

# Direct synthesis of N-functionalized indoles through isomerization of azomethine ylides

Jun-Rong Song<sup>a, b</sup> Xiong-Jiang Li,<sup>a, b</sup> Jun Shi,<sup>a, b</sup> Wei Wu<sup>a, b</sup>\* and Hai Ren<sup>a, b</sup>\*

State Key Laboratory of Functions and Applications of Medicinal Plants, Guizhou Medical University, Guiyang 550014, China; The Key Laboratory of Chemistry for Natural Products of Guizhou Province and Chinese Academy of Sciences, Guiyang 550014, China

**Email:** [wuwei@gmc.edu.cn](mailto:wuwei@gmc.edu.cn); [renhai@gmc.edu.cn](mailto:renhai@gmc.edu.cn)

## Supporting Information

### Content

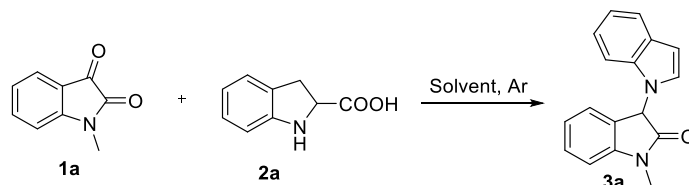
1. General information.....	2
2. Optimization of the Reaction Conditions.....	3
3. Mechanistic Studies.....	5
4. Experimental procedures and characterizations.....	6
5. Scale-up experiments.....	16
6. Transformations and applications.....	17
7. References.....	19
8. <sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of compounds.....	20

## 1. General information

All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use (unless stated otherwise). Column chromatography was performed on silica gel (Qingdao, 300 - 400 mesh) using the indicated eluents.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data were collected on a Varian Mercury 400 MHz or Agilent Mercury 600 MHz NMR spectrometer at room temperature using chloroform-*d*, DMSO-*d*<sub>6</sub> or Acetone-*d*<sub>6</sub> as a solvent and TMS as an internal standard, and chemical shift ( $\delta$ ) was expressed in parts per million (ppm).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were internally referenced to the proton ( $^1\text{H}$ ) of the internal TMS signal at 0.00 ppm, the solvent residue of DMSO-*d*<sub>6</sub> at 2.50 ppm or Acetone-*d*<sub>6</sub> at 2.05 ppm and the residual carbon nuclei ( $^{13}\text{C}$ ) of the solvent at 77.0 or 39.5 ppm, respectively. The following abbreviations were used in expressing the multiplicity: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS-ESI) were recorded on a Bruker ESI-QTOF mass spectrometer. Infrared (IR) spectra were recorded using a Fourier transform infrared spectrometer (IR 200) and the KBr disk method was adopted. The course of the reactions was monitored by thin-layer chromatography (TLC). All reactions that need to be heated were carried out in an oil bath.

## 2. Optimization of the Reaction Conditions

### 2.1 Screening of solvents <sup>a</sup>

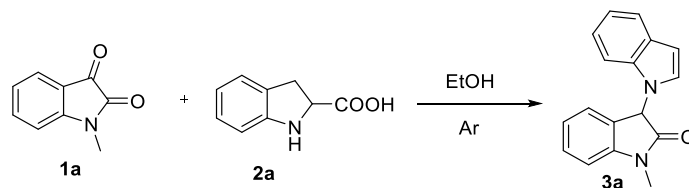


**Table S1**

Entry	Solvent	T (°C)	<i>t</i> (h)	Yield (%)
1	DMF	50	72	Trace
2	H <sub>2</sub> O	50	72	Trace
3	THF	50	48	17
4	DCM	50	72	38
5	TFE	50	48	35
6	EtOH	50	22	86
7	<sup>i</sup> PrOH	50	24	79
8	<sup>t</sup> BuOH	50	24	82
9	DMF/EtOH (1/1)	50	72	21
10	H <sub>2</sub> O/EtOH (1/1)	50	72	63
11	DCM/EtOH (1/1)	50	72	54
12	THF/EtOH (1/1)	50	72	28

<sup>a</sup> Unless noted otherwise, reactions were carried out with **1a** (0.20 mmol), **2a** (0.20 mmol), solvent (2.0 mL) and reaction carried out under Ar atmosphere, yields were isolated yields.

## 2.2 Screening of reaction temperature <sup>a</sup>



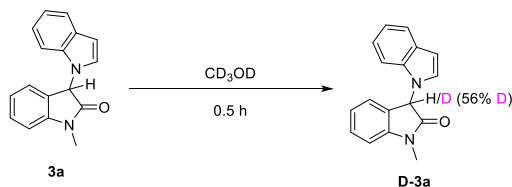
**Table S2**

Entry	Solvent	T (°C)	<i>t</i> (h)	Yield (%)
1	EtOH	25	22	20
2	EtOH	40	22	55
3	EtOH	50	22	86
4	EtOH	60	22	74
5	EtOH	70	22	74

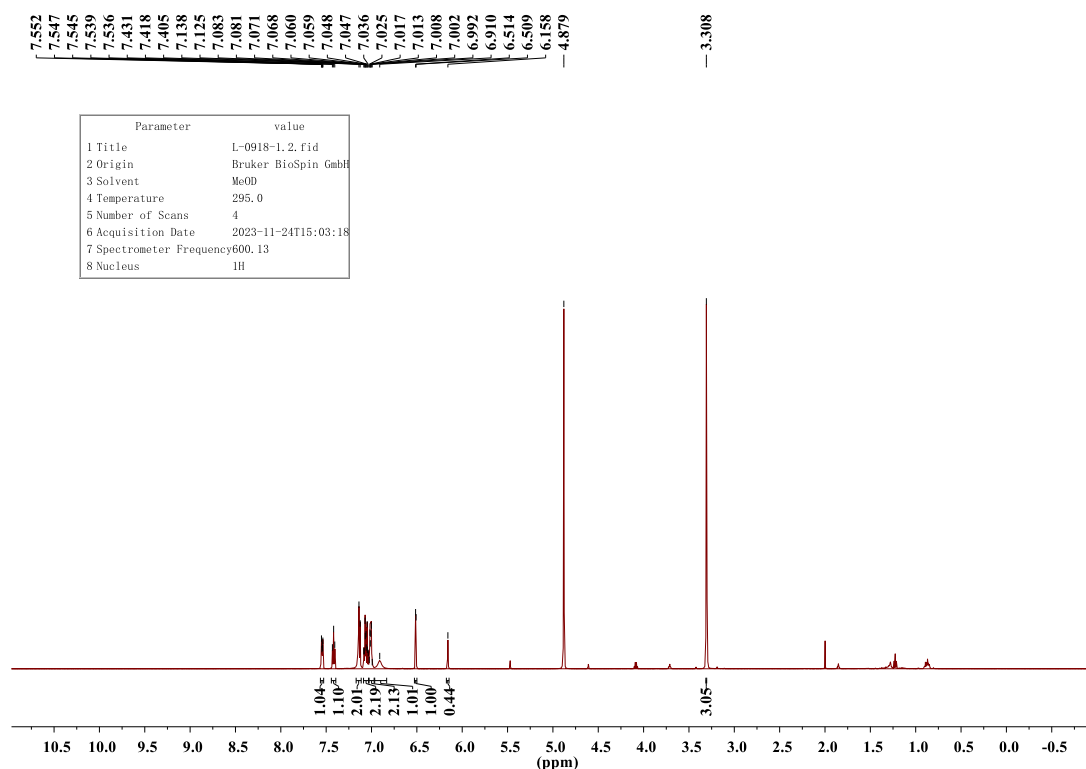
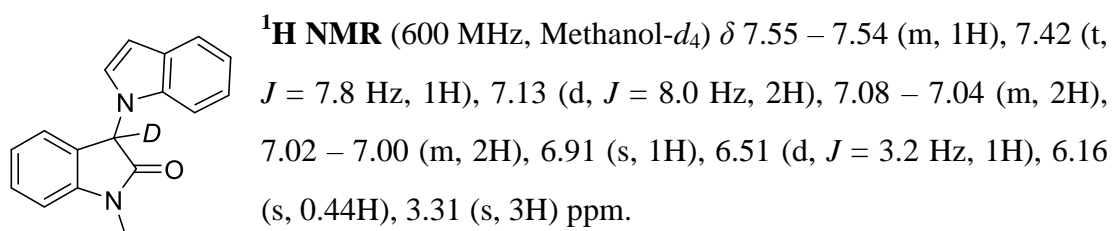
<sup>a</sup> Unless noted otherwise, reactions were carried out with **1a** (0.20 mmol), **2a** (0.20 mmol), EtOH (2.0 mL) and reaction carried out under Ar atmosphere, yields were isolated yields.

### 3. Mechanistic Studies

#### 3.1 Isotopic experiment using CD<sub>3</sub>OD

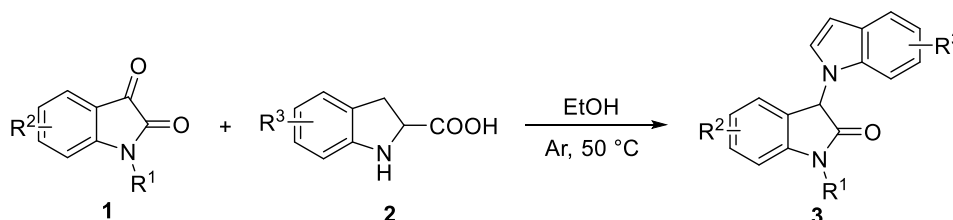


The **3a** was dissolved in 0.6 mL **CD<sub>3</sub>OD**, and after 0.5 hour, the mixture was scanned by <sup>1</sup>H NMR. **3-(1H-indol-1-yl)-1-methylindolin-2-one-3-d (D-3a)**



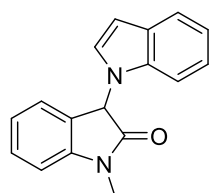
## 4. Experimental procedures and characterizations

### 4.1 Procedure for 3-(1H-indol-1-yl)-1-methylindolin-2-one



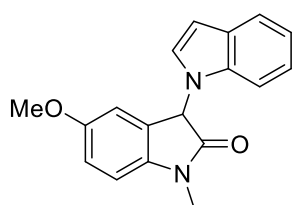
A mixture of **1** (0.2 mmol) and **2** (0.2 mmol) were added in a dried Schlenk tube, then EtOH (2 mL) was added under Ar atmosphere, and the reaction system was stirred at 50 °C. The reaction was monitored by TLC until 1-methylindoline-2,3-dione was fully consumed. The reaction was extracted with DCM. The combined organic portions were washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to afford 2-oxindole **3**.

#### 3-(1H-indol-1-yl)-1-methylindolin-2-one (3a)



Yellow solid, 22 h, 45.1 mg, 86% yield; <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 7.59-7.58 (m, 1H), 7.44-7.42 (m, 1H), 7.24 (d, *J* = 3.0 Hz, 1H), 7.15-7.11 (m, 2H), 7.06-7.03 (m, 4H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.20 (s, 1H), 3.30 (s, 3H) ppm. All analytical datas are consistent with literature <sup>[1]</sup>.

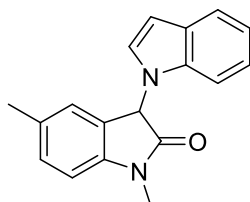
#### 3-(1H-indol-1-yl)-5-methoxy-1-methylindolin-2-one (3b)



Yellow solid, mp 155 – 156 °C, 69 h, 30.9 mg, 53% yield; <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.2 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.02 (d, *J* = 3.2 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 1.2 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 5.85 (s, 1H), 3.70 (s, 3H), 3.29 (s, 3H) ppm. IR (KBr): 3212, 1719, 1620, 1470, 1330, 1207, 908, 716 cm<sup>-1</sup>. <sup>13</sup>C NMR (150 MHz, Chloroform-*d*) δ 172.2, 156.5, 137.2, 136.2, 129.1, 127.0, 125.8, 122.1, 121.2, 120.1,

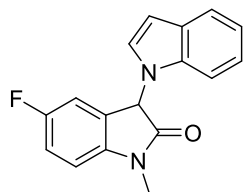
114.8, 111.8, 109.6, 109.2, 103.1, 58.7, 55.8, 26.7 ppm. **HRMS-ESI**: Exact mass calcd. for  $C_{18}H_{16}N_2O_2Na^+$  [ $M + Na$ ] $^+$ : 315.1104, Found: 315.1107.

### 3-(1H-indol-1-yl)-1,5-dimethylindolin-2-one (3c)



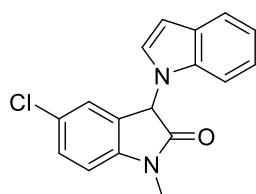
Yellow solid, mp 117 – 118 °C, 45 h, 43.6 mg, 79% yield;  $^1H$  **NMR** (600 MHz, Acetone- $d_6$ )  $\delta$  7.58 – 7.56 (m, 1H), 7.23 – 7.22 (m, 2H), 7.03 – 7.01 (m, 4H), 6.93 (s, 1H), 6.51 (d,  $J = 3.2$  Hz, 1H), 6.14 (s, 1H), 3.27 (s, 3H), 2.22 (s, 3H) ppm.  $^{13}C$  **NMR** (150 MHz, Chloroform- $d$ )  $\delta$  172.4, 141.4, 136.2, 133.0, 130.3, 129.1, 127.0, 125.7, 124.7, 122.1, 121.2, 120.0, 109.6, 108.5, 103.0, 58.5, 26.6, 21.0 ppm. **IR (KBr)**: 3569, 2927, 1719, 1648, 1460, 1330, 1207, 908, 779, 669  $cm^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $C_{18}H_{16}N_2ONa^+$  [ $M + Na$ ] $^+$ : 299.1154, Found: 299.1160.

### 5-fluoro-3-(1H-indol-1-yl)-1-methylindolin-2-one (3d)



Yellow solid, mp 165 – 167 °C, 47 h, 43.4 mg, 77% yield;  $^1H$  **NMR** (600 MHz, Chloroform- $d$ )  $\delta$  7.65 – 7.64 (m, 1H), 7.17 – 7.10 (m, 3H), 7.04 (s, 1H), 7.00 (d,  $J = 3.6$  Hz, 1H), 6.93 – 6.89 (m, 2H), 6.59 (d,  $J = 3.2$ , 1H), 5.86 (s, 1H), 3.31 (s, 3H) ppm.  $^{13}C$  **NMR** (150 MHz, Chloroform- $d$ )  $\delta$  172.1, 159.5 (d,  $^1J = 243.0$  Hz), 139.8 (d,  $^4J = 2.4$  Hz), 136.1, 129.2, 126.8, 126.2 (d,  $^3J = 8.0$  Hz), 122.3, 121.3, 120.2, 116.5 (d,  $^2J = 24.0$  Hz), 113.2 (d,  $^2J = 25.3$  Hz), 109.4, 109.3, 103.4, 58.5, 26.8 ppm.  $^{19}F$  **NMR** (564 MHz, Chloroform- $d$ )  $\delta$  -119.0 ppm, **IR (KBr)**: 3070, 2925, 1716, 1648, 1363, 1325, 1515, 920, 870, 690  $cm^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $C_{17}H_{13}N_2OFNa^+$  [ $M + Na$ ] $^+$ : 303.0910, Found: 303.0943.

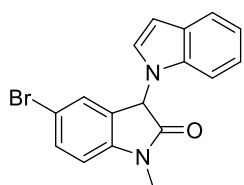
### 5-chloro-3-(1H-indol-1-yl)-1-methylindolin-2-one (3e)



Yellow solid, mp 157 – 158 °C, 42 h, 32.8 mg, 55% yield;  $^1H$  **NMR** (600 MHz, Chloroform- $d$ )  $\delta$  7.65 – 7.64 (m, 1H), 7.39 – 7.37 (m, 1H), 7.17 – 7.12 (m, 3H), 7.04 (s, 1H), 7.00 (s, 1H), 6.91 (d,  $J = 8.4$  Hz, 1H), 6.59 (d,  $J = 3.2$  Hz, 1H), 5.86 (s, 1H), 3.31 (s, 3H) ppm.  $^{13}C$  **NMR** (150 MHz, Chloroform- $d$ )  $\delta$  172.0, 142.3, 136.1, 130.1,

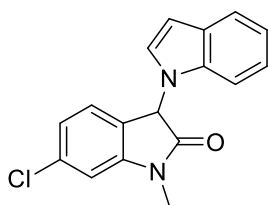
129.2, 128.8, 126.8, 126.3, 125.4, 122.4, 121.3, 120.3, 109.7, 109.4, 103.5, 58.2, 26.7 ppm. **IR (KBr)**: 3066, 2346, 1735, 1684, 1490, 1364, 1262, 881, 746, 670  $\text{cm}^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OCiNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 319.0609; Found: 319.0612.

### 5-bromo-3-(1H-indol-1-yl)-1-methylindolin-2-one (3f)



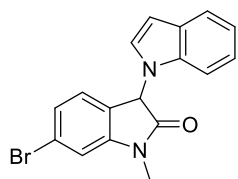
Yellow solid, mp 180 – 181  $^{\circ}\text{C}$ , 47 h, 57.1 mg, 84% yield;  $^1\text{H}$  **NMR** (600 MHz, Chloroform-*d*)  $\delta$  7.68 (dd,  $J = 6.6, 1.2$  Hz, 1H), 7.55 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.31 (s, 1H), 7.22 – 7.14 (m, 2H), 7.07 (s, 1H), 7.03 (d,  $J = 1.8$  Hz, 1H), 6.86 (d,  $J = 8.3$  Hz, 1H), 6.63 (d,  $J = 3.0$  Hz, 1H), 5.88 (s, 1H), 3.32 (s, 3H) ppm.  $^{13}\text{C}$  **NMR** (150 MHz, Chloroform-*d*)  $\delta$  171.8, 142.7, 136.0, 133.0, 129.1, 128.0, 126.8, 126.5, 122.3, 121.3, 120.2, 115.9, 110.2, 109.3, 103.4, 58.1, 26.7 ppm. **IR (KBr)**: 3226, 1735, 1612, 1490, 1364, 1328, 1103, 746, 670  $\text{cm}^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OBrNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 363.0103; Found: 363.0109.

### 6-chloro-3-(1H-indol-1-yl)-1-methylindolin-2-one (3g)



Yellow solid, mp 153 – 155  $^{\circ}\text{C}$ , 40 h, 45.0 mg, 76% yield;  $^1\text{H}$  **NMR** (600 MHz, Chloroform-*d*)  $\delta$  7.64 (d,  $J = 7.2$  Hz, 1H), 7.18 – 7.10 (m, 2H), 7.08 (d,  $J = 7.8$  Hz, 1H), 7.04 – 7.03 (m, 2H), 6.98 (d,  $J = 1.8$  Hz, 2H), 6.58 (d,  $J = 3.2$  Hz, 1H), 5.84 (s, 1H), 3.30 (s, 3H) ppm.  $^{13}\text{C}$  **NMR** (150 MHz, Chloroform-*d*)  $\delta$  172.4, 145.0, 136.1, 136.1, 129.2, 126.8, 125.9, 123.2, 122.9, 122.3, 121.3, 120.2, 109.6, 109.5, 103.3, 58.0, 26.7 ppm. **IR (KBr)**: 1735, 1612, 1535, 1459, 1305, 1200, 1115, 739, 652  $\text{cm}^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OCiNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 319.0614; Found: 319.0619.

### 6-bromo-3-(1H-indol-1-yl)-1-methylindolin-2-one (3h)

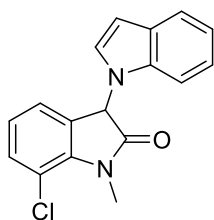


Yellow solid, mp 158 – 159  $^{\circ}\text{C}$ , 40 h, 57.8 mg, 90% yield;  $^1\text{H}$  **NMR** (600 MHz, Chloroform-*d*)  $\delta$  7.65 – 7.63 (m, 1H), 7.20 – 7.12 (m, 4H), 7.05 – 6.98 (m, 3H), 6.58 (d,  $J = 3.0$  Hz, 1H), 5.79 (s, 1H), 3.28 (s, 3H) ppm.  $^{13}\text{C}$  **NMR** (150 MHz, Chloroform-*d*)  $\delta$



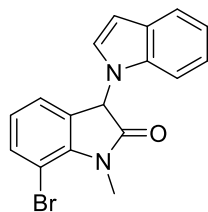
172.2, 145.1, 136.0, 129.1, 126.8, 126.2, 126.1, 123.8, 123.4, 122.2, 121.2, 120.2, 112.3, 109.4, 103.3, 58.0, 26.7 ppm. **IR (KBr):** 3066, 1773, 1604, 1559, 1460, 13118, 1253, 1088, 745, 652  $\text{cm}^{-1}$ . **HRMS-ESI:** Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OBrNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 363.0103; Found: 363.0109.

### 7-chloro-3-(1H-indol-1-yl)-1-methylindolin-2-one (3i)



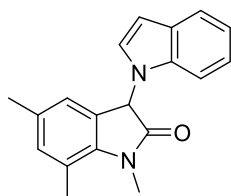
Yellow solid, mp 150 – 151  $^{\circ}\text{C}$ , 45 h, 35.0 mg, 60% yield;  $^1\text{H}$  **NMR** (600 MHz, Acetone- $d_6$ )  $\delta$  7.59 (d,  $J = 8.2$  Hz, 1H), 7.39 (d,  $J = 7.7$  Hz, 1H), 7.28 (s, 1H), 7.10 – 6.99 (m, 5H), 6.54 (d,  $J = 3.6$  Hz, 1H), 6.27 (s, 1H), 3.65 (d,  $J = 1.3$  Hz, 3H) ppm.  $^{13}\text{C}$  **NMR** (150 MHz, Chloroform- $d$ )  $\delta$  172.7, 1139.6, 136.1, 132.4, 129.2, 127.4, 126.8, 124.1, 123.4, 122.3, 121.3, 120.2, 116.2, 109.4, 103.4, 58.1, 30.1 ppm. **IR (KBr):** 1735, 1654, 1608, 1459, 1363, 1340, 1205, 1108, 739, 669  $\text{cm}^{-1}$ . **HRMS-ESI:** Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OCINa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 319.0614; Found: 319.0608.

### 7-bromo-3-(1H-indol-1-yl)-1-methylindolin-2-one (3j)



Yellow solid, mp 184 – 185  $^{\circ}\text{C}$ , 45 h, 46.2 mg, 68% yield;  $^1\text{H}$  **NMR** (600 MHz, Chloroform- $d$ )  $\delta$  7.66 (d,  $J = 7.8$  Hz, 1H), 7.53 (d,  $J = 8.2$  Hz, 1H), 7.21 – 7.14 (m, 2H), 7.08 (dt,  $J = 8.4, 1.2$  Hz, 1H), 7.01 (d,  $J = 2.4$  Hz, 1H), 6.90 (dd,  $J = 8.4, 7.2$  Hz, 1H), 6.61 (dd,  $J = 3.0, 0.6$  Hz, 1H), 5.87 (s, 1H), 3.73 (s, 3H) ppm.  $^{13}\text{C}$  **NMR** (150 MHz, Chloroform- $d$ )  $\delta$  172.9, 141.1, 136.1, 135.7, 129.1, 127.7, 126.8, 124.4, 124.0, 122.3, 121.3, 120.2, 109.4, 103.4, 103.0, 58.0, 30.3 ppm. **IR (KBr):** 1719, 1607, 1559, 1459, 1334, 1220, 1101, 735, 652  $\text{cm}^{-1}$ . **HRMS-ESI:** Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OBrNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 363.0103; Found: 363.0109.

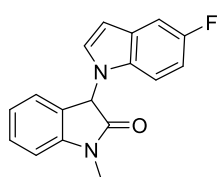
### 3-(1H-indol-1-yl)-1,5,7-trimethylindolin-2-one (3k)



White solid, mp 124 – 125  $^{\circ}\text{C}$ , 40 h, 45.1 mg, 78% yield;  $^1\text{H}$  **NMR** (600 MHz, Chloroform- $d$ )  $\delta$  7.64 (d,  $J = 7.6$  Hz, 1H), 7.19 – 7.07 (m, 3H), 7.01 (d,  $J = 3.2$  Hz, 1H), 6.93 (s, 1H), 6.80

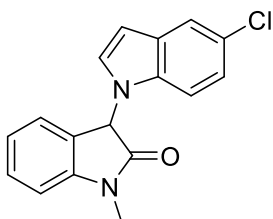
(s, 1H), 6.57 (d,  $J = 3.2$  Hz, 1H), 5.79 (s, 1H), 3.57 (s, 3H), 2.61 (s, 3H), 2.19 (s, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )  $\delta$  173.2, 139.0, 136.2, 134.2, 132.8, 129.1, 127.0, 125.4, 123.4, 122.0, 121.1, 120.1, 120.0, 109.6, 102.8, 58.2, 30.0, 20.6, 18.8 ppm. **IR (KBr):** 2919, 1735, 1608, 1559, 1469, 1345, 1331, 1080, 756, 699  $\text{cm}^{-1}$ . **HRMS-ESI:** Exact mass calcd. for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{ONa}^+$   $[\text{M} + \text{Na}]^+$ : 313.1311; Found: 313.1316.

### 3-(5-fluoro-1H-indol-1-yl)-1-methylindolin-2-one (3l)



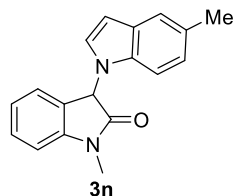
Yellow solid, m.p. 119.6-120.4  $^{\circ}\text{C}$ , 38 h, 13.9 mg, 25% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.42 (t,  $J = 7.8$  Hz, 1H), 7.27 – 7.25 (m, 1H), 7.18 – 7.17 (m, 1H), 7.07 (t,  $J = 7.4$  Hz, 1H), 7.05 (d,  $J = 3.2$  Hz, 1H), 6.98 – 6.91 (m, 2H), 6.89 – 6.86 (m, 1H), 6.52 (d,  $J = 3.4$  Hz, 1H), 5.82 (s, 1H), 3.31 (s, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )  $\delta$  172.3, 158.1 (d,  $^1J_{\text{C-F}} = 234.8$  Hz), 143.9, 132.7, 130.3, 129.5 (d,  $^3J_{\text{C-F}} = 10.0$  Hz), 128.6, 125.0, 124.2, 123.4, 110.5 (d,  $^2J_{\text{C-F}} = 26.6$  Hz), 110.3 (d,  $^3J_{\text{C-F}} = 9.8$  Hz), 108.8, 106.0 (d,  $^2J_{\text{C-F}} = 23.4$  Hz), 103.0 (d,  $^4J_{\text{C-F}} = 4.6$  Hz), 58.6, 26.6 ppm.  $^{19}\text{F}$  NMR (565 MHz, Chloroform- $d$ )  $\delta$  -124.6. IR (neat)  $\nu$ : 2922, 1700, 11614, 1147, 1199, 754, 722  $\text{cm}^{-1}$ . **HRMS (ESI)  $m/z$ :**  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{ON}_2\text{FNa}$  303.0904; Found 303.0892.

### 3-(6-chloro-1H-indol-1-yl)-1-methylindolin-2-one (3m)



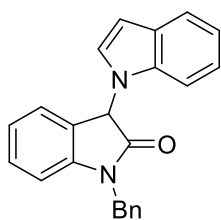
The **3l** was performed with the use of TFE as solvent instead of EtOH in 0.1 mmol scale. Yellow solid, mp 160 – 161  $^{\circ}\text{C}$ , 70 h, 13.0 mg, 44% yield;  $^1\text{H}$  NMR (600 MHz, Chloroform- $d$ )  $\delta$  7.61 (d,  $J = 1.8$  Hz, 1H), 7.45 (t,  $J = 7.8$  Hz, 1H), 7.19 (d,  $J = 7.2$  Hz, 1H), 7.13 – 7.04 (m, 3H), 7.00 (d,  $J = 7.8$  Hz, 2H), 6.53 (d,  $J = 3.6$  Hz, 1H), 5.85 (s, 1H), 3.33 (s, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Chloroform- $d$ )  $\delta$  172.2, 143.8, 134.6, 130.4, 130.2, 128.3, 125.8, 125.0, 124.1, 123.4, 122.4, 120.6, 120.7, 108.9, 102.6, 58.5, 26.6 ppm. **IR (KBr):** 3069, 1727, 1621, 1477, 1458, 1320, 1199, 732  $\text{cm}^{-1}$ . **HRMS-ESI:** Exact mass calcd. for  $\text{C}_{17}\text{H}_{13}\text{N}_2\text{OCINa}^+$   $[\text{M} + \text{Na}]^+$ : 319.0614; Found: 319.0619.

### 1-methyl-3-(5-methyl-1H-indol-1-yl)indolin-2-one (3n)



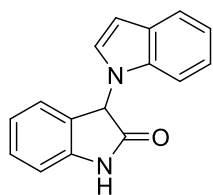
Grey solid, m.p. 119.0-121.1 °C 24 h, 12.8 mg, 23% yield.  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.38 (m, 2H), 7.16 (d,  $J = 7.2$  Hz, 1H), 7.04 (t,  $J = 7.2$  Hz, 1H), 6.97 – 6.91 (m, 4H), 6.48 (d,  $J = 3.2$  Hz, 1H), 5.83 (s, 1H), 3.31 (s, 3H), 2.41 (s, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  172.5, 143.8, 134.6, 130.1, 129.4, 129.3, 127.0, 125.0, 124.7, 123.7, 123.3, 120.9, 109.2, 108.7, 102.5, 58.5, 26.6, 21.3 ppm. IR (neat)  $\nu$  : 2921, 1703, 1612, 1470, 1199, 1125, 750, 714  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{ON}_2\text{Na}$  299.1155; Found 299.1145.

### 1-benzyl-3-(1H-indol-1-yl) indolin-2-one (3o)



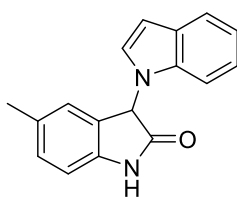
Yellow solid, 68 h, 51.4 mg, 76% yield;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.66 – 7.65 (m, 1H), 7.40 – 7.35 (m, 4H), 7.33 – 7.29 (m, 2H), 7.18 (d,  $J = 7.4$  Hz, 1H), 7.14 – 7.10 (m, 2H), 7.06 – 7.00 (m, 3H), 6.90 (d,  $J = 7.8$  Hz, 1H), 6.60 (d,  $J = 3.0$  Hz, 1H), 5.96 (s, 1H), 5.06 (d,  $J = 15.6$  Hz, 1H), 4.93 (d,  $J = 15.6$  Hz, 1H) ppm. All analytical data are consistent with literature <sup>[1]</sup>.

### 3-(1H-indol-1-yl) indolin-2-one (3p)



Yellow solid, 48 h, 36.7 mg, 74% yield;  $^1\text{H}$  NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  10.89 (s, 1H), 7.59 – 7.57 (m, 1H), 7.36 – 7.29 (m, 2H), 7.04 – 6.94 (m, 6H), 6.53 (d,  $J = 3.2$  Hz, 1H), 6.36 (s, 1H). ppm.  $^{13}\text{C}$  NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  174.2, 142.2, 135.6, 129.7, 128.7, 125.9, 124.4, 122.2, 121.5, 120.8, 119.6, 110.3, 109.9, 101.8, 58.8 ppm. All analytical data are consistent with literature <sup>[1]</sup>.

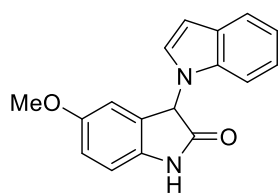
### 3-(1H-indol-1-yl)-5-methylindolin-2-one (3q)



Yellow solid, 28 h, 35.6 mg, 68% yield;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  9.03 (s, 1H), 7.70 – 7.66 (m, 1H), 7.20 – 7.15 (m, 3H), 7.12 – 7.08 (m, 2H), 6.96 (s, 1H), 6.80 (d,  $J = 7.8$  Hz, 1H), 6.63 (d,  $J = 3.0$  Hz, 1H), 5.88 (s, 1H), 2.25 (s, 3H) ppm.

All analytical data are consistent with literature <sup>[1]</sup>.

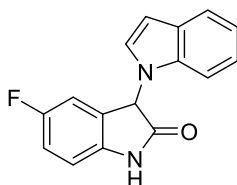
### 3-(1H-indol-1-yl)-5-methoxyindolin-2-one (3r)



yellow solid, 48 h, 50.6 mg, 91% yield;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  9.42 (s, 1H), 7.68 (d,  $J = 6.6$  Hz, 1H), 7.20 – 7.15 (m, 3H), 7.09 (s, 1H), 6.78 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.73 (d,  $J = 2.4$  Hz, 1H), 6.69 (d,  $J = 8.4$  Hz, 1H), 6.63 (d,  $J = 3.0$

Hz, 1H), 5.86 (s, 1H), 3.69 (s, 3H) ppm. All analytical data are consistent with literature <sup>[1]</sup>.

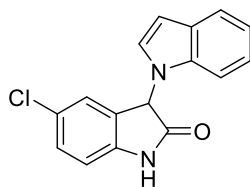
### 5-fluoro-3-(1H-indol-1-yl) indolin-2-one (3s)



Brown solid, 48 h, 43.1 mg, 81% yields;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  9.31 (s, 1H), 7.68 – 7.63 (m, 1H), 7.33 (d,  $J = 6.5$  Hz, 1H), 7.24 – 6.96 (m, 5H), 6.62 – 6.55 (m, 2H), 5.84 (s, 1H) ppm.  $^{19}\text{F NMR}$  (564 MHz, Chloroform-*d*)  $\delta$  -118.8 ppm,

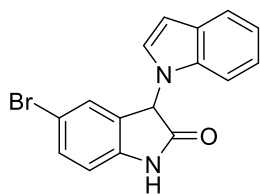
All analytical data are consistent with literature <sup>[1]</sup>.

### 5-chloro-3-(1H-indol-1-yl) indolin-2-one (3t)



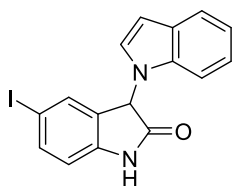
Pale yellow solid, 48 h, 49.9 mg, 88% yields;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  9.39 (s, 1H), 7.70 – 7.66 (m, 1H), 7.20 – 7.17 (m, 3H), 7.10 – 7.04 (m, 3H), 7.10 – 7.04 (m, 2H), 5.85 (s, 1H) ppm. All analytical data are consistent with literature <sup>[1]</sup>.

### 5-bromo-3-(1H-indol-1-yl) indolin-2-one (3u)



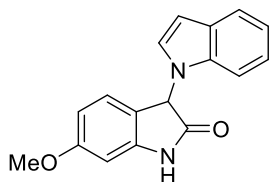
Brown solid, 42 h, 34.6 mg, 53% yields; **<sup>1</sup>H NMR** (600 MHz, acetone-*d*<sub>6</sub>): δ 9.92 (s, br, 1H), 7.61-7.58 (m, 1H), 7.54-7.50 (m, 1H), 7.31 (d, *J* = 3.3 Hz, 1H), 7.25 (s, br, 1H), 7.10-7.04 (m, 4H), 6.55 (d, *J* = 3.3 Hz, 1H), 6.28 (s, 1H); All analytical data are consistent with literature <sup>[1]</sup>.

### 3-(1H-indol-1-yl)-5-iodoindolin-2-one (3v)



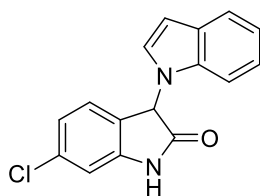
Yellow solid, mp 184 – 185 °C, 46 h, 60.6 mg, 81% yield; **<sup>1</sup>H NMR** (600 MHz, DMSO-*d*<sub>6</sub>) δ 11.01 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.35 (s, 1H), 7.26 (s, 1H), 7.07 – 6.96 (m, 3H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 3.6 Hz, 1H), 6.39 (s, 1H) ppm. **<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sub>6</sub>) δ 173.5, 141.9, 138.2, 132.4, 128.7, 128.6, 121.7, 120.8, 119.7, 112.8, 109.7, 102.0, 84.5, 58.4 ppm. **IR (KBr)**: 1710, 1664, 1624, 1559, 1515, 1469, 1314, 1216, 853, 792, 669 cm<sup>-1</sup>. **HRMS-ESI**: Exact mass calcd. for C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>OINa<sup>+</sup> [M + Na]<sup>+</sup>: 396.9811; Found: 396.9808.

### 3-(1H-indol-1-yl)-6-methoxyindolin-2-one (3w)



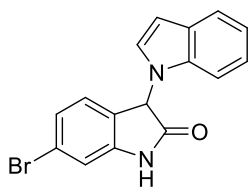
Yellow solid, mp 144 – 145 °C, 48 h, 39.5 mg, 71% yield; **<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.19 – 7.13 (m, 3H), 7.08 – 7.05 (m, 2H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.56 – 6.53 (m, 2H), 5.87 (s, 1H), 3.80 (s, 3H) ppm. **<sup>13</sup>C NMR** (150 MHz, Chloroform-*d*) δ 175.8, 161.5, 142.3, 136.1, 129.2, 127.0, 126.1, 122.2, 121.2, 120.1, 116.6, 109.7, 108.3, 103.0, 97.8, 58.6, 55.6 ppm. **IR (KBr)**: 1773, 1719, 1630, 1508, 1457, 1344, 1304, 1157, 738, 652 cm<sup>-1</sup>. **HRMS-ESI**: Exact mass calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Na<sup>+</sup> [M + Na]<sup>+</sup>: 301.0948; Found: 301.0953.

### 6-chloro-3-(1H-indol-1-yl) indolin-2-one (3x)



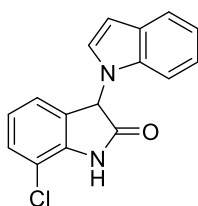
Yellow solid, mp 174 – 175 °C, 48 h, 47.3 mg, 84% yield;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  8.64 (s, 1H), 7.67 (d,  $J = 7.2$  Hz, 1H), 7.20 – 7.14 (m, 2H), 7.11 – 7.02 (m, 4H), 6.97 (d,  $J = 1.8$  Hz, 1H), 6.62 (d,  $J = 3.0$  Hz, 1H), 5.88 (s, 1H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Chloroform-*d*)  $\delta$  174.5, 141.9, 135.9, 129.2, 126.3, 123.5, 123.4, 122.4, 121.4, 120.3, 111.3, 109.5, 103.5, 29.7 ppm. IR (KBr): 2963, 1697, 1608, 1509, 1469, 1261, 1019, 756, 652  $\text{cm}^{-1}$ . HRMS-ESI: Exact mass calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{OCINa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 305.0452; Found: 305.0453.

### 6-bromo-3-(1H-indol-1-yl) indolin-2-one (3y)



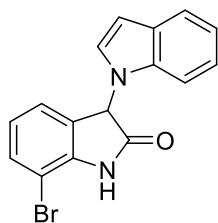
Yellow solid, mp 183 – 185 °C, 72 h, 57.6 mg, 88% yield;  $^1\text{H}$  NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.02 (s, 1H), 7.61 – 7.57 (m, 1H), 7.52 – 7.50 (m, 1H), 7.35 (br, 1H), 7.14 (s, 1H), 7.07 – 7.02 (m, 2H), 6.97 (d,  $J = 8.4$  Hz, 2H), 6.54 (dd,  $J = 3.6, 0.6$  Hz, 1H), 6.42 (s, 1H).  $^{13}\text{C}$  NMR (150 MHz, DMSO-*d*<sub>6</sub>) 173.7, 141.5, 132.4, 128.7, 128.3, 127.0, 121.7, 120.8, 119.7, 113.8, 112.3, 109.7, 102.1, 58.6 ppm. IR (KBr): 3040, 1717, 1620, 1470, 1327, 1196, 897, 866, 748  $\text{cm}^{-1}$ . HRMS-ESI: Exact mass calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{OBrNa}^+$  [ $\text{M} + \text{Na}$ ] $^+$ : 348.9947; Found: 348.9952.

### 7-chloro-3-(1H-indol-1-yl) indolin-2-one (3z)



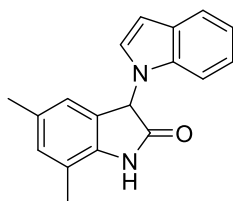
Yellow solid, 72 h, 51.3 mg, 91% yield;  $^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.96 (s, 1H), 7.67 (d,  $J = 7.8$  Hz, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 7.21 – 7.14 (m, 3H), 7.08 – 7.05 (m, 2H), 7.03 – 7.00 (m, 1H), 6.62 (d,  $J = 3.0$  Hz, 1H), 5.99 (s, 1H) ppm. All analytical data are consistent with literature <sup>[1]</sup>.

### 7-bromo-3-(1H-indol-1-yl) indolin-2-one (3aa)



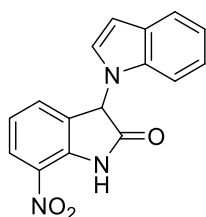
White solid, 28 h, 44.3 mg, 68% yield;  $^1\text{H NMR}$  (600 MHz, Acetone- $d_6$ )  $\delta$  9.98 (s, 1H), 7.61 (d,  $J = 7.2$  Hz, 1H), 7.55 (d,  $J = 7.2$  Hz, 1H), 7.32 (d,  $J = 3.0$  Hz, 1H), 7.14 – 7.05 (m, 4H), 6.98 (t,  $J = 7.2$  Hz, 1H), 6.57 (d,  $J = 3.6$  Hz, 1H), 6.36 (s, 1H) ppm. All analytical data are consistent with literature <sup>[1]</sup>.

### 3-(1H-indol-1-yl)-5,7-dimethylindolin-2-one (3ab)



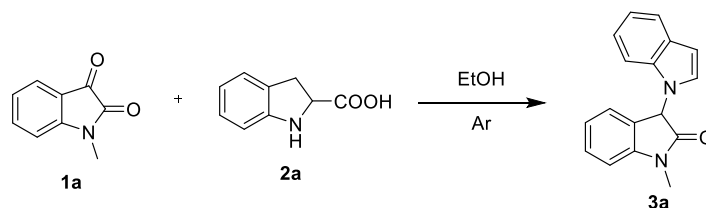
Yellow solid, mp 114 – 115 °C, 48 h, 46.4 mg, 84% yield;  $^1\text{H NMR}$  (600 MHz, Chloroform- $d$ )  $\delta$  8.83 (s, 1H), 7.65 (d,  $J = 7.2$  Hz, 1H), 7.15 – 7.09 (m, 3H), 7.06 (d,  $J = 3.0$  Hz, 1H), 6.93 (s, 1H), 6.80 (s, 1H), 6.59 (d,  $J = 3.6$  Hz, 1H), 5.87 (s, 1H), 2.20 (s, 6H) ppm.  $^{13}\text{C NMR}$  (150 MHz, Chloroform- $d$ )  $\delta$  175.1, 137.0, 136.2, 132.9, 131.9, 129.1, 127.2, 124.9, 123.1, 122.1, 121.2, 120.0, 119.8, 109.7, 102.9, 59.3, 20.9, 16 ppm; **IR (KBr)**: 2974, 2925, 1716, 1648, 1492, 1325, 1126, 834, 761, 690  $\text{cm}^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{ONa}^+$   $[\text{M} + \text{Na}]^+$ : 299.1155; Found: 299.1160.

### 3-(1H-indol-1-yl)-7-nitroindolin-2-one (3ac)

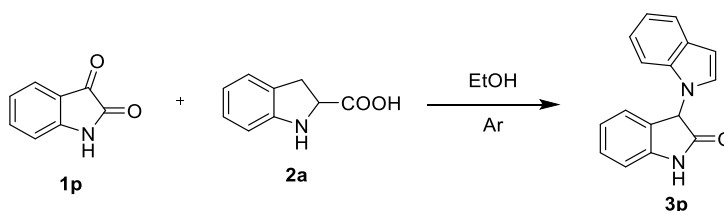


Yellow solid, mp 134 – 135 °C, 72 h, 37.0 mg, 63% yield;  $^1\text{H NMR}$  (600 MHz, DMSO- $d_6$ )  $\delta$  11.59 (s, 1H), 8.12 (d,  $J = 9.0$  Hz, 1H), 7.62 – 7.57 (m, 1H), 7.40 (d,  $J = 7.2$  Hz, 2H), 7.16 (dd,  $J = 9.0, 7.2$  Hz, 1H), 7.06 – 7.05 (m, 3H), 6.58 – 6.56 (m, 2H) ppm.  $^{13}\text{C NMR}$  (150 MHz, DMSO- $d_6$ )  $\delta$  174.7, 138.7, 131.6, 130.5, 129.3, 128.7, 124.5, 122.4, 121.8, 120.9, 119.8, 109.8, 102.4, 79.2, 57.6 ppm. **IR (KBr)**: 1773, 1725, 1671, 1654, 1459, 1196, 739, 646  $\text{cm}^{-1}$ . **HRMS-ESI**: Exact mass calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3\text{Na}^+$   $[\text{M} + \text{Na}]^+$ : 316.0698; Found: 316.0688.

## 5. Scale-up experiments



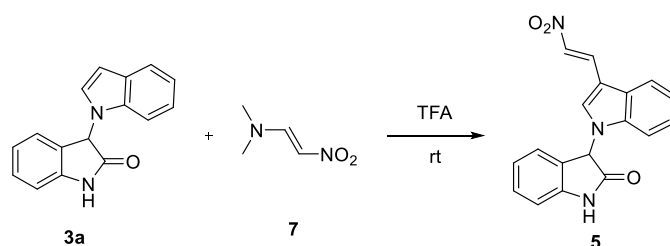
**Procedure:** A mixture of **1a** (1.13 g, 7.0 mmol) and **2a** (1.14 g, 7.0 mmol) were added in a dried Schlenk tube, then EtOH (70 mL) was added under Ar atmosphere, and the reaction system was stirred at 50 °C. The reaction was monitored by TLC until 1-methylindoline-2,3-dione was fully consumed. The reaction was extracted with DCM. The combined organic portions were washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to afford 2-oxindole **3a** (1.65 g, 90% yield).



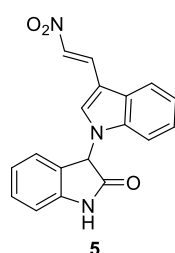
**Procedure:** A mixture of **1p** (1.03 g, 7.0 mmol) and **2a** (1.14 g, 7.0 mmol) were added in a dried Schlenk tube, then EtOH (70 mL) was added under Ar atmosphere, and the reaction system was stirred at 50 °C. The reaction was monitored by TLC until compound **1** was fully consumed. The reaction was extracted with DCM. The combined organic portions were washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) to afford 2-oxindole **3p** (1.36 g, 78% yield).



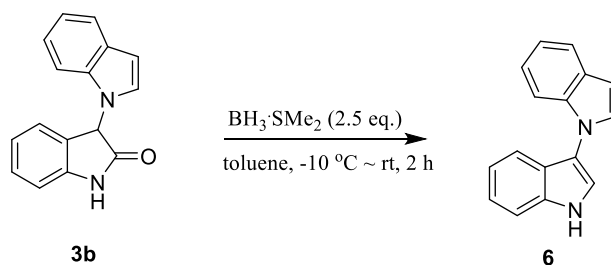
## 6. Transformations and applications



To a solution of 1,1-dimethylamino-2-nitroethylene (0.2 mmol) in trifluoroacetic acid (1 mL) was added **3a** (0.2 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 0.5 hours. The reaction mixture was treated to pH 9~10 using saturated NaHCO<sub>3</sub> and extracted with DCM. The combined organic layers were washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub>, the filtrate was concentrated under reduced pressure, purified by flash chromatography (Petroleum ether/ethyl acetate = 2/1) to give product **5** (45.5 mg, 71% yield).



Yellow solid, 45.5 mg, 71% yield. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 11.02 (s, 1H), 8.41 (d, *J* = 13.6 Hz, 1H), 8.27 (s, 1H), 8.07 (d, *J* = 13.6 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.24 (m, 4H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 173.3, 142.3, 133.6, 132.5, 130.2, 125.6, 124.8, 124.7, 123.9, 122.5, 122.5, 121.1, 111.2, 110.6, 108.6, 79.2 ppm. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>O<sub>3</sub>N<sub>3</sub>Na 342.0849; Found 342.0839.



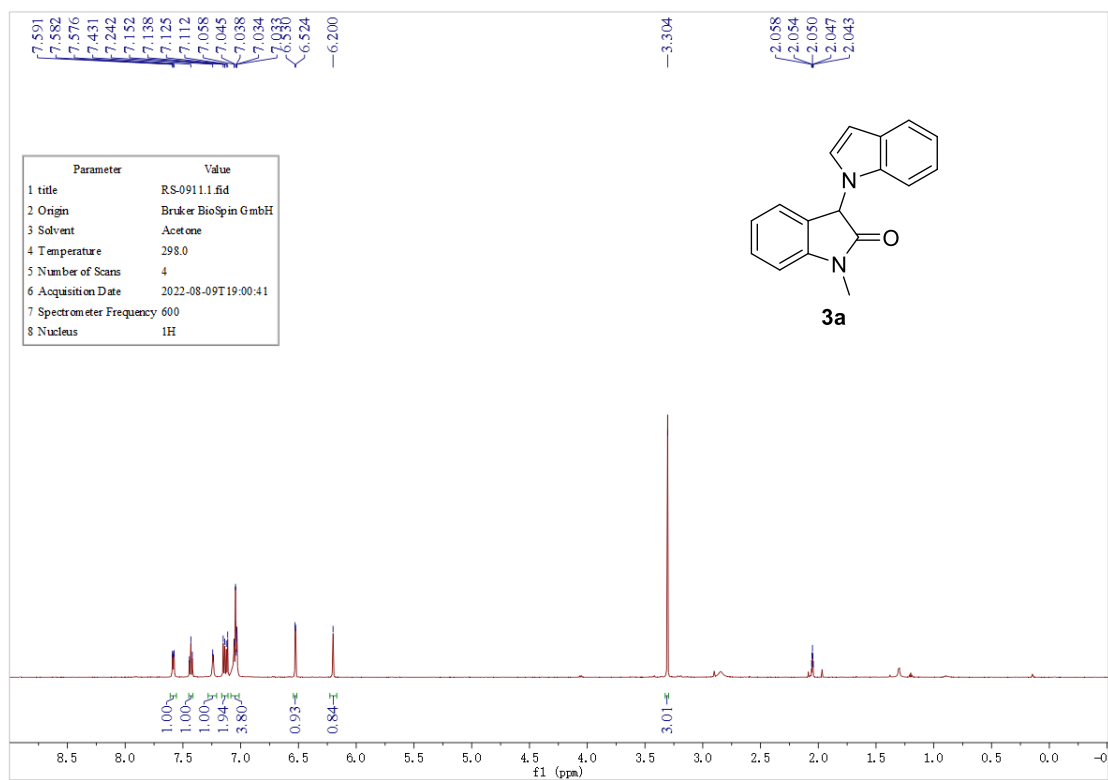
To a solution of compound **3b** (124 mg, 0.5 mmol) in toluene (5.0 mL) at -10 °C was added BH<sub>3</sub>.SMe<sub>2</sub> (2 M THF solution, 625 μL, 1.25 mmol) under Ar. The resulting mixture was then allowed to warm to room temperature and continued to stir for about

4 h before a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  was added to quench the reaction. The aqueous layer was separated and extracted with DCM. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and concentrated. Silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) afforded bi-indole **6** in 61% yield as colorless oil;  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  8.09 (s, 1H), 7.84 – 7.78 (m, 1H), 7.53 (d,  $J$  = 8.0 Hz, 1H), 7.47 (d,  $J$  = 8.3 Hz, 1H), 7.42 (dd,  $J$  = 9.6, 4.5 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 6.79 (d,  $J$  = 3.1 Hz, 1H) ppm.  $^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  137.4, 134.7, 129.6, 128.5, 12.7, 123.1, 122.0, 120.8, 120.4, 120.0, 119.2, 118.5, 117.5, 111.6, 110.8, 102.4 ppm. Analytical data were consistent with previously reported data.<sup>[1]</sup>

## 7. References

- [1] Y. H. Wang, J. S. Tian, W. P. Tan, Q. Cao, X. X. Zhang, Z. Y. Cao, F. Zhou, X. Wang and J. Zhou, *Angew. Chem., Int. Ed.* 2020, **50**, 1634-1643.
- [2] M. B. Chaudhari, Y. Sutar, S. Malpathak, A. Hazra and B. Gnanaprakasam, *Org. Lett.* 2017, **19**, 3628–3631
- [3] X. Y. Zhou and X. Chen, *Org. Biomol. Chem.*, 2021,**19**, 548-551.

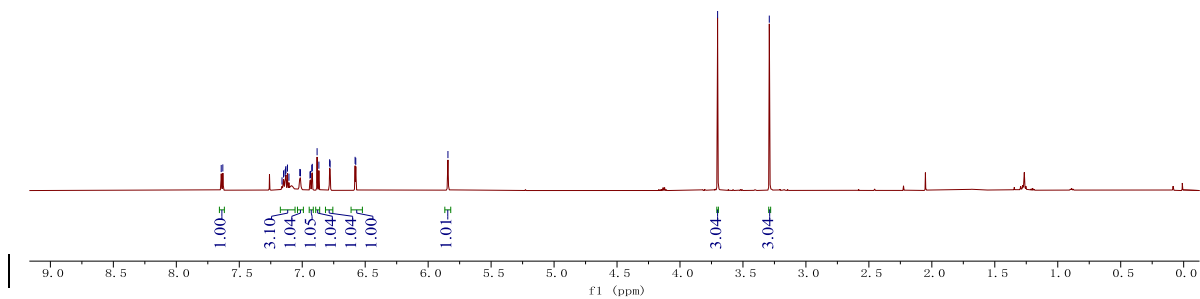
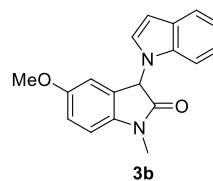
## 8. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compounds



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7.132  
7.130  
7.117  
7.106  
7.019  
7.014  
6.938  
6.934  
6.924  
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6.782  
6.779  
6.580  
6.575  
5.843

3.701  
3.291

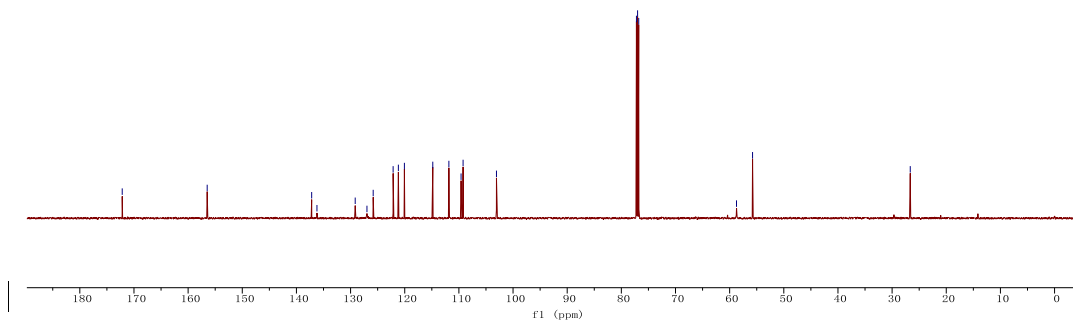
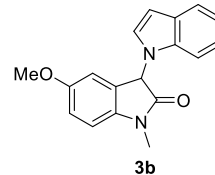
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7 Spectrometer Frequency	600
8 Nucleus	1H



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136.210  
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125.825  
122.143  
121.175  
120.062  
114.821  
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103.060

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76.789  
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55.769  
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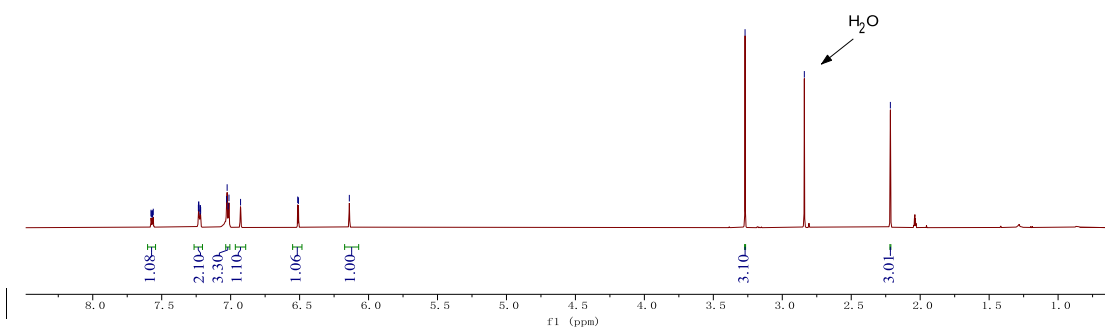
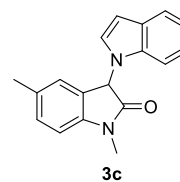
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7 Spectrometer Frequency	151
8 Nucleus	13C



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7.561  
7.234  
7.232  
7.231  
7.231  
7.230  
7.222  
7.221  
7.219  
7.218  
7.030  
7.025  
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6.509  
6.139

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7 Spectrometer Frequency	600
8 Nucleus	<sup>1</sup> H



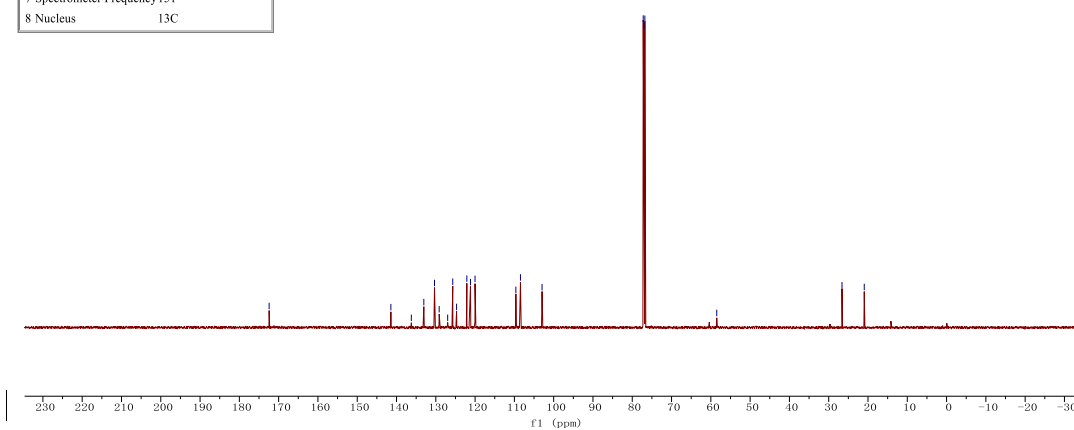
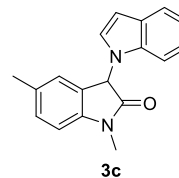
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102.958

77.211  
77.000  
76.788

58.497

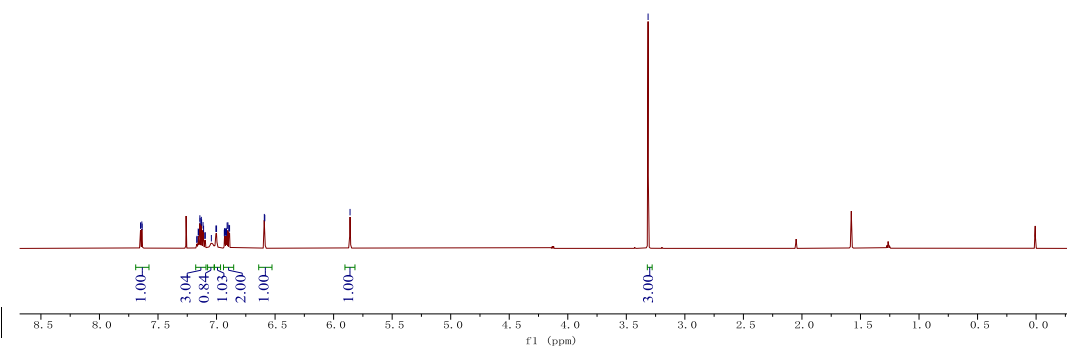
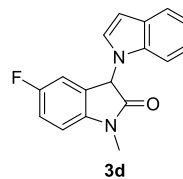
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7 Spectrometer Frequency	151
8 Nucleus	<sup>13</sup> C



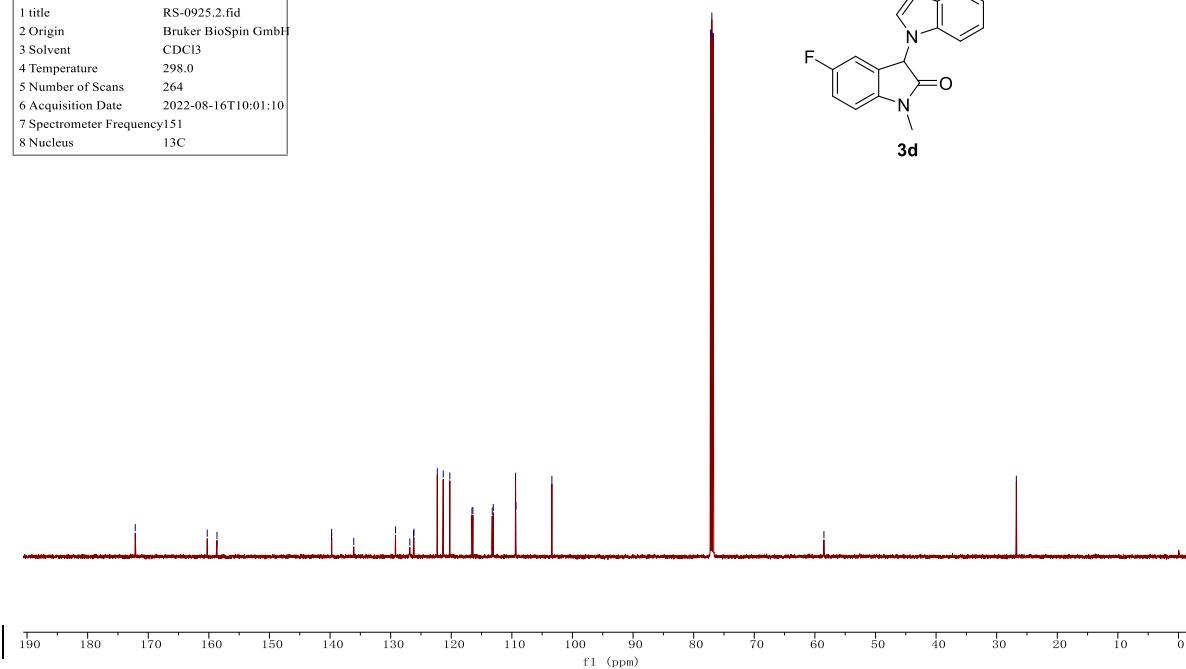
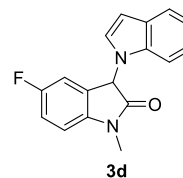
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6.921  
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Parameter	Value
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8 Nucleus	1H

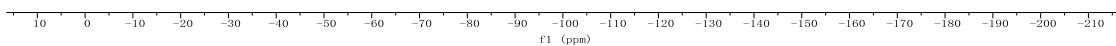
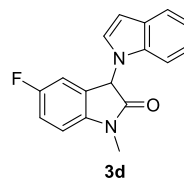


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121.326  
120.239  
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116.431  
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113.073  
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77.212  
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26.754

Parameter	Value
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3 Solvent	CDCl3
4 Temperature	298.0
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7 Spectrometer Frequency	151
8 Nucleus	13C



Parameter	value
1 title	LRS-0925.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
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7 Spectrometer Frequency	564.63
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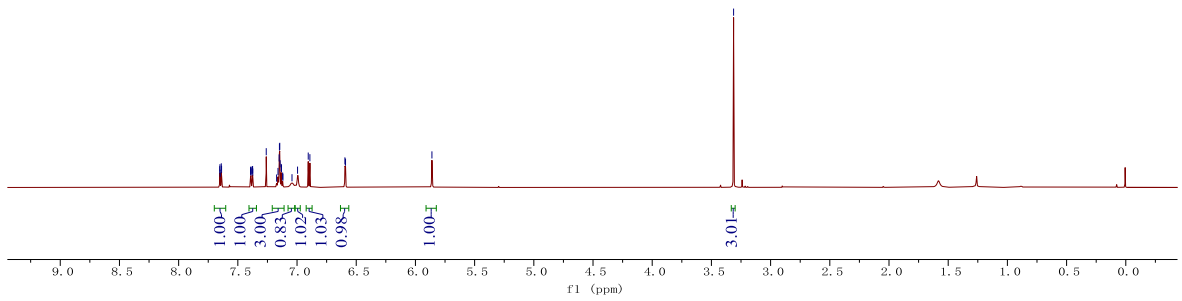
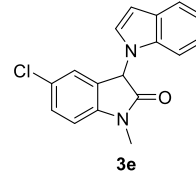




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7.375  
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7.133  
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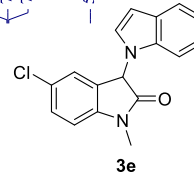
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7 Spectrometer Frequency	600
8 Nucleus	1H

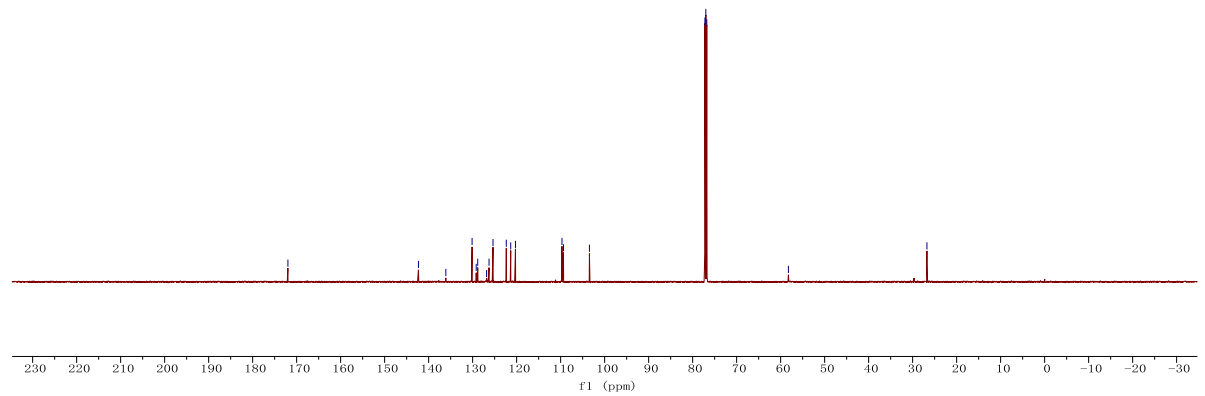


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58.236  
26.749

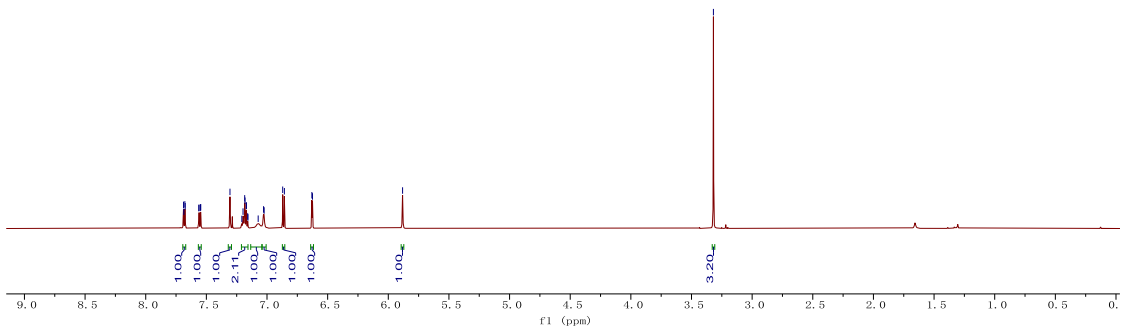
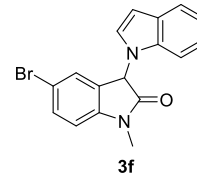


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7 Spectrometer Frequency	151
8 Nucleus	13C



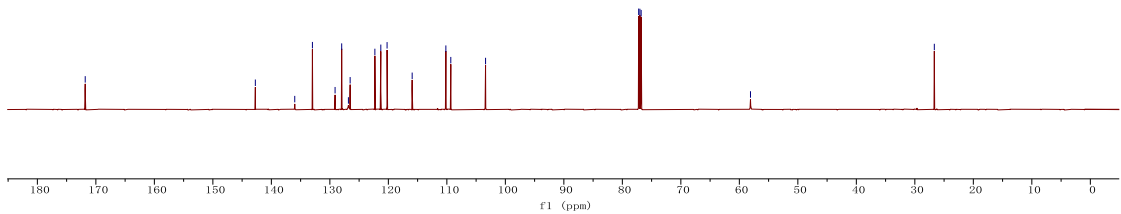
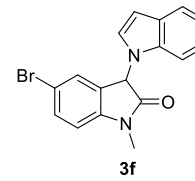
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 3.319

Parameter	value
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2 origin	Bruker BioSpin GmbH
3 solvent	CDCl3
4 temperature	295.0
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6 acquisition date	2023-09-26T01:41:12
7 spectrometer frequency	600.13
8 nucleus	1H



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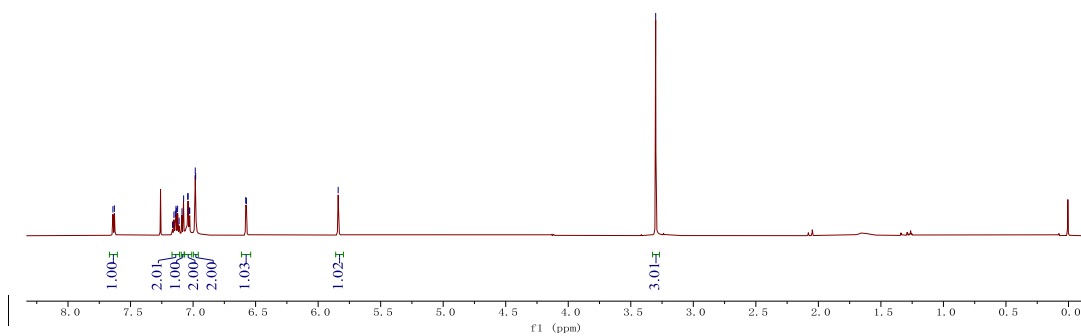
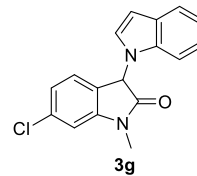
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7 spectrometer frequency	150.92
8 nucleus	13C



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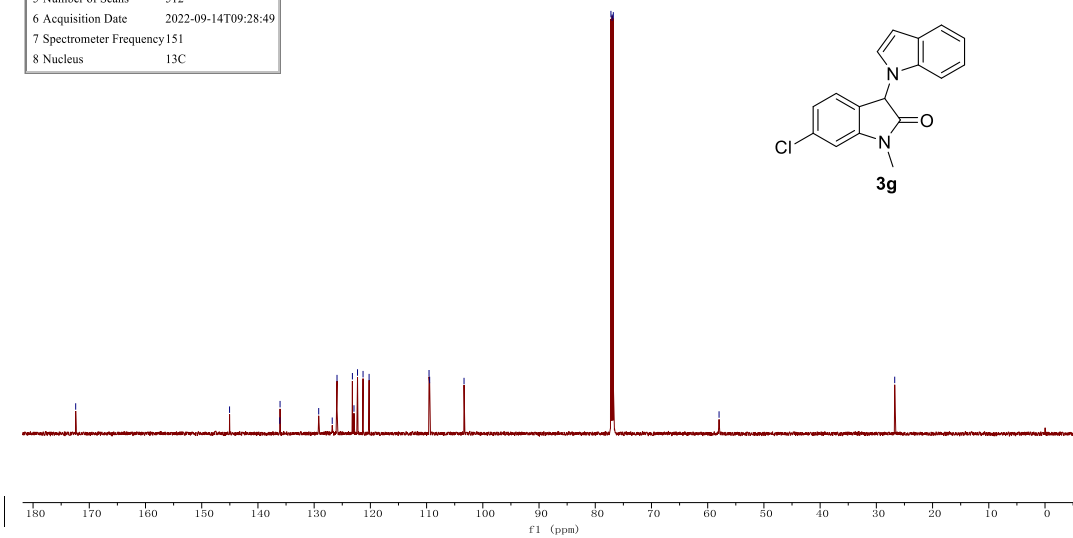
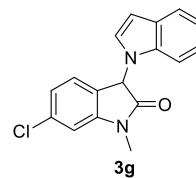
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7 Spectrometer Frequency	600
8 Nucleus	1H



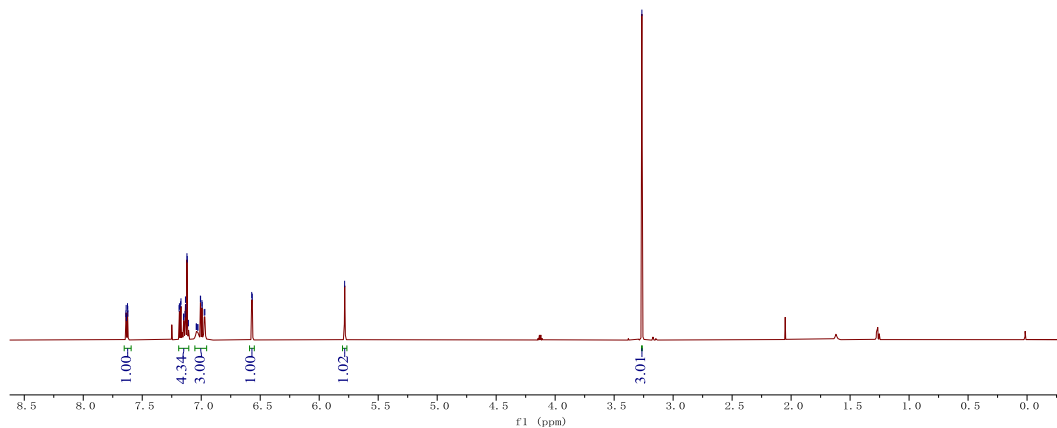
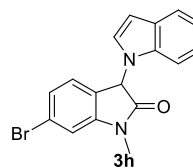
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26.734

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8 Nucleus	13C



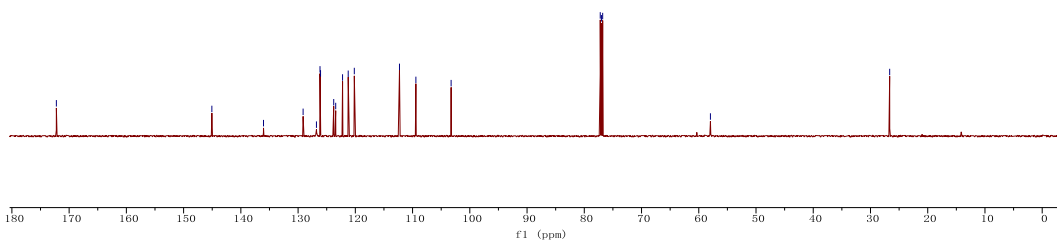
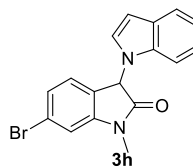
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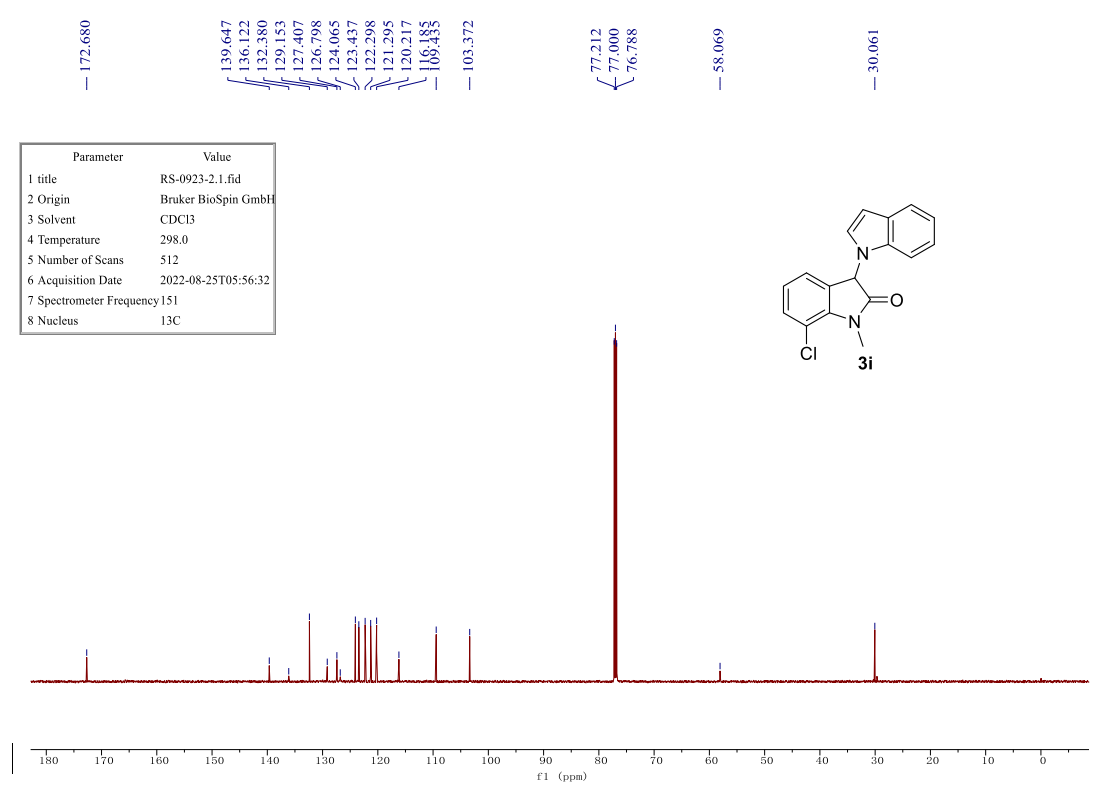
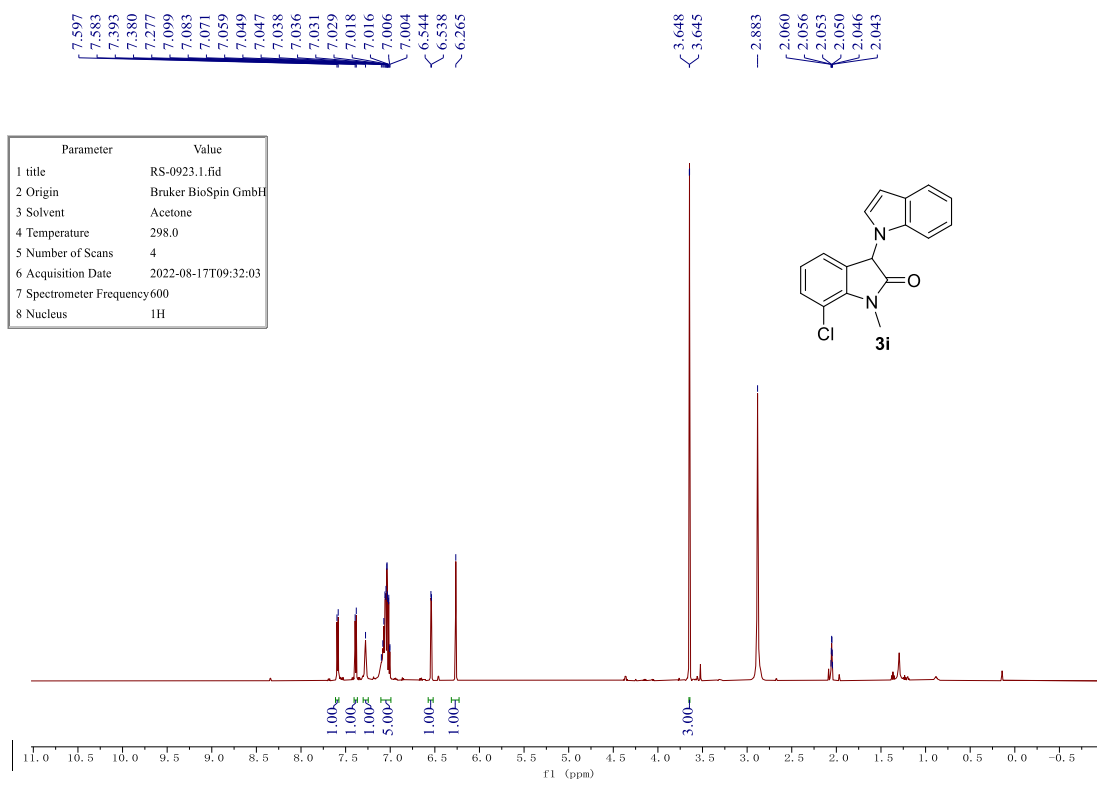
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8 Nucleus	1H



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76.788  
57.963  
26.648

Parameter	Value
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8 Nucleus	13C

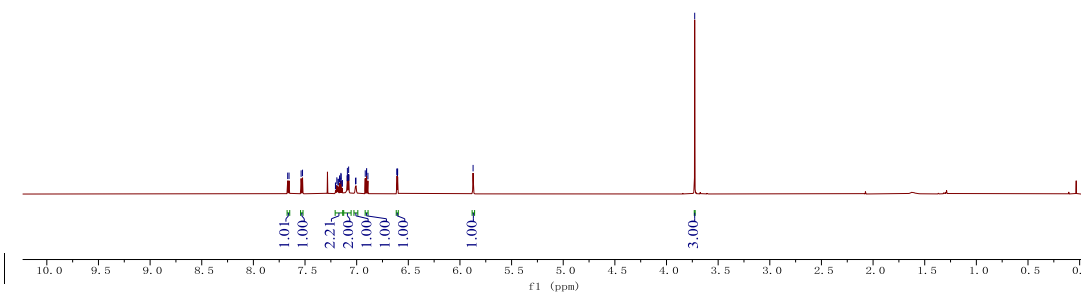
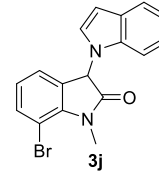




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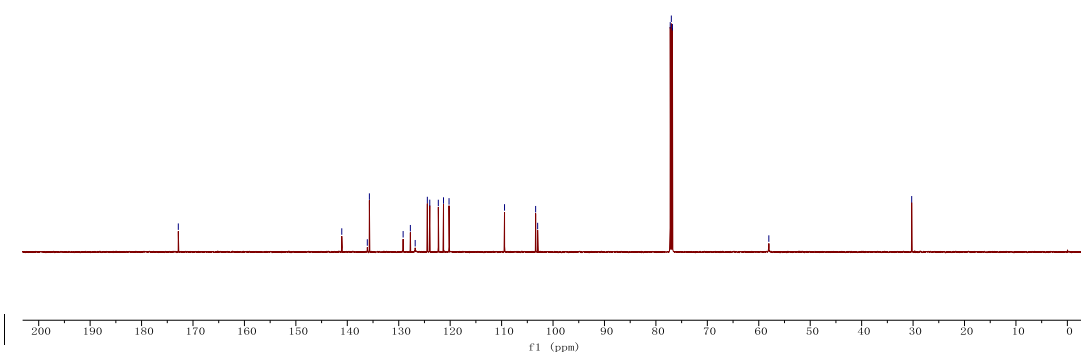
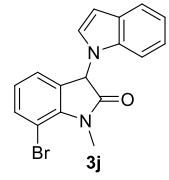
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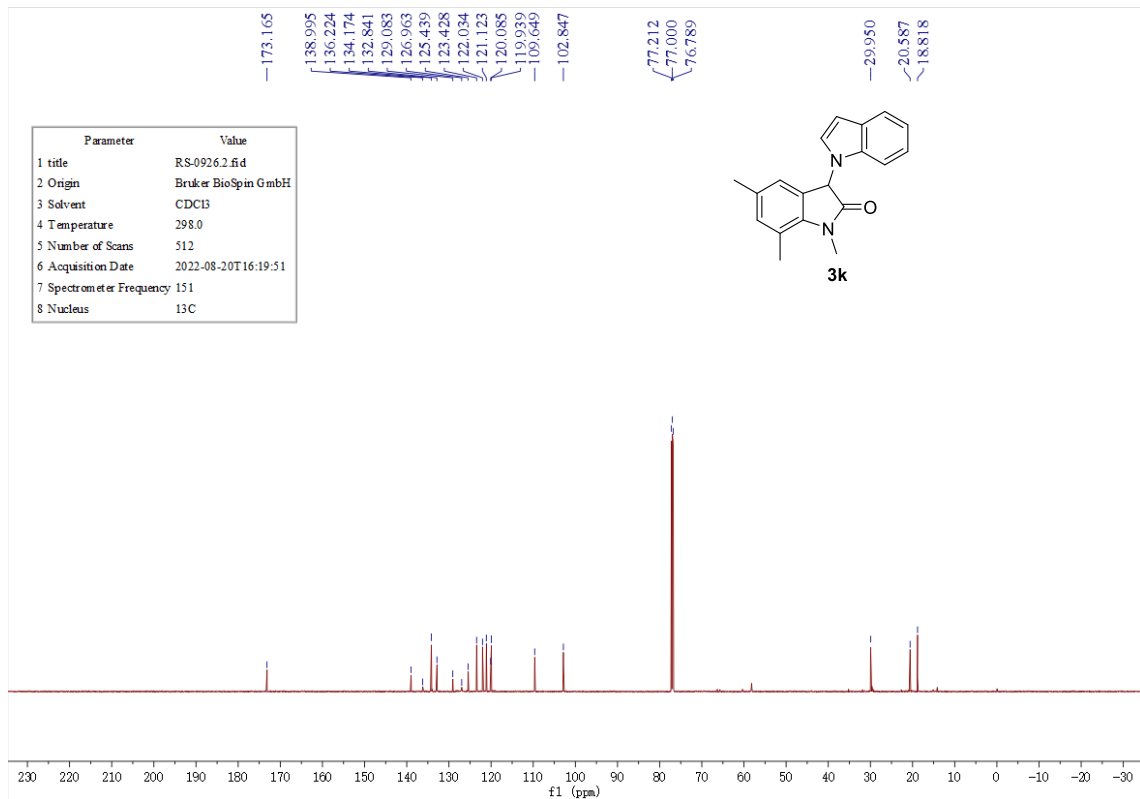
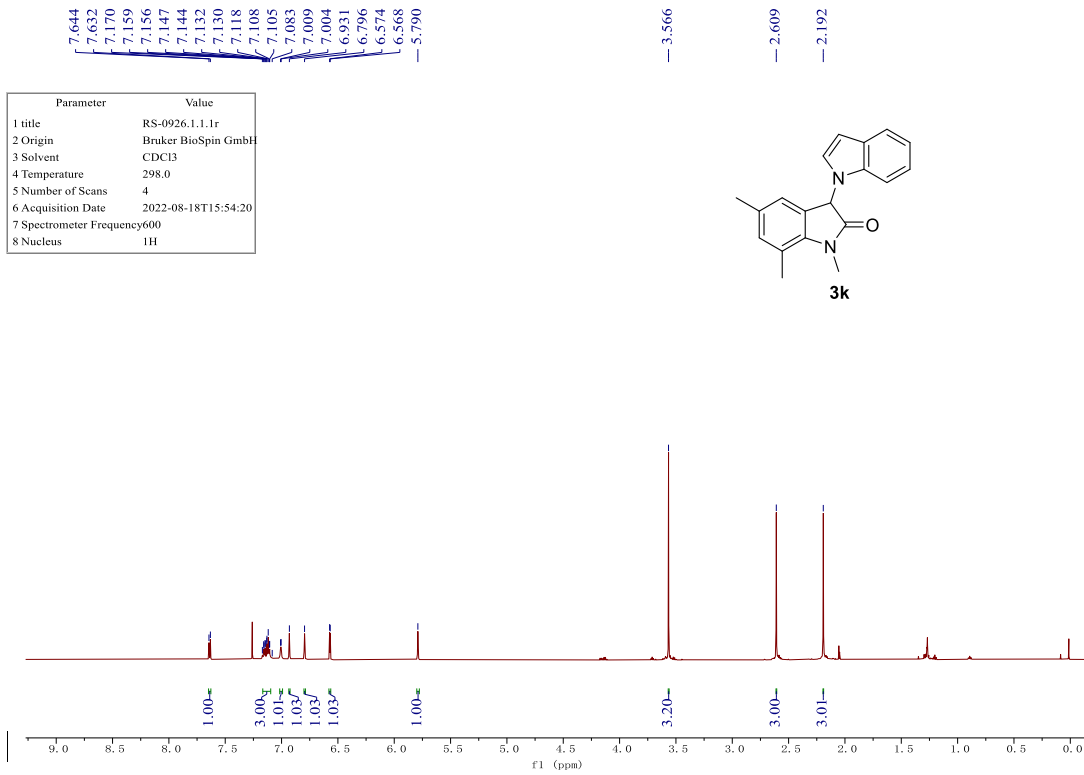
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8 Nucleus	<sup>1</sup> H

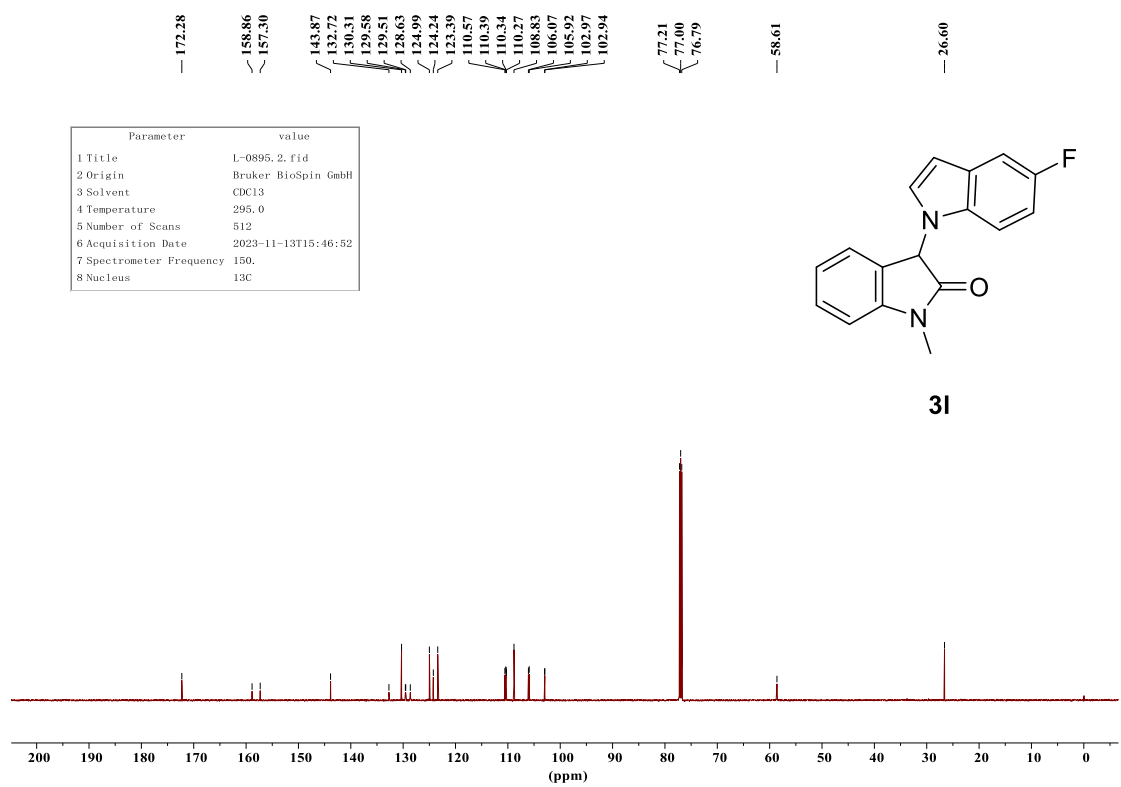
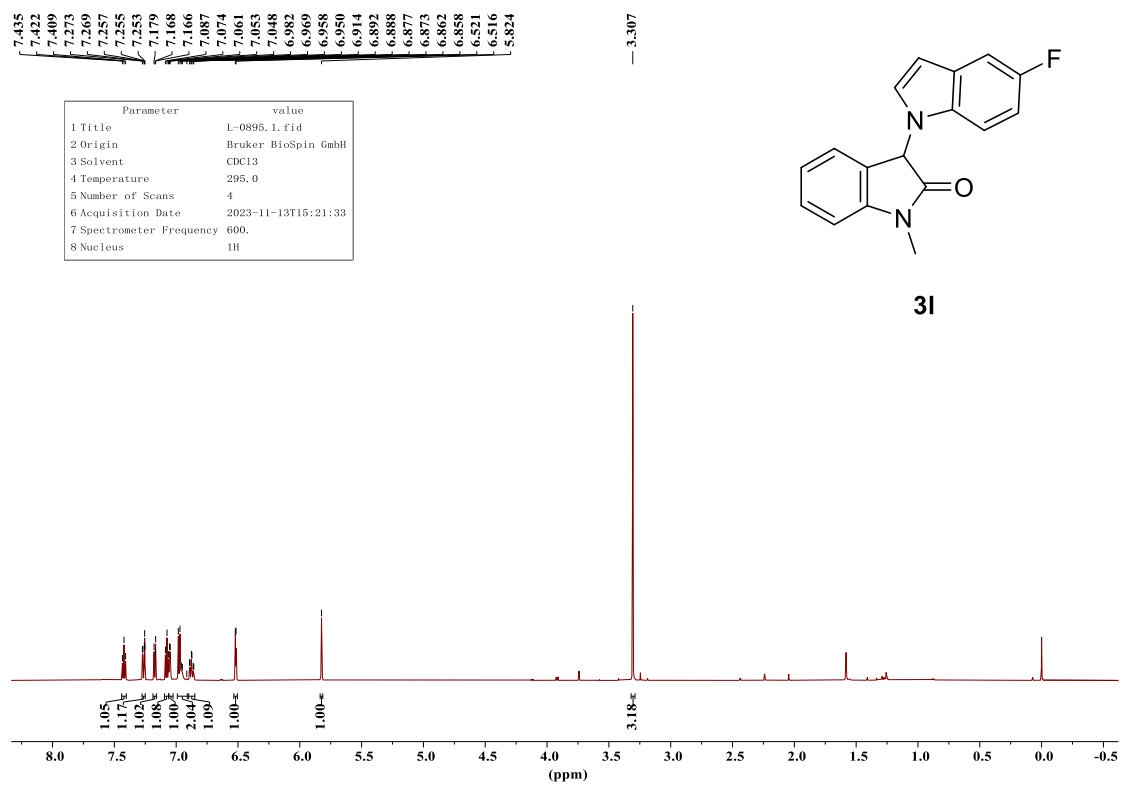


172.857  
141.075  
136.110  
135.707  
129.146  
127.738  
126.801  
124.440  
123.965  
122.306  
121.296  
120.222  
109.432  
103.382  
102.992  
77.211  
77.001  
76.788  
58.044  
30.269

Parameter	Value
1 title	RS-0931.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	512
6 Acquisition Date	2022-08-25T16:53:28
7 Spectrometer Frequency	151
8 Nucleus	<sup>13</sup> C



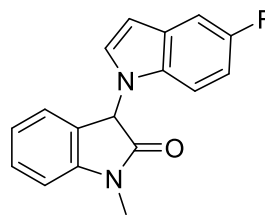




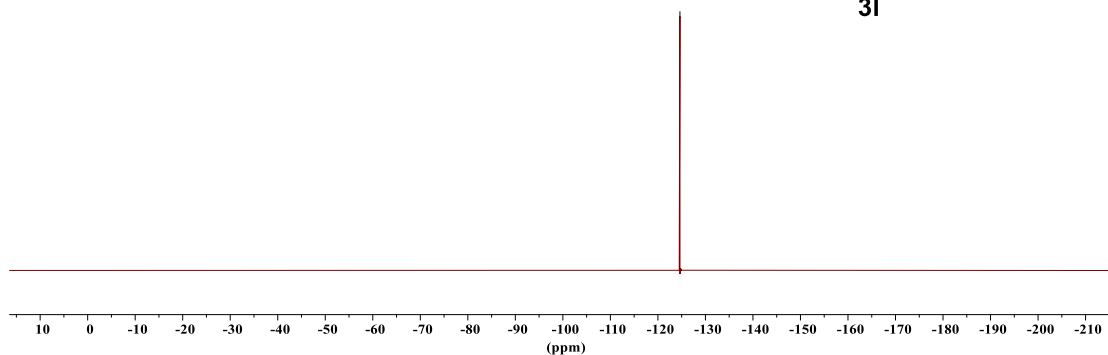


Parameter	value
1 Title	L-0895_3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.2
5 Number of Scans	16
6 Acquisition Date	2023-11-13T15:48:39
7 Spectrometer Frequency	565.
8 Nucleus	19F

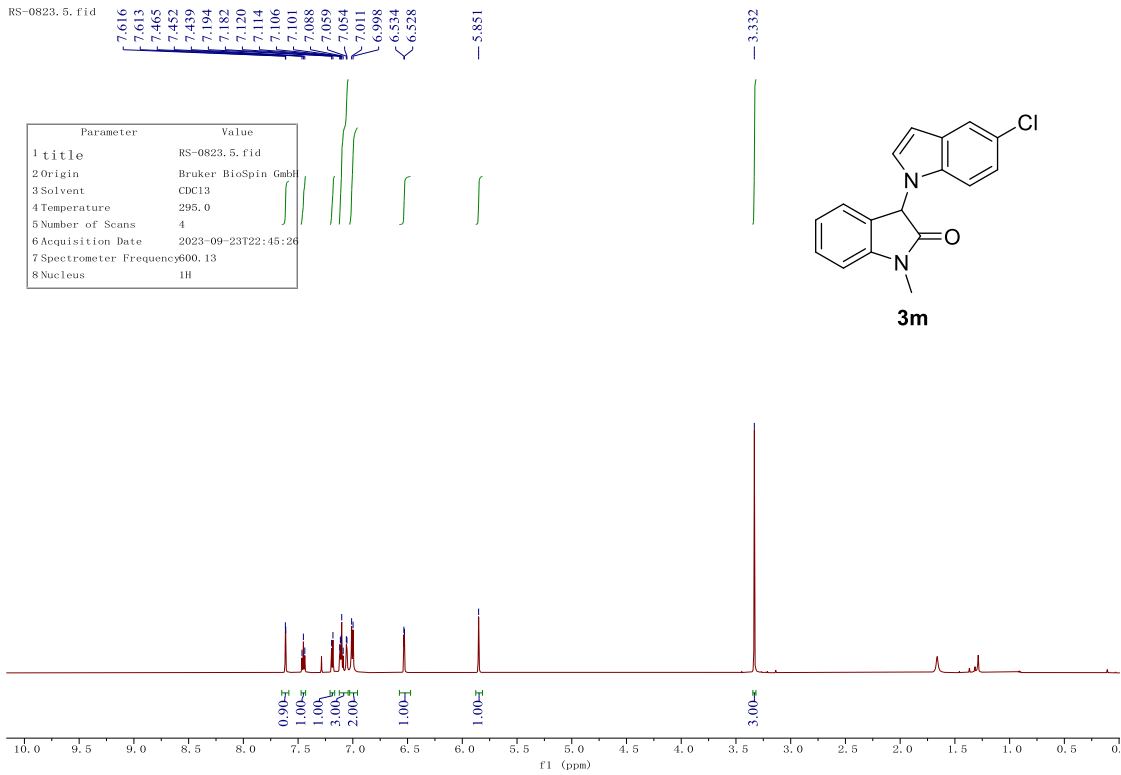
-124.64



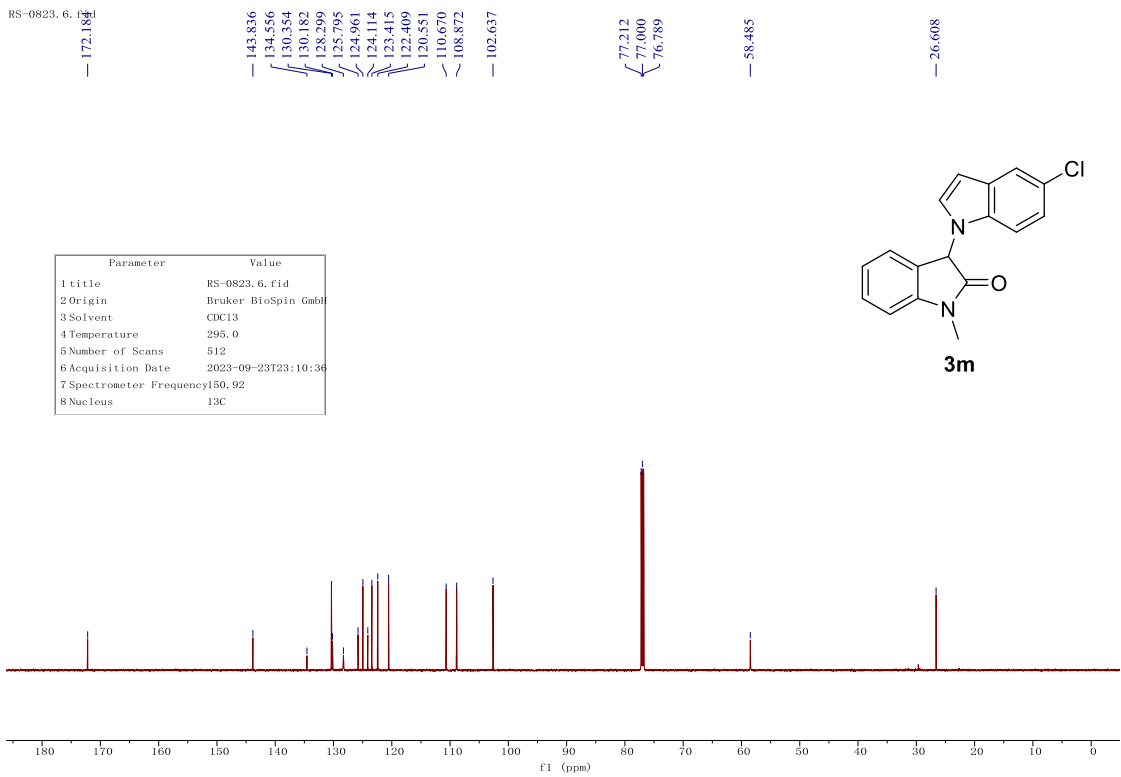
**31**



RS-0823.5.fid

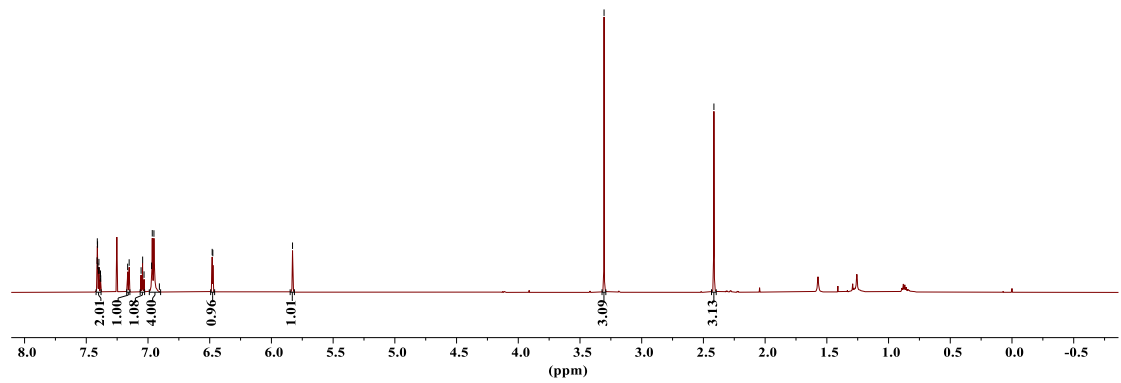
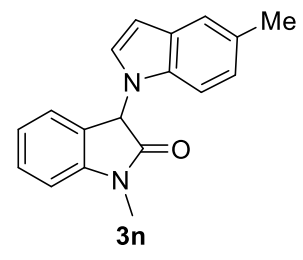


RS-0823.6.fid



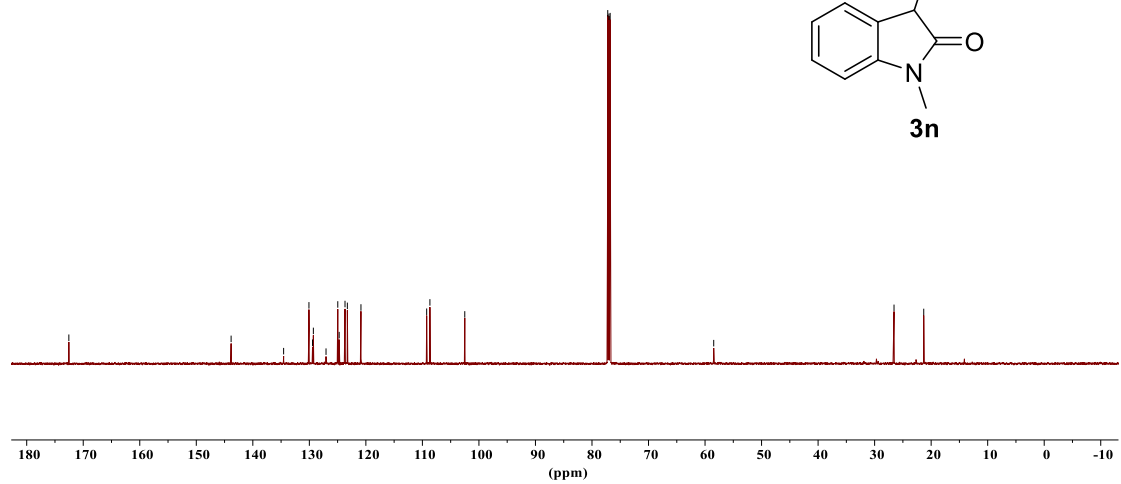
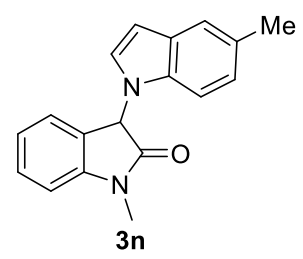
7.412  
7.411  
7.409  
7.407  
7.400  
7.398  
7.396  
7.387  
7.385  
7.383  
7.165  
7.153  
7.056  
7.043  
7.032  
6.971  
6.965  
6.952  
6.908  
6.480  
6.475  
5.829

Parameter	value
1 Title	L-0899-1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	4
6 Acquisition Date	2023-11-15T02:14:39
7 Spectrometer Frequency	600.
8 Nucleus	1H



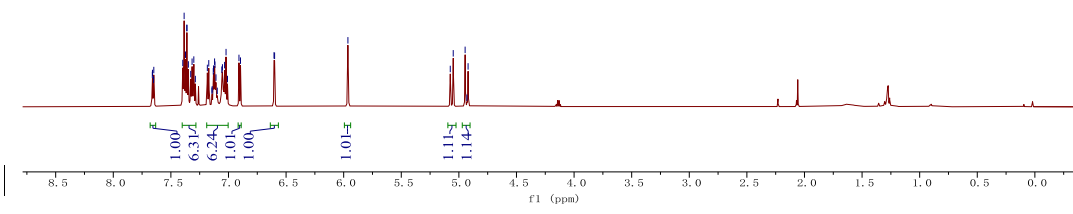
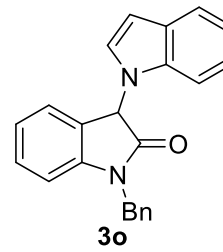
172.54  
143.84  
134.55  
130.07  
129.44  
129.29  
127.05  
124.97  
124.72  
123.69  
123.28  
120.87  
109.24  
108.67  
102.50  
77.21  
77.00  
76.79  
58.47  
26.57  
21.31

Parameter	value
1 Title	L-0899-1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	512
6 Acquisition Date	2023-11-15T02:39:54
7 Spectrometer Frequency	150.
8 Nucleus	13C



7.661  
7.660  
7.651  
7.648  
7.397  
7.385  
7.373  
7.361  
7.361  
7.348  
7.328  
7.316  
7.301  
7.288  
7.183  
7.171  
7.144  
7.141  
7.132  
7.130  
7.121  
7.117  
7.109  
7.097  
7.058  
7.052  
7.034  
7.021  
7.009  
6.909  
6.896  
6.605  
6.600  
5.963  
5.075  
5.049  
4.946  
4.930  
4.920

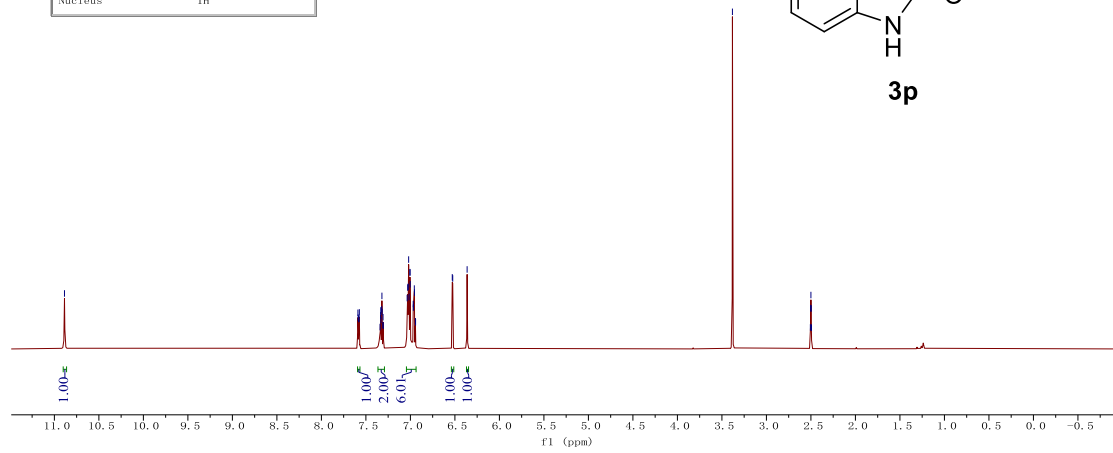
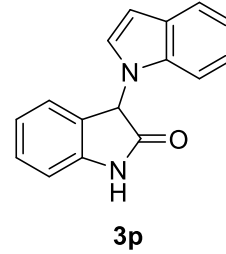
Parameter	Value
1 title	RS-0933.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Date	2022-09-03T17:35:03
7 Spectrometer Frequency	600
8 Nucleus	1H



10.886  
7.589  
7.587  
7.581  
7.578  
7.574  
7.341  
7.335  
7.333  
7.331  
7.322  
7.320  
7.318  
7.309  
7.307  
7.305  
7.036  
7.034  
7.030  
7.015  
7.005  
7.005  
7.002  
6.968  
6.967  
6.956  
6.954  
6.943  
6.942  
6.530  
6.524  
6.363

3.382  
2.506  
2.503  
2.500  
2.497  
2.494

Parameter	Value
title	LRS-0901.1.fid
Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	295.0
Number of Scans	4
Acquisition Date	2023-09-19T10:01:00
Spectrometer Frequency	600.13
Nucleus	<sup>1</sup> H

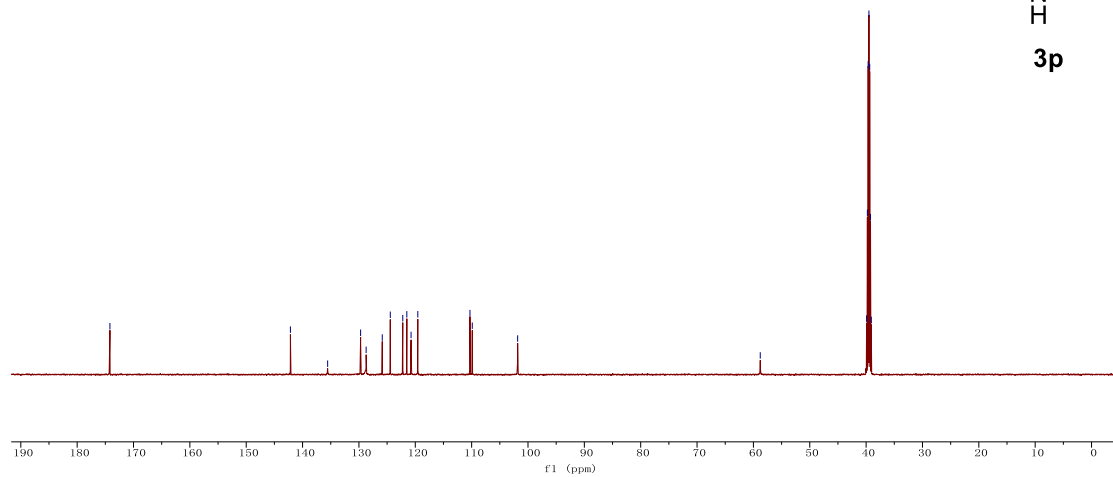
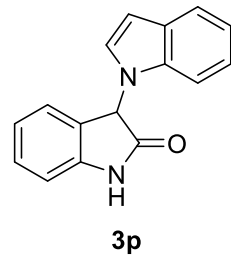


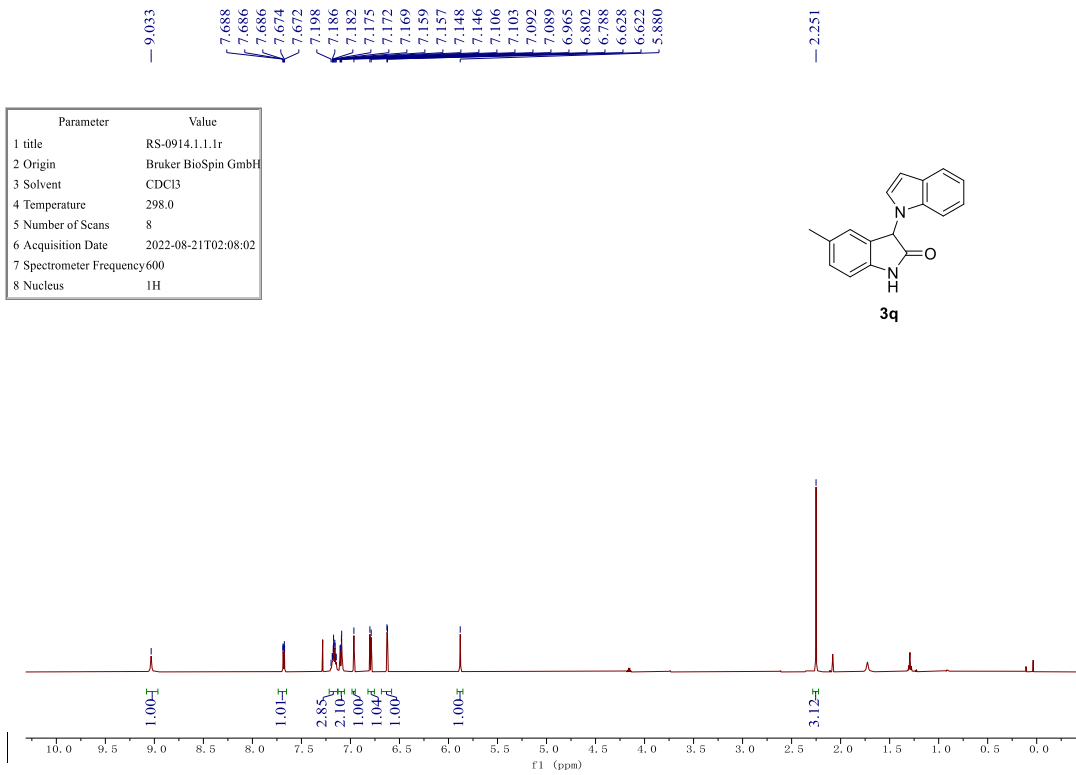
LRS-0901.2.fid

174.186  
142.158  
135.553  
129.704  
128.720  
125.861  
124.437  
122.220  
121.501  
120.749  
119.554  
110.298  
109.886  
101.835

58.785  
39.918  
39.778  
39.639  
39.500  
39.362  
39.222  
39.083

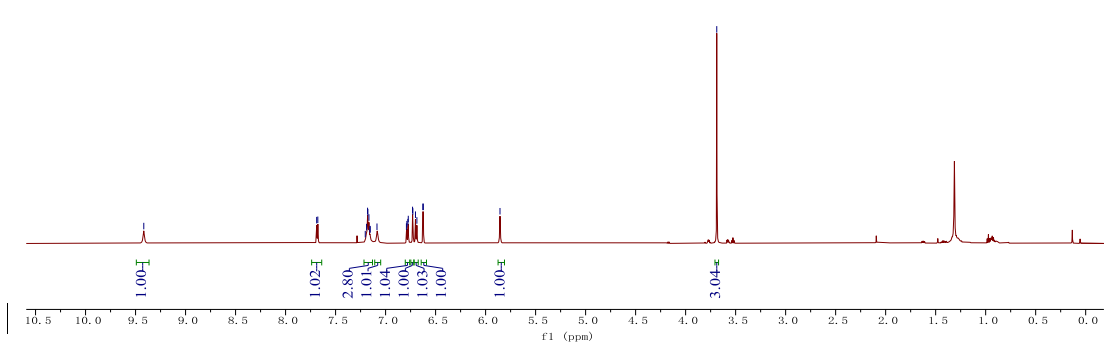
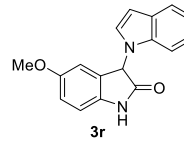
Parameter	value
1 title	LRS-0901.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	295.0
5 Number of Scans	512
6 Acquisition Date	2023-09-20T15:34:50
7 Spectrometer Frequency	150.92
8 Nucleus	<sup>13</sup> C





<sup>1</sup>H NMR (600 MHz, Chloroform-d)  $\delta$  6.73 (d,  $J = 1.9$  Hz, 1H), 6.69-6.62 (m, 7H), 3.689 (s, 3H).

Parameter	Value
1 title	RS-0902.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Date	2022-08-09T19:06:33
7 Spectrometer Frequency	600
8 Nucleus	<sup>1</sup> H

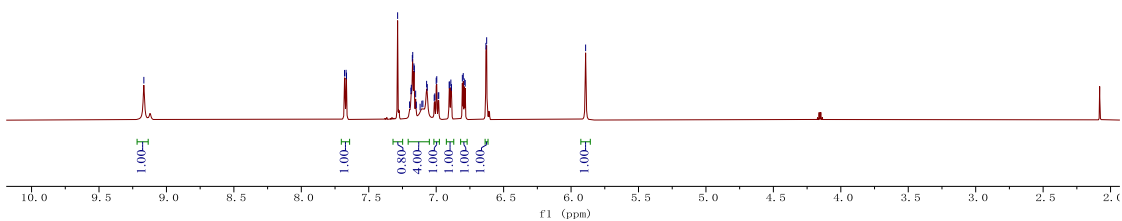
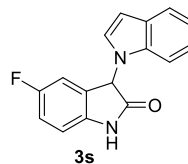


RS-0838-1.1.fid

9.167

7.680  
7.668  
7.665  
7.286  
7.197  
7.187  
7.184  
7.177  
7.174  
7.165  
7.162  
7.152  
7.147  
7.142  
7.102  
7.099  
7.071  
7.066  
7.015  
7.010  
7.000  
6.996  
6.985  
6.981  
6.904  
6.891  
6.887  
6.806  
6.799  
6.785  
6.631  
6.626  
5.892

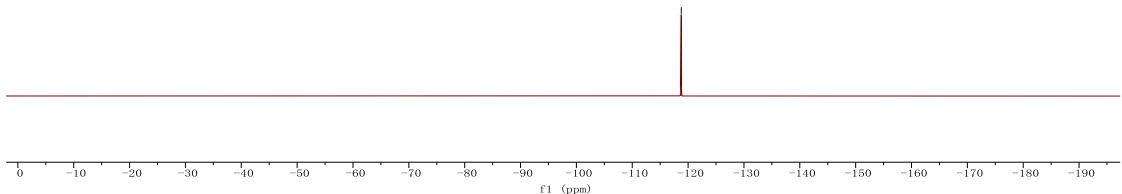
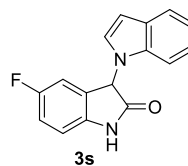
Parameter	value
1 title	RS-0838-1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	4
6 Acquisition Date	2023-10-20T19:21:56
7 Spectrometer Frequency	600.13
8 Nucleus	1H



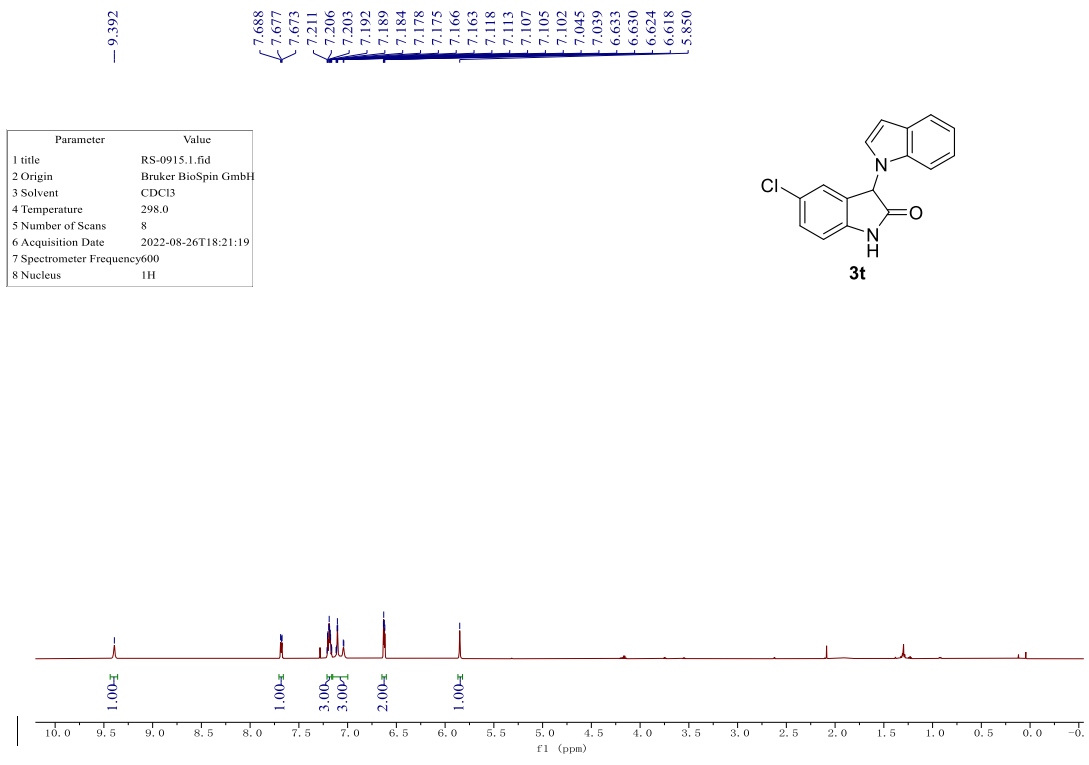
RS-0838-1.2.fid

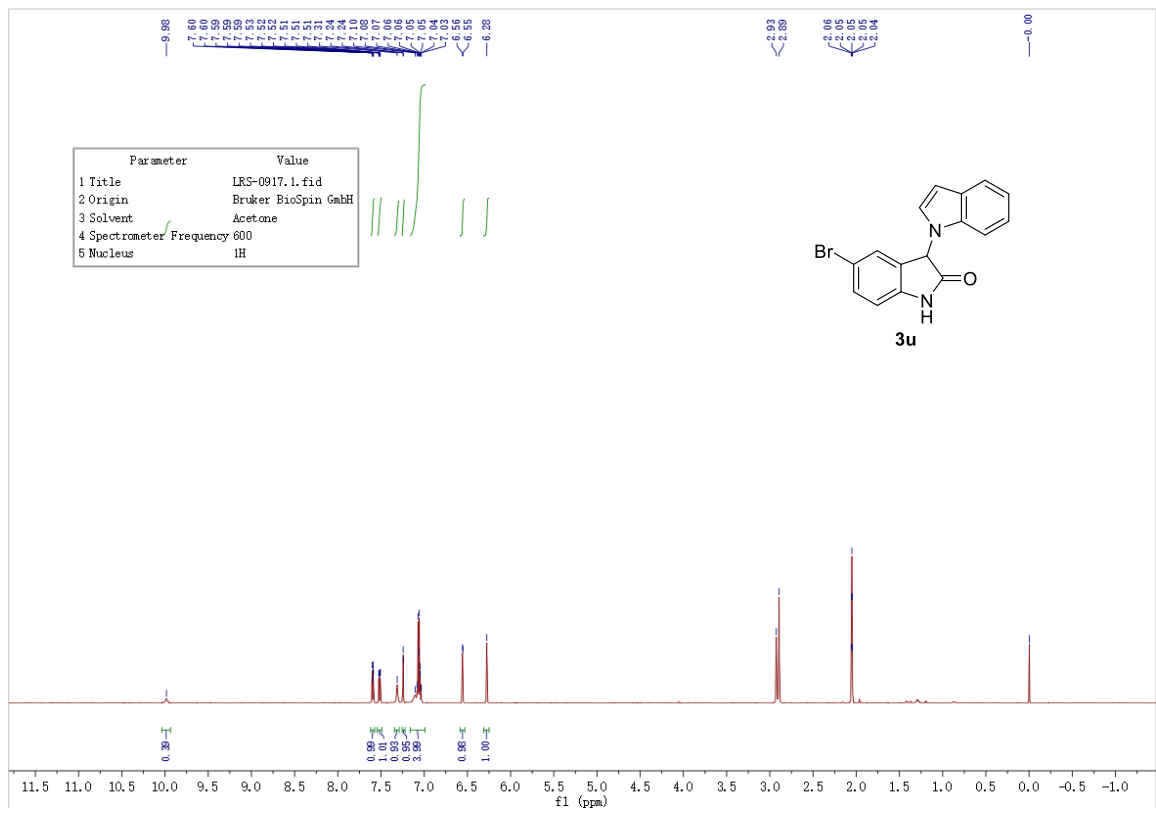
-118.777

Parameter	值
1 标题	RS-0838-1.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.2
5 Number of Scans	16
6 Acquisition Date	2023-10-21T22:01:57
7 Spectrometer Frequency	564.63
8 Nucleus	19F

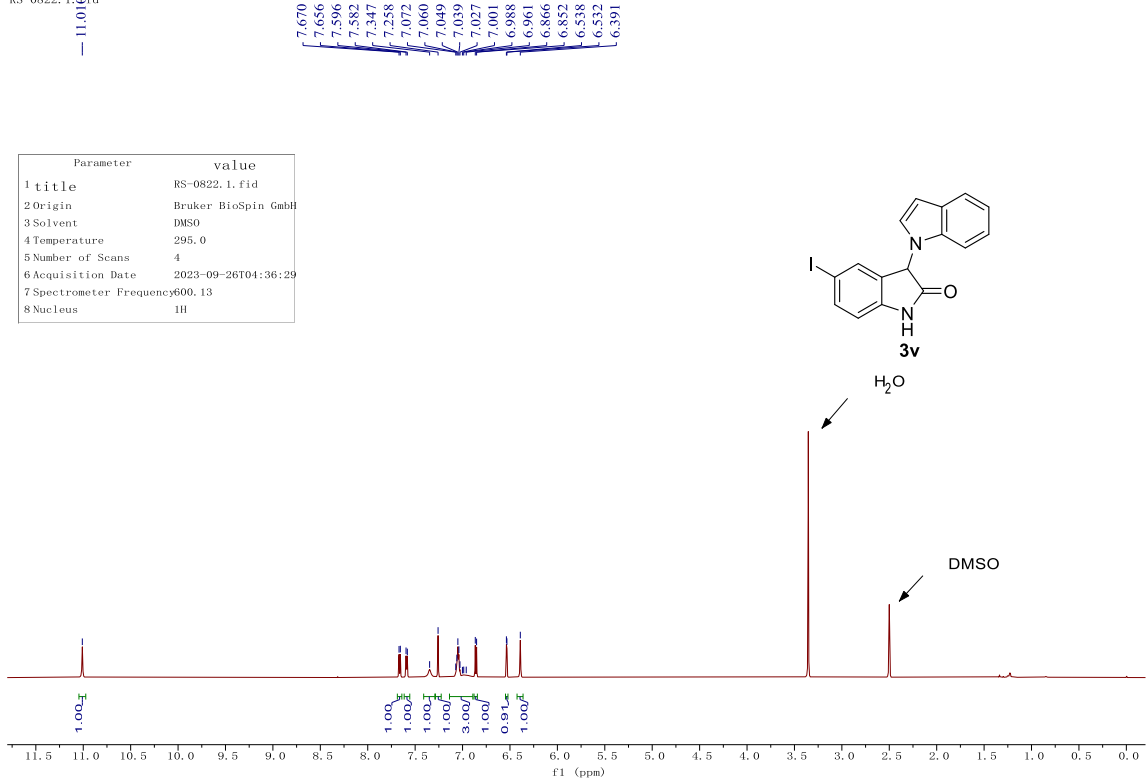




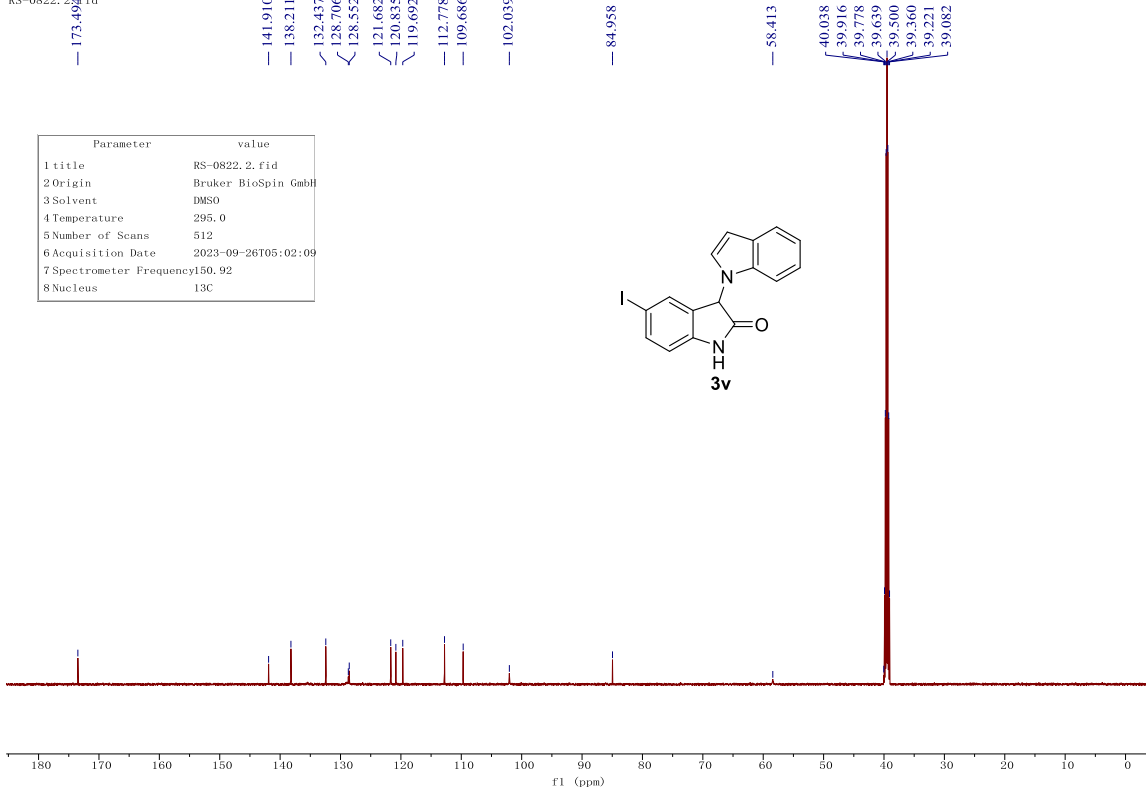




RS-0822.1.fid



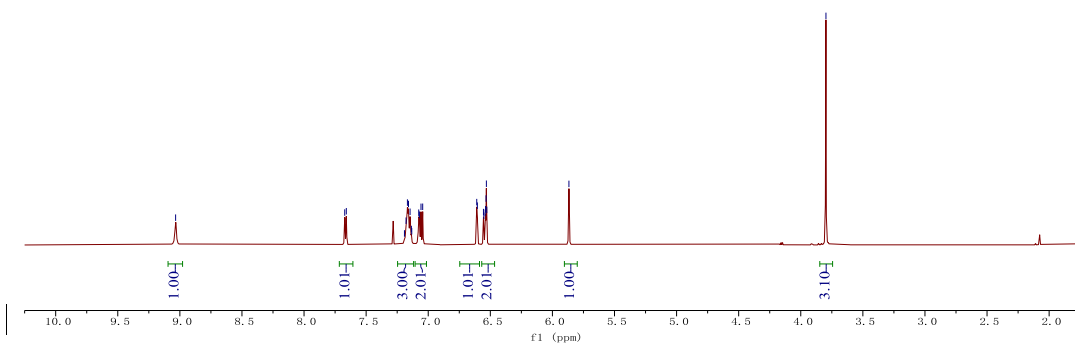
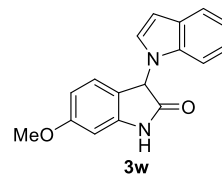
RS-0822.2.fid



9.034  
 7.672  
 7.660  
 7.191  
 7.179  
 7.168  
 7.159  
 7.146  
 7.136  
 7.133  
 7.076  
 7.071  
 7.058  
 7.045  
 6.609  
 6.604  
 6.555  
 6.552  
 6.541  
 6.538  
 6.534  
 6.532  
 6.528  
 5.867

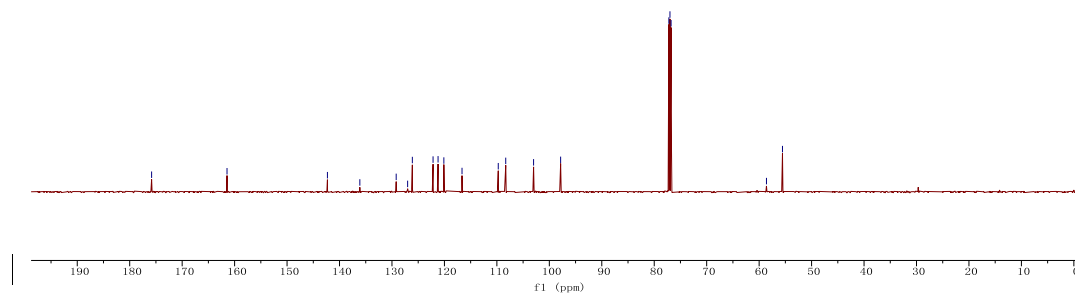
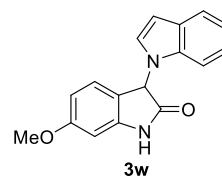
3.797

Parameter	Value
1 title	RS-0916.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Date	2022-08-16T11:18:11
7 Spectrometer Frequency	600
8 Nucleus	<sup>1</sup> H



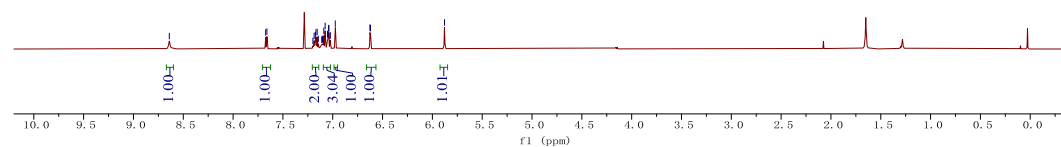
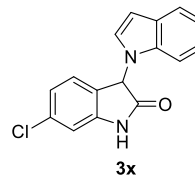
175.825  
 161.447  
 142.305  
 136.125  
 129.196  
 127.015  
 126.116  
 122.166  
 121.213  
 120.108  
 116.646  
 109.737  
 108.310  
 103.003  
 97.846  
 77.211  
 77.000  
 76.787  
 58.604  
 55.551

Parameter	Value
1 title	RS-0916.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	512
6 Acquisition Date	2022-08-16T11:43:33
7 Spectrometer Frequency	151
8 Nucleus	<sup>13</sup> C



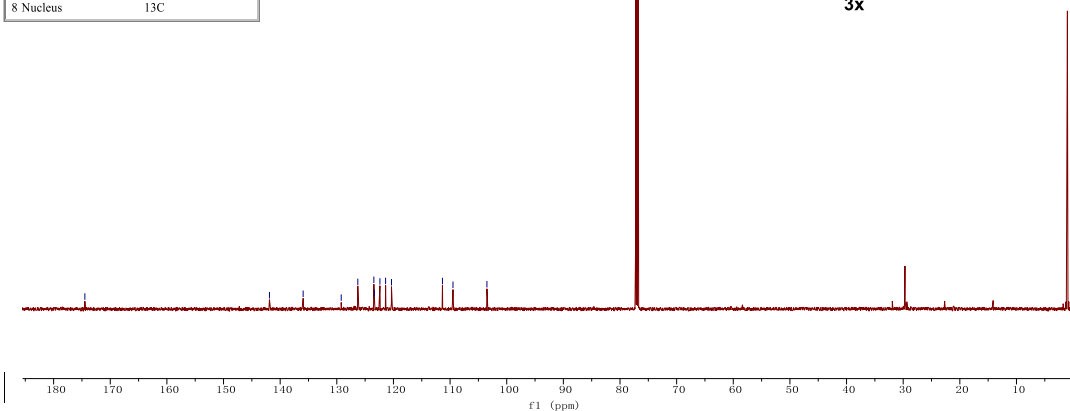
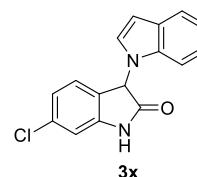
8.640  
 7.673  
 7.661  
 7.199  
 7.187  
 7.175  
 7.169  
 7.156  
 7.144  
 7.111  
 7.104  
 7.101  
 7.090  
 7.076  
 7.052  
 7.047  
 7.041  
 7.038  
 7.028  
 7.025  
 6.974  
 6.627  
 6.621  
 5.878

Parameter	Value
1 title	RS-0907.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Date	2022-08-09T19:03:22
7 Spectrometer Frequency	600
8 Nucleus	<sup>1</sup> H



174.485  
 141.893  
 135.944  
 126.293  
 123.459  
 123.369  
 122.387  
 121.383  
 120.349  
 111.346  
 109.488  
 103.494  
 77.212  
 77.000  
 76.789

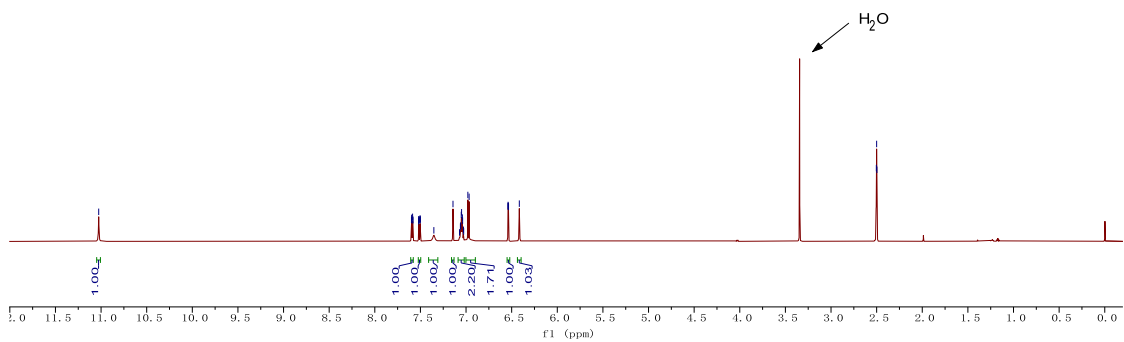
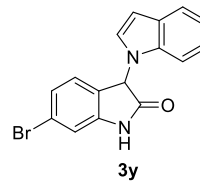
Parameter	Value
1 title	RS-0907.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	512
6 Acquisition Date	2022-08-27T15:05:08
7 Spectrometer Frequency	151
8 Nucleus	<sup>13</sup> C



LRS-0825\_1.fid  
 11.026  
 7.598  
 7.596  
 7.586  
 7.584  
 7.582  
 7.520  
 7.518  
 7.516  
 7.515  
 7.506  
 7.504  
 7.503  
 7.501  
 7.353  
 7.143  
 7.072  
 7.062  
 7.059  
 7.053  
 7.049  
 7.040  
 7.038  
 7.028  
 7.026  
 6.980  
 6.966  
 6.541  
 6.540  
 6.535  
 6.534  
 6.416

2.503  
 2.500  
 2.497

Parameter	value
1 title	LRS-0825_1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	295.0
5 Number of Scans	4
6 Acquisition Date	2023-10-15T17:30:18
7 Spectrometer Frequency	600.13
8 Nucleus	1H



LRS-0825\_2.fid

173.695

141.493

132.440

128.721

128.292

127.045

121.677

120.850

119.691

113.768

112.319

109.679

102.057

58.622

39.915

39.776

39.638

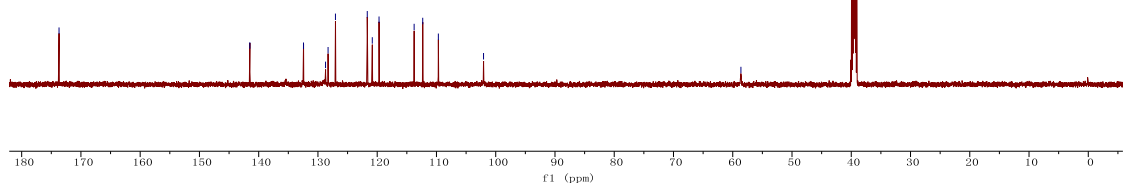
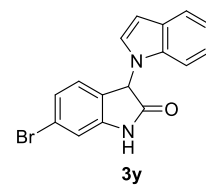
39.499

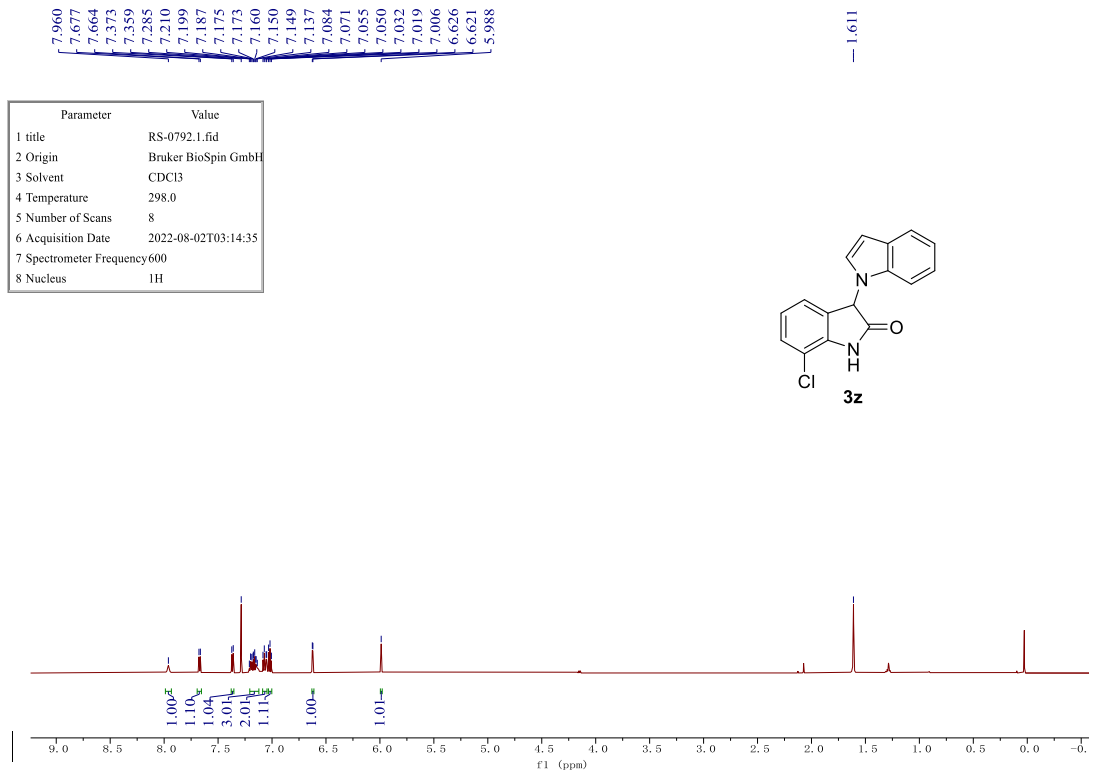
39.360

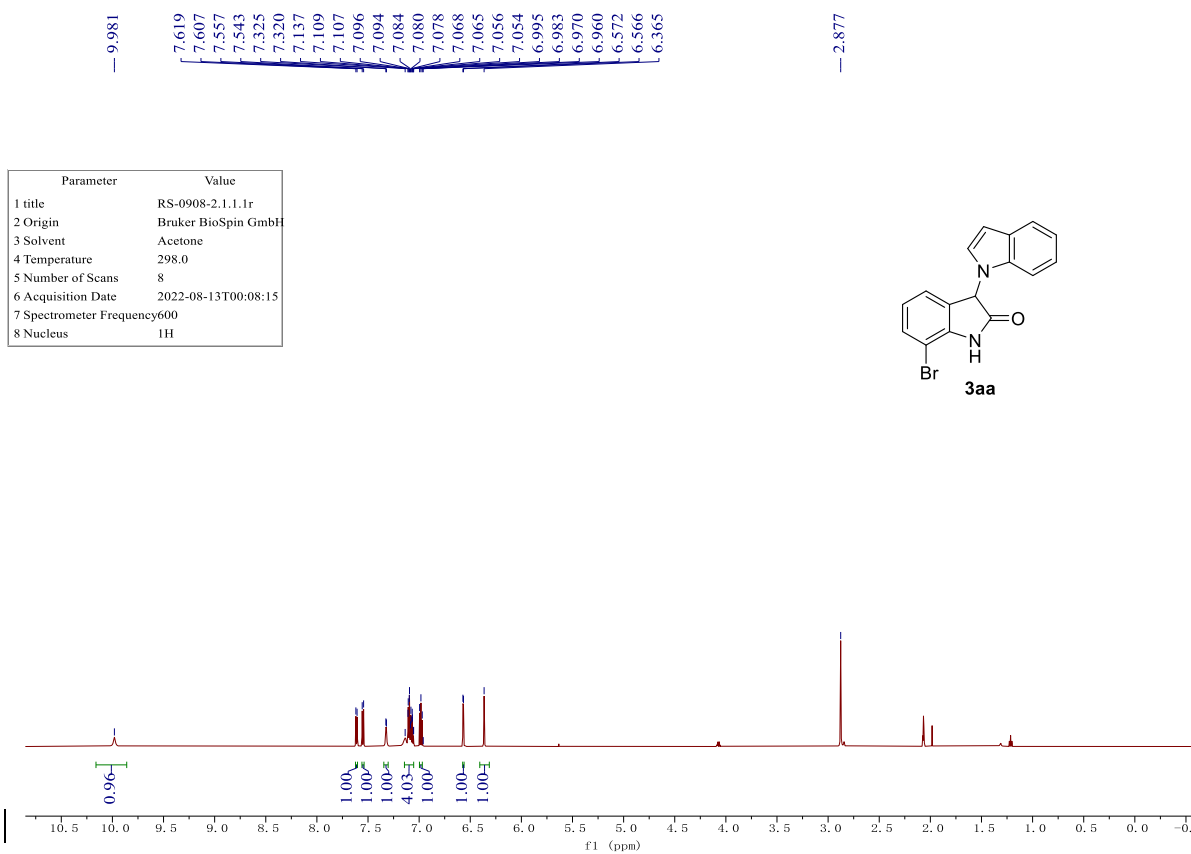
39.220

39.081

Parameter	value
1 title	LRS-0825_2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	295.0
5 Number of Scans	512
6 Acquisition Date	2023-10-15T17:55:29
7 Spectrometer Frequency	150.92
8 Nucleus	13C





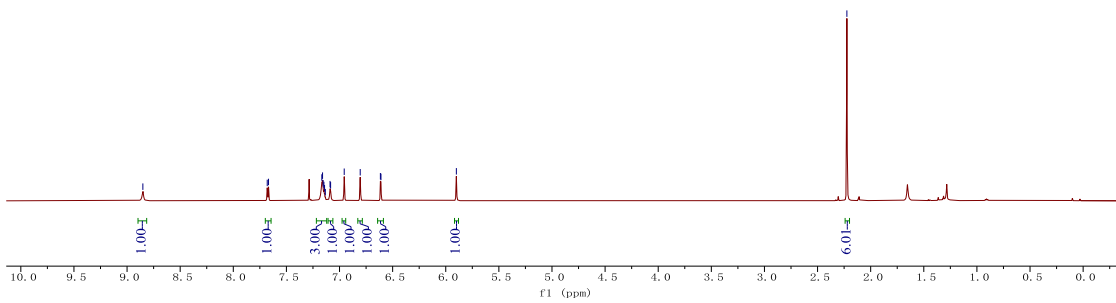
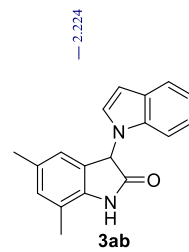




LRS-0905.1.fid

8.851  
7.681  
7.668  
7.167  
7.160  
7.154  
7.147  
7.141  
7.134  
7.089  
7.084  
6.956  
6.805  
6.615  
6.610  
5.900

Parameter	value
1 title	LRS-0905.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	4
6 Acquisition Date	2023-10-09T17:08:36
7 Spectrometer Frequency	600.13
8 Nucleus	1H

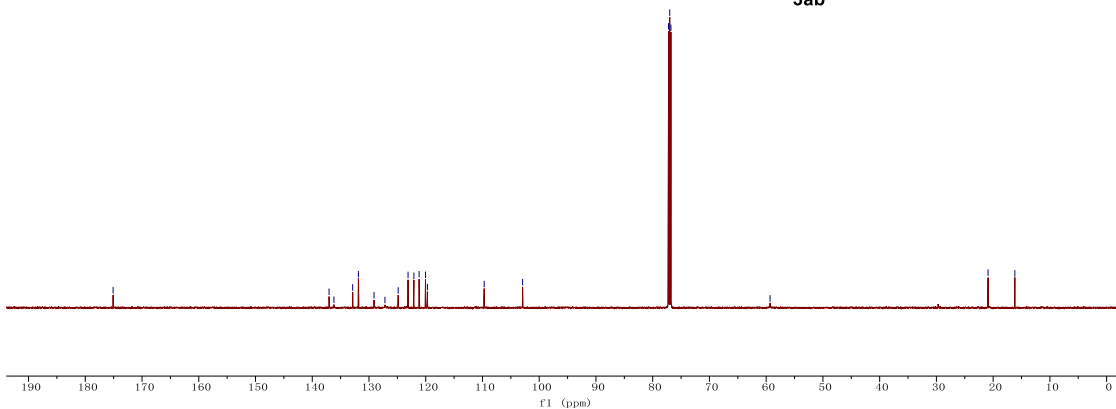
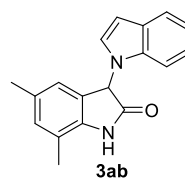


LRS-0905.2.fid

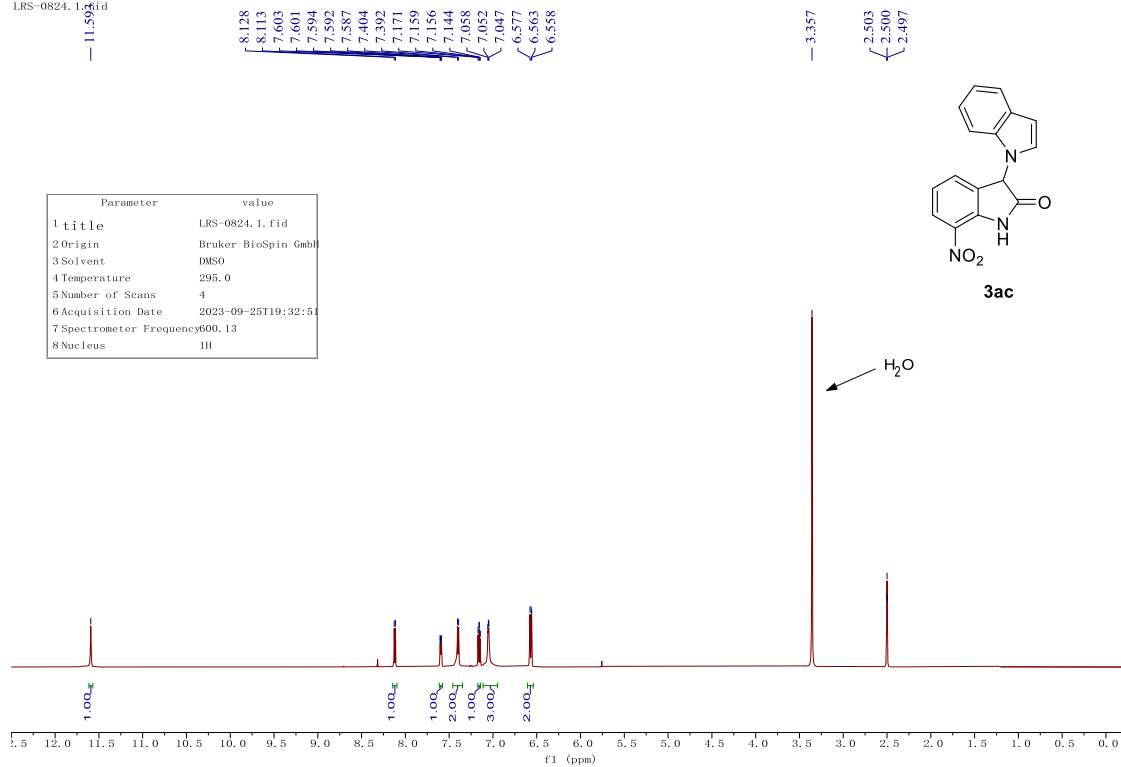
175.096  
137.038  
136.179  
132.881  
131.862  
129.112  
127.189  
124.855  
123.116  
122.089  
121.167  
120.037  
119.700  
109.698  
102.927

77.211  
77.000  
76.786  
59.315  
20.892  
16.172

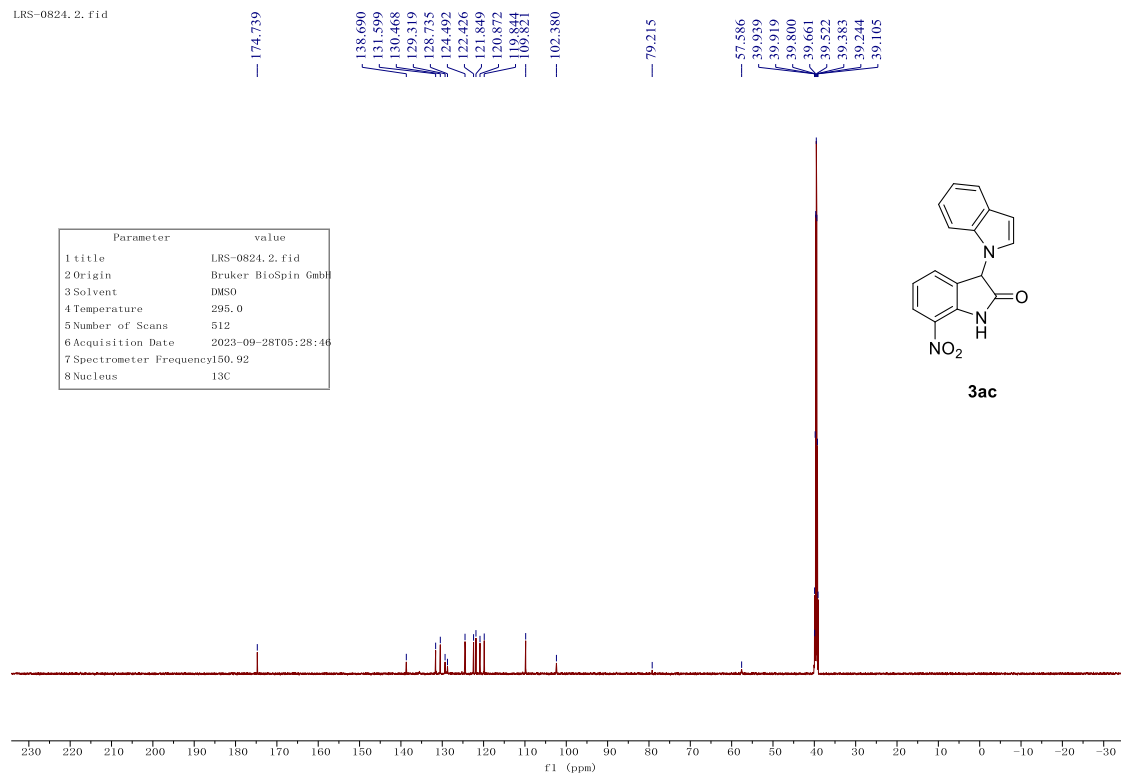
Parameter	Value
1 Title	LRS-0905.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	512
6 Acquisition Date	2023-10-09T17:33:53
7 Spectrometer Frequency	150.92
8 Nucleus	13C

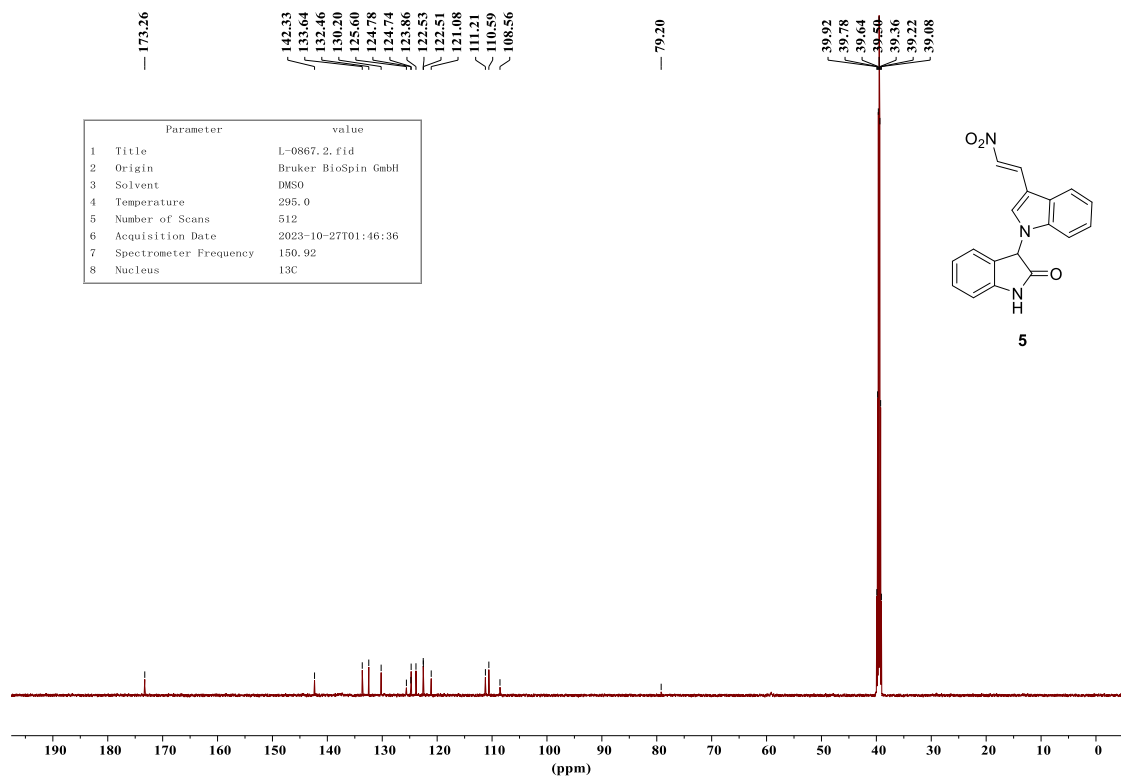
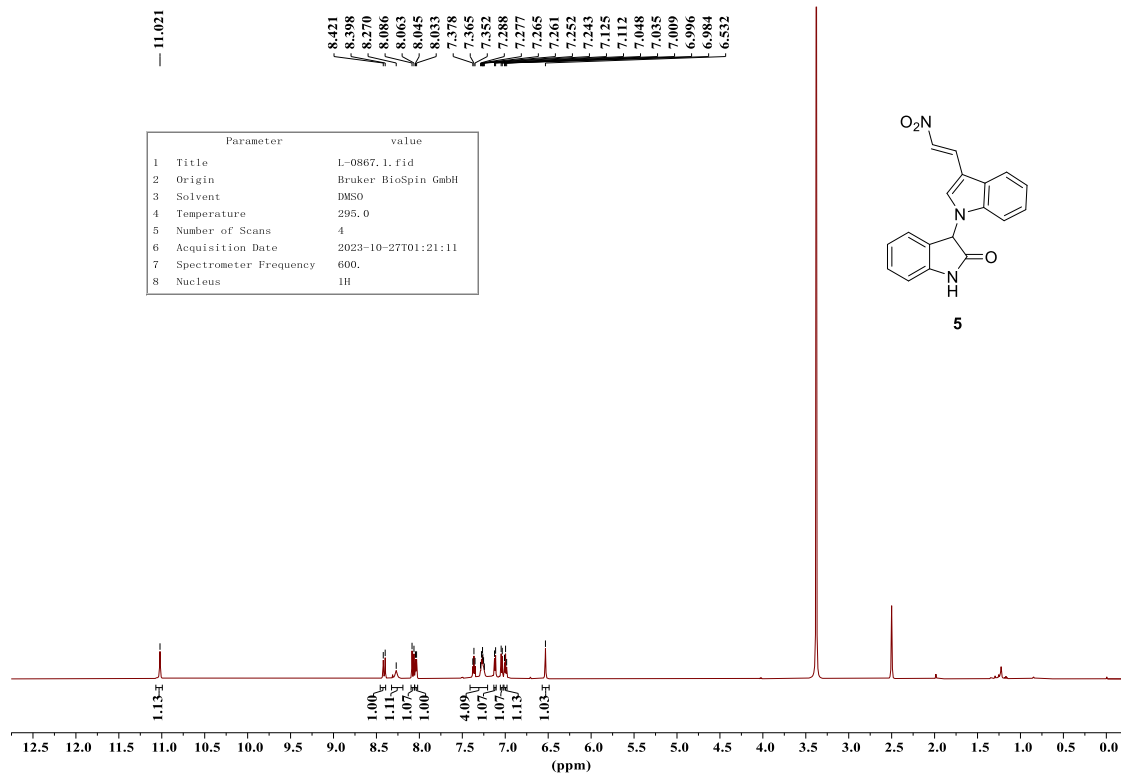


LRS-0824.1.fid



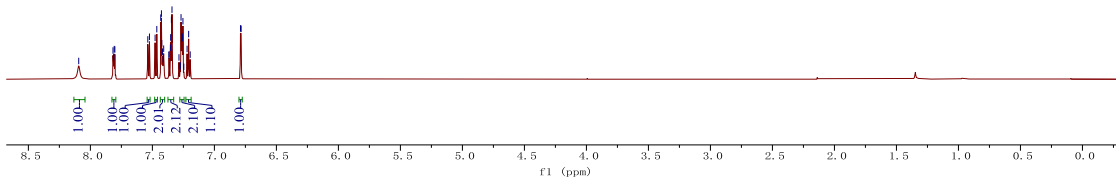
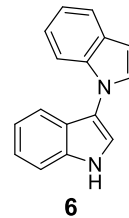
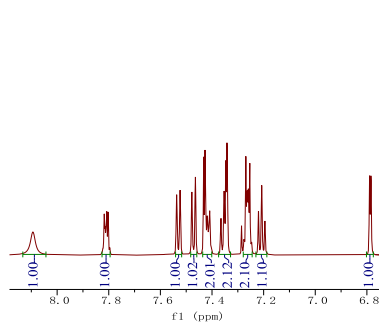
LRS-0824.2.fid





LRS-0827-3.1.fid  
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Parameter	值
1 标题	LRS-0827-3.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	4
6 Acquisition Date	2023-10-08T17:06:57
7 Spectrometer Frequency	600.13
8 Nucleus	1H



LRS-0827-3.2.fid  
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 110.809  
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 77.000  
 76.789

Parameter	value
1 title	LRS-0827-3.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.0
5 Number of Scans	512
6 Acquisition Date	2023-10-08T17:32:12
7 Spectrometer Frequency	150.92
8 Nucleus	13C

