

Supporting Information

An efficient transformation of primary halides into nitriles through palladium-catalyzed hydrogen transfer reaction

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1. General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^1H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer or a Bruker Avance II-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C); CDCl_3 and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was performed on an Agilent Technologies 7820A GC system. The products were separated on a 30 m length by 0.320mm id, HP-5. Nitrogen was employed as the carrier gas with a constant column flow of 0.8 mL/min. The injector temperature was held constant at 250 °C. The GC oven temperature program was as follows: start from 60 °C, ramp 15 °C/min to 300 °C, hold for 5 min. TLC was carried out on SiO_2 (silica gel 60 F₂₅₄, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous KMnO_4 . Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh) or basic Al_2O_3 (Al_2O_3 90, 100-200 mesh).

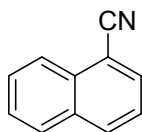
The starting materials **1a–1e**, **1g–1k**, **1n**, **1q–1s**, and **1t** are commercially available. **1f**,^[1] **1l**,^[2] **1m**,^[3] **1o**,^[1] **1p**,^[1] **1u**,^[4] **1v**,^[5] and **1w**^[5] were synthesized according the previous literatures.

2. Representative procedure for synthesis of nitriles from primary halides

1-(Chloromethyl)naphthalene (**1a**, 0.5 mmol, 88.3 mg) and NaN_3 (0.55 mmol, 35.8 mg) were added to a stirred suspension of $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol) and **L6** (XPhos, 9.5 mg, 0.02 mmol) in dry acetone (3.0 mL). The reaction mixture was heated at 80 °C under a N_2 atmosphere, and the reaction progress was monitored through thin-layer chromatography (TLC). The solvent was removed under reduced pressure after the starting material **1a** was consumed (6 h). The residue obtained was purified via column chromatography on basic alumina (eluent: petroleum ether/EtOAc = 20 : 1) to afford 1-naphthonitrile (**2a**) in 72% yield (55.1 mg) as a colorless solid.

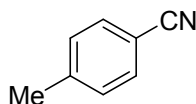
3. Spectral Data of Nitriles

1-Naphthonitrile (**2a**)⁴



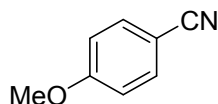
Colorless solid (55.1 mg, 72% yield), mp 36–38 °C (lit.:⁴ 37–38 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.86 (dd, J_1 = 10.2 Hz, J_2 = 4.2 Hz, 2H), 7.67–7.56 (m, 2H), 7.50–7.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 133.2, 132.8, 132.6, 132.3, 128.6, 128.5, 127.5, 125.1, 124.9, 117.8, 110.1.

4-Methylbenzonitrile (**2c**)⁶



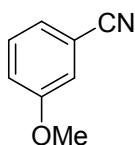
Colorless oil (49.1 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 131.6, 129.5, 118.8, 108.9, 21.5.

4-Methoxybenzonitrile (**2d**)⁶



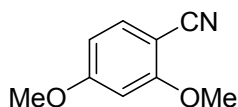
Yellow solid (55.2 mg, 83% yield), mp 60–62 °C (lit.:⁶ 61–62 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 133.7, 119.0, 114.5, 103.5, 55.3.

3-Methoxybenzonitrile (**2e**)⁶



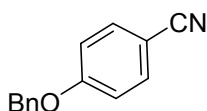
Yellow oil (53.9 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.33 (m, 1H), 7.19–7.17 (m, 1H), 7.12–7.11 (m, 1H), 6.91–6.89 (m, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 142.6, 129.7, 119.7, 112.9, 112.8, 100.0, 55.3.

2,4-Dimethoxybenzonitrile (**2f**)⁷



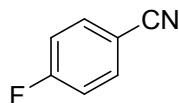
White solid (61.1 mg, 75% yield), mp 94–96 °C (lit.:⁷ 95–96 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 7.09 (d, $J = 2.0$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 149.0, 126.3, 119.1, 113.8, 111.1, 103.7, 56.0, 44.9.

4-(Benzyloxy)benzonitrile (**2g**)⁴



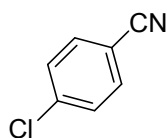
Yellow solid (92.0 mg, 88% yield), mp 86–88 °C (lit.:⁴ 87–88 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, $J = 8.8$ Hz, 2H), 7.40–7.33 (m, 5H), 7.00 (d, $J = 8.8$ Hz, 2H), 5.10 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 135.5, 133.8, 128.6, 127.3, 119.0, 115.4, 104.0, 70.1.

4-Fluorobenzonitrile (**2h**)⁸



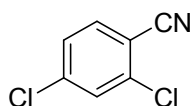
Yellow solid (49.6 mg, 82% yield), mp 35–37 °C (lit.:⁸ 35–36 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.67 (m, 2H), 7.21–7.17 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.9 (d, $^1J_{\text{C-F}} = 254.9$ Hz), 134.6 (d, $^3J_{\text{C-F}} = 9.3$ Hz), 117.9, 116.7 (d, $^2J_{\text{C-F}} = 22.6$ Hz), 108.5 (d, $^4J_{\text{C-F}} = 3.6$ Hz).

4-Chlorobenzonitrile (**2i**)⁶



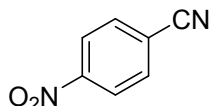
White solid (54.4 mg, 79% yield), mp 93–95 °C (lit.:⁶ 93–94 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.60 (m, 2H), 7.48–7.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 139.2, 133.2, 129.4, 117.7, 110.5.

2,4-dichlorobenzonitrile (**2j**)⁴



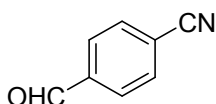
White solid (51.6 mg, 60% yield), mp 61–63 °C (lit.:⁴ 61–62 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.0, 137.7, 134.5, 130.2, 127.8, 115.2, 111.8.

4-Nitrobenzonitrile (**2k**)⁶



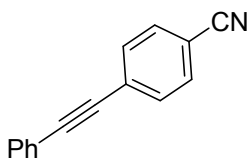
Yellow solid (48.1 mg, 65% yield), mp 148–150 °C (lit.:⁶ 148–149 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 150.0, 133.4, 124.2, 118.2, 116.7.

4-Formylbenzonitrile (**2l**)⁸



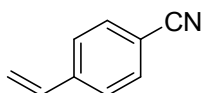
White solid (24.9 mg, 38% yield), mp 98–100 °C (lit.:⁸ 99–100 °C). ¹H NMR (400 MHz, CDCl₃) δ 10.14 (s, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 190.6, 138.5, 132.6, 129.6, 117.5, 117.2, 125.1.

4-(Phenylethynyl)benzonitrile (**2m**)⁹



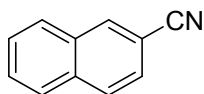
White solid (83.2 mg, 82% yield), mp 107–109 °C (lit.:⁹ 106–108 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.61–7.53 (m, 6H), 7.38–7.36 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 131.93, 131.91, 131.2, 129.0, 128.4, 128.1, 122.1, 118.4, 111.3, 93.7, 87.6.

4-Vinylbenzonitrile (**2n**)¹⁰



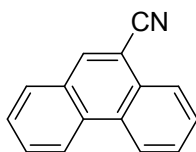
Black oil (45.2 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.61–7.59 (m, 2H), 7.49–7.47 (m, 2H), 6.72 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.87 (d, J = 17.6 Hz, 1H), 5.45 (d, J = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 135.1, 132.3, 126.6, 118.8, 117.6, 111.0.

2-Naphthonitrile (**2o**)⁸



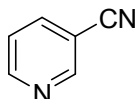
Yellow solid (58.1 mg, 76% yield), mp 65–67 °C (lit.:⁸ 66–67 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.90–7.86 (m, 3H), 7.65–7.57 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 134.6, 134.1, 132.1, 129.1, 129.0, 128.3, 128.0, 127.6, 126.3, 119.2, 109.3.

Phenanthrene-9-carbonitrile (**2p**)⁸



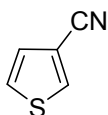
Yellow solid (79.2 mg, 78% yield), mp 110–112 °C (lit.:⁸ 111–112 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.56–8.52 (m, 2H), 8.20–8.18 (m, 1H), 8.07 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.73–7.58 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 131.4, 129.6, 129.6, 129.4, 129.2, 128.5, 127.9, 127.8, 127.4, 125.7, 122.8, 122.5, 117.7, 109.0.

Nicotinonitrile (**2q**)⁸



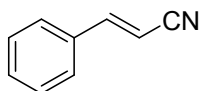
Yellow solid (36.4 mg, 70% yield), mp 50–52 °C (lit.:⁸ 51–52 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.91–8.90 (m, 1H), 8.84 (dd, J_1 = 5.2 Hz, J_2 = 2.0 Hz, 1H), 8.01–7.98 (m, 1H), 7.48–7.45 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.9, 152.4, 139.2, 123.6, 116.4, 110.1.

Thiophene-3-carbonitrile (**2r**)⁸



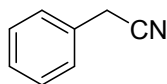
Yellow oil (39.2 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 2.8 Hz, 1H), 7.45–7.43 (m, 1H), 7.31 (d, J = 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 128.6, 127.2, 115.1, 110.6.

Cinnamonitrile (**2s**)¹¹



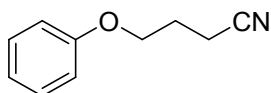
Colorless oil (45.2 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.44–7.36 (m, 6H), 5.87 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 133.4, 131.1, 129.0, 127.3, 118.1, 96.2.

2-Phenylacetonitrile (**2t**)⁵



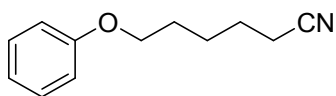
Colorless oil (49.7 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.21 (m, 5H), 3.57 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 129.7, 128.5, 127.3, 127.3, 117.7, 22.7.

4-Phenoxybutanenitrile (**2u**)¹²



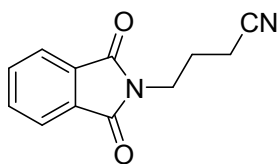
White solid (70.8 mg, 88% yield), mp 45–47 °C (lit.:¹² 45–46 °C). ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.25 (m, 2H), 6.97–6.93 (m, 1H), 6.89–6.87 (m, 2H), 4.01 (t, J = 5.6 Hz, 2H), 2.52 (d, J = 6.8 Hz, 2H), 2.10–2.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 129.4, 121.0, 119.1, 114.3, 65.0, 25.2, 13.9.

6-Phenoxyhexanenitrile (**2v**)¹³



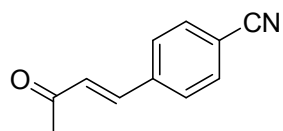
Colorless oil (80.3 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.29–7.25 (m, 2H), 6.95–6.91 (m, 1H), 6.89–6.86 (m, 2H), 3.94 (d, J = 6.2 Hz, 2H), 2.33 (d, J = 6.8 Hz, 2H), 1.81–1.59 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 129.3, 120.5, 119.5, 114.3, 67.0, 28.3, 25.2, 25.0, 16.9.

4-(1,3-Dioxisoindolin-2-yl)butanenitrile (**2w**)¹²



Yellow solid (72.8 mg, 68% yield), mp 147–149 °C (lit.:¹² 147–148 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.85–7.83 (m, 2H), 7.75–7.73 (m, 2H), 3.82 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.12–2.03 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 133.9, 131.6, 123.1, 118.7, 36.4, 24.5, 14.8.

(*E*)-4-(3-oxobut-1-enyl)benzonitrile (**4**)¹⁴



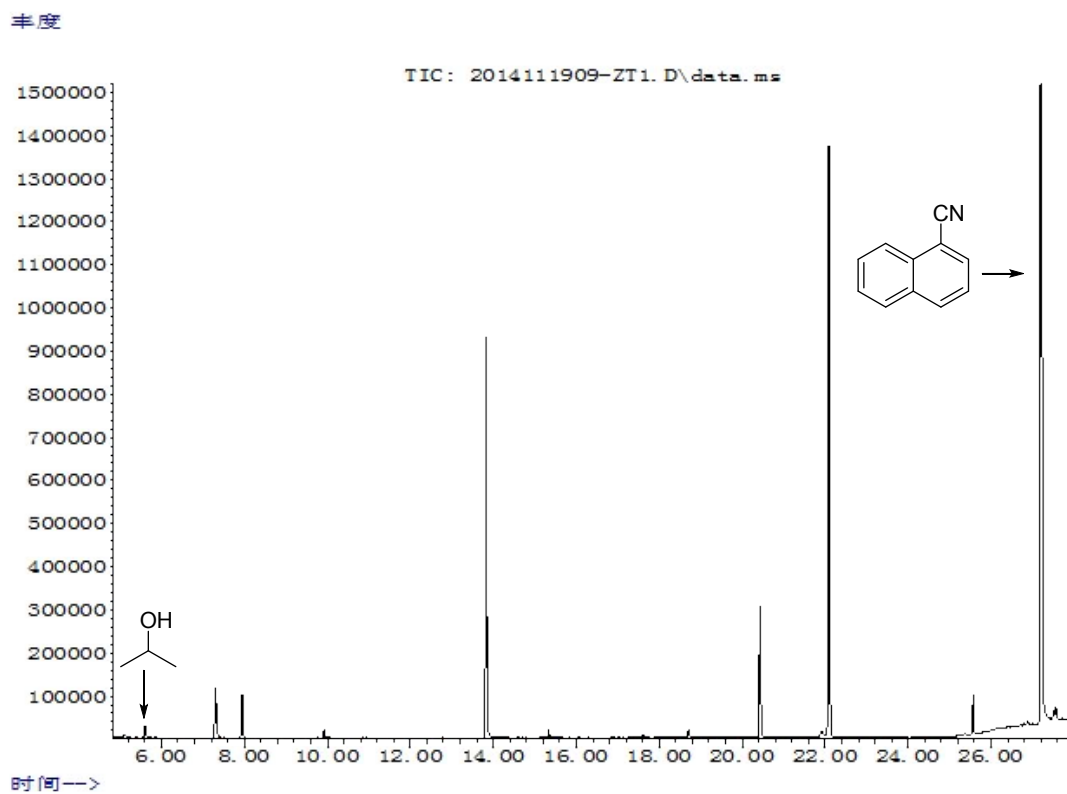
White solid (17.1 mg, 20% yield), mp 102–104 °C (lit.:¹⁴ 102–103 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.69 (m, 2H), 7.65–7.62 (m, 2H), 7.49 (d, *J* = 16.4 Hz, 1H), 6.78 (d, *J* = 16.4 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 140.6, 138.8, 132.7, 129.8, 128.5, 118.3, 113.6, 28.0.

4. References

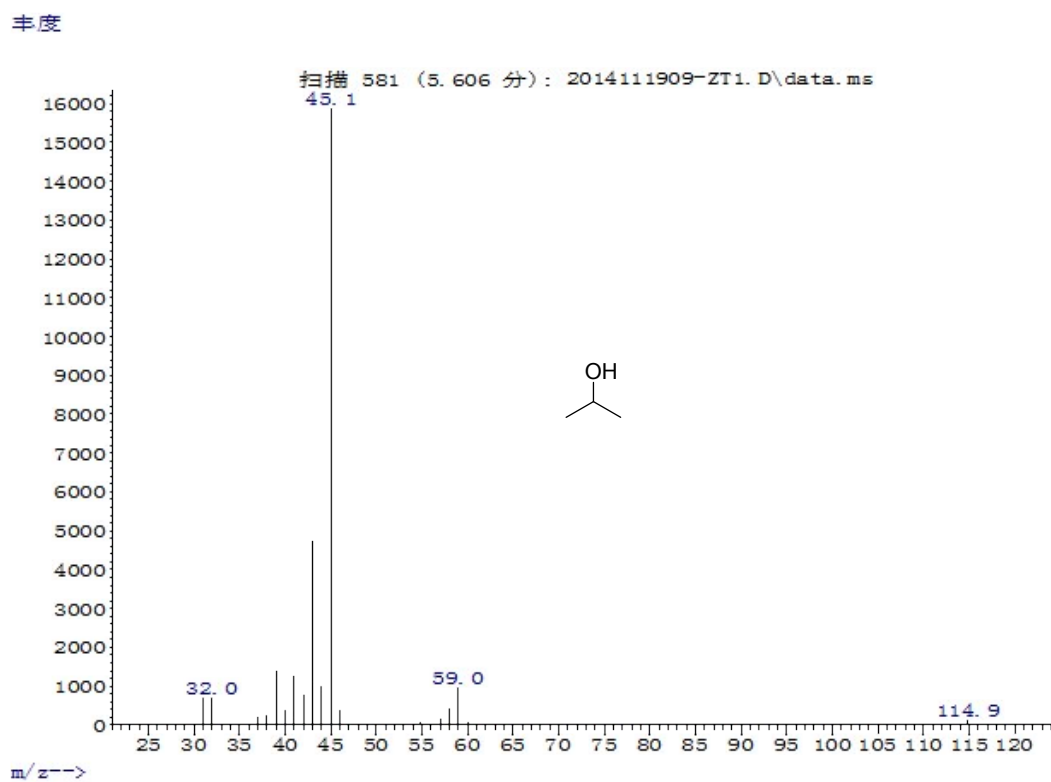
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7. GC-MS spectra of reaction mixture

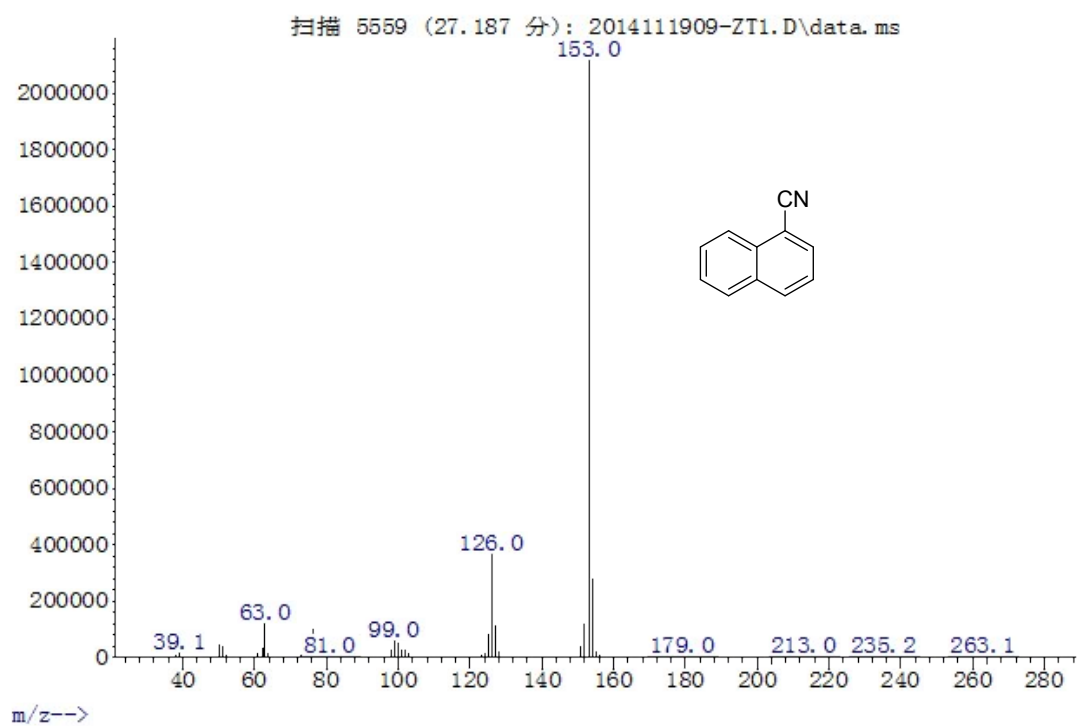
(1) GC spectrum



(2) MS spectra



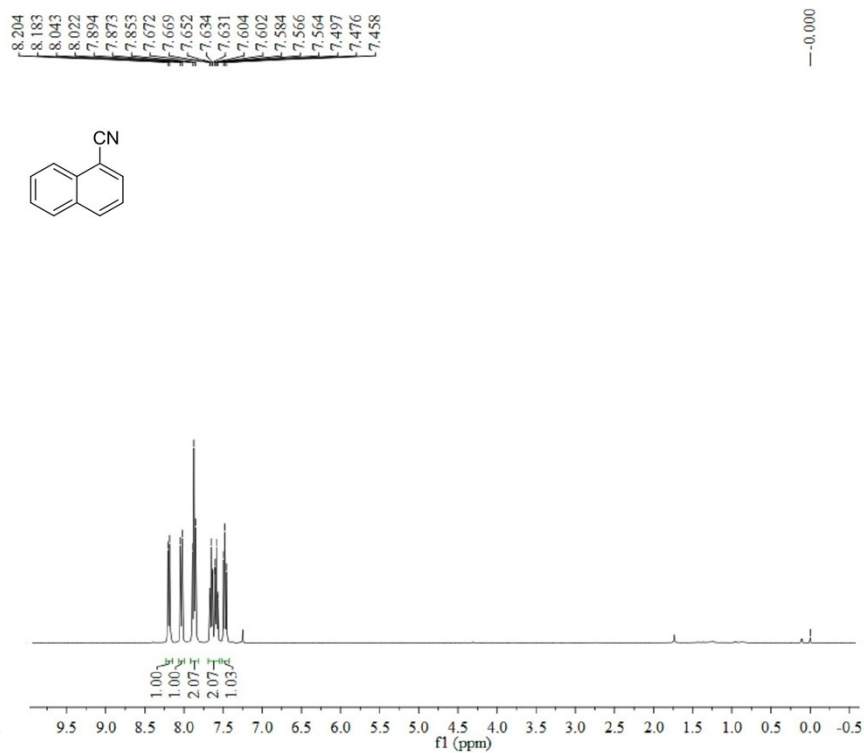
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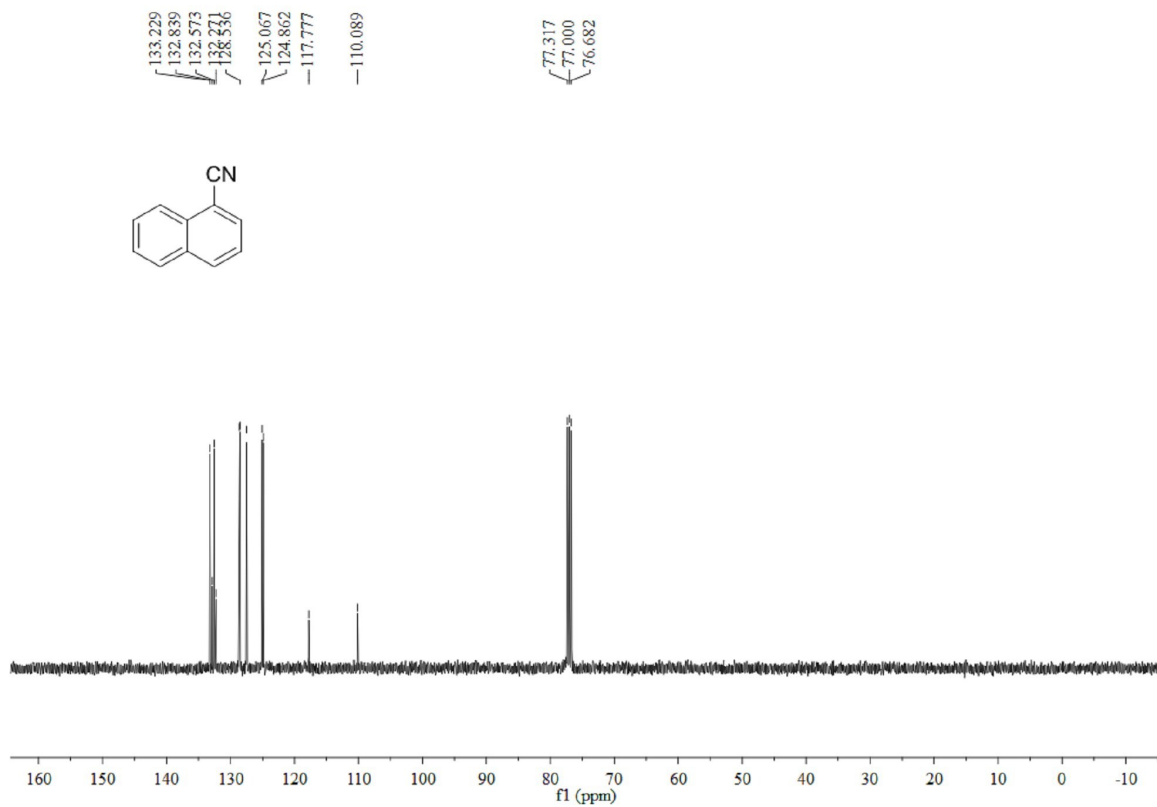
8. Copies of ^1H and ^{13}C NMR spectra of products

1-Naphthonitrile (**2a**)

^1H NMR, 400 MHz, CDCl_3



^{13}C NMR, 100 MHz, CDCl_3

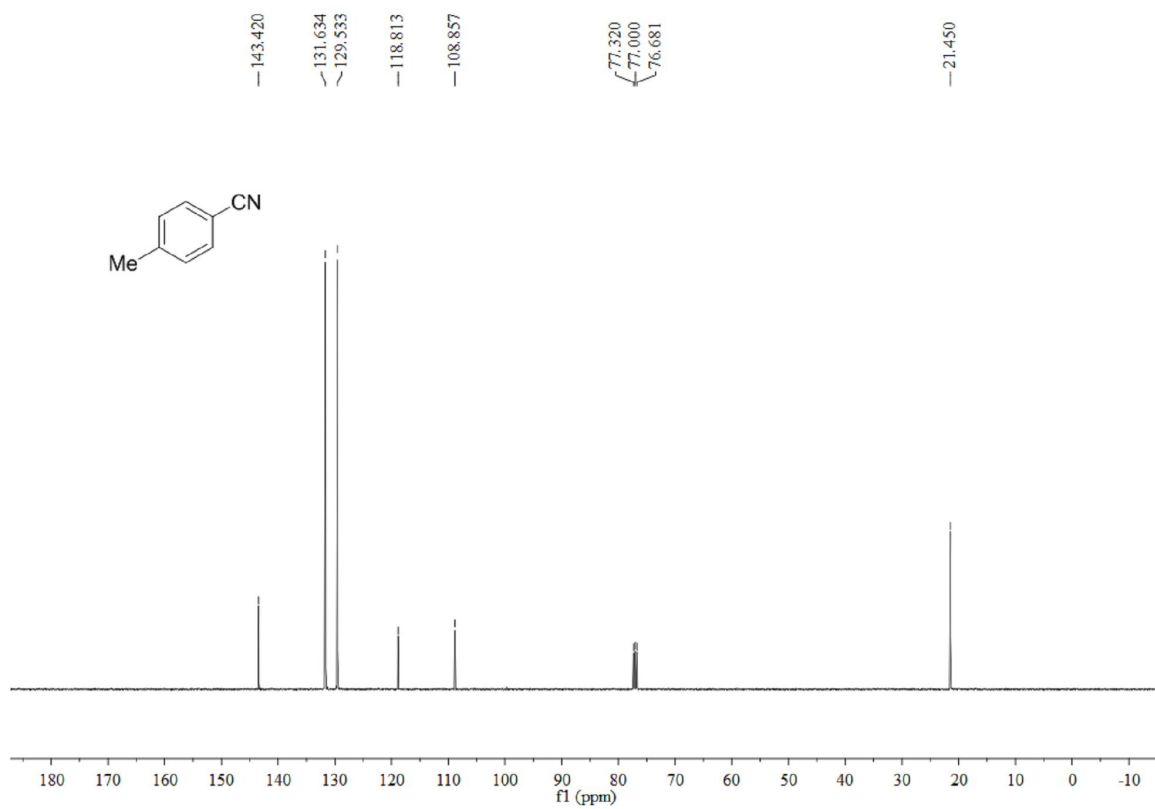


4-Methylbenzonitrile (**2c**)

^1H NMR, 400 MHz, CDCl_3

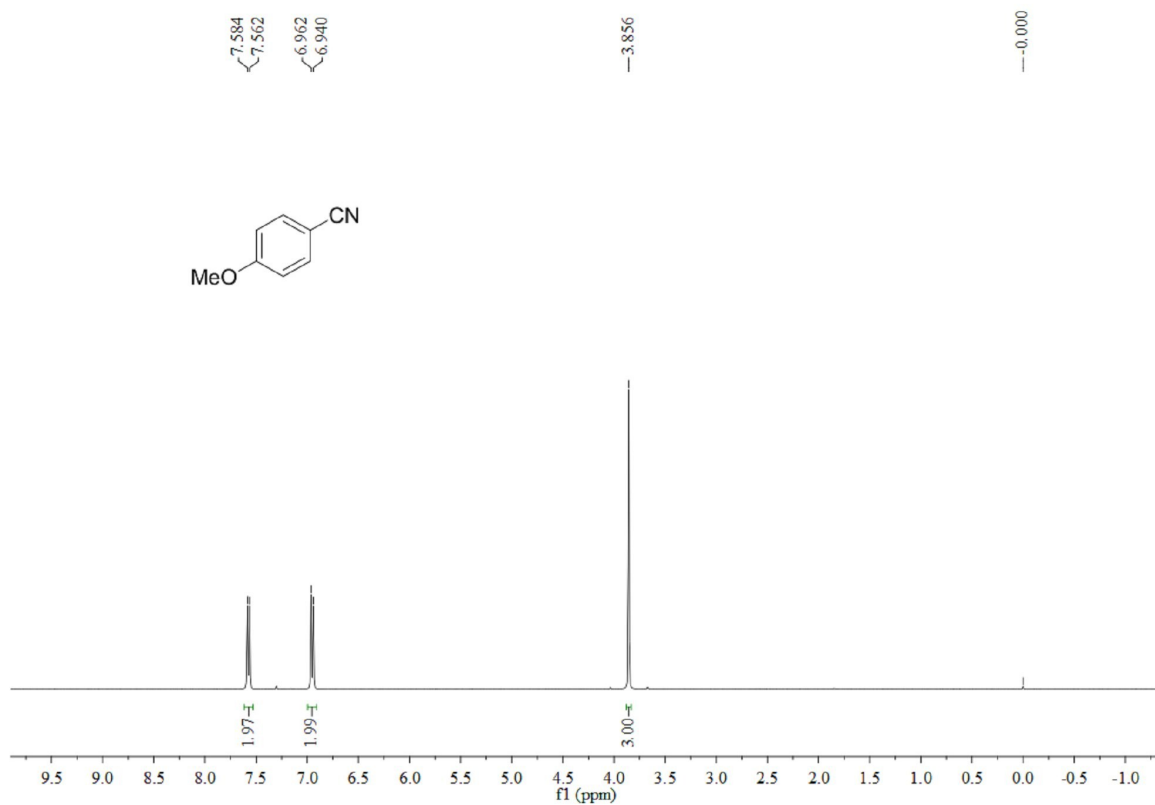


^{13}C NMR, 100 MHz, CDCl_3

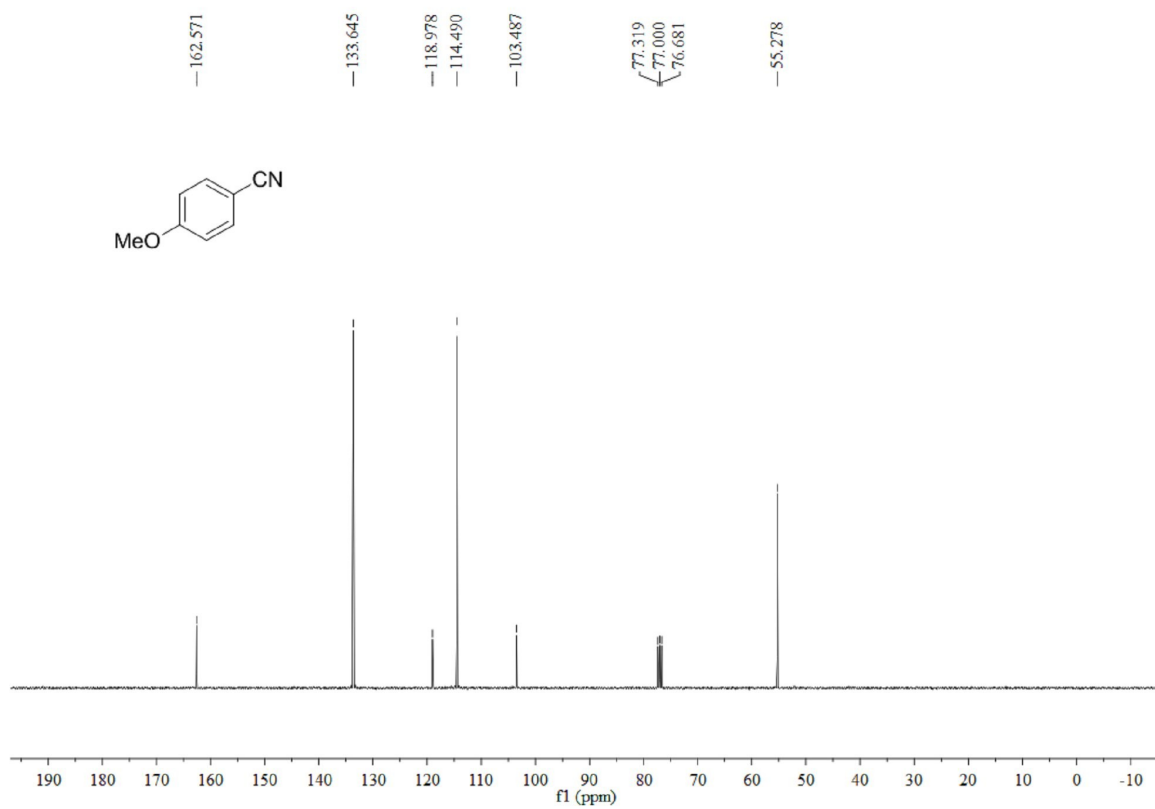


4-Methoxybenzonitrile (**2d**)

^1H NMR, 400 MHz, CDCl_3

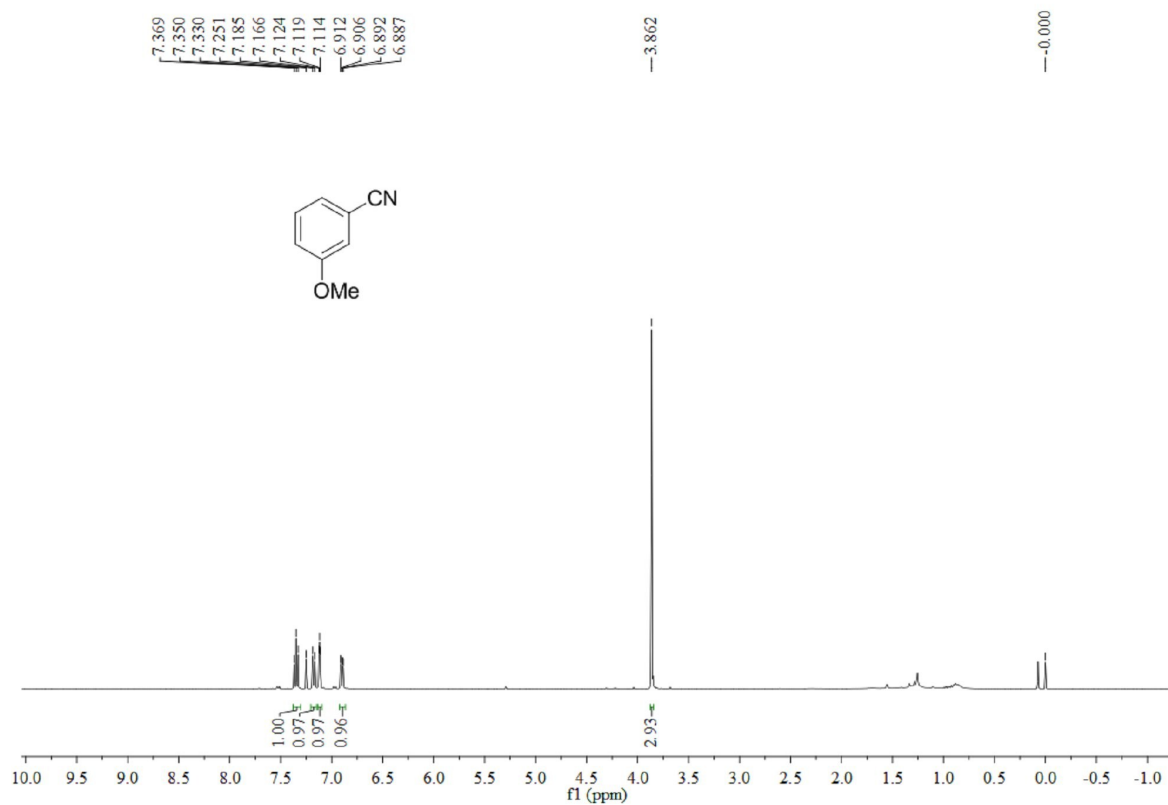


^{13}C NMR, 100 MHz, CDCl_3

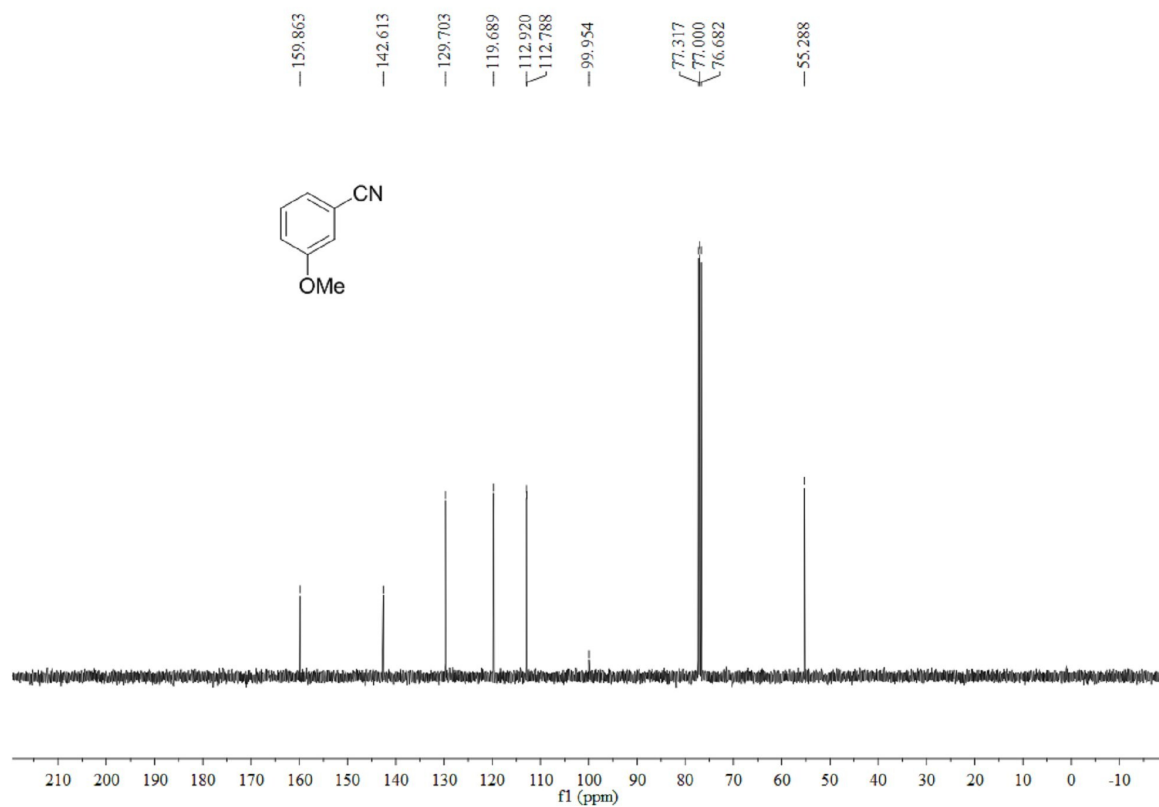


3-Methoxybenzonitrile (**2e**)

^1H NMR, 400 MHz, CDCl_3

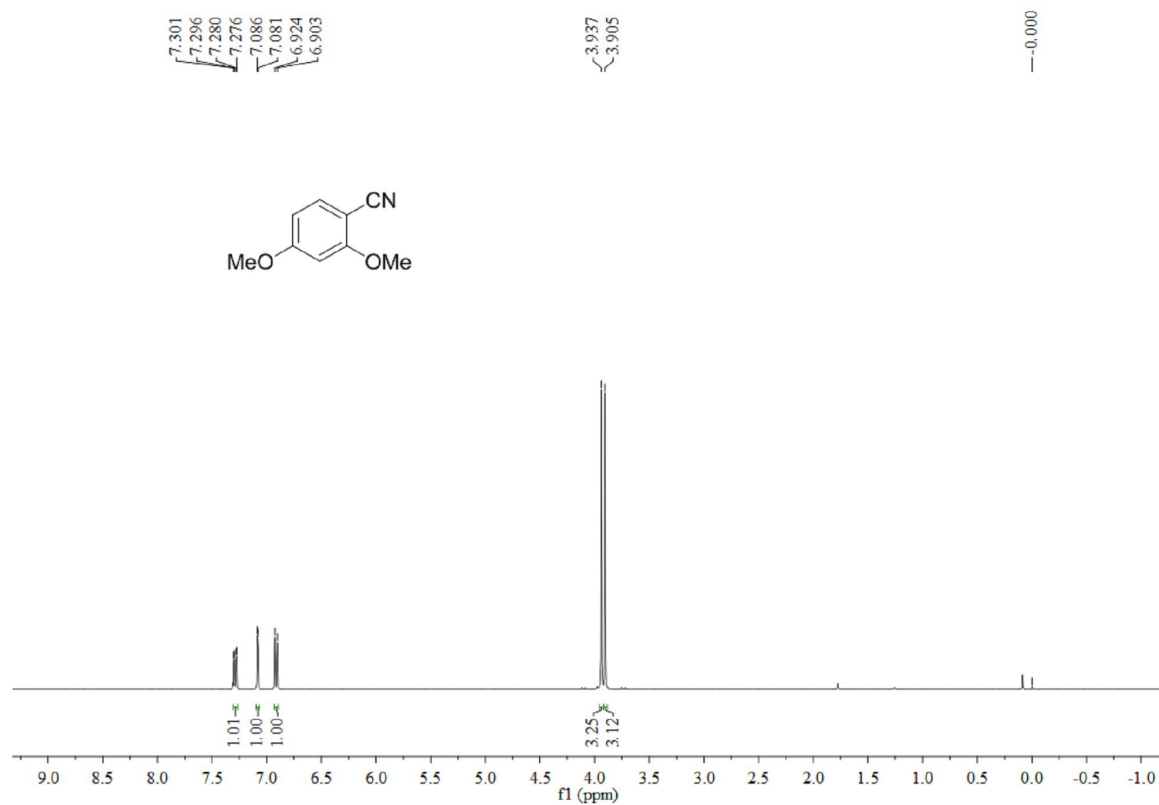


^{13}C NMR, 100 MHz, CDCl_3

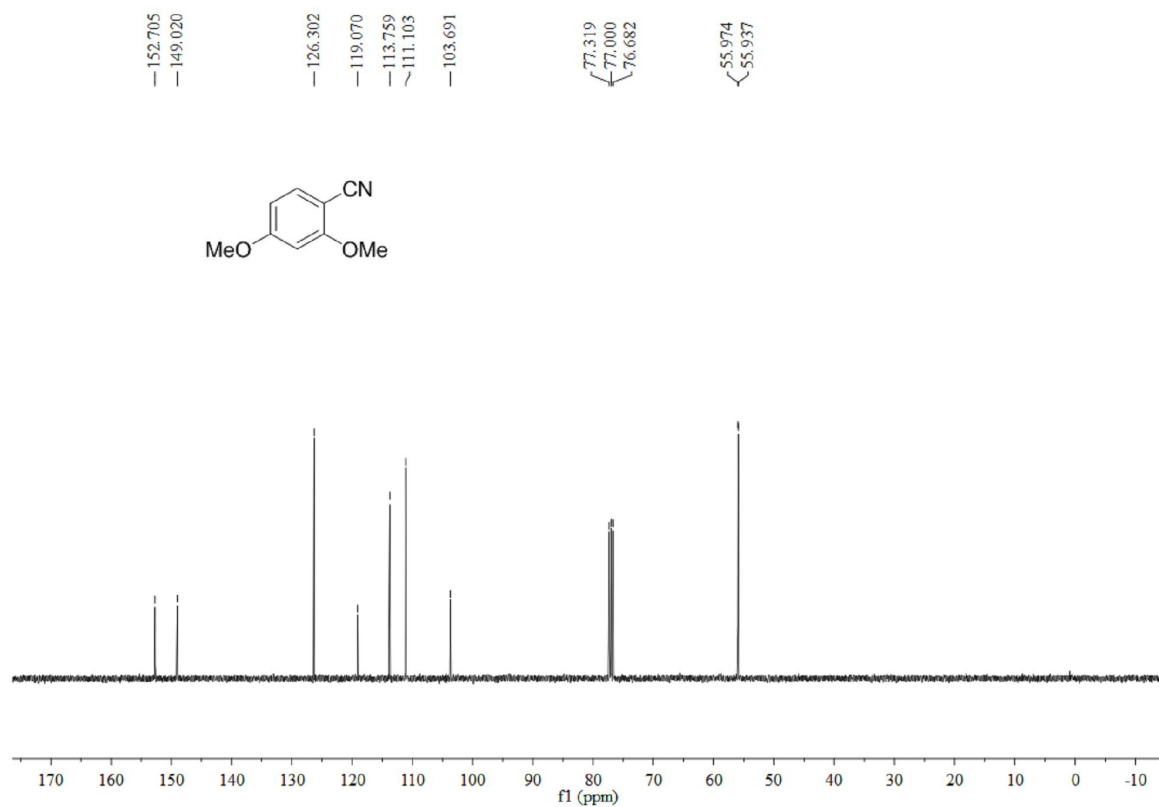


2,4-Dimethoxybenzonitrile (**2f**)

^1H NMR, 400 MHz, CDCl_3

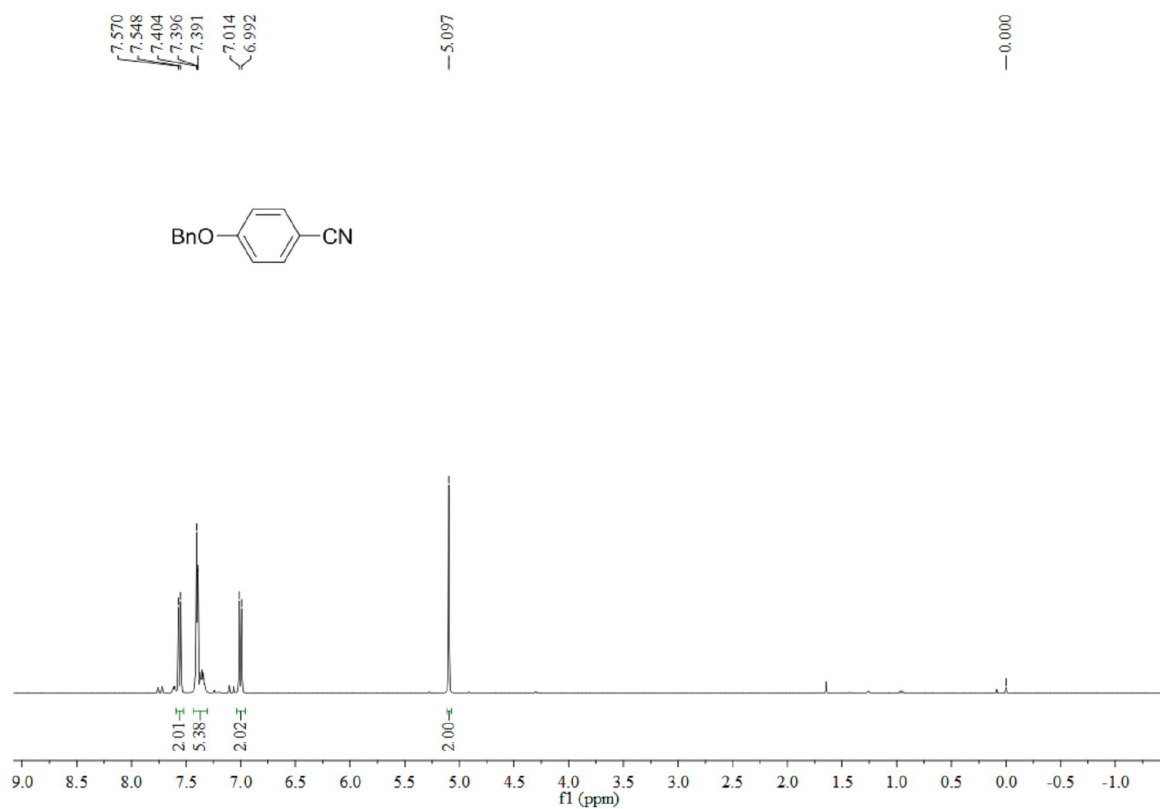


^{13}C NMR, 100 MHz, CDCl_3

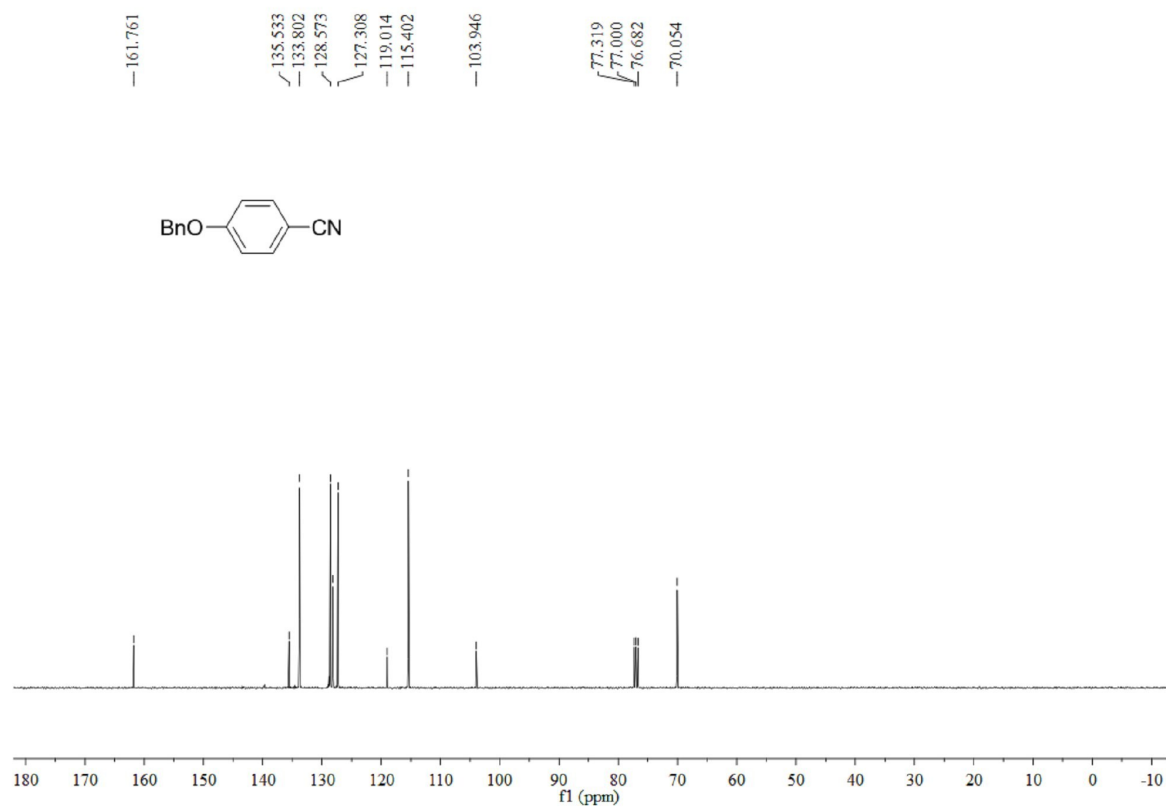


4-(Benzyloxy)benzonitrile (**2g**)

^1H NMR, 400 MHz, CDCl_3

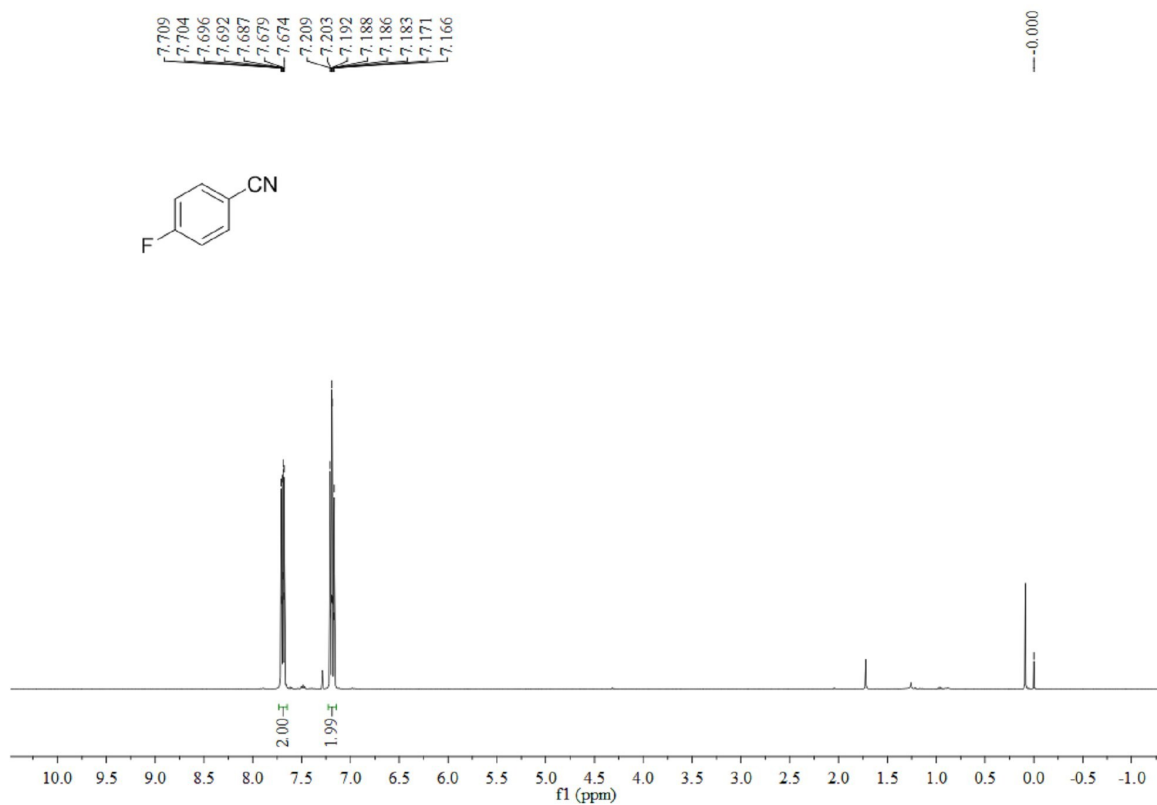


^{13}C NMR, 100 MHz, CDCl_3

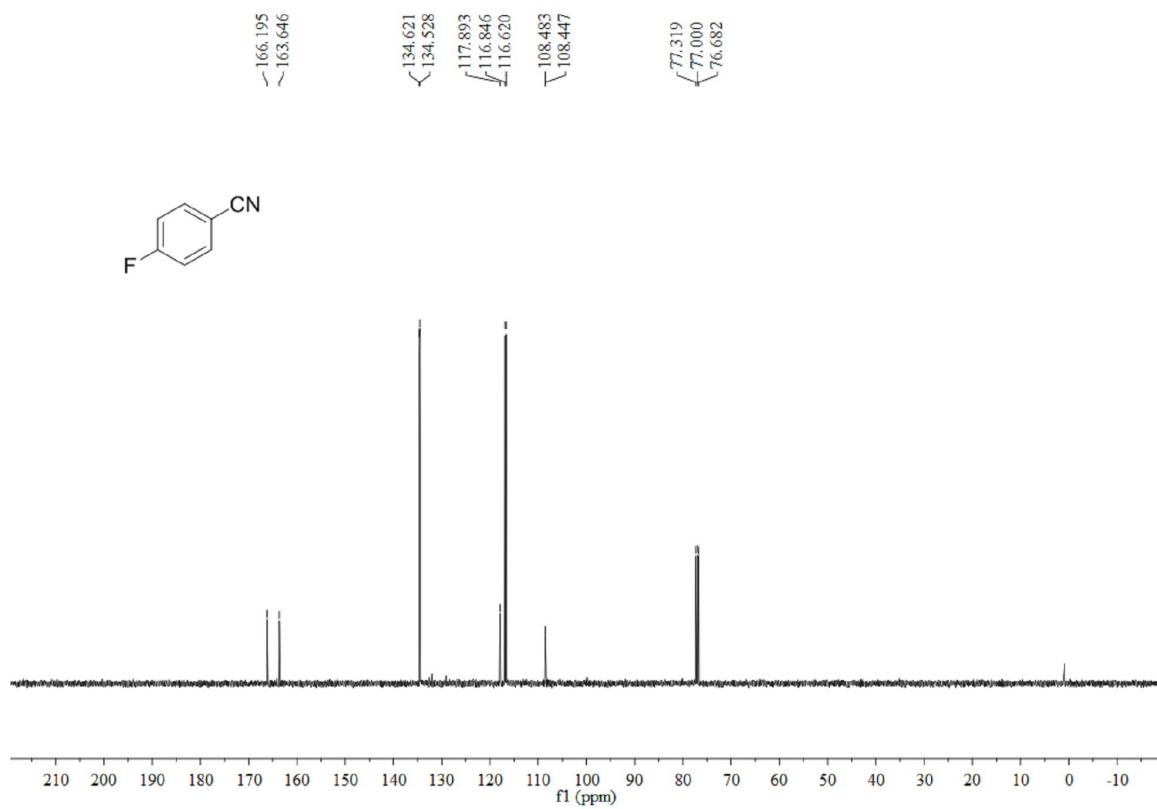


4-Fluorobenzonitrile (**2h**)

^1H NMR, 400 MHz, CDCl_3

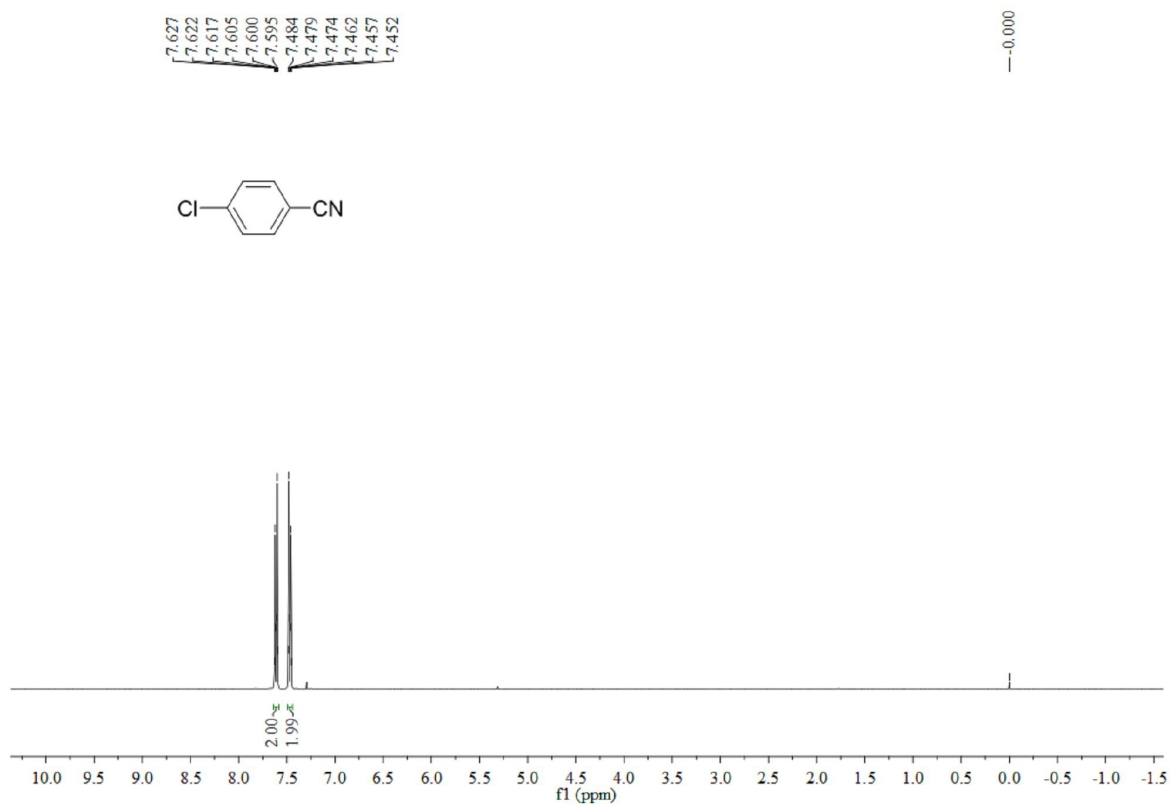


^{13}C NMR, 100 MHz, CDCl_3

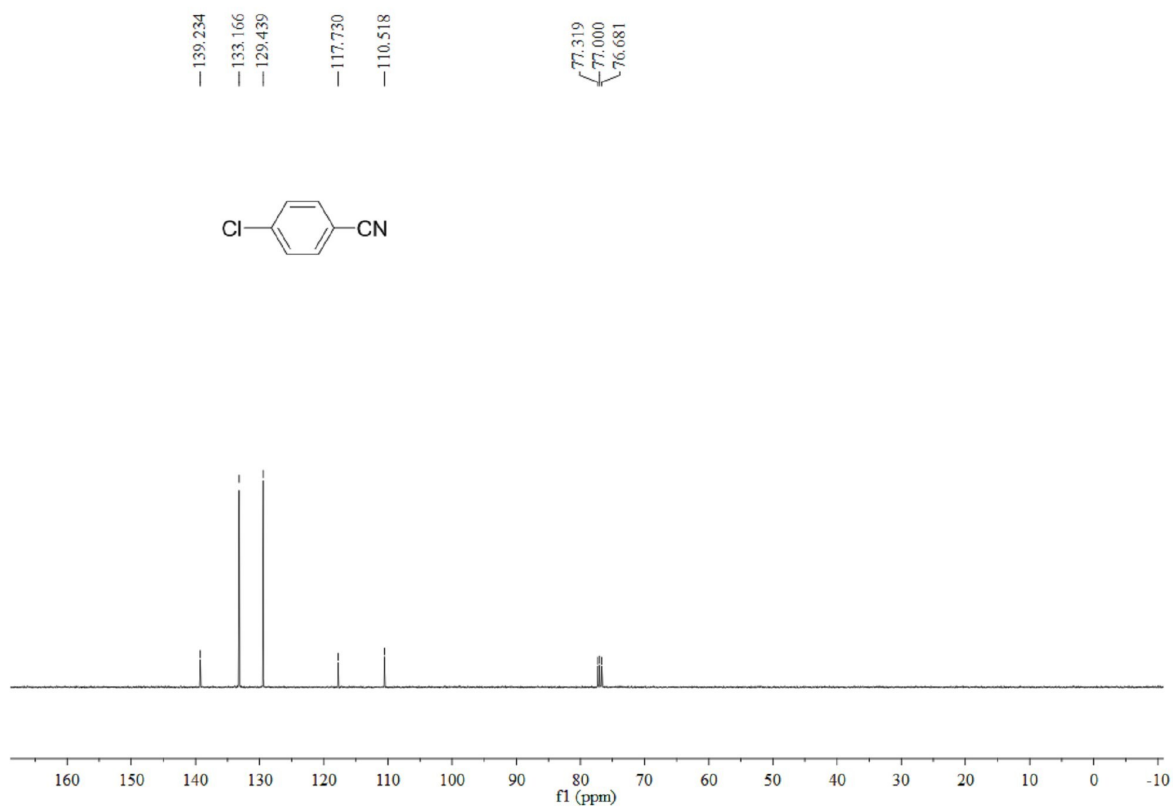


4-Chlorobenzonitrile (**2i**)

^1H NMR, 400 MHz, CDCl_3

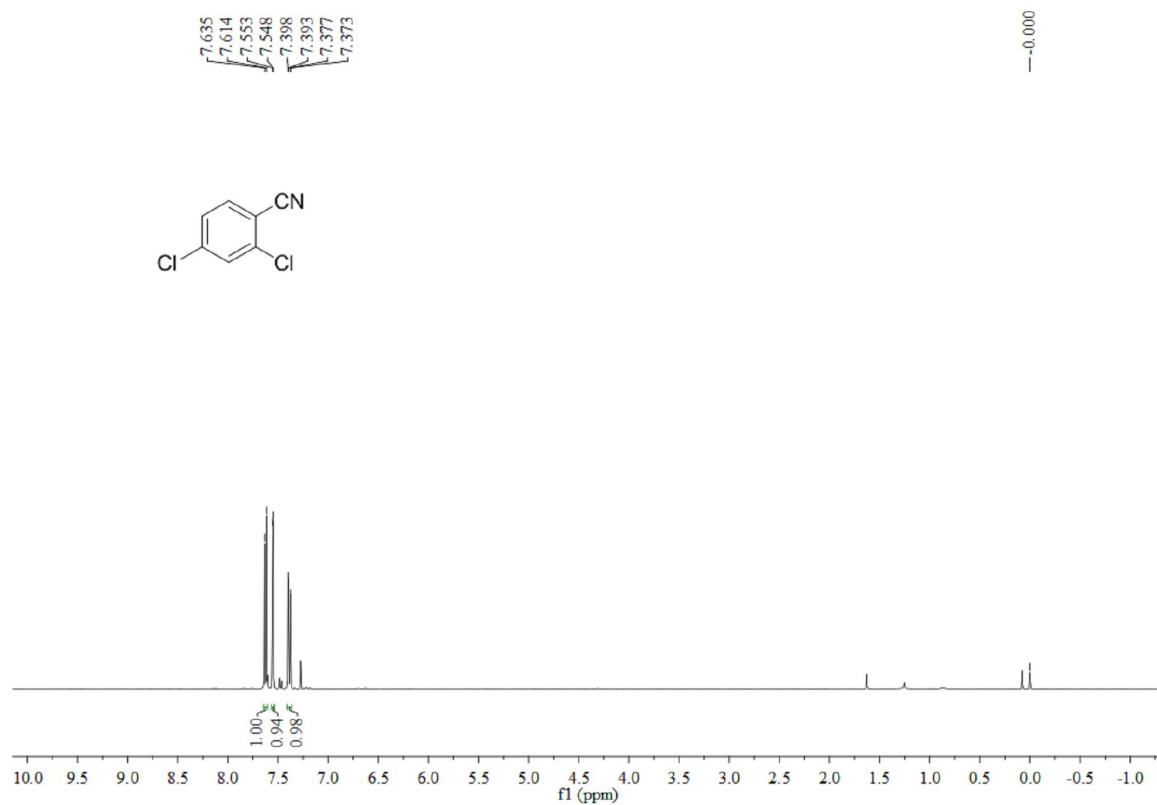


^{13}C NMR, 100 MHz, CDCl_3

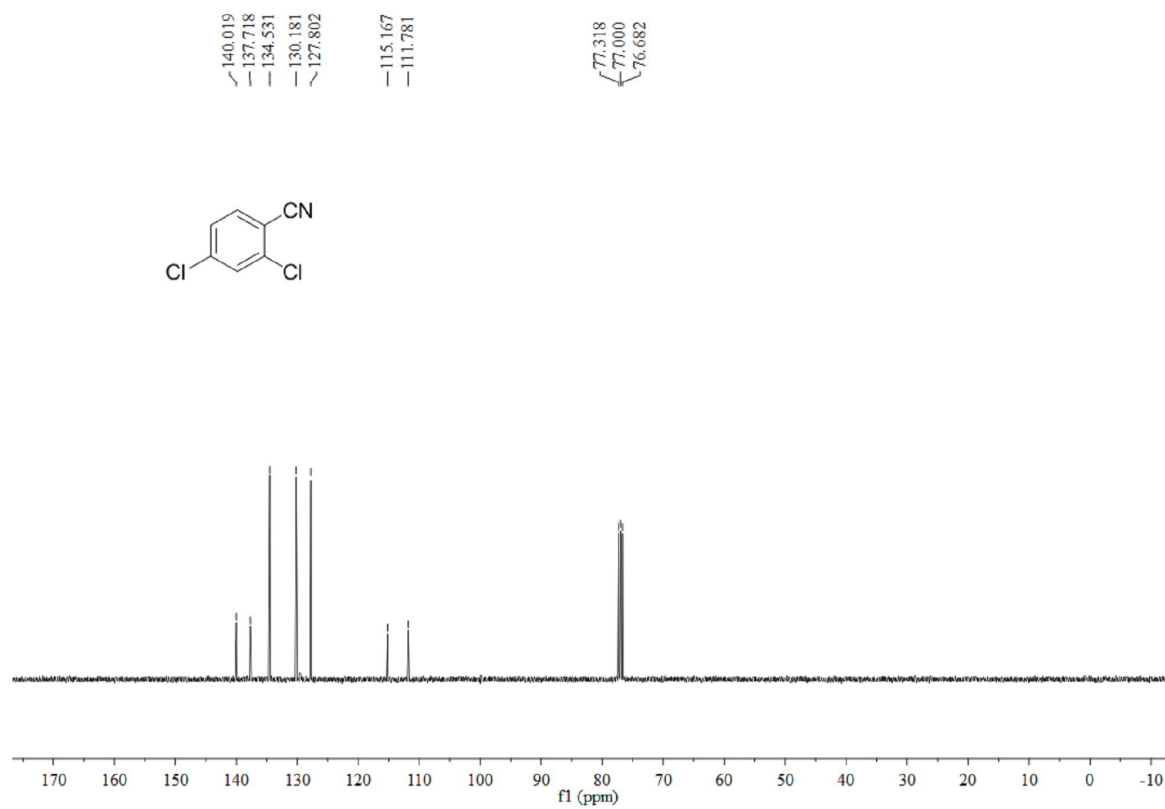


2,4-Dichlorobenzonitrile (**2j**)

^1H NMR, 400 MHz, CDCl_3

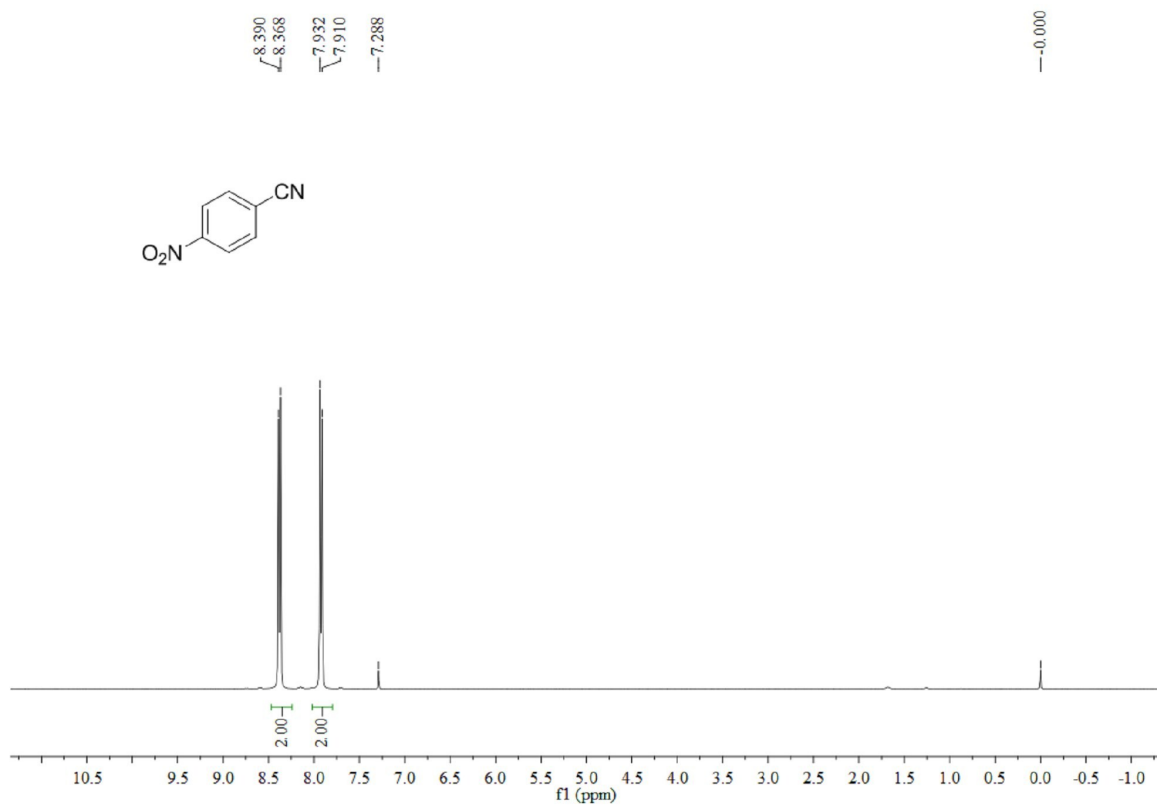


^{13}C NMR, 100 MHz, CDCl_3

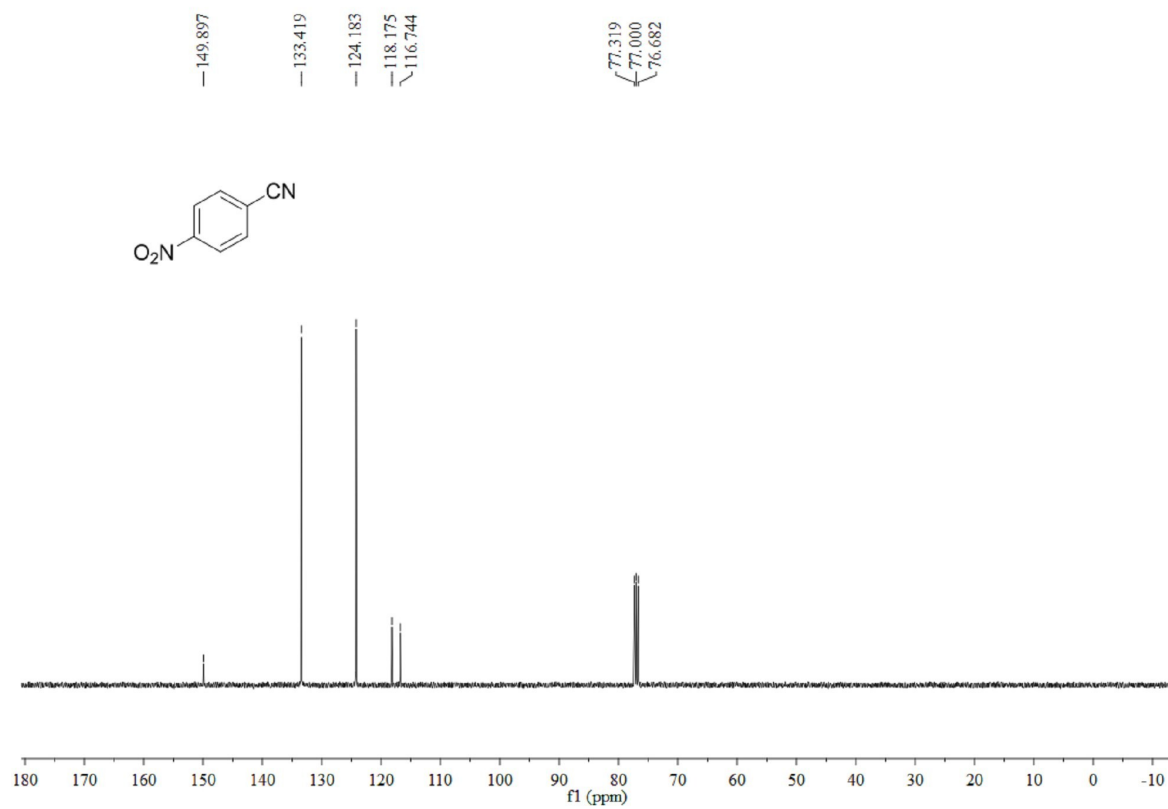


4-Nitrobenzonitrile (**2k**)

^1H NMR, 400 MHz, CDCl_3

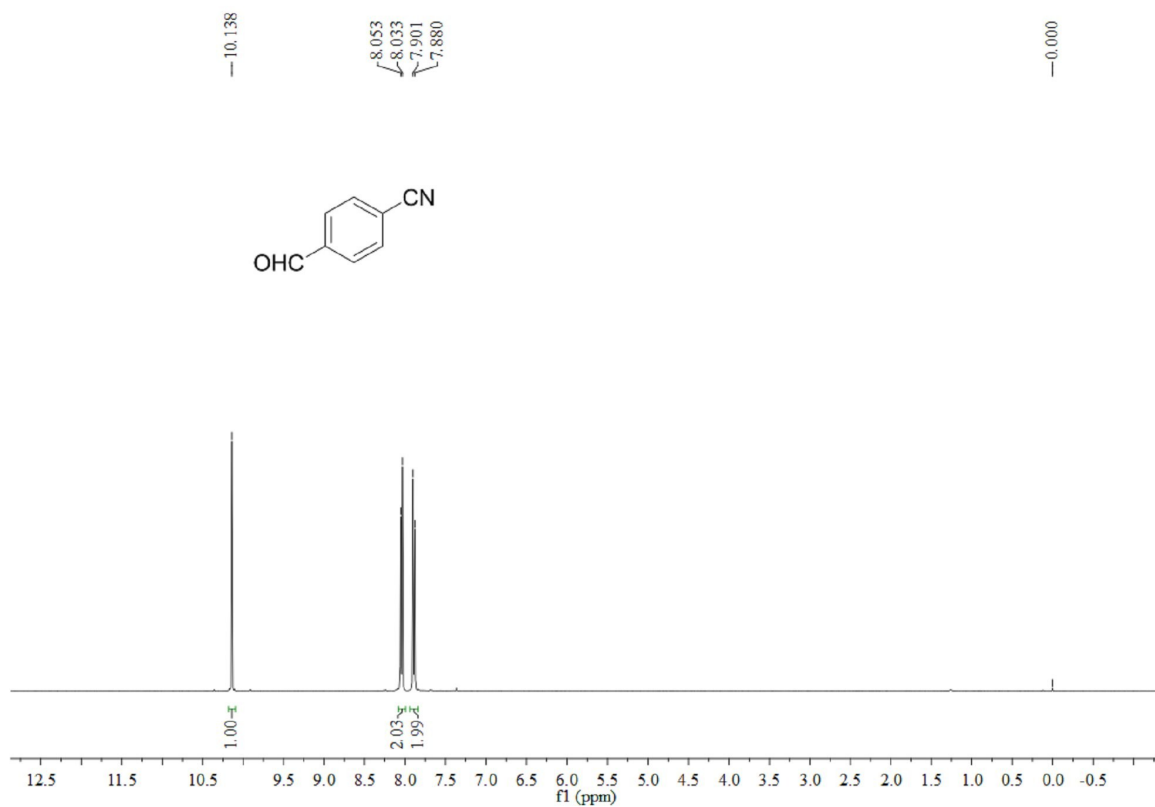


^{13}C NMR, 100 MHz, CDCl_3

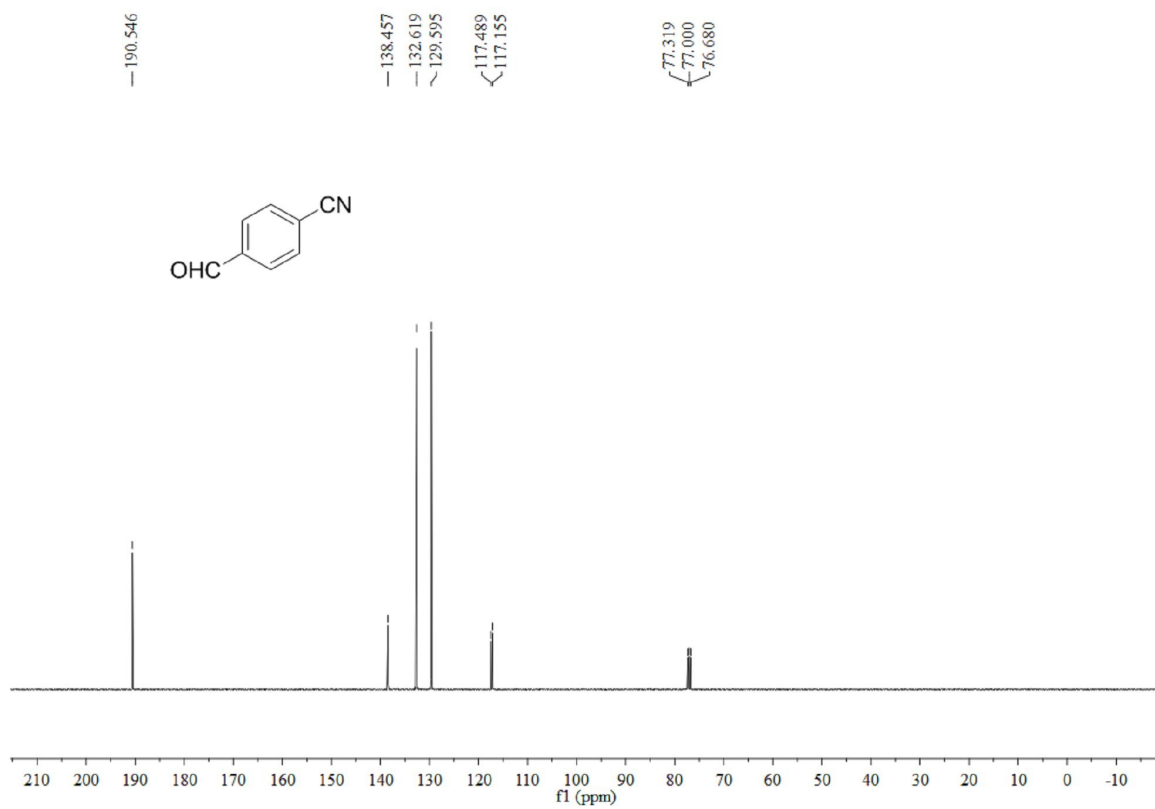


4-Formylbenzonitrile (**2l**)

^1H NMR, 400 MHz, CDCl_3

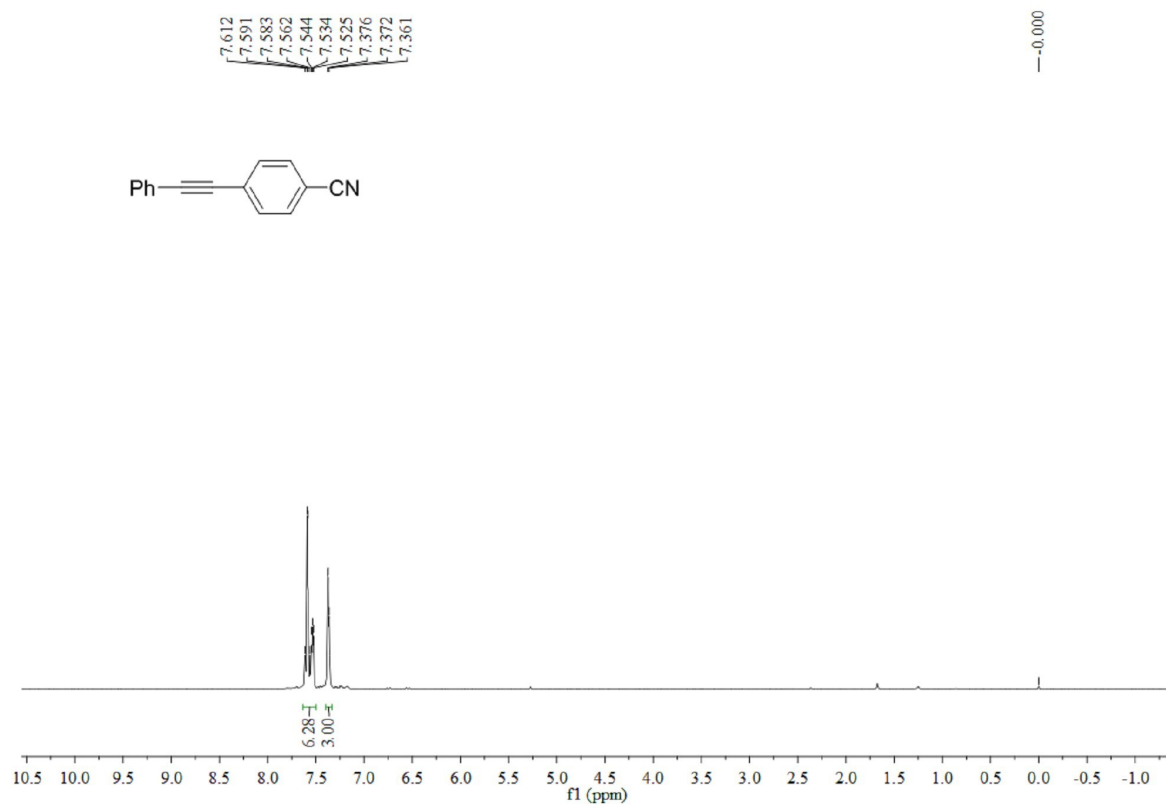


^{13}C NMR, 100 MHz, CDCl_3

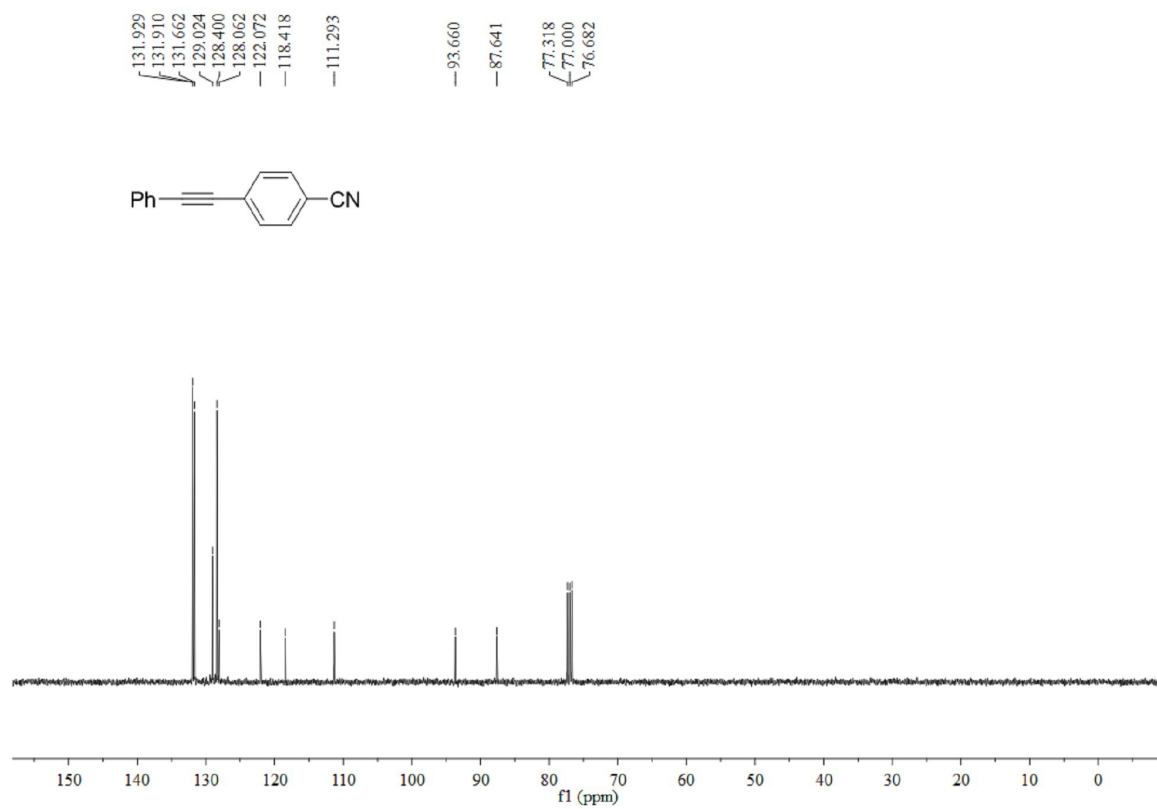


4-(Phenylethynyl)benzonitrile (**2m**)

^1H NMR, 400 MHz, CDCl_3

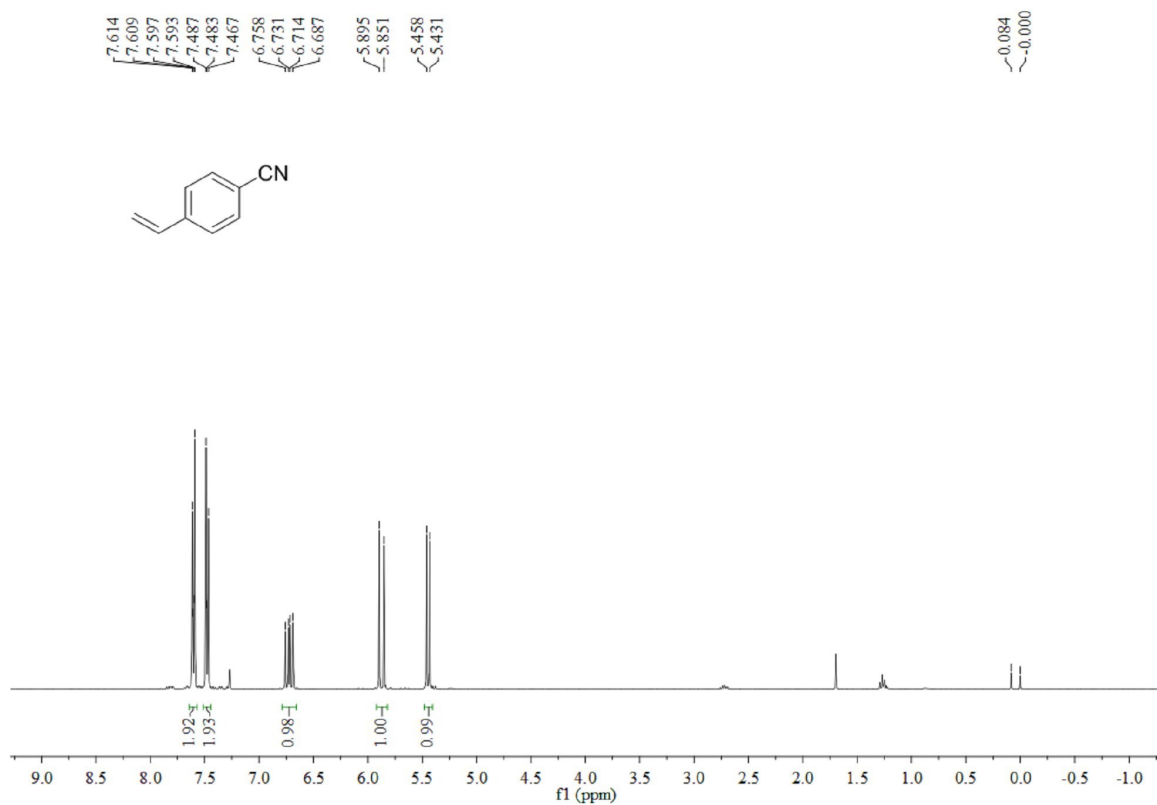


^{13}C NMR, 100 MHz, CDCl_3

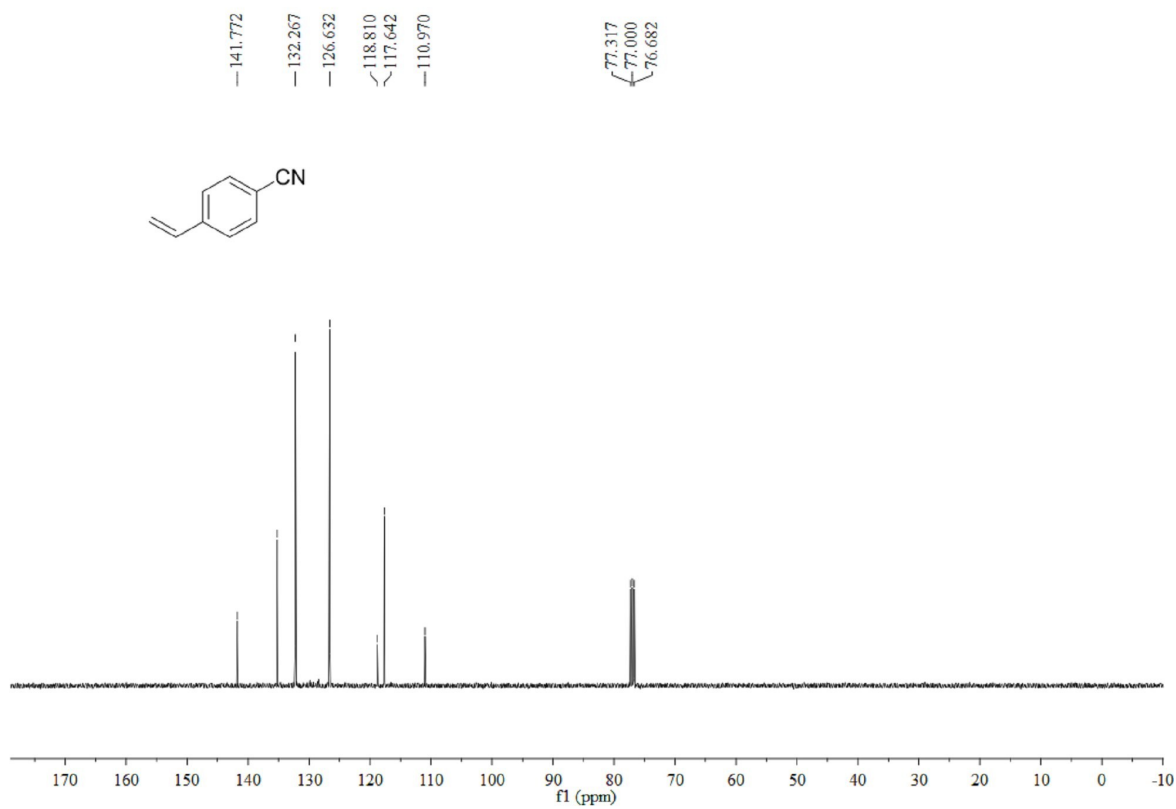


4-Vinylbenzonitrile (**2n**)

^1H NMR, 400 MHz, CDCl_3

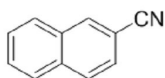
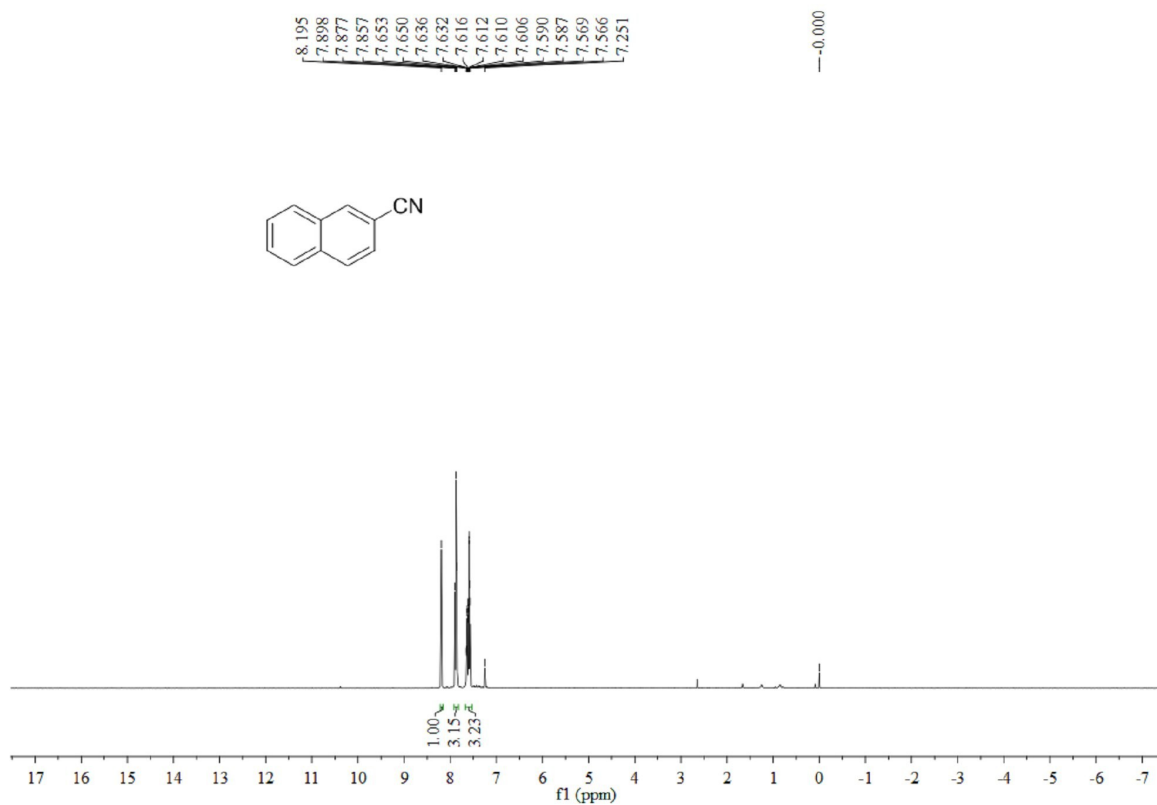


^{13}C NMR, 100 MHz, CDCl_3

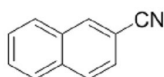
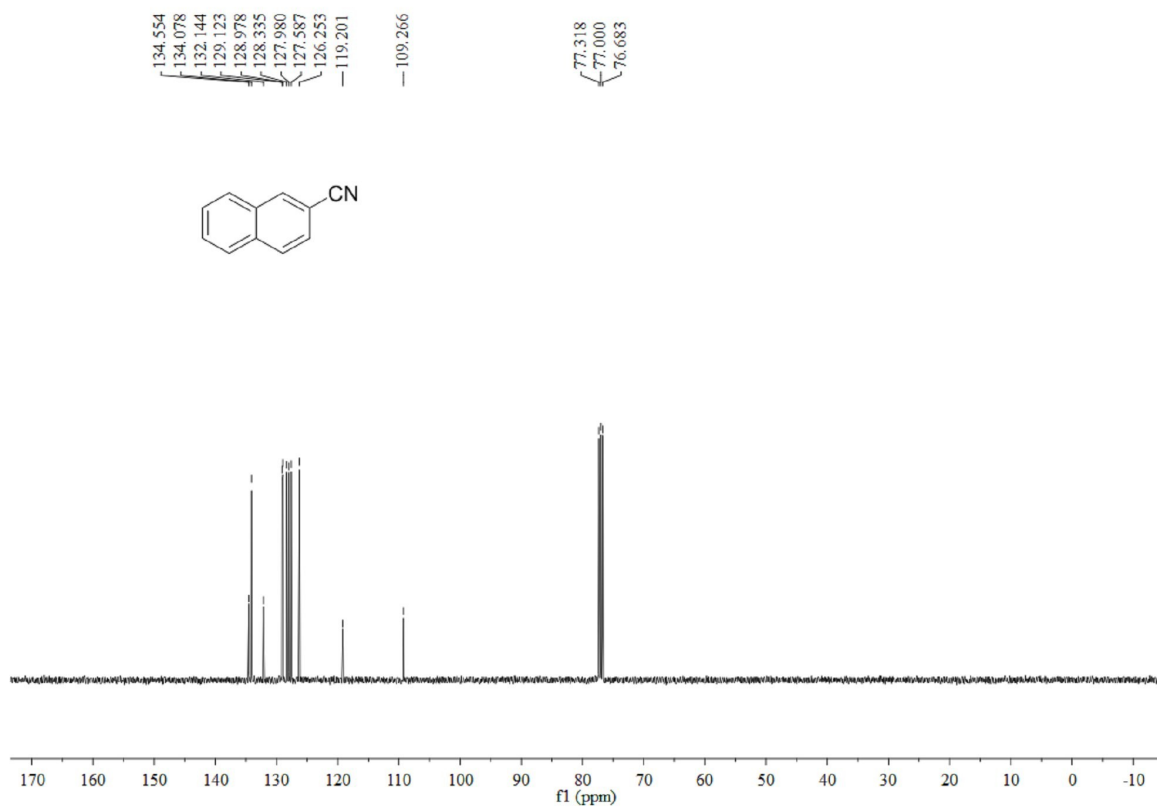


2-Naphthonitrile (**2o**)

^1H NMR, 400 MHz, CDCl_3

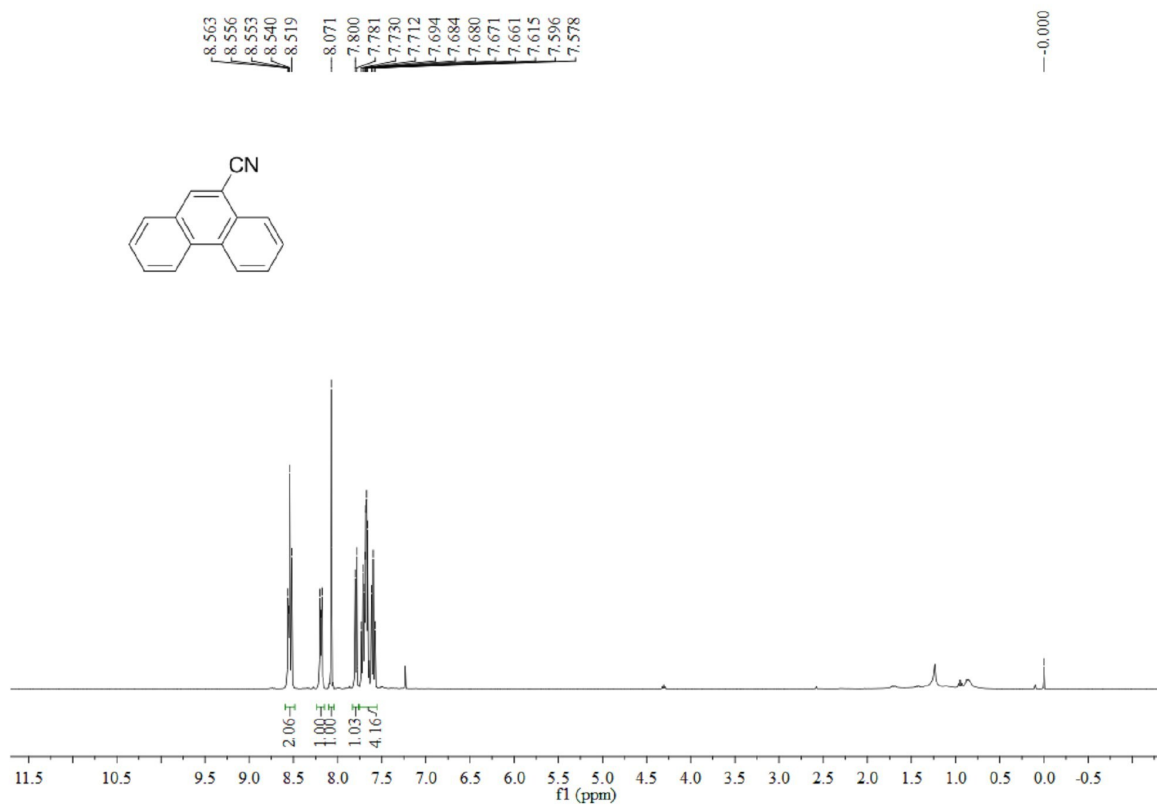


^{13}C NMR, 100 MHz, CDCl_3

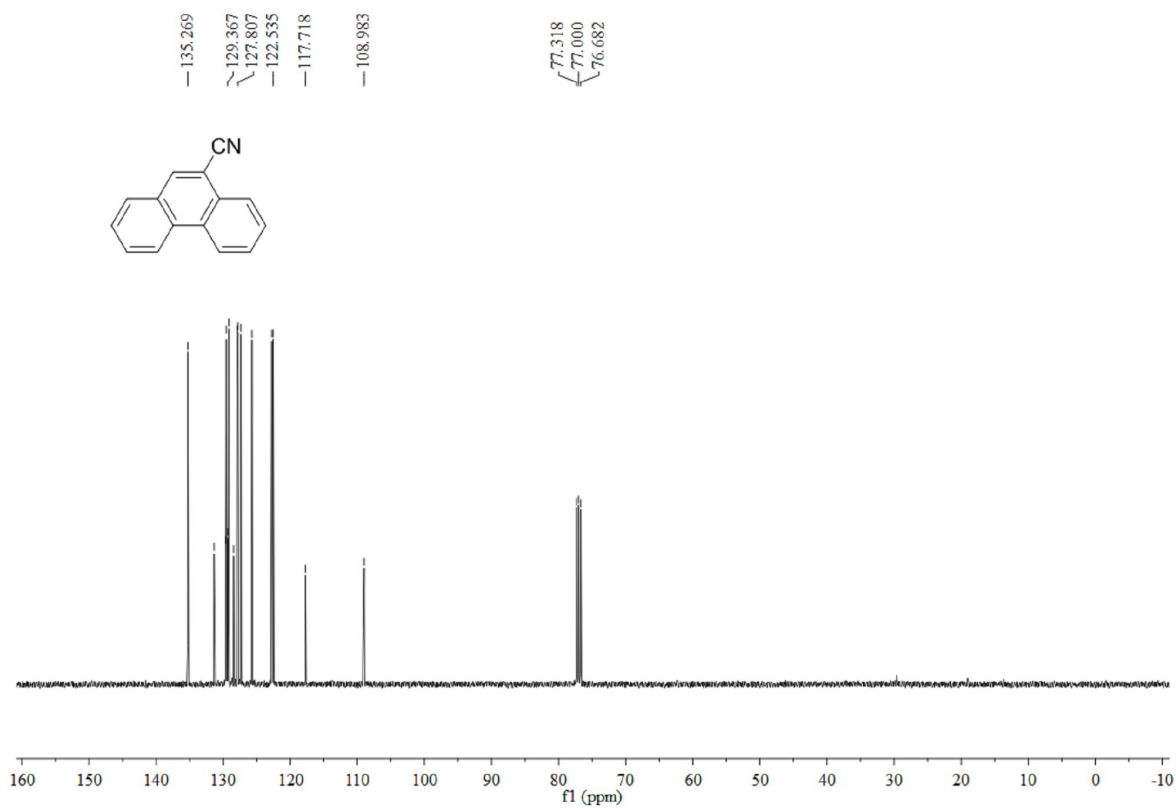


Phenanthrene-9-carbonitrile (**2p**)

^1H NMR, 400 MHz, CDCl_3

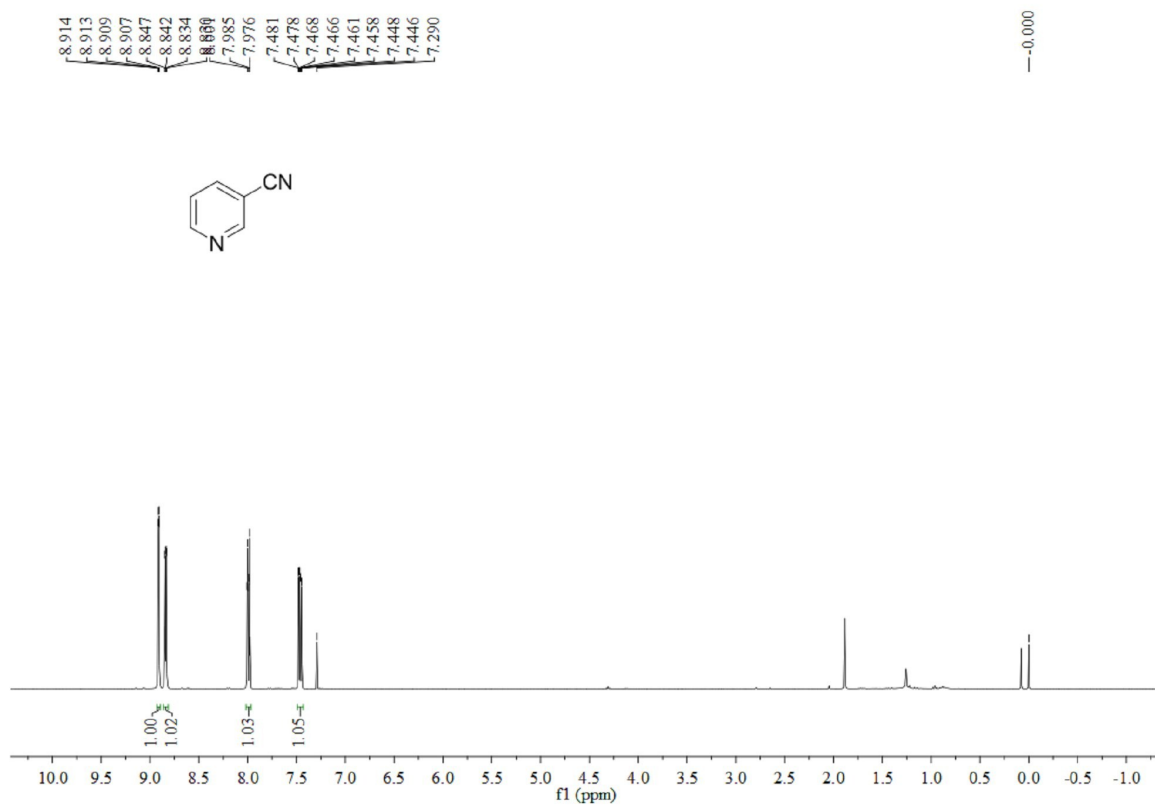


^{13}C NMR, 100 MHz, CDCl_3

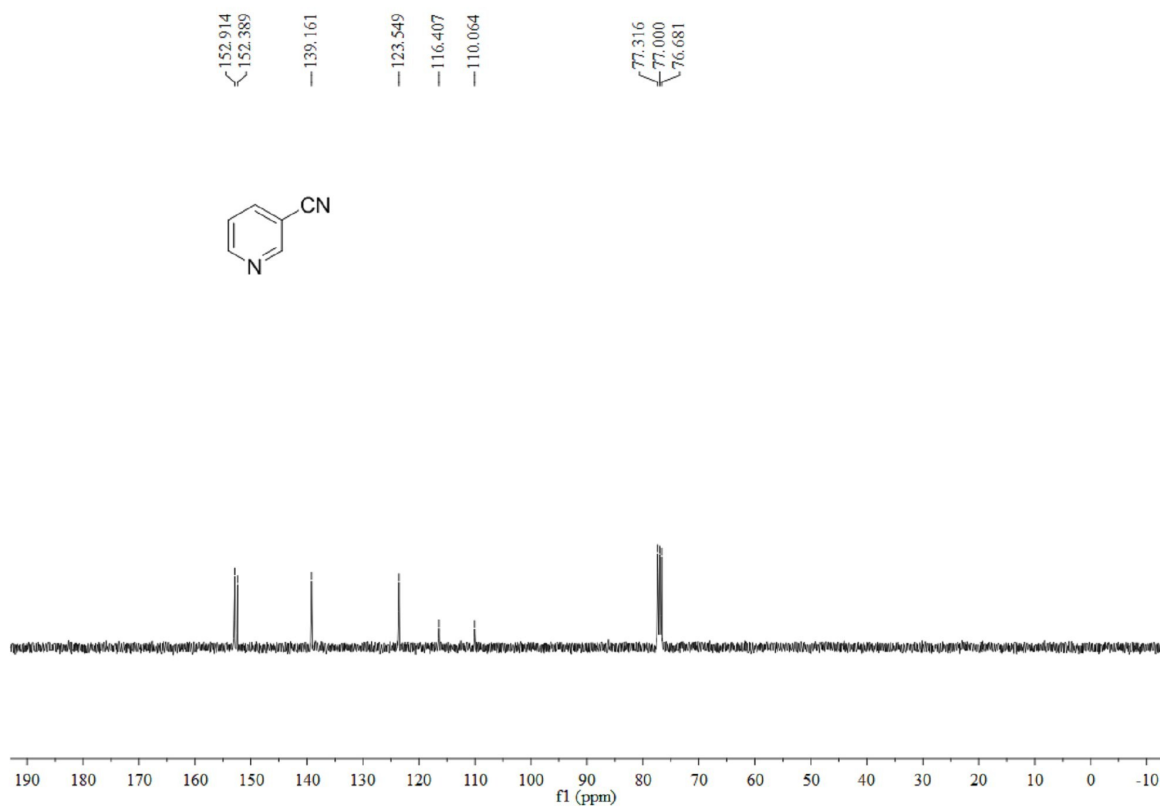


Nicotinonitrile (**2q**)

^1H NMR, 400 MHz, CDCl_3

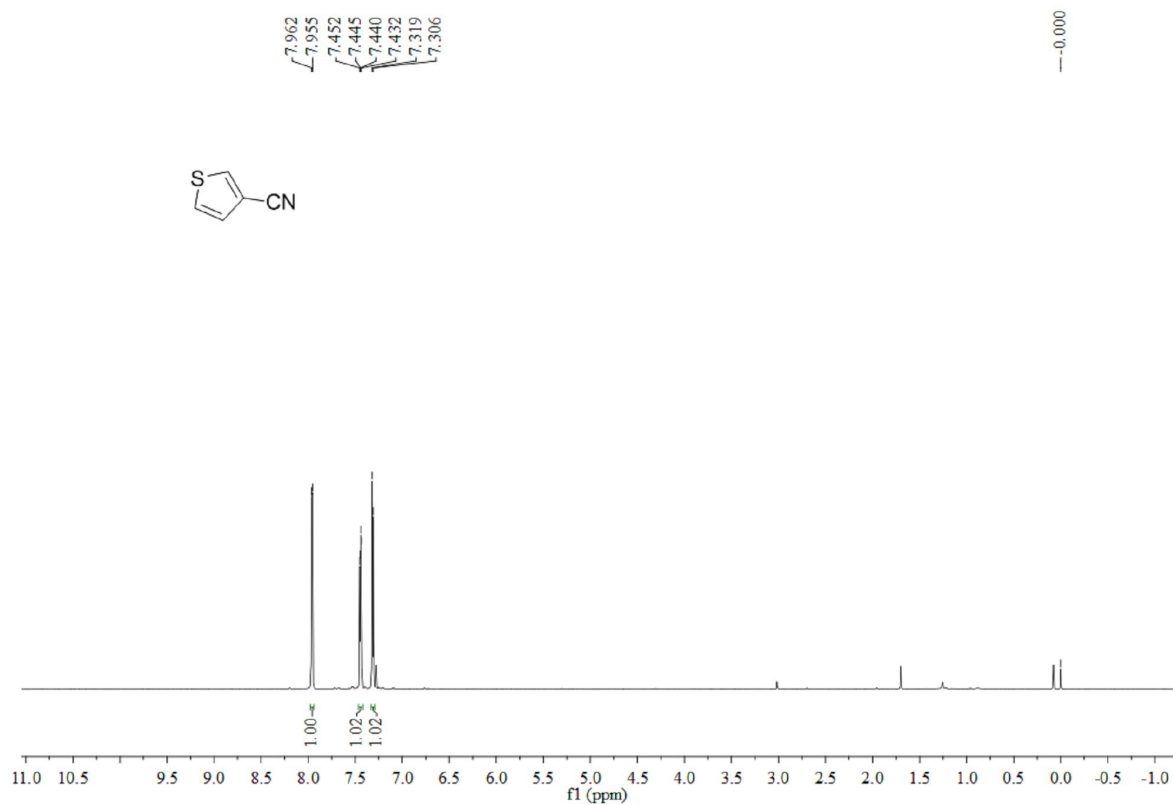


^{13}C NMR, 100 MHz, CDCl_3

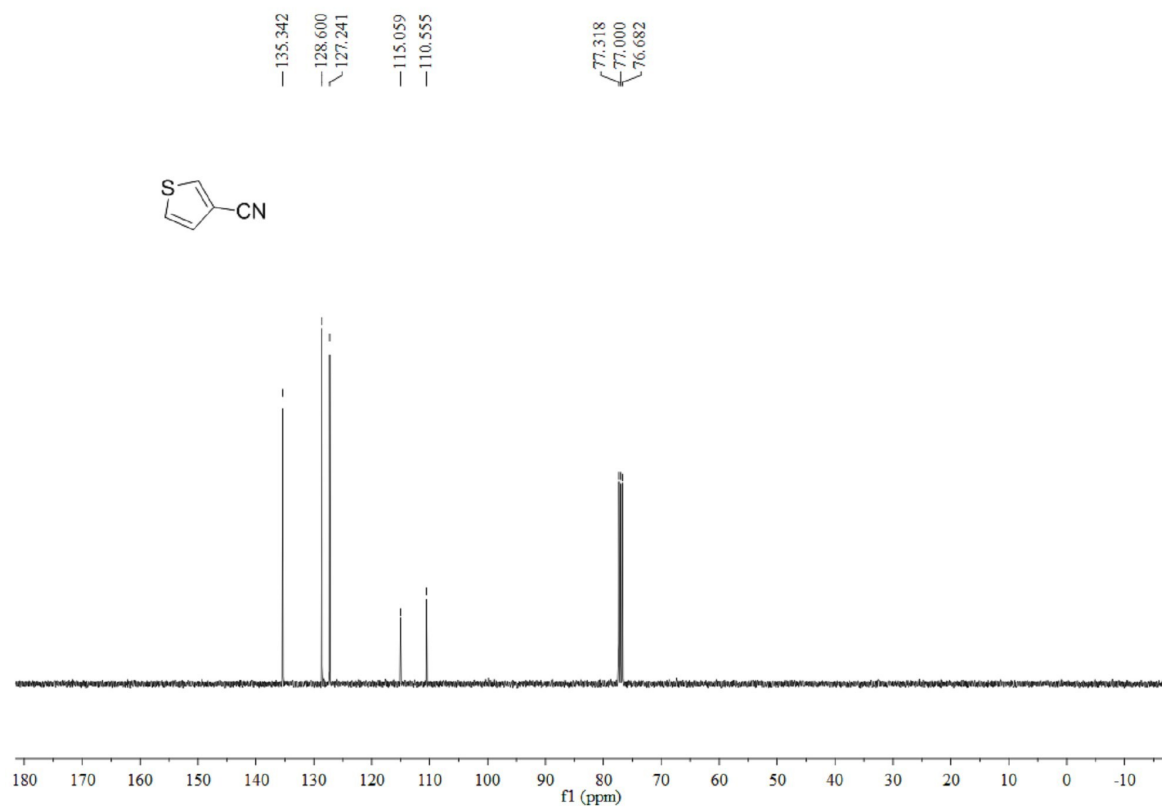


Thiophene-3-carbonitrile (**2r**)

^1H NMR, 400 MHz, CDCl_3

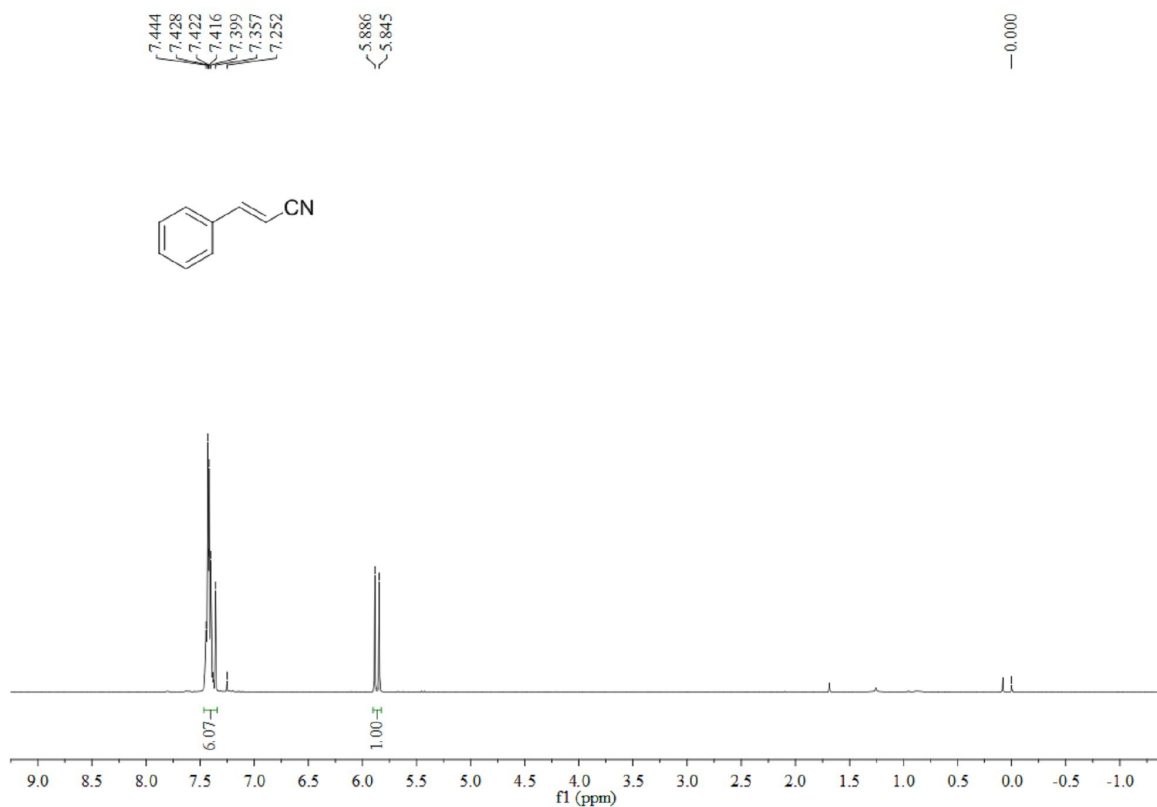


^{13}C NMR, 100 MHz, CDCl_3

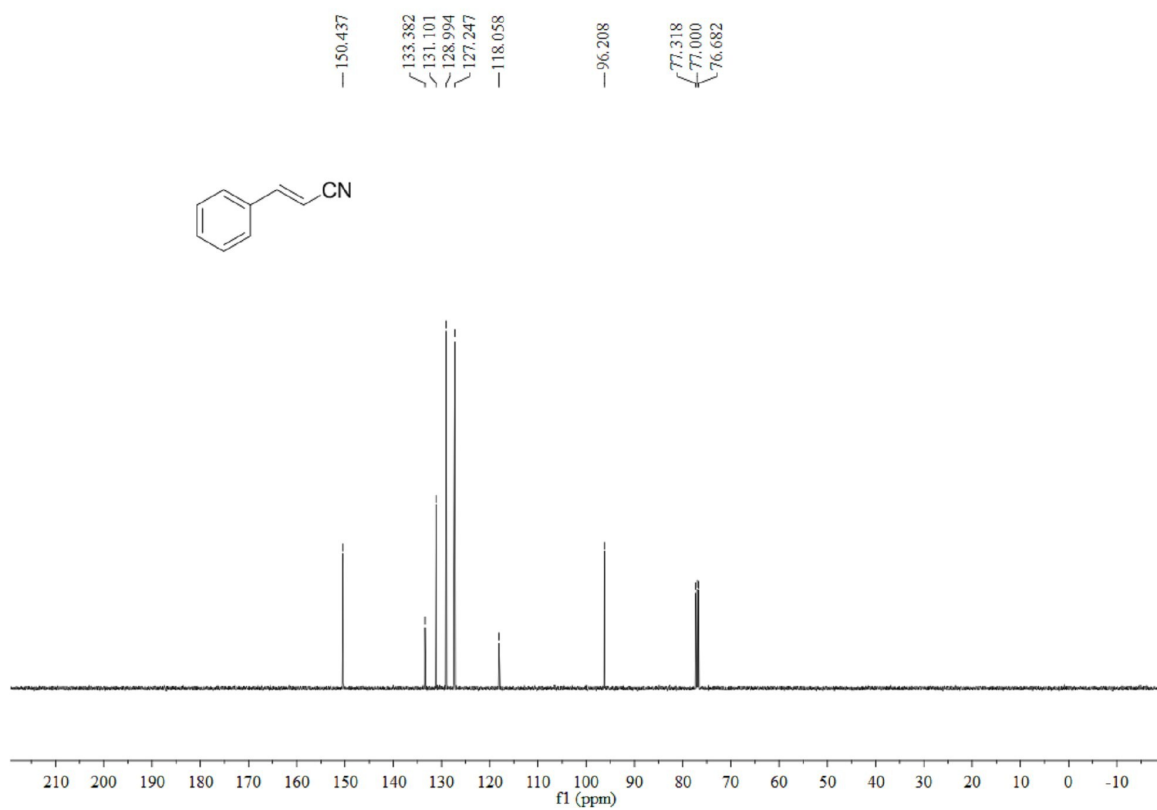


Cinnamonitrile (**2s**)

^1H NMR, 400 MHz, CDCl_3

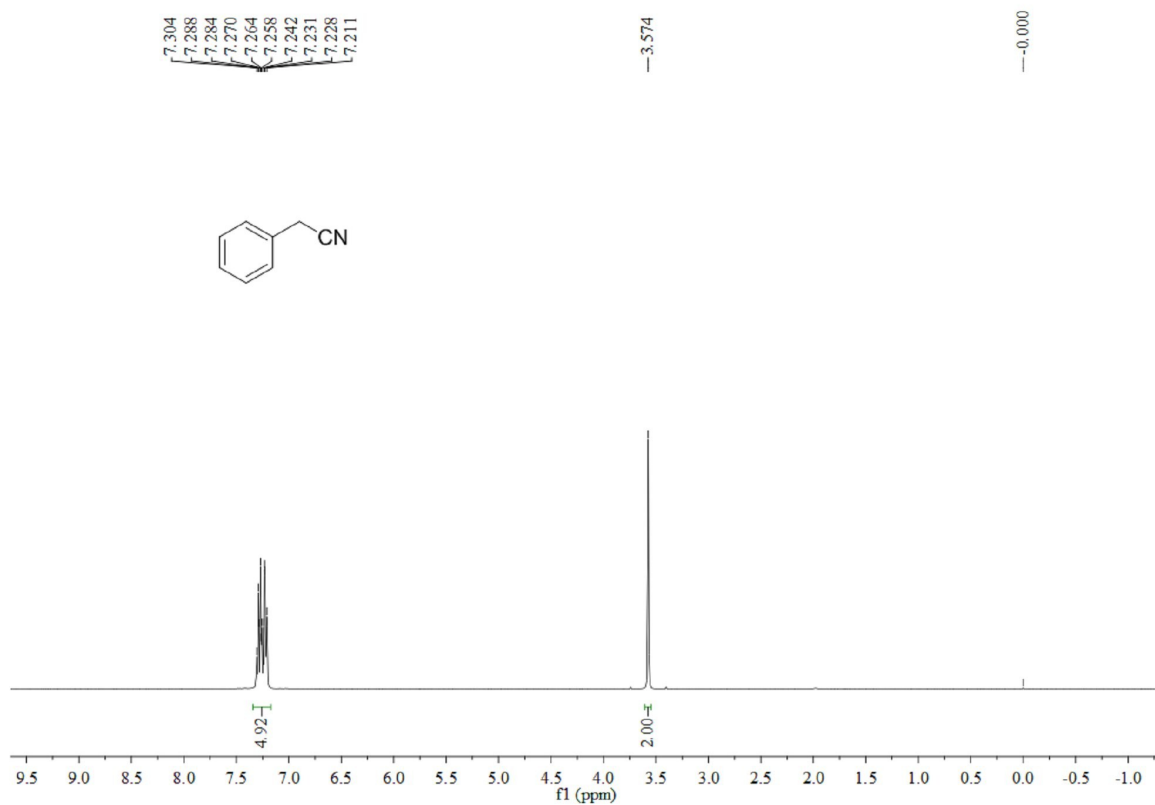


^{13}C NMR, 100 MHz, CDCl_3

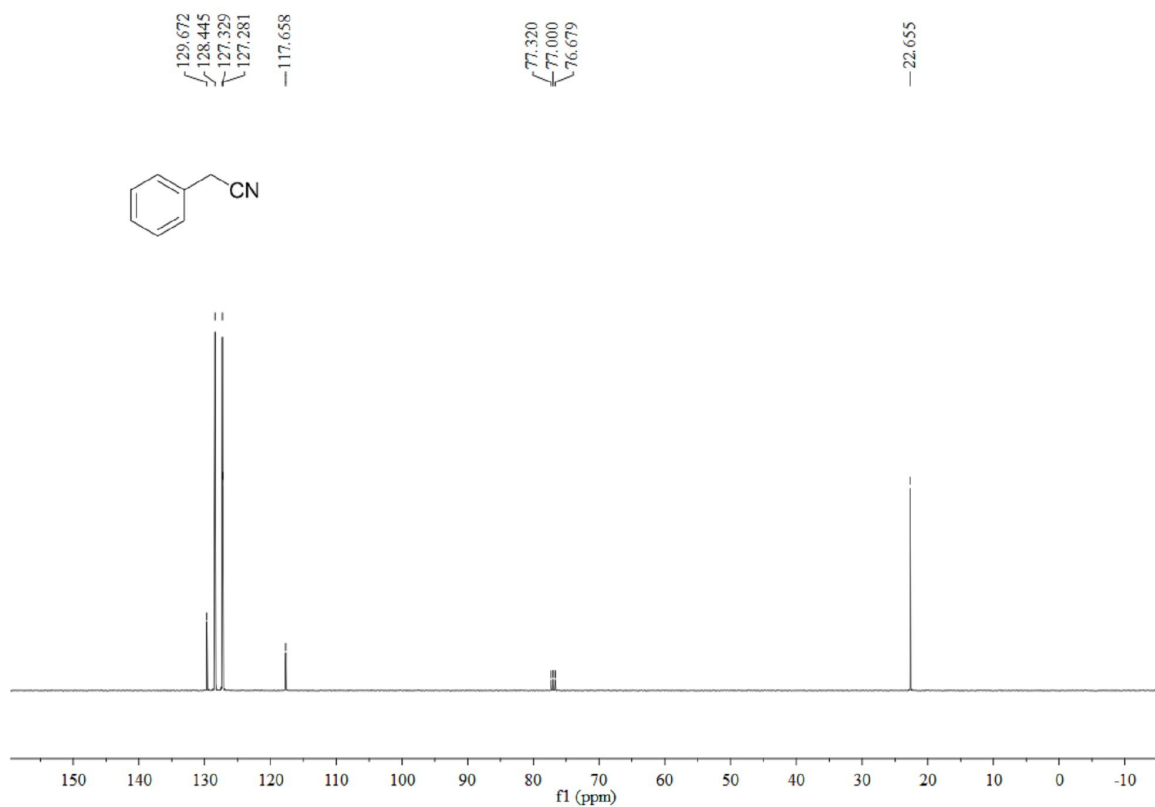


2-Phenylacetonitrile (**2t**)

^1H NMR, 400 MHz, CDCl_3

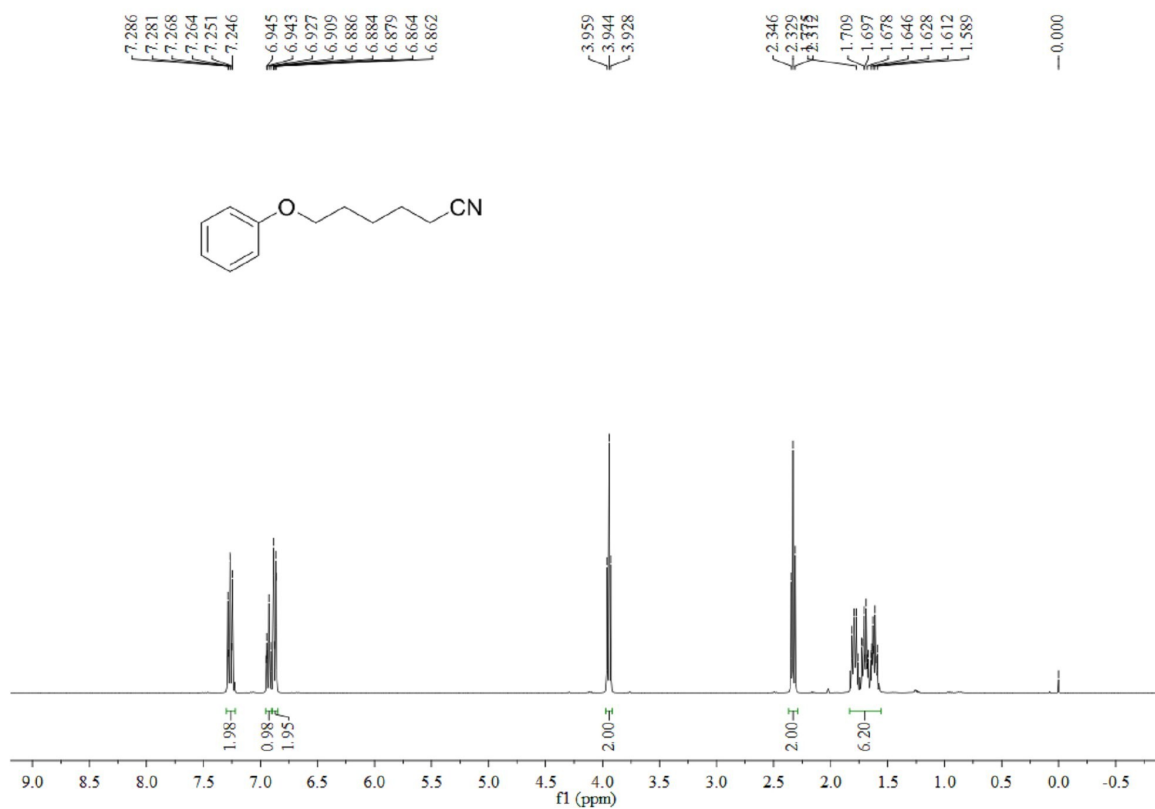


^{13}C NMR, 100 MHz, CDCl_3

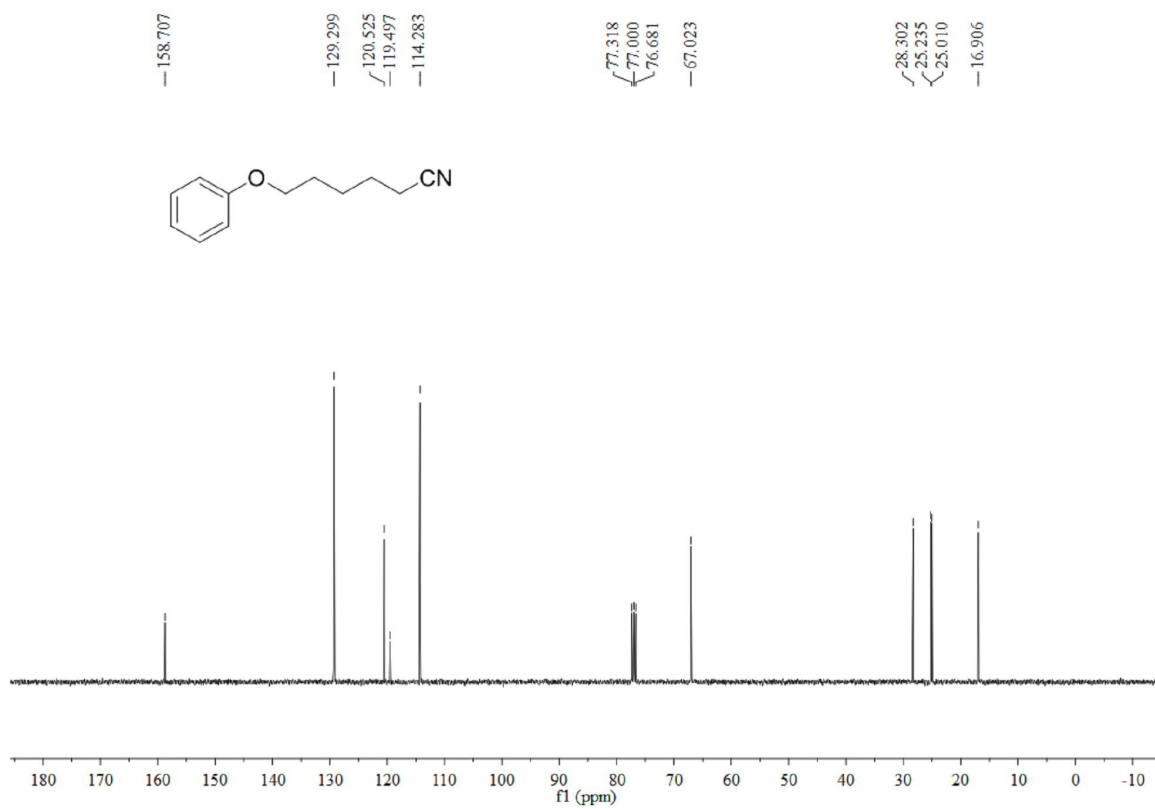


6-Phenoxyhexanenitrile (**2u**)

^1H NMR, 400 MHz, CDCl_3

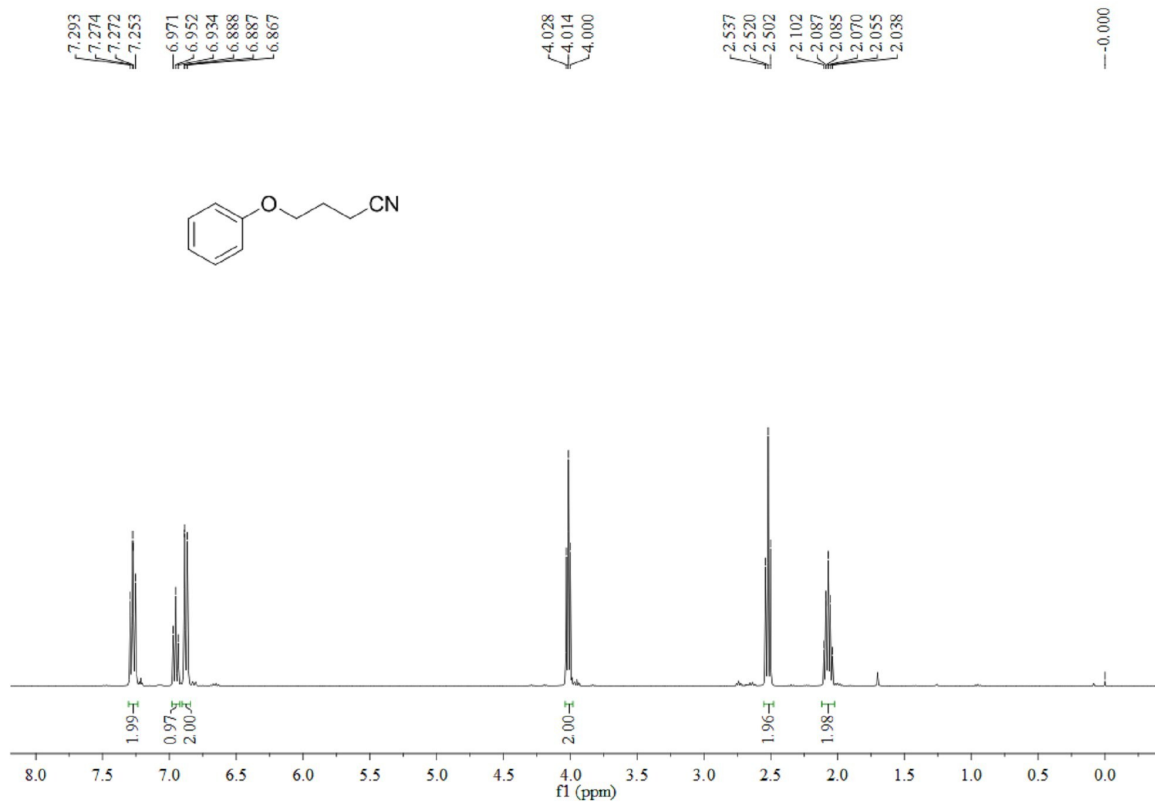


^{13}C NMR, 100 MHz, CDCl_3

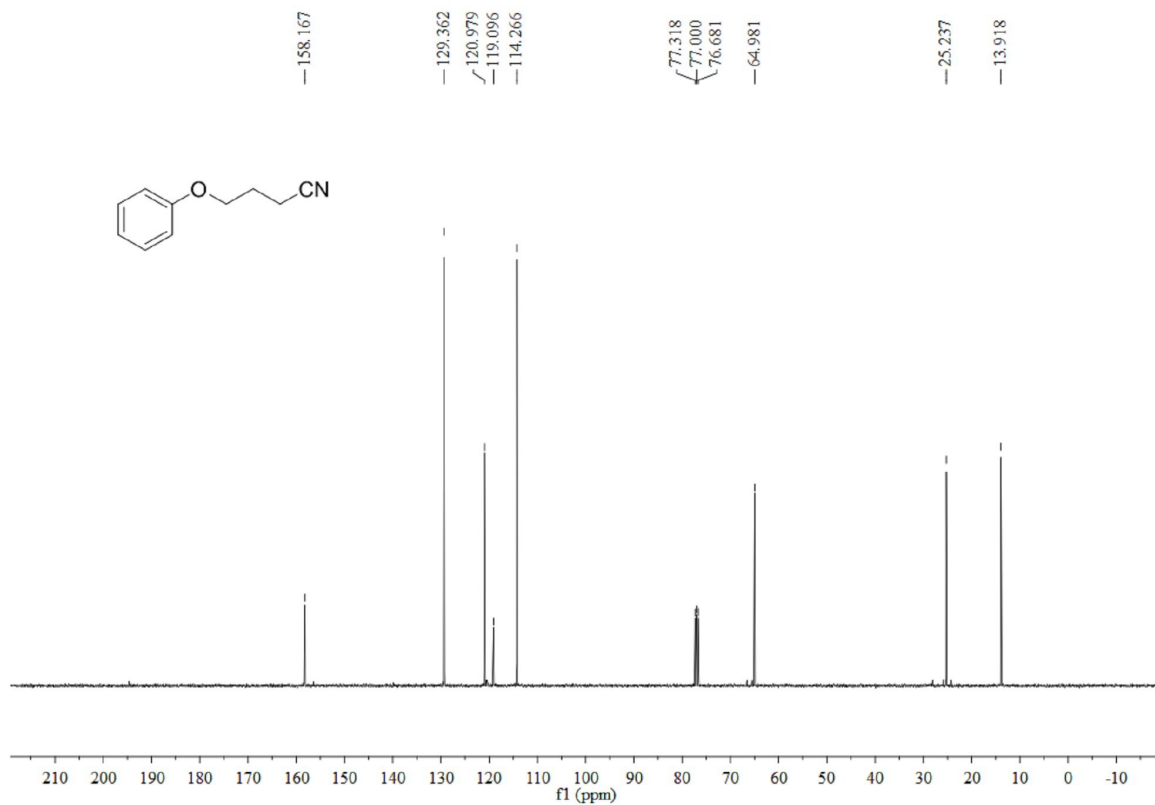


4-Phenoxybutanenitrile (**2v**)

¹H NMR, 400 MHz, CDCl₃

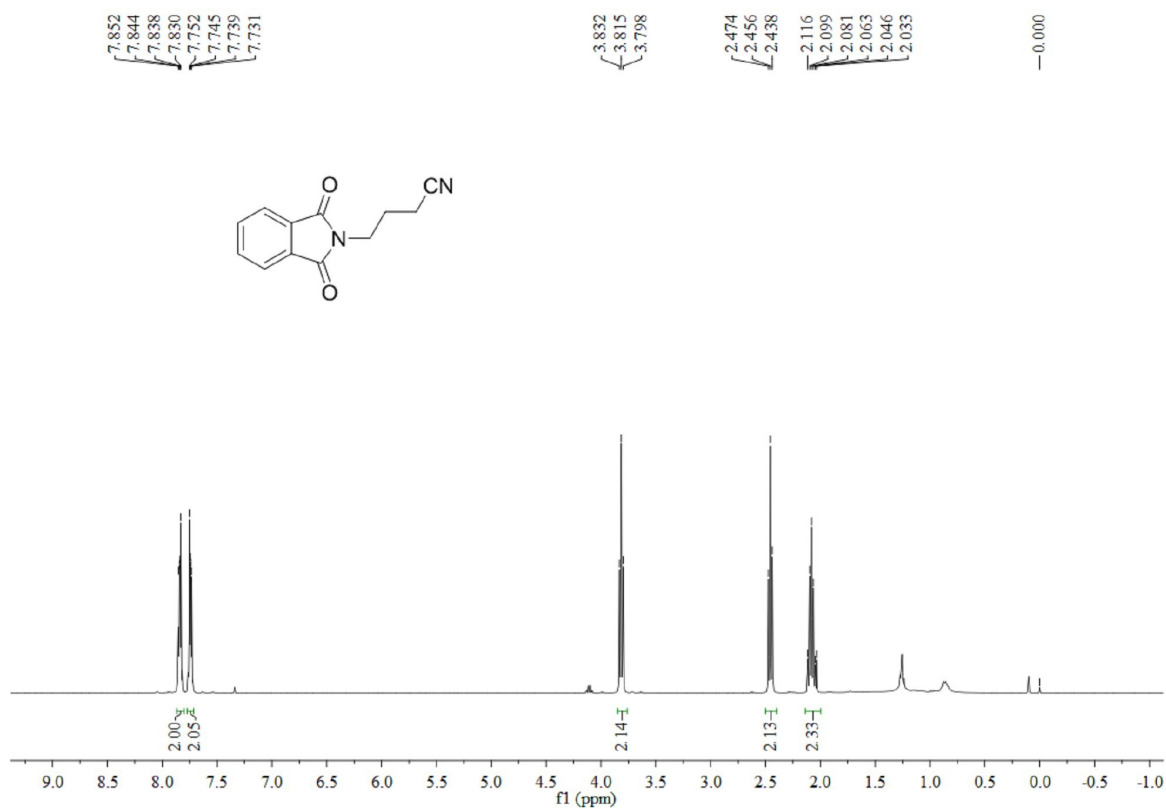


¹³C NMR, 100 MHz, CDCl₃

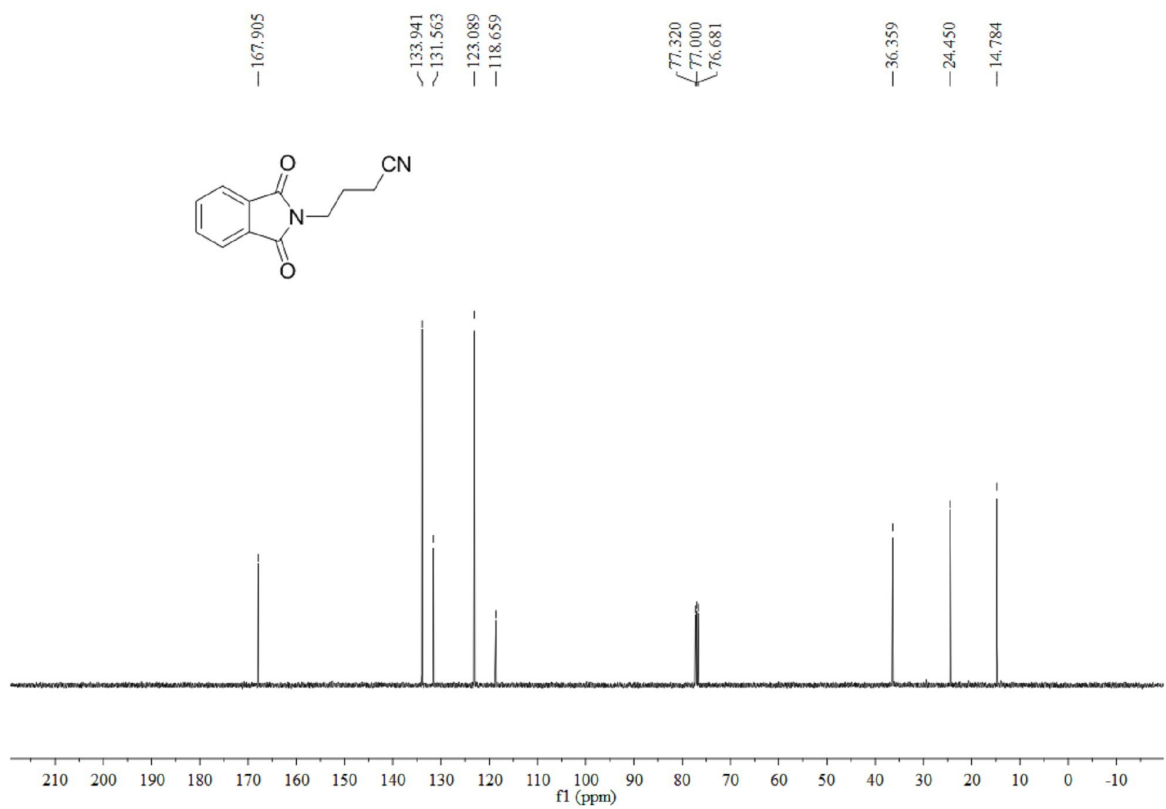


4-(1,3-Dioxisoindolin-2-yl)butanenitrile (**2w**)

^1H NMR, 400 MHz, CDCl_3

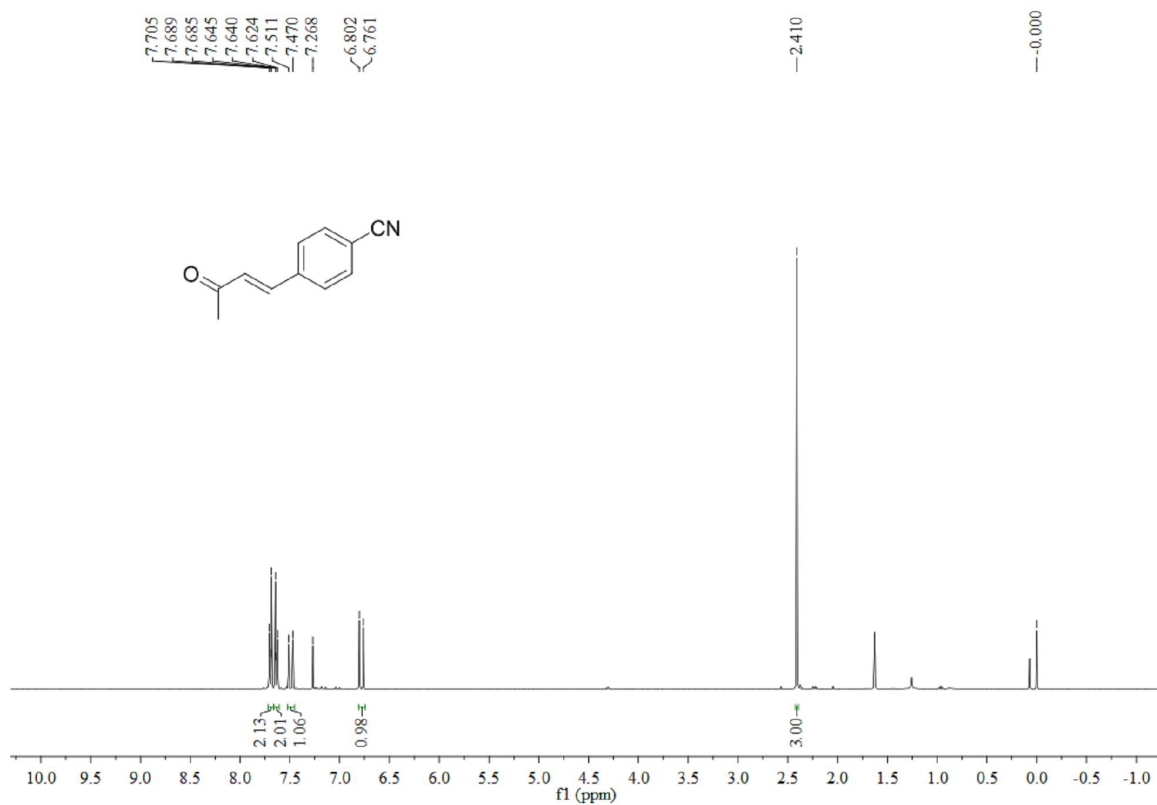


^{13}C NMR, 100 MHz, CDCl_3



(*E*)-4-(3-oxobut-1-enyl)benzonitrile (**4**)

^1H NMR, 400 MHz, CDCl_3



^{13}C NMR, 100 MHz, CDCl_3

