

## Supporting Information

### Expeditious Synthesis of Phenanthridines through Pd/MnO<sub>2</sub>-Mediated C-H Arylation/Oxidative Annulation Cascade from Aldehydes, Aryl Iodides and Amino Acid

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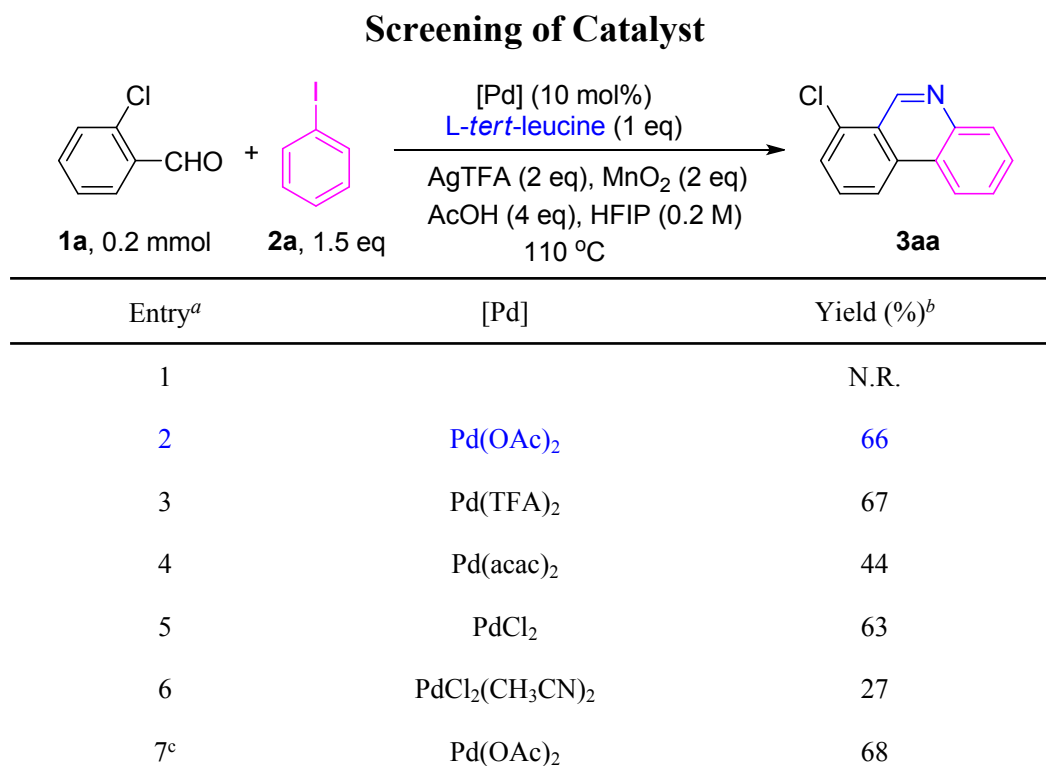
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Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, 241000, China

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## 1. General information:

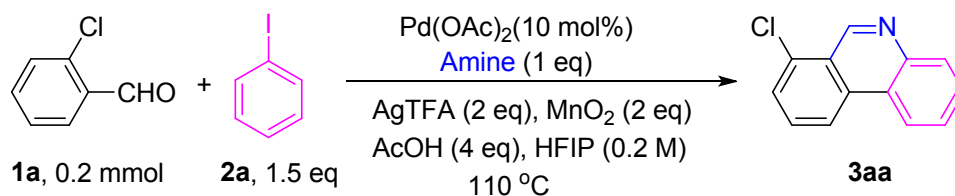
All commercial materials were used as received unless otherwise noted. Commercial reagents were purchased from Alfa Aesar, TCI, Energy Chemical, and used without further purification.  $^1\text{H}$  NMR spectra were recorded at 400 MHz or 500 MHz NMR spectrometers using TMS as an internal standard,  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz or 125 MHz NMR spectrometers using  $\text{CDCl}_3$  as an internal standard and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). Melting points were measured on a hot-stage microscope (XT4-A) and are uncorrected. High resolution mass spectra (HRMS) were obtained on an APEXM Fourier transform mass spectrometry (APCI). EPR spectra were obtained using Bruker EMX plus6/1 X-band variable-temperature apparatus.

## 2. Optimization of reaction conditions



<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), *L-tert-leucine* (0.2 mmol), [Pd] (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> 15 mmol% of Pd(OAc)<sub>2</sub>.

### Screening of Amino Acid

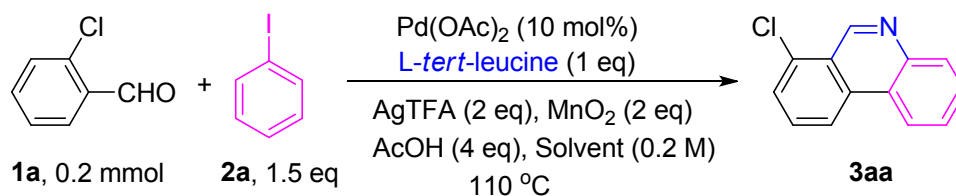


Entry <sup>a</sup>	Amine	Yield (%) <sup>b</sup>
1		N.D.
2	<i>L-tert-leucine</i>	66
3	L-alanine	trace
4	L-aspartic acid	trace
5	L-valine instead	15
6	L-isoleucine	12 <sup>g</sup>
7	Glycine	trace
8	D, <i>L-tert-leucine</i>	57
9	<i>L-tert-leucine</i>	65 <sup>c</sup>
10	<i>L-tert-leucine</i>	57 <sup>d</sup>
11	AcNH <sub>4</sub>	36 <sup>e</sup> , 42 <sup>f</sup>
12	<i>t</i> -BuNH <sub>2</sub>	28 <sup>e</sup> , 34 <sup>f</sup>
13	BnNH <sub>2</sub>	19 <sup>e</sup> , 14 <sup>f</sup>
14	AcNH <sub>4</sub>	N.D. <sup>h</sup>
15	<i>t</i> -BuNH <sub>2</sub>	N.D. <sup>h</sup>
16	BnNH <sub>2</sub>	N.D. <sup>h</sup>

<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), Amino acid (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> 1.2 equiv of *L-tert-leucine*. <sup>d</sup> 1.5 equiv of *L-tert-leucine*. <sup>e</sup> 30 mol% of *L-tert-leucine* was used. <sup>f</sup> 1

equiv of *L-tert-leucine* was used. <sup>g</sup> 10% yield of **B** was obtained.<sup>h</sup> 0.2 mmol amine was used.

### Screening of Solvent

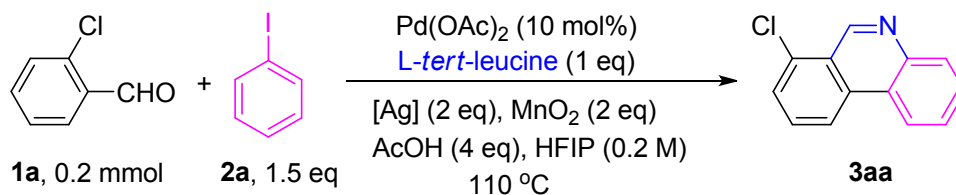


Entry <sup>a</sup>	Solvent	Yield (%) <sup>b</sup>
1	HFIP	66
2	TFE	43
3	1,4-dioxane	N.D
4	toluene	N.D
5	DCE	trace
6	MeCN	N.D
7	MeOH	trace
8	AcOH	trace
9	THF	trace
10	DMSO	N.D.
11	HFIP/TFE (v/v = 1:1)	48

<sup>a</sup> Reactions conditions: **1** (0.2 mmol), **2** (0.3 mmol), *L-tert-leucine* (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), AcOH (0.8 mmol), Solvent (1 mL), 110 °C, 24

h. <sup>b</sup> Isolated yield by flash column chromatography.

### Screening of [Ag]

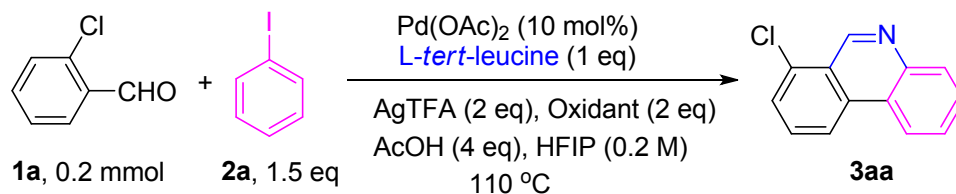


Entry <sup>a</sup>	[Ag]	Yield (%) <sup>b</sup>
1		5
2	AgTFA	66
3	Ag <sub>2</sub> CO <sub>3</sub>	55
4	AgOAc	42
5	Ag <sub>2</sub> O	21
6	AgNO <sub>3</sub>	49
7	AgOTf	57
8	AgF	44
9	AgTFA	57 <sup>c</sup>
10	AgTFA	50 <sup>d</sup>

<sup>a</sup> Reactions conditions: **1** (0.2 mmol), **2** (0.3 mmol), L-tert-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), [Ag] (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup>

Isolated yield by flash column chromatography. <sup>c</sup> 1.2 equiv of AgTFA. <sup>d</sup> 1.5 equiv of AgTFA.

### Screening of Oxidant



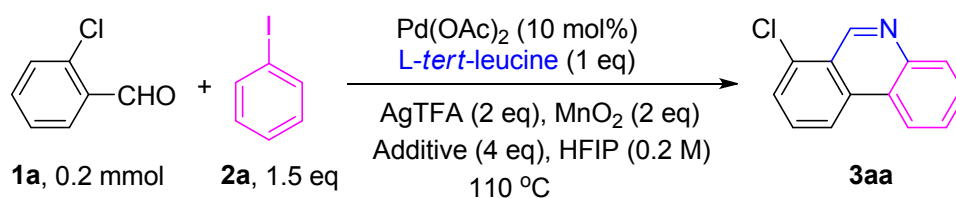
Entry <sup>a</sup>	Oxidant	Yield (%) <sup>b</sup>
1	/	N.D.
2	Mn(acac) <sub>2</sub>	N.D.
3	Mn(OAc) <sub>2</sub> ·4H <sub>2</sub> O	26
4	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	61

5	MnO <sub>2</sub>	66
6	BQ	21
7	PhI(OAc) <sub>2</sub>	N.D.
8	Selectflour	N.D.
9	DDQ	N.D.
10	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	trace
11	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	trace
12	Oxone	N.D.
13	Cu(OAc) <sub>2</sub>	23
14	CuO	21
15 <sup>c</sup>	MnO <sub>2</sub>	33
16 <sup>d</sup>	MnO <sub>2</sub>	64

<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), *L*-*tert*-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), Oxidant (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), 110 °C, 24 h.

<sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> 1.0 equiv of MnO<sub>2</sub>. <sup>d</sup> 4.0 equiv of MnO<sub>2</sub>.

### Screening of Additive

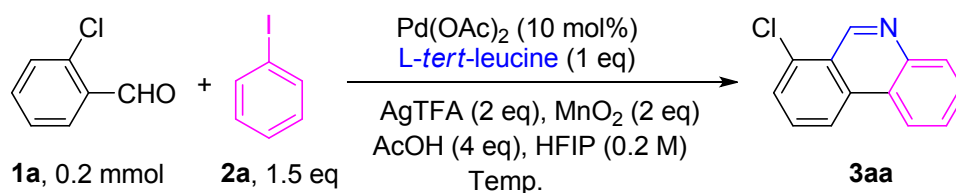


Entry <sup>a</sup>	Additive	Yield (%) <sup>b</sup>
1	/	16
2	AcOH	66
3	PivOH	47
4	TFA	trace
5	TsOH·H <sub>2</sub> O	trace
6	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	52
7	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COOH	52
8	PhCOOH	51

9	3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COOH	46
10	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COOH	42
11	<i>m</i> -CPBA	trace
12	KH <sub>2</sub> PO <sub>4</sub>	trace
13	K <sub>3</sub> PO <sub>4</sub>	trace
14	AcOH	54 <sup>c</sup>
15	AcOH	61 <sup>d</sup>

<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), *L*-*tert*-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), Additive (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> 2 equiv of AcOH. <sup>d</sup> 6 equiv of AcOH.

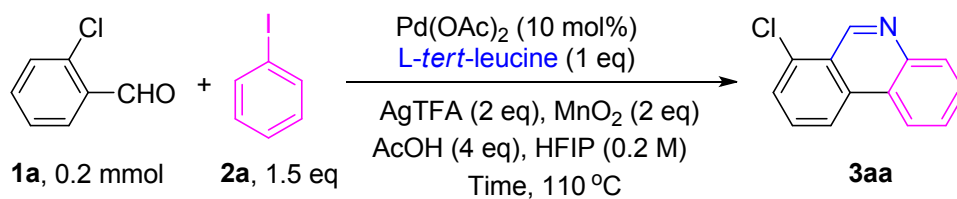
### Screening of Temperature



Entry <sup>a</sup>	T (°C)	Yield (%) <sup>b</sup>
1	100	41
2	110	66
3	120	59

<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), *L*-*tert*-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (0.4 mmol), AcOH (0.8 mmol), HFIP (1 mL), Temp., 24 h. <sup>b</sup> Isolated yield by flash column chromatography.

### Screening of Reaction Time



Entry <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
1	15	40
2	24	66
3	36	62
4	48	60

<sup>a</sup> Reactions conditons: **1** (0.2 mmol), **2** (0.3 mmol), *L-tert-leucine* (0.2 mmol),  $\text{Pd(OAc)}_2$  (0.02 mmol),  $\text{AgTFA}$  (0.4 mmol),  $\text{MnO}_2$  (0.4 mmol),  $\text{AcOH}$  (0.8 mmol), HFIP (1 mL), 110 °C, Time. <sup>b</sup> Isolated yield by flash column chromatography.

**Table S1 Optimization of reaction conditions<sup>a</sup>**

$\text{Pd(OAc)}_2$  (10 mol%)  
*L-tert-leucine* (1 eq)  
 $\text{Ag Salt}$ , Oxidant (2 eq)  
 Additive (4 eq), HFIP  
 110 °C

Entry	Ag Salt	Oxidant	Additive	Yield (%) <sup>b</sup>
1	$\text{AgOAc}$	$\text{MnO}_2$	$\text{AcOH}$	42
2	$\text{Ag}_2\text{CO}_3$	$\text{MnO}_2$	$\text{AcOH}$	55
3	$\text{Ag}_2\text{O}$	$\text{MnO}_2$	$\text{AcOH}$	21
4	$\text{AgNO}_3$	$\text{MnO}_2$	$\text{AcOH}$	49
5	$\text{AgOTf}$	$\text{MnO}_2$	$\text{AcOH}$	57
6	$\text{AgF}$	$\text{MnO}_2$	$\text{AcOH}$	44
7	$\text{AgTFA}$	$\text{MnO}_2$	$\text{AcOH}$	66
8	$\text{AgTFA}$	$\text{MnO}_2$	$\text{AcOH}$	64 <sup>c</sup>
9	$\text{AgTFA}$	$\text{Mn(acac)}_2$	$\text{AcOH}$	N.D.
10	$\text{AgTFA}$	$\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$	$\text{AcOH}$	26



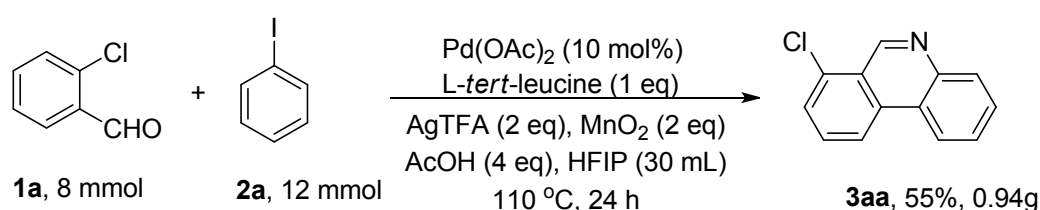
11	AgTFA	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	AcOH	61
12	AgTFA	BQ	AcOH	21
13	AgTFA	PhI(OAc) <sub>2</sub>	AcOH	N.D.
14	AgTFA	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	AcOH	Trace
15	AgTFA	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	AcOH	Trace
16	AgTFA	Cu(OAc) <sub>2</sub>	AcOH	23
17	AgTFA	CuO	AcOH	21
18	AgTFA	MnO <sub>2</sub>	TFA	Trace
19	AgTFA	MnO <sub>2</sub>	TsOH·H <sub>2</sub> O	Trace
20	AgTFA	MnO <sub>2</sub>	PivOH	47
21	AgTFA	MnO <sub>2</sub>	PhCO <sub>2</sub> H	51

<sup>a</sup> Reactions conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), *L-tert*-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), Ag Sat (0.4 mmol), Oxidant (0.4 mmol), Additive (0.8 mmol), HFIP (1 mL), 110 °C, 24 h. <sup>b</sup> Isolated yield by flash column chromatography. <sup>c</sup> Under argon atmosphere.

### 3. General procedure for synthesis of phenanthridine

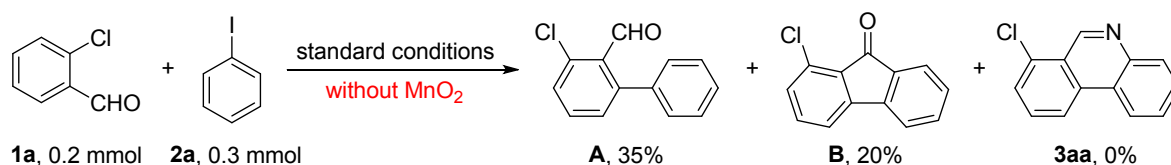
A mixture of aldehyde substrates (**1**, 0.2 mmol), aryl iodide (**2**, 0.3 mmol), *L-tert*-leucine (0.2 mmol), Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (**fresh**) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The combined organic was removed in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product.

### 4. Gram-scale preparation of **3aa** and competition experiment

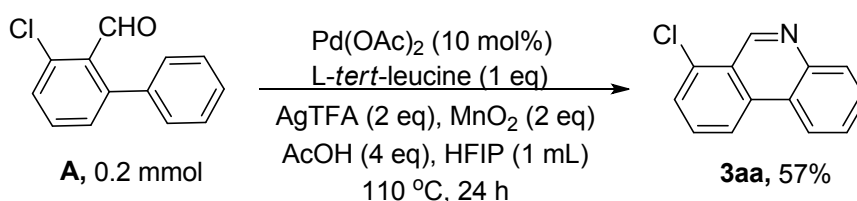


A 75 mL Schlenk tube was charged with *o*-chlorobenzaldehyde **1a** (8 mmol), **2a** (12 mmol), *L*-*tert*-leucine (8 mmol) and Pd(OAc)<sub>2</sub> (0.8 mmol), AgTFA (16 mmol), MnO<sub>2</sub> (**fresh**) (16 mmol). The mixture was dissolved in 30 mL HFIP followed by addition of AcOH (32 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product **3aa** (0.94 g, 55% isolated yield).

## 5. Control experiments

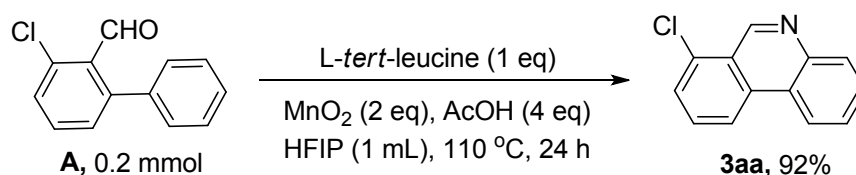


A 15 mL Schlenk tube was charged with *o*-chlorobenzaldehyde **1a** (0.2 mmol), **2a** (1.5 mmol), *L*-*tert*-leucine (1.0 mmol) and Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product **A** and **B**.

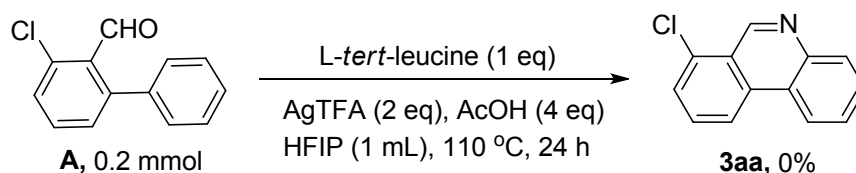


A 15 mL Schlenk tube was charged with biphenyl aldehyde **A** (0.2 mmol), *L*-*tert*-leucine (0.2 mmol) and Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol), MnO<sub>2</sub> (**fresh**) (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to

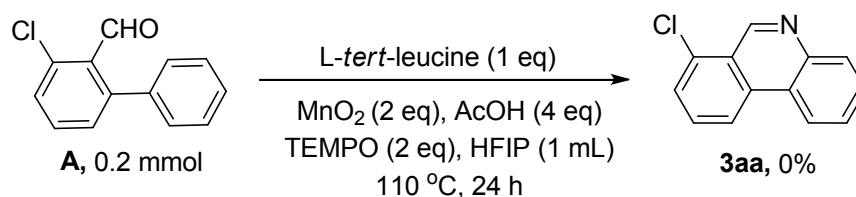
afford the pure product **3aa** (57% isolated yield).



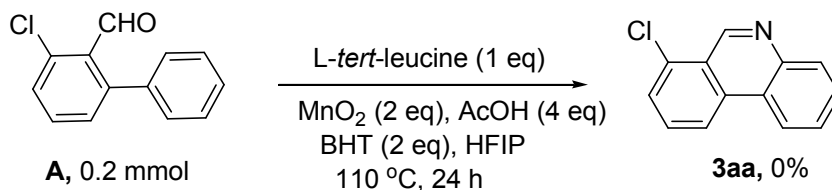
A mixture of biphenyl aldehyde **A** (0.2 mmol), *L-tert-leucine* (0.2 mmol),  $\text{MnO}_2$  (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product **3aa** (92% isolated yield).



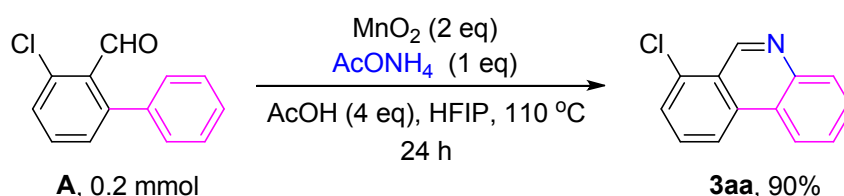
A mixture of biphenyl aldehyde **A** (0.2 mmol), *L-tert-leucine* (0.2 mmol), AgTFA (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no **3aa** was detected by TLC.



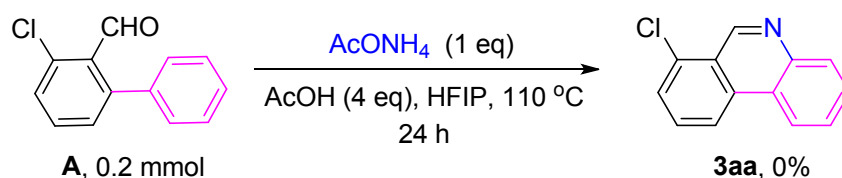
A mixture of biphenyl aldehyde **A** (0.2 mmol), *L-tert-leucine* (0.2 mmol), TEMPO (0.4 mmol),  $\text{MnO}_2$  (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no **3aa** was detected by TLC.



A mixture of biphenyl aldehyde **A** (0.2 mmol), *L-tert-leucine* (0.2 mmol), BHT (0.4 mmol), MnO<sub>2</sub> (**fresh**) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no **3aa** was detected by TLC.



A mixture of biphenyl aldehyde **A** (0.2 mmol), AcONH<sub>4</sub> (0.2 mmol), MnO<sub>2</sub> (**fresh**) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure product **3aa** (90% isolated yield).

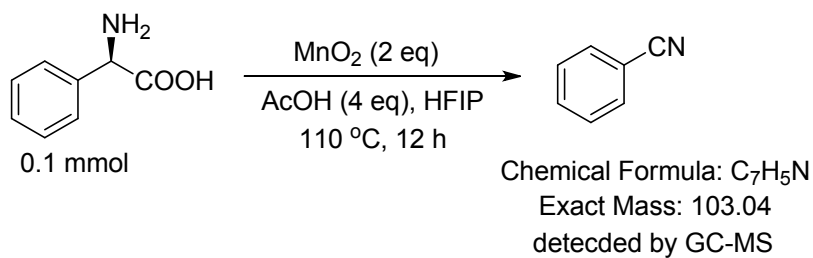


A mixture of biphenyl aldehyde **A** (0.2 mmol), AcONH<sub>4</sub> (0.2 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no **3aa** was detected by TLC.



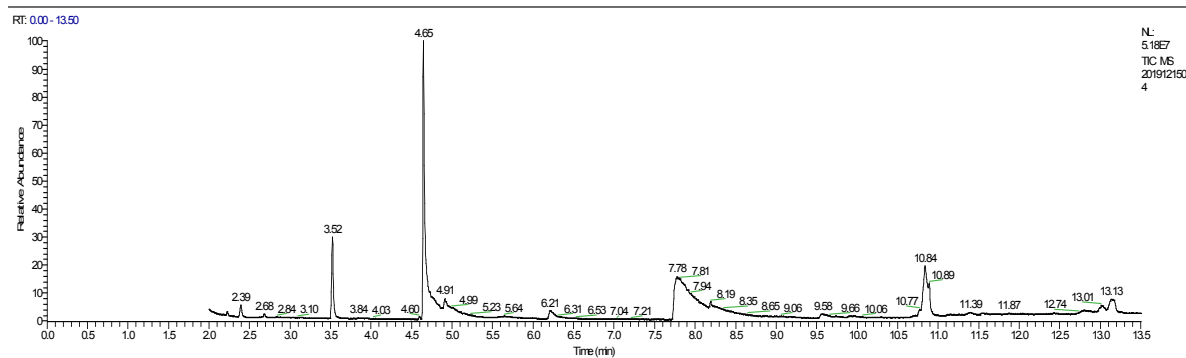
A mixture of biphenyl aldehyde **A** (0.2 mmol), AcONH<sub>4</sub> (0.2 mmol), TEMPO (0.4 mmol), MnO<sub>2</sub> (**fresh**) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 24 h. Then, the reaction mixture was cooled to room temperature. And no **3aa** was detected by TLC.

## 6. GC-MS analysis

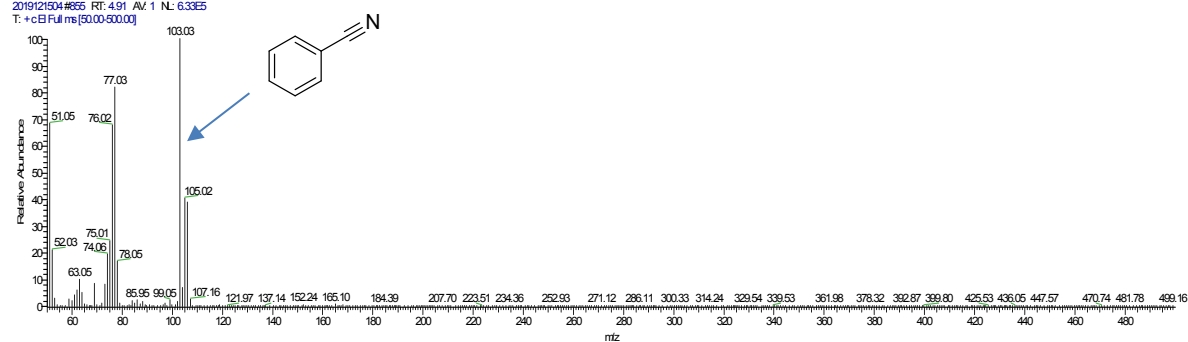


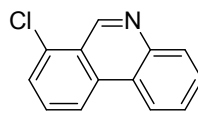
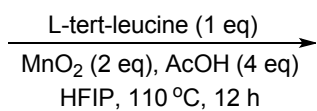
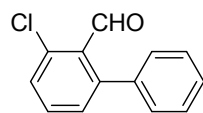
E:\ZIT\FanJian\20191215\2019121504

12/15/19 10:15:41

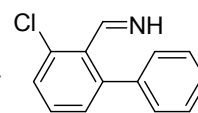


2019121504#666 RT: 4.91 AM: 1 N: 6.33E5  
T: +cEiFull.ms[50.00-500.00]





80%

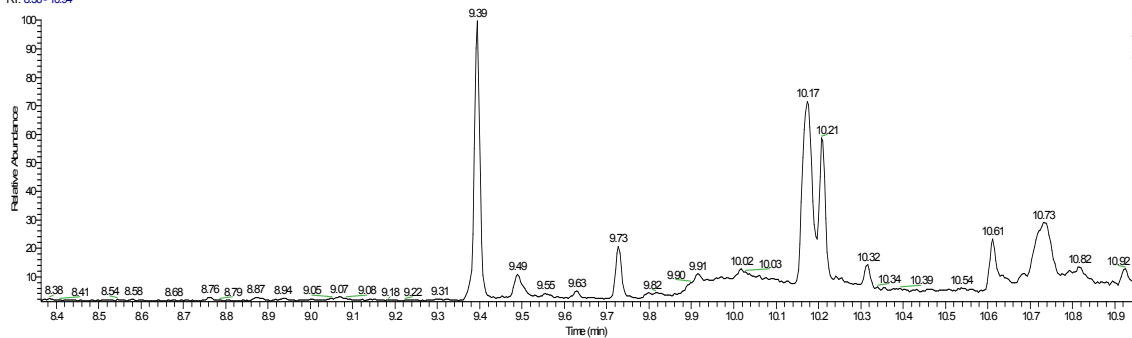


Chemical Formula:  $\text{C}_{13}\text{H}_{10}\text{ClN}$   
 Exact Mass: 215.05  
 detected by GC-MS

E:\Z\T\FanJan2019\2150219121503

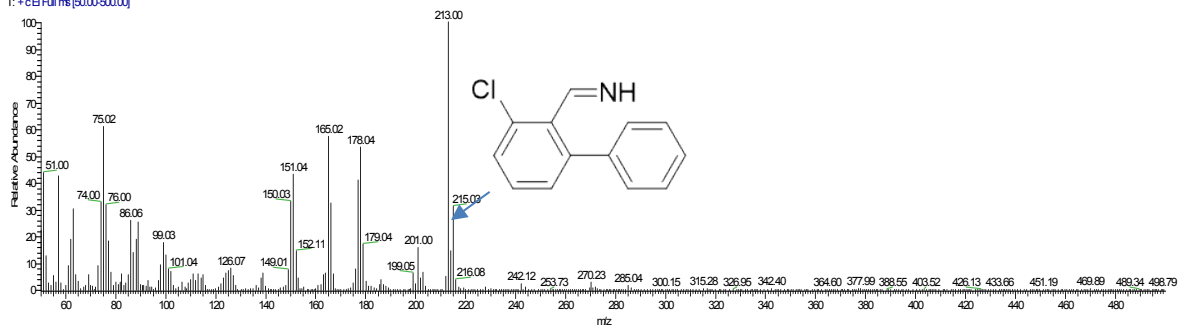
12/15/19 09:57:23

RT: 8.36 - 10.94

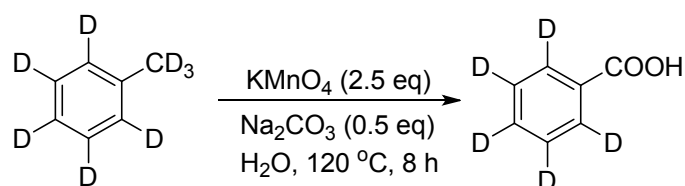


NL: 1.53E7  
 TIC MS  
 2019121503  
 3

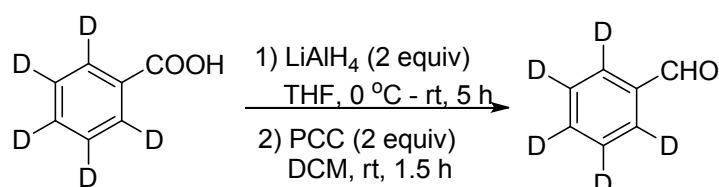
2019121503#204 RT: 10.17 AM: 1 NL: 8.83E5  
 T: +cB Full ms [500-500.0]



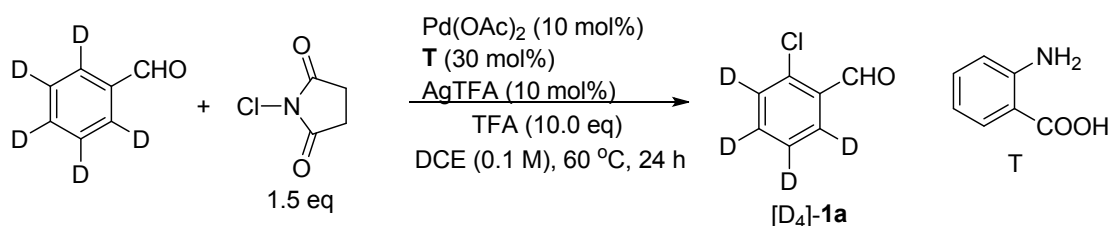
## 7. Deuteration Studies



A round-bottom flask equipped with a stir bar and a condenser was charged with  $d_8$ -toluene (99.9 atom % D) (1 g, 10 mmol),  $\text{KMnO}_4$  (4 g, 25 mmol),  $\text{Na}_2\text{CO}_3$  (0.26 g, 5 mmol), and  $\text{H}_2\text{O}$  (30 mL). The reaction mixture was refluxed for 8 h and then cooled to room temperature. The mixture was filtered through a pad of celite, and the filtrate was acidified with 12 M HCl and extracted with DCM ( $3 \times 30$  mL). The organic layer was washed with water and concentrated in vacuo. The crude product was recrystallized from water to give  $\text{C}_6\text{D}_5\text{CO}_2\text{H}$  as white needle solid (0.64 g, 50% yield). Synthesis of  $\text{C}_6\text{D}_5\text{CO}_2\text{H}$  was prepared using a similar procedure (P. Gandeepan, P. Rajamalli, C. Cheng, *Angew. Chem. Int. Ed.*, 2016, **55**, 4308-4311).



$[^2\text{H}_5]$ -Benzyl alcohol (0.45 g; 4 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was slowly dropped into the solution of pyridinium chlorochromate (Sigma-Aldrich) (1.5 g; 6 mmol) and  $\text{CH}_2\text{Cl}_2$  (12 mL). The mixture which turned quickly from orange to black was stirred for 1.5 h. Diethyl ether (20 mL) was added, and the residue was further extracted with diethyl ether ( $3 \times 10$  mL) until the gummy residue became granular solid. The combined extracts were passed through dry Florisil® (Sigma-Aldrich) (10 g), and the solvent was removed by  $\text{N}_2$  gas to obtain  $[^2\text{H}_5]$ - benzaldehyde (80% yield, 85.1% purity) (L. Li, B. Zhou, Y.-H. Wang, C. Shu, Y.-F. Pan, X. Lu, L.-W. Ye, *Angew. Chem. Int. Ed.*, 2015, **54**, 8245–8249).

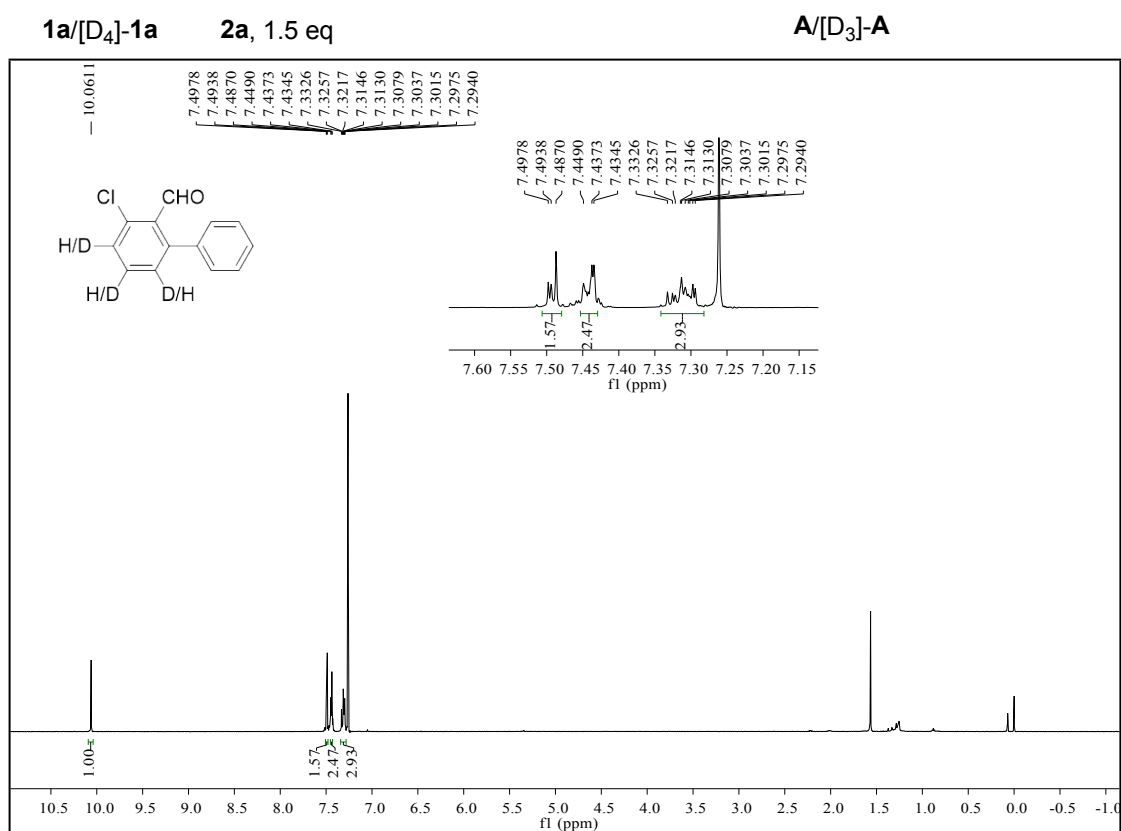
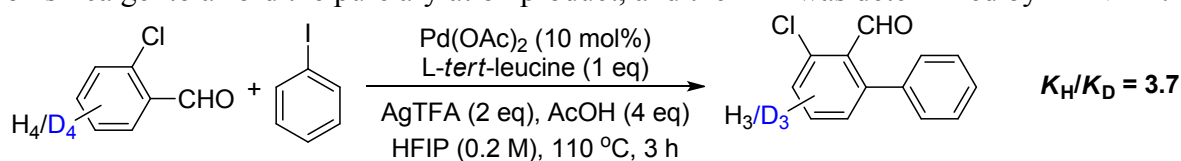


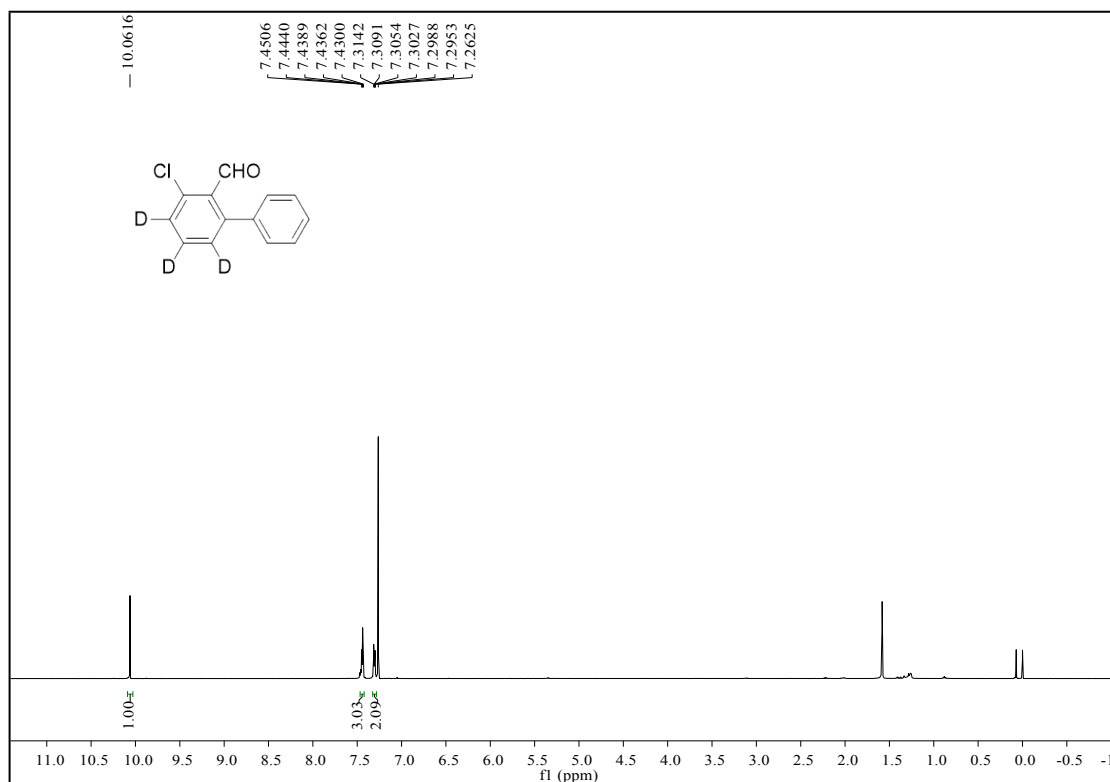
A sealed tube with magnetic stir bar was charged with  $[^2\text{H}_5]$ - benzaldehyde (0.3 mmol), NCS (0.45 mmol, 60.0 mg),  $\text{Pd}(\text{OAc})_2$  (0.03 mmol, 6.7 mg), **T** (0.09 mmol, 12.3 mg), and  $\text{AgTFA}$  (0.03 mmol, 6.6 mg) in air, followed by DCE (3.0 mL) and TFA (3.0 mmol, 342.0 mg). The reaction mixture was stirred at 60 °C for 24 hours. Upon completion, the reaction mixture was quenched by sat.  $\text{NaHCO}_3$  (aq) (30 mL), and extracted with DCM for 3 times. The combined organic layers were washed with water (50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude residue was purified by column



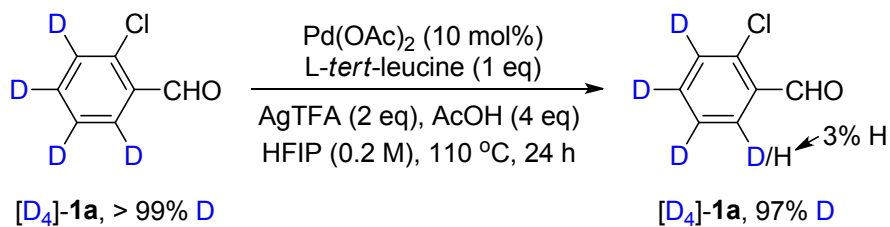
chromatography on silica gel using petroleum ether/EtOAc (50:1) as eluent to afford the [D<sub>4</sub>]-**1a** (65% yield) (X.-H. Liu, H. Park, J.-H. Hu, Y. Hu, Q.-L. Zhang, B.-L. Wang, B. Sun, K.-S. Yeung, F.-L. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* 2017, **139**, 888–896).

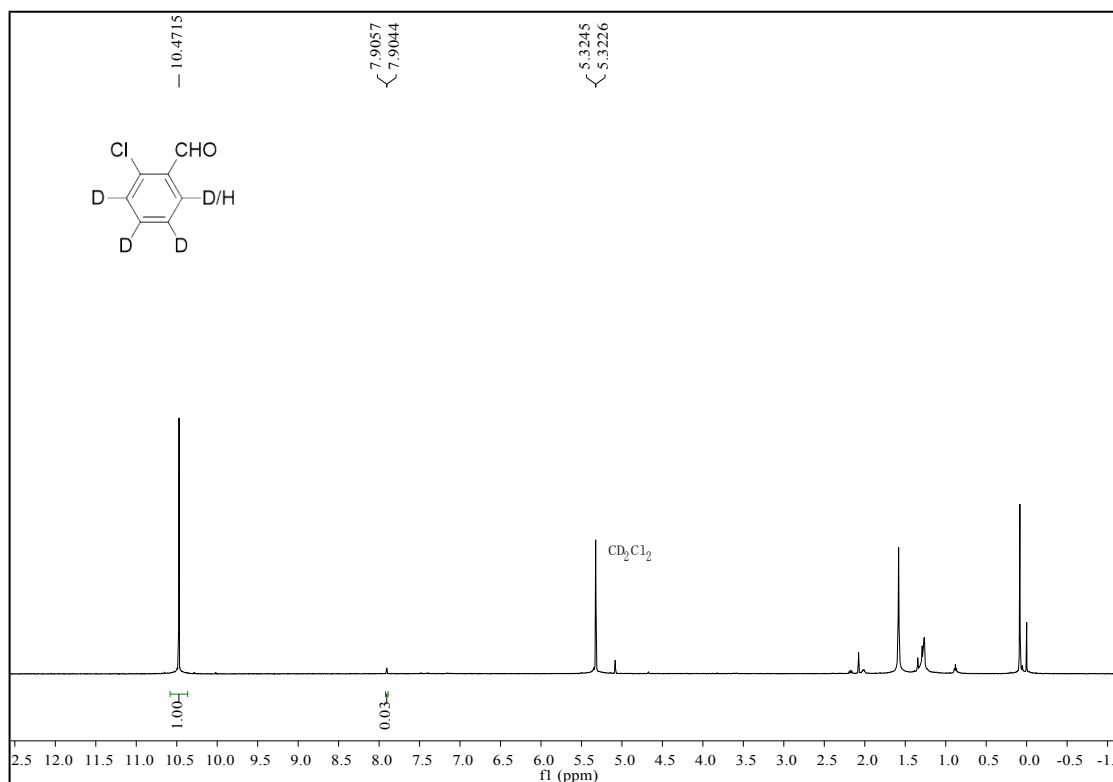
A 15 mL Schlenk tube was charged with *o*-chlorobenzaldehyde **1a** (0.1 mmol), [D<sub>4</sub>]-**1a** (0.1 mmol), **2a** (1.5 mmol), *L*-*tert*-leucine (1.0 mmol) and Pd(OAc)<sub>2</sub> (0.02 mmol), AgTFA (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 3 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure arylation product, and the KIE was determined by <sup>1</sup>H NMR.



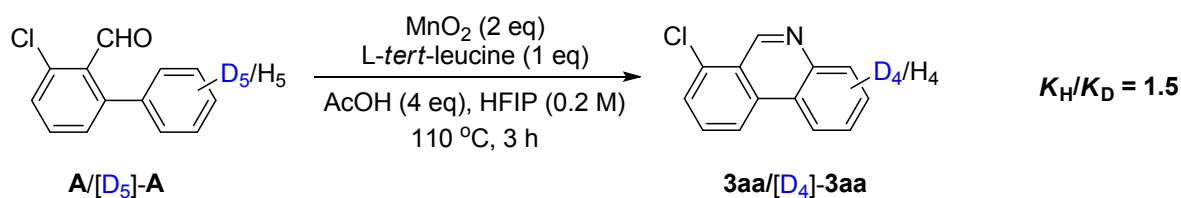


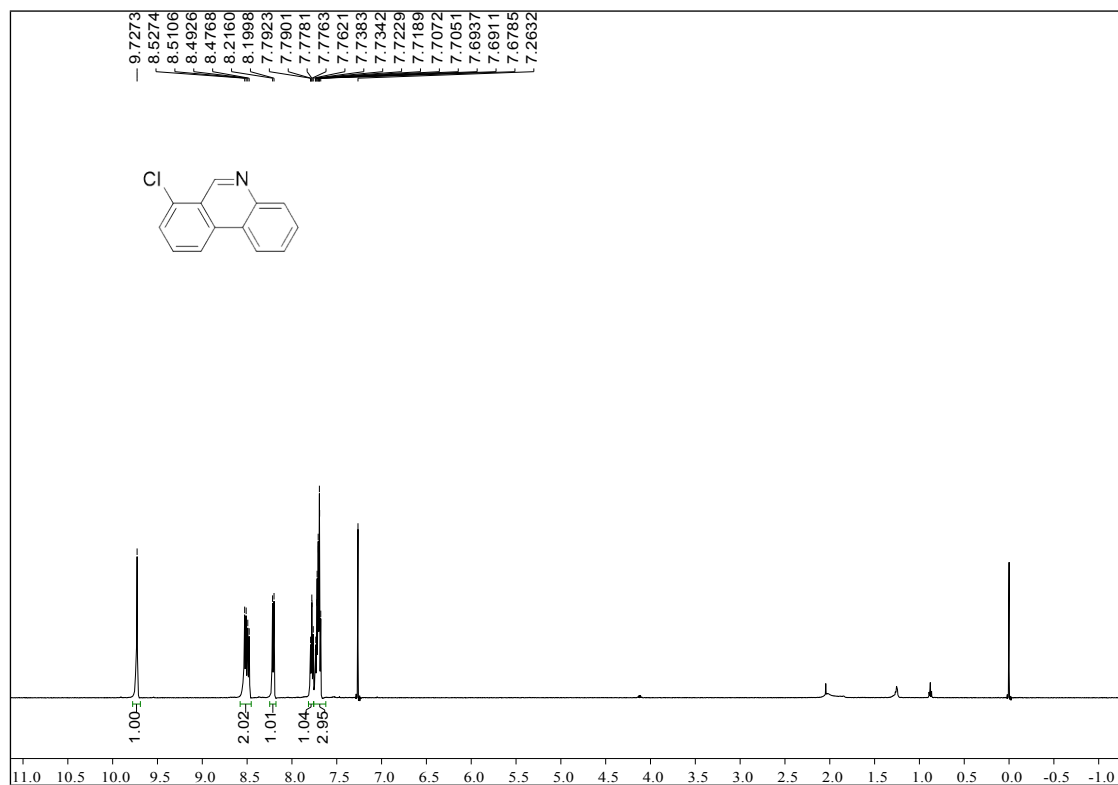
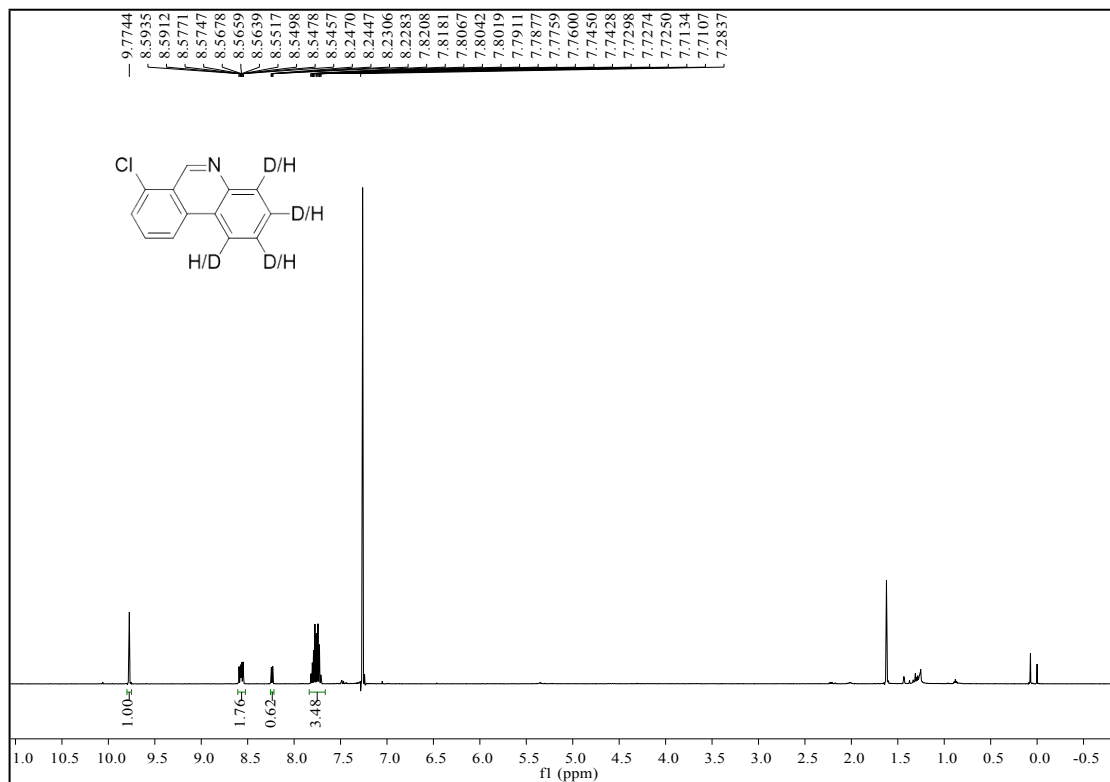
A 15 mL Schlenk tube was charged with  $[D_4]$ -**1a** (0.2 mmol), *L*-*tert*-leucine (1.0 mmol) and  $Pd(OAc)_2$  (0.02 mmol), AgTFA (0.4 mmol). The mixture was dissolved in 1 mL HFIP followed by addition of AcOH (0.8 mmol). The reaction mixture was stirred for 24 hours at 110 °C. After that it was filtered through a short pad of Celite® and washed with ethyl acetate. The solvent was then evaporated under reduced pressure and the aldehyde was recovered by column chromatography on silica gel and characterized by  $^1H$  NMR.



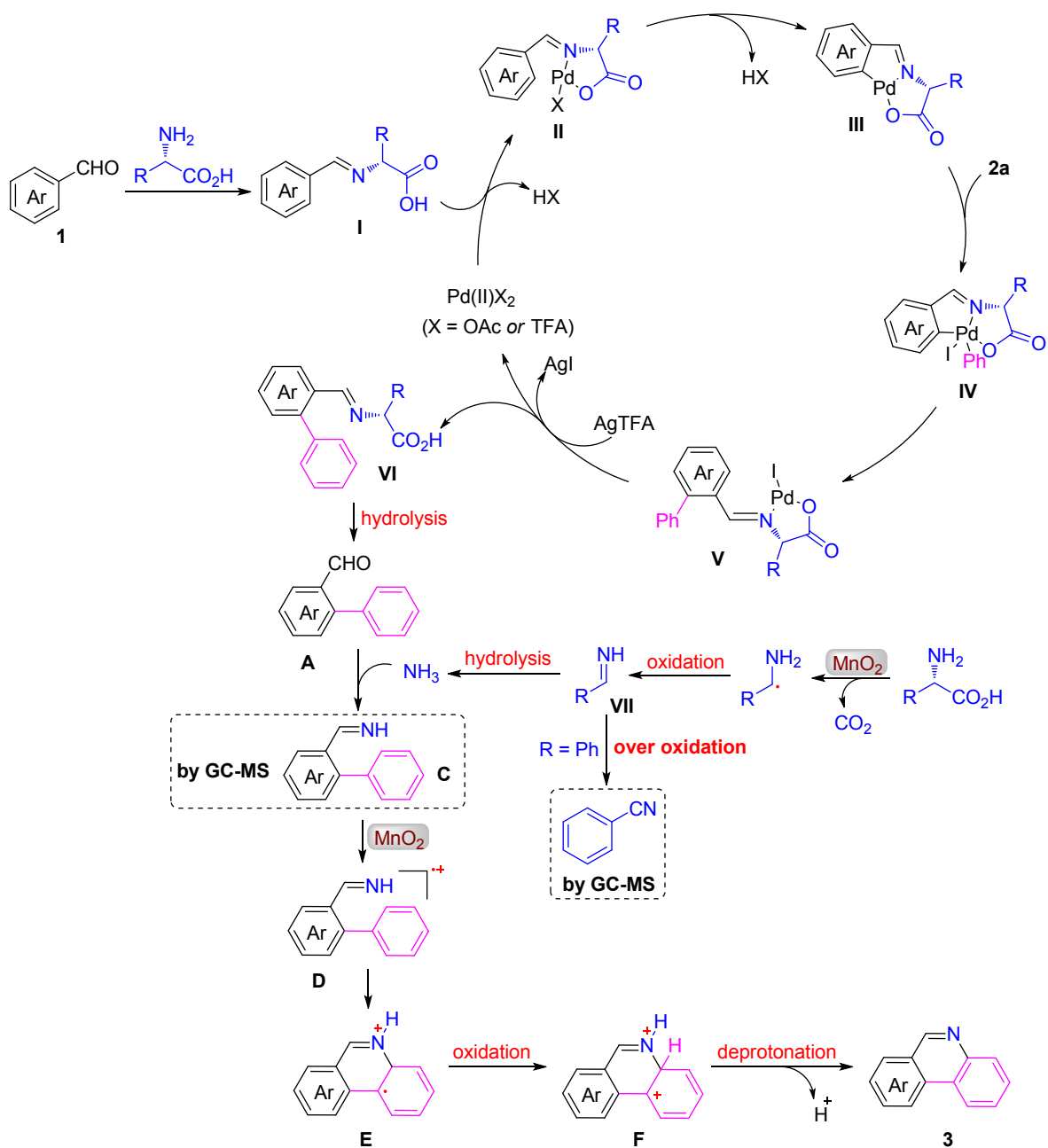


A mixture of biphenyl aldehyde **A** (0.1 mmol),  $[D_5]$ -**A** (0.1 mmol), *L*-*tert*-leucine (0.2 mmol),  $MnO_2$  (fresh) (0.4 mmol), AcOH (0.8 mmol) and HFIP (1.0 mL) was added to a 15 mL sealed tube. The tube was stirred at 110 °C for 3 h. Then, the reaction mixture was cooled to room temperature. The mixture was filtered through Celite®, and the filter cake was rinsed with EtOAc. The solvent was then evaporated under reduced pressure and the crude was purified by column chromatography on silica gel to afford the pure phenanthridine product, and the KIE was determined by  $^1H$  NMR.



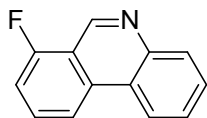


## 8. Proposed mechanism (Scheme S1)



## Analytic Data of Products

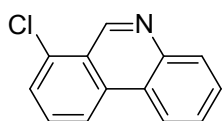
### 7-fluorophenanthridine (3ba)



White solid. Isolated yield: 66%. Melting point: 90-91 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.61 (s, 1H), 8.57-8.55 (m, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.83-7.78 (m, 2H), 7.73-7.70 (m, 1H), 7.38-7.34 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 160.6 (*J*<sub>F-C</sub> = 254.0 Hz), 146.8 (*J*<sub>F-C</sub> = 6.8 Hz), 144.9, 134.7 (*J*<sub>F-C</sub> = 3.2 Hz), 131.9 (*J*<sub>F-C</sub> = 8.9 Hz), 130.8, 129.7, 128.0, 123.5 (*J*<sub>F-C</sub> = 2.1 Hz), 122.9, 118.2 (*J*<sub>F-C</sub> = 4.3 Hz), 116.5 (*J*<sub>F-C</sub> = 13.9 Hz), 112.6 (*J*<sub>F-C</sub> = 19.4 Hz). **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>9</sub>FN (M+H<sup>+</sup>): 198.0713, found: 198.0712.

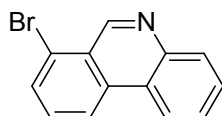
### 7-chlorophenanthridine (3aa)



White solid. Isolated yield: 66%. Melting point: 95-96 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.73 (s, 1H), 8.53-8.48 (m, 2H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.79-7.76 (m, 1H), 7.74-7.68 (m, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 150.0, 144.8, 134.7, 134.2, 131.3, 130.7, 129.7, 128.4, 128.0, 123.5, 123.46, 122.8, 121.3. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>9</sub>ClN (M+H<sup>+</sup>): 214.0418, found: 214.0416.

### 7-bromophenanthridine (3ca)

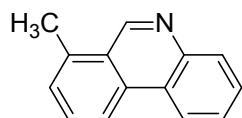


White solid. Isolated yield: 55%. Melting point: 151-152 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.70 (s, 1H), 8.57 (t, *J* = 8.7 Hz, 2H), 8.39 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.73-

7.66 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.6, 144.8, 135.0, 132.1, 131.7, 130.7, 129.8, 128.0, 124.7, 124.5, 123.4, 122.7, 122.0. HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_9\text{BrN}$  ( $\text{M}+\text{H}^+$ ): 257.9912, found: 257.9910.

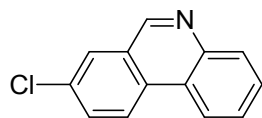
### 7-methylphenanthridine (3da)



White solid. Isolated yield: 31%. Melting point: 72-73 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.57 (s, 1H), 8.60 (d,  $J = 8.1$  Hz, 1H), 8.50 (d,  $J = 8.3$  Hz, 1H), 8.21-8.19 (m, 1H), 7.77-7.73 (m, 2H), 7.70-7.67 (m, 1H), 7.51-7.50 (m, 1H), 2.89 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  150.7, 144.5, 137.0, 133.2, 131.1, 130.4, 129.2, 129.0, 127.4, 125.3, 124.7, 122.8, 120.4, 19.3. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{12}\text{N}$  ( $\text{M}+\text{H}^+$ ): 194.0964, found: 194.0961.

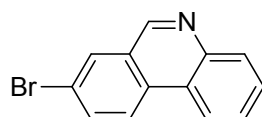
### 8-chlorophenanthridine (3ea)



White solid. Isolated yield: 57%. Melting point: 84-85 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.21 (s, 1H), 8.53 (t,  $J = 8.0$  Hz, 2H), 8.19 (d,  $J = 8.15$  Hz, 1H), 8.03-8.02 (m, 1H), 7.81-7.75 (m, 2H), 7.72-7.69 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.7, 144.8, 133.7, 132.0, 131.3, 130.7, 129.5, 128.2, 128.0, 127.6, 124.2, 124.0, 122.5. HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_9\text{ClN}$  ( $\text{M}+\text{H}^+$ ): 214.0418, found: 214.0415.

### 8-bromophenanthridine (3fa)

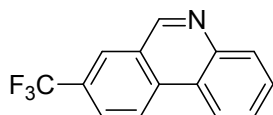


White solid. Isolated yield: 53%. Melting point: 72-73 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.20 (s, 1H), 8.52 (d,  $J = 9.2$  Hz, 1H), 8.46 (d,  $J = 8.8$  Hz, 1H), 8.20-8.18 (m, 2H), 7.94-7.9 (m, 1H), 7.79-7.76 (m, 1H),

7.72-7.68 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.6, 144.7, 134.6, 131.6, 131.4, 130.7, 129.5, 128.0, 127.9, 124.2, 124.0, 122.5, 121.7. HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_9\text{BrN}$  ( $\text{M}+\text{H}^+$ ): 257.9912, found: 257.9908.

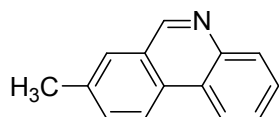
### 8-(trifluoromethyl)phenanthridine (3ga)



White solid. Isolated yield: 41%. Melting point: 118-119 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.39 (s, 1H), 8.76 (d,  $J = 8.6$  Hz, 1H), 8.63 (d,  $J = 8.1$  Hz, 1H), 8.38 (s, 1H), 8.29 (d,  $J = 7.9$  Hz, 1H), 8.09 (d,  $J = 8.7$  Hz, 1H), 7.86 (t,  $J = 7.4$  Hz, 1H), 7.78 (t,  $J = 7.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  153.1, 145.2, 134.7, 130.4, 130.0, 129.5 ( $J_{\text{F-C}} = 33.1$  Hz), 127.8, 126.8 ( $J_{\text{F-C}} = 3.1$  Hz), 126.2 ( $J_{\text{F-C}} = 4.2$  Hz), 125.6, 125.3, 123.2, 123.1, 122.6. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_9\text{F}_3\text{N}$  ( $\text{M}+\text{H}^+$ ): 248.0681, found: 248.0678.

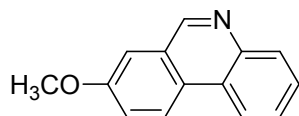
### 8-methylphenanthridine (3ha)



White solid. Isolated yield: 57%. Melting point: 139-140 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.21 (s, 1H), 8.53 (d,  $J = 8.1$  Hz, 1H), 8.48 (d,  $J = 8.35$  Hz, 1H), 8.18-8.16 (m, 1H), 7.80 (s, 1H). 7.73-7.64 (m, 3H), 2.59 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  153.8, 144.5, 137.9, 133.2, 130.4, 128.6, 128.56, 127.4, 127.0, 124.6, 122.5, 122.2, 21.9. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{12}\text{N}$  ( $\text{M}+\text{H}^+$ ): 194.0964, found: 194.0960.

### 8-methoxyphenanthridine (3ia)



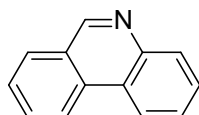
White solid. Isolated yield: 46%. Melting point: 92-93 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.24 (s, 1H), 8.52 (t,  $J = 9.6$



Hz, 2H), 8.17 (d,  $J = 7.85$  Hz, 1H), 7.71-7.65 (m, 2H), 7.34 (d,  $J = 8.7$  Hz, 1H), 7.39 (s, 1H), 4.00 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  159.3, 153.3, 144.0, 130.4, 128.1, 127.6, 127.4, 124.7, 124.0, 122.5, 122.2, 108.3, 56.0. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}$  ( $\text{M}+\text{H}^+$ ): 210.0913, found: 210.0911.

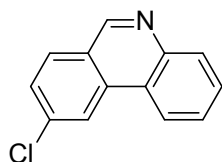
### Phenanthridine (3ja)



White solid. Isolated yield: 36%. Melting point: 93-94 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.29 (s, 1H), 8.61-8.57 (m, 2H), 8.20 (d,  $J = 8.0$  Hz, 1H), 8.04 (d,  $J = 7.9$  Hz, 1H), 7.86 (t,  $J = 8.0$  Hz, 1H), 7.77-7.67 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  153.6, 144.5, 132.6, 131.1, 130.2, 128.8, 128.7, 127.5, 127.1, 126.4, 124.1, 122.3, 121.9; HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_{10}\text{N}$  ( $\text{M}+\text{H}^+$ ): 180.0807, found: 180.0804.

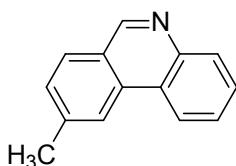
### 9-chlorophenanthridine (3ka)



White solid. Isolated yield: 30%. Melting point: 89-90 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.27 (s, 1H), 8.59 (d,  $J = 1.5$  Hz, 1H), 8.52-8.50 (m, 1H), 8.26 (d,  $J = 8.1$  Hz, 1H), 8.04 (d,  $J = 8.5$  Hz, 1H), 7.83-7.79 (m, 1H), 7.76-7.69 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  153.1, 145.1, 137.9, 134.1, 130.7, 130.6, 139.8, 128.6, 127.8, 125.0, 123.4, 122.6, 121.1. HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_9\text{ClN}$  ( $\text{M}+\text{H}^+$ ): 214.0418, found: 214.0416.

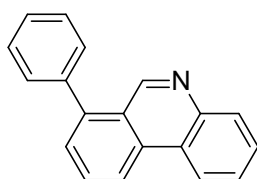
### 9-methylphenanthridine (3la)



White solid. Isolated yield: 30%. Melting point: 88-89 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.24 (s, 1H), 8.58-8.56 (m, 1H), 8.40 (s, 1H), 8.18-8.16 (m, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.75-7.72 (m, 1H), 7.68-7.65 (m, 1H), 7.55-7.53 (m, 1H), 2.66 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 153.3, 144.6, 132.7, 130.1, 128.7, 128.6, 126.9, 124.6, 124.0, 122.2, 121.6, 22.5. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>12</sub>N (M+H<sup>+</sup>): 194.0964, found: 194.0961.

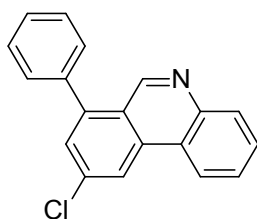
### 7-phenylphenanthridine (3jaa)



White solid. Isolated yield: 43%. Melting point: 195-196 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.36 (s, 1H), 8.66-8.64 (m, 2H), 8.19-8.17 (m, 1H), 7.91-7.88 (m, 1H), 7.78-7.75 (m, 1H), 7.72-7.69 (m, 1H), 7.65-7.63 (m, 1H), 7.55-7.48 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 151.9, 144.1, 142.3, 138.9, 133.0, 130.4, 130.3, 130.1, 128.81, 128.8, 128.5, 128.0, 127.2, 124.0, 123.99, 122.4, 121.2. **HRMS** (APCI) calcd for C<sub>19</sub>H<sub>14</sub>N (M+H<sup>+</sup>): 256.1120, found: 256.1117.

### 9-chloro-7-phenylphenanthridine (3kaa)

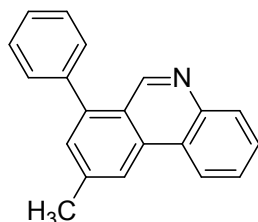


White solid. Isolated yield: 31%. Melting point: 120-121 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.29 (s, 1H), 8.60 (d, *J* = 2.0 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.18-8.16 (m, 1H), 7.80-7.77 (m, 1H), 7.73-7.70 (m, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.57-7.50 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 151.3, 144.4, 144.1, 137.5, 136.7, 134.4, 130.2, 130.1, 129.5, 129.2,

128.7, 128.5, 127.5, 123.0, 122.5, 122.4, 120.8. **HRMS** (APCI) calcd for  $C_{19}H_{13}ClN$  ( $M+H^+$ ): 290.0731, found: 290.0728.

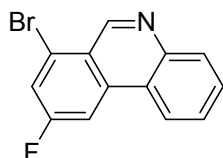
### 9-methyl-7-phenylphenanthridine (3laa)



White solid. Isolated yield: 36%. Melting point: 174-175 °C.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ , TMS as the internal standard):  $\delta$  9.30 (s, 1H), 8.63-8.61 (m, 1H), 8.43 (s, 1H), 8.17-8.15(m, 1H), 7.76-7.72 (m, 1H), 7.69-7.66 (m, 1H), 7.54-7.47 (m, 6H), 2.68 (s, 3H).  **$^{13}C$  NMR** (100 MHz,  $CDCl_3$ ,  $CDCl_3$  as the internal standard):  $\delta$  151.7, 144.3, 142.1, 140.8, 138.9, 133.2, 130.6, 130.3, 130.0, 128.7, 128.5, 127.9, 126.9, 123.9, 122.4, 122.2, 120.9, 22.4. **HRMS** (APCI) calcd for  $C_{20}H_{16}N$  ( $M+H^+$ ): 270.1277, found: 270.1274.

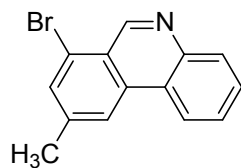
### 7-bromo-9-fluorophenanthridine (3ma)



White solid. Isolated yield: 42%. Melting point: 161-162 °C.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ , TMS as the internal standard):  $\delta$  9.64 (s, 1H), 8.45 (d,  $J = 9.0$  Hz, 1H), 8.24-8.21 (m, 2H), 7.84-7.81 (m, 1H), 7.75-7.72 (m, 2H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ,  $CDCl_3$  as the internal standard):  $\delta$  163.3 ( $J_{F-C} = 253.9$  Hz), 151.8, 144.9, 136.4 ( $J_{F-C} = 9.6$  Hz), 130.6 ( $J_{F-C} = 42.8$  Hz), 128.1, 125.8 ( $J_{F-C} = 11.0$  Hz), 122.9 ( $J_{F-C} = 4.2$  Hz), 122.8, 121.9, 121.7, 121.49, 107.3 ( $J_{F-C} = 21.9$  Hz). **HRMS** (APCI) calcd for  $C_{13}H_8FBrN$  ( $M+H^+$ ): 275.9818, found: 275.9815.

### 7-bromo-9-methylphenanthridine (3na)

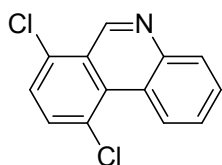


White solid. Isolated yield: 43%. Melting point: 145-146 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.60 (s, 1H), 8.50-8.49 (m, 1H), 8.29 (s, 1H), 8.19-8.17 (m, 1H), 7.77-7.73 (m, 2H), 7.68-7.65 (m, 1H), 2.59 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 152.2, 144.7, 142.6, 134.8, 133.6, 130.5, 129.6, 127.8, 124.2, 123.2, 122.8, 122.6, 121.7, 22.5. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>11</sub>BrN (M+H<sup>+</sup>): 272.0069, found: 272.0064.

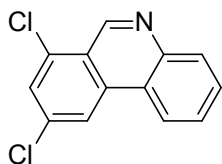
### 7,10-dichlorophenanthridine (3oa)



White solid. Isolated yield: 30%. Melting point: 188-189 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.81 (d, *J* = 8.6 Hz, 1H), 9.78 (s, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 2H), 7.73 (t, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 150.0, 145.9, 134.7, 133.5, 131.4, 130.9, 130.3, 130.1, 128.5, 127.6, 126.6, 125.3, 122.8. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N (M+H<sup>+</sup>): 248.0028, found: 248.0025.

### 7,9-dichlorophenanthridine (3pa)

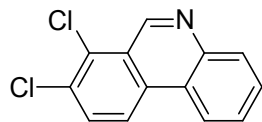


White solid. Isolated yield: 57%. Melting point: 157-158 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.62 (s, 1H), 8.41-8.39 (m, 2H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.70-7.66 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 149.4, 145.1, 137.2, 135.4, 135.2, 130.8, 130.4, 128.7, 128.3, 122.8, 122.4, 121.9, 121.1. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N

(M+H<sup>+</sup>): 248.0028, found: 248.0024.

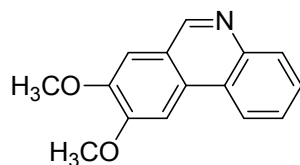
### 7,8-dichlorophenanthridine (3qa)



Yeiiow solid. Isolated yield: 60%. Melting point: 135-136 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.77 (s, 1H), 8.55-8.53 (m, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.25-8.23 (m, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.83-7.80 (m, 1H), 7.76-7.72 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 149.7, 144.6, 133.0, 132.5, 132.0, 130.8, 130.0, 128.4, 124.7, 123.0, 122.6, 121.1. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N (M+H<sup>+</sup>): 248.0028, found: 248.0025.

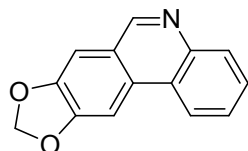
### 8,9-dimethoxyphenanthridine (3ra)



White solid. Isolated yield: 18%. Melting point: 172-173 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.15 (s, 1H), 8.44 (d, *J* = 10.3 Hz, 1H), 8.17-8.15 (m, 1H), 7.88 (s, 1H), 7.72-7.62 (m, 2H), 7.35 (s, 1H), 4.14 (s, 3H), 4.07 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 153.3, 152.2, 150.4, 144.4, 130.5, 128.6, 128.2, 127.0, 124.2, 122.2, 122.1, 108.2, 102.2, 56.6, 56.5. **HRMS** (APCI) calcd for C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub> (M+H<sup>+</sup>): 240.1019, found: 240.0115.

### [1,3]dioxolo[4,5-*j*]phenanthridine (3sa)

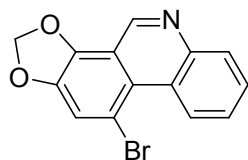


White solid. Isolated yield: 22%. Melting point: 144-145 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 8.98 (s, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.66-7.58 (m, 2H), 7.21 (s, 1H), 6.18 (s,

2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.1, 151.6, 148.6, 143.5, 130.8, 129.6, 128.5, 127.2, 124.6, 123.2, 122.3, 105.9, 102.4, 100.2. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{10}\text{NO}_2$  ( $\text{M}+\text{H}^+$ ): 224.0706, found: 224.0703.

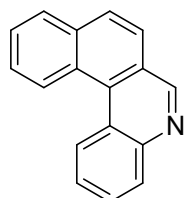
### 10-bromo-[1,3]dioxolo[4,5-*i*]phenanthridine (3ta)



Yellow solid. Isolated yield: 40%. Melting point: 225-226 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.51 (s, 1H), 8.83 (d,  $J = 8.0$  Hz, 1H), 8.16 (d,  $J = 8.2$  Hz, 1H), 7.76 (t,  $J = 7.2$  Hz, 1H), 7.66 (t,  $J = 7.2$  Hz, 1H), 7.55 (s, 1H), 6.36 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.6, 149.3, 144.6, 143.0, 130.0, 129.8, 127.6, 127.0, 121.3, 120.5, 119.8, 116.7, 114.9, 103.1. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_9\text{BrNO}_2$  ( $\text{M}+\text{H}^+$ ): 301.9811, found: 301.9810.

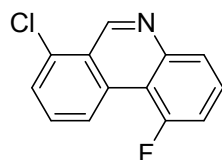
### benzo[*k*]phenanthridine (3ua)



White solid. Isolated yield: 25%. Melting point: 75-76 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.35 (s, 1H), 9.19 (d,  $J = 8.1$  Hz, 1H), 9.10 (d,  $J = 8.3$  Hz, 1H), 8.34-8.32 (m, 1H), 7.08-7.7.93 (m, 3H), 7.82-7.73 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  153.0, 147.0, 135.6, 131.6, 130.7, 129.41, 129.4, 129.2, 128.6, 128.5, 128.2, 127.4, 127.3, 127.2, 125.6, 125.5, 125.0. HRMS (APCI) calcd for  $\text{C}_{17}\text{H}_{12}\text{N}$  ( $\text{M}+\text{H}^+$ ): 230.0964, found: 230.0961.

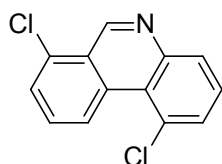
### 7-chloro-1-fluorophenanthridine (3ab)



White solid. Isolated yield: 45%. Melting point: 122-123 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.79 (s, 1H), 8.97-8.95 (m, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.81-7.71 (m, 3H), 7.46-7.42 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 160.8 (*J*<sub>F-C</sub> = 253.7 Hz), 151.1, 146.7 (*J*<sub>F-C</sub> = 2.0 Hz), 134.1, 132.7 (*J*<sub>F-C</sub> = 4.8 Hz), 132.0 (*J*<sub>F-C</sub> = 1.7 Hz), 129.3 (*J*<sub>F-C</sub> = 10.6 Hz), 128.9, 126.8 (*J*<sub>F-C</sub> = 3.5 Hz), 126.2 (*J*<sub>F-C</sub> = 23.3 Hz), 123.9, 114.5 (*J*<sub>F-C</sub> = 23.9 Hz), 113.5 (*J*<sub>F-C</sub> = 9.1 Hz). **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>ClFN (M+H<sup>+</sup>): 232.0323, found: 232.0321.

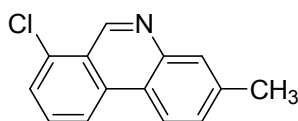
### 1,7-dichlorophenanthridine (3ac)



White solid. Isolated yield: 41%. Melting point: 145-146 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.82-9.80 (m, 2H), 8.18-8.17 (m, 1H), 7.79-7.75 (m, 3H), 7.66 (t, *J* = 7.7 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 150.5, 146.7, 133.7, 133.7, 131.4, 131.0, 130.4, 130.3, 128.7, 128.6, 125.3, 124.1, 121.1. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N (M+H<sup>+</sup>): 248.0028, found: 248.0024.

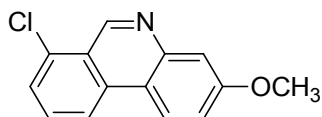
### 7-chloro-3-methylphenanthridine (3ad)



White solid. Isolated yield: 65%. Melting point: 115-116 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard) δ 9.74 (s, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.05 (s, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.71-7.69 (m, 1H), 7.57-7.55 (m, 1H), 2.62 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard) δ 149.2, 143.3, 140.7, 135.2, 134.6, 132.2, 130.3, 129.1, 128.2, 123.0, 122.6, 121.4, 121.2, 22.0. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>11</sub>ClN (M+H<sup>+</sup>): 228.0574, found: 228.0571.

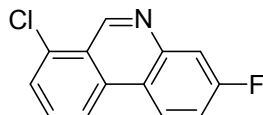
### 7-chloro-3-methoxyphenanthridine (3ae)



White solid. Isolated yield: 53%. Melting point: 149-150 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard) δ 9.71 (s, 1H), 8.43 (t, *J* = 8.8 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.65-7.61 (m, 2H), 7.35-7.33 (m, 1H), 4.00 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard) δ 160.9, 150.5, 146.6, 135.0, 134.3, 131.4, 127.3, 124.0, 122.8, 120.8, 119.2, 117.6, 110.3, 56.0. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>11</sub>ClNO (M+H<sup>+</sup>): 244.0523, found: 244.0522.

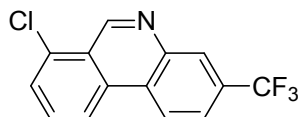
### 7-chloro-3-fluorophenanthridine (3af)



White solid. Isolated yield: 65%. Melting point: 84-85 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.77 (s, 1H), 8.57-8.54 (m, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 7.92-7.89 (m, 1H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.51-7.47 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 163.4 (d, *J* = 248.5 Hz), 151.1, 134.7 (*J*<sub>F-C</sub> = 3.2 Hz), 132.1, 128.4 (2C), 124.9 (*J*<sub>F-C</sub> = 9.5 Hz), 123.2, 121.1 (2C), 120.3 (*J*<sub>F-C</sub> = 1.8 Hz), 117.4 (*J*<sub>F-C</sub> = 23.8 Hz), 114.9 (*J*<sub>F-C</sub> = 20.6 Hz). **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>ClFN (M+H<sup>+</sup>): 232.0323, found: 232.0320.

### 7-chloro-3-(trifluoromethyl)phenanthridine (3ag)



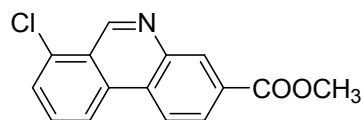
White solid. Isolated yield: 64%. Melting point: 224-225 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard): δ 9.83 (s, 1H), 8.67 (d, *J* = 8.7 Hz, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.54 (s, 1H), 7.93-7.91 (m, 1H), 7.87-7.81 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard): δ 151.4, 144.1, 134.6, 133.9, 132.0, 131.5 (*J*<sub>F-C</sub> = 33.0 Hz), 129.6, 128.3 (*J*<sub>F-C</sub> = 4.1 Hz), 125.8, 125.4, 124.1, 123.9 (*J*<sub>F-C</sub> = 4.6 Hz), 123.2, 121.6. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>8</sub>ClF<sub>3</sub>N (M+H<sup>+</sup>): 282.0291, found:



292.0288.

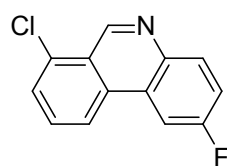
**methyl 7-chlorophenanthridine-3-carboxylate (3ah)**



White solid. Isolated yield: 57%. Melting point: 198-199 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.81 (s, 1H), 8.89 (s, 1H), 8.61-8.55 (m, 2H), 8.31 (d,  $J = 8.5$  Hz, 1H), 7.82-7.78 (m, 2H), 4.03 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  167.0, 151.0, 144.4, 134.5, 134.1, 132.8, 131.7, 131.2, 129.5, 127.9, 126.7, 124.2, 123.1, 121.8, 52.9. **HRMS** (APCI) calcd for C<sub>15</sub>H<sub>11</sub>ClO<sub>2</sub>N (M+H<sup>+</sup>): 272.0472, found: 272.0468.

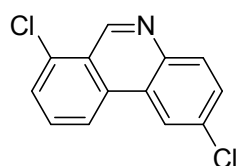
**7-chloro-2-fluorophenanthridine (3ai)**



White solid. Isolated yield: 36%. Melting point: 167-168 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.78 (s, 1H), 8.51 (d,  $J = 7.8$  Hz, 1H), 8.32 (d,  $J = 8.4$  Hz, 1H), 7.81-7.75 (m, 2H), 7.68-7.63 (m, 1H), 7.51-7.48 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  159.2 (d,  $J_{F-C} = 254.0$  Hz), 150.3, 134.6, 134.5, 134.1 ( $J_{F-C} = 2.8$  Hz), 131.9, 129.1, 128.0 ( $J_{F-C} = 8.5$  Hz), 125.5, 123.8, 121.6, 118.4 (d,  $J_{F-C} = 4.5$  Hz), 114.7 (d,  $J_{F-C} = 19.1$  Hz). **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>ClFN (M+H<sup>+</sup>): 232.0323, found: 232.0325.

**2,7-dichlorophenanthridine (3aj)**

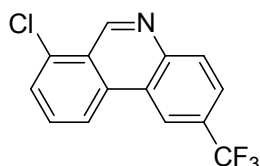


White solid. Isolated yield: 47%. Melting point: 161-162 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard)  $\delta$  9.74 (s, 1H), 8.52 (d,  $J = 2.8$

Hz, 1H), 8.48-8.45 (m, 1H), 8.16 (d,  $J = 10.9$  Hz, 1H), 7.82-7.72 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard)  $\delta$  150.3, 143.2, 134.5, 134.0, 133.8, 132.2, 131.7, 130.3, 129.1, 124.6, 123.8, 122.5, 121.3. HRMS (APCI) calcd for  $\text{C}_{13}\text{H}_8\text{Cl}_2\text{N}$  ( $\text{M}+\text{H}^+$ ): 248.0028, found: 248.0025.

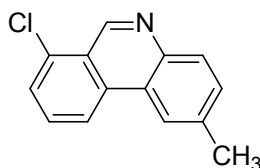
### 7-chloro-2-(trifluoromethyl)phenanthridine (3ak)



White solid. Isolated yield: 63%. Melting point: 136-137 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard):  $\delta$  9.77 (s, 1H), 8.76 (s, 1H), 8.49 (d,  $J = 8.0$  Hz, 1H), 8.29 (d,  $J = 8.5$  Hz, 1H), 7.96 (d,  $J = 8.4$  Hz, 1H), 7.81-7.75 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard):  $\delta$  152.1, 146.1, 134.6, 134.3, 132.1, 131.7, 129.6 ( $J_{\text{F-C}} = 32.3$  Hz), 129.3, 125.7 ( $J_{\text{F-C}} = 3.4$  Hz), 125.6, 123.8, 123.4, 123.1, 121.2, 120.6 ( $J_{\text{F-C}} = 4.6$  Hz). HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_8\text{ClF}_3\text{N}$  ( $\text{M}+\text{H}^+$ ): 282.0291, found: 282.0289.

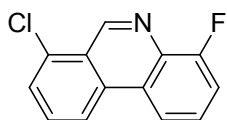
### 7-chloro-2-methylphenanthridine (3al)



White solid. Isolated yield: 58%. Melting point: 147-148 °C

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS as the internal standard)  $\delta$  9.69 (s, 1H), 8.51 (d,  $J = 7.9$  Hz, 1H), 8.33 (s, 1H), 8.11 (d,  $J = 8.3$  Hz, 1H), 7.75-7.69 (m, 2H), 7.62-7.60 (m, 1H), 2.64 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\text{CDCl}_3$  as the internal standard)  $\delta$  149.1, 143.1, 138.0, 134.5, 134.2, 131.5, 131.1, 130.4, 128.3, 123.7, 123.3, 122.4, 121.3, 22.4. HRMS (APCI) calcd for  $\text{C}_{14}\text{H}_{11}\text{ClN}$  ( $\text{M}+\text{H}^+$ ): 228.0574, found: 228.0572.

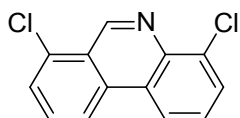
### 7-chloro-4-fluorophenanthridine (3ai')



White solid. Isolated yield: 37%. Melting point: 159-160 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.72 (s, 1H), 8.43 (d,  $J = 7.9$  Hz, 1H), 8.32-8.29 (m, 1H), 8.19-8.16 (m, 1H), 7.84-7.78 (m, 2H), 7.58-7.54 (m, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  162.0 ( $J_{F-C} = 247.3$  Hz), 149.0, 141.1, 134.5, 134.2 ( $J_{F-C} = 4.0$  Hz), 132.7 ( $J_{F-C} = 9.1$  Hz), 131.7, 129.2, 125.0 ( $J_{F-C} = 7.7$  Hz), 123.6, 121.4, 118.9 ( $J_{F-C} = 24.1$  Hz), 107.8 ( $J_{F-C} = 23.5$  Hz). HRMS (APCI) calcd for C<sub>13</sub>H<sub>8</sub>ClFN (M+H<sup>+</sup>): 232.0323, found: 232.0322.

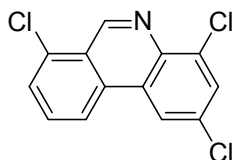
#### 4,7-dichlorophenanthridine (3aj')



White solid. Isolated yield: 31%. Melting point: 167-168 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.88 (s, 1H), 8.54-8.49 (m, 2H), 7.90 (d,  $J = 7.6$  Hz, 1H), 7.82-7.76 (m, 2H), 7.63 (d,  $J = 7.8$  Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  150.7, 141.1, 135.1, 134.6, 134.6, 131.9, 130.2, 129.1, 127.9, 125.3, 123.7, 121.8, 121.5; **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N (M+H<sup>+</sup>): 248.0028, found: 248.0026.

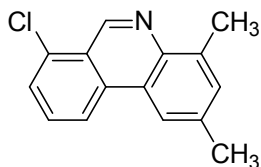
#### 2,4,7-trichlorophenanthridine (3am)



White solid. Isolated yield: 76%. Melting point: 199-200 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.86 (s, 1H), 8.46-8.45 (m, 2H), 7.89 (d,  $J = 2.2$  Hz, 1H), 7.85-7.81 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  150.8, 139.6, 136.0, 134.8, 133.6, 132.3, 130.4, 129.8, 125.9, 123.9, 121.6, 121.5. HRMS (APCI) calcd for C<sub>13</sub>H<sub>7</sub>Cl<sub>3</sub>N (M+H<sup>+</sup>): 281.9638, found: 281.9635.

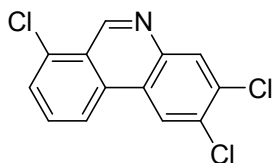
### 7-chloro-2,4-dimethylphenanthridine (3an)



White solid. Isolated yield: 46%. Melting point: 129-130 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.73 (s, 1H), 8.51 (d,  $J$  = 7.6 Hz, 1H), 8.20 (s, 1H), 7.73-7.68 (m, 2H), 7.48 (s, 1H), 2.85 (s, 3H), 2.59 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  147.3, 141.6, 137.7, 137.0, 134.4, 133.8, 131.9, 130.4, 127.6, 123.0, 122.9, 121.1, 119.8, 22.0, 18.4. **HRMS** (APCI) calcd for C<sub>15</sub>H<sub>13</sub>ClN (M+H<sup>+</sup>): 242.0731, found: 242.0728.

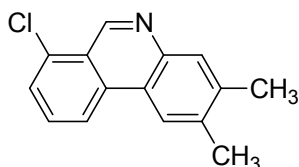
### 2,3,7-trichlorophenanthridine (3ao)



White solid. Isolated yield: 65%. Melting point: 184-185 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.75 (s, 1H), 8.63 (s, 1H), 8.42 (d,  $J$  = 8.8 Hz, 1H), 8.33 (s, 1H), 7.82-7.77 (m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  151.4, 143.8, 134.7, 134.0, 133.4, 132.5, 132.0, 131.8, 129.3, 124.3, 123.7, 123.1, 121.2. **HRMS** (APCI) calcd for C<sub>13</sub>H<sub>7</sub>Cl<sub>3</sub>N (M+H<sup>+</sup>): 281.9638, found: 281.9636.

### 7-chloro-2,3-dimethylphenanthridine (3ap)

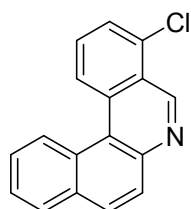


White solid. Isolated yield: 40%. Melting point: 162-163 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.66 (s, 1H), 8.48 (d,  $J$  = 8.1 Hz, 1H), 8.28 (s, 1H), 7.96 (s, 1H), 7.72-7.65 (m, 2H), 2.53 (s, 3H), 2.51 (s, 3H). **<sup>13</sup>C NMR**

(125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  149.1, 143.7, 139.5, 137.6, 134.5, 134.2, 131.0, 130.5, 127.8, 123.3, 122.8, 121.5, 121.1, 20.9, 20.6. **HRMS** (APCI) calcd for C<sub>15</sub>H<sub>13</sub>ClN (M+H<sup>+</sup>): 242.0731, found: 242.0728.

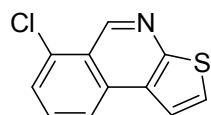
#### 4-chlorobenzo[*a*]phenanthridine (3aq)



White solid. Isolated yield: 35%. Melting point: 147-148 °C

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.86 (s, 1H), 9.00-8.97 (m, 2H), 8.14-8.12 (m, 1H), 8.07-8.05 (m, 2H), 7.79-7.67 (m, 4H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  149.4, 144.8, 134.7, 134.0, 133.9, 130.8, 130.7, 129.9, 129.3, 128.6, 128.1, 127.7, 127.2, 127.1, 126.0, 124.9, 120.4. **HRMS** (APCI) calcd for C<sub>17</sub>H<sub>11</sub>ClN (M+H<sup>+</sup>): 264.0574, found: 264.0571.

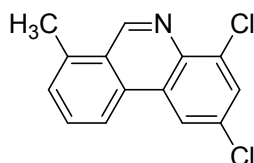
#### 6-chlorothieno[2,3-*c*]isoquinoline (3ar)



Yellow solid. Isolated yield: 20%. Melting point: 94-95 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.56 (s, 1H), 8.19-8.17 (m, 1H), 7.83 (d, *J* = 5.9 Hz, 1H), 7.70-7.64 (m, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  156.9, 146.6, 133.7, 133.3, 130.7, 126.94, 126.9, 122.9, 121.9, 199.7. **HRMS** (APCI) calcd for C<sub>11</sub>H<sub>7</sub>ClNS (M+H<sup>+</sup>): 219.9982, found: 219.9978.

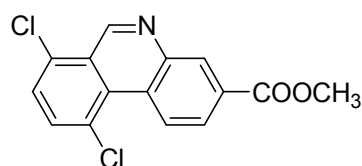
#### 2,4-dichloro-7-methylphenanthridine (3dm)



White solid. Isolated yield: 55%. Melting point: 171-172 °C.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.63 (s, 1H), 8.43 (s, 1H), 8.35 (d,  $J$  = 8.3 Hz, 1H), 7.81 (d,  $J$  = 1.7 Hz, 1H), 7.77 (t,  $J$  = 7.6 Hz, 1H), 7.56 (d,  $J$  = 7.2 Hz, 1H), 2.87 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  151.4, 139.4, 137.4, 135.7, 132.8, 132.0, 131.9, 130.5, 129.5, 126.9, 125.5, 121.5, 120.6, 19.1. **HRMS** (APCI) calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N (M+H<sup>+</sup>): 262.0184, found: 262.0182.

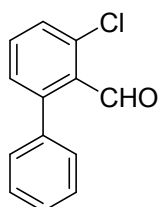
**methyl 7,10-dichlorophenanthridine-3-carboxylate (3nh)**



White solid. Isolated yield: 57%. Melting point: 177-178 °C.

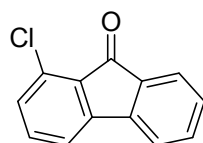
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  9.86 (d,  $J$  = 9.0 Hz, 1 H), 9.83 (s, 1H), 8.90 (d,  $J$  = 2 Hz, 1H), 8.32-8.30 (m, 1H), 7.88 (d,  $J$  = 8.3 Hz, 1H), 7.72 (t,  $J$  = 8.3 Hz, 1H), 4.04 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  166.8, 150.9, 145.7, 135.0, 133.7, 132.6, 131.3, 131.0, 130.8, 129.5, 127.3, 126.9, 126.0, 125.9, 52.9. **HRMS** (APCI) calcd for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>N (M+H<sup>+</sup>): 306.0083, found: 306.0081.

**3-chloro-[1,1'-biphenyl]-2-carbaldehyde (A)**



**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  10.06 (s, 1H), 7.49-7.48 (m, 2H), 7.44-7.42 (m, 3H), 7.33-7.29 (m, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  191.6, 147.0, 138.4, 134.9, 133.1, 132.3, 130.6, 128.9, 128.7.

**1-chloro-9H-fluoren-9-one (B)**

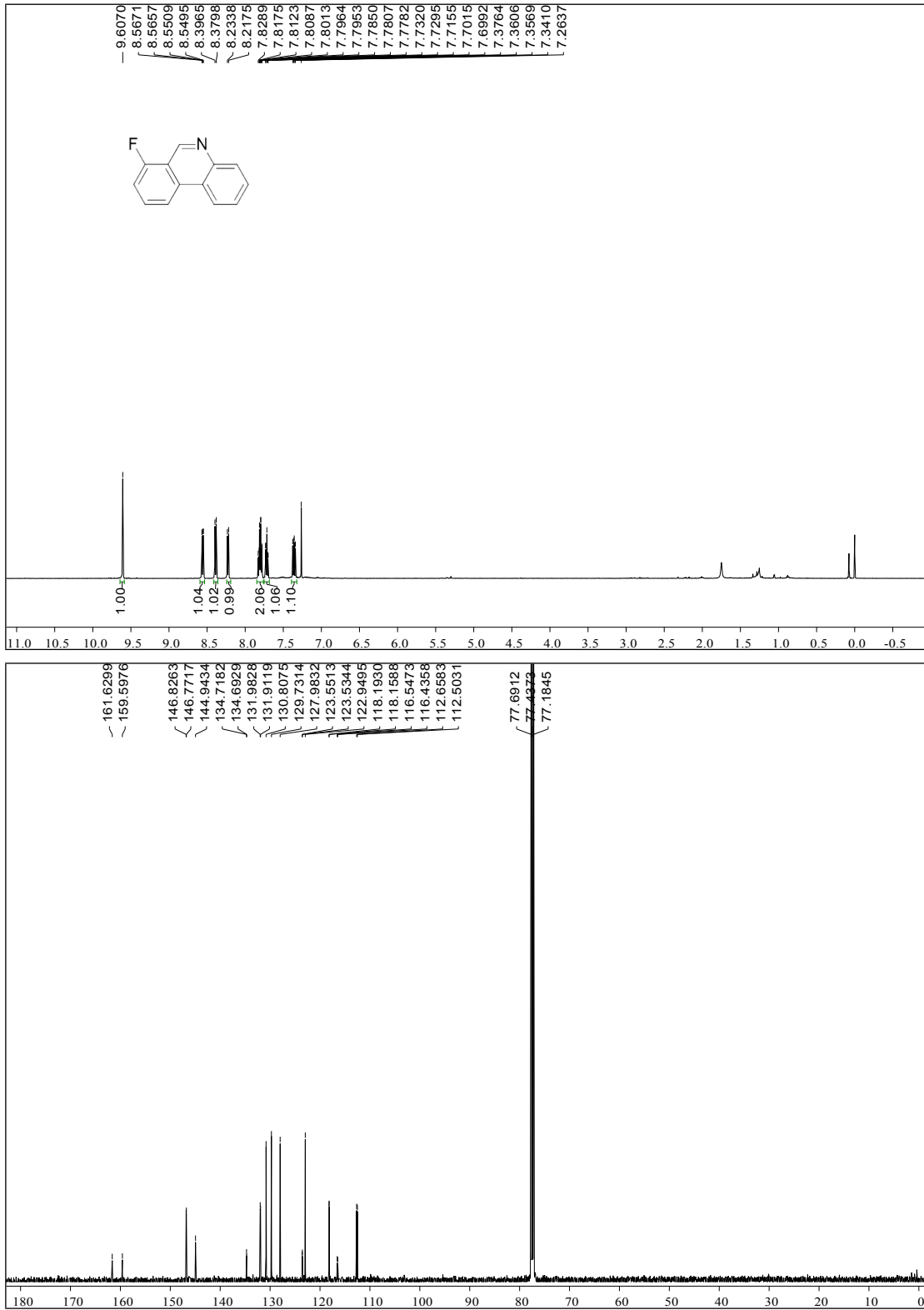


**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, TMS as the internal standard):  $\delta$  7.69 (d,  $J$  = 7.4 Hz, 1H), 7.54-7.49 (m, 2H), 7.45-7.38 (m, 2H), 7.35-7.32 (m, 1H), 7.23-7.21 (m, 1H); **<sup>13</sup>C NMR**

(125 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> as the internal standard):  $\delta$  191.2, 146.9, 143.0, 135.6, 135.1, 134.3, 133.2, 131.4, 130.1, 129.9, 124.9, 120.8, 119.1.

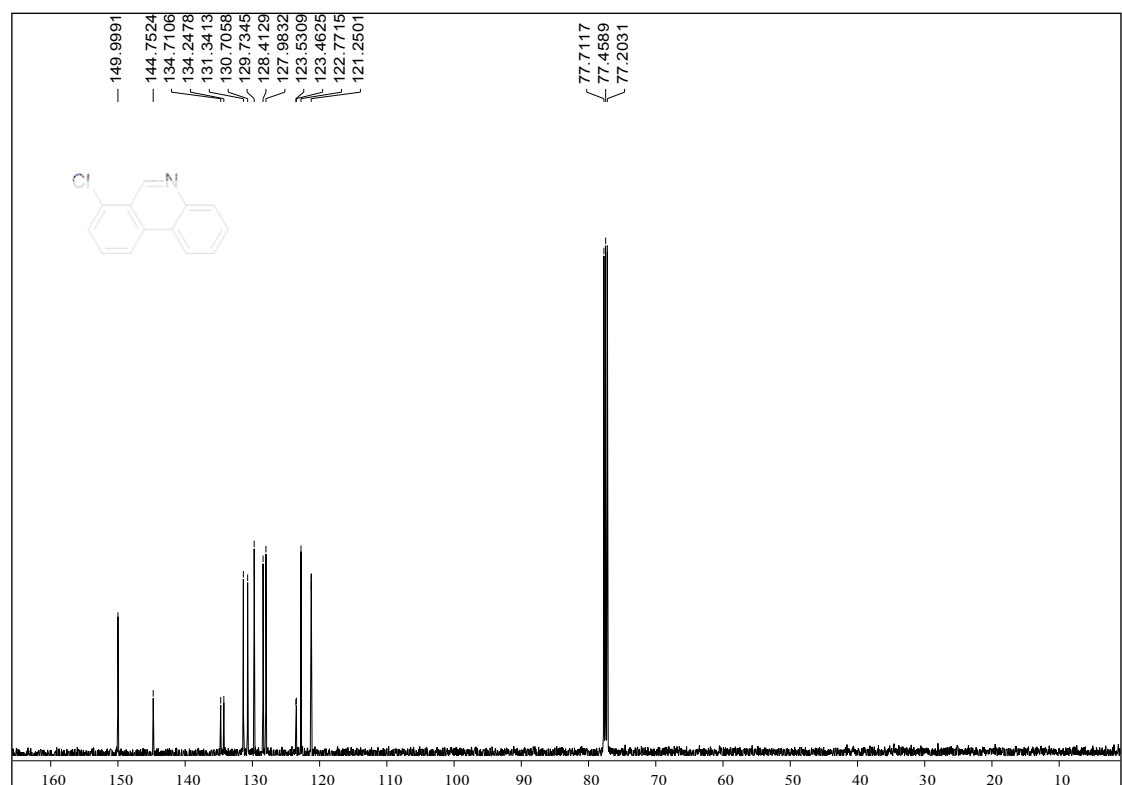
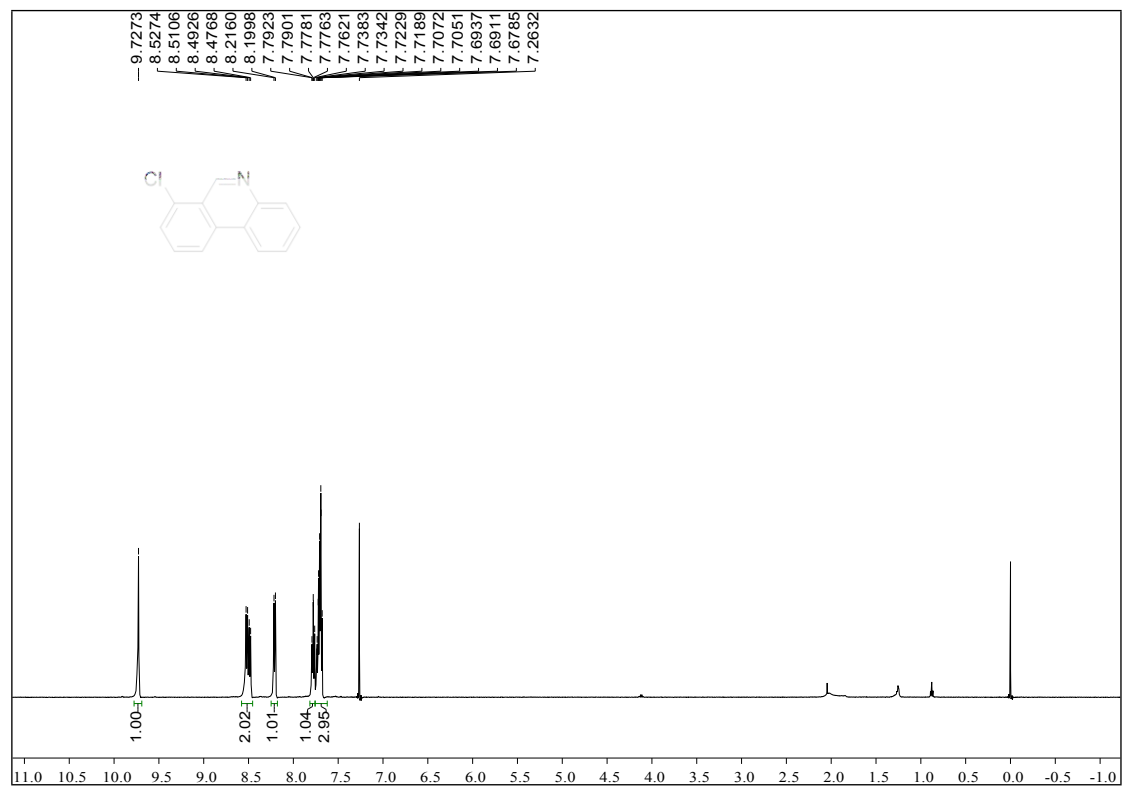
# Copies of $^1\text{H}$ , $^{13}\text{C}$ Spectra

## 7-fluorophenanthridine (3ba)

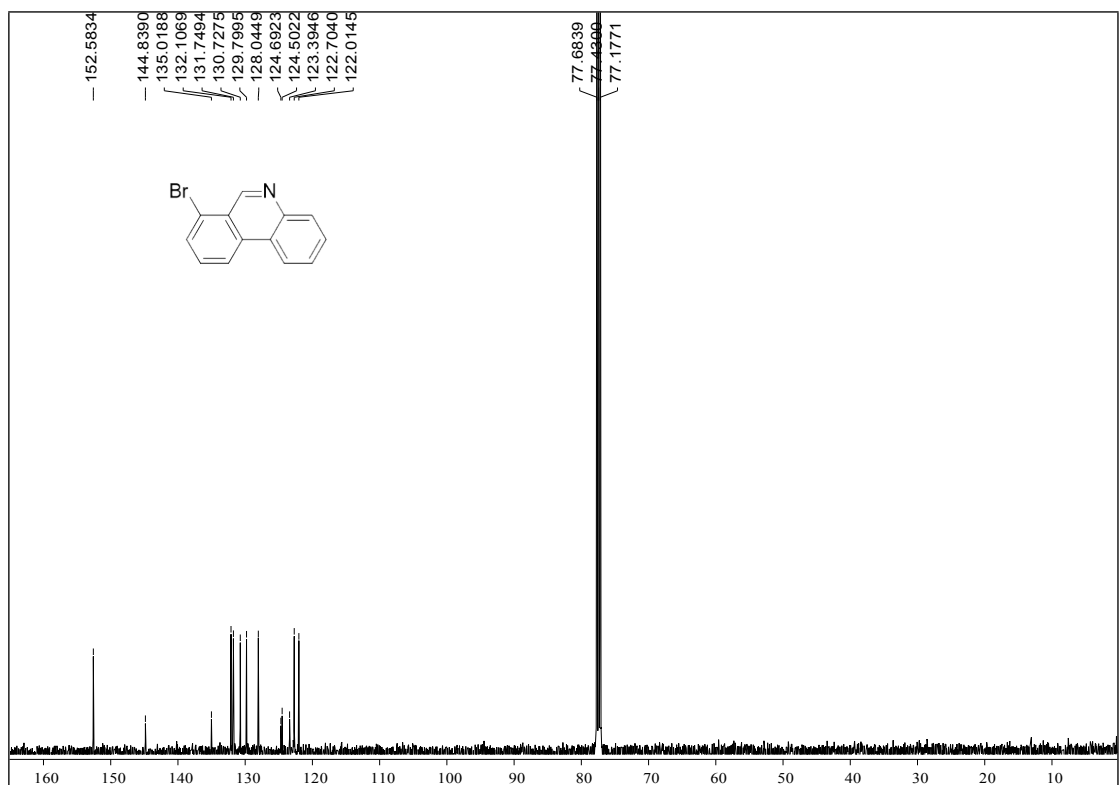
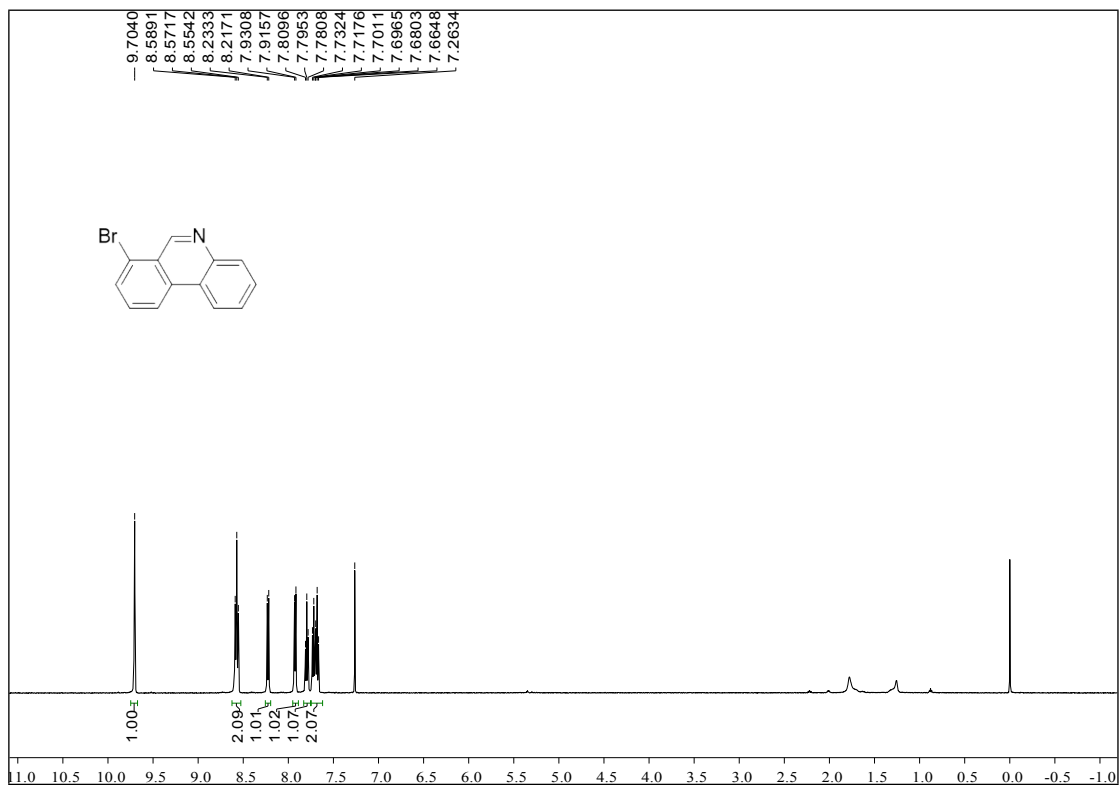




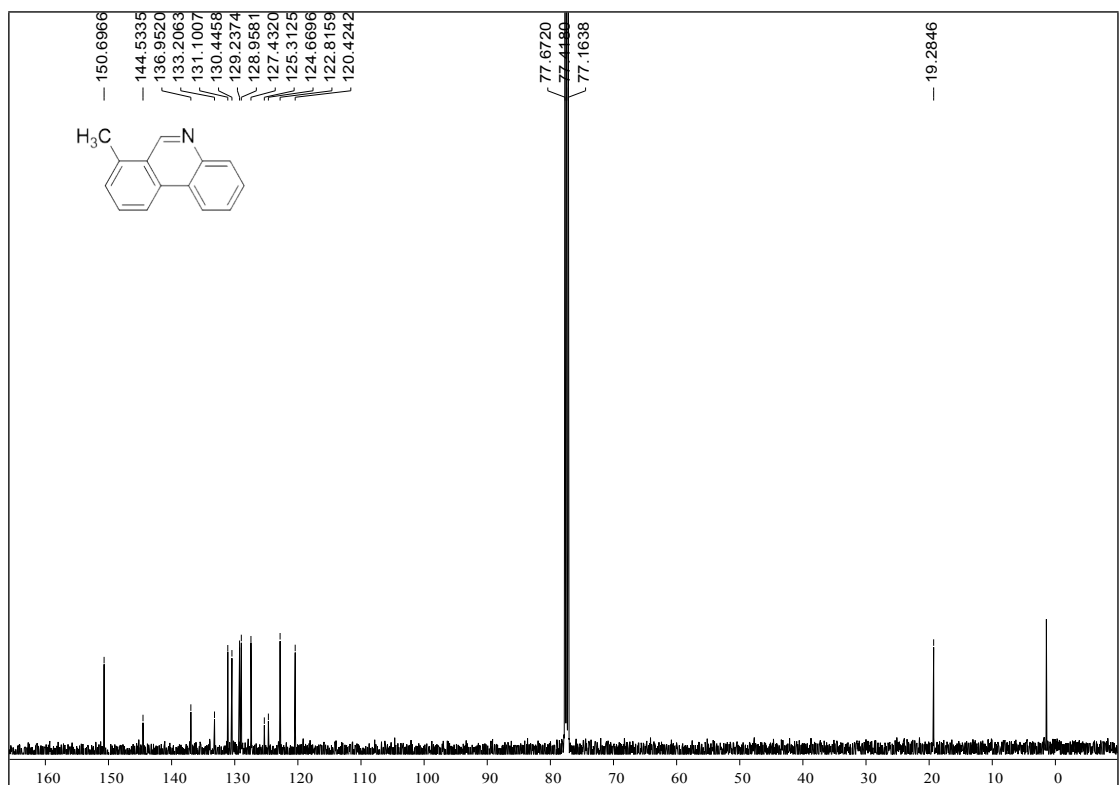
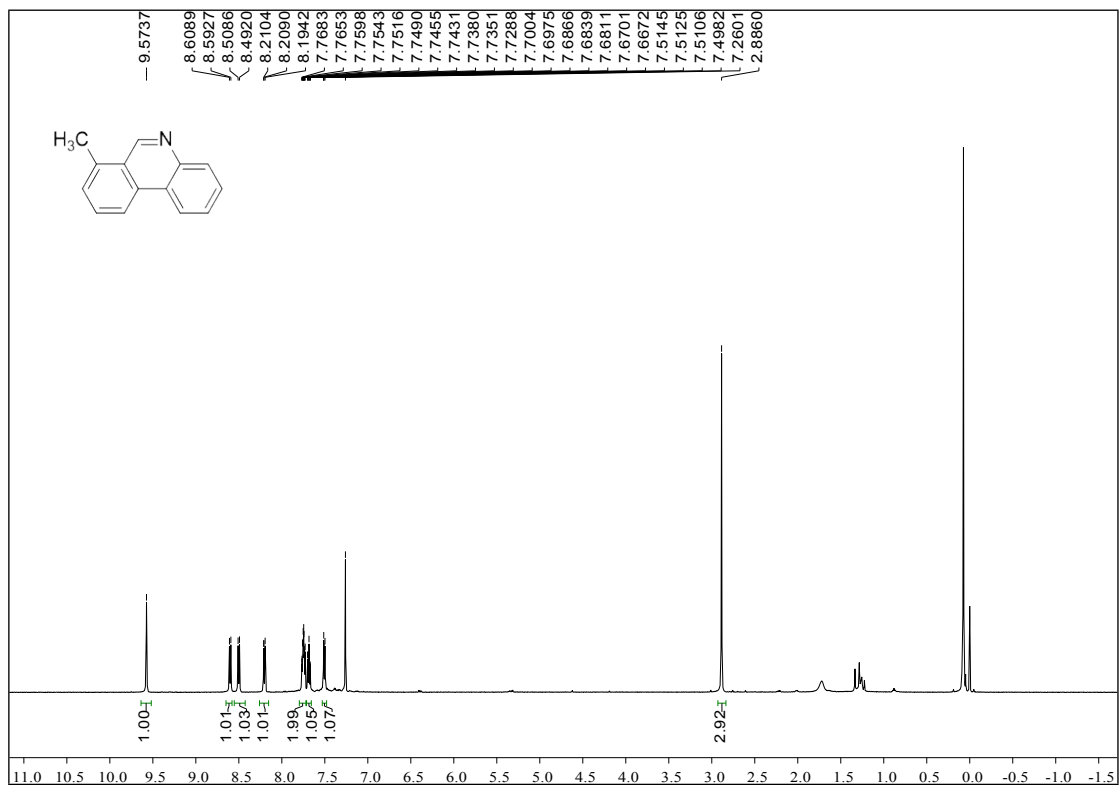
# 7-chlorophenanthridine (3aa)



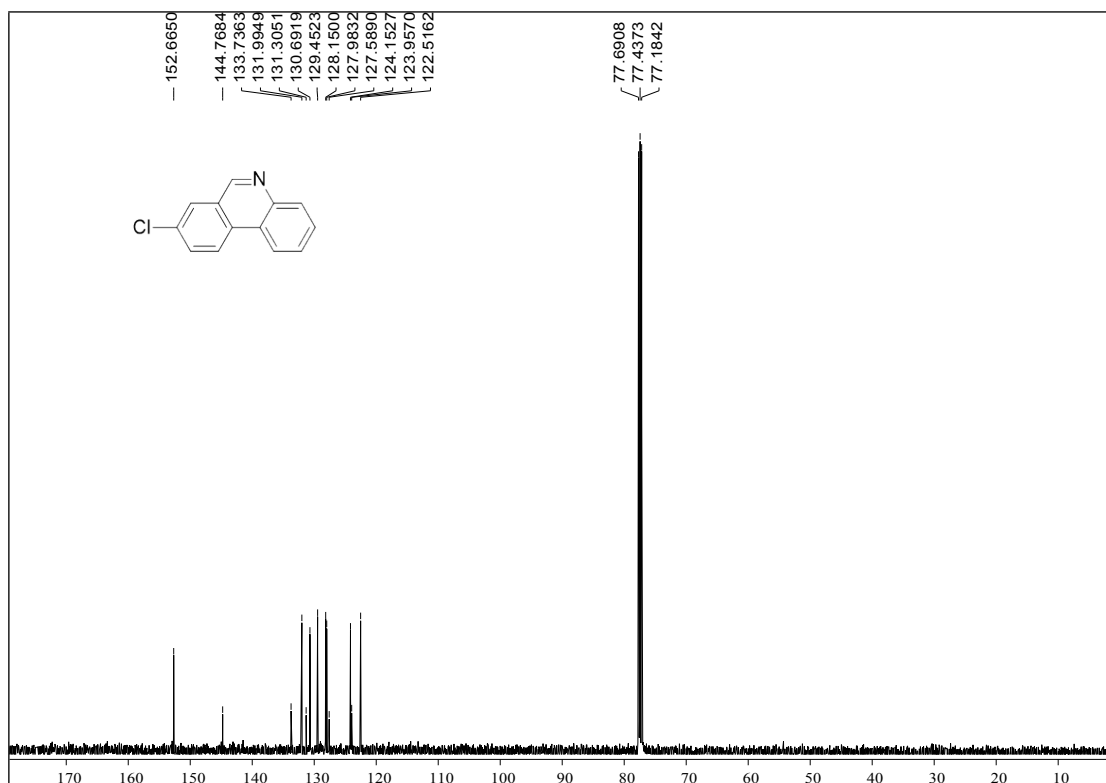
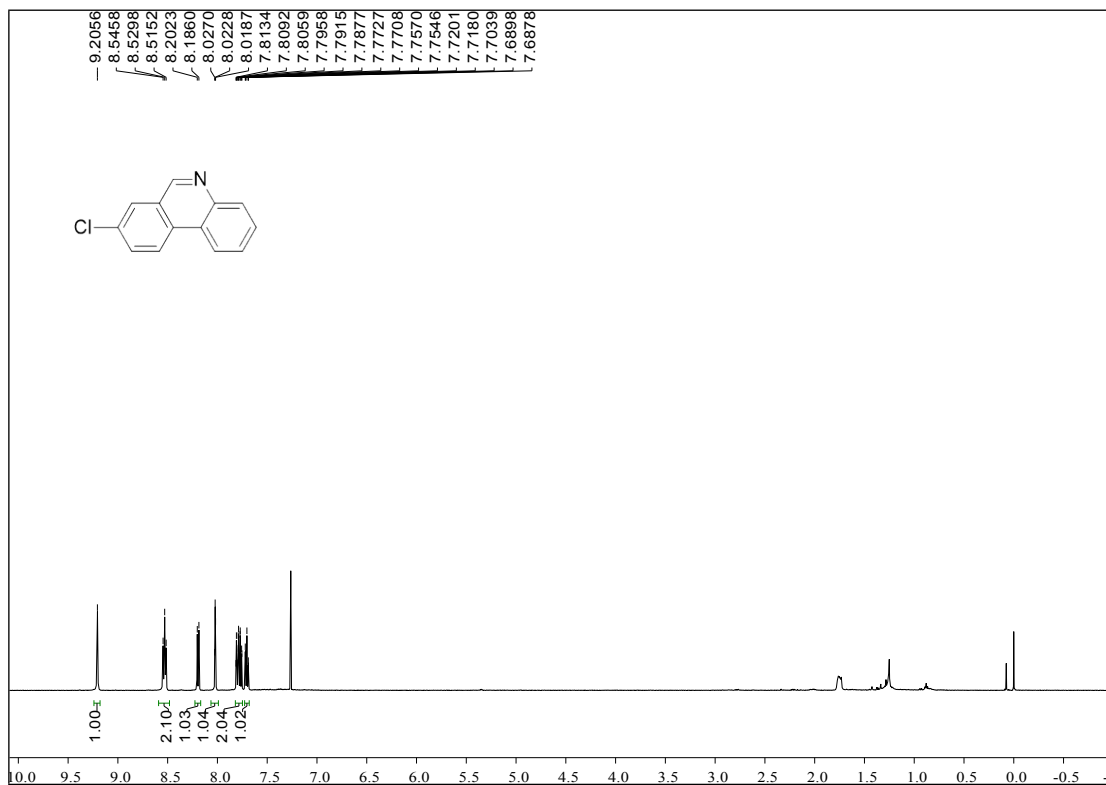
### 7-bromophenanthridine (3ca)



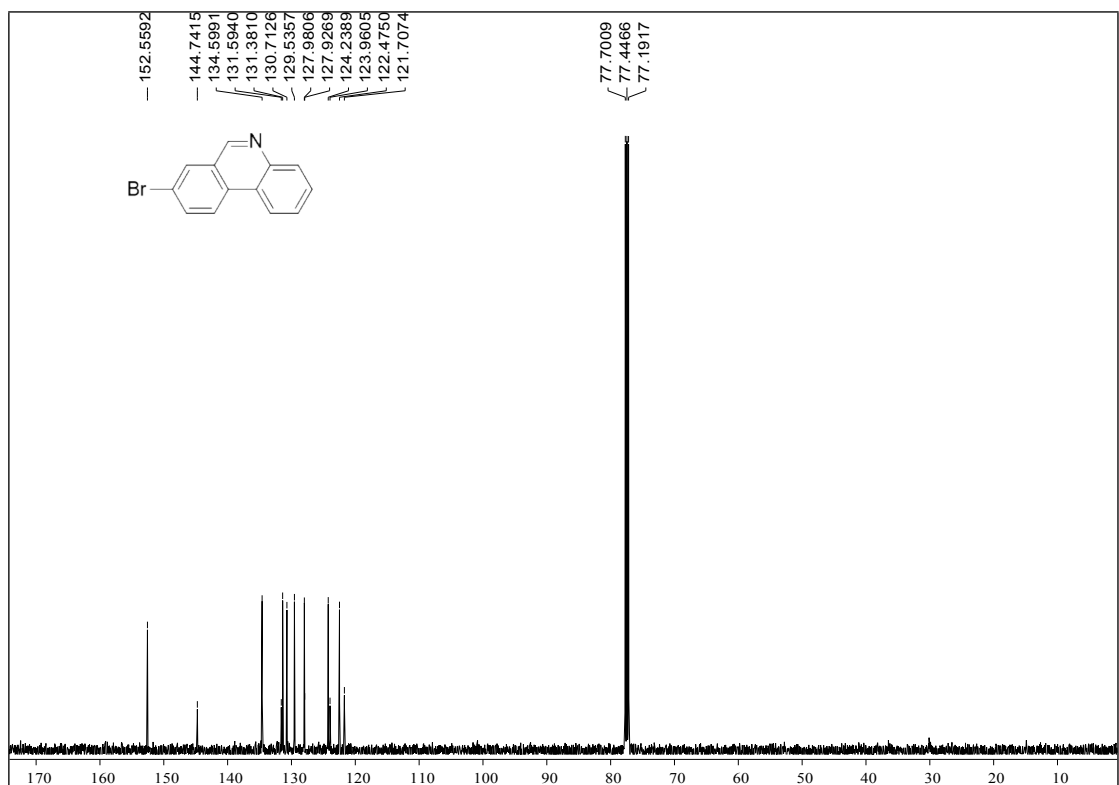
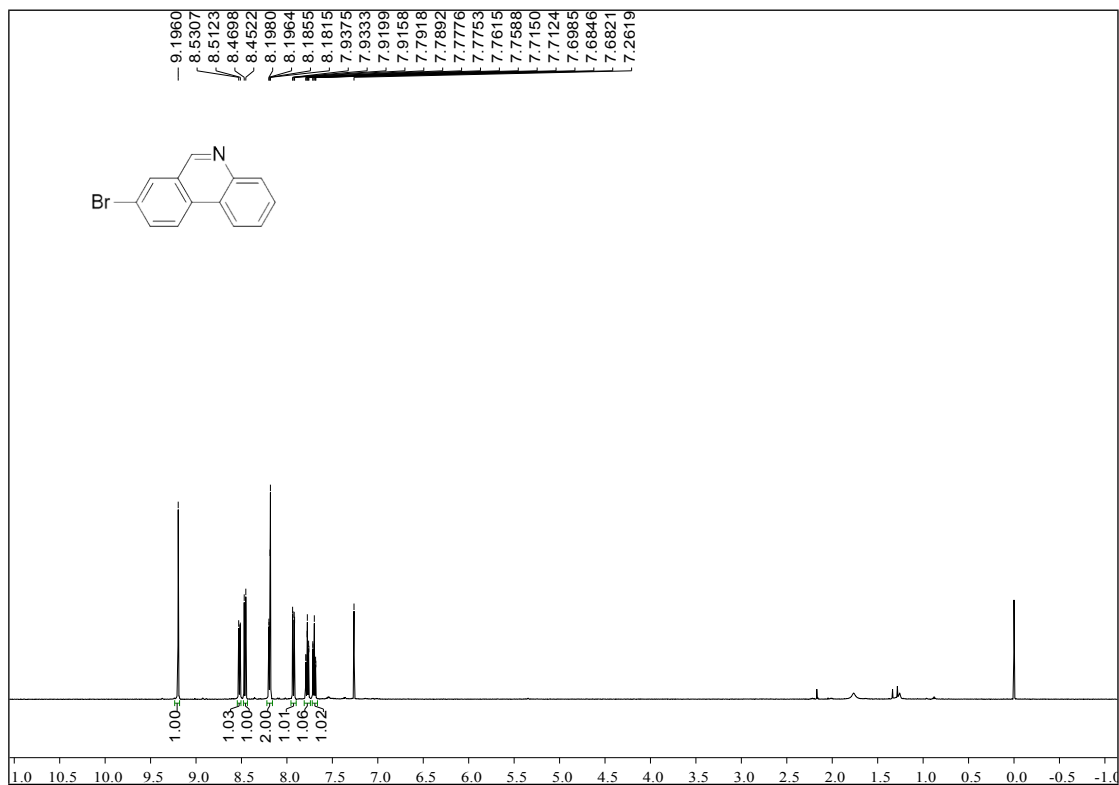
### 7-methylphenanthridine (3da)



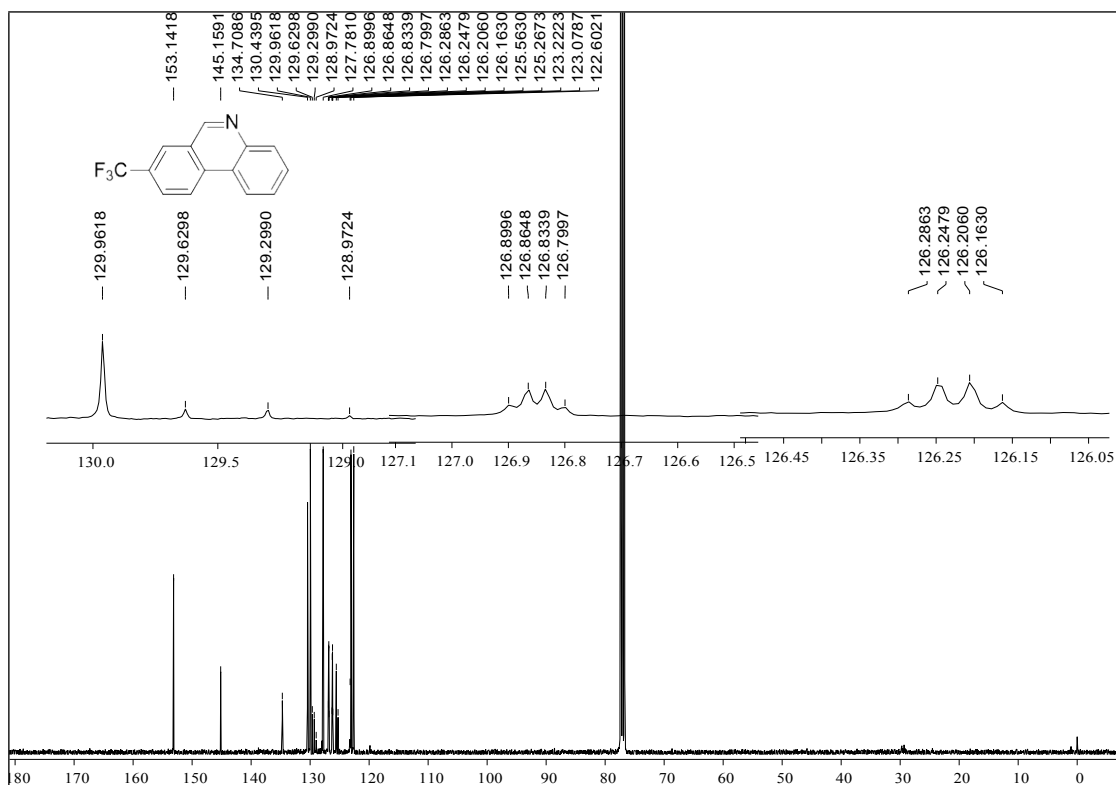
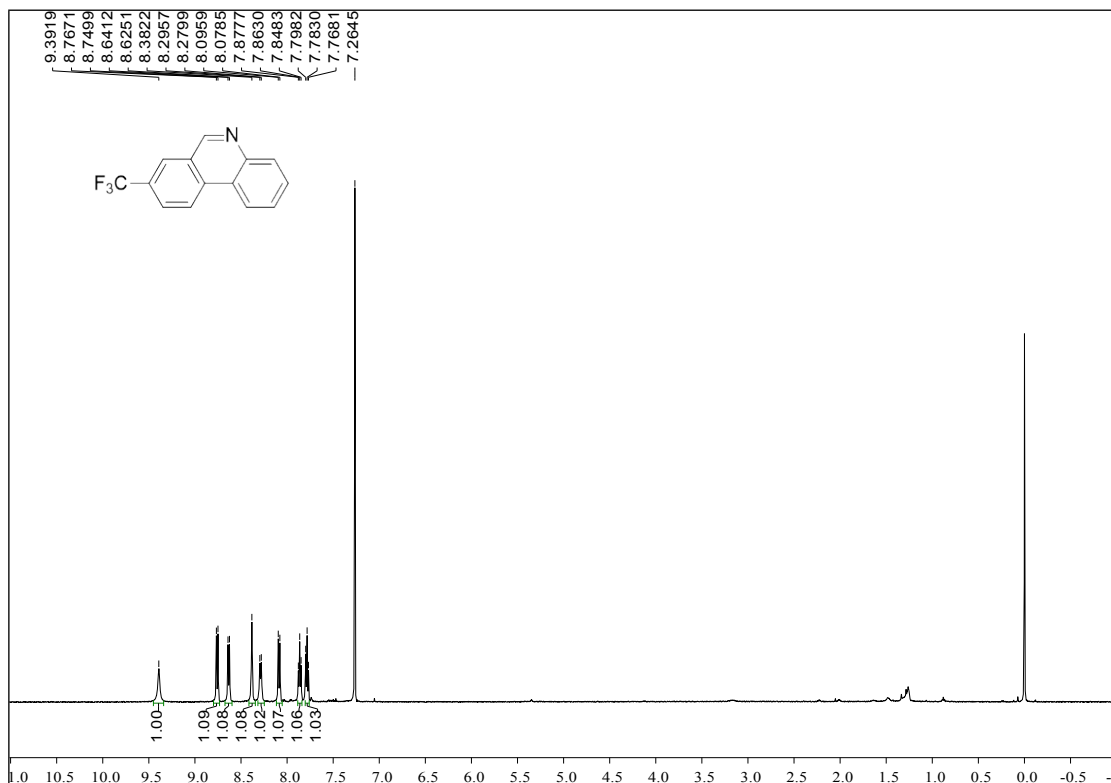
# 8-chlorophenanthridine (3ea)



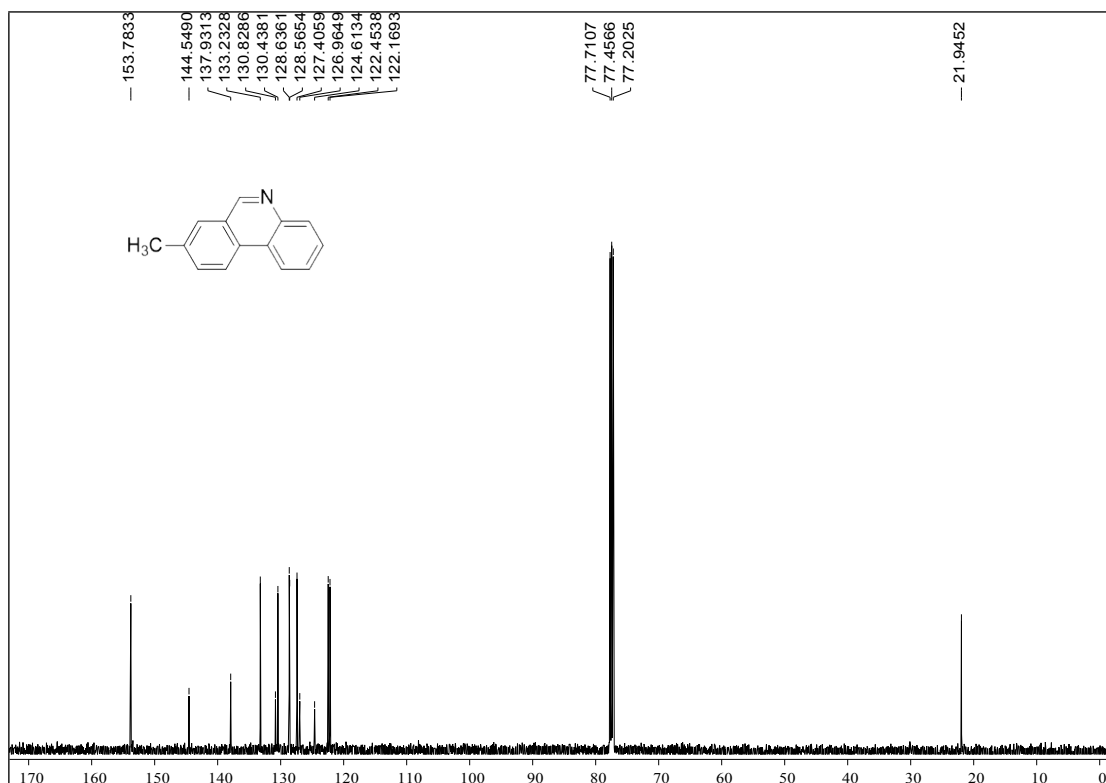
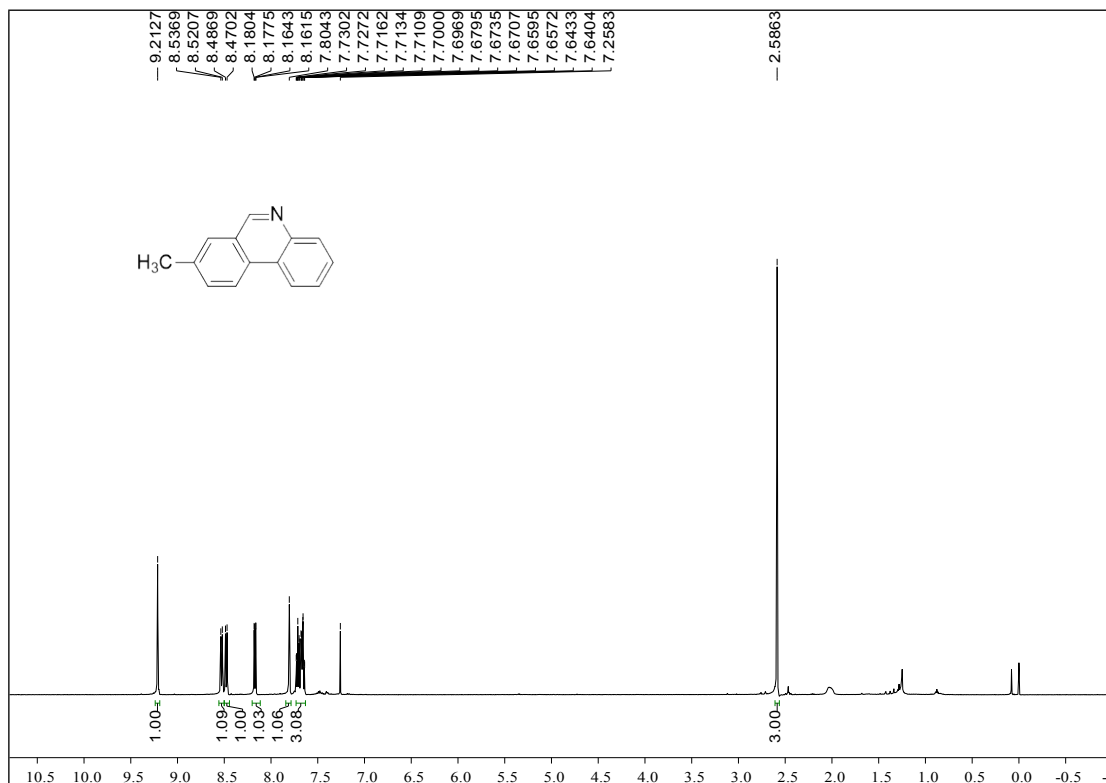
### 8-bromophenanthridine (3fa)



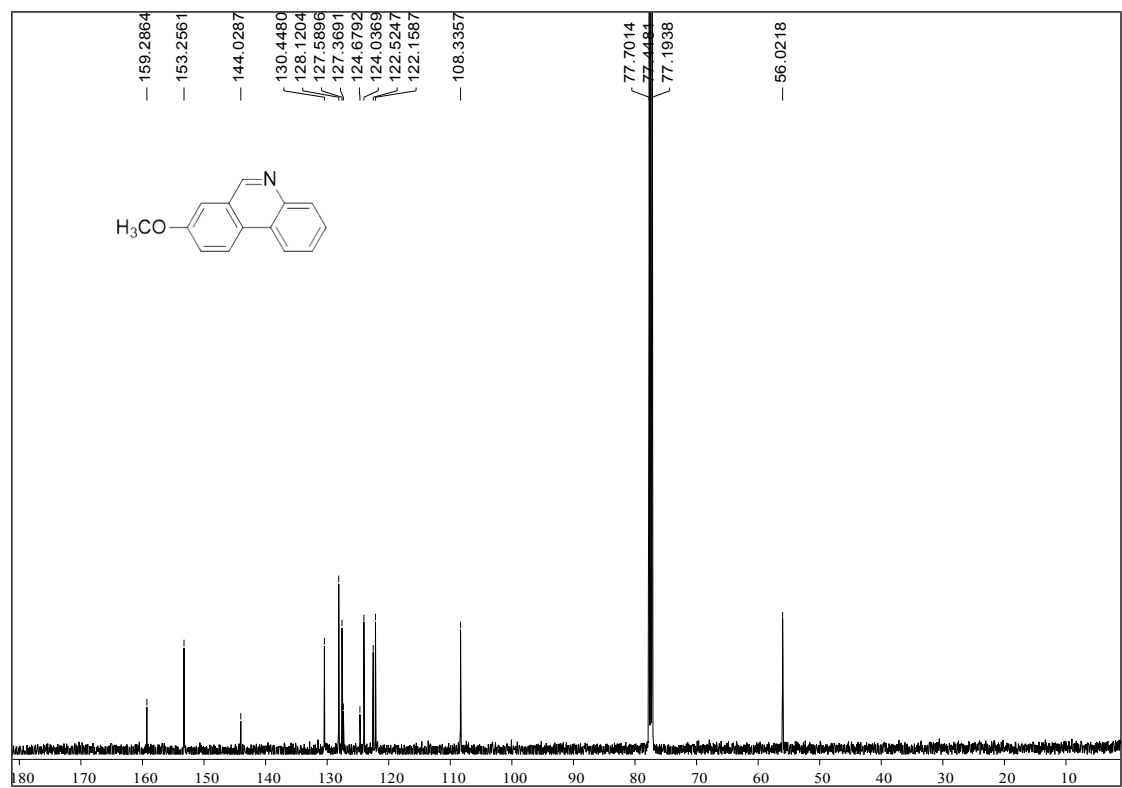
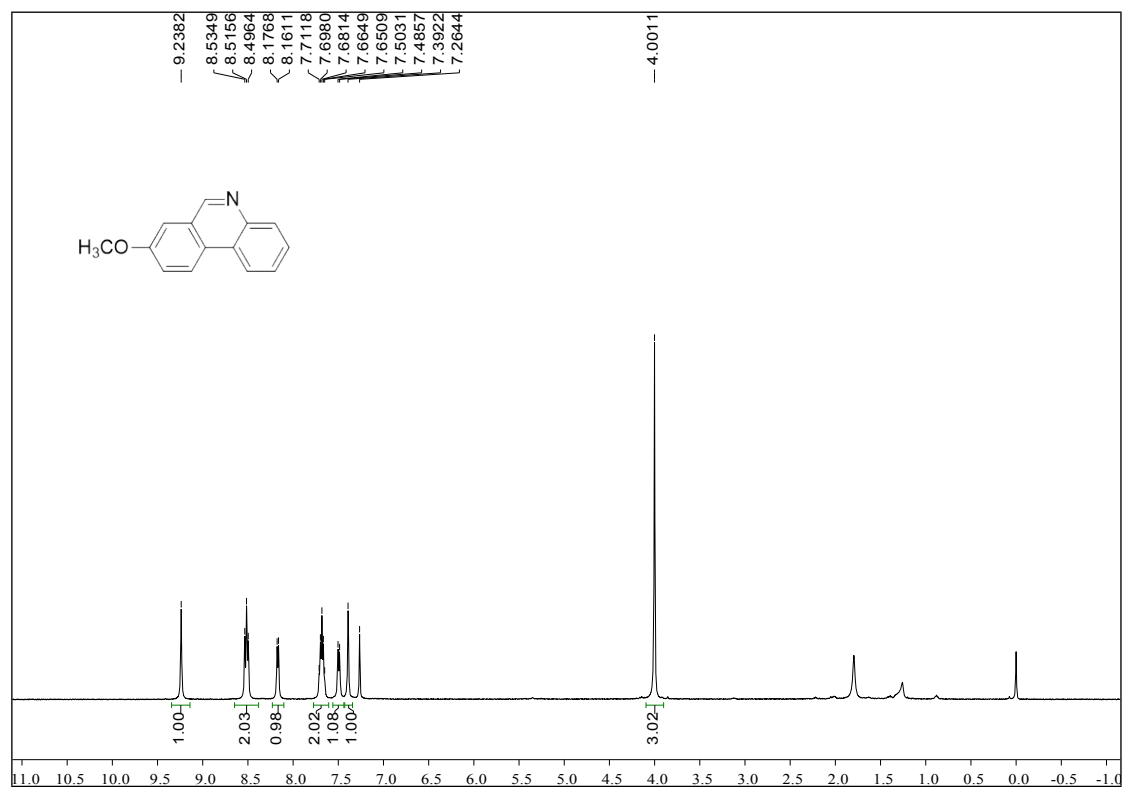
### 8-(trifluoromethyl)phenanthridine (3ga)



### 8-methylphenanthridine (3ha)

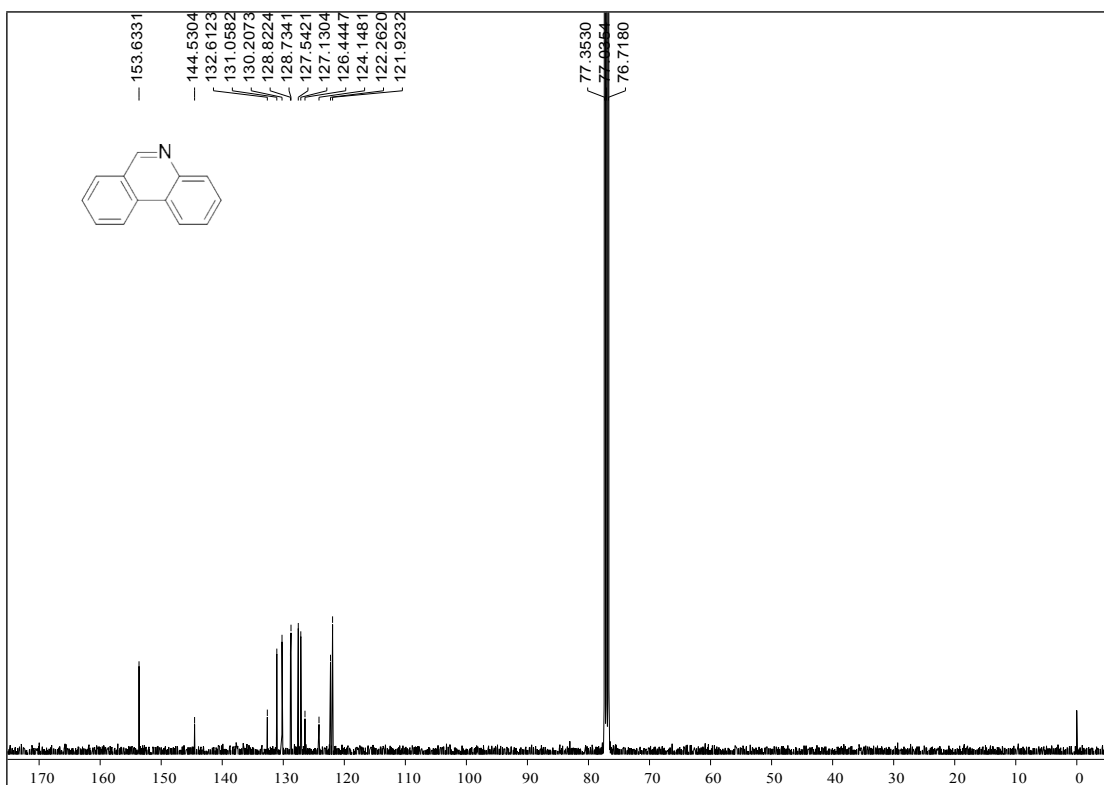
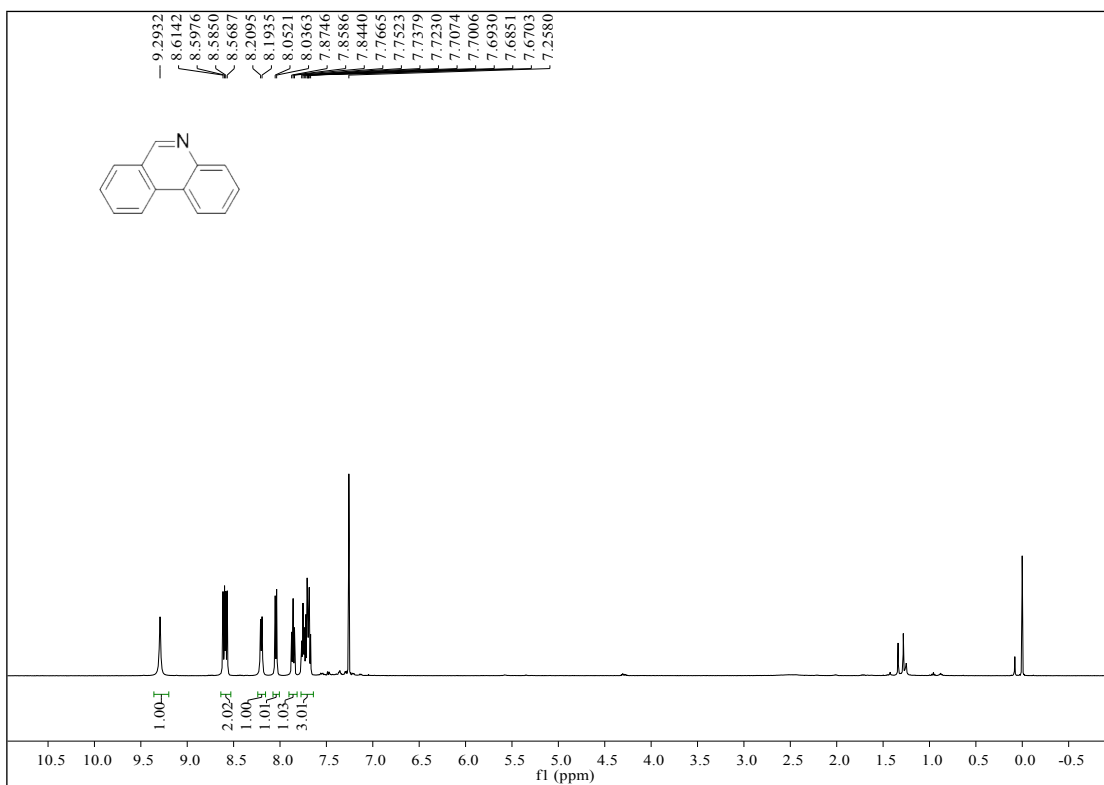


### 8-methoxyphenanthridine (3ia)

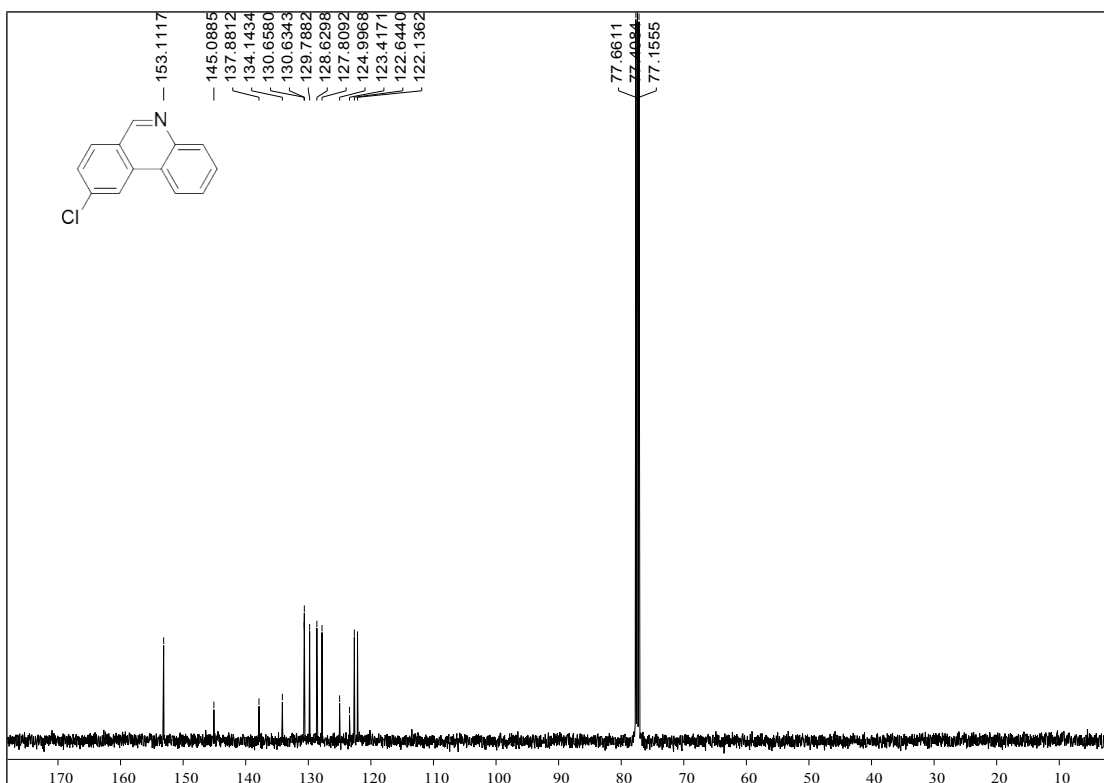
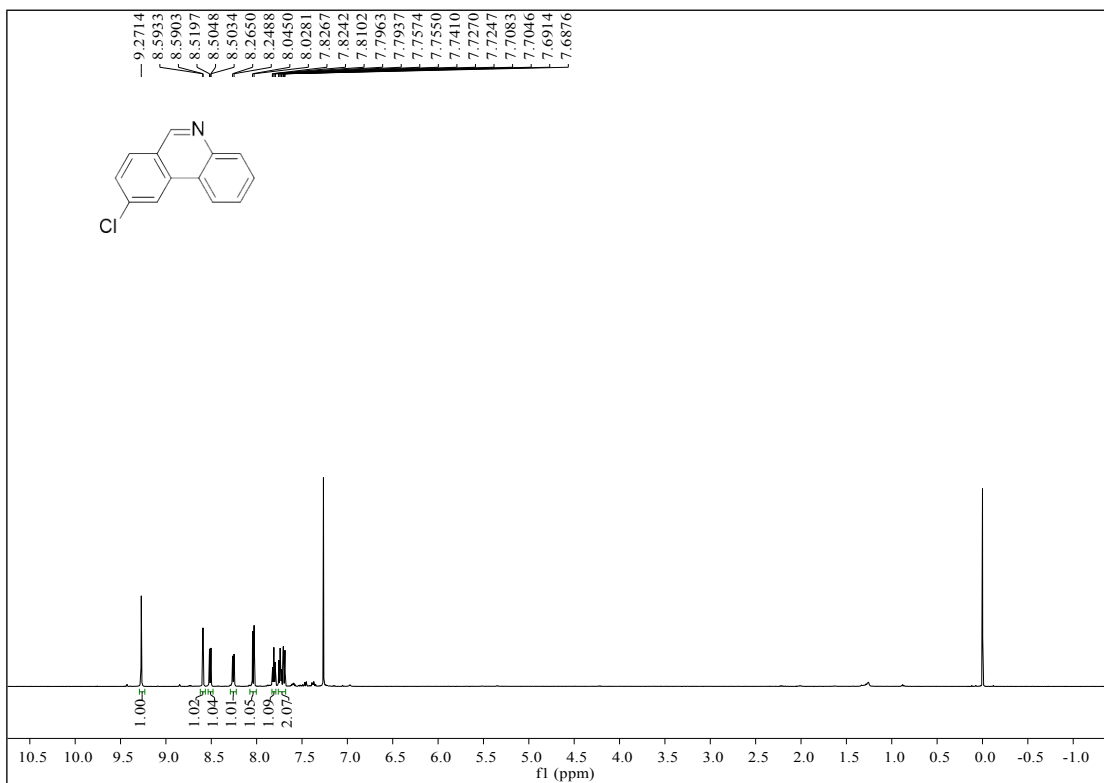




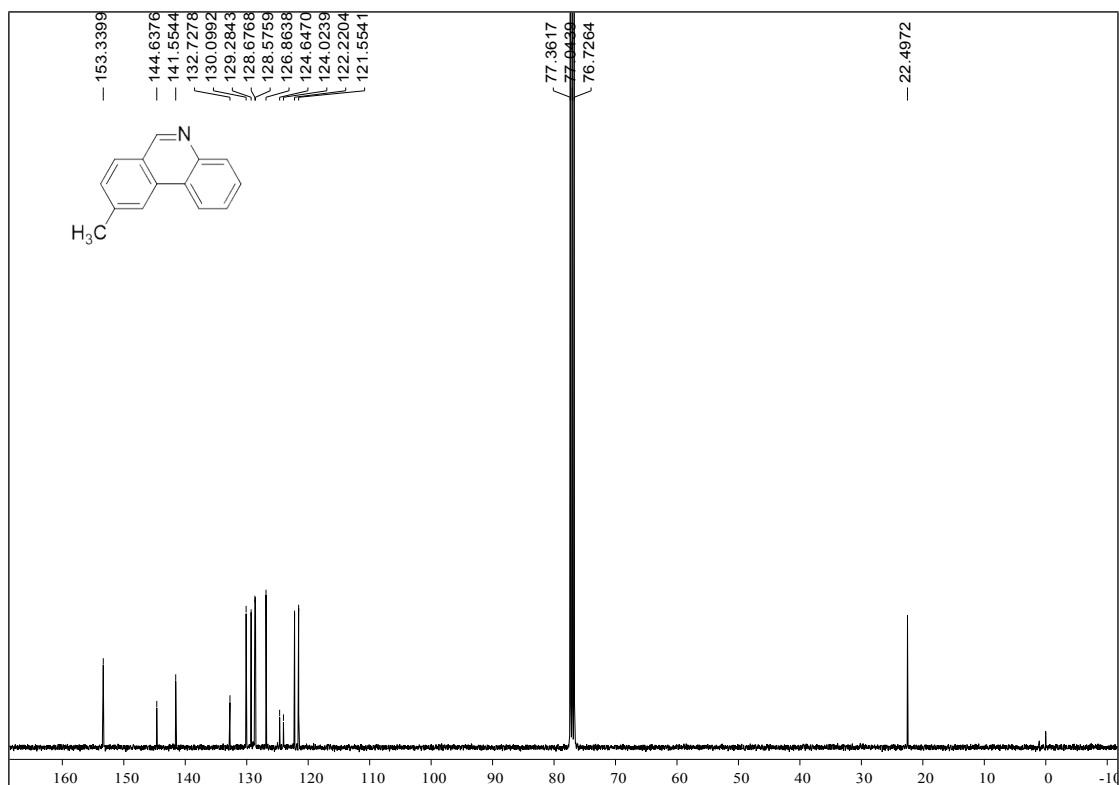
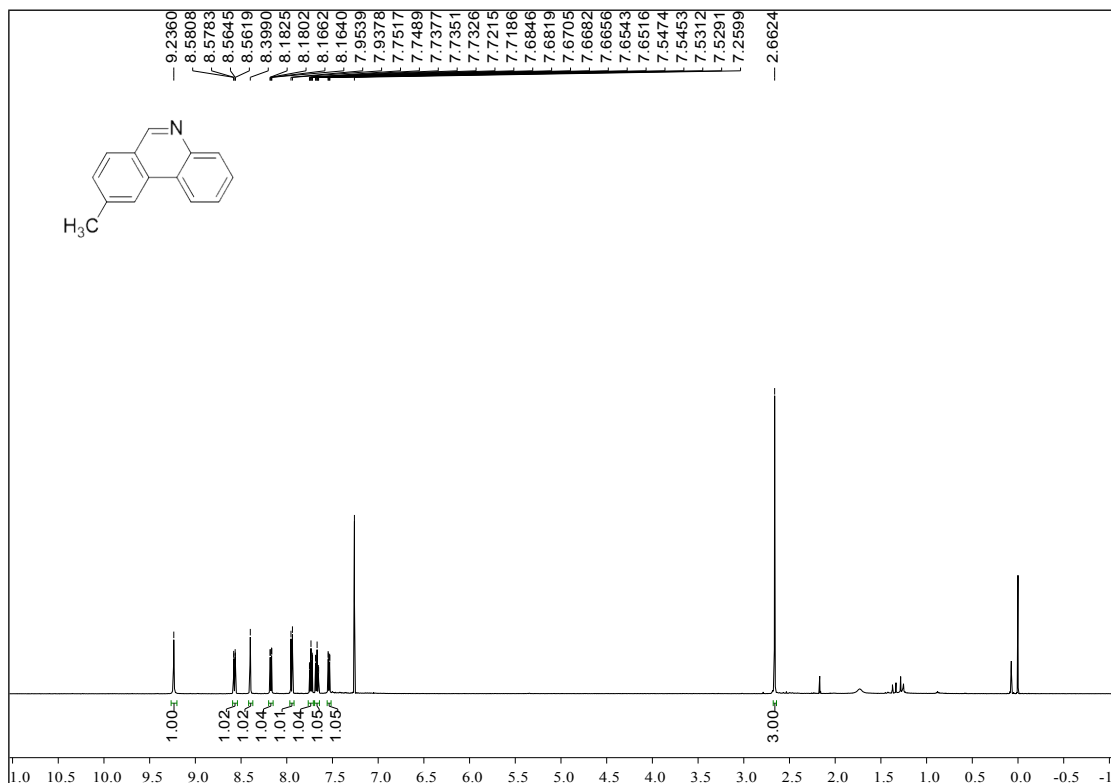
# Phenanthridine (3ja)



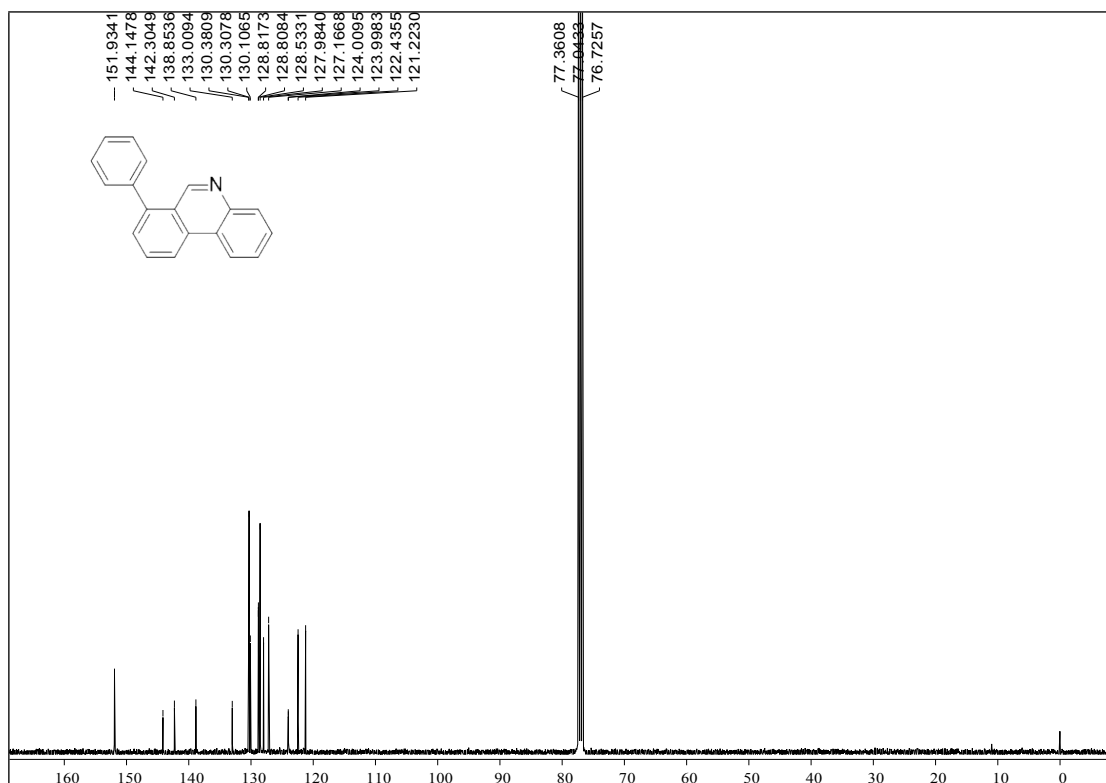
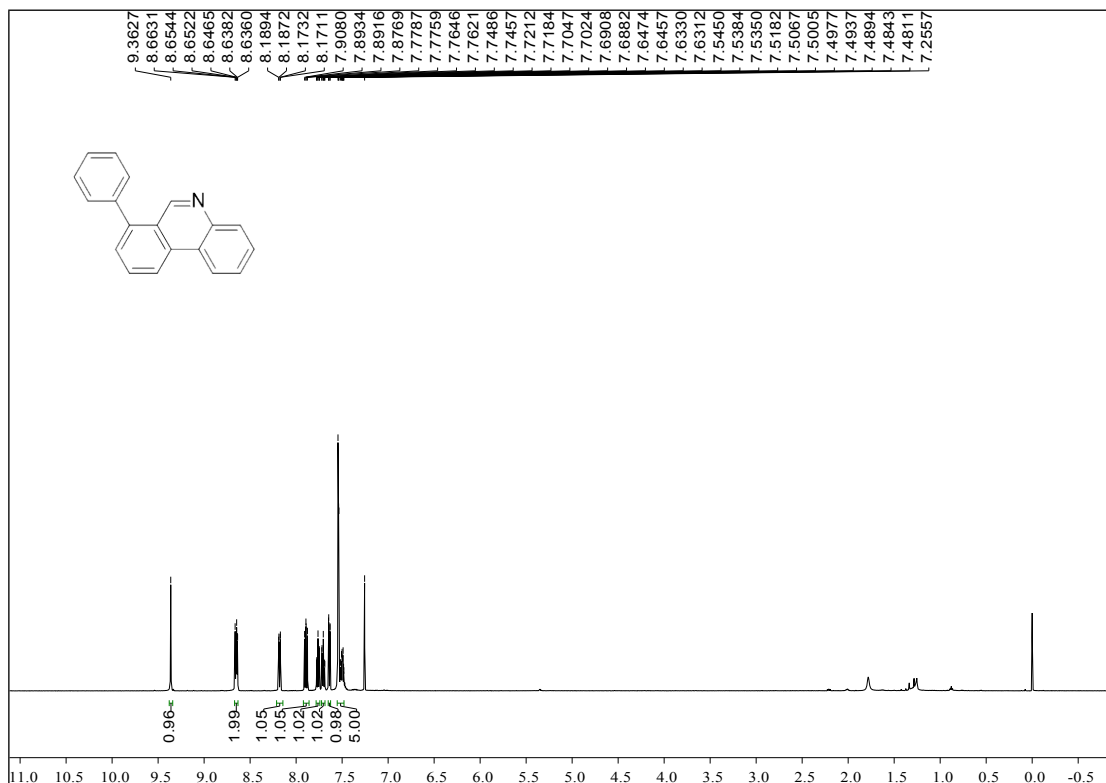
### 9-chlorophenanthridine (3ka)



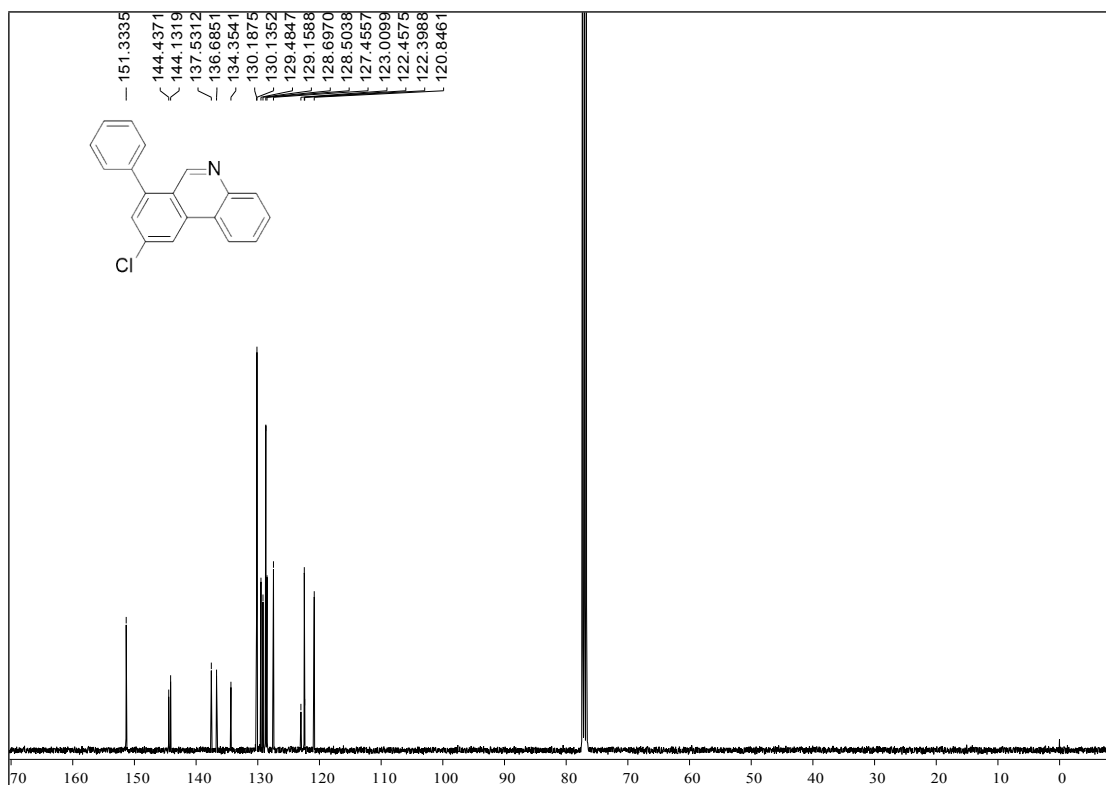
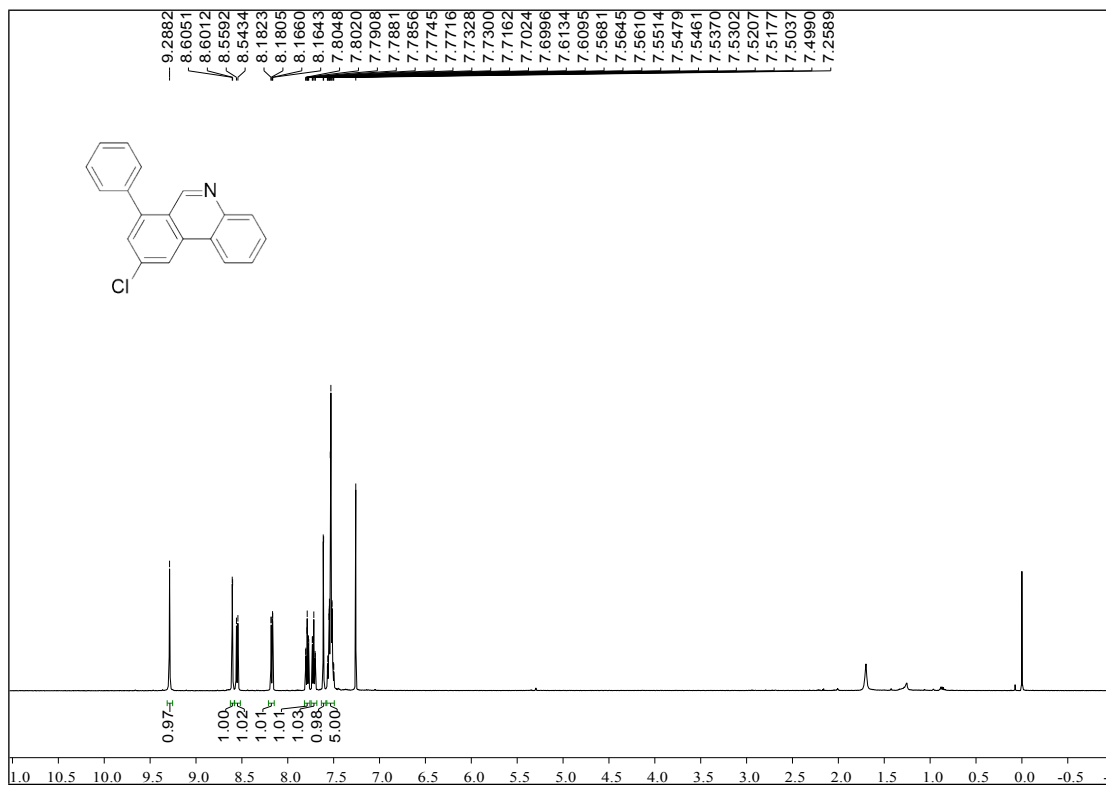
### 9-methylphenanthridine (31a)



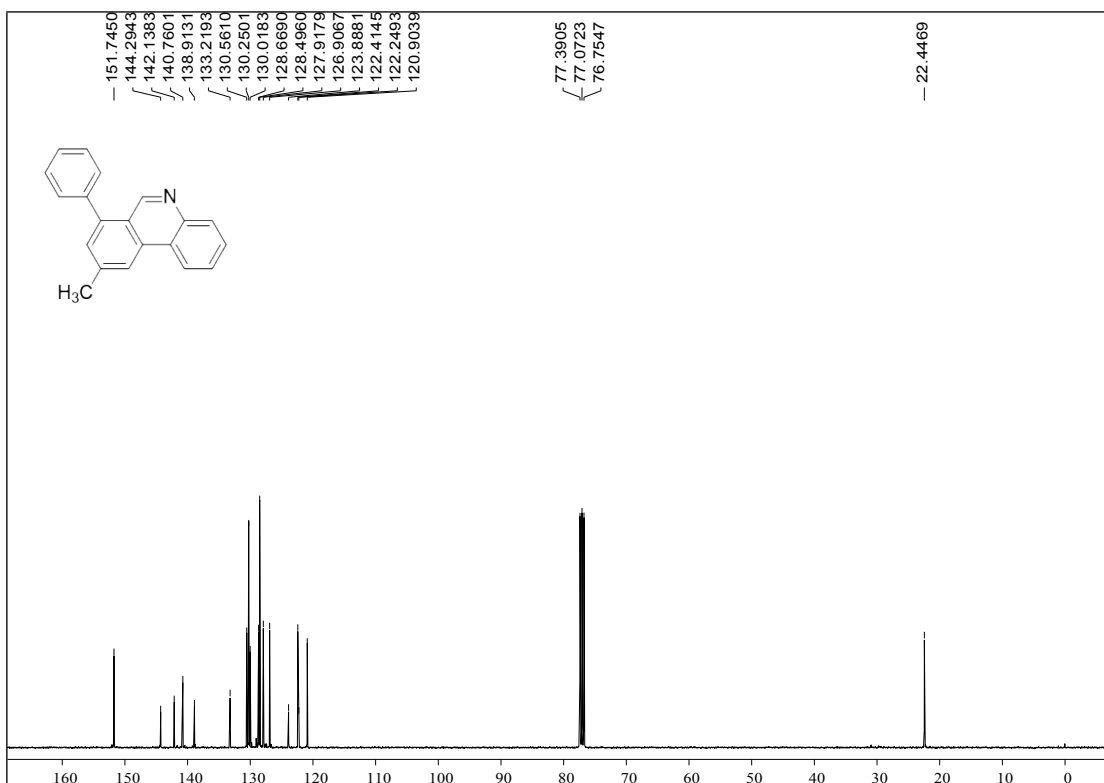
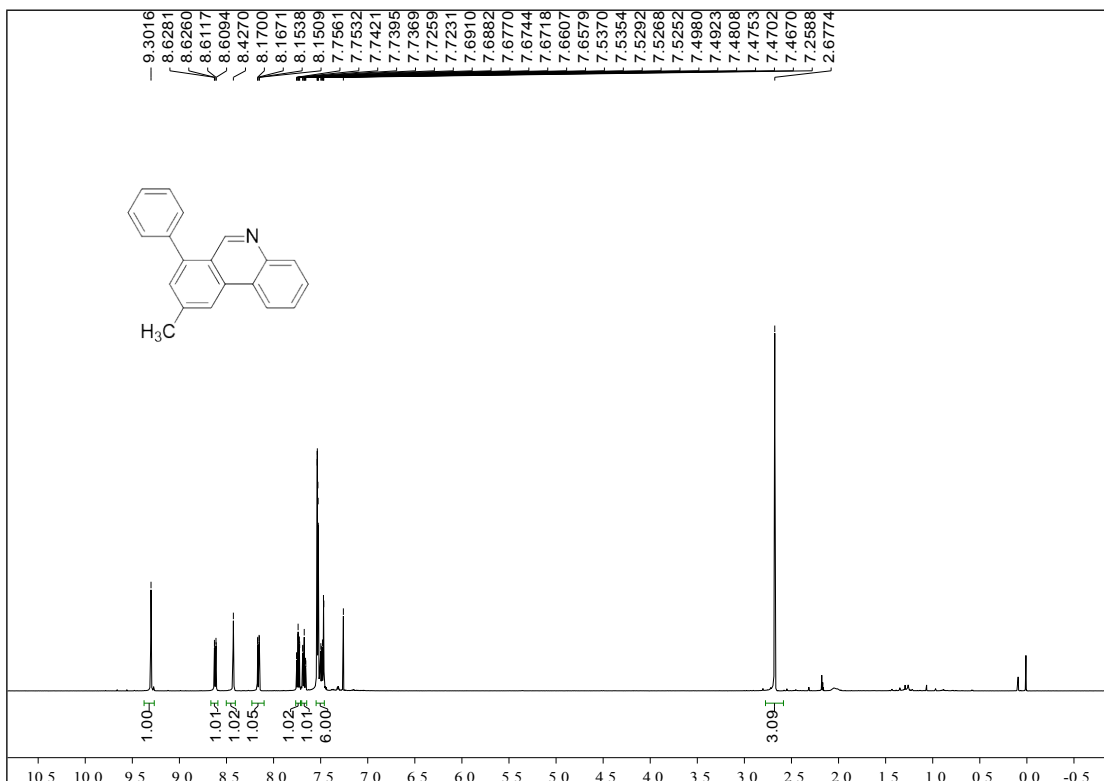
# 7-phenylphenanthridine (3jaa)



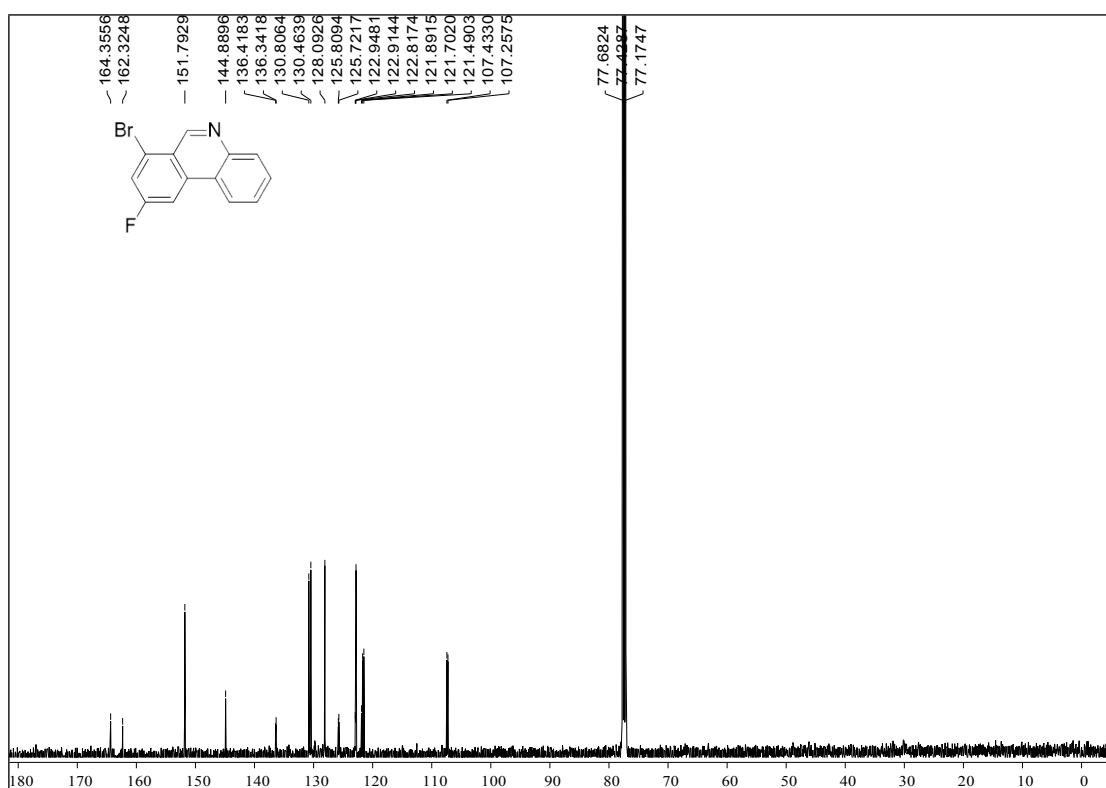
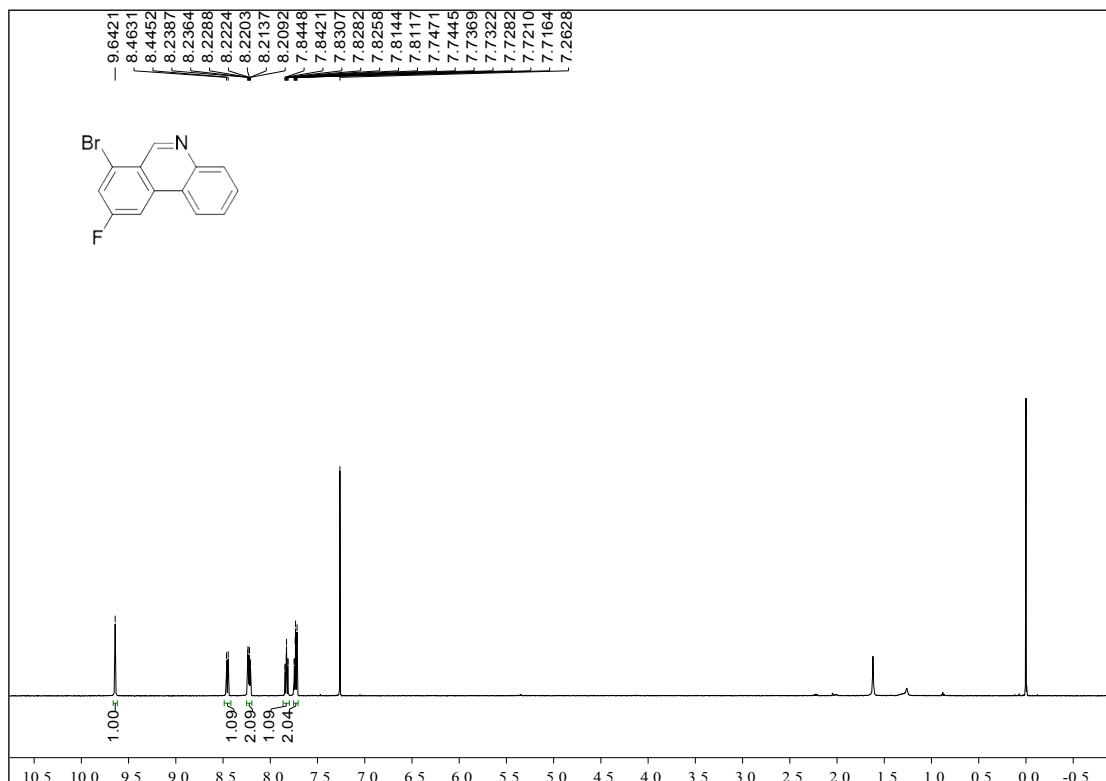
### 9-methyl-7-phenylphenanthridine (3kaa)



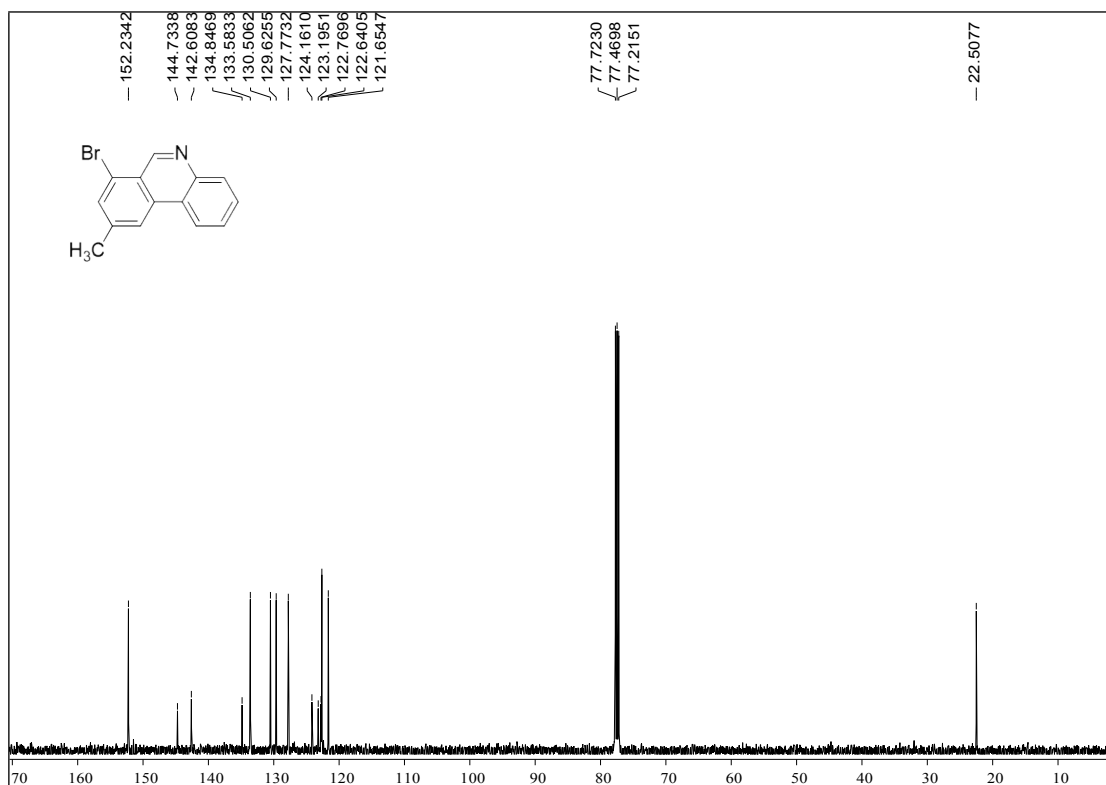
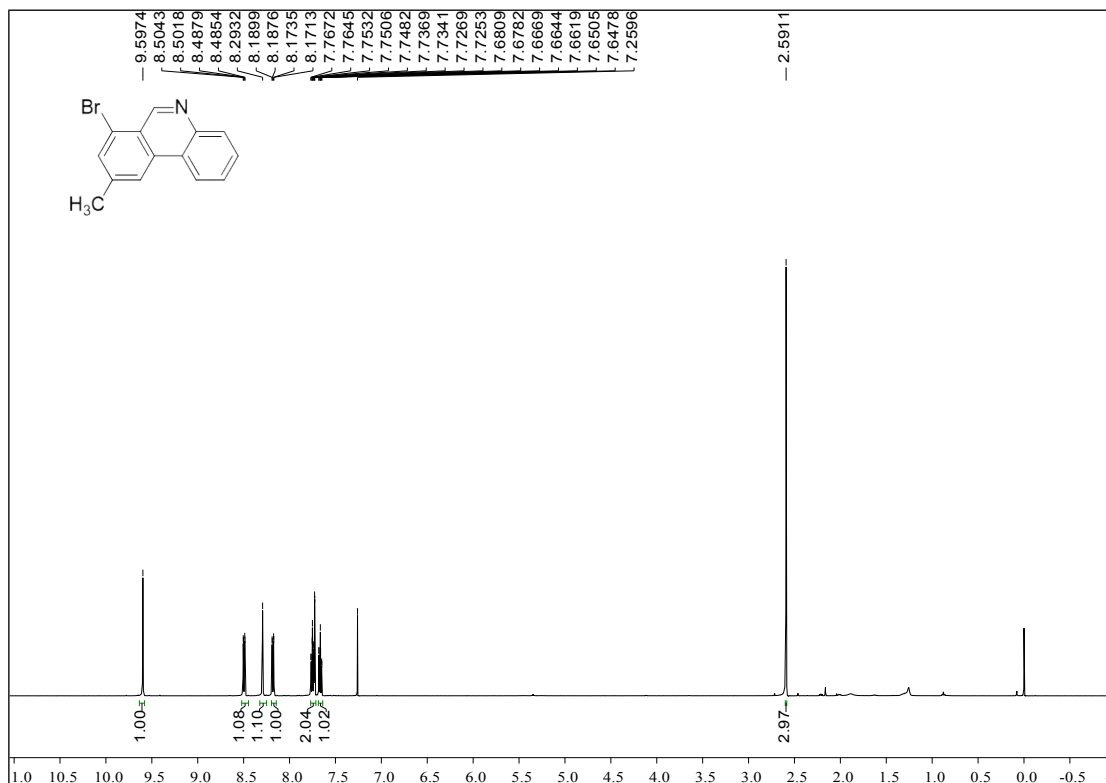
### 9-methyl-7-phenylphenanthridine (31aa)



### 7-bromo-9-fluorophenanthridine (3ma)

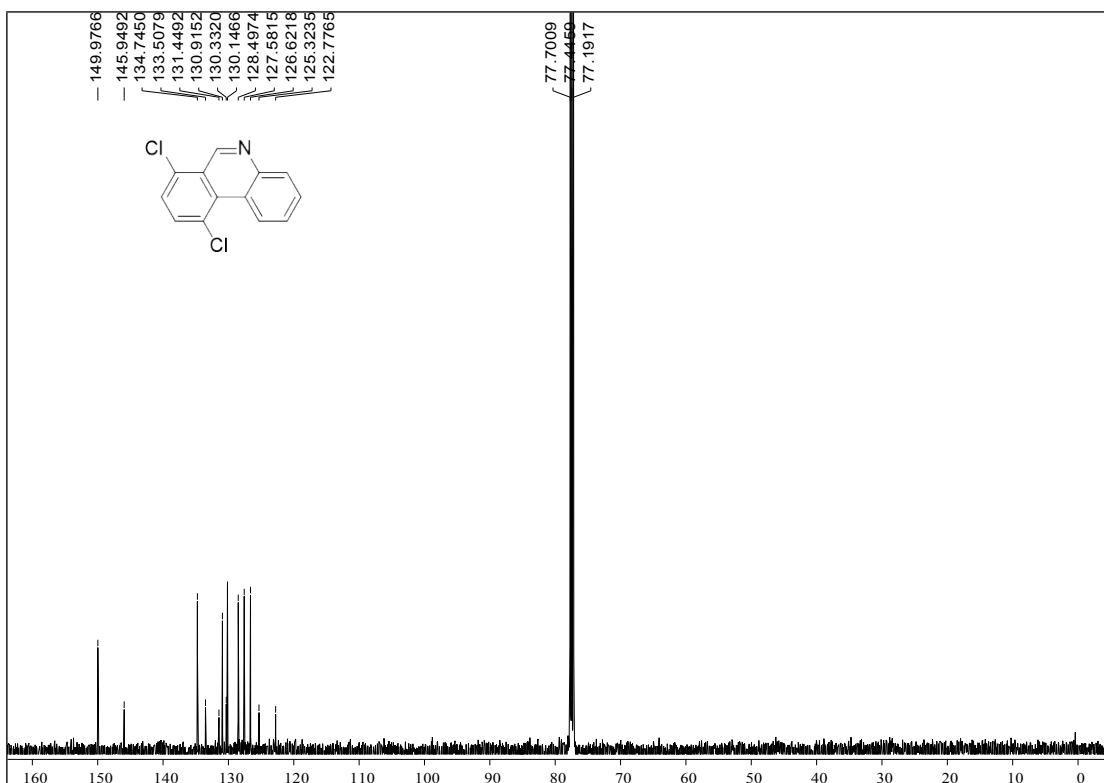
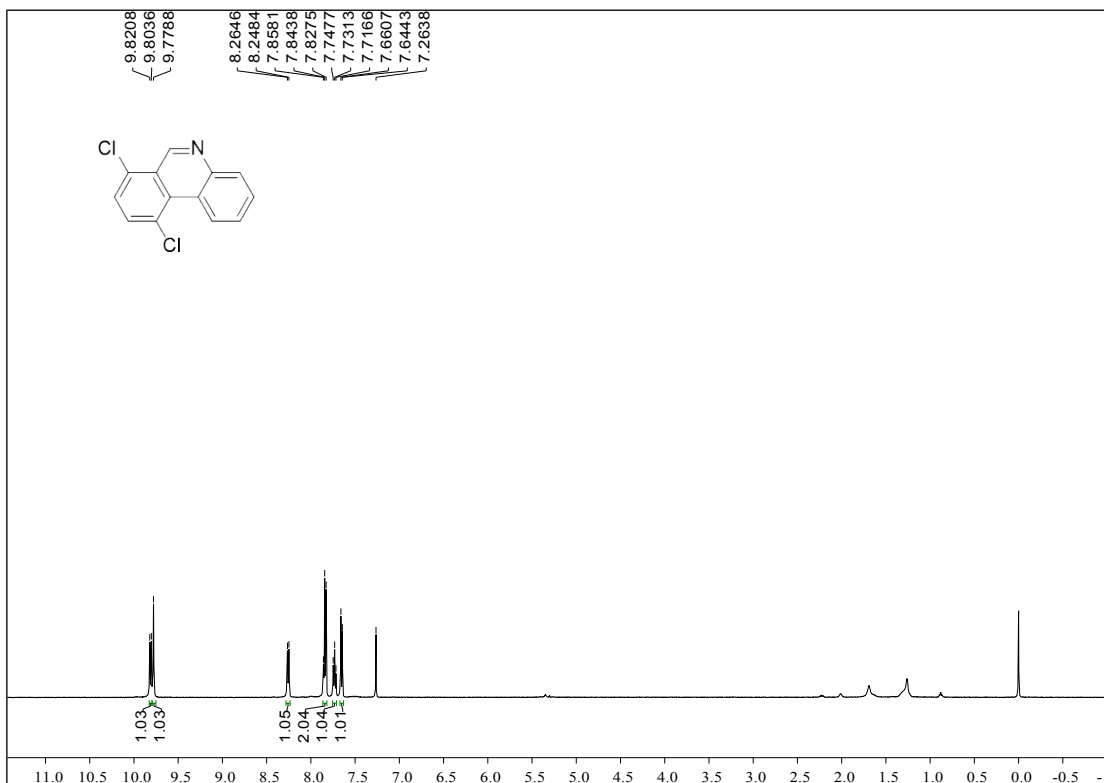


### 7-bromo-9-methylphenanthridine (3na)

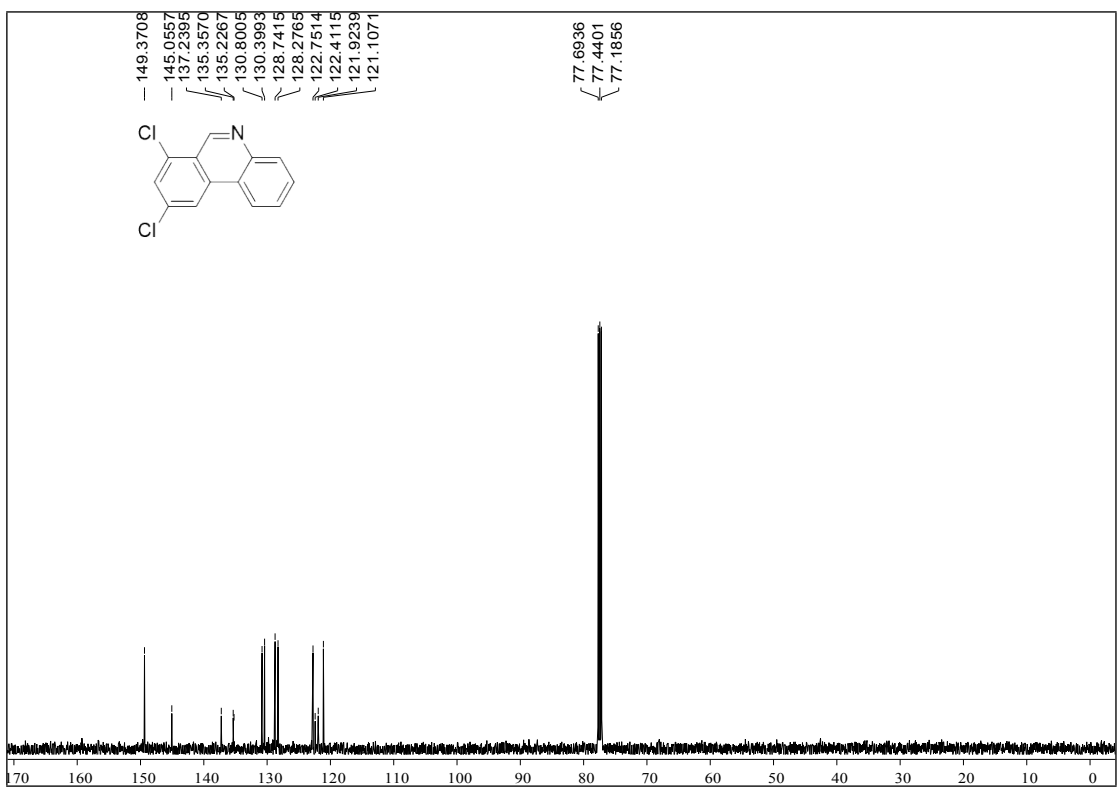
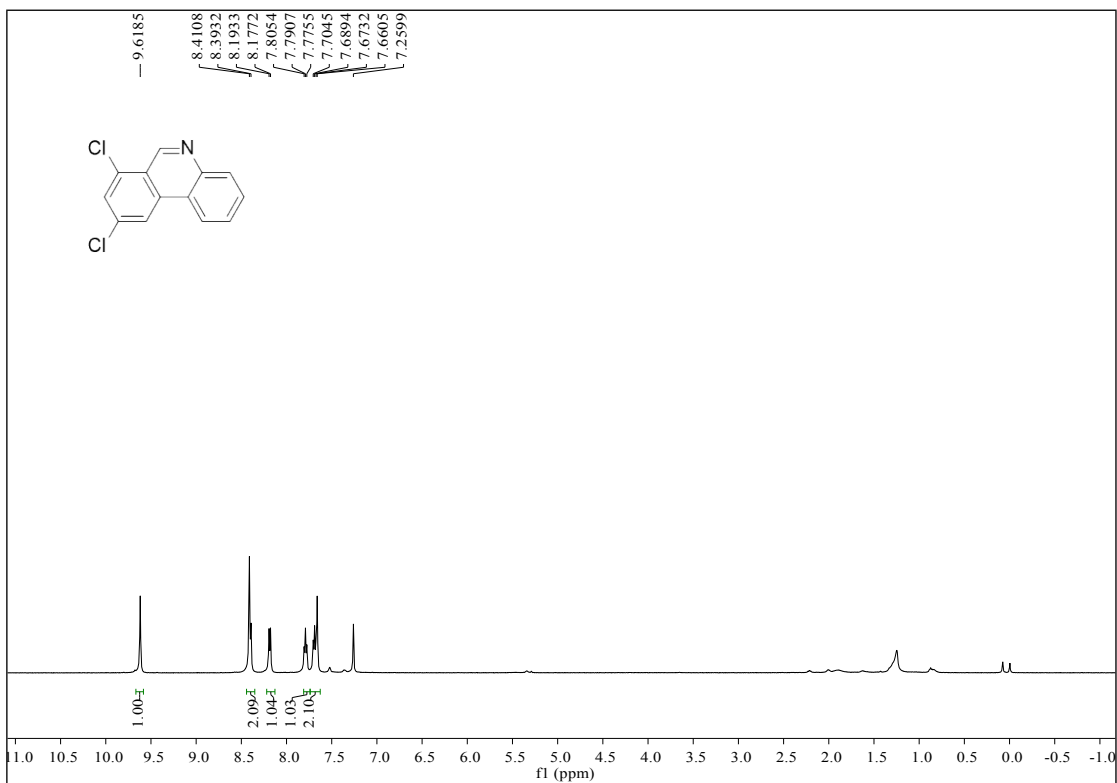




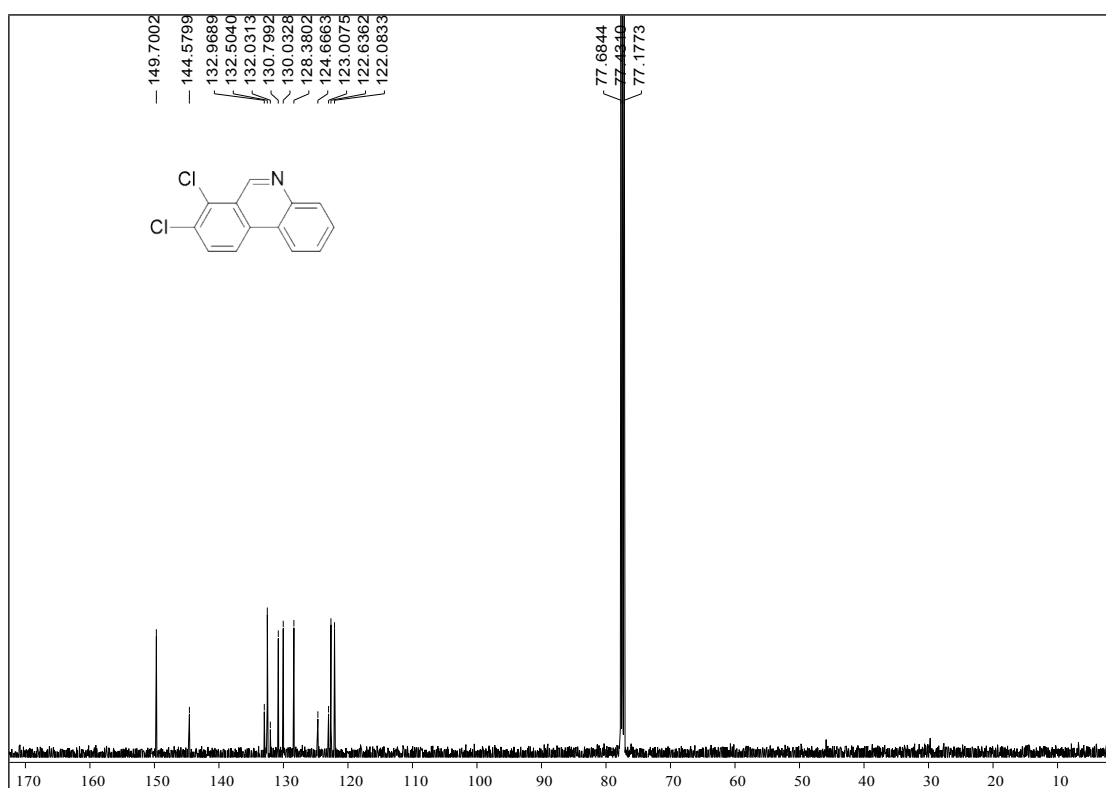
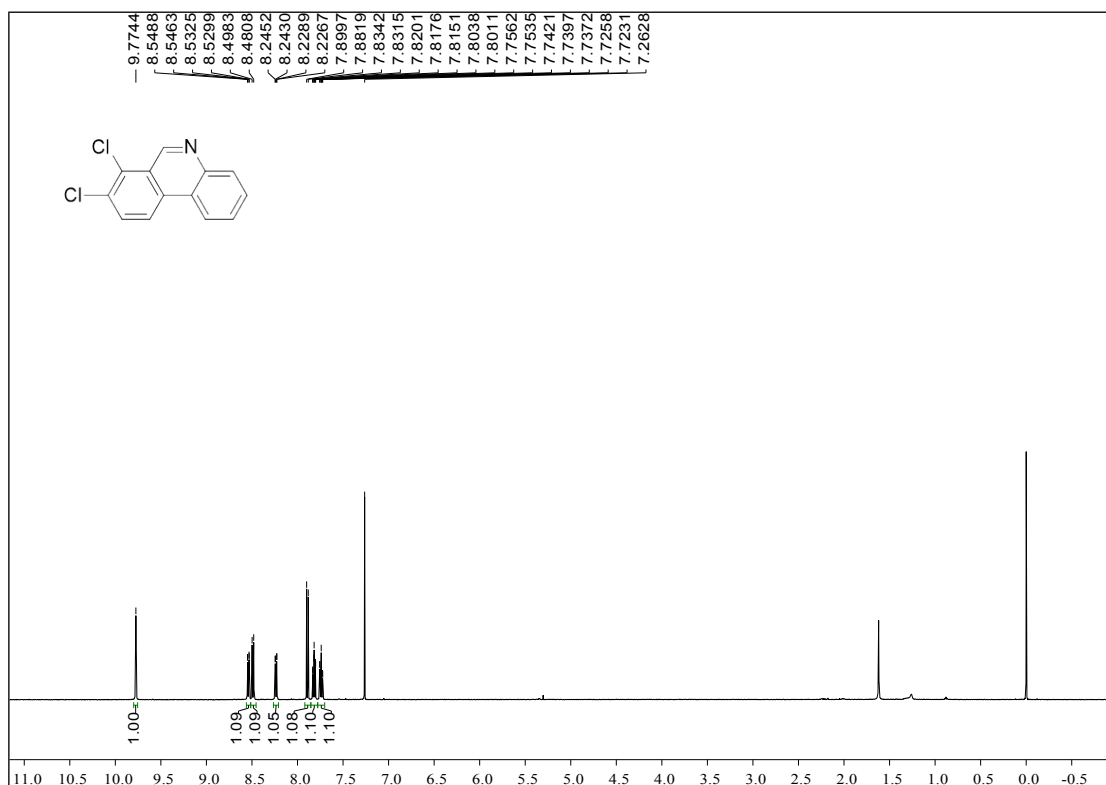
# 7,10-dichlorophenanthridine (30a)



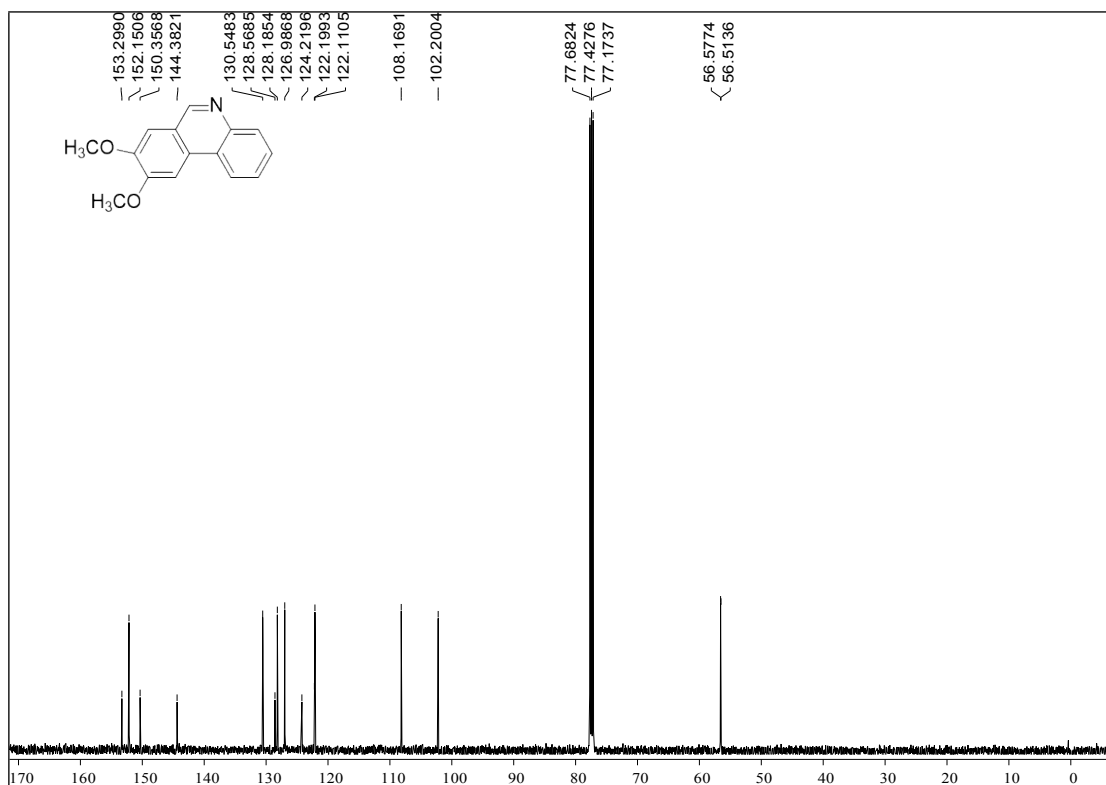
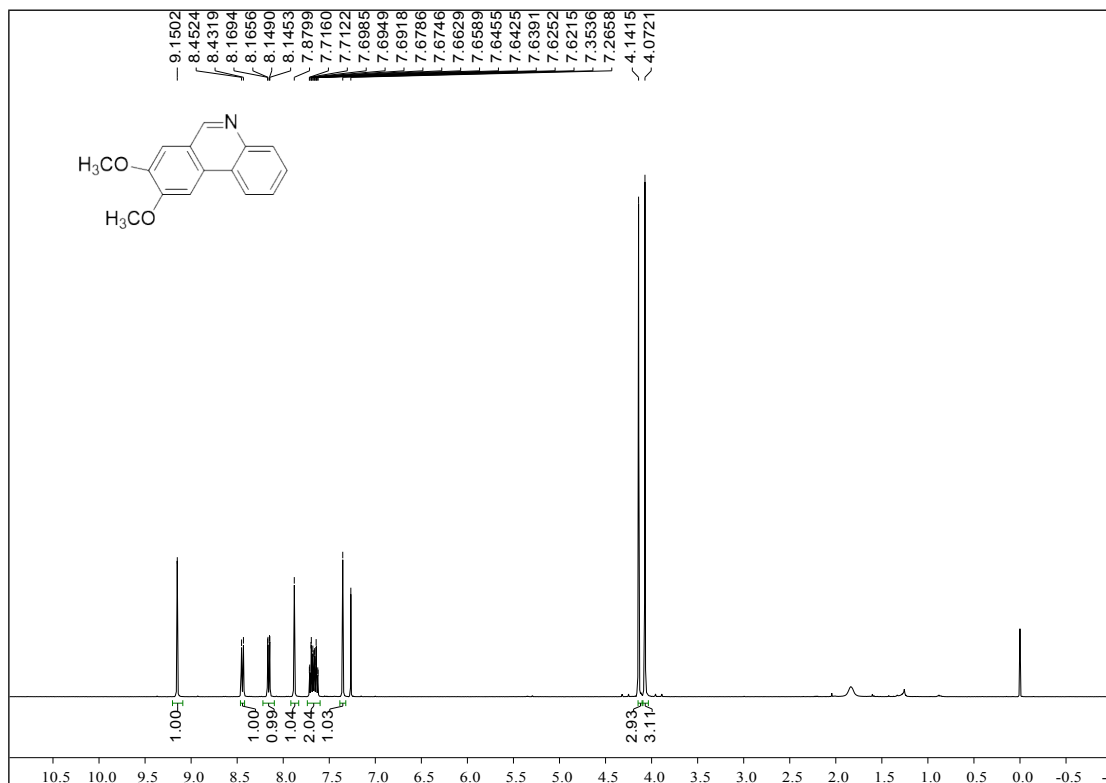
# 7,9-dichlorophenanthridine (3pa)



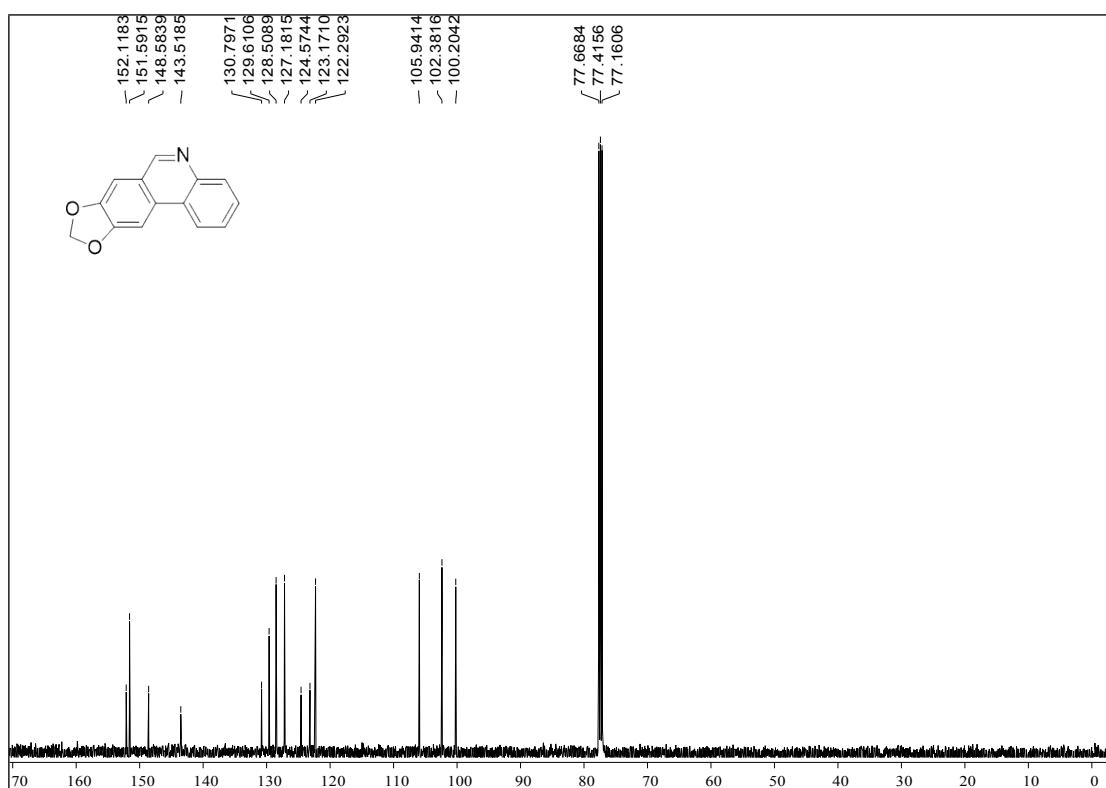
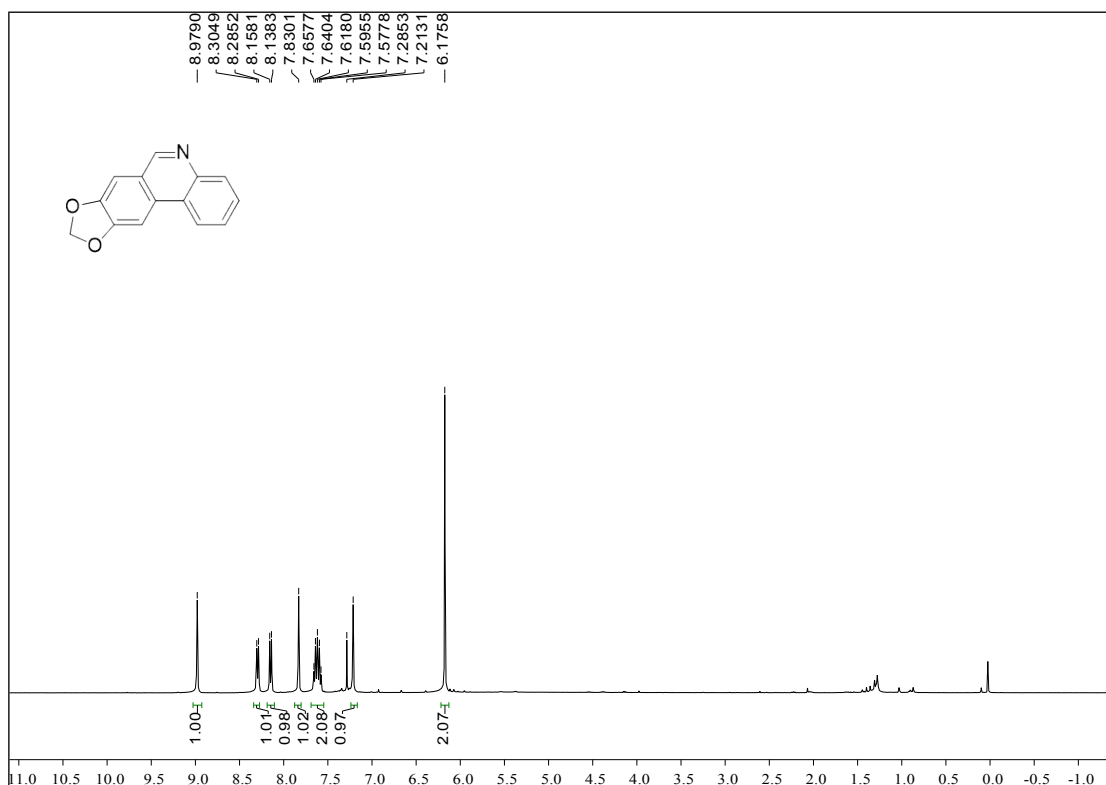
# 7,8-dichlorophenanthridine (3qa)



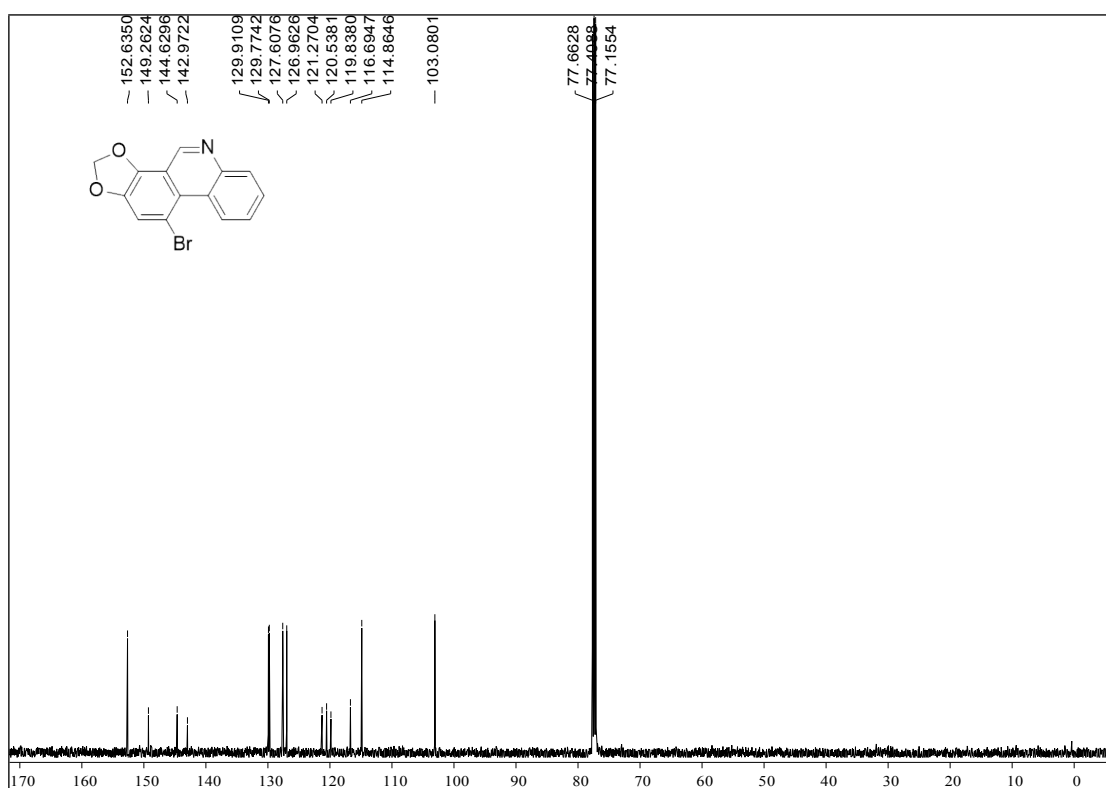
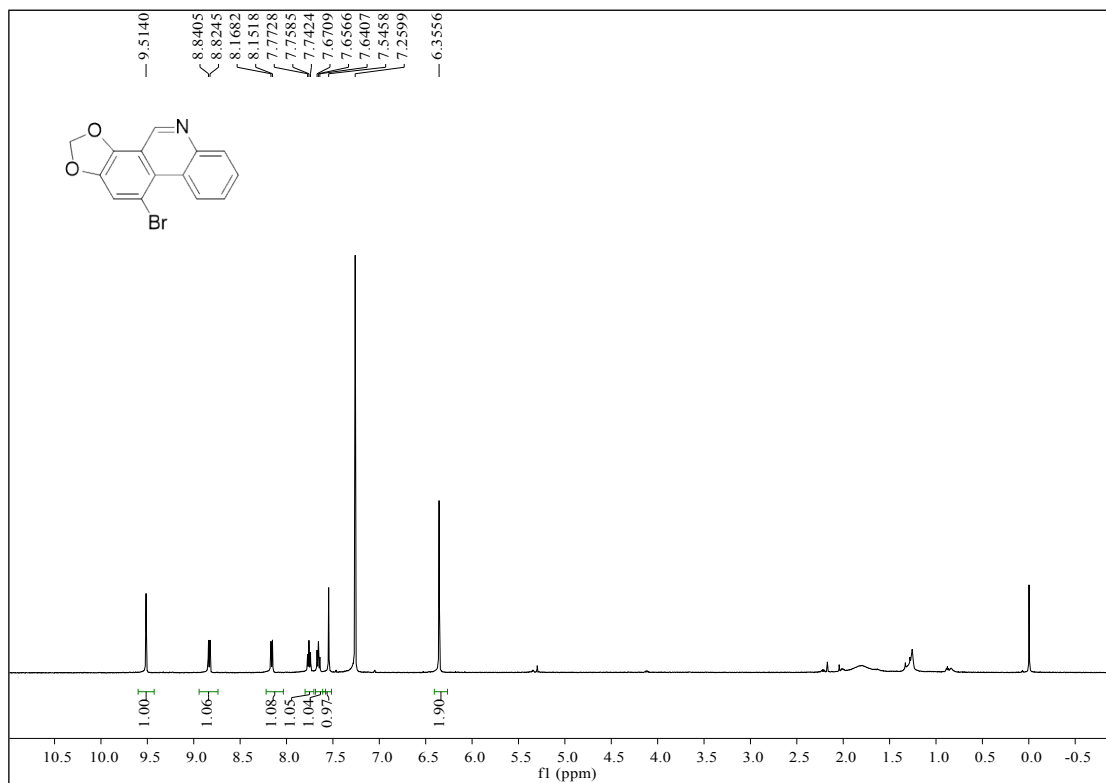
### 8,9-dimethoxyphenanthridine (3ra)



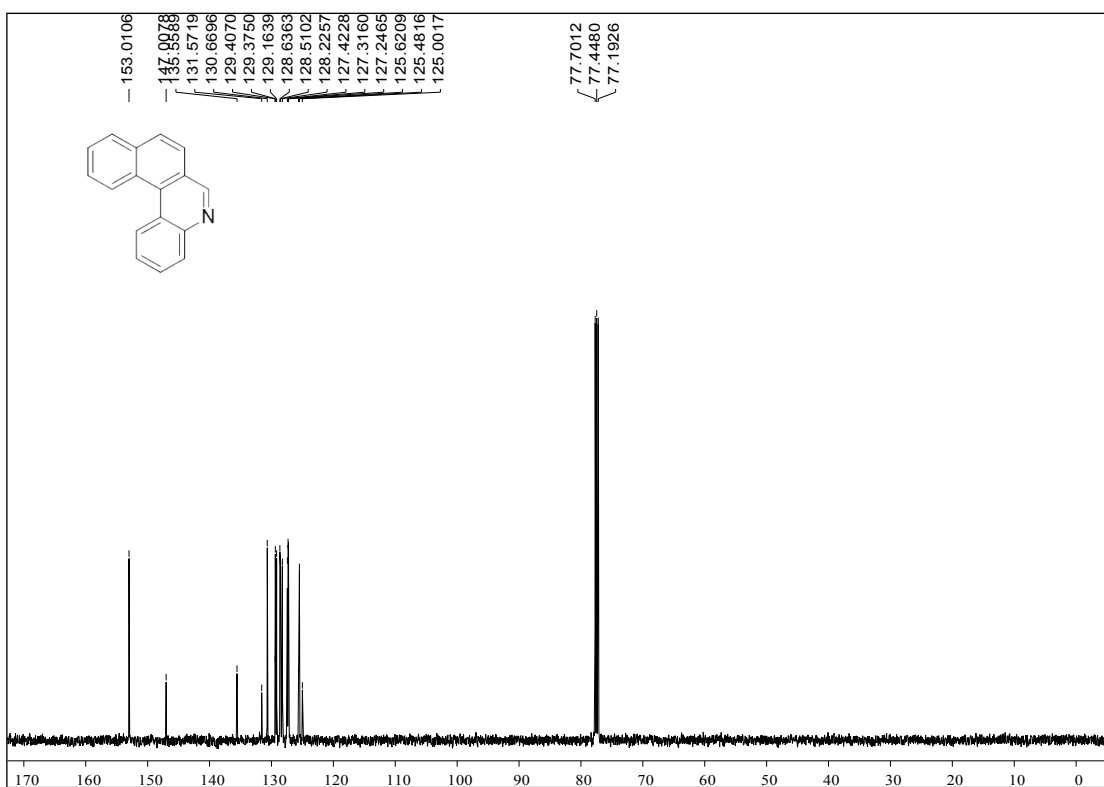
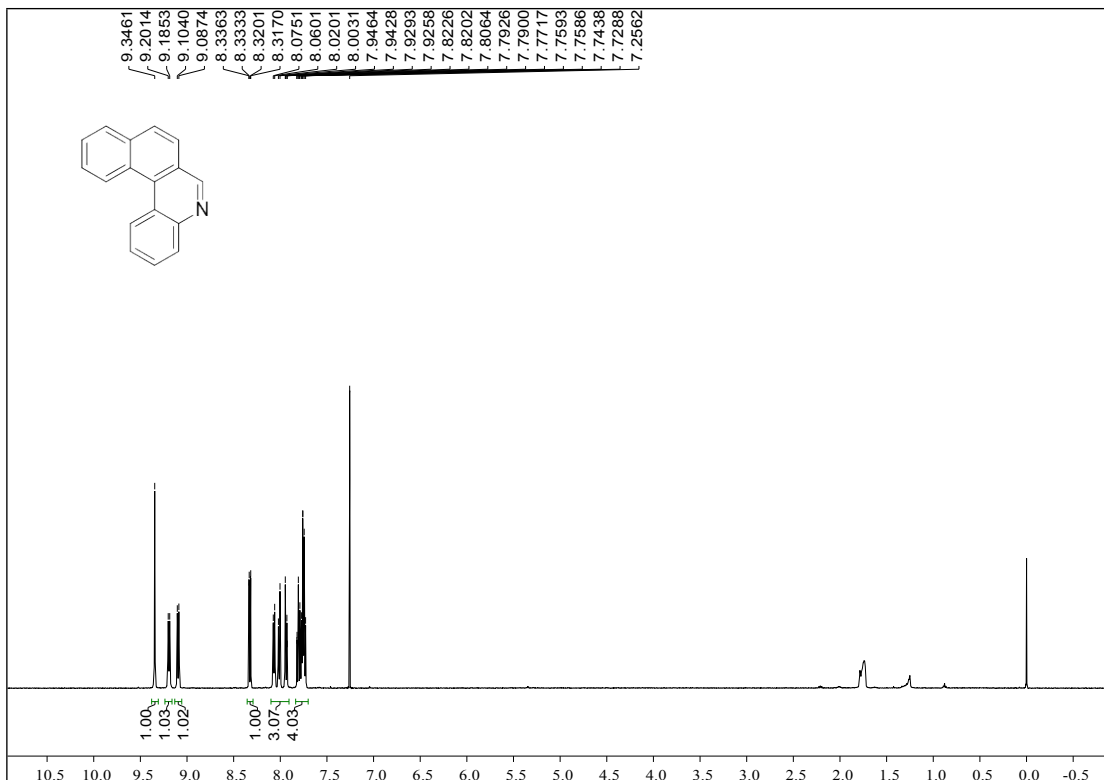
# [1,3]dioxolo[4,5-j]phenanthridine (3sa)



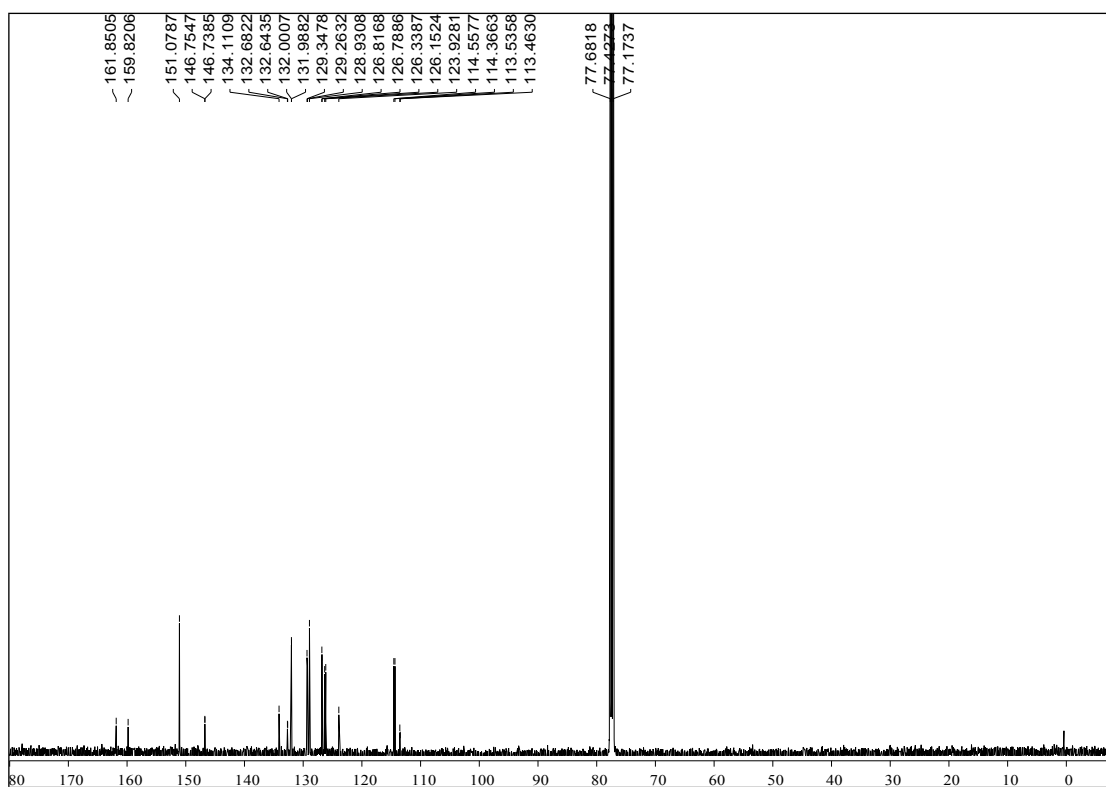
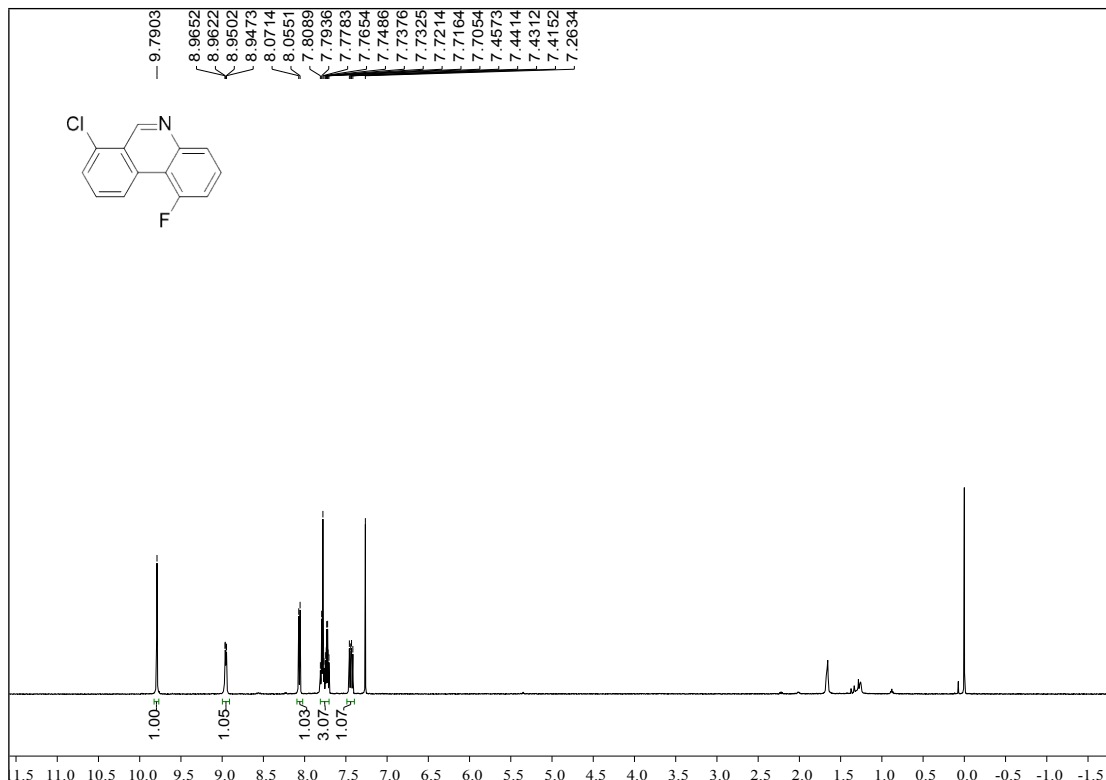
### 10-bromo-[1,3]dioxolo[4,5-i]phenanthridine (3ta)



# benzo[k]phenanthridine (3ua)

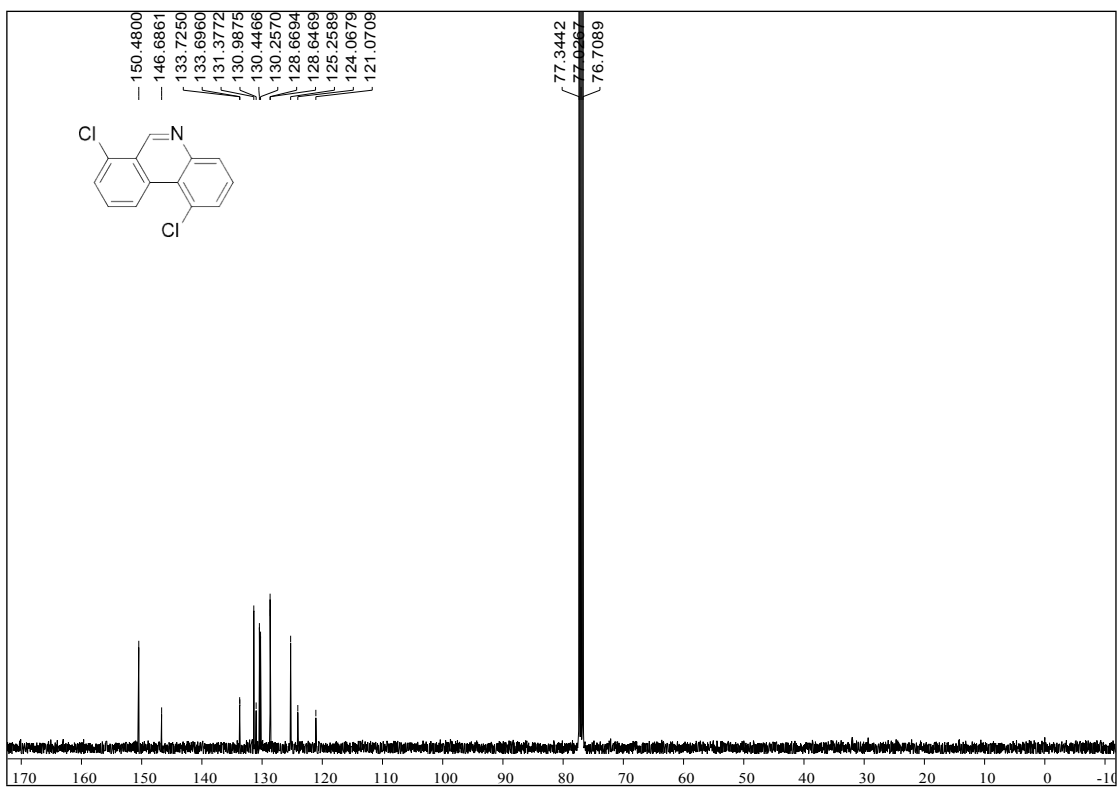
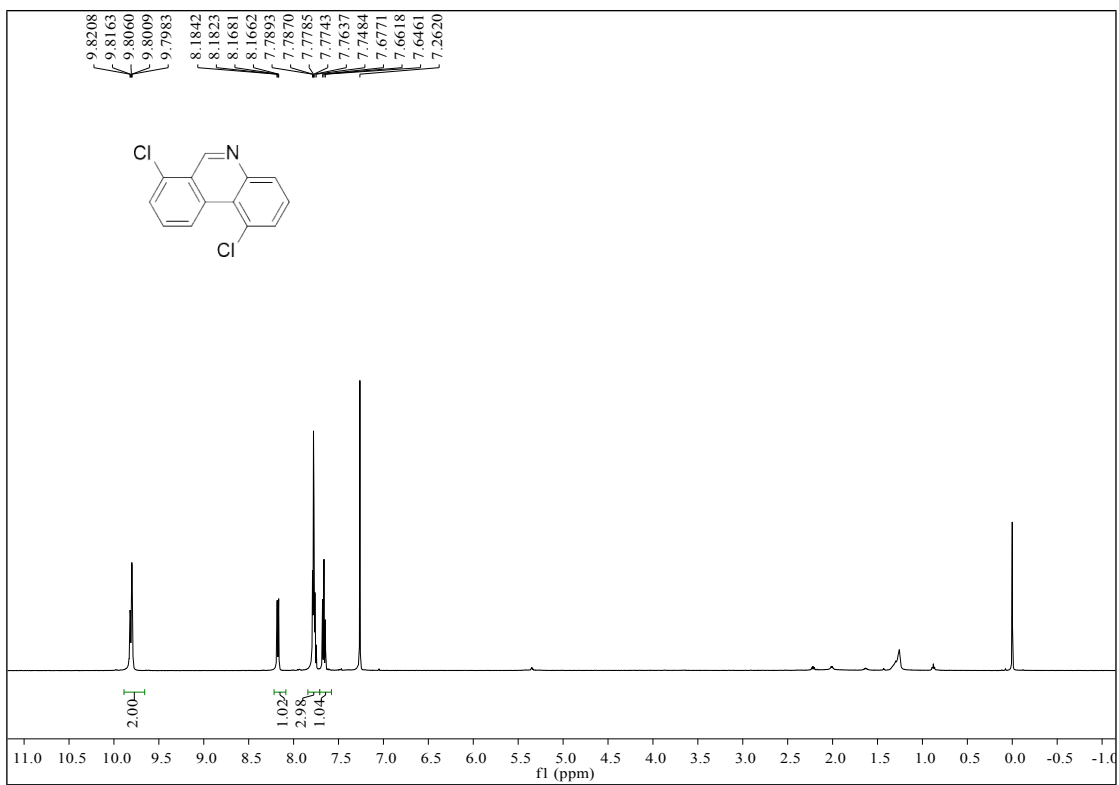


### 7-chloro-1-fluorophenanthridine (3ab)

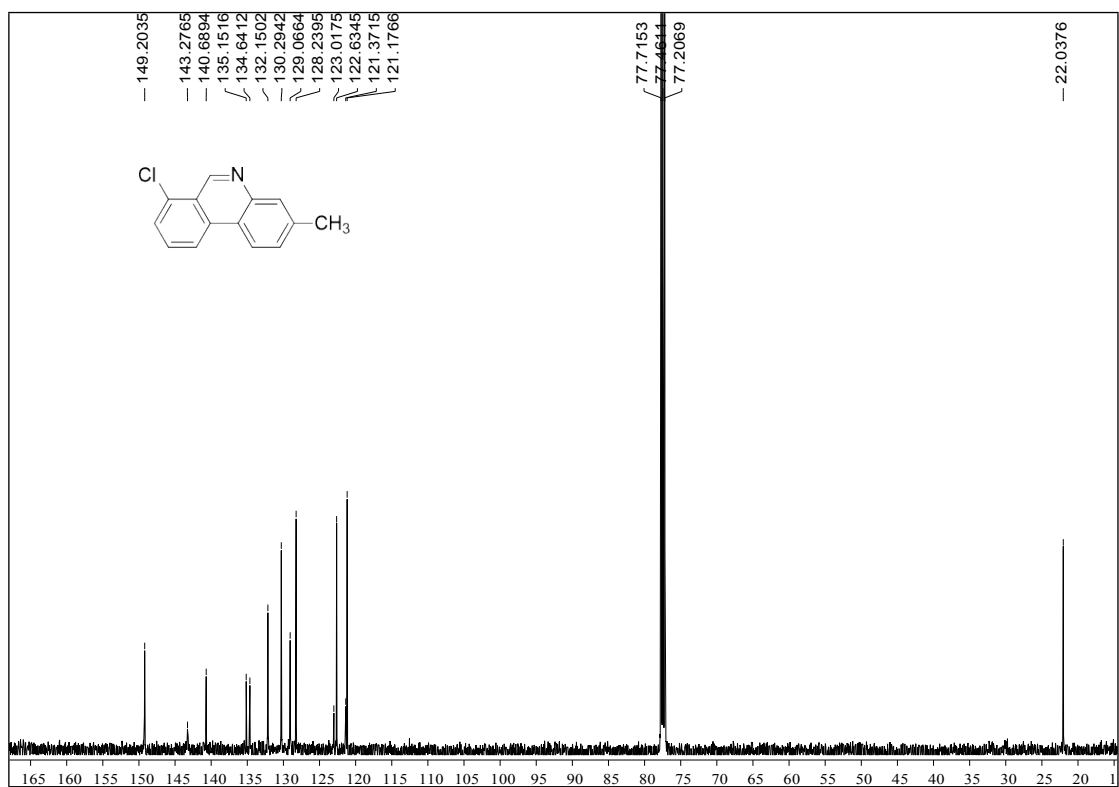
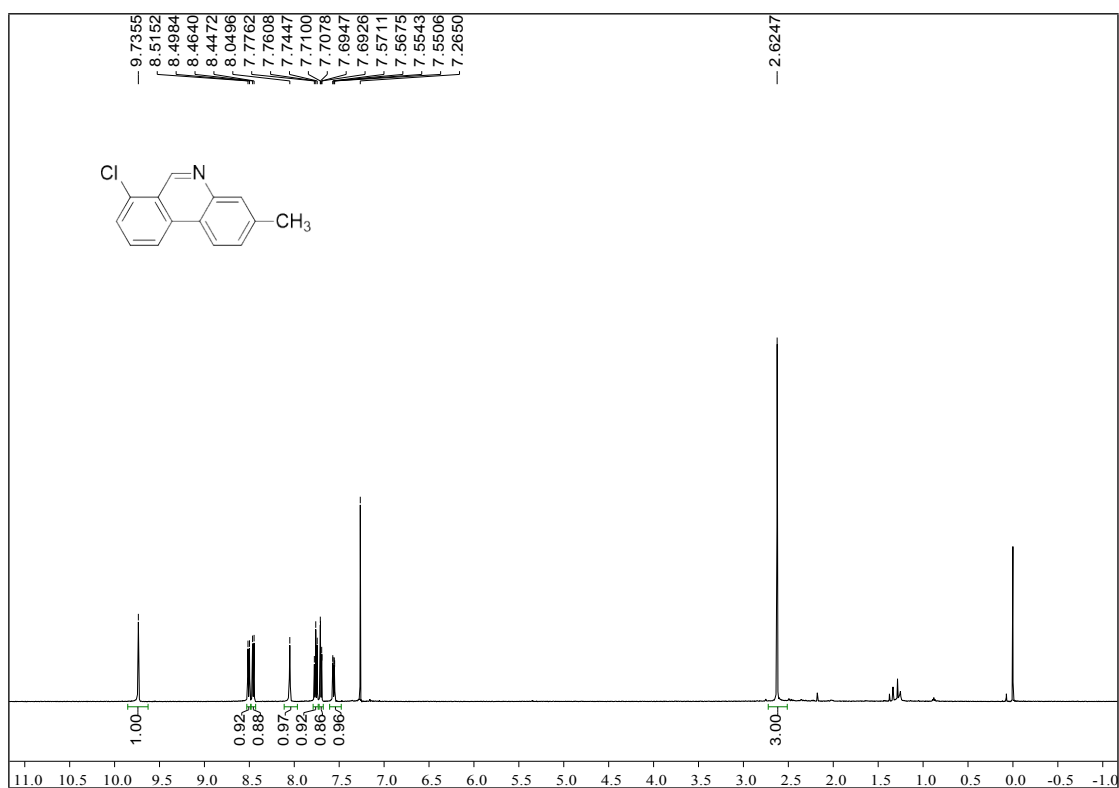




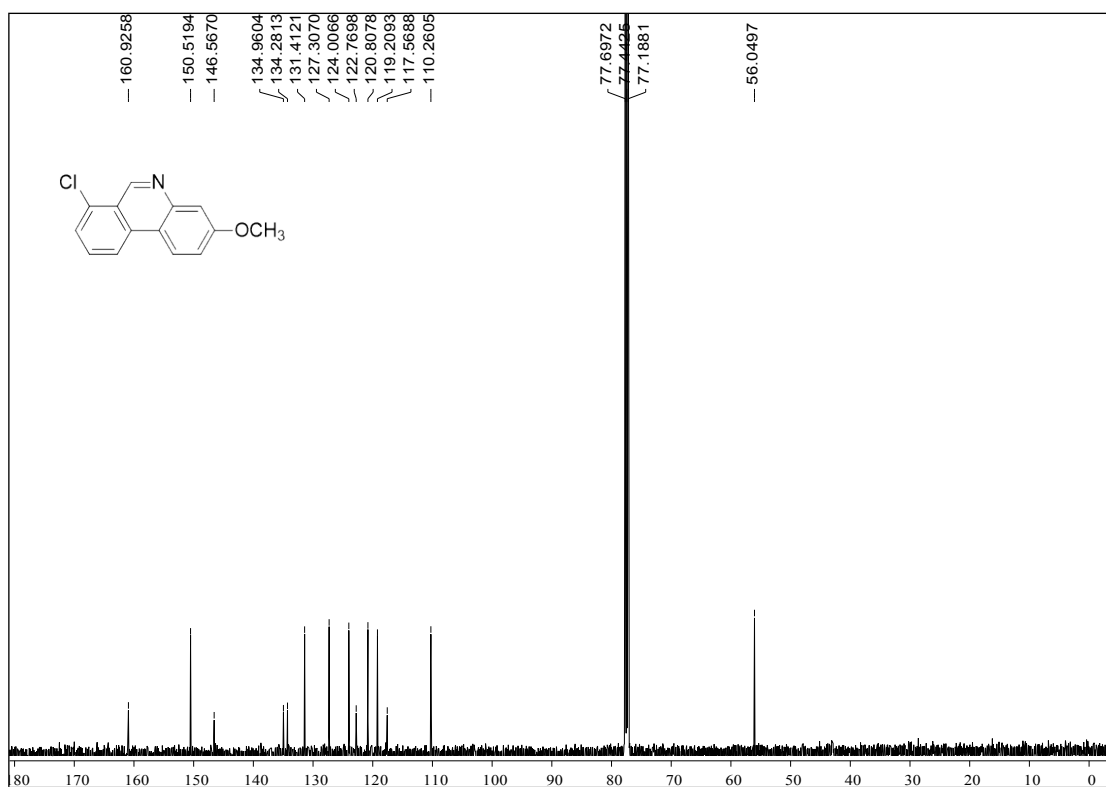
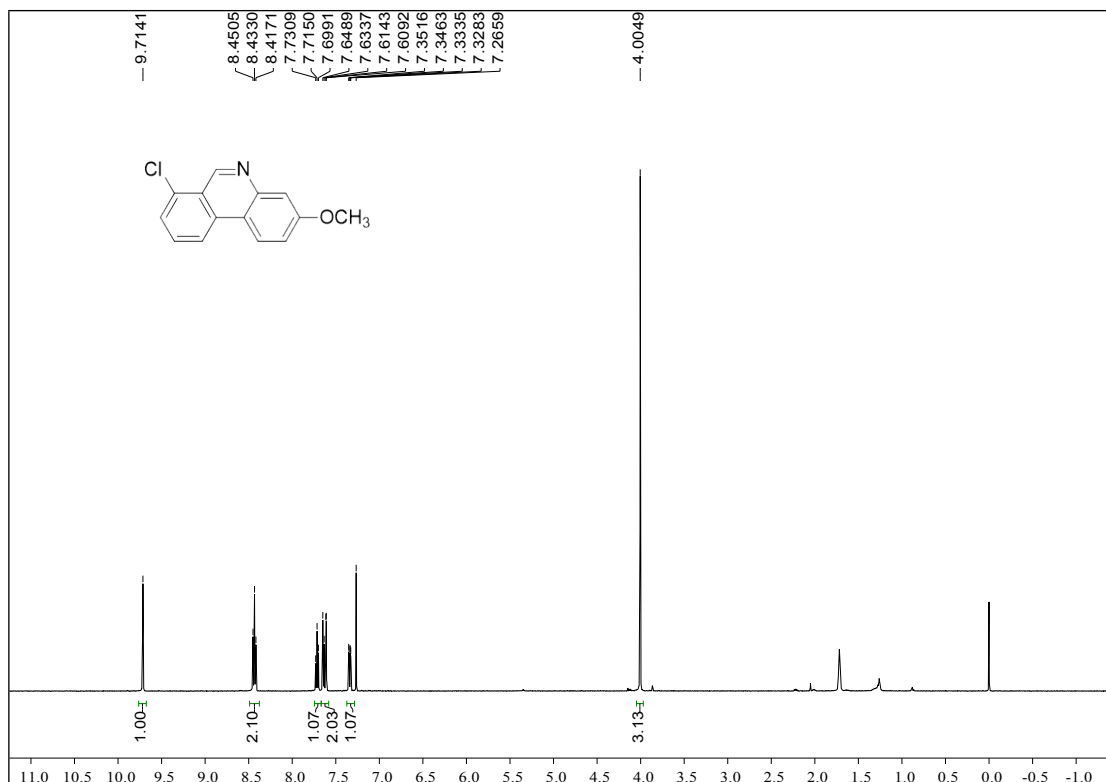
### 1,7-dichlorophenanthridine (3ac)



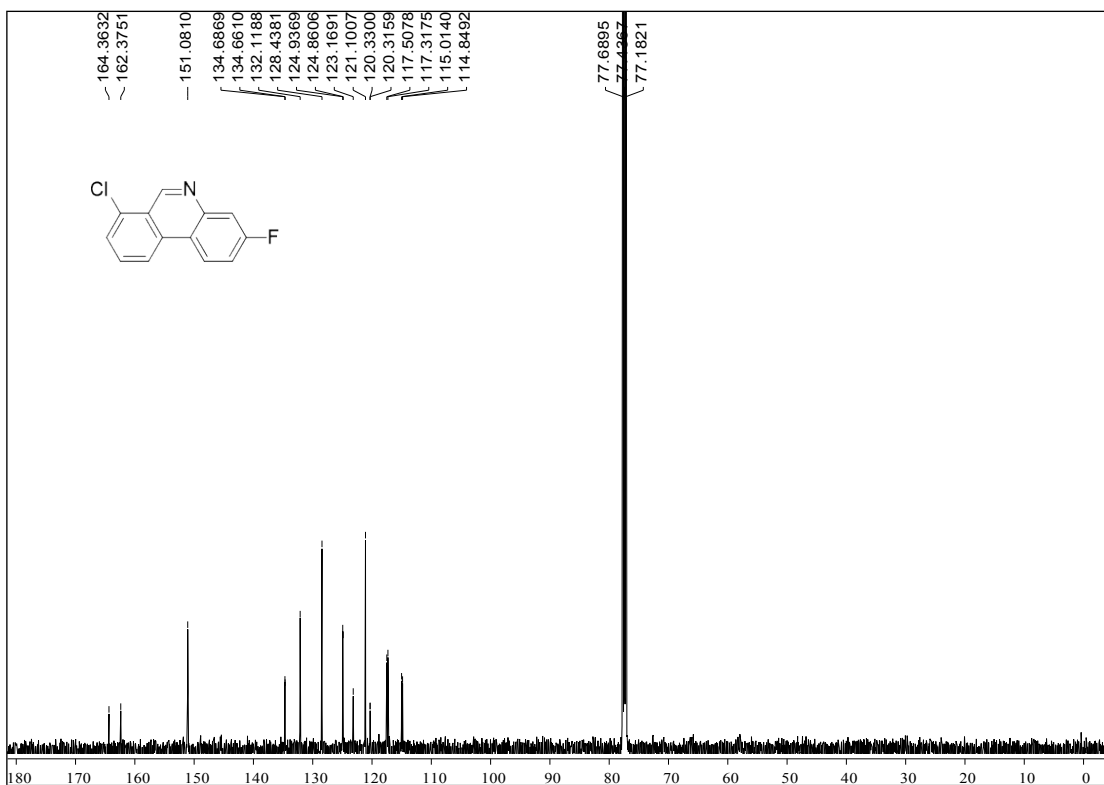
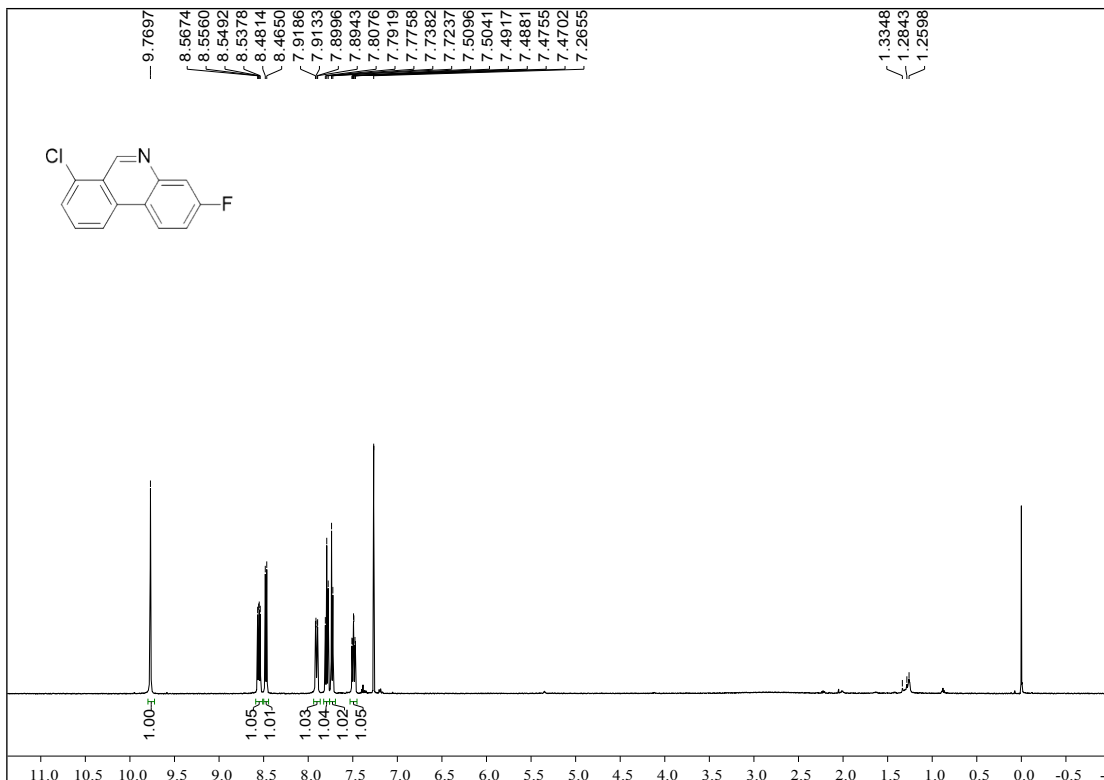
### 7-chloro-3-methylphenanthridine (3ad)



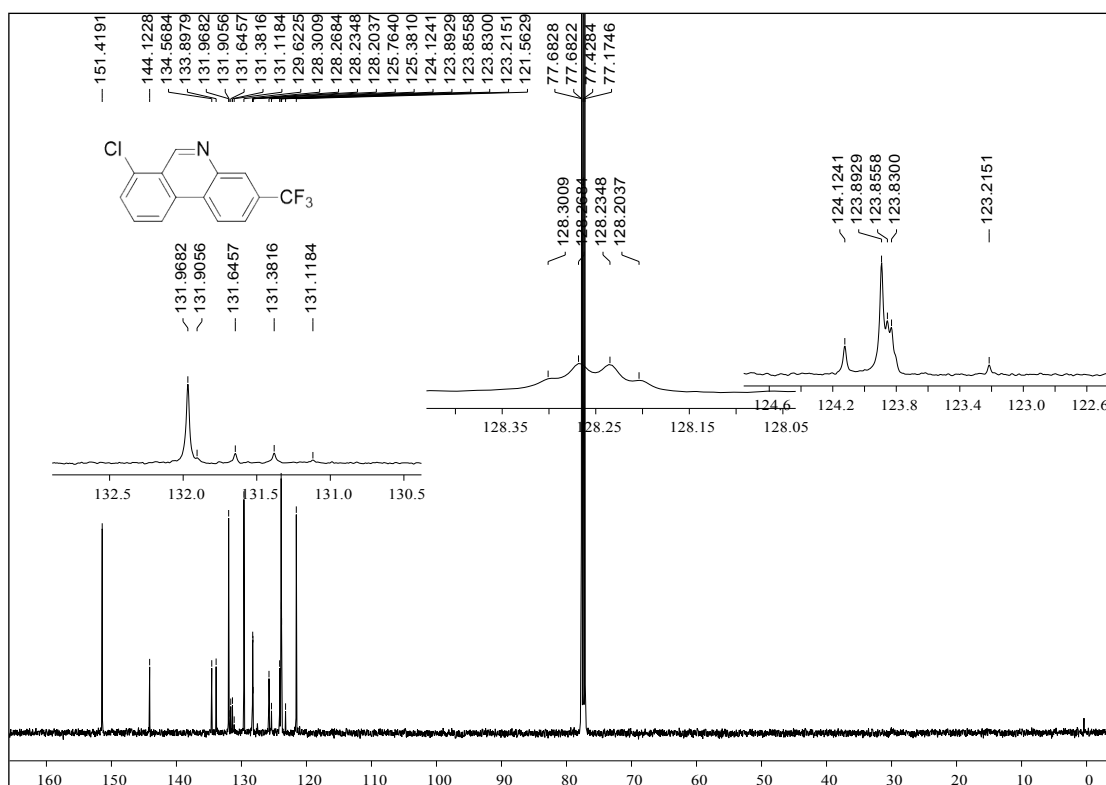
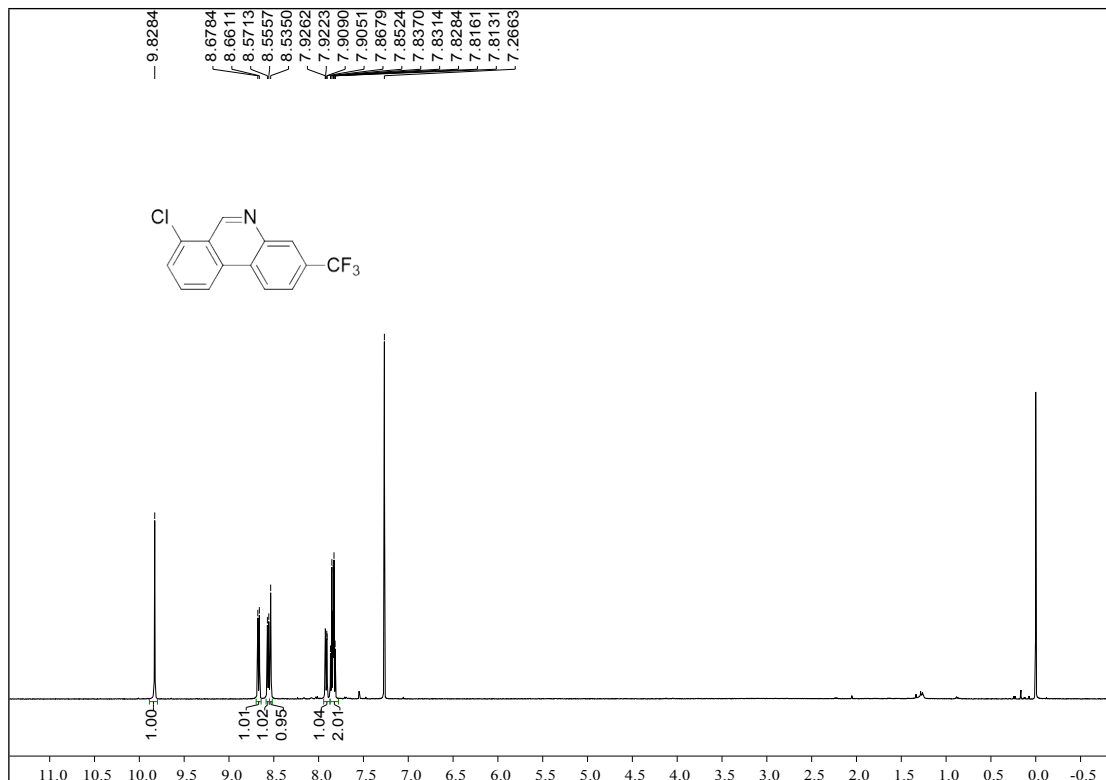
### 7-chloro-3-methoxyphenanthridine (3ae)



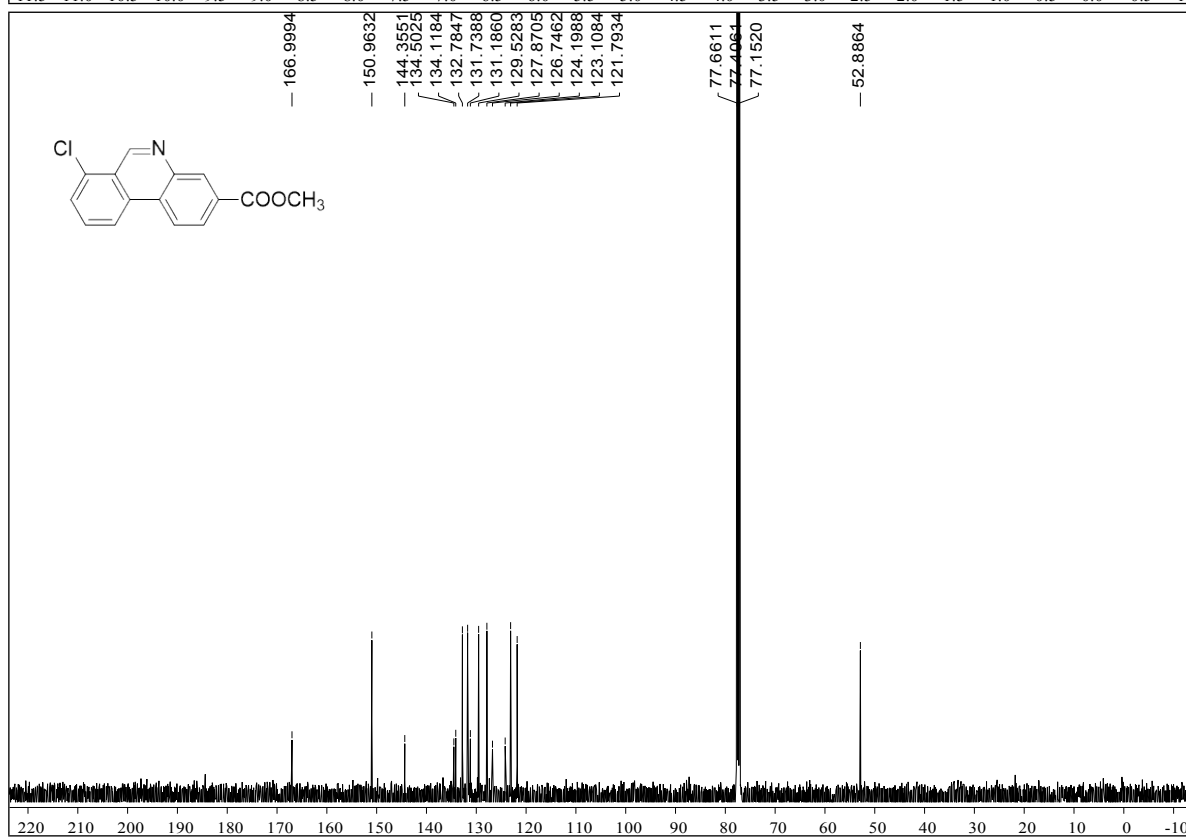
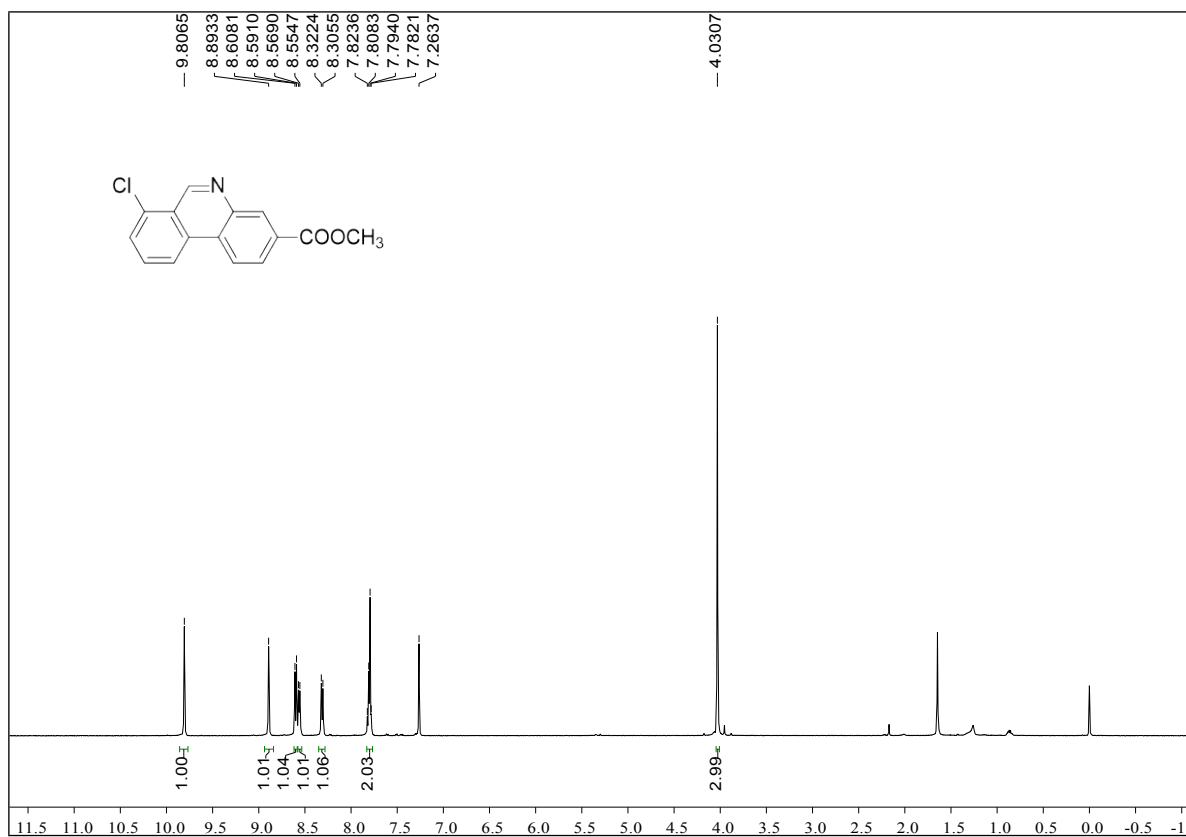
### 7-chloro-3-fluorophenanthridine (3af)



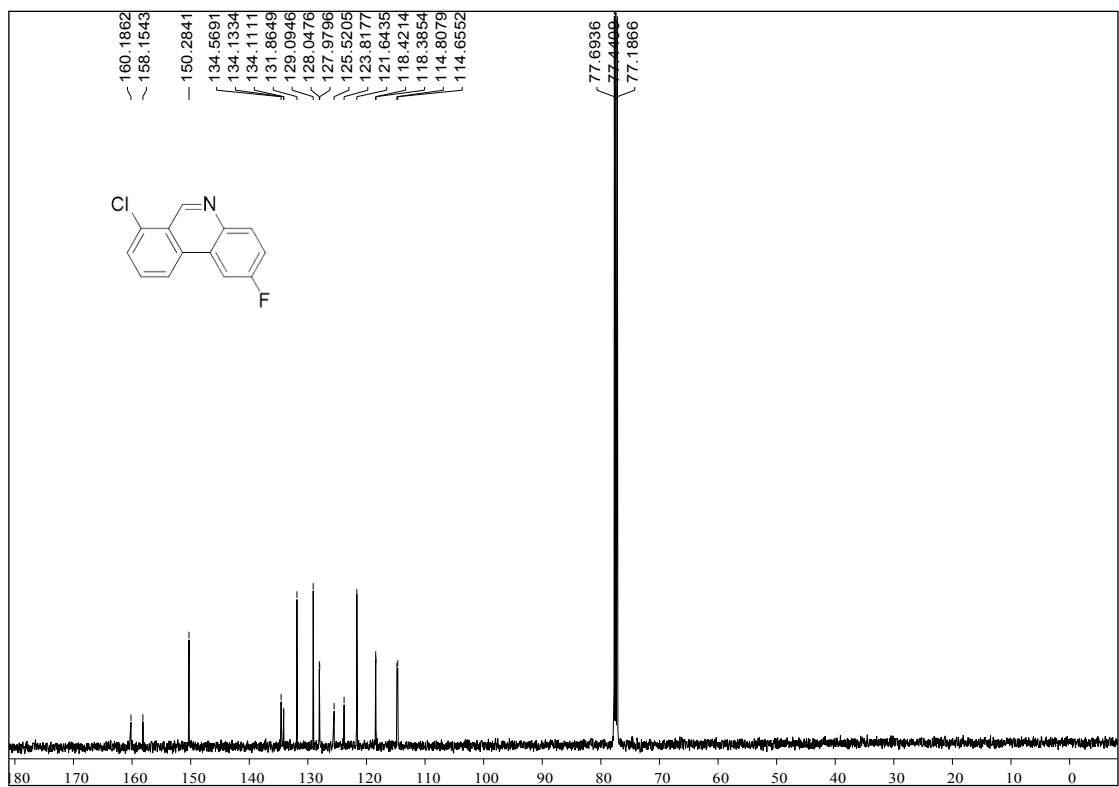
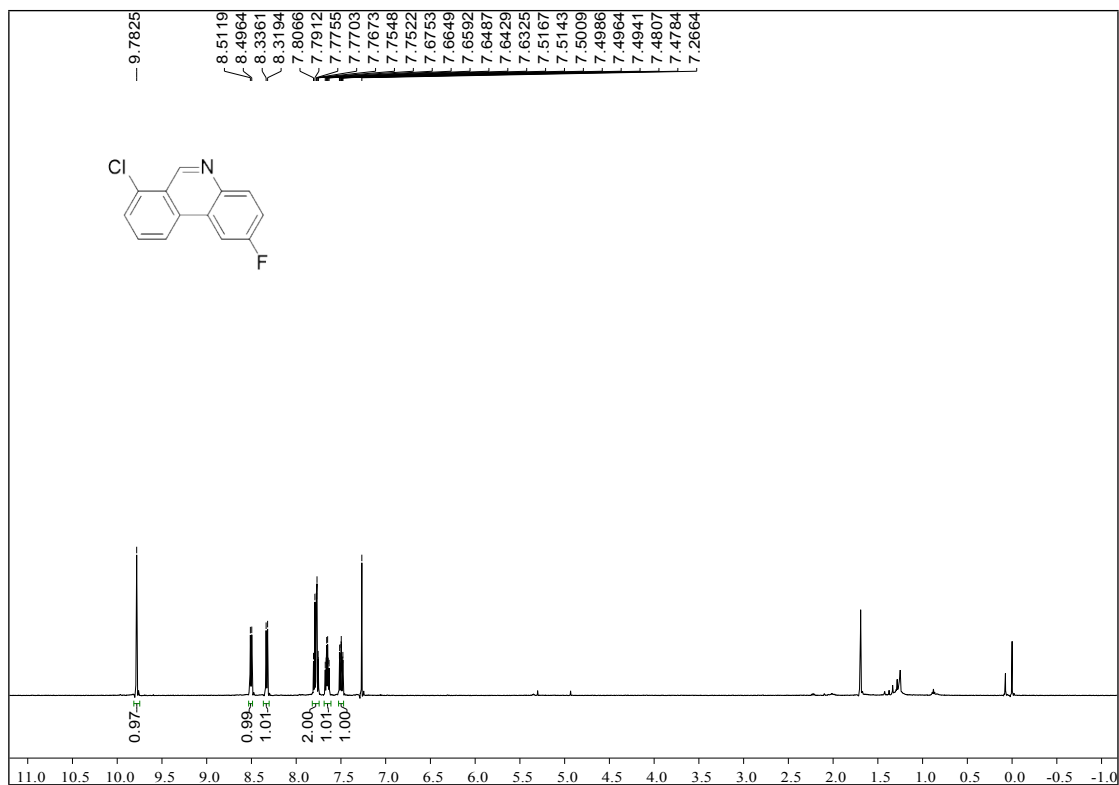
**7-chloro-3-(trifluoromethyl)phenanthridine (3ag)**



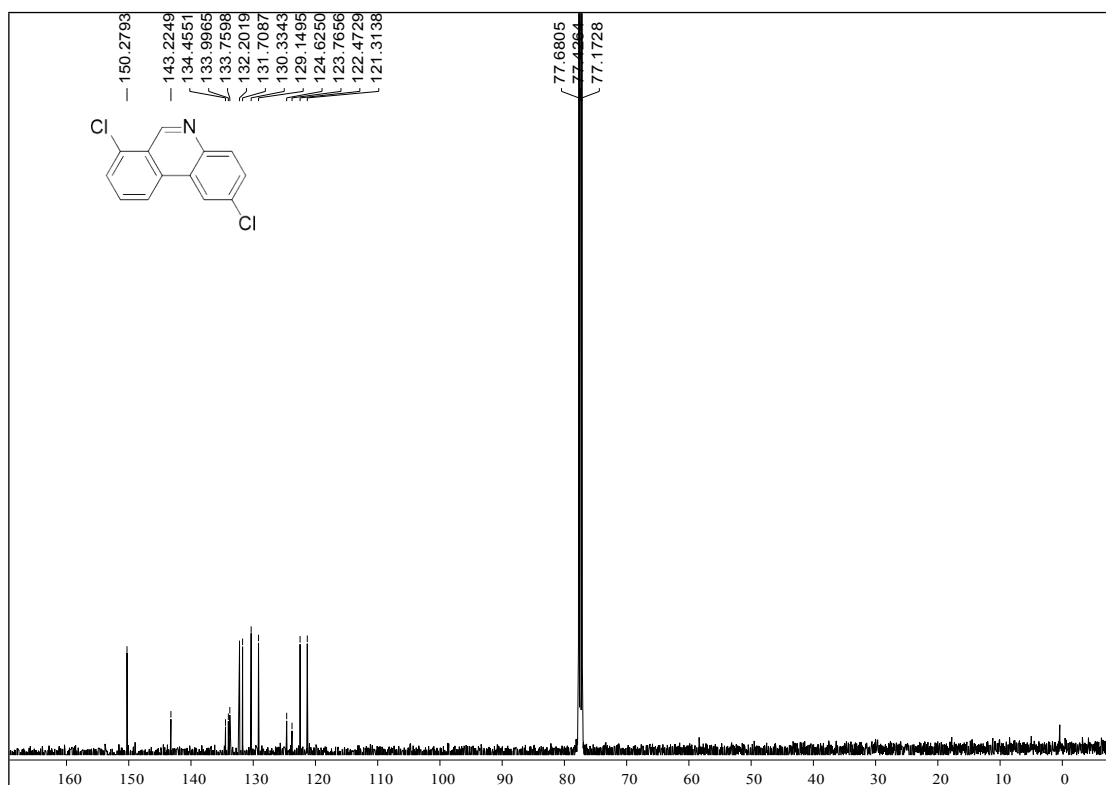
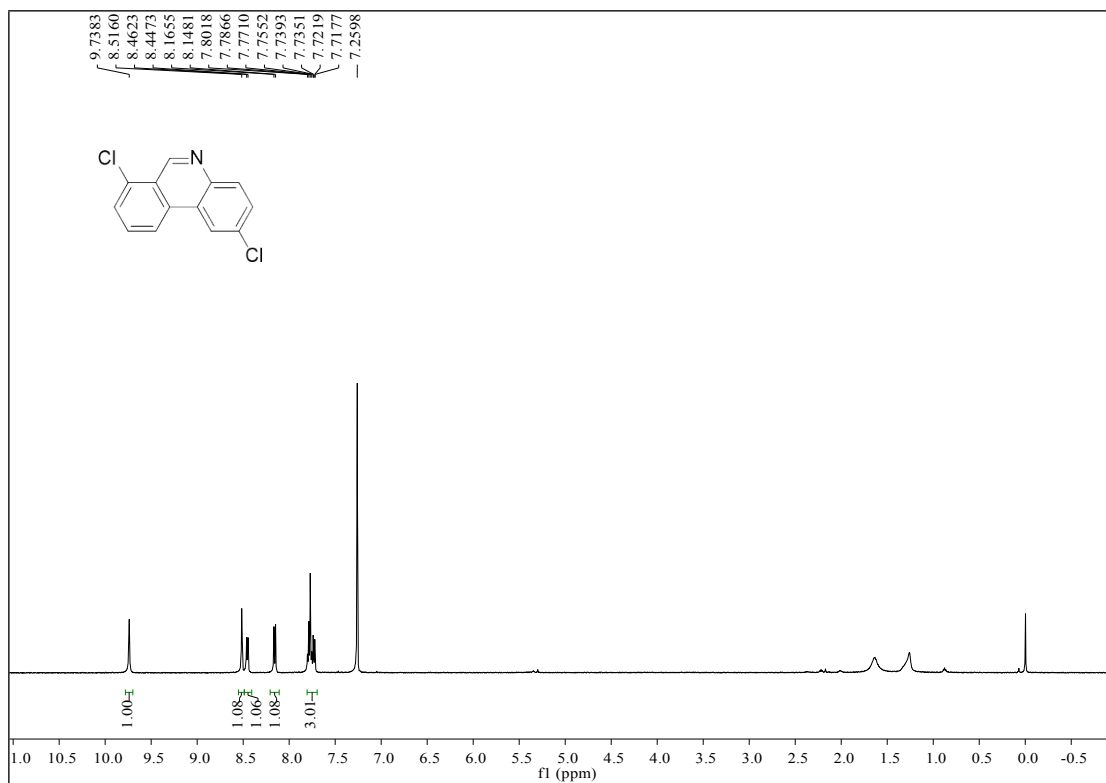
**methyl 7-chlorophenanthridine-3-carboxylate (3ah)**



### 7-chloro-2-fluorophenanthridine (3ai)

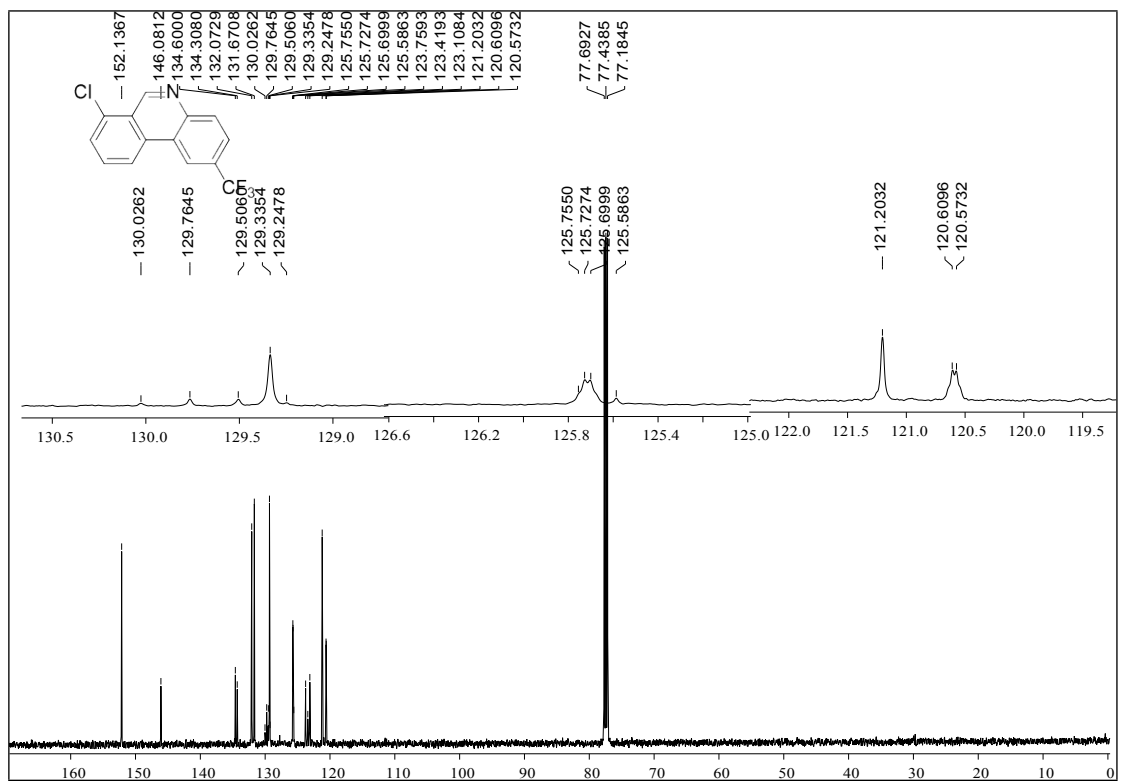
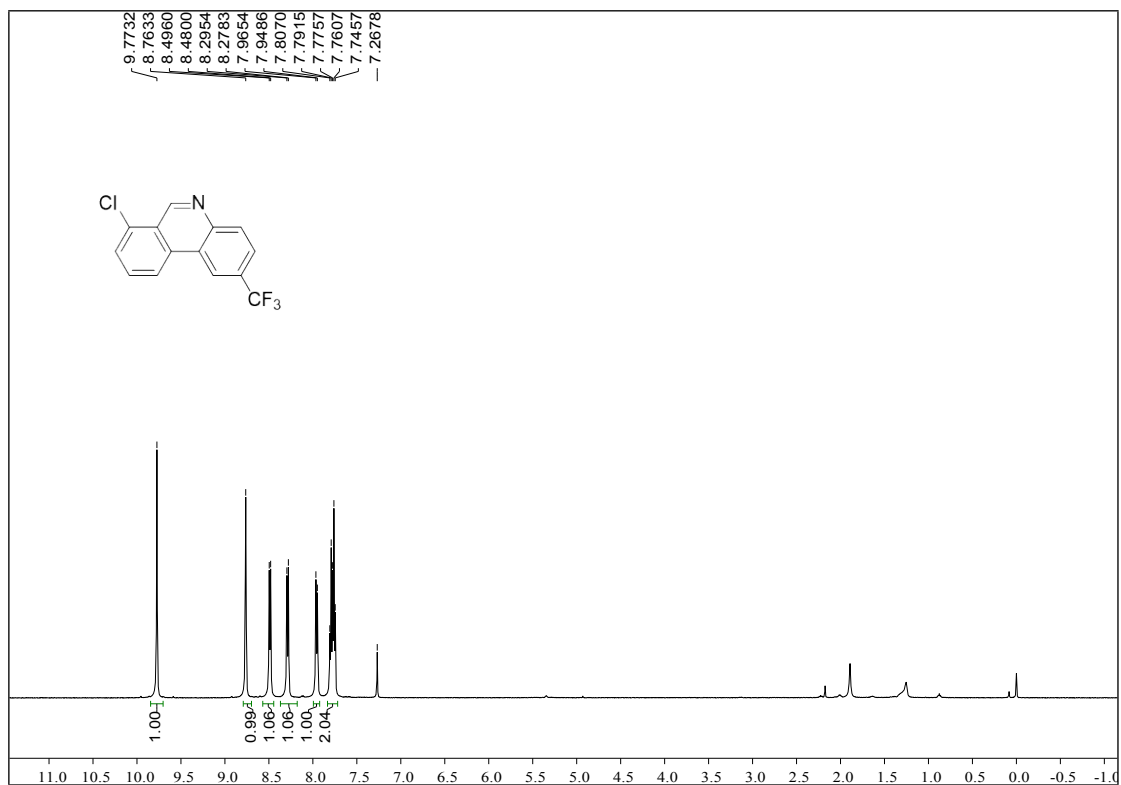


## 2,7-dichlorophenanthridine (3aj)

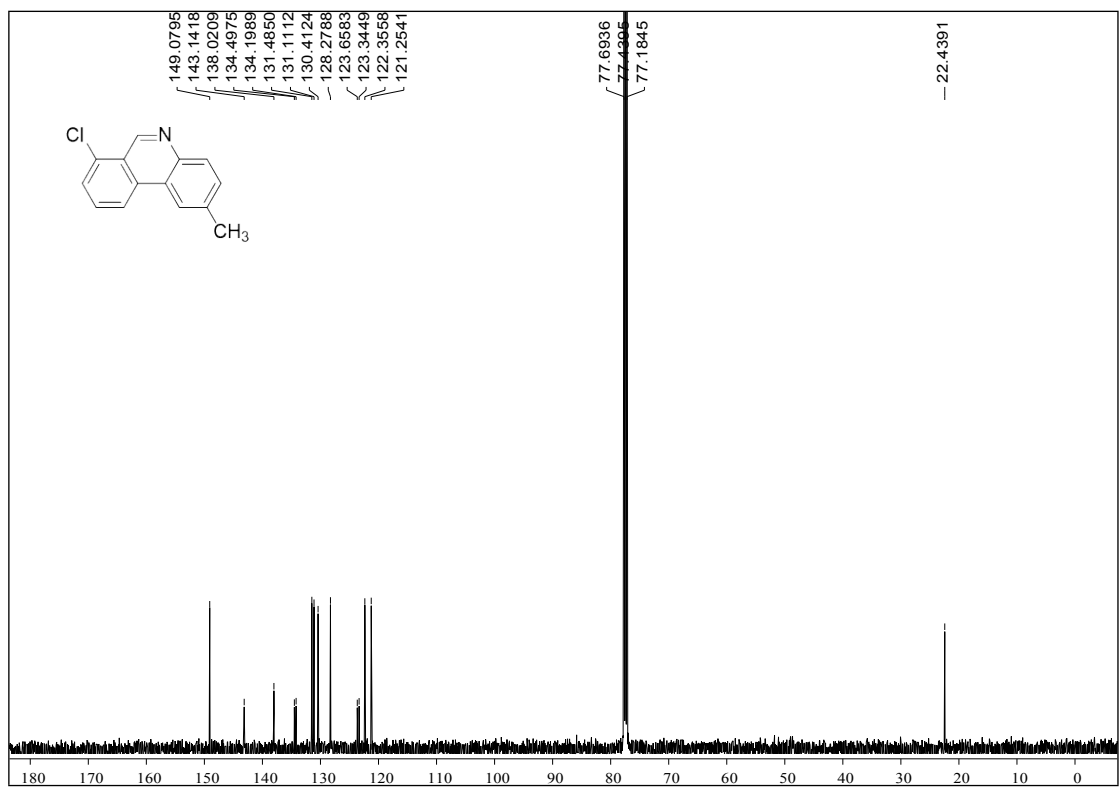
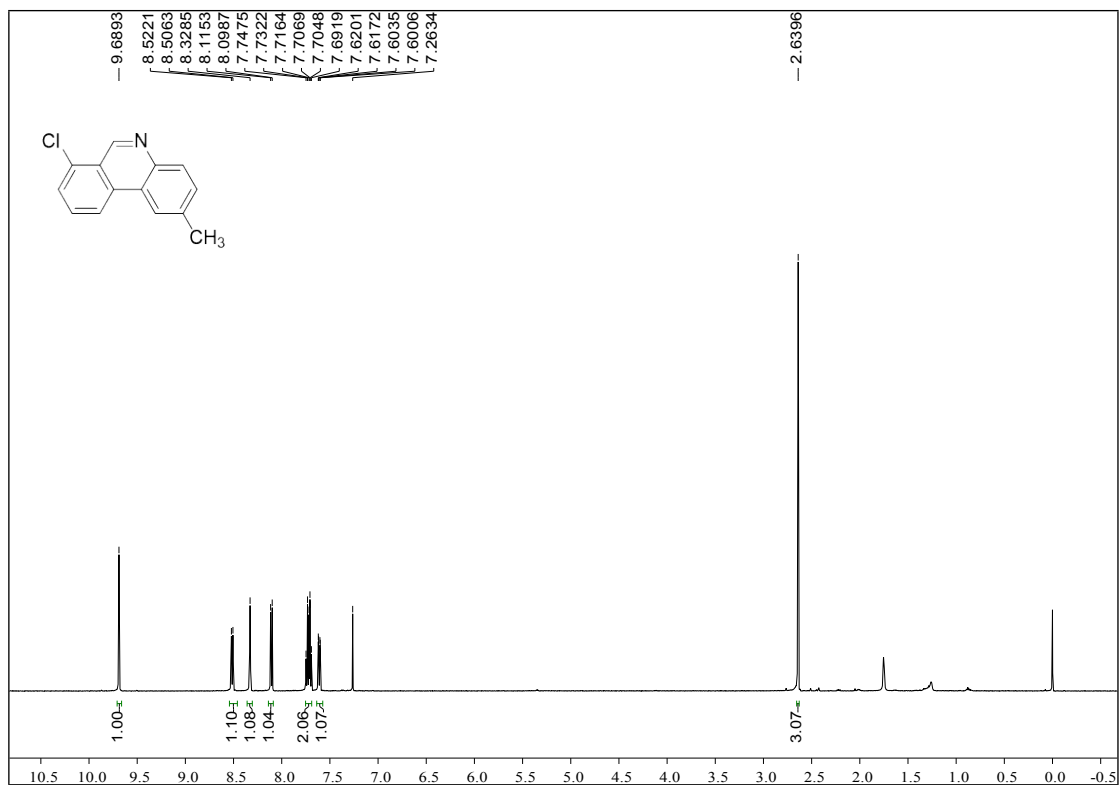




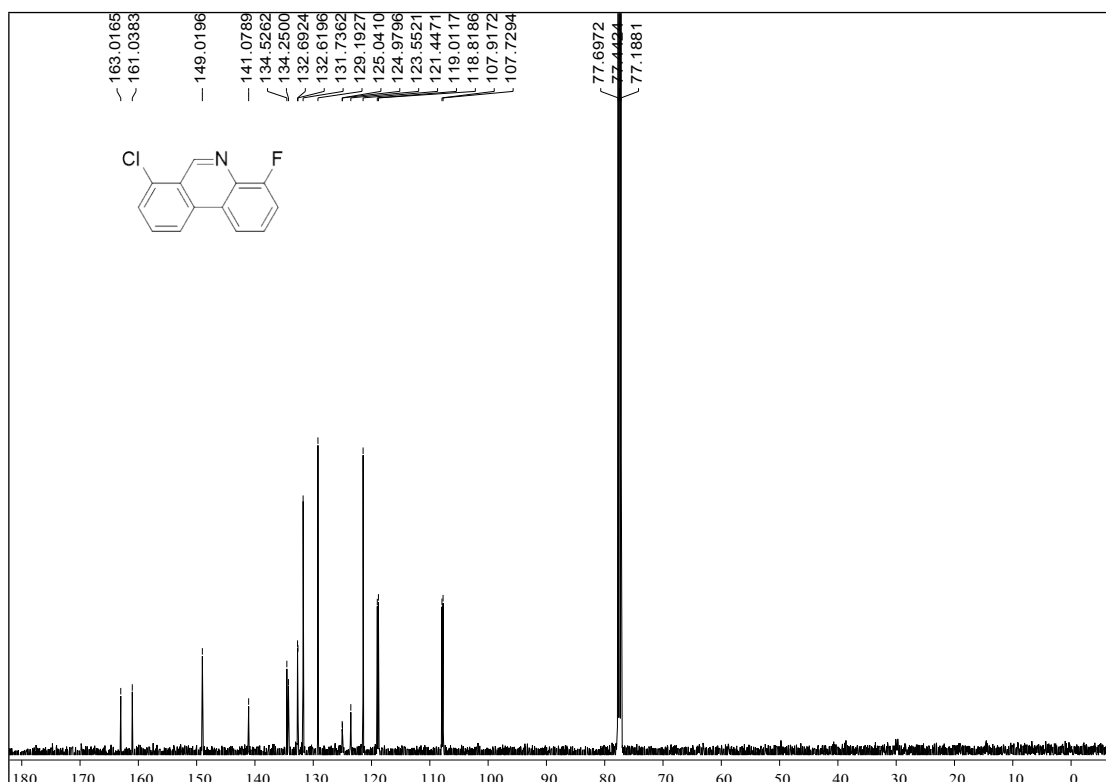
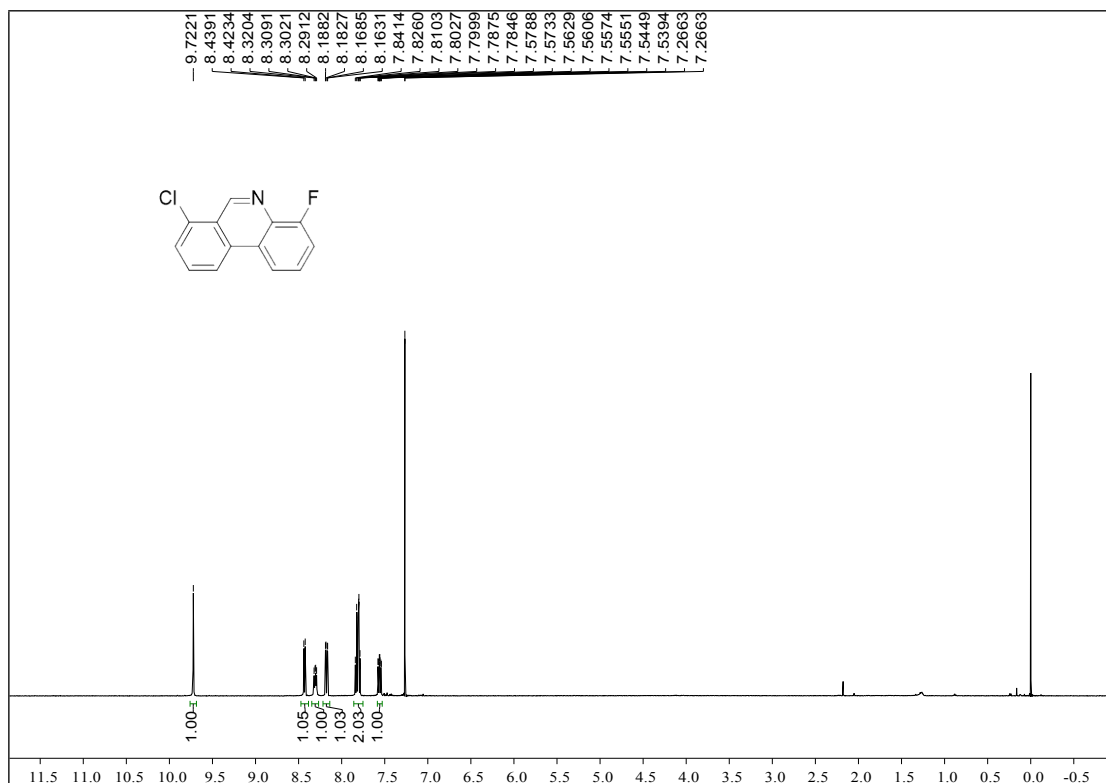
### 7-chloro-2-(trifluoromethyl)phenanthridine (3ak)



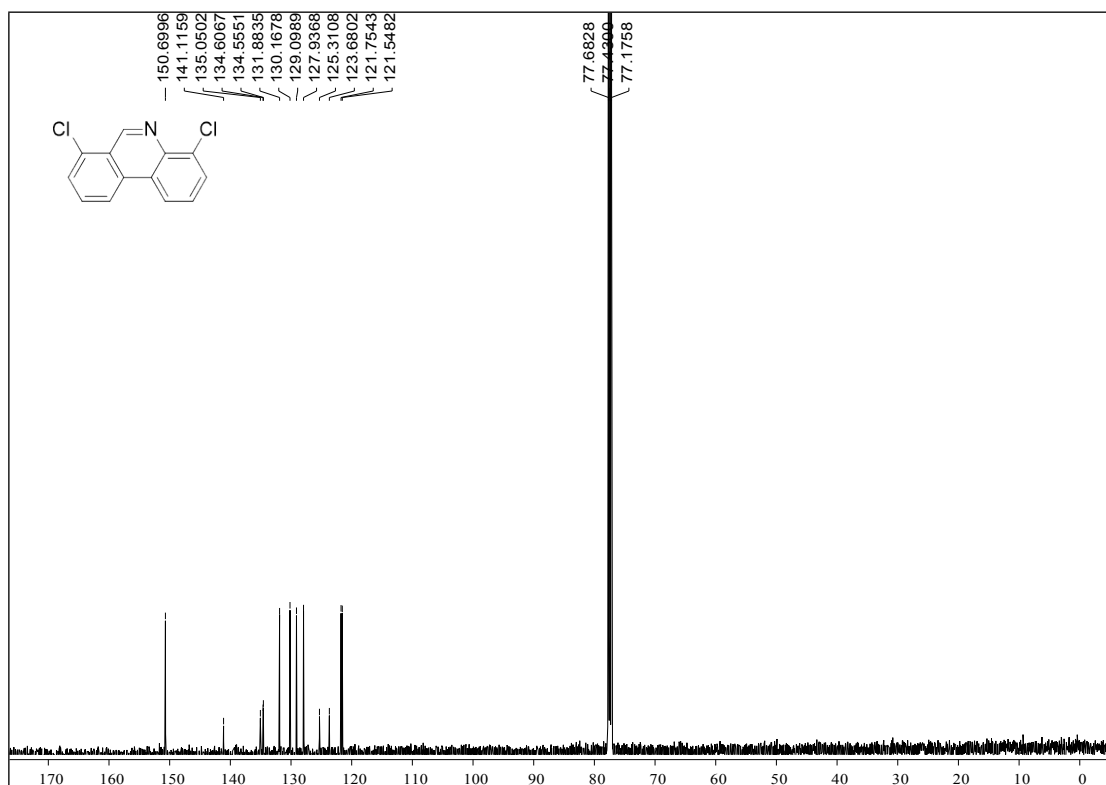
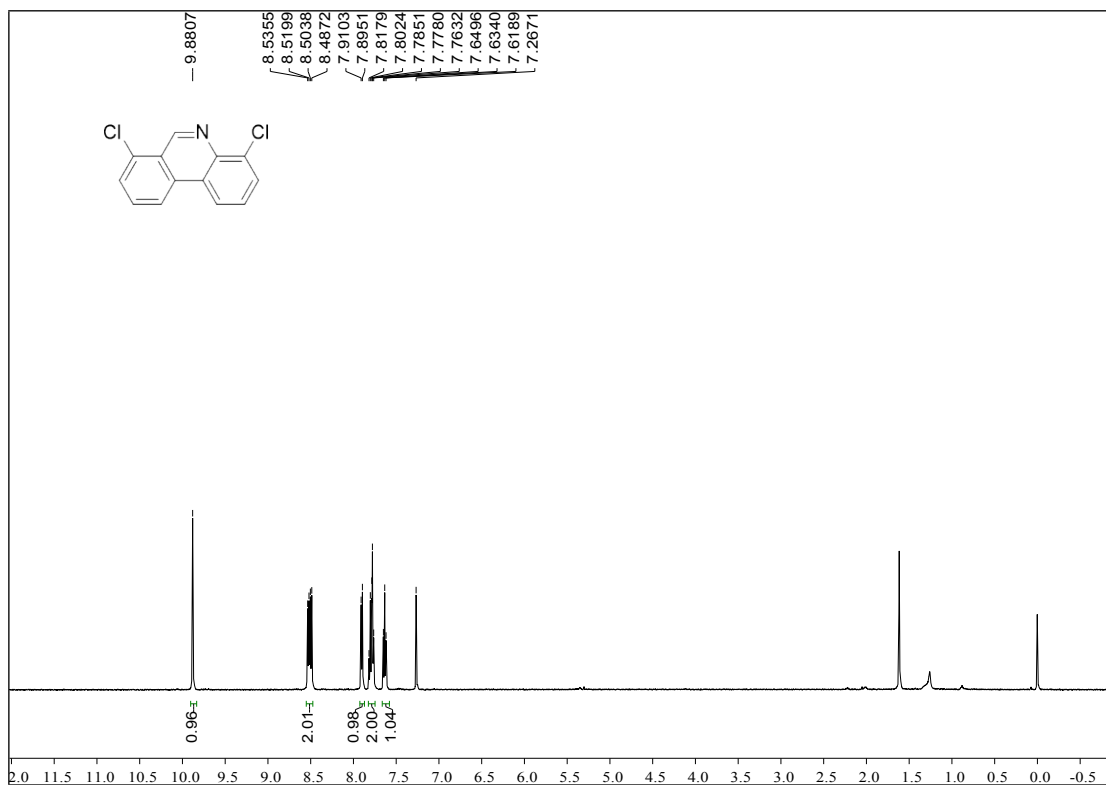
### 7-chloro-2-methylphenanthridine (3a)



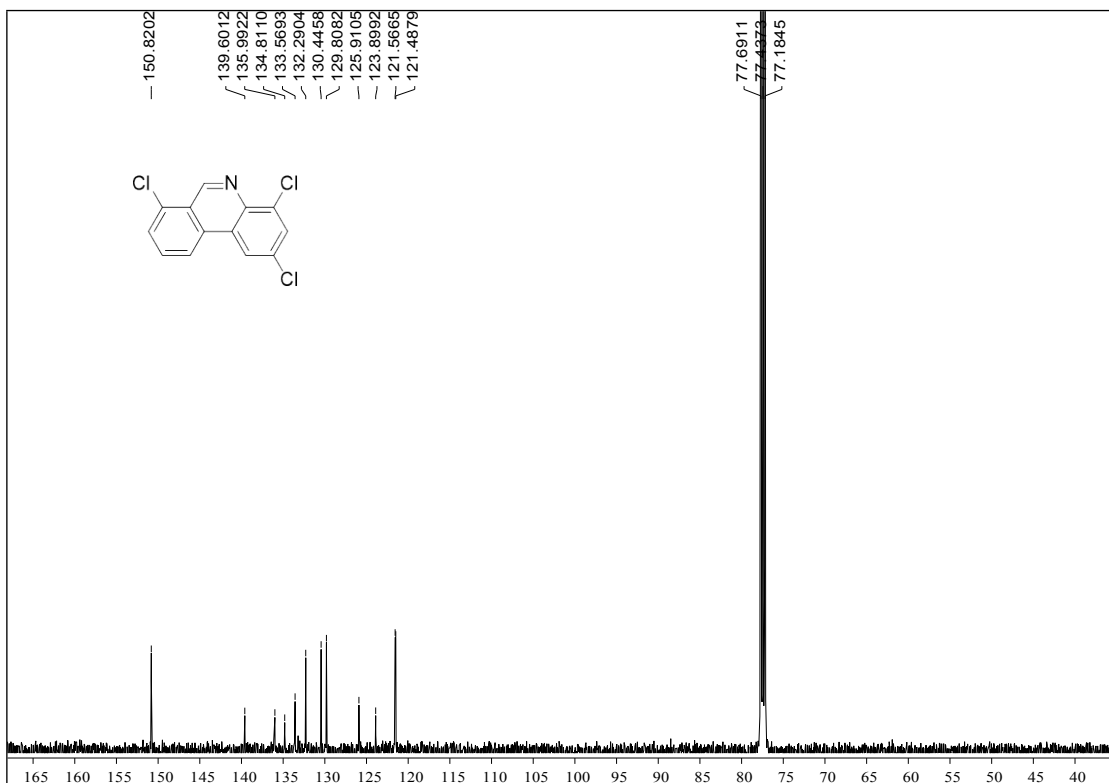
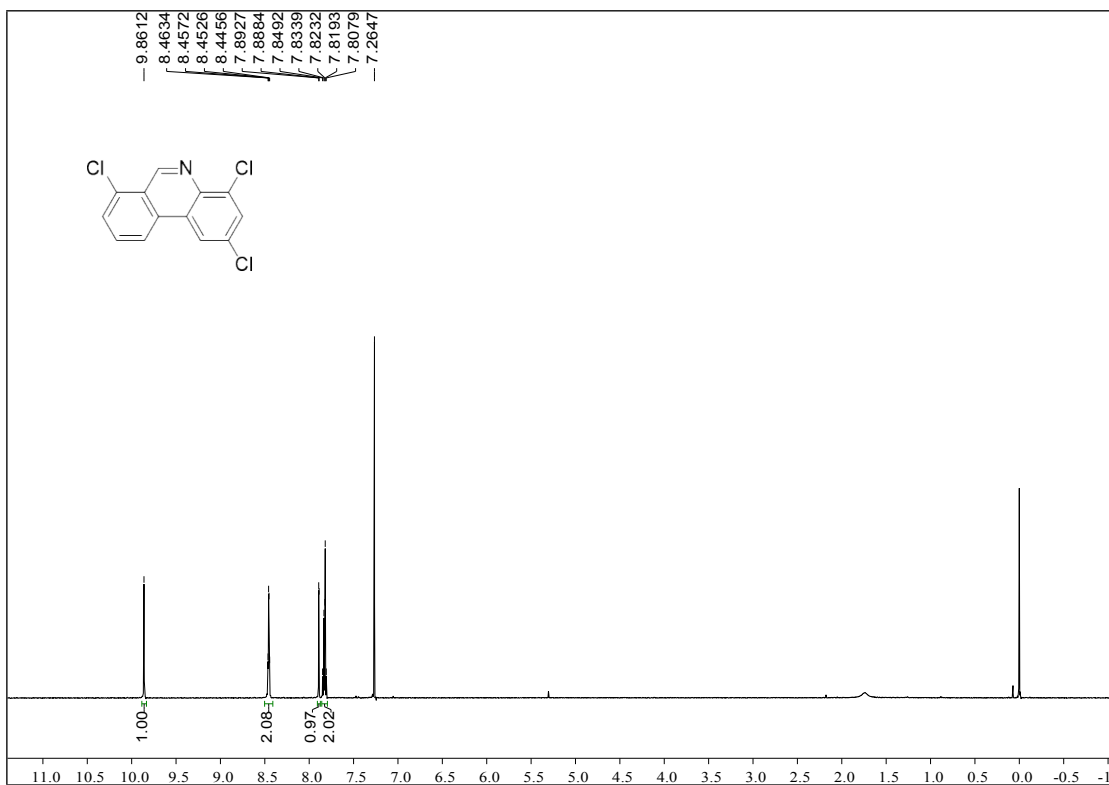
### 7-chloro-4-fluorophenanthridine (3ai')



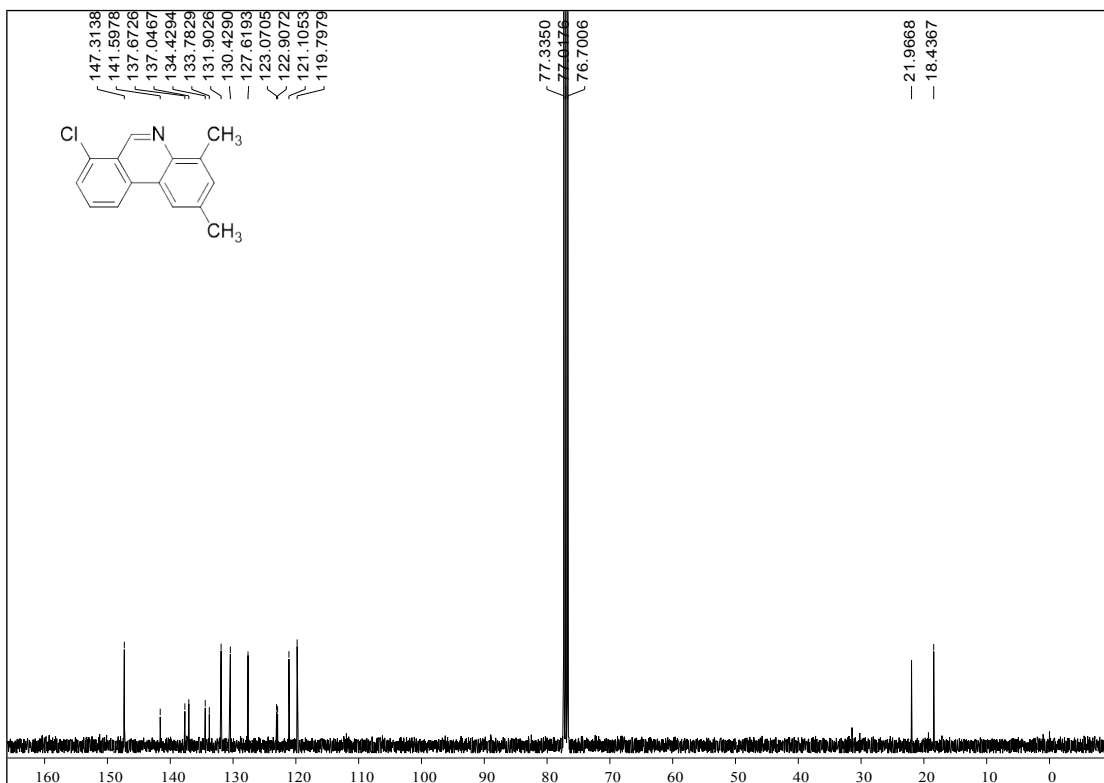
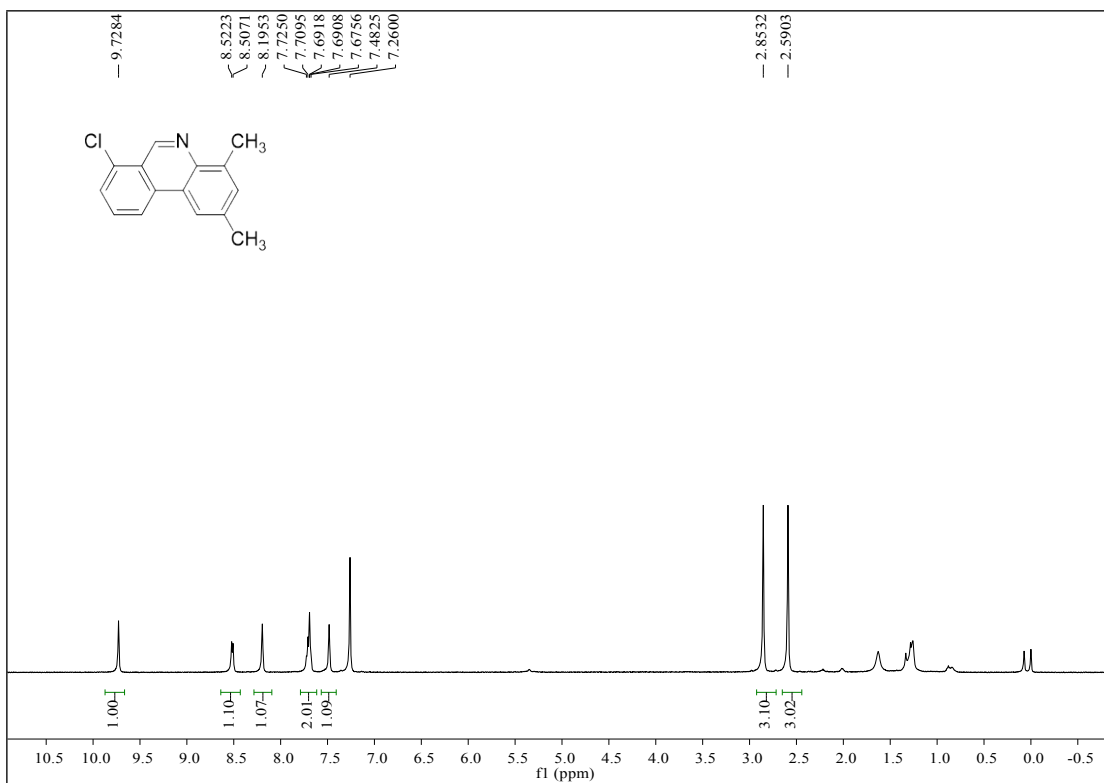
### 4,7-dichlorophenanthridine (3aj')



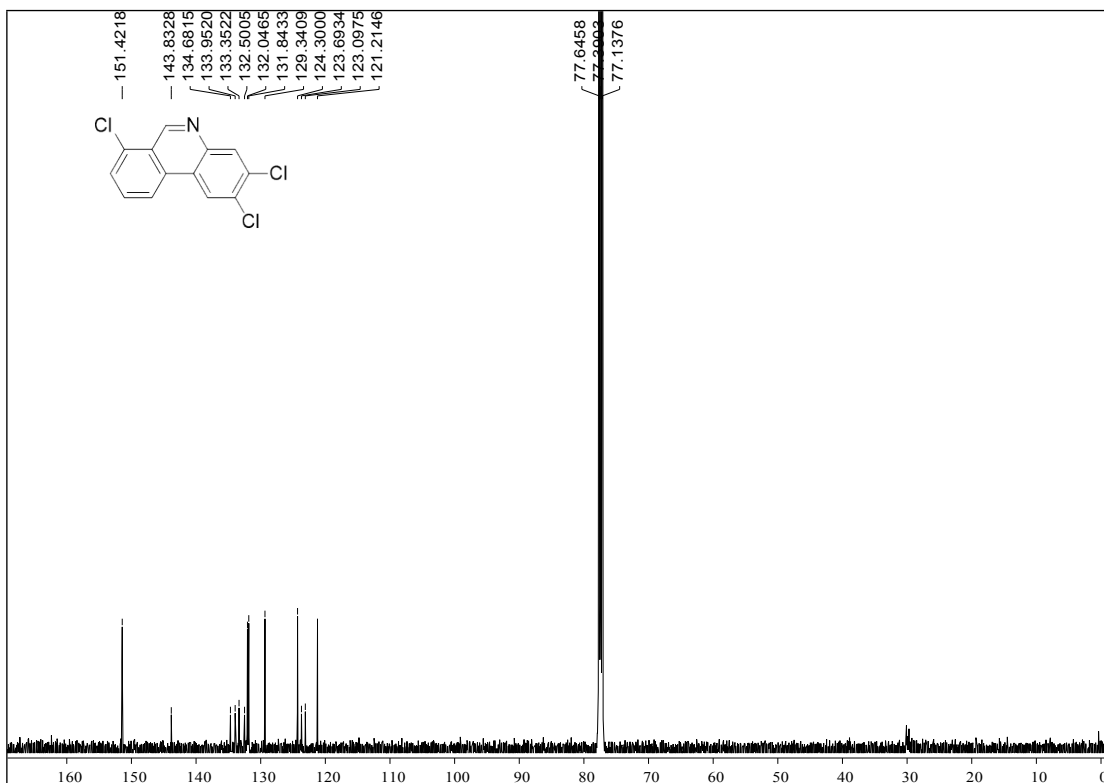
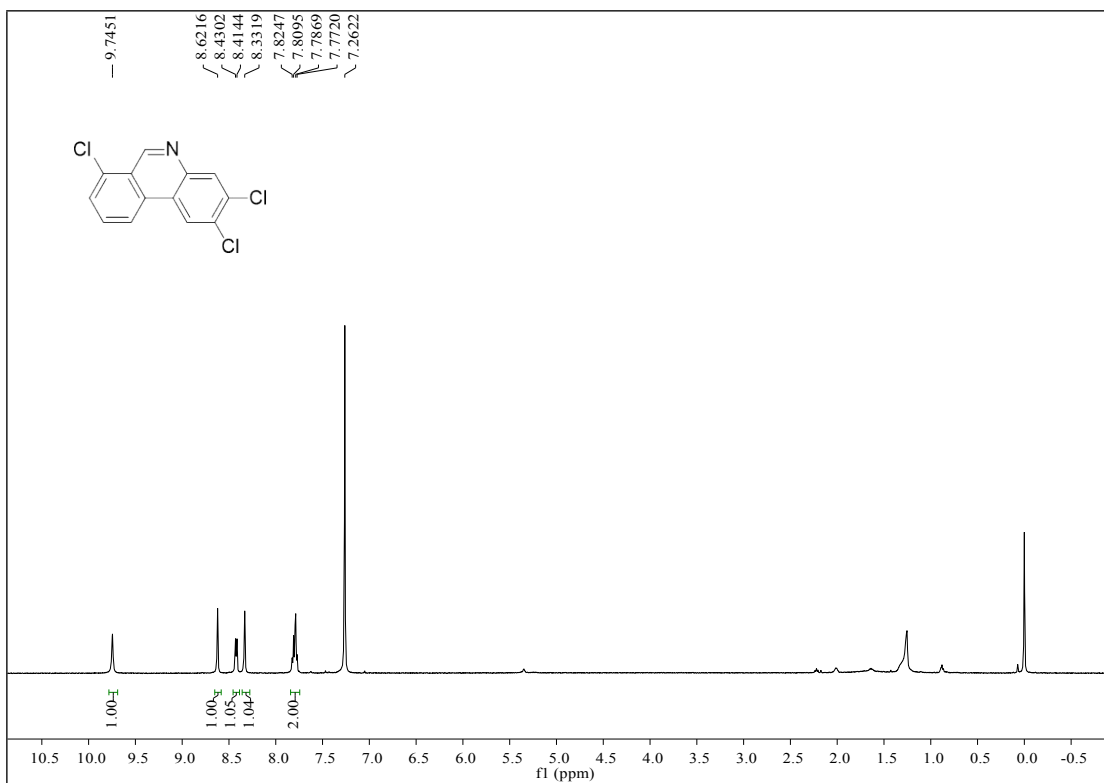
### 2,4,7-trichlorophenanthridine (3am)



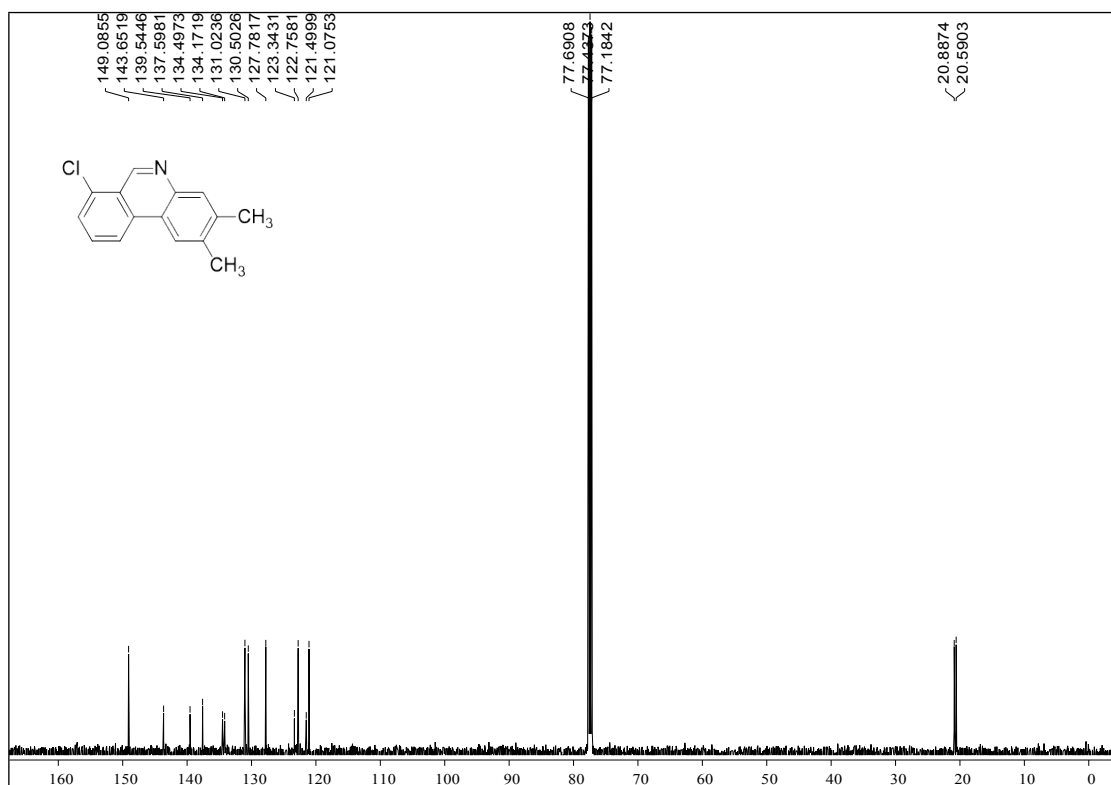
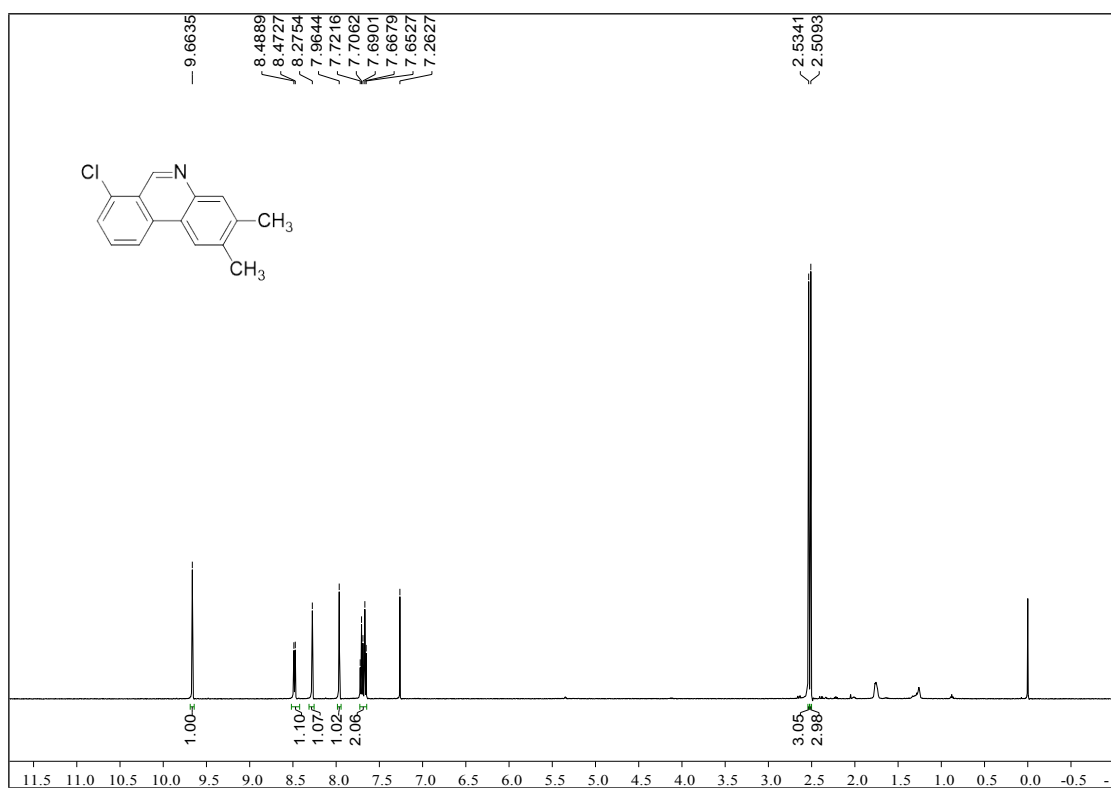
### 7-chloro-2,4-dimethylphenanthridine (3an)



### 2,3,7-trichlorophenanthridine (3ao)

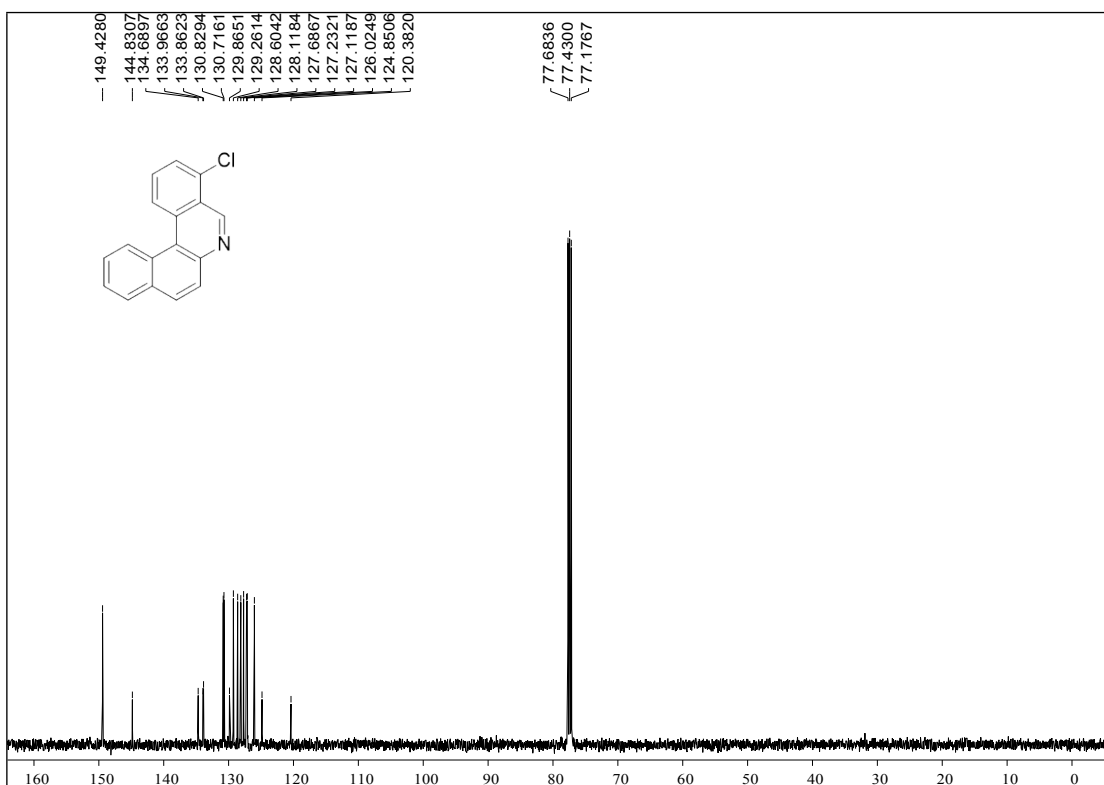
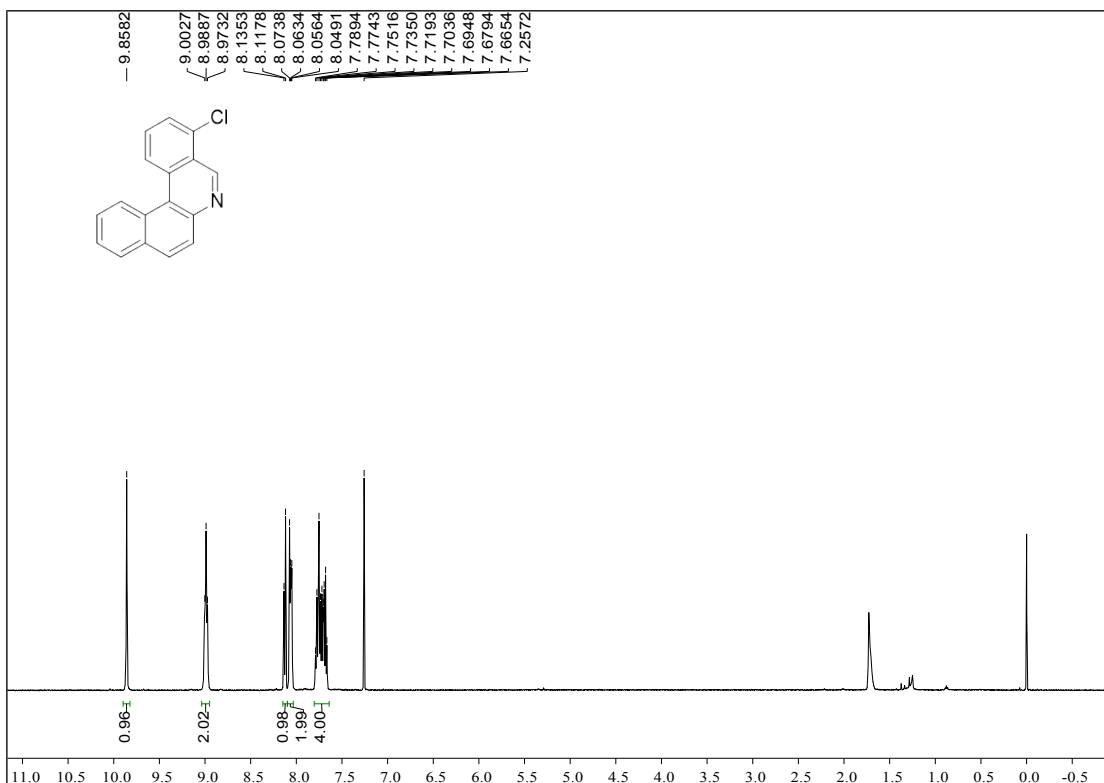


### 7-chloro-2,3-dimethylphenanthridine (3ap)

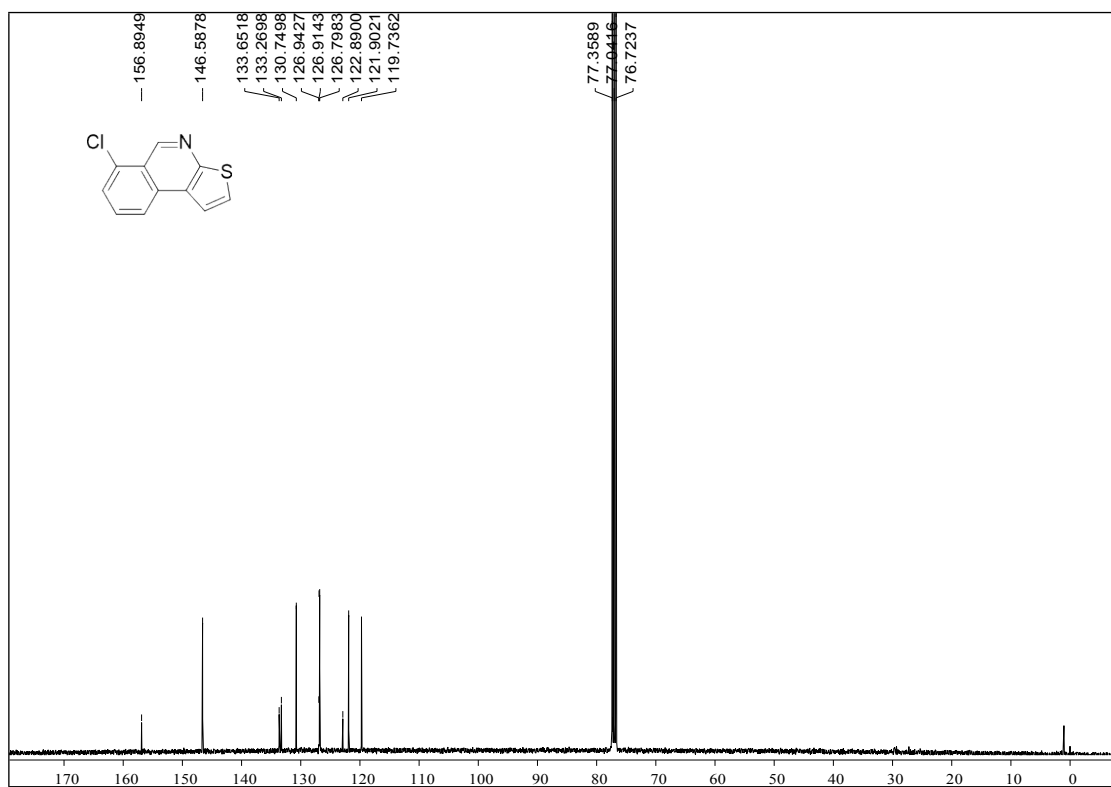
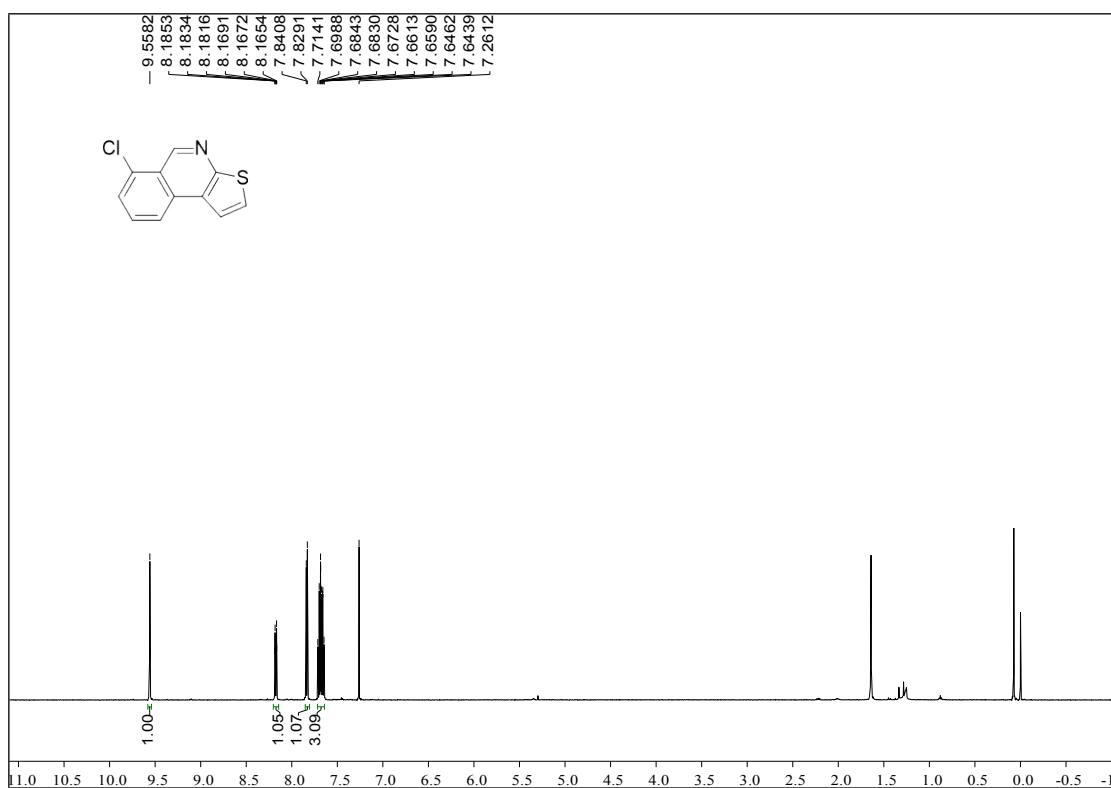




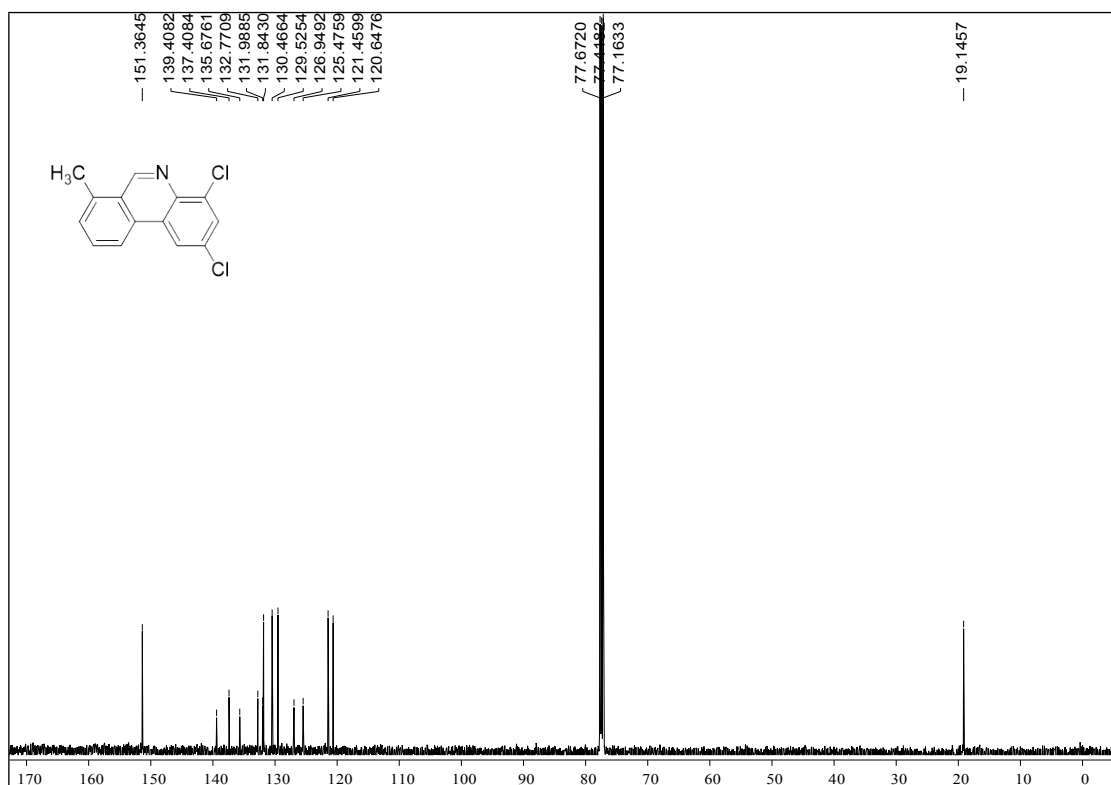
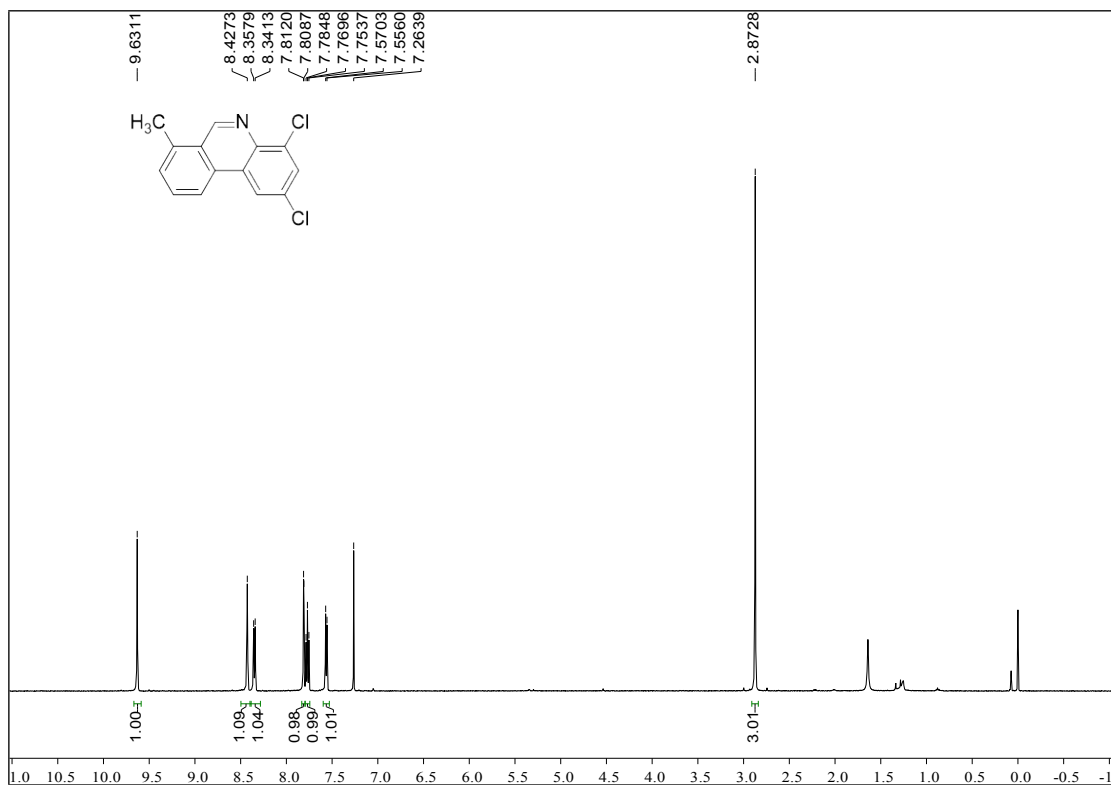
### 4-chlorobenzo[a]phenanthridine (3aq)



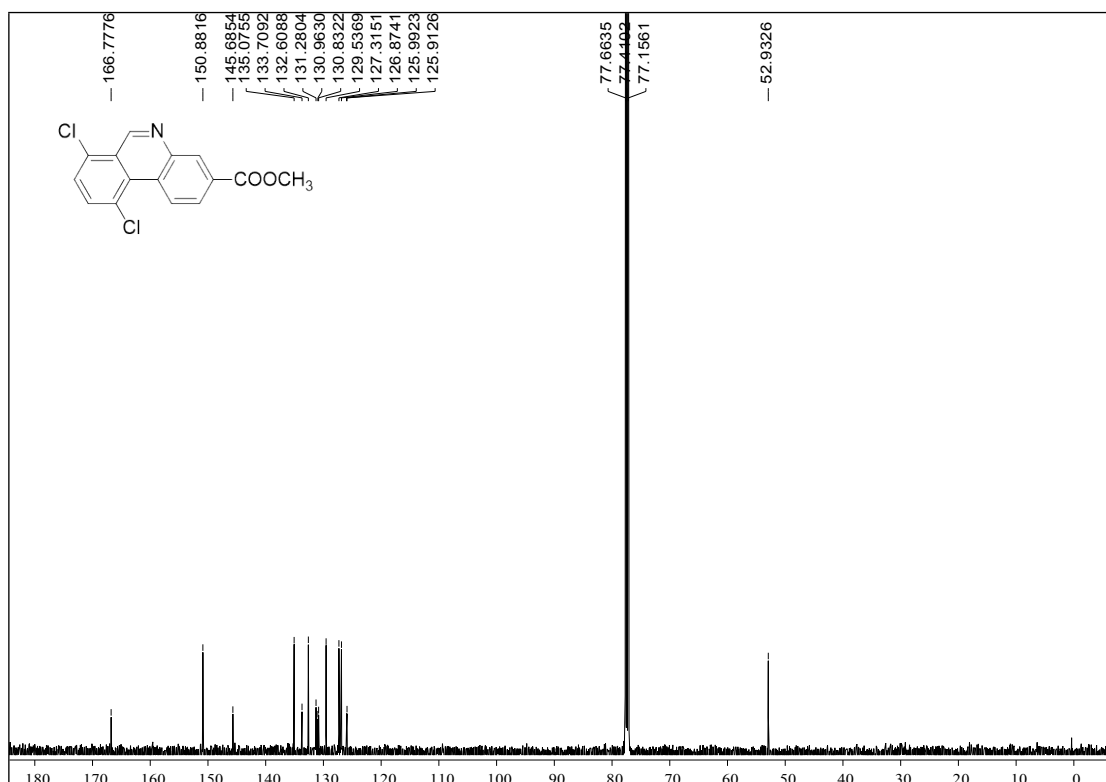
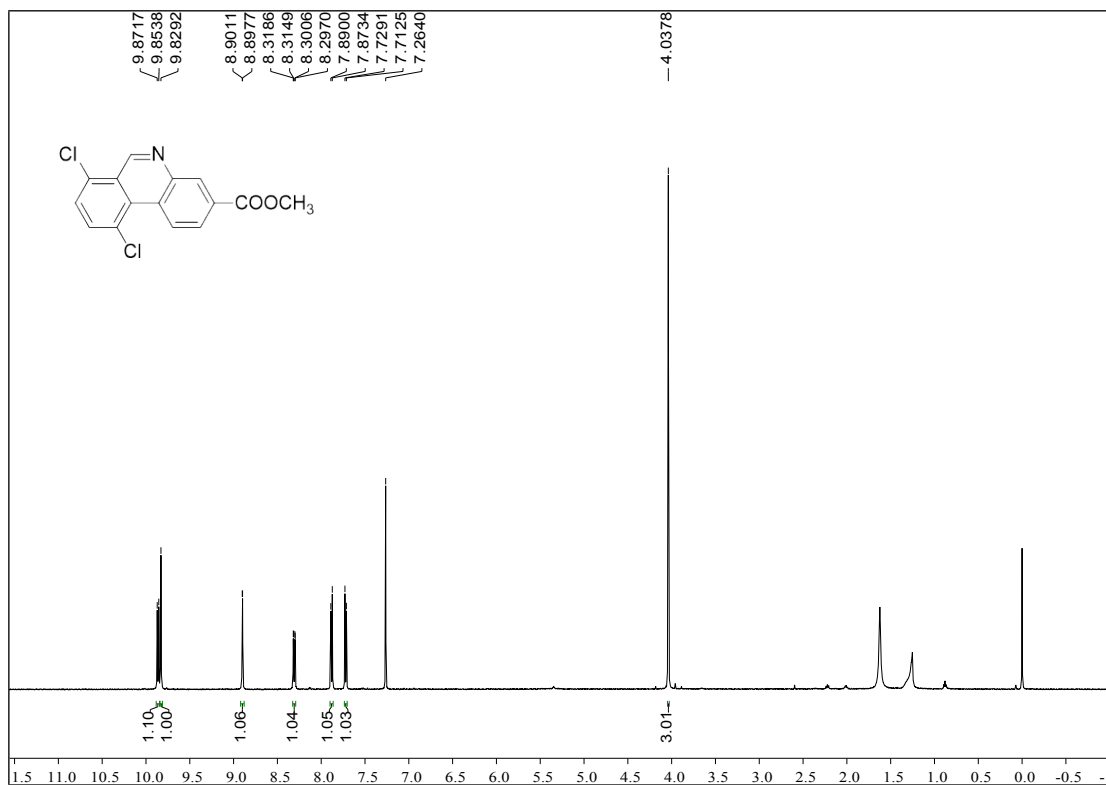
### 6-chlorothieno[2,3-c]isoquinoline (3ar)



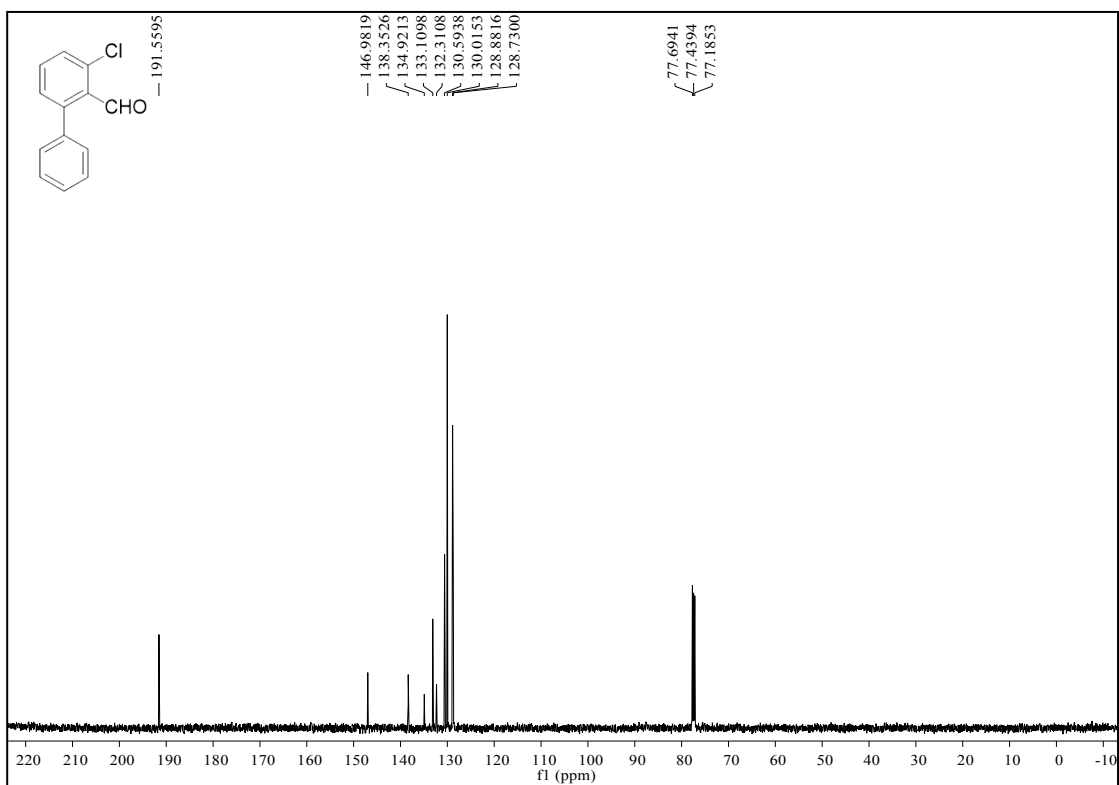
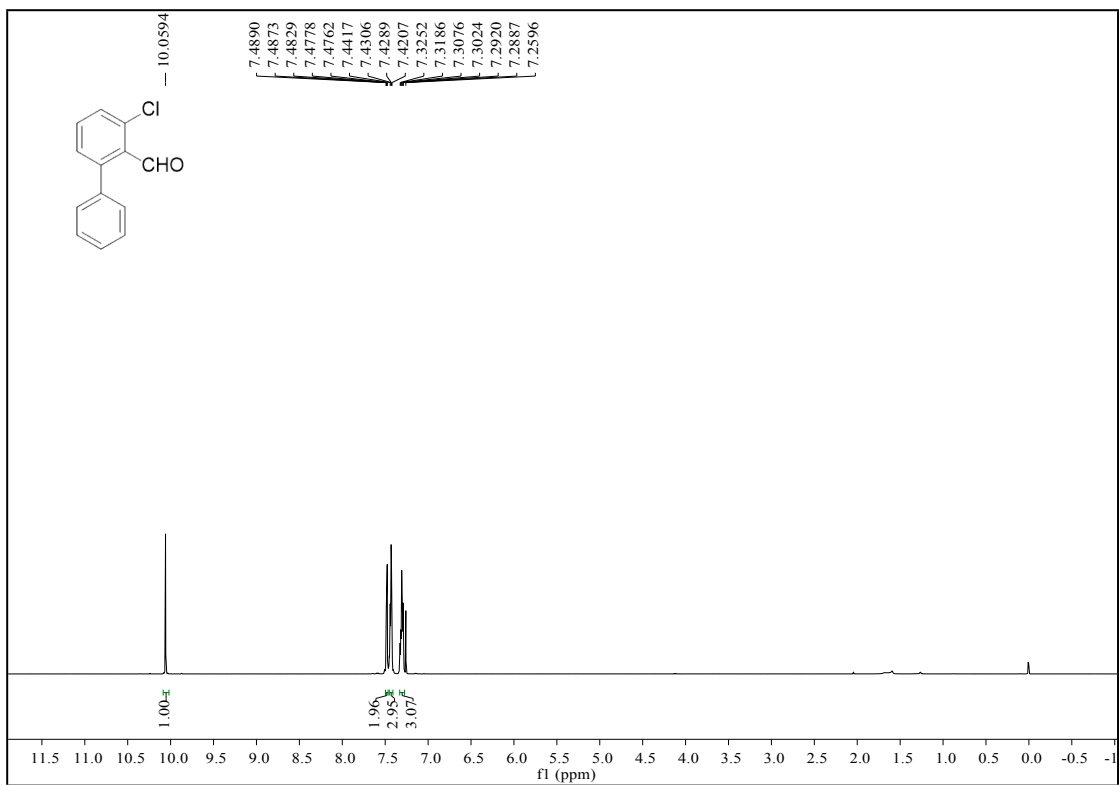
### 2,4-dichloro-7-methylphenanthridine (3dm)



**methyl 7,10-dichlorophenanthridine-3-carboxylate (3nh)**



### 3-chloro-[1,1'-biphenyl]-2-carbaldehyde (A)



### 1- chloro-9H-fluoren-9-one (B)

