

# Supplementary Information

## Iodine-catalyzed ammoxidation of methyl arenes †

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## 1. General Considerations

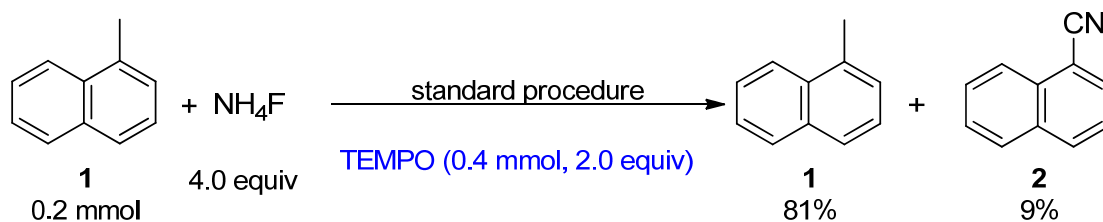
Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for  $^{13}\text{C}$ ). NMR experiments are reported in  $\delta$  units, parts per million (ppm), and were referenced to  $\text{CDCl}_3$  ( $\delta$  7.26 or 77.0 ppm) or  $\text{DMSO-d}_6$  ( $\delta$  2.50 or 39.52 ppm) as the internal standard. The coupling constants  $J$  are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). IR spectra were recorded on a FT-IR-480 spectrometer using KBr discs.

## 2. Experimental Procedures.

Under  $\text{O}_2$ , a 20 mL of Schlenk tube equipped with a stir bar was charged with **1** (0.2 mmol),  $\text{I}_2$  (10.2 mg, 0.04 mmol),  $\text{NH}_4\text{F}$  (29.6 mg, 0.8 mmol), TBHP (70% in water, 324  $\mu\text{L}$ , 2.4 mmol), DMSO (0.5 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 70  $^\circ\text{C}$  for 48 h in oil bath. After the completion of the reaction (monitored by TLC), the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.

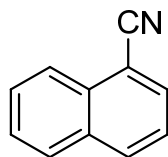
### 3. Free Radical Capture Experiments

Under O<sub>2</sub>, a 20 mL of Schlenk tube equipped with a stir bar was charged with **1a** (0.2 mmol), I<sub>2</sub> (10.2 mg, 0.04 mmol), NH<sub>4</sub>F (29.6 mg, 0.8 mmol), TBHP (70% in water, 324 μL, 2.4 mmol), DMSO (0.5 mL), **TEMPO** (62.5 mg, 0.4 mmol, 2 equiv). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 70 °C for 48 h in oil bath. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give product **2a** in 9% yield.



#### 4. Characterization Data for the Products

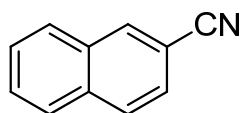
##### 1-Naphthonitrile (**2a**):<sup>[1]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2a** (24.5 mg, 80% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.22 (d,  $J$  = 8.3 Hz, 1H), 8.06 (d,  $J$  = 8.3 Hz, 1H), 7.92-7.88 (m, 2H), 7.70-7.66 (m, 1H), 7.63-7.59 (m, 1H), 7.50 (t,  $J$  = 7.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  133.2, 132.8, 132.5, 132.2, 128.6, 128.5, 127.4, 125.0, 124.8, 117.7, 110.0.

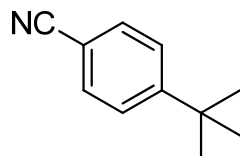
##### 2-Naphthonitrile (**2b**):<sup>[1]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2b** (23.8 mg, 78% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.22 (s, 1H), 7.92-7.87 (m, 3H), 7.67-7.58 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  134.6, 134.1, 132.2, 129.1, 129.0, 128.3, 128.0, 127.6, 126.3, 119.2, 109.3.

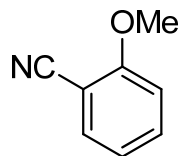
##### 4-(*tert*-Butyl)benzonitrile (**2c**):<sup>[1]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2c** (21.1 mg, 66% yield) as pale yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.58 (d,  $J$  = 8.5 Hz, 2H), 7.48 (d,  $J$  = 8.5 Hz, 2H), 1.33 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  156.6, 131.9, 126.1, 119.1, 109.3, 35.2, 30.9.

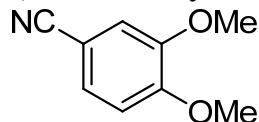
##### 2-Methoxybenzonitrile (**2d**):<sup>[1]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **2d** (15.7 mg, 59% yield) as colorless oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.56-7.51 (m, 2H), 7.02-6.96 (m, 2H), 3.93 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.2, 134.3, 133.7, 120.7, 116.5, 111.3, 101.8, 55.9.

##### 3,4-Dimethoxybenzonitrile (**2e**):<sup>[2]</sup>

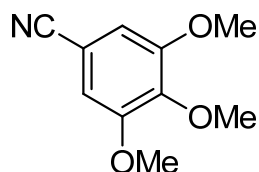


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10)

give **2e** (20.1 mg, 62% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.27 (dd,  $J = 8.4$  Hz,  $J = 1.8$  Hz, 1H), 7.06 (d,  $J = 1.8$  Hz, 1H), 6.89 (d,  $J = 8.3$  Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  152.8, 149.1, 126.4, 119.2, 113.9, 111.2, 103.8, 56.1, 56.0.

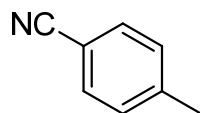
**3,4,5-Trimethoxybenzonitrile (2f):**<sup>[2]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **2f** (27.6 mg, 71% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  6.85 (s, 2H), 3.89 (s, 3H), 3.87 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  153.5, 142.3, 118.9, 109.4, 106.7, 61.0, 56.3.

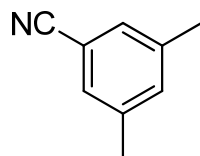
**4-Methylbenzonitrile (2g):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **2g** (14.6 mg, 62% yield) as colorless solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.53 (d,  $J = 8.1$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 2.42 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  143.6, 131.9, 129.7, 119.0, 109.2, 21.7.

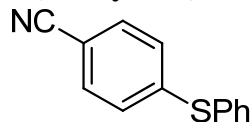
**3,5-Dimethylbenzonitrile (2h):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **2h** (14.3 mg, 55% yield) as colorless solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.26 (s, 2H), 7.21 (s, 1H), 2.34 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  139.0, 134.6, 129.6, 119.2, 112.0, 21.0.

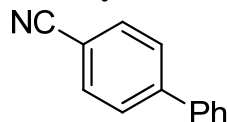
**4-(Phenylthio)benzonitrile (2i):**<sup>[4]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2i** (25.8 mg, 61% yield) as colorless oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.52-7.42 (m, 7H), 7.18-7.15 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  145.7, 134.4, 132.2, 130.8, 129.9, 129.3, 127.3, 118.7, 108.7.

**4-Phenylbenzonitrile (2j):**<sup>[3]</sup>

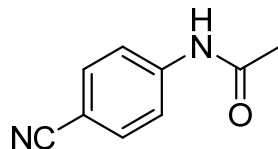


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50)

give **2j** (29.1 mg, 81% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.74-7.67 (m, 4H), 7.61-7.57 (m, 2H), 7.52-7.40 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.8.

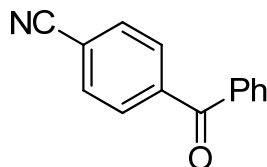
**N-(4-cyanophenyl)acetamide (2k):**<sup>[5]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give **2k** (26.6 mg, 83% yield) as white solid.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz): δ 10.37 (s, 1H), 7.75 (s, 4H), 2.09 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz): δ 169.2, 143.5, 133.2, 119.1, 118.9, 104.7, 24.2.

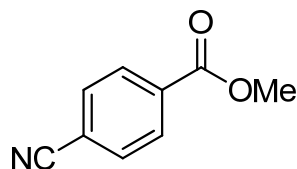
**4-Benzoylbenzotrile (2l):**<sup>[1]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give **2l** (20.8 mg, 50% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.88-7.86 (m, 2H), 7.80-7.77 (m, 4H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 195.0, 141.2, 136.3, 133.3, 132.1, 130.2, 130.0, 128.6, 118.0, 115.6.

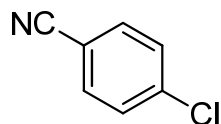
**Methyl 4-cyanobenzoate (2m):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **2m** (14.5 mg, 45% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 165.4, 133.9, 132.2, 130.1, 117.9, 116.4, 52.7.

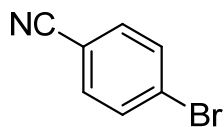
**4-Chlorobenzotrile (2n):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2n** (15.1 mg, 55% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 139.4, 133.3, 129.6, 117.9, 110.7.

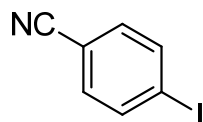
**4-Bromobenzotrile (2o):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2o** (18.4 mg, 51% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.63 (d,  $J = 8.5$  Hz, 2H), 7.52 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  133.4, 132.6, 128.0, 118.0, 111.2.

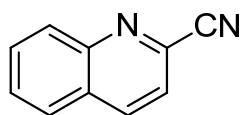
**4-Iodobenzonitrile (2p):**<sup>[3]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 150) give **2p** (26.5 mg, 58% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.84 (d,  $J = 8.4$  Hz, 2H), 7.36 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  138.5, 133.1, 118.2, 111.7, 100.3.

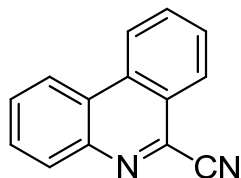
**Quinoline-2-carbonitrile (3a):**<sup>[6]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3a** (25.5 mg, 83% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.31 (d,  $J = 8.4$  Hz, 1H), 8.16 (d,  $J = 8.6$  Hz, 1H), 7.91-7.81 (m, 2H), 7.73-7.68 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  148.1, 137.5, 133.5, 131.2, 129.9, 129.4, 128.6, 127.7, 123.3, 117.5.

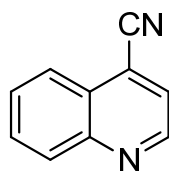
**Phenanthridine-6-carbonitrile (3b):**<sup>[7]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3b** (29.4 mg, 72% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.60 (d,  $J = 8.3$  Hz, 1H), 8.55-8.52 (m, 1H), 8.37 (d,  $J = 8.2$  Hz, 1H), 8.21-8.18 (m, 1H), 7.96-7.91 (m, 1H), 7.82-7.77 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  143.4, 135.6, 132.6, 132.2, 130.9, 129.9, 129.6, 128.7, 126.5, 125.2, 124.6, 122.3, 122.2, 115.7.

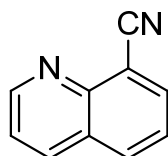
**Quinoline-4-carbonitrile (3c):**<sup>[8]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3c** (22.4 mg, 73% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.03 (d,  $J = 4.3$  Hz, 1H), 8.21-8.18 (m, 2H), 7.88-7.84 (m, 1H), 7.78-7.73 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  149.4, 148.1, 131.2, 130.3, 129.2, 125.7, 124.9, 124.8, 118.6, 115.5.

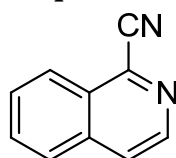
**Quinoline-8-carbonitrile (3d):**<sup>[9]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3d** (25.0 mg, 81% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.06 (dd,  $J = 4.2$  Hz,  $J = 1.6$  Hz, 1H), 8.23 (dd,  $J = 8.3$  Hz,  $J = 1.5$  Hz, 1H), 8.11-8.05 (m, 2H), 7.60 (t,  $J = 7.7$  Hz, 1H), 7.54 (dd,  $J = 8.3$  Hz,  $J = 4.2$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  152.4, 147.4, 136.4, 135.5, 132.9, 128.0, 125.8, 122.7, 117.2, 113.0.

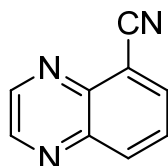
**Isoquinoline-1-carbonitrile (3e):**<sup>[10]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3e** (21.8 mg, 71% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.64 (d,  $J = 5.6$  Hz, 1H), 8.33 (d,  $J = 7.8$  Hz, 1H), 7.96-7.94 (m, 1H), 7.90 (d,  $J = 5.6$  Hz, 1H), 7.85-7.78 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  143.2, 135.8, 134.7, 131.7, 129.8, 129.3, 127.3, 125.3, 124.4, 115.8.

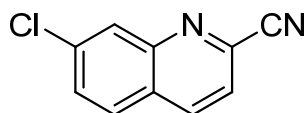
**Quinoxaline-5-carbonitrile (3f):**<sup>[11]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3f** (17.5 mg, 56% yield) as white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  9.03-8.99 (m, 2H), 8.36 (d,  $J = 8.5$  Hz, 1H), 8.20 (d,  $J = 7.2$  Hz, 1H), 7.86 (t,  $J = 7.9$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  146.7, 146.6, 142.6, 142.5, 135.9, 134.8, 129.4, 116.0, 113.3.

**7-Chloroquinoline-2-carbonitrile (3g):**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3g** (22.7 mg, 60% yield) as white solid. Mp: 135-136 °C.

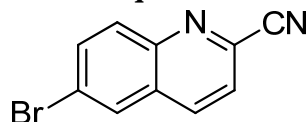
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.30 (d,  $J = 8.4$  Hz, 1H), 8.13 (s, 1H), 7.85-7.83 (m, 1H), 7.70 (d,  $J = 8.4$  Hz, 1H), 7.66-7.63 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  148.4, 137.4, 137.4, 134.6, 130.5, 128.9, 128.8, 127.0, 123.5, 117.1.



MS (EI): 188 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>10</sub>H<sub>6</sub>CIN<sub>2</sub> (M+H)<sup>+</sup> 189.0214, found 189.0214.

IR (neat)  $\nu$  3431, 3421, 3057, 3011, 2918, 2235, 1609, 1583, 1491, 1410, 1068, 926, 773, 635, 598, 478 cm<sup>-1</sup>.

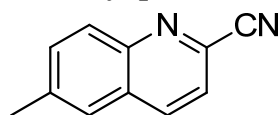
**6-Bromoquinoline-2-carbonitrile (3h):**<sup>[12]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3h** (31.0 mg, 67% yield) as white solid.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz):  $\delta$  8.60 (d, *J* = 8.5 Hz, 1H), 8.41 (s, 1H), 8.08-8.00 (m, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz):  $\delta$  145.9, 137.6, 134.6, 133.4, 131.2, 130.3, 129.7, 124.7, 122.9, 117.4.

**6-Methylquinoline-2-carbonitrile (3i):**



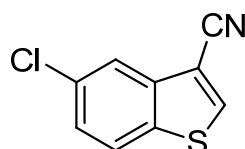
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3i** (16.4 mg, 49% yield) as white solid. Mp: 127-128 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.19 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.67-7.64 (m, 3H), 2.58 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  146.9, 140.0, 136.6, 133.6, 132.6, 129.6, 128.7, 126.5, 123.4, 117.7, 21.8.

MS (EI): 168 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>2</sub> (M+H)<sup>+</sup> 169.0760, found 169.0759.

IR (neat)  $\nu$  3447, 3421, 2918, 2230, 1620, 1587, 1555, 1489, 1375, 1219, 893, 831, 447 cm<sup>-1</sup>.

**5-Chlorobenzo[*b*]thiophene-3-carbonitrile (3j):**



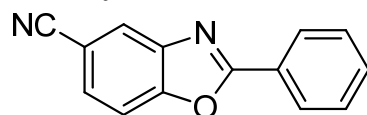
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 50) give **3j** (20.6 mg, 53% yield) as white solid. Mp: 134-135 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.17 (s, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.45 (dd, *J* = 8.6 Hz, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  139.1, 138.4, 136.6, 132.7, 126.9, 123.8, 122.2, 113.7, 106.6.

MS (EI): 193 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>9</sub>H<sub>3</sub>CINS (M-H)<sup>-</sup> 191.9680, found 191.9680.

IR (neat)  $\nu$  3421, 3099, 2924, 2228, 1651, 1589, 1549, 1497, 1423, 1290, 1252, 1078, 858, 827, 797, 621, 444 cm<sup>-1</sup>.

**2-Phenylbenzo[*d*]oxazole-5-carbonitrile (3k):**



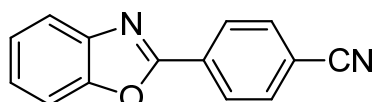
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3k** (22.4 mg, 51% yield) as white solid. Mp: 189-190 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.24 (d, *J* = 7.2 Hz, 2H), 8.06 (s, 1H), 7.68-7.62 (m, 2H), 7.61-7.53 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 165.1, 153.1, 142.5, 132.5, 129.1, 129.1, 128.0, 126.0, 124.5, 118.7, 111.8, 108.5.

MS (EI): 220 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>2</sub>O (M+H)<sup>+</sup> 221.0709, found 221.0708.

IR (neat) ν 3441, 3412, 3050, 2224, 1620, 1551, 1483, 1470, 1450, 1429, 1263, 1205, 1053, 814, 779, 708, 690, 627 cm<sup>-1</sup>.

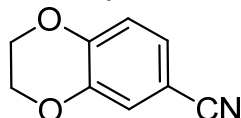
**4-(Benzo[d]oxazol-2-yl)benzonitrile (3l):**<sup>[13]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3l** (29.2 mg, 66% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.32 (d, *J* = 8.4 Hz, 2H), 7.80-7.77 (m, 3H), 7.60-7.58 (m, 1H), 7.43-7.36 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 160.8, 150.8, 141.8, 132.6, 131.0, 127.8, 126.1, 125.1, 120.5, 118.1, 114.6, 110.8.

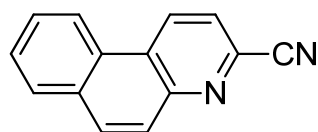
**2,3-Dihydrobenzo[b][1,4]dioxine-6-carbonitrile (3m):**<sup>[14]</sup>



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give **3m** (18.6 mg, 58% yield) as white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.14-7.12 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 4.33-4.26 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 147.7, 143.8, 125.9, 121.2, 118.8, 118.2, 104.5, 64.5, 64.1.

**Benzo[f]quinoline-3-carbonitrile (3n):**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **3n** (26.6 mg, 65% yield) as white solid. Mp: 152-153 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.99 (d, *J* = 8.5 Hz, 1H), 8.59-8.57 (m, 1H), 8.05-8.02 (m, 1H), 7.96-7.92 (m, 2H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.77-7.72 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 148.6, 132.9, 132.7, 132.4, 131.7, 129.0, 129.0, 128.5, 127.9, 127.4, 127.0, 124.2, 123.2, 117.6.

MS (EI): 204 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>14</sub>H<sub>9</sub>N<sub>2</sub> (M+H)<sup>+</sup> 205.0760, found 205.0758.

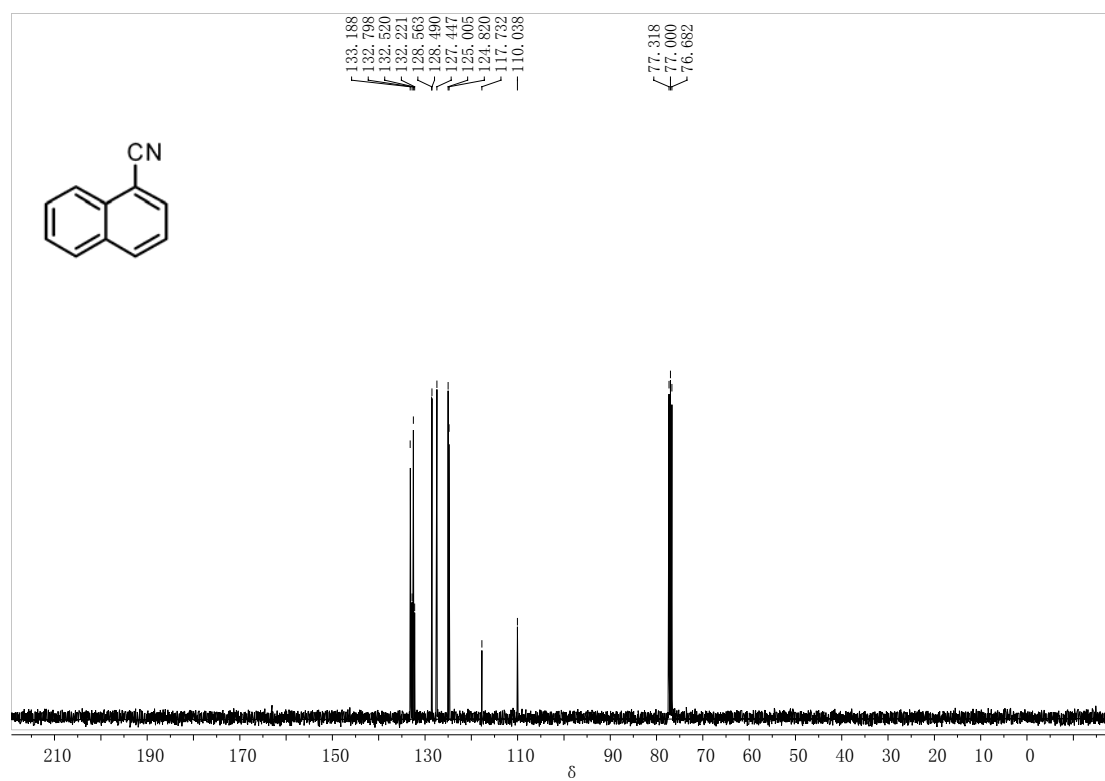
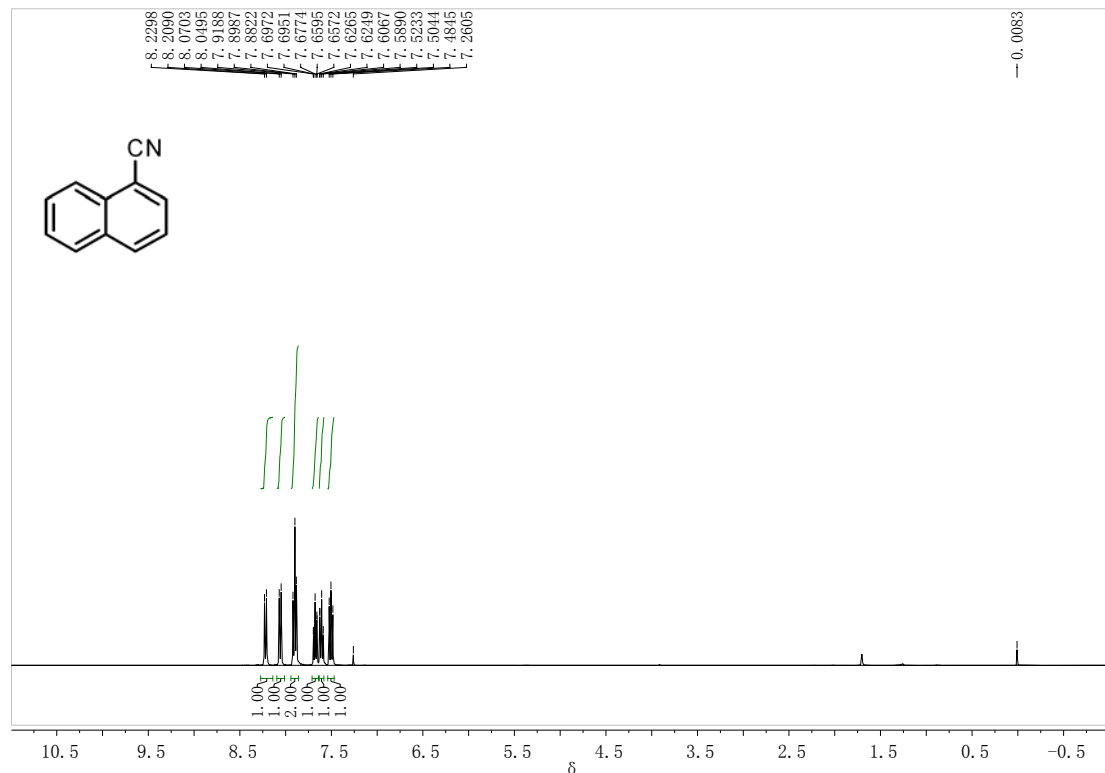
IR (neat) ν 3057, 2228, 1603, 1570, 1485, 1410, 1335, 1323, 999, 829, 754, 723, 457 cm<sup>-1</sup>.

## 5. References

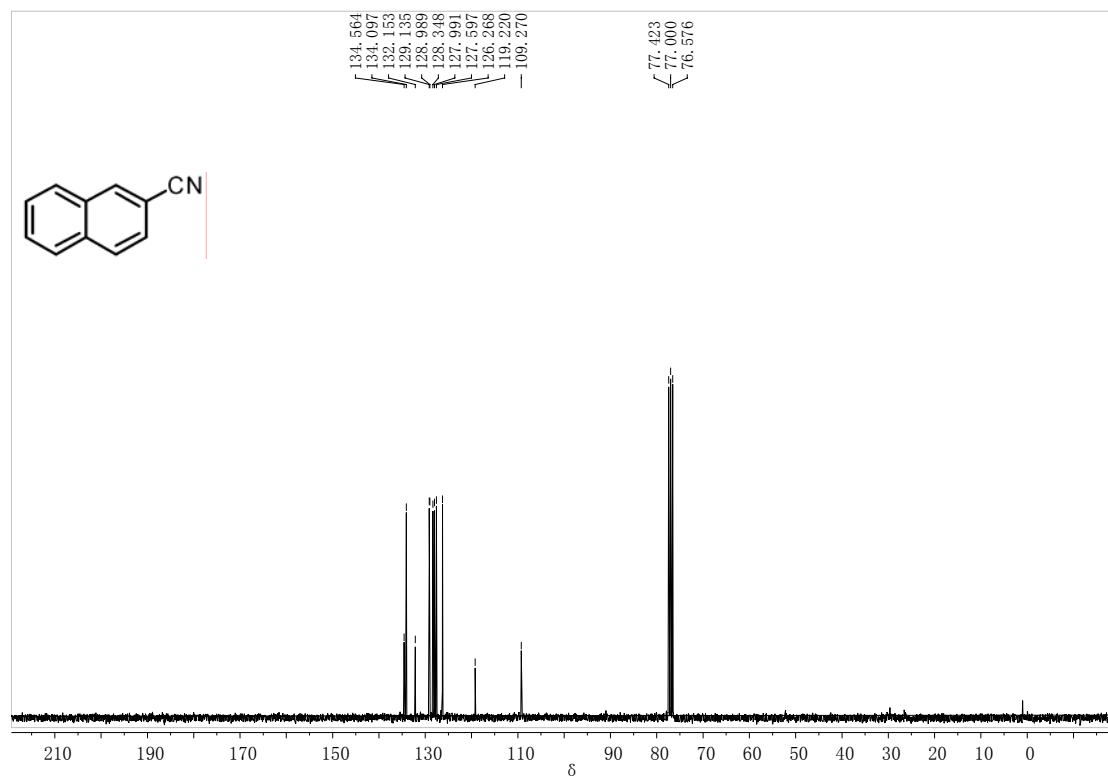
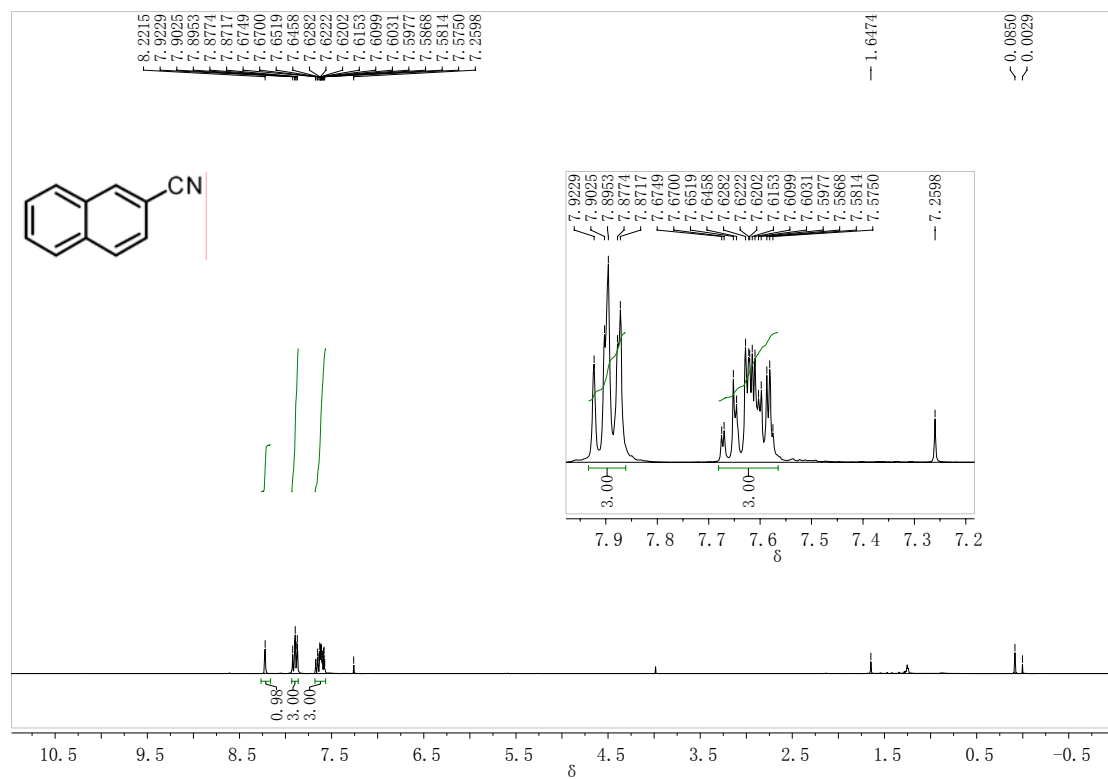
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- 2 B. V. Rokade and K. R. Prabhu, *J. Org. Chem.*, 2012, **77**, 5364.
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## 6. Copies of the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

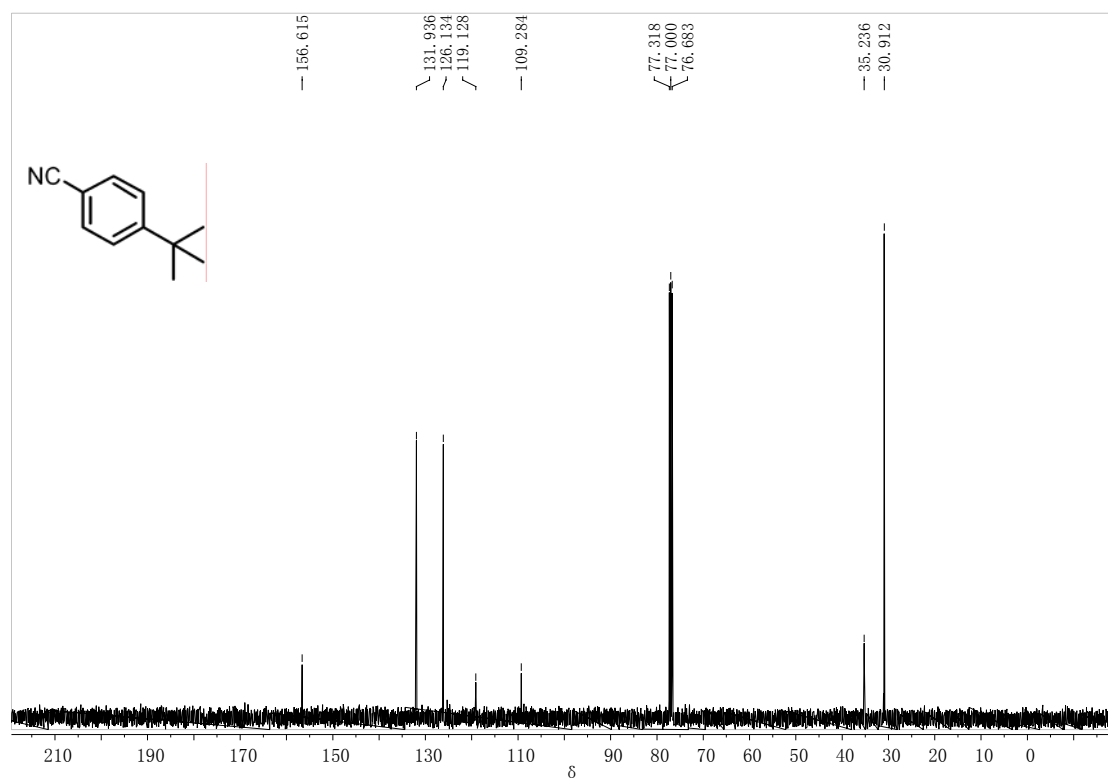
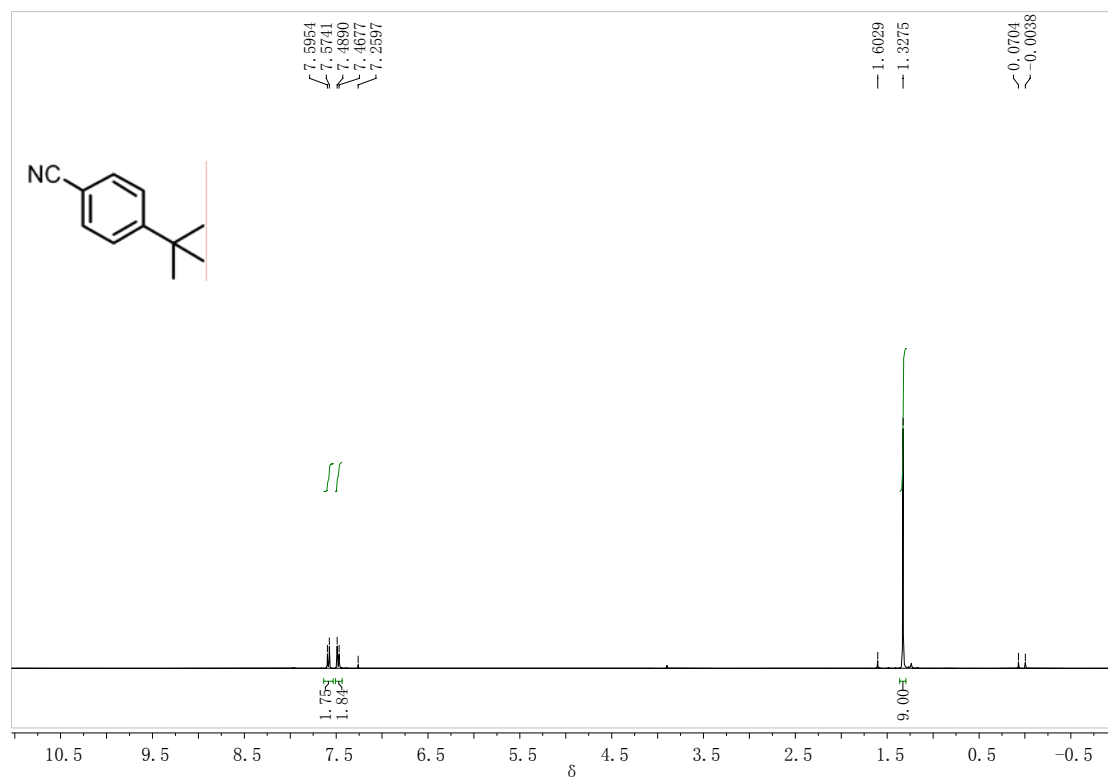
### 1-Naphthonitrile (2a)



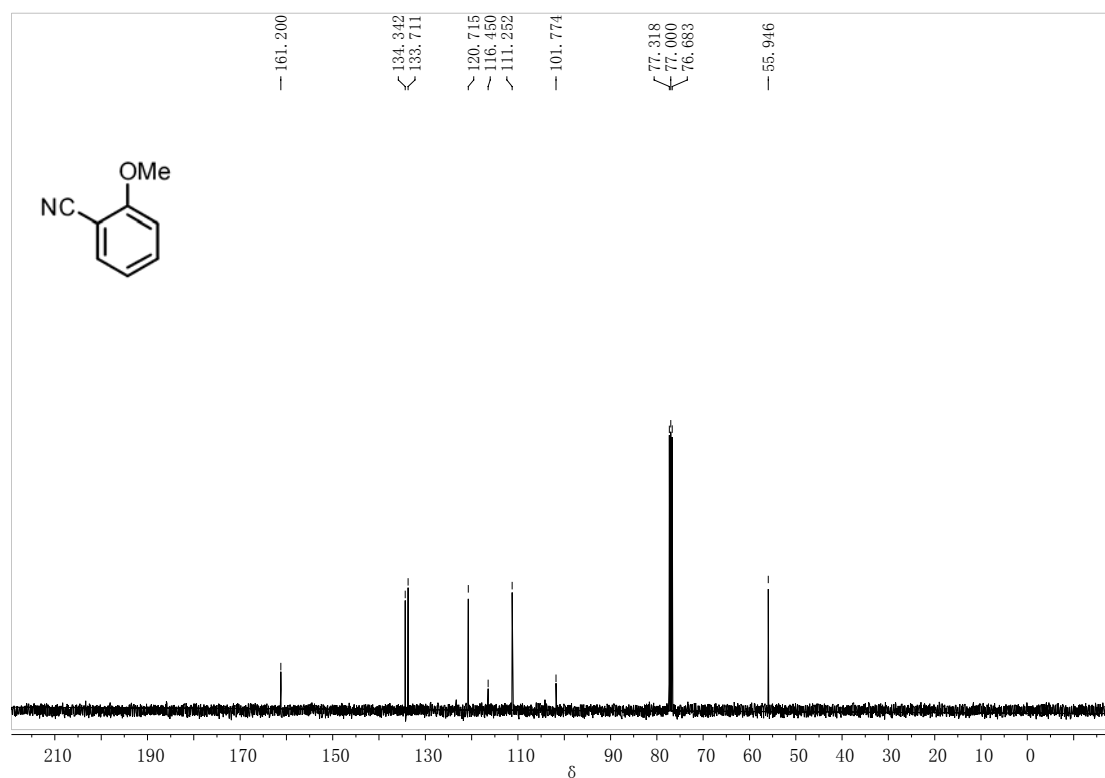
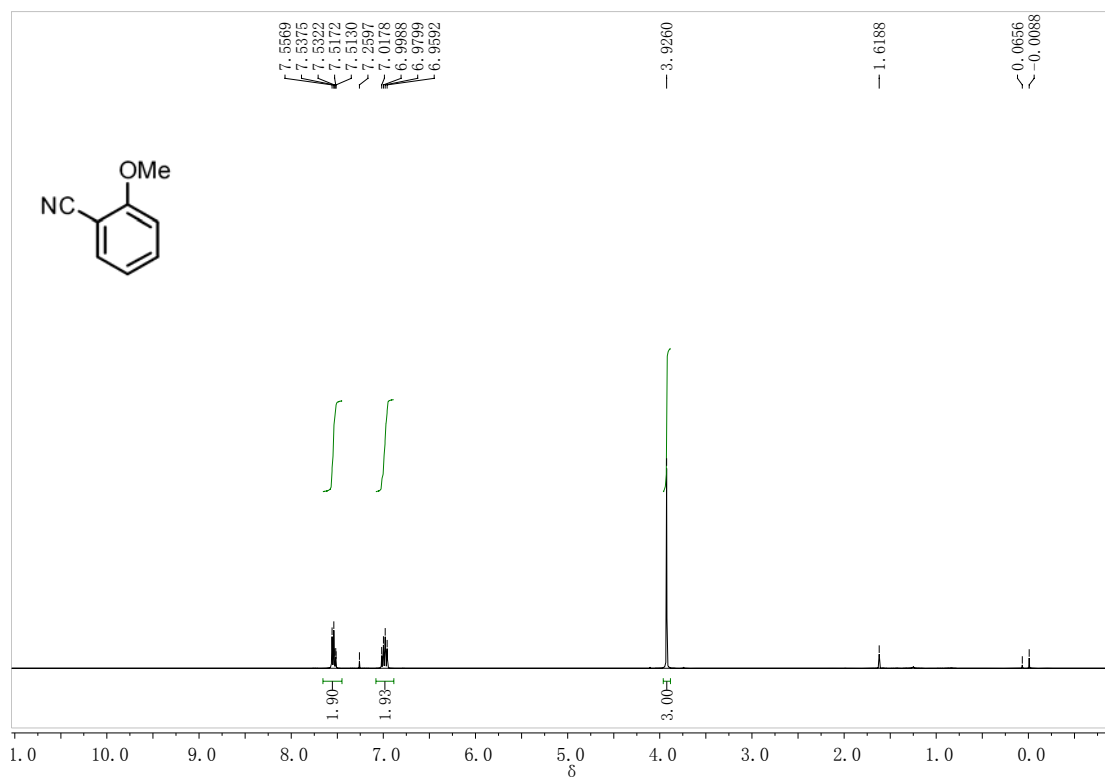
## 2-Naphthonitrile (2b)



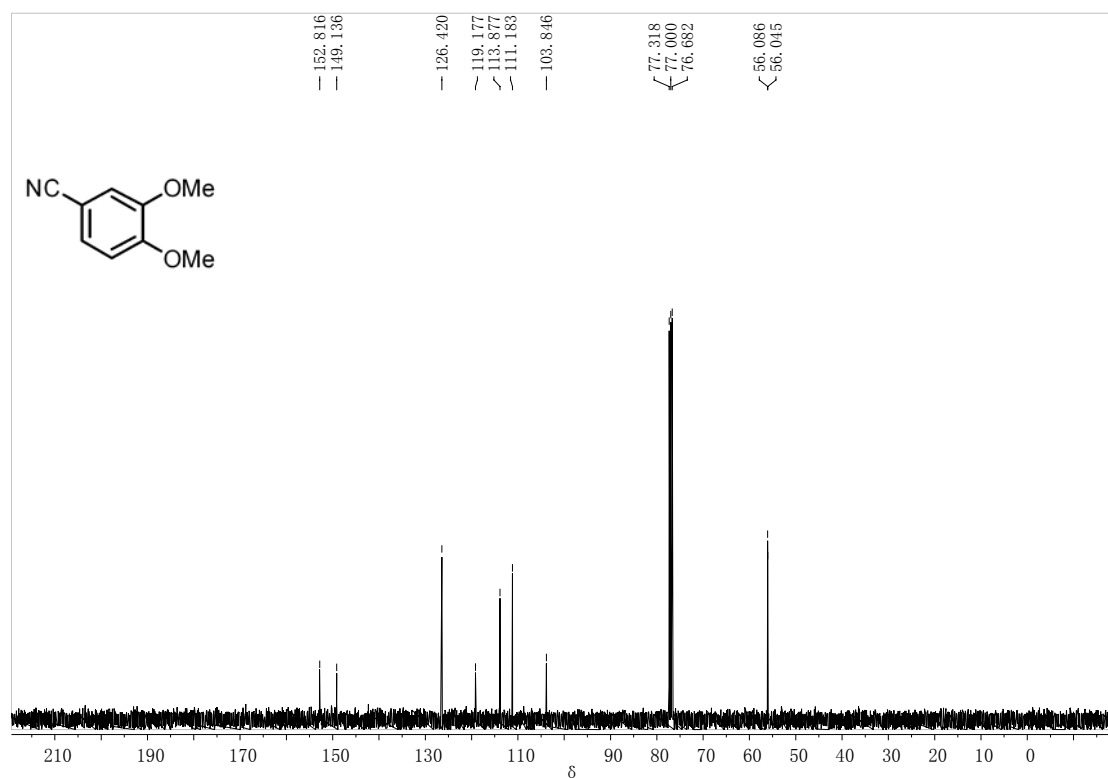
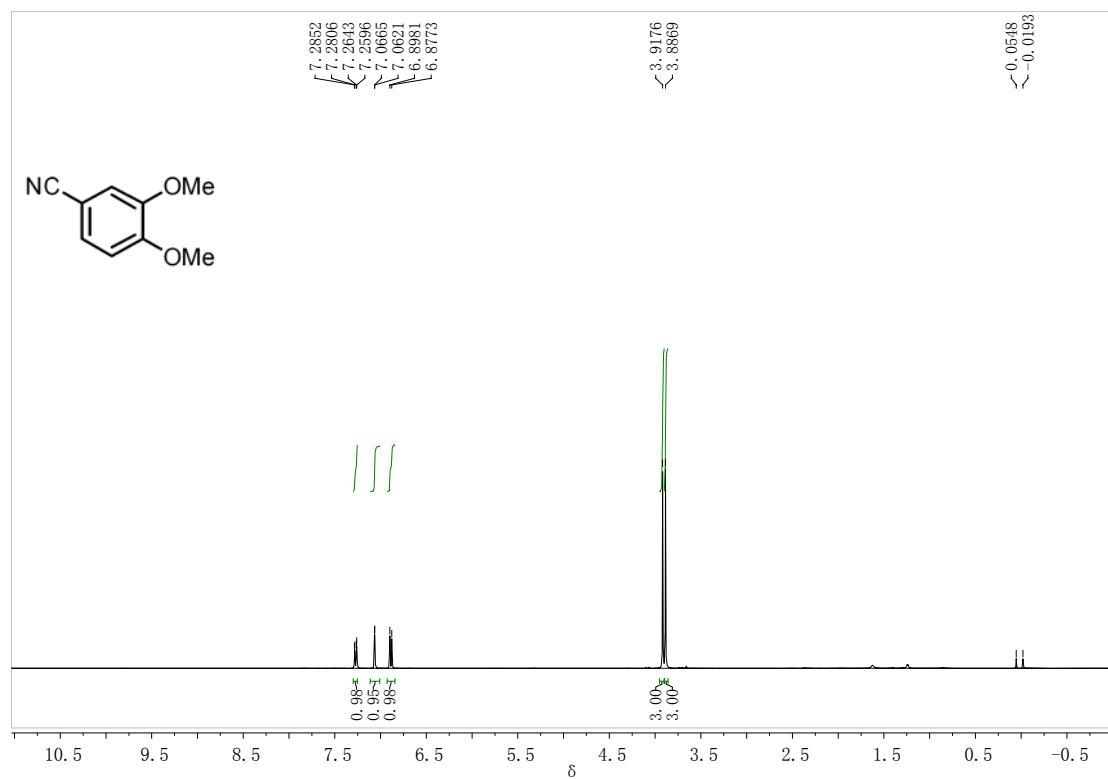
### 4-(*tert*-Butyl)benzonitrile (2c)



## 2-Methoxybenzonitrile (2d)

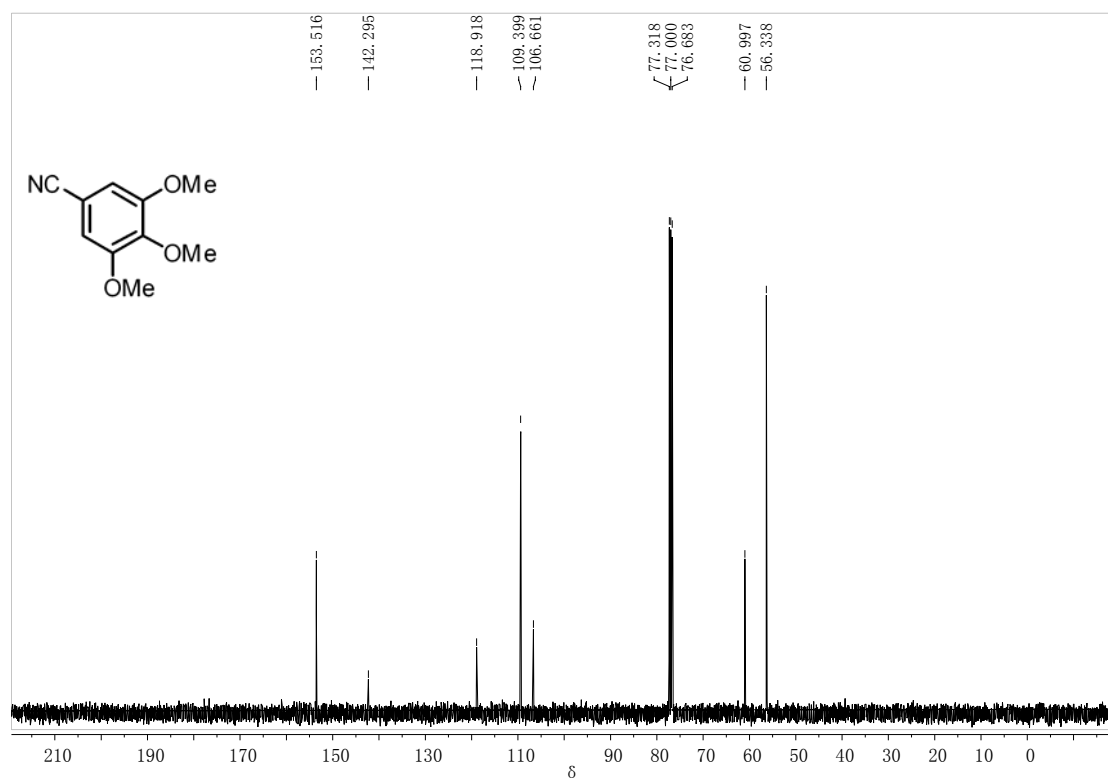
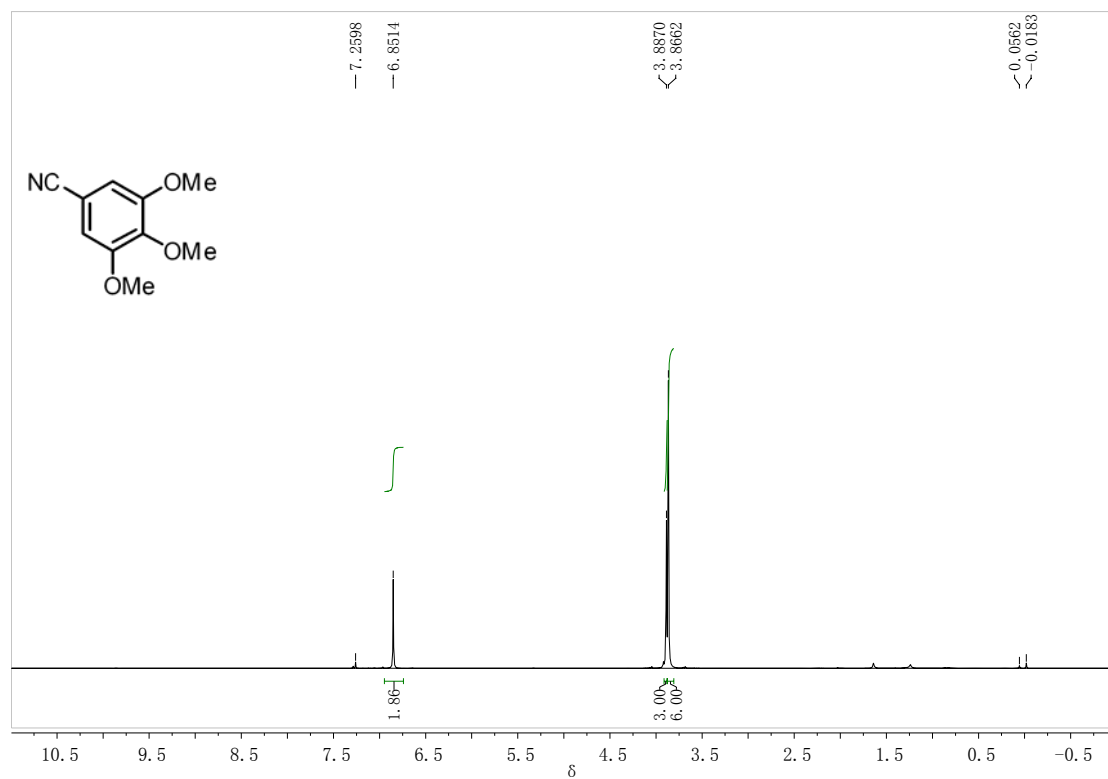


### 3,4-Dimethoxybenzonitrile (2e)

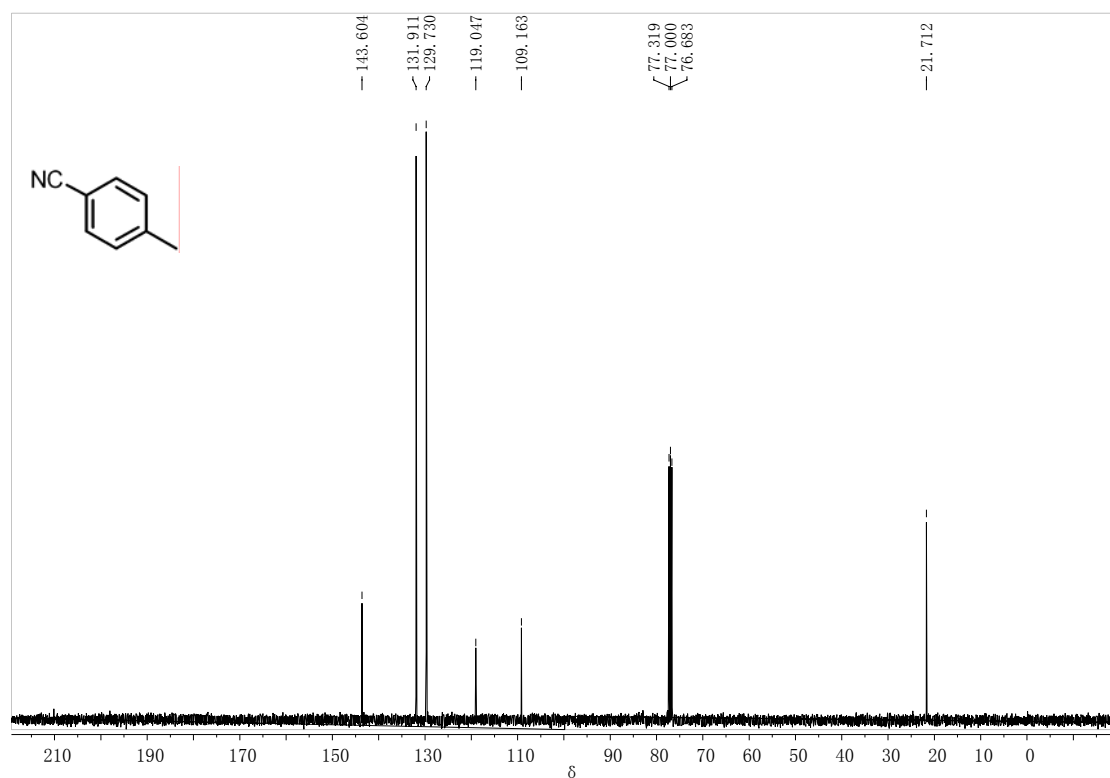
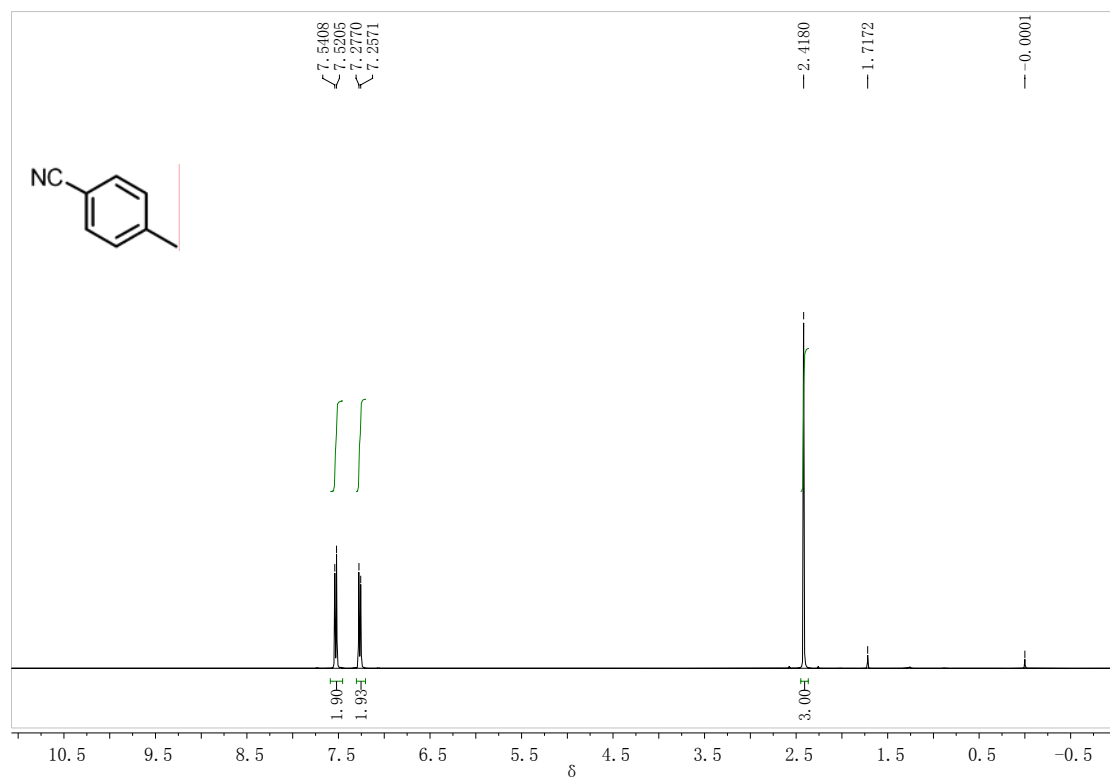




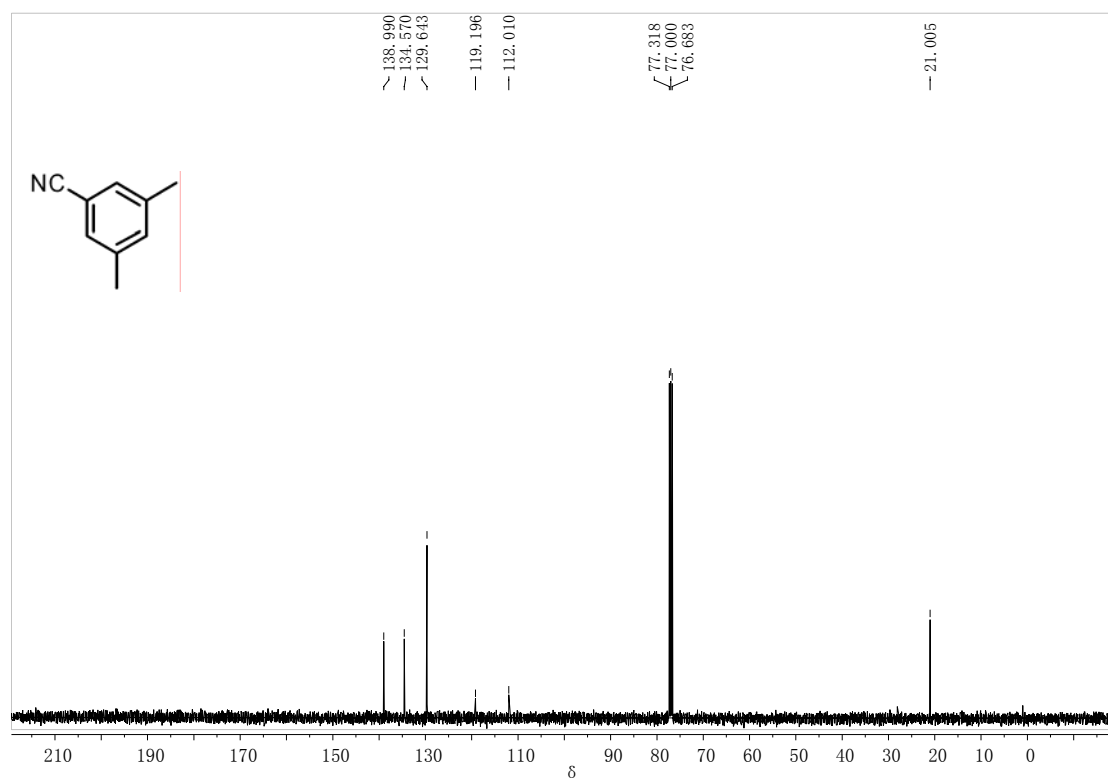
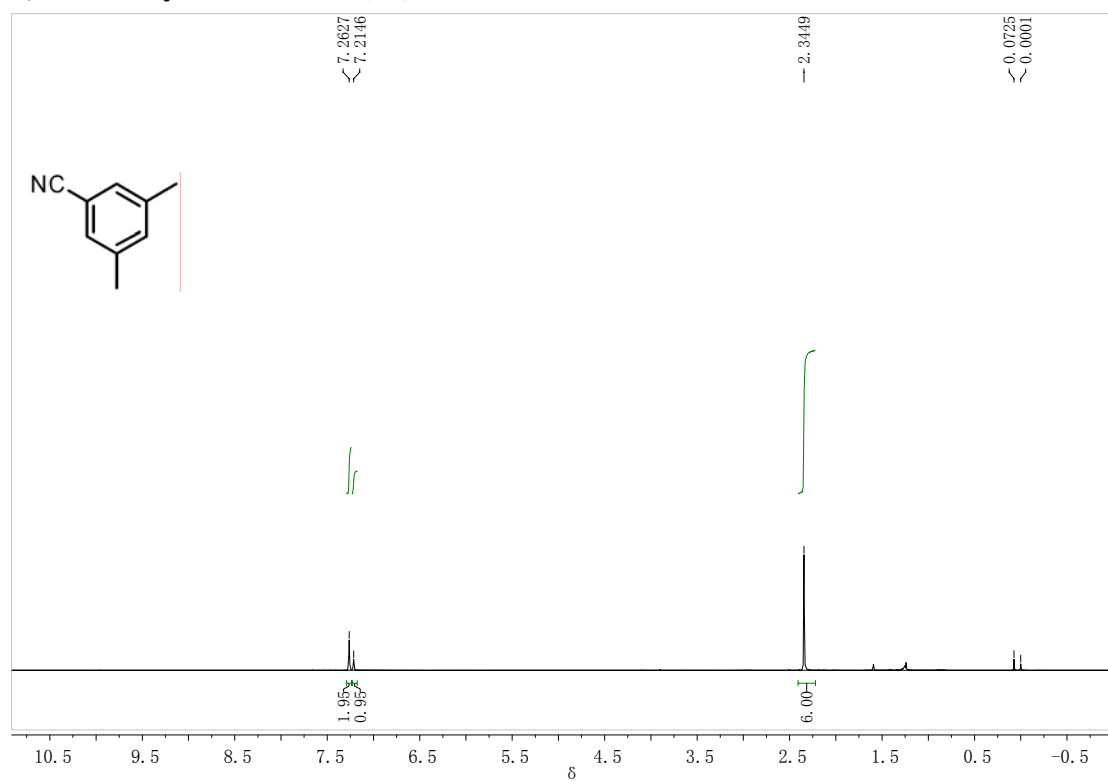
### 3,4,5-Trimethoxybenzonitrile (2f)



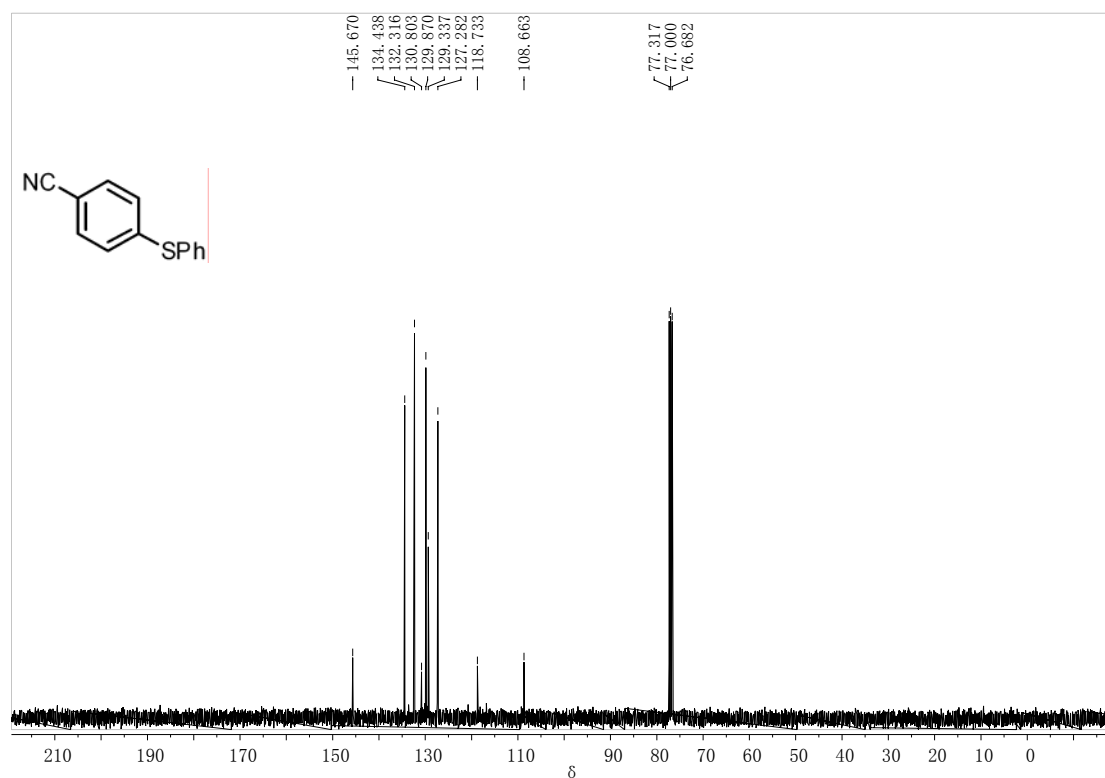
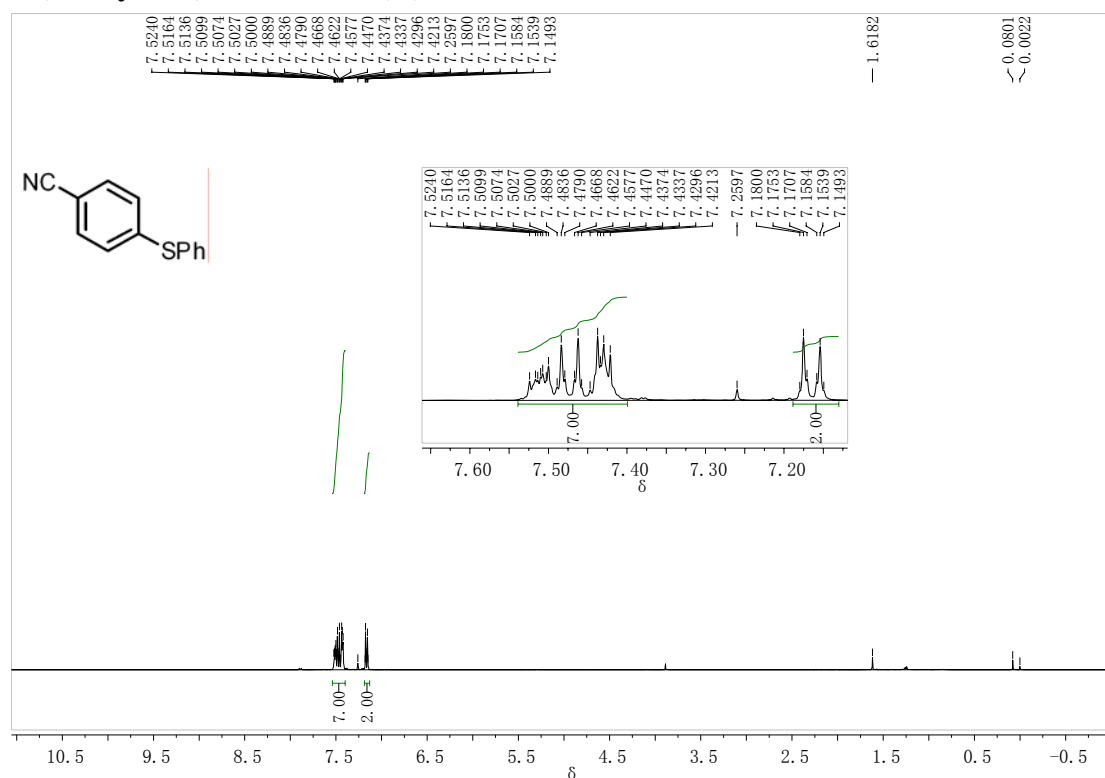
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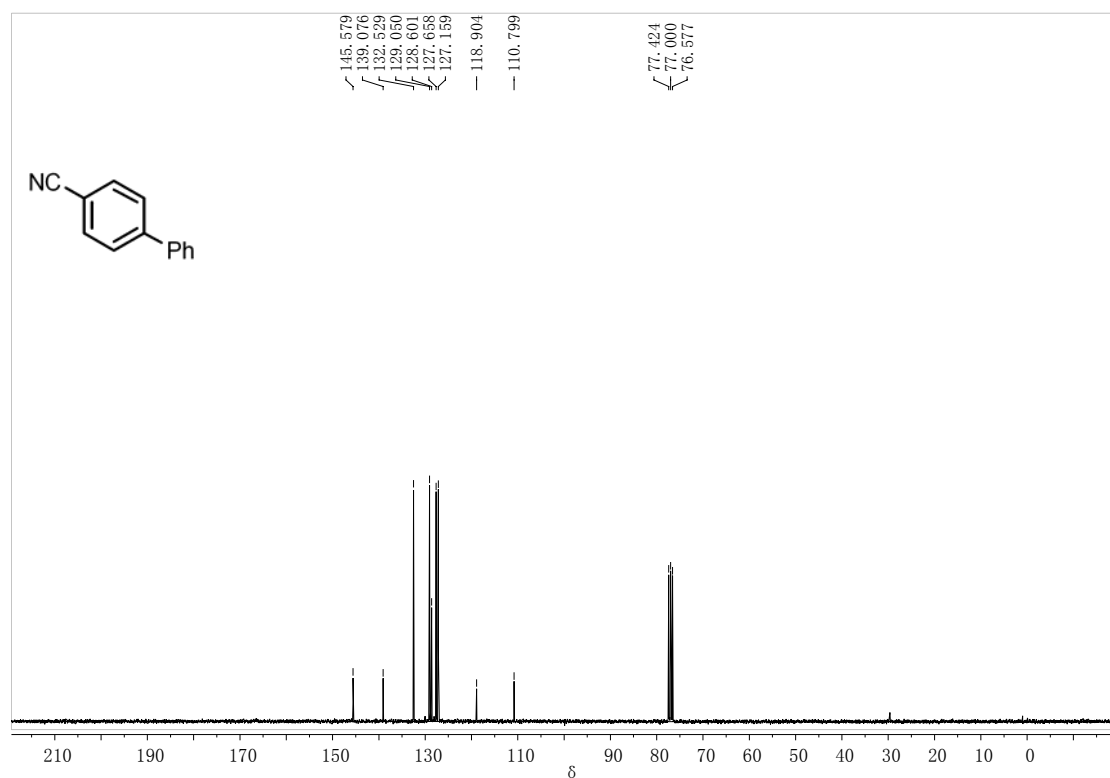
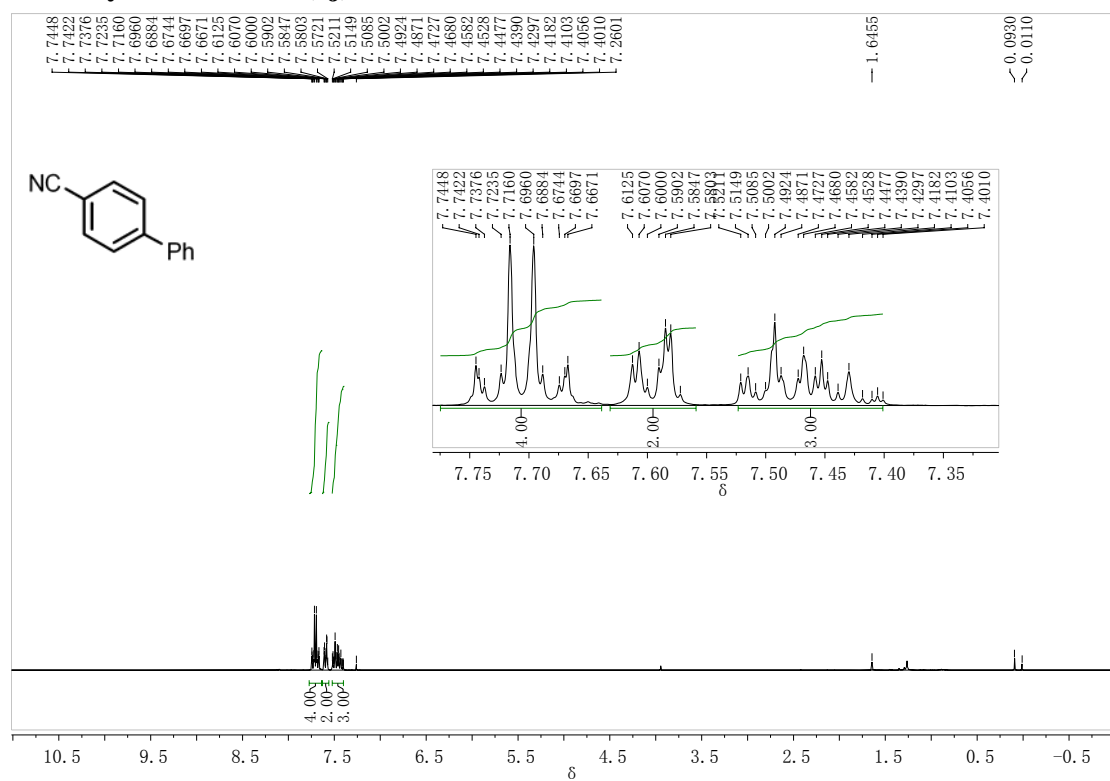
### 3,5-Dimethylbenzonitrile (2h)



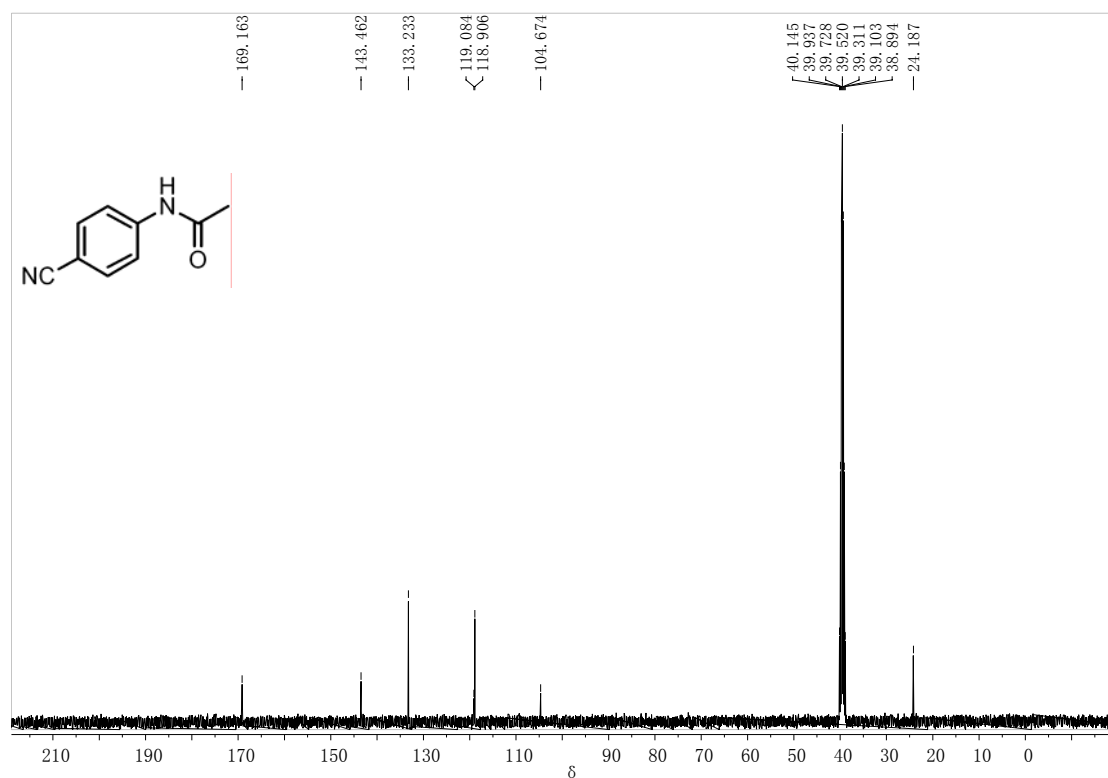
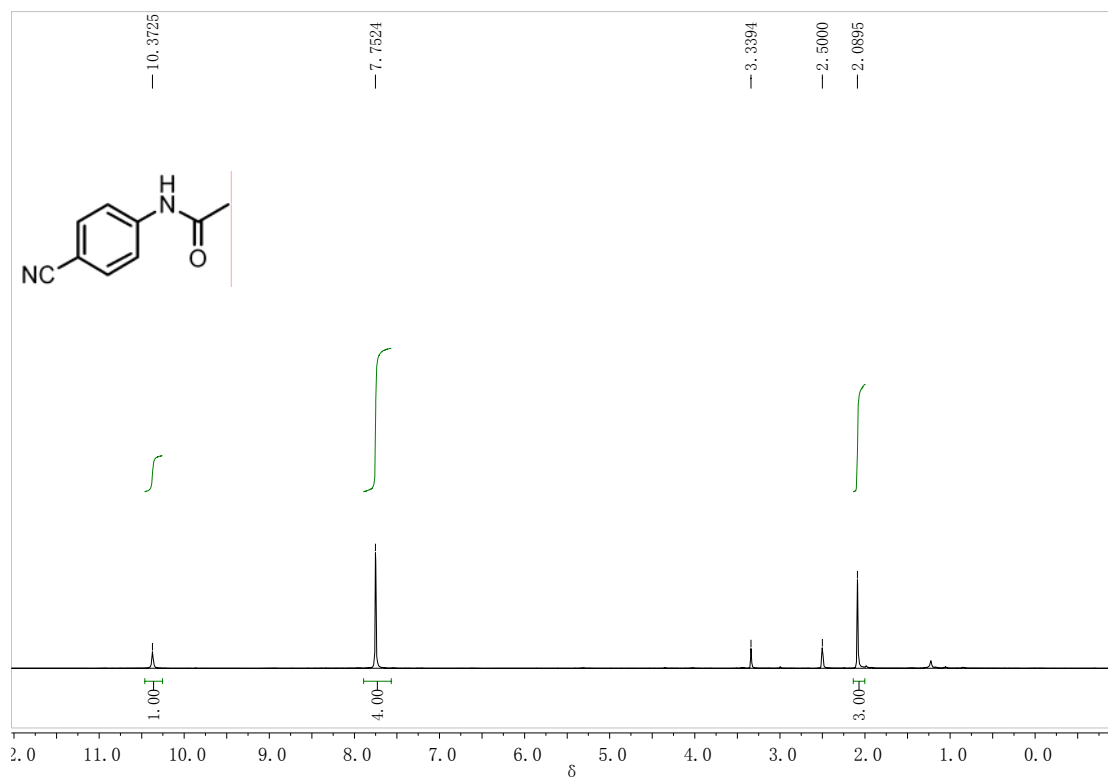
### 4-(Phenylthio)benzonitrile (2i)



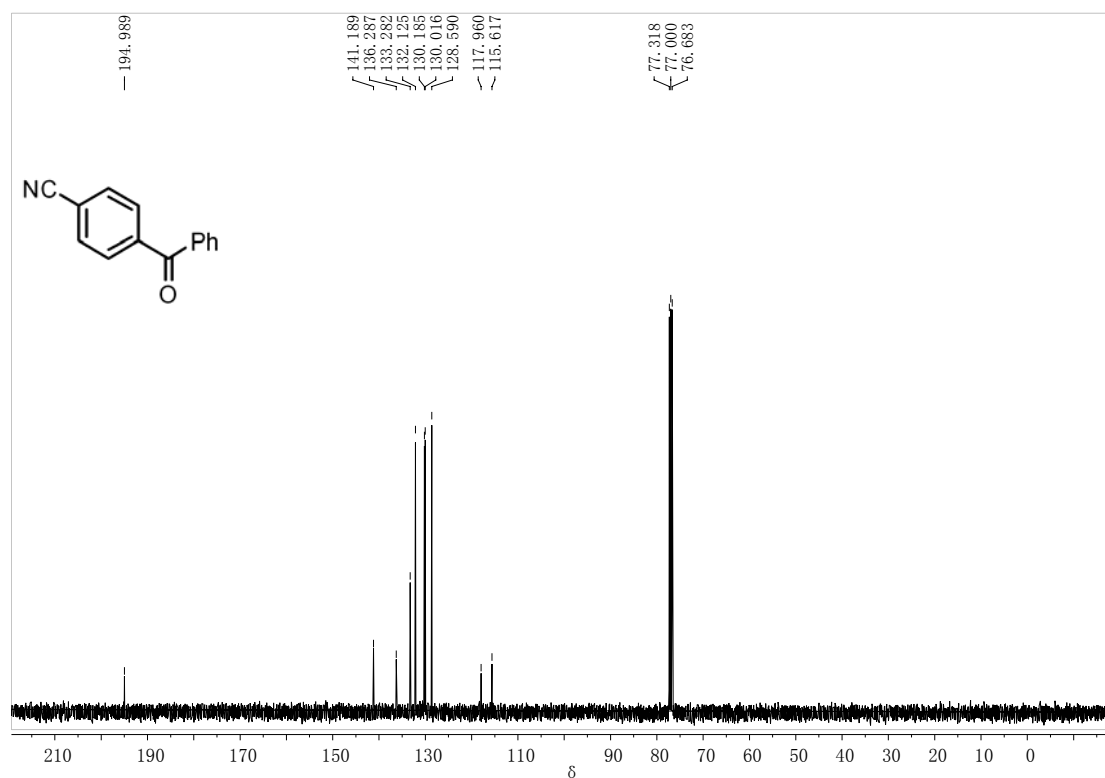
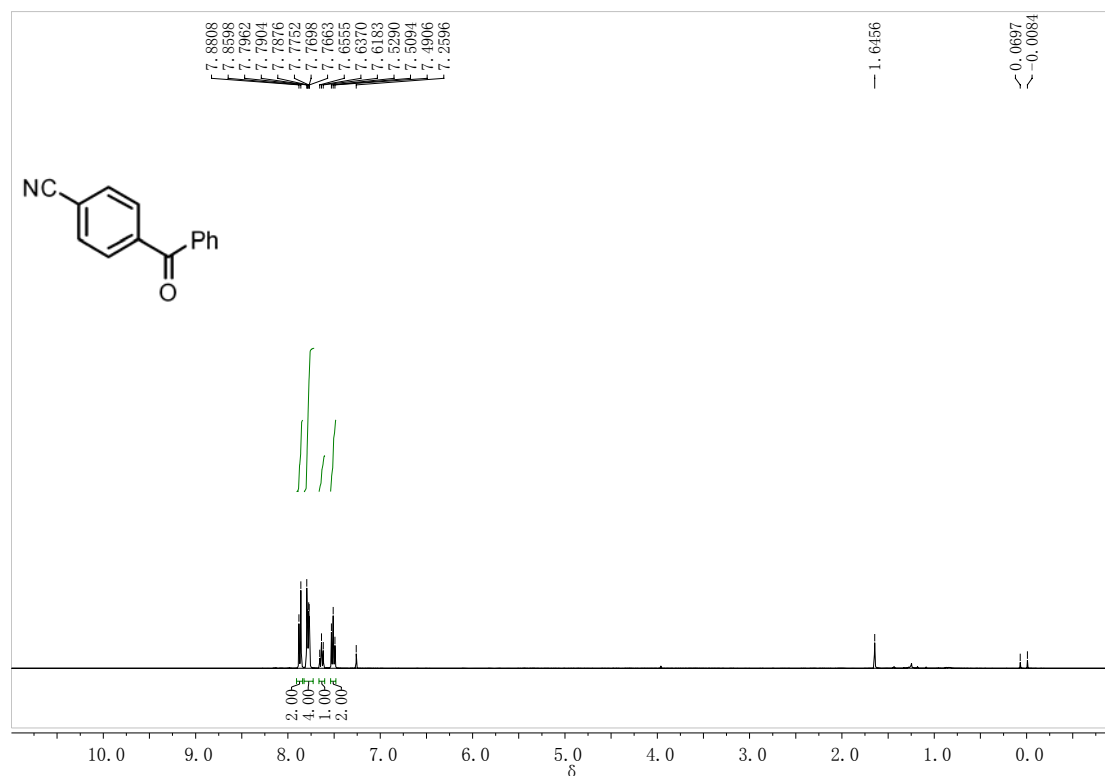
### 4-Phenylbenzonitrile (2j)



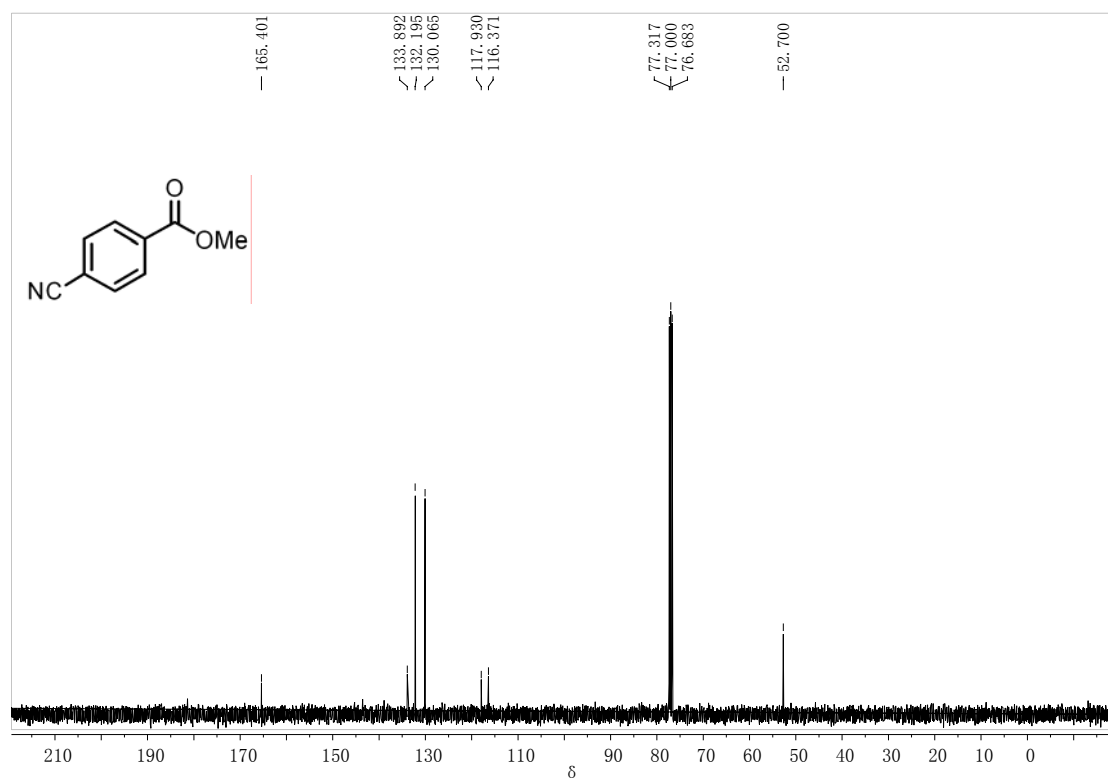
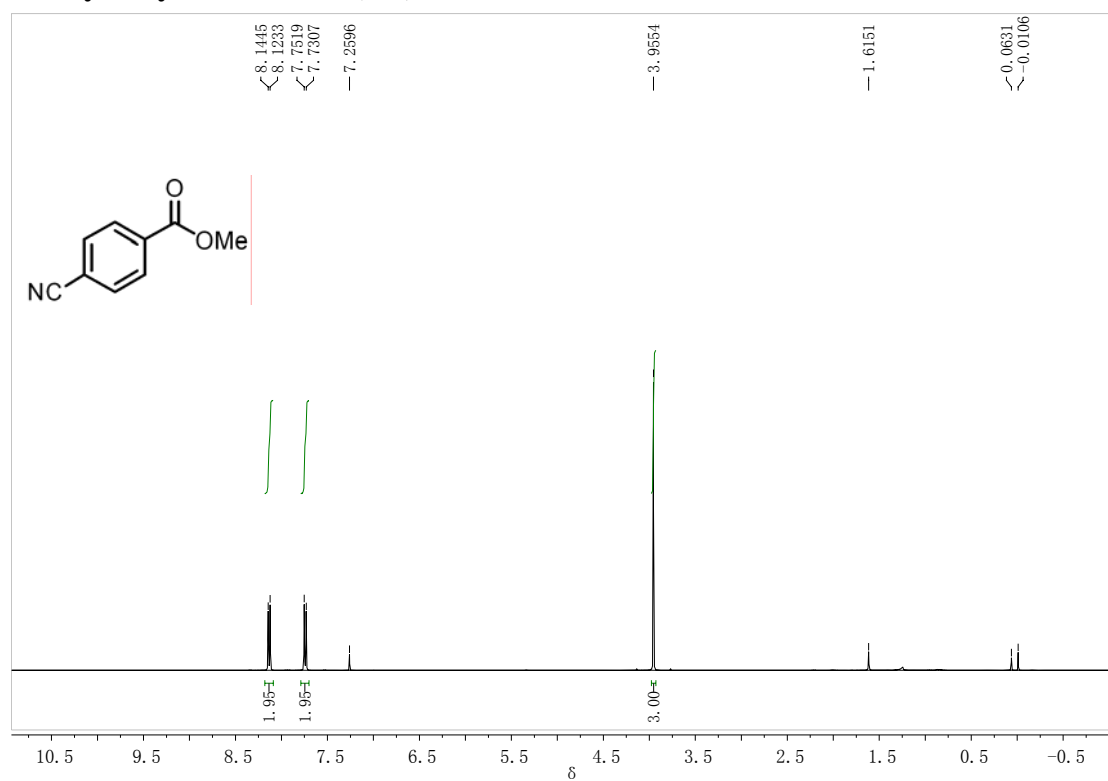
# N-(4-cyanophenyl)acetamide (2k)



# 4-Benzoylbenzonitrile (2l)

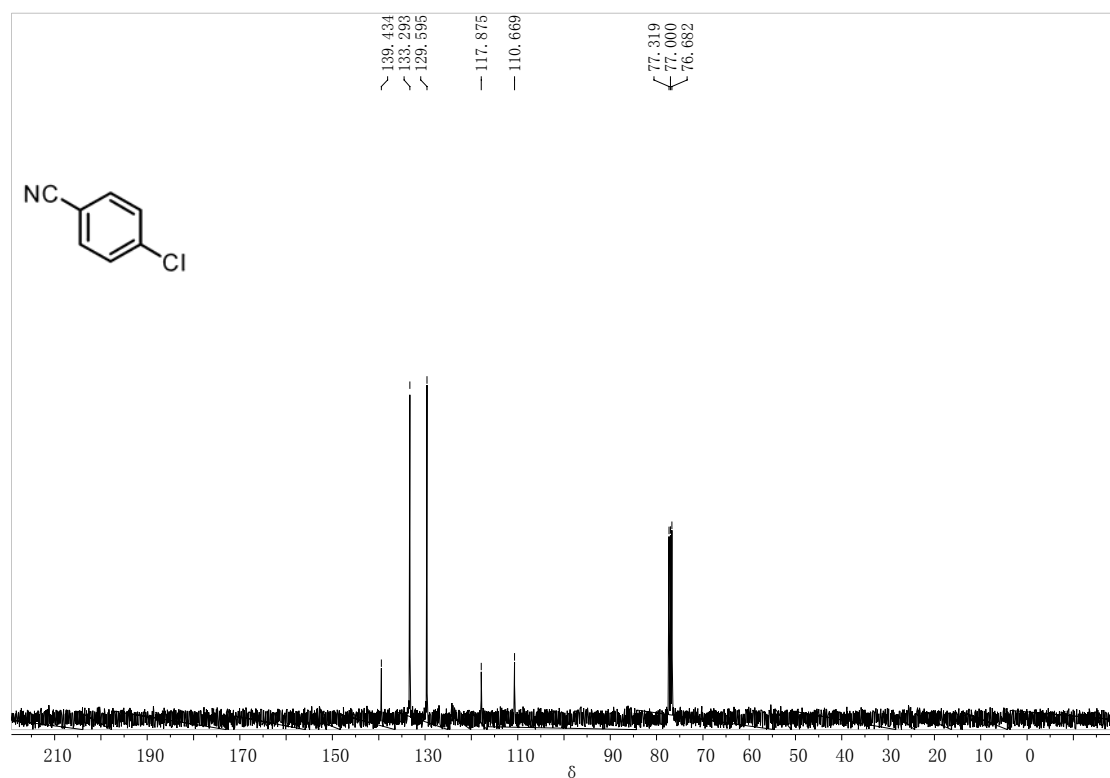
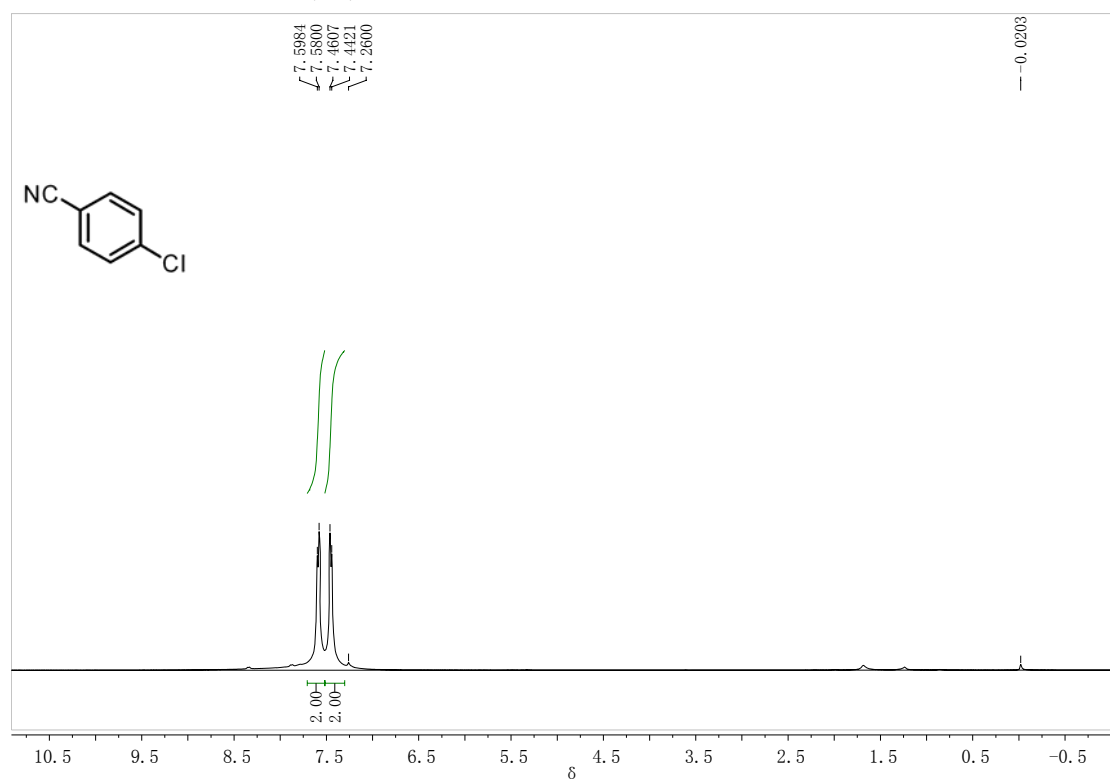


# Methyl 4-cyanobenzoate (2m)

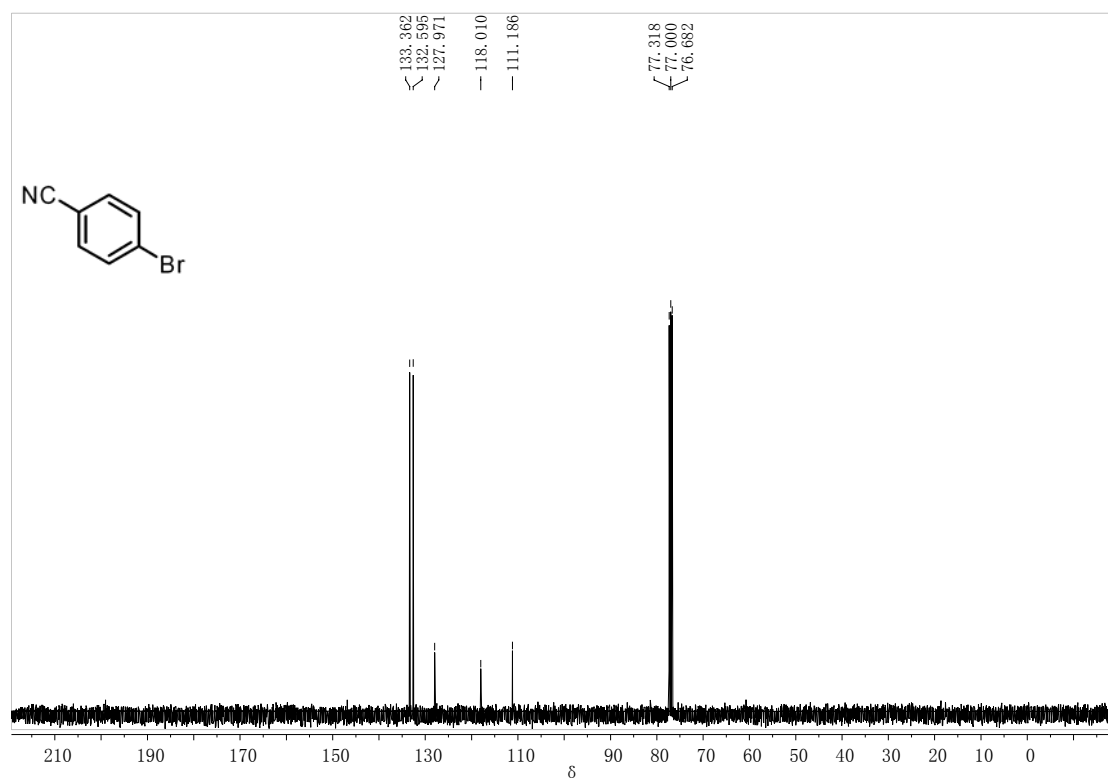
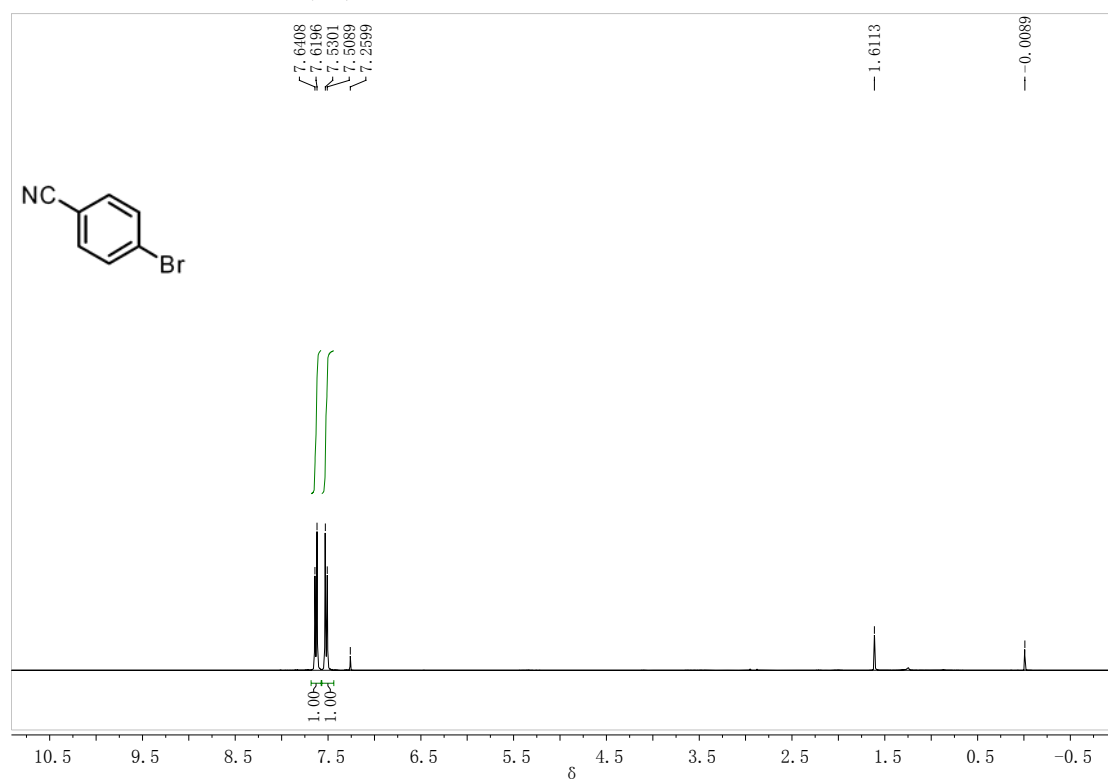




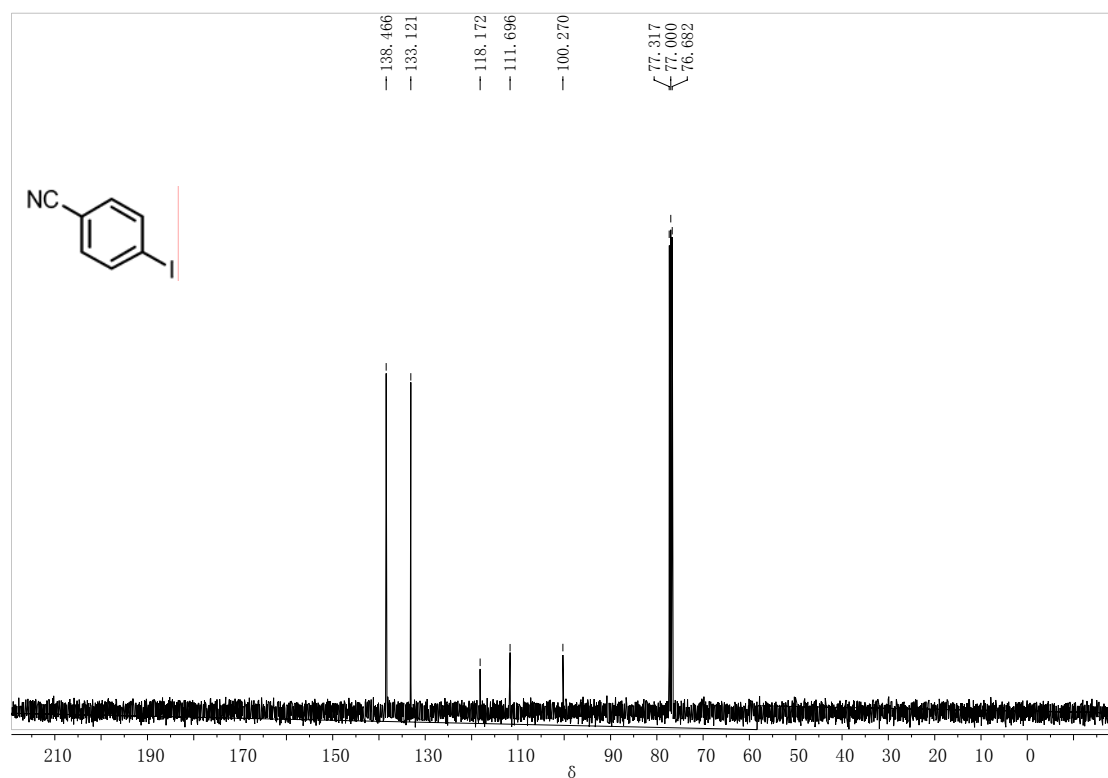
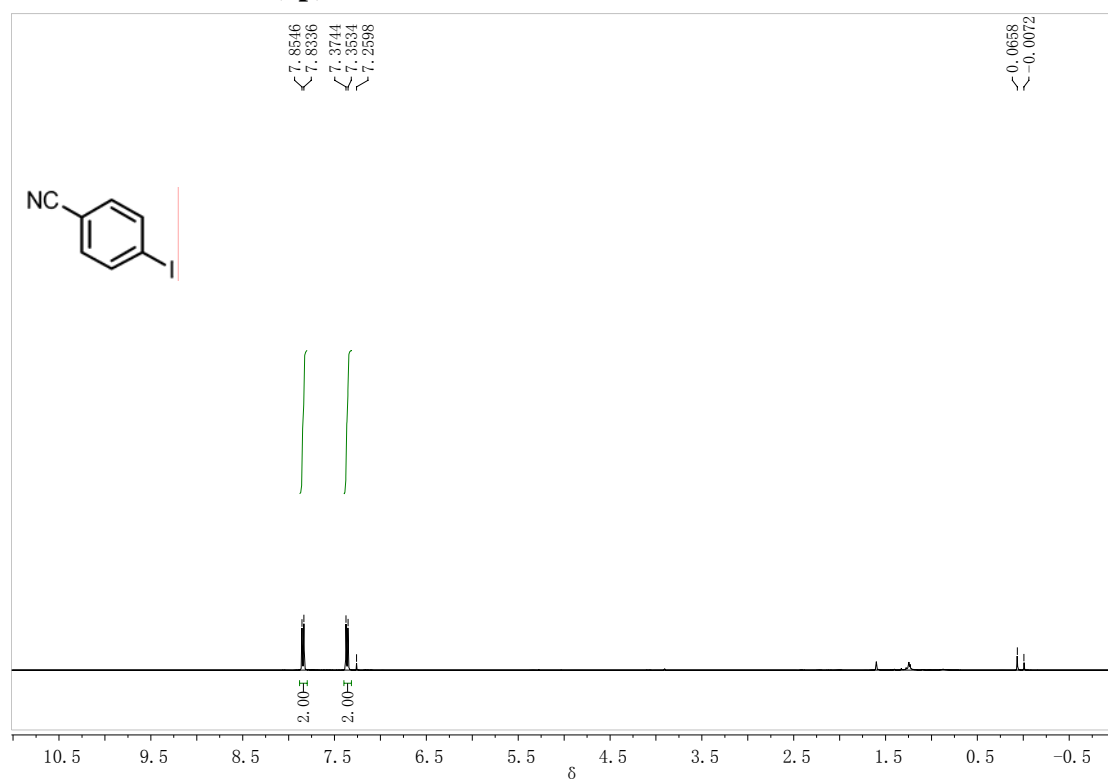
### 4-Chlorobenzonitrile (2n)



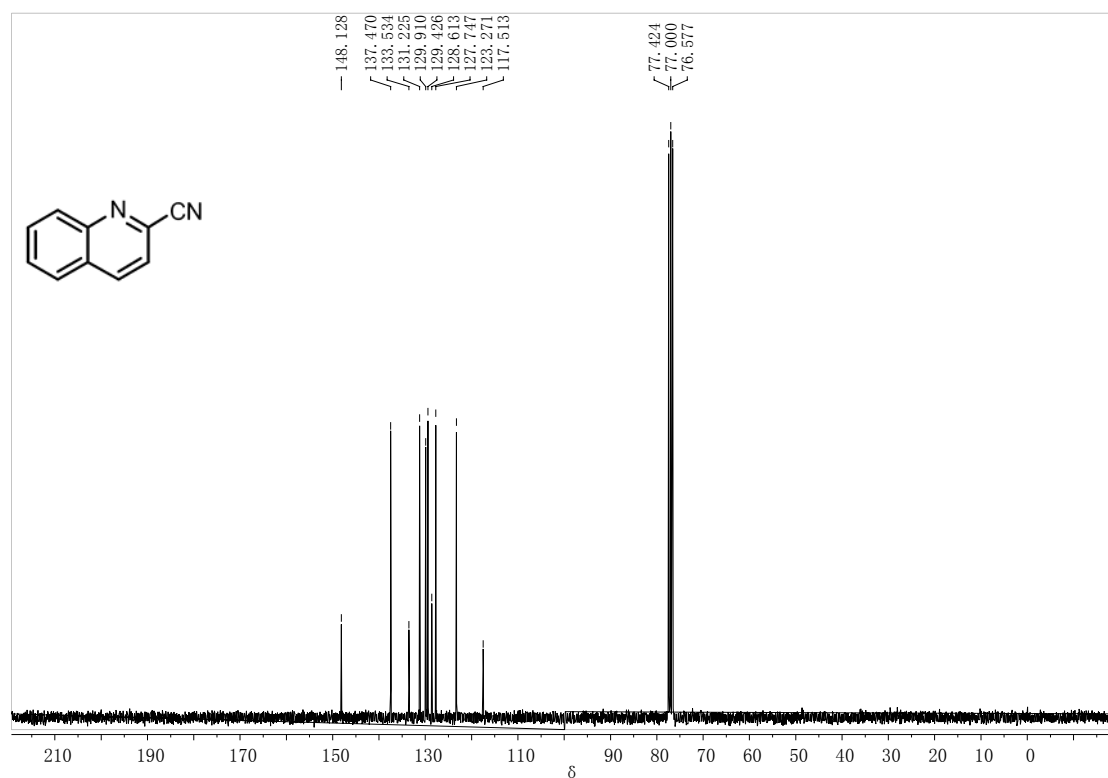
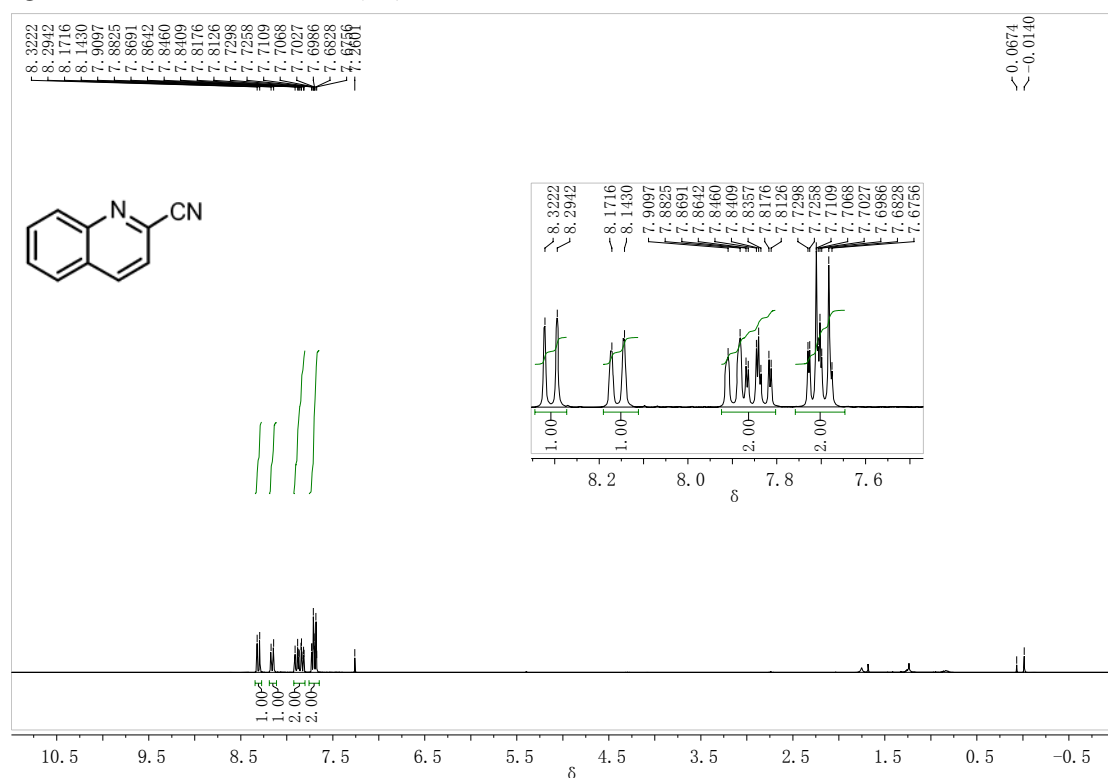
### 4-Bromobenzonitrile (2o)



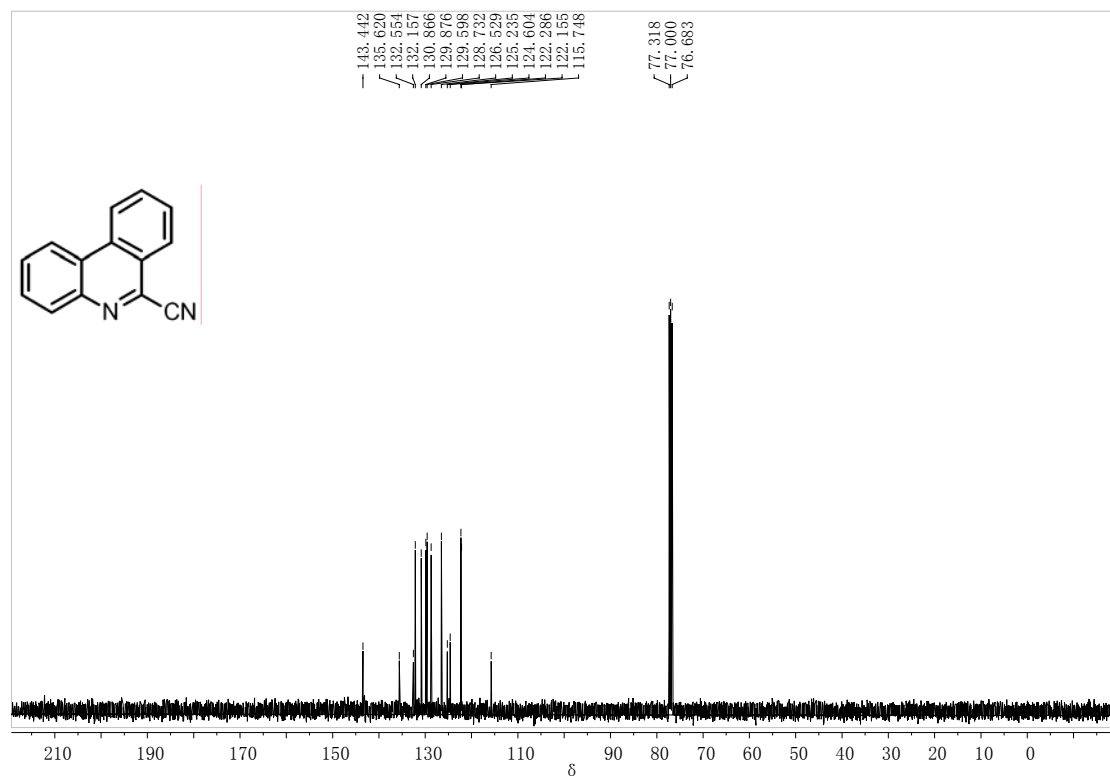
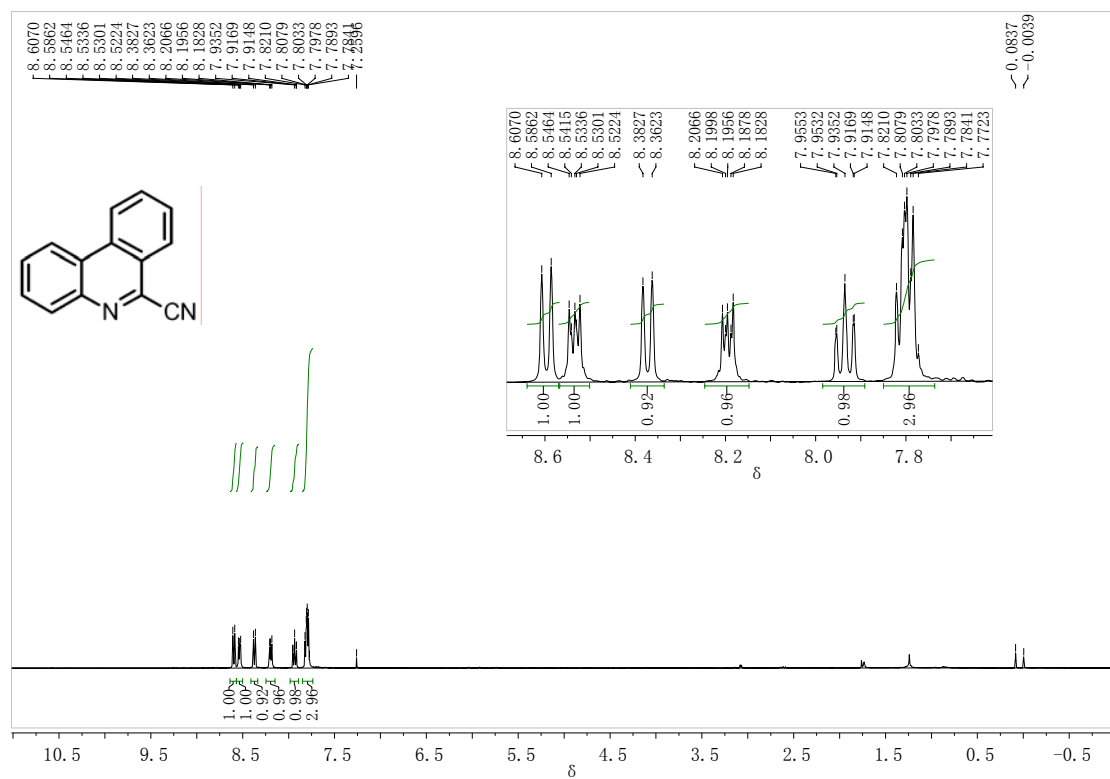
### 4-Iodobenzonitrile (2p)



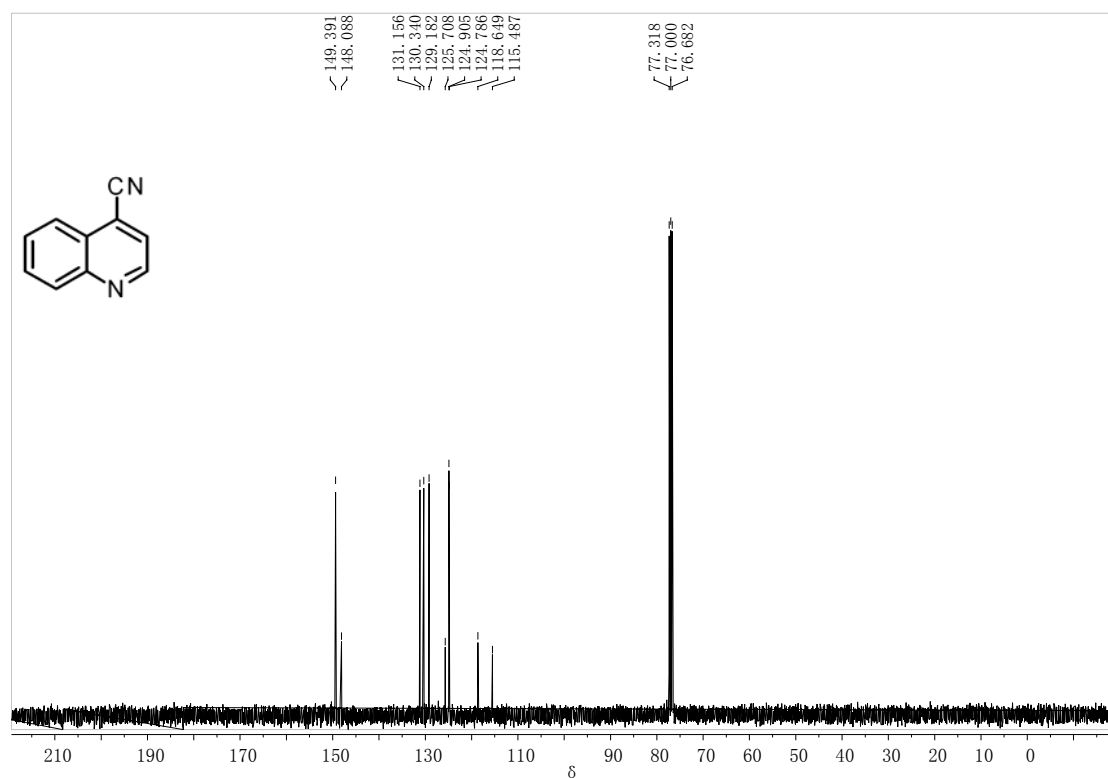
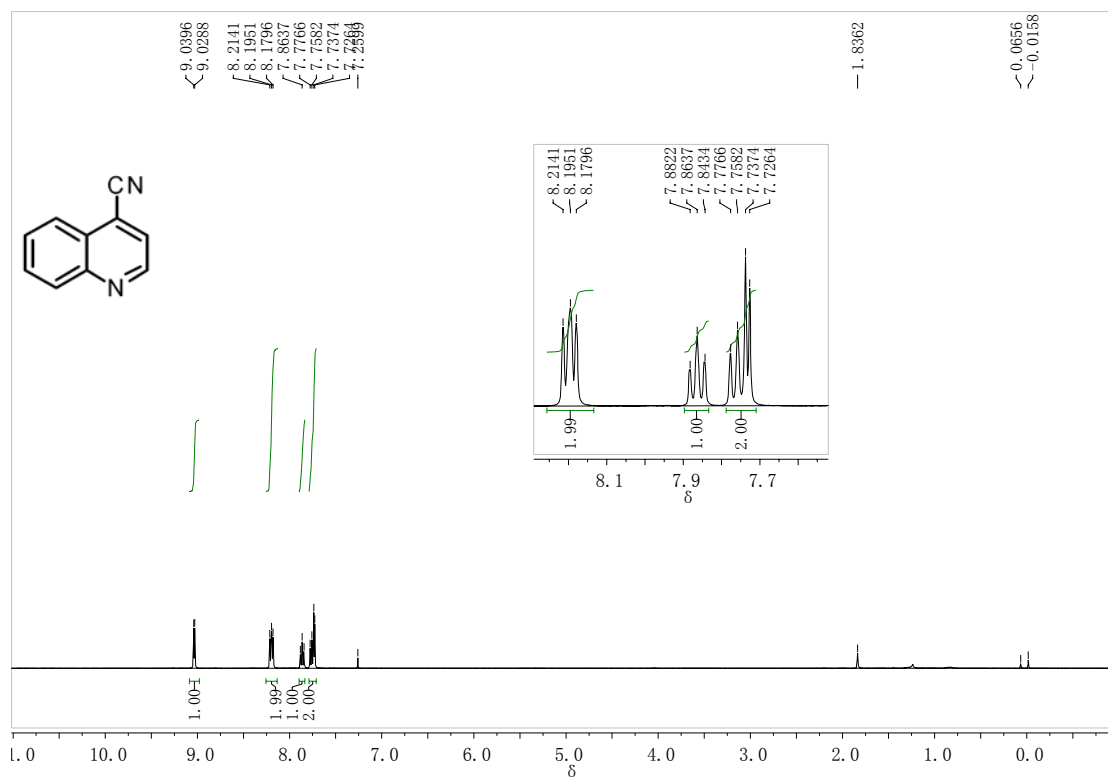
# Quinoline-2-carbonitrile (3a)



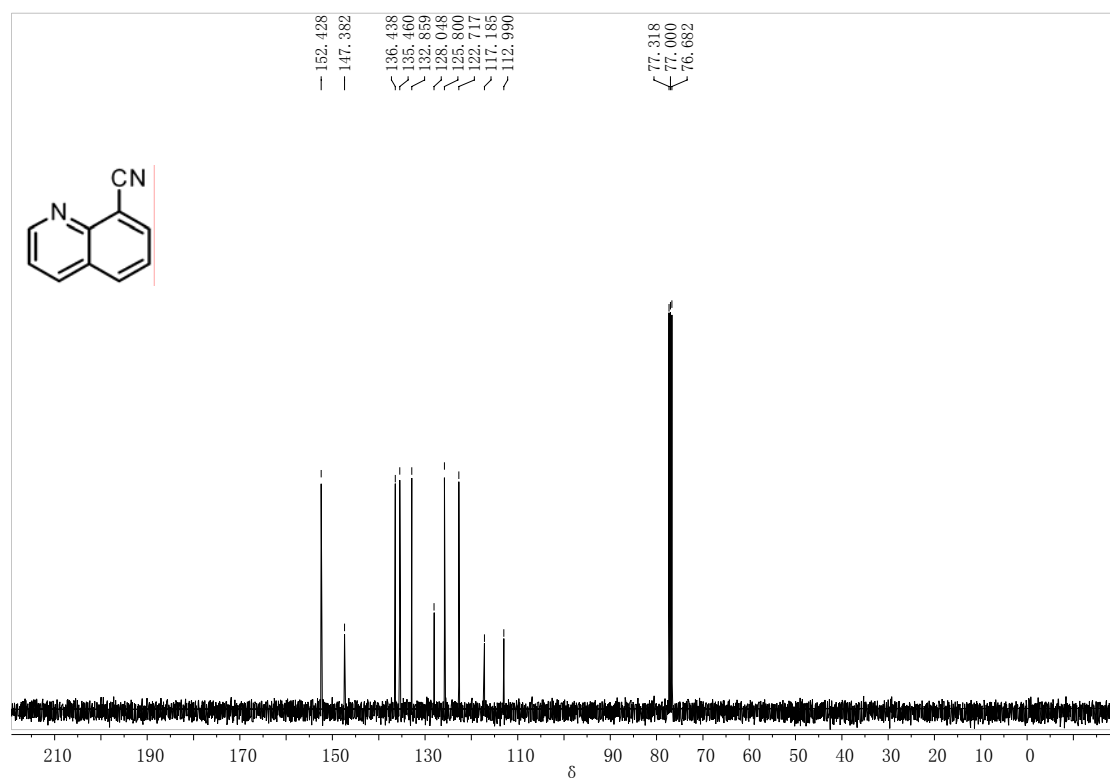
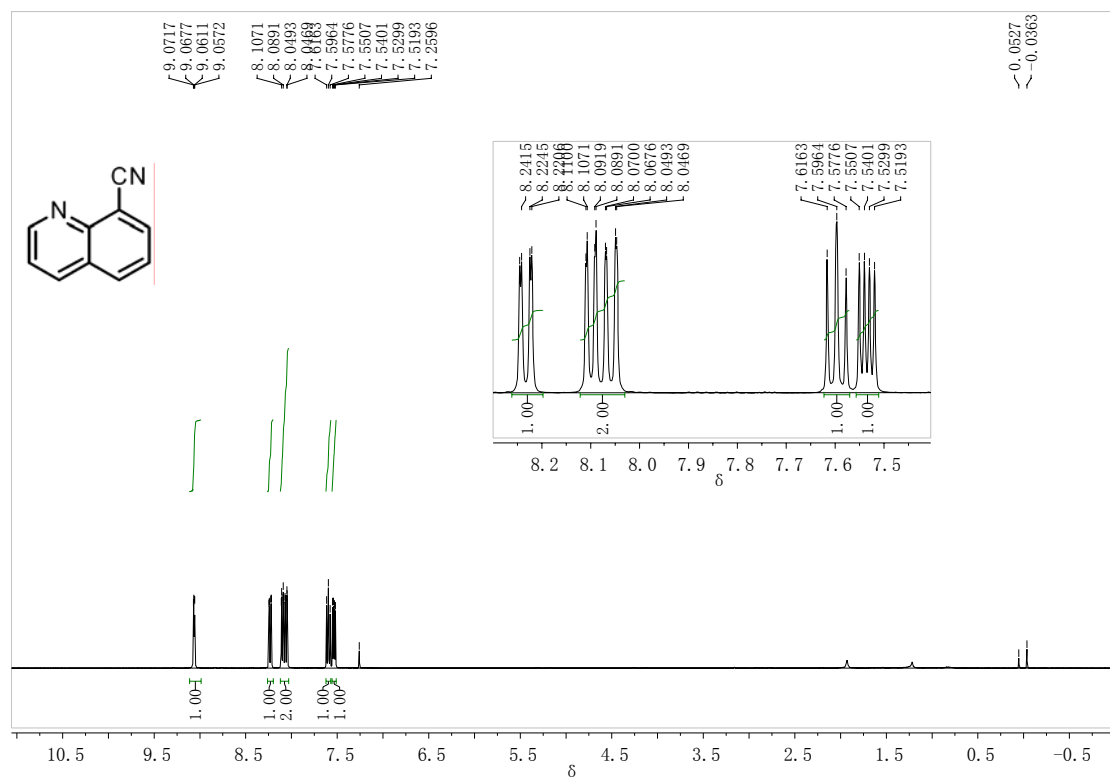
# Phenanthridine-6-carbonitrile (3b)



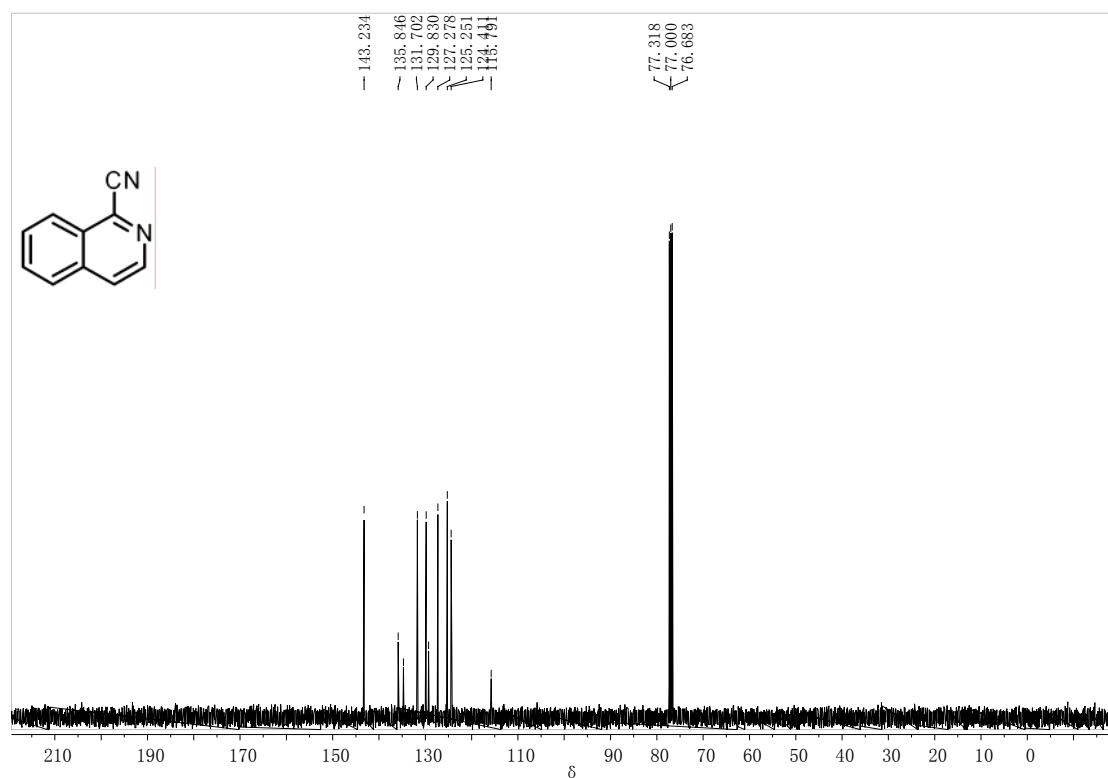
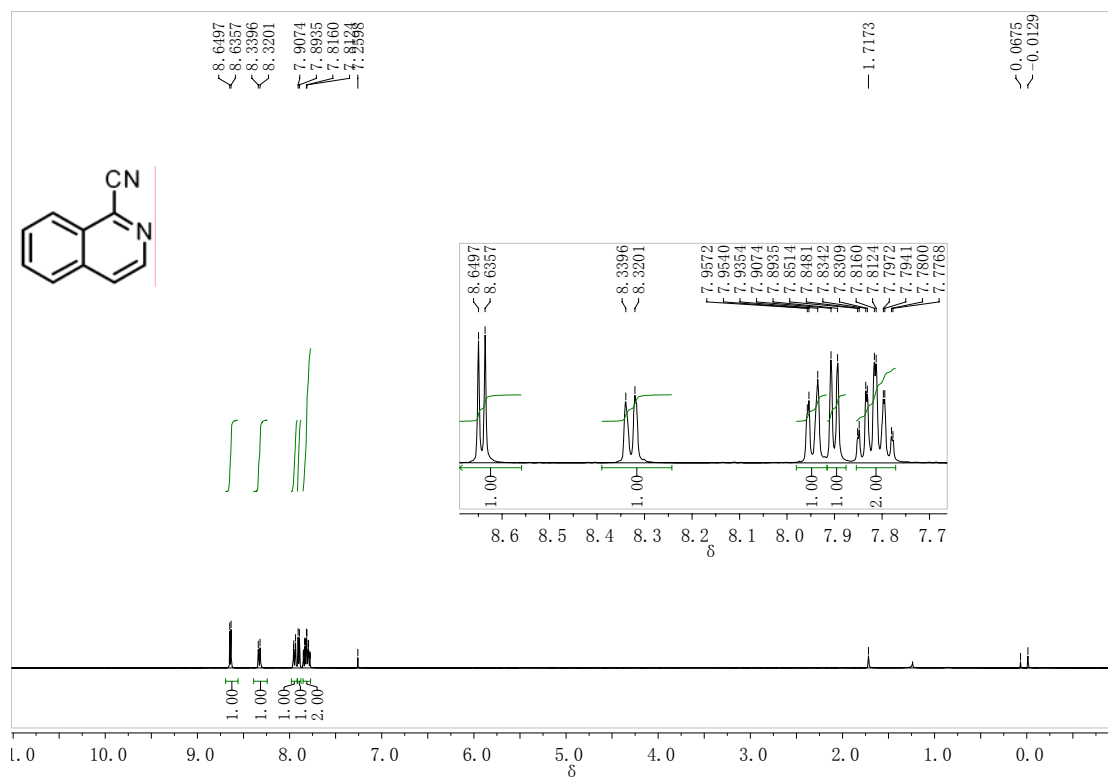
# Quinoline-4-carbonitrile (3c)



# Quinoline-8-carbonitrile (3d)

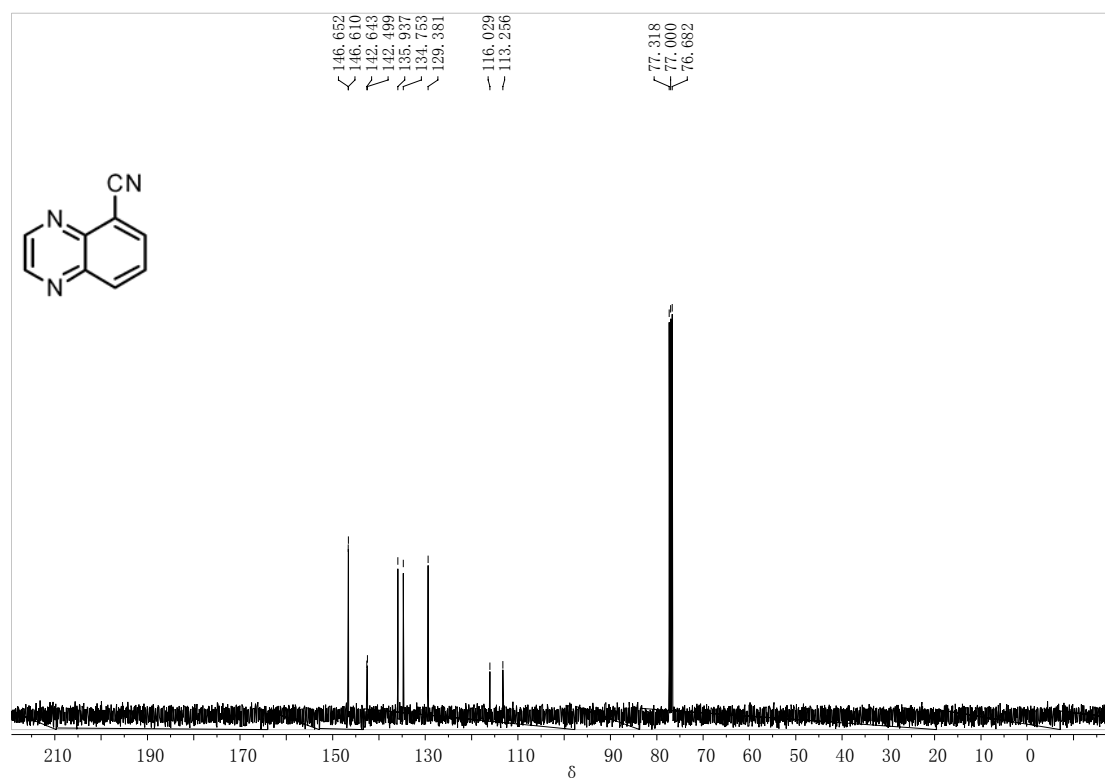
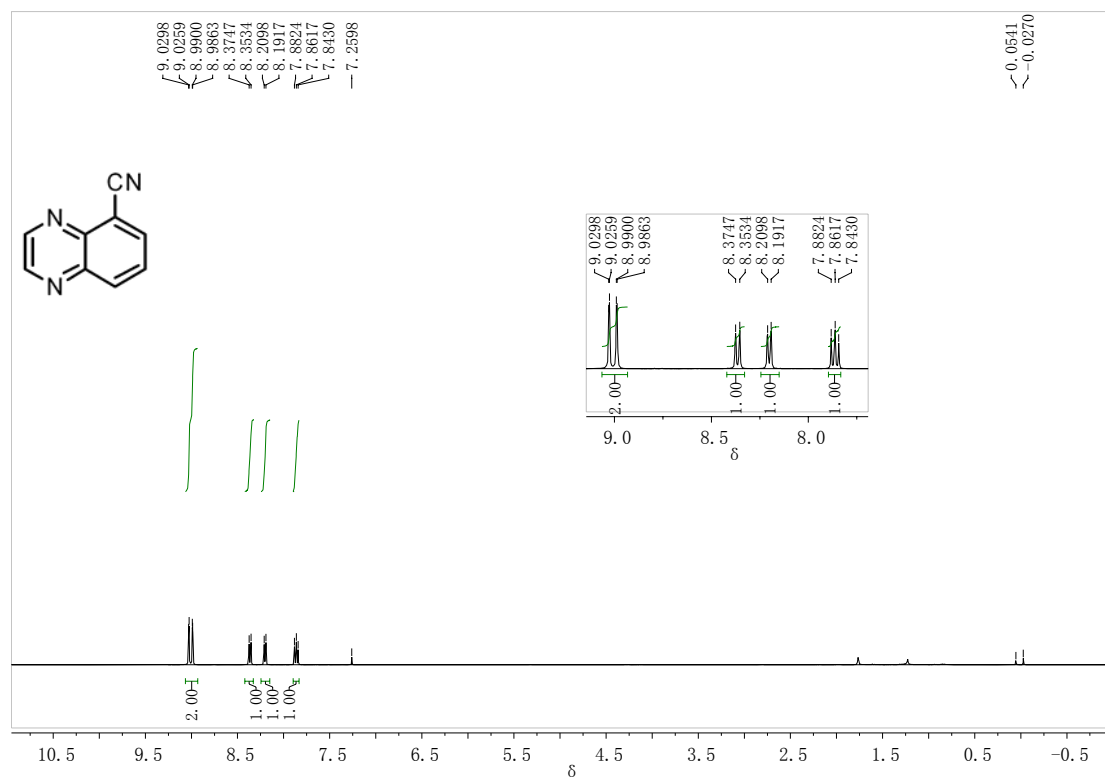


# Isoquinoline-1-carbonitrile (3e)

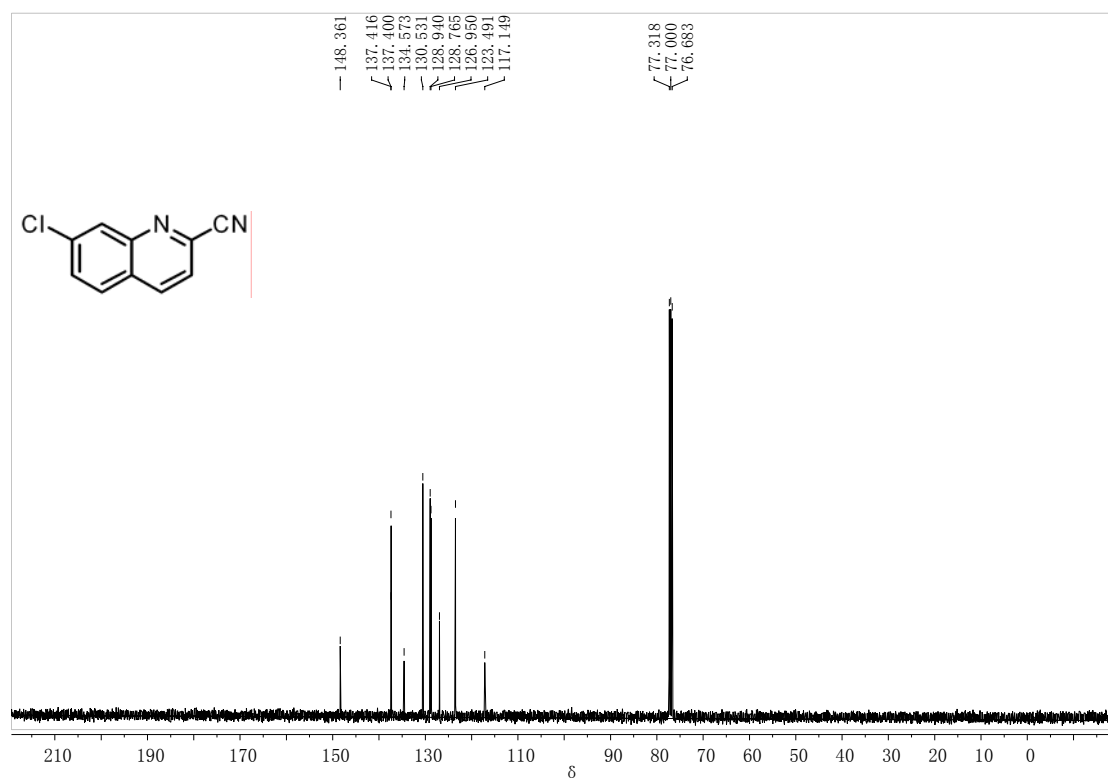
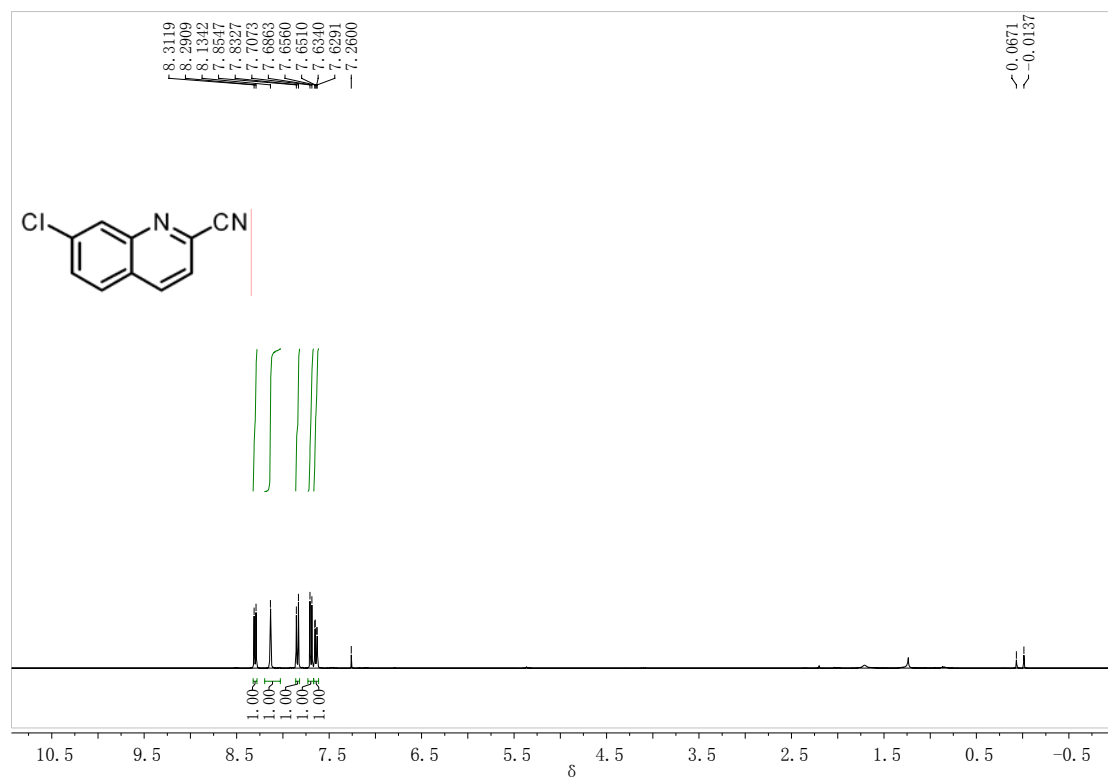




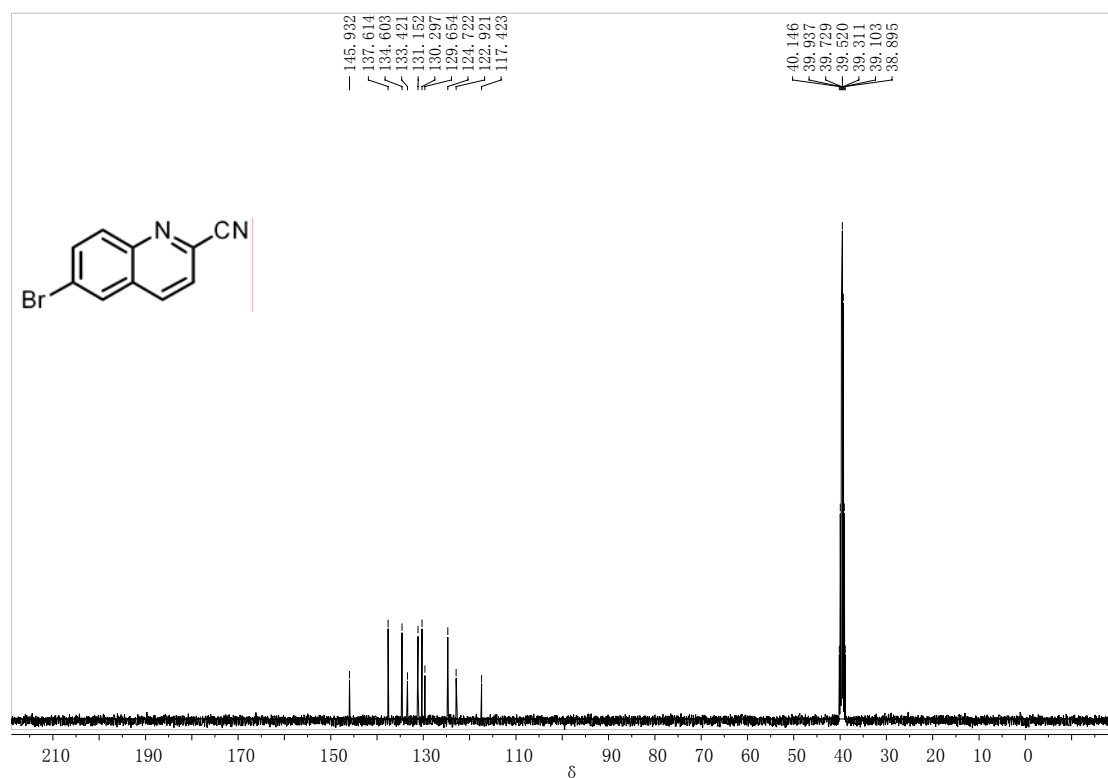
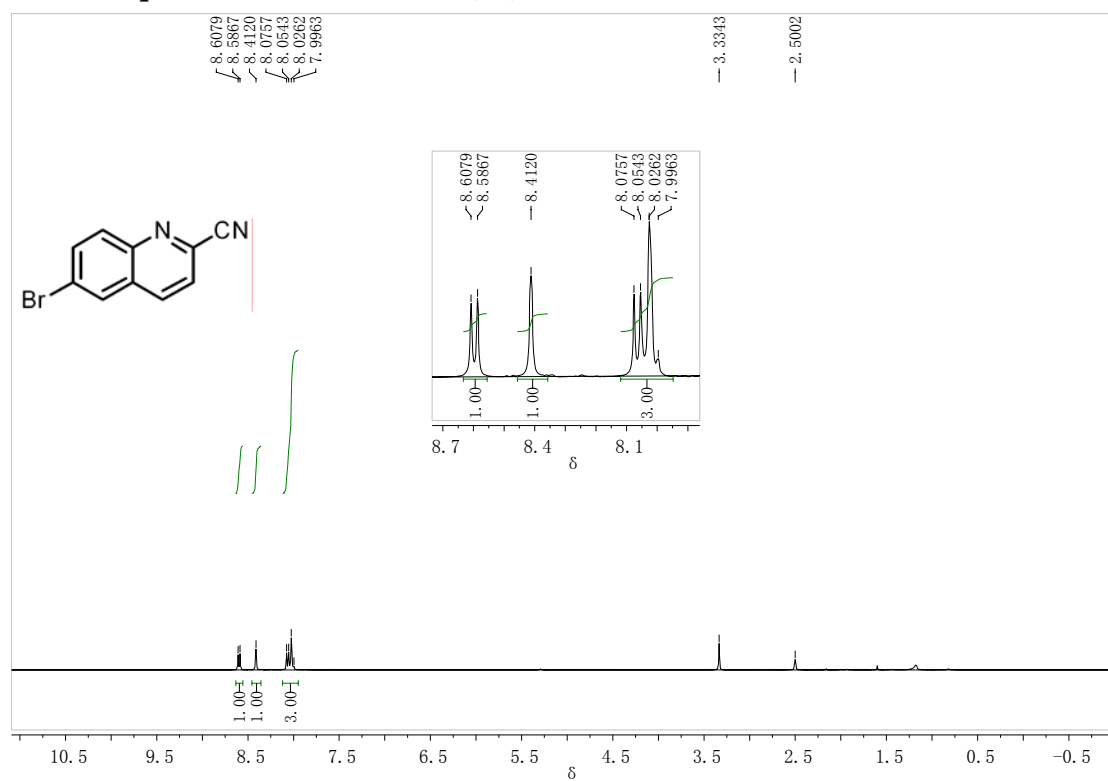
# Quinoxaline-5-carbonitrile (3f)



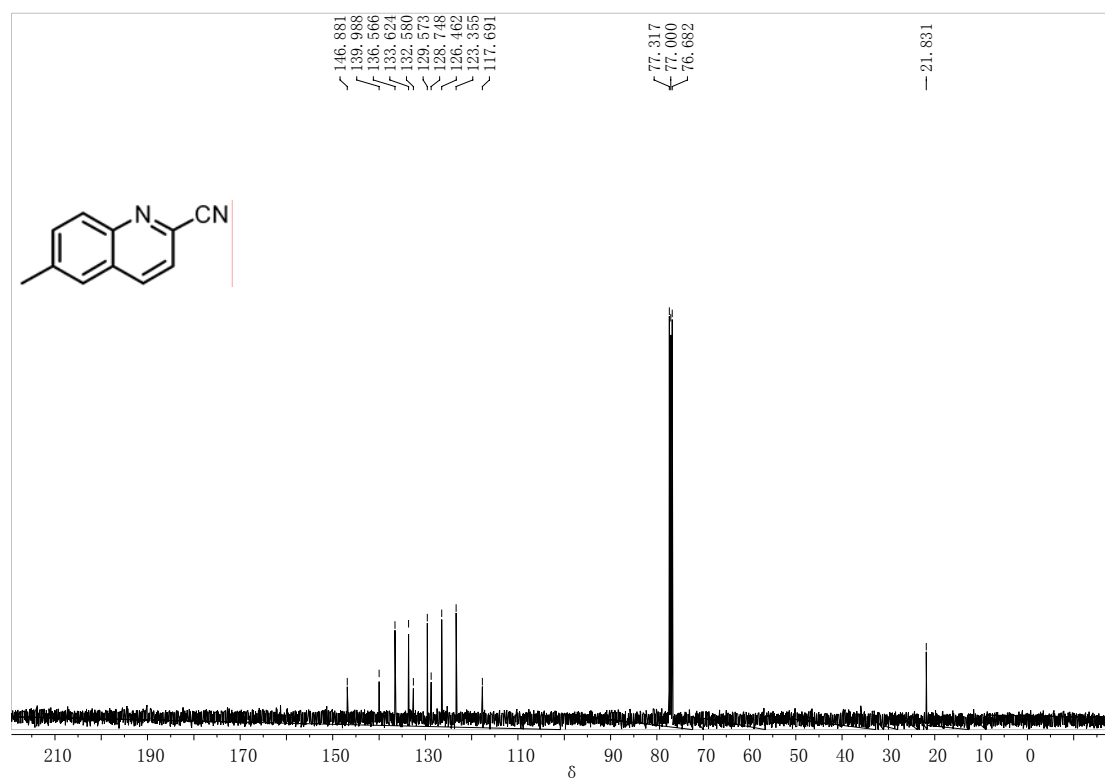
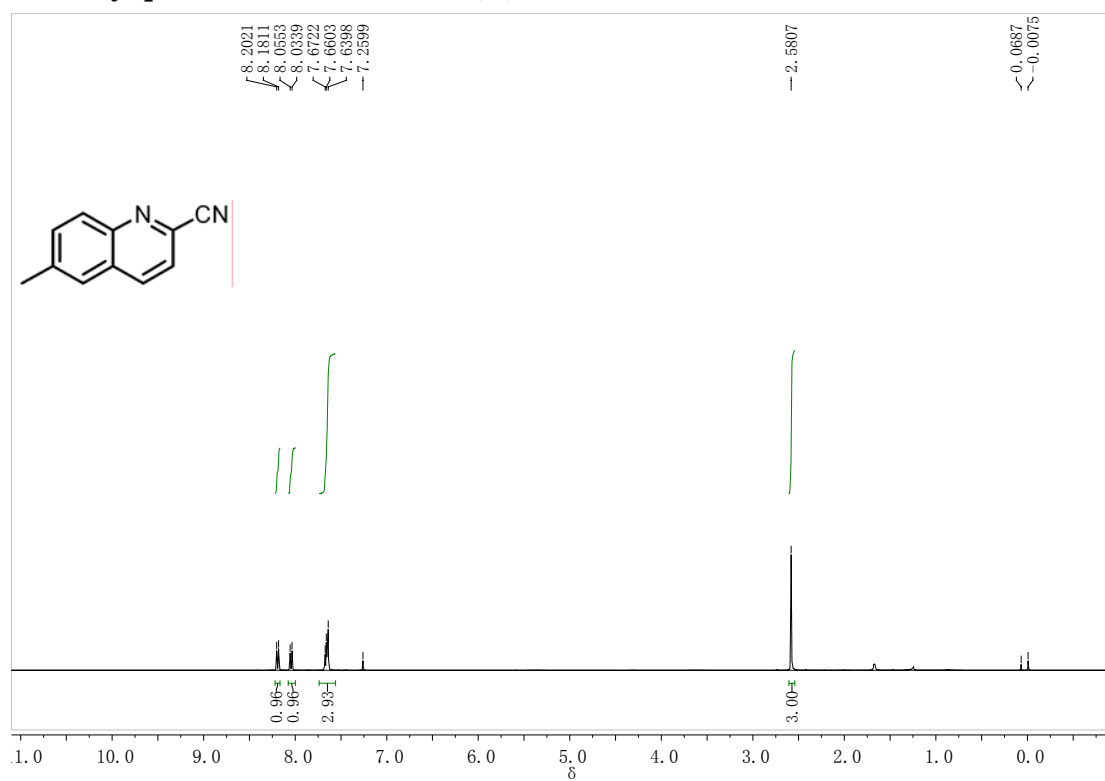
### 7-Chloroquinoline-2-carbonitrile (3g)



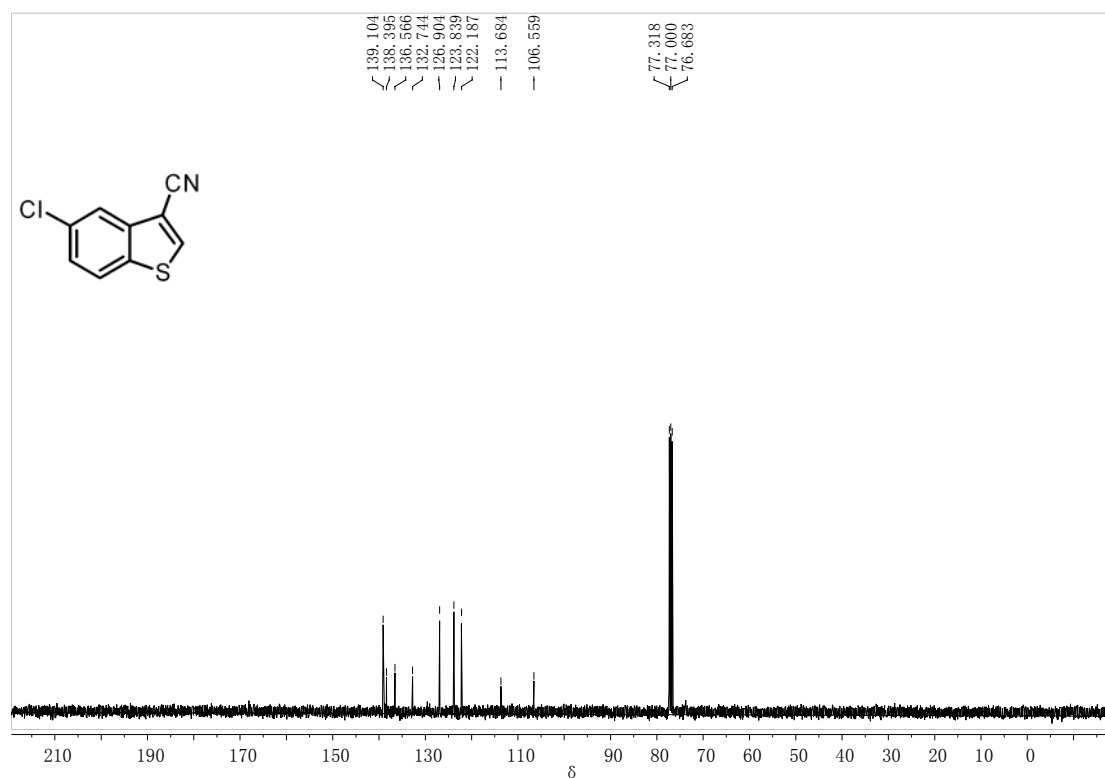
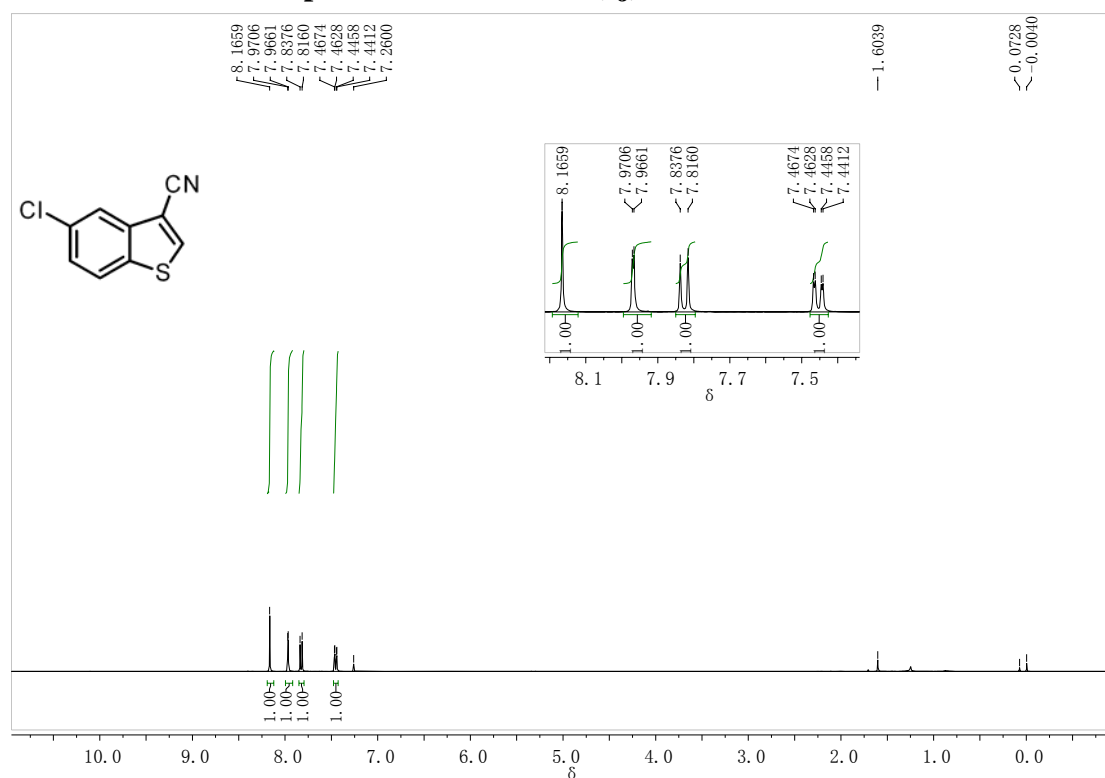
### 6-Bromoquinoline-2-carbonitrile (3h)



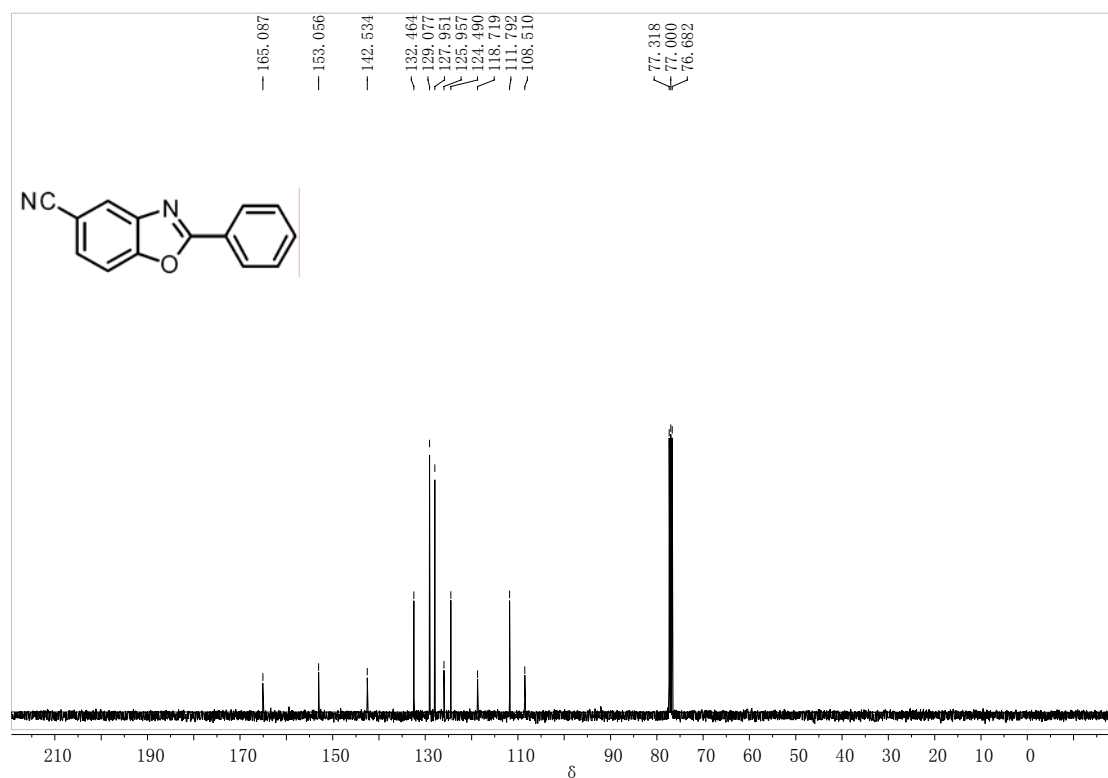
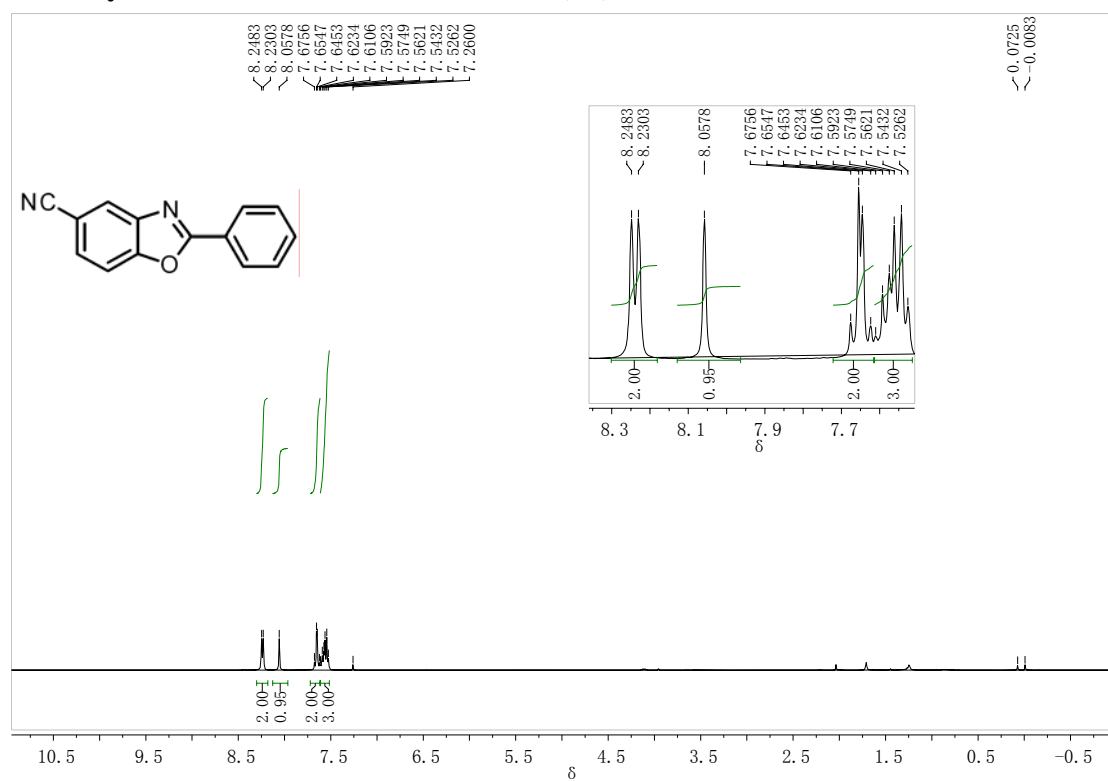
### 6-Methylquinoline-2-carbonitrile (3i)



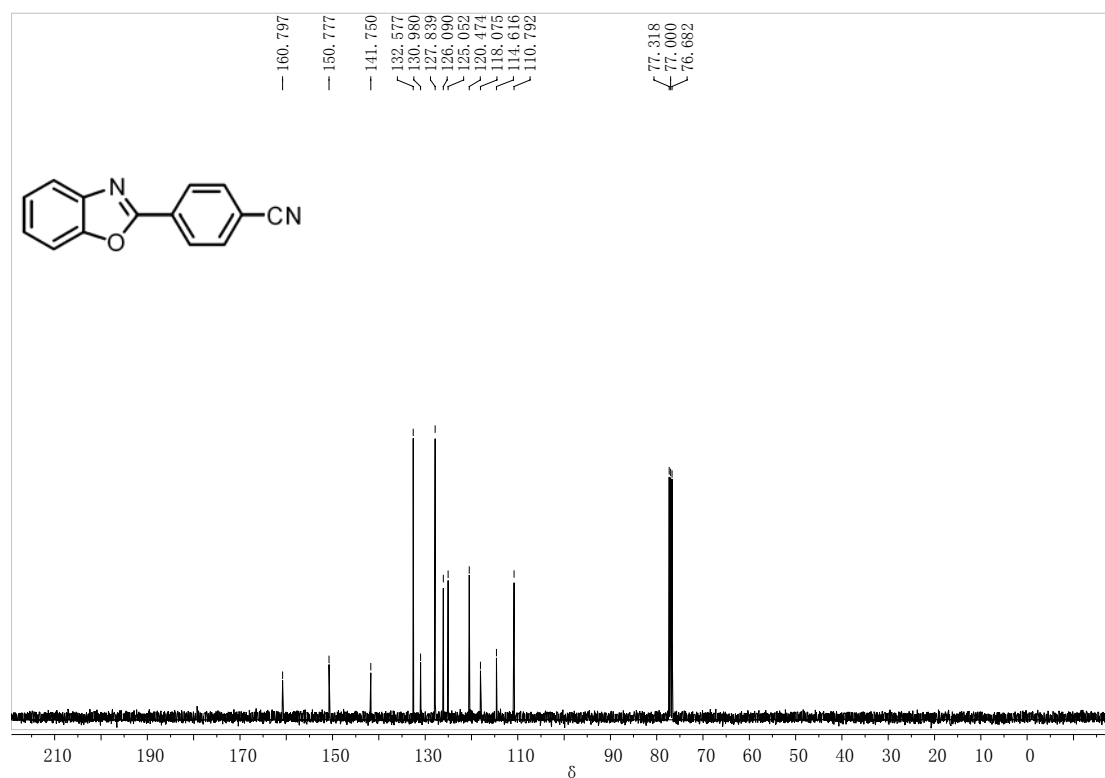
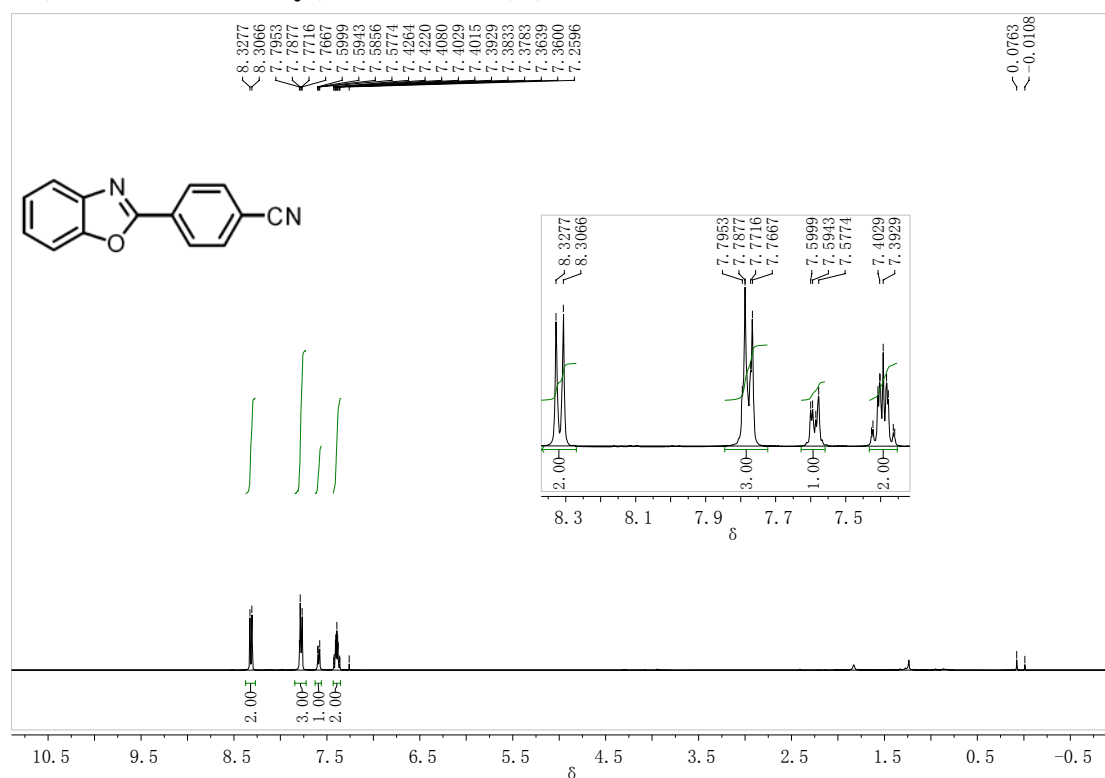
### 5-Chlorobenzo[*b*]thiophene-3-carbonitrile (3j)



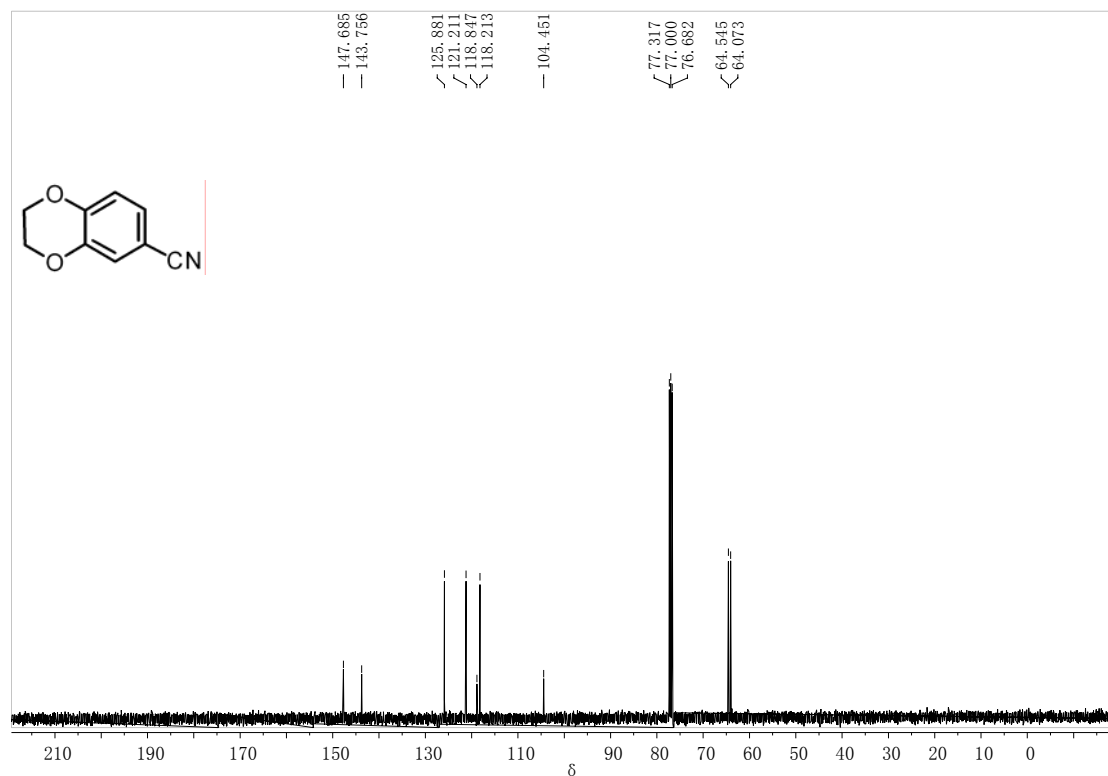
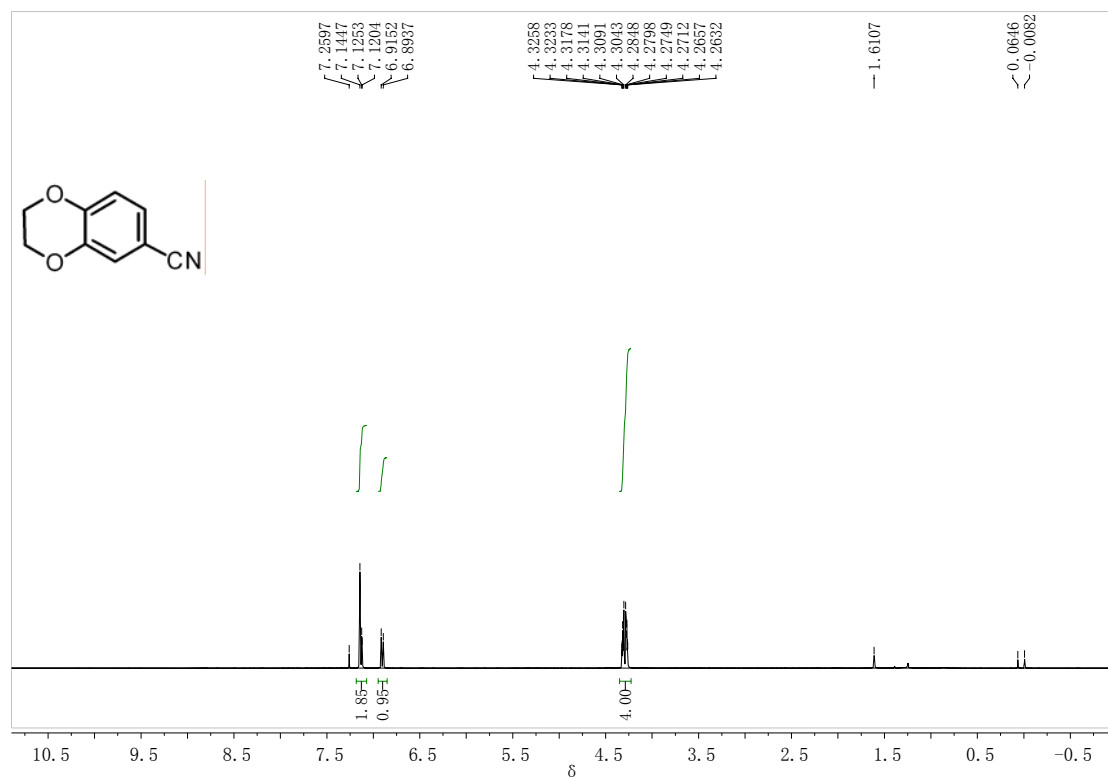
## 2-Phenylbenzo[d]oxazole-5-carbonitrile (3k)



### 4-(Benzo[d]oxazol-2-yl)benzonitrile (31)



### 2,3-Dihydrobenzo[*b*][1,4]dioxine-6-carbonitrile (3m)





# Benzo[f]quinoline-3-carbonitrile (3n)

