

## Supporting Information

### Enantioselective Construction of Triaryl-Substituted All-Carbon Quaternary Stereocenter via Organocatalytic Arylation of Oxindoles with Azonaphthalenes

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Junmin Zhang\* and Bin Tan\*

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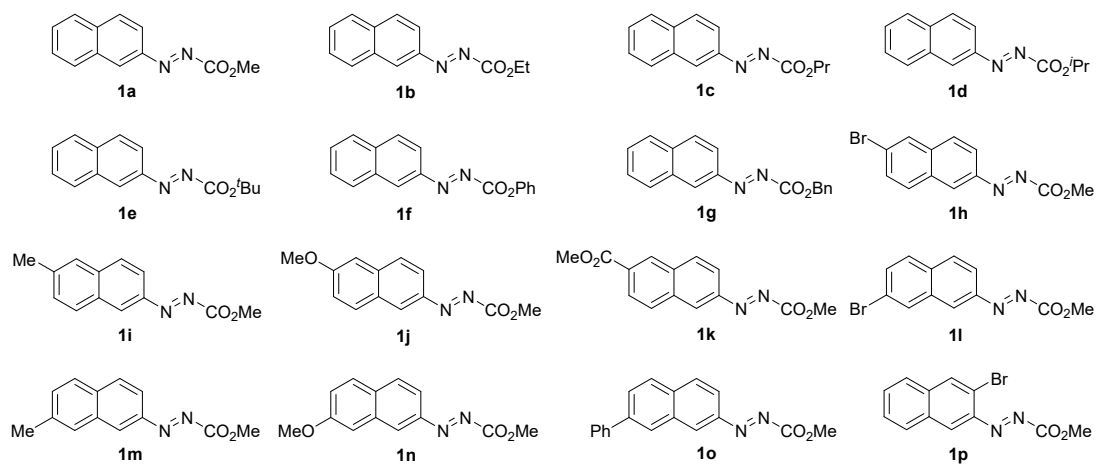
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## 1. General information

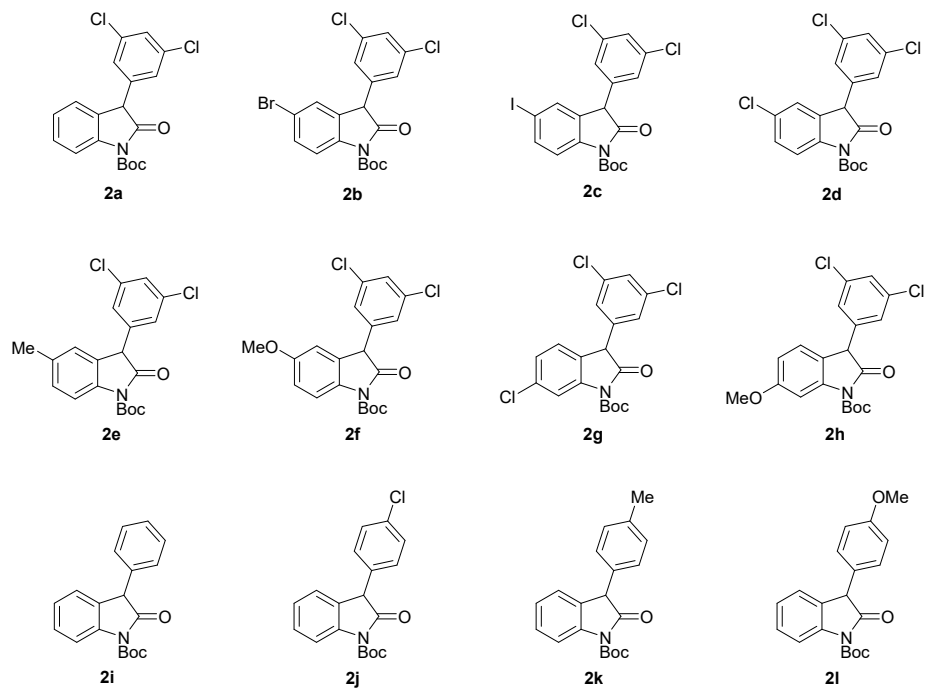
Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400 MHz or 600 MHz spectrometer in  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$ . The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). The enantiomeric excess values were determined by chiral HPLC with an Agilent instrument and a Daicel CHIRALCEL and CHIRALPAK column. High resolution mass spectroscopy (HRMS) analyses were performed at a Q-Exactive (Thermo Scientific) Inc mass instrument (HESI).

## 2. Substrates involved in the manuscript

### Azonaphthalene derivatives



### N-Boc 3-aryl-oxindoles derivatives



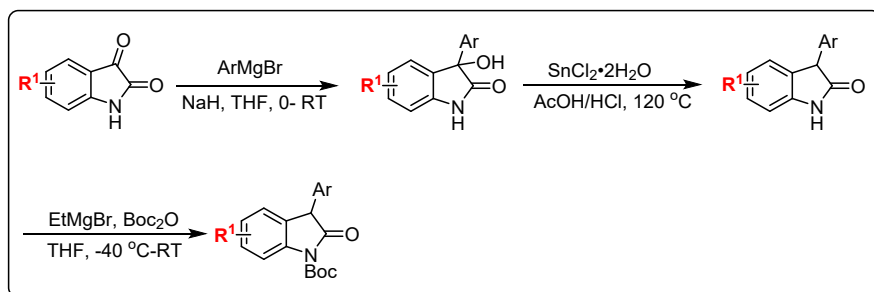
Scheme S1. Substrates involved in the manuscript

### 3. Procedures for the preparation of substrates

#### Preparation of azonaphthalene derivatives

Azonaphthalene derivatives **1a-1p** were prepared according to the procedure of reference.<sup>1</sup>

#### Preparation of *N*-Boc 3-aryl-oxindoles derivatives



*N*-Boc-3-aryl-oxindoles derivatives were synthesized according to a modified process.<sup>2</sup> To a solution of oxindole (25.0 mmol) in THF (50 mL), NaH (37.5 mmol) was added at 0 °C and the resulting mixture was stirred for 30 min.  $\text{ArMgBr}$  (50.0 mmol) in THF was then added dropwise to the mixture and the reaction was allowed to warm to room temperature. After the reaction was finish detected by TLC. The reaction mixture was quenched with aqueous sat.  $\text{NH}_4\text{Cl}$  and extracted with ethyl acetate. The combined extracts were washed with brine and dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was recrystallized in petroleum ether and ethyl acetate to give product as a light orange solid.

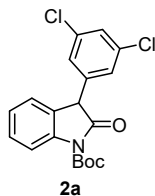
To a solution of the crude product obtained above in  $\text{AcOH/HCl}$  (60 mL/4 mL),  $\text{SnCl}_2$  (2 equiv.) was added at room temperature. Then the mixture was heated to 120 °C for 4 h to 12 h. The mixture was diluted with ethyl acetate and washed with  $\text{H}_2\text{O}$  multiple times. Then the organic phase was washed with aqueous sat.  $\text{Na}_2\text{CO}_3$  and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized in petroleum ether and ethyl acetate to give product as a white solid.

To a solution of obtained 3-aryl oxindole in THF (50 mL),  $\text{EtMgBr}$  (2.2 equiv.) in THF was added dropwise at -40 °C followed by adding  $(\text{Boc})_2\text{O}$  (2.2 equiv.) in one portion. Then the reaction was warmed to room temperature. After the reaction was finish detected by TLC. The mixture was quenched with aqueous sat.  $\text{NH}_4\text{Cl}$  and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by quickly flash column chromatography on silica gel (petroleum ether/ethyl



acetate = 20/1) to give the product with more than 90% purity, after recrystallizing from PE/EA or PE/DCM afforded the pure product as a white or yellow solid.

***tert*-butyl 3-(3,5-dichlorophenyl)-2-oxindoline-1-carboxylate**



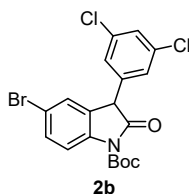
**2a** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.94 (d,  $J$  = 8.2 Hz, 1H), 7.43-7.37 (m, 1H), 7.31 (t,  $J$  = 1.9 Hz, 1H), 7.21 (td,  $J$  = 7.5, 1.1 Hz, 1H), 7.15 (dt,  $J$  = 7.4, 1.5 Hz, 1H), 7.09 (d,  $J$  = 1.9 Hz, 2H), 4.67 (s, 1H), 1.64 (s, 9H).

**<sup>13</sup>C NMR (100 MHz, Chloroform-*d*)**  $\delta$  172.73, 149.18, 140.63, 139.36, 135.53, 129.38, 128.37, 127.34, 125.86, 125.13, 125.06, 115.53, 84.93, 51.83, 28.16.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>17</sub>Cl<sub>2</sub>NNaO<sub>3</sub><sup>+</sup>,  $m/z$ : 400.0483, found: 400.0475.

***tert*-butyl 5-bromo-3-(3,5-dichlorophenyl)-2-oxindoline-1-carboxylate**



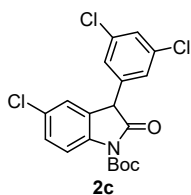
**2b** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.84 (d,  $J$  = 8.7 Hz, 1H), 7.52 (dd,  $J$  = 8.8, 2.1 Hz, 1H), 7.27-7.24 (m, 1H), 7.25 (s, 1H), 7.06 (d,  $J$  = 1.8 Hz, 2H), 4.64 (s, 1H), 1.62 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  171.93, 148.99, 139.64, 138.59, 135.76, 132.44, 128.72, 128.08, 128.01, 127.29, 118.03, 117.23, 85.40, 51.67, 28.15.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>16</sub>BrCl<sub>2</sub>NNaO<sub>3</sub><sup>+</sup>,  $m/z$ : 477.9588, found: 477.9584.

***tert*-butyl 5-chloro-3-(3,5-dichlorophenyl)-2-oxindoline-1-carboxylate**



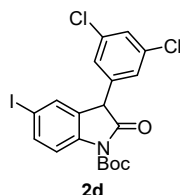
**2c** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.91 (d,  $J$  = 8.8 Hz, 1H), 7.38 (dd,  $J$  = 8.8, 2.2 Hz, 1H), 7.34 (t,  $J$  = 1.8 Hz, 1H), 7.13 (s, 1H), 7.07 (d,  $J$  = 1.8 Hz, 2H), 4.64 (s, 1H), 1.62 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  172.05, 149.02, 139.15, 138.60, 135.76, 130.57, 129.54, 128.72, 127.64, 127.30, 125.27, 116.85, 85.38, 51.74, 28.16.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>16</sub>Cl<sub>3</sub>NNaO<sub>3</sub><sup>+</sup>,  $m/z$ : 434.0093, found: 434.0089.

***tert*-butyl 3-(3,5-dichlorophenyl)-5-iodo-2-oxoindoline-1-carboxylate**



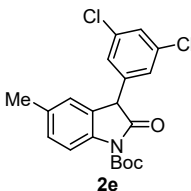
**2d** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.72 (s, 2H), 7.43 (d,  $J$  = 1.2 Hz, 1H), 7.33 (t,  $J$  = 1.9 Hz, 1H), 7.06 (d,  $J$  = 1.8 Hz, 2H), 4.63 (s, 1H), 1.62 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  171.78, 148.95, 140.36, 138.65, 138.37, 135.74, 133.73, 128.70, 128.30, 127.29, 117.56, 88.39, 85.38, 51.49, 28.14.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>16</sub>Cl<sub>2</sub>INNaO<sub>3</sub><sup>+</sup>,  $m/z$ : 525.9450, found: 525.9449.

***tert*-butyl 3-(3,5-dichlorophenyl)-5-methyl-2-oxoindoline-1-carboxylate**



**2e** was obtained as a white solid.

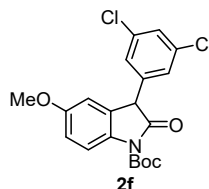
**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.80 (d,  $J$  = 8.4 Hz, 1H), 7.31 (t,  $J$  = 1.9 Hz, 1H), 7.19 (d,  $J$  = 8.4, 1H), 7.08 (d,  $J$  = 1.9 Hz, 2H), 6.94 (s, 1H), 4.62 (s, 1H), 2.34 (s, 3H), 1.63 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  172.99, 149.25, 139.59, 138.19, 135.51, 134.85, 129.88,

128.35, 127.39, 125.91, 125.63, 115.30, 84.80, 52.00, 28.19, 21.19.

**HRMS (ESI)** calcd for  $[M+Na]^+$   $C_{20}H_{19}Cl_2NNaO_3^+$ ,  $m/z$ : 414.0640, found: 414.0633.

***tert*-butyl 3-(3,5-dichlorophenyl)-5-methoxy-2-oxoindoline-1-carboxylate**



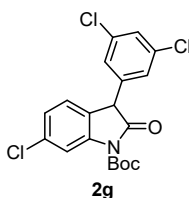
**2f** was obtained as a white solid.

**$^1H$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.86 (d,  $J$  = 8.9 Hz, 1H), 7.30 (t,  $J$  = 2.0 Hz, 1H), 7.09 (d,  $J$  = 1.9 Hz, 2H), 6.91 (dd,  $J$  = 8.9, 2.7 Hz, 1H), 6.69 (d,  $J$  = 2.2 Hz, 1H), 4.63 (s, 1H), 3.78 (s, 3H), 1.62 (s, 9H).

**$^{13}C$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  172.76, 157.22, 149.24, 139.34, 135.54, 133.92, 128.40, 127.36, 127.13, 116.50, 114.17, 111.17, 84.72, 55.79, 52.18, 28.17.

**HRMS (ESI)** calcd for  $[M+Na]^+$   $C_{20}H_{19}Cl_2NNaO_4^+$ ,  $m/z$ : 430.0589, found: 430.0583.

***tert*-butyl 6-chloro-3-(3,5-dichlorophenyl)-2-oxoindoline-1-carboxylate**



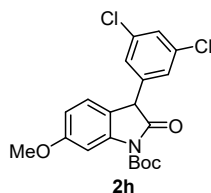
**2g** was obtained as a white solid.

**$^1H$  NMR (400 MHz, Chloroform-*d*)**  $\delta$  8.02 (t,  $J$  = 1.6 Hz, 1H), 7.34-7.30 (m, 1H), 7.20 (dt,  $J$  = 8.0, 2.1 Hz, 1H), 7.11-7.04 (m, 3H), 4.63 (s, 1H), 1.63 (s, 9H).

**$^{13}C$  NMR (101 MHz, Chloroform-*d*)**  $\delta$  172.28, 148.95, 141.52, 138.78, 135.69, 135.25, 128.61, 127.26, 126.00, 125.21, 124.18, 116.35, 85.51, 51.42, 28.13.

**HRMS (ESI)** calcd for  $[M+Na]^+$   $C_{19}H_{16}Cl_3NNaO_3^+$ ,  $m/z$ : 434.0093, found: 434.0089.

***tert*-butyl 3-(3,5-dichlorophenyl)-6-methoxy-2-oxoindoline-1-carboxylate**



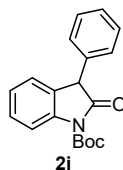
**2h** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.58 (d,  $J$  = 2.4 Hz, 1H), 7.30 (t,  $J$  = 1.9 Hz, 1H), 7.09 (d,  $J$  = 1.9 Hz, 2H), 7.04 (d,  $J$  = 8.3 Hz, 1H), 6.74 (dd,  $J$  = 8.3, 2.4 Hz, 1H), 4.61 (s, 1H), 3.87 (s, 3H), 1.63 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  173.32, 160.66, 149.20, 141.70, 139.84, 135.50, 128.31, 127.29, 125.75, 117.49, 110.81, 102.17, 84.95, 55.77, 51.38, 28.19.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>20</sub>H<sub>19</sub>Cl<sub>2</sub>NNaO<sub>4</sub><sup>+</sup>,  $m/z$ : 430.0589, found: 430.0583.

***tert*-butyl 2-oxo-3-phenylindoline-1-carboxylate**



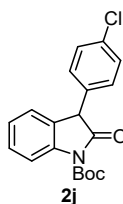
**2i** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.95 (d,  $J$  = 8.2 Hz, 1H), 7.41-7.28 (m, 4H), 7.24-7.13 (m, 4H), 4.74 (s, 1H), 1.65 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  173.97, 149.42, 140.51, 136.31, 128.96, 128.69, 127.93, 127.45, 125.13, 124.67, 115.16, 84.44, 52.57, 28.12.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>19</sub>NNaO<sub>3</sub><sup>+</sup>,  $m/z$ : 332.1263, found: 332.1251.

***tert*-butyl 3-(4-chlorophenyl)-2-oxoindoline-1-carboxylate**



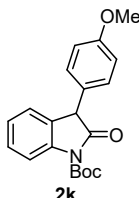
**2j** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.94 (d,  $J$  = 8.2 Hz, 1H), 7.37 (t,  $J$  = 7.8 Hz, 1H), 7.31 (d,  $J$  = 8.2 Hz, 2H), 7.18 (t,  $J$  = 7.4 Hz, 1H), 7.16-7.10 (m, 3H), 4.70 (s, 1H), 1.63 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  173.55, 149.29, 140.53, 134.73, 133.96, 130.04, 129.13, 128.95, 126.86, 125.06, 124.79, 115.29, 84.63, 51.89, 28.11.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>19</sub>H<sub>18</sub>ClNNaO<sub>3</sub><sup>+</sup>, *m/z*: 366.0873, found: 366.0865.

***tert*-butyl 3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate**



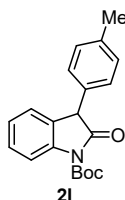
**2k** was obtained as a yellow solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.93 (d, *J* = 8.2 Hz, 1H), 7.39-7.32 (m, 1H), 7.18-7.14 (m, 2H), 7.14-7.08 (m, 2H), 6.90-6.84 (m, 2H), 4.67 (s, 1H), 3.78 (s, 3H), 1.63 (d, *J* = 1.1 Hz, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  174.33, 159.34, 149.49, 140.50, 129.75, 128.64, 128.35, 127.74, 125.12, 124.65, 115.15, 114.41, 84.40, 55.36, 51.83, 28.14.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>20</sub>H<sub>21</sub>NNaO<sub>4</sub><sup>+</sup>, *m/z*: 362.1368, found: 362.1357.

***tert*-butyl 2-oxo-3-(*p*-tolyl)indoline-1-carboxylate**



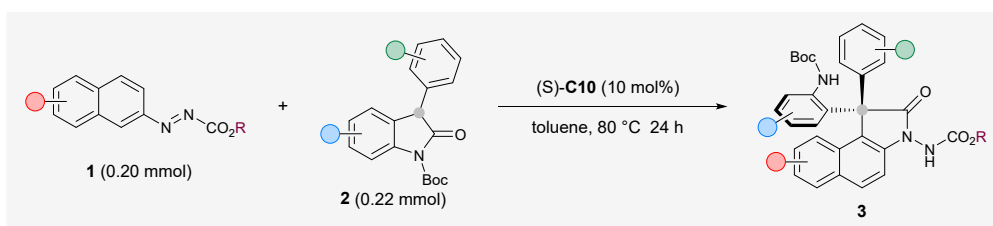
**2l** was obtained as a white solid.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)**  $\delta$  7.94 (d, *J* = 8.2 Hz, 1H), 7.41-7.32 (m, 1H), 7.20-7.12 (m, 4H), 7.12-7.05 (m, 2H), 4.70 (s, 1H), 2.34 (s, 3H), 1.64 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  174.19, 149.51, 140.56, 137.72, 133.36, 129.70, 128.65, 128.56, 127.71, 125.13, 124.66, 115.16, 84.41, 52.29, 28.16, 21.21.

**HRMS (ESI)** calcd for  $[M+Na]^+$  C<sub>20</sub>H<sub>21</sub>NNaO<sub>3</sub><sup>+</sup>, *m/z*: 346.1419, found: 346.1407.

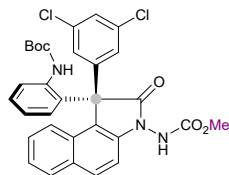
#### 4. General procedure for asymmetric synthesis of products **3**



To a dry Schlenk tube (10 mL) was added azonaphthalene derivative **1** (0.2 mmol, 1.0 equiv.), oxindole derivative **2** (0.22 mmol, 1.1 equiv.) and **(S)-C10** (10 mol%) in anhydrous toluene (4 mL). Then the reaction was stirred at 80 °C under argon atmosphere for 24 h. The resulted mixture was directly purified by flash chromatography on silica gel to afford product **3**. The corresponding racemic product was prepared with racemic **C10** as the catalyst.

## 5. Characterizations of products

### methyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate



**3a**, 93%, 96% ee

According to general procedure, **3a** was obtained in 93% yield and 96% ee as white solid.

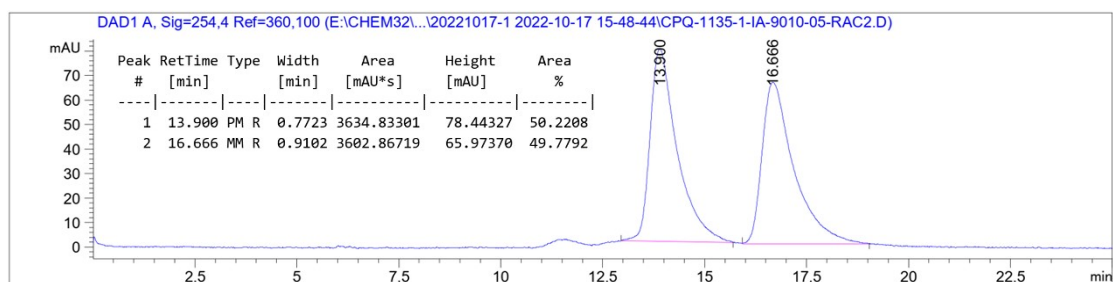
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.37 (s, 1H), 8.81 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.47-7.20 (m, 7H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.88, 155.26, 151.65, 141.75, 138.89, 137.68, 134.02, 131.60, 130.92, 129.63, 129.57, 129.16, 128.26, 127.44, 127.12, 126.86, 125.48, 124.25, 123.99, 121.77, 120.21, 109.68, 78.74, 61.42, 52.76, 27.48.

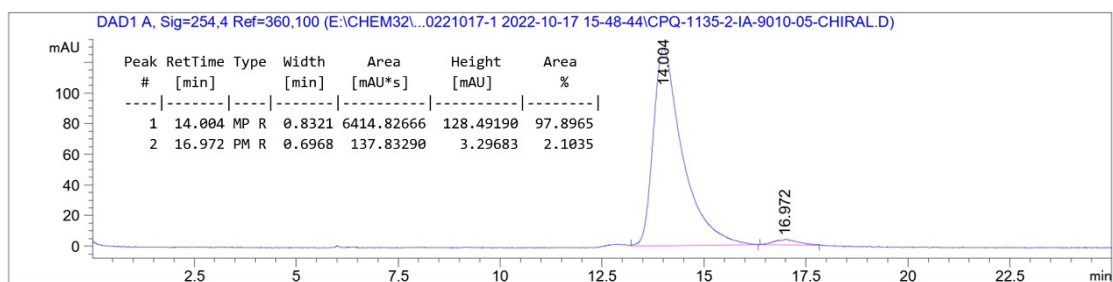
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 614.1225, found: 614.1222.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IA, hexane/isopropanol = 90/10, 0.5 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 14.00 min, *t*<sub>R</sub> (minor) = 16.97 min, ee = 96%.

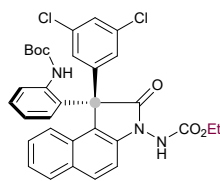
#### Chiral HPLC spectrum of racemic **3a**



#### Chiral HPLC spectrum of **3a**



ethyl (*S*)-(1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate



**3b**, 91%, 92% ee

According to general procedure, **3b** was obtained in 91% yield and 92% ee as white solid.

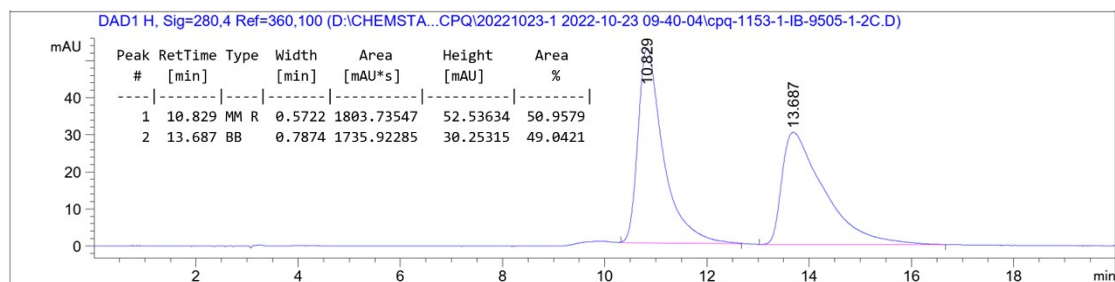
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.29 (s, 1H), 8.82 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.51-7.21 (m, 8H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.29 (s, 2H), 1.32 (s, 12H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.77, 154.76, 151.66, 141.76, 138.97, 137.70, 134.03, 131.59, 130.91, 129.64, 129.57, 129.15, 128.28, 127.43, 127.13, 126.86, 125.50, 124.25, 123.98, 121.76, 120.20, 109.67, 78.73, 61.77, 61.44, 27.49, 13.86.

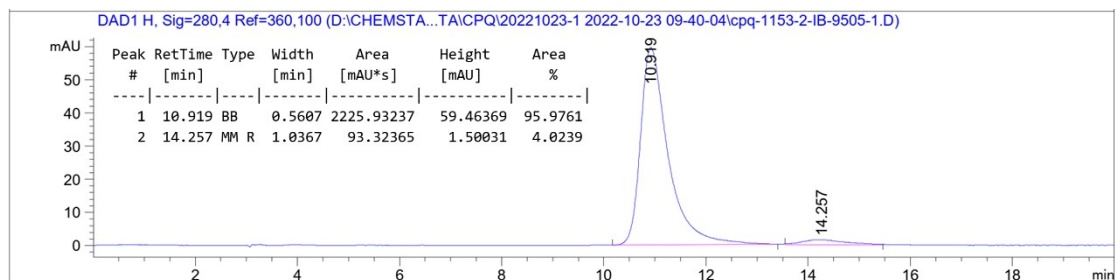
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 628.1382, found: 628.1378.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 280 nm, *t*<sub>R</sub> (major) = 10.92 min, *t*<sub>R</sub> (minor) = 14.26 min, ee = 92%.

Chiral HPLC spectrum of racemic **3b**

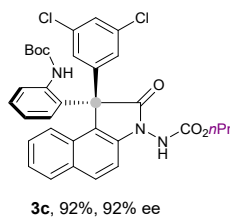


Chiral HPLC spectrum of **3b**





**propyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3c** was obtained in 92% yield and 92% ee as white solid.

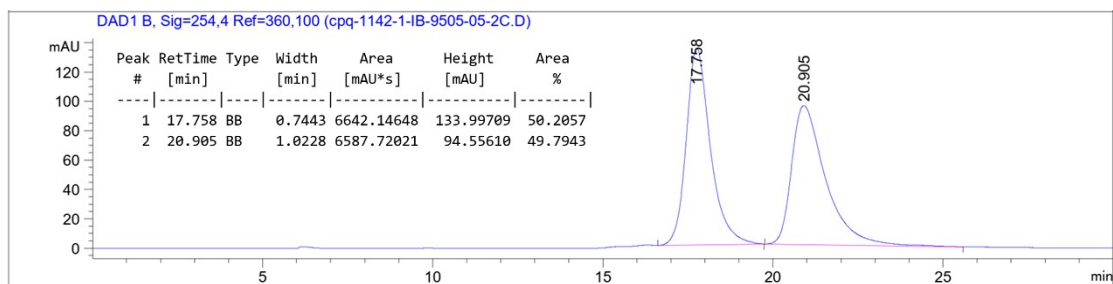
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.29 (s, 1H), 8.82 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.53-7.09 (m, 8H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.20 (s, 2H), 1.69 (s, 2H), 1.32 (s, 9H), 0.93 (s, 3H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.83, 154.78, 151.65, 141.75, 138.95, 137.68, 134.02, 131.60, 130.90, 129.64, 129.57, 129.14, 128.27, 127.44, 127.14, 126.85, 125.48, 124.25, 123.98, 121.75, 109.64, 78.71, 67.21, 61.43, 27.48, 21.38, 9.44.

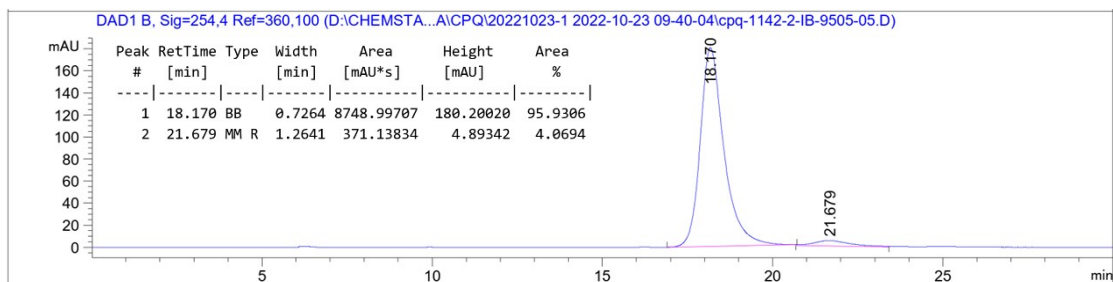
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>33</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 642.1538, found: 642.1533.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 18.18 min, *t<sub>R</sub>* (minor) = 21.68 min, ee = 92%.

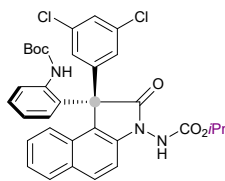
*Chiral HPLC spectrum of racemic 3c*



*Chiral HPLC spectrum of 3c*



**isopropyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



**3d**, 85%, 87% ee

According to general procedure, **3d** was obtained in 85% yield and 87% ee as white solid.

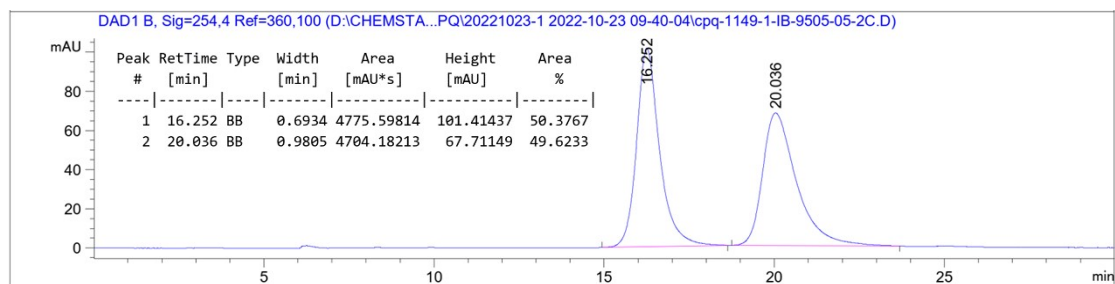
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.23 (s, 1H), 8.82 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.57-7.10 (m, 8H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 1.32 (s, 15H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 151.65, 141.74, 139.02, 137.69, 134.02, 131.57, 130.88, 129.62, 129.56, 129.11, 128.29, 127.41, 127.15, 126.86, 125.51, 124.23, 123.95, 121.73, 120.16, 109.63, 78.71, 69.68, 61.43, 27.48, 21.32.

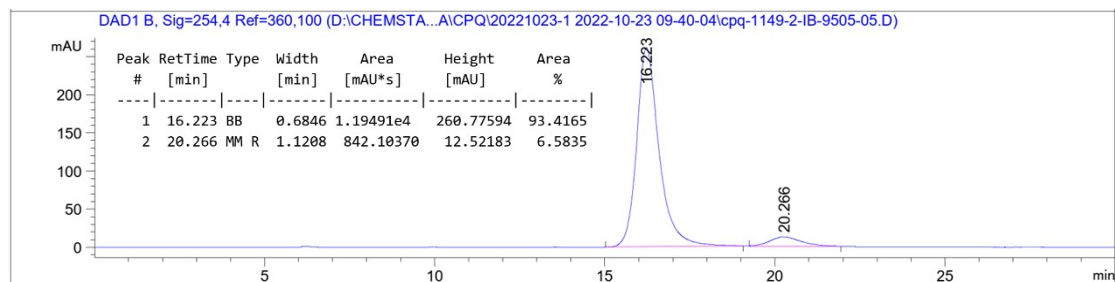
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>33</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 642.1538, found: 642.1533.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 16.22 min, *t*<sub>R</sub> (minor) = 20.27 min, ee = 87%.

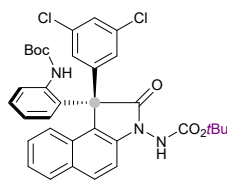
*Chiral HPLC spectrum of racemic 3d*



*Chiral HPLC spectrum of 3d*



***tert*-butyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



**3e**, 75%, 84% ee

According to general procedure, **3e** was obtained in 75% yield and 84% ee as white solid.

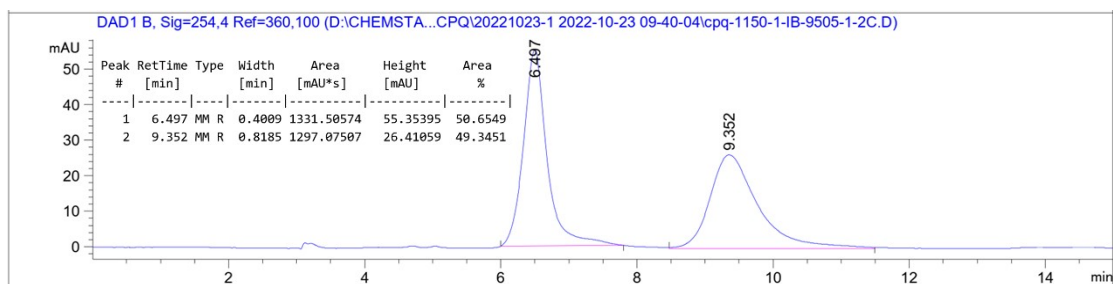
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 9.98 (s, 1H), 8.79 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.54-7.09 (m, 8H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 1.51 (s, 9H), 1.31 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.86, 153.62, 151.66, 141.79, 139.17, 137.66, 134.00, 131.53, 130.83, 129.62, 129.56, 129.08, 128.29, 127.40, 127.14, 126.88, 125.53, 124.25, 123.92, 121.72, 120.11, 109.65, 81.31, 78.74, 61.40, 27.56, 27.49.

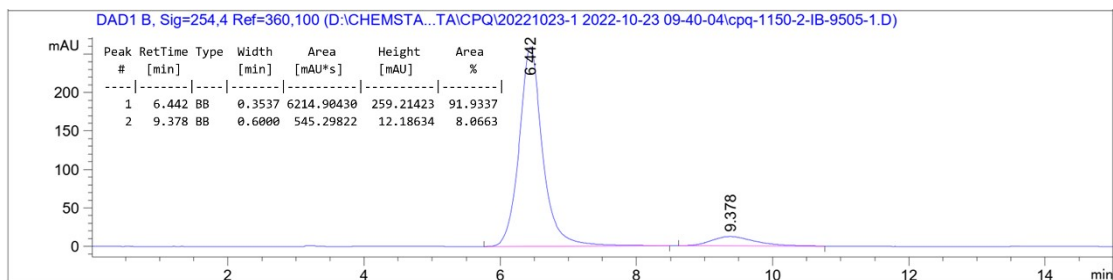
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>34</sub>H<sub>33</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 656.1695, found: 656.1691.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 6.44 min, *t<sub>R</sub>* (minor) = 9.38 min, ee = 84%.

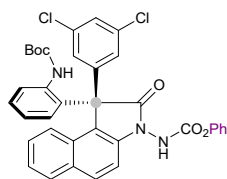
*Chiral HPLC spectrum of racemic 3e*



*Chiral HPLC spectrum of 3e*



**phenyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



**3f**, 84%, 95% ee

According to general procedure, **3f** was obtained in 84% yield and 95% ee as white solid.

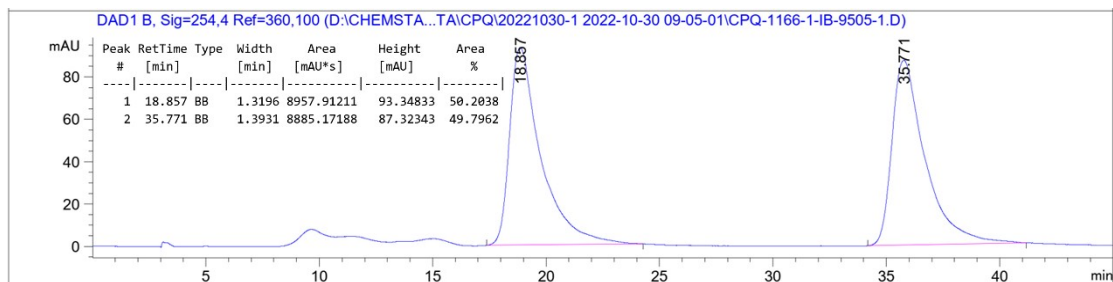
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 11.03 (s, 1H), 8.78 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.69 (dd, *J* = 28.9, 8.4 Hz, 2H), 7.60-7.09 (m, 12H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.67, 153.14, 151.67, 150.03, 141.61, 138.58, 137.68, 134.07, 131.75, 131.01, 129.68, 129.60, 129.23, 129.16, 128.28, 127.52, 127.20, 126.94, 125.58, 125.45, 124.34, 124.10, 121.79, 120.97, 120.27, 109.73, 78.79, 61.48, 27.49.

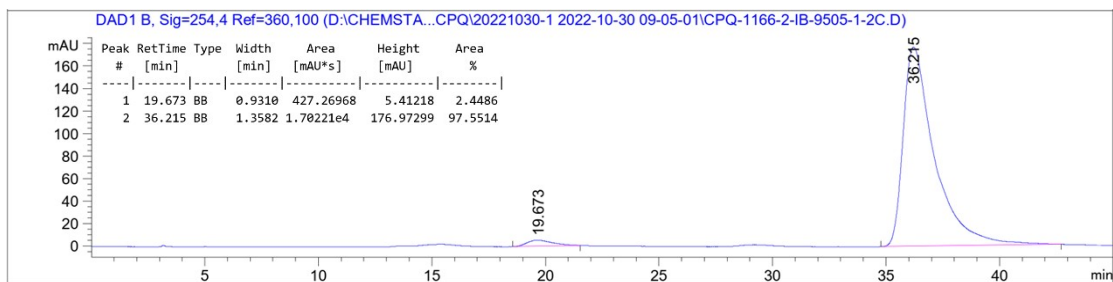
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>36</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 676.1382, found: 676.1372.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (minor) = 19.63 min, *t*<sub>R</sub> (major) = 36.22 min, ee = 95%.

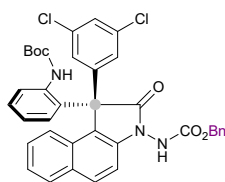
*Chiral HPLC spectrum of racemic 3f*



*Chiral HPLC spectrum of 3f*



**benzyl (S)-(1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



**3g**, 79%, 90% ee

According to general procedure, **3g** was obtained in 79% yield and 90% ee as white solid.

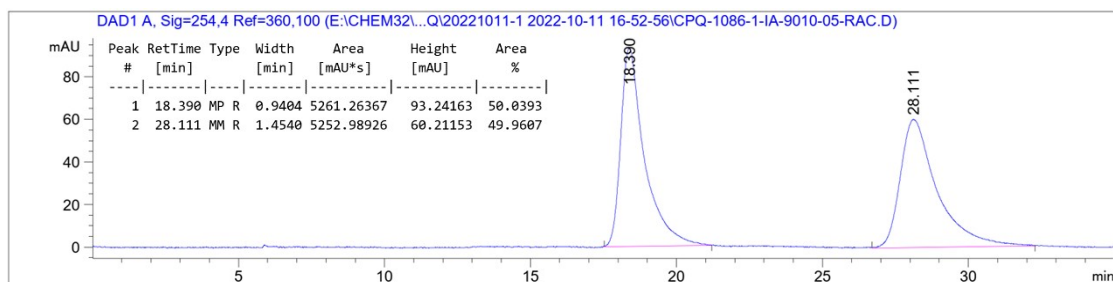
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.51 (s, 1H), 8.79 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.59-7.09 (m, 13H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.31 (s, 2H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.81, 154.71, 151.64, 141.71, 138.84, 137.66, 135.41, 134.03, 131.61, 130.92, 129.65, 129.57, 129.17, 128.25, 128.04, 127.79, 127.47, 127.15, 126.86, 125.47, 124.29, 124.02, 121.76, 120.21, 109.64, 78.73, 67.10, 61.42, 27.48.

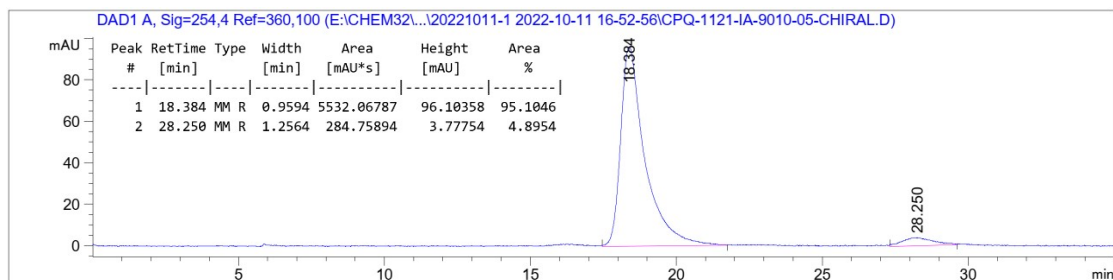
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>37</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 690.1538, found: 690.1534.

HPLC analysis: HPLC DAICEL CHIRALPAK IA, hexane/isopropanol = 90/10, 0.5 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 18.38 min, *t*<sub>R</sub> (minor) = 28.25 min, ee = 90%.

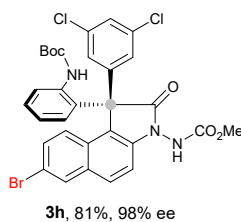
*Chiral HPLC spectrum of racemic 3g*



*Chiral HPLC spectrum of 3g*



**methyl (S)-(7-bromo-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3h** was obtained in 81% yield and 98% ee as white solid.

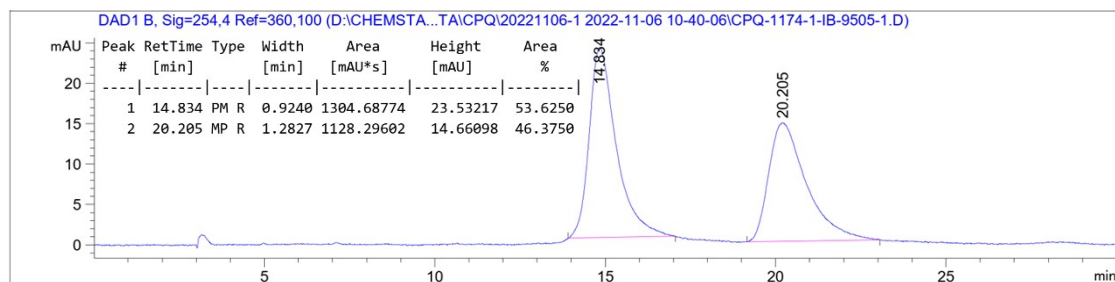
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.36 (s, 1H), 8.72 (s, 1H), 8.27 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 9.0, 3.6 Hz, 2H), 7.49-7.42 (m, 2H), 7.41-7.17 (m, 3H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 1.31 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.74, 155.24, 151.63, 141.52, 139.40, 137.62, 134.16, 132.14, 131.38, 130.99, 130.47, 129.47, 129.27, 127.31, 127.00, 126.81, 125.39, 124.47, 123.97, 120.52, 117.08, 110.95, 78.78, 61.29, 52.82, 27.49.

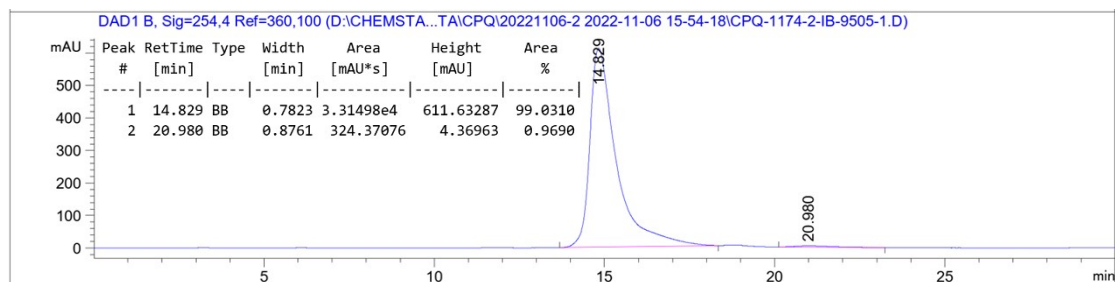
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>BrCl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 692.0331, found: 692.0325.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 14.83 min, *t*<sub>R</sub> (minor) = 20.98 min, ee = 98%.

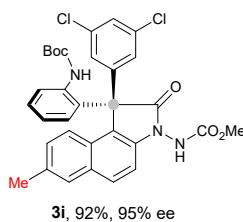
*Chiral HPLC spectrum of racemic 3h*



*Chiral HPLC spectrum of 3h*



**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-7-methyl-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3i** was obtained in 92% yield and 95% ee as white solid.

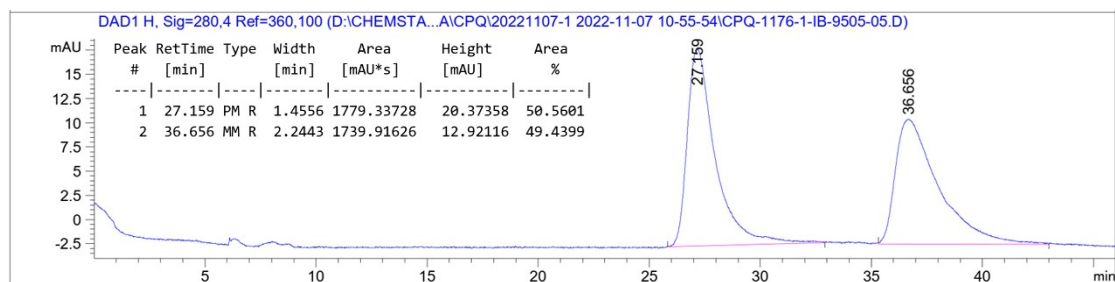
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.33 (s, 1H), 8.83 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.75 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.49-7.40 (m, 3H), 7.39-7.09 (m, 4H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H), 1.32 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.79, 155.20, 151.66, 141.90, 138.08, 137.69, 134.00, 133.40, 131.22, 130.79, 129.68, 129.59, 129.14, 128.35, 127.06, 126.82, 126.47, 125.43, 124.23, 121.63, 120.23, 109.63, 78.73, 61.42, 52.74, 27.49, 20.34.

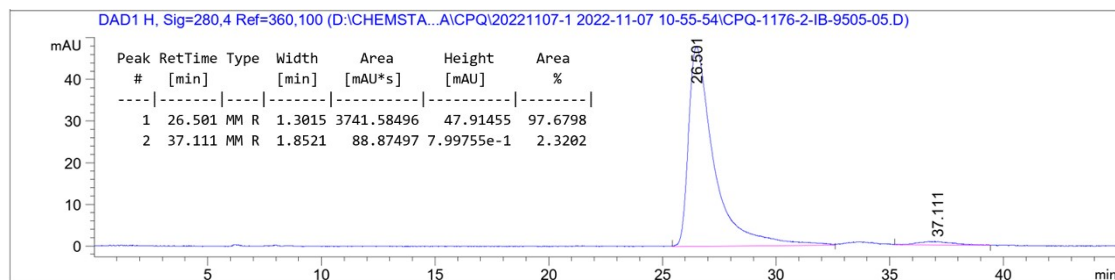
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 628.1382, found: 628.1375.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 280 nm, *t*<sub>R</sub> (major) = 26.50 min, *t*<sub>R</sub> (minor) = 37.11 min, ee = 95%.

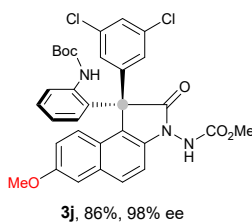
*Chiral HPLC spectrum of racemic 3i*



*Chiral HPLC spectrum of 3i*



**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-7-methoxy-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3j** was obtained in 86% yield and 98% ee as white solid.

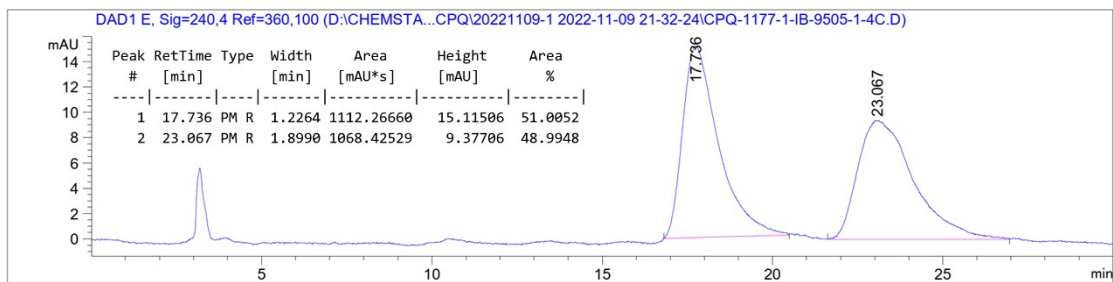
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.31 (s, 1H), 8.84 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.48-7.39 (m, 4H), 7.39-7.18 (m, 3H), 7.12 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 6H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.64, 155.71, 155.26, 151.65, 141.93, 137.70, 136.88, 134.02, 132.38, 130.09, 129.56, 129.12, 127.07, 126.80, 125.43, 124.25, 123.65, 123.22, 120.61, 119.94, 110.02, 108.43, 78.72, 61.44, 54.96, 52.72, 27.49.

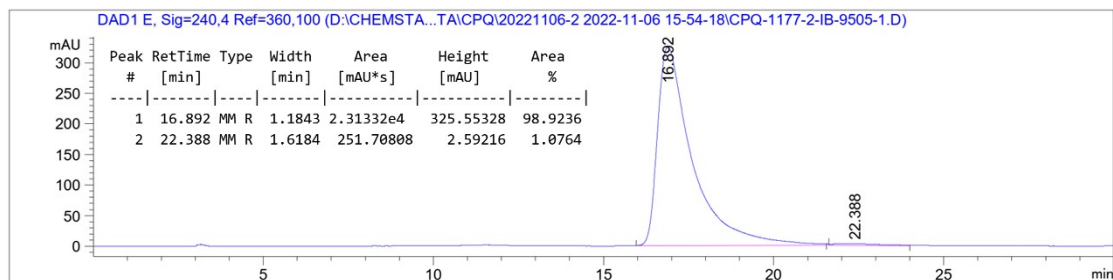
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>6</sub><sup>+</sup>, *m/z*: 644.1331, found: 644.1328.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 240 nm, *t*<sub>R</sub> (major) = 16.89 min, *t*<sub>R</sub> (minor) = 22.39 min, ee = 98%.

*Chiral HPLC spectrum of racemic 3j*

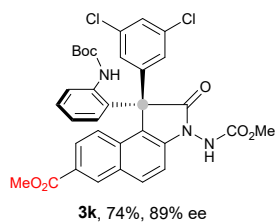


*Chiral HPLC spectrum of 3j*





**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-3-((methoxycarbonyl)amino)-2-oxo-2,3-dihydro-1H-benzo[e]indole-7-carboxylate**



According to general procedure, **3k** was obtained in 74% yield and 89% ee as white solid.

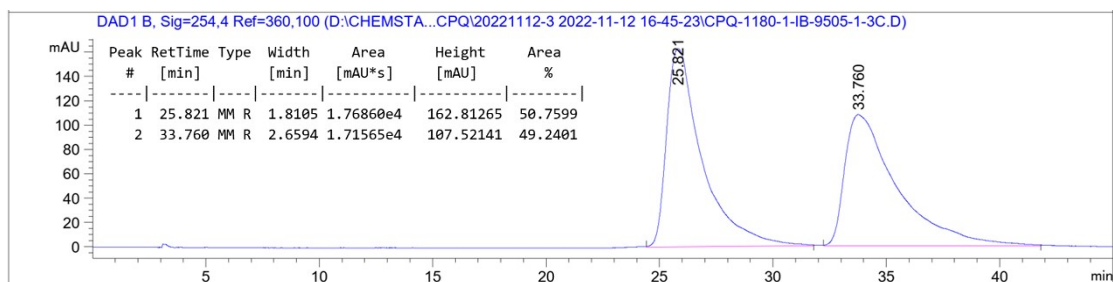
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 100 °C)** δ 10.28 (s, 1H), 8.66 (s, 1H), 8.64 (s, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 10.3 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.49-7.40 (m, 3H), 7.35 (s, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 1.32 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 100 °C)** δ 177.55, 165.42, 155.06, 151.56, 141.38, 141.07, 137.58, 134.06, 133.28, 132.06, 130.24, 129.93, 129.35, 129.13, 127.18, 126.87, 126.22, 125.42, 125.25, 124.29, 122.19, 120.25, 110.61, 78.70, 61.21, 52.67, 51.45, 27.39.

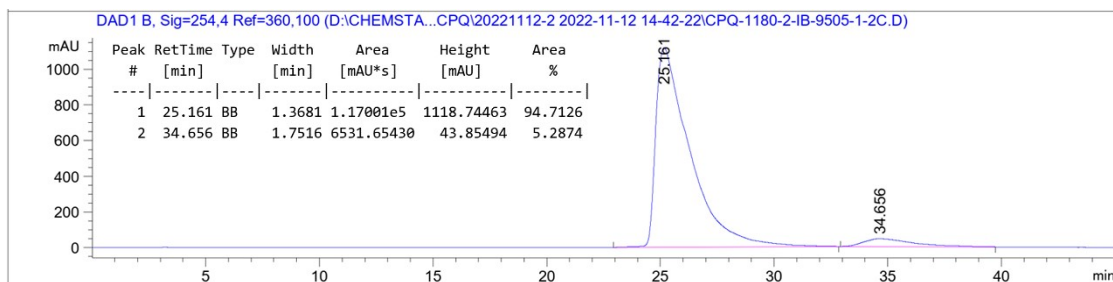
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>33</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>7</sub><sup>+</sup>, *m/z*: 672.1280, found: 672.1274.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 25.16 min, *t*<sub>R</sub> (minor) = 34.66 min, ee = 89%.

*Chiral HPLC spectrum of racemic 3k*

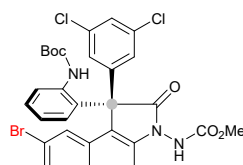


*Chiral HPLC spectrum of 3k*



**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-**

### oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate



**3I**, 87%, 98% ee

According to general procedure, **3I** was obtained in 87% yield and 99% ee as white solid.

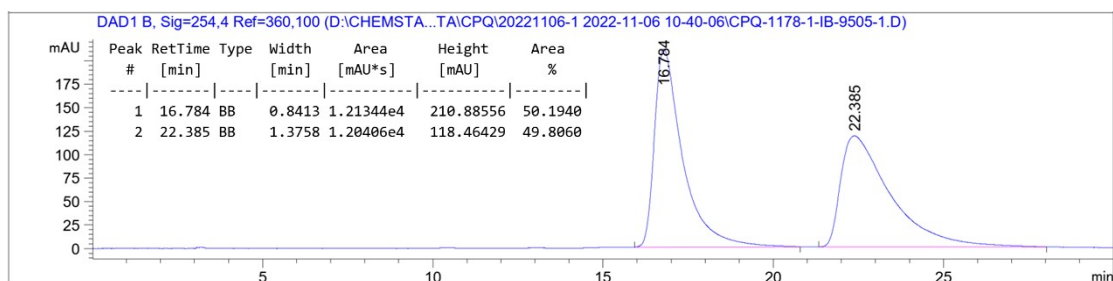
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.37 (s, 1H), 8.72 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.51-7.44 (m, 4H), 7.29 (s, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 1.31 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.63, 155.25, 151.68, 141.44, 140.01, 137.61, 134.25, 131.90, 131.86, 129.45, 129.36, 129.29, 129.20, 127.35, 127.24, 127.03, 125.32, 124.56, 123.72, 121.10, 119.09, 110.40, 78.83, 61.19, 52.82, 27.45.

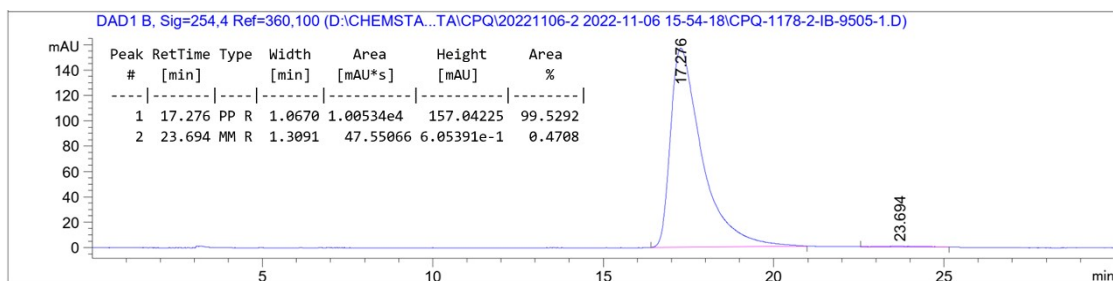
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>BrCl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, m/z: 692.0331, found: 692.0322.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, t<sub>R</sub> (major) = 17.28 min, t<sub>R</sub> (minor) = 23.69 min, ee = 99%.

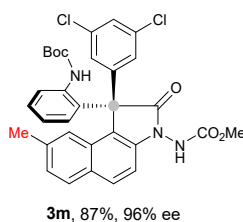
*Chiral HPLC spectrum of racemic 3I*



*Chiral HPLC spectrum of 3I*



**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-8-methyl-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3m** was obtained in 87% yield and 96% ee as white solid.

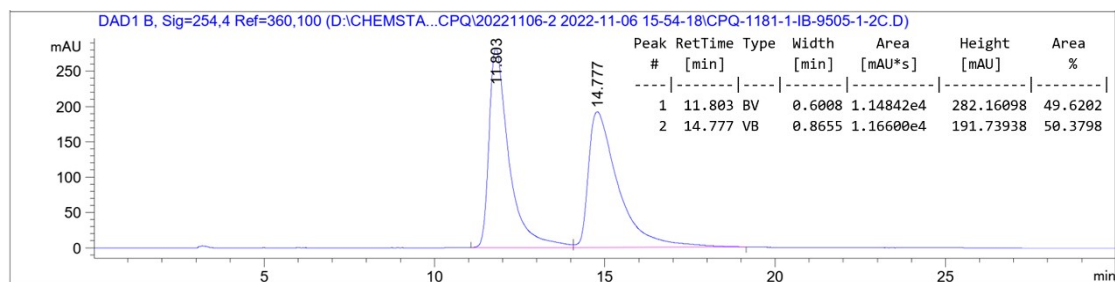
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.34 (s, 1H), 8.82 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.48-7.23 (m, 5H), 7.21 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.13 (s, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 2.26 (s, 3H), 1.32 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.92, 155.27, 151.72, 141.86, 138.94, 137.67, 137.00, 133.99, 131.26, 129.53, 129.46, 129.27, 129.21, 128.47, 127.02, 126.95, 126.18, 125.55, 124.29, 120.74, 119.44, 108.75, 78.74, 61.44, 52.75, 27.49, 21.08.

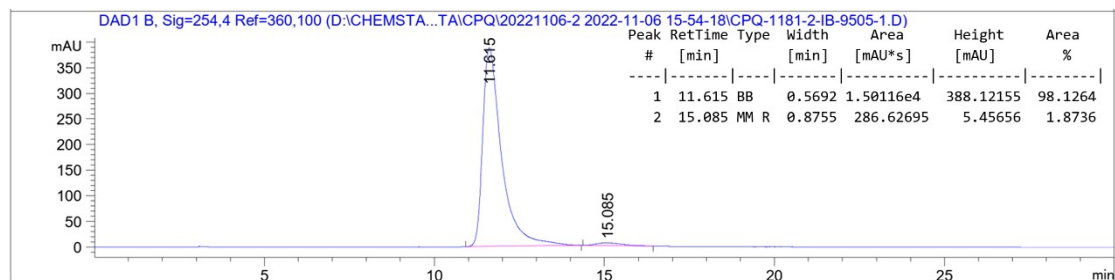
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 628.1382, found: 628.1378.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 11.62 min, *t<sub>R</sub>* (minor) = 15.09 min, ee = 96%.

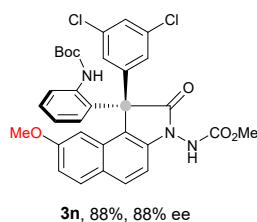
*Chiral HPLC spectrum of racemic 3m*



*Chiral HPLC spectrum of 3m*



**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-8-methoxy-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3n** was obtained in 88% yield and 88% ee as white solid.

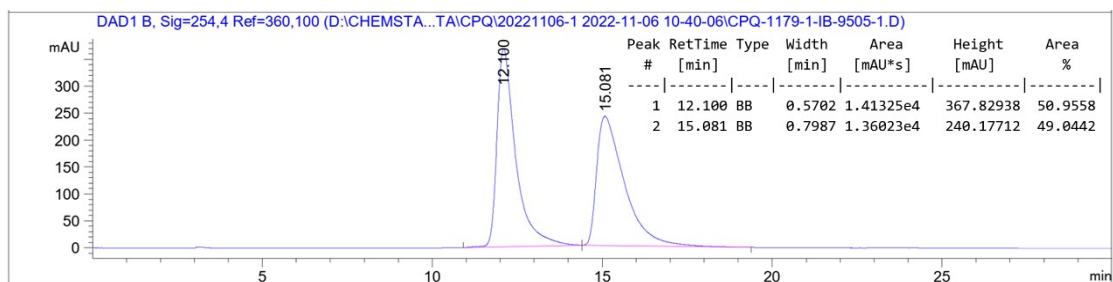
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.35 (s, 1H), 8.87 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.50-7.43 (m, 2H), 7.42-7.12 (m, 3H), 7.09-6.99 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H), 3.58 (s, 3H), 1.31 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.86, 158.03, 155.19, 151.74, 141.67, 139.46, 137.66, 134.03, 131.29, 131.19, 129.64, 129.51, 129.25, 127.15, 126.95, 126.38, 125.53, 124.23, 119.08, 116.62, 107.11, 100.61, 78.74, 61.32, 54.53, 52.75, 27.47.

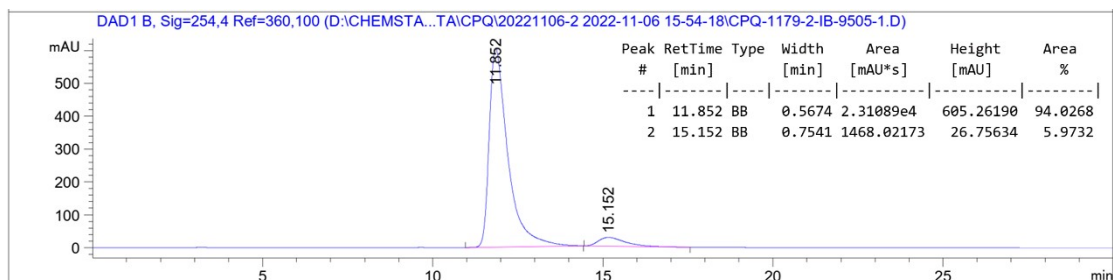
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>6</sub><sup>+</sup>, *m/z*: 624.1331, found: 624.1325.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 11.85 min, *t<sub>R</sub>* (minor) = 15.15 min, ee = 88%.

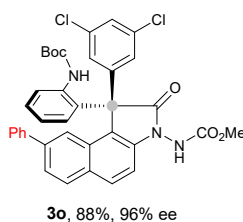
*Chiral HPLC spectrum of racemic 3n*



*Chiral HPLC spectrum of 3n*



**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-8-phenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3o** was obtained in 88% yield and 96% ee as white solid.

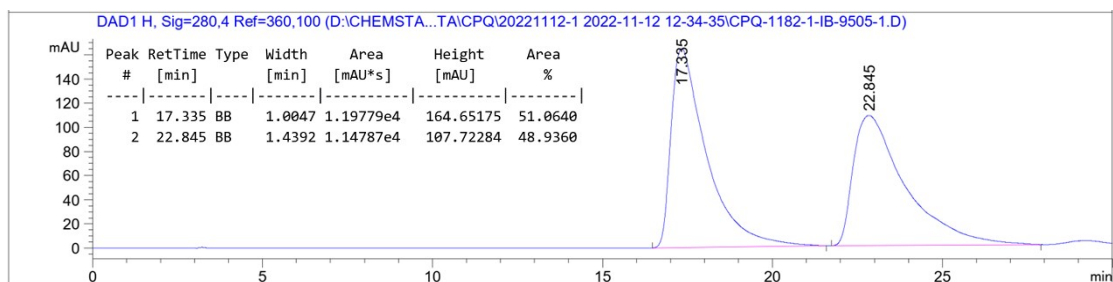
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.39 (s, 1H), 8.88 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.73-7.66 (m, 2H), 7.57 (s, 1H), 7.54-7.13 (m, 10H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 1.32 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 178.00, 155.27, 151.75, 141.93, 139.38, 139.15, 139.04, 137.68, 134.22, 131.39, 130.39, 130.10, 129.42, 129.35, 128.69, 128.52, 127.65, 127.29, 127.05, 126.34, 125.62, 124.38, 123.22, 120.27, 119.18, 109.81, 78.82, 61.44, 52.81, 27.48.

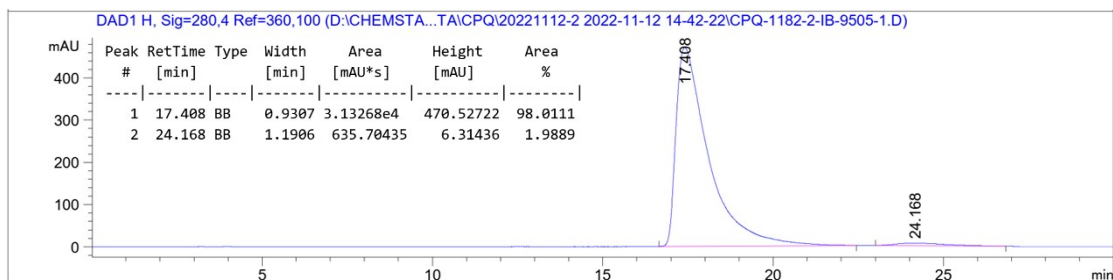
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>37</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 690.1538, found: 690.1535.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 280 nm, *t*<sub>R</sub> (major) = 17.41 min, *t*<sub>R</sub> (minor) = 24.17 min, ee = 96%.

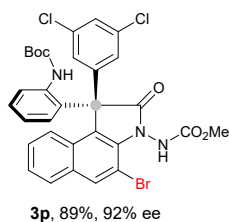
*Chiral HPLC spectrum of racemic 3o*



*Chiral HPLC spectrum of 3o*



**methyl (S)-(4-bromo-1-(2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3p** was obtained in 89% yield and 92% ee as white solid.

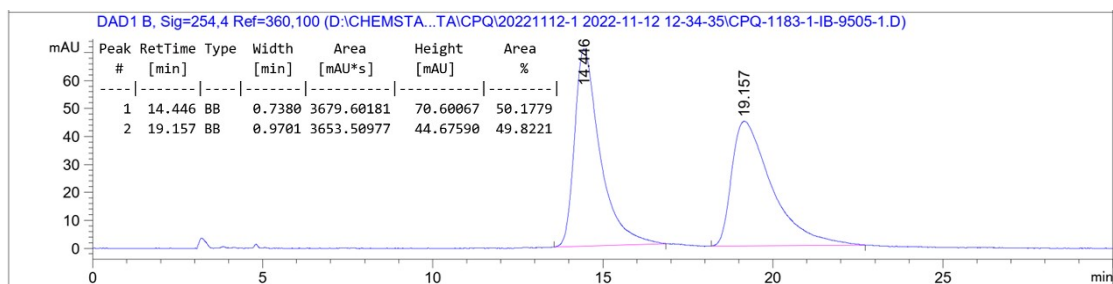
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.38 (s, 1H), 8.83 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.47-7.33 (m, 6H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 1.33 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.87, 155.32, 151.67, 141.77, 138.92, 137.72, 134.05, 131.60, 130.94, 129.63, 129.59, 129.16, 128.29, 127.43, 127.12, 126.88, 125.51, 124.24, 123.99, 121.79, 120.24, 109.69, 78.75, 61.45, 52.76, 27.50.

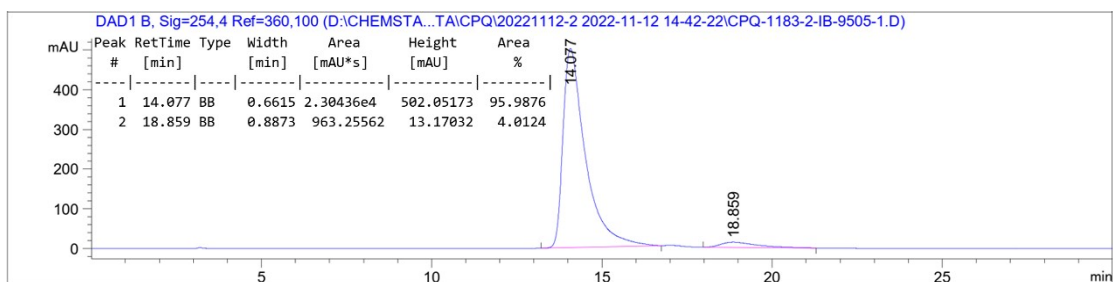
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>BrCl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 692.0331, found: 692.0338.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 14.08 min, *t<sub>R</sub>* (minor) = 18.86 min, ee = 92%.

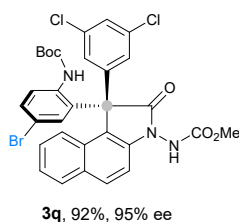
*Chiral HPLC spectrum of racemic 3p*



*Chiral HPLC spectrum of 3p*



**methyl (S)-1-(5-bromo-2-((tert-butoxycarbonyl)amino)phenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3q** was obtained in 92% yield and 95% ee as white solid.

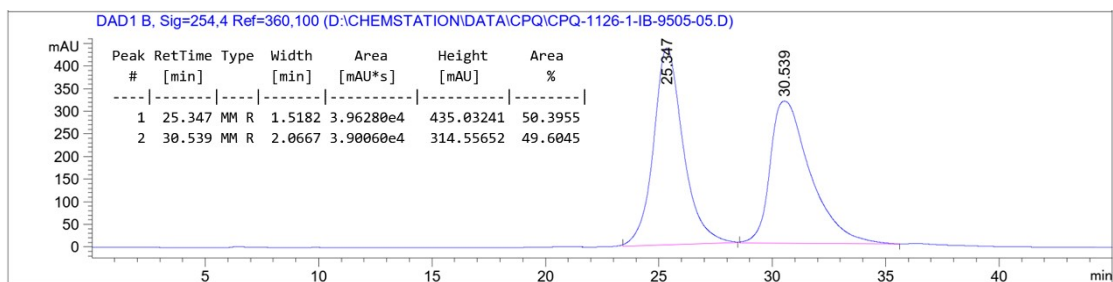
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.37 (s, 1H), 8.80 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.73-7.62 (m, 2H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.49-7.43 (m, 2H), 7.43-7.16 (m, 4H), 6.86 (s, 1H), 3.83 (s, 3H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.34, 155.16, 151.40, 140.97, 138.99, 137.15, 134.17, 132.09, 132.02, 130.92, 129.77, 128.65, 127.91, 127.76, 127.37, 125.34, 124.21, 121.51, 119.35, 116.26, 109.76, 79.18, 61.05, 52.82, 27.43.

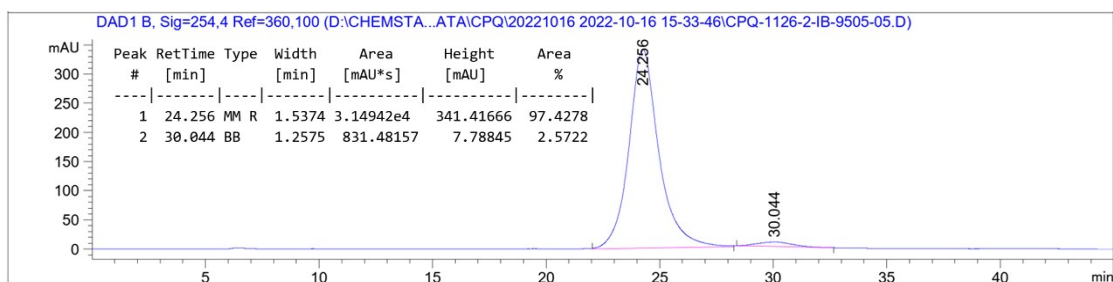
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>BrCl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, m/z: 692.0331, found: 692.0329.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, t<sub>R</sub> (major) = 24.26 min, t<sub>R</sub> (minor) = 30.04 min, ee = 95%.

Chiral HPLC spectrum of racemic **3q**

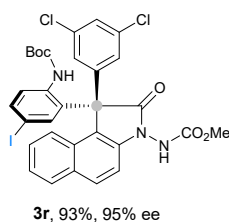


Chiral HPLC spectrum of **3q**





**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)-5-iodophenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3r** was obtained in 93% yield and 95% ee as white solid.

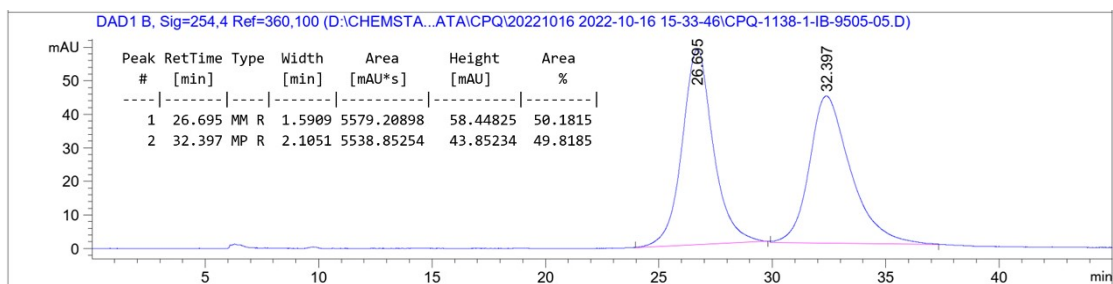
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.36 (s, 1H), 8.81 (s, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.58-7.17 (m, 8H), 7.05 (s, 1H), 3.84 (s, 3H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.39, 155.22, 151.35, 141.06, 138.92, 138.13, 137.95, 137.65, 134.15, 131.96, 130.89, 129.74, 128.71, 127.90, 127.68, 127.33, 125.29, 124.18, 121.52, 119.41, 109.74, 87.98, 79.15, 60.90, 52.81, 27.43.

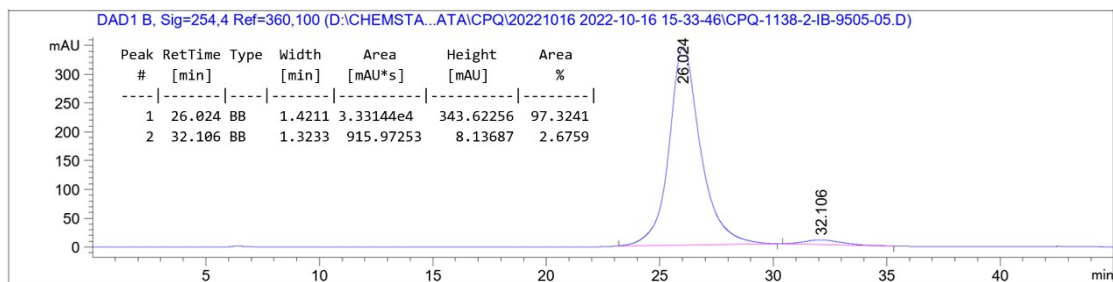
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>Cl<sub>2</sub>IN<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, m/z: 740.0192, found: 740.0182.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, t<sub>R</sub> (major) = 26.02 min, t<sub>R</sub> (minor) = 32.11 min, ee = 95%.

Chiral HPLC spectrum of racemic **3r**

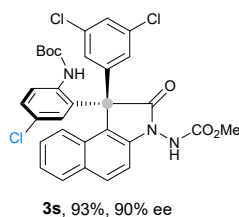


Chiral HPLC spectrum of **3r**





**methyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)-5-chlorophenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



According to general procedure, **3s** was obtained in 93% yield and 90% ee as white solid.

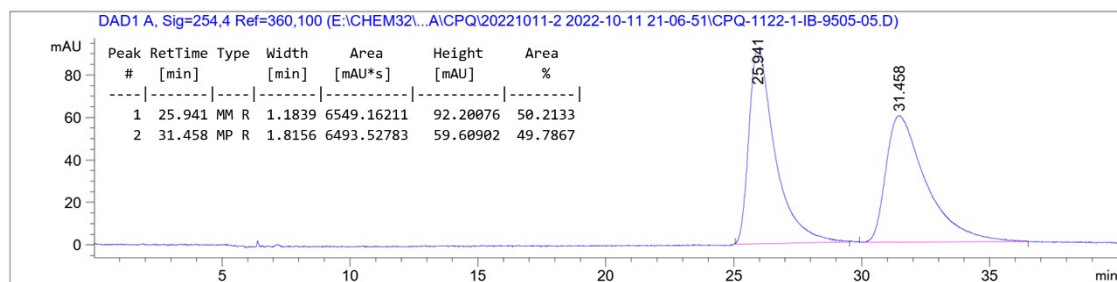
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.36 (s, 1H), 8.79 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.56-7.49 (m, 2H), 7.49-7.44 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.40-7.05 (m, 3H), 6.71 (s, 1H), 3.83 (s, 3H), 1.32 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.35, 155.20, 151.45, 140.95, 139.00, 136.70, 134.16, 132.02, 130.92, 129.78, 129.14, 128.40, 128.34, 127.92, 127.79, 127.37, 125.36, 124.21, 121.52, 119.35, 109.77, 79.15, 61.09, 52.82, 27.43.

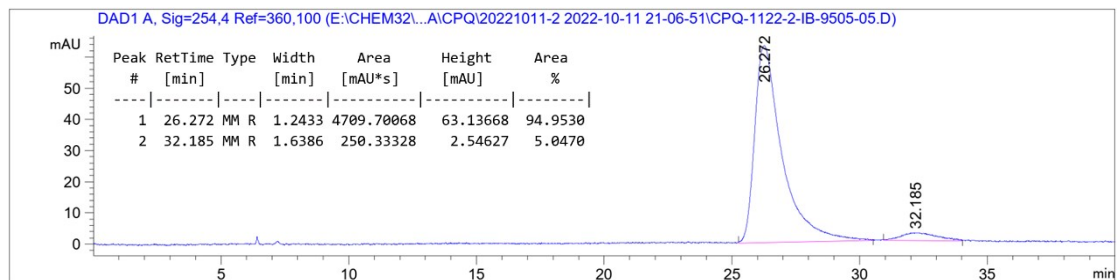
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>Cl<sub>3</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 648.0836, found: 648.0829.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 26.27 min, *t<sub>R</sub>* (minor) = 32.19 min, ee = 90%.

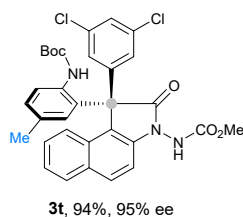
*Chiral HPLC spectrum of racemic 3s*



*Chiral HPLC spectrum of 3s*



**methyl (S)-1-(2-((tert-butoxycarbonyl)amino)-5-methylphenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3t** was obtained in 94% yield and 95% ee as white solid.

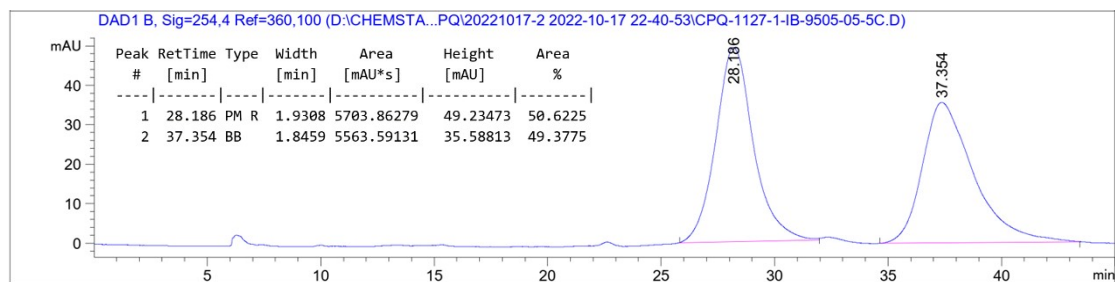
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.34 (s, 1H), 8.69 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.46-7.14 (m, 7H), 6.58 (s, 1H), 3.83 (s, 3H), 1.99 (s, 3H), 1.31 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.84, 151.75, 141.94, 138.86, 135.08, 133.97, 133.41, 131.57, 130.87, 129.96, 129.67, 129.62, 128.25, 127.33, 127.05, 126.97, 125.42, 123.99, 121.78, 120.25, 109.67, 78.55, 61.39, 52.75, 27.50, 19.97.

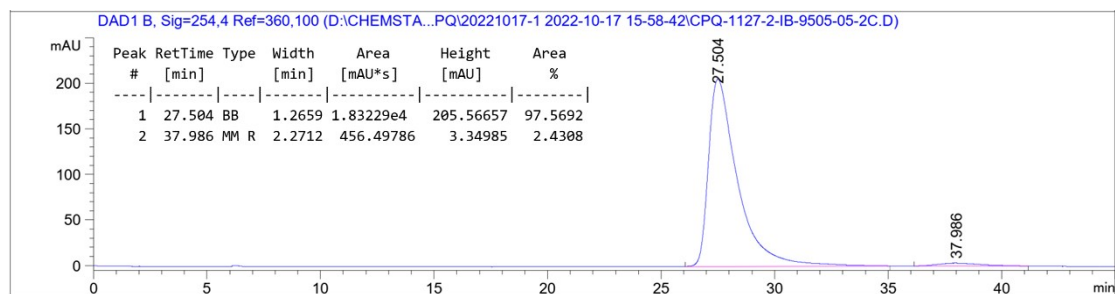
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 628.1382, found: 628.1376.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 27.50 min, *t*<sub>R</sub> (minor) = 37.99 min, ee = 95%.

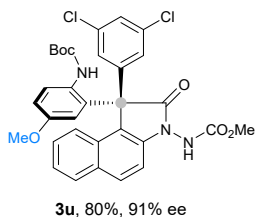
*Chiral HPLC spectrum of racemic 3t*



*Chiral HPLC spectrum of 3t*



**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)-5-methoxyphenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3u** was obtained in 80% yield and 91% ee as white solid.

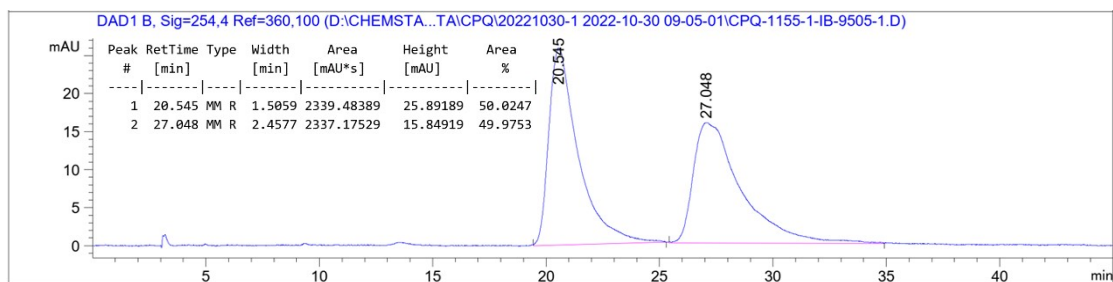
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.35 (s, 1H), 8.55 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.46-7.16 (m, 6H), 7.06 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.29 (s, 1H), 3.83 (s, 3H), 3.45 (s, 3H), 1.30 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 177.52, 155.82, 155.27, 151.98, 141.69, 138.90, 134.01, 131.68, 130.87, 130.44, 129.66, 128.67, 128.19, 127.46, 127.13, 125.52, 125.50, 124.03, 121.85, 120.07, 116.14, 113.85, 109.69, 78.45, 61.35, 54.79, 52.78, 27.53.

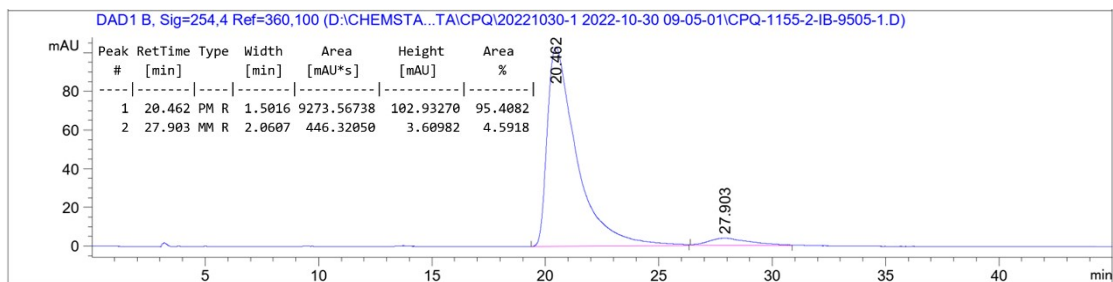
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>6</sub><sup>+</sup>, *m/z*: 644.1331, found: 644.1326.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 20.46 min, *t*<sub>R</sub> (minor) = 27.90 min, ee = 91%.

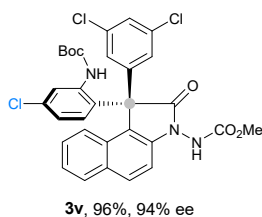
*Chiral HPLC spectrum of racemic 3u*



*Chiral HPLC spectrum of 3u*



**methyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)-4-chlorophenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



According to general procedure, **3v** was obtained in 96% yield and 94% ee as white solid.

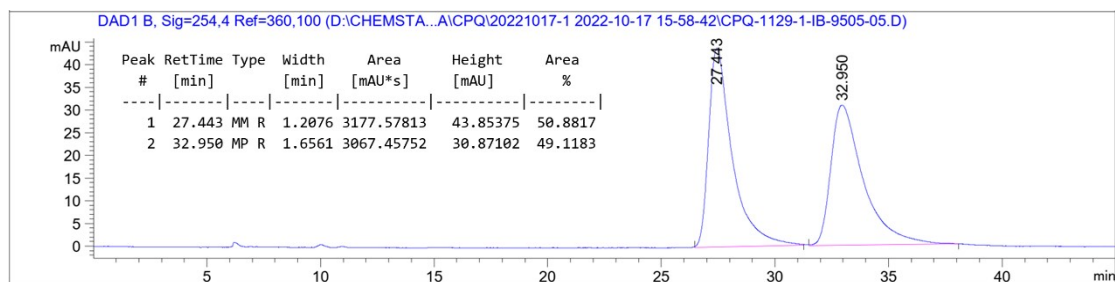
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 10.39 (s, 1H), 8.90 (s, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.76 (s, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.47-7.15 (m, 6H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 3H), 1.33 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)** δ 177.63, 155.18, 151.38, 141.21, 138.98, 138.96, 134.14, 133.69, 131.83, 131.21, 130.98, 129.67, 128.11, 127.70, 127.31, 125.86, 125.43, 124.12, 121.74, 119.73, 109.71, 79.36, 61.01, 52.80, 27.42.

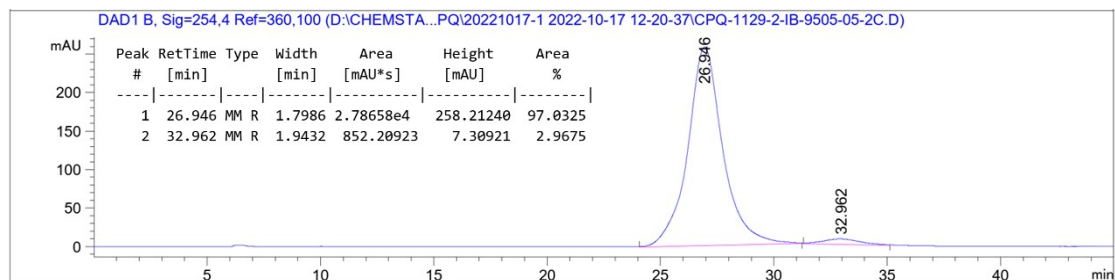
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>26</sub>Cl<sub>3</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 648.0836, found: 648.0836.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 0.5 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 26.95 min, *t<sub>R</sub>* (minor) = 32.96 min, ee = 94%.

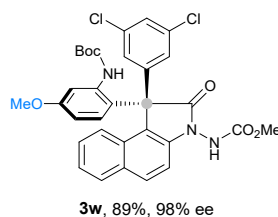
*Chiral HPLC spectrum of racemic 3v*



*Chiral HPLC spectrum of 3v*



**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)-4-methoxyphenyl)-1-(3,5-dichlorophenyl)-2-oxo-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



According to general procedure, **3w** was obtained in 89% yield and 98% ee as white solid.

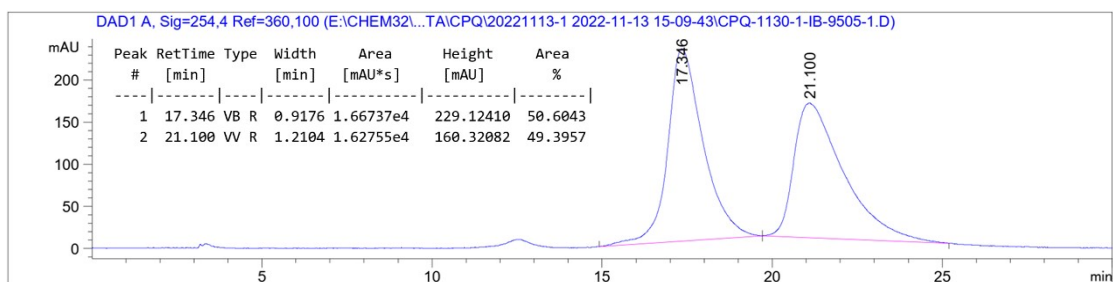
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.37 (s, 1H), 8.84 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.46-7.14 (m, 7H), 6.72-6.54 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 1.33 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 178.20, 159.71, 151.55, 142.06, 138.85, 133.98, 131.52, 130.90, 130.61, 129.60, 128.28, 127.44, 127.04, 125.55, 123.96, 121.80, 120.45, 112.15, 109.69, 109.66, 78.83, 60.83, 54.98, 52.74, 27.51.

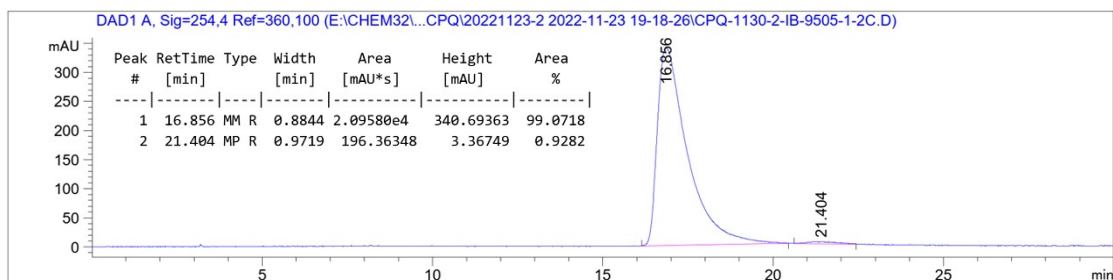
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>6</sub><sup>+</sup>, *m/z*: 644.1331, found: 644.1328.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 16.86 min, *t*<sub>R</sub> (minor) = 21.40 min, ee = 98%.

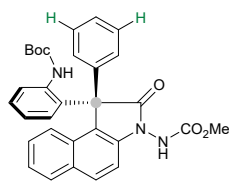
Chiral HPLC spectrum of racemic **3w**



Chiral HPLC spectrum of **3w**



**methyl (S)-(1-(2-((tert-butoxycarbonyl)amino)phenyl)-2-oxo-1-phenyl-1,2-dihydro-3H-benzo[e]indol-3-yl)carbamate**



**3x**, 91%, 78% ee

According to general procedure, **3x** was obtained in 91% yield and 78% ee as white solid.

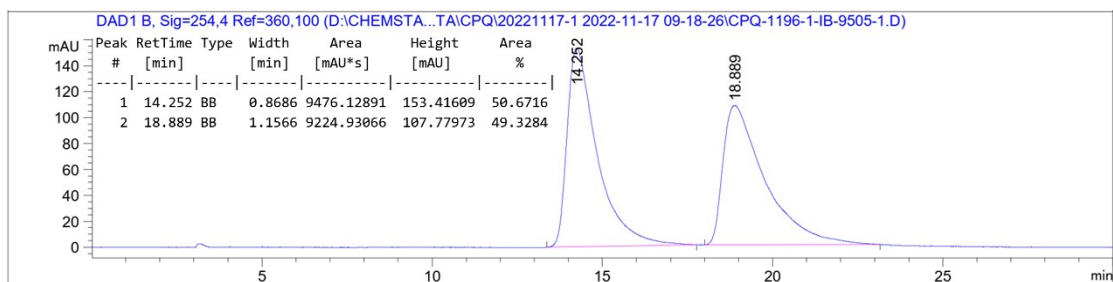
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.29 (s, 1H), 8.77 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.49-7.18 (m, 10H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 3.81 (s, 3H), 1.27 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 178.89, 155.29, 151.83, 138.74, 138.08, 137.44, 130.78, 130.76, 129.57, 129.28, 128.65, 128.48, 128.01, 126.90, 126.87, 126.19, 123.69, 123.63, 122.43, 121.71, 109.52, 78.33, 61.95, 52.60, 27.59.

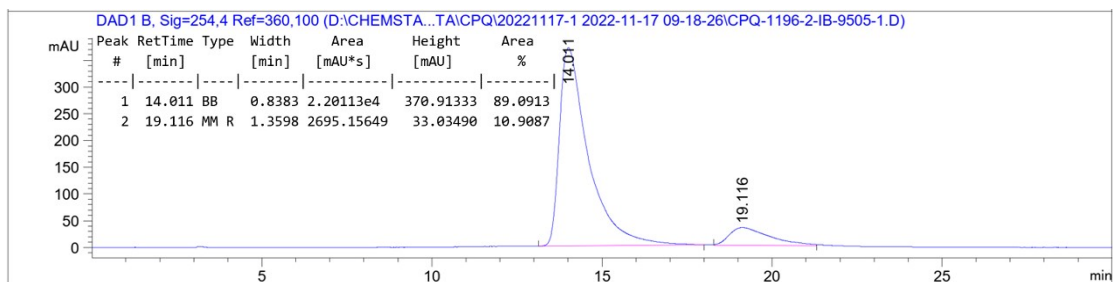
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 546.2005, found: 546.2001.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 14.01 min, *t*<sub>R</sub> (minor) = 19.12 min, ee = 78%.

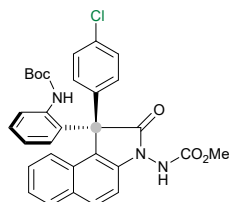
Chiral HPLC spectrum of racemic **3x**



Chiral HPLC spectrum of **3x**



**methyl (*S*)-1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-chlorophenyl)-2-oxo-1,2-dihydro-3*H*-benzo[*e*]indol-3-yl)carbamate**



**3y**, 83%, 81% ee

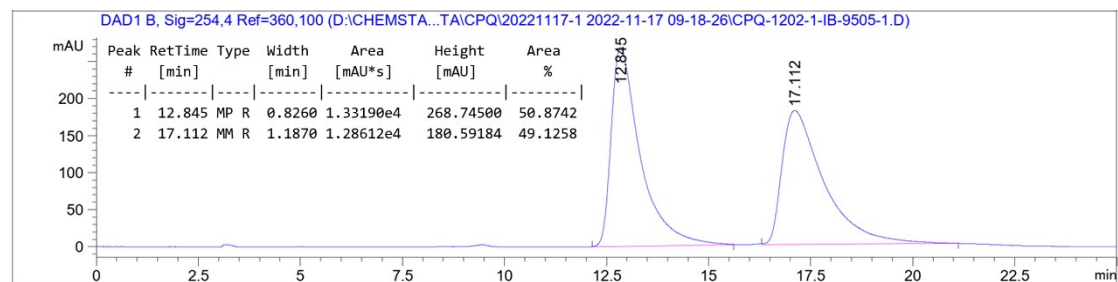
According to general procedure, **3y** was obtained in 83% yield and 81% ee as white solid. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 100 °C) δ 10.20 (s, 1H), 8.66 (s, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.43-7.38 (m, 2H), 7.38-7.28 (m, 6H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 1.30 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 100 °C) δ 178.29, 155.11, 151.69, 138.73, 137.80, 136.55, 131.69, 130.88, 130.74, 129.35, 129.24, 128.62, 128.52, 128.44, 127.91, 126.95, 126.38, 123.78, 123.62, 122.14, 120.98, 109.43, 78.39, 61.37, 52.48, 27.42.

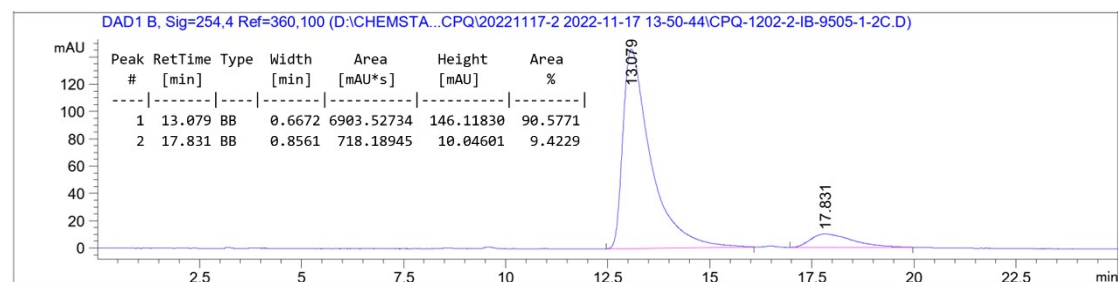
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>28</sub>ClN<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 580.1615, found:580.1609.

HPLC analysis: HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 13.08 min, *t*<sub>R</sub> (minor) = 17.83 min, ee = 81%.

*Chiral HPLC spectrum of racemic 3y*

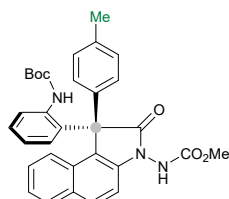


*Chiral HPLC spectrum of 3y*





**methyl (*S*)-(1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-2-oxo-1-(*p*-tolyl)-1,2-dihydro-3H-benzo[*e*]indol-3-yl)carbamate**



**3z**, 94%, 81% ee

According to general procedure, **3z** was obtained in 94% yield and 81% ee as white solid.

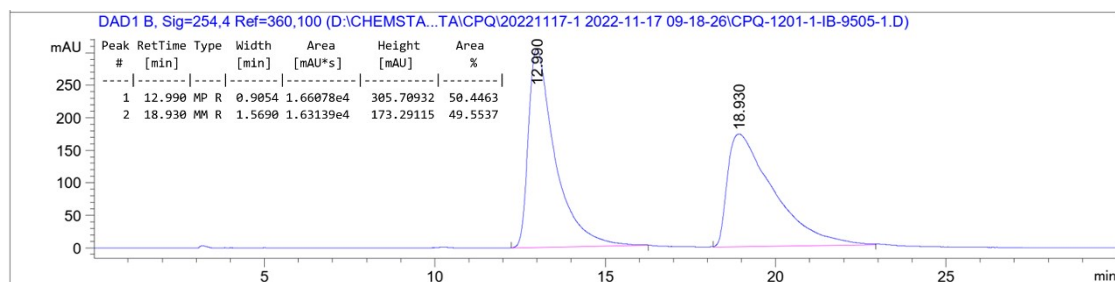
<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 10.26 (s, 1H), 8.73 (s, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.35-7.28 (m, 2H), 7.23 (s, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.77 (s, 1H), 3.80 (s, 3H), 2.22 (s, 3H), 1.26 (s, 9H).

<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C) δ 178.87, 155.27, 151.85, 138.71, 138.05, 136.06, 134.51, 130.77, 130.63, 129.51, 129.26, 128.65, 128.60, 128.39, 126.83, 126.77, 126.24, 123.64, 123.59, 122.55, 121.75, 109.50, 78.24, 61.65, 52.57, 27.52, 19.98.

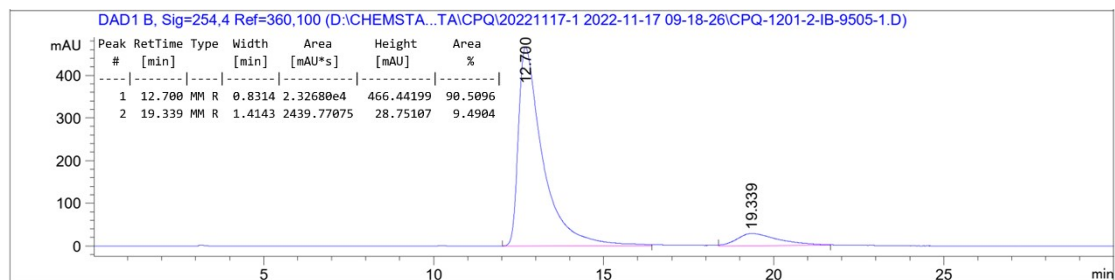
HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>31</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 560.2161, found:560.2154.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t*<sub>R</sub> (major) = 12.70 min, *t*<sub>R</sub> (minor) = 19.34 min, ee = 81%.

*Chiral HPLC spectrum of racemic 3z*



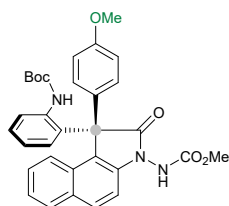
*Chiral HPLC spectrum of 3z*



**methyl (*S*)-(1-(2-((*tert*-butoxycarbonyl)amino)phenyl)-1-(4-methoxyphenyl)-2-oxo-1,2-**



## dihydro-3H-benzo[e]indol-3-yl)carbamate



**3aa**, 93%, 81% ee

According to general procedure, **3aa** was obtained in 93% yield and 81% ee as white solid.

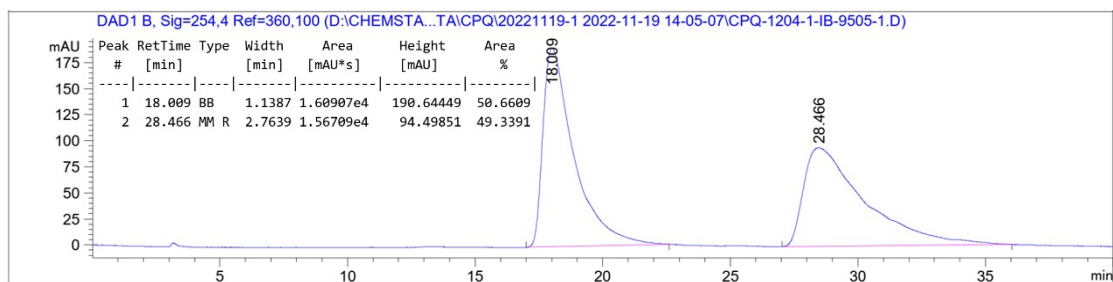
**<sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>, 100 °C)** δ 10.15 (s, 1H), 8.64 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 2H), 7.37 (td, *J* = 7.7, 1.6 Hz, 1H), 7.35-7.22 (m, 4H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 1.28 (s, 9H).

**<sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>, 100 °C)** δ 178.71, 158.07, 155.19, 151.80, 138.64, 138.02, 130.72, 130.41, 129.41, 129.25, 129.13, 128.68, 128.22, 128.16, 126.67, 126.01, 123.47, 123.45, 122.45, 121.83, 113.59, 109.38, 78.23, 61.24, 54.64, 52.43, 27.49.

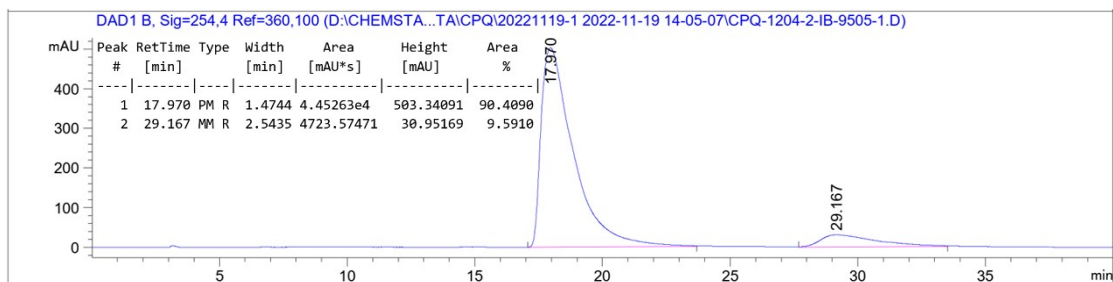
**HRMS (ESI)** calcd for [M+Na]<sup>+</sup> C<sub>32</sub>H<sub>31</sub>N<sub>3</sub>NaO<sub>6</sub><sup>+</sup>, *m/z*: 576.2111, found:576.2103.

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, *t<sub>R</sub>* (major) = 17.97 min, *t<sub>R</sub>* (minor) = 29.17 min, ee = 81%.

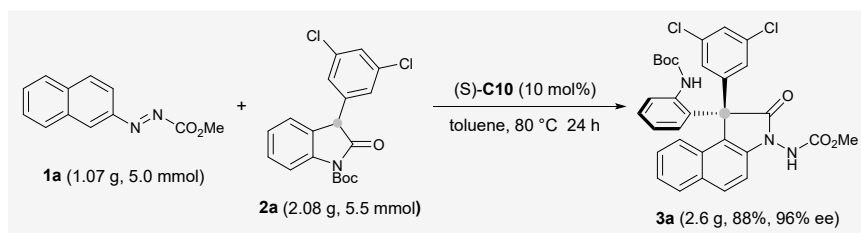
### Chiral HPLC spectrum of racemic **3aa**



### Chiral HPLC spectrum of **3aa**



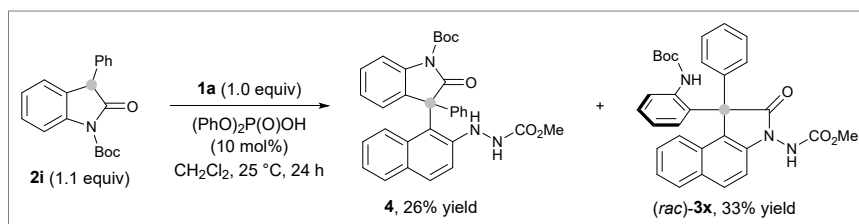
## 6. Gram-scale synthesis for **3a**



To a dry Schlenk tube (250 mL) was added azonaphthalene derivative **1a** (1.07 g, 5.0 mmol), oxindole derivative **2a** (2.08 g, 5.5 mmol, 1.1 equiv.) and (*S*)-**C10** (10 mol%) in anhydrous toluene (100 mL) at room temperature under argon atmosphere. The reaction was stirred at 80 °C for 24 h and the resulted mixture was directly purified by flash chromatography on silica gel to afford the products **3a** (2.6 g, 88% yield, 96% ee).

## 7. Mechanistic investigations

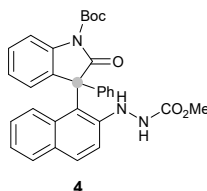
### The trap of key intermediate 4



To a dry Schlenk tube (25 mL) was added azonaphthalene derivative **1a** (1.5 mmol, 1.0 equiv.), oxindole derivative **2a** (1.65 mmol, 1.1 equiv.) and (PhO)<sub>2</sub>P(O)OH (10 mol%) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at 25 °C under argon atmosphere. The reaction was stirred at this temperature for 24 h. The resulted mixture was directly purified by quickly flash chromatography on silica gel to afford intermediate **4** (0.39 mmol, 26% yield), *(rac)*-**3x** (0.5 mmol, 33% yield) and recycled raw material **1a** (0.42 mmol, 28% yield).

Due to the instability of intermediate **4**, <sup>1</sup>H NMR and <sup>13</sup>C NMR was collected at room temperature.

#### *tert*-butyl 3-(2-(2-(methoxycarbonyl)hydrazinyl)naphthalen-1-yl)-2-oxo-3-phenylindoline-1-carboxylate

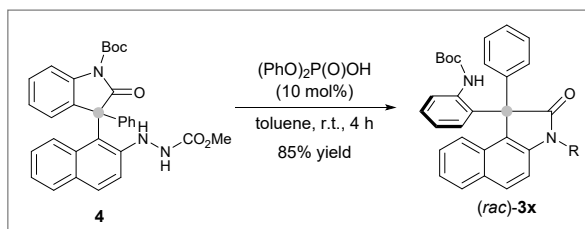


<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.72 (s, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.74-7.65 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.45-7.35 (m, 4H), 7.27-7.19 (m, 2H), 7.18-7.08 (m, 3H), 7.07-6.99 (m, 1H), 3.42 (s, 3H), 1.56 (s, 9H).

<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 172.02, 157.29, 156.59, 148.73, 146.19, 139.14, 134.16, 133.43, 129.56, 128.85, 128.65, 128.42, 128.20, 127.98, 127.88, 127.57, 126.31, 126.15, 124.85, 124.66, 122.45, 115.20, 114.65, 105.13, 84.17, 72.01, 53.56, 27.65.

HRMS (ESI) calcd for [M+Na]<sup>+</sup> C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>NaO<sub>5</sub><sup>+</sup>, *m/z*: 546.2005, found:546.1988.

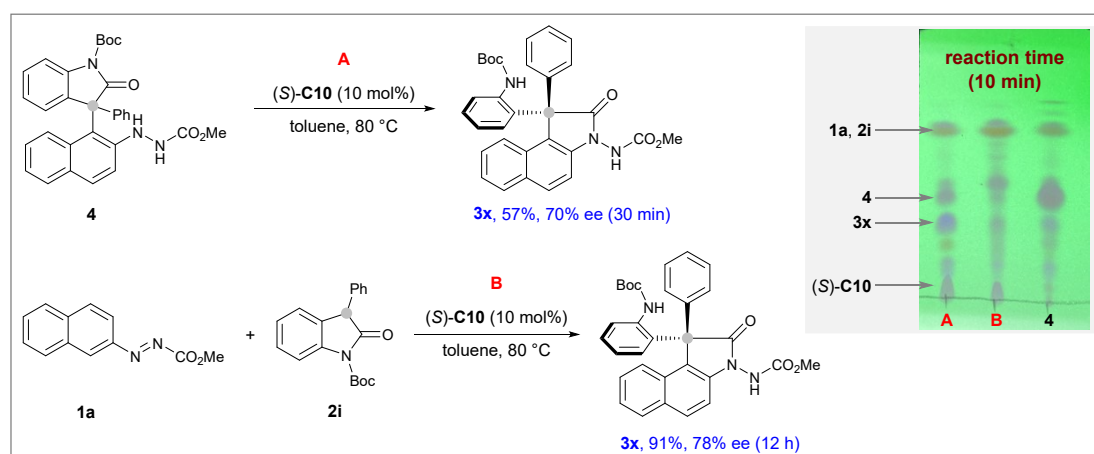
## The conversion of racemic intermediate to product catalyzed by $(\text{PhO})_2\text{P}(\text{O})\text{OH}$



To a dry Schlenk tube (10 mL) was added compound **4** (0.05 mmol) and  $(\text{PhO})_2\text{P}(\text{O})\text{OH}$  (10 mol%) in anhydrous toluene (1 mL) at room temperature under argon atmosphere. The reaction was stirred at this temperature for 4 h. The resulted mixture was directly purified by quickly flash chromatography on silica gel to afford product (*rac*)-**3x** (22 mg, 85% yield).

## The verification experiment of rate-determining step

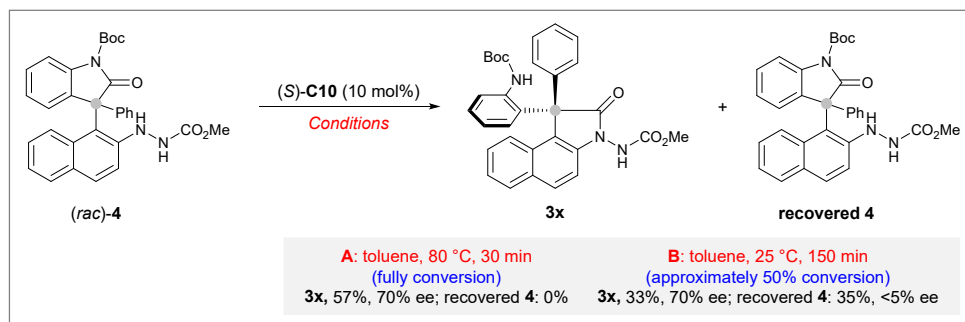
By subjecting intermediate **4** to standard conditions at 80 °C, a quick conversion to **3x** that completed in 30 min was seen. However, about 12 h were required for fully conversion of the reaction between **1a** and **2i** under same set of conditions. Meanwhile, TLC analysis (10 min) revealed that more than 50% of **4** was converted to the desired product **3x**, while only small amount of **3x** and trace amount of intermediate **4** for the reaction of **1a** and **2i** within the same time span (10 min). These observations suggested facile conversion of intermediate **4** under standard conditions and that the initial addition-coupling step is likely to be rate-determining.



For reaction conducted at room temperature (about 25 °C), intermediate **4** would be more easily detected on TLC, which means that the transamidation could be slowed down at lower temperature. Accordingly, the arylation intermediate trapping experiment was conducted at 25 °C. In addition,

the study was conducted with **1a** and **2i** but not the model substrates (**1a** and **2a**) which showed high reactivity and hindered the interception of intermediate.

### The conversion of racemic intermediate to product catalyzed by (*S*)-C10



It was noted that the racemic intermediate **4** could be transformed to enantioenriched product **3x** in 57% yield with 70% ee under the standard conditions in about 30 min. This suggested that a secondary kinetic resolution could be in effect to enhance the product enantioselectivity. Furthermore, when this conversion was carried out at 25 °C and halted at approximately 50% (about 2.5 h) conversion, product **3x** was obtained in 33% yield with 70% ee along with the recovery of **4** in 35% yield. However, less than 5% ee was observed for the recovered **4**. This may be due to the instability of this intermediate and the unfavored enantiomer of compound **4** was decomposed rapidly under this set of reaction conditions. These results supported that the transformation of **4** to **3x** is a kinetic resolution process.

### Synthetic procedure for the fully conversion of **4** under (*S*)-C10 catalysis:

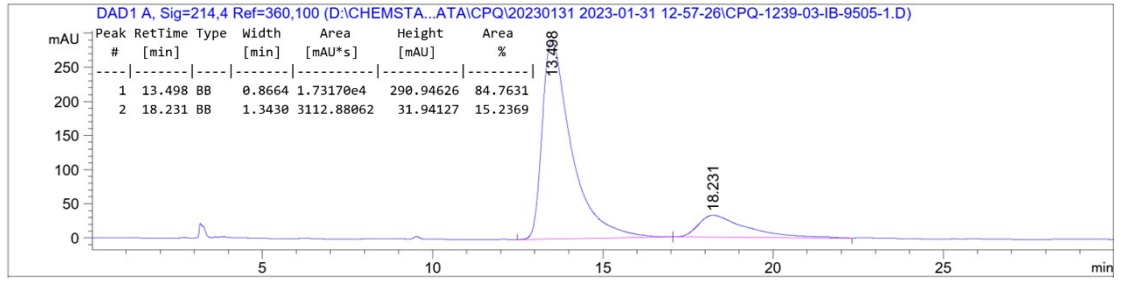
To a dry Schlenk tube (10 mL) was added intermediate **4** (0.05 mmol) and (*S*)-C10 (10 mol%) in anhydrous toluene (1 mL). Then the reaction was stirred at 80 °C under argon atmosphere for 30 min. The resulted mixture was directly purified by quickly flash chromatography on silica gel to afford product **3x** (22 mg, 57% yield, 70% ee).

**HPLC analysis:** HPLC DAICEL CHIRALPAK IB, hexane/isopropanol = 95/5, 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  (major) = 13.50 min,  $t_R$  (minor) = 18.23 min, ee = 70%.

*Chiral HPLC spectrum of racemic 3x*

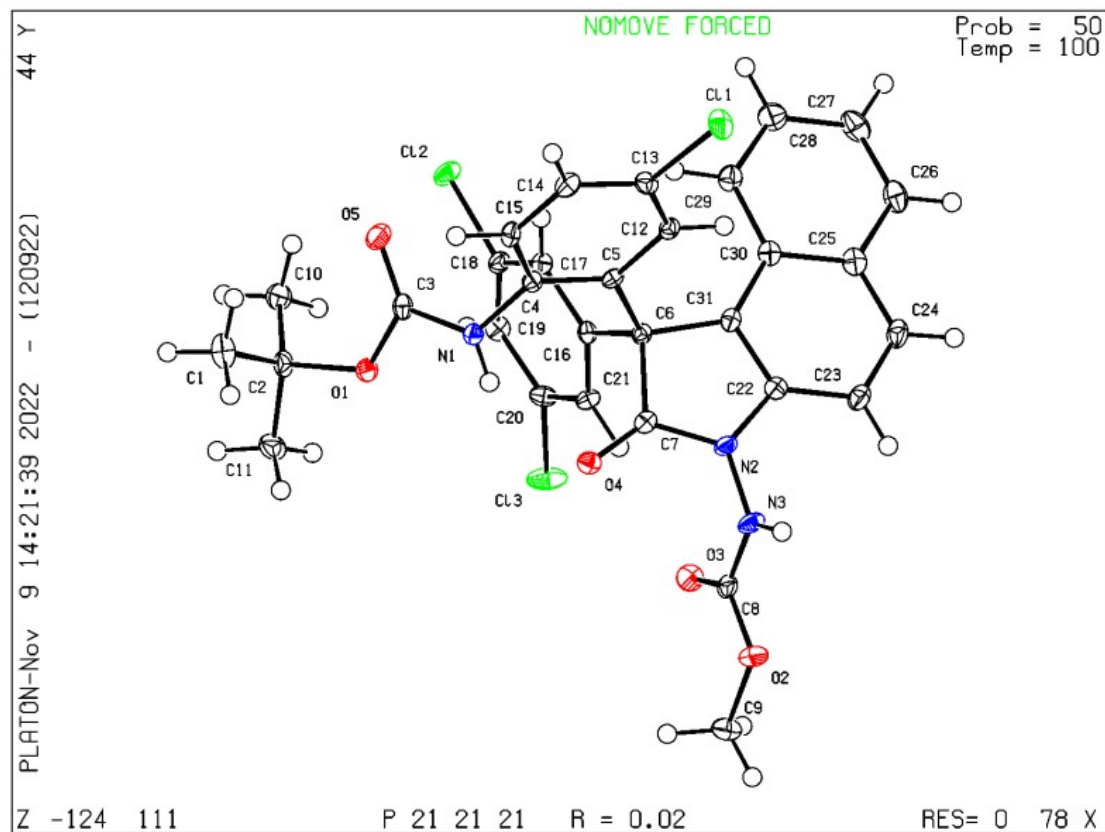


*Chiral HPLC spectrum of 3x*



## 8. Crystal data and structure refinement for 3s

Compound 3s: The crystal structure of compound 1aa has been deposited at the Cambridge Crystallographic Data Centre (CCDC: 2226208)



**Table S1 Crystal data and structure refinement for 111.**

Identification code	111
Empirical formula	C <sub>31</sub> H <sub>26</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>5</sub>
Formula weight	626.90
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	9.9368(2)
b/Å	17.0962(3)
c/Å	17.1478(3)
α/°	90
β/°	90

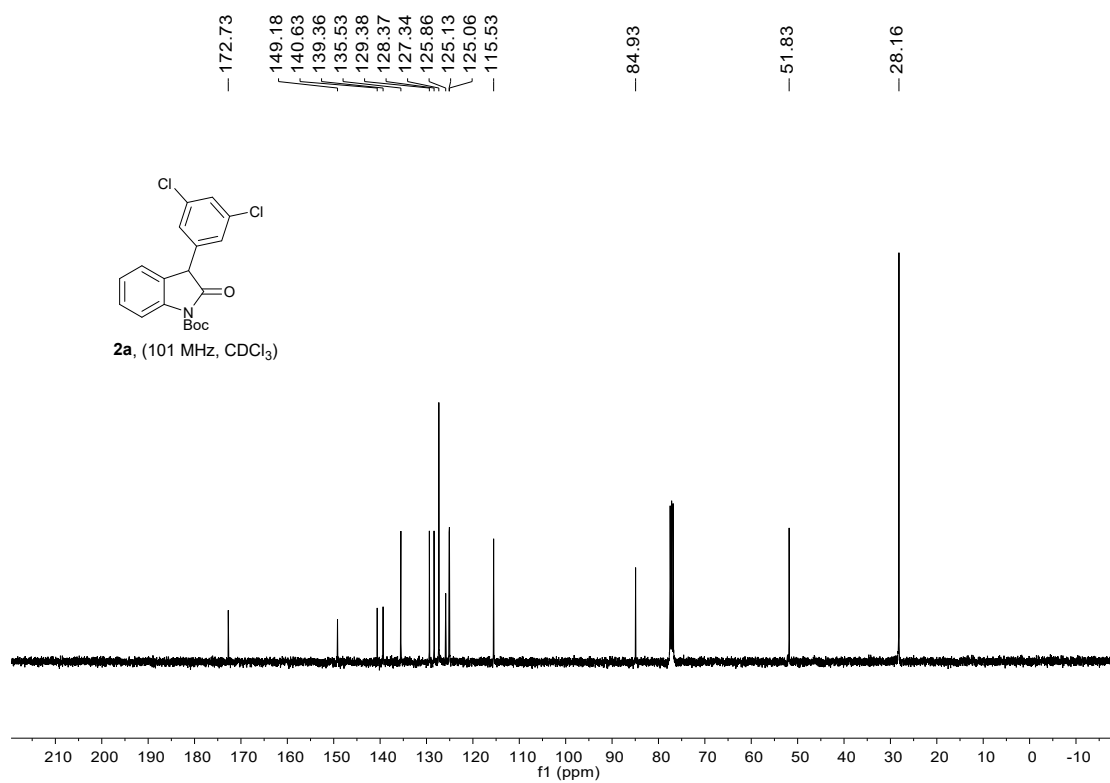
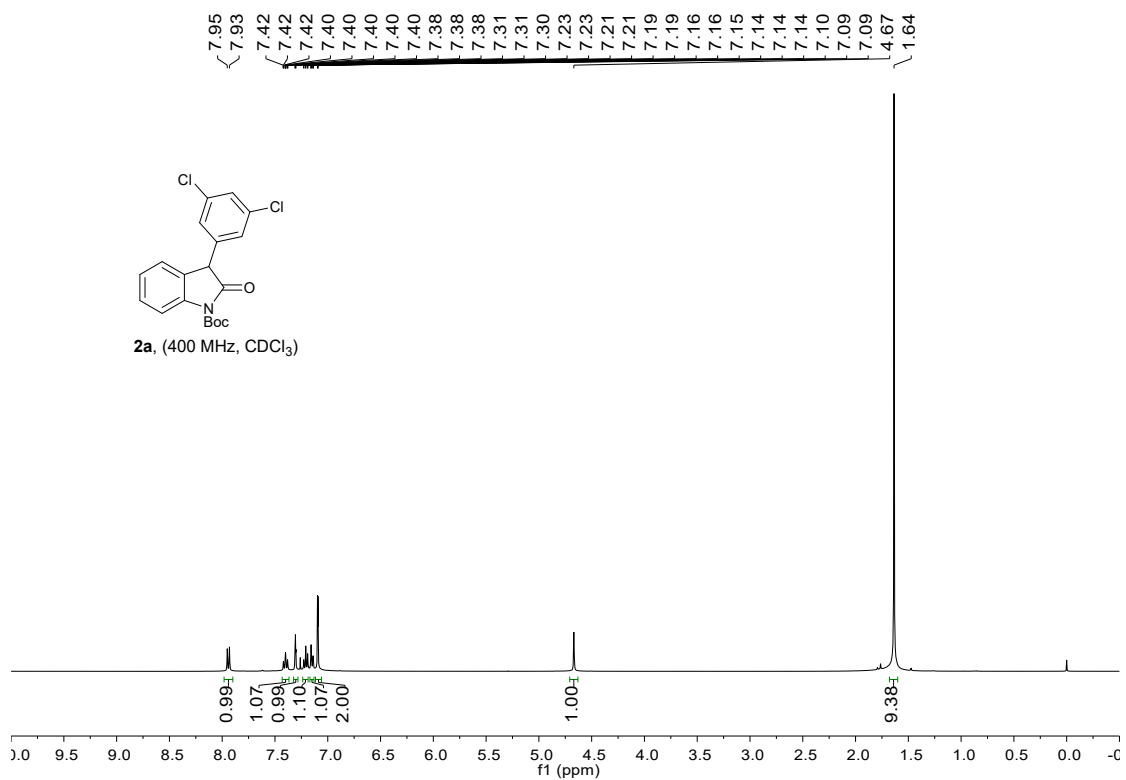
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2913.09(9)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.429
$\mu/\text{mm}^{-1}$	3.235
F(000)	1296.0
Crystal size/ $\text{mm}^3$	$0.2 \times 0.15 \times 0.1$
Radiation	CuK $\alpha$ ( $\lambda = 1.54178$ )
$2\Theta$ range for data collection/ $^\circ$	7.302 to 136.414
Index ranges	$-11 \leq h \leq 11, -20 \leq k \leq 20, -20 \leq l \leq 20$
Reflections collected	45400
Independent reflections	5328 [ $R_{\text{int}} = 0.0324, R_{\text{sigma}} = 0.0206$ ]
Data/restraints/parameters	5328/0/388
Goodness-of-fit on $F^2$	1.056
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0184, wR_2 = 0.0464$
Final R indexes [all data]	$R_1 = 0.0187, wR_2 = 0.0465$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.18/-0.17
Flack parameter	0.019(2)



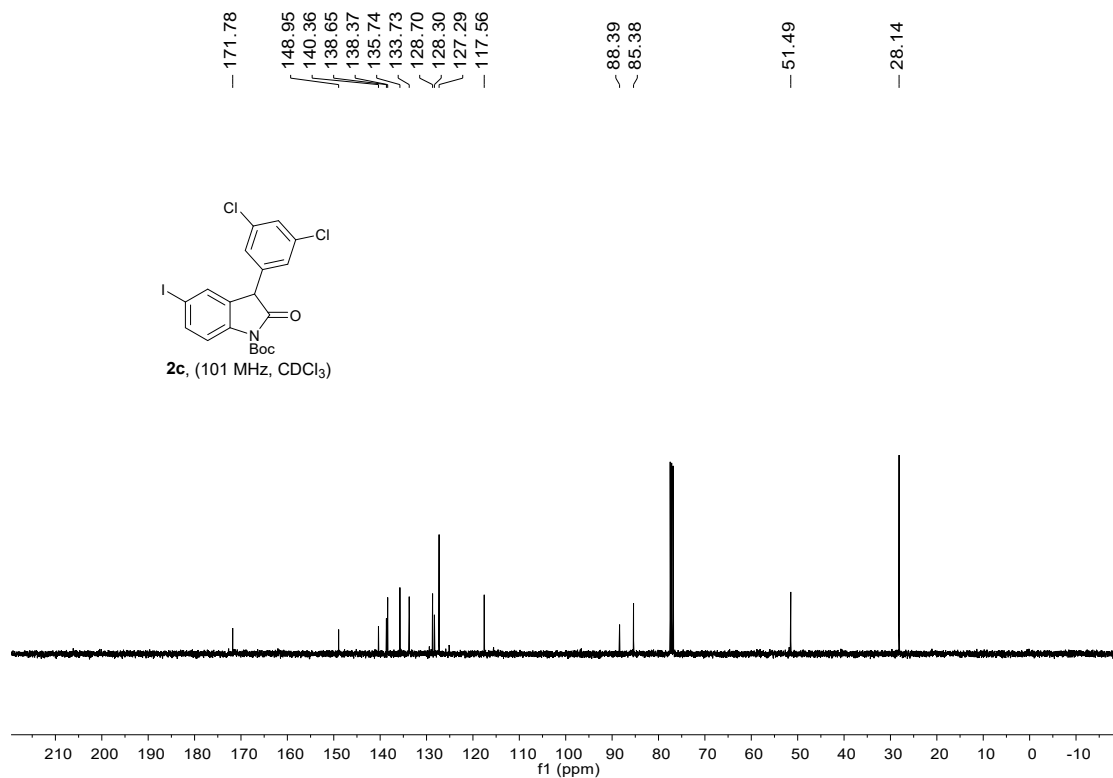
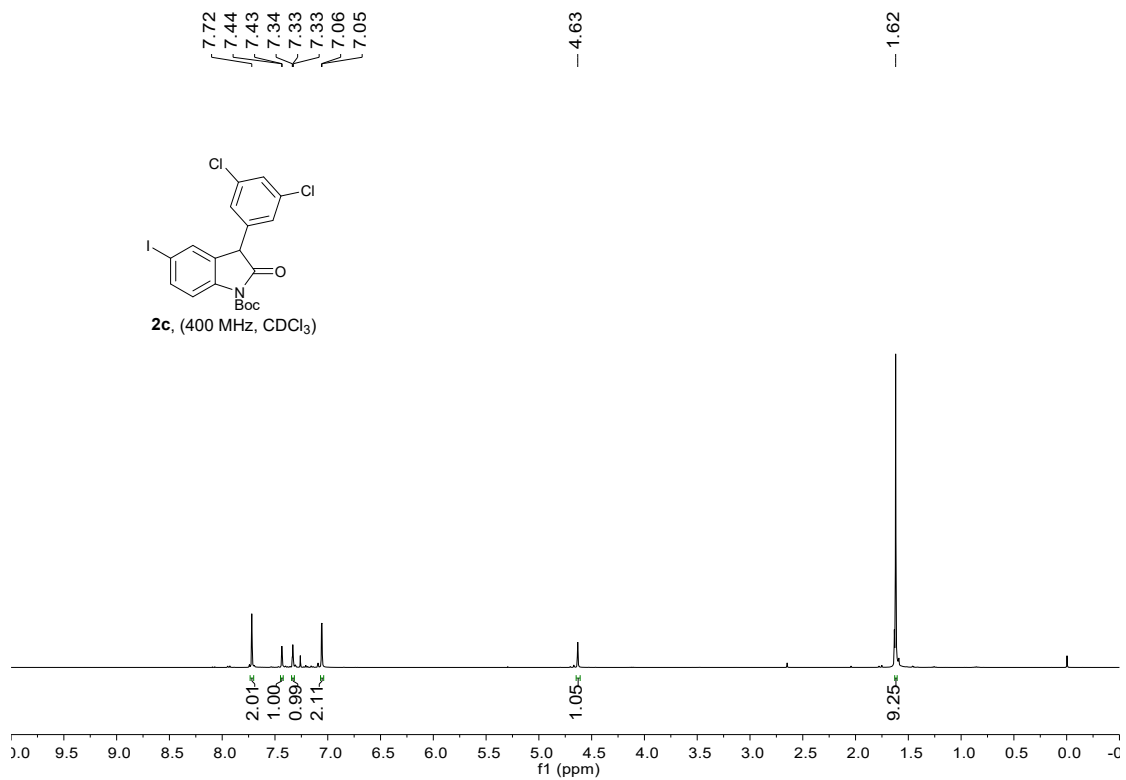
## 9. References

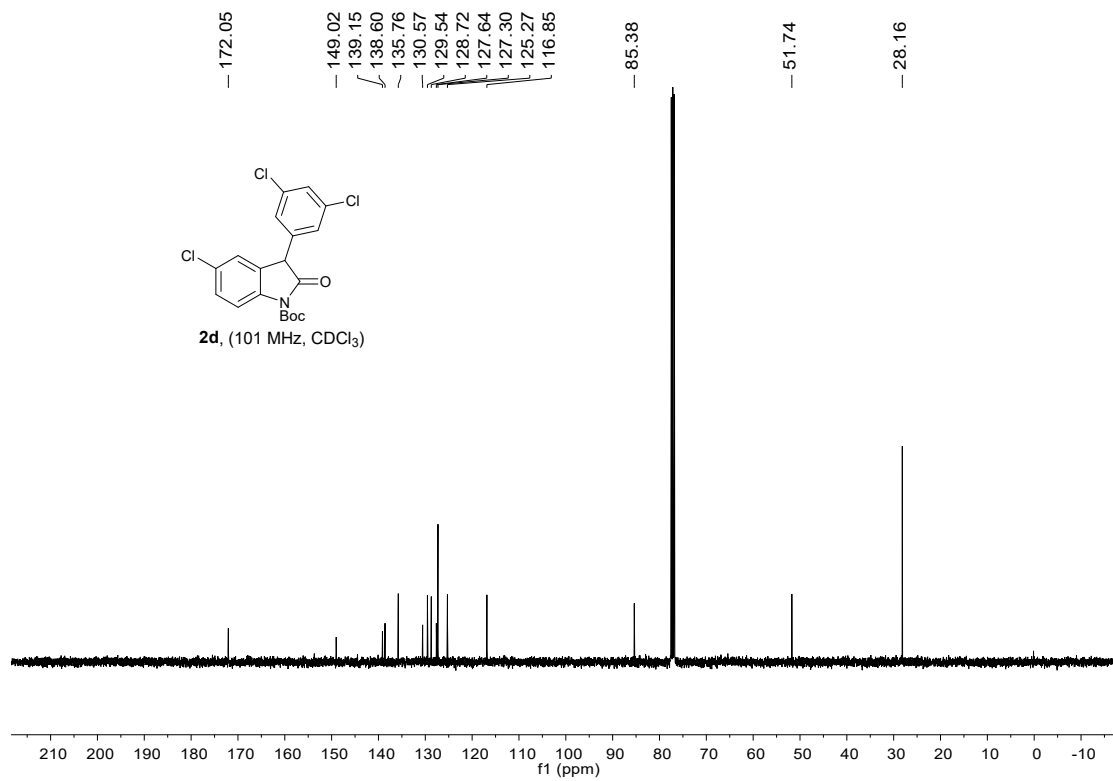
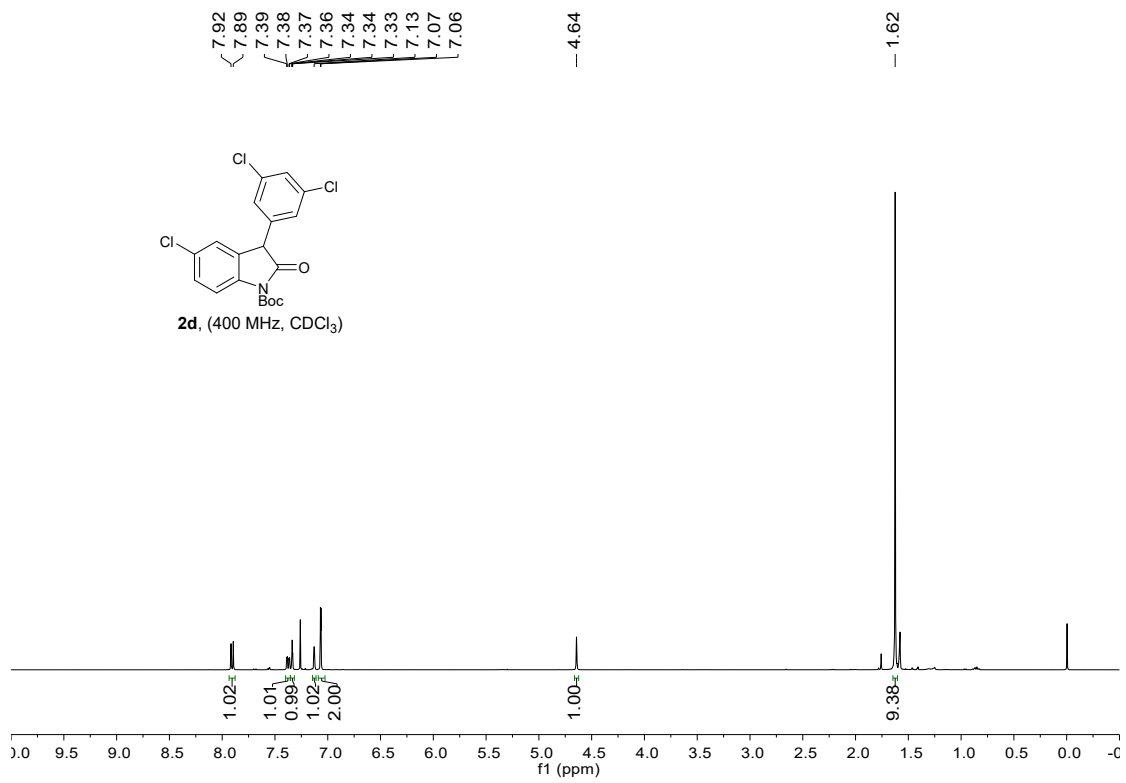
1. L.-W. Q, J.-H. Mao, J. Zhang and B. Tan, *Nat. Chem.* 2018, **10**, 58-64.
2. X.-L. Zhu, J.-H. Xu, D.-J. Cheng, L.-J. Zhao, X.-Y. Liu and B. Tan, *Org. Lett.* 2014, **16**, 2192-2195

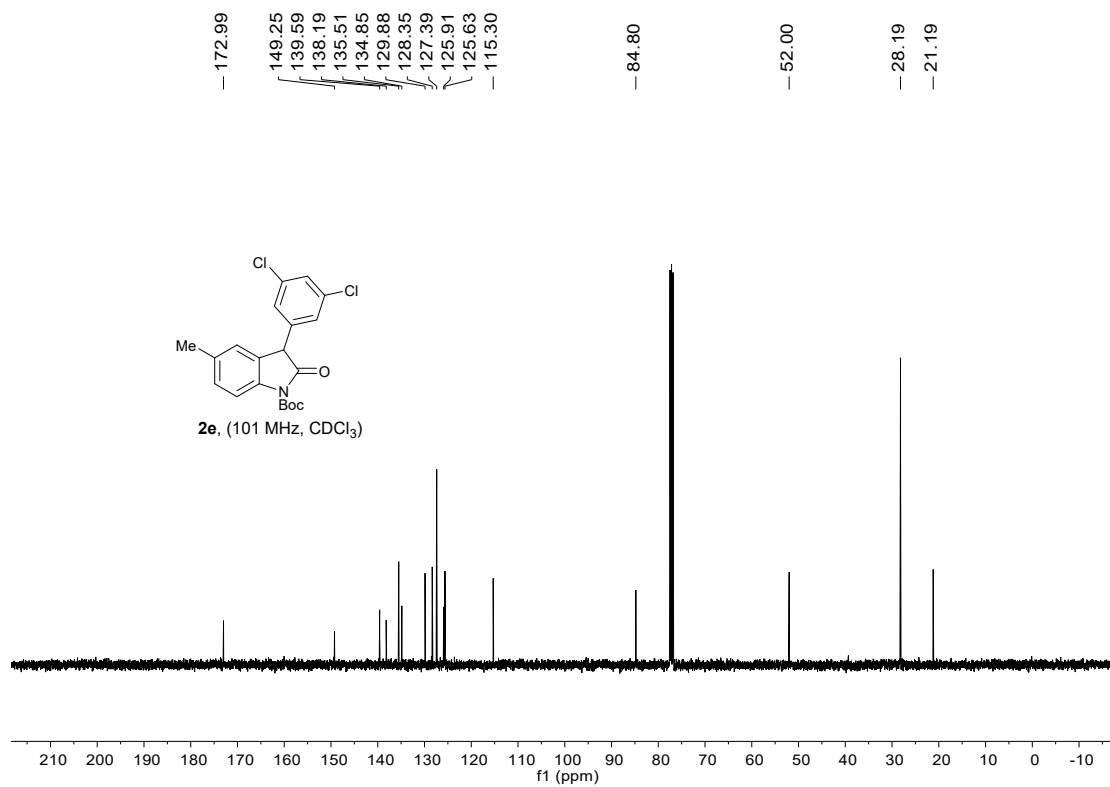
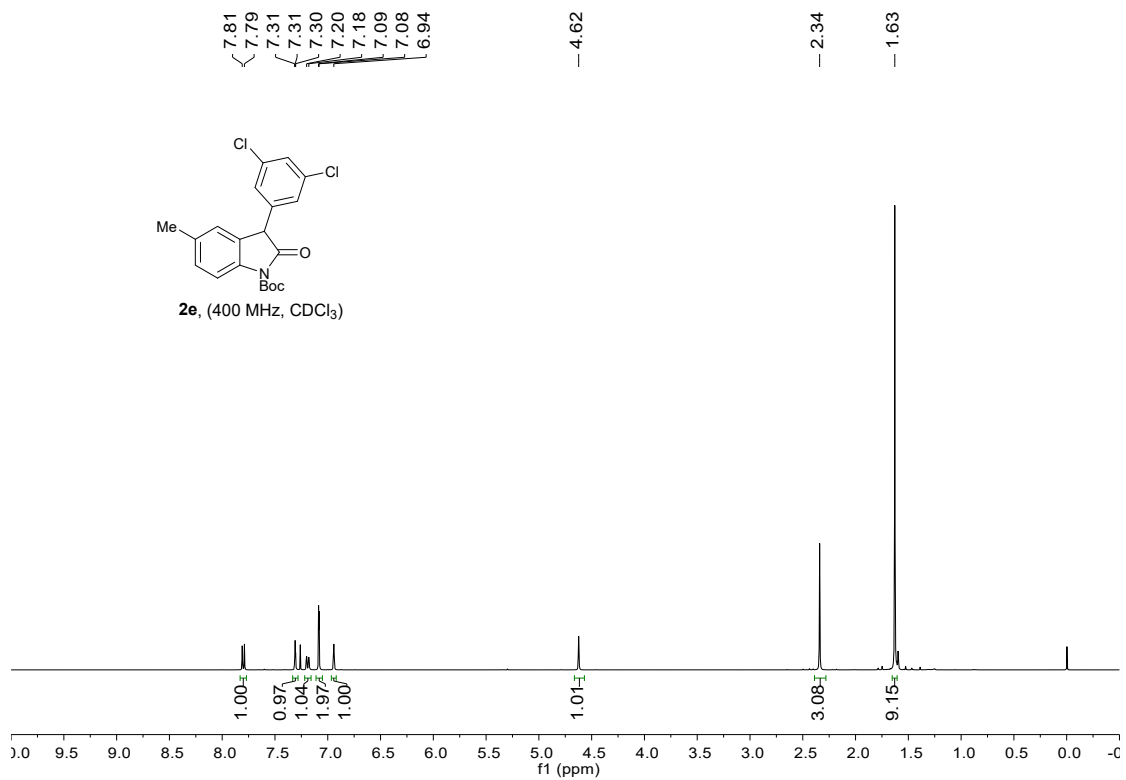
## 10. NMR spectra of new compounds

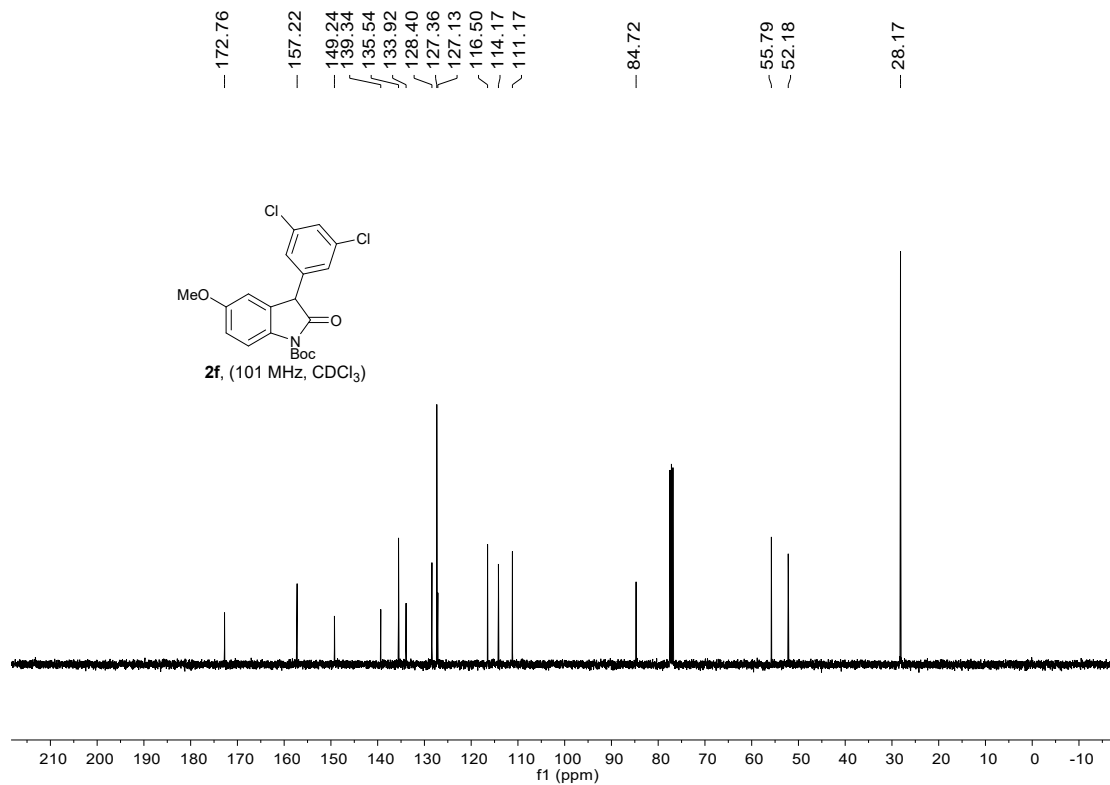
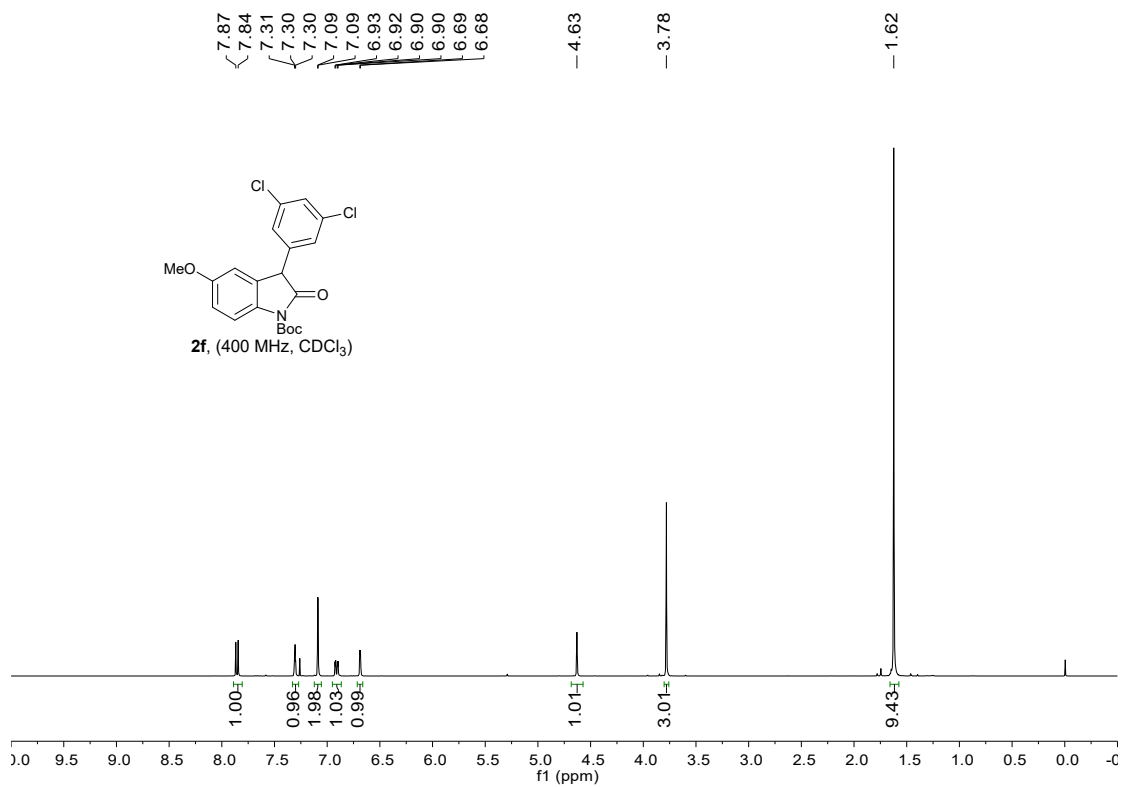


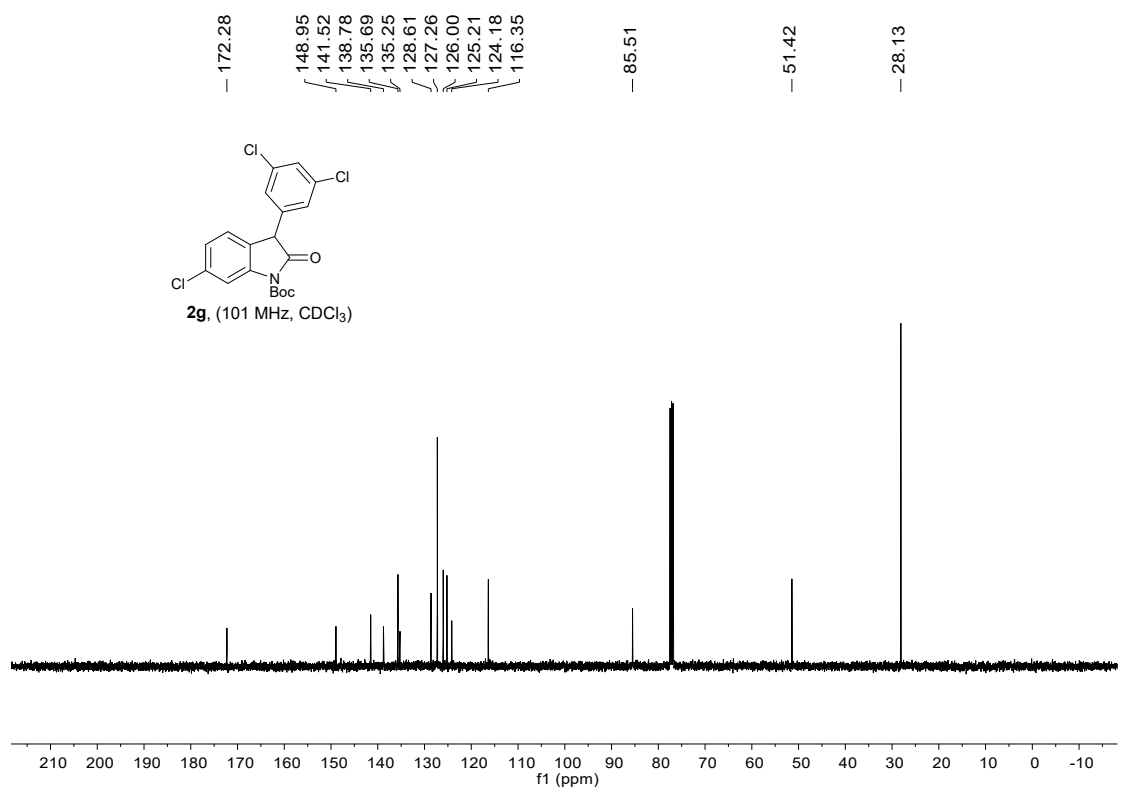
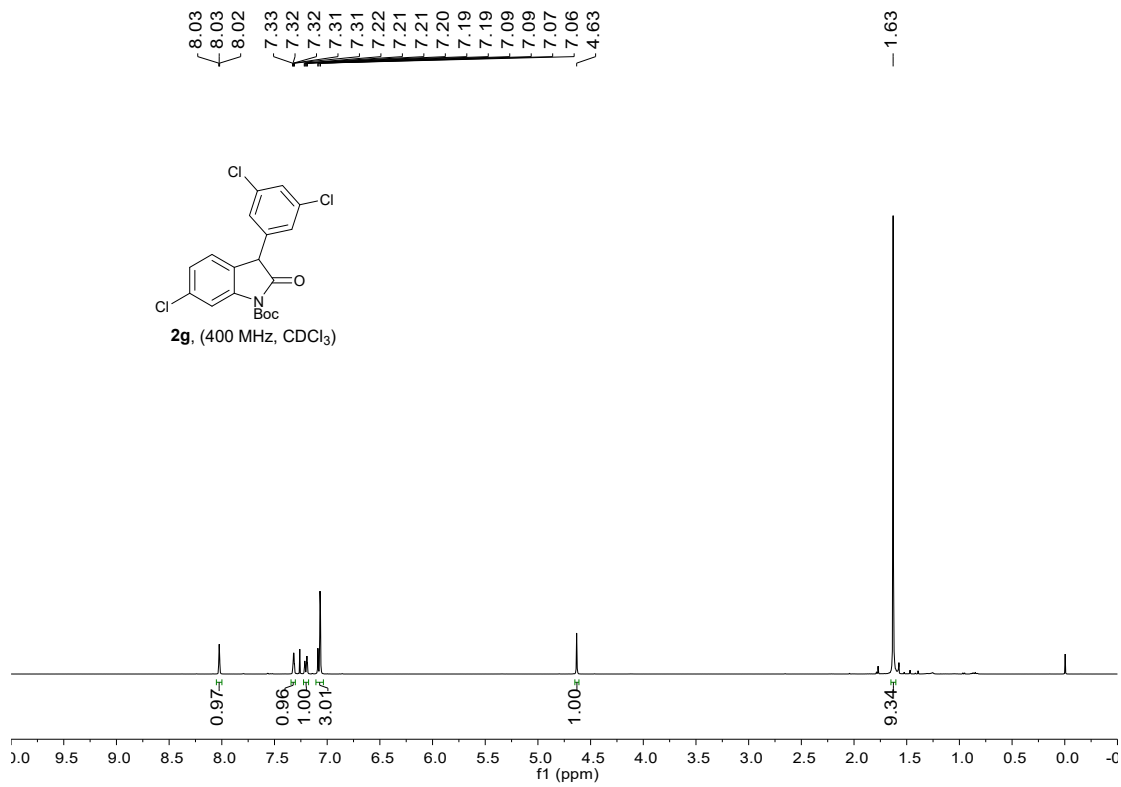






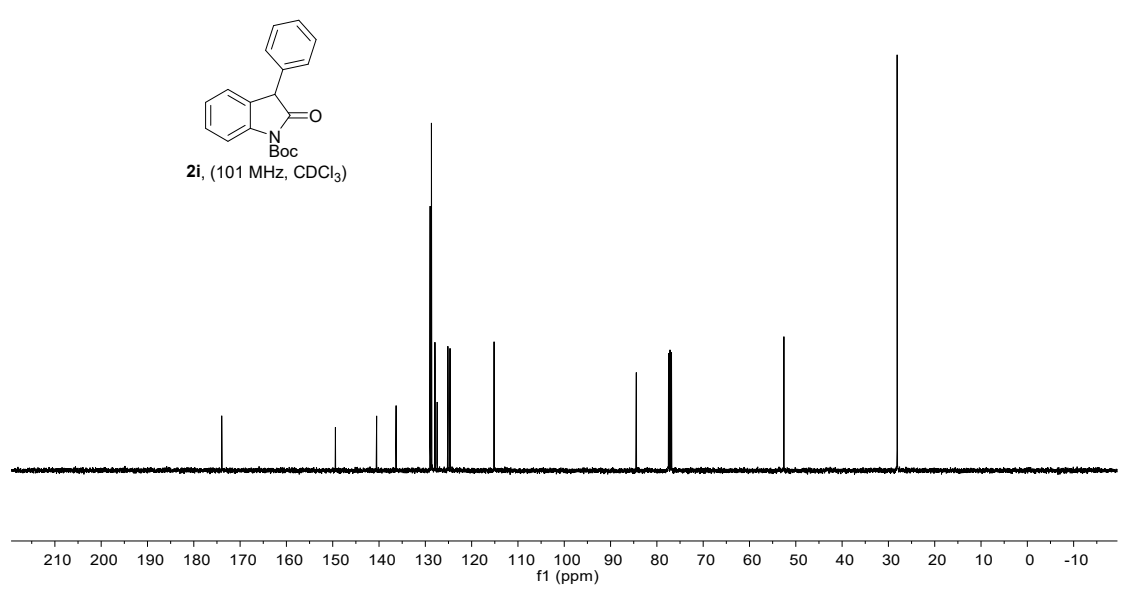
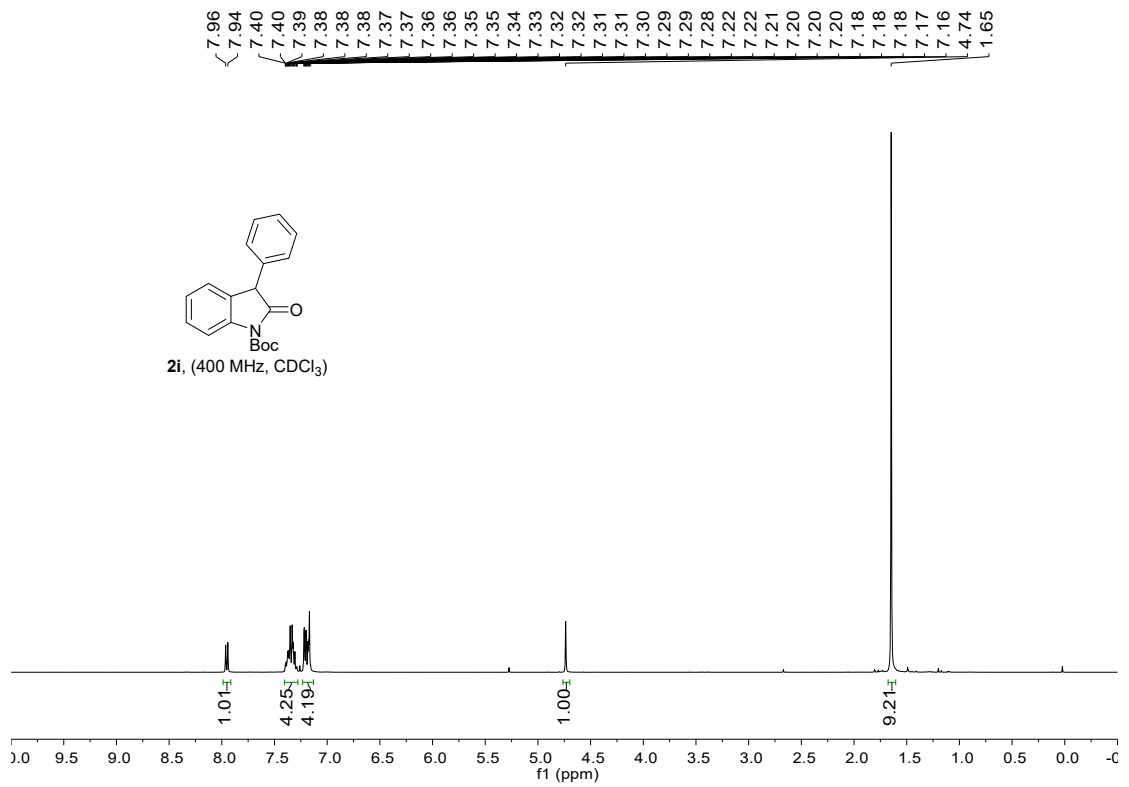


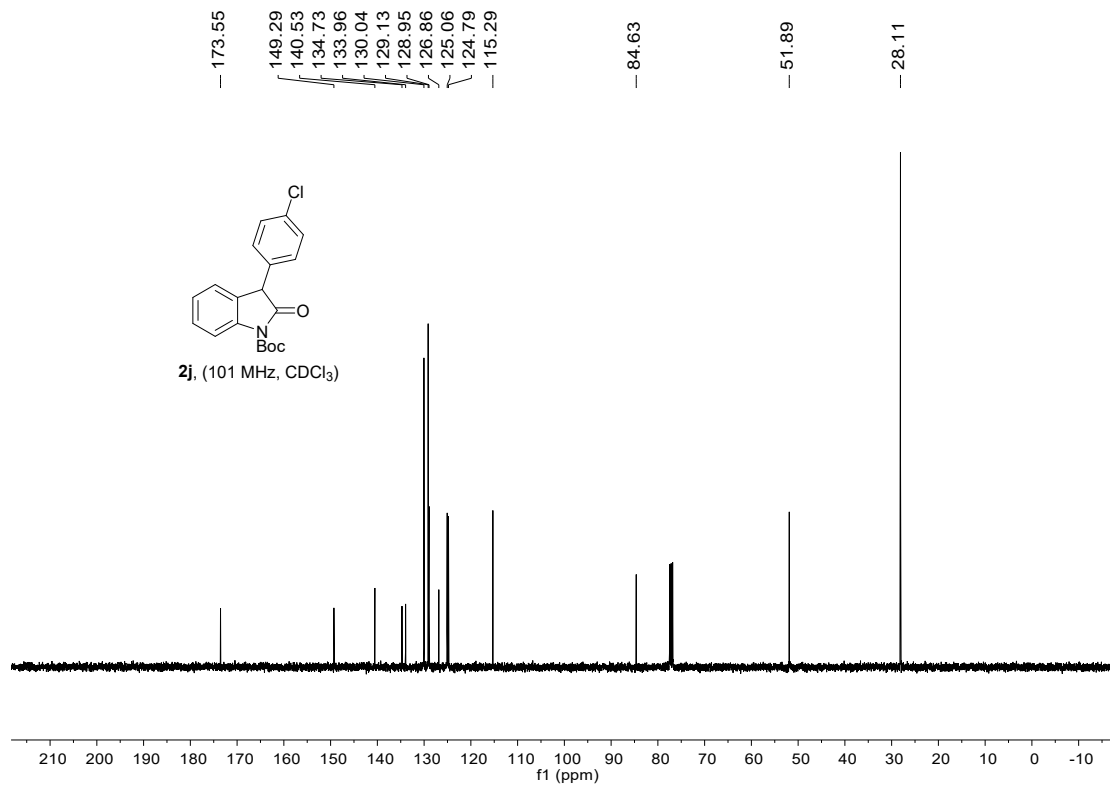
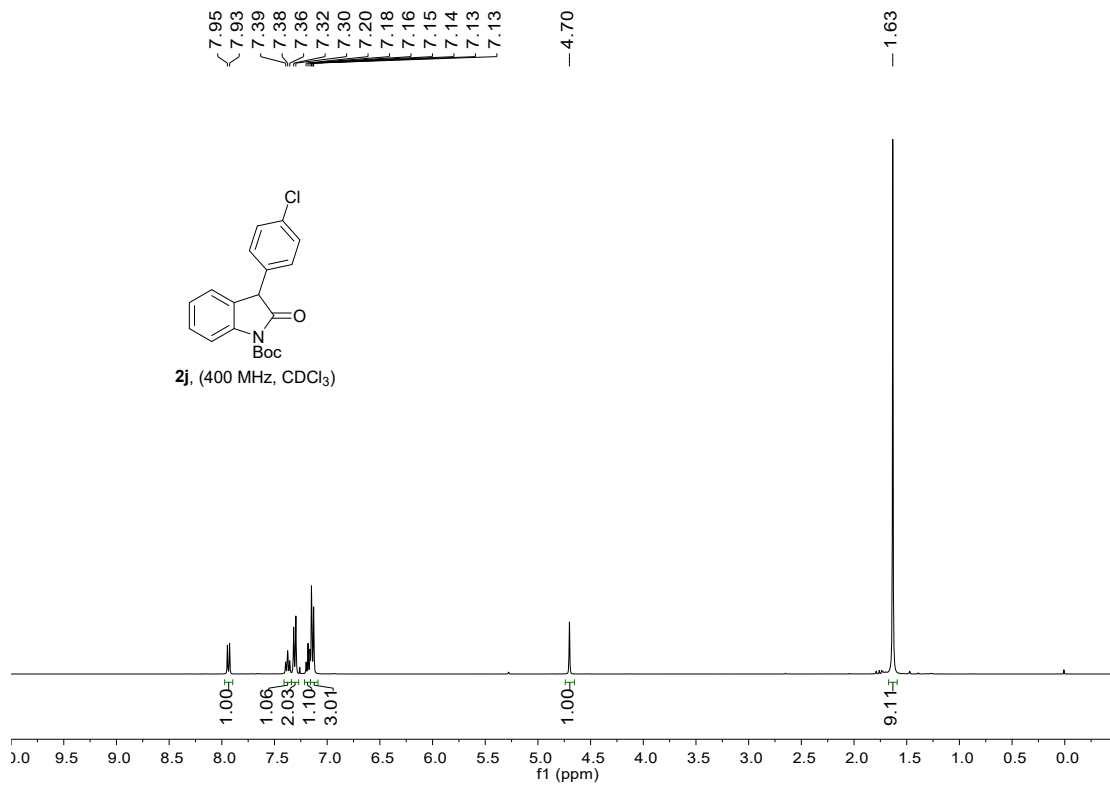


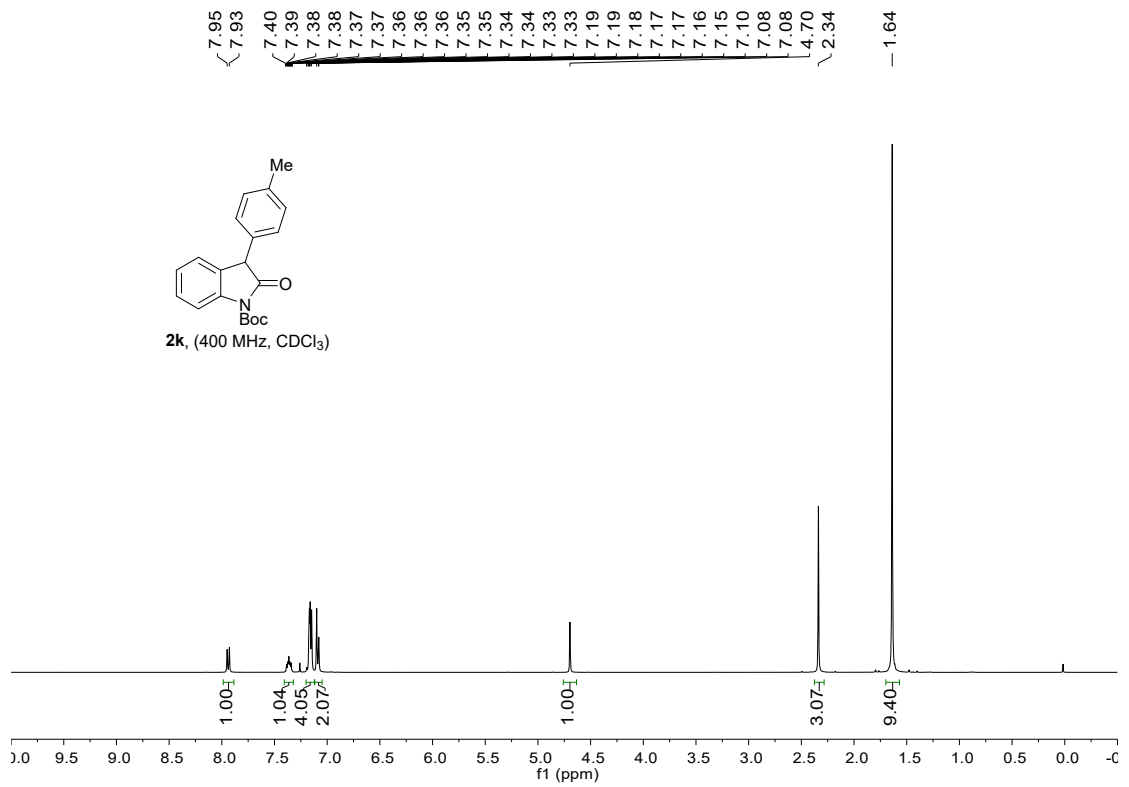


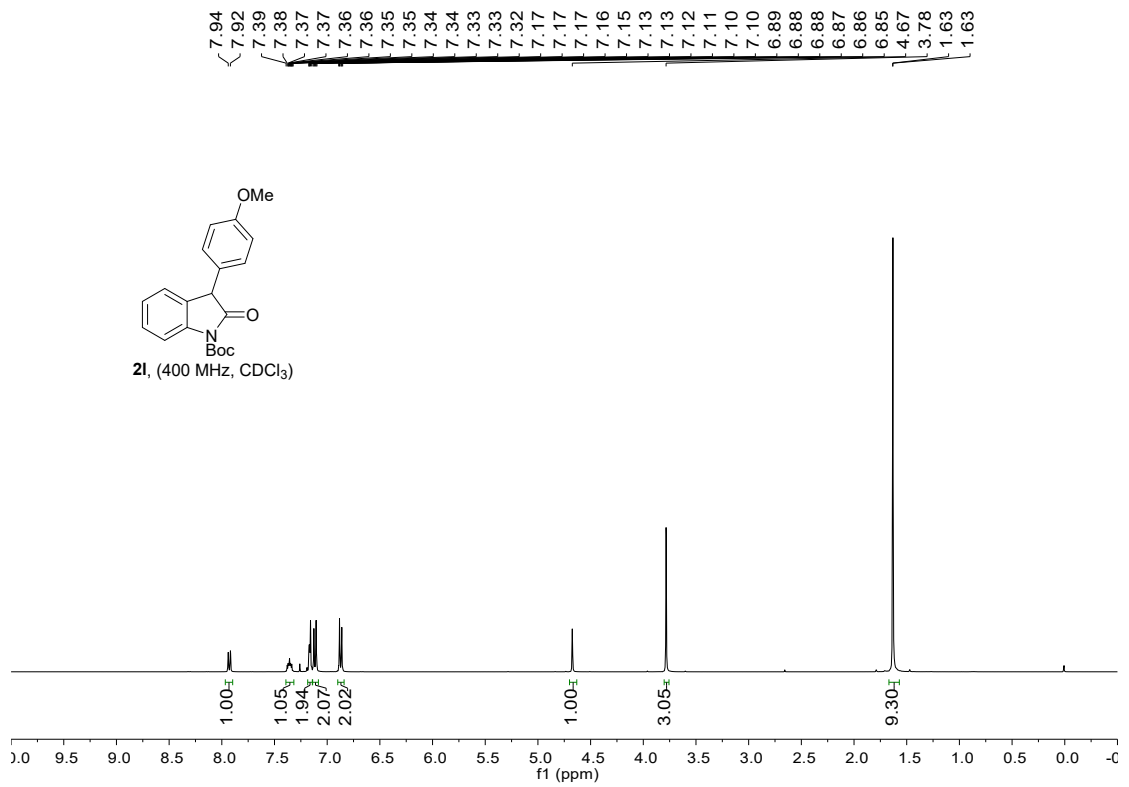




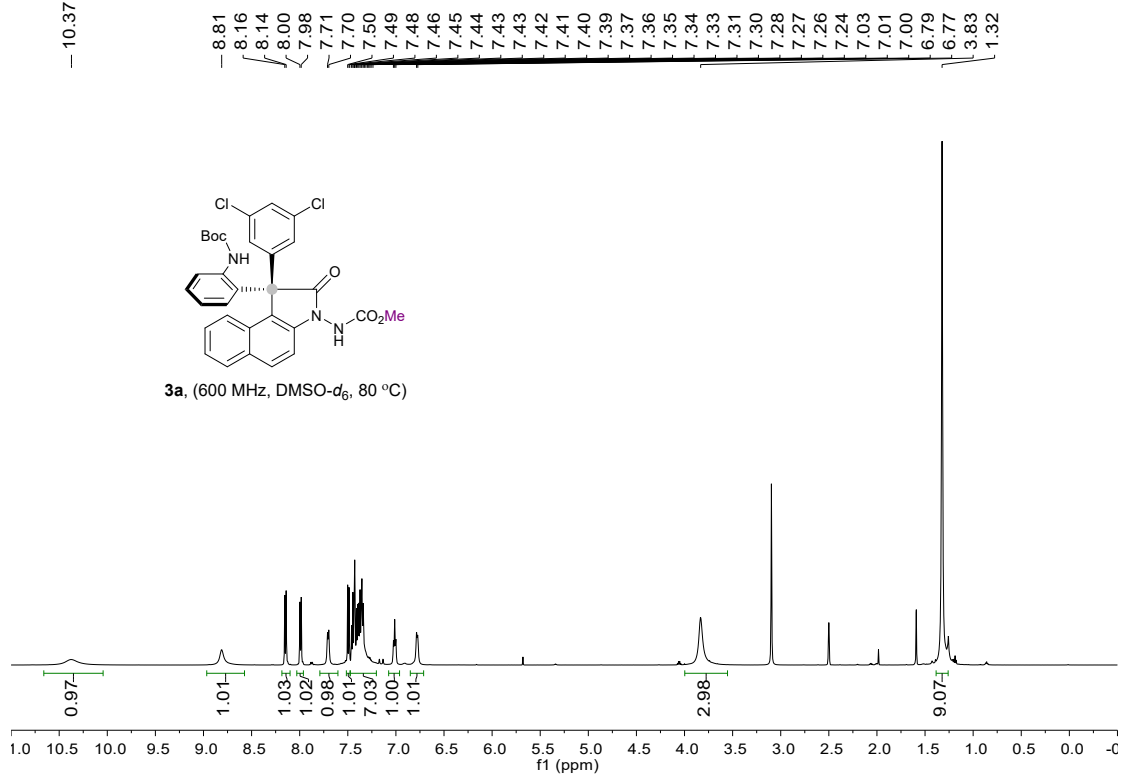








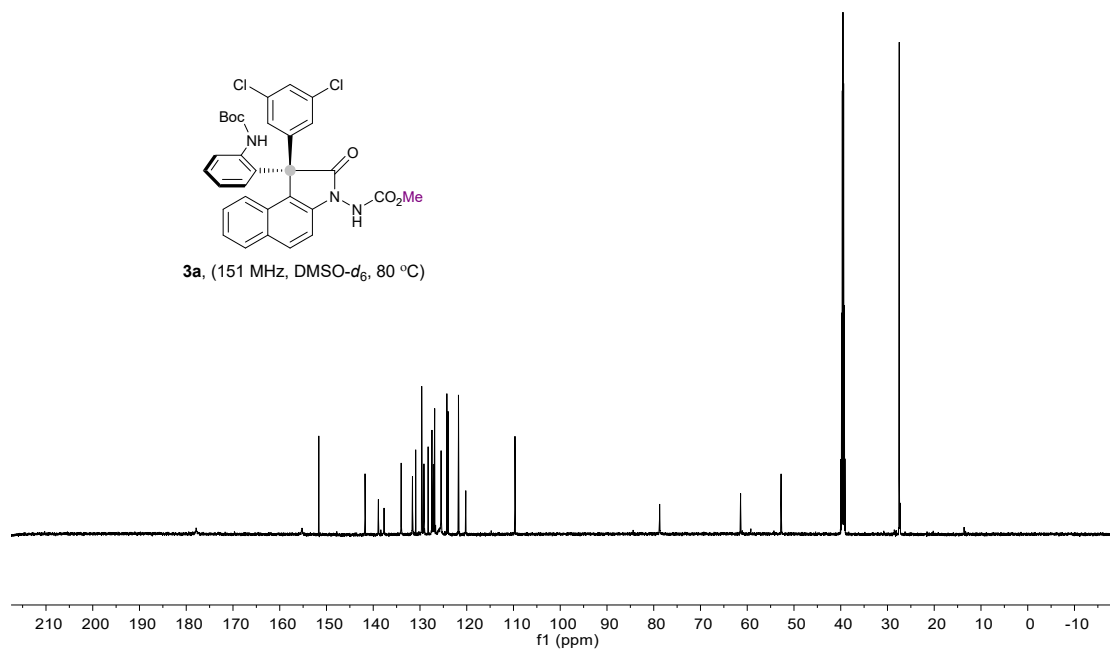
-10.37



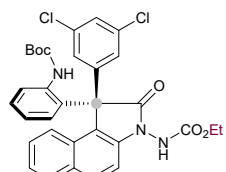
Chemical structure of **3a**: COC(=O)N[C@@H](c1ccc2ccccc12)c1ccc(NC(=O)c2ccc(Cl)c(Cl)c2)cc1

**3a**, (151 MHz, DMSO- $d_6$ , 80 °C)

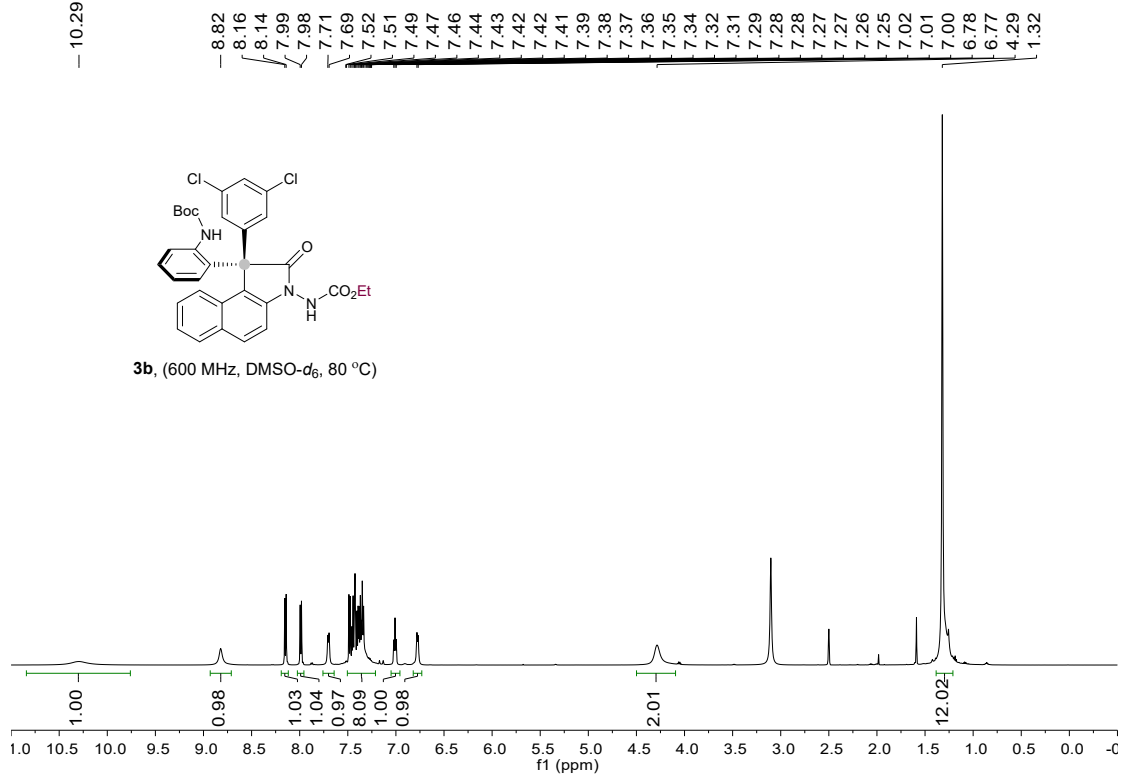
Chemical Shift (ppm)
177.88
155.26
151.65
141.75
138.89
137.68
134.02
131.60
130.92
129.63
129.57
129.16
128.26
127.44
127.12
126.86
125.48
124.25
123.99
121.77
120.21
109.68
78.74
61.42
52.76
27.48



- 10.29

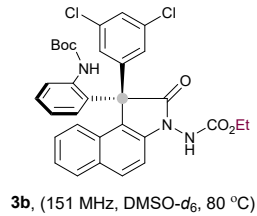


**3b**, (600 MHz, DMSO-*d*<sub>6</sub>, 80 °C)



Chemical structure of **3b** is shown above the spectrum. The spectrum displays the following chemical shifts (ppm):

Chemical Shift (ppm)
177.77
154.76, 151.66, 141.76, 138.97, 137.70, 134.03, 131.59, 130.91, 129.64, 129.57, 129.15, 128.28, 127.43, 127.13, 126.86, 125.50, 124.25, 123.98, 121.76, 120.20, 109.67, 78.73, 61.77, 61.44
27.49
13.86



**3b**, (151 MHz, DMSO-*d*<sub>6</sub>, 80 °C)

