

## Supporting Information

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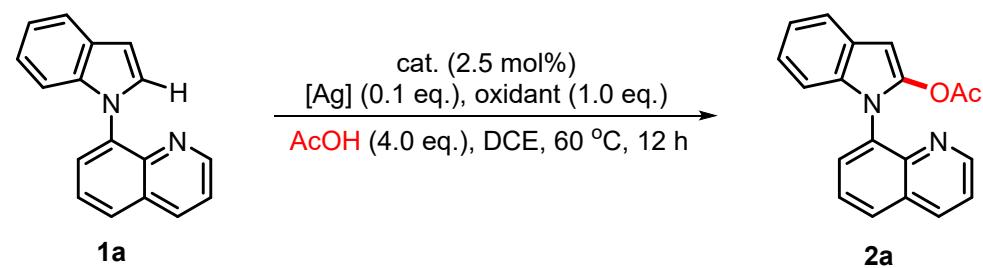
## I. General Experimental Information

The raw materials and solvents used in the reaction are all analytically pure. If there is no other instructions, they can be used directly.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were measured using a Bruker Avance (400 MHz and 100 MHz) and nuclear magnetic resonance instrument with TMS as an internal standard and were fully decoupled by broad band proton decoupling. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad resonances (br). High-resolution mass spectrometry was measured by APEXM Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

## II. Experimental Procedures for the Preparation of Starting Materials

Take **1a** as an example: Indole (2.4 mmol), 8-bromoquinoline (2 mmol), CuI (5 mol%),  $\text{K}_3\text{PO}_4$  (4.2 mmol), trans-N, N'-dimethyl-1, 2-cyclohexaneamine (20 mol%) was dissolved in DMF (1.0 M) and reacted at 110 °C in an argon atmosphere for 24 hours. After the reaction is completed, it is cooled to room temperature, and the organic substance obtained by washing with ethyl acetate is dried with anhydrous sodium sulfate, then concentrated under reduced pressure, and purified by column chromatography to obtain the target product.

## III. Optimization of Reaction Conditions



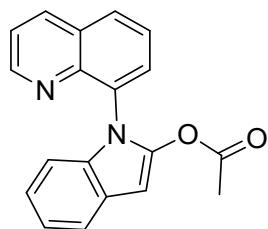
entry <sup>a</sup>	cat.	[Ag]	oxidant	AcOH	yield (%) <sup>b</sup>
1	$[\text{Cp}^*\text{IrCl}_2]_2$	AgOAc	$\text{MnO}_2$	AcOH	nr
2	$\text{Pd}(\text{OAc})_2$	AgOAc	$\text{MnO}_2$	AcOH	nr
3	$[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$	AgOAc	$\text{MnO}_2$	AcOH	nr
4	/	AgOAc	$\text{MnO}_2$	AcOH	nr
5	$[\text{Cp}^*\text{RhCl}_2]_2$	AgOAc	$\text{MnO}_2$	AcOH	75
6	$[\text{Cp}^*\text{RhCl}_2]_2$	$\text{Ag}_2\text{CO}$	$\text{MnO}_2$	AcOH	73

7	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Ag <sub>2</sub> O	MnO <sub>2</sub>	AcOH	69
8	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgTFA	MnO <sub>2</sub>	AcOH	38
9	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgF	MnO <sub>2</sub>	AcOH	68
10	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgSbF <sub>6</sub>	MnO <sub>2</sub>	AcOH	trace
11	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	/	MnO <sub>2</sub>	AcOH	34
12	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	AcOH	59
13	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	Mn(OAc) <sub>2</sub> ·4H <sub>2</sub> O	AcOH	64
14	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	AcOH	nr
15	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub> (2.0 eq.)	AcOH	46
16	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub> (1.5 eq.)	AcOH	65
17	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub> (0.5 eq.)	AcOH	52
18	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub>	AcOH (5.0 eq.)	73
19	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub>	AcOH (3.0 eq.)	80
20	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub>	AcOH (2.0 eq.)	83
21	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	MnO <sub>2</sub>	AcOH (1.0 eq.)	74

<sup>a</sup>Reaction conditions:**1a** (0.1 mmol), AcOH (4.0 eq.), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2.5 mol%), AgOAc (0.1 eq.), MnO<sub>2</sub> (1.0 eq.), DCE (0.5 mL), 60 °C (oil bath), 12 h. <sup>b</sup> Isolated yield by flash column chromatography.

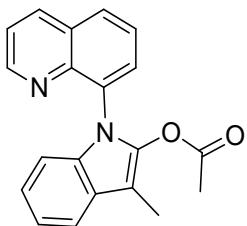
#### IV. Synthesis and Characterization of Compounds 2

An oven-dried Schlenk tube was charged with **1** (0.1 mmol, 24.4 mg), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 1.6 mg), AgOAc (0.01 mmol, 1.67 mg), MnO<sub>2</sub> (0.10 mmol, 8.69 mg), AcOH (0.20 mmol, 12 mg) and DCE (0.5 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 60 °C (oil bath) for 12 hours followed by cooling to ambient temperature. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc as the eluent to afford the product **2**.



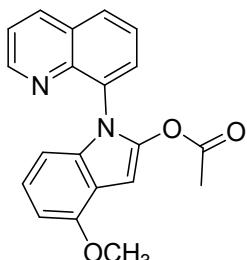
**1-(Quinolin-8-yl)-1H-indol-2-yl acetate (2aa)**

Eluent: petroleum ether/ethyl acetate (10:1). Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 83% (25.1 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.87 (m, 1H), 8.28-8.26 (m, 1H), 7.98-7.96 (m, 1H), 7.84-7.82 (m, 1H), 7.71-7.65 (m, 2H), 7.47-7.44 (m, 1H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.55 (s, 1H), 1.89 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.2, 151.1, 144.7, 143.3, 136.1, 134.1, 133.4, 129.3, 128.7, 126.7, 126.2, 121.9, 121.7, 120.7, 120.6, 110.1, 89.9, 20.7. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 303.1128, found: 303.1131.



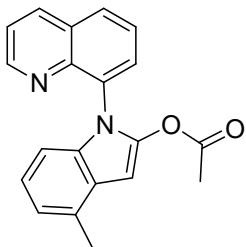
**3-Methyl-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ba)**

Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 89% (28.1 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.90-8.89 (m, 1H), 7.95-7.93 (m, 1H), 7.78-7.76 (m, 1H), 7.68-7.61 (m, 2H), 7.47-7.44 (m, 1H), 7.19-7.15 (m, 1H), 7.11-7.07 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 2.30 (s, 3H), 1.90 (s, 3H), **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.9, 151.1, 144.8, 139.8, 136.2, 134.3, 133.7, 129.3, 128.5, 127.4, 126.3, 121.8, 120.0, 118.9, 110.2, 98.4, 77.4, 77.1, 76.8, 20.3, 8.0. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 317.1285, found: 317.1287.



**4-Methoxy-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ca)**

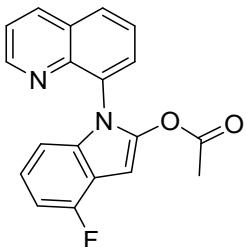
Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 62% (20.6 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.87 (m, 1H), 8.27-8.24 (m, 1H), 7.97-7.95 (m, 1H), 7.83-7.81 (m, 1H), 7.70-7.66 (m, 1H), 7.46-7.43 (m, 1H), 7.03-6.99 (m, 1H), 6.64 (s, 1H), 6.61-6.56 (m, 2H), 3.98 (s, 3H), 1.88 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.3, 153.4, 151.1, 144.7, 142.0, 136.1, 135.3, 133.5, 129.4, 129.3, 128.8, 126.2, 122.3, 121.9, 117.1, 103.6, 101.0, 87.4, 55.5, 20.6. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup>: 333.1234, found: 333.1239.



**4-Methyl-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2da)**

Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 84% (26.5 mg).

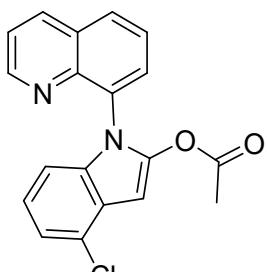
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.89-8.87 (m, 1H), 8.28-8.25 (m, 1H), 7.98-7.95 (m, 1H), 7.84-7.82 (m, 1H), 7.71-7.67 (m, 1H), 7.47-7.44 (m, 1H), 7.03-6.95 (m, 2H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 2.61 (s, 3H), 1.89 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.3, 151.1, 144.7, 142.8, 136.1, 133.7, 133.6, 130.1, 129.3, 128.7, 126.4, 126.2, 121.9, 121.8, 121.0, 107.7, 88.3, 20.6, 18.8. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 317.1285, found: 317.1284.



**4-Fluoro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ea)**

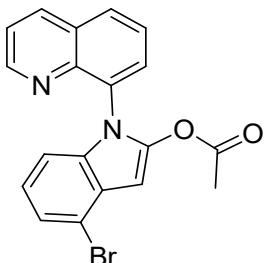
Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 63% (20.2 mg).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.87 (m, 1H), 8.29-8.27 (m, 1H), 8.00-7.98 (m, 1H), 7.83-7.81 (m, 1H), 7.72-7.68 (m, 1H), 7.49-7.46 (m, 1H), 7.02-6.96 (m, 1H), 6.86-6.81 (m, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 1H), 1.89 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.0, 157.6 (d, *J* = 244.8 Hz), 151.3, 144.6, 142.9, 136.4 (d, *J* = 11.1 Hz), 136.2, 133.2, 129.4, 129.3, 129.1, 126.2, 122.0 (d, *J* = 3.9 Hz), 122.0, 115.7, (d, *J* = 22.9 Hz), 106.3 (d, *J* = 3.5 Hz), 105.7 (d, *J* = 18.9 Hz), 86.1, 20.6. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -123.4. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 321.1034, found: 321.1037.



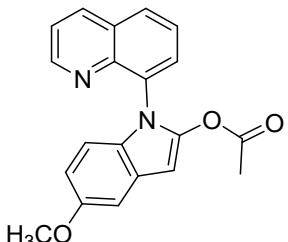
**4-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2fa)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 70% (23.5 mg).  
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.86 (m, 1H), 8.29-8.27 (m, 1H), 8.01-7.98 (m, 1H), 7.82-7.80 (m, 1H), 7.72-7.68 (m, 1H), 7.49-7.47 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.02-6.98 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.67 (s, 1H), 1.90 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.9, 151.3, 144.5, 143.6, 136.2, 129.4, 129.3, 129.2, 126.2, 122.2, 122.0, 120.5, 108.8, 88.7, 20.6. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 337.0738, found: 337.0742.



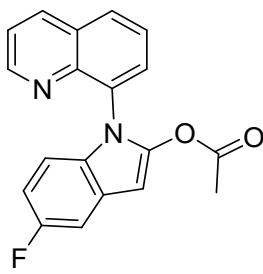
**4-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ga)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 83% (31.5 mg).  
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.86 (m, 1H), 8.29-8.27 (m, 1H), 8.01-7.98 (m, 1H), 7.82-7.80 (m, 1H), 7.72-7.68 (m, 1H), 7.49-7.46 (m, 1H), 7.33-7.31 (m, 1H), 6.96-6.92 (m, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.62 (s, 1H), 1.90 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.9, 151.3, 144.5, 143.6, 136.2, 134.3, 133.0, 129.4, 129.3, 129.2, 127.5, 126.2, 123.6, 122.5, 122.0, 114.9, 109.3, 90.3, 20.7. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 381.0233, found: 381.0235.



**5-Methoxy-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ha)**

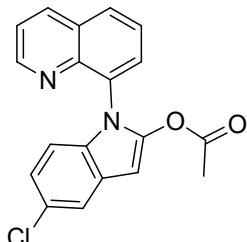
Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 80% (26.6 mg).  
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.87 (m, 1H), 8.27-8.24 (m, 1H), 7.96-7.94 (m, 1H), 7.82-7.79 (m, 1H), 7.70-7.66 (m, 1H), 7.46-7.43 (m, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.75-6.73 (m, 1H), 6.48 (s, 1H), 3.86 (s, 3H), 1.88 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.3, 156.2, 151.2, 144.7, 142.5, 136.1, 134.8, 133.5, 129.4, 129.3, 128.8, 126.2, 121.9, 121.4, 120.7, 109.8, 94.6, 89.6, 55.7, 20.7. **HRMS** (ESI) m/z calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup>: 333.1234, found: 333.1238.



**5-Fluoro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ia)**

Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 59% (18.9 mg).

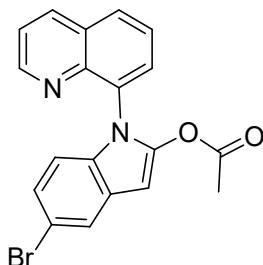
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.87 (m, 1H), 8.29-8.27 (m, 1H), 8.00-7.97 (m, 1H), 7.82-7.80 (m, 1H), 7.72-7.68 (m, 1H), 7.49-7.45 (m, 1H), 7.33-7.30 (m, 1H), 6.87-6.79 (m, 2H), 6.52 (s, 1H), 1.90 (s, 3H); **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>) δ 167.0, 158.5 (d, *J* = 233.1 Hz), 151.2, 144.6, 144.4, 136.2, 133.2, 130.6, 129.3, 129.3, 128.9, 127.1 (d, *J* = 10.7 Hz), 126.2, 122.0, 111.0 (d, *J* = 9.5 Hz), 109.8 (d, *J* = 25.6 Hz), 105.8 (d, *J* = 24.1 Hz), 90.1 (d, *J* = 4.2 Hz), 20.6. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -123.7. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>FN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 321.1034, found: 321.1038.



**5-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ja)**

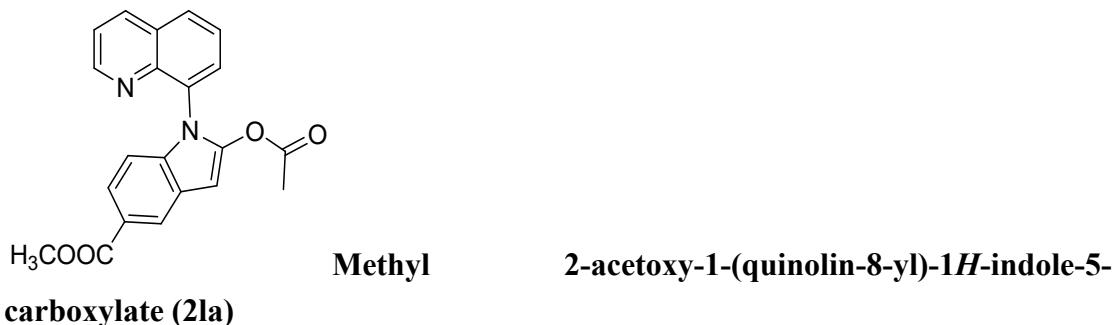
Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 61% (20.5 mg).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.87-8.86 (m, 1H), 8.29-8.26 (m, 1H), 8.00-7.98 (m, 1H), 7.81-7.79 (m, 1H), 7.71-7.68 (m, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.48-7.45 (m, 1H), 7.05-7.02 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.51 (s, 1H), 1.90 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.9, 151.3, 144.5, 144.2, 136.2, 133.0, 132.5, 129.3, 129.3, 129.1, 127.7, 126.2, 126.2, 122.0, 121.9, 120.1, 111.3, 89.6, 20.6. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>ClN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 337.0738, found: 337.0740.

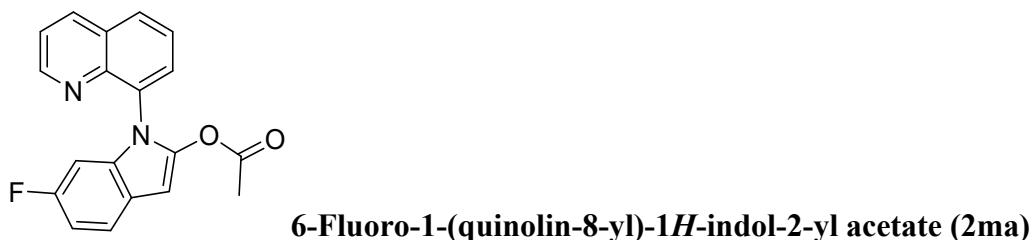


**5-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ka)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 52% (19.8 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.87-8.85 (m, 1H), 8.29-8.27 (m, 1H), 8.00-7.98 (m, 1H), 7.81-7.79 (m, 2H), 7.72-7.68 (m, 1H), 7.49-7.46 (m, 1H), 7.18-7.15 (m, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.50 (s, 1H), 1.90 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.9, 151.3, 144.5, 144.0, 136.2, 132.95, 132.7, 129.3, 129.3, 129.1, 128.3, 126.2, 124.5, 123.1, 122.0, 113.7, 111.7, 89.4, 20.6. **HRMS** (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 381.0233, found: 381.0237.

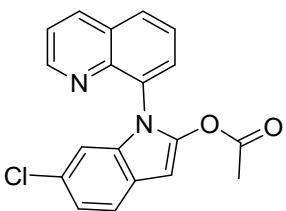


Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 50% (18 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.86-8.85 (m, 1H), 8.42 (d, *J* = 1.2 Hz, 1H), 8.29-8.27 (m, 1H), 8.01-7.98 (m, 1H), 7.82-7.79 (m, 2H), 7.72-7.69 (m, 1H), 7.48-7.46 (m, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.63 (s, 1H), 3.92 (s, 3H), 1.89 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.1, 166.9, 151.3, 144.5, 144.2, 136.7, 136.2, 132.8, 129.3, 129.2, 126.2, 126.2, 123.5, 123.2, 122.6, 122.1, 109.9, 90.8, 51.9, 20.6. **HRMS** (ESI) m/z calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup>: 361.1183, found: 361.1187.



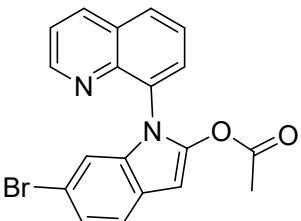
Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 68% (21.8 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.87-8.85 (m, 1H), 8.27-2.24 (m, 1H), 7.98-7.96 (m, 1H), 7.79-7.77 (m, 1H), 7.69-7.65 (m, 1H), 7.55-7.52 (m, 1H), 7.47-7.44 (m, 1H), 6.91-6.86 (m, 1H), 6.60-6.58 (m, 1H), 6.49 (s, 1H), 3.92 (s, 1H), 1.89 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.2, 159.7 (d, *J* = 235.3 Hz), 151.3, 144.5, 143.4, 136.2, 133.0, 129.4, 129.2, 129.0, 126.2, 122.9, 122.0, 121.5 (d, *J* = 9.6 Hz), 121.4, 109.1 (d, *J* = 24.0

Hz), 97.0 (d,  $J$  = 26.8 Hz), 89.8, 20.6.  **$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.8. **HRMS** (ESI) m/z calcd for  $\text{C}_{19}\text{H}_{14}\text{FN}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 321.1034, found: 321.1036.



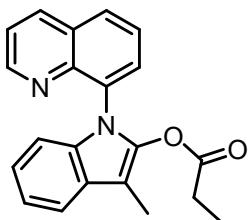
**6-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2na)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 72% (24.2 mg).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88-8.86 (m, 1H), 8.28-8.26 (m, 1H), 8.00-7.97 (m, 1H), 7.81-7.79 (m, 1H), 7.72-7.68 (m, 1H), 7.56 (d,  $J$  = 8.4 Hz, 1H), 7.48-7.45 (m, 1H), 7.13-7.10 (m, 1H), 6.92 (d,  $J$  = 1.5 Hz, 1H), 6.54 (s, 1H), 1.89 (s, 3H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 151.3, 144.6, 143.8, 136.2, 134.4, 132.8, 129.3, 129.3, 129.2, 127.4, 126.2, 125.2, 122.0, 121.7, 121.3, 110.2, 89.8, 20.6. **HRMS** (ESI) m/z calcd for  $\text{C}_{19}\text{H}_{14}\text{BrN}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 381.0233, found: 381.0238.



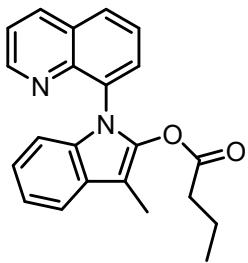
**6-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2oa)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 73% (27.7 mg).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88-8.86 (m, 1H), 8.28-8.26 (m, 1H), 8.00-7.98 (m, 1H), 7.82-7.79 (m, 1H), 7.72-7.68 (m, 1H), 7.52 (d,  $J$  = 8.4 Hz, 1H), 7.49-7.46 (m, 1H), 7.27-7.24 (m, 1H), 7.07 (d,  $J$  = 1.5 Hz, 1H), 6.53 (s, 1H), 1.88 (s, 3H);  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 151.3, 144.6, 143.7, 136.2, 134.8, 132.8, 129.4, 129.2, 126.2, 125.6, 123.9, 122.1, 122.0, 114.9, 113.1, 89.9, 20.6. **HRMS** (ESI) m/z calcd for  $\text{C}_{19}\text{H}_{14}\text{BrN}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 381.0233, found: 381.0235.



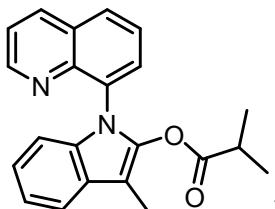
**3-Methyl-1-(quinolin-8-yl)-1*H*-indol-2-yl propionate (2bb)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 51% (17.0 mg).  
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.90-8.89 (m, 1H), 8.27-8.24 (m, 1H), 7.94-7.92 (m, 1H), 7.78-7.76 (m, 1H), 7.65 (dd, *J* = 15.7, 7.8 Hz, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.19-7.15 (m, 1H), 7.12-7.08 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H), 2.19-2.12 (m, 2H), 0.84 (t, *J* = 7.6 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 171.4, 151.1, 144.8, 139.9, 136.2, 134.2, 133.7, 129.5, 129.3, 128.4, 127.5, 126.3, 121.8, 121.7, 120.0, 118.8, 110.1, 98.3, 27.1, 8.8, 7.9. **HRMS** (ESI) *m/z* calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 331.1441, found: 331.1437.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl butyrate (2bc)**

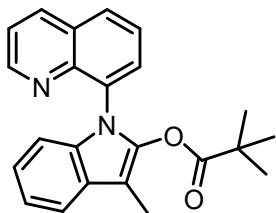
Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 84% (28.8 mg).  
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.91-8.89 (m, 1H), 8.27-8.24 (m, 1H), 7.94-7.92 (m, 1H), 7.78-7.76 (m, 1H), 7.67-7.61 (m, 2H), 7.47-7.44 (m, 1H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 2.28 (s, 3H), 2.14-2.12 (m, 2H), 1.36-1.29 (m, 2H), 0.64 (t, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 170.6, 151.2, 144.9, 139.9, 136.1, 134.3, 133.7, 129.6, 129.3, 128.5, 127.4, 126.2, 121.8, 121.7, 120.0, 118.8, 110.1, 98.2, 35.5, 18.1, 13.2, 7.9. **HRMS** (ESI) *m/z* calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 345.1598, found: 345.1594.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl isobutyrate (2bd)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 80% (27.6 mg).  
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.91-8.90 (m, 1H), 8.26-8.24 (m, 1H), 7.94-7.92 (m, 1H), 7.79-7.77 (m, 1H), 7.67-7.61 (m, 2H), 7.47-7.43 (m, 1H), 7.19-7.15 (m, 1H), 7.12-7.08 (m, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 2.44-2.37 (m, 1H), 2.27 (s, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 174.0, 151.2, 145.0, 139.9, 136.1, 134.3, 133.7, 129.7, 129.3, 128.8, 128.5, 127.5, 126.2,

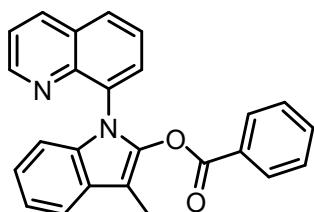
121.8, 121.7, 119.9, 118.8, 110.0, 98.1, 33.6, 18.5, 18.3, 7.8. **HRMS** (ESI) m/z calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>(M+H)<sup>+</sup>: 345.1598, found: 345.1599.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl pivalate (2be)**

Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil. Isolated yield: 58% (20.9 mg).

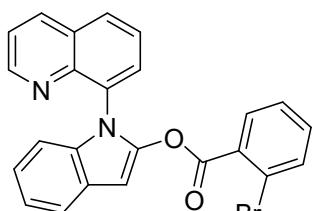
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.92-8.91 (m, 1H), 8.26-8.23 (m, 1H), 7.93-7.91 (m, 1H), 7.79-7.76 (m, 1H), 7.67-7.60 (m, 2H), 7.47-7.43 (m, 1H), 7.18-7.14 (m, 1H), 7.12-7.08 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 2.25 (s, 3H), 0.84 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 175.4, 151.1, 145.0, 140.2, 136.1, 133.7, 129.8, 129.3, 128.5, 127.6, 126.2, 121.8, 121.6, 119.9, 118.8, 109.9, 98.0, 38.8, 26.5, 7.8. **HRMS** (ESI) m/z calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>(M+H)<sup>+</sup>: 359.1754, found: 359.1754.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl benzoate (2bf)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 83% (31.3 mg).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.88-8.86 (m, 1H), 8.18-8.16 (m, 1H), 7.87-7.83 (m, 1H), 7.68-7.67 (m, 1H), 7.66-7.65 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.30-7.26 (m, 2H), 7.21-7.18 (m, 1H), 7.16-7.12 (m, 1H), 7.03-7.00 (m, 1H), 2.35 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 163.6, 151.1, 144.7, 139.9, 136.1, 134.2, 133.7, 133.6, 130.0, 129.3, 129.2, 128.5, 128.4, 128.3, 127.6, 126.3, 121.8, 121.7, 120.1, 118.9, 110.2, 98.7, 8.1. **HRMS** (ESI) m/z calcd for C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>(M+H)<sup>+</sup>: 379.1441, found: 379.1443.

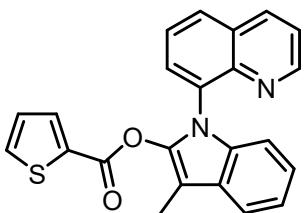


**1-(Quinolin-8-yl)-1H-indol-2-yl 2-bromobenzoate (2ag)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 67% (29.5 mg).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.86-8.85 (m, 1H), 8.25-8.22 (m, 1H), 7.96-7.91

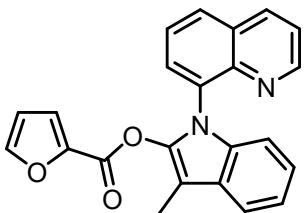
(m, 2H), 7.73-7.67 (m, 2H), 7.54 (d,  $J = 9.1$  Hz, 1H), 7.42-7.39 (m, 1H), 7.22-7.17 (m, 2H), 7.15-7.10 (m, 2H), 7.05-7.02 (m, 1H), 6.79 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  161.5, 151.3, 144.9, 143.4, 136.1, 134.7, 134.1, 133.5, 133.2, 131.6, 129.9, 129.6, 129.3, 128.8, 126.9, 126.9, 126.3, 122.6, 121.9, 120.9, 120.8, 110.0, 90.0. HRMS (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{16}\text{BrN}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 442.0390, found: 442.0384.



### **3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl thiophene-2-carboxylate (2bh)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 97% (37.3 mg).

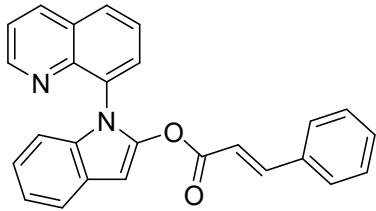
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.86-8.84 (m, 1H), 8.20-8.17 (m, 1H), 7.88-7.86 (m, 1H), 7.84-7.82 (m, 1H), 7.66-7.60 (m, 2H), 7.48-7.48 (m, 1H), 7.39-7.36 (m, 1H), 7.21-7.17 (m, 1H), 7.15-7.10 (m, 1H), 6.99 (d,  $J = 8.0$  Hz, 1H), 6.86-6.85 (m, 1H), 6.36-6.34 (m, 1H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  155.3, 151.0, 147.4, 144.6, 143.0, 139.1, 136.1, 134.2, 133.6, 129.3, 129.2, 128.3, 127.5, 126.3, 122.0, 121.7, 120.1, 119.5, 119.0, 112.0, 110.2, 99.0, 8.0. HRMS (ESI) m/z calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_2\text{S}$  ( $\text{M}+\text{H}$ ) $^+$ : 385.1005, found: 385.1012.



### **3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl furan-2-carboxylate (2bi)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 77% (28.5 mg).

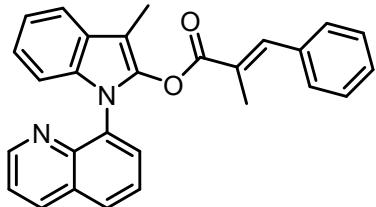
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.67-8.65 (m, 1H), 8.19-8.16 (m, 1H), 7.87-7.83 (m, 2H), 7.67-7.65 (m, 1H), 7.64-7.60 (m, 2H), 7.59-7.57 (m, 1H), 7.46-7.44 (m, 1H), 7.38-7.35 (m, 1H), 7.22-7.18 (m, 1H), 7.16-7.12 (m, 1H), 7.03 (d,  $J = 8.1$  Hz, 1H), 6.96-6.94 (m, 1H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  158.9, 151.0, 144.6, 139.6, 136.0, 134.8, 134.1, 133.8, 133.6, 131.6, 129.3, 129.2, 128.3, 127.8, 127.6, 126.2, 121.9, 121.7, 120.1, 119.0, 110.2, 98.9, 8.1. HRMS (ESI) m/z calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 369.1234, found: 369.1229.



**1-(Quinolin-8-yl)-1H-indol-2-yl cinnamate (2aj)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 65% (25.4 mg).

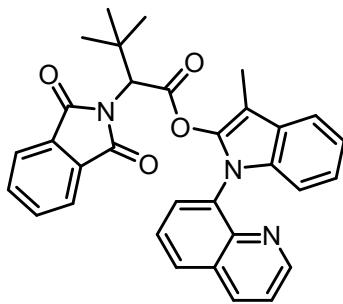
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.89-8.88 (m, 1H), 8.27-8.25 (m, 1H), 7.98-7.96 (m, 1H), 7.90-7.88 (m, 1H), 7.74-7.69 (m, 2H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 1H), 7.35-7.32 (m, 2H), 7.30-7.28 (m, 3H), 7.20-7.16 (m, 1H), 7.14-7.09 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1 H), 6.70 (s, 1H), 6.18 (d, *J* = 16.0 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 162.9, 151.2, 146.9, 144.8, 143.6, 136.1, 134.1, 133.8, 133.6, 130.8, 129.5, 129.4, 128.9, 128.7, 128.2, 126.9, 126.3, 121.9, 121.7, 120.8, 120.7, 116.2, 110.1, 89.7. **HRMS** (ESI) m/z calcd for C<sub>26</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 391.1441, found: 391.1440.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl (E)-2-methyl-3-phenylacrylate (2bk)**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 89% (37.4 mg).

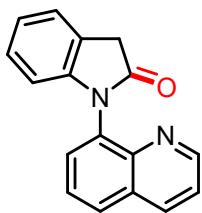
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.93-8.92 (m, 1H), 8.24-8.21 (m, 1H), 7.92-7.90 (m, 1H), 7.86-7.84 (m, 1H), 7.68-7.64 (m, 2H), 7.44-7.41 (m, 1H), 7.36-7.30 (m, 4H), 7.22-7.18 (m, 1H), 7.17-7.12 (m, 3H), 7.05-7.03 (m, 1H), 2.37 (s, 3H), 1.86 (d, *J* = 1.5 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 165.6, 151.0, 144.8, 140.9, 140.2, 136.2, 135.3, 134.1, 133.8, 129.7, 129.4, 129.3, 128.7, 128.4, 128.3, 127.7, 126.7, 126.3, 121.8, 120.0, 118.9, 110.1, 98.6, 13.9, 8.1. **HRMS** (ESI) m/z calcd for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 419.1754, found: 419.1752.



**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl 2-(1,3-dioxoisooindolin-2-yl)-3,3-dimethylbutanoate (2bj)**

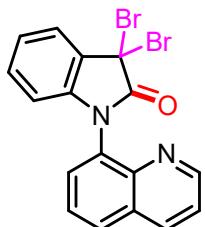
Eluent: petroleum ether/ethyl acetate (5:1). Yellow oil. Isolated yield: 78% (40.2 mg).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.73-8.71 (m, 1H), 8.56-8.55 (m, 1H), 8.26-8.24 (m, 1H), 8.05-8.02 (m, 1H), 7.93-7.90 (m, 1H), 7.82-7.80 (m, 2H), 7.78-7.74 (m, 3H), 7.72-7.70 (m, 1H), 7.69-7.66 (m, 2H), 7.63-7.62 (m, 2H), 7.60-7.58 (m, 3H), 7.40-7.36 (m, 1H), 7.27-7.24 (m, 1H), 7.15-7.10 (m, 2H), 7.10-7.04 (m, 2H), 6.96-6.91 (m, 2H), 4.31 (s, 1H), 3.99 (s, 1H), 2.31 (s, 3H), 2.27 (s, 3H), 1.01 (s, 9H), 0.92 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 167.4, 164.8, 164.0, 151.0, 150.8, 144.7, 139.2, 136.0, 135.9, 134.3, 134.1, 134.0, 133.5, 131.6, 131.2, 129.5, 129.3, 129.0, 128.5, 128.4, 127.5, 126.2, 123.6, 123.6, 121.9, 121.8, 121.7, 121.5, 120.0, 119.0, 118.8, 109.8, 109.8, 98.8, 98.3, 59.3, 59.1, 35.8, 35.5, 27.5, 27.4, 8.1, 7.7. **HRMS** (ESI) m/z calcd for C<sub>32</sub>H<sub>28</sub>N<sub>3</sub>O<sub>4</sub>(M+H)<sup>+</sup>: 518.2074, found: 518.2071.



**1-(Quinolin-8-yl)indolin-2-one (2ag-1)**

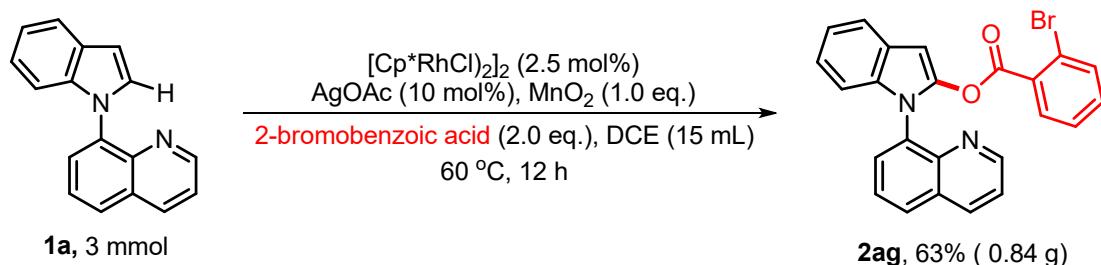
Eluent: petroleum ether/ethyl acetate (1:1). Red oil. Isolated yield: 58% (30.2 mg). **<sup>1</sup>H NMR** (500 MHz, Chloroform-*d*) δ 8.88-8.87 (m, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.80-7.78 (m, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.46-7.44 (m, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.12-7.09 (m, 1H), 7.07-7.04 (m, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 3.96 (d, *J* = 22.3 Hz, 1H), 3.80 (d, *J* = 22.4 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, Chloroform-*d*) δ 175.8, 151.4, 146.9, 144.6, 136.7, 132.8, 130.2, 130.1, 129.7, 128.0, 126.9, 124.9, 124.8, 122.9, 122.3, 110.1, 36.7. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>O (M+H)<sup>+</sup>: 261.1022, found: 261.1017.



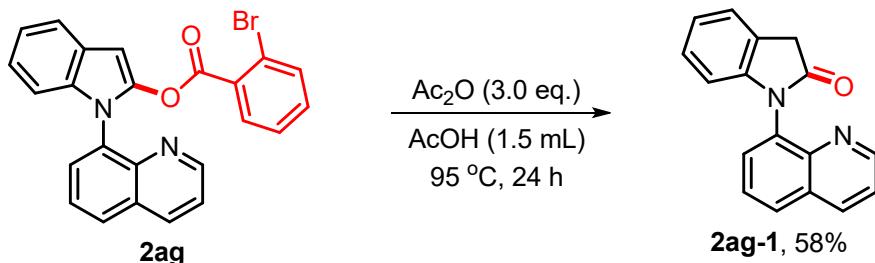
**3,3-Dibromo-1-(quinolin-8-yl)indolin-2-one (2ag-2)**

Eluent: petroleum ether/ethyl acetate (5:1). Pink solid. Melting point: 160-162 °C. Isolated yield: 74% (61.5 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.86-8.85 (m, 1H), 8.25-8.23 (m, 1H), 8.00-7.98 (m, 1H), 7.84-7.82 (m, 1H), 7.75-7.67 (m, 2H), 7.47-7.44 (m, 1H), 7.20-7.13 (m, 2H), 6.34-6.29 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 169.9, 151.3, 144.0, 141.5, 136.2, 131.3, 130.9, 130.8, 130.0, 129.7, 129.6, 126.4, 125.9, 124.1, 122.2, 110.9, 45.7. **HRMS** (ESI) m/z calcd for C<sub>17</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O (M+H)<sup>+</sup>: 416.9233, found: 416.9233.

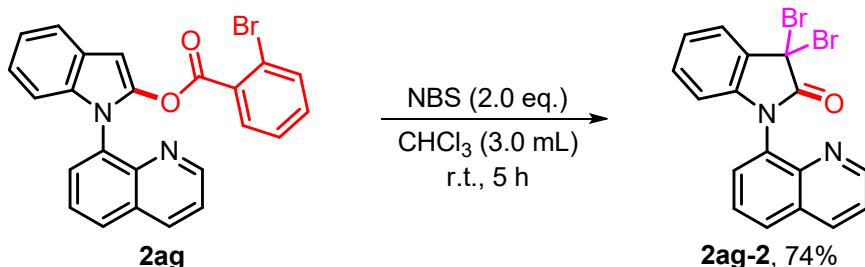
## V. Scale-up Synthesis and Further Transformation



An oven-dried Schlenk tube was charged with **1a** (3 mmol, 0.73 g), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.075 mmol, 48 mg), AgOAc (0.3 mmol, 50.1 mg), MnO<sub>2</sub> (3 mmol, 260.7 mg), AcOH (10 mmol, 360 mg) and DCE (15 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 60 °C (oil bath) for 12 hours followed by cooling to ambient temperature. The resulting mixture was quenched by filtered through a celite pad and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc as the eluent to afford the product **2ag** in 63% yield (0.84 g).



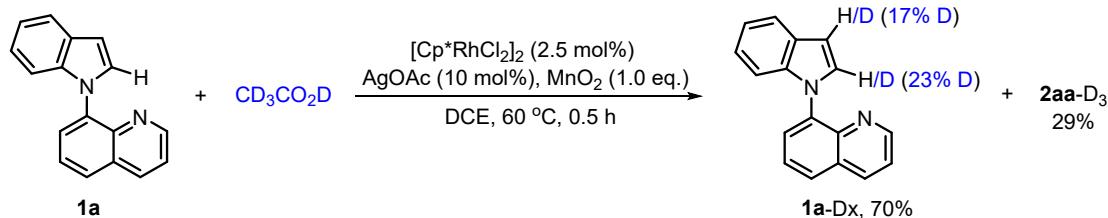
**2ag** (0.3 mmol) was dissolved in acetic acid (1.5 mL) and the reaction mixture was heated to 95 °C for 24 hours. The reaction was then cooled to room temperature, which was then extracted with ethyl acetate. The combined organic layer were dried and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1/1, v/v) to afford corresponding product **2ag-1** (58% yield).



To a solution of **2ag** (0.2 mmol) in CHCl<sub>3</sub> (3.0 mL), NBS (N-bromosuccinimide) (0.4 mmol) was added portionwisely and then the mixture was heated at rt. under air for 5 h. The reaction solution was concentrated and purified by column chromatography on silica gel to provide the desired product **2ag-2** (74% yield).

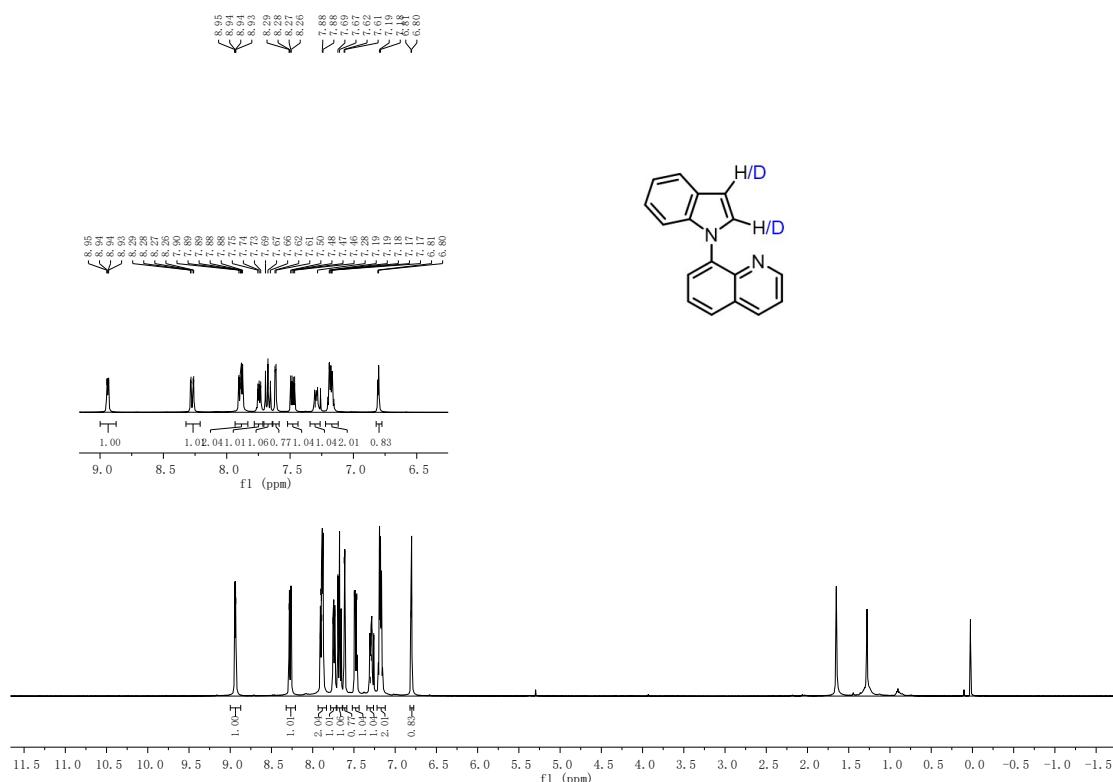
## VI. Mechanistic Studies

### H/D exchange reaction

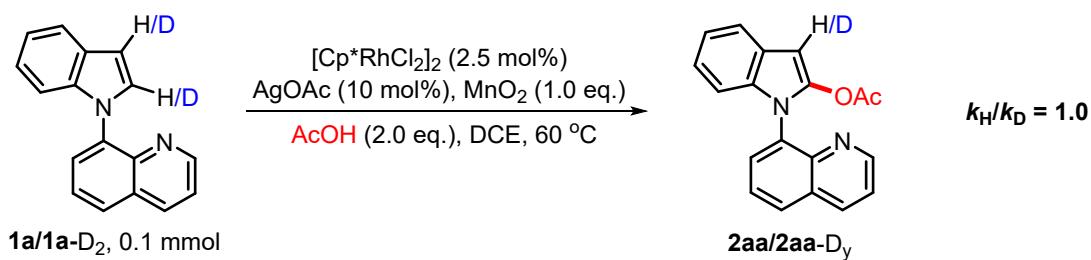


To an oven-dried sealed tube charged with **1a** (0.1 mmol, 24.4 mg), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2.5 mol%, 1.6 mg), MnO<sub>2</sub> (0.1 mmol, 8.69 mg), AgOAc (0.01 mmol, 1.67 mg), CD<sub>3</sub>CO<sub>2</sub>D (12 uL, 20 mmol) and DCE (0.5 mL) was added under air atmosphere. The

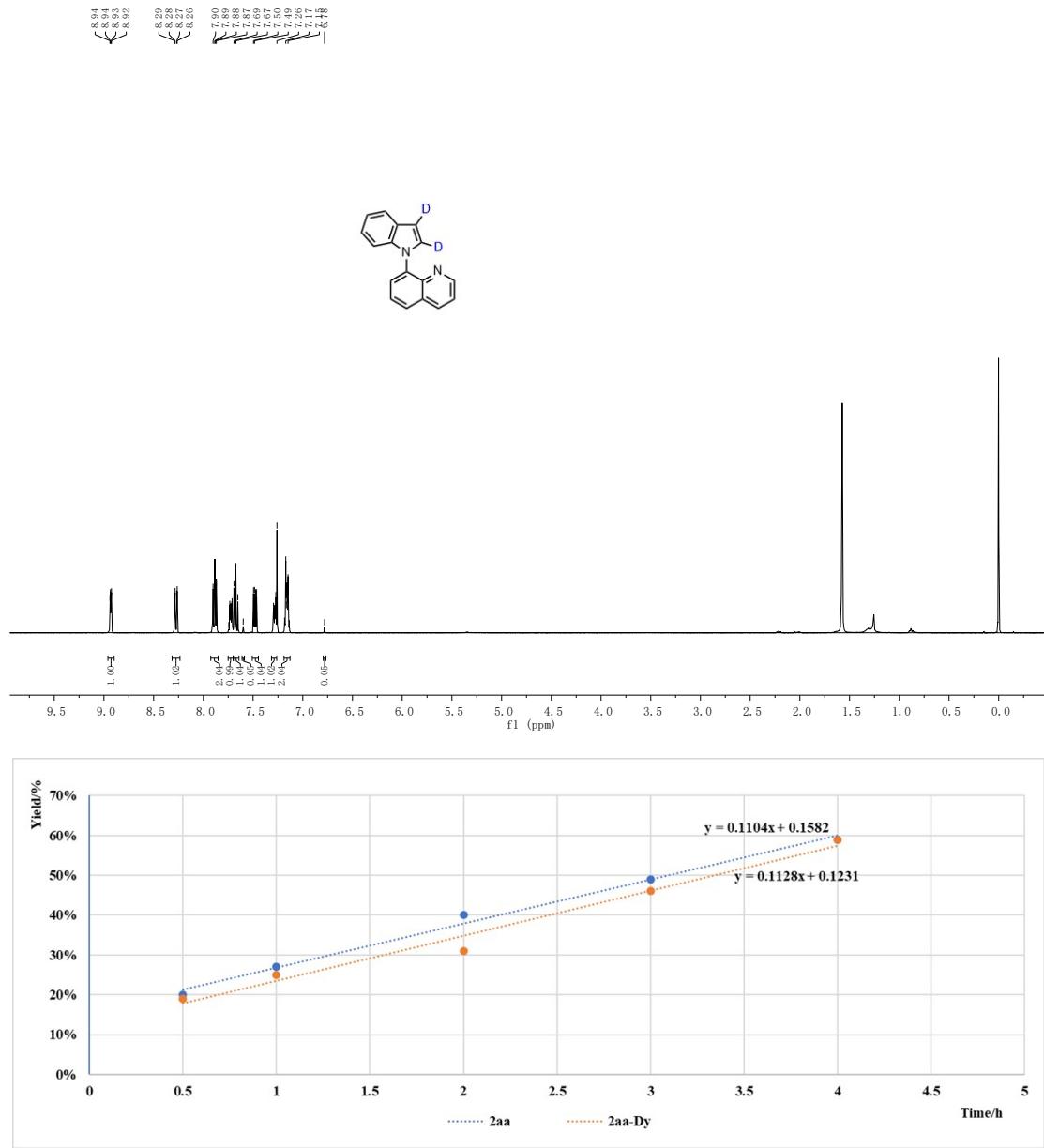
reaction mixture was then allowed to stir at 60 °C (oil bath) for 0.5 h. The reaction was followed by TLC, cooled after the reaction, diluted with ethyl acetate, filtered through Celite. Then the filtrate was concentrated and purified by flash column chromatography to give **1a-D<sub>x</sub>** in 70% yield.



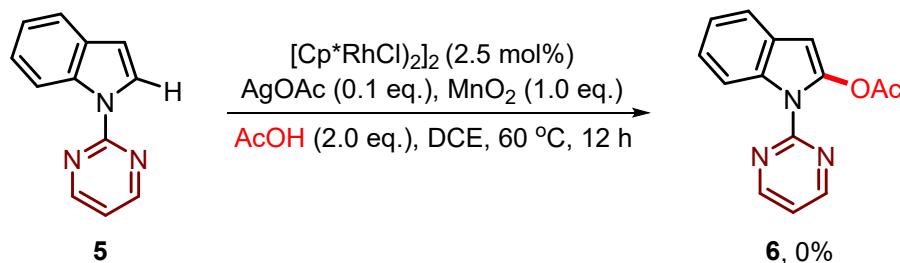
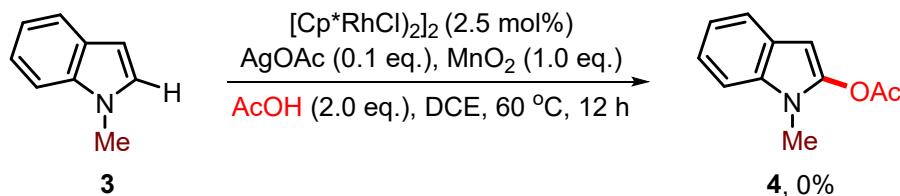
### *kinetic isotope effect (parallel)*



To an oven-dried sealed tube charged with **1a** (0.1 mmol, 24.4 mg) or **1a-D<sub>2</sub>** (0.1 mmol, 26.4 mg), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (2.5 mol%, 1.6 mg), MnO<sub>2</sub> (0.1 mmol, 8.69 mg), AgOAc (0.01 mmol, 1.67 mg), AcOH (0.2 mmol, 12 mg) and DCE (0.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at 60 °C (oil bath). The reaction was followed by TLC, cooled after the reaction, diluted with ethyl acetate, filtered through Celite. Then the filtrate was concentrated and purified by flash column chromatography to give the product **2aa** or **2aa-D<sub>y</sub>**.

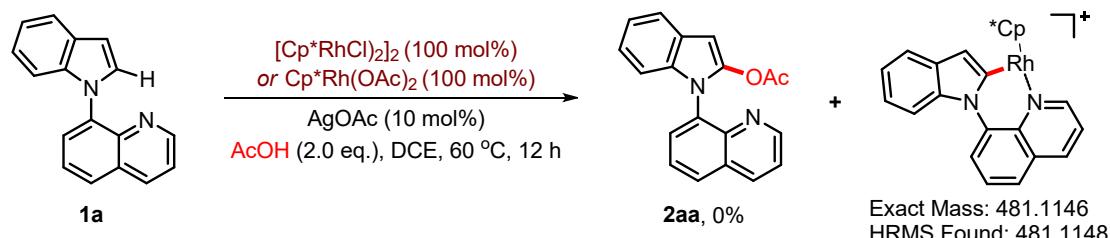


### *directing-group variation*

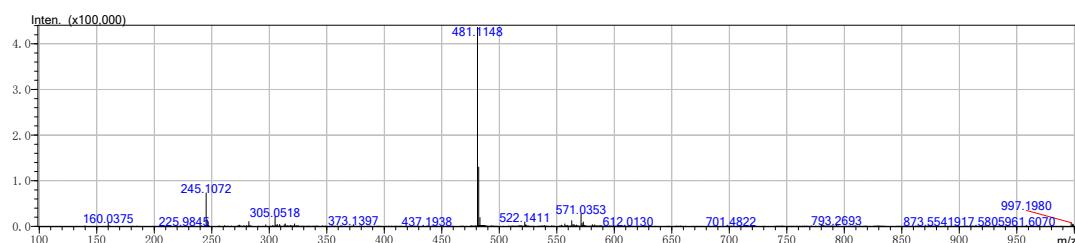


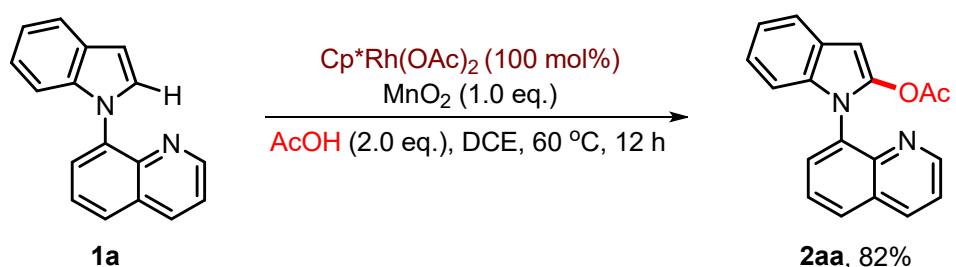
To an oven-dried sealed tube charged with **3** (0.1 mmol, 13.1 mg) or **5** (0.1 mmol, 19.5 mg),  $[\text{Cp}^*\text{RhCl}_2]_2$  (2.5 mol%, 1.6 mg),  $\text{MnO}_2$  (0.1 mmol, 8.69 mg),  $\text{AgOAc}$  (0.01 mmol, 1.67 mg),  $\text{AcOH}$  (0.2 mmol, 12 mg) and  $\text{DCE}$  (0.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at  $60\text{ }^\circ\text{C}$  (oil bath) for 12 h and followed by TLC.

### catalyst investigation



To an oven-dried sealed tube charged with **1a** (0.1 mmol, 24.4 mg),  $[\text{Cp}^*\text{RhCl}_2]_2$  (0.1 mmol, 64 mg) or  $\text{Cp}^*\text{Rh}(\text{OAc})_2$  (0.1 mmol, 35.6 mg),  $\text{AgOAc}$  (0.01 mmol, 1.67 mg),  $\text{AcOH}$  (0.2 mmol, 12 mg) and  $\text{DCE}$  (0.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at  $60\text{ }^\circ\text{C}$  (oil bath) for 12 h and followed by TLC and HRMS.

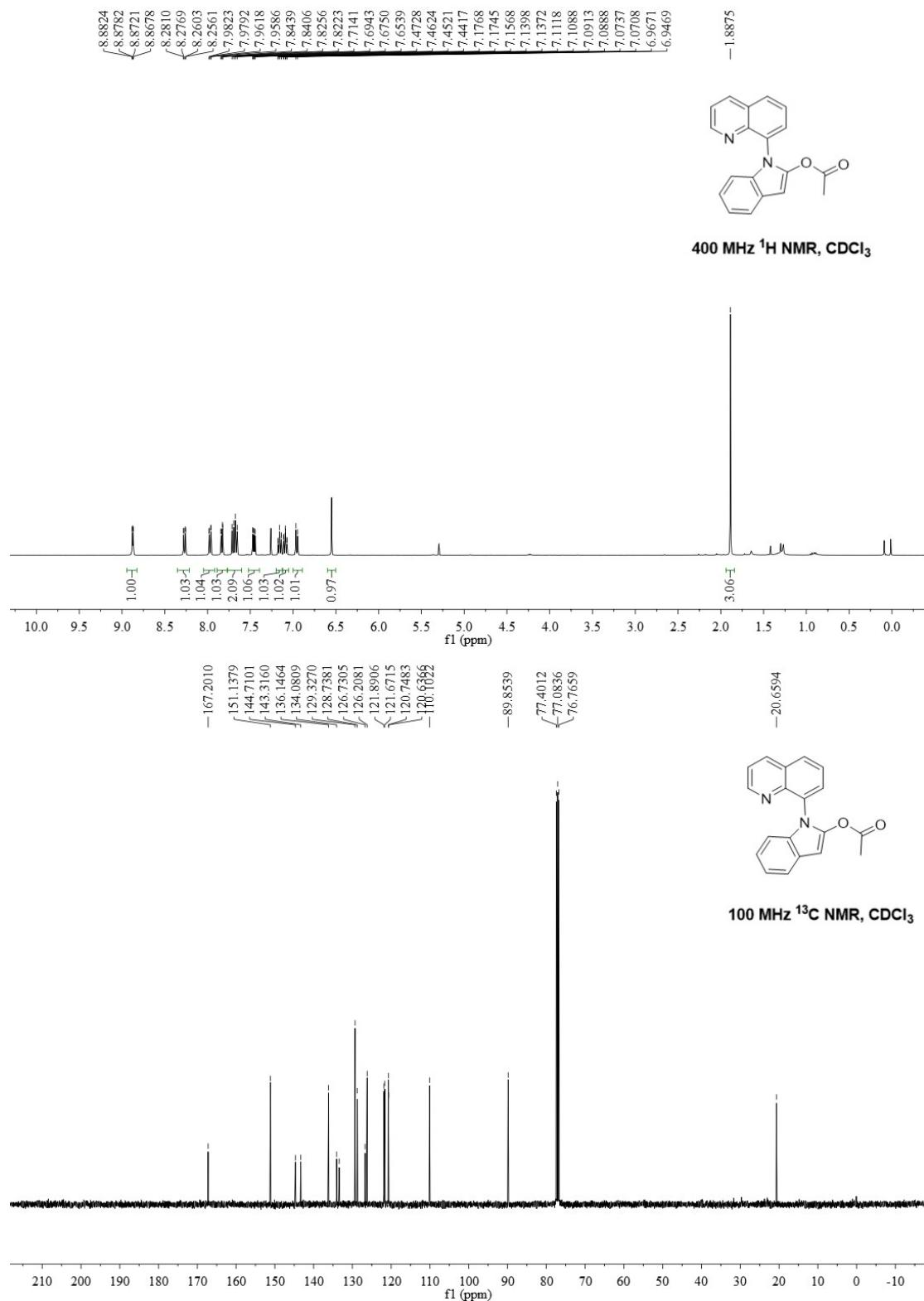




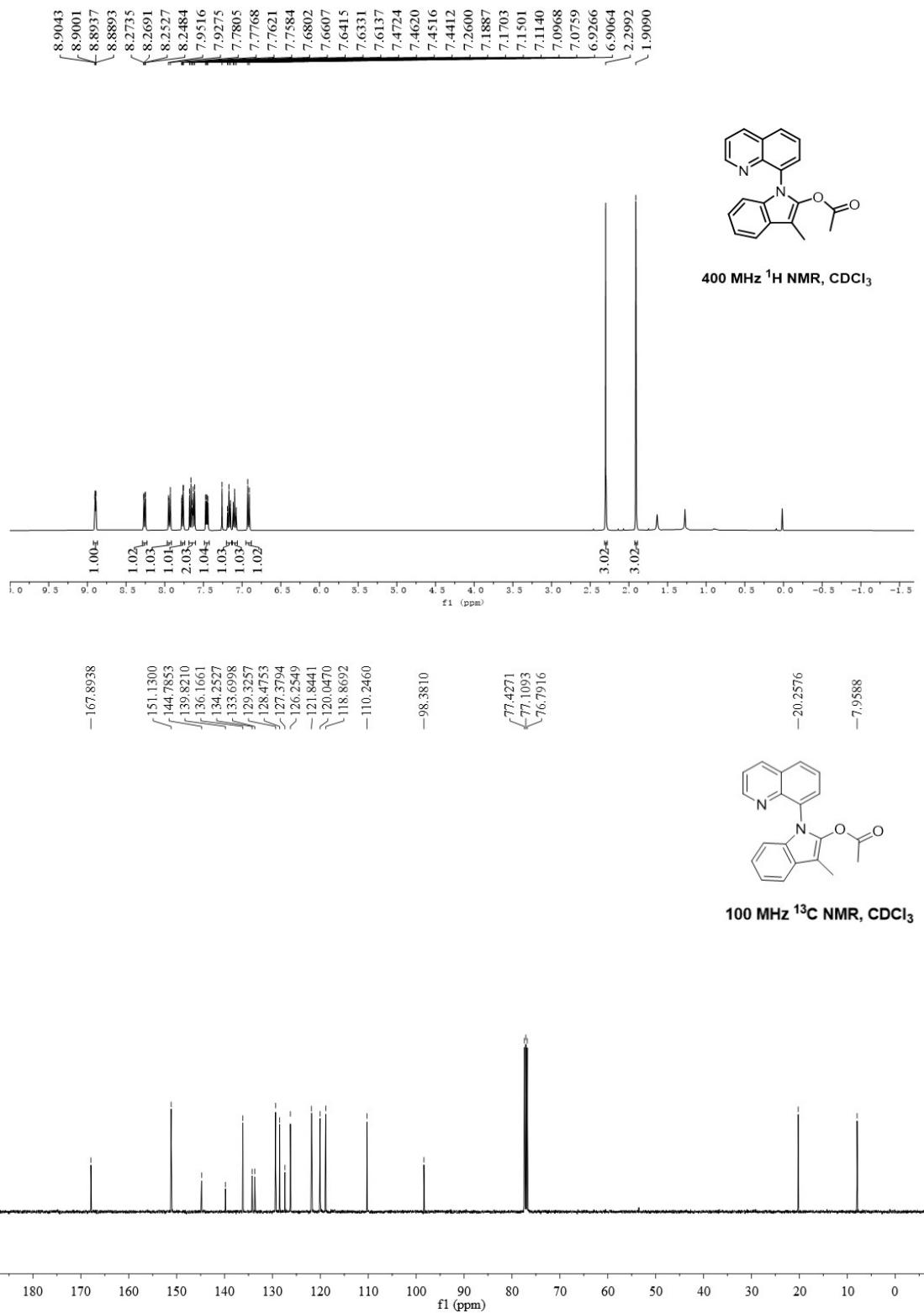
To an oven-dried sealed tube charged with **1a** (0.1 mmol, 24.4 mg) [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (0.1 mmol, 35.6 mg), MnO<sub>2</sub> (0.1 mmol, 8.69 mg), AcOH (0.2 mmol, 12 mg) and DCE (0.5 mL) was added under air atmosphere. The reaction mixture was then allowed to stir at 60 °C (oil bath). The reaction was followed by TLC, cooled after the reaction, diluted with ethyl acetate, filtered through Celite. Then the filtrate was concentrated and purified by flash column chromatography to give the product **2aa** in 82% yield.

## VII. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectrum

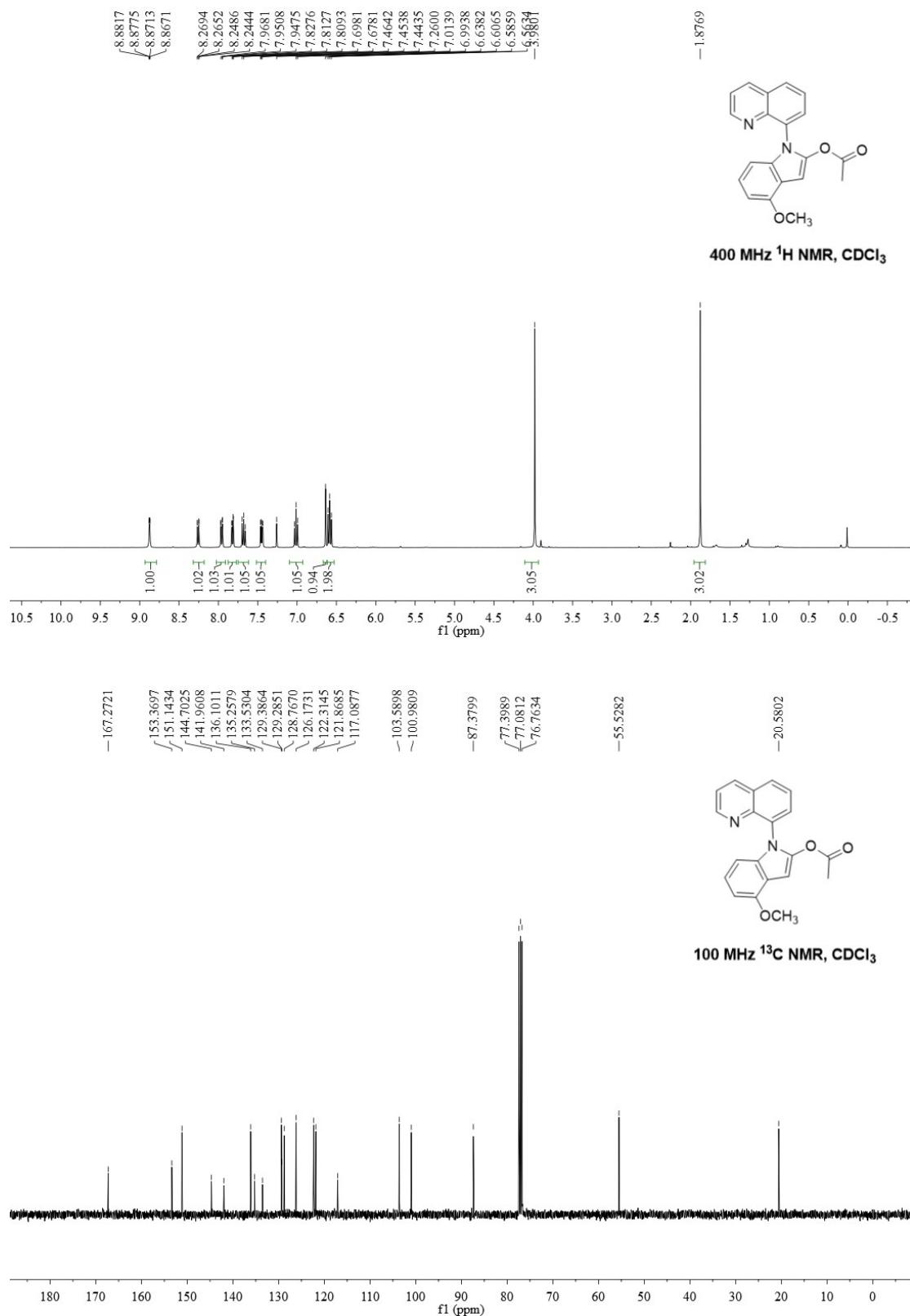
### 1-(Quinolin-8-yl)-1*H*-indol-2-yl acetate (2aa)



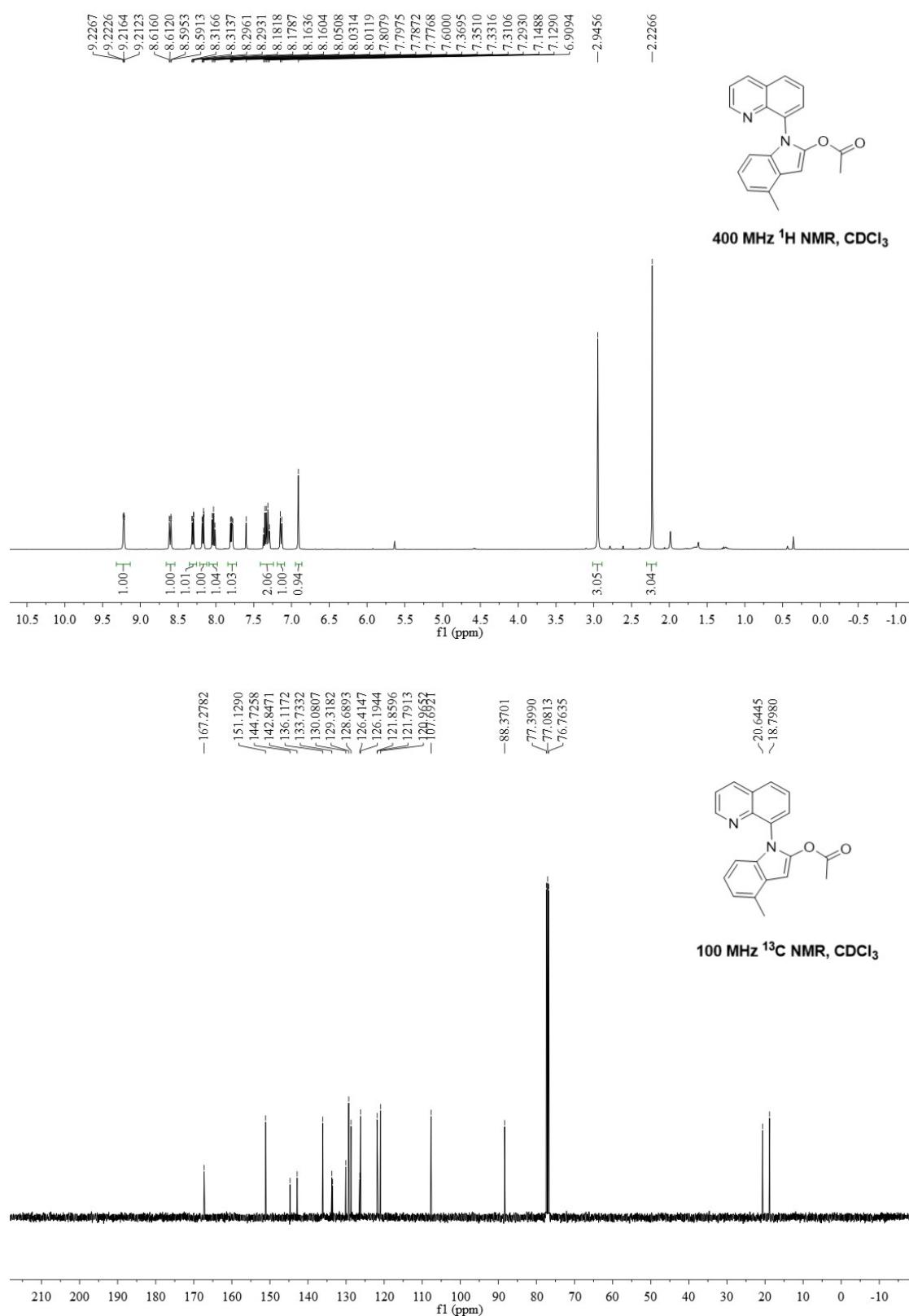
**3-Methyl-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ba)**



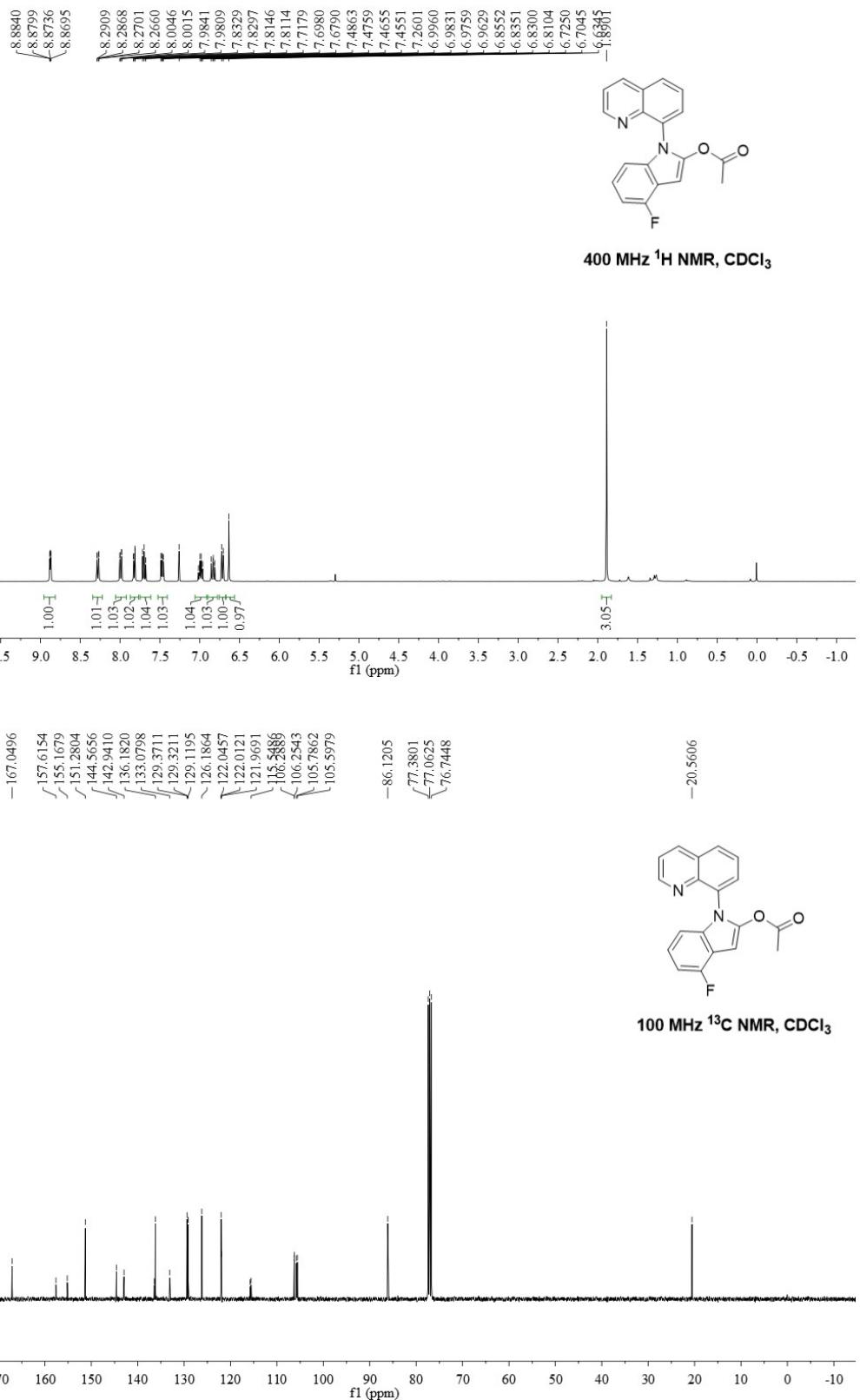
**4-Methoxy-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ca)**



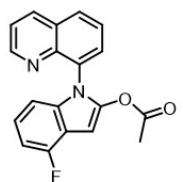
**4-Methyl-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2da)**



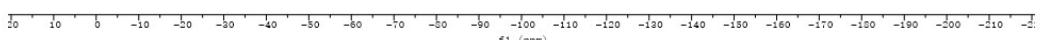
**4-Fluoro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ea)**



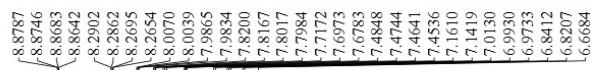
-123.4073



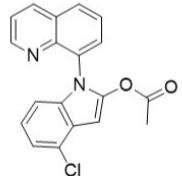
376 MHz  $^{19}\text{F}$  NMR,  $\text{CDCl}_3$



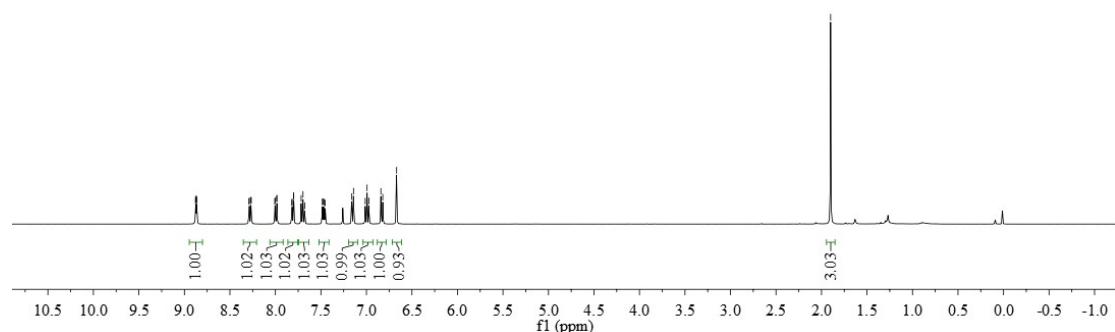
**4-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2fa)**



-1.8999



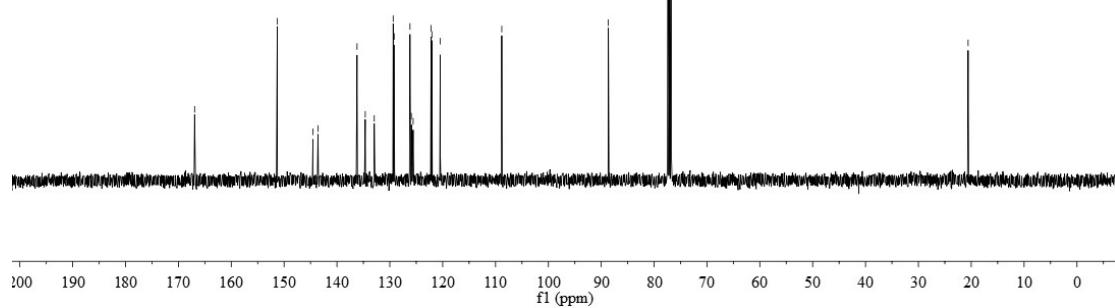
400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



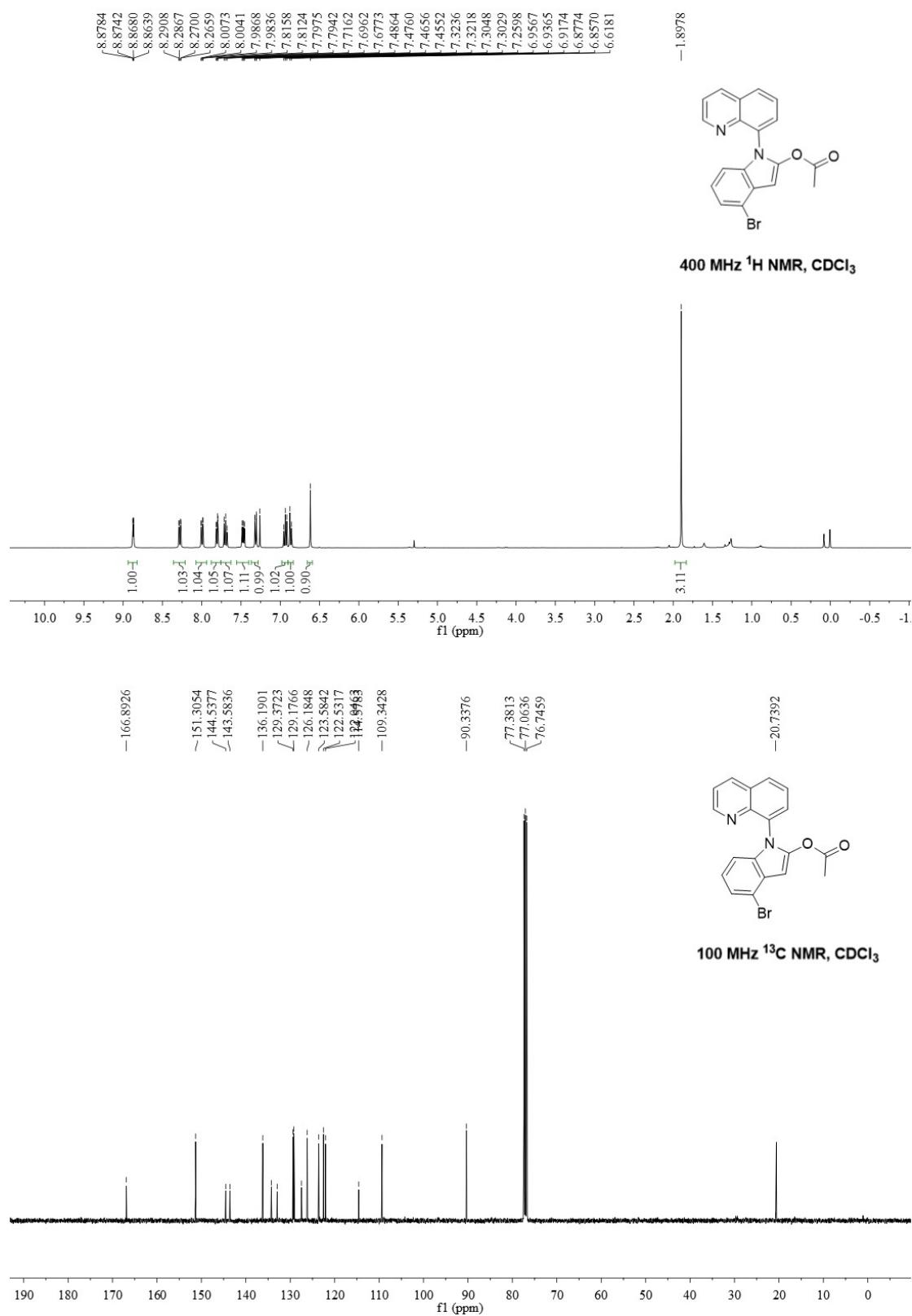
-166.9329



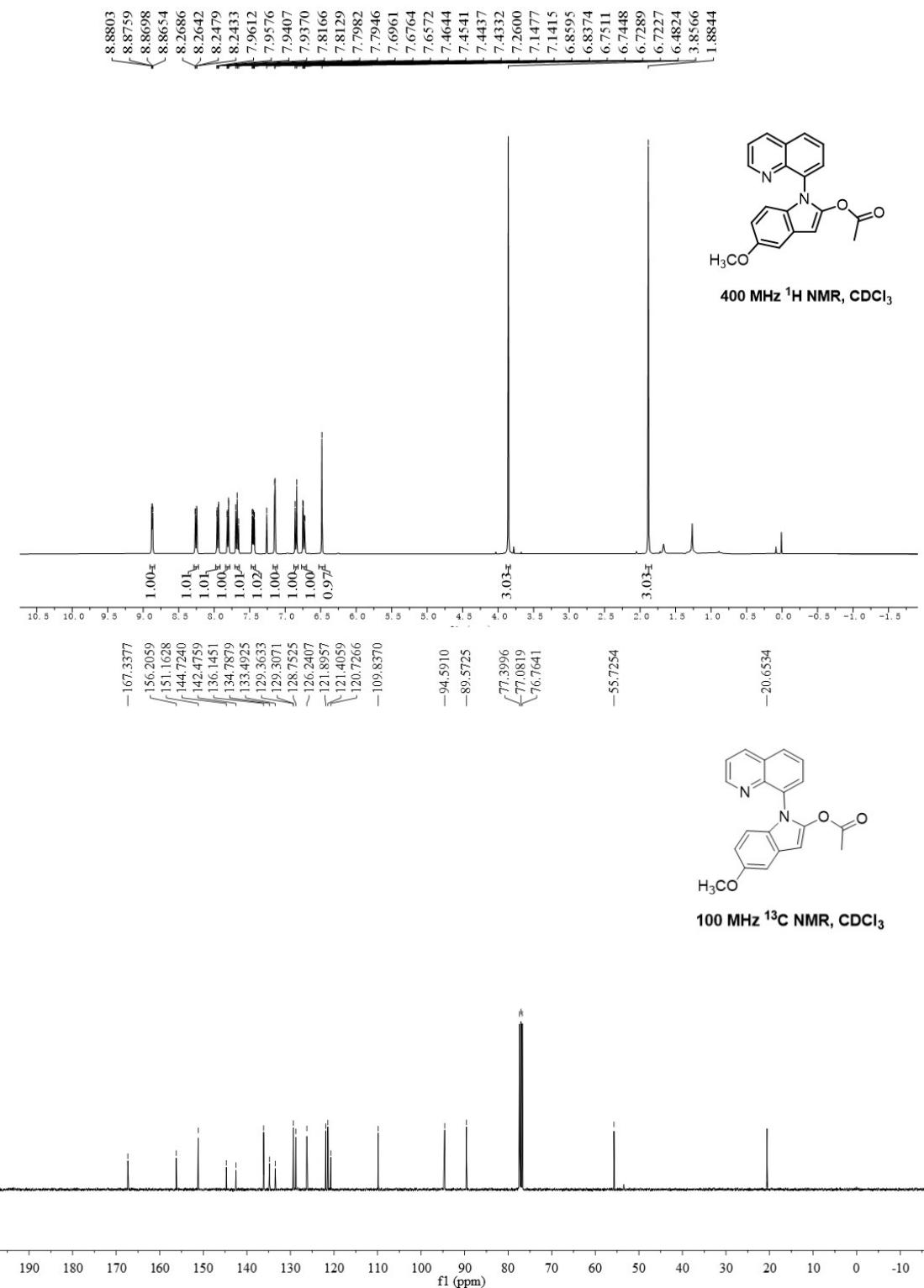
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



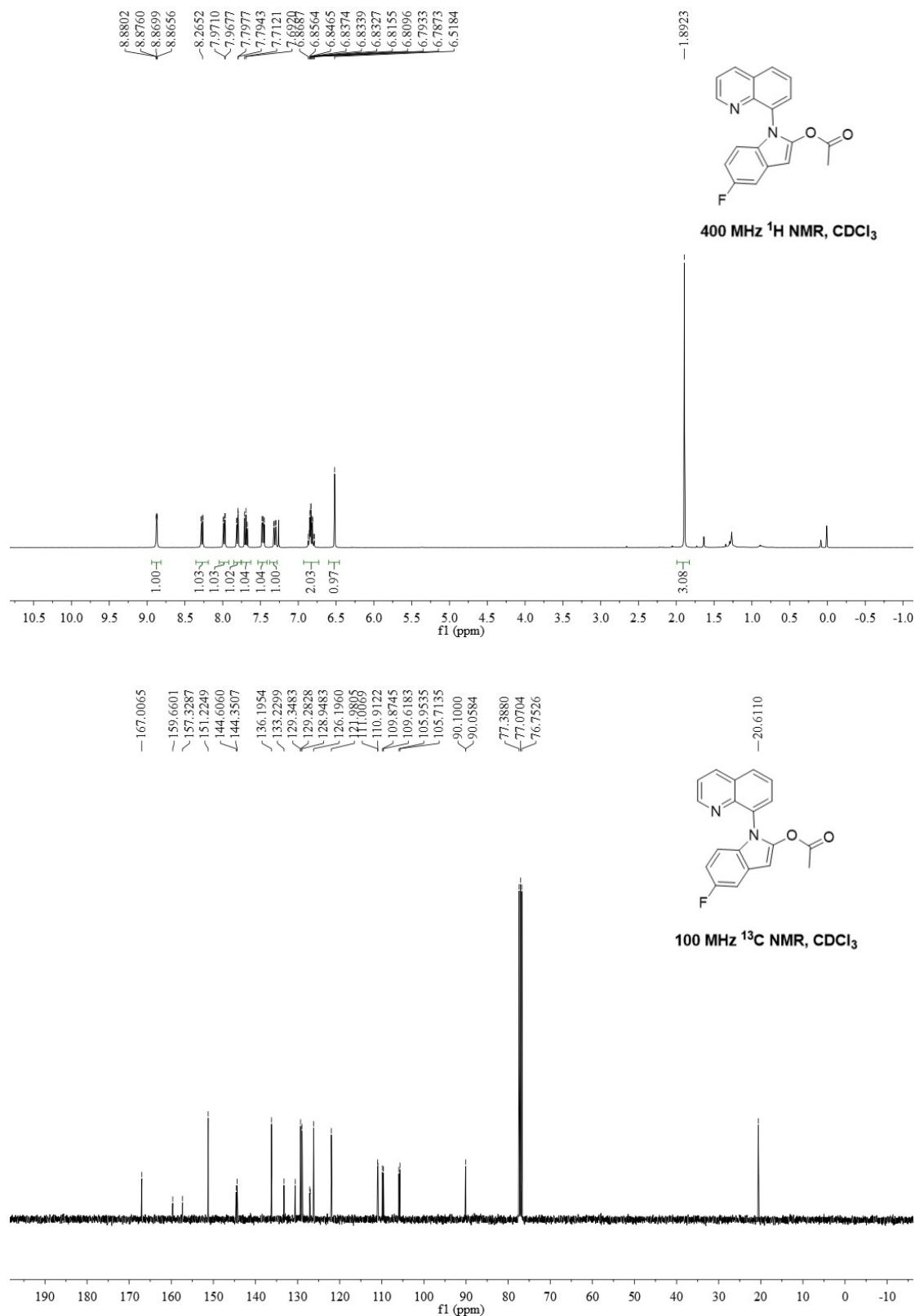
**4-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ga)**

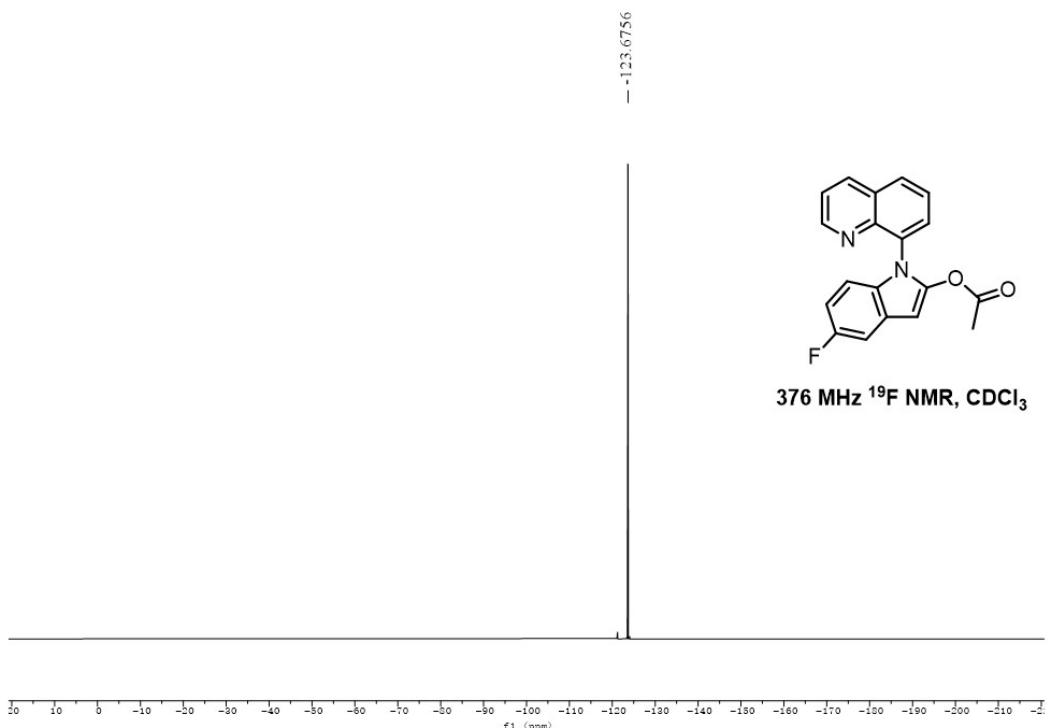


**5-Methoxy-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ha)**

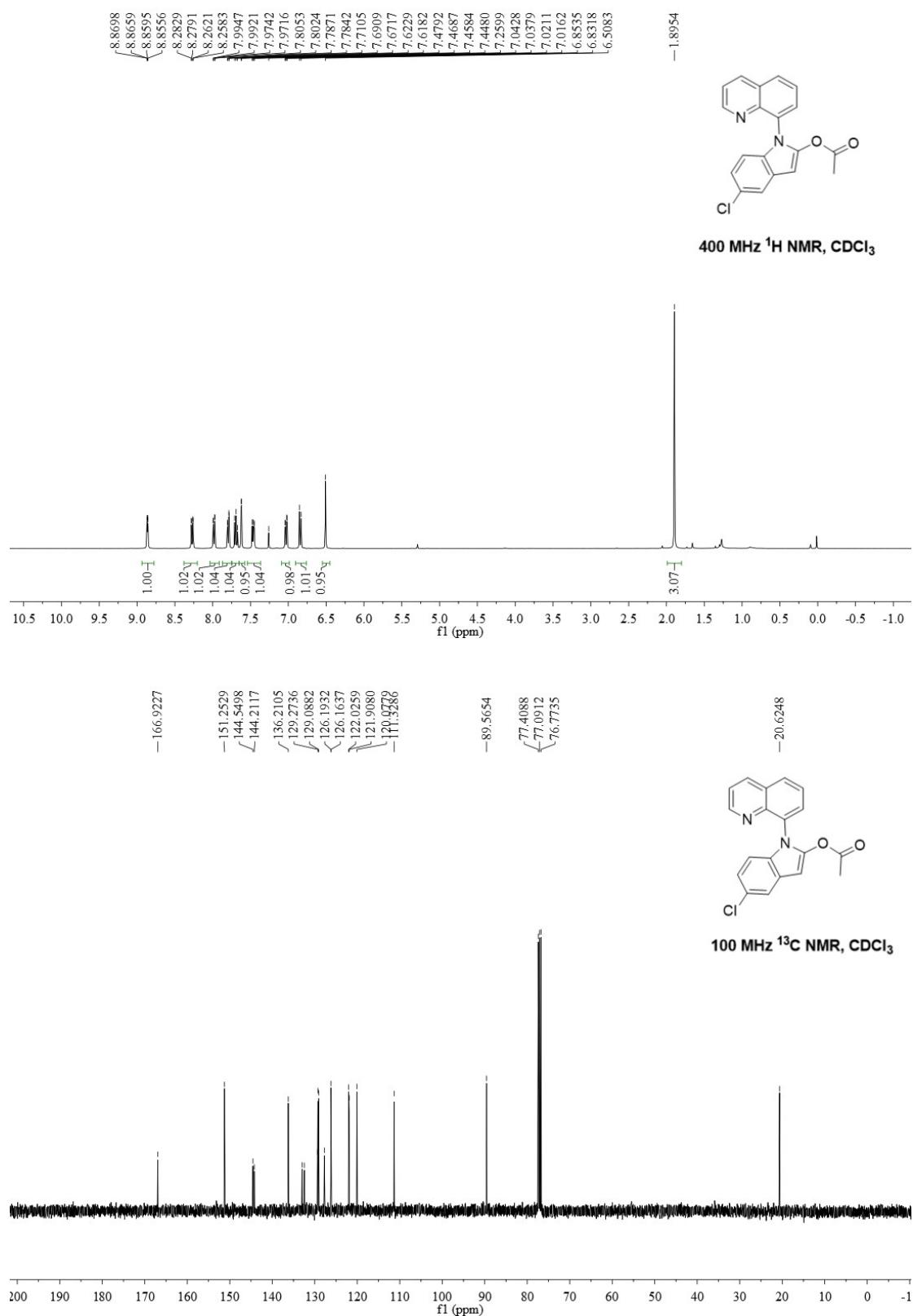


**5-Fluoro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ia)**

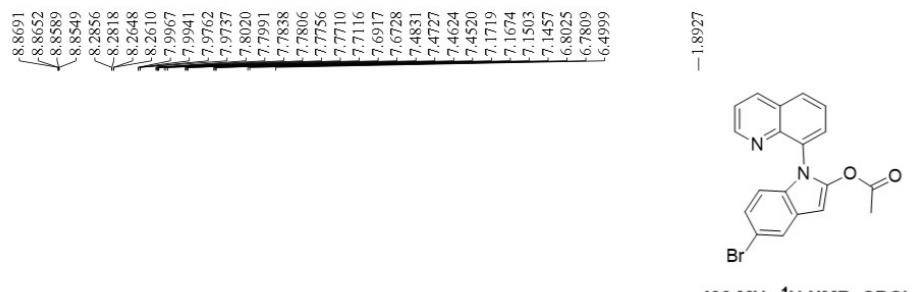




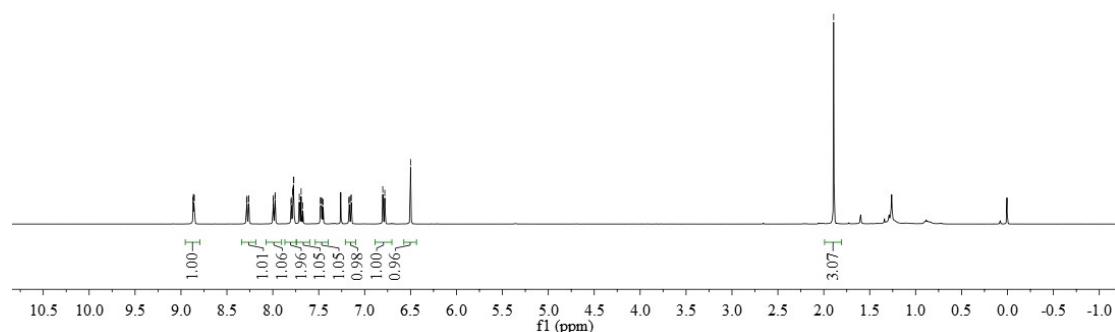
**5-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ja)**



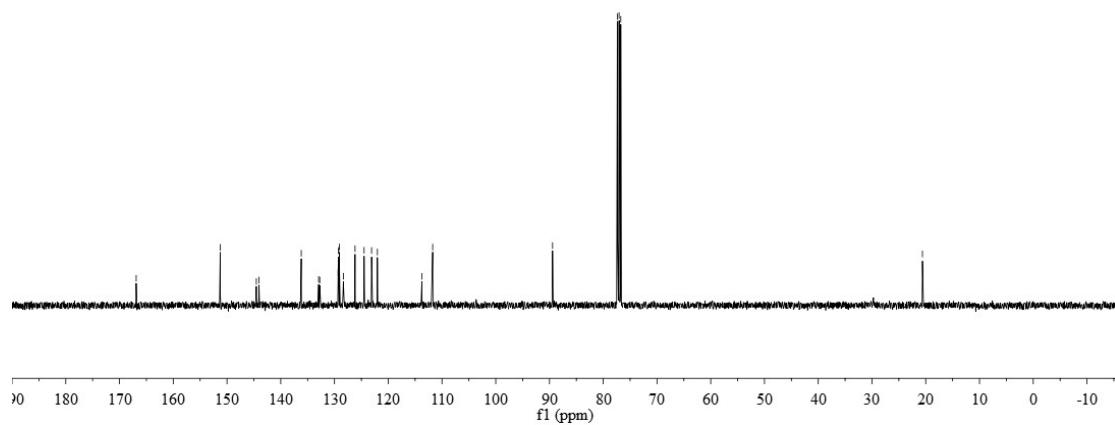
**5-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ka)**



400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



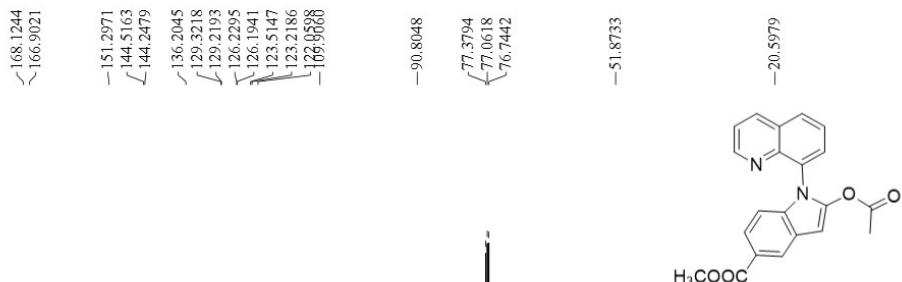
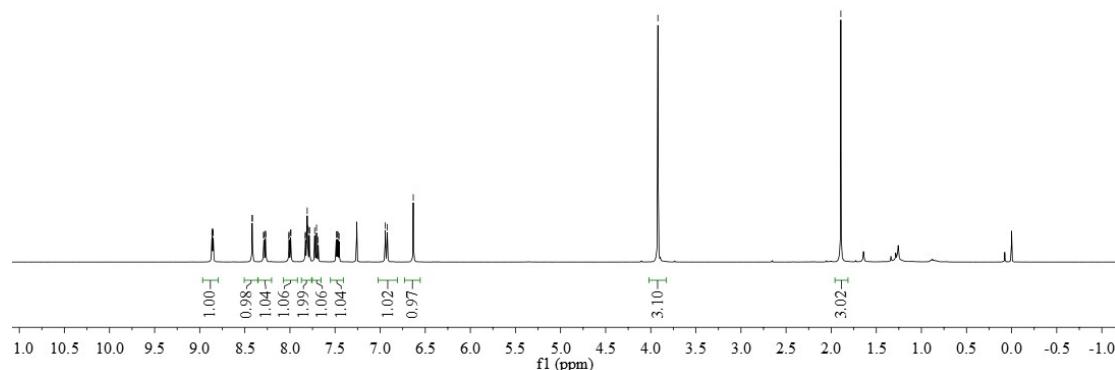
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



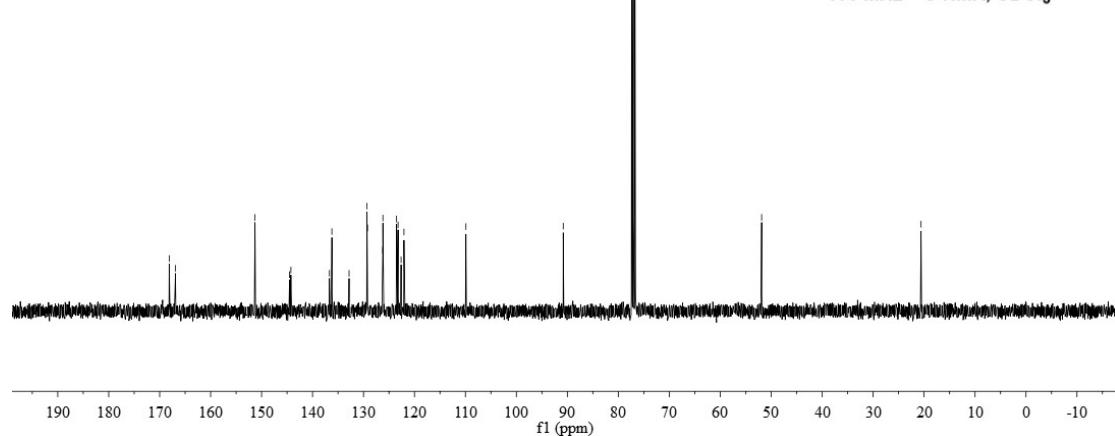
**Methyl 2-acetoxymethyl-1-(quinolin-8-yl)-1*H*-indole-5-carboxylate (2la)**



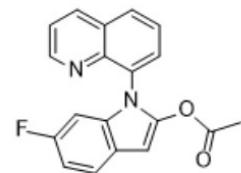
400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



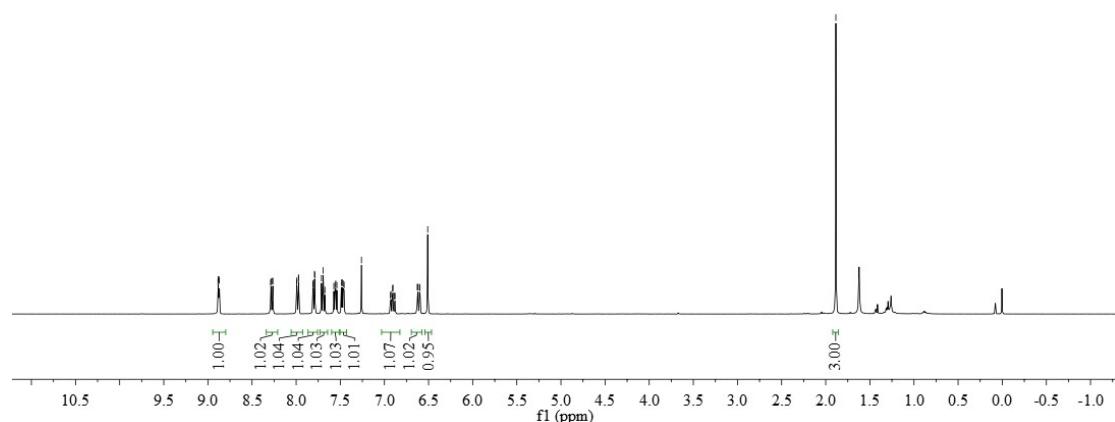
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



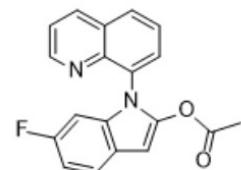
**6-Fluoro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2ma)**



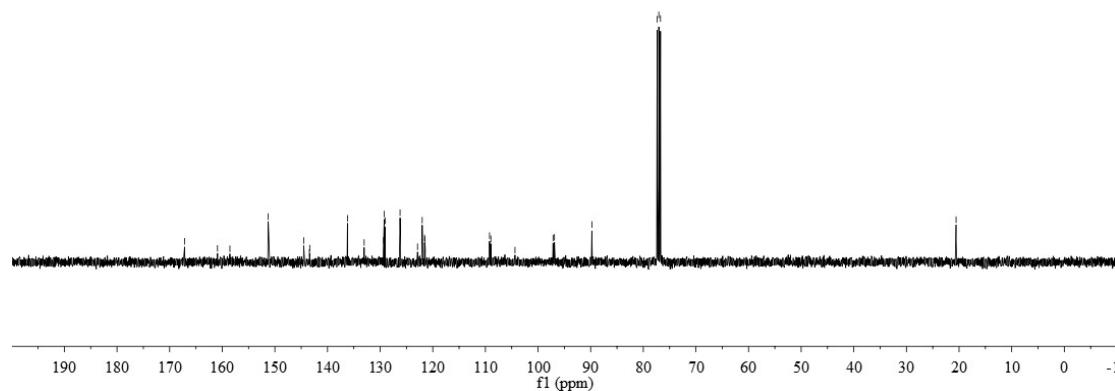
400 MHz <sup>1</sup>H NMR, CDCl<sub>3</sub>

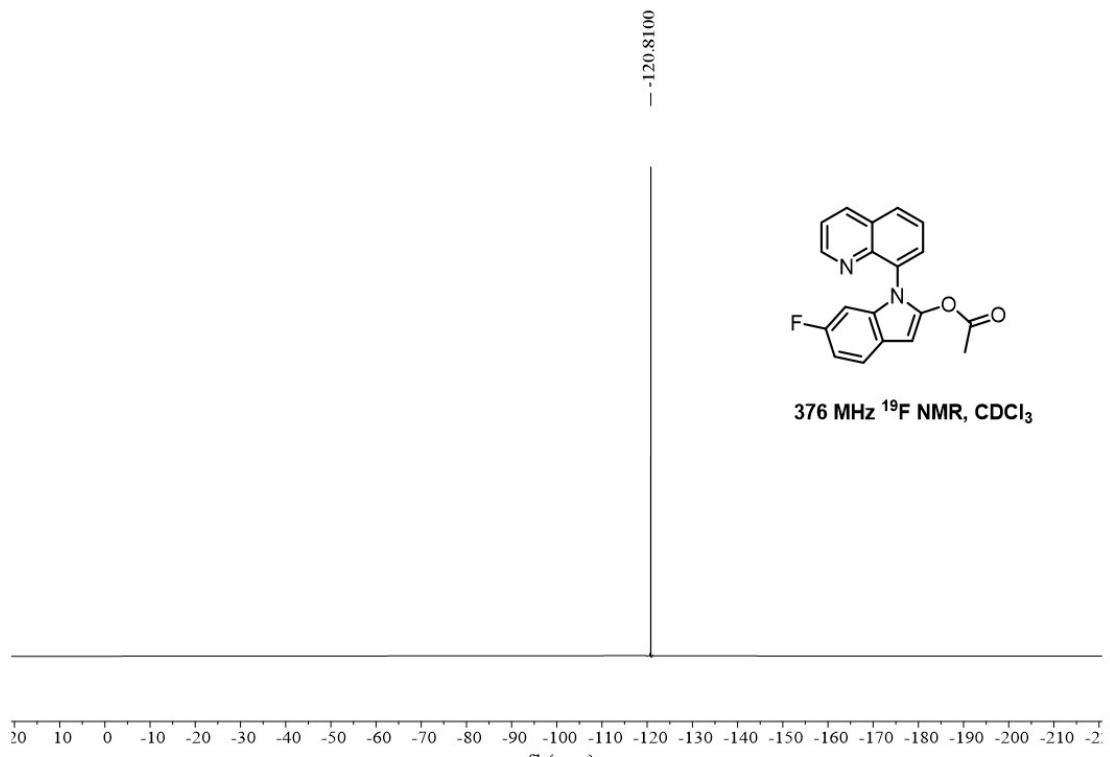


~167.1523  
~158.5488  
~151.2677  
~144.5221  
~136.2097  
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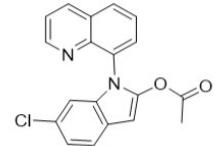
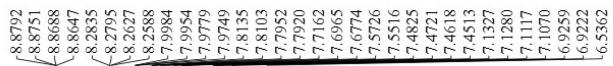


100 MHz <sup>13</sup>C NMR, CDCl<sub>3</sub>

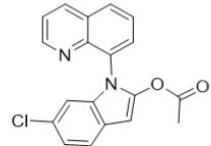
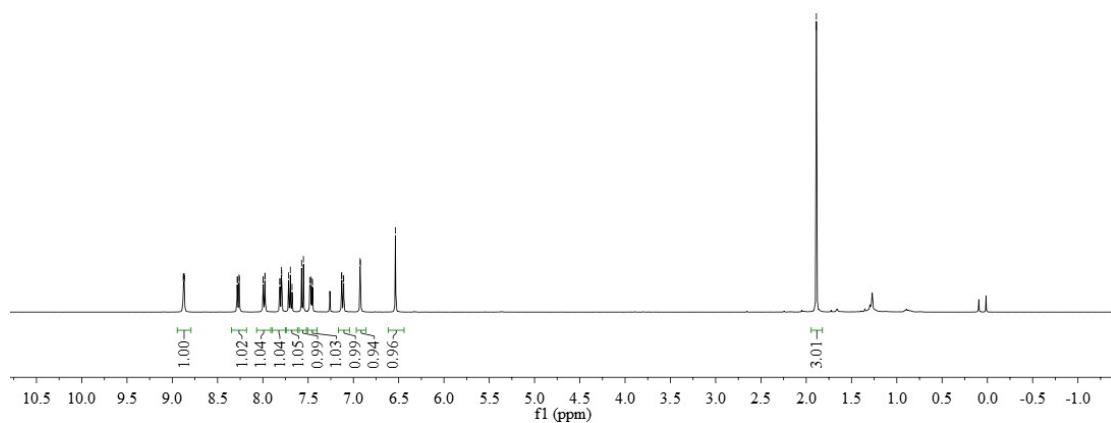




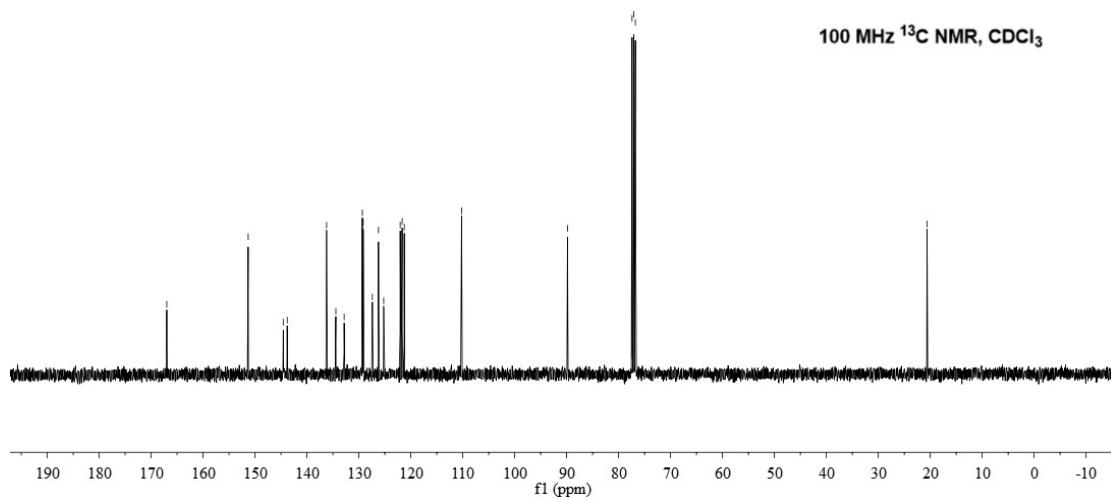
### 6-Chloro-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2na)



400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$

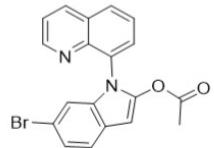


**6-Bromo-1-(quinolin-8-yl)-1*H*-indol-2-yl acetate (2oa)**

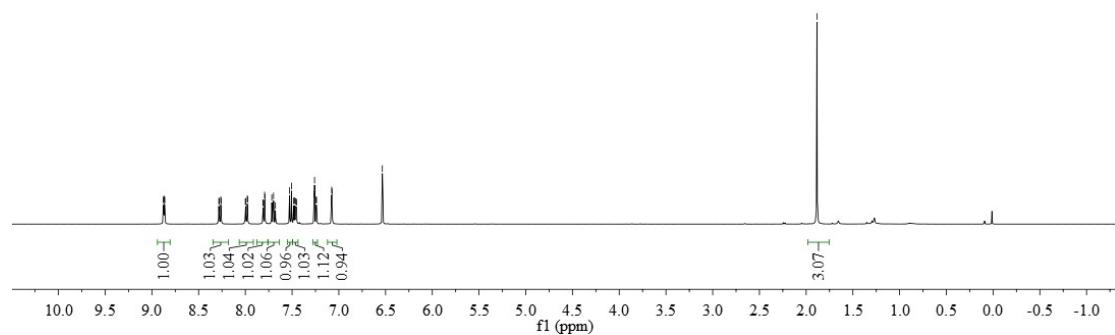
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8.8664  
8.8622

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7.7909  
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7.5275  
7.5066  
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7.2597  
7.0764  
6.9349

—1.8847



400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

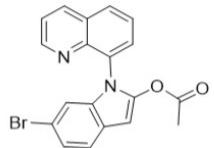


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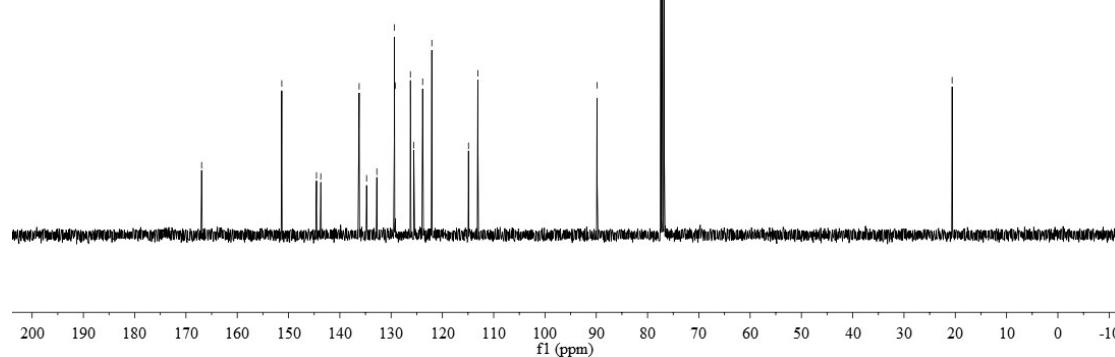
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—123.8551  
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—113.0920

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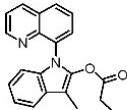
—20.6187



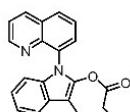
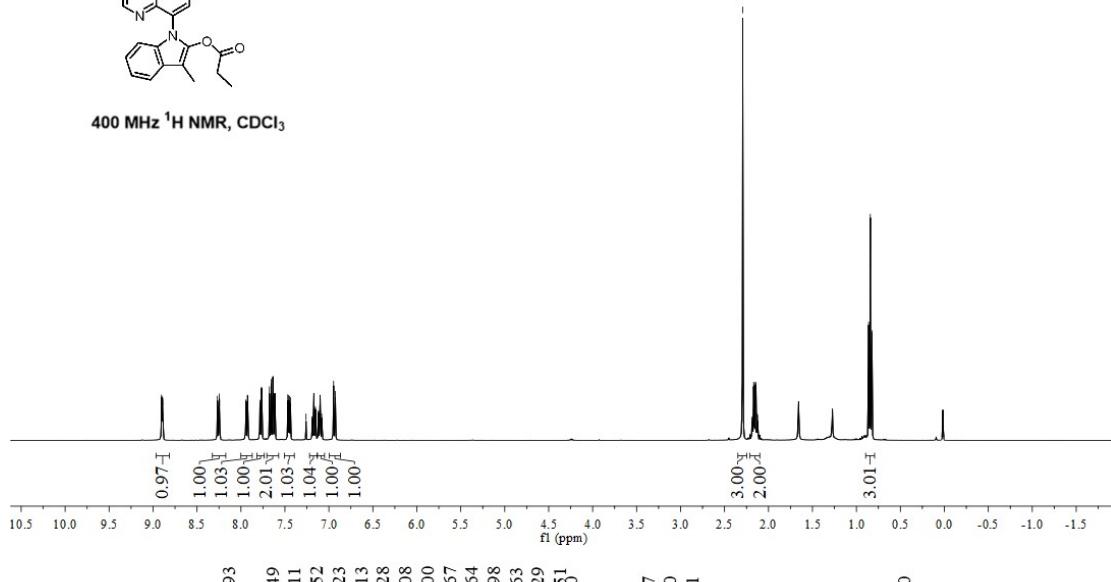
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



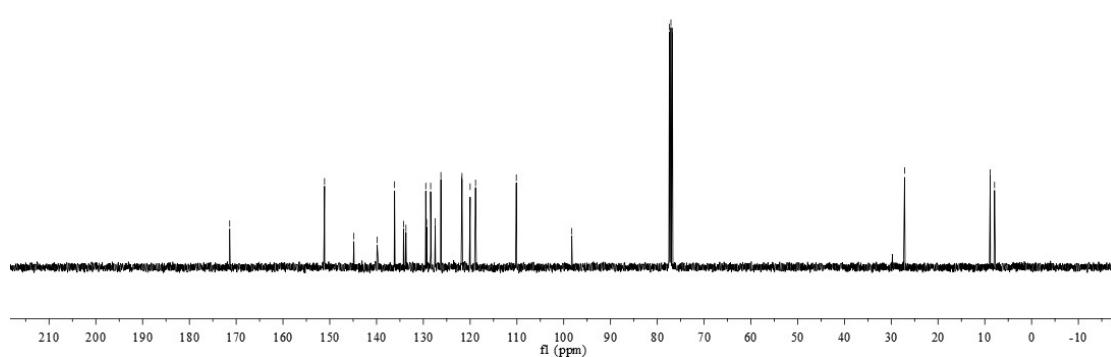
### 3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl propionate (2bb)



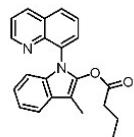
400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



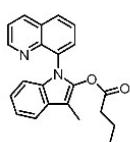
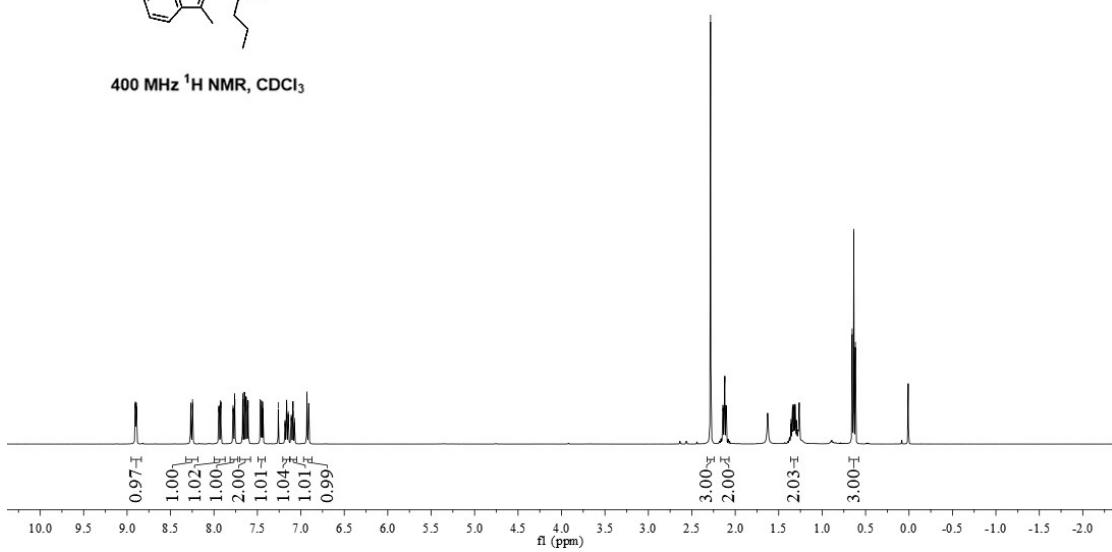
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



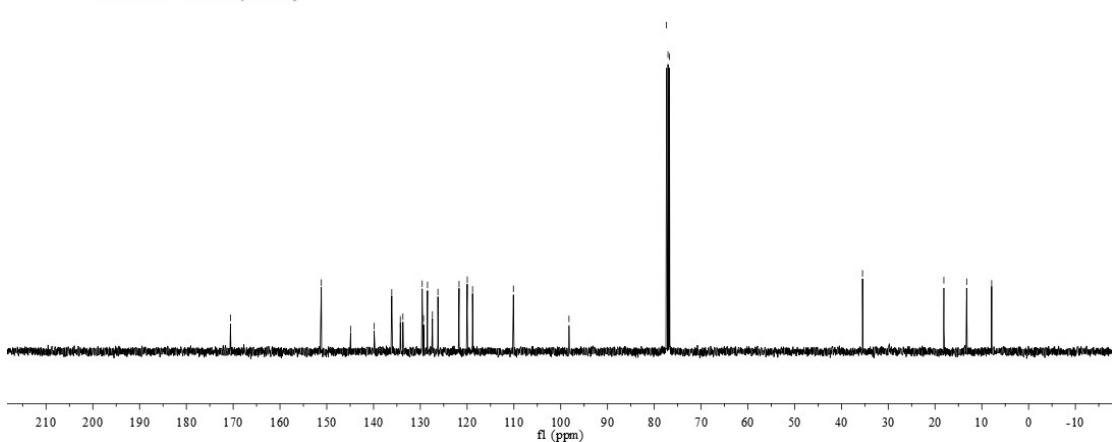
### 3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl butyrate (2bc)



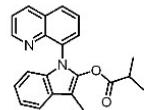
400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



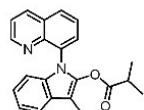
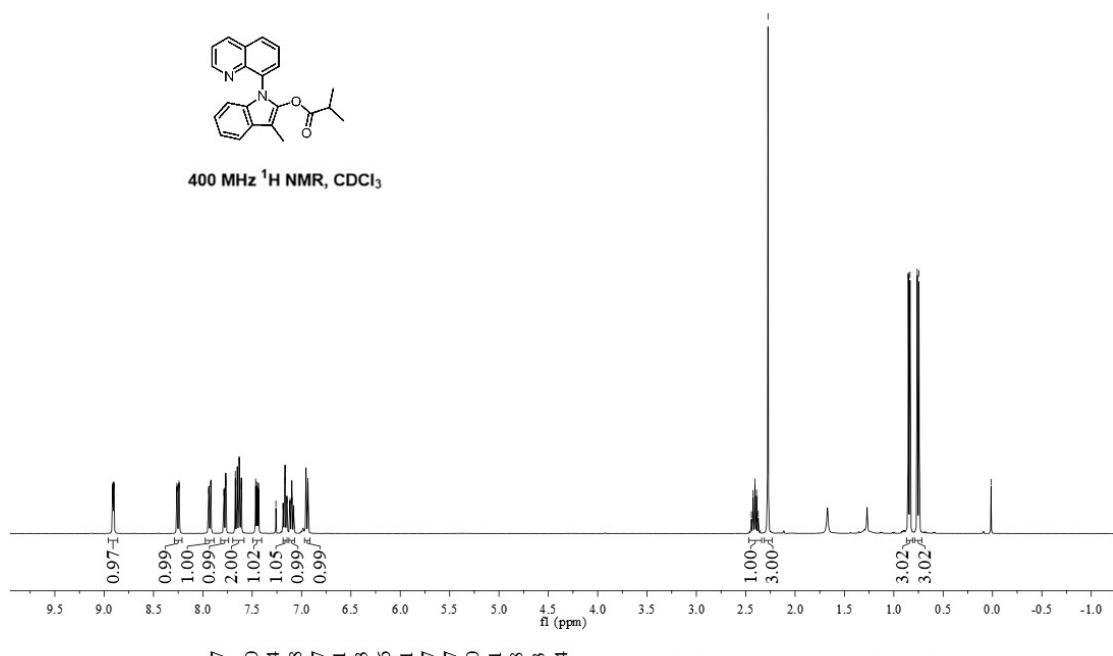
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



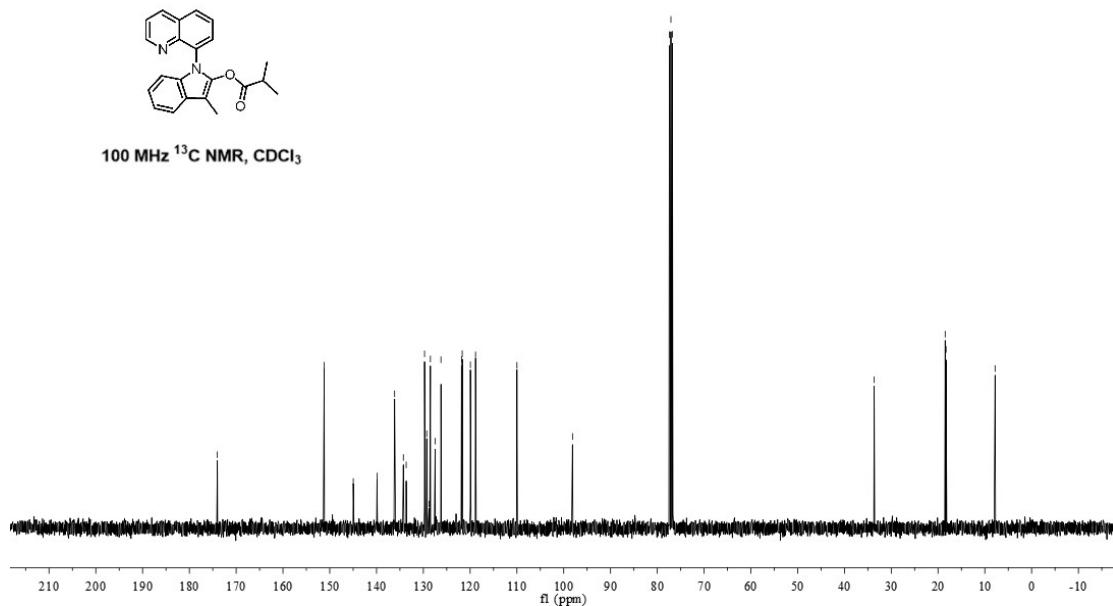
### 3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl isobutyrate (2bd)



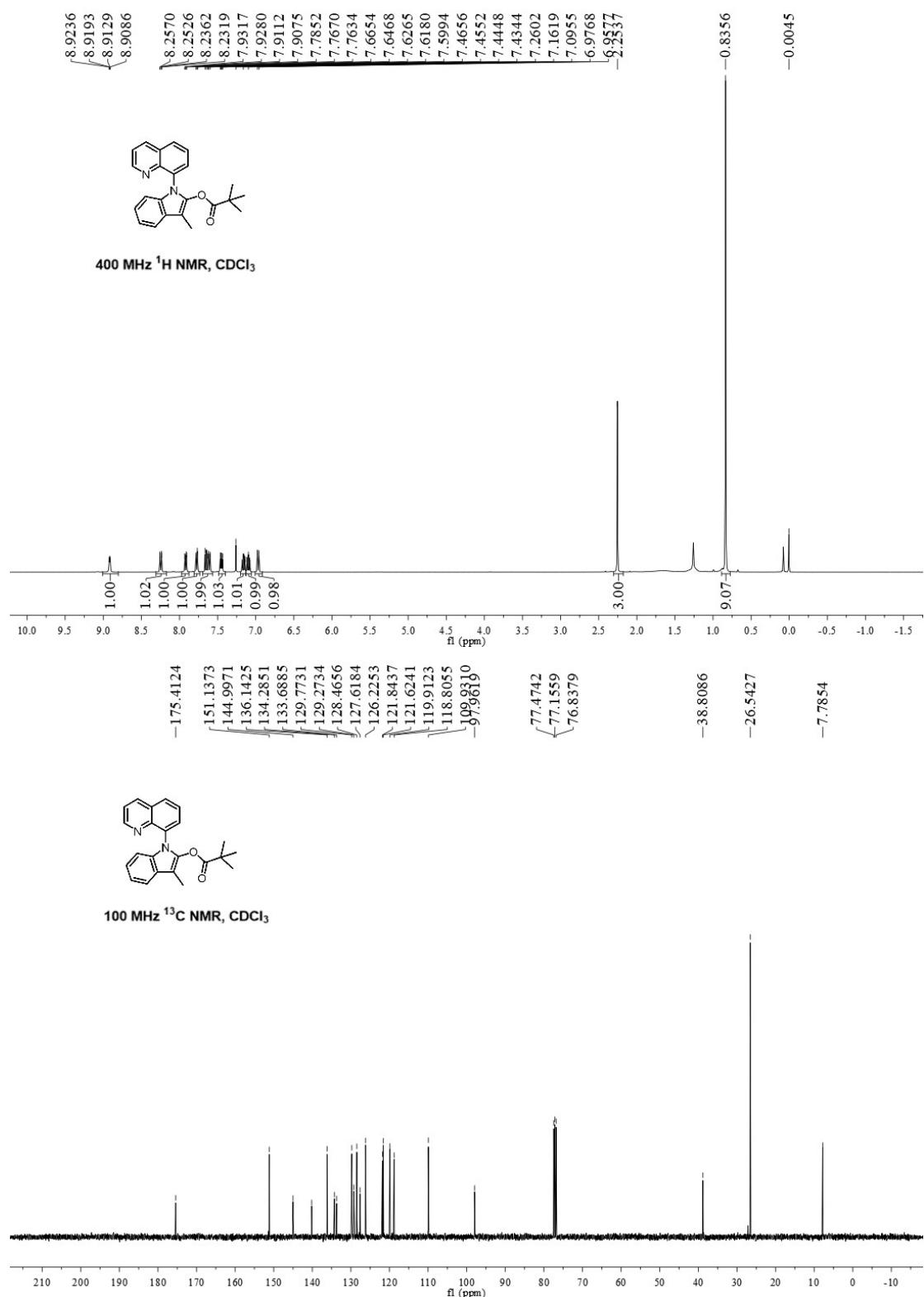
400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$



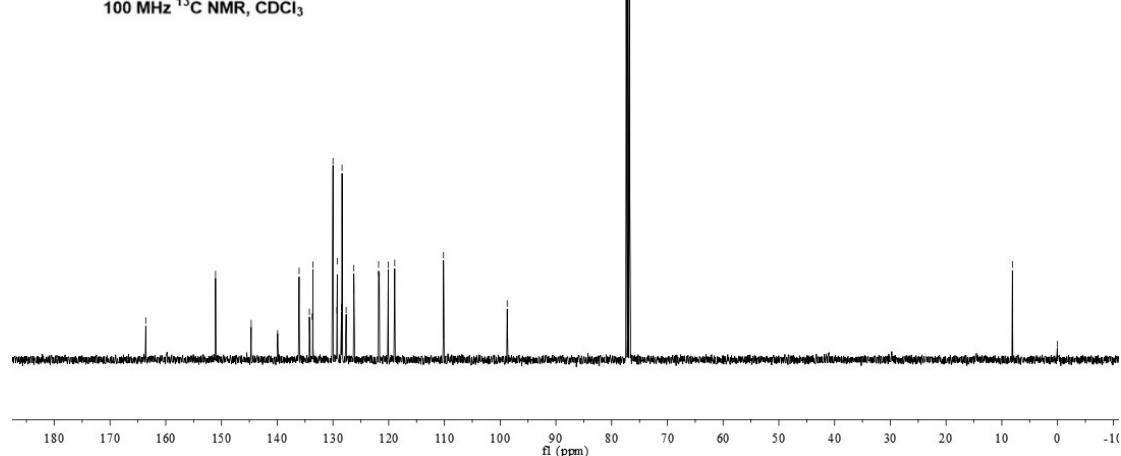
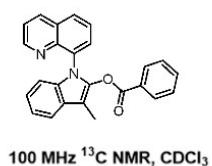
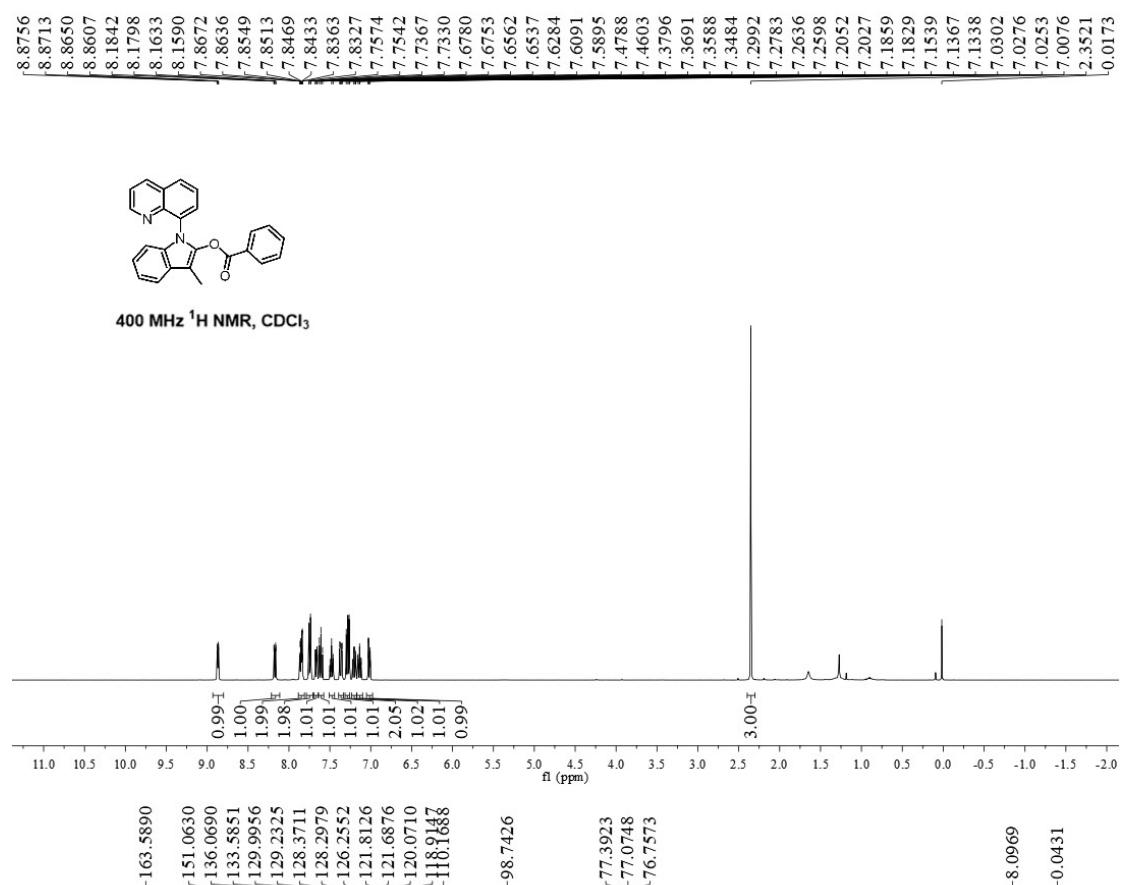
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



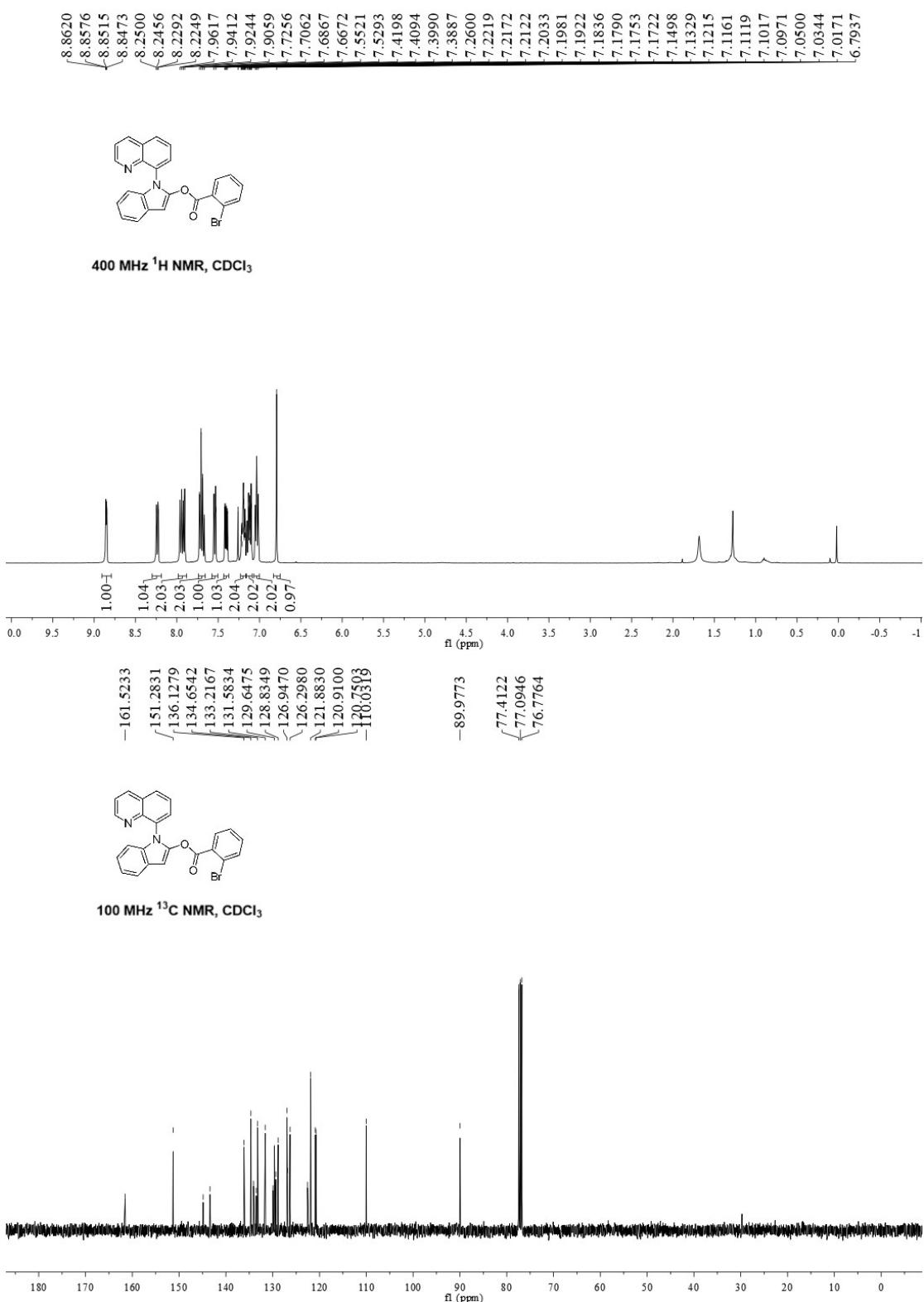
**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl pivalate (2be)**



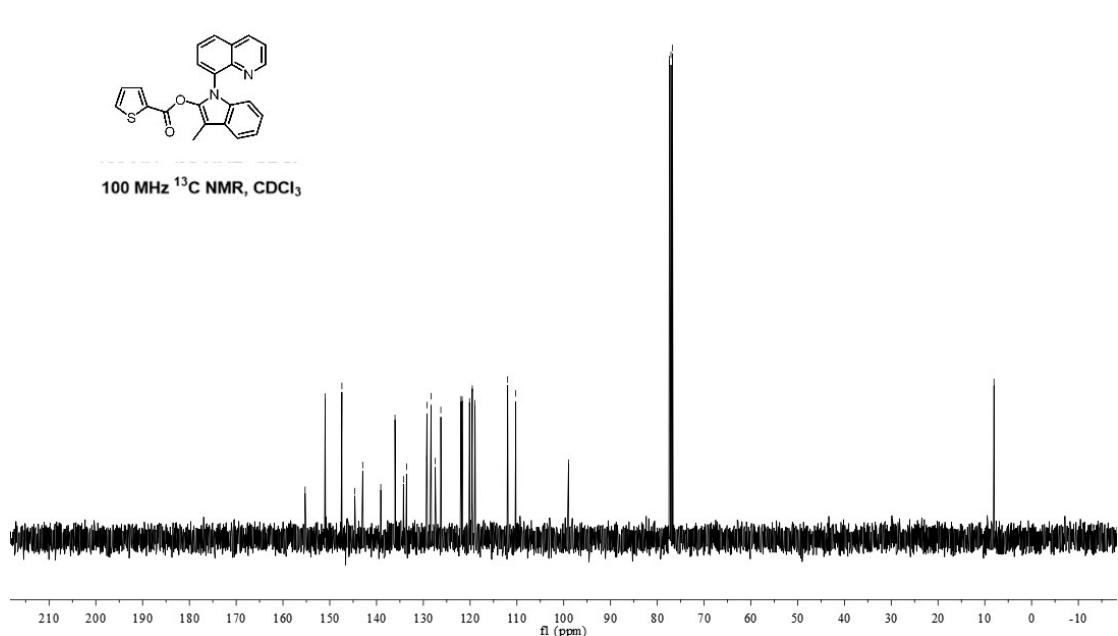
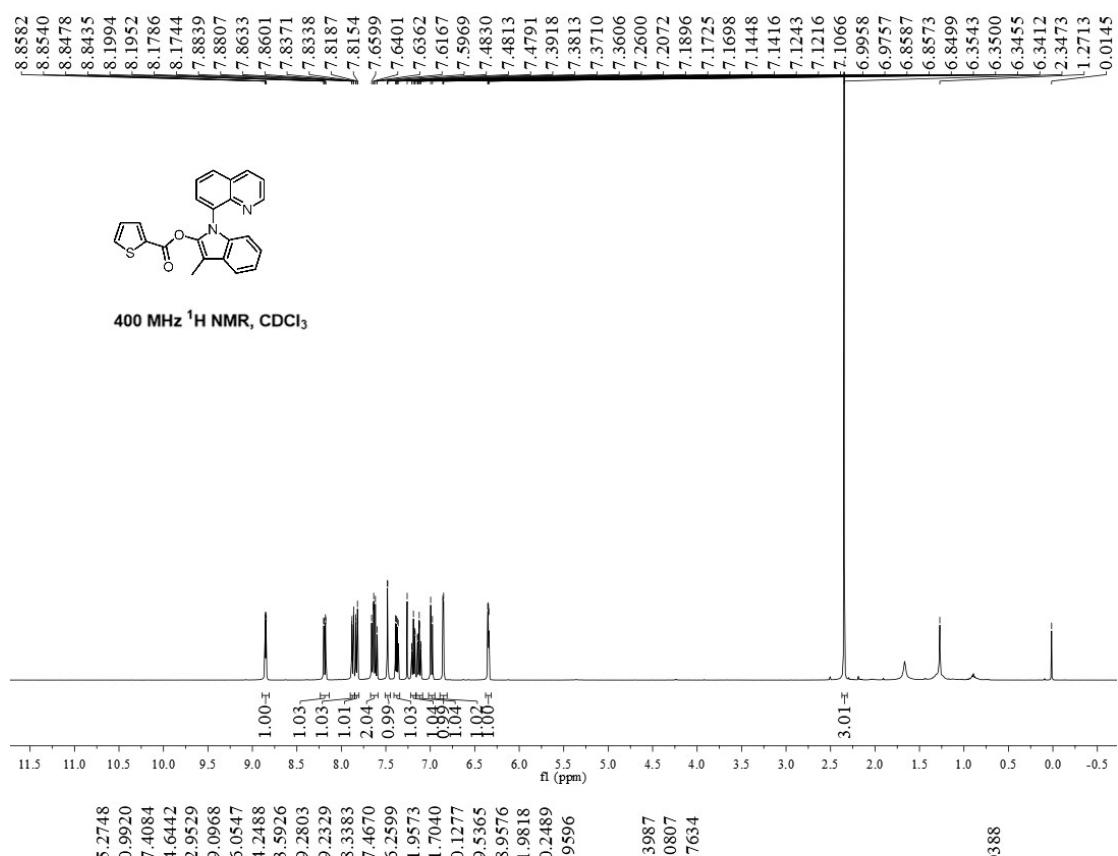
**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl benzoate (2bf)**



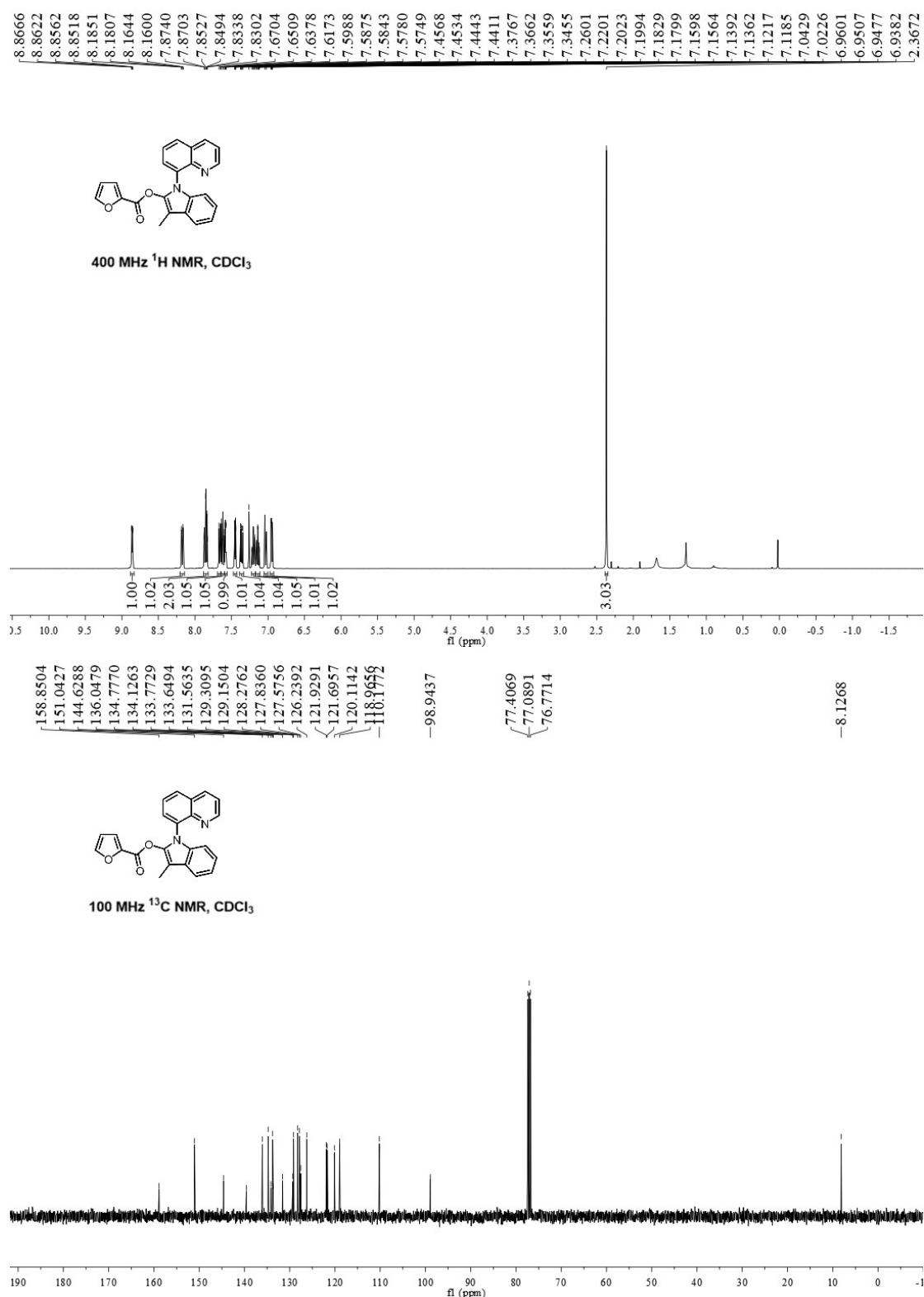
**1-(Quinolin-8-yl)-1H-indol-2-yl 2-bromobenzoate (2ag)**



### 3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl thiophene-2-carboxylate (2bh)

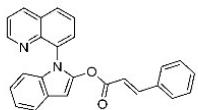


**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl furan-2-carboxylate (2bi)**

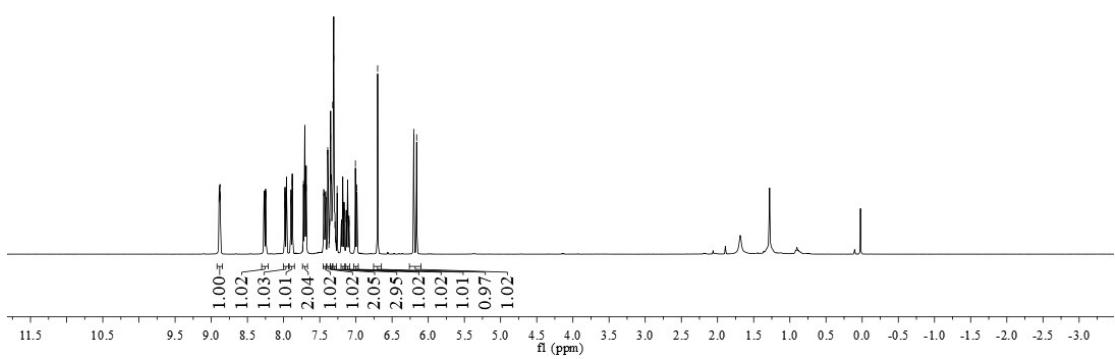


**1-(Quinolin-8-yl)-1H-indol-2-yl cinnamate (2aj)**

8.8908	8.8865	8.8803	8.8759	8.2700	8.2656	8.2493	8.2450	7.9837	7.9802	7.9631	7.9596	7.8996	7.8961	7.8811	7.8776	7.7367	7.7251	7.7066	7.6910	7.6866	7.4472	7.4368	7.4265	7.4160	7.3899	7.3730	7.3619	7.2842	7.2600	7.2017	7.1989	7.1836	7.1645	7.1616	7.1357	7.1324	7.1154	7.0975	7.0943	7.0072	6.9870	6.6997	6.2001	6.1602
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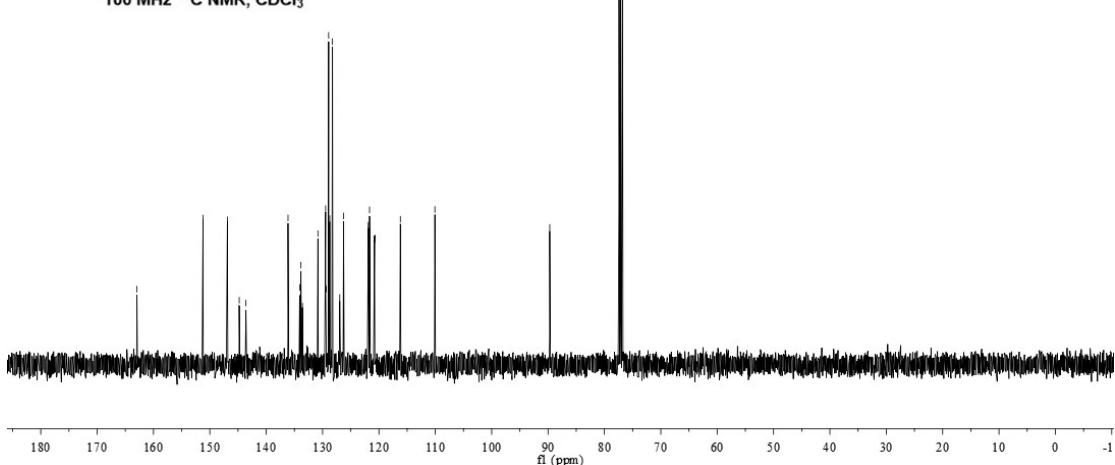


400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

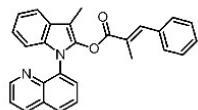


-162.9314  
-151.2085  
-146.8895  
-136.1278  
-134.0615  
-133.8381  
-130.8252  
-129.4610  
-128.9196  
-128.7250  
-128.2398  
-126.2748  
-121.8911  
-121.6674  
-120.7846  
-120.6665  
-116.1990  
-89.698847  
77.4092  
77.0944  
76.7751

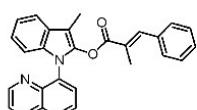
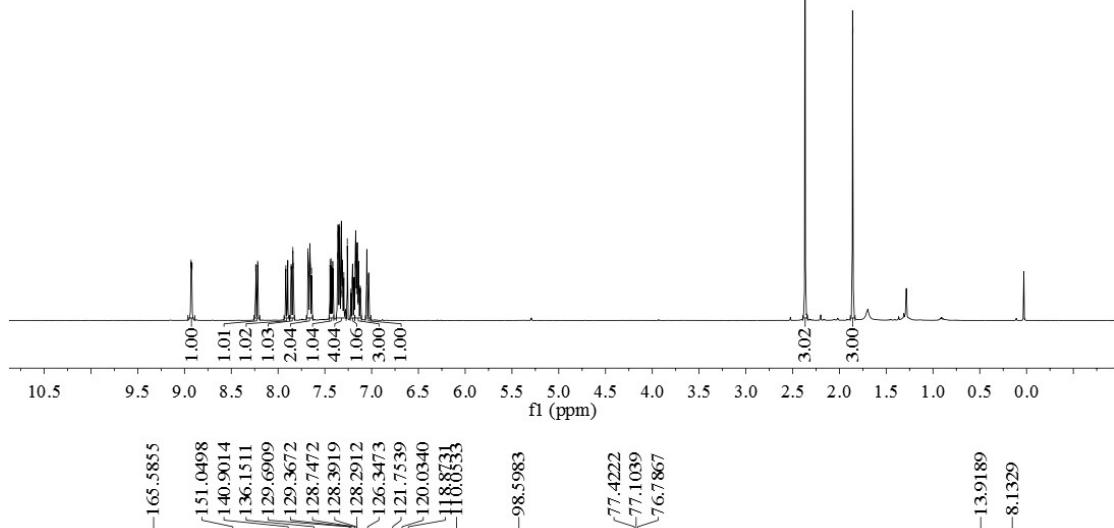
100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



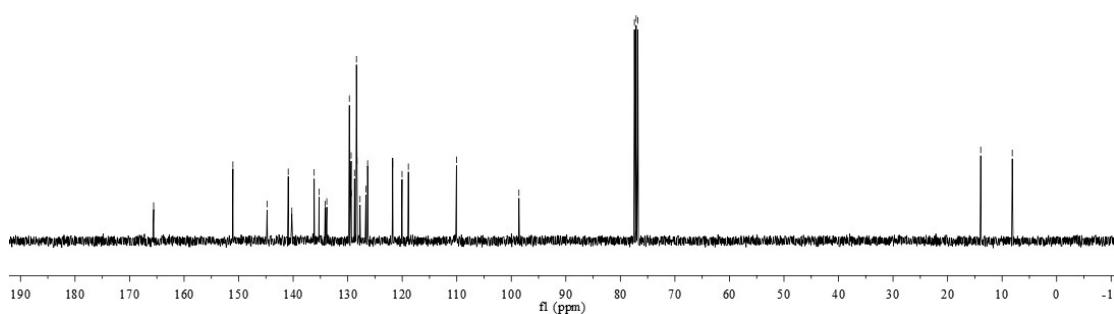
### 3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl (E)-2-methyl-3-phenylacrylate (2bk)



400 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

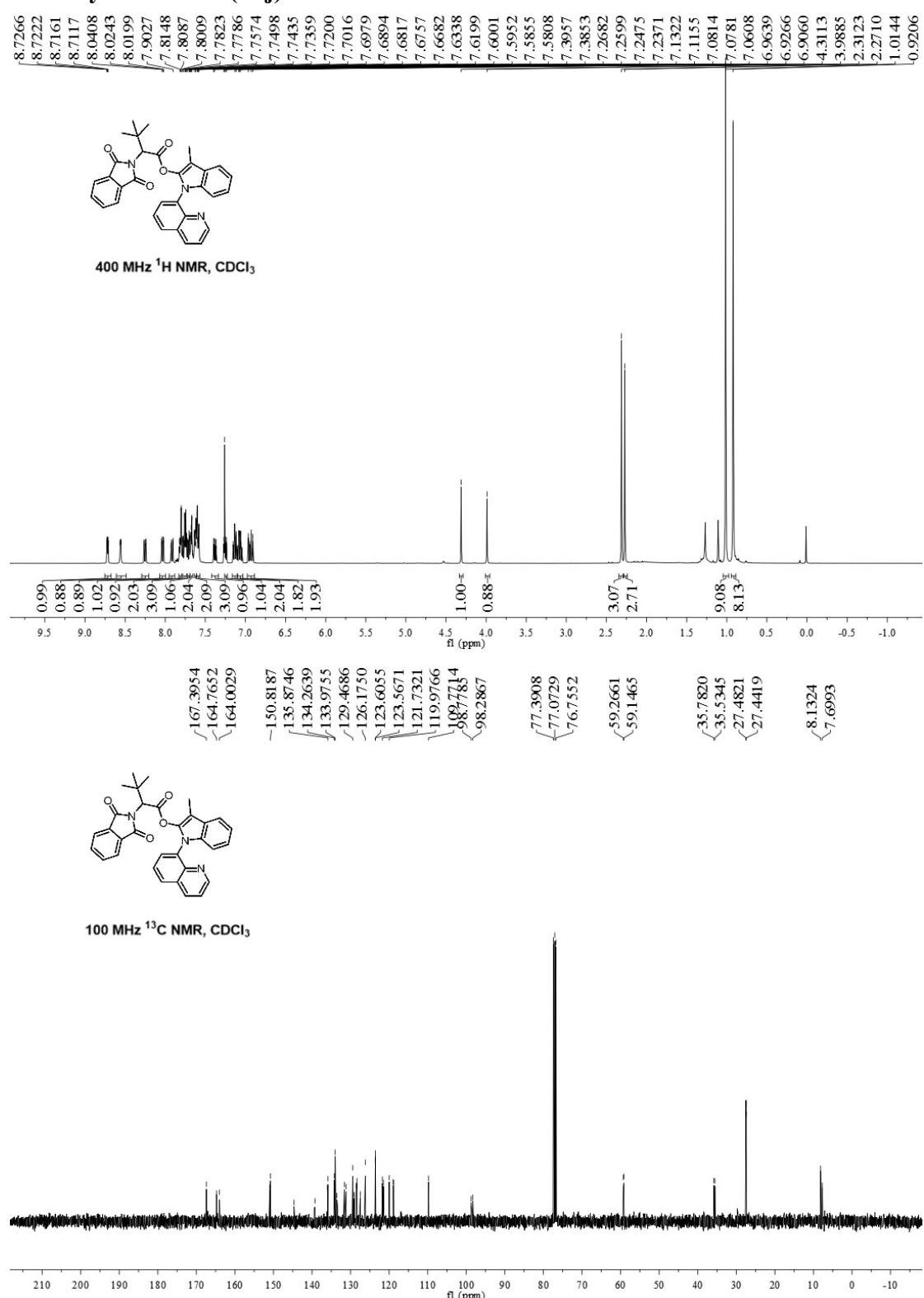


100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$

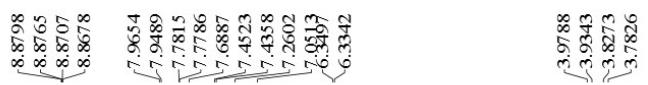


**3-Methyl-1-(quinolin-8-yl)-1H-indol-2-yl dimethylbutanoate (2bj)**

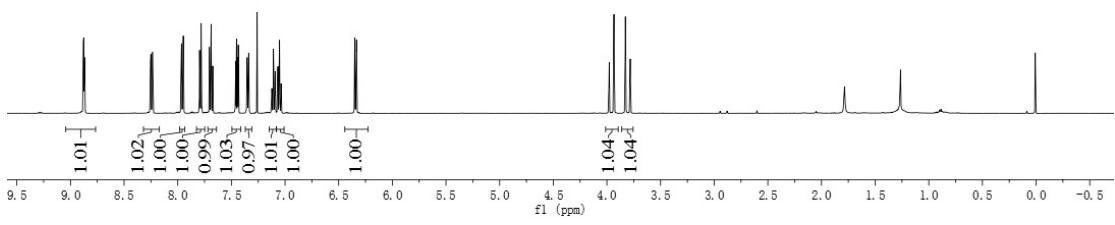
**2-(1,3-dioxoisooindolin-2-yl)-3,3-dimethylbutanoate (2bj)**



**1-(Quinolin-8-yl)indolin-2-one (2ag-1)**

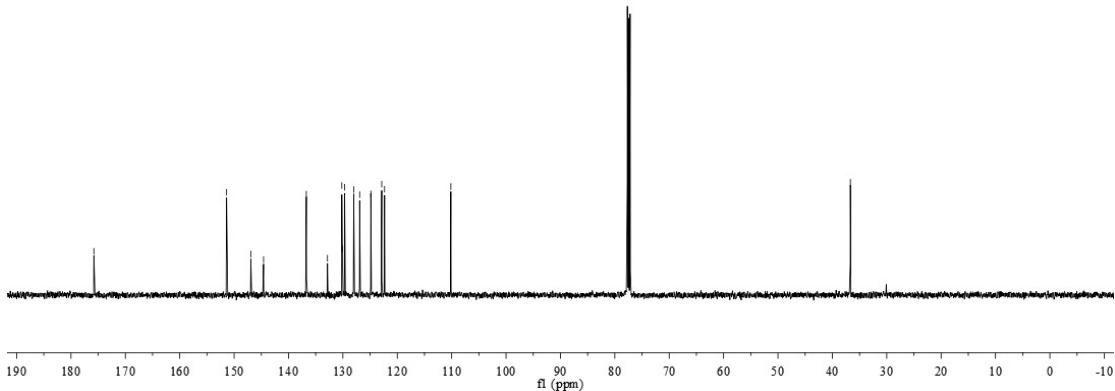


500 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

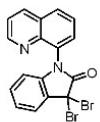


Chemical shifts ( $\delta$ ) in ppm: -175.7892, 151.3830, 146.9234, 144.5883, 136.7206, 132.8322, 130.1949, 130.0917, 129.6790, 128.0041, 126.9191, 124.8653, 124.8347, 122.8576, 122.3336, -110.1450, -36.6852.

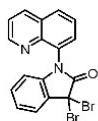
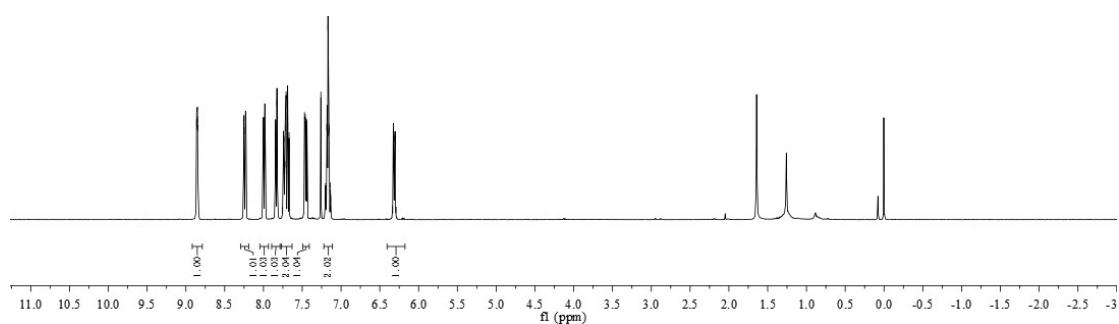
125 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$



### **3,3-Dibromo-1-(quinolin-8-yl)indolin-2-one (2ag-2)**



400 MHz  $^{13}\text{H}$  NMR,  $\text{CDCl}_3$



100 MHz  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$

