

**Supporting Information**  
*for*  
**Palladium-Catalyzed C-H Bond Activation and Decarboxylation for  
the Assembly of Indolo[1,2-f]phenanthridine**

Xiaobing Liu,<sup>a</sup> Yong-Liang Ban,<sup>a</sup> Yanjie Liu,<sup>a</sup> Mengdie Zhuang<sup>a</sup> and Yao Zhou<sup>\*b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou, Henan 466000, People's Republic of China

<sup>b</sup> Hubei Key Laboratory of Pollutant Analysis & Reuse Technology, College of Chemistry and Chemical Engineering, Hubei Normal University, Huangshi, Hubei 435002, People's Republic of China

\*E-mail: yaozhou@hbnu.edu.cn

## Table of Contents

1. General information.....	3
2. General procedure for the synthesis of <b>3</b> and <b>4</b> .....	4
3. Crystal data of <b>4e</b> .....	5
4. Characterization data for products.....	6
5. NMR spectroscopic data .....	17

## 1. General information

All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. Unless otherwise stated, all experiments were conducted in a 25 mL Schlenk reaction tube under N<sub>2</sub> atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker Avance 500 spectrometer (500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl<sub>3</sub> ( $\delta$  = 7.26 for <sup>1</sup>H-NMR,  $\delta$  = 77.00 for <sup>13</sup>C-NMR) or DMSO-*d*<sub>6</sub> ( $\delta$  = 2.50 for <sup>1</sup>H-NMR,  $\delta$  = 39.60 for <sup>13</sup>C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz).

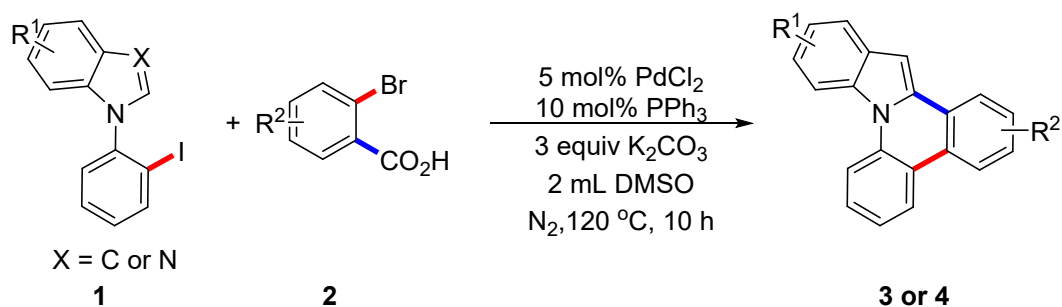
The starting materials **1** were synthesized according to methods reported previous literatures.<sup>1,2</sup>

---

<sup>1</sup> R. Liu, Q. Wang, Y. Wei and M. Shi, *Chem. Commun.*, **2018**, 54, 1225.

<sup>2</sup> K. Naveen, S. Nikson, P. Perumal *Adv. Synth. Catal.*, **2017**, 359, 2407.

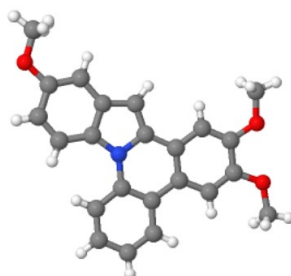
## 2. General procedure for the synthesis of **3** and **4**



The mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), PdCl<sub>2</sub> (1.7 mg, 0.01 mmol, 5 mol %), PPh<sub>3</sub> (5.2 mg, 0.02 mmol, 10 mol %) and K<sub>3</sub>CO<sub>3</sub> (82.8 mg, 0.6 mmol, 3.0 equiv) in DMSO (2 mL) was stirred under nitrogen atmosphere at 120 °C for 10 h (oil bath temperature). After the completion of the reaction (monitored by TLC), the reaction mixture was washed by saturated NH<sub>4</sub>Cl solution and then evaporated under reduced pressure, the crude product was purified by column chromatography to provide the desired product **3** or **4**.

### 3. Crystal data of 4e

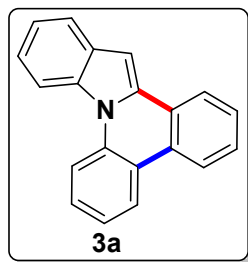
Crystallographic data for compound **4e** (CCDC-2016614) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk).



ORTEP view with ellipsoids (at the 30% probability level)

Bond precision: C-C = 0.0033 Å		Wavelength=0.71073	
Cell:	a=14.5848 (15)	b=8.7233 (10)	c=15.8098 (18)
	alpha=90	beta=115.796 (13)	gamma=90
Temperature:	300 K		
	Calculated	Reported	
Volume	1811.0 (4)	1811.0 (4)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H19 N O3	C23 H19 N O3	
Sum formula	C23 H19 N O3	C23 H19 N O3	
Mr	357.39	357.39	
Dx, g cm-3	1.311	1.311	
Z	4	4	
Mu (mm-1)	0.087	0.087	
F000	752.0	752.0	
F000'	752.35		
h, k, lmax	20, 11, 21	19, 11, 21	
Nref	4916	4122	
Tmin, Tmax	0.990, 0.991	0.783, 1.000	
Tmin'	0.990		
Correction method= # Reported T Limits: Tmin=0.783 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.838		Theta (max)= 29.246	
R(reflections)= 0.0644 ( 2264)		wR2(reflections)= 0.1626 ( 4122)	
S = 1.021		Npar= 258	

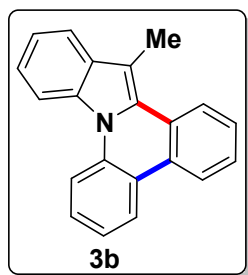
#### 4. Characterization data for products



##### indolo[1,2-f]phenanthridine (3a) (CAS: 945472-69-5)

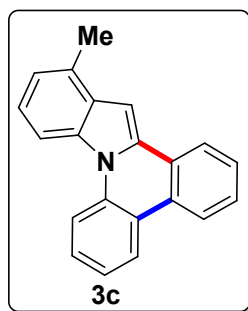
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (50.2 mg, 94%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.30 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.25 – 8.16 (m, 1H), 8.15 – 8.08 (m, 1H), 7.86 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.30 (m, 3H), 7.26 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 136.0, 135.3, 133.9, 130.4, 128.8, 128.2, 127.8, 126.9, 126.2, 124.2, 124.0, 123.1, 122.4, 122.1, 122.1, 121.8, 121.1, 116.4, 114.3, 96.3.

##### 14-methylindolo[1,2-f]phenanthridine (3b) (CAS: 2226086-29-7)



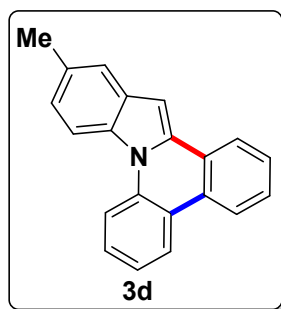
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (50.1 mg, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.44 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.31 (ddd, *J* = 22.6, 7.3, 1.6 Hz, 2H), 8.21 (ddd, *J* = 16.9, 8.1, 1.4 Hz, 2H), 7.90 – 7.78 (m, 1H), 7.55 – 7.47 (m, 2H), 7.47 – 7.36 (m, 3H), 7.28 (td, *J* = 7.6, 7.0, 1.1 Hz, 1H), 2.79 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 136.01, 132.5, 131.3, 130.2, 128.6, 128.0, 127.8, 127.6, 126.8, 125.1, 123.8, 122.7, 122.3, 122.2, 122.1, 121.1, 118.8, 116.2, 114.0, 106.9, 11.9.

##### 13-methylindolo[1,2-f]phenanthridine (3c) (CAS: 945472-68-4)



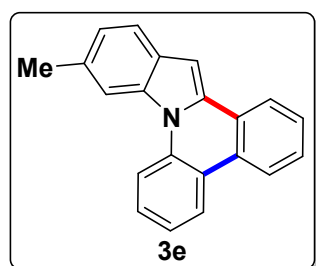
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (47.8 mg, 85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.51 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.27 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.17 (dd, *J* = 7.0, 2.1 Hz, 1H), 8.15 – 8.10 (m, 1H), 7.55 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.46 (tt, *J* = 7.2, 5.4 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.26 (s, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 2.73 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 135.9, 134.6, 133.6, 130.2, 130.1, 128.6, 128.0, 127.5, 126.7, 126.2, 124.0, 123.8, 122.9, 122.3, 122.1, 122.1, 121.9, 116.3, 111.8, 94.6, 19.0.

### 12-methylindolo[1,2-f]phenanthridine (3d) (CAS: 945472-67-3)



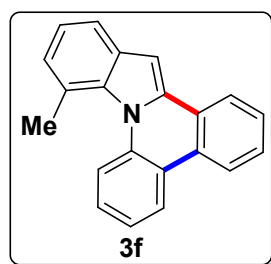
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (49.5 mg, 88%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J = 8.4$  Hz, 1H), 8.29 (d,  $J = 7.9$  Hz, 1H), 8.24 (d,  $J = 8.6$  Hz, 1H), 8.22 – 8.16 (m, 1H), 8.15 – 8.05 (m, 1H), 7.61 (s, 1H), 7.59 – 7.53 (m, 1H), 7.48 (td,  $J = 6.3, 5.7, 3.5$  Hz, 2H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.24 – 7.12 (m, 2H), 2.56 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 135.2, 132.2, 131.12, 130.6, 128.6, 128.1, 127.6, 126.8, 126.2, 124.0, 123.9, 123.6, 122.7, 122.3, 121.9, 120.6, 116.1, 113.8, 95.7, 21.4.

### 11-methylindolo[1,2-f]phenanthridine (3e) (CAS: 2226086-21-9)

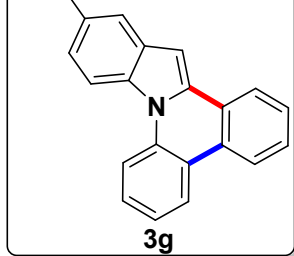


The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (46.6 mg, 83%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J = 8.4$  Hz, 1H), 8.26 (dd,  $J = 8.1, 1.5$  Hz, 1H), 8.16 (q,  $J = 3.1, 2.2$  Hz, 2H), 8.11 – 8.03 (m, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.56 (ddd,  $J = 8.4, 7.1, 1.5$  Hz, 1H), 7.45 (tt,  $J = 7.2, 5.4$  Hz, 2H), 7.35 – 7.28 (m, 1H), 7.21 (d,  $J = 8.0$  Hz, 2H), 2.66 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.0, 134.7, 134.3, 131.7, 128.5, 128.1, 128.0, 127.4, 126.6, 126.3, 123.9, 123.8, 123.4, 122.8, 122.3, 122.0, 120.5, 116.2, 114.2, 96.0, 22.4.

### 10-methylindolo[1,2-f]phenanthridine (3f)



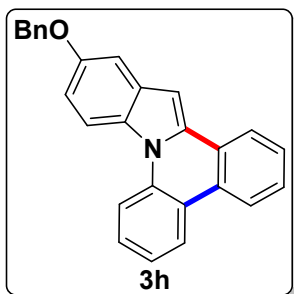
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (48.9 mg, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 – 8.15 (m, 2H), 8.12 – 8.02 (m, 1H), 7.69 (d,  $J = 7.8$  Hz, 1H), 7.56 (dd,  $J = 8.3, 1.2$  Hz, 1H), 7.54 – 7.44 (m, 3H), 7.38 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 2.63 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 135.6, 134.5, 131.7, 128.1, 128.1, 127.8, 127.2, 125.5, 124.3, 124.0, 122.9, 122.8, 122.7, 122.5, 120.8, 118.1, 97.4, 22.5. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{16}\text{N}$   $[\text{M}+\text{H}]^+$ : 282.1277; found: 282.1281



**12-methoxyindolo[1,2-f]phenanthridine (3g) (CAS: 945472-65-1)**

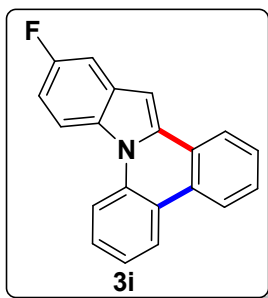
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 10 : 1, v/v) to give the product as a pale yellow solid (48.1 mg, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.30 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 8.23 – 8.18 (m, 1H), 8.13 – 8.06 (m, 1H), 7.56 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 2.6 Hz, 1H), 7.16 (s, 1H), 7.02 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.94 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 155.1, 135.8, 135.8, 131.3, 129.1, 128.7, 128.1, 127.7, 126.8, 126.0, 124.1, 124.0, 122.8, 122.4, 121.8, 115.9, 115.0, 111.9, 102.1, 95.8, 55.6.

**12-(benzyloxy)indolo[1,2-f]phenanthridine (3h) (CAS: 2226086-24-2)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 8:1, v/v) to give the product as a pale yellow solid (56.0 mg, 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.48 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.34 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 8.26 – 8.21 (m, 1H), 8.15 – 8.09 (m, 1H), 7.61 – 7.48 (m, 5H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.19 (s, 1H), 7.11 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.20 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.4, 137.4, 135.9, 135.8, 131.3, 129.2, 128.8, 128.6, 128.2, 127.9, 127.75, 127.6, 126.8, 126.0, 124.1, 124.0, 122.9, 122.4, 121.9, 115.9, 115.1, 112.6, 103.6, 95.9, 70.6.

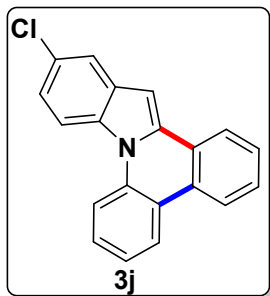
**12-fluoroindolo[1,2-f]phenanthridine (3i) (CAS: 2226086-27-5)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (46.7 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.25 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.20 (dd, *J* = 9.2, 4.3 Hz, 1H), 8.18 – 8.11 (m, 1H), 7.52 (ddd, *J* = 8.6, 7.1, 1.5 Hz, 1H), 7.46 (td, *J* = 5.5, 4.6, 3.2 Hz, 2H), 7.40 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.15 – 7.02 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.5 (d, *J* = 236.3 Hz), 136.6, 135.5, 131.1 (d, *J* = 11.3 Hz), 130.4, 128.7, 128.1 (d, *J* = 13.8 Hz), 126.8, 125.6, 124.0 (d, *J* = 18.8 Hz), 123.1, 122.3, 121.9, 115.8, 114.9 (d, *J* = 8.8 Hz), 110.1, 109.9, 105.6, 105.4, 95.9 (d, *J* = 3.8 Hz). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -121.7.

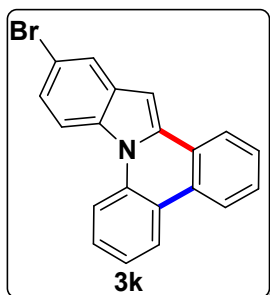
**12-chloroindolo[1,2-f]phenanthridine (3j) (CAS: 2169291-29-4)**





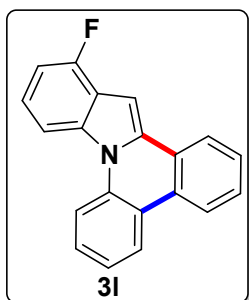
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (51.8 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 8.4$  Hz, 1H), 8.30 (dd,  $J = 8.1, 1.5$  Hz, 1H), 8.25 – 8.15 (m, 2H), 8.12 – 8.01 (m, 1H), 7.74 (d,  $J = 2.2$  Hz, 1H), 7.60 – 7.52 (m, 1H), 7.49 (td,  $J = 7.0, 6.3, 3.6$  Hz, 2H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.28 (dd,  $J = 9.0, 2.2$  Hz, 1H), 7.12 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 135.5, 132.2, 131.5, 128.8, 128.3, 128.2, 127.3, 126.9, 125.6, 124.2, 124.1, 123.4, 122.4, 122.1, 122.0, 120.1, 116.1, 115.1, 95.6.

### 12-bromoindolo[1,2-f]phenanthridine (3k)



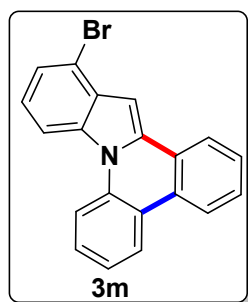
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (49.0 mg, 71%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 8.4$  Hz, 1H), 8.30 (d,  $J = 8.0$  Hz, 1H), 8.25 – 8.14 (m, 2H), 8.13 – 8.01 (m, 1H), 7.90 (d,  $J = 2.0$  Hz, 1H), 7.56 (t,  $J = 7.8$  Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.30 (m, 2H), 7.12 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.3, 135.5, 132.5, 132.1, 128.9, 128.3, 128.3, 127.0, 125.7, 124.6, 124.3, 124.2, 123.5, 123.3, 122.5, 122.2, 116.2, 115.5, 115.1, 95.5. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{20}\text{H}_{12}\text{BrKN}$   $[\text{M}+\text{K}]^+$ : 383.9785; found: 383.9779.

### 13-fluoroindolo[1,2-f]phenanthridine (3l)



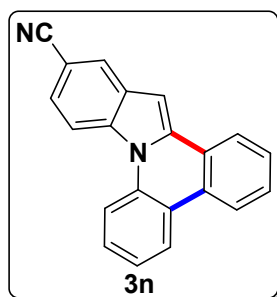
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (44.5 mg, 78%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (d,  $J = 8.4$  Hz, 1H), 8.26 (dd,  $J = 8.1, 1.5$  Hz, 1H), 8.16 (dt,  $J = 7.4, 3.7$  Hz, 1H), 8.12 – 8.05 (m, 2H), 7.54 (ddd,  $J = 8.6, 7.2, 1.5$  Hz, 1H), 7.47 (dt,  $J = 6.1, 3.5$  Hz, 2H), 7.37 – 7.31 (m, 1H), 7.30 – 7.24 (m, 2H), 7.02 (dd,  $J = 9.7, 7.8$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2 (d,  $J = 245.0$  Hz), 136.0 (d,  $J = 10.0$  Hz), 135.5, 135.2, 128.7, 128.3, 128.1, 126.8, 125.8, 124.1, 124.0, 123.4, 122.3, 122.2 (d,  $J = 7.5$  Hz), 122.2, 119.7 (d,  $J = 22.5$  Hz), 116.3, 110.3 (d,  $J = 3.8$  Hz), 106.4 (d,  $J = 18.8$  Hz), 91.7.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.8. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{23}\text{H}_{13}\text{FN}$   $[\text{M}+\text{H}]^+$ : 286.1027; found: 286.1032.

### 13-bromoindolo[1,2-f]phenanthridine (3m) (CAS: 2226086-25-3)



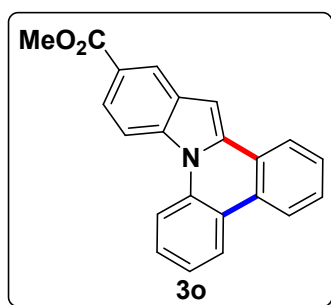
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (48.3 mg, 70%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (d,  $J = 8.4$  Hz, 1H), 8.31 – 8.22 (m, 2H), 8.17 (dq,  $J = 7.3, 4.0$  Hz, 1H), 8.12 (dt,  $J = 7.2, 3.7$  Hz, 1H), 7.54 (ddd,  $J = 8.7, 7.3, 1.5$  Hz, 1H), 7.52 – 7.43 (m, 3H), 7.35 (td,  $J = 7.6, 7.0, 1.1$  Hz, 1H), 7.27 (s, 1H), 7.20 (t,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 135.5, 133.9, 130.8, 128.8, 128.3, 128.3, 126.8, 125.6, 124.6, 124.3, 124.1, 123.5, 122.5, 122.4, 122.3, 116.3, 114.9, 113.2, 96.5.

### indolo[1,2-f]phenanthridine-12-carbonitrile (3n) (CAS: 945472-71-9)



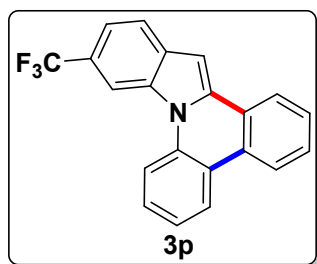
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 5:1, v/v) to give the product as a pale yellow solid (32.7 mg, 56%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (dd,  $J = 8.4, 1.2$  Hz, 1H), 8.34 – 8.30 (m, 2H), 8.24 – 8.18 (m, 1H), 8.13 – 8.00 (m, 2H), 7.62 – 7.49 (m, 4H), 7.41 (ddd,  $J = 8.2, 7.2, 1.1$  Hz, 1H), 7.19 (d,  $J = 0.8$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 137.2, 135.0, 135.0, 129.9, 129.0, 128.8, 128.5, 127.0, 125.9, 125.2, 124.4, 124.3, 124.2, 122.5, 122.4, 120.1, 116.5, 114.7, 104.8, 96.3.

### methyl indolo[1,2-f]phenanthridine-12-carboxylate (3o)



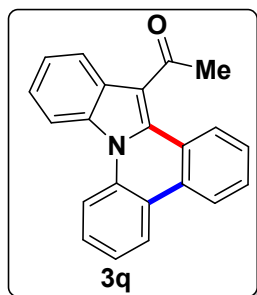
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 5:1, v/v) to give the product as a pale yellow solid (47.5 mg, 73%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J = 1.8$  Hz, 1H), 8.40 (dd,  $J = 8.4, 1.1$  Hz, 1H), 8.30 – 8.20 (m, 2H), 8.18 – 8.10 (m, 1H), 8.01 (ddd,  $J = 22.1, 7.6, 3.3$  Hz, 2H), 7.53 (ddd,  $J = 8.5, 7.2, 1.4$  Hz, 1H), 7.50 – 7.41 (m, 2H), 7.33 (ddd,  $J = 8.2, 7.2, 1.1$  Hz, 1H), 7.20 (s, 1H), 3.99 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 136.4, 135.9, 135.4, 129.8, 128.8, 128.3, 128.2, 126.8, 125.6, 124.2, 124.0, 123.7, 123.4, 123.4, 122.9, 122.4, 122.3, 116.4, 113.7, 97.1, 52.0. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{16}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 326.1176; found: 326.1180.

### 11-(trifluoromethyl)indolo[1,2-f]phenanthridine (3p)



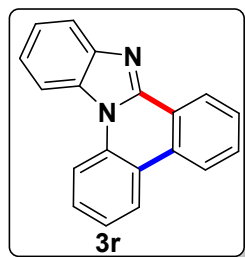
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow oil (58.3 mg, 87%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.55 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.26 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.1, 2.1 Hz, 1H), 8.10 – 7.99 (m, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.49 (tt, *J* = 7.2, 5.5 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.17 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.6, 135.2, 132.6, 132.5, 129.0, 128.5, 128.3, 127.1, 125.3 (q, *J* = 270.0 Hz), 125.3, 124.3, 124.1, 123.7, 123.4 (q, *J* = 31.3 Hz), 122.4, 122.1, 121.1, 118.4, (q, *J* = 3.8 Hz), 116.23, 111.5 (q, *J* = 5.0 Hz) 96.1. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -60.0. HRMS (ESI, *m/z*) calcd for C<sub>21</sub>H<sub>13</sub>F<sub>3</sub>N [M+H]<sup>+</sup>: 336.0995; found: 336.0995.

### 1-(indolo[1,2-f]phenanthridin-14-yl)ethan-1-one (3q)



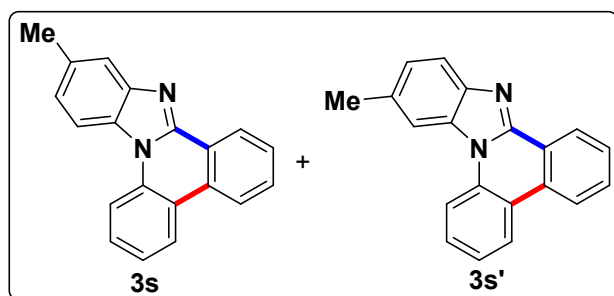
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 10 : 1, v/v) to give the product as a yellow solid (26.6 mg, 43%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.41 (dt, *J* = 7.0, 2.3 Hz, 2H), 8.35 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.26 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.22 – 8.11 (m, 1H), 7.65 (dddd, *J* = 8.4, 7.2, 5.7, 1.4 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.48 (ddd, *J* = 7.7, 3.7, 1.9 Hz, 3H), 2.80 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 199.4, 135.8, 134.7, 133.1, 129.3, 129.1, 128.8, 128.7, 128.4, 128.0, 124.7, 124.2, 124.2, 123.4, 123.3, 122.6, 122.5, 120.8, 117.0, 114.4, 114.2, 32.1. HRMS (ESI, *m/z*) calcd for C<sub>22</sub>H<sub>16</sub>NO [M+H]<sup>+</sup>: 310.1226; found: 310.1229.

### benzo[4,5]imidazo[1,2-f]phenanthridine (3r) (CAS: 201-71-8)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 4 : 1, v/v) to give the product as a pale yellow solid (28.4 mg, 53%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.42 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.31 (dd, *J* = 11.0, 8.1 Hz, 2H), 8.10 – 7.99 (m, 1H), 7.74 – 7.60 (m, 3H), 7.54 – 7.40 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.5, 144.5, 134.4, 131.8, 130.4, 129.5, 129.1, 128.6, 126.0, 124.4, 124.2, 124.1, 123.4, 122.9, 122.2, 121.7, 120.3, 116.0 113.9.

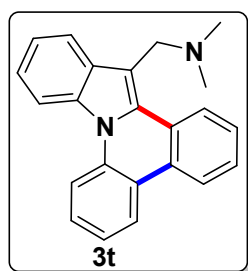
**11-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (3s) (CAS: 2376924-18-2) and 12-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (3s') (CAS: 2376924-19-3)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 4 : 1, v/v) to give the product as a White solid (27.6 mg, 49%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.82 (ddd, *J* =

8.0, 4.5, 1.7 Hz, 1H), 8.47 (dd, *J* = 14.4, 8.4 Hz, 1H), 8.41 (dd, *J* = 8.2, 2.9 Hz, 1H), 8.32 (dd, *J* = 8.1, 3.7 Hz, 1H), 8.19 – 8.02 (m, 1H), 7.95 – 7.76 (m, 1H), 7.73 – 7.59 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 2.60 (d, *J* = 32.8 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.5, 147.1, 144.9, 142.6, 134.5, 134.4, 133.9, 132.8, 132.1, 130.2, 130.1, 129.9, 129.4, 129.3, 129.1, 129.0, 128.5, 128.5, 126.0, 125.9, 125.6, 124.4, 124.2, 124.2, 124.1, 123.6, 123.5, 122.2, 121.7, 121.6, 120.1, 119.8, 119.0, 115.99, 113.9, 113.3, 22.3, 21.6.

**1-(indolo[1,2-f]phenanthridin-14-yl)-N,N-dimethylmethanamine (3t)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, DCM:EtOH = 100:1, v/v) to give the product as a pale yellow oil (47.3 mg, 73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.72 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.41 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.33 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.05 – 7.86 (m, 1H), 7.58 (tdd, *J* = 8.8, 7.2, 1.4 Hz, 2H), 7.52 (td, *J* = 7.7, 7.1, 1.3 Hz, 1H), 7.45 – 7.33 (m, 3H), 3.97 (s, 2H), 2.44 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 135.8, 132.8, 132.6, 131.8, 128.6, 128.4, 127.8, 127.5, 127.2, 127.1, 124.0, 123.1, 122.5, 122.2, 122.0, 121.5, 118.9, 116.7, 114.1, 108.8, 54.2, 45.4. HRMS (ESI, *m/z*) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 325.1699; found: 325.1672.

**2-methylindolo[1,2-f]phenanthridine (4a) and 3-methylindolo[1,2-f]phenanthridine (4a') (CAS: 1658455-12-9)**

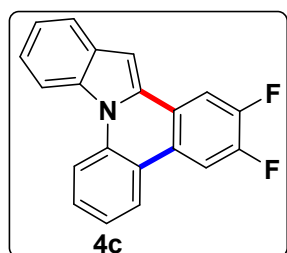
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (52.3 mg, 93% 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.52 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.38 (dd, *J* = 7.9, 5.2 Hz, 1H), 8.27 (ddd, *J* = 16.3, 8.1, 1.5 Hz, 1H), 8.10 – 7.88 (m, 2H), 7.84 (ddd, *J* = 6.8, 3.7, 1.4 Hz, 1H), 7.62 – 7.49 (m, 1H), 7.44 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 7.27 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.21 (d, *J* = 24.6 Hz, 1H), 2.50 (s, 0.69H), 2.49 (s, 2.29H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ

138.0, 137.6, 136.0, 135.6, 135.5, 135.3, 133.9, 133.8, 130.5, 130.4, 129.4, 129.1, 128.5, 128.2, 126.7, 126.0, 124.4, 124.1, 124.1, 123.9, 123.7, 123.6, 122.9, 122.9, 122.5, 122.3, 122.2, 122.1, 121.9, 121.7, 121.7, 121.0, 120.8, 116.3, 116.2, 114.2, 114.1, 96.0, 95.5, 21.8, 21.5.

**2-methoxyindolo[1,2-f]phenanthridine (4b) and 3-methoxyindolo[1,2-f]phenanthridine (4b') (CAS: 1658455-26-5)**

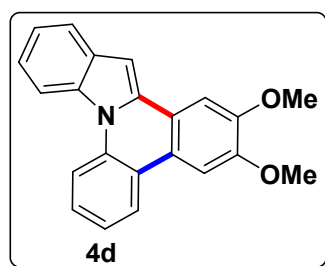
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 10 : 1, v/v) to give the product as a yellow solid (56.4 mg, 95%, 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.47 (d, *J* = 8.4 Hz, 1H), 8.35 (dd, *J* = 16.7, 8.6 Hz, 1H), 8.14 (td, *J* = 8.9, 8.1, 1.5 Hz, 1H), 7.98 (dd, *J* = 42.5, 8.8 Hz, 1H), 7.88 – 7.75 (m, 1H), 7.59 – 7.43 (m, 2H), 7.43 – 7.33 (m, 2H), 7.29 (td, *J* = 7.6, 7.0, 1.1 Hz, 1H), 7.11 (d, *J* = 61.5 Hz, 1H), 7.01 (ddd, *J* = 8.8, 5.4, 2.6 Hz, 1H), 3.91 (s, 2.12H), 3.90 (s, 0.76H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.4, 159.4, 136.1, 135.4, 135.0, 135.0, 133.9, 133.6, 130.6, 130.2, 128.7, 128.2, 127.5, 127.2, 125.7, 124.0, 123.9, 123.3, 122.9, 122.7, 122.1, 122.0, 121.8, 121.7, 121.6, 121.4, 121.0, 120.6, 120.3, 119.7, 116.2, 116.1, 116.1, 115.9, 114.2, 114.1, 106.3, 105.6, 96.2, 94.6, 55.3.

**2,3-difluoroindolo[1,2-f]phenanthridine (4c)**



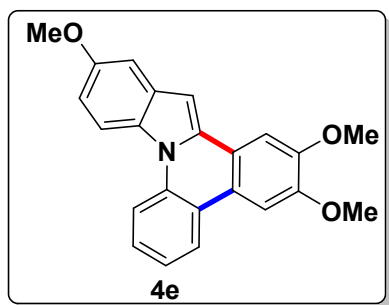
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (50.9 mg, 84%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.26 (dd, *J* = 10.3, 6.5 Hz, 1H), 8.17 (t, *J* = 7.7 Hz, 1H), 7.80 (dd, *J* = 11.7, 6.6 Hz, 1H), 7.72 (qd, *J* = 5.5, 3.6, 3.0 Hz, 1H), 7.62 (ddd, *J* = 19.1, 9.2, 5.9 Hz, 1H), 7.55 – 7.39 (m, 2H), 7.34 (p, *J* = 7.3 Hz, 2H), 7.18 (p, *J* = 6.0 Hz, 1H), 6.91 – 6.73 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.3 (dd, *J* = 250.0, 10.0 Hz), 150.1 (dd, *J* = 250.0, 10.0 Hz), 135.5, 133.6, 133.1, 129.9, 128.9, 123.7 (dd, *J* = 7.5, 3.8 Hz), 123.7, 122.9, 122.8 (dd, *J* = 7.5, 3.8 Hz), 122.3, 121.9, 121.0, 120.3, 116.0, 114.1, 111.7 (dd, *J* = 16.3, 3.8 Hz), 110.7 (d, *J* = 17.5 Hz), 96.5. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -136.75 – -136.79 (m), -136.80 – -136.87 (m), -136.88 – -136.92 (m). HRMS (ESI, *m/z*) calcd for C<sub>20</sub>H<sub>12</sub>F<sub>2</sub>N [M+H]<sup>+</sup>: 304.0932; found: 304.0926.

**2,3-dimethoxyindolo[1,2-f]phenanthridine (4d)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 8:1) to give the product as a pale yellow solid (55.6 mg, 85%).

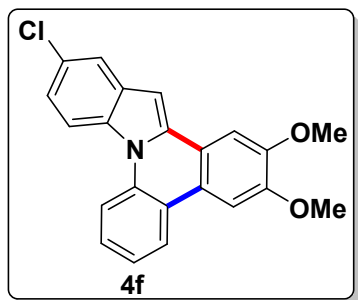
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.29 – 8.21 (m, 1H), 7.90 – 7.81 (m, 1H), 7.81 – 7.72 (m, 1H), 7.43 – 7.30 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.01 (s, 1H), 6.85 (s, 1H), 3.82 (d, *J* = 7.5 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.4, 149.2, 135.1, 135.0, 133.5, 130.3, 127.3, 122.9, 122.3, 121.6, 121.5, 121.2, 120.4, 120.3, 119.4, 115.9, 114.2, 104.7, 103.4, 94.2, 55.6, 55.6. HRMS (ESI, *m/z*) calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 328.1332; found: 328.1334.



### 2,3,12-trimethoxyindolo[1,2-f]phenanthridine (4e)

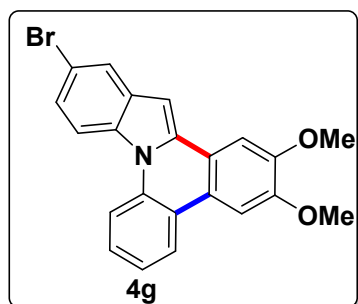
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 5:1) to give the product as a pale yellow solid (59.3 mg, 83%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 8.00 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.34 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.97 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.86 (s, 1H), 3.93 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 155.0, 149.7, 149.5, 135.7, 135.1, 131.4, 128.8, 127.5, 123.1, 122.4, 121.5, 120.4, 119.6, 115.7, 115.0, 111.0, 105.0, 103.7, 101.9, 94.0, 55.8, 55.6. HRMS (ESI, *m/z*) calcd for C<sub>23</sub>H<sub>20</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 358.1438; found: 328.1443.

### 12-chloro-2,3-dimethoxyindolo[1,2-f]phenanthridine (4f)



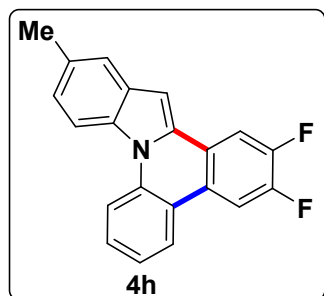
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 5:1) to give the product as a pale yellow solid (47.7 mg, 66%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.38 – 7.33 (m, 2H), 7.28 (d, *J* = 2.2 Hz, 1H), 6.95 (s, 1H), 4.03 (d, *J* = 6.0 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.0, 150.0, 136.4, 134.9, 132.0, 131.6, 127.9, 127.3, 123.4, 123.2, 121.9, 121.4, 120.8, 119.7, 119.4, 116.1, 115.1, 105.3, 104.0, 93.9, 56.0, 56.0. HRMS (ESI, *m/z*) calcd for C<sub>22</sub>H<sub>17</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup>: 362.0942; found: 362.0950.

### 12-bromo-2,3-dimethoxyindolo[1,2-f]phenanthridine (4g)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 5:1) to give the product as a pale yellow solid (56.8 mg,

70%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (dd,  $J = 8.5, 1.1$  Hz, 1H), 8.19 (d,  $J = 8.9$  Hz, 1H), 8.15 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.88 (d,  $J = 2.1$  Hz, 1H), 7.57 – 7.50 (m, 2H), 7.40 (dd,  $J = 8.9, 2.1$  Hz, 1H), 7.38 – 7.34 (m, 2H), 6.95 (s, 1H), 4.03 (d,  $J = 5.7$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 150.0, 136.3, 134.9, 132.3, 132.2, 127.9, 124.0, 123.4, 123.2, 122.9, 122.0, 120.8, 119.4, 116.2, 115.5, 115.0, 105.3, 104.0, 93.8, 56.0, 56.0. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{22}\text{H}_{17}\text{BrNO}_2$   $[\text{M}+\text{H}]^+$ : 406.0437; found: 406.0437.

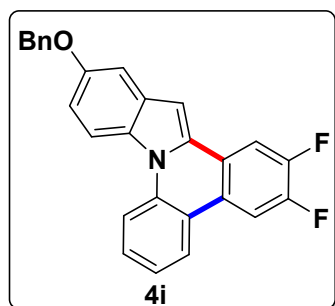


#### 2,3-difluoro-12-methylindolo[1,2-f]phenanthridine (4h)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a pale yellow solid (52.6 mg, 83%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (dd,  $J = 8.5, 1.1$  Hz, 1H), 8.14 (d,  $J = 8.7$  Hz, 1H), 7.99 (dd,  $J = 8.1, 1.5$  Hz, 1H), 7.82 (dd,  $J = 11.9, 7.8$  Hz, 1H), 7.69 (dd,  $J = 10.9, 7.9$  Hz, 1H), 7.58 – 7.48 (m, 2H), 7.28 (ddd,  $J = 8.3, 7.2, 1.2$  Hz, 1H), 7.19 (dd,  $J = 8.7, 1.8$  Hz, 1H), 6.92 (s, 1H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4 (dd,  $J = 251.3, 16.3$  Hz), 150.3, (dd,  $J = 251.3, 17.5$  Hz), 135.8, 133.4, 132.2, 131.5, 130.4, 129.1, 124.1, 124.0 (dd,  $J = 6.3, 2.5$  Hz), 123.9, 123.2 (dd,  $J = 6.3, 2.5$  Hz), 122.9, 120.8, 120.4, 116.2, 113.8, 111.9 (d,  $J = 17.5$  Hz), 110.9, (d,  $J = 18.8$  Hz), 96.2, 21.3.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -136.82, -136.87, -137.00, -137.05. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{21}\text{H}_{14}\text{F}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 318.1089; found: 318.1092.

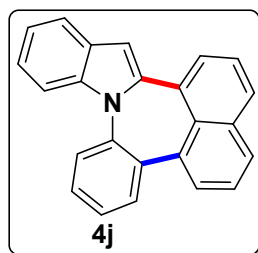


### 12-(benzyloxy)-2,3-difluorindolo[1,2-f]phenanthridine (4i)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether : AcOEt = 8:1) to give the product as a pale yellow solid (70.3 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 – 8.21 (m, 1H), 8.09 (d,  $J = 9.2$  Hz, 1H), 7.91 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.74 (dd,  $J = 11.8, 7.8$  Hz, 1H), 7.66 – 7.51 (m, 3H), 7.51 – 7.41 (m, 3H), 7.41 – 7.32 (m, 1H), 7.26 – 7.22 (m, 1H), 7.21 (d,  $J = 2.6$  Hz, 1H), 7.06 (dd,  $J = 9.2, 2.6$  Hz, 1H), 6.80 (s, 1H), 5.17 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 150.4 (dd,  $J = 250.0, 13.8$  Hz), 150.2 (dd,  $J = 250.0, 13.8$  Hz), 137.4, 135.5, 133.8, 130.9, 129.1, 129.0, 128.6, 127.9, 127.6, 123.8, 123.8 (dd,  $J = 7.5, 3.8$  Hz), 122.9, 122.8 (dd,  $J = 7.5, 3.8$  Hz), 120.2, 115.8, 115.0, 113.0, 111.8 (dd,  $J = 18.1, 2.5$  Hz), 110.8 (d,  $J = 18.8$  Hz), 103.5, 96.2, 70.5.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -136.75, -136.80, -136.87, -136.91. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{27}\text{H}_{18}\text{F}_2\text{NO}$   $[\text{M}+\text{H}]^+$ : 410.1351; found: 410.1357.

### benzo[6,7]naphtho[1',8':3,4,5]azepino[1,2-a]indole (4j)

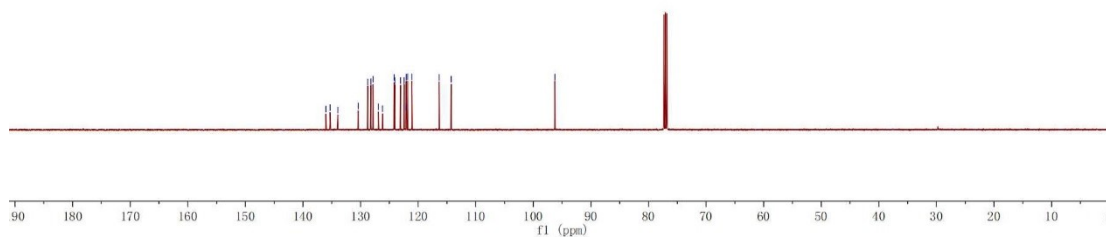
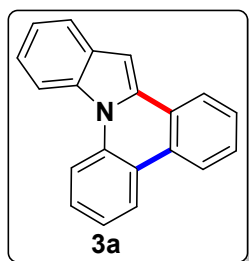
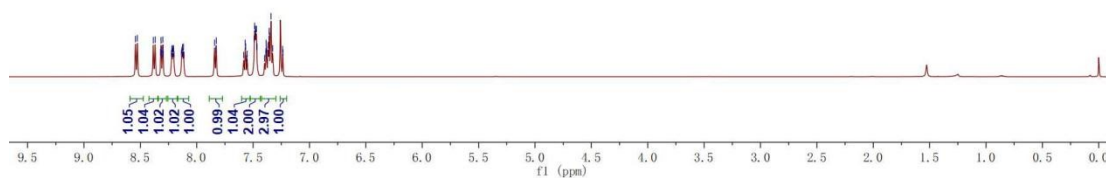
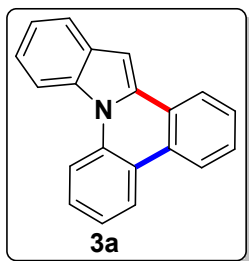


The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, 100% petroleum) to give the product as a bright yellow solid (29.1 mg, 46%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.83 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.80 – 7.68 (m, 4H), 7.59 (d,  $J = 7.7$  Hz, 1H), 7.51 (t,  $J = 7.6$  Hz, 1H), 7.45 (t,  $J = 7.6$  Hz, 1H), 7.37 (td,  $J = 7.7, 1.7$  Hz, 1H), 7.28 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.21 (ddd,  $J = 15.4, 8.1, 1.5$  Hz, 2H), 7.14 (t,  $J = 7.4$  Hz, 1H), 6.52 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 137.6, 136.8, 135.7, 135.7, 135.0, 133.5, 133.40, 130.2, 128.8, 128.4, 128.1, 128.0, 127.2, 126.6, 126.1, 125.9, 124.6, 124.3, 122.4, 121.1, 120.7, 112.6, 107.4. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{24}\text{H}_{16}\text{N}$   $[\text{M}+\text{H}]^+$ : 318.1277; found: 318.1273.

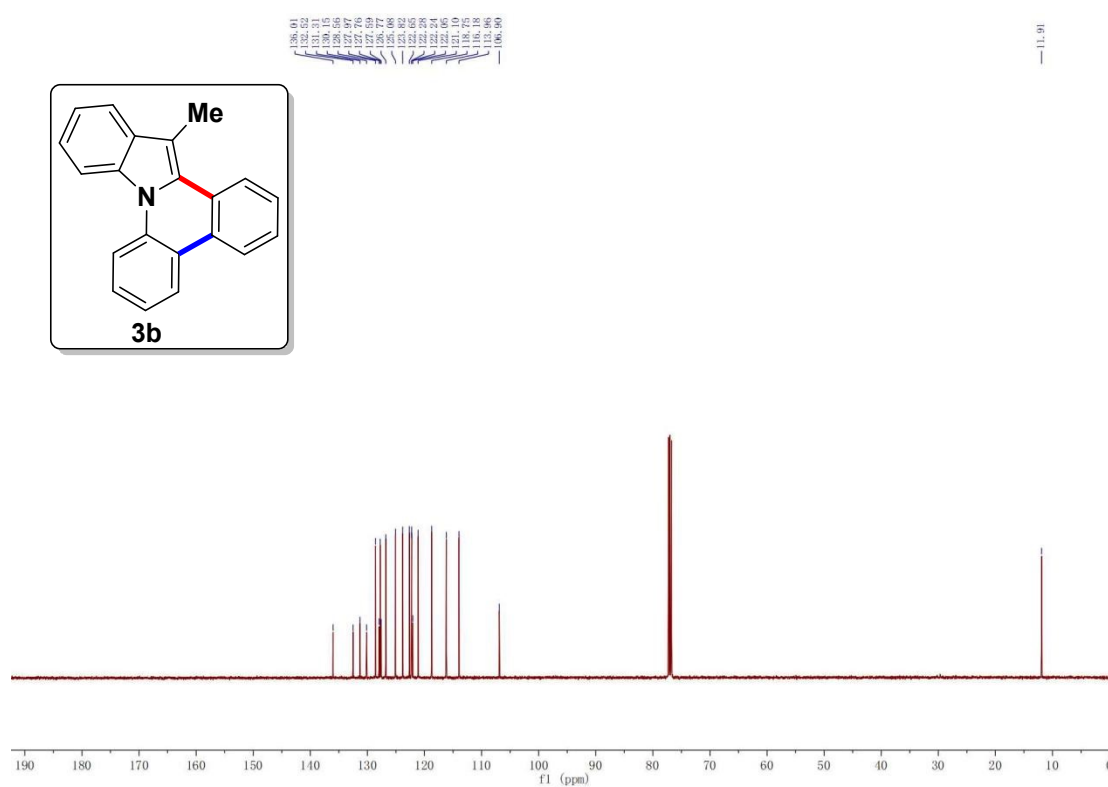
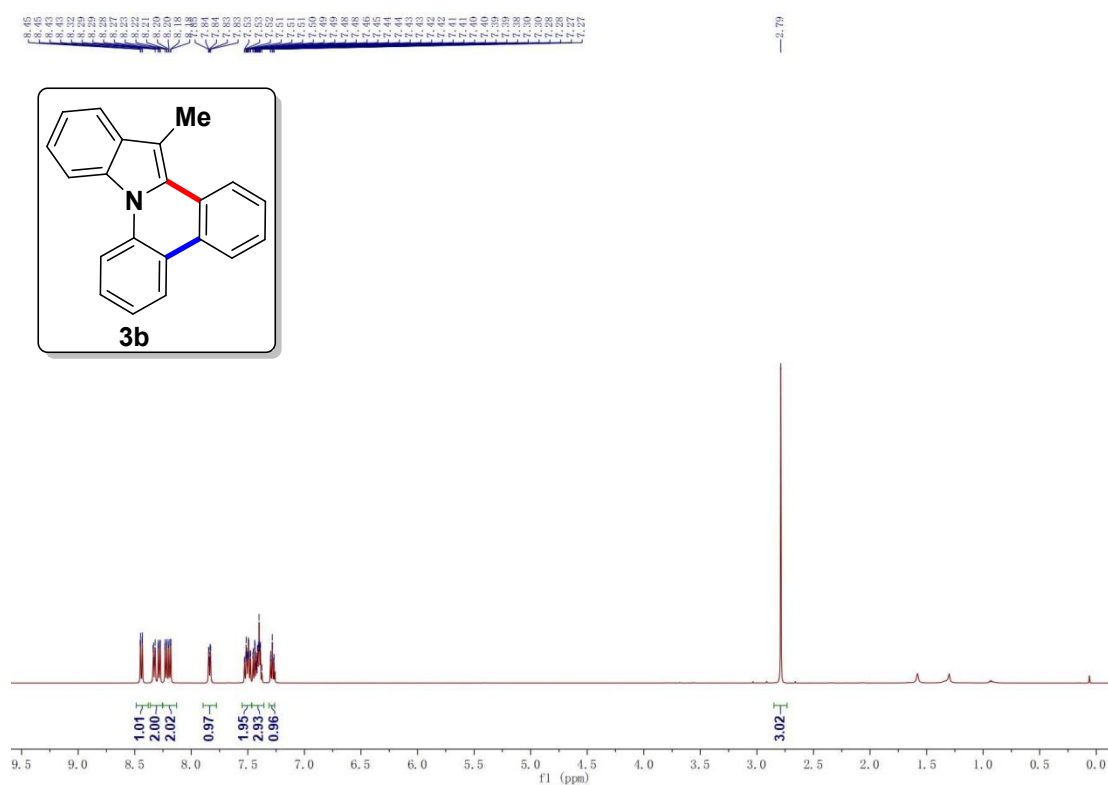


## 5. NMR spectroscopic data

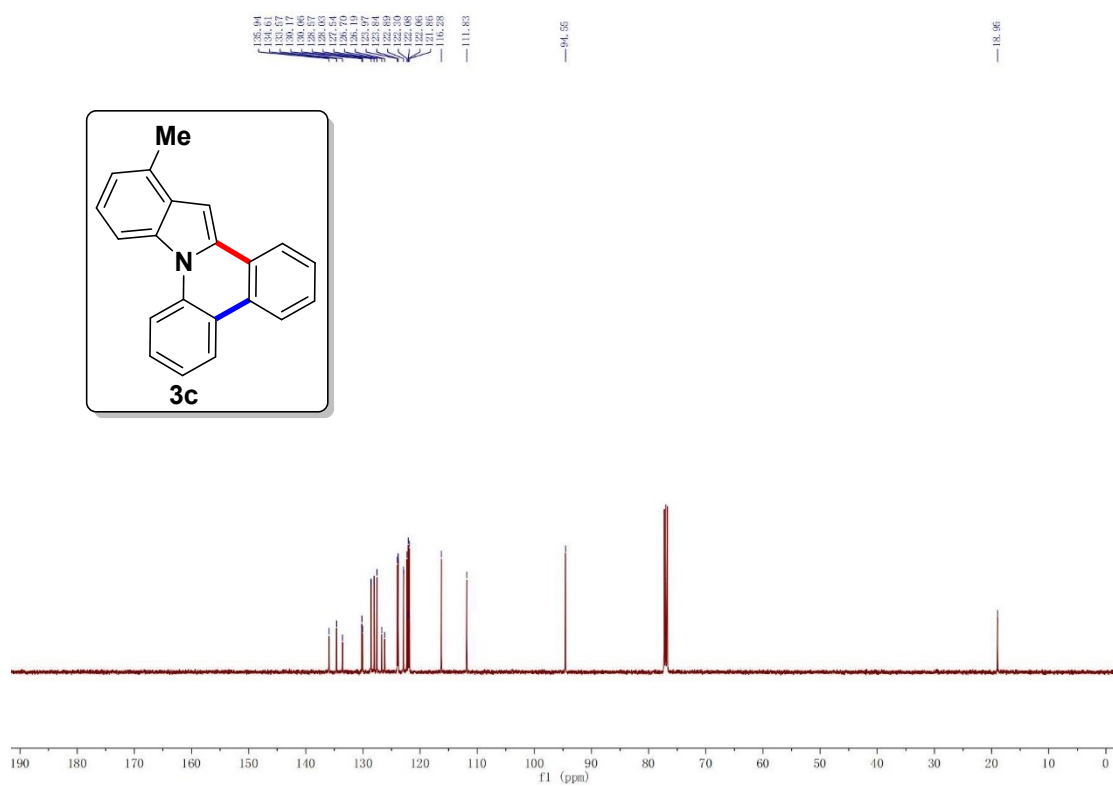
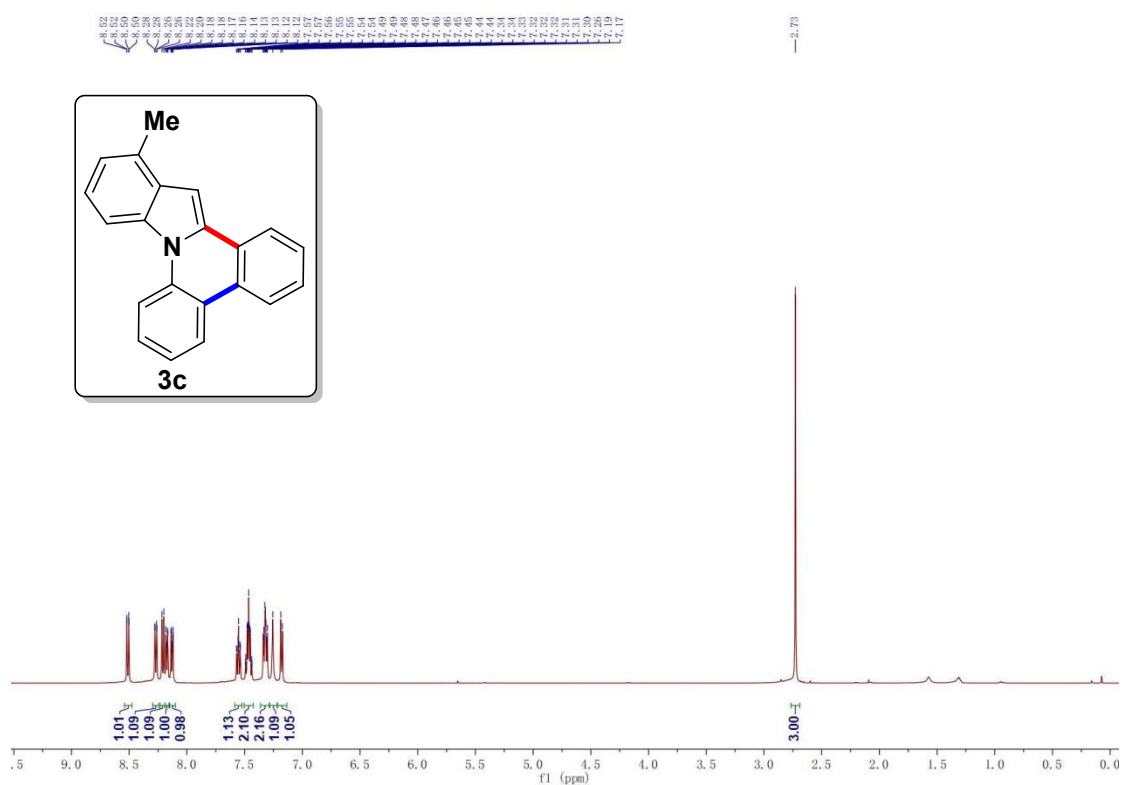
### indolo[1,2-f]phenanthridine (3a)



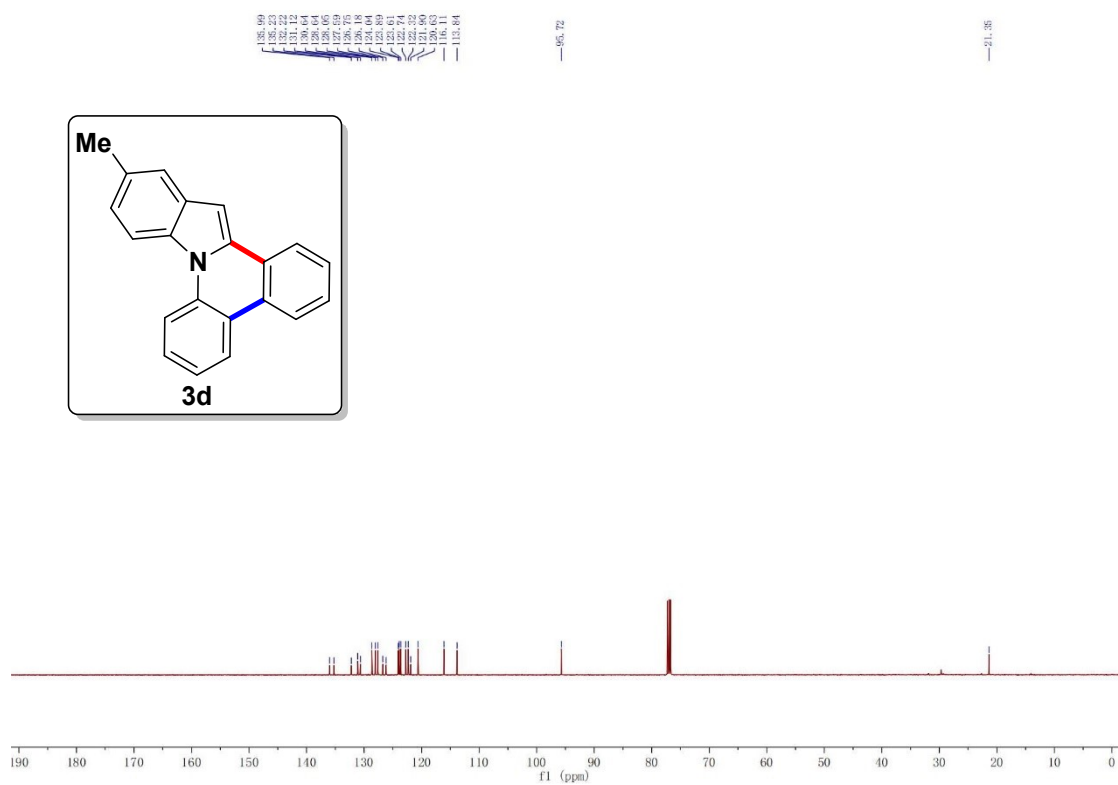
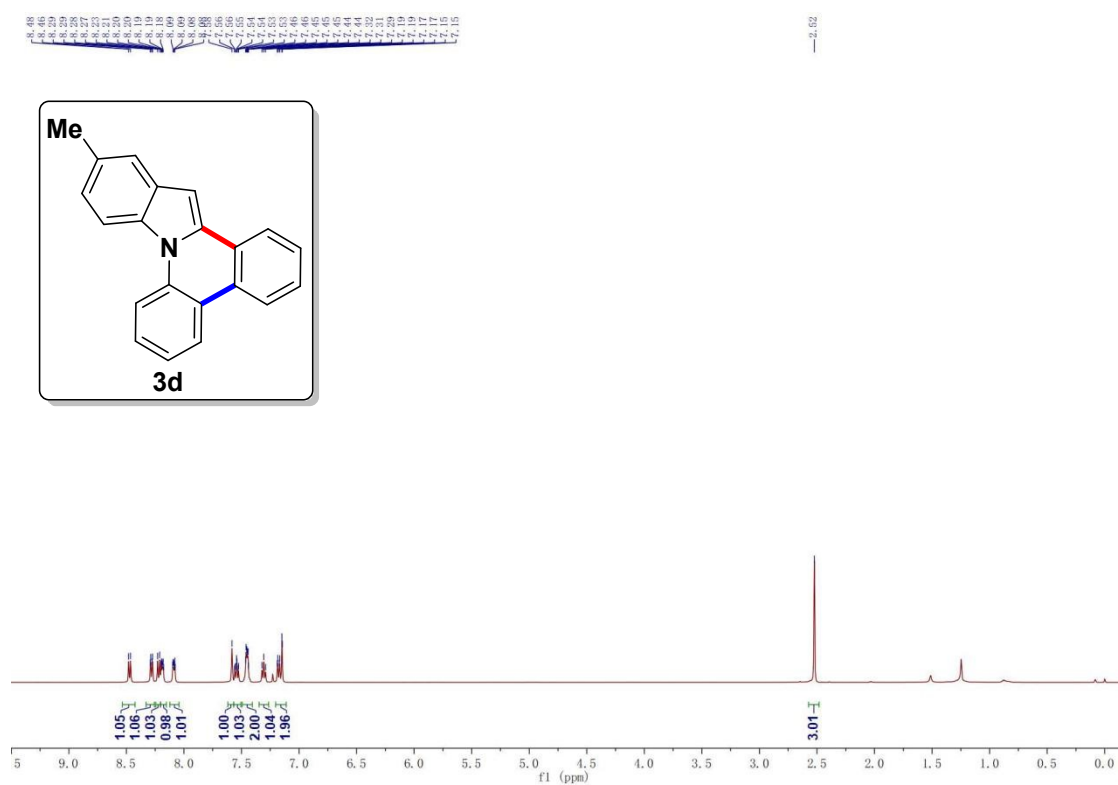
# 14-methylindolo[1,2-f]phenanthridine (3b)



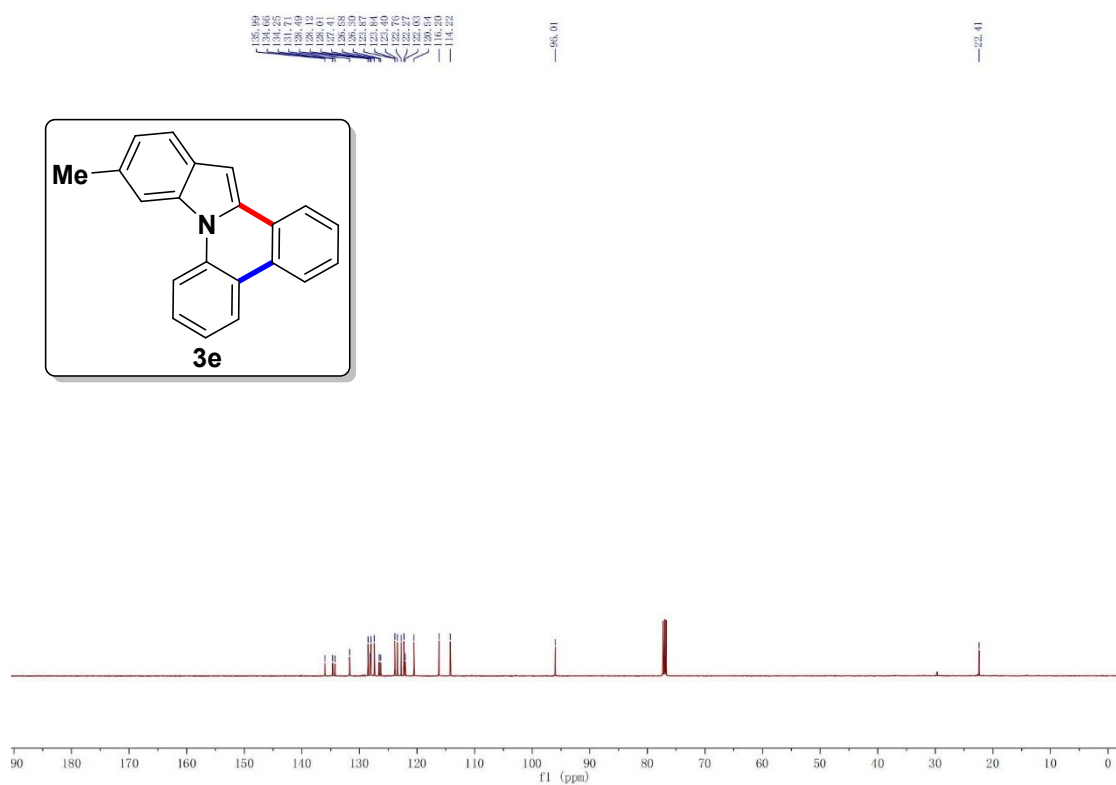
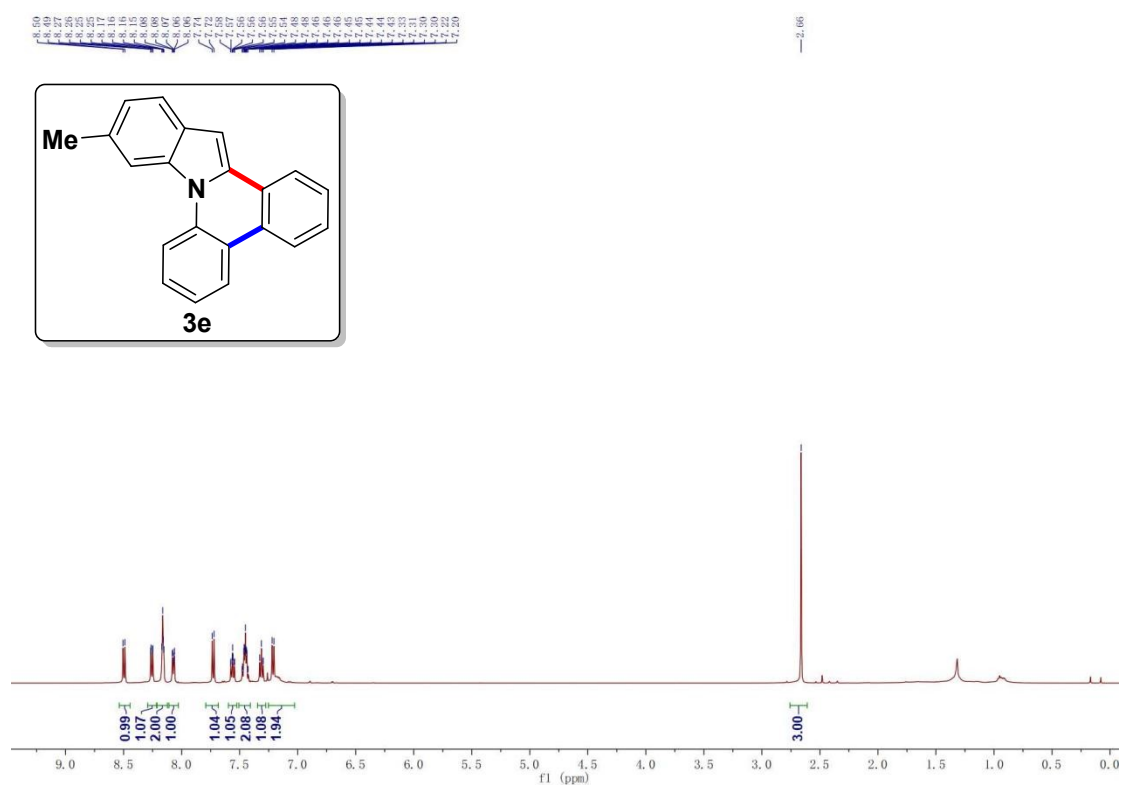
### 13-methylindolo[1,2-f]phenanthridine (3c)



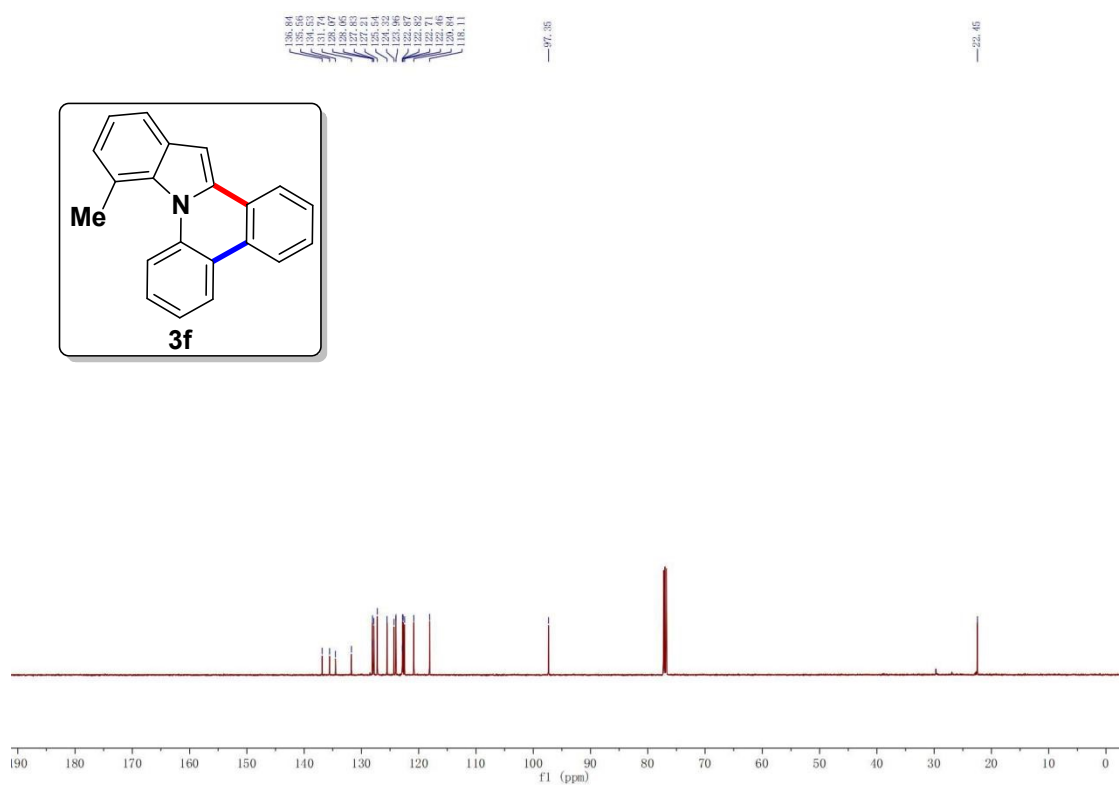
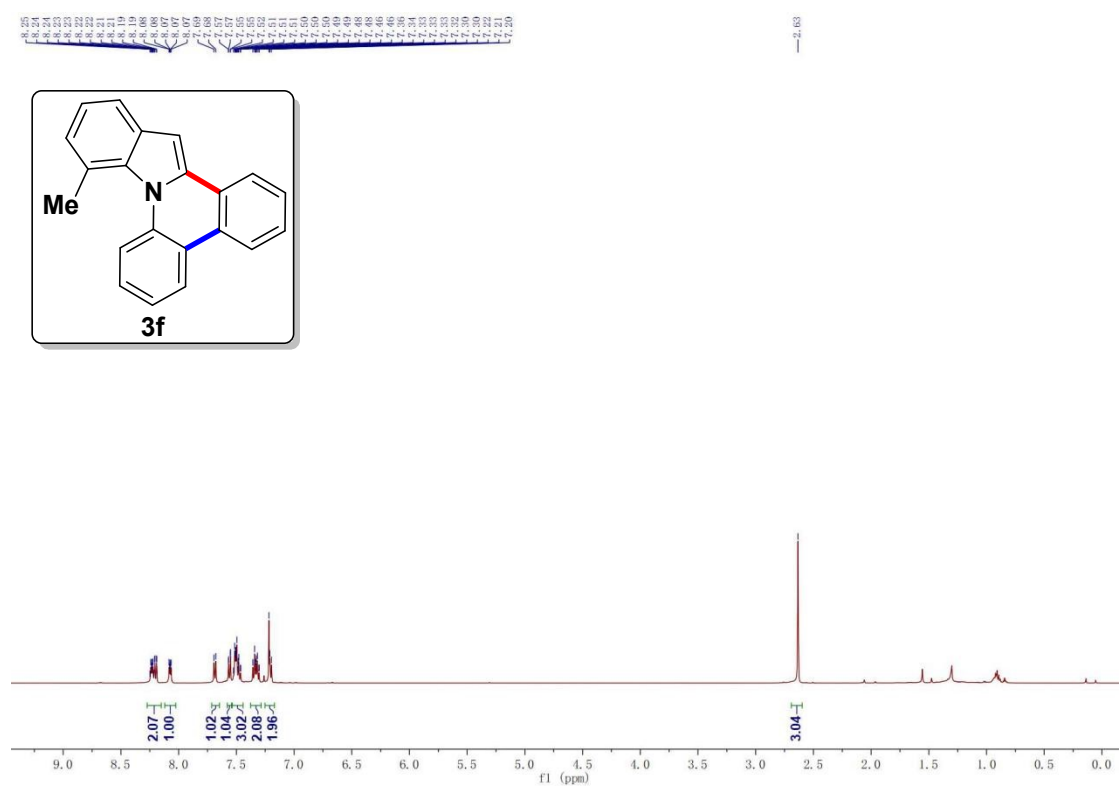
### 12-methylindolo[1,2-f]phenanthridine (3d)



# 11-methylindolo[1,2-f]phenanthridine (3e)



# 10-methylindolo[1,2-f]phenanthridine (3f)



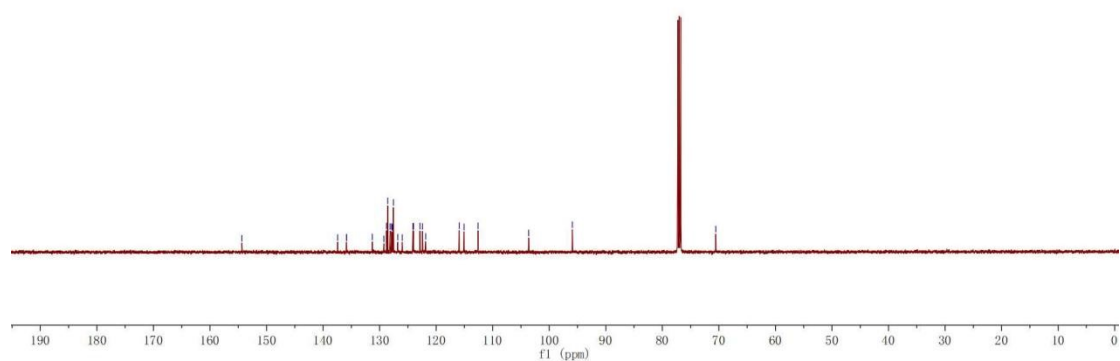
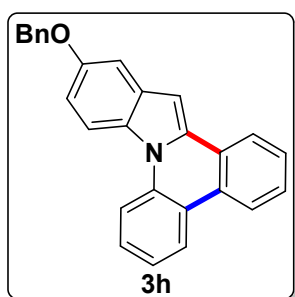
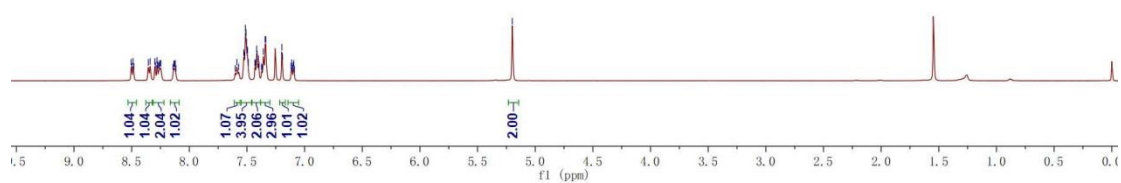
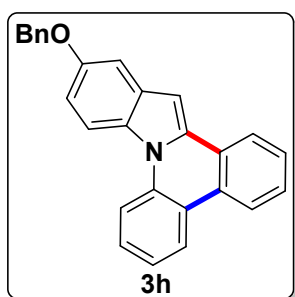
Chemical structure of compound **3g** is shown, which is a tricyclic indole derivative. The structure features a methoxy group (MeO) and is labeled **3g**.

The  $^1\text{H}$  NMR spectrum (CDCl<sub>3</sub>) shows the following peaks and integrations:

- Aromatic region (7.0–8.5 ppm): Multiple peaks with integrations of 1.00, 1.01, 1.00, 0.98, 1.02, 1.01, 1.01, 0.98, and 0.98.
- Methoxy singlet (3.94 ppm): Integration of 2.98.

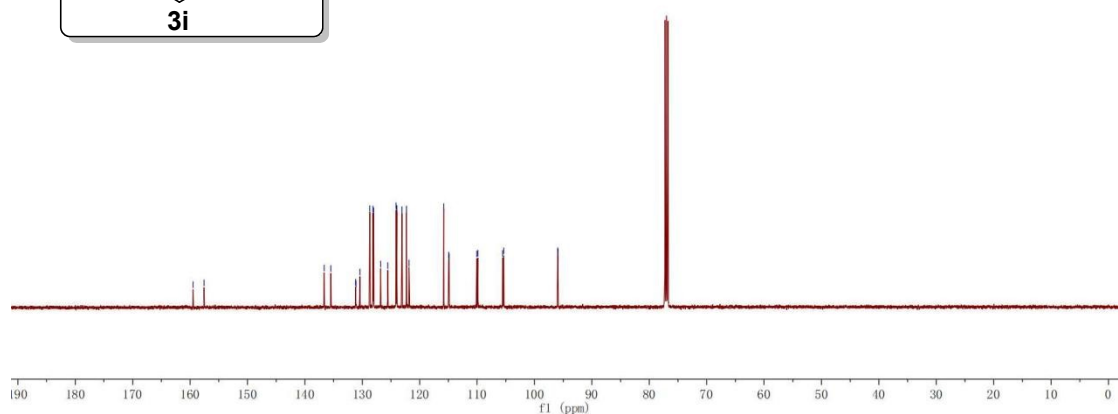
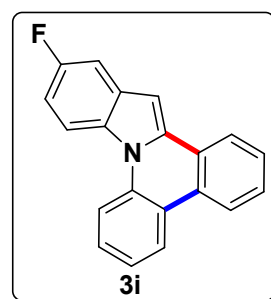
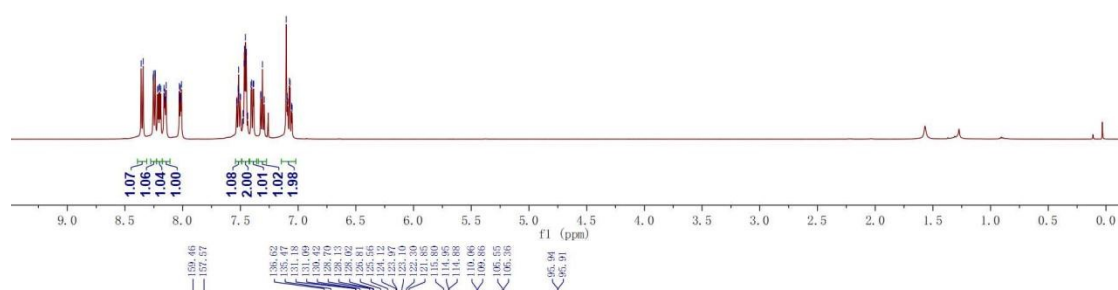
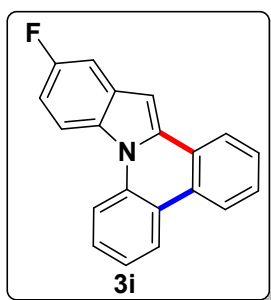


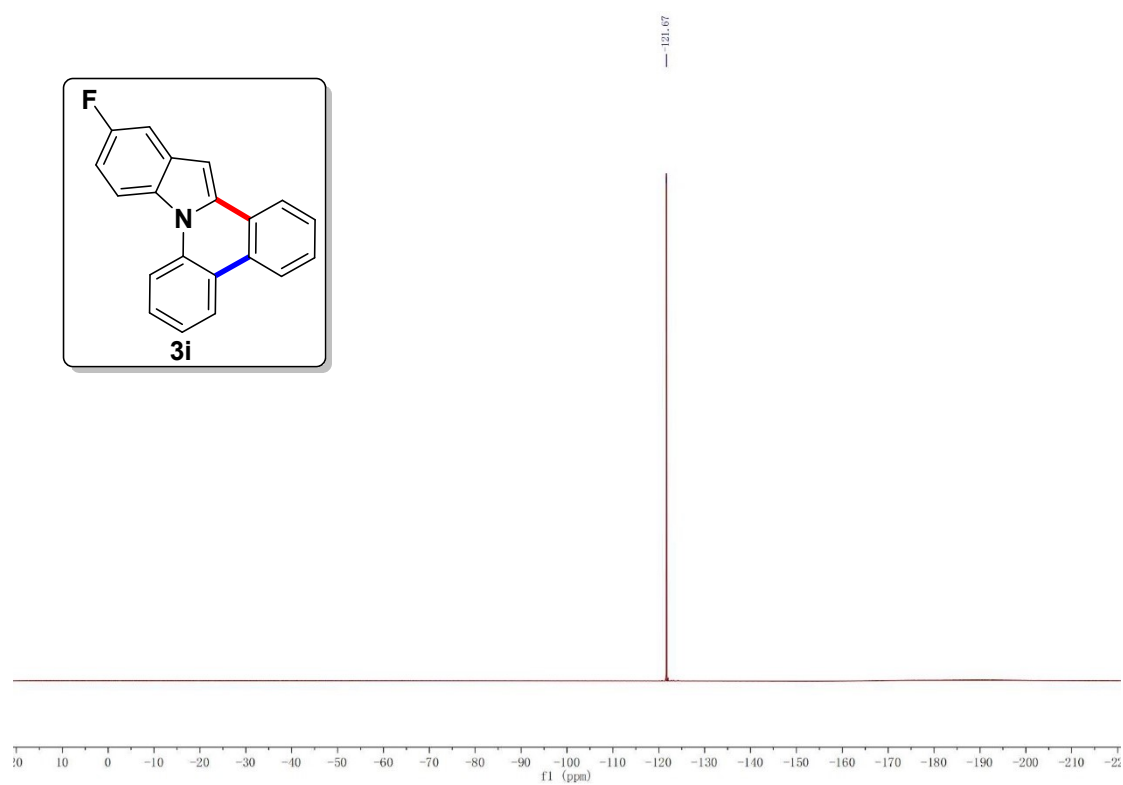
## 12-(benzyloxy)indolo[1,2-f]phenanthridine (3h)



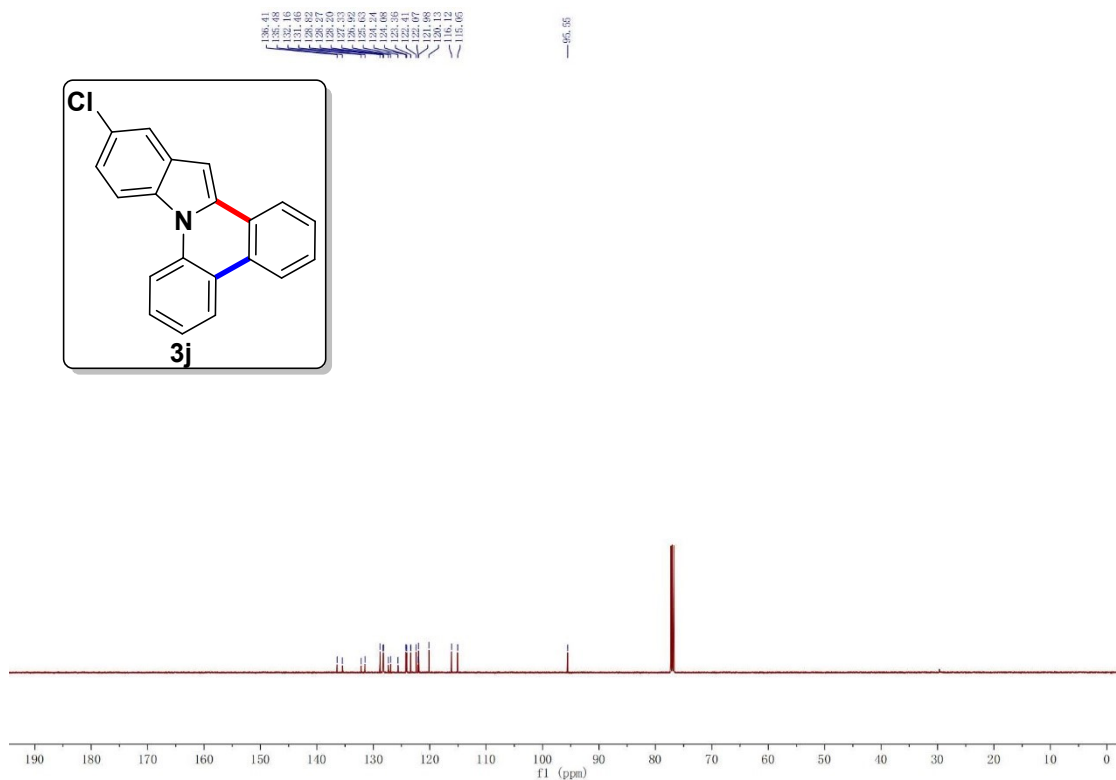
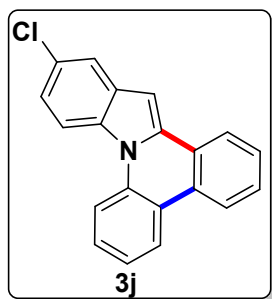
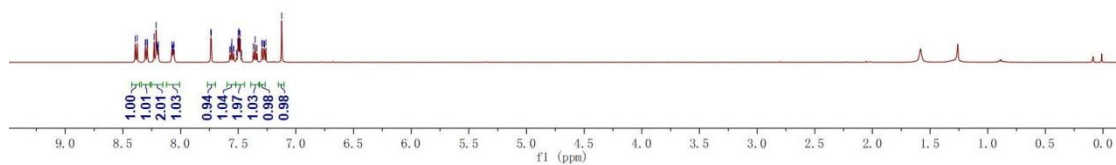
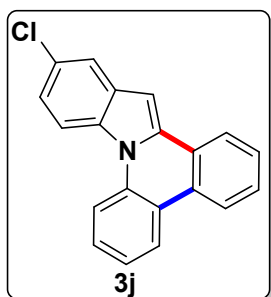


# 12-fluoroindolo[1,2-f]phenanthridine (3i)

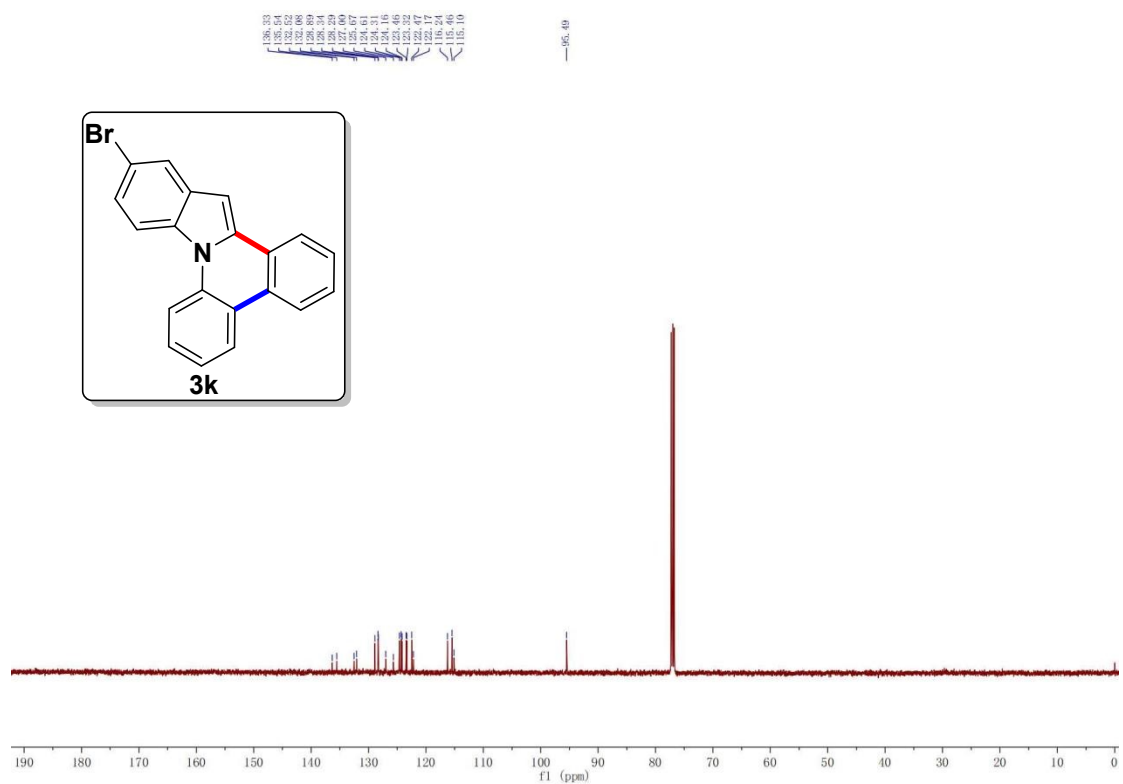
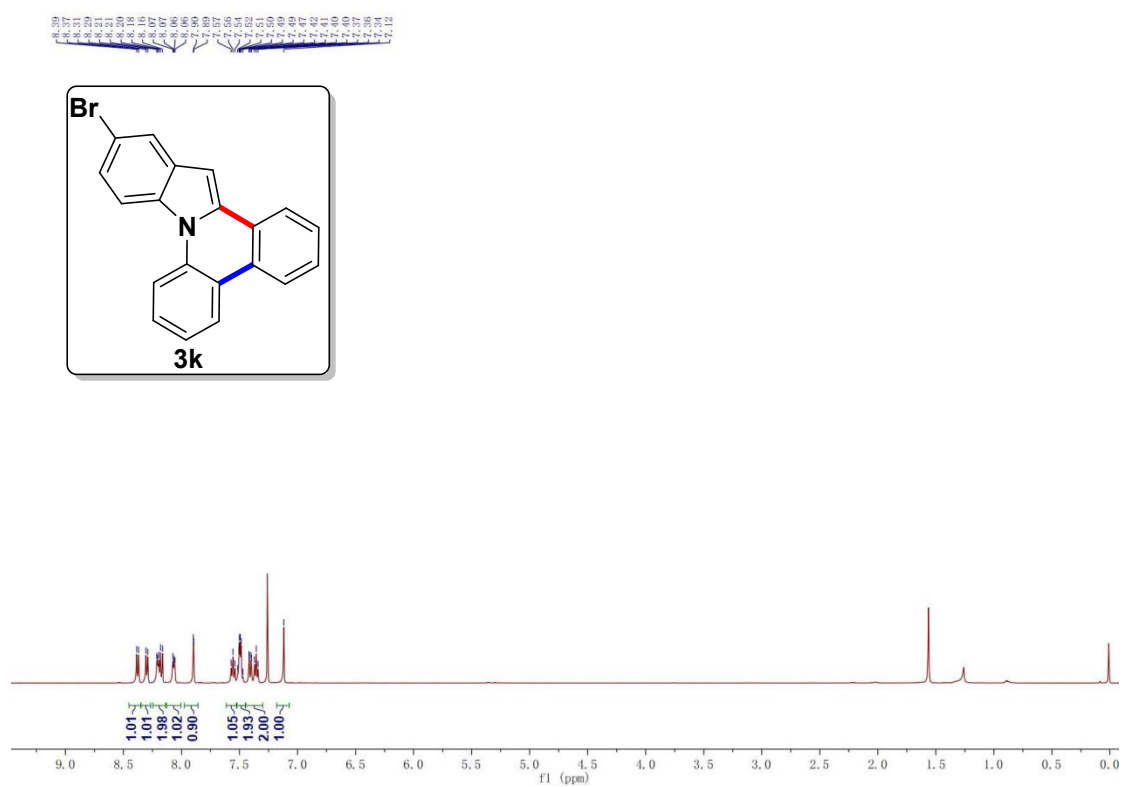




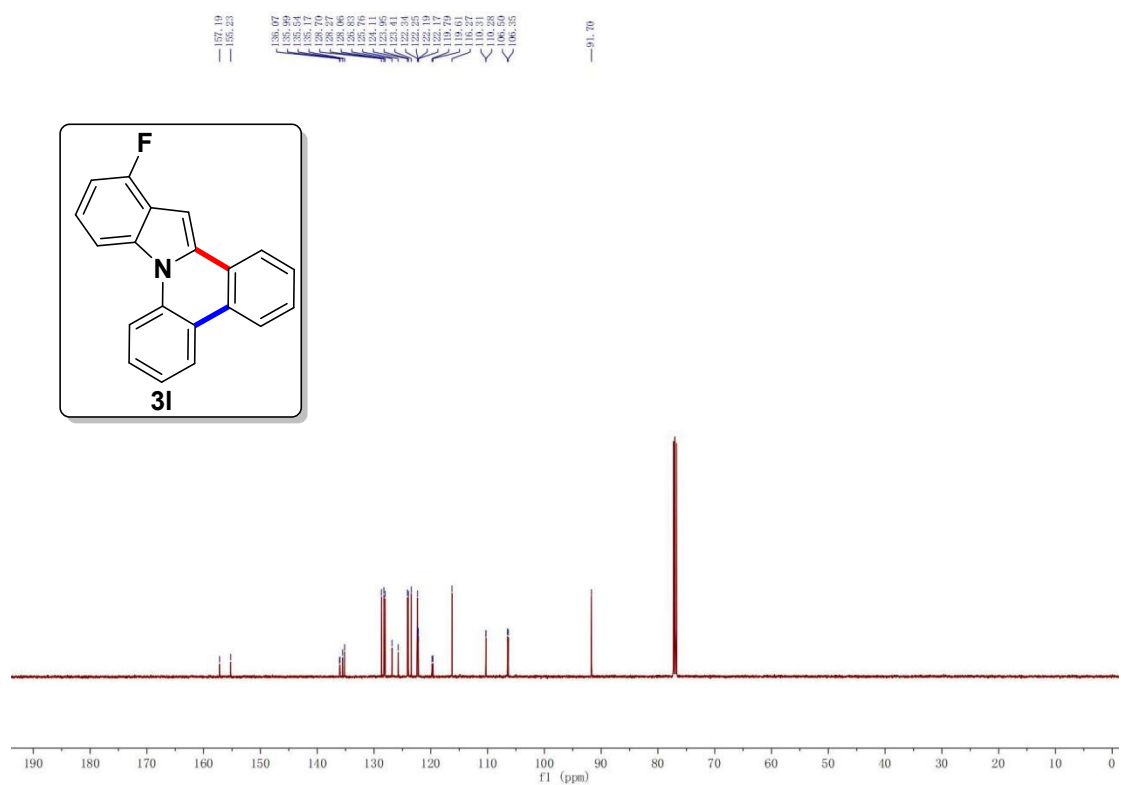
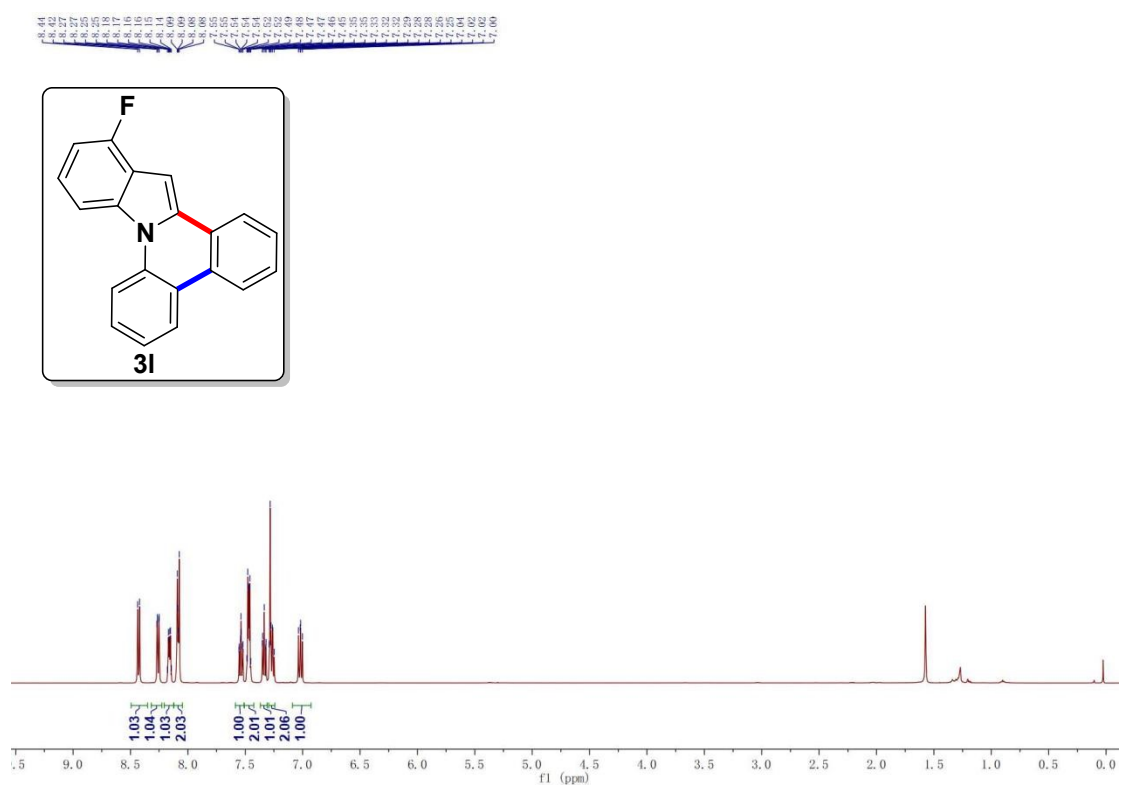
# 12-chloroindolo[1,2-f]phenanthridine (3j)

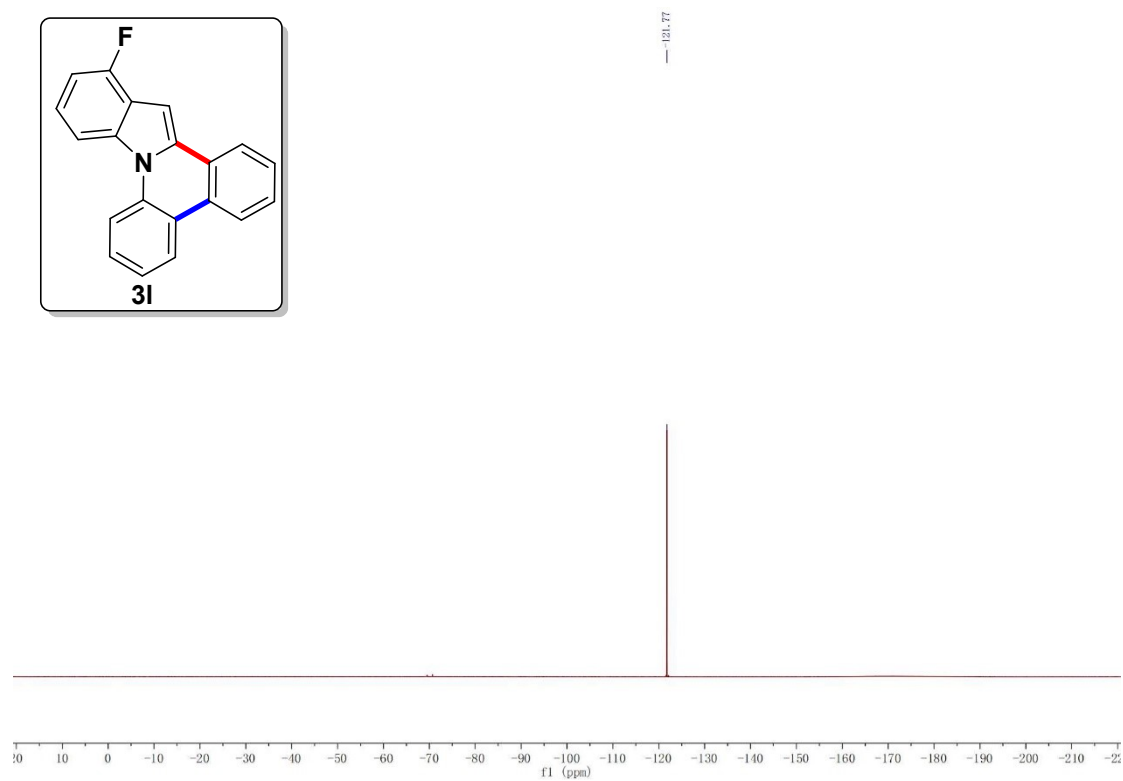


### 12-bromoindolo[1,2-f]phenanthridine (3k)

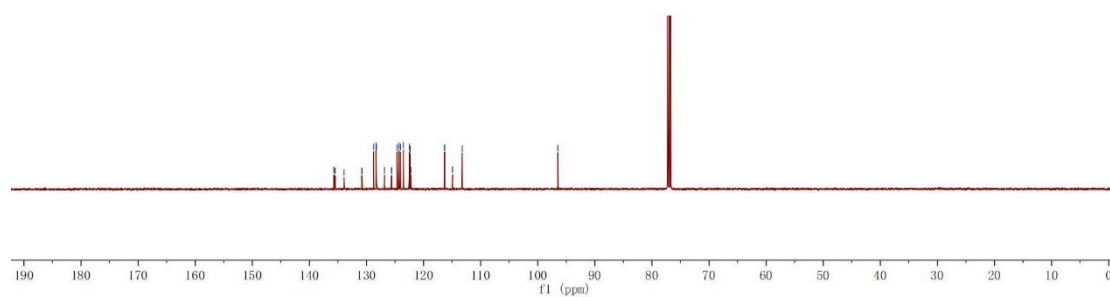
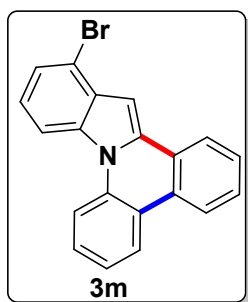
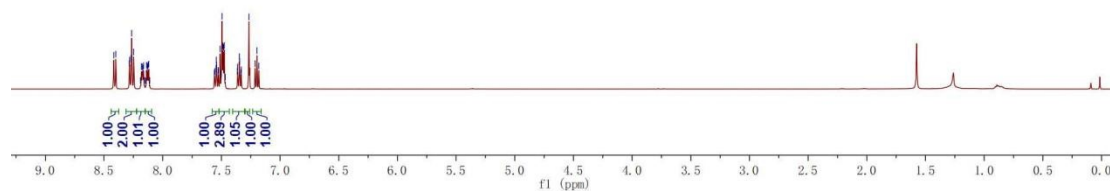
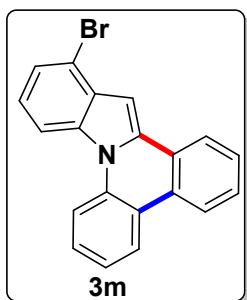


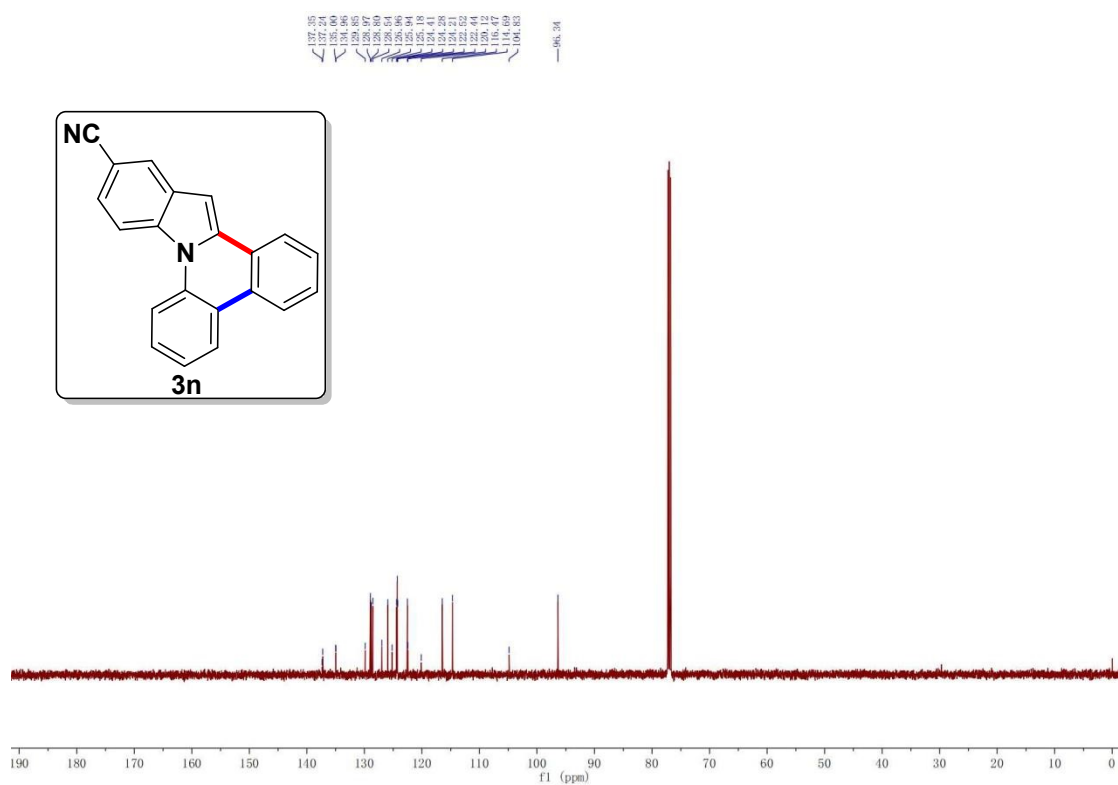
# 13-fluoroindolo[1,2-f]phenanthridine (3I)





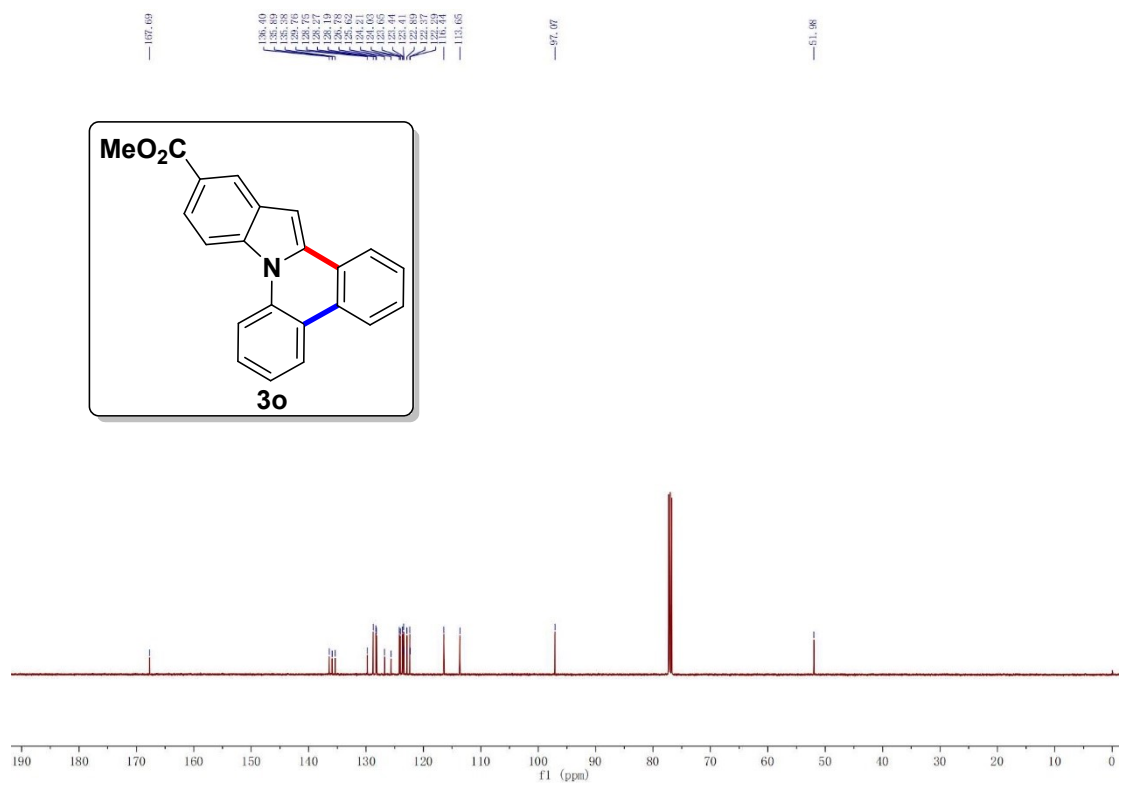
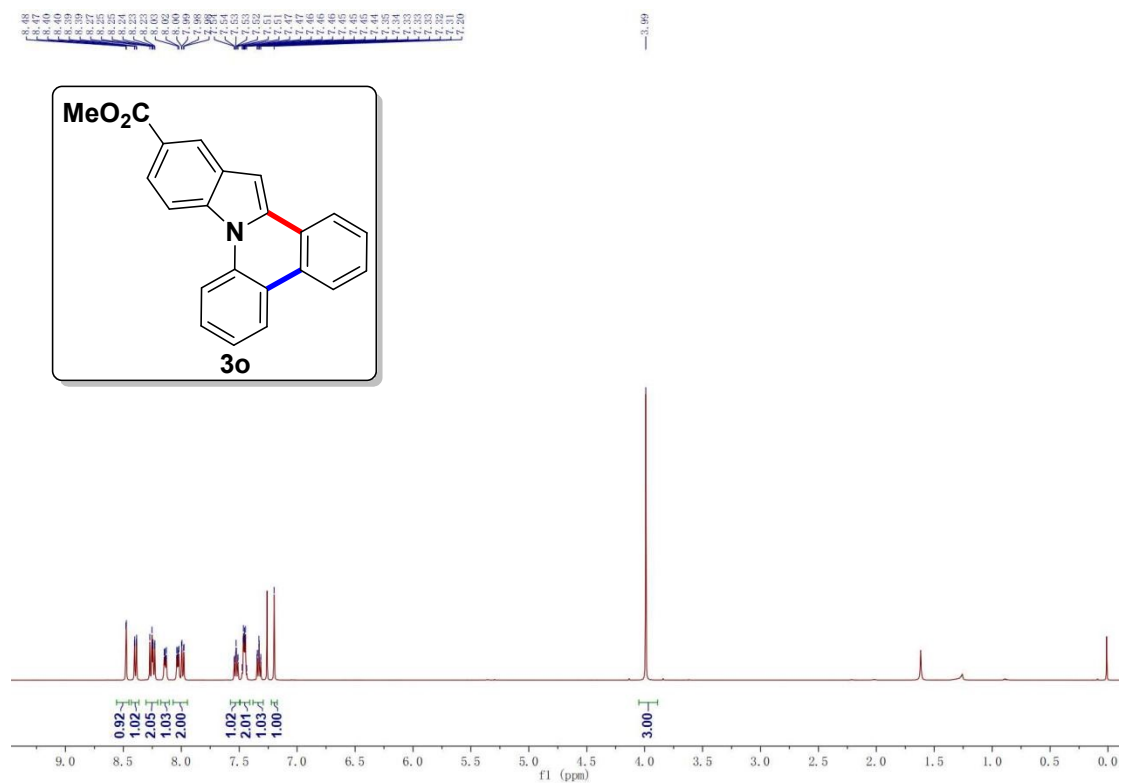
# 13-bromoindolo[1,2-f]phenanthridine (3m)



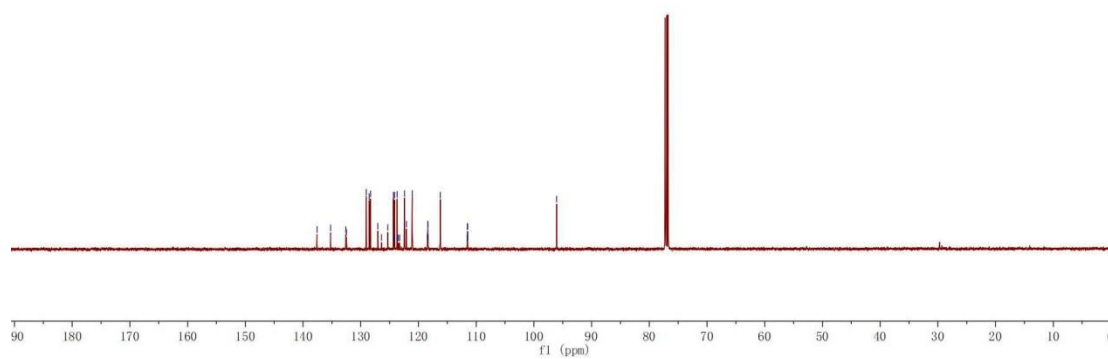
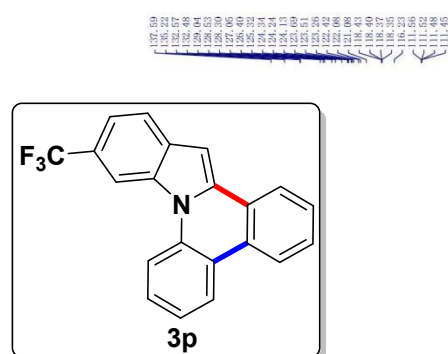
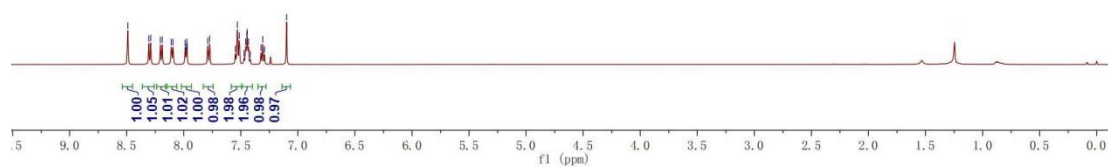
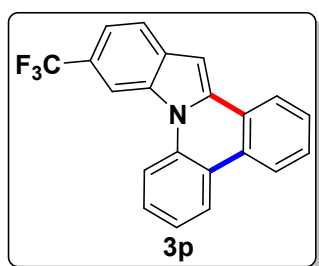
[illegible]

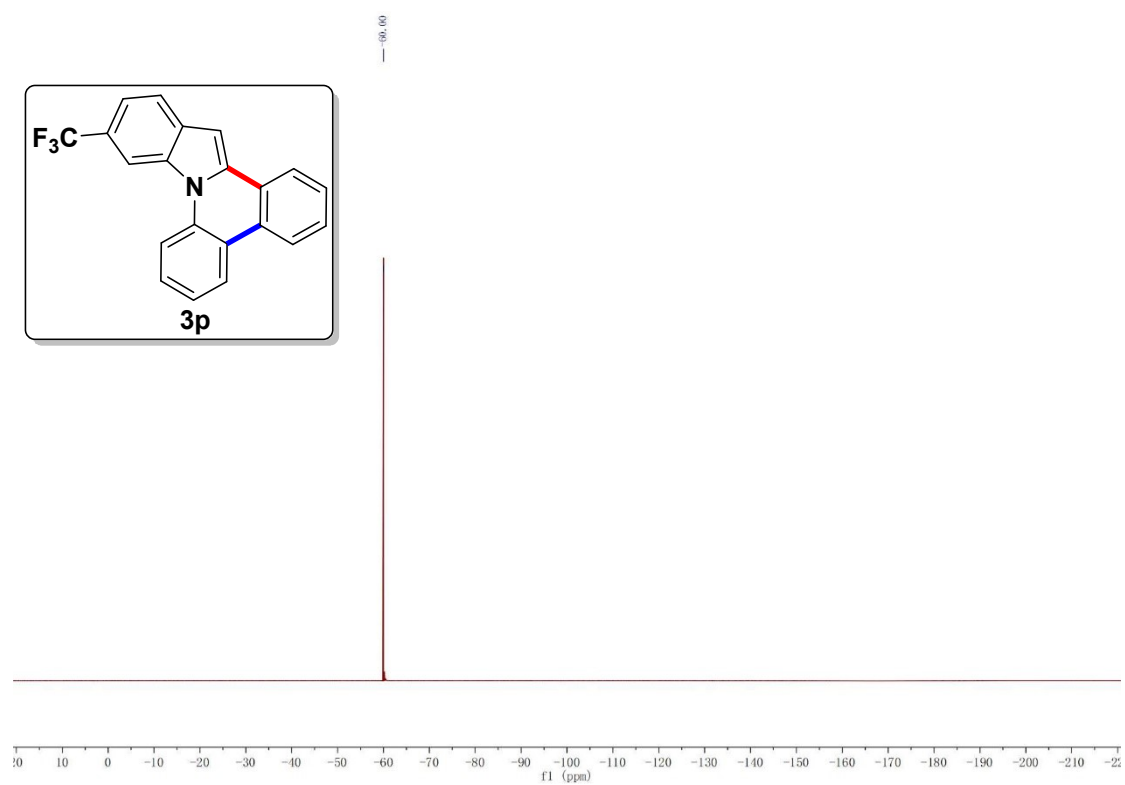


**methyl indolo[1,2-f]phenanthridine-12-carboxylate (3o)**

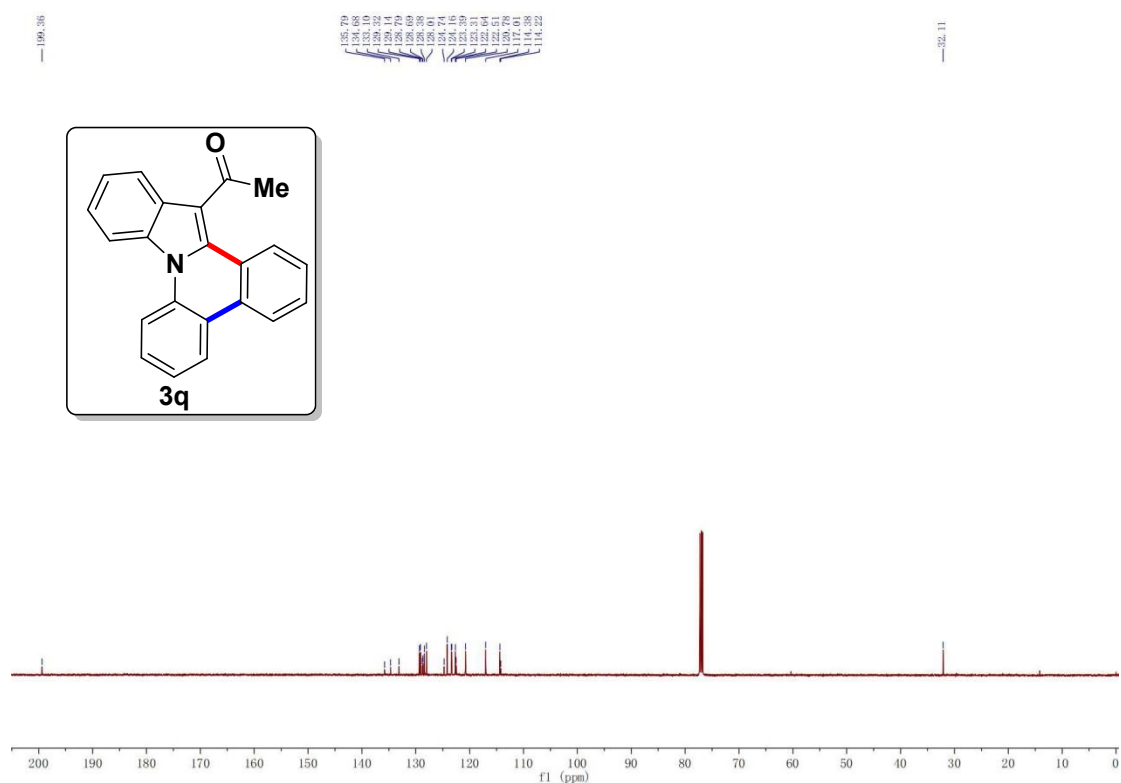
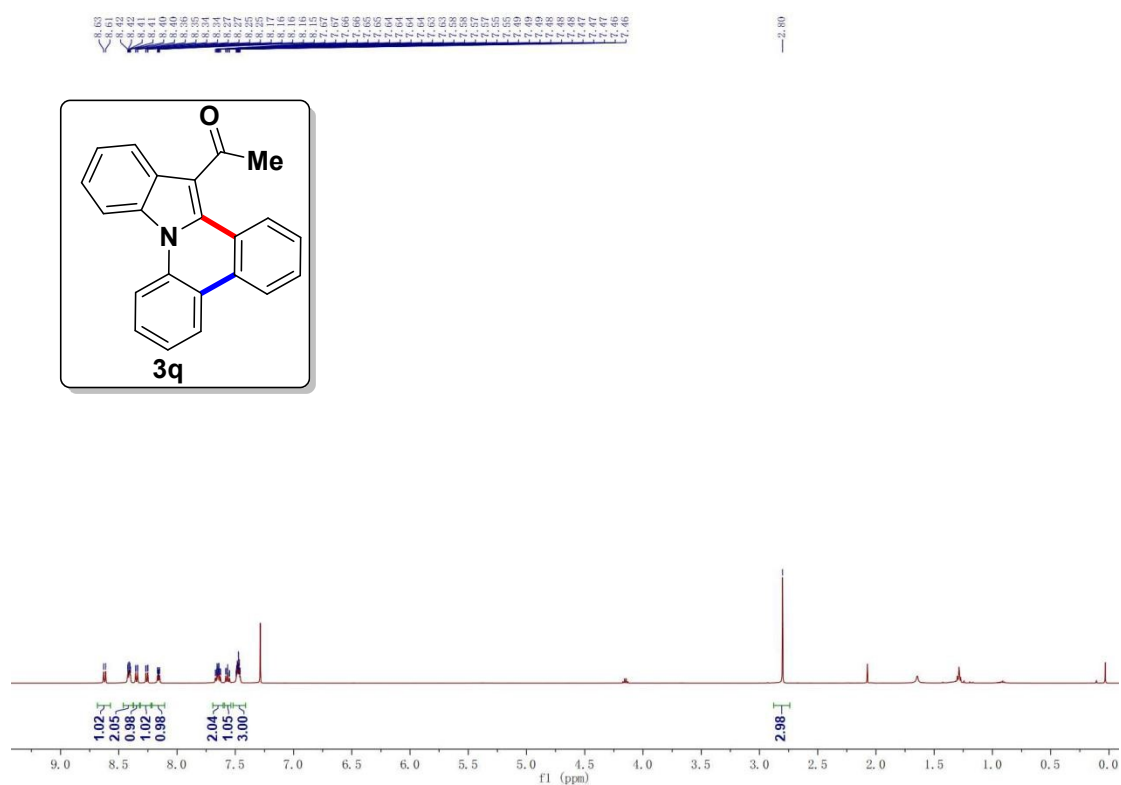


# 11-(trifluoromethyl)indolo[1,2-f]phenanthridine (3p)

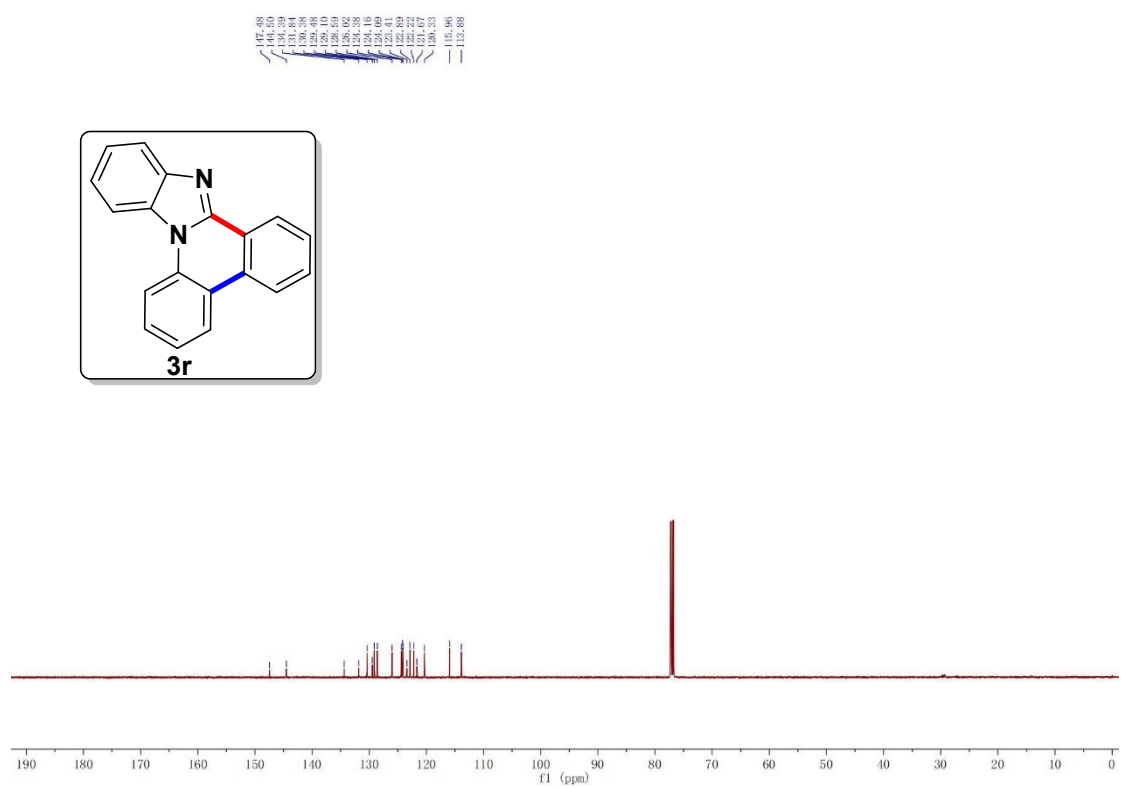
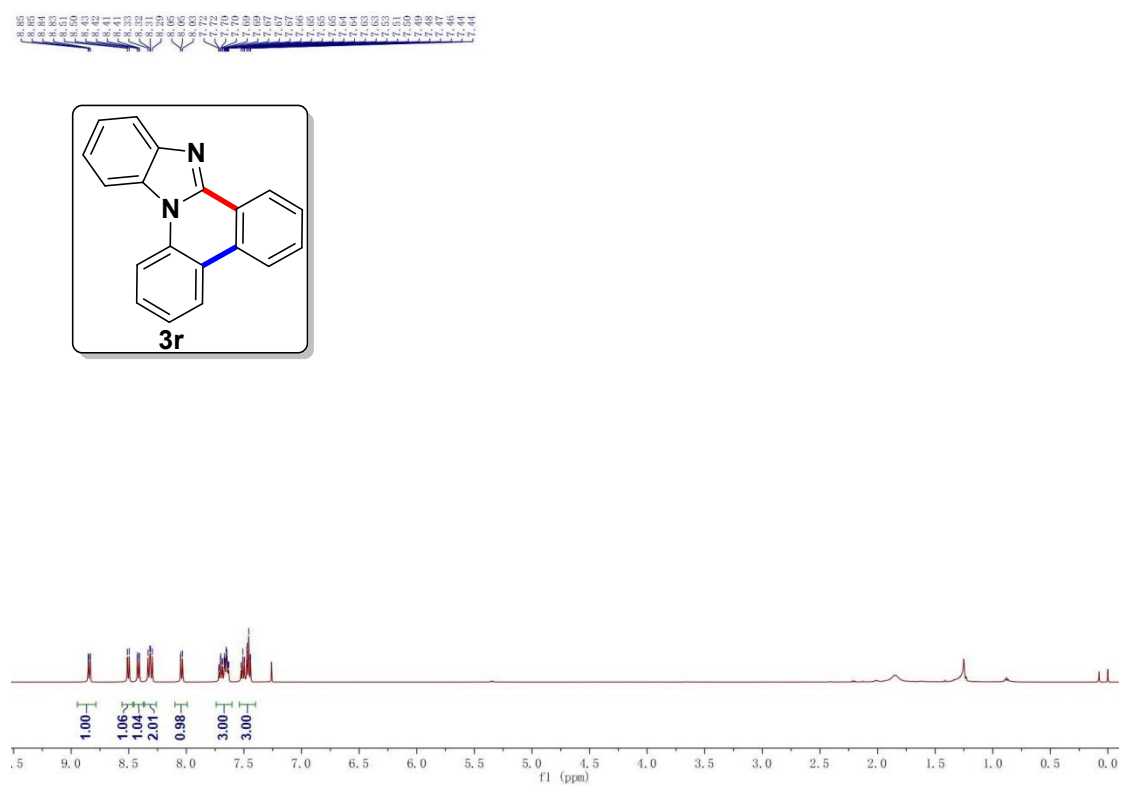




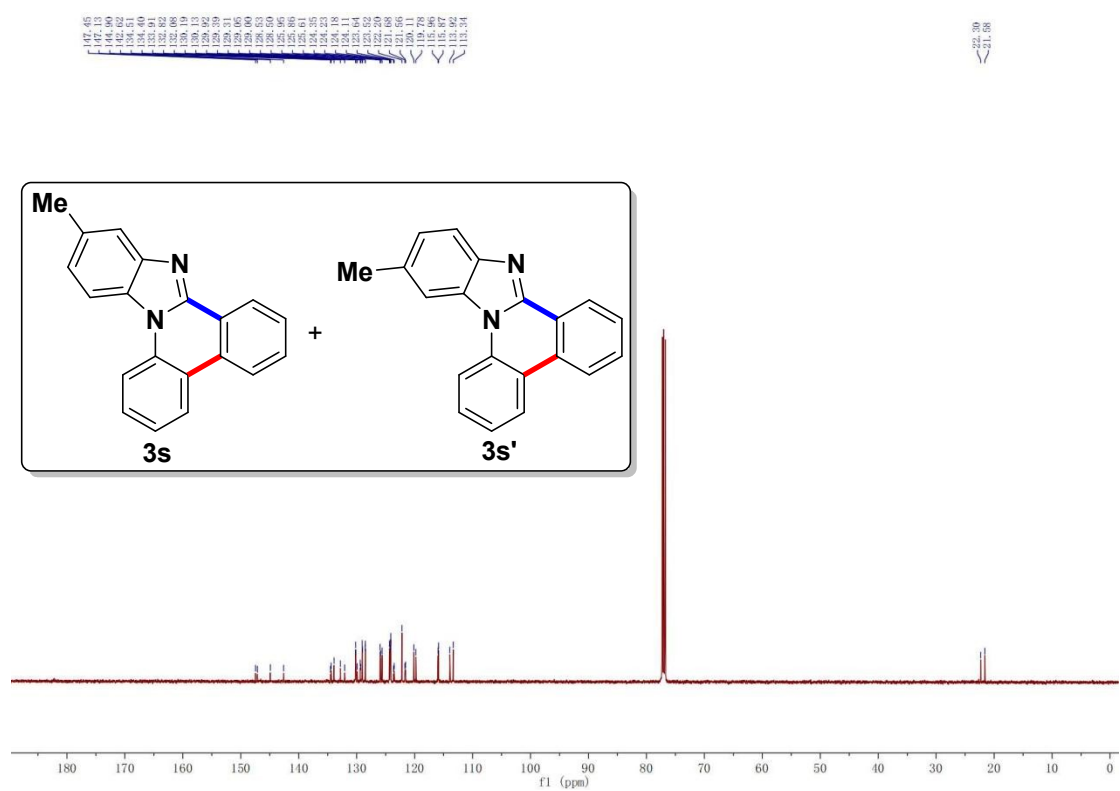
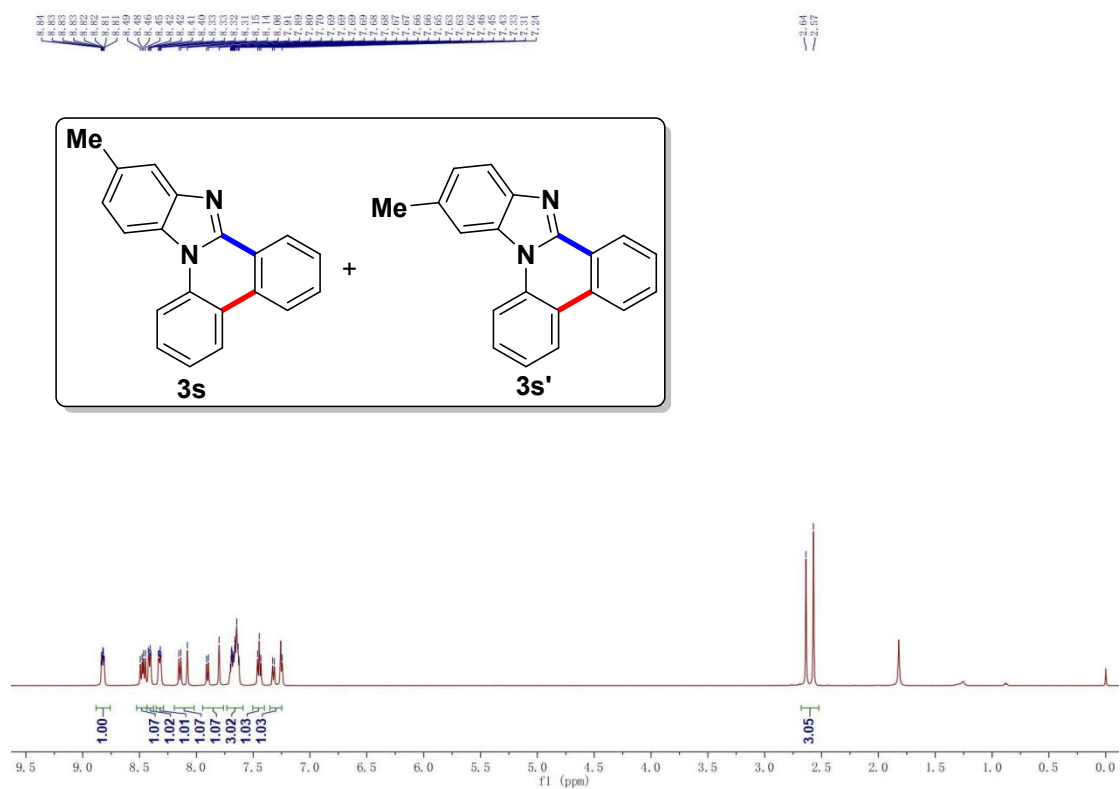
# 1-(indolo[1,2-f]phenanthridin-14-yl)ethan-1-one (3q)



**benzo[4,5]imidazo[1,2-f]phenanthridine (3r)**



11-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (3s) and 12-methylbenzo[4,5]imidazo[1,2-f]phenanthridine (3s')



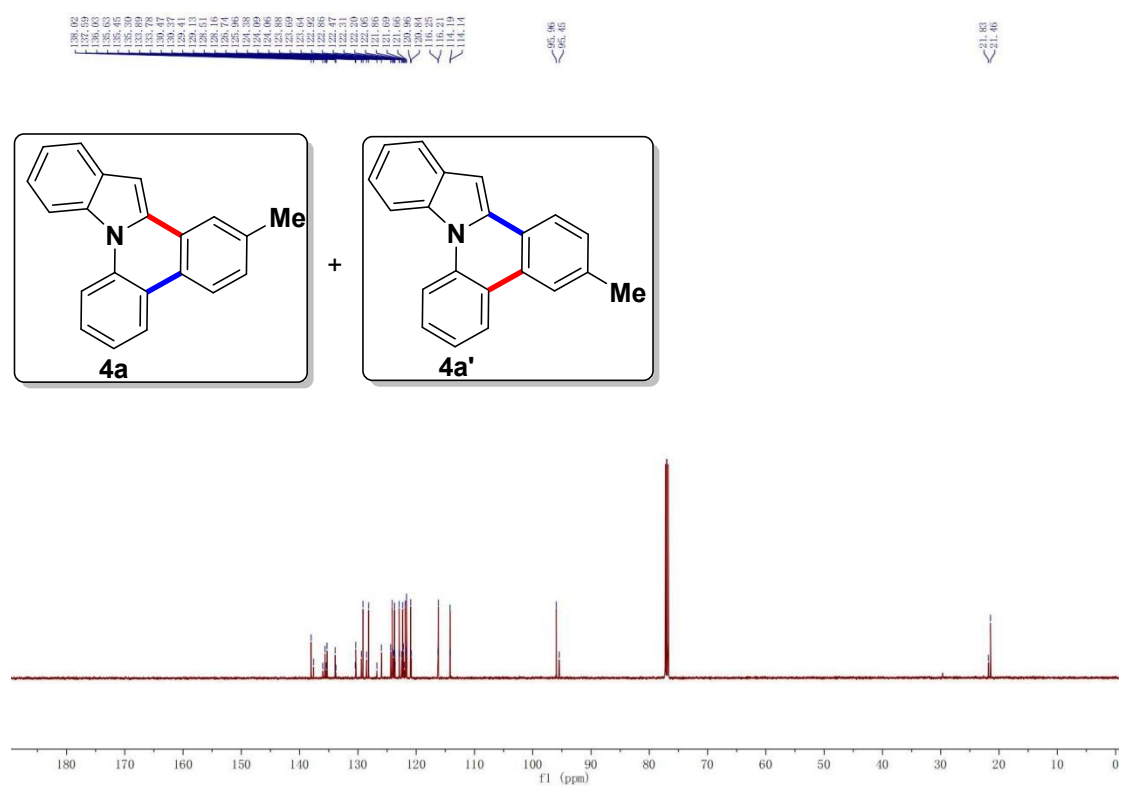
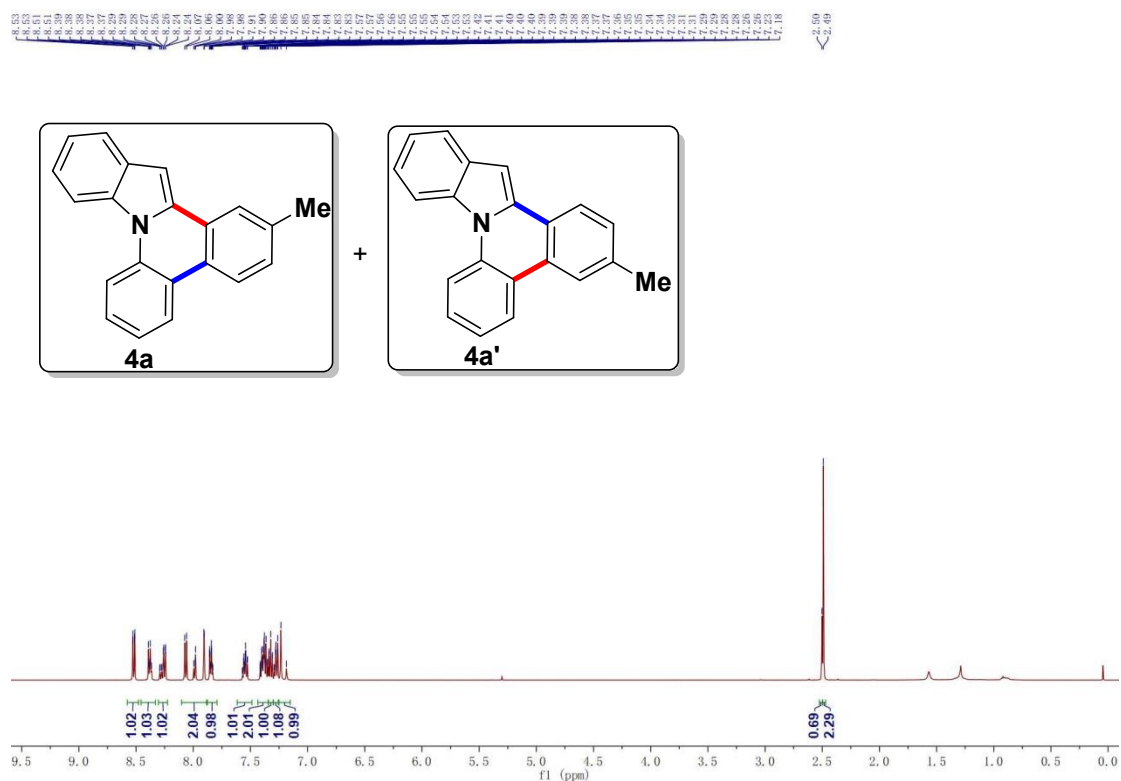
The chemical structure of **3t** is shown in a box. It is a spirocyclic compound consisting of a benzimidazole core fused to a benzene ring. The benzimidazole part has a dimethylamino group (-NMe<sub>2</sub>) attached to the 2-position. The benzene ring is fused to the 1-position of the benzimidazole. The structure is labeled **3t**.

The <sup>1</sup>H NMR spectrum is displayed below the structure. The x-axis is labeled 'f1 (ppm)' and ranges from 0 to 10. The spectrum shows several peaks with corresponding integrations:

- Peak at ~7.2 ppm: integration 1.01
- Peak at ~7.1 ppm: integration 1.02
- Peak at ~7.0 ppm: integration 1.03
- Peak at ~6.9 ppm: integration 1.02
- Peak at ~6.8 ppm: integration 1.03
- Peak at ~6.7 ppm: integration 1.98
- Peak at ~6.6 ppm: integration 1.02
- Peak at ~6.5 ppm: integration 3.07
- Peak at ~4.0 ppm: integration 2.02
- Peak at ~2.5 ppm: integration 6.00

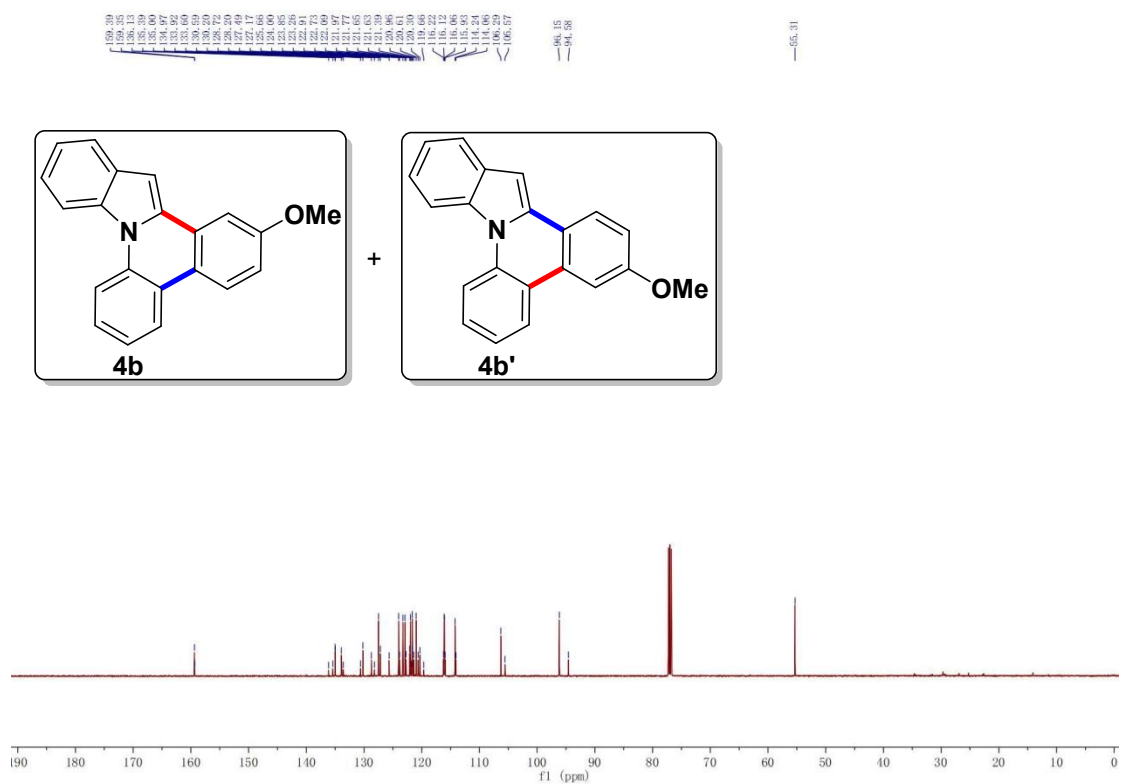
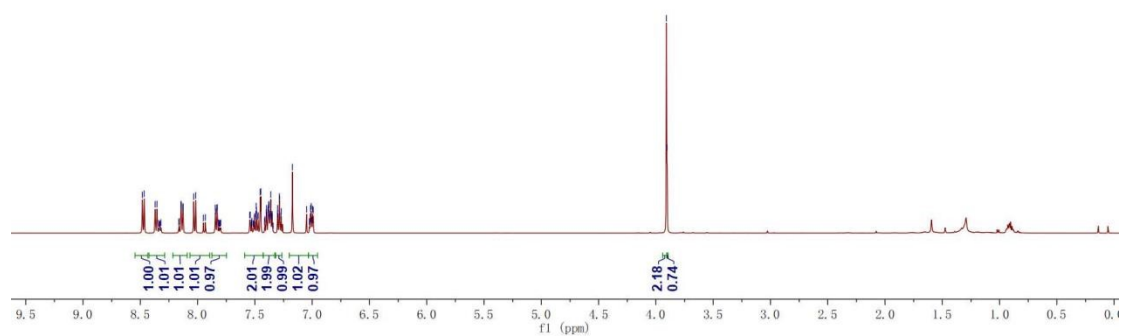


**2-methylindolo[1,2-f]phenanthridine (4a) and 3-methylindolo[1,2-f]phenanthridine (4a')**

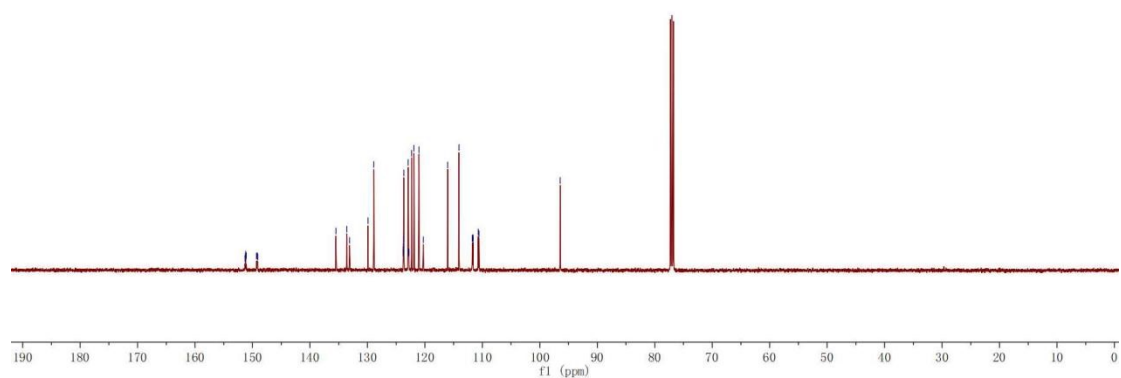
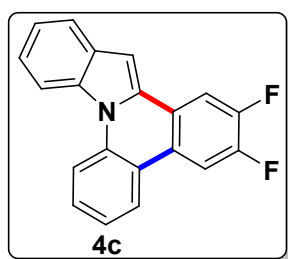
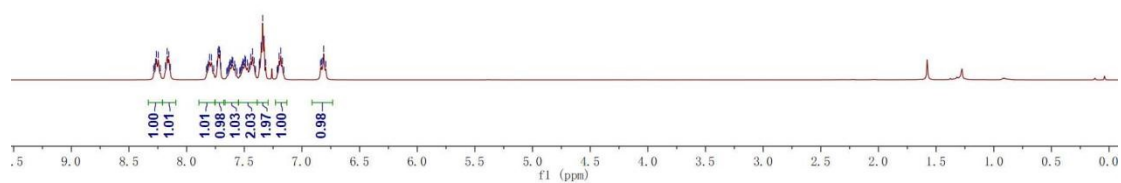
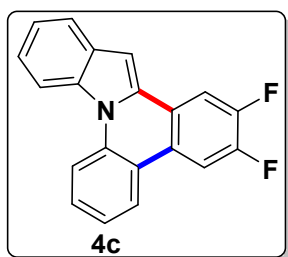


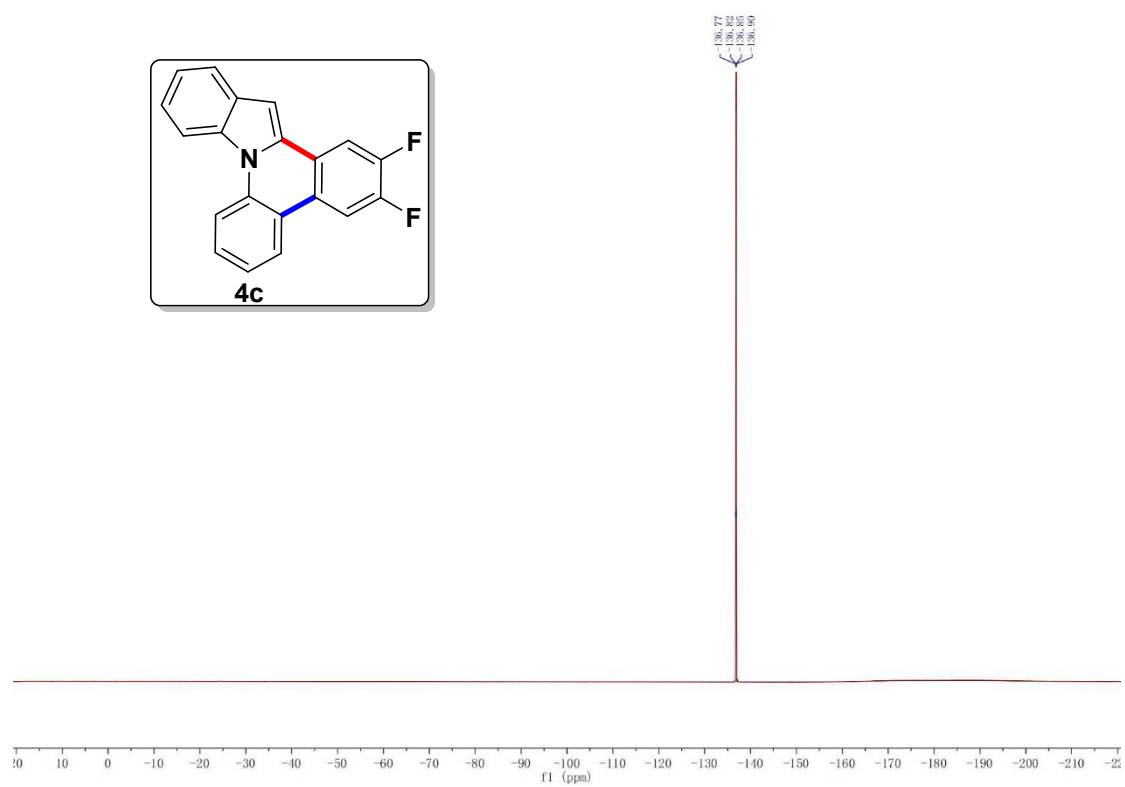


8.48	8.47	8.46	8.45	8.44	8.43	8.42	8.41	8.40	8.39	8.38	8.37	8.36	8.35	8.34	8.33	8.32	8.31	8.30	8.29	8.28	8.27	8.26	8.25	8.24	8.23	8.22	8.21	8.20	8.19	8.18	8.17	8.16	8.15	8.14	8.13	8.12	8.11	8.10	8.09	8.08	8.07	8.06	8.05	8.04	8.03	8.02	8.01	8.00	7.99	7.98	7.97	7.96	7.95	7.94	7.93	7.92	7.91	7.90	7.89	7.88	7.87	7.86	7.85	7.84	7.83	7.82	7.81	7.80	7.79	7.78	7.77	7.76	7.75	7.74	7.73	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65	7.64	7.63	7.62	7.61	7.60	7.59	7.58	7.57	7.56	7.55	7.54	7.53	7.52	7.51	7.50	7.49	7.48	7.47	7.46	7.45	7.44	7.43	7.42	7.41	7.40	7.39	7.38	7.37	7.36	7.35	7.34	7.33	7.32	7.31	7.30	7.29	7.28	7.27	7.26	7.25	7.24	7.23	7.22	7.21	7.20	7.19	7.18	7.17	7.16	7.15	7.14	7.13	7.12	7.11	7.10	7.09	7.08	7.07	7.06	7.05	7.04	7.03	7.02	7.01	7.00	6.99	6.98	6.97	6.96	6.95	6.94	6.93	6.92	6.91	6.90	6.89	6.88	6.87	6.86	6.85	6.84	6.83	6.82	6.81	6.80	6.79	6.78	6.77	6.76	6.75	6.74	6.73	6.72	6.71	6.70	6.69	6.68	6.67	6.66	6.65	6.64	6.63	6.62	6.61	6.60	6.59	6.58	6.57	6.56	6.55	6.54	6.53	6.52	6.51	6.50	6.49	6.48	6.47	6.46	6.45	6.44	6.43	6.42	6.41	6.40	6.39	6.38	6.37	6.36	6.35	6.34	6.33	6.32	6.31	6.30	6.29	6.28	6.27	6.26	6.25	6.24	6.23	6.22	6.21	6.20	6.19	6.18	6.17	6.16	6.15	6.14	6.13	6.12	6.11	6.10	6.09	6.08	6.07	6.06	6.05	6.04	6.03	6.02	6.01	6.00	5.99	5.98	5.97	5.96	5.95	5.94	5.93	5.92	5.91	5.90	5.89	5.88	5.87	5.86	5.85	5.84	5.83	5.82	5.81	5.80	5.79	5.78	5.77	5.76	5.75	5.74	5.73	5.72	5.71	5.70	5.69	5.68	5.67	5.66	5.65	5.64	5.63	5.62	5.61	5.60	5.59	5.58	5.57	5.56	5.55	5.54	5.53	5.52	5.51	5.50	5.49	5.48	5.47	5.46	5.45	5.44	5.43	5.42	5.41	5.40	5.39	5.38	5.37	5.36	5.35	5.34	5.33	5.32	5.31	5.30	5.29	5.28	5.27	5.26	5.25	5.24	5.23	5.22	5.21	5.20	5.19	5.18	5.17	5.16	5.15	5.14	5.13	5.12	5.11	5.10	5.09	5.08	5.07	5.06	5.05	5.04	5.03	5.02	5.01	5.00	4.99	4.98	4.97	4.96	4.95	4.94	4.93	4.92	4.91	4.90	4.89	4.88	4.87	4.86	4.85	4.84	4.83	4.82	4.81	4.80	4.79	4.78	4.77	4.76	4.75	4.74	4.73	4.72	4.71	4.70	4.69	4.68	4.67	4.66	4.65	4.64	4.63	4.62	4.61	4.60	4.59	4.58	4.57	4.56	4.55	4.54	4.53	4.52	4.51	4.50	4.49	4.48	4.47	4.46	4.45	4.44	4.43	4.42	4.41	4.40	4.39	4.38	4.37	4.36	4.35	4.34	4.33	4.32	4.31	4.30	4.29	4.28	4.27	4.26	4.25	4.24	4.23	4.22	4.21	4.20	4.19	4.18	4.17	4.16	4.15	4.14	4.13	4.12	4.11	4.10	4.09	4.08	4.07	4.06	4.05	4.04	4.03	4.02	4.01	4.00	3.99	3.98	3.97	3.96	3.95
------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------

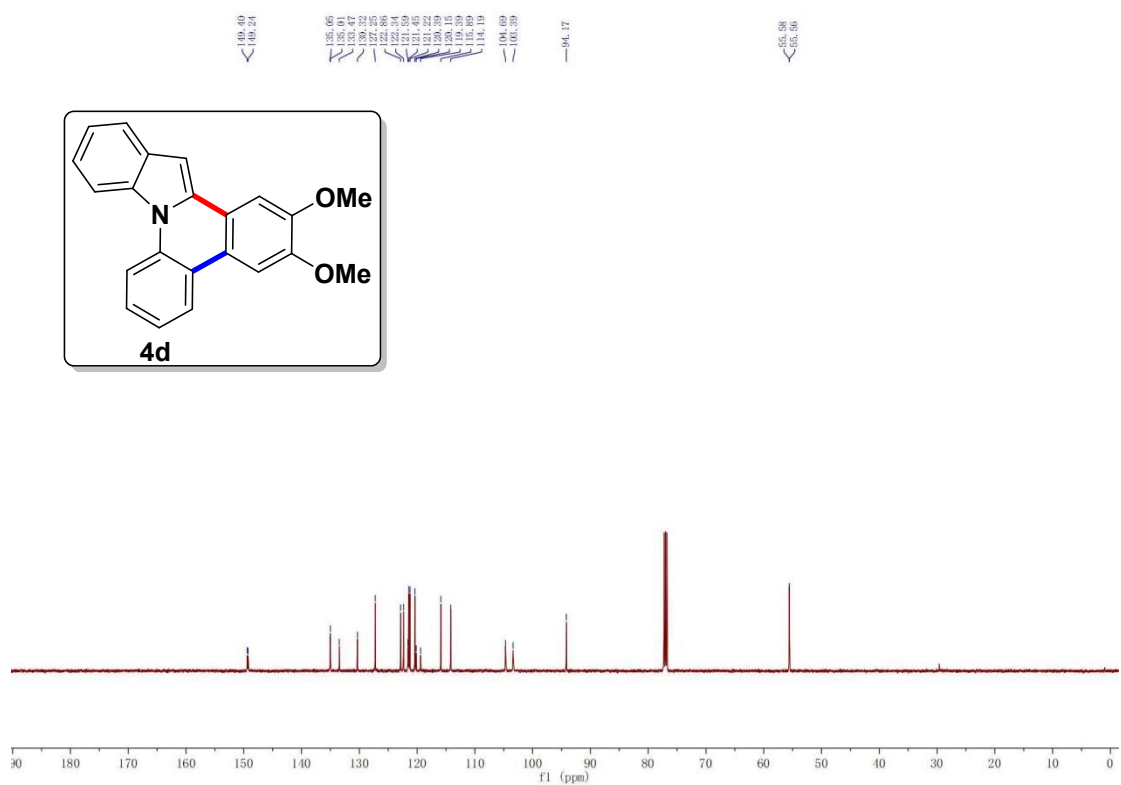
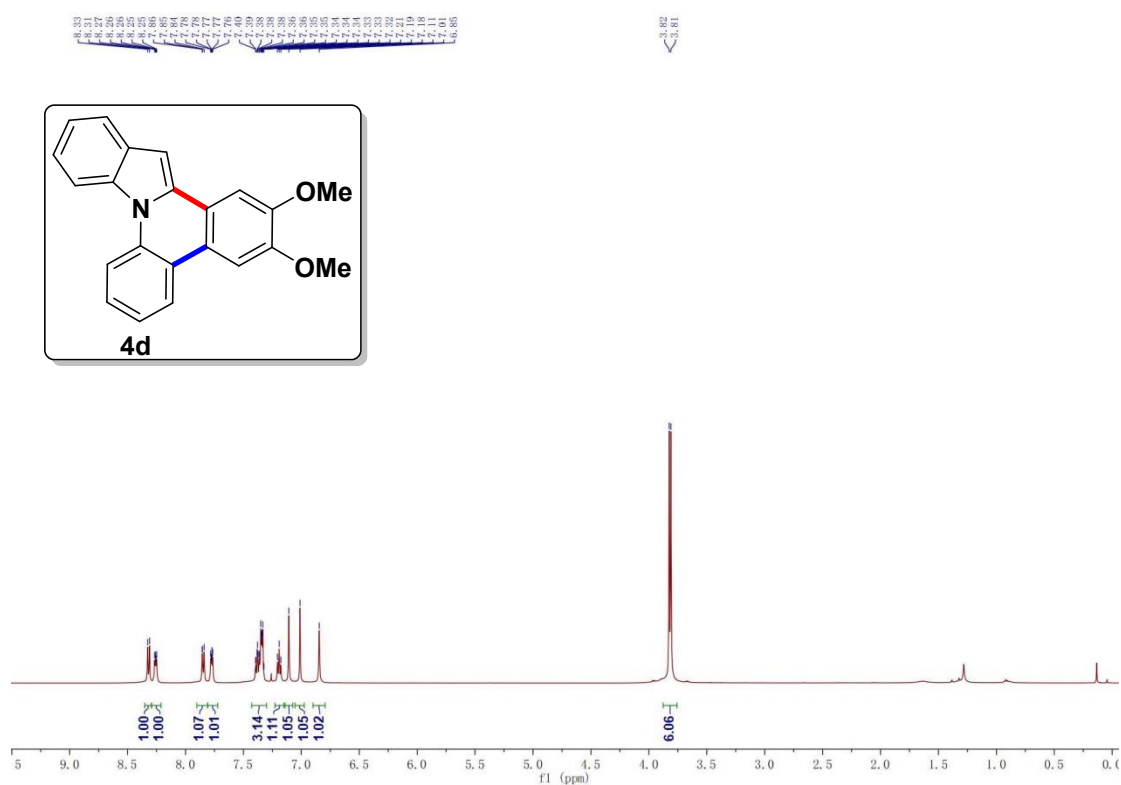


## 2,3-difluoroindolo[1,2-f]phenanthridine (4c)

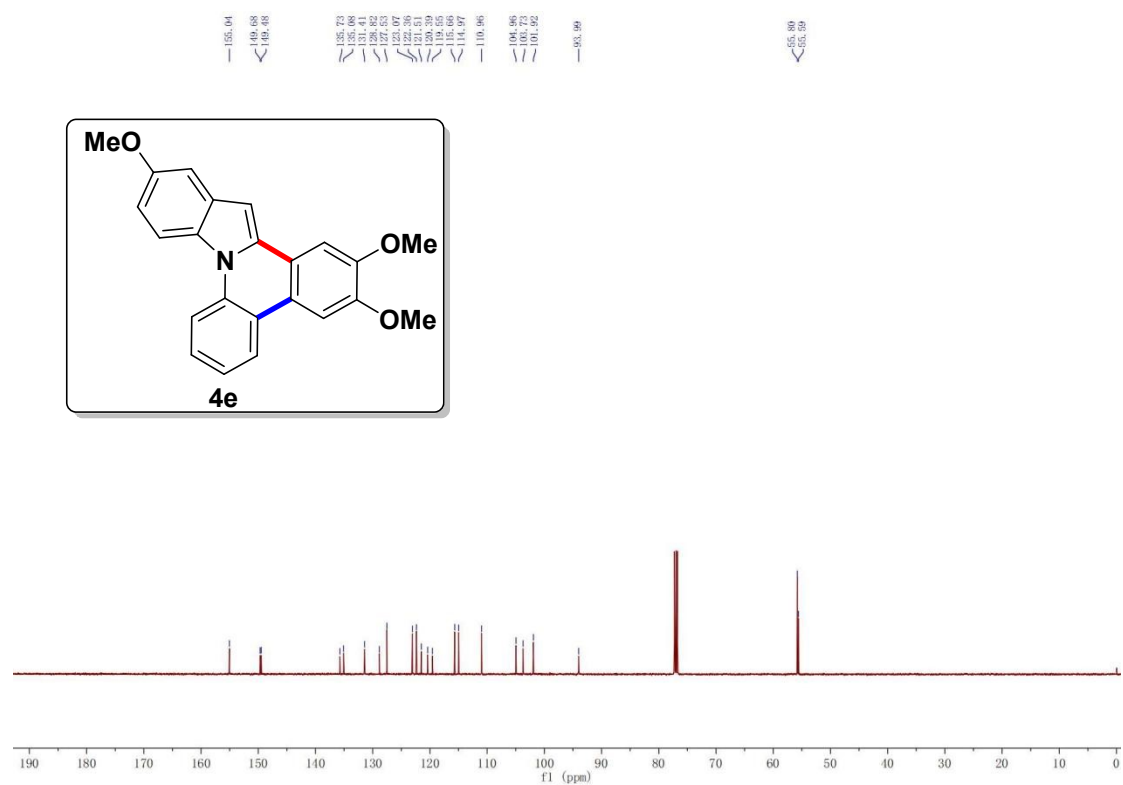
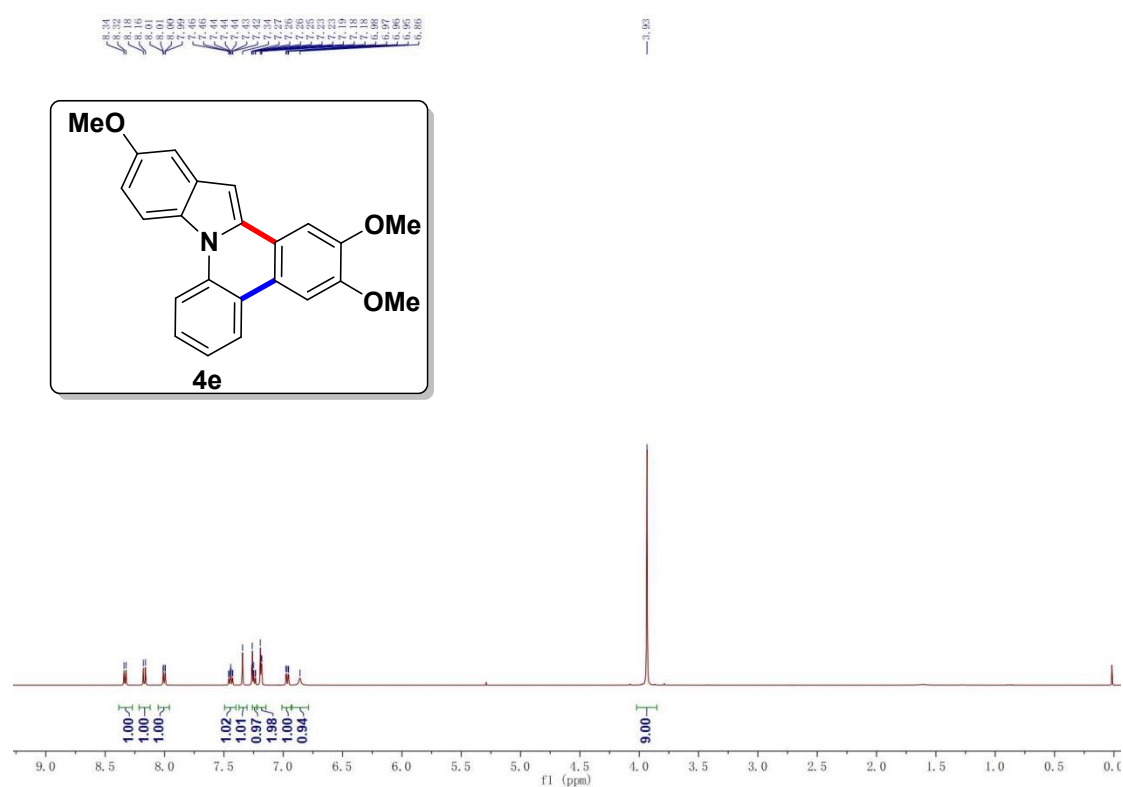




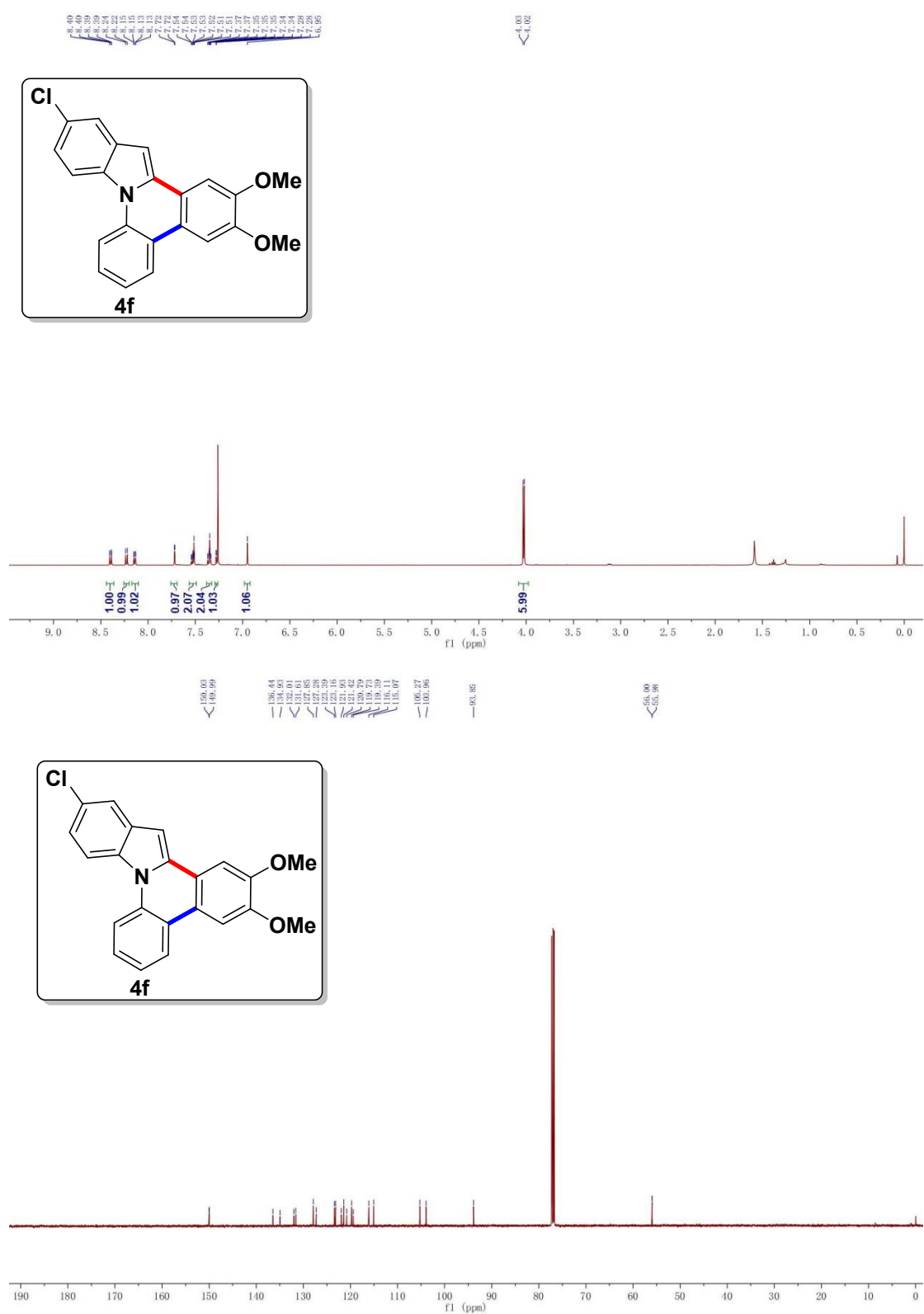
### 2,3-dimethoxyindolo[1,2-f]phenanthridine (4d)



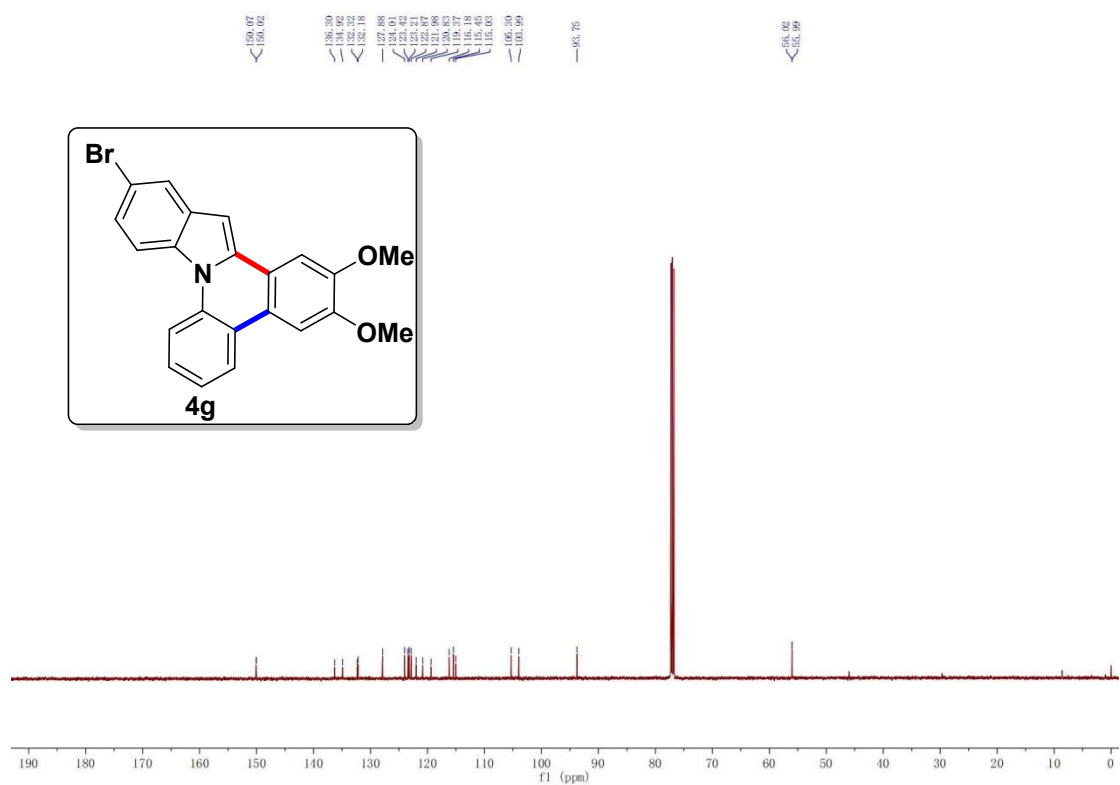
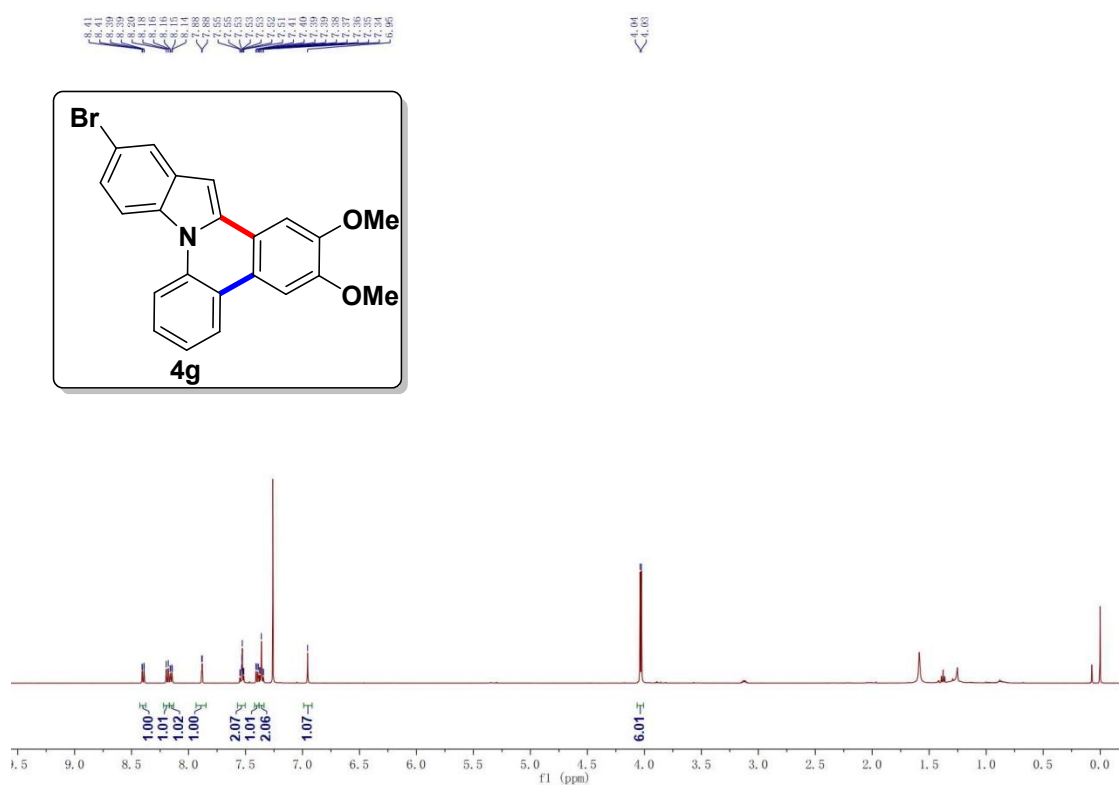
## 2,3,12-trimethoxyindolo[1,2-f]phenanthridine (4e)



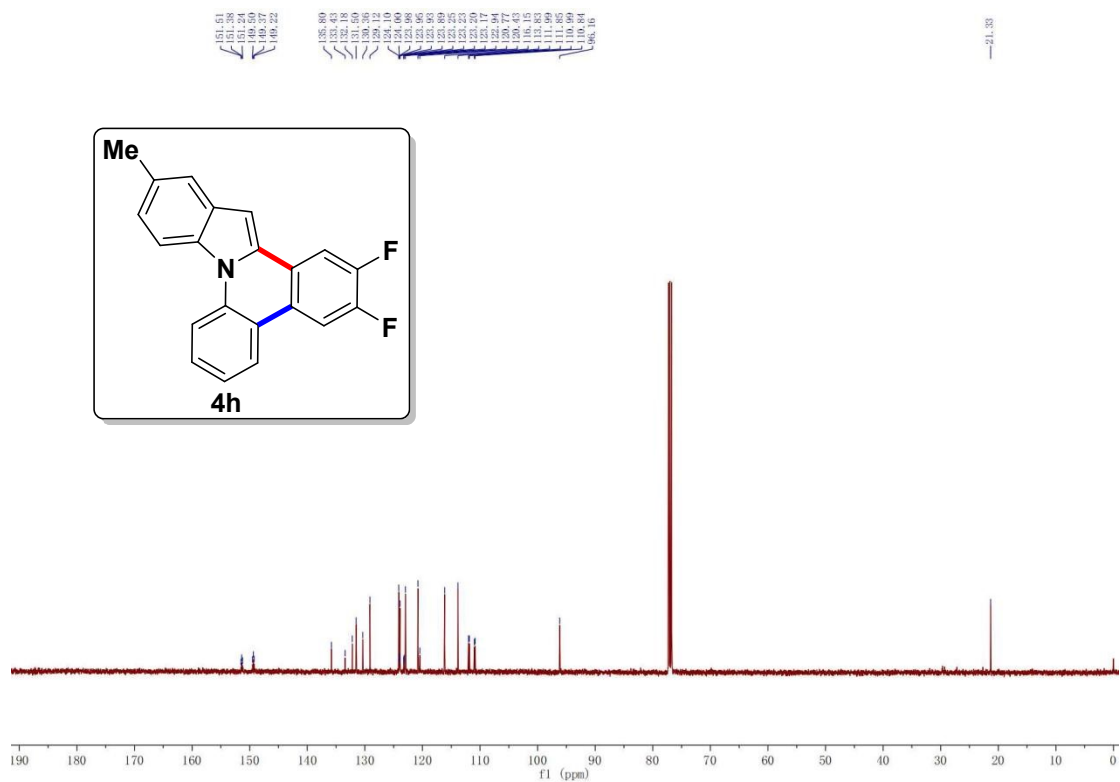
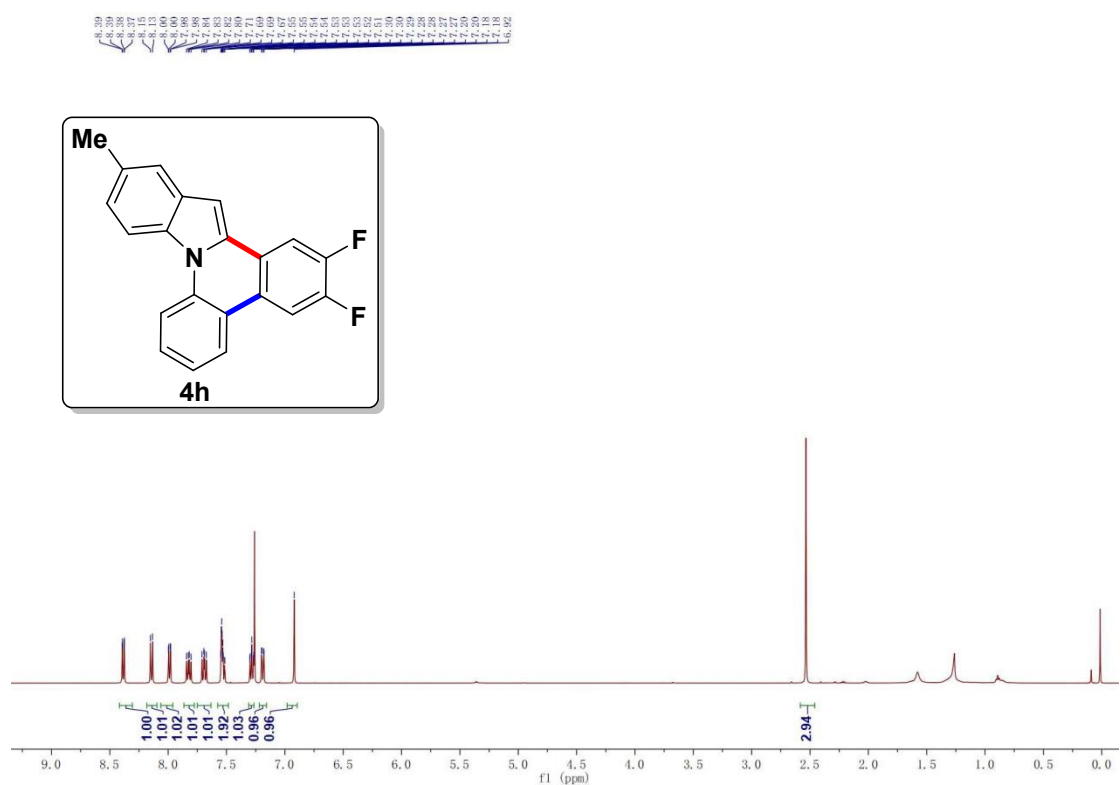
# 12-chloro-2,3-dimethoxyindolo[1,2-f]phenanthridine (4f)



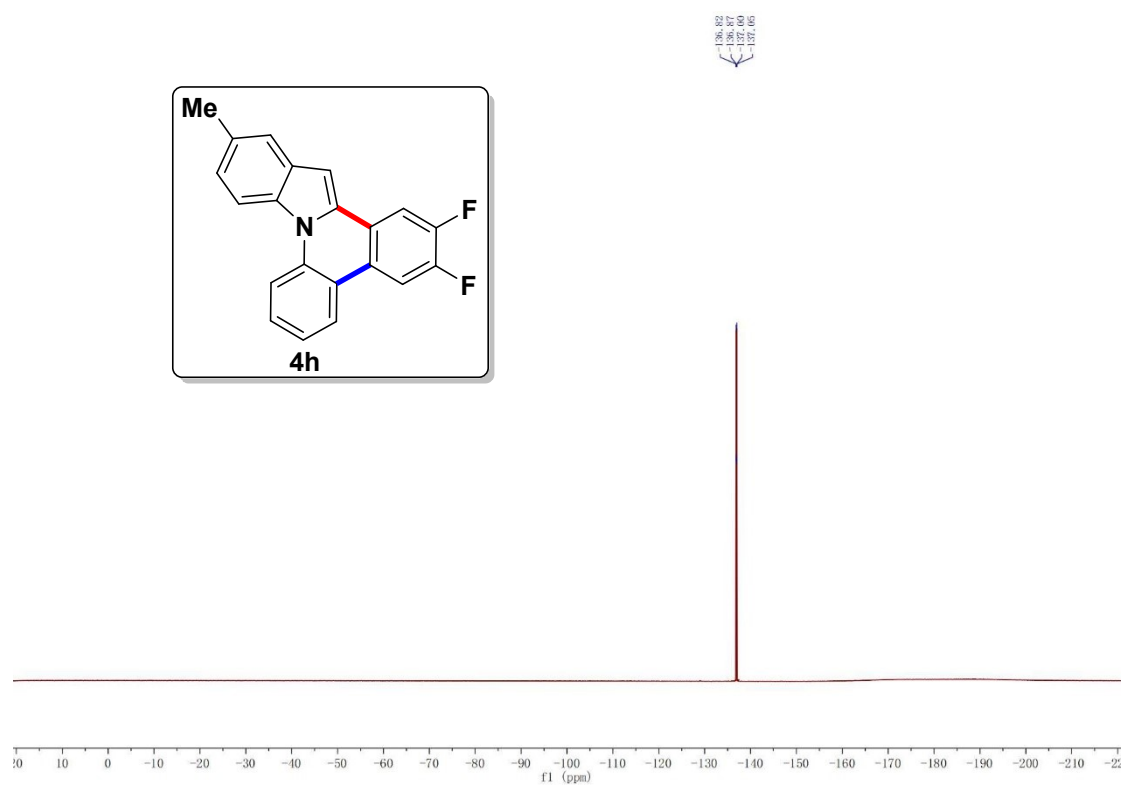
# 12-bromo-2,3-dimethoxyindolo[1,2-f]phenanthridine (4g)



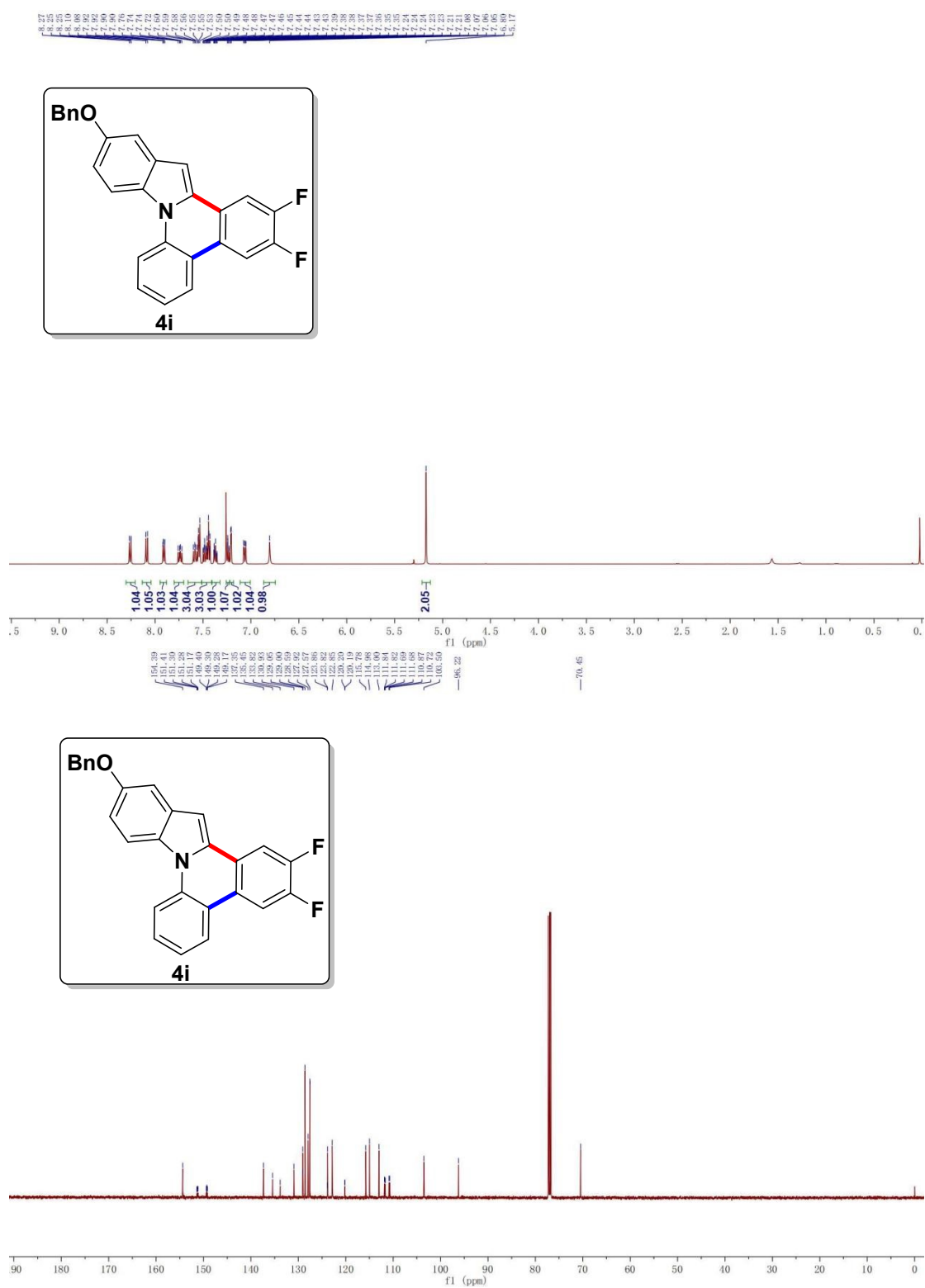
## 2,3-difluoro-12-methylindolo[1,2-f]phenanthridine (4h)

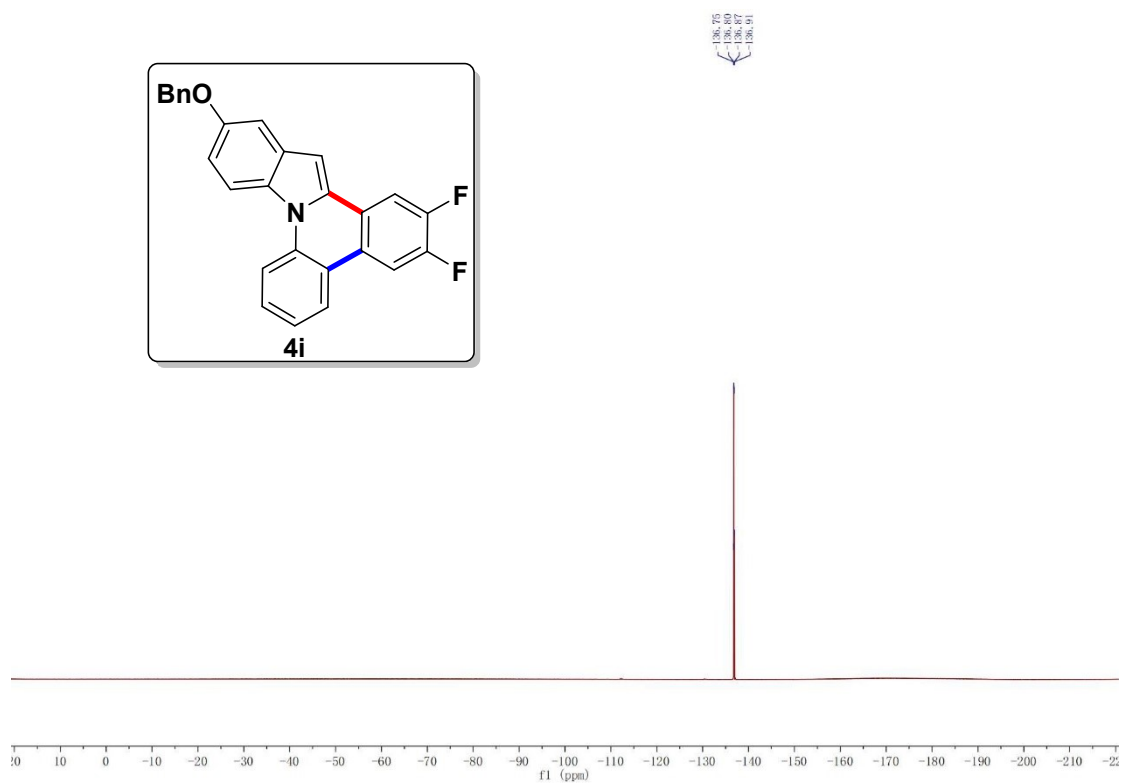






# 12-(benzyloxy)-2,3-difluoroindolo[1,2-f]phenanthridine (4i)





**benzo[6,7]naphtho[1',8':3,4,5]azepino[1,2-a]indole (4j)**

