

# Supporting Information

## Expeditious Synthesis of Pyrano[2,3,4-*de*]quinolines via Rh(III)-Catalyzed Cascade C–H Activation/Annulation/Lactonization of Quinolin-4-ol with Alkynes

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### Table of Contents:

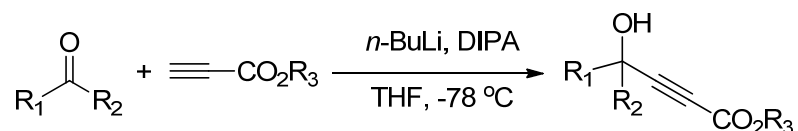
1. General information	S2
2. Experimental Section	S2
2.1 General Procedure for the Preparation of tertiary propargylic alcohols(GP1)	S2
2.2 General Procedure for the Rh(III)-Catalyzed reaction (GP2)	S4
3. References	S21
4. NMR Spectra	S22

## 1. General Information:

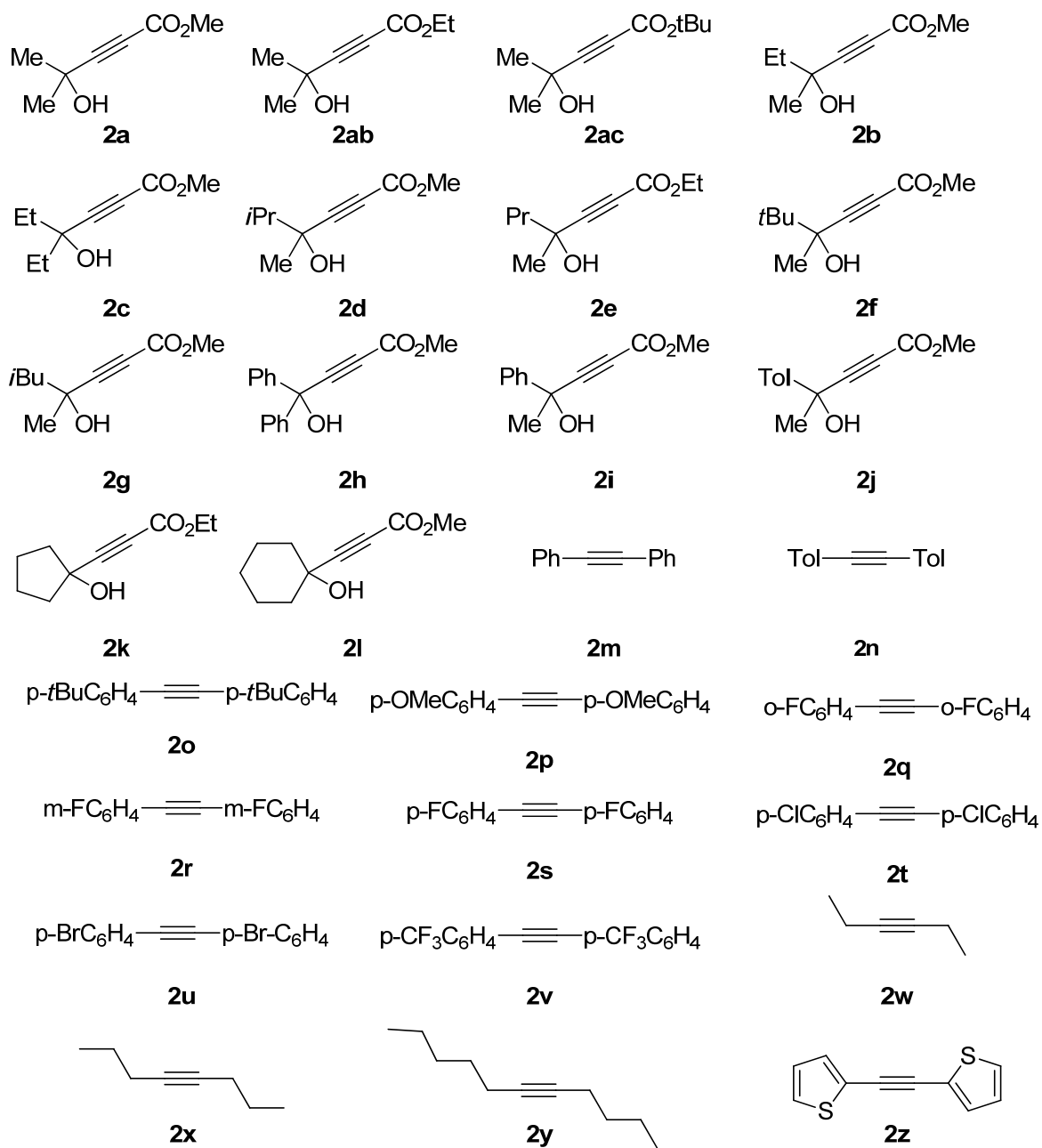
1,2-dimethoxyethane was dried by Sodium and stored under nitrogen. All 4-Hydroxyquinoline substrate were purchased from commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for  $^1\text{H}$  NMR at 400 MHz,  $^{13}\text{C}$  NMR at 100 MHz, and  $^{19}\text{F}$  NMR at 376 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for  $^{13}\text{C}$  NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

## 2. Experimental Section

### 2.1 General Procedure for the Preparation of tertiary propargylic alcohols (GP1)



A solution of *n*-butyllithium in hexanes (1.6 M, 33.0 mmol) was added dropwise to a solution of freshly distilled diisopropylamine (33.0 mmol) in dried THF (30 mL) at 0 °C. The solution was stirred for 1 h at 0 °C, then cooled to -78 °C. Propargyl ester (31.3 mmol) in dried THF (10 mL) was then added dropwise to the reaction mixture. After 1 h at the same temperature, ketone (62.6 mmol) was added, and the resulting mixture was stirred at -78 °C for 3 h. The reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  solution, and the mixture was extracted four times with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine, dried with anhydrous  $\text{MgSO}_4$ , and the solvents evaporated to dryness. The oily residue was purified by flash silica gel column chromatography (hexanes/ $\text{EtOAc}$ ) to get propargylic alcohol.



Compounds **2a**, **2ab**, **2h**, **2k**, **2l**; <sup>[1a]</sup> **2m**, **2n**, **2o**; <sup>[1b]</sup> **2c** <sup>[1c]</sup> ; **2d** <sup>[1d]</sup> ; **2h-2z** <sup>[1e]</sup> were known compounds was knows compound and were prepared accounting to literature. <sup>[1]</sup> **2ac**, **2b**, **2e**, **2f**, **2g** were prepared accounting to the **GP1**.

#### Tert-butyl 4-hydroxy-4-methylpent-2-ynoate (**2ac**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.55 (s, 6H), 1.49 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.8, 88.7, 83.7, 75.6, 65.1, 30.7, 28.1; HRMS (EI) calcd for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> (M<sup>+</sup>): 184.1099 ; found 184.1100.

#### Methyl 4-hydroxy-4-methylhex-2-ynoate (**2b**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.77 (s, 1H), 2.44 (s, 1H), 1.84 – 1.69 (m, 1H), 1.51 (s, 1H), 1.04 (t,  $J = 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 90.9, 75.0, 68.7, 52.9, 36.0, 28.5, 8.8. HRMS (EI) calcd for  $\text{C}_8\text{H}_{12}\text{O}_3(\text{M}^+)$ : 156.0786; found 156.0783.

#### **Ethyl 4-hydroxy-4-methylhept-2-ynoate (2e)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.23 (q,  $J = 7.1$  Hz, 2H), 2.26 (s, 1H), 1.74 – 1.63 (m, 2H), 1.58 – 1.47 (m, 5H), 1.31 (t,  $J = 7.1$  Hz, 3H), 0.96 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 90.7, 75.2, 68.1, 62.2, 45.2, 29.0, 17.9, 14.2, 14.1. HRMS (EI) calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3(\text{M}^+)$ : 184.1099; found 184.1096.

#### **Methyl 4-hydroxy-4,5,5-trimethylhex-2-ynoate (2f)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.77 (s, 3H), 2.13 (s, 1H), 1.48 (s, 3H), 1.05 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 91.2, 75.9, 74.1, 52.8, 38.4, 25.1, 24.3. HRMS (EI) calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3(\text{M}^+)$ : 184.1099 ; found 184.1101.

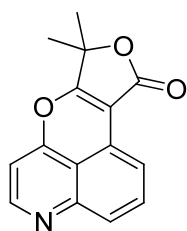
#### **Methyl 4-hydroxy-4,6-dimethylhept-2-ynoate (2g)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.77 (s, 3H), 2.14 (s, 1H), 1.98 – 1.87 (m, 1H), 1.64 (d,  $J = 6.3$  Hz, 2H), 1.54 (s, 3H), 1.01 (dd,  $J = 6.6, 4.0$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 91.4, 75.2, 68.0, 52.9, 51.1, 30.2, 25.1, 24.2, 24.1. HRMS (EI) calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_3(\text{M}^+)$ : 184.1099 ; found 184.1097 .

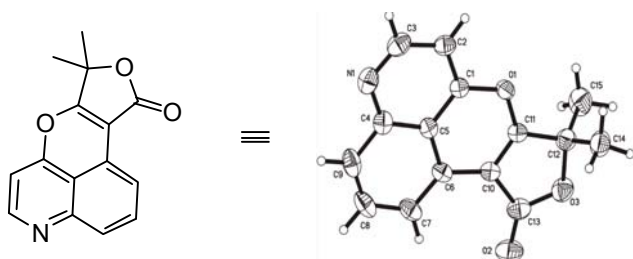
## **2.2 General Procedure for the Rh(III)-Catalyzed reaction (GP2)**

A mixture of quinolin-4-ol **1** (0.2 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.005 mmol, 0.0025 equiv),  $\text{AgSbF}_6$  (0.02 mmol, 0.1 equiv), alkyne **2** (0.4 mmol, 2.0 equiv),  $\text{Cu}(\text{OAc})_2$  (0.4 mmol, 2.0 equiv),  $\text{LiOTf}$  (0.4 mmol, 2.0 equiv) in 2 mL DME in a 50-mL Schlenk tube (Purged with  $\text{N}_2$ ) was heated at 100 °C for 12 h. Then a 1mL ammonium hydroxide was added and then the whole solution was stirred for 5 min. The resulting mixture was filtered with celite. The organic layer was concentrated under reduced pressure and separated on a silica gel column to provide the desired product.

### 8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3a)



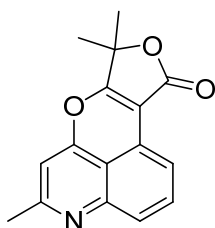
The title compound **3a** was prepared according to **GP2** and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (32.9mg 65% yield)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J = 5.1$  Hz, 1H), 7.78 (d,  $J = 8.6$  Hz, 1H), 7.73 (d,  $J = 6.9$  Hz, 1H), 7.67 – 7.60 (m, 1H), 6.91 (d,  $J = 5.1$  Hz, 1H), 1.67 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5, 166.5, 158.8, 152.4, 150.3, 131.8, 127.0, 122.0, 118.0, 116.1, 105.3, 104.2, 81.1, 24.4; HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$  ( $\text{M}^+$ ): 253.0739 ; found 253.0737.



Bond precision:	C-C = 0.0027 Å	Wavelength=0.71073
Cell:	a=7.2462(9)      b=8.215(1)	c=20.228(3)
	$\alpha=90$ $\beta=93.583(10)$	$\gamma=90$
Temperature:	293 K	
	Calculated	Reported
Volume	1201.8(3)	1201.7(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$\text{C}_{15}\text{H}_{11}\text{N O}_3$	$\text{C}_{15}\text{H}_{11}\text{N O}_3$
Sum formula	$\text{C}_{15}\text{H}_{11}\text{N O}_3$	$\text{C}_{15}\text{H}_{11}\text{N O}_3$
Mr	253.25	253.25
$D_x, \text{g cm}^{-3}$	1.400	1.400
Z	4	4

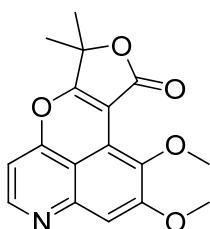
Mu (mm <sup>-1</sup> )	0.099	0.099
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F000'	528.27	
h,k,l <sub>max</sub>	8,9,24	8,9,24
N <sub>ref</sub>	2194	2190
T <sub>min</sub> ,T <sub>max</sub>	0.978, 0.984	0.968, 0.984
T <sub>min</sub> '	0.968	
Correction method= MULTI-SCAN		
Data completeness=	0.998	Theta(max)= 25.350
R(reflections)=	0.0423( 1421)	wR2(reflections)= 0.1198( 2190)
S =	1.031	N <sub>par</sub> = N <sub>par</sub> = 175

### 8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3aa)



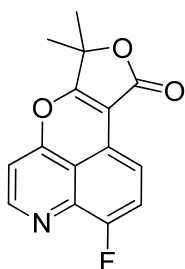
The title compound **3aa** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (27.0mg 51% yield) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 – 7.67 (m, 2H), 7.63 (dd, *J* = 8.3, 7.4 Hz, 1H), 6.83 (s, 1H), 2.66 (s, 3H), 1.68 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.5, 166.7, 161.7, 159.0, 149.8, 131.9, 126.4, 121.9, 116.3, 115.5, 105.5, 104.1, 81.1, 25.7, 24.4. HRMS (EI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>3</sub>N (M<sup>+</sup>): 267.0895; found 267.0895.

### 1,2-dimethoxy-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3ab)



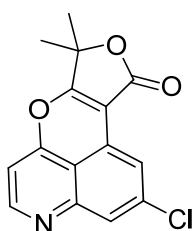
The title compound **3ab** was prepared according to **GP2** and was purified by chromatography (EtOAc) to give the product as a faint yellow solid (38.8mg, 76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54 (d, *J* = 5.2 Hz, 1H), 7.20 (s, 1H), 6.76 (d, *J* = 5.2 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 1.65 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.6, 164.5, 158.2, 157.8, 151.5, 149.3, 142.5, 113.9, 113.2, 107.0, 103.6, 103.3, 79.6, 62.6, 56.1, 24.6. HRMS (EI) calcd for C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>N(M<sup>+</sup>): 313.0950; found 313.0942.

### 3-fluoro-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-on (**3ac**)



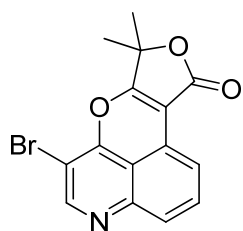
The title compound **3ac** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (29.8mg, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.40 (dd, *J* = 10.9, 8.0 Hz, 1H), 7.04 (t, *J* = 10.1 Hz, 1H), 1.69 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.6(d, *J*<sub>C-F</sub>=2.0 Hz), 166.3, 159.0(d, *J*<sub>C-F</sub>=3.1 Hz), 156.3(d, *J*<sub>C-F</sub>=256.8Hz), 152.9, 140.8 (d, *J*<sub>C-F</sub>=14.6Hz), 119.8(d, *J*<sub>C-F</sub>=3.8 Hz), 118.2 (d, *J*<sub>C-F</sub>=5.0 Hz), 116.0, 115.9 (d, *J*<sub>C-F</sub>=12.1 Hz), 106.4, 104.2, 81.3, 24.4. HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>NF(M<sup>+</sup>): 271.0654; found 271.0648.

### 2-chloro-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (**3ad**)



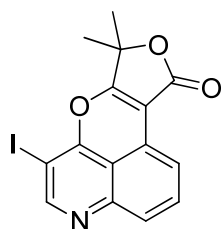
The title compound **3ad** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (37mg, 64% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 5.1 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 1.7 Hz, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 1.68 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.3, 166.0, 158.9, 153.4, 150.9, 138.5, 126.0, 123.6, 117.2, 116.5, 105.6, 103.6, 81.4, 24.4. HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>NCl(M<sup>+</sup>): 287.0349; found 287.0356.

**6-bromo-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3ae)**



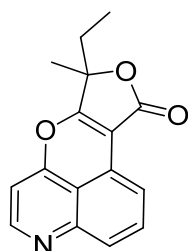
The title compound **3ae** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (47.1mg, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 1H), 7.87 – 7.78 (m, 2H), 7.70 (dd, *J* = 8.6, 7.2 Hz, 1H), 1.73 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 166.2, 155.1, 154.0, 148.7, 131.9, 127.3, 121.5, 118.9, 117.0, 104.8, 100.7, 81.4, 24.4. HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>NBr (M<sup>+</sup>): 330.9844 ; found 330.9841.

**6-iodo-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3af)**



The title compound **3af** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (56.1mg, 74% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.91 (s, 1H), 7.88 – 7.78 (m, 2H), 7.75 – 7.67 (m, 1H), 1.73 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.1, 166.1, 158.4, 158.0, 149.1, 132.0, 127.0, 121.3, 118.9, 116.7, 104.8, 81.3, 73.5, 24.3. HRMS (EI) calcd for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>NI (M<sup>+</sup>) 378.9705; found 378.9705.

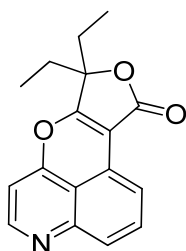
**8-ethyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3b)**





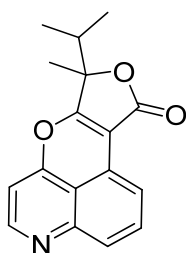
The title compound **3b** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (35.8mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 5.0 Hz, 1H), 7.92 – 7.75 (m, 2H), 7.69 (dd, *J* = 8.6, 7.2 Hz, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.92 (m, 1H), 1.67 (s, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 166.9, 158.8, 152.4, 150.4, 131.8, 127.0, 122.0, 118.0, 116.1, 105.4, 105.3, 83.9, 30.2, 22.9, 7.8. HRMS (EI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>3</sub>N(M<sup>+</sup>): 267.0895; found 267.0898.

### 8,8-diethylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3c)



The title compound **3c** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (33.7mg, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 4.9 Hz, 1H), 7.94 – 7.76 (m, 2H), 7.69 (dd, *J* = 8.6, 7.2 Hz, 1H), 6.93 (d, *J* = 5.1 Hz, 1H), 2.07 (dq, *J* = 14.9, 7.4 Hz, 2H), 1.97 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.3, 167.3, 158.8, 152.4, 150.4, 131.9, 127.0, 121.9, 116.0, 106.7, 105.3, 87.0, 77.2, 28.9, 7.6. HRMS (EI) calcd for C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>N (M<sup>+</sup>) 281.1052; found 281.1051.

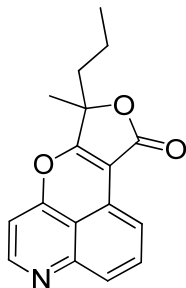
### 8-isopropyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-*de*]quinolin-10(8*H*)-one (3d)



The title compound **3d** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (37.7mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.86 – 7.75 (m, 2H), 7.68 (dd, *J* = 8.4, 7.4 Hz, 1H), 6.93 (d, *J* = 5.1 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.67 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 167.1, 158.8, 152.4, 150.3,

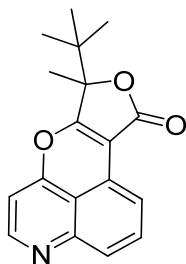
131.9, 126.9, 122.0, 118.0, 116.0, 105.4, 105.3, 86.1, 34.6, 21.3, 17.2, 16.8. HRMS (EI) calcd for  $C_{17}H_{15}O_3N(M^+)$ : 281.1052; found 281.1052.

**8-methyl-8-propylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3e)**



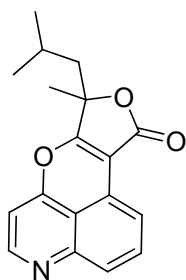
The title compound **3e** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (35.4mg, 63% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.72 (s, 1H), 7.81 (d,  $J = 8.5$  Hz, 1H), 7.77 (d,  $J = 7.1$  Hz, 1H), 7.66 (t,  $J = 7.8$  Hz, 1H), 6.93 (d,  $J = 4.7$  Hz, 1H), 2.04 – 1.93 (m, 1H), 1.92 – 1.81 (m, 1H), 1.66 (s, 3H), 1.53 – 1.39 (m, 1H), 1.36 – 1.26 (m, 1H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  174.8, 166.9, 158.8, 152.4, 150.5, 146.9, 131.8, 127.1, 122.1, 116.1, 105.4, 105.2, 83.7, 39.1, 23.3, 16.8, 14.0. HRMS (EI) calcd for  $C_{17}H_{15}O_3N(M^+)$ : 281.1052 ; found 281.1055.

**8-(tert-butyl)-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3f)**



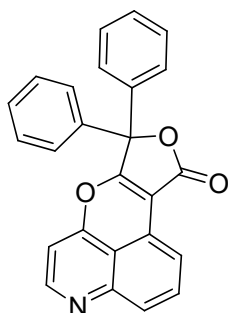
The title compound **3f** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (31.7mg, 54% yield).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.71 (d,  $J = 5.1$  Hz, 1H), 7.86 – 7.76 (m, 2H), 7.68 (t,  $J = 7.8$  Hz, 1H), 6.93 (d,  $J = 5.1$  Hz, 1H), 1.67 (s, 3H), 1.13 (s, 9H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  175.3, 167.2, 158.7, 152.4, 150.4, 131.9, 127.0, 122.1, 118.0, 116.1, 105.6, 105.3, 88.4, 37.5, 25.4, 19.3. HRMS (EI) calcd for  $C_{18}H_{17}O_3N(M^+)$ : 295.1208; found 295.1211.

**8-isobutyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3g)**



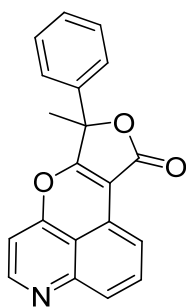
The title compound **3g** was prepared according to **GP2** and was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (41.3 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 7.4 Hz, 1H), 6.94 (d, *J* = 5.1 Hz, 1H), 1.99 (dd, *J* = 7.8 Hz, 1H), 1.82 – 1.73 (m, 2H), 1.66 (s, 3H), 0.97 (d, *J* = 6.3 Hz, 3H), 0.92 (d, *J* = 6.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 166.9, 158.8, 152.5, 150.4, 131.9, 127.0, 122.1, 118.0, 116.2, 105.3, 105.2, 83.7, 45.4, 24.4, 24.1, 24.0, 23.6. HRMS (EI) calcd for C<sub>18</sub>H<sub>17</sub>O<sub>3</sub>N(M<sup>+</sup>): 295.1208 ; found 295.1205.

#### 8,8-diphenylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (**3h**)



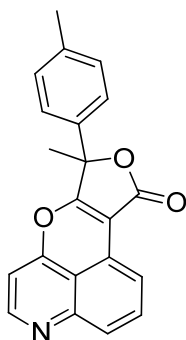
The title compound **3h** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (38.5mg, 51% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (s, 1H), 7.89 – 7.81 (m, 2H), 7.74 – 7.66 (m, 1H), 7.53 – 7.46 (m, 4H), 7.43 – 7.39 (m, 6H), 6.98 (d, *J* = 4.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.4, 166.5, 158.8, 152.5, 150.3, 137.3, 131.9, 129.5, 129.0, 127.5, 127.1, 121.9, 116.6, 105.8, 87.5. HRMS (EI) calcd for C<sub>25</sub>H<sub>15</sub>O<sub>3</sub>N(M<sup>+</sup>): 377.1052 ; found 377.1056.

#### 8-methyl-8-phenylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (**3i**)



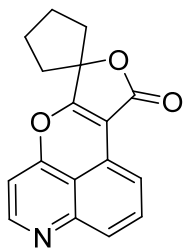
The title compound **3i** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (33.4mg, 53% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 5.2 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.44 – 7.39 (m, 3H), 7.04 (d, *J* = 5.2 Hz, 1H), 6.78 (d, *J* = 6.7 Hz, 1H), 2.18 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.4, 159.3, 153.0, 150.6, 139.9, 138.8, 136.5, 131.0, 129.8, 129.6, 129.3, 126.3, 122.9, 119.7, 117.5, 105.8, 85.4, 23.9. HRMS (EI) calcd for C<sub>20</sub>H<sub>13</sub>O<sub>3</sub>N(M<sup>+</sup>): 315.0895; found 315.0895.

**8-methyl-8-(p-tolyl)furo[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3j)**



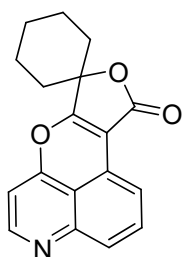
The title compound **3j** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (30.3mg, 46% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 5.2 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 5.2 Hz, 1H), 6.77 (d, *J* = 7.1 Hz, 1H), 2.35 (s, 4H), 2.18 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 159.3, 153.0, 150.6, 139.9, 139.9, 138.7, 133.4, 131.0, 129.9, 129.6, 126.3, 122.9, 119.7, 117.5, 105.8, 85.4, 23.9, 21.3. HRMS (EI) calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>N(M<sup>+</sup>): 329.1052 ; found 329.1051.

**10'H-spiro[cyclopentane-1,8'-furo[3',4':5,6]pyrano[2,3,4-de]quinolin]-10'-one (3k)**



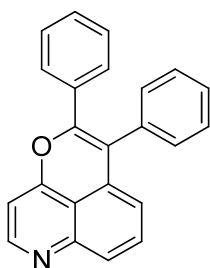
The title compound **3k** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (34.6 mg, 62% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (s, 1H), 7.81 (d,  $J = 8.5$  Hz, 1H), 7.76 (d,  $J = 7.1$  Hz, 1H), 7.66 (d,  $J = 7.8$  Hz, 1H), 2.49 – 1.76 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 166.8, 159.0, 152.4, 150.5, 131.9, 127.0, 122.2, 116.0, 105.4, 105.3, 90.9, 36.5, 25.2. HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}(\text{M}^+)$  279.0895; found 279.0899.

### 10'H-spiro[cyclohexane-1,8'-furo[3',4':5,6]pyrano[2,3,4-de]quinolin]-10'-one (3l)



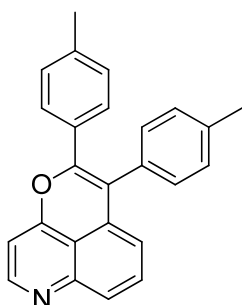
The title compound **3l** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (42.2 mg, 71% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (d,  $J = 5.1$  Hz, 1H), 7.81 (t,  $J = 8.2$  Hz, 2H), 7.68 (dd,  $J = 8.4, 7.4$  Hz, 1H), 6.93 (d,  $J = 5.1$  Hz, 1H), 2.02 – 1.91 (m, 2H), 1.87 – 1.80 (m, 8H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.9, 166.9, 158.9, 152.4, 150.3, 131.8, 126.9, 122.2, 118.1, 116.0, 105.3, 104.4, 82.9, 33.3, 24.4, 21.7. HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}(\text{M}^+)$ : 293.1052; found 293.1057.

### 5,6-diphenylpyrano[2,3,4-de]quinoline (4a)



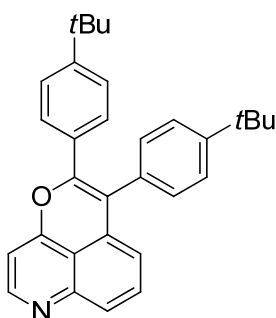
The title compound **4a** was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (60.4 mg, 94% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.28 – 7.17 (m, 4H), 6.82 (d, *J* = 4.9 Hz, 1H), 6.65 (d, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 152.3, 150.1, 149.2, 134.8, 133.4, 131.4, 130.7, 129.3, 129.1, 128.9, 128.1, 127.9, 125.2, 119.5, 118.5, 116.2, 103.2. HRMS (EI) calcd for C<sub>23</sub>H<sub>15</sub>ON(M<sup>+</sup>) 321.1154; found 321.1153.

#### 5,6-di-*p*-tolylpyrano[2,3,4-*de*]quinoline (**4b**)



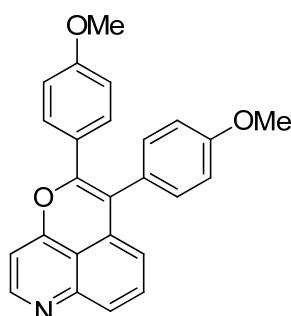
The title compound **4b** was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (66.4mg 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 5.1 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.24 – 7.17 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 5.2 Hz, 1H), 6.64 (d, *J* = 7.3 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 152.1, 150.0, 149.1, 138.8, 137.6, 131.8, 131.6, 131.3, 130.6, 130.5, 129.9, 128.8, 128.6, 124.7, 118.8, 118.3, 116.0, 103.0, 21.4, 21.3. HRMS (EI) calcd for C<sub>25</sub>H<sub>19</sub>ON(M<sup>+</sup>): 349.1467; found 349.1470.

#### 5,6-bis(4-(*tert*-butyl)phenyl)pyrano[2,3,4-*de*]quinoline (**4c**)



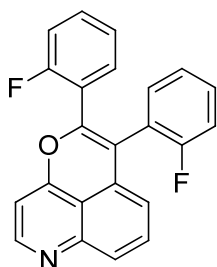
The title compound **4c** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (81.5 mg, 94% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.61 (d, *J* = 5.3 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.13 (m, 6H), 6.79 (d, *J* = 5.3 Hz, 1H), 6.66 (d, *J* = 7.3 Hz, 1H), 1.35 (s, 9H), 1.26 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.8, 152.0, 151.1, 149.8, 149.0, 131.8, 131.7, 131.5, 130.5, 130.3, 128.6, 126.2, 124.8, 124.6, 119.0, 118.4, 116.3, 103.1, 34.8, 34.7, 31.5, 31.2. HRMS (EI) calcd for C<sub>31</sub>H<sub>31</sub>ON(M<sup>+</sup>): 433.2400; found 433.2403.

#### 5,6-bis(4-methoxyphenyl)pyrano[2,3,4-*de*]quinoline (**4d**)



The title compound **4d** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (70.2 mg, 92% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (d, *J* = 5.2 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.45 (m, 1H), 7.30 – 7.23 (m, 2H), 7.18 (d, *J* = 2.7 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 5.2 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.68 (d, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.9, 159.79, 159.3, 152.1, 150.0, 149.1, 132.0, 131.9, 131.5, 130.5, 127.1, 125.9, 124.6, 118.3, 118.0, 115.9, 114.8, 113.4, 103.1, 55.4, 55.3. HRMS (EI) calcd for C<sub>25</sub>H<sub>19</sub>ON<sub>3</sub>(M<sup>+</sup>): 381.1359; found 381.1356.

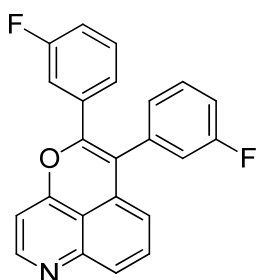
#### 5,6-bis(2-fluorophenyl)pyrano[2,3,4-*de*]quinoline (**4e**)



The title compound **4e** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (57.9

mg, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (d,  $J = 4.7$  Hz, 1H), 7.68 (d,  $J = 8.5$  Hz, 1H), 7.42 (t,  $J = 7.9$  Hz, 1H), 7.27 – 7.14 (m, 3H), 7.09 (t,  $J = 6.9$  Hz, 1H), 7.02 – 6.85 (m, 4H), 6.70 (d,  $J = 5.1$  Hz, 1H), 6.51 (d,  $J = 7.2$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.8 (d,  $J = 2.3$  Hz, 1F), -112.9 (d,  $J = 2.3$  Hz, 1F).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 160.6 (d,  $J_{\text{C-F}} = 248.7$  Hz), 160.0 (d,  $J_{\text{C-F}} = 252.6$  Hz), 159.7, 152.1, 149.8, 146.7, 132.2 (d,  $J_{\text{C-F}} = 3.0$  Hz), 131.6 (d,  $J_{\text{C-F}} = 8.3$  Hz), 131.5, 131.2 (d,  $J_{\text{C-F}} = 2.2$  Hz), 130.4 (d,  $J_{\text{C-F}} = 8.1$  Hz), 129.7, 125.5, 124.5 (d,  $J_{\text{C-F}} = 3.6$  Hz), 123.9 (d,  $J_{\text{C-F}} = 3.6$  Hz), 121.6 (d,  $J_{\text{C-F}} = 16.3$  Hz), 121.4 (d,  $J_{\text{C-F}} = 14.9$  Hz), 118.4, 116.6, 116.0, 115.9 (d,  $J_{\text{C-F}} = 24.4$  Hz), 115.9 (d,  $J_{\text{C-F}} = 19.1$  Hz), 103.4. HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{13}\text{OF}_2\text{N}$  ( $\text{M}^+$ ): 357.0960; found 357.0959.

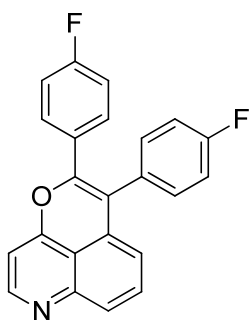
#### 5,6-bis(3-fluorophenyl)pyrano[2,3,4-*de*]quinoline (4f)



The title compound **4f** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (57.2 mg, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (d,  $J = 5.1$  Hz, 1H), 7.73 (d,  $J = 8.6$  Hz, 1H), 7.49 (t,  $J = 7.9$  Hz, 1H), 7.40 (dd,  $J = 14.2, 7.6$  Hz, 1H), 7.17 (dd,  $J = 14.2, 7.6$  Hz, 1H), 7.09 (t,  $J = 9.0$  Hz, 1H), 7.06 – 6.93 (m, 5H), 6.82 (d,  $J = 5.1$  Hz, 1H), 6.63 (d,  $J = 7.3$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.4, -112.5.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 163.5 (d,  $J_{\text{C-F}} = 248.7$  Hz), 162.3 (d,  $J_{\text{C-F}} = 247.1$  Hz), 159.2, 152.5, 150.0, 148.0 (d,  $J_{\text{C-F}} = 2.7$  Hz), 136.6 (d,  $J_{\text{C-F}} = 8.0$  Hz), 135.1 (d,  $J_{\text{C-F}} = 8.2$  Hz), 131.4, 131.2 (d,  $J_{\text{C-F}} = 8.5$  Hz), 130.5, 129.6 (d,  $J_{\text{C-F}} = 8.2$  Hz), 126.5 (d,  $J_{\text{C-F}} = 3.1$  Hz), 125.8, 124.8 (d,  $J_{\text{C-F}} = 3.1$  Hz), 119.1 (d,  $J_{\text{C-F}} = 2.0$  Hz), 118.3, 117.6 (d,  $J_{\text{C-F}} = 21.6$  Hz), 116.5, 116.4, 116.1 (d,  $J_{\text{C-F}} = 21.2$  Hz), 115.9 (d,  $J_{\text{C-F}} = 23.7$  Hz), 115.5 (d,  $J_{\text{C-F}} = 21.0$  Hz), 103.3. HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{13}\text{OF}_2\text{N}$  ( $\text{M}^+$ ): 357.0960; found 357.0956.

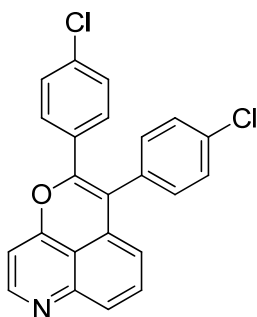
#### 5,6-bis(4-fluorophenyl)pyrano[2,3,4-*de*]quinolone (4g)





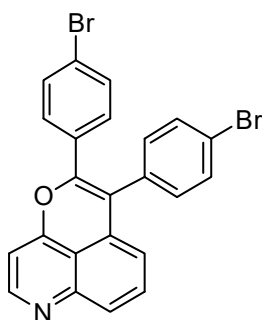
The title compound **4g** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (57.9 mg, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (d,  $J = 5.1$  Hz, 1H), 7.72 (d,  $J = 8.6$  Hz, 1H), 7.53 – 7.42 (m, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 7.10 (t,  $J = 8.6$  Hz, 2H), 6.95 – 6.85 (m, 2H), 6.79 (d,  $J = 5.2$  Hz, 1H), 6.61 (d,  $J = 7.3$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.8, -113.0  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 162.8 (d,  $J_{\text{C-F}}=251.5$  Hz), 161.5 (d,  $J_{\text{C-F}}=249.0$  Hz), 159.4, 152.2, 149.9, 148.6, 132.5 (d,  $J_{\text{C-F}}=8.1$  Hz), 131.4, 131.1, 131.0, 130.4 (d,  $J_{\text{C-F}}=3.6$  Hz), 129.3 (d,  $J_{\text{C-F}}=3.5$  Hz), 125.3, 118.5, 118.2, 116.6 (d,  $J_{\text{C-F}}=21.6$  Hz), 116.2, 115.2 (d,  $J_{\text{C-F}}=21.8$  Hz), 103.2. HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{13}\text{OF}_2\text{N}$  ( $\text{M}^+$ ): 357.0960; found 357.0961

#### 5,6-bis(4-chlorophenyl)pyrano[2,3,4-*de*]quinoline (**4h**)



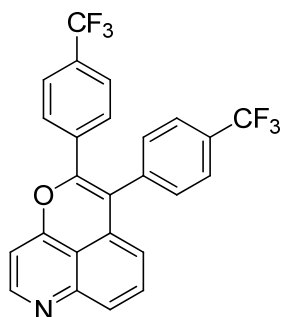
The title compound **4h** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (73.4 mg, 94% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (s, 1H), 7.72 (d,  $J = 8.5$  Hz, 1H), 7.48 (t,  $J = 7.9$  Hz, 1H), 7.40 (d,  $J = 8.2$  Hz, 2H), 7.23 – 7.15 (m, 6H), 6.81 (d,  $J = 4.6$  Hz, 1H), 6.61 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 152.5, 150.1, 148.4, 135.2, 134.3, 133.0, 132.1, 131.6, 131.4, 130.7, 130.4, 129.9, 128.5, 125.7, 118.8, 116.3, 103.4. HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{13}\text{O}_3\text{NCl}_2$  ( $\text{M}^+$ ): 389.0374; found 389.0378.

### 5,6-bis(4-bromophenyl)pyrano[2,3,4-*de*]quinoline (4i)



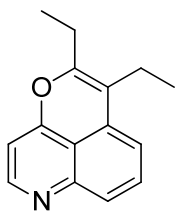
The title compound **4i** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (43.1 mg, 41% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (s, 1H), 7.72 (d,  $J = 8.5$  Hz, 1H), 7.55 (d,  $J = 8.3$  Hz, 2H), 7.48 (t,  $J = 8.0$  Hz, 1H), 7.37 (d,  $J = 8.6$  Hz, 2H), 7.19 – 7.07 (m, 4H), 6.80 (d,  $J = 5.1$  Hz, 1H), 6.61 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 152.4, 150.0, 148.4, 133.4, 133.2, 132.8, 132.4, 132.0, 131.4, 130.6, 129.0, 125.6, 123.6, 122.5, 118.9, 118.3, 116.3, 103.3. HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{13}\text{OBr}_2\text{N}$  ( $\text{M}^+$ ): 476.9358; found 476.9361

### 5,6-bis(4-(trifluoromethyl)phenyl)pyrano[2,3,4-*de*]quinoline (4j)



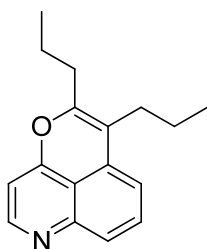
The title compound **4j** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (75.0 mg, 82% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 5.2$  Hz, 1H), 7.78 (d,  $J = 8.5$  Hz, 1H), 7.70 (d,  $J = 8.1$  Hz, 2H), 7.57 – 7.45 (m, 3H), 7.42 – 7.36 (m, 4H), 6.83 (d,  $J = 5.3$  Hz, 1H), 6.59 (d,  $J = 7.3$  Hz, 1H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.7, -62.97.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 159.3, 152.3, 149.7, 148.2, 138.1, 136.3, 131.6, 131.2, 131.1 (q,  $J_{\text{C-F}}=33.6$  Hz), 130.5 (q,  $J_{\text{C-F}}=33.0$  Hz), 129.4, 126.6 (q,  $J_{\text{C-F}}=3.7$  Hz), 125.9, 125.2 (q,  $J_{\text{C-F}}=3.8$  Hz), 123.8 (q,  $J_{\text{C-F}}=273.4$  Hz), 124.0 (q,  $J_{\text{C-F}}=273.5$  Hz), 119.7, 118.3, 116.7, 103.3. HRMS (EI) calcd for  $\text{C}_{25}\text{H}_{13}\text{OF}_6\text{N}$  ( $\text{M}^+$ ): 457.0896; found 457.0899.

### 5,6-diethylpyrano[2,3,4-*de*]quinoline (4k)



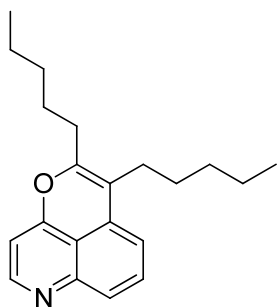
The title compound **4k** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (41.0 mg, 91% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (s, 1H), 7.68 (d,  $J = 8.5$  Hz, 1H), 7.59 (t,  $J = 7.9$  Hz, 1H), 6.97 (d,  $J = 7.3$  Hz, 1H), 6.69 (d,  $J = 5.2$  Hz, 1H), 2.62 – 2.40 (m, 4H), 1.26 (t,  $J = 7.5$  Hz, 3H), 1.18 (t,  $J = 7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 153.2, 151.3, 149.7, 131.8, 130.1, 123.5, 115.5, 113.1, 102.9, 23.9, 19.8, 12.9, 12.6. HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{15}\text{ON}$  ( $\text{M}^+$ ): 225.1148; found 225.1147.

### 5,6-dipropylpyrano[2,3,4-*de*]quinoline (4l)



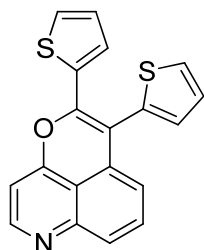
The title compound **4l** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (39.5 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (d,  $J = 5.0$  Hz, 1H), 7.64 (d,  $J = 8.5$  Hz, 1H), 7.56 (t,  $J = 7.9$  Hz, 1H), 6.92 (d,  $J = 7.2$  Hz, 1H), 6.66 (d,  $J = 5.2$  Hz, 1H), 2.54 – 2.34 (m, 4H), 1.79 – 1.64 (m, 2H), 1.63 – 1.41 (m, 2H), 1.10 – 0.96 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 152.2, 151.8, 150.3, 131.4, 130.3, 124.0, 118.7, 114.5, 113.1, 102.8, 32.5, 28.7, 21.4, 21.2, 14.4, 14.0. HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{19}\text{ON}$  ( $\text{M}^+$ ): 253.1461; found 253.1465.

### 5,6-dibutylpyrano[2,3,4-*de*]quinoline (4m)



The title compound **4m** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (34.3 mg, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (s, 1H), 7.63 (d,  $J = 8.5$  Hz, 1H), 7.56 (t,  $J = 7.8$  Hz, 1H), 6.91 (d,  $J = 7.3$  Hz, 1H), 6.66 (d,  $J = 3.1$  Hz, 1H), 2.54 – 2.36 (m, 6H), 1.71 – 1.62 (m, 3H), 1.59 – 1.50 (m, 3H), 1.45 – 1.28 (m, 11H), 1.00 – 0.86 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 152.3, 151.7, 150.4, 131.4, 130.4, 129.3, 124.1, 114.5, 113.0, 102.9, 32.2, 31.6, 30.6, 27.9, 27.6, 26.7, 22.7, 22.6, 14.2, 14.1. HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{27}\text{ON}$  ( $\text{M}^+$ ):309.2087; found 309.2086.

#### 5,6-di(thiophen-2-yl)pyrano[2,3,4-*de*]quinoline (**4n**)



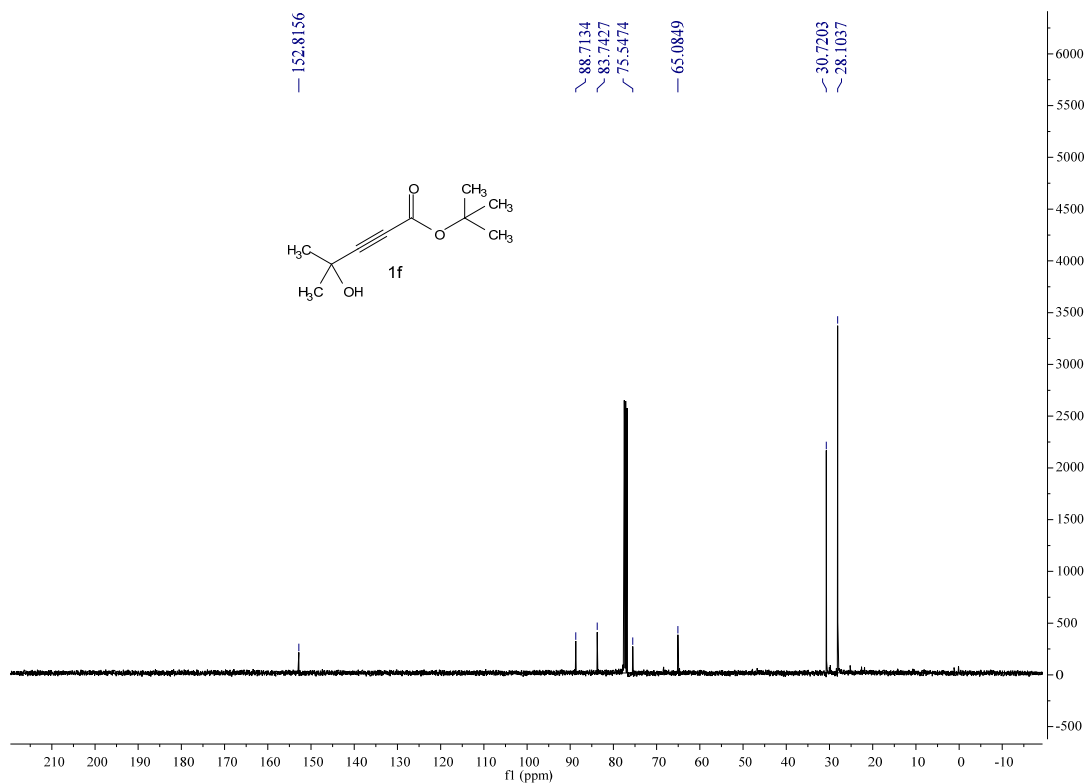
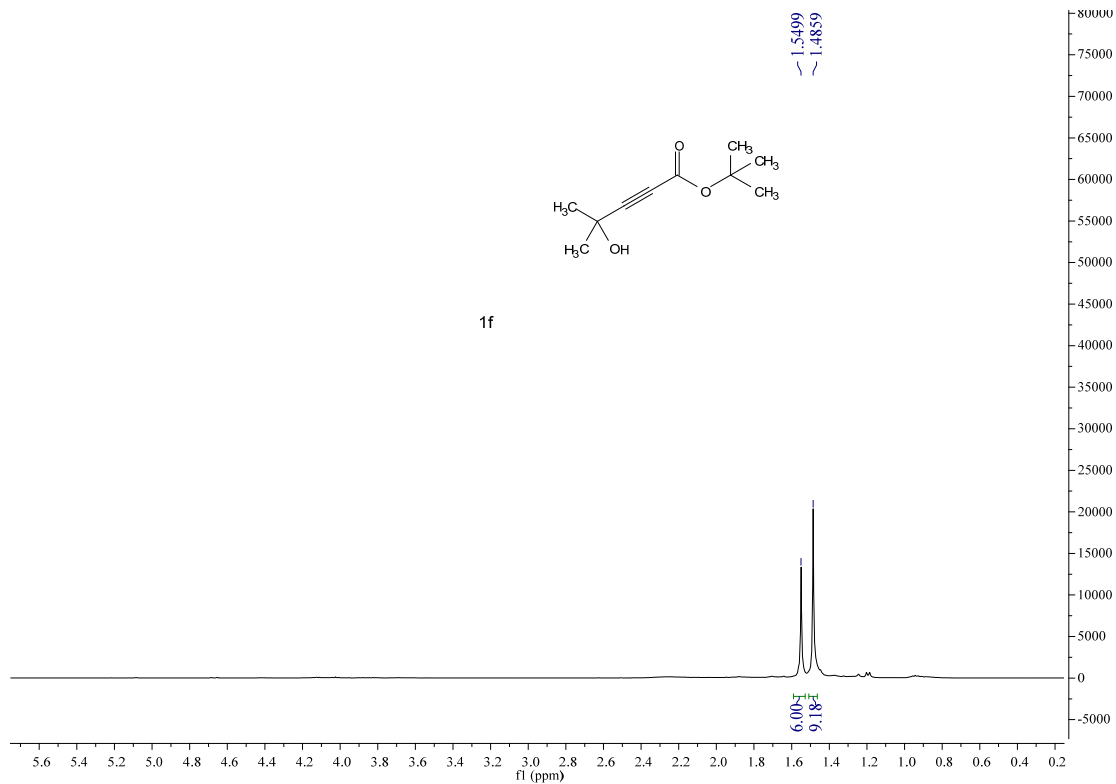
The title compound **4n** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (30.0 mg, 45% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (s, 1H), 7.70 (d,  $J = 8.5$  Hz, 1H), 7.60 (d,  $J = 5.0$  Hz, 1H), 7.50 (t,  $J = 7.9$  Hz, 1H), 7.30 (d,  $J = 4.9$  Hz, 1H), 7.27 – 7.23 (m, 1H), 7.19 (d,  $J = 3.5$  Hz, 1H), 7.09 (d,  $J = 3.0$  Hz, 1H), 6.96 (t,  $J = 4.4$  Hz, 1H), 6.86 (d,  $J = 4.9$  Hz, 1H), 6.63 (d,  $J = 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 152.4, 149.7, 146.2, 135.0, 134.4, 131.9, 131.6, 129.9, 129.2, 128.7, 128.6, 128.5, 127.0, 125.2, 116.6, 110.4, 103.3. HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{11}\text{ONS}_2$  ( $\text{M}^+$ ):333.0277; found 333.0280.

### 3. References

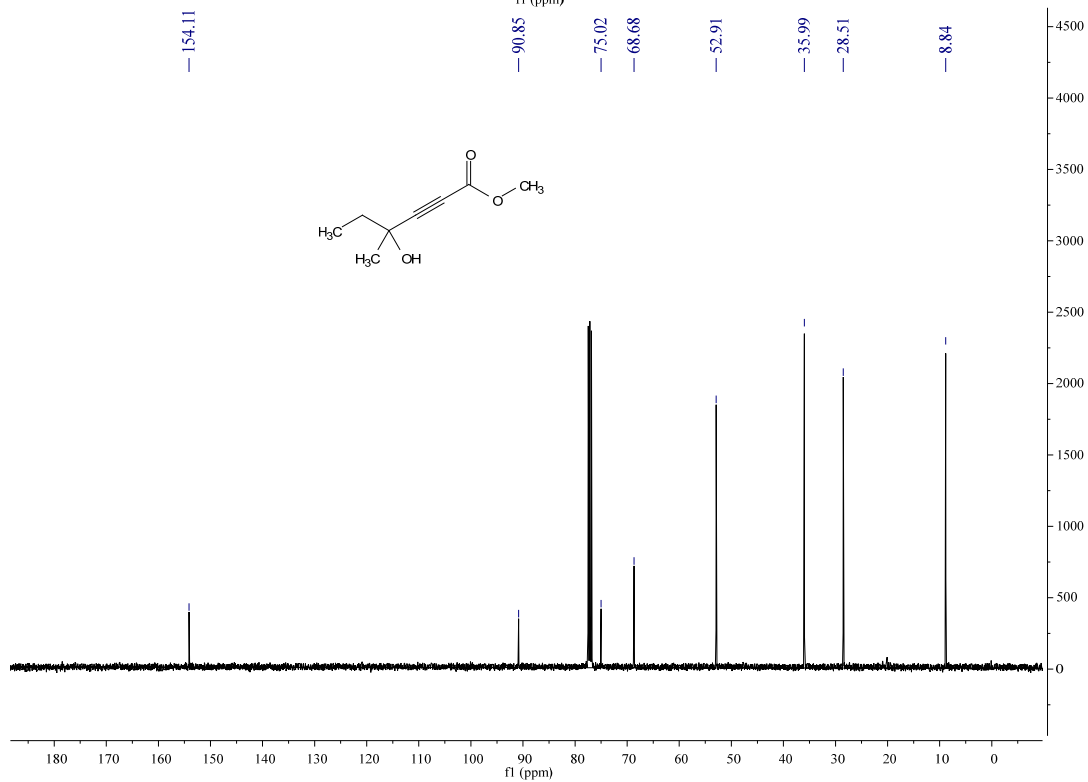
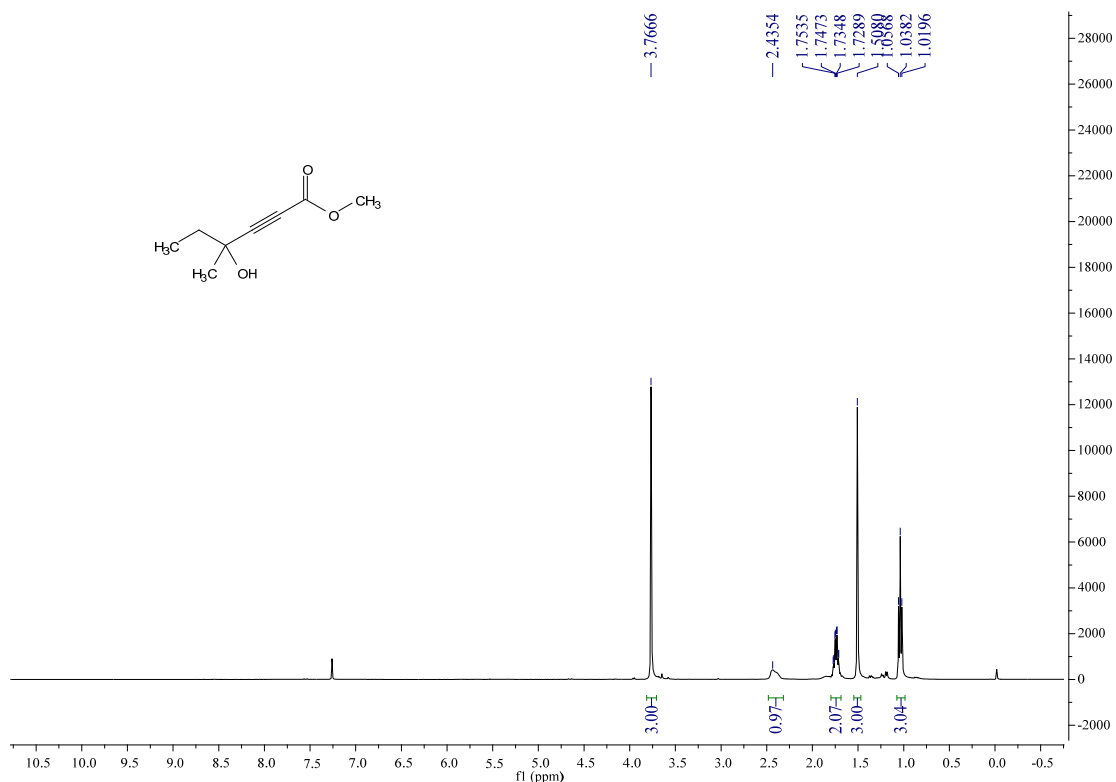
- [1] (a) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* 2010, **132**, 8550;  
(b) M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and Paul A. Grieco, *Org. Lett.* 2002, **4**, 3199;  
(c) R. M. Carlson, J. R. Peterson, B. J. Hoop, K. J. Jensen, *Synthetic Communications*, 1982, **12**, 977;  
(d) S. Yu, N. Keiichi, K. Tanaka, *J. Am. Chem. Soc.* 2010, **132**, 7896;  
(e) H.-T. zhu, L.-J. wang, K.-G. Ji, X.-Y. Liu and Y.-M. Liang, *Chem. Asian J.* 2012, **7**, 1862 ;

## 4. NMR Spectra

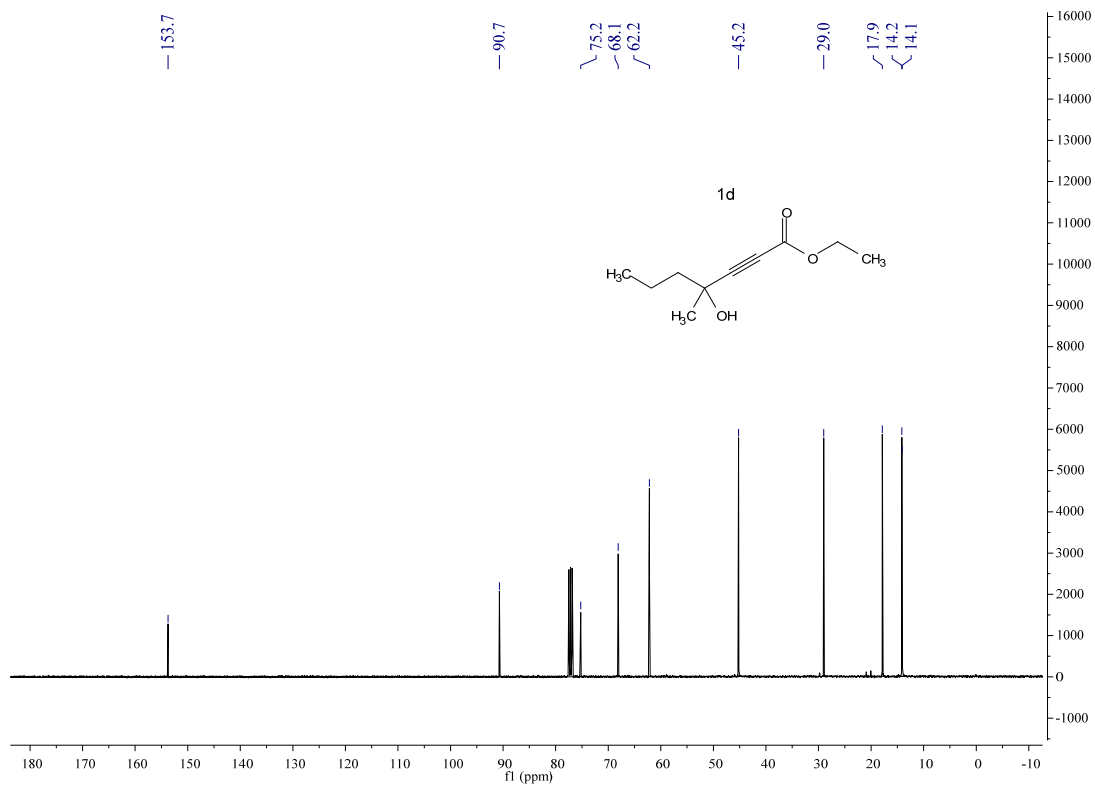
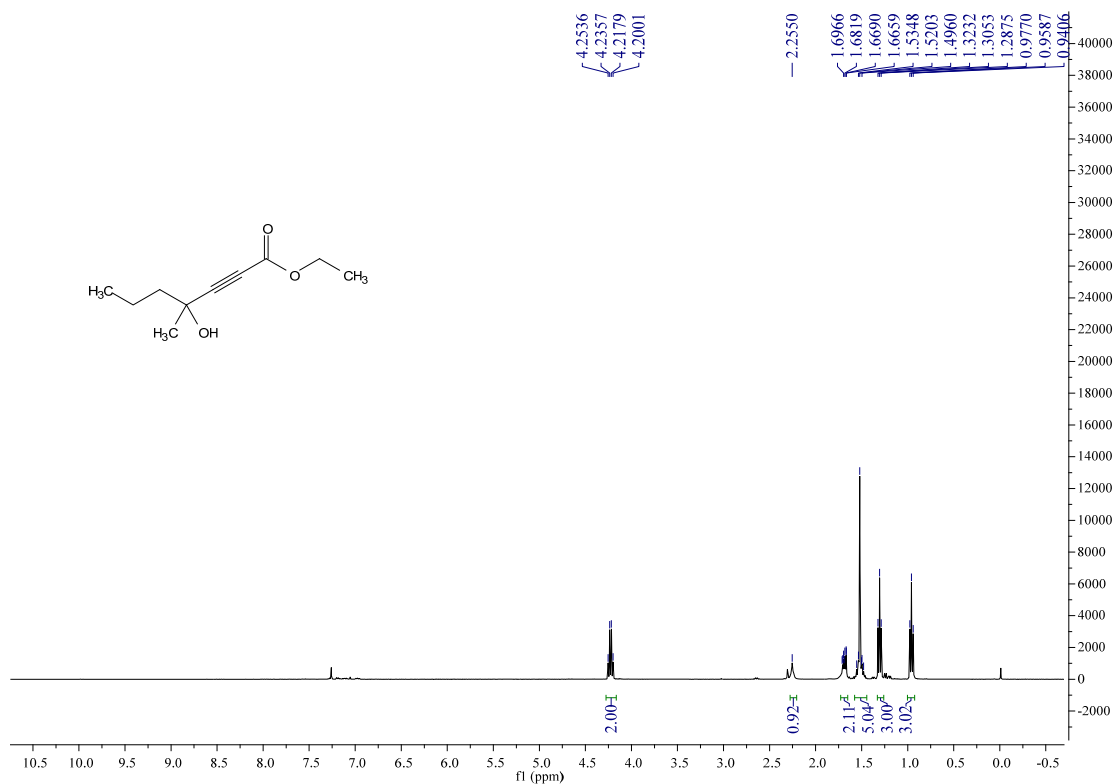
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2b

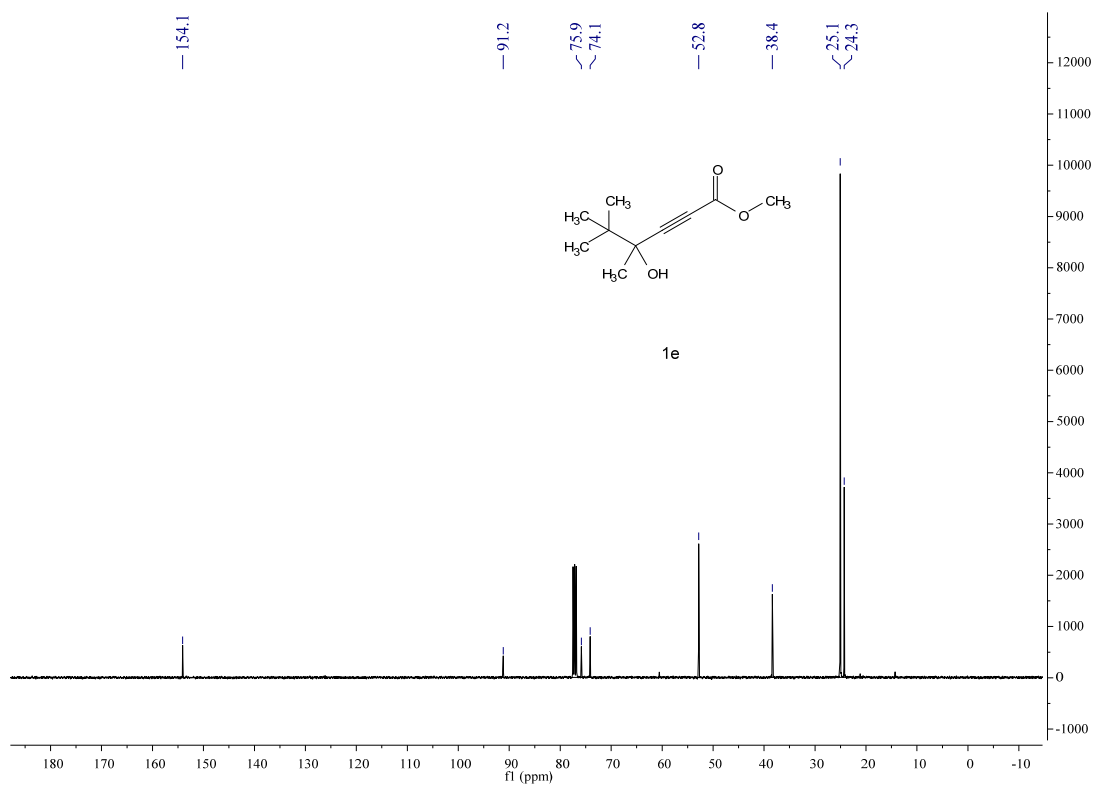
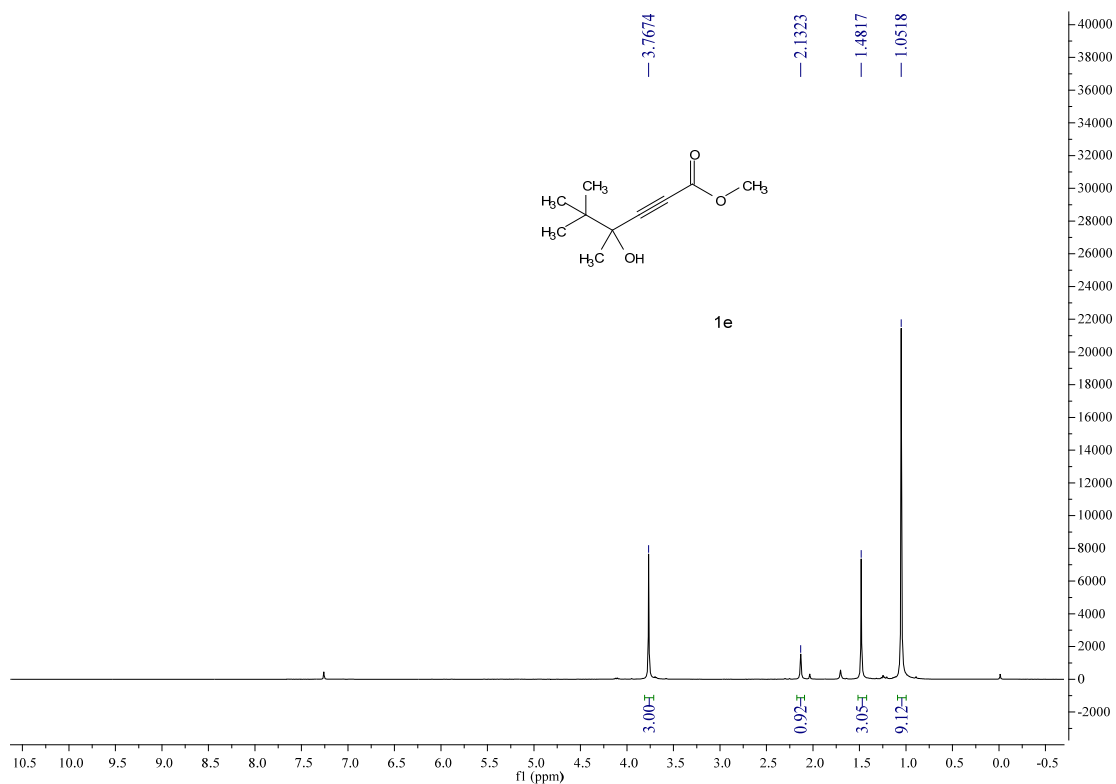


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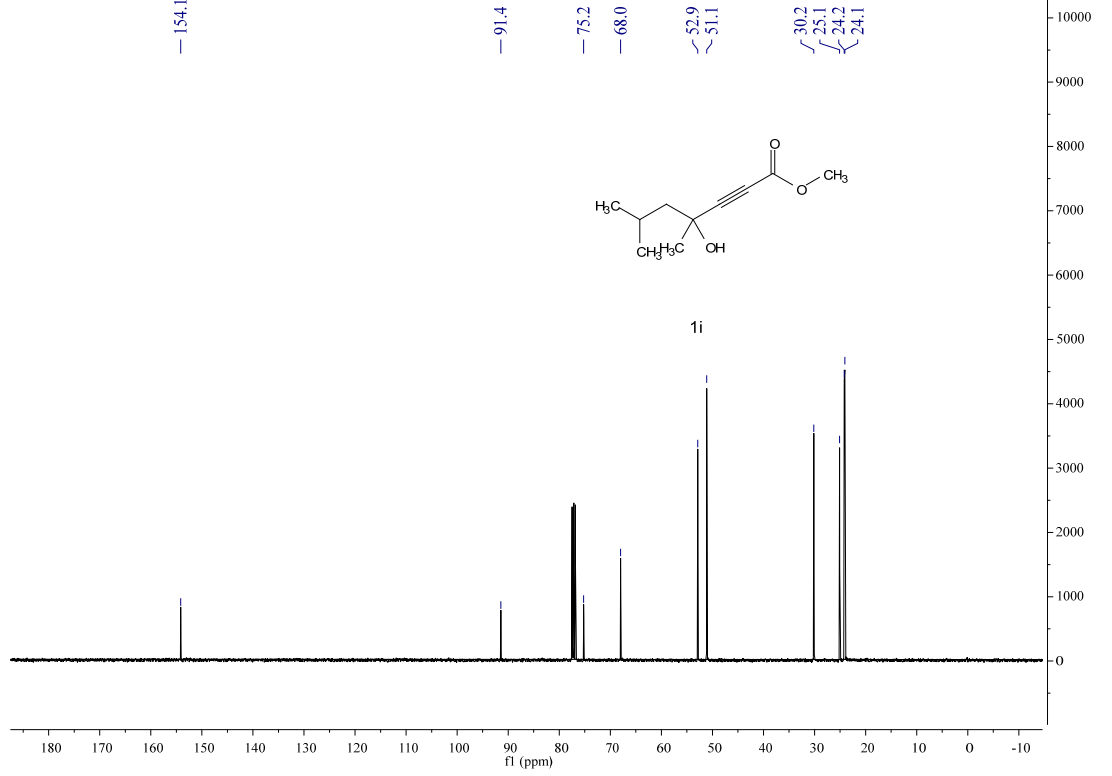
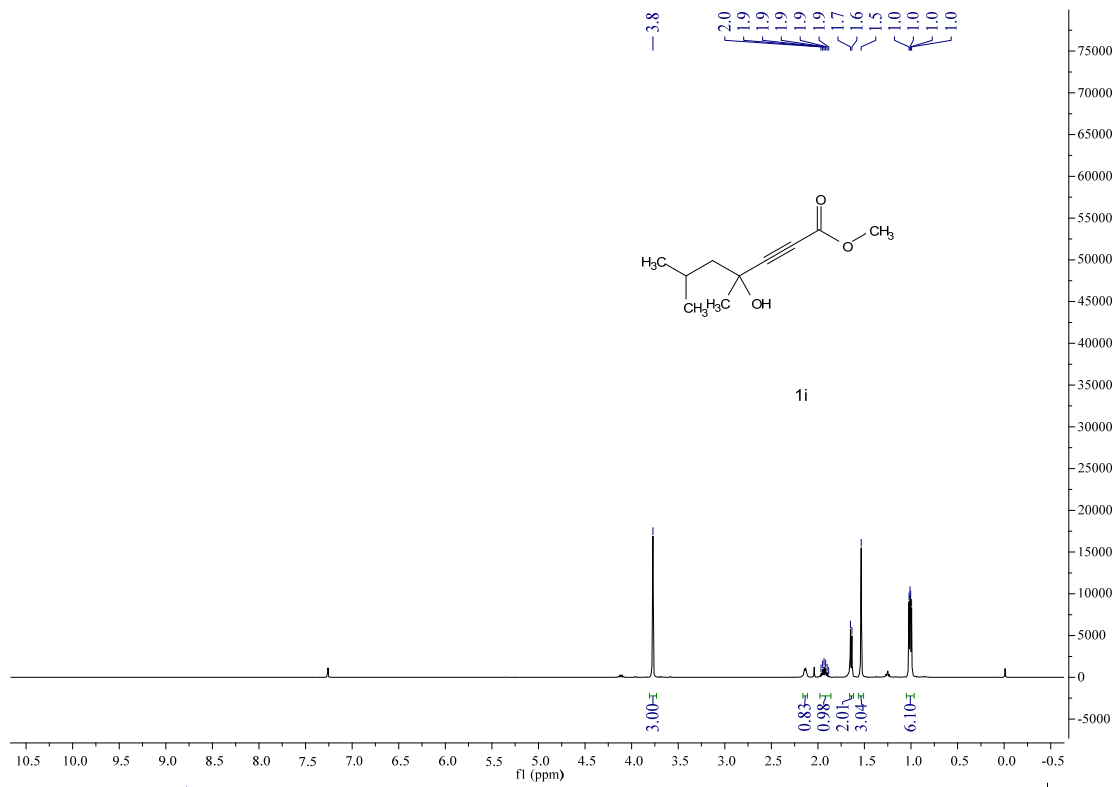




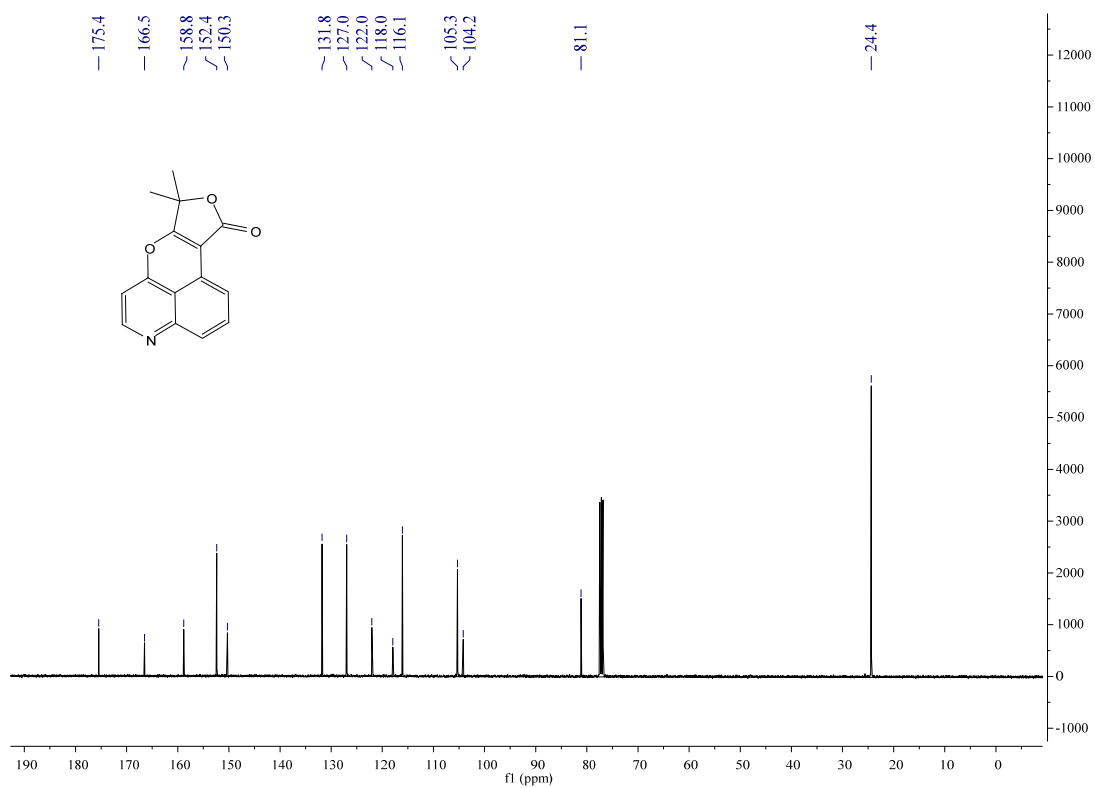
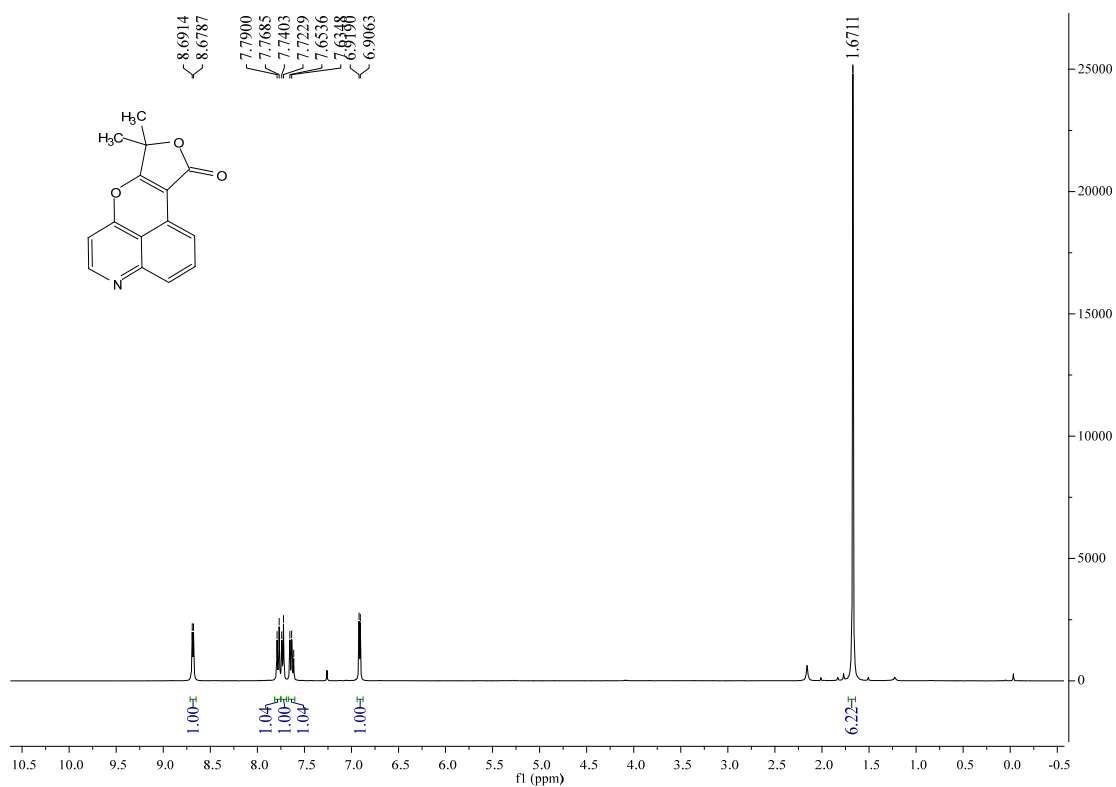
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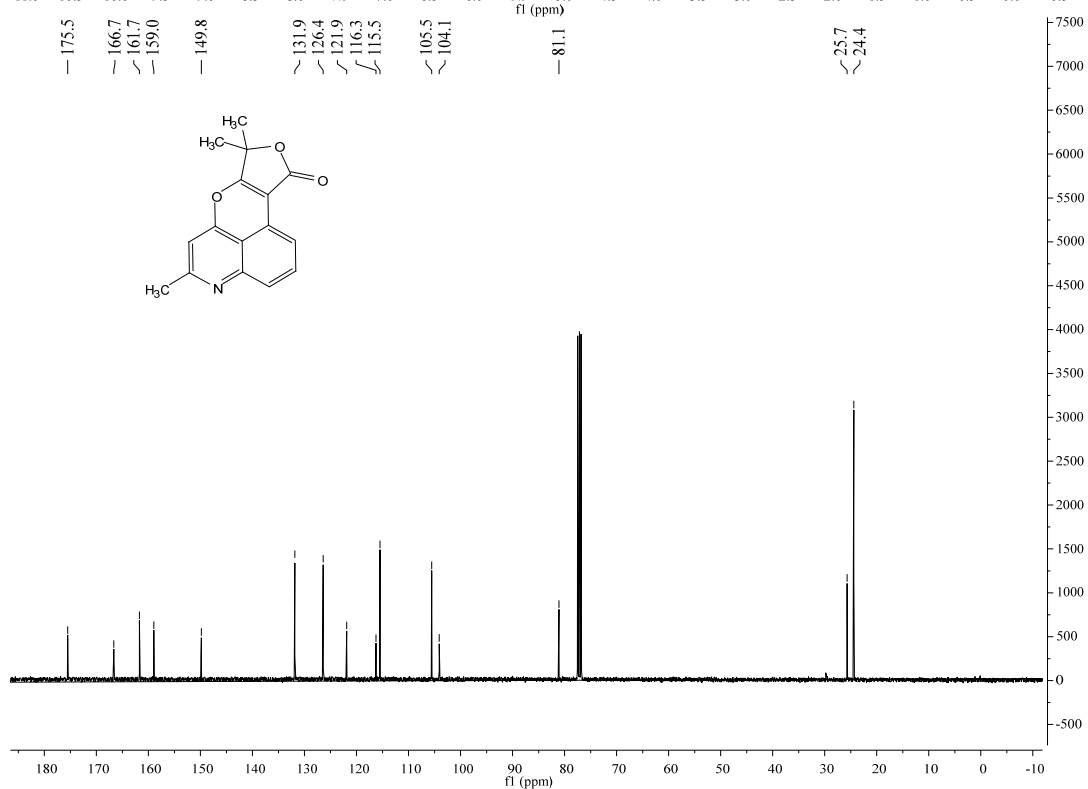
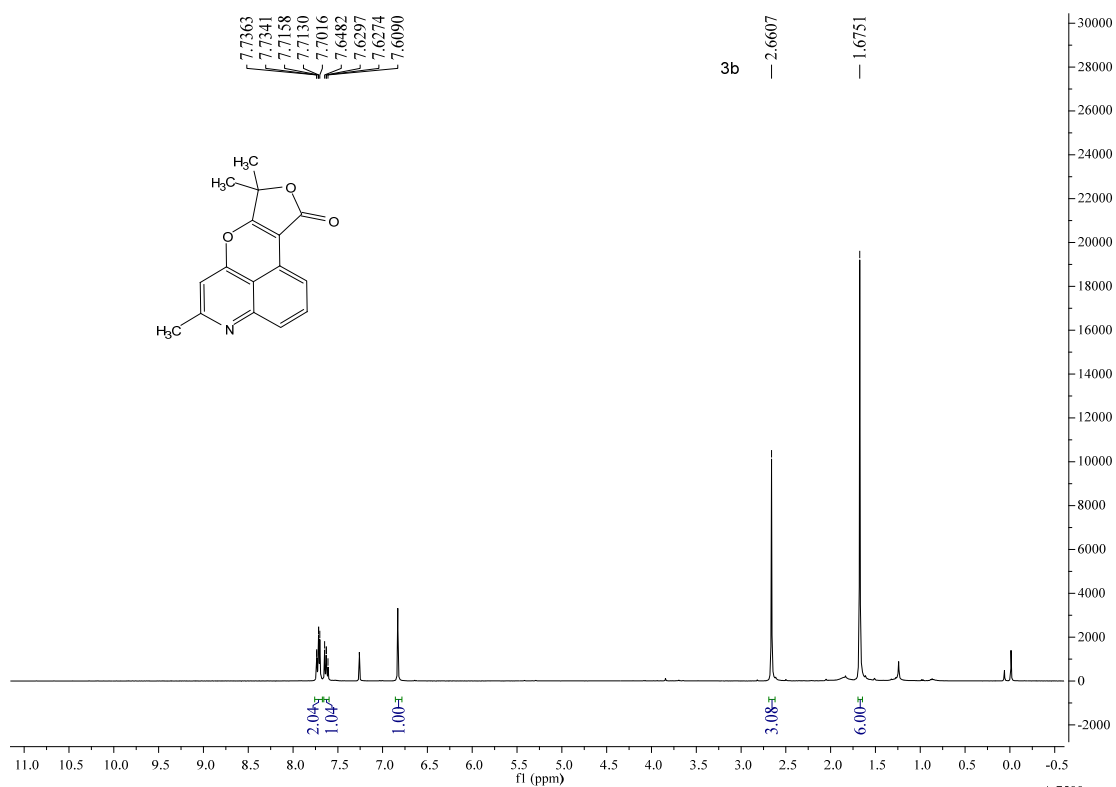
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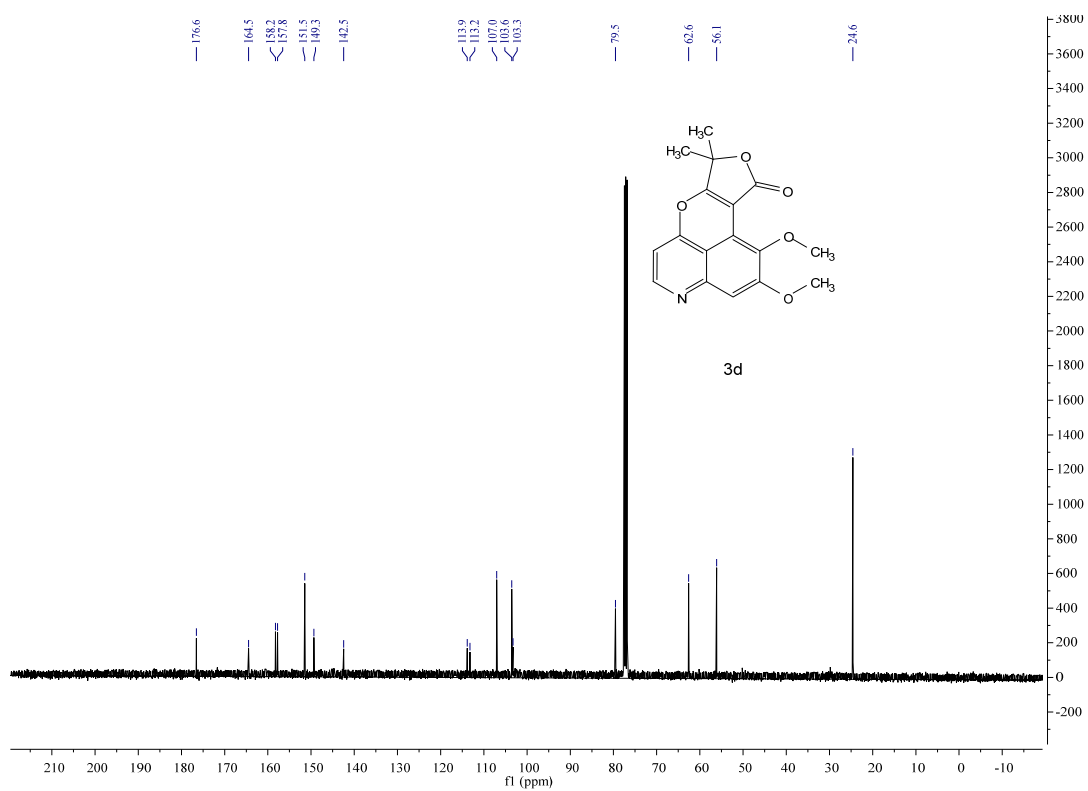
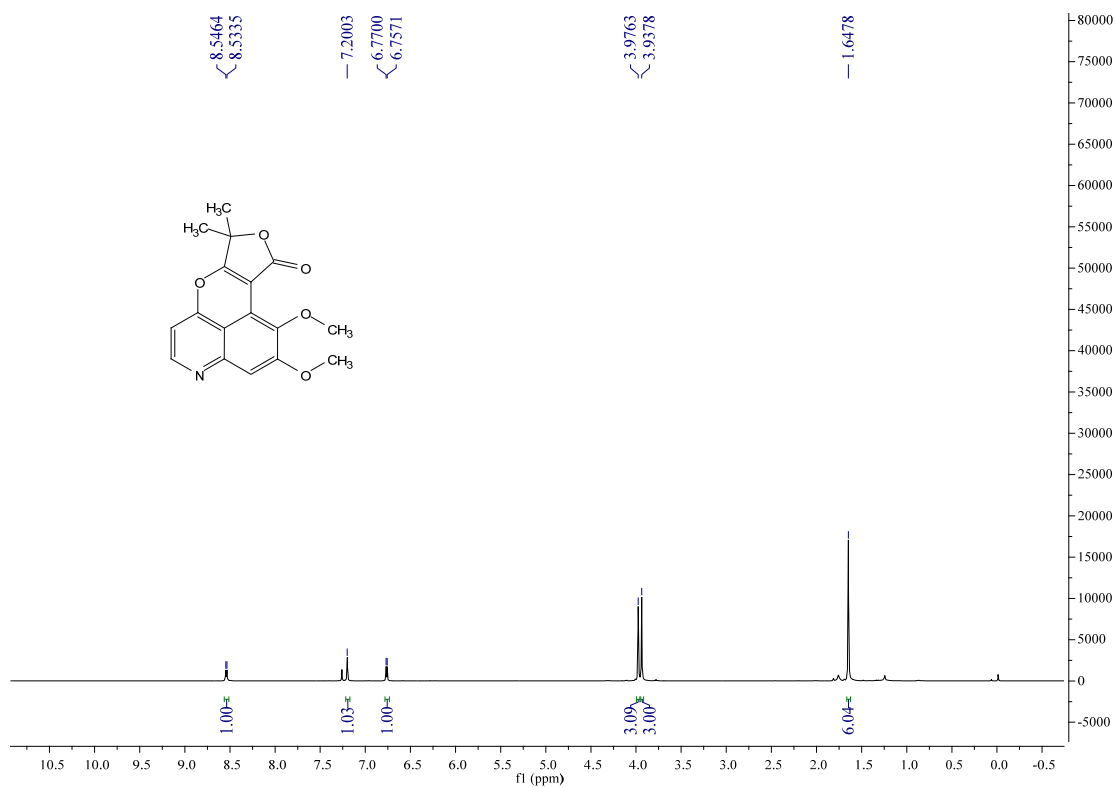
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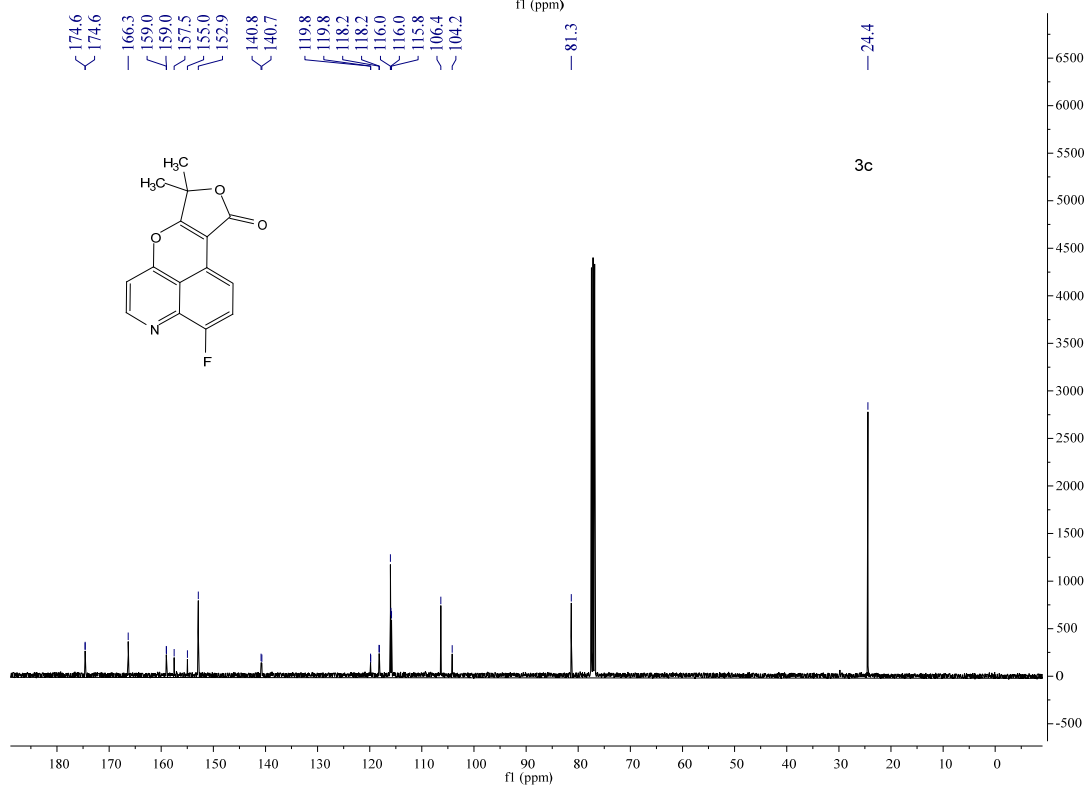
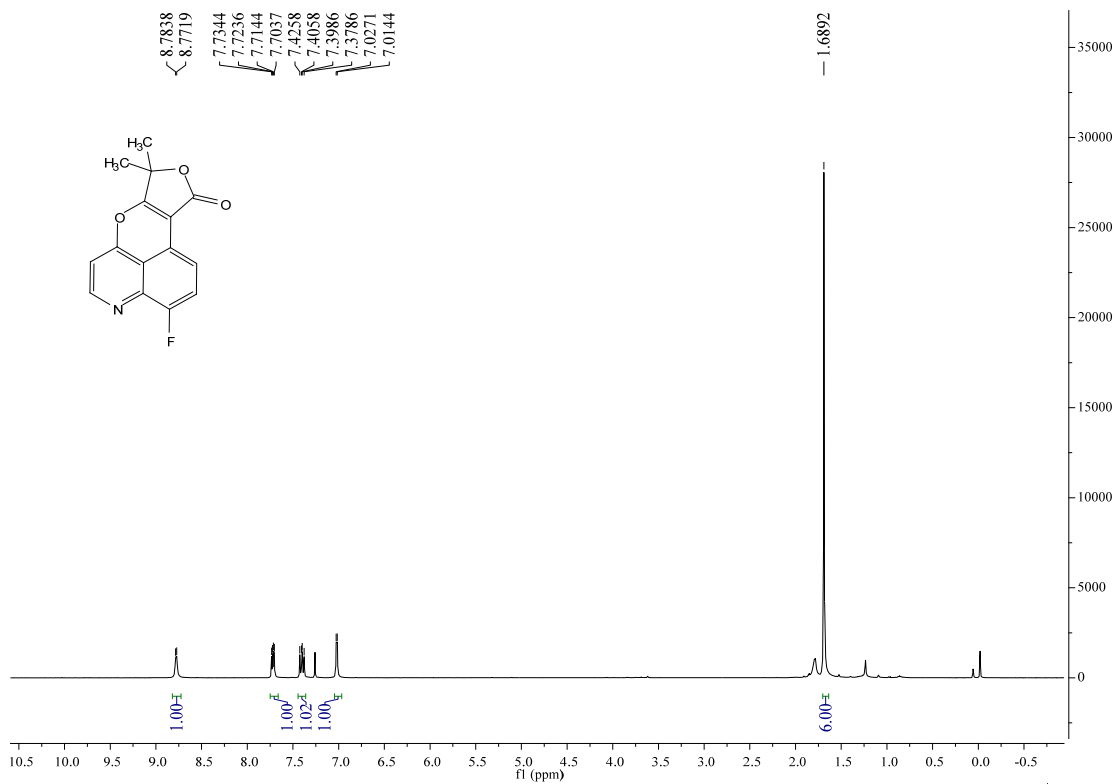
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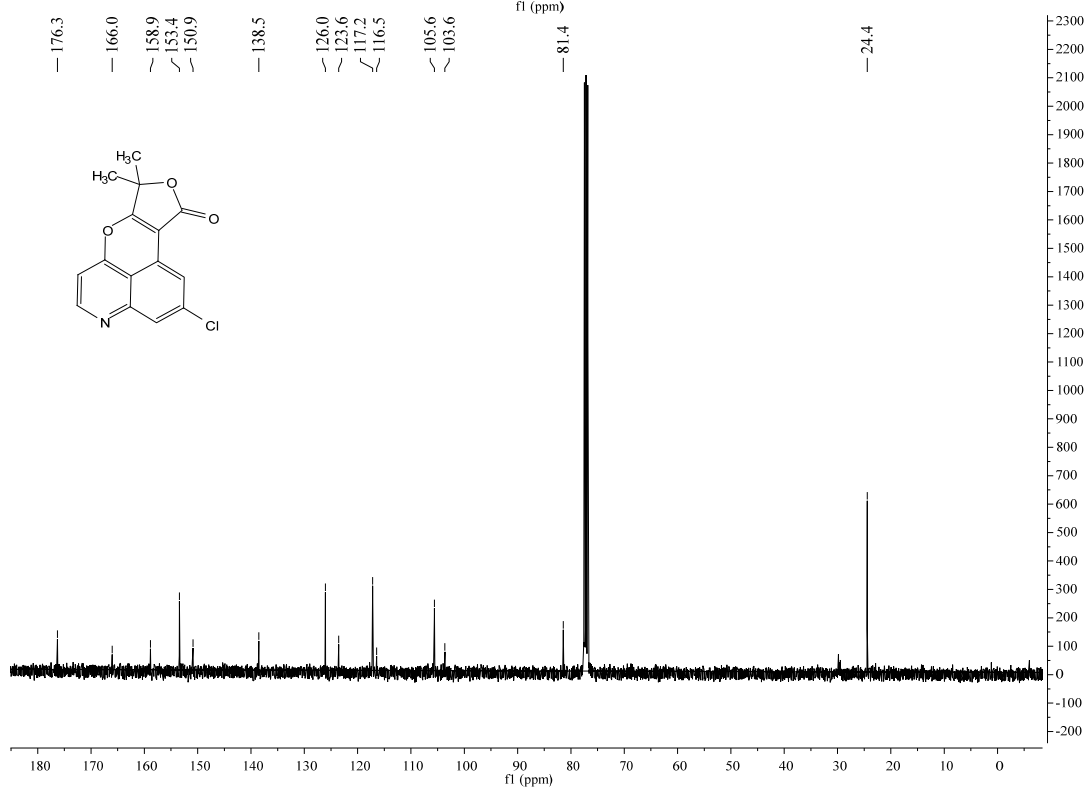
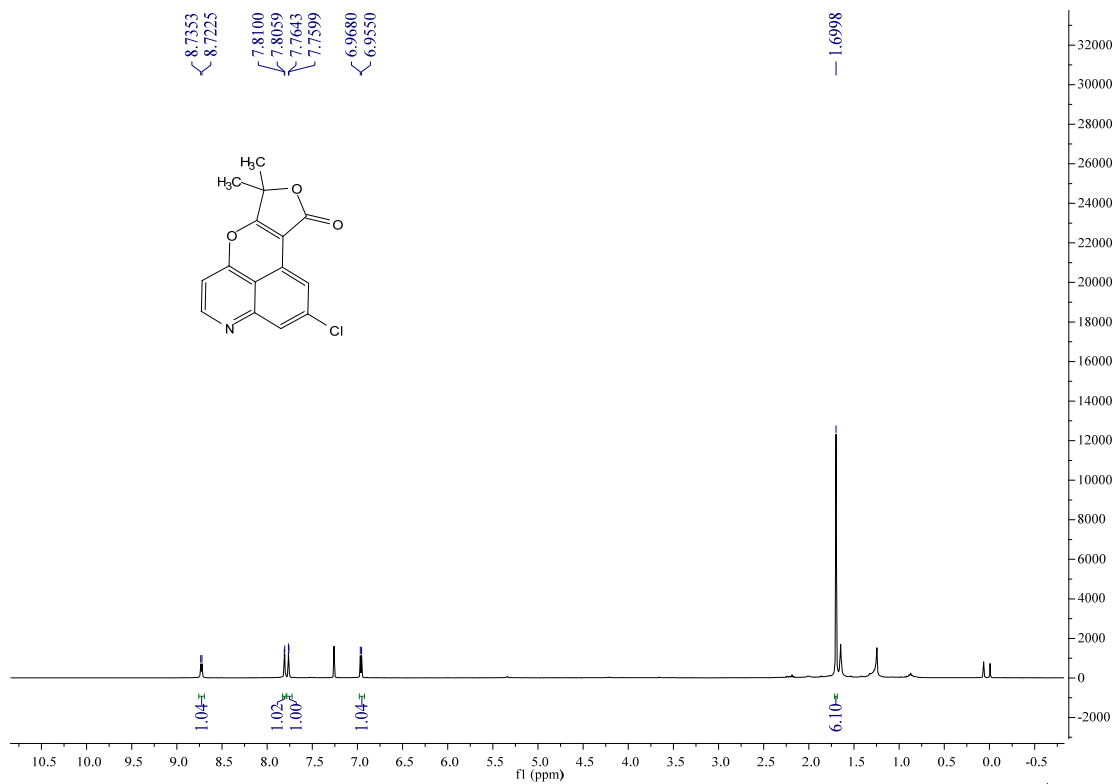
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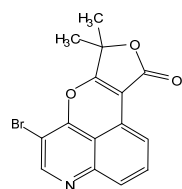
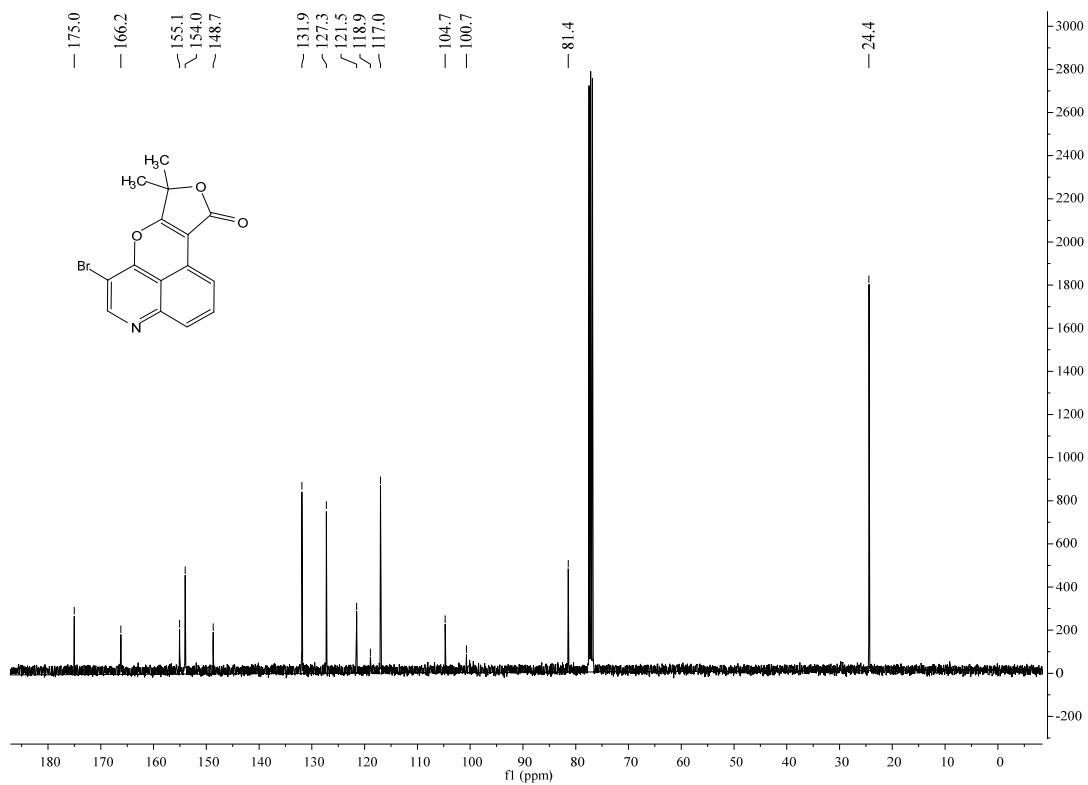
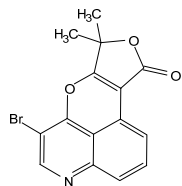
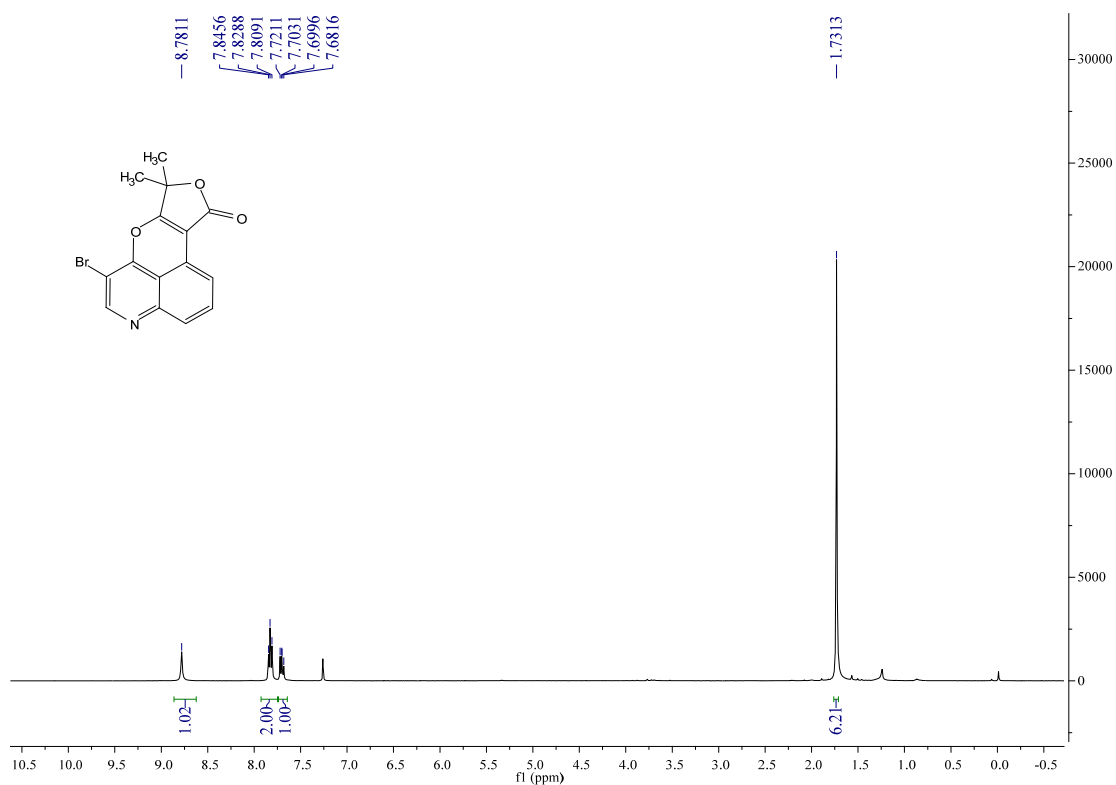
**3ac**



3ad

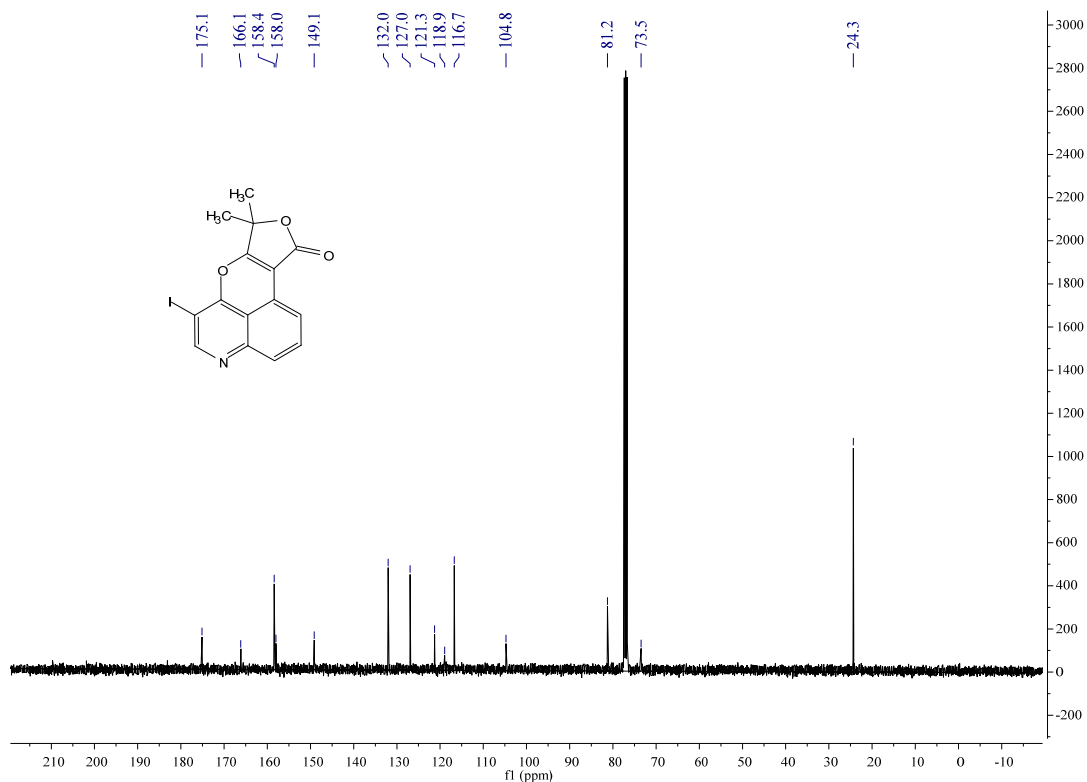
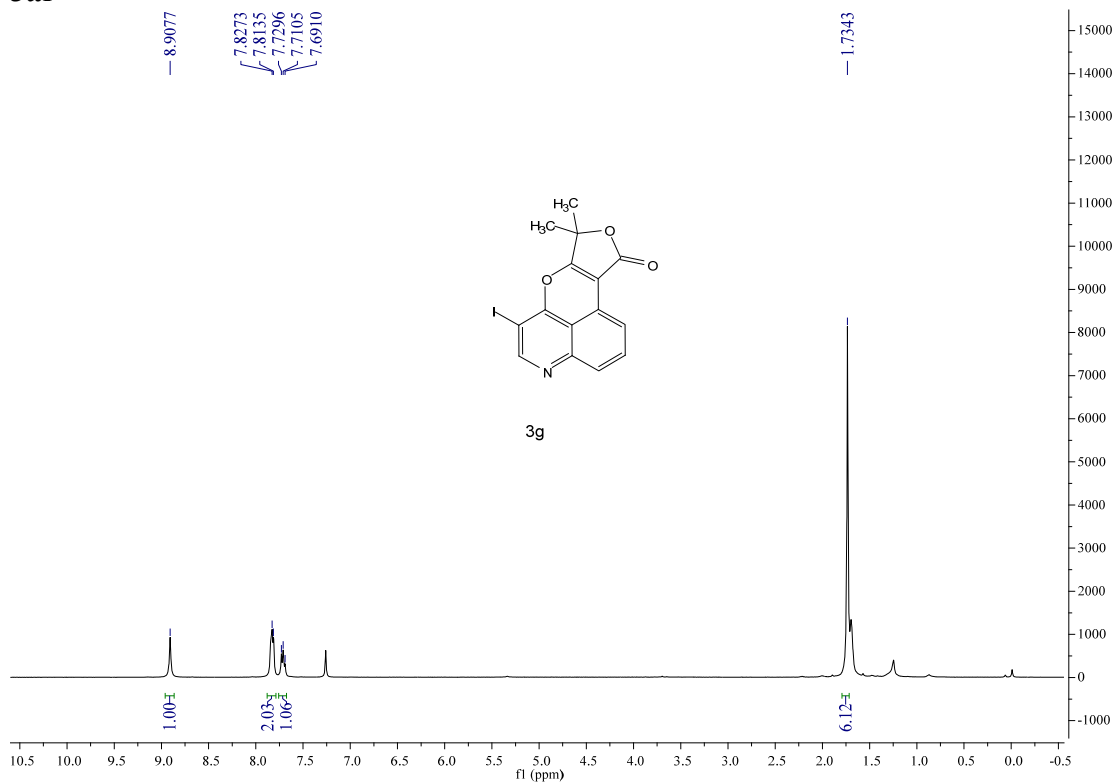


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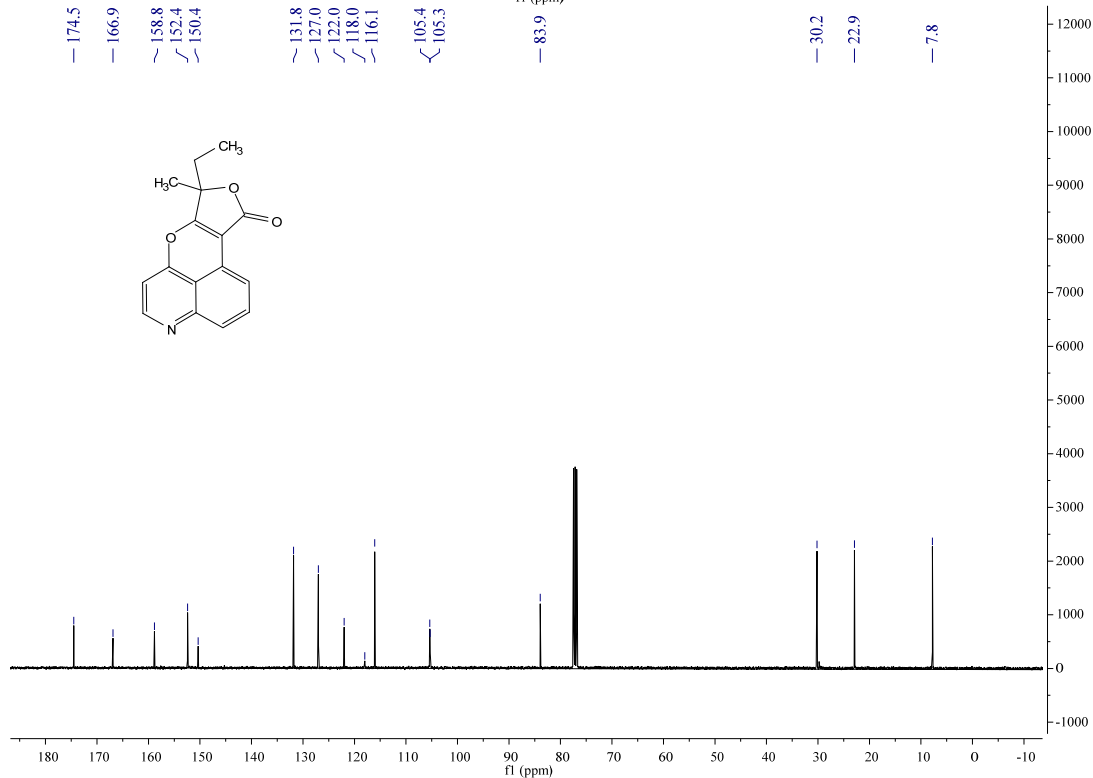
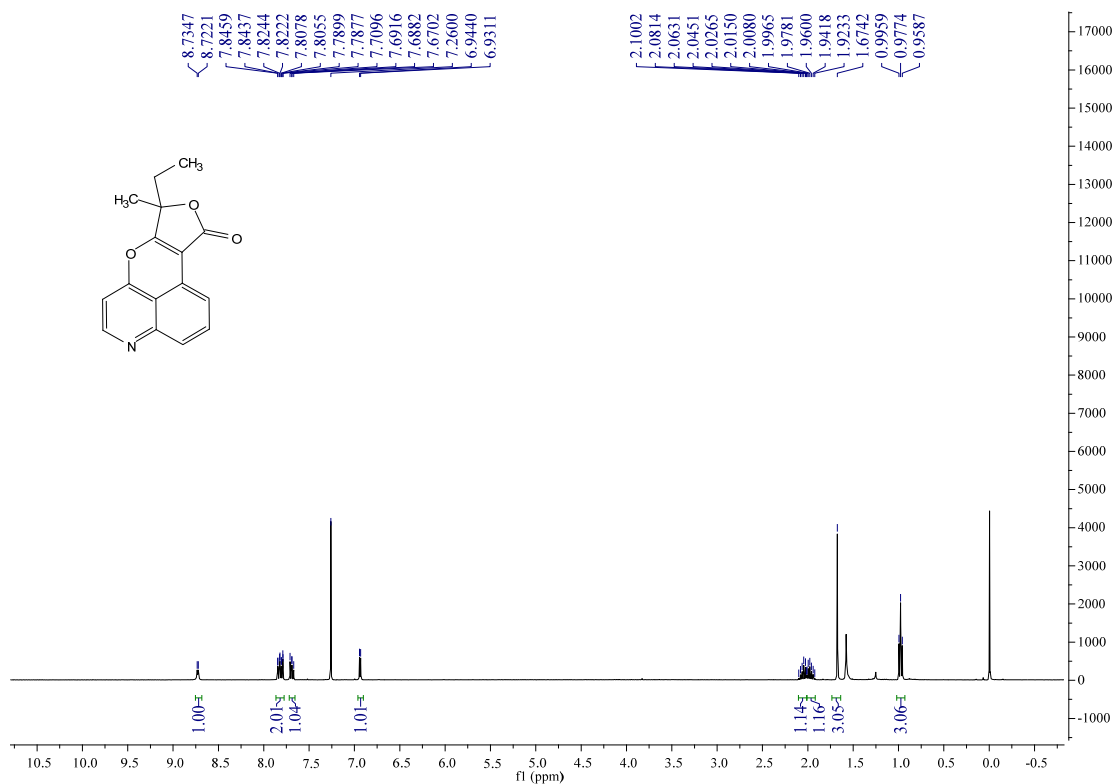




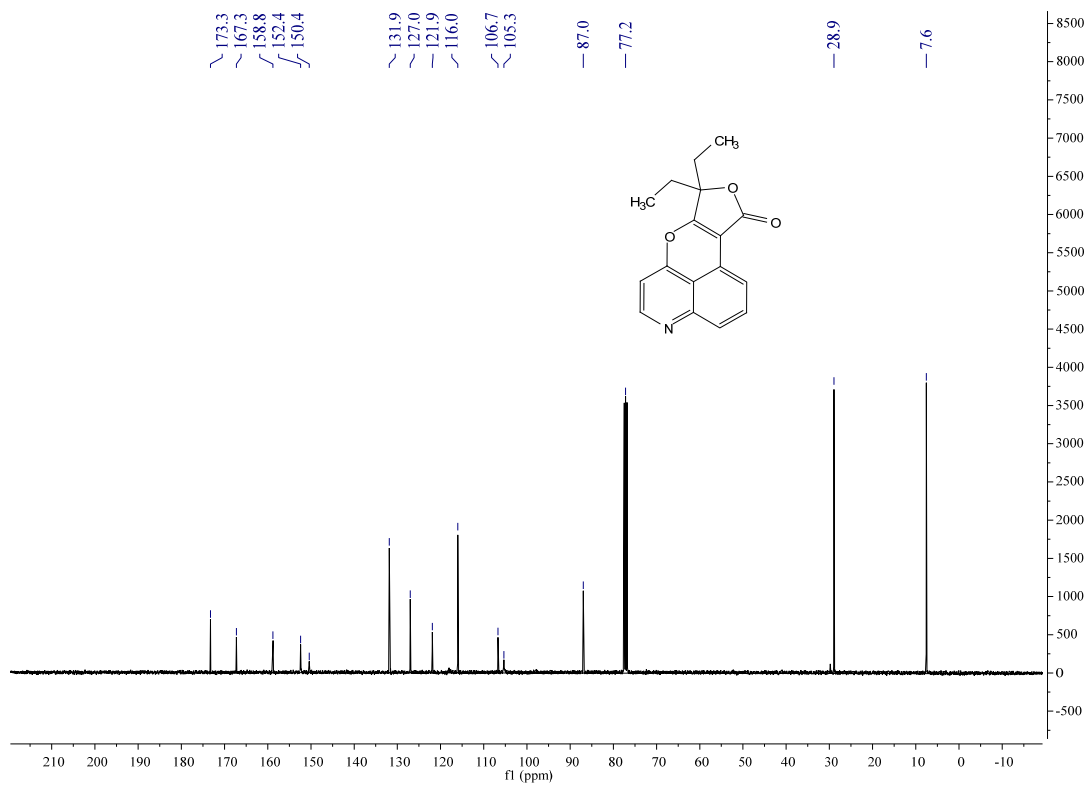
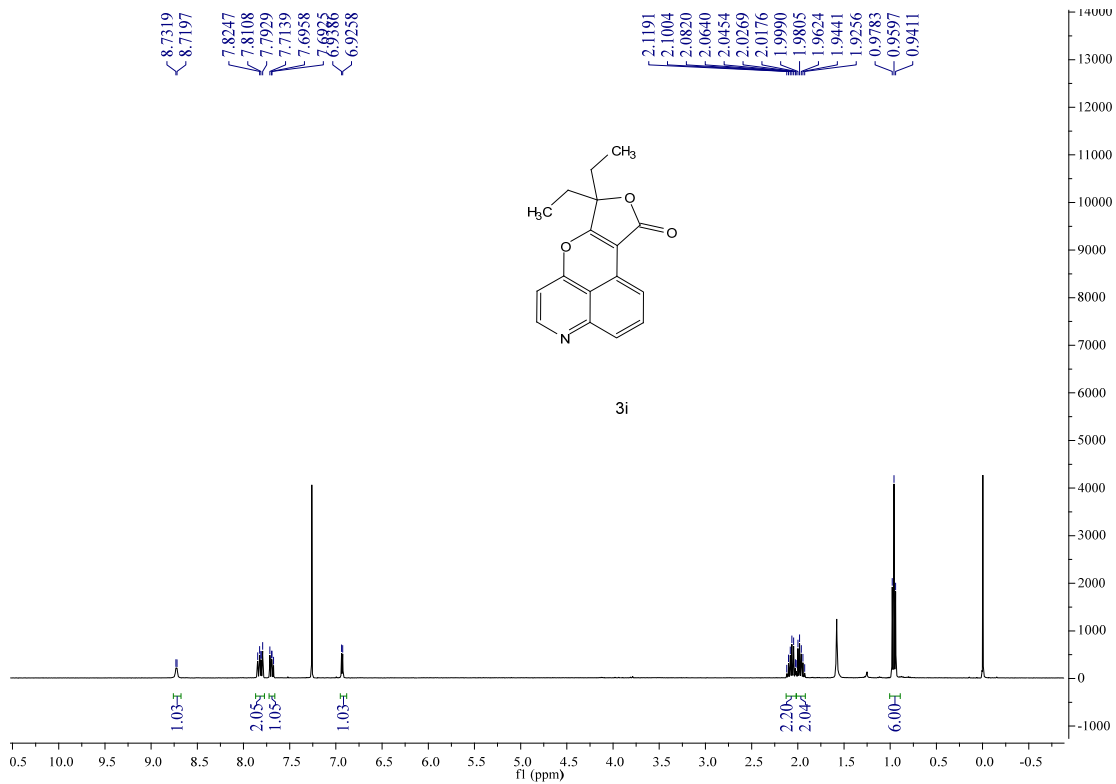
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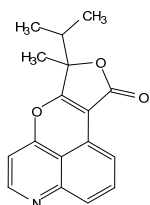
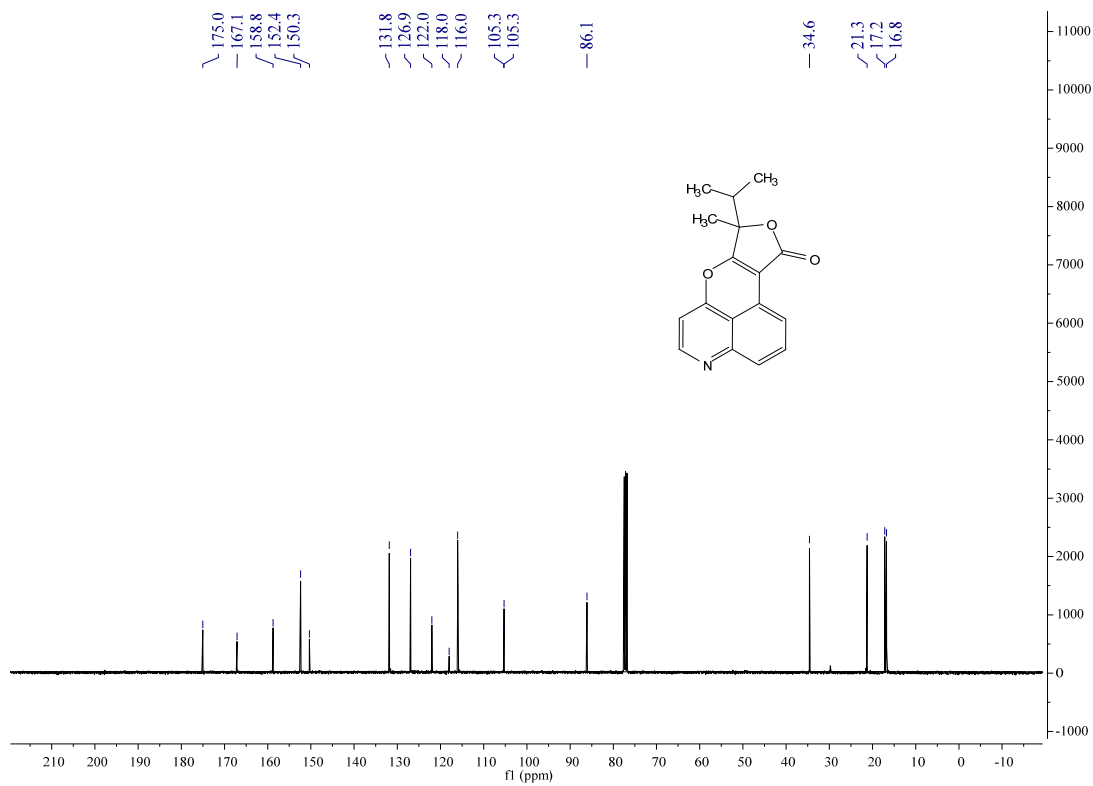
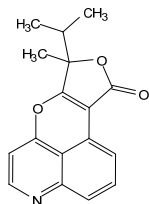
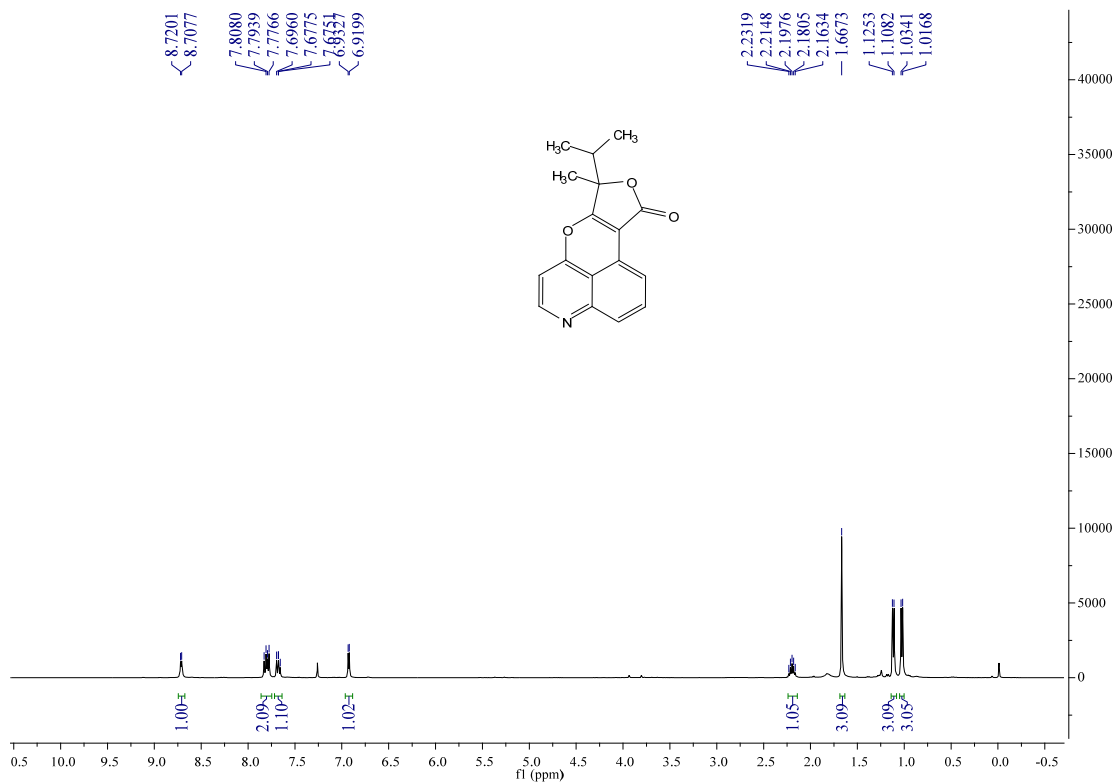
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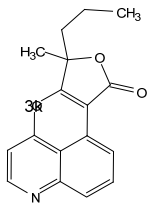
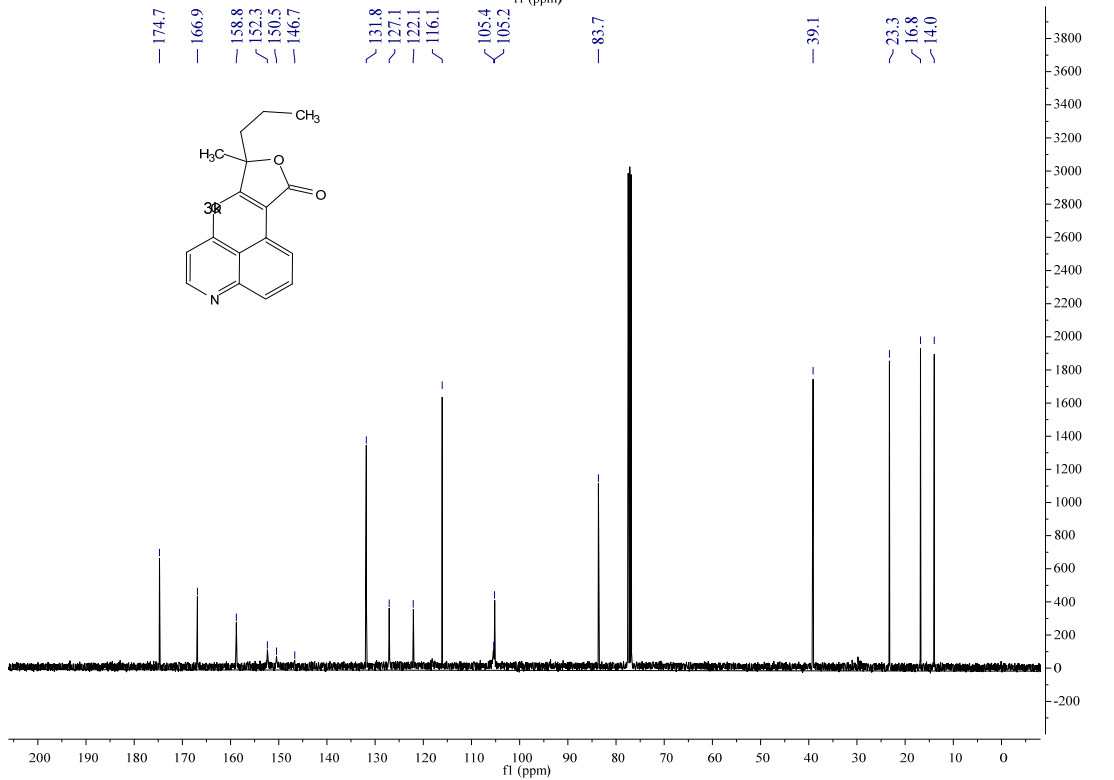
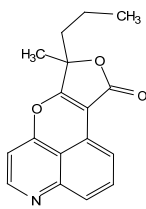
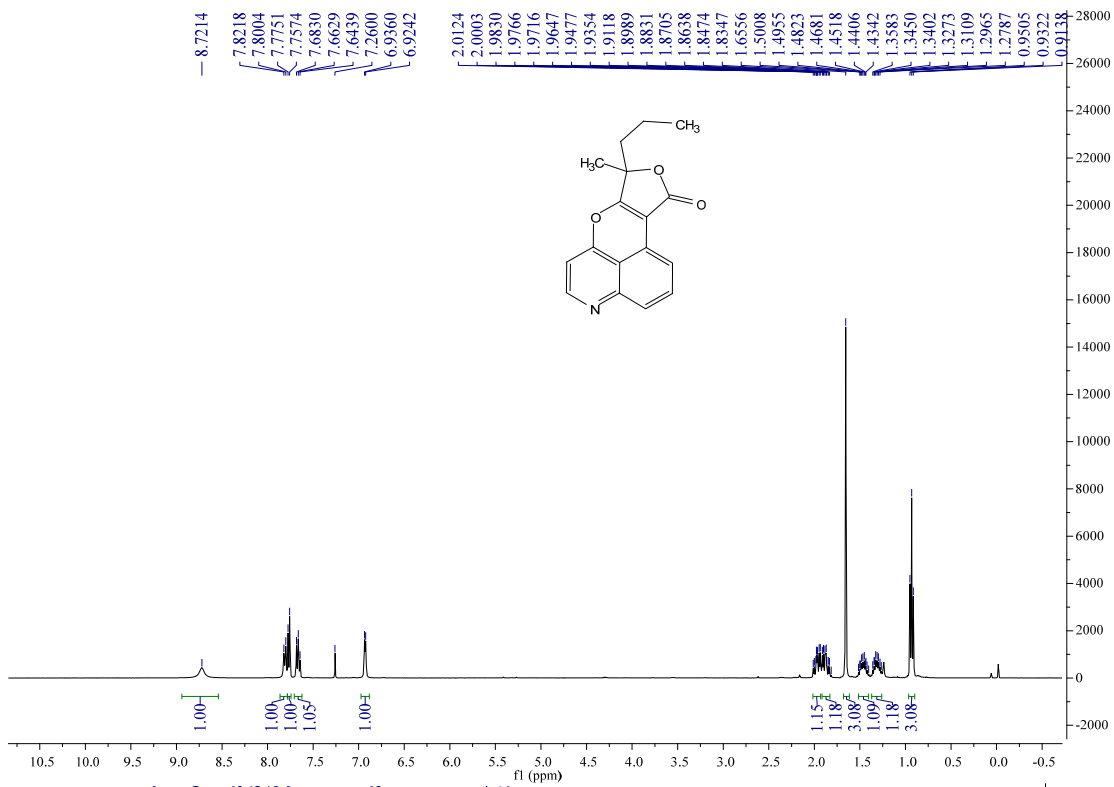
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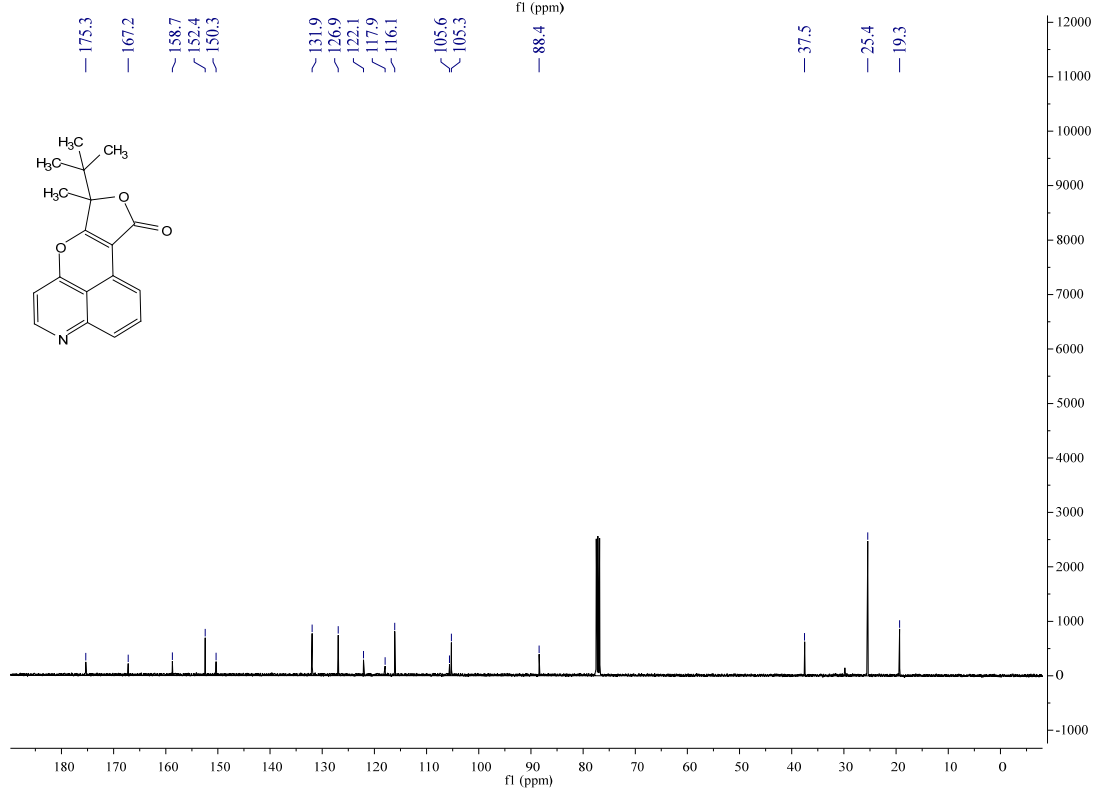
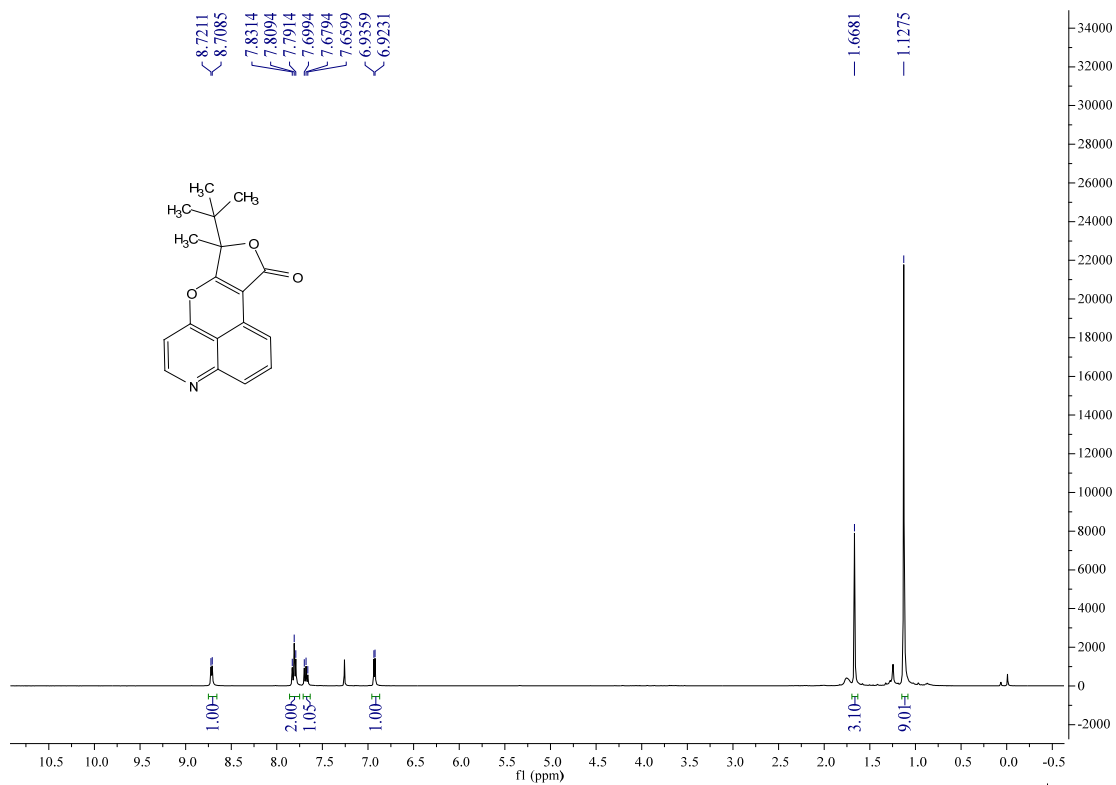
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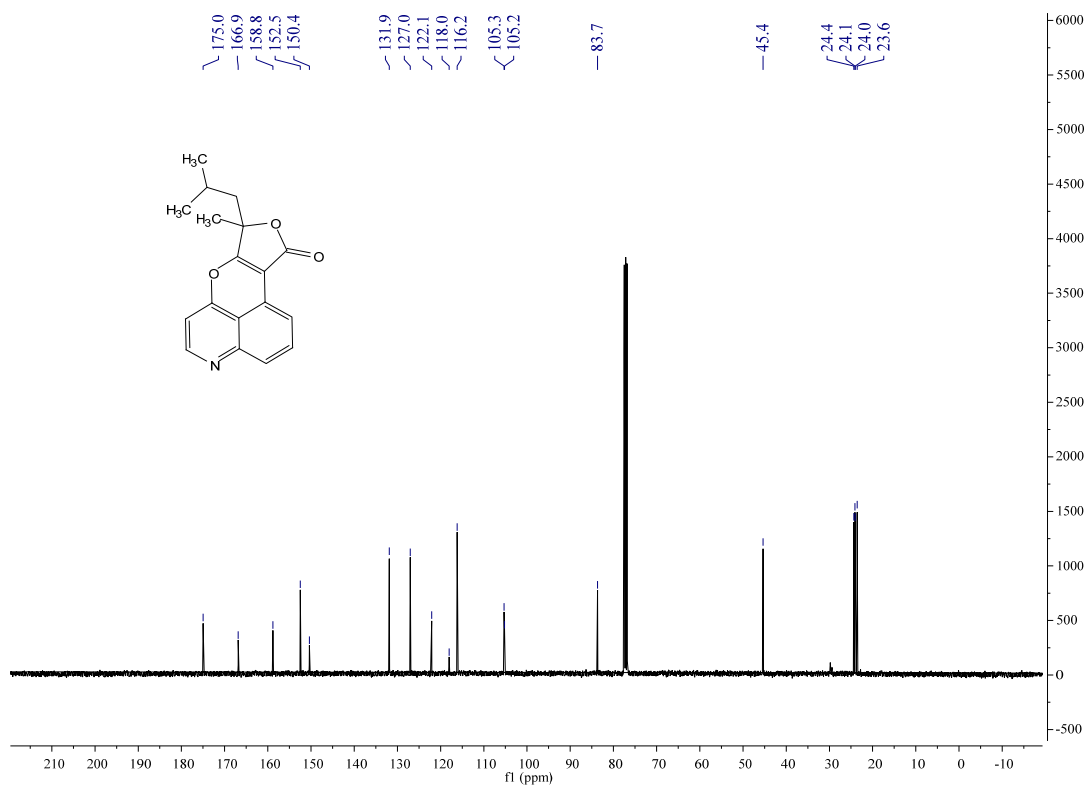
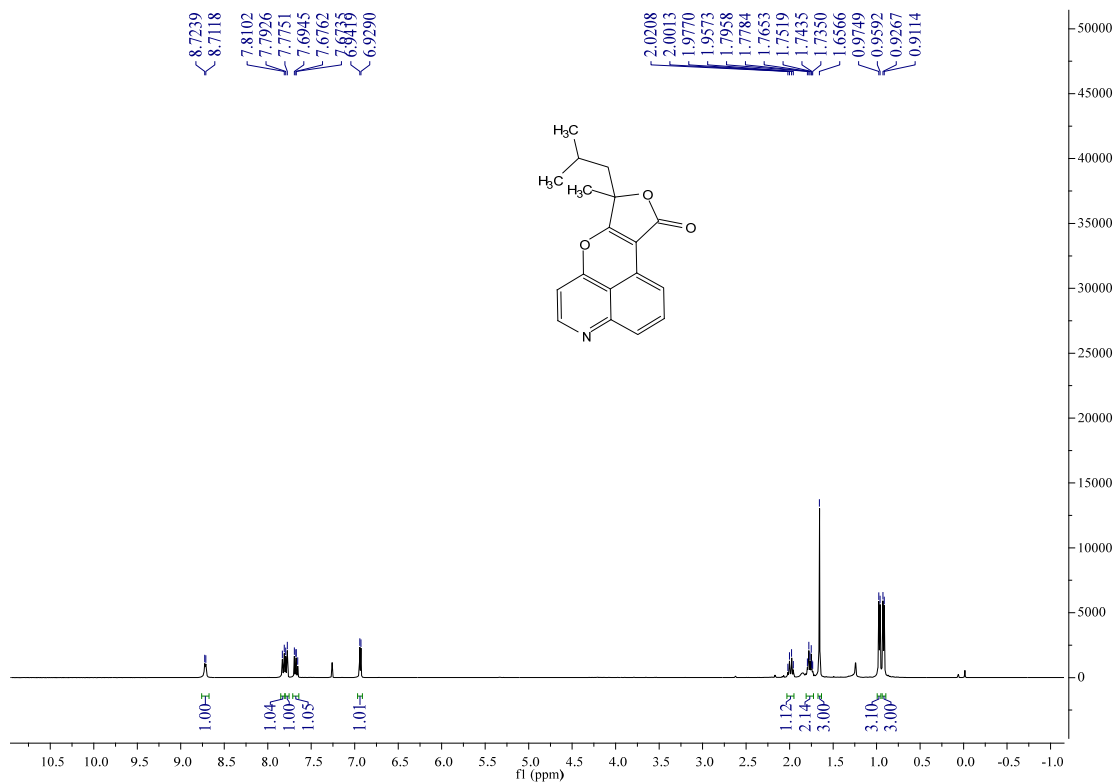
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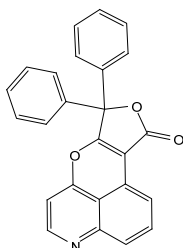
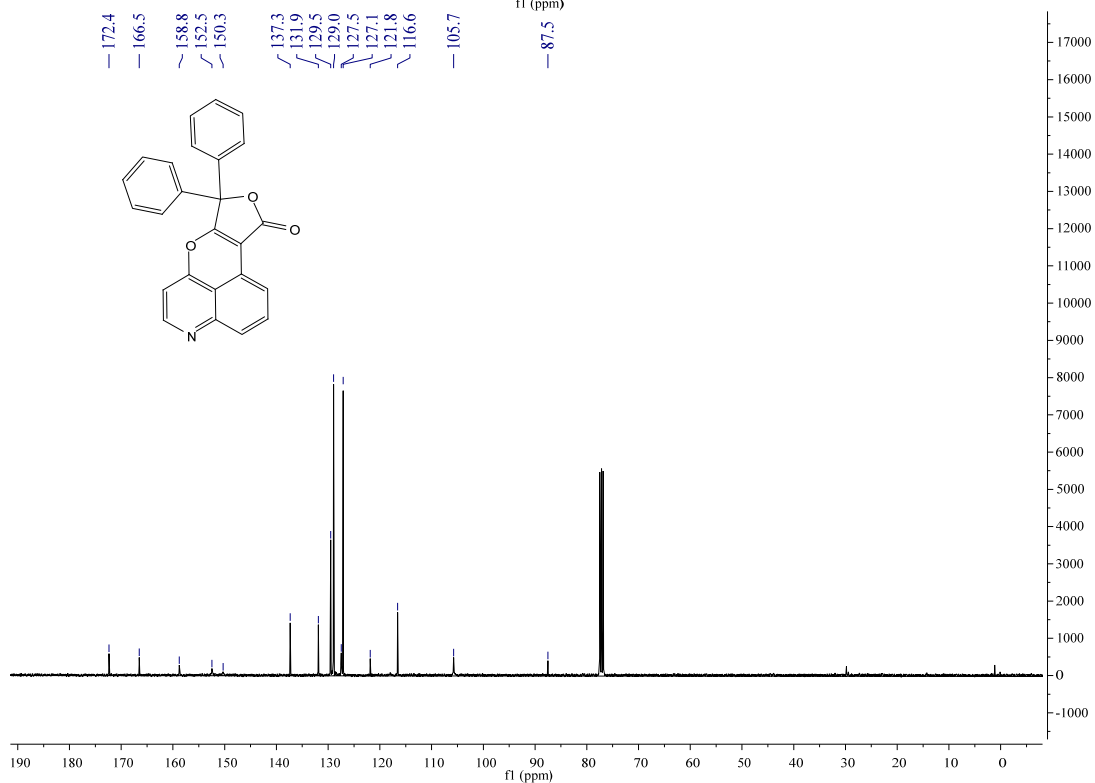
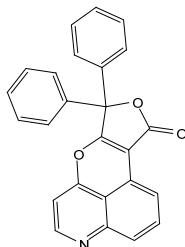
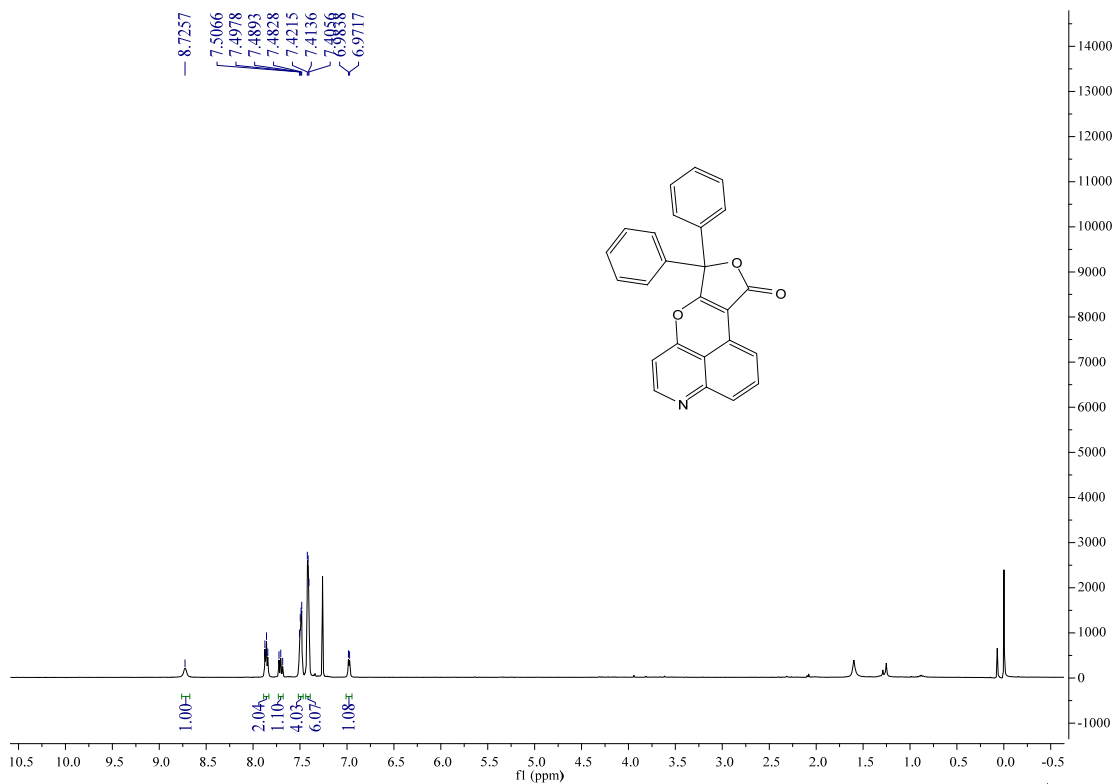
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3g

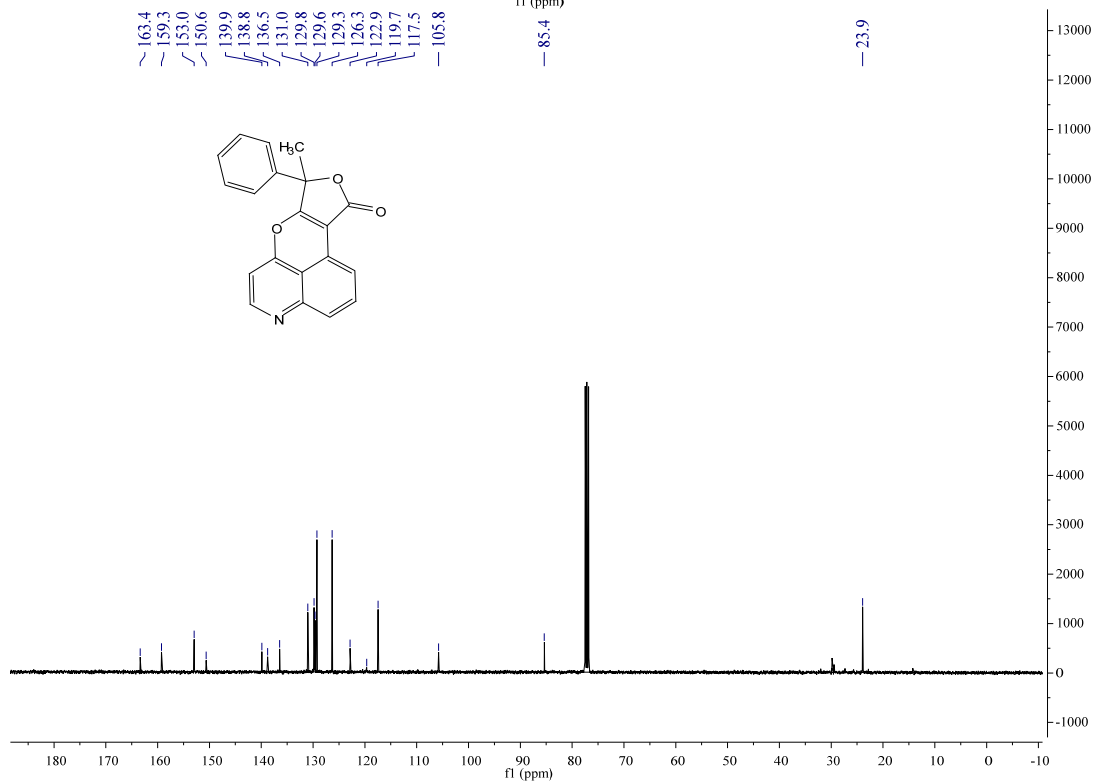
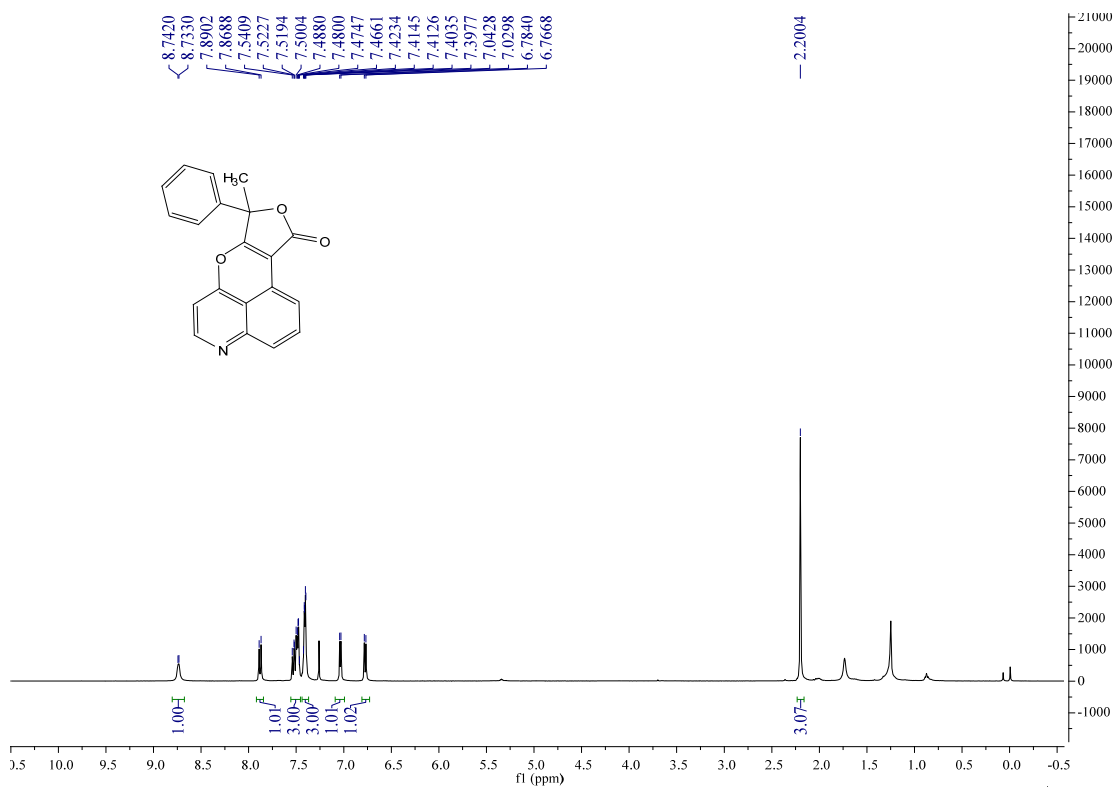


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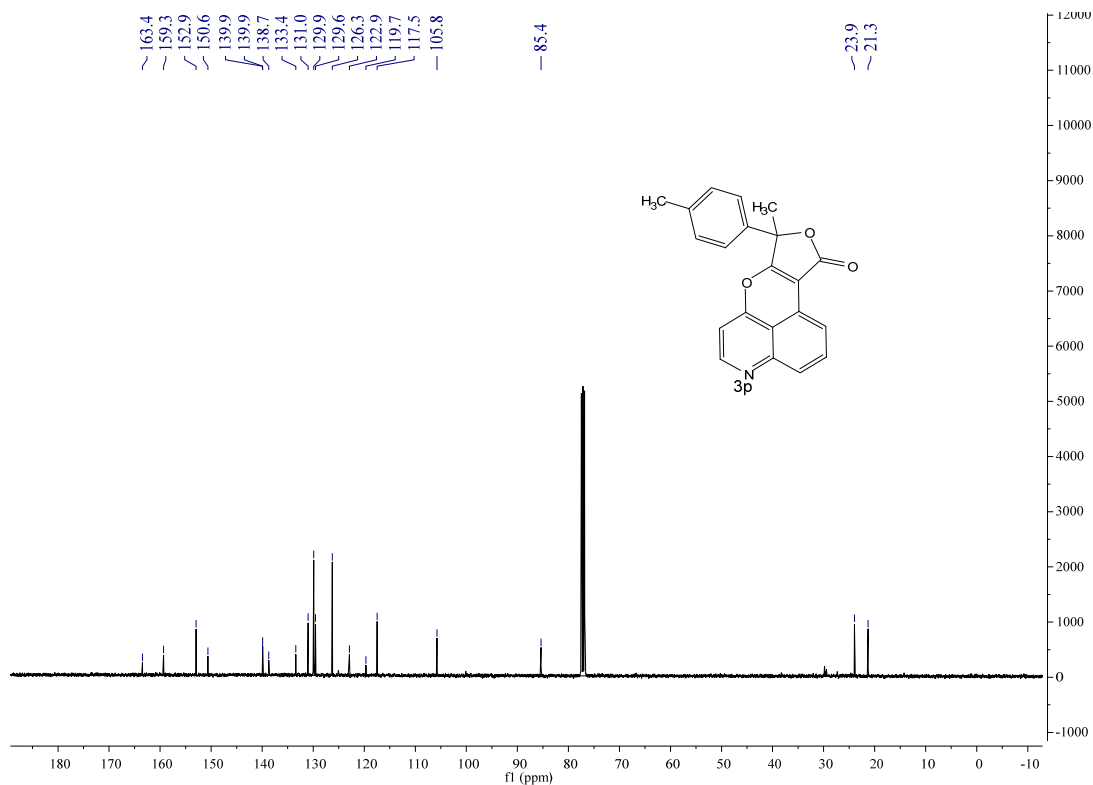
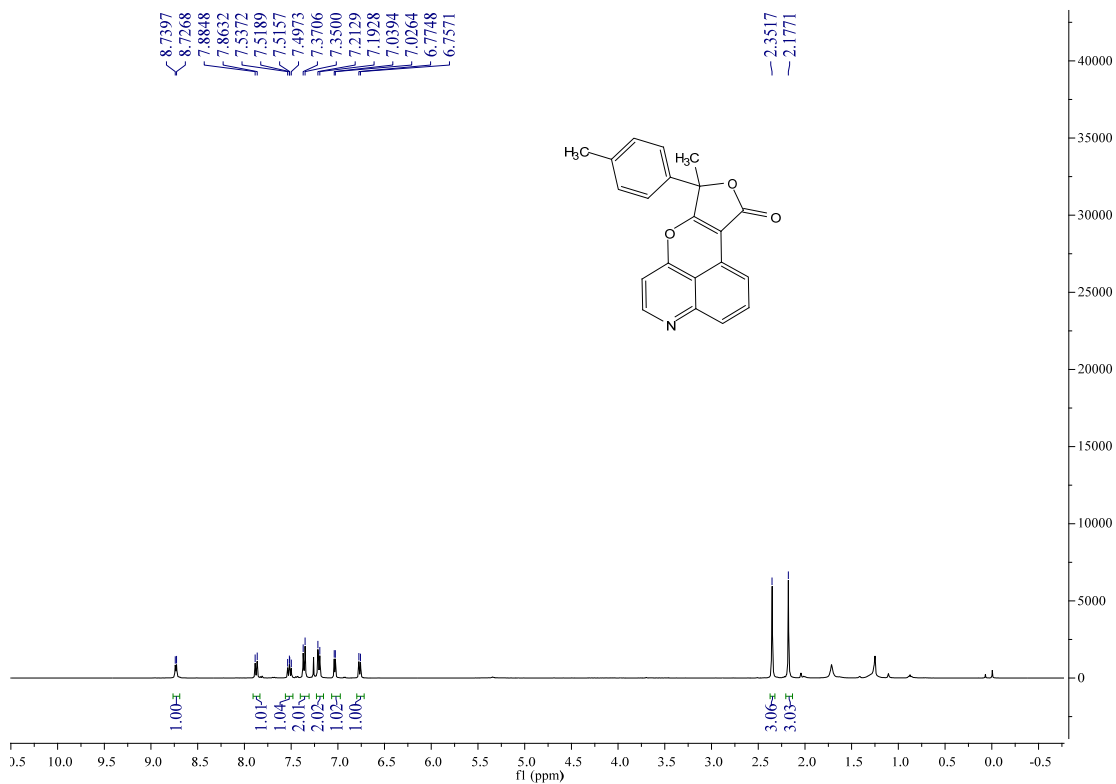




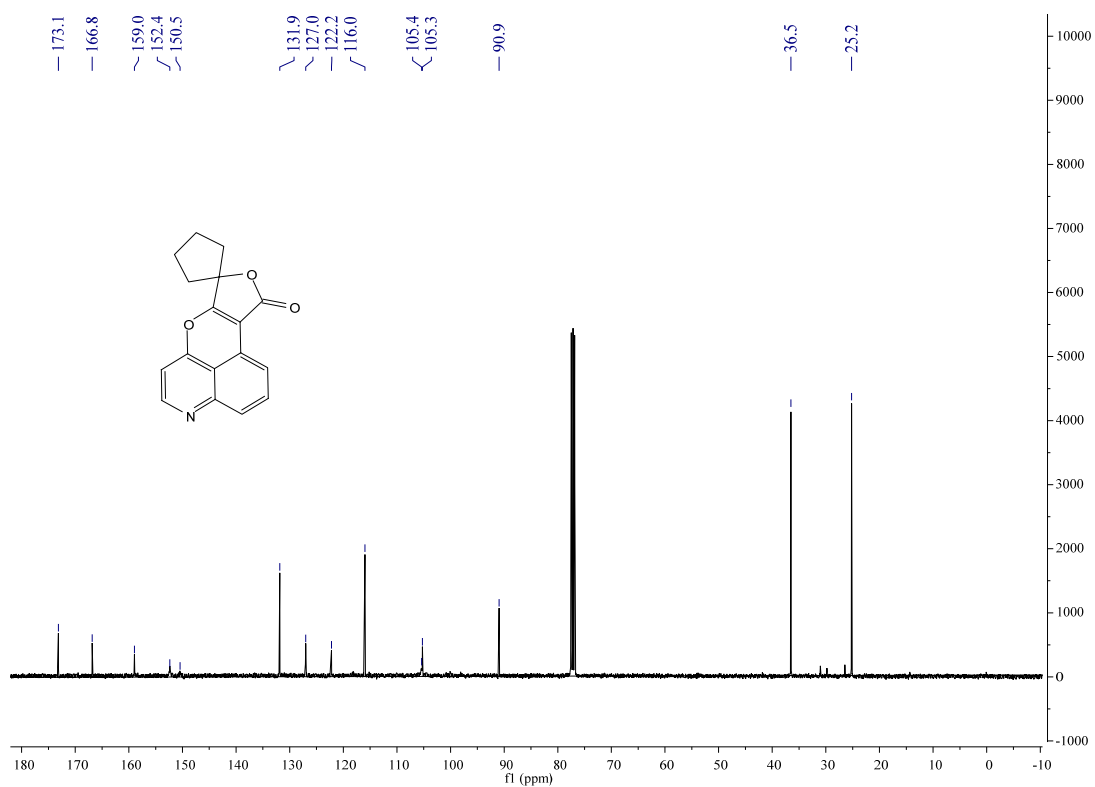
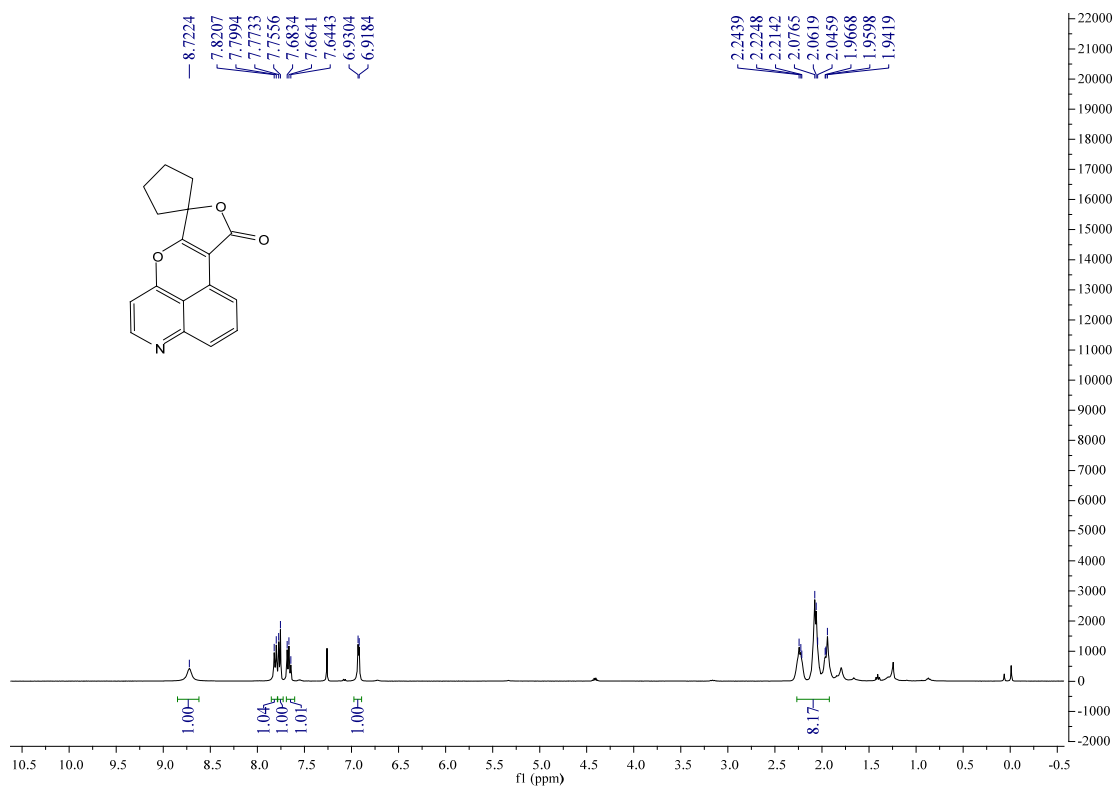
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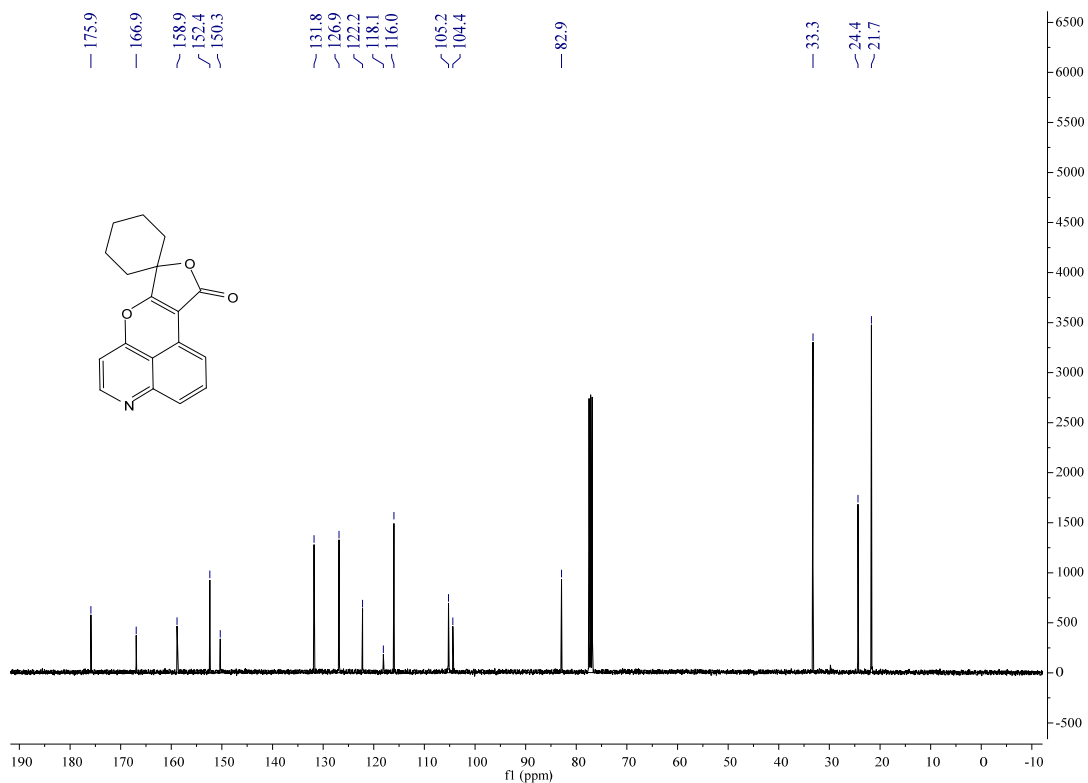
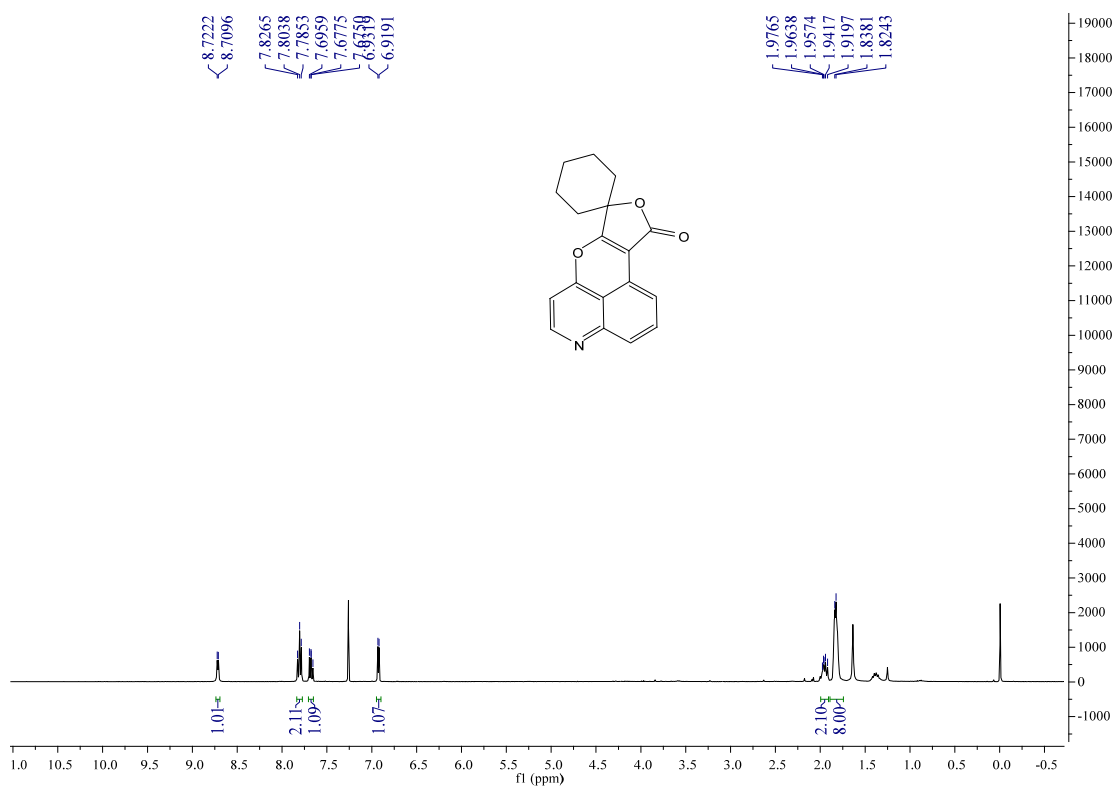
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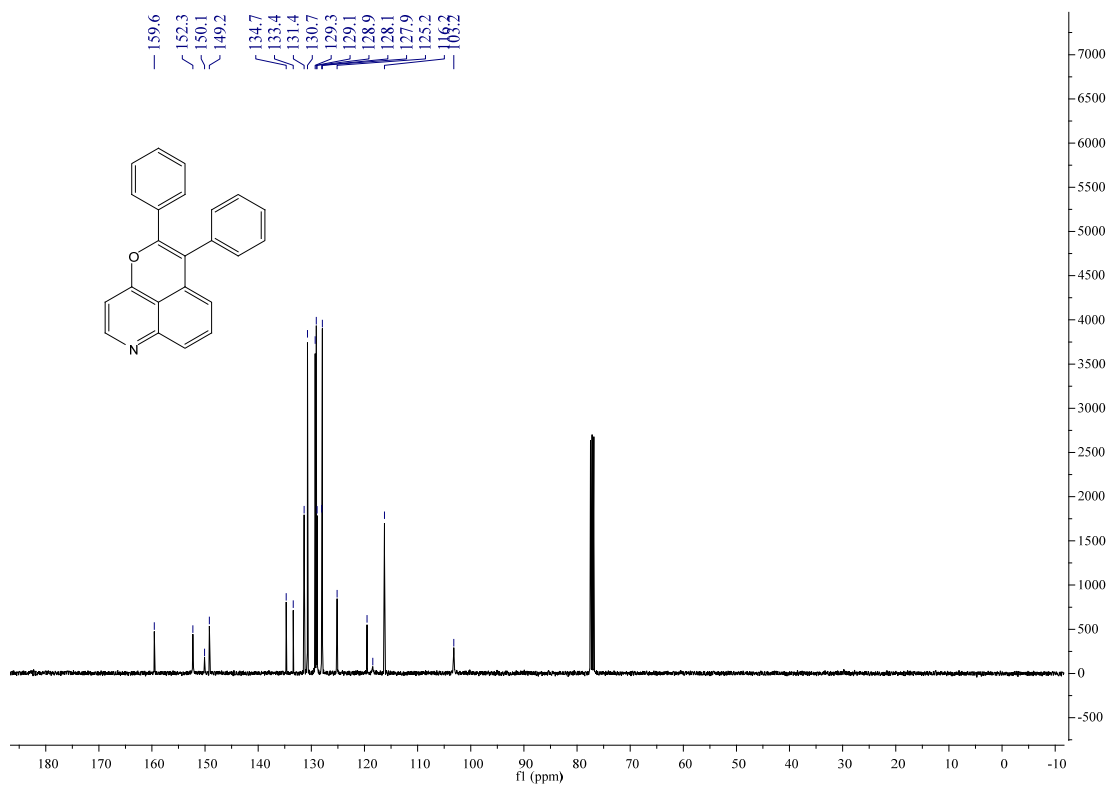
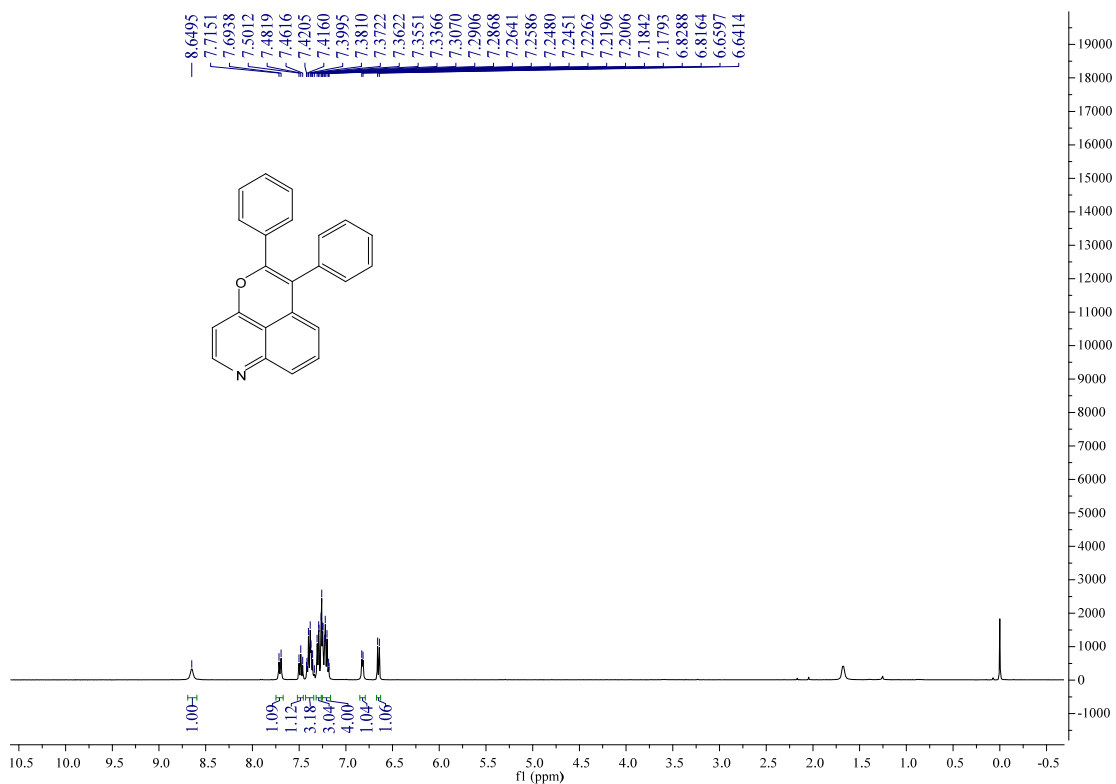
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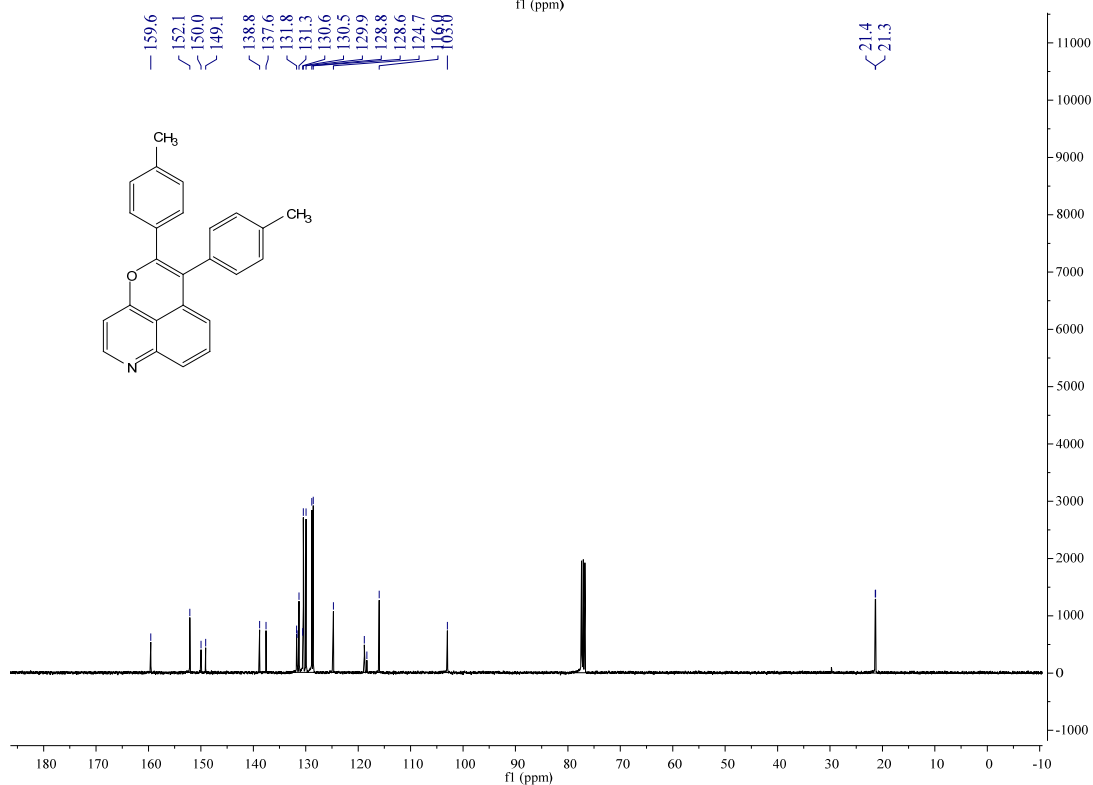
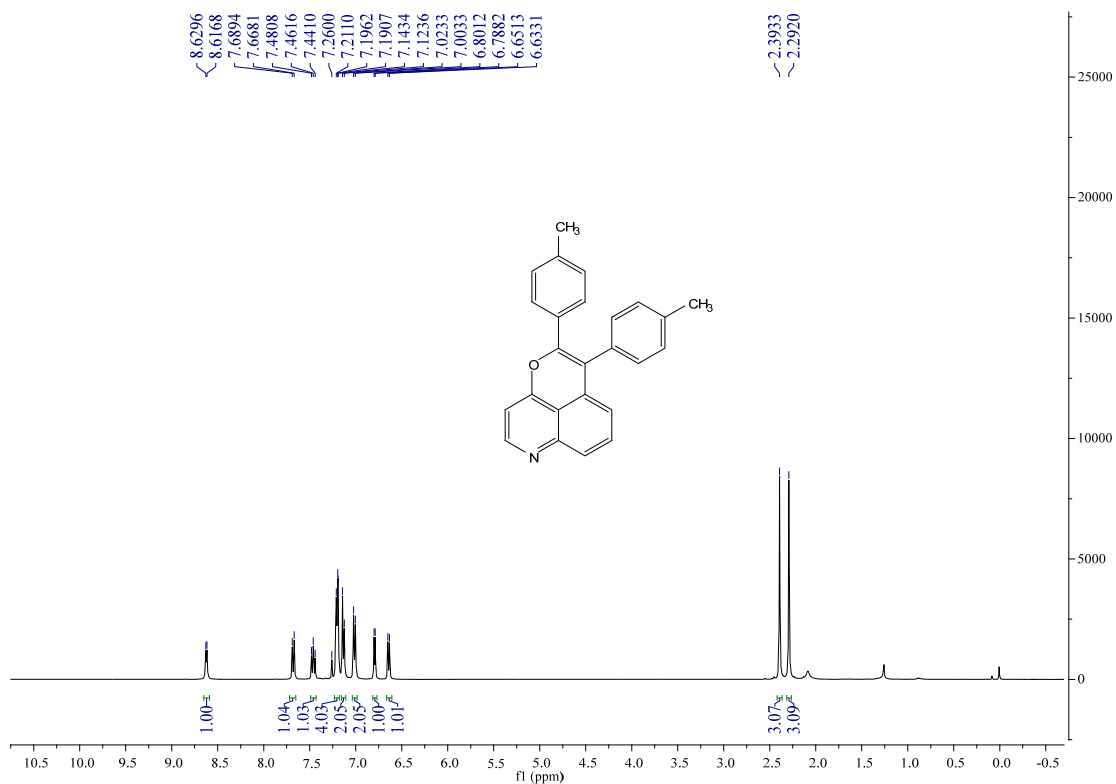
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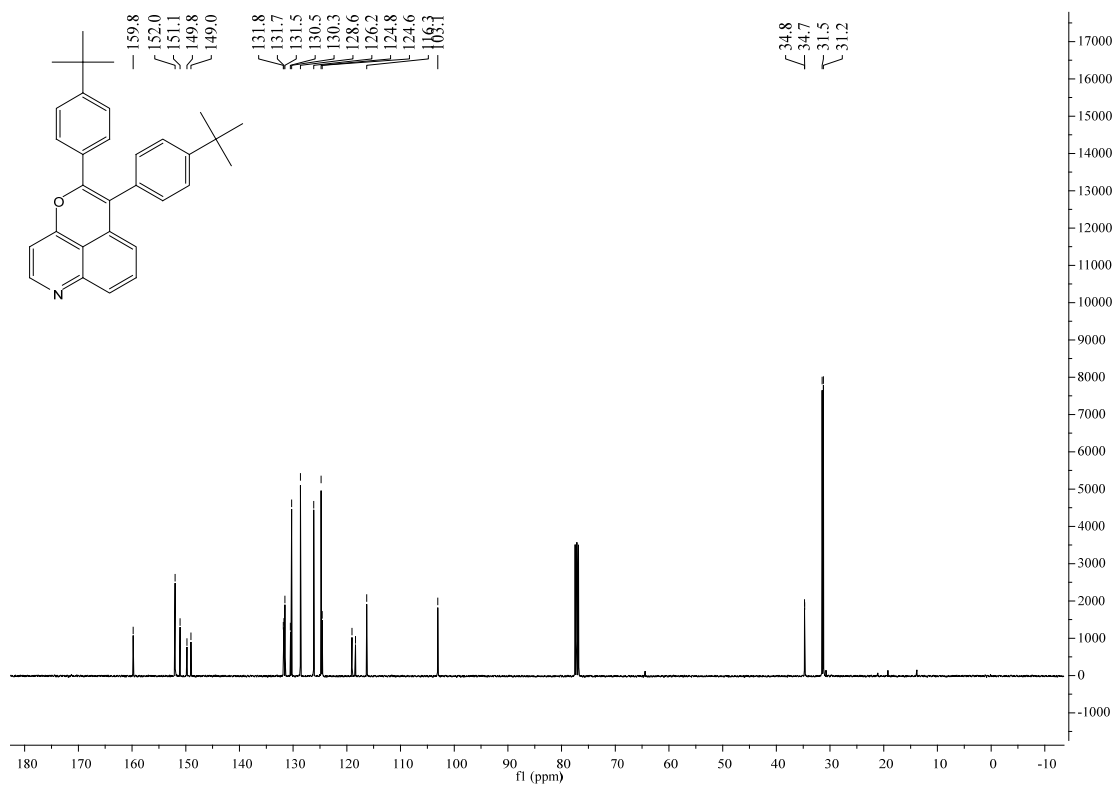
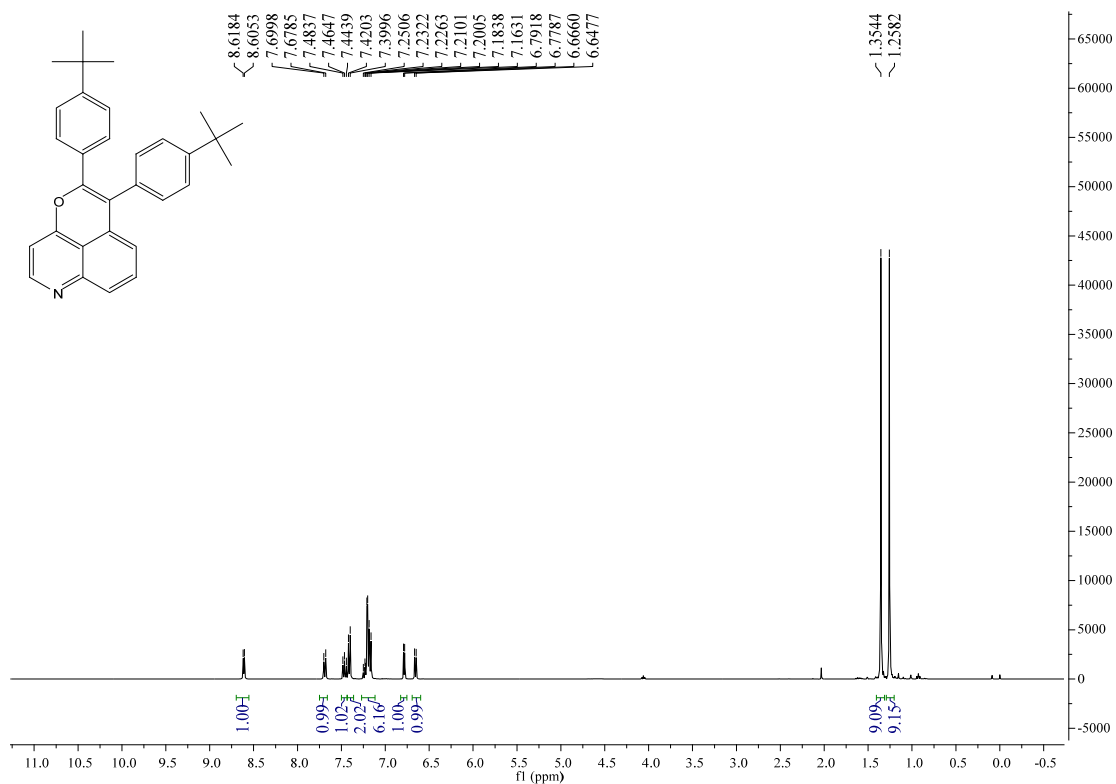
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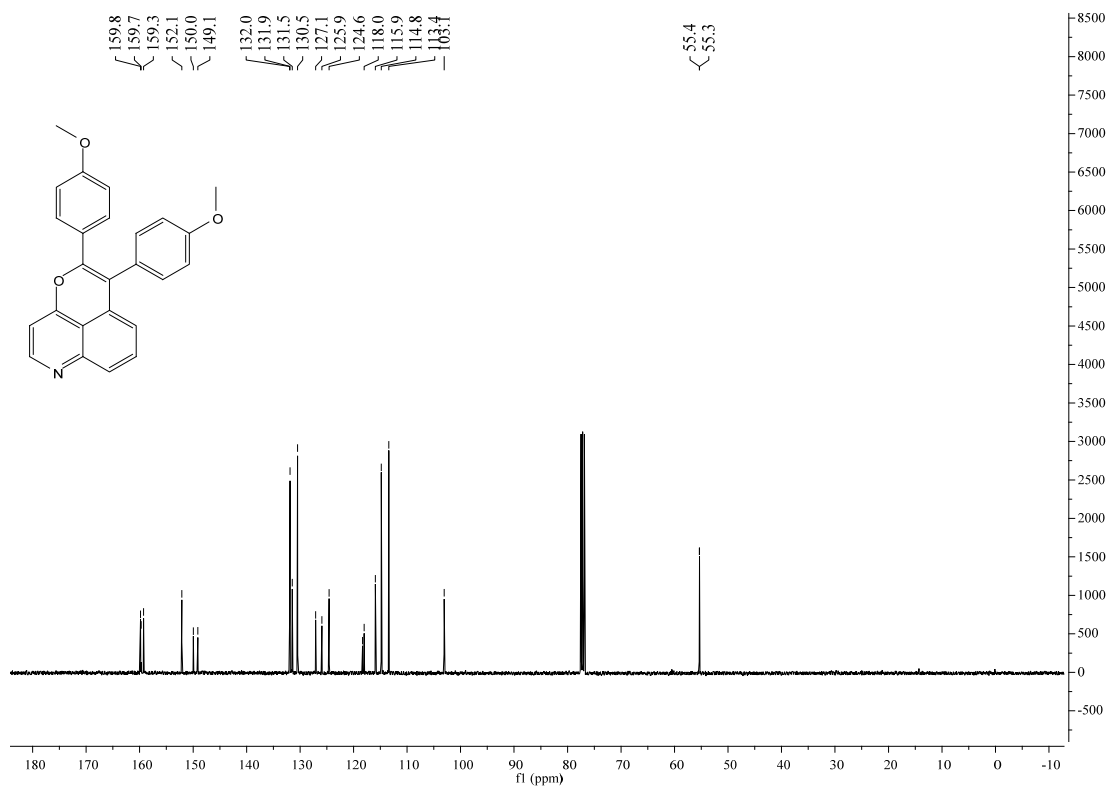
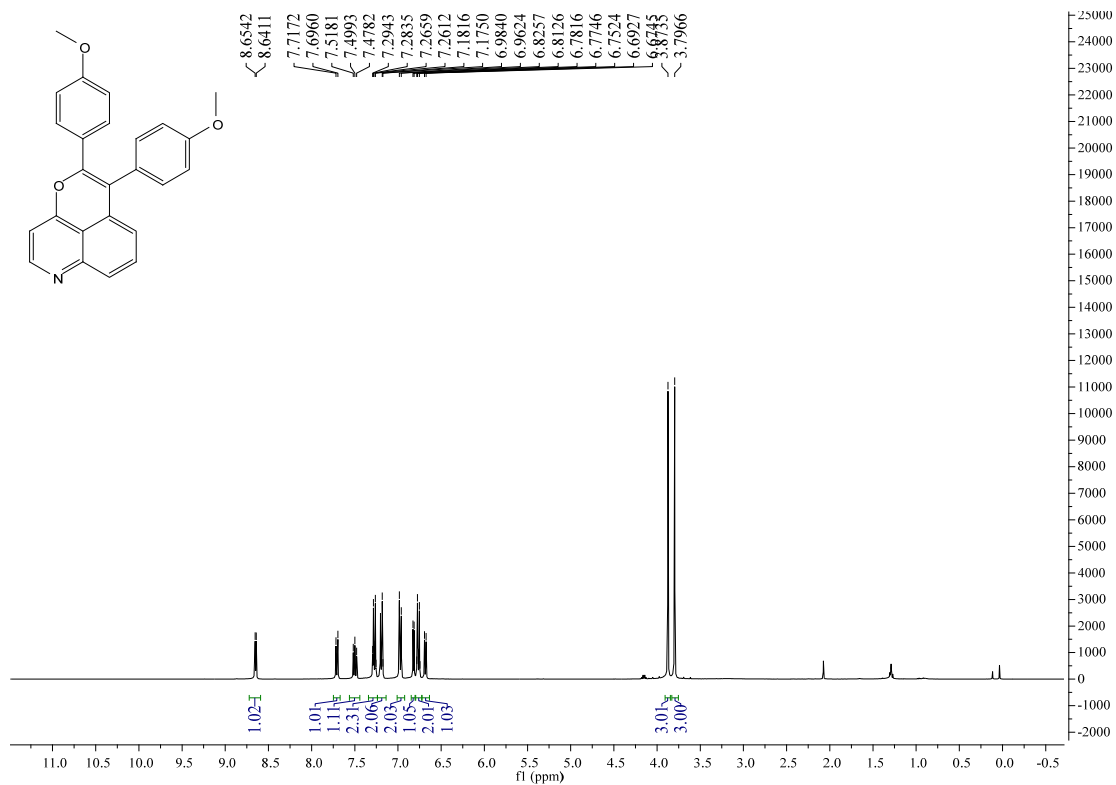
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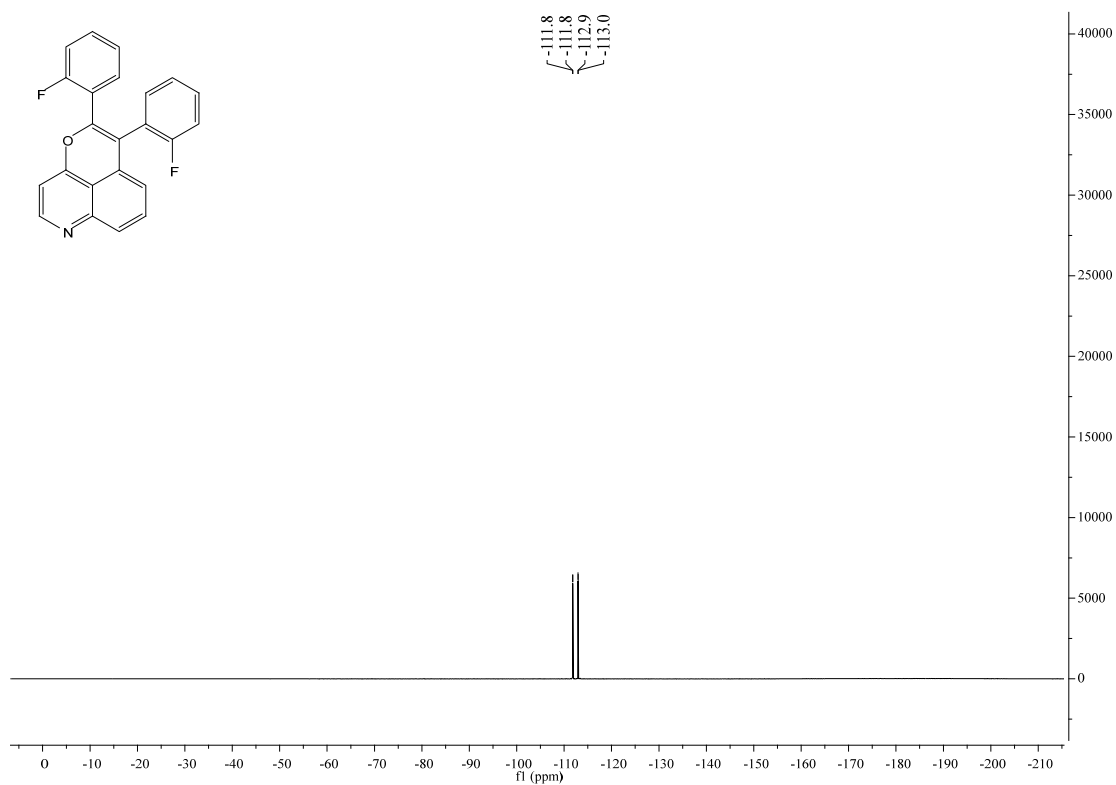
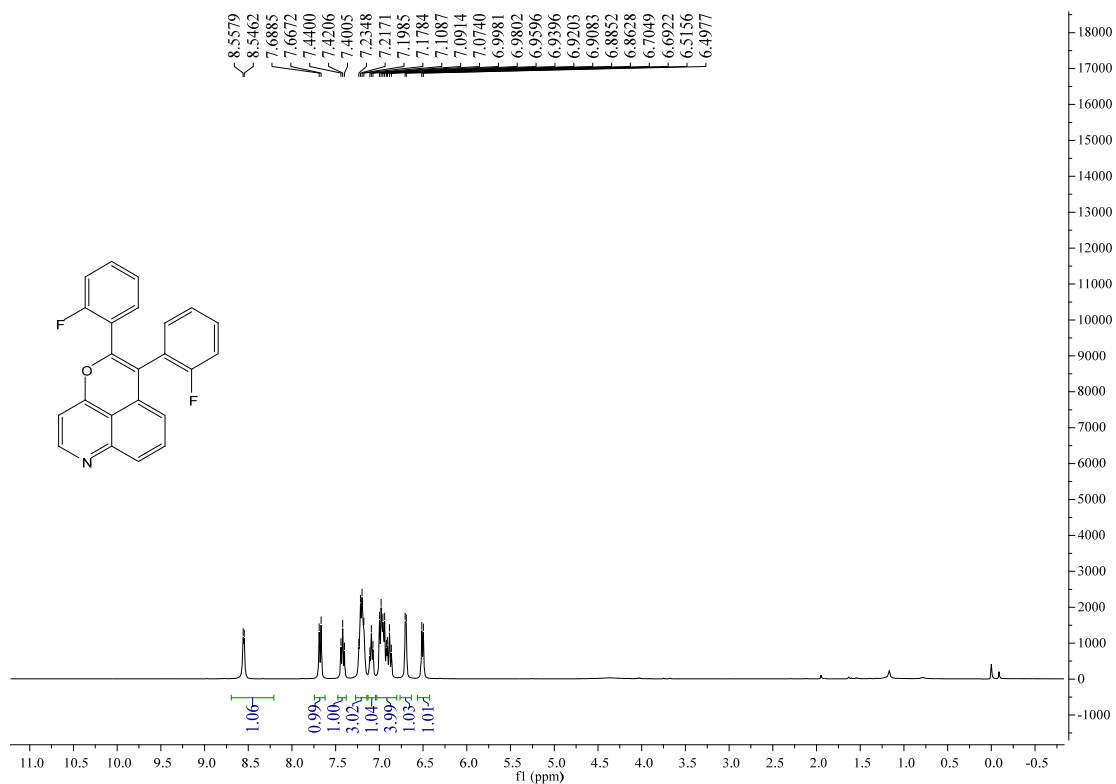


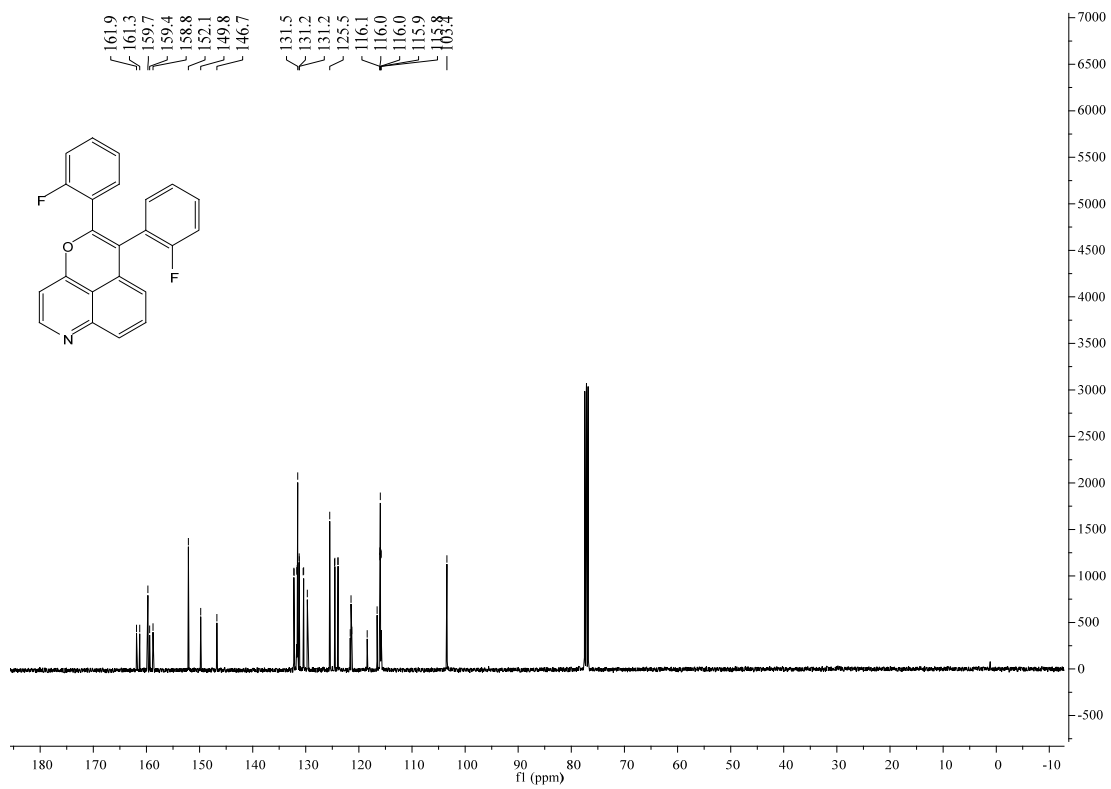
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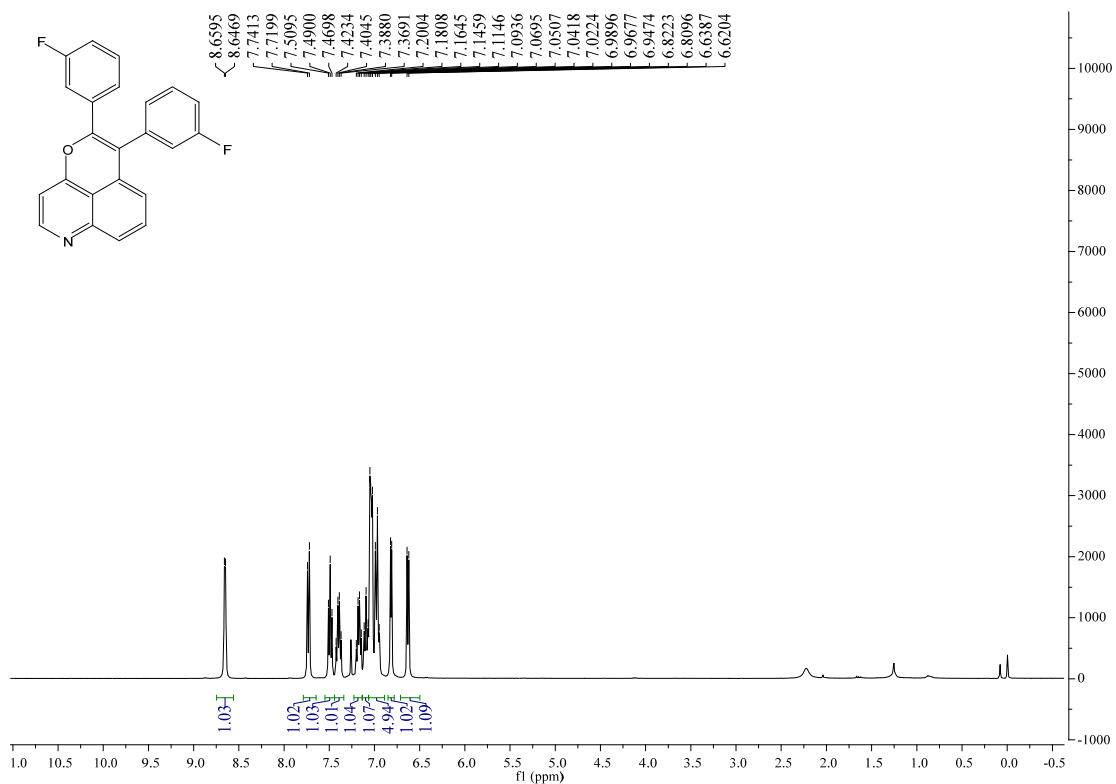


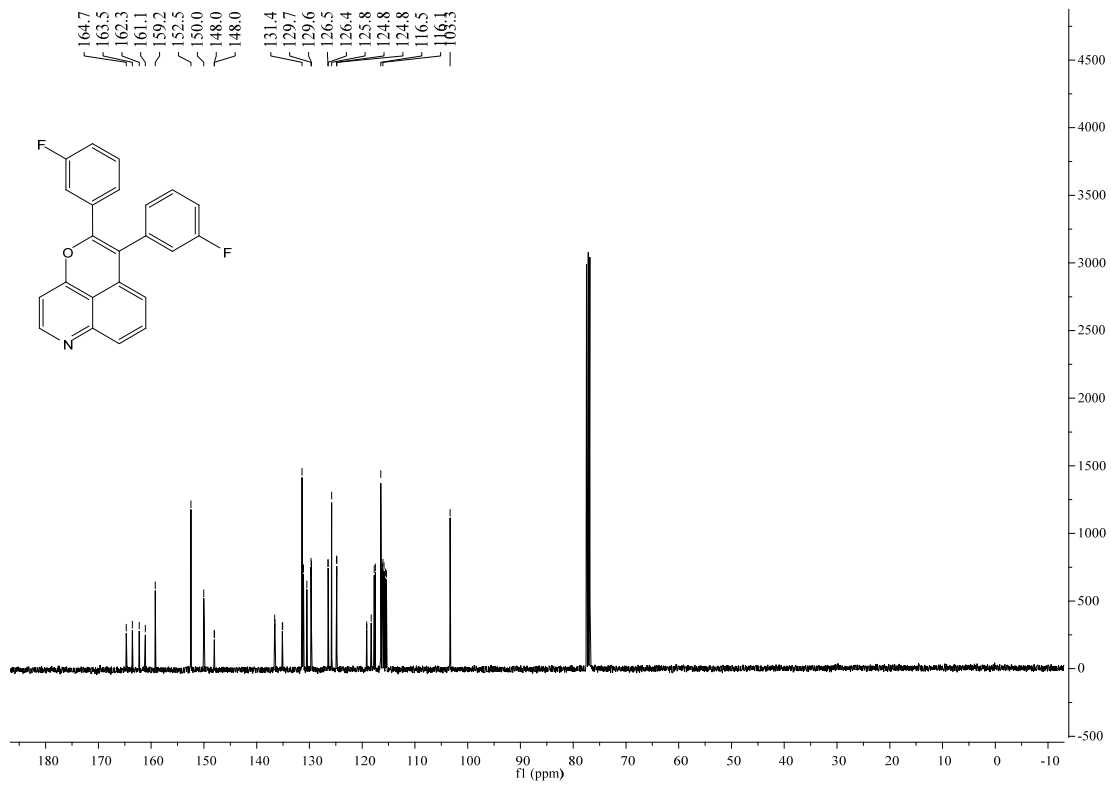
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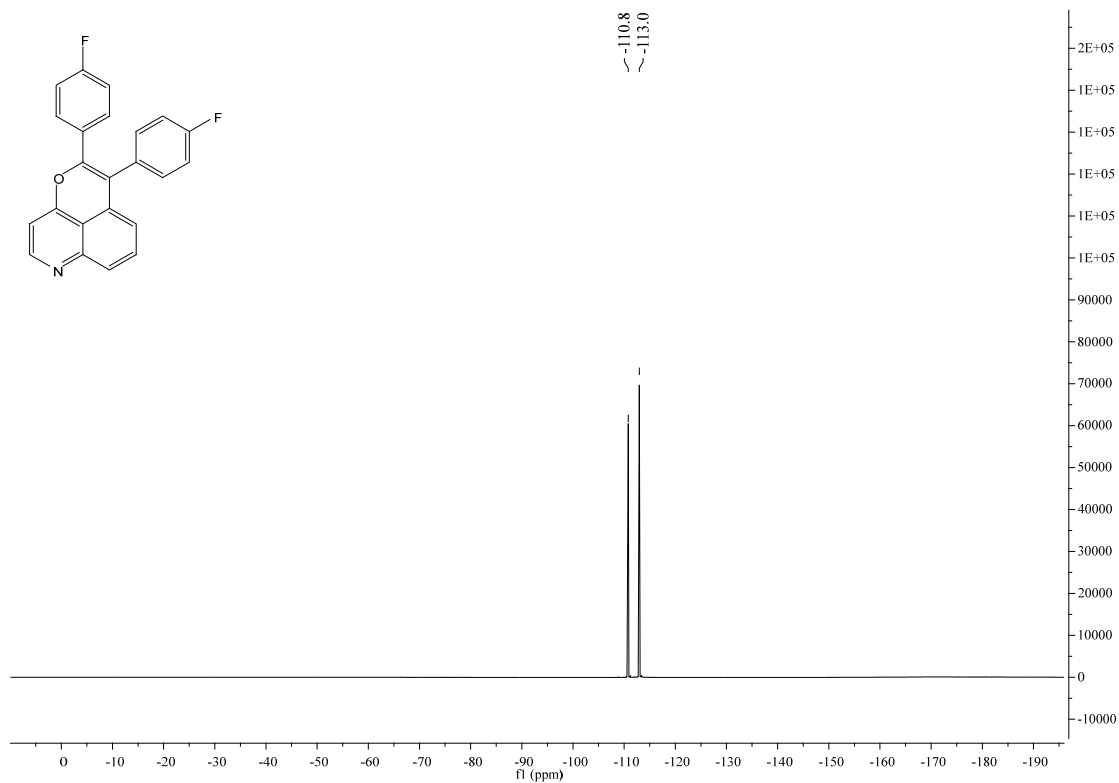
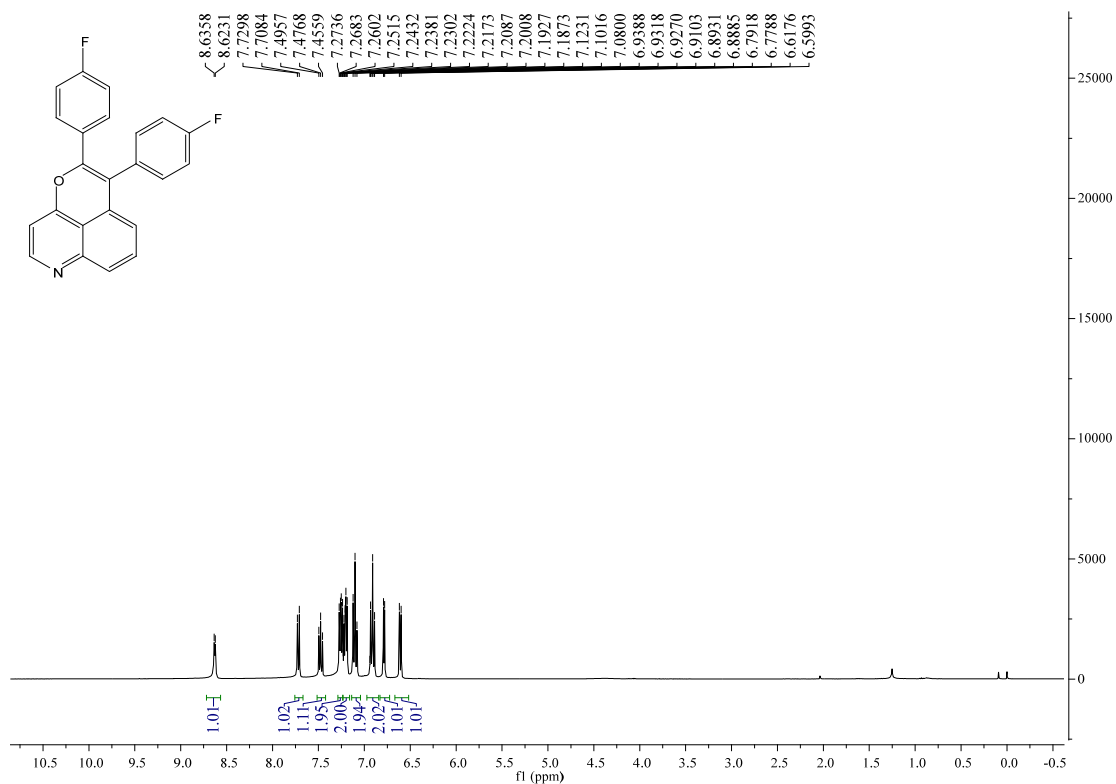


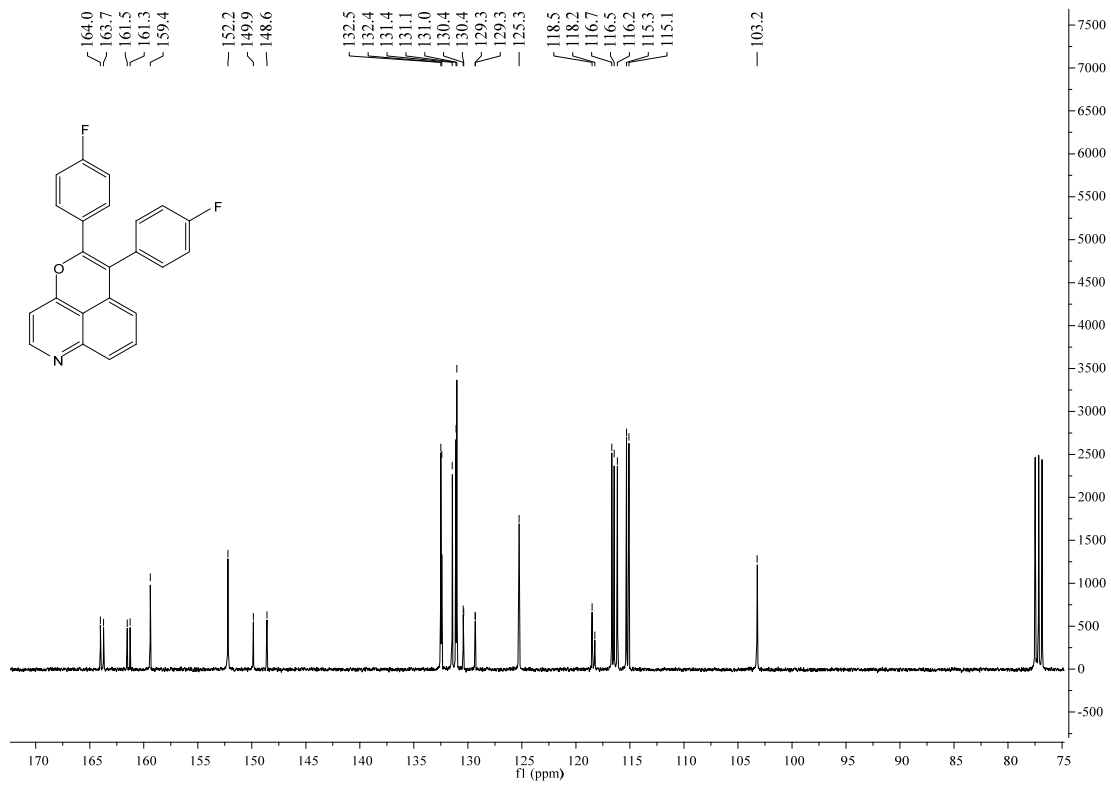
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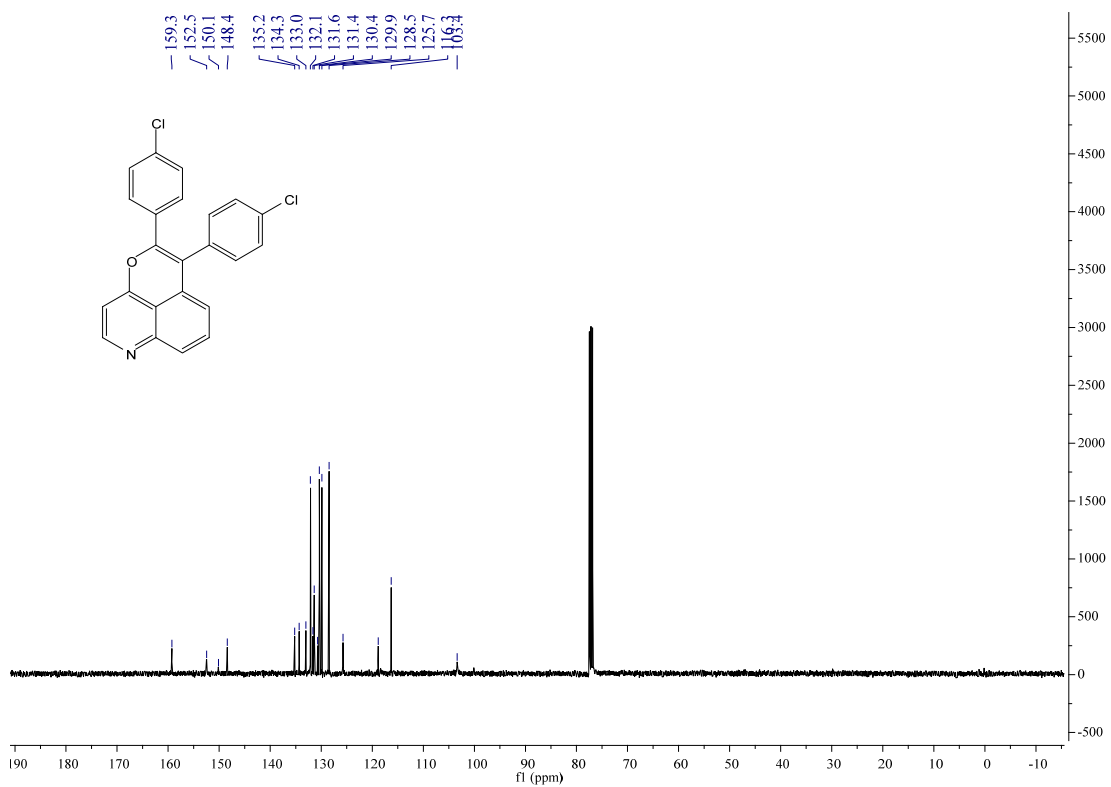
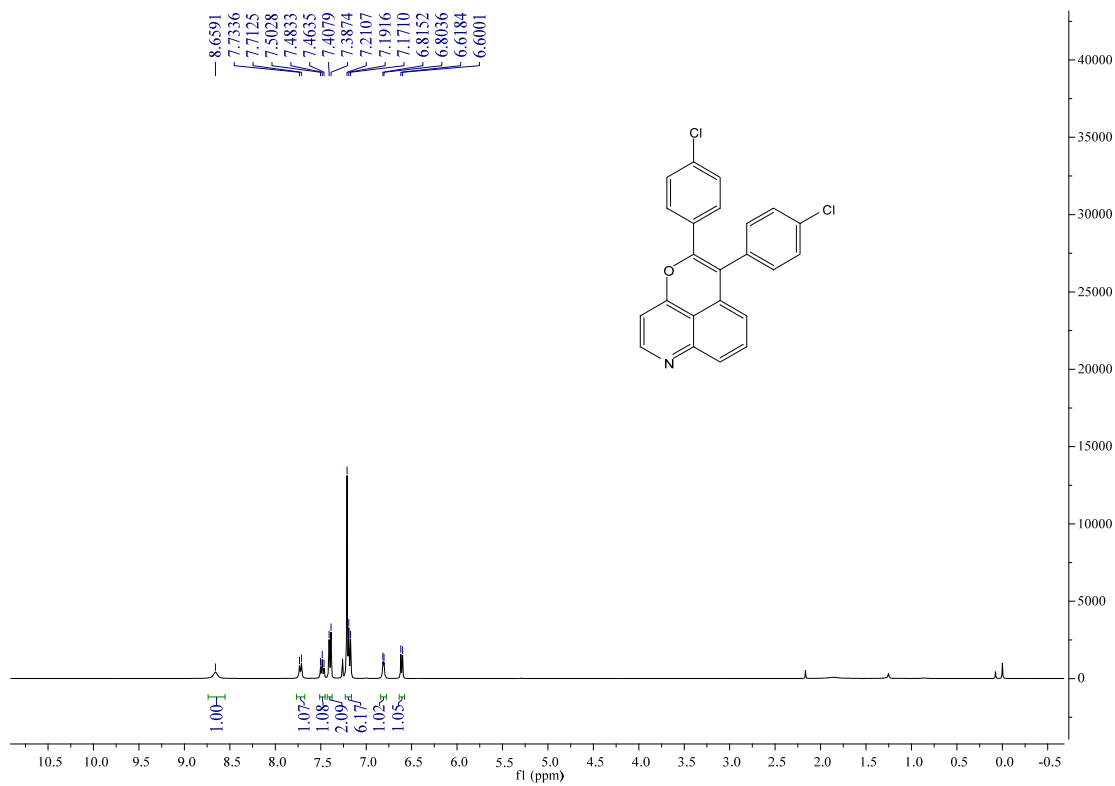


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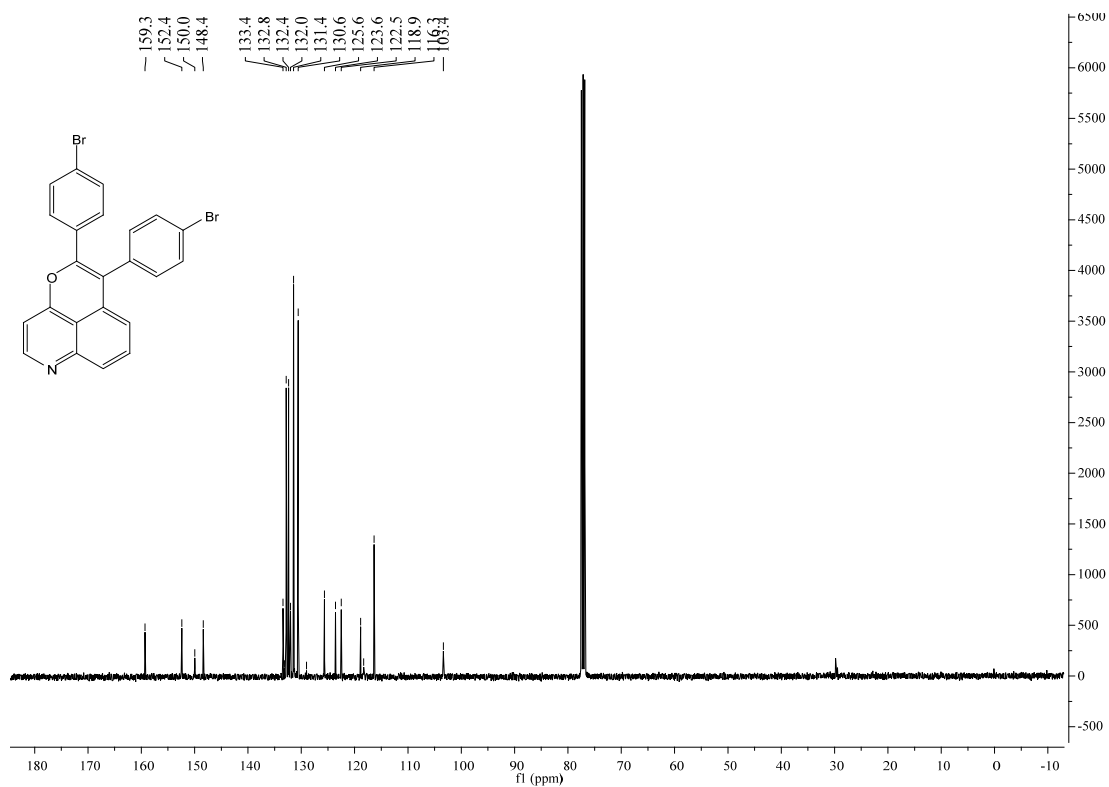
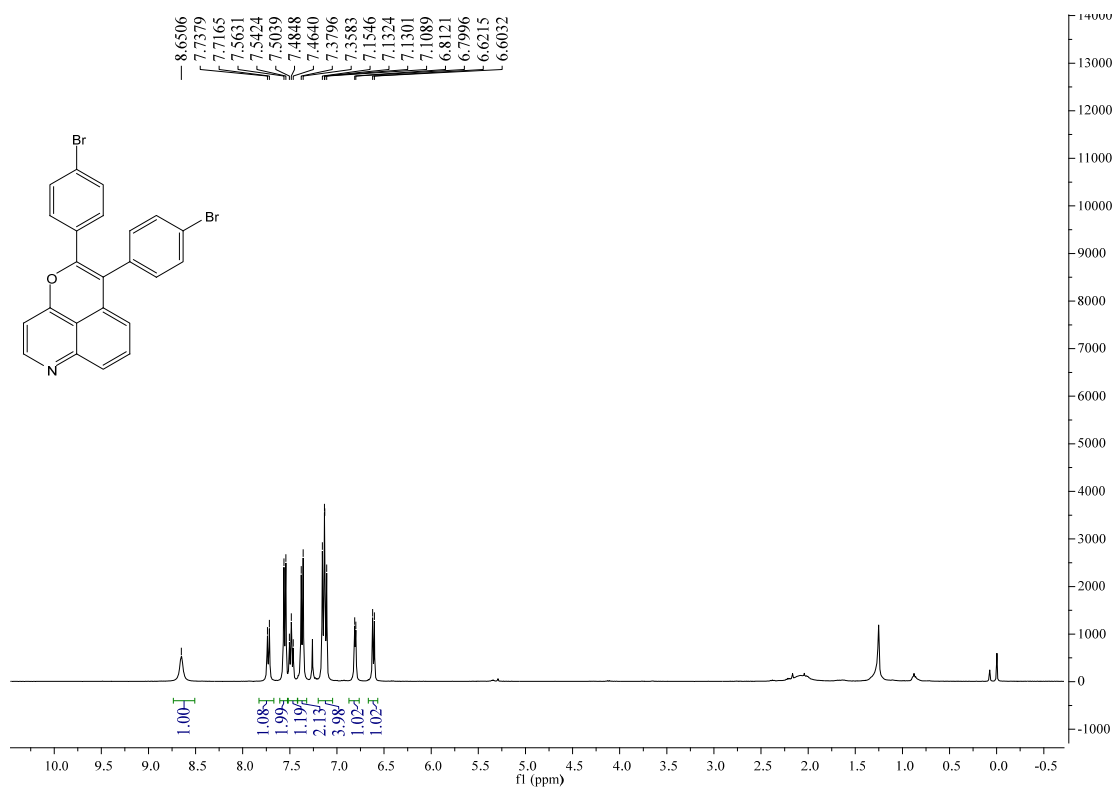




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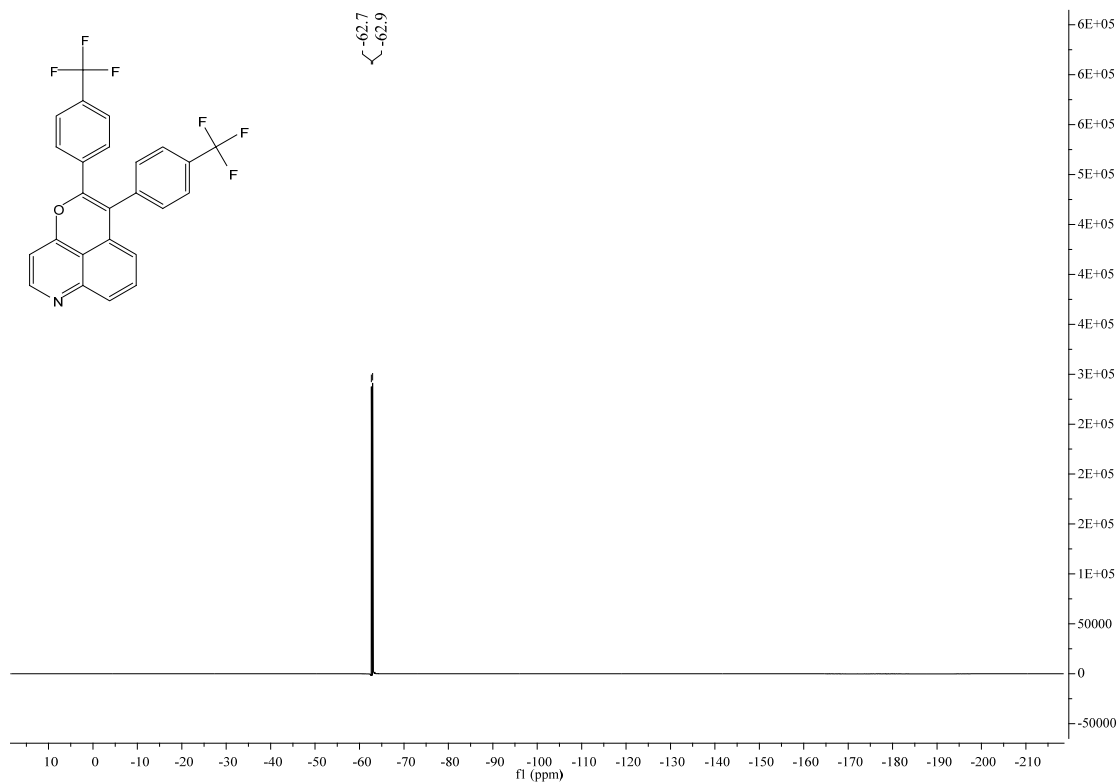
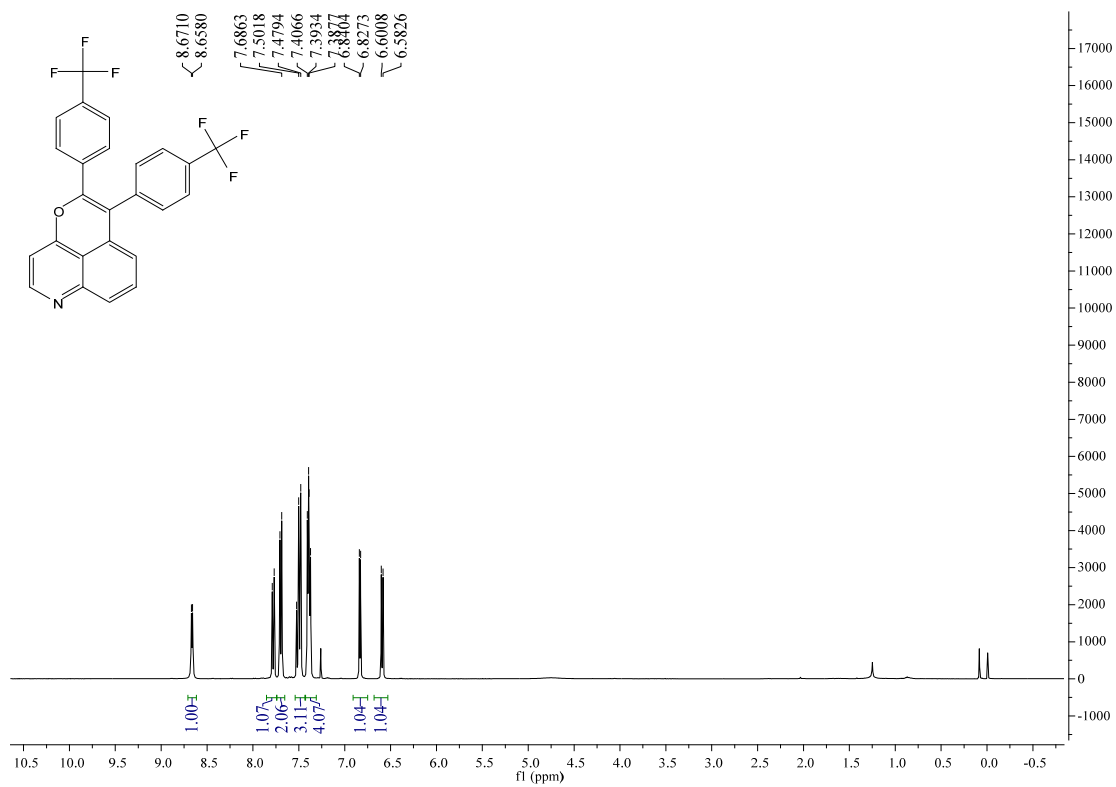


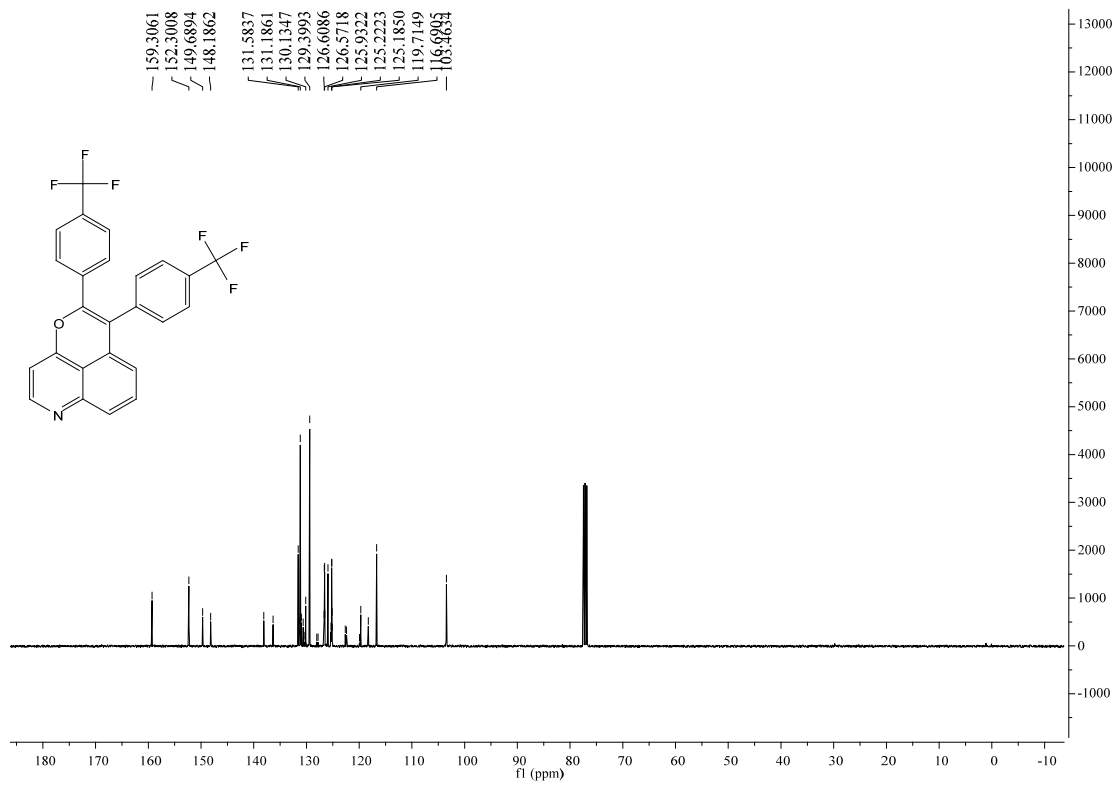
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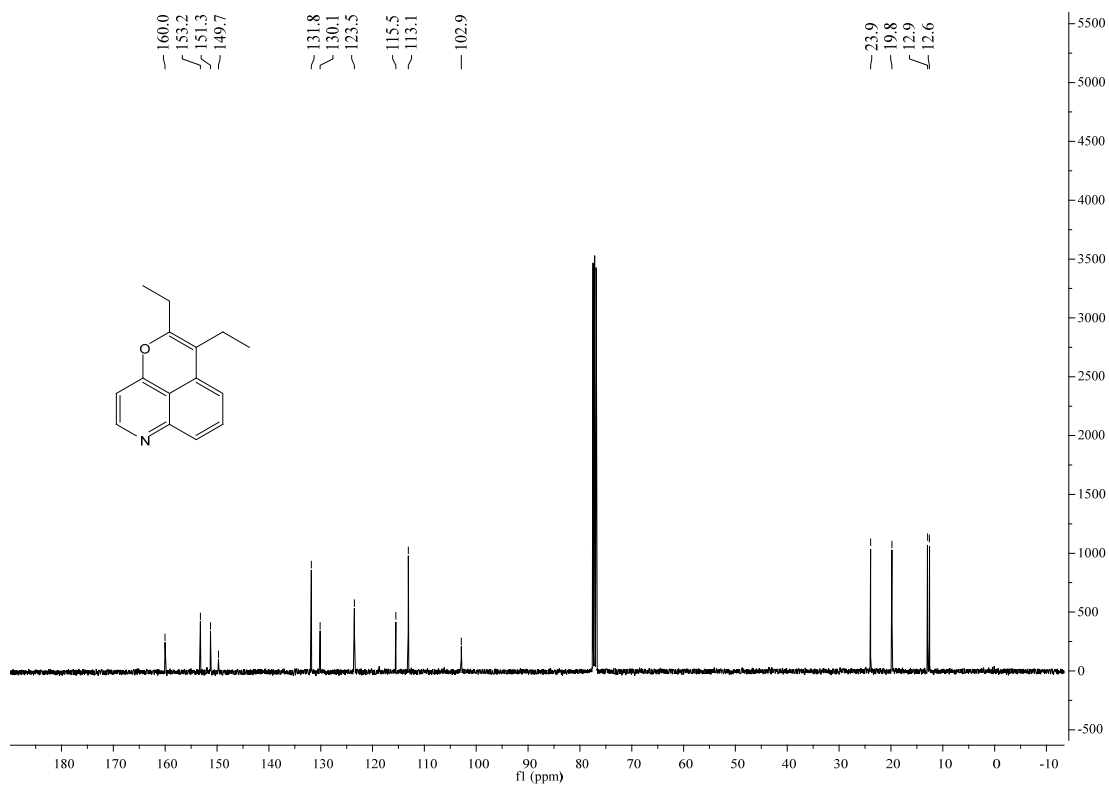
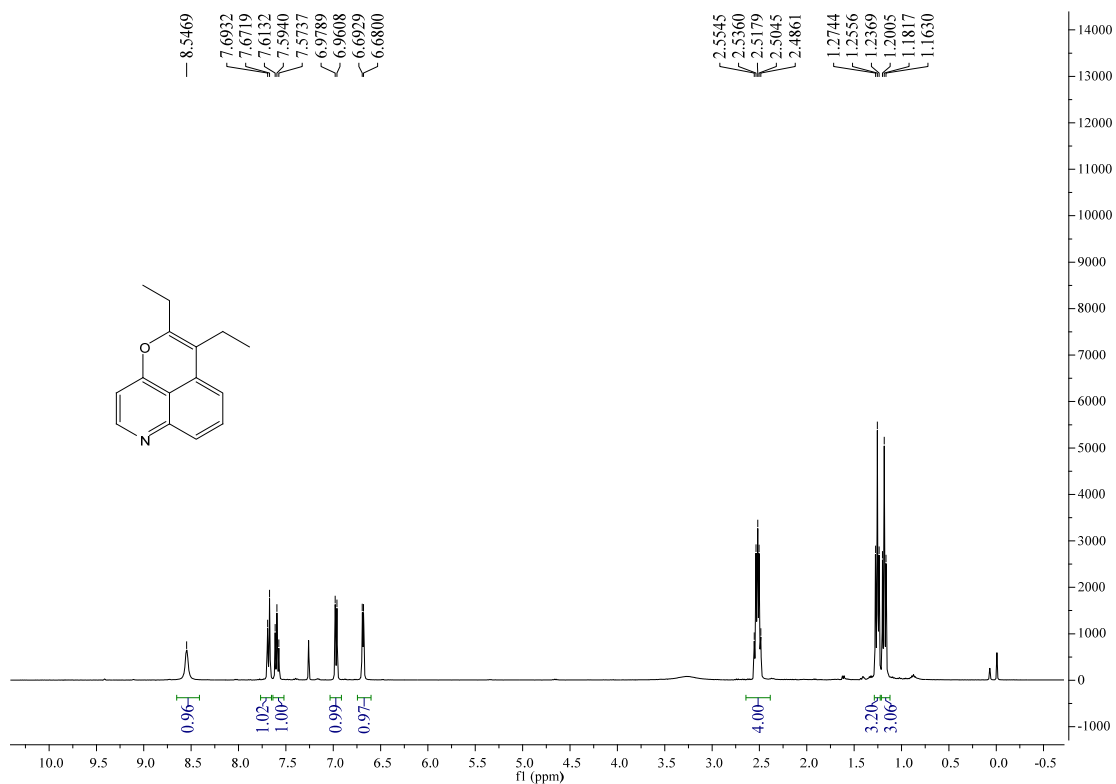


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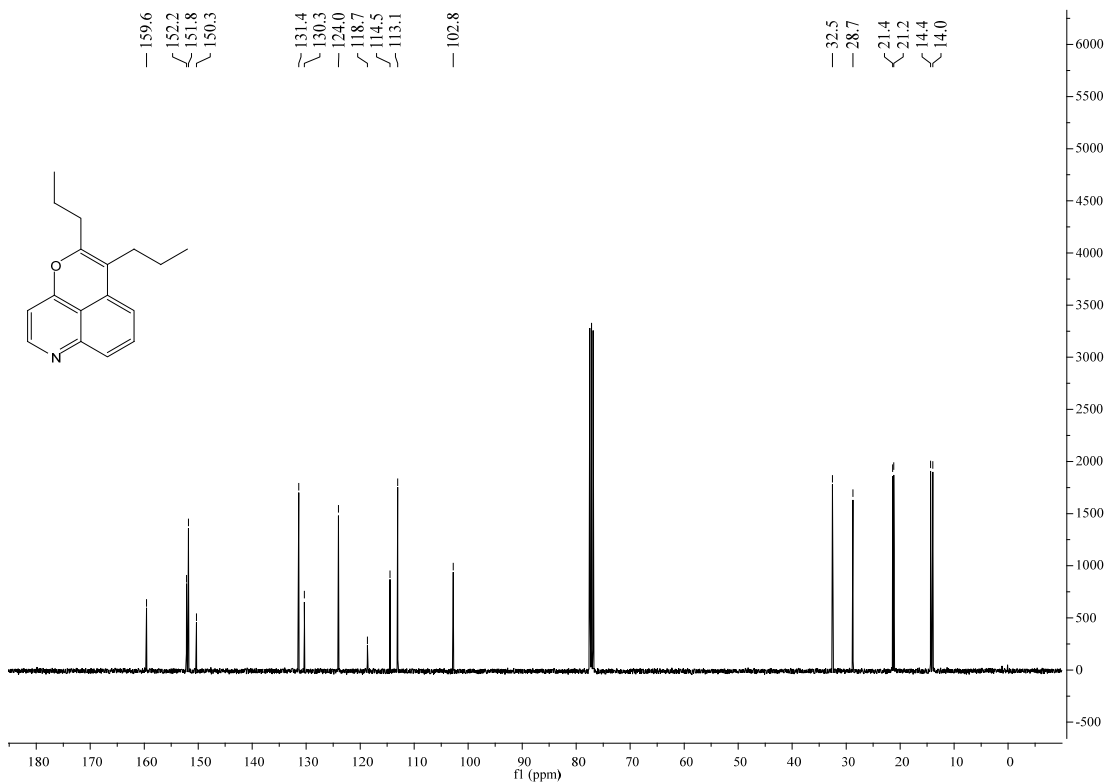
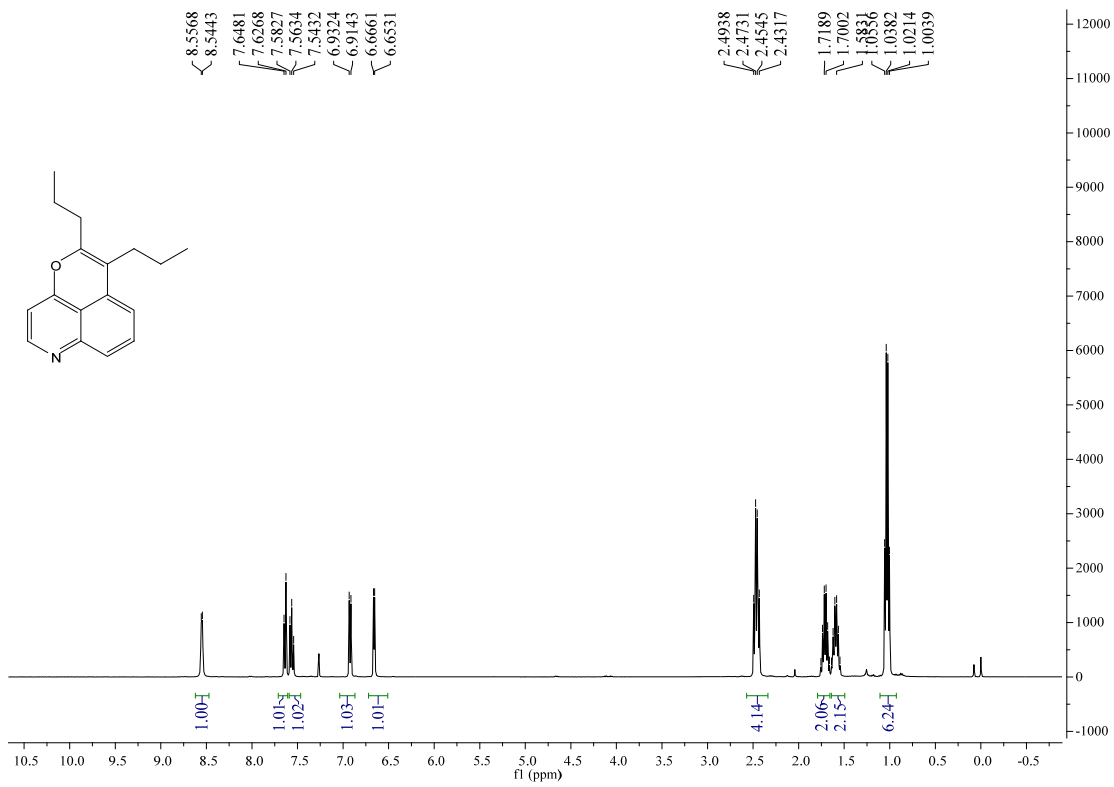




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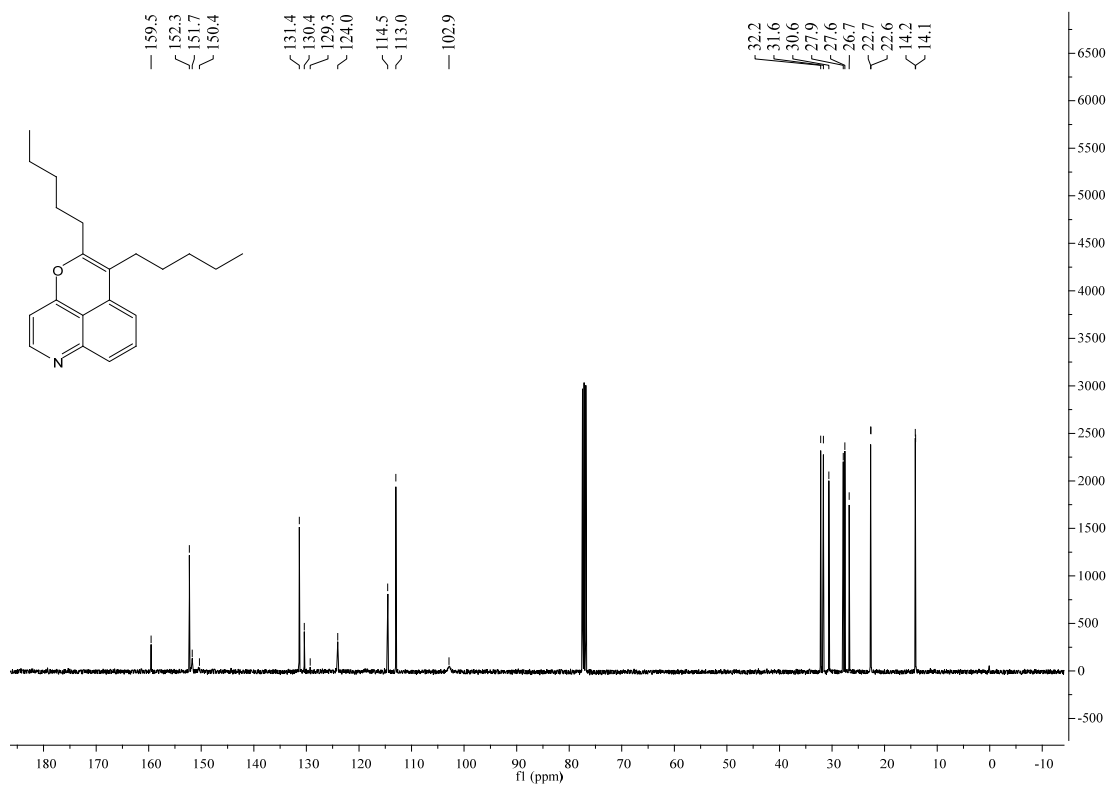
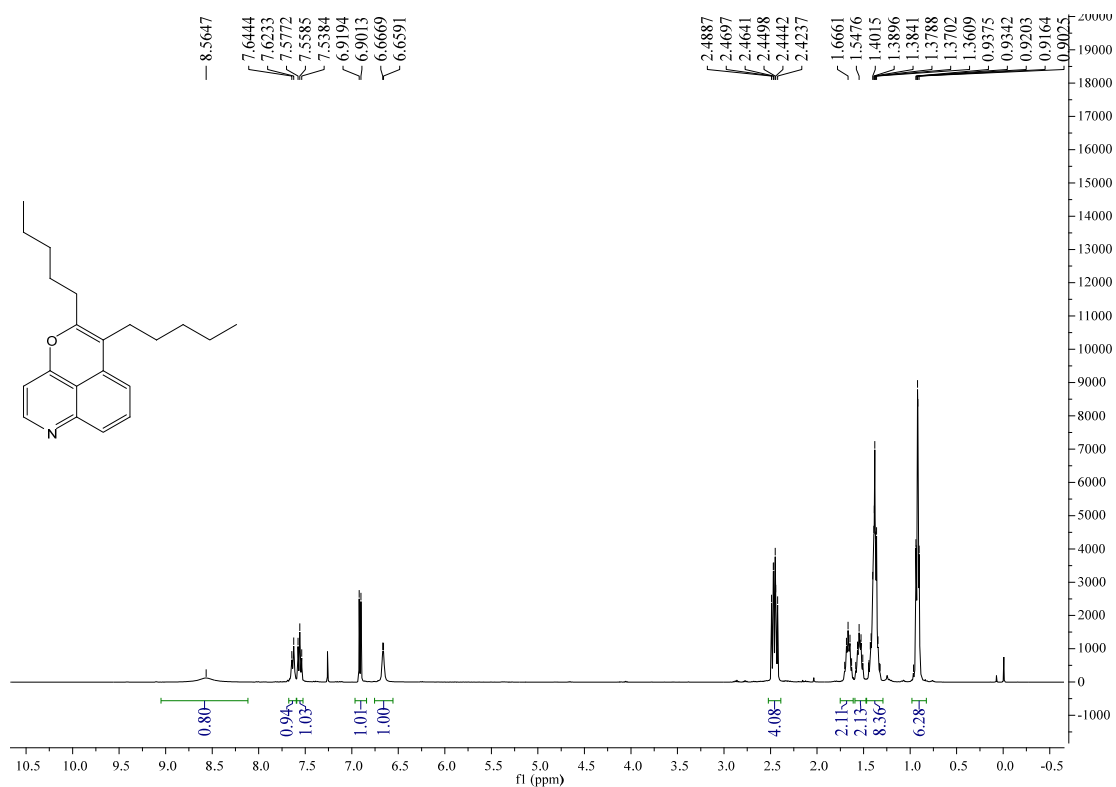


41



60

4m



4n

