

## Supporting Information

### **Metal-Free Radical Cascade Dichloromethylation of Activated Alkenes**

#### **Using CH<sub>2</sub>Cl<sub>2</sub>: Highly Selective Activation of the C-H Bond**

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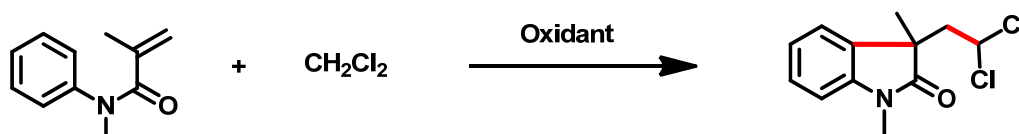
#### **General Information**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker advance III 400 spectrometer in CDCl<sub>3</sub> with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by <sup>1</sup>H and <sup>13</sup>C NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification.

## Typical procedure

A mixture of *N*-arylacrylamide (1 equiv., 0.2 mmol), DCP (3 eq, 0.60 mmol) and dichloromethane (3.5 mL) was heated under reflux at 110 °C in sealed tube for 18 h. After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.

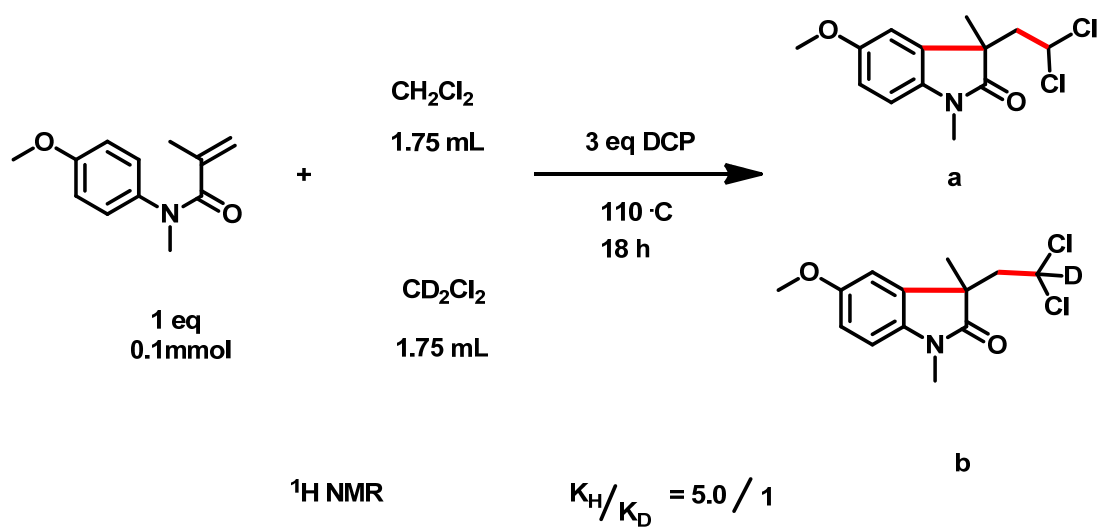
## The modification of the reaction condition



entry	Radical initiator (equiv)	DCM (mL)	T (°C) <sup>b</sup>	Yield (%) <sup>c</sup>
1	TBHP (3) <sup>d</sup>	3.5	110	-
2	TBHP (3) <sup>e</sup>	3.5	110	39
3	DTBP (3)	3.5	110	54
4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3)	3.5	110	-
5	BPO (3)	3.5	110	79
<b>6</b>	<b>DCP (3)</b>	<b>3.5</b>	<b>110</b>	<b>98</b>
7	DCP (2)	3.5	110	93
8	DCP (4)	3.5	110	51
9	DCP (3)	2.0	110	58
10	DCP (3)	4.0	110	91
11	DCP (3)	3.5	100	33
12	DCP (3)	3.5	90	-

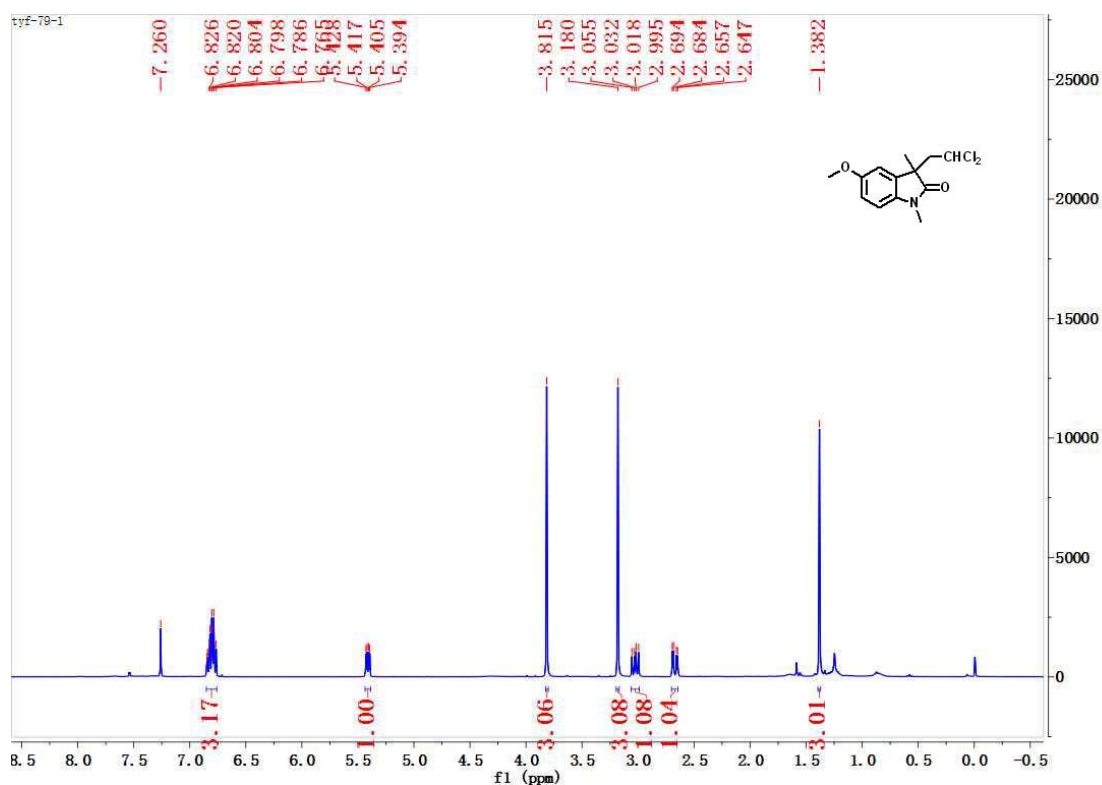
<sup>a</sup> Reaction conditions: *N*-methyl-*N*-phenylmethacrylamide (1 equiv, 0.2 mmol), dichloromethane as solvent, sealed tube, 18 h. <sup>b</sup> Measured temperature of the oil bath. <sup>c</sup> Isolated yields. <sup>d</sup> TBHP (in decane). <sup>e</sup> TBHP (in water).

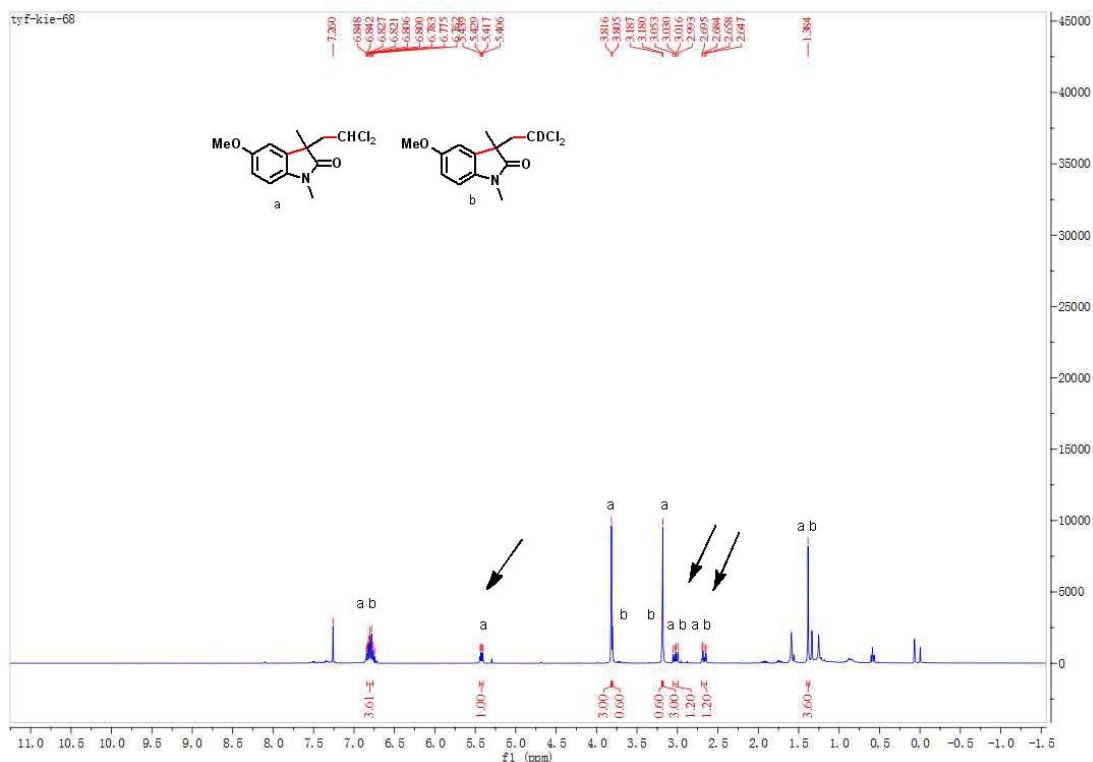
### Competing Kinetic Isotope Effect (KIE) Experiment:



raw material conversion 30%

$^1\text{H NMR}$





### Physical data and references for the following products

All known compounds are determined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

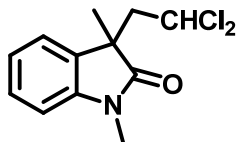
### References:

1. Z. Cui, X. Shang, X.-F. Shao, Z.-Q. Liu, *Chem, Sci.* 2012, **3**, 2853.
2. Z. Li, Y. Zhang, L. Zhang, Z.-Q. Liu, *Org. Lett.* 2014, **16**, 382-385.
3. J. Xie, P. Xu, H. Li, Q. Xue, H. Jin, Y. Cheng, and C.-J. Zhu, *Chem. Commun.*, 2013, **49**, 5672 – 5674
4. S.Zhou, L. Guo, H. Wang and X.-H. Duan, *Chem. Eur. J.* 2013, **19**, 12970
5. X. Mu, T. Wu, H. Wang, Y. Guo and G.-S. Liu, *J. Am. Chem. Soc.*, 2012, **134(2)**, 878 - 881
6. M. Zhou, R.-J. Song, X. Ouyang, Y. Liu, W. Wei, G. Deng and J.-H. Li, *Chem, Sci.* 2013, **4**, 2690-2694.

Physical data for the following products:

**1: 3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



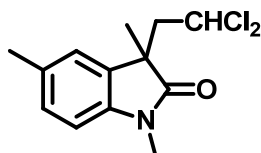
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.10 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.38 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.70 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.0, 143.4, 131.1, 128.6, 122.7, 108.6, 69.6, 50.2, 47.2, 26.4, 25.4.

**HRMS (ESI, *m/z*):** Calculated for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 258.0447, found 258.0446

**2: 3-(2,2-dichloroethyl)-1,3,5-trimethylindolin-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



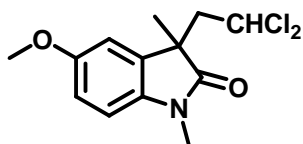
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.11 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.00 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.40 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.18 (s, 3H), 3.02 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.9, 141.1, 132.3, 131.1, 128.9, 123.4, 108.3, 69.7, 50.2, 47.2, 26.5, 25.5, 21.1.

**HRMS (ESI, *m/z*):** Calculated for C<sub>13</sub>H<sub>16</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 272.0603, found 272.0612

**3: 3-(2,2-dichloroethyl)-5-methoxy-1,3-dimethylindolin-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



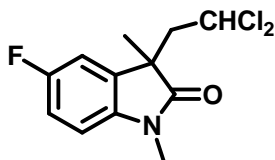
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.85 – 6.77 (m, 3H), 5.41 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.82 (s, 3H), 3.18 (s, 3H), 3.02 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.67 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.6, 156.1, 136.9, 132.5, 112.4, 110.5, 108.9, 69.6, 55.8, 50.1, 47.6, 26.5, 25.4.

**HRMS (ESI, *m/z*):** Calculated for C<sub>13</sub>H<sub>16</sub>Cl<sub>2</sub>NO<sub>2</sub>(M+H)<sup>+</sup> 288.0553, found 288.0559

#### 4: 3-(2,2-dichloroethyl)-5-fluoro-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



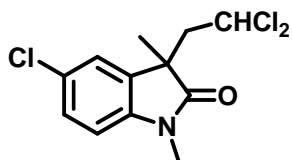
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.02 (td, *J* = 8.8, 2.4 Hz, 1H), 6.96 (dd, *J* = 7.6, 2.4 Hz, 1H), 6.79 (dd, *J* = 8.8, 4.4 Hz, 1H), 5.42 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.8 Hz, 1H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.6, 160.5, 158.1, 139.3, 132.9, 132.8, 115.0, 114.7, 111.1, 110.8, 109.1, 109.0, 69.3, 50.0, 47.6, 47.5, 26.6, 25.4.

**HRMS (ESI, *m/z*):** Calculated for C<sub>12</sub>H<sub>13</sub>Cl<sub>2</sub>FNO (M+H)<sup>+</sup> 276.0353, found 276.0351

#### 5: 5-chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



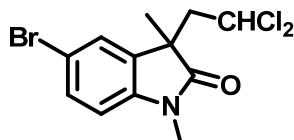
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.41 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.20 (s, 3H), 3.03 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.69 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.5, 142.0, 132.9, 128.6, 128.1, 123.2, 109.5, 69.3, 49.9, 47.4, 26.6, 25.4.

**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>13</sub>Cl<sub>3</sub>NO (M+H)<sup>+</sup> 292.0057, found 292.0059

### 6: 5-bromo-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



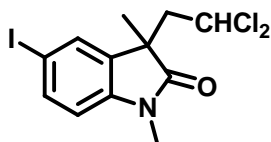
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.44 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.41 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.18 (s, 3H), 3.02 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.8 Hz, 1H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.3, 142.5, 133.3, 131.5, 125.9, 115.3, 110.0, 69.3, 49.9, 47.3, 26.5, 25.4

**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>13</sub>BrCl<sub>2</sub>NO (M+H)<sup>+</sup> 335.9552, found 335.9557

### 7: 3-(2,2-dichloroethyl)-5-iodo-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.44 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.18 (s, 3H), 3.02 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 178.2, 143.2, 137.5, 133.6, 131.5, 110.6, 85.0, 69.4, 49.9, 47.2, 26.5, 25.5.

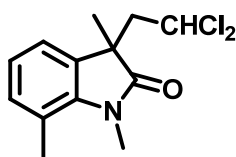
**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>13</sub>Cl<sub>2</sub>INO (M+H)<sup>+</sup> 383.9413, found 383.9418

### 8: 3-(2,2-dichloroethyl)-1,3,7-trimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl



acetate = 20/1)



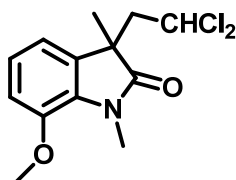
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.05 – 6.96 (m, 3H), 5.38 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.48 (s, 3H), 3.02 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.66 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.58 (s, 3H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.7, 141.2, 132.3, 131.7, 122.6, 120.5, 120.3, 69.7, 50.5, 46.5, 29.8, 25.8, 19.1

**HRMS (ESI, *m/z*):** Calculated for C<sub>13</sub>H<sub>16</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 272.0603, found 272.0608

### 9: 3-(2,2-dichloroethyl)-7-methoxy-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



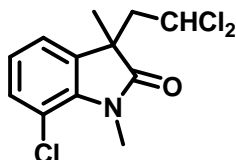
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.04 (t, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.39 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.87 (s, 3H), 3.47 (s, 3H), 3.01 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.66 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.2, 145.7, 132.7, 131.3, 123.3, 115.2, 112.3, 69.7, 55.9, 50.4, 47.2, 29.7, 25.6.

**HRMS (ESI, *m/z*):** Calculated for C<sub>13</sub>H<sub>16</sub>Cl<sub>2</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 288.0553, found 288.0554

### 10: 7-chloro-3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



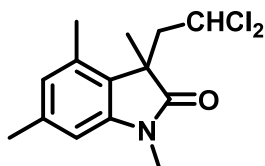
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.24 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.07 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.03 – 6.99 (m, 1H), 5.39 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.57 (s, 3H), 3.03 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.4 Hz, 1H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.2, 139.4, 134.0, 130.9, 123.4, 121.2, 116.1, 69.3, 50.2, 46.9, 29.8, 25.8.

**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>13</sub>Cl<sub>3</sub>NO (M+H)<sup>+</sup> 292.0057, found 292.0060

### 11: 3-(2,2-dichloroethyl)-1,3,4,6-tetramethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



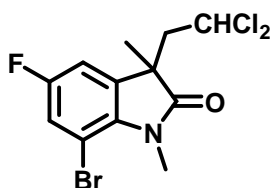
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.67 (s, 1H), 6.54 (s, 1H), 5.27 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.17 (s, 3H), 3.07 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.86 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.42 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.4, 143.9, 138.7, 133.6, 125.7, 124.8, 107.3, 69.9, 49.0, 47.7, 26.5, 23.3, 21.6, 18.1.

**HRMS (ESI, m/z):** Calculated for C<sub>14</sub>H<sub>18</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 286.0760, found 286.0758

### 12: 7-bromo-3-(2,2-dichloroethyl)-5-fluoro-1,3-dimethylindolin-2-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



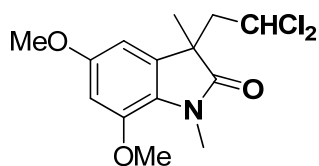
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.18 (dt, *J* = 8.8, 2.4 Hz, 1H), 6.90 (dd, *J* = 6.8, 2.4 Hz, 1H), 5.43 (ddd, *J* = 8.4, 5.2, 1.2 Hz, 1H), 3.55 (s, 3H), 3.01 (ddd, *J* = 14.8, 8.4, 2.0 Hz, 1H), 2.65 (dd, *J* = 14.8, 4.8 Hz, 1H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 179.0, 159.5, 157.1, 137.1, 137.0, 135.6, 135.5, 120.6, 120.4, 110.2, 110.0, 102.4, 102.3, 69.0, 50.1, 47.5, 47.4, 30.0, 25.8.

**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>12</sub>BrCl<sub>2</sub>FNO (M+H)<sup>+</sup> 353.9458, found 353.9457

**13: 3-(2,2-dichloroethyl)-5,7-dimethoxy-1,3-dimethylindolin-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



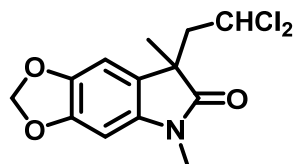
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.45 (d,  $J = 2.4$  Hz, 1H), 6.37 (d,  $J = 2.0$  Hz, 1H), 5.43 (dd,  $J = 9.2, 4.4$  Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.00 (dd,  $J = 14.8, 9.2$  Hz, 1H), 2.63 (dd,  $J = 14.8, 4.0$  Hz, 1H), 1.35 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  178.8, 156.8, 146.3, 133.3, 124.8, 100.4, 99.9, 99.4, 69.7, 55.9, 55.8, 50.35, 47.8, 29.6, 25.7.

**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  318.0658, found 318.0659

**14:****7-(2,2-dichloroethyl)-5,7-dimethyl-5,7-dihydro-6H-[1,3]dioxolo[4,5-f]indol-6-one.**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



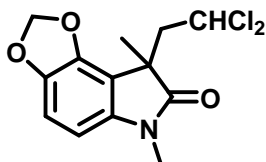
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  6.72 (s, 1H), 6.48 (s, 1H), 5.97 (dd,  $J = 5.2, 1.2$  Hz, 2H), 5.41 (dd,  $J = 9.2, 4.4$  Hz, 1H), 3.16 (s, 3H), 3.00 (dd,  $J = 14.8, 9.2$  Hz, 1H), 2.63 (dd,  $J = 14.8, 4.4$  Hz, 1H), 1.35 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) :  $\delta$  179.1, 147.8, 143.4, 137.8, 122.7, 104.3, 101.3, 92.5, 69.6, 50.3, 47.5, 26.6, 25.5.

**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  302.0345, found 302.0344

**14':****8-(2,2-dichloroethyl)-6,8-dimethyl-6,8-dihydro-7H-[1,3]dioxolo[4,5-e]indol-7-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



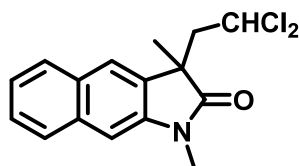
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** : δ 6.74 (d, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 6.01(d, *J* = 1.2 Hz, 1H), 5.98(d, *J* = 1.2 Hz, 1H), 5.48 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.16 (s, 3H), 2.99 (dd, *J* = 14.8, 8.8 Hz, 1H), 2.83 (dd, *J* = 14.8, 4.8 Hz, 1H), 1.44 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** : δ 177.9, 144.3, 143.2, 138.5, 111.8, 107.1, 101.8, 100.2, 69.9, 48.8, 46.6, 26.9, 23.7

**HRMS (ESI, m/z)**: Calculated for C<sub>13</sub>H<sub>14</sub>Cl<sub>2</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 302.0345, found 302.0343

**15: 3-(2,2-dichloroethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[f]indol-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



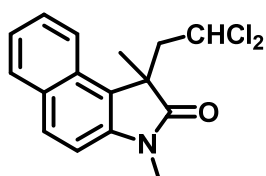
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** : δ 7.81 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.62 (s, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.40 (m, 1H), 7.15 (s, 1H), 5.45 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.31 (s, 3H), 3.13 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.80 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** : δ 178.5, 141.7, 134.0, 132.1, 130.2, 128.0, 127.2, 126.8, 124.5, 122.2, 104.3, 69.6, 50.4, 46.7, 26.7, 26.0.

**HRMS (ESI, m/z)**: Calculated for C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 308.0603, found 308.0606

**15': 1-(2,2-dichloroethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-one**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



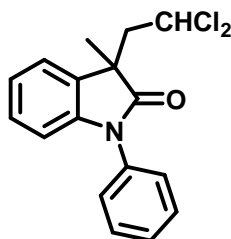
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** :δ 7.91 (d, *J*= 8.4 Hz, 1H), 7.75 (d, *J*= 8.4 Hz, 1H), 7.59– 7.54 (m, 1H), 7.42 – 7.38 (m, 1H), 7.23 (d, *J*= 8.8 Hz, 1H), 5.20 (dd, *J*= 10.0, 3.2Hz, 1H), 3.33 (s, 3H), 3.31 – 3.26 (m, 1H), 3.18 – 3.14 (m, 1H), 1.61 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** :δ 180.5, 141.5, 130.5, 130.1, 129.4, 128.0, 123.7, 122.0, 121.0, 112.5, 109.9, 70.0, 50.3, 48.7, 26.8, 24.9.

**HRMS (ESI, m/z)**: Calculated for C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 308.0603, found 308.0607

### 17: 3-(2,2-dichloroethyl)-3-methyl-1-phenylindolin-2-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



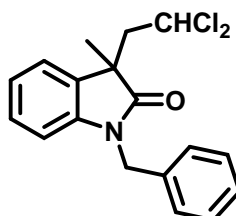
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** :δ 7.52 (t, *J*= 8.4 Hz, 1H), 7.41 (t, *J*= 8.4 Hz, 1H), 7.27– 7.23 (m, 1H), 7.14 (t, *J*= 7.6Hz, 1H), 6.86 (d, *J*= 8.0 Hz, 1H), 5.50 (dd, *J*= 9.2, 4.0 Hz, 1H), 3.16 (dd, *J*= 14.8, 9.2 Hz, 1H), 2.80 (dd, *J*= 14.8, 4.0 Hz, 1H), 1.52 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** : δ 178.3, 143.4, 134.4, 130.8, 129.6, 128.5, 128.1, 126.4, 123.1, 122.9, 110.0, 69.8, 50.3, 47.3, 26.1.

**HRMS (ESI, m/z)**: Calculated for C<sub>17</sub>H<sub>16</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 320.0603, found 320.0606

### 18: 1-benzyl-3-(2,2-dichloroethyl)-3-methylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** :δ 7.32 – 7.27 (m, 1H), 7.23 – 7.19 (m, 1H), 7.08 – 7.05 (m, 1H), 6.80 – 6.78 (m, 1H), 5.46 (dd, *J*= 8.8, 4.4 Hz, 1H), 5.01 (d, *J*= 15.6 Hz, 1H), 4.81 (d, *J*= 15.6 Hz, 1H), 3.09 (dd, *J*= 14.8, 9.2 Hz, 1H), 2.76 (dd, *J*= 14.8, 4.4 Hz,

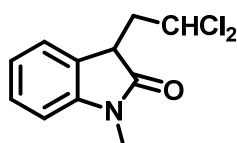
1H), 1.45 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 179.0, 142.6, 135.7, 131.1, 128.7, 128.5, 127.7, 127.5, 122.7, 122.6, 109.7, 69.6, 49.9, 47.2, 44.1, 26.1.

**HRMS (ESI, m/z)**: Calculated for C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 334.0760, found 334.0765

### 19: 3-(2,2-dichloroethyl)-1-methylindolin-2-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



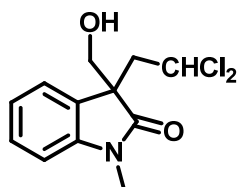
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.32 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.09 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.36 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.74 – 3.70 (m, 1H), 3.21 (s, 3H), 2.72 – 2.67 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 176.4, 144.2, 128.6, 126.9, 123.7, 122.7, 108.4, 70.6, 44.6, 42.8, 26.2.

**HRMS (ESI, m/z)**: Calculated for C<sub>11</sub>H<sub>12</sub>Cl<sub>2</sub>NO (M+H)<sup>+</sup> 244.0290, found 244.0288

### 20: 3-(2,2-dichloroethyl)-3-(hydroxymethyl)-1-methylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



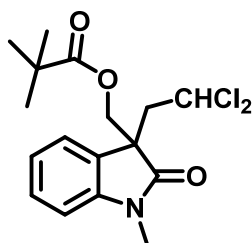
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 7.37 (td, *J* = 8.0, 1.2 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.13 (td, *J* = 7.6, 0.8 Hz, 1H), 6.91 (d, *J* = 7.6, 1H), 5.45 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.78 (dd, *J* = 10.8, 9.2 Hz, 1H), 3.69 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.23 (s, 3H), 3.21 – 3.18 (m, 1H), 2.86 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.44 (dd, *J* = 9.2, 4.0 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 177.7, 144.3, 129.3, 127.1, 123.3, 122.9, 108.9, 69.7, 67.8, 52.9, 45.6, 26.5.

**HRMS (ESI, m/z)**: Calculated for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 274.0396, found 274.0393

**21: (3-(2,2-dichloroethyl)-1-methyl-2-oxoindolin-3-yl)methyl pivalate**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate =10/1)



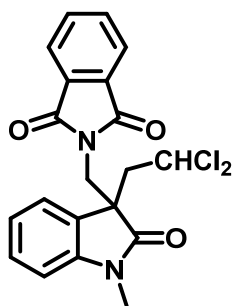
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** : $\delta$  7.34 (t,  $J$ = 7.6Hz, 1H), 7.24 (d,  $J$ = 7.6 Hz, 1H), 7.09 (t,  $J$ = 7.6 Hz, 1H), 6.87 (d,  $J$ = 8.0 Hz, 1H), 5.50 (dd,  $J$ = 9,2Hz,4.4 Hz, 1H), 4.57 (d,  $J$ = 10.8 Hz, 1H), 4.07 (d,  $J$ = 10.4 Hz, 1H), 3.22 (s, 3H), 3.01 (dd,  $J$ = 14.8, 9.2 Hz, 1H), 2.77 (dd,  $J$ = 14.8, 4.4 Hz, 1H), 0.95 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** : $\delta$  177.2, 176.0, 144.5, 129.3, 126.9, 123.7, 122.7, 108.5, 69.0, 66.9, 51.5, 45.4, 38.7, 26.8, 26.5.

**HRMS (ESI, m/z)**: Calculated for C<sub>17</sub>H<sub>22</sub>Cl<sub>2</sub>NO<sub>3</sub> (M+H)<sup>+</sup> 358.0971, found 358.0970

**22:****2-((3-(2,2-dichloroethyl)-1-methyl-2-oxoindolin-3-yl)methyl)isoindoline-1,3-dione**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



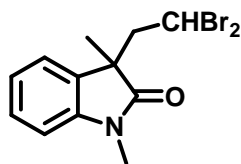
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** : $\delta$  7.81 (dd,  $J$ = 5.6, 3.2 Hz, 1H), 7.70 (dd,  $J$ = 5.6, 3.2Hz, 1H), 7.32 – 7.28 (m, 1H), 7.19 (d,  $J$ = 7.2 Hz, 1H), 7.03 (t,  $J$ = 7.6 Hz, 1H), 6.84 (d,  $J$ = 7.6 Hz, 1H), 5.44 (dd,  $J$ = 8.4, 4.8 Hz, 1H), 4.02 (d,  $J$ = 14.0 Hz, 1H), 3.95(d,  $J$ = 14.0 Hz, 1H), 3.21 (s, 3H), 3.19 – 3.16(m, 1H), 3.07 (dd,  $J$ = 14.8, 4.8 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** :  $\delta$  176.1, 167.9, 144.0, 134.2, 131.6, 129.4, 126.9, 123.8, 123.6, 122.5, 108.8, 69.3, 51.4, 47.0, 44.1, 26.6.

**HRMS (ESI, m/z)**: Calculated for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 403.0611, found 403.0627.

### 23: 3-(2,2-dibromoethyl)-1,3-dimethylindolin-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



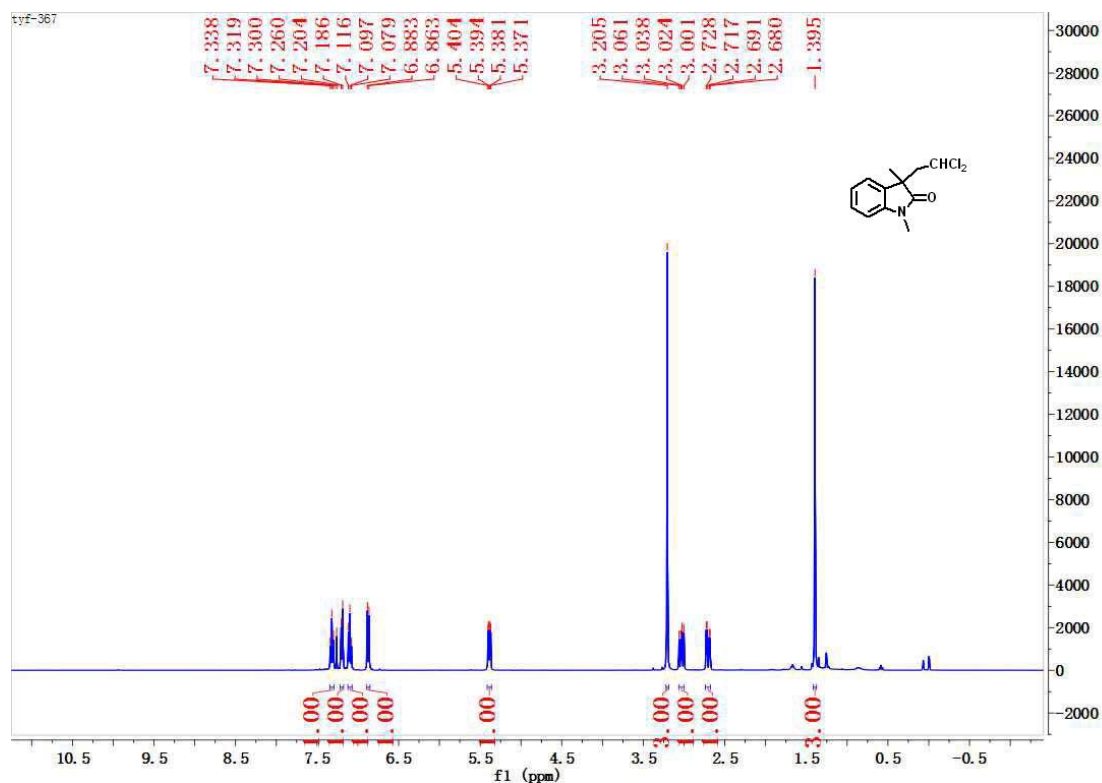
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.19 (d,  $J = 7.2$  Hz, 1H), 7.11 (t,  $J = 7.6$  Hz, 1H), 6.88 (d,  $J = 8.0$  Hz, 1H), 5.31 (dd,  $J = 9.6, 4.4$  Hz, 1H), 3.28 (dd,  $J = 14.8, 9.2$  Hz, 1H), 3.21 (s, 3H), 3.00 (dd,  $J = 15.2, 4.4$  Hz, 1H), 1.38 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  178.8, 143.6, 130.8, 128.6, 122.7, 108.6, 51.6, 48.6, 39.6, 26.5, 25.6.

HRMS (ESI,  $m/z$ ): Calculated for  $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{NO}$  ( $\text{M}+\text{H}$ ) $^+$  347.9437, found 347.9415

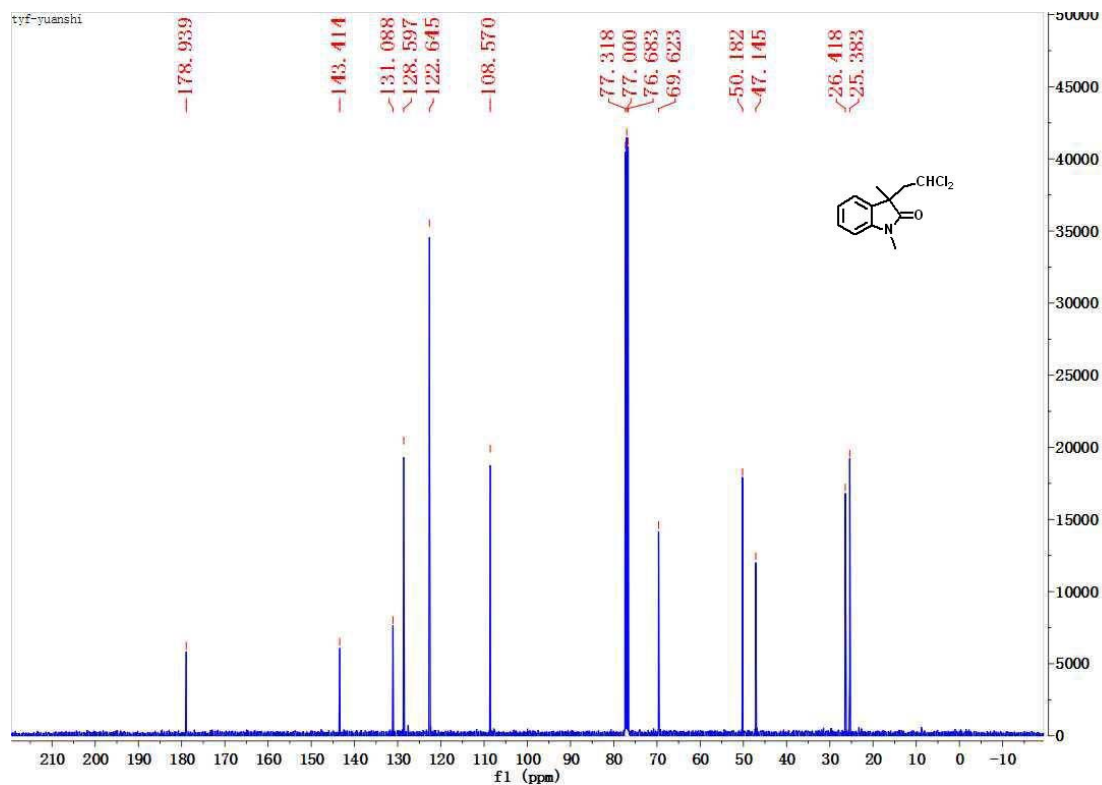
### Copies of the $^1\text{H NMR}$ , $^{13}\text{C NMR}$

#### 1- $^1\text{H NMR}$

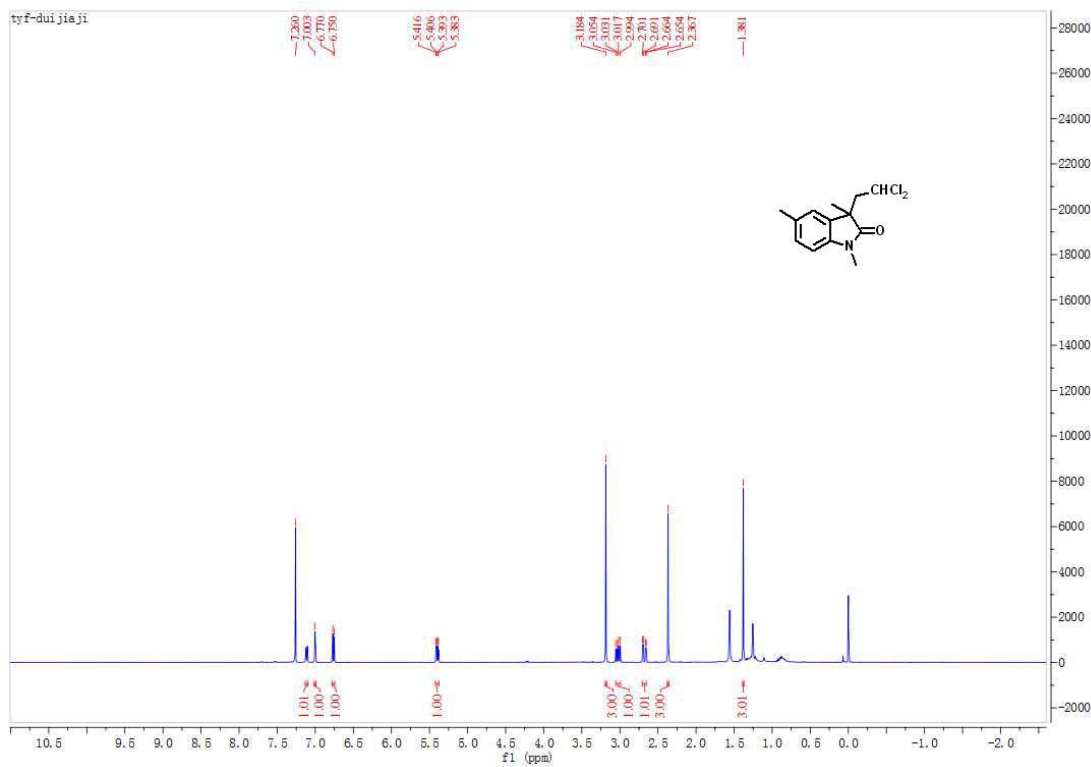




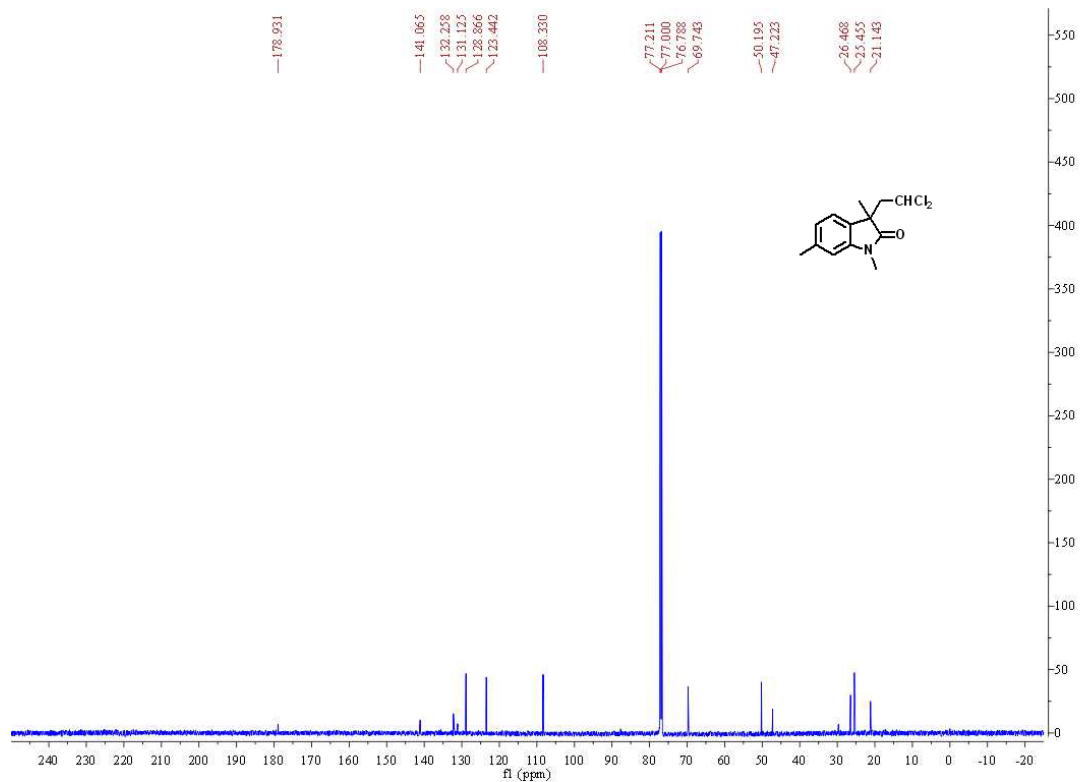
## 1-<sup>13</sup>C NMR



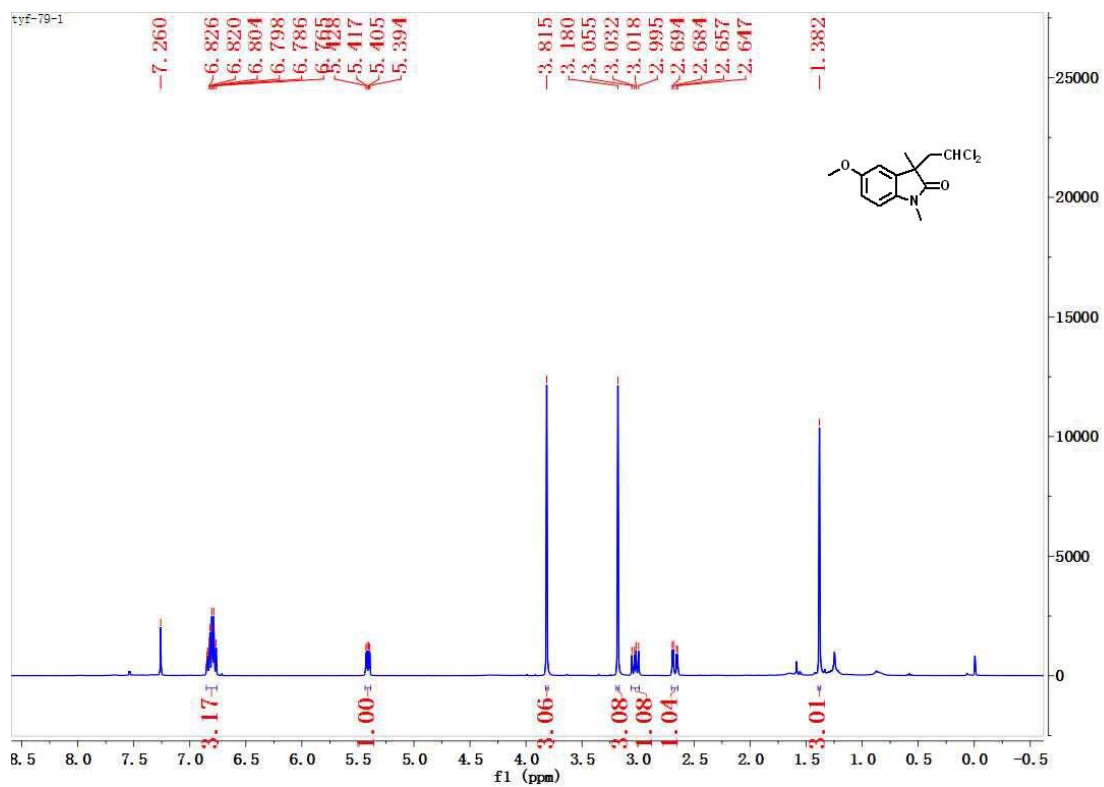
## 2-<sup>1</sup>H NMR



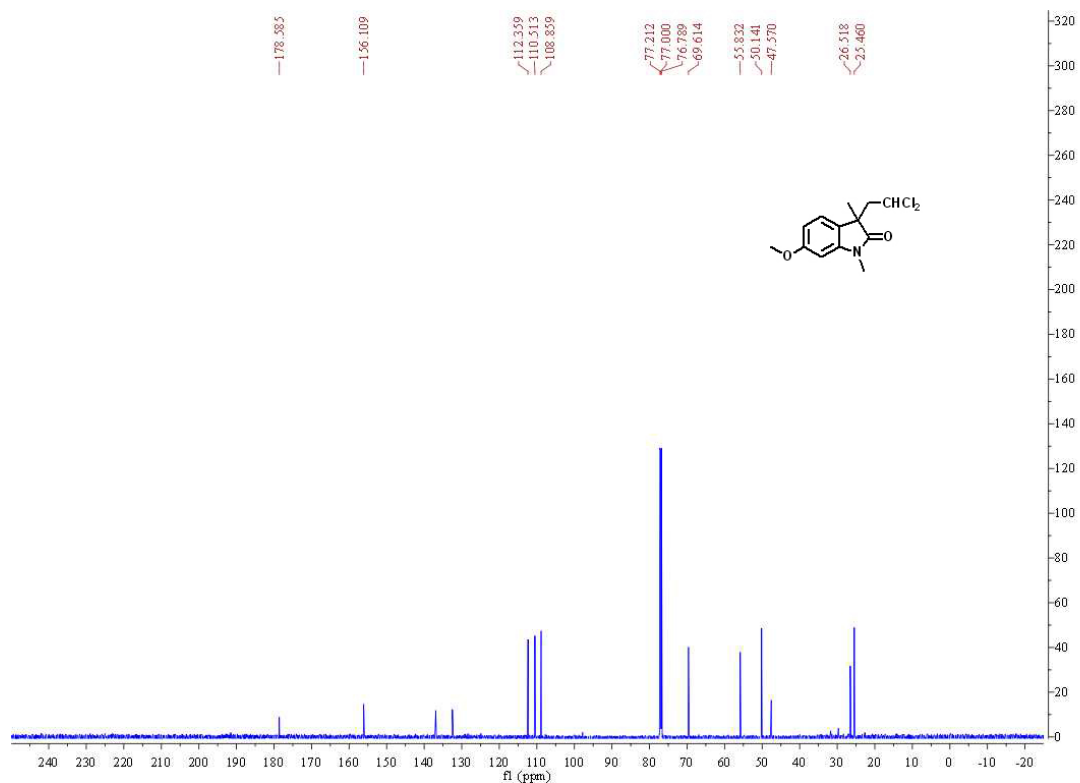
## 2-<sup>13</sup>C NMR



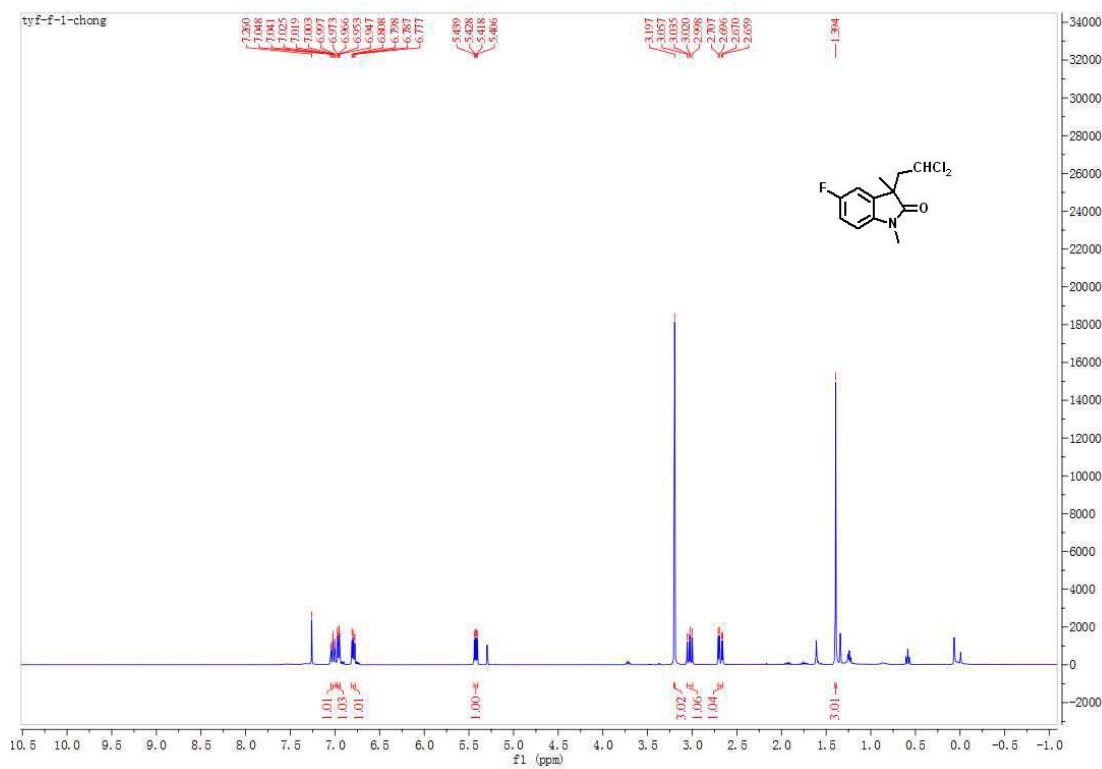
## 3-<sup>1</sup>H NMR



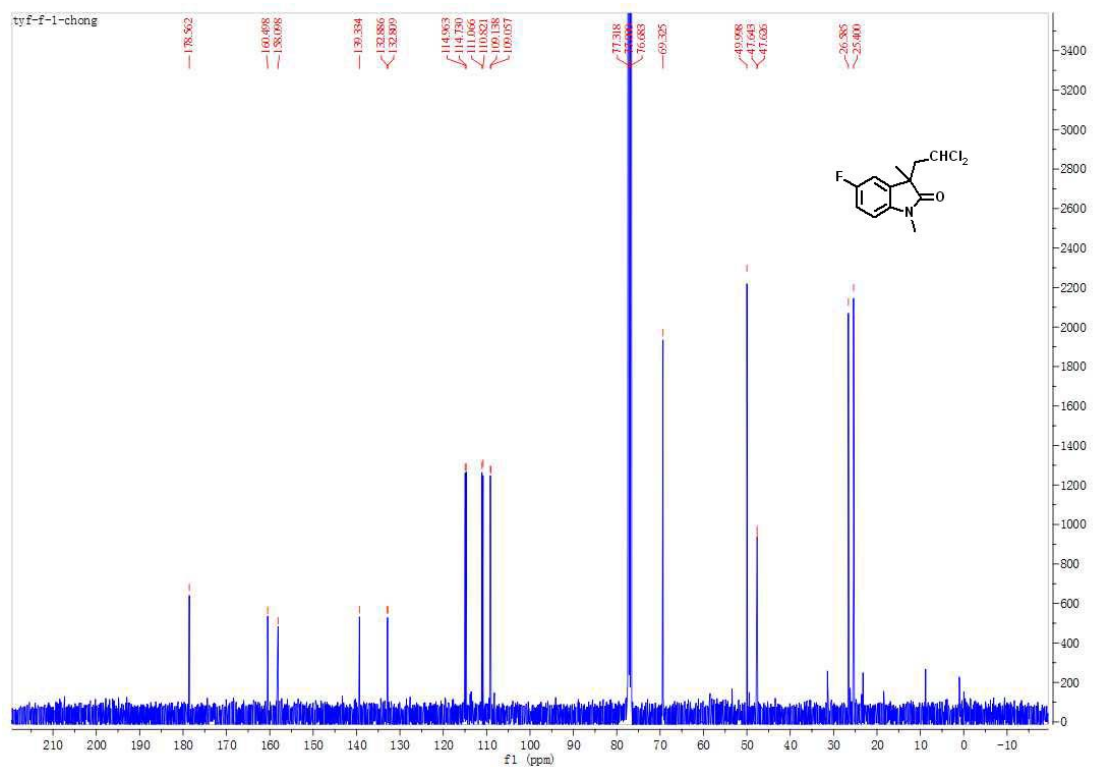
### 3-<sup>13</sup>C NMR



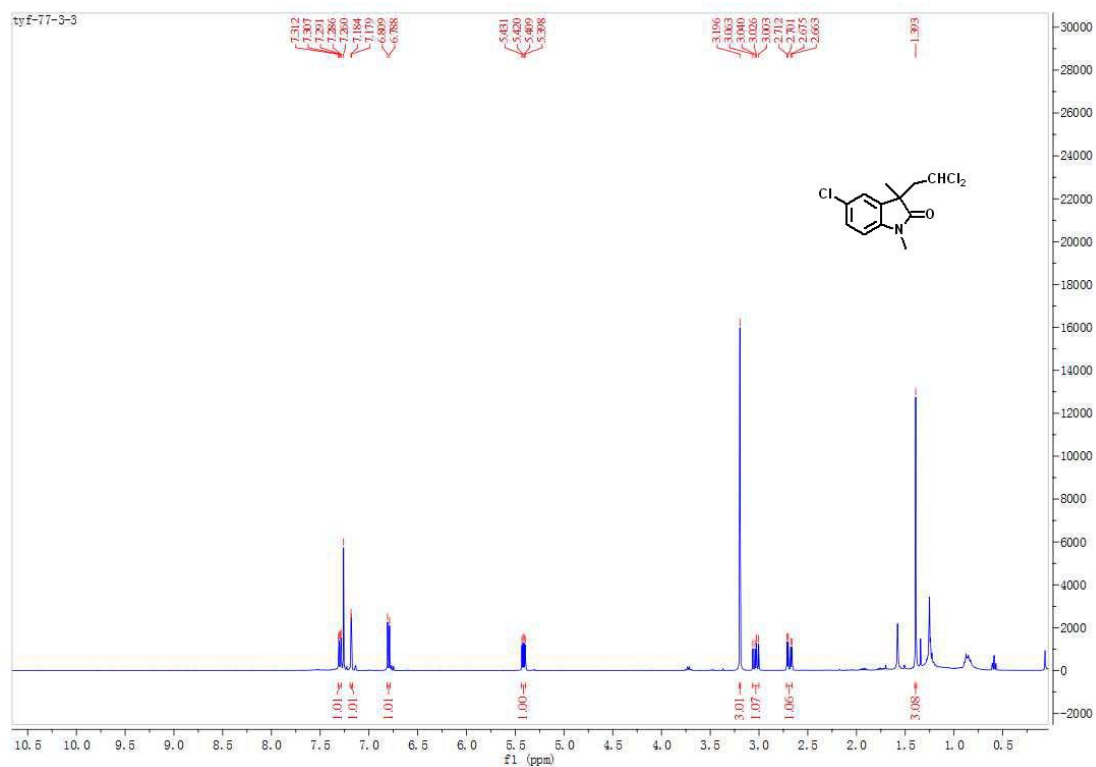
### 4-<sup>1</sup>H NMR



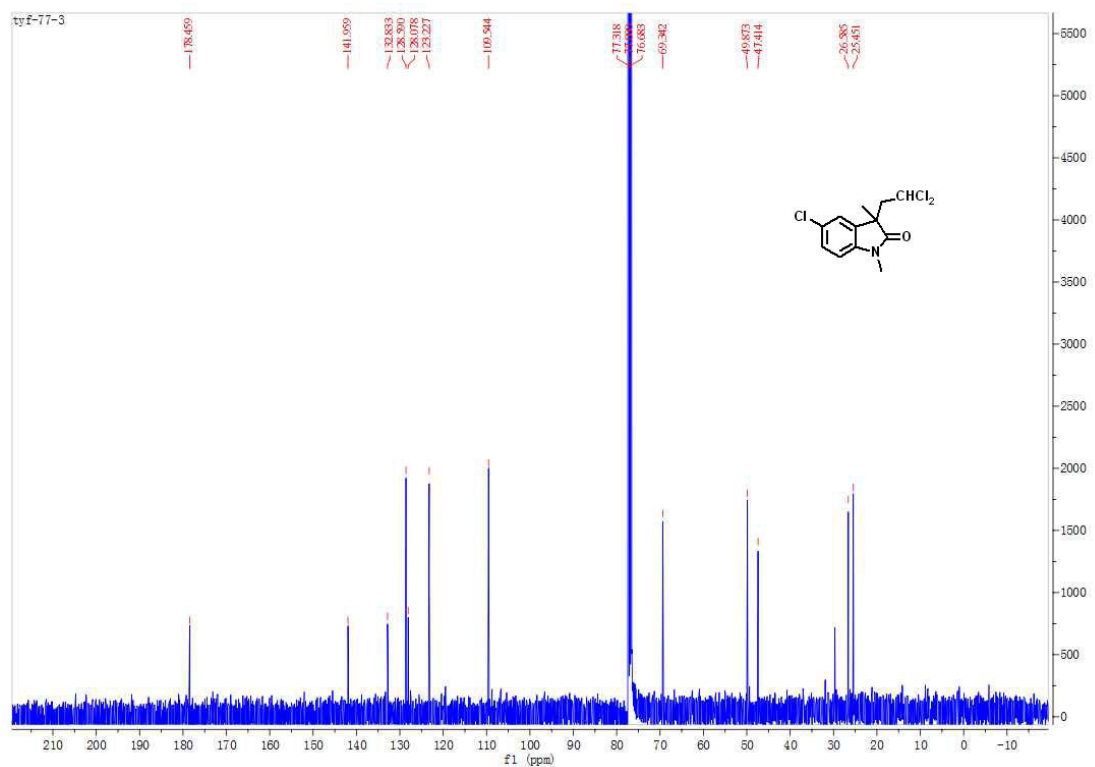
## 4-<sup>13</sup>C NMR



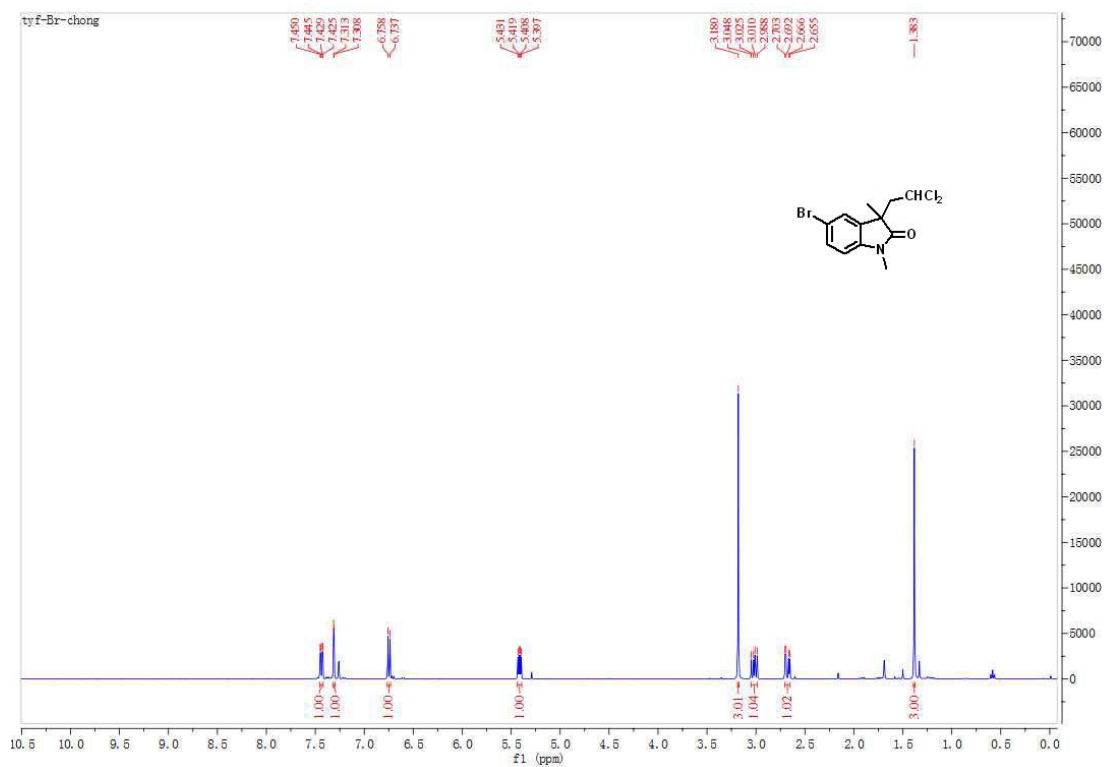
## 5-<sup>1</sup>H NMR



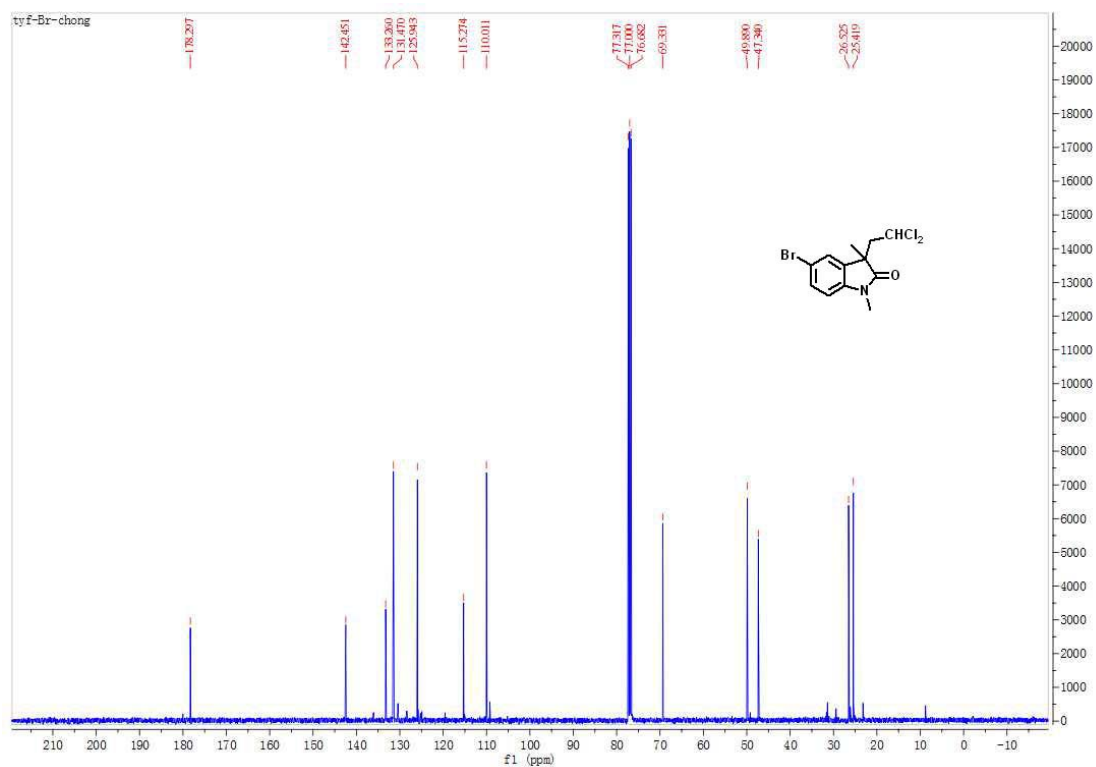
## 5-<sup>13</sup>C NMR



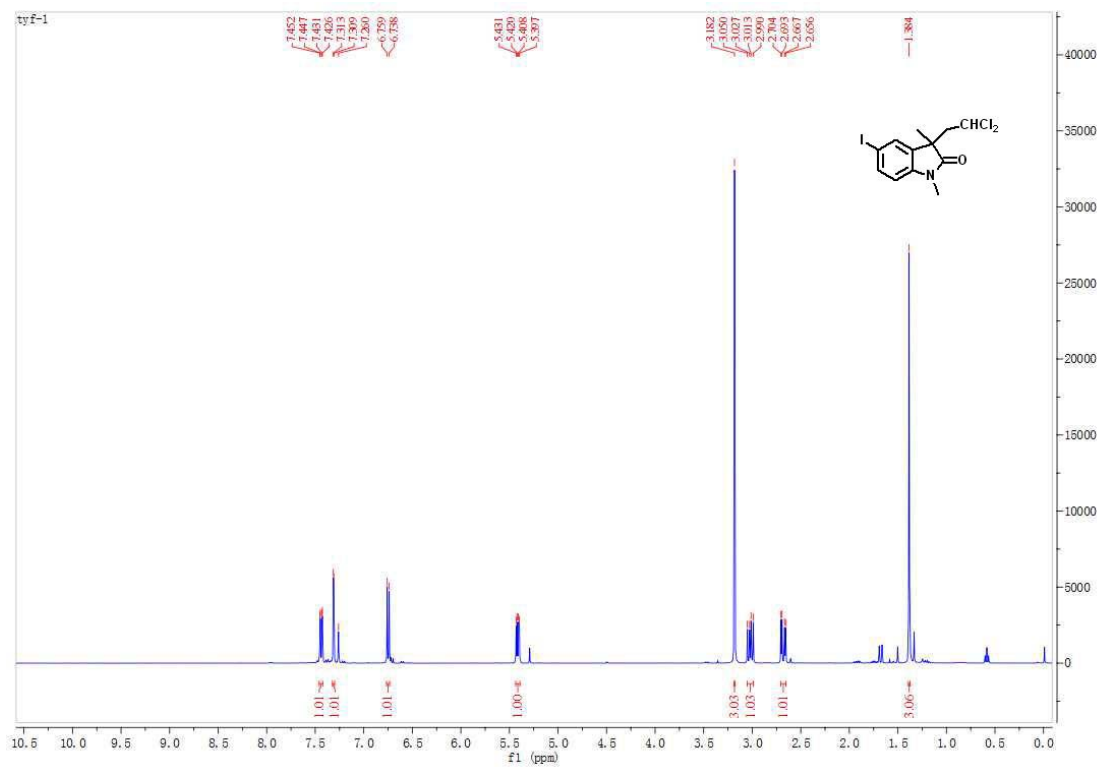
## 6-<sup>1</sup>H NMR



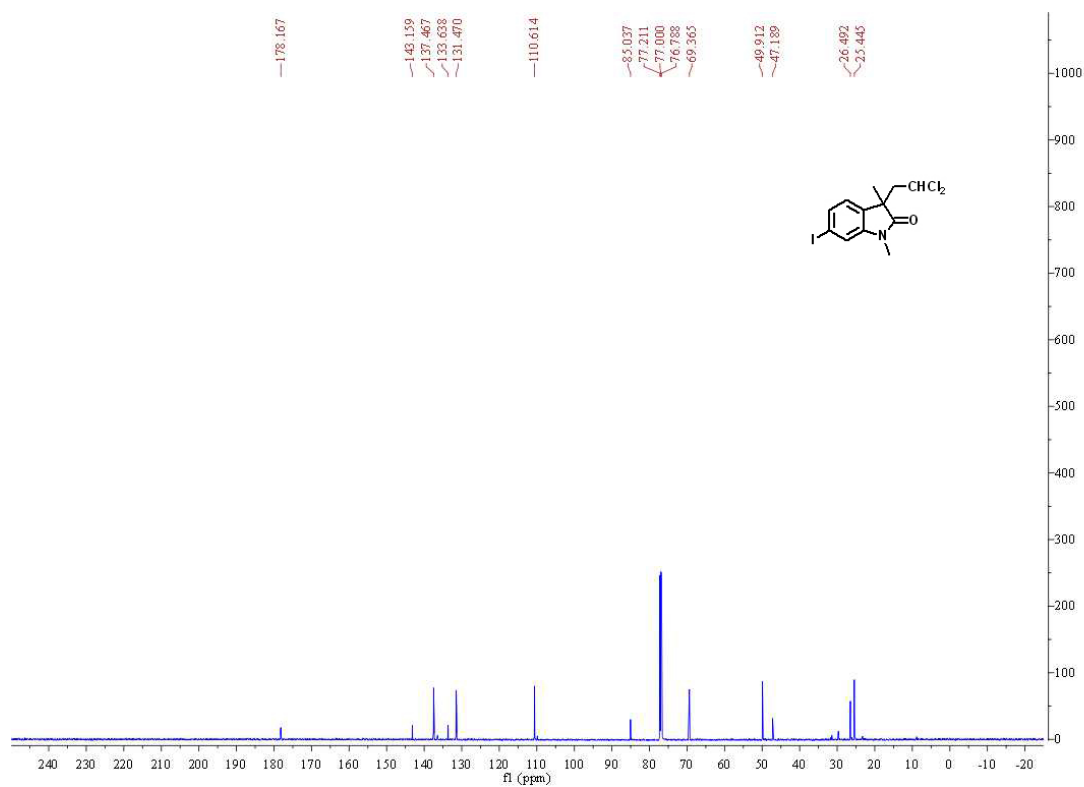
## 6-<sup>13</sup>C NMR



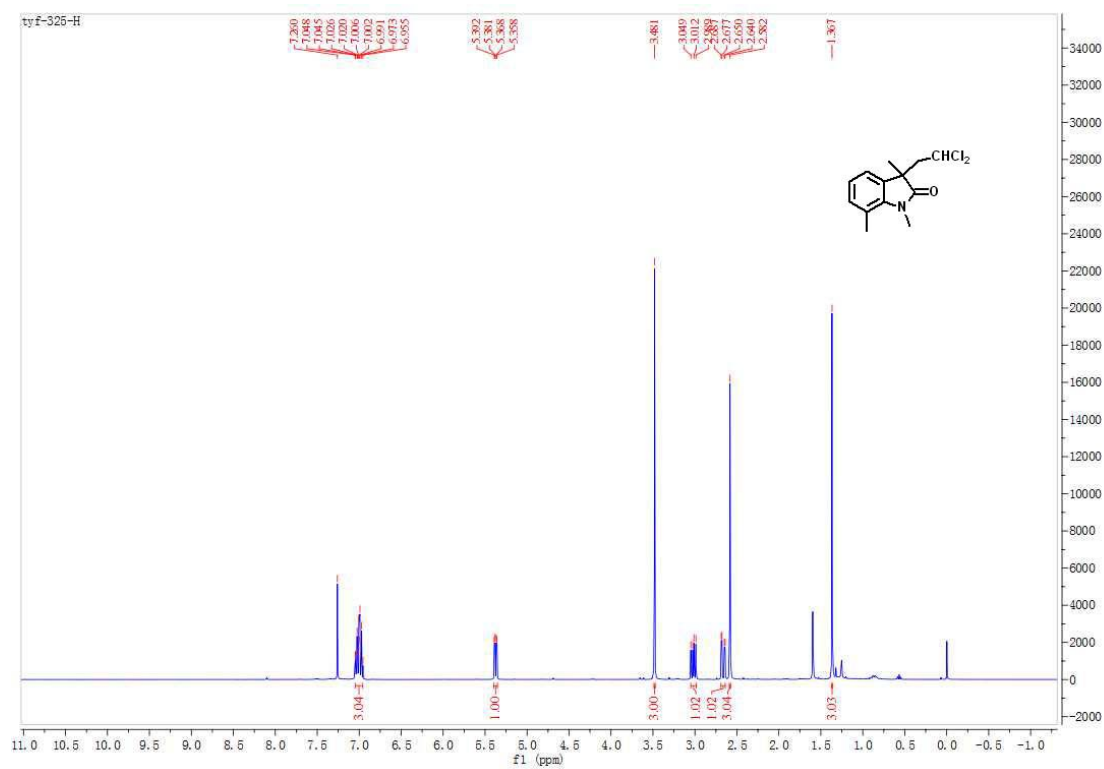
## 7-<sup>1</sup>H NMR



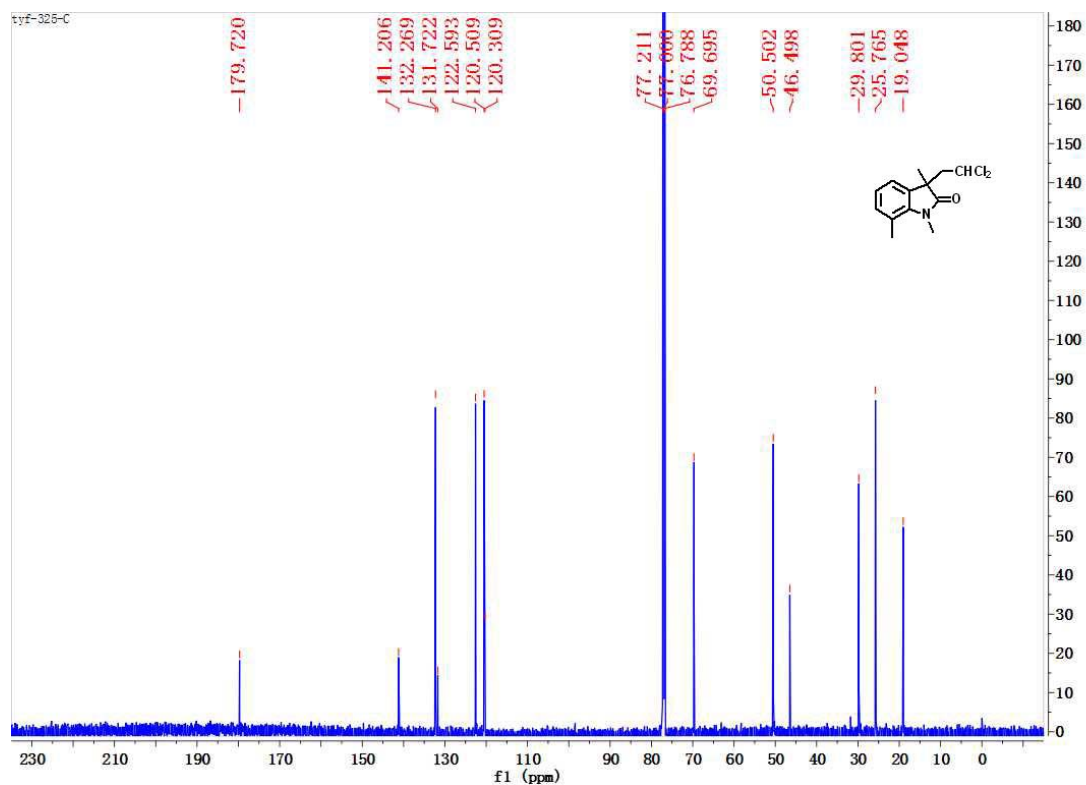
## 7-<sup>13</sup>C NMR



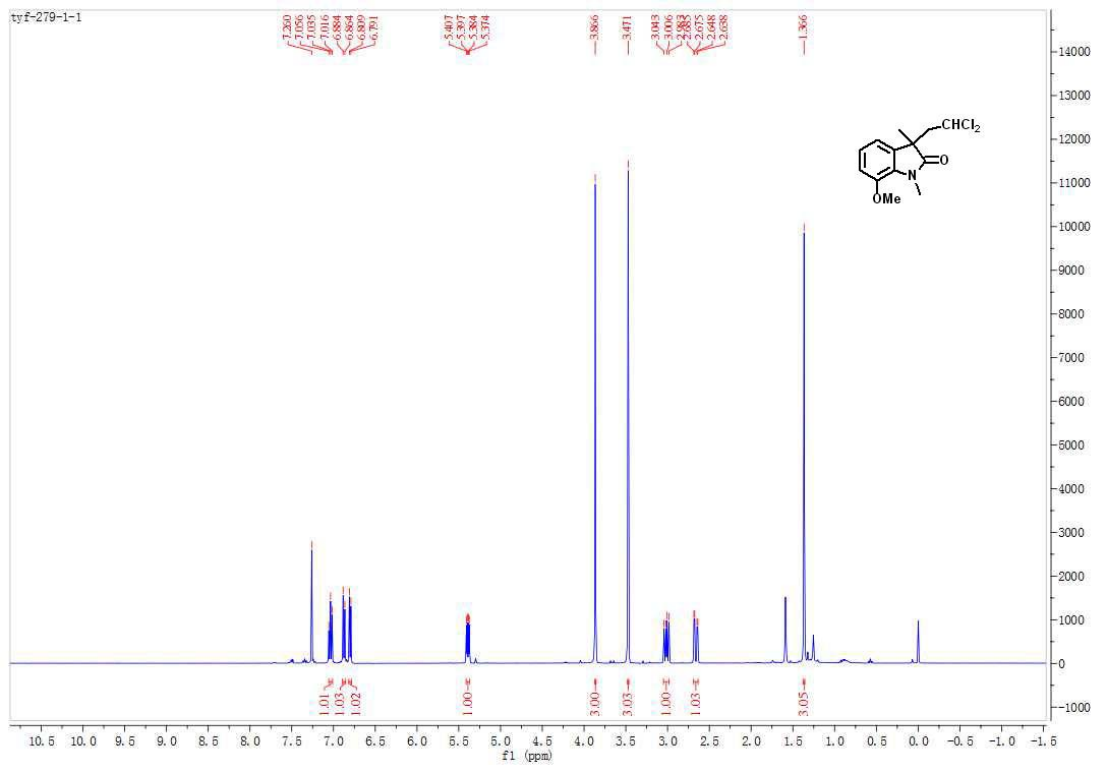
## 8-<sup>1</sup>H NMR



## 8-<sup>13</sup>C NMR

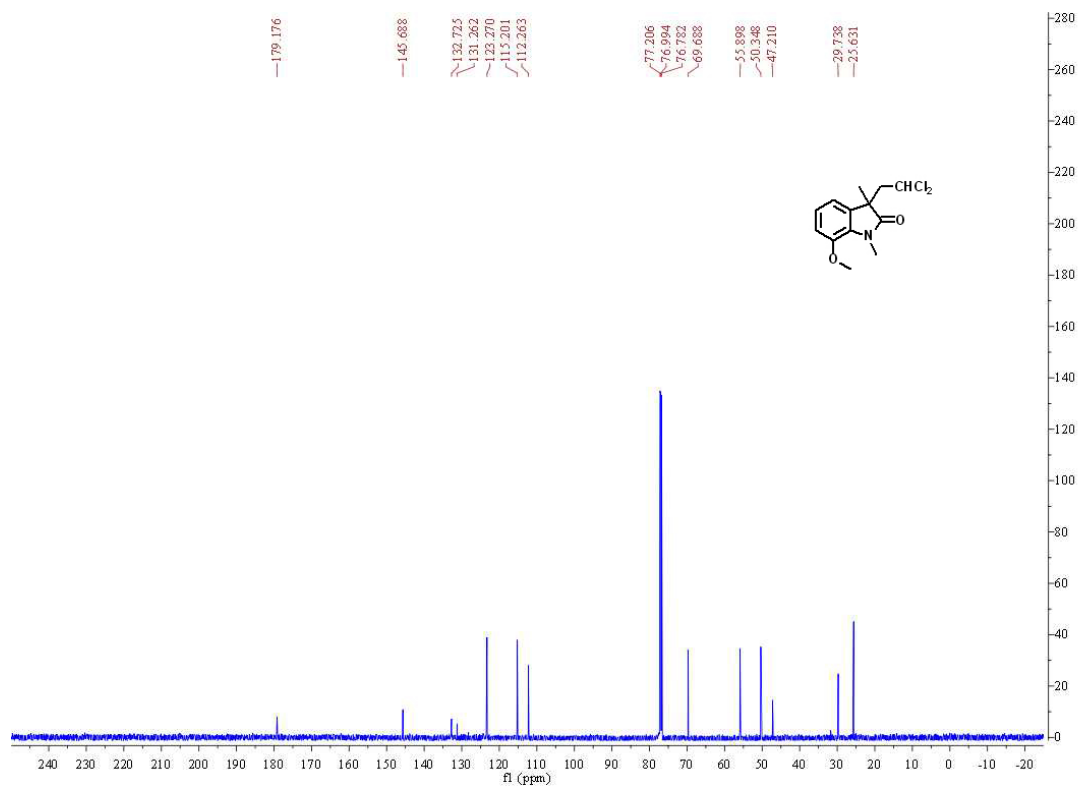


## 9-<sup>1</sup>H NMR

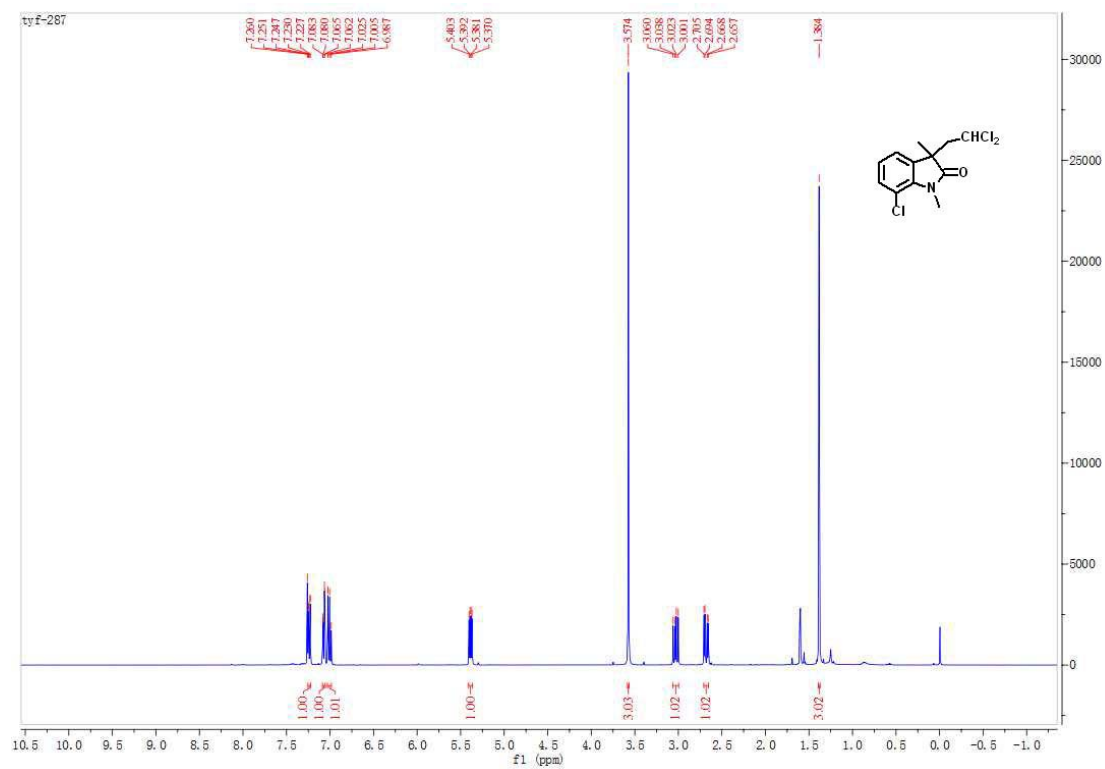




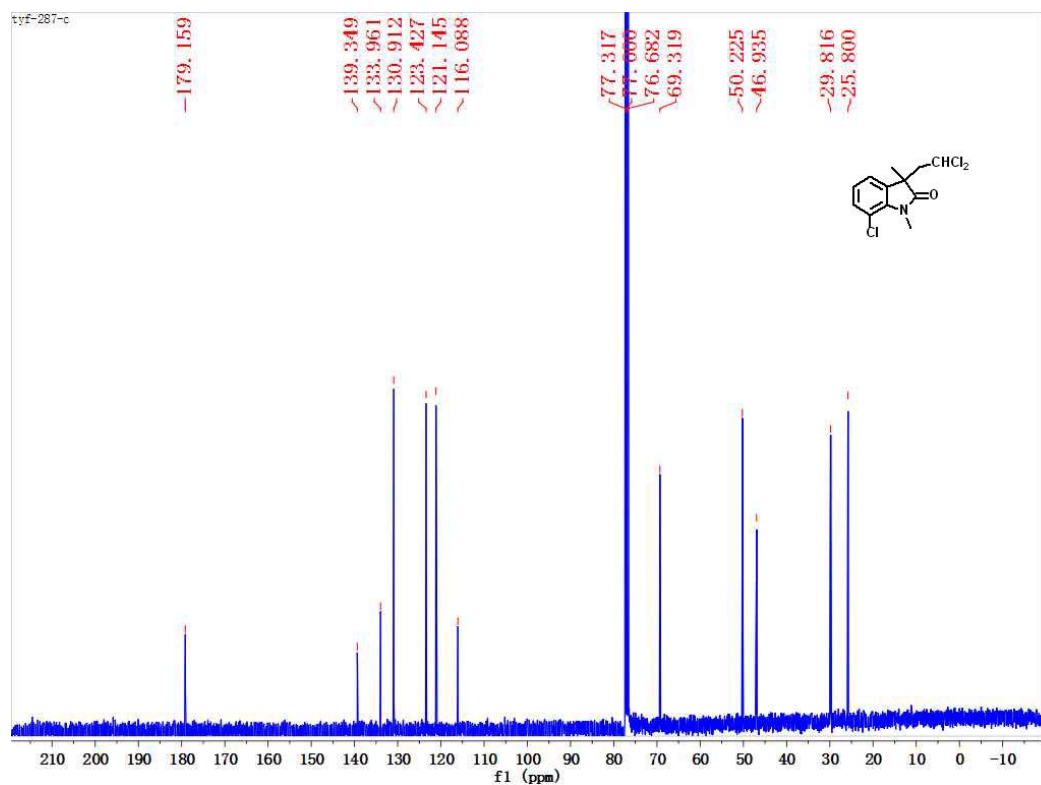
## 9-<sup>13</sup>C NMR



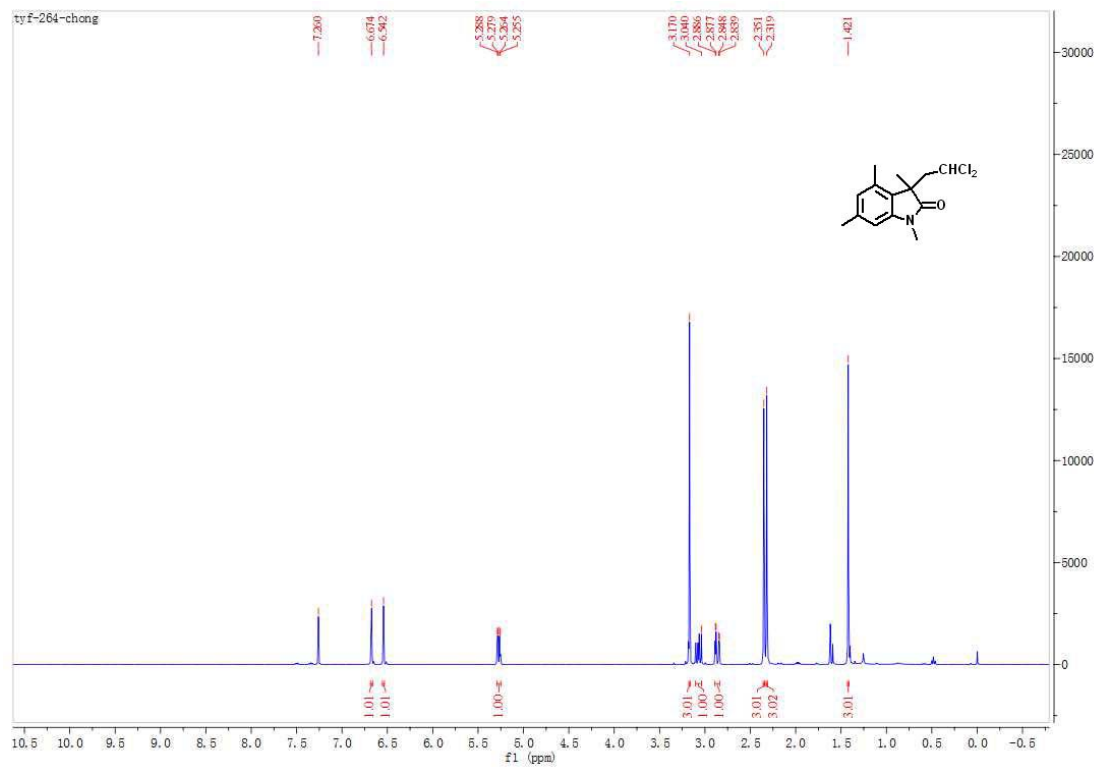
## 10-<sup>1</sup>H NMR



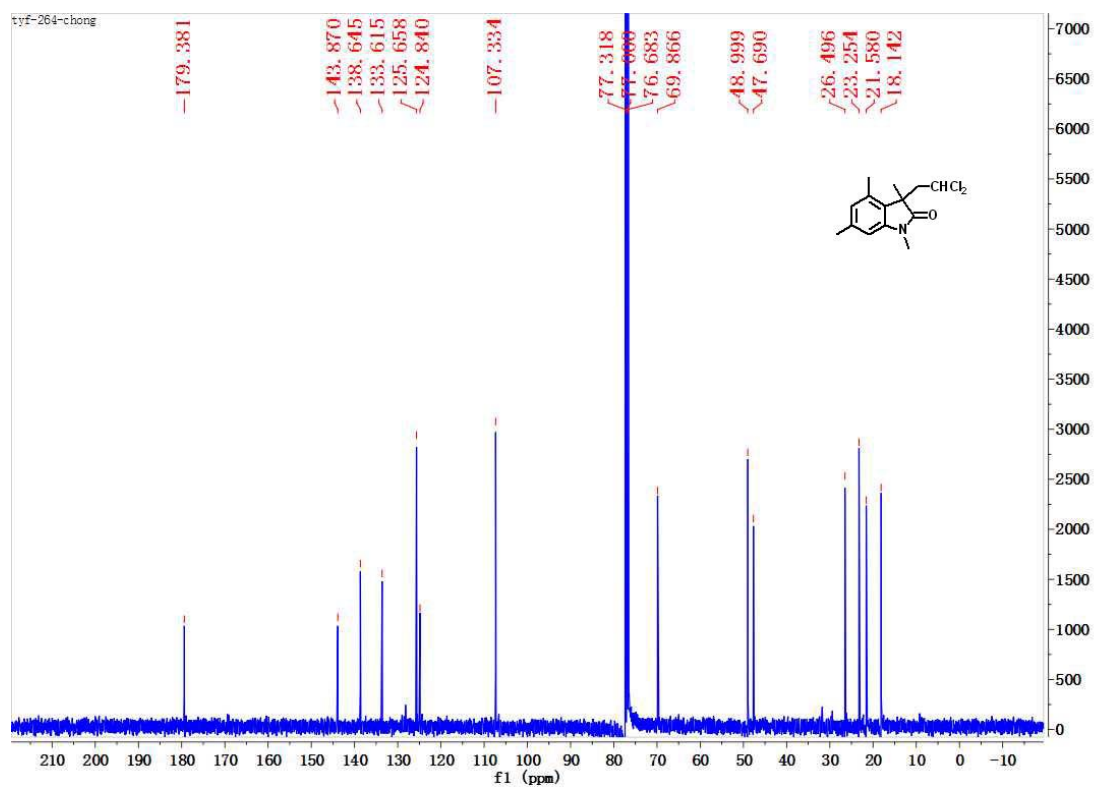
### 10-<sup>13</sup>C NMR



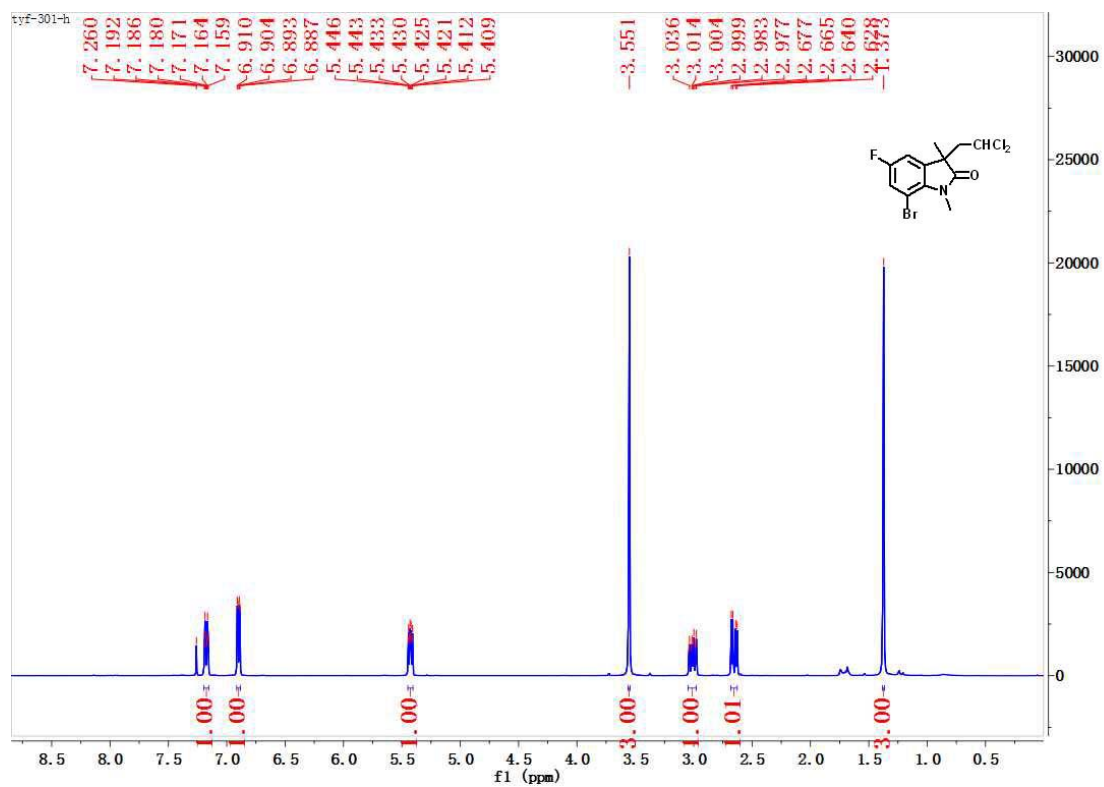
### 11-<sup>1</sup>H NMR



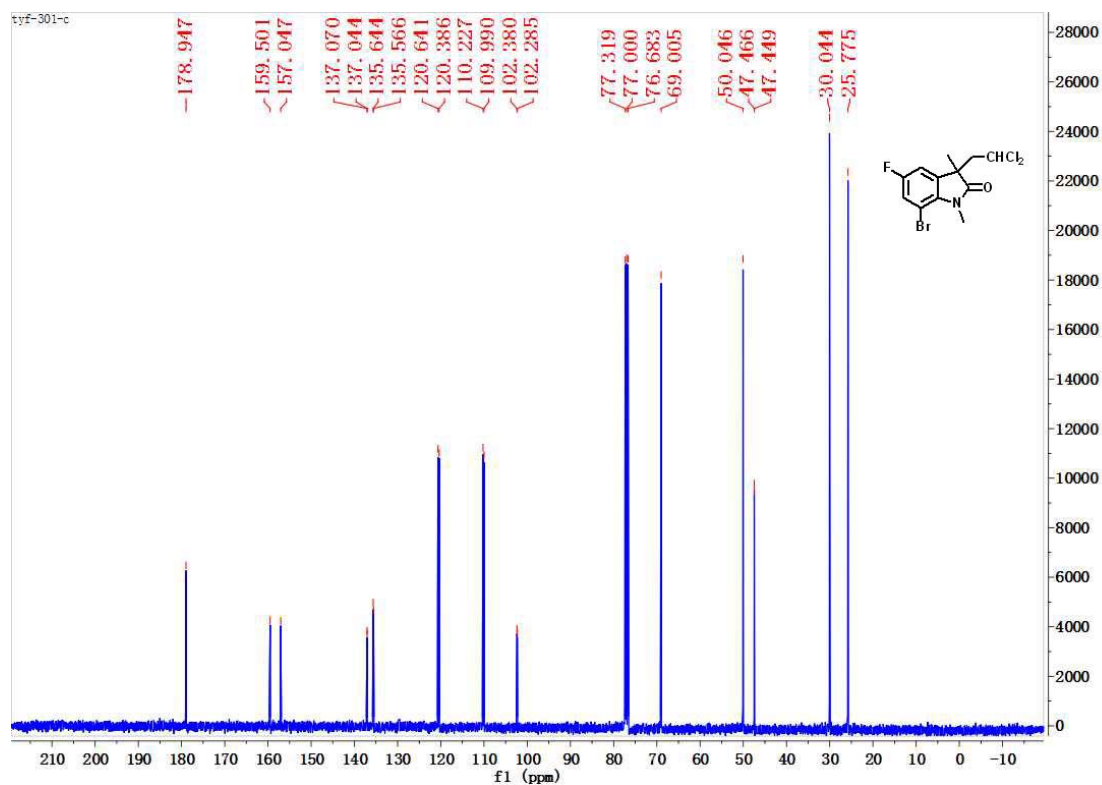
## 11-<sup>13</sup>CNMR



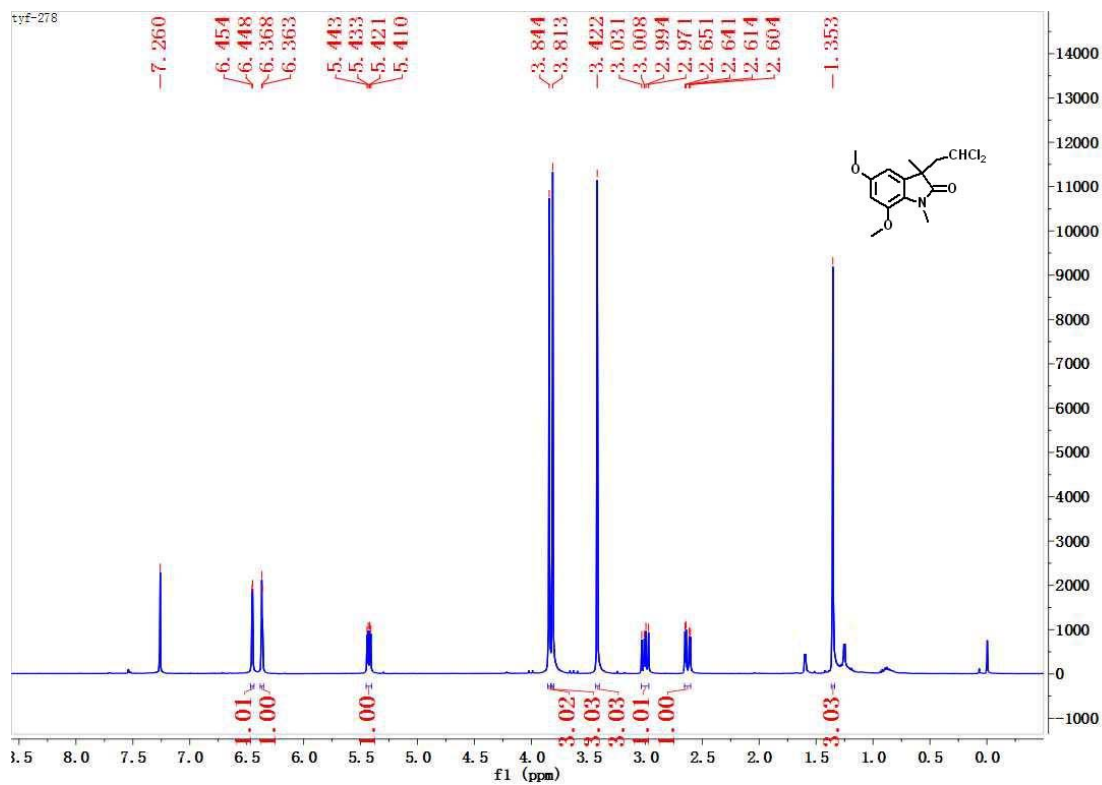
## 12-<sup>1</sup>H NMR



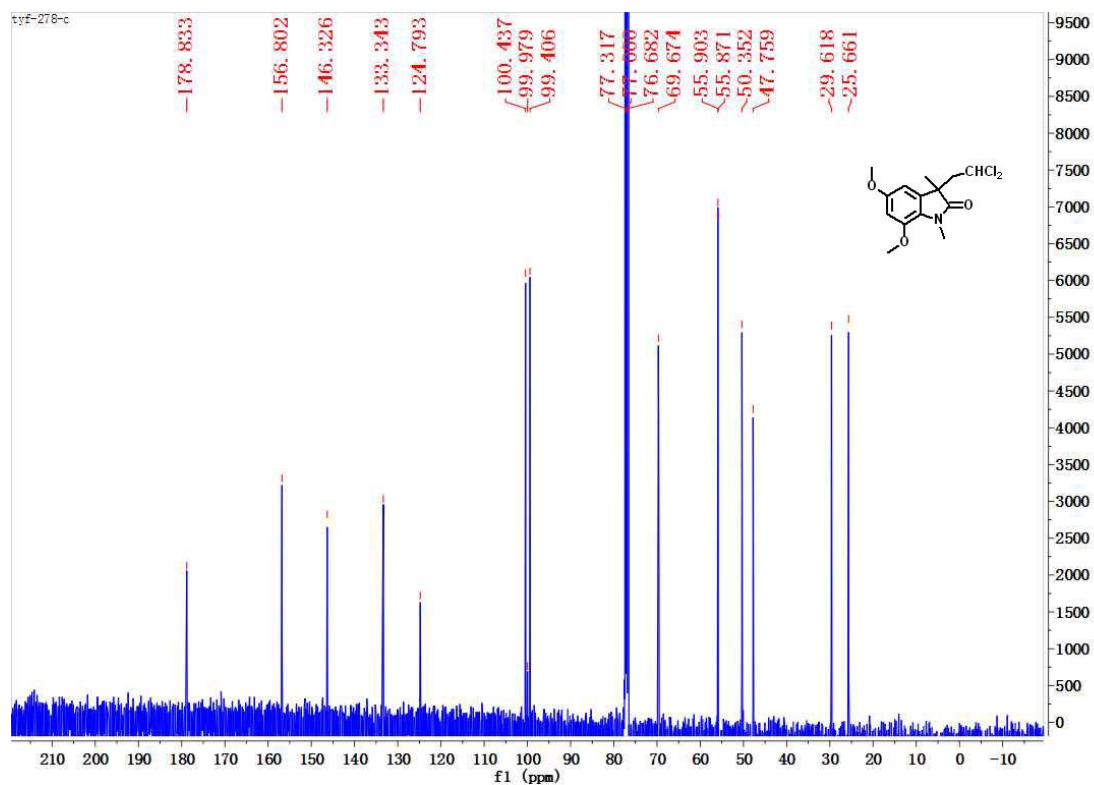
### 12-<sup>13</sup>C NMR



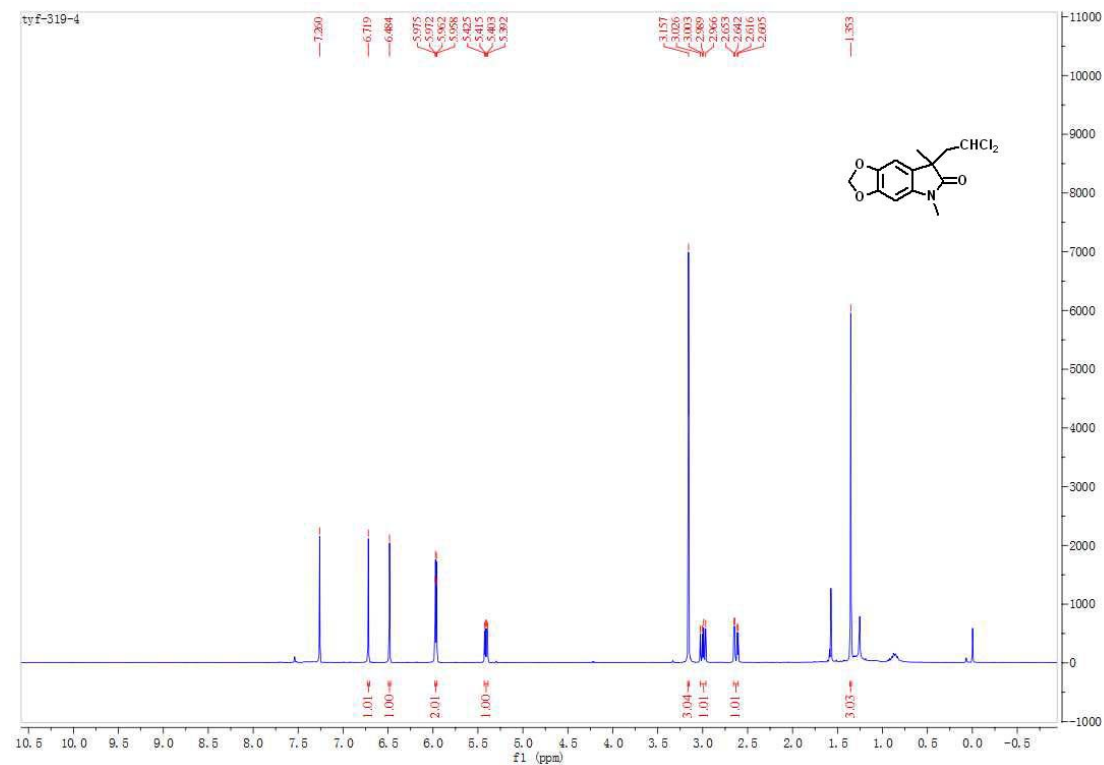
### 13-<sup>1</sup>H NMR



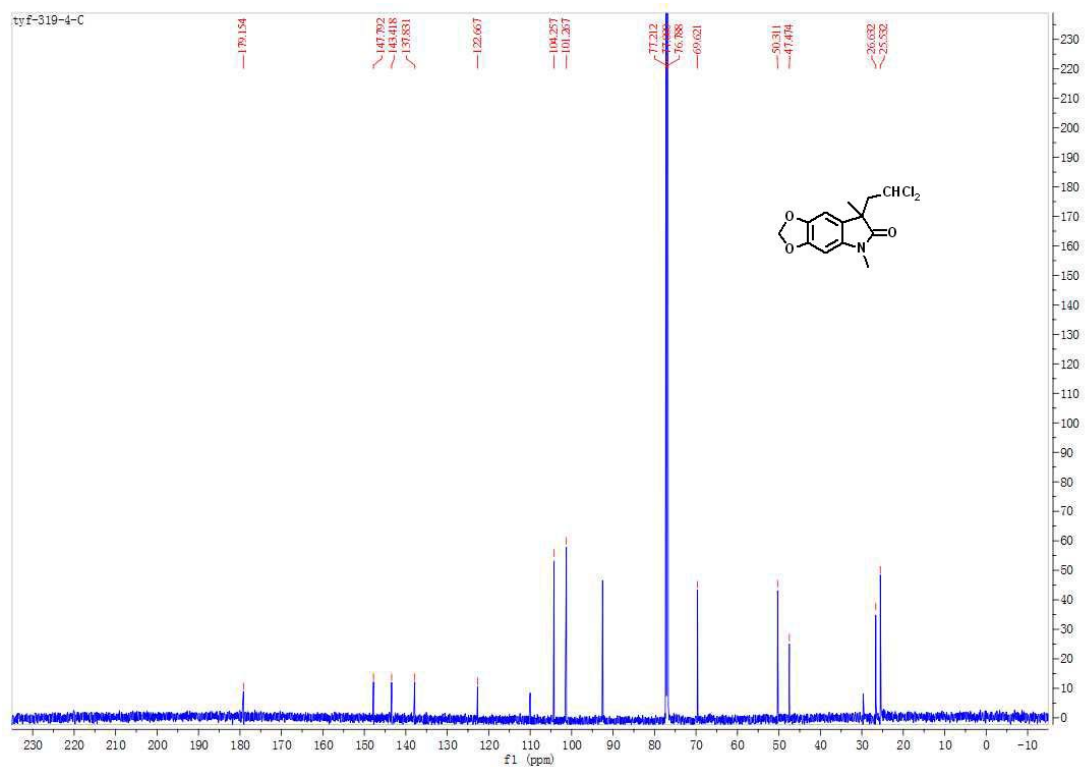
### 13-<sup>13</sup>C NMR



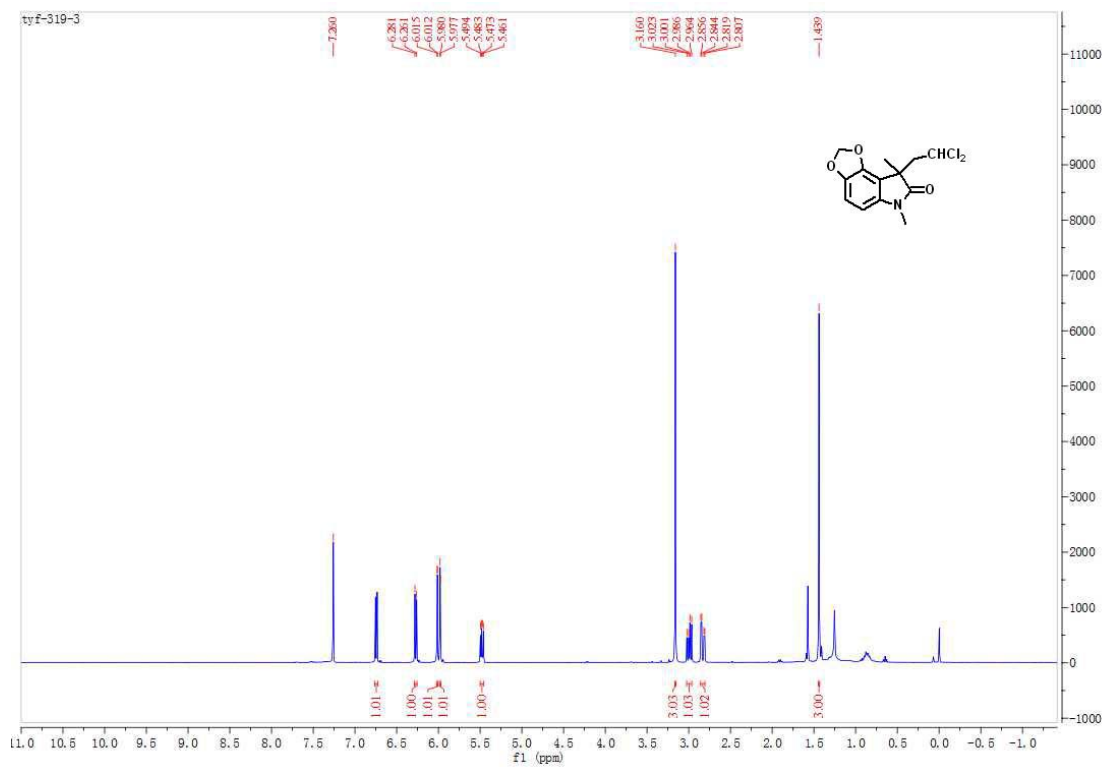
### 14-<sup>1</sup>H NMR



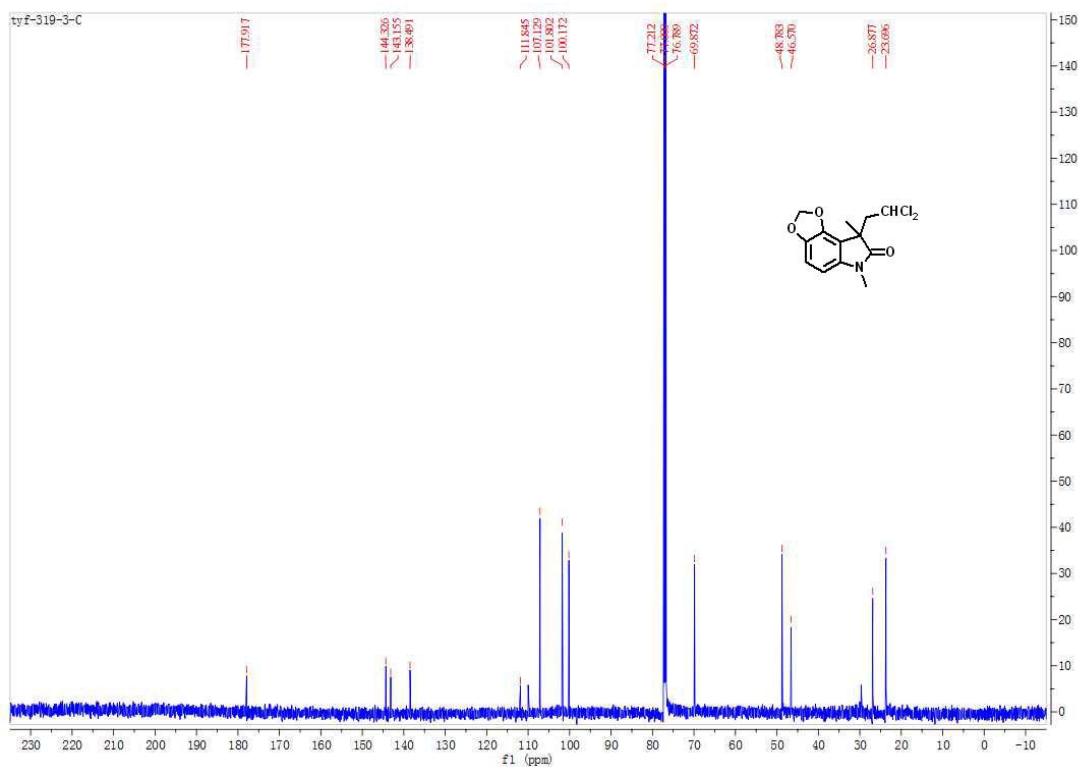
### 14-<sup>13</sup>C NMR



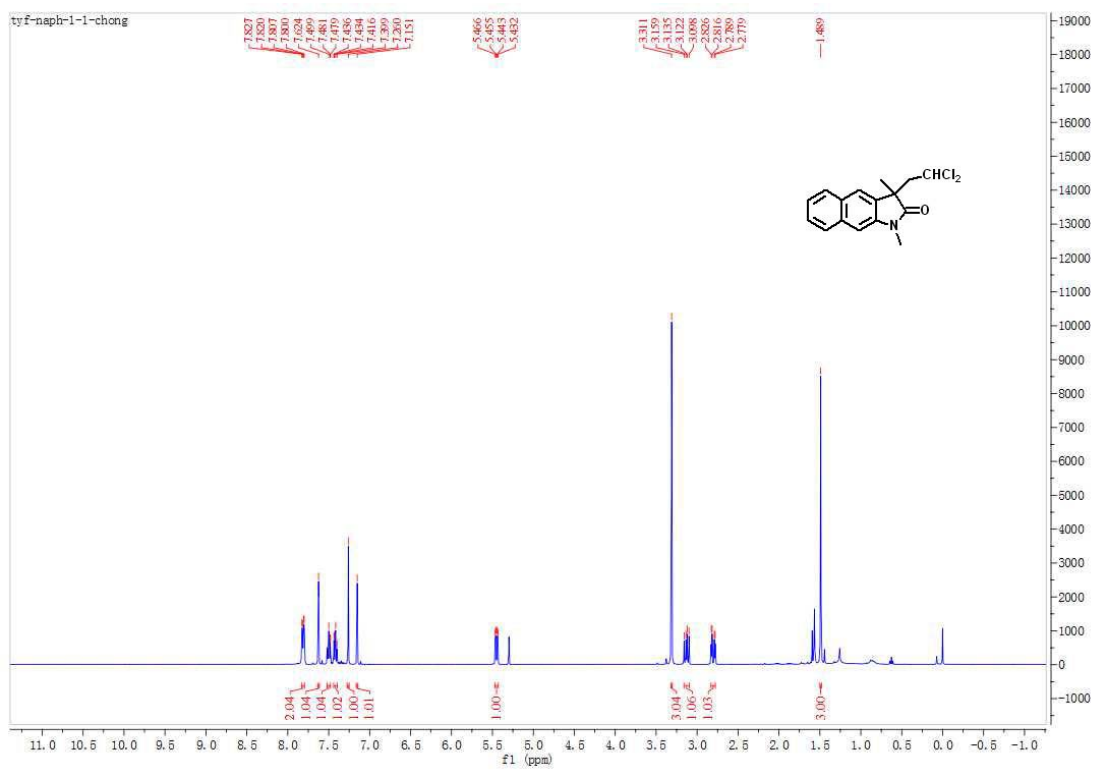
### 14'-<sup>1</sup>H NMR



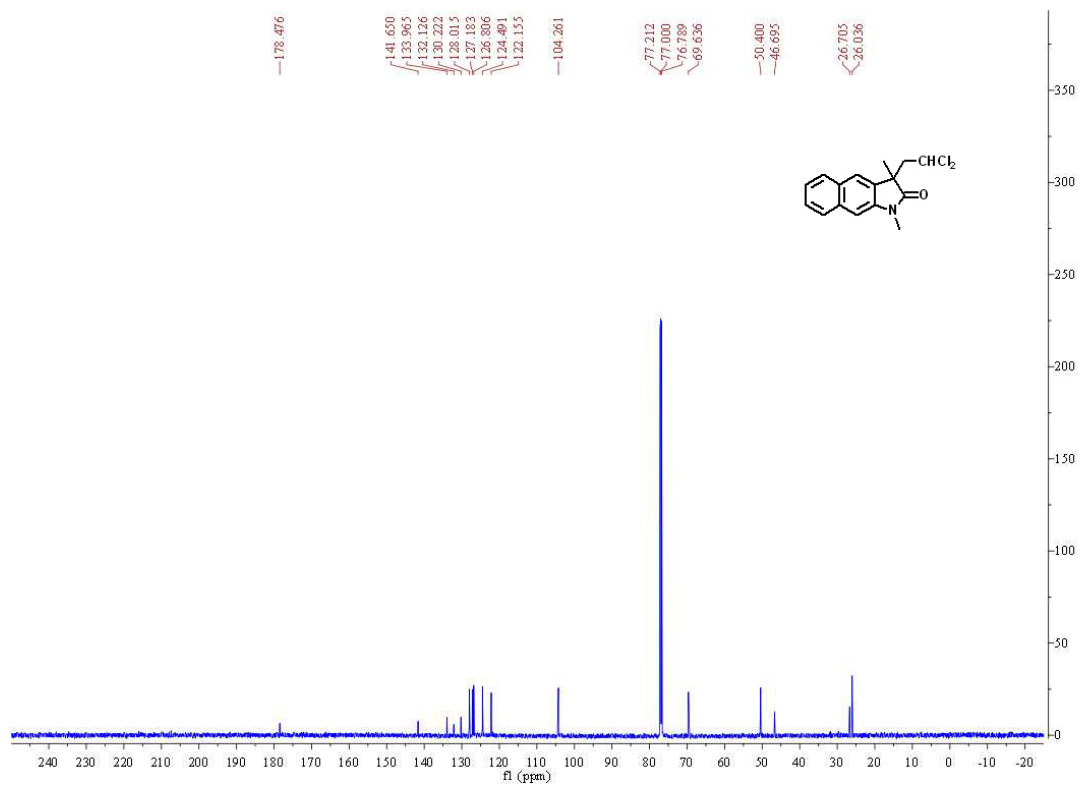
## 14'-<sup>13</sup>C NMR



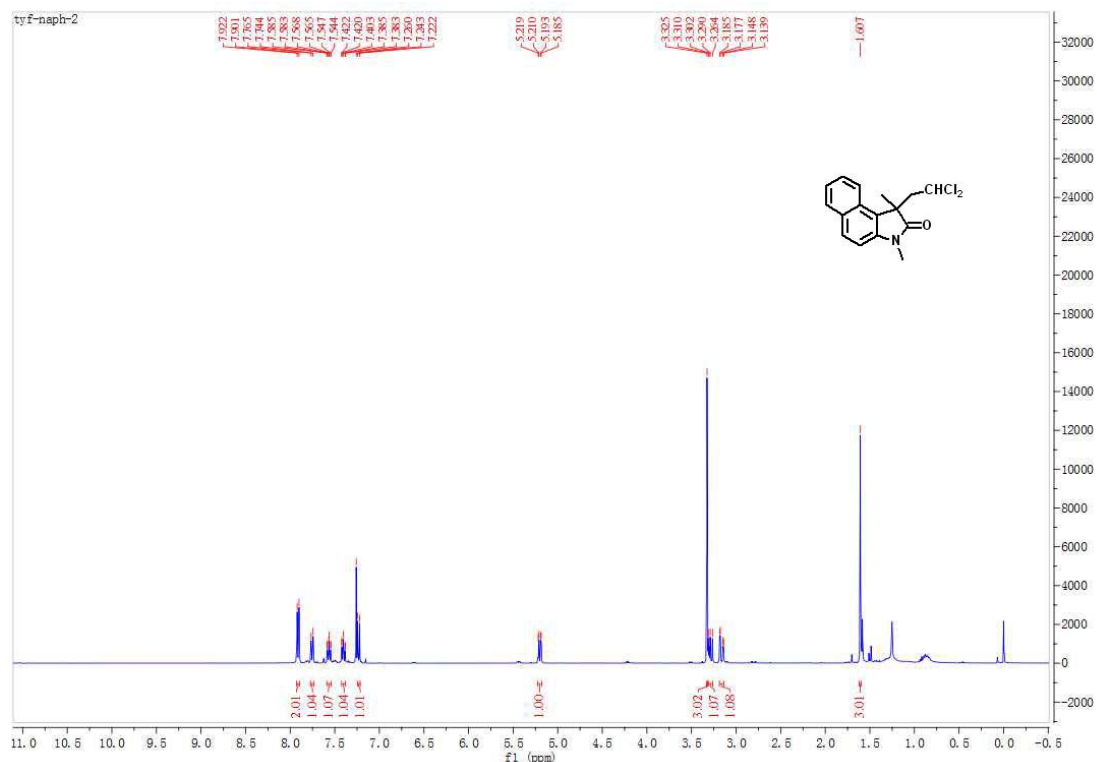
## 15-<sup>1</sup>H NMR



### 15-<sup>13</sup>C NMR

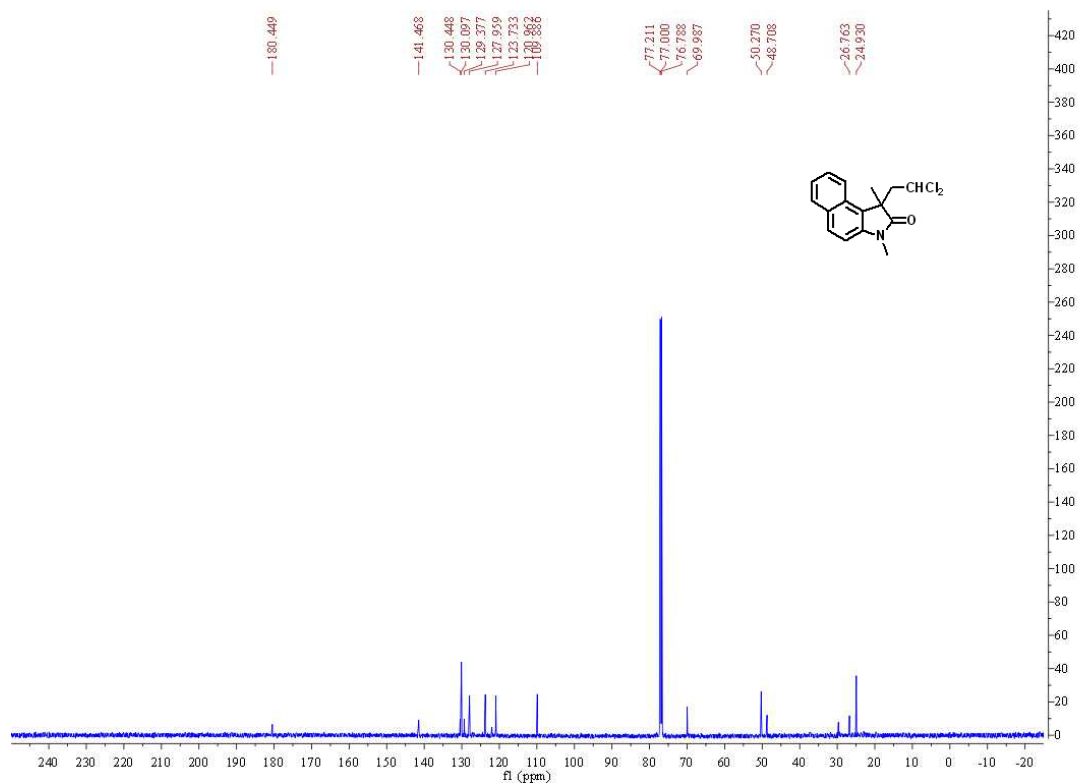


### 15'-<sup>1</sup>H NMR

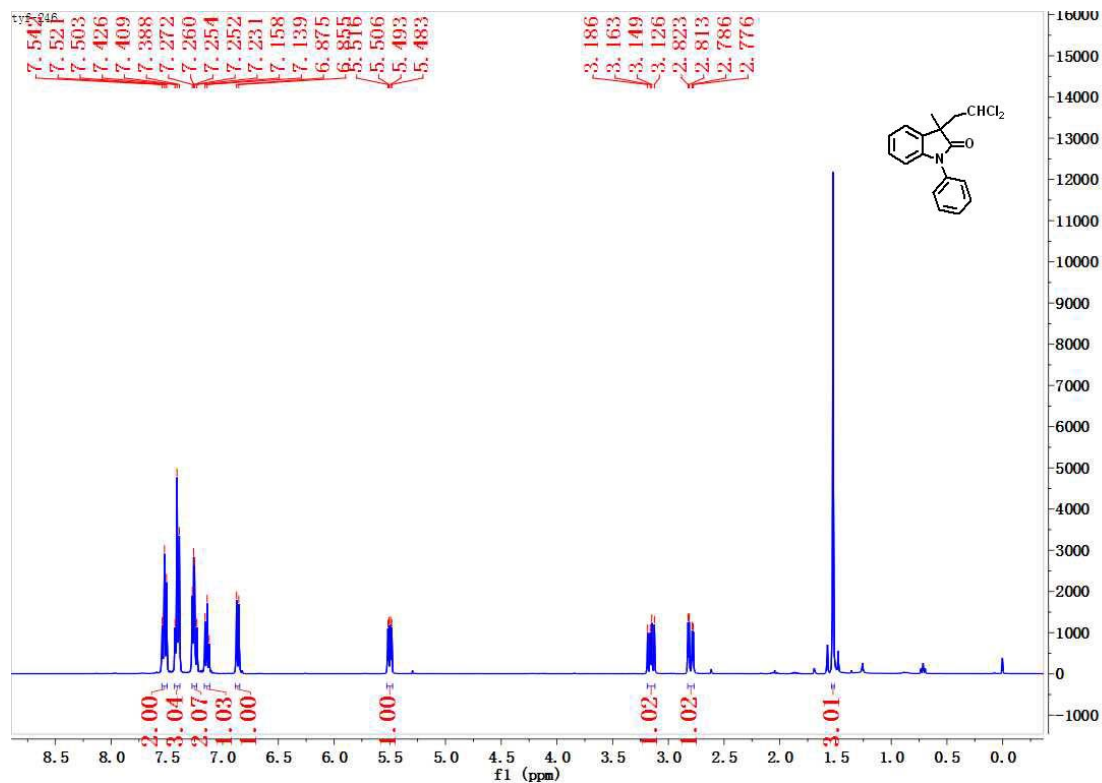




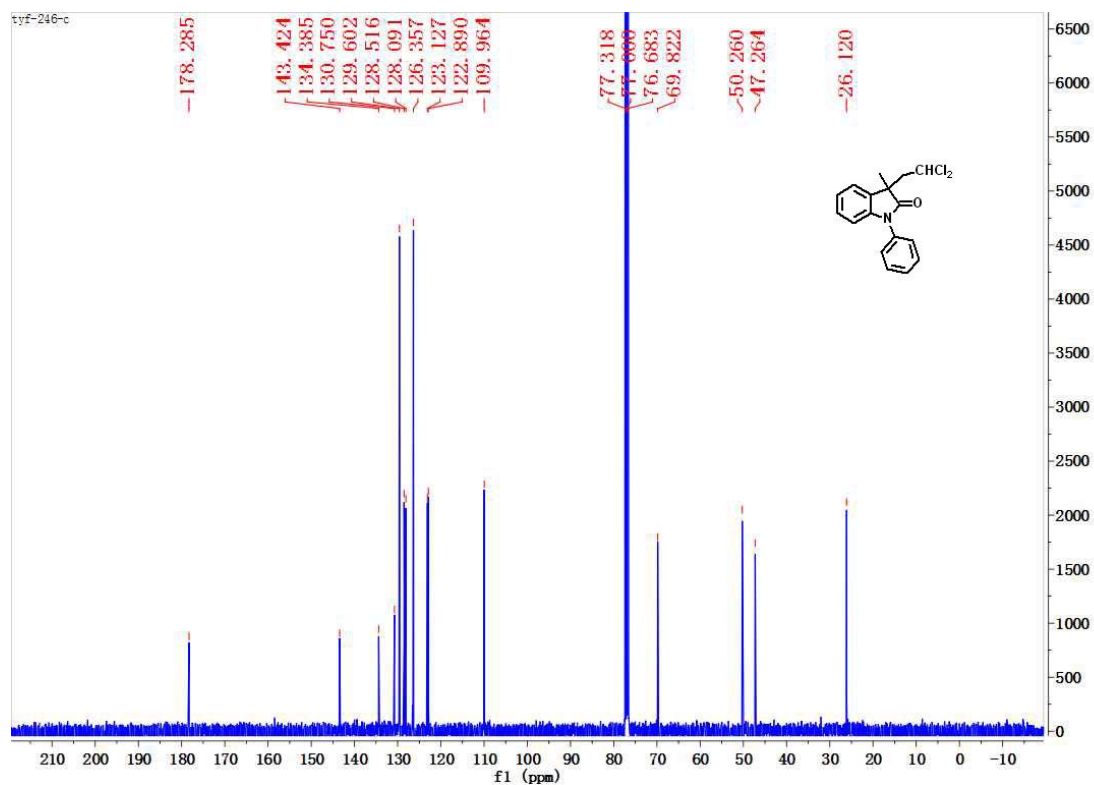
### 15'-<sup>13</sup>C NMR



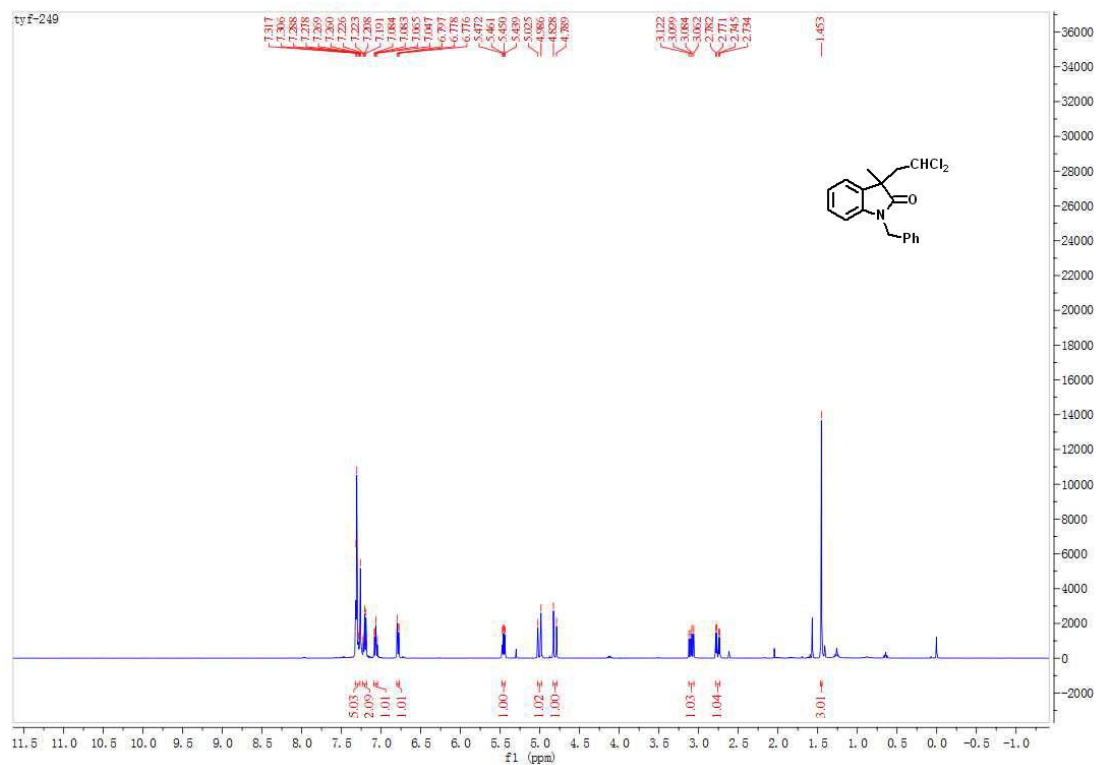
### 17-<sup>1</sup>H NMR



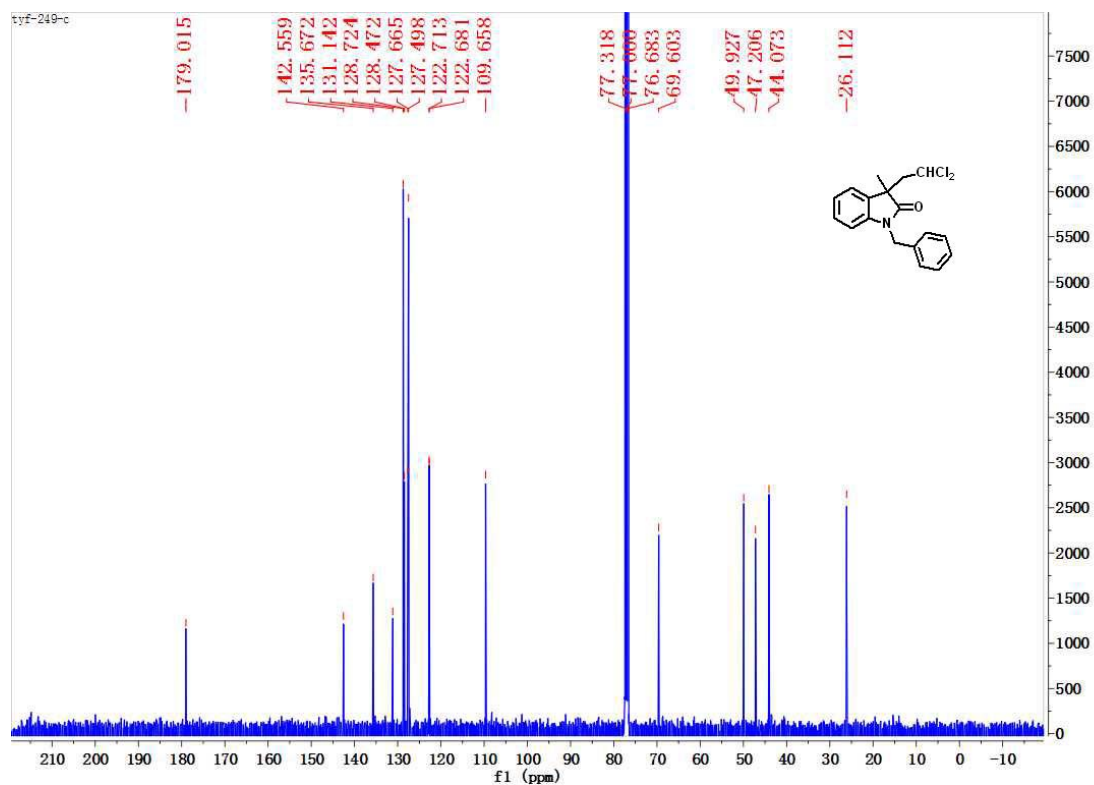
### 17-<sup>13</sup>C NMR



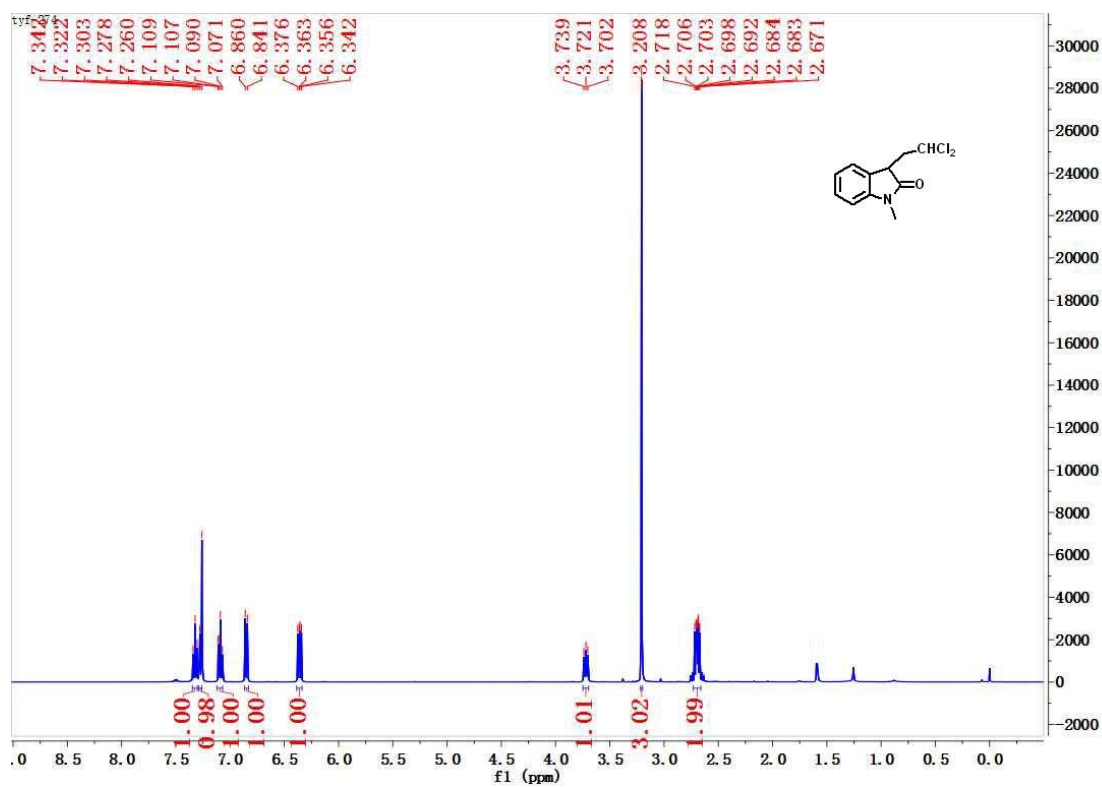
### 18-<sup>1</sup>H NMR



### 18-<sup>13</sup>C NMR

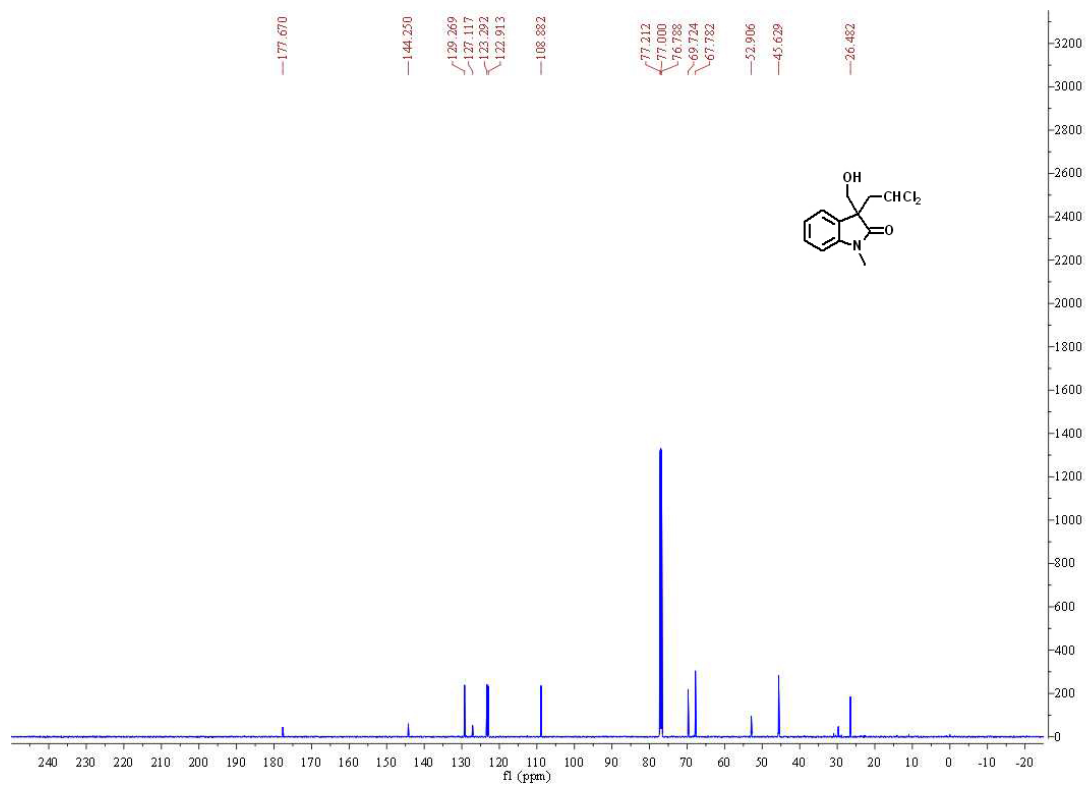


### 19-<sup>1</sup>H NMR

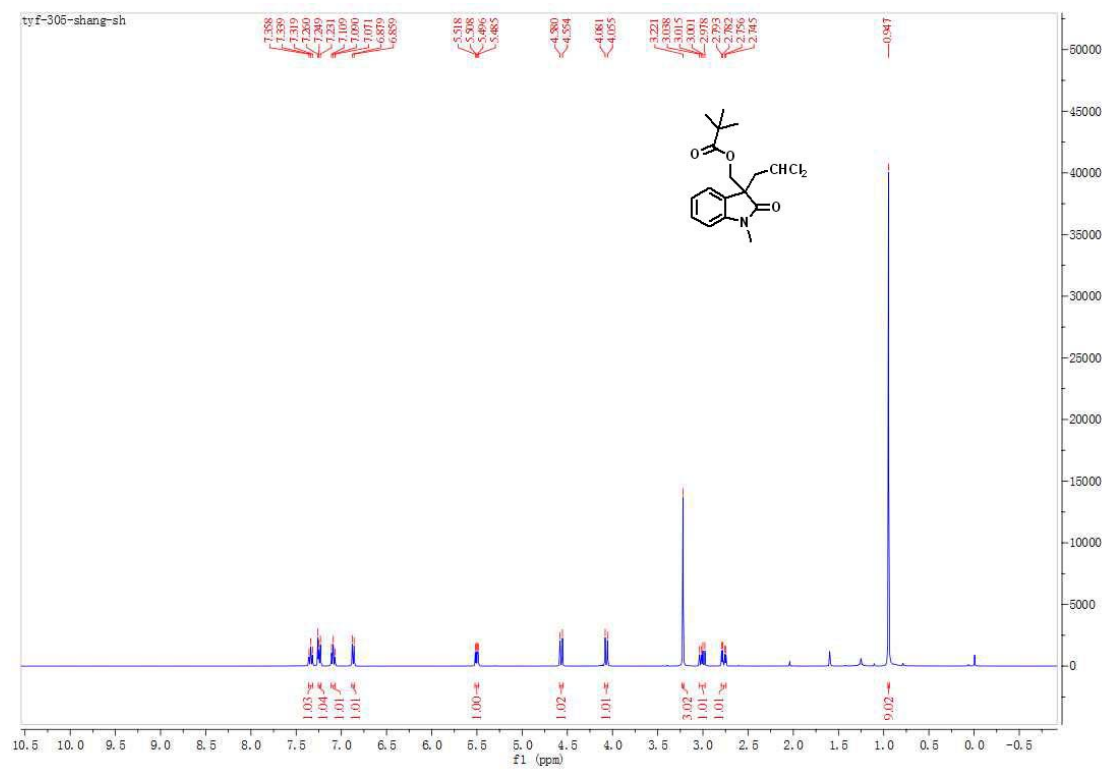




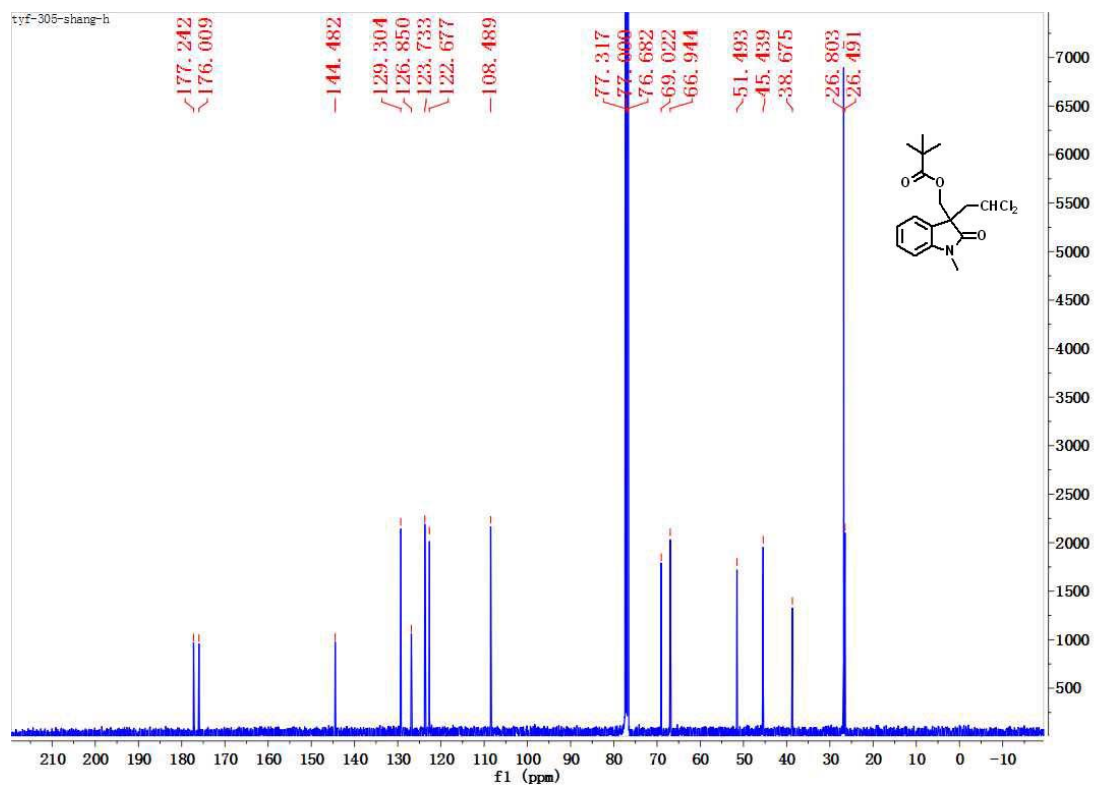
## 20-<sup>13</sup>C NMR



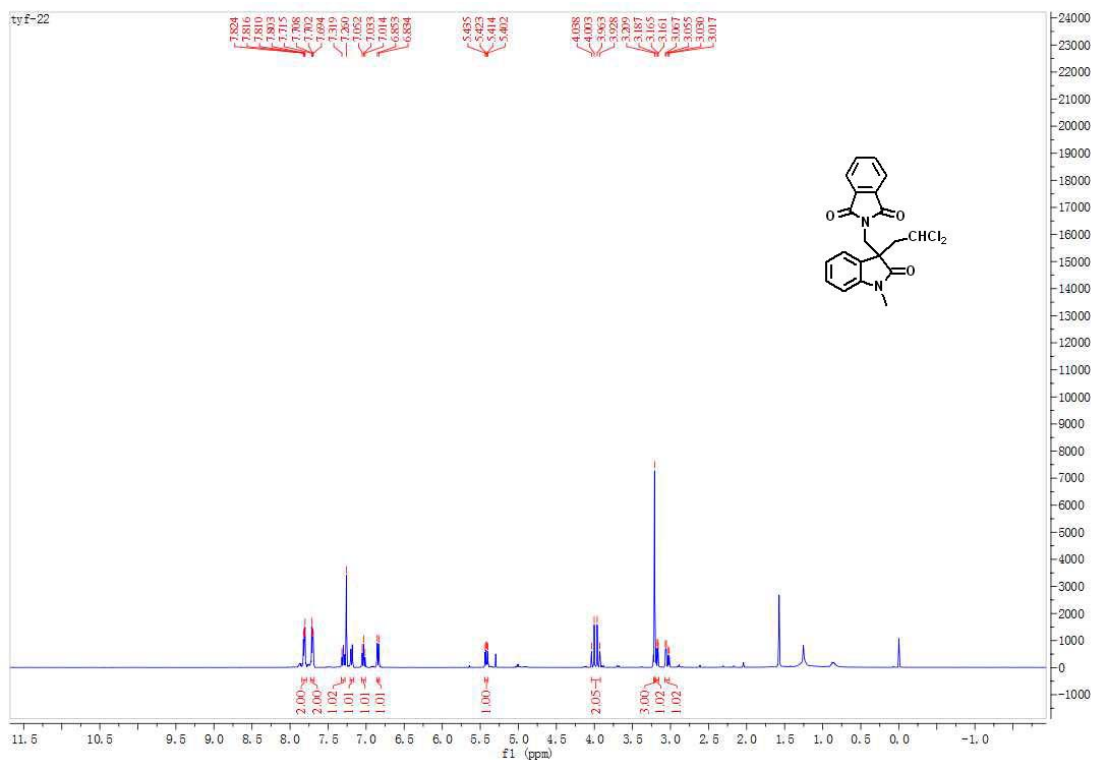
## 21-<sup>1</sup>H NMR



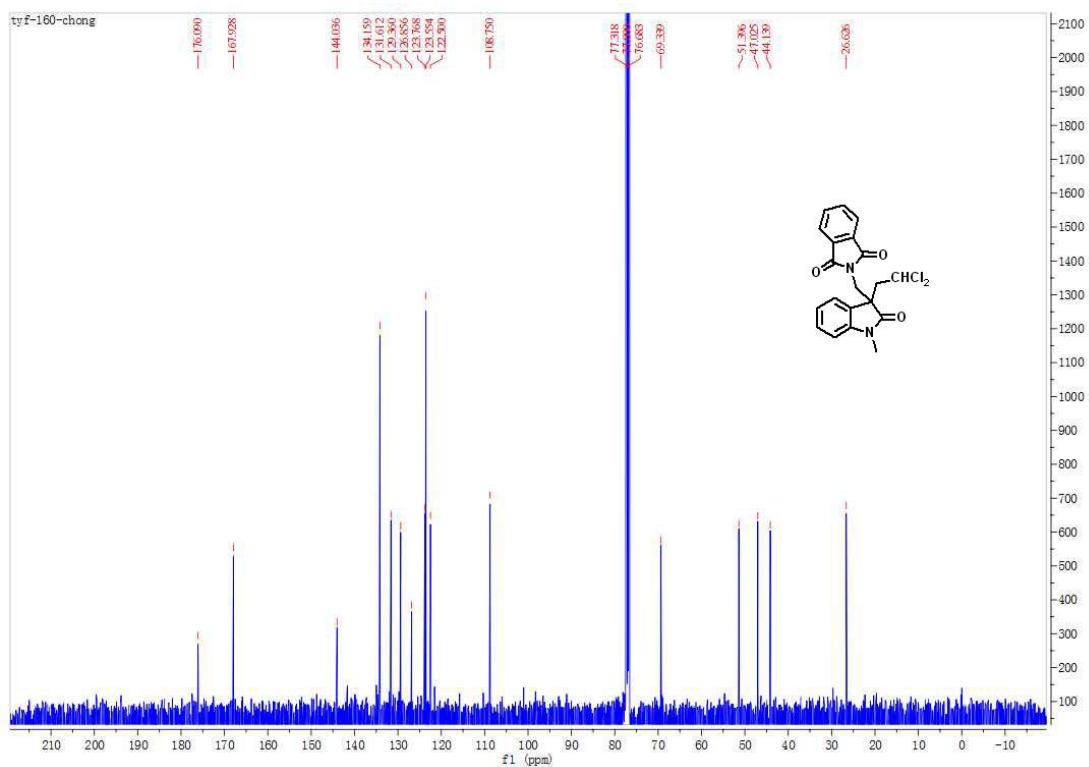
## 21-<sup>13</sup>C NMR



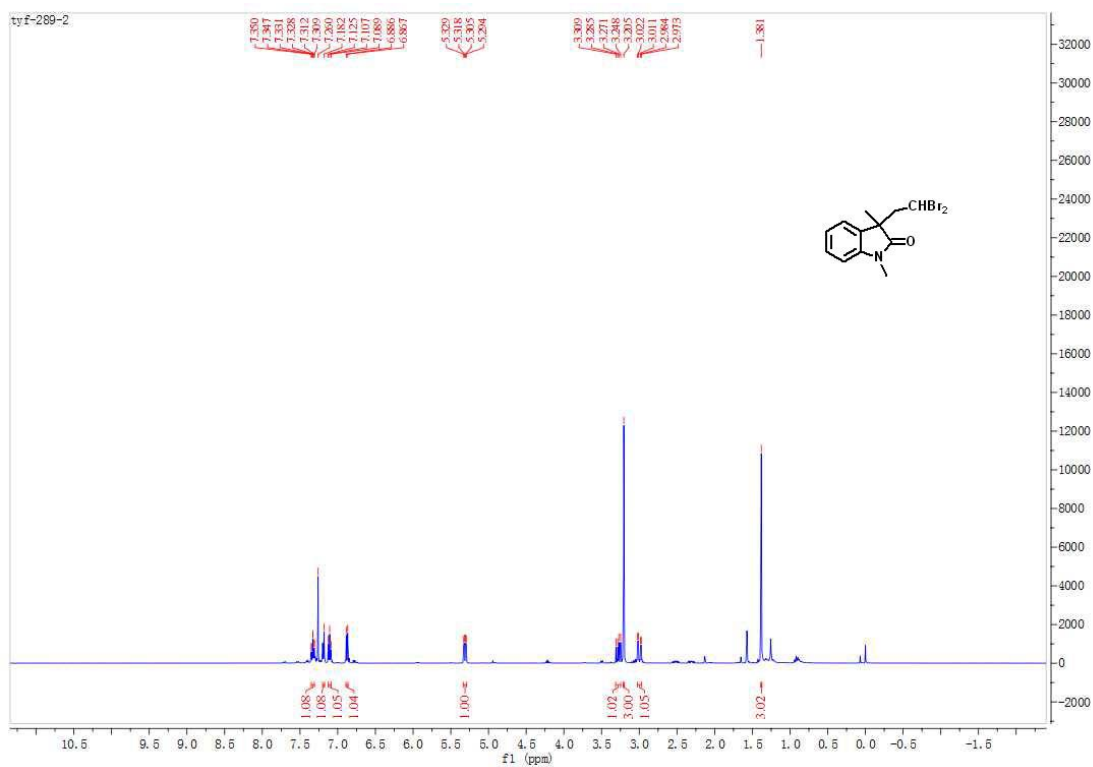
## 22-<sup>1</sup>H NMR



## 22-<sup>13</sup>C NMR



## 23-<sup>1</sup>H NMR



# 23-<sup>13</sup>C NMR

