Supporting Information

Efficient copper-catalyzed coupling of aryl chlorides, bromides and iodides with aqueous ammonia

Hanhui Xu and Christian Wolf*

Department of Chemistry, Georgetown University, Washington DC, 20057

cw27@georgetown.edu

Experimental Procedures

General Procedures. All chemicals used were of reagent grade. Flash chromatography was performed on Kieselgel 60, particle size 0.032-0.063 mm. NMR spectra were obtained at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) using $CDCl_3$ as solvent unless noted otherwise. Chemical shifts are reported in ppm relative to TMS.

General procedure for the Cu-catalyzed amination of aryl halides

A 10 mL reaction vessel was charged with Cu_2O (14.3 mg, 0.10 mmol), aryl halide (2.0 mmol), 1.3 mL of *N*-methyl pyrrolidinone (NMP), 1.3 mL of ammonium hydroxide solution (29% NH_3, 20.0 mmol) and a magnetic stir bar. The vessel was sealed with a Teflon screw cap, immersed in a preheated oil bath and the reaction mixture was stirred at 80 ^{o}C. Upon completion, the reaction mixture was cooled to 25 ^{o}C, quenched with water, extracted with diethyl ether and dried over anhydrous $MgSO_4$. The solvents were removed under vacuum and the residue was purified by flash chromatography on silica gel as described below.

General microwave-assisted procedure for the Cu-catalyzed amination of aryl chlorides

A mixture of Cu_2O (14.3 mg, 0.10 mmol), aryl chloride (2.0 mmol) and 1.3 mL of *N*-methyl pyrrolidinone (NMP) was placed with 1.3 mL of ammonium hydroxide solution (29% NH_3, 20.0 mmol) into a 10 mL glass tube. The reaction mixture was placed in a microwave oven and heated to 110^{o}C (150 W) while the temperature was monitored using a calibrated infrared temperature control. Upon completion, the mixture was allowed to cool to room temperature, quenched with water, extracted with diethyl ether and dried over anhydrous $MgSO_4$. The solvents were removed under vacuum and the residue was purified by flash chromatography on silica gel as described below.

Product identification (yields are corresponding to the reactions of the aryl halides given in Table 1)

Aniline.[1] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 186.0 mg of a colorless oil (2.00 mmol, 100%). ^{1}H NMR: δ 3.54 (s, br, 2H), 6.59-6.61 (m, 2H), 6.70-6.74 (m, 1H), 7.09-7.13 (m, 2H). ^{13}C NMR: δ 115.2, 118.6, 129.4, 146.6.

***o*-Toluidine**.[2] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 205.7 mg of a colorless oil (1.92 mmol, 96%). ^{1}H NMR: δ 2.09 (s, 3H), 3.47 (s, br, 2H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.98-7.01 (m, 2H). ^{13}C NMR: δ 17.4, 115.0, 118.7, 122.4, 127.1, 130.6, 144.8.

***p*-Toluidine**.[1] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 209.7 mg of slight yellow crystals (1.96 mmol, 98%). ^{1}H NMR: δ 2.19 (s, 3H), 3.40 (s, br, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR: δ 20.6, 115.4, 127.7, 129.9, 144.2.

3,5-Dimethylaniline.[3] Purification by flash chromatography (hexanes:ethyl acetate =10:1) gave 242.4 mg of a colorless oil (2.00 mmol, 100%). ^{1}H NMR: δ 2.20 (s, 6H), 3.47 (s, br, 2H), 6.27 (s, 2H), 6.91 (s, 1H). ^{13}C NMR: δ 21.8, 113.7, 121.0, 139.4, 146.8.

2-Isopropylaniline.[4] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 221.7 mg of a colorless oil (1.64 mmol, 82%). ^{1}H NMR: δ 1.23 (d, *J* = 6.8 Hz, 6H), 2.81-2.88 (m, 1H), 3.56 (s, br, 2H), 6.61 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.74-6.78 (m, 1H), 6.96-6.70 (m, 1H), 7.11 (dd, *J* = 7.6, 1.0 Hz, 1H). ^{13}C NMR: δ 22.4, 27.7, 115.9, 119.1, 125.5, 126.6, 132.7, 143.5.

2-Aminobiphenyl.[1] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 253.8 mg of slight brown crystals (1.50 mmol, 75%). ^{1}H NMR: δ 3.71 (s, br, 2H), 6.72-6.83 (m, 2H), 7.11-7.19 (m, 2H), 7.30-7.44 (m, 5H). ^{13}C NMR: δ 115.6, 118.6, 127.2, 127.6, 128.5, 128.9, 129.1, 130.5, 139.6, 143.5.

1-Aminonaphthalene.[1] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 257.8 mg of purple crystals (1.80 mmol, 90%). ^{1}H NMR: δ 4.01 (s, br, 2H), 6.68 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.22-7.29(m, 2H), 7.36-7.43 (m, 2H), 7.71-7.77 (m, 2H). ^{13}C NMR: δ 109.7, 119.0, 120.9, 123.7, 124.9, 125.9, 126.4, 128.6, 134.5, 142.2.

1,3-Phenylenediamine.[1] Purification by flash chromatography (hexanes:ethyl acetate=9:1) gave 203.3 mg of purple crystals (1.88 mmol, 94%). ^{1}H NMR: δ 3.55 (s, br, 4H), 5.94 (d, *J* = 2.0 Hz, 1H), 6.08 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.91(t, *J* = 8.0 Hz, 1H). ^{13}C NMR: δ 102.5, 106.4, 130.6, 148.1.

3-Chloroaniline.[5] Purification by flash chromatography (hexanes:ethyl acetate=10:1) gave 237.3 mg of slight yellow crystals (1.86 mmol, 93%). ^{1}H NMR: δ 3.66 (s, br, 2H), 6.46-6.48 (m, 1H), 6.60 (t, *J* = 2.0 Hz, 1H), 6.69 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.01(t, *J* = 8.0 Hz, 1H). ^{13}C NMR: δ 113.3, 114.9, 118.4, 130.4, 134.8, 147.8.

***p*-Anisidine**.[1] Purification by flash chromatography (hexanes:ethyl acetate=9:1) gave 231.5 mg of slight purple crystals (1.88 mmol, 94%). ^{1}H NMR: δ 3.41 (s, br, 2H), 3.71 (s, 3H), 6.60 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.72 (dd, *J* = 6.8, 2.0 Hz, 2H). ^{13}C NMR: δ 55.7, 114.8, 116.4, 140.1, 152.7.

4-Aminobenzonitrile.[1] Purification by flash chromatography (hexanes:ethyl acetate=9:1) gave 191.4 mg of white crystals (1.62 mmol, 81%). ^{1}H NMR: δ 4.32 (s, br, 2H), 6.64 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.37 (dd, *J* = 6.8, 2.0 Hz, 2H). ^{13}C NMR: δ 99.5, 114.4, 120.4, 133.7, 150.8.

4-Nitroaniline.[6] Purification by flash chromatography (hexanes:ethyl acetate=8:2) gave 237.6 mg of slight yellow crystals (1.72 mmol, 86%). ^{1}H NMR: δ 4.40 (s, br, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR: δ 113.4, 126.3, 139.0, 152.5.

3-Aminoacetophenone.[7] Purification by flash chromatography (hexanes:ethyl acetate=9:1) gave 248.7 mg of slight yellow crystals (1.84 mmol, 92%). ^{1}H NMR: δ 2.52 (s, 3H), 4.00 (s, br, 2H), 6.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17-7.29 (m, 3H). ^{13}C NMR: δ 26.7, 113.9, 118.5, 119.7, 129.4, 138.1, 147.1, 198.7.

4-Aminobenzaldehyde.[1] Purification by flash chromatography (hexanes:ethyl acetate=7:3) gave 191.4 mg of slight yellow crystals (1.58 mmol, 79%). ^{1}H NMR (in $(CD_3)_2SO$): δ 5.78 (s, br, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 9.61 (s, 1H). ^{13}C NMR: δ 113.4, 125.5, 132.2, 154.7, 189.6.

4-Aminopyridine.[8] Purification by flash chromatography (hexanes:ethyl acetate=7:3) gave 139.3 mg of white crystals (1.48 mmol, 74%). ^{1}H NMR (CD_3OD): δ 5.06 (s, br, 2H), 6.55 (d, *J* = 6.4 Hz, 2H), 7.95 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR: δ 110.3, 149.7, 156.8.

4-Amino-2-methylquinoline.[9] Purification by flash chromatography (dichloromethane:ethanol:triethylamine=100:10:3) gave 256.3 mg of white crystals (1.62 mmol, 81%). ^{1}H NMR: δ 2.58 (s, 3H), 4.74 (s, 2H), 6.49 (s, 1H), 7.38 (m, 1H), 7.60 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR: δ 25.2, 103.9, 117.4, 120.0, 124.1, 129.0, 129.4, 148.6, 149.6, 159.3.

Ethyl 4-aminobenzoate.[10] Purification by flash chromatography (hexanes:ethyl acetate=8:2) gave 274.2 mg of slight yellow crystals (1.66 mmol, 83%). ^{1}H NMR: δ 1.35 (t, *J* = 7.2 Hz, 3H), 4.16 (s, br, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.62 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.84 (dd, *J* = 8.8, 2.0 Hz, 2H). ^{13}C NMR: δ 14.4, 60.3, 113.7, 119.7, 131.5, 151.0, 166.8.

Methyl 2-aminobenzoate.[11] Purification by flash chromatography (hexanes:ethyl acetate=8:2) gave 278.1 mg of slight yellow crystals (1.84 mmol, 92%). ^{1}H NMR: δ 3.84 (s, 3H), 5.71 (s, br, 2H), 6.62 (t, *J* = 7.6 Hz, 2H), 7.24 (m, 1H), 7.84 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR: δ 51.5, 110.7, 116.2, 116.7, 131.2, 134.1, 150.5, 168.6.

2-Aminobenzoic acid.[12] Purification by flash chromatography (hexanes:ethyl acetate=6:4) gave 257.8 mg of white crystals (1.88 mmol, 94%). ^{1}H NMR: δ 5.19 (s, br, 2H), 6.55-6.61 (m, 1H), 6.73 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.20-7.26 (m, 1H), 7.84 (dd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR: δ 111.9, 116.9, 118.0, 132.9, 135.3, 152.9, 171.9.

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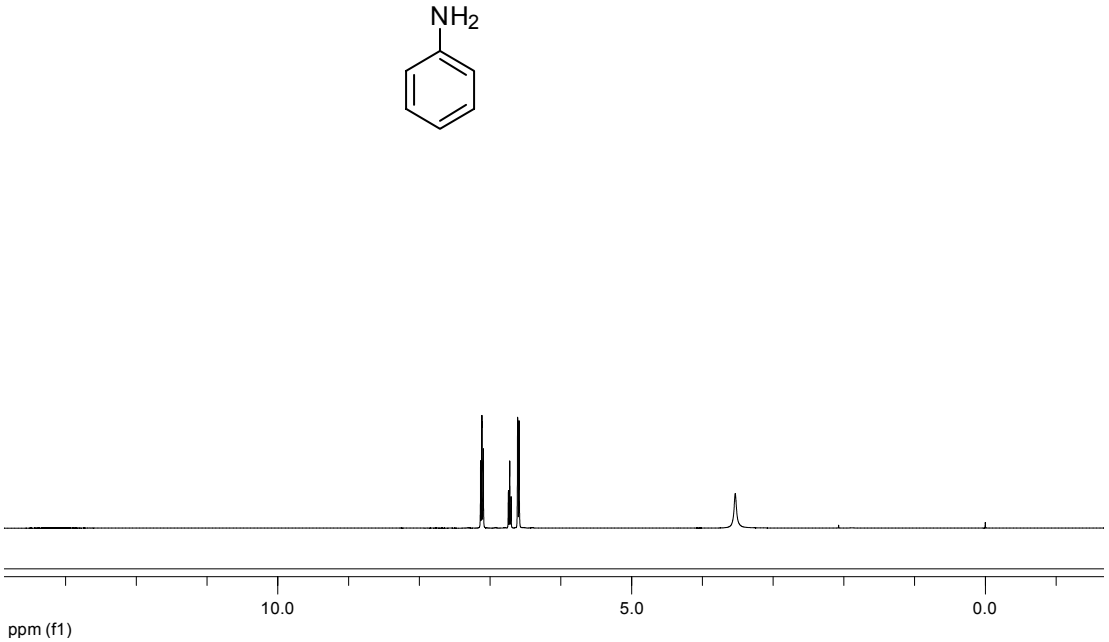

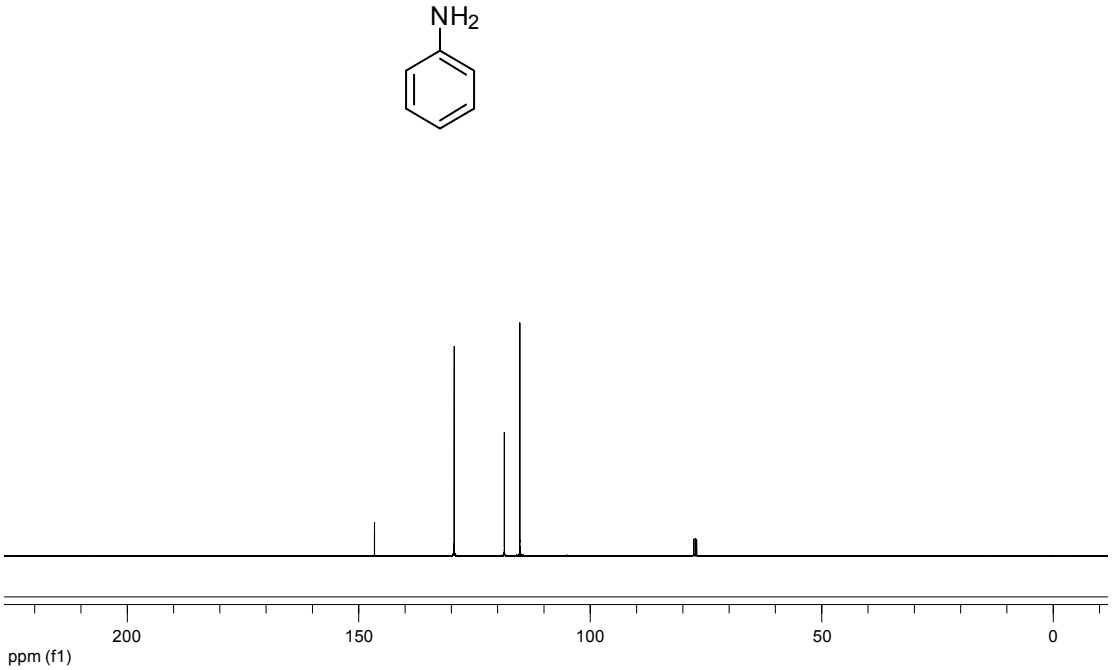

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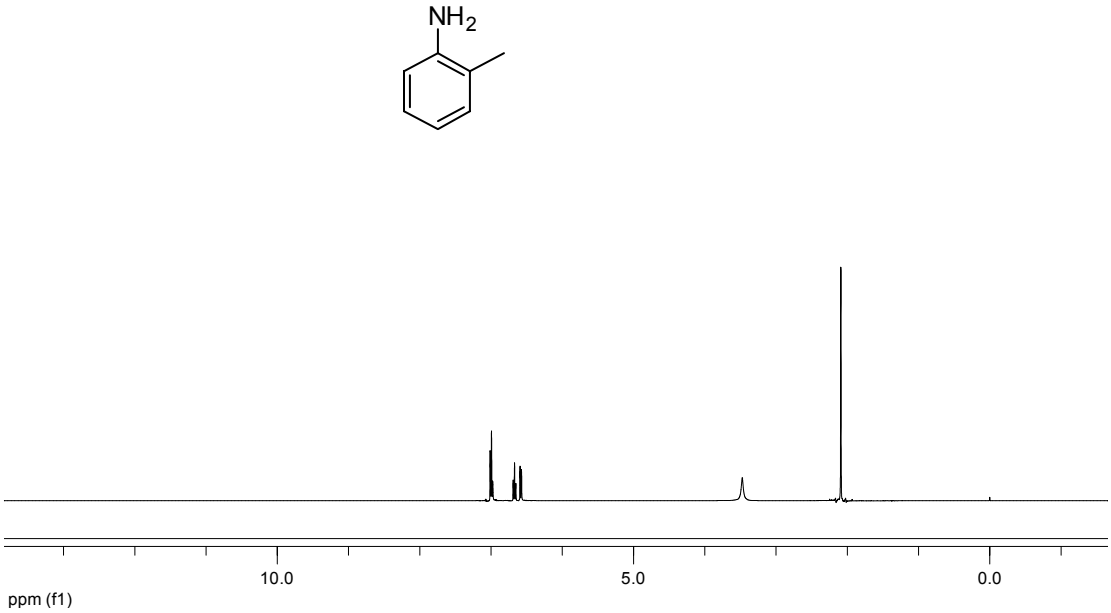

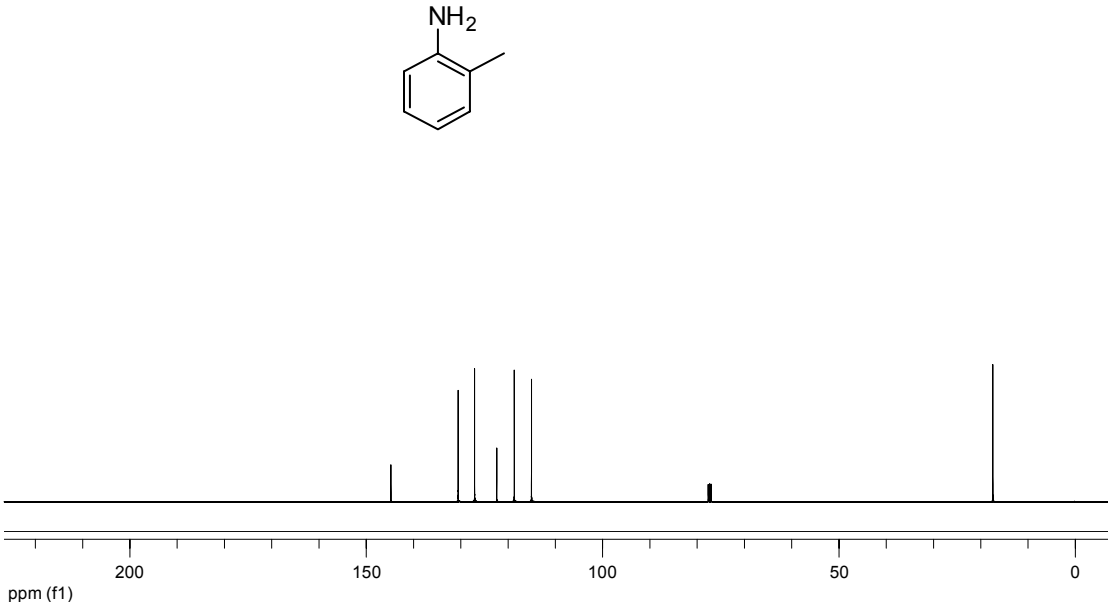

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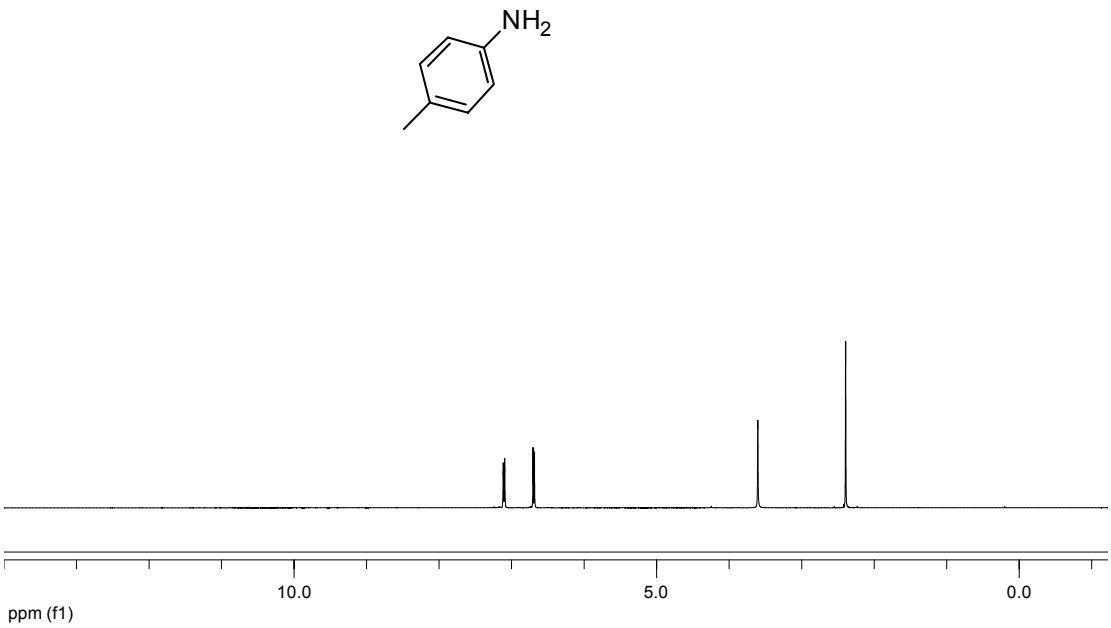

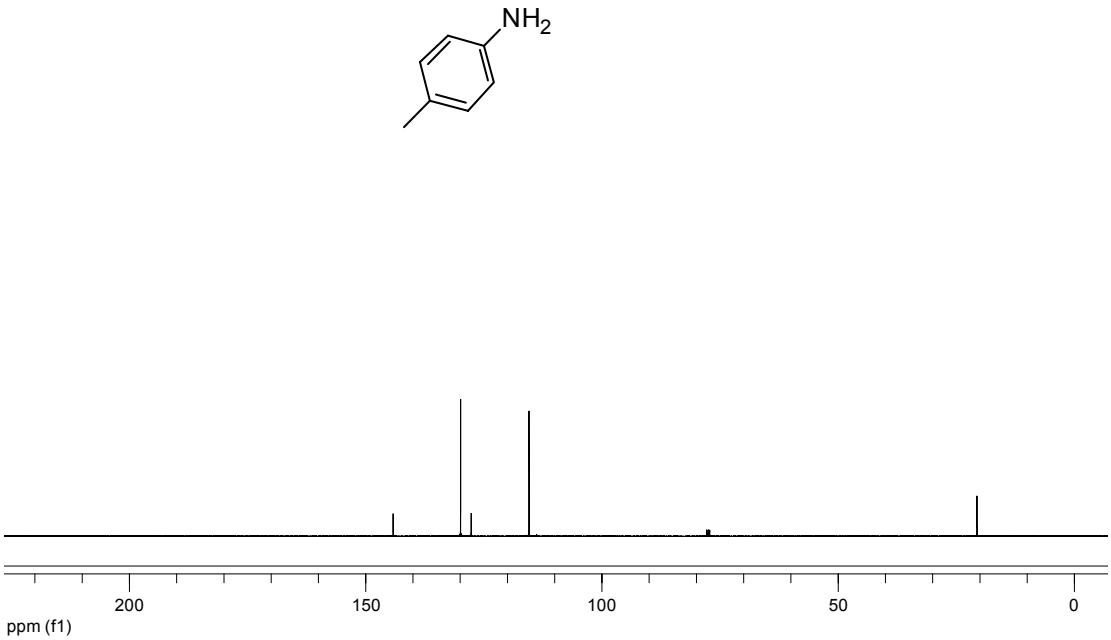

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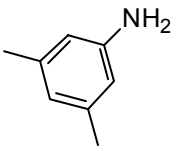

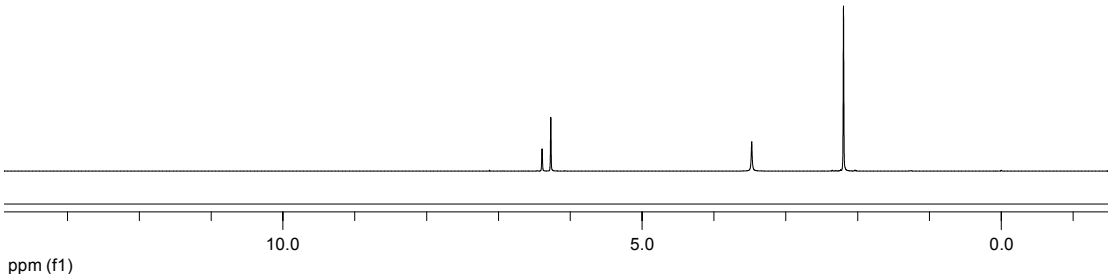

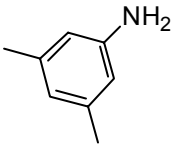

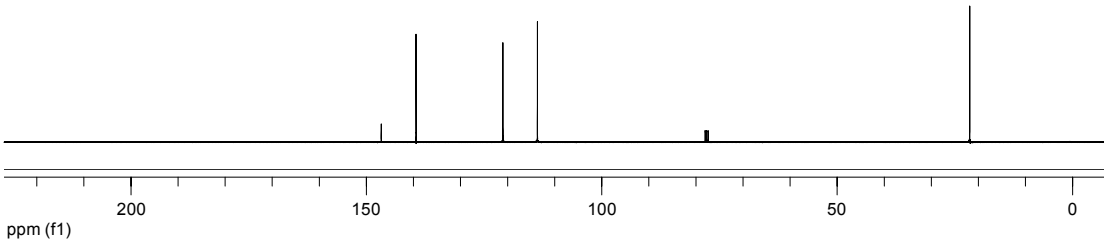

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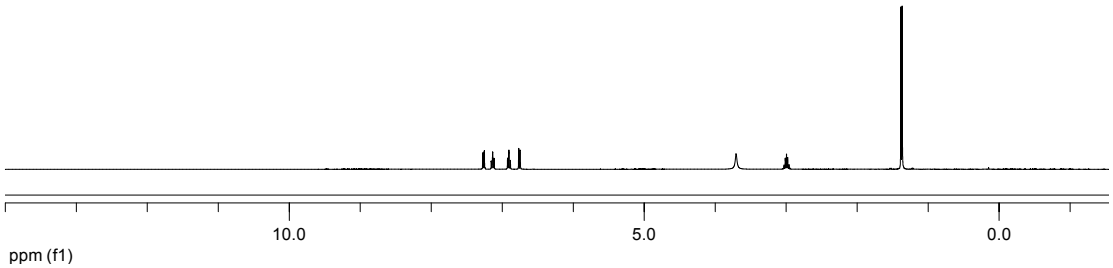

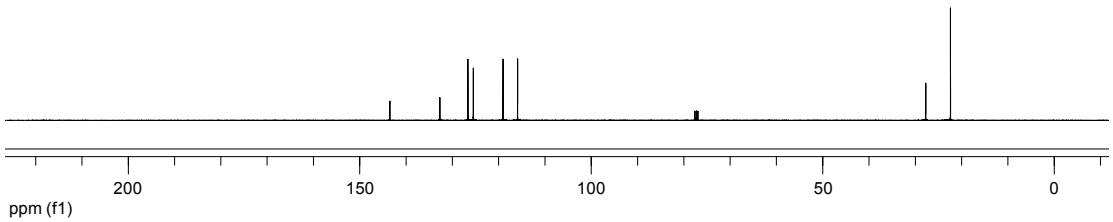

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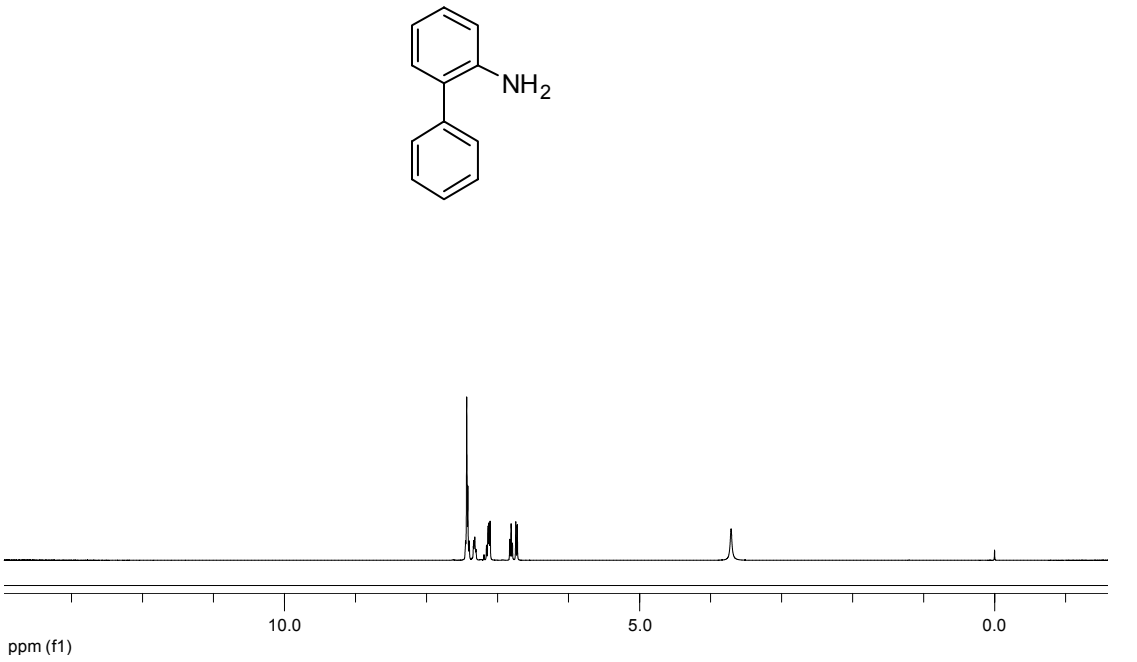

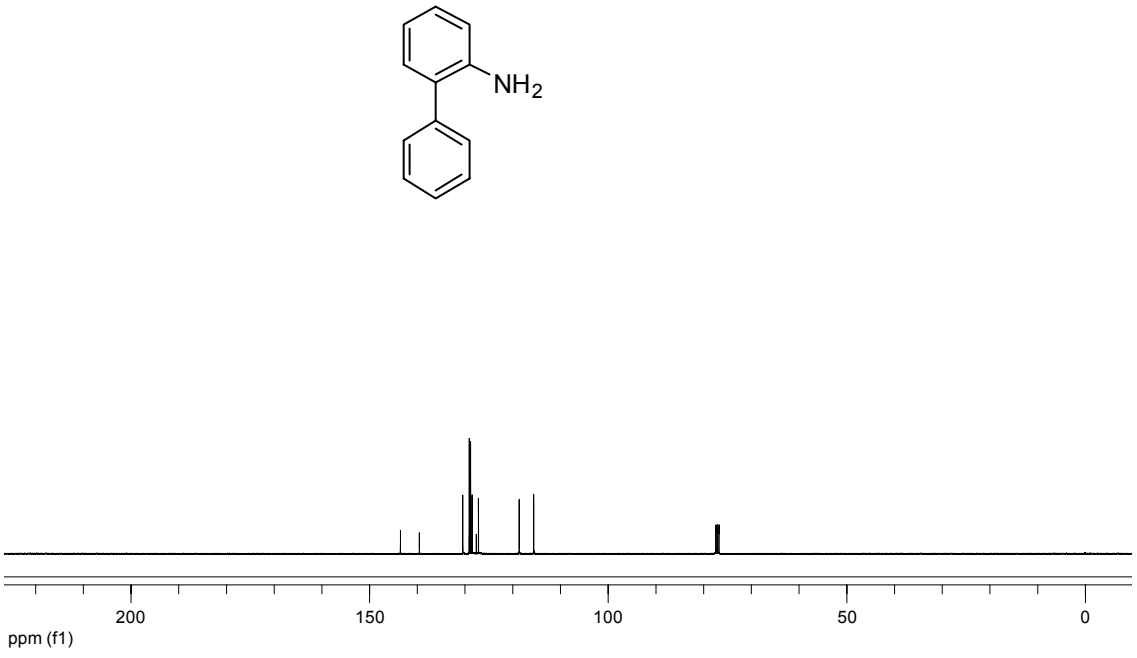

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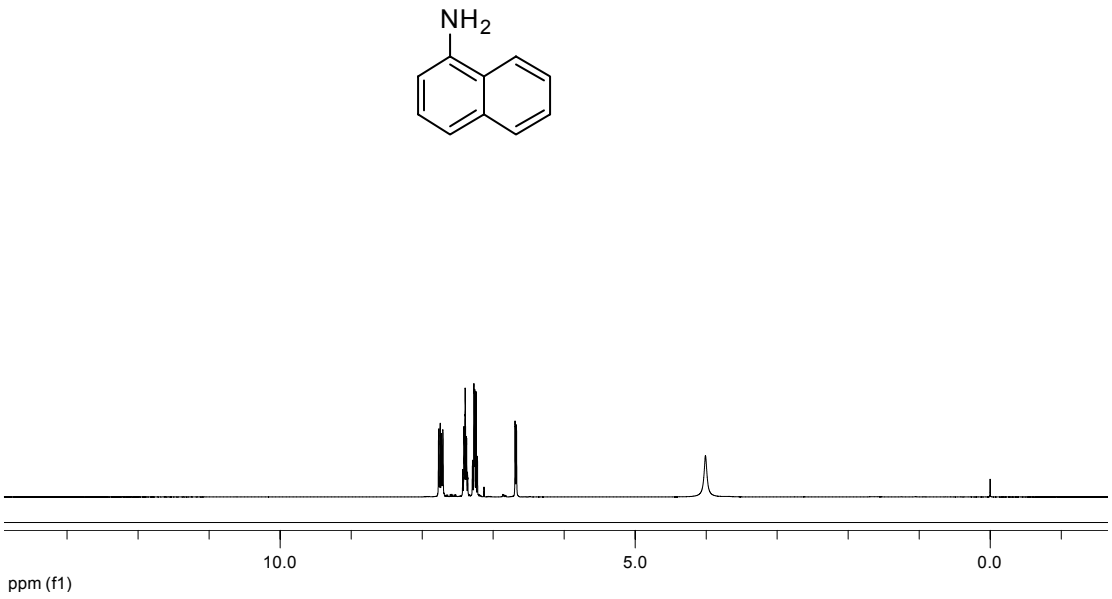

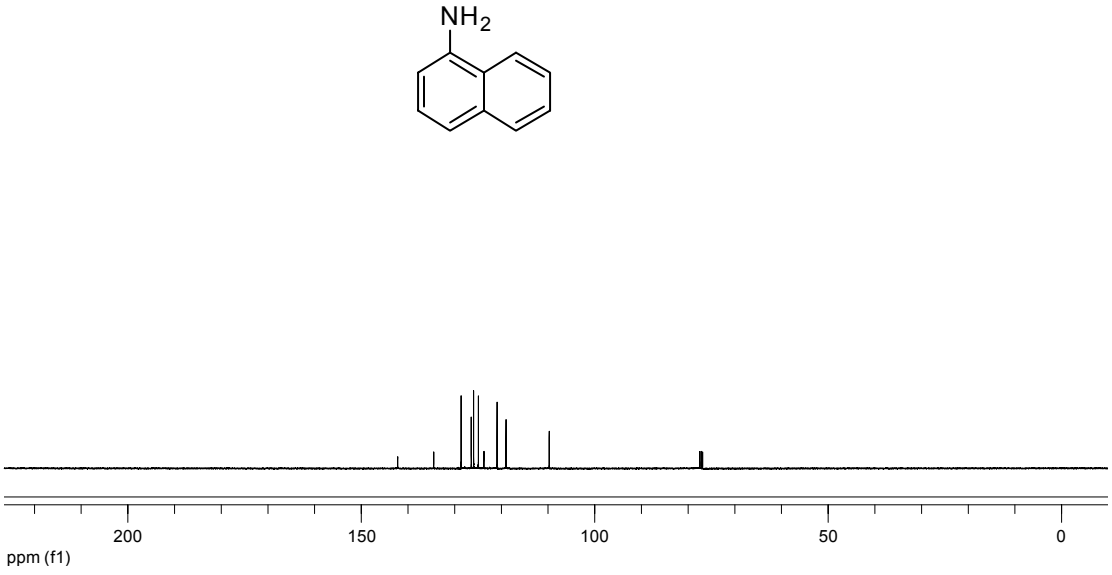

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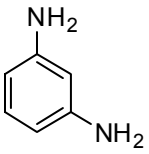

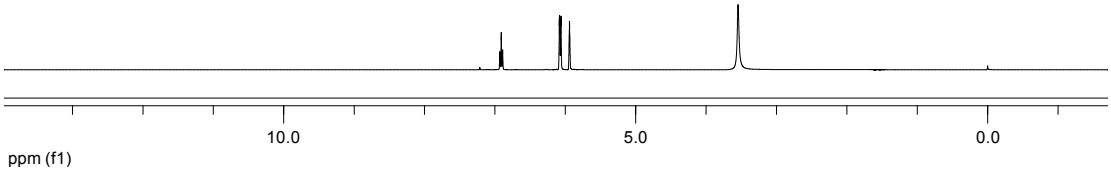

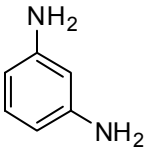

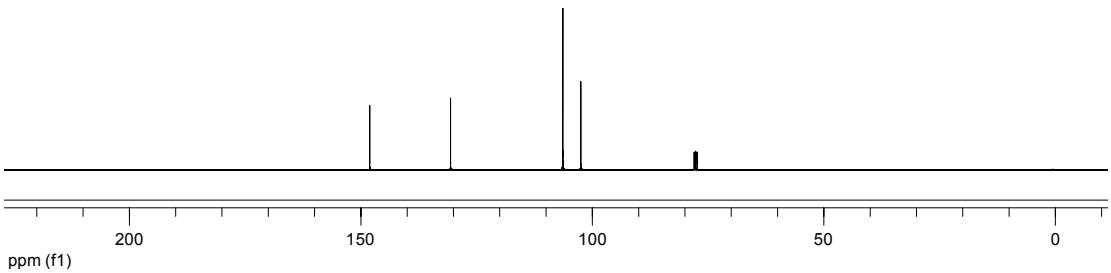

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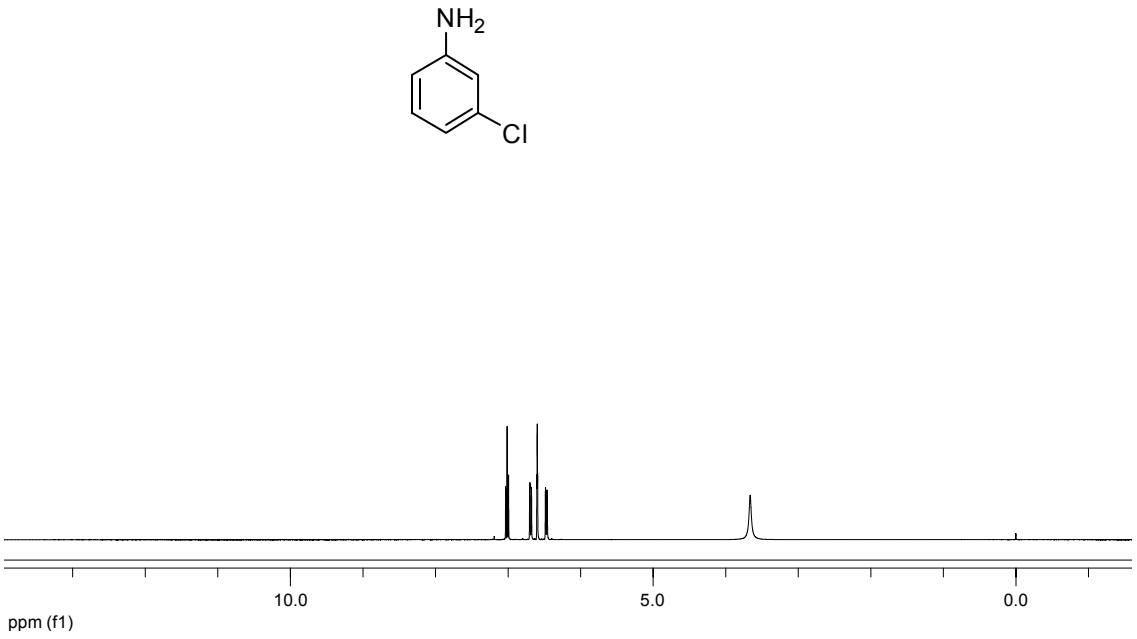

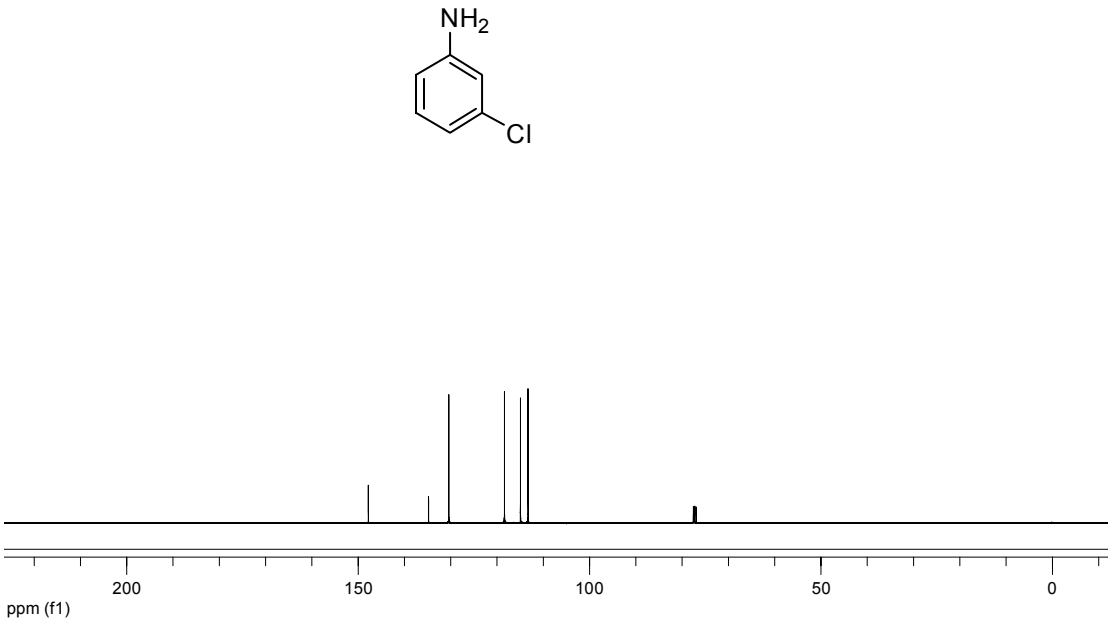

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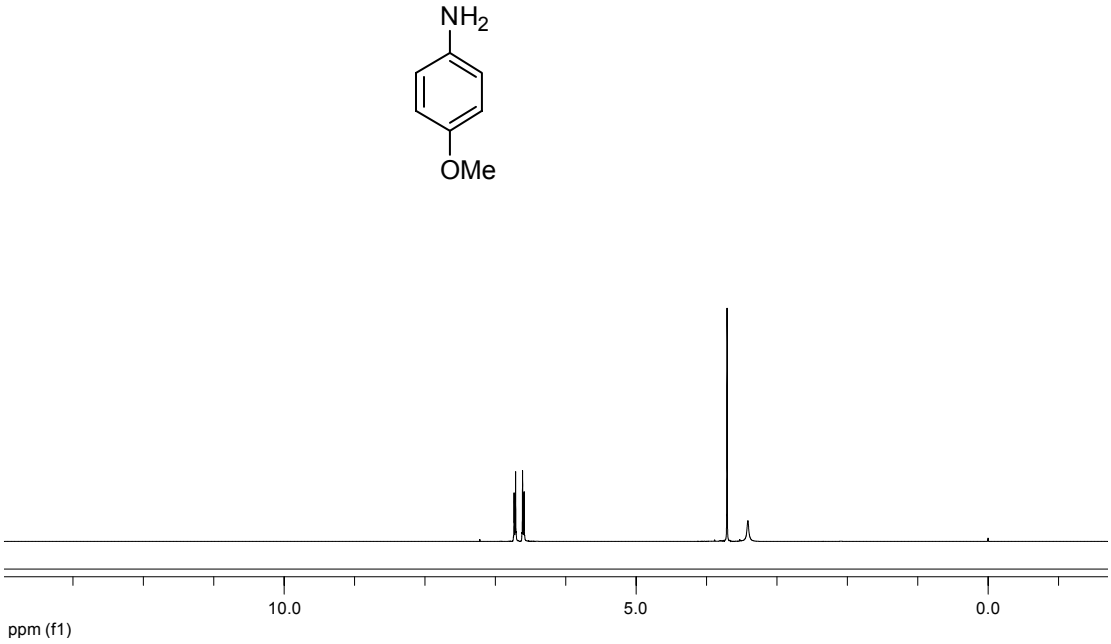

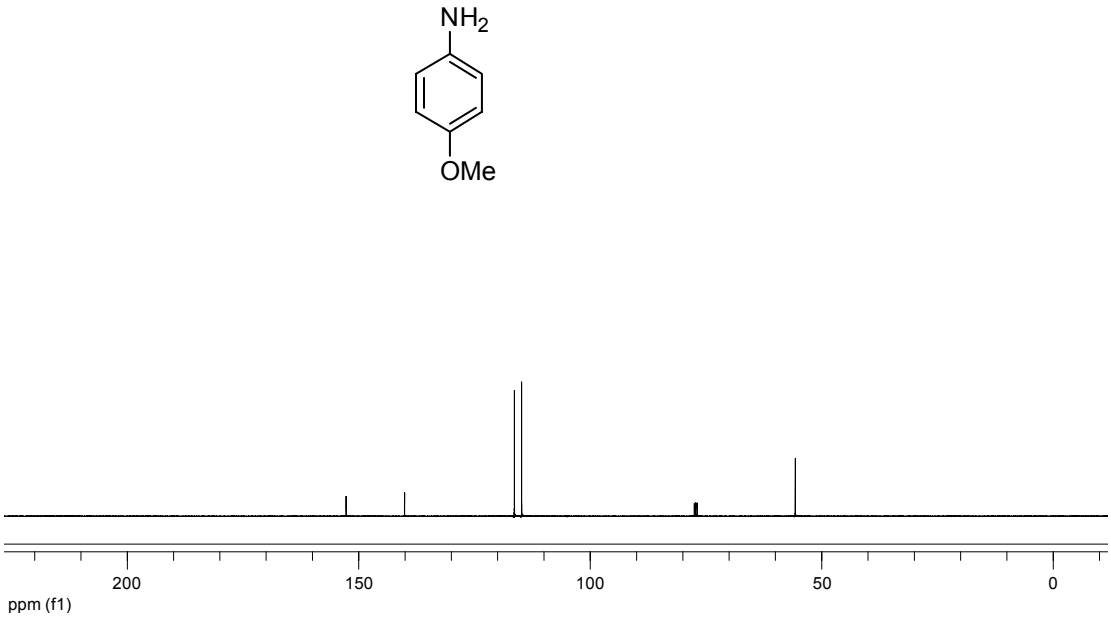

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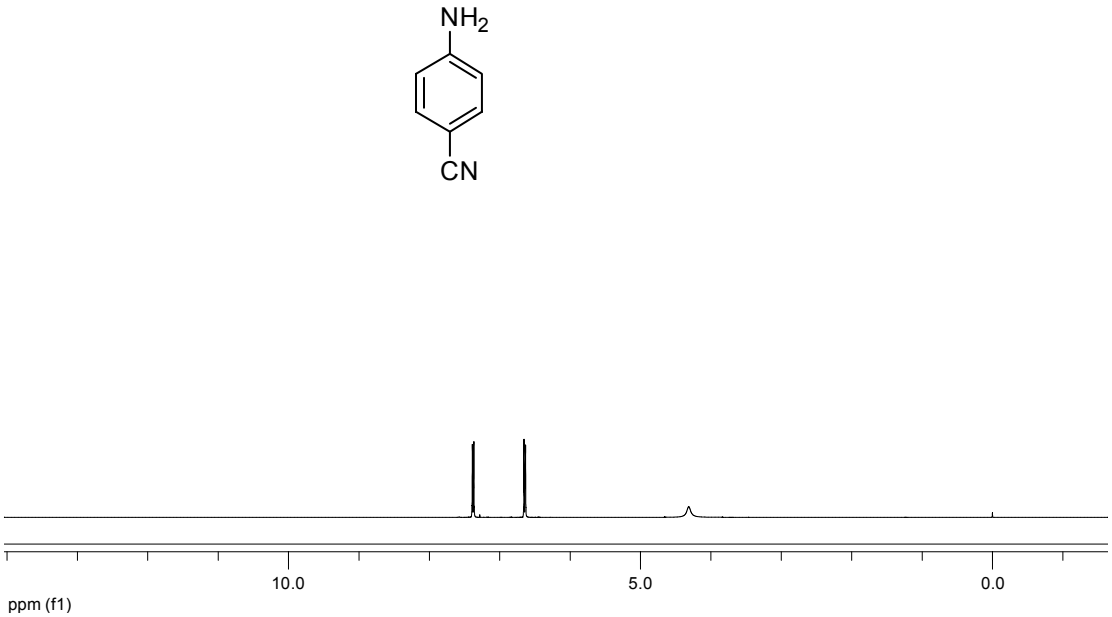

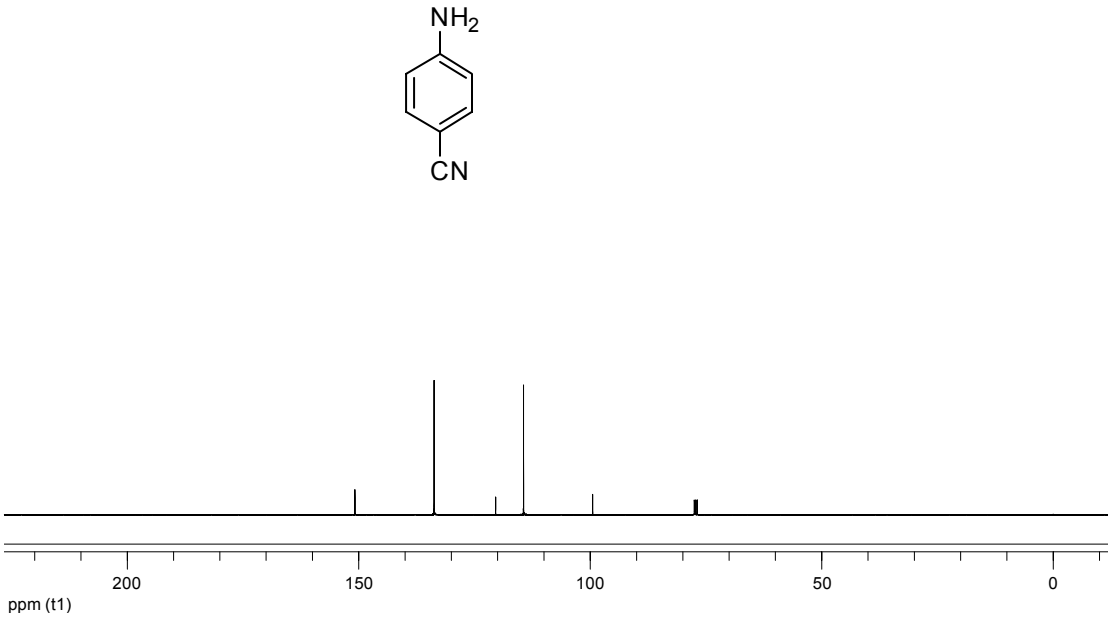

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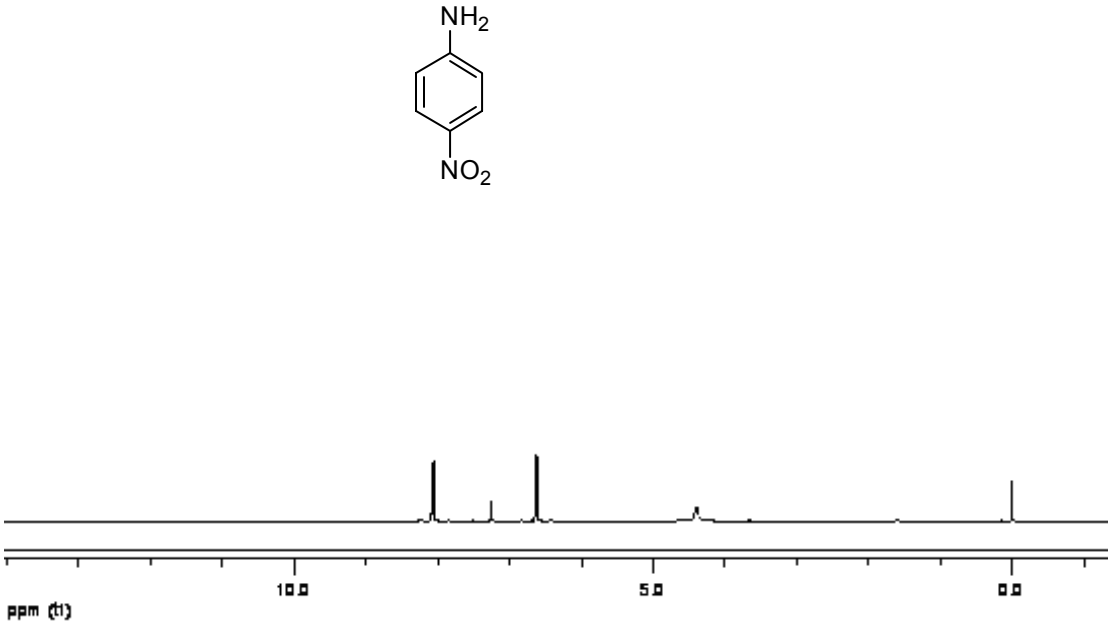
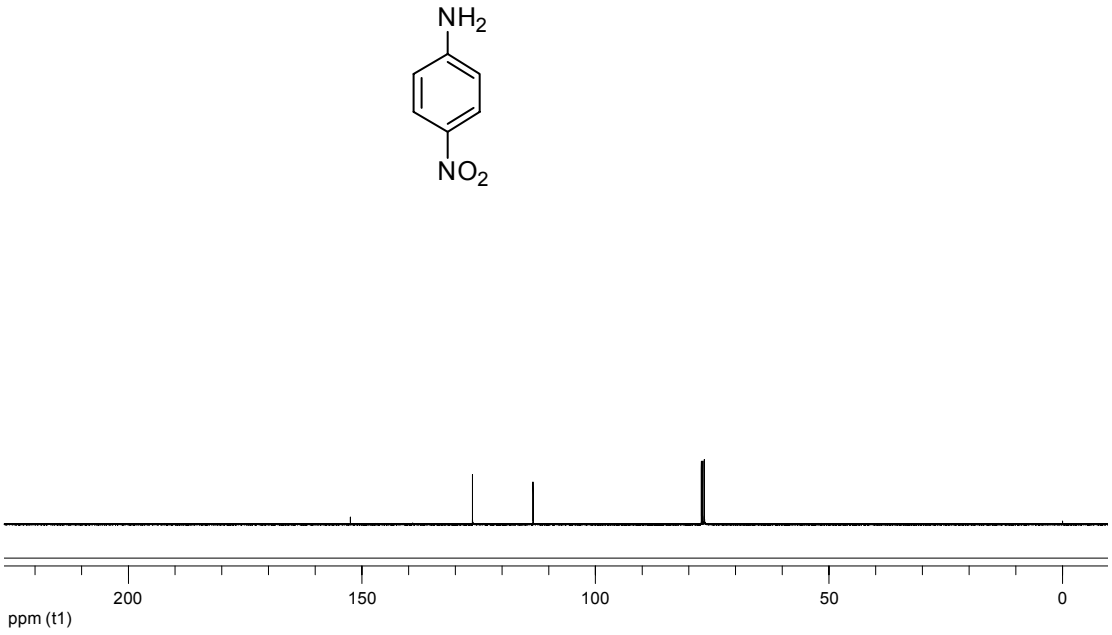
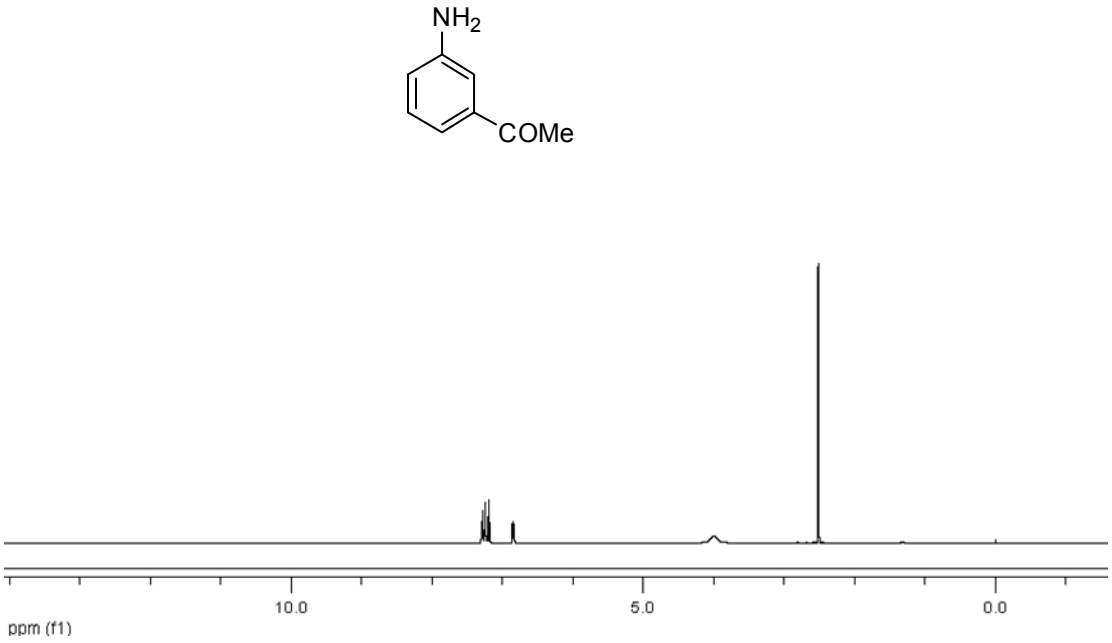
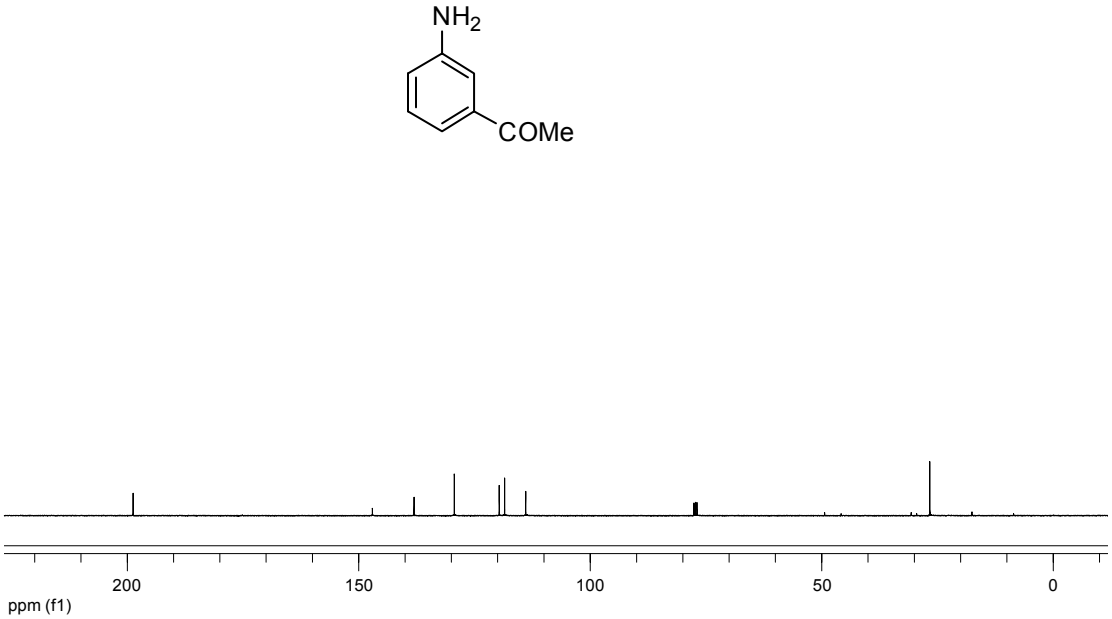


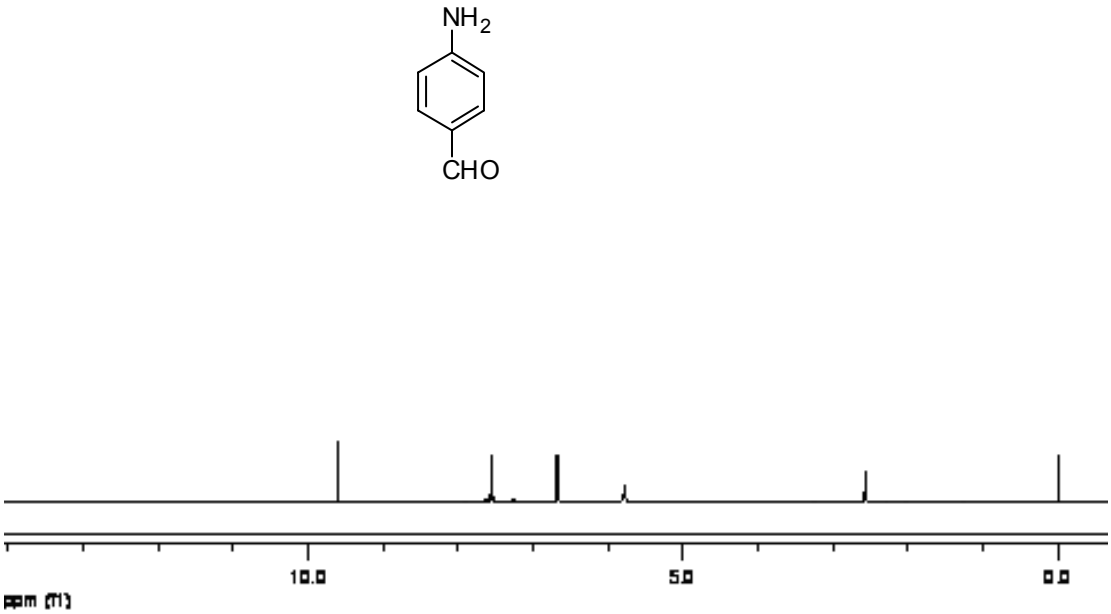


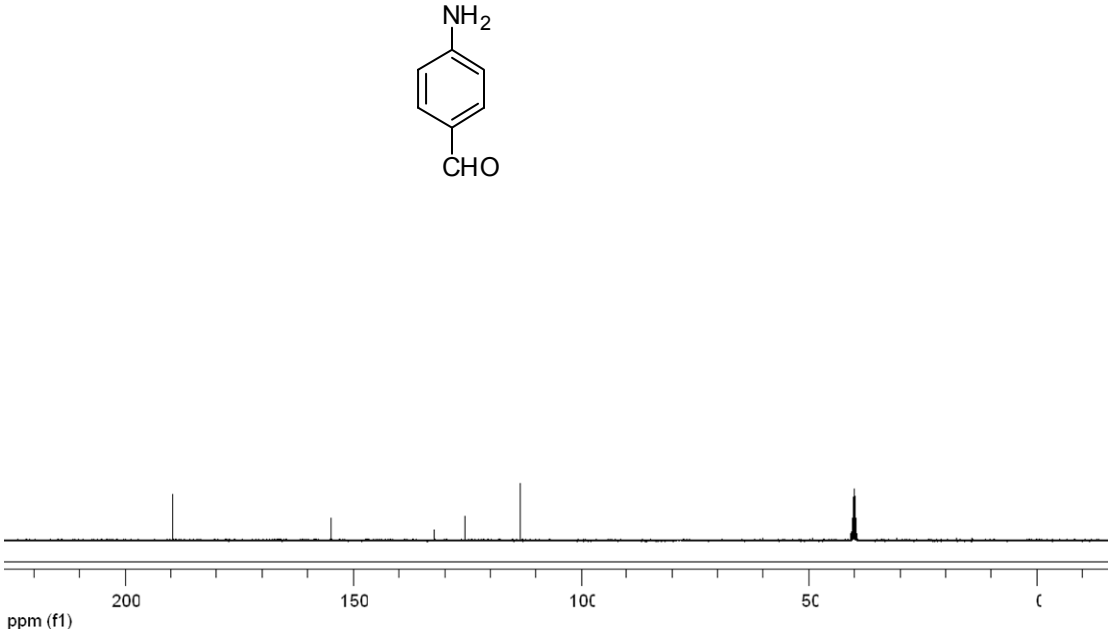
^{1}H NMR and ^{13}C NMR spectra of 3-aminoacetophenone in $CDCl_3$:



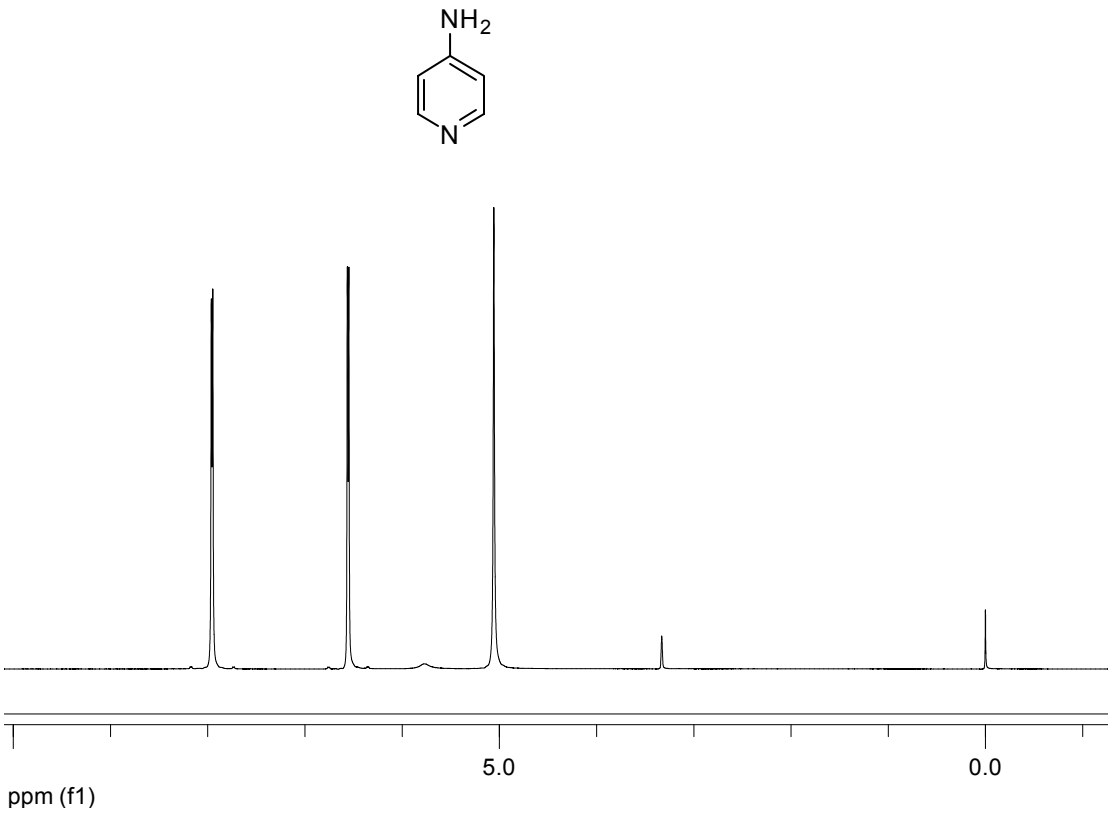


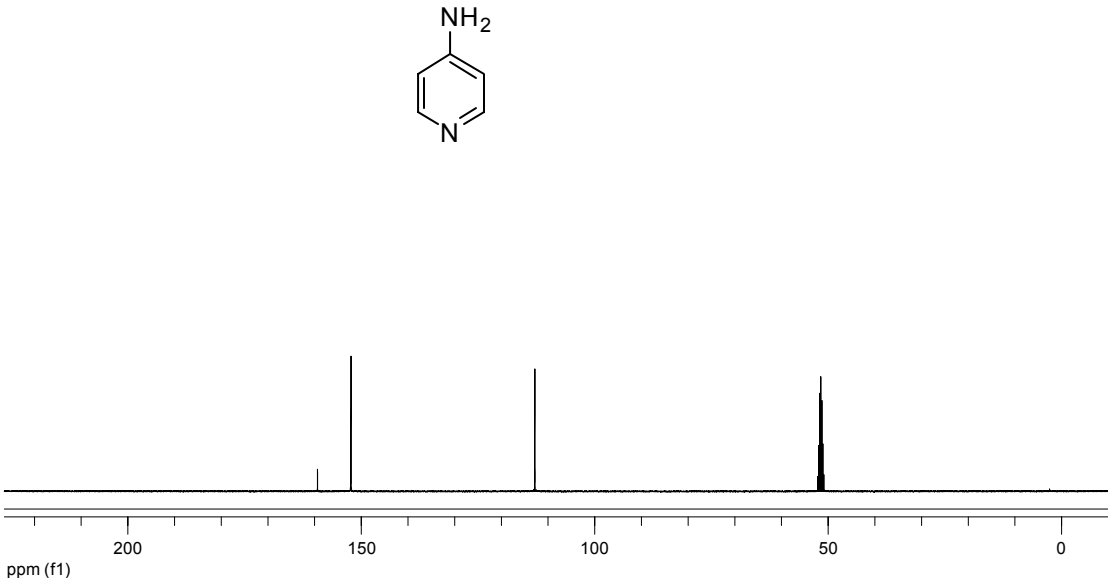
^{1}H NMR and ^{13}C NMR spectra of 4-aminobenzaldehyde in d_6-DMSO:



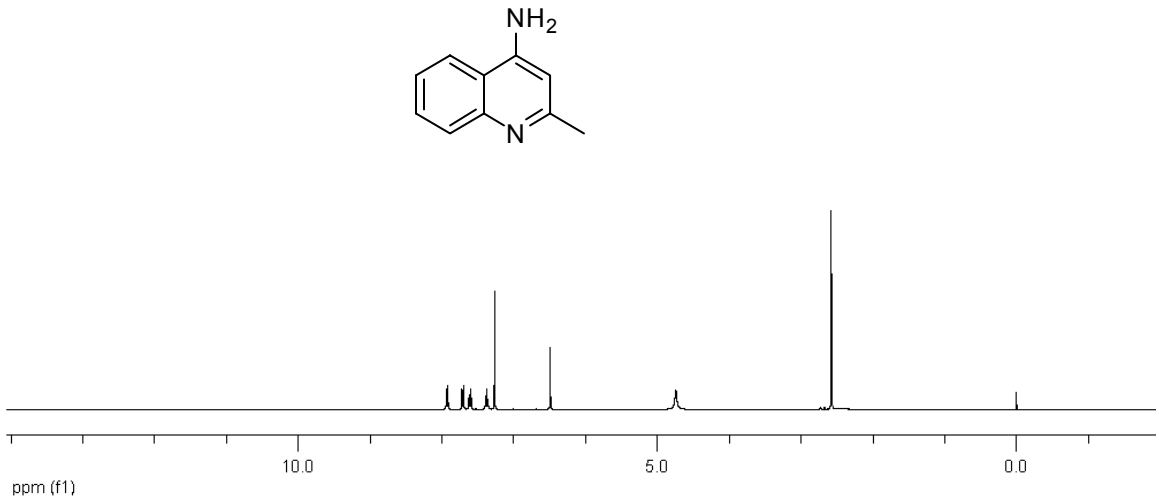


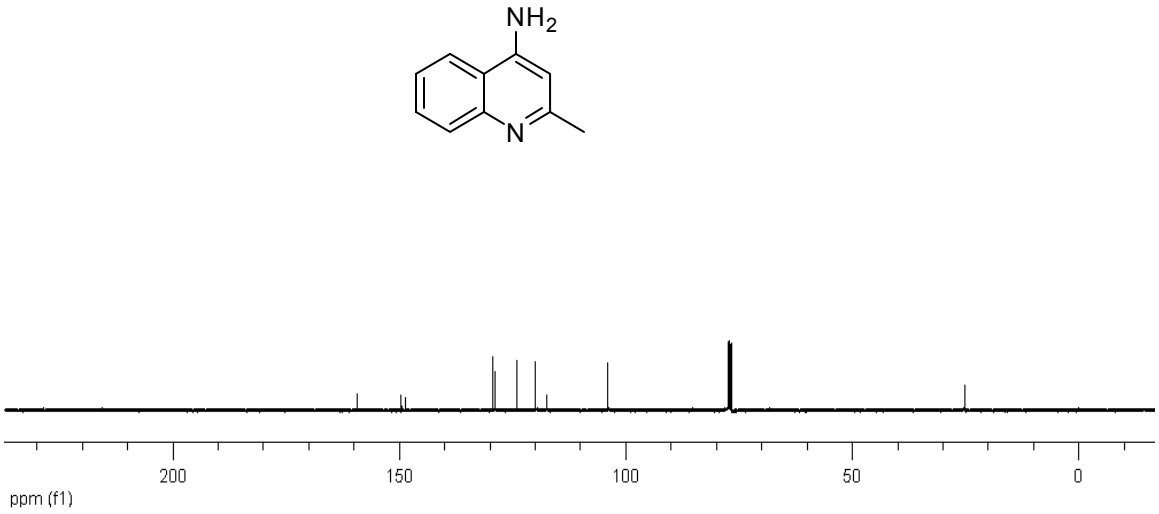
^{1}H NMR and ^{13}C NMR spectra of 4-aminopyridine in CD_3OD:



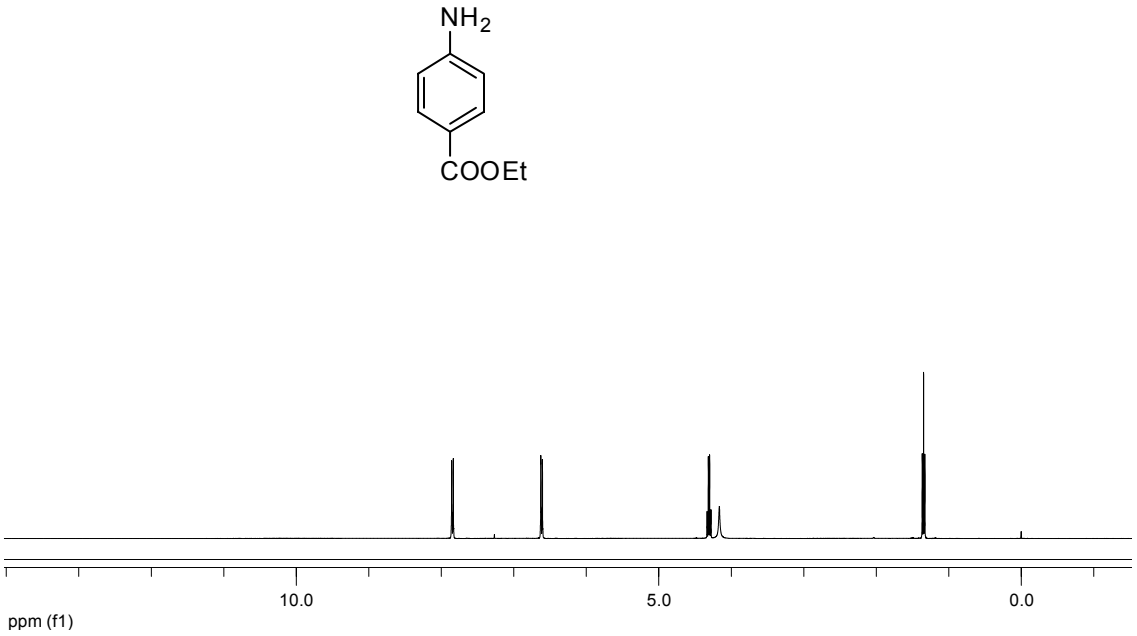


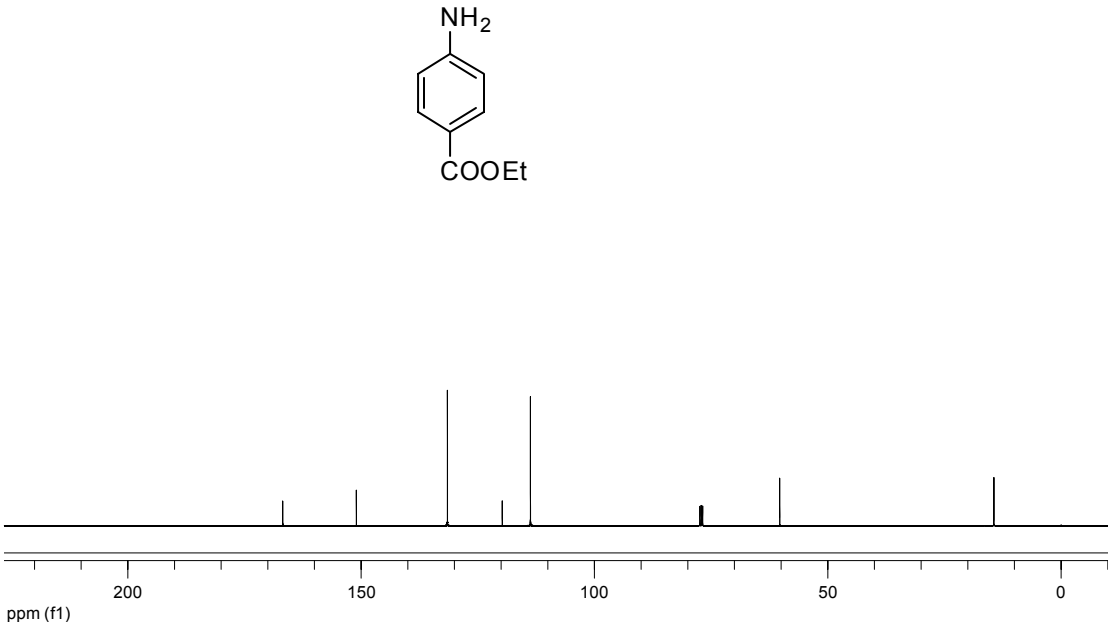
^{1}H NMR and ^{13}C NMR spectra of 4-amino-2-methylquinoline, in $CDCl_3$:



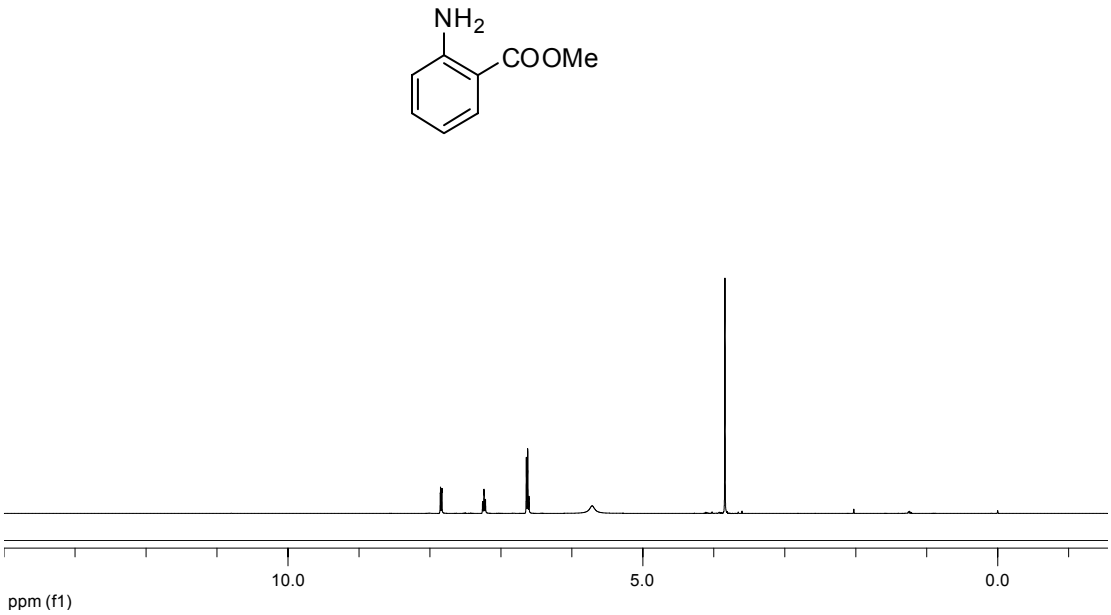


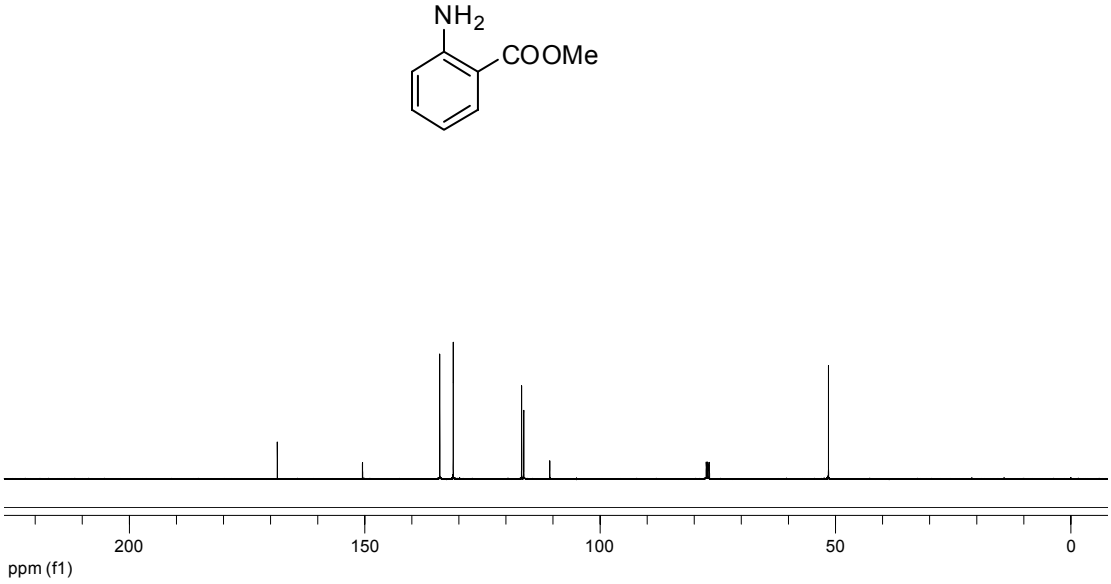
^{1}H NMR and ^{13}C NMR spectra of ethyl 4-aminobenzoate in $CDCl_3$:





^{1}H NMR and ^{13}C NMR spectra of methyl 2-aminobenzoate in $CDCl_3$:





^{1}H NMR and ^{13}C NMR spectra of 2-aminobenzoic acid in CD_3OD: