Supporting Information

Copper catalyzed nitrile synthesis from aryl halides using formamide as a nitrile source

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Table of Contents

I. General Information…….....S2

II. General experimental procedure for nitrile synthesis…….……..S2

III. ^{1}H NMR and ^{13}C NMR data of products….....S3-S4

IV. ^{1}H NMR and ^{13}C NMR copies of products …….…....S5-S12

General information

Materials and Methods:

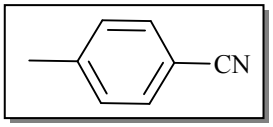
All the reagents were purchased from Sigma-Aldrich and Alfa Aesar. The solvents were purchased from commercial suppliers and used without further purification. GC equipped with flame ionization detector and a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm) was used for gas chromatography analysis. The mass of the products were identified using GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm) (column flow 2 $mLmin^{-1}$, 80 °C to 240 °C at 10 °C/min rise). The products were purified by column chromatography on silica gel (100-200 mesh). The ^{1}H NMR spectra was recorded at 400 MHz spectrometer in $CDCl_3$ using TMS as an internal standard. The ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ using TMS as an internal standard. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as bs (broad singlet), s (singlet), d (doublet), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC-MS spectra, ^{1}H and ^{13}C NMR spectra with those of authentic data.

General experimental procedure for nitrile synthesis from aryl halide:

The 4-iodotoluene (**1a**, 1 mmol), CuI (20 mol%) and PPh_3 (20 mol%) were added in formamide (10 $mLmmol^{-1}$) into two-necked round-bottomed flask (25 mL) equipped with a condenser at room temperature under nitrogen atmosphere. The mixture was stirred for 2–3 minutes at room temperature and $POCl_3$ (2 mmol) was added to the reaction mixture. The reaction flask equipped with a condenser placed in oil bath and stirred the reaction mixture for 24 h at 140 ^{o}C under nitrogen atmosphere. After cooling to room temperature, the resultant mixture was added to saturated solution of $NaHCO_3$ (50 mL) and extracted with diethyl ether (3×15 mL). The organic layer was dried over anhydrous Na_2SO_4 and it was evaporated under reduced pressure. The GC yield is quantified by using the external standard method using *p*-tolunitrile. The residue was then purified by column chromatography on silica gel (100-200 mesh; petroleum ether/ethyl acetate) and the products were confirmed by GCMS, ^{1}H and ^{13}C NMR spectroscopic analysis.

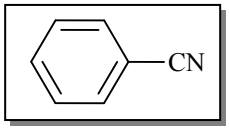
Spectral data:

4-Methylbenzonitrile (3a)



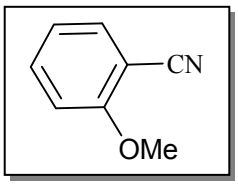
Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, J = 8 Hz, 2H), 7.27 (d, J = 8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.74, 132.02, 129.96, 119.16, 109.28, 21.82. GC-MS (EI): *m/z* 117(100) $[M]^+$, 116 (55.1), 90 (36.6), 63 (18.7).

Benzonitrile (3c)



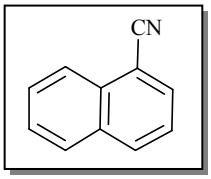
Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.65 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.77, 132.17, 129.12, 118.85, 112.48. GC-MS (EI): *m/z* 103(100) $[M]^+$, 76 (38.8), 50 (12).

2-Methoxybenzonitrile (3e)



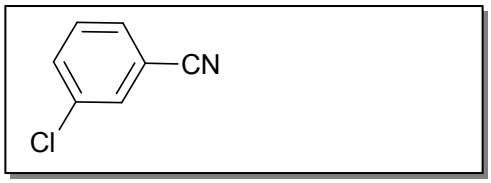
Light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57-7.53 (m, 2H), 7.03-6.97 (m, 2H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.23, 134.43, 133.74, 120.77, 116.53, 111.31, 101.76, 56.00. GC-MS (EI): *m/z* 133(100) $[M]^+$, 105 (49.8), 90 (51.5), 77(23.5), 63(42.5), 51(16.5).

1-Naphthonitrile (3f)



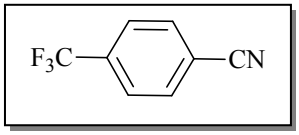
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.93-7.90 (m, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.28, 132.92, 132.63, 132.36, 128.66, 128.60, 127.55, 125.12, 124.92, 117.82, 110.19. GC-MS (EI): *m/z* 153(100) $[M]^+$, 126 (25.4), 63 (10.9).

3-Chlorobenzonitrile (3k)



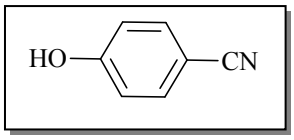
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.64 (m, 1H), 7.61-7.56 (m, 2H), 7.44 (t, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.26, 133.25, 131.94, 130.51, 130.31, 117.45, 113.98. GC-MS (EI): *m/z* 137 (100) $[M]^+$, 102 (30.4), 75 (14).

4-(trifluoromethyl)benzonitrile (3l)



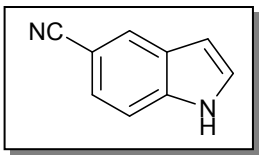
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.44, 132.76, 126.27, 124.48, 117.50, 116.14. GC-MS (EI): *m/z* 171 (100) $[M]^+$, 170 (23.2), 152 (38.4), 121 (56.7), 102 (10.3), 76 (10.6), 44 (17.1).

4-Hydroxybenzonitrile (3m)



White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.38, 134.35, 119.30, 116.51, 102.86. GC-MS (EI): *m/z* 119 (100) $[M]^+$, 91 (27.2), 64 (30.3), 63 (17.7), 44 (11.5).

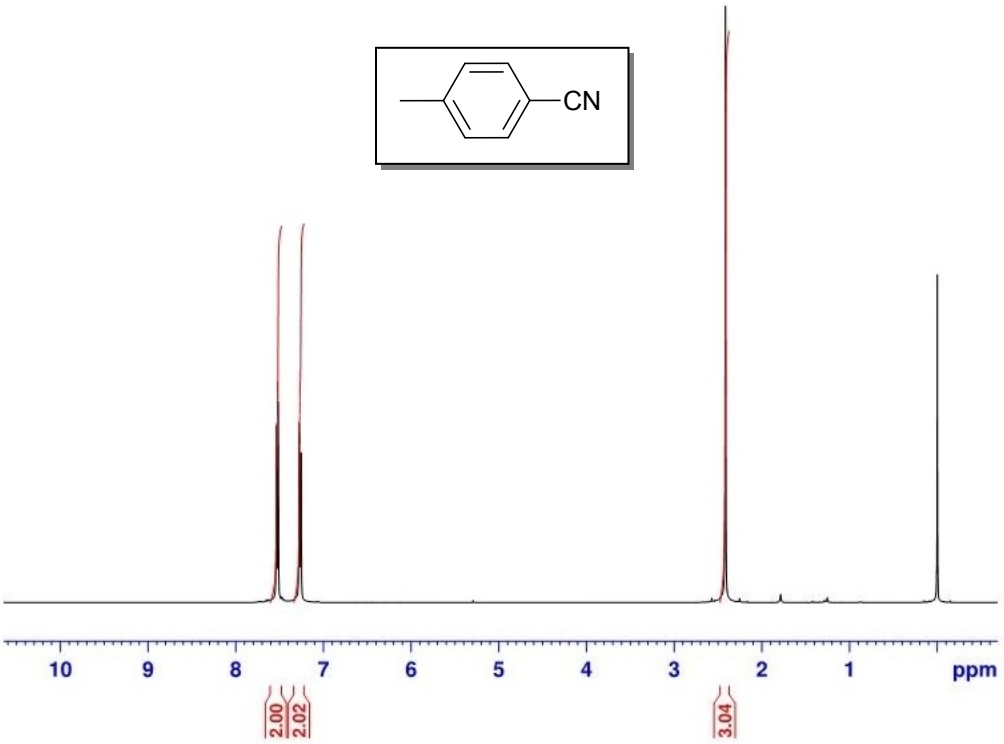
1H-Indole-5-carbonitrile (3n)



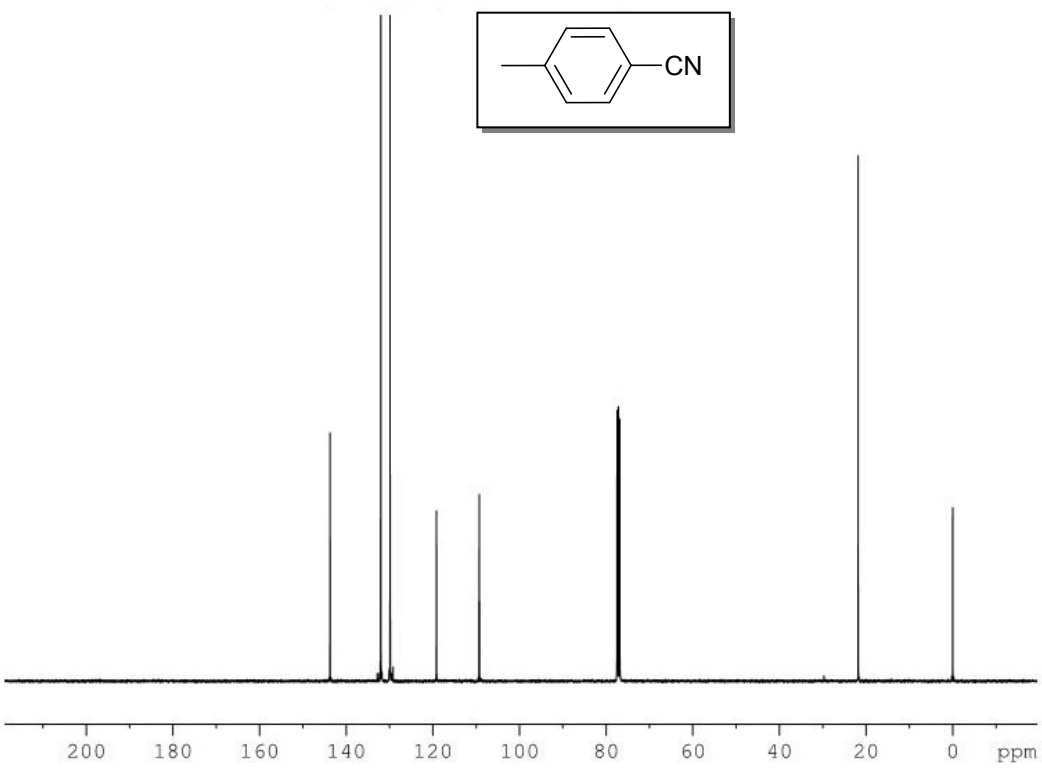
Yellowish solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (bs, 1H), 7.99 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.41 (dd, J = 8.4, 1.2 Hz, 1H), 7.35 (t, J = 2.8 Hz, 1H), 6.63-6.62 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.55, 127.67, 126.57, 126.39, 124.80, 120.95, 112.08, 103.35, 102.95. GC-MS (EI): *m/z* 142 (100) $[M]^+$, 115 (38.3), 114 (18), 89 (10), 88 (14.5), 45 (18.3), 44 (11.4).

^{1}H and ^{13}C NMR Spectra of Products:

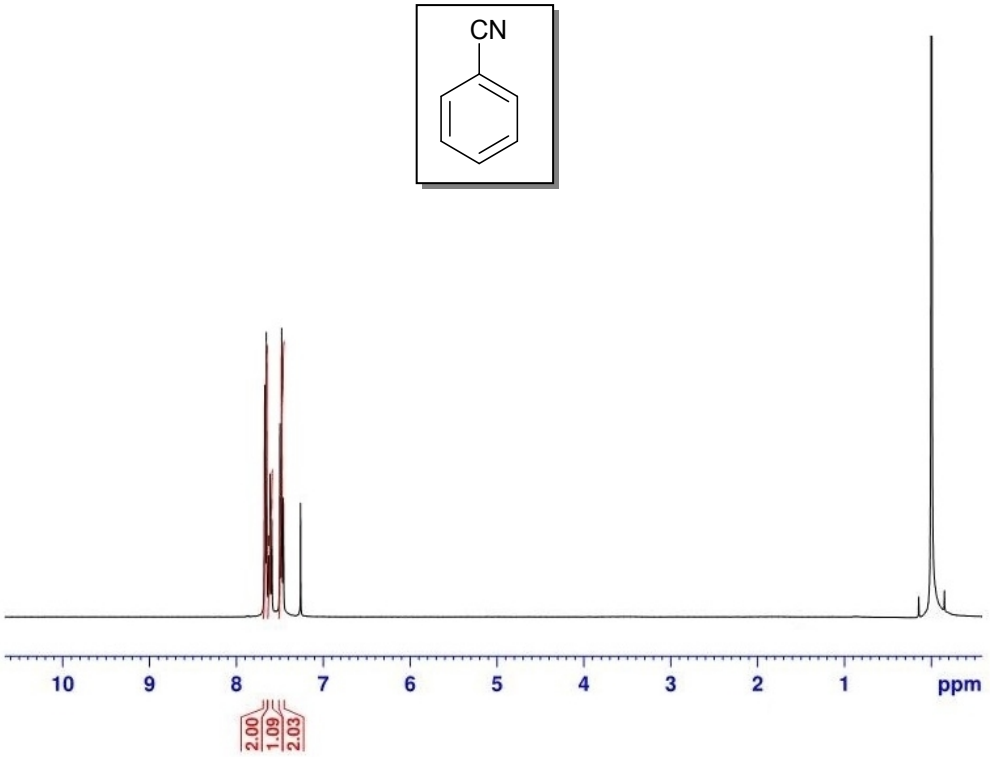
4-Methylbenzonitrile (^{1}H NMR) (3a)



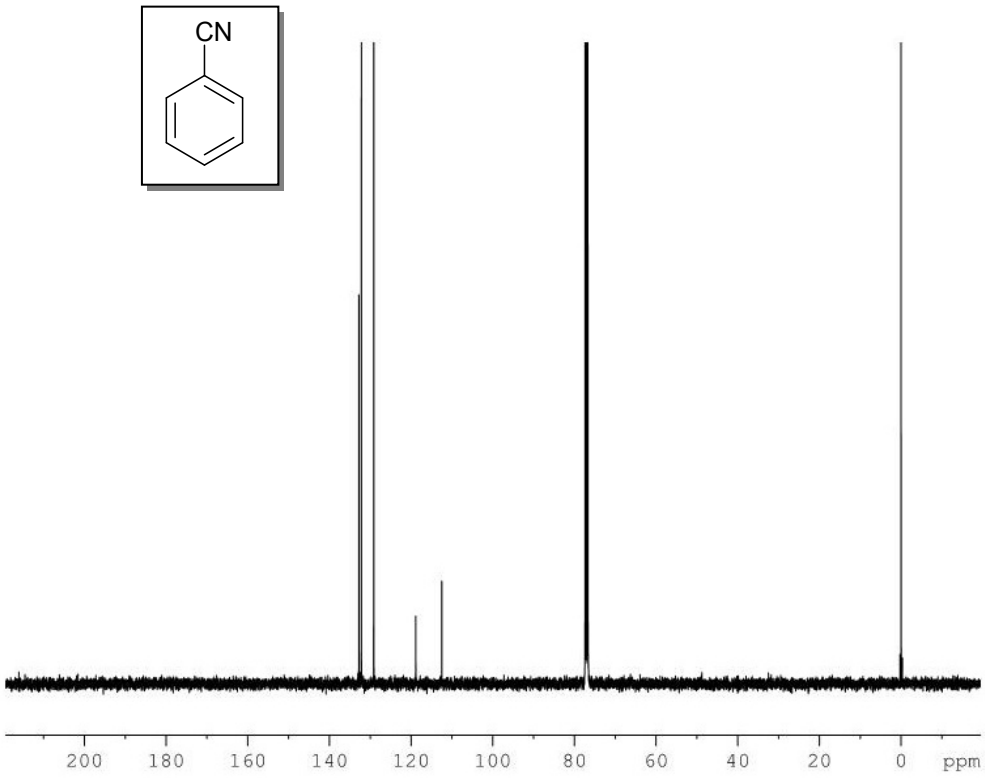
4-Methylbenzonitrile (^{13}C NMR) (3a)



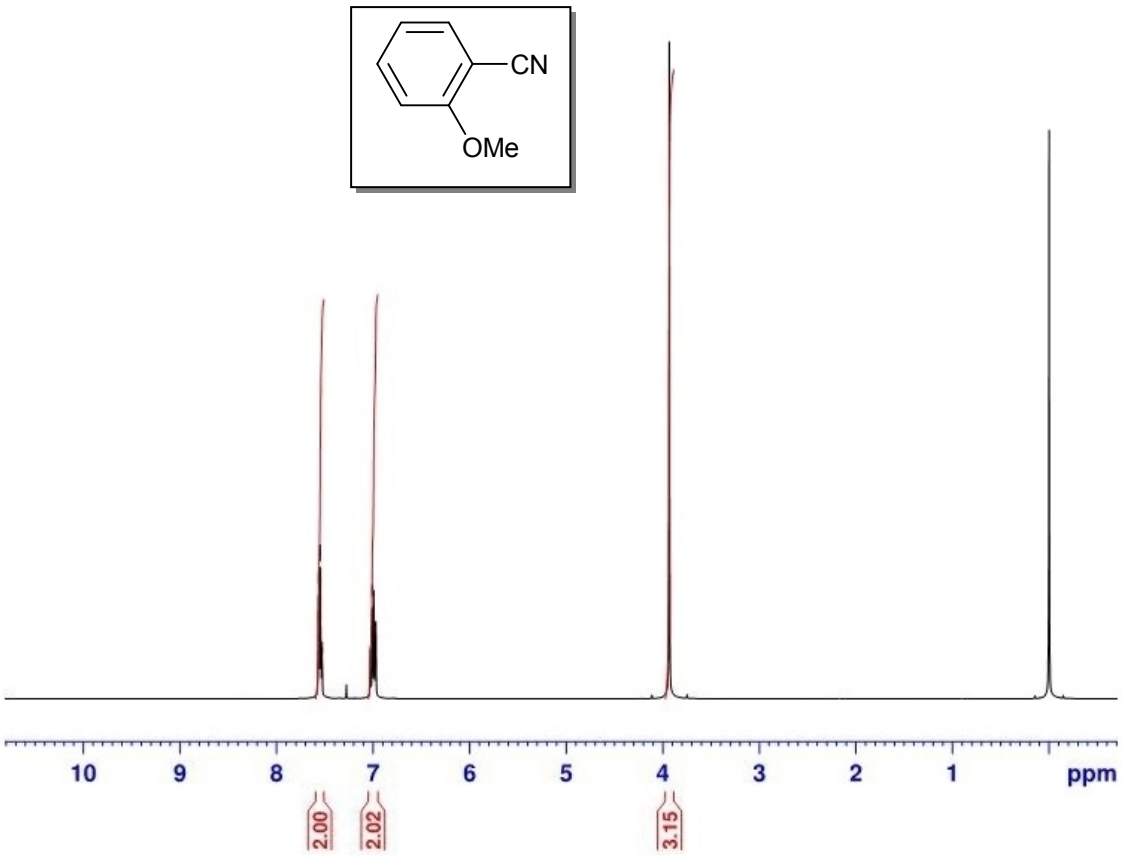
Benzonitrile (^{1}H NMR) (3c)



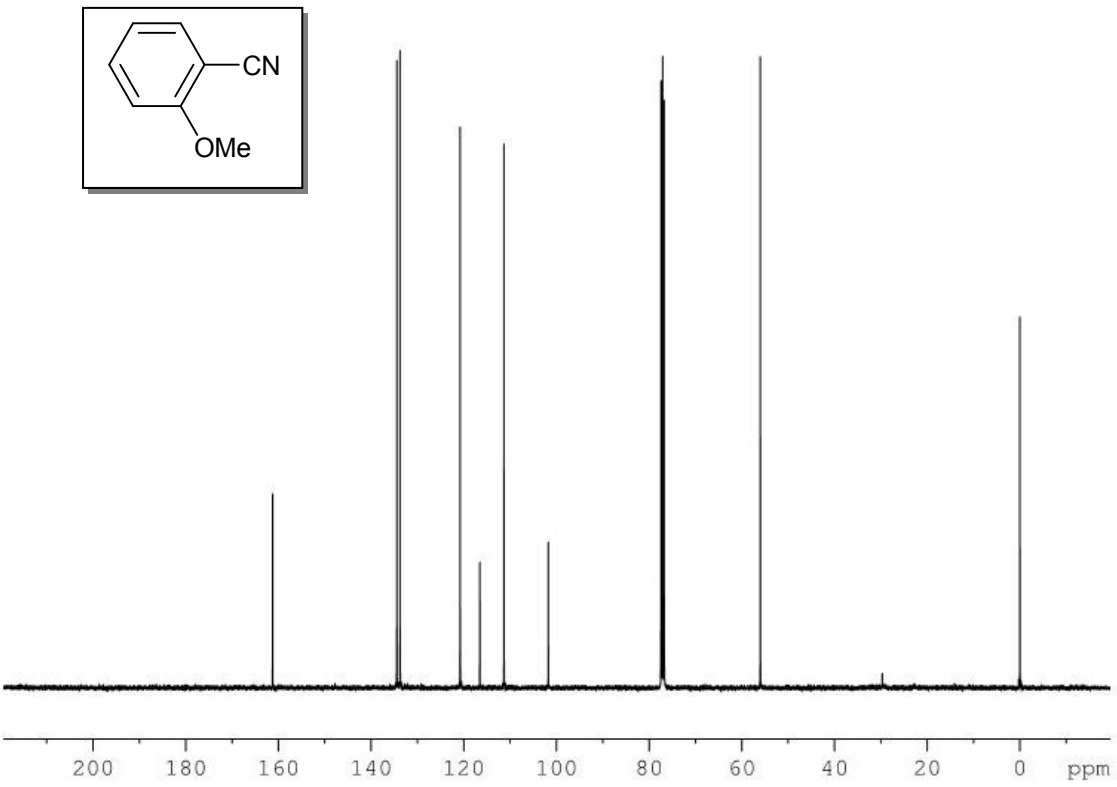
Benzonitrile (^{13}C NMR) (3c)



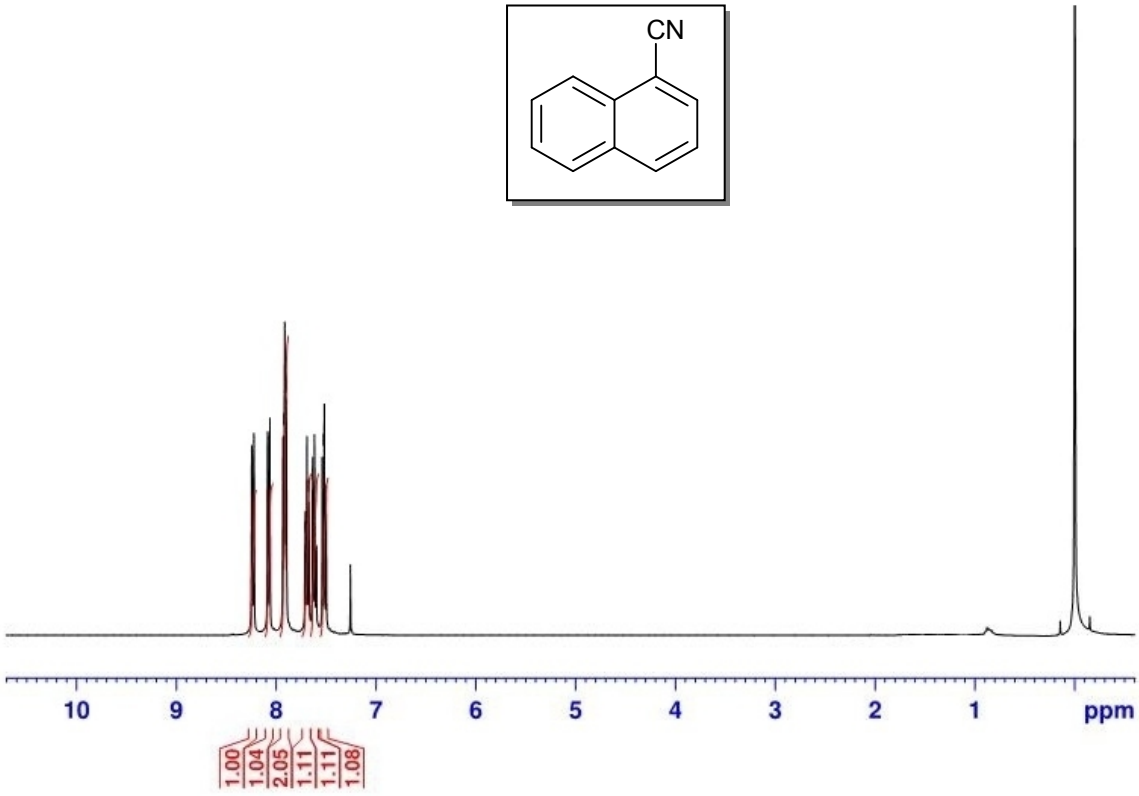
2-Methoxybenzonitrile (^{1}H NMR) (3e)



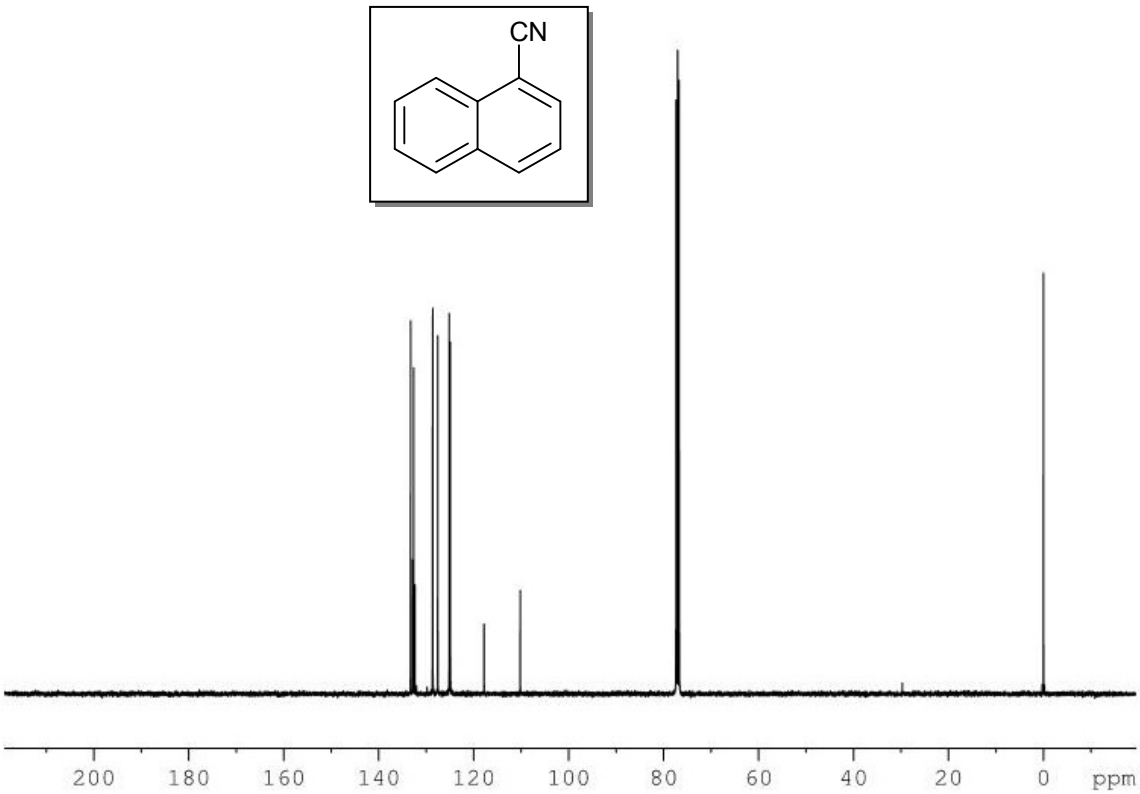
2-Methoxybenzonitrile (^{13}C NMR) (3e)



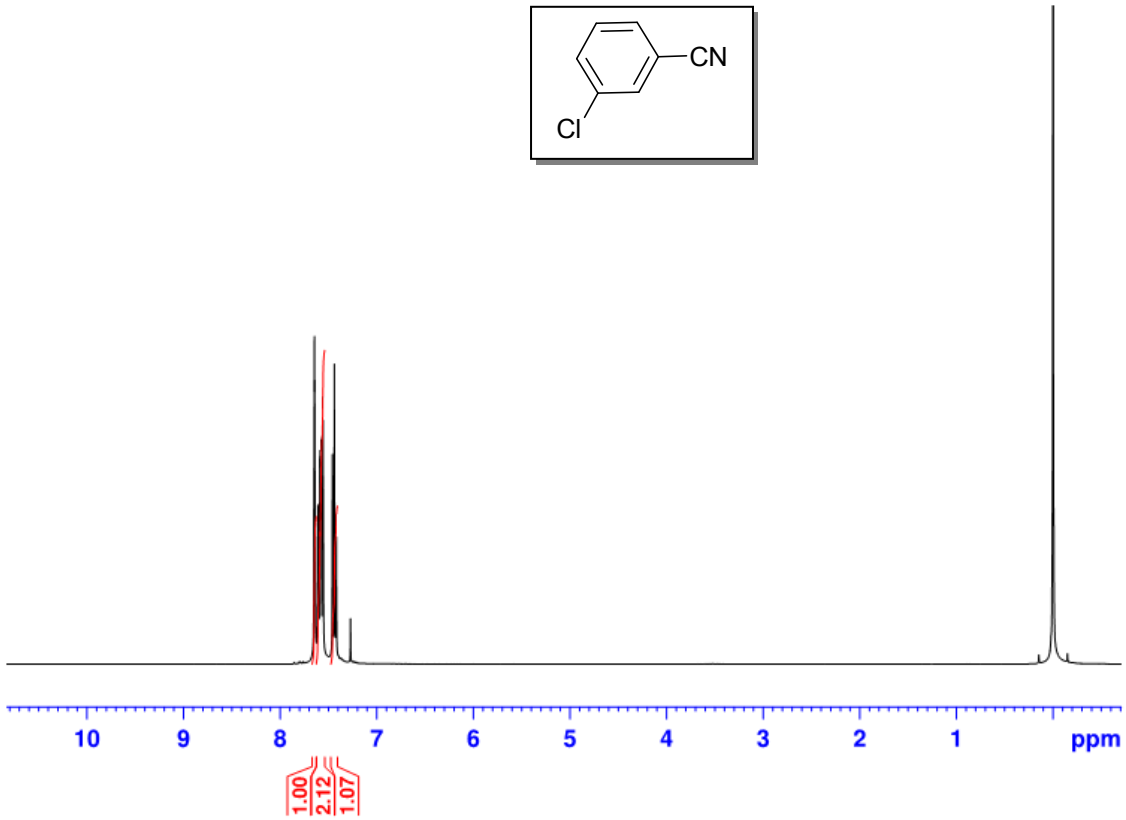
1-Naphthonitrile (^{1}H NMR) (3f)



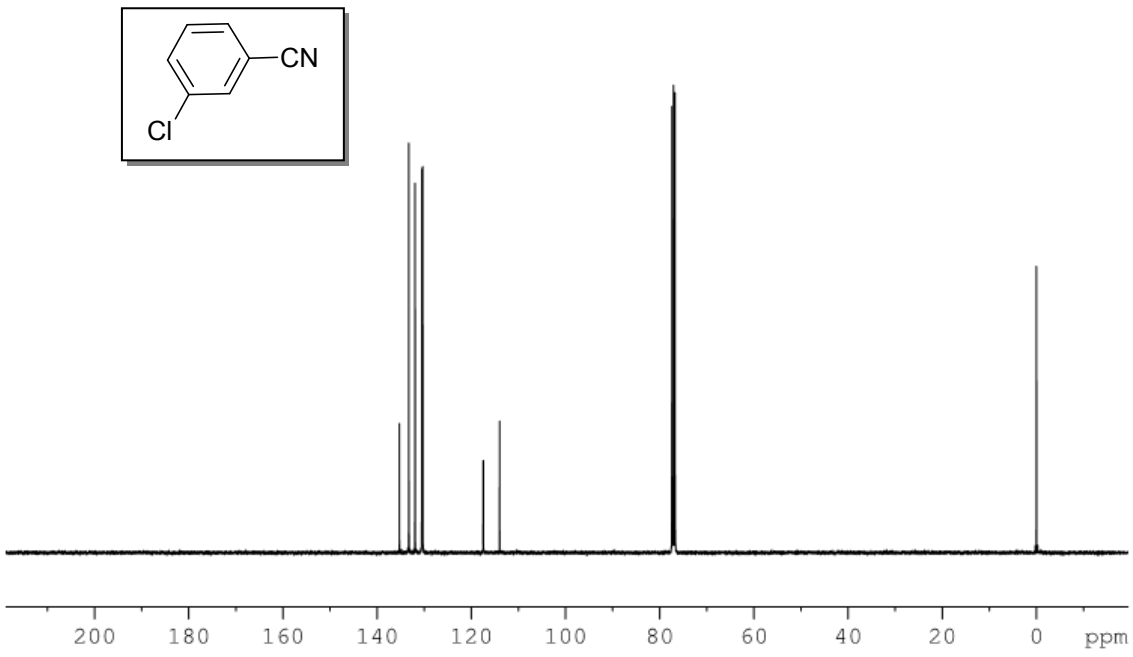
1-Naphthonitrile (^{13}C NMR) (3f)



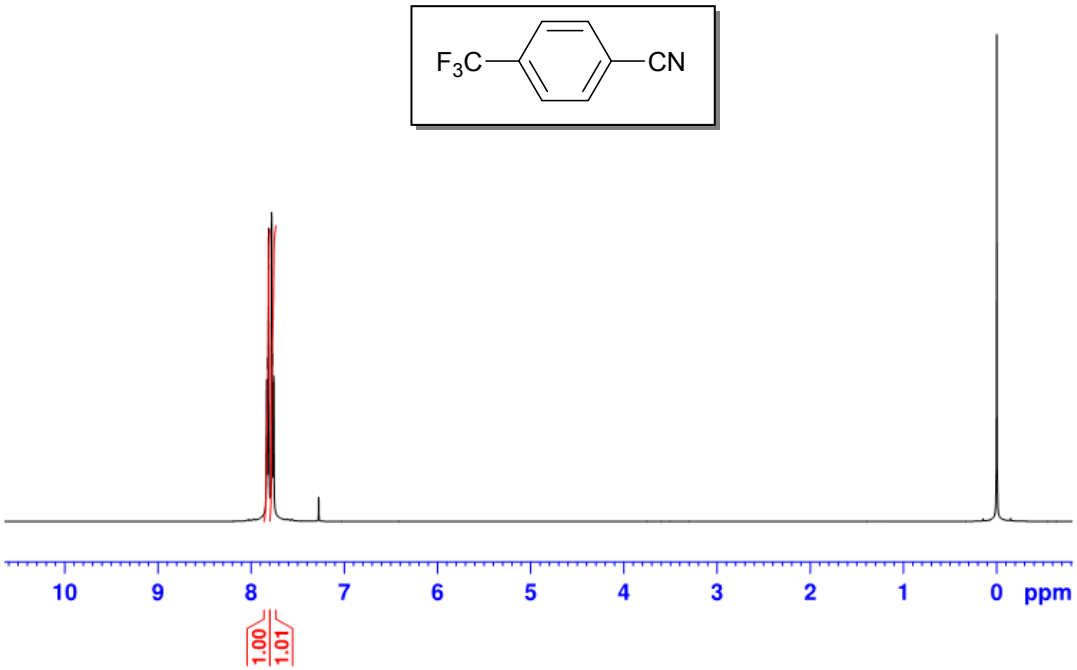
3-Chlorobenzonitrile (^{1}H NMR) (3k)



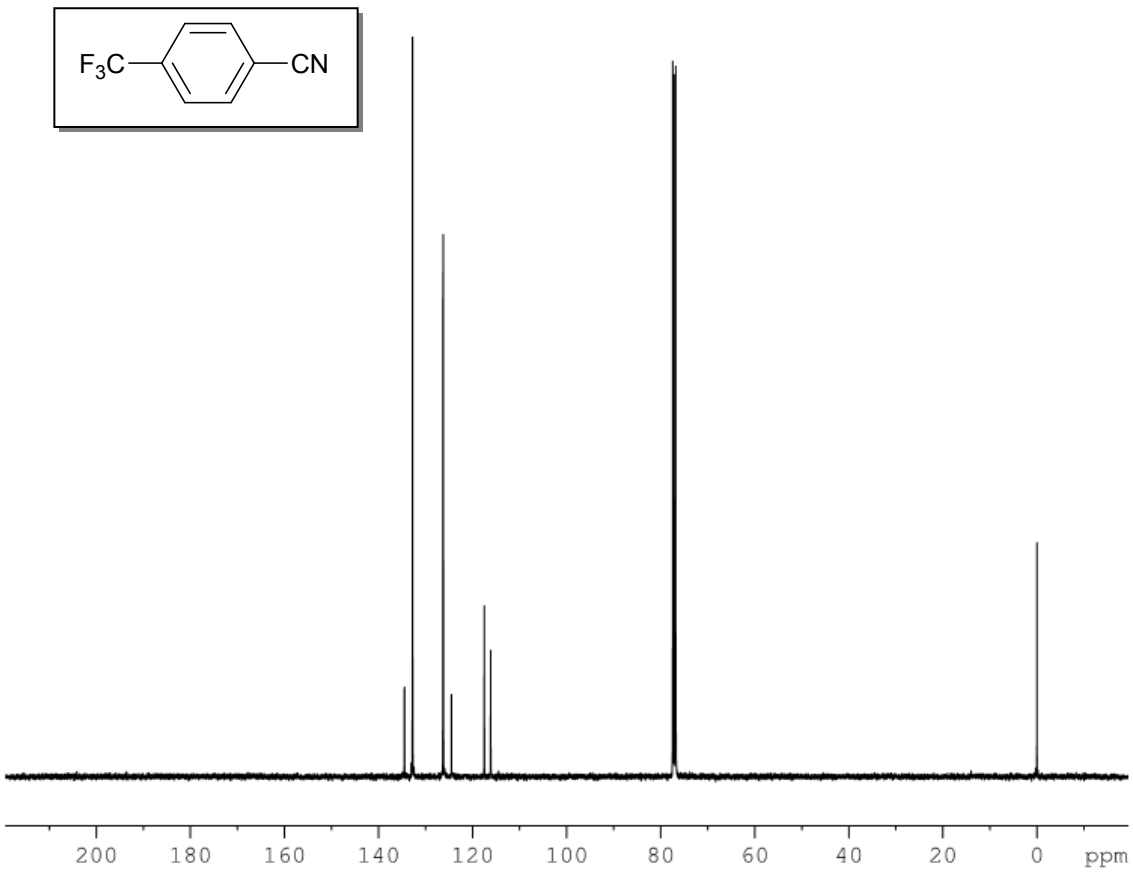
3-Chlorobenzonitrile (^{13}C NMR) (3k)



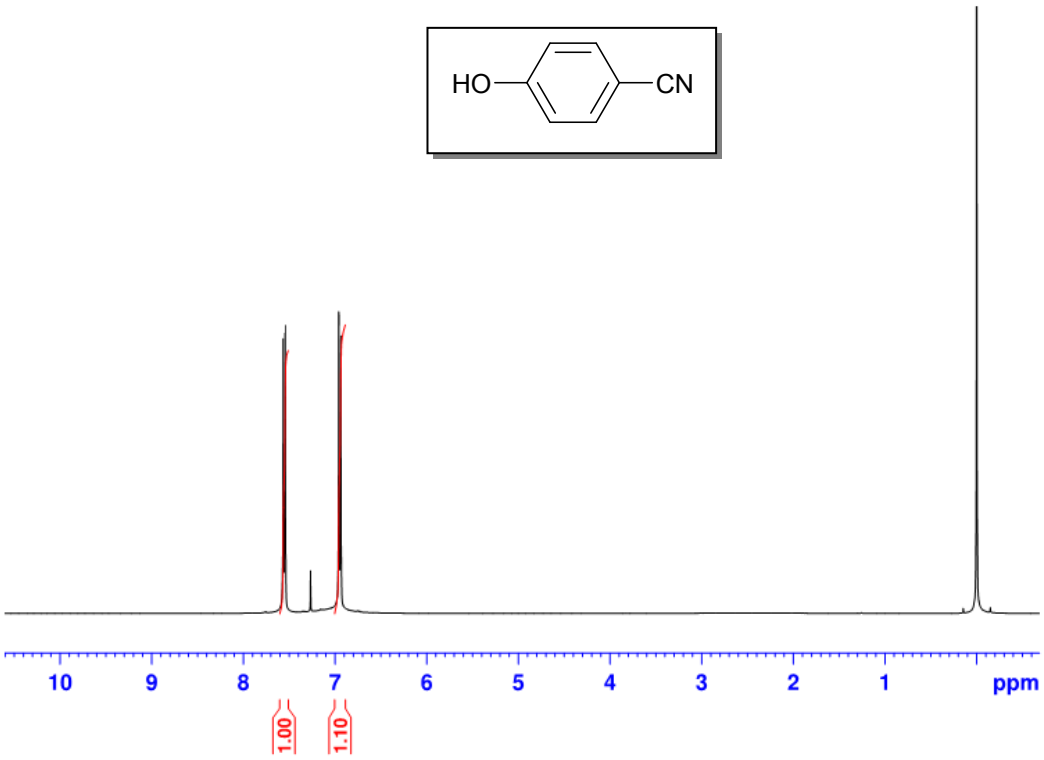
4-(trifluoromethyl)benzonitrile (^{1}H NMR) (3l)



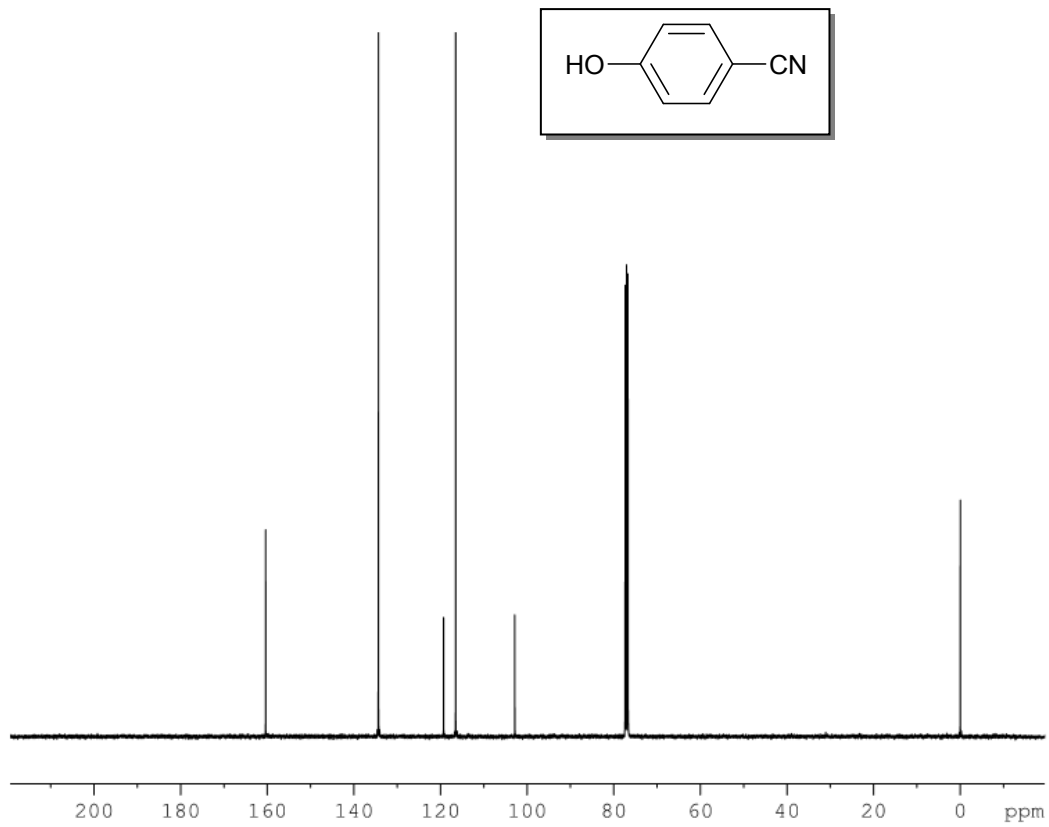
4-(trifluoromethyl)benzonitrile (^{13}C NMR) (3l)



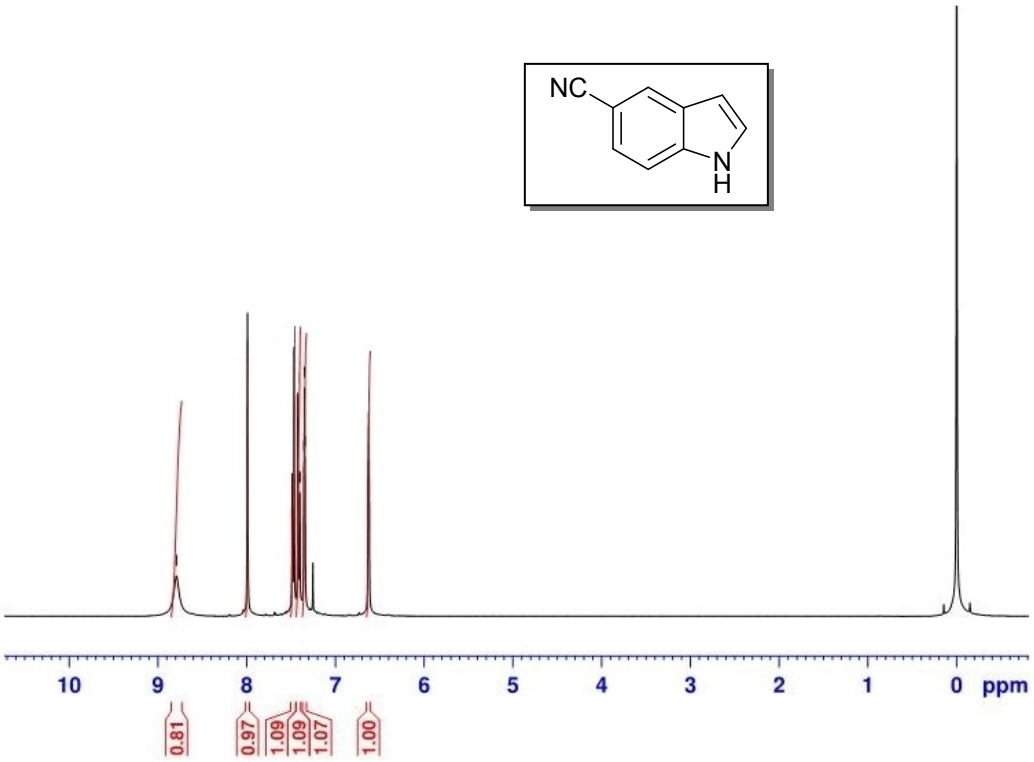
4-Hydroxybenzonitrile (^{1}H NMR) (3m)



4-Hydroxybenzonitrile (^{13}C NMR) (3m)



1H-Indole-5-carbonitrile (^{1}H NMR) (3n)



1H-Indole-5-carbonitrile (^{13}C NMR) (3n)