Metal-Free Catalysis of Nitrogen-Doped Nanocarbons for the Ammoxidation of Alcohols to Nitriles

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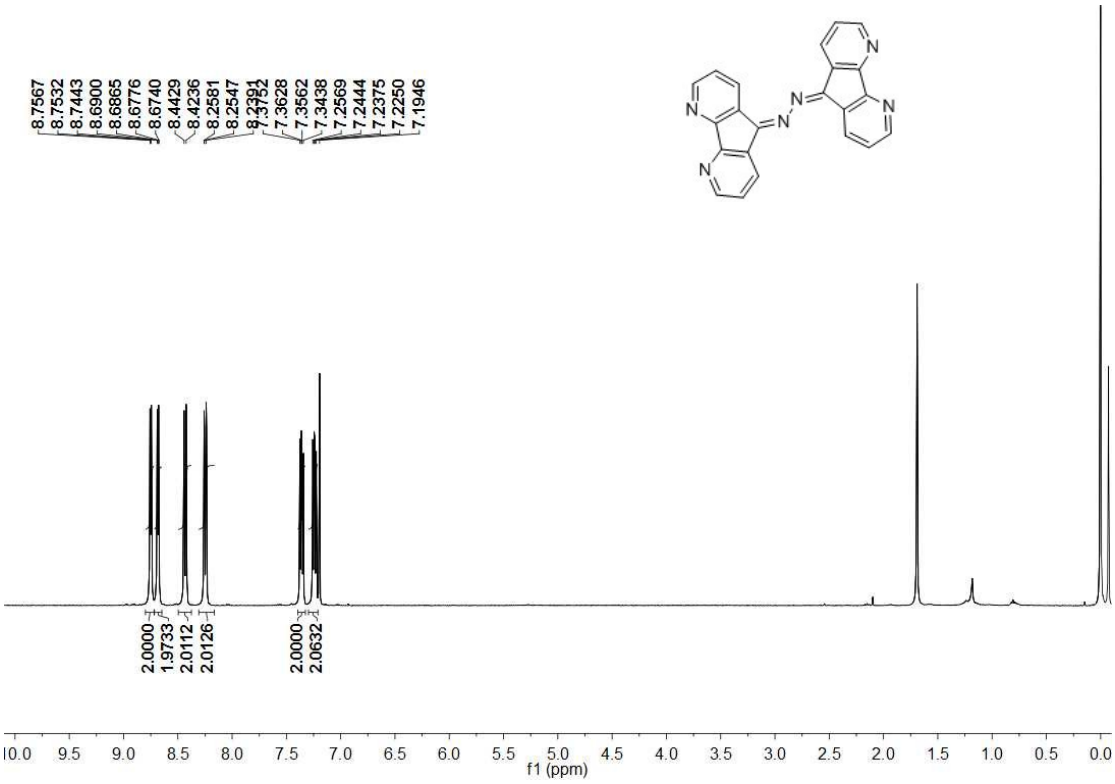
Materials

All starting materials and solvents were obtained from commercial suppliers and used without further purification.

Synthesis of DAA ligand[1]

4,5-Diazafluoren-9-one (DA): 1,10-Phenanthroline (9 g, 0.05 M) and KOH (5 g, 0.09 M) were added to 850 ml of water and brought to reflux. $KMnO_4$ (25.30 g, 0.16 M) in 400 ml water was added dropwise to the refluxing mixture. After addition the solution was refluxed for 1 h and filtered to remove MnO_2; when the solution was cooled, crude 4,5-diazafluoren-9-one precipitated as yellow needles.

4,5-diazafluorene-9-one azine (DAA): An acetic acid solution (5 mL) containing DA (1.10 g, 6.1 mmol) and hydrazine (0.14 mL, 2.8 mmol) was refluxed for 0.5 h, and the red precipitate was separated and washed by ethanol, dimethylsulfone and acetone in turn. Yield: 80 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, J = 4.9, 1.4 Hz, 1H), 8.68 (dd, J = 5.0, 1.4 Hz, 1H), 8.43 (dd, J = 7.7, 1.4 Hz, 1H), 8.25 (dd, J = 7.6, 1.4 Hz, 1H), 7.36 (dd, J = 7.6, 5.0 Hz, 1H), 7.24 (dd, J = 7.7, 5.0 Hz, 1H).



Synthesis of meso-N/C-x

The typical meso-N/C-x catalysts were prepared as follows: 270 mg (0.49 mmol) DAA was added into 40 mL DMF under vigorous stirring. The mixture was refluxed at 130 ^{o}C for 0.5h. Then 1200 mg 40% dispersion of 12-nm SiO_2 particles (Ludox HS-40) in water was added into the mixture under vigorous stirring. After evaporation of DMF at 180 ^{o}C, the obtained DAA/SiO_2 composites were then pyrolyzed under flowing nitrogen with a heating ramp rate of 5 ^{o}C/min to desired temperatures (800-1000 ^{o}C) and the temperature was kept for 2 h. Finally, meso-N/C-*x* catalysts, where x indicated the pyrolysis temperature, were obtained after removal of templates by 0.5 M NaOH etching for 5 h at 100 ^{o}C.

Synthesis of meso-C

270 mg sucrose was added into 40 mL H_2O under vigorous stirring. Then 1200 mg Ludox HS-40 was added into the mixture and then the whole reaction mixture was

stirred at 60 °C for 5-6 hours. After evaporation of H_2O at 100 ^oC, the obtained composites were then pyrolyzed under flowing nitrogen with a heating ramp rate of 5 ^oC/min to 800 ^oC) and the temperature was kept for 2 h. Finally, meso-C catalyst was obtained after removal of templates by 0.5 M NaOH etching for 5 h at 100 ^oC.

Synthesis of mpg-C_3N_4[2]

Cyanamide was dissolved in Ludox HS-40 with stirring at 60 °C overnight. After evaporation of the solvent at 100 ^oC, the obtained solid was pyrolyzed at 550 °C (ramp rate: 2.3 °C min^{-1}) for 4 h under flowing nitrogen. The obtained powder was treated with 10 wt % hydrofluoric acid for 12 h, and this procedure was repeated once for removing the silicon template completely. Finally, the powder was thoroughly washed to neutral with water and dried in vacuum at 100 °C overnight.

Synthesis of N/AC

1,10-phenanthroline (183.5 mg, 1.0 mmol) was stirred in ethanol for 20-30 minutes at room temperature. Then, vulcan XC72R carbon powder (689.7 mg) was added and the whole reaction mixture was stirred at 60 °C for 5-6 hours. The reaction mixture was cooled to room temperature and ethanol was removed slowely under vacuum. The remaining solid sample obtained was dried at 60 °C for 12 hours. The dried sample was grinded to a powder. Then, the grinded powder was pyrolyzed at 800°C for 2 hours in nitrogen atmosphere and cooled to room temperature.

Catalyst characterization

N_2 sorption isotherms were measured at 77K using a QuadraSorb SI4 Station, and the samples were degassed at 300 ^oC for 6 h before the measurements. The pore size

distribution (PSD) plot was recorded from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) model. Scanning electron microscope (SEM) images were conducted on a JSM-7800F microscope operating at an acceleration voltage of 20 kV. Transmission electron microscope (TEM) images were acquired with JEM-2100 microscope. Surface compositions were determined by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific ESCALAB 250Xi instrument with Al Kα radiation anode (hv =1486.6 eV), and the C 1s line (284.8 eV) was used as the reference to correct the binding energies (BE).

Procedure for the synthesis of nitriles

The magnetic stirring bar and corresponding alcohol were transferred to the glass vial and then solvent was added. The catalyst was added followed by the addition of aq. NH_3. Then the vial was fitted with septum, cap and needle. The reaction vials were placed into an autoclave and the autoclave was pressurized to 5 bar molecular oxygen. The autoclave was placed into the oil bath to get the required reaction temperature. The reaction was stirred for required time and after the completion of the reaction, the autoclave was cooled to room temperature. The remaining oxygen was discharged and the samples were removed from the autoclave. To the individual vials, biphenyl as standard was added and the reaction product was diluted with *t*-amyl alcohol followed by filtration and then analysed by GC and GC mass spectrometry (GC-MS). Qualitative and quantitative analysis of all products were made using GC and GC-MS analysis.

Recovery and reuse of meso-N/C-900

The recycling of catalyst experiments was carried out using benzyl alcohol, as model

substrate applying standard procedure under following reaction conditions: 0.5 mmol benzyl alcohol, 50 mg meso-N/C-900, 140 µl aq. NH_3, 130 ^oC, 24 h, 5 bar O_2, 1 ml *t*-amyl alcohol. After completion of the reaction, in each run the catalyst was separated by centrifugation, washed with methanol and calcined at 400 ^oC under N_2 for 2h. Then the catalyst was used for the next run. Alternatively, after completion of the reaction, the reaction solution was carefully decanted and the fresh solvent, substrate and ammonia were added and the reaction was performed. Conversion and yield were determined by GC analysis using naphthalene as standard.

Procedure for gram scale reaction

To a Teflon-fitted 300-ml autoclave, the magnetic stirring bar and corresponding alcohol were transferred and then solvent was added. The meso-N/C-900 catalyst was added followed by the addition of aq. NH_3. The autoclave was pressurized to 5 bar molecular oxygen. The autoclave was placed into a oil bath to get the required reaction temperature. The reactions were stirred for required time and after the completion of the reaction, the autoclave was cooled to room temperature. naphthalene as standard was added and the reaction product was diluted with *t*-amyl alcohol followed by filtration and then analysed by GC.

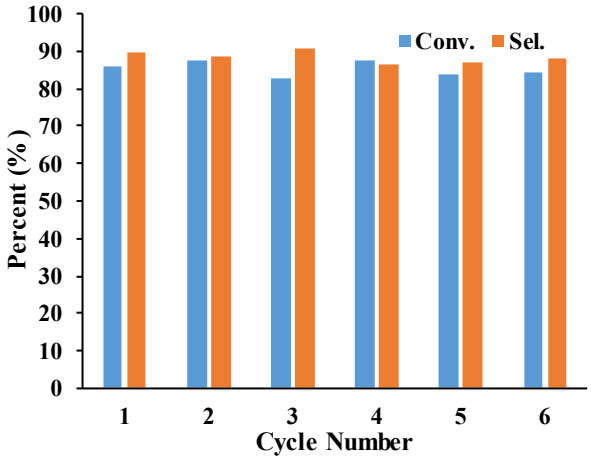


Figure S1. Recycling test of meso-N/C-900 in aerobic oxidative synthesis of benzonitrile. Reaction conditions: **1a** (0.5 mmol), 50 mg catalyst, 3.7 equiv. aq. NH_3 (25-28% NH_3 basis), 5 bar O_2, 1 ml *t*-amyl alcohol, 130 °C, 24 h. Yields were determined by GC.

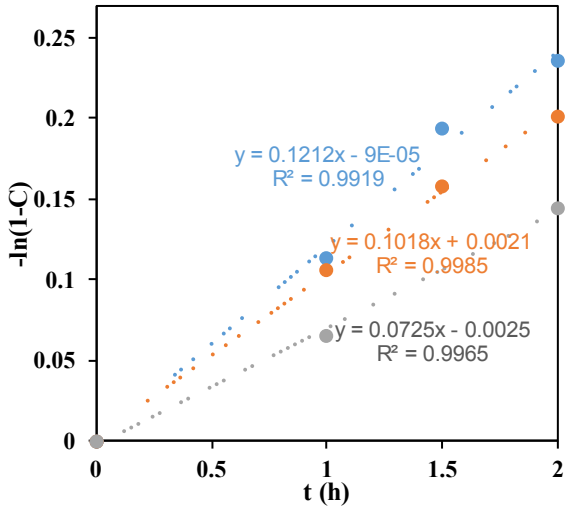


Figure S2. Time-on-stream course of conversion under different temperatures. Reaction conditions: benzyl alcohol (0.5 mmol), 3.7 equiv. aq. NH_3 (25-28% NH_3 basis), 5 bar O_2, 1 ml *t*-amyl alcohol, 50 mg meso-N/C-800(blue), -900(orange), -1000(gray).

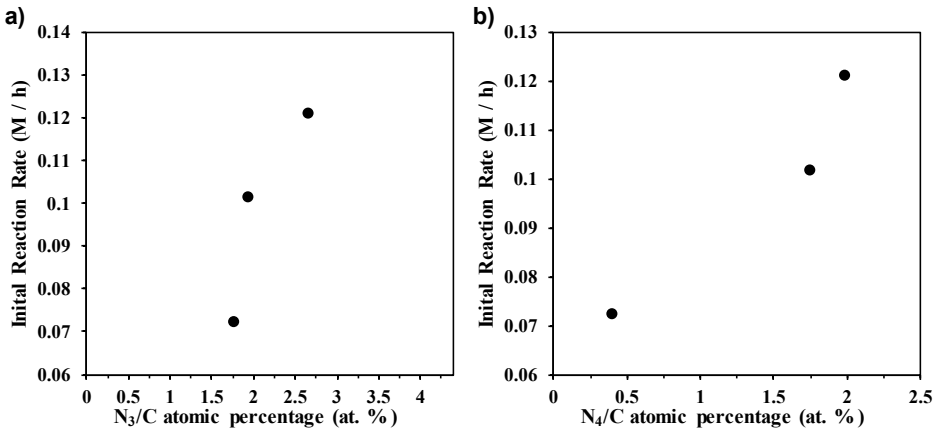
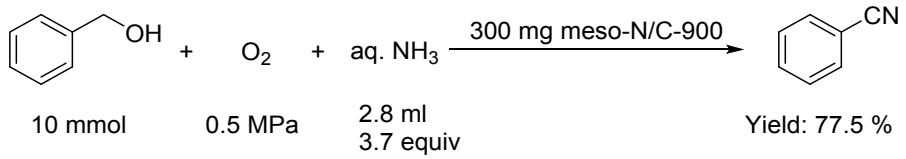


Fig. S3 Relationship between benzyl alcohol conversion rate and (a) graphitic N3/C, (b) pyridinic N-oxide N4/C atomic ratio of meso-N/C-x.

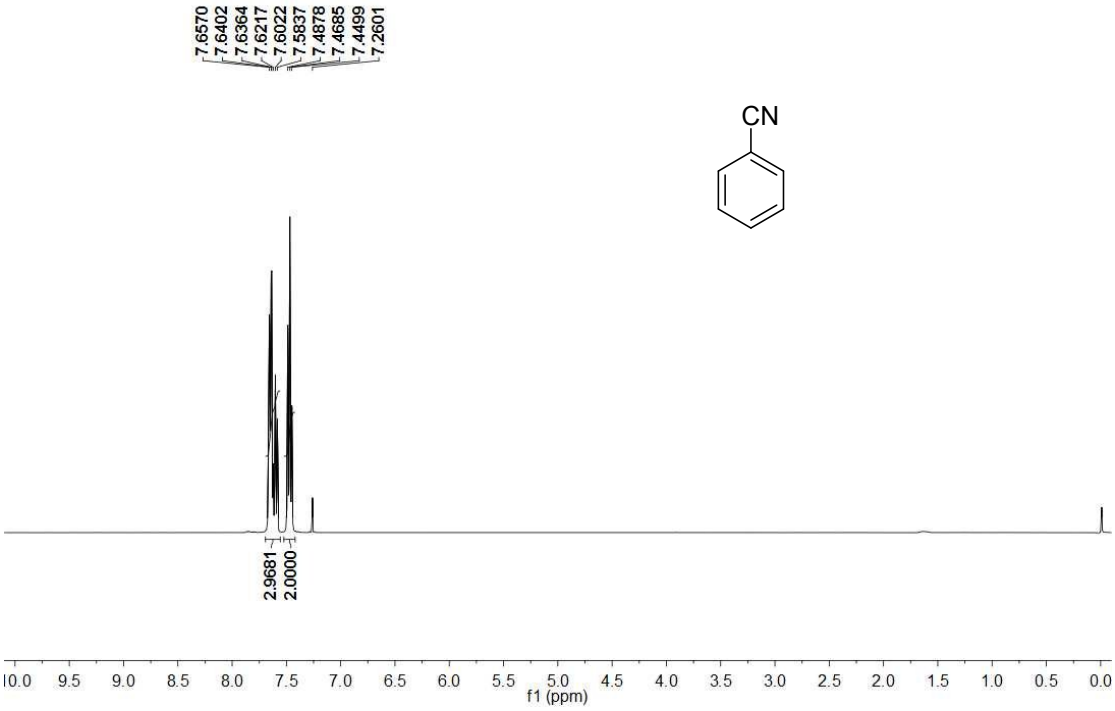
Table S1 Distribution of element species obtained from the De-Convolution of N1s peaks by XPS.

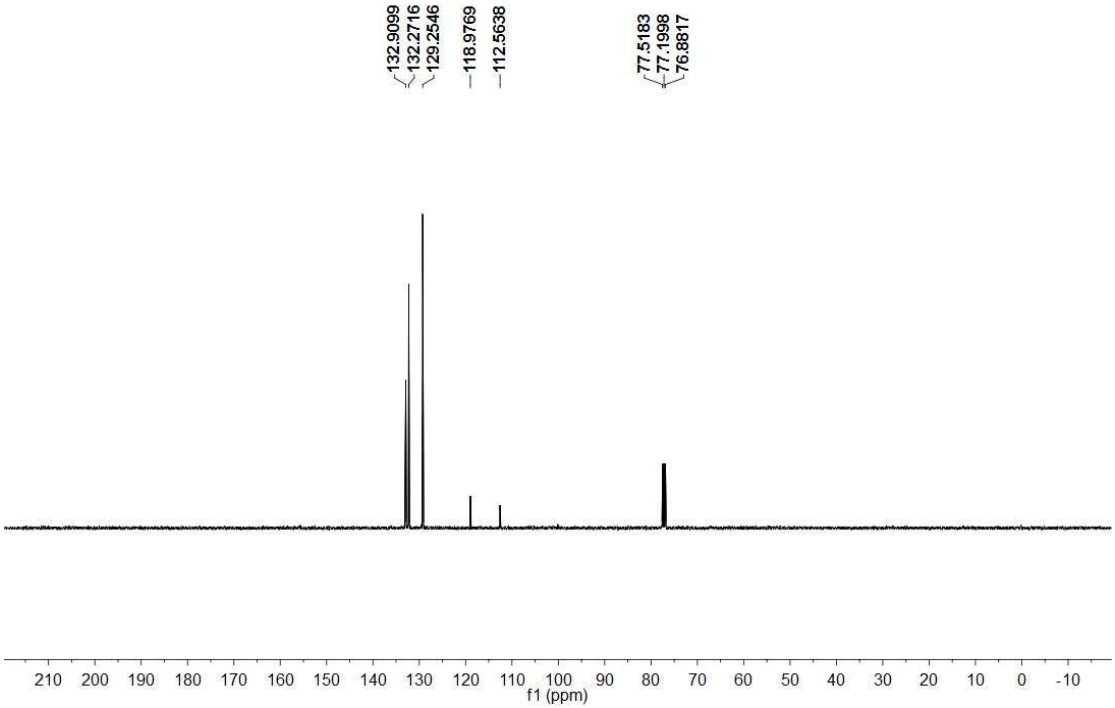
		at.%		
entry	binding energy (eV)	800	900	1000
surface area (m^2g^{-1})	–	869	906	840
total pore volume (cm^3g^{-1})		2.42	2.20	2.44
total C	–	82.8	85.4	84.8
total N	–	8.80	6.56	4.02
pyridinic nitrogen N1	398.4-398.6	2.91	1.94	1.13
pyrrolic nitrogen N2	399.9-400.1	2.06	1.50	1.08
graphitic nitrogen N3	400.7-401.0	2.18	1.63	1.48
pyridine-*N*-oxide N4	402-405	1.65	1.49	0.33
N/C (at.%)	–	10.6	7.68	4.74
N1/C (at.%)	–	3.51	2.27	1.33
N2/C (at.%)	–	2.49	1.76	1.27
N3/C (at.%)	–	2.63	1.91	1.75
N4/C (at.%)	–	1.97	1.74	0.39

Scheme S1. Gram-scale experiment:10 mmol benzyl alcohol, 2.8 ml aq. NH_3 (25-28 % NH_3 basis), 300 mg catalyst, 5 bar O_2, 9 ml *t*-amyl alcohol, 130 ^oC, 60 h. Yields were determined by GC.

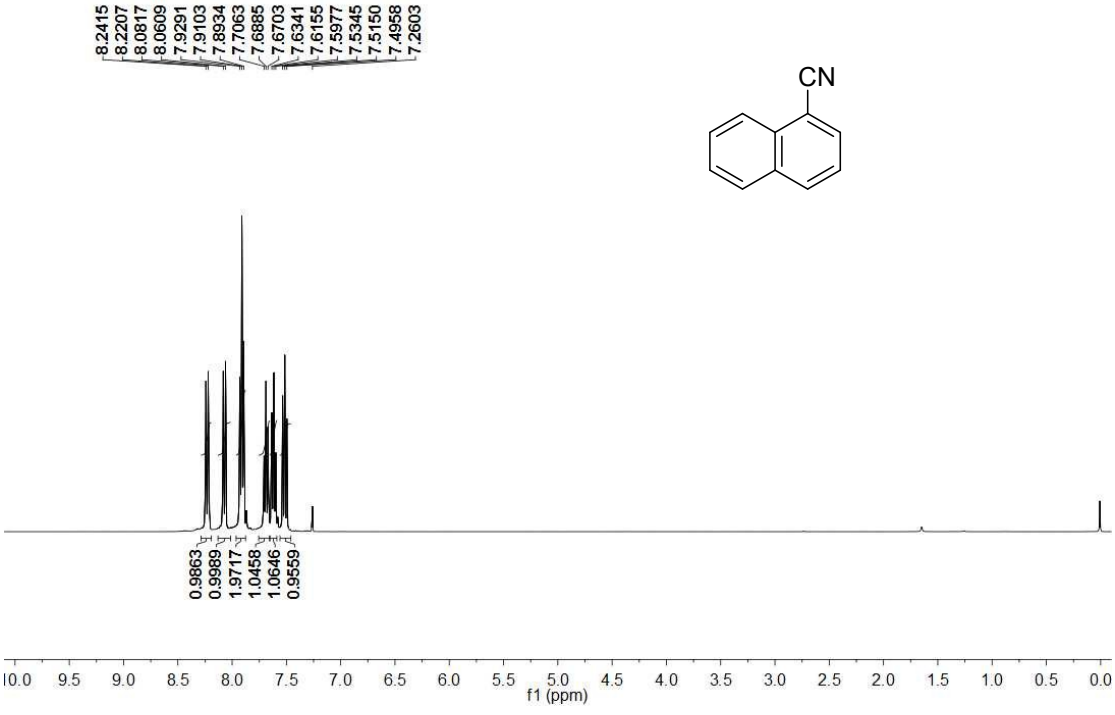


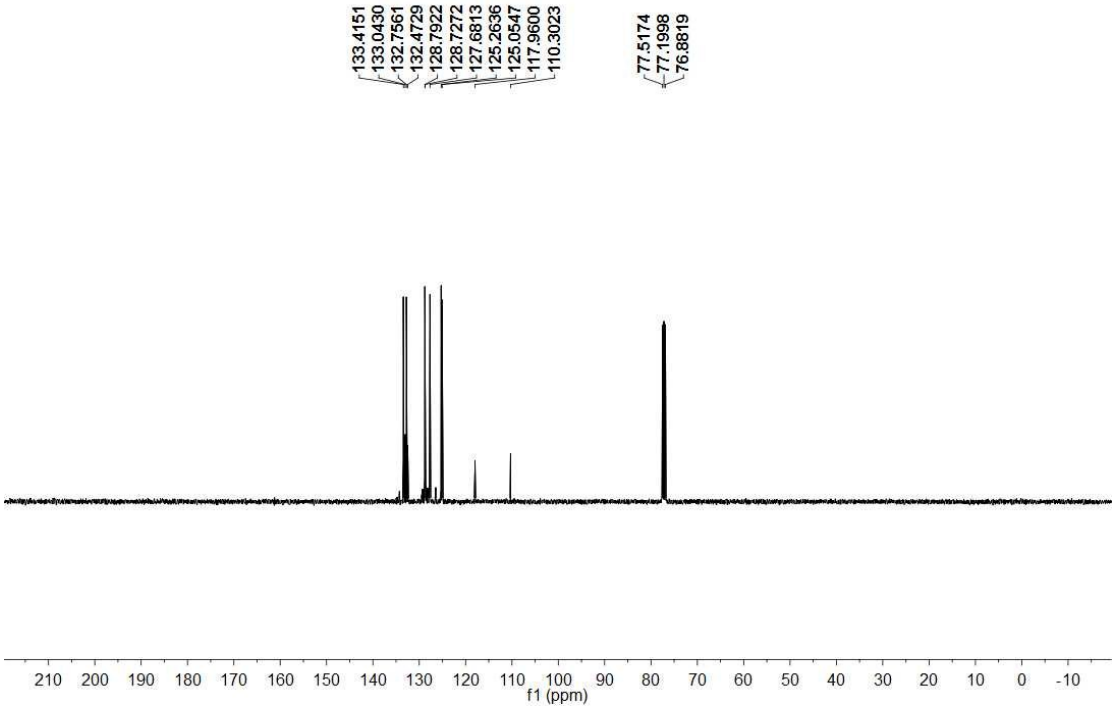
Characterization of the Products



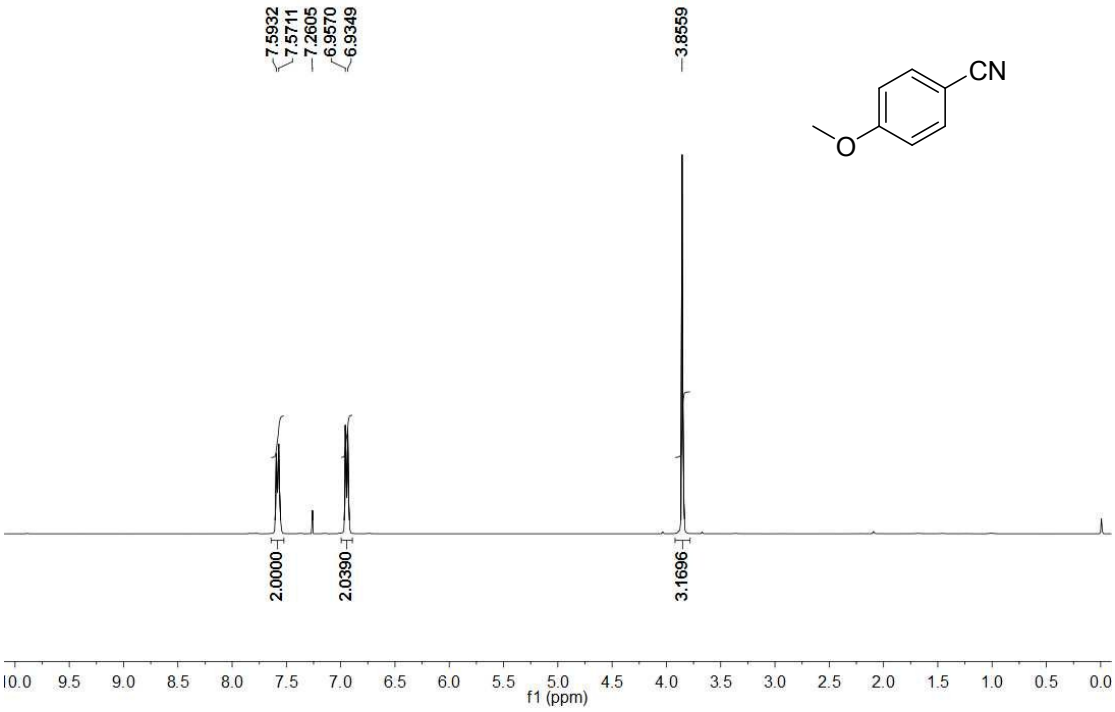


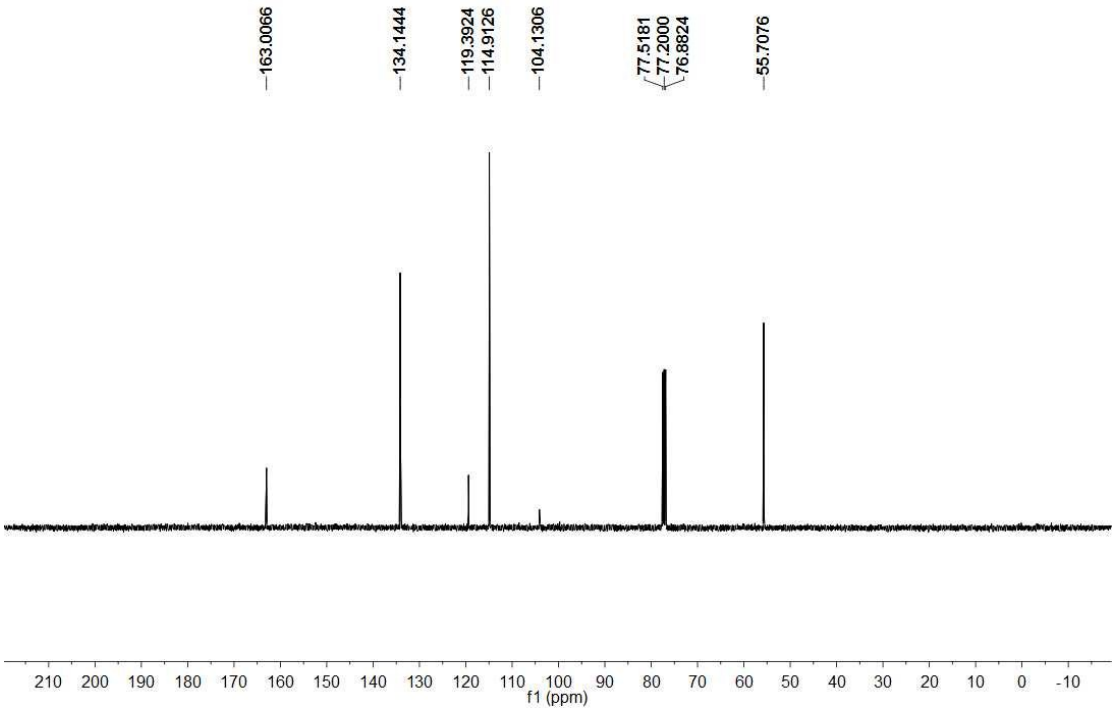
Benzonitrile (2a)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 3H), 7.47 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 132.3, 129.3, 119.0, 112.6; MS (70 eV): m/z (%) 103.3(M^+, 100).



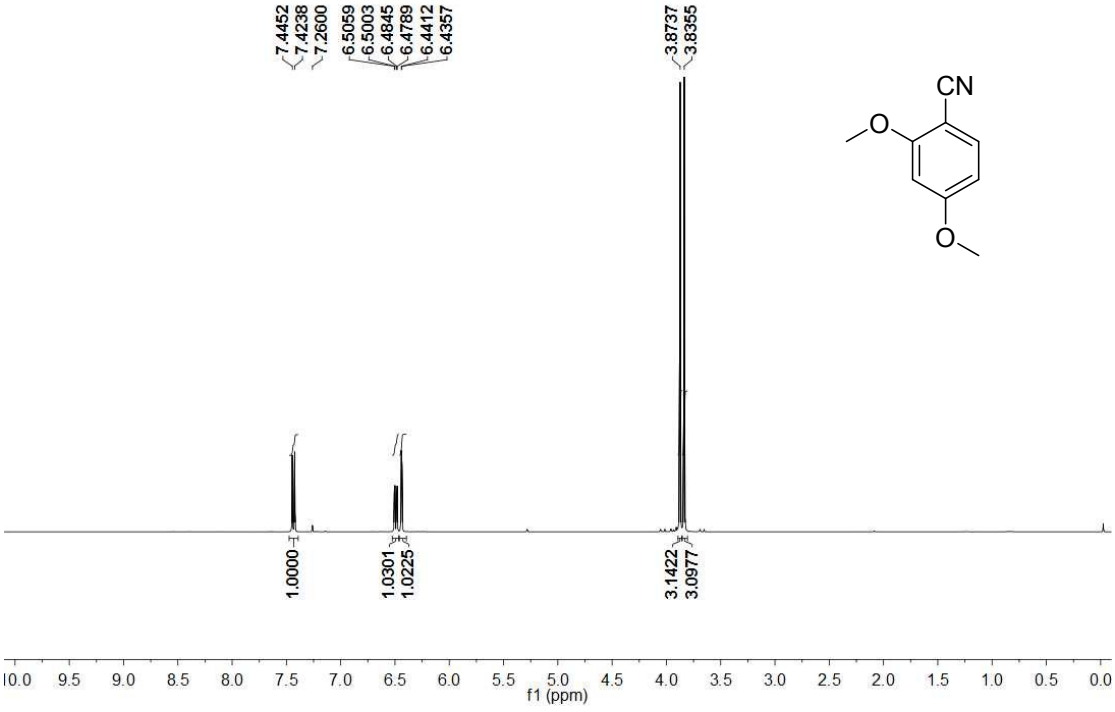


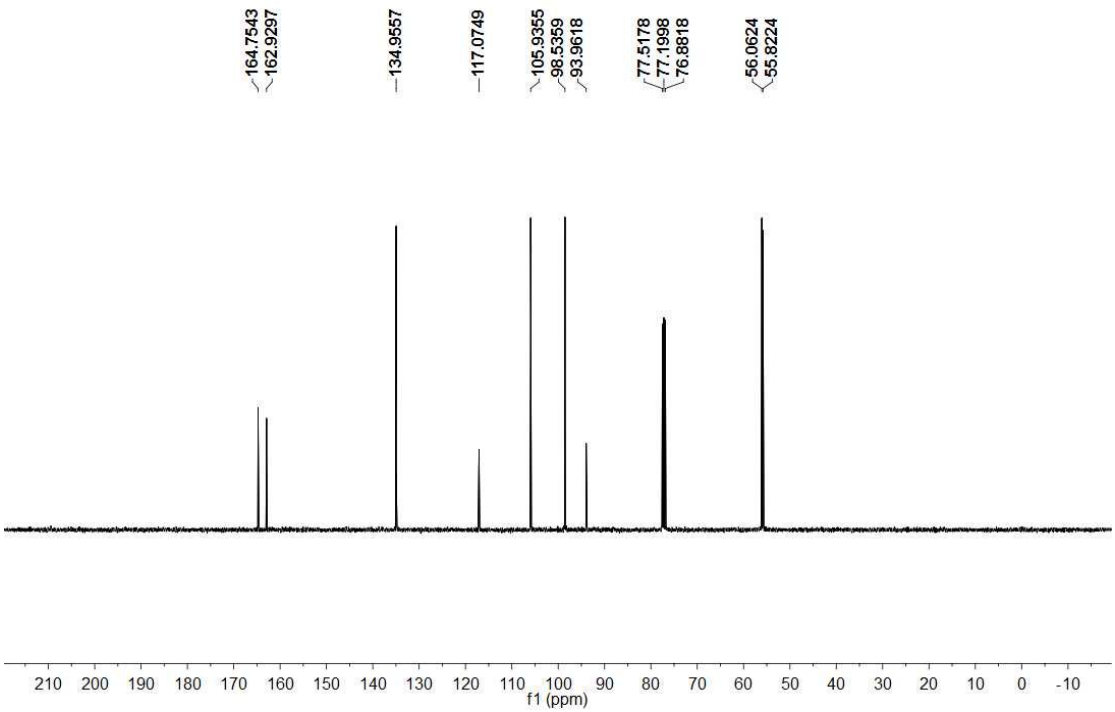
Naphthonitrile (2b)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.91 (t, *J* = 7.1 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 133.0, 132.8, 132.5, 128.8, 128.7, 127.7, 125.3, 125.1, 118.0, 110.3; MS (EI, 70 eV): m/z (%) 153.3 (M^+, 100).



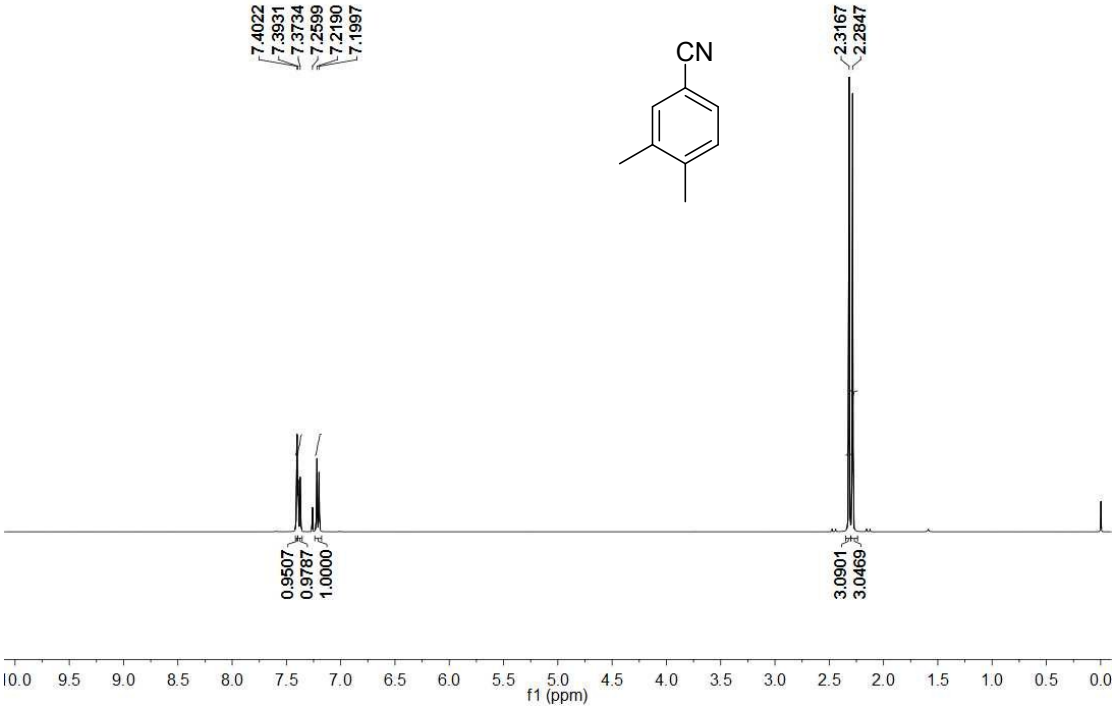


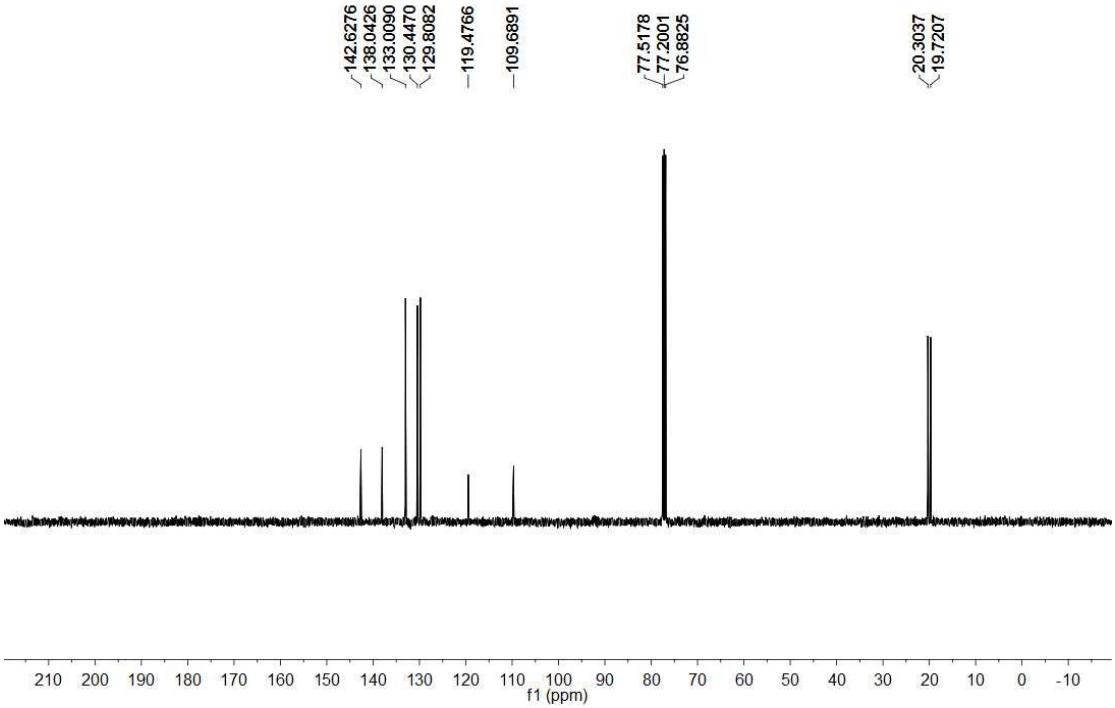
4-Methoxybenzonitrile (2c)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 134.1, 119.4, 114.9, 104.1, 55.7; MS (EI, 70 eV): m/z (%) 133.3 (M^+, 100).



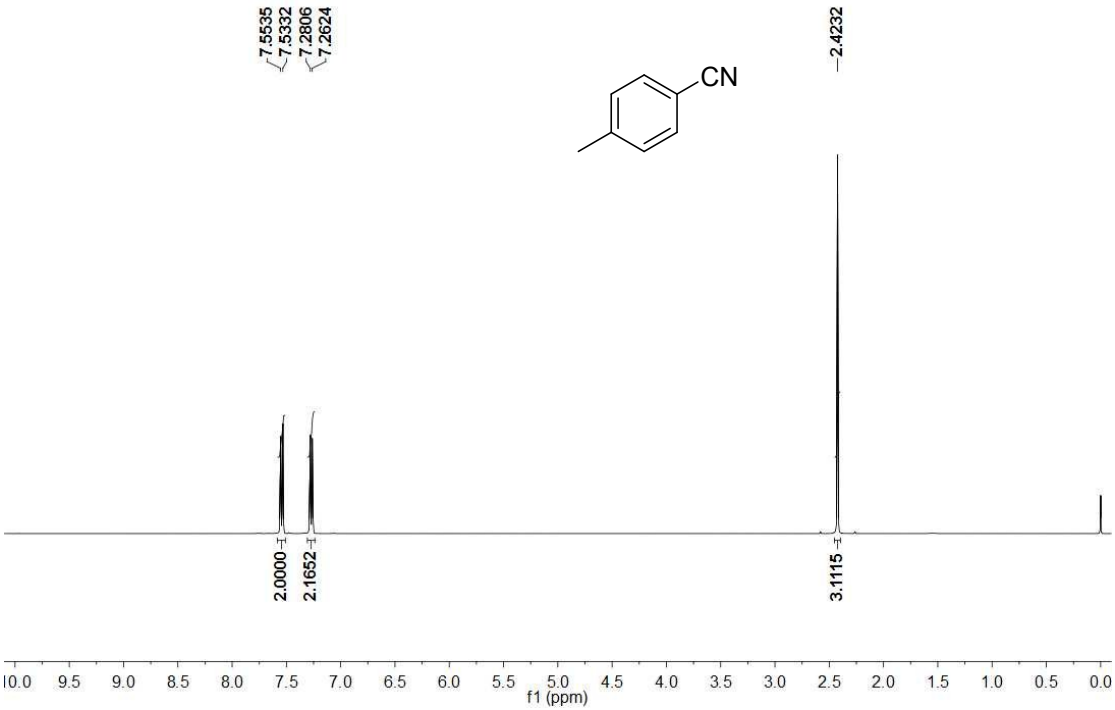


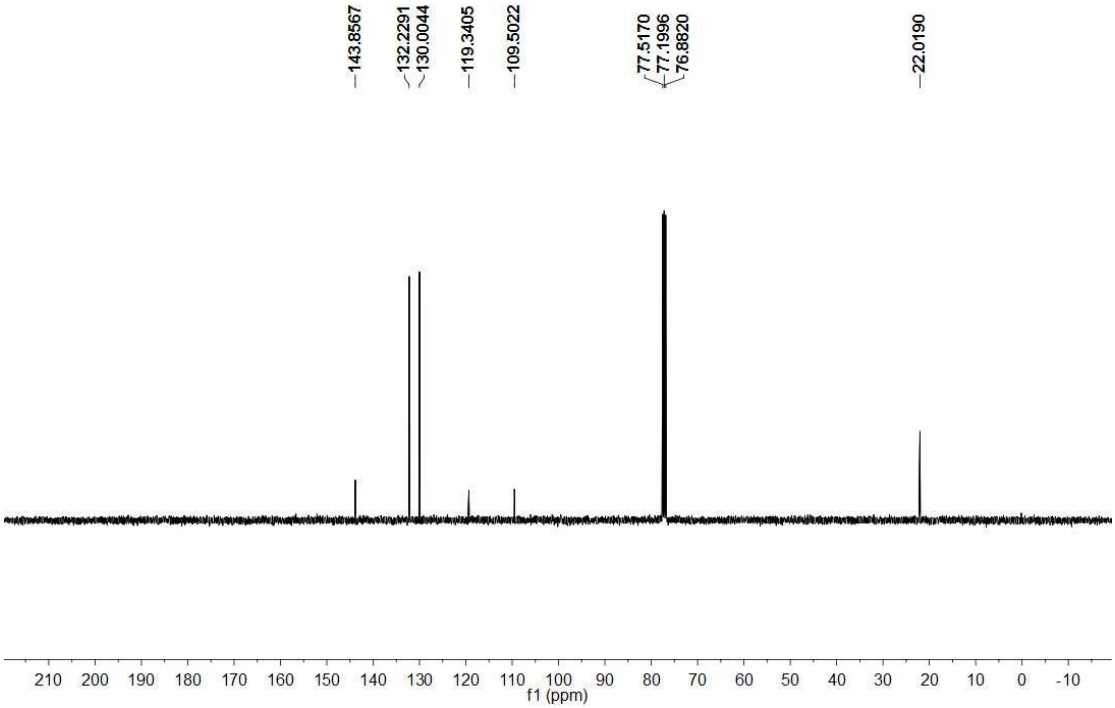
2,4-Dimethoxybenzonitrile (2d)[4]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.6 Hz, 1H), 6.49 (dd, J = 8.6, 2.2 Hz, 1H), 6.44 (d, J = 2.2 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 162.9, 135.0, 117.1, 105.9, 98.5, 94.0, 56.1, 55.8; MS (EI, 70 eV): m/z (%) 163.2 (M^+, 100).



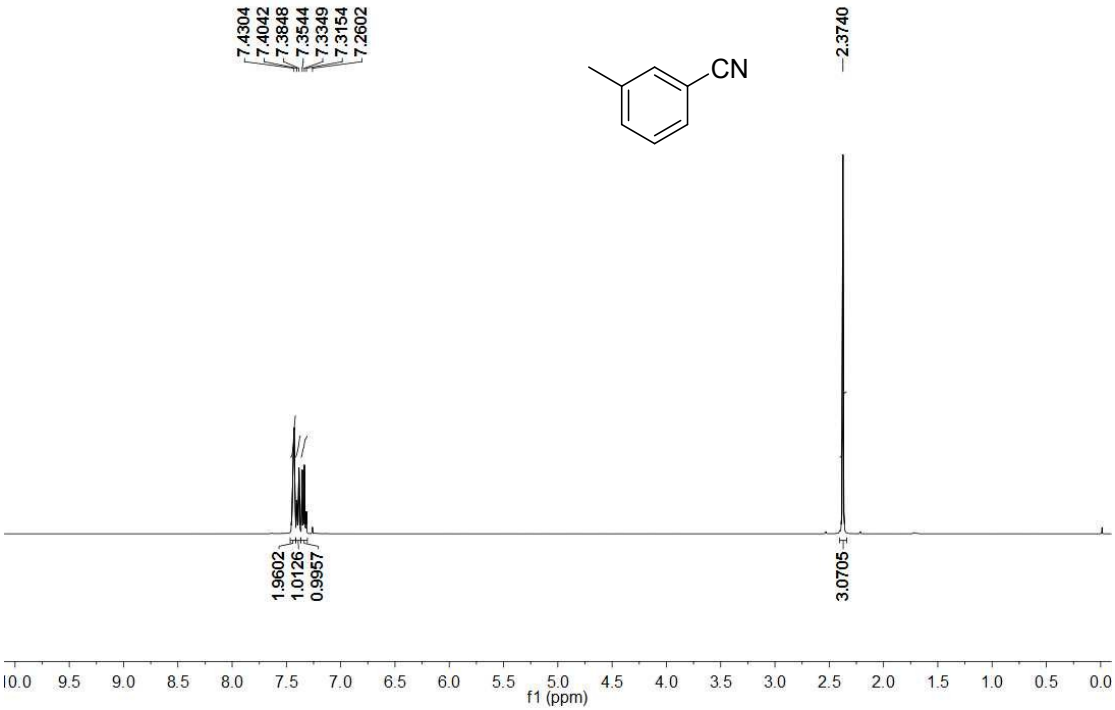


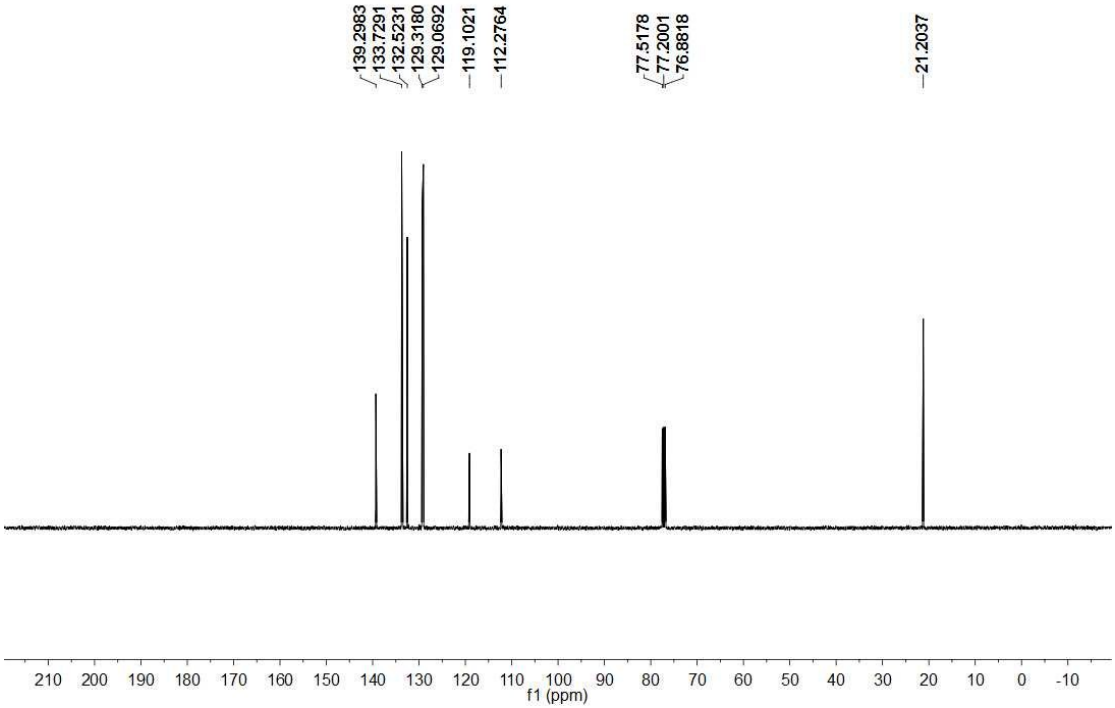
3,4-Dimethylbenzonitrile (2e)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 138.0, 133.0, 130.4, 129.8, 119.5, 109.7, 20.3, 19.7; MS (EI, 70 eV): m/z (%) 131.3 (M^+, 72.2), 116.2(100).



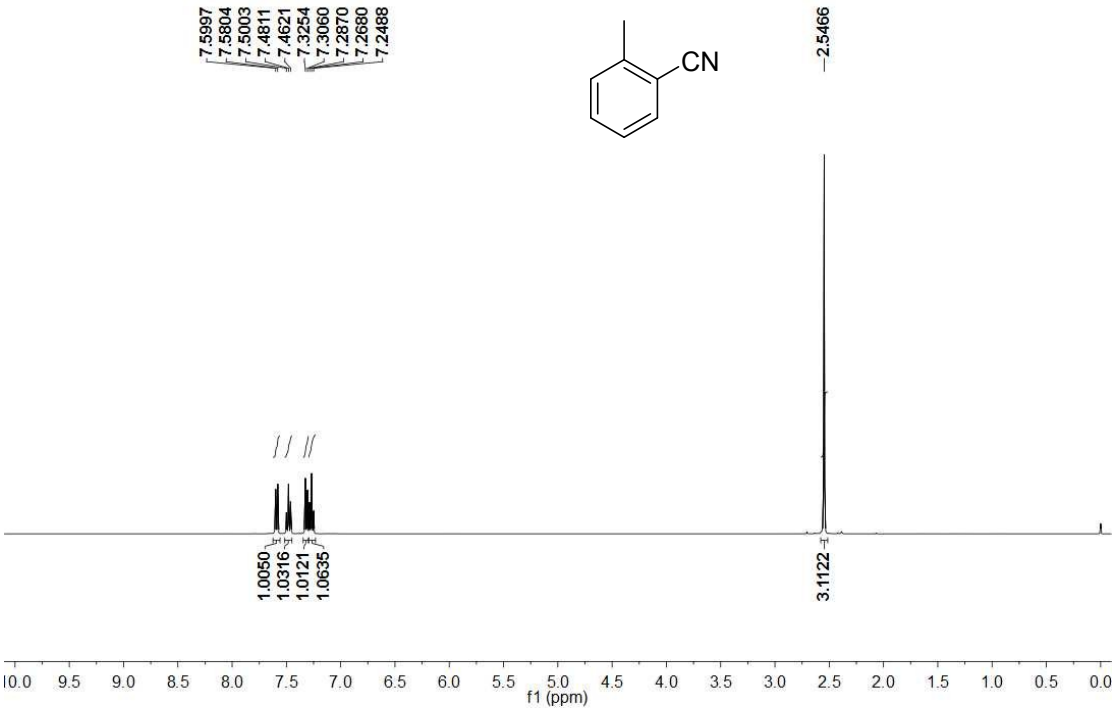


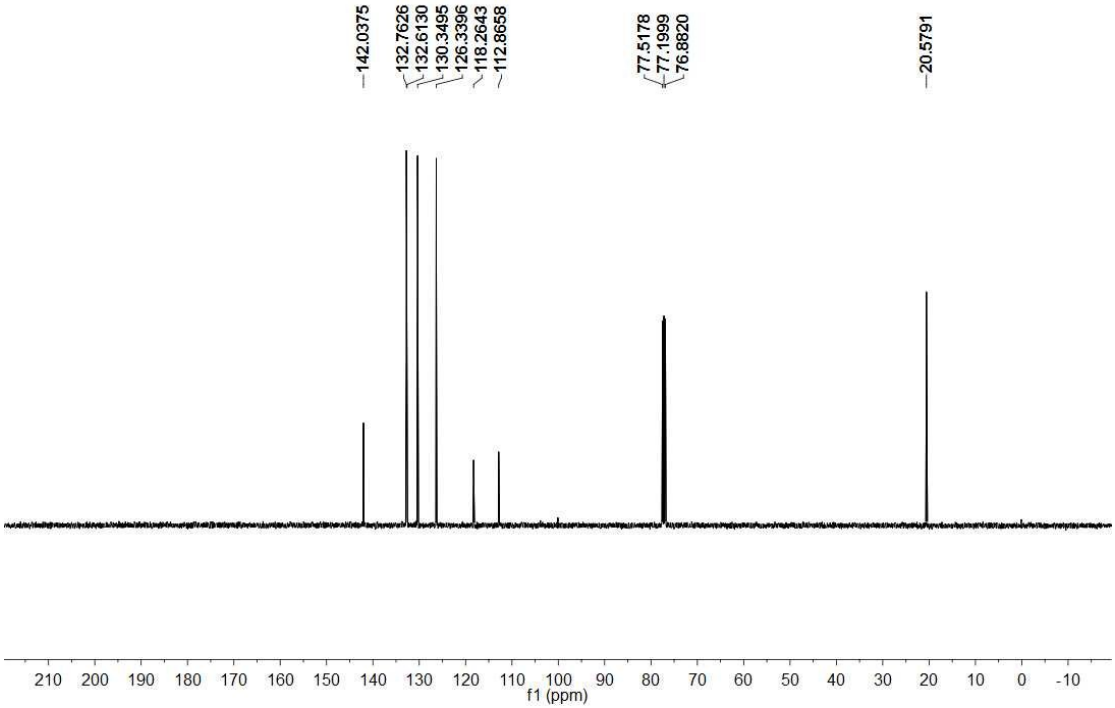
4-Methylbenzonitrile (2f)[3]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 132.2, 130.0, 119.3, 109.5, 22.0; MS (EI, 70 eV): m/z (%) 117.3 (M^+, 100).



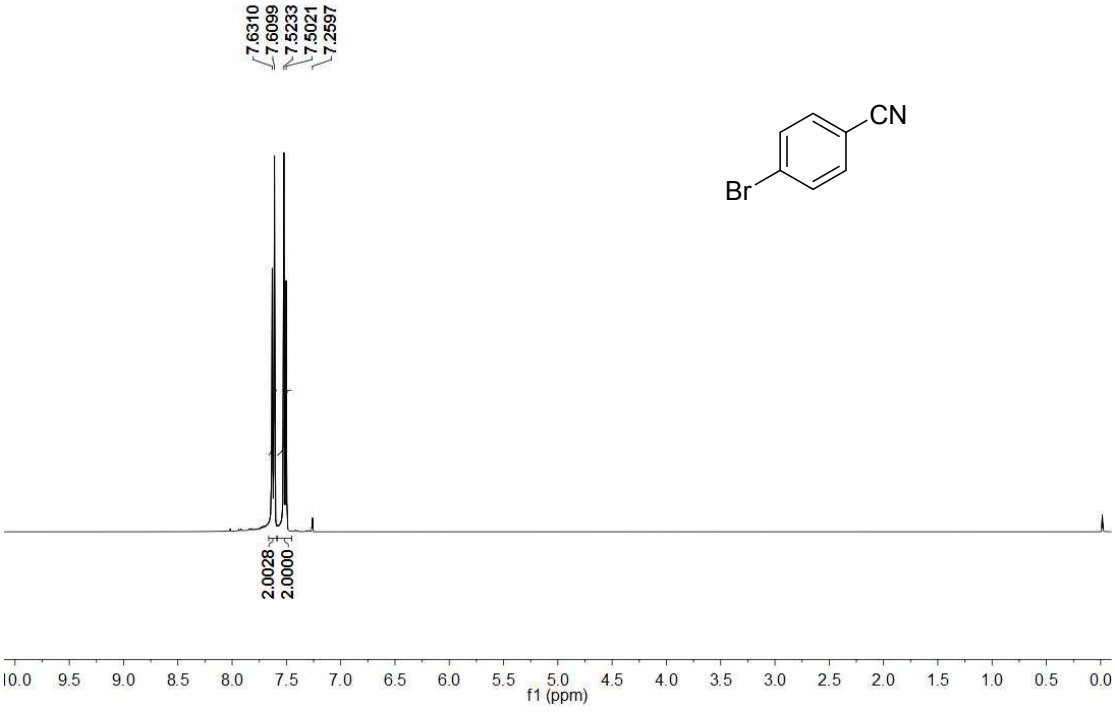


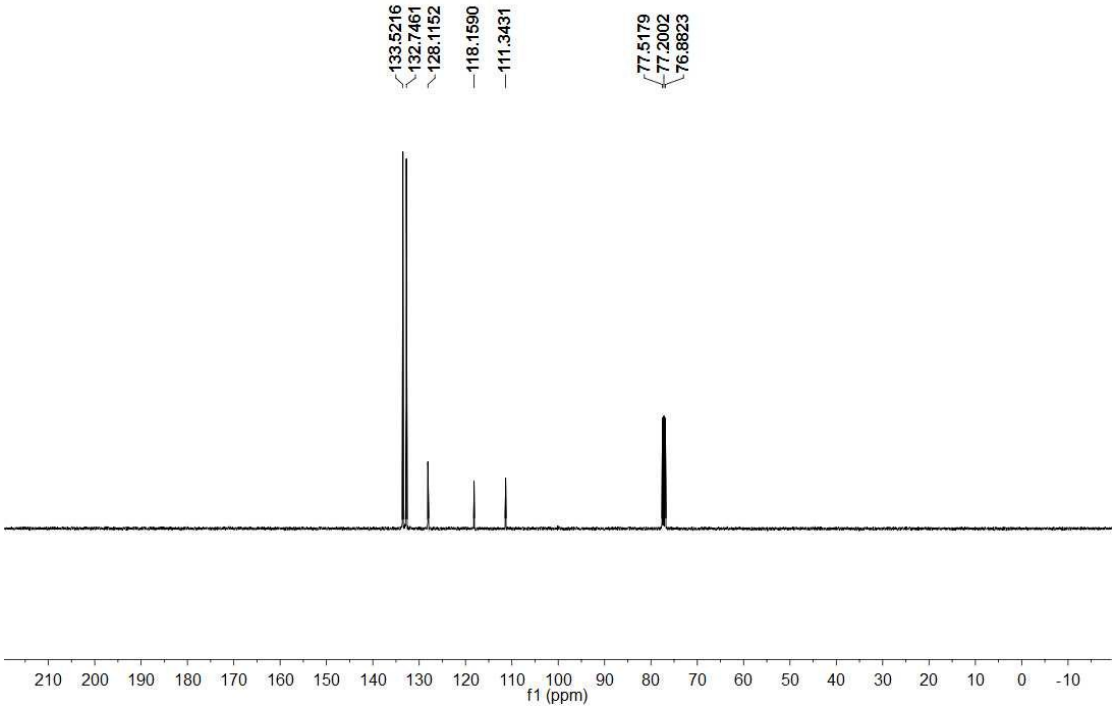
3-Methylbenzonitrile (2g)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 133.7, 132.5, 129.3, 129.1, 119.1, 112.3, 21.2; MS (EI, 70 eV): m/z (%) 117.3 (M^+, 100).



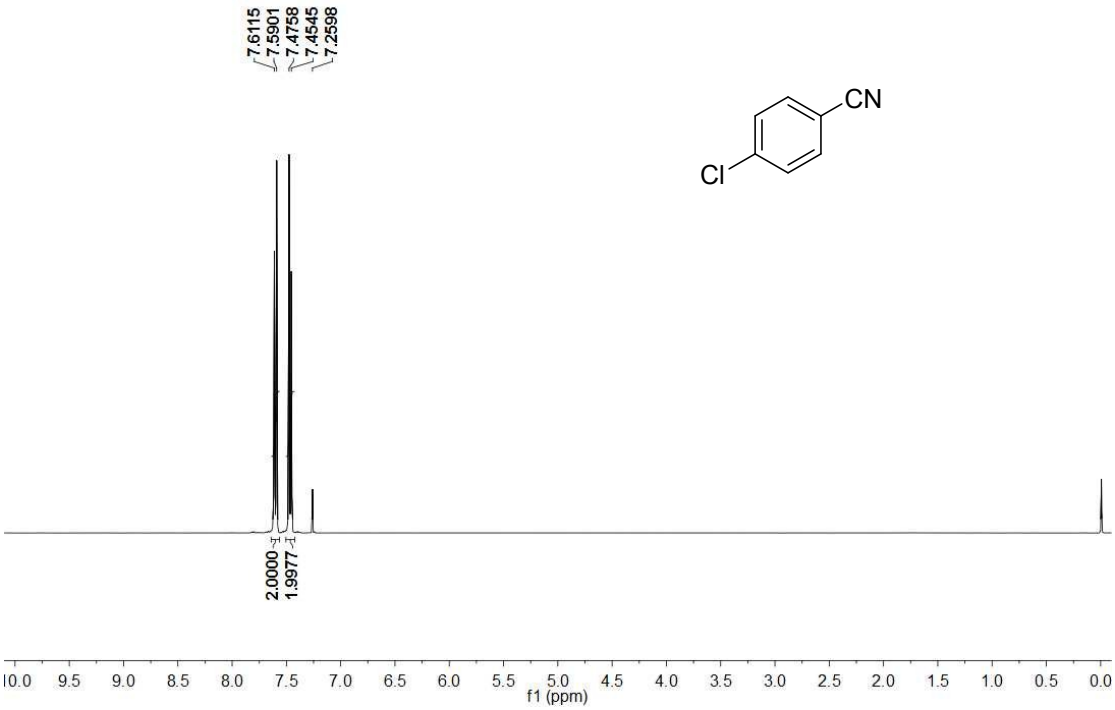


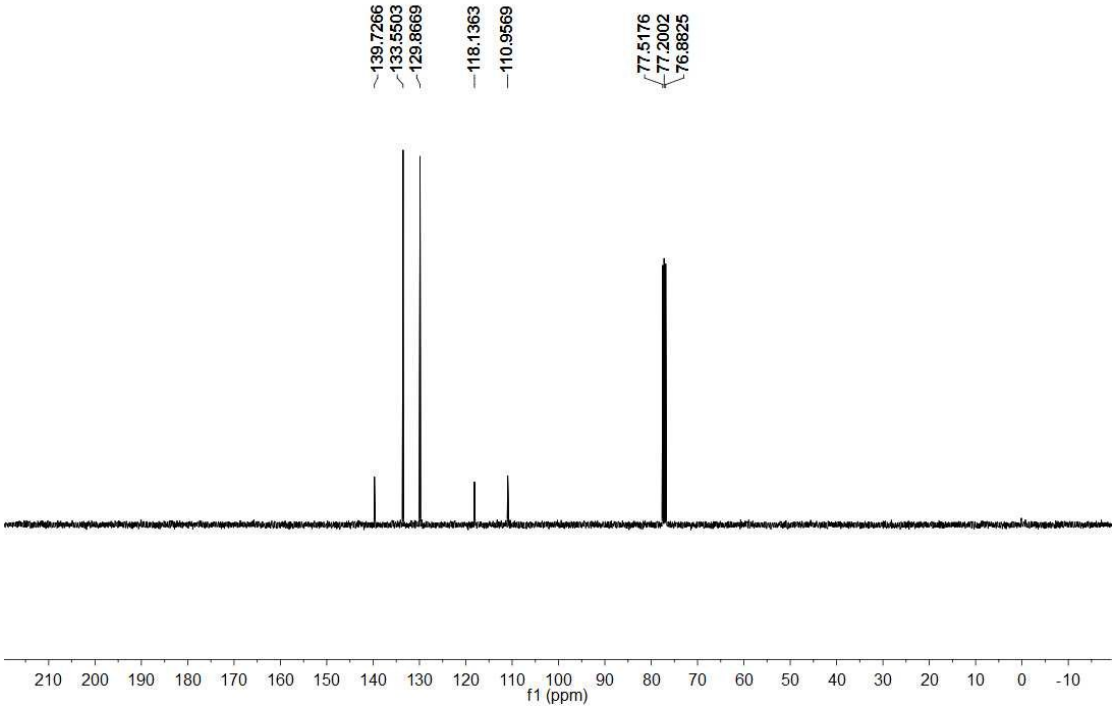
2-Methylbenzonitrile (2h)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 132.8, 132.6, 130.3, 126.3, 118.3, 112.9, 20.6; MS (EI, 70 eV): m/z (%) 117.3 (M^+, 100).



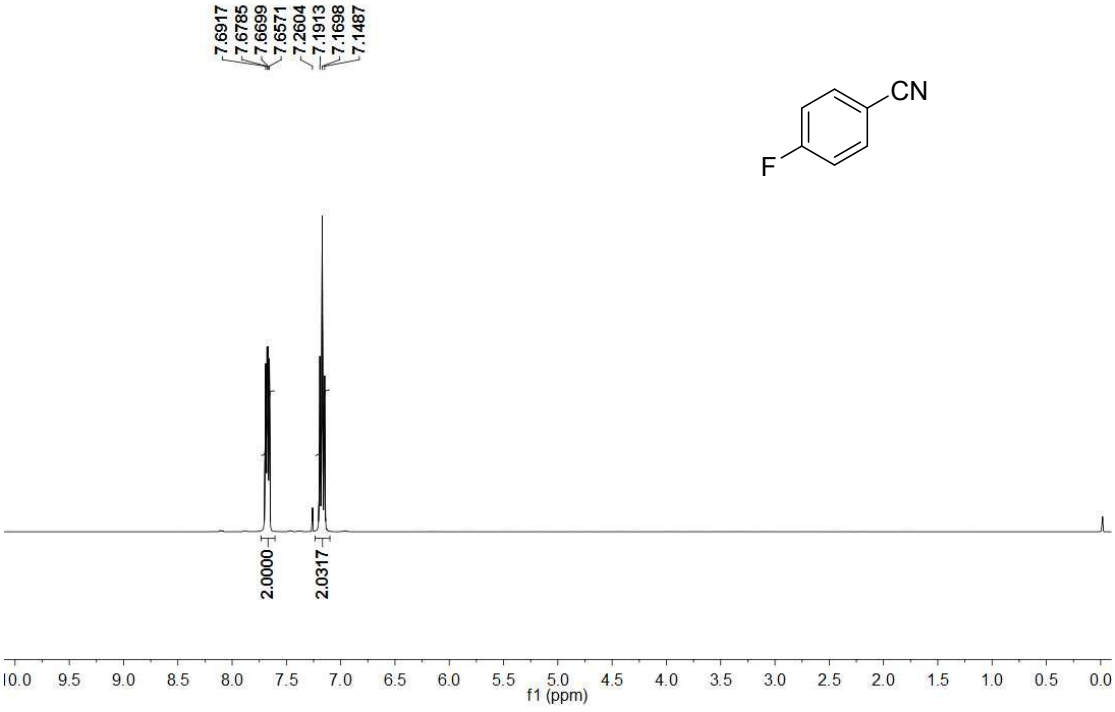


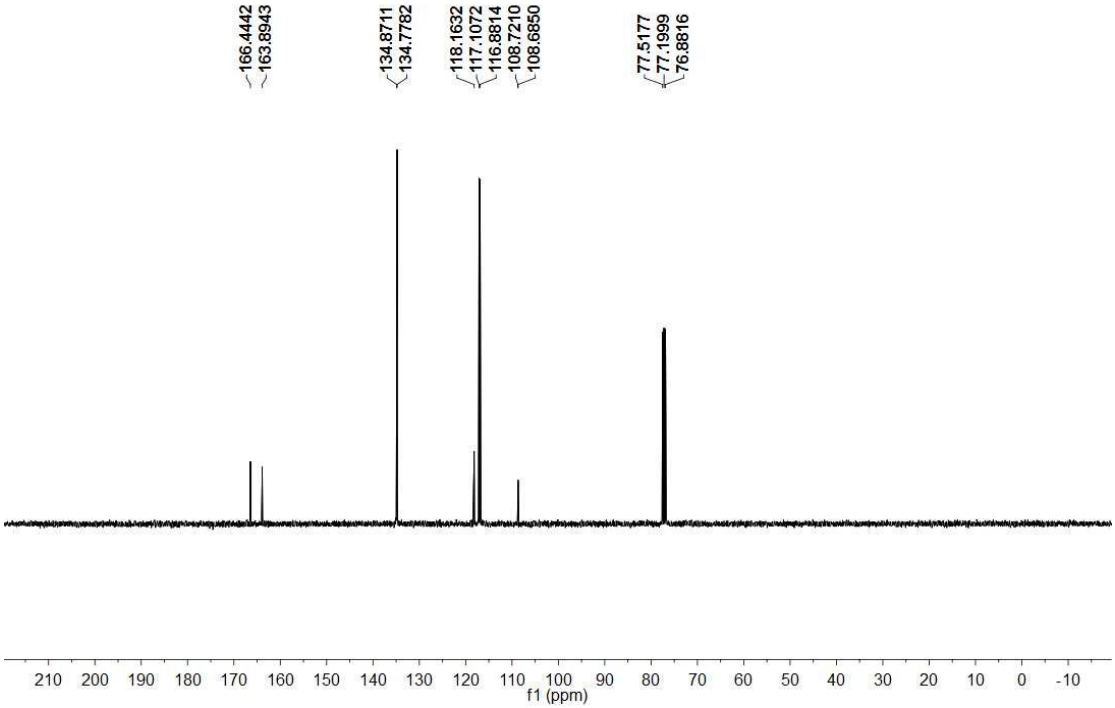
4-Bromobenzonitrile (2i)[3]: ^{1}H NMR (400 MHz, CDCl3) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.5, 132.7, 128.1, 118.2, 111.3; MS (EI, 70 eV): m/z (%) 181.2 (M^+, 100), 102.2(97), 75.2(30), 50.3(11).

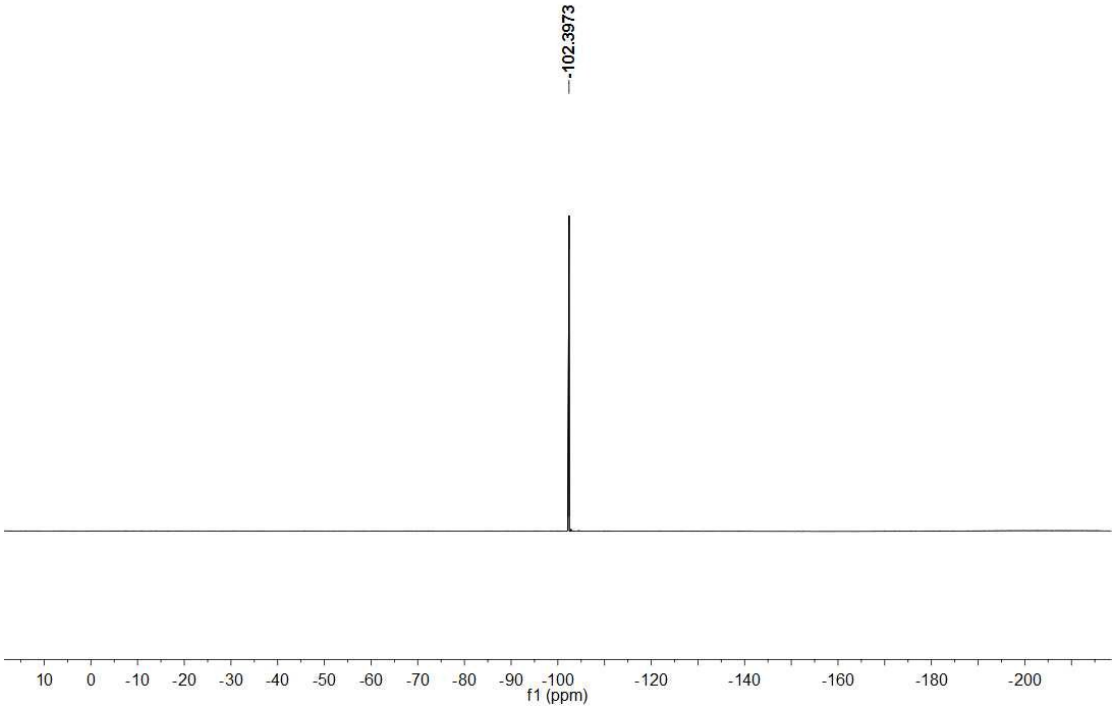




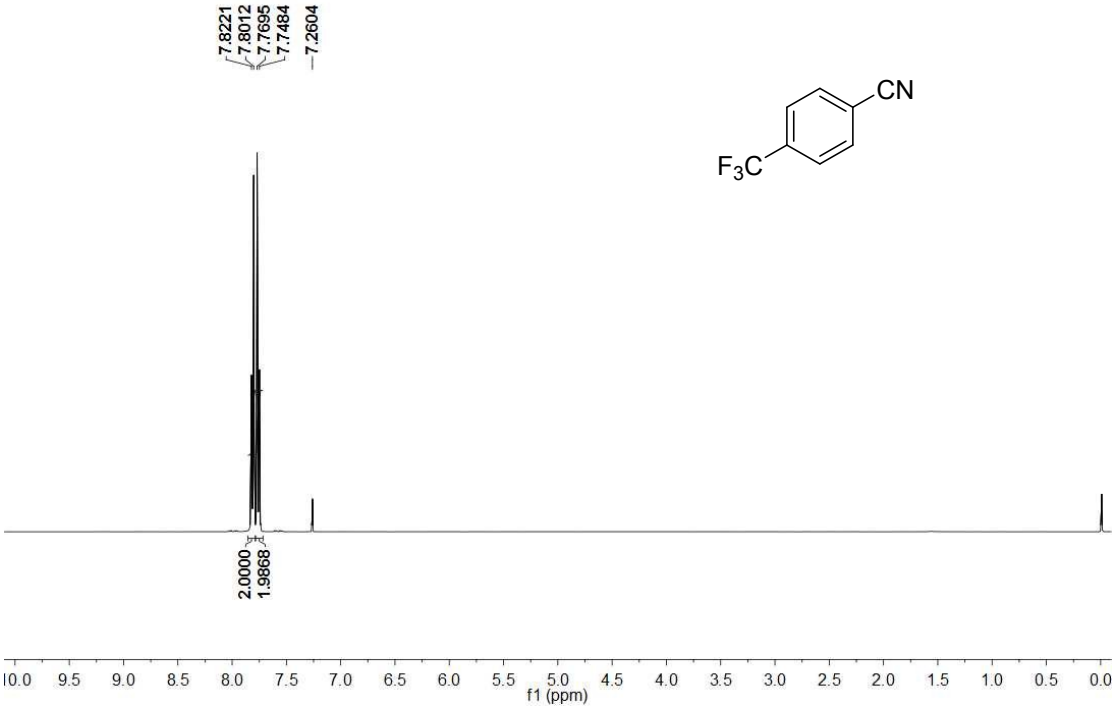
4-Chlorobenzonitrile (2j)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 133.6, 129.9, 118.1, 111.0; MS (EI, 70 eV): m/z (%) 137.2 (M^+, 100).

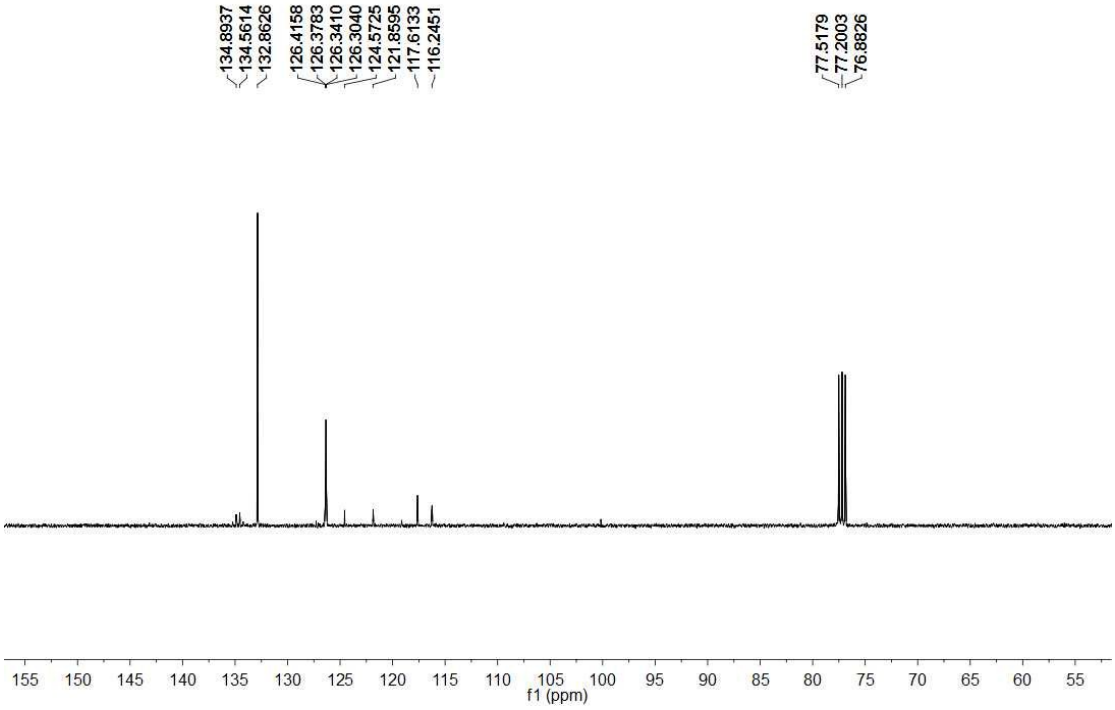


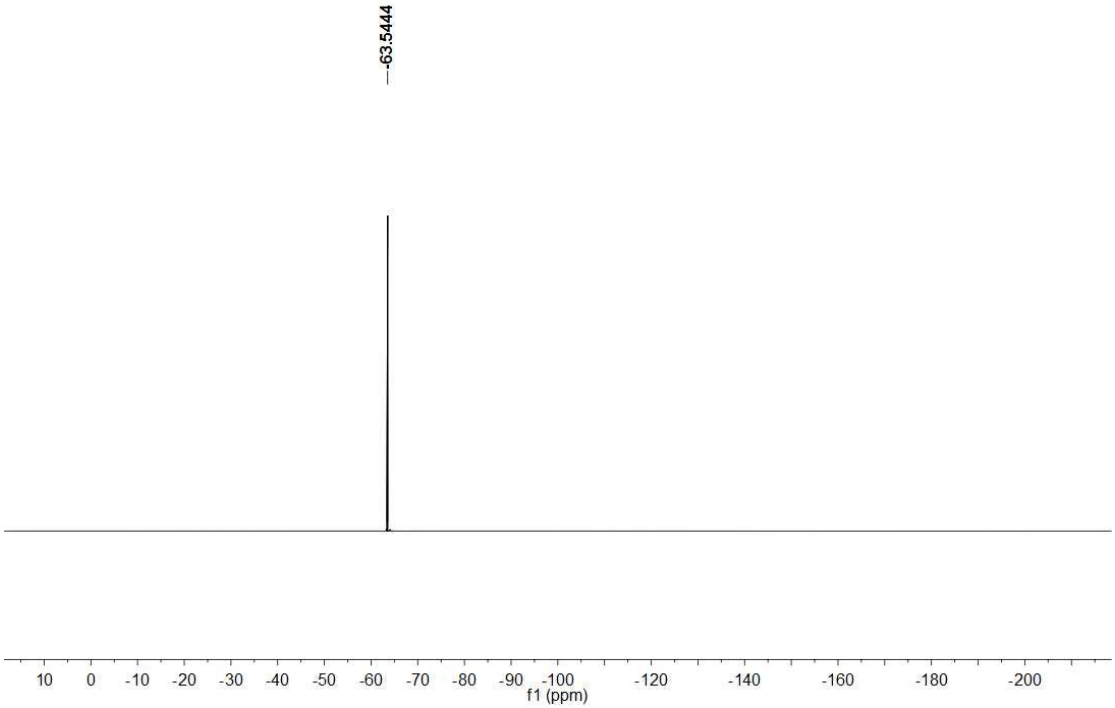




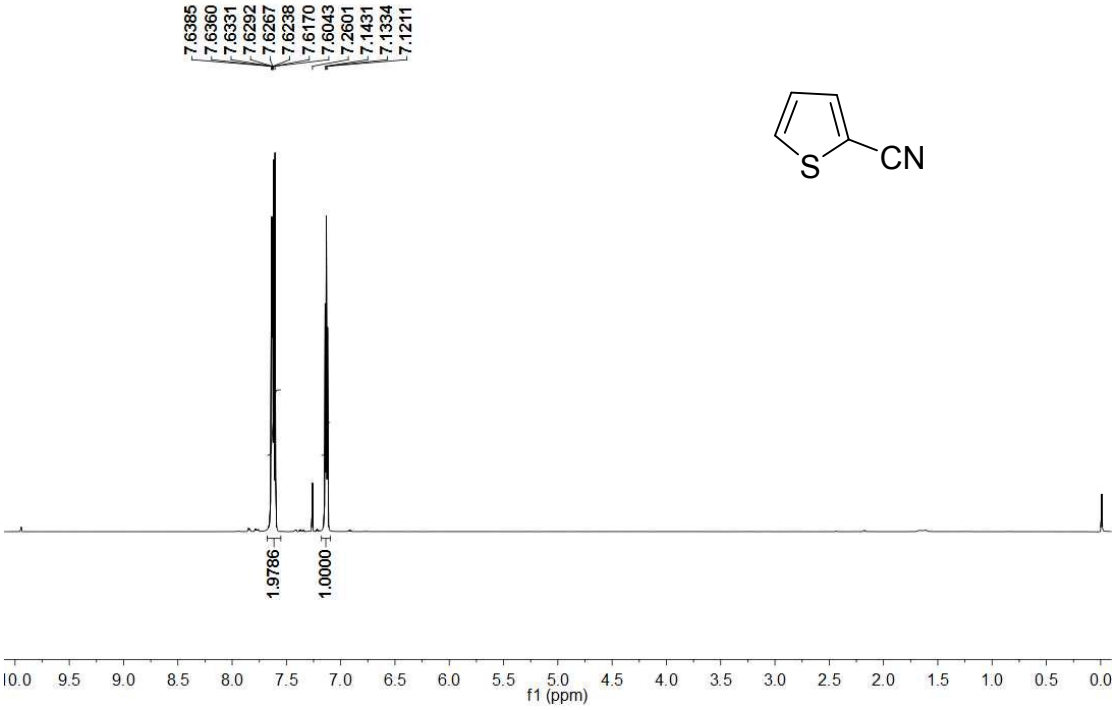
4-Fluorobenzonitrile (2k)[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.6, 5.2 Hz, 2H), 7.17 (t, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (d, $J_{C\text{-}F}$ = 257.5 Hz), 134.8 (d, $J_{C\text{-}F}$ = 9.4 Hz), 118.2, 117.0 (d, $J_{C\text{-}F}$ = 22.8 Hz), 108.7 (d, $J_{C\text{-}F}$ = 3.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.4; MS (EI, 70 eV): m/z (%) 121.2 (M^+, 100).

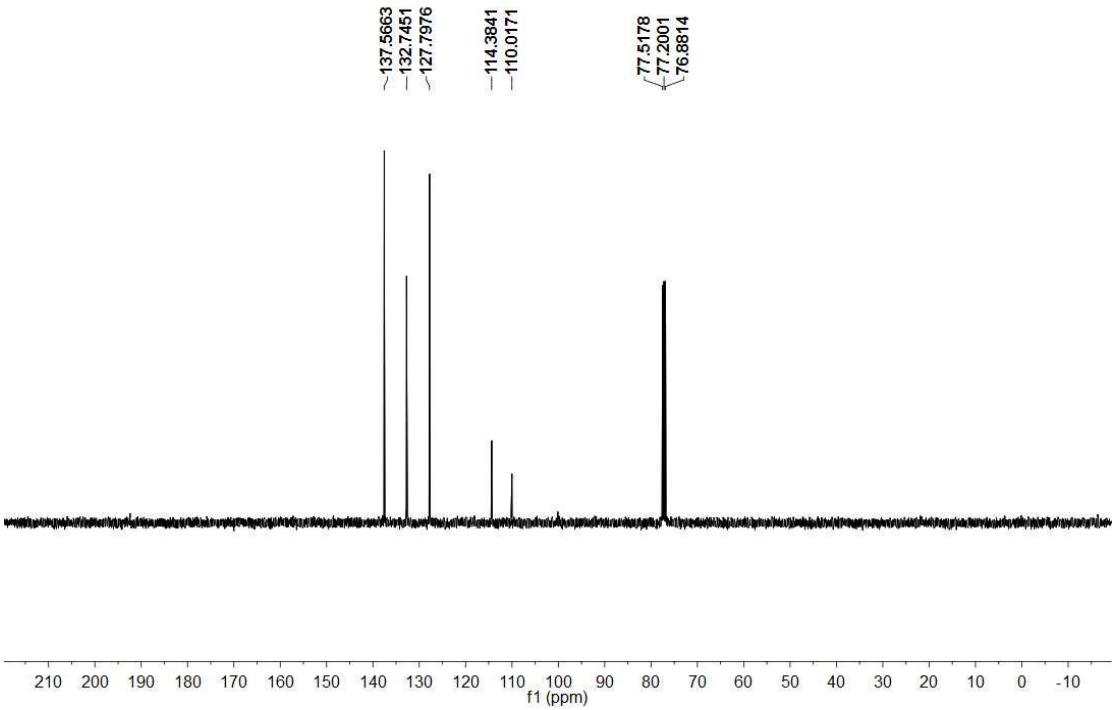

7.8221
7.8012
7.7695
7.7484
7.2604
CN
F3C
2.0000
1.9868
f1 (ppm)


134.8937
134.5614
132.8626
126.4158
126.3783
126.3410
126.3040
124.5725
121.8595
117.6133
116.2451
77.5179
77.2003
76.8826
f1 (ppm)



4-(Trifluoromethyl)benzonitrile (2l)[6]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7 (d, $J_{C\text{-}F}$ = 33.6 Hz), 132.9, 126.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.2 (d, $J_{C\text{-}F}$ = 274.0 Hz), 117.6, 116.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.5; MS (EI, 70 eV): m/z (%) 171.2 (M^+, 100), 121.2(48).





Thiophene-2-carbonitrile(2m)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 2H), 7.14 – 7.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 132.7, 127.8, 114.4, 110.0; MS (EI, 70 eV): m/z (%) 109.3 (M^+, 100).

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