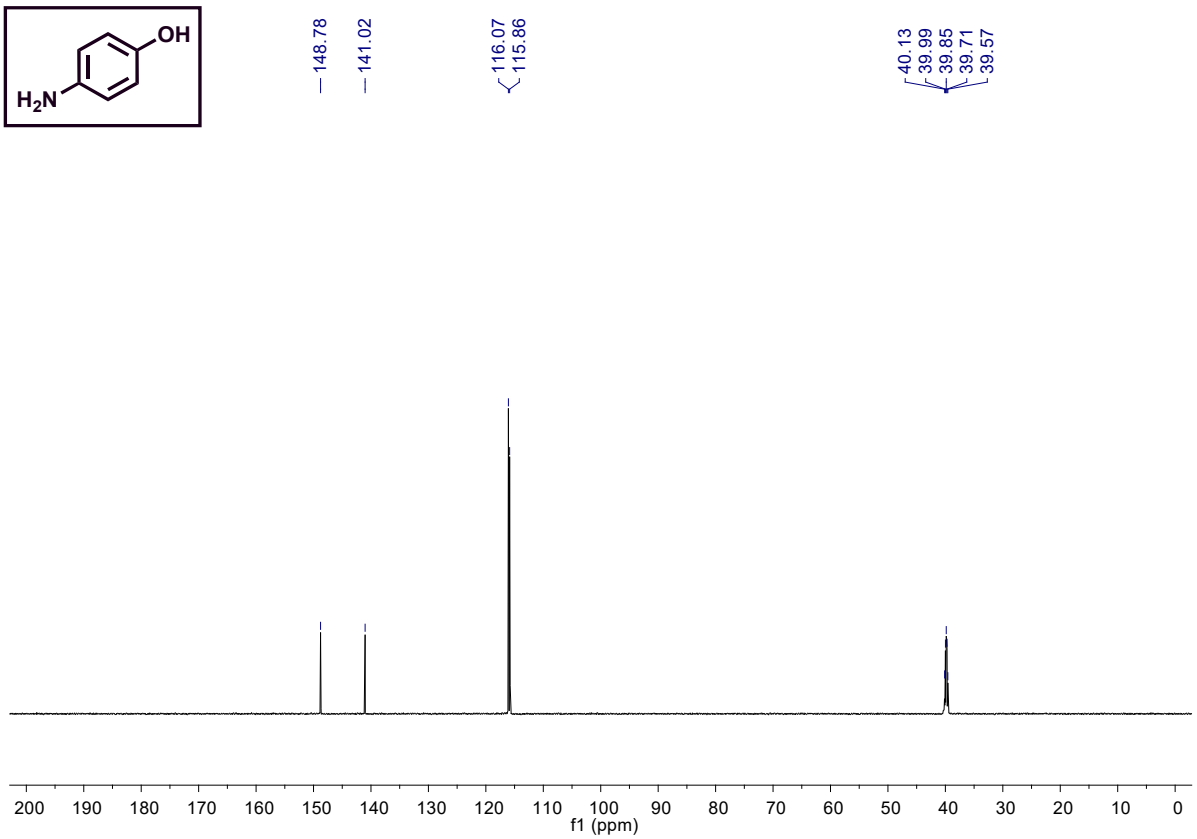

Figure S53: ^{1}H NMR spectrum of *p*-anisidine (27)

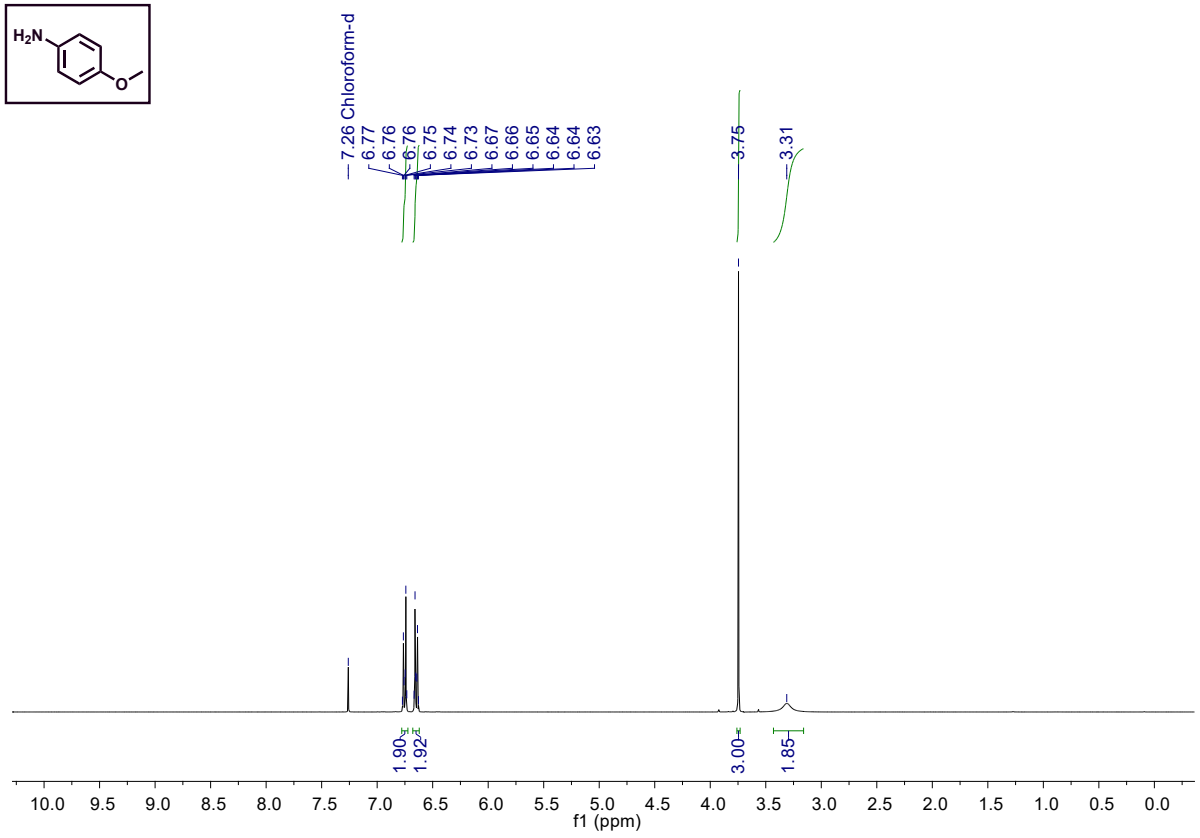

Figure S54: $^{13}C\{1H\}$ NMR spectrum of *p*-anisidine (27)

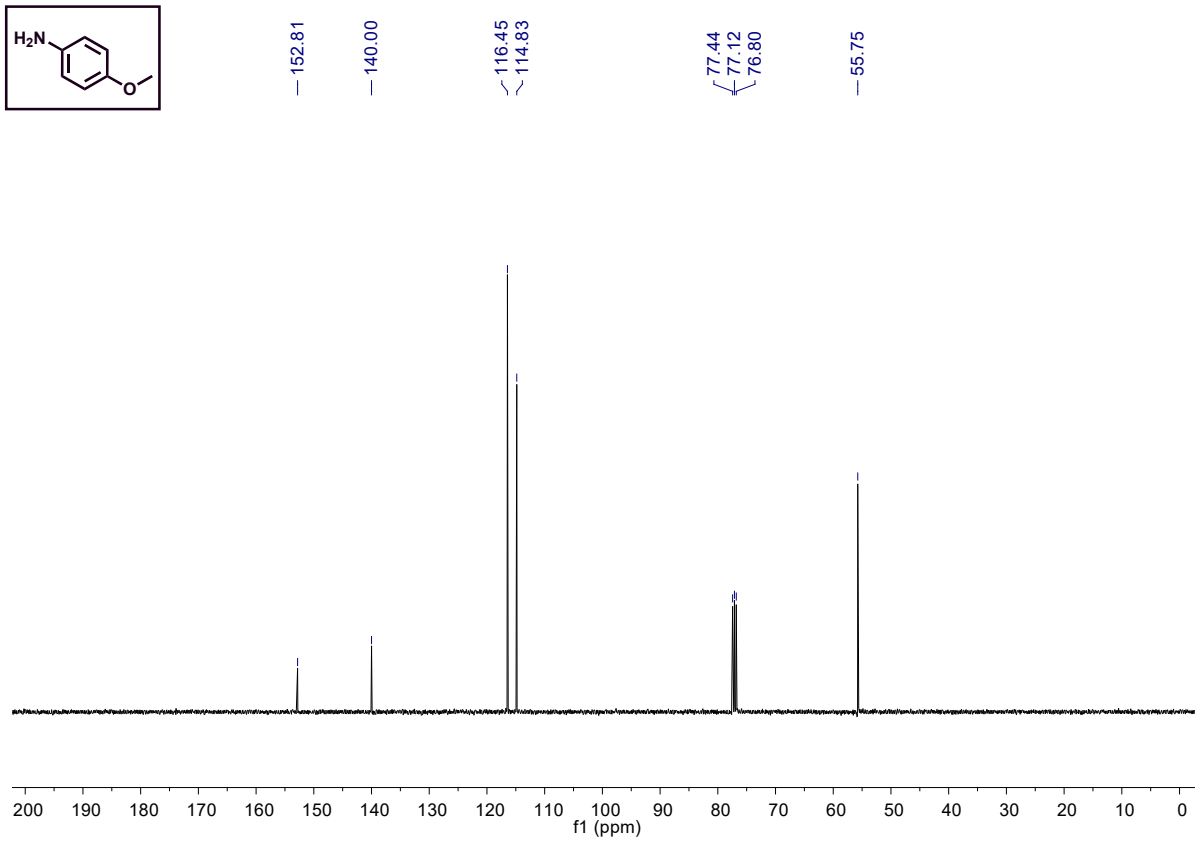

Figure S55: ^{1}H NMR spectrum of (4-Aminophenyl)methanol (28)

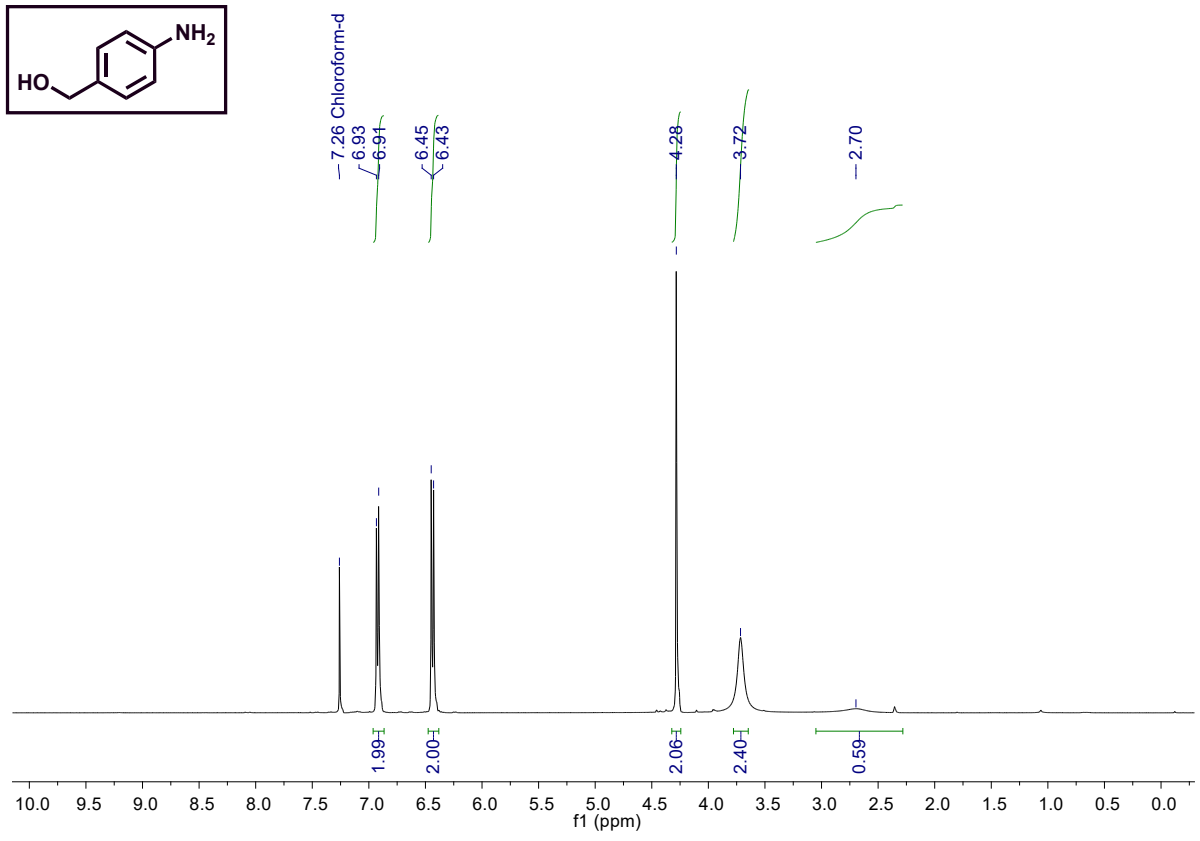

Figure S56: ^{13}C NMR spectrum of (4-Aminophenyl)methanol (28)

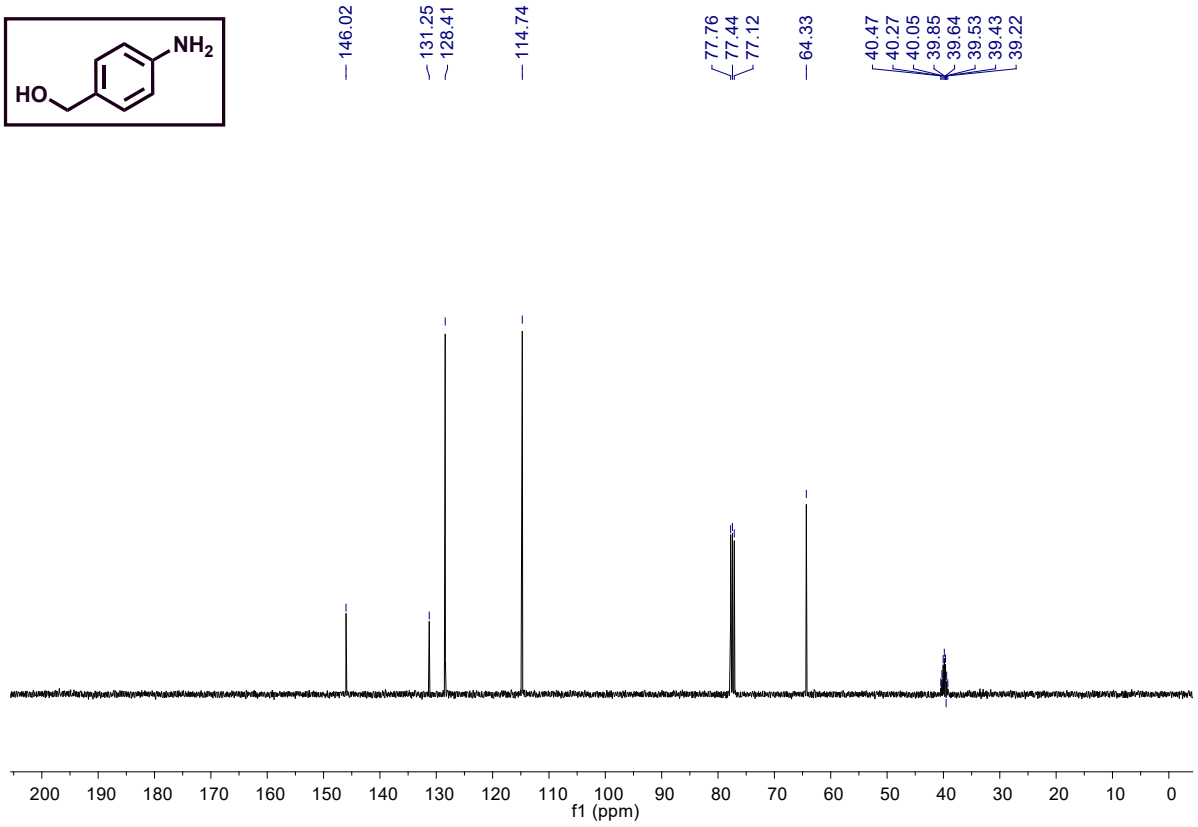

Figure S57: ^{1}H NMR spectrum of 3,4-(Methylenedioxy)aniline (29)

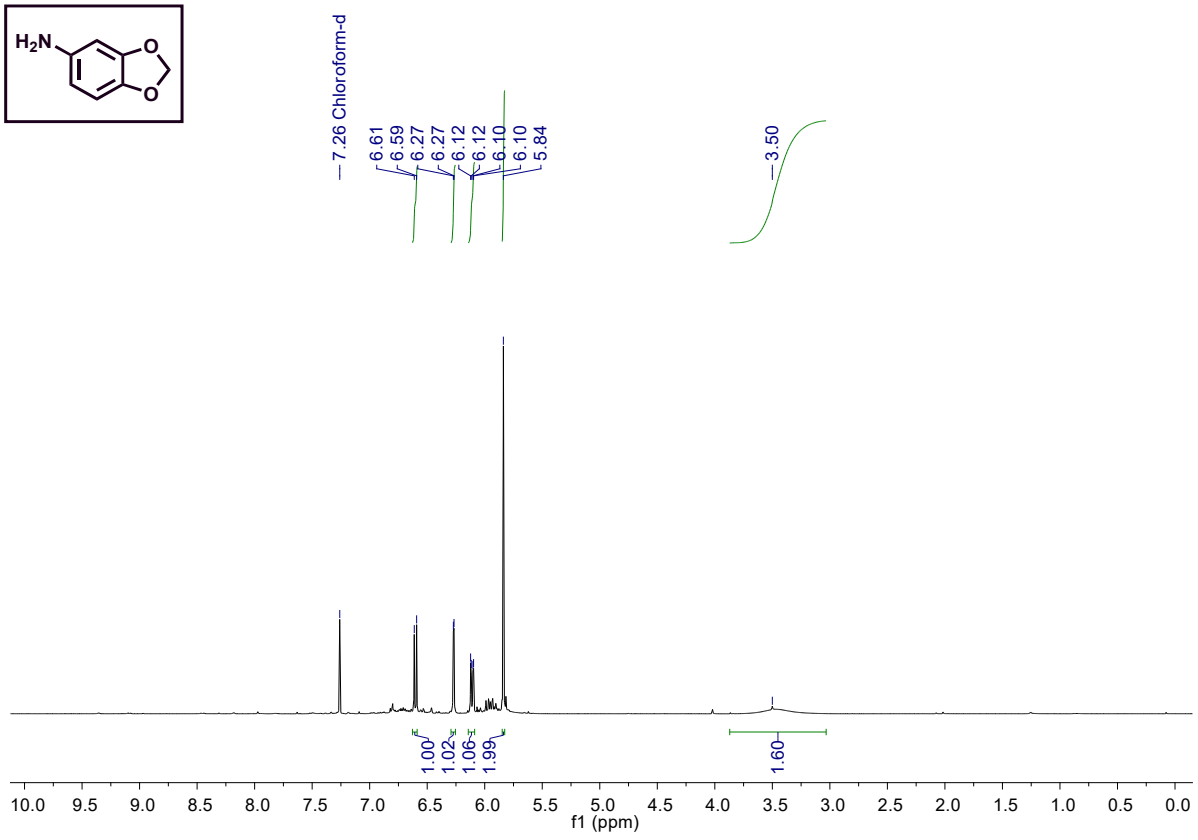

Figure S58: ^{13}C NMR spectrum of 3,4-(Methylenedioxy)aniline (29)

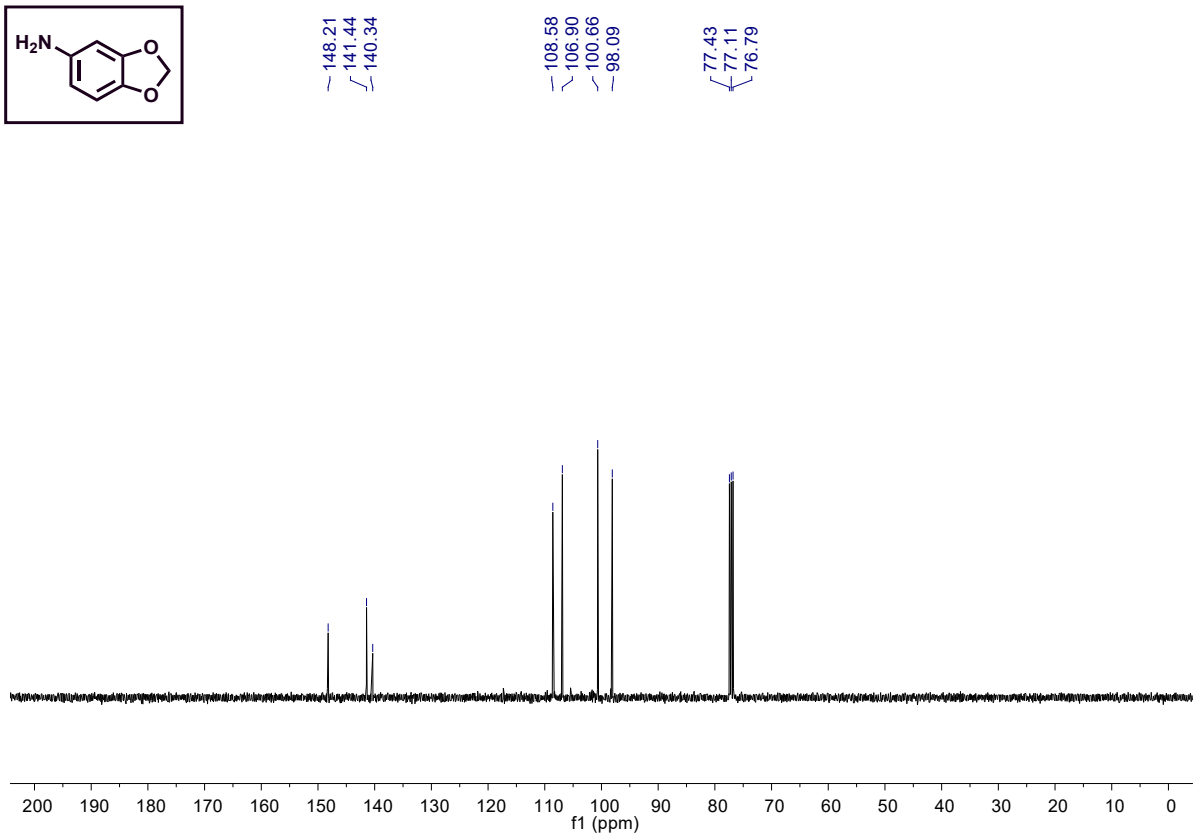

Figure S59: ^{1}H NMR spectrum of *p*-toluidine (30)

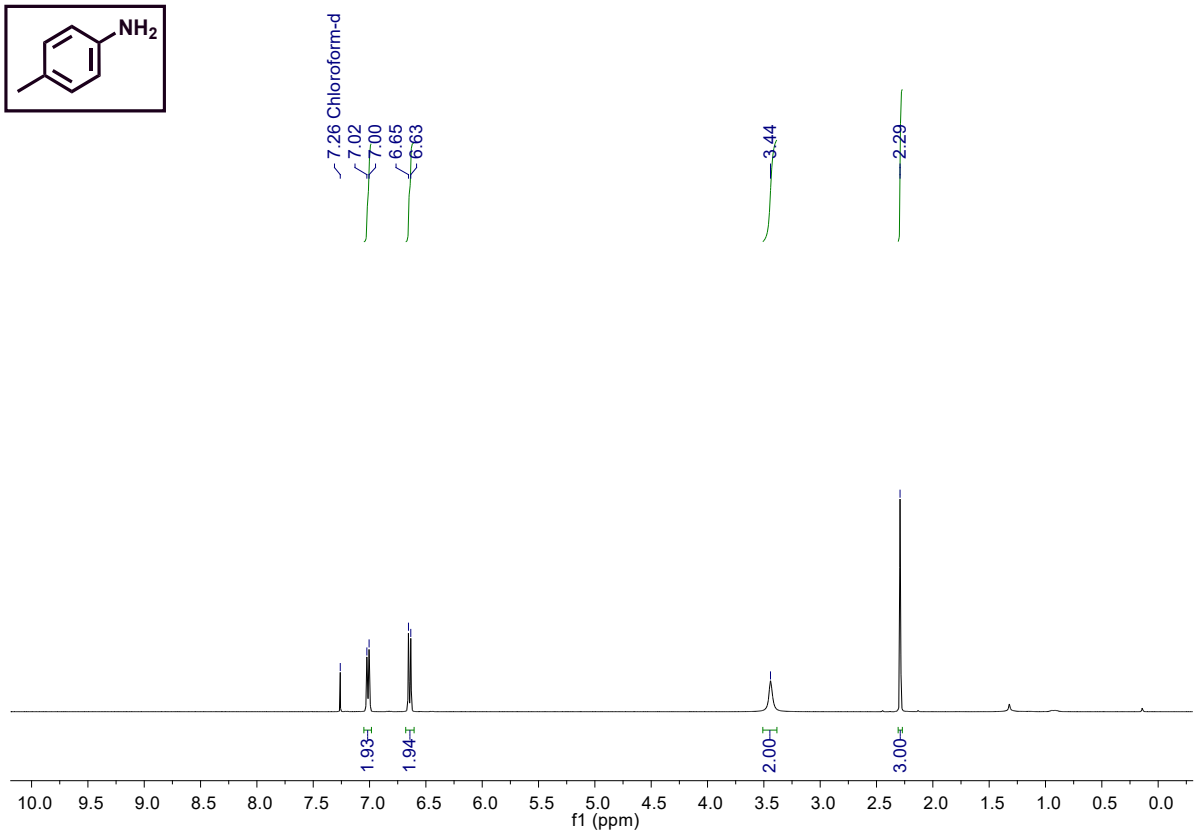

Figure S60: ^{13}C NMR spectrum of *p*-toluidine (30)

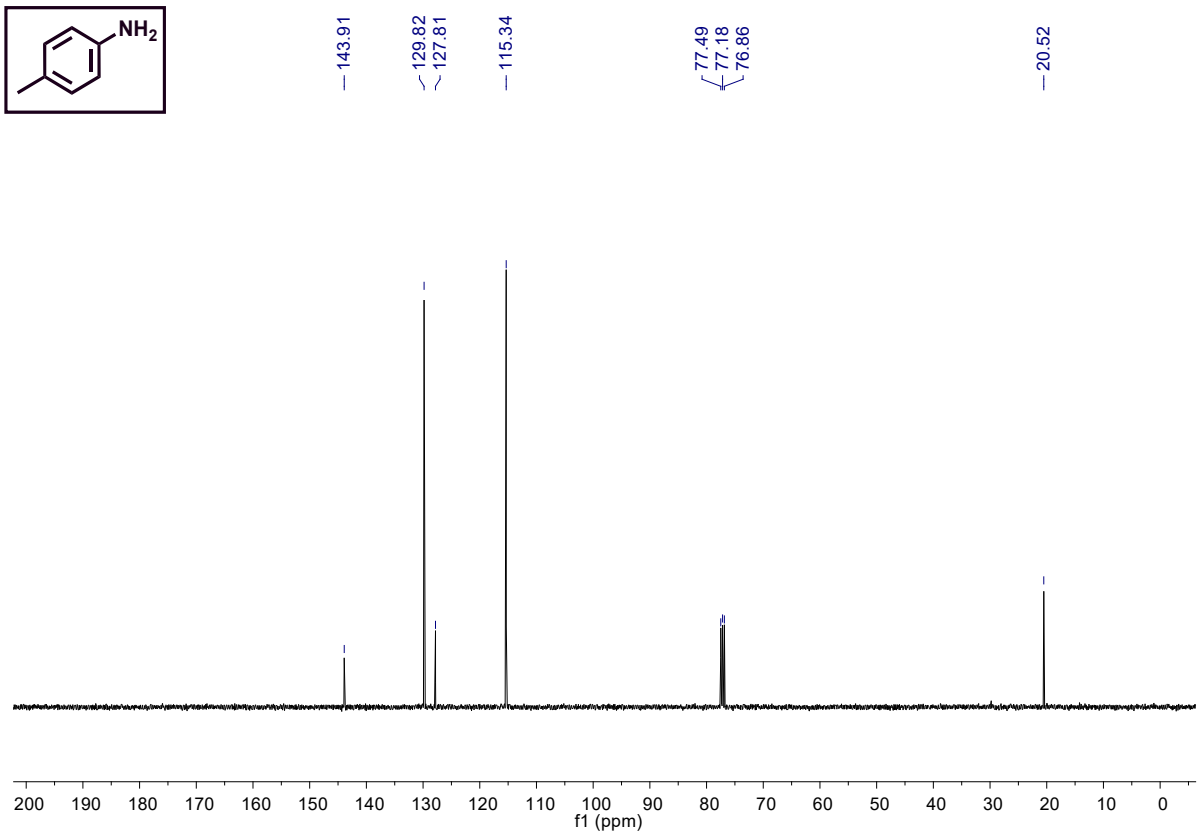

Figure S61: ^{1}H NMR spectrum of *o*-toluidine (31)

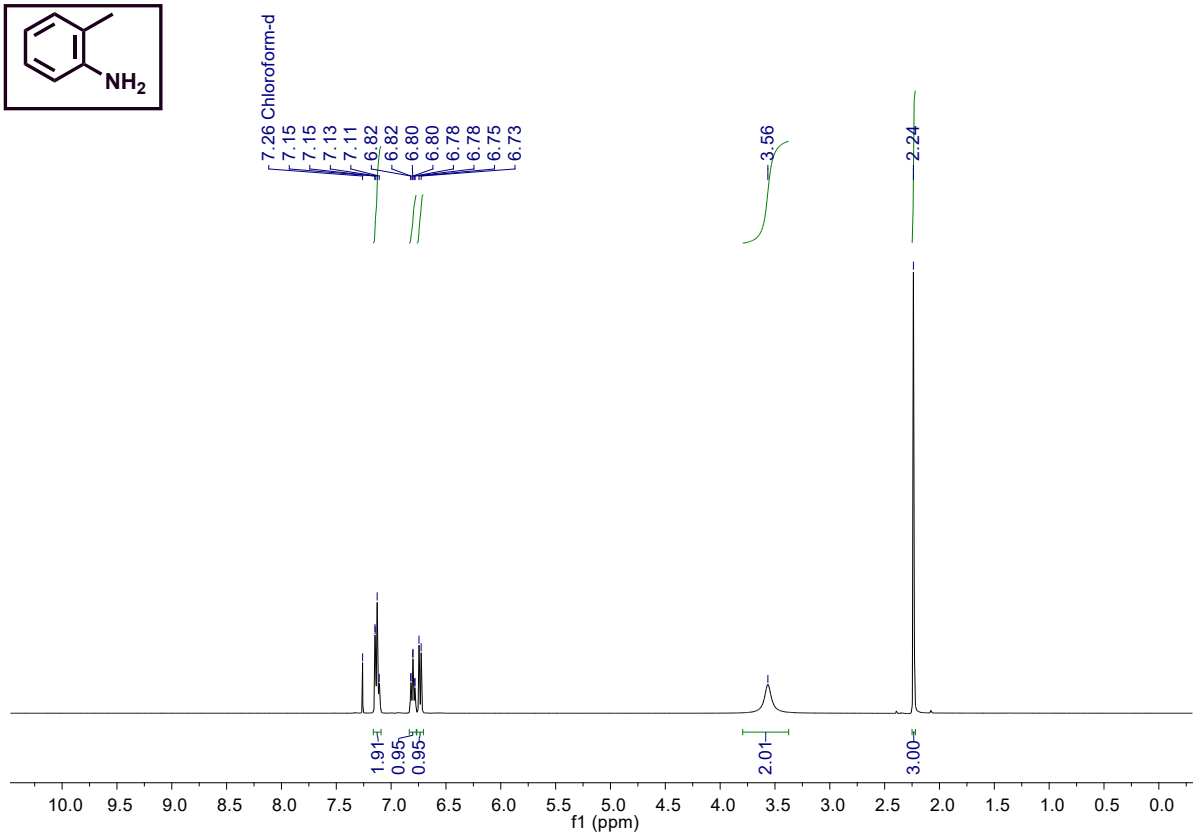

Figure S62: ^{13}C NMR spectrum of *o*-toluidine (31)

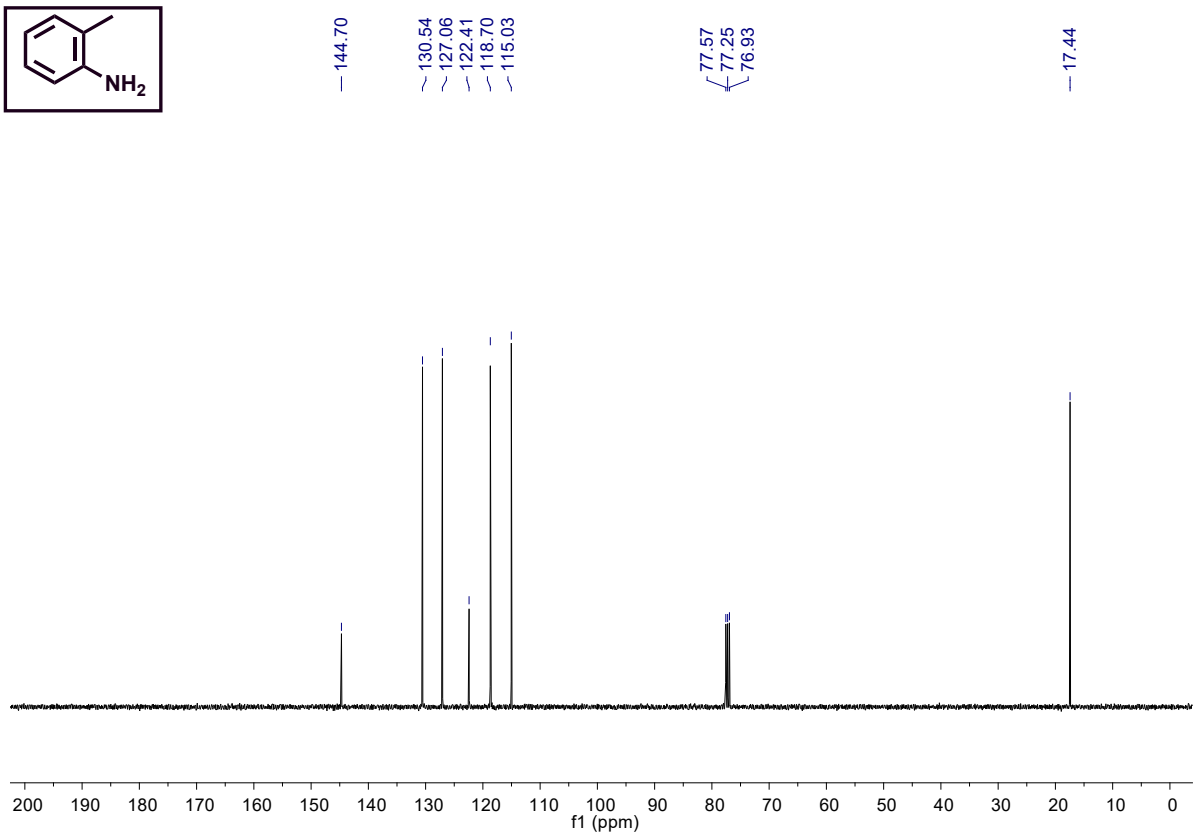

Figure S63: ^{1}H NMR spectrum of 3,5-Dimethylaniline (32)

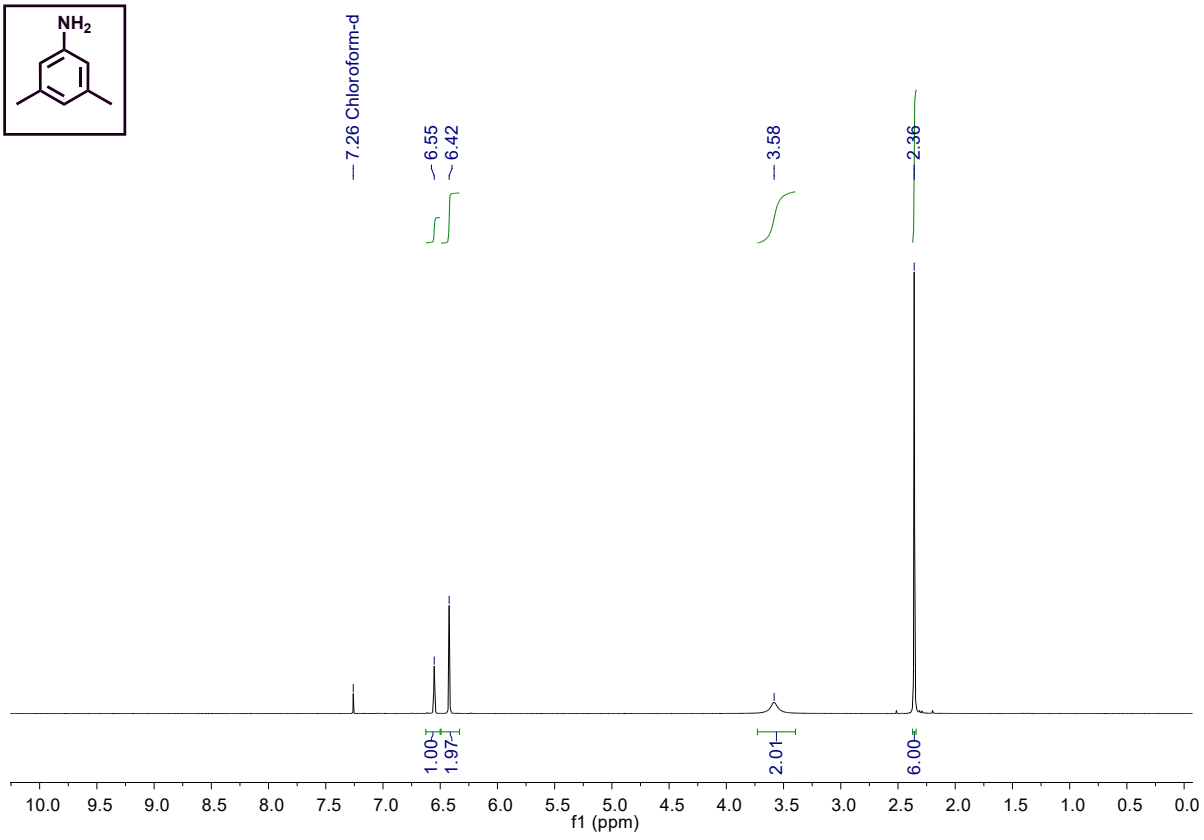

Figure S64: ^{13}C NMR spectrum of 3,5-Dimethylaniline (32)

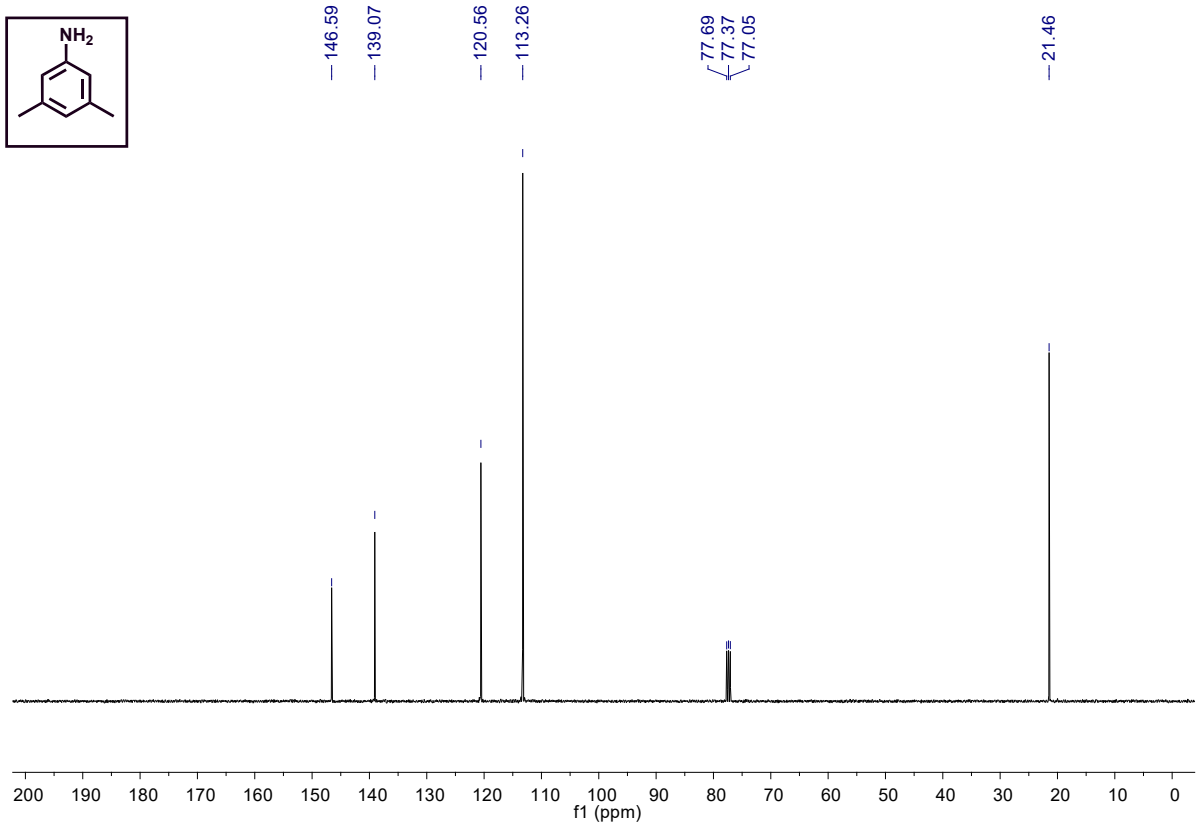

Figure S67: ^{1}H NMR spectrum of Benzene-1,2-diamine (34)

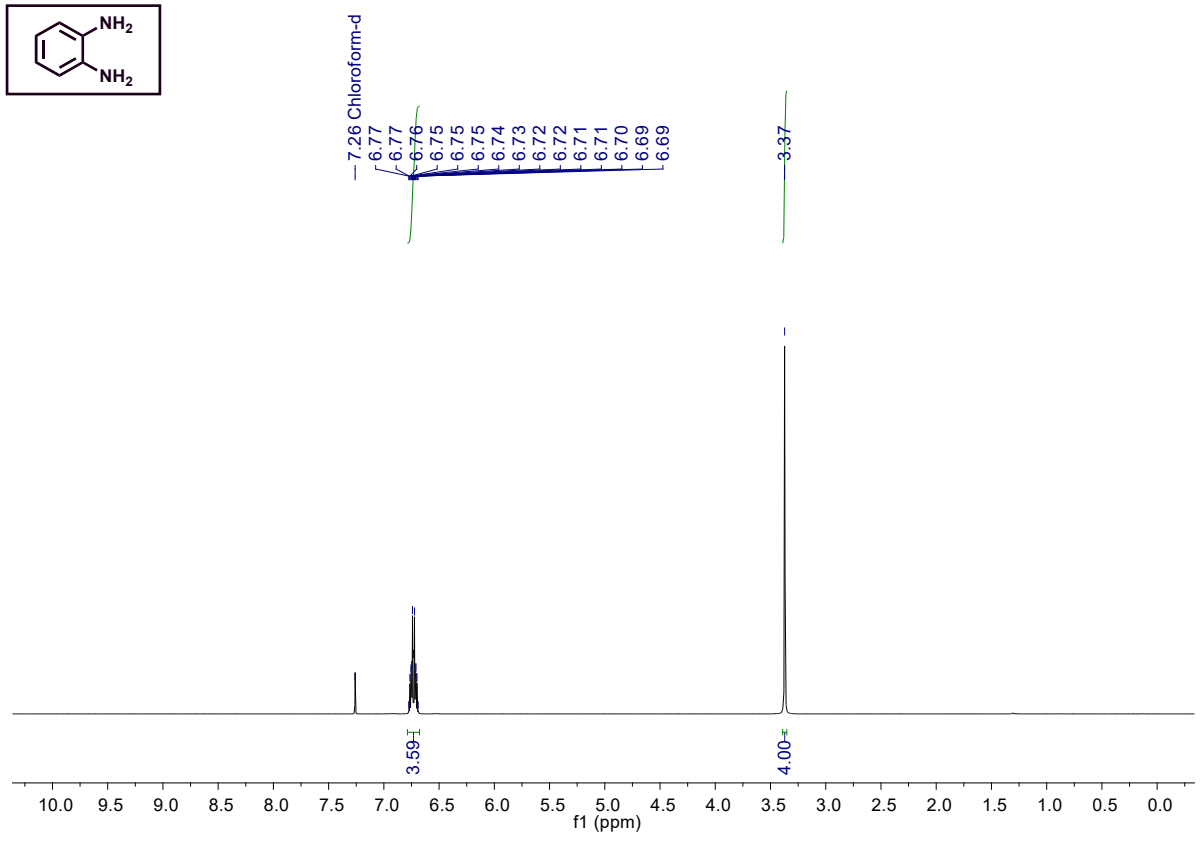

Figure S68: ^{13}C NMR spectrum of Benzene-1,2-diamine (34)

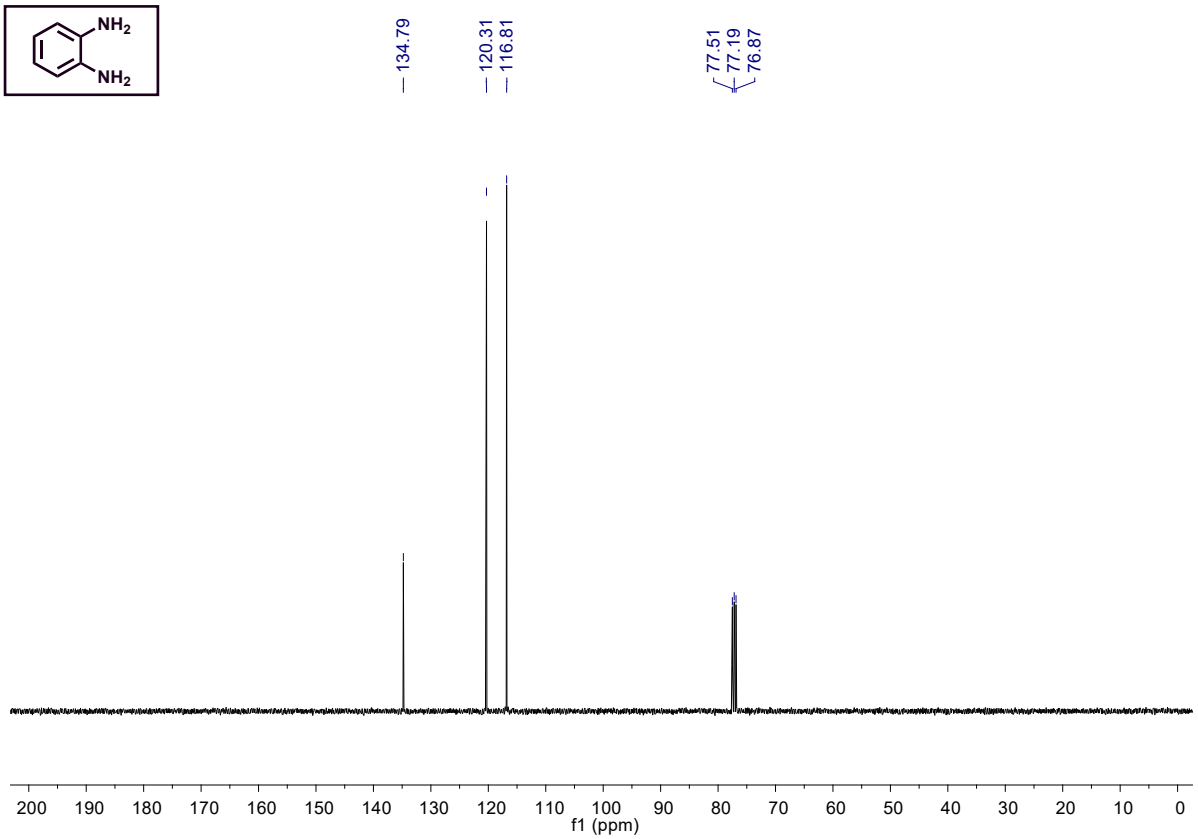

Figure S69: ^{1}H NMR spectrum of 2,2'-(Ethane-1,2-diyl)dianiline (35)

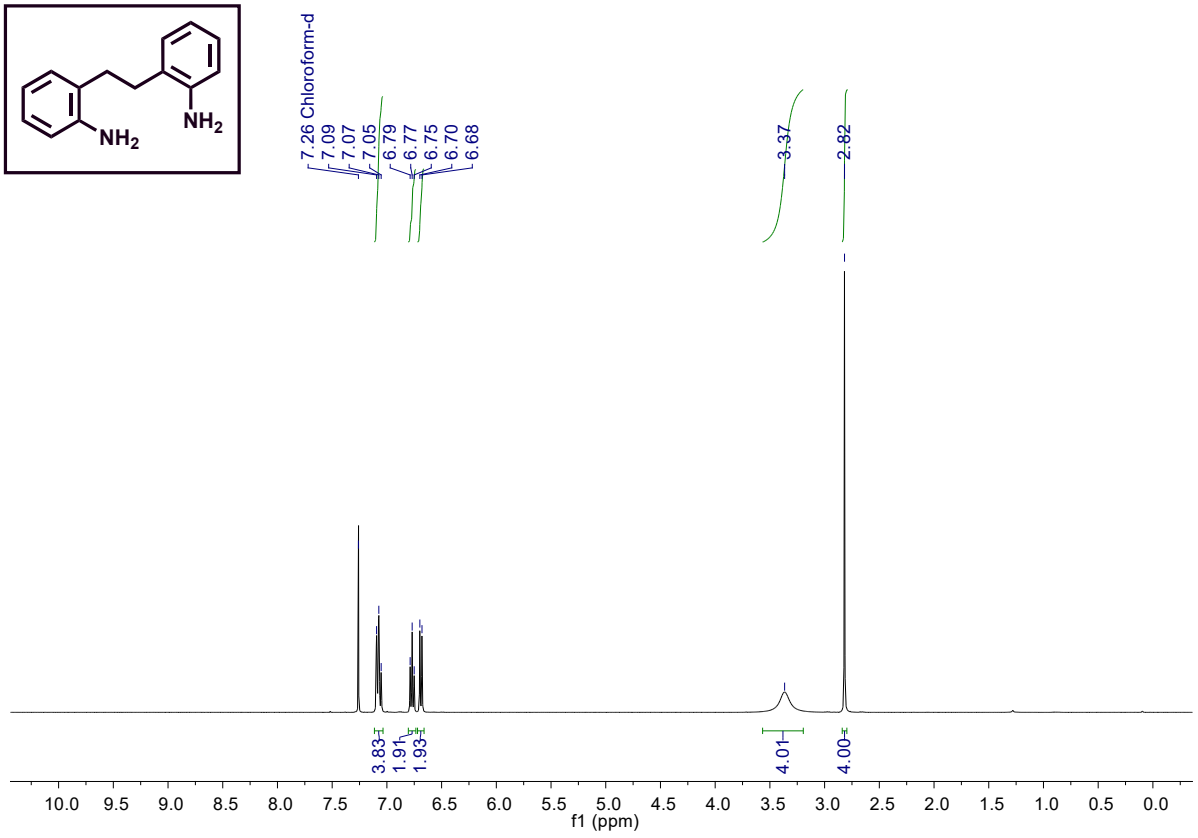

Figure S70: ^{13}C NMR spectrum of 2,2'-(Ethane-1,2-diyl)dianiline (35)

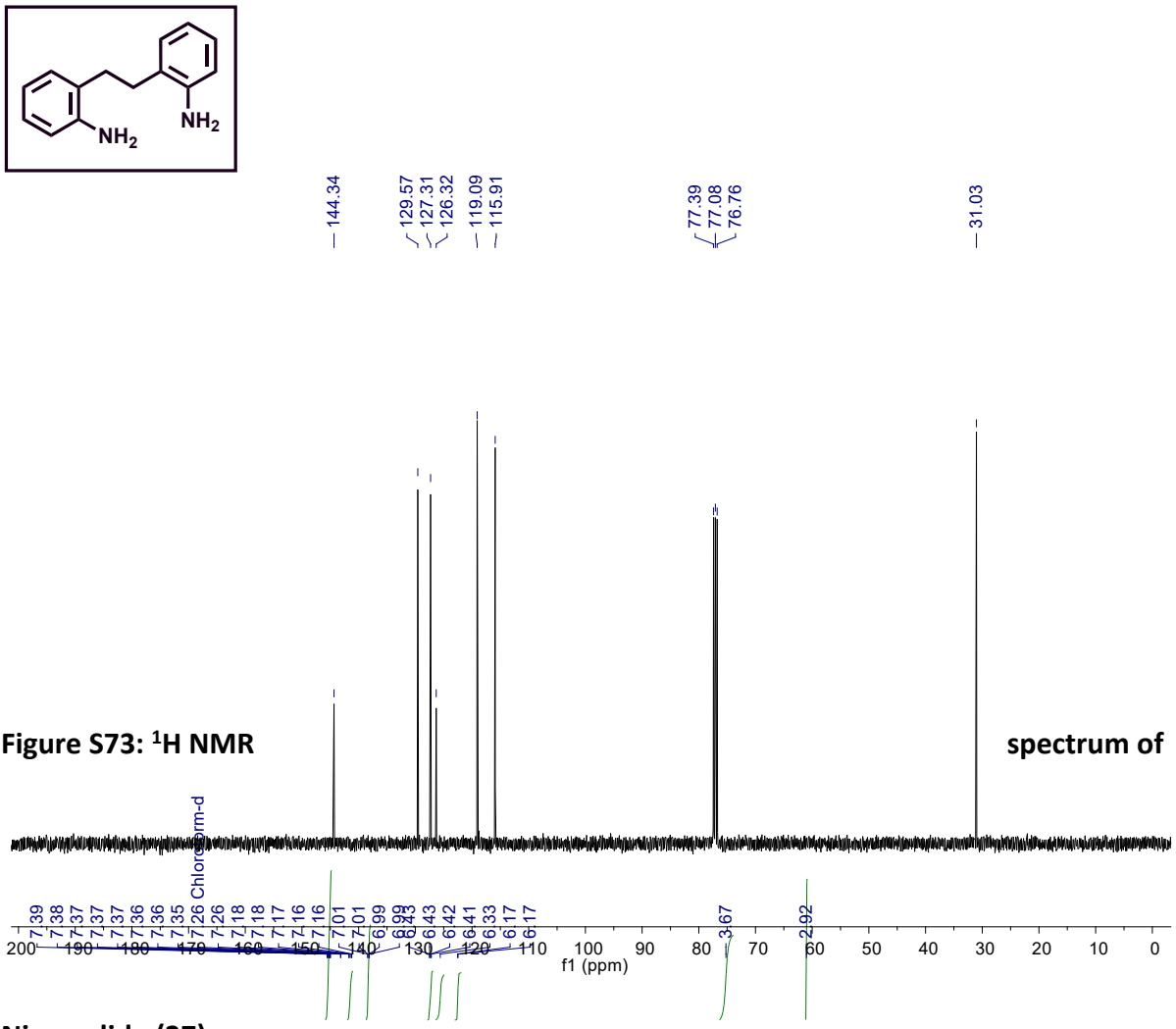

Figure S73: ^{1}H NMR spectrum of Nimesulide (37)

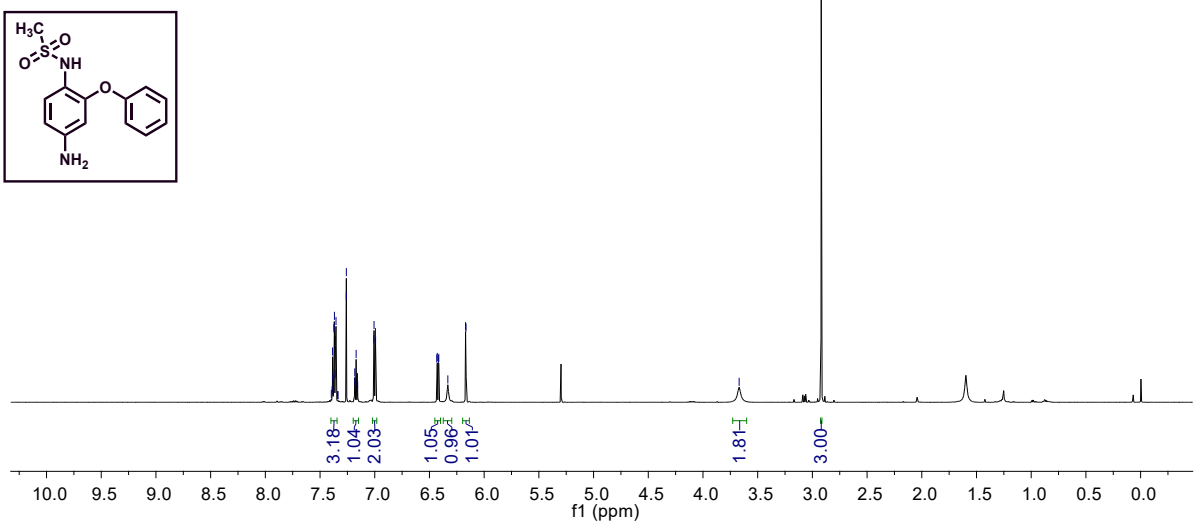

Figure S74: ^{13}C NMR spectrum of Nimesulide (37)

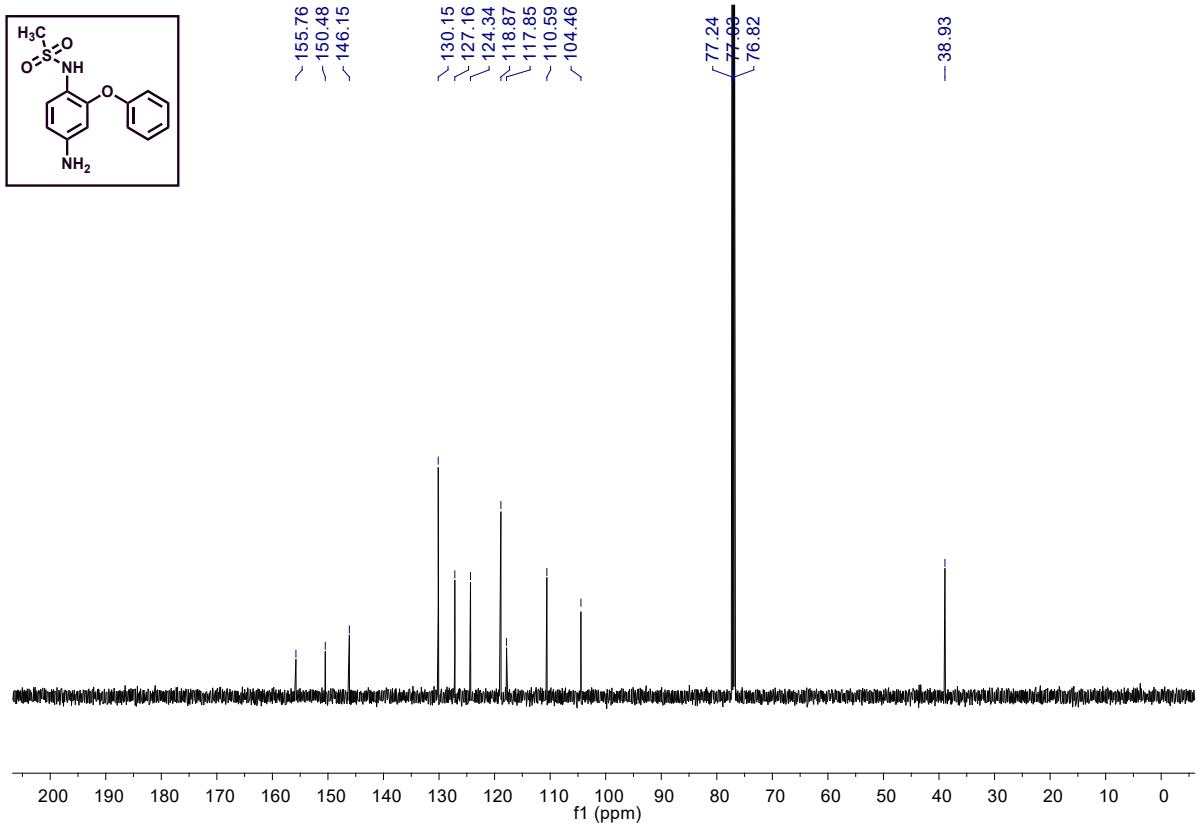

Figure S77: ^{1}H NMR spectrum of 2-Aminopyridine (39)

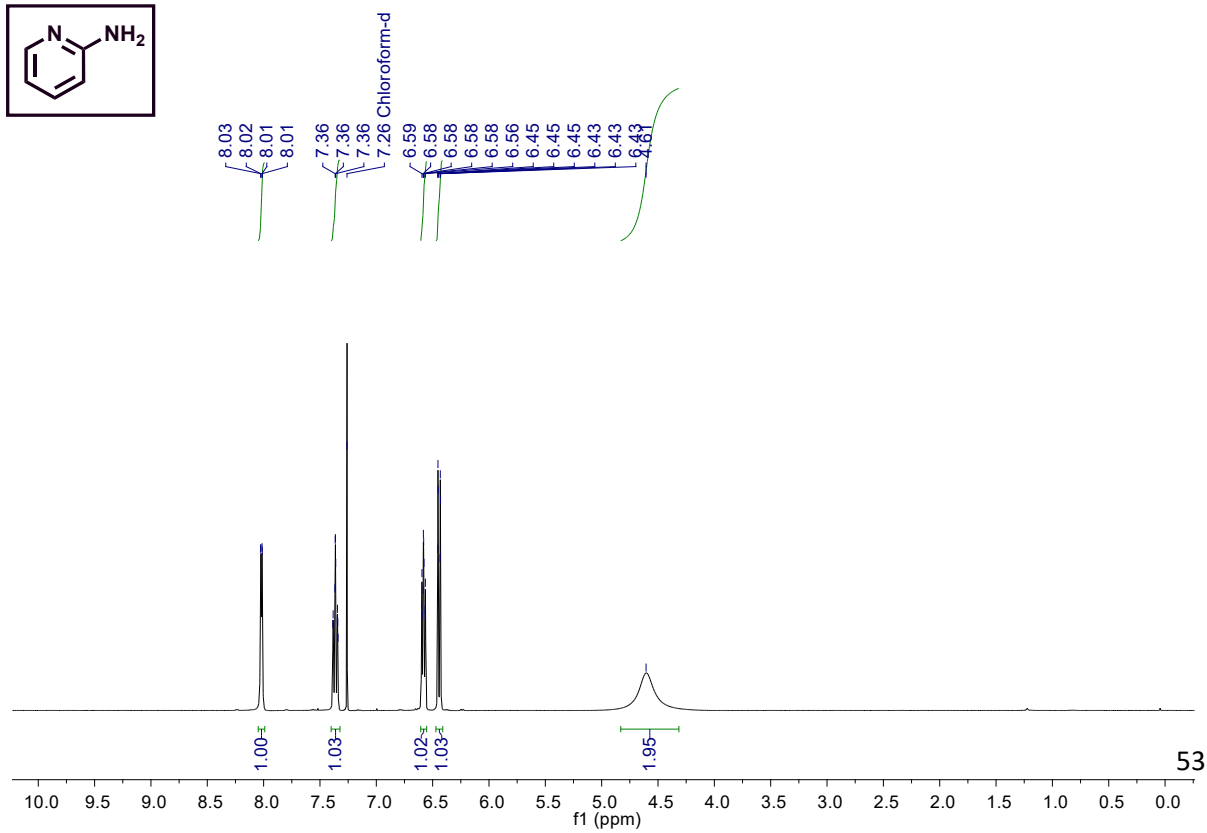

Figure S78: ^{13}C NMR spectrum of 2-Aminopyridine (39)

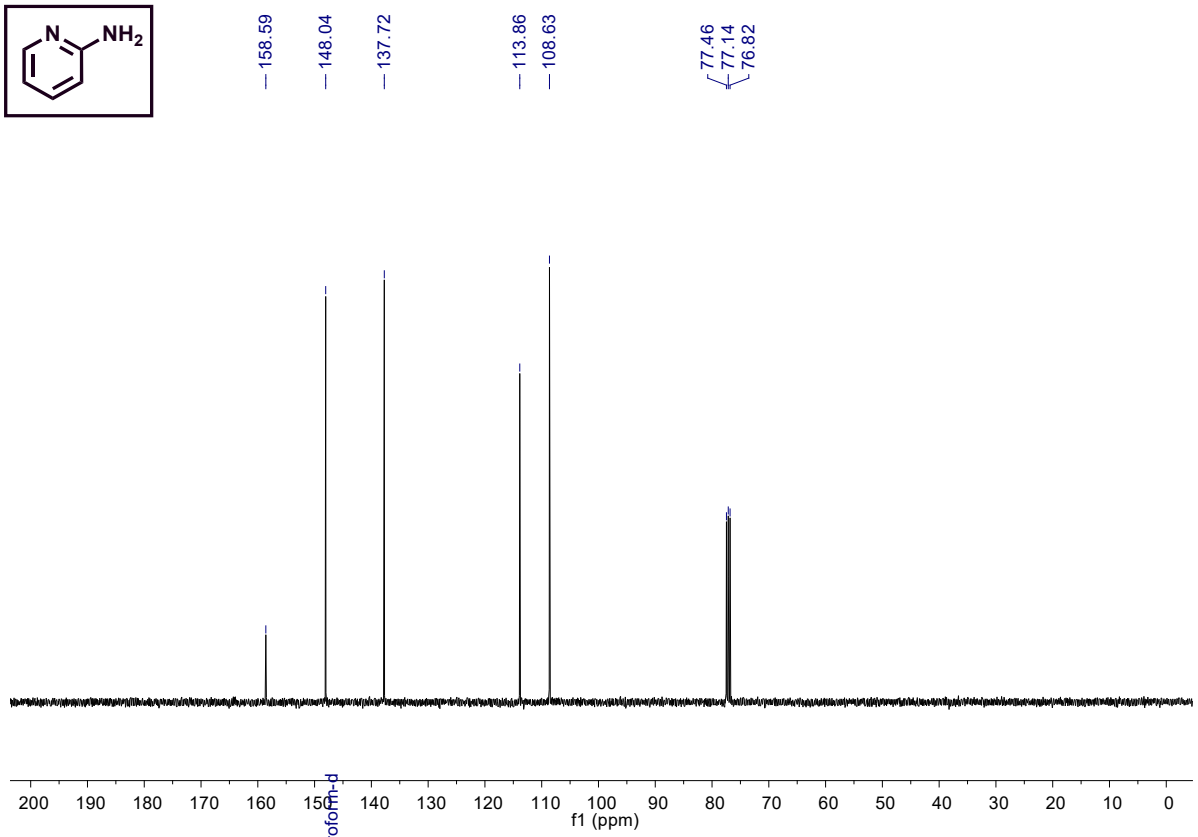

Figure S79: ^{1}H NMR spectrum of 3-Aminopyridine (40)

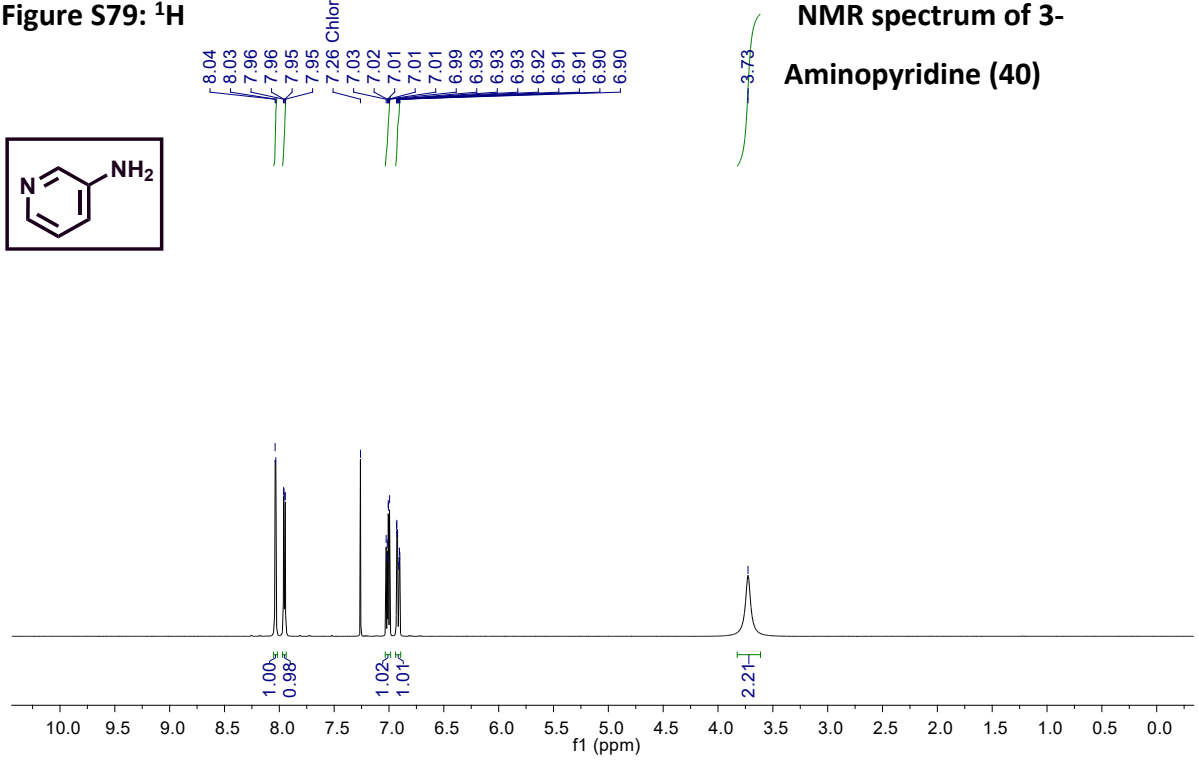

Figure S80: ^{13}C NMR spectrum of 3-Aminopyridine (40)

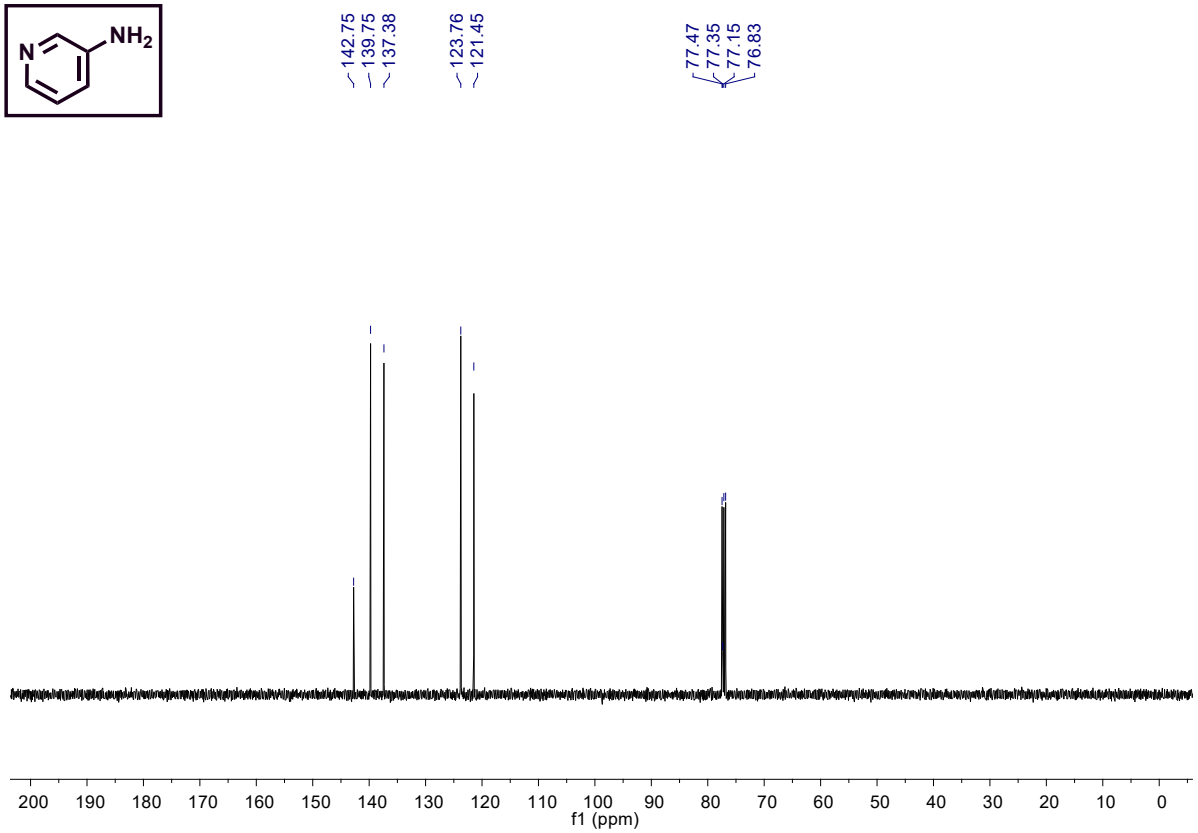

Figure S81: ^{1}H NMR spectrum of 3-Aminopyridine (41)

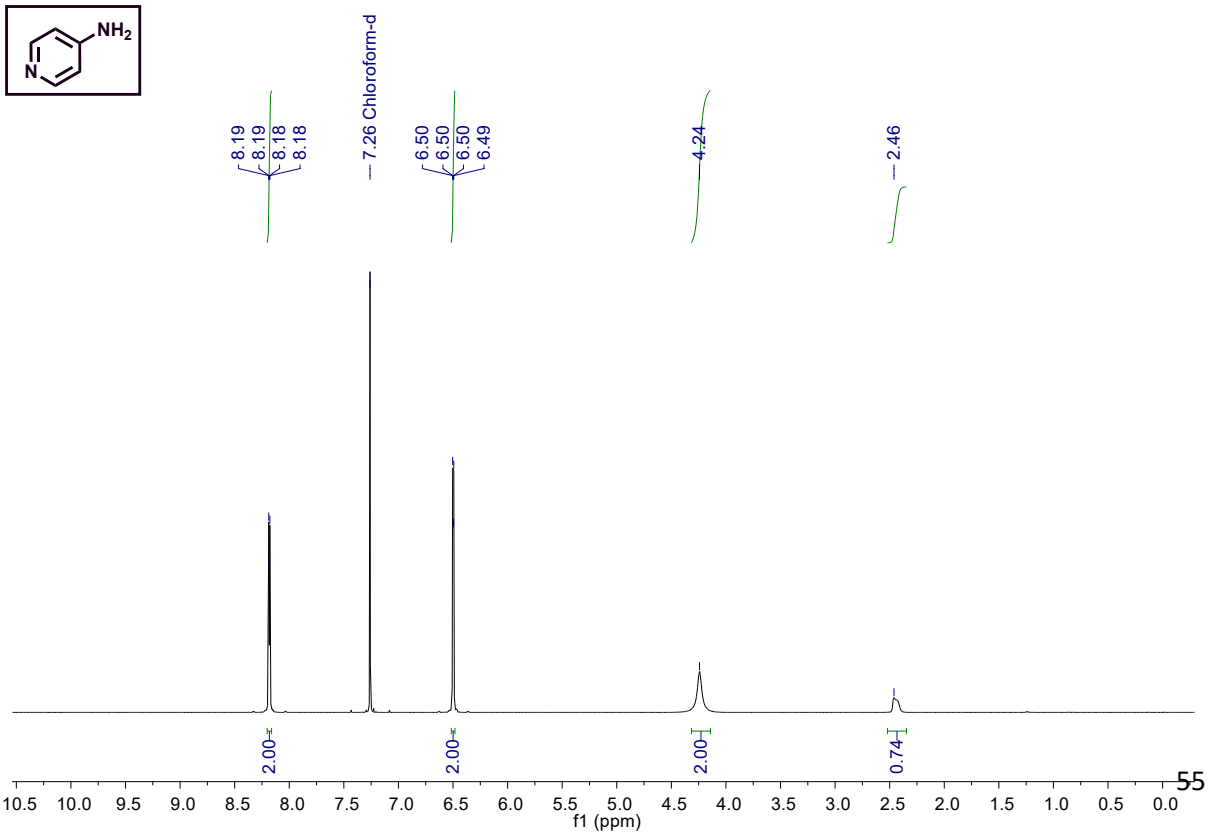

Figure S82: ^{13}C NMR spectrum of 3-Aminopyridine (41)

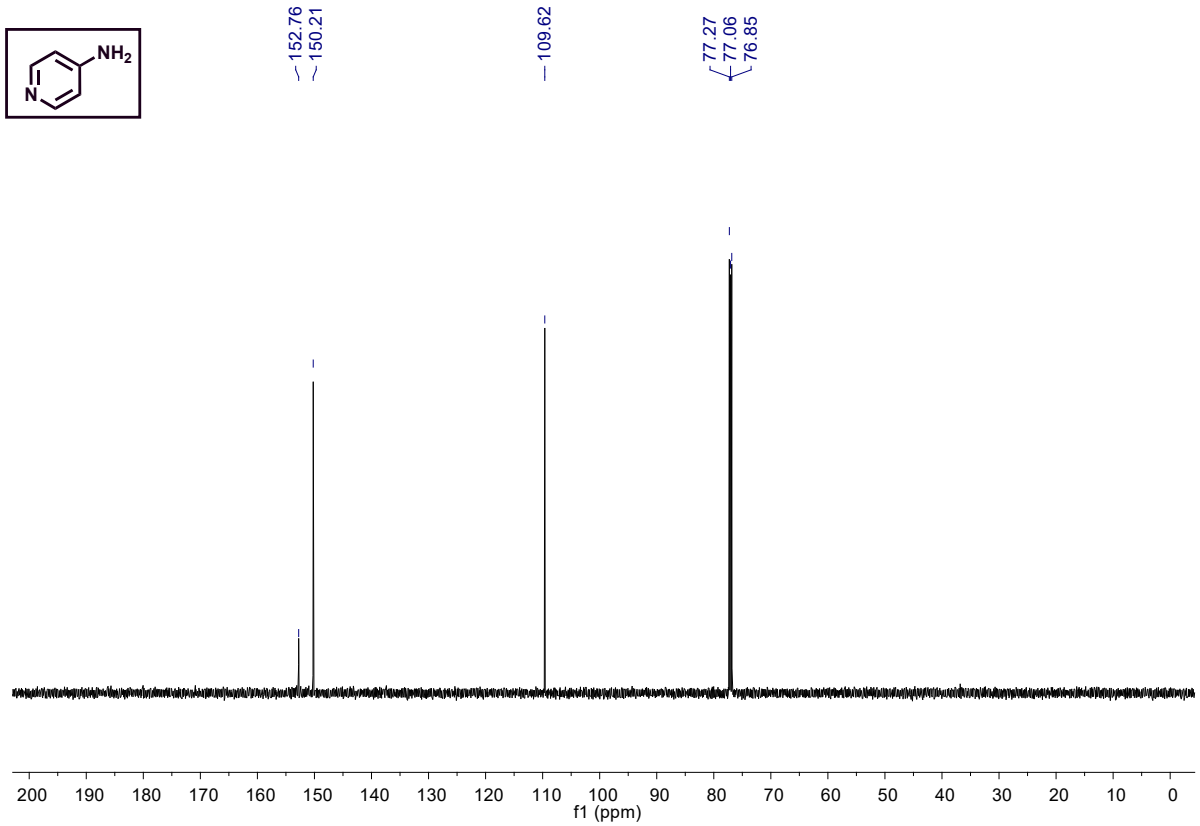

Figure S83: ^{1}H NMR spectrum of Quinolin-8-amine (42)

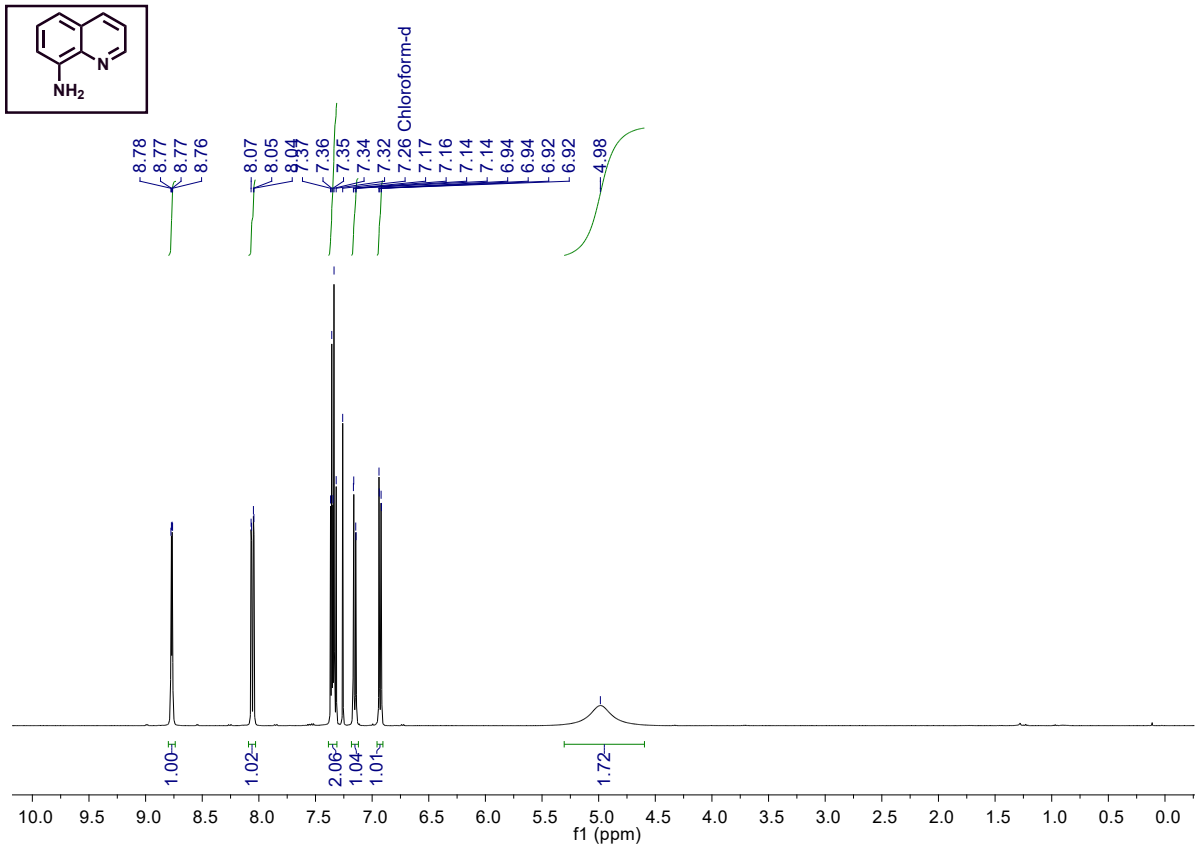

Figure S84: ^{13}C NMR spectrum of Quinolin-8-amine (42)

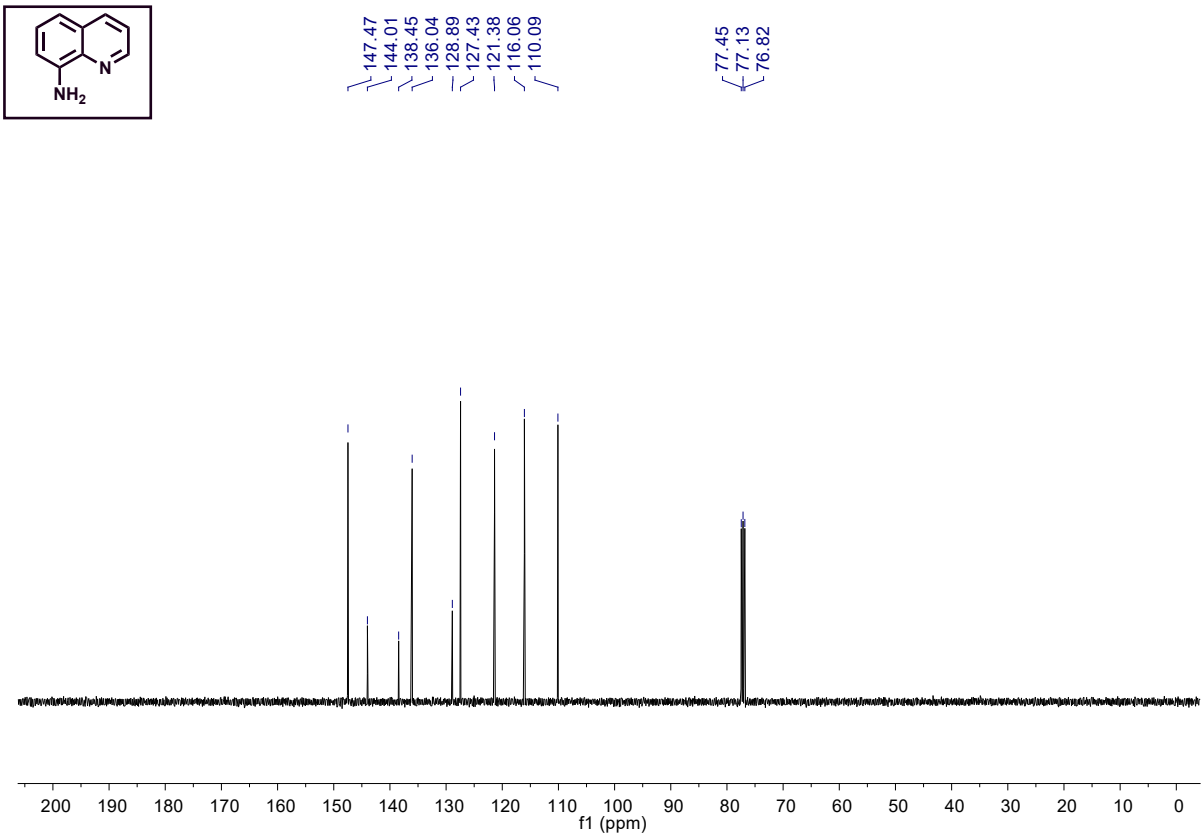

Figure S85: ^{1}H NMR spectrum of 4-(4-Aminophenyl)morpholin-3-one (43)

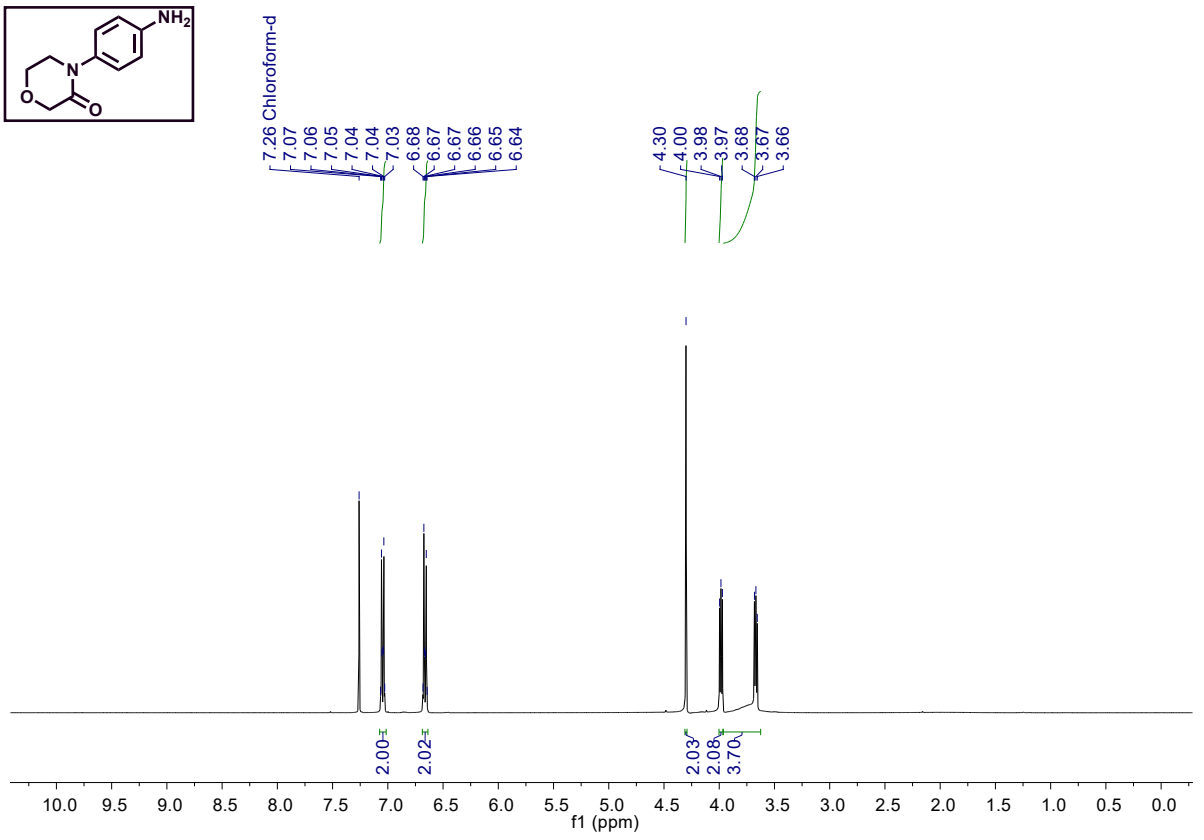

Figure S86: ^{13}C NMR spectrum of 4-(4-Aminophenyl)morpholin-3-one (43)

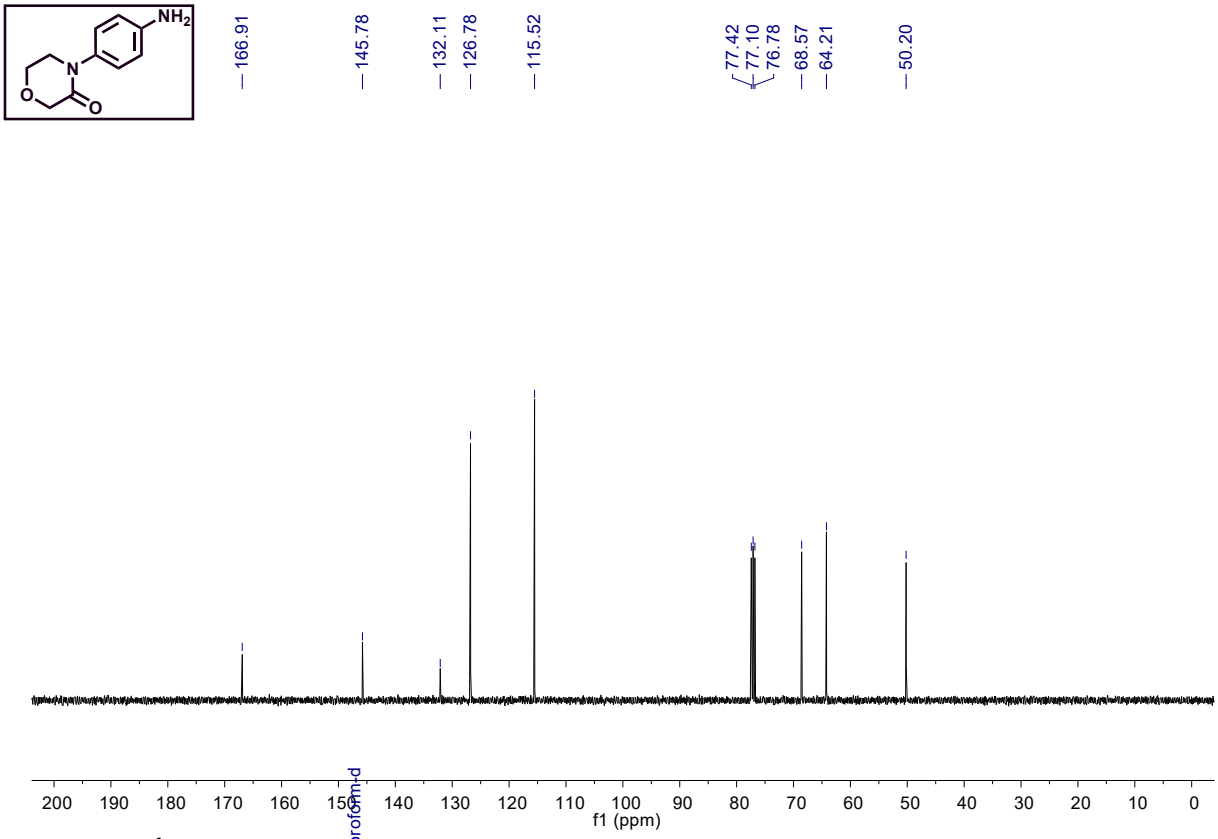

Figure S87: ^{1}H NMR spectrum of 2-((2,4-Dimethylphenyl)thio)aniline (44)

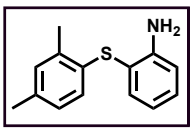

Figure S88: ^{13}C NMR spectrum of 2-((2,4-Dimethylphenyl)thio)aniline (44)

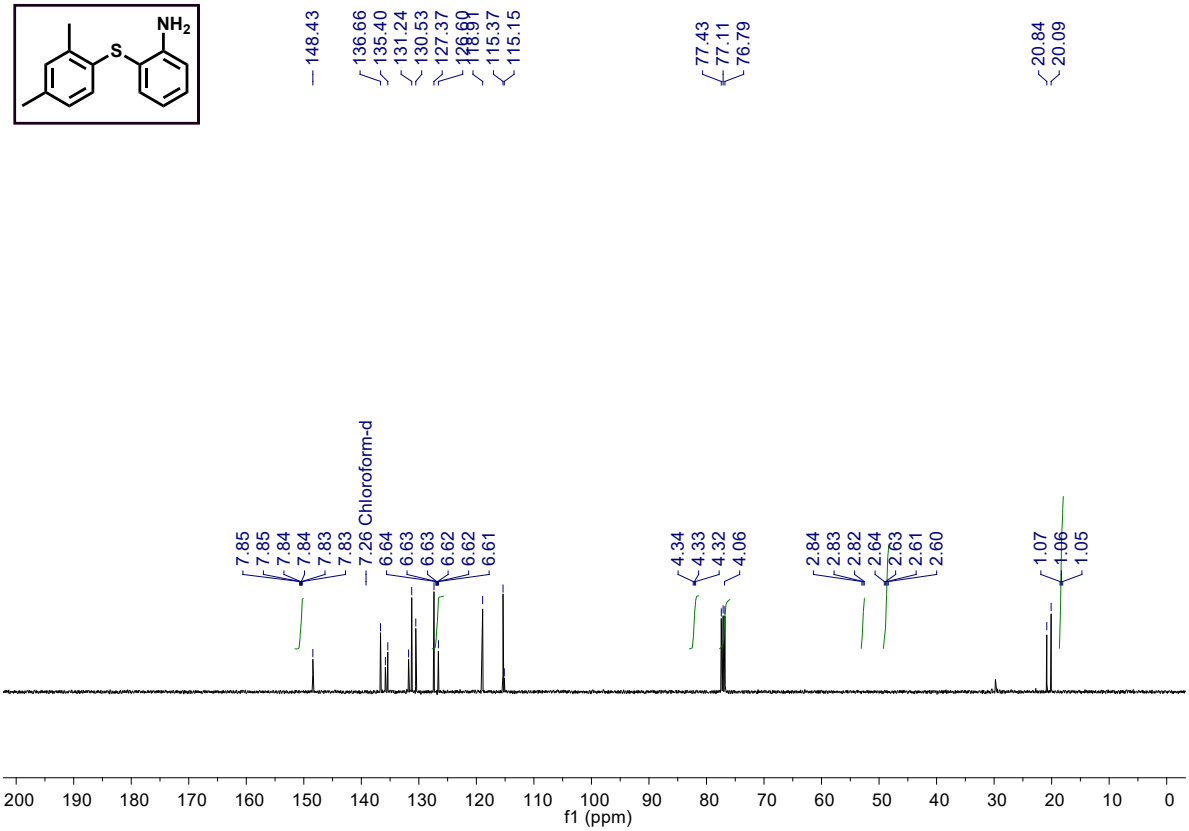

Figure S89: ^{1}H NMR spectrum of Procaine (45)

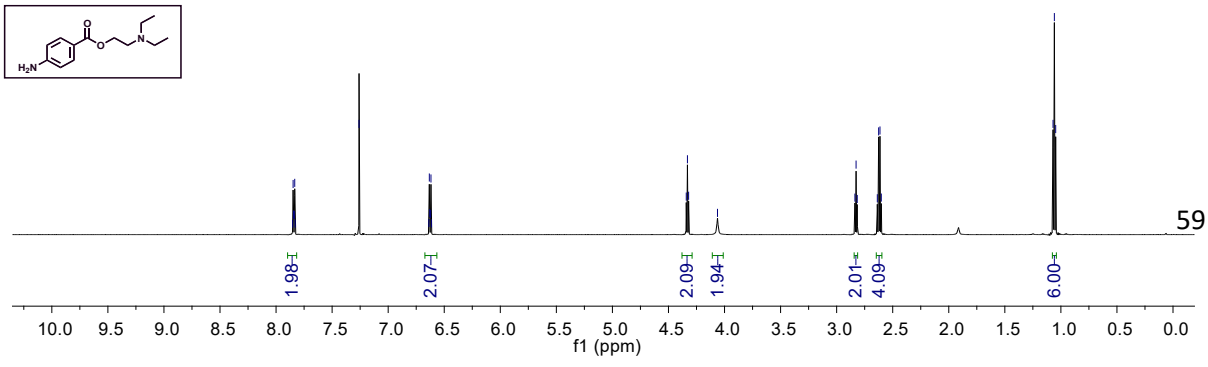

Figure S90: ^{13}C NMR spectrum of Procaine (45)

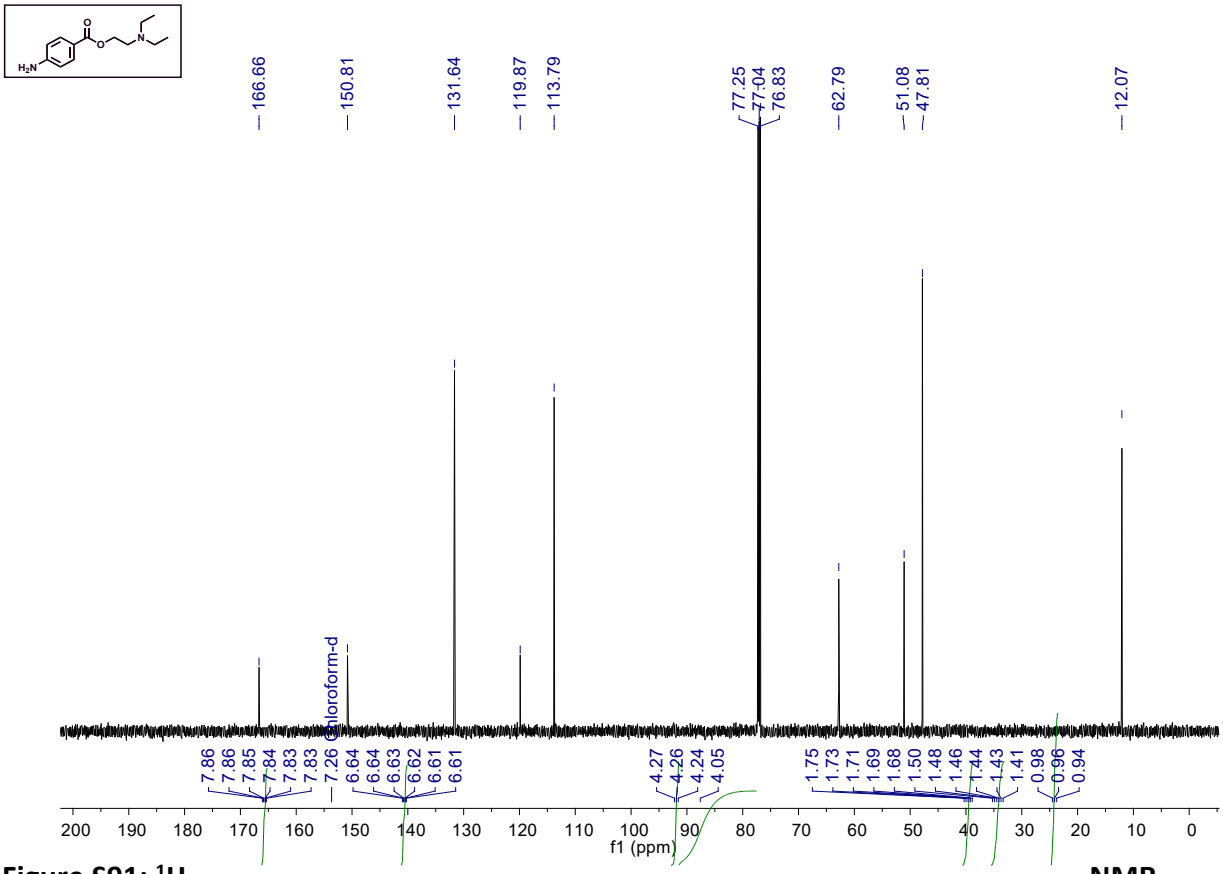

Figure S91: ^{1}H NMR spectrum of Butyl 4-aminobenzoate (46)

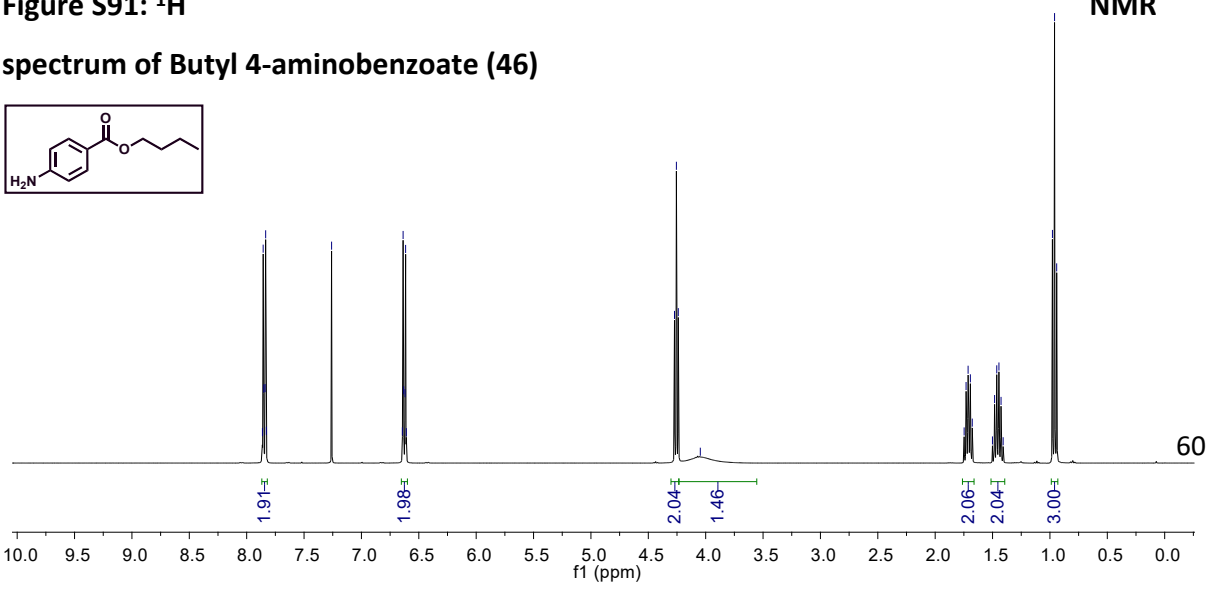

Figure S92: ^{13}C NMR spectrum of Butyl 4-aminobenzoate (46)

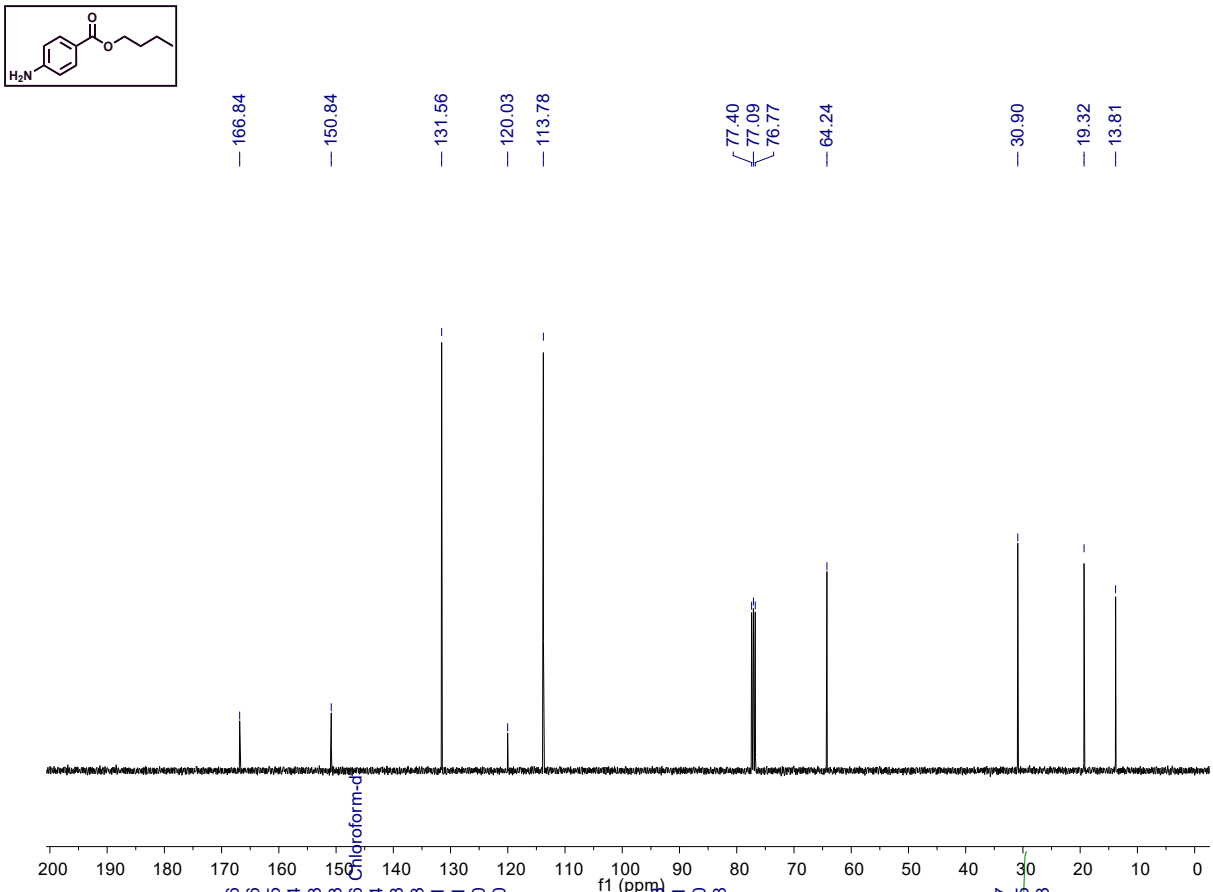

Figure S93: ^{1}H NMR spectrum of Ethyl 4-aminobenzoate (47)

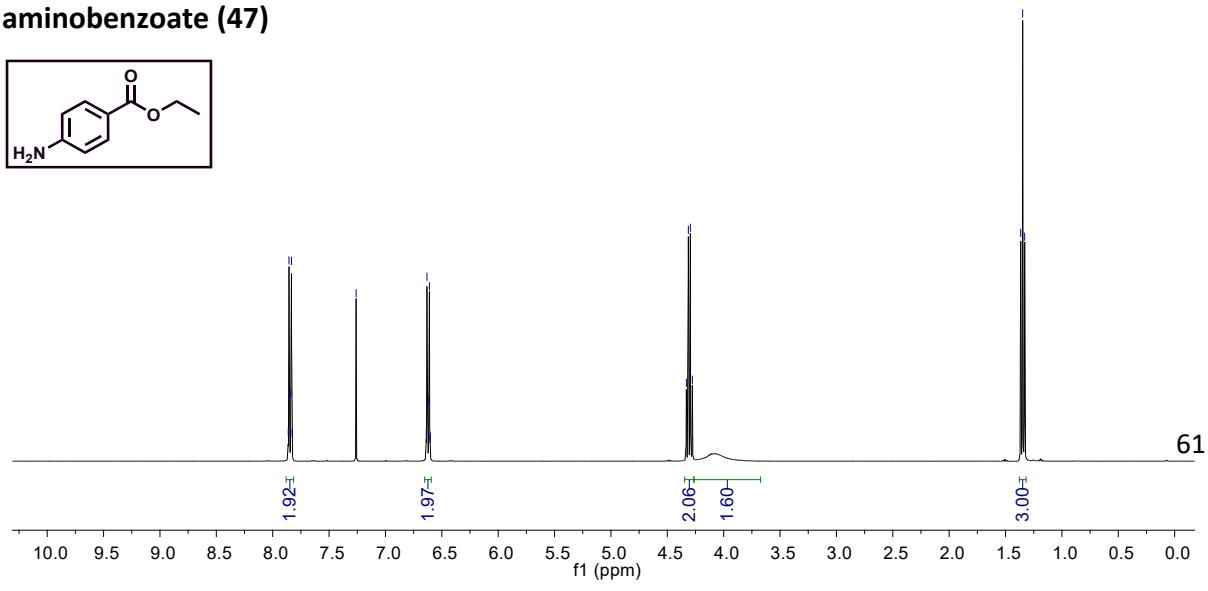

Figure S94: ^{13}C NMR spectrum of Ethyl 4-aminobenzoate (47)

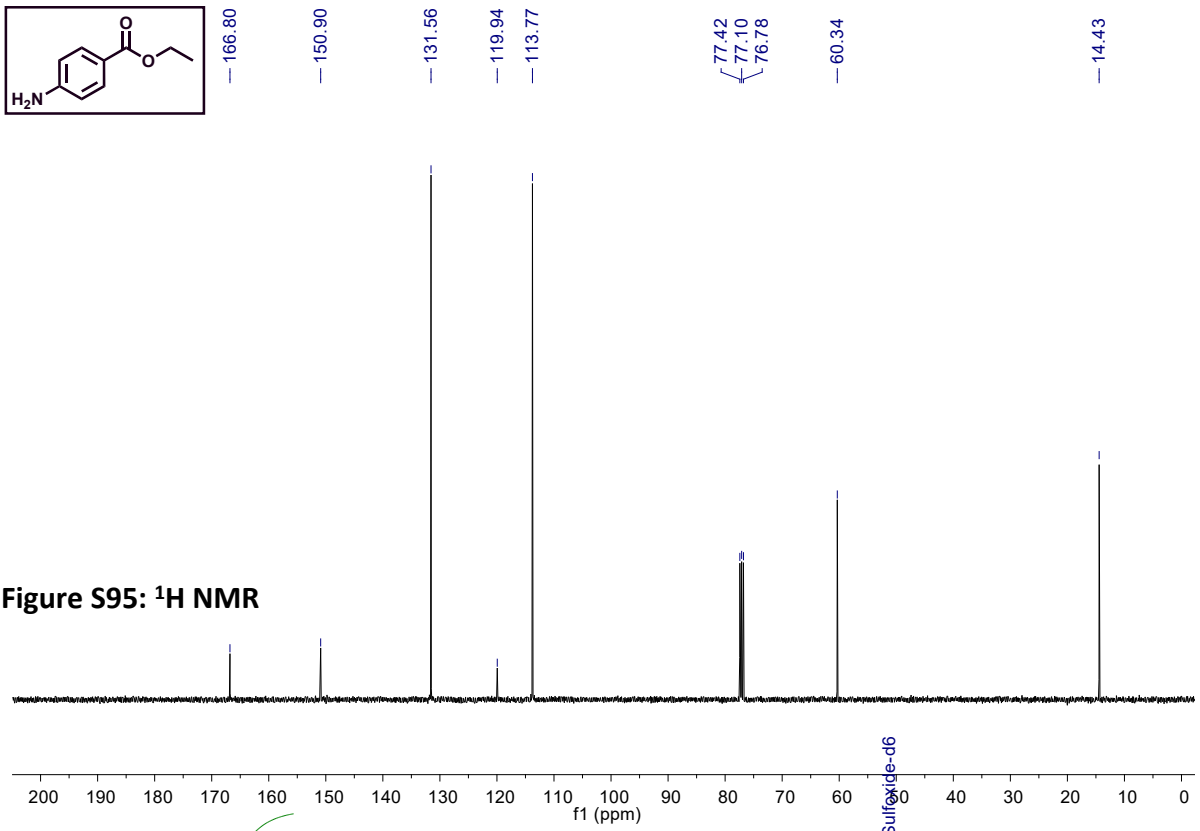

Figure S95: ^{1}H NMR spectrum of 5-Aminosalicylicacid (48)

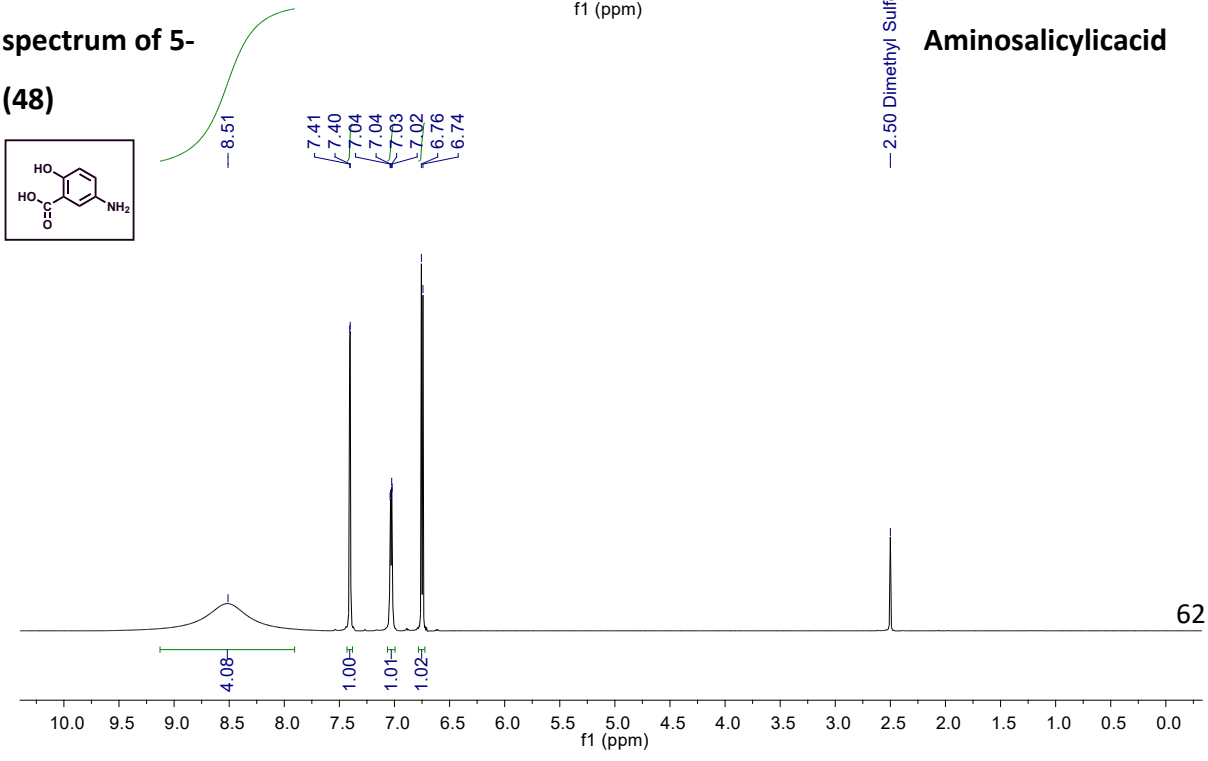

Figure S96: ^{13}C NMR spectrum of 5-Aminosalicylicacid (48)