

# Tf<sub>2</sub>O-Mediated [4+2]-Annulation of Anthranils with 2-Chloropyridines: Enabling Access to Pyridoquinazolinones and Euxylophoricine B

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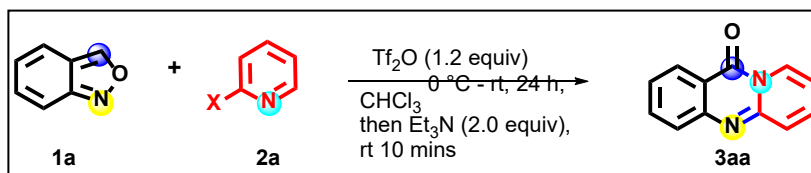
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## EXPERIMENTAL SECTION

### General Information

All reagents were purchased from Sigma Aldrich, Thermo-Fischer, and local vendors and were used without further purification. All experiments were carried out in screw-pressure reaction tubes purchased from Sigma Aldrich. All the solvents used for the reaction were distilled before use. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on Avance III, and Bruker at 400 MHz, 100 MHz, and 376 MHz spectrometers respectively using  $\text{CDCl}_3$ . In the experimental section, the  $^1\text{H}$  NMR chemical shifts are expressed in the form of ppm ( $\delta$ ) relative to  $\delta = 7.26$  for  $\text{CDCl}_3$  whereas  $^{13}\text{C}$  NMR chemical shift are expressed relative to  $\delta = 77.00$ . Multiplicities in the  $^1\text{H}$  NMR spectra are described as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate- Mass Q-TOF LC/MS.

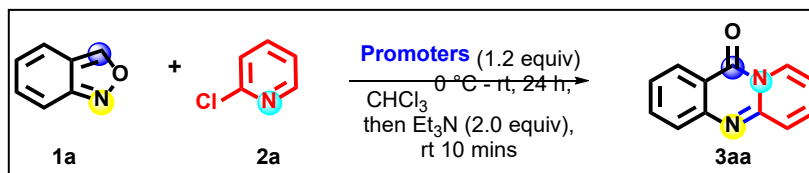
**Table S1. Optimization of nature of Pyridine:**



A mixture of anthranil (**1a**, 0.33 mmol), 2-haloopyridines (**2a**, 0.33 mmol), and chloroform (1.0 mL) were taken in an ace pressure reaction sealed tube at  $0^\circ\text{C}$  and added  $\text{Tf}_2\text{O}$  (1.2 equiv.), screw of the screw pressure reaction tube and stirred at  $0^\circ\text{C}$  for 5 minutes then allowed to stir at  $70^\circ\text{C}$  for 24 h, then the reaction mixture was quenched with  $\text{Et}_3\text{N}$  (2.0 mmol) after completion and stirred for an additional 10 minutes at room temperature. When the reaction was completed (determined by TLC) and the solvent was evaporated under reduced pressure to get the crude product (**3aa**) which was purified by column chromatography using 50% (ethyl acetate: hexane) on 100-200 mesh silica gel to get the product **3aa**.

S. No.	Promters	Isolated Yield
1	X = Br	82%
2	X = I	63%
3	X = F	Trace
4	X = H	Not observed

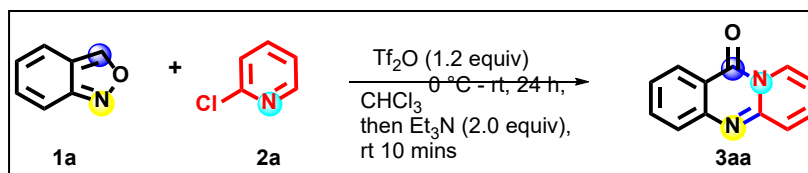
**Table S2: . Optimization of Anhydrides (Promoters):**



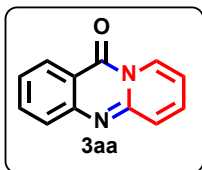
A mixture of anthranil (**1a**, 0.33 mmol), 2-chloropyridines (**2a**, 0.33 mmol), and chloroform (1.0 mL) were taken in an ace pressure reaction sealed tube at 0 °C and added different **promoters/anhydrides** (1.2 equiv.), screw of the screw pressure reaction tube and stirred at 0 °C for 5 minutes then allowed to stir at 70 °C for 24 h, then the reaction mixture was quenched with Et<sub>3</sub>N (2.0 mmol) after completion and stirred for an additional 10 minutes at room temperature. When the reaction was completed (determined by TLC) and solvent was evaporated under reduced pressure to get the crude product (**3aa**) which was purified by column chromatography using 50% (ethyl acetate: hexane) on 100-200 mesh silica gel to get the product **3aa**.

S. No.	2-X pyridines	Isolated Yield
1	Tf <sub>2</sub> O	94%
2	Acetic anhydride (Ac <sub>2</sub> O)	0%
3	Methanesulfonic anhydride (Ms <sub>2</sub> O)	0%
4	Trifluoroacetic anhydride (TFAA)	0%

**General Experimental Procedure for the synthesis of 11H-pyrido[2,1-b]quinazolin-11-one (3aa)<sup>1</sup>:**



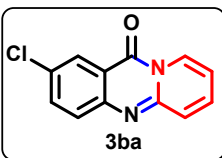
A mixture of anthranil (**1a**, 0.33 mmol), 2-chloropyridine (**2a**, 0.33 mmol), and chloroform (1.0 mL) were taken in an ace pressure reaction sealed tube at 0 °C and added Tf<sub>2</sub>O (1.2 equiv.), screw of the screw pressure reaction tube and stirred at 0 °C for 5 minutes then allowed to stir at 70 °C for 24 h , then the reaction mixture was quenched with Et<sub>3</sub>N (2.0 mmol) after completion and stirred for an additional 10 minutes at room temperature When the reaction was completed (determined by TLC) and solvent was evaporated under reduced pressure to get the crude product (**3aa**) which was purified by column chromatography using 50% (ethyl acetate: hexane) on 100-200 mesh silica gel to get the product **3aa** in 94% yield (62 mg), as a



yellow solid; Mp: 208 - 210 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.89 (d, *J* = 7.4 Hz, 1H), 8.45 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.56 – 7.47 (m, 3H), 6.91 – 6.87 (m, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.86, 148.12, 147.67, 135.22, 134.47, 127.34, 126.74, 126.58, 126.02, 125.33, 116.14, 112.70; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O [M+H]<sup>+</sup> is 197.0709, found 197.0713.

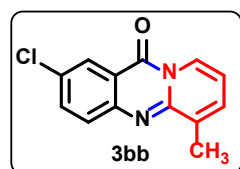
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“**Note:** Following the same above experimental procedure all the desired products (**3ba - 3ai**) and **Euxylophoricine-B** were prepared”.

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



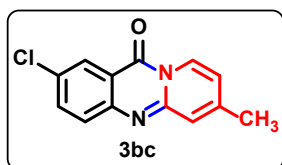
Compound **3ba** (69 mg, yield = 90%) was isolated as a light brown solid; Mp: 176 - 178 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.83 (d, *J* = 7.4 Hz, 1H), 8.35 (d, *J* = 2.3 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.57 – 7.43 (m, 2H), 6.93 – 6.83 (m, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.99, 147.70, 147.00, 135.57, 134.39, 130.66, 128.63, 126.66, 126.35, 126.19, 116.93, 112.95; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> is 231.0320, found 231.0317.

### **2-chloro-6-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3bb):<sup>2</sup>**



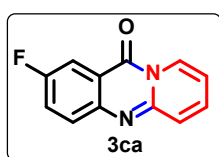
Compound **3bb** (75 mg, yield = 92%) was isolated as yellow solid; Mp: 153 - 155 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.77 (d, *J* = 7.4 Hz, 1H), 8.37 (d, *J* = 2.3 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.39 (d, *J* = 6.6 Hz, 1H), 6.81 (t, *J* = 7.0 Hz, 1H), 2.58 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.55, 147.61, 146.70, 135.27, 134.68, 132.53, 130.50, 129.21, 126.10, 124.80, 116.76, 112.57, 18.51; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> is 245.0476, found 245.0485.

### 2-chloro-7-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3bc):



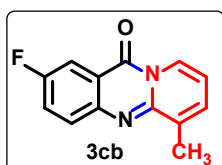
Compound **3bc** (74 mg, yield = 91%) was isolated as a yellow solid; Mp: 184 - 186 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.68 (d, *J* = 7.5 Hz, 1H), 8.27 (d, *J* = 2.3 Hz, 1H), 7.67– 7.59 (m, 2H), 7.19 (s, 1H), 6.70 – 6.68 (m, 1H), 2.38 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.90, 147.74, 147.23, 146.28, 135.39, 130.01, 128.32, 126.06, 125.83, 123.62, 116.51, 115.96, 21.42; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> is 245.0476, found 245.0481.

### 2-fluoro-11H-pyrido[2,1-b]quinazolin-11-one (3ca):<sup>3</sup>



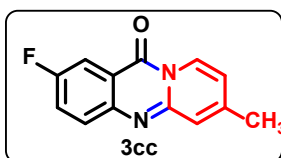
Compound **3ca** (63 mg, yield = 89%) was isolated as a yellow solid; Mp: 180 - 182 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.82 (d, *J* = 7.4 Hz, 1H), 8.05 – 8.02 (m, 1H), 7.80 – 7.77 (m, 1H), 7.61 – 7.54 (m, 1H), 7.54 – 7.43 (m, 2H), 6.89 – 6.86 (m, 1H). ; **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 159.67 (d, *J*<sub>C-F</sub> = 247.4 Hz), 158.37, (d, *J*<sub>C-F</sub> = 4.1 Hz), 147.07 (d, *J*<sub>C-F</sub> = 1.8 Hz), 145.51, 145.50, 134.07, 129.39 (d, *J*<sub>C-F</sub> = 8.1 Hz), 126.54, 126.47, 124.49 (d, *J*<sub>C-F</sub> = 25.0 Hz), 116.94 (d, *J*<sub>C-F</sub> = 8.8 Hz), 113.03, 111.20 (d, *J*<sub>C-F</sub> = 23.5 Hz); **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):** δ -113.97; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 215.0615, found 215.0636.

### 2-fluoro-6-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3cb):<sup>5</sup>



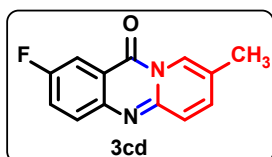
Compound **3cb** (69 mg, yield = 91%) was isolated as a yellow solid; Mp: 132 - 136 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.75 (d, *J* = 7.4 Hz, 1H), 8.02 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.83 (dd, *J* = 9.1, 4.9 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.36 (d, *J* = 6.6 Hz, 1H), 6.79 (t, *J* = 7.0 Hz, 1H), 2.57 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 159.62 (d, *J*<sub>C-F</sub> = 246.91 ), 158.88 (d, *J*<sub>C-F</sub> = 4.1 Hz), 146.92 (d, *J*<sub>C-F</sub> = 1.8 Hz), 145.06, 134.60, 131.97, 129.98 (d, *J*<sub>C-F</sub> = 8.1 Hz), 124.53, 124.23, 123.99, 116.71 (d, *J*<sub>C-F</sub> = 8.8 Hz), 110.98 (d, *J*<sub>C-F</sub> = 23.4 Hz), 18.51; **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):** δ -114.43; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 229.0772, found 229.0776.

### 2-fluoro-7-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3cc):<sup>5</sup>



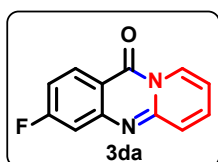
Compound **3cc** (68 mg, yield = 90%) was isolated as a brown solid; Mp: 149 - 151 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.72 (d, *J* = 7.5 Hz, 1H), 7.99 (dd, *J* = 8.6, 2.9 Hz, 1H), 7.72 (dd, *J* = 9.1, 4.9 Hz, 1H), 7.58 – 7.46 (m, 1H), 7.23 (s, 1H), 6.71 (dd, *J* = 7.5, 1.7 Hz, 1H), 2.40 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 159.34 (d, *J*<sub>C-F</sub> = 246.68), 158.38 (d, *J*<sub>C-F</sub> = 4.0 Hz), 147.17 (d, *J*<sub>C-F</sub> = 1.7 Hz), 145.73, 145.64, 129.17 (d, *J*<sub>C-F</sub> = 8.1 Hz), 125.63, 124.48, 124.23, 123.64, 116.54 (d, *J*<sub>C-F</sub> = 8.7 Hz), 115.91, 111.08 (d, *J*<sub>C-F</sub> = 23.4 Hz), 21.40; **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)**: δ -114.83; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 229.0772, found 229.0773.

### **2-fluoro-8-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3cd):**



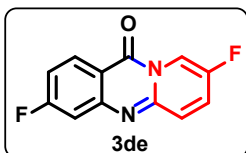
Compound **3cd** (70 mg, yield = 92%) was isolated as a yellow solid; Mp: 182 - 185 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.53 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.68 (dd, *J* = 8.7, 4.7 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.35 – 7.29 (m, 2H), 2.30 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 159.38 (d, *J*<sub>C-F</sub> = 247.0 Hz), 157.97 (d, *J*<sub>C-F</sub> = 3.9 Hz), 146.11, 145.13, 137.16, 129.22 (d, *J*<sub>C-F</sub> = 8.1 Hz), 125.60, 124.18, 123.93, 123.07, 122.69, 116.67 (d, *J*<sub>C-F</sub> = 8.8 Hz), 110.93 (d, *J*<sub>C-F</sub> = 23.4 Hz), 18.19; **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)**: δ -114.35; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 229.0772, found 229.0773.

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



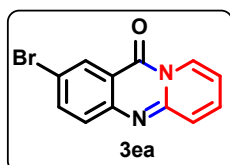
Compound **3da** (63 mg, yield = 89%) was isolated as a yellow solid; Mp: 104 - 106 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.87 (d, *J* = 7.3 Hz, 1H), 8.45 (dd, *J* = 8.9, 6.3 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.22 – 7.17 (m, 1H), 6.91 (t, *J* = 6.8 Hz, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 167.08 (d, *J*<sub>C-F</sub> = 255.6 Hz); 158.22, 150.54 (d, *J*<sub>C-F</sub> = 11.9 Hz), 148.55, 135.04, 130.31 (d, *J*<sub>C-F</sub> = 11.1 Hz), 126.83, 125.97, 114.84 (d, *J*<sub>C-F</sub> = 24.5 Hz), 113.00, 112.85, 111.23 (d, *J*<sub>C-F</sub> = 21.6 Hz); **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)**: δ -101.46; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 215.0615, found 215.0623.

### **3,8-difluoro-11H-pyrido[2,1-b]quinazolin-11-one (3de):**



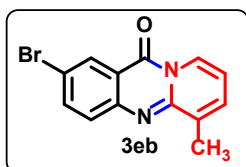
Compound **3de** (70 mg, yield = 91%) was isolated as a yellow solid; Mp: 176 - 180 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.82 – 8.72 (m, 1H), 8.45 (dd, *J* = 8.9, 6.2 Hz, 1H), 7.52 (d, *J* = 5.9 Hz, 2H), 7.41 (dd, *J* = 10.0, 2.3 Hz, 1H), 7.24 (dt, *J* = 8.8, 3.0 Hz, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 166.95 (d, *J*<sub>C-F</sub> = 255.8 Hz), 157.74 (d, *J*<sub>C-F</sub> = 2.1 Hz), 153.64, 151.21, 150.28 (d, *J*<sub>C-F</sub> = 14.1 Hz), 146.58, 130.10 (d, *J*<sub>C-F</sub> = 11.1 Hz), 128.12 (d, *J*<sub>C-F</sub> = 7.4 Hz), 115.60, 115.35, 112.44, 112.05, 111.53 (d, *J*<sub>C-F</sub> = 21.5 Hz); **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)**: δ -101.33, -136.58; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>7</sub>F<sub>2</sub>N<sub>2</sub>O [M+H]<sup>+</sup> is 233.0521, found 233.0521.

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



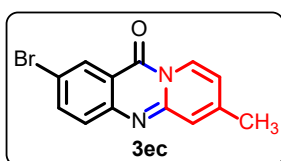
Compound **3ea** (84 mg, yield = 93%) was isolated as a brown solid; Mp: 166 - 168 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.83 (d, *J* = 7.4 Hz, 1H), 8.53 (d, *J* = 2.1 Hz, 1H), 7.86 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.44 (m, 2H), 6.88 (t, *J* = 6.4 Hz, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 157.86, 147.83, 147.29, 138.19, 134.48, 129.48, 128.75, 126.73, 126.38, 118.28, 117.38, 112.97; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> is 274.9815, found 274.9820.

### **2-bromo-6-methyl-11H-pyrido[2,1-b]quinazolin-11-one(3eb):<sup>6</sup>**



Compound **3eb** (87 mg, yield = 91%) was isolated as an off-white solid; Mp: 140 - 141 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.83 (d, *J* = 7.1 Hz, 1H), 8.55 (d, *J* = 2.1 Hz, 1H), 7.98 – 7.84 (m, 2H), 7.50 (d, *J* = 6.3 Hz, 1H), 6.90 (t, *J* = 6.9 Hz, 1H), 2.67 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 158.43, 147.73, 147.00, 137.90, 134.72, 132.65, 129.40, 129.35, 124.86, 118.12, 117.22, 112.60, 18.53; **HRMS** (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> is 288.9971, found 288.9979.

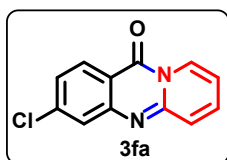
### **2-bromo-7-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3ec):<sup>6</sup>**



Compound **3ec** (89 mg, yield = 93%) was isolated as an off-white solid; Mp: 184 - 186 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.73 (d, *J* = 7.5 Hz, 1H), 8.48 (d, *J* = 2.2 Hz, 1H), 7.82 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 6.73 (dd, *J* = 7.5, 1.7 Hz, 1H), 2.40 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 157.72, 147.82, 147.22, 146.80, 138.16, 129.44, 128.27, 125.98, 123.49,

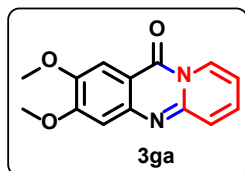
117.73, 116.92, 116.16, 21.52; **HRMS** (ESI) m/z calcd for C<sub>13</sub>H<sub>10</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> is 288.9971, found 288.9999.

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



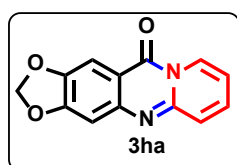
Compound **3fa** (69 mg, yield = 90%) was isolated as a yellow solid; Mp: 116 - 118 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.89 (d, *J* = 7.3 Hz, 1H), 8.38 (d, *J* = 8.7 Hz, 1H), 7.82 (s, 1H), 7.60 (d, *J* = 4.7 Hz, 2H), 7.43 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.95 (d, *J* = 5.2 Hz, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.33, 148.49, 141.57, 135.17, 128.86, 126.85, 126.06, 125.91, 114.49, 113.06; **HRMS** (ESI) m/z calcd for C<sub>12</sub>H<sub>8</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> is 231.0320, found 231.0322.

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



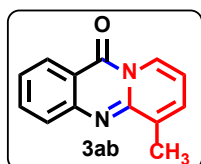
Compound **3ga** (76 mg, yield = 89%) was isolated as a yellow solid; Mp: 199 - 201 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.89 (d, *J* = 7.3 Hz, 1H), 7.70 (s, 1H), 7.53 - 7.42 (m, 2H), 7.15 (s, 1H), 6.89 - 6.85 (m, 1H), 4.03 (s, 6H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.79, 156.24, 148.58, 146.84, 145.42, 133.31, 126.58, 125.76, 112.44, 109.75, 106.35, 105.13, 77.32, 77.00, 76.68, 56.36, 56.32; **HRMS** (ESI) m/z calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> is 257.0921, found 257.0913.

### **11H-[1,3]dioxolo[4,5-g]pyrido[2,1-b]quinazolin-11-one (3ha):<sup>4</sup>**



Compound **3ha** (73 mg, yield = 92%) was isolated as an off-white solid; Mp: 244 - 246 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.84 (d, *J* = 7.4 Hz, 1H), 7.67 (s, 1H), 7.49 - 7.42 (m, 2H), 7.07 (s, 1H), 6.88 - 6.81 (m, 1H), 6.12 (s, 2H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.77, 154.50, 147.04, 146.75, 146.64, 133.45, 126.44, 125.77, 112.62, 111.10, 104.23, 103.00, 102.16; **HRMS** (ESI) m/z calcd for C<sub>13</sub>H<sub>9</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> is 241.0608, found 241.0607.

### **6-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3ab):<sup>1</sup>**



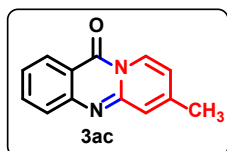
Compound **3ab** (64 mg, yield = 91%) was isolated as a yellowish solid; Mp: 127 - 129 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.79 (d, *J* = 7.4 Hz, 1H), 8.42 (d, *J* = 8.1 Hz, 1H), 7.84 - 7.78 (m, 2H), 7.45 (ddd, *J* = 8.1, 4.9, 3.1 Hz, 1H),



7.35 (d,  $J = 6.5$  Hz, 1H), 6.76 (t,  $J = 7.0$  Hz, 1H), 2.58 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**:  $\delta$  159.46, 148.21, 147.53, 134.67, 134.50, 132.12, 127.42, 127.13, 125.01, 124.79, 116.07, 112.02, 18.54; **HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  is 211.0866, found 211.0866.

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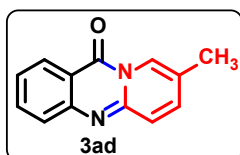
### **7-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3ac):<sup>1</sup>**



Compound **3ac** (63 mg, yield = 90%) was isolated as a yellow solid; Mp: 135 - 137 °C;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**:  $\delta$  8.69 (d,  $J = 7.5$  Hz, 1H), 8.34 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.78 - 7.72 (m, 1H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.40 - 7.32 (m, 1H), 7.19 (s, 1H), 6.62 (dd,  $J = 7.5, 1.7$  Hz, 1H), 2.33 (s, 1H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**:  $\delta$  158.77, 148.66, 147.63, 145.77, 134.83, 127.11, 126.48, 125.77, 124.55, 123.45, 115.81, 115.41, 21.31; **HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  is 211.0866, found 211.0873.

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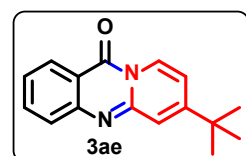
### **8-methyl-11H-pyrido[2,1-b]quinazolin-11-one (3ad):<sup>1</sup>**



Compound **3ad** (64 mg, yield = 92%) was isolated as a yellow solid; Mp: 130 - 132 °C;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**:  $\delta$  8.64 (s, 1H), 8.41 (d,  $J = 8.1$  Hz, 1H), 7.84 - 7.72 (m, 2H), 7.44 (t,  $J = 8.2$  Hz, 2H), 7.37 (d,  $J = 9.3$  Hz, 1H), 2.34 (s, 3H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**:  $\delta$  158.64, 148.10, 146.80, 137.67, 134.83, 127.21, 126.52, 125.46, 125.00, 123.47, 122.48, 116.01, 18.24; **HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  is 211.0866, found 211.0872.

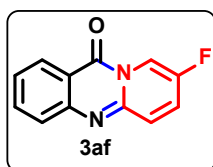
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### **7-(tert-butyl)-11H-pyrido[2,1-b]quinazolin-11-one (3ae):**



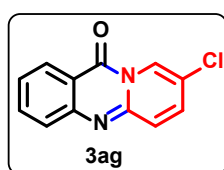
Compound **3ae** (67 mg, yield = 89%) was isolated as a yellow solid;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**:  $\delta$  8.79 (d,  $J = 7.8$  Hz, 1H), 8.40 (dd,  $J = 8.1, 0.9$  Hz, 1H), 7.79 (dd,  $J = 6.9, 1.4$  Hz, 1H), 7.73 (d,  $J = 8.2$  Hz, 1H), 7.46 - 7.36 (m, 2H), 6.92 (dd,  $J = 7.8, 2.0$  Hz, 1H), 1.36 (s, 9H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**:  $\delta$  158.71, 157.96, 148.82, 148.02, 134.79, 127.10, 126.46, 125.86, 124.53, 119.93, 115.91, 112.13, 35.06, 29.43; **HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  is 253.1335, found 253.1353.

### **8-fluoro-11H-pyrido[2,1-b]quinazolin-11-one (3af):<sup>1</sup>**



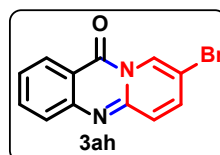
Compound **3af** (65 mg, yield = 91%) was isolated as a yellow solid; Mp: 174 - 176 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.78 (dd, *J* = 4.4, 2.6 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.56 – 7.47 (m, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.52, 152.38 (d, *J*<sub>C-F</sub> = 243.3 Hz), 148.16, 145.76, 135.11, 128.37 (d, *J*<sub>C-F</sub> = 7.4 Hz), 127.76 (d, *J*<sub>C-F</sub> = 27.4 Hz), 127.16, 127.11, 125.93, 115.67, 112.11 (d, *J*<sub>C-F</sub> = 41.8 Hz); **<sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)** δ -137.06; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> is 215.0615, found 215.0616.

### **8-chloro-11H-pyrido[2,1-b]quinazolin-11-one (3ag):<sup>1</sup>**



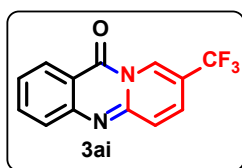
Compound **3ag** (70 mg, yield = 92%) was isolated as a yellow solid; Mp: 166 - 167 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.82 (dd, *J* = 1.8, 1.0 Hz, 1H), 8.38 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.81 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.40 – 7.38 (m, 2H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.85, 148.00, 145.75, 135.44, 135.15, 127.32, 127.27, 127.04, 125.81, 124.08, 121.02, 116.06; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> is 231.0320, found 231.0325.

### **8-bromo-11H-pyrido[2,1-b]quinazolin-11-one (3ah):<sup>1</sup>**



Compound **3ah** (82 mg, yield = 91%) was isolated as a light brown solid. Mp: 164 - 166 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.95 (s, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.36 (dd, *J* = 9.7, 0.8 Hz, 1H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.83, 148.03, 145.81, 137.45, 135.24, 127.36, 127.34, 127.06, 126.50, 125.85, 116.17, 107.60; **HRMS** (ESI) *m/z* calcd for C<sub>12</sub>H<sub>8</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> is 274.9815, found 274.9814.

### **8-(trifluoromethyl)-11H-pyrido[2,1-b]quinazolin-11-one (3ai):<sup>1</sup>**

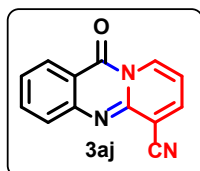


Compound **3ai** (78 mg, yield = 89%) was isolated as a white solid; Mp: 160-162 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 9.24 – 9.17 (m, 1H), 8.46 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.90 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.50 (m, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.62, 148.19, 146.69, 135.84, 128.93 (d, *J*<sub>C-F</sub> = 2.3 Hz), 127.76, 127.58, 127.35, 126.60 (q, *J*<sub>C-F</sub> = 6.0 Hz), 126.39, 122.90 (q, *J*<sub>C-F</sub> = 271.2 Hz), 116.58, 116.47 (d, *J*<sub>C-F</sub> = 35.0 Hz); **<sup>19</sup>F NMR (375**

**MHz, CDCl<sub>3</sub>):**  $\delta$  -63.75; **HRMS** (ESI)  $m/z$  calcd for C<sub>13</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O [M+H]<sup>+</sup> is 265.0583, found 265.0586.

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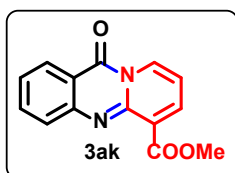
### **11-oxo-11H-pyrido[2,1-b]quinazoline-6-carbonitrile (3aj):**



Compound **3aj** (64 mg, yield = 87%) was isolated as a yellow solid; Mp: 228 - 230 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.99 (d,  $J$  = 7.4 Hz, 1H), 8.44 (d,  $J$  = 8.2 Hz, 1H), 8.00 (d,  $J$  = 6.8 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.61 – 7.52 (m, 1H), 6.89 (t,  $J$  = 7.1 Hz, 1H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  158.34, 147.66, 144.49, 142.31, 135.93, 131.13, 127.86, 127.39, 126.72, 116.66, 114.72, 111.49, 110.53; **HRMS** (ESI)  $m/z$  calcd for C<sub>13</sub>H<sub>8</sub>N<sub>3</sub>O [M+H]<sup>+</sup> is 222.0662, found 222.0674.

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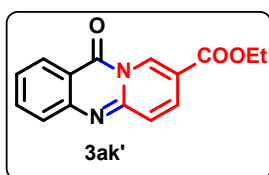
### **Methyl 11-oxo-11H-pyrido[2,1-b]quinazoline-6-carboxylate (3ak):**



Compound **3ak** (69 mg, yield = 91%) was isolated as a yellow solid; Mp: 228 - 230 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.64 (dd,  $J$  = 4.8, 1.9 Hz, 1H), 8.51 (dd,  $J$  = 7.7, 1.9 Hz, 1H), 8.38 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.85 (d,  $J$  = 8.4 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.47 (dd,  $J$  = 7.7, 4.8 Hz, 1H), 7.35 (t,  $J$  = 7.7 Hz, 1H), 3.83 (s, 3H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  166.61, 163.39, 156.01, 152.47, 142.04, 138.85, 135.83, 132.28, 124.96, 123.16, 119.39, 118.75, 115.89, 52.77; **HRMS** (ESI)  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O [M+H]<sup>+</sup> is 255.0764, found 255.0767.

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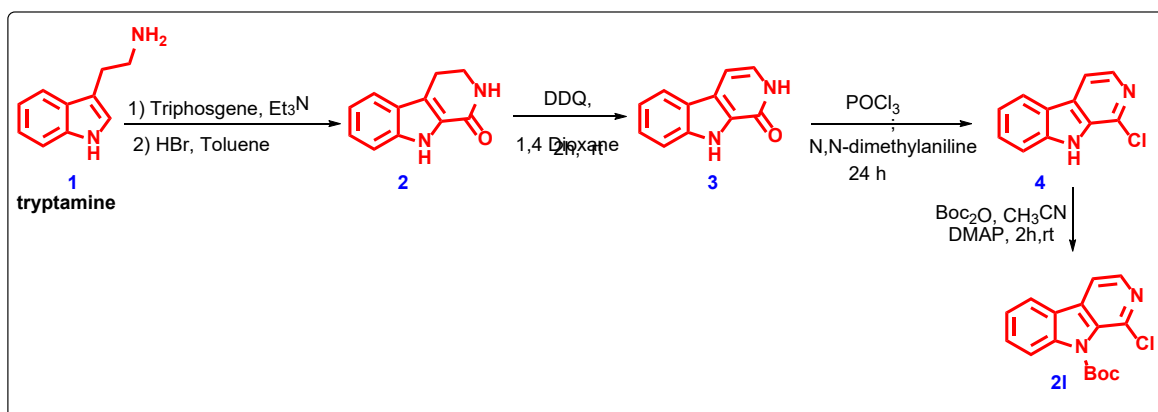
### **Ethyl 11-oxo-11H-pyrido[2,1-b]quinazoline-8-carboxylate (3ak')**



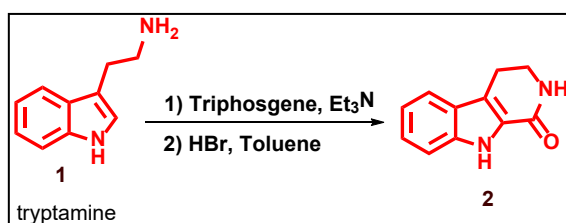
Compound **3ak'** (72 mg, yield = 90%) was isolated as a yellow solid; Mp: 228 - 230 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  9.52 (d,  $J$  = 1.6 Hz, 1H), 8.41 (d,  $J$  = 8.1 Hz, 1H), 7.92 (dd,  $J$  = 9.5, 1.9 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.76 (d,  $J$  = 8.2 Hz, 1H), 7.48 (t,  $J$  = 7.5 Hz, 1H), 7.44 (d,  $J$  = 9.5 Hz, 1H), 4.42 (q,  $J$  = 7.1 Hz, 2H), 1.42 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  163.90, 158.75, 148.10, 147.22, 135.70, 132.61, 131.51, 127.56, 127.07, 125.93, 125.87, 116.58, 116.32, 61.83, 14.26; **HRMS** (ESI)  $m/z$  calcd for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> is 269.0921, found 269.0931.

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### **Schematic route for the synthesis of tert-butyl 1-chloro-9H-pyrido[3,4-b]indole-9-carboxylate(2l) from Tryptamine (1):**



## Experimental Procedure for the Synthesis of 2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-one (2):<sup>7</sup>



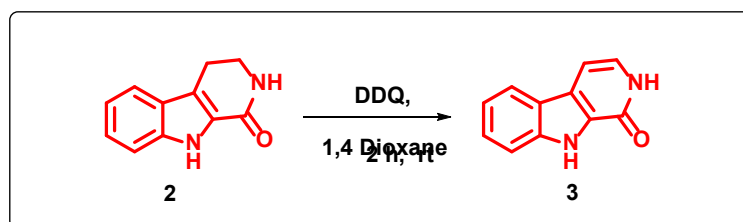
Tryptamine **1** (3.0 g, 18.7 mmol, 1.0 equiv.) was dissolved in toluene (267 mL) and warmed to increase solubility. Once completely dissolved, the solution was cooled to room temperature and sparged with a stream of nitrogen for 5 minutes. Triethylamine (6.3 mL, 45.2 mmol, 2.4 equiv.) was then added to the reaction mixture. In an addition funnel, triphosphogene (2.2 g, 7.50 mmol, 0.40 equiv.) was dissolved in toluene (11.8 mL) and added dropwise to the reaction mixture over 5 minutes. The yellowish-brown solution was left to stir at room temperature for 1 hour. A solution of 48% HBr in acetic acid (4.3 mL) was added to the reaction mixture in a steady stream over 30 seconds. The resulting greenish-yellow solution was heated at reflux for 1 hour. The solution was then cooled to roughly 4 °C and water (150 mL) was added to the product mixture dropwise. The diluted mixture was then poured into a separatory funnel and extracted with ethyl acetate (4 x 60 mL). The organic layer was then dried over magnesium sulfate, filtered, and concentrated. The residue obtained was recrystallized using ethyl acetate (15 mL) to yield the solid, pale-yellow cyclized crude product **2** (1.99 g) as a yellow solid in 58% yield. The spectra of crude **2** were consistent with a literature procedure.<sup>5</sup>

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 10.41 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 13.2, 5.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 3.73 (td, *J* = 7.0, 2.5

Hz, 2H), 3.07 (t,  $J = 7.0$  Hz, 2H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  163.75, 137.60, 126.32, 125.23, 125.15, 120.29, 120.20, 119.98, 112.76, 42.18, 20.86.

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### **Experimental Procedure for the Synthesis of 2,9-dihydro-1H-pyrido[3,4-b]indol-1-one (3):**<sup>8</sup>

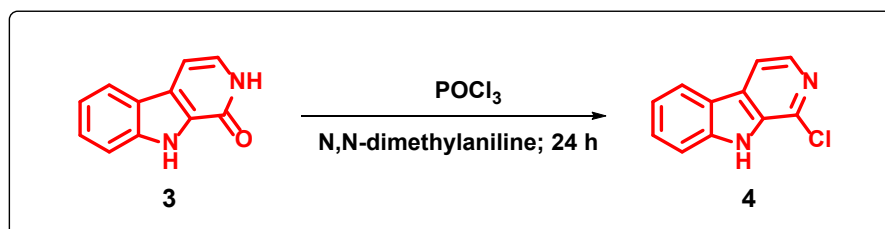


The crude Lactam **2** (750 mg, 4.0 mmol, 1.0 equiv.) was dissolved in anhydrous dioxane (57.3 mL), cooled to 15 °C, and sparged with a stream of nitrogen for 5 minutes. In a separate flask, 2,3 - dichloro-5,6-dicyano-1,4-benzoquinone (1.098 g, 4.839 mmol, 1.200 equiv.) was dissolved in anhydrous dioxane, sparged with a stream of nitrogen for 5 minutes, and then added to the reaction flask containing **2**. The reddish brown solution was warmed to room temperature and stirred for 2 hours. The product mixture was then poured into a separatory funnel containing 120 mL water. The diluted mixture was extracted with ethyl acetate (3 x 40 mL). The organic layer obtained was washed with 0.1 M sodium hydroxide (4 x 40 mL). The combined organic layers obtained were then dried over magnesium sulfate, filtered, and concentrated to provide an orange-brown solid **3** (707 mg, 94%), whose spectra were consistent with a literature procedure.

**$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )**:  $\delta$  11.96 (s, 1H), 11.43 (s, 1H), 8.03 (d,  $J = 7.9$  Hz, 1H), 7.52 (d,  $J = 8.3$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.18 (t,  $J = 7.5$  Hz, 1H), 7.09 (s, 1H), 6.99 (d,  $J = 6.8$  Hz, 1H);  **$^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )**:  $\delta$  156.15, 139.42, 128.46, 126.68, 125.00, 124.70, 122.42, 121.79, 119.93, 112.90, 100.19.

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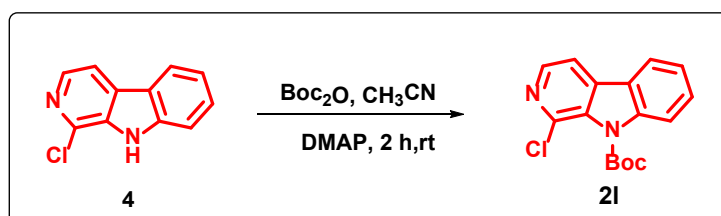
### **Experimental Procedure for the Synthesis of 1-chloro-9H-pyrido[3,4-b]indole (4):**



Compound **3** (400 mg, 2.17 mmol, 1.0 equiv.) was taken in N, N-dimethylaniline (10 mL), and phosphorus oxychloride was added dropwise to the reaction, heated under reflux in an oil bath (125 °C) for 24 hours. Then the solution was poured onto ice and neutralized with sodium carbonate. It is then extracted with ethyl acetate (4 x 30 mL), the combined organic phase is dried with magnesium sulfate and the solvent was evaporated under reduced pressure to get the crude product **4**. The crude product was purified by column chromatography using 20% (ethyl acetate: hexane) on 100-200 mesh silica gel to get the product **4** in 50 % yield (220 mg); **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.67 (s, 1H), 8.24 (d, *J* = 5.2 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 5.2 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.38 – 7.30 (m, 1H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 139.94, 138.54, 133.85, 132.76, 130.62, 129.04, 122.01, 121.84, 120.78, 114.31, 111.90.

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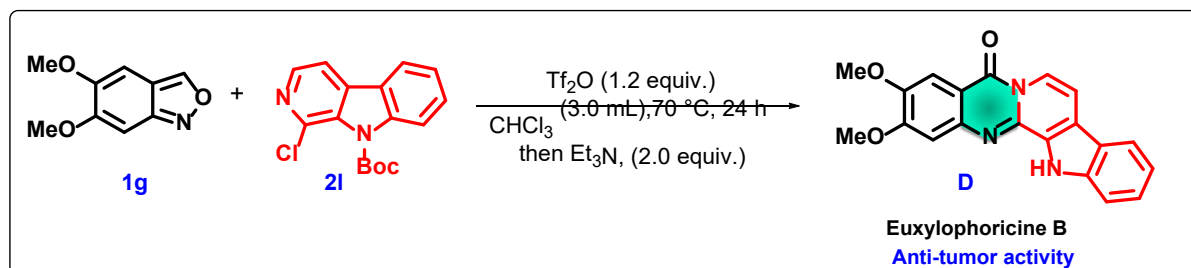
### **Experimental Procedure for the Synthesis of *tert*-butyl 1-chloro-9H-pyrido[3,4-*b*]indole-9-carboxylate (**21**):**



Compound **4** (250 mg, 1.23 mmol, 1.0 equiv.) was dissolved in dry acetonitrile (7 mL). Di-*tert*-butyldicarbonate (512 mg, 2.35 mmol, 1.9 equiv.) was added as a neat liquid. DMAP (150 mg, 1.23 mmol, 1.0 equiv.) was added in one portion. The reaction mixture was stirred for 2 hours. After column chromatography (15% ethyl acetate: hexane) an off-white solid product **21** (186 mg, yield = 50%) was obtained; Mp: 83 - 85 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.36 (d, *J* = 5.1 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 5.1 Hz, 1H), 7.67 – 7.57 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 1.71 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.22, 142.32, 140.92, 138.17, 135.86, 132.34, 130.22, 123.59, 123.07, 121.21, 115.03, 113.34, 85.46, 27.95; **HRMS** (ESI) *m/z* calcd for C<sub>16</sub>H<sub>16</sub>ClN<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> is 303.0895, found 303.0887.

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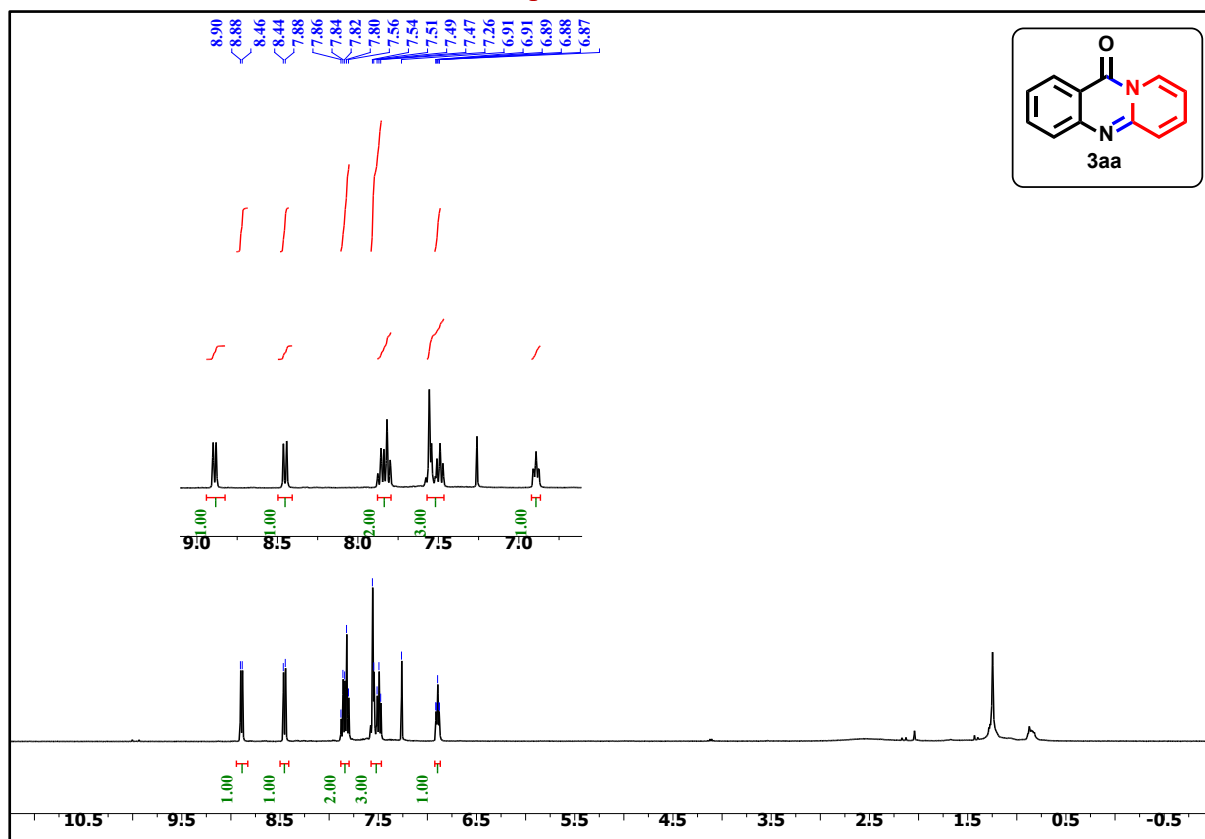
**Experimental Procedure for the synthesis of 2,3-dimethoxyindolo[2',3':3,4]pyrido[2,1-b]quinazolin-5(13H)-one (Euxylophoricine - B) (D):**



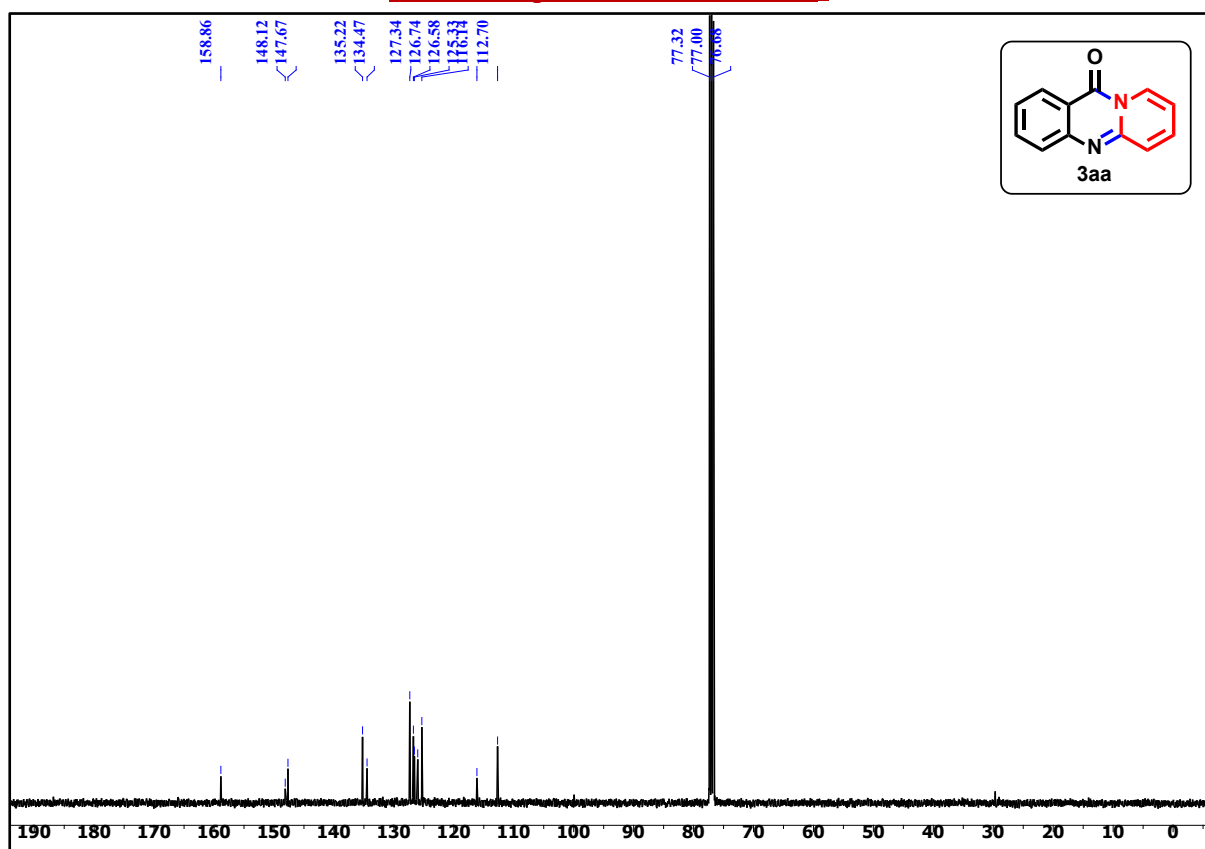
The Euxylophorocone B (**3gl**) was prepared following the same experimental procedure as described for **3aa**. Isolated as yellow solid; 56% yield; Mp: 228 - 230 °C; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 10.22 (s, 1H), 8.75 (d, *J* = 7.1 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.56 – 7.44 (m, 3H), 7.38 – 7.28 (m, 1H), 7.11 (s, 1H), 4.03 (s, 3H), 3.95 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 158.16, 156.03, 148.21, 144.35, 139.37, 129.27, 127.09, 122.55, 121.15, 120.76, 120.54, 118.66, 112.19, 109.87, 107.38, 105.79, 56.31, 56.23; **HRMS** (ESI) *m/z* calcd for C<sub>20</sub>H<sub>16</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup> is 346.1186, found 346.1177.

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**<sup>1</sup>H NMR spectra of 3aa in CDCl<sub>3</sub>**

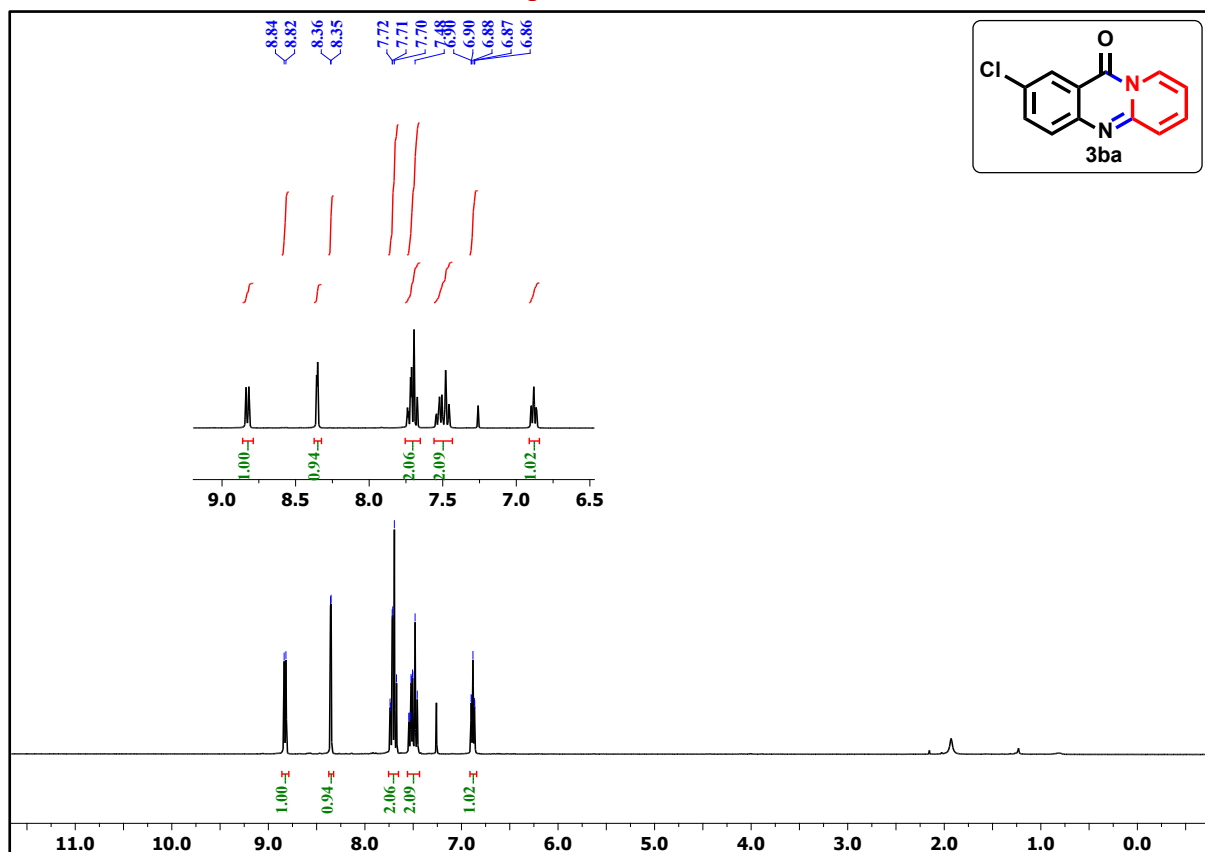


**<sup>13</sup>C NMR spectra of 3aa in CDCl<sub>3</sub>**

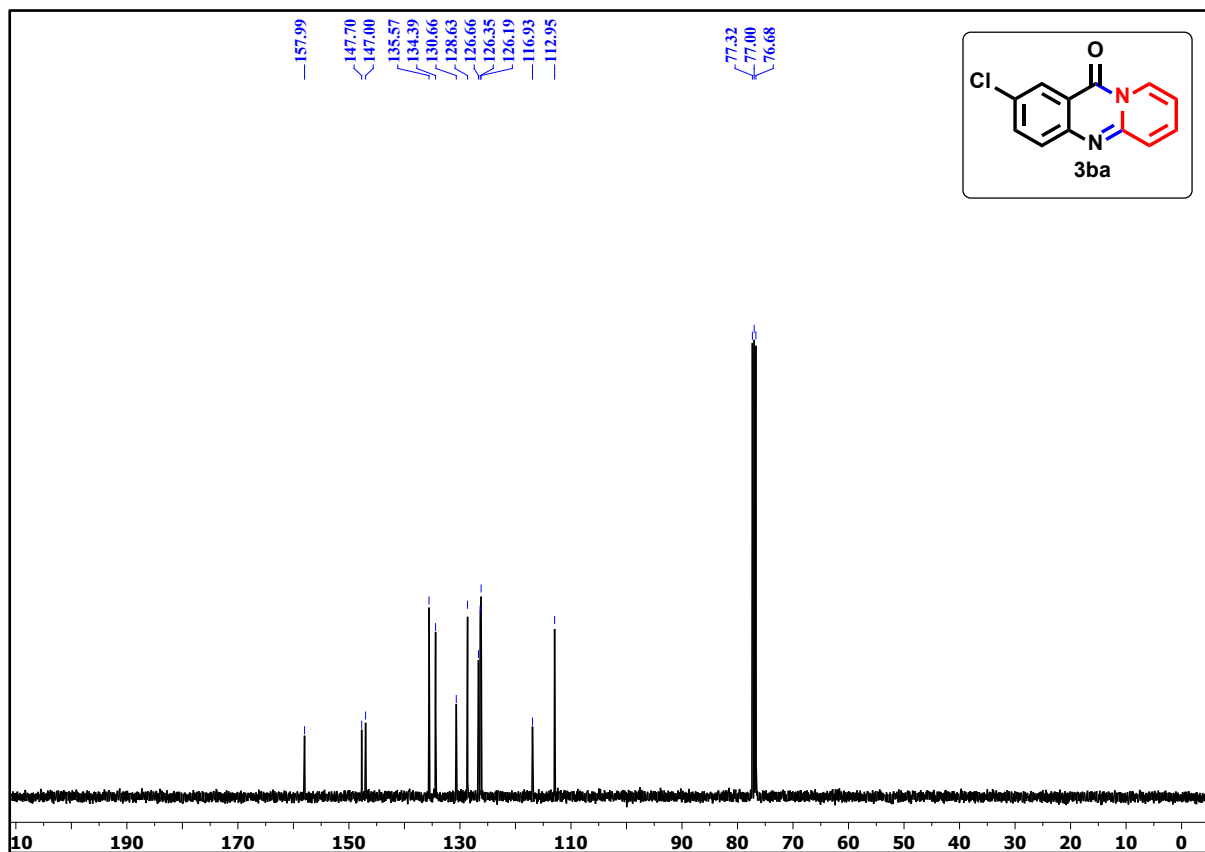




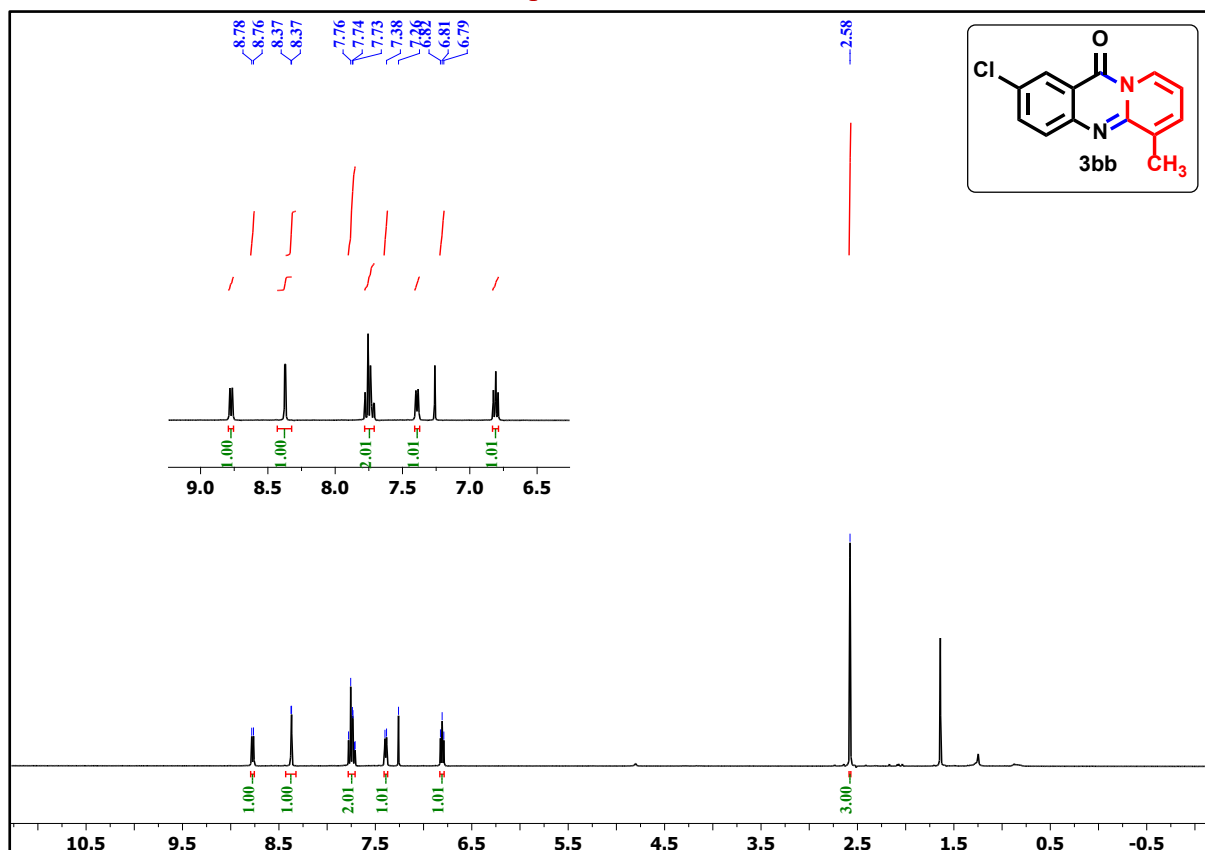
**<sup>1</sup>H NMR spectra of 3ba in CDCl<sub>3</sub>**



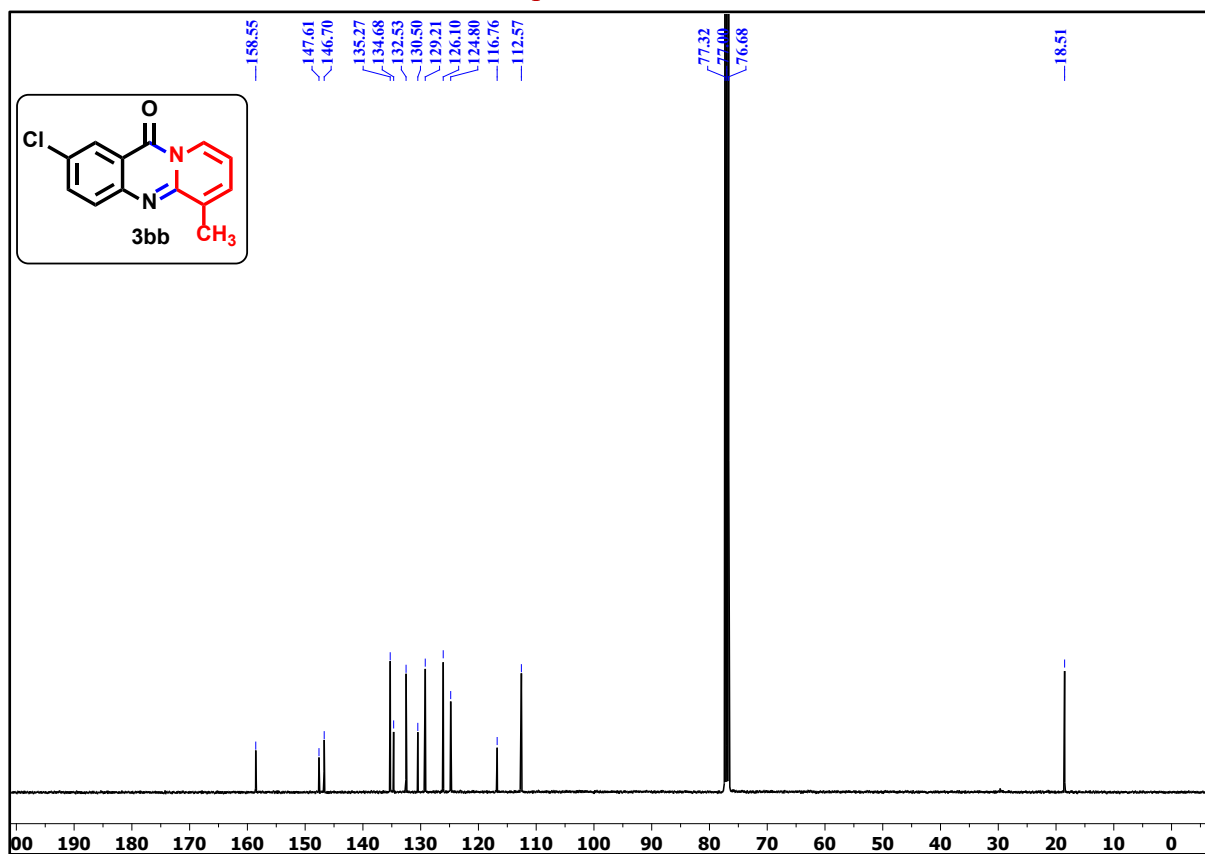
**<sup>13</sup>C NMR spectra of 3ba in CDCl<sub>3</sub>**



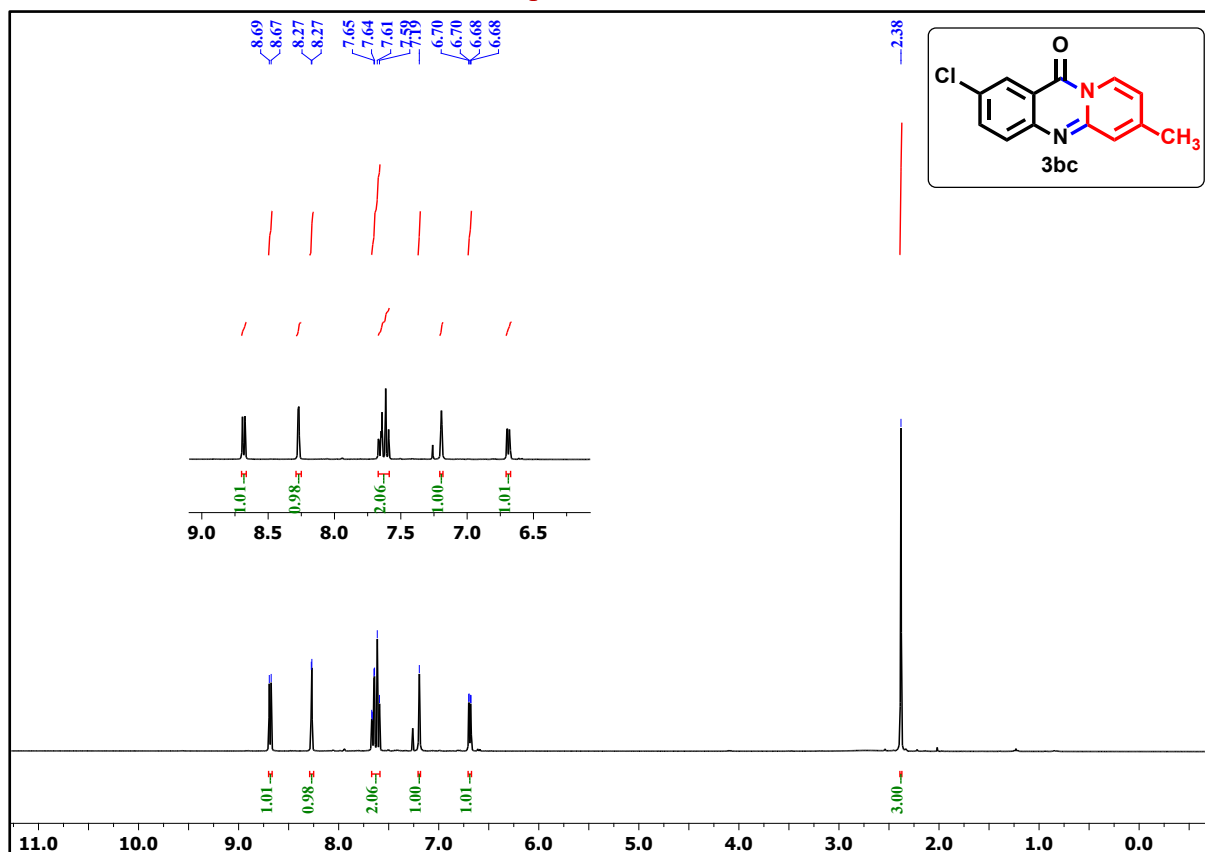
**<sup>1</sup>H NMR spectra of 3bb in CDCl<sub>3</sub>**



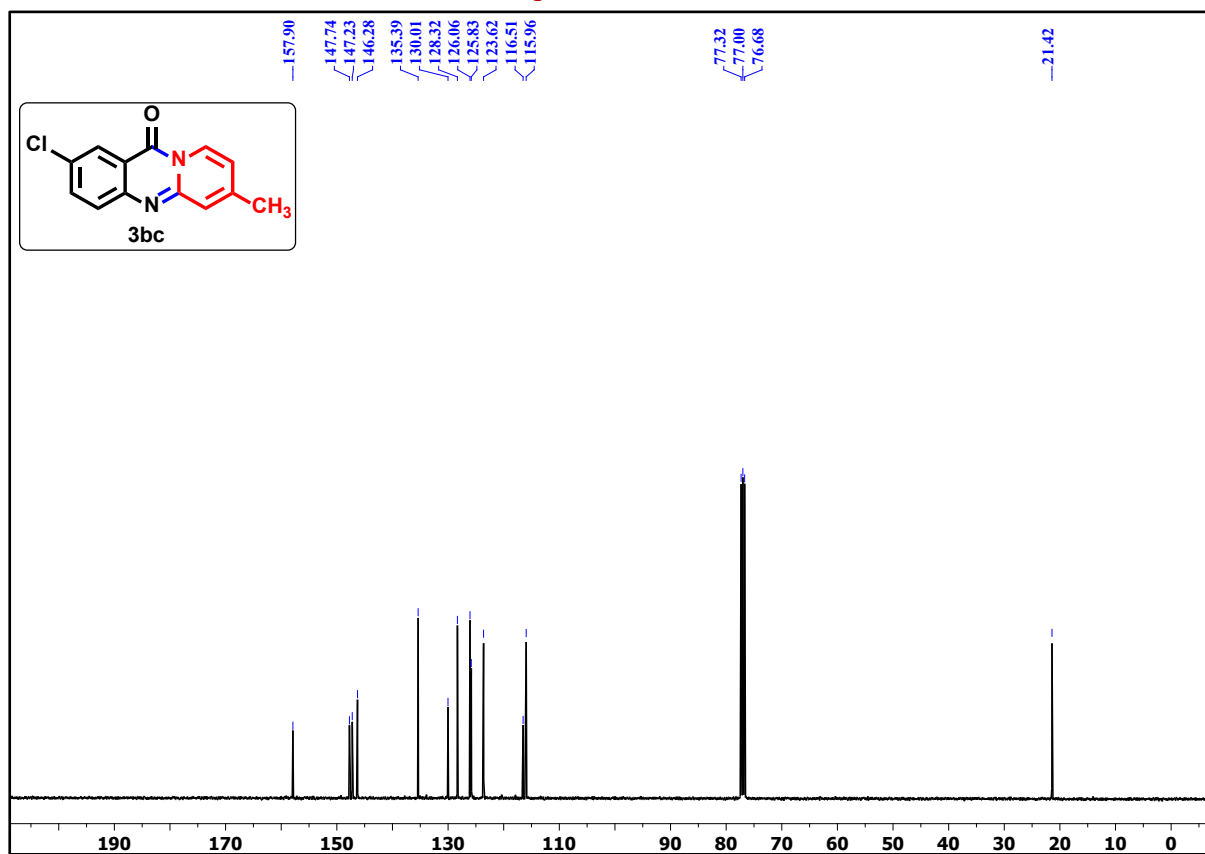
**<sup>13</sup>C NMR spectra of 3bb in CDCl<sub>3</sub>**



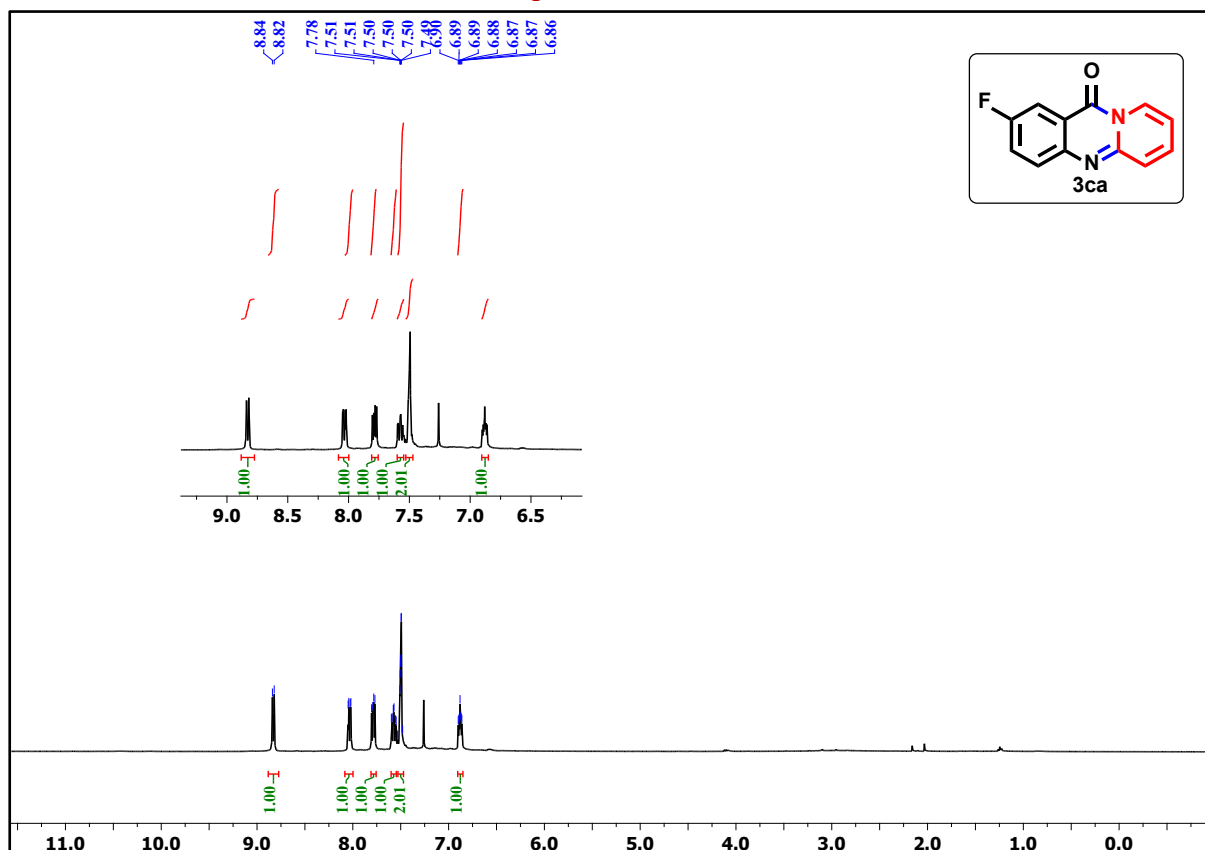
**<sup>1</sup>H NMR spectra of 3bc in CDCl<sub>3</sub>**



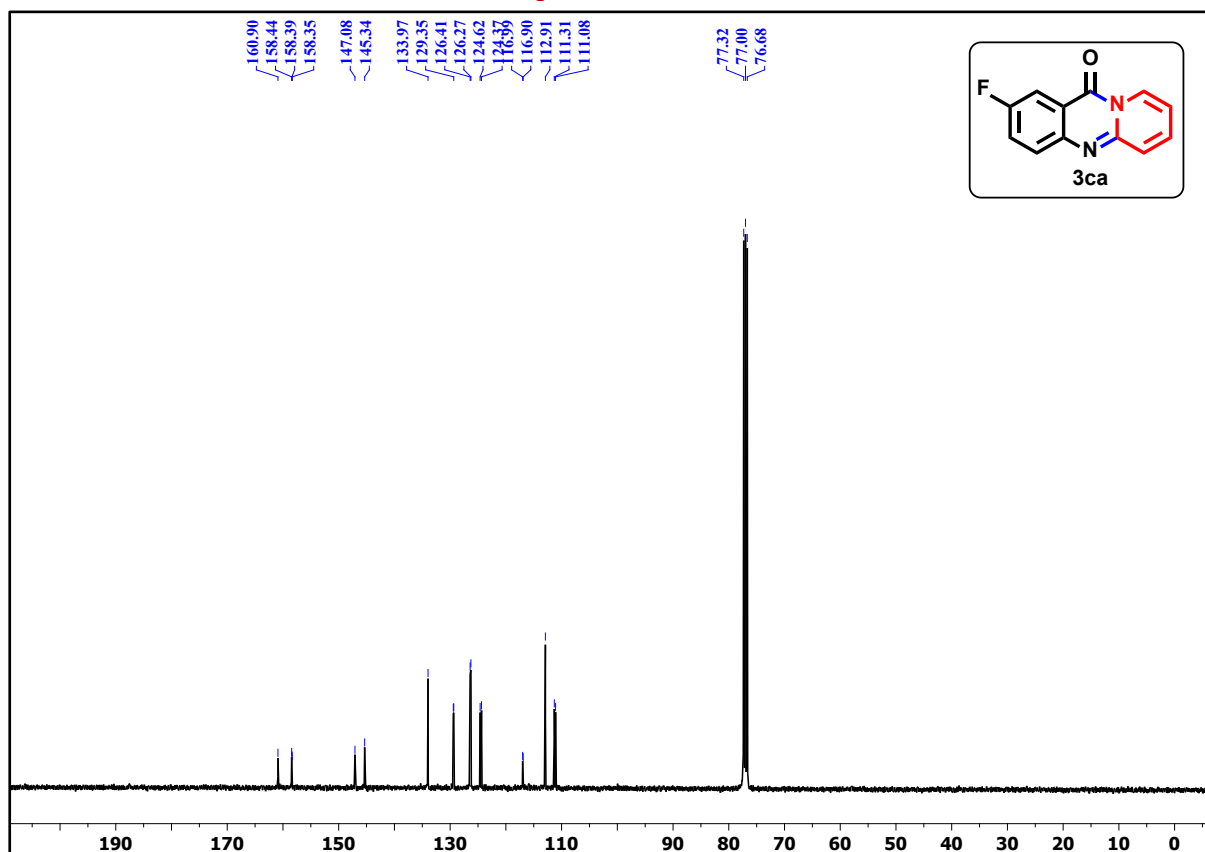
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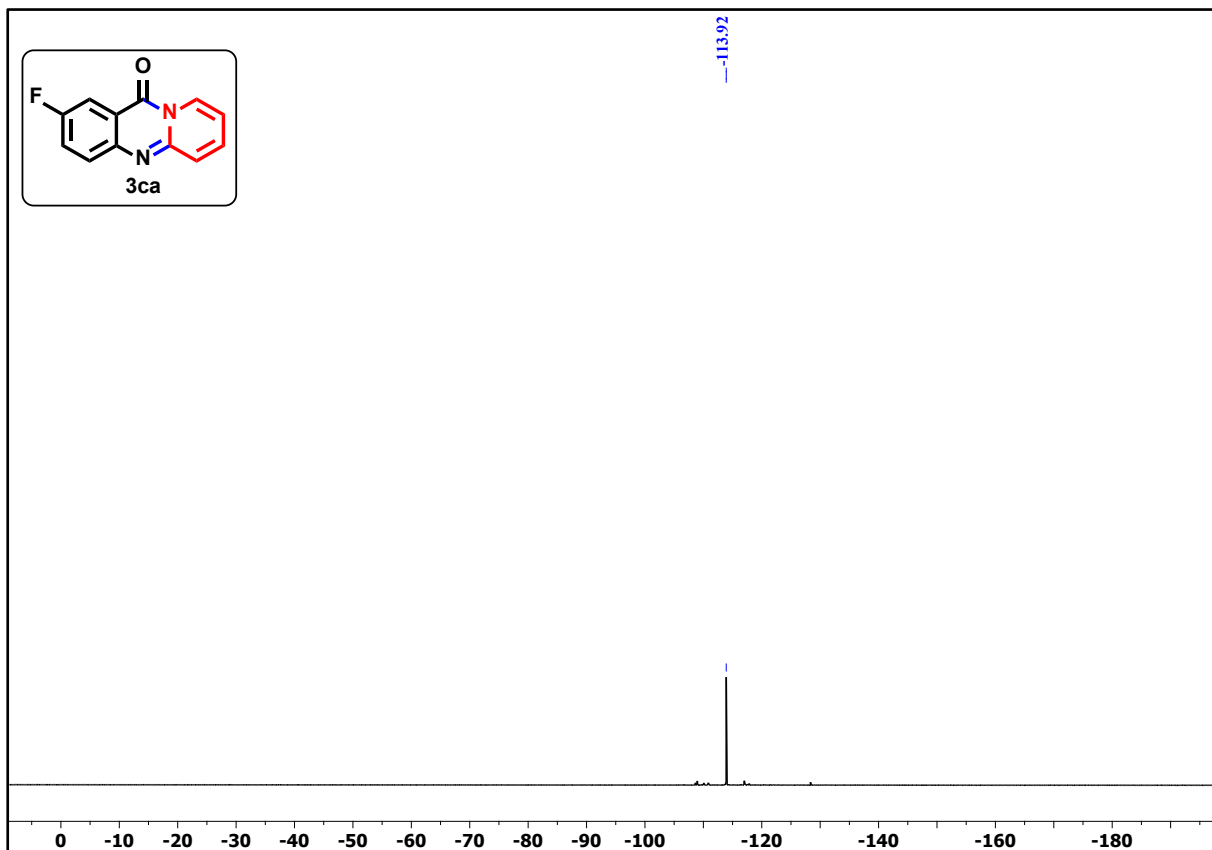
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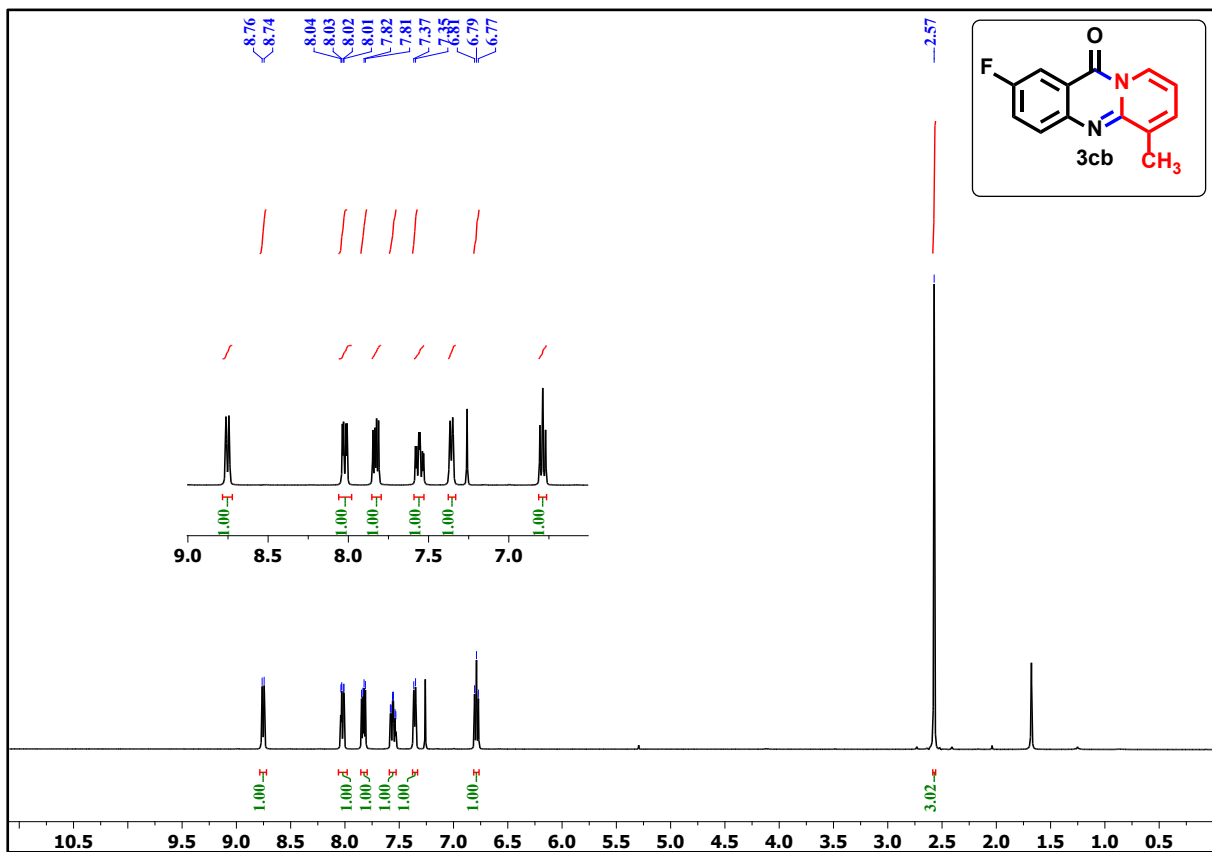
**<sup>13</sup>C NMR spectra of 3ca in CDCl<sub>3</sub>**



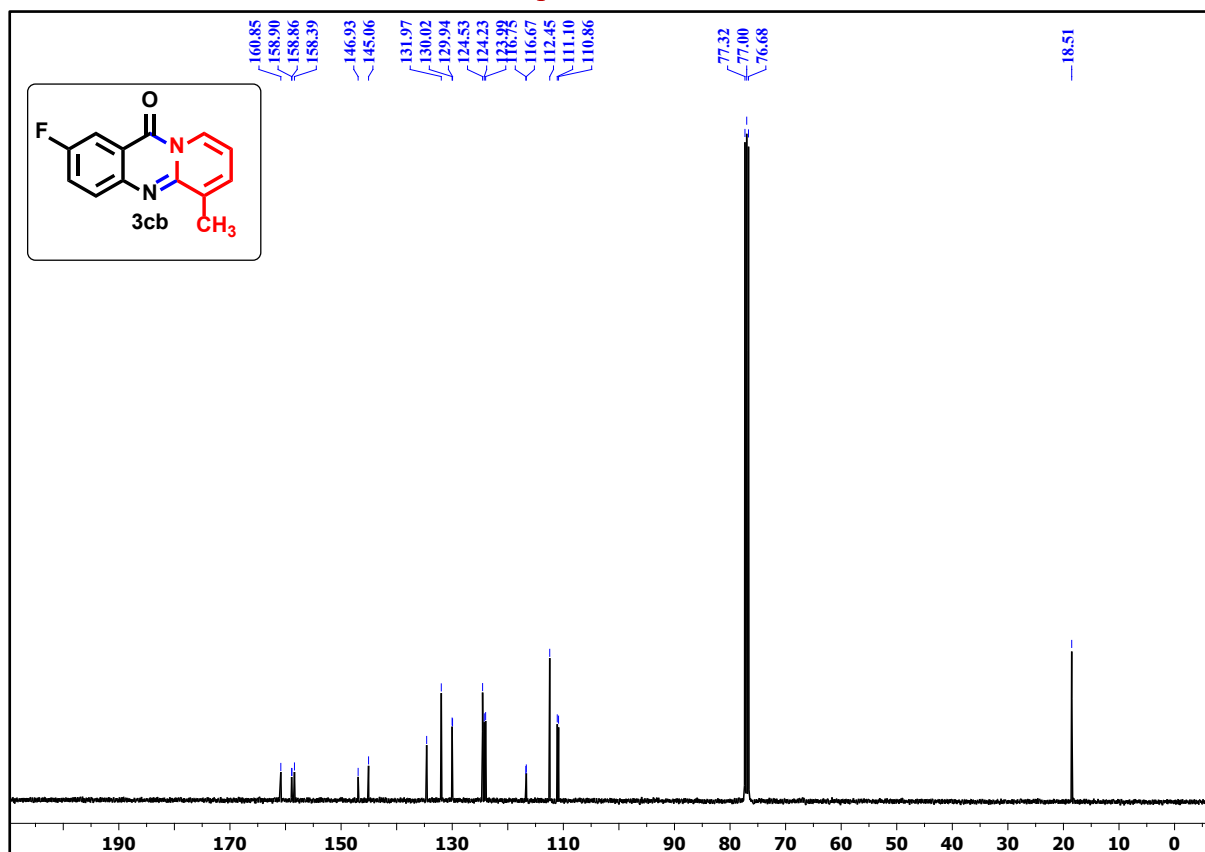
**<sup>19</sup>F NMR spectra of 3ca in CDCl<sub>3</sub>**



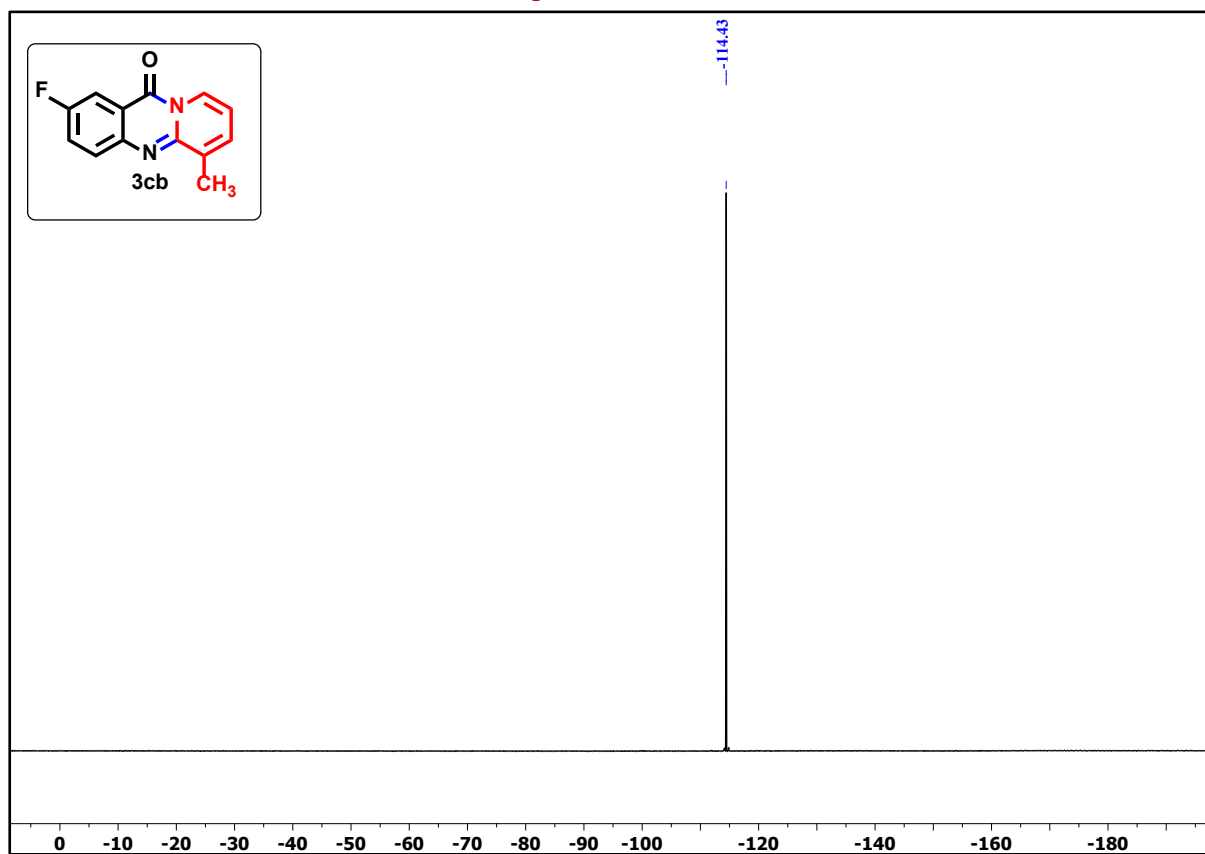
**<sup>1</sup>H NMR spectra of 3cb in CDCl<sub>3</sub>**



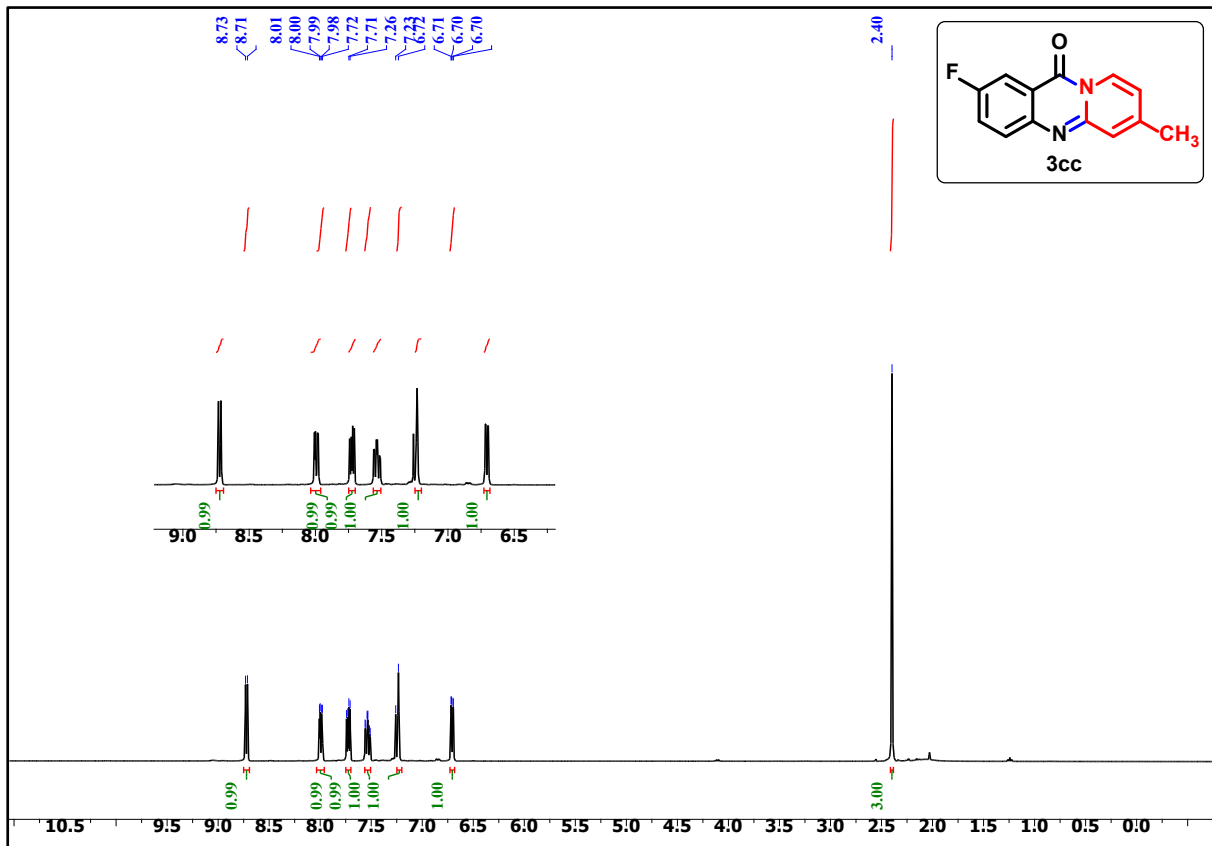
**<sup>13</sup>C-NMR spectra of 3cb in CDCl<sub>3</sub>**



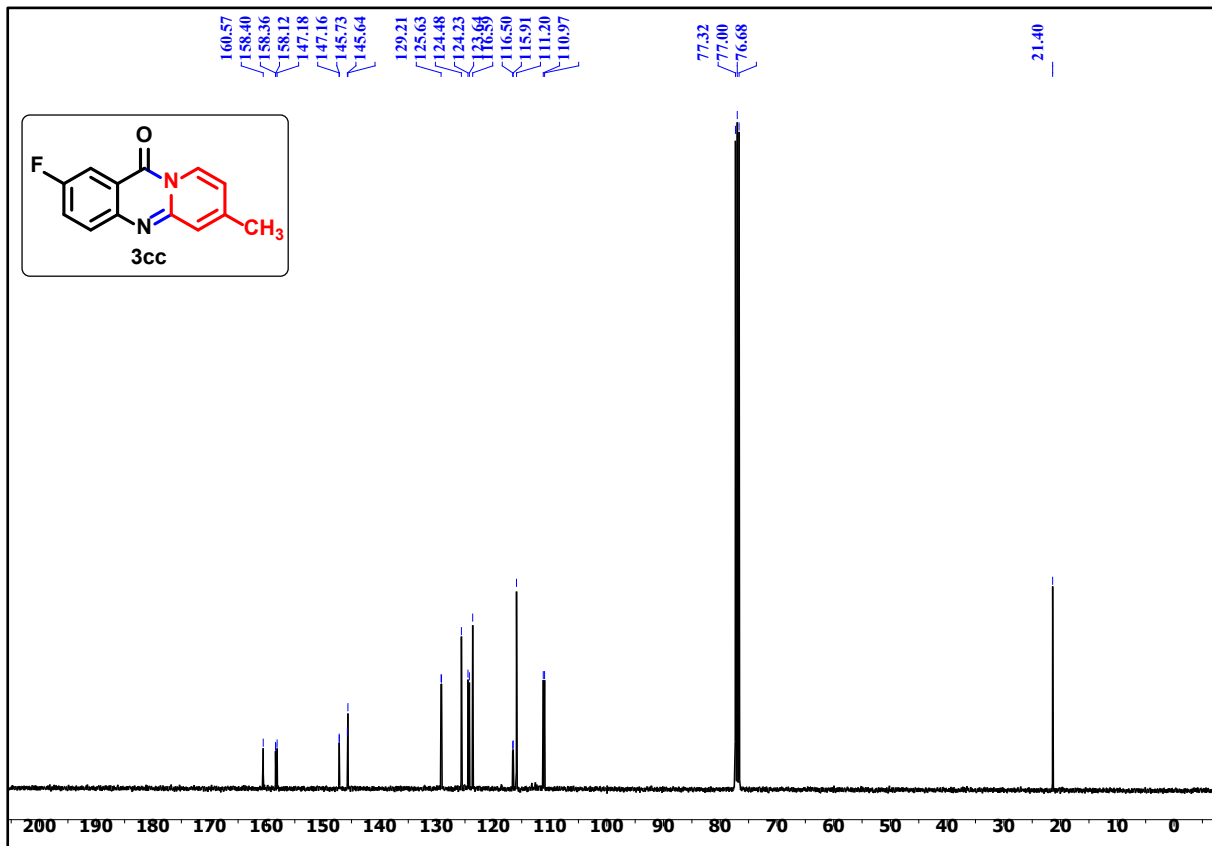
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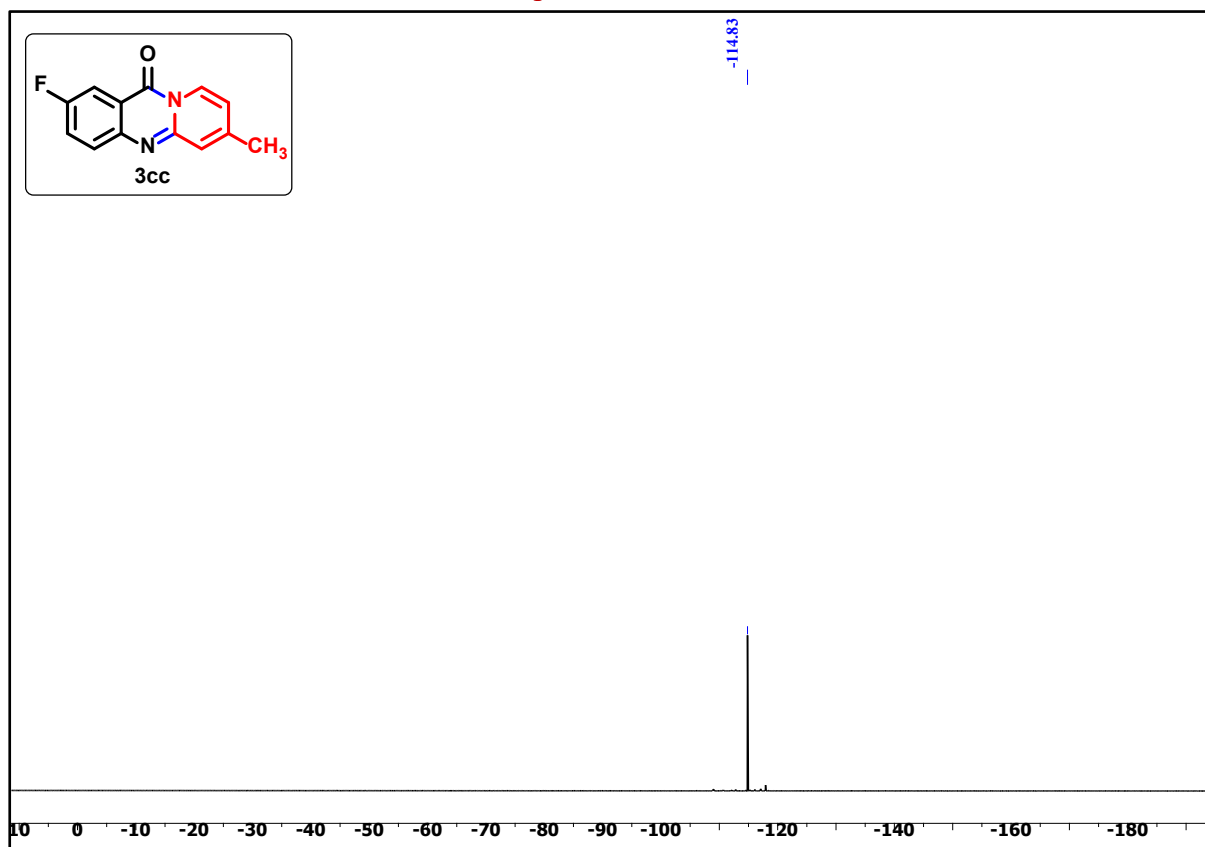
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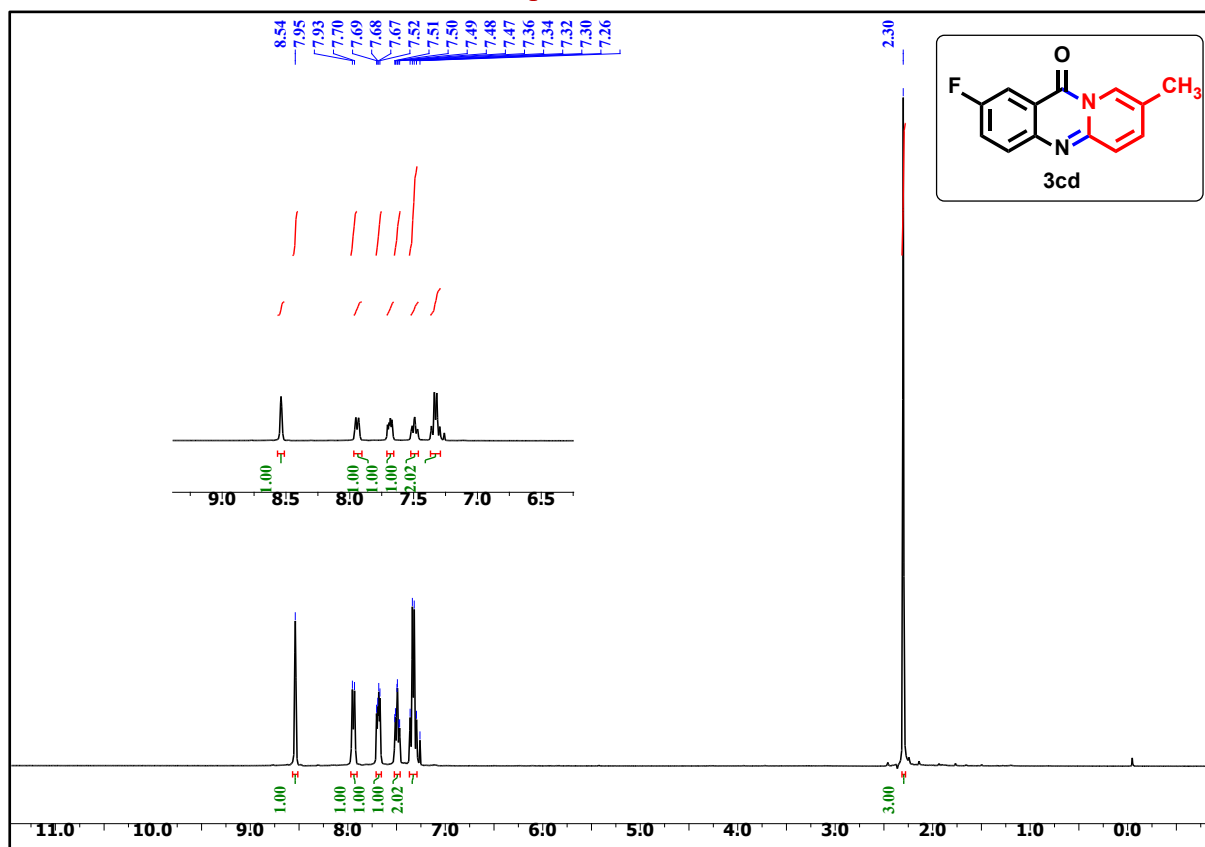
**<sup>13</sup>C NMR spectra of 3cc in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR spectra of 3cc in CDCl<sub>3</sub>**

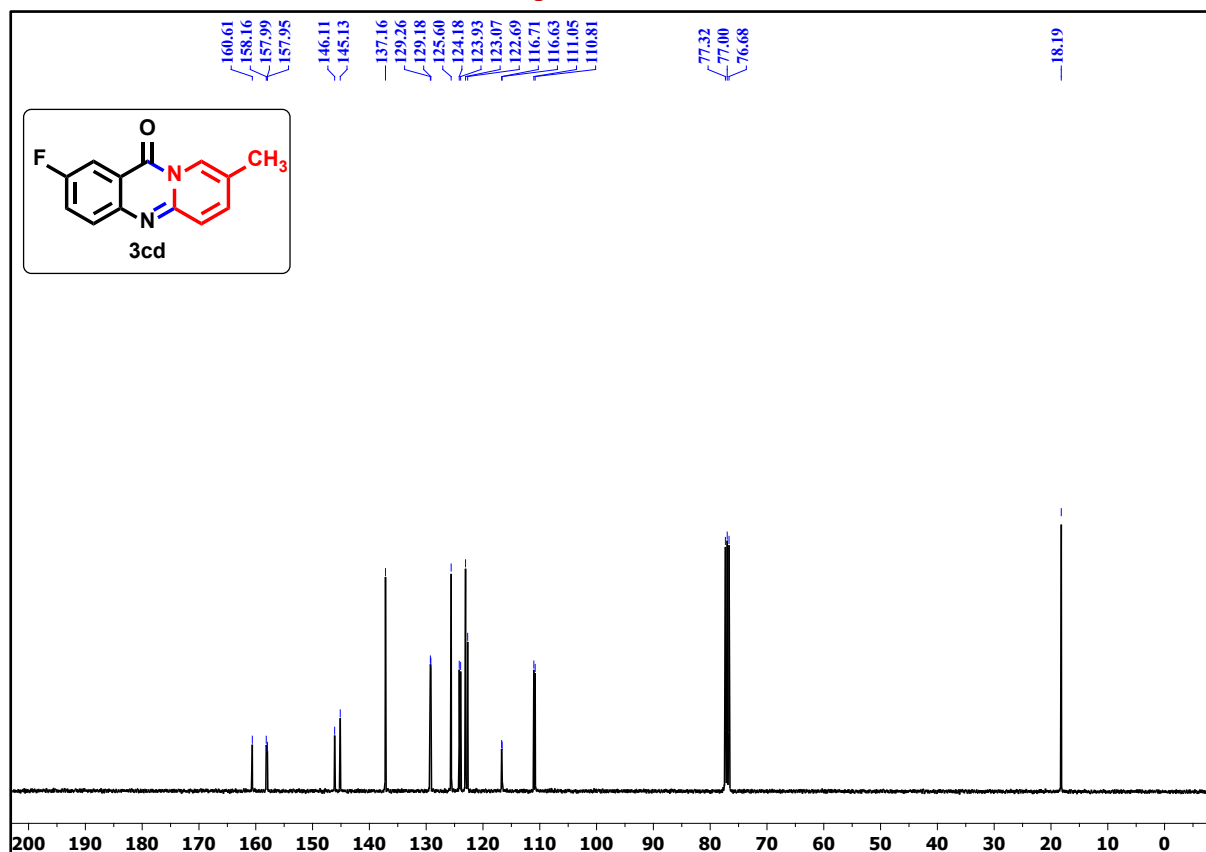


**<sup>1</sup>H NMR spectra of 3cd in CDCl<sub>3</sub>**

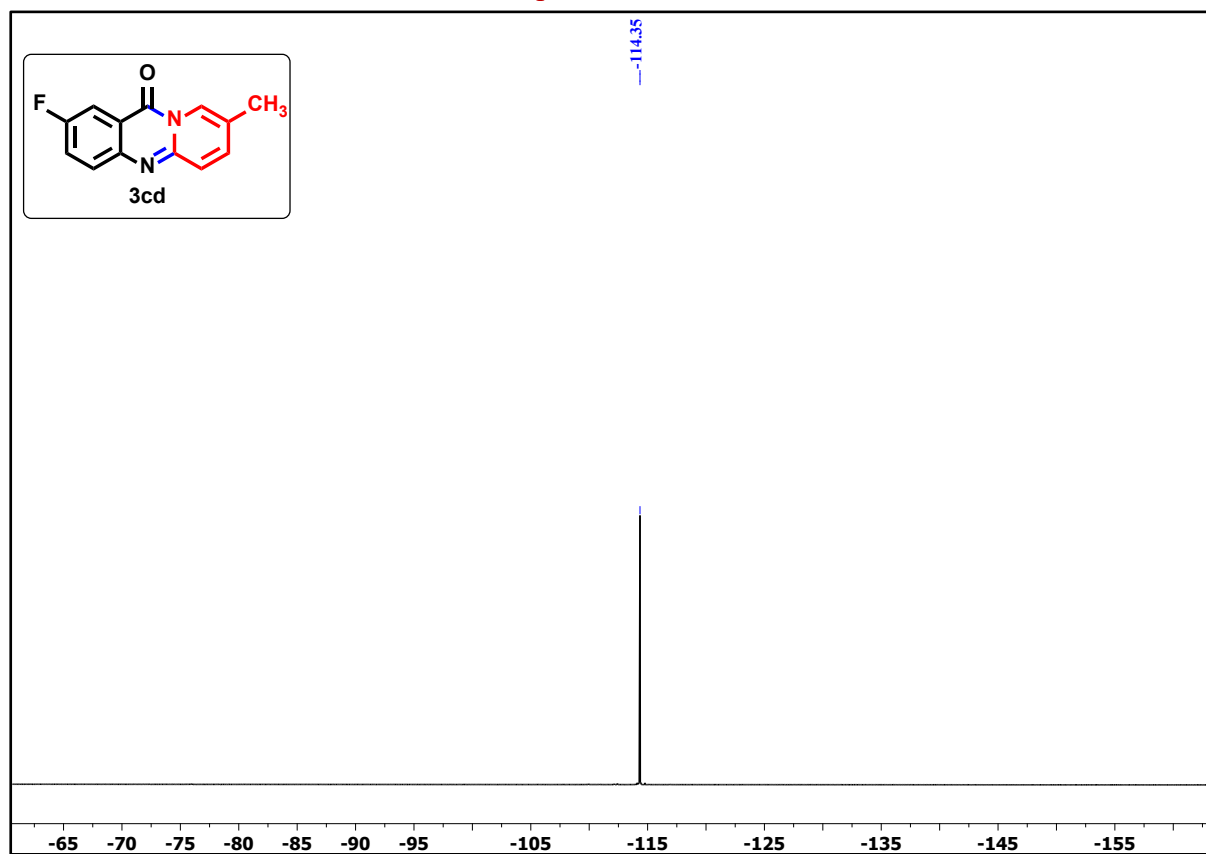




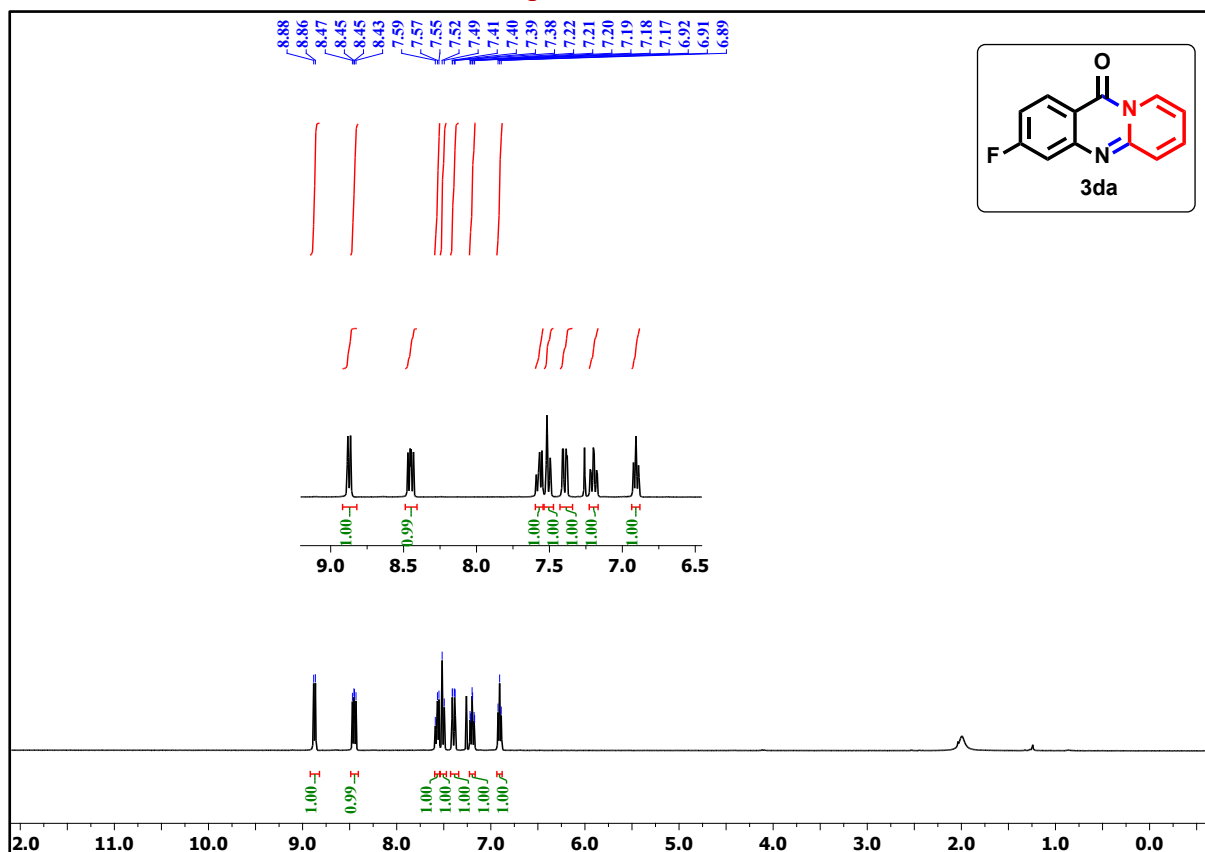
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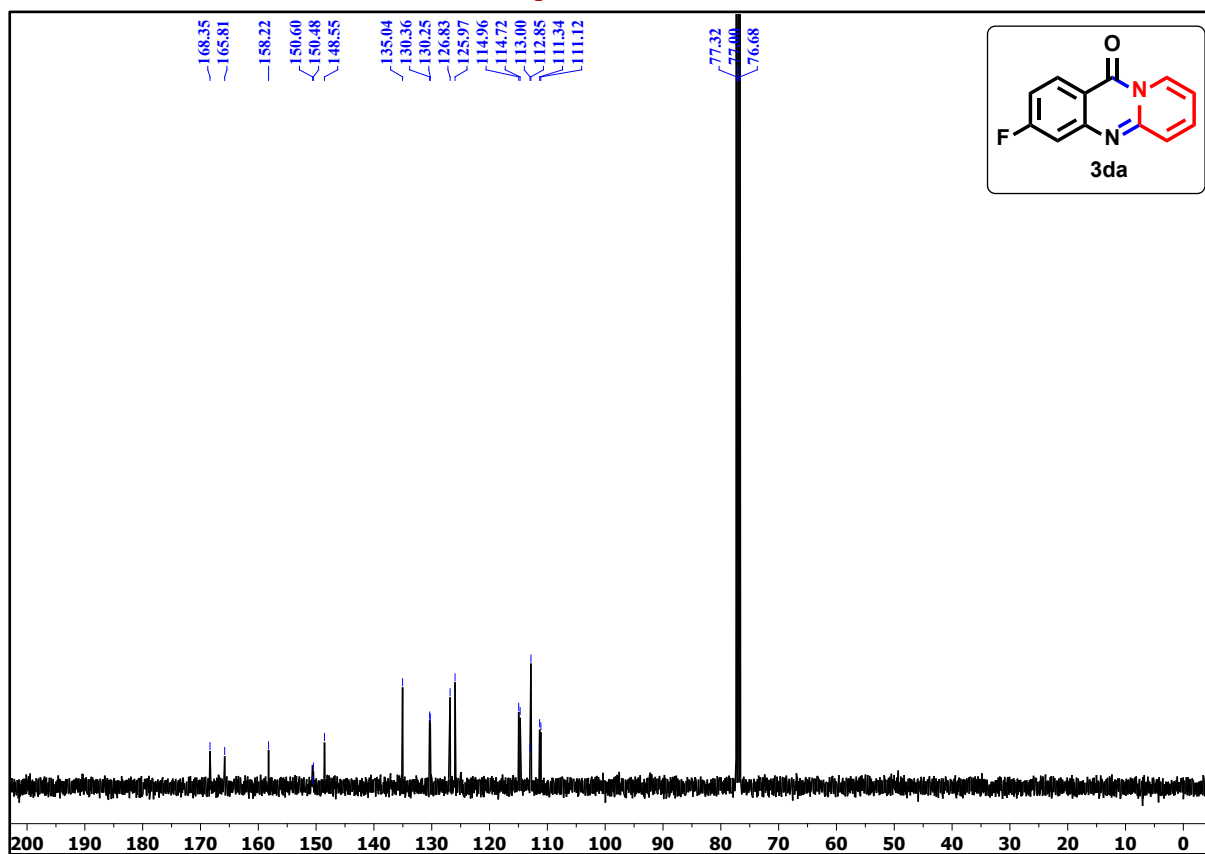
**<sup>19</sup>F-NMR spectra of 3cd in CDCl<sub>3</sub>**



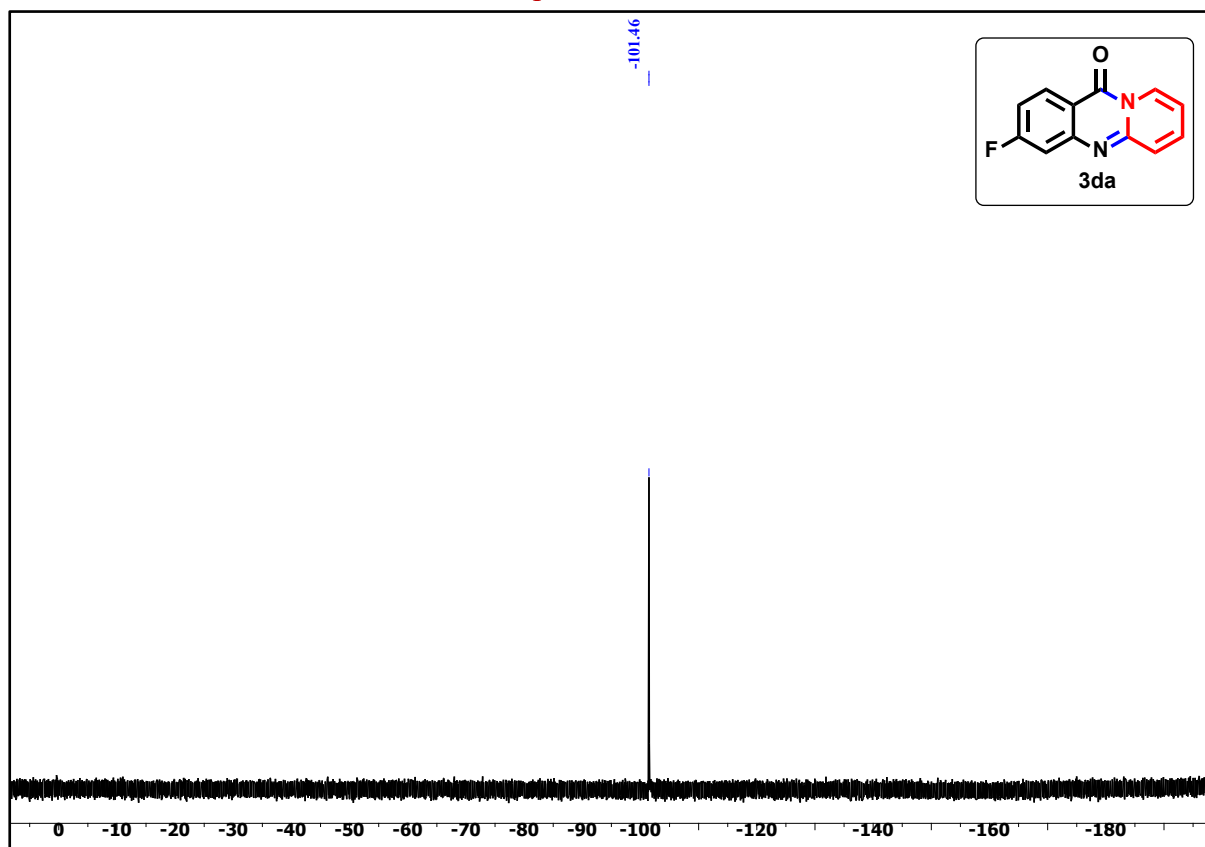
### <sup>1</sup>H NMR spectra of 3da in CDCl<sub>3</sub>



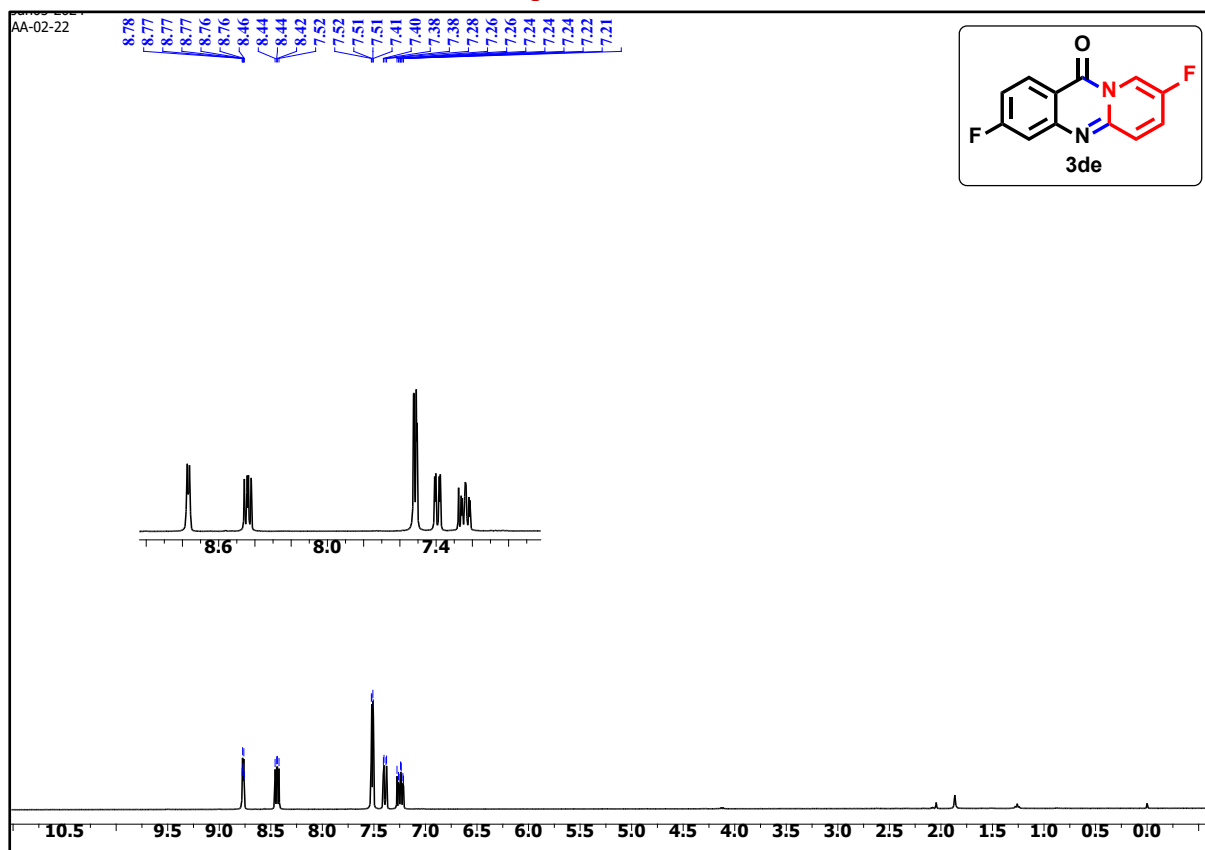
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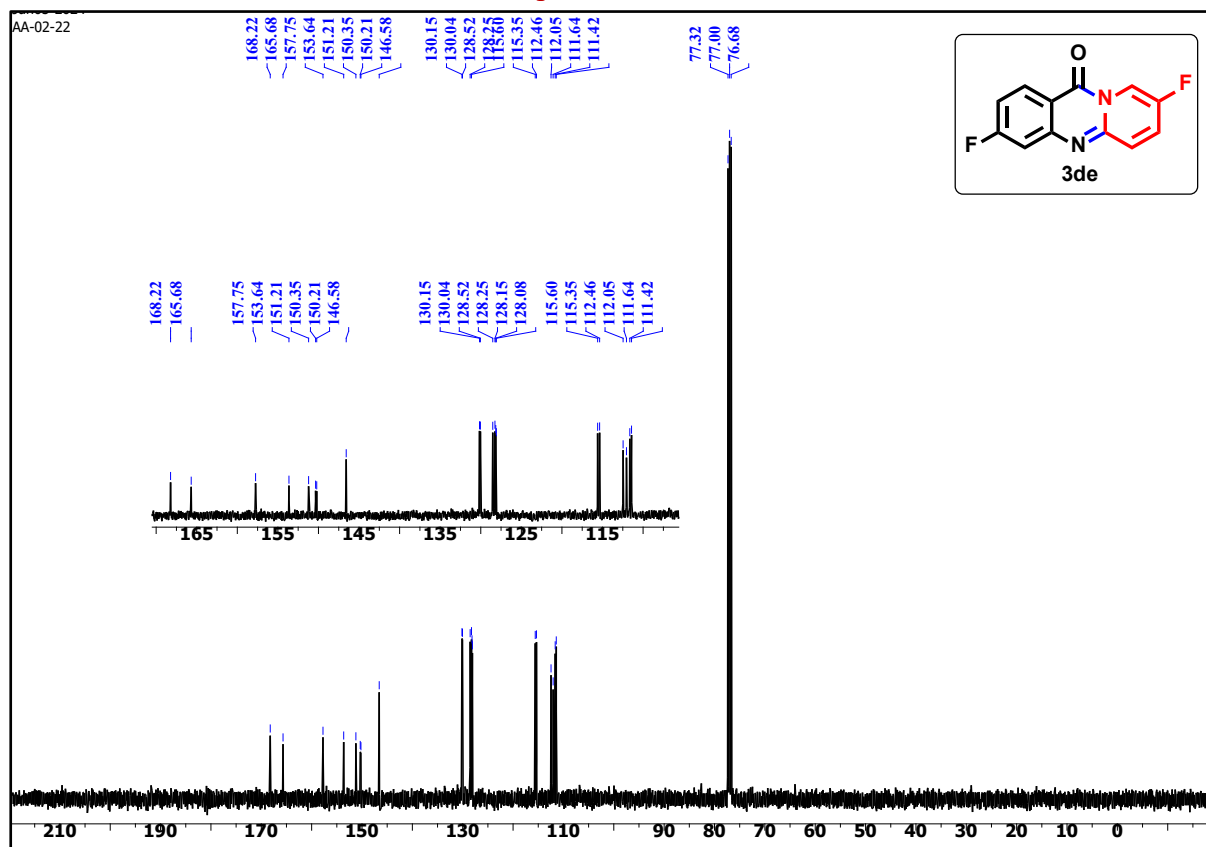
**<sup>19</sup>F NMR spectra of 3da in CDCl<sub>3</sub>**



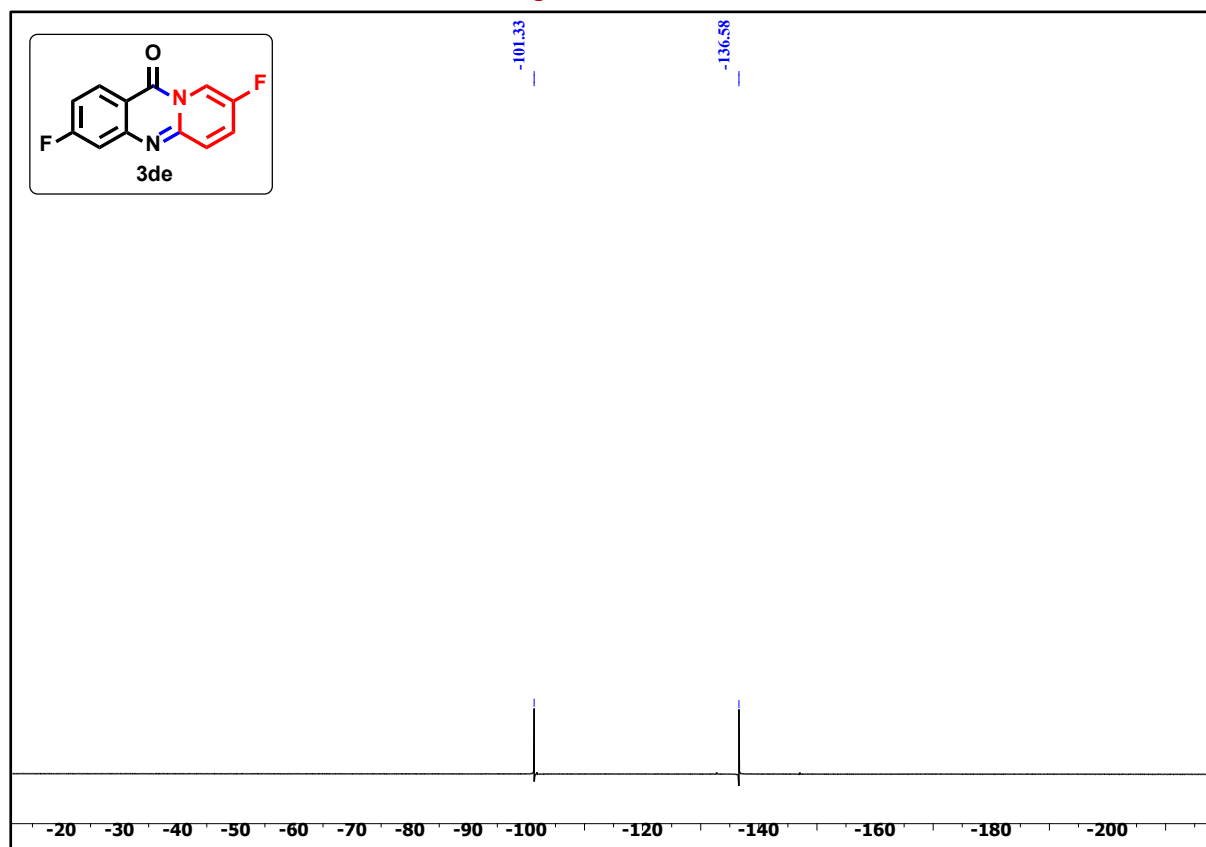
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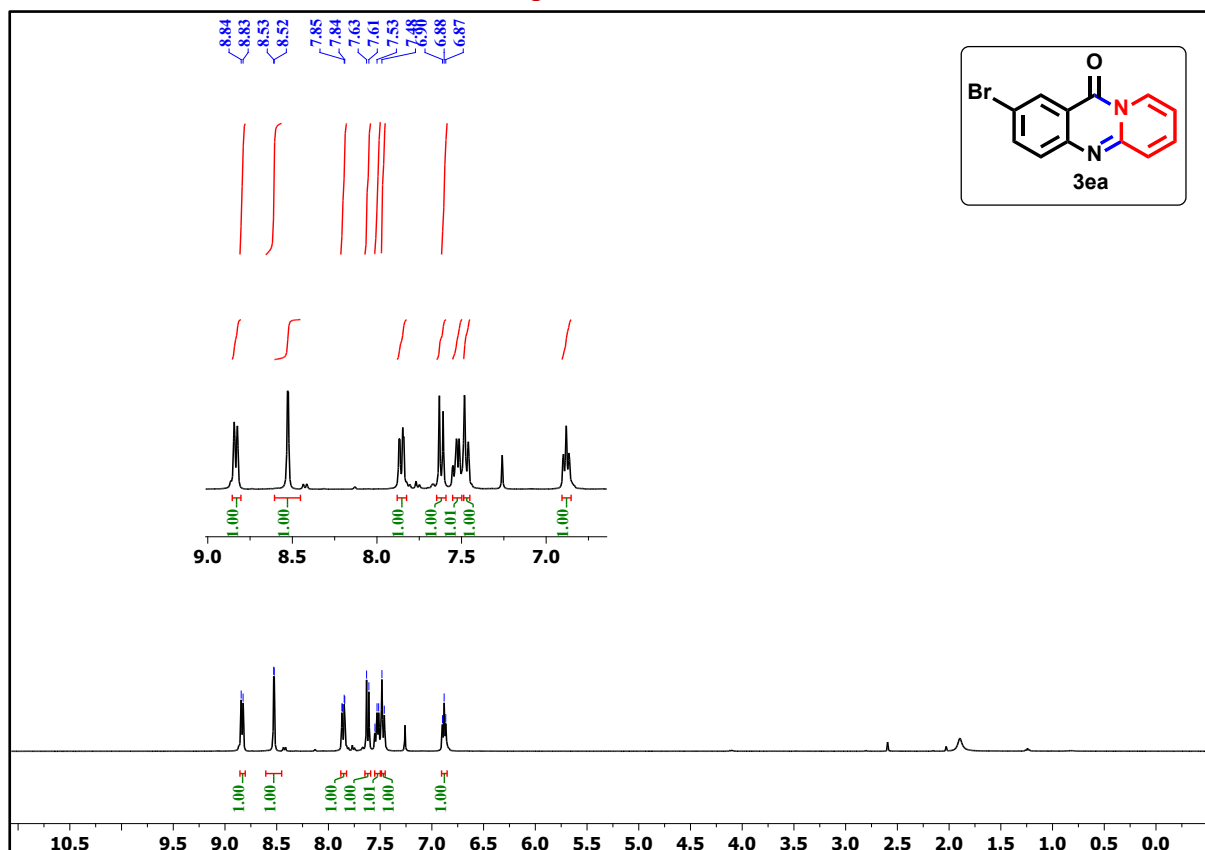
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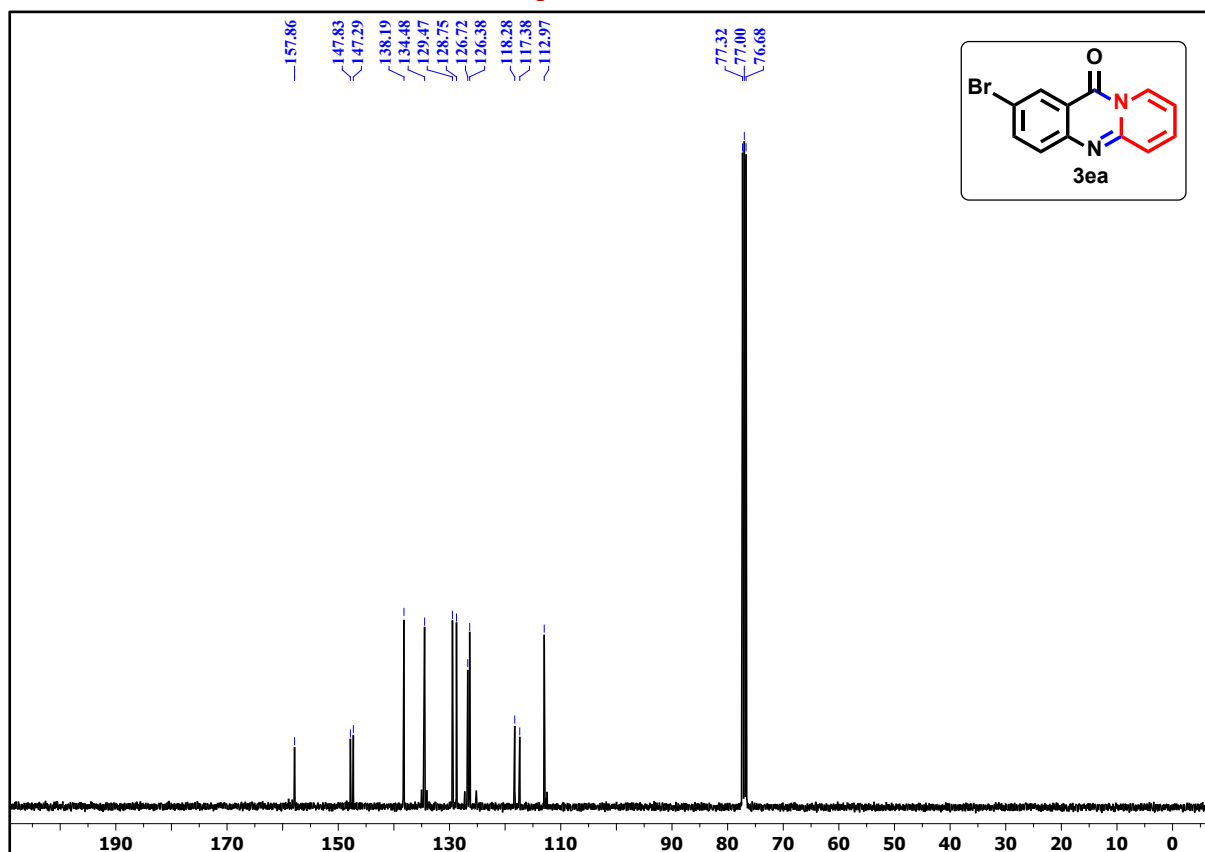
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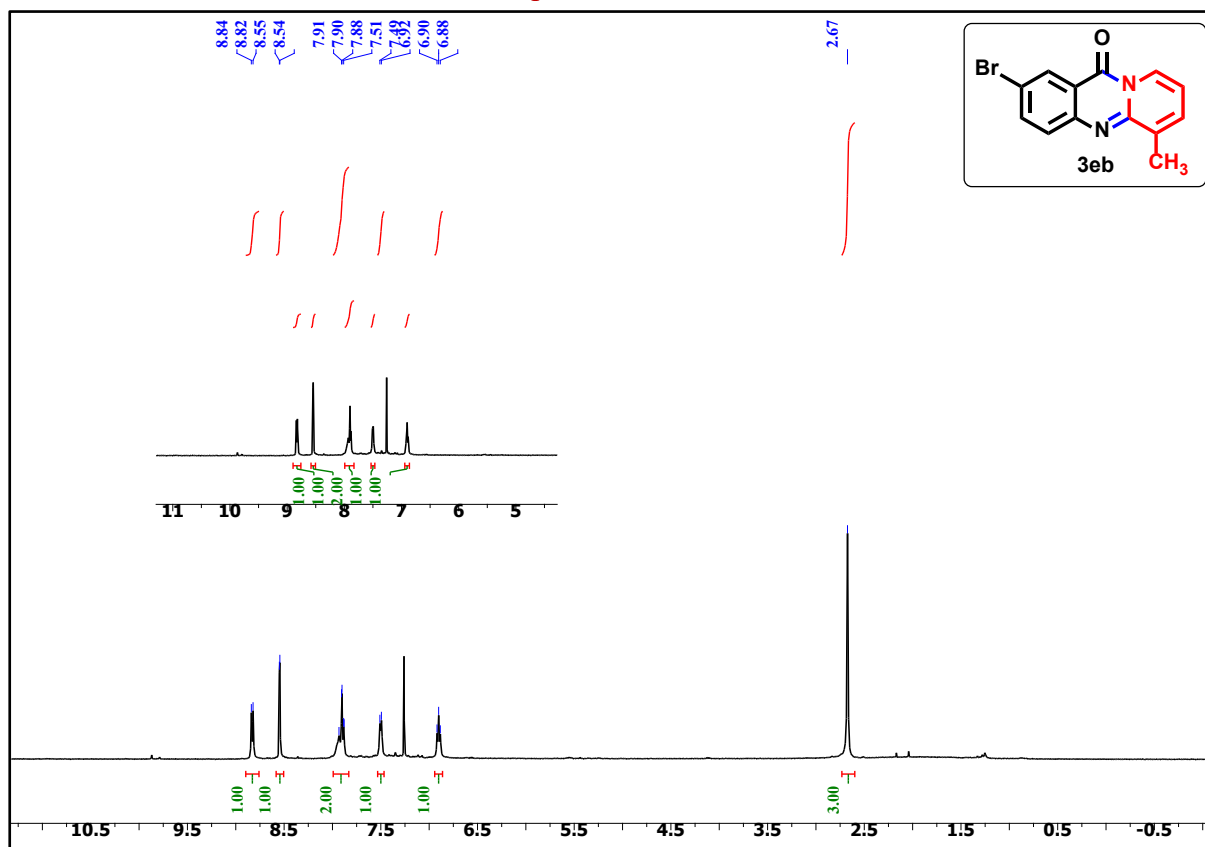
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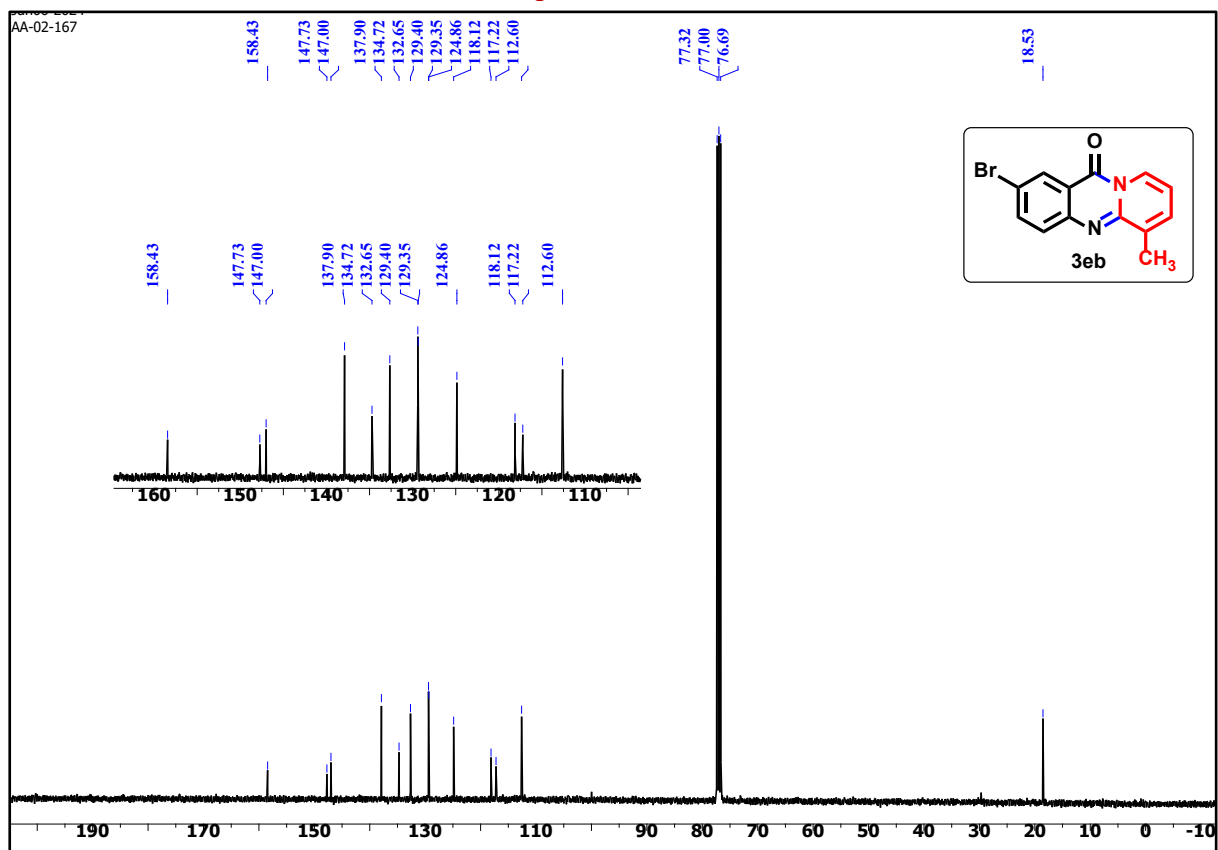
**<sup>13</sup>C NMR spectra of 3ea in CDCl<sub>3</sub>**



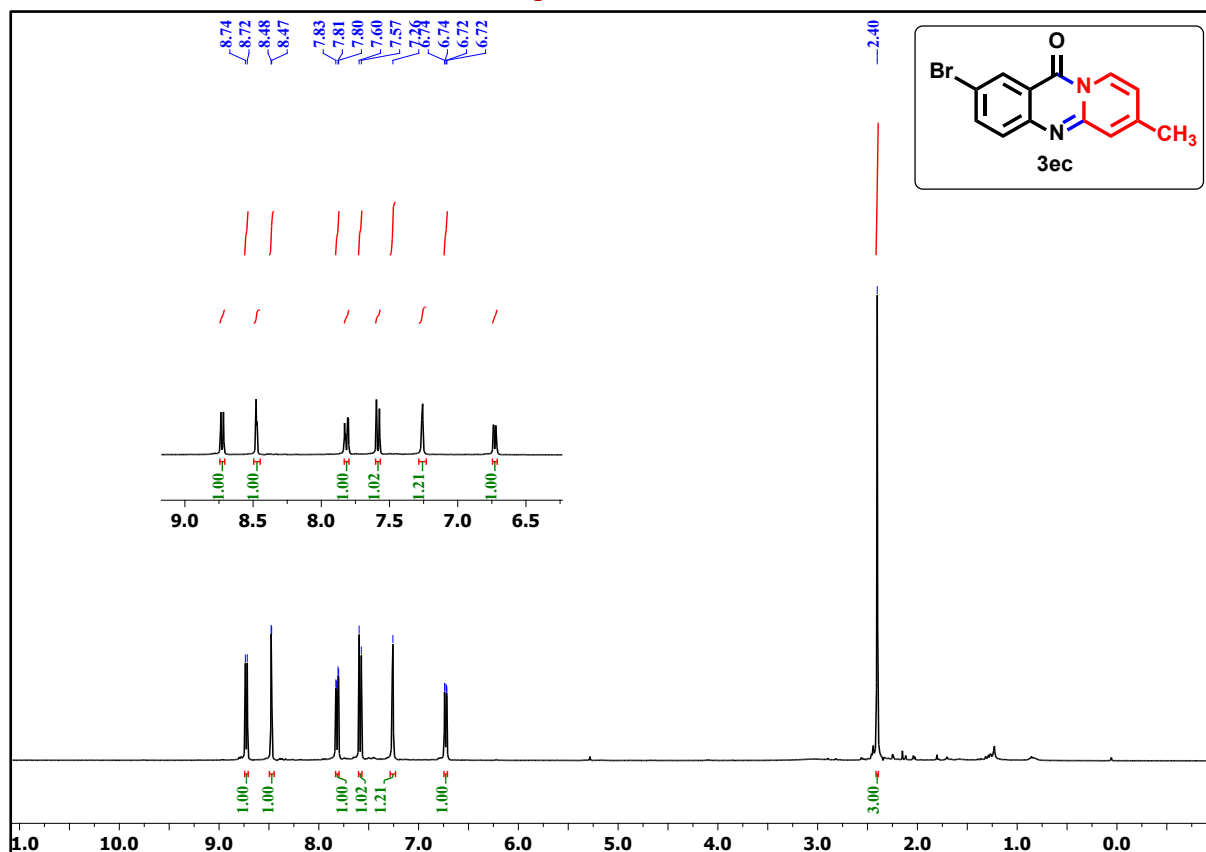
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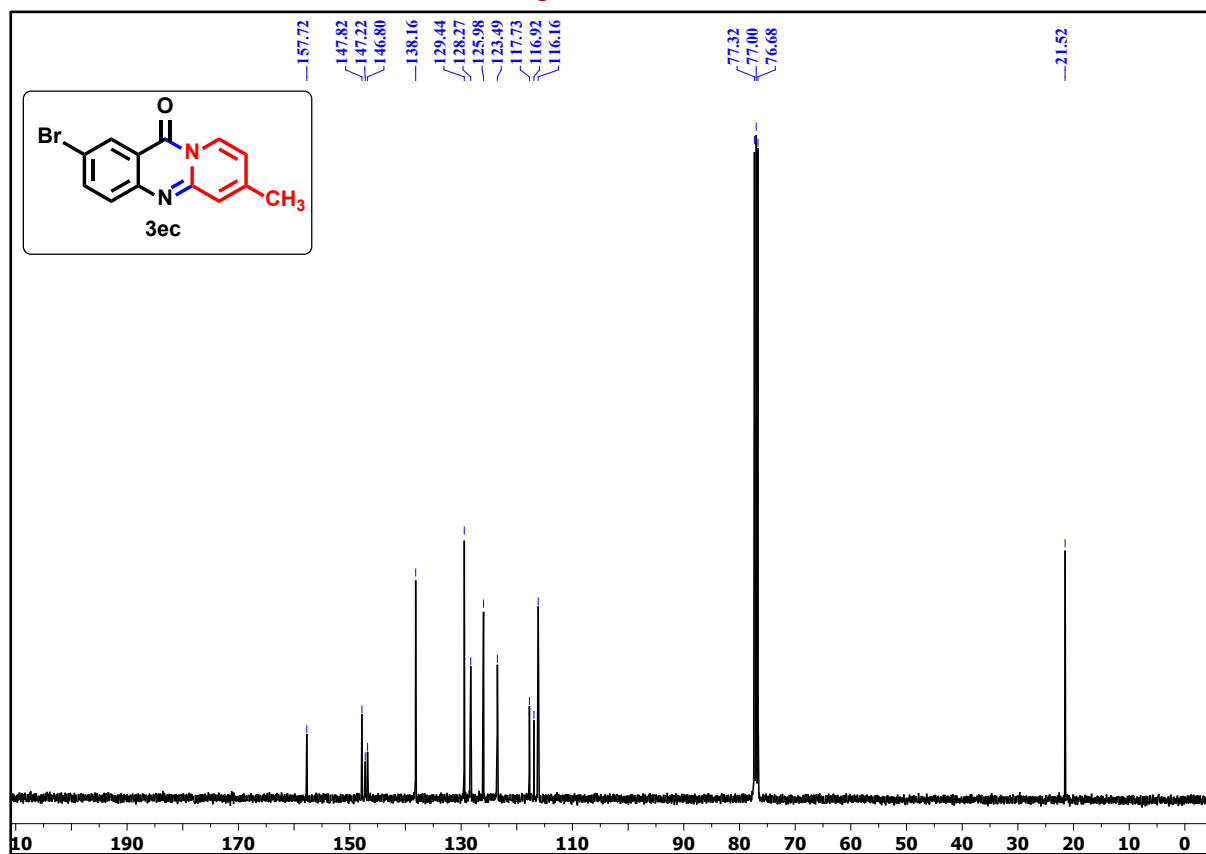
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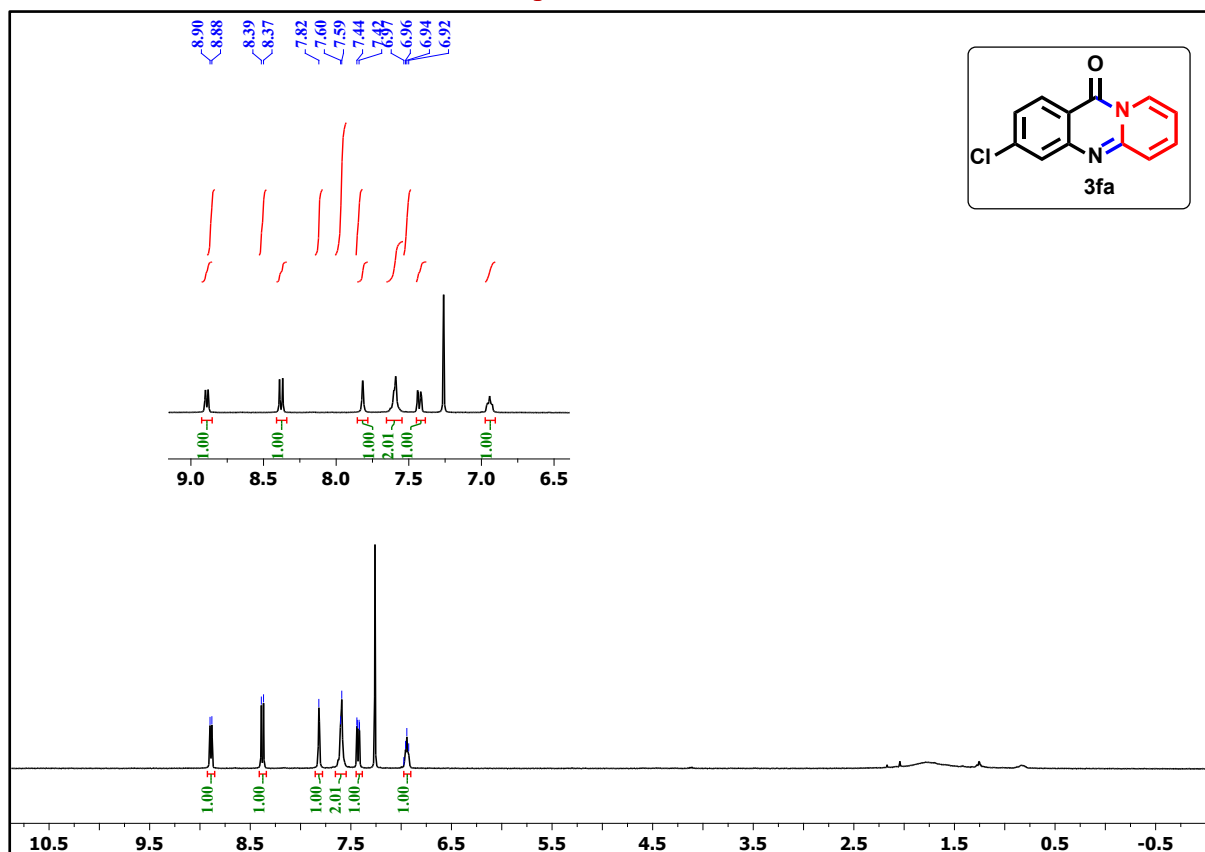
**<sup>1</sup>H NMR spectra of 3ec in CDCl<sub>3</sub>**



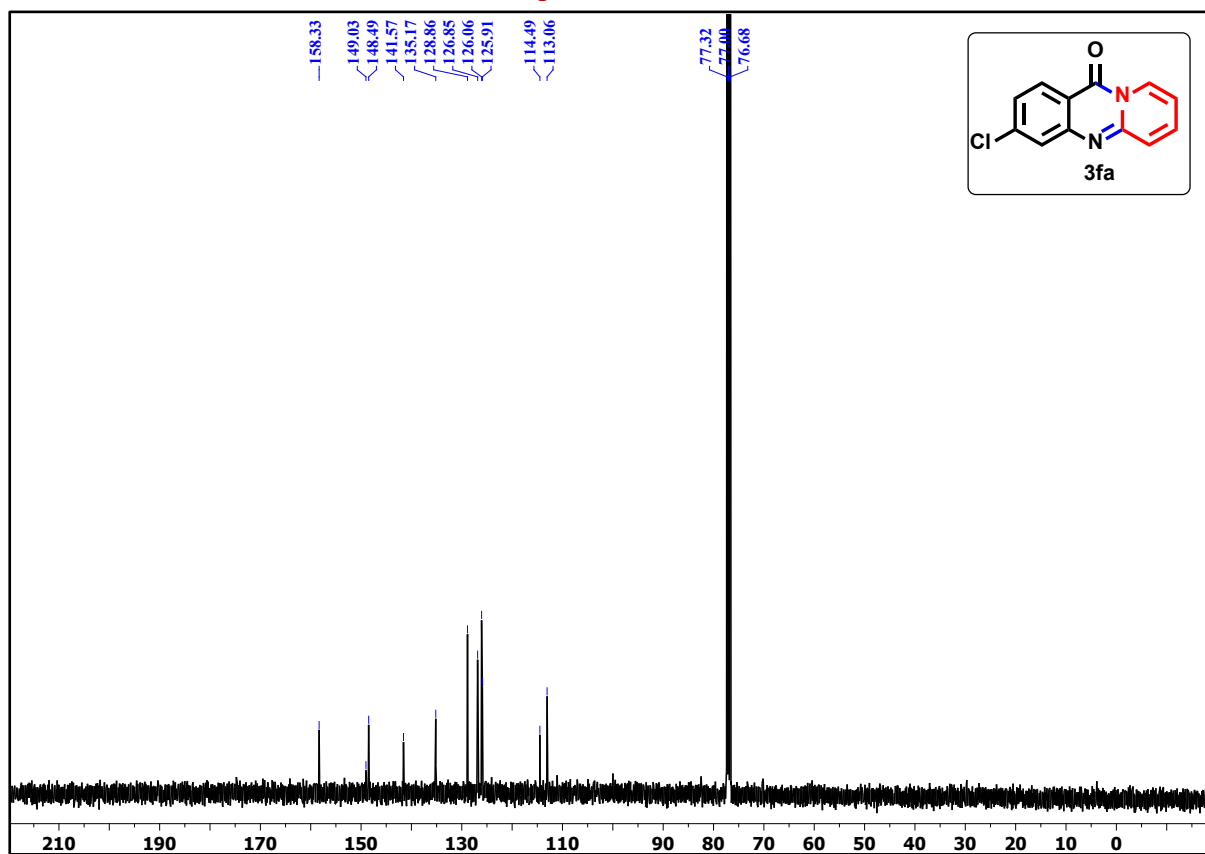
**<sup>13</sup>C NMR spectra of 3ec in CDCl<sub>3</sub>**



### <sup>1</sup>H NMR spectra of 3fa in CDCl<sub>3</sub>

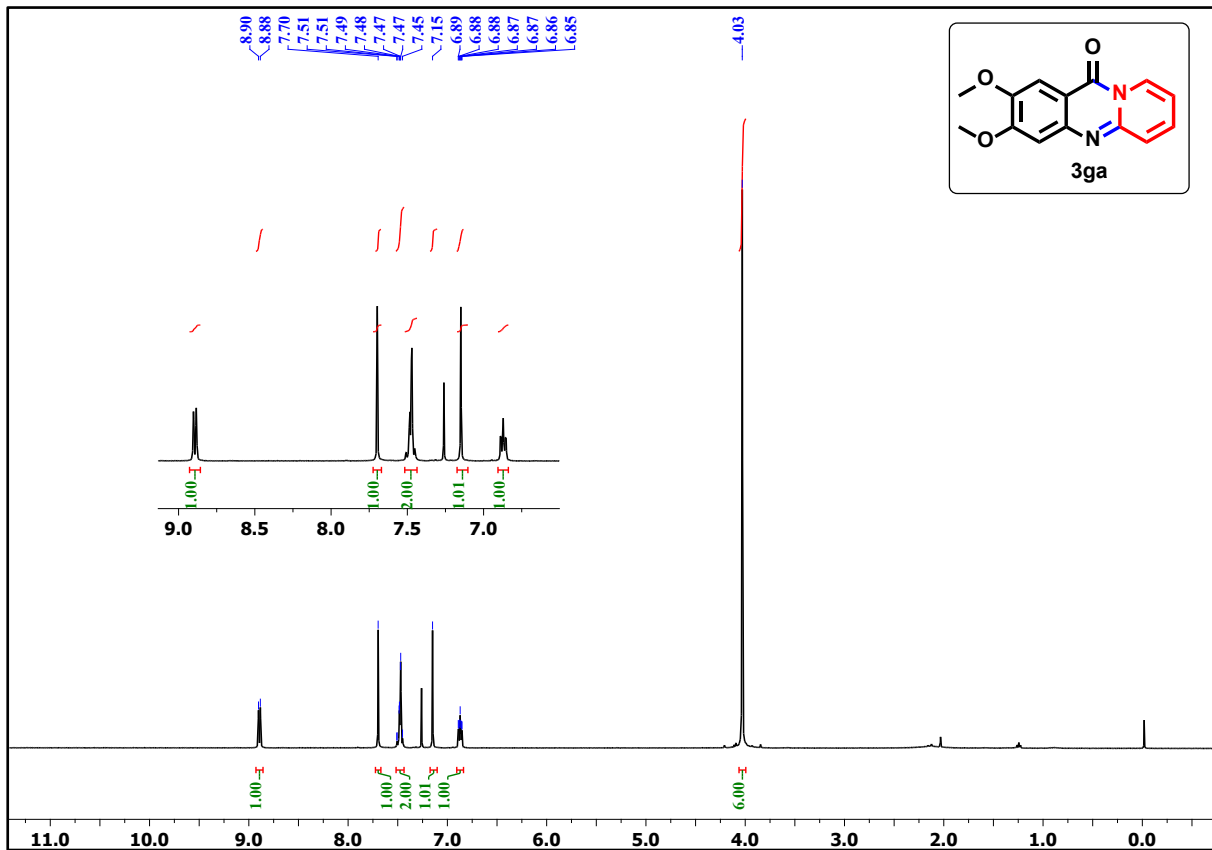


### <sup>13</sup>C NMR spectra of 3fa in CDCl<sub>3</sub>

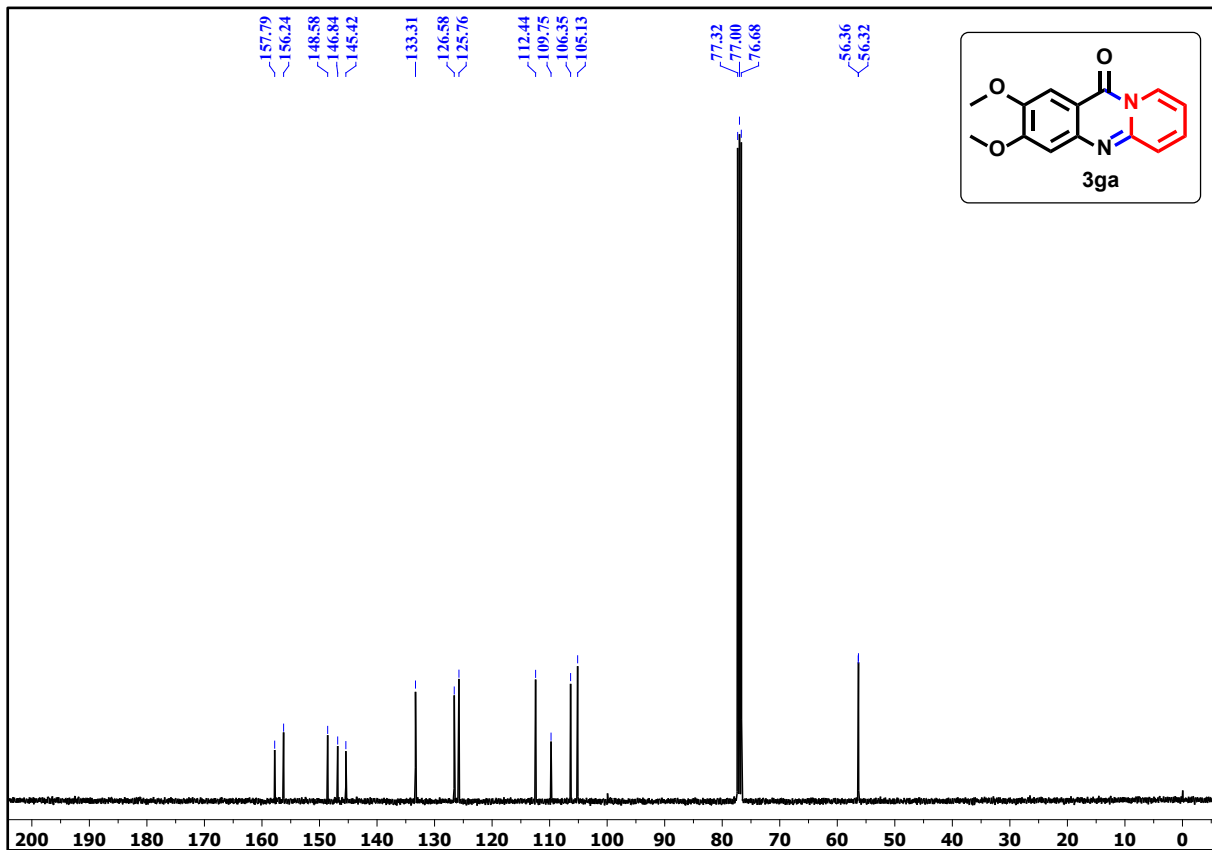




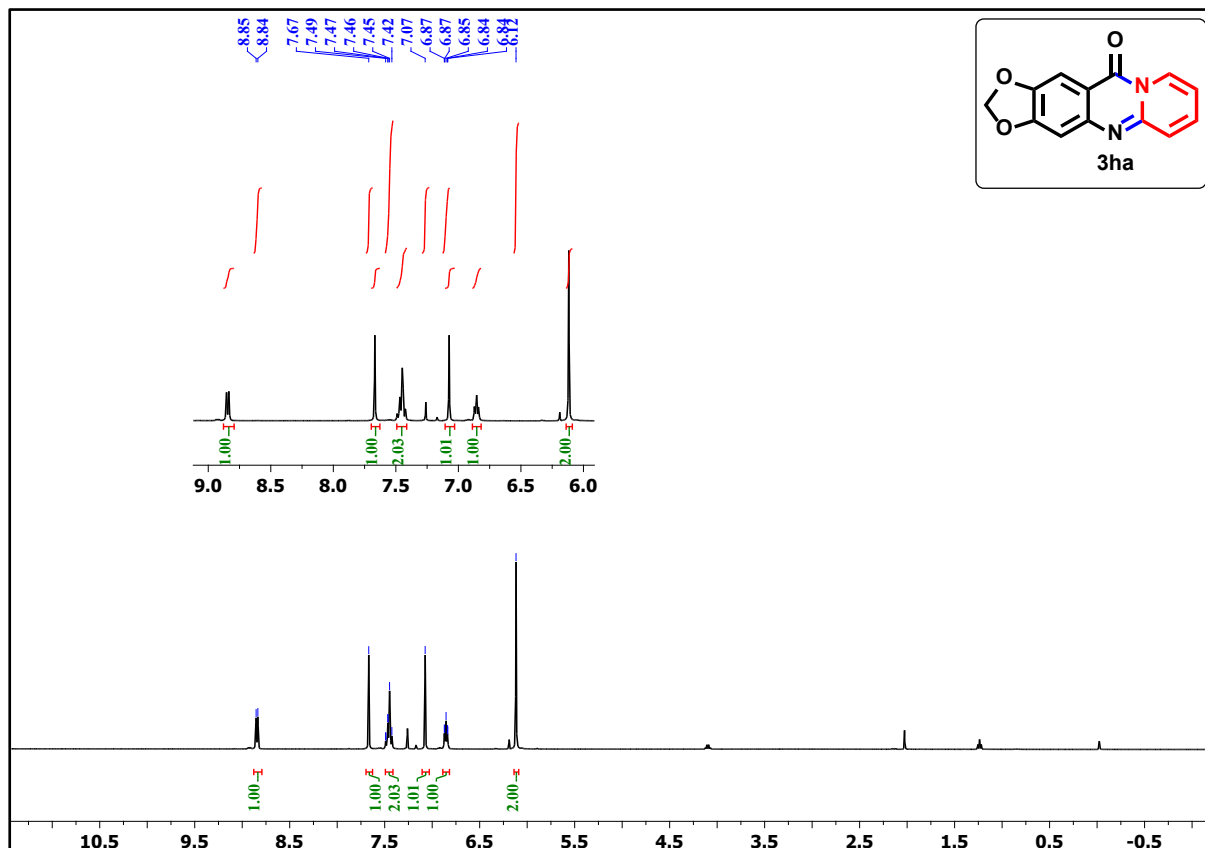
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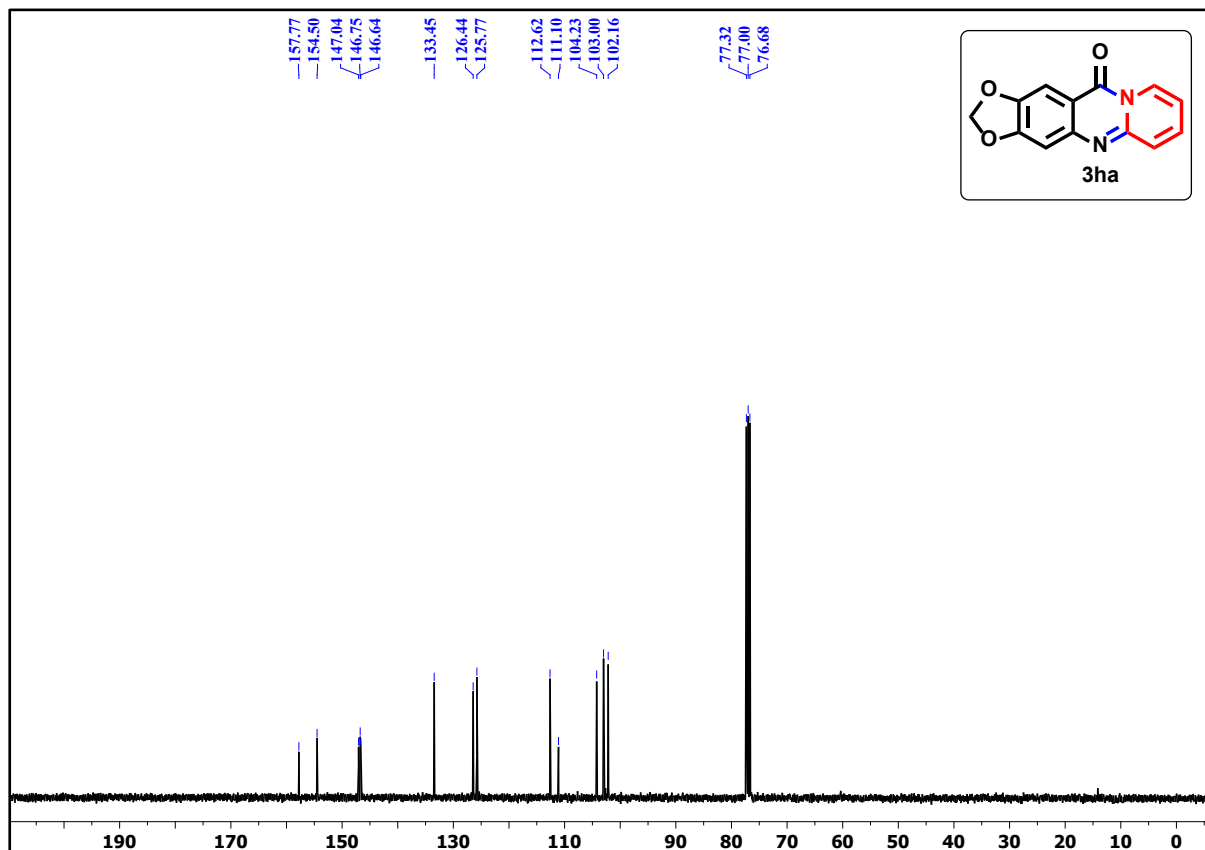
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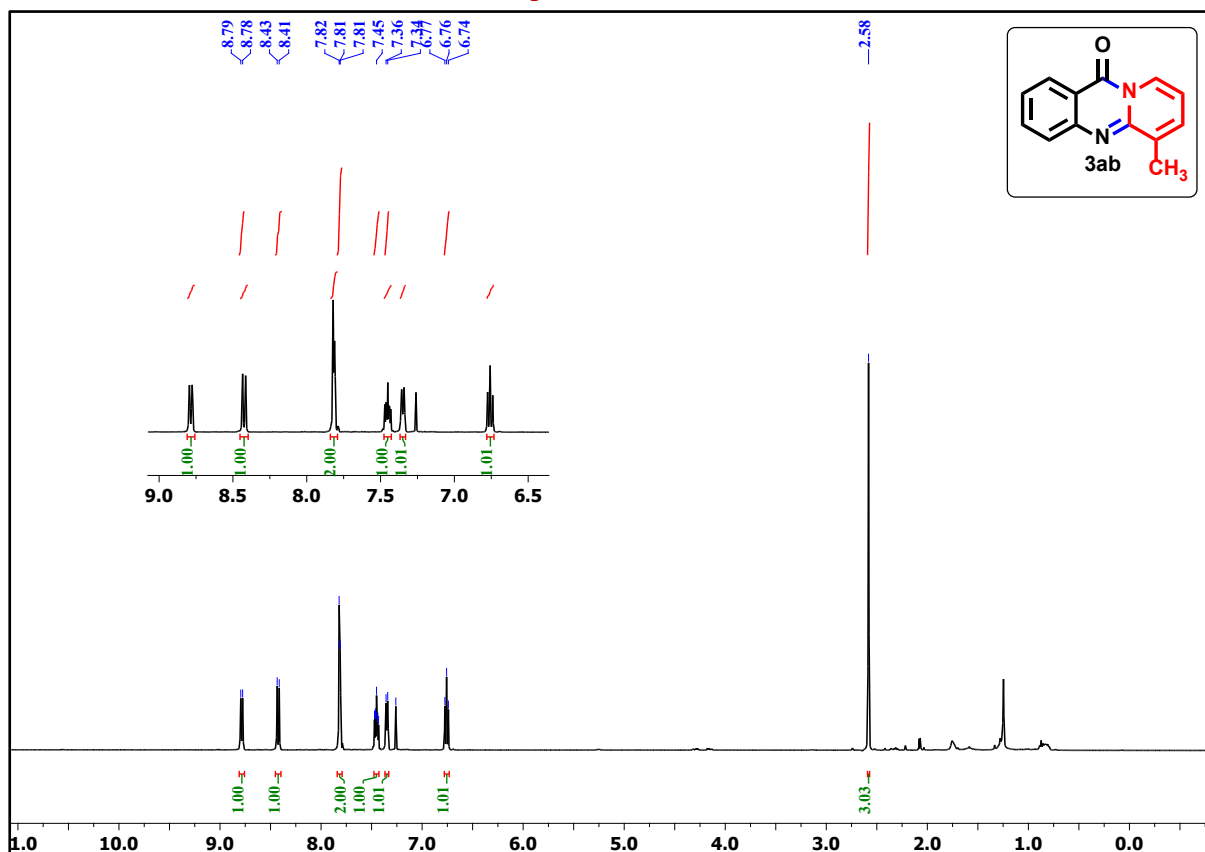
### <sup>1</sup>H NMR spectra of 3ha in CDCl<sub>3</sub>



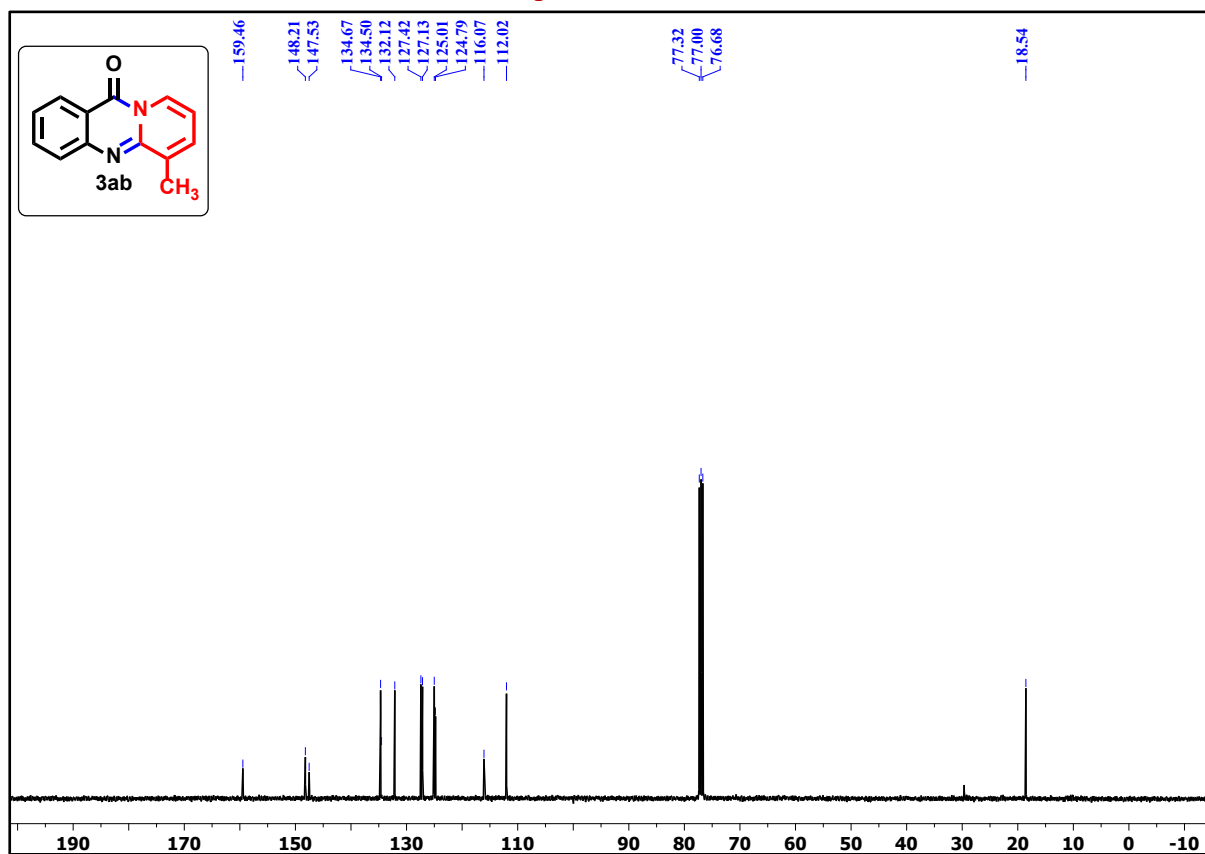
### <sup>13</sup>C NMR spectra of 3ha in CDCl<sub>3</sub>



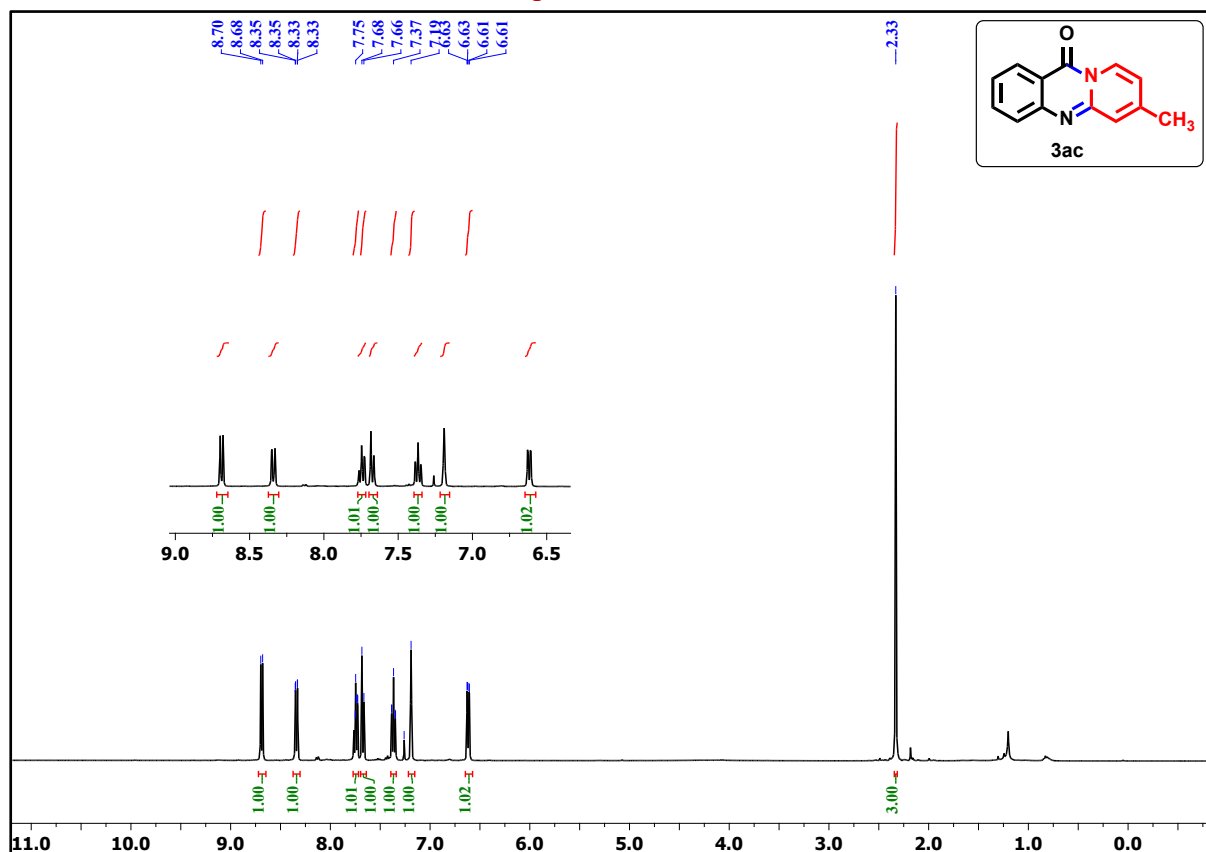
**<sup>1</sup>H NMR spectra of 3ab in CDCl<sub>3</sub>**



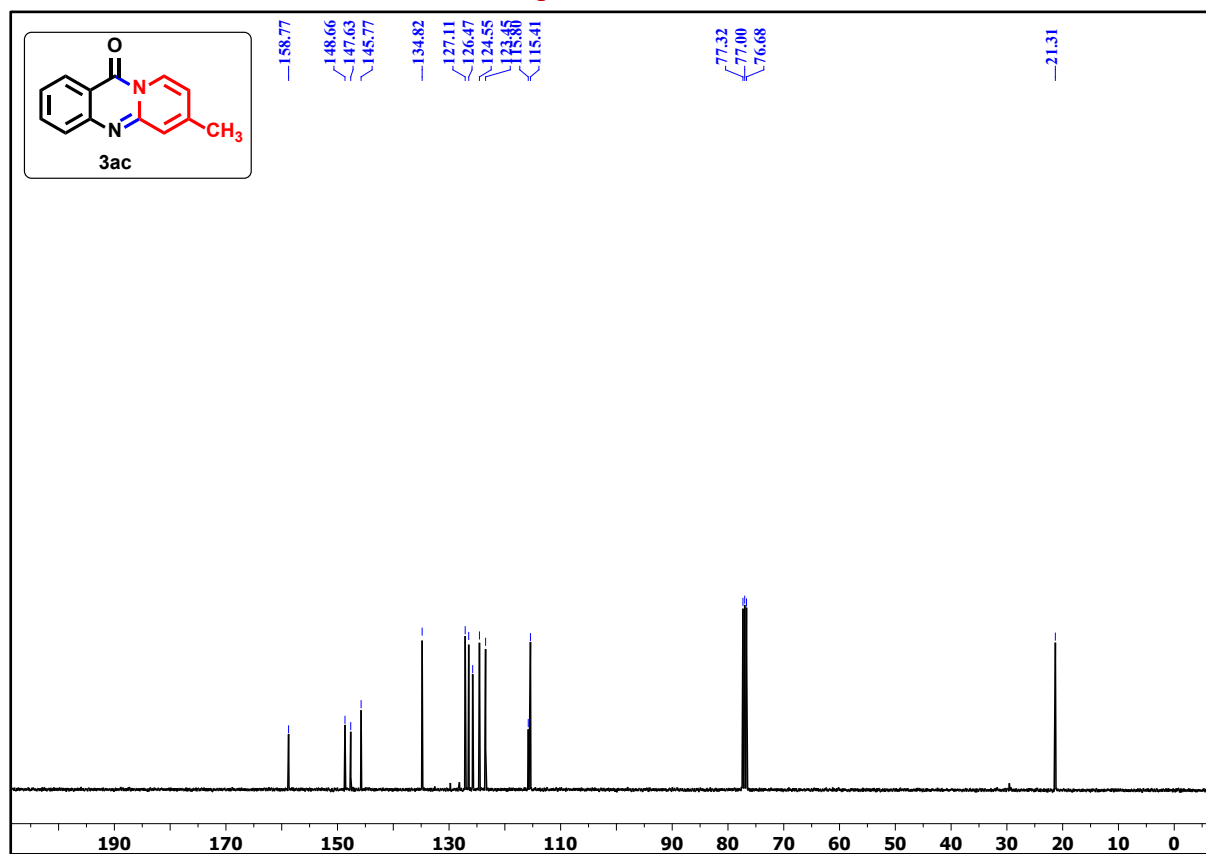
**<sup>13</sup>C NMR spectra of 3ab in CDCl<sub>3</sub>**



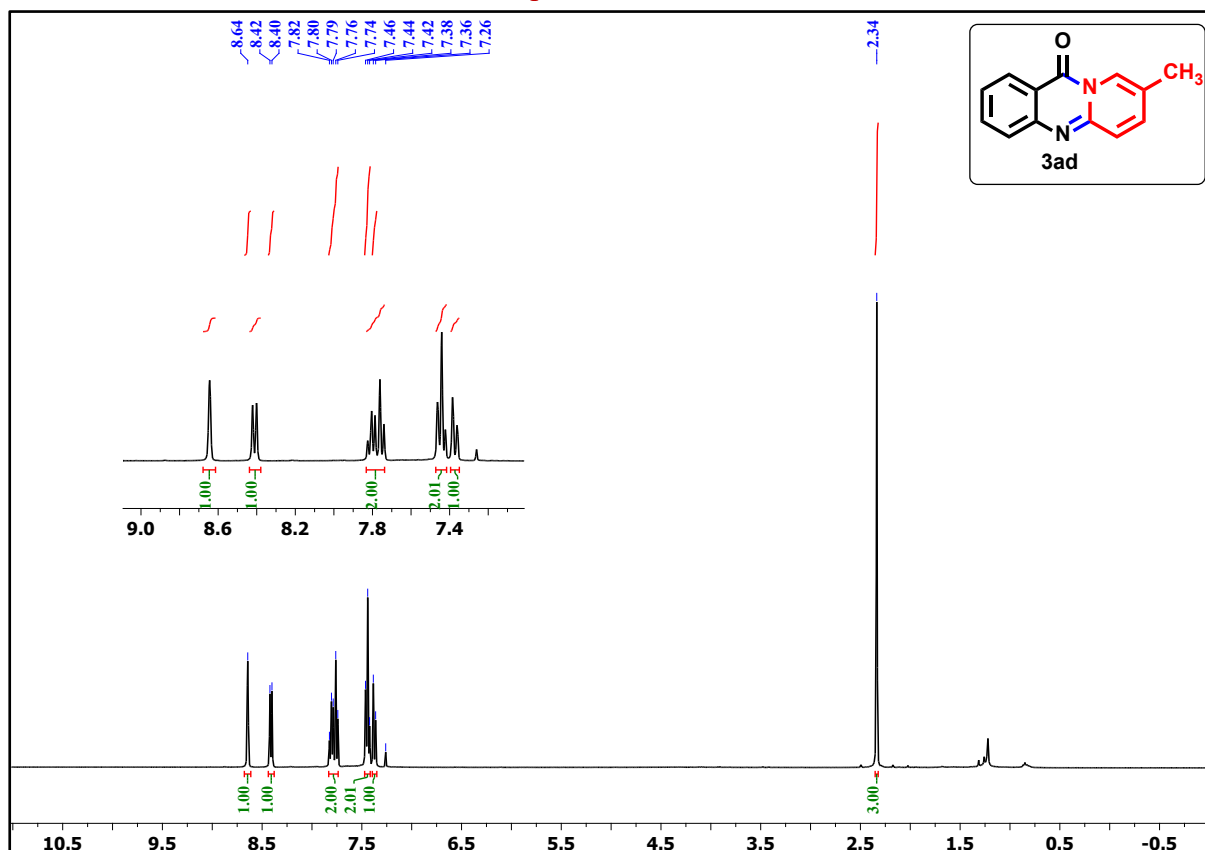
**<sup>1</sup>H NMR spectra of 3ac in CDCl<sub>3</sub>**



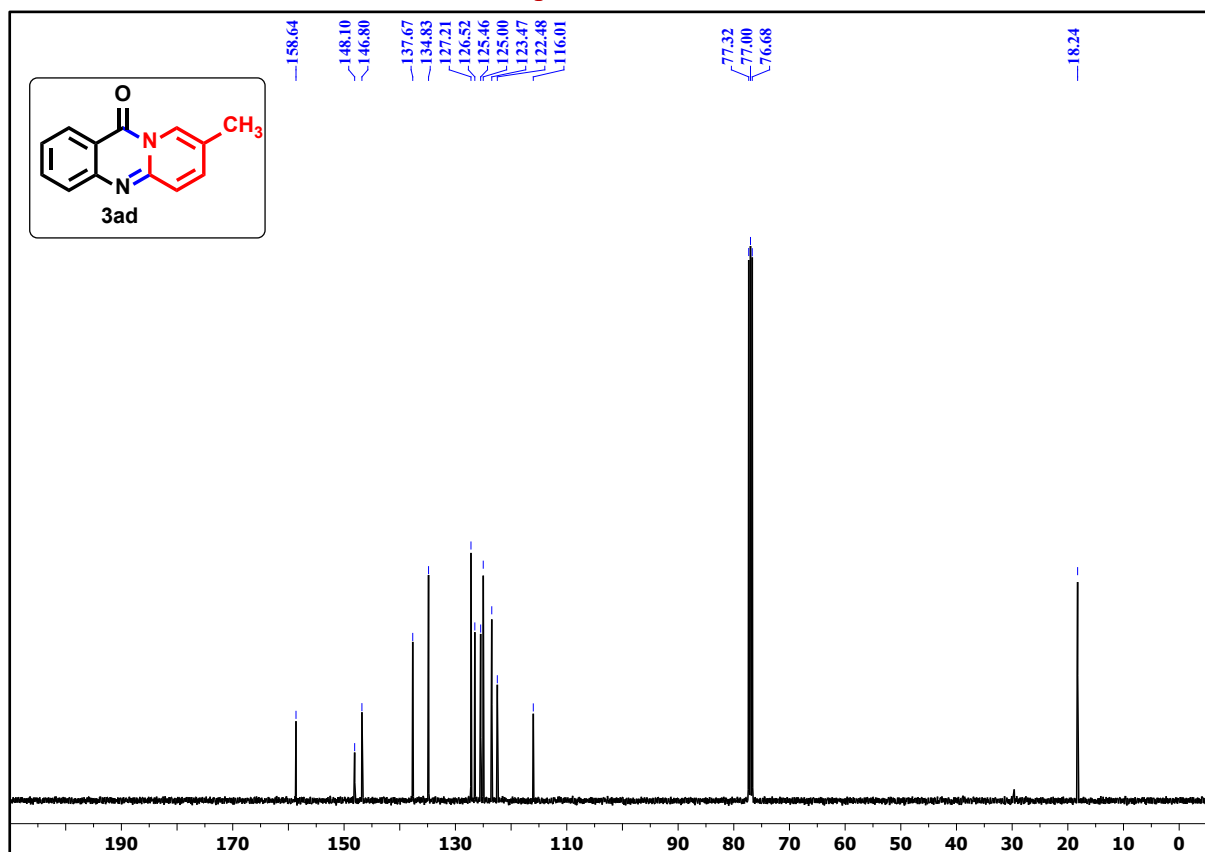
**<sup>13</sup>C NMR spectra of 3ac in CDCl<sub>3</sub>**



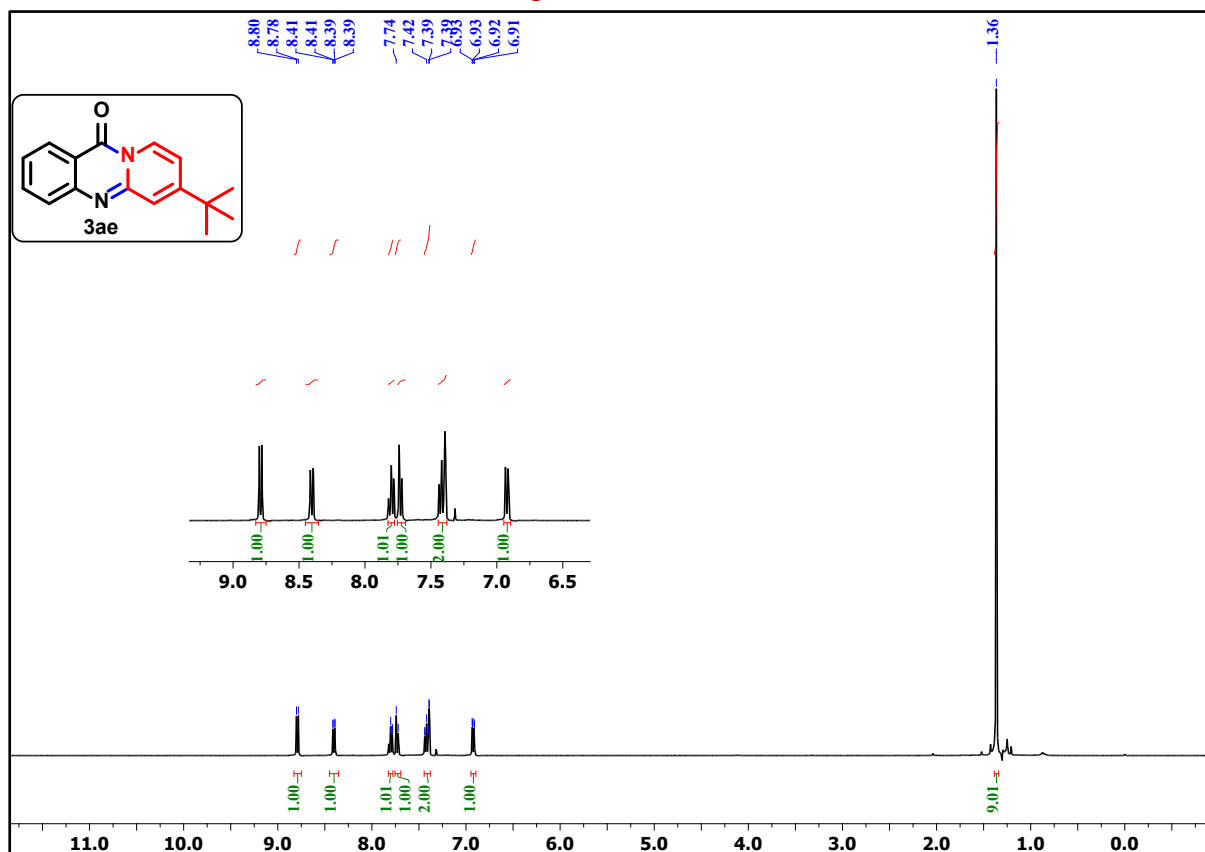
**<sup>1</sup>H NMR spectra of 3ad in CDCl<sub>3</sub>**



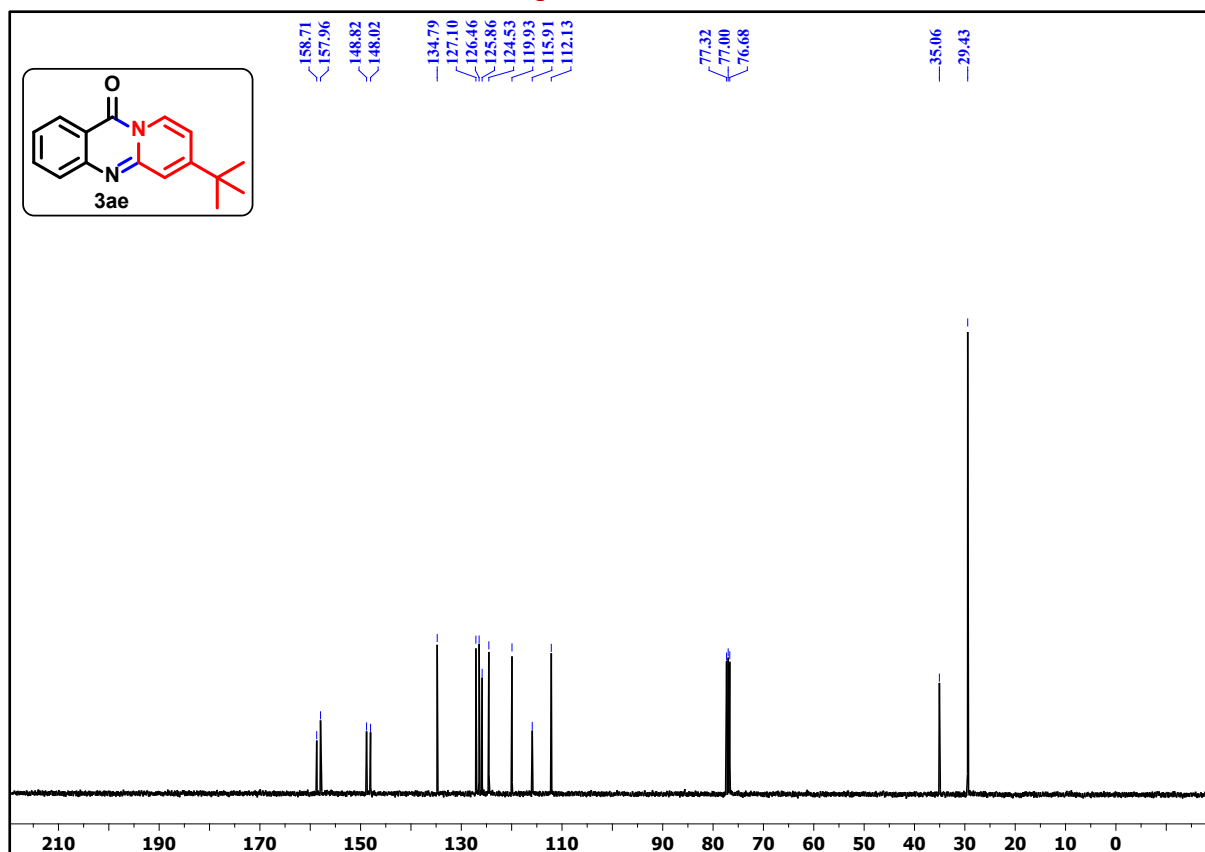
**<sup>13</sup>C NMR spectra of 3ad in CDCl<sub>3</sub>**



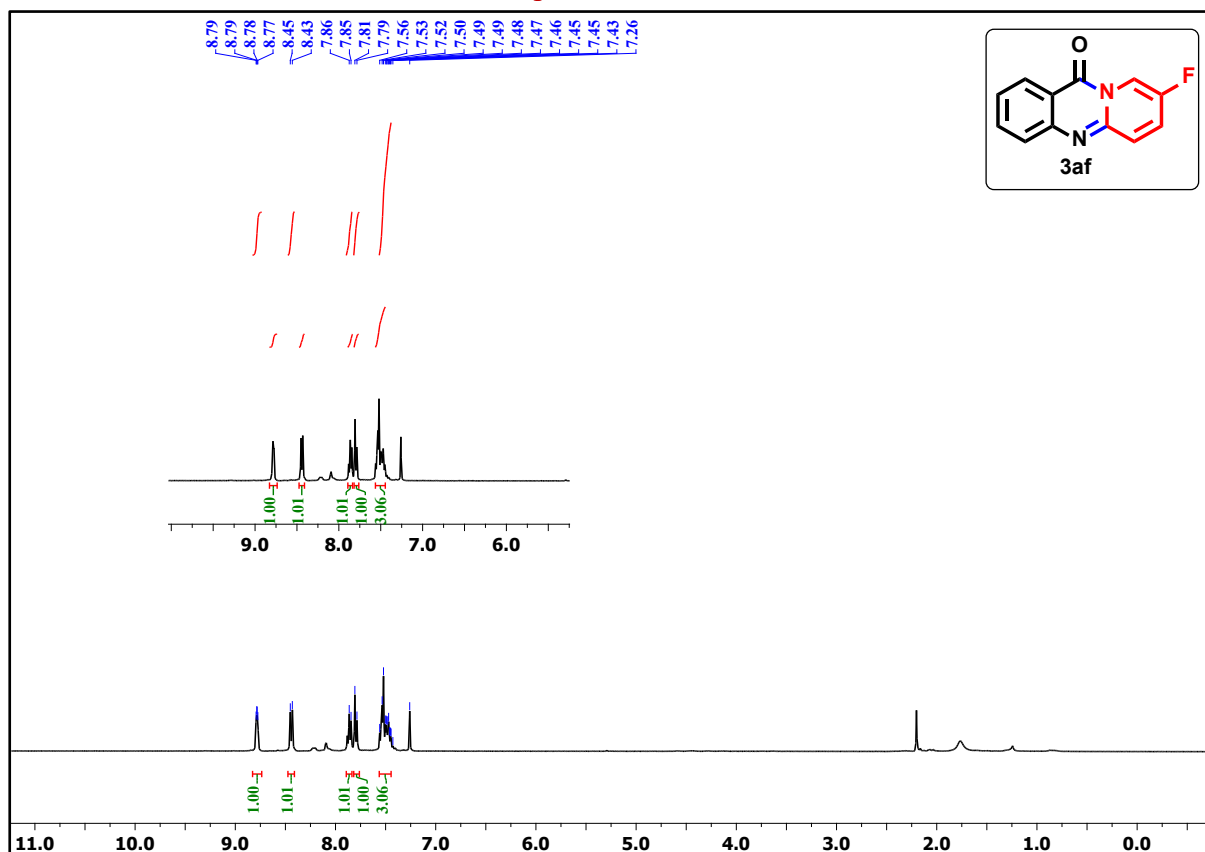
### <sup>1</sup>H NMR spectra of 3ae in CDCl<sub>3</sub>



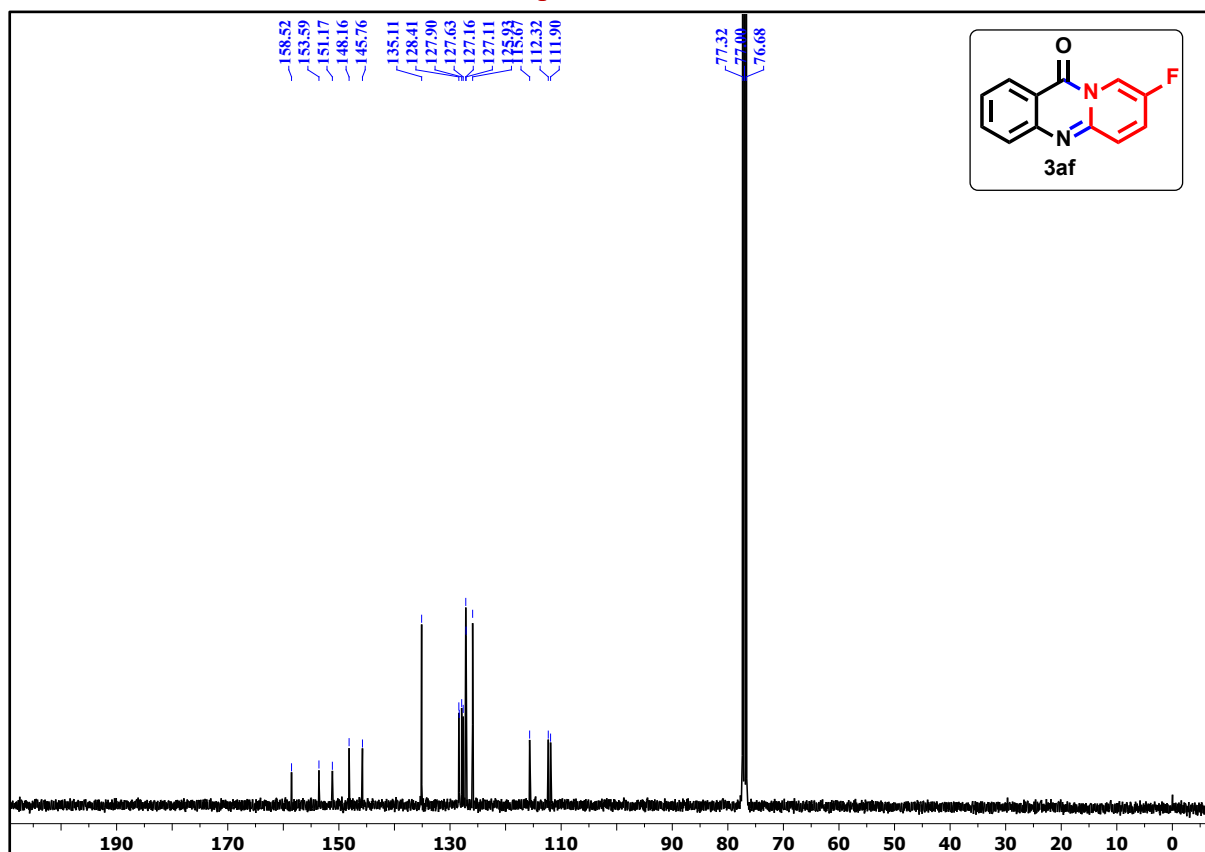
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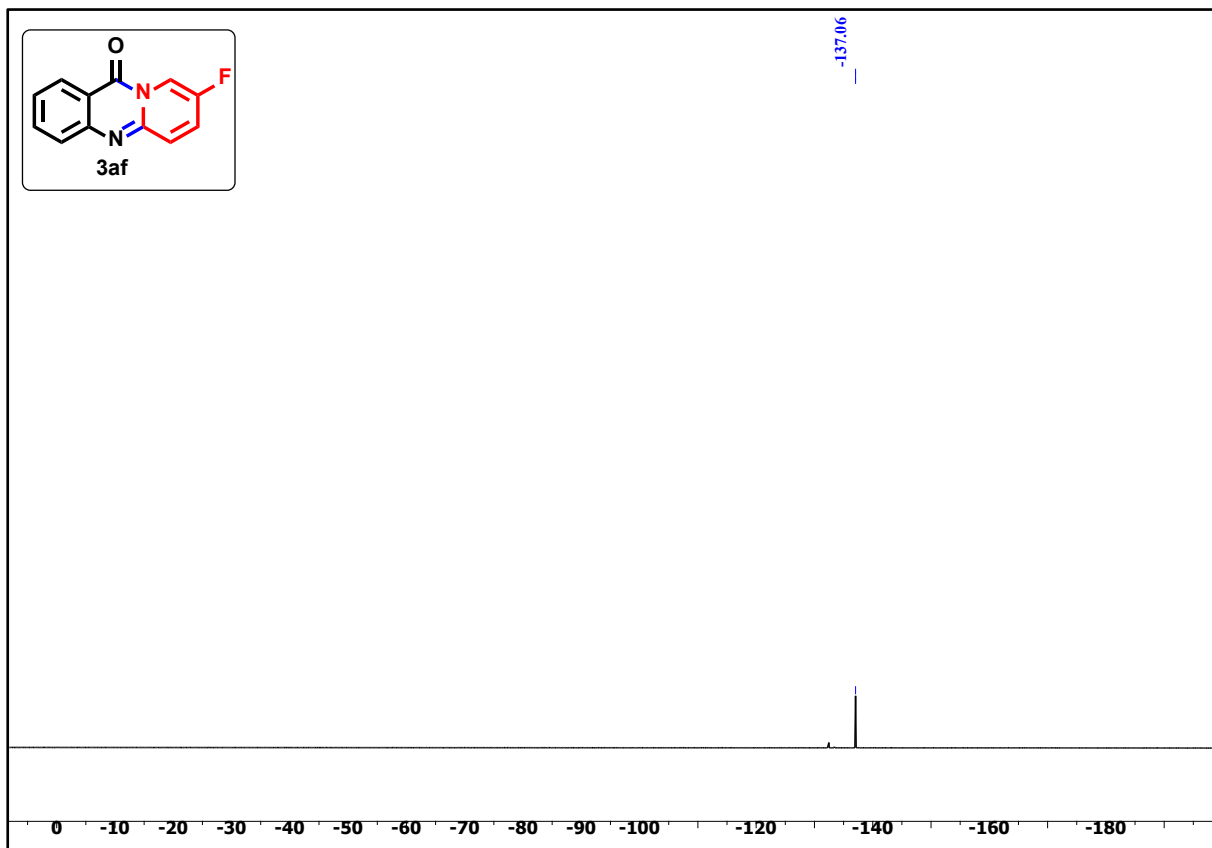
### <sup>1</sup>H NMR spectra of 3af in CDCl<sub>3</sub>



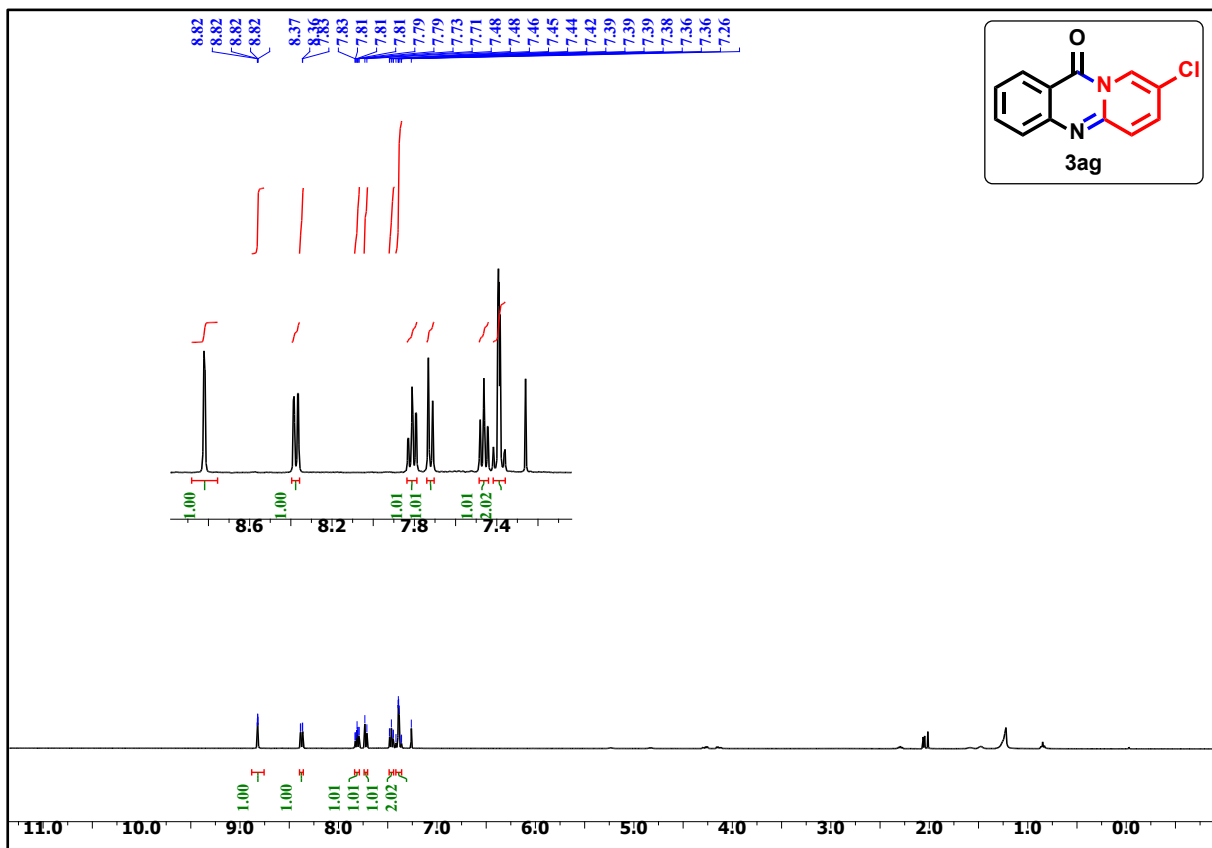
### <sup>13</sup>C NMR spectra of 3af in CDCl<sub>3</sub>



**<sup>19</sup>F NMR spectra of 3af in CDCl<sub>3</sub>**

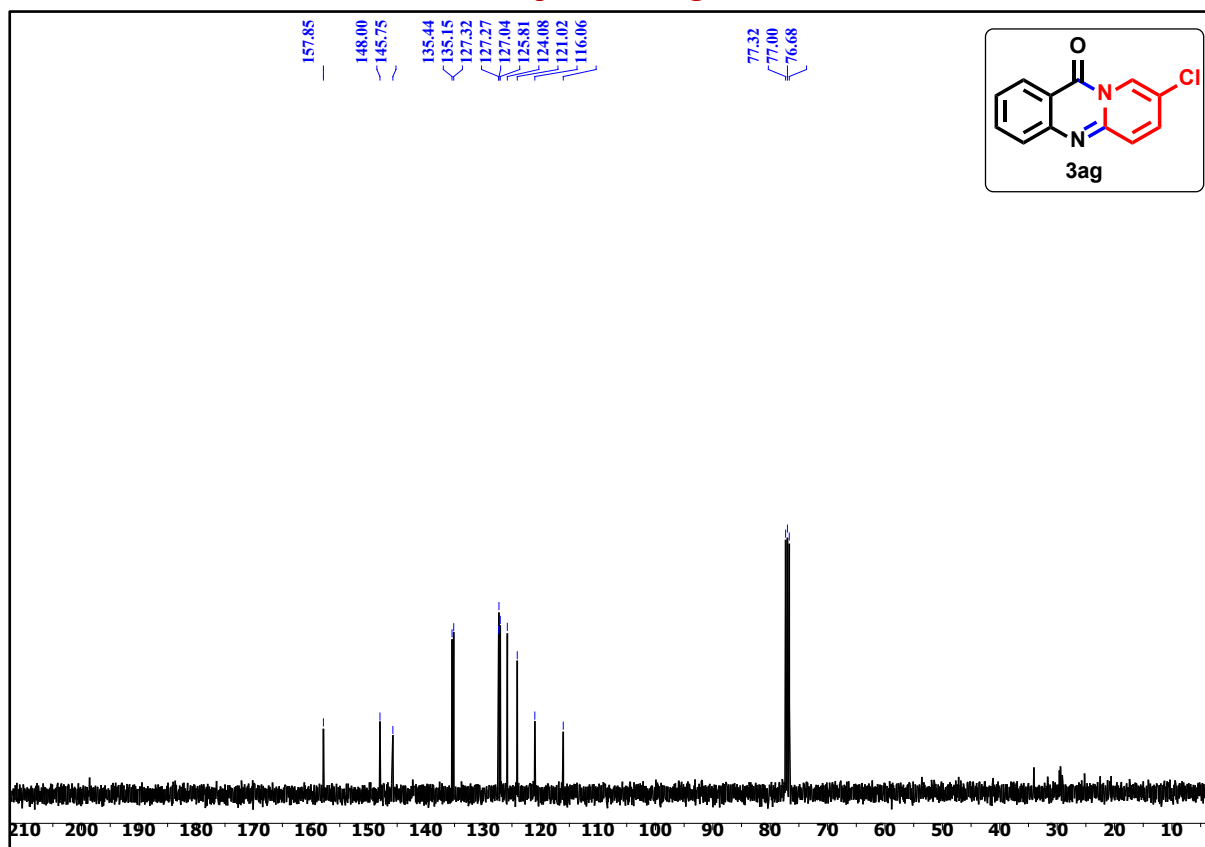


**<sup>1</sup>H NMR spectra of 3ag in CDCl<sub>3</sub>**

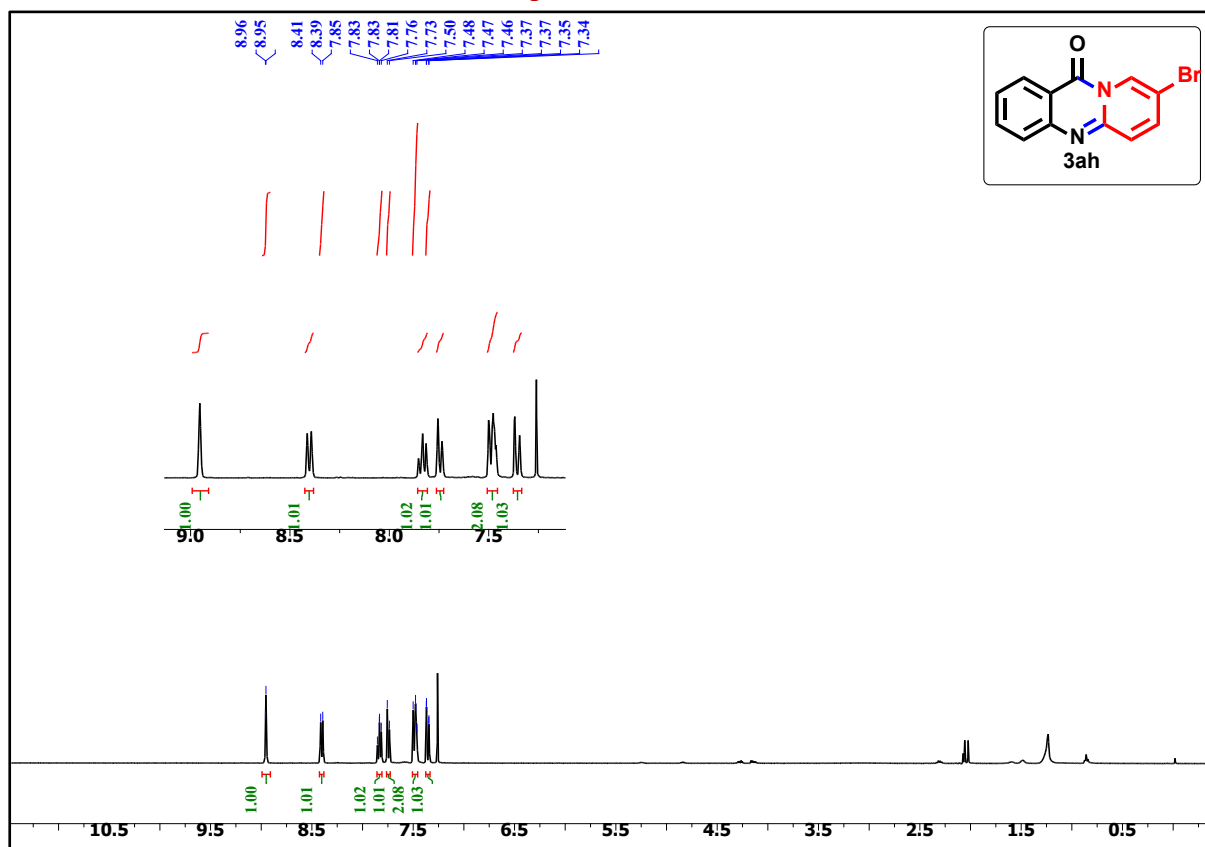




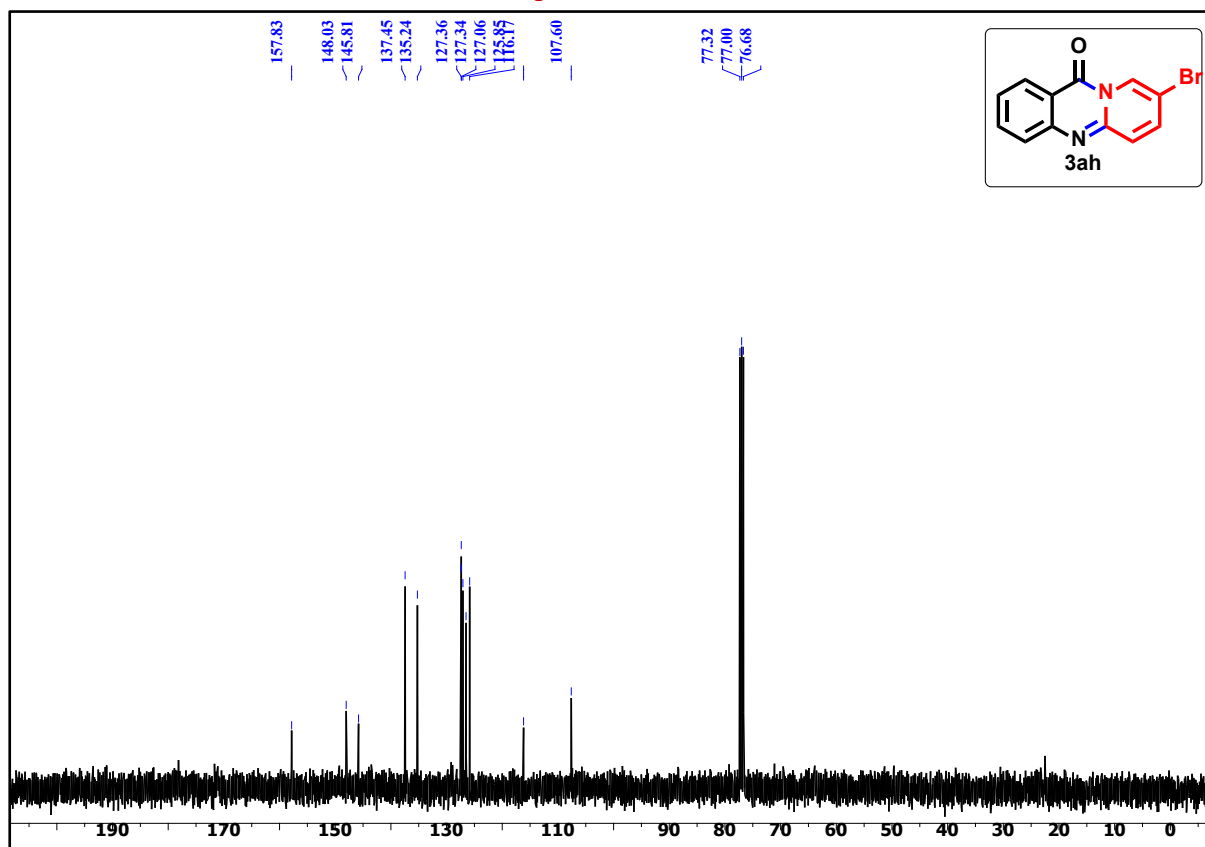
**<sup>13</sup>C NMR spectra of 3ag in CDCl<sub>3</sub>**



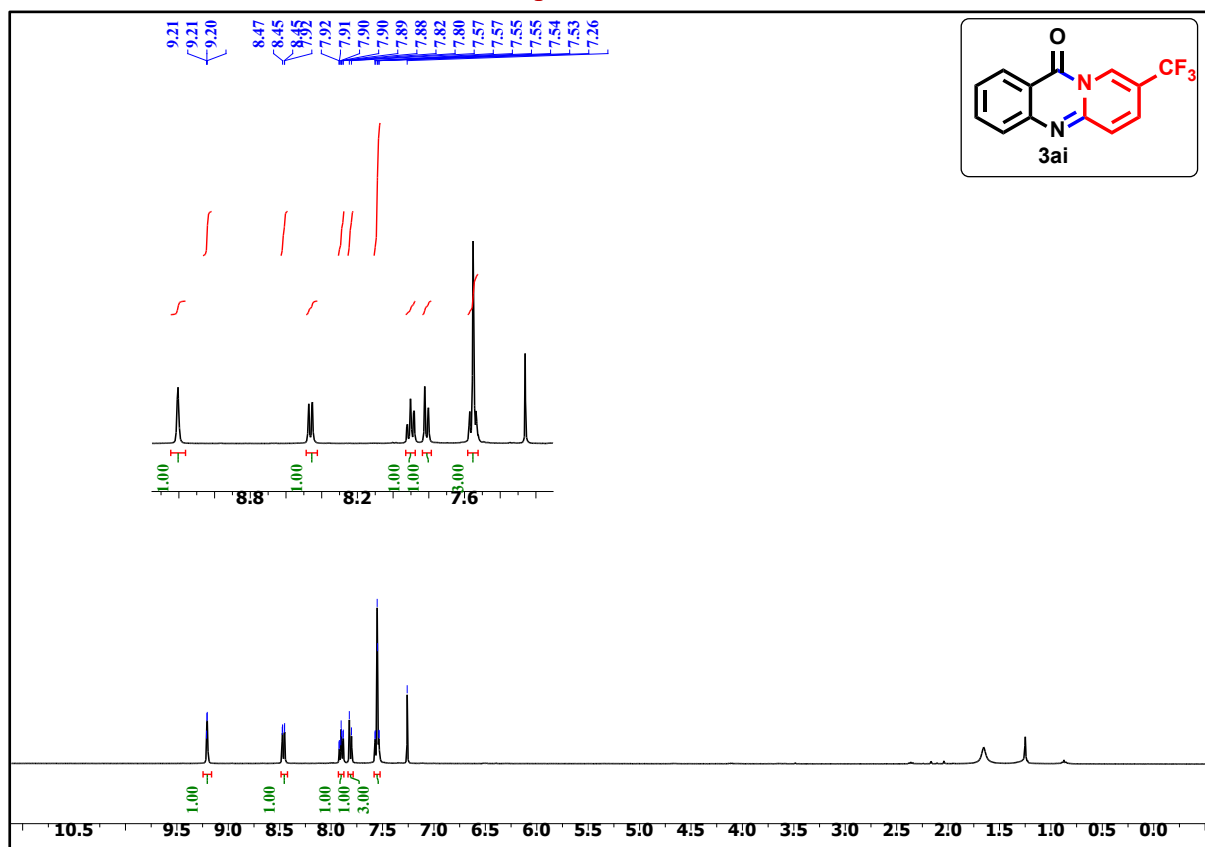
**<sup>1</sup>H NMR spectra of 3ah in CDCl<sub>3</sub>**



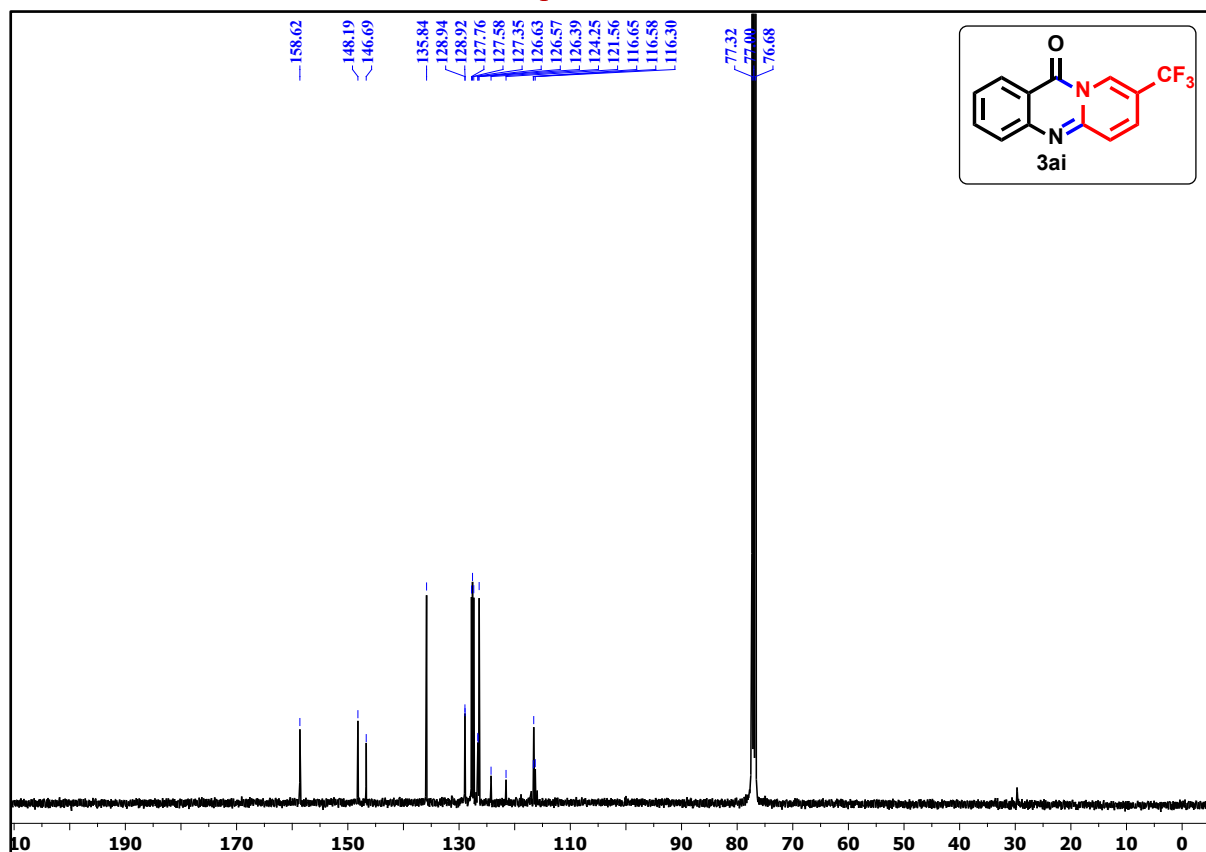
**<sup>13</sup>C NMR spectra of 3ah in CDCl<sub>3</sub>**



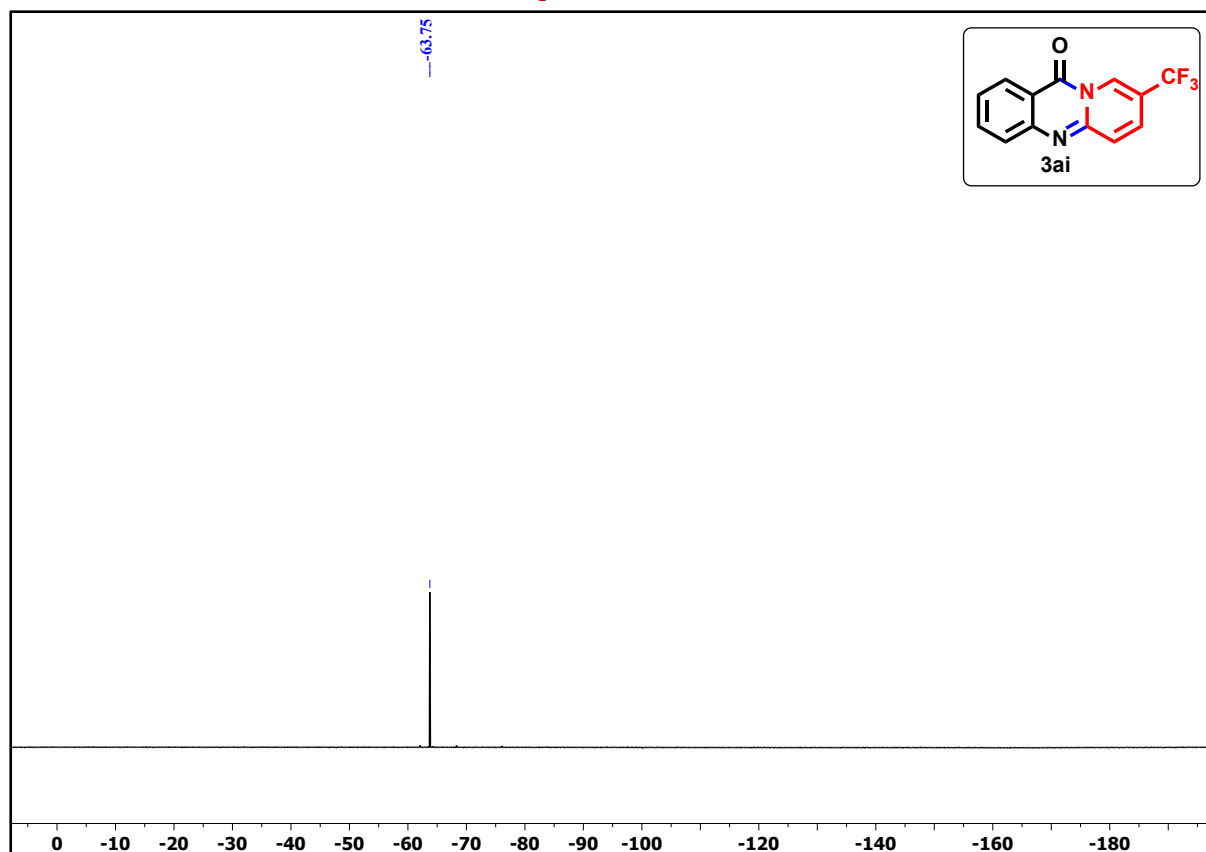
**<sup>1</sup>H NMR spectra of 3ai in CDCl<sub>3</sub>**



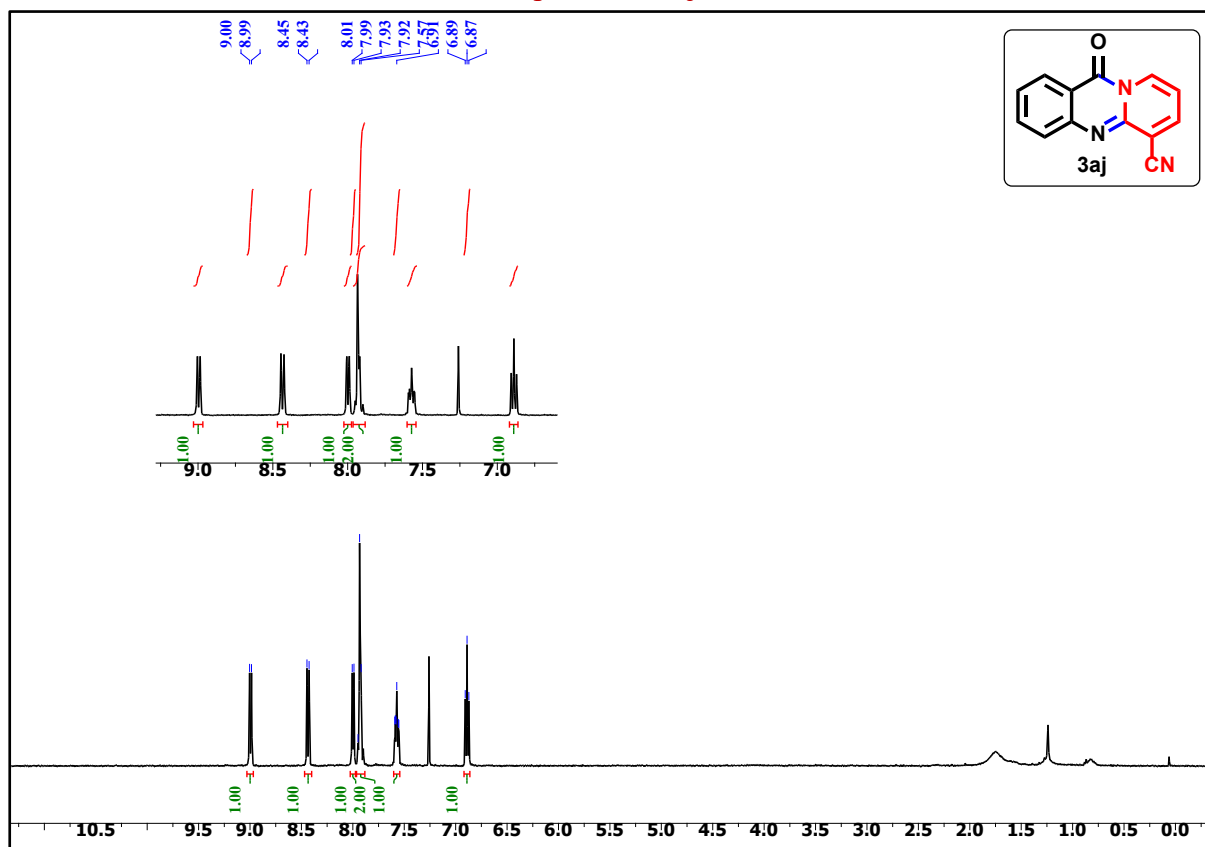
**<sup>13</sup>C NMR spectra of 3ai in CDCl<sub>3</sub>**



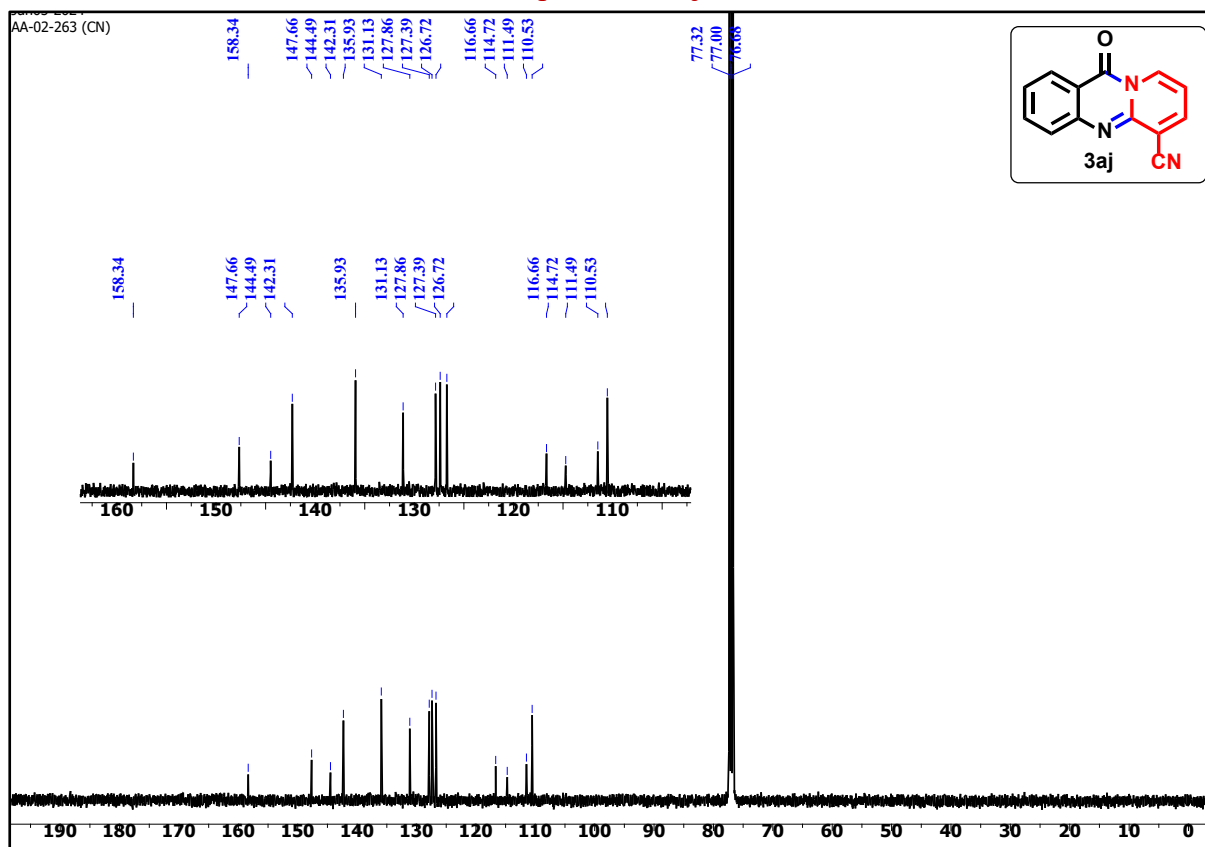
**<sup>19</sup>F NMR spectra of 3ai in CDCl<sub>3</sub>**



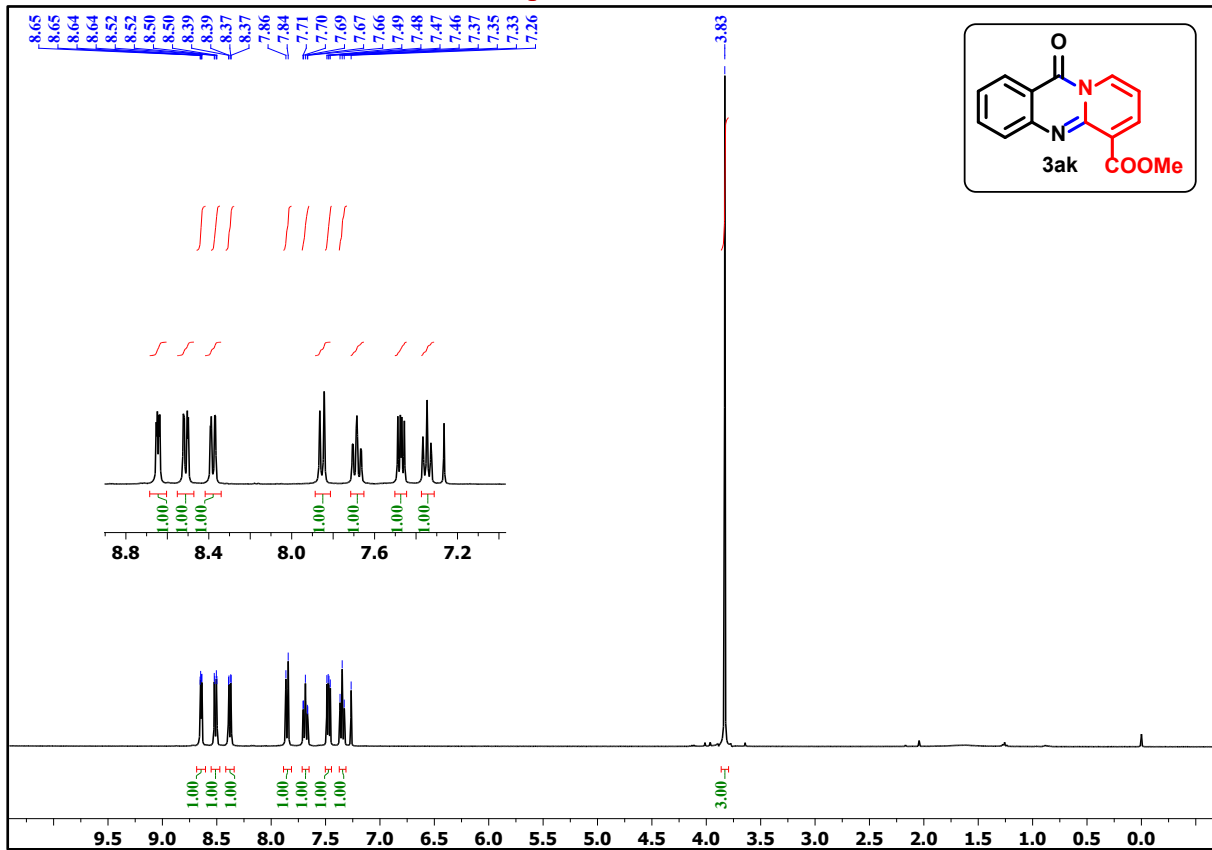
### <sup>1</sup>H NMR spectra of 3aj in CDCl<sub>3</sub>



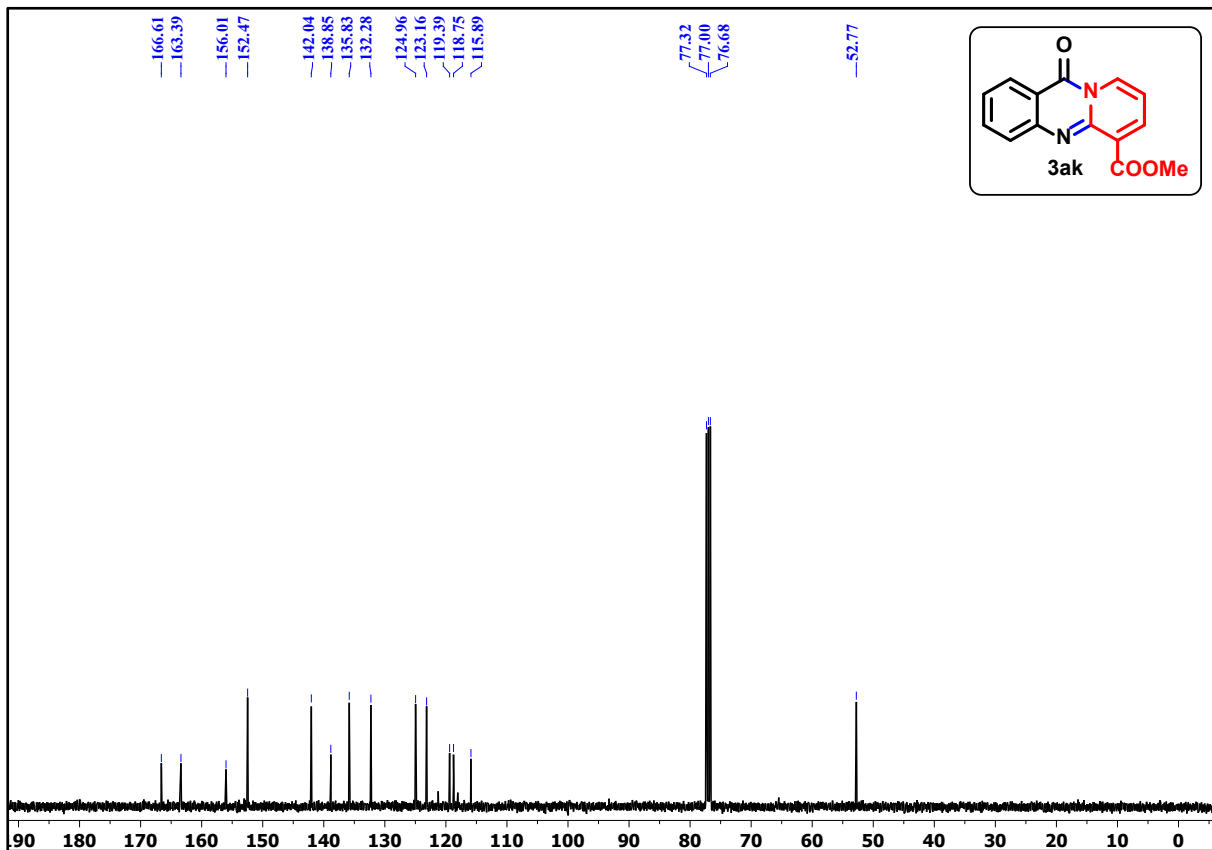
### <sup>13</sup>C NMR spectra of 3aj in CDCl<sub>3</sub>



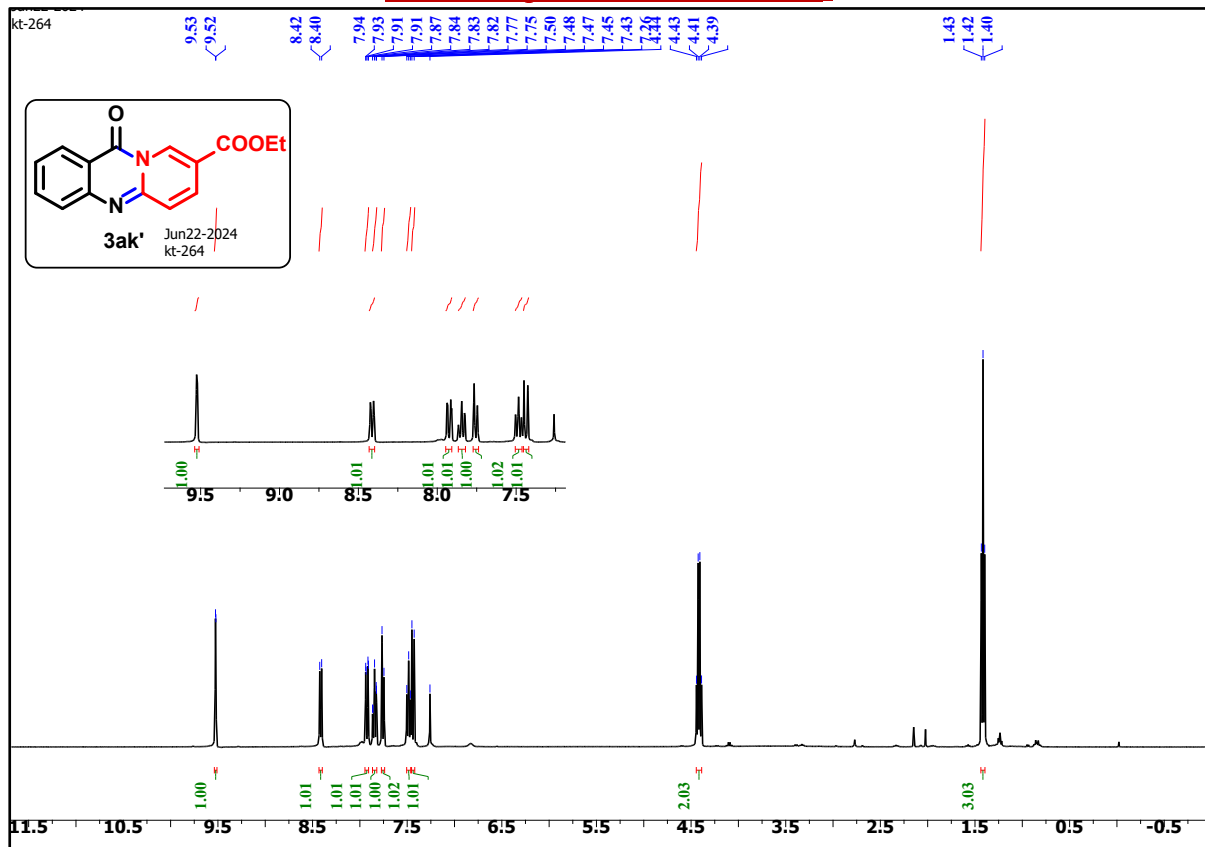
### <sup>1</sup>H NMR spectra of 3ak in CDCl<sub>3</sub>



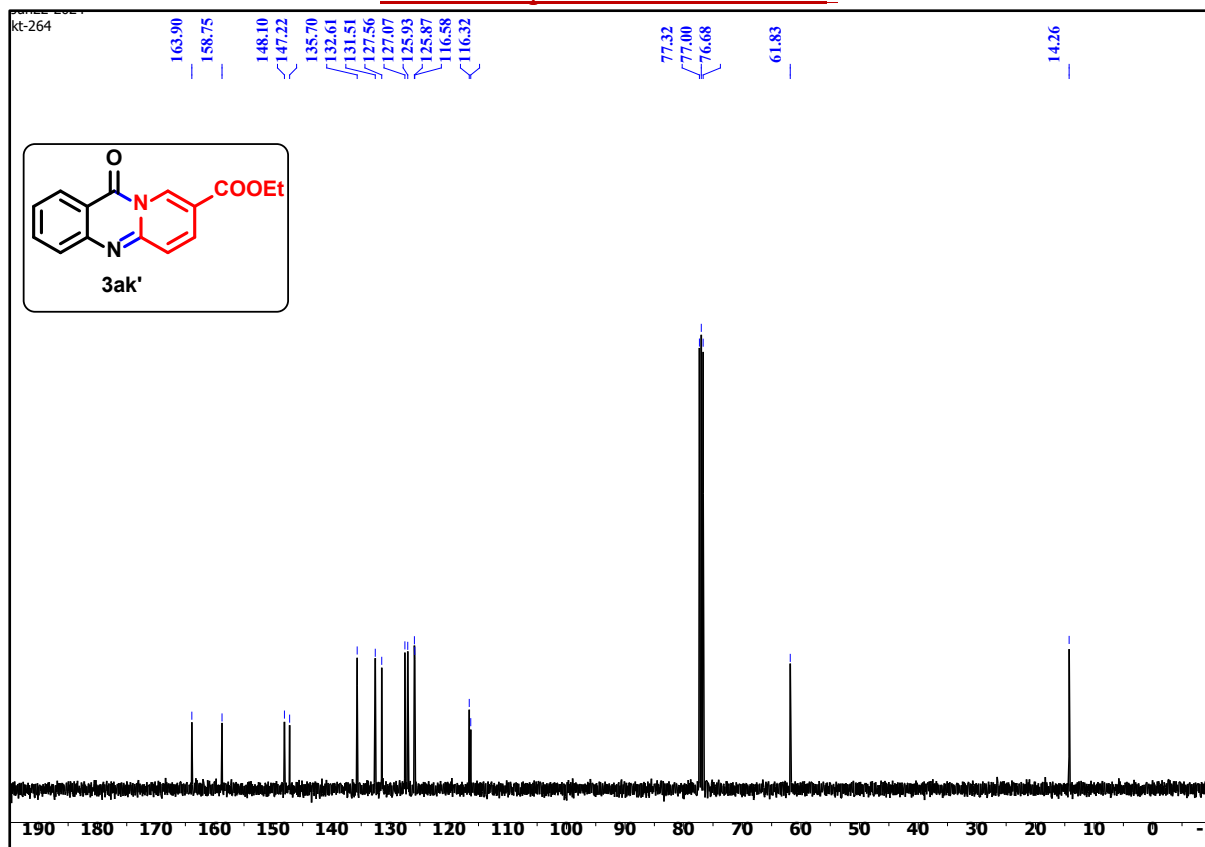
### <sup>13</sup>C NMR spectra of 3ak in CDCl<sub>3</sub>



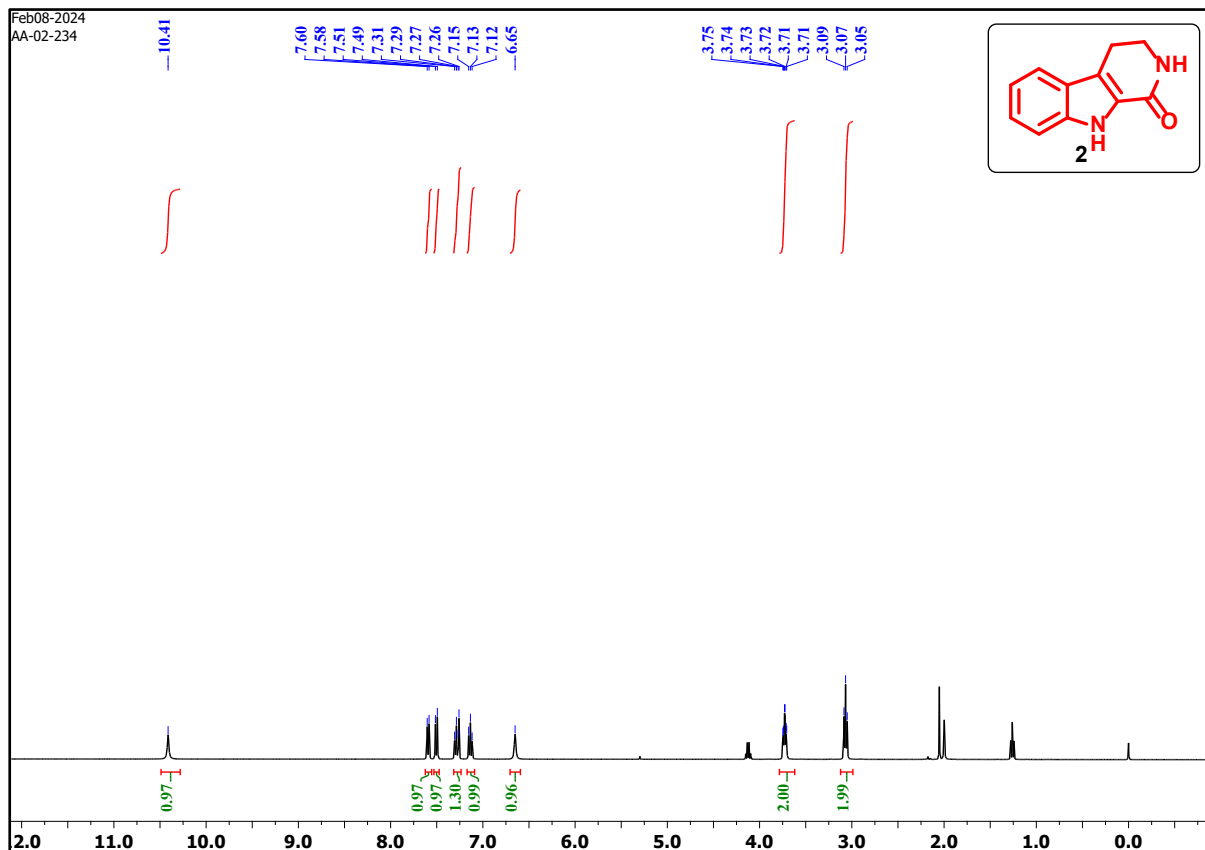
### <sup>1</sup>H NMR spectra of 3ak' in CDCl<sub>3</sub>



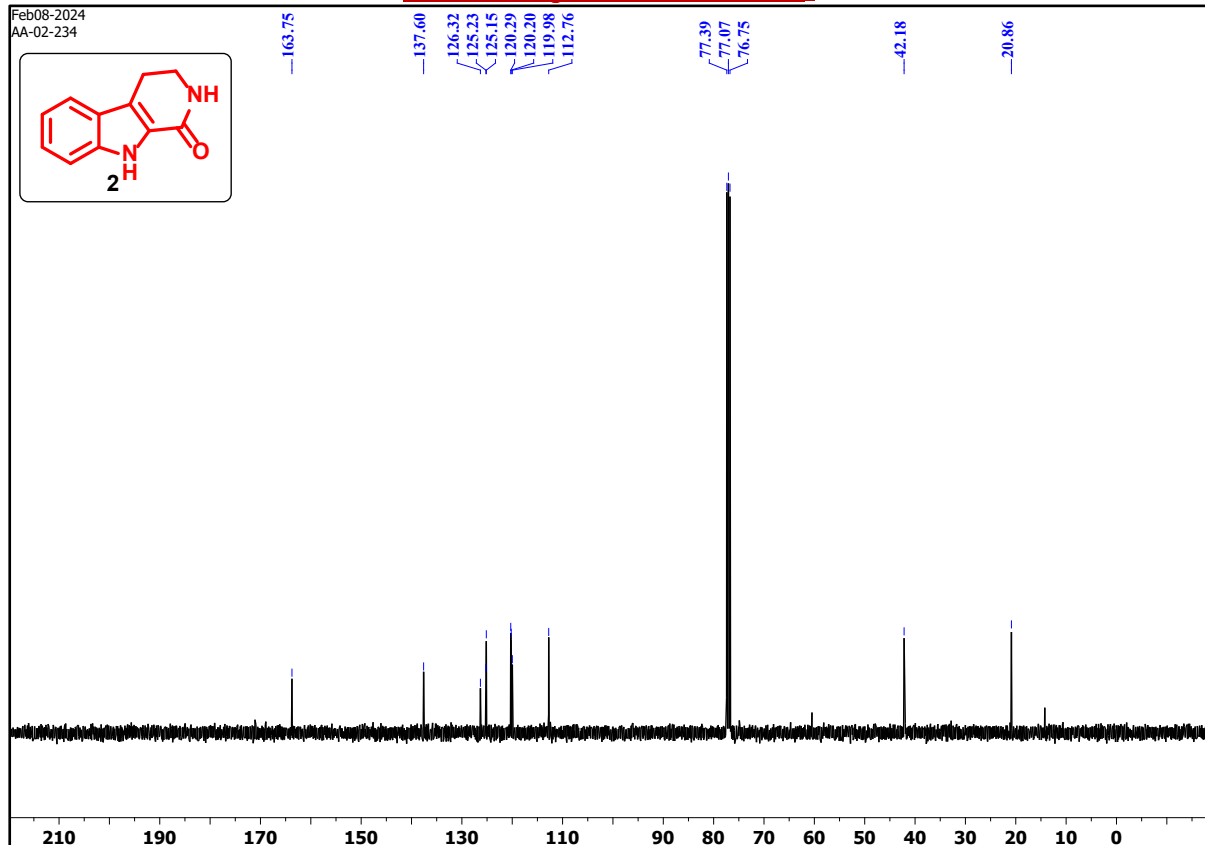
### <sup>13</sup>C NMR spectra of 3ak' in CDCl<sub>3</sub>



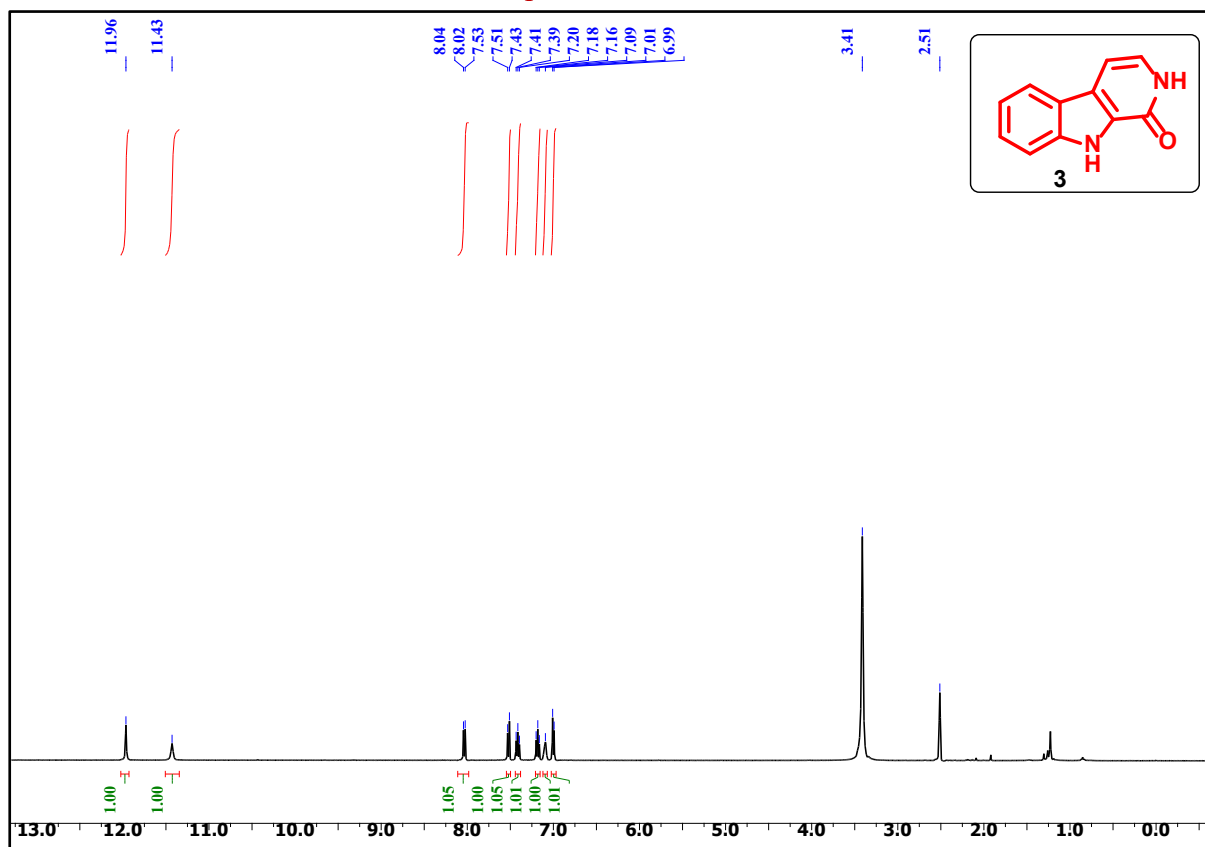
### $^1\text{H}$ NMR spectra of **2** in $\text{CDCl}_3$



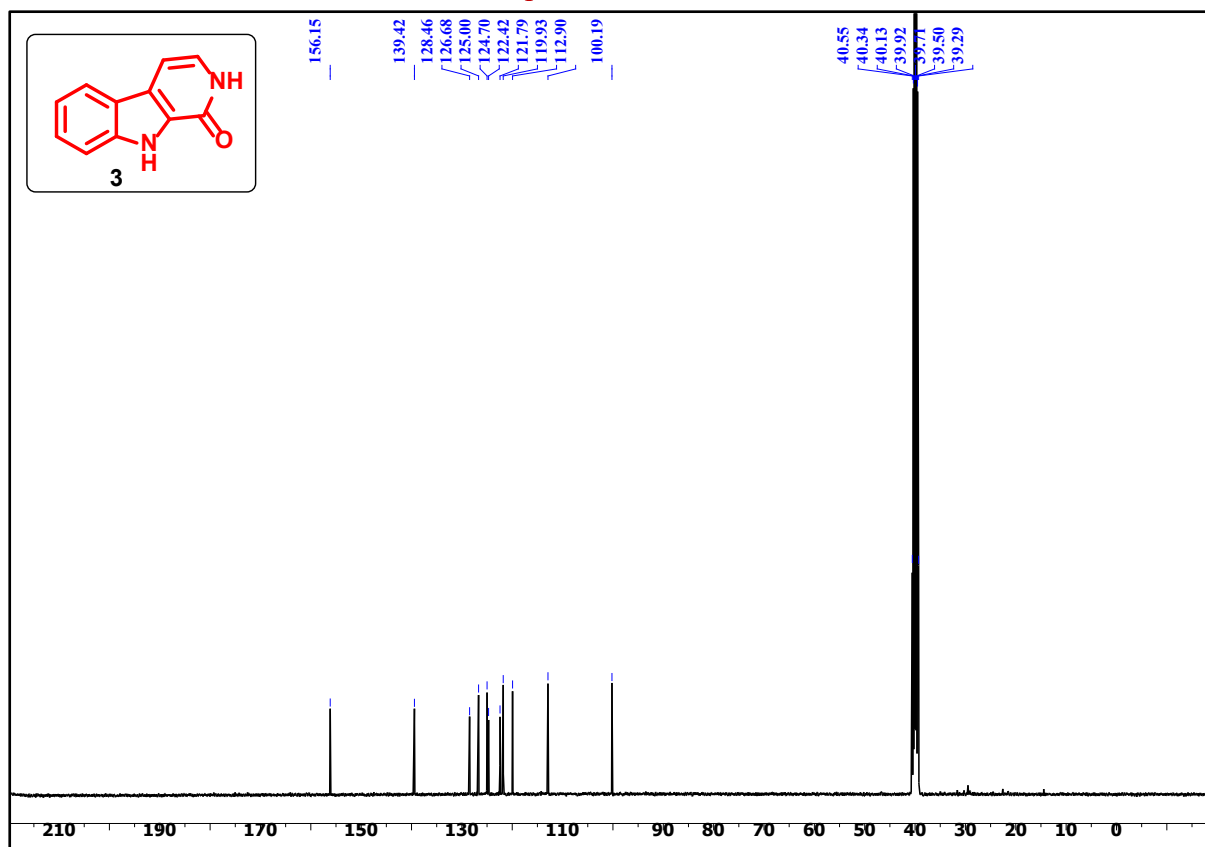
### $^{13}\text{C}$ NMR spectra of **2** in $\text{CDCl}_3$



**<sup>1</sup>H NMR spectra of 3 in DMSO-d<sub>6</sub>**

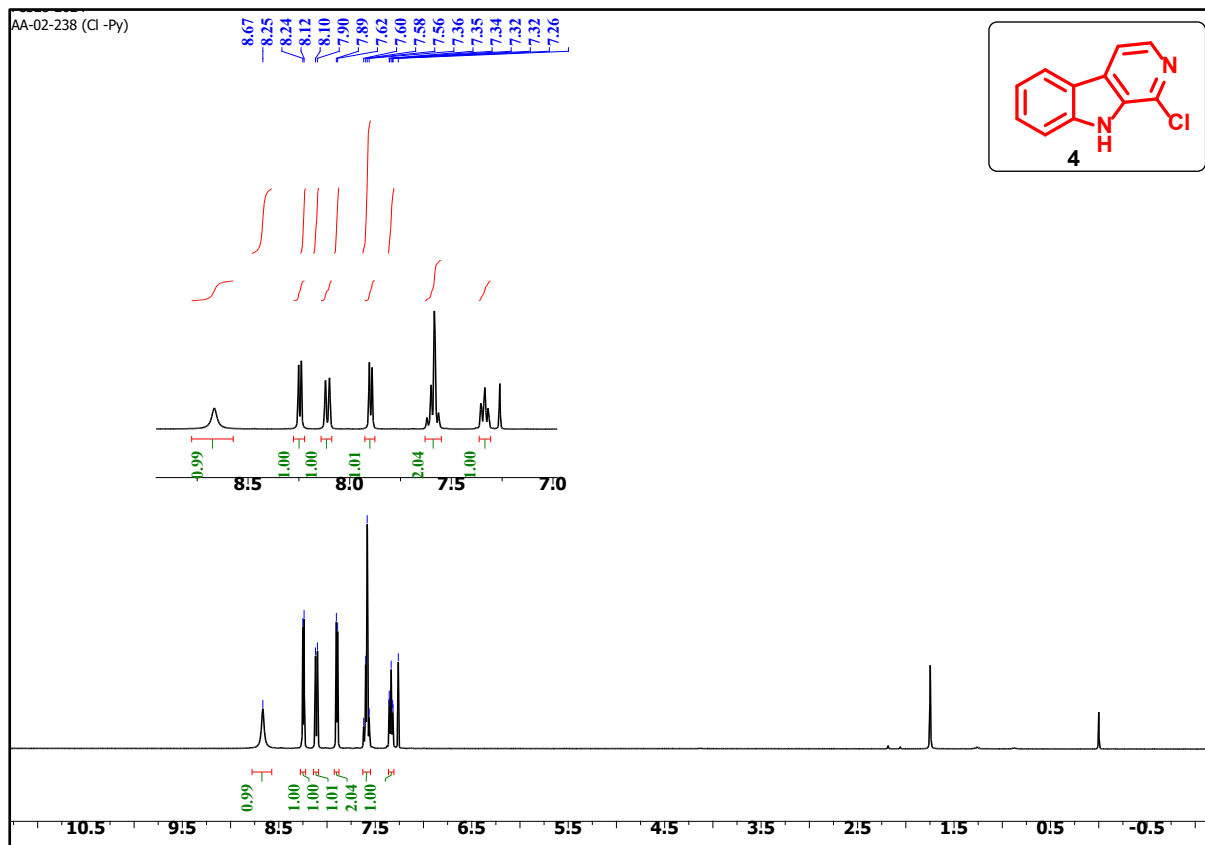


**<sup>13</sup>C NMR spectra of 3 in DMSO-d<sub>6</sub>**

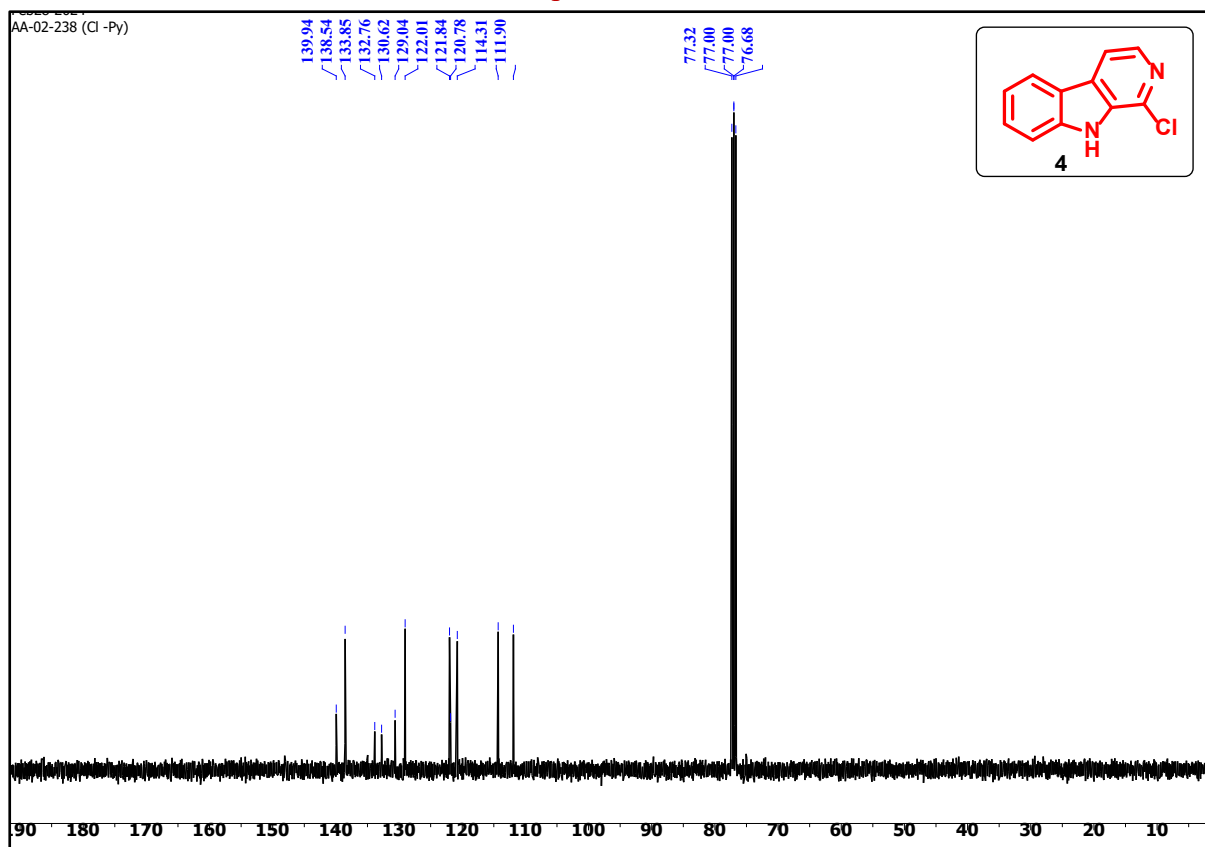




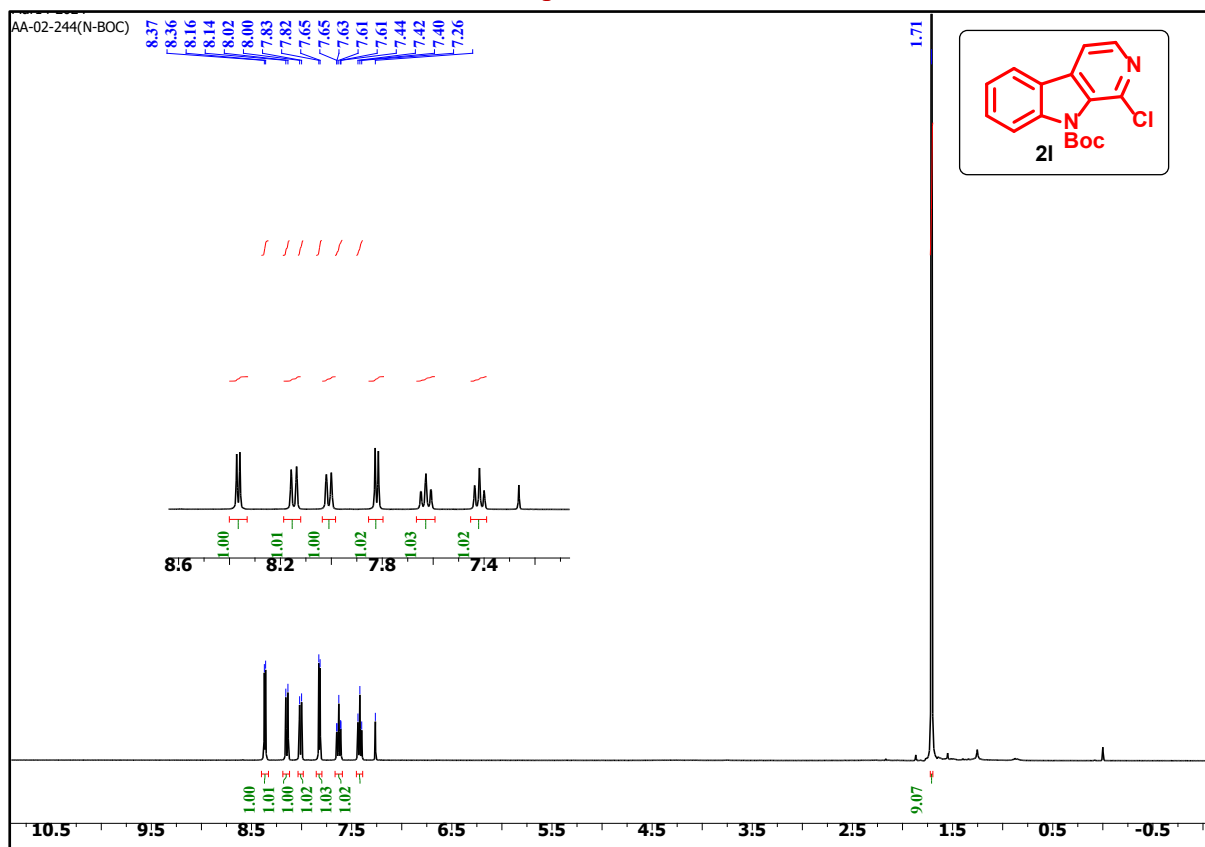
### <sup>1</sup>H NMR spectra of 4 in CDCl<sub>3</sub>



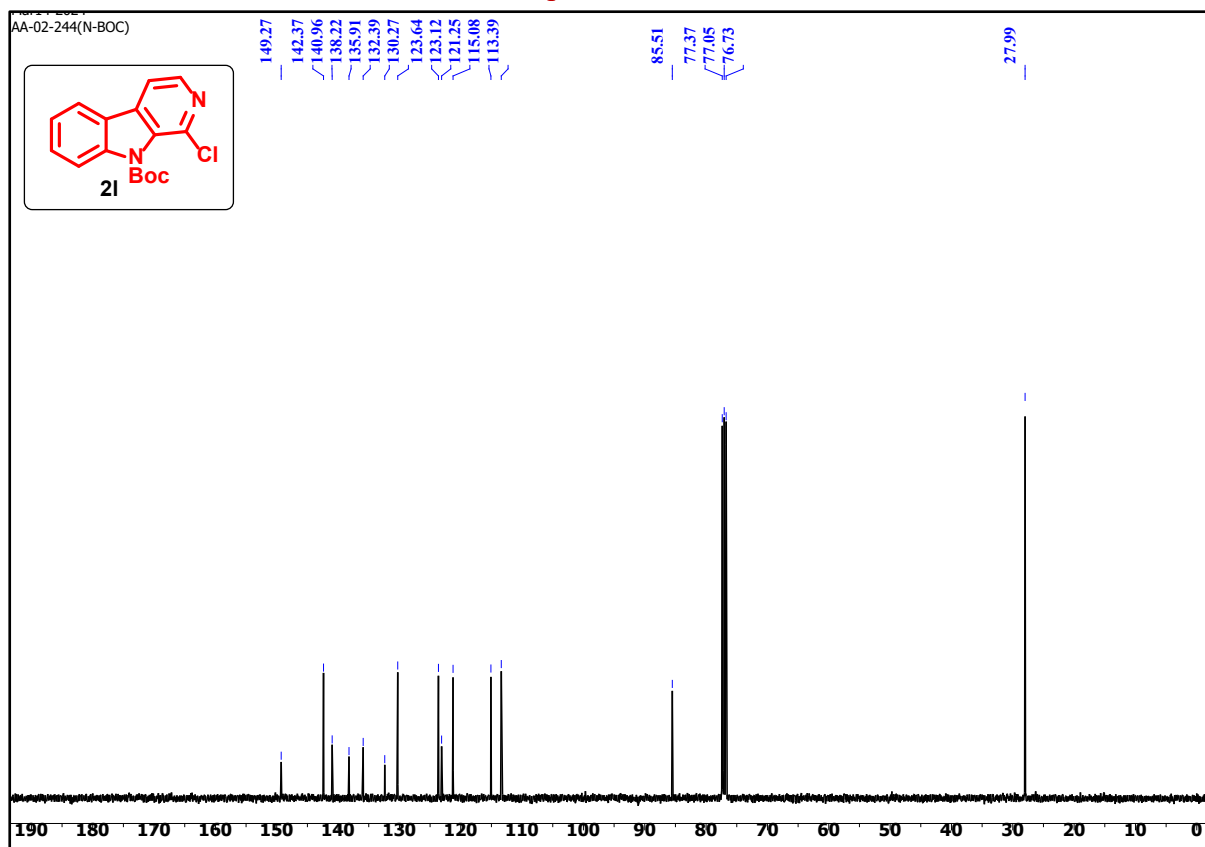
### <sup>13</sup>C NMR spectra of 4 in CDCl<sub>3</sub>



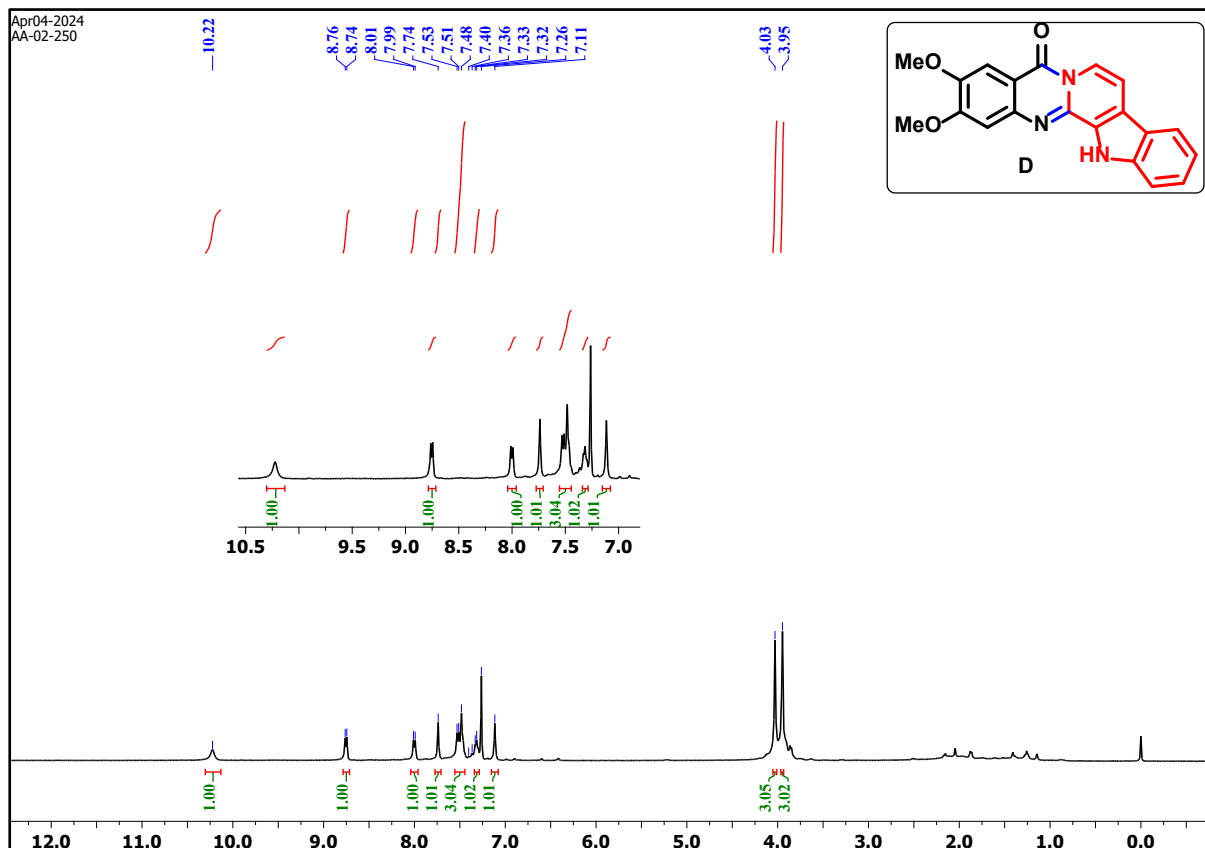
### <sup>1</sup>H NMR spectra of **21** in CDCl<sub>3</sub>



### <sup>13</sup>C NMR spectra of **21** in CDCl<sub>3</sub>



### <sup>1</sup>H NMR spectra of Euxylophoricine – B (D) in CDCl<sub>3</sub>



### <sup>13</sup>C NMR spectra of Euxylophoricine – B (D) in CDCl<sub>3</sub>

