

# Supplementary Information

## Palladium-Catalyzed CO-Free Cyclizative Carbonyla-tion of 2-Benzylpyridines leading to Pyridoisoquinolinones

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## 1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers 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  $\text{DMSO-d}_6$  ( $\delta$  2.5 or 40.0 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). All melting points were uncorrected.

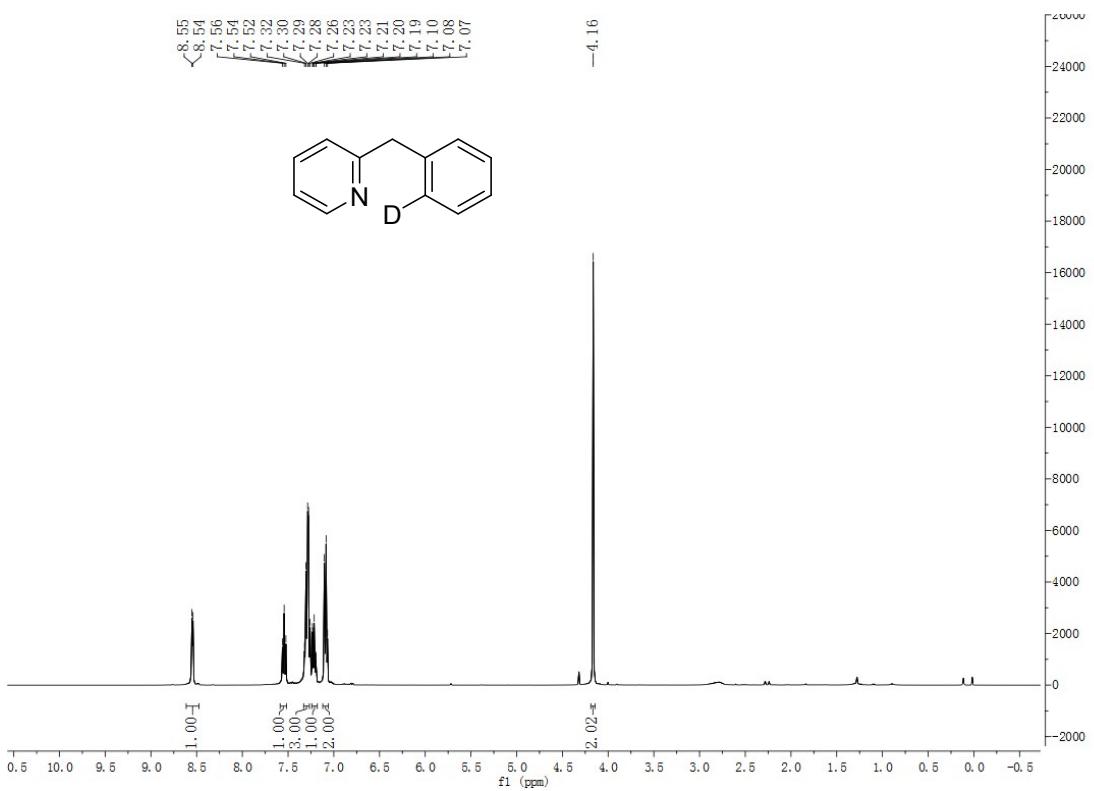
## 2. Synthesis and Reaction

### 2.1 General Procedure for the Synthesis of 2

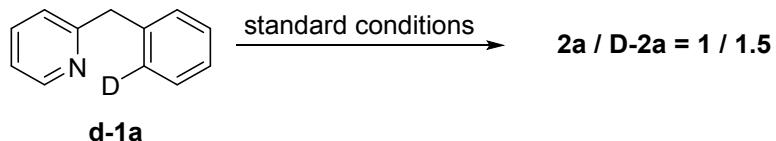
Substrates **1** were prepared according to literature reported procedures.<sup>1a, 1b</sup> To a Schlenk tube were added  $\text{Pd}(\text{OAc})_2$  (0.02 mmol),  $\text{Cu}(\text{TFA})_2 \cdot \text{xH}_2\text{O}$  (0.24 mmol) and 2 mL of dry toluene. Then, 2-benzyl heterocycle **1** (0.2 mmol) were added and  $\text{Ac}_2\text{O}$  (1.6 mmol),  $\text{HCOOH}$  (1.6 mmol) were followed in. The reaction mixture was stirred at 110 °C for 12 h. Finally, the reaction was cooled down to room temperature before addition of saturated aqueous  $\text{NaCl}$  and  $\text{NH}_4\text{-OH}$  and  $\text{EtOAc}$  to the reaction mixture. The aqueous phase was further extracted with  $\text{EtOAc}$  ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash chromatography to provide the desired product **2**.

### 2.2 Isotope Labelling Experiments

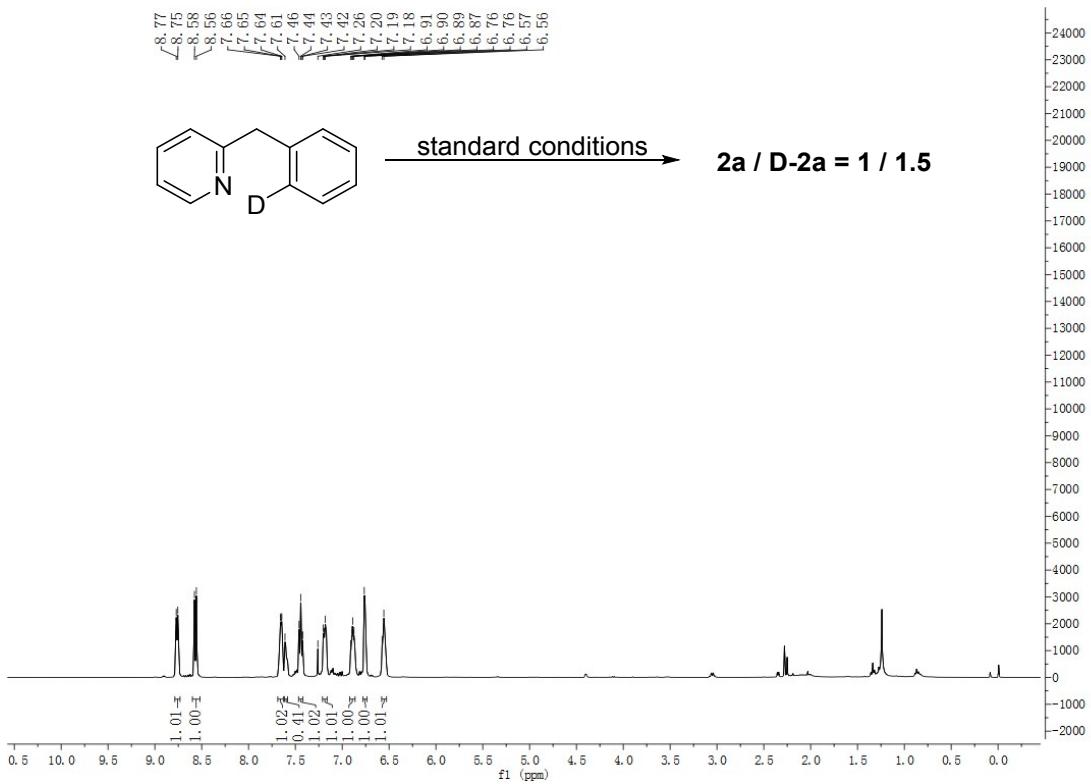
Deuterated substrate **d-1a** was synthesized according to the literature reported method<sup>1a</sup> using potassium 2-(pyridin-2-yl)acetate and 1-bromobenzene-2-d as substrates. **d-1a** was obtained in 63% yield as a liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 8.5 (d,  $J = 4.0$  Hz, 1H); 7.54 (t,  $J = 8.0$  Hz, 1H), 7.32-7.28 (m, 3H), 7.23-7.19 (m, 1H), 7.10-7.07 (m, 2H), 4.16 (s, 2H).



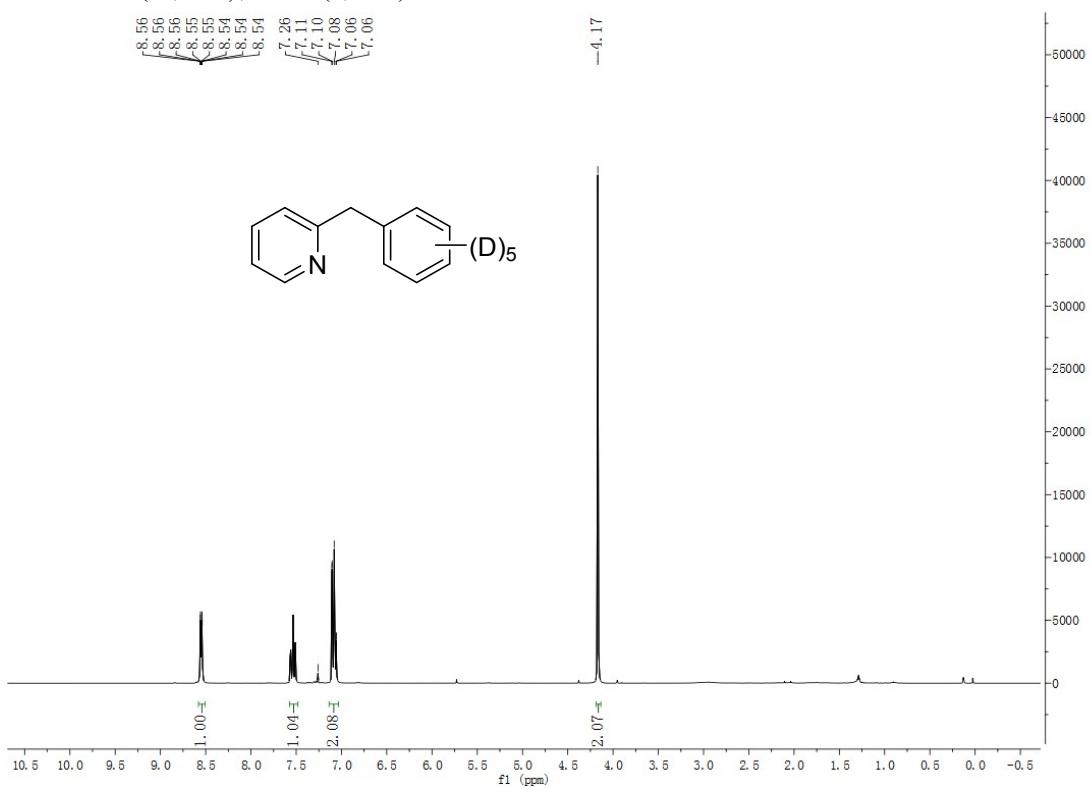
Intermolecular KIE study:



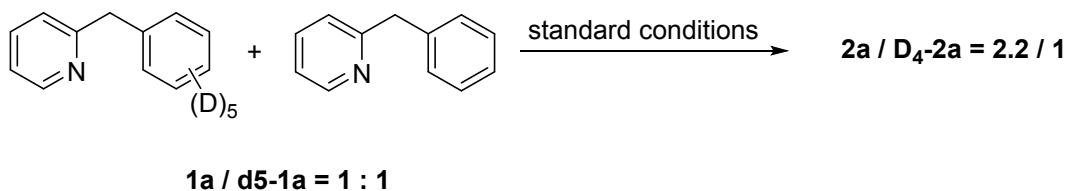
**d-1a** (0.2 mmol) were used in standard conditions and the concentrated residue was purified by column chromatography to give a mixture of **2a** and **D-2a** in a ratio of 1:1.5 as determined by  $^1\text{H}$  NMR in a total yield of 58%.



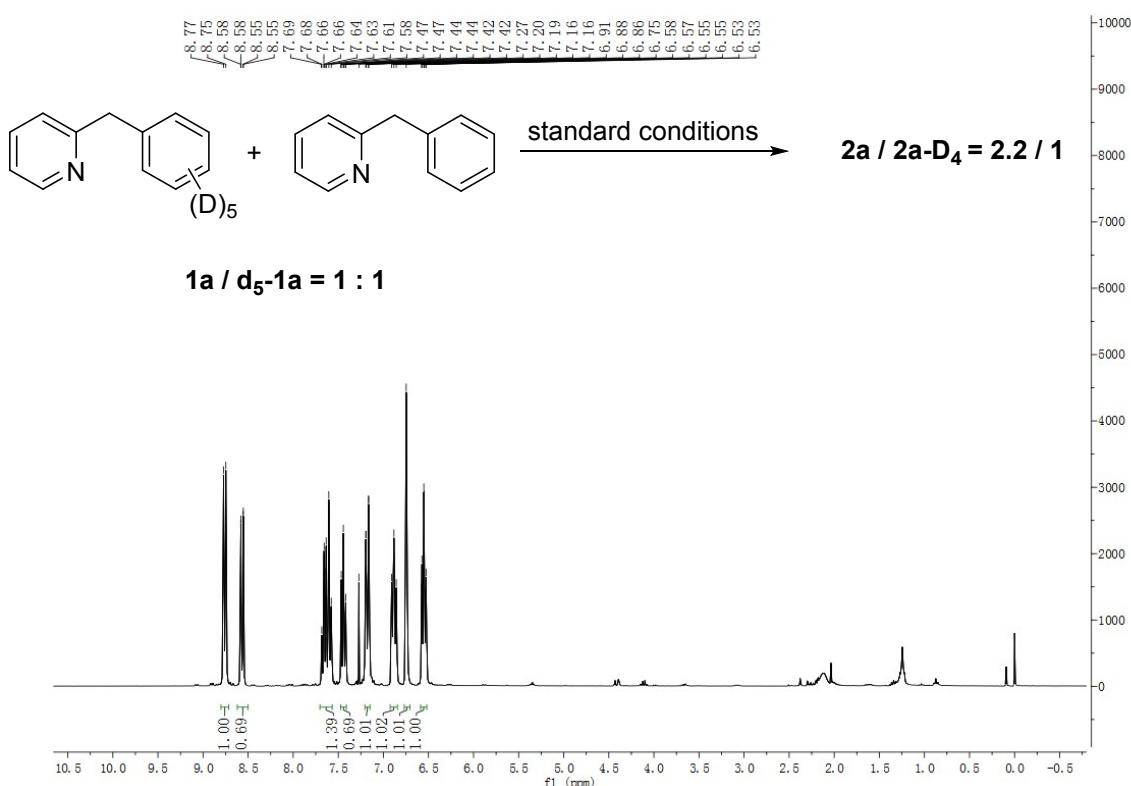
Deuterated substrate **d<sub>5</sub>-1a** was synthesized according to the literature reported method<sup>1a</sup> using potassium 2-(pyridin-2-yl)acetate 2-Pyridineacetic acid, potassium salt and pentadeuterated bromobenzene as substrates. **d<sub>5</sub>-1a** was obtained in 80% yield as a liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.56-8.54 (m, 1H); 7.57-7.51 (m, 1H), 7.11-7.06 (m, 2H); 4.17 (s, 2H).



Intermolecular KIE study:



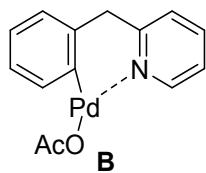
A mixture of **1a** (0.1 mmol), **d<sub>5</sub>-1a** (0.1 mmol) were used in standard conditions for 0.5 h and the concentrated residue was purified by column chromatography to give a mixture of **2a** and **D<sub>4</sub>-2a** in a ratio of 2.2:1 as determined by <sup>1</sup>H NMR in a total yield of 18%.



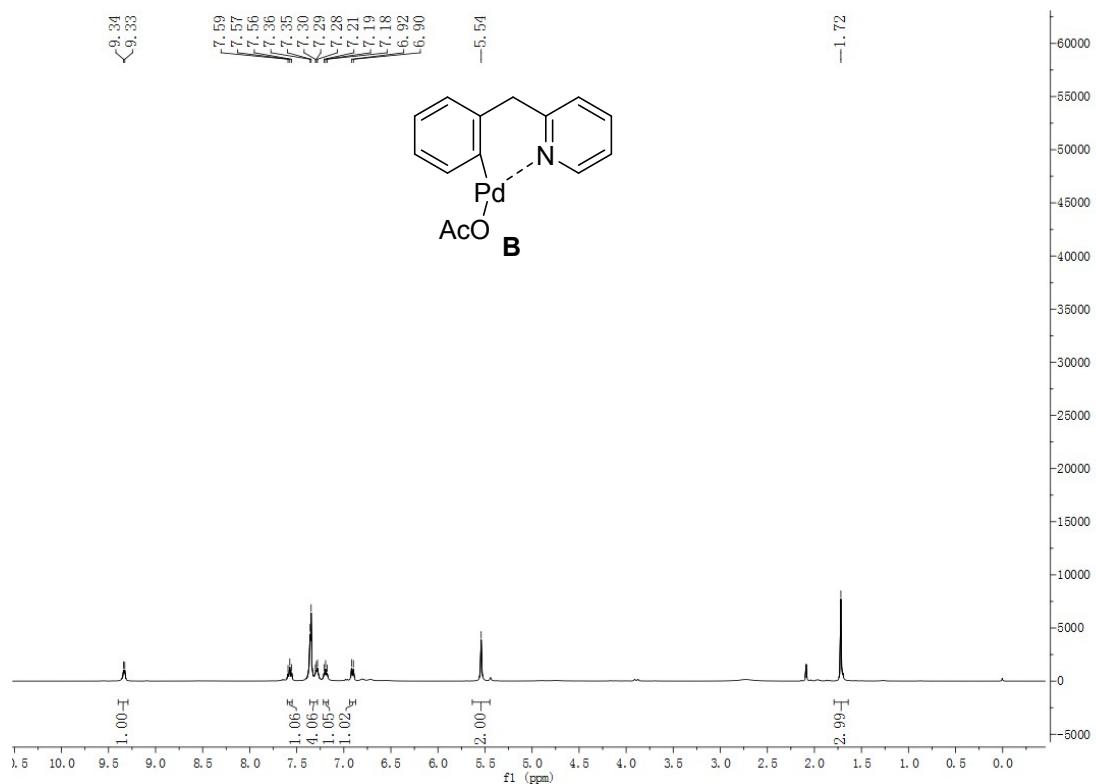
Parallel competition reactions of **1a** and **d<sub>5</sub>-1a**:

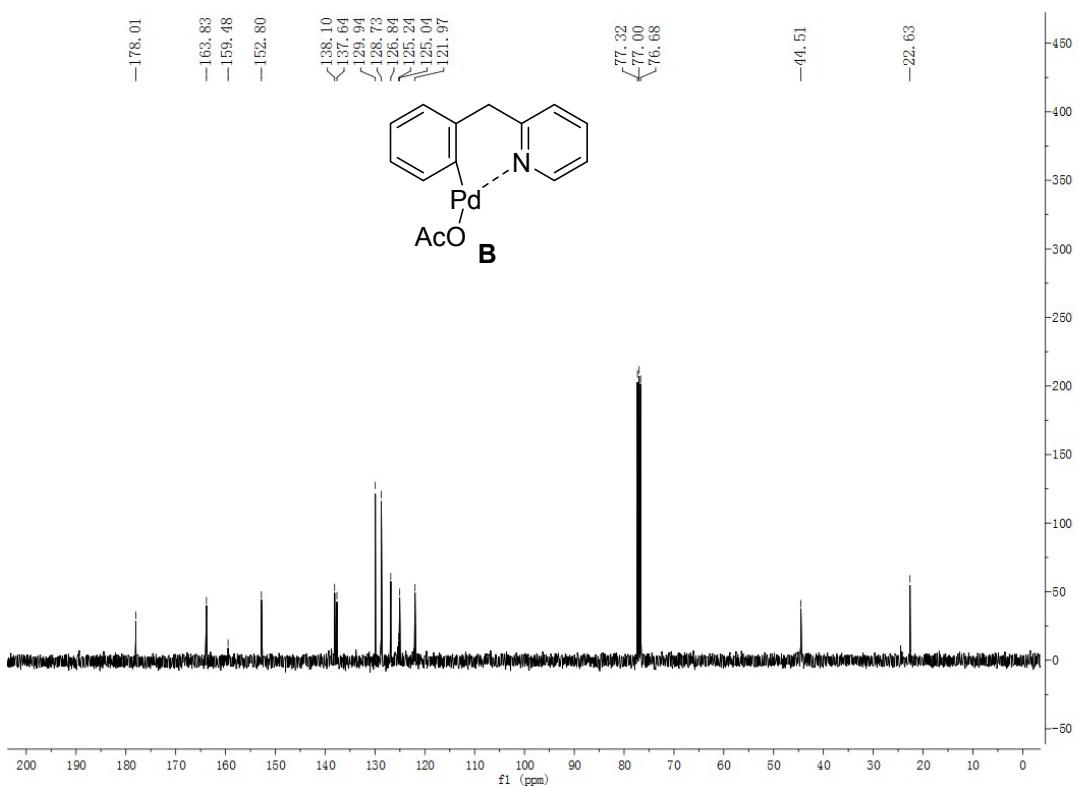
### 2.3 Preparation of Palladacycle B:

A mixture of 2-benzylpyridine (1.4 mmol) and Pd(OAc)<sub>2</sub> (1 mmol), in MeOH (10 mL) was stirred in a 20 mL vial for 24 h at room temperature.<sup>2</sup> The resulting yellow complex was collected by filtration and washed with diethyl ether (3 × 5 mL) to get **B** in 78% yield.



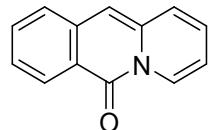
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.33 (d, *J* = 4.0 Hz, 1H), 7.59-7.56 (m, 1H), 7.36-7.28 (m, 4H), 7.21-7.18 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.54 (s, 2H), 1.72 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 178.0, 163.8, 159.5, 152.8, 138.1, 137.6, 129.9, 128.7, 126.8, 125.2, 125.0, 121.9, 44.5, 22.6; HRMS (ESI) m/z calcd for [C<sub>14</sub>H<sub>14</sub>NO<sub>2</sub>Pd]<sup>+</sup> (M+H)<sup>+</sup> 334.0054, found 334.0069.





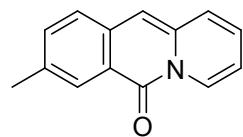
### 3 Characterization Data for the Products

#### **6H-pyrido[1,2-*b*]isoquinolin-6-one (2a)<sup>1a</sup>**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2a** (32.3 mg, 83% yield) as a yellow solid. m.p. 168-170 °C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 8.66-8.64 (m, 1H), 8.39-8.37 (m, 1H), 7.75-7.74 (m, 2H), 7.48-7.46 (m, 2H), 7.11-7.08 (m, 1H), 7.02 (s, 1H), 6.78-6.74 (m, 1H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ 158.2, 137.1, 136.1, 132.5, 127.5, 126.6, 125.9, 125.8, 125.3, 125.1, 119.1, 112.7, 100.4; MS (EI): 195 (M<sup>+</sup>).

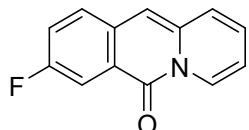
#### **8-methyl-6H-pyrido[1,2-*b*]isoquinolin-6-one (2b)<sup>1a</sup>**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2b** (22.2 mg, 53% yield) as a yellow solid. m.p. 159-161 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.75 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 7.52-7.47 (m, 2H), 7.17-7.14 (m, 1H), 6.86-6.82 (m, 1H), 6.73 (s, 1H), 6.54-6.51 (m, 1H), 2.50 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 159.0, 136.4, 135.0, 134.2, 134.1, 127.1, 125.9, 125.6, 125.5,

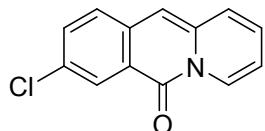
125.2, 119.9, 111.7, 100.9, 21.5; MS (EI): 209 ( $M^+$ ).

**8-fluoro-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2c)**



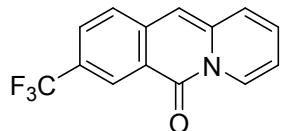
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2c** (20.8 mg, 49% yield) as a yellow solid. m.p. 140-142 °C  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.74 (d,  $J = 8.0$  Hz, 1H), 8.20-8.16 (m, 1H), 7.66-7.61 (m, 1H), 7.47-7.40 (m, 1H), 7.26-7.21 (m, 1H), 6.95-6.90 (m, 1H), 6.80 (s, 1H), 6.64-6.59 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  160.1 (d,  $J_{\text{C}-\text{F}} = 245.3$  Hz), 158.5 (d,  $J_{\text{C}-\text{F}} = 4.5$  Hz), 136.5, 133.1, 128.1 (d,  $J_{\text{C}-\text{F}} = 7.5$  Hz), 125.8, 125.6 (d,  $J_{\text{C}-\text{F}} = 4.5$  Hz), 122.1 (d,  $J_{\text{C}-\text{F}} = 24.7$  Hz), 120.9 (d,  $J_{\text{C}-\text{F}} = 8.2$  Hz), 112.3, 112.2 (d,  $J_{\text{C}-\text{F}} = 23.3$  Hz), 100.6.; MS (EI): 213 ( $M^+$ ); HRMS (ESI) m/z calcd for  $\text{C}_{13}\text{H}_9\text{FNO}$  ( $M+\text{H}^+$ ) 214.0663, found 214.0657.

**8-chloro-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2d)<sup>1a</sup>**



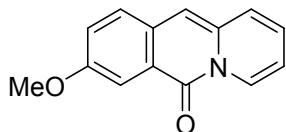
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2d** (22.4 mg, 49% yield) as a yellow solid. m.p. 114-116 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.75-8.72 (m, 1H), 8.49-8.50 (m, 1H), 7.56-7.51 (m, 2H), 7.23-7.20 (m, 1H), 6.98-6.92 (m, 1H), 6.73 (s, 1H), 6.64-6.59 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  158.2, 137.3, 134.5, 132.8, 130.5, 127.2, 127.1, 126.3, 126.0, 125.6, 120.5, 112.4, 100.4; MS (EI): 229 ( $M^+$ ).

**8-(trifluoromethyl)-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2e)**



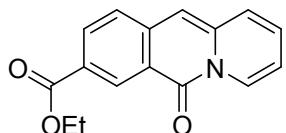
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2e** (43.1 mg, 82% yield) as a yellow solid. m.p. 143-145 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.77-8.73 (m, 2H), 7.76-7.73 (m, 1H), 7.63-7.60 (m, 1H), 7.23-7.20 (m, 1H), 7.04-6.99 (m, 1H), 6.72-6.62 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  158.7, 138.8, 138.0, 129.5 (q,  $J_{\text{C}-\text{F}} = 35.3$  Hz), 127.7 (q,  $J_{\text{C}-\text{F}} = 2.3$  Hz), 127.6, 126.4, 126.2, 126.1, 125.9 (q,  $J_{\text{C}-\text{F}} = 5.3$  Hz), 125.4, 124.1 (q,  $J_{\text{C}-\text{F}} = 270.0$  Hz), 118.6, 112.6, 100.1; MS (EI): 263 ( $M^+$ ); HRMS (ESI) m/z calcd for  $\text{C}_{14}\text{H}_9\text{F}_3\text{NO}$  ( $M+\text{H}^+$ ) 264.0631, found 264.0627.

**8-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2f)**



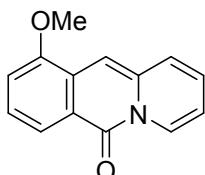
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **3f** (18.5 mg, 41% yield) as a yellow solid. m.p. 165-167 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.75 (d, *J* = 8.0 Hz, 1H), 7.89-7.88 (m, 1H), 7.55-7.53 (m, 1H), 7.32-7.30 (m, 1H), 7.18-7.16 (m, 1H), 6.85-6.81 (m, 1H), 6.75 (s, 1H), 6.58-6.54 (m, 1H), 3.93 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.5, 157.5, 135.2, 131.0, 127.3, 125.6, 124.5, 124.4, 120.9, 112.1, 106.1, 101.2, 55.6; MS (EI): 225 (M<sup>+</sup>); HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>12</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 226.0863, found 226.0859.

#### **ethyl 6-oxo-6*H*-pyrido[1,2-*b*]isoquinoline-8-carboxylate (2g)**



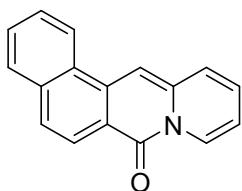
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2g** (48.5 mg, 91% yield) as yellow solid. m.p. 171-173 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.14 (s, 1H), 8.72-8.70 (m, 1H), 8.15-8.13 (m, 1H), 7.52-7.50 (m, 1H), 7.17-7.15 (m, 1H), 6.98-6.94 (m, 1H), 6.65-6.57 (m, 2H), 4.41-4.35 (m, 2H), 1.42-1.38 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz) δ 165.2, 158.1, 139.2, 138.7, 132.3, 131.1, 129.9, 128.6, 126.2, 125.8, 125.2, 117.9, 113.5, 100.0, 60.9, 14.3; MS (EI): 267 (M<sup>+</sup>); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 268.0968, found 268.0962.

#### **10-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2h)**



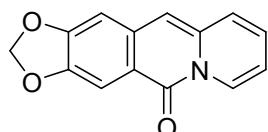
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **2h** (19.8, 44% yield) as a yellow solid. m.p. 155-157 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.62-6.59 (m, 1H), 3.98 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.8, 153.9, 136.6, 128.2, 126.1, 125.8, 125.4, 124.9, 120.7, 119.6, 112.2, 109.9, 95.7, 55.6; MS (EI): 225 (M<sup>+</sup>); HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>12</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 226.0863, found 226.0857.

#### **7*H*-benzo[f]pyrido[1,2-*b*]isoquinolin-7-one (2i)<sup>1a</sup>**



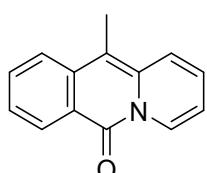
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **2i** (32.8 mg, 67% yield) as a yellow solid. m.p. 200-202 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.97 (d, *J* = 8.0 Hz, 1H), 8.54-8.47 (m, 2H), 7.91-7.89 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69-7.62 (m, 2H), 7.59 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.13-7.09 (m, 1H), 6.80-6.76 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.7, 137.9, 135.3, 134.8, 128.8, 128.7, 128.1, 126.9, 126.5, 126.4, 125.9, 125.7, 124.3, 123.9, 116.7, 113.1, 97.2; MS (EI): 245 (M<sup>+</sup>).

#### **5*H*-[1,3]dioxolo[4,5-*g*]pyrido[1,2-*b*]isoquinolin-5-one (2j)**<sup>1a</sup>



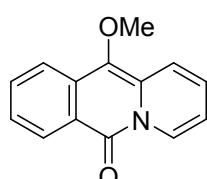
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2j** (36.8 mg, 77% yield) as a yellow solid. m.p. 229-231 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.66-8.63 (m, 1H), 7.65 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.11-7.07 (m, 1H), 6.98 (s, 1H), 6.80-6.76 (m, 1H), 6.19 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 157.0, 152.3, 146.9, 136.1, 134.2, 126.0, 125.5, 125.1, 114.6, 112.8, 103.6, 102.6, 102.1, 100.7; MS (EI): 239 (M<sup>+</sup>).

#### **11-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2k)**<sup>1a</sup>



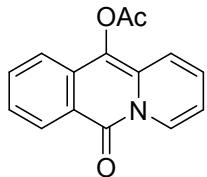
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2k** (35.1 mg, 84% yield) as a yellow solid. m.p. 150-152 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 7.79-7.68 (m, 2H), 7.47-7.41 (m, 2H), 6.90-6.86 (m, 1H), 6.53-6.49 (m, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.7, 135.9, 133.6, 132.0, 128.4, 126.5, 125.4, 124.7, 122.6, 122.2, 119.9, 111.2, 104.2, 11.9; MS (EI): 209 (M<sup>+</sup>).

#### **11-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2l)**<sup>1a</sup>



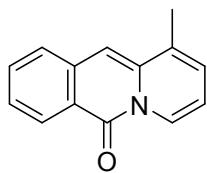
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2l** (36.4 mg, 81% yield) as a yellow solid. m.p. 148-150 °C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz) δ 8.70-8.67 (m, 1H), 8.50-8.47 (m, 1H), 7.99-7.87 (m, 2H), 7.70-7.57 (m, 2H), 7.20-7.14 (m, 1H), 6.81-6.76 (m, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 75 MHz) δ 156.6, 132.7, 131.3, 131.1, 129.8, 128.1, 126.4, 125.6, 125.5, 120.4, 119.8, 118.9, 112.4, 61.9; MS (EI): 225 (M<sup>+</sup>).

### **6-oxo-6*H*-pyrido[1,2-*b*]isoquinolin-11-yl acetate (**2m**) <sup>1a</sup>**



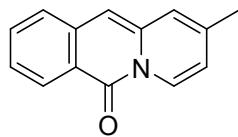
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2m** (36.9 mg, 73% yield) as a yellow solid. m.p. 196-198 °C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.89-7.85 (m, 1H), 7.75-7.73 (m, 1H), 7.61-7.51 (m, 2H), 7.24-7.20 (m, 1H), 6.85-6.82 (m, 1H), 2.55 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 170.0, 157.1, 133.2, 130.8, 129.9, 127.9, 127.8, 125.8, 125.6, 121.6, 120.2, 119.5, 118.3, 112.6, 20.5; MS (EI): 253 (M<sup>+</sup>).

### **1-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (**2n**) <sup>1a</sup>**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2n** (25.1 mg, 60% yield) as a yellow solid. m.p. 119-121 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.76 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 2H), 7.46-7.42 (m, 1H), 6.81-6.79 (m, 2H), 6.54-6.51 (m, 1H), 2.37 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 159.6, 137.6, 136.0, 132.2, 131.5, 127.9, 125.9, 125.6, 124.9, 124.7, 119.7, 111.3, 97.9, 19.3; MS (EI): 209 (M<sup>+</sup>).

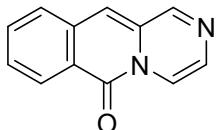
### **2-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (**2o**)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give **2o** (14.6 mg, 35% yield) as a yellow solid. m.p. 120-122 °C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.71-7.66 (m, 2H), 7.43-7.40 (m, 1H), 7.11 (s, 1H), 6.79 (s, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.16 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 158.2, 137.2, 136.9, 136.5, 132.3, 127.4, 125.7, 124.9, 124.5, 122.6, 118.6, 115.5, 98.8, 20.5; MS (EI): 209 (M<sup>+</sup>); HRMS (ESI) m/z calcd for

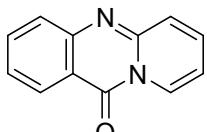
$C_{14}H_{12}NO$  ( $M+H$ )<sup>+</sup> 210.0913, found 210.0907.

**6*H*-pyrazino[1,2-*b*]isoquinolin-6-one (2p)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **2p** (22.1 mg, 57% yield) as a yellow solid. m.p. 190-192 °C; <sup>1</sup>H NMR ( $CDCl_3$ , 400 MHz) δ 8.68 (s, 1H), 8.60 (d,  $J$  = 8.0 Hz, 1H), 8.37 (d,  $J$  = 8.0 Hz, 1H), 7.81-7.76 (m, 2H), 7.64-7.60 (m, 1H), 7.45 (d,  $J$  = 8.0 Hz, 1H), 7.06 (s, 1H); <sup>13</sup>C NMR ( $CDCl_3$ , 100 MHz) δ 157.9, 153.9, 135.5, 132.9, 130.8, 128.2, 127.6, 126.9, 126.9, 122.7, 116.3, 104.9; MS (EI): 196 ( $M^+$ ); HRMS (ESI) m/z calcd for  $C_{12}H_9N_2O$  ( $M+H$ )<sup>+</sup> 197.0709, found 197.0702.

**11*H*-pyrido[2,1-*b*]quinazolin-11-one (2q)<sup>3</sup>**



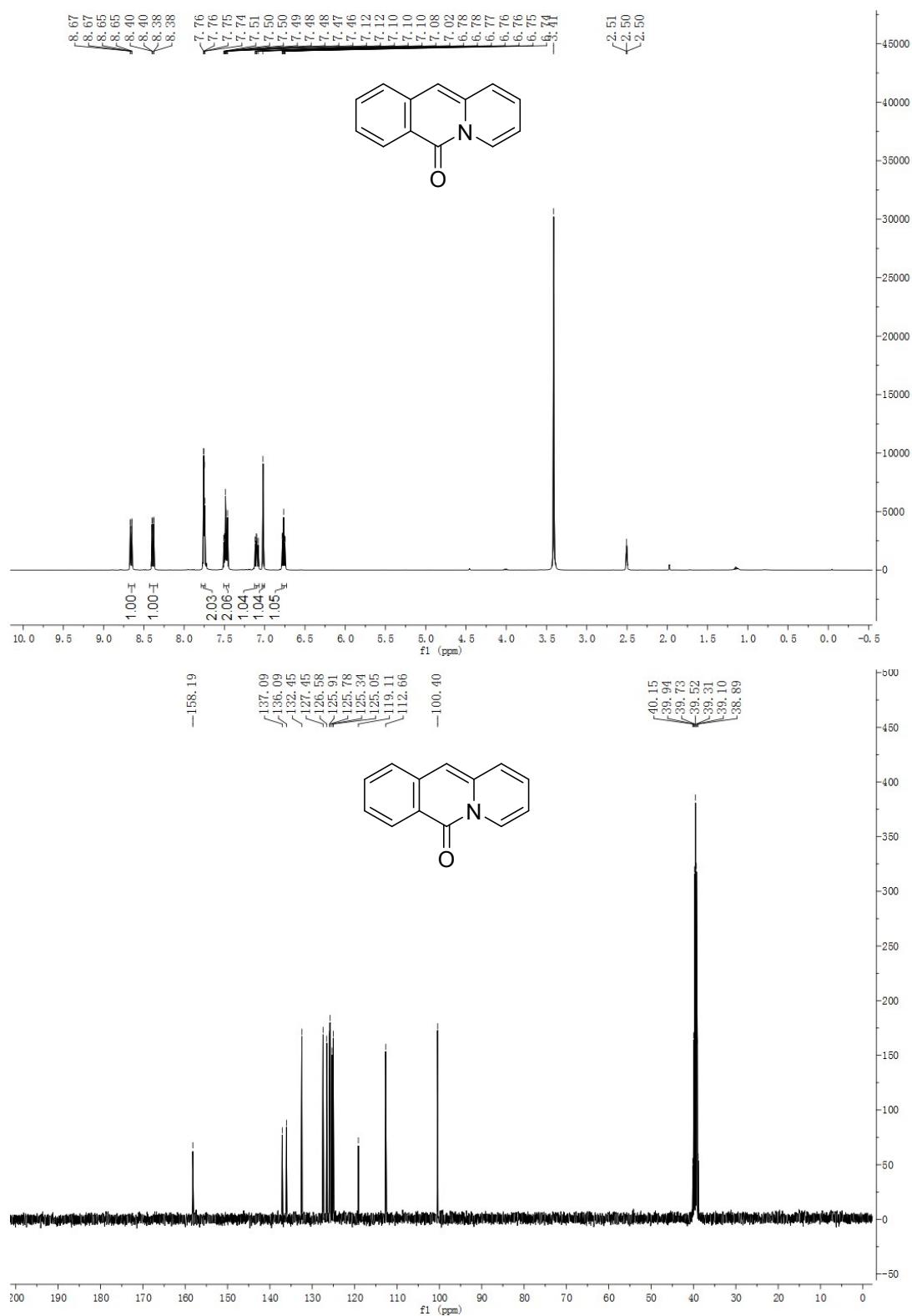
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **2q** (22.3 mg, 57% yield) as a yellow solid. mp 210-212 °C; <sup>1</sup>H NMR ( $CDCl_3$ , 300 MHz) δ 8.88-8.85 (m, 1H), 8.46-8.42 (m, 1H), 7.87-7.75 (m, 2H), 7.51-7.45 (m, 3H), 6.89-6.83 (m, 1H); <sup>13</sup>C NMR ( $CDCl_3$ , 75 MHz) δ 158.9, 148.5, 147.7, 135.1, 134.1, 127.3, 126.8, 126.7, 126.3, 125.2, 116.2, 112.5; MS (EI): 196 ( $M^+$ ).

#### 4. Reference

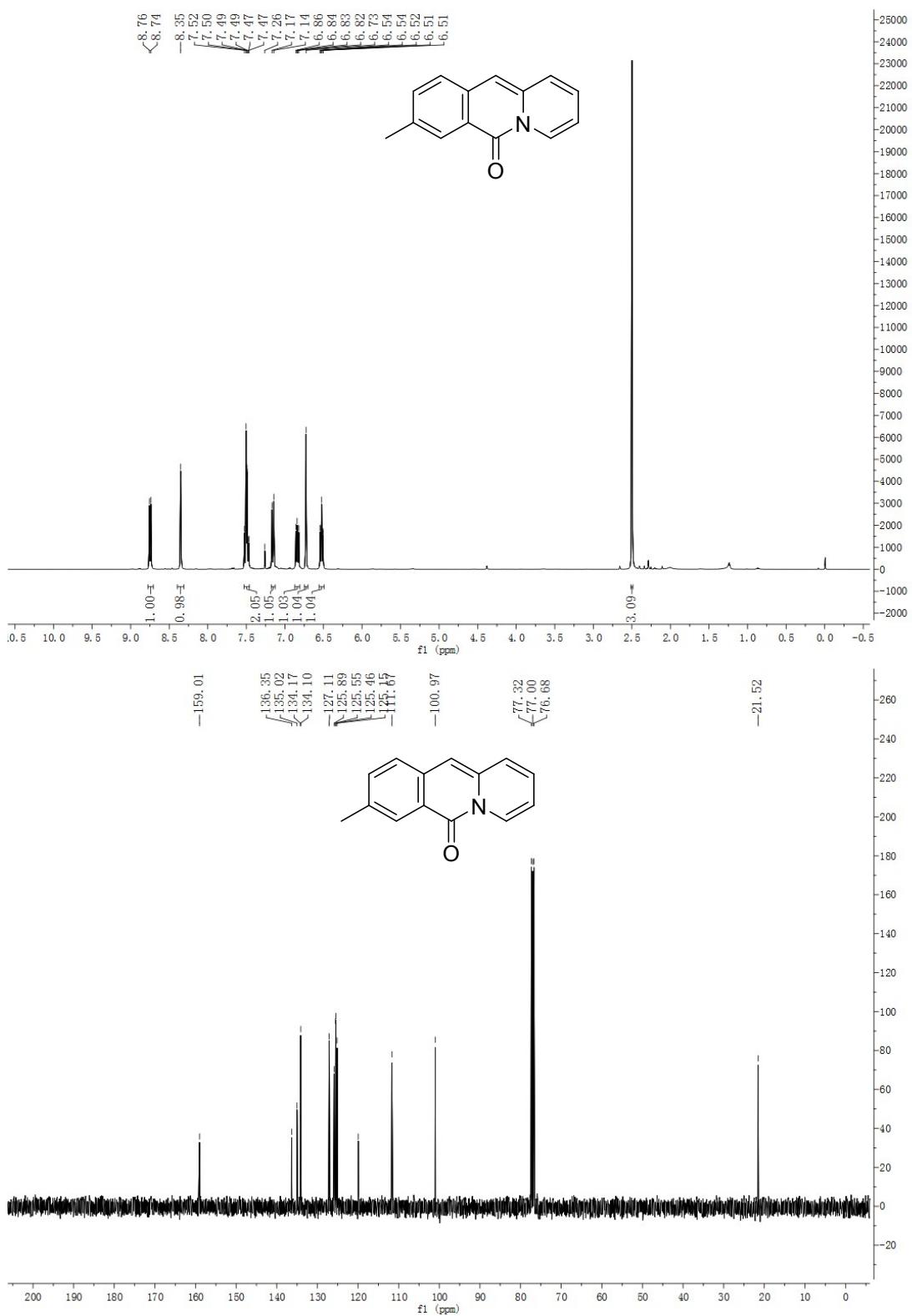
- (1) (a) Z. Xie, S. Luo and Q. Zhu, *Chem. Commun.* 2016, **52**, 12873; (b) L. Ren, L. Wang, Y. Lv, G. Li and S. Gao, *Org. Lett.* 2015, **17**, 2078.
- (2) X. Jia, D. Yang, S. Zhang and J. Cheng, *Org. Lett.* 2009, **11**, 4716.
- (3) D. Liang, Y. He and Q. Zhu, *Org. Lett.* 2014, **16**, 2748.

## 5. Copies of the $^1\text{H}$ NMR, $^{13}\text{C}$ NMR Spectra

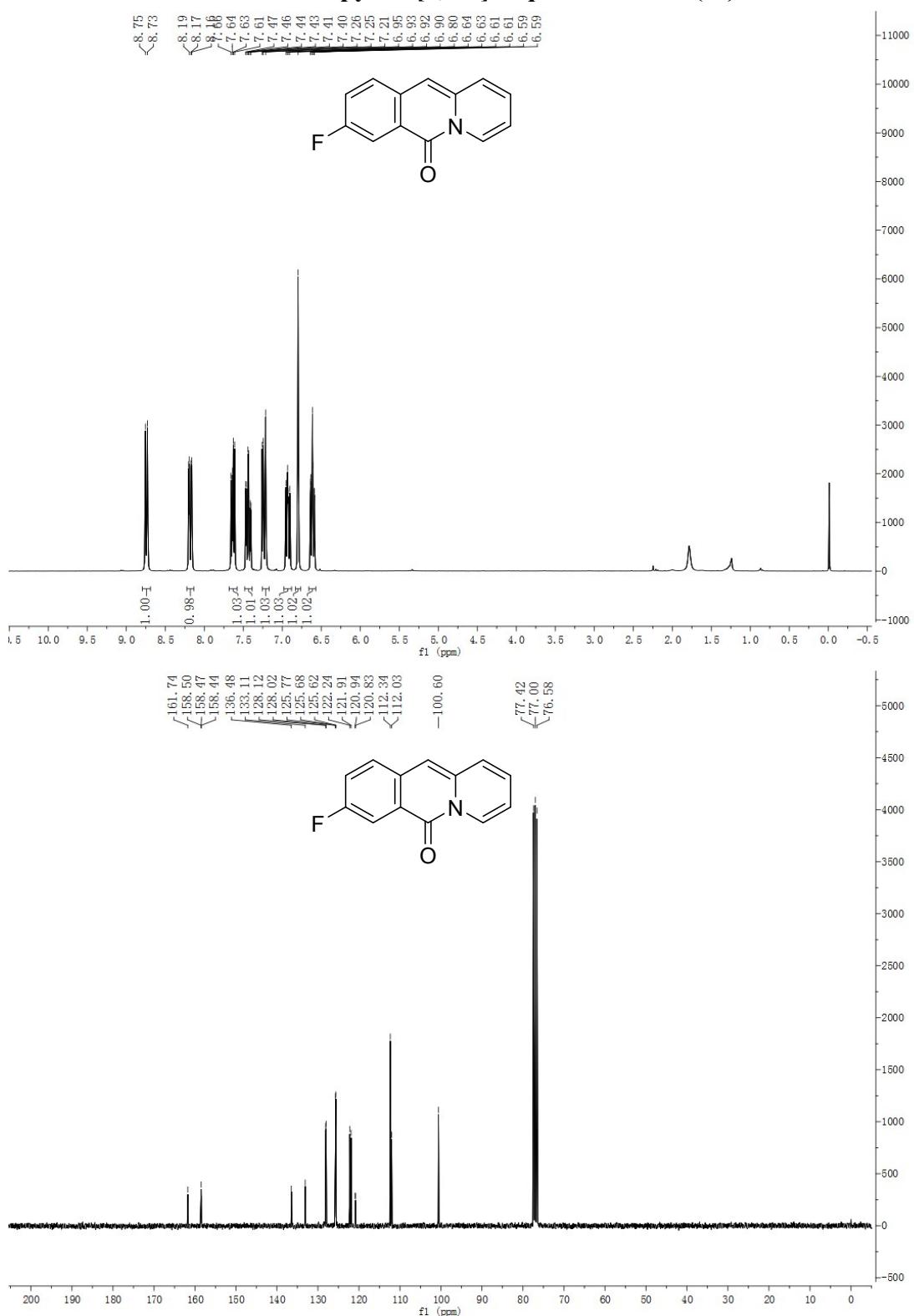
### **6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2a):**



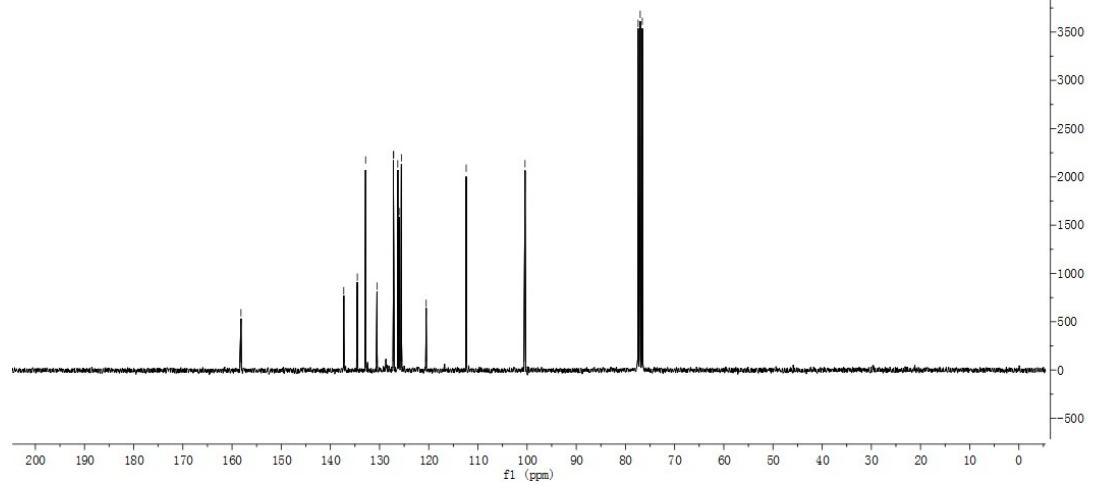
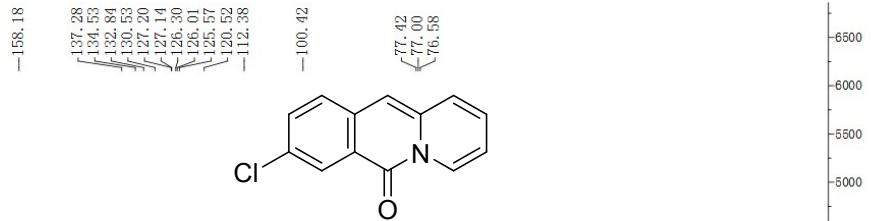
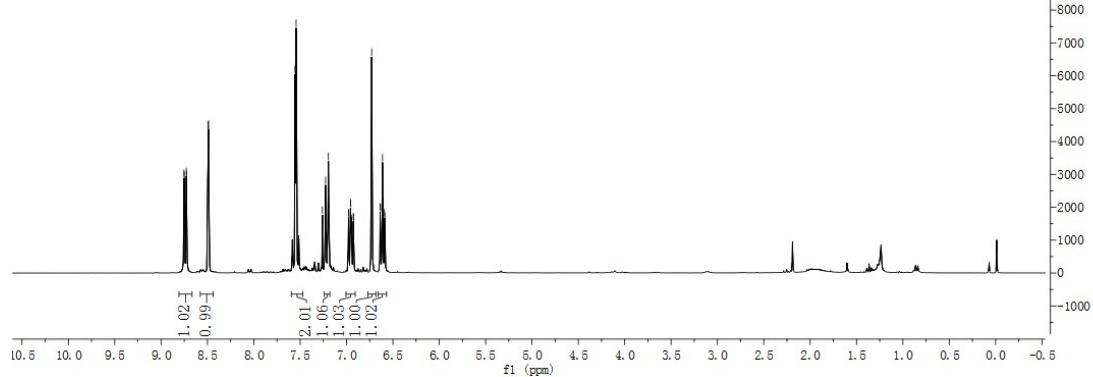
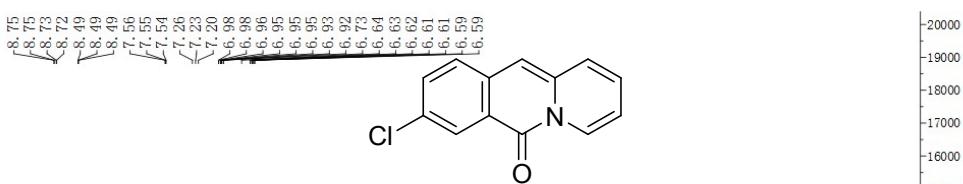
### **8-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2b):**



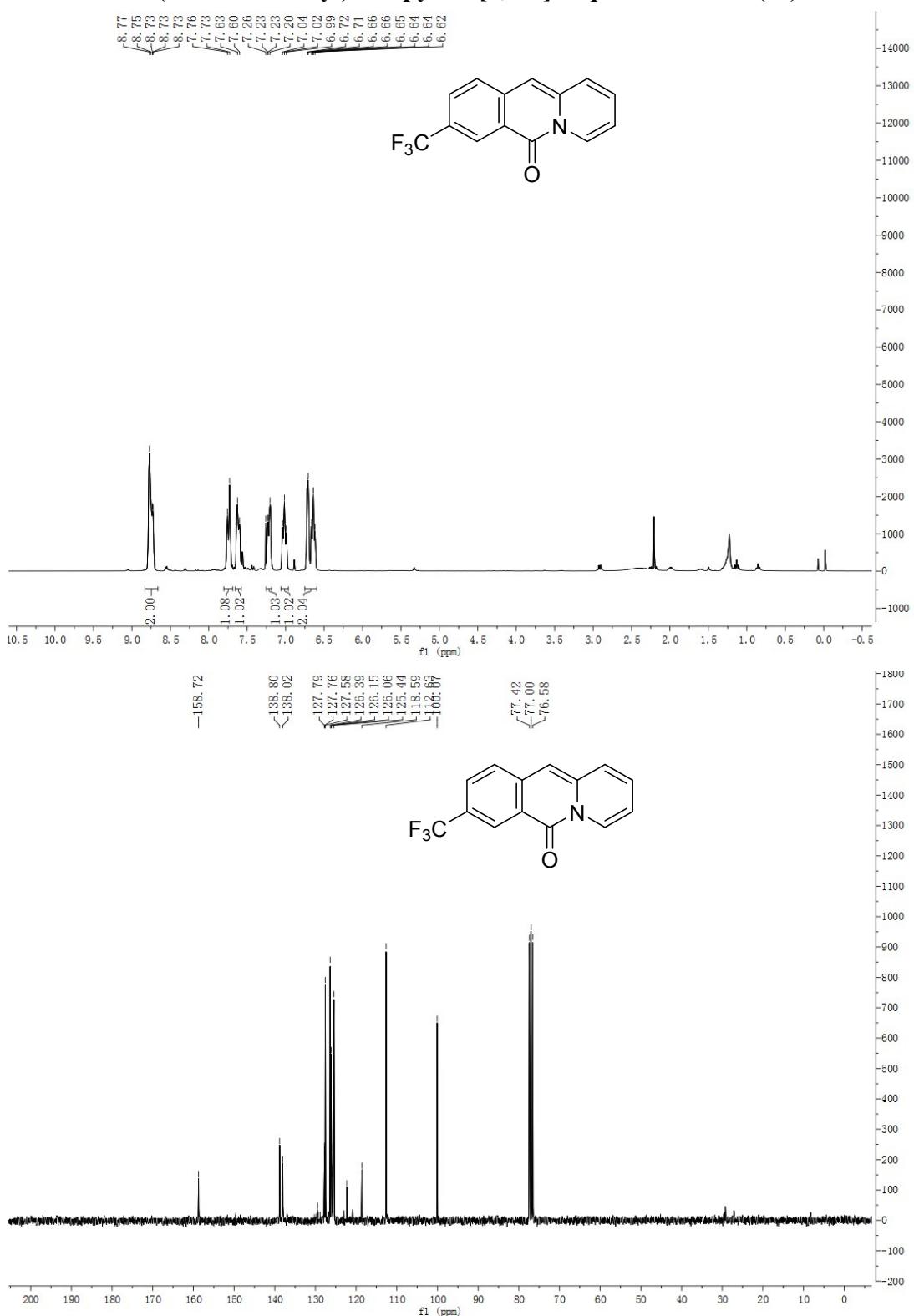
**8-fluoro-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2c):**



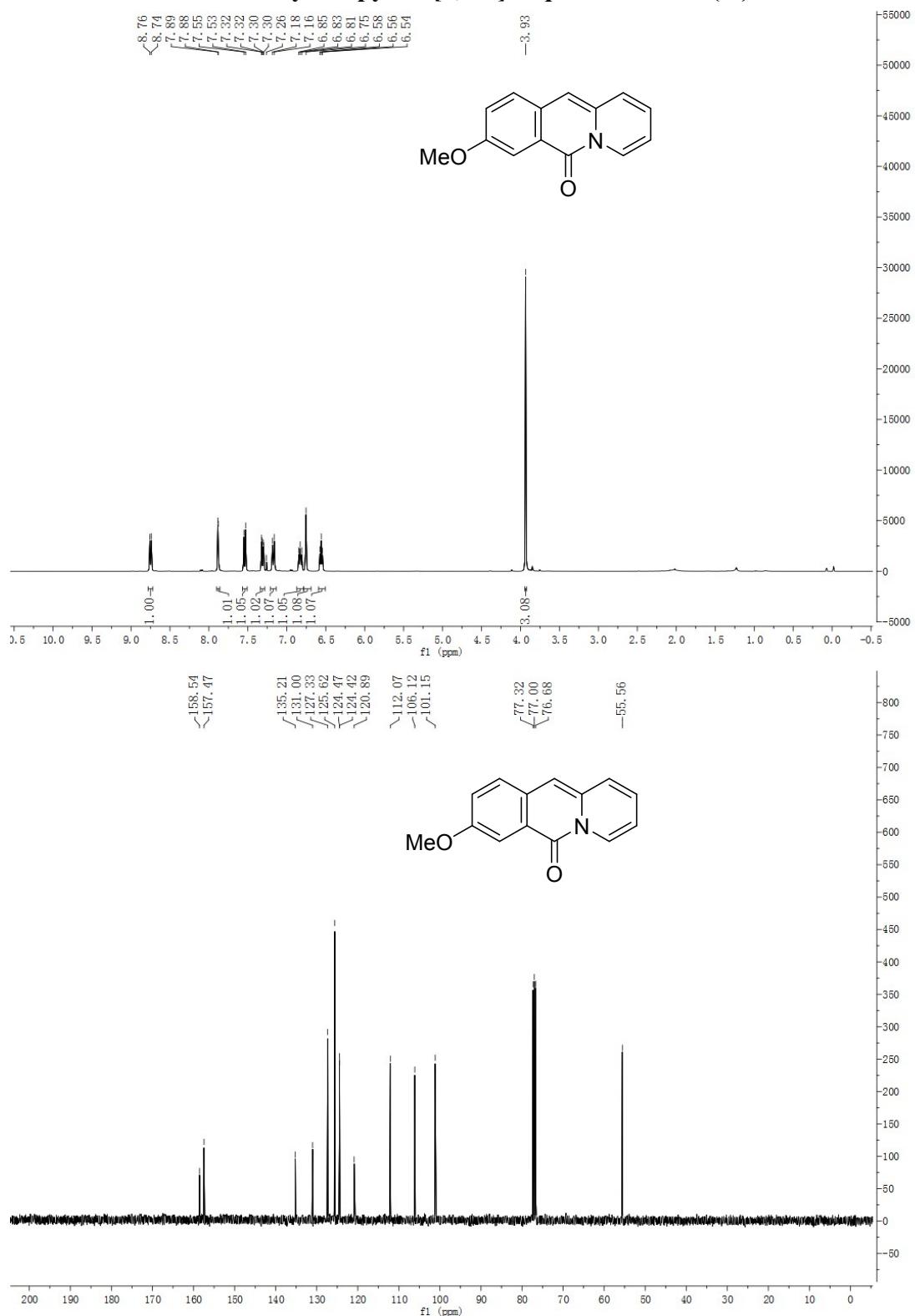
**8-chloro-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2d):**



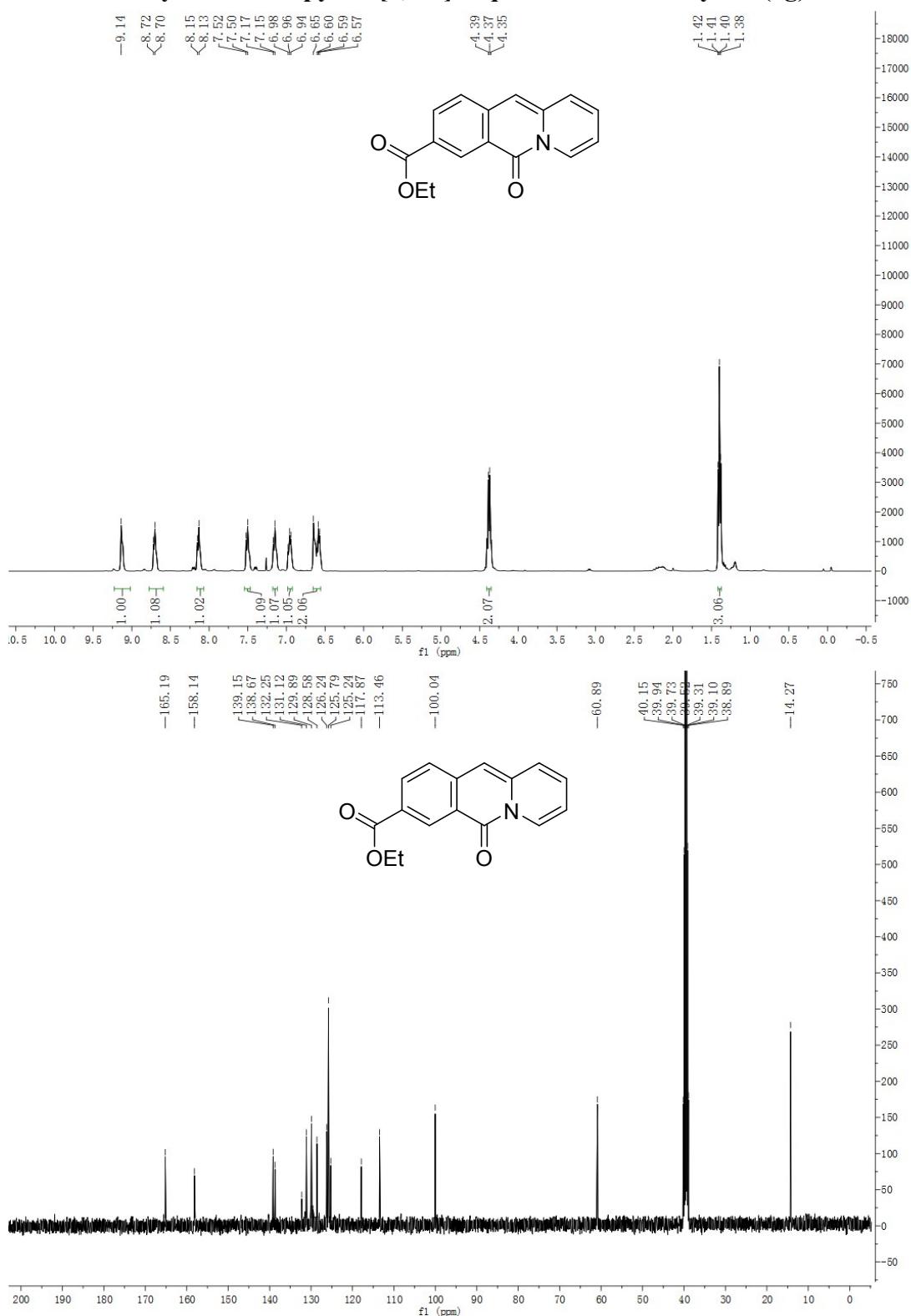
**8-(trifluoromethyl)-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2e):**



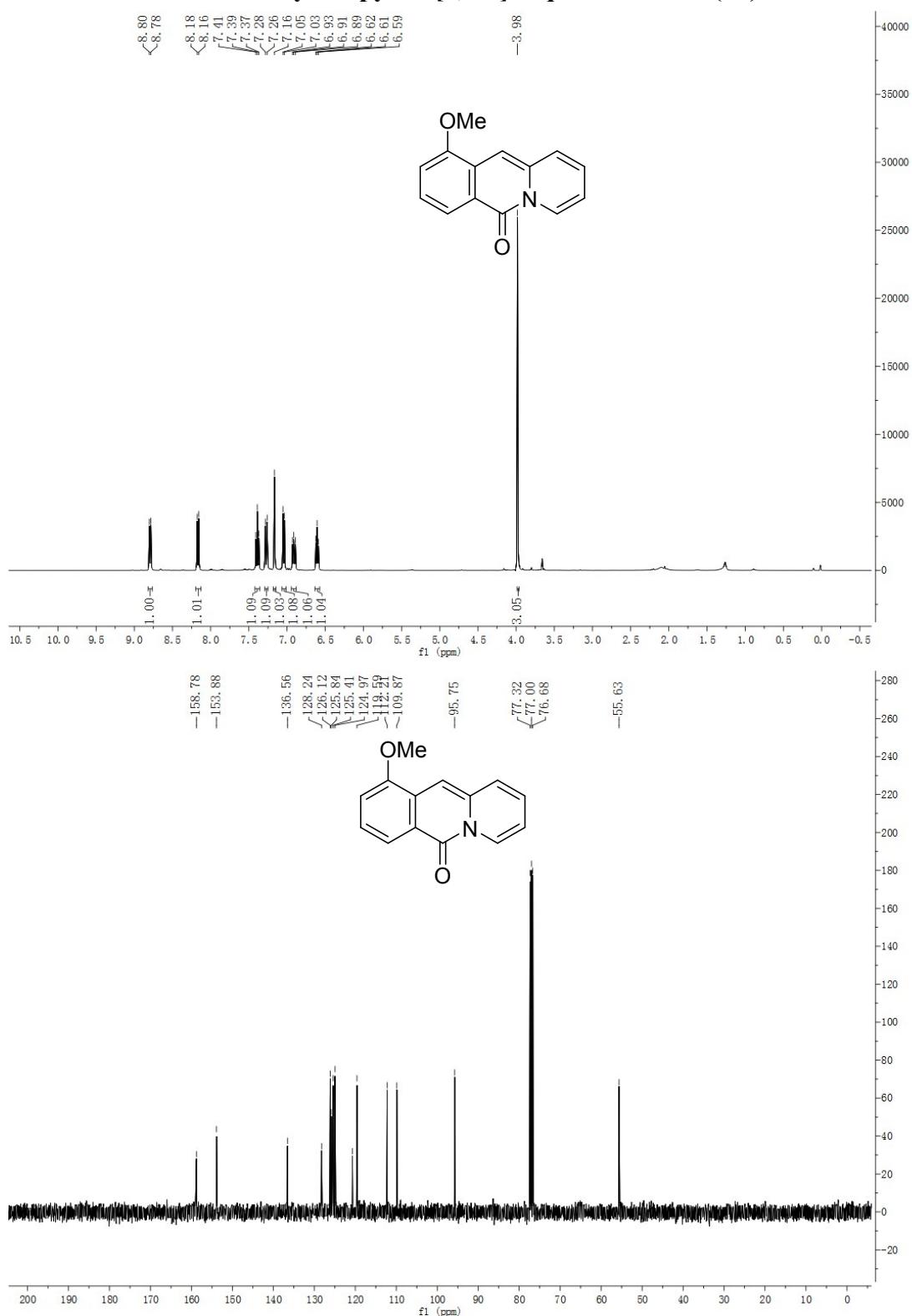
**8-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2f):**



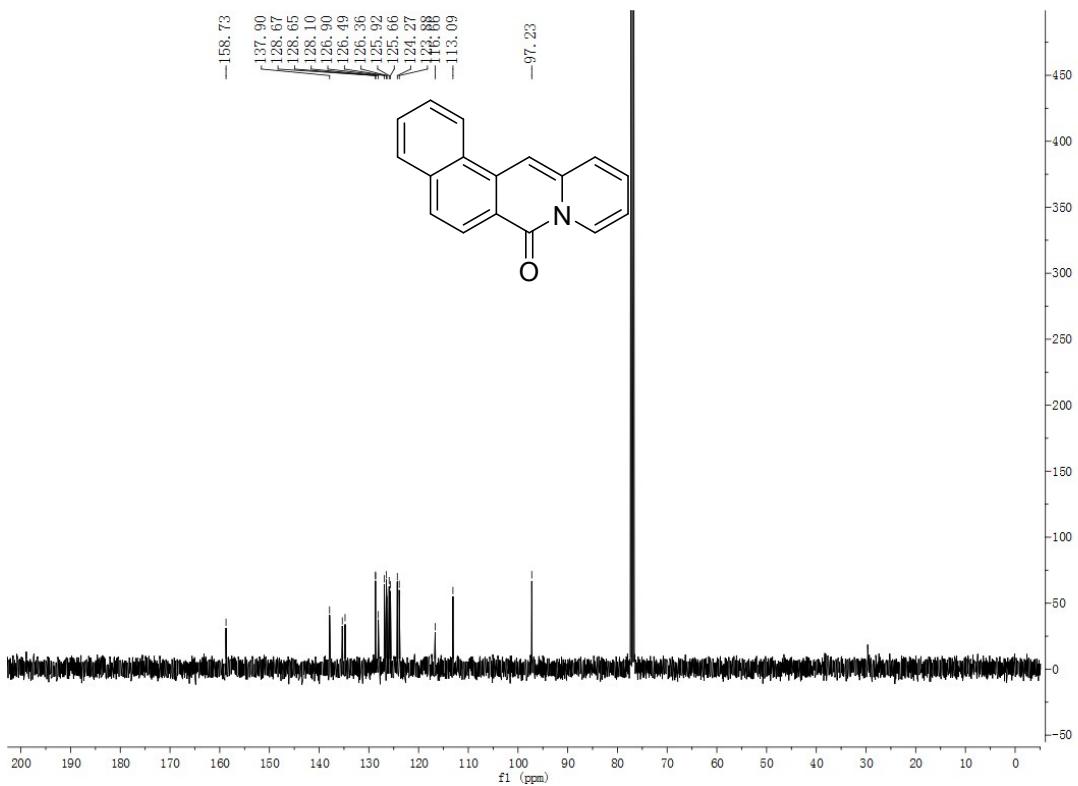
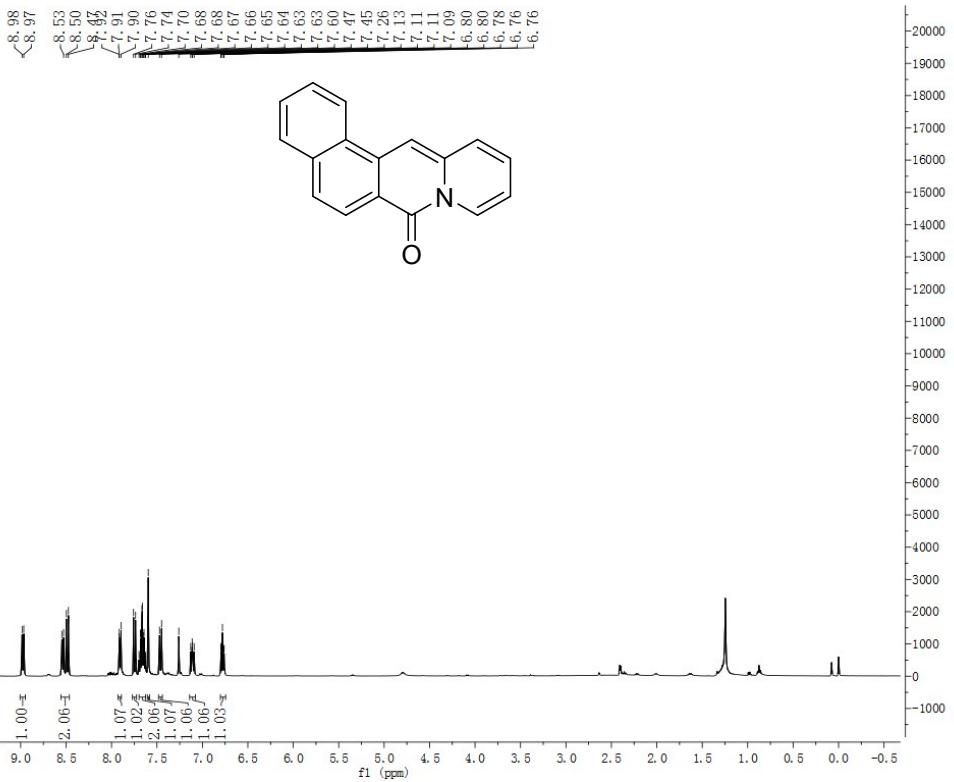
**ethyl 6-oxo-6*H*-pyrido[1,2-*b*]isoquinoline-8-carboxylate (2g):**



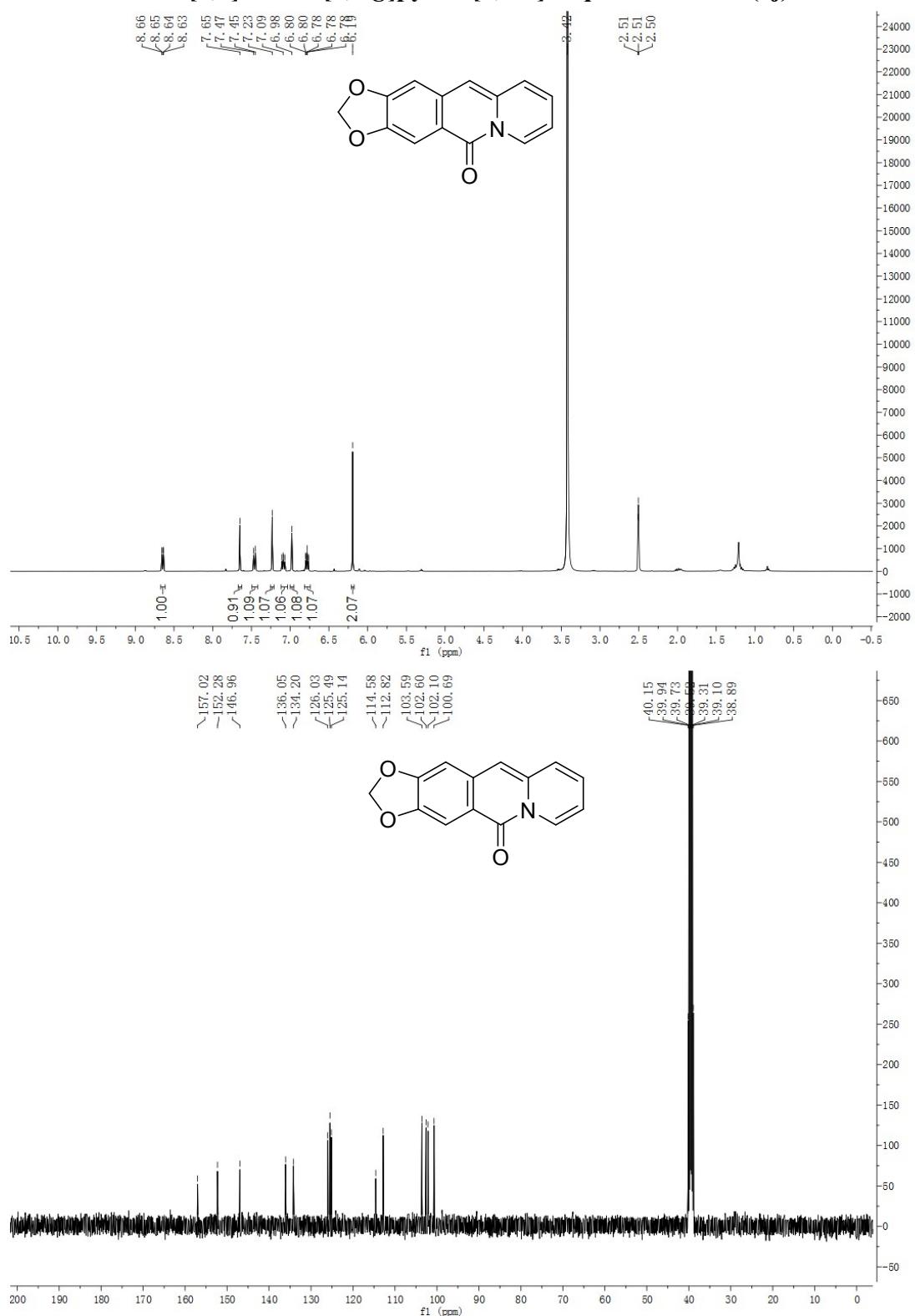
**10-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2h):**



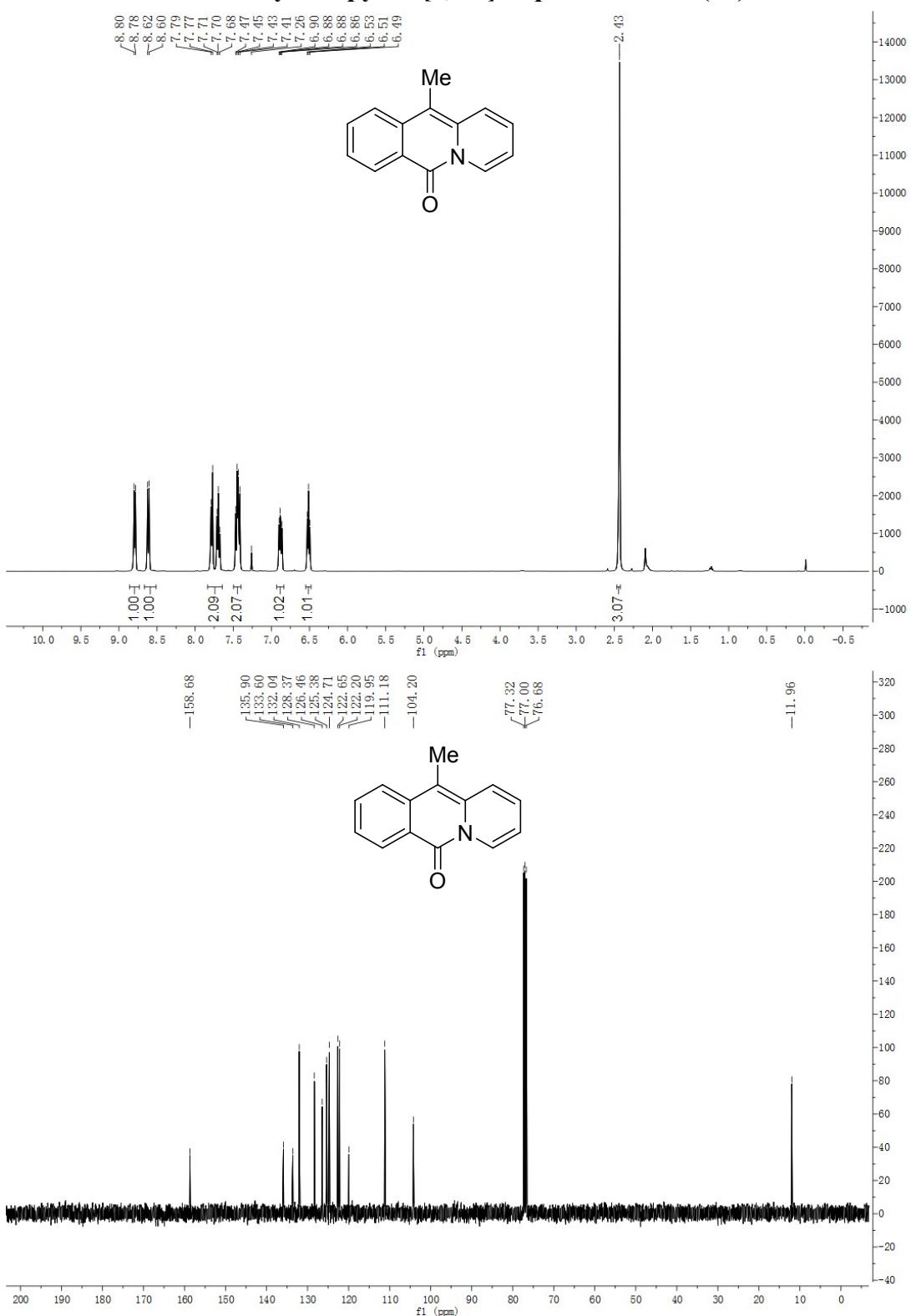
**7*H*-benzo[*f*]pyrido[1,2-*b*]isoquinolin-7-one (2i):**



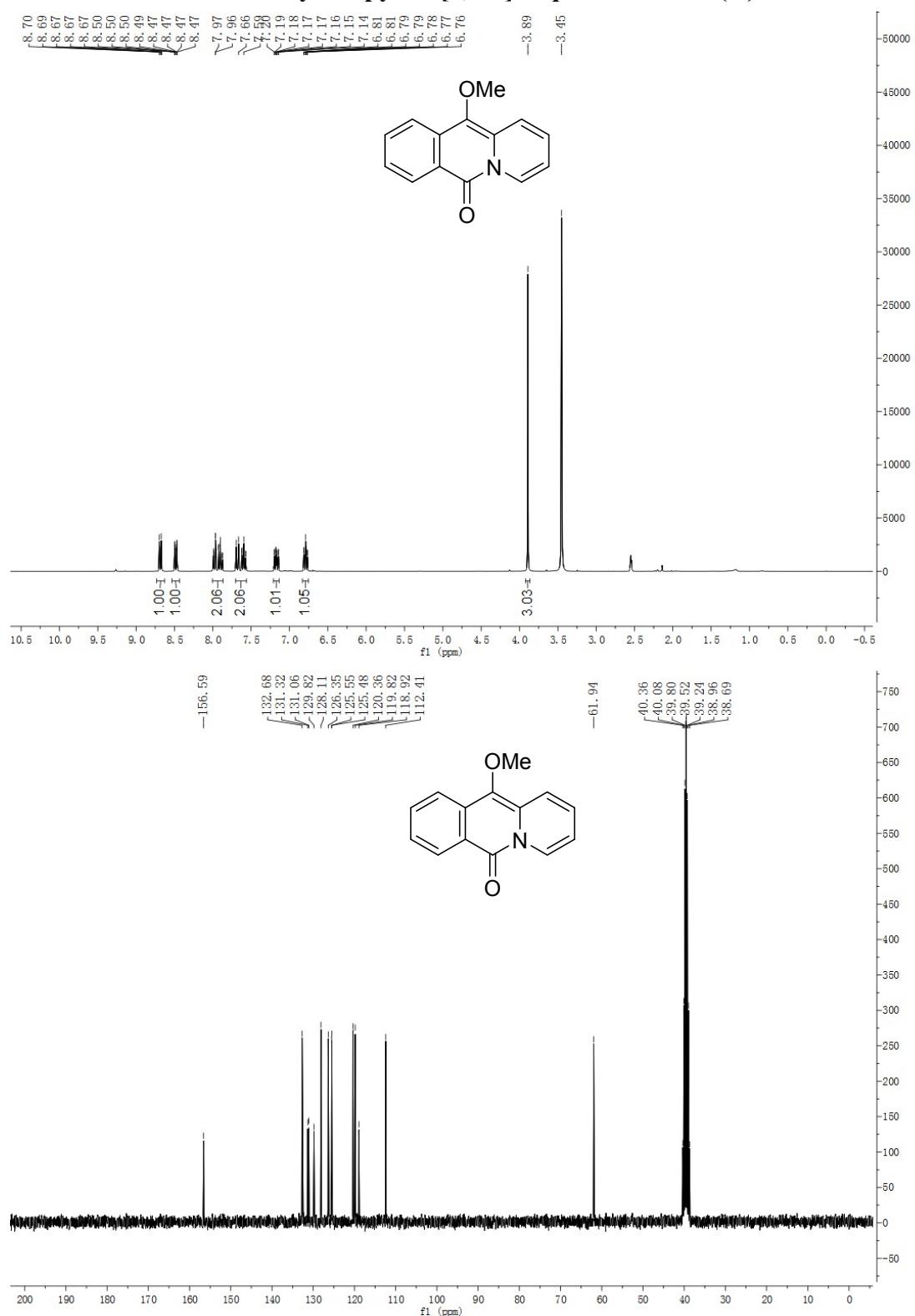
**5*H*-[1,3]dioxolo[4,5-*g*]pyrido[1,2-*b*]isoquinolin-5-one (**2j**):**



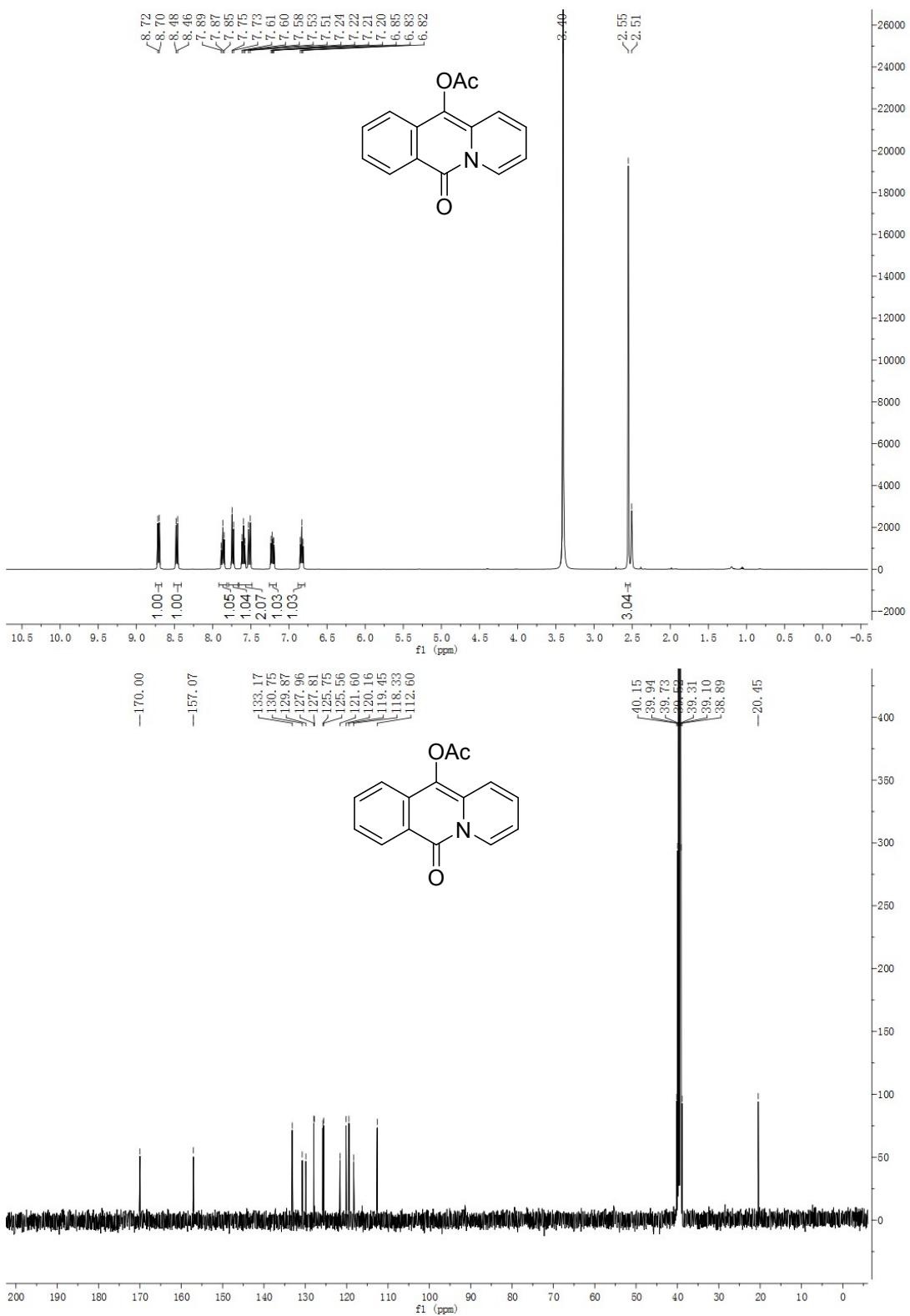
**11-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2k):**



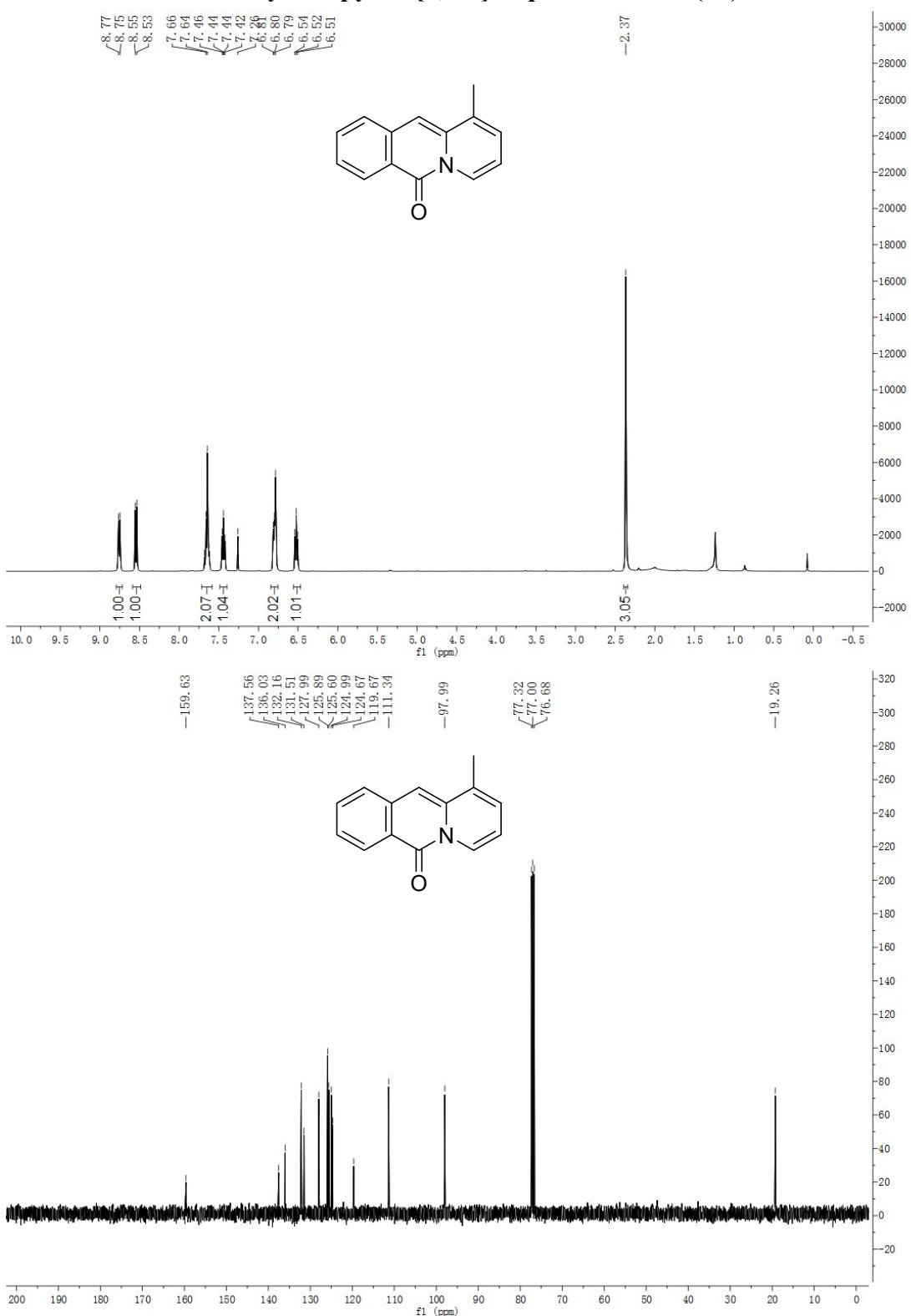
**11-methoxy-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2l):**



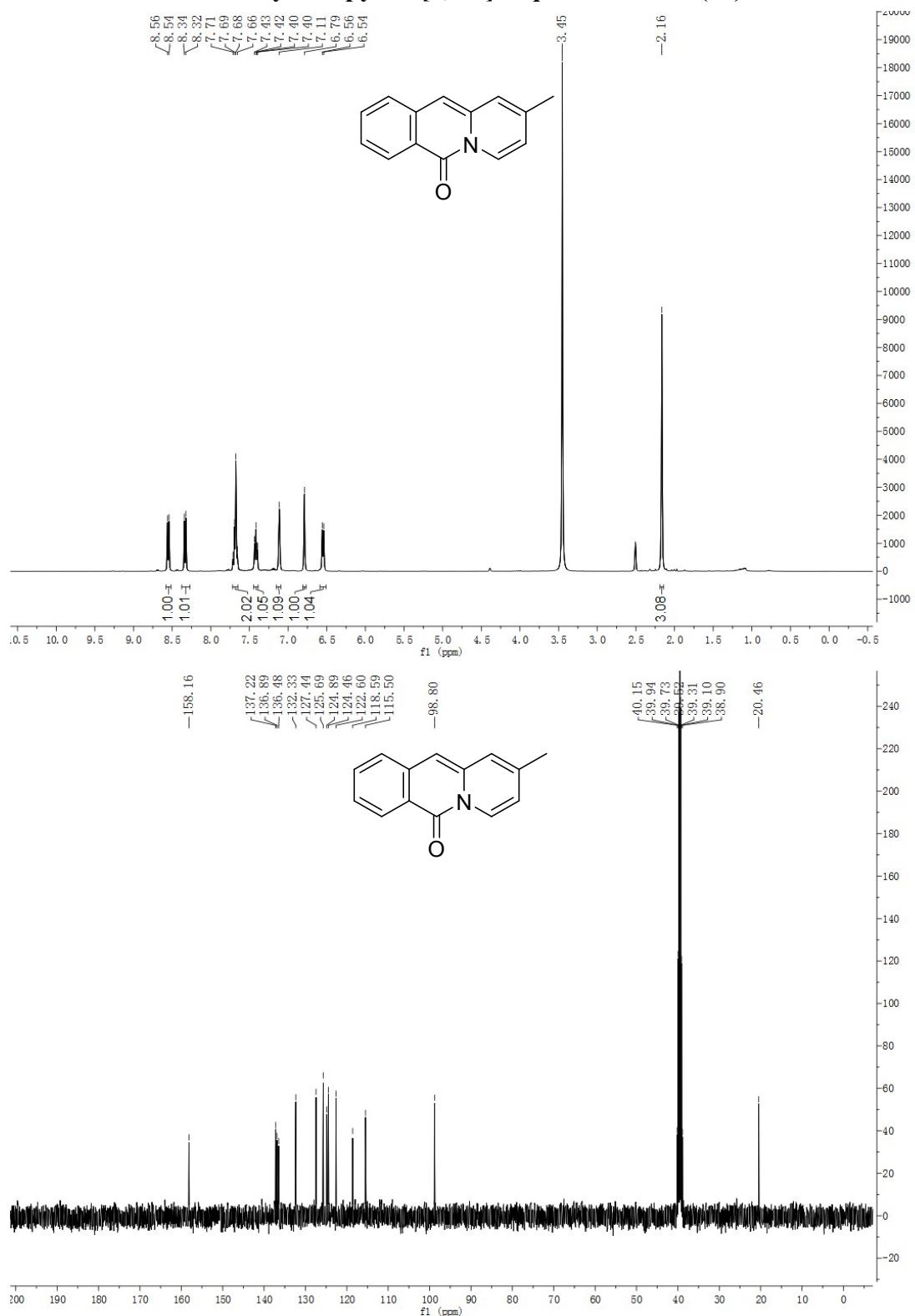
### **6-oxo-6*H*-pyrido[1,2-*b*]isoquinolin-11-yl acetate (2m):**



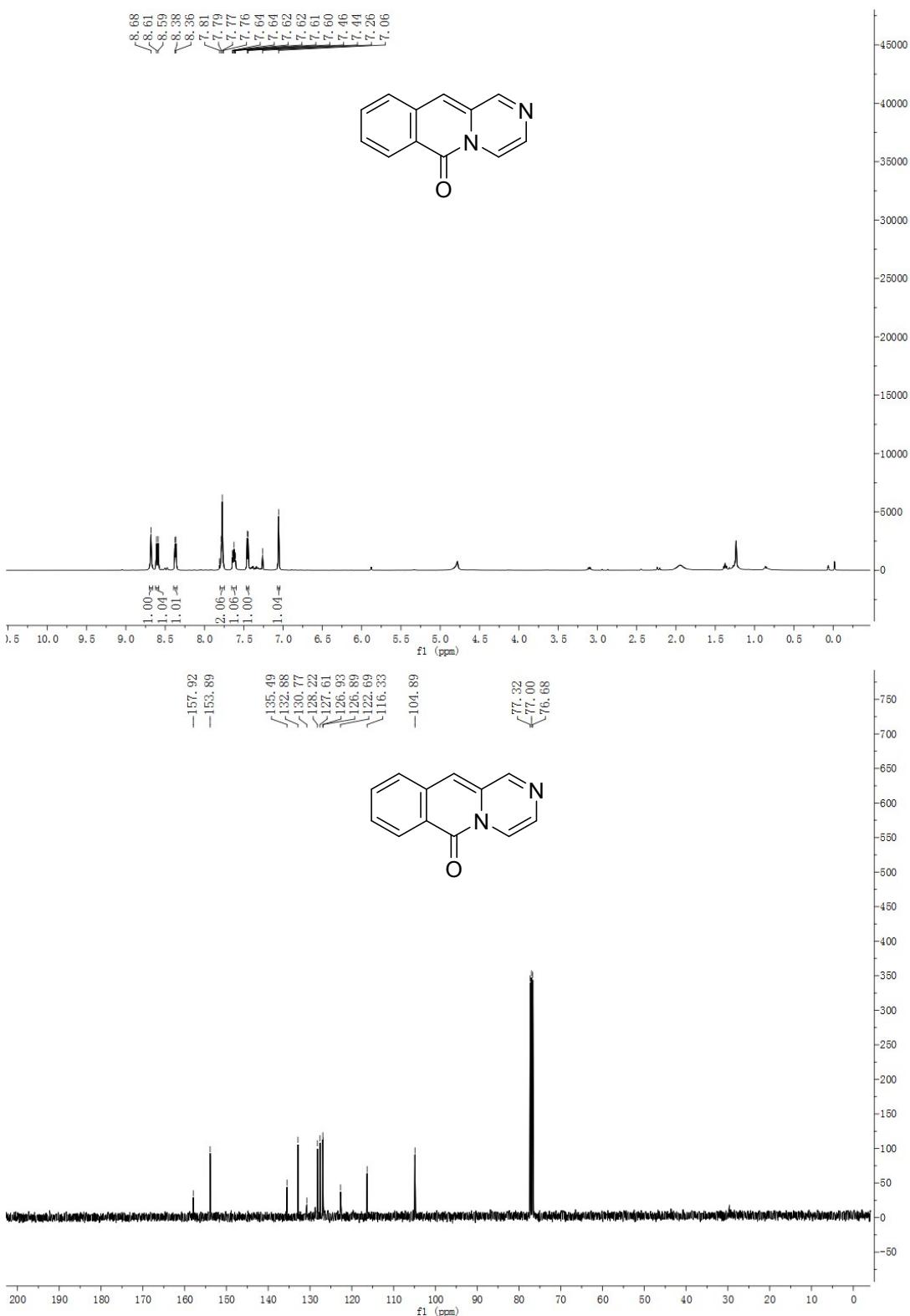
**1-methyl-6*H*-pyrido[1,2-*b*]isoquinolin-6-one (2n):**



**2-methyl-6H-pyrido[1,2-*b*]isoquinolin-6-one (2o):**



**6H-pyrazino[1,2-*b*]isoquinolin-6-one (2p):**



**11*H*-pyrido[2,1-*b*]quinazolin-11-one (2q):**

