Supporting Information

Ethanol as an H_2 Source: Transfer Hydrogenation of Sulfur and Halogen Containing Nitroarenes with Anti-Poisoning Platinum on Carbon Catalyst

Chitrarekha Dewangan[a], Reeshma Rameshan,[b] Suresh Perumal,[b] Narayana V. Kalevaru,[c] Sebastian Wohlrab,[c]* Rajenahally V. Jagadeesh,[c]* and Kishore Natte[a]*

[a]Laboratory for Sustainable Catalysis and Organic Synthesis, Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy 502 285, Telangana, India.

[b]Laboratory for Energy and Advanced Devices (LEAD), Department of Materials Science and Metallurgical Engineering, Indian Institute of Technology Hyderabad, Kandi, Sangareddy 502 285, Telangana, India.

[c]Leibniz-Institut für Katalyse e.V., Albert-Einstein-Str. 29A, Rostock 18059, Germany. Email: jagadeesh.rajenahally@catalysis.de

*Email: kishore.natte@chy.iith.ac.in ; sebastian.wohlrab@catalysis.de ; jagadeesh.rajenahally@catalysis.de

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1) Experimental section

a) General information

Substrates and related compounds were purchased from different companies and were used without any purification. The Pt/C (10 wt%) was purchased from HIMEDIA with the product no. GRM4777-1G. 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. ^{1}H 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. HRMS data were obtained on a Bruker micro TOF-QII or Agilent 5975C high-resolution mass spectrometers. Melting points were calculated using a manual melting point apparatus (280 Volts).

b) General Procedure for the Transfer Hydrogenation of Nitro Compound

A dried, 21 mL screw-cap pressure tube was charged with a magnetic stir bar, Pt/C 10 wt% Pt/C (25 mg), 4 equivalents of KO^{t}Bu (225 mg), and 0.5 mmol 4-chloronitrobenzene (79 mg). 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 aluminum block, and reactions were allowed to progress for the desired time (48 h) and temperature (150 ˚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.

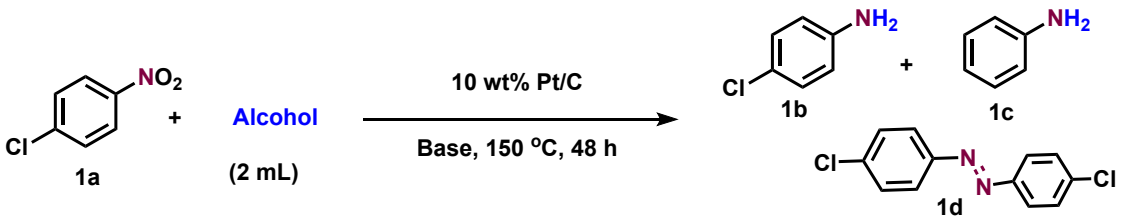
c) Gram-scale synthesis of 4-chloroaniline

A dry, 50 mL screw-cap Ace Schlenk tube was charged with a magnetic stir bar, 10 wt% Pt/C (312 mg), 4 Equivalent of KO^{t}B*u* (3 gm) and 1 gm (6.4 mmol) 4-Nitrochlorobenzene. Then, ethanol (20 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 an oil bath, and reactions were allowed to progress for the desired time (48 h) and temperature (150 ˚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 89% yield (726.64 mg), which was further submitted for NMR analysis.

d) Safety advice

All transfer hydrogenation reactions are carried out in ACE® pressure tubes. Hydrogenation reactions with KO^{t}Bu in the presence of Pt/C at high temperatures are, in general, exothermic. Hence, appropriate safety measurements are required.

2) Table T1. Transfer hydrogenation of 4-chloronitrobenzene with different alcohols[a]



Entry	Catalyst	Base (4 equiv.)	Yield 1b (%)	Yield 1c (%)	Yield 1d (%)
1	Isopropanol	KO^{t}Bu	58	12	8
2	Butanol	KO^{t}Bu	28	2	9
3	Pentanol	KO^{t}Bu	26	5	7

[a]General reaction conditions: 1a (0.5 mmol), alcohol (2 mL), 10 wt% Pt/C (25 mg), base (4 equiv.), 150 °C, 48 h.

3) XPS of Pt/C catalyst

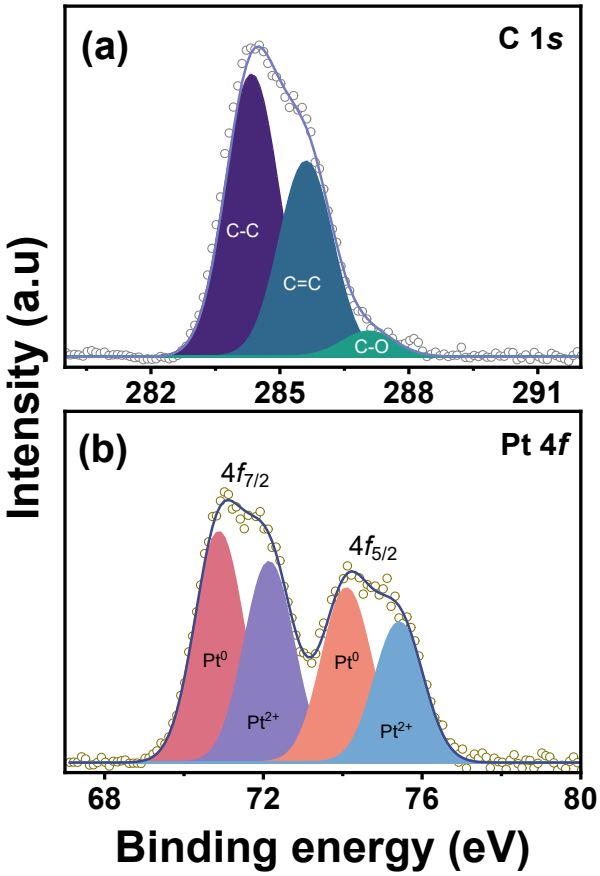


Figure S1: XPS core level spectra of (a) C 1*s* and (b) Pt 4*f*

4) XRD Pattern of Pt/C catalyst

The XRD pattern of the Pt/C catalyst is shown in **Figure S2**. The broad diffraction peak centered at ~24.3º corresponds to the (002) plane of amorphous carbon, indicating a disordered carbon support. The 2θ reflections at ~39.8º, 46.2º, 67.5º, and 81.3º are indexed to the (111), (200), (220), and (311) planes of face-centred cubic metallic Pt, respectively (JCPDS no. 04–0802). The broad nature of the Pt peaks suggests nanosized Pt crystallites with high dispersion on the carbon support.

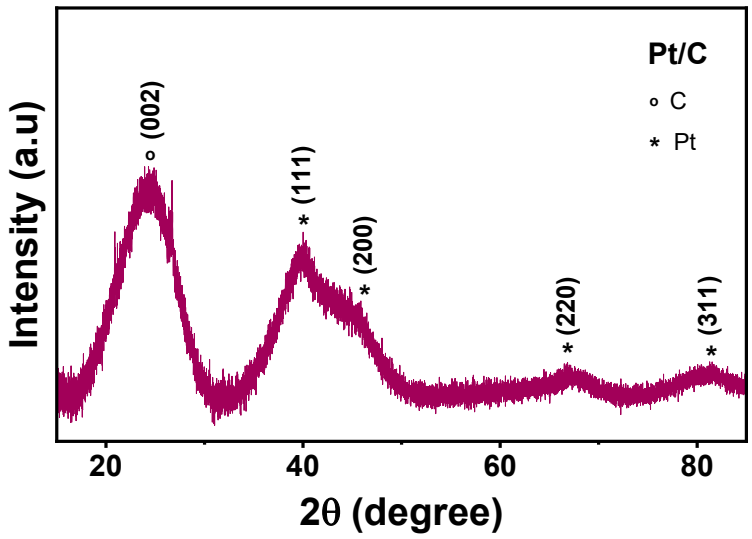
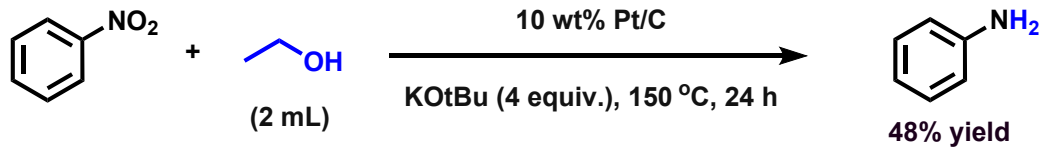


Figure S2: XRD Pattern of Pt/C catalyst

5) Catalyst leaching experiments

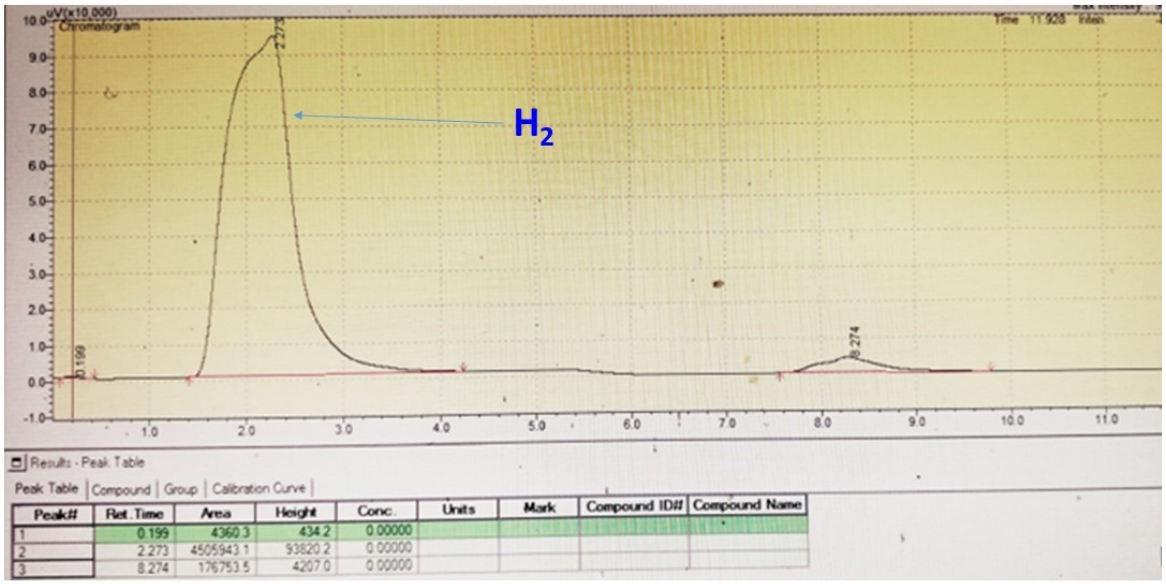
For the study of catalyst leaching, we performed the reaction of nitrobenzene with ethanol at a 24 h reaction time and obtained a 48% yield.



Reaction conditions: Substrate (0.5 mmol), ethanol (2 mL), 10 wt% Pt/C (25 mg), KO^{t}Bu (4 equiv.), 150 °C, 24 h, isolated yield.

Following that, we filtered the catalyst out of the reaction mixture and kept the reaction solution for 24 hours at 150 °C, obtaining 60% of the product. This indicated that some catalyst had been deactivated in the reaction media.

6) GC-FID of ethanol degradation experiment

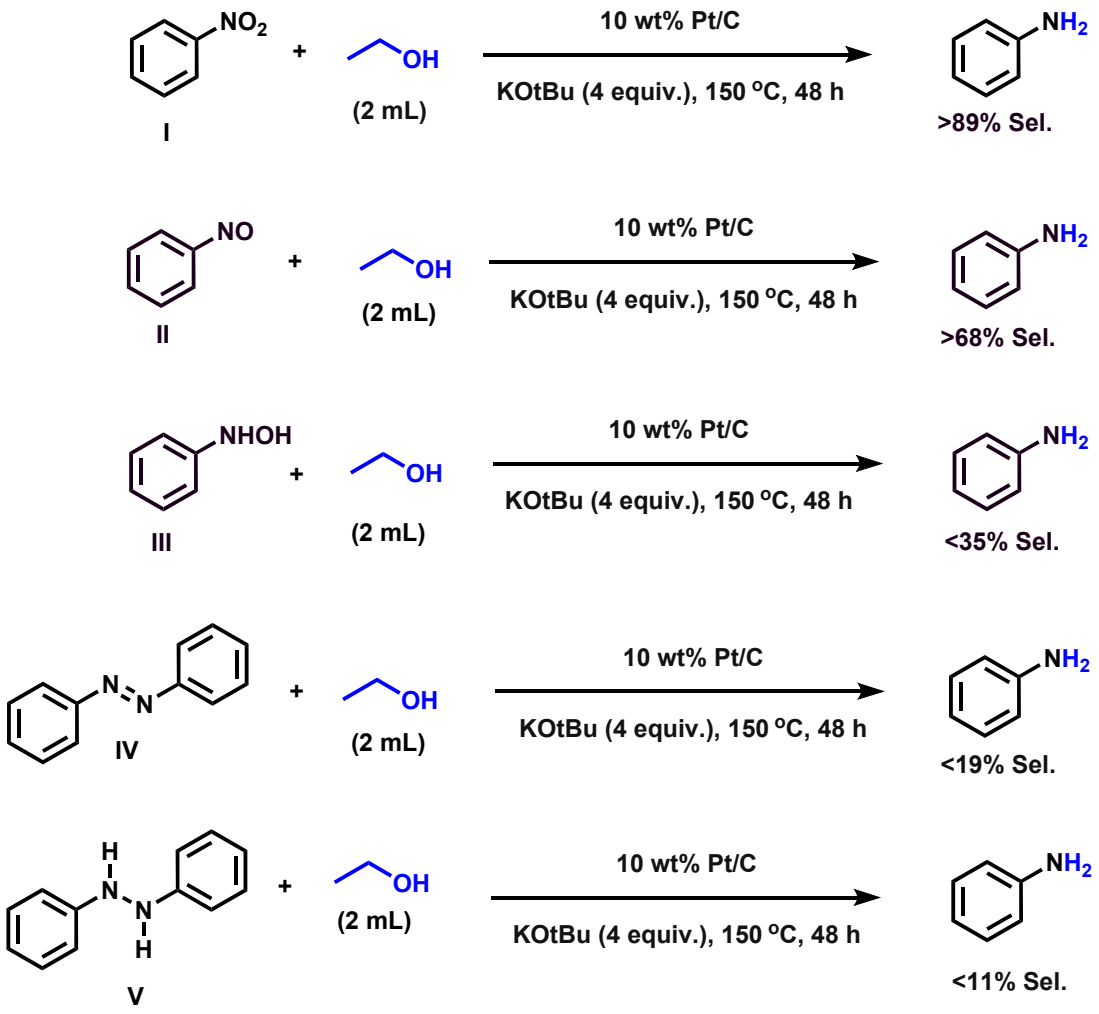


Peak#	Ret. Time	Area	Height	Conc.	Units	Mark	Compound ID#	Compound Name
1	0.199	4360.3	434.2	0.00000				
2	2.273	4505943.1	93820.2	0.00000				
3	8.274	176753.5	4207.0	0.00000				

Figure S3. Evolution of H_2 from ethanol

7) Mechanistic Study

To study the mechanism of our reaction, we performed control experiments with possible intermediates.

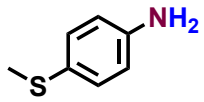


Reaction conditions: Substrate (0.5 mmol), ethanol (2 mL), 10 wt% Pt/C (25 mg), KO^{t}Bu (4 equiv.), 150 °C, 48 h.

Nitroso benzene and phenyl hydroxyl amine yield aniline with >68% and <35% selectivity, respectively. Azobenzene and hydrazobenzene produced aniline with <19% and <11% selectivity. Based on the above results, the nitro group undergoes direct reduction in the presence of the Pt/C system.

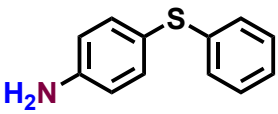
8) Spectroscopic data (^{1}H & ^{13}C)

4-(Methylthio)aniline (1)



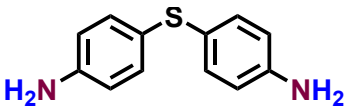
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 2H), 6.67 – 6.56 (m, 2H), 3.56 (s, 2H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.2, 131.1, 125.6, 115.8, 18.8.

4-Aminophenyl(phenyl)sulfane (2)



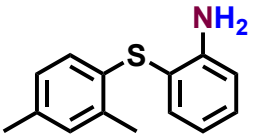
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 6.73 – 6.66 (m, 2H), 3.68 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 139.8, 136.2, 128.9, 127.3, 125.3, 120.4, 115.9.

4((4-Aminophenyl)thio)aniline (3)



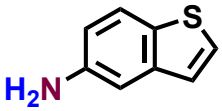
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.8 Hz, 4H), 6.56 (d, *J* = 7.9 Hz, 4H), 3.62 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8, 132.8, 124.8, 115.8.

3-((2,4-dimethyl phenyl)thio)aniline (4)



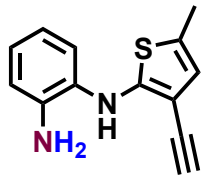
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.03 (s, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.83 – 6.66 (m, 3H), 3.90 (s, 2H), 2.42 (s, 3H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 148.4, 136.6, 135.8, 135.4, 131.8, 131.2, 130.5, 127.6, 126.6, 118.9, 115.4, 115.1, 20.8, 20.1.

5-Aminobenzothiophene (5)



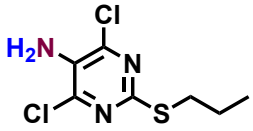
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 1H), 7.16 (d, *J* = 5.4 Hz, 1H), 7.09 (s, 1H), 6.78 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.48 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 140.9, 130.5, 127.2, 123.1, 122.9, 114.9, 108.4.

2-((2-Aminohenyl)amino-5-methyl-thiophene-3-carbonitrile (6)



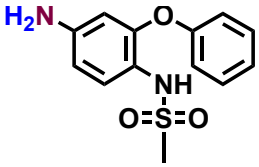
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.12 – 7.03 (m, 1H), 6.88 – 6.74 (m, 2H), 6.53 (s, 1H), 6.44 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.9, 141.4, 127.9, 127.6, 124.9, 122.2, 119.5, 117.0, 116.3, 86.7, 15.0.

4,6-Dichloro-2-(propylthio)pyrimidine-5-amine (7)



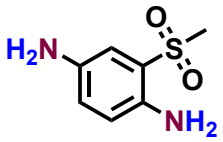
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.19 – 2.62 (m, 2H), 1.87 – 1.64 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 145.2, 131.5, 33.4, 22.4, 13.4.

Nimesulide (8)



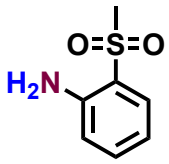
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 10.3, 6.2, 2.4 Hz, 3H), 7.21 – 7.14 (m, 1H), 7.07 – 6.94 (m, 2H), 6.43 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.33 (s, 1H), 6.17 (d, *J* = 2.5 Hz, 1H), 3.67 (s, 2H), 2.92 (s, 3H). **^{13}CNMR (151 MHz, $CDCl_3$)** δ 155.8, 150.5, 146.1, 130.1, 127.2, 124.3, 118.9, 117.8, 110.6, 104.5, 38.9.

2-(Methylsulfonyl) benzene-1,4-diamine (9)



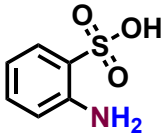
^{1}H NMR (400 MHz, DMSO) δ 6.88 (d, *J* = 2.4 Hz, 1H), 6.72 (dt, *J* = 16.5, 5.5 Hz, 2H), 5.09 (s, 4H), 3.04 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 138.9, 138.5, 123.3, 122.2, 119.3, 113.0, 41.9. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_7H_{11}N_2O_2S$ 187.0541; Found 187.0534.

1-Methylsulfonyl-2-aniline (10)



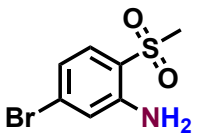
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.34 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 6.79 (ddd, *J* = 19.1, 9.5, 4.5 Hz, 2H), 5.05 (s, 2H), 3.04 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3, 135.2, 129.3, 121.8, 117.9, 117.7, 42.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_7H_{10}NO_2S$ 172.0432; Found 172.0432.

2-Aminosulfonicacid (11)



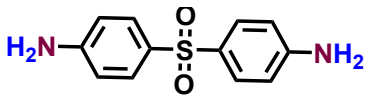
^{1}H NMR (400 MHz, DMSO) δ 9.50 (s, 3H, NH_3^+), 7.78 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (td, *J* = 7.7, 1.6 Hz, 1H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.8, 0.9 Hz, 1H). **^{13}C NMR (101 MHz, DMSO)** 140.5, 131.1, 128.7, 128.3, 128.1, 124.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_6H_8NO_3S$ 174.0225; Found 174.0210. Melting Point: 300 °C.

5-Bromo-2-(methylsulfonyl)aniline (12)



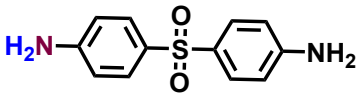
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.3 Hz, 1H), 7.44 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 5.04 (s, 2H), 3.06 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 145.1, 137.9, 131.6, 123.3, 119.4, 109.3,42.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_7H_9BrNO_2S$ 249.9537; Found 249.9532.

4-(4-sulfonyldianiline) (13)



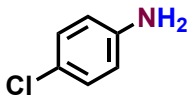
^{1}H NMR (400 MHz, DMSO) δ 7.45 (d, *J* = 8.7 Hz, 4H), 6.58 (d, *J* = 8.7 Hz, 4H), 6.00 (s, 4H). **^{13}C NMR (101 MHz, DMSO)** δ 153.2, 129.0, 128.6, 113.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2S$ 249.0698; Found 249.0681. Melting Point: 175 to 176 °C.

4-(4-sulfonyldianiline) (14)



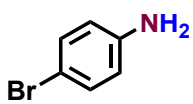
^{1}H NMR (400 MHz, DMSO) δ 7.45 (d, *J* = 8.7 Hz, 4H), 6.58 (d, *J* = 8.7 Hz, 4H), 6.00 (s, 4H). **^{13}C NMR (101 MHz, DMSO)** δ 153.2, 129.0, 128.6, 113.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2S$ 249.0698; Found 249.0681. Melting Point: 175 to 176 °C.

4-Chloroaniline (15)



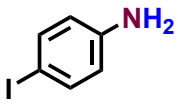
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 3.45 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.9, 129.1, 123.1, 116.3.

4-Bromoaniline (16)



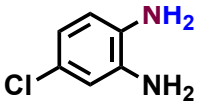
^{1}H NMR (400 MHz, $CDCl_3$) 7.25 – 7.20 (m, 2H), 6.58 – 6.52 (m, 2H), 3.51 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.5, 132.0, 116.7, 110.2.

4-Iodoaniline (17)



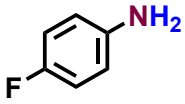
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 6.51 – 6.31 (m, 2H), 3.50 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.1, 137.9, 117.3, 79.4.

4-Chlorobenzene-1,2-diamine (18)



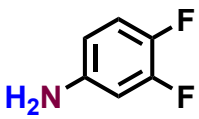
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (d, J = 2.2 Hz, 1H), 6.66 (dd, J = 8.2, 2.3 Hz, 1H), 6.61 (d, J = 8.2 Hz, 1H), 3.33 (s, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.1, 133.1, 124.8, 119.6, 117.6, 116.3.

4-Fluoroaniline (19)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 – 6.83 (m, 2H), 6.64 – 6.56 (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).

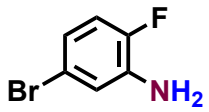
3,4-Difluoroaniline (20)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dt, J = 10.3, 8.8 Hz, 1H), 6.45 (ddd, J = 12.1, 6.7, 2.8 Hz, 1H), 6.36 – 6.29 (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, $J_{C\text{-}F}$ = 230 Hz), 143.4 (dd, $J_{C\text{-}F}$ = 11 Hz, $J_{C\text{-}F}$ = 6 Hz), 143.7 (dd, $J_{C\text{-}F}$ = 248 Hz, $J_{C\text{-}F}$

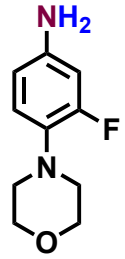
= 223 Hz), 117.5 (dd, $J_{C\text{-}F}$ = 18 Hz, $J_{C\text{-}F}$ = 18 Hz), 110.3 (dd, $J_{C\text{-}F}$ = 9 Hz, $J_{C\text{-}F}$ = 2 Hz) 103.9 (d, $J_{C\text{-}F}$ = 20 Hz).

5-Bromo-2-fluoroaniline (21)



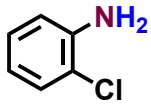
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.58 (m, 3H), 3.70 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.7 (d, $J_{C\text{-}F}$ = 230 Hz), 136.1 (d, $J_{C\text{-}F}$ = 14 Hz), 121.1 (d, $J_{C\text{-}F}$ = 6 Hz), 119.4 (d, $J_{C\text{-}F}$ = 4 Hz), 116.8 (d, $J_{C\text{-}F}$ = 3 Hz), 116.6 (d, $J_{C\text{-}F}$ = 20 Hz).

3-Fluoro-4-morpholinoaniline (22)



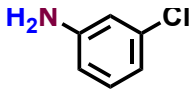
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dd, J = 13.1, 5.2 Hz, 1H), 6.53 – 6.05 (m, 2H), 3.94 – 3.70 (m, 4H), 3.45 (s, 2H), 3.03 – 2.81 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.8 (d, $J_{C\text{-}F}$ = 244 Hz), 142.9 (d, $J_{C\text{-}F}$ = 10 Hz), 131.7 (d, $J_{C\text{-}F}$ = 10 Hz), 120.3 (d, $J_{C\text{-}F}$ = 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).

2-Chloroaniline (23)



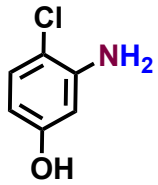
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 1H), 6.96 (td, J = 7.7, 1.4 Hz, 1H), 6.65 (dd, J = 8.1, 1.4 Hz, 1H), 6.59 (td, J = 7.7, 1.4 Hz, 1H), 3.81 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.9, 129.4, 127.7, 119.3, 119.1, 115.9.

3-Chloroaniline (24)



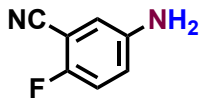
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.75 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 6.67 (t, *J* = 2.1 Hz, 1H), 6.59 – 6.50 (m, 1H), 3.63 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.8, 134.8, 130.4, 118.4, 114.9, 113.3.

3-Amino-4-chlorophenol (25)



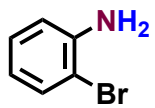
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.03 – 6.75 (m, 1H), 6.34 – 5.96 (m, 2H), 3.98 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$& DMSO-d_6)** δ 156.8, 143.7, 129.6, 109.8, 106.7, 102.8.

5-Amino-2-fluorobenzonitrile (26)



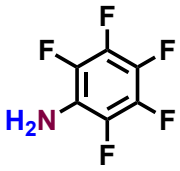
^{1}H NMR (400 MHz, DMSO) δ 7.12 (t, *J* = 9.1 Hz, 1H), 6.94 – 6.77 (m, 2H), 5.46 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.5 (d, $J_{C\text{-}F}$ = 241 Hz), 146.5(d, $J_{C\text{-}F}$ = 1 Hz), 120.7(d, $J_{C\text{-}F}$ = 7Hz), 117.28 (d, $J_{C\text{-}F}$ = 20 Hz), 115.6 (d, $J_{C\text{-}F}$ = 82 Hz), 99.9 (d, $J_{C\text{-}F}$ = 16 Hz). HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_7H_6FN_2$ 137.0515 Found 137.0500. Melting Point: 92 to 96 °C.

2-Bromoaniline (27)



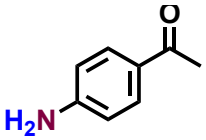
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.3, 1.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.65 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 4.09 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** 144.2, 132.6, 128.4, 119.5, 115.9, 109.4.

2,3,4,5,6-Pentafluoroaniline (28)



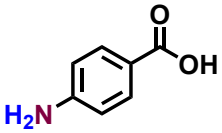
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.2, 137.8, 136.8, 135.4, 134.6, 132.1, 121.9.

1-(4-Aminophenyl)ethane-1-one (29)



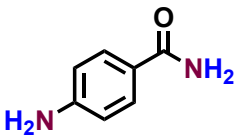
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.59 (m, 2H), 6.71 – 6.40 (m, 2H), 4.27 (s, 2H), 2.48 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.7, 151.4, 130.8, 127.6, 113.7, 26.1.

4-Aminobenzoic acid (30)



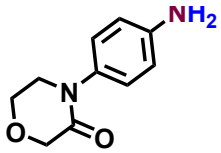
^{1}H NMR (400 MHz, MeOD) δ 9.49 – 9.23 (m, 2H), 8.36 – 8.03 (m, 2H), 6.25 (s, 3H, NH_3^+). **^{13}C NMR (101 MHz, MeOD)** δ 169.5, 152.1, 131.8, 118.6, 113.6.

4-Aminobenzamide (31)



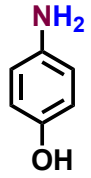
^{1}H NMR (400 MHz, MeOD) δ 9.37 – 8.93 (m, 2H), 8.39 – 8.05 (m, 2H), 6.44 (s, 4H). **^{13}C NMR (101 MHz, MeOD)** δ 171.4, 152.1, 129.1, 120.9, 113.3.

4-(4-Aminophenyl)Morholin-3-one (32)



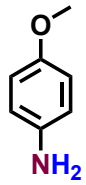
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.95 (m, 2H), 6.68 – 6.61 (m, 2H), 4.30 (s, 2H), 3.98 (dd, *J* = 5.8, 4.4 Hz, 2H), 3.67 (dd, *J* = 5.7, 4.5 Hz, 4H, CH_2 and NH_2). **^{13}C NMR (101 MHz, $CDCl_3$)** 166.9, 145.8, 132.1, 126.8, 115.5, 68.6, 64.2, 50.2.

4-Aminophenol (33)



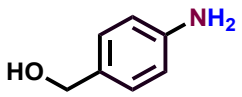
^{1}H NMR (600 MHz, DMSO) δ 8.42 (s, 1H), 6.53 – 6.41 (m, 4H), 4.37 (s, 2H). **^{13}C NMR (151 MHz, DMSO)** δ 148.8, 141.0, 116.1, 115.9.

***p*-Anisidine (34)**



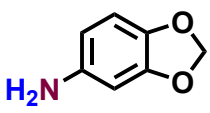
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 – 6.71 (m, 2H), 6.69 – 6.59 (m, 2H), 3.75 (s, 3H), 3.31 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 140.0, 116.4, 114.8,55.7.

4-Aminobenzylalcohol (35)



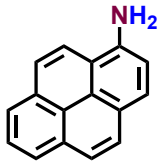
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.28 (s, 2H), 3.72 (s, 2H), 2.70 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** 146.0, 131.2, 128.4, 114.7, 64.3.

3,4-(Methylenedioxy)aniline (36)



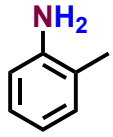
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (d, *J* = 8.2 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.11 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.84 (s, 2H), 3.45 (s, *J* = 94.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.2, 141.4, 140.3, 108.6, 106.9, 100.7, 98.1.

Pyrene-1-amine (37)



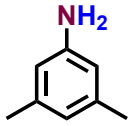
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 8.00 – 7.89 (m, 5H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 4.42 (s, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.9, 132.2, 131.7, 127.7, 127.5, 126.1, 126.0, 125.5, 125.0, 124.3, 124.1, 123.8, 123.6, 120.2, 116.8, 114.0.

***o*-Toluidine (38)**



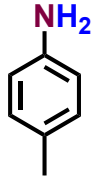
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.4 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 3.54 (s, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** 144.7, 130.6, 127.1, 122.4, 118.7, 115.1, 17.5.

3,5-dimethylaniline (39)



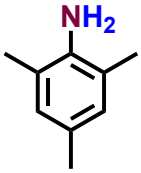
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 1H), 6.42 (s, 2H), 3.58 (s, 2H), 2.36 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 139.1, 120.6, 113.3, 21.5.

***p*-Toluidine (40)**



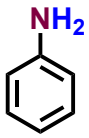
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.44 (s, 2H), 2.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.9, 129.8, 127.8, 115.3, 20.5.

2,4,6-trimethylamine (41)



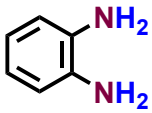
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 3.48 (s, 2H), 2.35 (s, 3H), 2.28 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.6, 124.2, 122.4, 117.2, 15.8, 12.9.

Aniline (42)



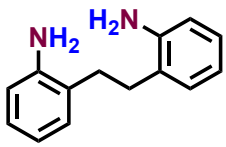
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 2H), 6.99 (td, *J* = 7.4, 0.9 Hz, 1H), 6.80 (dt, *J* = 3.0, 1.5 Hz, 2H), 3.74 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.9, 129.6, 118.6, 115.4.

Benzene-1,2-diamine (43)



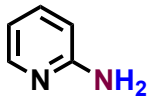
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 – 6.56 (m, 4H), 3.37 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.8, 120.3, 116.8.

2,2'-(Ethane-1,2-diyl)dianiline (44)



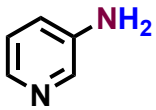
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, *J* = 8.4 Hz, 4H), 6.77 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 3.37 (s, 4H), 2.82 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.3, 129.6, 127.3, 126.3, 119.1, 115.9, 31.0.

2-Aminopyridine (45)



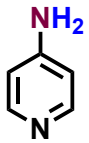
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 5.3 Hz, 1H), 7.37 (ddd, *J* = 13.1, 4.2, 3.3 Hz, 1H), 6.63 – 6.54 (m, 1H), 6.46 – 6.43 (m, 1H), 4.60 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6, 148.0, 137.7, 113.9, 108.6.

3-Aminopyridine (46)



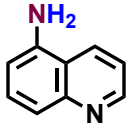
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.5 Hz, 1H), 7.95 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.92 (ddd, *J* = 8.2, 2.8, 1.4 Hz, 1H), 3.73 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.7, 139.7, 137.4, 123.8, 121.4.

4-Aminopyridine (47)



^{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). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 152.8, 150.2, 109.6.

Quinoline-8-amine (48)



^{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), 7.40 – 7.28 (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, 138.4, 136.0, 128.9, 127.4, 121.4, 116.0, 110.1.

Figure S4: ^{1}H NMR of 4-Methylthioaniline (1)

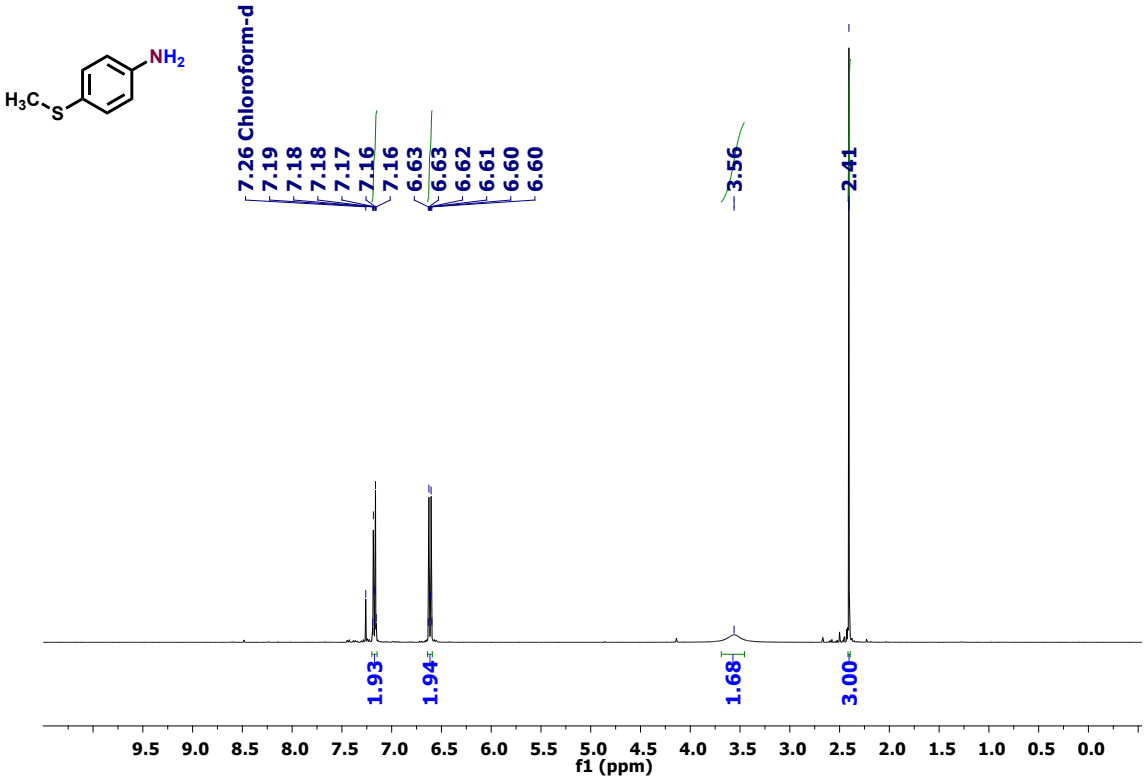


Figure S5: ^{13}C NMR of 4-Methylthioaniline (1)

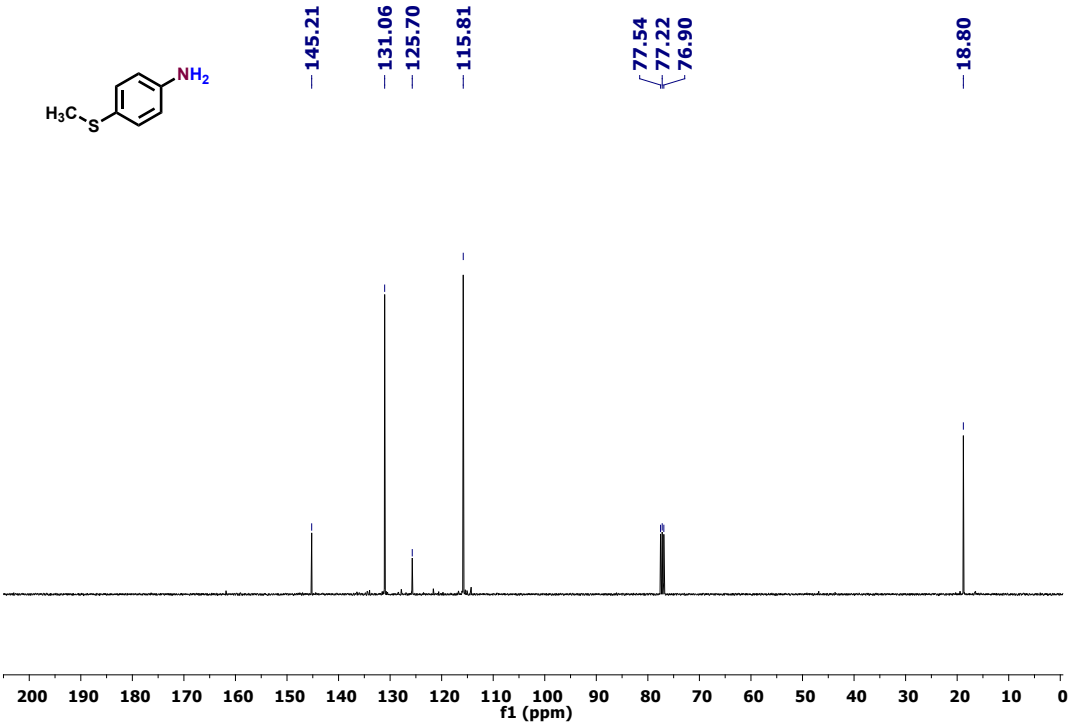


Figure S6: ^{1}H NMR of 4-Aminophenyl(phenyl)sulfane (2)

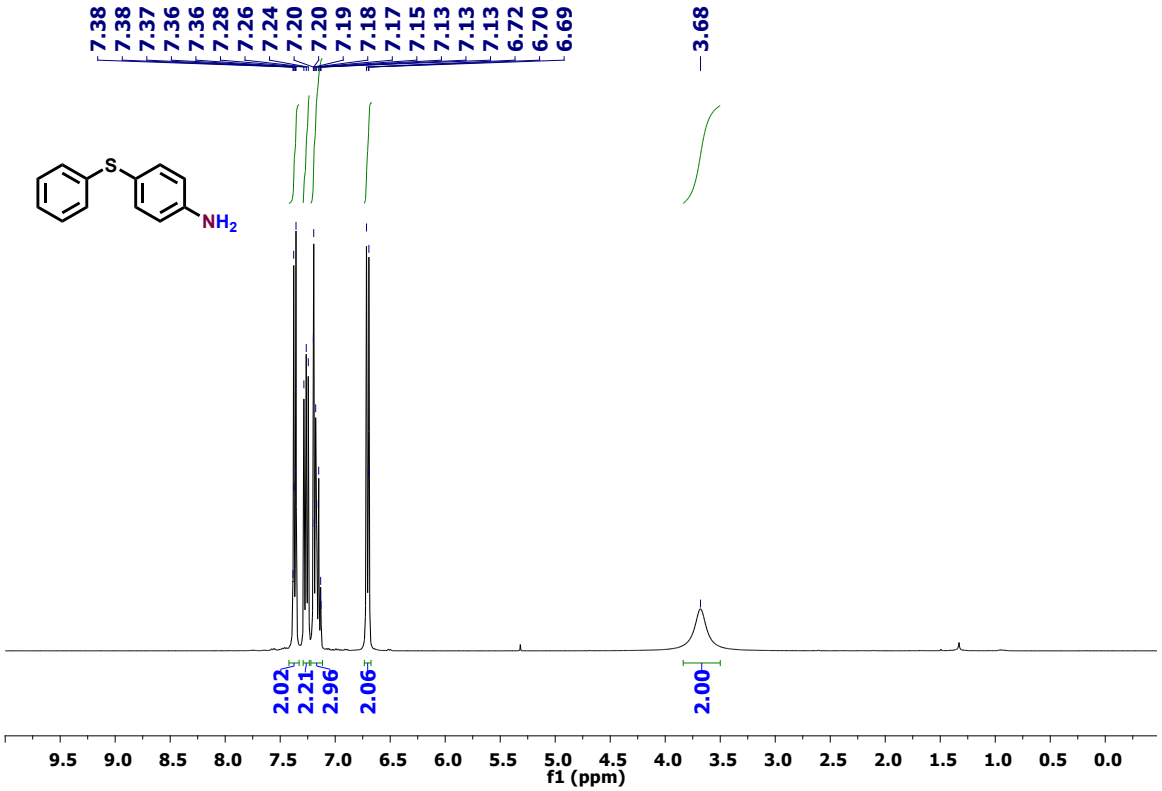


Figure S7: ^{13}C NMR of 4-Aminophenyl(phenyl)sulfane (2)

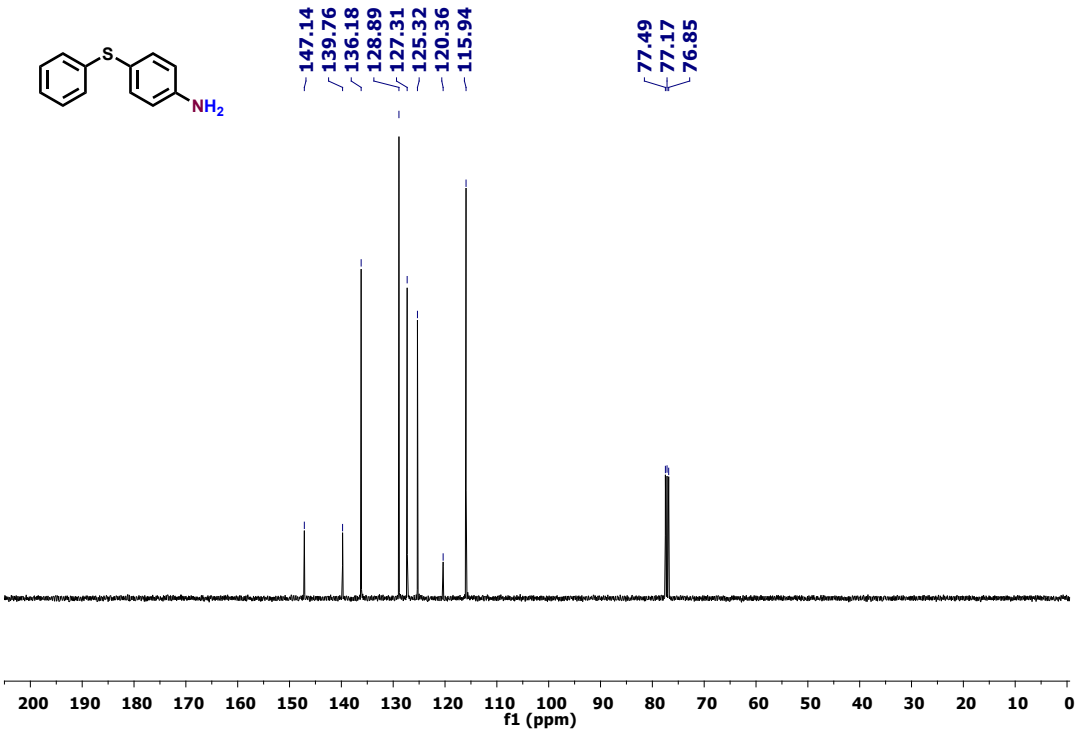


Figure S8: ^{1}H NMR of 4-((4-Aminophenyl)thioaniline (3)

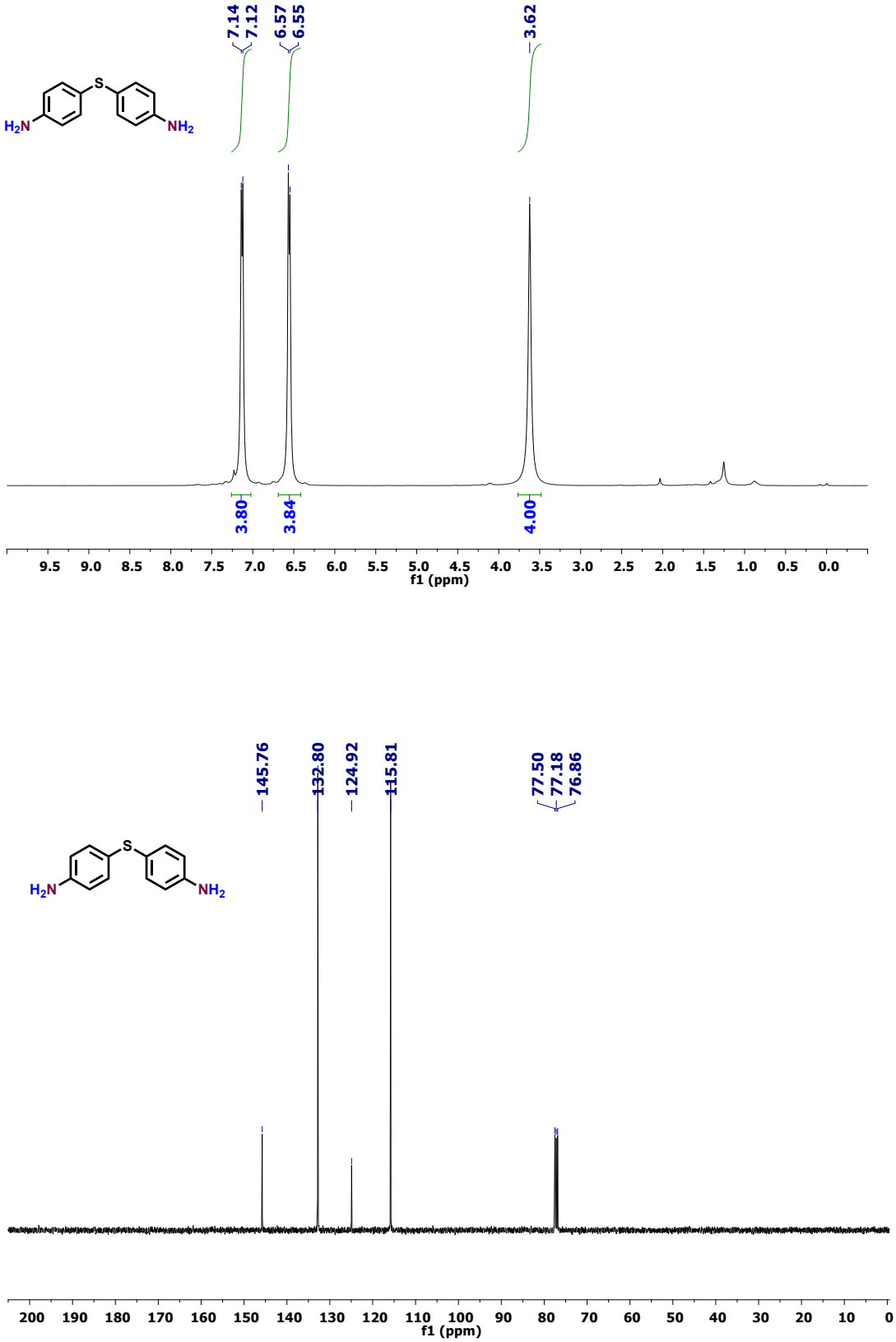


Figure S9: ^{13}C NMR of 4-((4-Aminophenyl)thioaniline (3)

Figure S10: ^{1}H NMR of 3-((2,4-Dimethyl phenyl)thio)aniline (4)

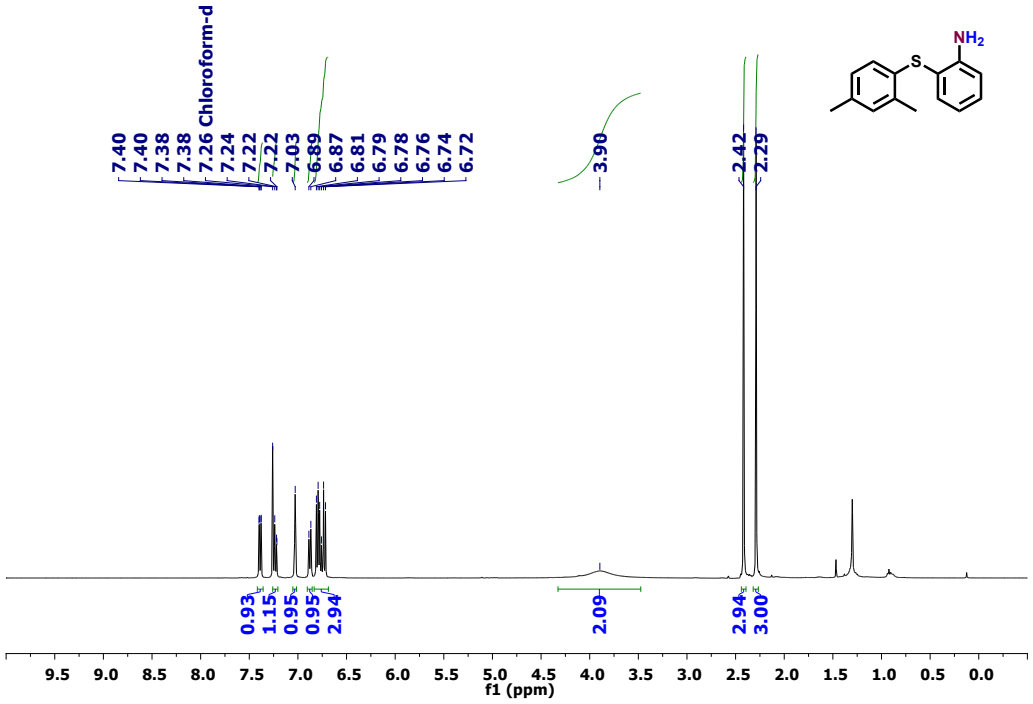


Figure S11: ^{13}C NMR of 3-((2,4-Dimethyl phenyl)thio)aniline (4)

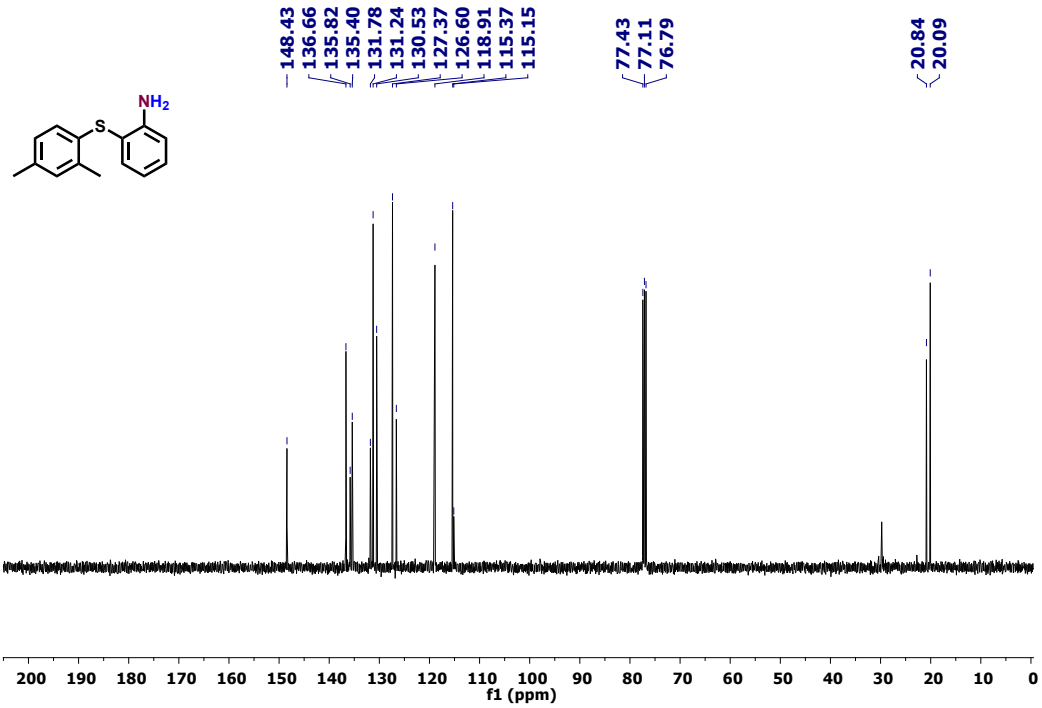


Figure S12: ^{1}H NMR of 5-Aminobenzothiohene (5)

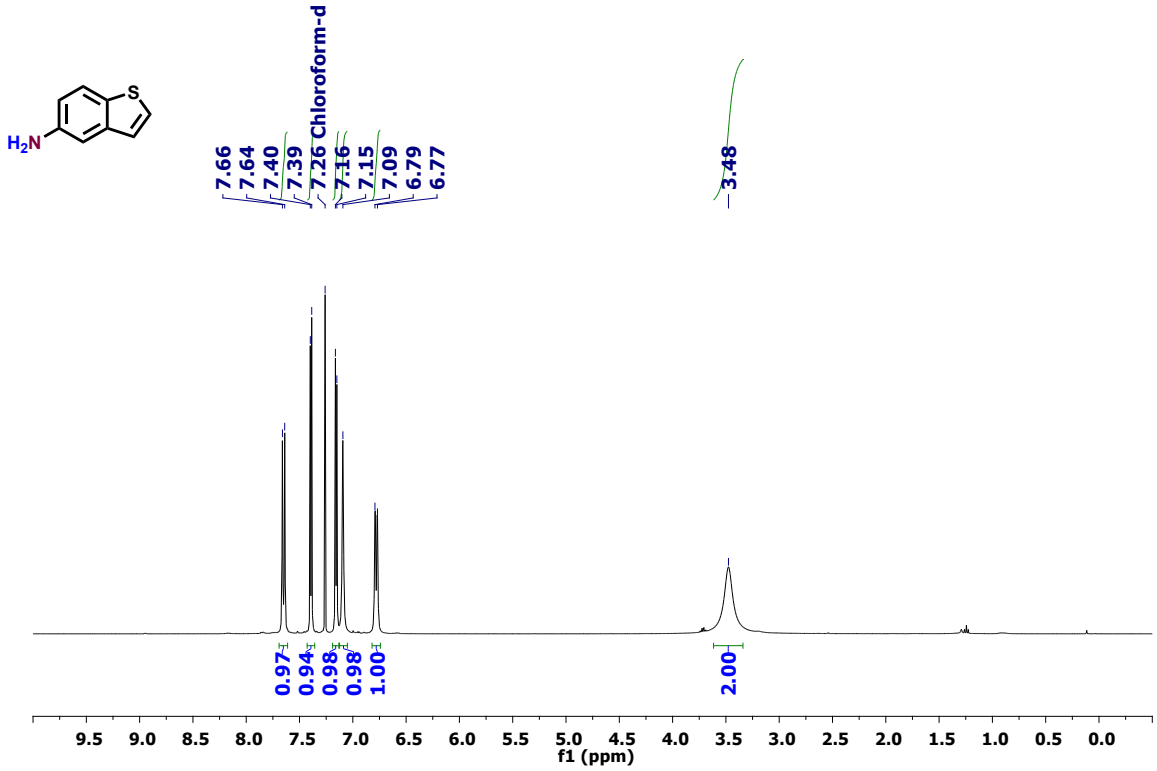


Figure S13: ^{13}C NMR of 5-Aminobenzothiohene (5)

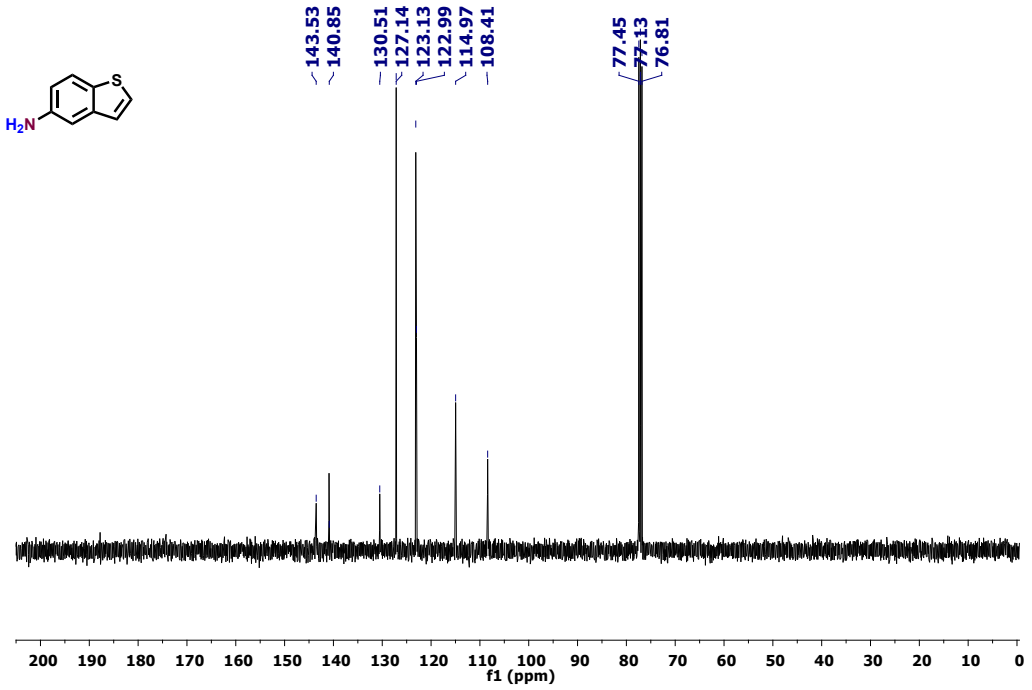


Figure S14: ^{1}H NMR of 5-(Methyl)-2-((-2aminophenyl) aminothiophene-3-carbonitrile (6)

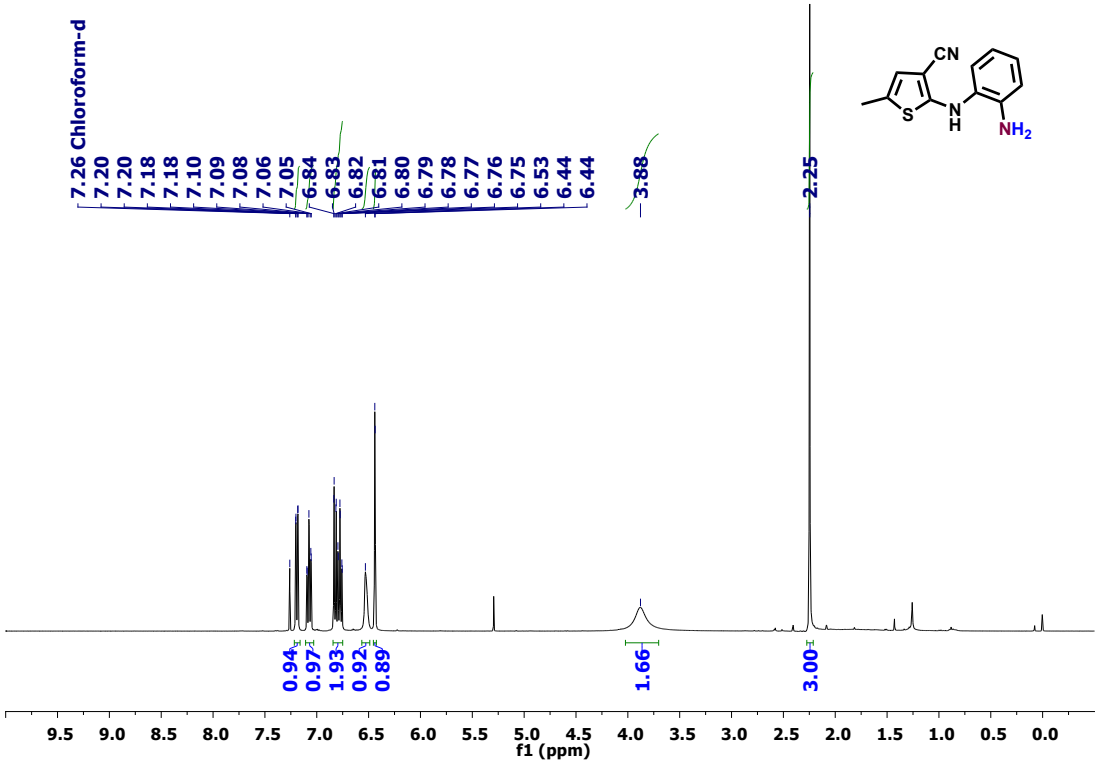


Figure S15: ^{13}C NMR spectrum of 5-(Methyl)-2-((-2aminophenyl) aminothiophene-3 carbonitrile (6)

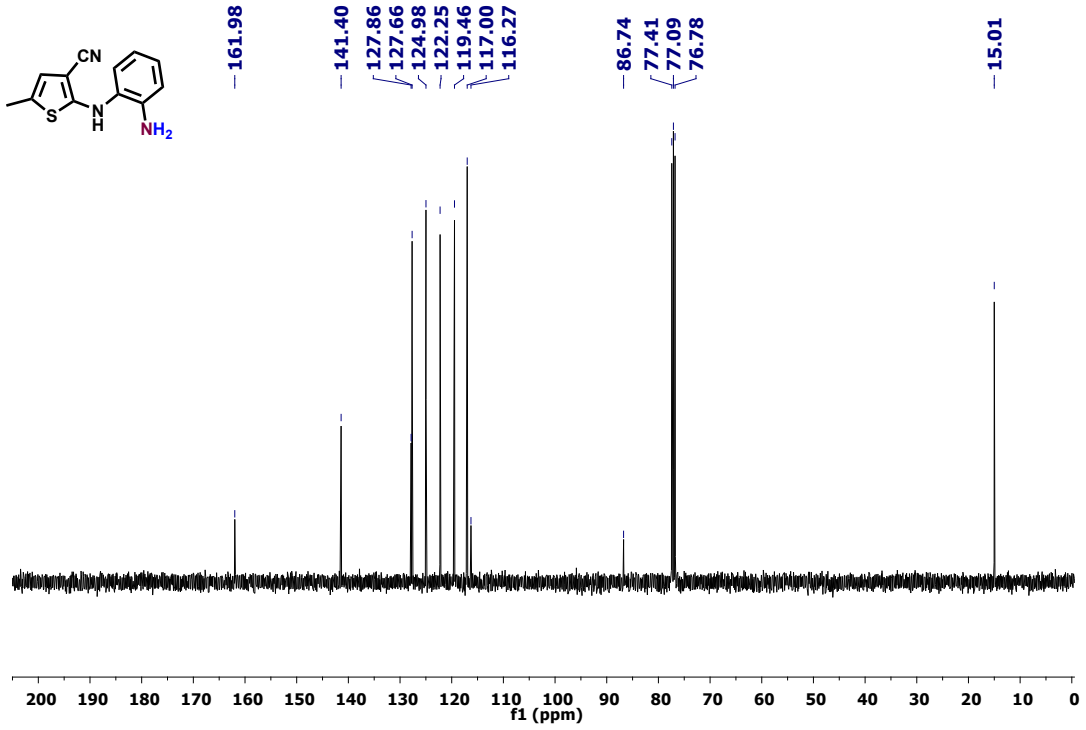


Figure S16: ^{1}H NMR of 4,6-Dichloro-5-Amino-2(propylthio)pyrimidine (7)

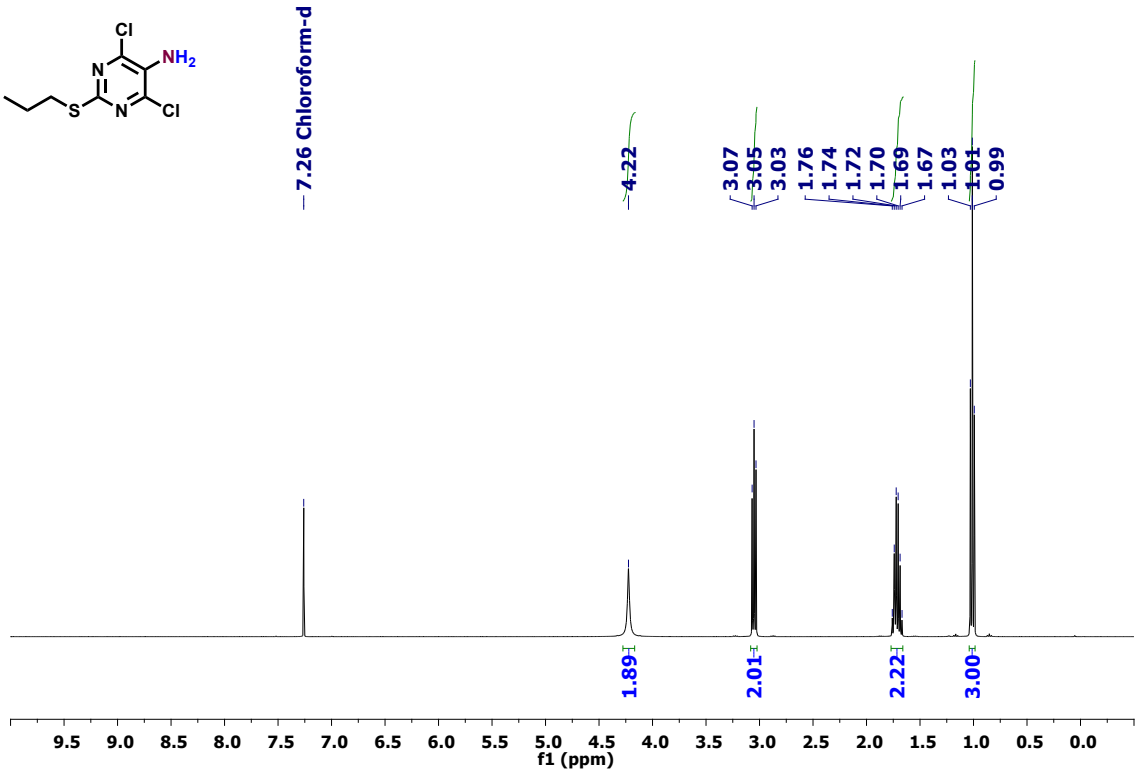


Figure S17: ^{13}C NMR of 4,6-Dichloro-5-Amino-2(propylthio)pyrimidine (7)

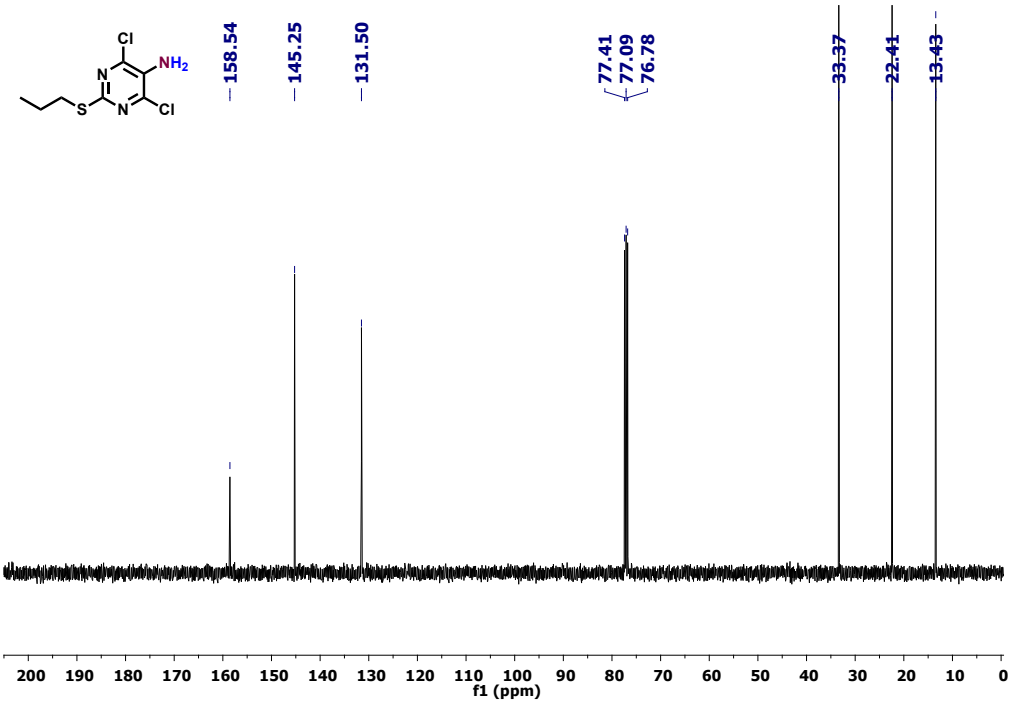


Figure S18: ^{1}H NMR of Nimesulide (8)

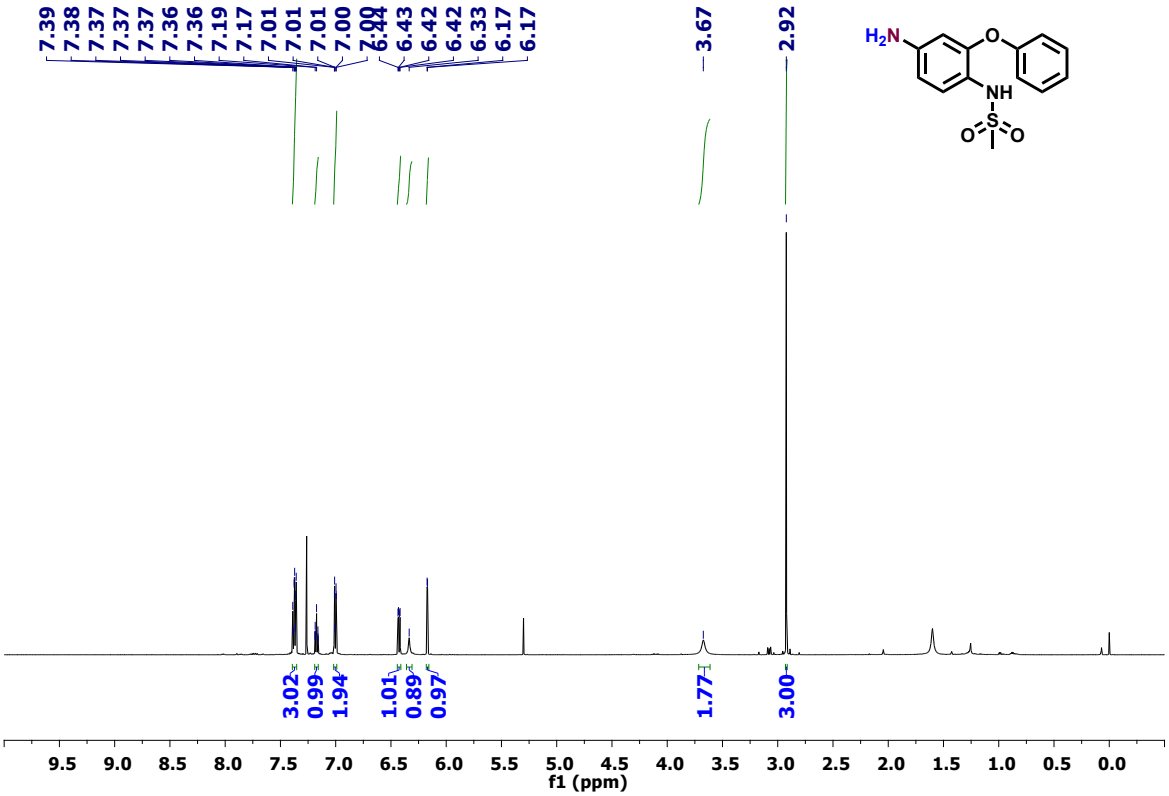


Figure S19: ^{13}C NMR of Nimesulide (8)

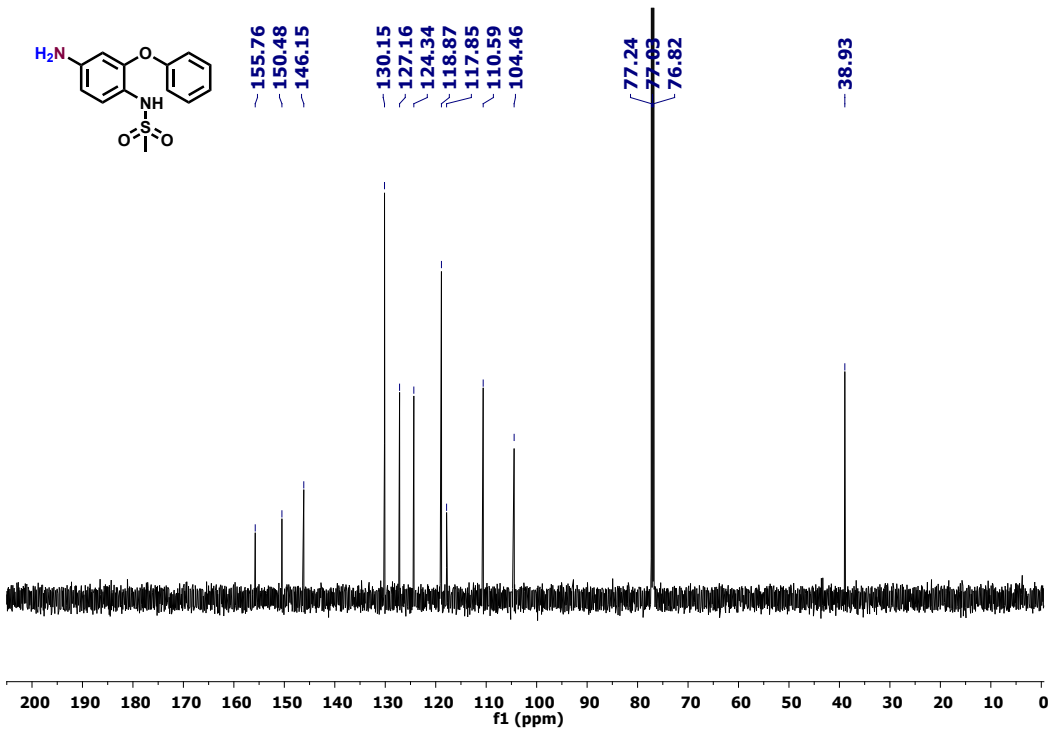


Figure S20: ^{1}H NMR of 2-(Methylsulfonyl) benzene-1,4-diamine (9)

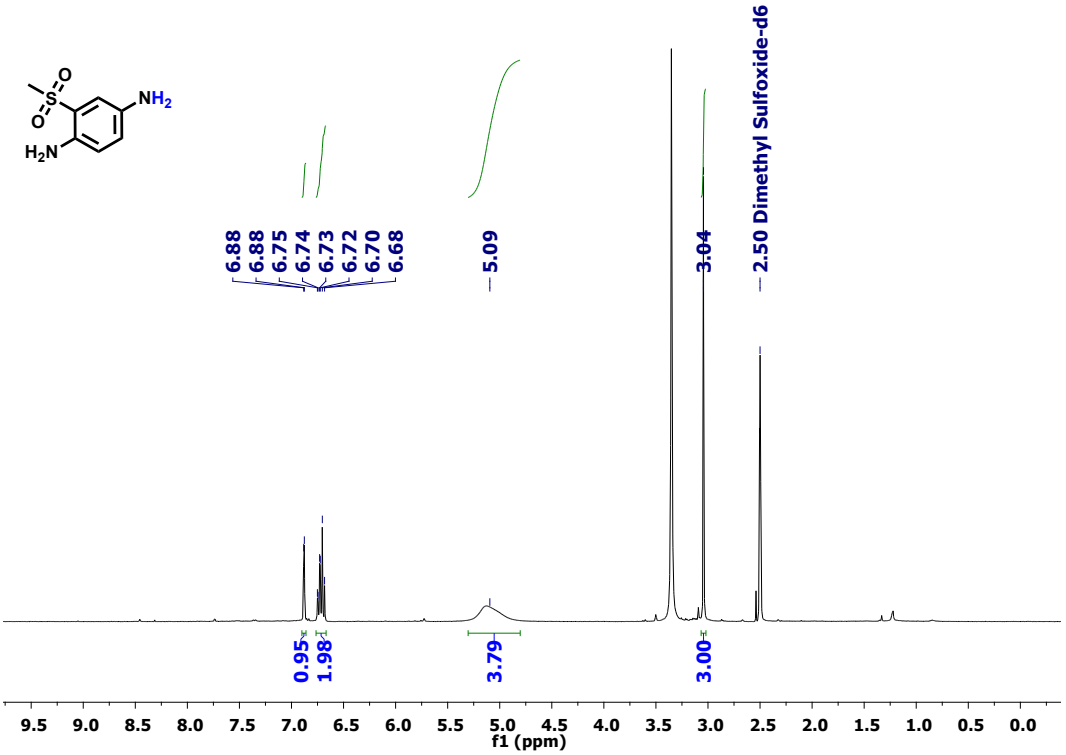


Figure S21: ^{13}C NMR of 2-(Methylsulfonyl) benzene-1,4-diamine (9)

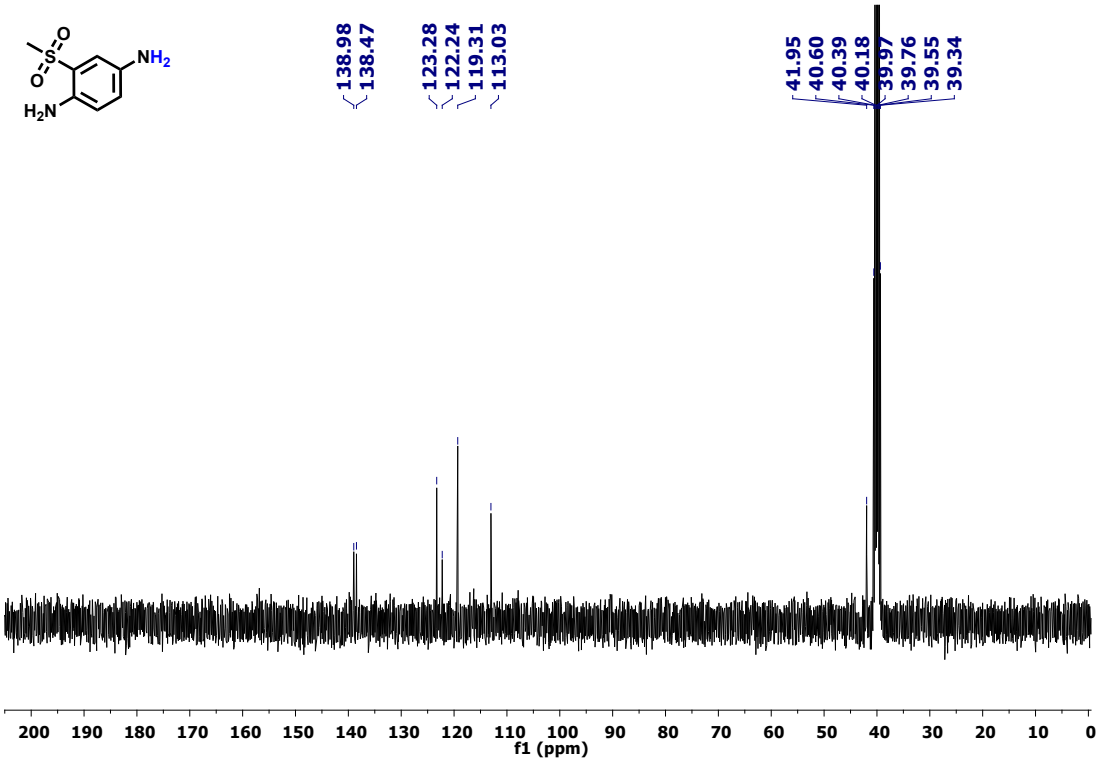


Figure S22: ^{1}H NMR of 1-Methylsulfonyl-2-aniline (10)

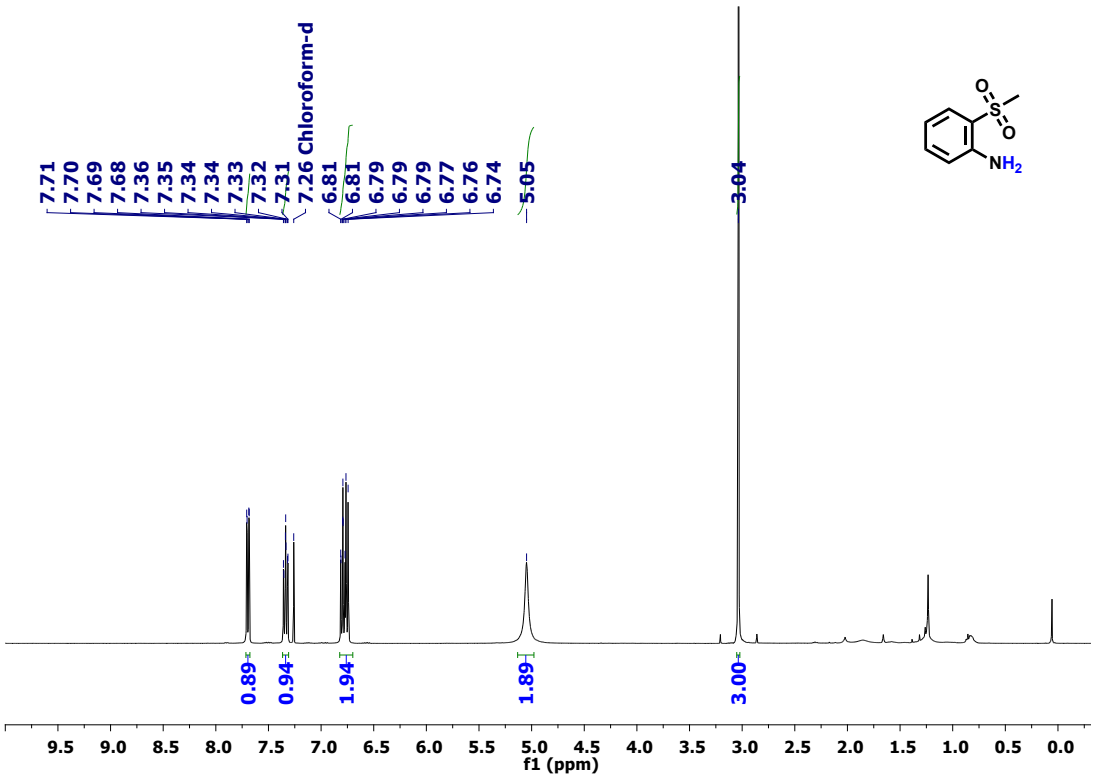


Figure S23: ^{13}C NMR of 1-Methylsulfonyl-2-aniline (10)

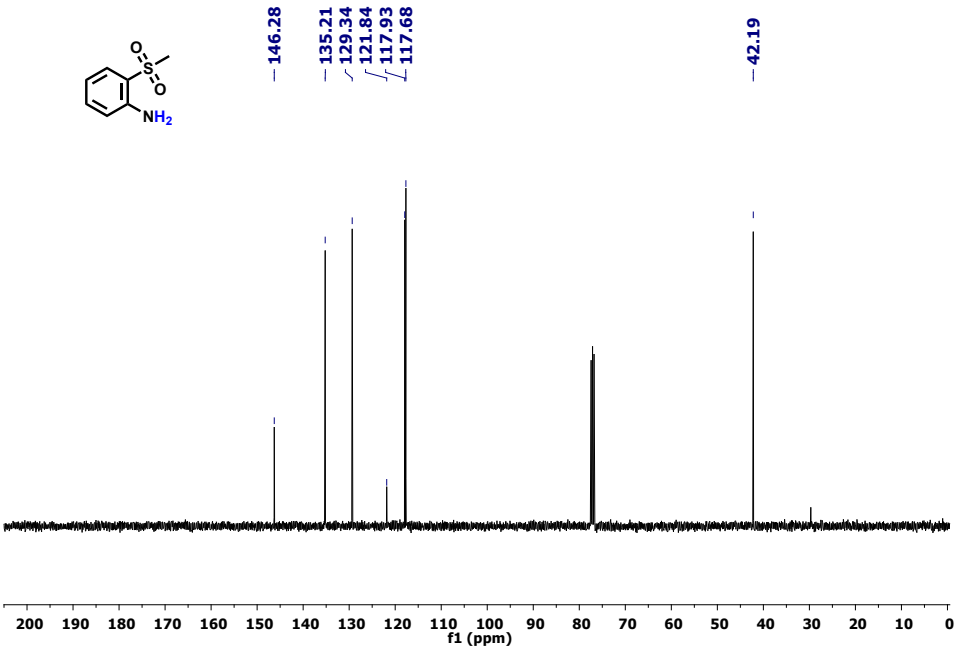


Figure S24: ^{1}H NMR of 2-Aminobenzenesulfonic acid (11)

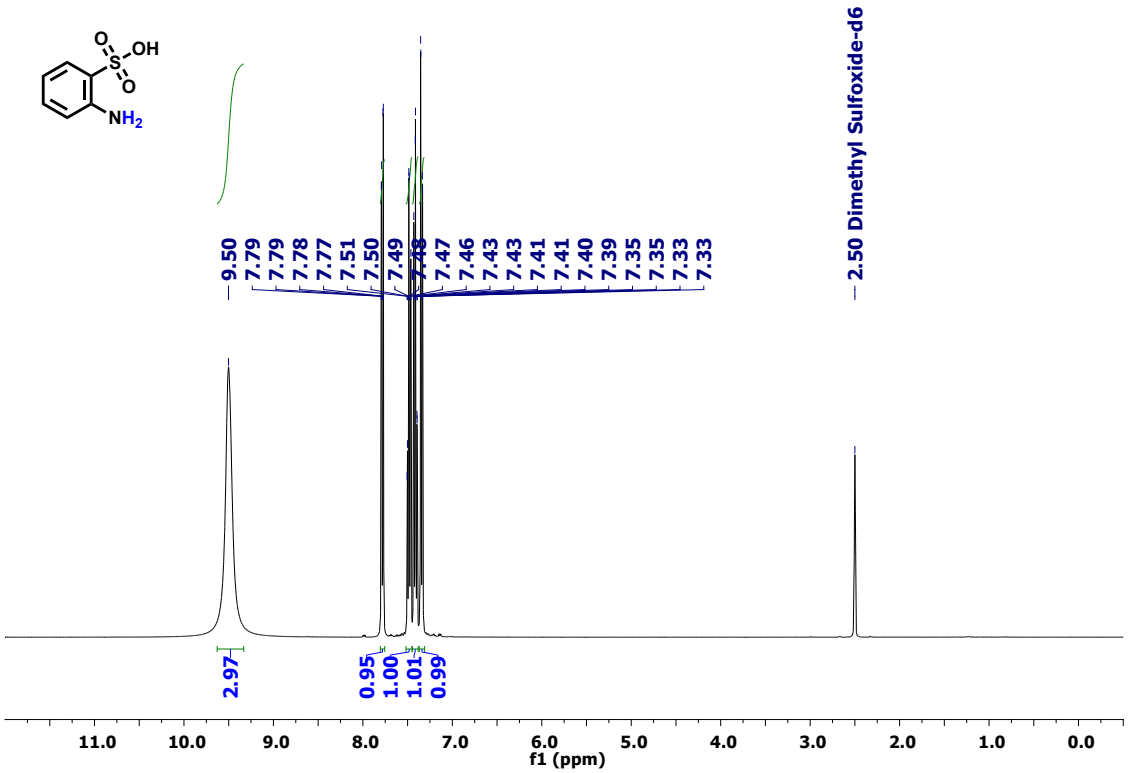


Figure S25: ^{13}C NMR of 2-Aminobenzenesulfonic acid (11)

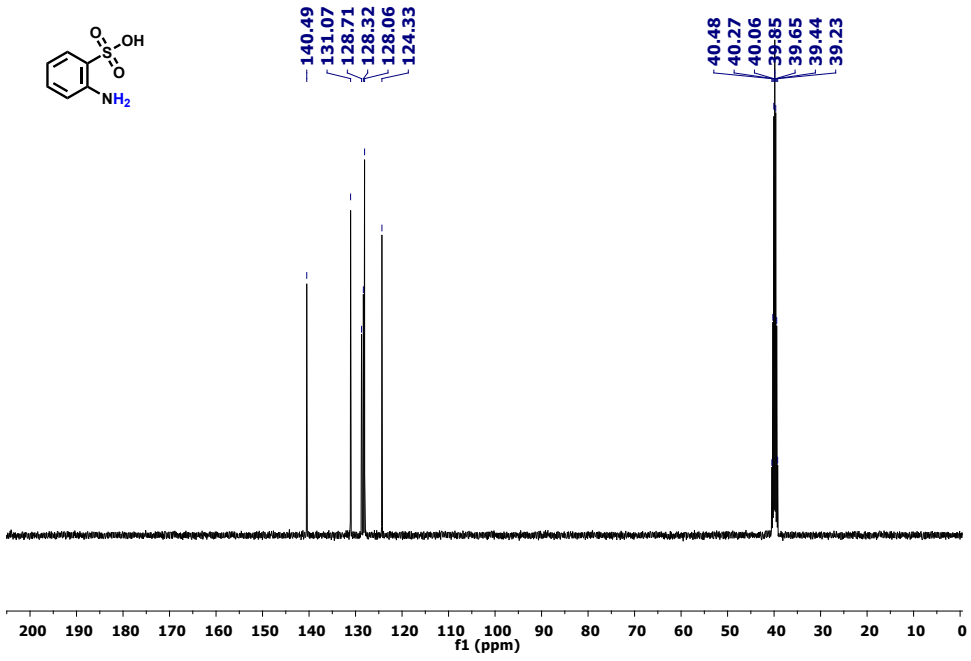


Figure S26: ^{1}H NMR of 5-Bromo-2-(methylsulfonyl)aniline (12)

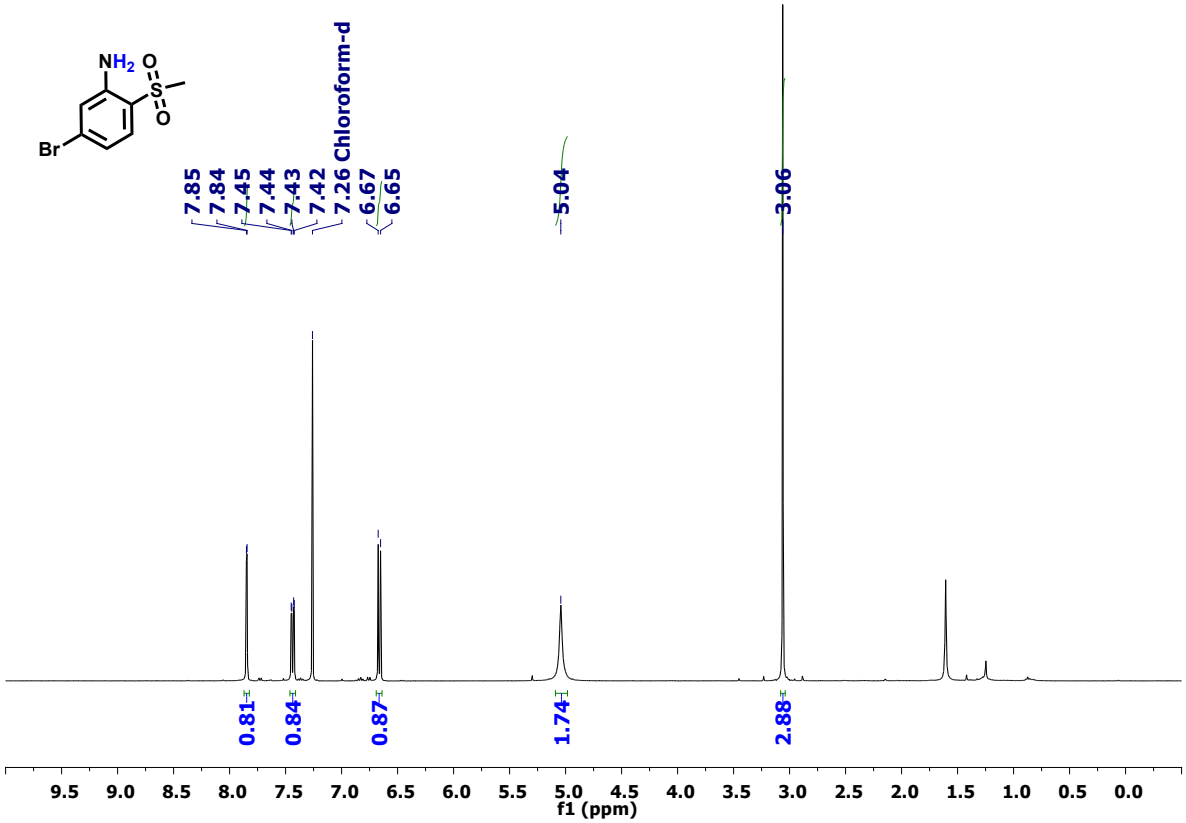


Figure S27: ^{13}C NMR of 5-Bromo-2-(methylsulfonyl)aniline (12)

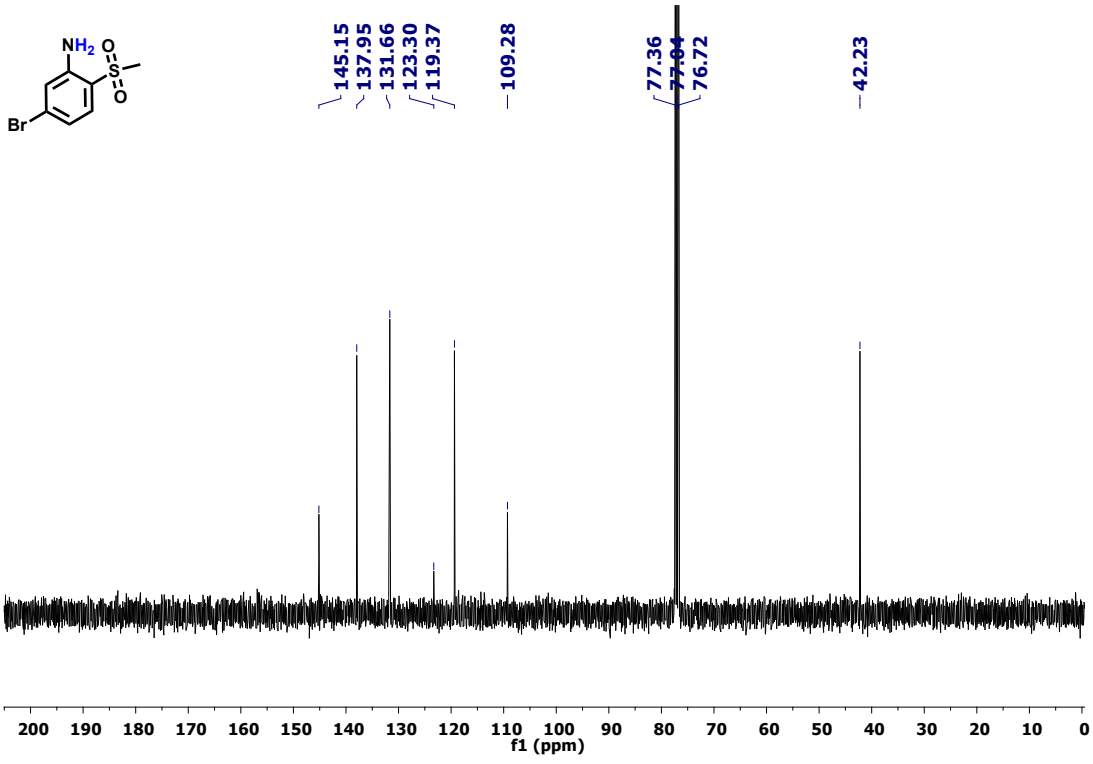


Figure S28: ^{1}H NMR of 4-(4-sulfonyldianiline) (13)

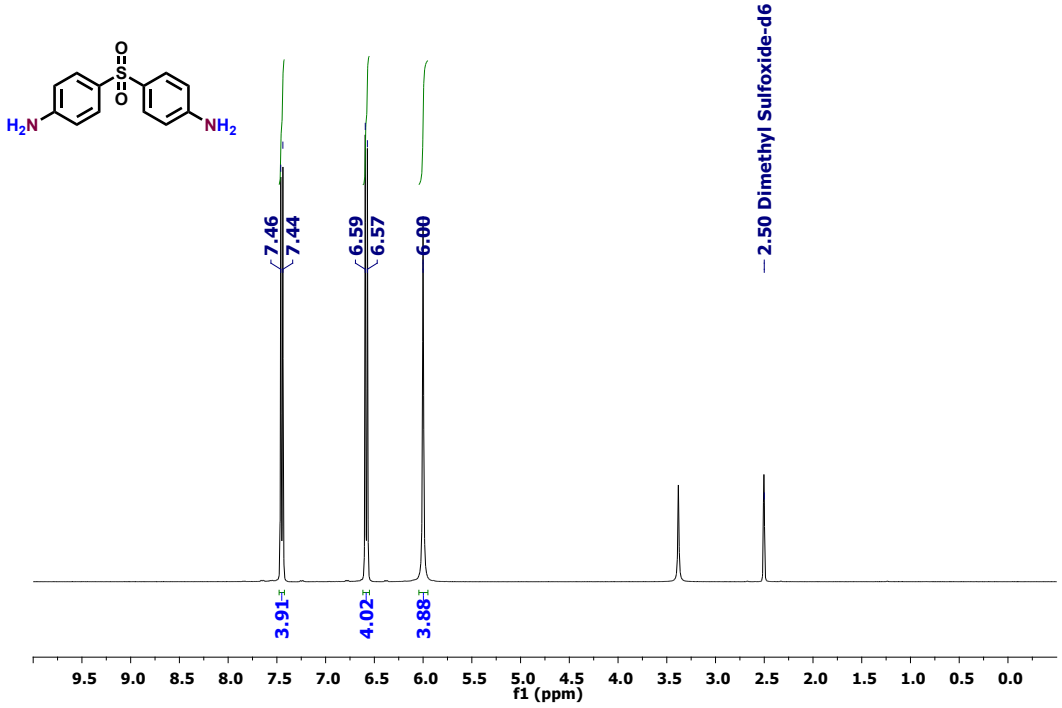


Figure S29: ^{13}C NMR of 4-(4-sulfonyldianiline) (13)

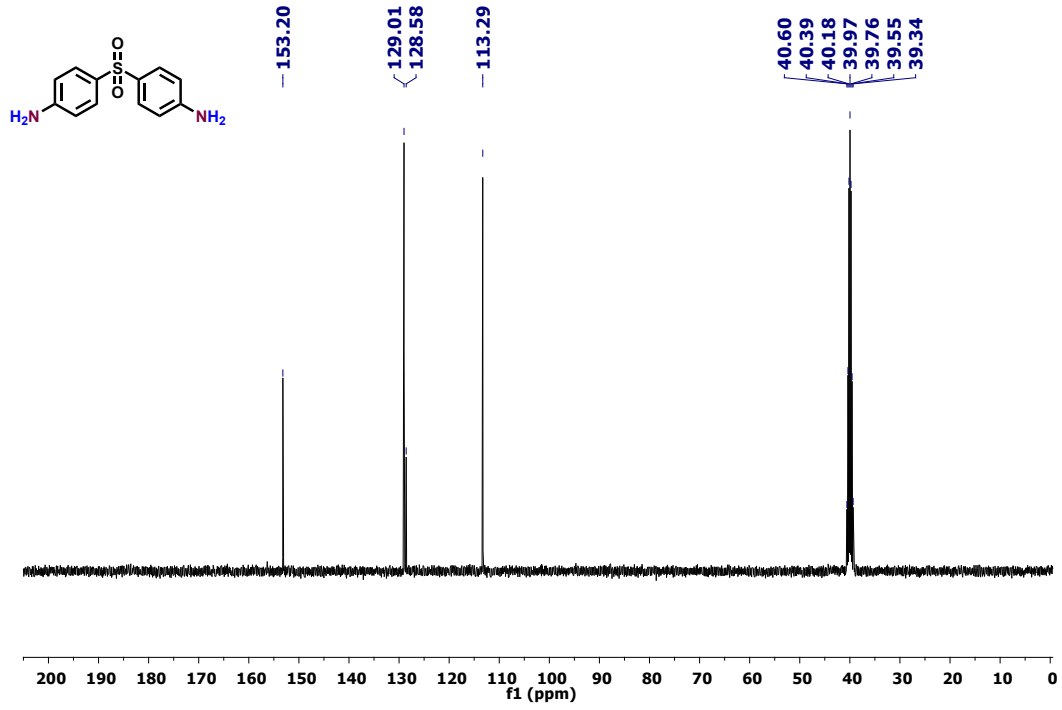


Figure S30: ^{1}H NMR of 4-(4-sulfonyldianiline) (14)

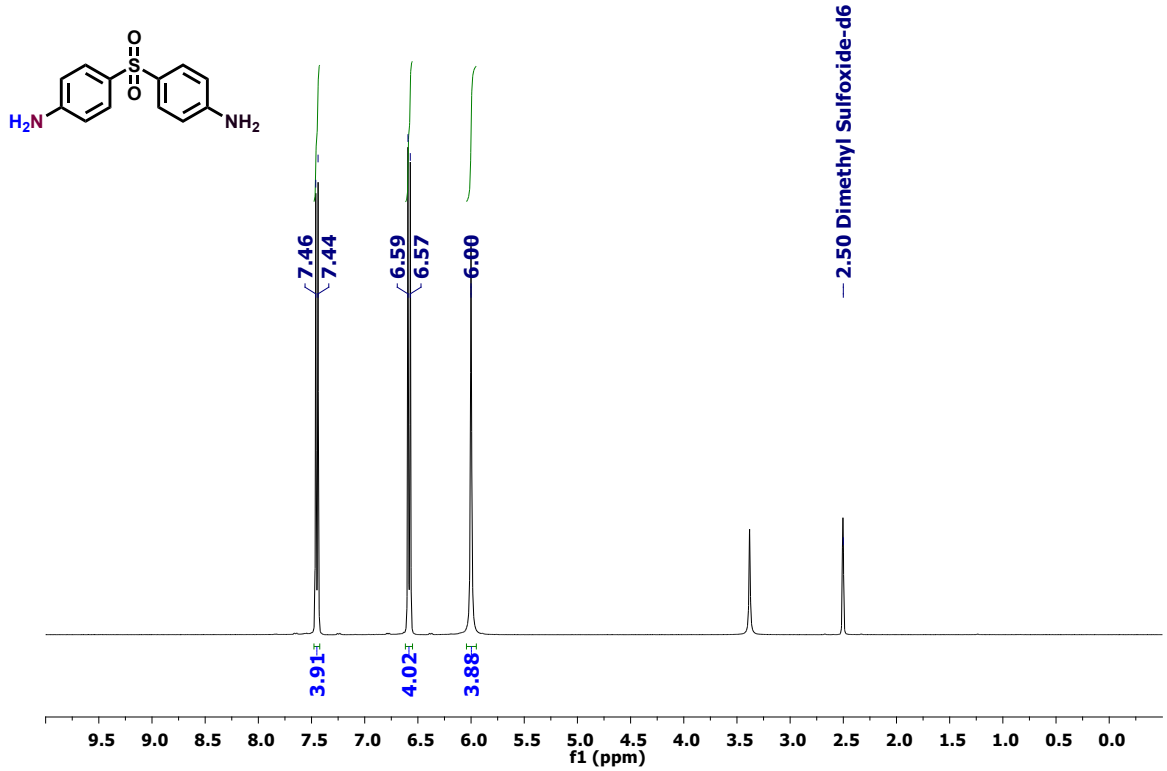


Figure S31: ^{13}C NMR of 4-(4-sulfonyldianiline) (14)

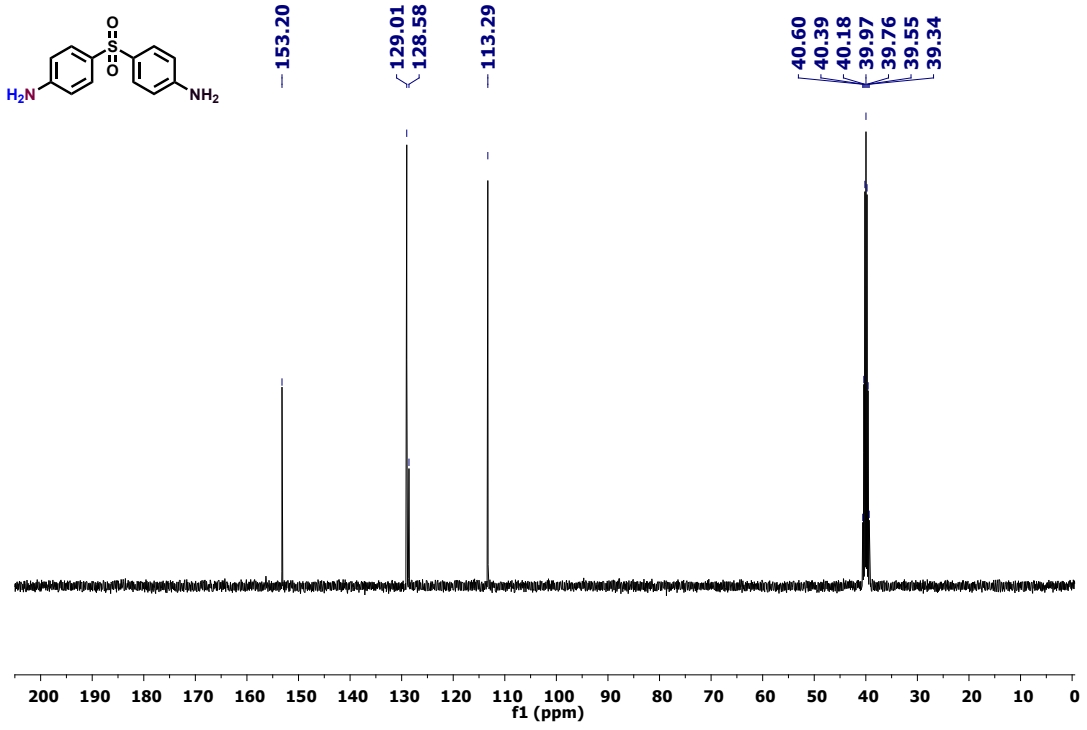


Figure S32: ^{1}H NMR of 4-Chloroaniline (15)

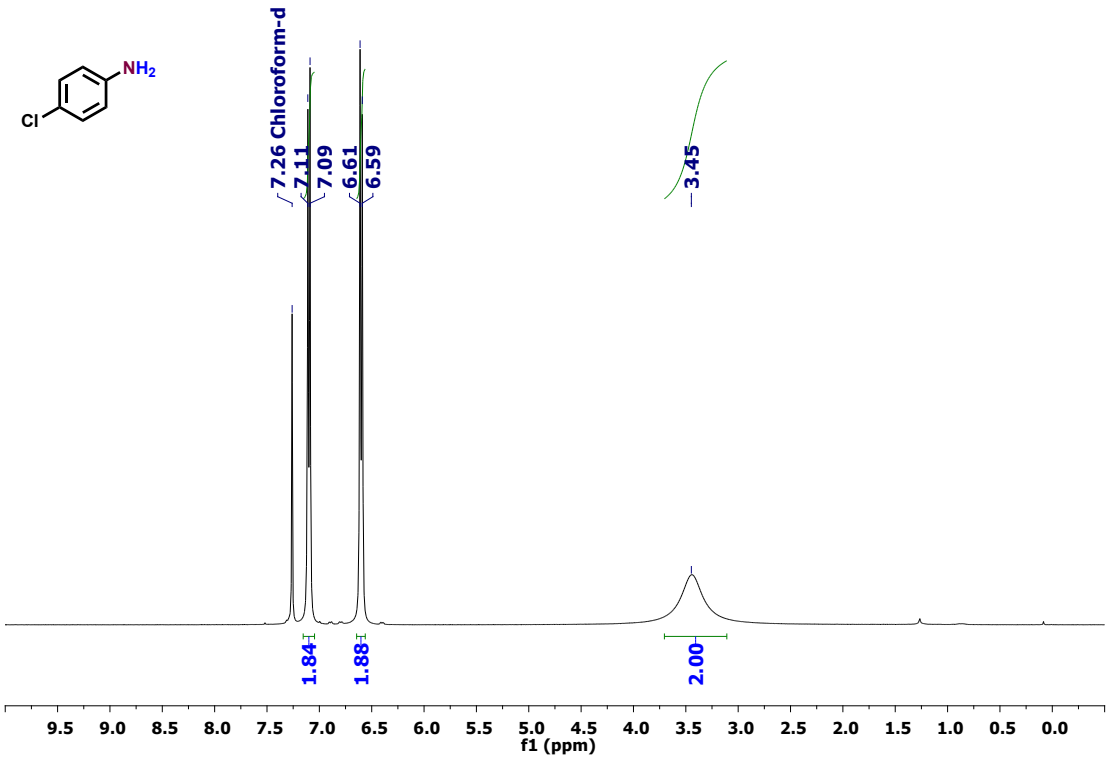


Figure S33: ^{13}C NMR of 4-Chloroaniline (15)

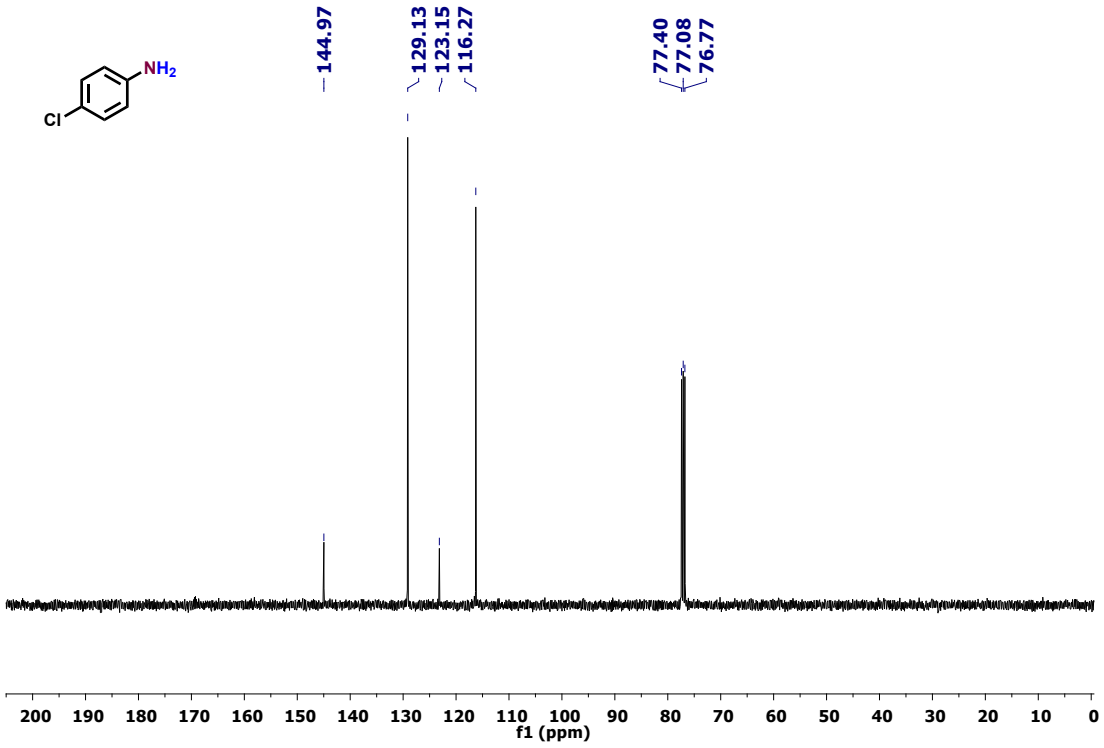


Figure S34: ^{1}H NMR of 4-Bromoaniline (16)

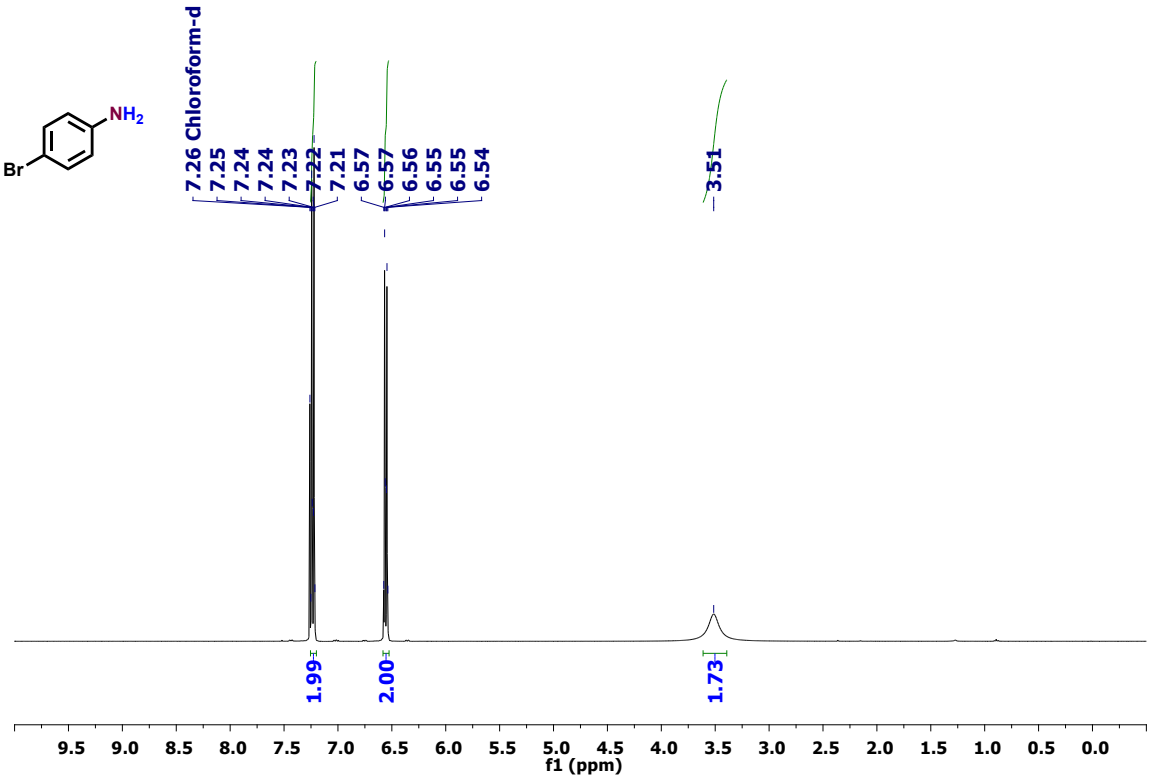


Figure S35: ^{13}C NMR of 4-Bromoaniline (16)

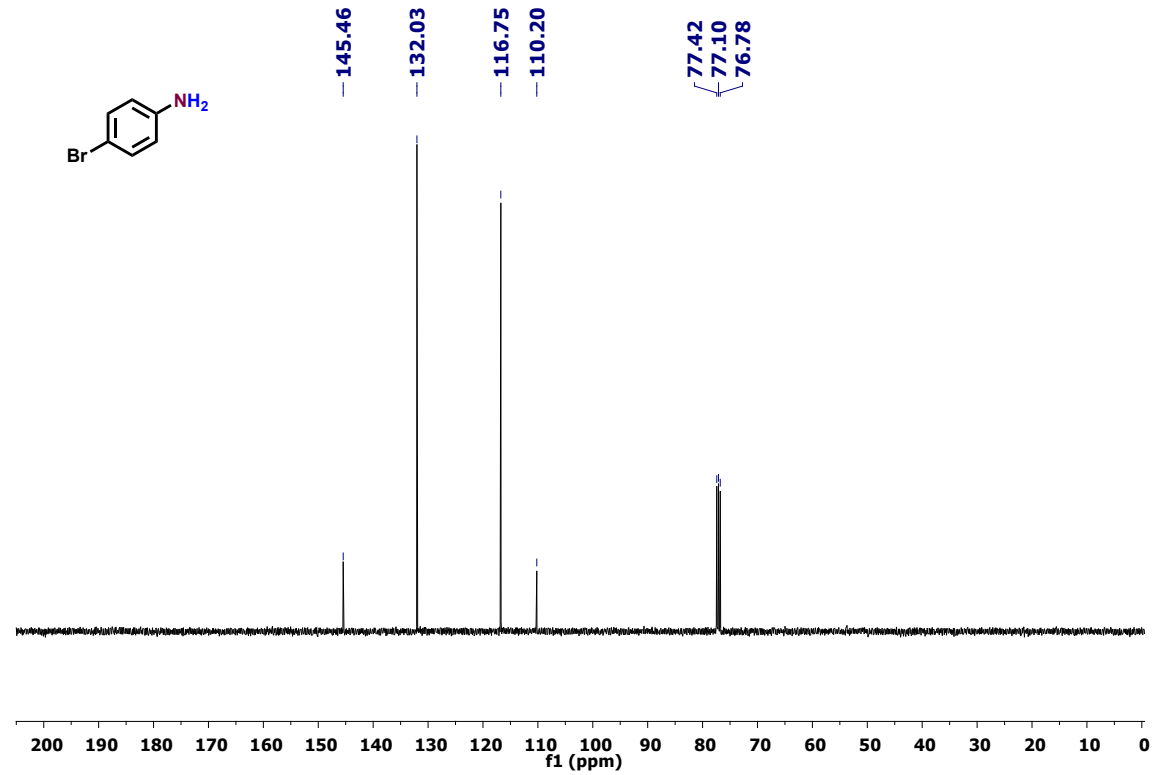


Figure S36: ^{1}H NMR of 4-Iodoaniline (17)

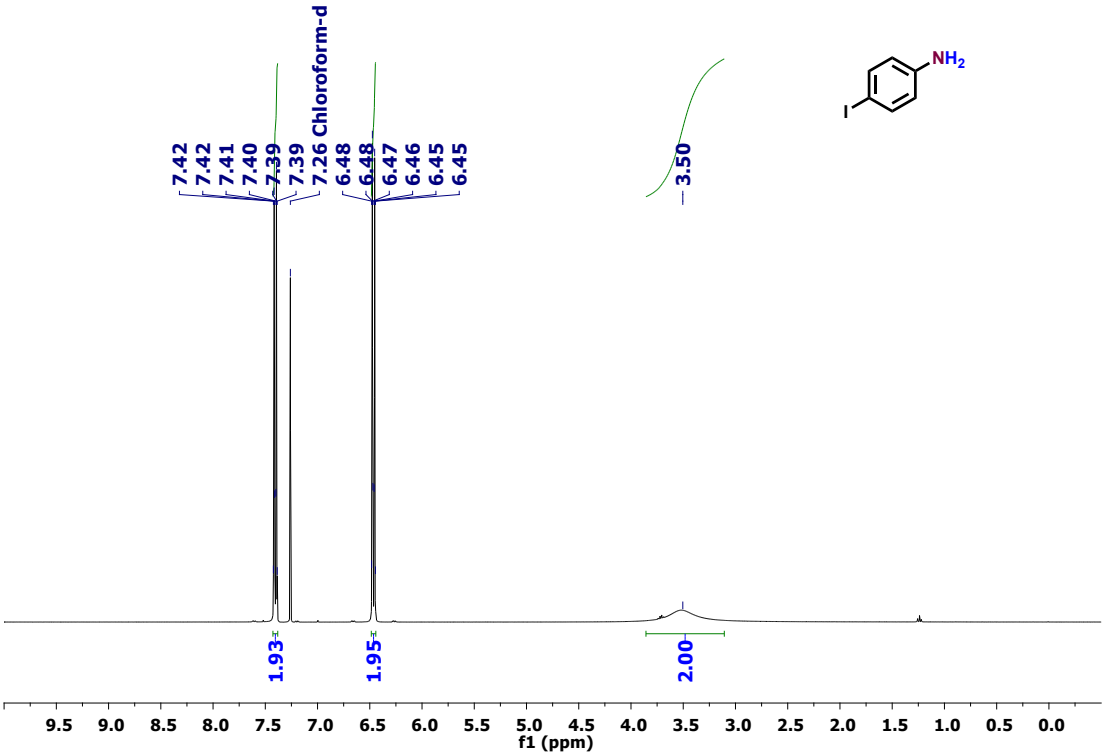


Figure S37: ^{13}C NMR of 4-Iodoaniline (17)

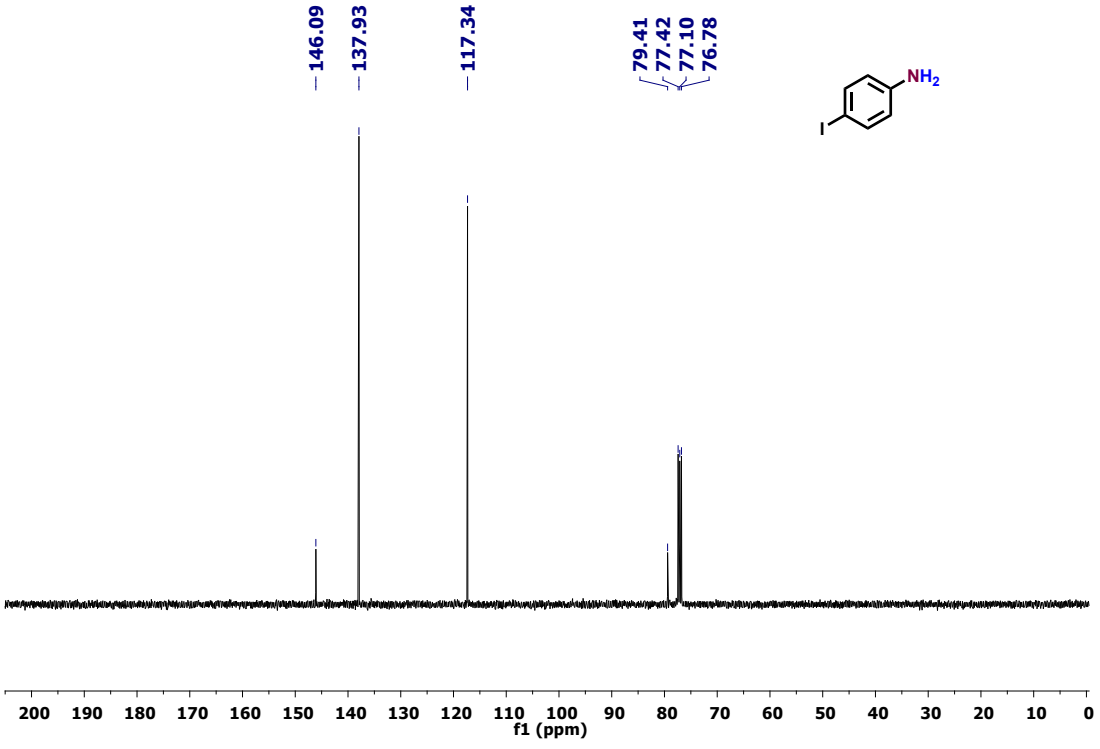


Figure S38: ^{1}H NMR of 4-Chlorobenzene-1,2-diamine (18)

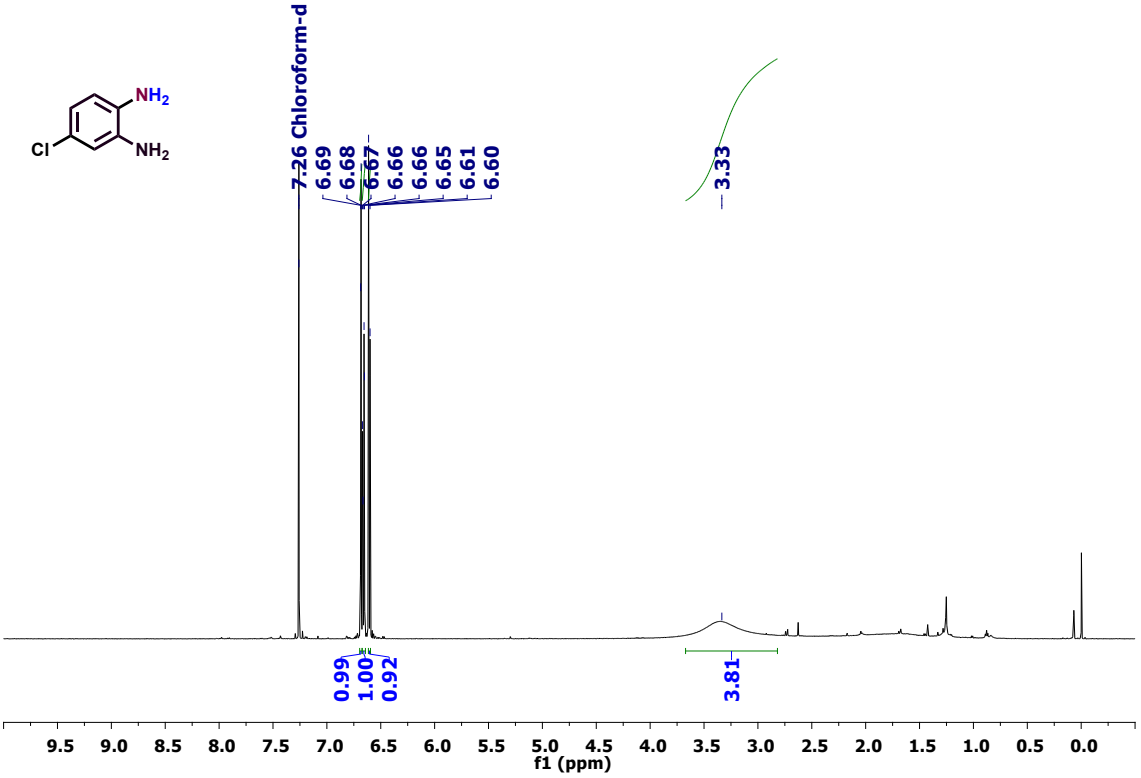


Figure S39: ^{13}C NMR of 4-Chlorobenzene-1,2-diamine (18)

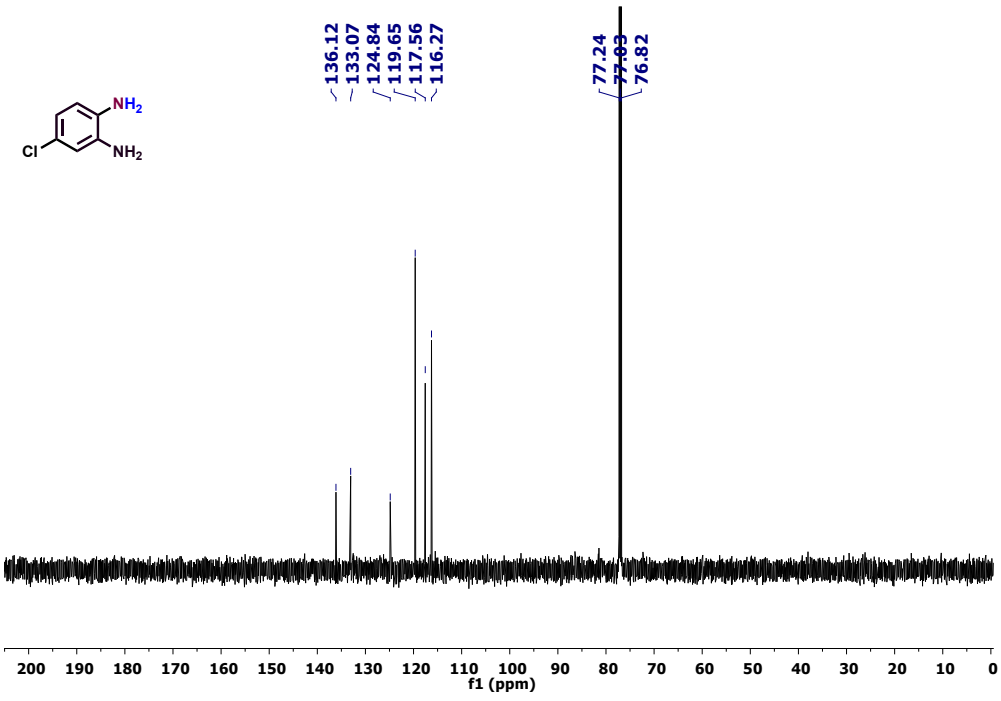


Figure S40: ^{1}H NMR of 4-Fluorooaniline (19)

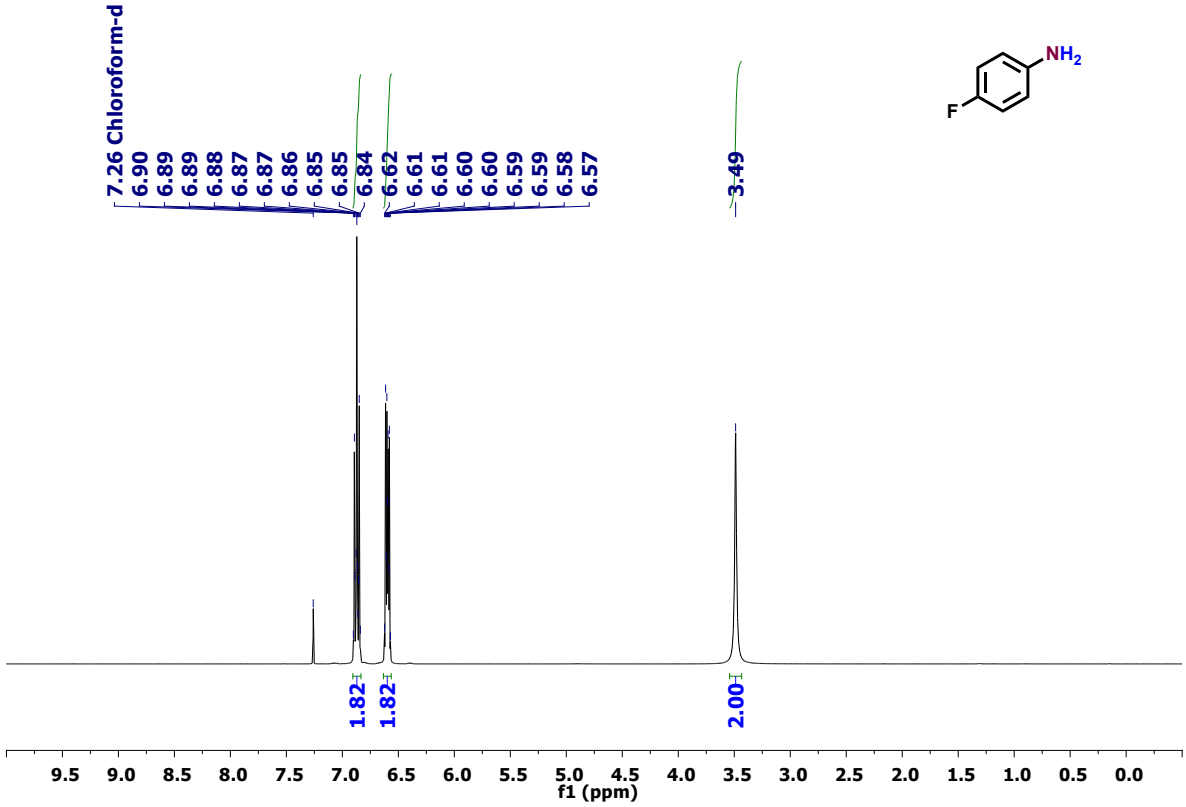


Figure S41: ^{13}C NMR of 4-Fluorooaniline (19)

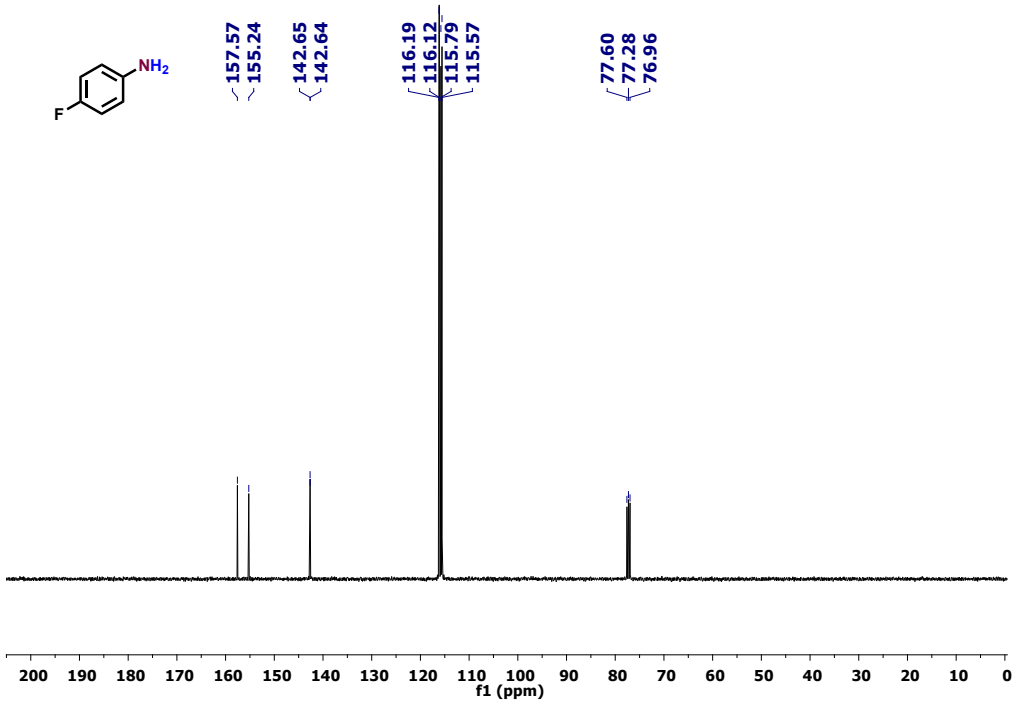


Figure S42:H NMR of 3,4-Difluoroaniline (20)

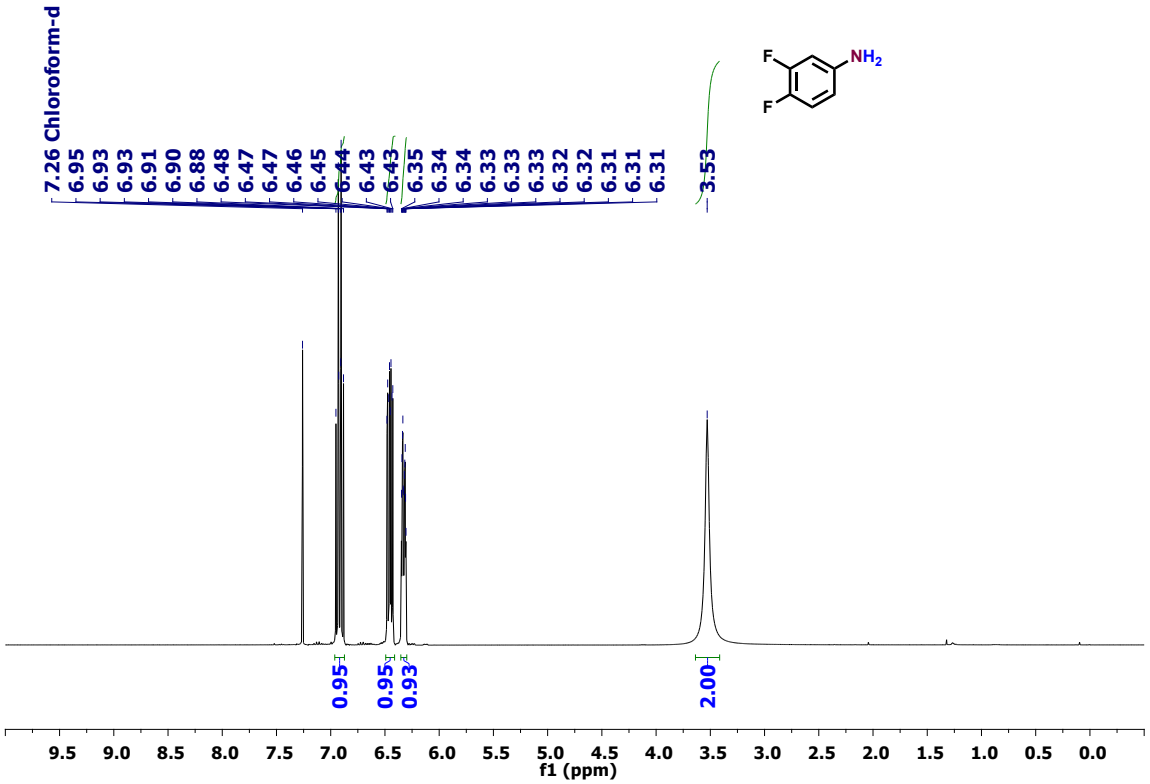


Figure S43: ^{13}C NMR of 3,4-Difluoroaniline (20)

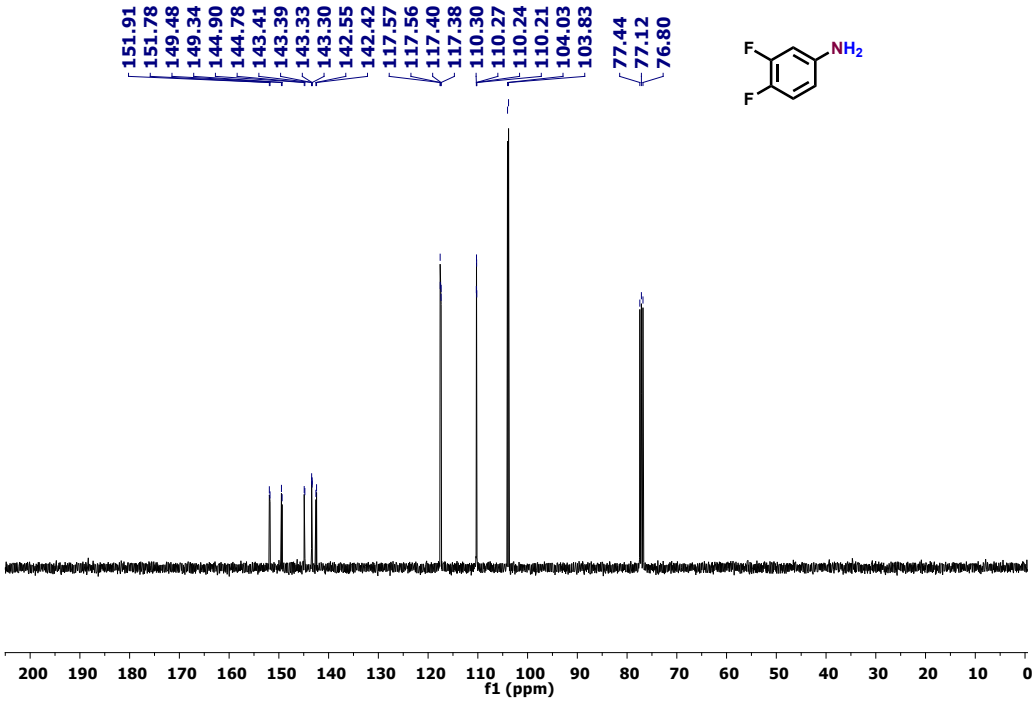


Figure S44: ^{1}H NMR of 5-Bromo-2-fluoroaniline (21)

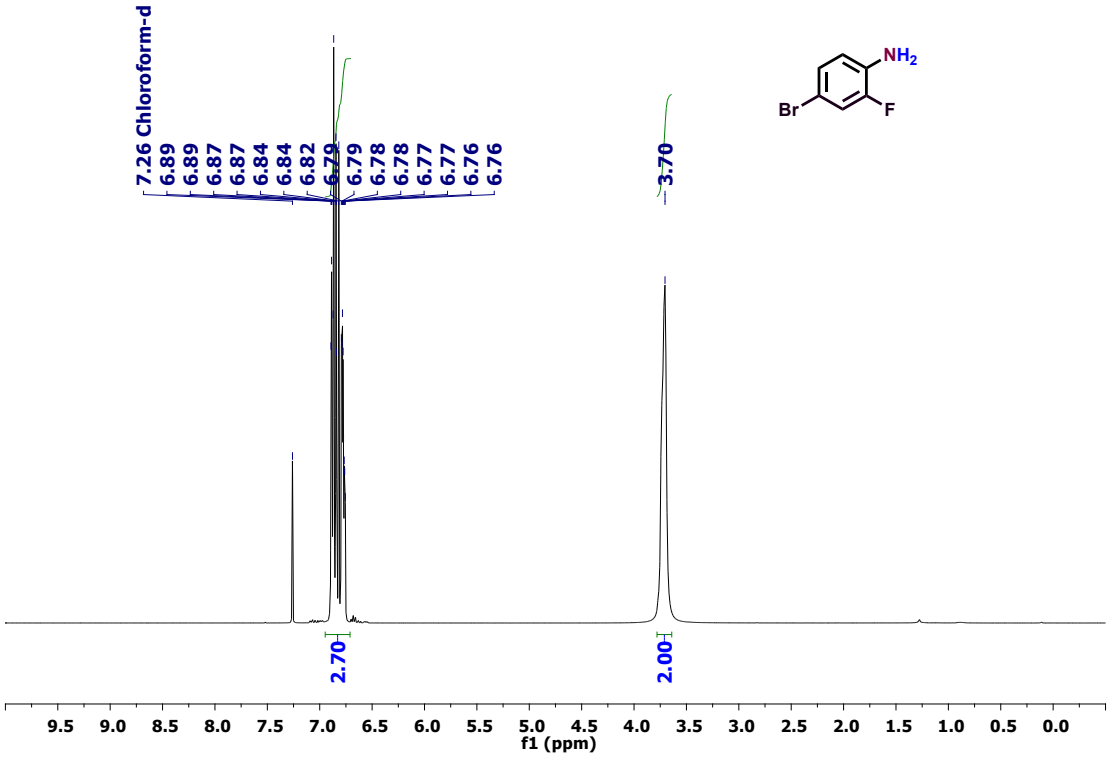


Figure S45: ^{13}C NMR spectrum of 5-Bromo-2-fluoroaniline (21)

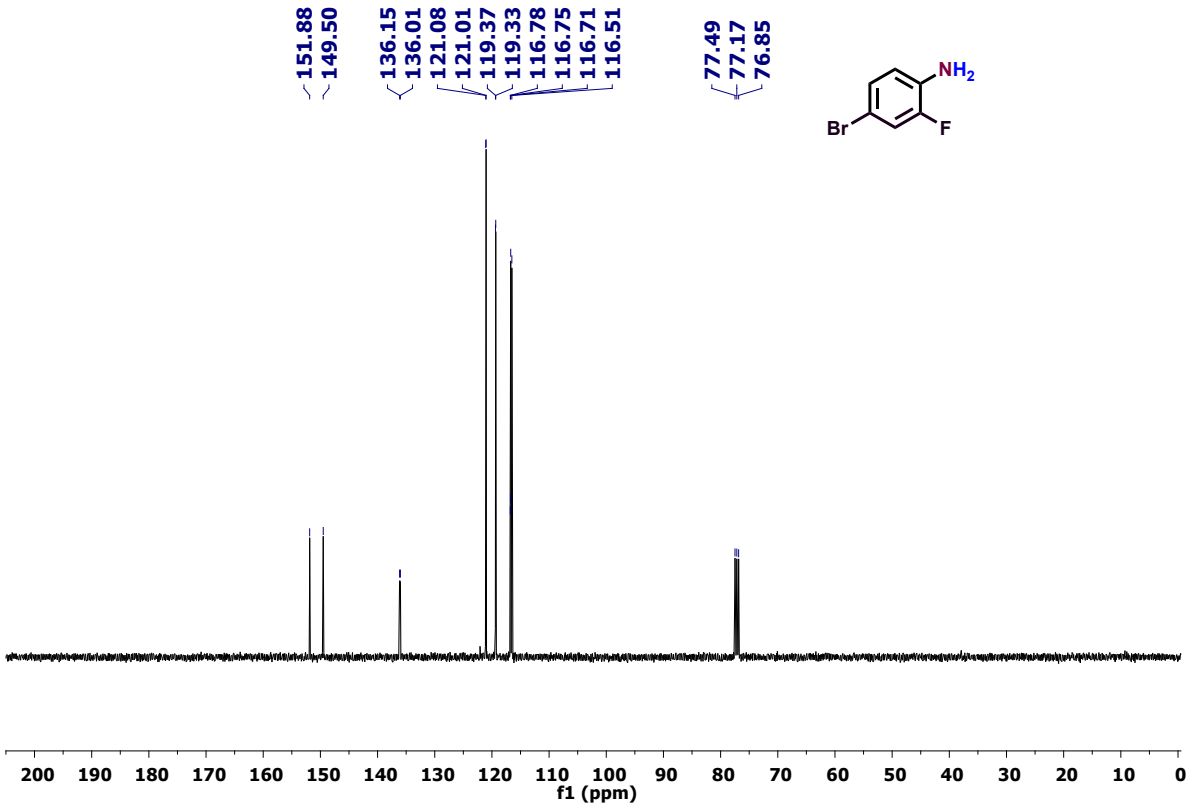


Figure S46: ^{1}H NMR of 3-Fluoro-4-morpholinoaniline (22)

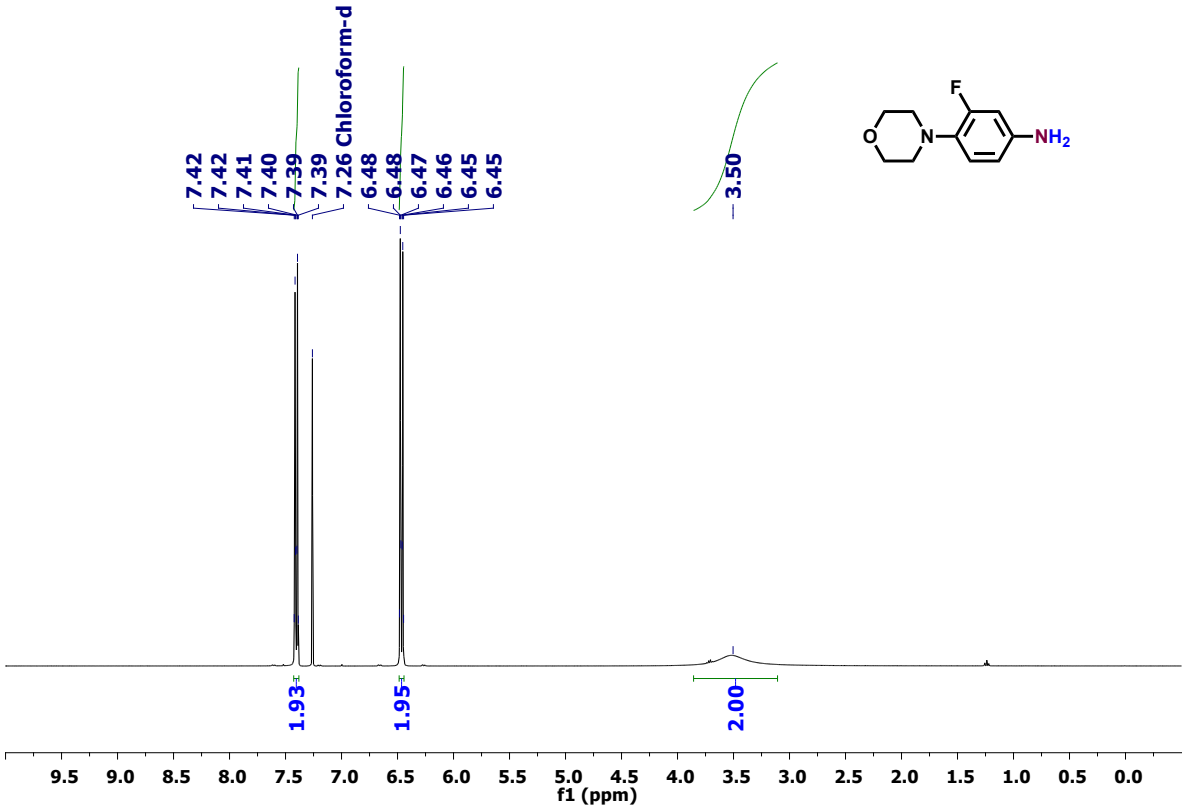


Figure S47: ^{13}C NMR of 3-Fluoro-4-morpholinoaniline (22)

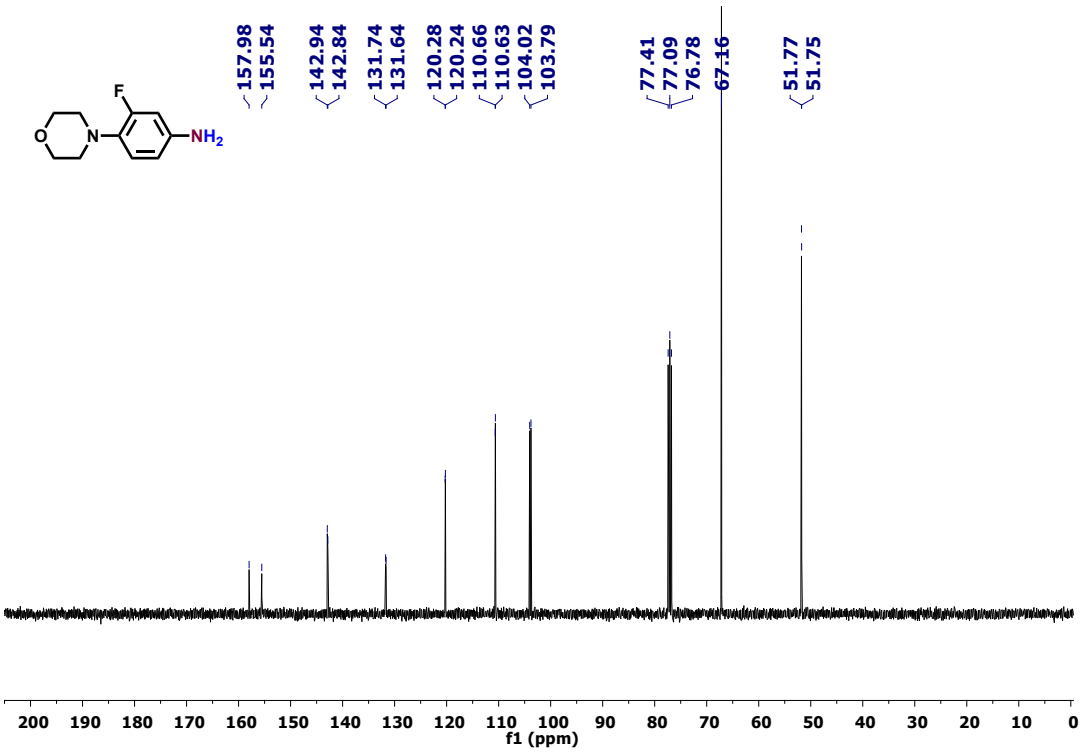


Figure S48: ^{1}H NMR of 2-Chloroaniline (23)

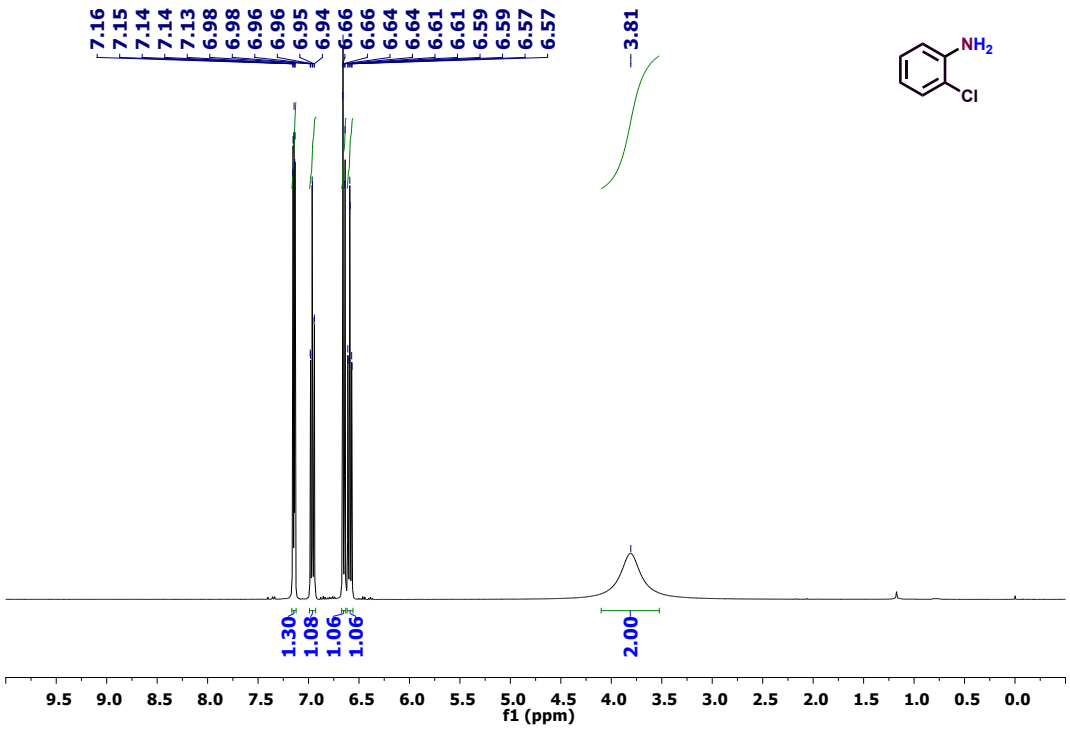


Figure S49: ^{13}C NMR of 2-Chloroaniline (23)

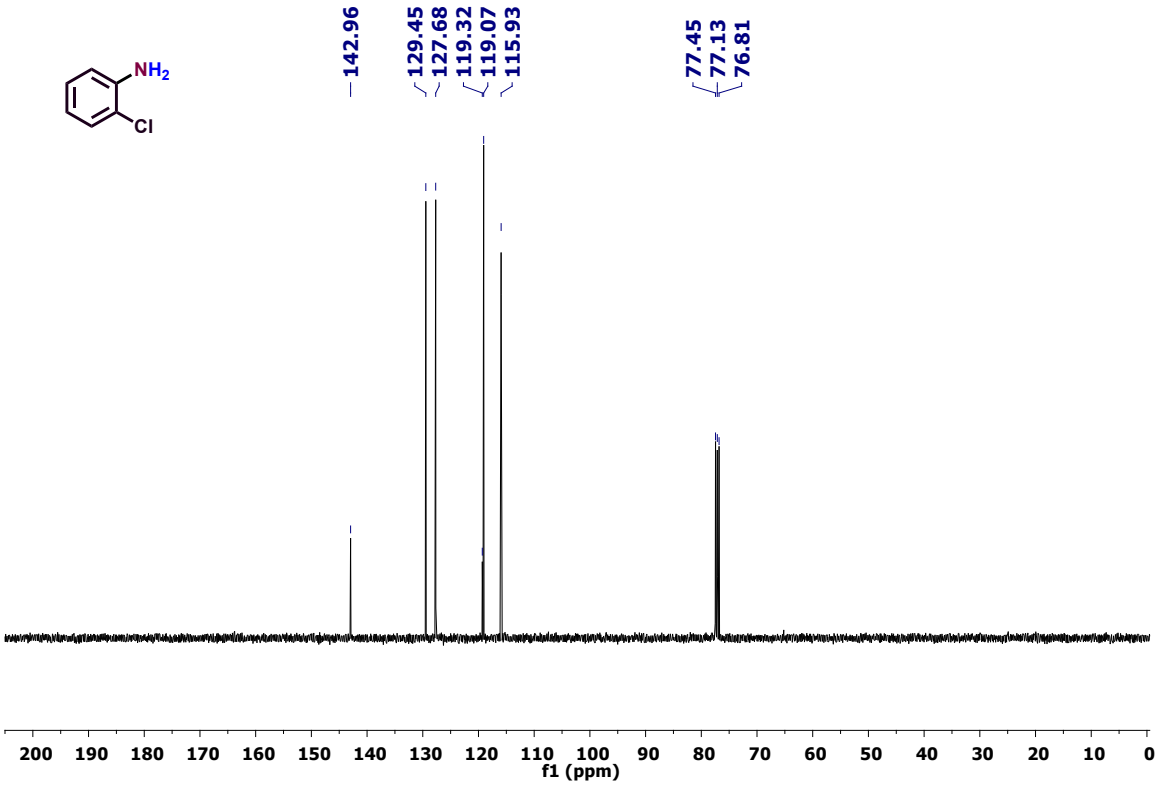


Figure S50: ^{1}H NMR of 3-Chloroaniline (24)

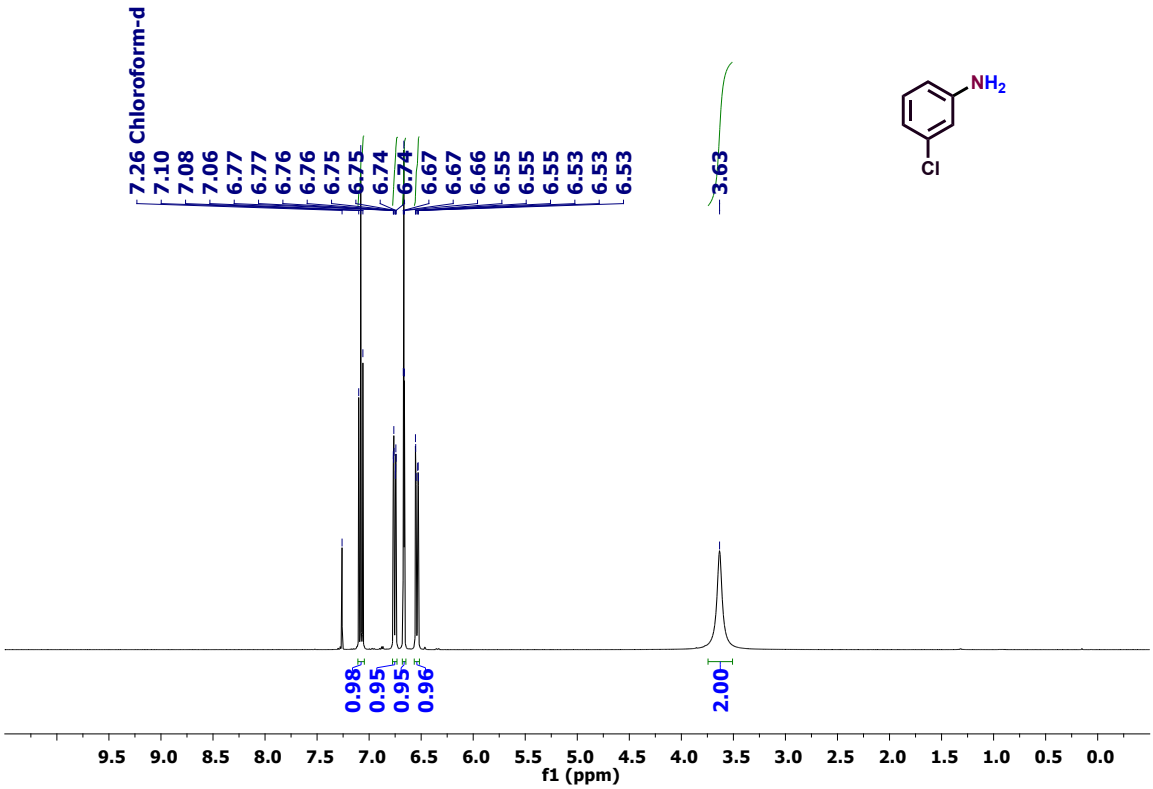


Figure S51: ^{13}C NMR of 3-Chloroaniline (24)

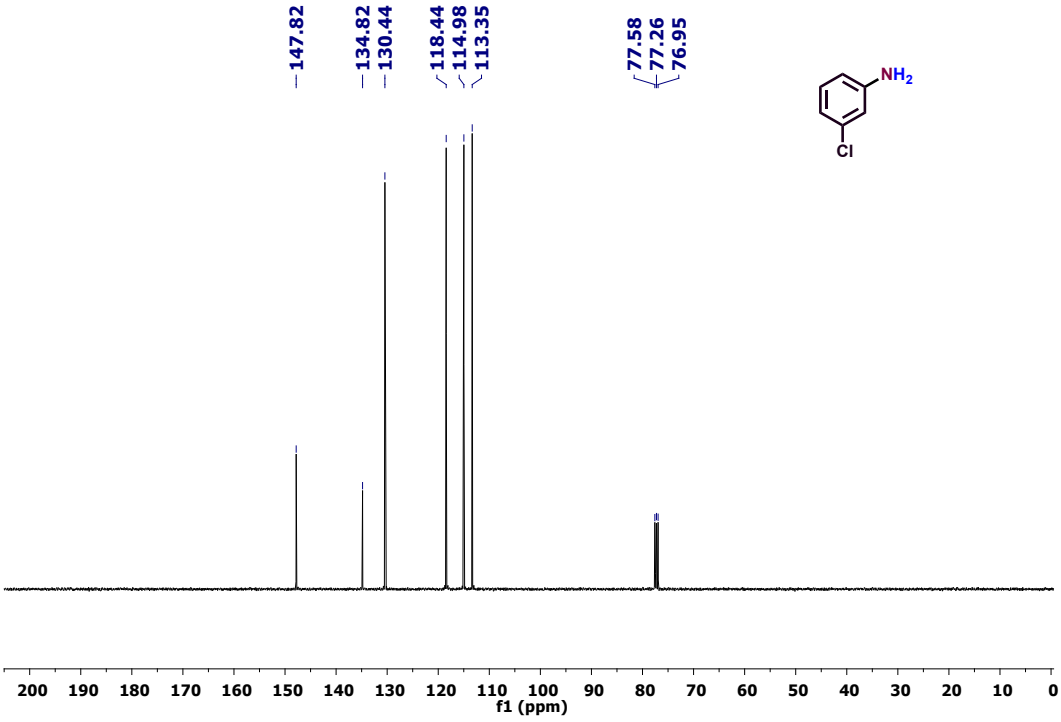


Figure S52: ^{1}H NMR of 4-Chloro-3-aminophenol (25)

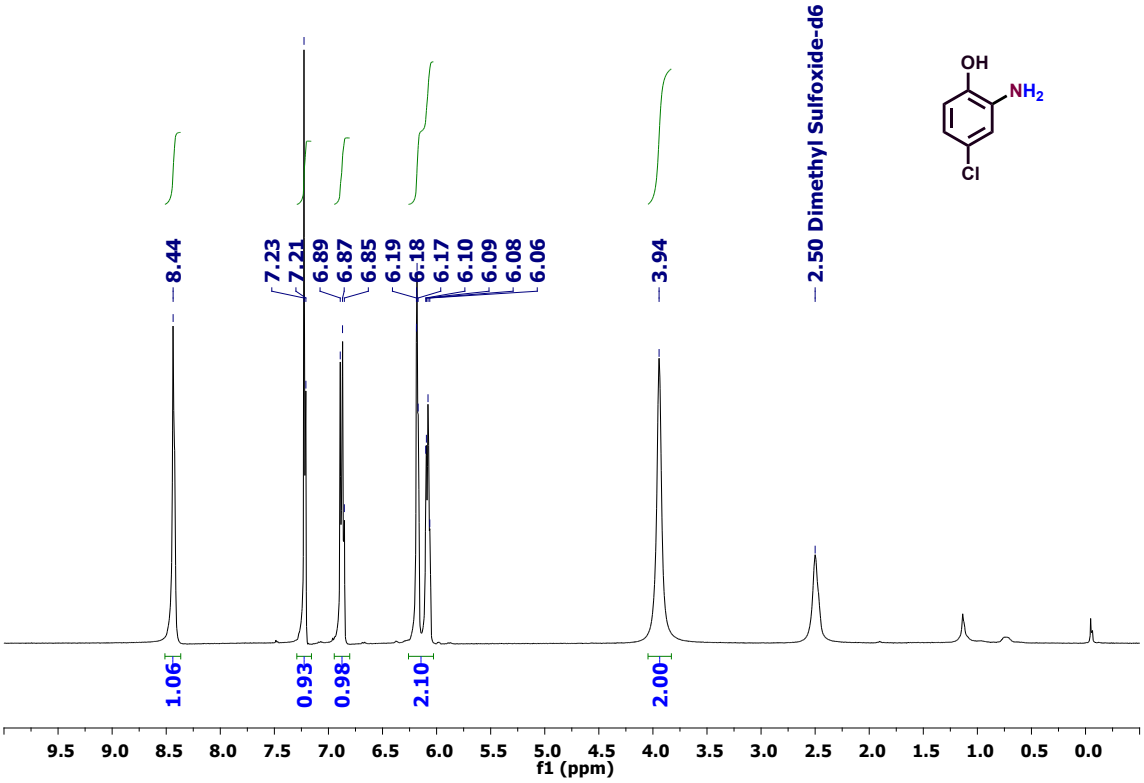


Figure S53: ^{13}C NMR of 4-Chloro-3-aminophenol (25)

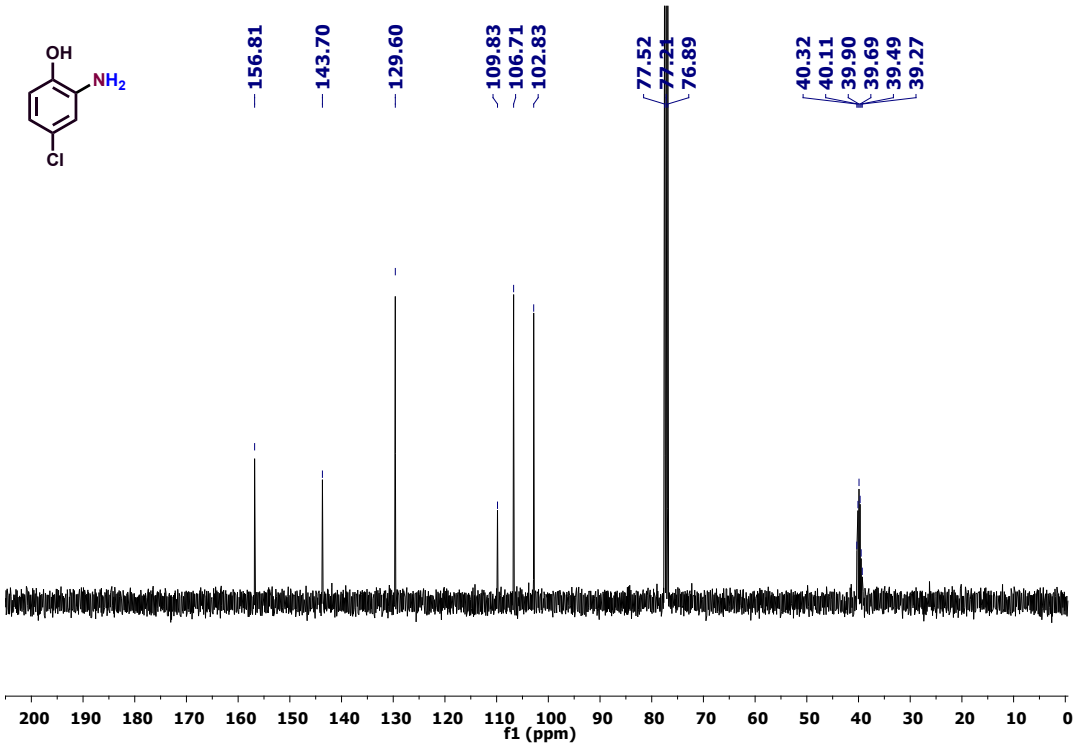


Figure S54: ^{1}H NMR of 5-Amino-2-fluorobenzonitrile (26)

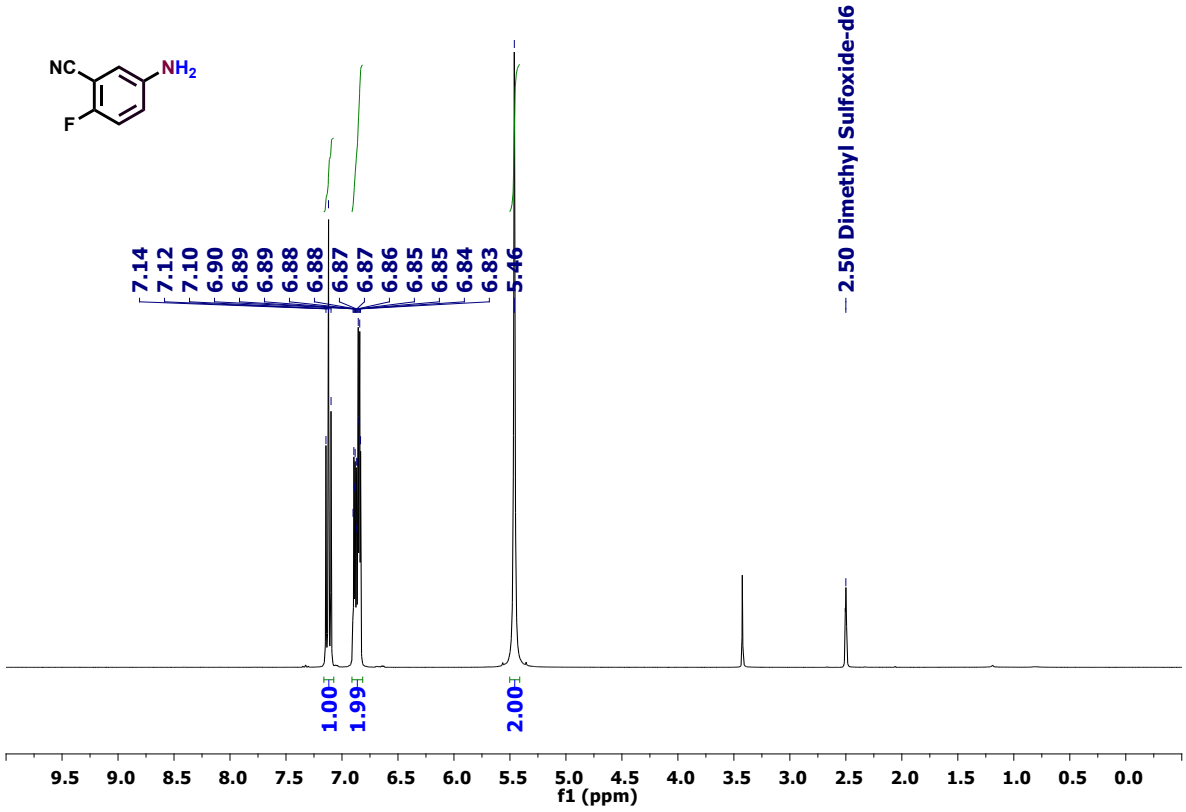


Figure S55: ^{13}C NMR of 5-Amino-2-fluorobenzonitrile (26)

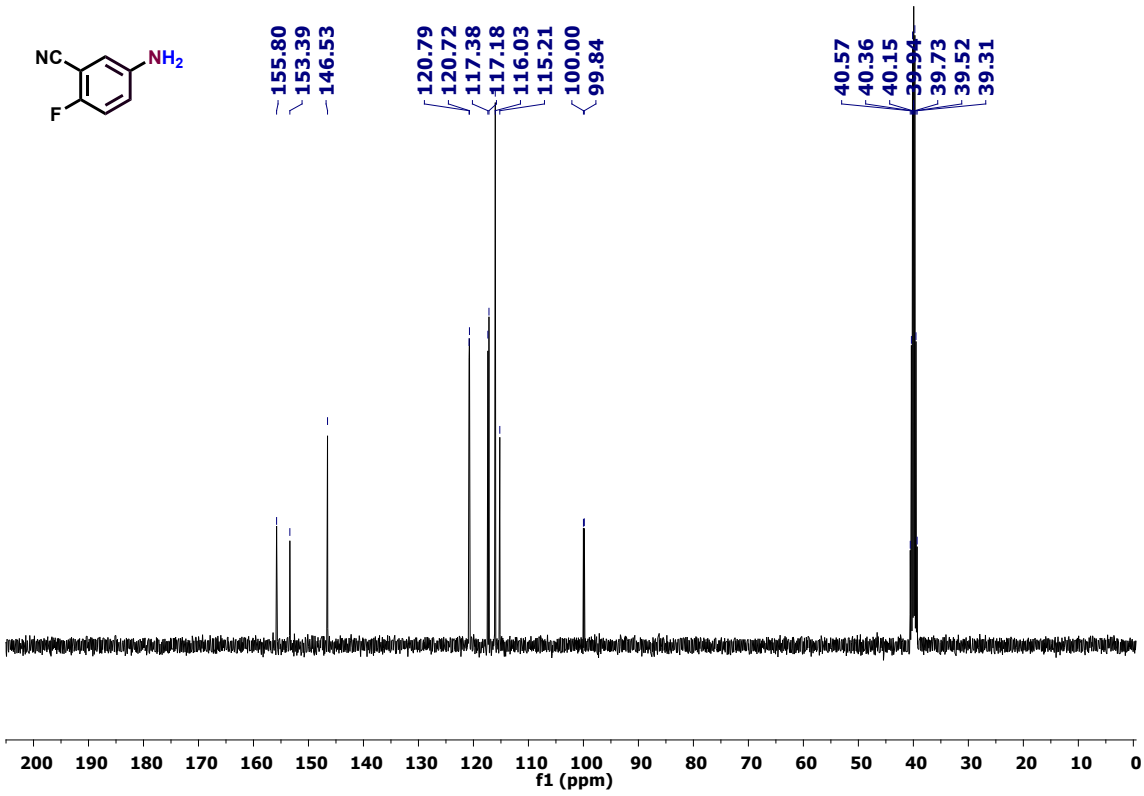


Figure S56:[1]H NMR of 2-Bromoaniline (27)

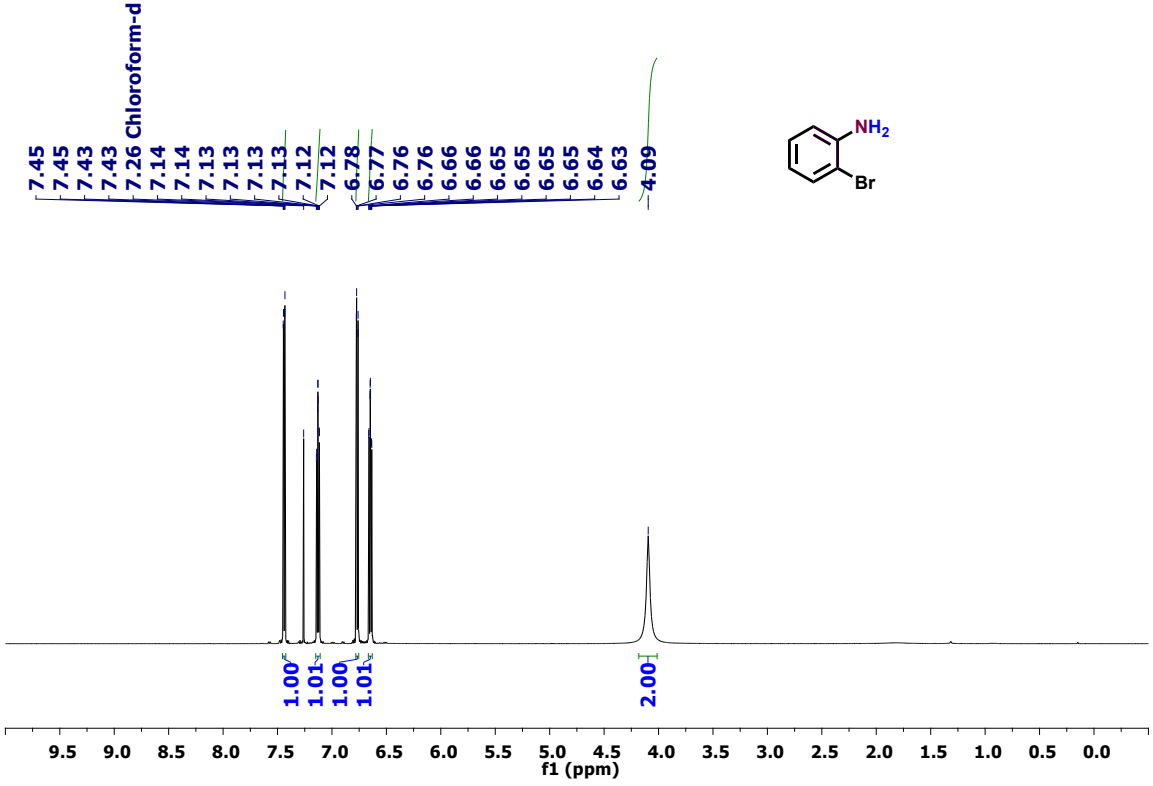


Figure S57: [13]C NMR of 2-Bromoaniline (27)

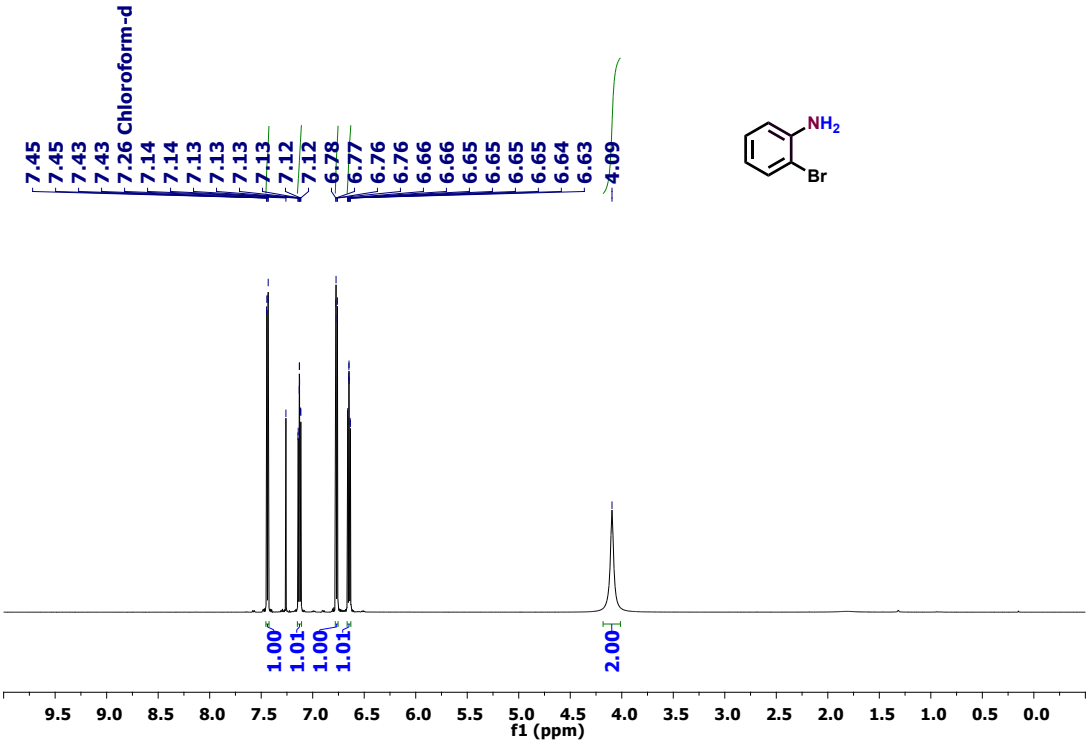


Figure S58: ^{1}H NMR of Pentafluoroaniline (28)

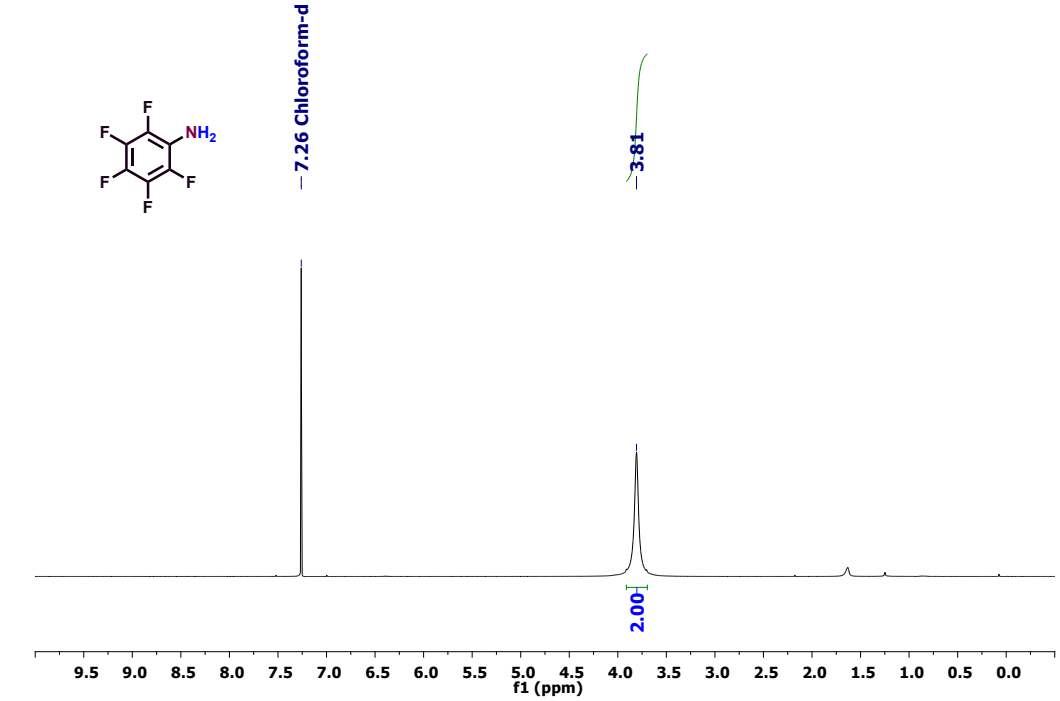


Figure S59: ^{13}C NMR of Pentafluoroaniline (28)

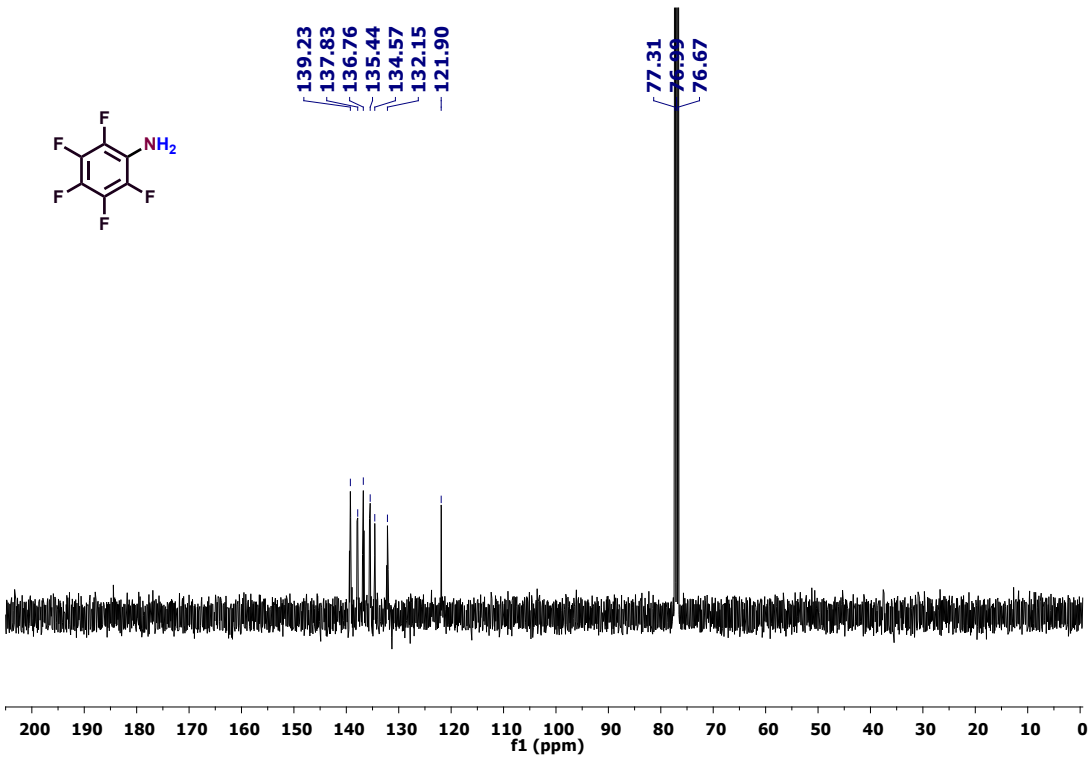


Figure S60: ^{1}H NMR of 4-Aminoacetophenone (29)

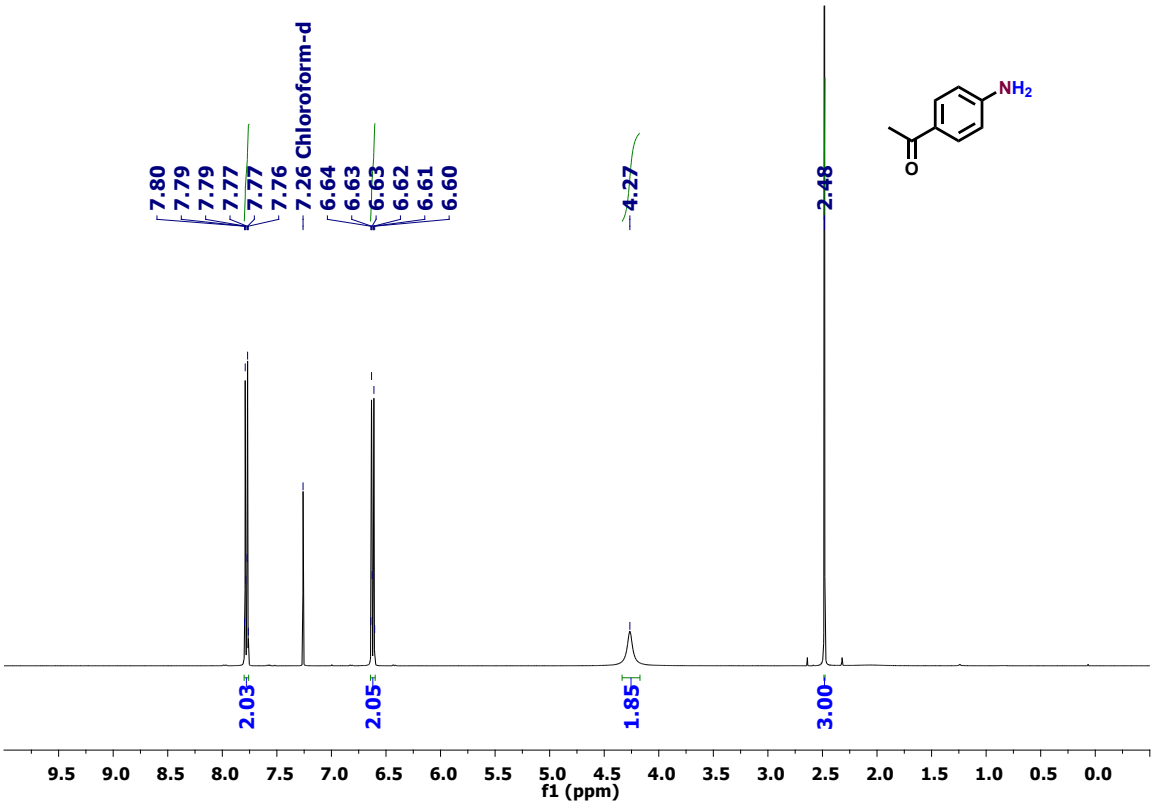


Figure S61: ^{13}C NMR of 4-Aminoacetophenone (29)

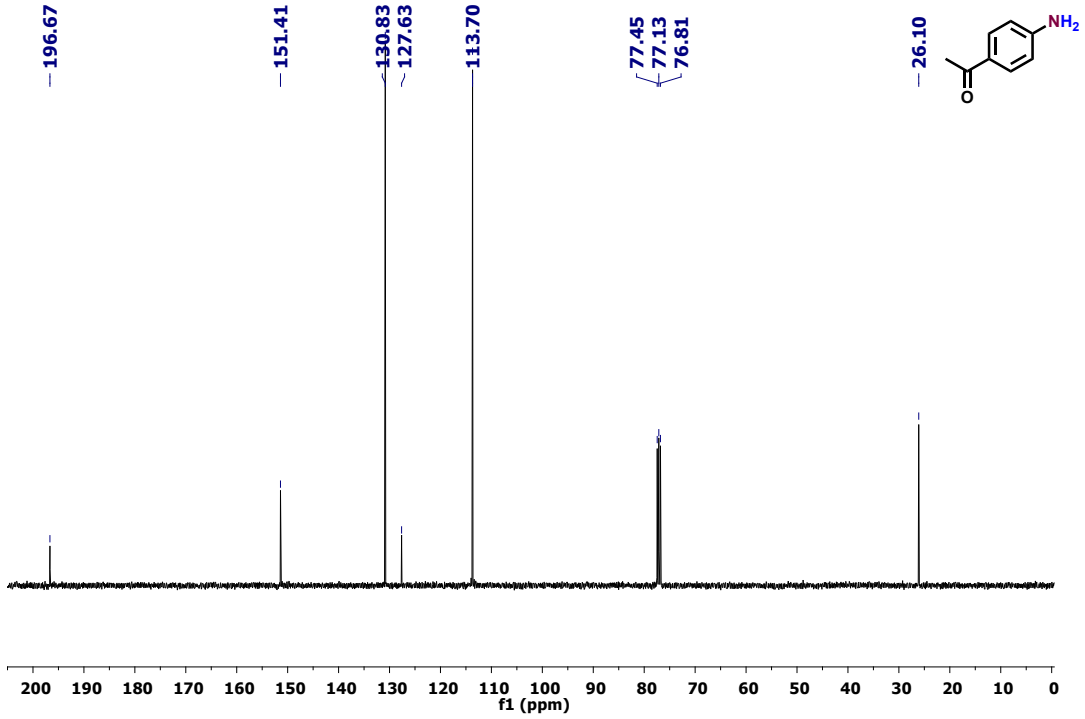


Figure S62: ^{1}H NMR of 4-Aminobenzoic acid (30)

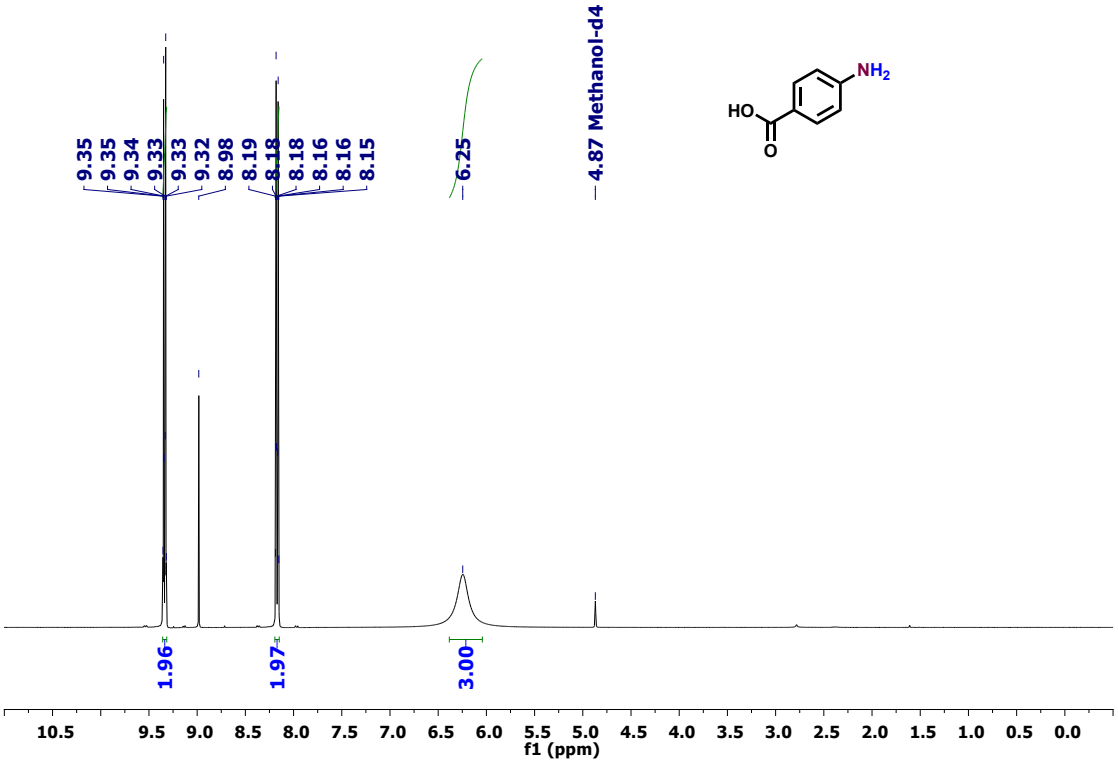


Figure S63: ^{13}C NMR of 4-Aminobenzoic acid (30)

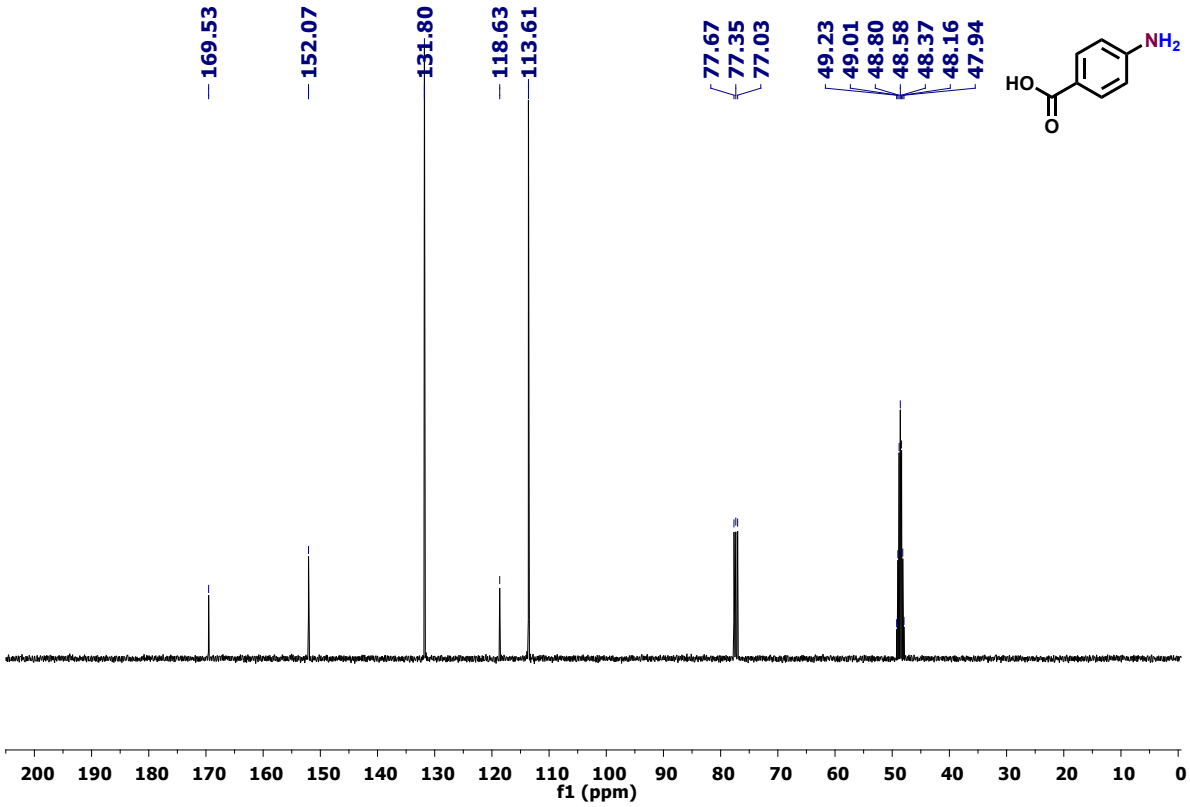


Figure S64: ^{1}H NMR of 4-Aminobenzamide (31)

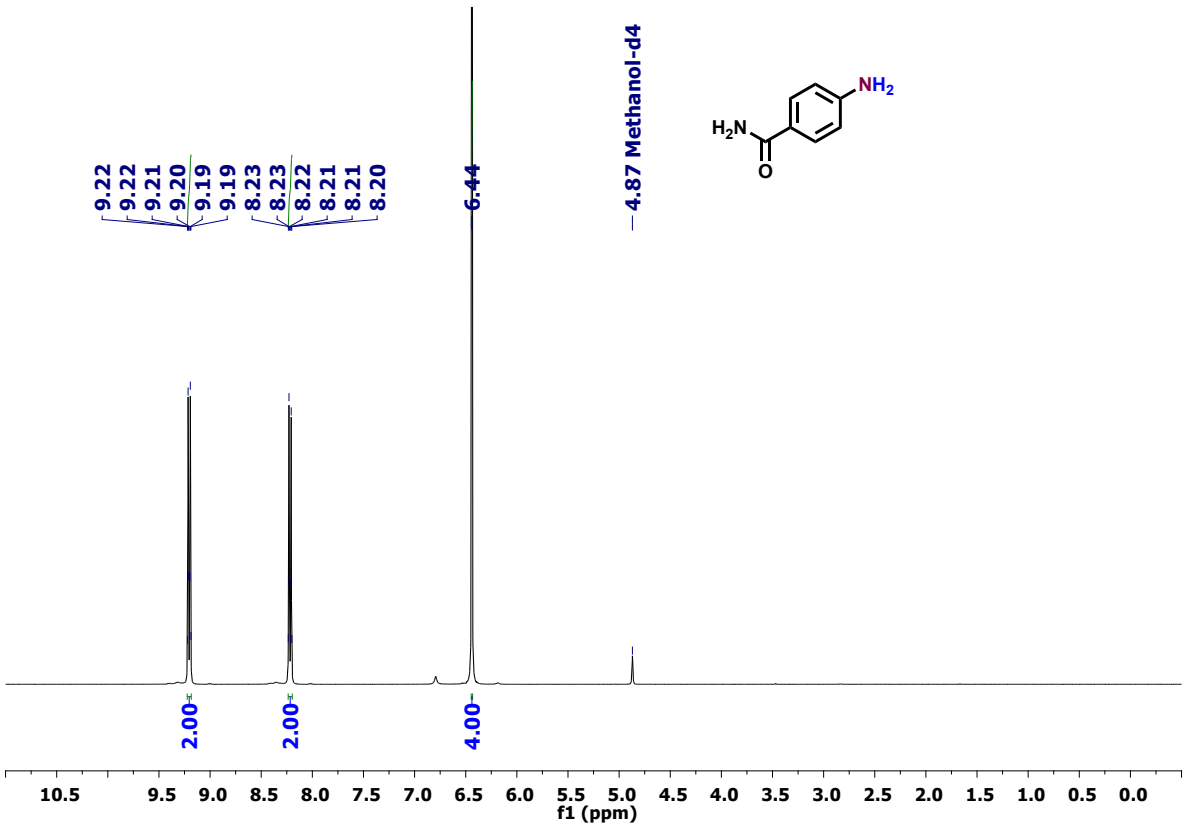


Figure S65: ^{13}C NMR spectrum of 4-Aminobenzamide (31)

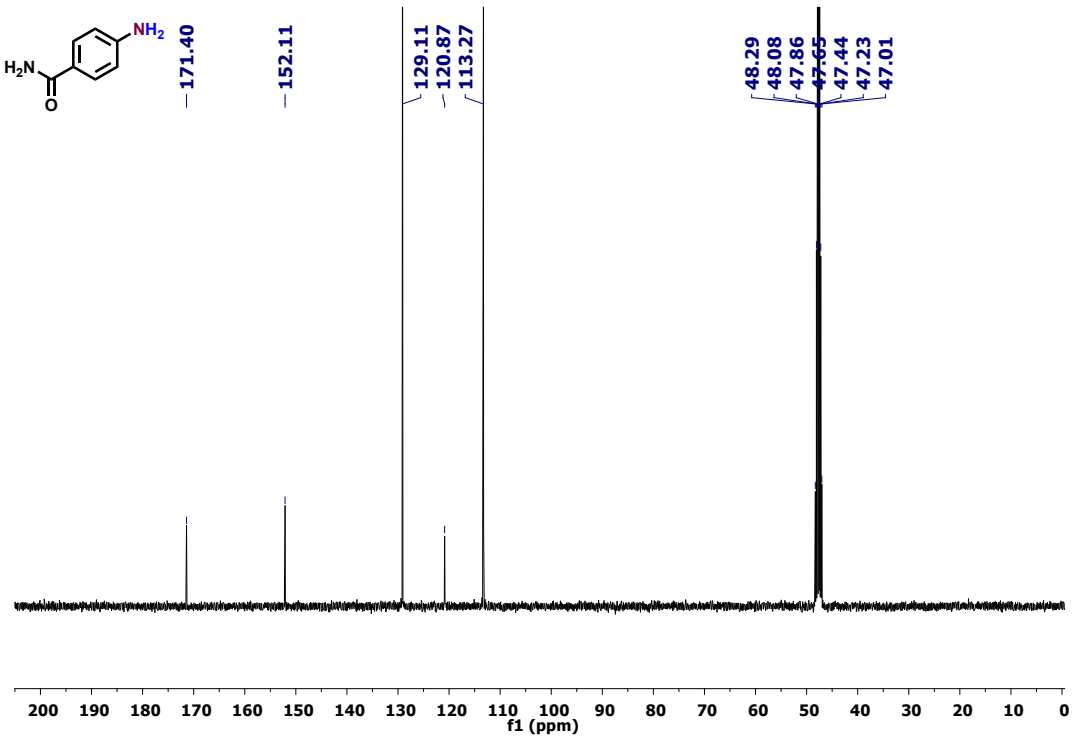


Figure S66: ^{1}H NMR of 4-(4-Aminophenyl) Morholin-3-one (32)

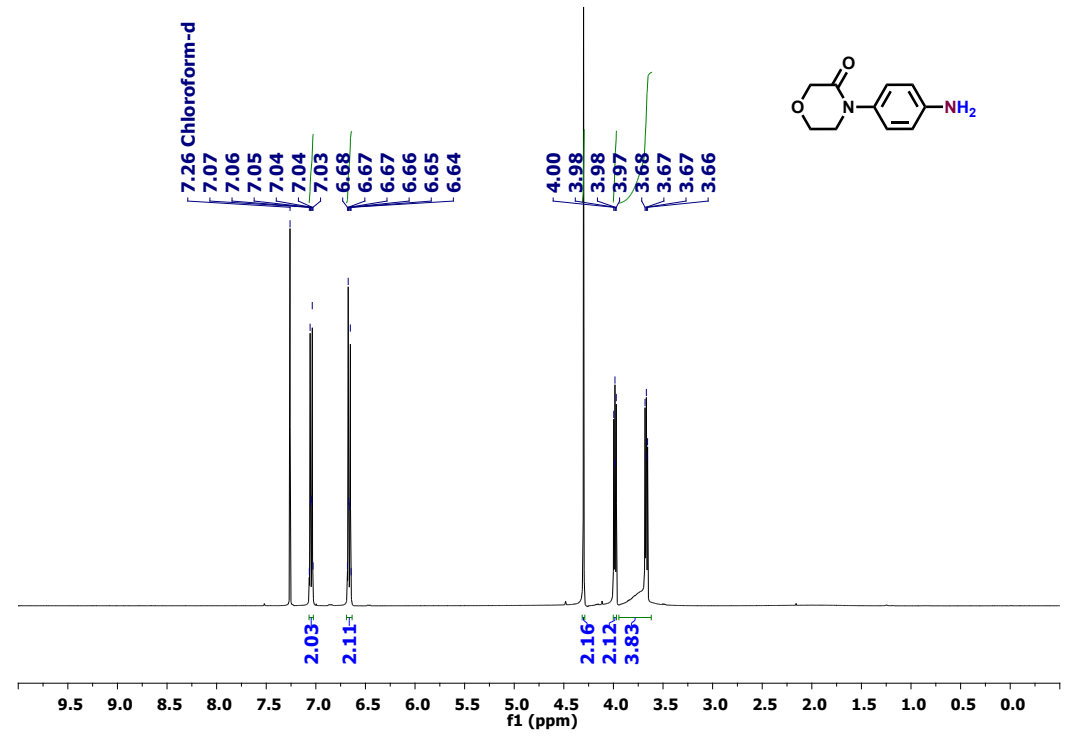


Figure S67: ^{13}C NMR of 4-(4-Aminophenyl) Morholin-3-one (32)

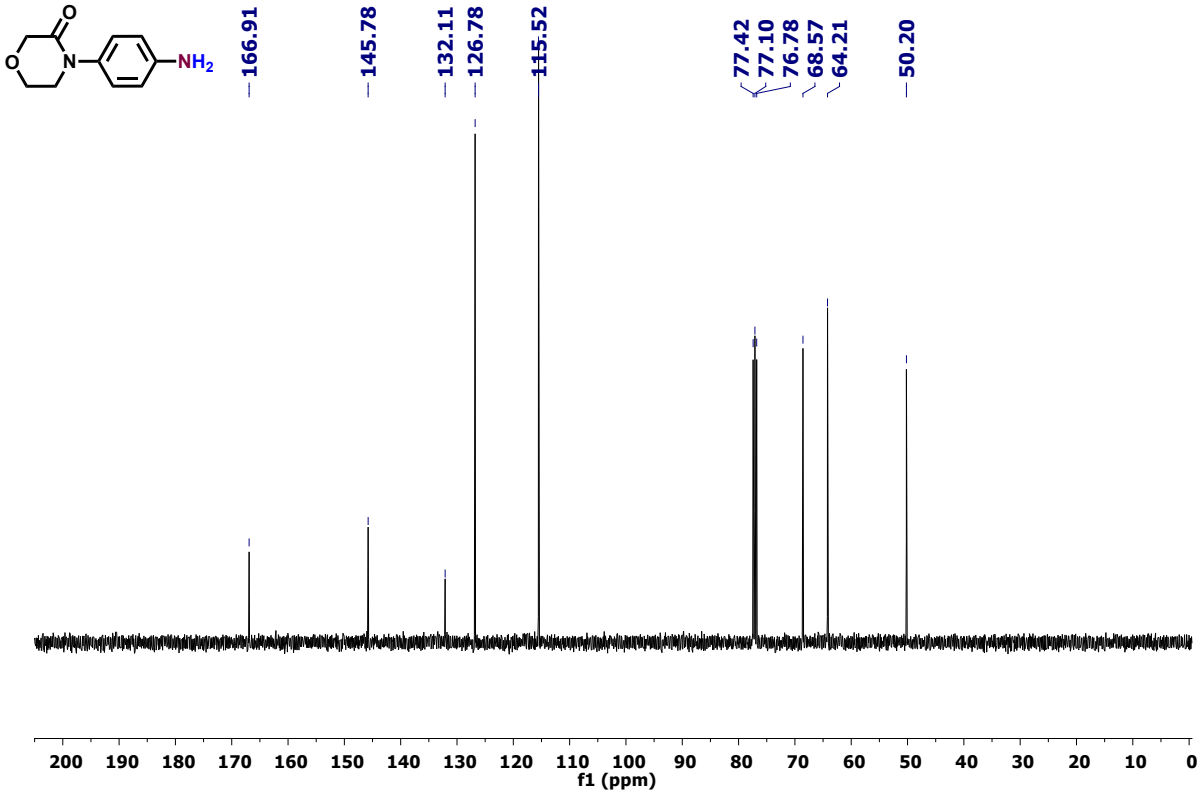


Figure S68: ^{1}H NMR of 4-Aminophenol (33)

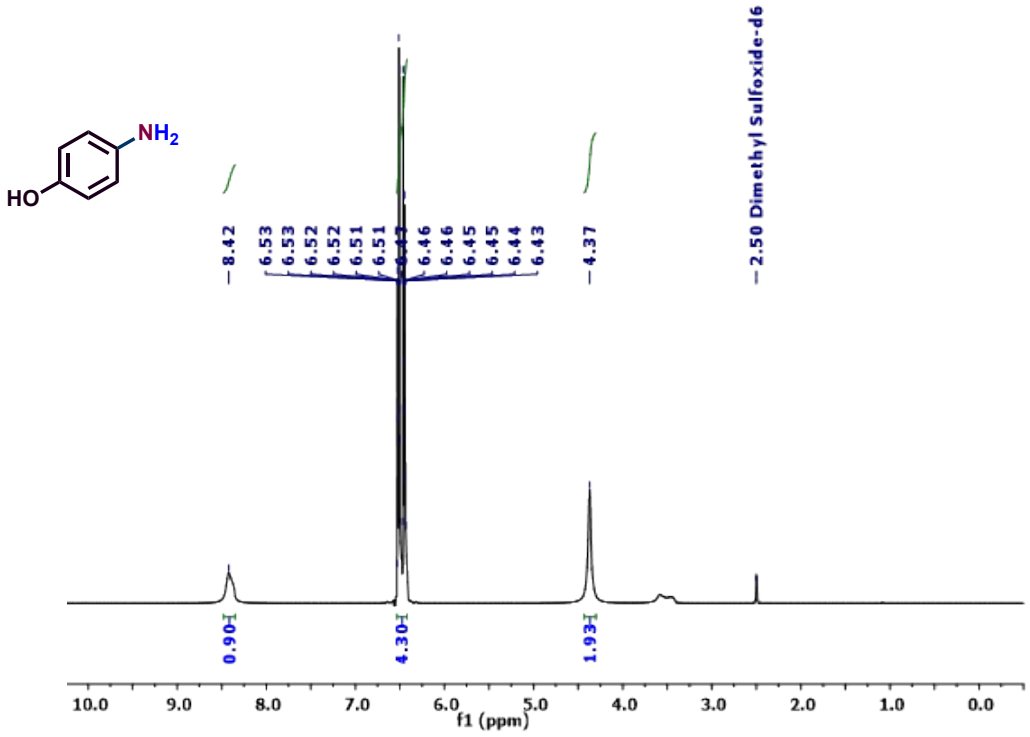


Figure S69: ^{13}C NMR of 4-Aminophenol (33)

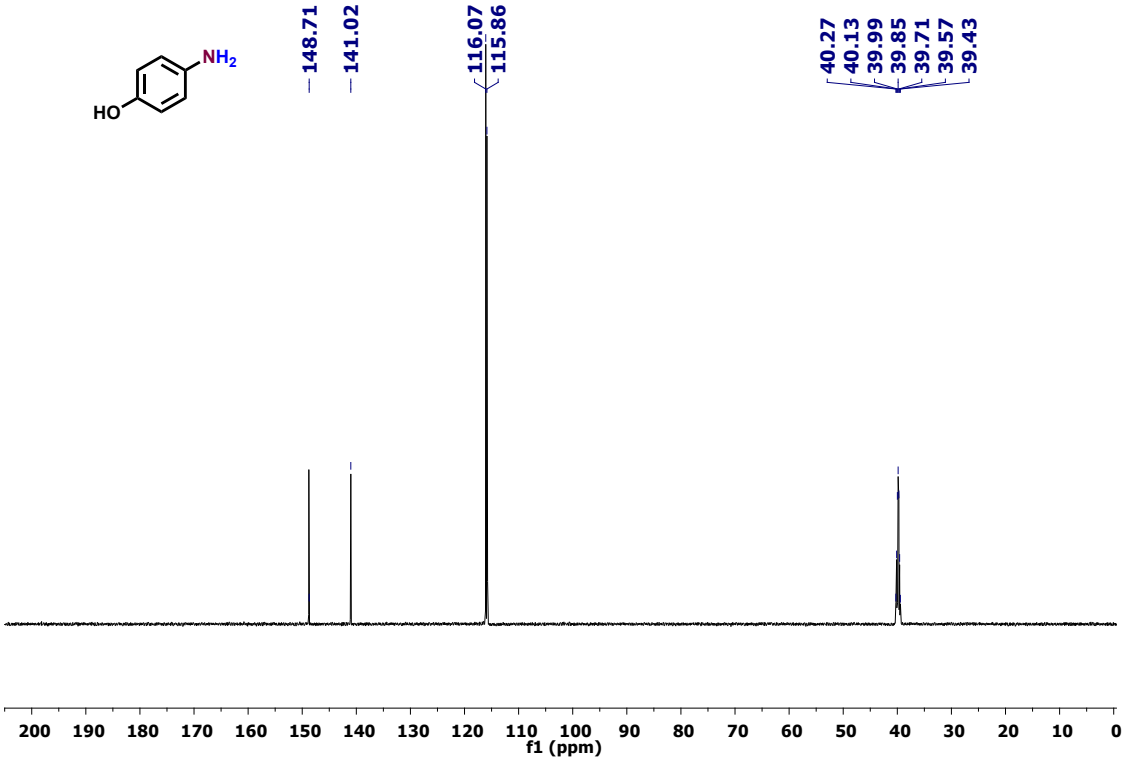


Figure S70: ^{1}H NMR of *p*-Anisidine (34)

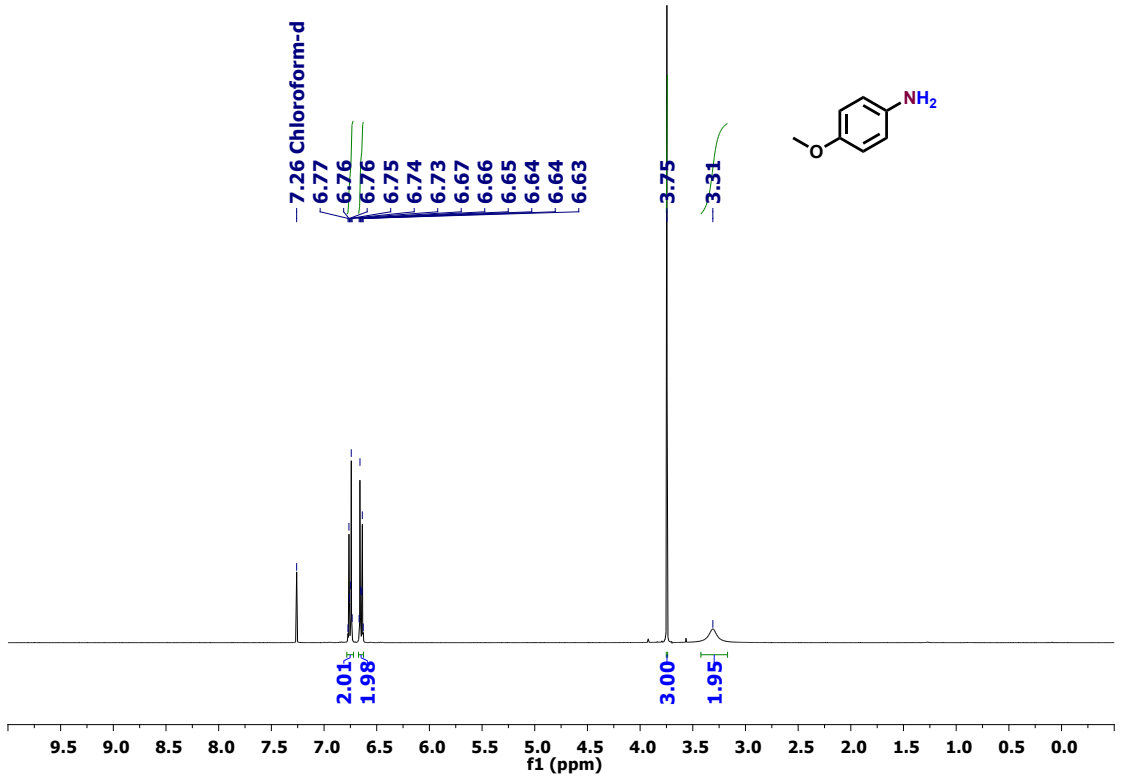


Figure S71: ^{13}C NMR of *p*-Anisidine (34)

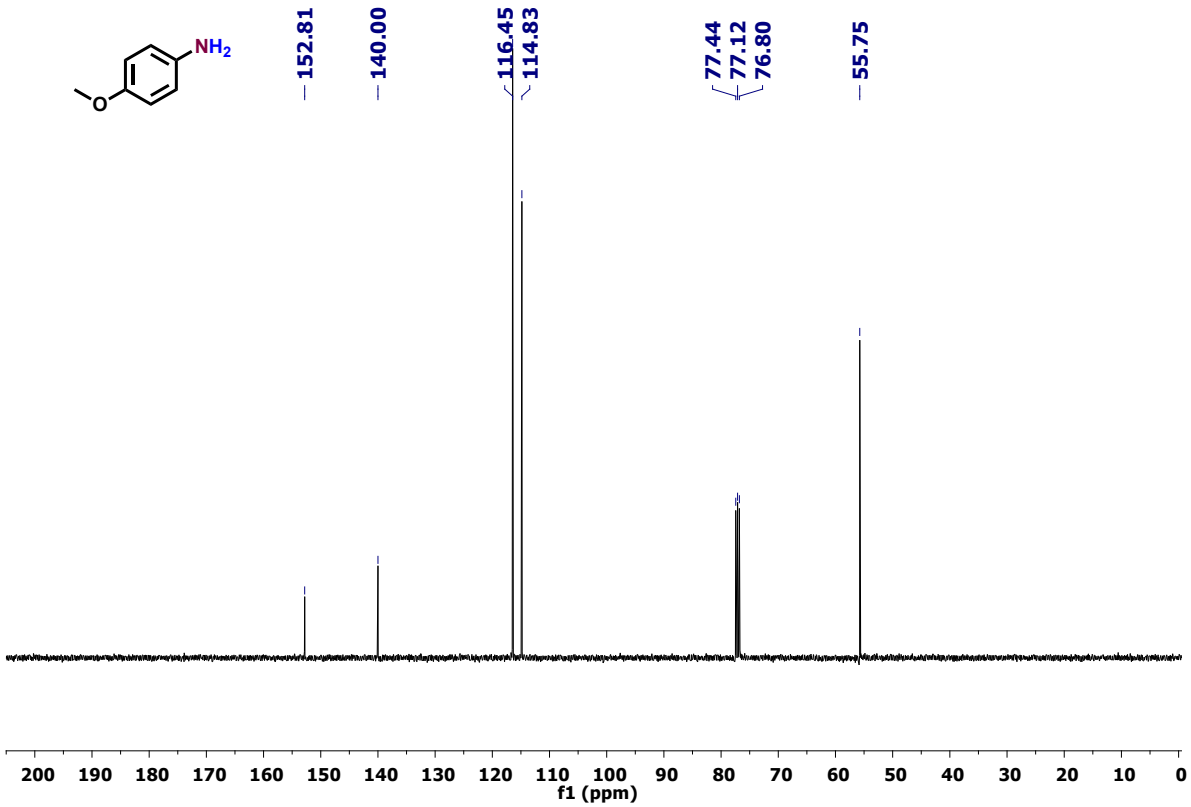


Figure S72: ^{1}H NMR of 4-Aminobenzylalcohol (35)

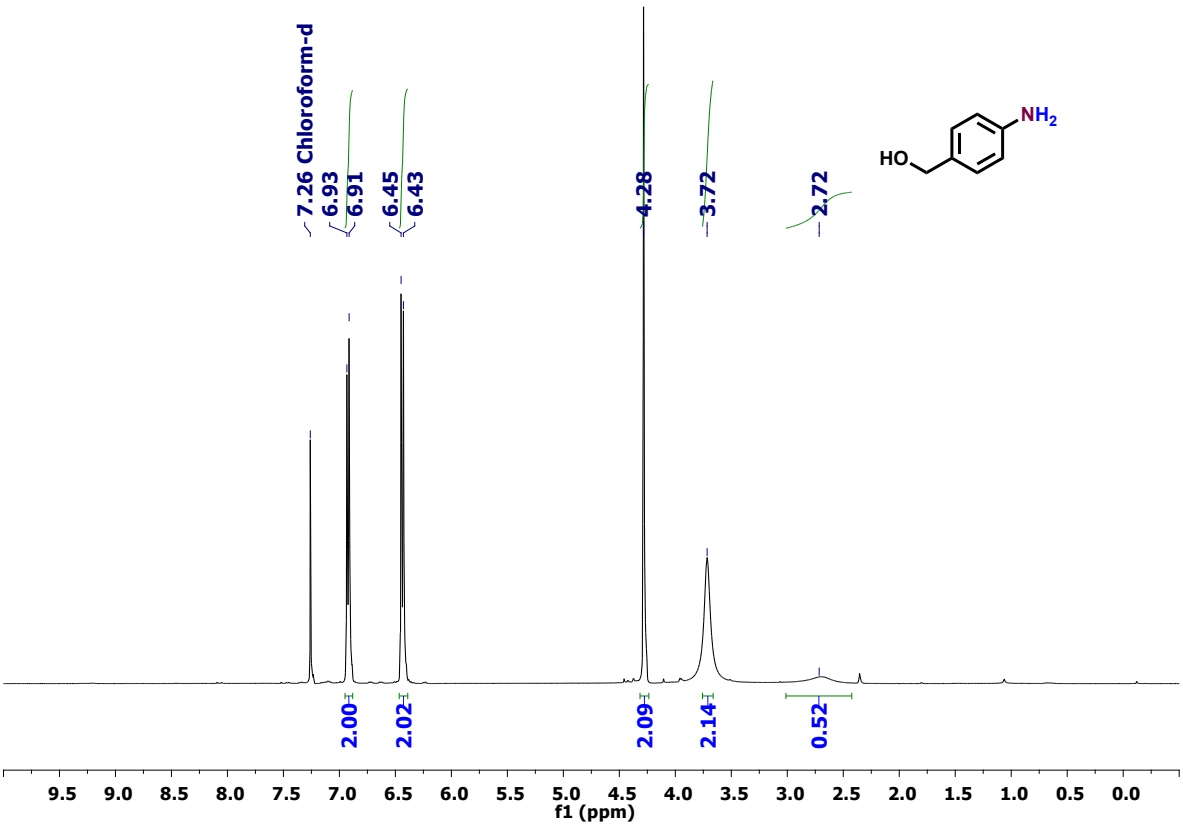


Figure S73: ^{13}C NMR of 4-Aminobenzylalcohol (35)

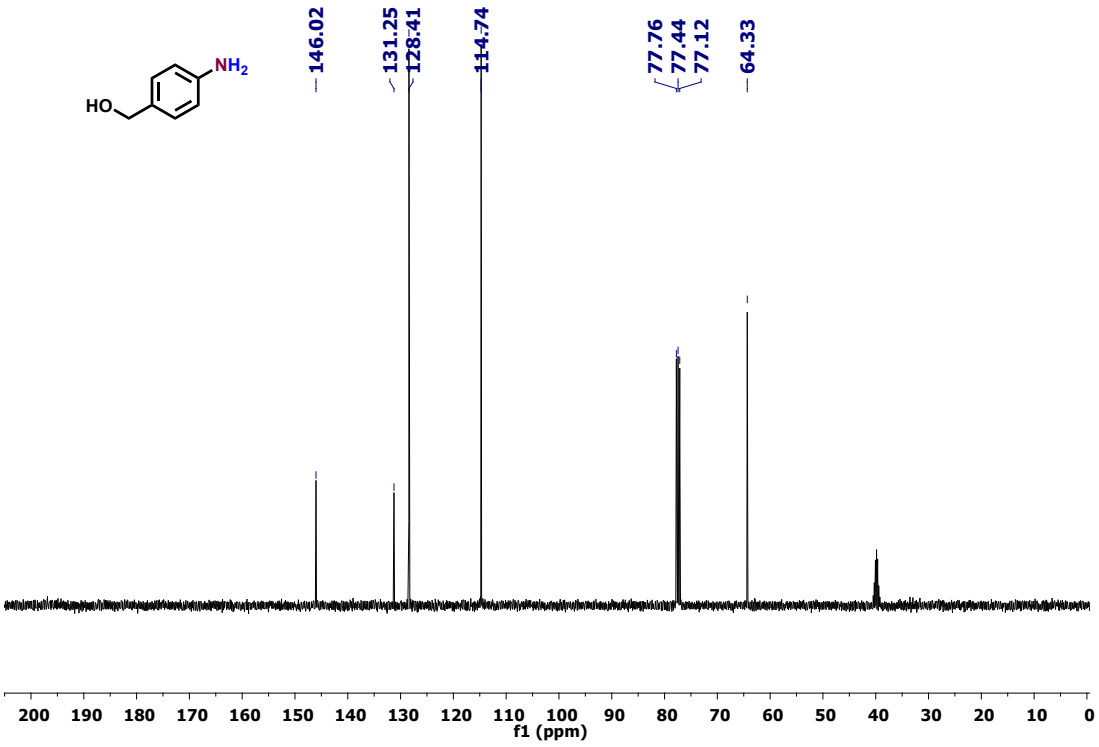


Figure S74: ^{1}H NMR of 3,4-Methylinedioxyaniline (36)

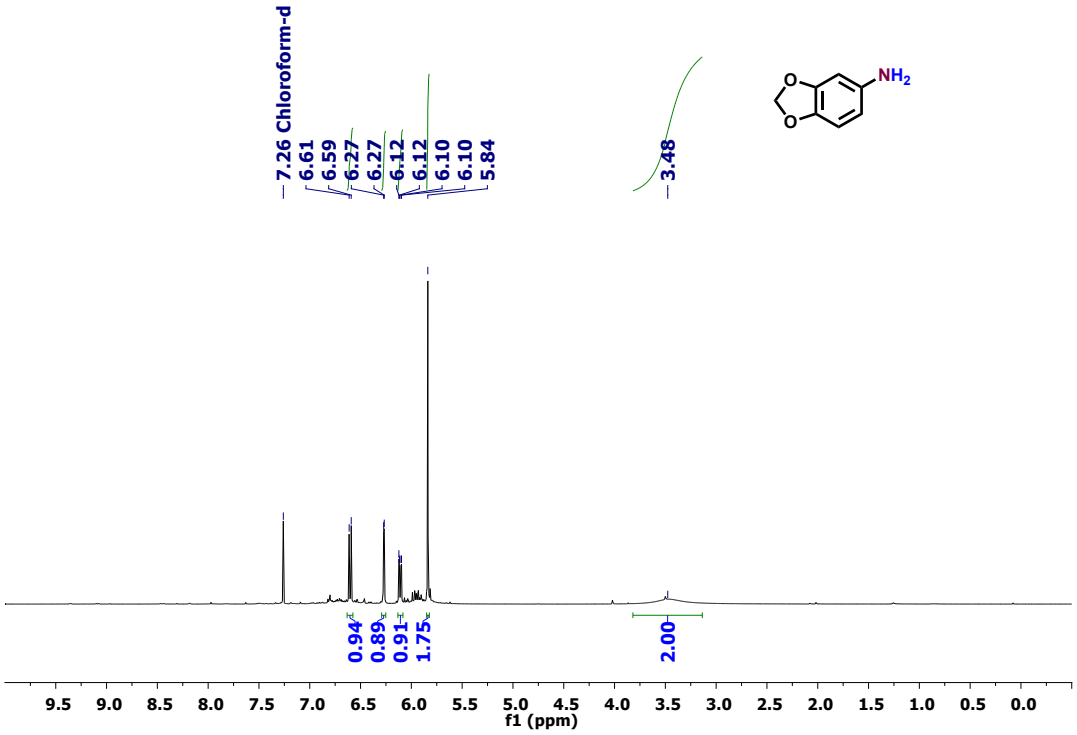


Figure S75: ^{13}C NMR of 3,4-Methylinedioxyaniline (36)

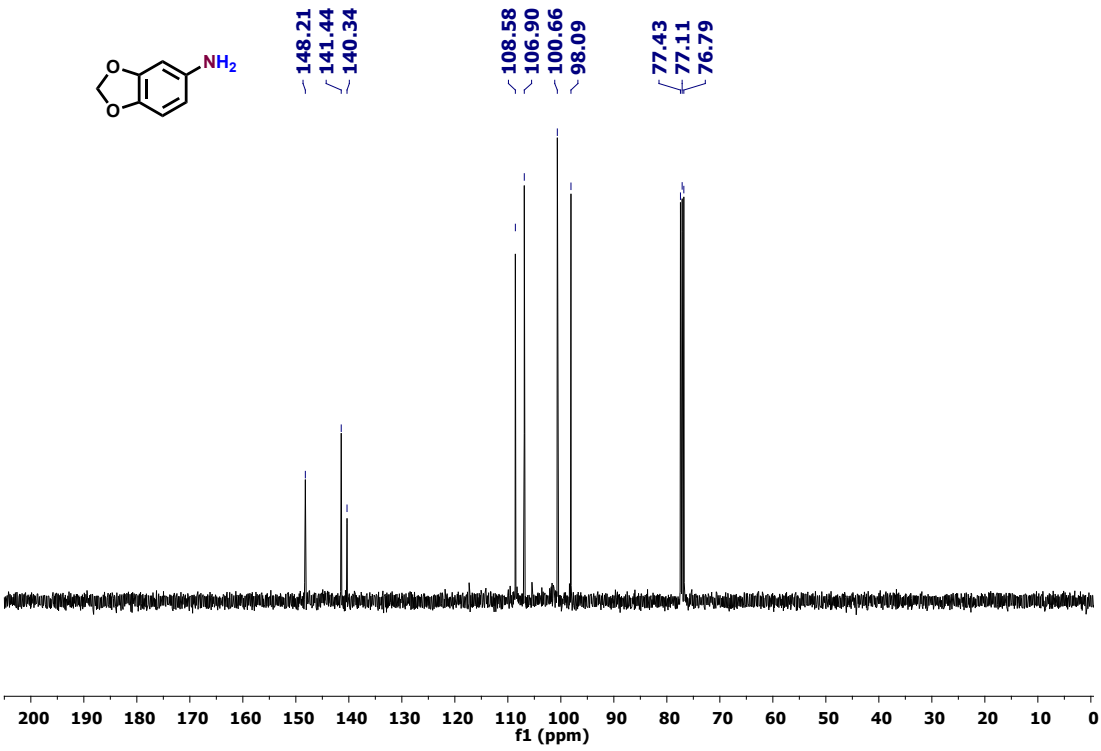


Figure S76: ^{1}H NMR of Pyrene-1-amine (37)

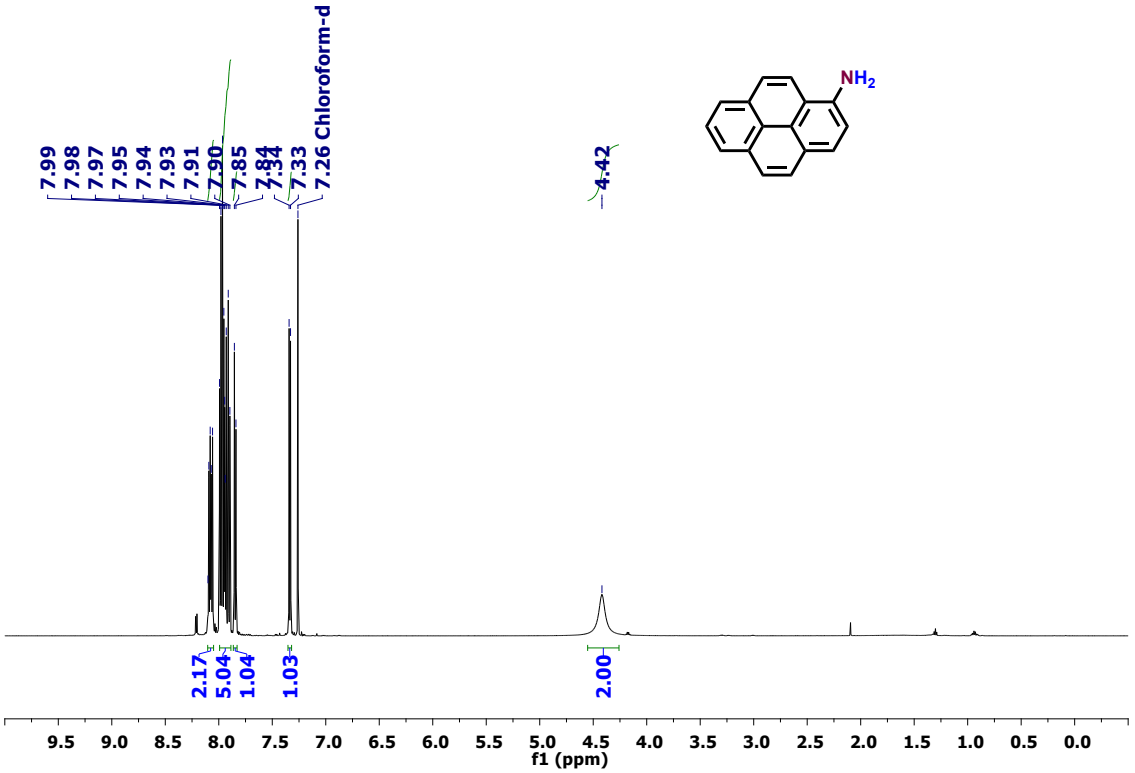


Figure S77: ^{13}C NMR of Pyrene-1-amine (37)

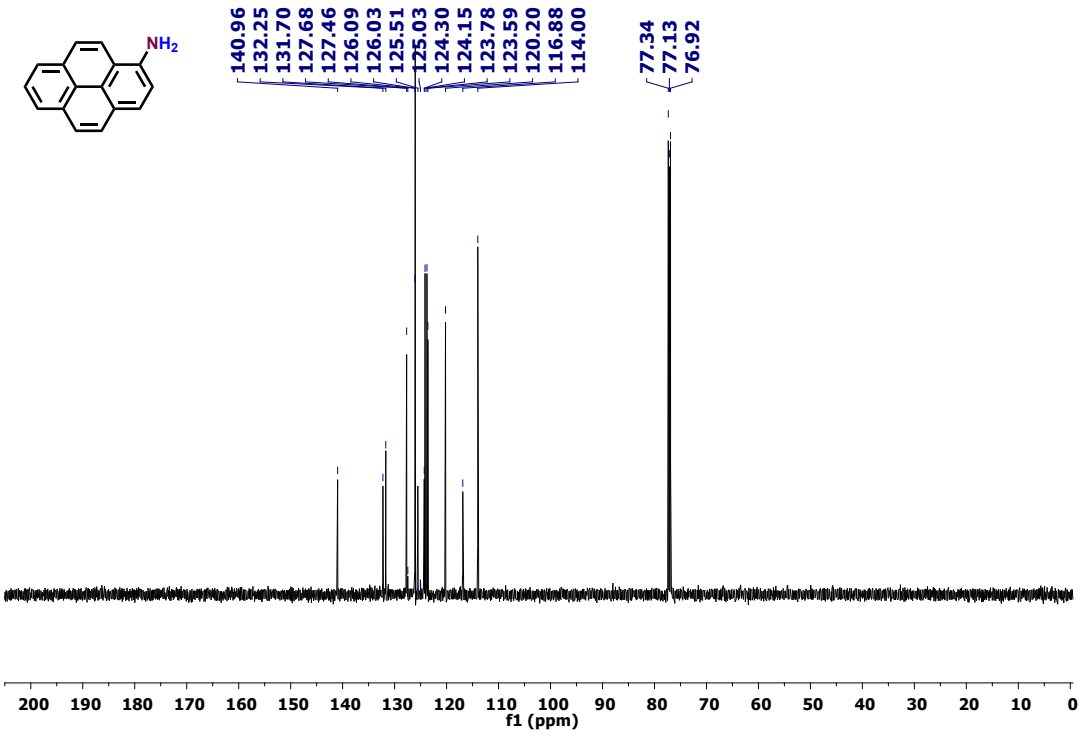


Figure S78: ^{1}H NMR of *o*-Toluidine (38)

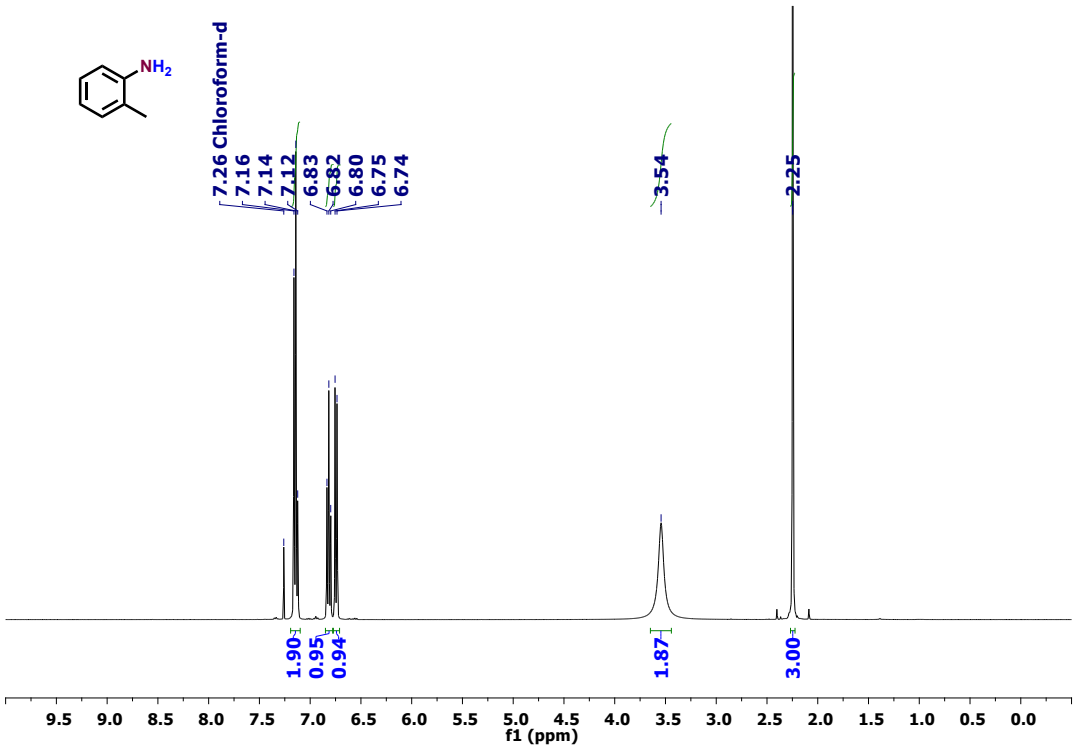


Figure S79: ^{13}C NMR of *o*-Toluidine (38)

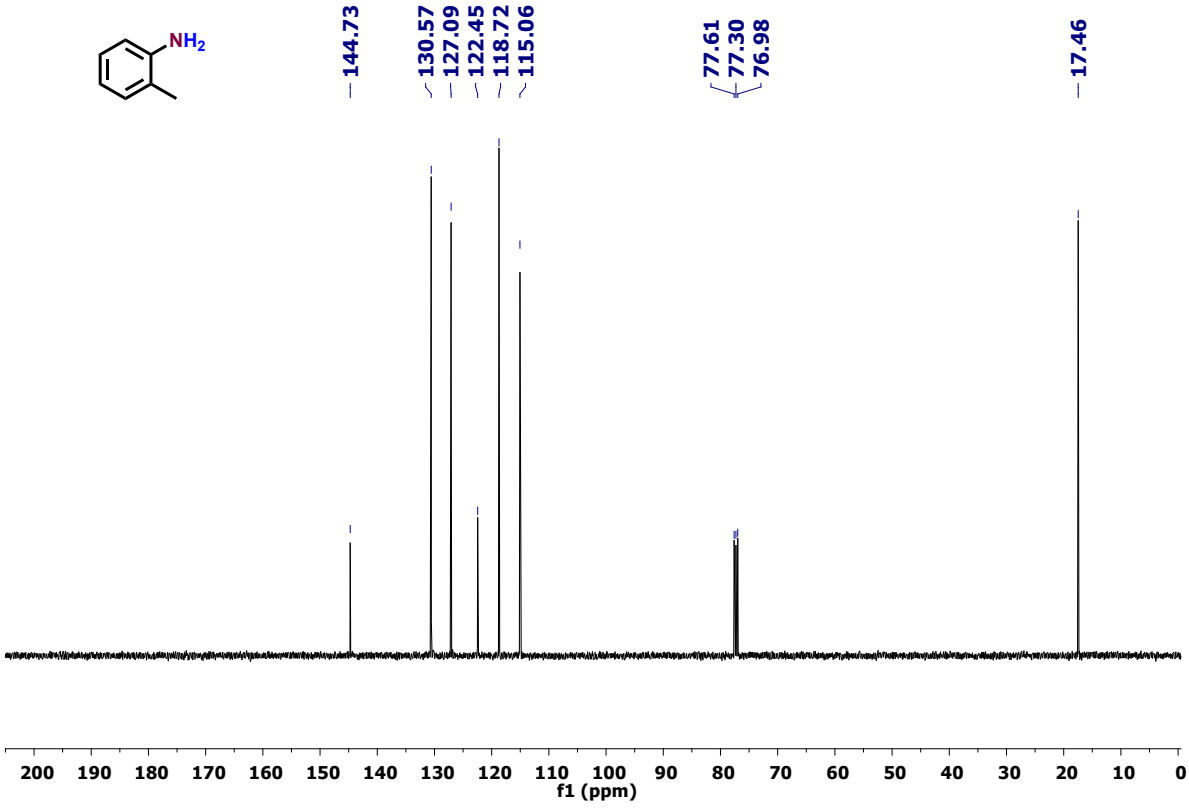


Figure S80: ^{1}H NMR of 3,5-Dimethylaniline (39)

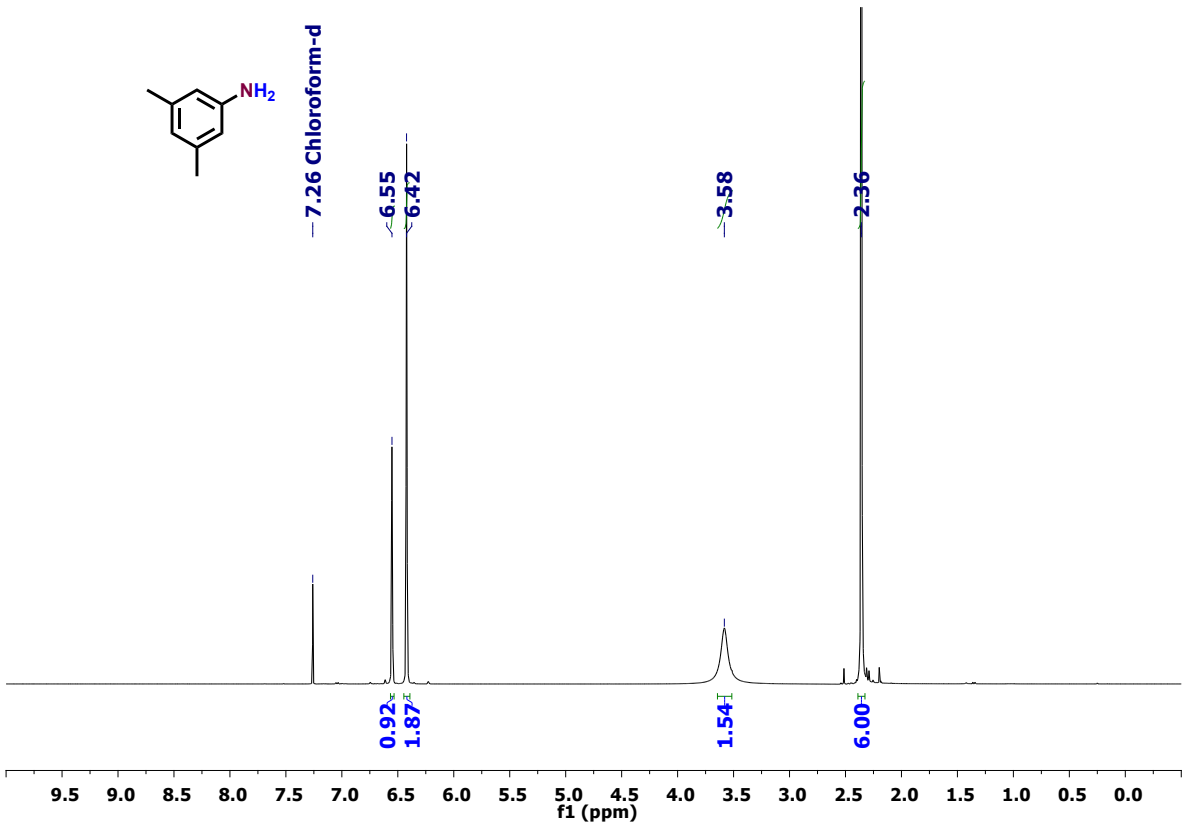


Figure S81: NMR of 3,5-Dimethylaniline (39)

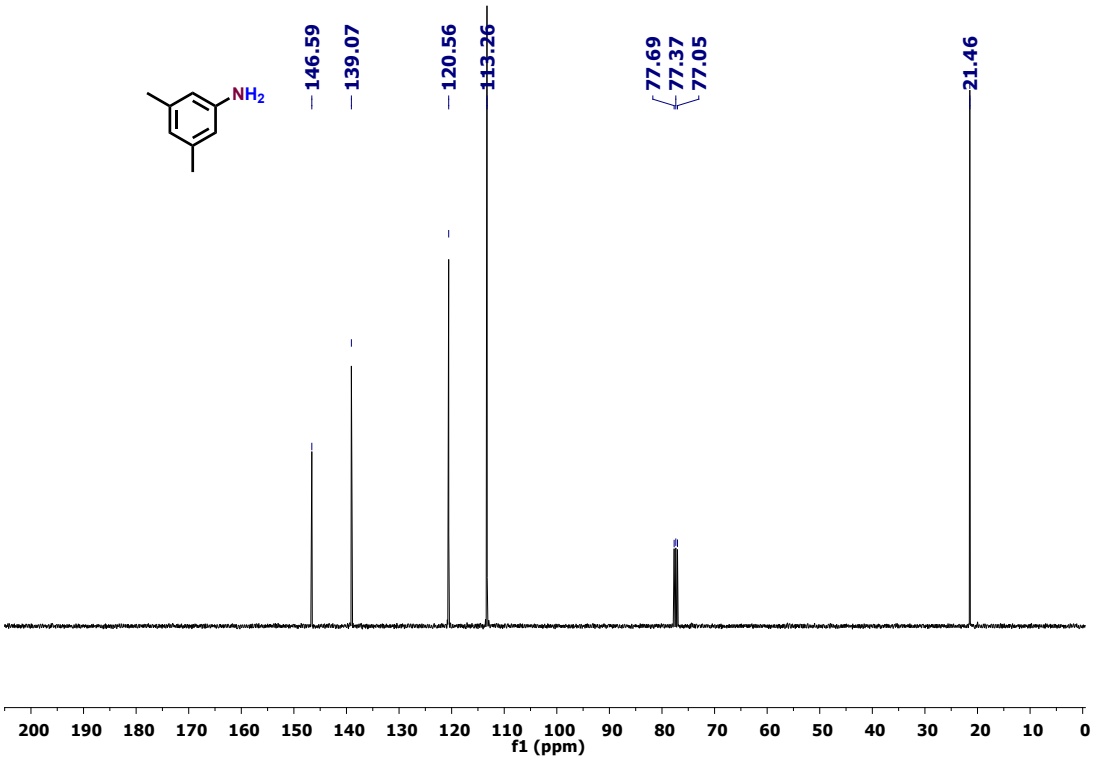


Figure S82: ^{1}H NMR of *p*-Toluidine (40)

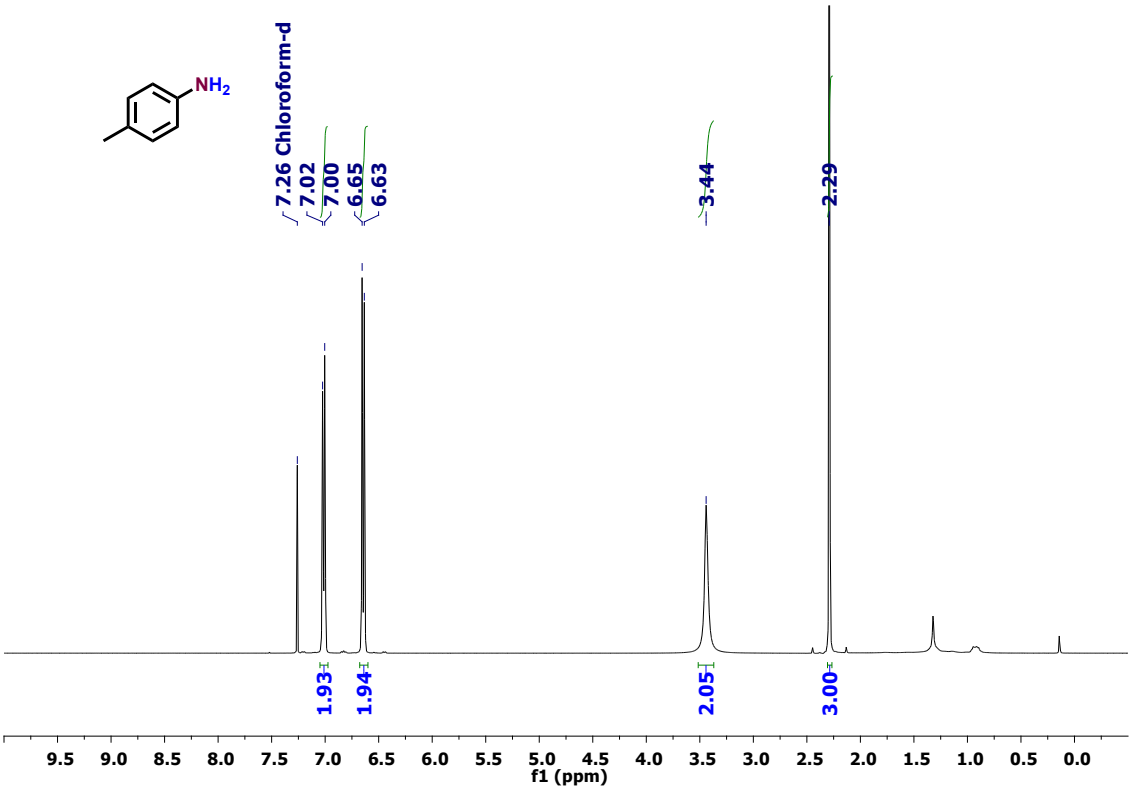


Figure S83: ^{13}C NMR of *p*-Toluidine (40)

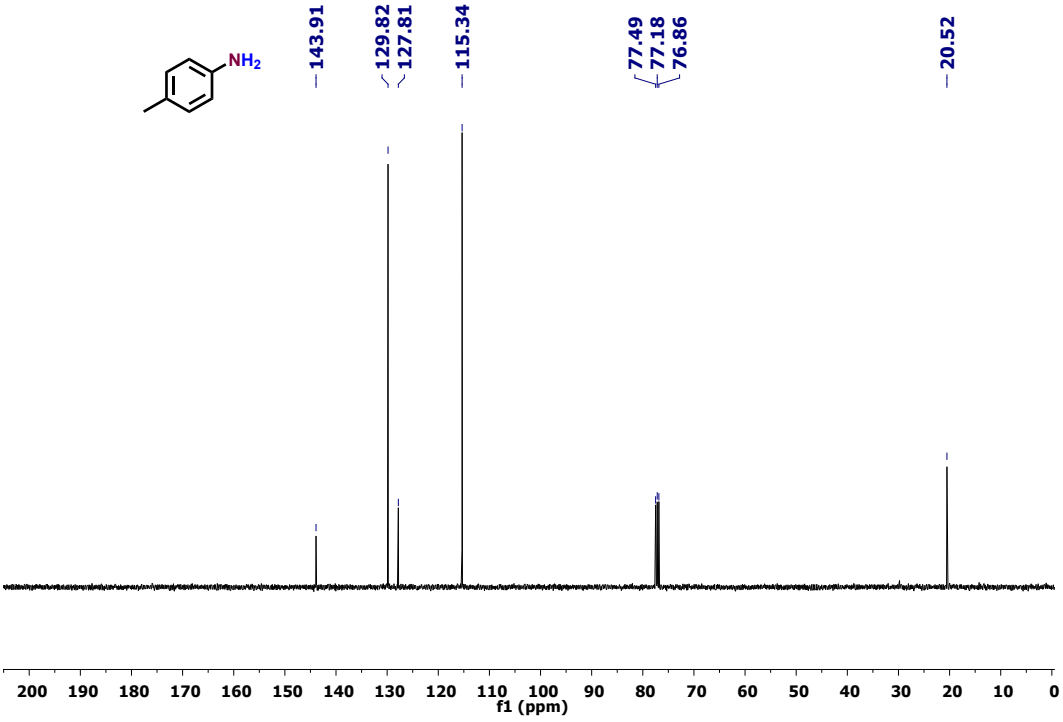


Figure S84: ^{1}H NMR of 2,3,5-Trimethylaniline (41)

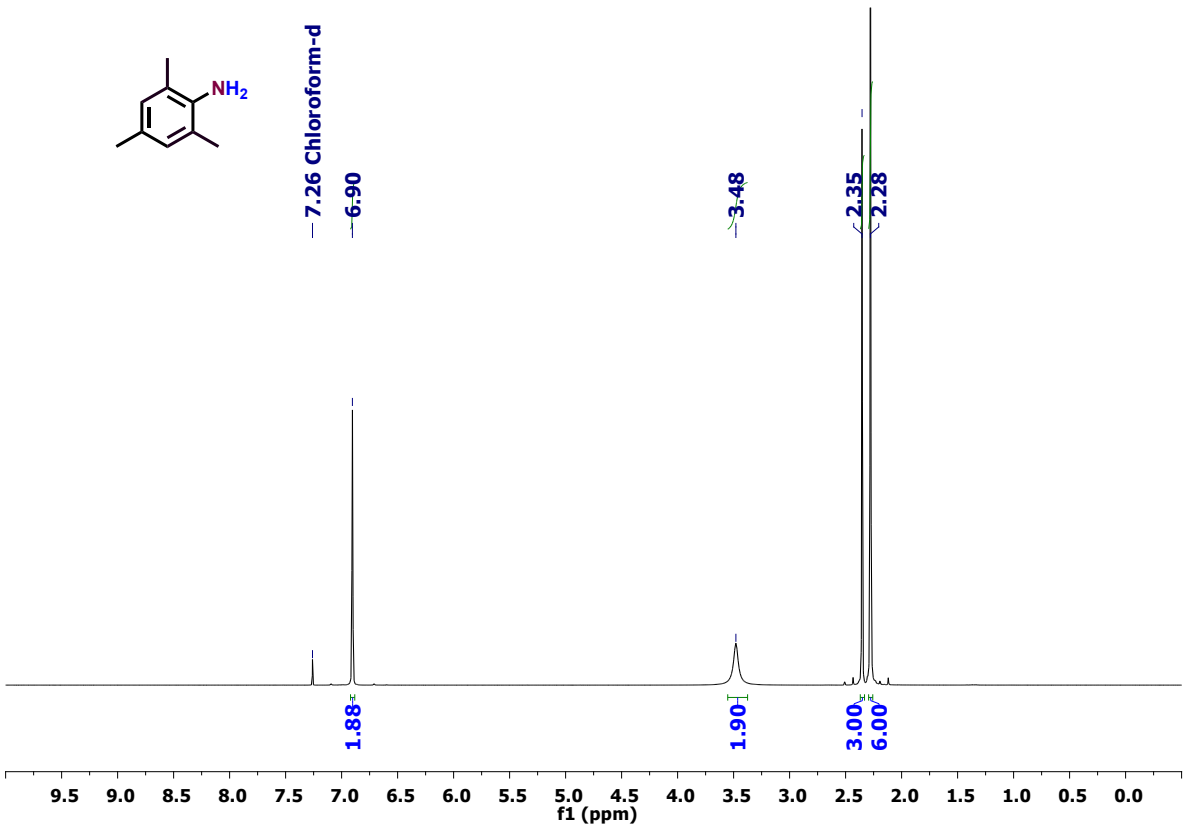


Figure S85: ^{13}C NMR of 2,3,5-Trimethylaniline (41)

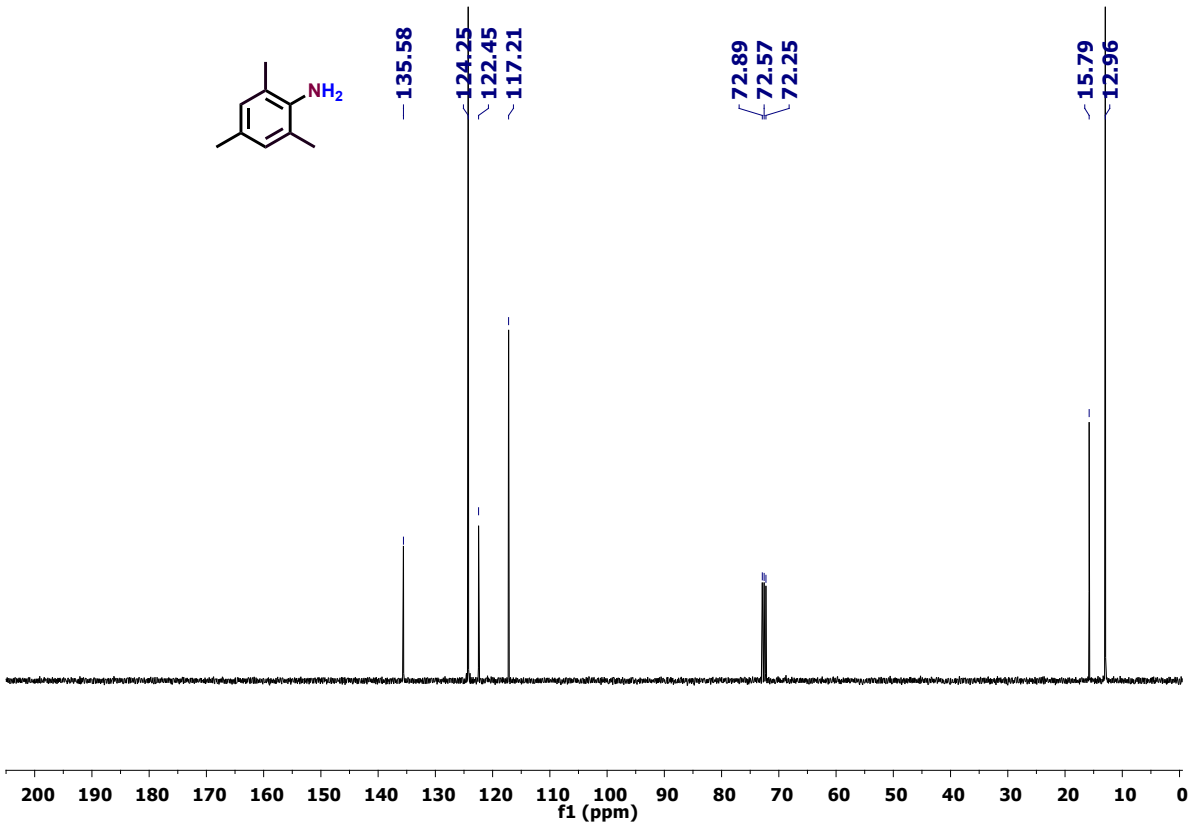


Figure S86: ^{1}H NMR of Aniline (42)

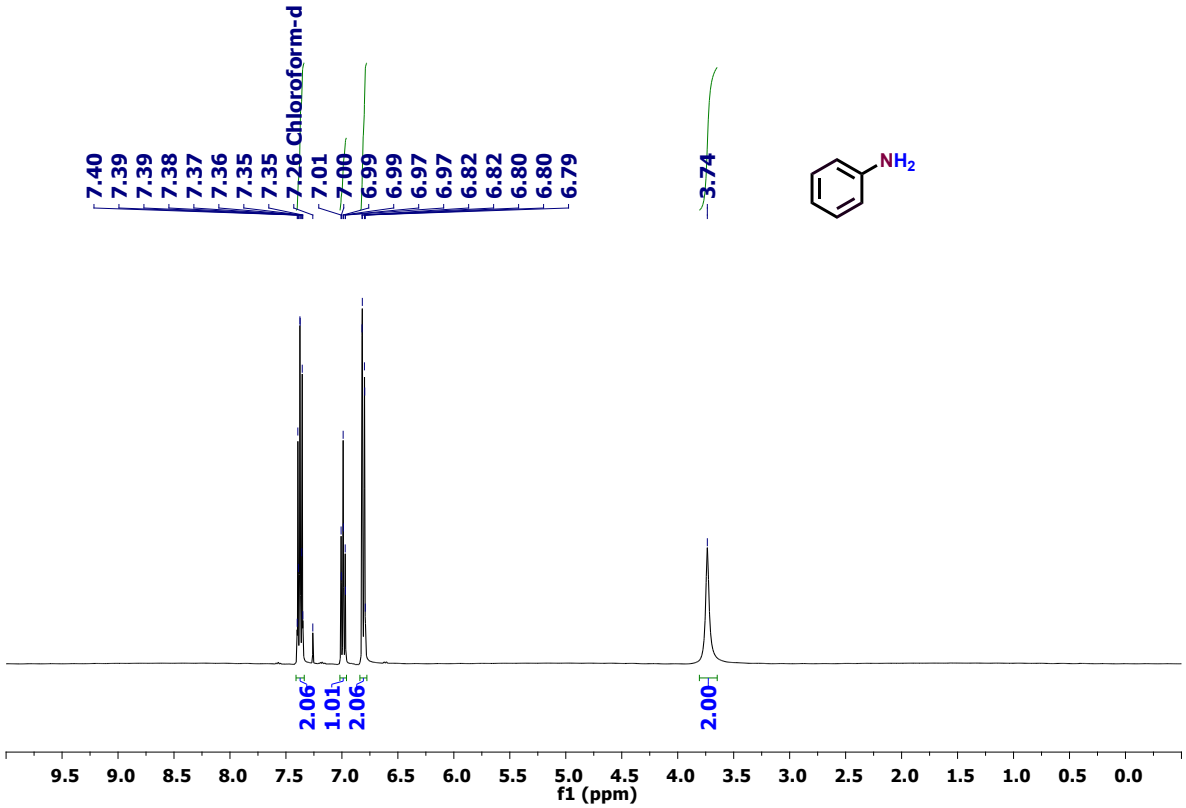


Figure S87: ^{13}C NMR of Aniline (42)

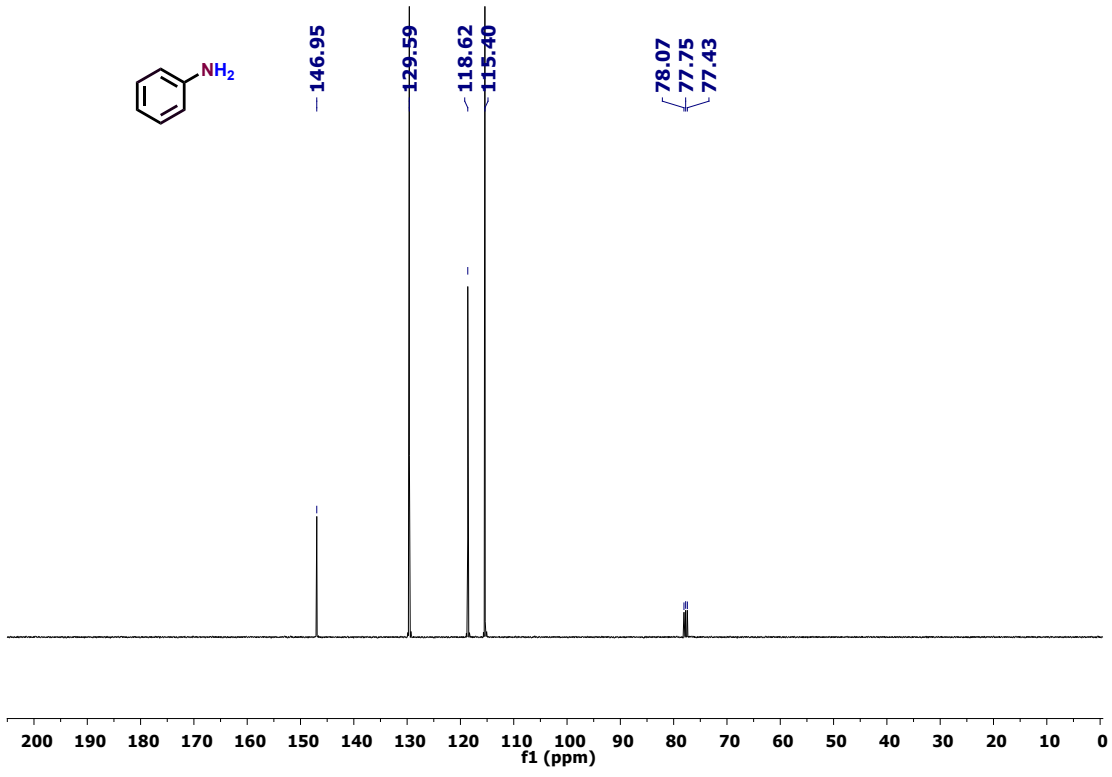


Figure S88: ^{1}H NMR of 1,2-Diaminobenzene (43)

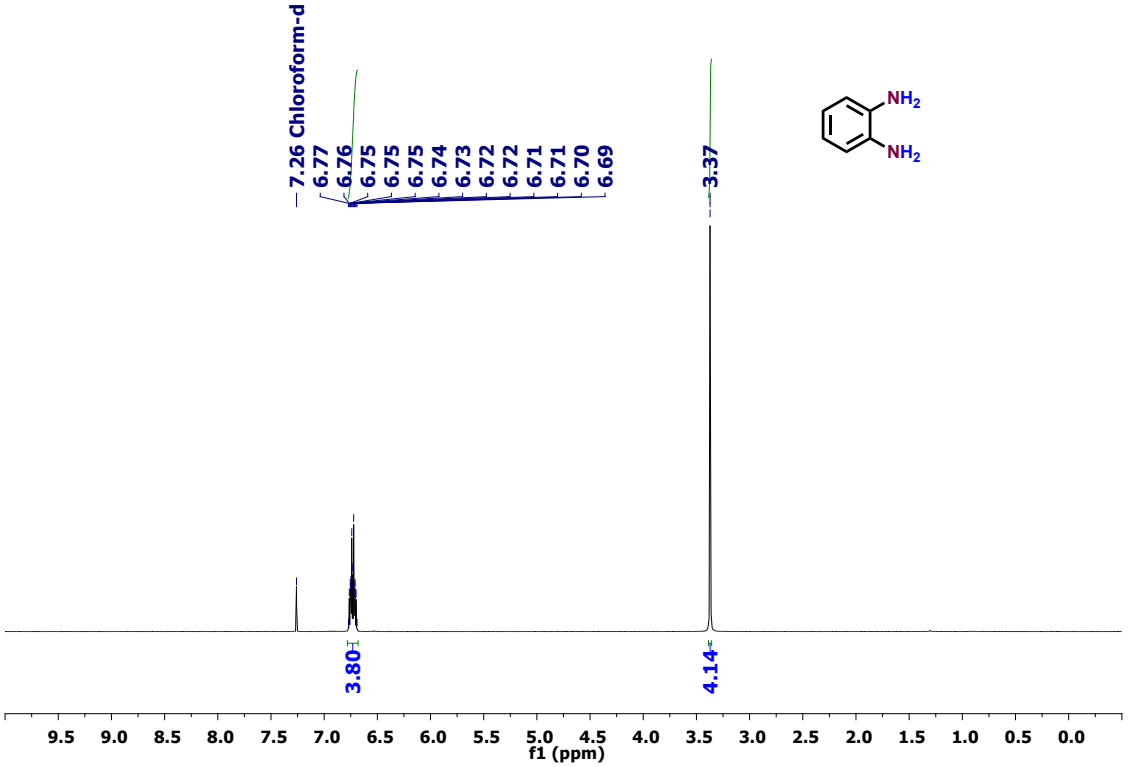


Figure S89: ^{13}C NMR of 1,2-Diaminobenzene (43)

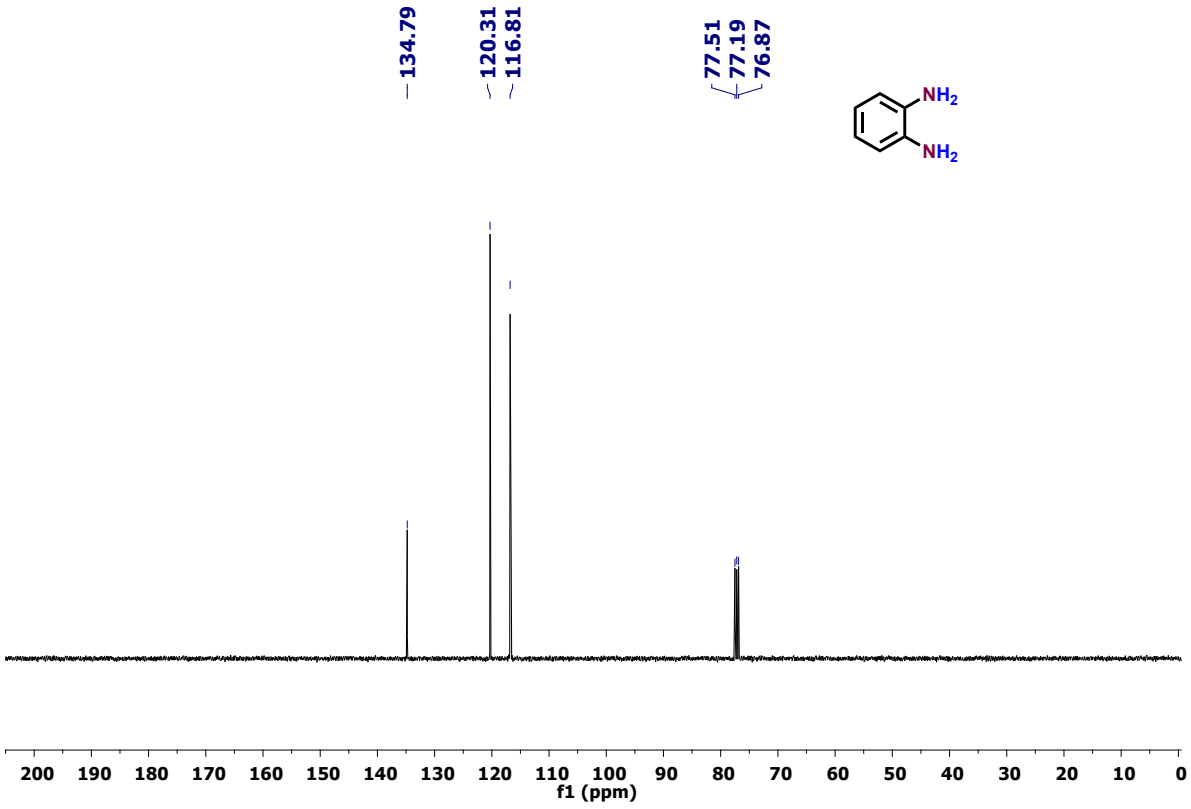


Figure S90: ^{1}H NMR of 1,2-(Ethane-1,2-diyl)dianiline (44)

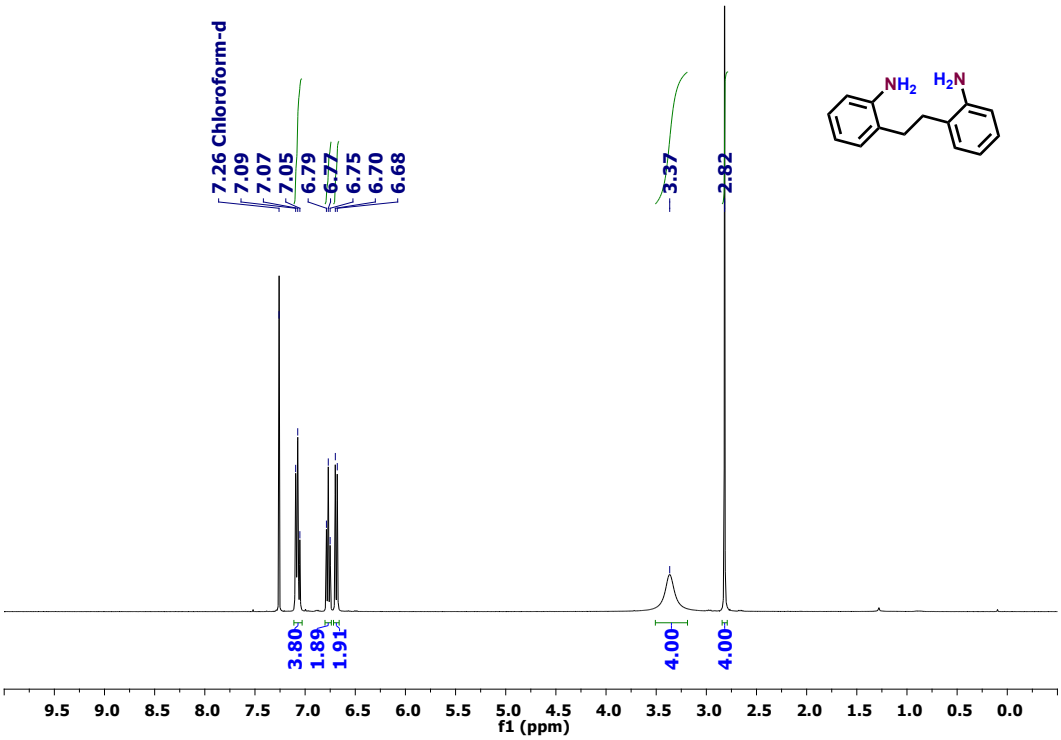


Figure S91: ^{13}C NMR of 1,2-(Ethane-1,2-diyl)dianiline (44)

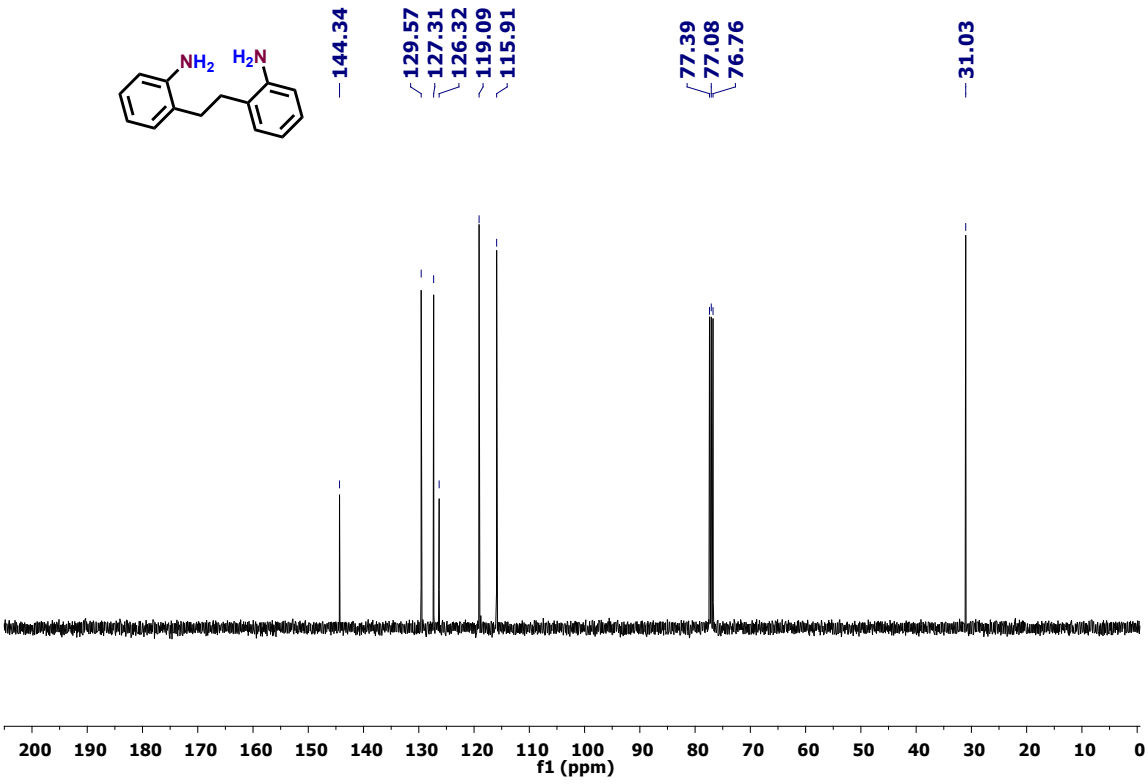


Figure S92: ^{1}H NMR of 2-Aminopyridine (45)

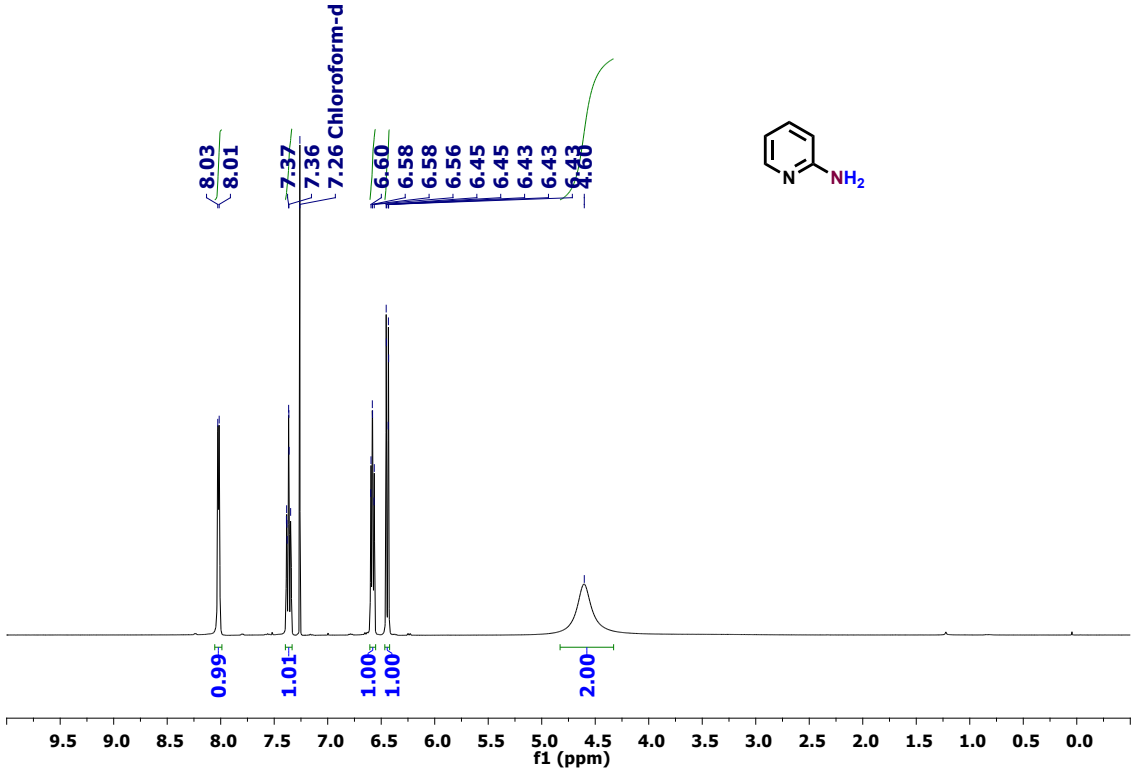


Figure S93: ^{13}C NMR of 2-Aminopyridine (45)

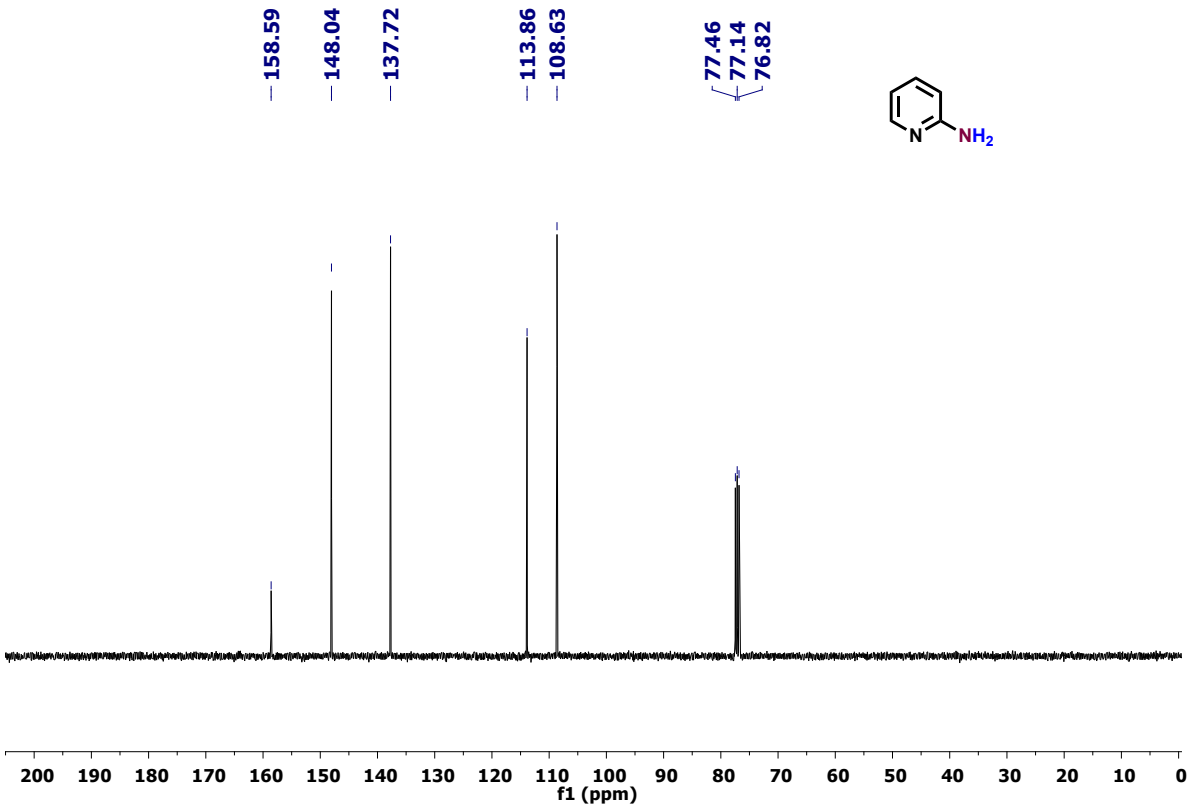


Figure S94: ^{1}H NMR of 3-Aminopyridine (46)

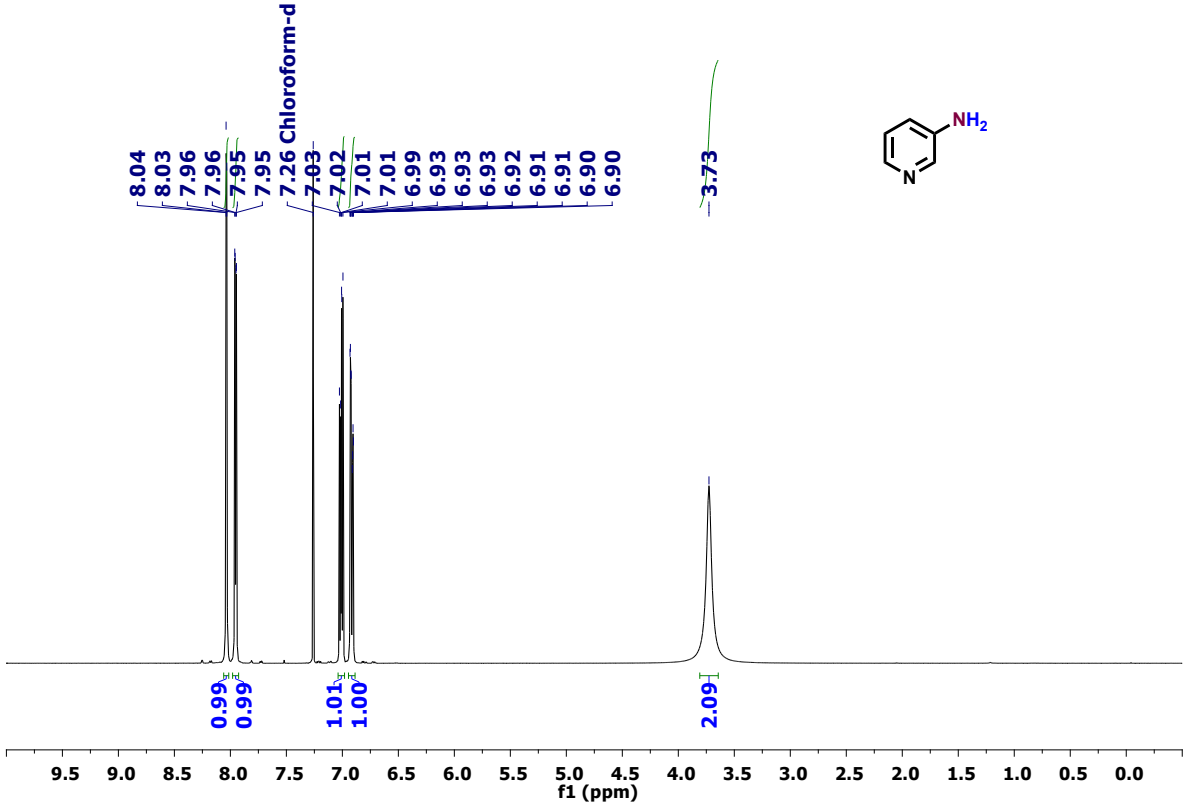


Figure S95: ^{13}C NMR of 3-Aminopyridine (46)

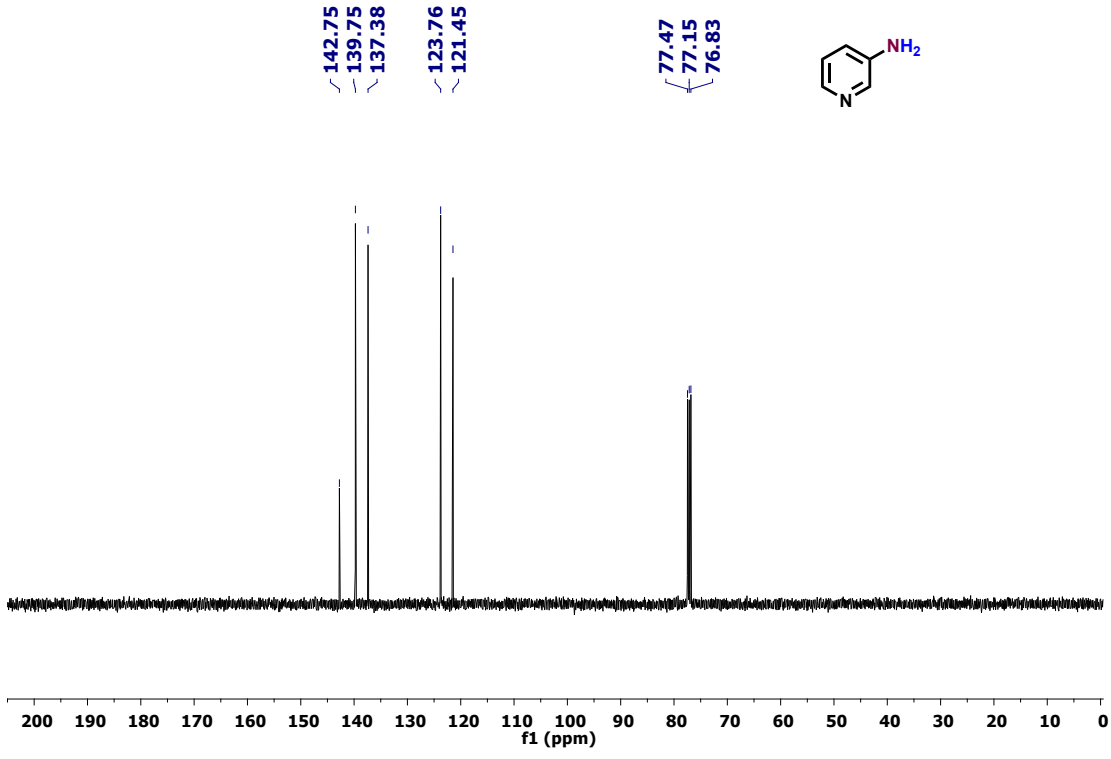


Figure S96: ^{1}H NMR of 4-Aminopyridine (47)

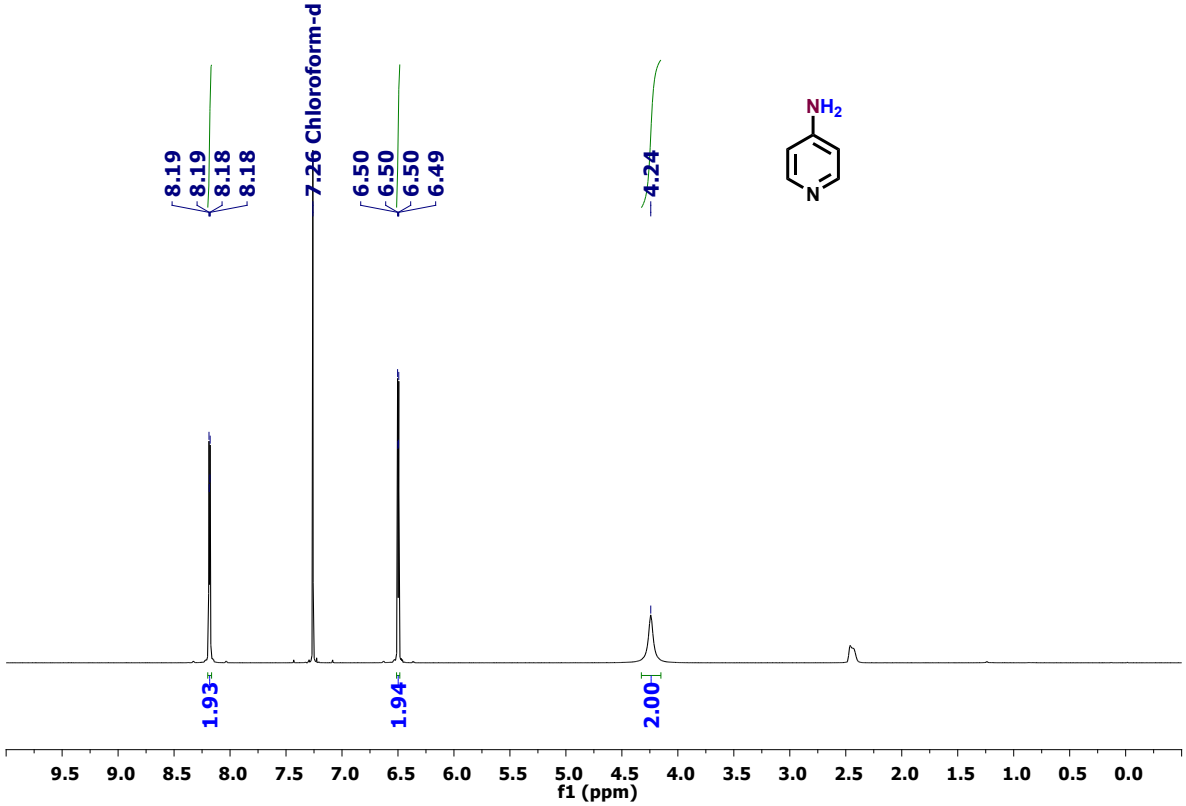


Figure S97: ^{13}C NMR of 4-Aminopyridine (47)

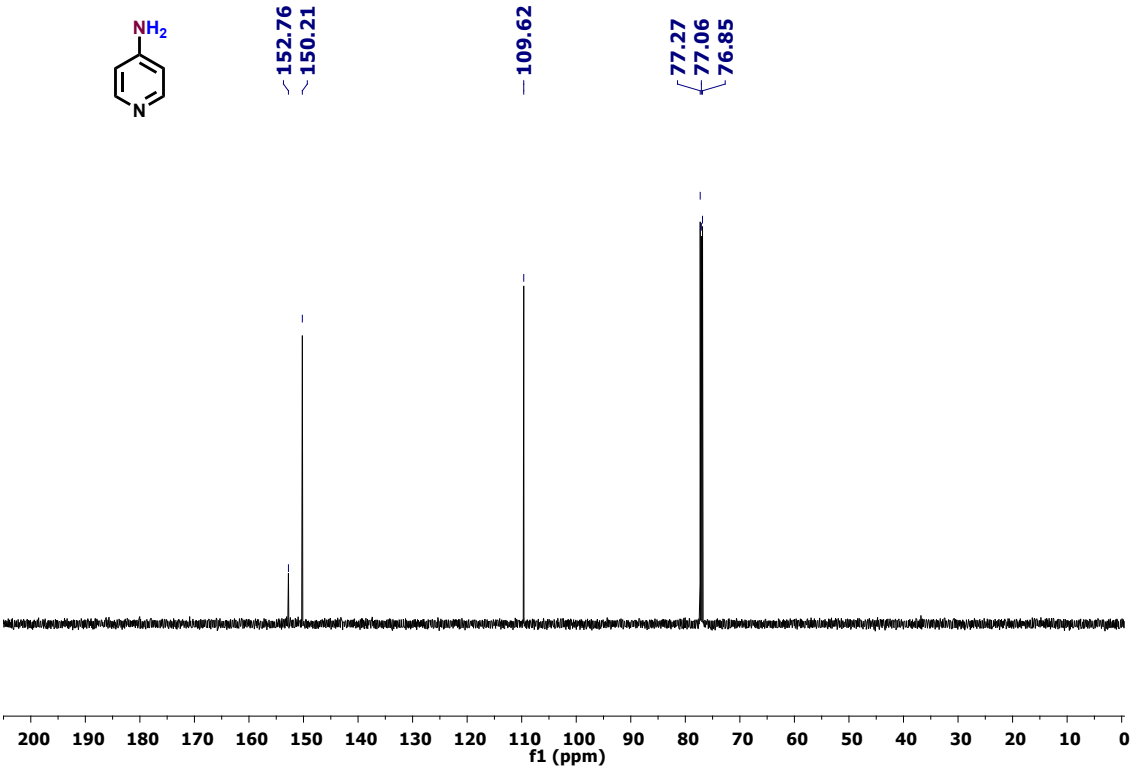


Figure S98: ^{1}H NMR of 8-Aminoquinoline (48)

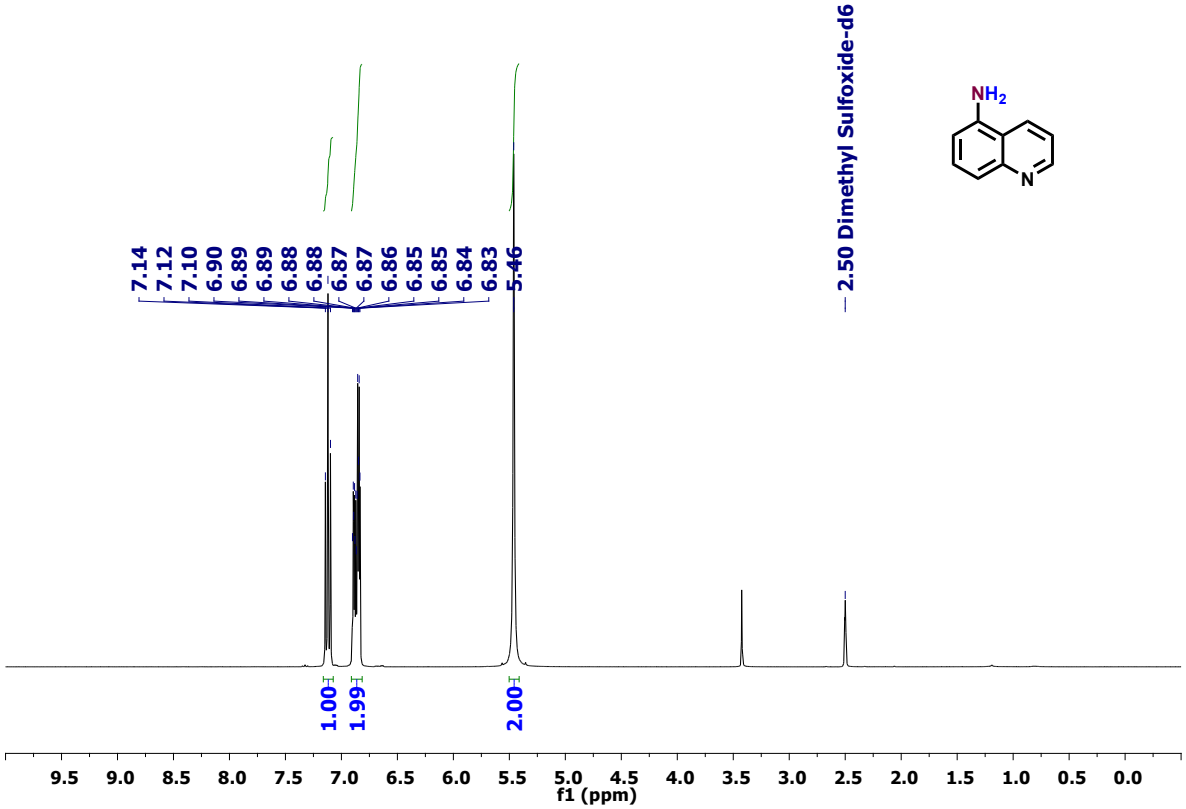


Figure S99: ^{13}C NMR of 8-Aminoquinoline (48)