

# Catalytic Asymmetric Electrophilic Cyanation of 3-Substituted Oxindoles

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## *Supporting Information*

## Contents

1. General information.....	S2
2. Materials .....	S2
3. Asymmetric reactions and copies of HPLC chromatograms .....	S3
3.1 General procedure for the synthesis of <b>3</b> .....	S3
4. X-Ray structure of <b>3s</b> (CCDC 1539670) .....	S26
5. References.....	S32
6. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra.....	S33

## 1. General information

All reactions were carried out with oven dried glassware under argon atmosphere, unless otherwise stated. All chemicals were purchased from Acros, Alfa, Aladdin, or InnoChem and used as it comes unless otherwise stated. TLC was performed on silica gel F<sub>254</sub> TLC glass plates and visualized with UV light. All the HPLC columns and **L3-L5** were purchased from Daicel Chemical Industries. Solvent of petroleum ether (PE) and ethyl acetate (EA) were used directly in column chromatography. Toluene, THF were dried over sodium (diphenyl ketone) and distilled; CH<sub>2</sub>Cl<sub>2</sub> were distilled over CaH<sub>2</sub> before use. <sup>1</sup>H NMR spectra were recorded on a Brucker Avance400 (400 MHz) spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm as the standard. The data is reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration, assignment). <sup>13</sup>C NMR spectra were recorded with <sup>1</sup>H-decoupling on a Brucker Avance400 (100 MHz) spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as the standard. Other analysis was carried out on the following instruments.

Infrared spectrometer: Bruker ALPHA FT-IR-Spektrometer.

High resolution mass spectrum: Bruker Apex IV FTMS.

Rotation polarity: Krüss P8000.

High Performance Liquid Chromatography: Shimadzu LC-20A.

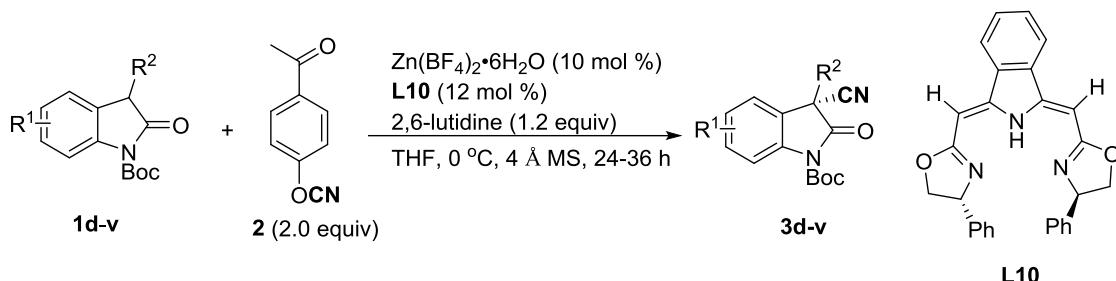
Melting point detector: Binocular microscope XT4A melting point apparatus (without correct).

## 2. Materials

Chiral bisoxazoline ligands **L1-L2**<sup>[1]</sup>, **L6-L8**<sup>[2]</sup>, **L9**<sup>[3]</sup> and chiral pincer ligand **L10**<sup>[4]</sup> were prepared according to the reported procedures. 3-Substituted oxindoles **1a-v** were synthesized according to the literature procedure.<sup>[5]</sup> Electrophilic CN reagents **2** was prepared following our previous literature procedures.<sup>[6]</sup>

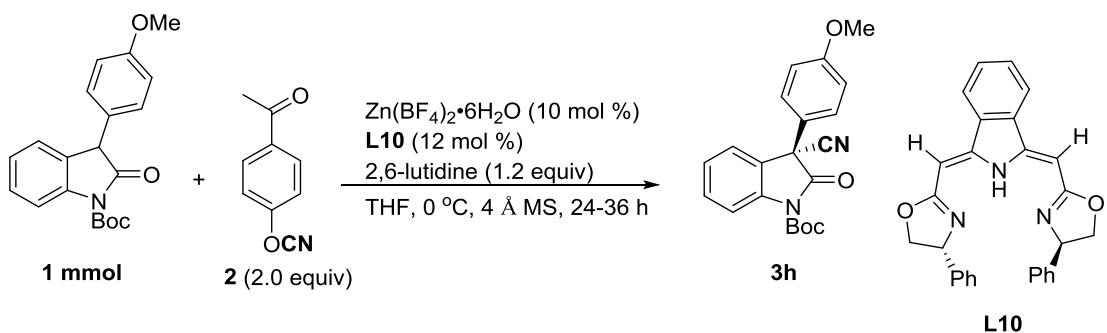
### 3. Asymmetric reactions and copies of HPLC chromatograms

#### 3.1 General procedure for the synthesis of 3



After stirring a mixture of  $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.005 mmol, 10 mol %, 1.8 mg) and **L10** (0.006 mmol, 12 mol %, 2.6 mg) in THF (0.5 mL) with dry 4 Å MS (5 mg) at room temperature for 2 h, substrates **1d-1v** (0.05 mmol) was added. After stirring 30 min, cooled to 0 °C, cyanate reagent **2** (0.1 mmol, 2.0 equiv, 16 mg) and 2,6-lutidine (0.06 mmol, 1.2 equiv, 7 µL) were added successively. The reaction mixture was stirred for 24–36 h at 0 °C under argon atmosphere. Routine aqueous workup and silica gel column chromatography was performed to purify the crude product **3d-3v**.

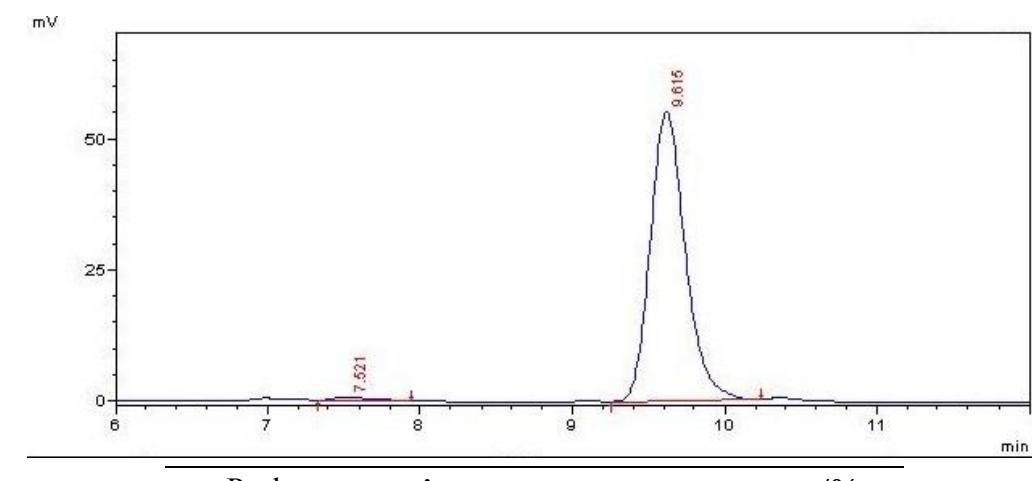
#### 1 mmol scale reaction for substrate **1h** for representative example.



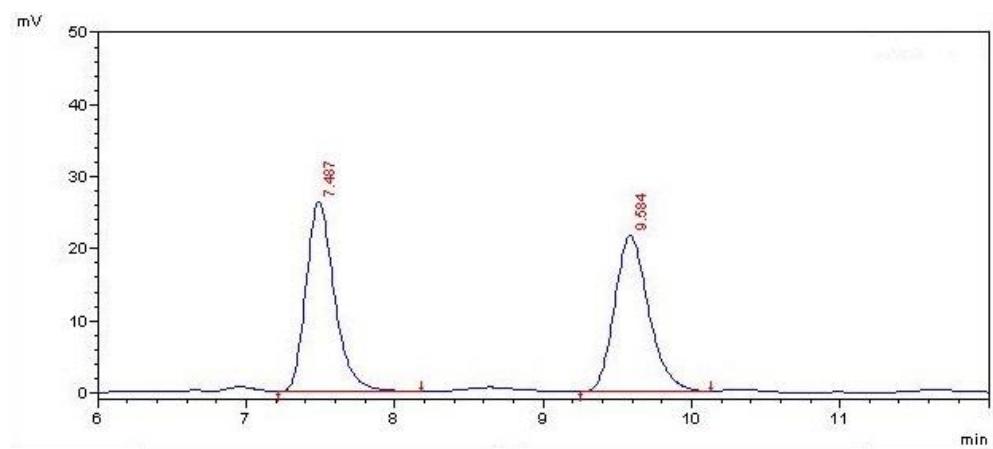
After stirring a mixture of  $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 10 mol %, 35.6 mg) and **L10** (0.12 mmol, 12 mol %, 52 mg) in THF (10 mL) with dry 4 Å MS (100 mg) at room temperature for 2 h, substrate **1h** (1 mmol, 1.0 equiv, 339 mg) was added. After stirring 30 min, cooled to 0 °C, cyanate reagent **2** (2 mmol, 2.0 equiv, 322 mg) and 2,6-lutidine (1.2 mmol, 1.2 equiv, 140 µL) were added successively. The reaction mixture was stirred at 0 °C under argon atmosphere until the substrate completely consumed by TLC. The volatiles removed under reduced pressure and the residue was purified by column chromatography (15:1 PE:EA) to give the product **3h** (317 mg, 87 % yield, 96 % ee).

**tert-Butyl (R)-3-cyano-2-oxo-3-phenylindoline-1-carboxylate (3d)**

Colorless oil, 15.4 mg, 92 % yield, 97 % ee, eluent PE/EA (15/1, V/V),  $R_f = 0.50$ ,  $[\alpha]^{20}_D = 34.9$  ( $c$  0.60,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.51 (dt,  $J = 7.2, 1.6$  Hz, 1H, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.35-7.31 (m, 3H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 148.5, 139.8, 133.7, 131.0, 129.5, 129.4, 126.8, 125.9, 124.5, 116.4 (CN), 116.0, 85.8, 52.7, 27.9 ppm. IR (KBr) 2245, 1774, 1743  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 352.1656 found: 352.1653. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_S$ (minor) = 7.5 min,  $t_R$ (major) = 9.6 min.



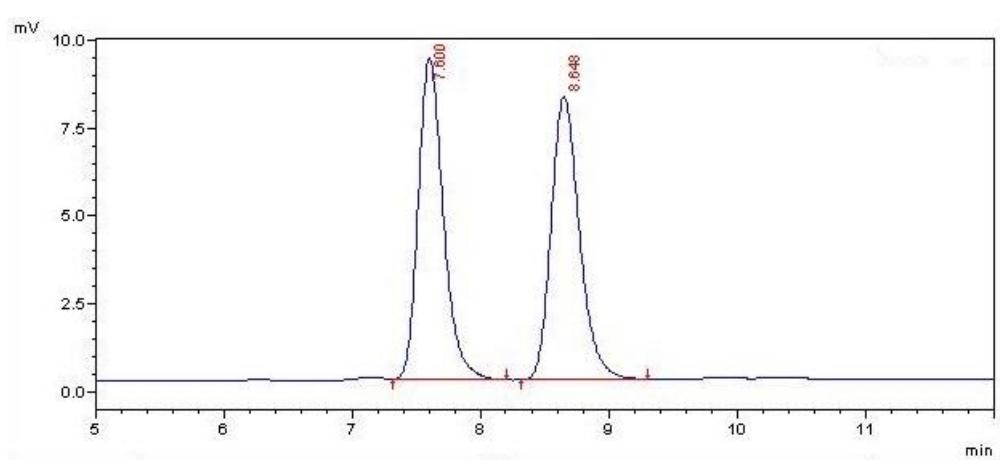
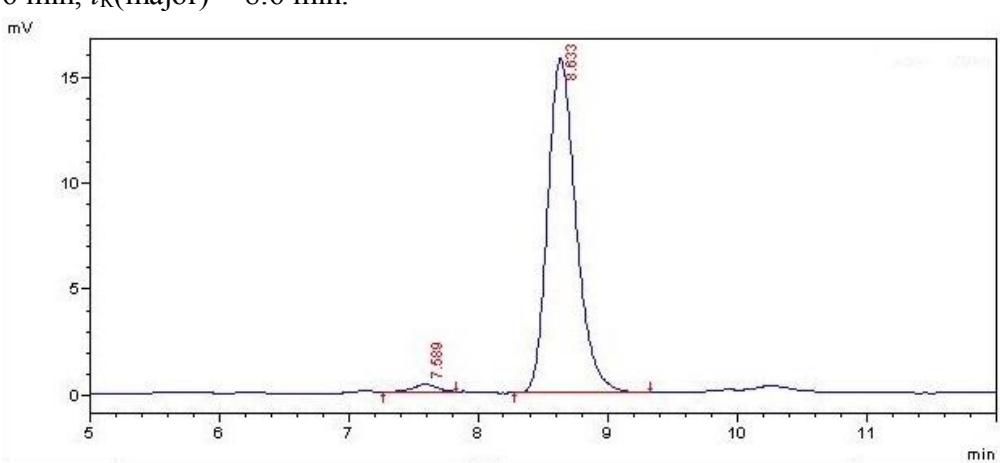
Peak	time	area	area/%
1	<b>7.521</b>	11790	<b>1.310</b>
2	<b>9.615</b>	888194	<b>98.690</b>
total		899984	<b>100.000</b>



Peak	time	area	area/%
1	<b>7.487</b>	349995	<b>50.219</b>
2	<b>9.584</b>	346938	<b>49.781</b>
total		696933	<b>100.000</b>

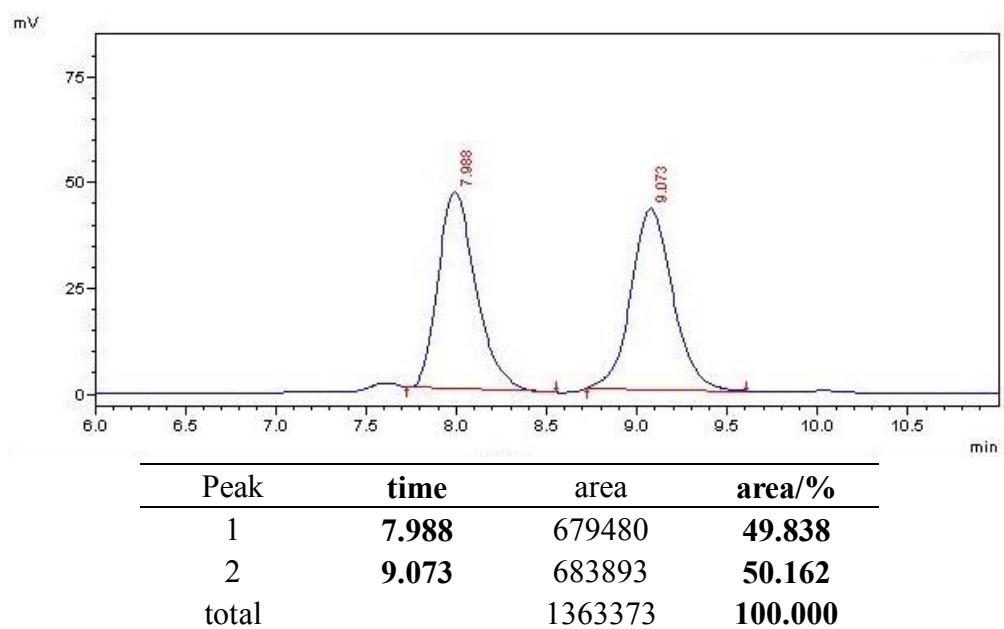
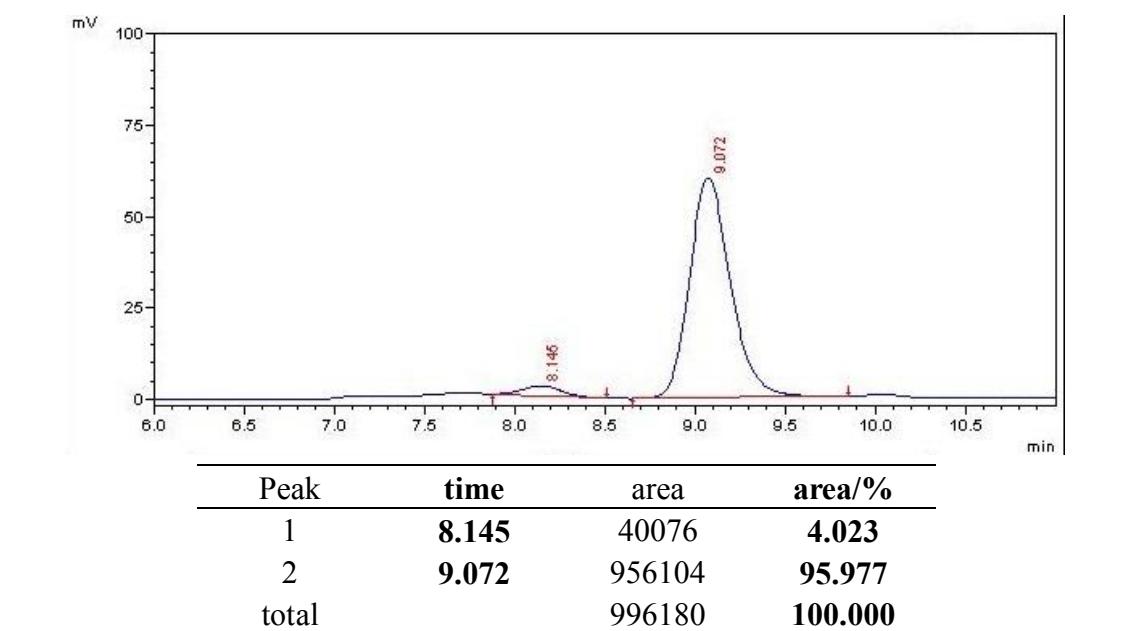
**tert-Butyl (R)-3-cyano-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate (3e)**

Colorless oil, 16.5 mg, 95 % yield, 95 % ee, eluent PE/EA (15:1, V/V),  $R_f = 0.50$ ,  $[\alpha]^{20}_D = 60.1$  ( $c$  0.70,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.51 (dt,  $J = 8.4, 1.6$  Hz, 1H, Ar-H), 7.39-7.31 (m, 4H, Ar-H), 7.09 (t,  $J = 8.4$  Hz, 2H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 163.3 (d,  $^1J_{\text{C}-\text{F}} = 248.5$  Hz), 148.4, 139.8, 131.2, 129.5 (d,  $^4J_{\text{C}-\text{F}} = 3.2$  Hz), 128.8 (d,  $^3J_{\text{C}-\text{F}} = 8.6$  Hz), 126.0, 125.4, 124.1, 116.4 (d,  $^2J_{\text{C}-\text{F}} = 45.8$  Hz), 116.34, 116.27(CN), 86.0, 51.9, 27.9 ppm. IR (KBr) 2247, 1778, 1740  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{FN}_3\text{O}_3$   $[M+\text{NH}_4]^+$ : 370.1561 found: 370.1561. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 7.6 min,  $t_R$ (major) = 8.6 min.

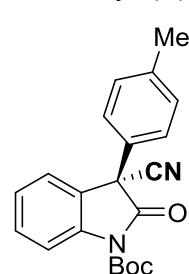


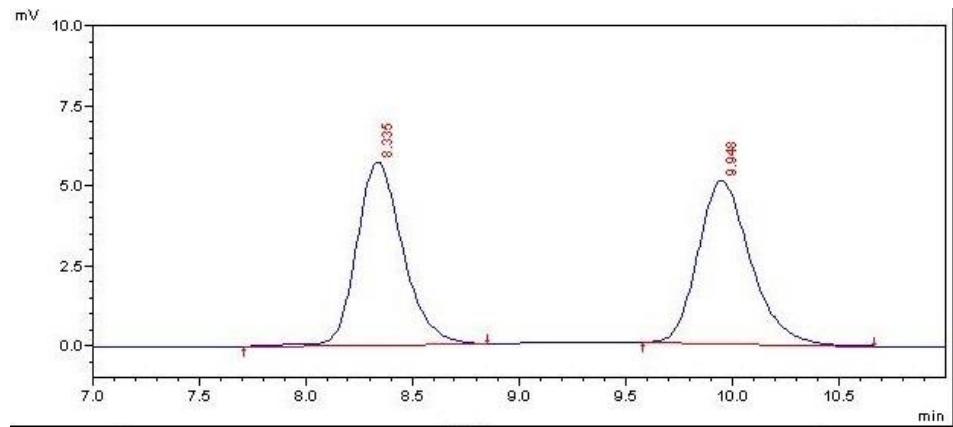
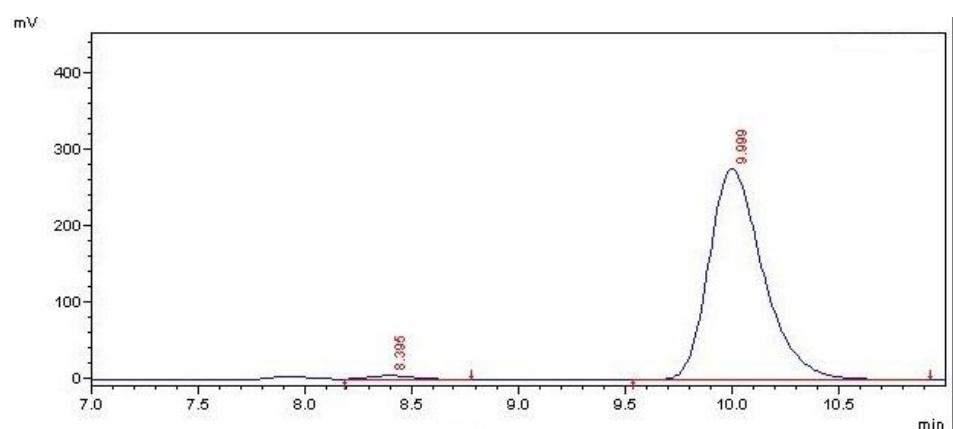
**tert-Butyl (R)-3-cyano-3-(4-chlorophenyl)-2-oxoindoline-1-carboxylate (3f)**

Colorless oil, 16.1 mg, 89 % yield, 92 % ee, eluent PE/EA (15:1, V/V),  $R_f = 0.45$ ,  $[\alpha]^{20}_D = 30.4$  ( $c$  0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.52 (dt,  $J = 8.4, 1.6$  Hz, 1H, Ar-H), 7.38-7.28 (m, 6H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 148.3, 139.8, 135.9, 132.2, 131.2, 129.6, 128.2, 126.0, 125.4, 123.9, 116.1, 116.06(CN), 86.0, 52.1, 27.9 ppm. IR (KBr) 2245, 1777, 1743  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{ClN}_3\text{O}_3$   $[M+\text{NH}_4]^+$ : 386.1266 found: 386.1265. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_s$ (minor) = 8.1 min,  $t_R$ (major) = 9.1 min.



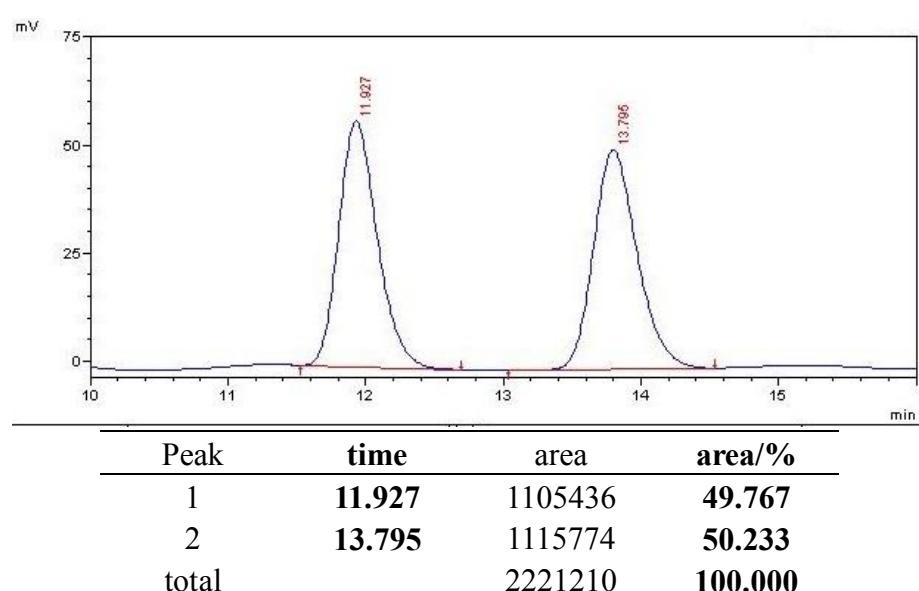
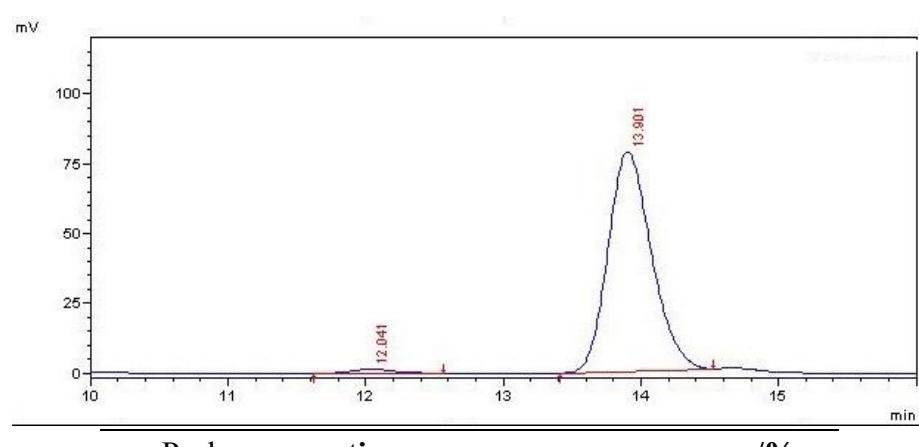
**tert-Butyl (R)-3-cyano-2-oxo-3-(p-tolyl)indoline-1-carboxylate (3g)**


  
 Colorless oil, 16.0 mg, 92 % yield, 98 % ee, eluent PE/EA (15:1, V/V),  $R_f = 0.50$ ,  $[\alpha]^{20}_D = 33.3$  ( $c$  0.50,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.50 (dt,  $J = 8.4, 1.2$  Hz, 1H, Ar-H), 7.38-7.36 (m, 1H, Ar-H), 7.30 (t,  $J = 7.6$  Hz, 1H, Ar-H), 7.23-7.18 (m, 4H, Ar-H), 2.35 (s, 3H,  $\text{CH}_3$ ), 1.62 (s, 9H,  $t\text{Bu}-\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 148.5, 139.8, 139.6, 130.9, 130.8, 130.5, 126.6, 125.8, 125.4, 124.6, 116.5(CN), 115.9, 85.7, 52.4, 27.9, 21.1 ppm. IR (KBr) 2246, 1776, 1740  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_3$   $[M+\text{NH}_4]^+$ : 366.1812 found: 366.1811. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_{\text{S}}(\text{minor}) = 8.3$  min,  $t_{\text{R}}(\text{major}) = 10.0$  min.

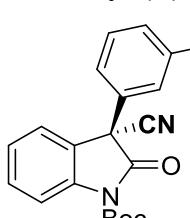


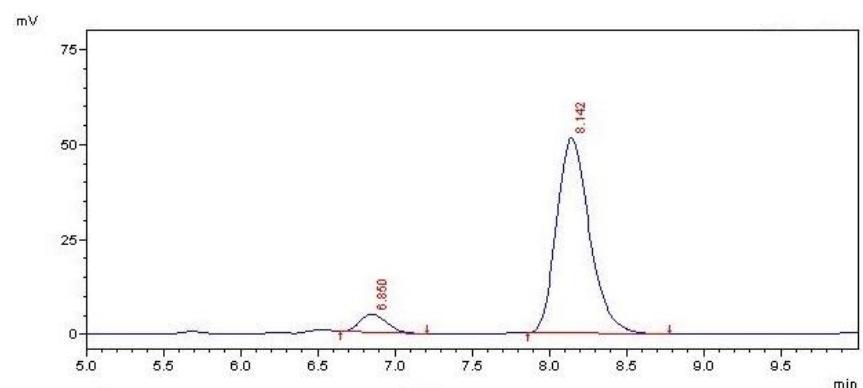
**tert-Butyl (R)-3-cyano-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate (3h)**

Colorless oil, 15.6 mg, 86 % yield, 97 % ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 51.6$  (*c* 0.45, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.50 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.39 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.31 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.26-7.24 (m, 2H, Ar-H), 6.90 (d, *J* = 8.0 Hz, 1H, Ar-H), 3.80 (s, 3H, OCH<sub>3</sub>), 1.62 (s, 9H, *t*Bu-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.5, 160.4, 148.5, 139.8, 130.9, 128.1, 125.8, 125.5, 125.4, 124.5, 116.5(CN), 115.9, 114.7, 85.7, 55.4, 52.0, 27.9 ppm. IR (KBr) 2251, 1781, 1731 cm<sup>-1</sup>. HRMS: calc. for C<sub>21</sub>H<sub>24</sub>N<sub>3</sub>O<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 382.1761 found: 382.1761. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm), *t*<sub>s</sub>(minor) = 12.0 min, *t*<sub>R</sub>(major) = 13.9 min.

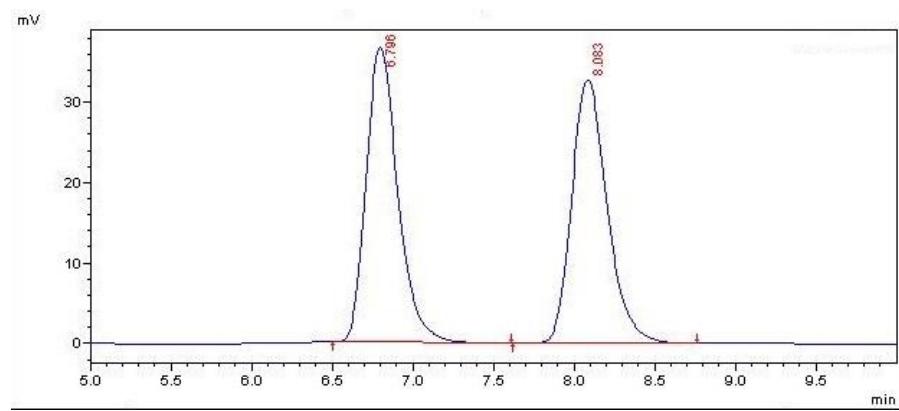


**tert-Butyl (R)-3-cyano-3-(3-fluorophenyl)-2-oxoindoline-1-carboxylate (3i)**


 Colorless oil, 15.3 mg, 87% yield, 86% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.60$ ,  $[\alpha]^{20}_D = 44.6$  ( $c$  0.35,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.53 (dt,  $J = 8.8, 1.6$  Hz, 1H, Ar-H), 7.40-7.33 (m, 3H, Ar-H), 7.19 (dd,  $J = 8.0, 0.4$  Hz, 1H, Ar-H), 7.10 (dt,  $J = 8.4, 2.0$  Hz, 1H, Ar-H), 7.00 (td,  $J = 9.2, 2.0$  Hz, 1H, Ar-H), 1.63 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 163.0 (d,  ${}^1J_{C-F} = 247.3$  Hz), 148.3, 139.8, 135.8 (d,  ${}^3J_{C-F} = 7.5$  Hz), 131.3, 131.0 (d,  ${}^3J_{C-F} = 8.2$  Hz), 126.0, 125.4, 123.8, 122.7 (d,  ${}^3J_{C-F} = 3.1$  Hz), 116.7 (d,  ${}^2J_{C-F} = 20.9$  Hz), 116.1, 116.0(CN), 114.2 (d,  ${}^2J_{C-F} = 24.0$  Hz), 86.0, 52.3 (d,  ${}^4J_{C-F} = 2.2$  Hz), 27.9 ppm. IR (KBr) 2244, 1776, 1742  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{FN}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 370.1561 found: 370.1561. HPLC on AD-H column (*n*-hexane / *iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_s$ (minor) = 6.8 min,  $t_R$ (major) = 8.1 min.



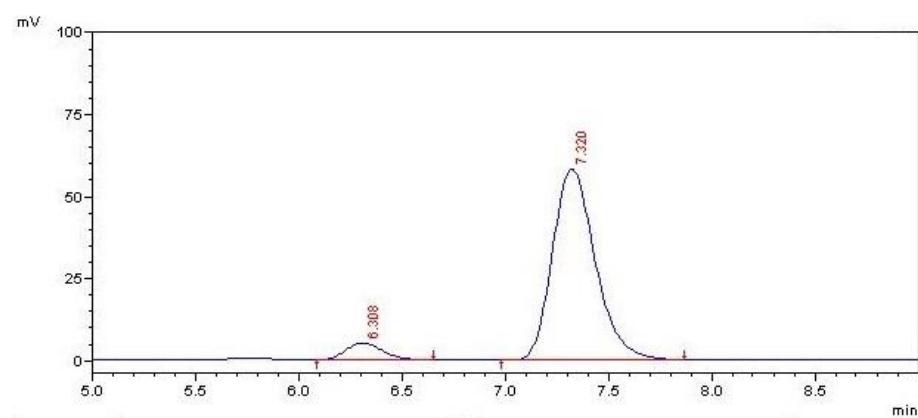
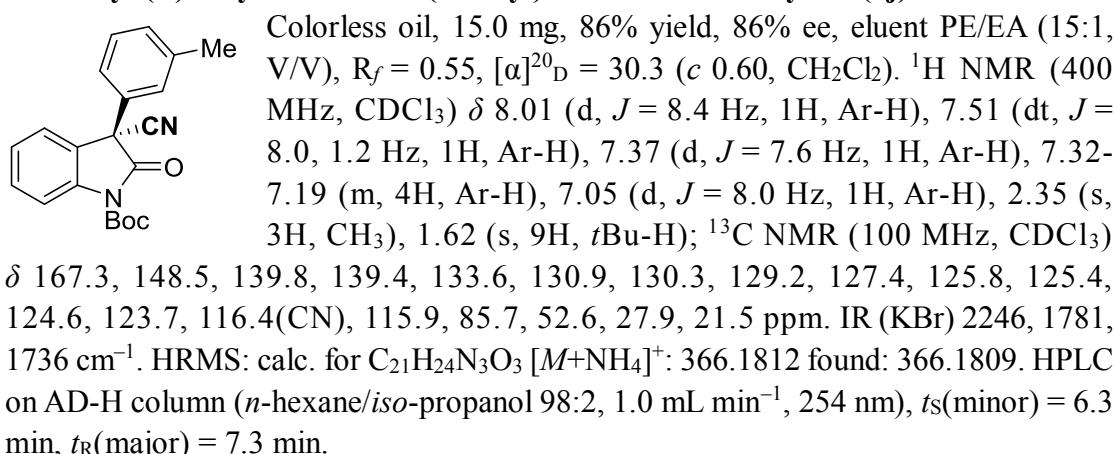
Peak	time	area	area/%
1	<b>6.850</b>	58667	<b>7.135</b>
2	<b>8.142</b>	763623	<b>92.865</b>
total		822290	<b>100.000</b>



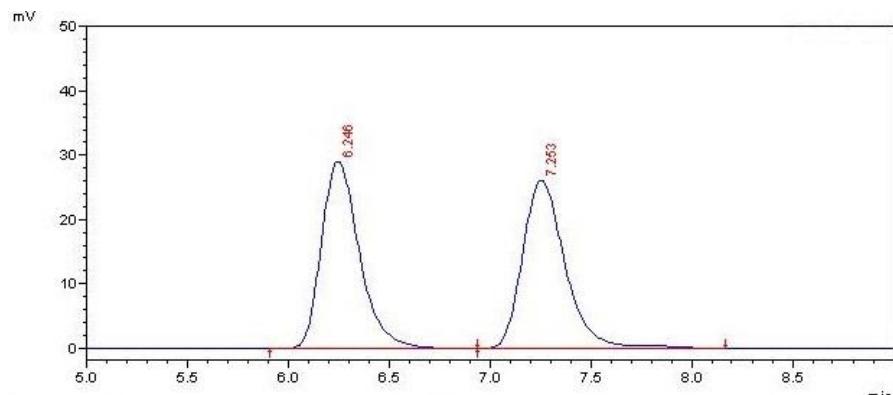
Peak	time	area	area/%
1	<b>6.796</b>	500798	<b>50.046</b>
2	<b>8.083</b>	499870	<b>49.954</b>
total		1000668	<b>100.000</b>

**tert-Butyl (R)-3-cyano-2-oxo-3-(m-tolyl)indoline-1-carboxylate (3j)**

Colorless oil, 15.0 mg, 86% yield, 86% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.55$ ,  $[\alpha]^{20}_D = 30.3$  ( $c$  0.60,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.51 (dt,  $J = 8.0, 1.2$  Hz, 1H, Ar-H), 7.37 (d,  $J = 7.6$  Hz, 1H, Ar-H), 7.32–7.19 (m, 4H, Ar-H), 7.05 (d,  $J = 8.0$  Hz, 1H, Ar-H), 2.35 (s, 3H,  $\text{CH}_3$ ), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 148.5, 139.8, 139.4, 133.6, 130.9, 130.3, 129.2, 127.4, 125.8, 125.4, 124.6, 123.7, 116.4(CN), 115.9, 85.7, 52.6, 27.9, 21.5 ppm. IR (KBr) 2246, 1781, 1736  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_3 [M+\text{NH}_4]^+$ : 366.1812 found: 366.1809. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 6.3 min,  $t_R$ (major) = 7.3 min.

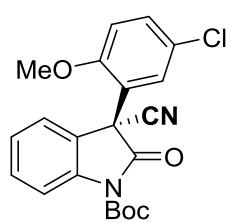


Peak	time	area	area/%
1	<b>6.308</b>	65200	<b>7.228</b>
2	<b>7.320</b>	836887	<b>92.772</b>
total		902087	<b>100.000</b>

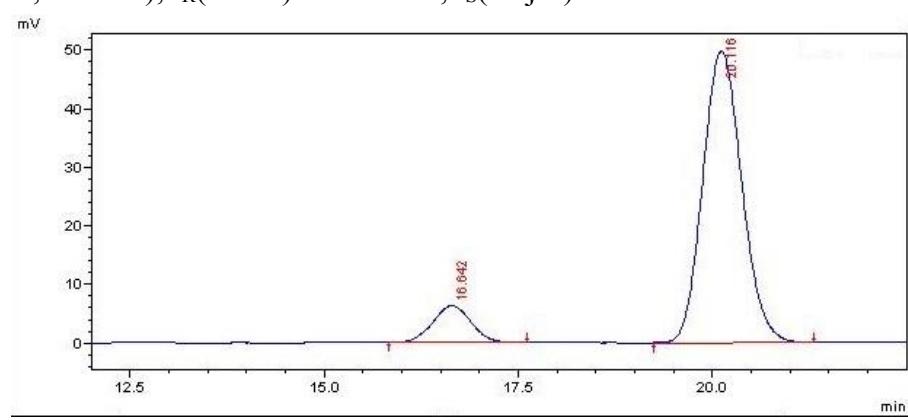


Peak	time	area	area/%
1	<b>6.246</b>	381379	<b>49.953</b>
2	<b>7.253</b>	382089	<b>50.047</b>
total		763468	<b>100.000</b>

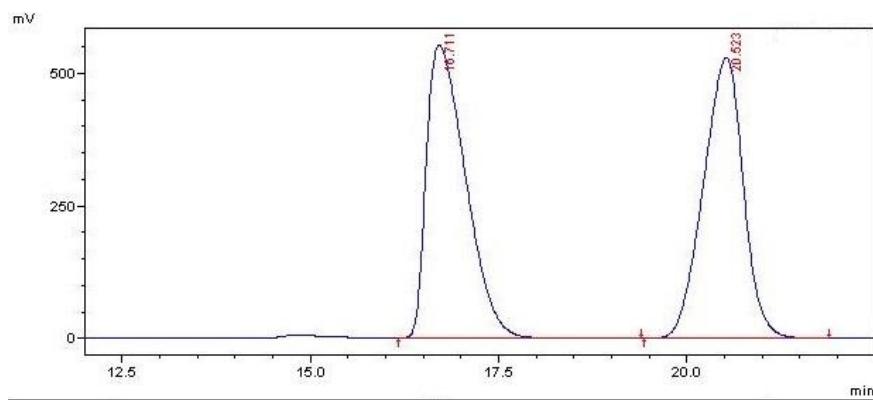
**tert-Butyl (S)-3-(5-chloro-2-methoxyphenyl)-3-cyano-2-oxoindoline-1-carboxylate (3k)**



Colorless oil, 13.0 mg, 65% yield, 78% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.35$ ,  $[\alpha]^{20}_D = -88.7$  ( $c$  0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.86 (d,  $J = 2.4$  Hz, 1H, Ar-H), 7.40 (dt,  $J = 7.2, 1.6$  Hz, 1H, Ar-H), 7.35 (dd,  $J = 8.8, 2.4$  Hz, 4H, Ar-H), 7.18-7.10 (m, 2H, Ar-H), 6.76 (d,  $J = 8.8$  Hz, 1H, Ar-H), 3.50 (s, 3H,  $\text{OCH}_3$ ), 1.67 (s, 9H,  $t\text{Bu}-\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 154.3, 148.7, 139.7, 130.7, 129.2, 126.5, 125.3, 124.5, 124.4, 123.8, 115.3, 115.2, 113.6, 85.4, 56.1, 51.4, 28.0 ppm. IR (KBr) 2247, 1779, 1739  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{ClO}_4$  [ $M+\text{NH}_4$ ] $^+$ : 416.1372 found: 416.1373. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_R$ (minor) = 16.6 min,  $t_S$ (major) = 20.1 min.



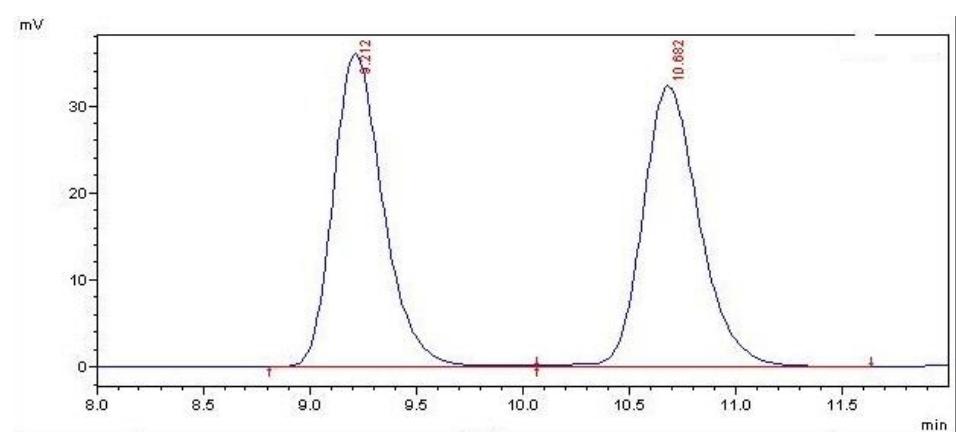
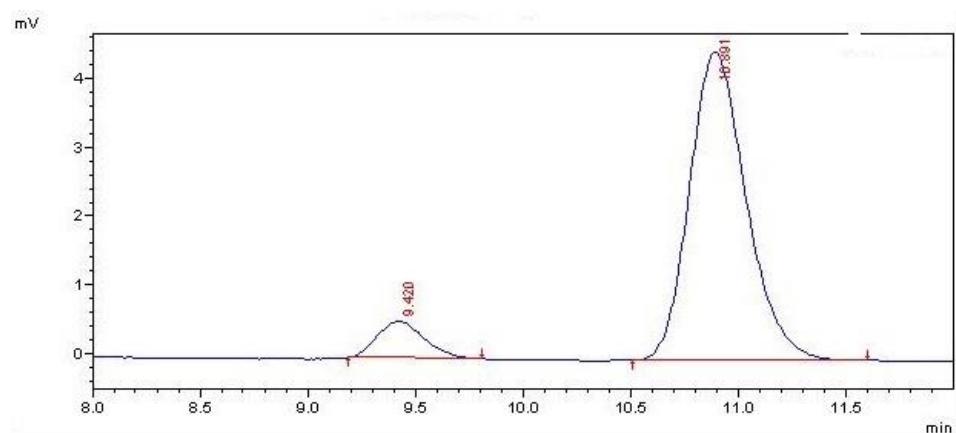
Peak	time	area	area/%
1	<b>16.642</b>	217646	<b>11.097</b>
2	<b>20.116</b>	1743626	<b>88.903</b>
total		1961272	<b>100.000</b>



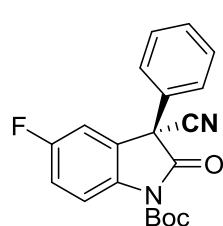
Peak	time	area	area/%
1	<b>16.711</b>	19968252	<b>50.609</b>
2	<b>20.523</b>	19487595	<b>49.391</b>
total		39455847	<b>100.000</b>

**tert-Butyl (R)-3-cyano-3-(naphthalen-1-yl)-2-oxoindoline-1-carboxylate (3l)**

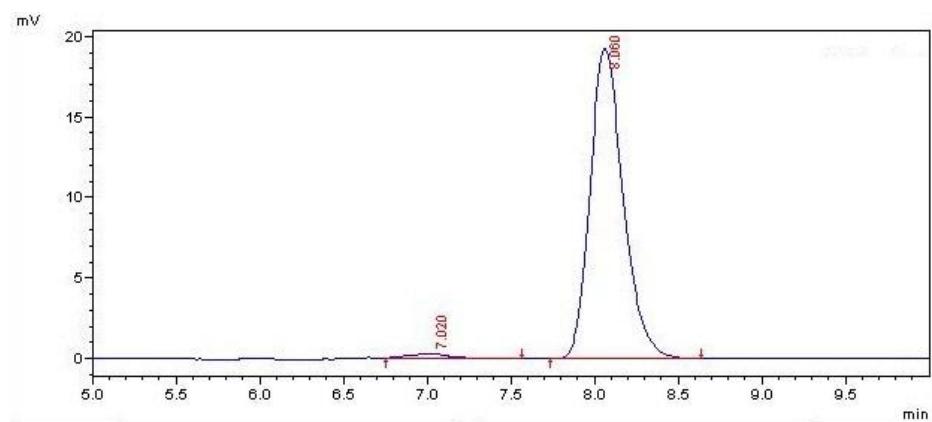
Colorless oil, 15.4 mg, 80 % yield, 82 % ee, eluent PE/EA (15:1, V/V),  $R_f = 0.55$ ,  $[\alpha]^{20}_D = 29.7$  ( $c$  0.50,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.91 (dd,  $J = 15.2, 8.0$  Hz, 2H, Ar-H), 7.74-7.72 (m, 2H, Ar-H), 7.54-7.44 (m, 4H, Ar-H), 7.26-7.24 (m, 2H, Ar-H), 1.65 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 148.6, 139.1, 134.7, 131.2, 131.0, 129.7, 129.4, 128.0, 127.2, 126.3, 126.0, 125.5, 125.1, 124.9, 123.8, 116.3(CN), 116.1, 85.9, 53.4, 28.0 ppm. IR (KBr) 2240, 1773, 1735  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_3 [M+\text{NH}_4]^+$ : 402.1812 found: 402.1810. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 9.4 min,  $t_R$ (major) = 10.9 min.



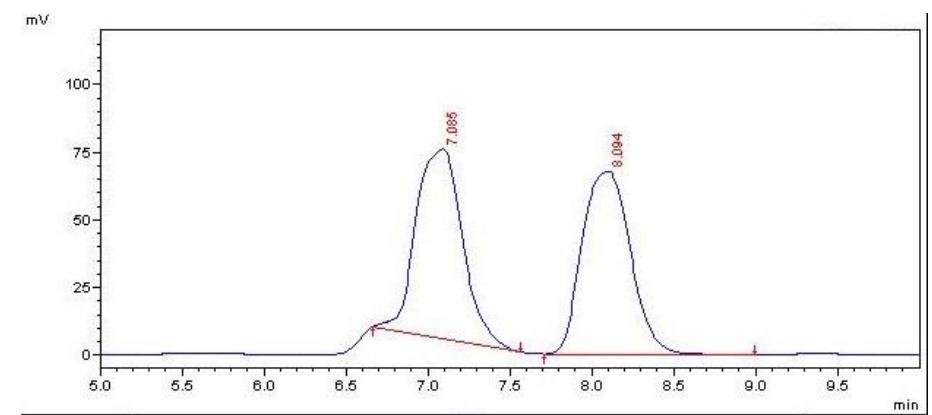
**tert-Butyl (R)-3-cyano-5-fluoro-2-oxo-3-phenylindoline-1-carboxylate (3m)**



Colorless oil, 14.8 mg, 84% yield, 97% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.50$ ,  $[\alpha]^{20}_D = 35.0$  ( $c$  0.65,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (dd,  $J = 9.2, 4.4$  Hz, 1H, Ar-H), 7.43-7.41 (m, 3H, Ar-H), 7.33 (dd,  $J = 6.0, 3.2$  Hz, 2H, Ar-H), 7.21 (dt,  $J = 8.8, 2.4$  Hz, 1H, Ar-H), 7.11 (dd,  $J = 7.2, 2.4$  Hz, 1H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 160.3 (d,  $^1J_{C-F} = 245.6$  Hz), 148.4, 135.8 (d,  $^4J_{C-F} = 2.7$  Hz), 133.1, 129.7, 129.5, 126.6, 126.0 (d,  $^3J_{C-F} = 8.5$  Hz), 117.9 (d,  $^2J_{C-F} = 22.7$  Hz), 117.6 (d,  $^3J_{C-F} = 7.8$  Hz), 115.8(CN), 112.9 (d,  $^2J_{C-F} = 25.0$  Hz), 86.1, 52.7 (d,  $^4J_{C-F} = 1.6$  Hz), 27.9 ppm. IR (KBr) 2250, 1770, 1739  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{FN}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 370.1560 found: 370.1561. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_s$ (minor) = 7.0 min,  $t_R$ (major) = 8.0 min.



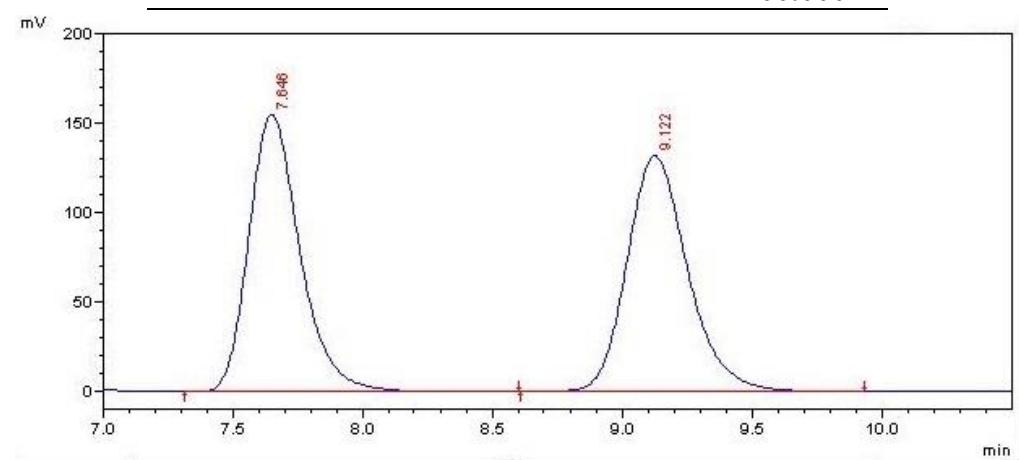
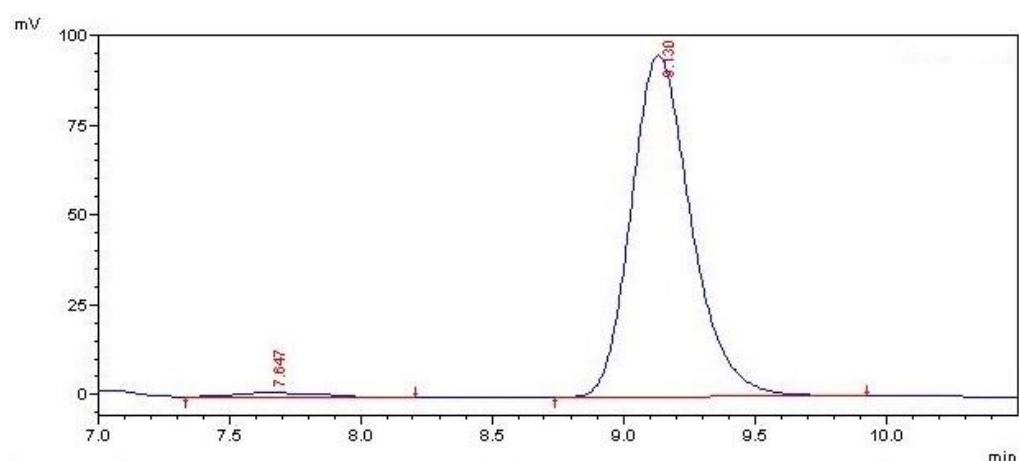
Peak	time	area	area/%
1	<b>7.020</b>	4617	<b>1.707</b>
2	<b>8.060</b>	265894	<b>98.293</b>
total		270511	<b>100.000</b>



Peak	time	area	area/%
1	<b>7.085</b>	1379412	<b>49.956</b>
2	<b>8.094</b>	1381858	<b>50.044</b>
total		2761270	<b>100.000</b>

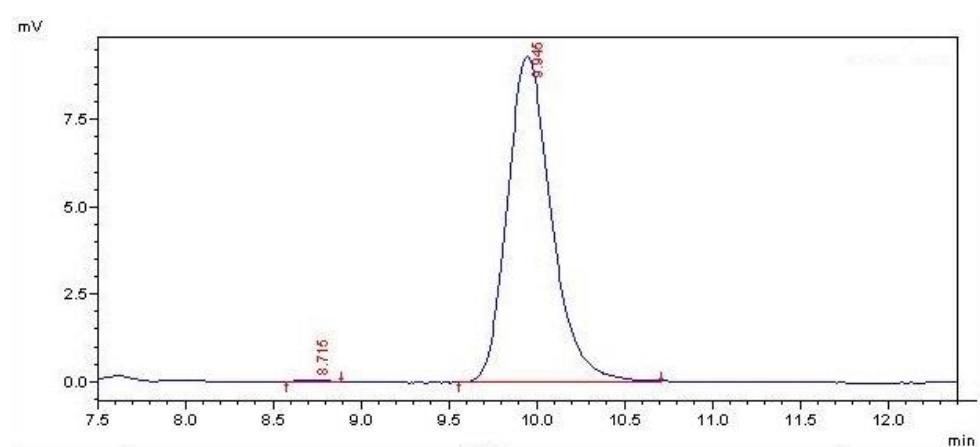
**tert-Butyl (R)-5-chloro-3-cyano-2-oxo-3-phenylindoline-1-carboxylate (3n)**

Colorless oil, 16.9 mg, 92% yield, 97% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.45$ ,  $[\alpha]^{20}_D = 63.7$  ( $c$  0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.8$  Hz, 1H, Ar-H), 7.48 (dd,  $J = 8.8, 2.0$  Hz, 1H, Ar-H), 7.43-7.42 (m, 3H, Ar-H), 7.36 (d,  $J = 2.0$  Hz, 1H, Ar-H), 7.34-7.32 (m, 2H, Ar-H), 1.61 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 148.3, 138.3, 133.0, 131.4, 131.1, 129.7, 129.6, 126.6, 126.0, 125.5, 117.3, 115.7(CN), 86.2, 52.5, 27.9 ppm. IR (KBr) 2247, 1784, 1743  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{ClN}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 386.1266 found: 386.1266. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_{\text{s}}$ (minor) = 7.6 min,  $t_{\text{R}}$ (major) = 9.1 min.

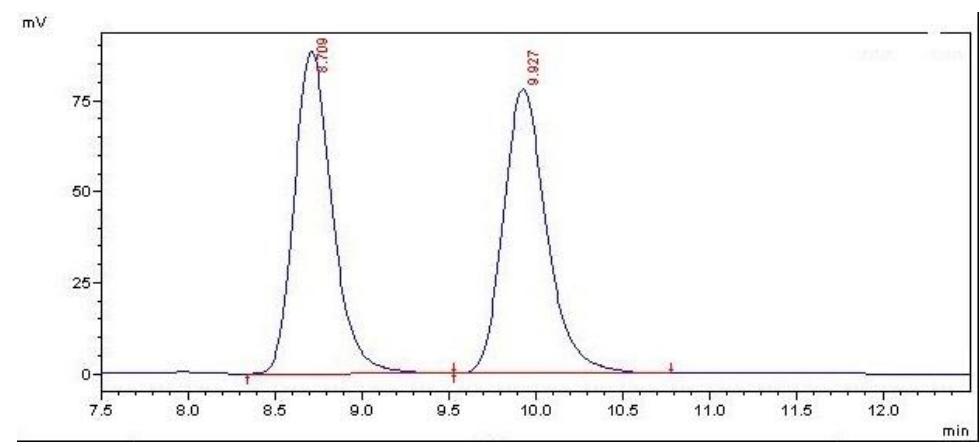


**tert-Butyl (R)-5-bromo-3-cyano-2-oxo-3-phenylinidoline-1-carboxylate (3o)**

Colorless oil, 16.9 mg, 82% yield, >99% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.45$ ,  $[\alpha]^{20}_D = 74.5$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.8$  Hz, 1H, Ar-H), 7.63 (dd,  $J = 8.8$ , 2.0 Hz, 1H, Ar-H), 7.50 (d,  $J = 2.0$  Hz, 1H, Ar-H), 7.43-7.42 (m, 3H, Ar-H), 7.33-7.32 (m, 2H, Ar-H), 1.61 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 148.3, 138.8, 134.1, 133.1, 129.7, 129.6, 128.4, 126.6, 126.3, 118.7, 117.7, 115.8(CN), 86.3, 52.4, 27.9 ppm. IR (KBr) 2247, 1780, 1734  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{BrN}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 430.0761 found: 430.0760. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_{\text{s}}$ (minor) = 8.7 min,  $t_{\text{R}}$ (major) = 9.9 min.

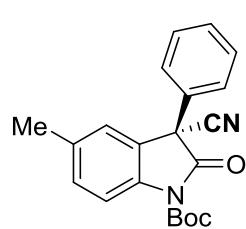


Peak	time	area	area/%
1	<b>8.715</b>	433	<b>0.266</b>
2	<b>9.945</b>	162113	<b>99.734</b>
total		162545	<b>100.000</b>

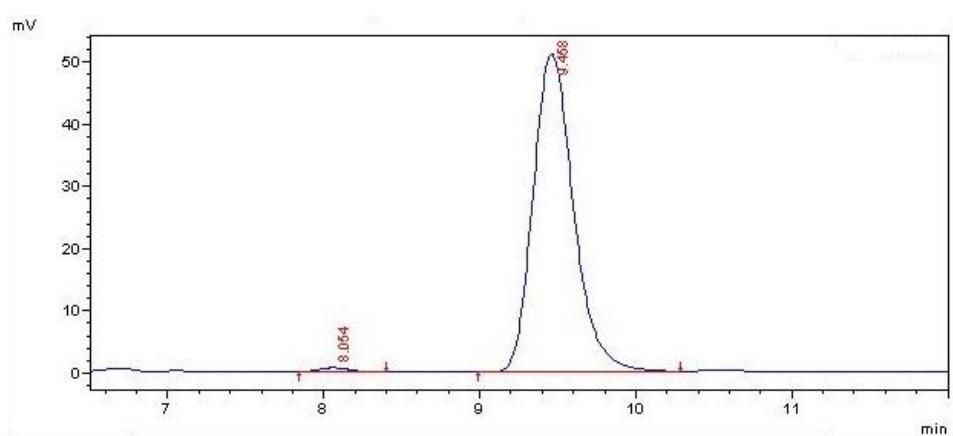


Peak	time	area	area/%
1	<b>8.709</b>	1350581	<b>49.849</b>
2	<b>9.927</b>	1358757	<b>50.151</b>
total		2709338	<b>100.000</b>

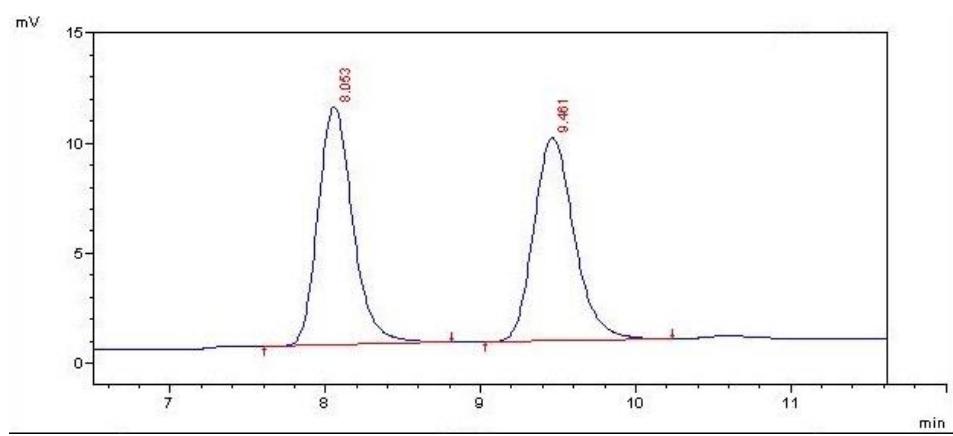
**tert-Butyl (R)-3-cyano-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (3p)**



Colorless oil, 16.2 mg, 93% yield, 98% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.55$ ,  $[\alpha]^{20}_D = 50.0$  ( $c$  0.70,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.41-7.39 (m, 3H, Ar-H), 7.38-7.29 (m, 3H, Ar-H), 7.18 (s, 1H, Ar-H), 2.38 (s, 3H,  $\text{CH}_3$ ), 1.61 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 148.5, 137.4, 135.9, 133.9, 131.5, 129.39, 129.35, 126.8, 125.7, 124.4, 116.5(CN), 115.7, 85.6, 52.8, 28.0, 21.0 ppm. IR (KBr) 2245, 1778, 1739  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}$  [ $M+\text{Na}$ ] $^+$ : 371.1366 found: 371.1363. HPLC on AD-H column (*n*-hexane *iso*-propanol 98:2, 1.0 mL min $^{-1}$ , 254 nm),  $t_s$ (minor) = 8.0 min,  $t_R$ (major) = 9.4 min.



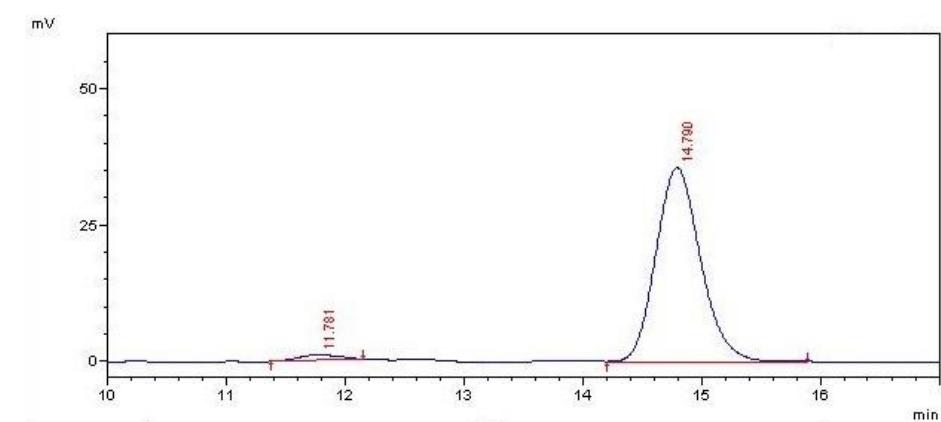
Peak	time	area	area/%
1	<b>8.054</b>	9240	<b>0.991</b>
2	<b>9.458</b>	923160	<b>99.009</b>
total		932400	<b>100.000</b>



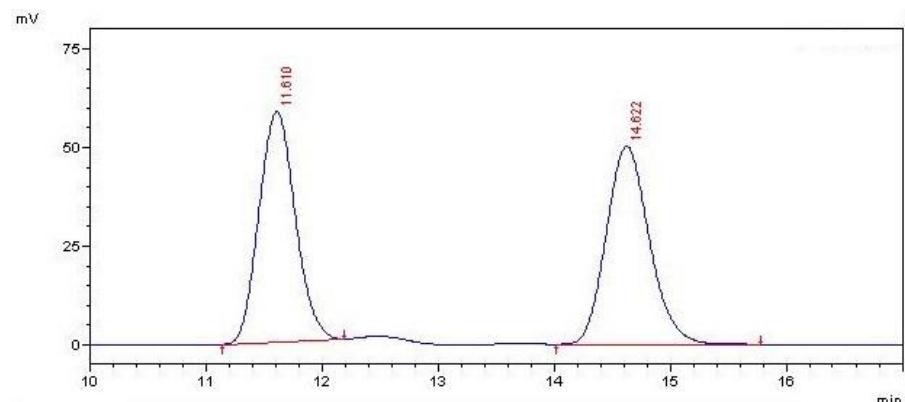
Peak	time	area	area/%
1	<b>8.053</b>	169139	<b>50.269</b>
2	<b>9.461</b>	167326	<b>49.731</b>
total		336465	<b>100.000</b>

**tert-Butyl (R)-3-cyano-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (3q)**

Colorless oil, 14.6 mg, 80% yield, 95% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = +57.8$  ( $c$  0.70,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.8$  Hz, 1H, Ar-H), 7.41-7.39 (m, 3H, Ar-H), 7.39-7.34 (m, 2H, Ar-H), 7.03 (dd,  $J = 9.2$ , 2.8 Hz, 1H, Ar-H), 6.90 (d,  $J = 2.8$  Hz, 1H, Ar-H), 3.81 (s, 3H,  $\text{OCH}_3$ ), 1.61 (s, 9H,  $t\text{Bu}-\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 157.8, 148.6, 133.8, 133.1, 129.5, 129.4, 126.8, 125.5, 117.2, 116.6, 116.4(CN), 110.7, 85.6, 55.8, 53.0, 28.0 ppm. IR (KBr) 2247, 1772, 1739  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4 [M+\text{H}]^+$ : 365.1496 found: 365.1494. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 11.7 min,  $t_R$ (major) = 14.7 min.

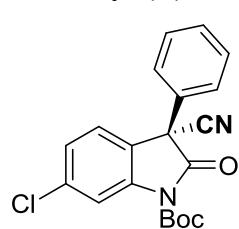


Peak	time	area	area/%
1	<b>11.781</b>	22720	<b>2.399</b>
2	<b>14.790</b>	924414	<b>97.601</b>
total		947134	<b>100.000</b>

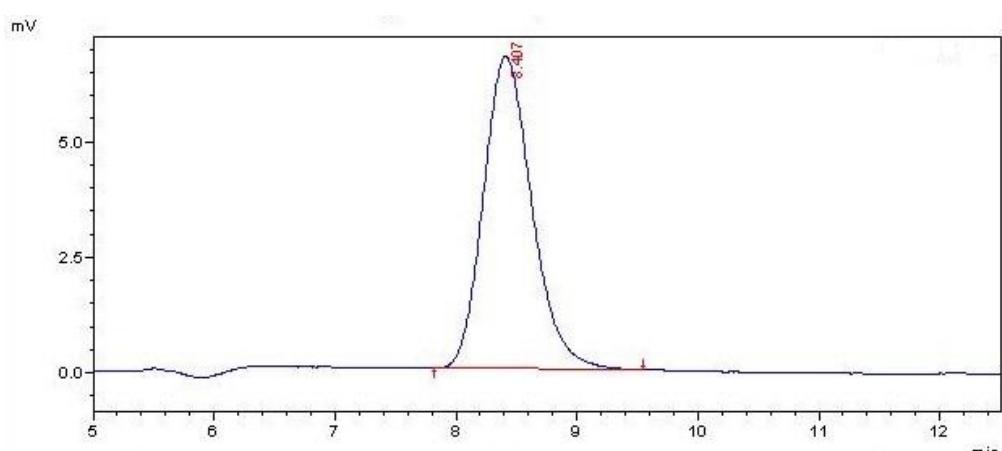


Peak	time	area	area/%
1	<b>11.610</b>	1268993	<b>49.513</b>
2	<b>14.622</b>	1293954	<b>50.487</b>
total		2562947	<b>100.000</b>

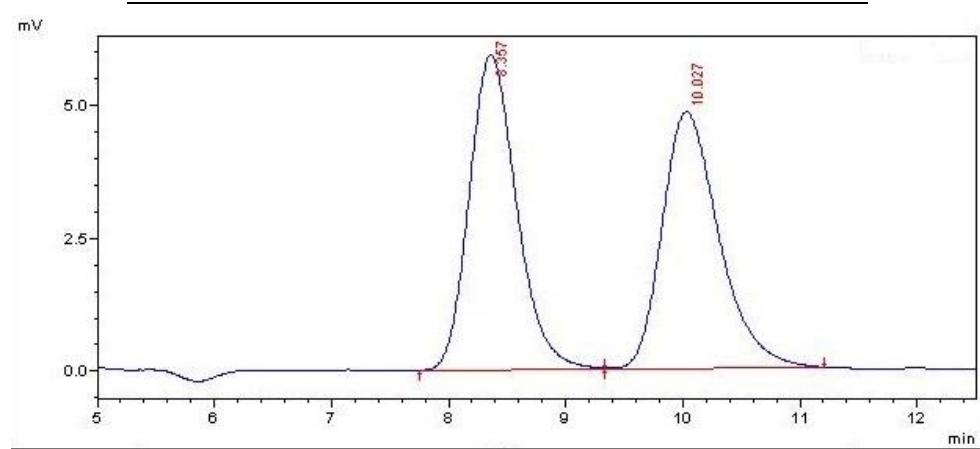
**tert-Butyl (R)-6-chloro-3-cyano-2-oxo-3-phenylindoline-1-carboxylate (3r)**



White solid, 17.0 mg, 92% yield, >99% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 43.8$  ( $c$  0.20,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (s, 1H, Ar-H), 7.41 (t,  $J = 2.8$  Hz, 3H, Ar-H), 7.33-7.31 (m, 4H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 148.2, 140.7, 137.0, 133.2, 129.7, 129.5, 126.7, 126.3, 126.1, 122.8, 116.8, 115.9(CN), 86.4, 52.3, 27.9 ppm. IR (KBr) 2247, 1791, 1736  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{ClN}_3\text{O}_3$  [ $M+\text{NH}_4$ ] $^+$ : 386.1265 found: 386.1264. HPLC on AS-H column (*n*-hexane / *iso*-propanol 95:5, 1.0 mL min $^{-1}$ , 254 nm),  $t_R$ (major) = 8.4 min,  $t_s$ (minor) = 10.0 min.

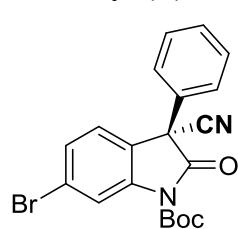


Peak	time	area	area/%
1	<b>8.407</b>	188821	<b>100.000</b>
2			
total		188821	<b>100.000</b>

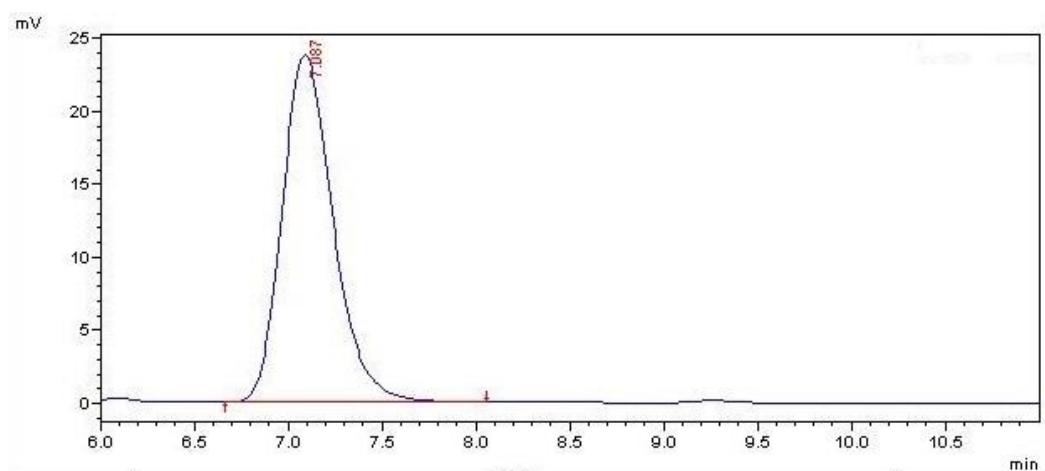


Peak	time	area	area/%
1	<b>8.357</b>	166456	<b>50.587</b>
2	<b>10.027</b>	162593	<b>49.413</b>
total		329048	<b>100.000</b>

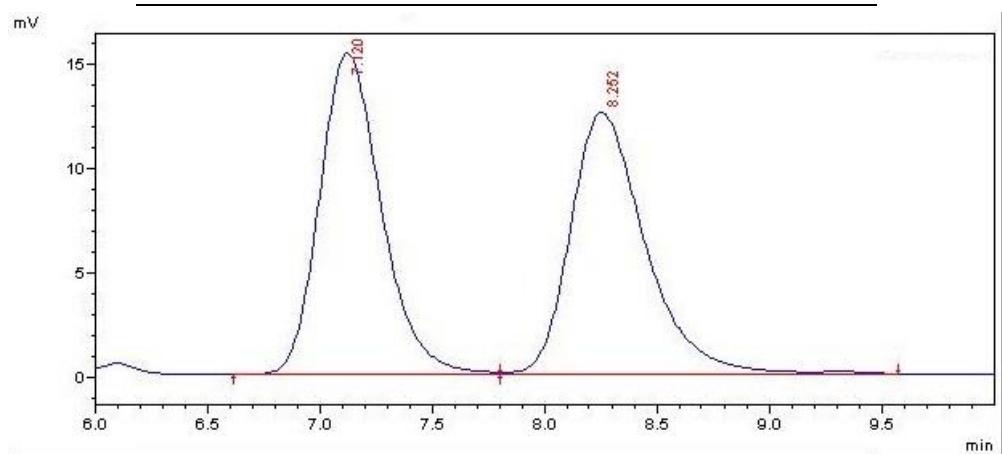
**tert-Butyl (R)-6-bromo-3-cyano-2-oxo-3-phenylindoline-1-carboxylate (3s)**



White solid, 16.9 mg, 82% yield, >99% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 24.3$  ( $c$  0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 1.6$  Hz, 1H, Ar-H), 7.47 (dd,  $J = 8.4, 2.0$  Hz, 1H, Ar-H), 7.41 (t,  $J = 2.8$  Hz, 3H, Ar-H), 7.33–7.31 (m, 2H, Ar-H), 7.25 (d,  $J = 9.2$  Hz, 1H, Ar-H), 1.62 (s, 9H, *t*Bu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 148.2, 140.7, 133.1, 129.7, 129.5, 129.0, 126.7, 126.5, 124.9, 123.3, 119.5, 115.8(CN), 86.4, 52.3, 27.9 ppm. IR (KBr) 2247, 1785, 1734  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{20}\text{H}_{21}\text{BrN}_3\text{O}_3$   $[M+\text{NH}_4]^+$ : 430.0761 found: 430.0760. HPLC on AS-H column (*n*-hexane/*iso*-propanol 90:10, 1.0 mL min $^{-1}$ , 254 nm),  $t_R$ (major) = 7.1 min,  $t_s$ (minor) = 8.3 min.

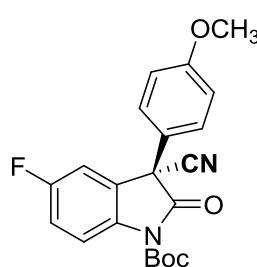


Peak	time	area	area/%
1	7.087	449974	100.000
2			
total		449974	100.000

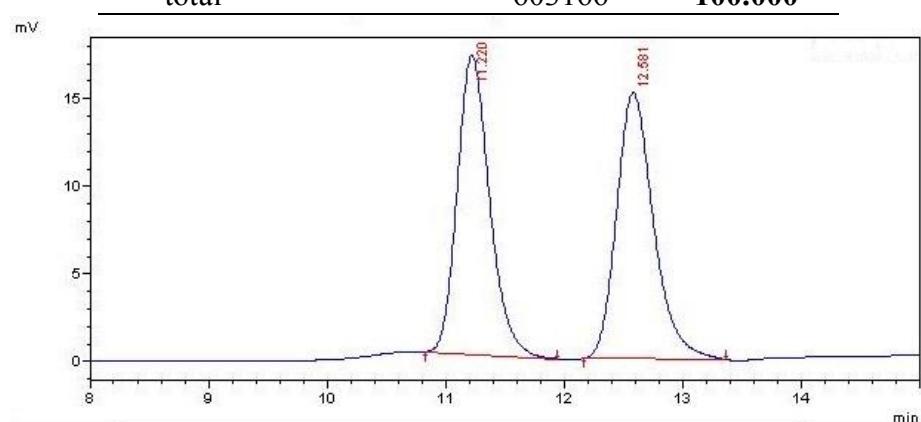
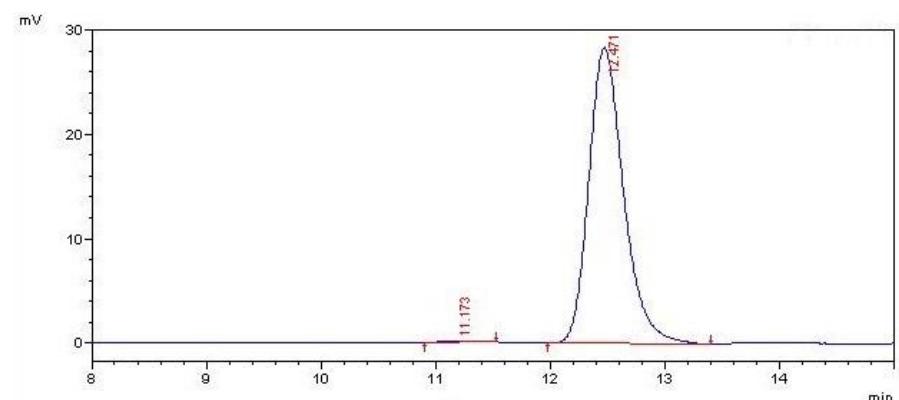


Peak	time	area	area/%
1	7.120	293811	50.296
2	8.252	290351	49.704
total		584162	100.000

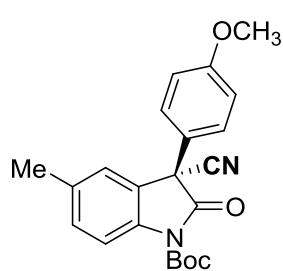
**tert-Butyl(R)-3-cyano-5-fluoro-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate  
(3t)**



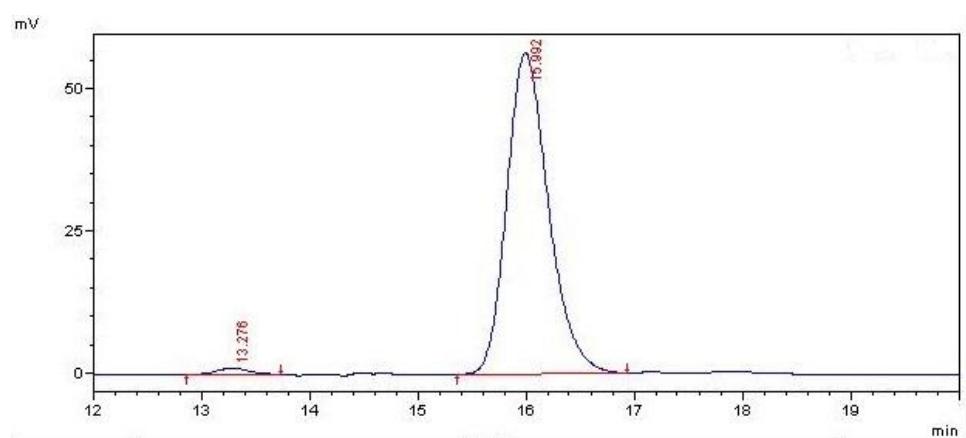
Colorless oil, 16.2 mg, 85% yield, 99% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 42.1$  ( $c$  0.60,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (dd,  $J = 8.8, 4.4$  Hz, 1H, Ar-H), 7.24–7.20 (m, 3H, Ar-H), 7.11 (dd,  $J = 7.2, 2.8$  Hz, 1H, Ar-H), 6.91 (d,  $J = 8.8$  Hz, 2H, Ar-H), 3.80 (s, 3H, OCH<sub>3</sub>), 1.62 (s, 9H, tBu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 160.6, 160.3 (d,  ${}^1J_{C-F} = 245.6$  Hz), 148.5, 135.7 (d,  ${}^4J_{C-F} = 2.7$  Hz), 128.0, 126.1 (d,  ${}^3J_{C-F} = 8.3$  Hz), 124.9, 117.8 (d,  ${}^2J_{C-F} = 22.7$  Hz), 117.5 (d,  ${}^3J_{C-F} = 7.7$  Hz), 116.0(CN), 114.9, 112.9 (d,  ${}^2J_{C-F} = 25.0$  Hz), 86.0, 55.4, 55.0 ( ${}^4J_{C-F} = 1.4$  Hz), 27.9 ppm. IR (KBr) 2247, 1780, 1739 cm<sup>-1</sup>. HRMS: calc. for C<sub>21</sub>H<sub>23</sub>FN<sub>3</sub>O<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 400.1667 found: 400.1668. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm), *ts*(minor) = 11.2 min, *ts*(major) = 12.5 min.



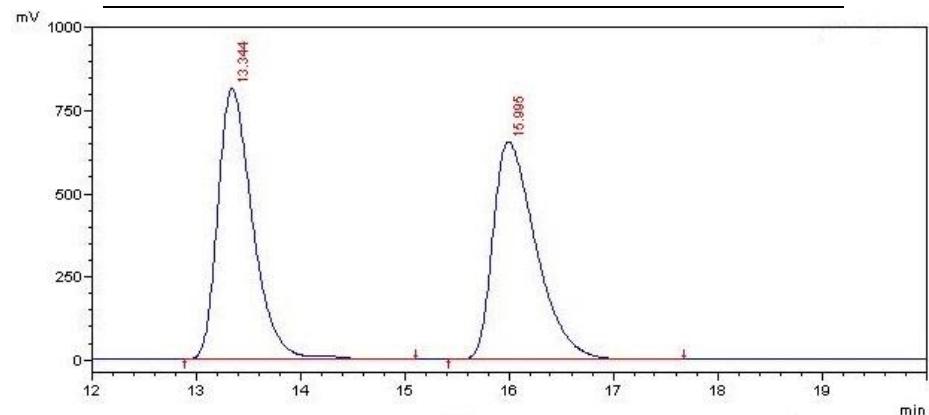
**tert-Butyl (R)-3-cyano-3-(4-methoxyphenyl)-5-methyl-2-oxoindoline-1-carboxylate (3u)**



Colorless oil, 15.7 mg, 83% yield, 97% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 67.9$  ( $c$  0.55, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.30-7.24 (m, 3H, Ar-H), 7.19 (s, 1H, Ar-H), 6.90 (d,  $J = 9.2$  Hz, 2H, Ar-H), 3.80 (s, 3H, OCH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 1.61 (s, 9H, tBu-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 160.4, 148.6, 137.3, 135.8, 131.4, 128.1, 125.72, 125.69, 124.5, 116.7(CN), 115.7, 114.7, 85.5, 55.4, 52.1, 27.9, 21.0 ppm. IR (KBr) 2245, 1774, 1739 cm<sup>-1</sup>. HRMS: calc. for C<sub>22</sub>H<sub>26</sub>N<sub>3</sub>O<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 396.1918 found: 396.1914. HPLC on AD-H column (*n*-hexane/*iso*-propanol 98:2, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 13.3 min,  $t_R$ (major) = 16.0 min.

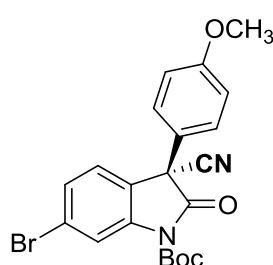


Peak	time	area	area/%
1	<b>13.276</b>	21155	<b>1.382</b>
2	<b>15.992</b>	1509864	<b>98.618</b>
total		1531019	<b>100.000</b>

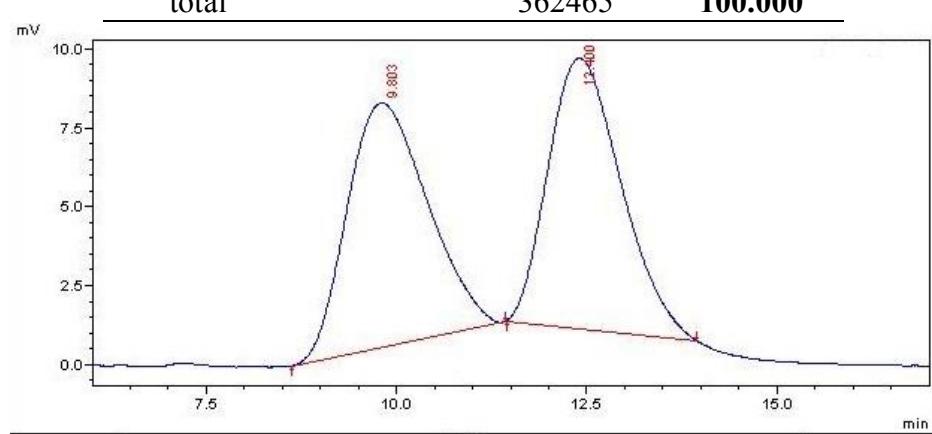
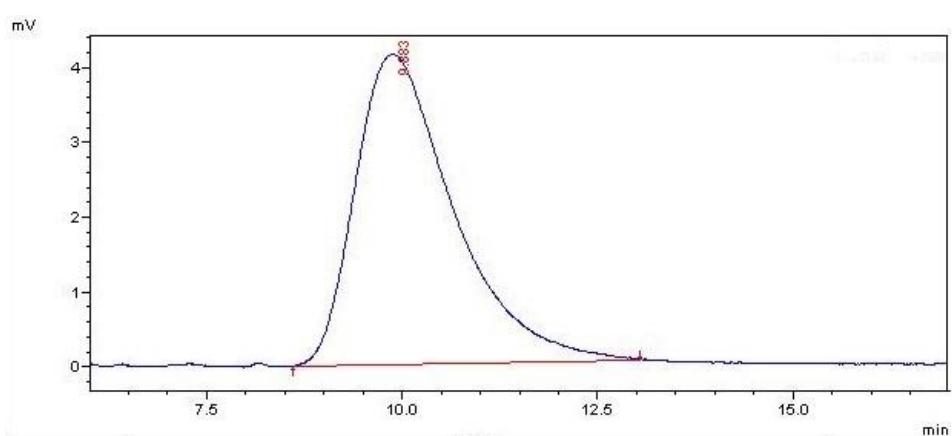


Peak	time	area	area/%
1	<b>13.344</b>	18977782	<b>50.228</b>
2	<b>15.995</b>	18805256	<b>49.772</b>
total		37783038	<b>100.000</b>

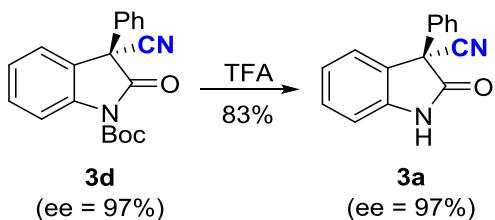
**tert-Butyl (R)-6-bromo-3-cyano-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate (3v)**



Colorless oil, 19.3 mg, 87% yield, >99% ee, eluent PE/EA (15:1, V/V),  $R_f = 0.40$ ,  $[\alpha]^{20}_D = 42.3$  ( $c$  0.60,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 2.0$  Hz, 1H, Ar-H), 7.46 (dd,  $J = 8.4, 2.0$  Hz, 1H, Ar-H), 7.24-7.21 (m, 3H, Ar-H), 6.90 (dd,  $J = 6.8, 2.0$  Hz, 2H, Ar-H), 3.80 (s, 3H, OCH<sub>3</sub>), 1.61 (s, 9H, tBu-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 160.6, 148.3, 140.7, 128.9, 128.0, 126.5, 124.9, 124.8, 123.4, 119.5, 116.0(CN), 114.8, 86.3, 55.4, 51.7, 27.9 ppm. IR (KBr) 2247, 1780, 1743 cm<sup>-1</sup>. HRMS: calc. for C<sub>21</sub>H<sub>23</sub>BrN<sub>3</sub>O<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 460.0866 found: 460.0865. HPLC on AS-H column (*n*-hexane/*iso*-propanol 90:10, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_R$ (major) = 9.8 min,  $t_s$ (minor) = 12.4 min.

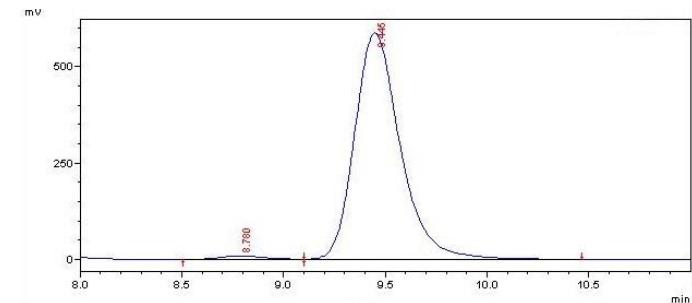


## Control Experiment

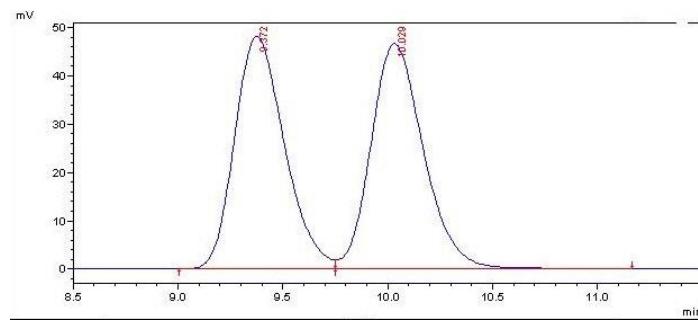


### (R)-2-oxo-3-phenylindoline-3-carbonitrile (3a)

97% ee **3d** (0.1 mmol, 33.4 mg) treats with TFA (3.0 equiv) in DCM (2.0 mL) at room temperature for 24h, quenching with  $\text{NaHCO}_3$  (aq.). Routine aqueous workup and silica gel column chromatography was performed to purify and get the white solid **3a**, 19.4 mg, 83%, m.p. 152-153 °C, 97% ee, eluent PE/EA (2:1, V/V),  $R_f = 0.50$ ,  $[\alpha]^{20}_D = 86.5$  (*c* 0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (s, 1H, NH), 7.42-7.38 (m, 6H, Ar-H), 7.33 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.18 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.03 (d, *J* = 7.6 Hz, 1H, Ar-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 140.5, 133.5, 130.8, 129.4, 129.3, 126.8, 126.5, 125.7, 124.3, 116.5(CN), 111.2, 52.4 ppm. IR (neat) 2245, 1730  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$  [ $M+\text{NH}_4$ ] $^+$ : 252.1132 found: 252.1134. HPLC on AD-H column (*n*-hexane/*iso*-propanol 85:15, 1.0 mL min $^{-1}$ , 254 nm),  $t_{\text{s}}(\text{minor}) = 8.7$  min,  $t_{\text{R}}(\text{major}) = 9.4$  min.



Peak	time	area	area/%
1	<b>8.780</b>	121179	<b>1.311</b>
2	<b>9.445</b>	9121461	<b>98.689</b>
total		9242640	<b>100.000</b>

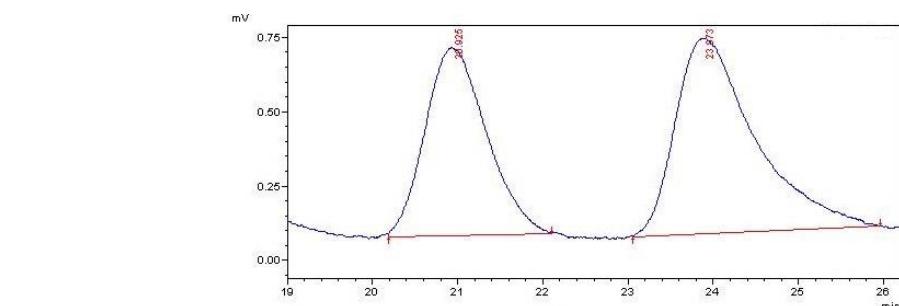


Peak	time	area	area/%
1	<b>9.372</b>	793027	<b>49.474</b>
2	<b>10.029</b>	809884	<b>50.526</b>
total		1602912	<b>100.000</b>

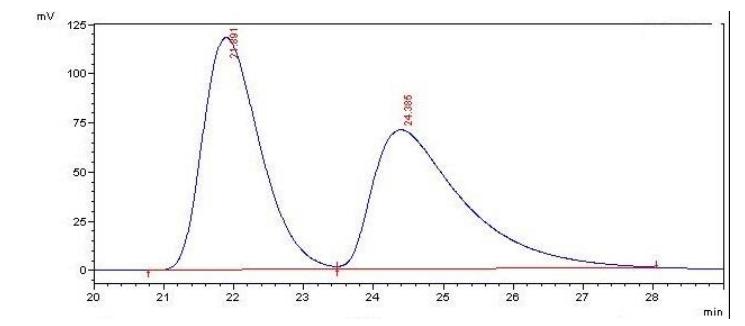
After stirring a mixture of  $Zn(BF_4)_2 \cdot 6H_2O$  (1.8 mg, 0.005 mmol, 10 mol %) and  $(R,R)$ -DBFOX/Ph (2.8 mg, 0.006 mmol, 12 mol %) in  $CH_2Cl_2$  (1.0 mL) with dry 4 Å MS (20 mg) at room temperature for 2 h, substrates **1b-1c** (0.05 mmol) was added. After stirring 30 min, cyanate reagent **2** (16 mg, 0.1 mmol, 2.0 equiv) and 2,6-lutidine (0.12 mmol, 1.2 equiv, 7  $\mu$ L) were added successively. And the reaction mixture was stirred for 24 h at rt under argon atmosphere. Routine aqueous workup and silica gel column chromatography was performed to purify the crude product **3b-3c**.

### **(R)-1-benzyl-2-oxo-3-phenylindoline-3-carbonitrile (3b)**

Colorless oil, 6.5 mg, 40% yield, 15% ee, eluent PE/EA (10:1, V/V),  $R_f = 0.25$ .  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.51-7.46 (m, 5 H), 7.39-7.19 (m, 9 H, Ar-H), 7.17-7.09 (m, 2 H, Ar-H), 6.98 (t,  $J = 7.0$  Hz, 1 H, Ar-H), 6.76 (d,  $J = 6.7$  Hz, 1 H, Ar-H), 5.05 (ab,  $J = 15.6$  Hz, 1 H, CH<sub>2</sub>), 4.99 (ab,  $J = 15.6$  Hz, 1 H, CH<sub>2</sub>);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  169.8, 142.7, 136.0, 134.2, 130.1, 129.8, 129.4, 128.3, 127.7, 126.6, 126.2, 125.7, 124.8, 117.3(CN), 111.5, 52.0, 44.3 ppm. IR (neat): 2244, 1731  $cm^{-1}$ . HRMS: calc. for  $C_{22}H_{17}N_2O$  [ $M+H$ ]<sup>+</sup>: 325.1335 found: 325.1335. HPLC on AD-H column (*n*-hexane/*iso*-propanol 90:10, 1.0 mL min<sup>-1</sup>, 254 nm),  $t_s$ (minor) = 21.0 min,  $t_R$ (major) = 24.1 min.



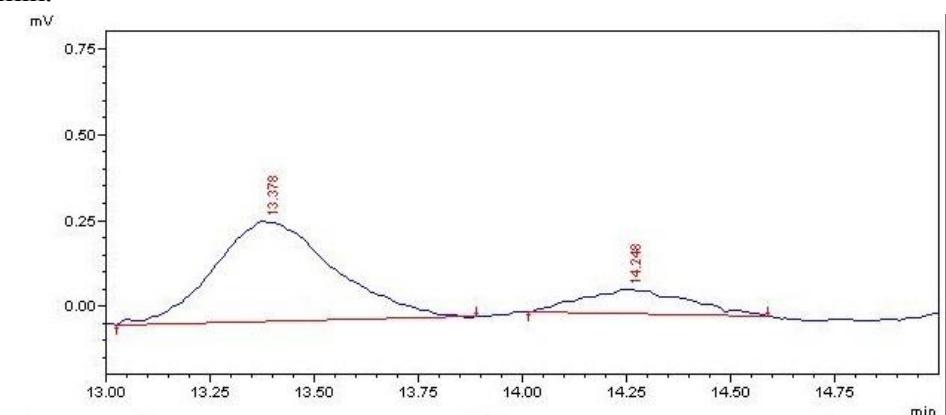
Peak	time	area	area/%
1	<b>20.925</b>	31706	<b>42.660</b>
2	<b>23.873</b>	42617	<b>57.340</b>
total		74324	<b>100.000</b>



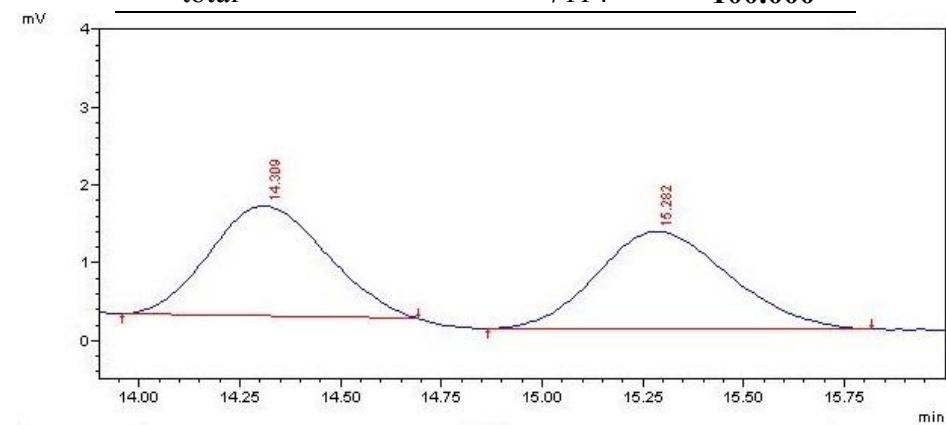
Peak	time	area	area/%
1	<b>21.891</b>	6734454	<b>51.317</b>
2	<b>24.385</b>	6388913	<b>48.683</b>
total		13123366	<b>100.000</b>

**(R)-benzyl 3-cyano-2-oxo-3-phenylindoline-1-carboxylate (3c)**

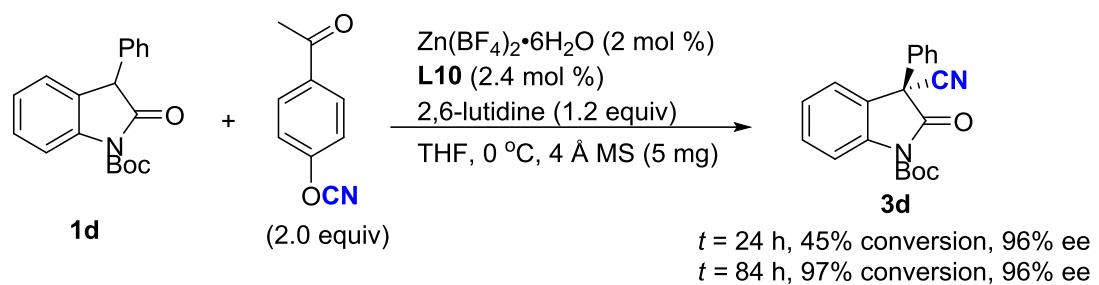
White solid, 13.8 mg, 75% yield, 65% ee, eluent PE/EA (10:1, V/V),  $R_f = 0.30$ .  $[\alpha]^{20}_D = 25.6$  ( $c$  0.30,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.4$  Hz, 1H, Ar-H), 7.52-7.47 (m, 3H, Ar-H), 7.41-7.34 (m, 10H, Ar-H), 5.44 (dd,  $J = 27.6, 12$  Hz, 2H,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 150.1, 139.3, 134.2, 133.5, 131.1, 129.6, 129.5, 128.7, 128.2, 126.7, 126.3, 125.5, 124.5, 116.1(CN), 116.08, 69.4, 52.6 ppm. IR (KBr) 2242, 1775, 1720  $\text{cm}^{-1}$ . HRMS: calc. for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3$   $[M+\text{H}]^+$ : 369.1234 found: 369.1236. HPLC on AD-H column (*n*-hexane / *iso*-propanol 90:10, 1.0 mL min $^{-1}$ , 254 nm),  $t_{\text{R}}$ (major) = 13.4 min,  $t_{\text{s}}$ (minor) = 14.3 min.



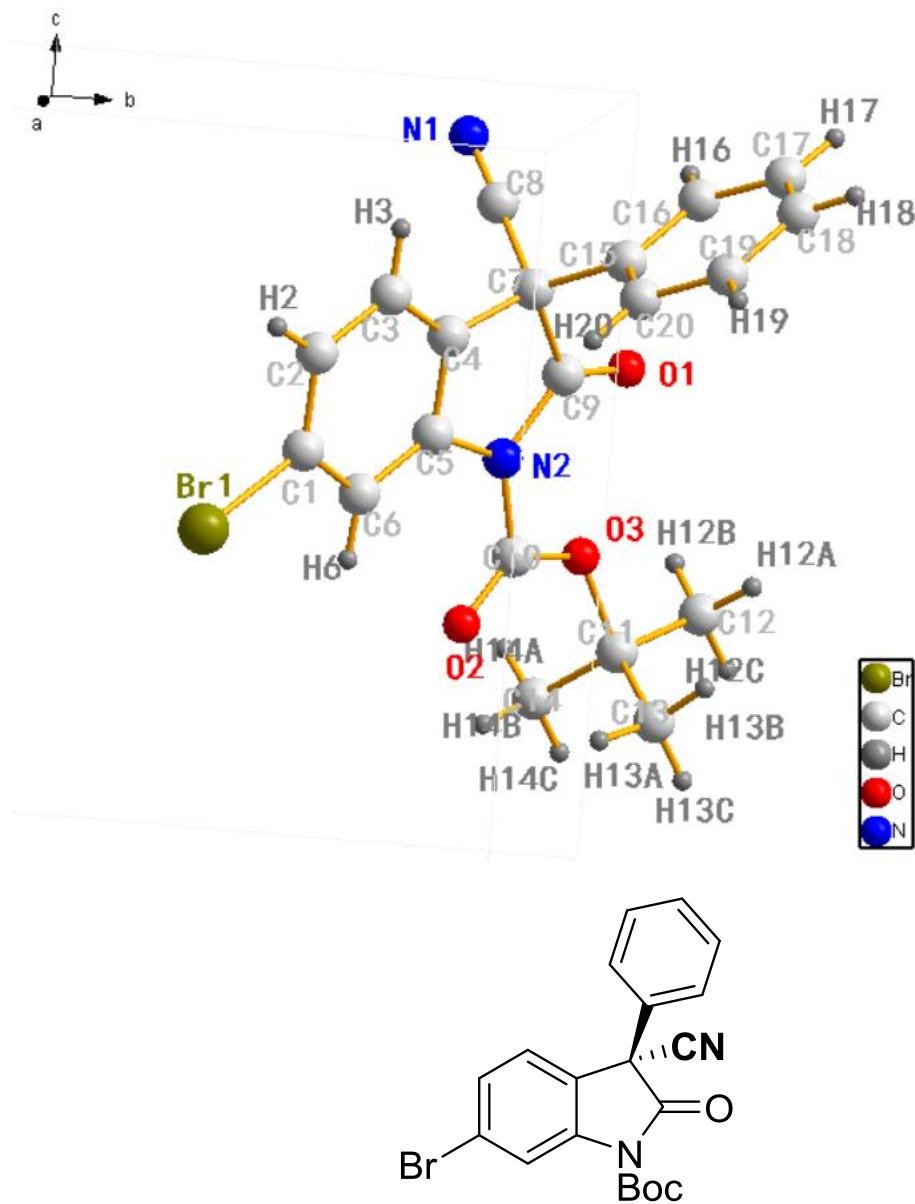
Peak	time	area	area/%
1	<b>13.378</b>	5844	<b>82.152</b>
2	<b>14.248</b>	1270	<b>17.848</b>
total		7114	<b>100.000</b>



Peak	time	area	area/%
1	<b>14.309</b>	28484	<b>49.655</b>
2	<b>15.282</b>	28879	<b>50.345</b>
total		57363	<b>100.000</b>



#### 4. X-Ray structure of **3s** (CCDC 1539670)



**Table S1.** Crystal data and structure refinement for **3s**.

Formula sum	Br <sub>2</sub> C <sub>40</sub> H <sub>34</sub> O <sub>6</sub> N <sub>4</sub>
Formula weight	826.54 g/mol
Crystal system	monoclinic
Space-group	P 1 21 1 (4)
Cell parameters	a=6.3659(7) Å b=14.6244(17) Å c=10.2478(12) Å β=97.97(0)°
Cell ratio	a/b=0.4353 b/c=1.4271 c/a=1.6098
Cell volume	944.84(56) Å <sup>3</sup>
Calc. density	1.45255 g/cm <sup>3</sup>
Pearson code	mP86
Formula type	NO <sub>2</sub> P <sub>3</sub> Q <sub>17</sub> R <sub>20</sub>
Wyckoff sequence	a43
_diffrn_ambient_temperature	296(2)
_diffrn_radiation_wavelength	0.71073
_diffrn_radiation_type	MoK\alpha
_diffrn_reflns_number	11456
_diffrn_reflns_av_unetI/netI	0.0531
_diffrn_reflns_av_R_equivalents	0.0246
_diffrn_reflns_limit_h_min	-8
_diffrn_reflns_limit_h_max	8
_diffrn_reflns_limit_k_min	-19
_diffrn_reflns_limit_k_max	19
_diffrn_reflns_limit_l_min	-13
_diffrn_reflns_limit_l_max	13
_diffrn_reflns_theta_min	2.007
_diffrn_reflns_theta_max	28.410
_diffrn_reflns_theta_full	25.242
_diffrn_measured_fraction_theta_max	0.996
_diffrn_measured_fraction_theta_full	0.999
_diffrn_reflns_Laue_measured_fraction_max	0.996
_diffrn_reflns_Laue_measured_fraction_full	0.999
_diffrn_reflns_point_group_measured_fraction_max	0.981
_diffrn_reflns_point_group_measured_fraction_full	0.984
_reflns_number_total	4666
_reflns_number_gt	4043
_reflns_threshold_expression	'I > 2\s(I)'
_reflns_Friedel_coverage	0.898
_reflns_Friedel_fraction_max	0.965
_reflns_Friedel_fraction_full	0.968

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for **3s**.

U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Br1 Br	0.82631(5)	0.69702(2)	0.45906(3)	0.06453(13)
C1 C	0.6567(4)	0.7694(2)	0.5573(3)	0.0414(6)
C9 C	0.1002(4)	0.95875(19)	0.6355(3)	0.0332(6)
C3 C	0.6025(5)	0.83397(19)	0.7636(3)	0.0405(6)
H3 H	0.6436	0.8418	0.8536	0.049
C15 C	0.3626(4)	1.03008(19)	0.8111(3)	0.0363(6)
O3 O	-0.0950(3)	0.97275(16)	0.3847(2)	0.0465(5)
C2 C	0.7208(5)	0.78015(19)	0.6904(3)	0.0441(7)
H2 H	0.8431	0.7513	0.7307	0.053
C10 C	0.0769(5)	0.9240(2)	0.3926(3)	0.0394(6)
O1 O	-0.0524(3)	1.00452(17)	0.6374(2)	0.0481(5)
C4 C	0.4221(4)	0.87584(17)	0.7008(3)	0.0331(5)
C7 C	0.2713(4)	0.93877(19)	0.7578(3)	0.0321(5)
N2 N	0.1691(3)	0.91469(17)	0.5263(2)	0.0348(5)
C18 C	0.5143(6)	1.1976(3)	0.9053(4)	0.0775(12)
H18 H	0.5674	1.2534	0.9386	0.093
C13 C	-0.0580(8)	1.0567(3)	0.1815(4)	0.0859(14)
H13A H	0.0537	1.0168	0.1624	0.129
H13B H	0.0016	1.1067	0.2349	0.129
H13C H	-0.1332	1.0799	0.1005	0.129
N1 N	0.0892(5)	0.8524(2)	0.9348(3)	0.0627(8)
C20 C	0.5526(5)	1.0618(2)	0.7807(4)	0.0527(8)
H20 H	0.6305	1.0267	0.7289	0.063
C5 C	0.3586(4)	0.86382(17)	0.5665(2)	0.0338(5)
C12 C	-0.3770(8)	1.0641(4)	0.2983(4)	0.0927(17)
H12A H	-0.3119	1.1173	0.3415	0.139
H12B H	-0.4518	1.0311	0.3585	0.139
H12C H	-0.4746	1.0825	0.2230	0.139
C17 C	0.3249(7)	1.1676(3)	0.9341(4)	0.0736(12)
H17 H	0.2466	1.2037	0.9844	0.088
C14 C	-0.3016(7)	0.9230(3)	0.1780(4)	0.0718(11)
H14A H	-0.3776	0.8858	0.2329	0.108
H14B H	-0.1895	0.8877	0.1491	0.108
H14C H	-0.3969	0.9434	0.1027	0.108
C11 C	-0.2094(5)	1.0041(2)	0.2547(3)	0.0483(7)
C16 C	0.2473(6)	1.0833(2)	0.8889(3)	0.0541(8)
H16 H	0.1185	1.0623	0.9103	0.065

C6 C	0.4743(5)	0.8097(2)	0.4908(3)	0.0397(6)
H6 H	0.4325	0.8009	0.4011	0.048
C8 C	0.1661(4)	0.8907(2)	0.8578(3)	0.0406(6)
C19 C	0.6287(6)	1.1467(3)	0.8274(5)	0.0718(12)
H19 H	0.7566	1.1687	0.8060	0.086
O2 O	0.1550(4)	0.8881(2)	0.3057(2)	0.0665(8)

**Table S3.** Bond lengths [Å] and angles [°] for **3s**.

Br1 C1 1.898(3)

C1 C2 1.377(4)

C1 C6 1.393(4)

C9 O1 1.182(3)

C9 N2 1.413(3)

C9 C7 1.570(4)

C3 C4 1.379(4)

C3 C2 1.381(4)

C15 C20 1.371(4)

C15 C16 1.394(4)

C15 C7 1.527(4)

O3 C10 1.300(4)

O3 C11 1.499(4)

C10 O2 1.199(4)

C10 N2 1.421(4)

C4 C5 1.391(4)

C4 C7 1.505(4)

C7 C8 1.478(4)

N2 C5 1.428(3)

C18 C17 1.354(6)

C18 C19 1.372(6)

C13 C11 1.511(5)

N1 C8 1.133(4)

C20 C19 1.392(5)

C5 C6 1.390(4)

C12 C11 1.497(5)

C17 C16 1.383(5)

C14 C11 1.497(5)

C2 C1 C6 123.3(3)

C2 C1 Br1 118.5(2)

C6 C1 Br1 118.2(2)

O1 C9 N2 128.1(3)

O1 C9 C7 125.0(2)  
N2 C9 C7 106.9(2)  
C4 C3 C2 118.8(3)  
C20 C15 C16 119.5(3)  
C20 C15 C7 121.3(3)  
C16 C15 C7 119.3(3)  
C10 O3 C11 121.6(2)  
C1 C2 C3 119.6(3)  
O2 C10 O3 128.8(3)  
O2 C10 N2 121.1(3)  
O3 C10 N2 110.1(2)  
C3 C4 C5 121.0(2)  
C3 C4 C7 128.7(2)  
C5 C4 C7 110.3(2)  
C8 C7 C4 110.7(2)  
C8 C7 C15 110.8(2)  
C4 C7 C15 116.2(2)  
C8 C7 C9 108.1(2)  
C4 C7 C9 102.3(2)  
C15 C7 C9 108.1(2)  
C9 N2 C10 126.1(2)  
C9 N2 C5 110.6(2)  
C10 N2 C5 123.2(2)  
C17 C18 C19 120.7(4)  
C15 C20 C19 120.0(3)  
C4 C5 C6 121.4(2)  
C4 C5 N2 109.7(2)  
C6 C5 N2 128.9(2)  
C18 C17 C16 120.3(4)  
C12 C11 O3 101.1(3)  
C12 C11 C14 112.2(4)  
O3 C11 C14 109.4(3)  
C12 C11 C13 112.3(4)  
O3 C11 C13 109.4(3)  
C14 C11 C13 111.9(3)  
C17 C16 C15 119.8(4)  
C5 C6 C1 116.0(3)  
N1 C8 C7 178.4(3)  
C18 C19 C20 119.7(4)

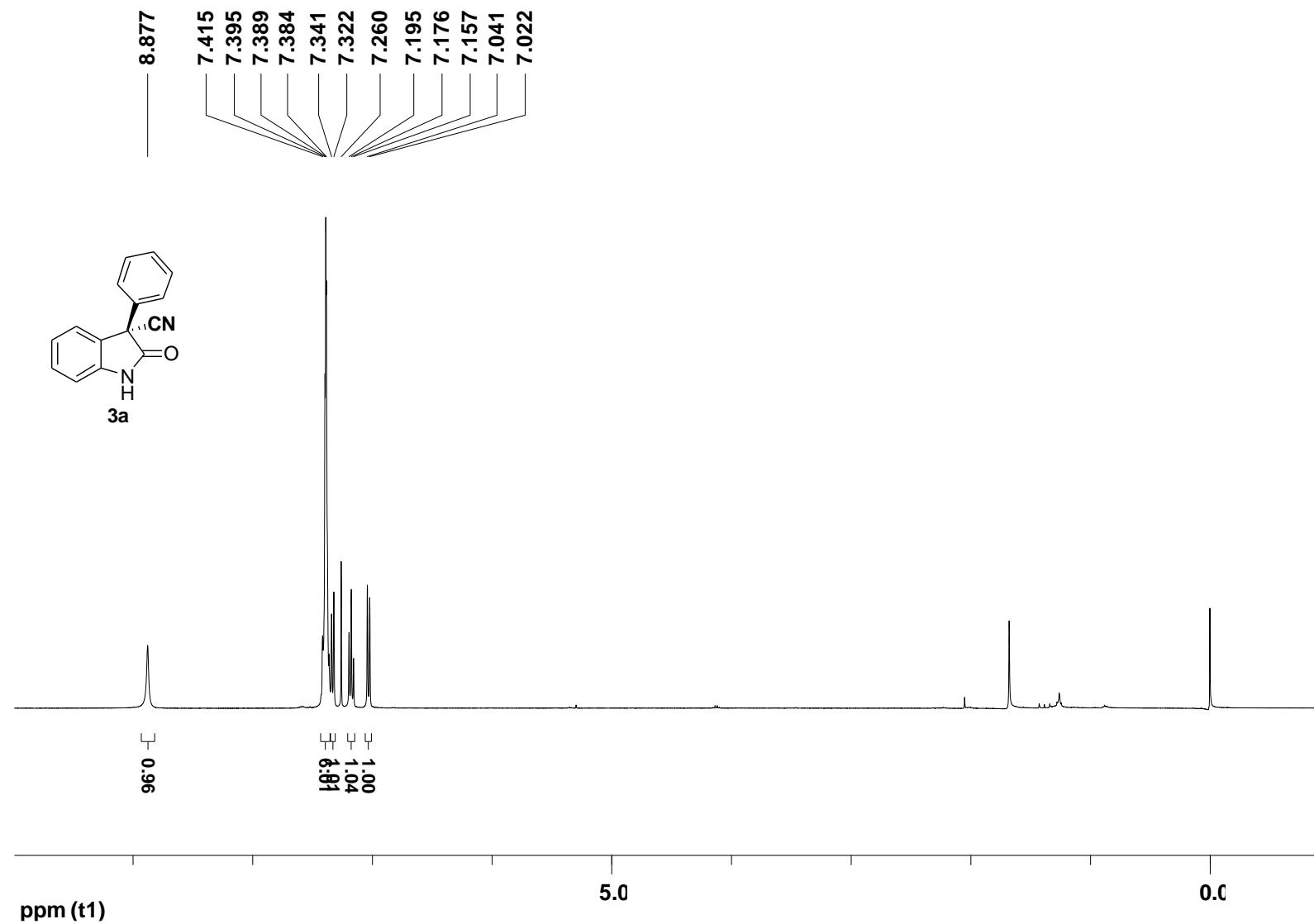
**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2$ ) for **3s**.

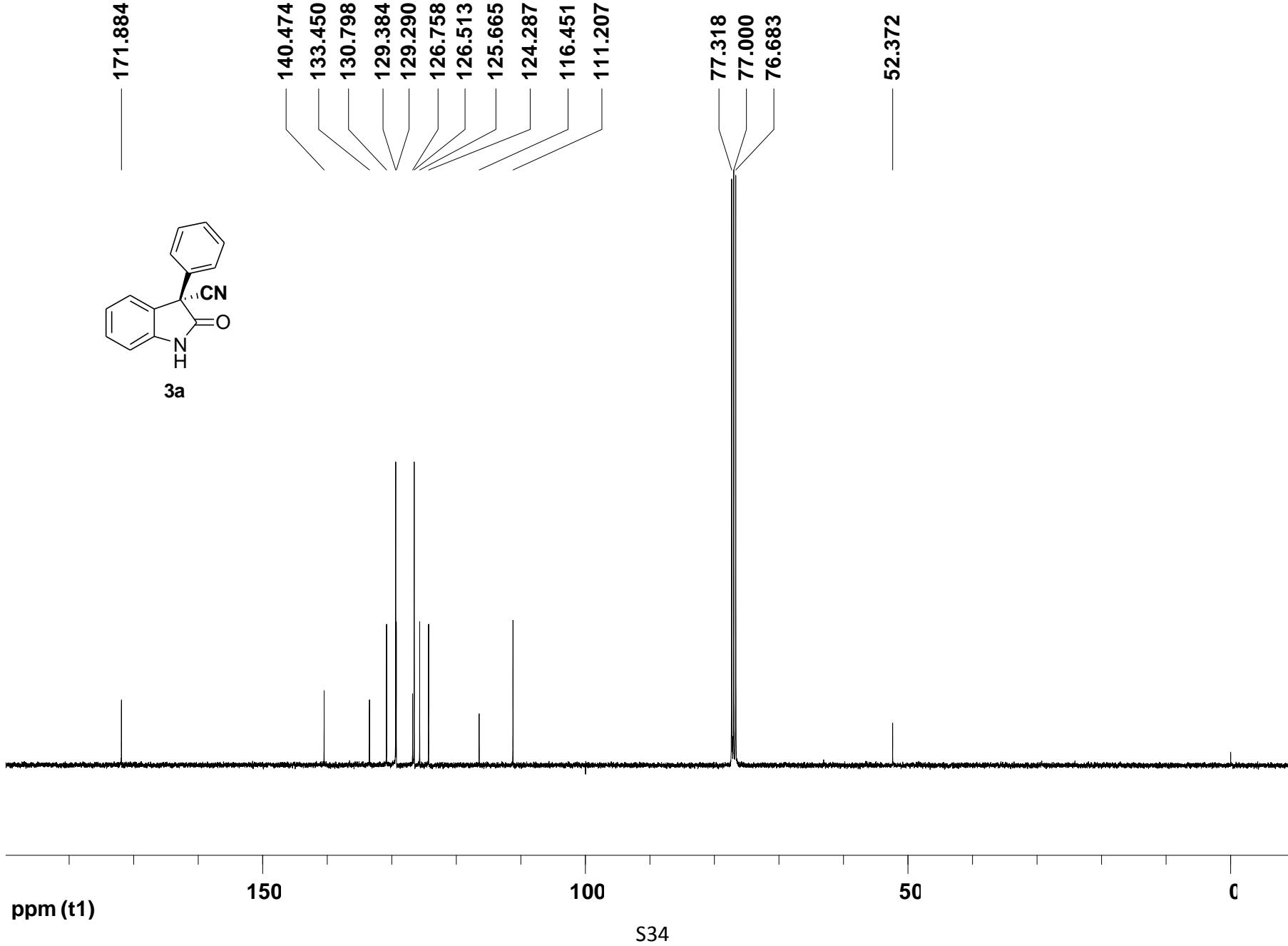
	U11	U22	U33	U23	U13	U12
Br1	0.06006	0.06201	0.07063	0.02270	0.00962	-0.02240
C1	0.04095	0.03372	0.04935	0.00614	0.00755	-0.00824
C9	0.02948	0.04157	0.02761	-0.00003	0.00536	0.00020
C3	0.04332	0.03865	0.03619	0.00646	-0.00108	-0.00085
C15	0.03564	0.03884	0.03159	0.00506	-0.00167	-0.00221
O3	0.04493	0.06243	0.03044	0.01624	-0.00280	-0.00030
C2	0.04009	0.03743	0.05306	0.01053	-0.00324	-0.00227
C10	0.03671	0.05020	0.03087	0.00145	0.00062	-0.00047
O1	0.03682	0.07397	0.03388	0.01713	0.00444	-0.00065
C4	0.03326	0.03080	0.03502	0.00416	0.00353	0.00104
C7	0.03018	0.03810	0.02760	0.00213	0.00447	-0.00090
N2	0.03231	0.04416	0.02827	0.00667	0.00391	-0.00049
C18	0.08630	0.04605	0.08751	0.00266	-0.03222	-0.01834
C13	0.08538	0.08988	0.07077	-0.02123	-0.01044	0.03654
N1	0.05570	0.08516	0.04566	-0.00656	0.00849	0.01870
C20	0.03411	0.04450	0.07876	0.00237	0.00640	-0.00329
C5	0.03150	0.03450	0.03366	0.00277	0.00171	0.00050
C12	0.08668	0.12135	0.06641	0.06249	-0.01061	-0.00159
C17	0.10326	0.05888	0.05911	0.01182	0.00213	-0.02295
C14	0.06880	0.07977	0.05971	-0.00964	-0.01509	-0.00606
C11	0.04814	0.05642	0.03457	0.00470	-0.00874	0.00517
C16	0.06545	0.05592	0.04325	0.00874	0.01391	-0.00880
C6	0.04184	0.04217	0.03417	0.00401	0.00409	-0.00638
C8	0.03669	0.05439	0.03169	0.00131	0.00287	0.00375
C19	0.04528	0.05093	0.11346	-0.00579	-0.01290	0.00255
O2	0.06153	0.10435	0.03148	0.03268	0.00490	-0.00591

## 5. References

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## 6. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra





S34

