

# Supporting Information

## Palladium-catalyzed Cascade Reactions of $\delta$ -ketonitriles with Arylboronic Acids: Synthesis of Pyridines

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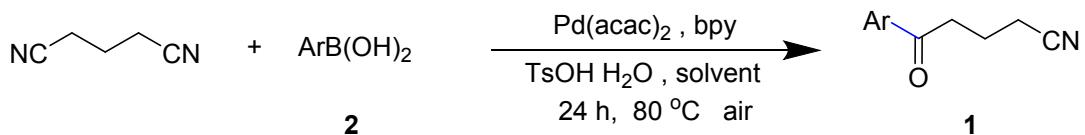
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## General Information

Chemicals were received from commercial sources without further purification or prepared by literature methods. Melting points are uncorrected and recorded on Digital Melting Point Apparatus WRS-1B.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a 400 MHz or 500 MHz Bruker spectrometer, using DMSO- $d_6$  or  $\text{CDCl}_3$  as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in  $\delta$  relative to TMS, the coupling constants  $J$  are given in Hz. High-resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF mass spectrometer.

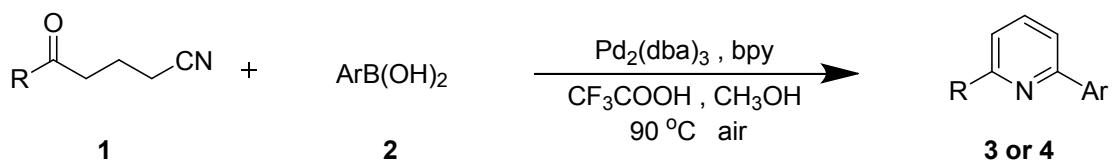
## Experimental section

## General Procedures for the Synthesis of 5-oxo-5-arylpentanenitrile



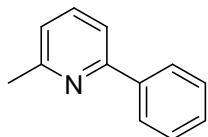
Arylboronic acid **2** (0.4 mmol, 0.5 equiv), Pd(acac)<sub>2</sub> (5 mol%), bpy (10 mol%), TsOH·H<sub>2</sub>O (2 equiv), toluene (2.5 mL), H<sub>2</sub>O (0.5 mL) and glutaronitrile (38 µL, 0.8 mmol, 1 equiv) were successively added to a 25 ml sealing tube. The reaction mixture was stirred vigorously at 80 °C for 24 hours. After the reaction mixture was cooled to room temperature, washed with saturated NaHCO<sub>3</sub>, and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under a vacuum. The residue was purified by flash column chromatography with petroleum ether/ethyl acetate to afford 5-oxo-5-arylpentanenitrile **1**.

## General Procedures for the Synthesis of pyridine

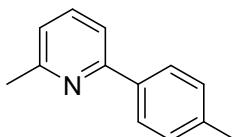


In air atmosphere, arylboronic acid **2** (0.4 mmol, 2 equiv), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mmol%), bpy (10 mol%), CH<sub>3</sub>OH (2 ml), **1** (0.2 mmol, 1 equiv) and CF<sub>3</sub>COOH (0.15 ml) were successively added to a 25 ml sealing tube. The reaction mixture was stirred vigorously at 90 °C and observed by TLC point plate until the end of the reaction. After the reaction mixture was cooled to room temperature, washed with saturated NaHCO<sub>3</sub>, and extracted with ethyl acetate (3 × 10 ml). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under a vacuum. The residue was purified by flash column chromatography with petroleum ether/ethyl acetate to afford **3** or **4**.

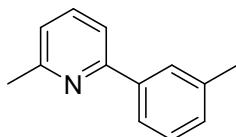
## **Analytical data for all products**



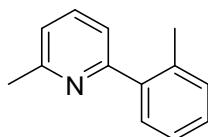
**2-methyl-6-phenylpyridine (3a);** yellow oil (29.1 mg, 86%), (lit.<sup>1</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00-7.97 (m, 2H), 7.66-7.62 (m, 1H), 7.53-7.51 (m, 1H), 7.49-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.11-7.09 (m, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.3, 157.0, 139.6, 137.0, 128.8, 128.7, 127.1, 121.7, 117.7, 24.7.



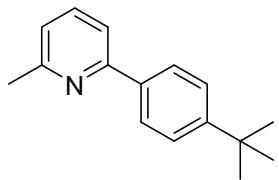
**2-methyl-6-(p-tolyl)pyridine (3b);** Pale yellow oil (30.0 mg, 82%), (lit.<sup>2</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.62-7.59 (m 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 2.63 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.3, 157.0, 138.6, 137.0, 136.8, 129.4, 126.9, 121.3, 117.3, 24.8, 21.2.



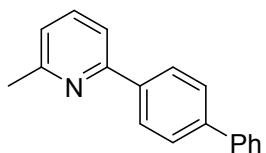
**2-methyl-6-(m-tolyl)pyridine (3c);** yellow oil (28.6 mg, 78%), (lit.<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.69-7.65 (m, 1H), 7.53-7.51 (m, 1H), 7.38-7.34 (m, 1H), 7.24-7.22 (m, 1H), 7.13-7.11 (m, 1H), 2.67 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.1, 156.9, 138.4, 137.6, 129.9, 128.7, 128.0, 124.4, 121.9, 118.3, 24.3, 21.5.



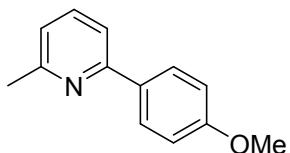
**2-methyl-6-(o-tolyl)pyridine (3d);** yellow oil (26.0 mg, 71%), (lit.<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63-7.60 (m, 1H), 7.38-7.36 (m, 1H), 7.27-7.26 (m, 1H), 7.25-7.23 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 2.61 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.5, 157.8, 140.7, 136.3, 135.7, 130.7, 129.6, 128.1, 125.9, 121.1, 121.0, 24.6, 20.3.



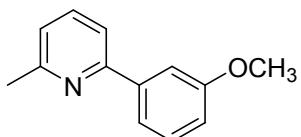
**2-(4-(tert-butyl)phenyl)-6-methylpyridine (3e);** yellow oil (34.2 mg, 76%) (lit.<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.64-7.60 (m, 1H), 7.51-7.48 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.63 (s, 3H), 1.36 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.2, 157.0, 151.9, 136.9, 126.8, 125.6, 121.3, 117.5, 34.7, 31.3, 24.6.



**2-([1,1'-biphenyl]-4-yl)-6-methylpyridine (3f);** yellow oil (39.7 mg, 81%), (lit.<sup>4</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.72-7.65 (m, 5H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48-7.45 (m, 2H), 7.38-7.35 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 2.68 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.4, 140.7, 137.3, 137.3, 128.8, 127.5, 127.5, 127.4, 127.2, 127.1, 121.8, 117.8, 100.0, 24.5.

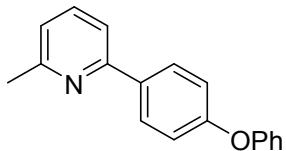


**2-(4-methoxyphenyl)-6-methylpyridine (3g);** yellow oil (32.7 mg, 82%), (lit.<sup>2</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.62-7.59 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.62 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.4, 158.1, 156.5, 137.0, 132.2, 128.3, 121.0, 117.0, 114.1, 55.4, 24.6.

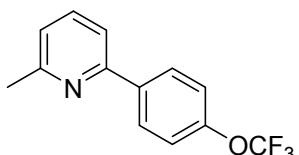


**2-(3-methoxyphenyl)-6-methylpyridine (3h);** Pale yellow oil (33.8 mg, 85%) (lit.<sup>5</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.61 (m, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.54-7.49 (m, 2H), 7.38-7.35 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.96-6.94 (m, 1H), 3.89 (s, 3H), 2.63 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.1, 158.3, 156.8, 141.3, 136.8,

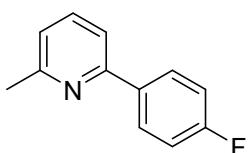
129.6, 121.7, 119.5, 117.7, 114.7, 112.4, 55.4, 24.7.



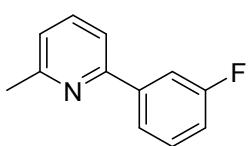
**2-methyl-6-(4-phenoxyphenyl)pyridine (3i);** yellow oil (41.3 mg, 79%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.95 (m, 2H), 7.65-7.61 (m, 1H), 7.49-7.47 (m, 1H), 7.37-7.34 (m, 2H), 7.14-7.04 (m, 6H), 2.63 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 158.0, 157.1, 156.3, 137.0, 134.8, 129.8, 128.6, 123.4, 121.3, 119.0, 119.0, 117.3, 24.7. HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{16}\text{NO} [\text{M} + \text{H}]^+$ : 262.1227, found 262.1226.



**2-methyl-6-(4-(trifluoromethoxy)phenyl)pyridine (3j);** yellow oil (41.0 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.8$  Hz, 2H), 7.69-7.65 (m, 1H), 7.50 (d,  $J = 7.9$  Hz, 1H), 7.32-7.30 (m, 2H), 7.13 (d,  $J = 7.6$  Hz, 1H), 2.64 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 155.5, 137.3, 130.1, 129.9, 128.6, 128.0, 122.1, 121.1, 117.7, 37.9, 24.6. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NO} [\text{M} + \text{H}]^+$ : 254.0787, found 254.0790.



**3-(4-fluorophenyl)-6-methylpyridine (3k);** yellow oil (19.5 mg, 52%), (lit.<sup>6</sup>).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.95 (m, 2H), 7.64-7.61 (m, 1H), 7.46 (d,  $J = 7.8$  Hz, 1H), 7.16-7.12 (m, 2H), 7.09 (d,  $J = 7.6$  Hz, 1H), 2.62 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4 (d,  $J_{\text{C}-\text{F}} = 247.9$  Hz), 158.4, 155.9, 136.9, 135.9 (d,  $J_{\text{C}-\text{F}} = 3.1$  Hz), 128.8 (d,  $J_{\text{C}-\text{F}} = 8.3$  Hz), 121.5, 117.2, 115.5 (d,  $J_{\text{C}-\text{F}} = 21.5$  Hz), 24.7.



**2-(3-fluorophenyl)-6-methylpyridine (3l);** yellow oil (25.6 mg, 63%), (lit.<sup>3</sup>).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76-7.71 (m, 2H), 7.69-7.65 (m, 1H), 7.52-7.50 (m, 1H), 7.45-7.39 (m, 1H), 7.15-7.07 (m, 2H), 2.65 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3 (d,

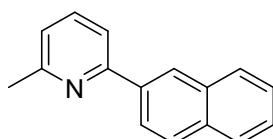
$J_{C-F} = 245.4$  Hz), 158.5, 155.5, 155.4, 137.3,  $\delta$  130.2 (d,  $J_{C-F} = 8.1$  Hz),  $\delta$  122.6 (d,  $J_{C-F} = 2.6$  Hz), 122.3, 117.8,  $\delta$  115.7 (d,  $J_{C-F} = 21.5$  Hz),  $\delta$  114.1 (d,  $J_{C-F} = 22.8$  Hz), 24.5.



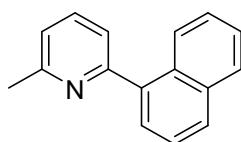
**2-(4-chlorophenyl)-6-methylpyridine (3m);** yellow oil (26.8 mg, 66%), (lit.<sup>7</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d,  $J = 8.3$  Hz, 2H), 7.64-7.61 (m, 1H), 7.48 (d,  $J = 7.8$  Hz, 1H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.10 (d,  $J = 7.6$  Hz, 1H), 2.62 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 155.7, 138.2, 137.0, 134.8, 128.8, 128.3, 121.9, 117.3, 24.7.



**2-(4-bromophenyl)-6-methylpyridine (3n);** yellow oil (28.7 mg, 58%) (lit.<sup>7</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d,  $J = 8.5$  Hz, 2H), 7.67-7.64 (m, 1H), 7.59 (d,  $J = 8.5$  Hz, 2H), 7.50 (d,  $J = 7.8$  Hz, 1H), 7.13 (d,  $J = 7.6$  Hz, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.4, 155.5, 137.5, 131.9, 128.7, 123.5, 122.2, 117.7, 24.4.

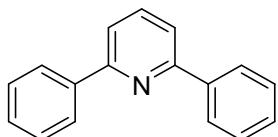


**2-methyl-6-(naphthalen-2-yl)pyridine (3o);** yellow oil (36.4 mg, 83%) (lit.<sup>8</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (s, 1H), 8.18-8.13 (m, 1H), 7.98-7.93 (m, 2H), 7.91-7.86 (m, 1H), 7.69-7.68 (m, 2H), 7.54-7.50 (m, 2H), 7.15-7.13 (m, 1H), 2.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.4, 156.8, 137.1, 133.6, 133.6, 128.7, 128.4, 127.7, 126.4, 126.4, 126.2, 124.8, 121.7, 118.0, 24.7.

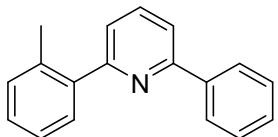


**2-methyl-6-(naphthalen-1-yl)pyridine (3p);** yellow oil (37.2 mg, 85%) (lit.<sup>9</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05-8.03 (d,  $J = 8.1$  Hz, 1H), 7.91-7.89 (m, 2H), 7.75-7.71 (m, 1H), 7.61-7.44 (m, 4H), 7.38 (d,  $J = 7.6$  Hz, 1H), 7.22 (d,  $J = 7.8$  Hz, 1H), 2.70 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  158.2, 136.8, 134.0, 131.3, 128.8, 128.3, 127.5,

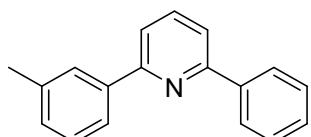
126.3, 125.8, 125.7, 125.3, 122.2, 121.7, 24.6.



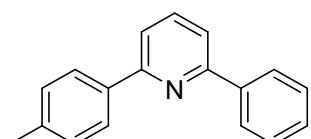
**2,6-diphenylpyridine (4a);** White solid (42.1 mg, 91%), mp 75-77 °C (lit.<sup>10</sup> 76–77 °C).  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 7.6 Hz, 4H), 7.85-7.81 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.54-7.50 (m, 4H), 7.47-7.43 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.9, 139.5, 137.5, 129.0, 128.7, 127.0, 118.6.



**2-phenyl-6-(o-tolyl)pyridine (4b);** White solid (43.1 mg, 88%), mp 62-64 °C (lit.<sup>11</sup> 63-64 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.84-7.81 (m, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.51-7.46 (m, 3H), 7.43-7.40 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32-7.30 (m, 3H), 2.50 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.8, 156.5, 140.5, 139.4, 137.0, 136.2, 130.9, 129.8, 128.9, 128.7, 128.3, 127.1, 125.9, 122.4, 118.3, 20.7.

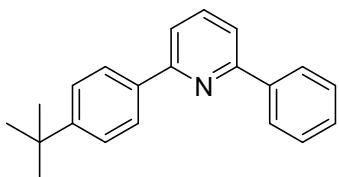


**2-phenyl-6-(m-tolyl)pyridine (4c);** White solid (45.1 mg, 92%), mp 63-65 °C (lit.<sup>11</sup> 66-67 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.6 Hz, 2H), 7.98 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.83-7.79 (m, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.52-7.49 (m, 2H), 7.45-7.38 (m, 2H), 7.25 (s, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.0, 156.8, 139.4, 139.3, 138.3, 137.6, 129.8, 129.0, 128.7, 128.6, 127.8, 127.1, 124.2, 118.9, 118.7, 21.6.

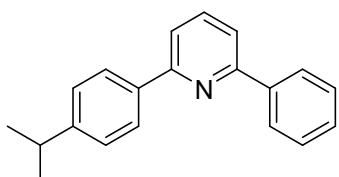


**2-phenyl-6-(p-tolyl)pyridine (4d);** White solid (45.6 mg, 93%), mp 95-96 °C (lit.<sup>12</sup> 91-92 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.85-7.81 (m, 1H),

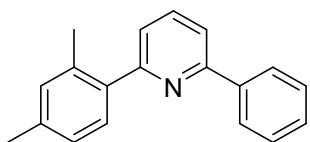
7.71 (d,  $J = 7.9$  Hz, 1H), 7.51-7.46 (m, 3H), 7.43-7.40 (m, 1H), 7.37 (d,  $J = 7.6$  Hz, 1H), 7.32-7.30 (m, 3H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 156.7, 139.4, 139.0, 137.5, 136.5, 129.4, 129.0, 128.7, 127.1, 127.0, 118.5, 21.3.



**2-(4-(tert-butyl)phenyl)-6-phenylpyridine (4e);** White solid (53.4 mg, 93%), mp 92–93 °C (lit.<sup>12</sup> 93–95 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 7.6$  Hz, 2H), 8.09 (d,  $J = 8.3$  Hz, 2H), 7.82-7.79 (m, 1H), 7.68 (d,  $J = 7.8$  Hz, 2H), 7.54-7.49 (m, 4H), 7.45-7.42 (m, 1H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 156.7, 152.2, 139.4, 137.5, 136.6, 129.0, 128.7, 127.0, 126.8, 125.7, 118.5, 118.4, 34.7, 31.3.

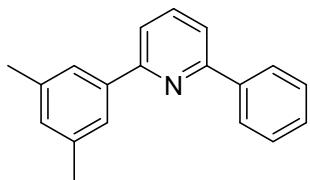


**2-(4-isopropylphenyl)-6-phenylpyridine (4f);** White solid (48.6 mg, 89%), mp 89–92 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 7.5$  Hz, 2H), 8.08 (d,  $J = 8.1$  Hz, 2H), 7.82-7.79 (m, 1H), 7.67 (d,  $J = 7.7$  Hz, 2H), 7.52-7.49 (m, 2H), 7.44 (d,  $J = 7.3$  Hz, 1H), 7.37 (d,  $J = 8.0$  Hz, 2H), 3.01-2.95 (m, 1H), 1.31 (d,  $J = 6.9$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 156.7, 150.0, 139.3, 137.6, 136.9, 129.0, 128.7, 127.1, 127.1, 126.8, 118.6, 118.5, 34.0, 24.0. HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{20}\text{N}^+$  [M + H]<sup>+</sup>: 274.1590, found 274.1592.

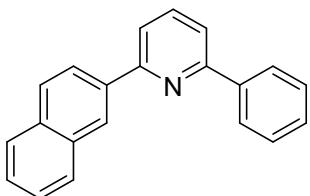


**2-(2,4-dimethylphenyl)-6-phenylpyridine (4g);** White solid (47.7 mg, 92%), mp 78–79 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 7.5$  Hz, 2H), 7.83-7.79 (m, 1H), 7.69 (d,  $J = 7.9$  Hz, 1H), 7.50-7.47 (m, 2H), 7.42 (d,  $J = 7.7$  Hz, 2H), 7.36 (d,  $J = 7.6$  Hz, 1H), 7.16-7.12 (m, 2H), 2.49 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 156.4, 139.6, 138.1, 137.8, 136.9, 136.0, 131.7, 129.8, 128.9, 128.7, 127.1, 126.6,

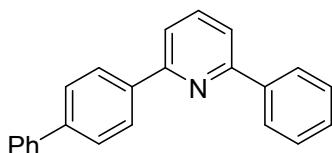
122.4, 118.0, 21.2, 20.7. HRMS (ESI) calcd for C<sub>19</sub>H<sub>18</sub>N [M + H]<sup>+</sup>: 260.1434, found 260.1435.



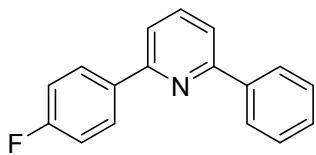
**2-(3,5-dimethylphenyl)-6-phenylpyridine (4h);** White solid (48.7 mg, 94%), mp 82-84 °C (lit.<sup>13</sup> 178-180 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16-8.15 (m, 2H), 7.82-7.79 (m, 1H), 7.76 (s, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.53-7.50 (m, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.09 (s, 1H), 2.44 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.3, 156.9, 139.6, 139.5, 138.2, 137.4, 130.7, 128.9, 128.7, 127.1, 124.9, 118.8, 118.6, 21.5. HRMS (ESI) calcd for C<sub>19</sub>H<sub>18</sub>N [M + H]<sup>+</sup>: 260.1434, found 260.1435.



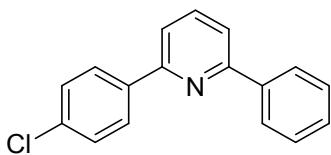
**2-(naphthalen-2-yl)-6-phenylpyridine (4i);** White solid (34.9 mg, 62%), mp 153-155 °C (lit.<sup>1</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 3H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.60-7.43 (m, 7H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.0, 156.9, 139.2, 138.6, 137.3, 134.1, 131.3, 129.1, 129.0, 128.8, 128.4, 127.7, 127.2, 126.4, 125.9, 125.9, 125.3, 123.5, 118.7.



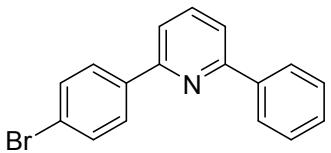
**2-([1,1'-biphenyl]-4-yl)-6-phenylpyridine (4j);** White solid (51.0 mg, 83%), mp 151-153 °C (lit.<sup>11</sup> 149-150 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.86-7.82 (t, *J* = 7.7 Hz, 1H), 7.76-7.68 (m, 6H), 7.54-7.44 (m, 5H), 7.41-7.38 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.9, 156.4, 141.8, 140.7, 139.4, 138.3, 137.6, 129.1, 128.9, 128.7, 127.5, 127.5, 127.4, 127.1, 127.1, 118.7, 118.6.



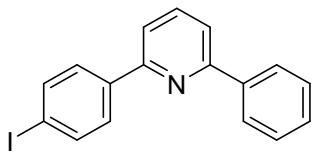
**2-(4-fluorophenyl)-6-phenylpyridine (4k);** White solid (28.9 mg, 58%), mp 91-93 °C (lit.<sup>11</sup> 94-95 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 7.1 Hz, 4H), 7.83-7.79 (m, 1H), 7.70-7.64 (m, 2H), 7.51 (t, *J* = 7.1 Hz, 2H), 7.45 (d, *J* = 6.6 Hz, 1H), 7.21-7.16 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 163.6 (d, *J*<sub>C-F</sub> = 248.3 Hz), 156.9, 155.8, 139.4, 137.6, 135.6 (d, *J*<sub>C-F</sub> = 3.0 Hz), 129.1, 128.8 (d, *J*<sub>C-F</sub> = 8.3 Hz), 128.7, 127.0, 118.6, 118.3, 115.6 (d, *J*<sub>C-F</sub> = 21.5 Hz).



**2-(4-chlorophenyl)-6-phenylpyridine (4l);** White solid (31.8 mg, 60%), mp 102-103 °C (lit.<sup>10</sup> 104-105 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14-8.09 (m, 4H), 7.85-7.82 (m, 1H), 7.72-7.66 (m, 2H), 7.53-7.46 (m, 5H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.0, 155.6, 139.1, 137.8, 137.7, 135.2, 129.2, 128.9, 128.8, 128.4, 127.1, 119.1, 118.6.

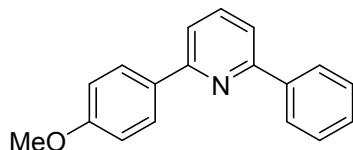


**2-(4-bromophenyl)-6-phenylpyridine (4m);** White solid (40.2 mg, 65%), mp 119-120 °C (lit.<sup>11</sup> 115-116 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 7.1 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.68-7.61 (m, 3H), 7.53-7.49 (m, 2H), 7.47-7.43 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.0, 155.7, 139.2, 138.3, 137.7, 131.8, 129.2, 128.8, 128.6, 127.0, 123.5, 119.0, 118.4.

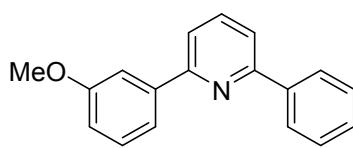


**2-(4-iodophenyl)-6-phenylpyridine (4n);** White solid (48.6 mg, 68%), mp 135-137°C (lit.<sup>11</sup> 139-141 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15-8.13 (m, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.84-7.80 (m, 3H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.53-7.50 (m, 2H), 7.45 (d, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.0, 155.8,

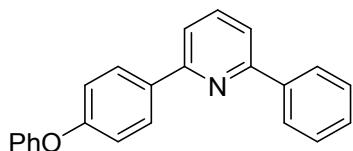
139.3, 139.0, 137.8, 137.6, 129.1, 128.8, 128.7, 127.0, 119.1, 118.3, 95.3.



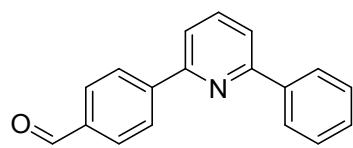
**2-(4-methoxyphenyl)-6-phenylpyridine (4o);** White solid (48.0 mg, 92%), mp 132-133 °C (lit.<sup>11</sup> 132-133 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17-8.12 (m, 4H), 7.79-7.76 (m, 1H), 7.65-7.63 (m, 2H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.6, 156.7, 156.5, 139.6, 137.4, 132.2, 128.9, 128.7, 128.3, 127.0, 118.0, 117.9, 114.1, 55.4.



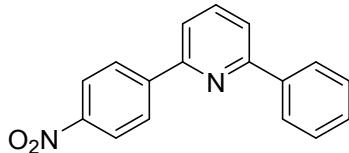
**2-(3-methoxyphenyl)-6-phenylpyridine (4p);** White solid (44.9 mg, 86%), mp 127-128 °C (lit.<sup>1</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.74 (s, 1H), 8.43 (d, *J* = 7.4 Hz, 1H), 8.16-8.11 (m, 3H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.78-7.74 (m, 2H), 7.61-7.58 (m, 1H), 7.53-7.51 (m, 2H), 7.47-7.44 (m, 1H), 3.98 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.1, 157.0, 155.8, 139.4, 138.9, 138.0, 131.8, 130.7, 130.2, 129.3, 128.9, 128.8, 128.1, 127.2, 119.4, 119.1, 52.3.



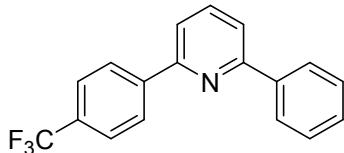
**2-(4-phenoxyphenyl)-6-phenylpyridine (4q);** White solid (58.2 mg, 90%), mp 155-157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 6.5 Hz, 4H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.52-7.49 (m, 2H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.39-7.36 (m, 2H), 7.16-7.12 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.6, 157.3, 156.9, 156.8, 156.2, 138.0, 129.9, 129.7, 129.3, 128.8, 128.7, 127.3, 123.6, 123.2, 119.3, 118.9, 118.8. HRMS (ESI) calcd for C<sub>23</sub>H<sub>18</sub>NO [M + H]<sup>+</sup>: 324.1383, found 324.1388.



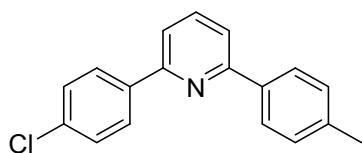
**4-(6-phenylpyridin-2-yl)benzaldehyde (4r);** White solid (30.6 mg, 59%), mp 112–113 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.10 (s, 1H), 8.33 (d,  $J = 8.0$  Hz, 2H), 8.15 (d,  $J = 7.7$  Hz, 2H), 8.02 (d,  $J = 7.9$  Hz, 2H), 7.90–7.87 (m, 1H), 7.78 (d,  $J = 7.7$  Hz, 2H), 7.54–7.51 (m, 2H), 7.47 (d,  $J = 7.1$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  192.1, 157.3, 155.3, 145.0, 139.0, 137.8, 136.5, 130.2, 129.3, 128.8, 127.6, 127.0, 119.8, 119.4. HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{14}\text{NO} [\text{M} + \text{Na}]^+$ : 282.0895, found 282.0900.



**2-(4-nitrophenyl)-6-phenylpyridine (4s);** White solid (32.6 mg, 59%), mp 128–129 °C (lit.<sup>12</sup> 127–129 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.0$  Hz, 2H), 8.15 (d,  $J = 7.6$  Hz, 2H), 7.87 (d,  $J = 7.8$  Hz, 1H), 7.77–7.62 (m, 4H), 7.53–7.44 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 155.3, 142.8, 139.0, 137.8, 129.3, 128.8, 127.3, 127.1, 125.6, 125.6, 119.6, 119.0.

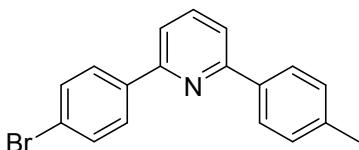


**2-phenyl-6-(4-(trifluoromethyl)phenyl)pyridine (4t);** White solid (30.5 mg, 51%), mp 115–116 °C (lit.<sup>11</sup> 117–118 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.0$  Hz, 2H), 8.15 (d,  $J = 7.8$  Hz, 2H), 7.88–7.84 (m, 1H), 7.77–7.72 (m, 4H), 7.54–7.44 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 155.3, 142.8, 139.2, 137.7, 130.8 (d,  $J_{\text{C}-\text{F}} = 32.4$  Hz), 129.2, 128.8, 127.3, 127.0, 125.6 (q,  $J_{\text{C}-\text{F}} = 3.8$  Hz), 124.3 (d,  $J_{\text{C}-\text{F}} = 272.2$  Hz), 119.5, 118.9.

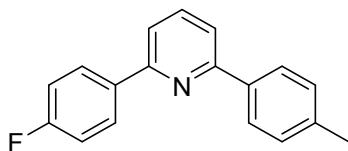


**2-(4-chlorophenyl)-6-(p-tolyl)pyridine (4u);** White solid (36.8 mg, 66%), mp 113–115 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10–8.03 (m, 4H), 7.79 (d,  $J = 7.7$  Hz, 1H), 7.69–7.62 (m, 2H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.31 (d,  $J = 7.8$  Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 155.5, 139.2, 138.0, 137.6, 136.5, 135.1, 129.5, 128.9, 128.3, 126.9, 118.7, 118.1, 21.3. HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{ClN}_2 [\text{M} + \text{H}]^+$ :

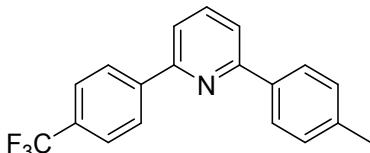
280.0888, found 280.0892.



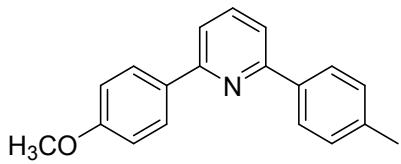
**2-(4-bromophenyl)-6-(p-tolyl)pyridine (4v);** White solid (29.1 mg, 45%), mp 124-126 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.02 (m, 4H), 7.81-7.78 (m, 1H), 7.68 (d,  $J$  = 7.8 Hz, 1H), 7.64-7.61 (m, 3H), 7.31 (d,  $J$  = 8.0 Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 155.5, 139.2, 138.4, 137.6, 136.5, 131.8, 129.5, 128.6, 126.9, 123.4, 118.7, 118.1, 21.3. HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{BrN} [\text{M} + \text{H}]^+$ : 324.0383 and 326.0362 found 324.0386 and 326.0364.



**2-(4-fluorophenyl)-6-(p-tolyl)pyridine (4w);** White solid (24.7 mg, 47%), mp 117-118 °C (lit.<sup>14</sup> 116-118 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16-8.13 (m, 2H), 8.05 (d,  $J$  = 8.0 Hz, 2H), 7.80-7.77 (m, 1H), 7.66 (d,  $J$  = 7.8 Hz, 1H), 7.61 (d,  $J$  = 7.8 Hz, 1H), 7.31 (d,  $J$  = 7.9 Hz, 2H), 7.20-7.17 (m, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6 (d,  $J_{\text{C}-\text{F}} = 248.1$  Hz), 156.9, 155.7, 139.1, 137.5, 136.6, 135.7 (d,  $J_{\text{C}-\text{F}} = 2.9$  Hz), 129.5, 128.8 (d,  $J_{\text{C}-\text{F}} = 8.3$  Hz), 126.9, 128.2 (d,  $J_{\text{C}-\text{F}} = 35.6$  Hz), 115.6 (d,  $J_{\text{C}-\text{F}} = 21.5$  Hz), 21.3.

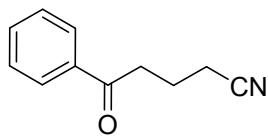


**2-(p-tolyl)-6-(4-(trifluoromethyl)phenyl)pyridine (4x);** White solid (23.8 mg, 38%), mp 120-122 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J$  = 8.1 Hz, 2H), 8.05 (d,  $J$  = 8.1 Hz, 2H), 7.85-7.82 (m, 1H), 7.76-7.69 (m, 4H), 7.32 (d,  $J$  = 7.9 Hz, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 155.2, 139.3, 137.6, 136.4, 130.7 (d,  $J_{\text{C}-\text{F}} = 32.5$  Hz), 129.5, 127.3, 126.9, 125.6 (q,  $J_{\text{C}-\text{F}} = 3.8$  Hz), 124.3 (d,  $J_{\text{C}-\text{F}} = 272.1$  Hz), 119.2, 118.6, 100.0, 21.3. HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N} [\text{M} + \text{H}]^+$ : 314.1151, found 314.1156.

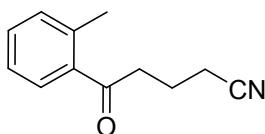


**2-(4-methoxyphenyl)-6-(p-tolyl)pyridine (4y);** White solid (48.4 mg, 88%), mp 129-132 °C (lit.<sup>15</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.79-7.76 (m, 1H), 7.62-7.60 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.6, 156.6, 156.3, 139.1, 137.6, 129.4, 128.4, 127.0, 117.9, 114.1, 55.4, 21.3.

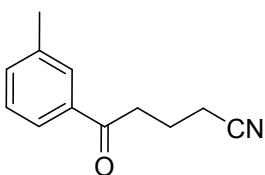
## Analytical data for reactants



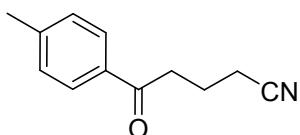
**5-oxo-5-phenylpentanenitrile (1b);** colorless oil (30.0 mg, 86%) (lit.<sup>16</sup> 32-33 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.60-7.57 (m, 1H), 7.50-7.47 (m, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.15-2.09 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 198.2, 136.5, 133.5, 128.8, 128.0, 119.4, 36.3, 19.7, 16.7.



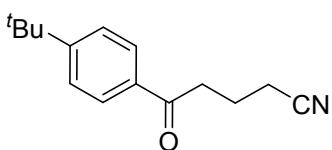
**5-oxo-5-(o-tolyl)pentanenitrile (1c);** colorless oil (26.9 mg, 72%) (lit.<sup>17</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.62 (m, 1H), 7.36-7.32 (m, 1H), 7.25-7.20 (m, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.46 (s, 3H), 2.45-2.43 (m, 2H) 2.05-1.98 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 201.9, 138.2, 137.2, 132.1, 131.7, 128.6, 125.8, 119.4, 39.1, 21.4, 19.9, 16.5.



**5-oxo-5-(m-tolyl)pentanenitrile (1d);** yellow solid (30.3 mg, 81%) mp 59-61 °C (lit.<sup>18</sup> 164–170 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77-7.70 (m, 2H), 7.35-7.29 (m, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 2.07-2.01 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 198.3, 138.5, 136.6, 134.1, 128.6, 128.5, 125.2, 119.4, 36.4, 21.3, 19.8, 16.6.

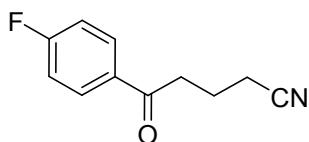


**5-oxo-5-(p-tolyl)pentanenitrile (1e);** yellow solid (31.4 mg, 84%) mp 58-59 °C (lit.<sup>16</sup> 58-59 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 2.06-1.98 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.8, 144.2, 134.1, 129.4, 128.1, 119.5, 36.3, 21.6, 19.9, 16.6.

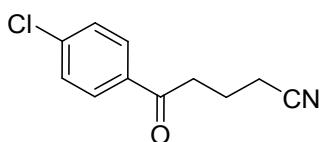


**5-(4-(tert-butyl)phenyl)-5-oxopentanenitrile (1f);** yellow solid (39.9 mg, 87%) mp 53-55 °C (lit.<sup>16</sup> 55-57 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 6.7 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.05-2.01 (m, 2H),

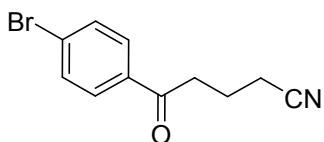
1.40-1.20 (m, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7, 157.1, 134.0, 127.9, 125.6, 119.4, 36.3, 35.1, 31.0, 19.9, 16.6.



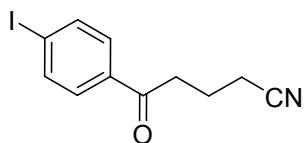
**5-(4-fluorophenyl)-5-oxopentanenitrile (1g);** yellow solid (22.5 mg, 59%) mp 71-73 °C (lit.<sup>16</sup> 72-73 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99-7.97 (m, 2H), 7.15-7.11 (m, 2H), 3.14 (t,  $J = 6.7$  Hz, 2H), 2.51 (t,  $J = 6.9$  Hz, 2H), 2.12-2.07 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 165.9 (d,  $J_{\text{C}-\text{F}} = 255.4$  Hz), 133.0 (d,  $J_{\text{C}-\text{F}} = 2.9$  Hz), 130.6 (d,  $J_{\text{C}-\text{F}} = 9.4$  Hz), 119.2, 115.8 (d,  $J_{\text{C}-\text{F}} = 21.9$  Hz), 36.24, 19.73, 16.60.



**5-(4-chlorophenyl)-5-oxopentanenitrile (1h);** yellow solid (29.0 mg, 70%) mp 63-65 °C (lit.<sup>16</sup> 61-62 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.2$  Hz, 2H), 7.47-7.43 (m, 2H), 3.15 (t,  $J = 6.6$  Hz, 2H), 2.53 (t,  $J = 6.8$  Hz, 2H), 2.13-2.10 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  196.9, 140.1, 134.9, 129.4, 129.1, 119.2, 36.3, 19.7, 16.7.

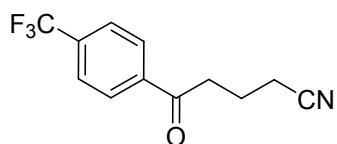


**5-(4-bromophenyl)-5-oxopentanenitrile (1i);** yellow solid (26.1 mg, 52%) mp 57-58 °C (lit.<sup>16</sup> 53-54 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.74 (m, 2H), 7.55-7.51 (m, 2H), 3.07 (t,  $J = 6.8$  Hz, 2H), 2.46 (t,  $J = 7.0$  Hz, 2H), 2.07-2.00 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 135.2, 132.0, 129.5, 128.5, 119.3, 36.4, 19.7, 16.6.



**5-(4-iodophenyl)-5-oxopentanenitrile (1j);** White oil (28.7 mg, 48%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.1$  Hz, 2H), 7.59 (d,  $J = 8.2$  Hz, 2H), 3.06 (t,  $J = 6.8$  Hz, 2H), 2.46 (t,  $J = 7.0$  Hz, 2H), 2.06-2.00 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 138.0, 135.7, 129.3, 119.3, 101.4, 36.3, 19.7, 16.6. HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{11}\text{INO}$

[M + H]<sup>+</sup>: 299.9880, found 299.9884.



**5-oxo-5-(4-(trifluoromethyl)phenyl)pentanenitrile (1k);** yellow oil (20.7 mg, 43%) (lit.<sup>16</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.15-2.08 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.2, 139.1, 134.7 (q, *J*<sub>C-F</sub> = 32.7 Hz), 128.3, 125.8 (q, *J*<sub>C-F</sub> = 3.7 Hz), 123.5 (q, *J*<sub>C-F</sub> = 272.8 Hz), 119.2, 36.7, 19.5, 16.5.

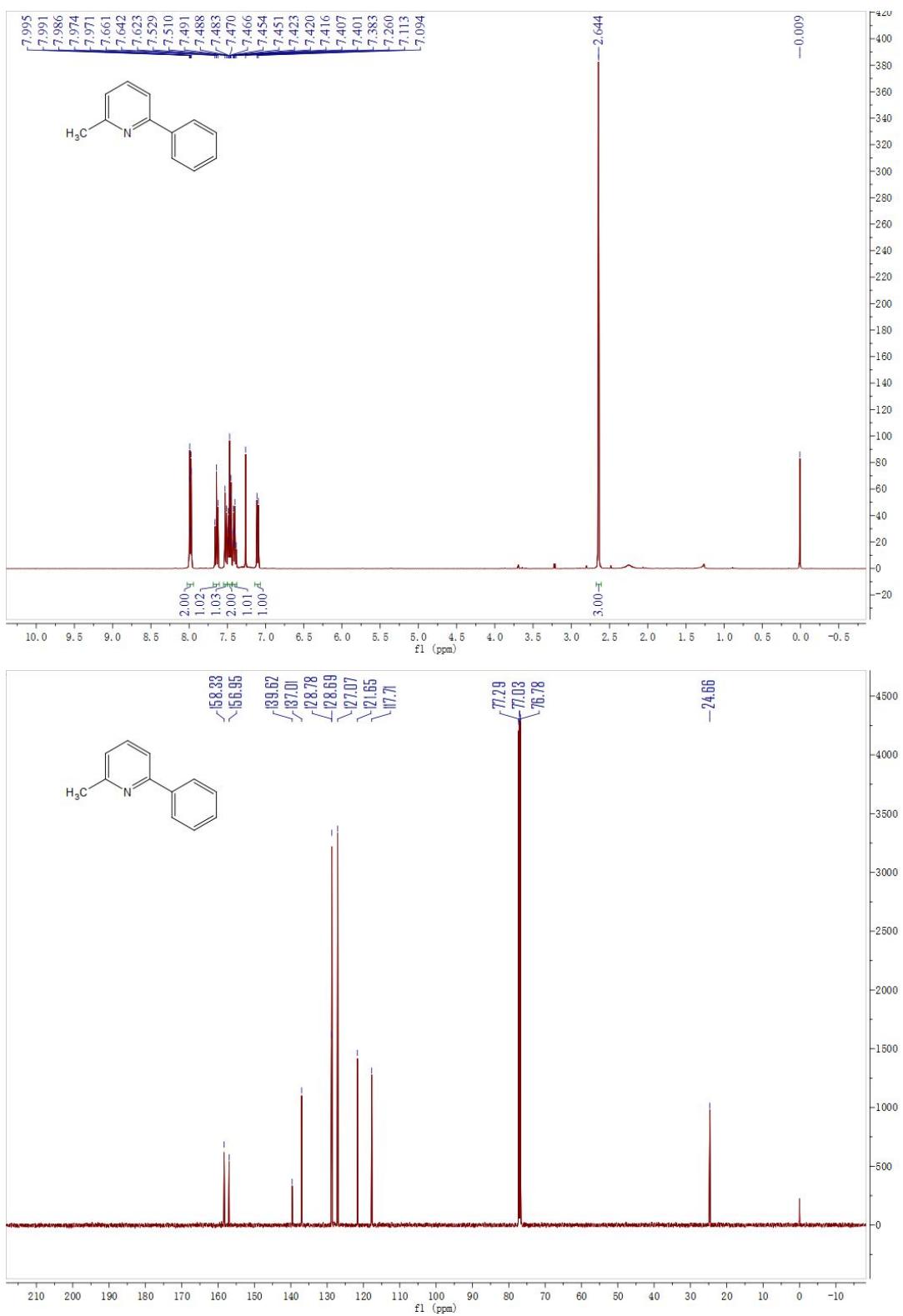
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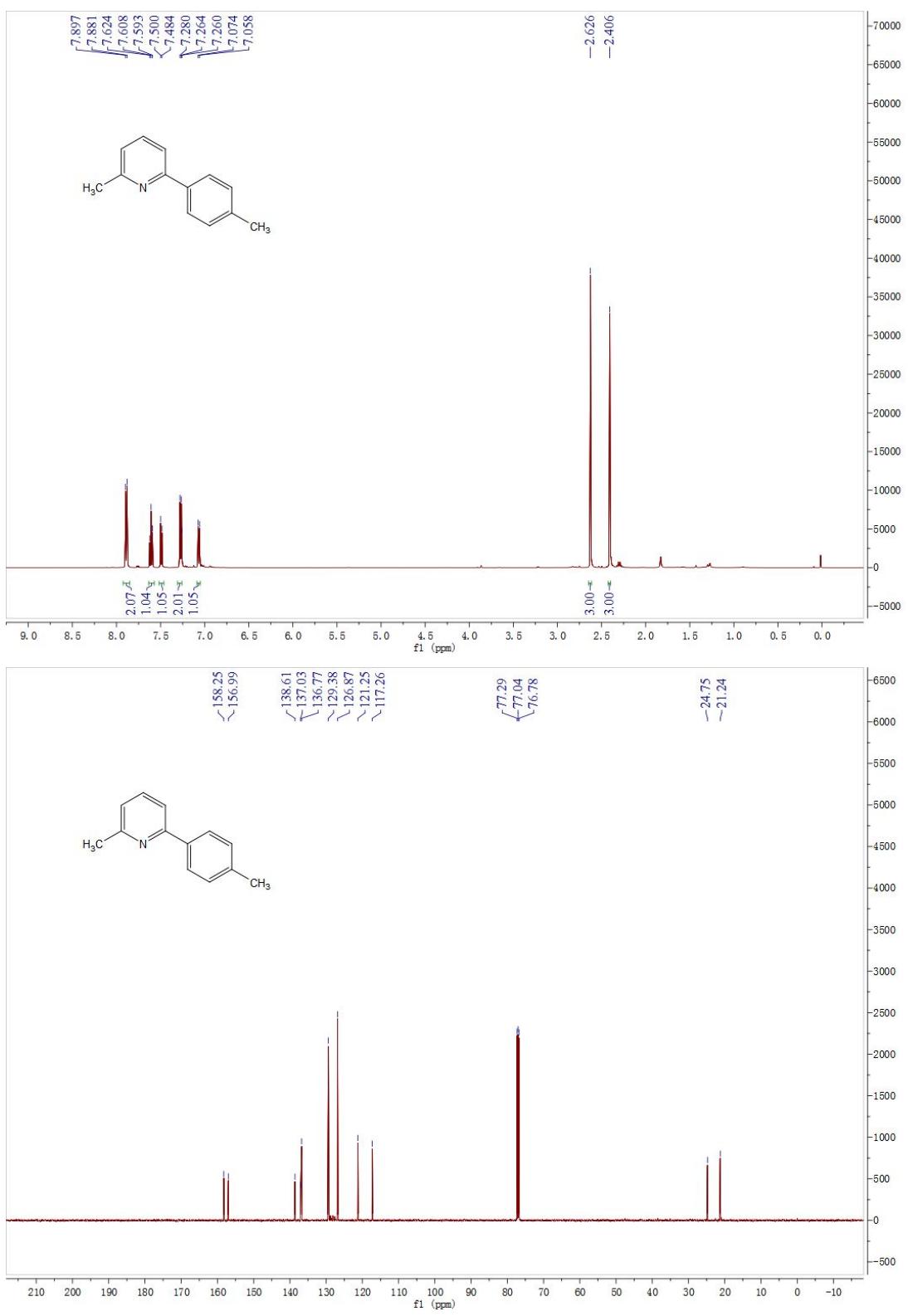
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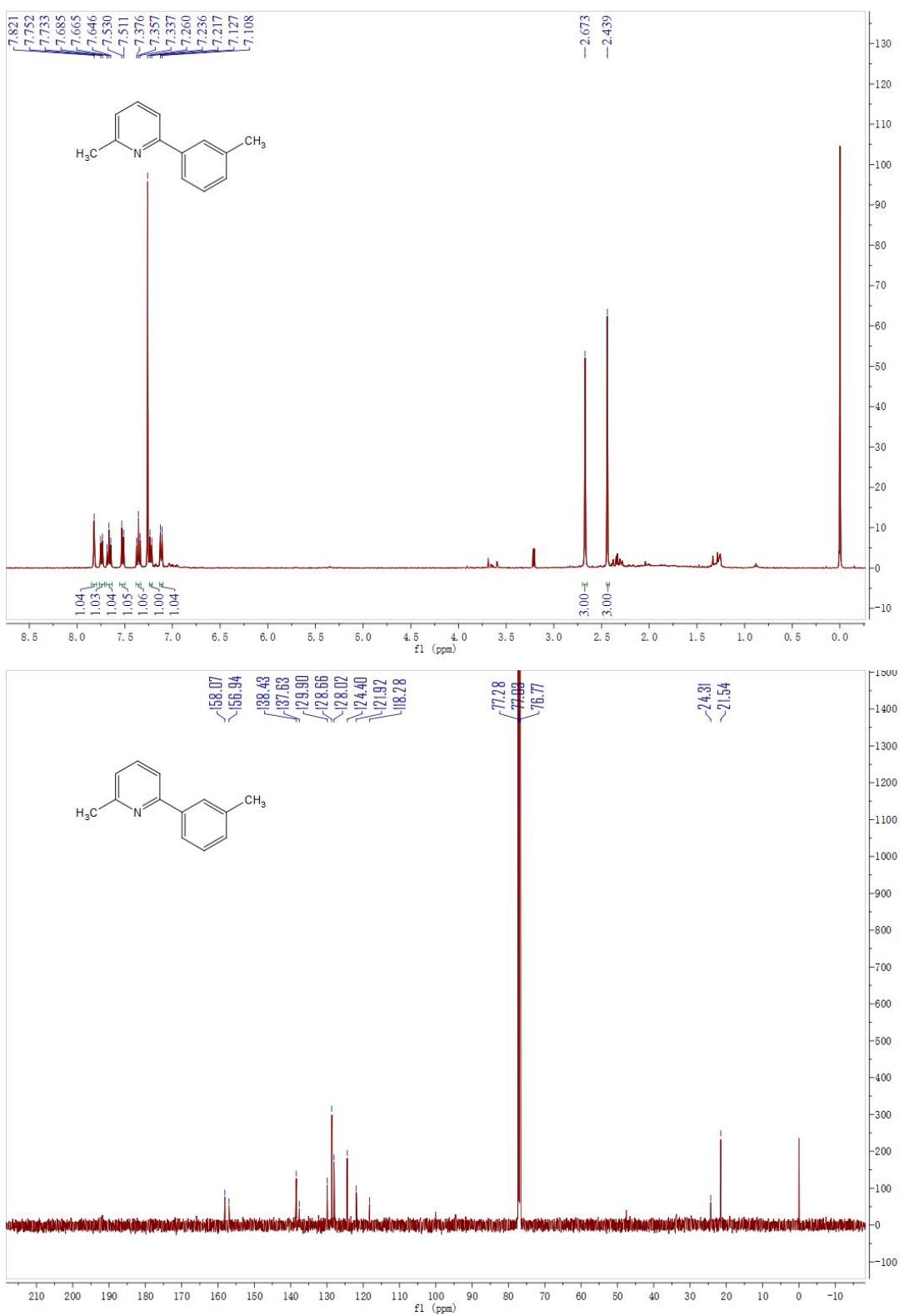
## NMR spectra for all products



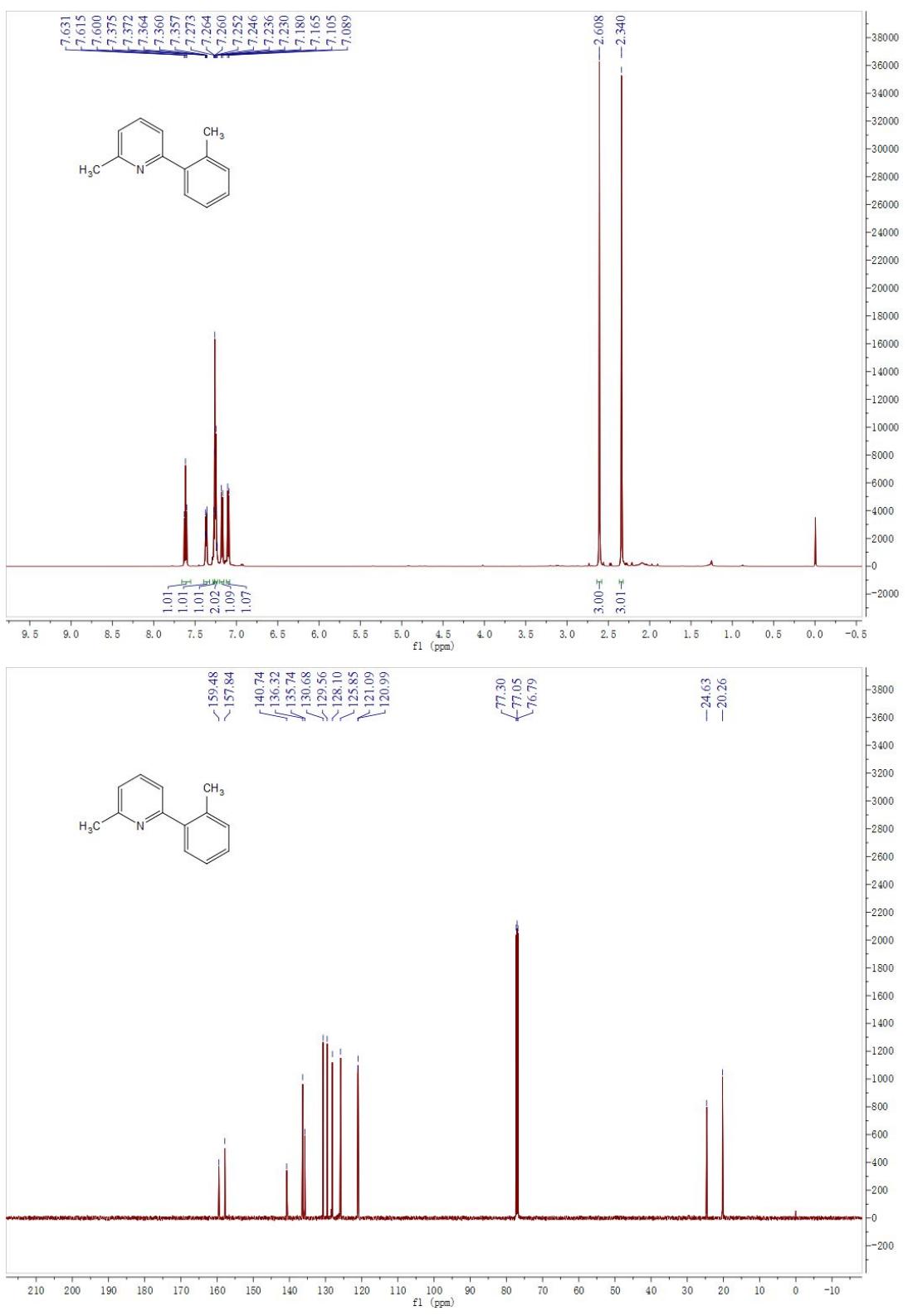
**Figure S1.**  $^1\text{H}$  NMR of **3a** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3a** (125 MHz,  $\text{CDCl}_3$ )



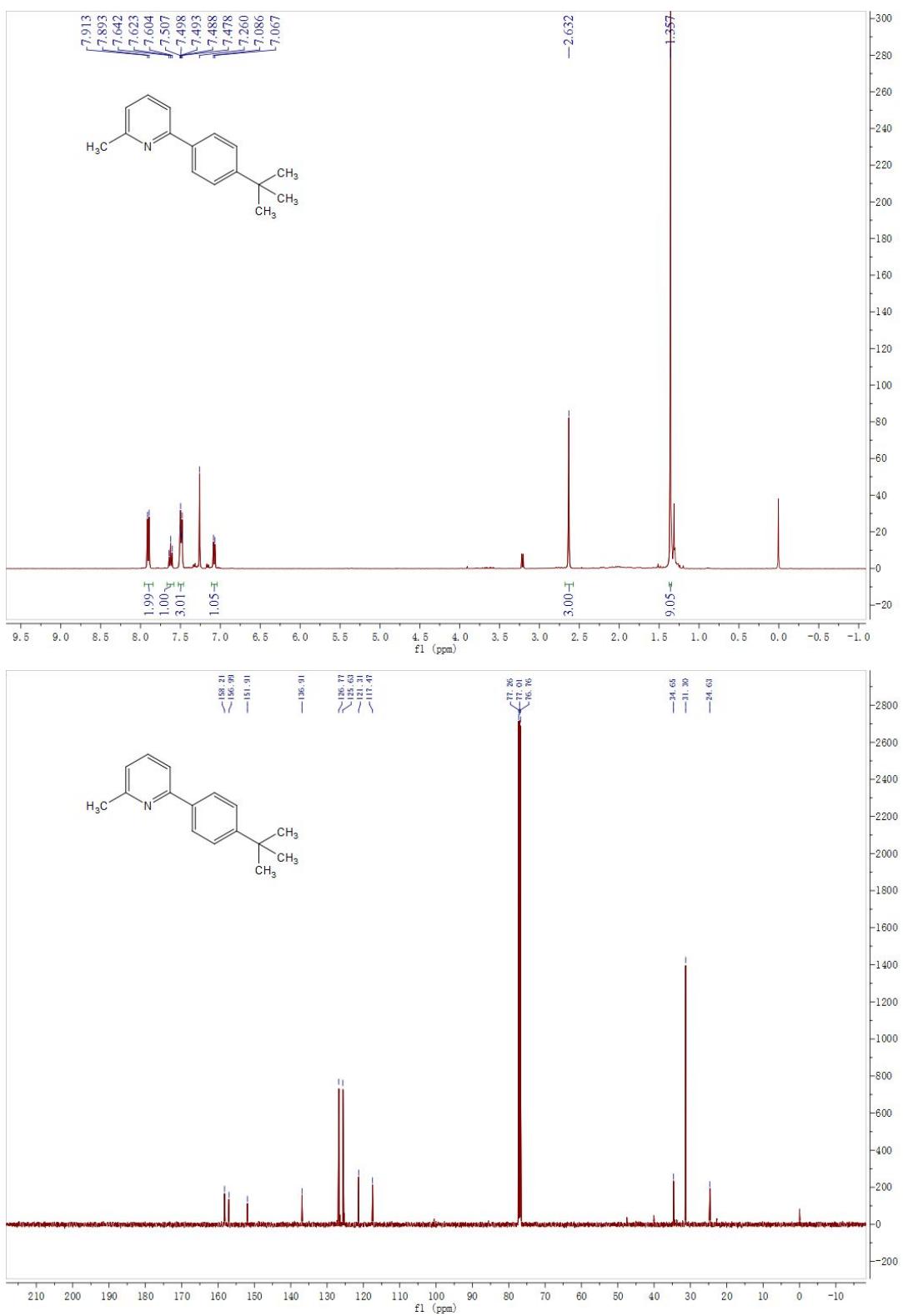
**Figure S2.**  $^1\text{H}$  NMR of **3b** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3b** (125 MHz,  $\text{CDCl}_3$ )



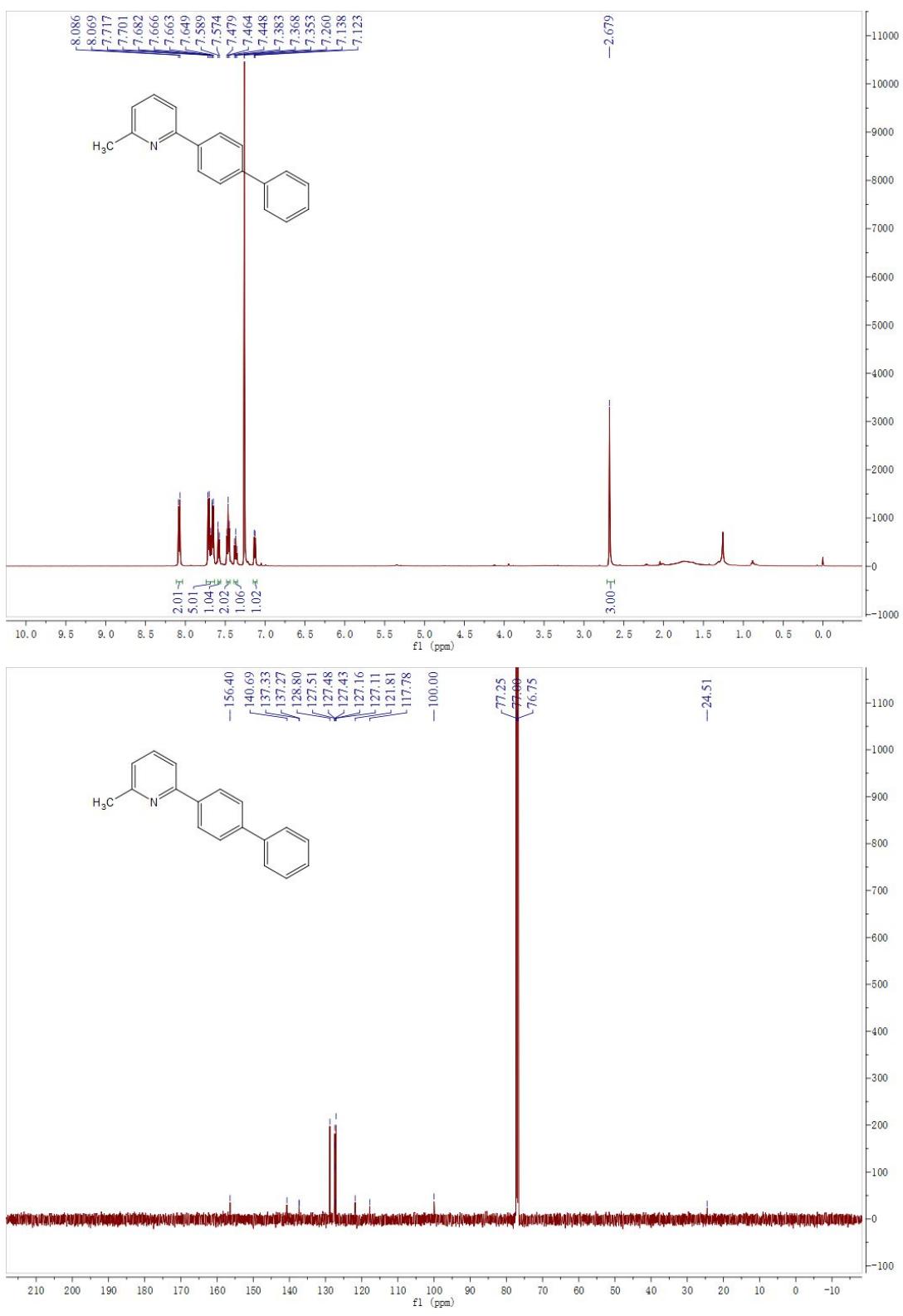
**Figure S3.**  $^1\text{H}$  NMR of **3c** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3c** (125 MHz,  $\text{CDCl}_3$ )



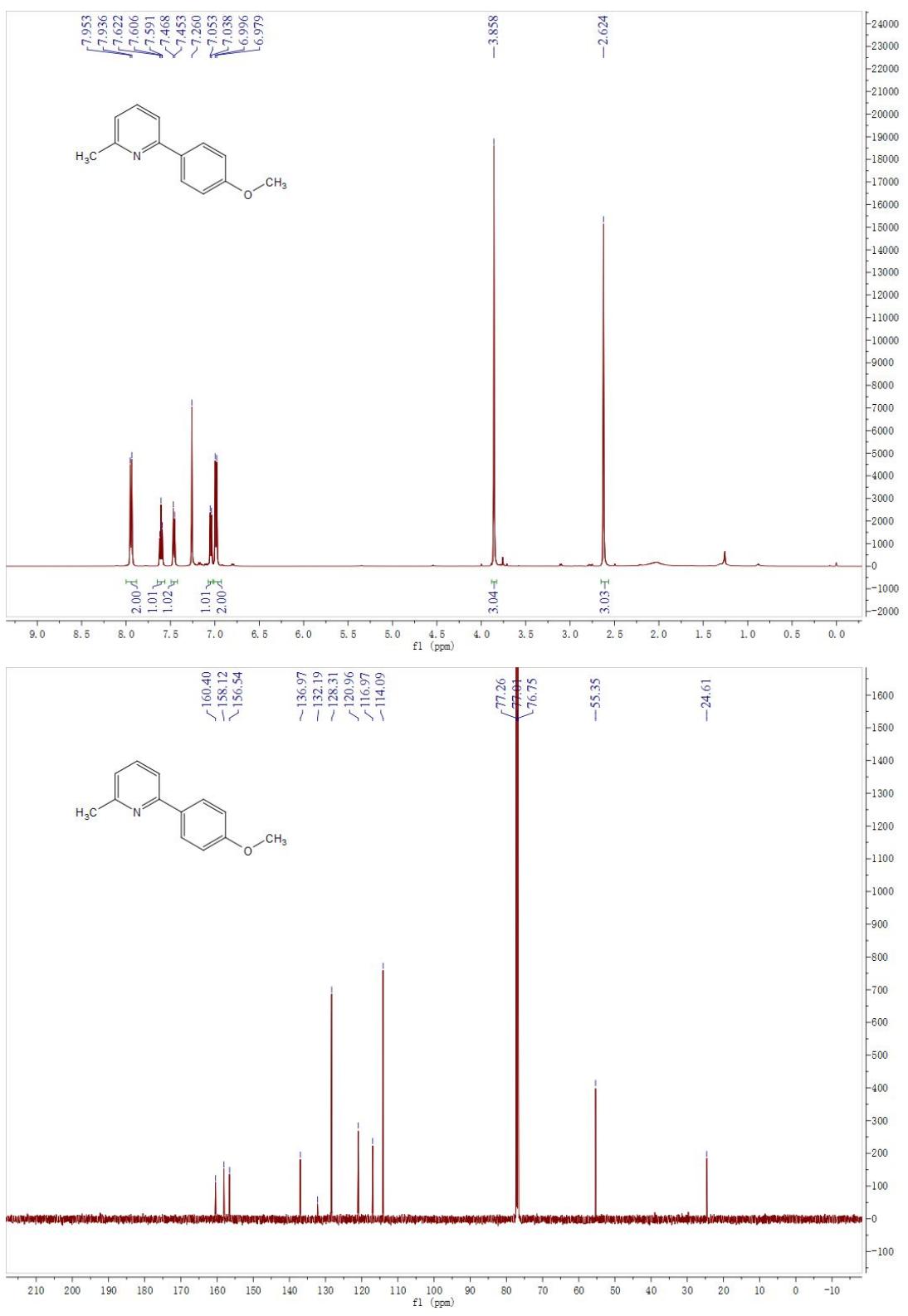
**Figure S4.**  $^1\text{H}$  NMR of **3d** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3d** (125 MHz,  $\text{CDCl}_3$ )



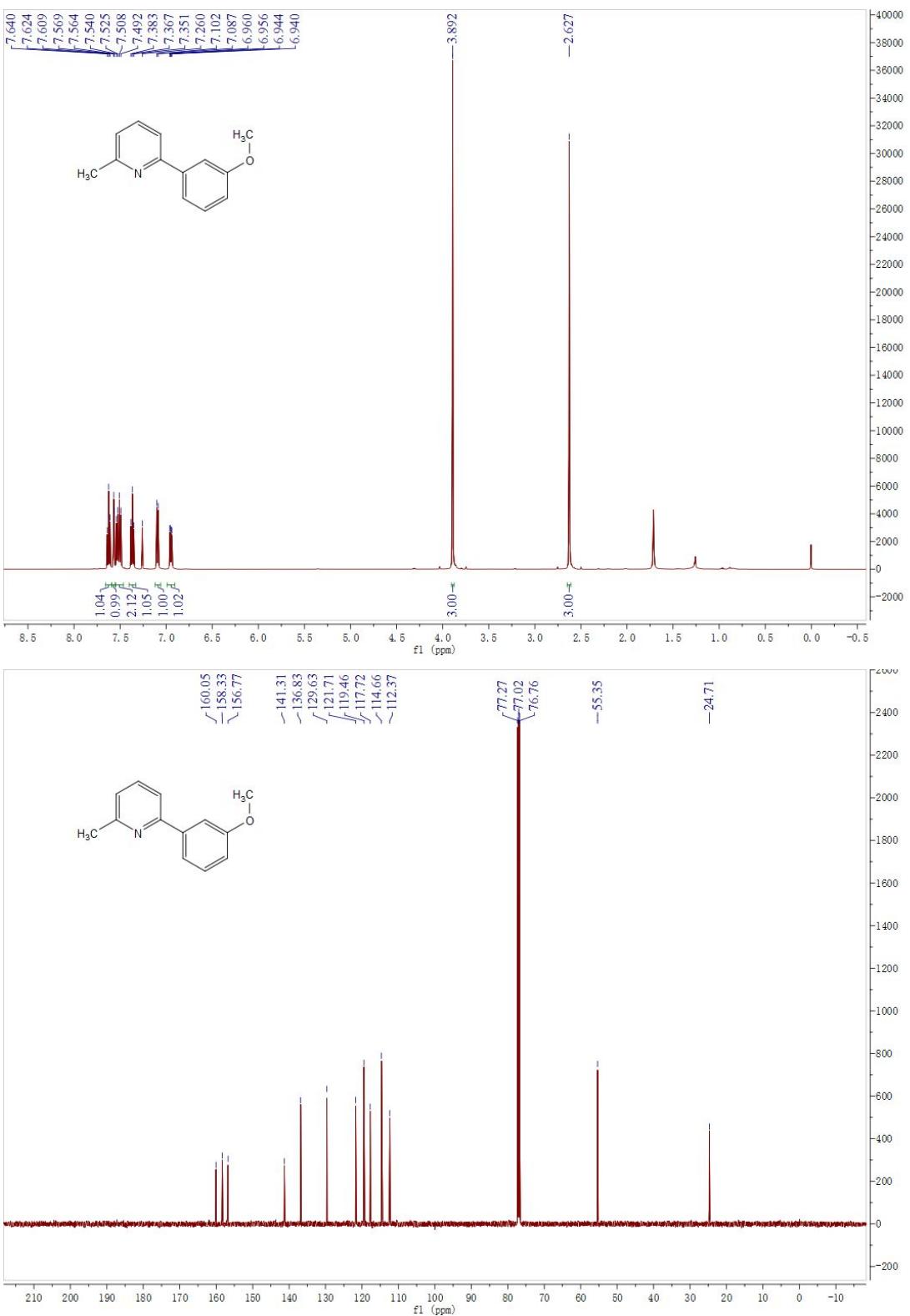
**Figure S5.**  $^1\text{H}$  NMR of **3e** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3e** (125 MHz,  $\text{CDCl}_3$ )



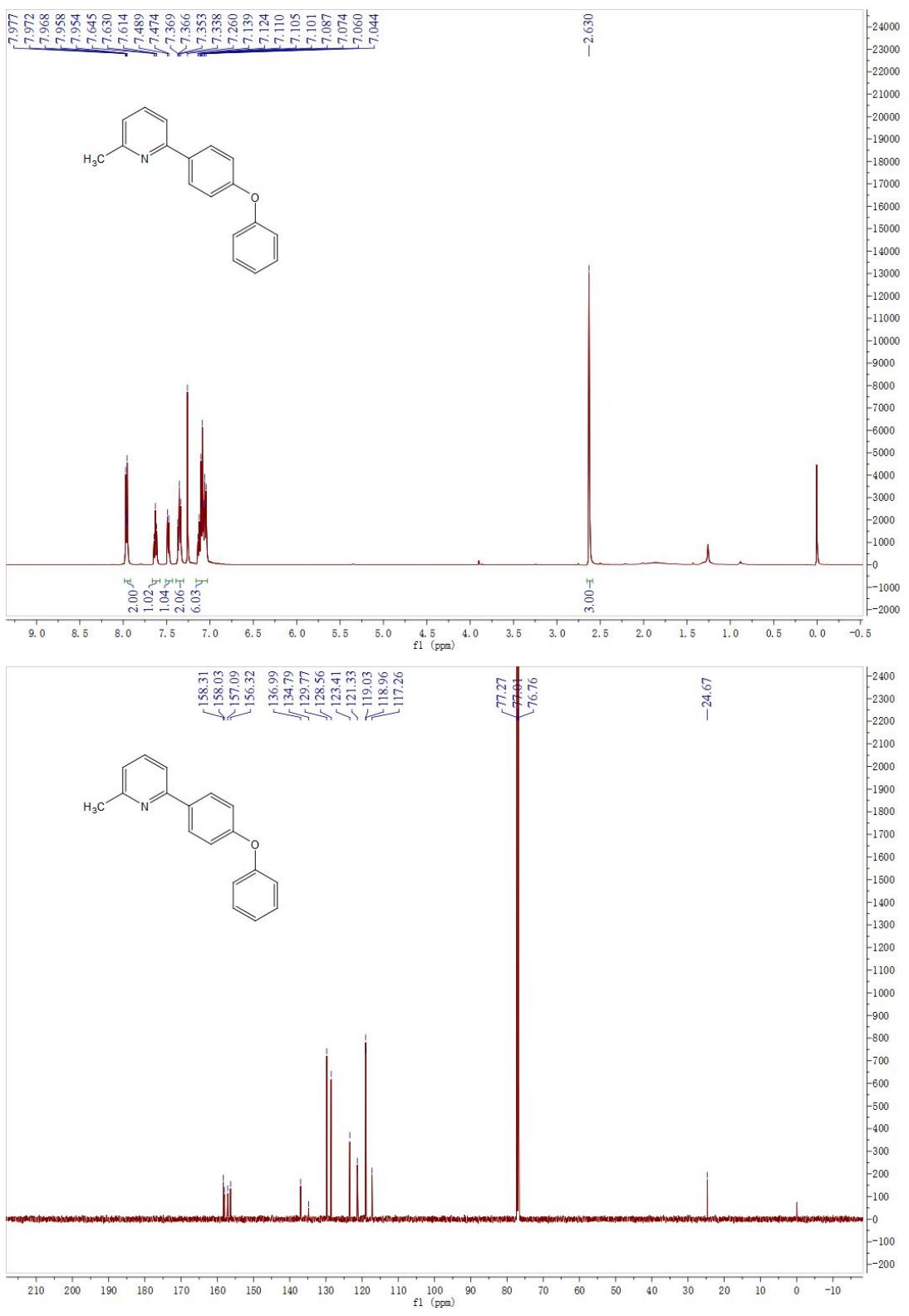
**Figure S6.**  $^1\text{H}$  NMR of **3f** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3f** (125 MHz,  $\text{CDCl}_3$ )



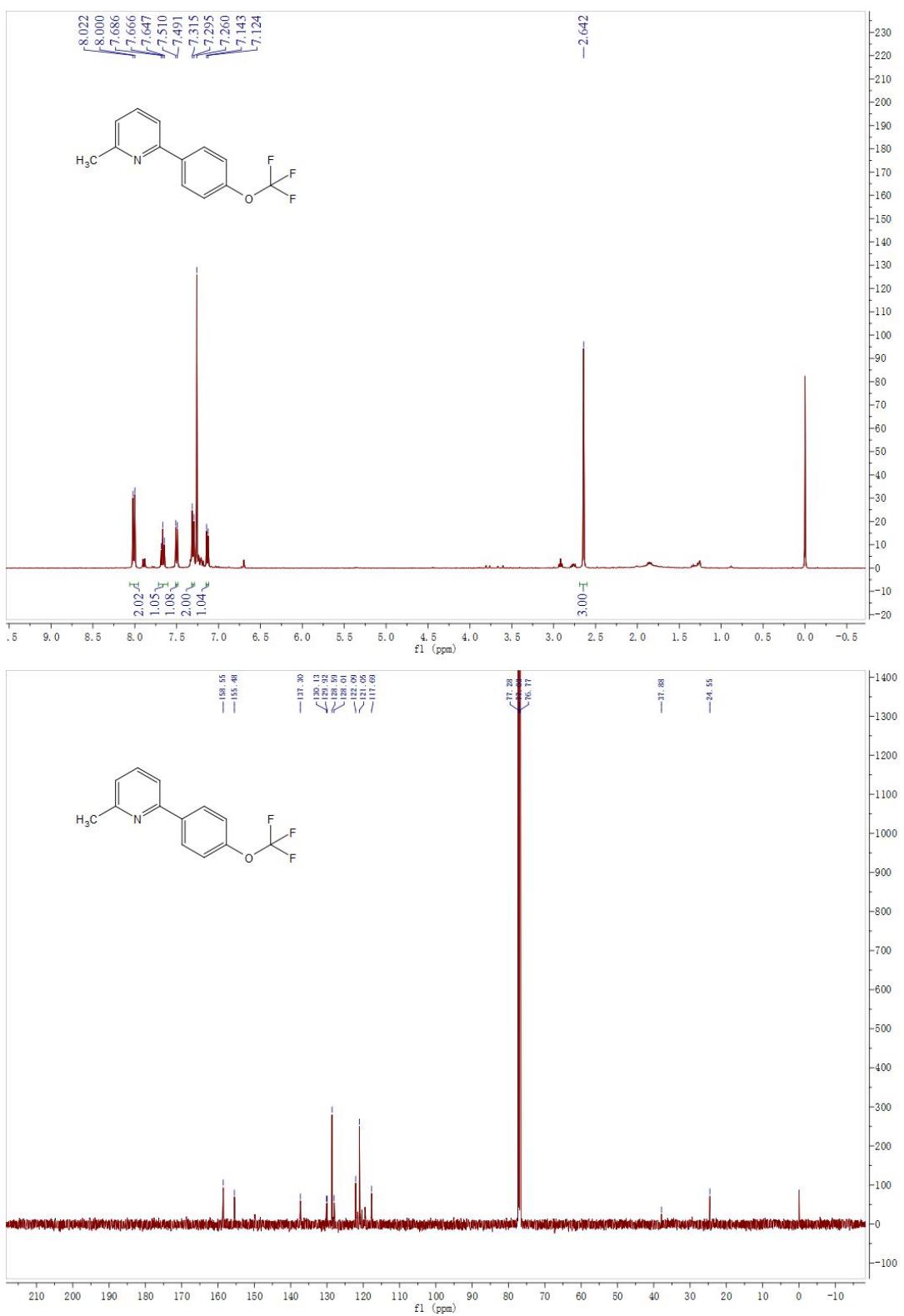
**Figure S7.**  $^1\text{H}$  NMR of **3g** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3g** (125 MHz,  $\text{CDCl}_3$ )



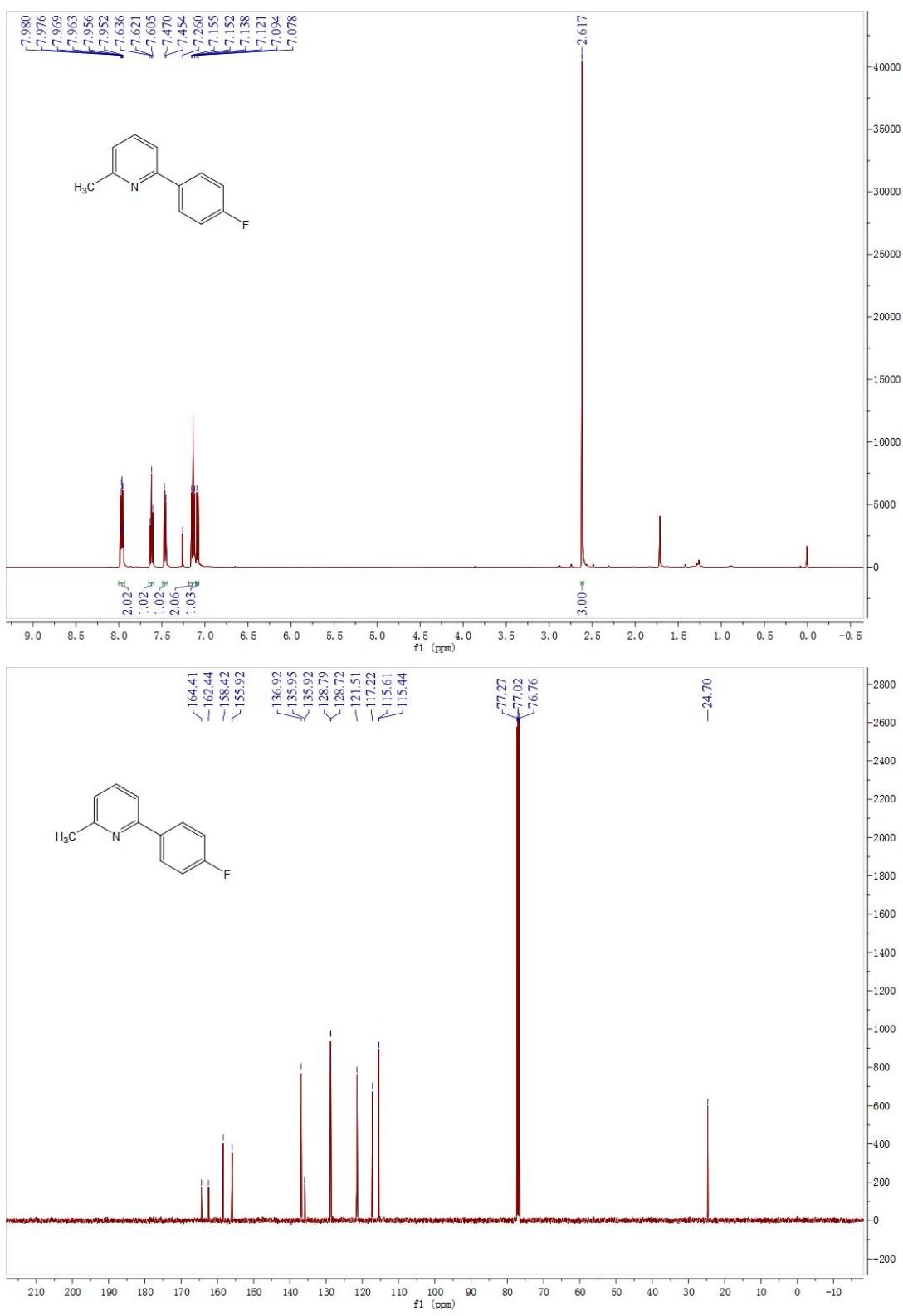
**Figure S8.**  $^1\text{H}$  NMR of **3h** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3h** (125 MHz,  $\text{CDCl}_3$ )



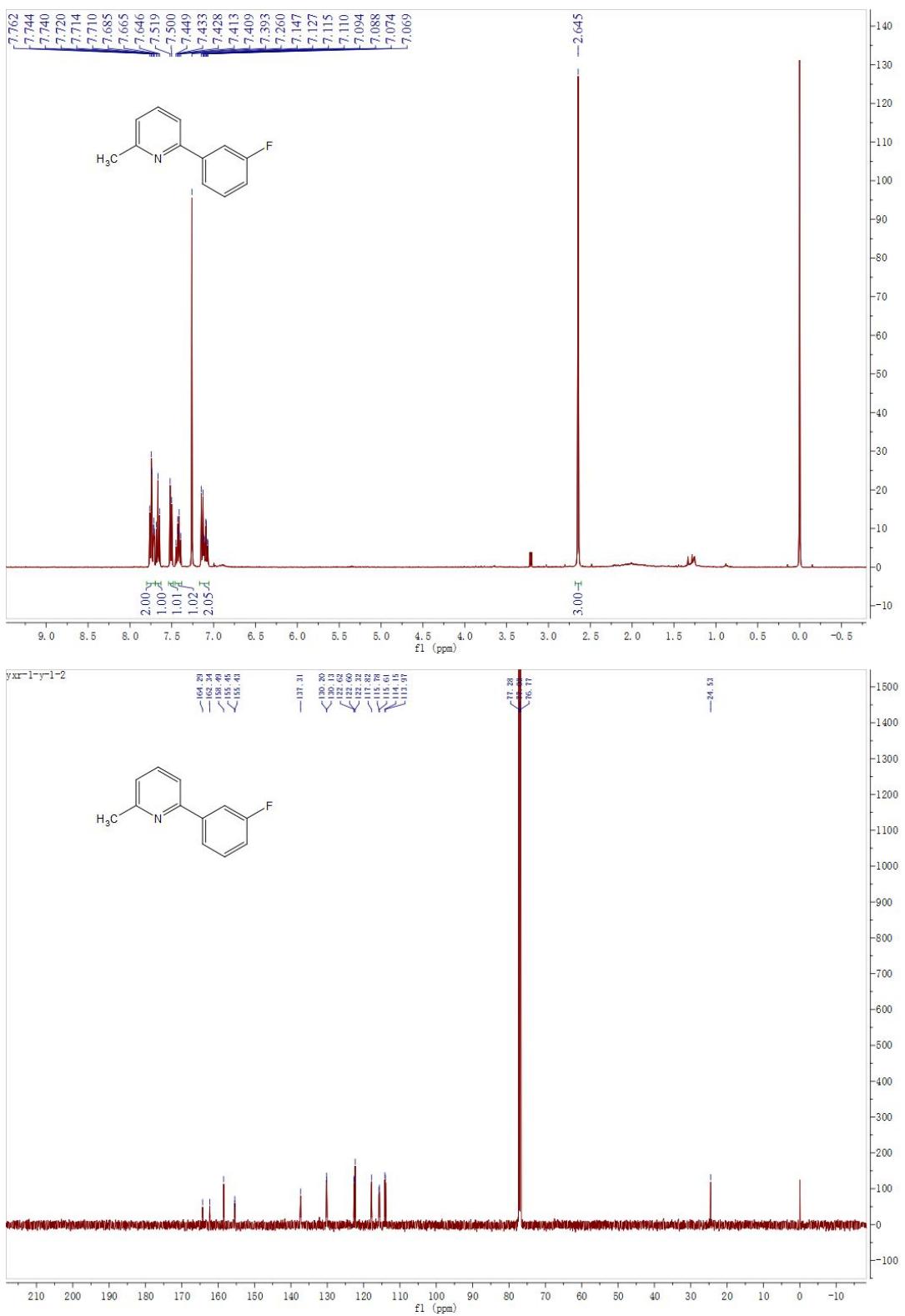
**Figure S9.**  $^1\text{H}$  NMR of **3i** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3i** (125 MHz,  $\text{CDCl}_3$ )



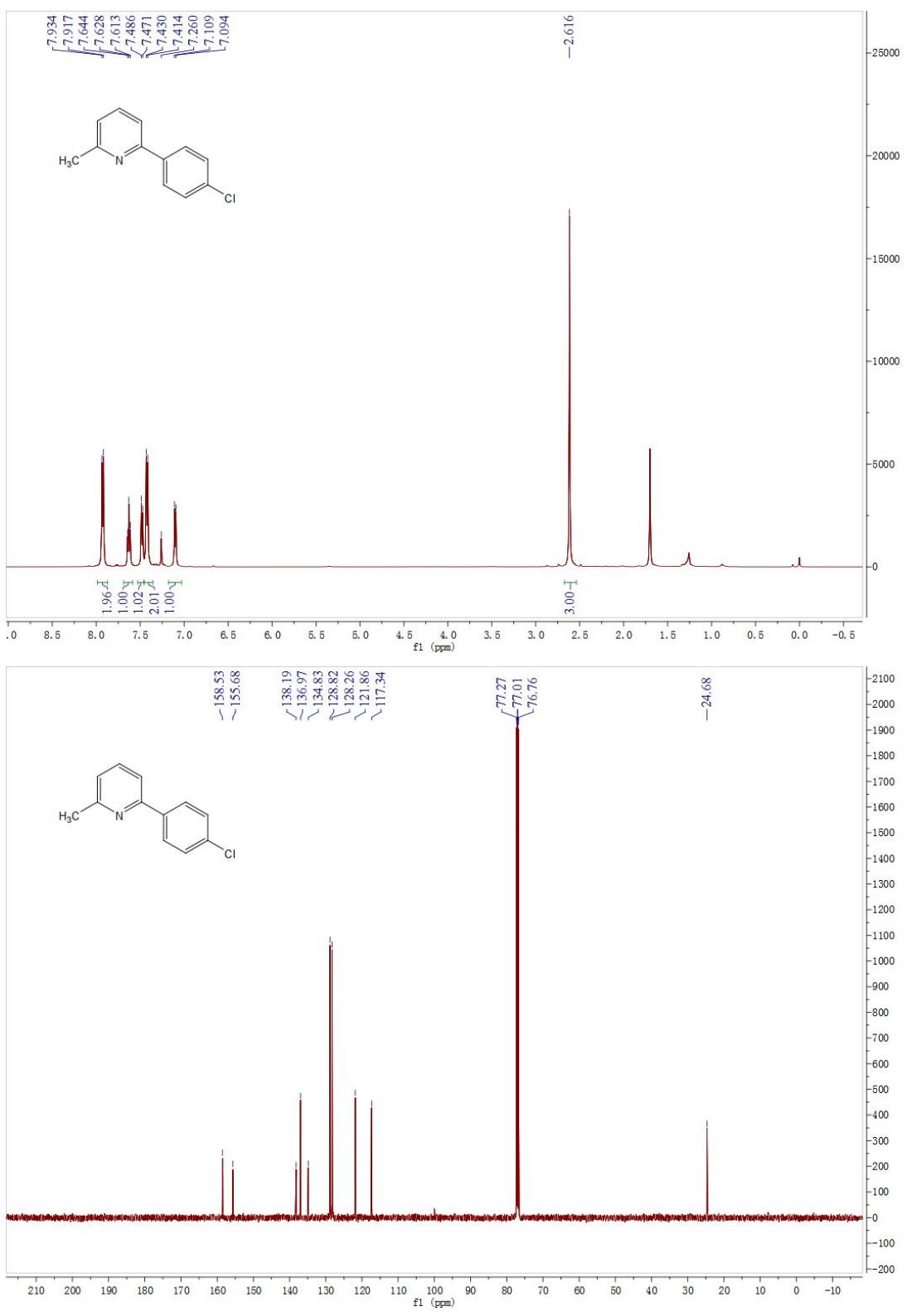
**Figure S10.** <sup>1</sup>H NMR of **3j** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3j** (125 MHz, CDCl<sub>3</sub>)



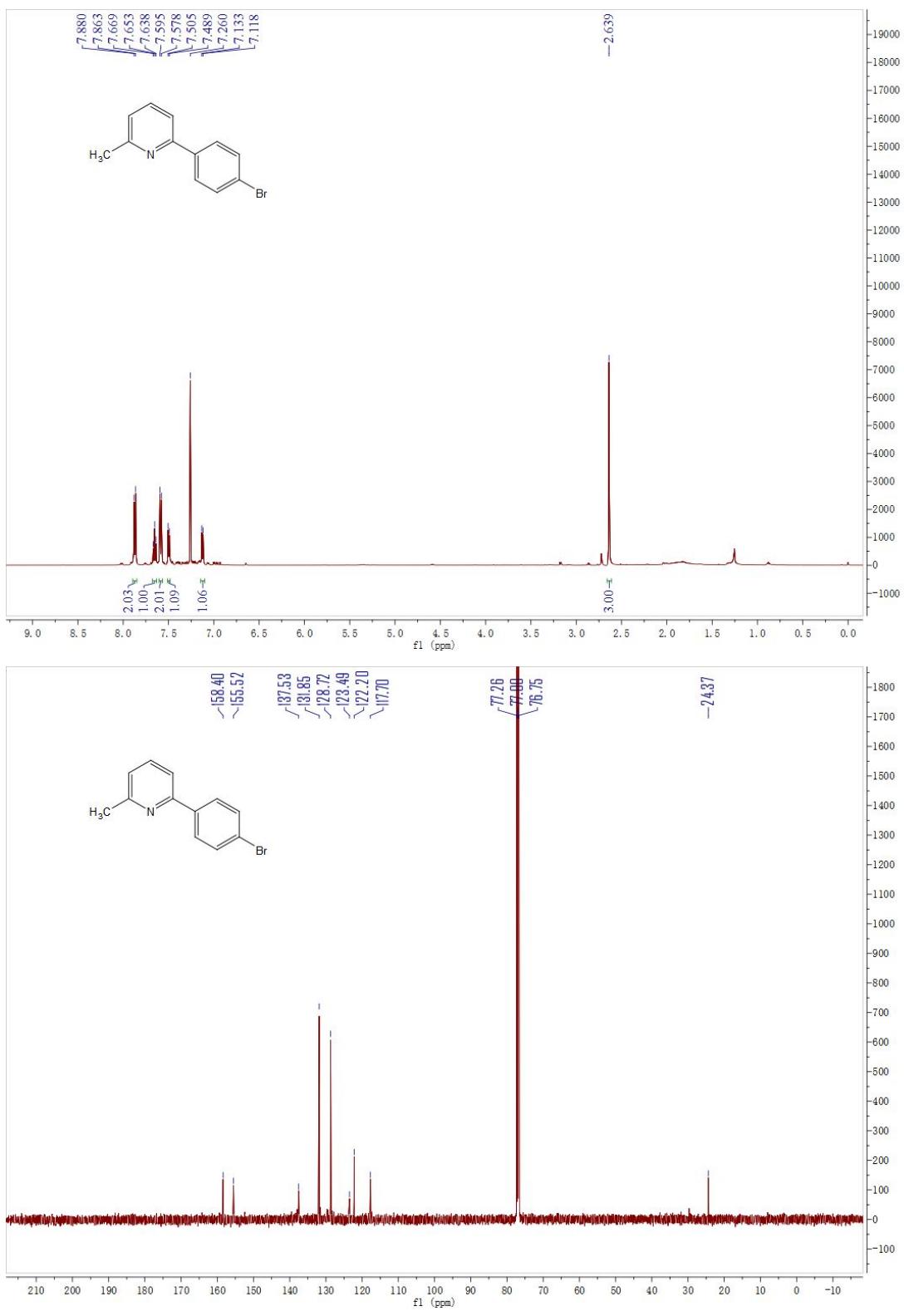
**Figure S11.**  $^1\text{H}$  NMR of **3k** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3k** (125 MHz,  $\text{CDCl}_3$ )



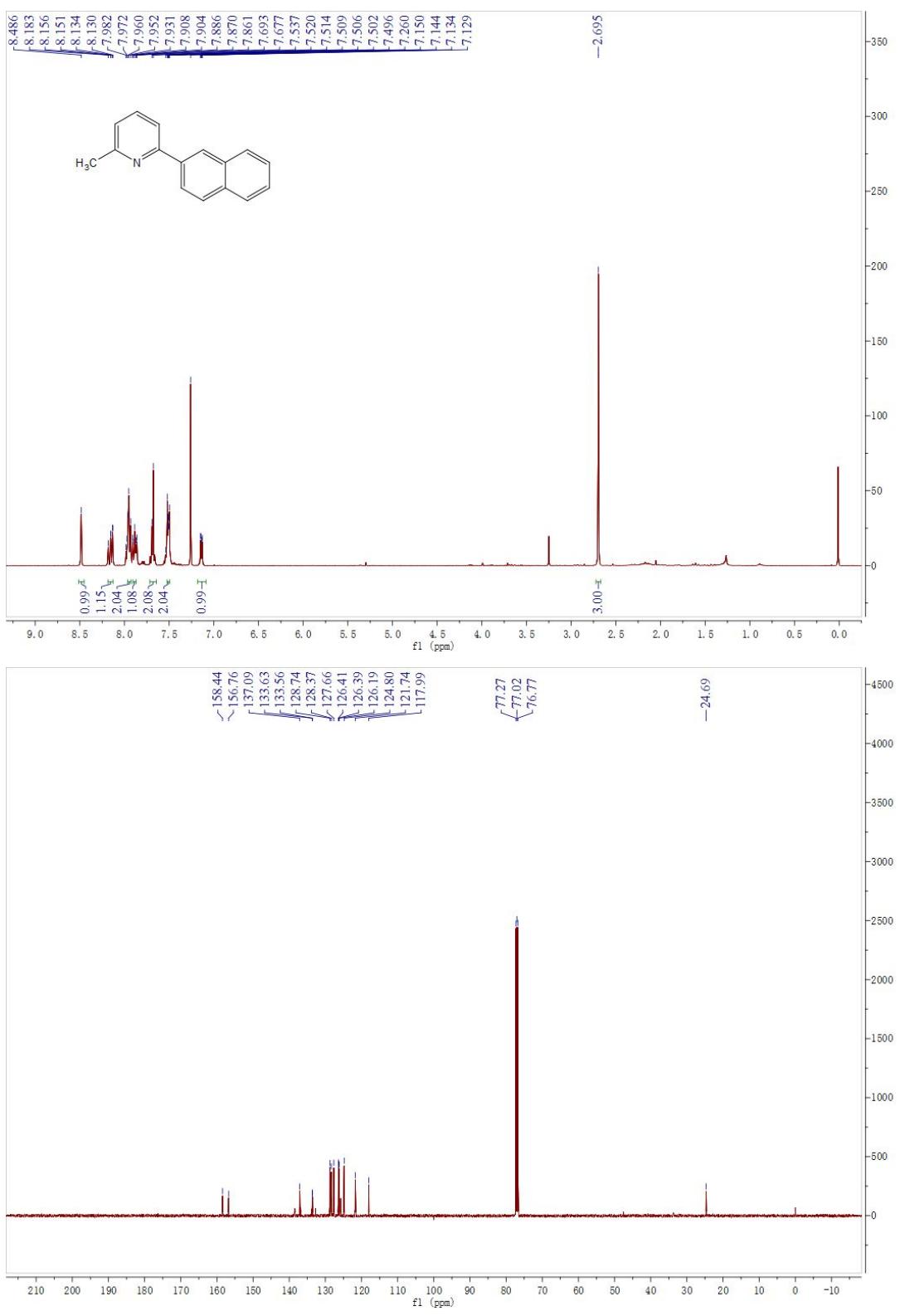
**Figure S12.**  $^1\text{H}$  NMR of **3I** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3I** (125 MHz,  $\text{CDCl}_3$ )



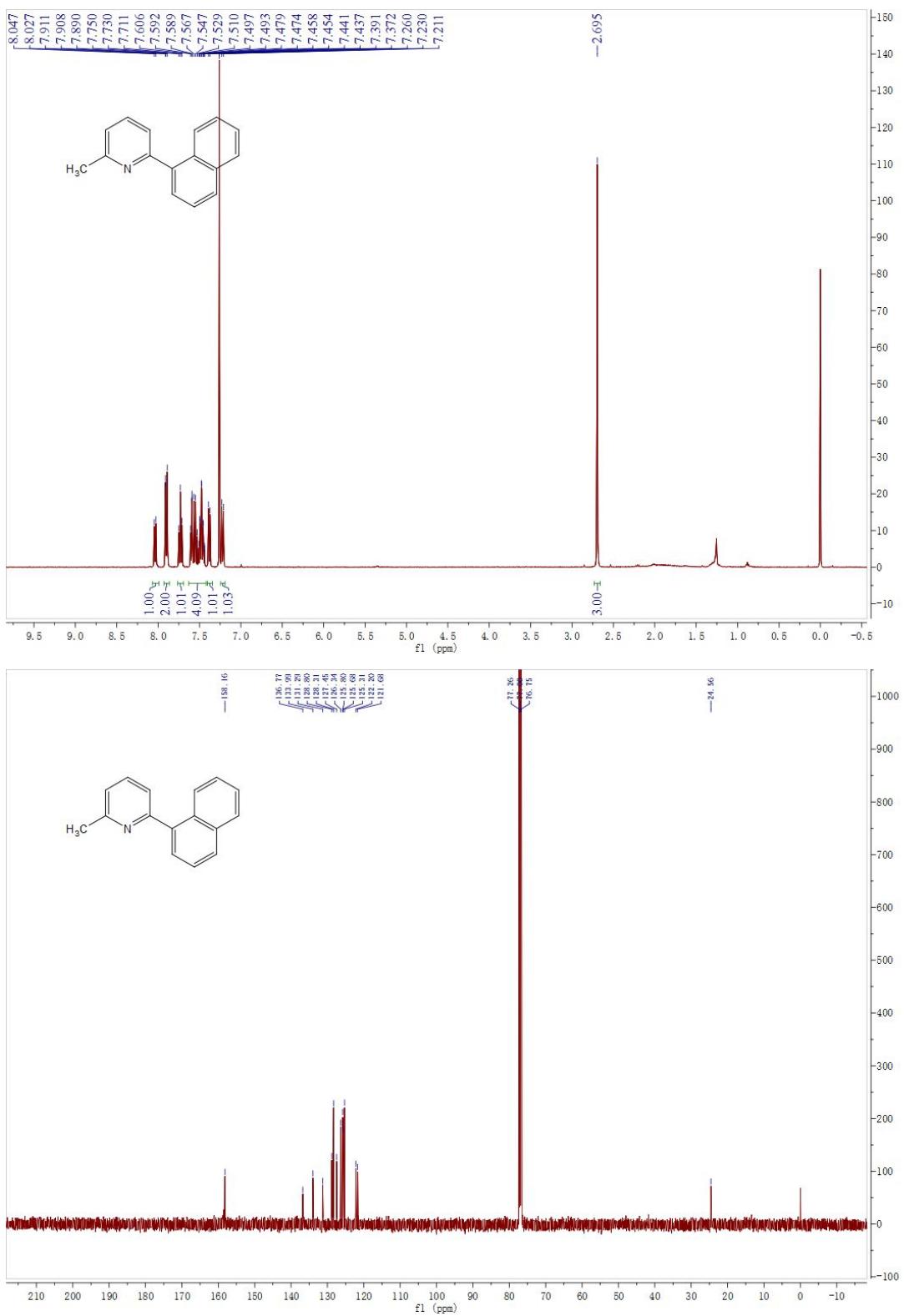
**Figure S13.** <sup>1</sup>H NMR of **3m** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **3m** (125 MHz, CDCl<sub>3</sub>)



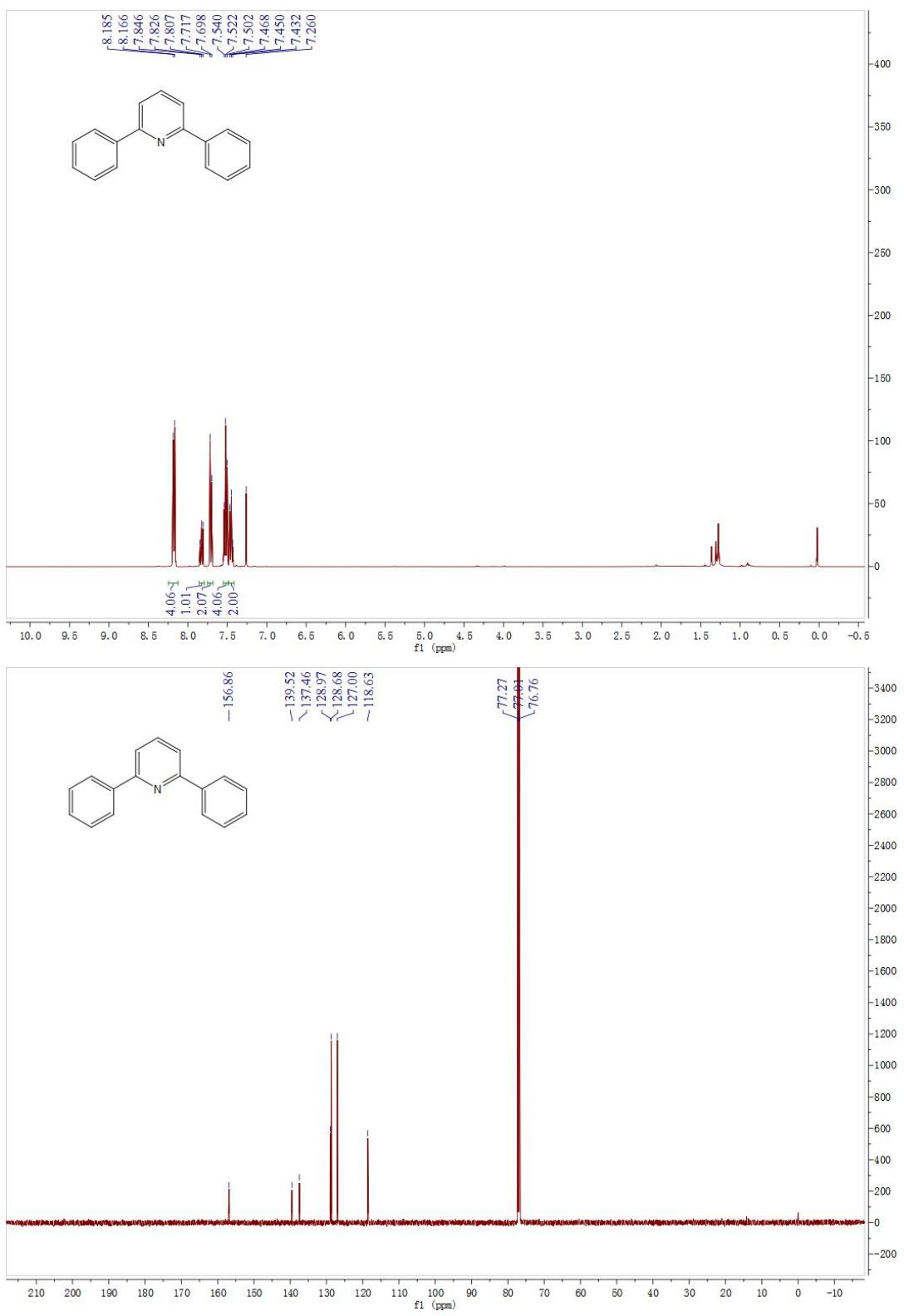
**Figure S14.**  $^1\text{H}$  NMR of **3n** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3n** (125 MHz,  $\text{CDCl}_3$ )



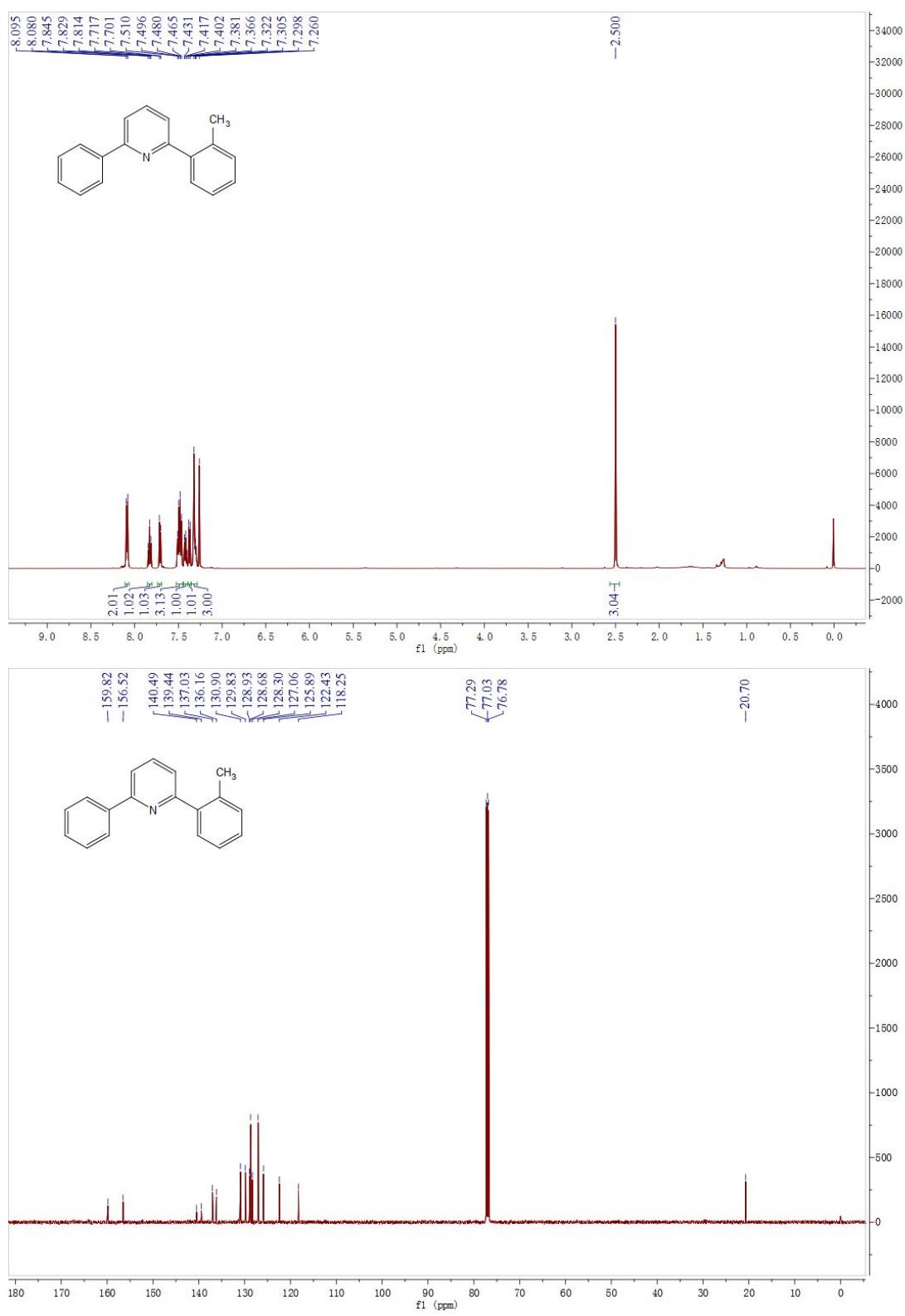
**Figure S15.**  $^1\text{H}$  NMR of **3o** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3o** (125 MHz,  $\text{CDCl}_3$ )



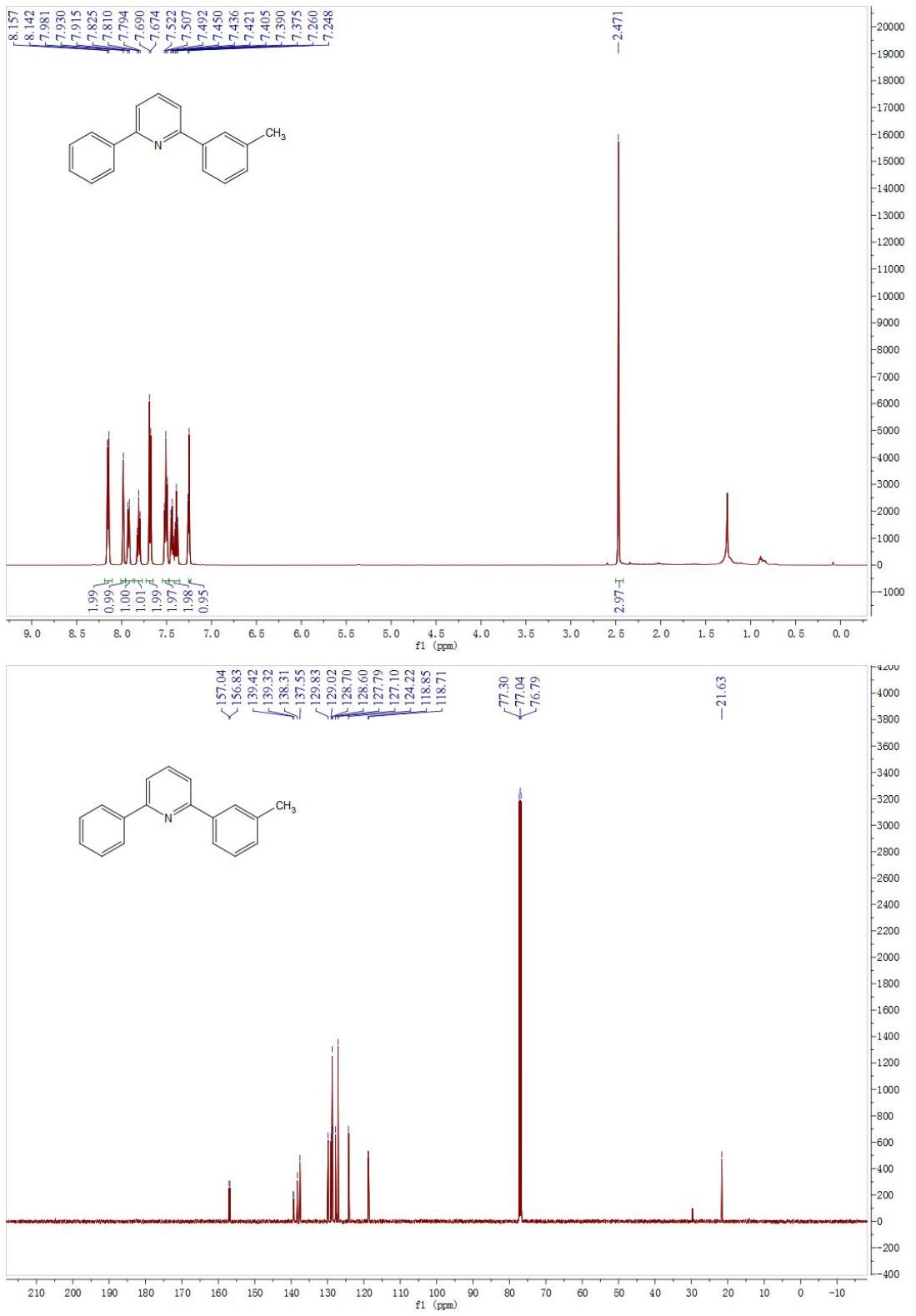
**Figure S16.**  $^1\text{H}$  NMR of **3p** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **3p** (125 MHz,  $\text{CDCl}_3$ )



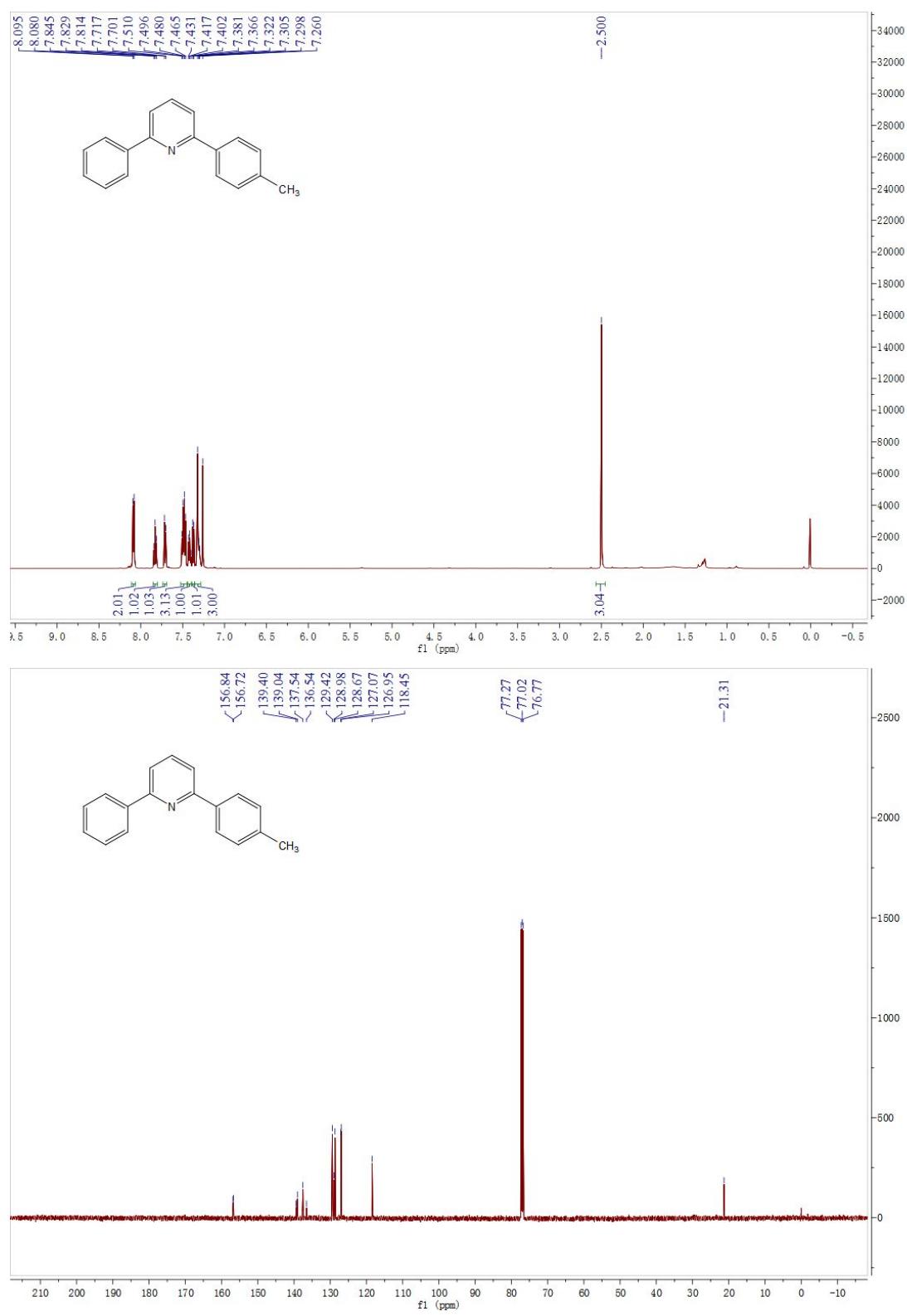
**Figure S17.**  $^1\text{H}$  NMR of **4a** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4a** (125 MHz,  $\text{CDCl}_3$ )



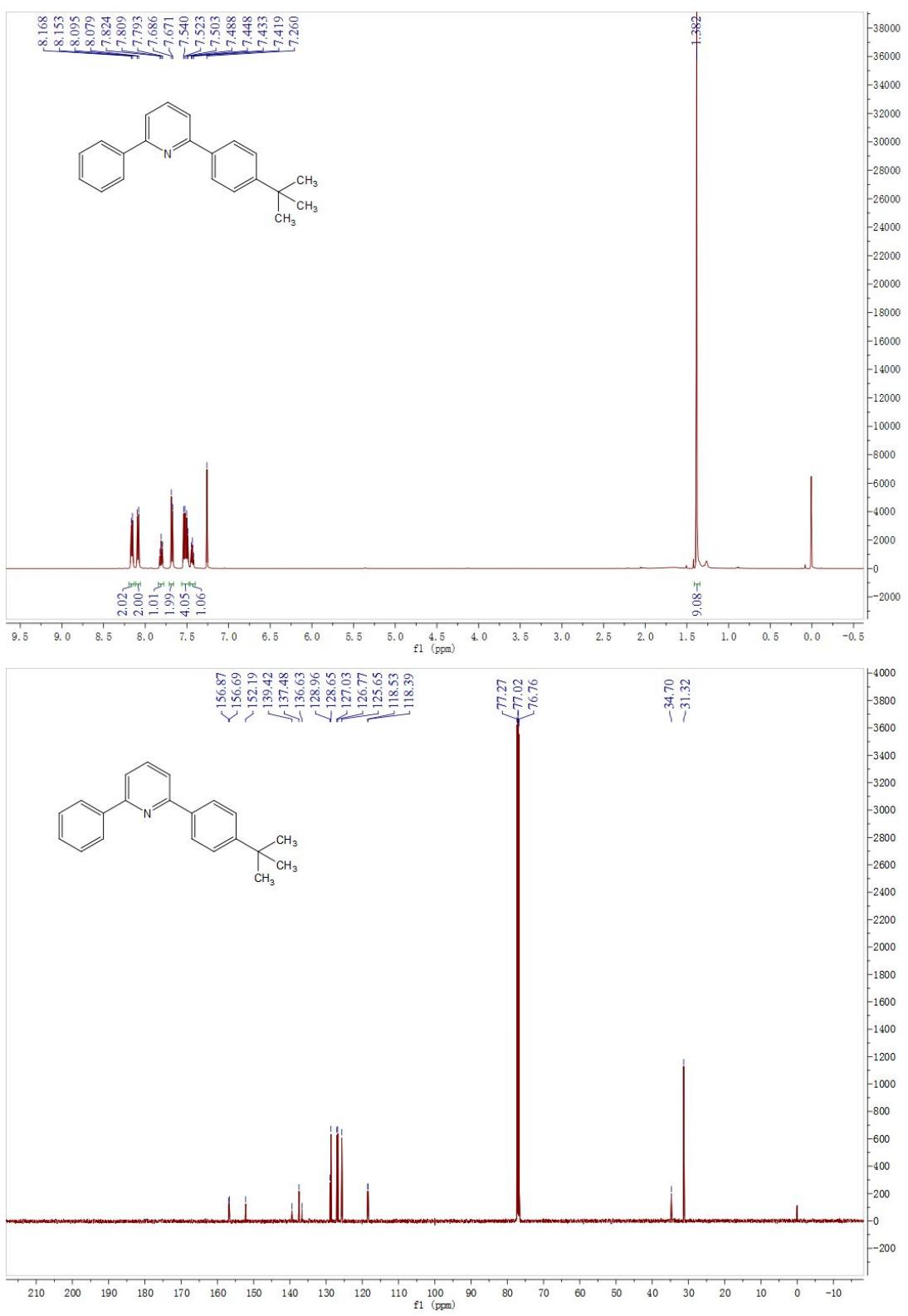
**Figure S18.**  $^1\text{H}$  NMR of **4b** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4b** (125 MHz,  $\text{CDCl}_3$ )



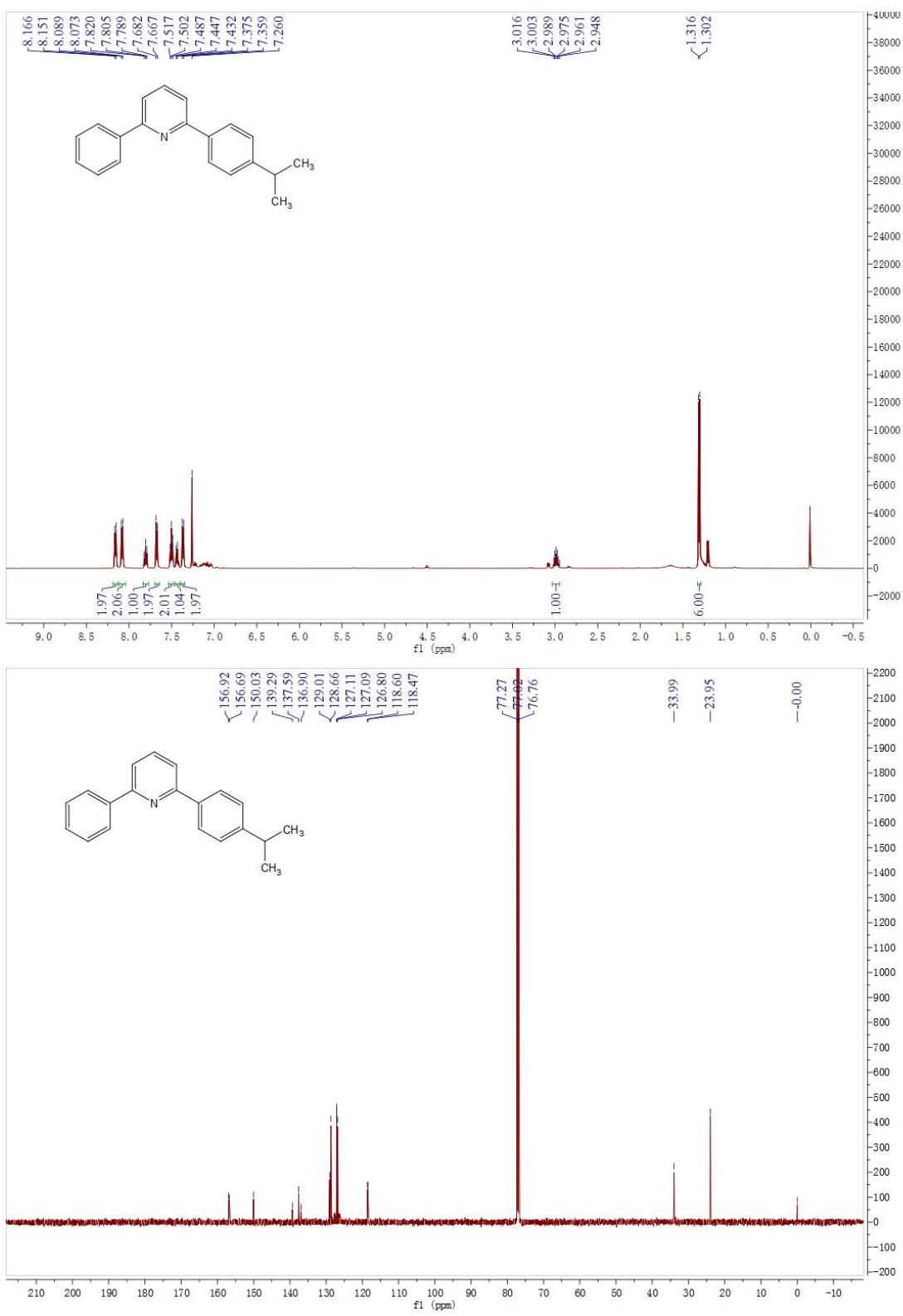
**Figure S19.**  $^1\text{H}$  NMR of **4c** (400 MHz, CDCl<sub>3</sub>) and  $^{13}\text{C}$  NMR of **4c** (125 MHz, CDCl<sub>3</sub>)



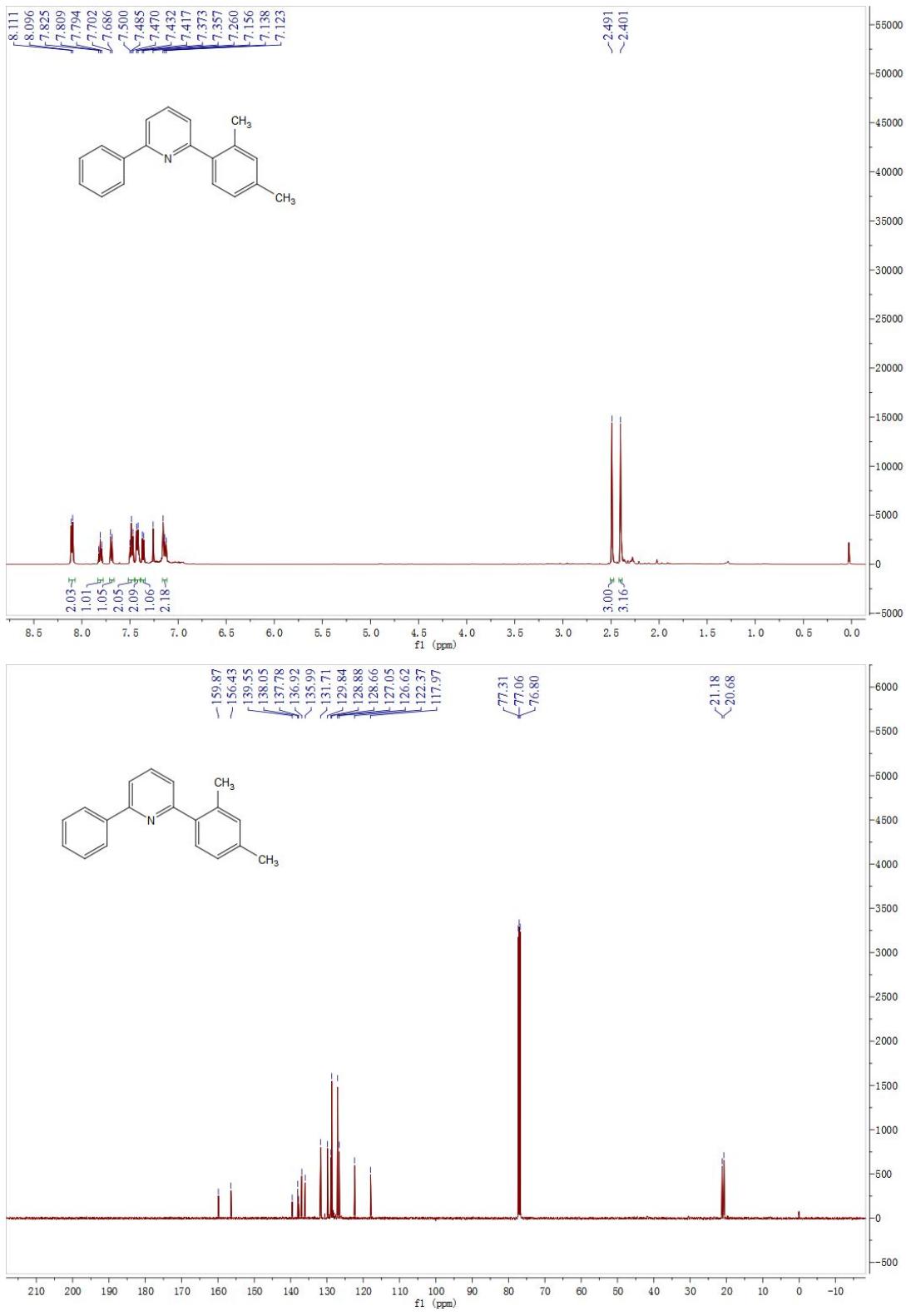
**Figure S20.** <sup>1</sup>H NMR of **4d** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4d** (125 MHz, CDCl<sub>3</sub>)



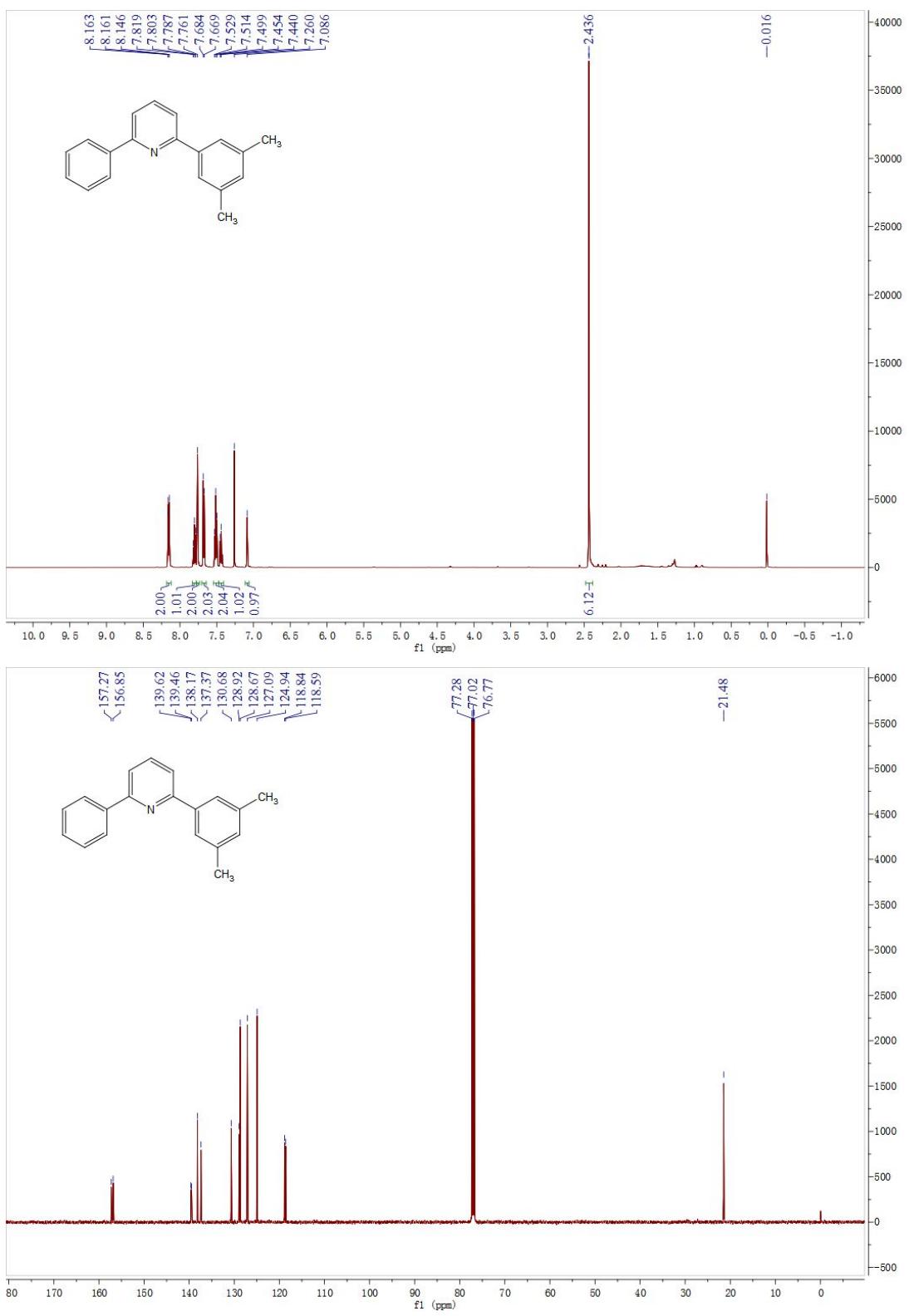
**Figure S21.**  $^1\text{H}$  NMR of **4e** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4e** (125 MHz,  $\text{CDCl}_3$ )



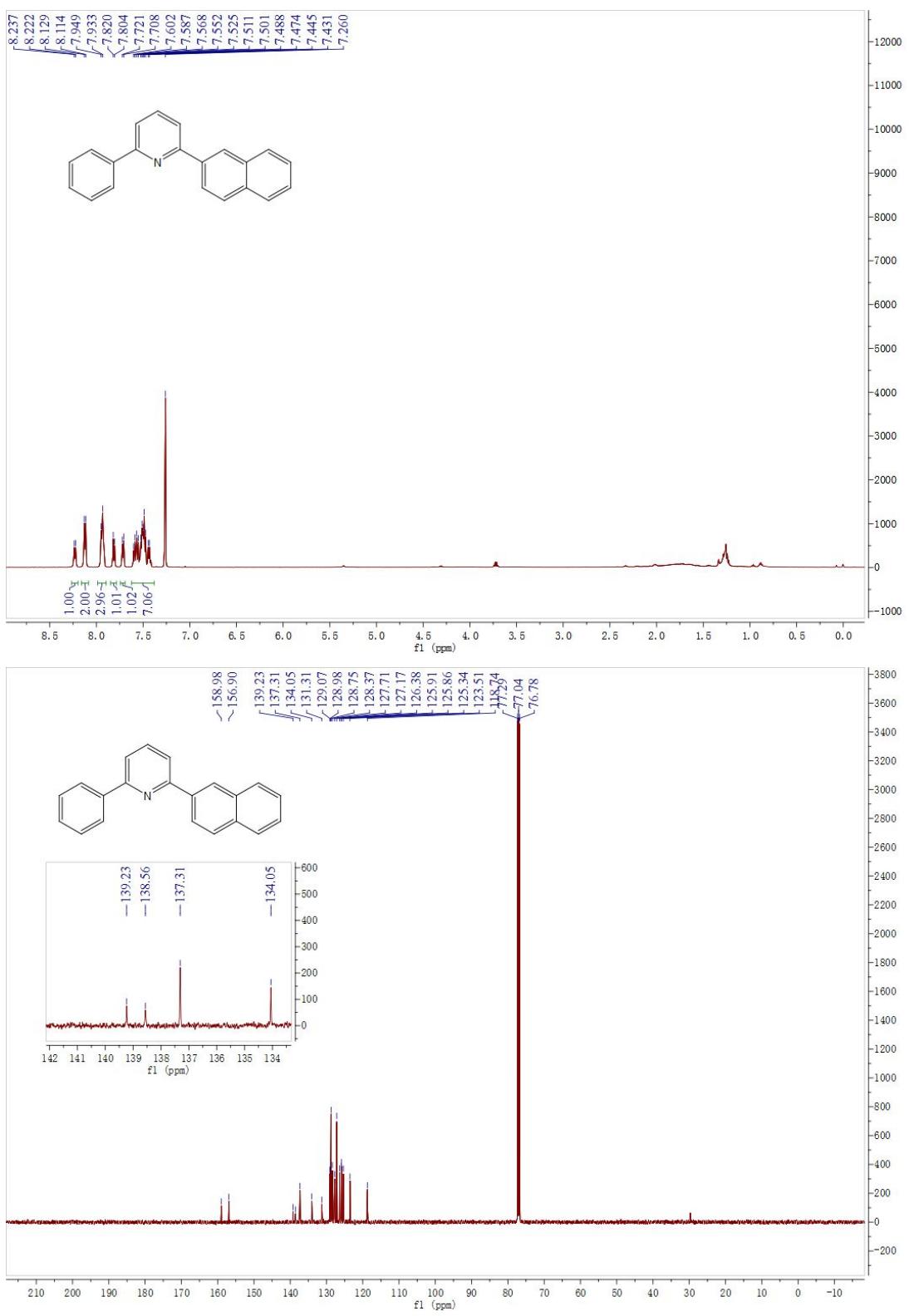
**Figure S22.**  $^1\text{H}$  NMR of **4f** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4f** (125 MHz,  $\text{CDCl}_3$ )



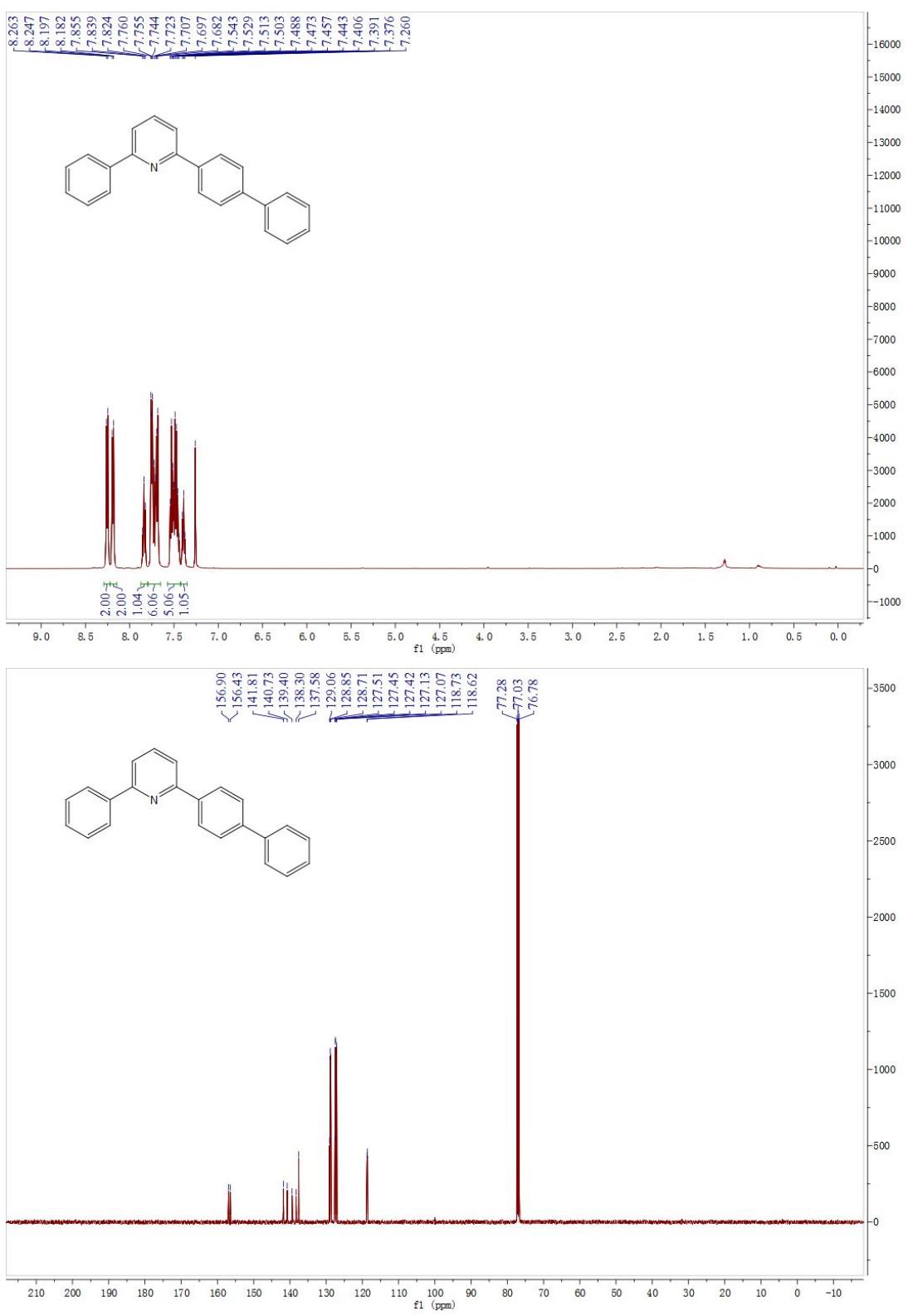
**Figure S23.**  $^1\text{H}$  NMR of **4g** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4g** (125 MHz,  $\text{CDCl}_3$ )



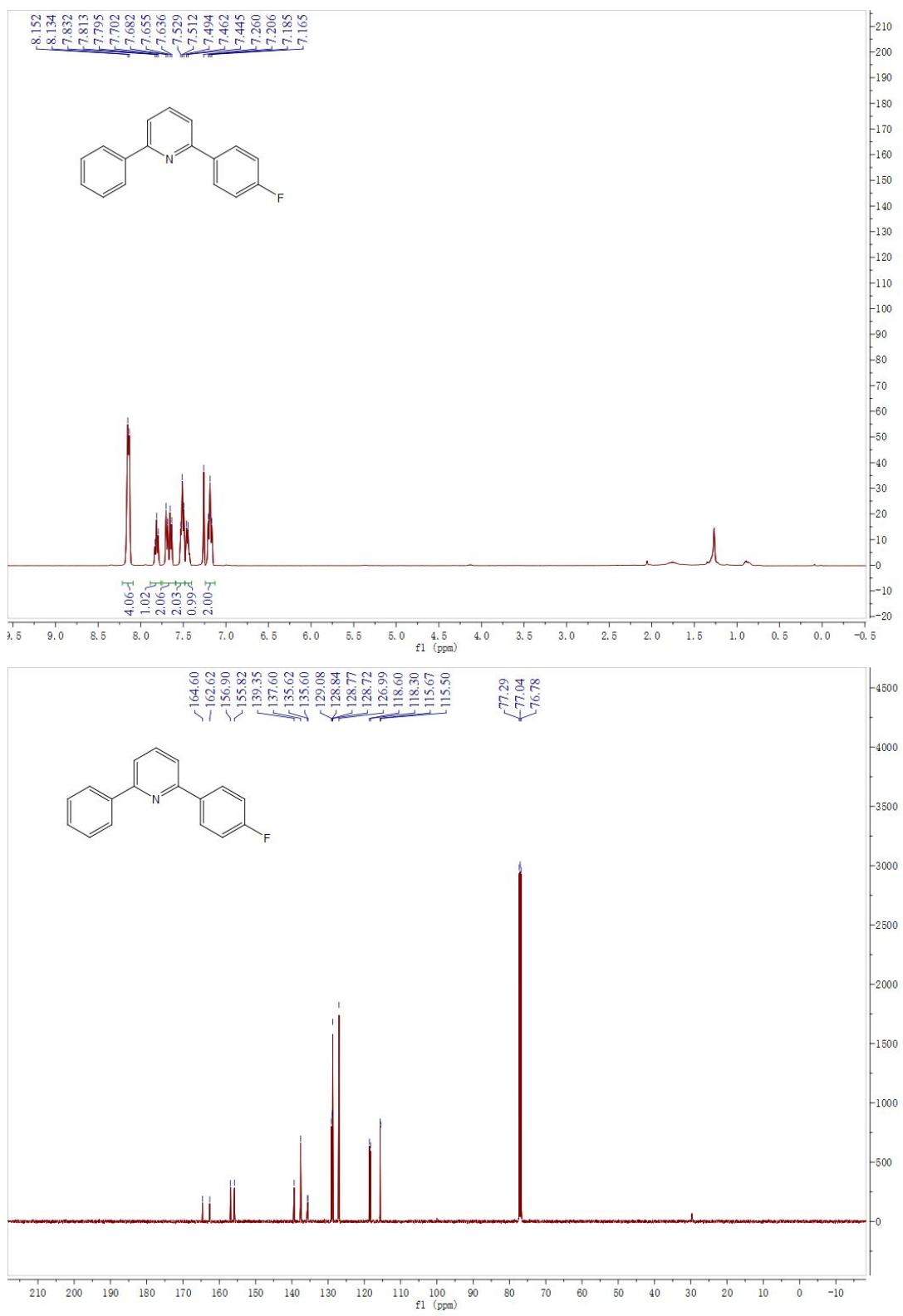
**Figure S24.**  $^1\text{H}$  NMR of **4h** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4h** (125 MHz,  $\text{CDCl}_3$ )



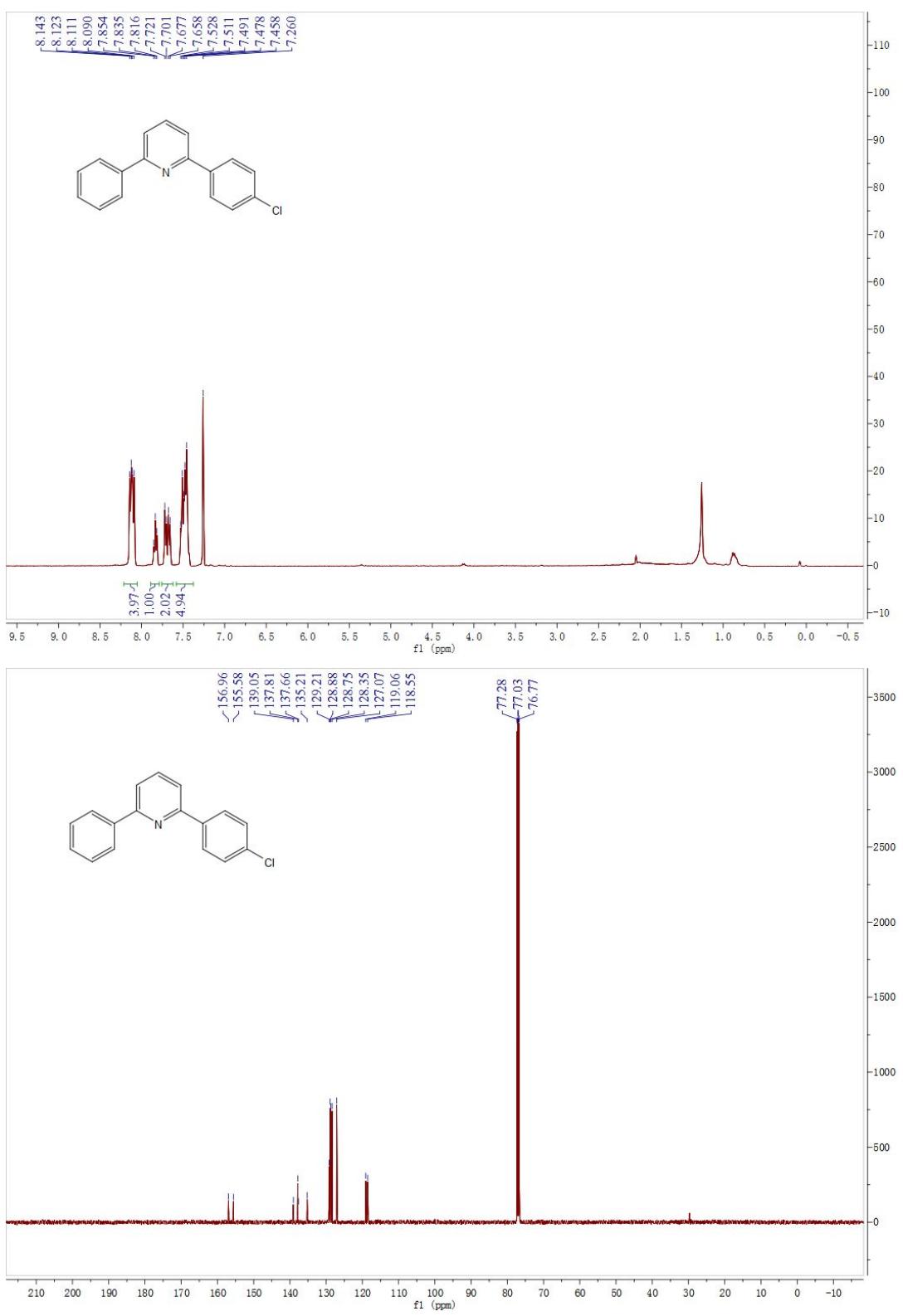
**Figure S25.**  $^1\text{H}$  NMR of **4i** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4i** (125 MHz,  $\text{CDCl}_3$ )



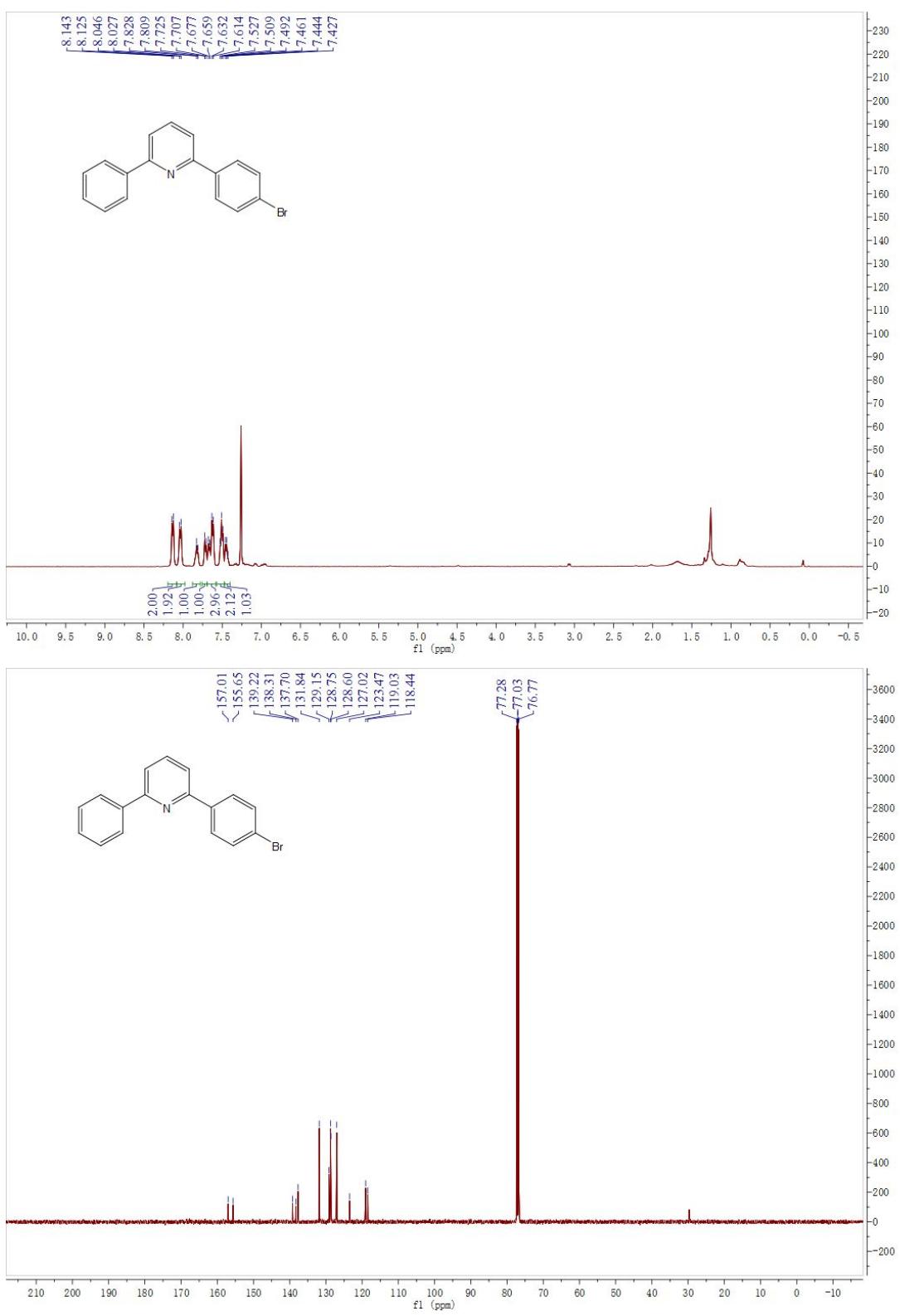
**Figure S26.**  $^1\text{H}$  NMR of **4j** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4j** (125 MHz,  $\text{CDCl}_3$ )



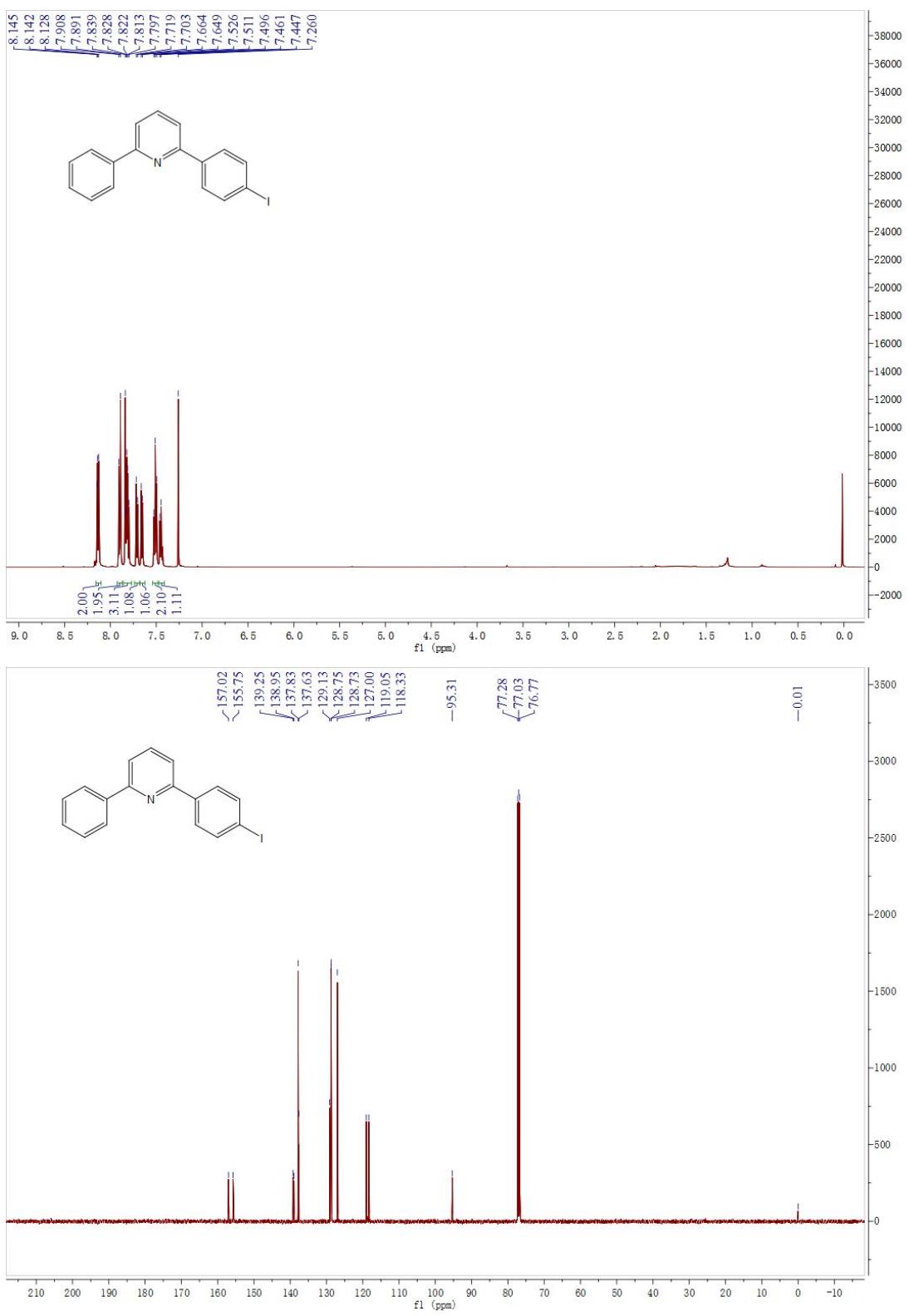
**Figure S27.**  $^1\text{H}$  NMR of **4k** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4k** (125 MHz,  $\text{CDCl}_3$ )



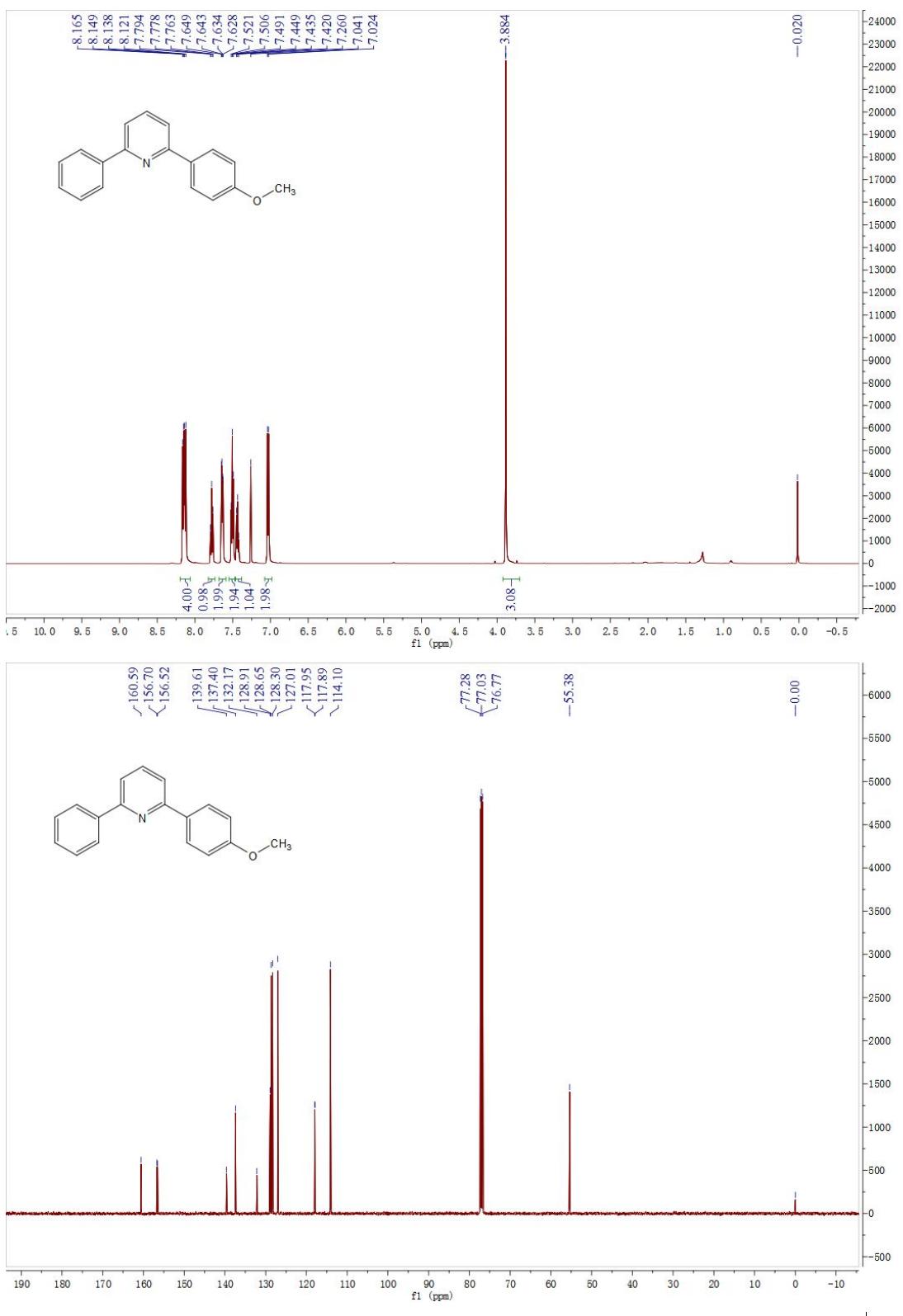
**Figure S28.**  $^1\text{H}$  NMR of **4l** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4l** (125 MHz,  $\text{CDCl}_3$ )



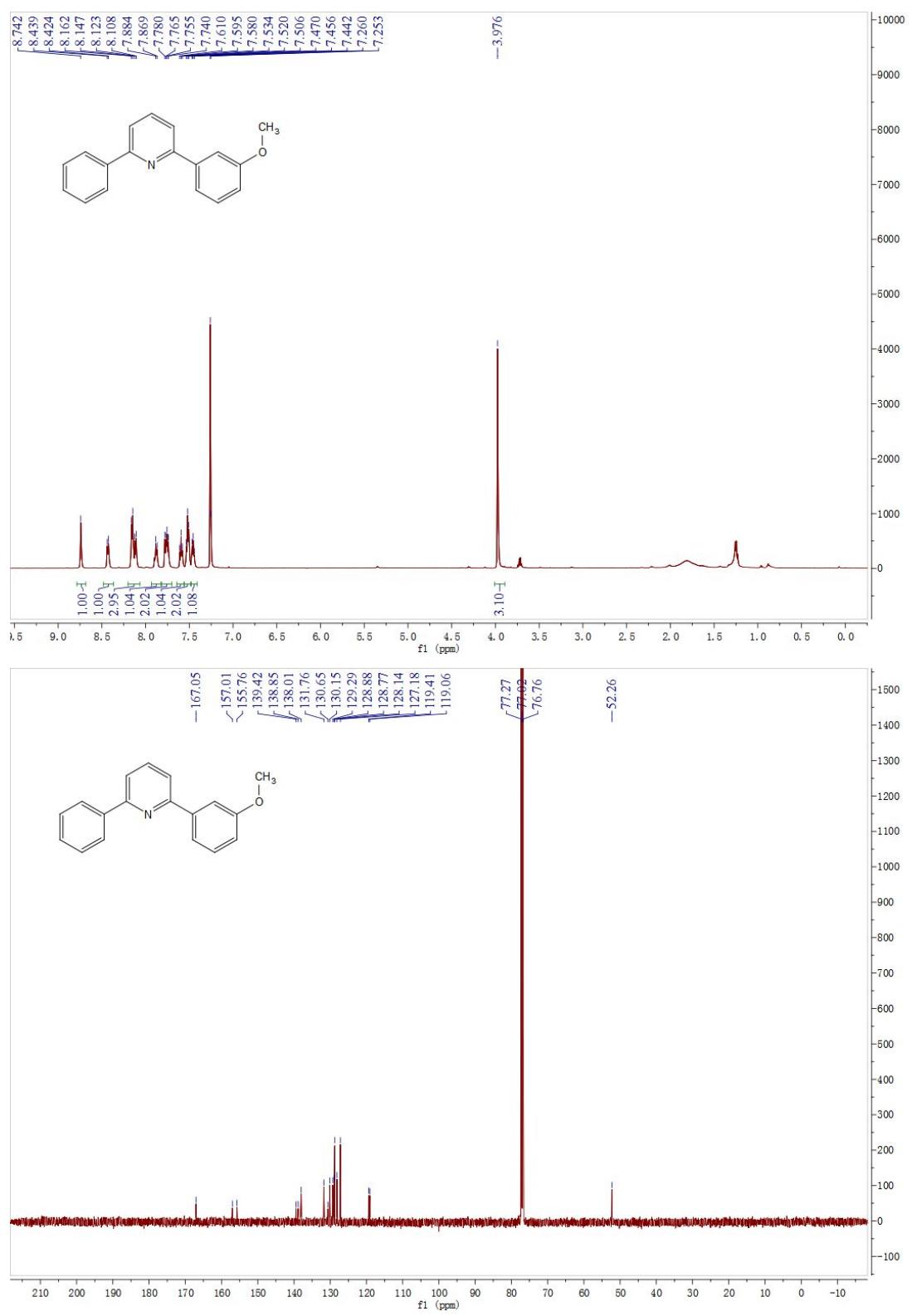
**Figure S29.**  $^1\text{H}$  NMR of **4m** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4m** (125 MHz,  $\text{CDCl}_3$ )



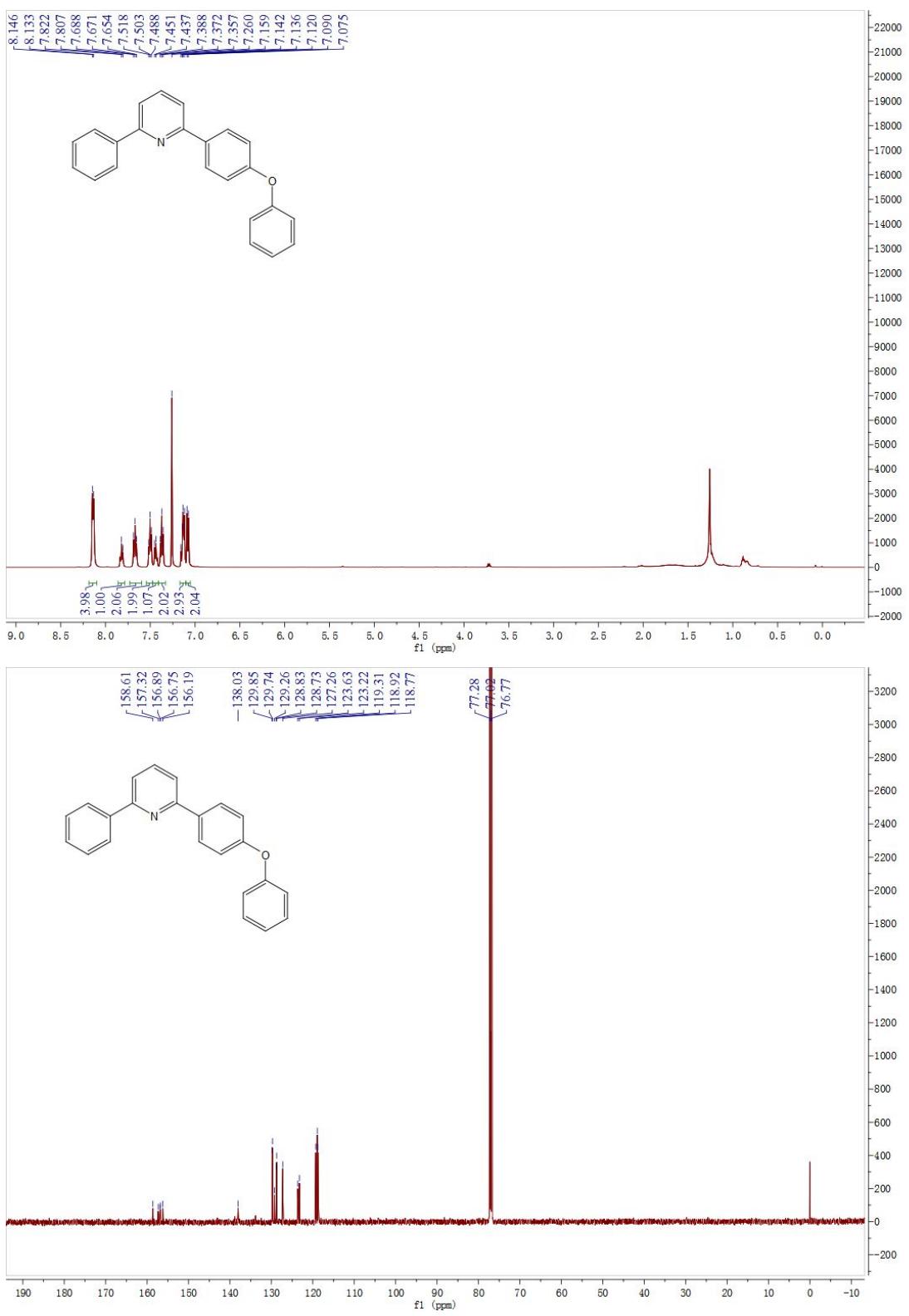
**Figure S30.**  $^1\text{H}$  NMR of **4n** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4n** (125 MHz,  $\text{CDCl}_3$ )



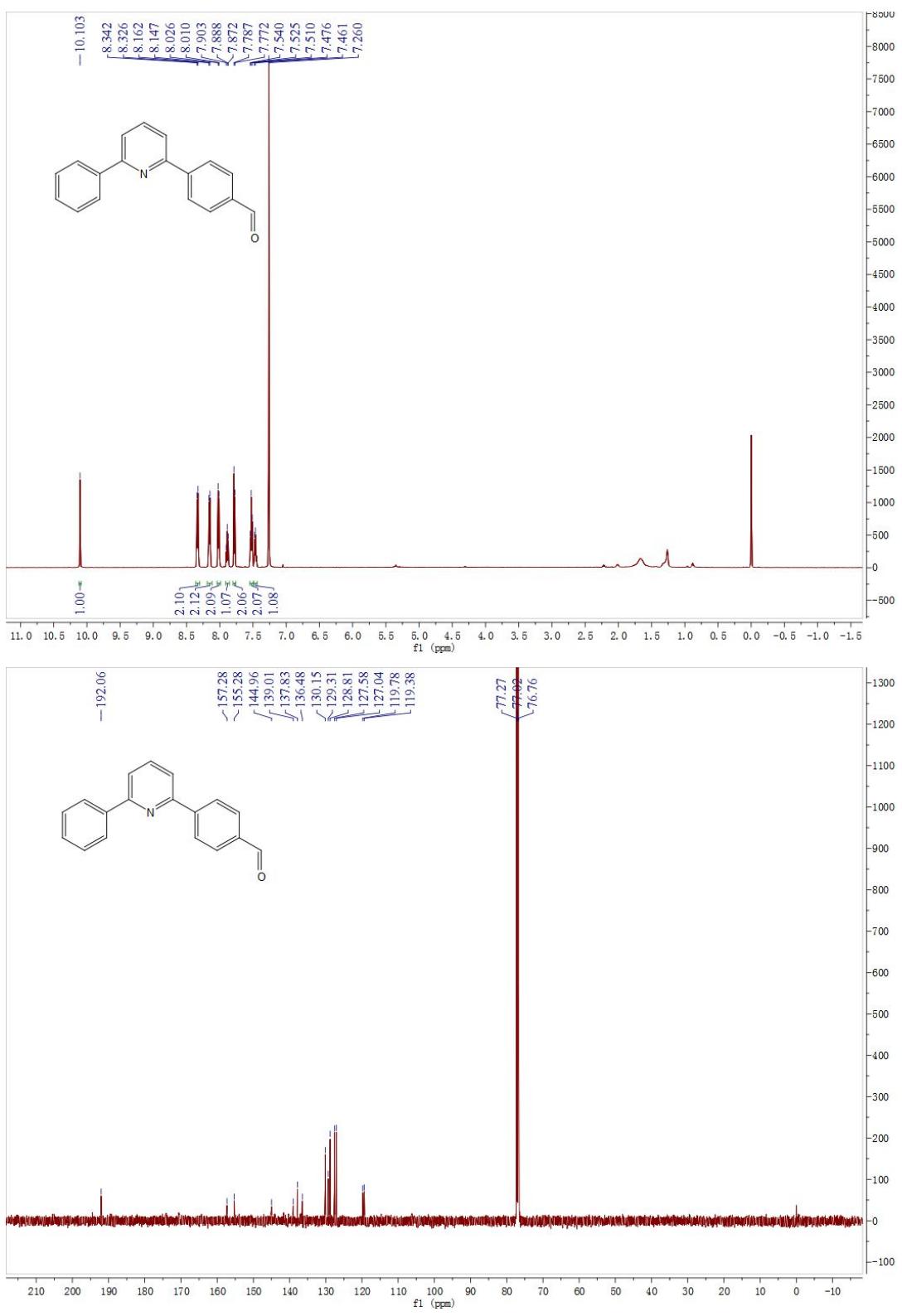
**Figure S31.**  $^1\text{H}$  NMR of **4o** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4o** (125 MHz,  $\text{CDCl}_3$ )



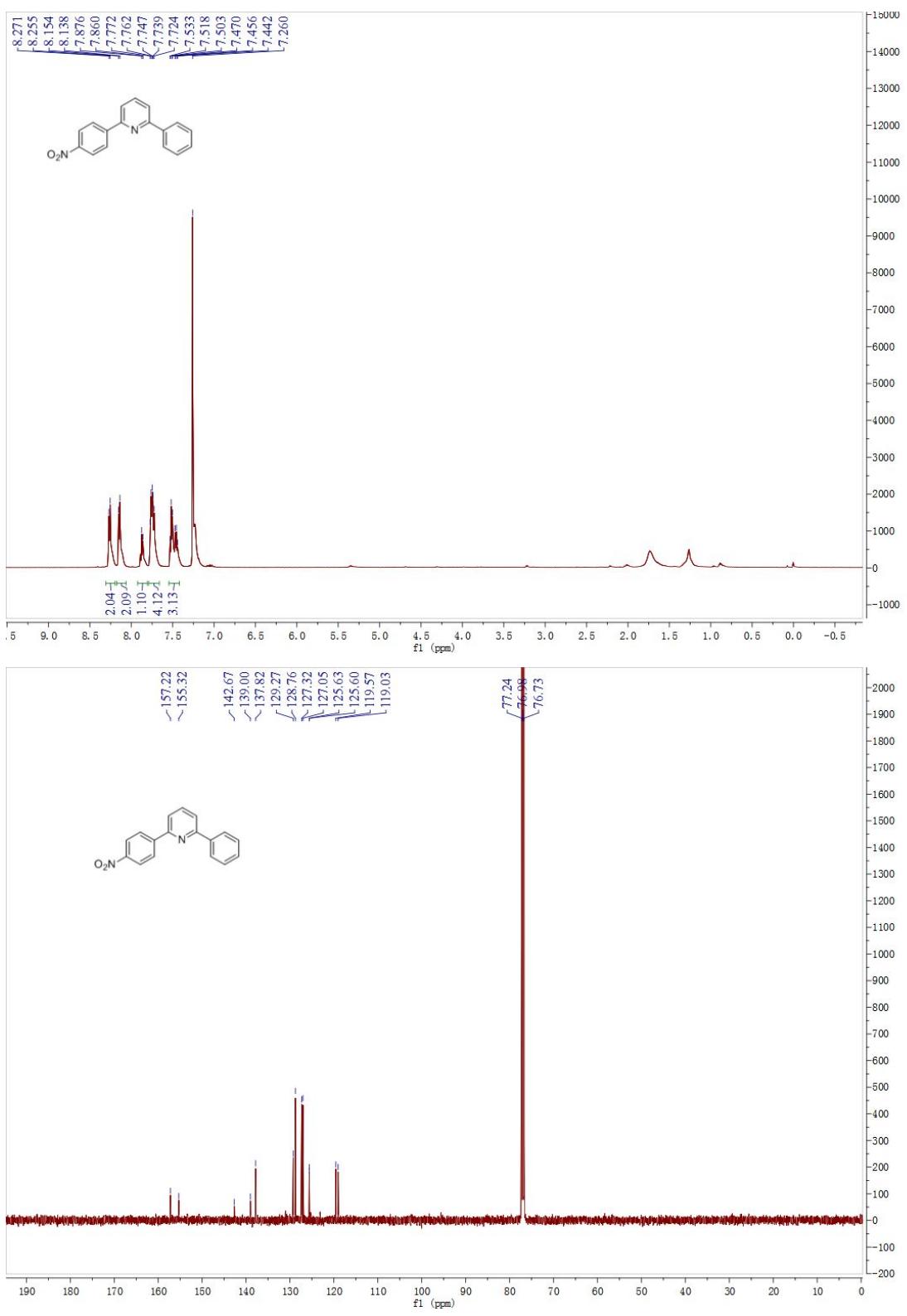
**Figure S32.**  $^1\text{H}$  NMR of **4p** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4p** (125 MHz,  $\text{CDCl}_3$ )



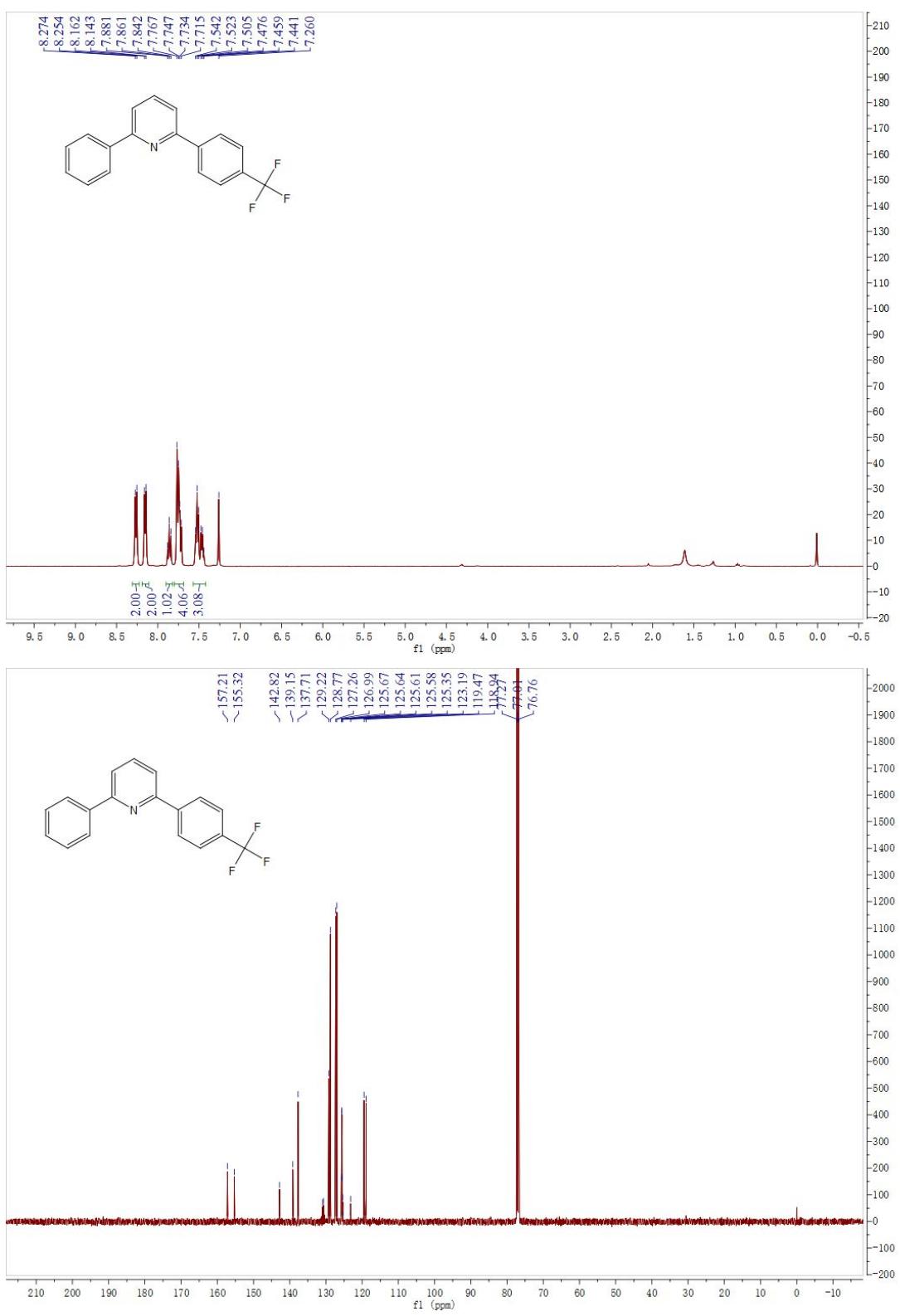
**Figure S33.**  $^1\text{H}$  NMR of **4q** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4q** (125 MHz,  $\text{CDCl}_3$ )



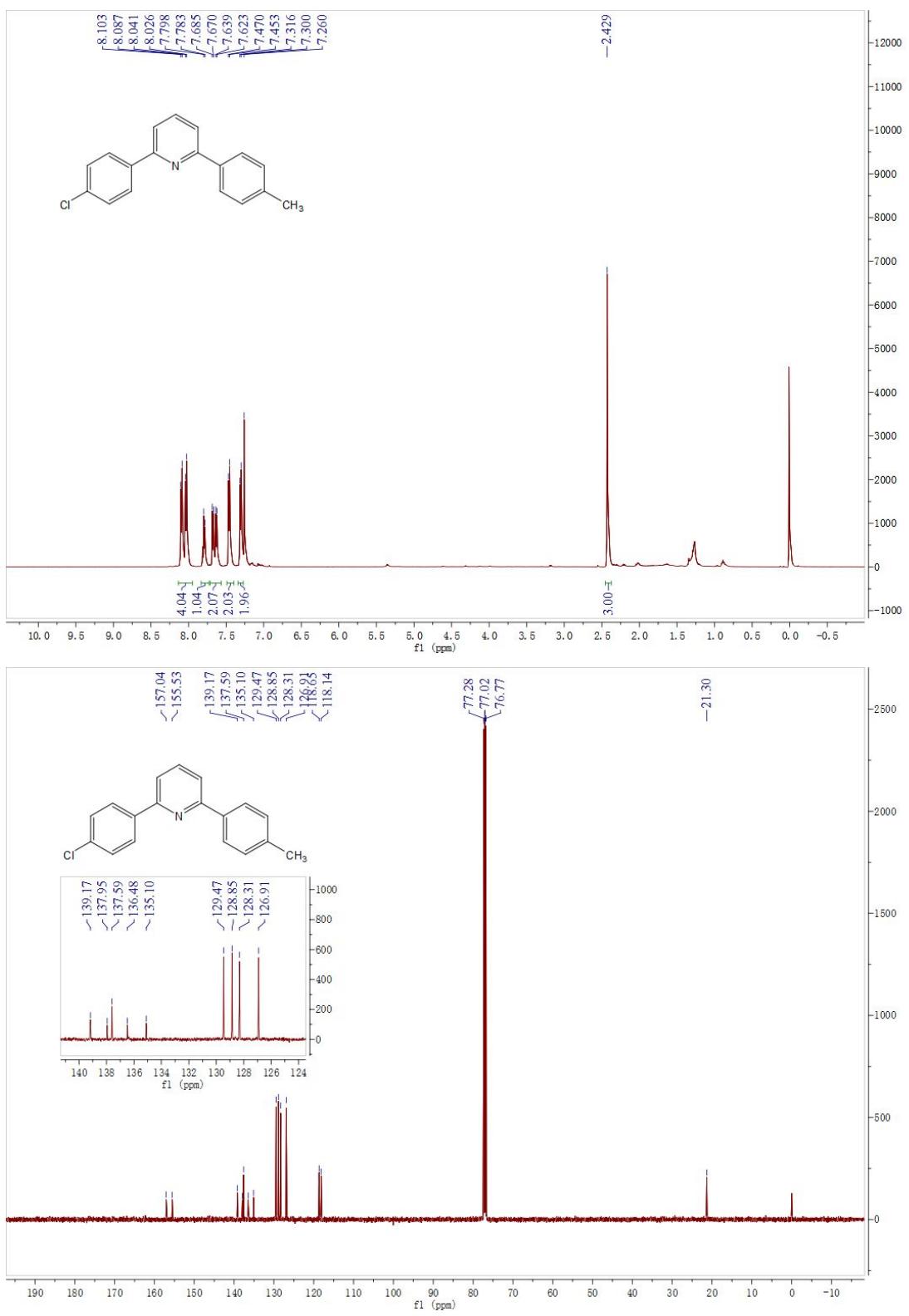
**Figure S34.**  $^1\text{H}$  NMR of **4r** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4r** (125 MHz,  $\text{CDCl}_3$ )



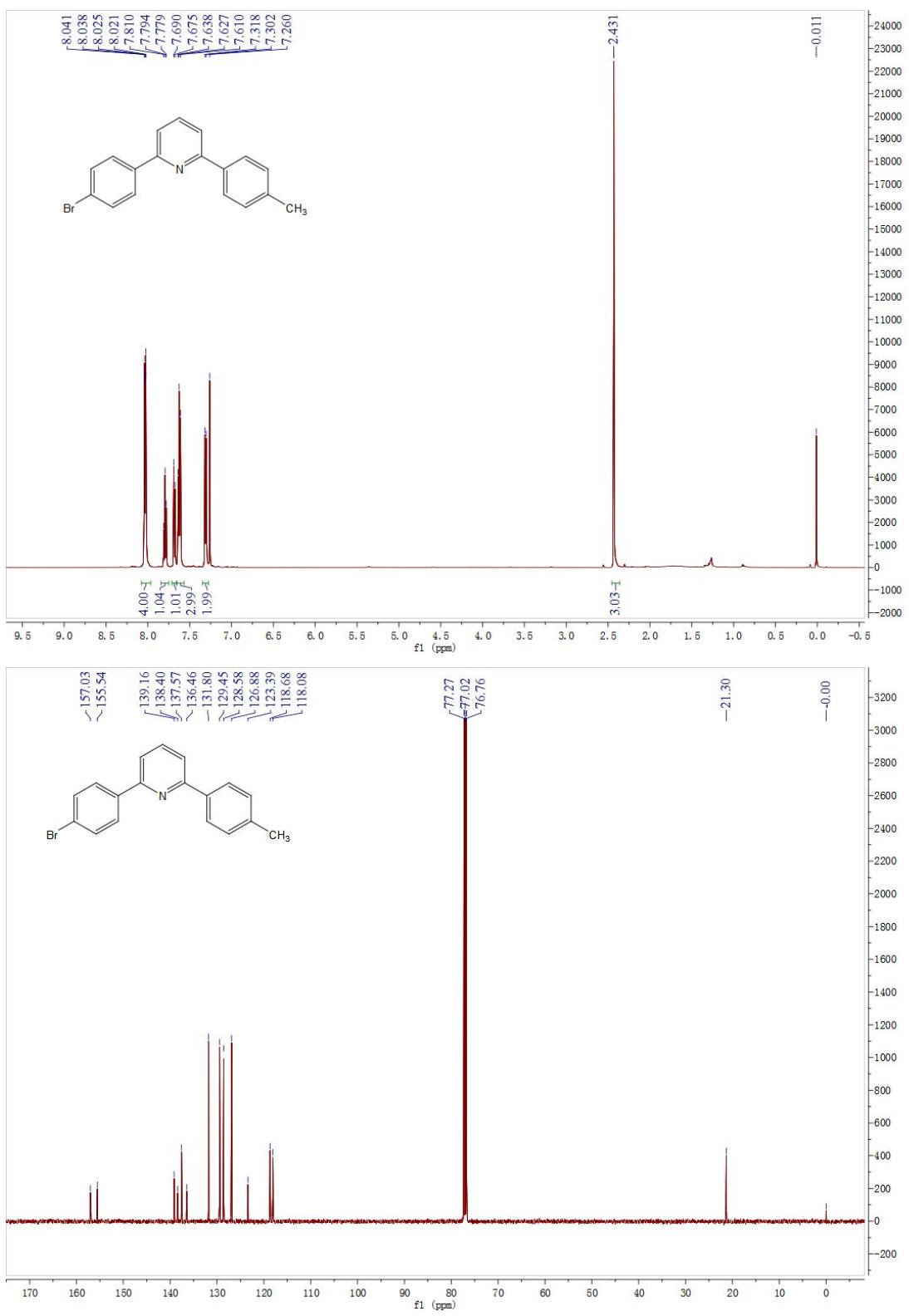
**Figure S35.**  $^1\text{H}$  NMR of **4s** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4s** (125 MHz,  $\text{CDCl}_3$ )



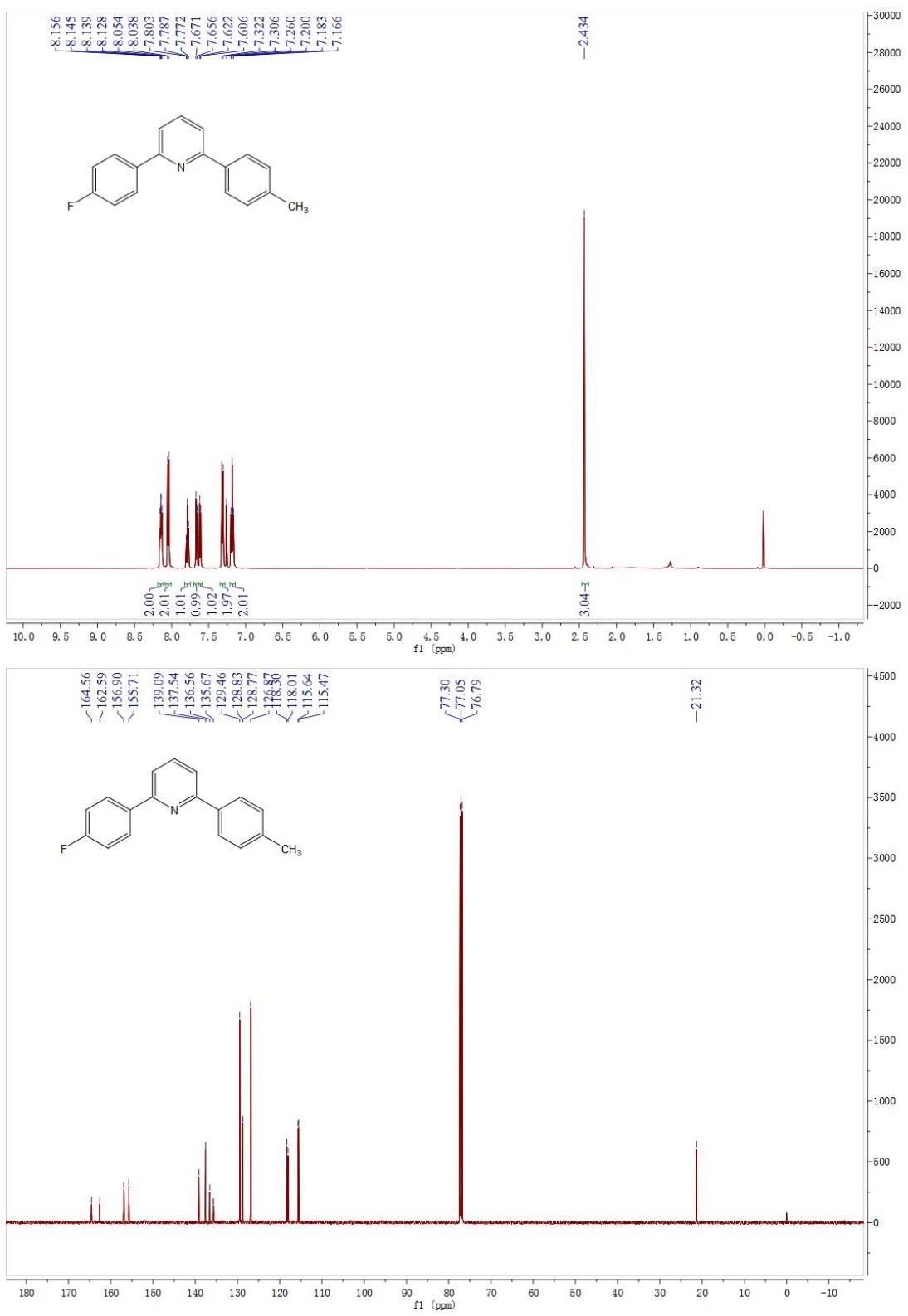
**Figure S36.** <sup>1</sup>H NMR of **4t** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4t** (125 MHz, CDCl<sub>3</sub>)



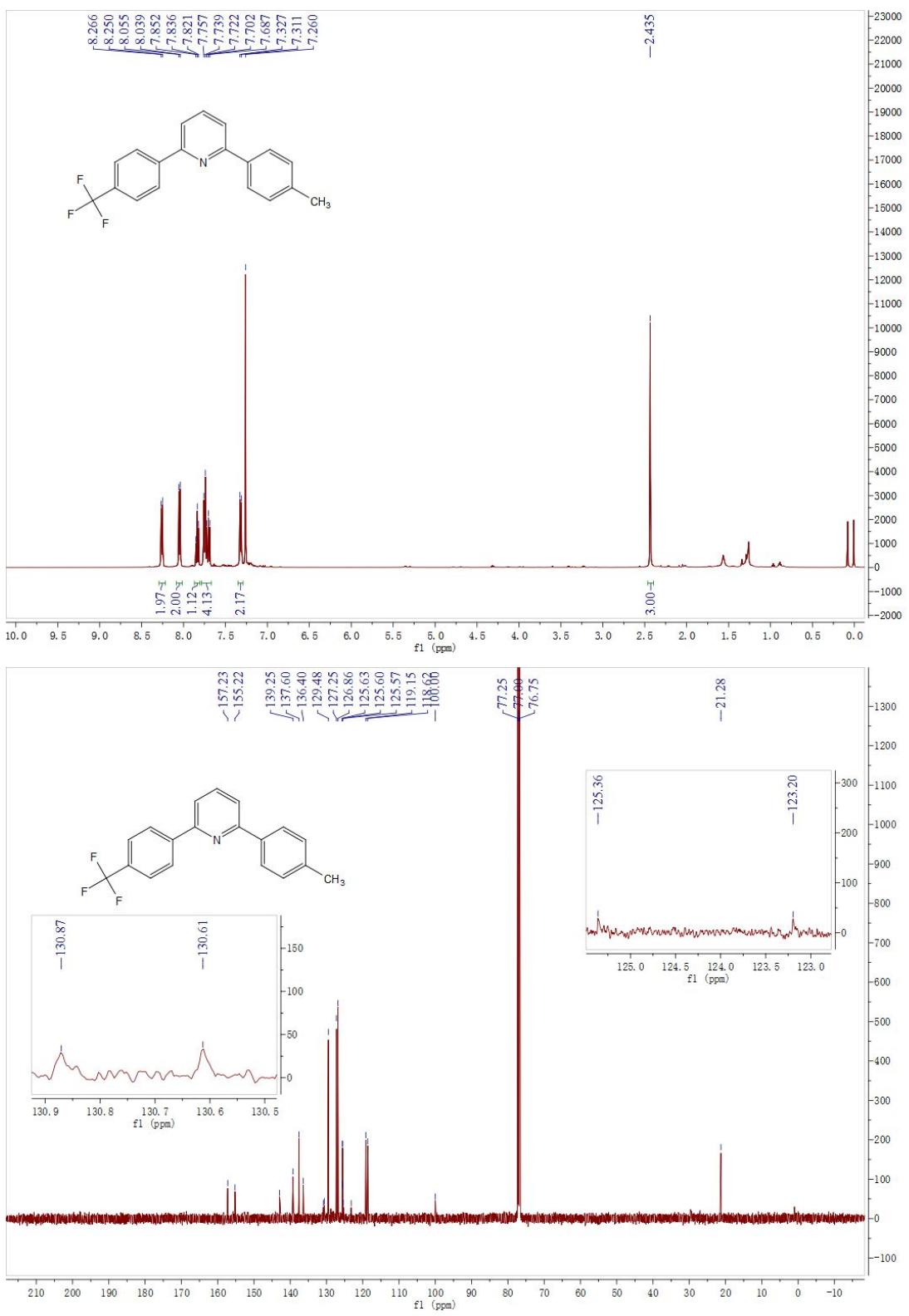
**Figure S37.**  $^1\text{H}$  NMR of **4u** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4u** (125 MHz,  $\text{CDCl}_3$ )



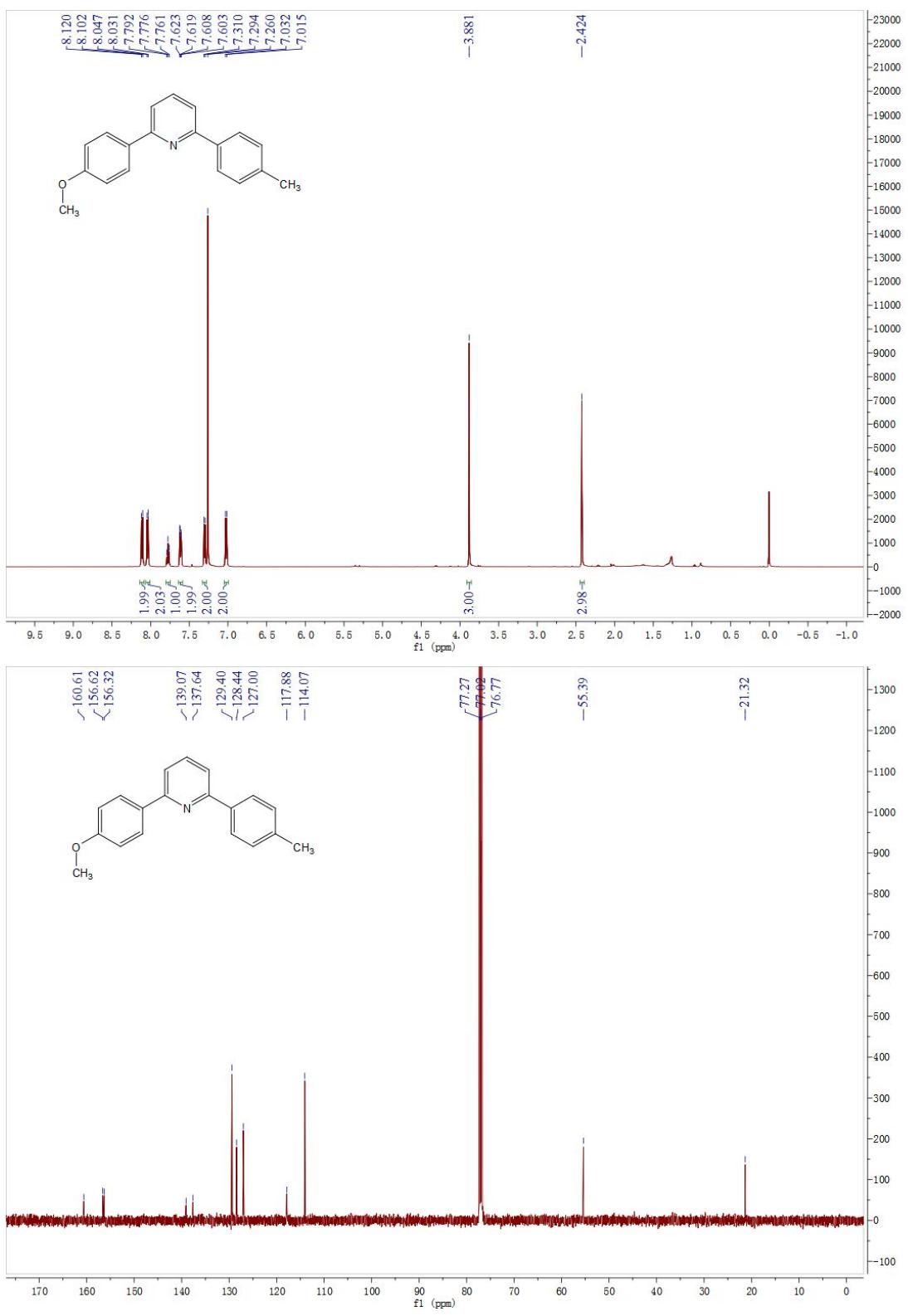
**Figure S38.**  $^1\text{H}$  NMR of **4v** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4v** (125 MHz,  $\text{CDCl}_3$ )



**Figure S39.**  $^1\text{H}$  NMR of **4w** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **4w** (125 MHz,  $\text{CDCl}_3$ )

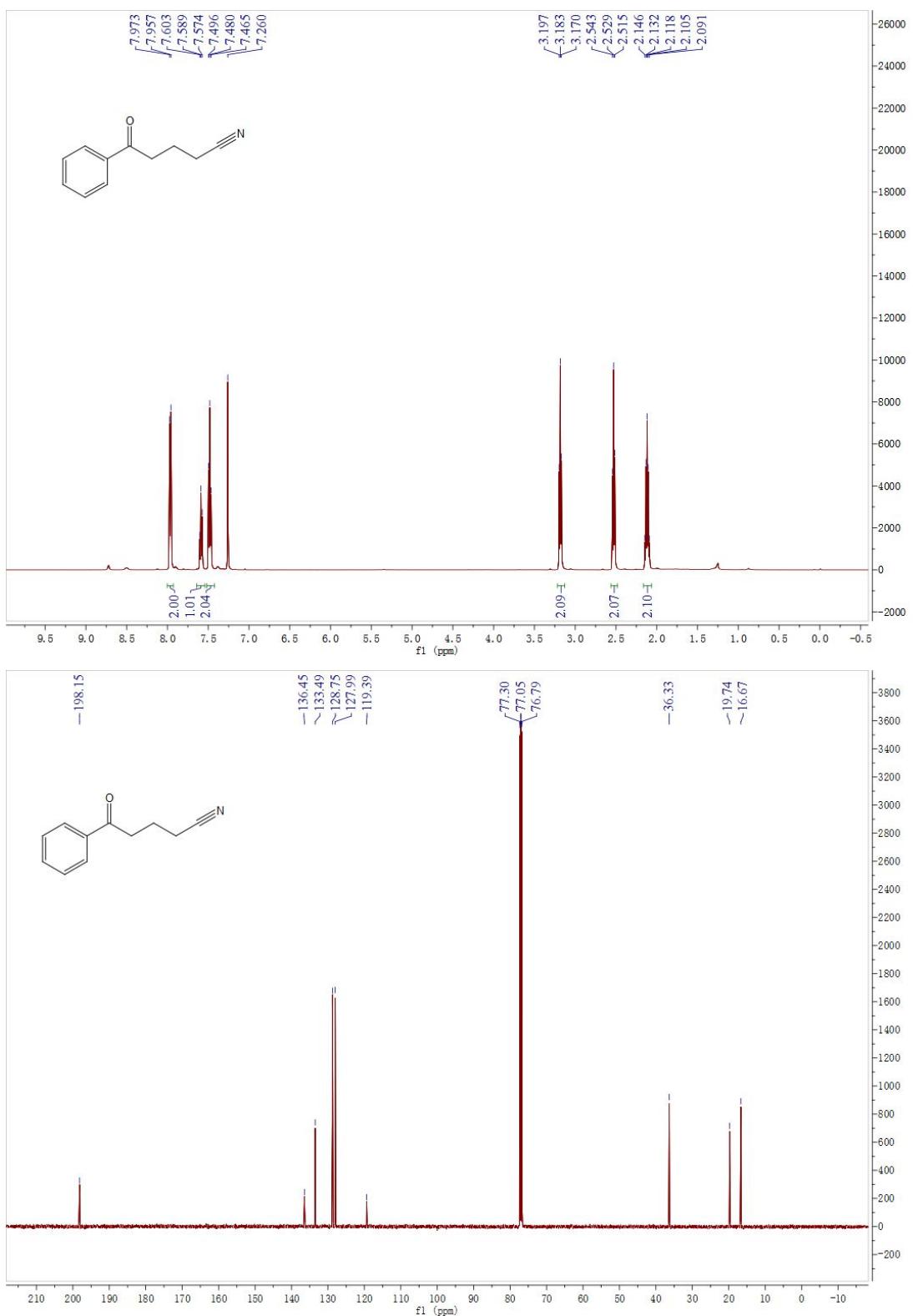


**Figure S40.** <sup>1</sup>H NMR of **4x** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4x** (125 MHz, CDCl<sub>3</sub>)

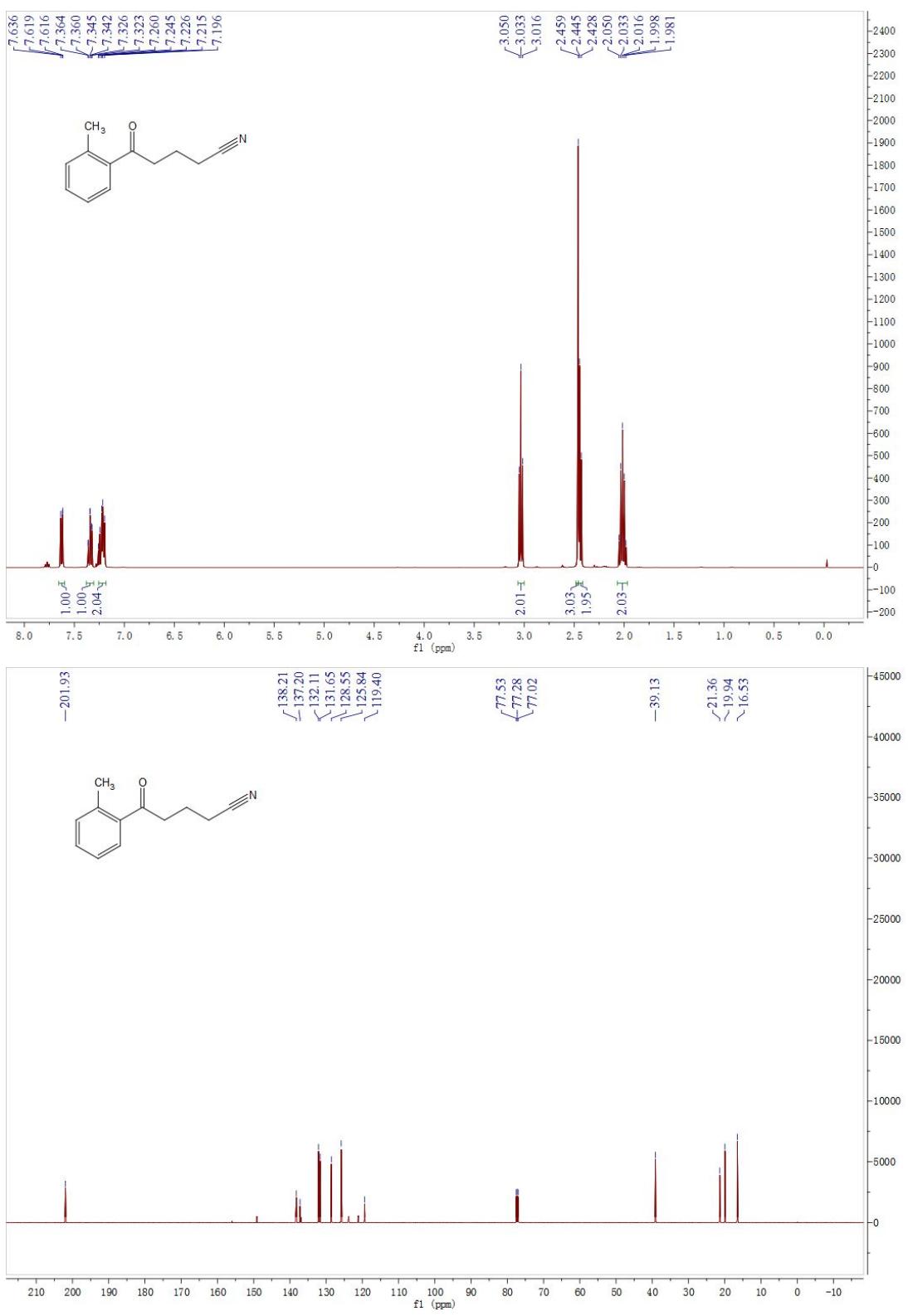


**Figure S41.** <sup>1</sup>H NMR of **4y** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **4y** (125 MHz, CDCl<sub>3</sub>)

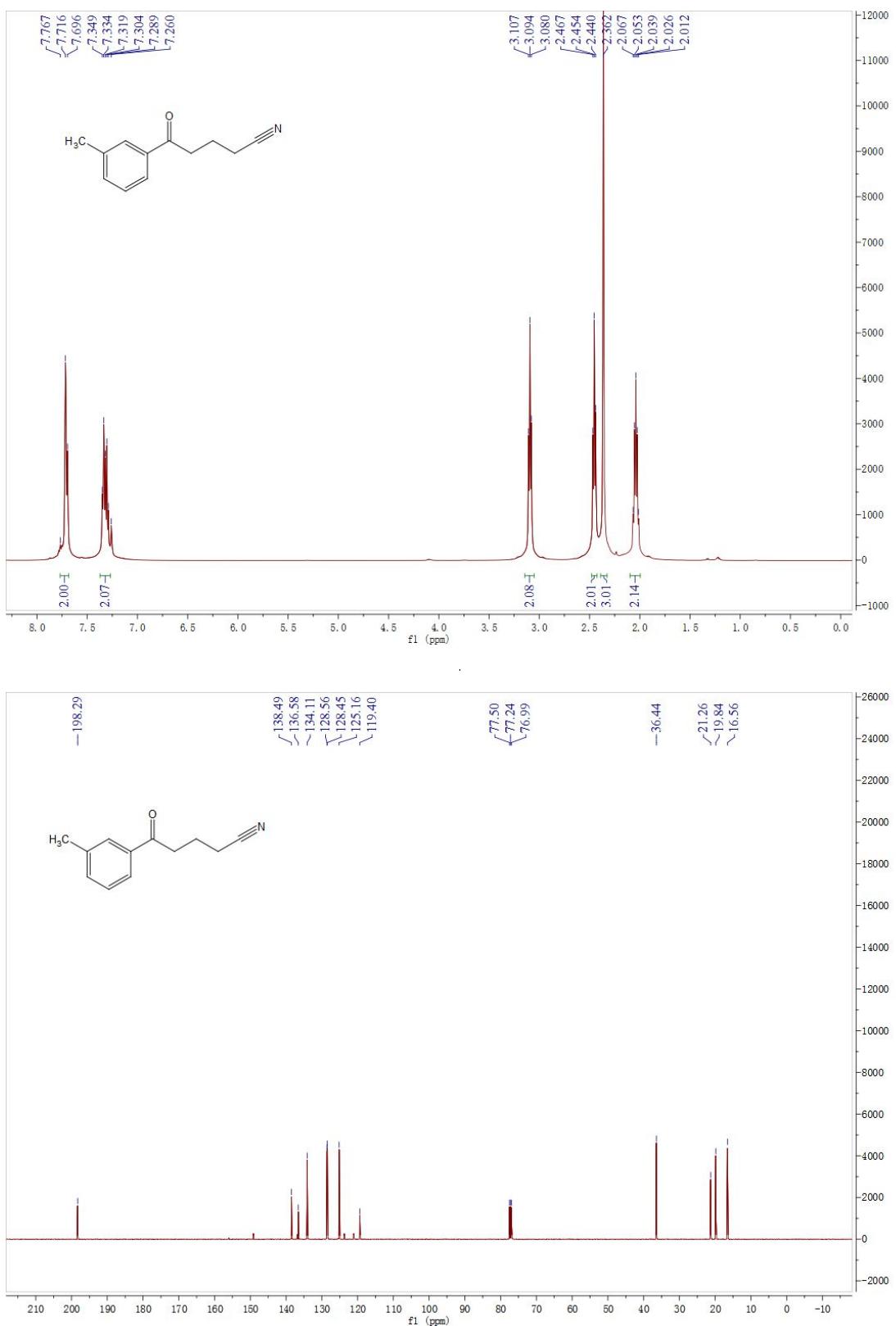
## NMR spectra for reactants



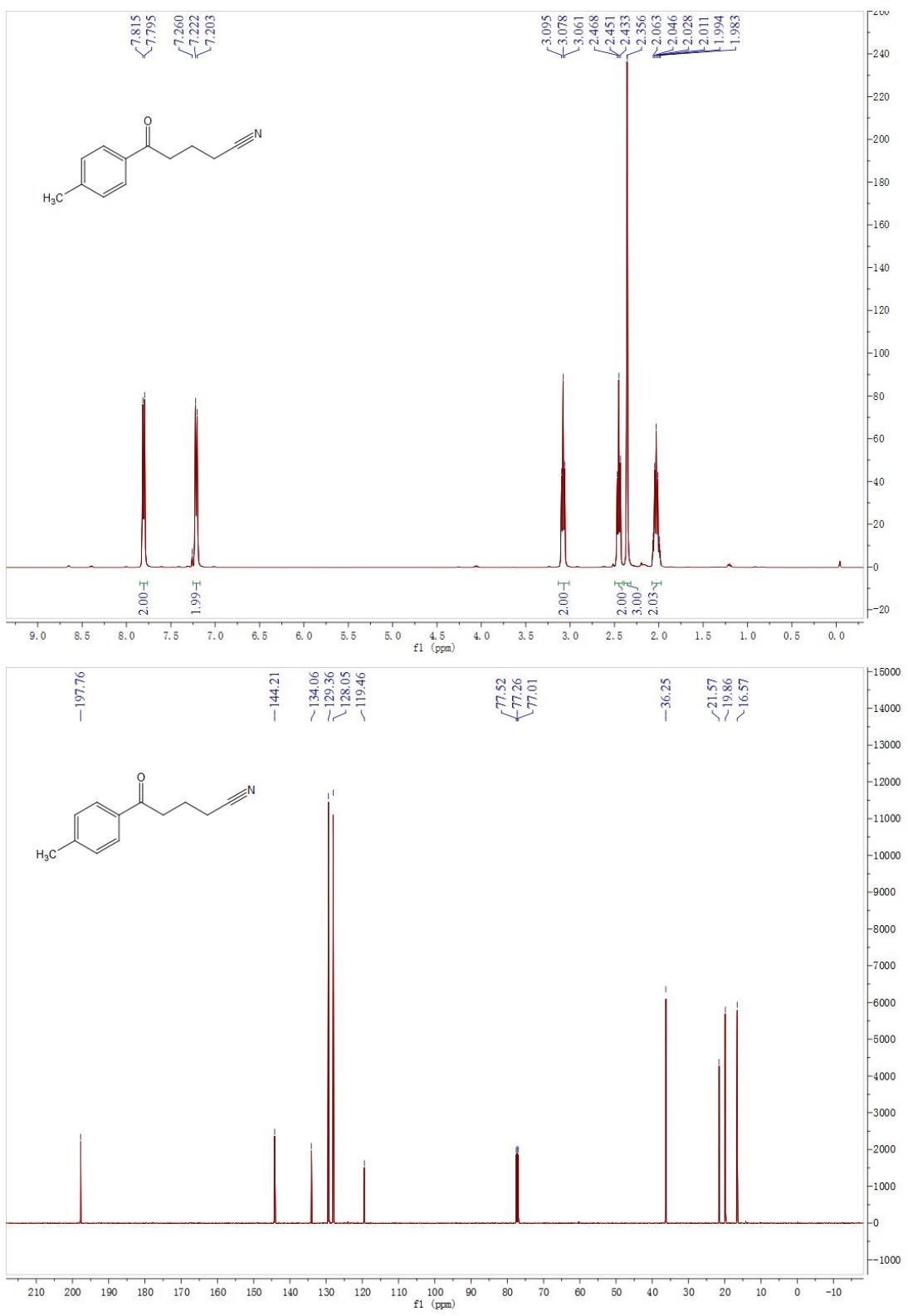
**Figure S42.**  $^1\text{H}$  NMR of **1b** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1b** (125 MHz,  $\text{CDCl}_3$ )



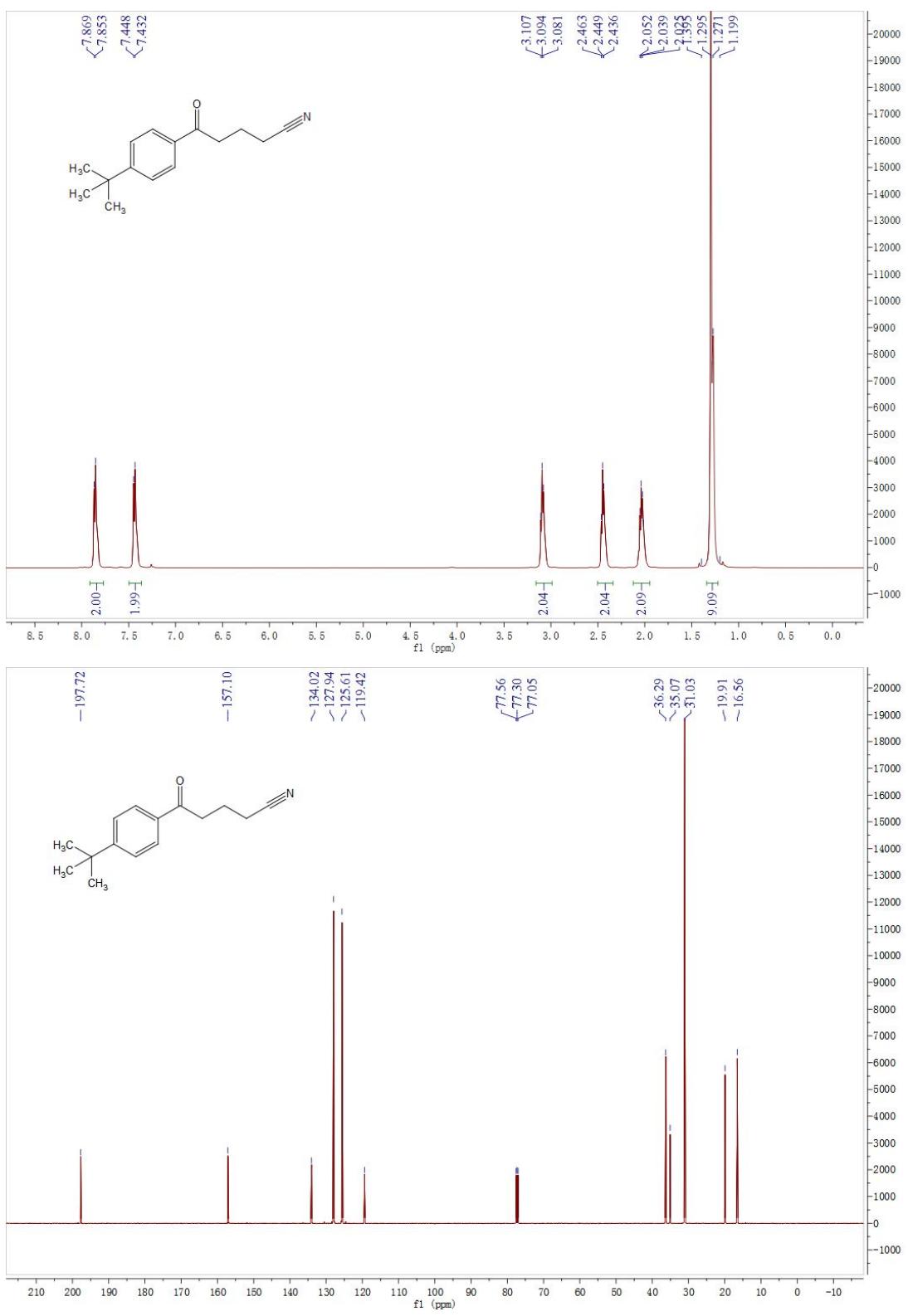
**Figure S43.**  $^1\text{H}$  NMR of **1c** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1c** (125 MHz,  $\text{CDCl}_3$ )



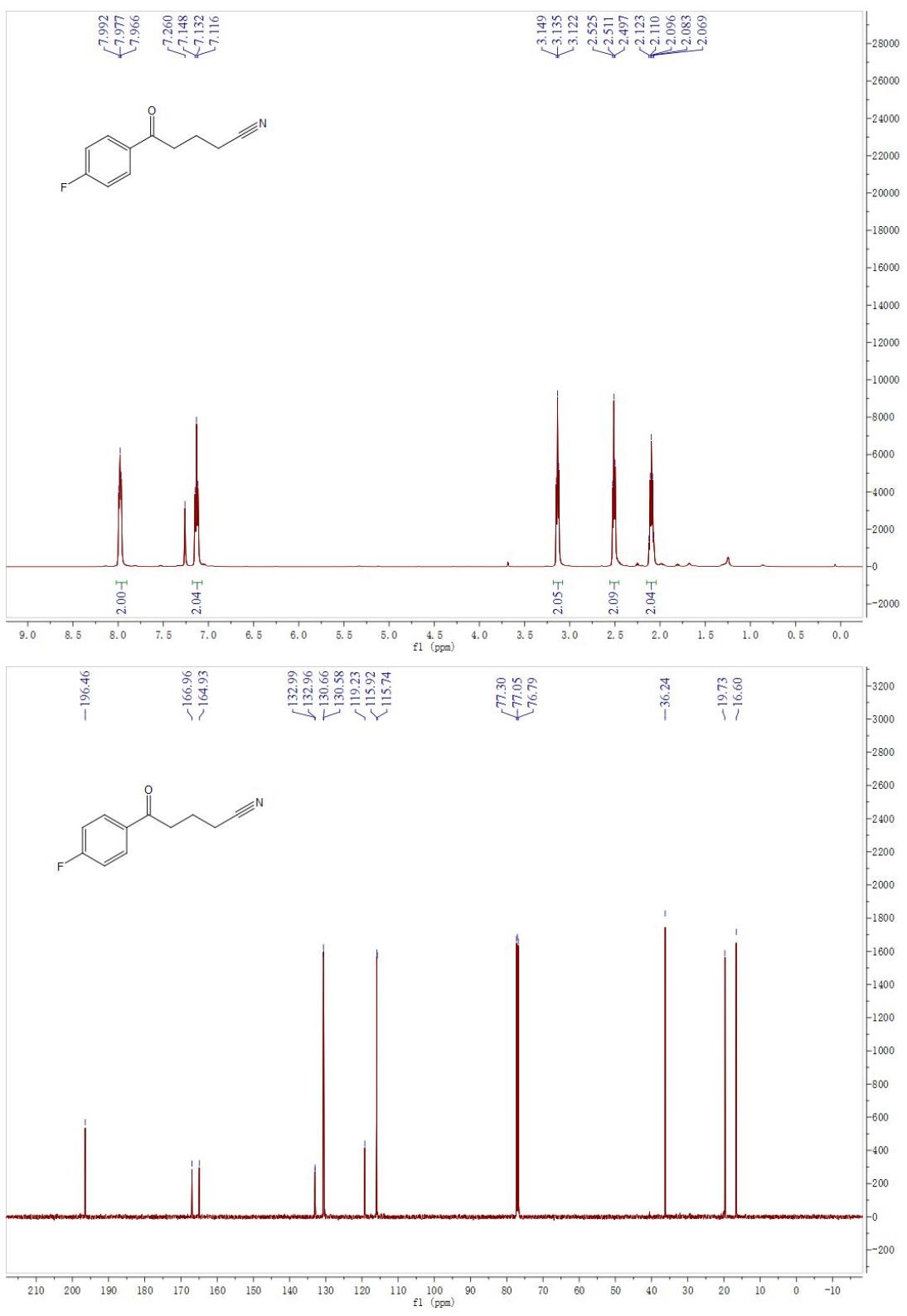
**Figure S44.**  $^1\text{H}$  NMR of **1d** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1d** (125 MHz,  $\text{CDCl}_3$ )



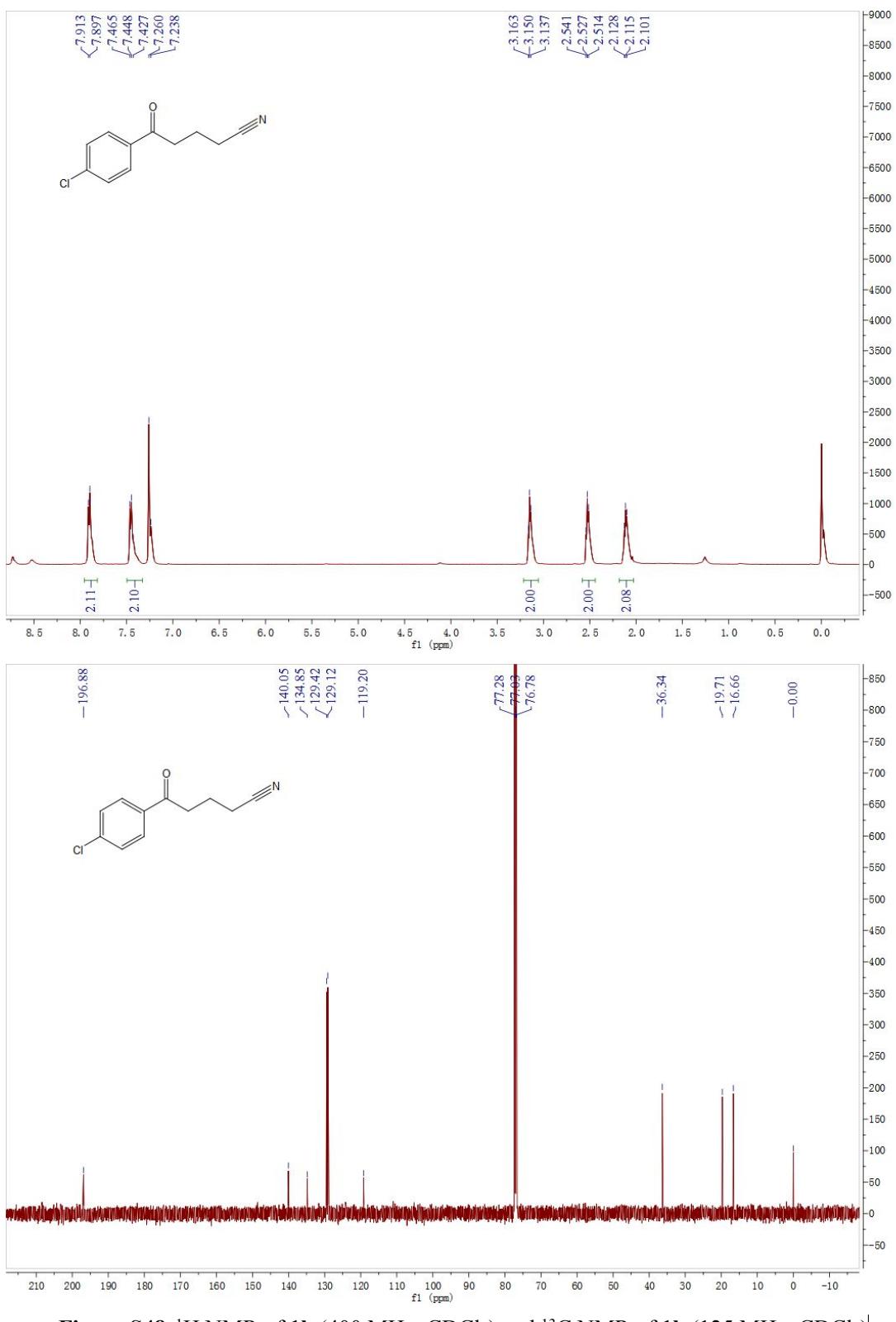
**Figure S45.**  $^1\text{H}$  NMR of **1e** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1e** (125 MHz,  $\text{CDCl}_3$ )



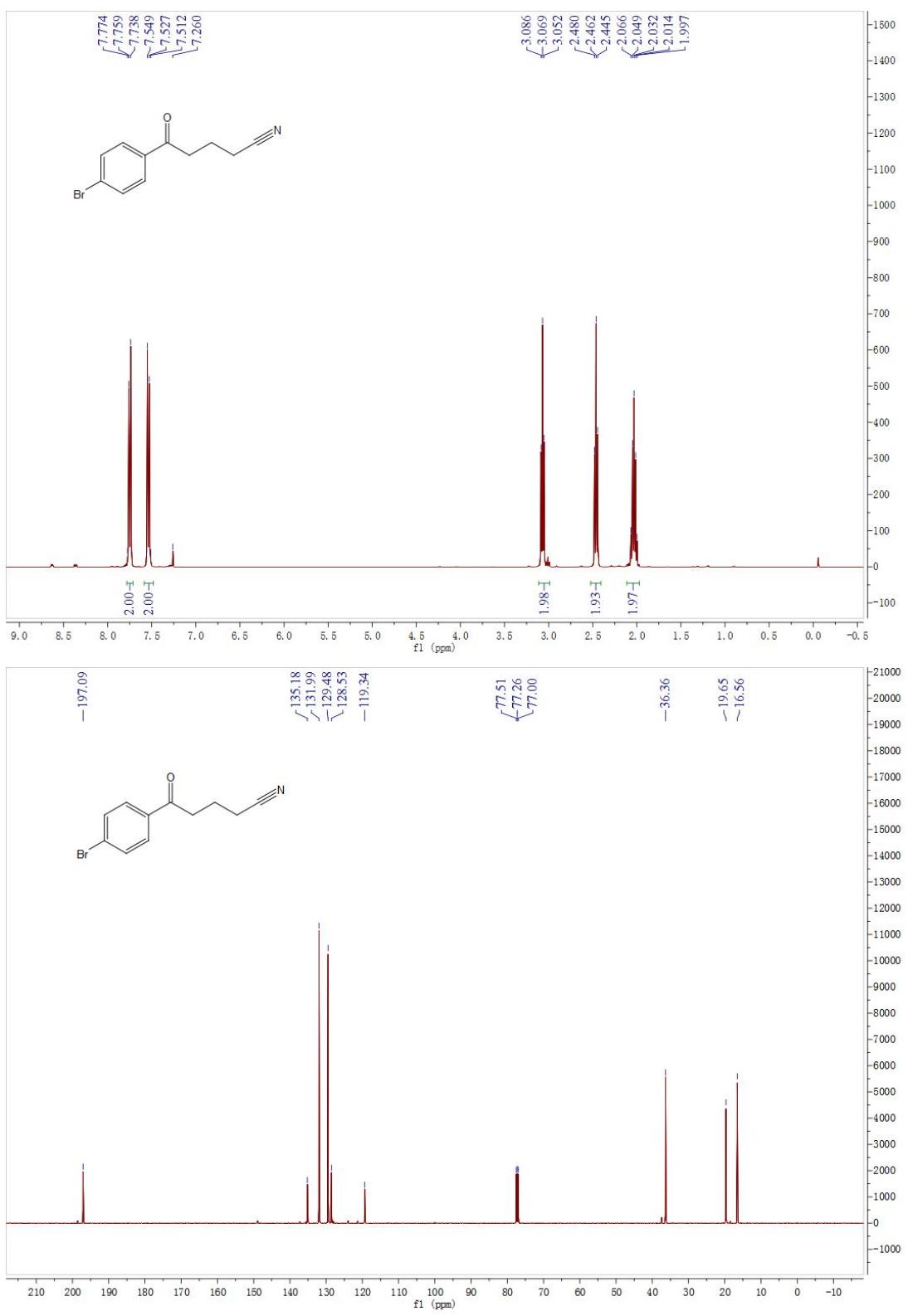
**Figure S46.**  $^1\text{H}$  NMR of **1f** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1f** (125 MHz,  $\text{CDCl}_3$ )



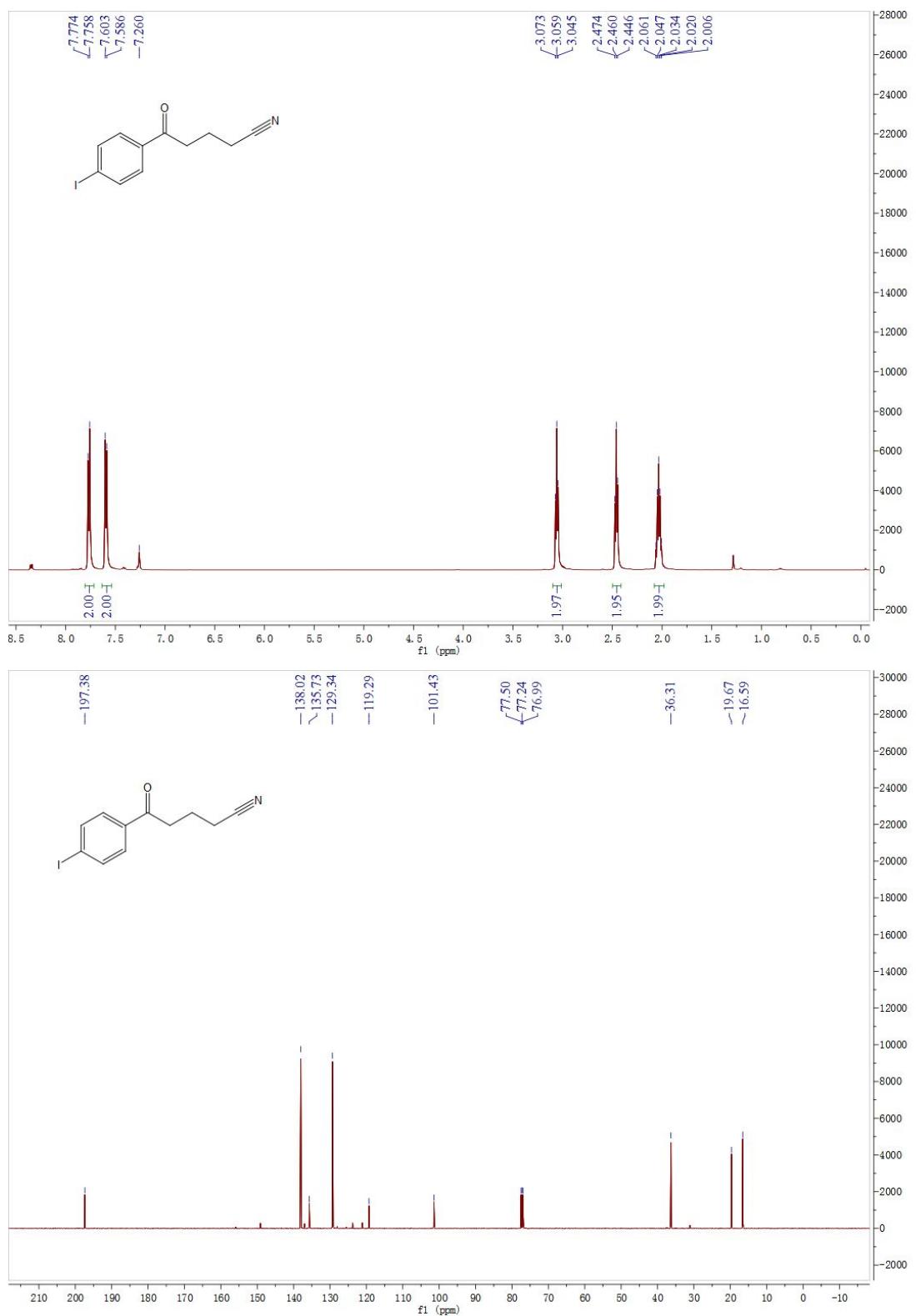
**Figure S47.**  $^1\text{H}$  NMR of **1g** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1g** (125 MHz,  $\text{CDCl}_3$ )



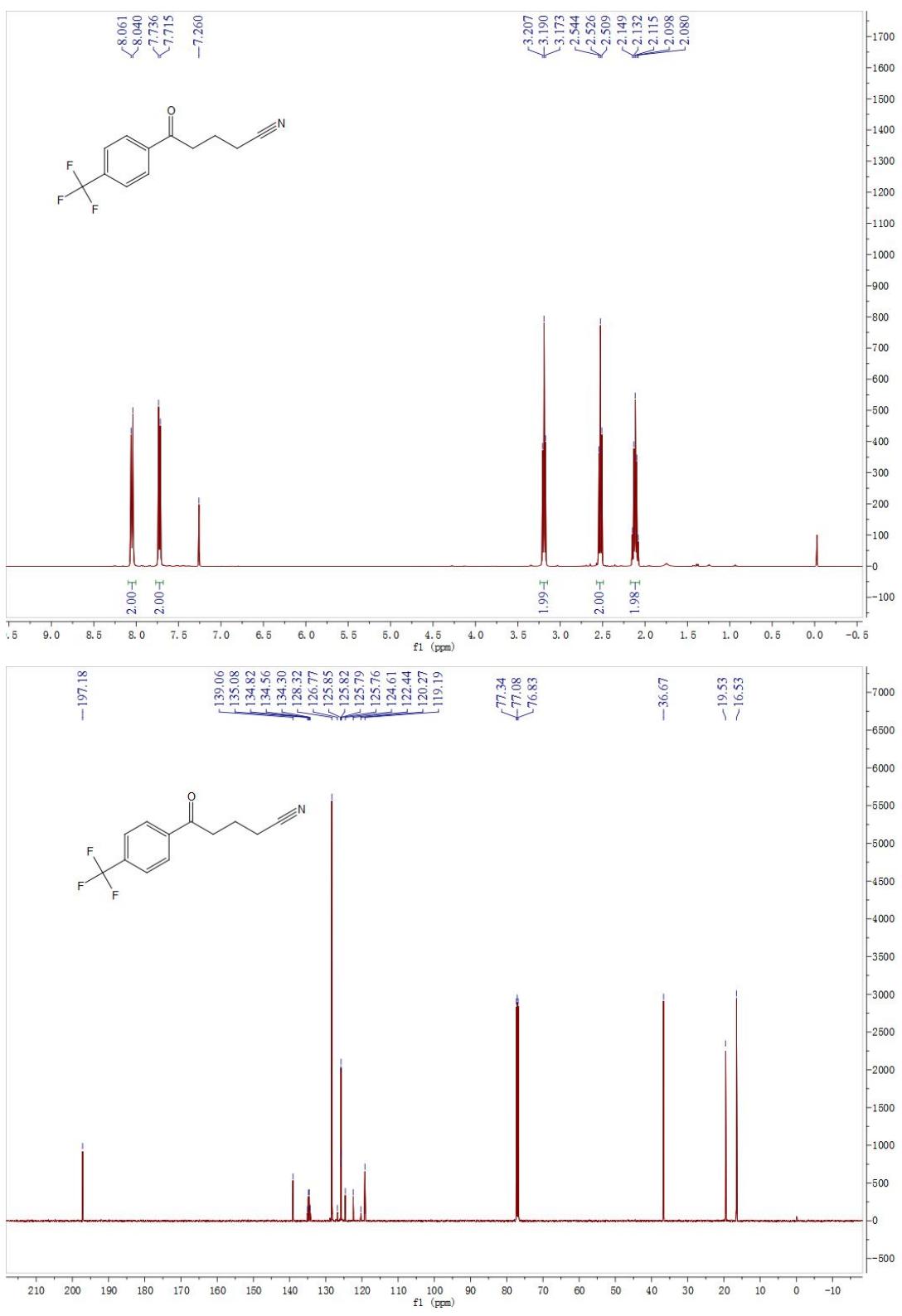
**Figure S48.**  $^1\text{H}$  NMR of **1h** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1h** (125 MHz,  $\text{CDCl}_3$ )



**Figure S49.** <sup>1</sup>H NMR of **1i** (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR of **1i** (125 MHz, CDCl<sub>3</sub>)



**Figure S50.**  $^1\text{H}$  NMR of **1j** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1j** (125 MHz,  $\text{CDCl}_3$ )



**Figure S51.**  $^1\text{H}$  NMR of **1k** (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR of **1k** (125 MHz,  $\text{CDCl}_3$ )