

## Supporting Information

### Silver-Catalyzed TEMPO Oxidative Homocoupling of Indoles for the Synthesis of 3,3'-Biindolin-2-ones

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#### CONTENTS

1. General Methods and Materials .....	2
2. Initial Studies: Screen of Solvents and Reaction Temperature.....	2
3. General Procedure.....	2
4. Spectroscopic Data of the Products <b>4</b> , <b>12</b> and <b>13</b> .....	3
5. Copies of <sup>1</sup> H, <sup>13</sup> C Spectra .....	10
6. References.....	31

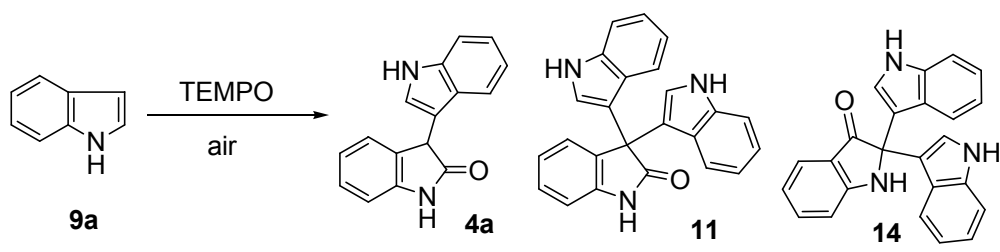
## 1. General Methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

## Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

## 2. Initial Studies: Screen of Solvents and Reaction Temperature <sup>a</sup>



entry	solvent	temperature (°C)	yield (%) (4a/11/14) <sup>b</sup>
1	trimethylamine	65	45/0/0
2	diisopropylamine	65	23/0/0
3	Aniline	65	17/0/0
4	<i>N,N</i> -dimethyl aniline	65	36/0/0
5	<i>N,N</i> -diethyl ethylenediamine	65	30/0/0
6	tri- <i>n</i> -propylamine	65	23/0/0
7	tri- <i>n</i> -butylamine	65	15/0/0
8	pyridine	65	73/0/0
9	THF	65	0/0/37
10	$\text{CH}_3\text{CN}$	65	0/0/30
11	benzene	65	0/0/26
12	pyridine	45	12/0/0
13	pyridine	55	57/0/0
14	pyridine	65	73/0/0
15	pyridine	75	61/0/0

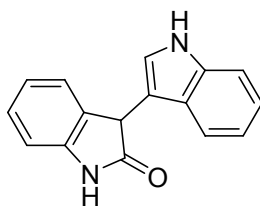
<sup>a</sup> Condition: 9a (0.5 mmol),  $\text{AgNO}_3$  (0.1 mmol), TEMPO (0.35 mmol), benzoic acid (0.1 mmol), solvent (1 mL), 65 °C, 48 h, under open air. <sup>b</sup> Isolated yields.

## 3. General Procedure for the Preparation of 4 or 13.

To a solution of indole (0.5 mmol),  $\text{AgNO}_3$  (0.1 mmol), and TEMPO (0.35 mmol) in pyridine (1 mL) was added benzoic acid (0.1 mmol) under an air atmosphere and the mixture was stirred at 65 °C for 48 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:2) to yield the corresponding product 4 or 13.

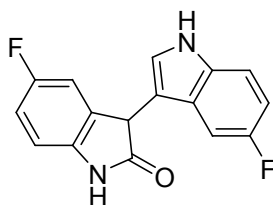
#### 4. Spectroscopic Data of the Products 4, 12 and 13.

##### 3,3'-Biindolin-2-one (**4a**)



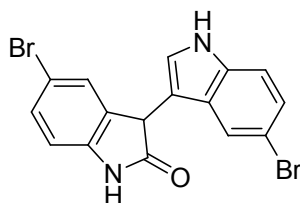
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3283 (br s), 1715, 1620, 1469, 1335, 749  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  10.94 (s, 1H, NH), 10.30 (s, 1H, NH), 7.29 (t,  $J = 7.6$  Hz, 2H, Ar-H), 7.21 (t,  $J = 7.6$  Hz, 1H, Ar-H), 7.19 (dd,  $J = 7.6, 2.5$  Hz, 1H, Ar-H), 7.02 (d,  $J = 2.5$  Hz, 1H, Ar-H), 6.98 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.91 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.86 (d,  $J = 7.6$  Hz, 1H, Ar-H), 6.82 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.31 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.9, 142.1, 137.2, 133.9, 129.5, 125.4, 125.2, 123.9, 122.1, 121.5, 120.8, 118.9, 115.9, 111.9, 110.0, 75.3. MS (ESI): 249 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ : C, 77.40; H, 4.87; N, 11.28. Found C, 77.57; H, 4.53; N, 10.96. These assignments matched with those previously published.<sup>1</sup>

##### 5,5'-Difluoro-3,3'-biindolin-2-one (**4b**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3412, 1719, 1484, 1182, 1138  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  11.15 (s, 1H, NH), 10.37 (s, 1H, NH), 7.33 (dt,  $J = 8.8, 4.7$  Hz, 1H, Ar-H), 7.18 (dt,  $J = 10.4, 2.5$  Hz, 1H, Ar-H), 7.11 (dt,  $J = 10.4, 2.5$  Hz, 1H, Ar-H), 7.09 (d,  $J = 8.8$  Hz, 1H, Ar-H), 7.05 (d,  $J = 2.5$  Hz, 1H, Ar-H), 6.90 (dt,  $J = 8.8, 2.5$  Hz, 2H, Ar-H), 6.53 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.7, 158.5 (d,  $J = 237.3$  Hz), 157.0 (d,  $J = 230.8$  Hz), 138.2, 135.1 (d,  $J = 7.3$  Hz), 134.0, 126.1, 115.9 (d,  $J = 23.2$  Hz), 115.4 (d,  $J = 4.7$  Hz), 113.0, 112.9 (d,  $J = 2.7$  Hz), 112.7, 111.0 (d,  $J = 7.8$  Hz), 109.9 (d,  $J = 26.1$  Hz), 105.7 (d,  $J = 23.9$  Hz), 60.2. MS (ESI): 285 ( $\text{M}+\text{H}^+$ , 100), 307 ( $\text{M}+\text{Na}^+$ , 15). Anal calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_2\text{N}_2\text{O}$ : C, 67.60; H, 3.55; N, 9.85. Found C, 67.91; H, 3.78; N, 9.54.

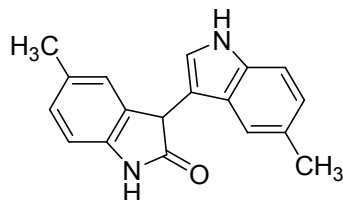
##### 5,5'-Dibromo-3,3'-biindolin-2-one (**4c**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3340 (br s), 1707, 1625, 1431, 1310, 1152  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  11.21 (d,  $J = 2.0$  Hz, 1H, NH), 10.47 (s, 1H, NH), 7.71 (s, 1H, Ar-H), 7.43 (dd,  $J = 8.2, 2.0$  Hz, 1H, Ar-H), 7.33 (d,  $J = 2.0$  Hz, 1H, Ar-H), 7.30 (d,  $J = 8.6$  Hz, 1H, Ar-H), 7.14 (dd,  $J = 8.6, 2.0$  Hz, 1H, Ar-H), 6.97 (d,  $J = 2.6$  Hz, 1H, Ar-H), 6.84 (d,  $J = 8.2$  Hz, 1H, Ar-H), 6.55 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.1, 141.4, 136.0, 135.7, 132.4, 127.9,

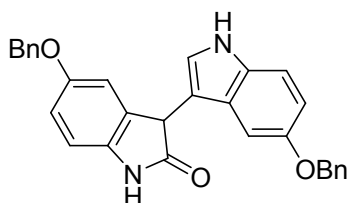
127.2, 125.6, 124.2, 123.5, 114.9, 114.1, 113.9, 112.3, 111.8, 75.2. MS (ESI): 405 (M+H<sup>+</sup>, 50), 407 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>16</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O: C, 47.32; H, 2.48; N, 6.90. Found C, 47.14; H, 2.61; N, 6.52.

5,5'-Dimethyl-3,3'-biindolin-2-one (**4d**)



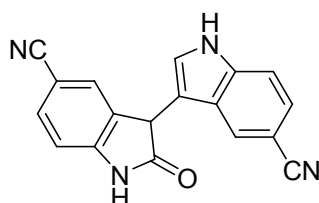
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3423 (br s), 1699, 1625, 1137 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.78 (s, 1H, NH), 10.18 (s, 1H, NH), 7.17 (d, *J* = 8.3 Hz, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 7.00 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.82 (d, *J* = 1.0 Hz, 1H, Ar-H), 6.81 (dd, *J* = 7.7, 1.0 Hz, 1H, Ar-H), 6.74 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.20 (s, 1H), 2.23 (s, 3H, CH<sub>3</sub>), 2.17 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  183.7, 144.4, 140.4, 138.8, 135.6, 134.3, 131.8, 130.5, 130.4, 128.7, 127.8, 125.2, 120.3, 116.3, 114.5, 80.2, 26.6, 25.9. MS (ESI): 277 (M+H<sup>+</sup>, 100), 299 (M+Na<sup>+</sup>, 25). Anal calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O: C, 78.24; H, 5.84; N, 10.14. Found C, 77.93; H, 6.05; N, 9.92.

5,5'-Bis(benzyloxy)-3,3'-biindolin-2-one (**4e**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3427 (br s), 1709, 1612, 1235, 1120 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.85 (d, *J* = 2.4 Hz, 1H, NH), 10.17 (s, 1H, NH), 7.42-7.28 (m, 10H, Ar-H), 7.24 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.02 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.99 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.95-6.80 (m, 2H, Ar-H), 6.83 (dd, *J* = 7.4, 1.6 Hz, 1H, Ar-H), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H, Ar-H), 6.34 (s, 1H), 5.00 (s, 2H, CH<sub>2</sub>), 4.94 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  178.8, 154.4, 152.2, 138.0, 137.7, 135.6, 135.0, 132.6, 128.8 (4C), 128.2, 128.1, 128.0, 125.8, 124.8, 115.5, 115.4, 113.1, 112.4, 112.0, 110.5, 104.8, 75.7, 70.2. MS (ESI): 461 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 78.24; H, 5.25; N, 6.08. Found C, 78.02; H, 5.57; N, 5.94.

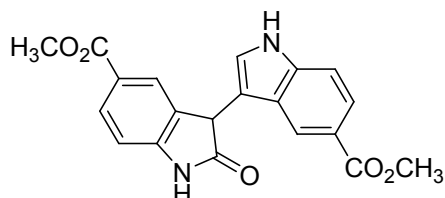
2-Oxo-3,3'-biindoline-5,5'-dicyanitrile (**4f**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3321 (br s), 2228, 1727, 1619, 1484, 1120 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.65 (d, *J* = 1.6 Hz, 1H, NH), 10.89 (s, 1H, NH), 8.22 (s, 1H, Ar-H), 7.79 (dd, *J* = 8.1, 1.8 Hz, 1H, Ar-H), 7.75 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.53 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H, Ar-H), 7.09 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.06 (d, *J* = 8.1 Hz, 1H, Ar-

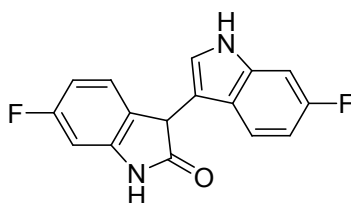
H), 6.78 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  178.4, 146.5, 139.2, 135.3, 129.7, 129.0, 127.5, 126.9, 125.4, 124.5, 121.2, 119.8, 115.6, 113.6, 111.2, 104.5, 101.3, 74.6. MS (ESI): 299 (M+H $^+$ , 100), 321 (M+Na $^+$ , 10). Anal calcd for C $_{18}$ H $_{10}$ N $_4$ O: C, 72.23; H, 3.70; N, 18.72. Found C, 71.89; H, 3.85; N, 18.46.

Dimethyl 2-oxo-3,3'-biindoline-5,5'-dicarboxylate (**4g**)



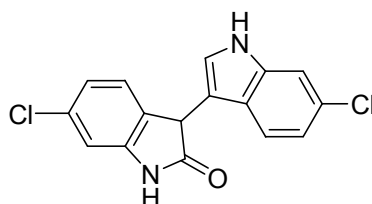
White solid, mp: 144-146 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\text{max}}$ : 3332 (br s), 1705, 1620, 1435, 1315, 1256  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.40 (d,  $J$  = 2.3 Hz, 1H, NH), 10.79 (s, 1H, NH), 8.36 (d,  $J$  = 1.8 Hz, 1H, Ar-H), 7.92 (dd,  $J$  = 8.2, 1.8 Hz, 1H, Ar-H), 7.81 (d,  $J$  = 1.8 Hz, 1H, Ar-H), 7.67 (dd,  $J$  = 8.6, 1.8 Hz, 1H, Ar-H), 7.40 (d,  $J$  = 8.6 Hz, 1H, Ar-H), 7.03 (d,  $J$  = 2.3 Hz, 1H, Ar-H), 7.00 (d,  $J$  = 8.2 Hz, 1H, Ar-H), 6.64 (s, 1H), 3.78 (s, 3H, CH $_3$ ), 3.75 (s, 3H, CH $_3$ ).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  178.8, 167.7, 166.5, 146.8, 140.0, 133.7, 132.1, 126.0, 125.8, 125.1, 124.3, 123.6, 122.7, 120.6, 116.7, 112.1, 110.2, 74.9, 52.3, 52.1. MS (ESI): 365 (M+H $^+$ , 100), 387 (M+Na $^+$ , 40). Anal calcd for C $_{20}$ H $_{16}$ N $_2$ O $_5$ : C, 65.93; H, 4.43; N, 7.69. Found C, 66.12; H, 4.29; N, 7.92.

6,6'-Difluoro-3,3'-biindolin-2-one (**4i**)



Amorphous solid. IR (KBr)  $\nu_{\text{max}}$ : 3246, 1726, 1623, 1141  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.08 (s, 1H, NH), 10.49 (s, 1H, NH), 7.45 (dt,  $J$  = 8.8, 5.8 Hz, 1H, Ar-H), 7.25 (dt,  $J$  = 8.0, 5.8 Hz, 1H, Ar-H), 7.10 (dd,  $J$  = 10.0, 2.2 Hz, 1H, Ar-H), 6.97 (d,  $J$  = 2.2 Hz, 1H, Ar-H), 6.77 (dt,  $J$  = 10.0, 2.2 Hz, 2H, Ar-H), 6.70 (dd,  $J$  = 10.0, 2.2 Hz, 1H, Ar-H), 6.44 (s, 1H, Ar-H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  178.9, 162.3 (d,  $J$  = 401.8 Hz), 160.0 (d,  $J$  = 393.7 Hz), 143.8 (d,  $J$  = 12.4 Hz), 137.2 (d,  $J$  = 12.5 Hz), 129.5 (d,  $J$  = 2.7 Hz), 126.7 (d,  $J$  = 10.0 Hz), 124.7 (d,  $J$  = 3.0 Hz), 122.3, 122.1 (d,  $J$  = 10.1 Hz), 115.8, 108.2 (d,  $J$  = 22.1 Hz), 107.6 (d,  $J$  = 24.2 Hz), 98.3 (d,  $J$  = 26.9 Hz), 97.9 (d,  $J$  = 25.3 Hz), 74.7. MS (ESI): 285 (M+H $^+$ , 100), 307 (M+Na $^+$ , 12). Anal calcd for C $_{16}$ H $_{10}$ F $_2$ N $_2$ O: C, 67.60; H, 3.55; N, 9.85. Found C, 67.27; H, 3.93; N, 9.49.

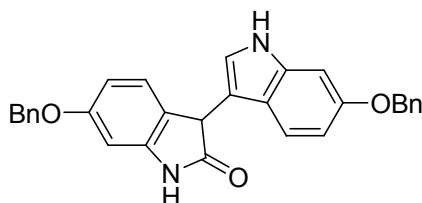
6,6'-Dichloro-3,3'-biindolin-2-one (**4j**)



Amorphous solid. IR (KBr)  $\nu_{\text{max}}$ : 3321 (br s), 1708, 1620, 1435, 1152  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,

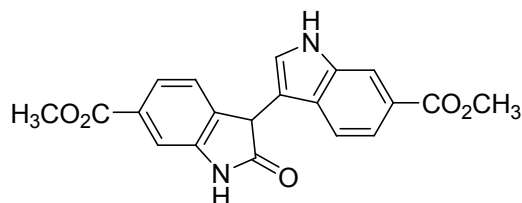
DMSO-*d*<sub>6</sub>):  $\delta$  11.16 (s, 1H, NH), 10.50 (s, 1H, NH), 7.51-7.47 (m, 2H, Ar-H), 7.38 (d,  $J$  = 1.8 Hz, 1H, Ar-H), 7.25 (d,  $J$  = 7.9 Hz, 1H, Ar-H), 7.03 (d,  $J$  = 1.9 Hz, 1H, Ar-H), 7.02 (t,  $J$  = 1.9 Hz, 1H, Ar-H), 6.95 (dd,  $J$  = 8.6, 1.9 Hz, 1H, Ar-H), 6.91 (d,  $J$  = 1.9 Hz, 1H, Ar-H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  178.5, 143.6, 137.7, 132.4, 129.7, 129.0, 126.7, 125.2, 124.2, 122.4, 122.0, 119.5, 115.6, 111.6, 110.2, 74.8. MS (ESI): 317 (M+H<sup>+</sup>, 100), 319 (M+H<sup>+</sup>, 64). Anal calcd for C<sub>16</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O: C, 60.59; H, 3.18; N, 8.83. Found C, 60.44; H, 3.37; N, 8.65.

6,6'-Bis(benzyloxy)-3,3'-biindolin-2-one (**4k**)



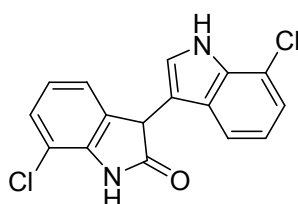
Amorphous solid. IR (KBr)  $\nu_{\text{max}}$ : 3427 (br s), 1710, 1615, 1231, 1123 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.76 (s, 1H, NH), 10.27 (s, 1H, NH), 7.47-7.31 (m, 10H, Ar-H), 7.27 (d,  $J$  = 8.8 Hz, 1H, Ar-H), 7.13 (d,  $J$  = 8.2 Hz, 1H, Ar-H), 6.89-6.90 (m, 2H, Ar-H), 6.64 (dd,  $J$  = 8.8, 2.2 Hz, 1H, Ar-H), 6.59 (dd,  $J$  = 8.2, 2.2 Hz, 1H, Ar-H), 6.53 (d,  $J$  = 2.2 Hz, 1H, Ar-H), 6.20 (s, 1H), 5.12 (s, 2H, OCH<sub>2</sub>), 5.09 (s, 2H, OCH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  179.3, 159.7, 154.8, 143.4, 138.1, 137.9, 137.5, 128.9, 128.8, 128.3, 128.0, 127.9, 126.2, 126.0, 125.4, 122.8, 121.6, 120.1, 116.2, 109.8, 107.8, 97.8, 96.4, 75.0, 69.9, 69.8. MS (ESI): 461 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 78.24; H, 5.25; N, 6.08. Found C, 78.07; H, 5.41; N, 5.72.

Dimethyl 2-oxo-3,3'-biindoline-6,6'-dicarboxylate (**4l**)



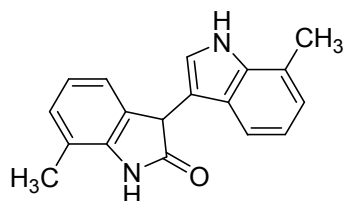
White solid, mp: 240-242 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\text{max}}$ : 3329 (br s), 1703, 1617, 1436, 1312, 1253 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.43 (d,  $J$  = 2.3 Hz, 1H, NH), 10.57 (s, 1H, NH), 8.00 (s, 1H, Ar-H), 7.60 (dd,  $J$  = 7.7, 1.2 Hz, 1H, Ar-H), 7.56 (dd,  $J$  = 8.5, 1.0 Hz, 1H, Ar-H), 7.51 (dd,  $J$  = 8.5, 1.2 Hz, 1H, Ar-H), 7.41 (d,  $J$  = 1.0 Hz, 1H, Ar-H), 7.38 (d,  $J$  = 7.7 Hz, 1H, Ar-H), 7.25 (d,  $J$  = 2.3 Hz, 1H, Ar-H), 6.64 (s, 1H), 3.82 (s, 3H, CH<sub>3</sub>), 3.79 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  178.4, 167.6, 166.4, 142.5, 138.6, 136.6, 130.9, 128.9, 127.9, 125.4, 123.9, 122.8, 120.8, 119.7, 115.7, 114.1, 110.3, 75.0, 52.7, 52.2. MS (ESI): 365 (M+H<sup>+</sup>, 100), 387 (M+Na<sup>+</sup>, 30). Anal calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C, 65.93; H, 4.43; N, 7.69. Found C, 65.69; H, 4.71; N, 7.60.

7,7'-Dichloro-3,3'-biindolin-2-one (**4m**)



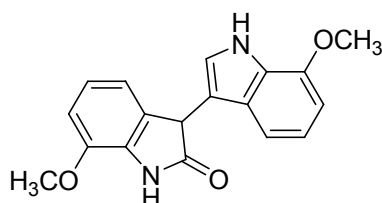
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3327 (br s), 1705, 1623, 1430, 1153  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  11.44 (d,  $J = 2.3$  Hz, 1H, NH), 10.84 (s, 1H, NH), 7.40 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.35 (dd,  $J = 7.8, 1.0$  Hz, 1H, Ar-H), 7.22 (d,  $J = 7.6$  Hz, 1H, Ar-H), 7.15 (dd,  $J = 7.6, 1.0$  Hz, 1H, Ar-H), 7.07 (d,  $J = 2.3$  Hz, 1H, Ar-H), 7.01 (dd,  $J = 7.6, 1.0$  Hz, 1H, Ar-H), 6.95 (t,  $J = 7.8$  Hz, 1H, Ar-H), 6.64 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.5, 139.8, 133.3, 129.7, 129.6, 129.0, 125.2, 123.8, 123.7, 121.2, 120.2, 119.9, 116.7, 116.4, 114.5, 75.7. MS (ESI): 317 ( $\text{M}+\text{H}^+$ , 100), 319 ( $\text{M}+\text{H}^+$ , 64). Anal calcd for  $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}$ : C, 60.59; H, 3.18; N, 8.83. Found C, 60.83; H, 3.35; N, 8.47.

7,7'-Dimethyl-3,3'-biindolin-2-one (**4n**)



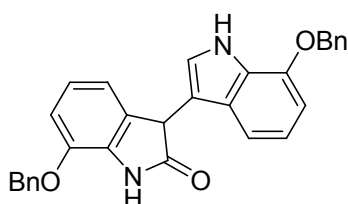
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3420 (br s), 1703, 1627, 1131  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  10.99 (s, 1H, NH), 10.38 (s, 1H, NH), 7.14 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.03-6.99 (m, 3H, Ar-H), 6.85 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.80 (d,  $J = 7.6$  Hz, 1H, Ar-H), 6.75 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.24 (s, 1H), 2.40 (s, 3H,  $\text{CH}_3$ ), 2.25 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  179.4, 140.6, 136.7, 133.6, 130.6, 125.0, 123.6, 122.5, 122.0, 121.9, 120.9, 119.2, 119.1, 118.4, 116.5, 75.6, 17.2, 16.8. MS (ESI): 277 ( $\text{M}+\text{H}^+$ , 100), 299 ( $\text{M}+\text{Na}^+$ , 20). Anal calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ : C, 78.24; H, 5.84; N, 10.14. Found C, 78.05; H, 6.11; N, 10.07.

7,7'-Dimethoxy-3,3'-biindolin-2-one (**4o**)



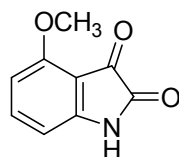
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3422 (br s), 1704, 1617, 1230, 1125  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  11.07 (d,  $J = 2.0$  Hz, 1H, NH), 10.36 (s, 1H, NH), 6.98 (dd,  $J = 7.3, 1.0$  Hz, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.92 (t,  $J = 8.0$  Hz, 1H, Ar-H), 6.90 (d,  $J = 8.0$  Hz, 1H, Ar-H), 6.84 (dd,  $J = 7.3, 1.0$  Hz, 1H, Ar-H), 6.78 (t,  $J = 8.0$  Hz, 1H, Ar-H), 6.59 (d,  $J = 7.3$  Hz, 1H, Ar-H), 6.32 (s, 1H), 3.87 (s, 3H,  $\text{OCH}_3$ ), 3.85 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  178.9, 146.5, 144.0, 134.6, 130.5, 127.3, 126.8, 123.4, 122.7, 119.4, 117.5, 116.5, 113.5, 112.5, 101.9, 75.6, 56.2, 55.5. MS (ESI): 309 ( $\text{M}+\text{H}^+$ , 100), 331 ( $\text{M}+\text{Na}^+$ , 30). Anal calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$ : C, 70.12; H, 5.23; N, 9.09. Found C, 69.78; H, 5.35; N, 8.92.

7,7'-Bis(benzyloxy)-3,3'-biindolin-2-one (**4p**)



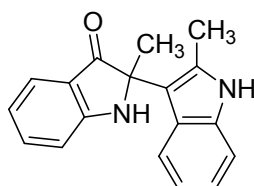
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3423 (br s), 1706, 1614, 1230, 1126  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.11 (s, 1H, NH), 10.50 (s, 1H, NH), 7.58 (d,  $J = 7.5$  Hz, 2H, Ar-H), 7.54 (d,  $J = 7.5$  Hz, 2H, Ar-H), 7.40 (dt,  $J = 1.3, 7.5$  Hz, 4H, Ar-H), 7.33 (d,  $J = 7.5$  Hz, 2H, Ar-H), 7.05 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.00 (d,  $J = 2.6$  Hz, 1H, Ar-H), 6.89 (dt,  $J = 2.6, 7.8$  Hz, 2H, Ar-H), 6.84 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.75 (t,  $J = 7.8$  Hz, 1H, Ar-H), 6.68 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.35 (s, 1H), 5.23 (s, 2H, OCH<sub>2</sub>), 5.21 (s, 2H, OCH<sub>2</sub>).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  179.9, 145.4, 142.8, 137.8, 137.6, 134.9, 131.2, 129.0, 128.8, 128.7, 128.2, 128.1, 127.9, 127.8, 127.6, 123.6, 122.6, 119.4, 117.8, 116.5, 114.3, 113.8, 103.4, 75.7, 70.1, 69.6. MS (ESI): 461 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>: C, 78.24; H, 5.25; N, 6.08. Found C, 77.93; H, 5.48; N, 5.96.

4-Methoxyindoline-2,3-dione (**12**)



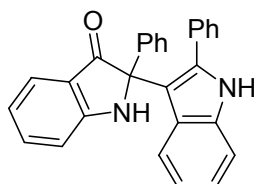
Orange-red solid.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.95 (s, 1H, NH), 7.49 (t,  $J = 8.2$  Hz, 1H, Ar-H), 6.66 (d,  $J = 8.2$  Hz, 1H, Ar-H), 6.41 (d,  $J = 8.2$  Hz, 1H, Ar-H), 3.83 (s, 3H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  181.0, 160.0, 158.6, 151.8, 141.1, 107.3, 106.3, 104.8, 56.4. MS (ESI): 178 (M+H<sup>+</sup>, 100). These assignments matched with those of an authentic sample.

2,2'-Dimethyl-2,3'-biindolin-3-one (**13a**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3422, 3244, 1668, 1614  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  10.87 (s, 1H, NH), 7.71 (s, 1H, NH), 7.47 (dt,  $J = 16.4, 8.2$  Hz, 2H, Ar-H), 7.23 (dt,  $J = 14.1, 8.0$  Hz, 2H, Ar-H), 6.93 (t,  $J = 7.5$  Hz, 1H, Ar-H), 6.88 (t,  $J = 8.2$ , 1H, Ar-H), 6.78 (t,  $J = 7.5$  Hz, 1H, Ar-H), 6.71 (t,  $J = 7.4$  Hz, 1H, Ar-H), 2.39 (s, 3H, CH<sub>3</sub>), 1.74 (s, 3H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  204.3, 160.4, 137.9, 135.2, 133.4, 127.7, 124.8, 120.4, 119.9, 118.8, 118.2, 117.4, 112.2, 110.9, 109.0, 66.7, 24.8, 14.4. MS (ESI): 277 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O: C, 78.24; H, 5.84; N, 10.14. Found C, 78.61; H, 5.75; N, 9.87.

2,2'-Diphenyl-2,3'-biindolin-3-one (**13b**)

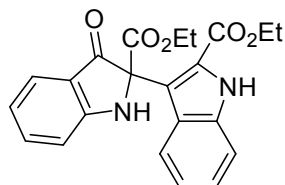


Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3394, 1692, 1615, 1452  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.33 (s, 1H, NH), 8.33 (s, 1H, NH), 7.51 (t,  $J = 7.6$  Hz, 1H, Ar-H), 7.40-7.36 (m, 2H, Ar-H), 7.33 (d,  $J = 8.1$ , 1H, Ar-H), 7.24 (d,  $J = 7.6$ , 1H, Ar-H), 7.17-7.10 (m, 3H, Ar-H), 7.08-7.00 (m, 6H, Ar-H), 6.97 (d,  $J = 8.1$  Hz, 1H, Ar-H), 6.76 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.71 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.60 (d,  $J = 8.1$  Hz, 1H, Ar-H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  200.9, 160.5, 140.3, 138.4, 137.9, 136.2, 133.6, 130.0, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 124.8, 121.6, 120.8, 119.1, 118.9, 117.9, 112.3, 111.7, 111.5, 71.6. MS (ESI): 401 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O: C,



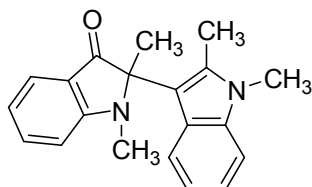
83.98; H, 5.03; N, 7.00. Found C, 84.21; H, 4.72; N, 6.84.

Diethyl 3-oxo-2,3'-biindoline-2,2'-dicarboxylate (**13c**)



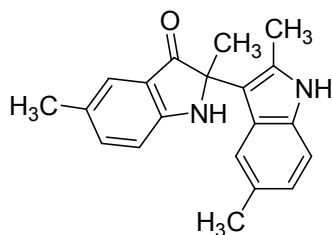
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3367, 1705, 1615, 1251  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  12.07 (s, 1H, NH), 7.92 (s, 1H, NH), 7.59 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.4-7.45 (m, 2H, Ar-H), 7.25 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.21 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.97 (d,  $J = 8.4$  Hz, 1H, Ar-H), 6.94 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.80 (t,  $J = 7.4$  Hz, 1H, Ar-H), 4.31 (q,  $J = 7.1$  Hz, 2H,  $\text{CH}_2$ ), 4.08 (q,  $J = 7.1$  Hz, 2H,  $\text{CH}_2$ ), 1.33 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ), 1.08 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  195.8, 168.3, 162.7, 161.7, 138.4, 136.4, 129.7, 129.0, 126.4, 125.2, 124.9, 121.9, 120.5, 118.6, 116.4, 113.3, 113.0, 73.0, 61.9, 61.3, 14.5, 14.3. MS (ESI): 393 ( $\text{M}+\text{H}^+$ , 100), 415 ( $\text{M}+\text{Na}^+$ , 15). Anal calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_5$ : C, 67.34; H, 5.14; N, 7.14. Found C, 67.70; H, 5.03; N, 6.87.

1,1',2,2'-Tetramethyl-2,3'-biindolin-3-one (**13d**)



Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3435, 1692, 1612  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.57 (t,  $J = 8.3$  Hz, 1H, Ar-H), 7.50 (d,  $J = 7.7$  Hz, 1H, Ar-H), 7.37 (d,  $J = 8.1$  Hz, 1H, Ar-H), 7.18 (d,  $J = 8.1$  Hz, 1H, Ar-H), 7.03 (t,  $J = 7.7$  Hz, 1H, Ar-H), 6.98 (d,  $J = 8.3$  Hz, 1H, Ar-H), 6.85 (t,  $J = 7.4$  Hz, 1H, Ar-H), 6.74 (t,  $J = 7.4$  Hz, 1H, Ar-H), 3.64 (s, 3H,  $\text{CH}_3$ ), 2.80 (s, 3H,  $\text{CH}_3$ ), 2.28 (s, 3H,  $\text{CH}_3$ ), 1.75 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  203.0, 159.2, 138.4, 136.7, 136.3, 127.0, 124.9, 120.7, 119.6, 119.3, 118.0, 117.0, 109.9, 109.2, 106.6, 70.9, 29.8, 28.0, 22.1, 11.8. MS (ESI): 305 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$ : C, 78.92; H, 6.62; N, 9.20. Found C, 79.30; H, 6.54; N, 8.97.

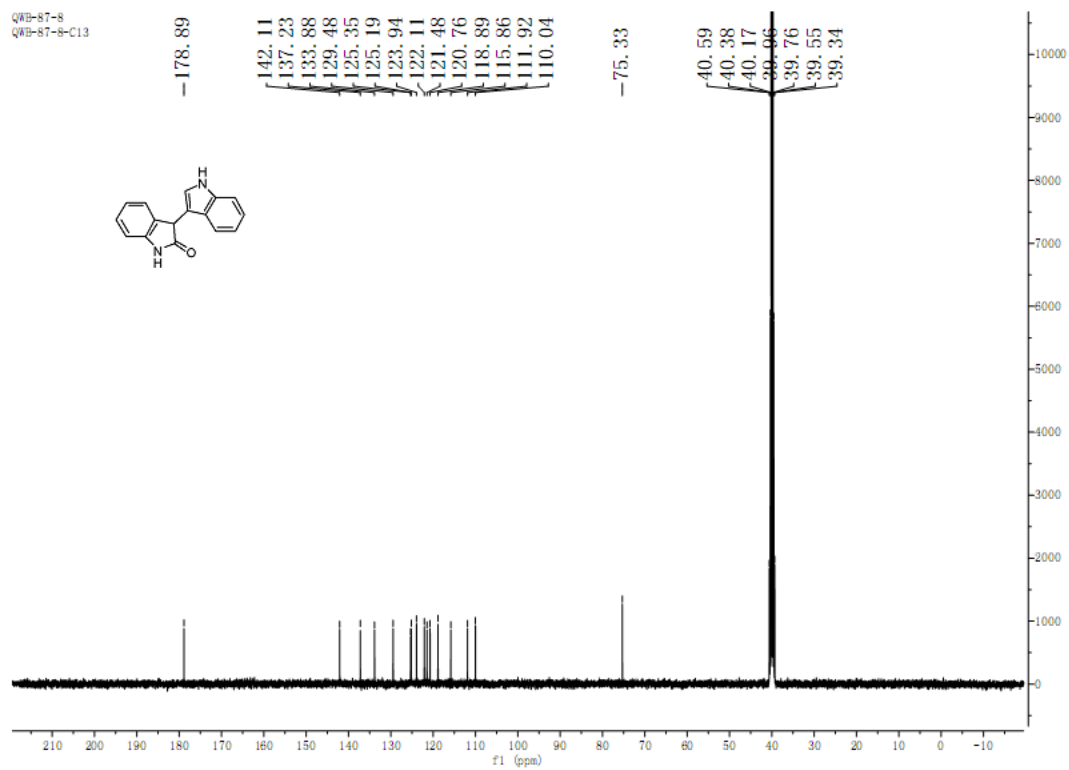
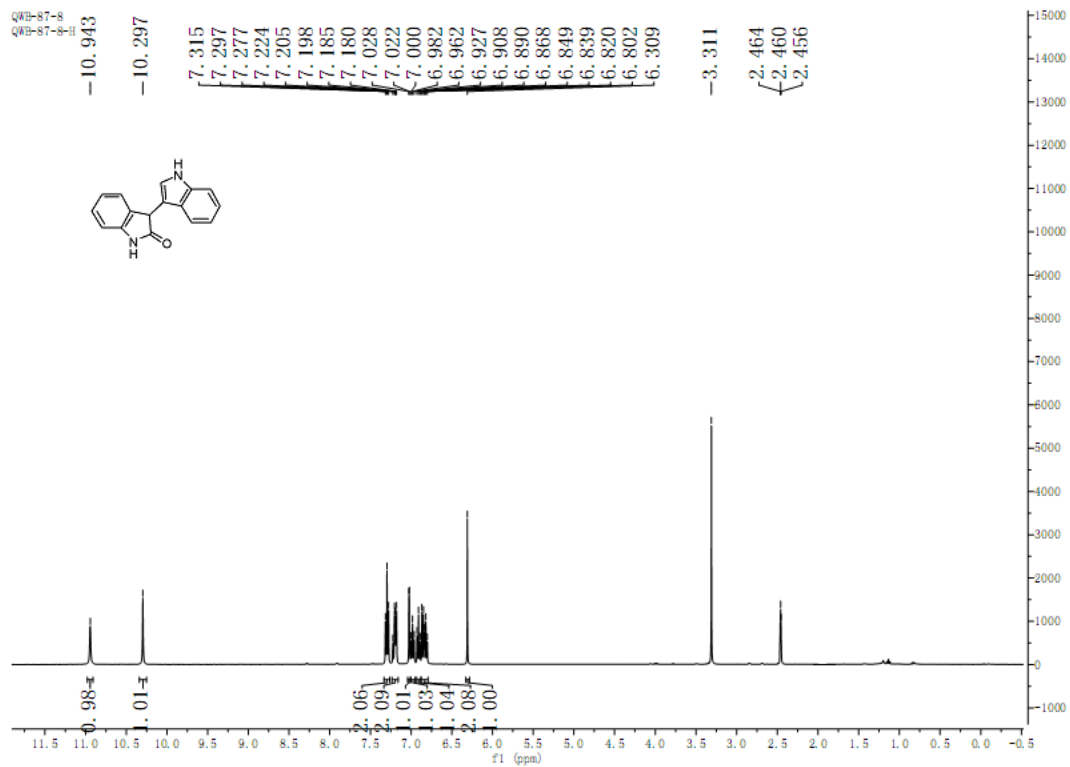
2,2',5,5'-Tetramethyl-2,3'-biindolin-3-one (**13e**)



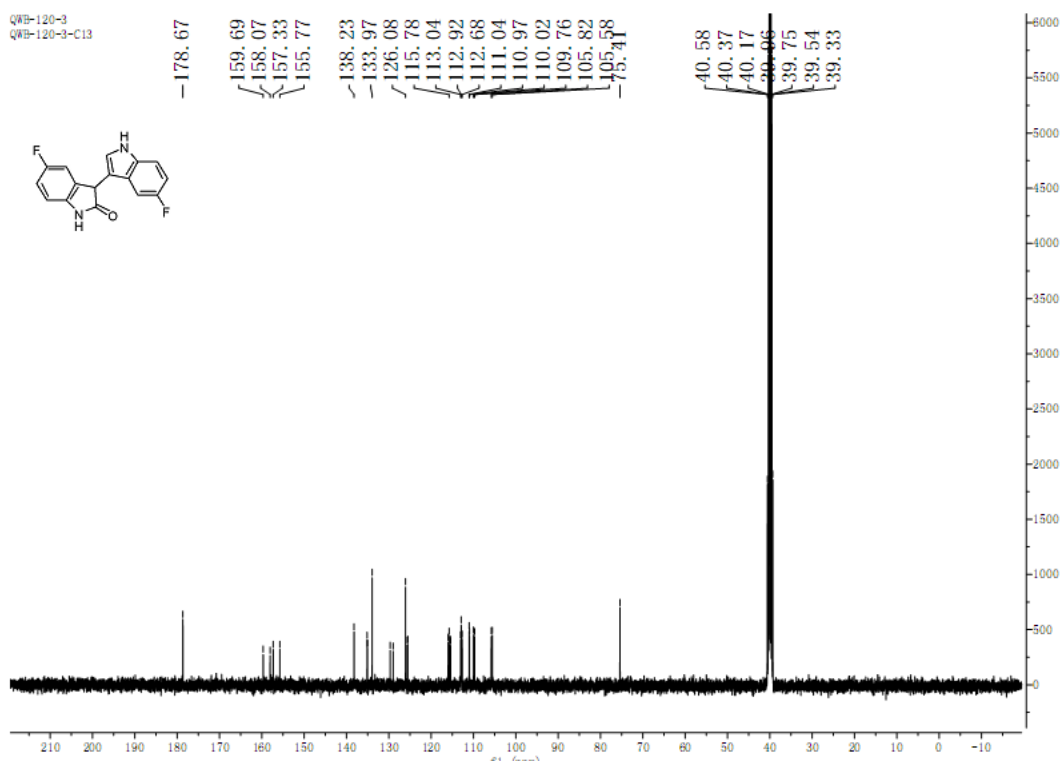
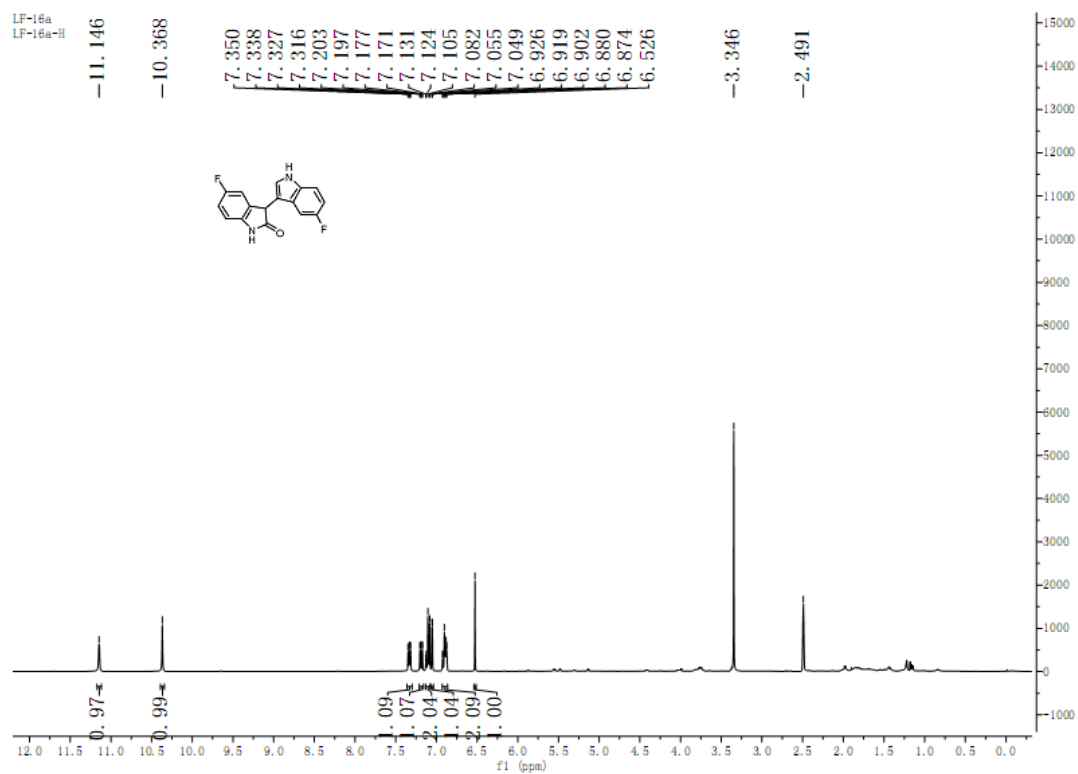
Amorphous solid. IR (KBr)  $\nu_{\max}$ : 3384, 1667, 1626, 1498  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  10.71 (s, 1H, NH), 7.43 (s, 1H, NH), 7.32 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.25 (s, 1H, Ar-H), 7.11 (t,  $J = 7.3$  Hz, Ar-H), 6.82 (d,  $J = 8.3$  Hz, 1H, Ar-H), 6.76 (d,  $J = 8.2$  Hz, 1H, Ar-H), 2.49 (s, 3H,  $\text{CH}_3$ ), 2.24 (s, 6H,  $\text{CH}_3$ ), 1.73 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  204.3, 159.0, 139.2, 133.6, 133.2, 128.0, 126.8, 126.2, 124.0, 121.8, 119.8, 118.4, 112.3, 110.6, 108.7, 67.1, 25.1, 22.0, 20.6, 14.4. MS (ESI): 305 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$ : C, 78.92; H, 6.62; N, 9.20. Found C, 78.69; H, 6.94; N, 8.86.

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

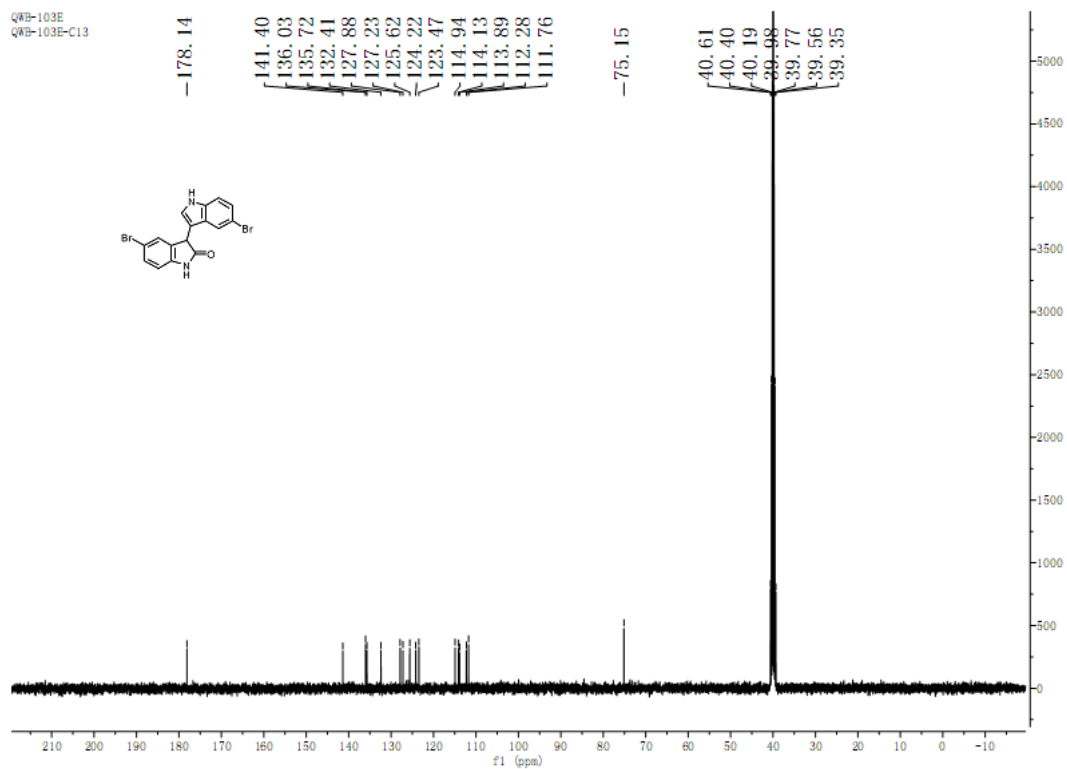
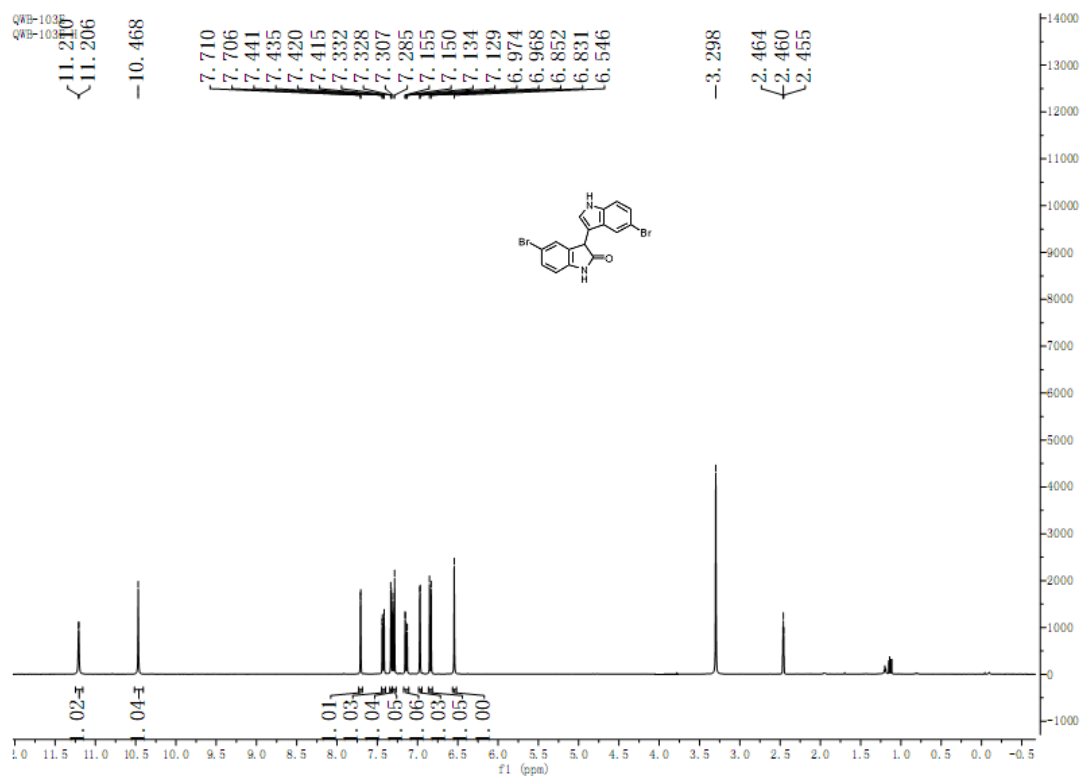
$^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra for 4a



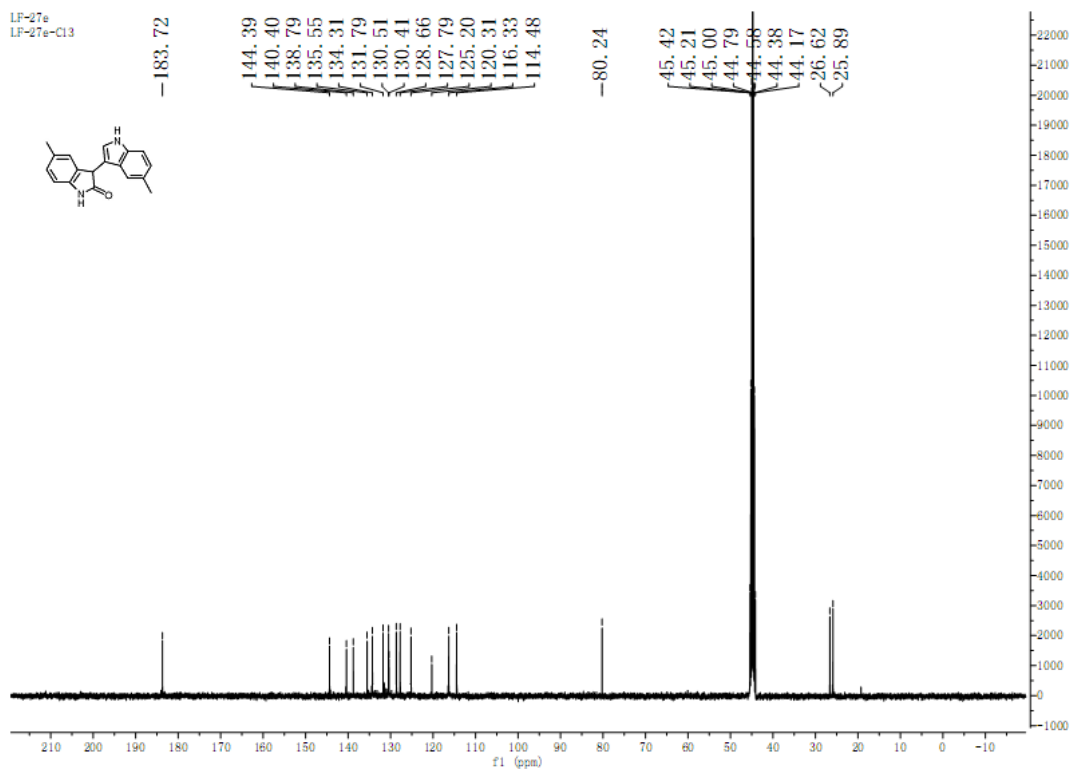
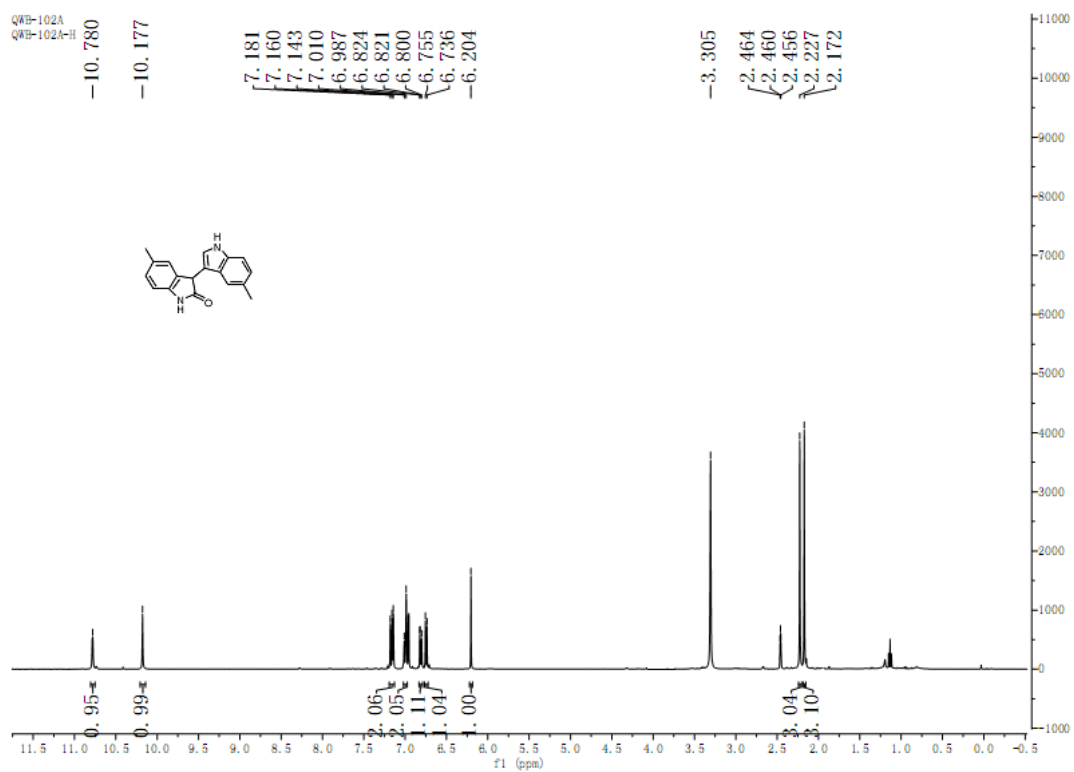
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4b



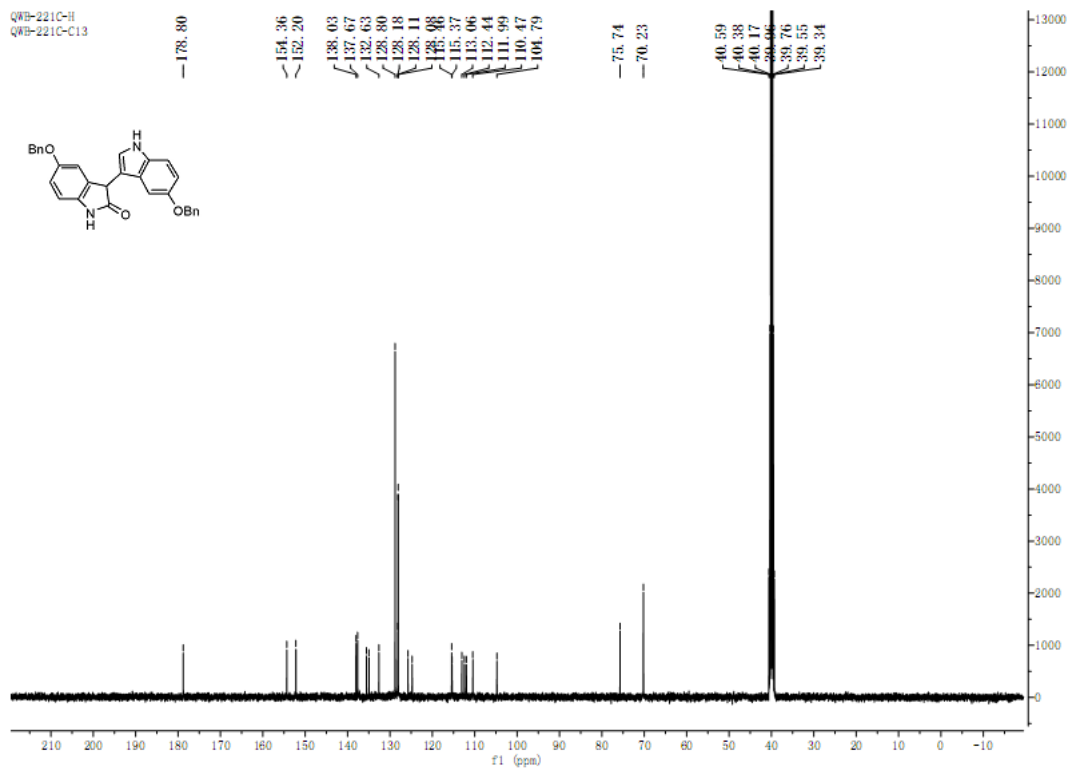
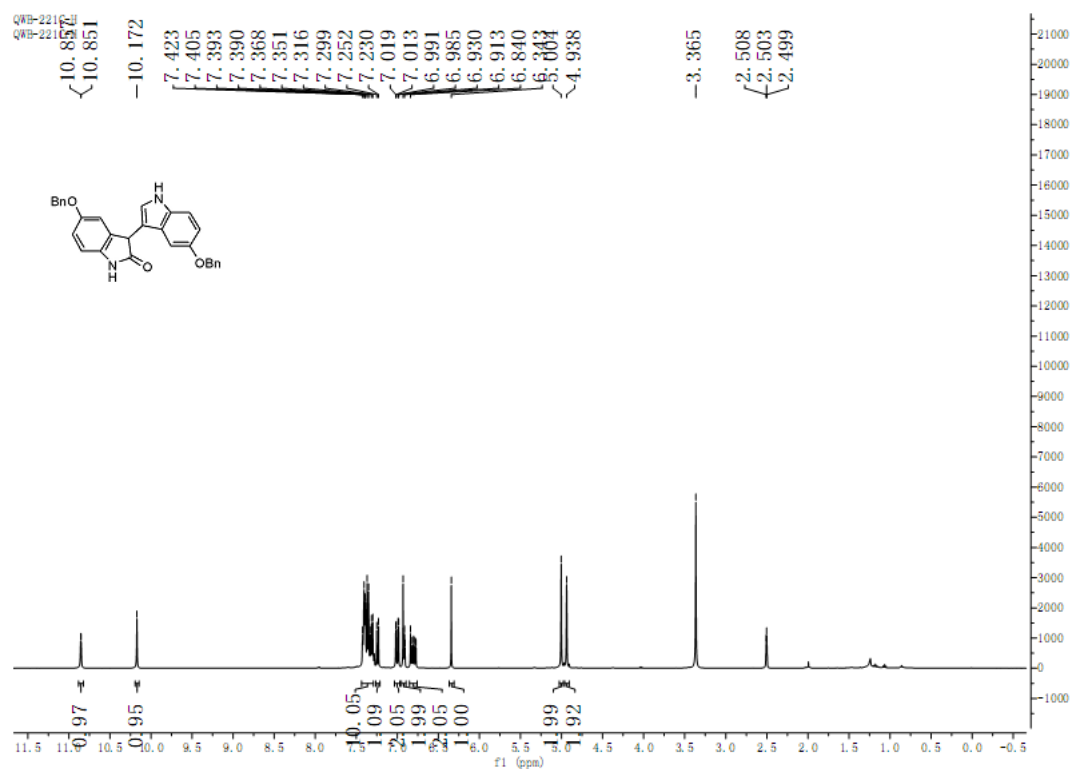
<sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4c



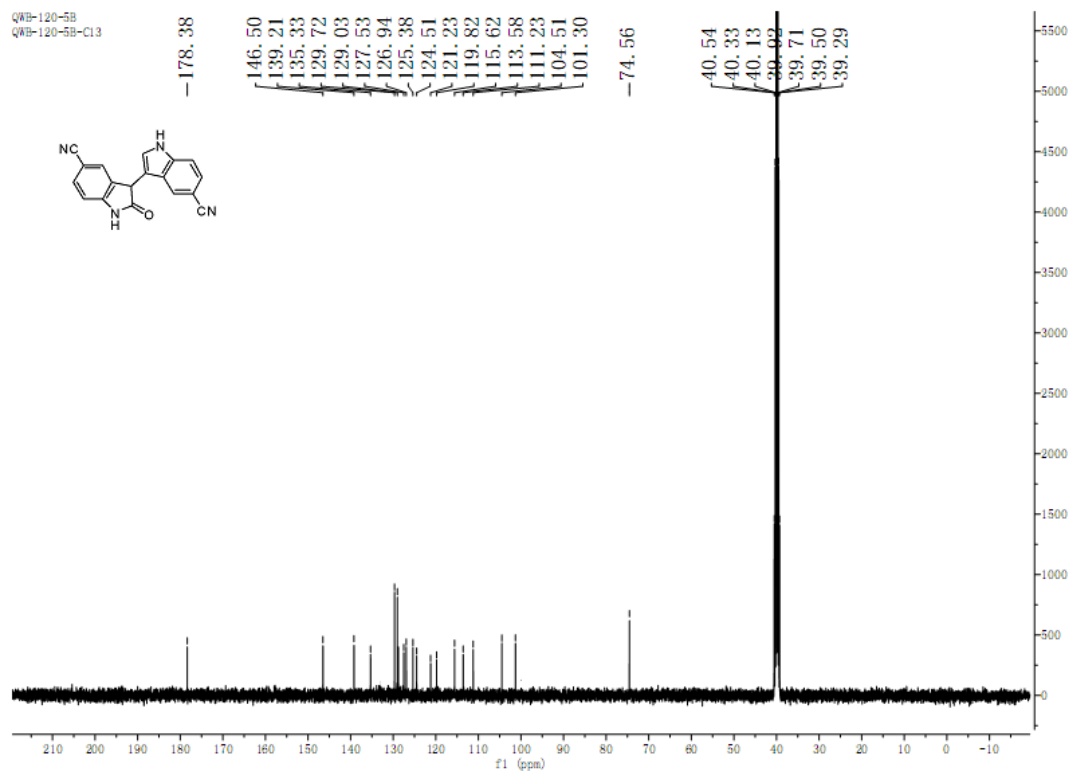
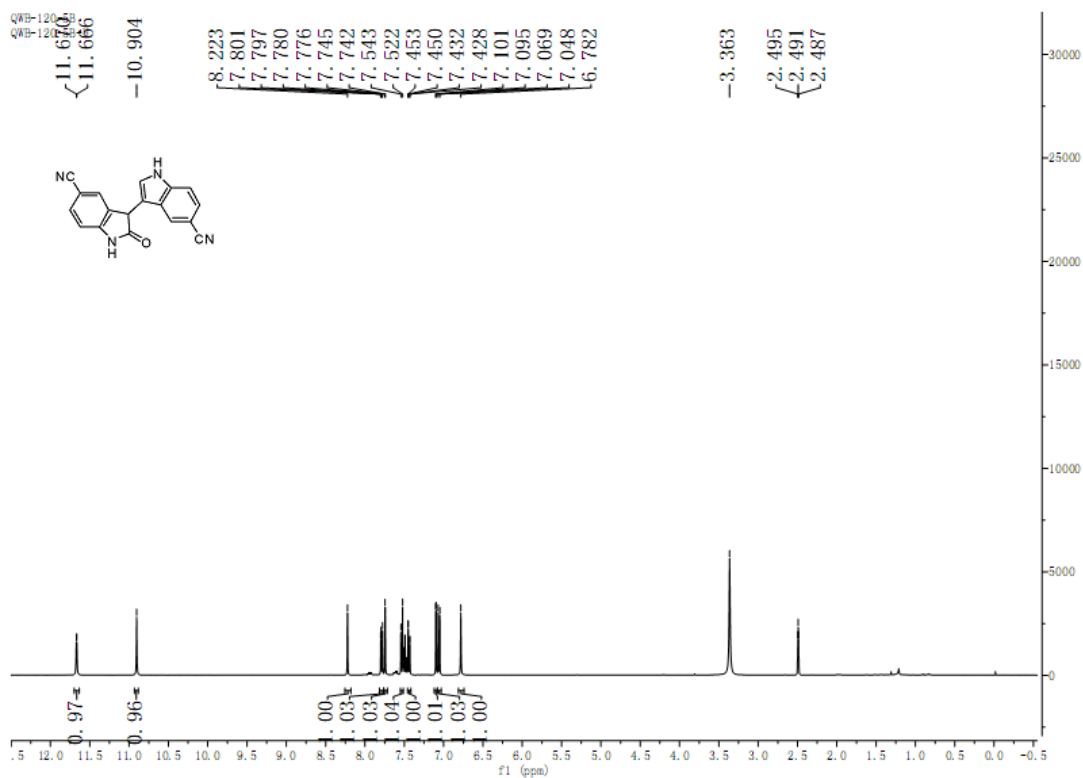
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4d



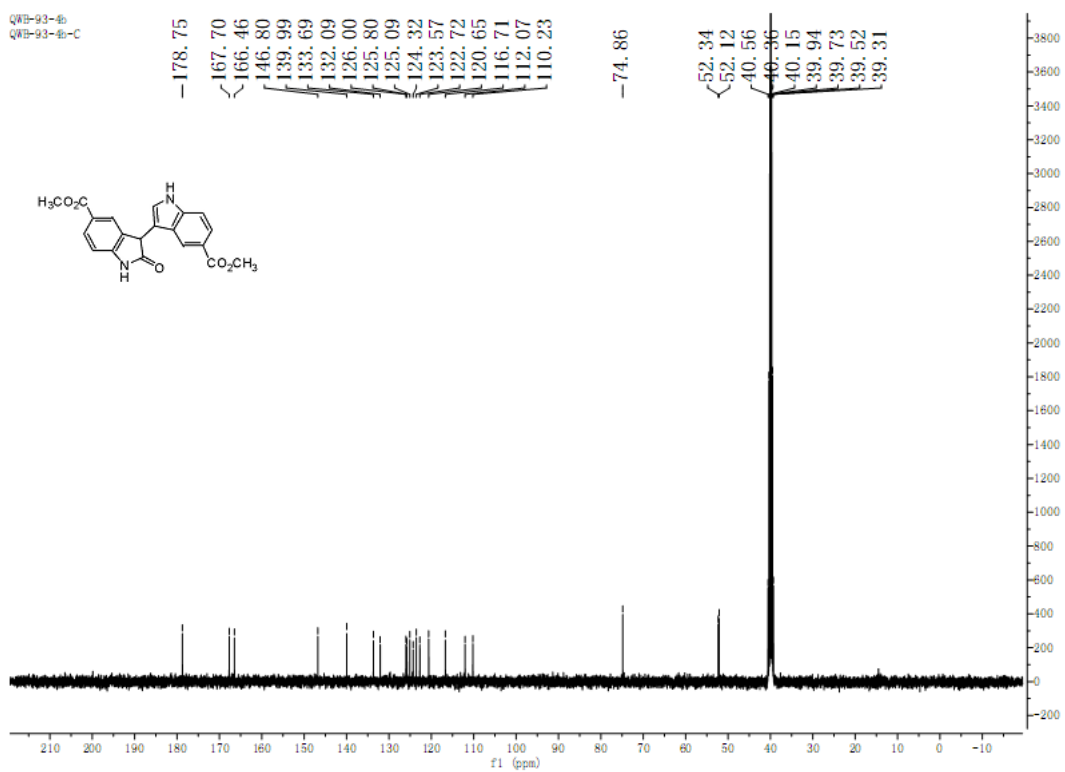
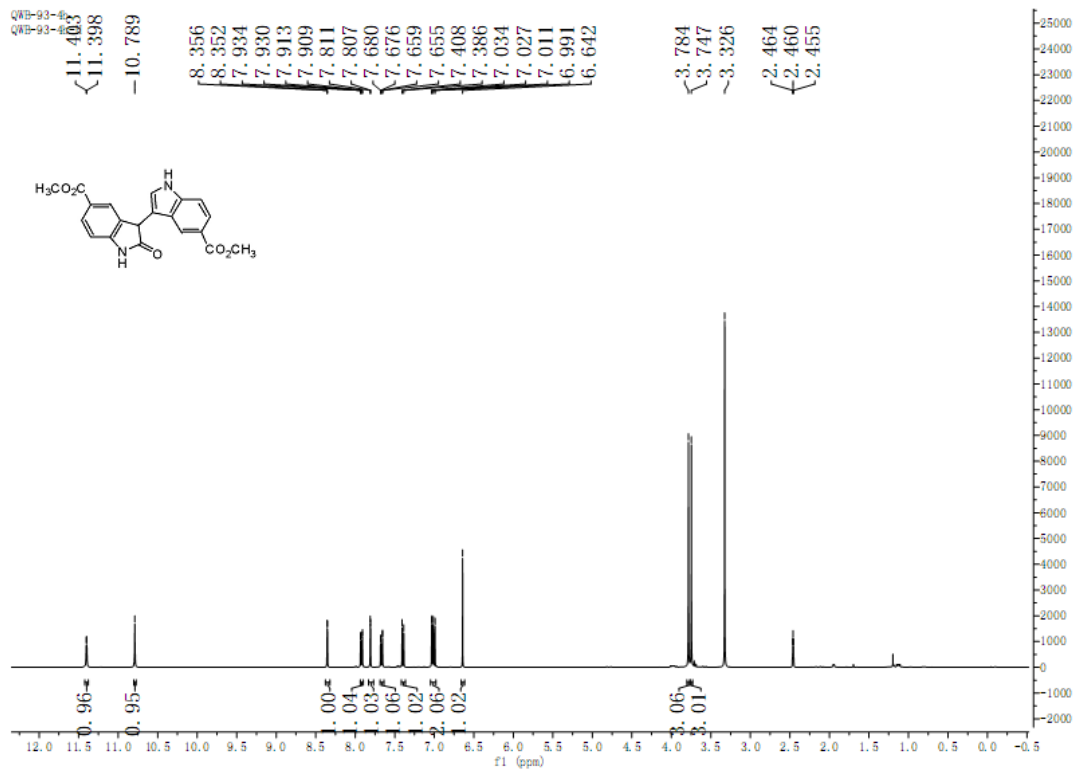
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4e



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4f

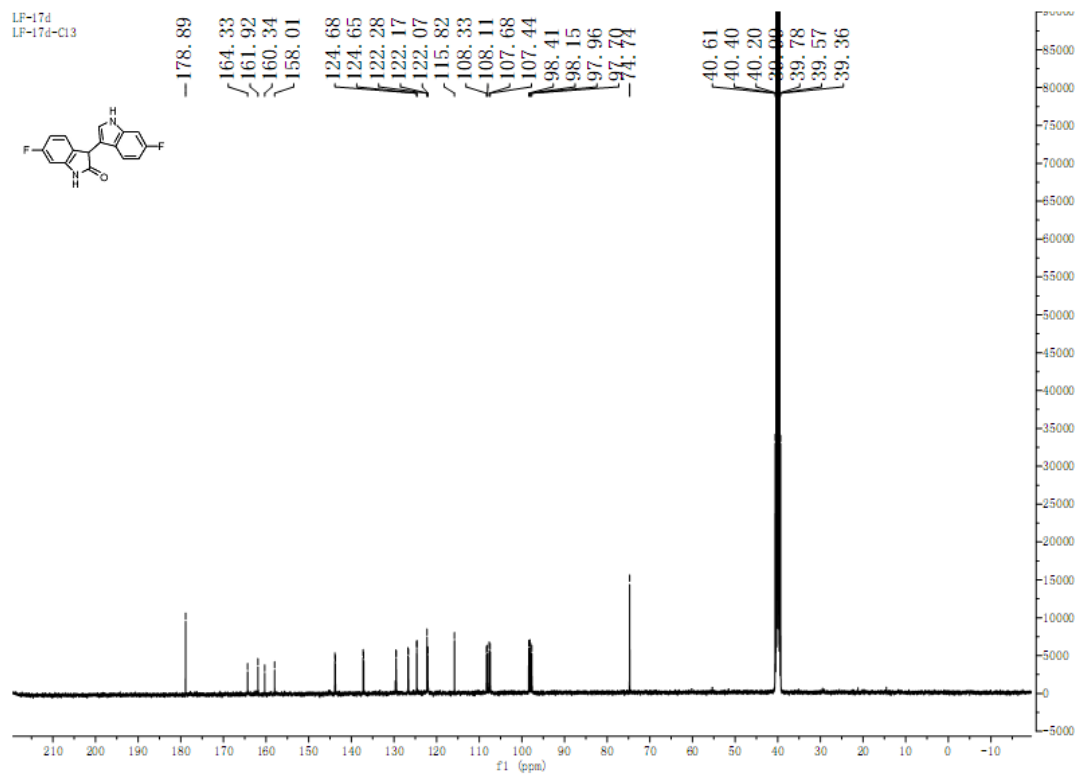
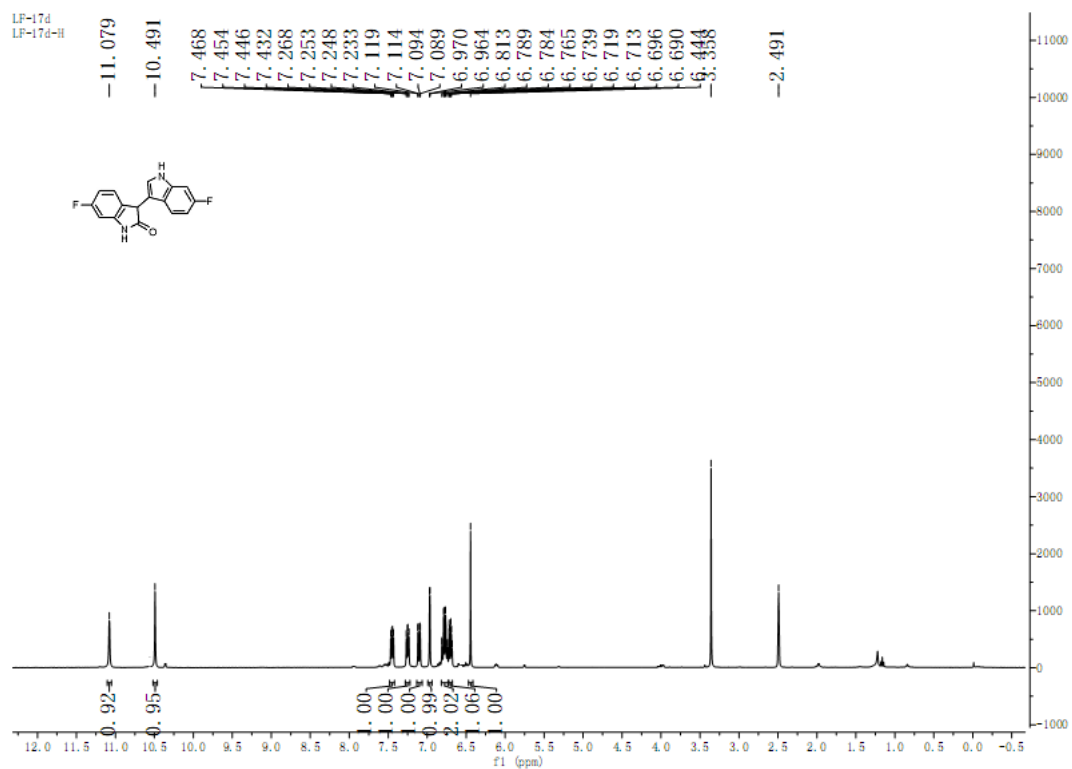


<sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4g

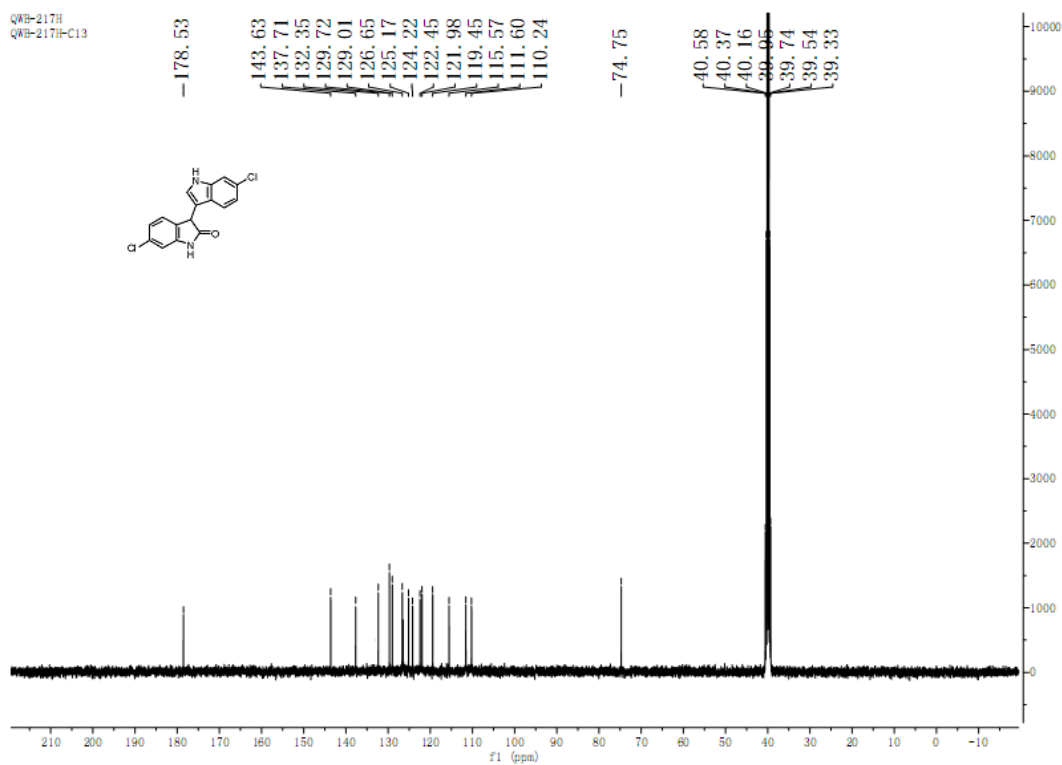
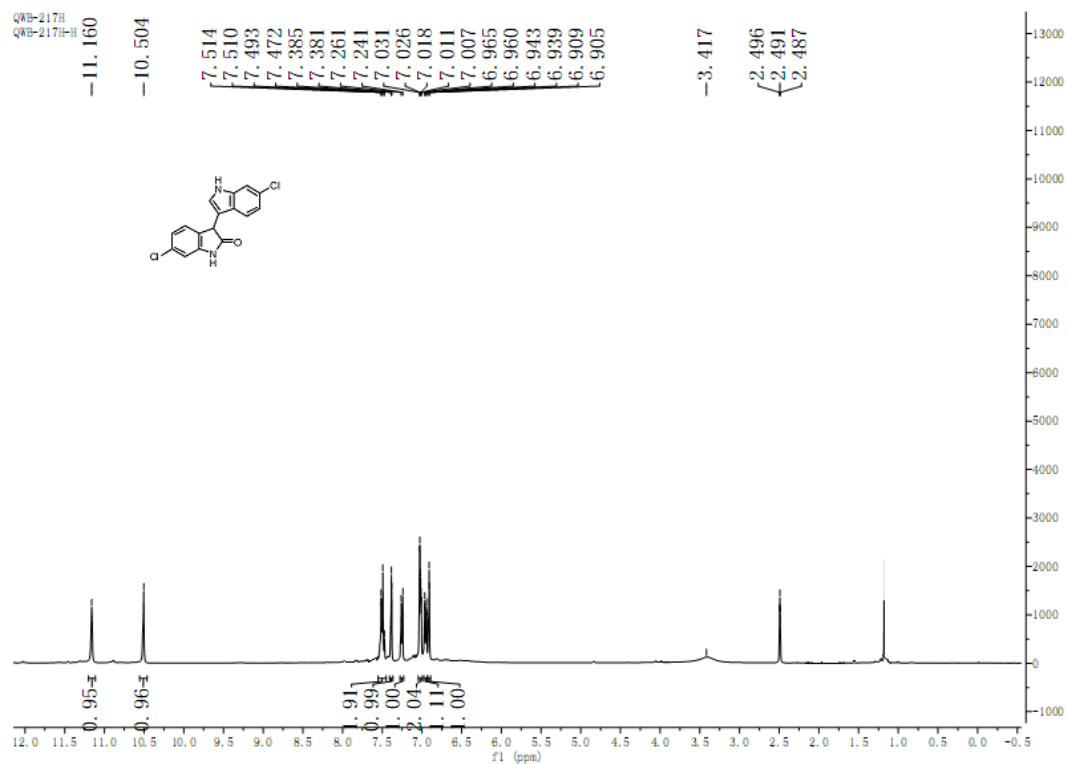




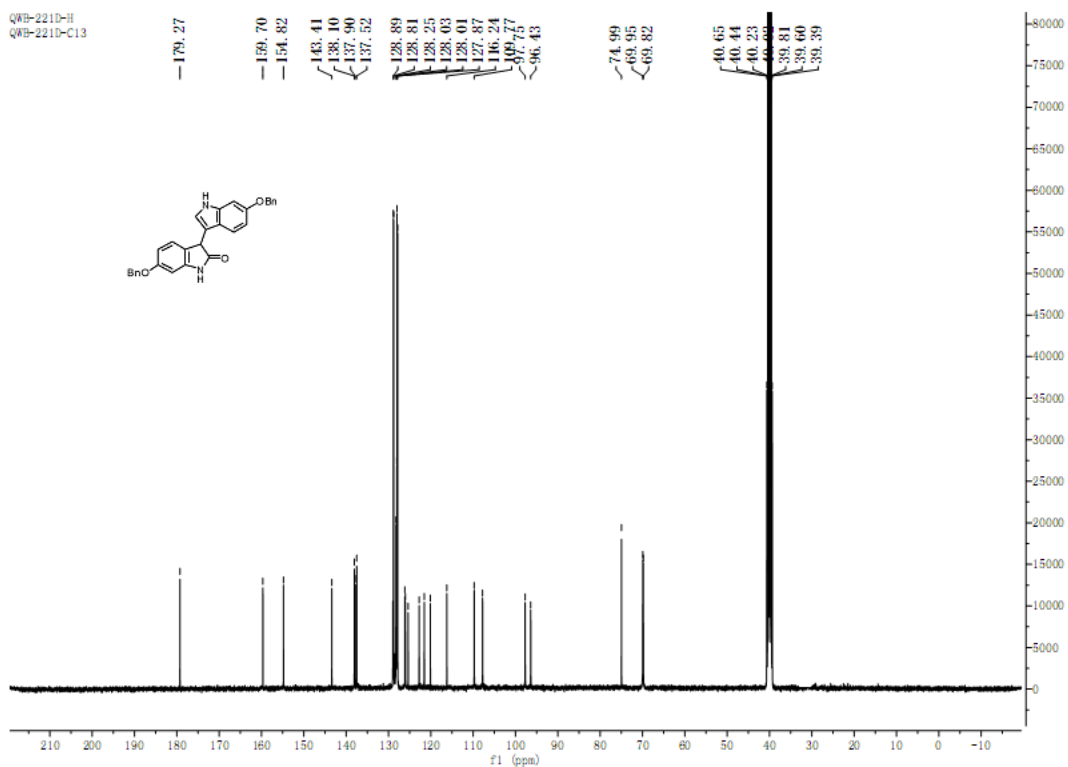
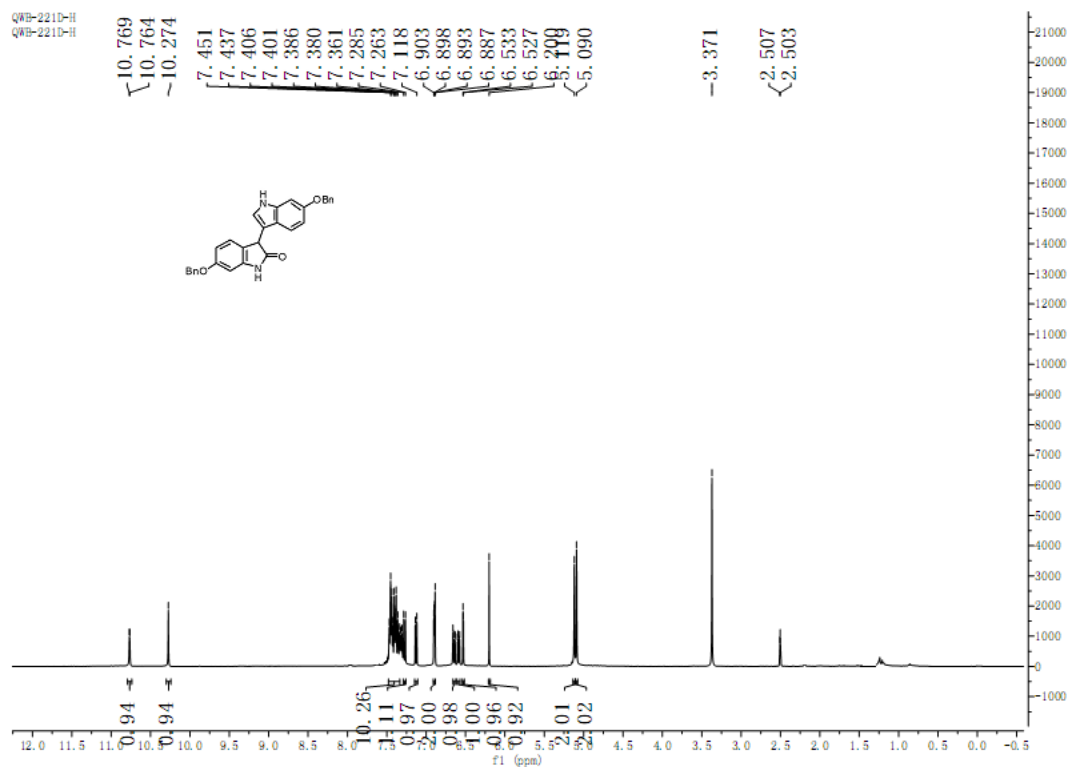
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4i



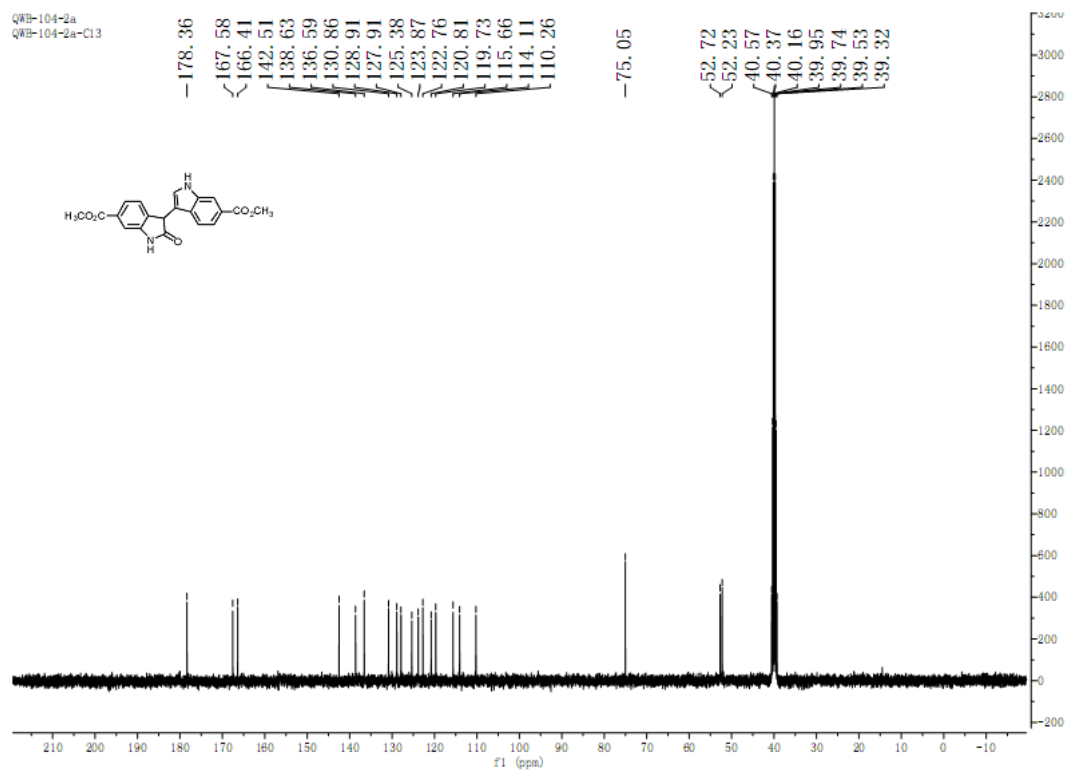
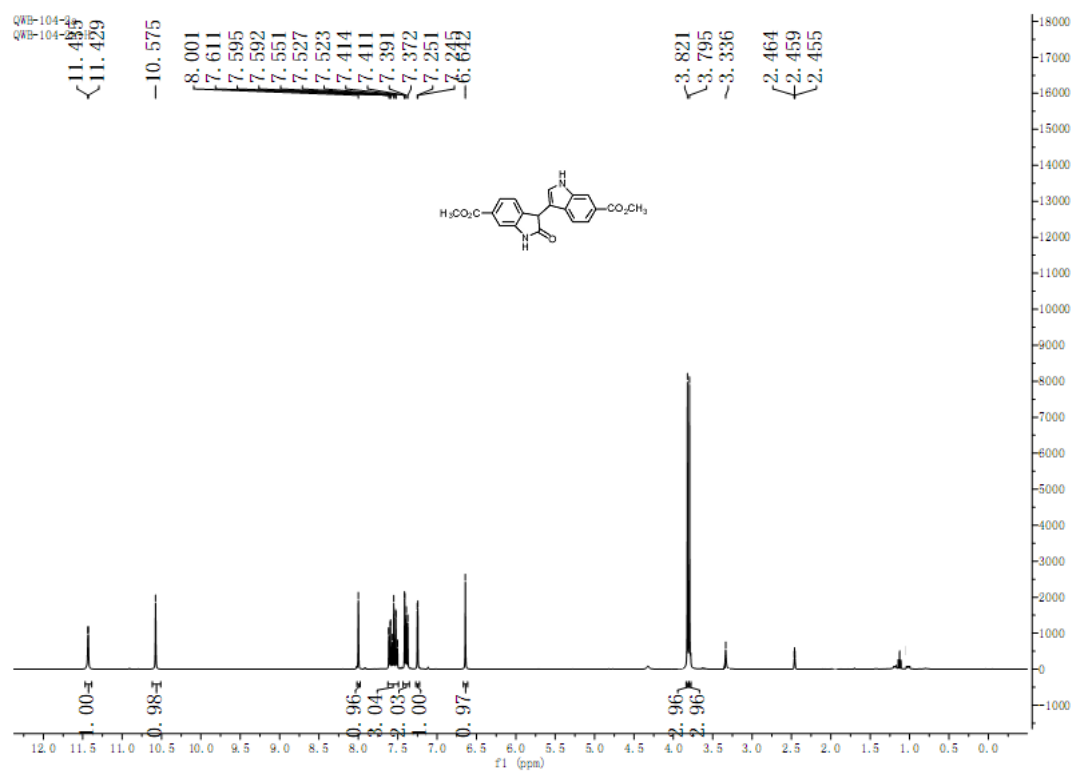
<sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4j



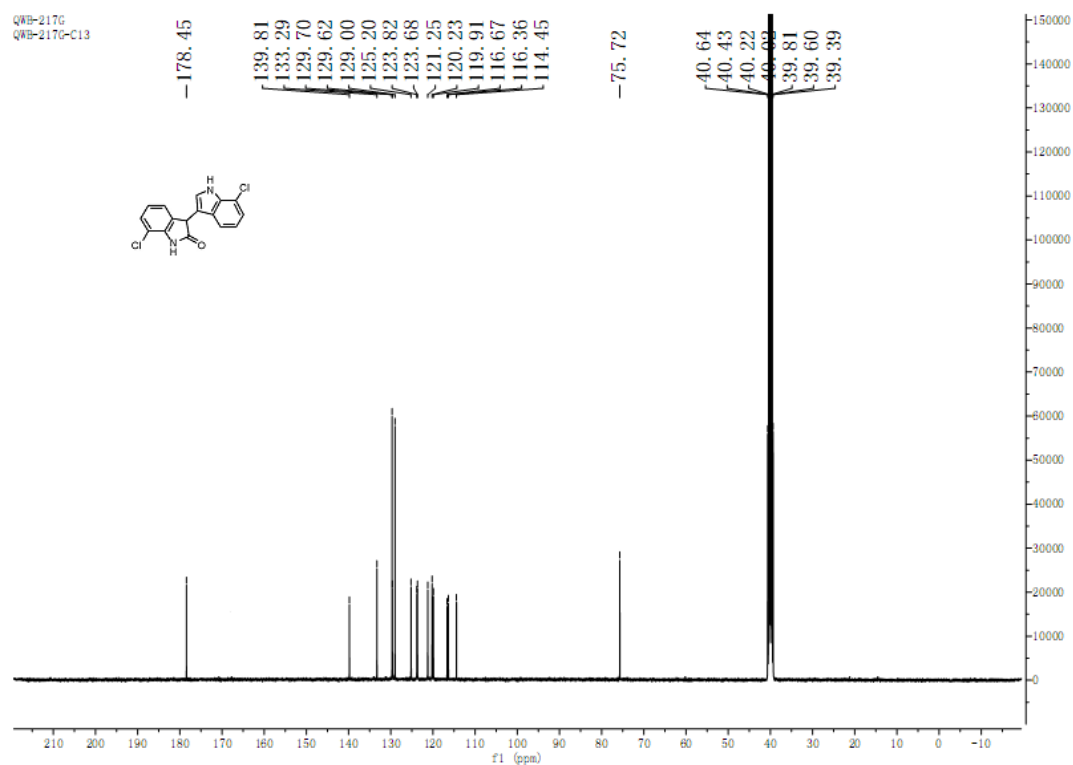
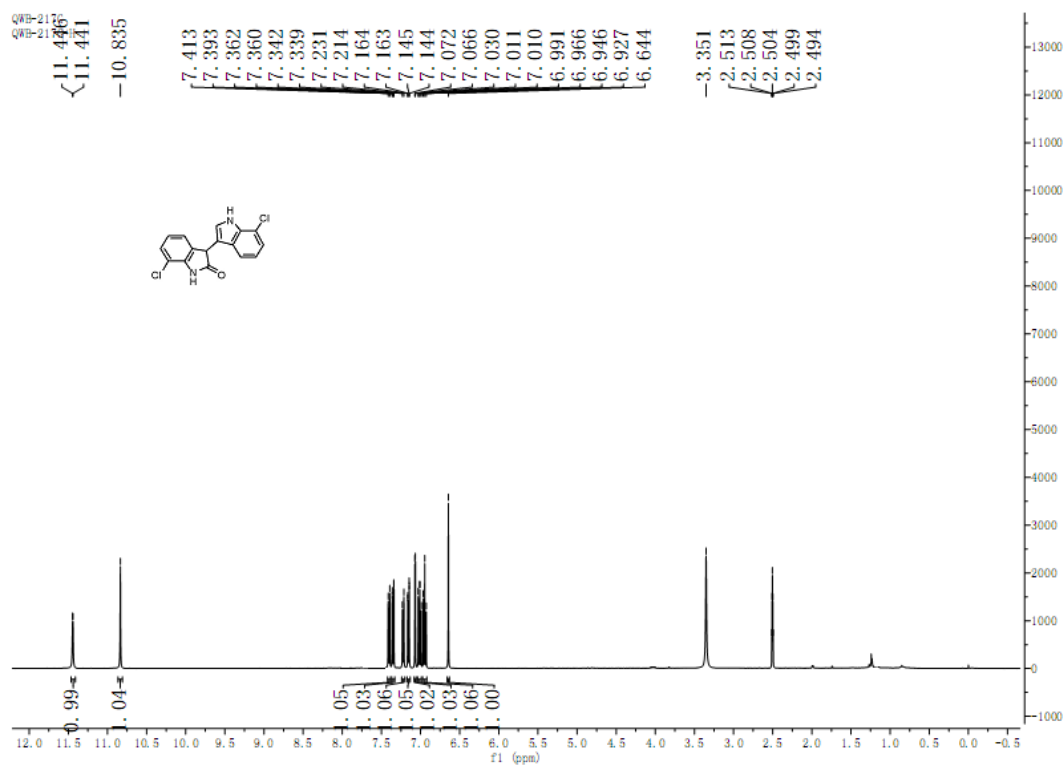
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4k



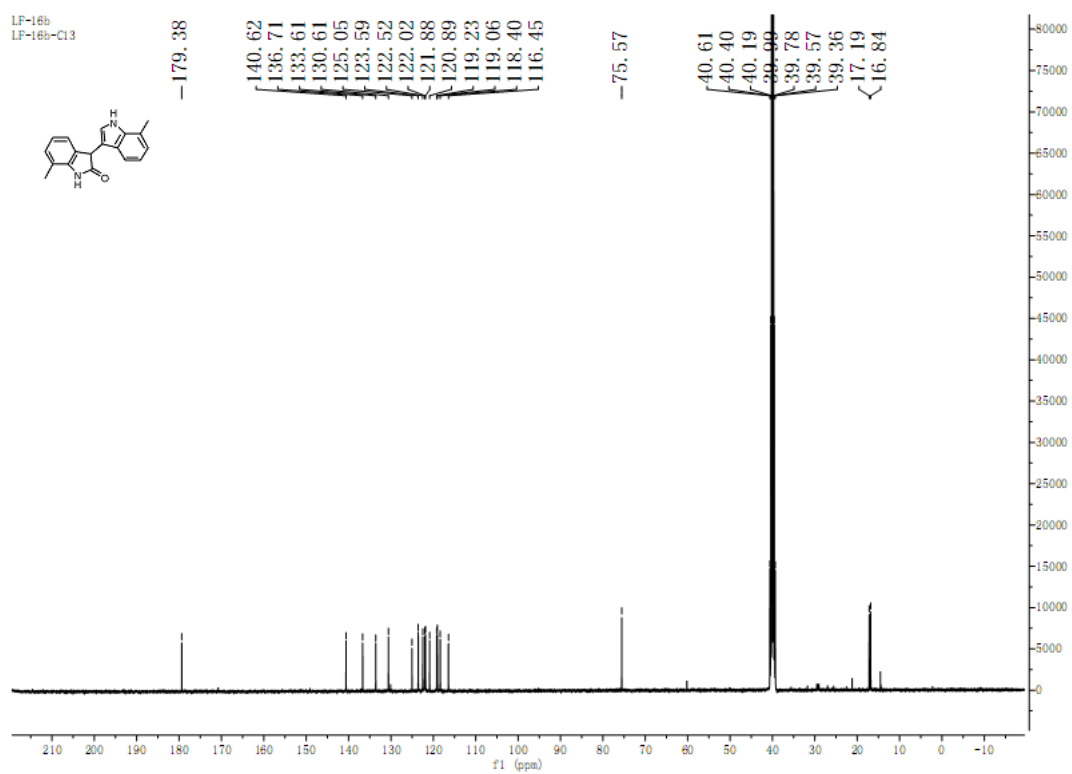
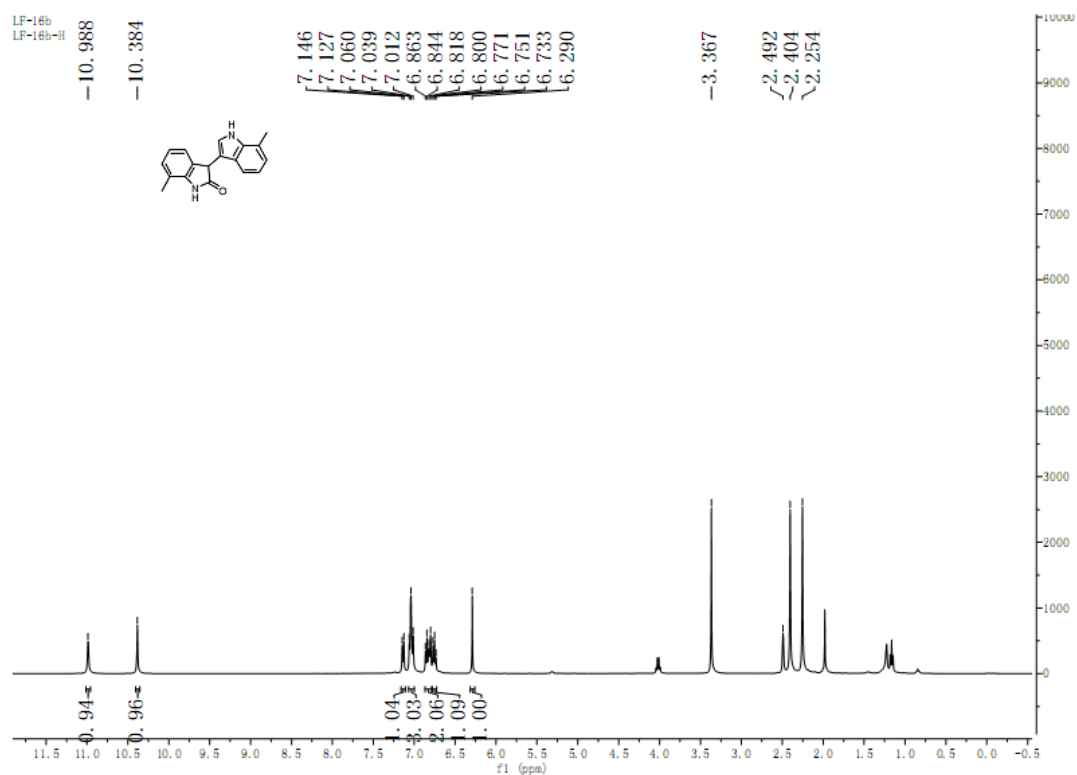
<sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4l



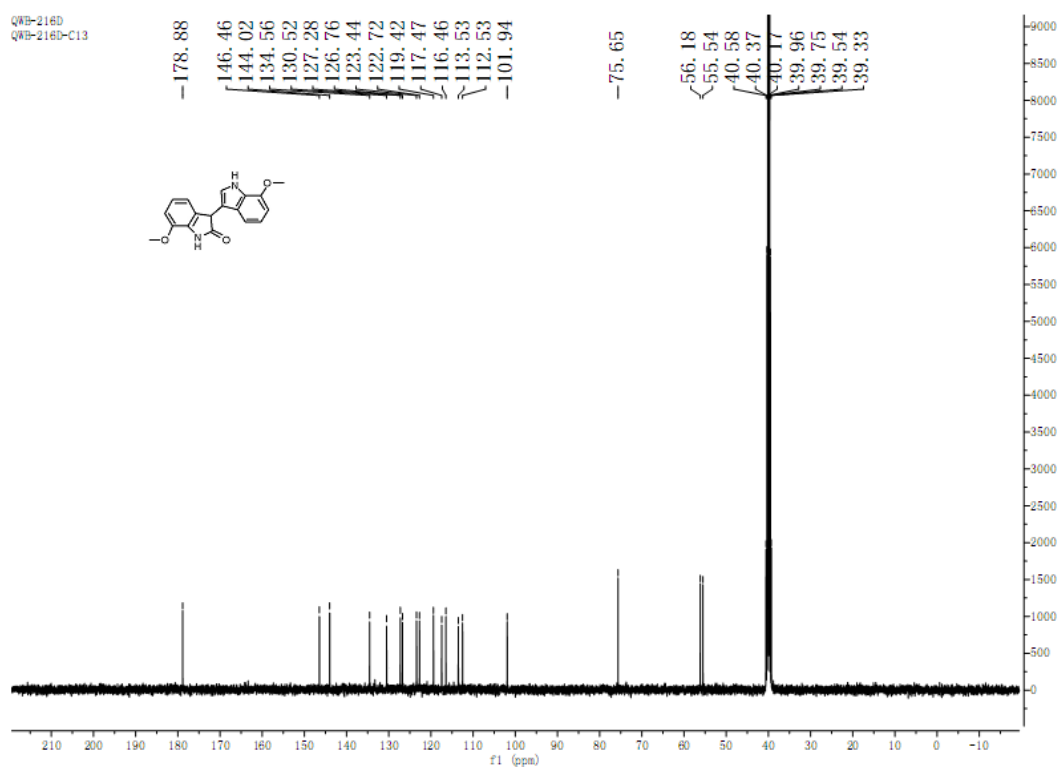
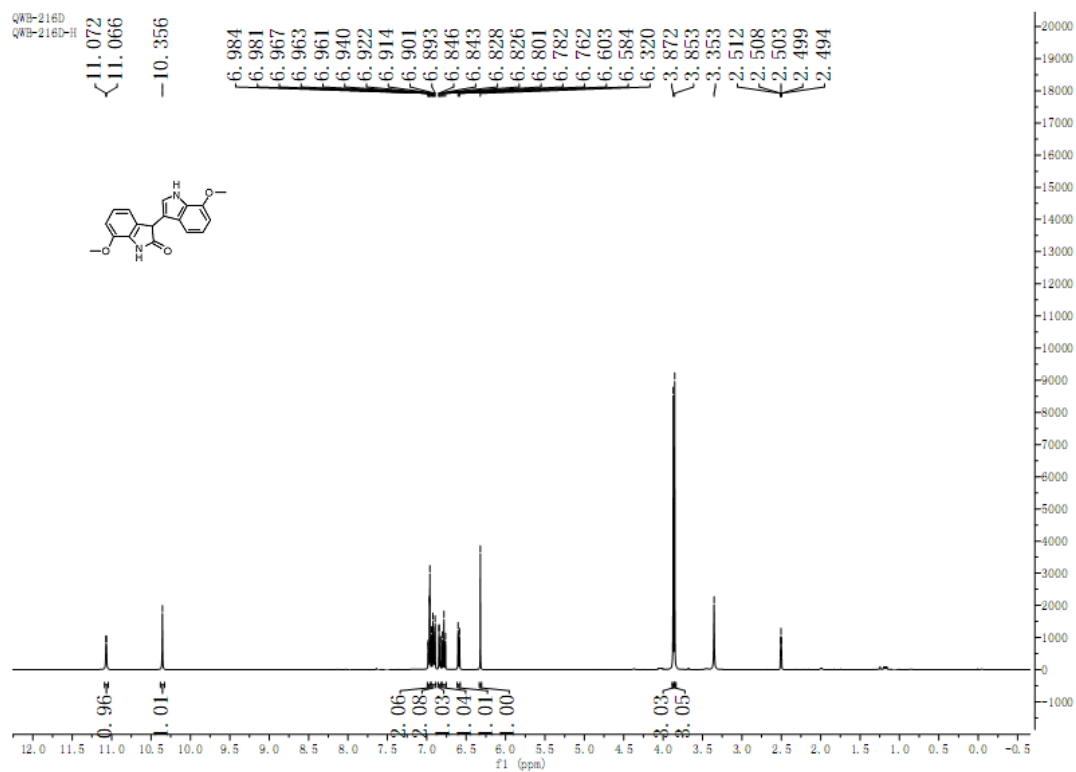
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4m



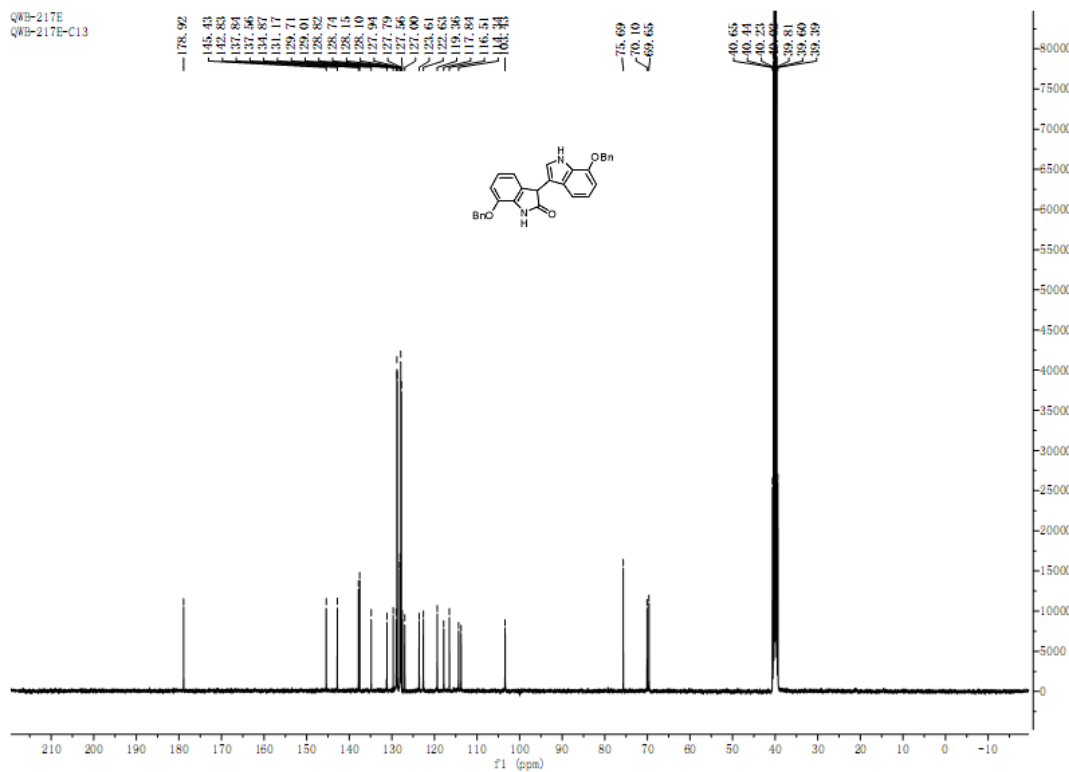
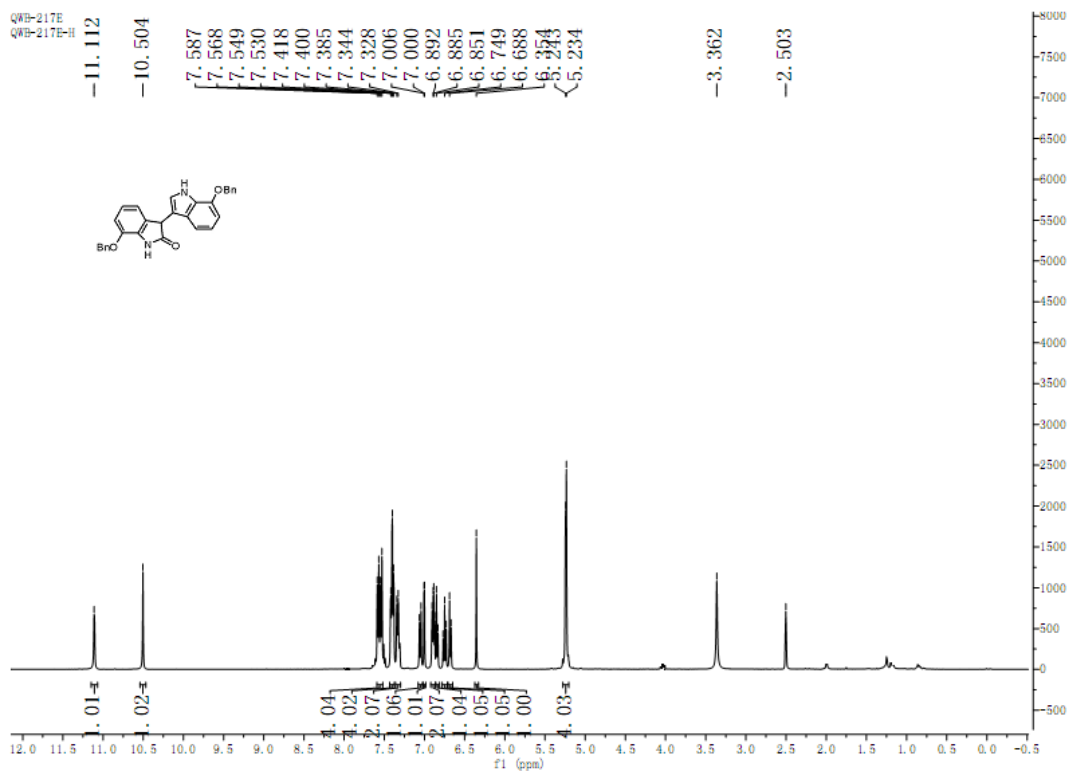
<sup>1</sup>H and <sup>13</sup>C NMR Spectra for **4n**



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4o

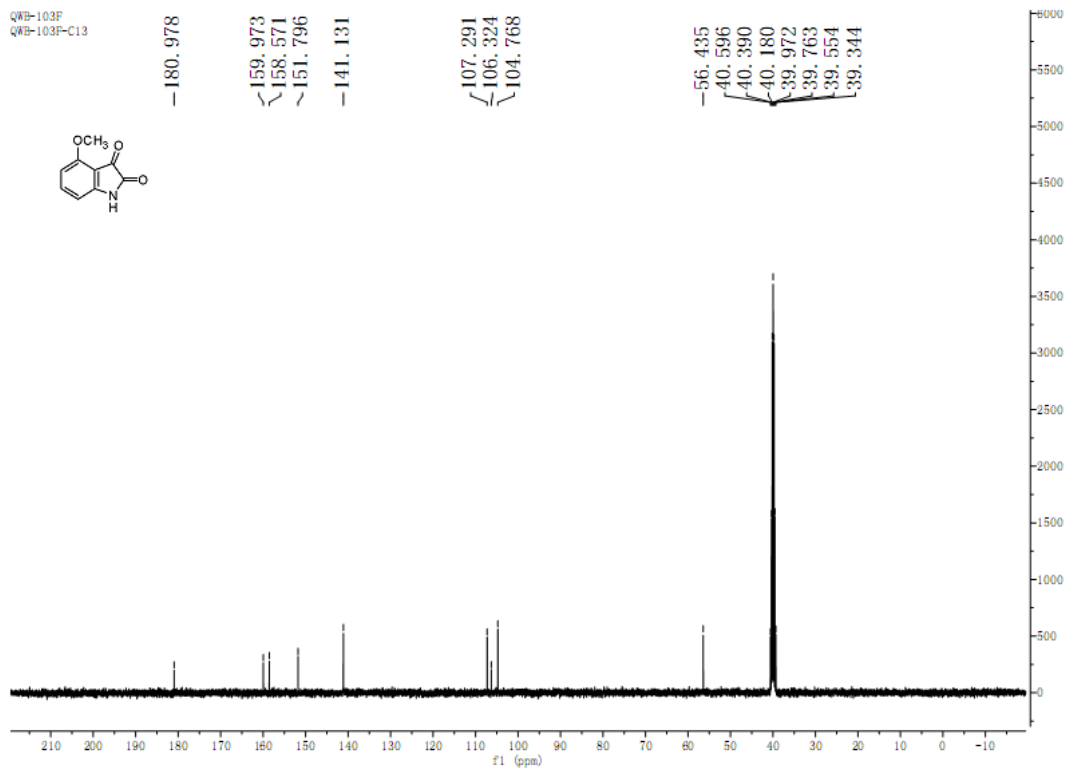
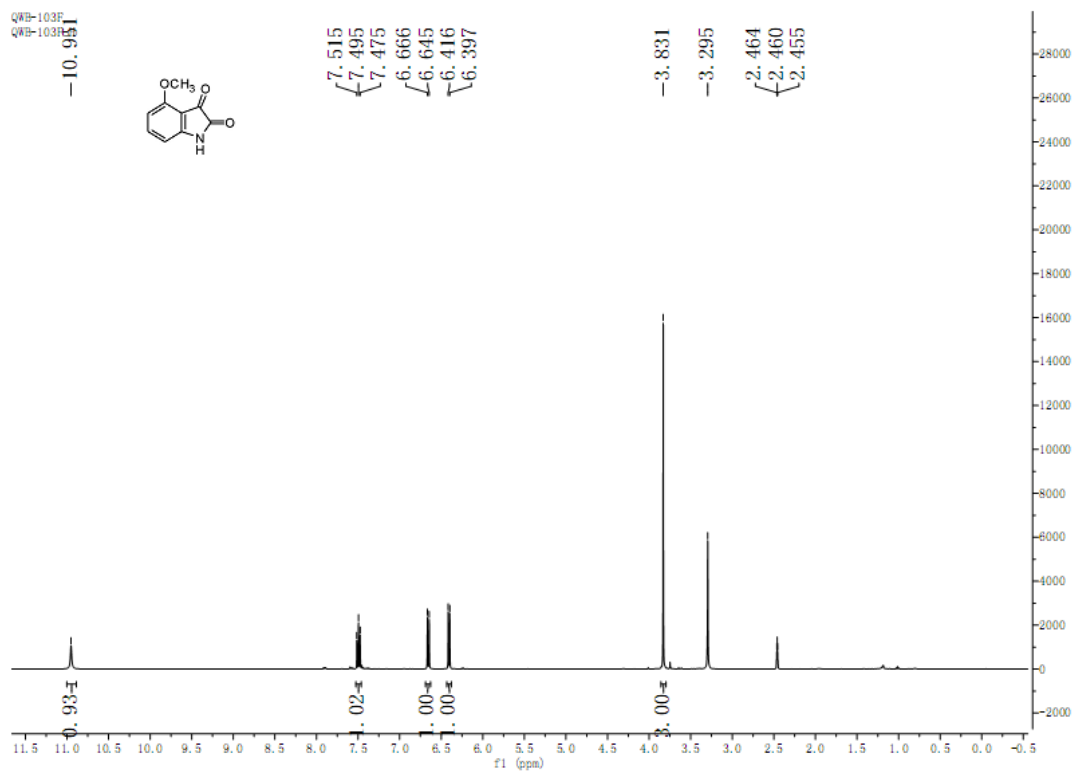


# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 4p

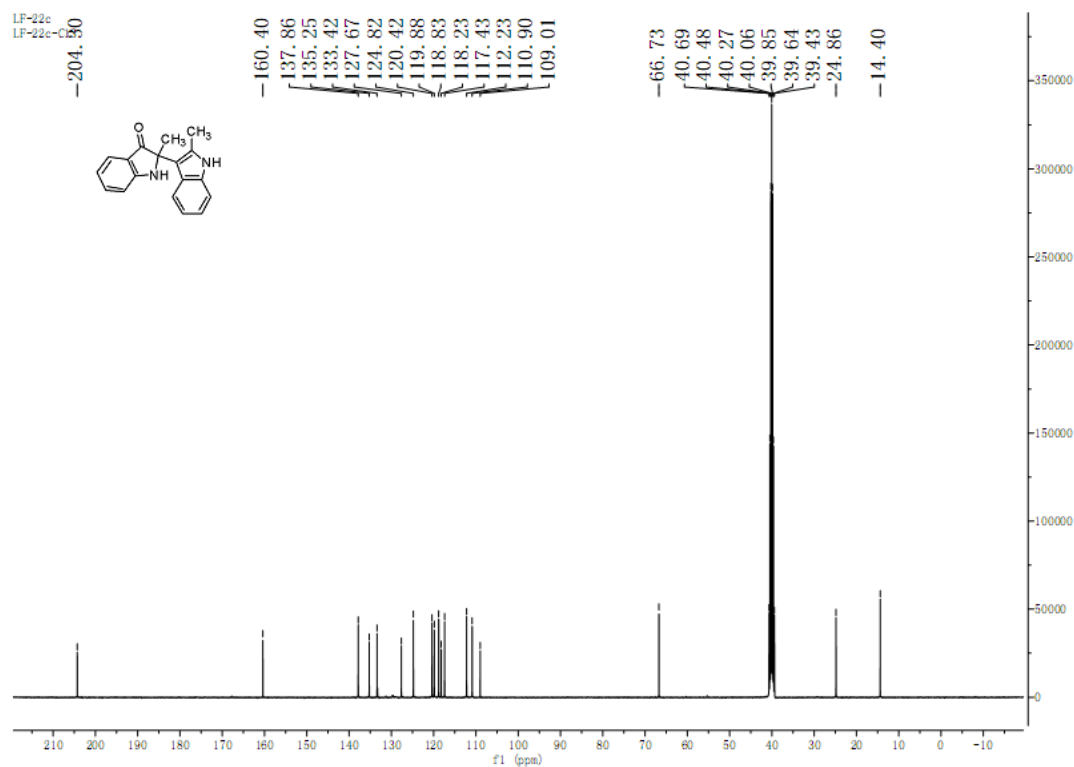
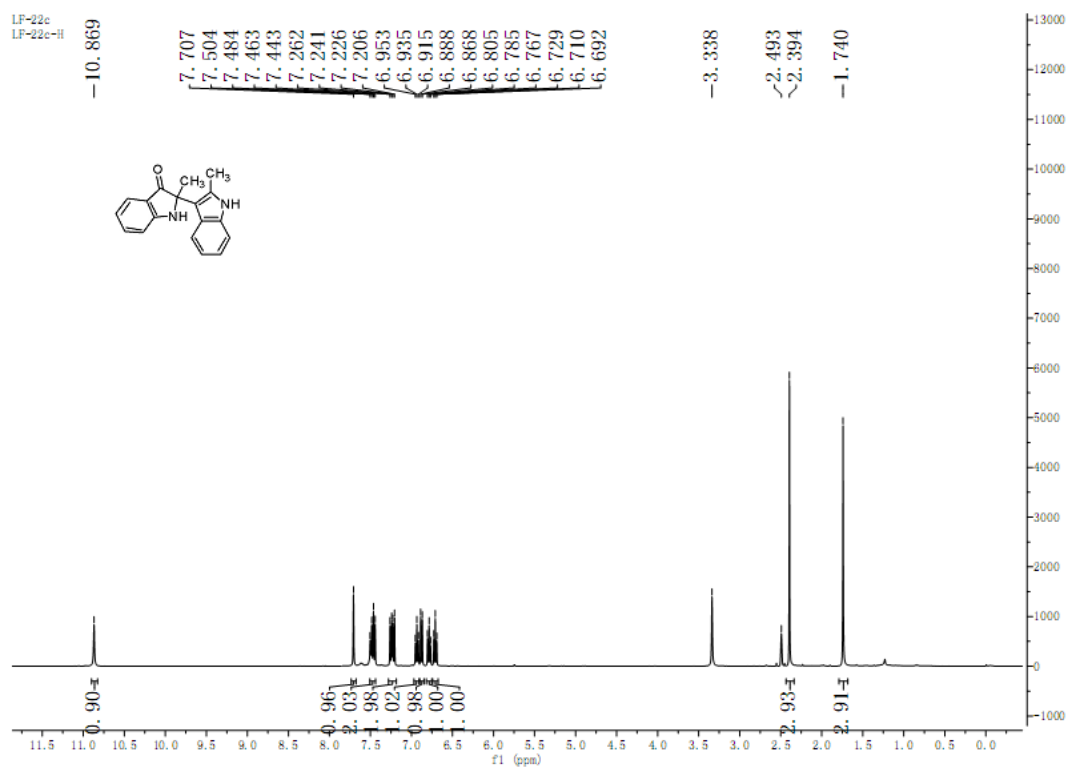




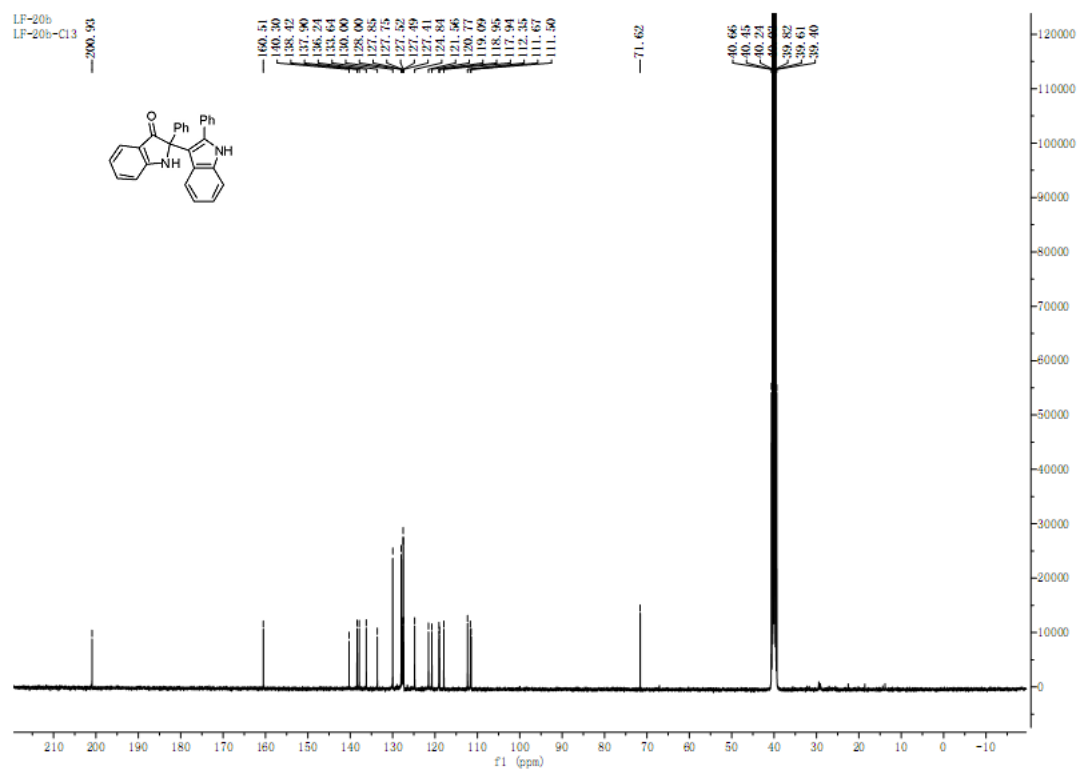
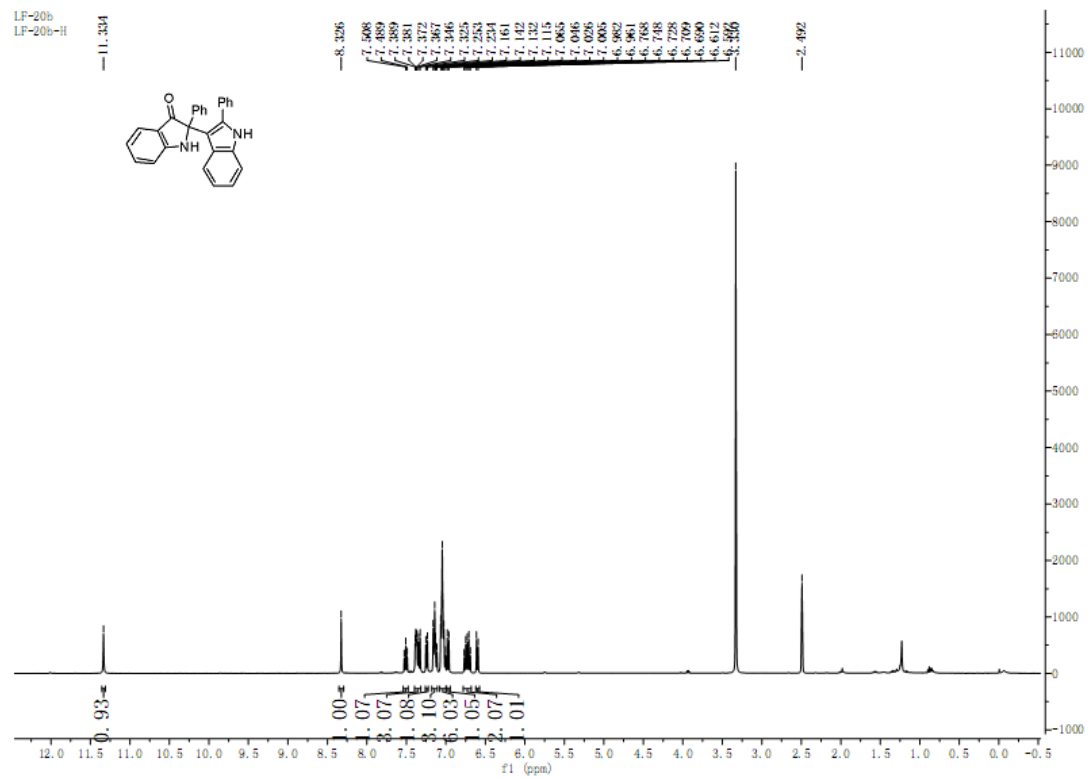
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for 12



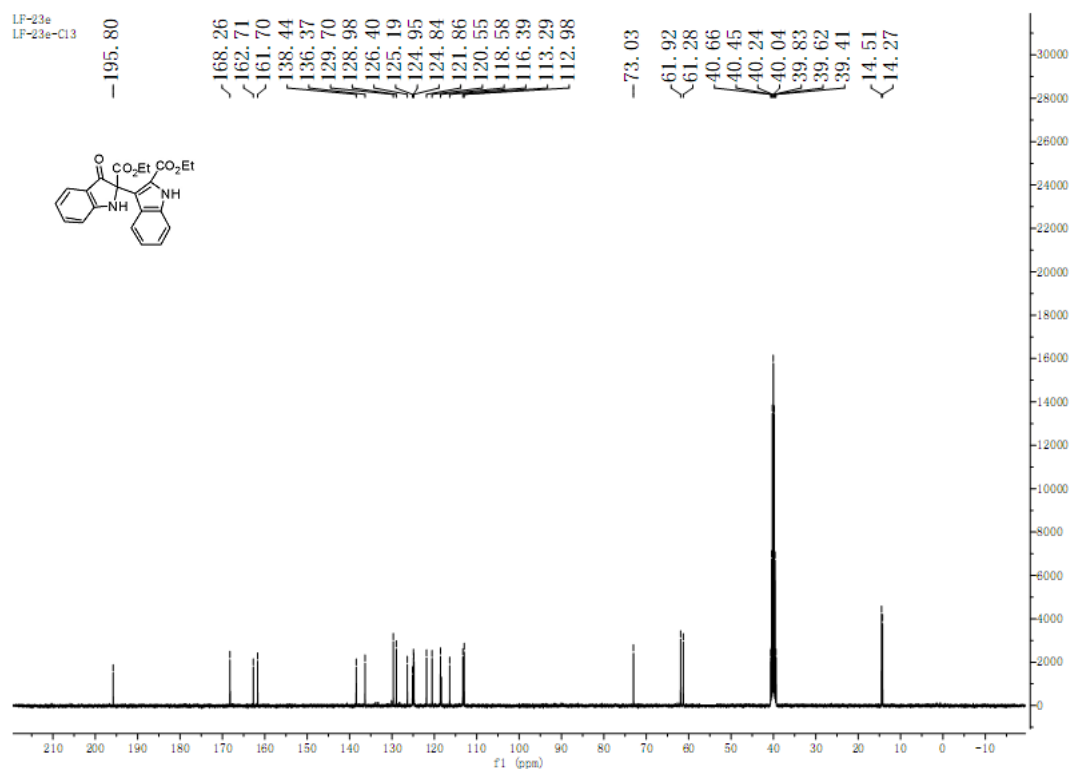
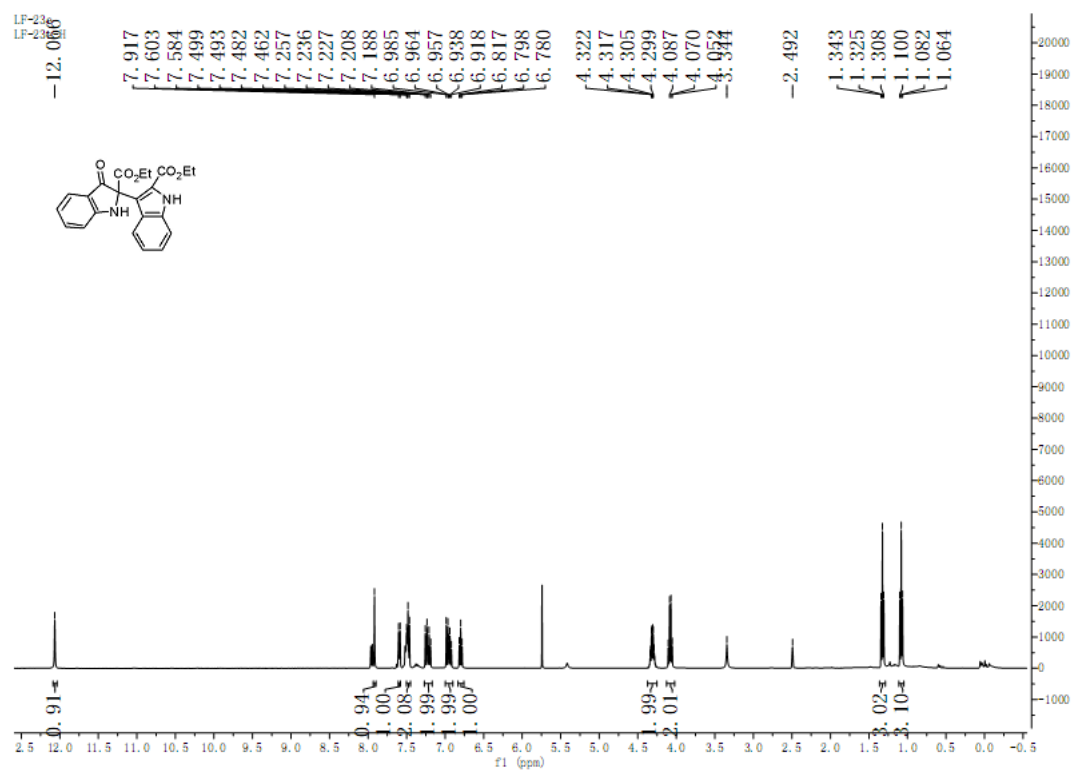
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for **13a**



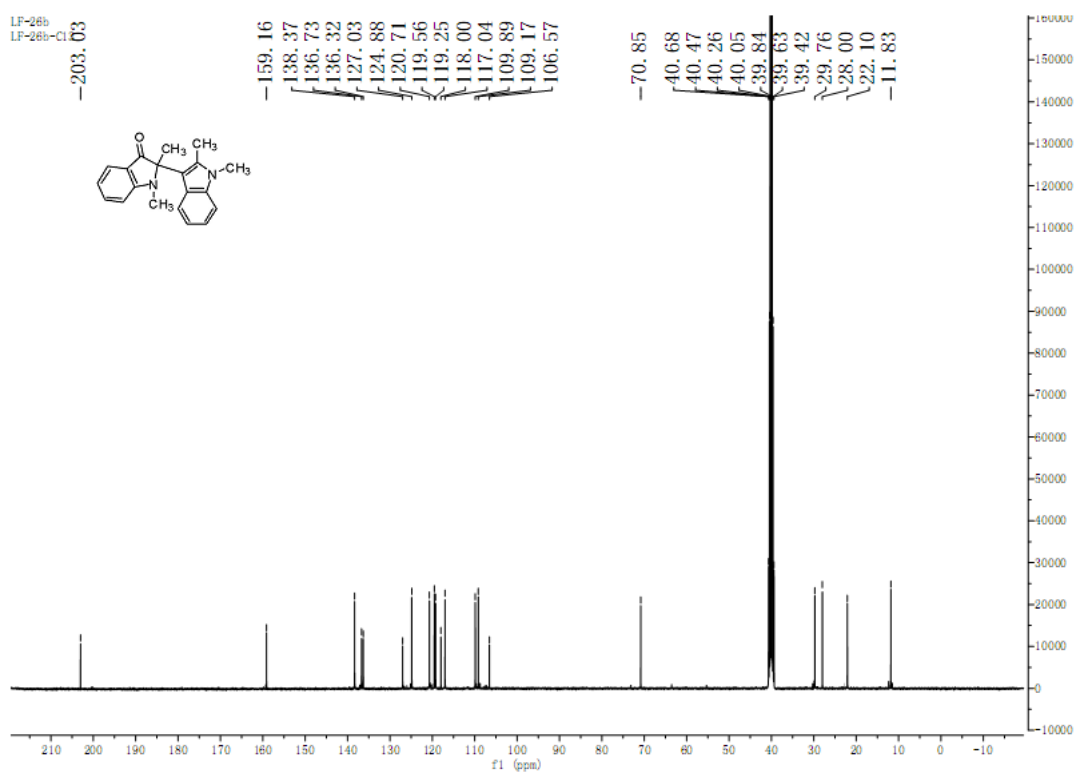
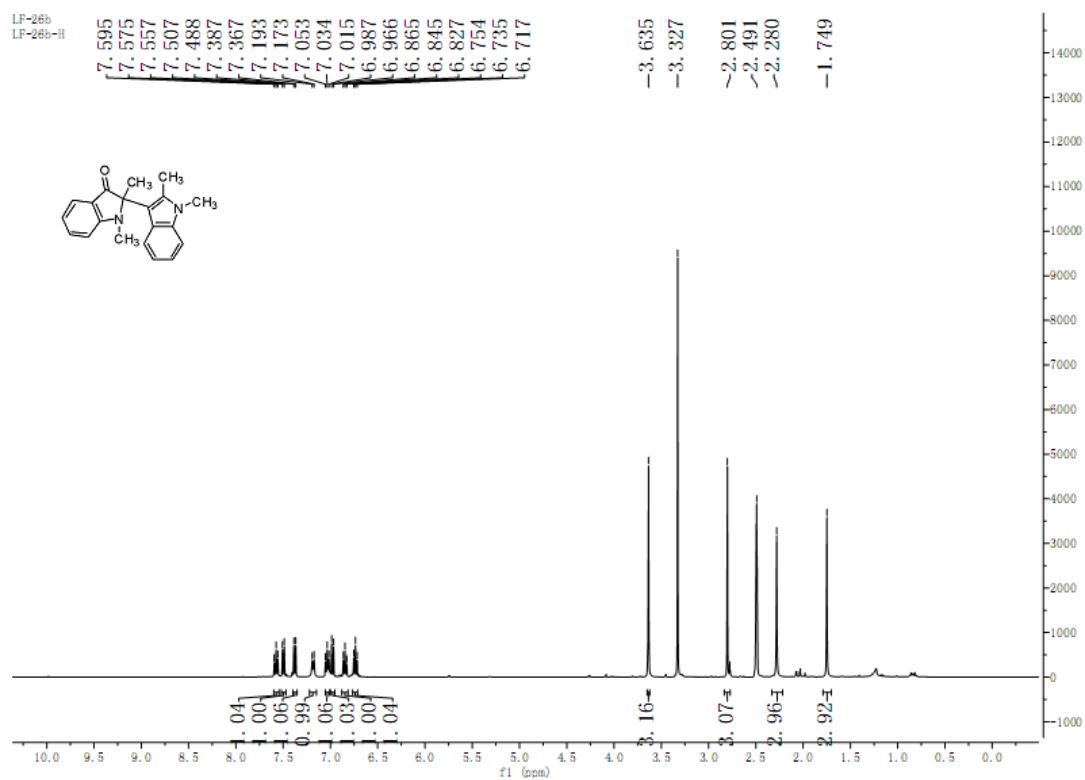
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for **13b**



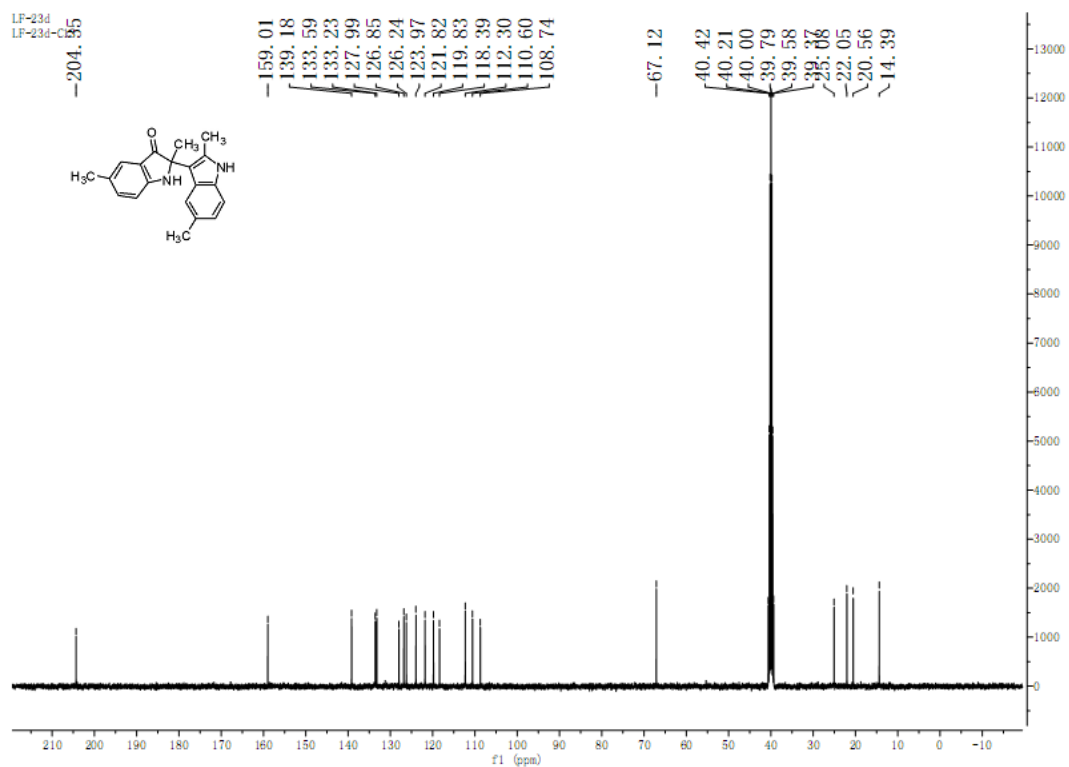
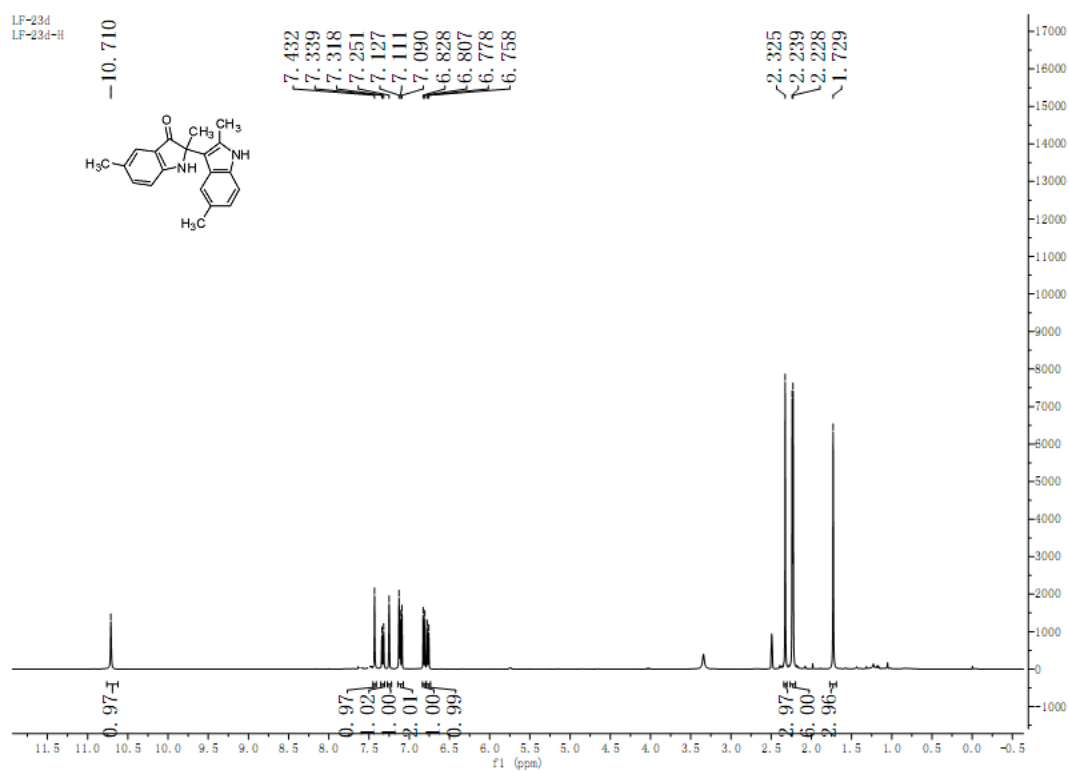
<sup>1</sup>H and <sup>13</sup>C NMR Spectra for **13c**



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra for **13d**



# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra for **13e**



## 6. References

- 1 S. Muthusamy, C. Gunanathan, S. A. Babu, E. Sures and P. Dastidar, *Chem. Commun.* **2002**, 824-825.