

## Supporting Information

### Use of Unprotected Amino Acids in Metal-Free Tandem Radical Cyclization Reactions: Divergent Synthesis of 6-Alkyl/Acyl

#### Phenanthridines

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## 1. General Considerations

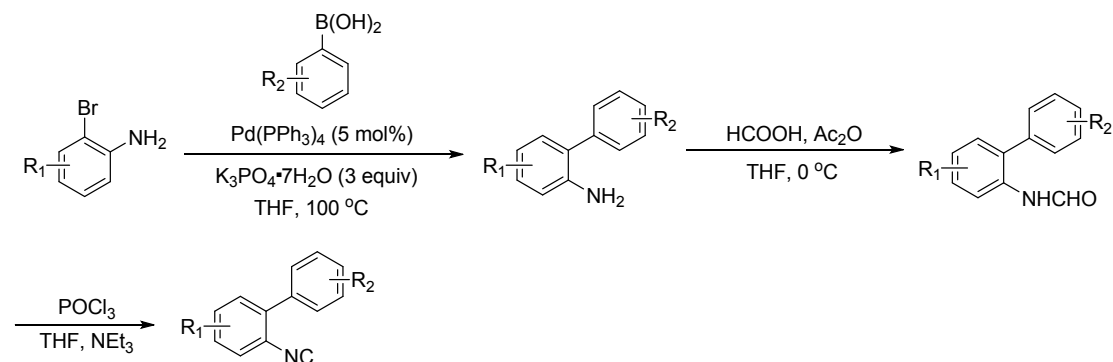
Analytical and preparative thin layer chromatography (TLC) plates were purchased from Yantai Jiangyou Silica Gel Development Co., Ltd. The silica gel (200-300 mesh) for column chromatography was purchased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd. The liquid chromatograph-mass spectrometer (LC-MS) analysis was performed on a Thermo Finnigan LCQ Advantage mass spectrometer equipped with an Agilent HPLC system and an eluent splitter (5% eluent was split into the MS system). High-resolution MS (HR MS) was analyzed by a TOF analyzer. The ion source was electrospray ionization (ESI). Both proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C-NMR}$ ) spectra were recorded on Bruker 400 MHz spectrometer, using  $\text{CDCl}_3$  or  $\text{CD}_3\text{OD}$  as the solvents with tetramethylsilane (TMS) as the internal standard at 25 °C.  $\text{K}_2\text{CO}_3$  (99.997%) and  $\text{K}_2\text{S}_2\text{O}_8$  (99.99%) were purchased from Alfa Aesar. Other chemicals were purchased as reagent grade and used without further purification. All reactions were performed under an Ar atmosphere in a 25 mL sealed tube unless otherwise noted.

Abbreviations in this paper: DMF: *N,N*-Dimethylformamide; DMSO: Dimethyl sulfoxide; DCE: 1,2-Dichloroethane; Ar: Argon; TEMPO: 2,2,6,6-Tetramethylpiperidine 1-oxyl; BHT: 2,6-di-*tert*-butyl-*p*-cresol

## 2. Experimental procedures

### (1) General procedure for synthesis of 2-isocyanobiphenyls:

2-Isocyanobiphenyls were prepared according to the reported method.<sup>1</sup>



**Scheme 1** General procedure for synthesis of 2-isocyanobiphenyls

### (2) General procedure for synthesis of 6-alkyl/acyl phenanthridines:

General procedure: A 25 mL oven-dried sealed tube was charged with 2-isocyanobiphenyls (**1**, 0.20 mmol, 1.0 equiv), amine acids (**2**, 0.40 mmol, 2.0 equiv), K<sub>2</sub>CO<sub>3</sub> (55 mg, 0.40 mmol, 2.0 equiv) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (216 mg, 0.80 mmol, 4.0 equiv) in CH<sub>3</sub>CN/H<sub>2</sub>O (6.0 mL, v/v = 5:1). The tube was sealed and heated at 100 °C for 1 h under an Ar atmosphere. After completion of the reaction, the reaction mixture was added water (5 mL), and then extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) to afford **3**.

### (3) Experimental procedure for synthesis of 1,3-dimethyl-3-neopentylindolin- 2-one (**3y**):

Following procedure for synthesis of 6-alkyl/aryl phenanthridines, **3y** was obtained by employing *N*-methyl-*N*-(*p*-tolyl)methacrylamide as the substrate instead of 2-isocyanobiphenyl **1a** in 38% yield.

### (4) Experimental procedure for mechanistic studies with TEMPO:

To a mixture of 2-isocyanobiphenyl **1a** (0.20 mmol), L-tert-Leucine **2a** (0.40 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.40 mmol), TEMPO (0.40 mmol) in CH<sub>3</sub>CN/H<sub>2</sub>O (6.0 mL, v/v = 5:1) was added K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.80 mmol). The reaction was allowed to stir at 100 °C for 1 h under an Ar atmosphere. After completion of the reaction, no desired product was detected by LC-MS.

**(5) Experimental procedure for mechanistic studies with BHT:**

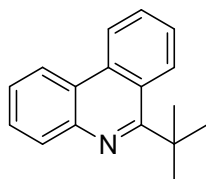
The experimental procedure is the same as above (4), and no desired product was detected by LC-MS.

**(6) Experimental procedure for synthesis of 6-isopropylphenanthridine with isobutyraldehyde as a radical precursor:**

Following the procedure for synthesis of general procedure for synthesis of 6-alkyl/acyl phenanthridines, **3n** was obtained in 35% yield.

### 3. Spectroscopic data

#### 6-(*tert*-butyl)phenanthridine (**3a**)<sup>2</sup>



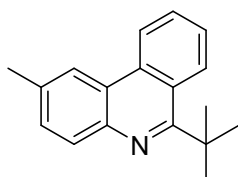
Colorless oil, 78% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.75-7.83 (m, 1H), 7.57-7.73 (m, 3H), 1.74 (s, 9H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.8, 143.1, 134.2, 130.4, 129.4, 128.5, 128.4, 126.6, 126.1, 124.5, 123.6, 123.1, 121.7, 40.3, 31.3.

HRMS (ESI-TOF) calcd for C<sub>17</sub>H<sub>18</sub>N [M + H]<sup>+</sup> (236.1434), found 236.1430.

#### 6-(*tert*-butyl)-2-methylphenanthridine (**3b**)<sup>3</sup>



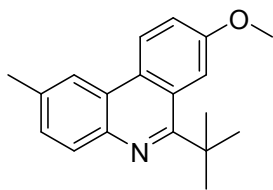
Colorless oil, 72% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.31 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.74-7.78 (m, 1H), 7.61-7.65 (m, 1H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.62 (s, 3H), 1.73 (s, 9H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.7, 141.3, 136.2, 133.9, 130.12, 130.08, 129.1, 128.3, 125.8, 124.5, 123.3, 123.0, 121.3, 40.1, 31.3, 22.1.

HRMS (ESI-TOF) calcd for C<sub>18</sub>H<sub>20</sub>N [M + H]<sup>+</sup> (250.1590), found 250.1593.

#### 6-(*tert*-butyl)-8-methoxy-2-methylphenanthridine (**3c**)<sup>3</sup>



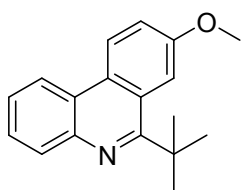
Colorless oil, 68% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (d,  $J = 8.8$  Hz, 1H), 8.22 (s, 1H), 7.98 (d,  $J = 6.0$  Hz, 1H), 7.97 (s, 1H), 7.46 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.41 (dd,  $J = 8.8, 2.4$  Hz, 1H), 3.99 (s, 3H), 2.60 (s, 3H), 1.73 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 157.2, 140.6, 136.3, 130.0, 129.2, 128.1, 125.6, 124.5, 123.4, 120.8, 119.0, 109.7, 55.5, 40.0, 31.1, 22.1.

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}$   $[\text{M} + \text{H}]^+$  (280.1696), found 280.1695.

### 6-(*tert*-butyl)-8-methoxyphenanthridine (3d)<sup>4</sup>



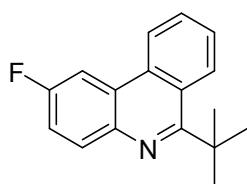
Colorless oil, 81% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (d,  $J = 9.2$  Hz, 1H), 8.44 (dd,  $J = 8.0, 1.2$  Hz, 1H), 8.09 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.99 (d,  $J = 2.4$  Hz, 1H), 7.56-7.64 (m, 2H), 7.44 (dd,  $J = 8.0, 1.2$  Hz, 1H), 4.00 (s, 3H), 1.74 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 157.4, 142.3, 130.3, 128.3, 127.5, 126.6, 125.6, 124.5, 123.6, 121.2, 119.2, 109.8, 55.6, 40.1, 31.1.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}$   $[\text{M} + \text{H}]^+$  (266.1539), found 266.1540.

### 6-(*tert*-butyl)-2-fluorophenanthridine (3e)<sup>5</sup>



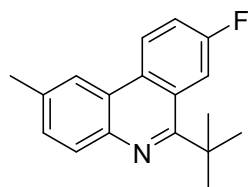
Colorless oil, 70% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (d,  $J = 8.4$  Hz, 1H), 8.54 (d,  $J = 8.0$  Hz, 1H), 8.09-8.13 (m, 2H), 7.77-7.81 (m, 1H), 7.66-7.70 (m, 1H), 7.40-7.45 (m, 1H), 1.73 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9 (d,  $J = 2.5$  Hz), 161.2 (d,  $J = 244.0$  Hz), 139.9, 133.5 (d,  $J = 4.1$  Hz), 132.5 (d,  $J = 9.1$  Hz), 129.4, 128.4, 126.6, 124.7 (d,  $J = 9.1$  Hz), 124.4, 123.2, 117.2 (d,  $J = 24.0$  Hz), 106.6 (d,  $J = 23.1$  Hz), 40.2, 31.2.

HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{17}\text{FN}$   $[\text{M} + \text{H}]^+$  (254.1340), found 254.1343.

### 6-(*tert*-butyl)-8-fluoro-2-methylphenanthridine (3f)



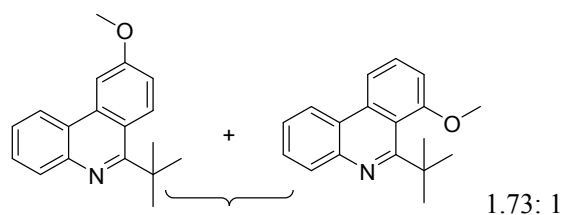
Colorless oil, 65% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64-8.67 (m, 1H), 8.20-8.24 (m, 2H), 8.00 (d,  $J = 8.0$  Hz, 1H), 7.50-7.54 (m, 2H), 2.61 (s, 3H), 1.70 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8 (d,  $J = 3.8$  Hz), 160.2 (d,  $J = 244.1$  Hz), 141.0, 136.7, 130.5, 130.2, 130.0, 125.5 (d,  $J = 7.6$  Hz), 125.5 (d,  $J = 8.6$  Hz), 122.9, 121.1, 118.2 (d,  $J = 23.6$  Hz), 113.1 (d,  $J = 22.1$  Hz), 40.1, 31.1, 22.1.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{19}\text{FN}$   $[\text{M} + \text{H}]^+$  (268.1496), found 268.1498.

### 6-(*tert*-butyl)-9-methoxyphenanthridine (3g) and 6-(*tert*-butyl)-7-methoxyphenanthridine (3h)



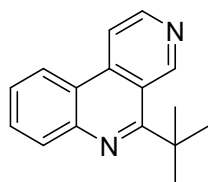
Colorless oil, 62% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J = 9.2$  Hz, 1H), 8.45 (d,  $J = 8.4$  Hz, 2H), 8.26 (d,  $J = 8.0$  Hz, 1H), 8.09 (dd,  $J = 8.4, 1.2$  Hz, 1H), 8.04 (dd,  $J = 8.4, 1.2$  Hz, 1H), 8.00 (d,  $J = 2.4$  Hz, 1H), 7.64-7.72 (m, 3H), 7.53-7.60 (m, 2H), 7.24 (dd,  $J = 8.0, 2.8$  Hz, 1H), 7.10 (d,  $J = 7.6$  Hz, 1H), 4.04 (s, 3H), 4.02 (s, 3H), 1.71 (s, 9H), 1.62 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.45, 166.42, 159.9, 156.9, 143.4, 142.5, 136.38, 136.35, 130.4, 130.1, 129.9, 129.7, 128.54, 128.49, 126.2, 126.1, 123.4, 122.7, 122.2, 121.7, 119.3, 117.1, 115.9, 115.0, 108.4, 103.7, 55.5, 54.6, 42.2, 40.1, 31.3, 31.0.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}$   $[\text{M} + \text{H}]^+$  (266.1539), found 266.1541.

### 5-(*tert*-butyl)benzo[*c*][2,7]naphthyridine (3i)



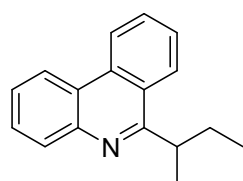
Colorless oil, 47% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.03 (s, 1H), 8.86 (d,  $J = 5.2$  Hz, 1H), 8.50 (d,  $J = 8.0$  Hz, 1H), 8.44 (d,  $J = 5.2$  Hz, 1H), 8.16 (d,  $J = 8.0$  Hz, 1H), 7.79-7.84 (m, 1H), 7.65-7.69 (m, 1H), 1.75 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 151.4, 146.9, 144.3, 139.3, 130.8, 130.6, 127.2, 122.2, 121.4, 119.7, 116.4, 40.3, 31.4.

HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_2$   $[\text{M} + \text{H}]^+$  (237.1386), found 237.1383.

### 6-(*sec*-butyl)phenanthridine (3j)



Colorless oil, 64% yield.

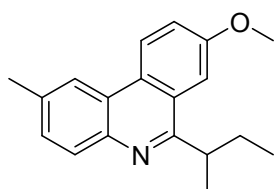


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (d,  $J = 8.0$  Hz, 1H), 8.55 (dd,  $J = 8.0, 1.2$  Hz, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 8.16 (d,  $J = 8.0$  Hz, 1H), 7.80-7.84 (m, 1H), 7.67-7.73 (m, 2H), 7.60-7.64 (m, 1H), 3.73-3.82 (m, 1H), 2.13-2.24 (m, 1H), 1.78-1.88 (m, 1H), 1.50 (d,  $J = 6.8$  Hz, 3H), 1.00 (t,  $J = 7.2$  Hz, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 143.9, 133.1, 130.02, 129.98, 128.4, 127.2, 126.2, 125.7, 125.3, 123.4, 122.6, 121.9, 38.4, 29.2, 19.9, 12.5.

HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{18}\text{N}$   $[\text{M} + \text{H}]^+$  (236.1434), found 236.1430.

### 6-(*sec*-butyl)-8-methoxy-2-methylphenanthridine (3k)



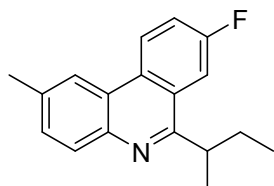
Colorless oil, 73% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J = 8.8$  Hz, 1H), 8.24 (s, 1H), 8.00 (d,  $J = 8.0$  Hz, 1H), 7.63 (d,  $J = 2.4$  Hz, 1H), 7.47 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.44 (dd,  $J = 8.8, 2.4$  Hz, 1H), 4.00 (s, 3H), 3.61-3.69 (m, 1H), 2.60 (s, 3H), 2.11-2.21 (m, 1H), 1.75-1.87 (m, 1H), 1.48 (d,  $J = 6.8$  Hz, 3H), 0.98 (t,  $J = 7.2$  Hz, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 158.5, 141.4, 136.0, 129.7, 129.2, 127.2, 126.7, 124.2, 123.3, 121.0, 119.8, 106.4, 55.6, 38.5, 29.1, 22.0, 19.7, 12.6.

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{22}\text{NO}$   $[\text{M} + \text{H}]^+$  (280.1696), found 280.1695.

### 6-(*sec*-butyl)-8-fluoro-2-methylphenanthridine (3l)



Colorless oil, 66% yield.

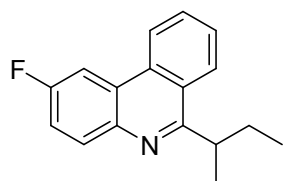
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61-8.64 (m, 1H), 8.26 (s, 1H), 8.03 (d,  $J = 8.0$  Hz,

1H), 7.90 (dd,  $J = 10.4, 2.8$  Hz, 1H), 7.51-7.56 (m, 2H), 3.55-3.64 (m, 1H), 2.61 (s, 3H), 2.09-2.19 (m, 1H), 1.75-1.85 (m, 1H), 1.47 (d,  $J = 6.8$  Hz, 3H), 0.97 (t,  $J = 7.2$  Hz, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6 (d,  $J = 3.8$  Hz), 161.5 (d,  $J = 245.3$  Hz), 141.9, 136.4, 130.0, 129.9, 129.5, 126.7 (d,  $J = 7.3$  Hz), 125.1 (d,  $J = 8.4$  Hz), 122.7, 121.3, 118.9 (d,  $J = 23.6$  Hz), 110.3 (d,  $J = 21.4$  Hz), 38.5, 29.1, 22.0, 19.7, 12.5.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{19}\text{FN}$   $[\text{M} + \text{H}]^+$  (268.1496), found 268.1494.

### 6-(*sec*-butyl)-2-fluorophenanthridine (3m)



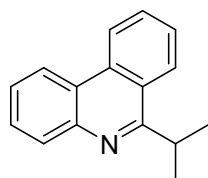
Colorless oil, 62% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J = 8.2$  Hz, 1H), 8.31 (d,  $J = 8.2$  Hz, 1H), 8.16 – 8.08 (m, 2H), 7.80 (ddd,  $J = 8.2, 7.0, 1.3$  Hz, 1H), 7.70 (ddd,  $J = 8.3, 7.0, 1.3$  Hz, 1H), 7.45 – 7.39 (m, 1H), 3.73 (q,  $J = 6.8$  Hz, 1H), 2.19-2.08 (m, 1H), 1.86 – 1.73 (m, 1H), 1.46 (d,  $J = 6.8$  Hz, 3H), 0.97 (t,  $J = 7.4$  Hz, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7 (d,  $J = 2.8$  Hz), 161.0 (d,  $J = 244$  Hz), 140.8, 132.5 (d,  $J = 3.9$  Hz), 132.1 (d,  $J = 8.8$  Hz), 130.3, 127.8, 125.8, 125.3, 124.6 (d,  $J = 9.0$  Hz), 122.8, 117.2 (d,  $J = 23.9$  Hz), 106.8 (d,  $J = 22.7$  Hz), 38.3, 29.2, 19.8, 12.5.

HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{17}\text{FN}$   $[\text{M} + \text{H}]^+$  (254.1340), found 254.1342.

### 6-isopropylphenanthridine (3n)<sup>6</sup>



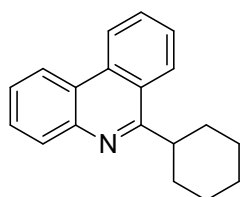
Colorless oil, 58% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (d,  $J = 8.4$  Hz, 1H), 8.53 (dd,  $J = 8.0, 1.2$  Hz, 1H), 8.32 (d,  $J = 8.4$  Hz, 1H), 8.14 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.79-7.83 (m, 1H), 7.66-7.72 (m, 2H), 7.58-7.62 (m, 1H), 3.95-4.05 (m, 1H), 1.52 (d,  $J = 6.8$  Hz, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 143.8, 133.0, 129.94, 129.92, 128.4, 127.1, 126.2, 125.7, 124.7, 123.4, 122.6, 121.8, 31.5, 22.0.

HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{16}\text{N}$  [ $\text{M} + \text{H}$ ] $^+$  (222.1277), found 222.1280.

### 6-cyclohexylphenanthridine (3o)<sup>7</sup>



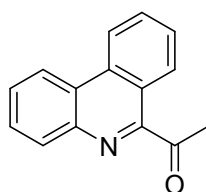
Colorless oil, 68% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (d,  $J = 8.3$  Hz, 1H), 8.52 (d,  $J = 8.2$  Hz, 1H), 8.31 (d,  $J = 8.3$  Hz, 1H), 8.14 (d,  $J = 8.1$  Hz, 1H), 7.80 (t,  $J = 7.6$  Hz, 1H), 7.72 – 7.65 (m, 2H), 7.62 – 7.57 (m, 1H), 3.65 – 3.57 (m, 1H), 2.12 – 2.04 (m, 2H), 2.01 – 1.80 (m, 5H), 1.63 – 1.52 (m, 2H), 1.50 – 1.40 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.59, 144.18, 133.30, 130.23, 128.69, 127.37, 126.43, 125.92, 125.02, 123.64, 122.88, 122.12, 42.30, 32.61, 27.20, 26.64.

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{20}\text{N}$  [ $\text{M} + \text{H}$ ] $^+$  (262.1590), found 262.1587.

### 1-(phenanthridin-6-yl)ethan-1-one (3p)<sup>8</sup>



Colorless oil, 60% yield.

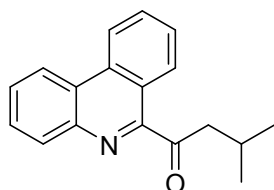
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90 (d,  $J = 8.3$  Hz, 1H), 8.67 (d,  $J = 8.3$  Hz, 1H), 8.58-8.63 (m, 1H), 8.22-8.26 (m, 1H), 7.87 (ddd,  $J = 8.3, 7.1, 1.3$  Hz, 1H), 7.71-7.80

(m, 3H), 2.96 (s, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.0, 154.0, 142.6, 133.7, 131.2, 130.9, 129.1, 129.0, 128.3, 128.0, 125.5, 123.2, 122.2, 122.2, 28.7.

HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{12}\text{NO}$   $[\text{M} + \text{H}]^+$  (222.0913), found 222.0910.

### 3-methyl-1-(phenanthridin-6-yl)butan-1-one (3q)



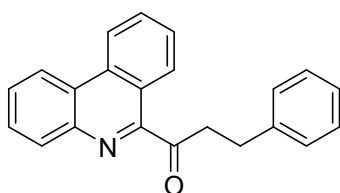
Colorless oil, 67% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68 (dd,  $J = 8.4, 0.6$  Hz, 1H), 8.60 (d,  $J = 8.3$  Hz, 1H), 8.52-8.55 (m, 1H), 8.14-8.19 (m, 1H), 7.80 (ddd,  $J = 8.3, 7.1, 1.3$  Hz, 1H), 7.62-7.74 (m, 3H), 3.22 (d,  $J = 6.9$  Hz, 2H), 2.32 (dt,  $J = 13.5, 6.7$  Hz, 1H), 1.00 (d,  $J = 6.7$  Hz, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.0, 155.1, 142.7, 133.7, 131.1, 130.9, 129.0, 128.8, 128.2, 127.8, 125.3, 123.2, 122.2, 49.4, 25.2, 23.0.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}$   $[\text{M} + \text{H}]^+$  (264.1383), found 264.1379.

### 1-(phenanthridin-6-yl)-3-phenylpropan-1-one (3r)



Colorless oil, 54% yield.

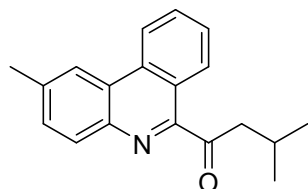
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (d,  $J = 8.4$  Hz, 1H), 8.67 (d,  $J = 8.4$  Hz, 1H), 8.61 (d,  $J = 9.0$  Hz, 1H), 8.20-8.23 (m, 1H), 7.69-7.90 (m, 4H), 7.21-7.33 (m, 5H), 3.78 (t,  $J = 7.5$  Hz, 2H), 3.18 (t,  $J = 7.5$  Hz, 2H);

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 154.1, 142.6, 141.4, 133.6, 131.1, 130.9, 129.0,

128.9, 128.62, 128.55, 128.1, 127.8, 126.1, 125.4, 123.2, 122.2, 122.1, 42.1, 30.3.

HRMS (ESI-TOF) calcd for C<sub>22</sub>H<sub>18</sub>NO [M + H]<sup>+</sup> (312.1383), found 312.1385.

### 3-methyl-1-(2-methylphenanthridin-6-yl)butan-1-one (3s)



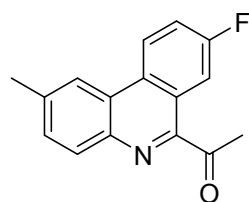
Colorless oil, 62% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (dd, *J* = 8.4, 0.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.38 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.82-7.87 (m, 1H), 7.68-7.72 (m, 1H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.29 (d, *J* = 7.2 Hz, 2H), 2.66 (s, 3H), 2.32-2.43 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.0, 154.0, 140.9, 139.0, 133.3, 130.80, 130.76, 130.6, 128.0, 127.7, 125.1, 123.3, 122.1, 121.8, 49.3, 25.2, 23.0, 22.3.

HRMS (ESI-TOF) calcd for C<sub>19</sub>H<sub>20</sub>NO [M + H]<sup>+</sup> (278.1539), found 278.1536.

### 1-(8-fluoro-2-methylphenanthridin-6-yl)ethan-1-one (3t)



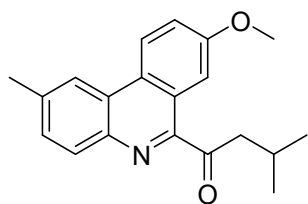
Colorless oil, 56% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (dd, *J* = 10.8, 2.8 Hz, 1H), 8.61-8.65 (m, 1H), 8.31 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.57-7.62 (m, 2H), 2.94 (s, 3H), 2.66 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.6, 162.0 (d, *J* = 246.4 Hz), 151.2 (d, *J* = 4.4 Hz), 140.6, 139.9, 131.1, 130.7, 130.1, 125.1, 124.6 (d, *J* = 9.2 Hz), 124.4 (d, *J* = 8.7 Hz), 121.6, 119.9 (d, *J* = 24.2 Hz), 112.8 (d, *J* = 23.3 Hz), 28.4, 22.4.

HRMS (ESI-TOF) calcd for C<sub>16</sub>H<sub>13</sub>FNO [M + H]<sup>+</sup> (254.0976), found 254.0977.

### 1-(8-methoxy-2-methylphenanthridin-6-yl)-3-methylbutan-1-one (3u)



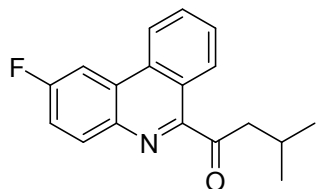
Colorless oil, 67% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (d,  $J = 9.2$  Hz, 1H), 8.36 (d,  $J = 2.4$  Hz, 1H), 8.28 (s, 1H), 8.09 (d,  $J = 8.4$  Hz, 1H), 7.54 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.47 (dd,  $J = 9.2, 2.8$  Hz, 1H), 3.99 (s, 3H), 3.32 (d,  $J = 6.8$  Hz, 2H), 2.64 (s, 3H), 2.34-2.44 (m, 1H), 1.07 (d,  $J = 6.4$  Hz, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  205.3, 159.3, 152.1, 140.2, 139.2, 130.8, 129.8, 127.9, 125.5, 124.9, 123.6, 121.9, 121.3, 107.0, 55.6, 49.1, 25.3, 23.0, 22.3.

HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_2$   $[\text{M} + \text{H}]^+$  (308.1645), found 308.1642.

### 1-(2-fluorophenanthridin-6-yl)-3-methylbutan-1-one (3v)



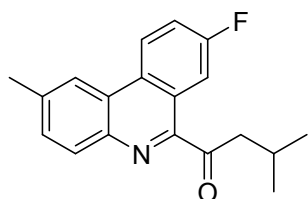
Colorless oil, 61% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.50 (d,  $J = 8.4$  Hz, 1H), 8.20-8.23 (m, 1H), 8.16 (d,  $J = 10.0$  Hz, 1H), 7.84-7.88 (m, 1H), 7.73-7.77 (m, 1H), 7.48-7.53 (m, 1H), 3.28 (d,  $J = 6.8$  Hz, 2H), 2.33-2.44 (m, 1H), 1.07 (d,  $J = 6.8$  Hz, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.6, 162.5 (d,  $J = 248.2$  Hz), 154.1 (d,  $J = 2.8$  Hz), 139.4, 133.4 (d,  $J = 9.4$  Hz), 133.0 (d,  $J = 4.3$  Hz), 130.9, 128.7, 127.9, 126.8 (d,  $J = 9.4$  Hz), 123.2, 122.3, 118.1 (d,  $J = 24.4$  Hz), 107.2 (d,  $J = 23.3$  Hz), 49.2, 25.1, 22.9.

HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{17}\text{FNO}$   $[\text{M} + \text{H}]^+$  (282.1289), found 282.1292.

### 1-(8-fluoro-2-methylphenanthridin-6-yl)-3-methylbutan-1-one (3w)



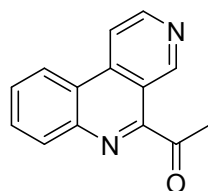
Colorless oil, 59% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (dd,  $J = 10.8, 2.8$  Hz, 2H), 8.28 (s, 1H), 8.11 (d,  $J = 8.4$  Hz, 1H), 7.55-7.60 (m, 2H), 3.30 (d,  $J = 7.2$  Hz, 2H), 2.65 (s, 3H), 2.33-2.44 (m, 1H), 1.07 (d,  $J = 6.8$  Hz, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.6, 161.9 (d,  $J = 246.5$  Hz), 152.1, 140.6, 139.7, 131.0, 130.7, 130.0, 124.9, 124.6, 124.5 (d,  $J = 8.5$  Hz), 121.5, 119.9 (d,  $J = 24.1$  Hz), 112.5 (d,  $J = 23.2$  Hz), 48.8, 25.3, 22.9, 22.3.

HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{19}\text{FNO}$  [ $\text{M} + \text{H}$ ] $^+$  (296.1445), found 296.1447.

### 1-(benzo[*c*][2,7]naphthyridin-5-yl)ethan-1-one (3x)



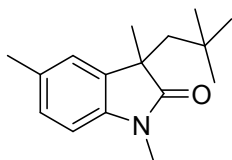
Colorless oil, 42% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.30 (s, 1H), 8.96 (d,  $J = 5.6$  Hz, 1H), 8.60 (dd,  $J = 8.4, 0.8$  Hz, 1H), 8.41 (d,  $J = 5.6$  Hz, 1H), 8.30 (dd,  $J = 8.4, 0.8$  Hz, 1H), 7.91-7.95 (m, 1H), 7.83-7.87 (m, 1H), 2.98 (s, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.8, 153.1, 152.2, 148.6, 143.8, 138.2, 131.5, 131.2, 129.7, 123.5, 122.7, 118.6, 115.2, 28.1.

HRMS (ESI-TOF) calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}$  [ $\text{M} + \text{H}$ ] $^+$  (223.0866), found 223.0863.

### 1,3,5-trimethyl-3-neopentylindolin-2-one (3y)<sup>9</sup>



Colorless oil, 38% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.05 (d,  $J = 7.9$  Hz, 1H), 7.01 (s, 1H), 6.73 (d,  $J = 7.8$  Hz, 1H), 3.20 (s, 3H), 2.34 (s, 3H), 2.14 (d,  $J = 14.4$  Hz, 1H), 1.83 (d,  $J = 14.4$  Hz, 1H), 1.58 (s, 2H), 1.28 (s, 3H), 0.61 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  181.1, 140.6, 134.4, 131.5, 127., 124.8, 107.8, 50.9, 47.5, 31.9, 30.9, 28.4, 26.4, 21.3.

HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{24}\text{NO}$   $[\text{M} + \text{H}]^+$  (246.1852), found 246.1850.

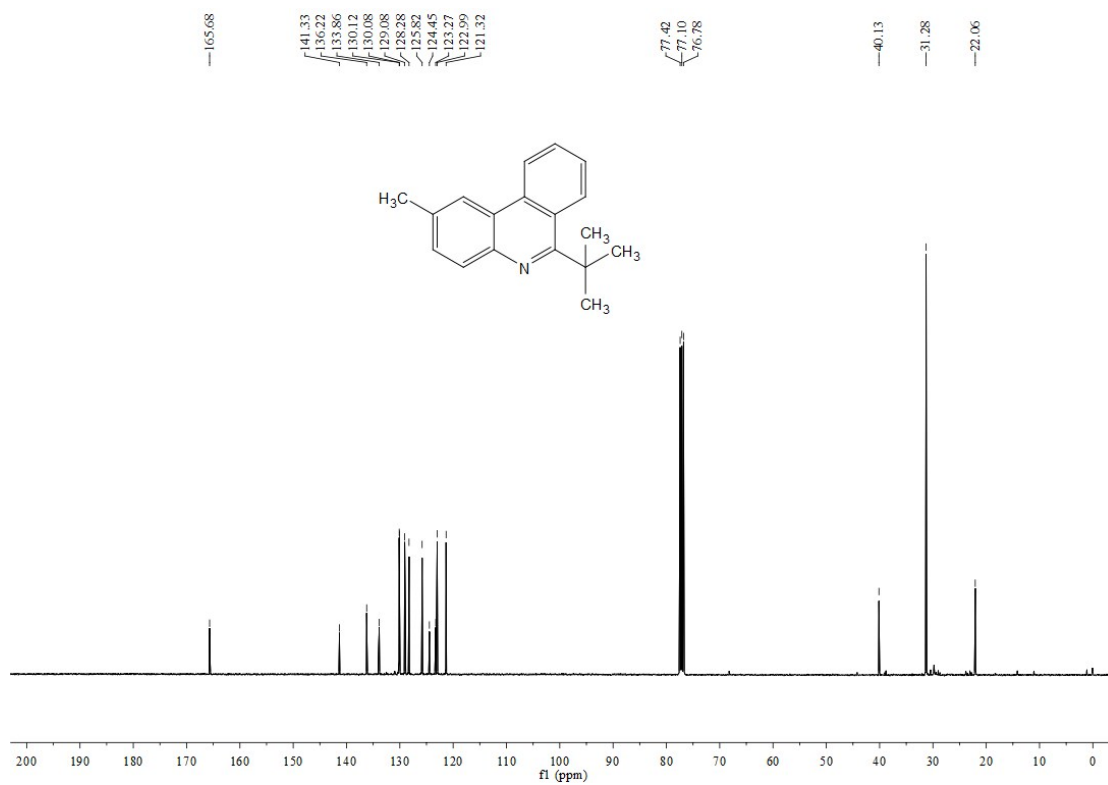
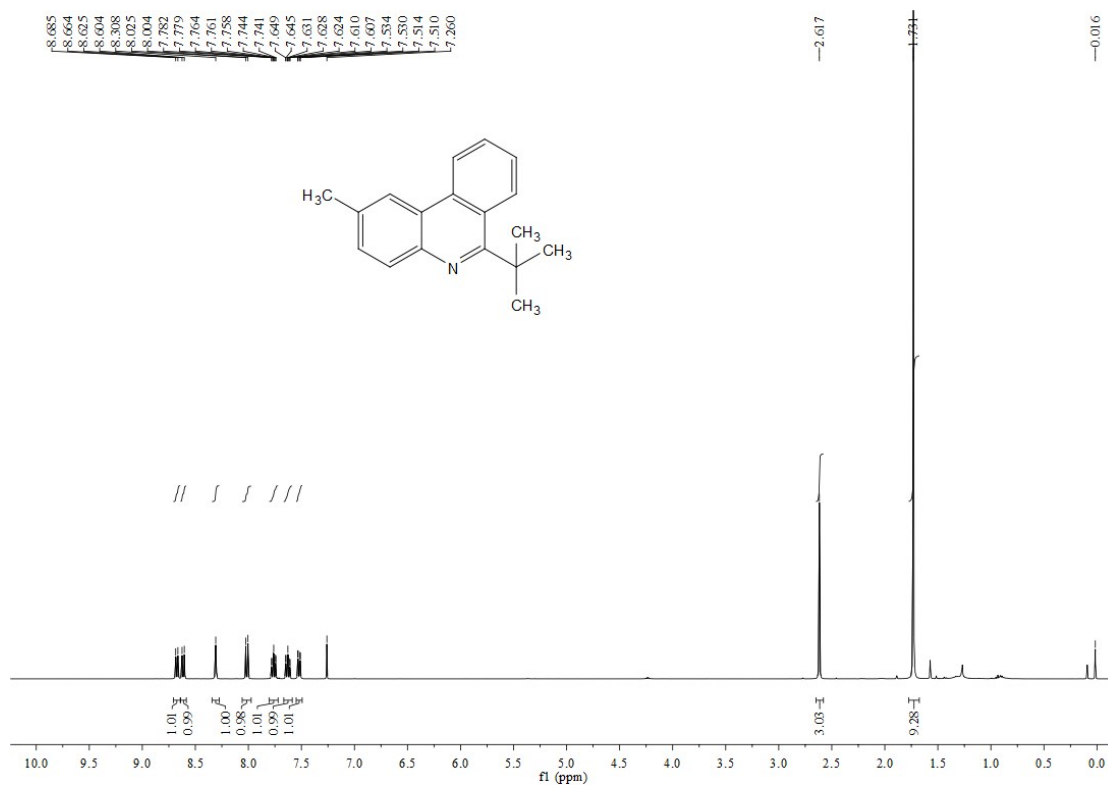


#### **4. References**

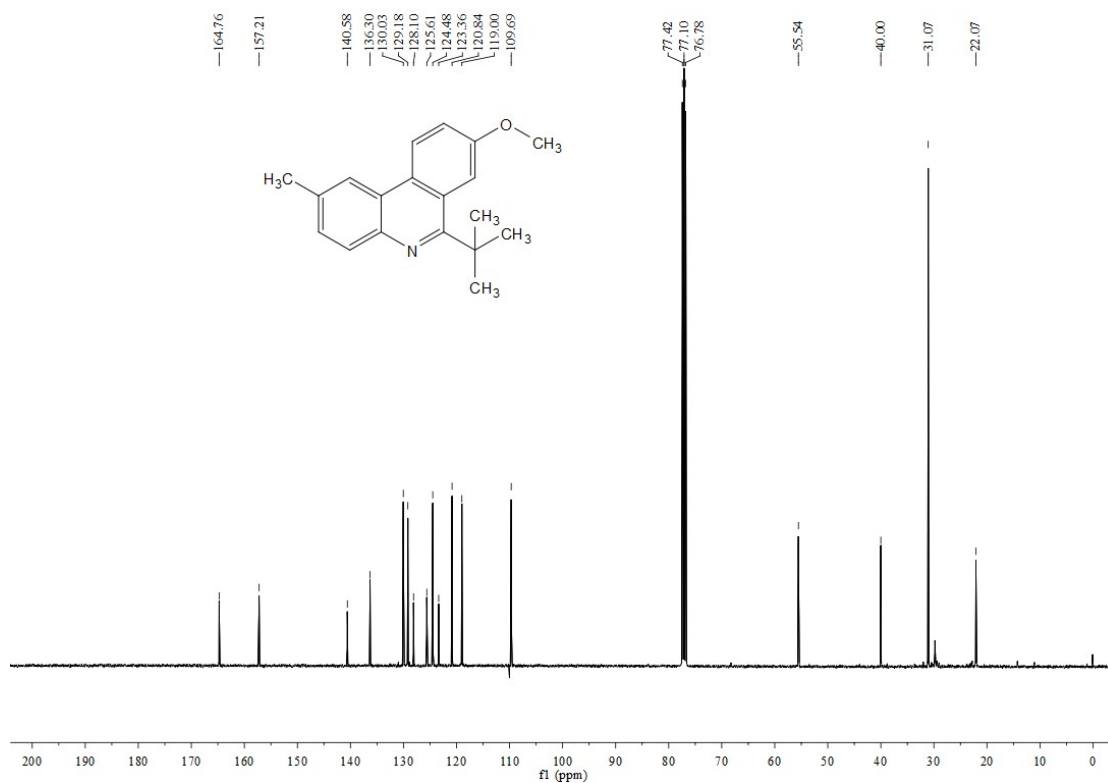
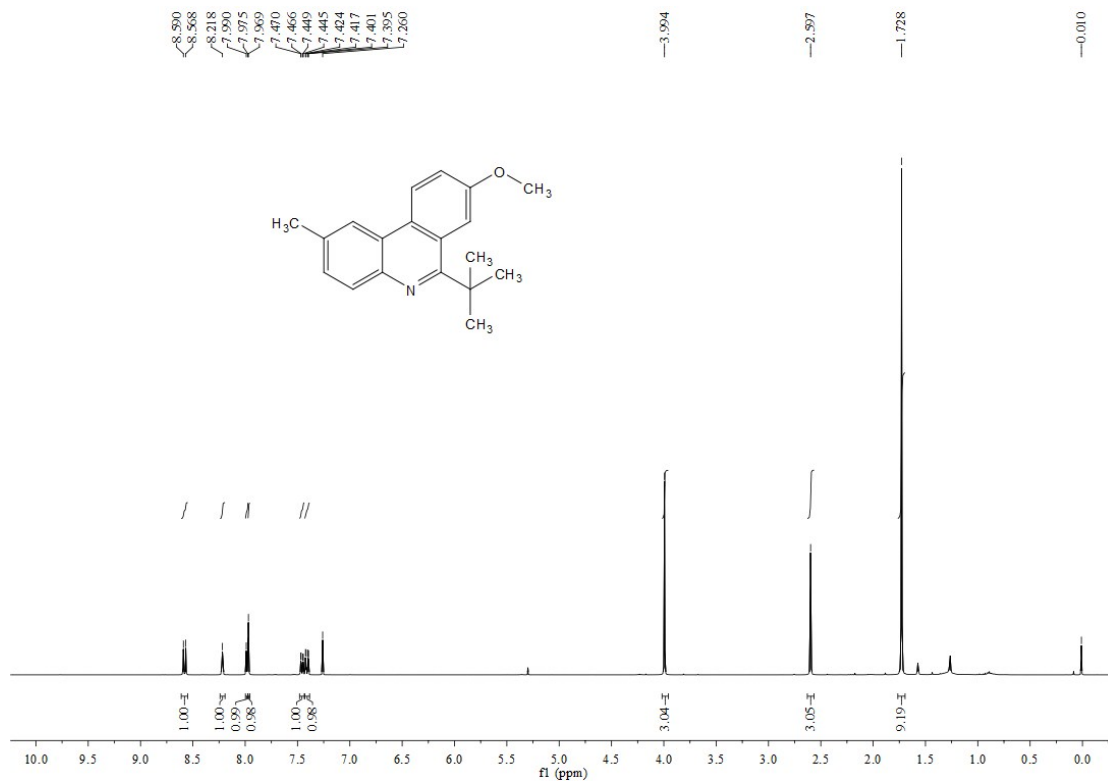
1. Wang, Q. L.; Dong, X. C.; Xiao, T. B.; Zhou, L. *Org. Lett.* **2013**, *15*, 4846.
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9. Yang, L.; Lu, W.; Zhou, W.; Zhang, F. *Green Chem.* **2016**, *18*, 2941.



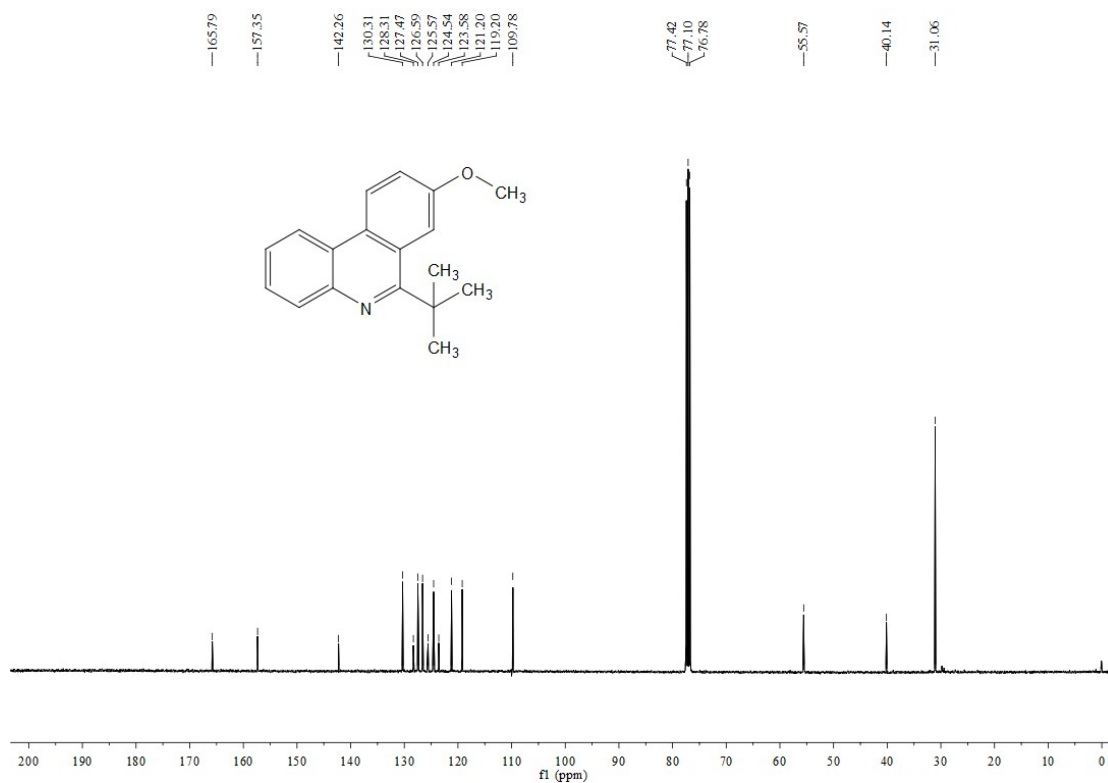
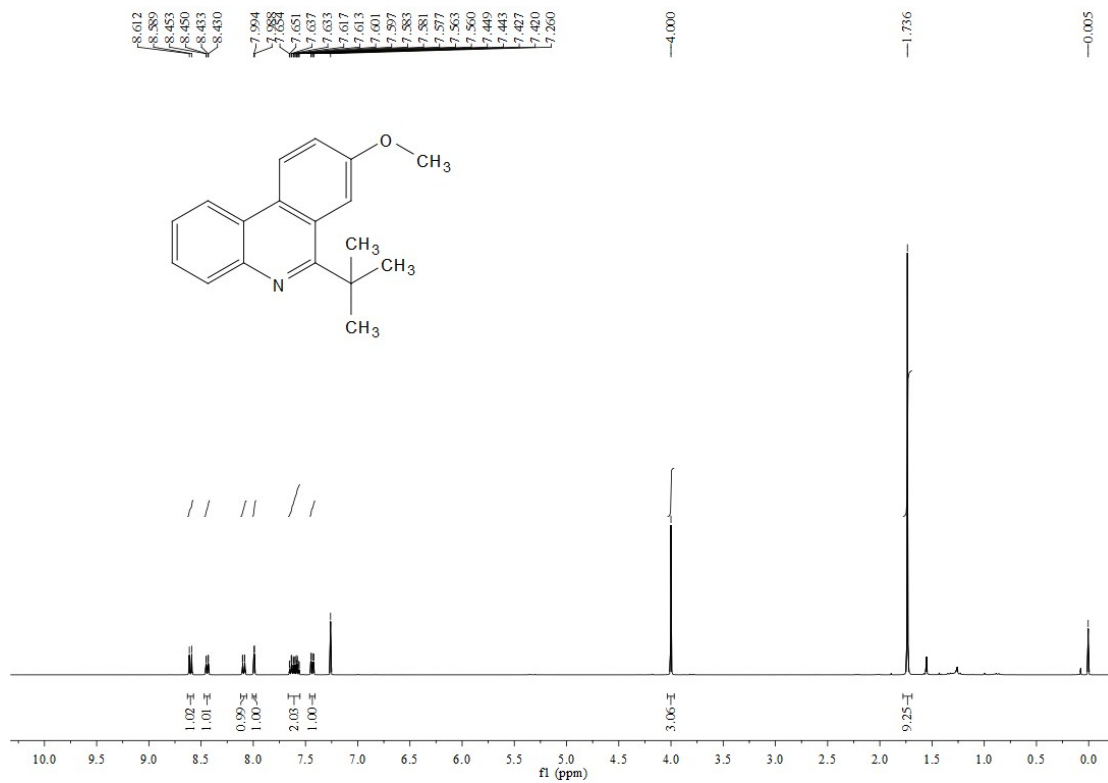
# 6-(*tert*-butyl)-2-methylphenanthridine (3b)



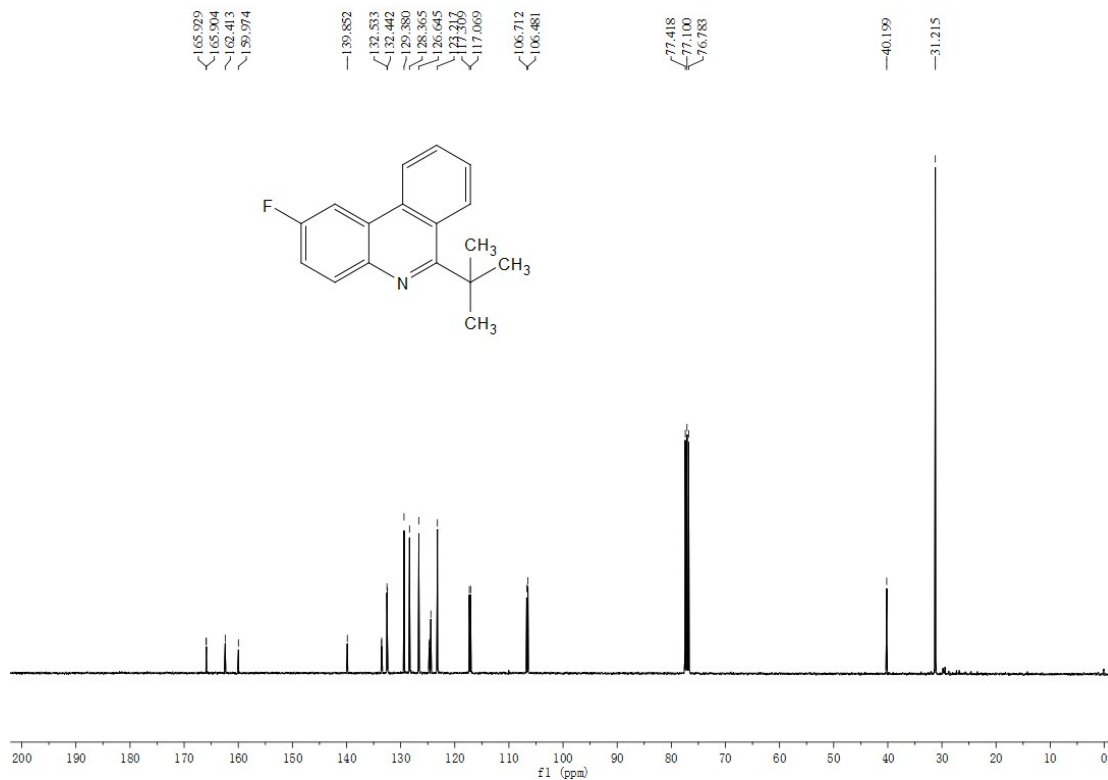
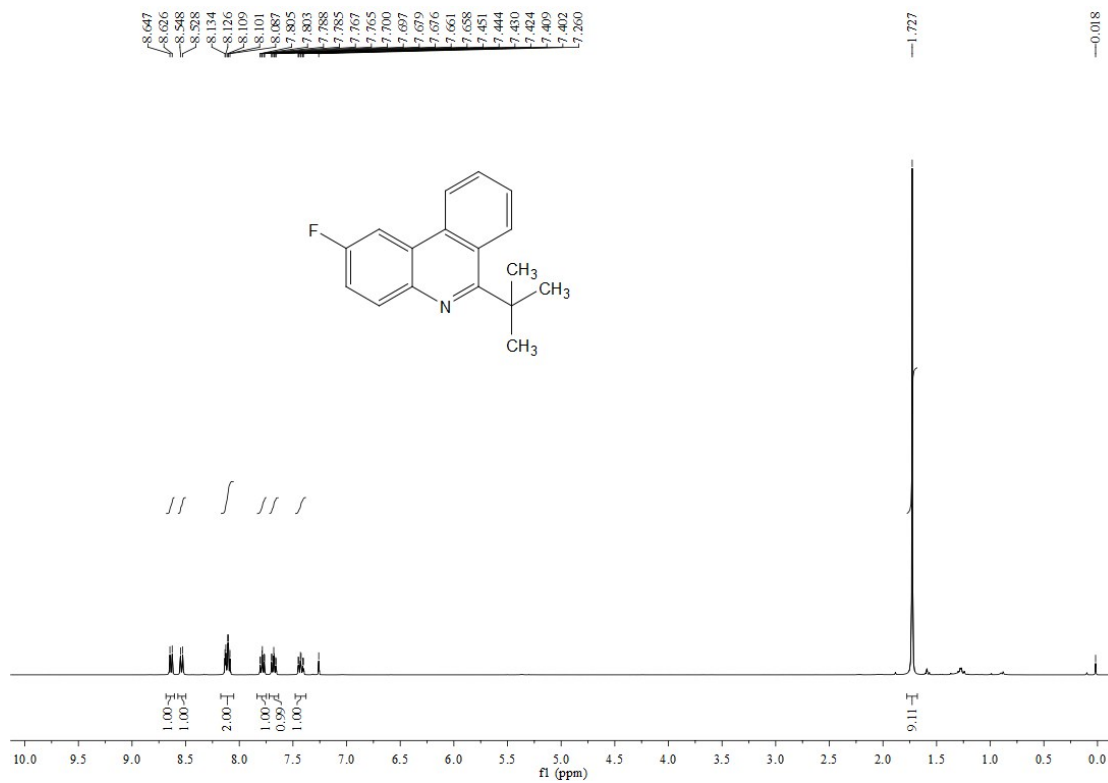
# 6-(*tert*-butyl)-8-methoxy-2-methylphenanthridine (3c)



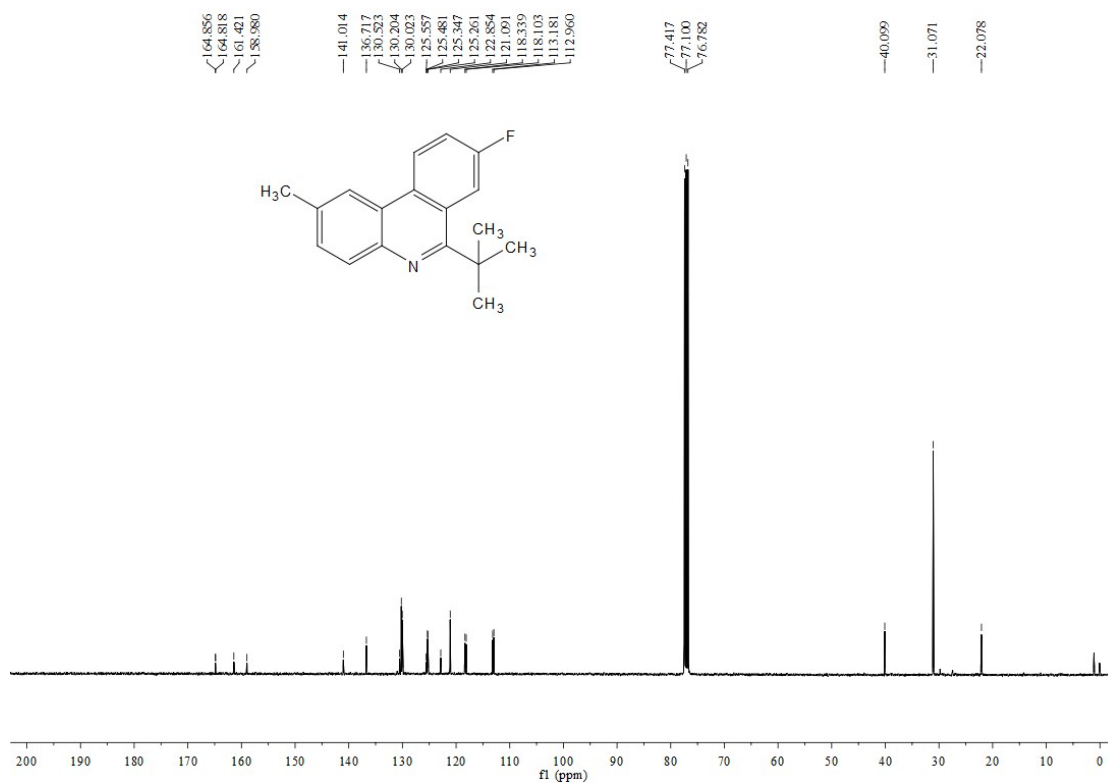
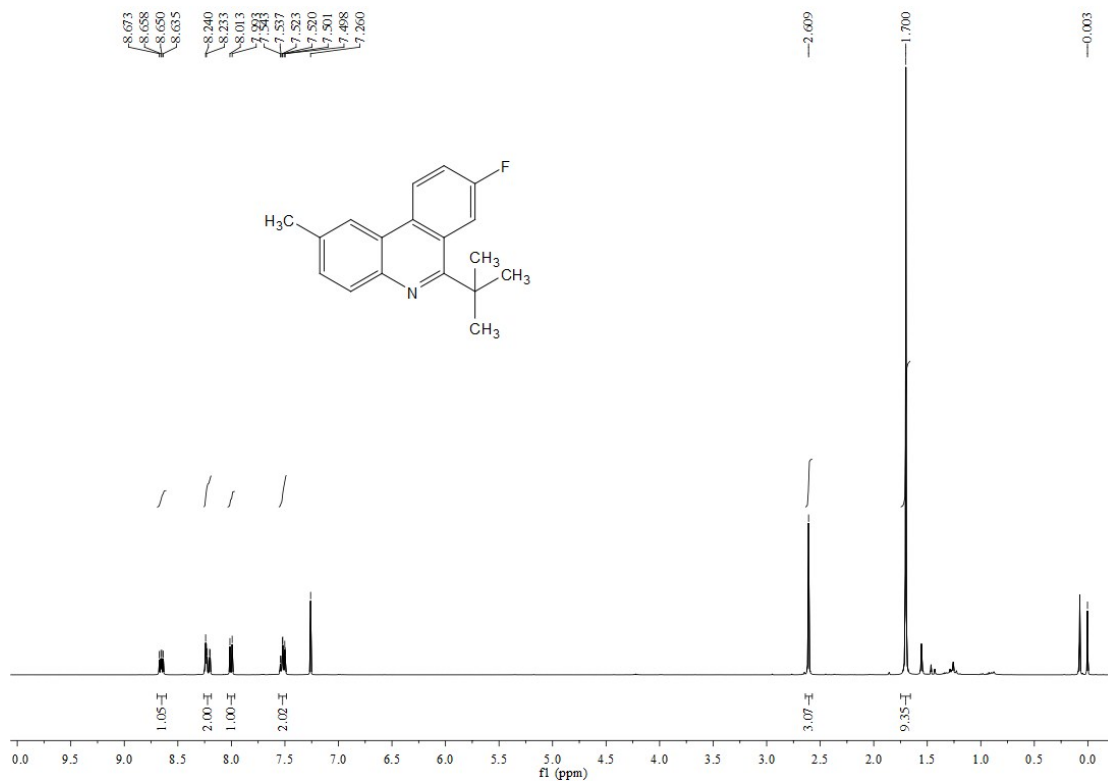
# 6-(*tert*-butyl)-8-methoxyphenanthridine (3d)



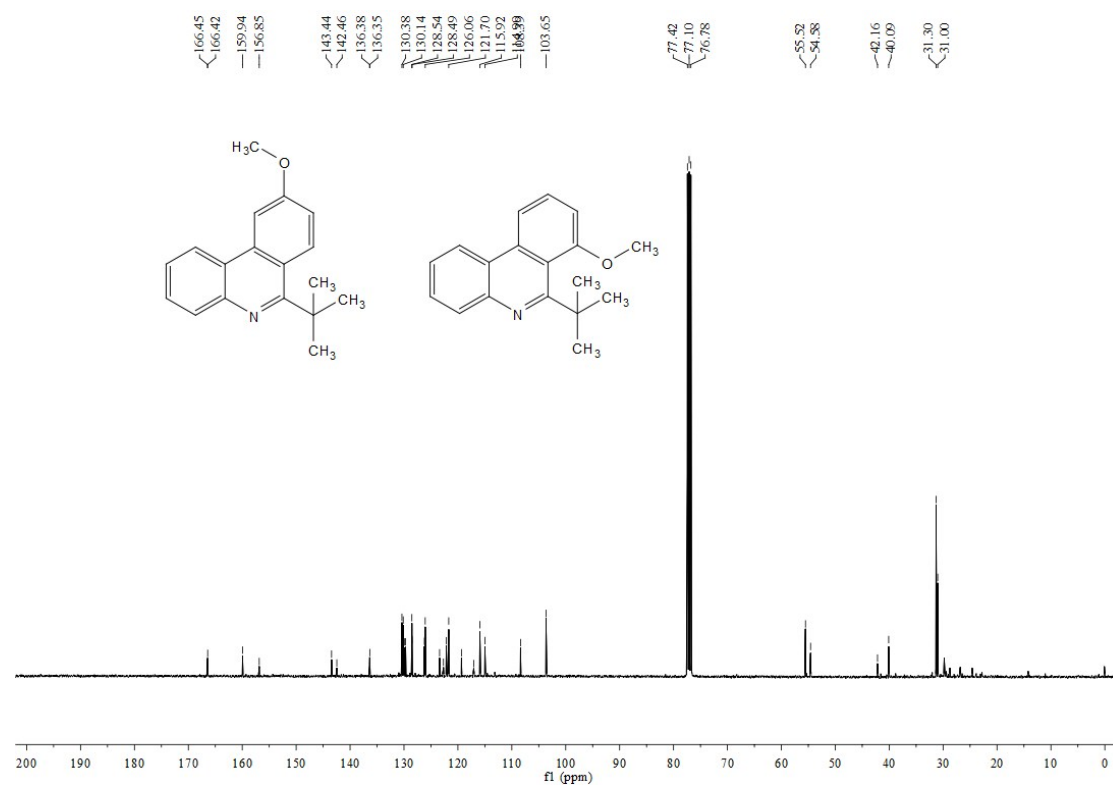
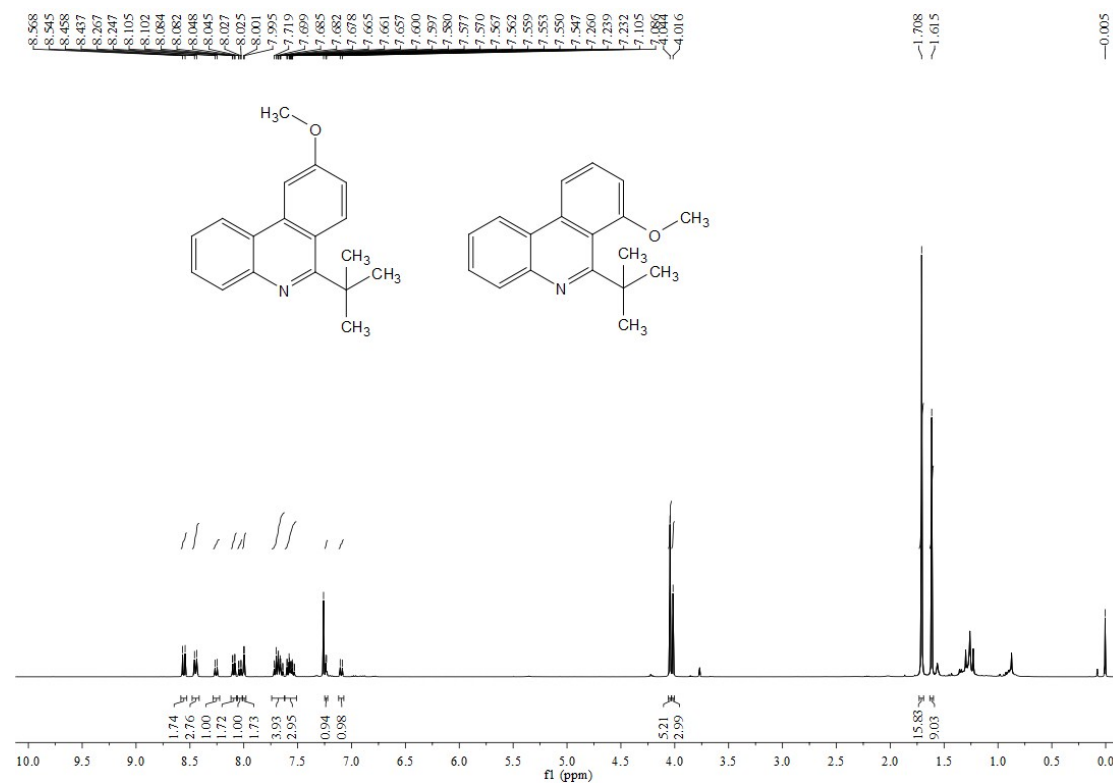
# 6-(*tert*-butyl)-2-fluorophenanthridine (3e)



# 6-(*tert*-butyl)-8-fluoro-2-methylphenanthridine (3f)

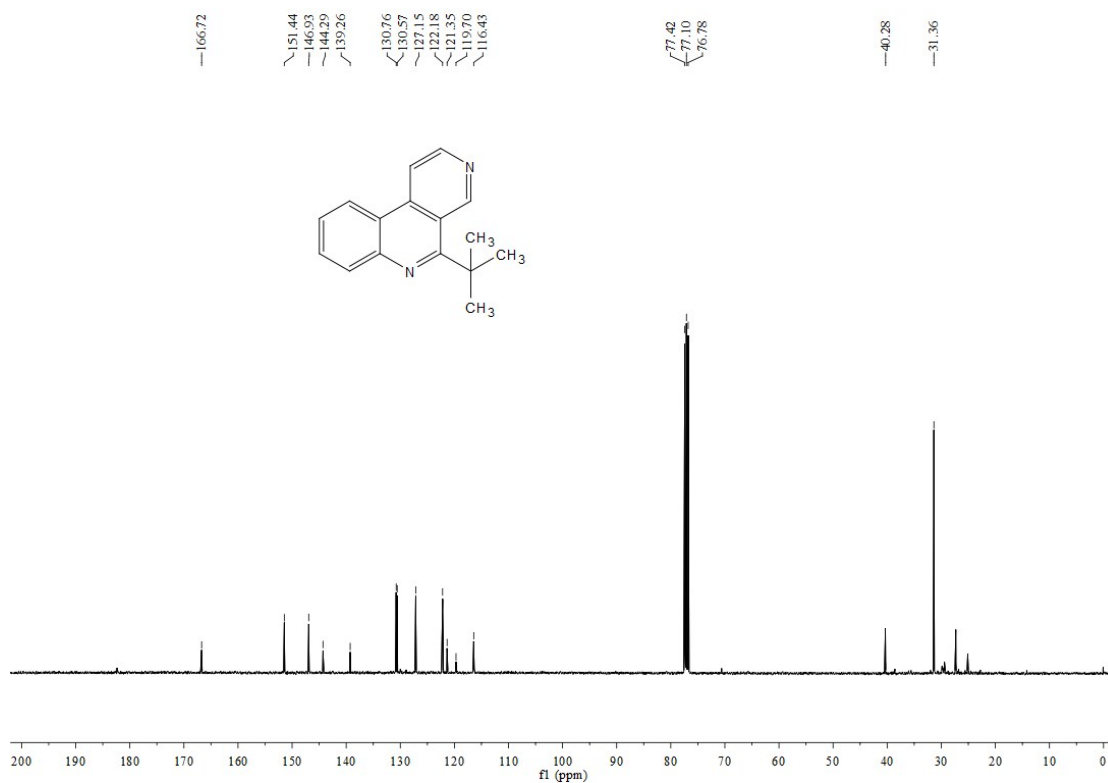
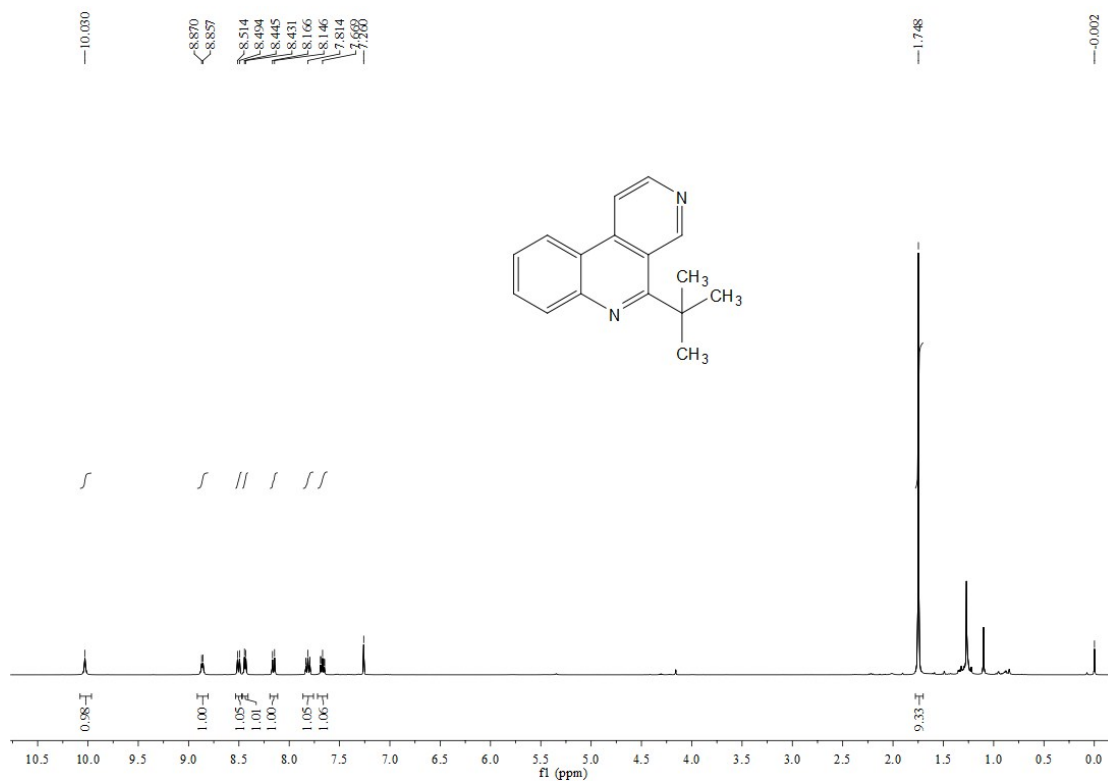


**6-(*tert*-butyl)-9-methoxyphenanthridine (3g) and 6-(*tert*-butyl)-7-methoxyphenanthridine (3h)**

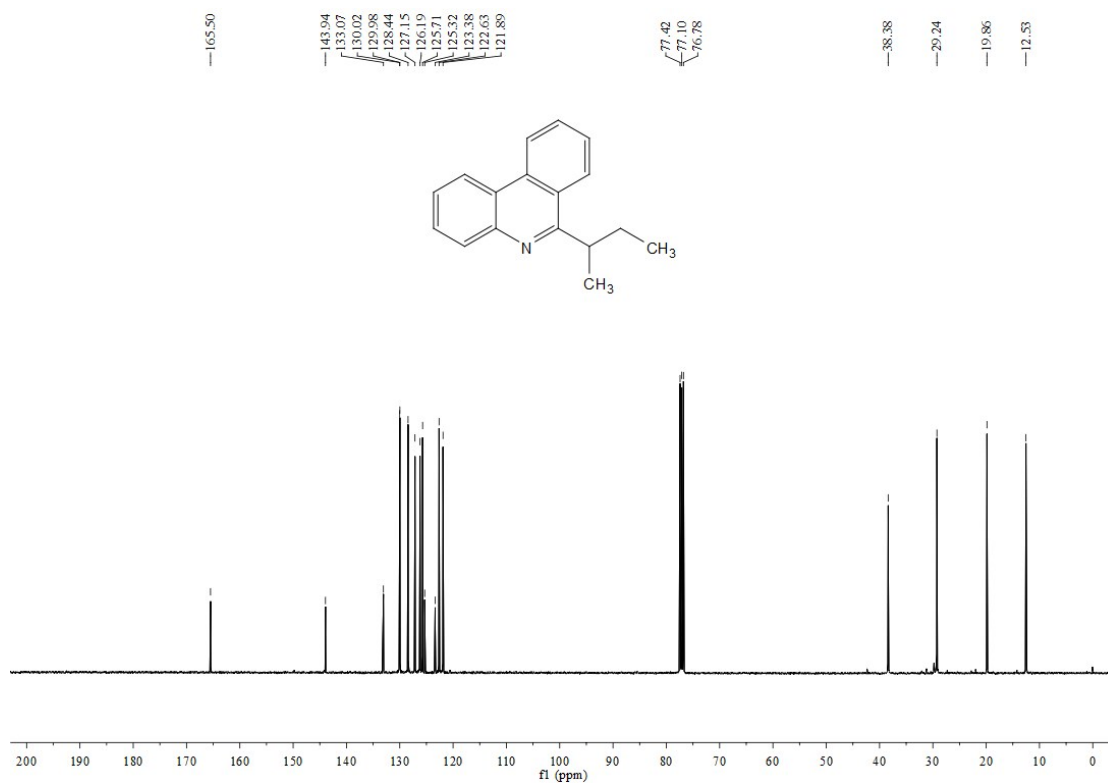
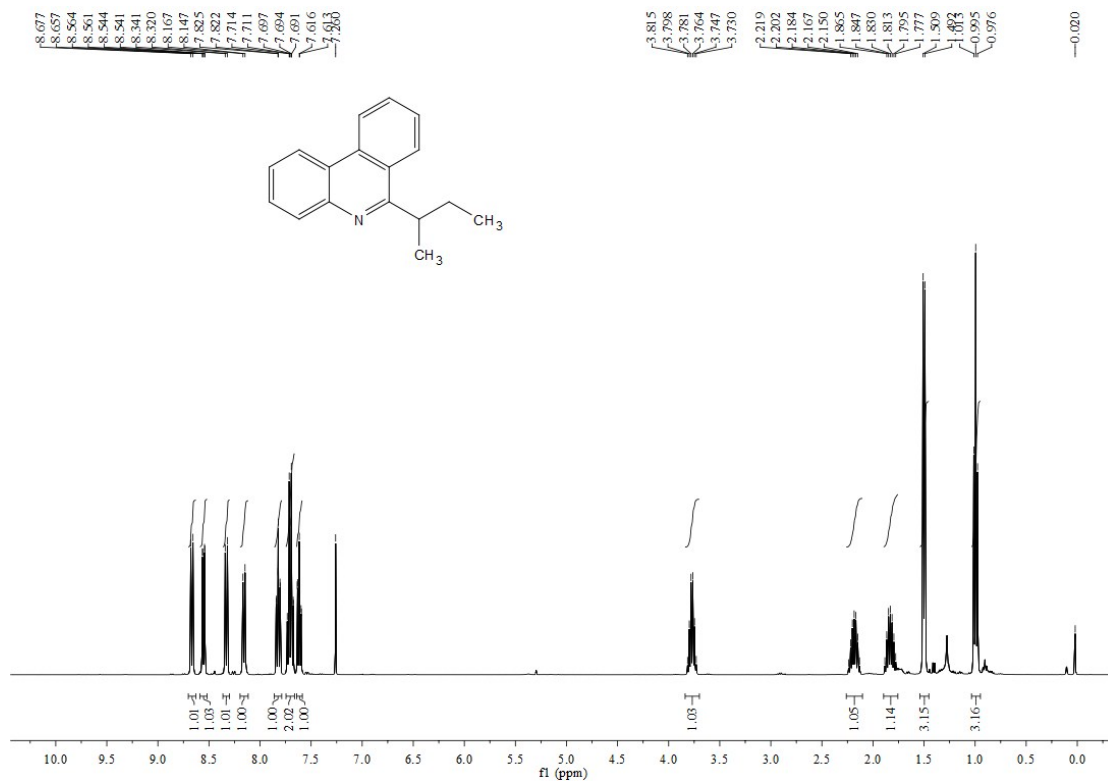




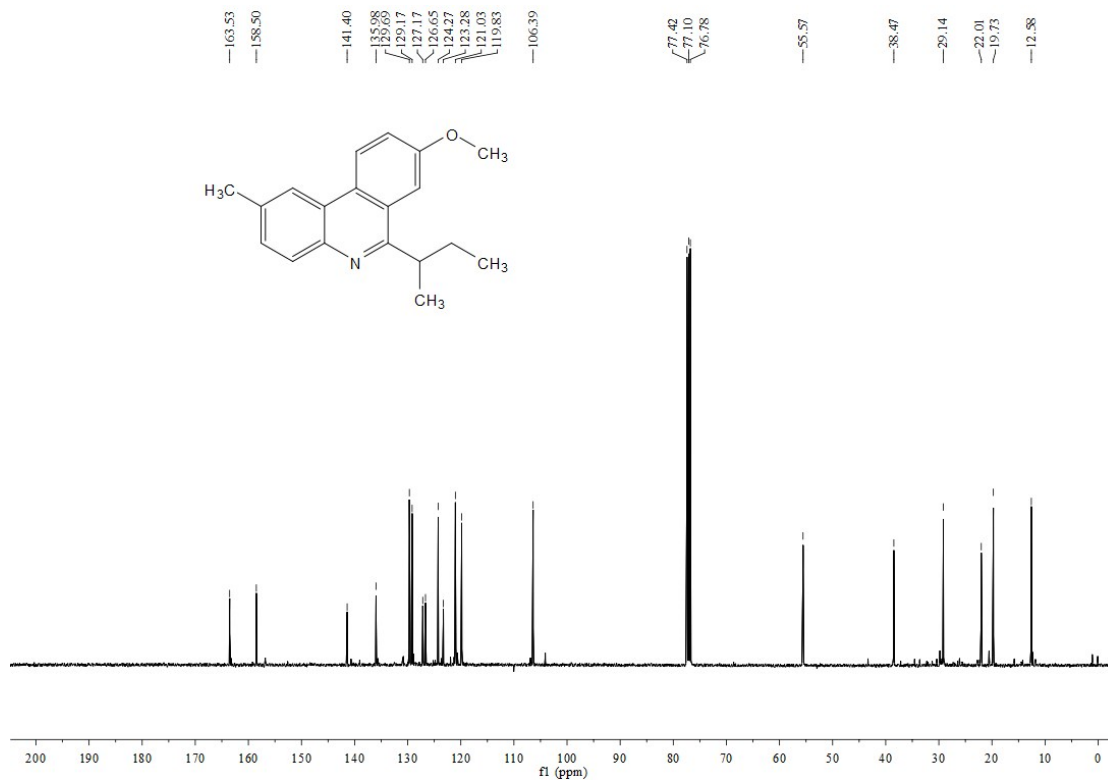
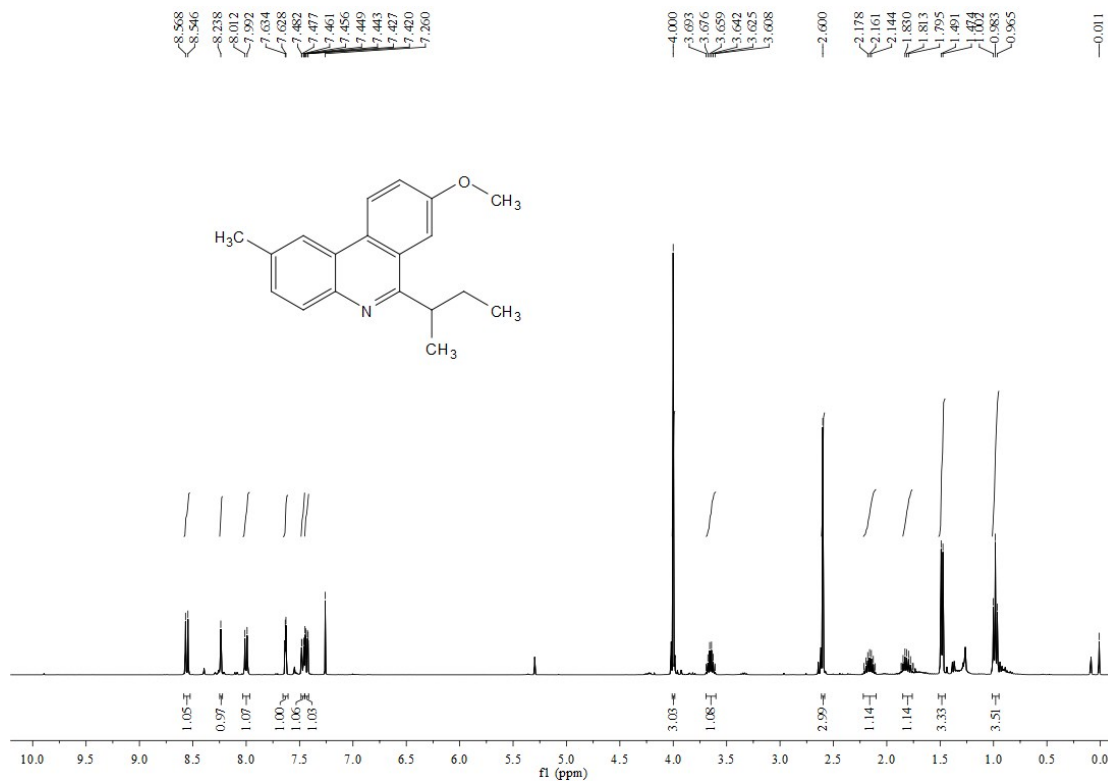
# 5-(*tert*-butyl)benzo[*c*][2,7]naphthyridine (3i)



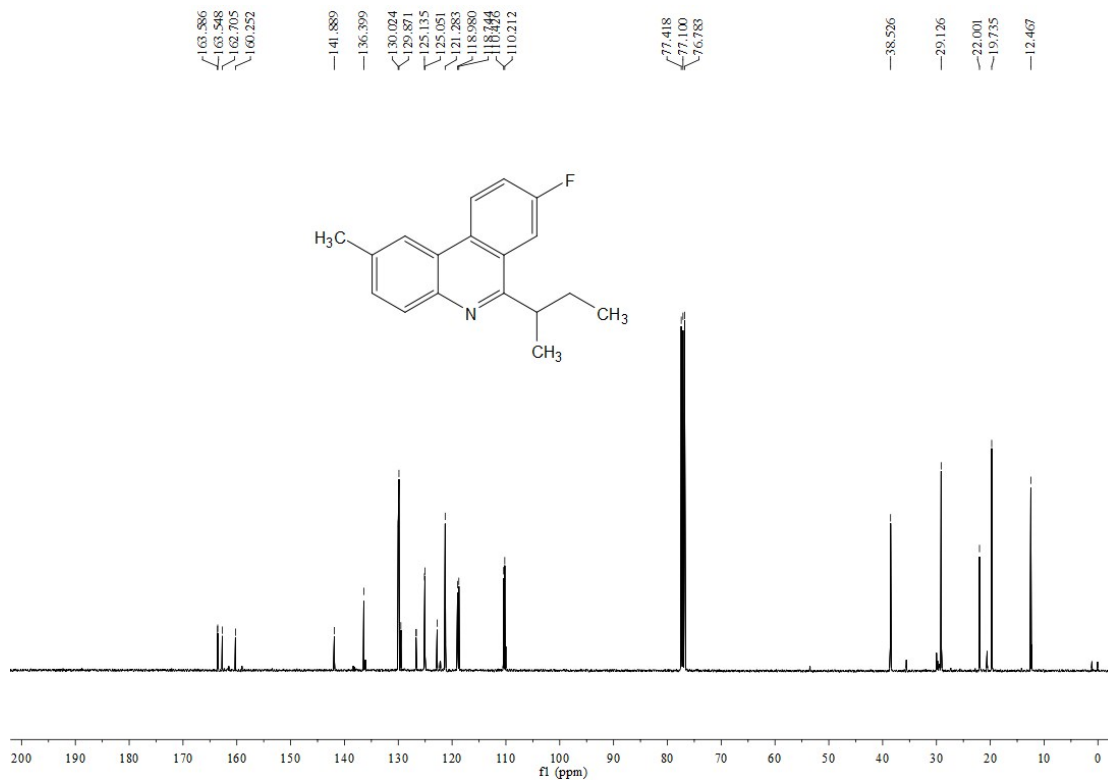
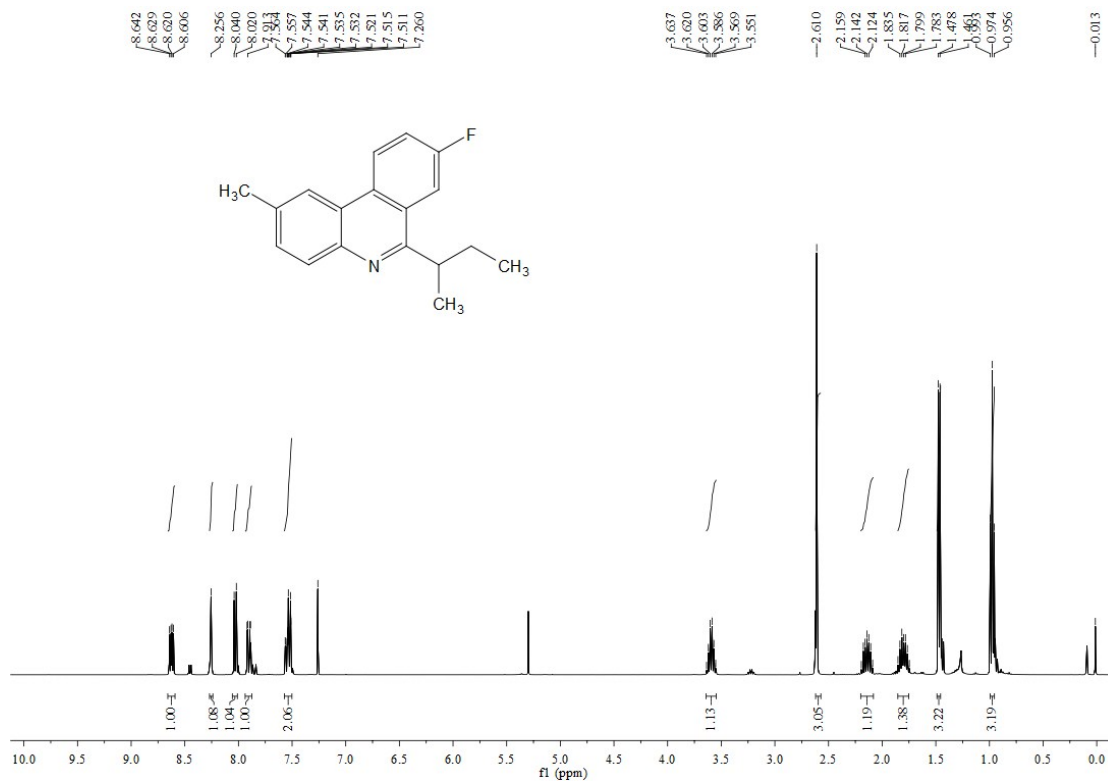
# 6-(*sec*-butyl)phenanthridine (3j)



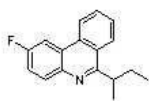
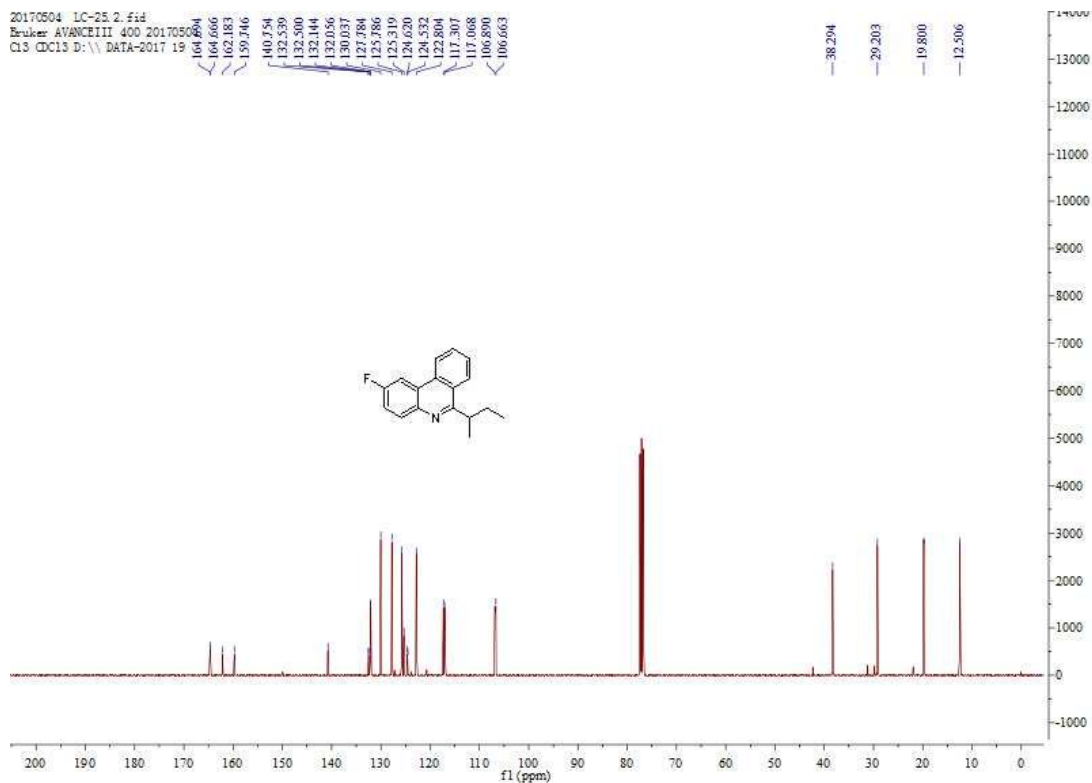
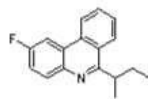
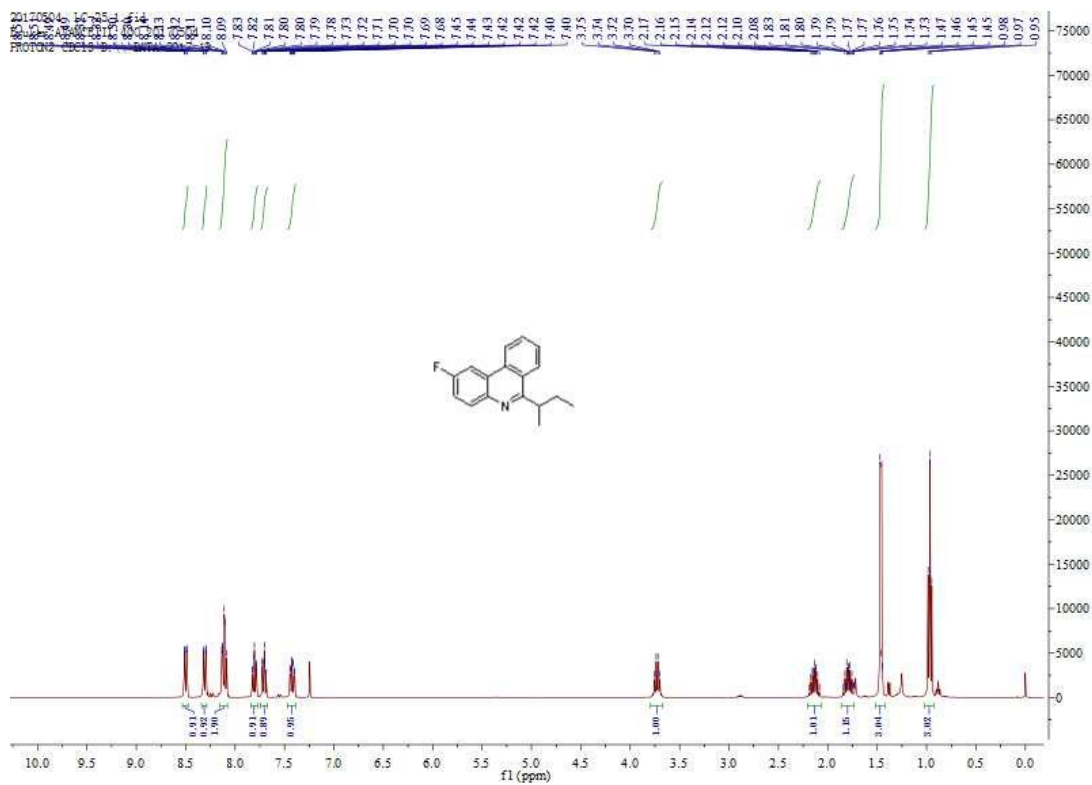
# 6-(*sec*-butyl)-8-methoxy-2-methylphenanthridine (3k)



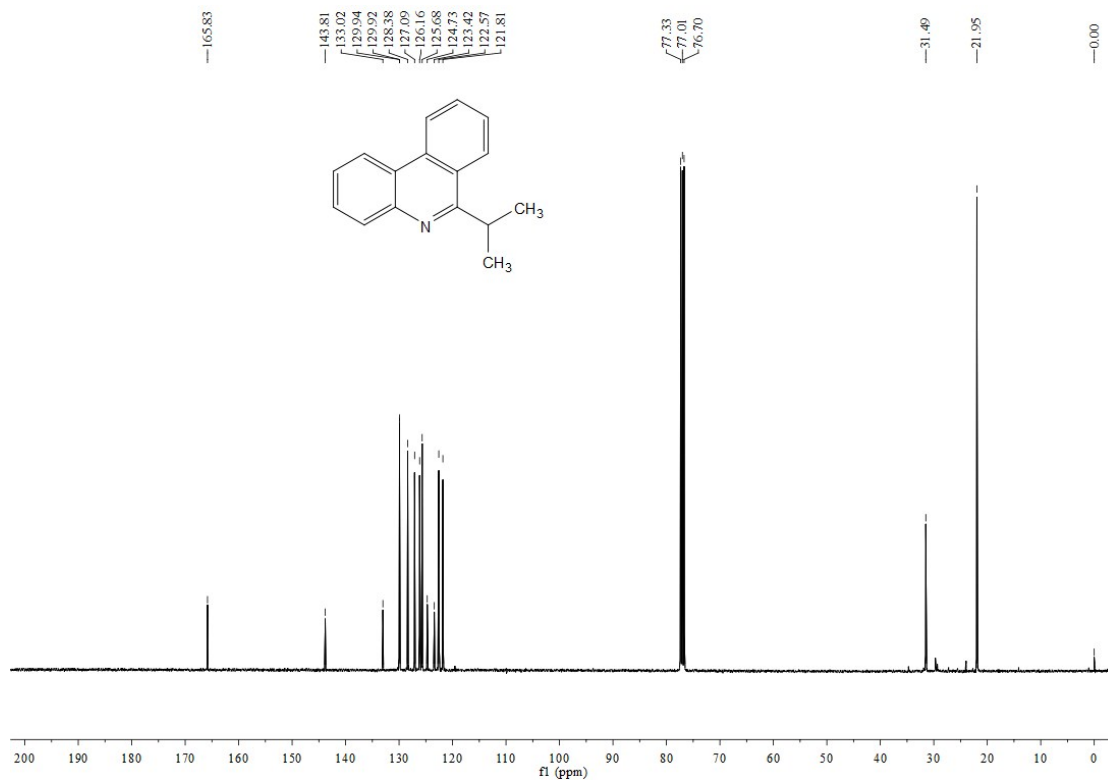
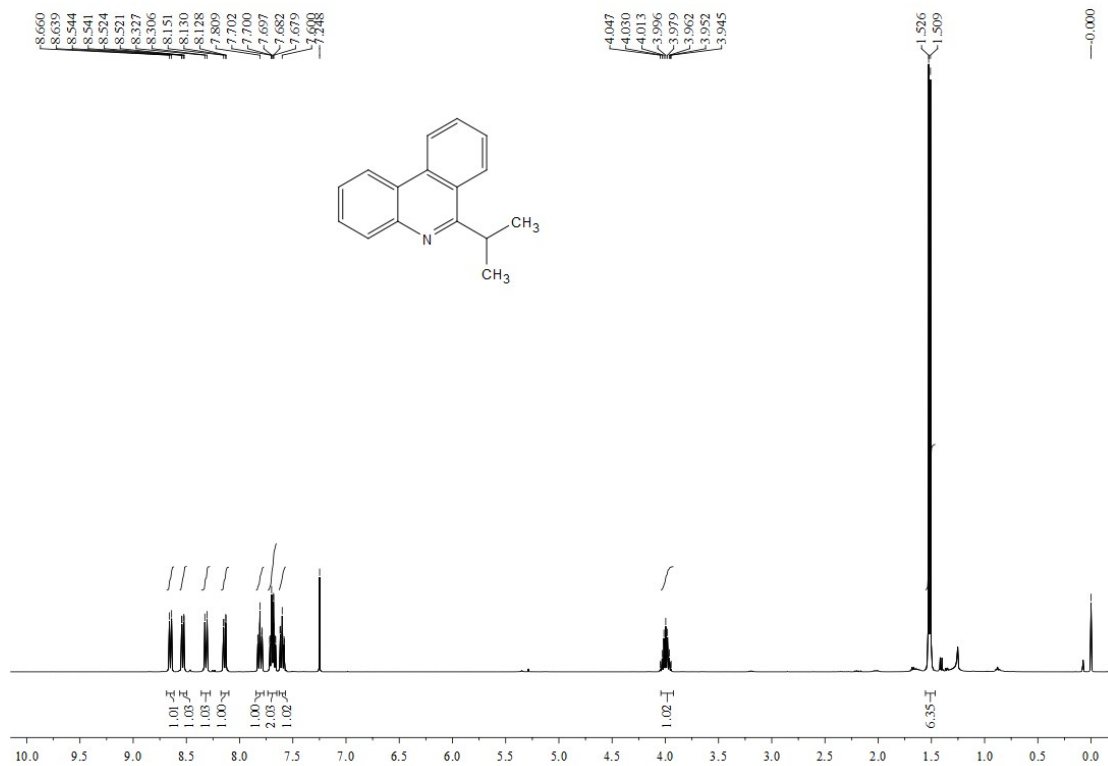
# 6-(*sec*-butyl)-8-fluoro-2-methylphenanthridine (31)



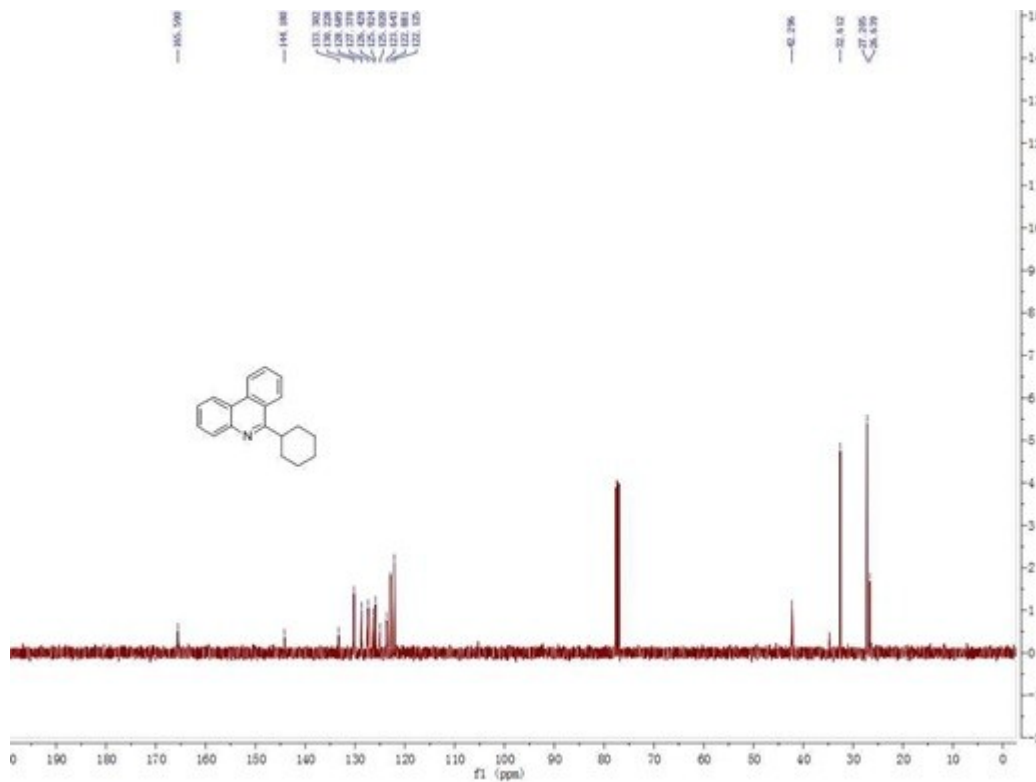
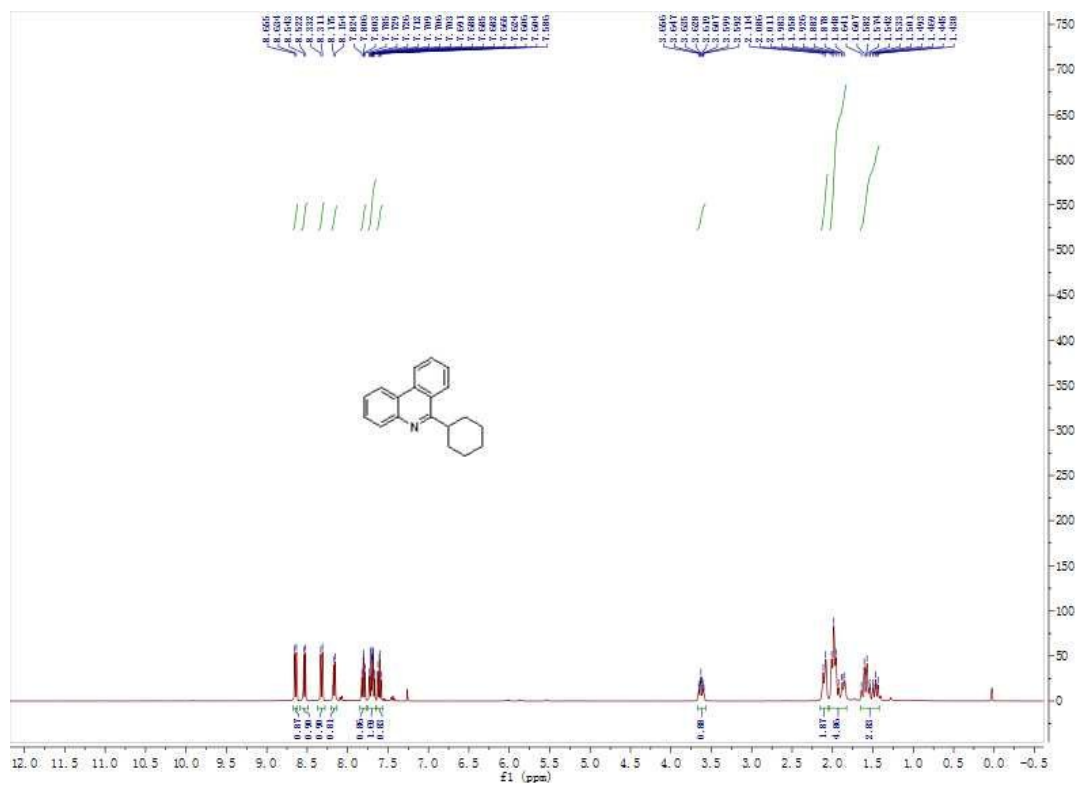
# 6-(*sec*-butyl)-2-fluorophenanthridine (3m)



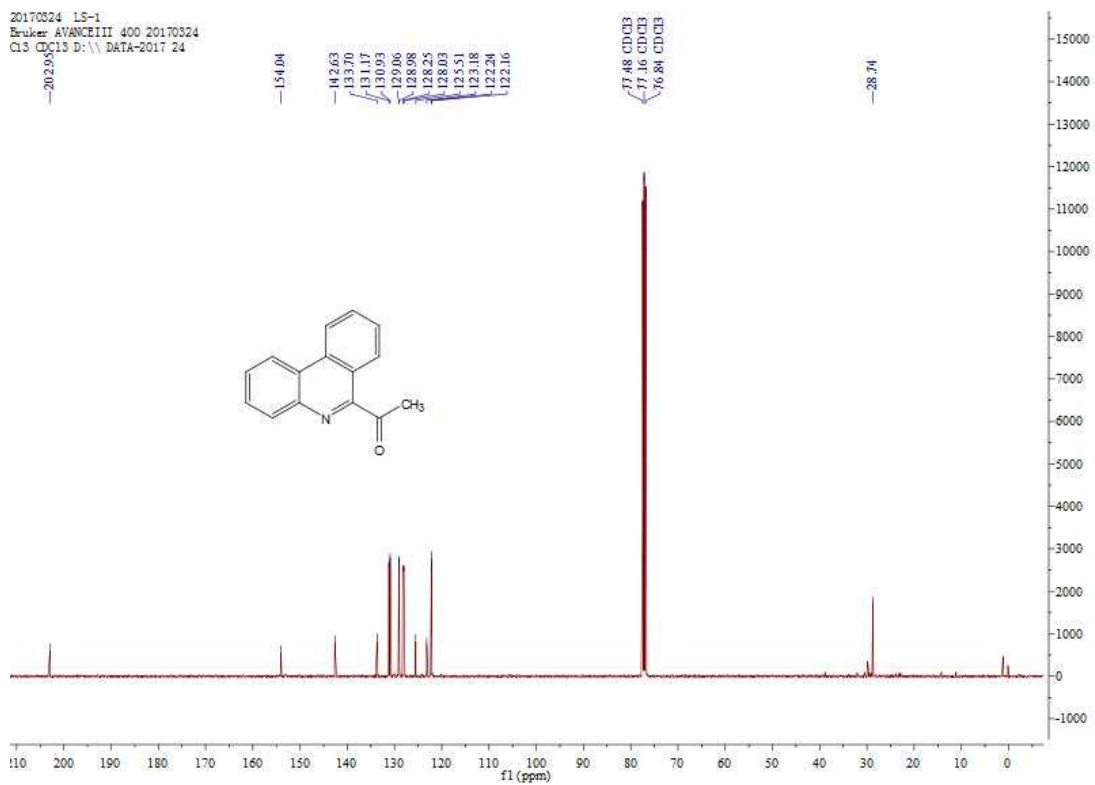
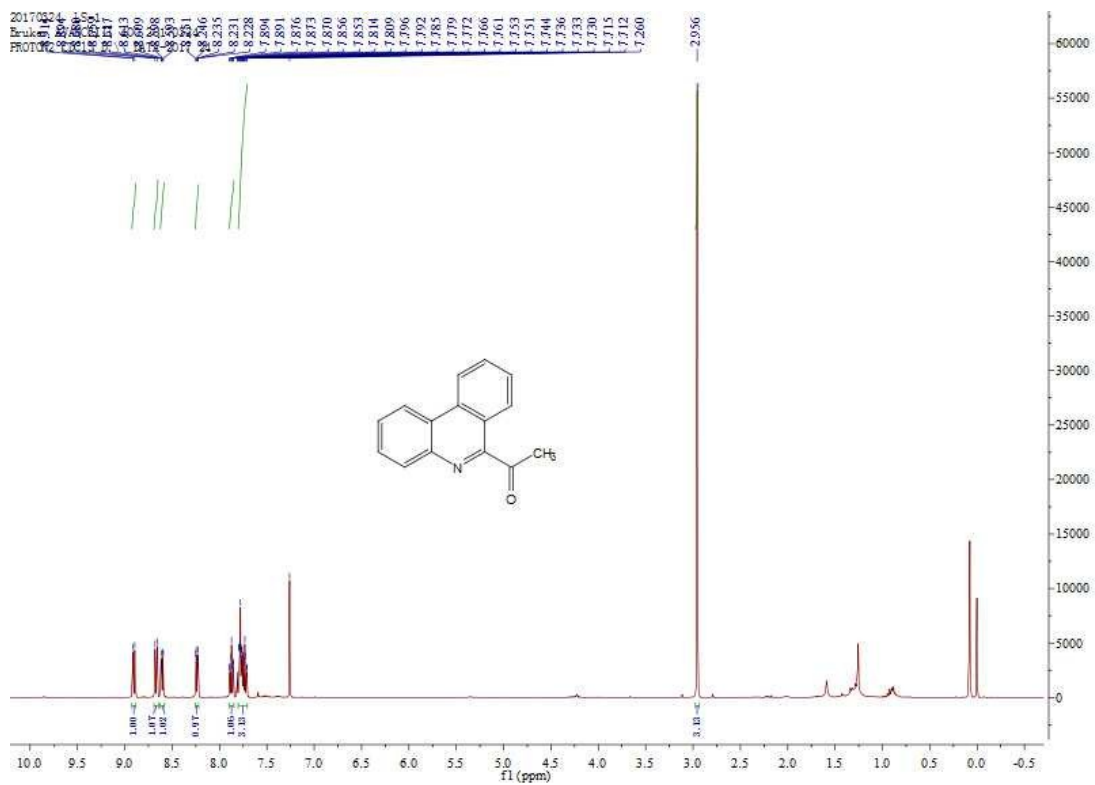
# 6-isopropylphenanthridine (3n)



## 6-cyclohexylphenanthridine (3o)

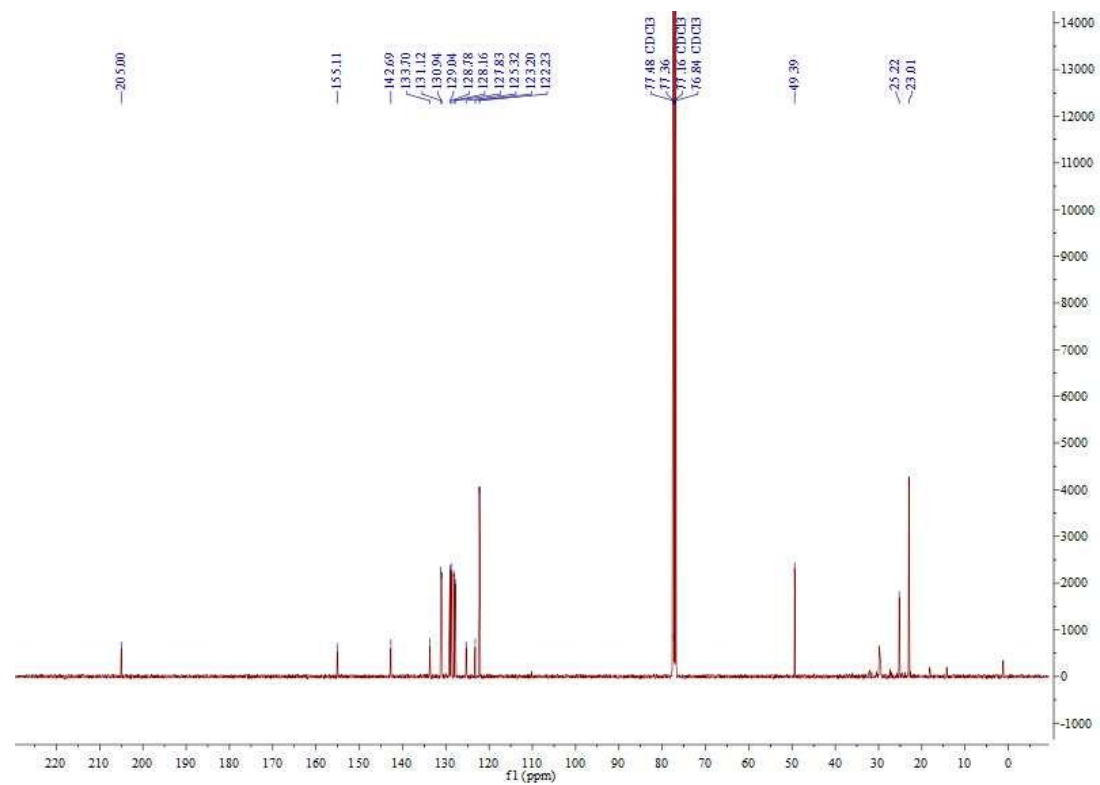
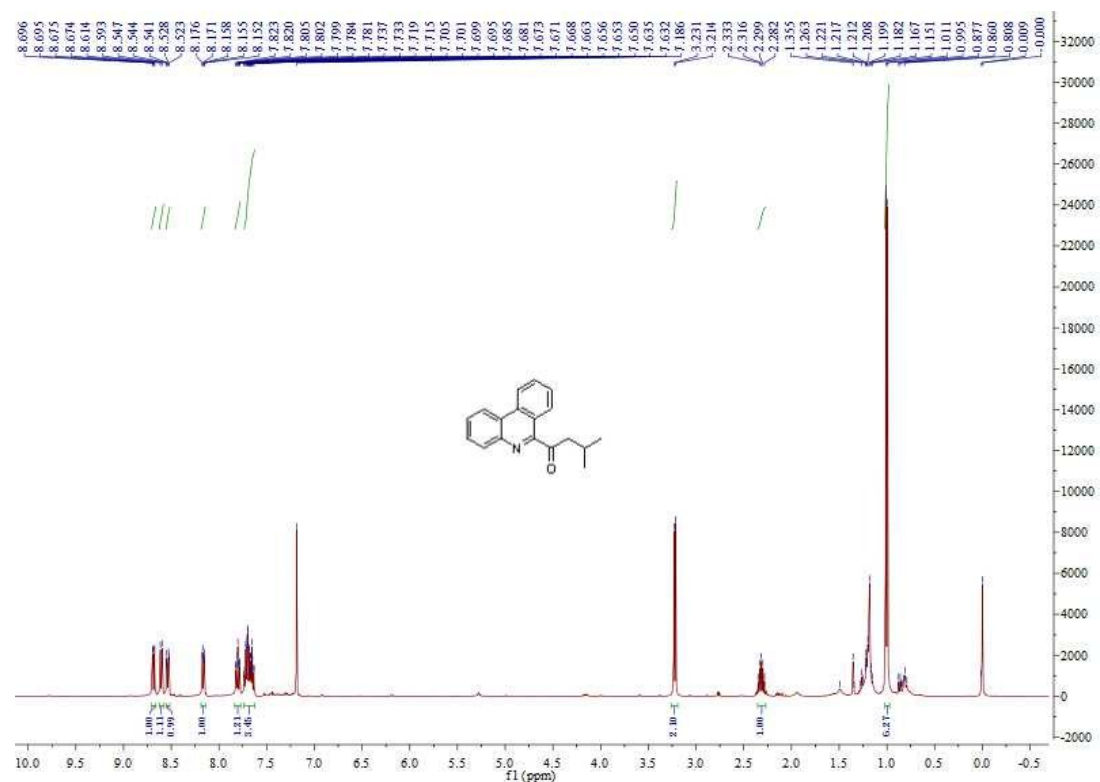


# 1-(phenanthridin-6-yl)ethan-1-one (3p)

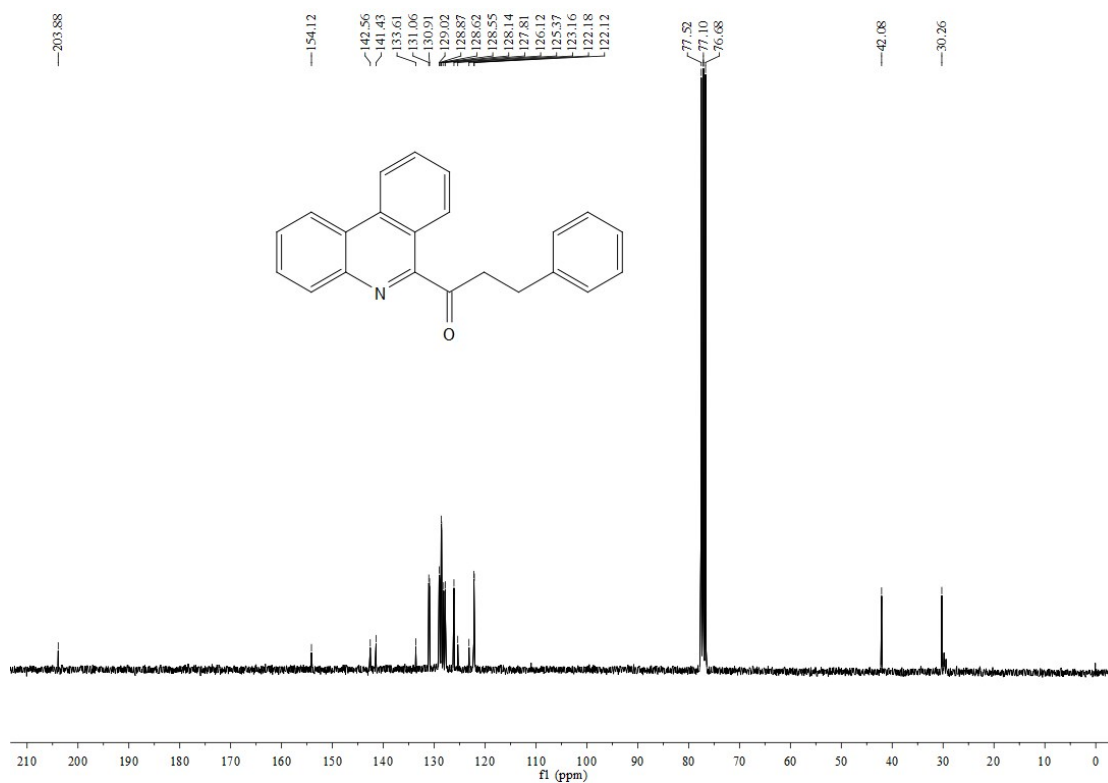
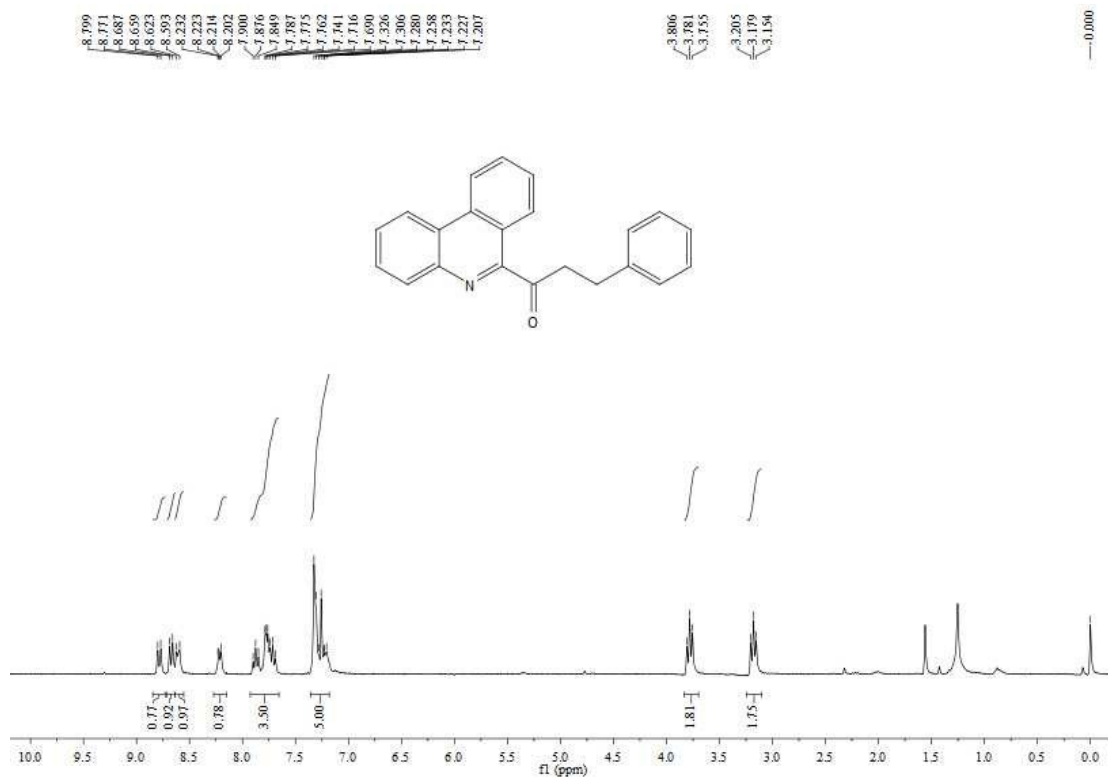




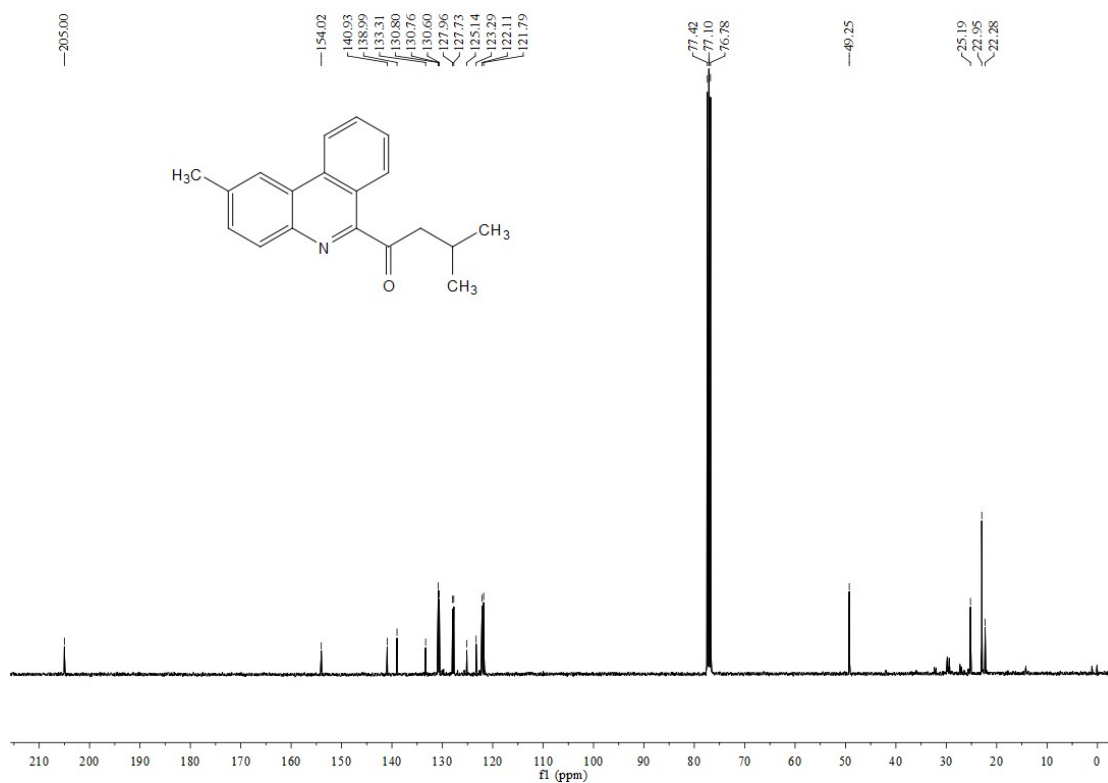
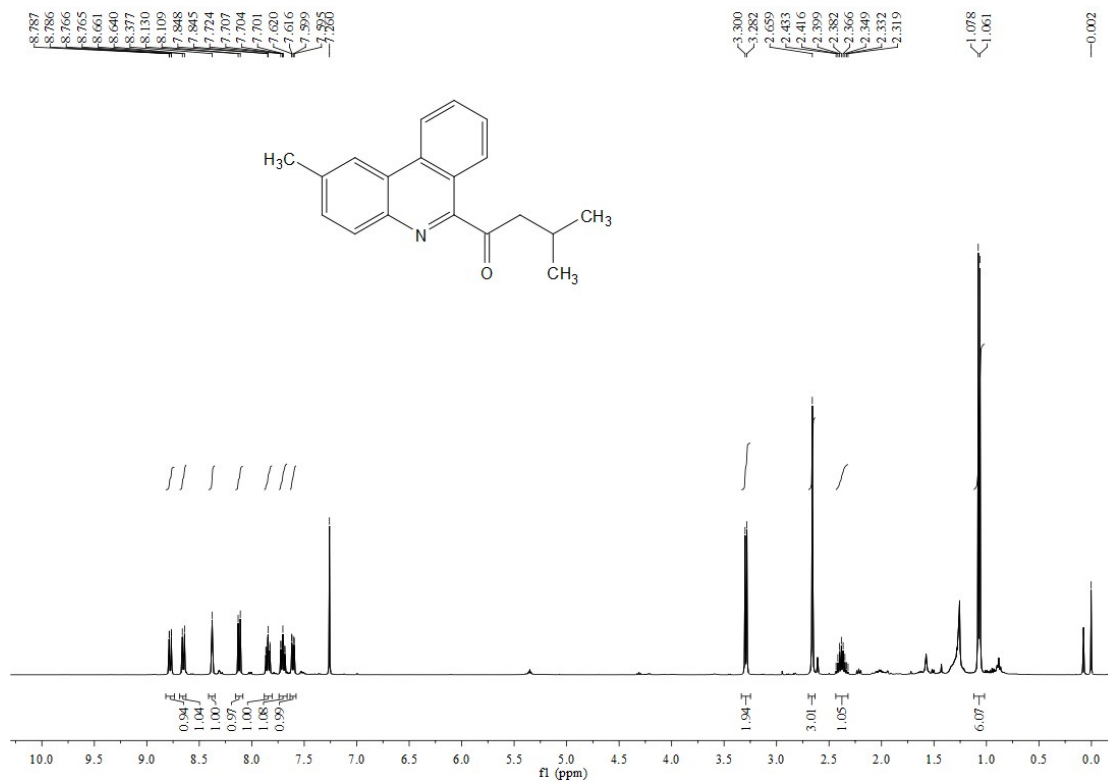
### 3-methyl-1-(phenanthridin-6-yl)butan-1-one (3q)



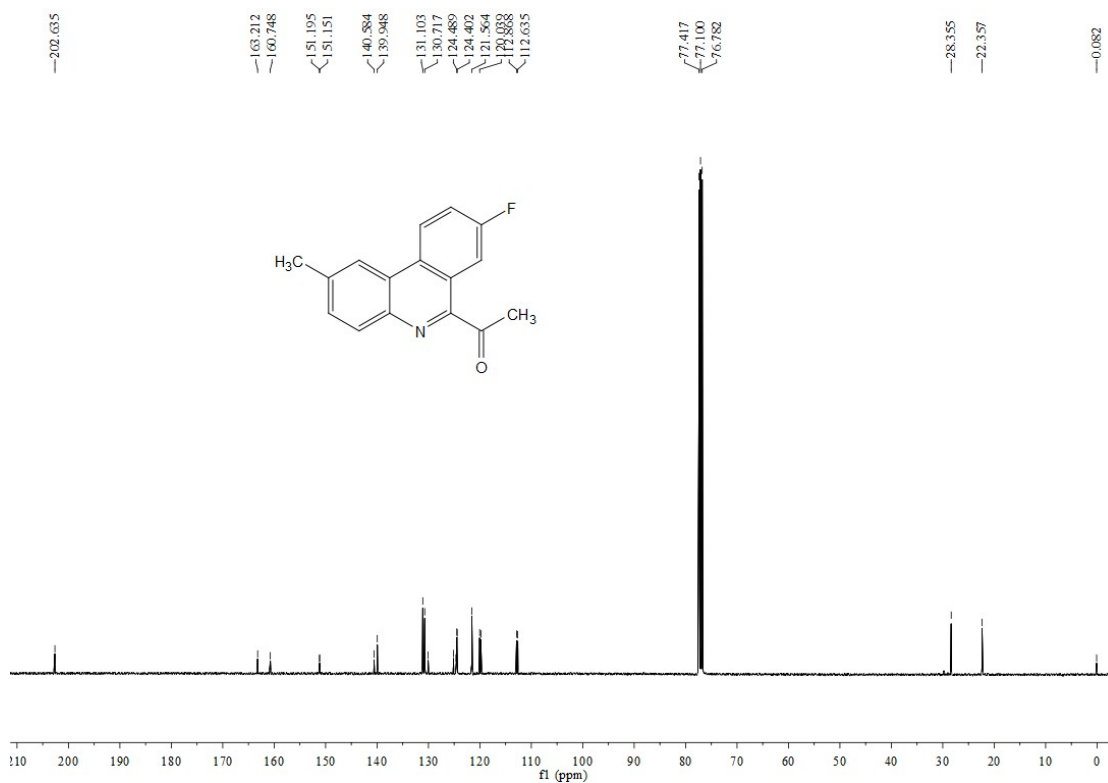
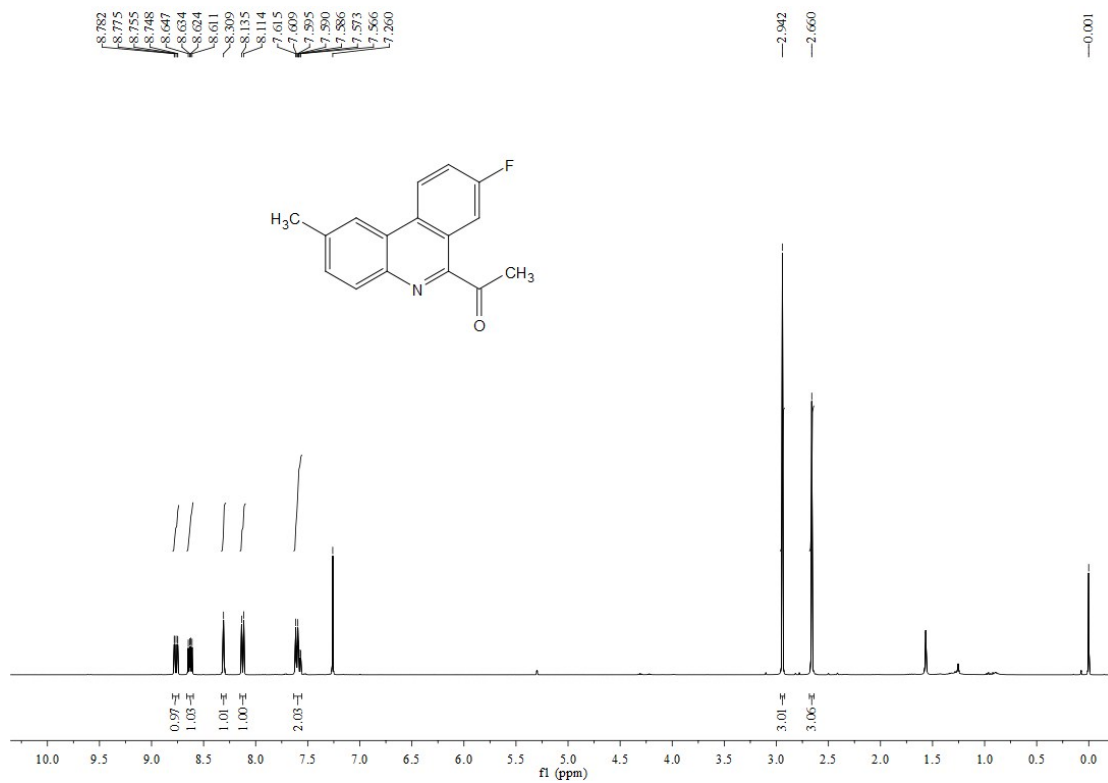
# 1-(phenanthridin-6-yl)-3-phenylpropan-1-one (3r)



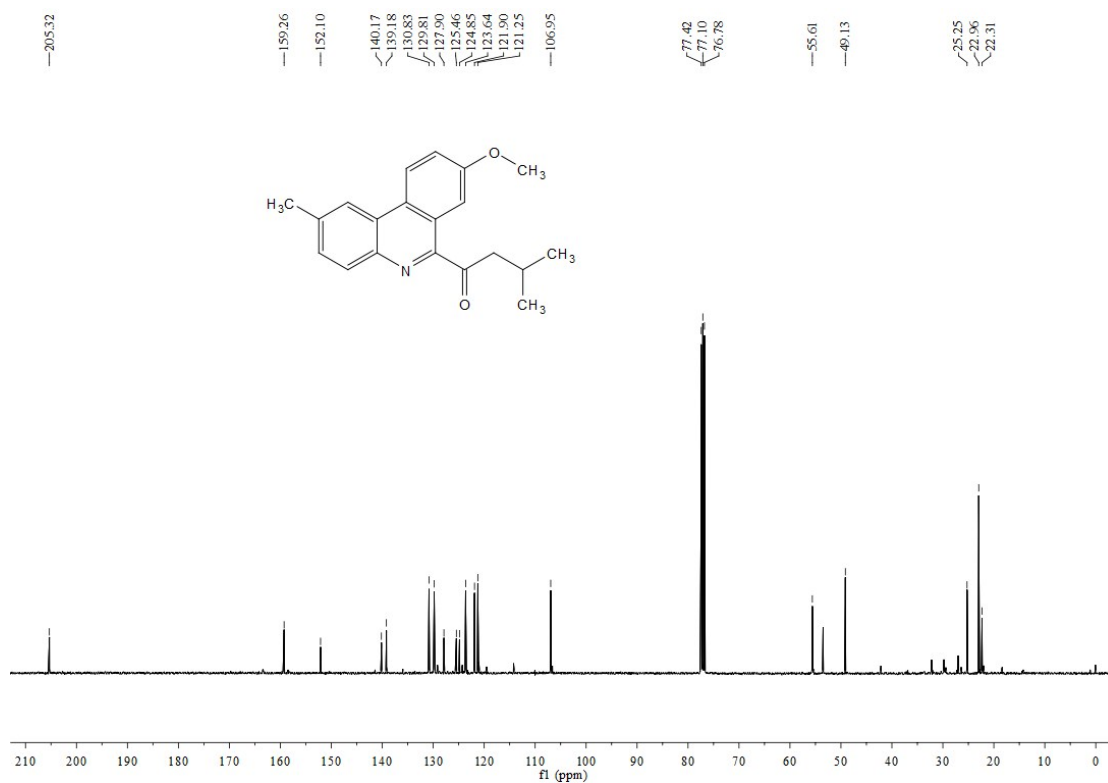
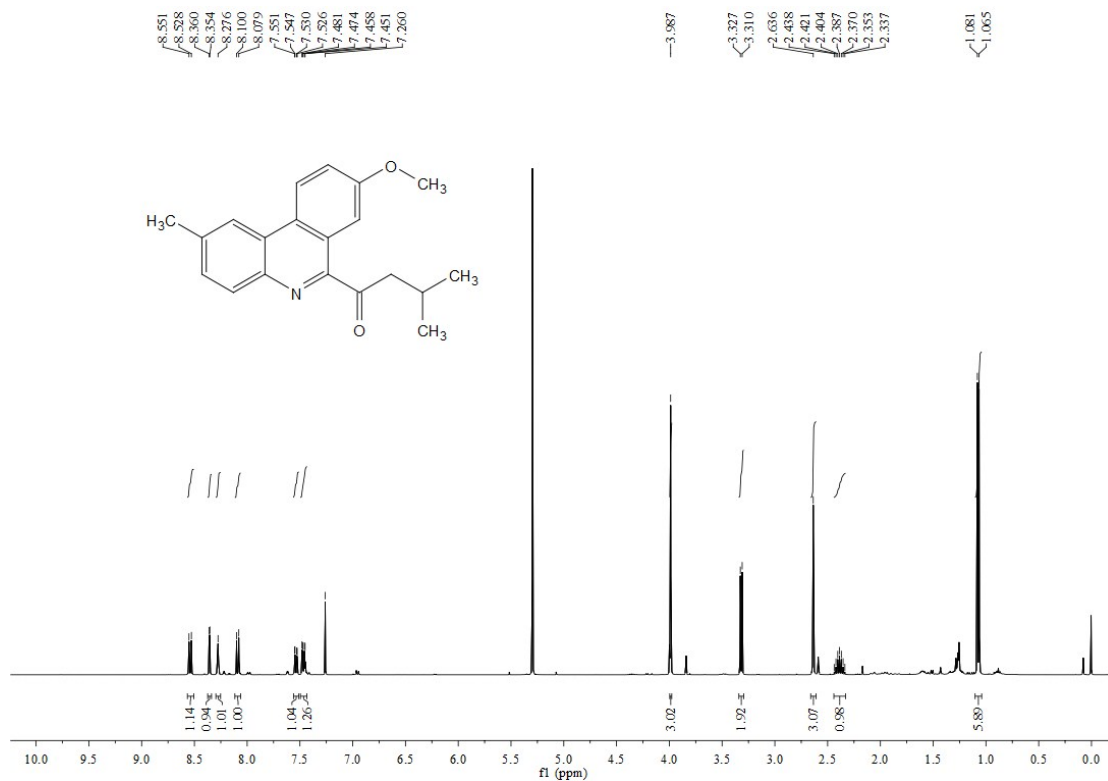
### 3-methyl-1-(2-methylphenanthridin-6-yl)butan-1-one (3s)



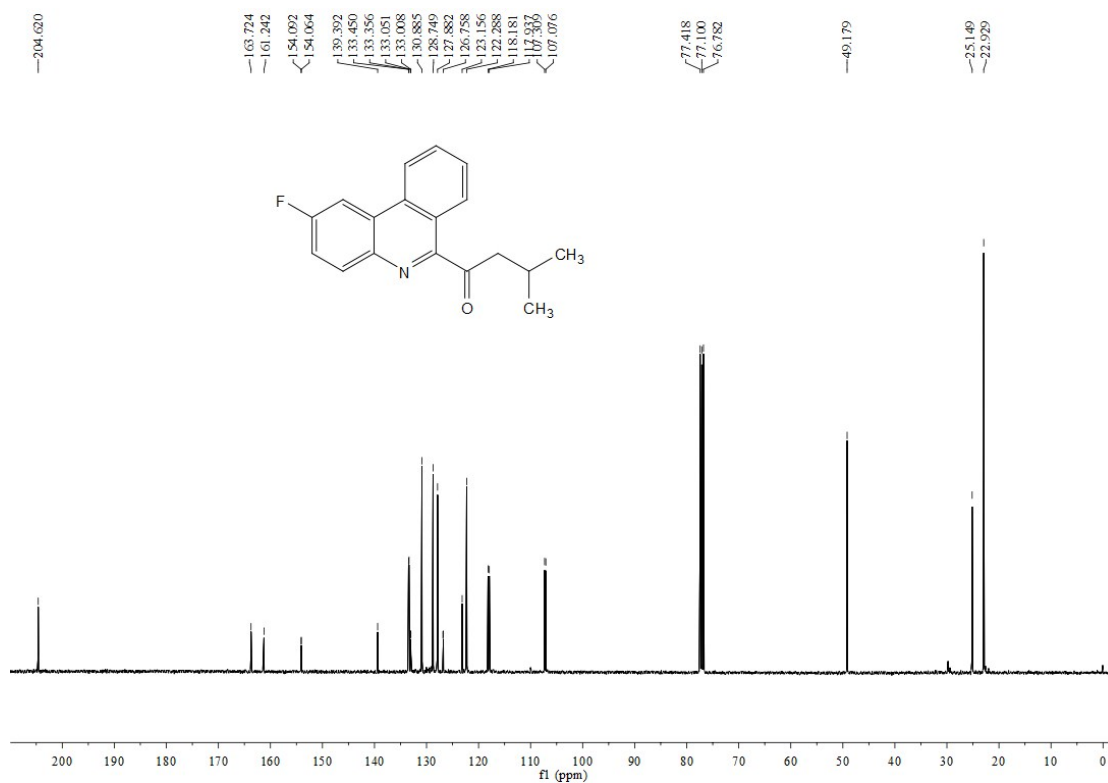
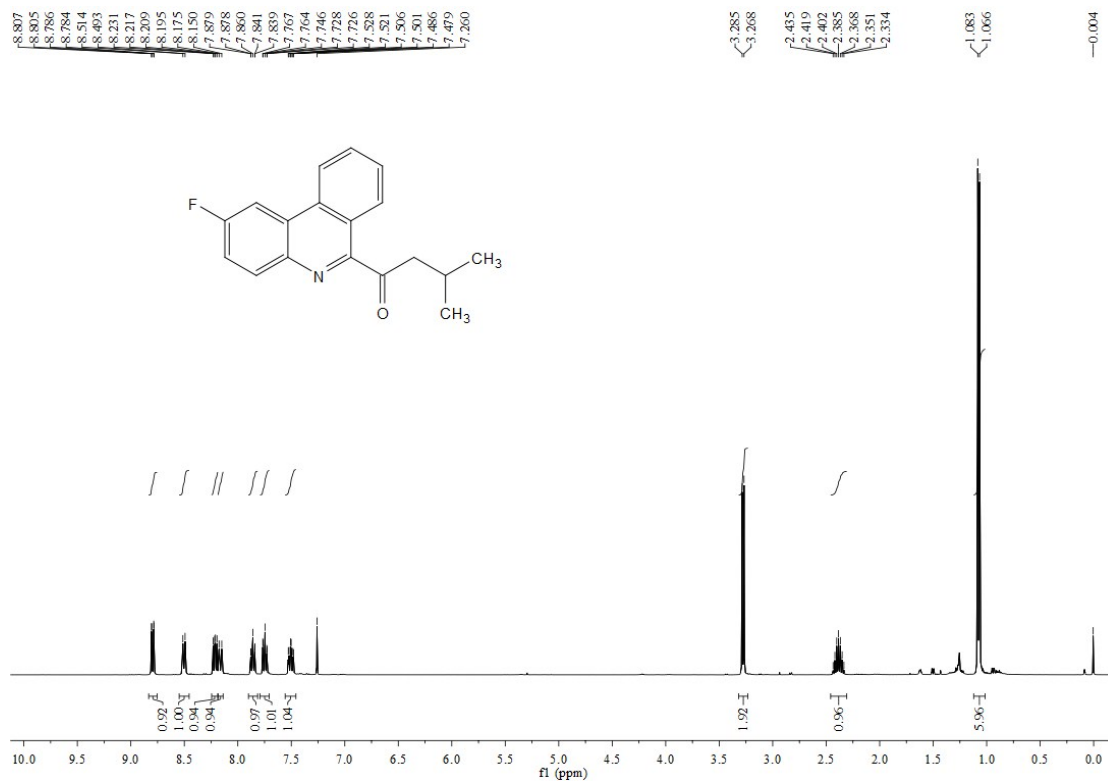
# 1-(8-fluoro-2-methylphenanthridin-6-yl)ethan-1-one (3t)



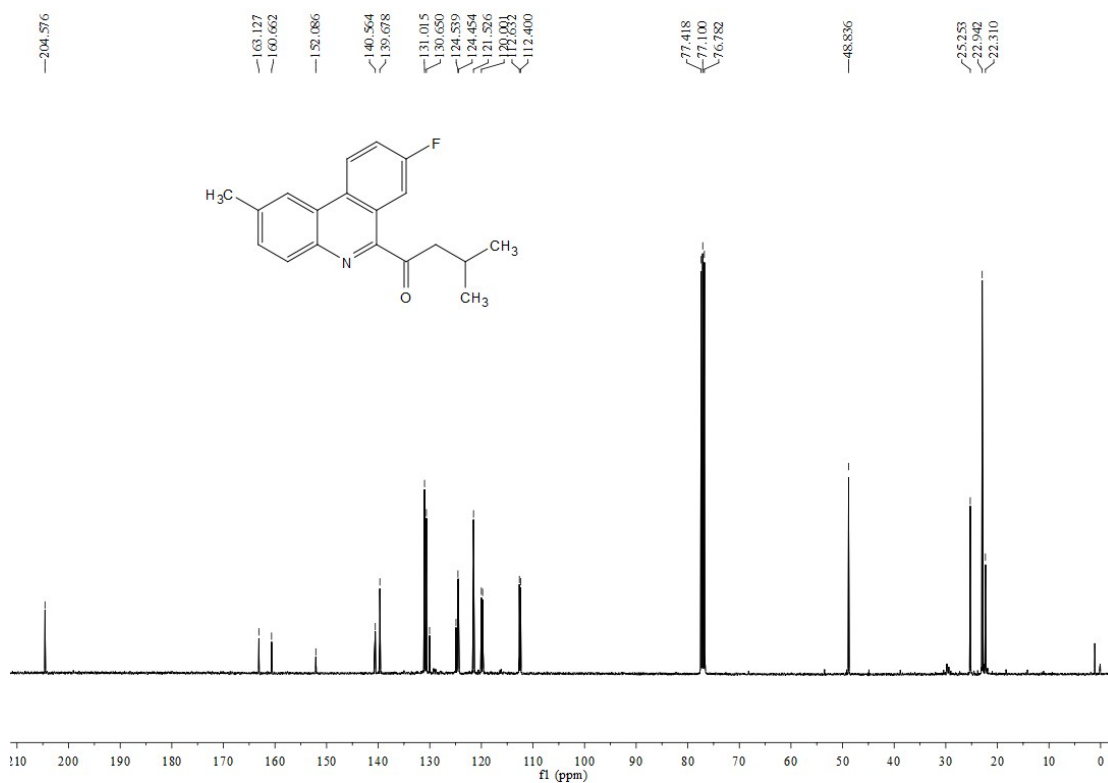
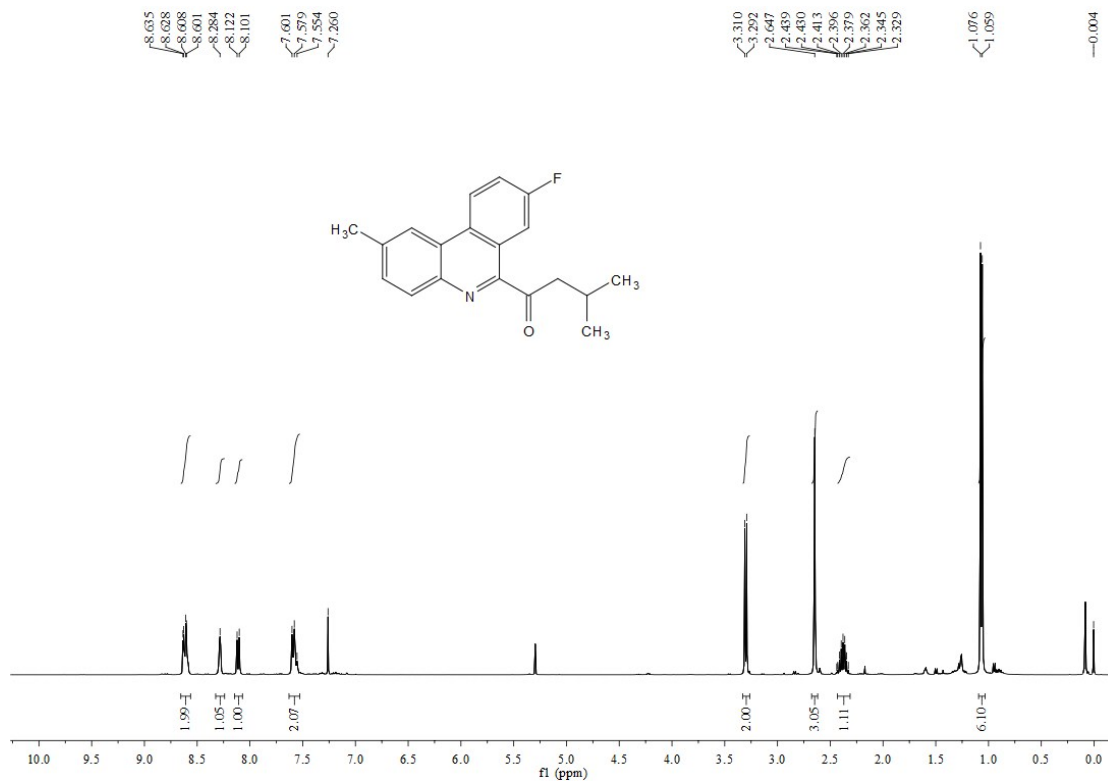
# 1-(8-methoxy-2-methylphenanthridin-6-yl)-3-methylbutan-1-one (3u)



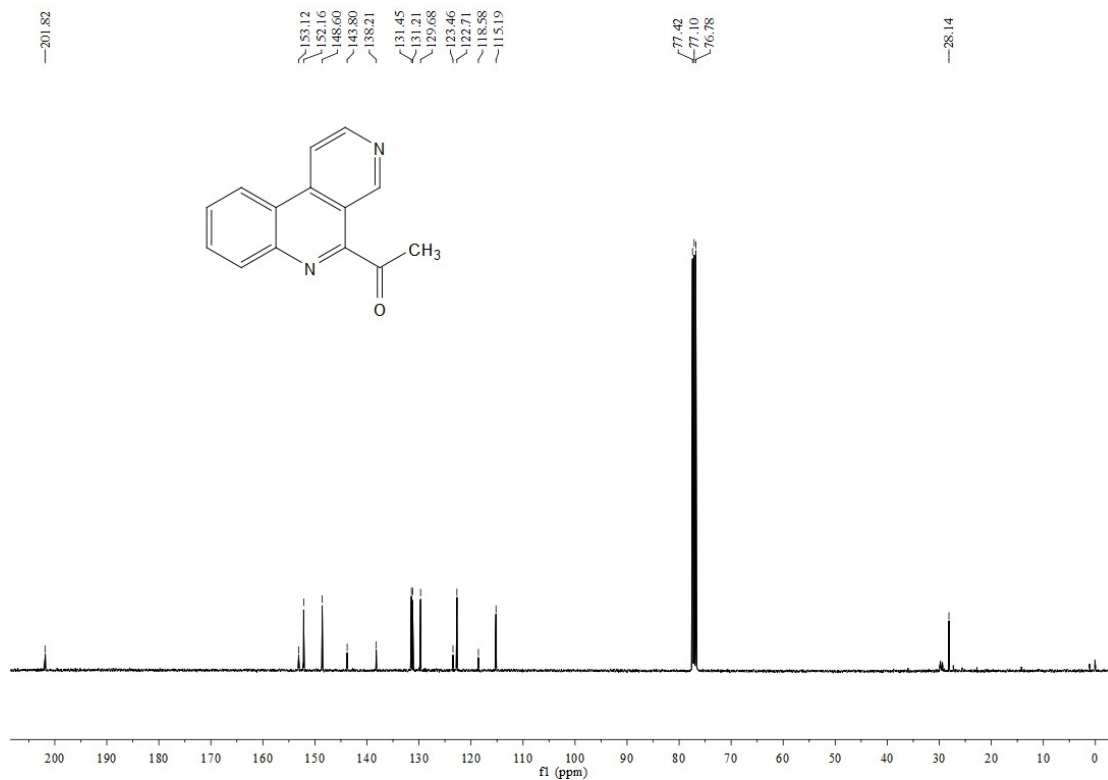
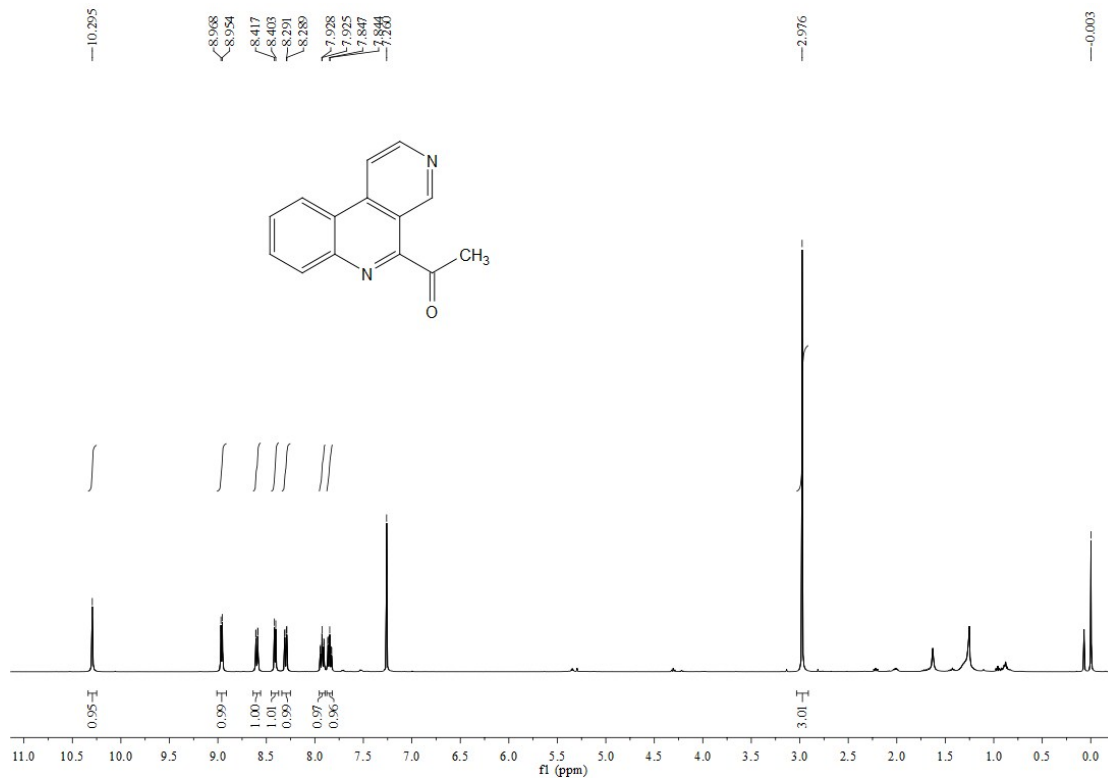
# 1-(2-fluorophenanthridin-6-yl)-3-methylbutan-1-one (3v)



# 1-(8-fluoro-2-methylphenanthridin-6-yl)-3-methylbutan-1-one (3w)



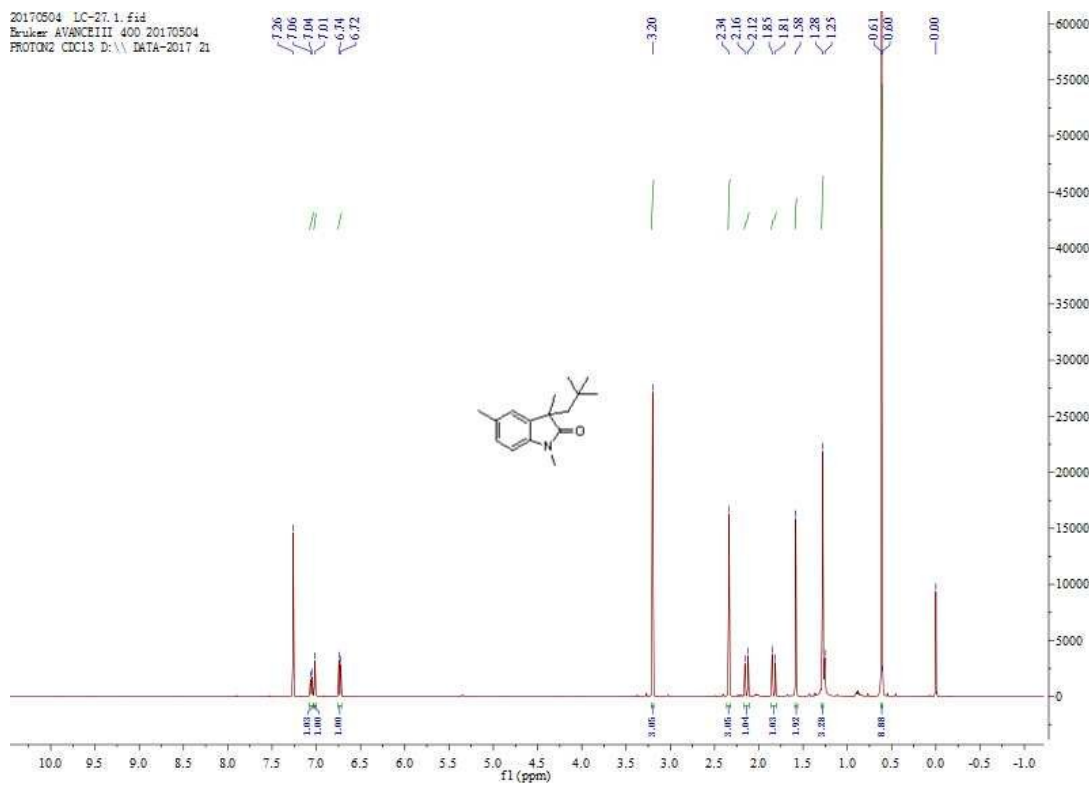
# 1-(benzo[c][2,7]naphthyridin-5-yl)ethan-1-one (3x)





# 1,3,5-trimethyl-3-neopentylindolin-2-one (3y)

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20170504 LC-27.2.fid  
Bruker AVANCEIII 400 20170504  
C13 CDCl3 D:\DATA-2017 21

