Supporting Information for

Catalytic Asymmetric Chemodivergent Arylative Dearomatization of Tryptophols

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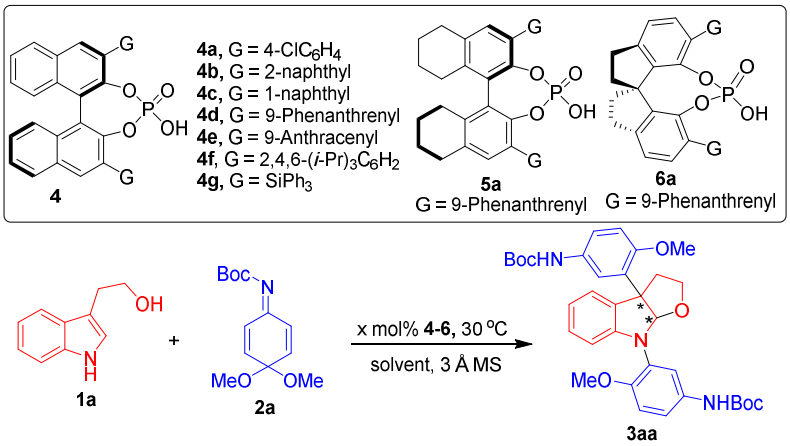
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Enantiomeric excesses (*ee*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric ratios by chiral HPLC were Chiralpak IA, IB, AD-H and IC columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compound **8** was CuKα (λ = 1.54178), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography were distilled before use. All starting materials commercially available were used directly. Substrates **1** and **2** were synthesized according to the literature method.[1]

2. Screening of catalysts and condition optimization

Table 1. Screening of Catalysts and optimization of reaction conditions[a]



entry	**Cat.**	solvent	**2a**:**1a**	x	yield (%)[b]	dr[c]	ee (%)[d]
1	**4a**	THF	1:1.2	20	44	>95:5	58
2	**4b**	THF	1:1.2	20	34	>95:5	89
3	**4c**	THF	1:1.2	20	51	>95:5	70
4	**4d**	THF	1:1.2	20	31	>95:5	96
5	**4e**	THF	1:1.2	20	31	>95:5	95

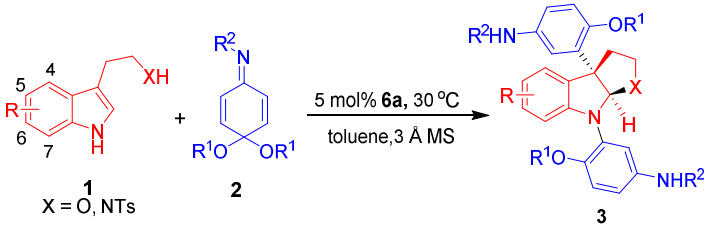
1. a) L. Han, C. Liu, W. Zhang, X.-X. Shi, S.-L. You, *Chem. Commun.* **2014**, *50*, 1231; b) T. Hashimoto, H. Nakatsu, Y. Takiguchi, K. Maruoka, *J. Am. Chem. Soc.* **2013**, *135*, 16010.

6	**4f**	THF	1:1.2	20	21	>95:5	96
7	**4g**	THF	1:1.2	20	23	>95:5	93
8	**4d**	EtOAc	1:1.2	20	60	>95:5	97
9	**4d**	CH_3CN	1:1.2	20	60	>95:5	92
10	**4d**	$CHCl_3$	1:1.2	20	58	>95:5	96
11	**4d**	acetone	1:1.2	20	26	>95:5	90
12	**4d**	toluene	1:1.2	20	78	>95:5	96
13	**5a**	toluene	1:1.2	20	59	>95:5	96
14	**6a**	toluene	1:1.2	20	48	>95:5	-99
15	**6a**	toluene	1:2	20	65	>95:5	-99
16	**6a**	toluene	1:4	20	58	>95:5	-98
17	**6a**	toluene	2.5:1	20	99	>95:5	-99
18	**6a**	toluene	4:1	20	99	>95:5	-96
19	**6a**	toluene	2.5:1	10	99	>95:5	-98
20	**6a**	toluene	2.5:1	5	92	>95:5	-99

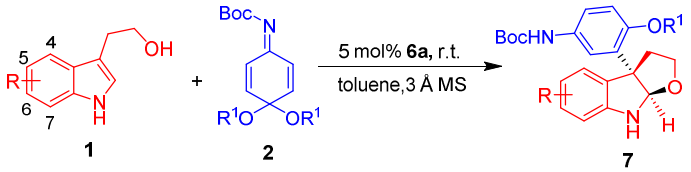
[a] Unless otherwise indicated, the reaction was carried out at the 0.05 mmol scale in a solvent (0.5mL) for 12 h. [b] Isolated yield. [c] The *dr* value was determined by HPLC and ^{1}H NMR. [d] The *ee* value was determined by HPLC.

3. General procedure for the synthesis of products 3 and 7

For chiral products 3 and 7:



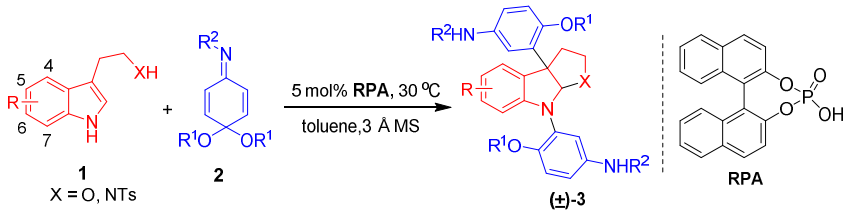
The solution of quinone imine ketal **2** (0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1** (0.1 mmol), catalyst **6a** (0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure compound **3**.



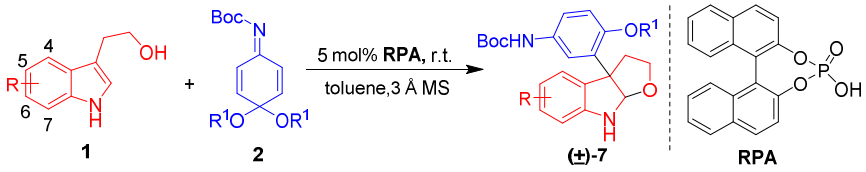
To the mixture of tryptophol **1** (0.4 mmol), catalyst **6a** (0.005 mmol) and 3 Å MS (100 mg),

was added toluene (2 mL). Then, the solution of quinone imine ketal **2** (0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure compound **7**.

For racemic products 3 and 7:



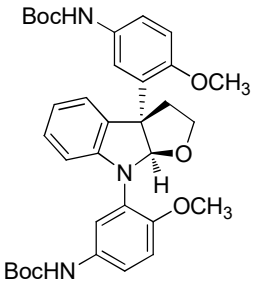
The solution of quinone imine ketal **2** (0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1** (0.1 mmol), racemic phosphoric acid **RPA** (0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford racemic compound (±)-**3**.



To the mixture of tryptophol **1** (0.4 mmol), racemic phosphoric acid **RPA** (0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2** (0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford racemic compound (±)-**7**.

4. Characterization data of products 3 and 7

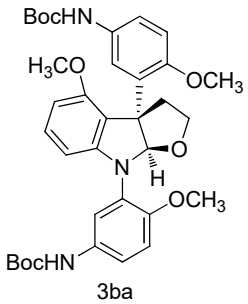
di-*tert*-butyl (((3a*R*,8a*R*)-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene)) dicarbamate (3aa):



3aa

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1a** (16.1 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3aa** (55.5 mg) in 92% yield as white solid.

m.p. 117–120 °C; $[\alpha]_D^{20}$ = +94.5 (c 0.9, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44 – 7.31 (m, 3H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.31 (s, 1H), 6.11 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.77 – 3.67 (m, 7H), 2.89 – 2.80 (m, 1H), 2.53 – 2.45 (m, 1H), 1.50 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.8, 153.1, 150.8, 148.4, 132.7, 132.3, 131.8, 131.1, 130.3, 127.7, 124.5, 118.2, 112.8, 112.2, 108.0, 102.2, 80.1, 67.1, 59.4, 55.8, 55.7, 39.8, 28.3, 28.2; IR (KBr): 2976, 1699, 1598, 1512, 1232, 1161, 1025, 847, 811, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{41}N_3O_7+Na)^+$ requires m/z 626.2843, found m/z 626.2842; The enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.663 (major), t_R = 9.230 (minor).



3ba

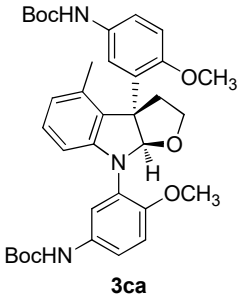
di-*tert*-butyl (((3a*S*,8a*R*)-4-methoxy-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ba):

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of

tryptophol **1b** (19.1 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ba** (47 mg) in 74% yield as white solid.

m.p. 116–118 °C; $[\alpha]_D^{20}$ = +51.0 (c 0.8, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (s, 1H), 7.32 (s, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.88 – 6.80 (m, 3H), 6.39 (s, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 6.29 (s, 1H), 6.12 (d, *J* = 7.9 Hz, 1H), 5.87 (s, 1H), 4.15 (t, *J* = 7.3 Hz, 1H), 3.79 – 3.74 (m, 4H), 3.73 (s, 3H), 3.62 (s, 3H), 2.91 – 2.81 (m, 1H), 2.67 – 2.60 (m, 1H), 1.49 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.4, 153.7, 153.2, 153.1, 150.8, 150.1, 131.7, 130.8, 130.6, 130.4, 129.2, 117.3, 113.0, 111.8, 102.8, 102.4, 101.7, 80.0, 68.1, 59.2, 55.9, 55.6, 55.2, 36.6, 28.3; IR (KBr): 2976, 1723, 1589, 1512, 1234, 1161, 1026, 810, 773, 724 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{43}N_3O_8+Na)^+$ requires m/z 656.2948, found m/z 656.2949; The enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 23.807 (minor), t_R = 27.107 (major).

di-*tert*-butyl (((3a*R*,8a*R*)-4-methyl-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ca):



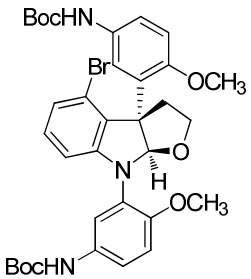
3ca

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1c** (17.5 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ca** (52.1 mg) in 84% yield as white solid.

m.p. 117–119 °C; $[\alpha]_D^{20}$ = +141.6 (c 0.8, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (s, 1H), 7.38 – 7.28 (m, 2H), 7.24 – 7.15 (m, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.50 (d, *J* = 7.4 Hz, 1H), 6.41 (s, 1H), 6.37 (s, 1H), 6.26 (d, *J* = 7.8 Hz, 1H), 5.87 (s, 1H), 4.13 (t, *J*

= 6.8 Hz, 1H), 3.85 – 3.79 (m, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.00 – 2.89 (m, 1H), 2.47 – 2.39 (m, 1H), 2.07 (s, 3H), 1.49 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.1, 153.1, 151.2, 148.9, 143.3, 131.8, 131.0, 130.4, 130.3, 127.7, 120.6, 112.9, 112.6, 105.6, 103.4, 80.2, 59.3, 55. 9, 55.8, 50.4, 36.9, 28.4, 18.7; IR (KBr): 2927, 1698, 1588, 1514, 1234, 1162, 1026, 811, 767 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{43}N_3O_7+Na)^+$ requires m/z 640.2999, found m/z 640.3001; The enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IB, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.200 (minor), t_R = 14.873 (major).

di-*tert*-butyl (((3a*S*,8a*R*)-4-bromo-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3da):



3da

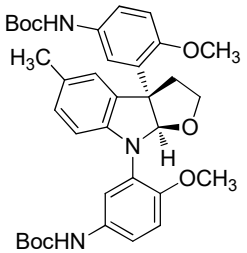
Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1d** (23.9 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3da** (42.4 mg) in 62% yield as white solid.

m.p. 120–123 °C; $[\alpha]_D^{20}$ = +377 (c 0.1, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.35 (m, 2H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 2H), 6.37 (s, 1H), 6.11 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.75 – 3.68 (m, 7H), 2.89 – 2.79 (m, 1H), 2.51 – 2.44 (m, 1H), 1.50 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.2, 150.8, 148.4, 148.3, 132.7, 132.2, 131.8, 131.1, 130.3, 127.7, 124.5, 118.2, 112.8, 112.2, 108.1, 102.2, 80.1, 39.8, 28.3; IR (KBr): 2927, 1704, 1598, 1513, 1232, 1161, 1025, 847, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}BrN_3O_7+Na)^+$ requires m/z 704.1947, 706.1927, found m/z 704.1941, 706.1922; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.607 (major), t_R = 9.203 (minor).

di-*tert*-butyl

(((3a*R*,8a*R*)-5-methyl-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ea):

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1e** (17.5 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ea** (57.6 mg) in 93% yield as white solid.

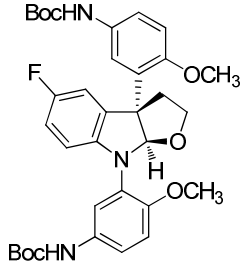


3ea

m.p. 120–123 °C; $[\alpha]_D^{20}$ = +115.8 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 – 7.30 (m, 3H), 7.21 (d, *J* = 2.3 Hz, 1H), 6.93 – 6.83 (m, 4H), 6.46 – 6.37 (m, 3H), 6.13 (s, 1H), 4.11 (t, *J* = 7.7 Hz, 1H), 3.77 – 3.71 (m, 7H), 2.89 – 2.80 (m, 1H), 2.53 – 2.47 (m, 1H), 2.27 (s, 3H), 1.53 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.2, 153.1, 150.5, 146.1, 132.9, 132.4, 131.8, 131.1, 130.8, 128.1, 127.4, 125.1, 112.8, 112.2, 108.1, 102.4, 80.1, 67.1, 59.5, 55.8, 55.7, 39.8, 28.4, 20.9; IR (KBr): 2976, 1722, 1605, 1511, 1231, 1162, 1026, 809, 769, 731 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{43}N_3O_7+Na)^+$ requires m/z 640.2999, found m/z 640.3013; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IB, hexane/ isopropanol = 95/ 5, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 29.567 (minor), t_R = 34.590 (major).

di-*tert*-butyl

(((3a*R*,8a*R*)-5-fluoro-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3fa):



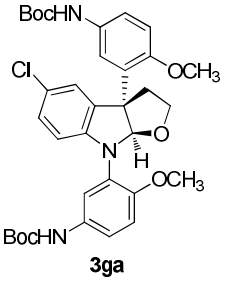
3fa

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1f** (17.9 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly

purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3fa** (39.1 mg) in 63% yield as white solid.

m.p. 126–129 °C; $[\alpha]_D^{20}$ = -72.0 (c 0.6, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.27 (m, 3H), 7.19 (d, *J* = 2.6 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.76 – 6.69 (m, 1H), 6.41 (s, 1H), 6.37 (s, 1H), 6.34 – 6.29 (m, 1H), 6.11 (s, 1H), 4.09 (t, *J* = 7.6 Hz, 1H), 3.79 – 3.67 (m, 7H), 2.85 – 2.74 (m, 1H), 2.54 – 2.43 (m, 1H), 1.50 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.6 (d, *J* = 233.3 Hz), 153.6, 153.1 (d, *J* = 13.6 Hz), 150.6, 144.4, 134.3 (d, *J* = 7.4 Hz), 113.8 (d, *J* = 23.0 Hz), 131.2, 130.4, 113.9, 113.7, 112.8, 112.2, 111.6 (d, *J* = 24.0 Hz), 108.2 (d, *J* = 7.9 Hz), 102.6, 80.2, 67.1, 59.5, 59.4, 55.8, 55.6, 39.7, 28.4; IR (KBr): 2977, 1723, 1601, 1513, 1231, 1162, 1027, 809, 770, 731 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}FN_3O_7+Na)^+$ requires m/z 644.2748, found m/z 644.2756; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.710 (major), t_R = 8.080 (minor).

di-*tert*-butyl (((3a*R*,8a*R*)-5-chloro-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ga):



3ga

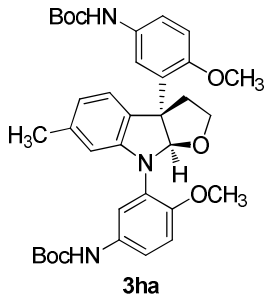
Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1g** (19.5 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ga** (48.1 mg) in 76% yield as white solid.

m.p. 117–119 °C; $[\alpha]_D^{20}$ = +157.3 (c 0.8, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 – 7.41 (m, 1H), 7.40 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 6.99 (s, 1H), 6.97 – 6.93 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.43 (s, 1H), 6.40 (s, 1H), 6.28 (d, *J* = 8.4 Hz, 1H), 6.12 (s, 1H), 4.08 (t, *J* = 7.8 Hz, 1H), 3.82 – 3.71 (m, 4H), 3.70 (s, 3H), 2.85 – 2.74 (m, 1H), 2.50 – 2.43 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.6, 153.1, 153.0, 150.8, 147.1, 134.7, 131.9, 131.7, 131.2, 129.6, 127.5, 124.3, 122.3, 112.7, 112.2, 108.5,

102.5, 80.2, 66.7, 59.3, 55.7, 55.6, 39.8, 28.3; IR (KBr): 2976, 1703, 1596, 1512, 1231, 1161, 1026, 809, 767, 729 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}ClN_3O_7+Na)^+$ requires m/z 660.2452, 661.2486, found m/z 660.2487, 661.2514; The enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IB, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 15.723 (minor), t_R = 18.183 (major).

di-*tert*-butyl (((3a*R*,8a*R*)-6-methyl-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ha):

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1h** (17.5 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ha** (61.5 mg) in 99% yield as white solid.

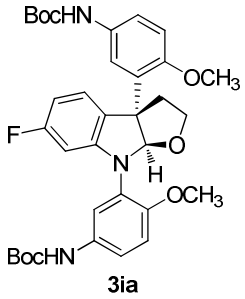


3ha

m.p. 130–133 °C; $[\alpha]_D^{20}$ = +120.5 (c 1.0, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46 – 7.31 (m, 3H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 6.32 (s, 1H), 6.25 (s, 1H), 6.08 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.78 – 3.72 (m, 4H), 3.72 (s, 3H), 2.86 – 2.78 (m, 1H), 2.48 – 2.42 (m, 1H), 2.24 (s, 3H), 1.50 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.2, 150.9, 148.5, 137.6, 132.3, 131.8, 131.0, 130.4, 129.9, 124.3, 119.1, 112.9, 112.2, 108.8, 102.5, 80.1, 67.3, 59.2, 55.8, 55.7, 39.8, 28.3, 21.6; IR (KBr): 2996, 1723, 1600, 1513, 1223, 1162, 1026, 808 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{43}N_3O_7+Na)^+$ requires m/z 640.2999, found m/z 640.3035; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 34.143 (major), t_R = 42.883 (minor).

di-*tert*-butyl (((3a*R*,8a*R*)-6-fluoro-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phe

nylene))dicarbamate (3ia):



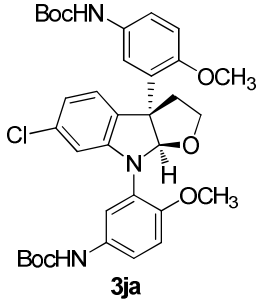
3ia

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1i** (17.9 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ia** (29.9 mg) in 48% yield as white solid.

m.p. 115–117 °C; $[\alpha]_D^{20}$ = +94.3 (c 0.2, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 – 7.28 (m, 3H), 7.25 – 7.22 (m, 1H), 6.95 – 6.88 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.46 (s, 1H), 6.40 (s, 1H), 6.36 – 6.30 (m, 1H), 6.14 (s, 1H), 6.05 (d, *J* = 10.4 Hz, 1H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.77 – 3.71 (m, 4H), 3.70 (s, 3H), 2.85 – 2.74 (m, 1H), 2.46 – 2.38 (m, 1H), 1.50 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.5 (d, *J* = 239.5 Hz), 153.7, 153.1 (d, *J* = 18.9 Hz), 150.9, 150.1 (d, *J* = 12.2 Hz), 149.2, 144.9, 132.3, 132.1, 131.9, 131.2, 129.3, 128.3 (d, *J* = 1.9 Hz), 124.7 (d, *J* = 10.5 Hz), 119.7, 119.1, 118.0, 117.5, 112.7, 112.3, 111.5, 104.0 (d, *J* = 22.8 Hz), 102.9, 95.4 (d, *J* = 27.2 Hz), 66.9, 58.9, 55.8, 55.7, 39.9, 28.4; IR (KBr): 2977, 1703, 1605, 1514, 1232, 1162, 1026, 945, 810, 764 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}FN_3O_7+Na)^+$ requires m/z 644.2748, found m/z 644.2769; The enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 31.667 (major), t_R = 41.277 (minor).

di-*tert*-butyl

(((3a*R*,8a*R*)-6-chloro-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-ph enylene))dicarbamate (3ja):



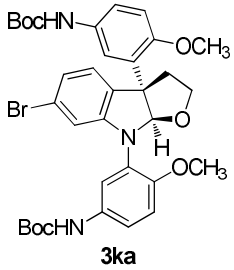
3ja

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1j** (19.5 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the

reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ja** (33.8 mg) in 53% yield as white solid.

m.p. 120–123 °C; $[\alpha]_D^{20}$ = -32.8 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 – 7.29 (m, 3H), 7.23 (d, *J* = 2.4 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.65 – 6.59 (m, 1H), 6.38 (s, 1H), 6.33 (s, 1H), 6.30 (s, 1H), 6.12 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.82 – 3.72 (m, 4H), 3.70 (s, 3H), 2.85 – 2.76 (m, 1H), 2.46 – 2.39 (m, 1H), 1.50 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 152.5, 151.0, 150.9, 149.7, 133.4, 132.0, 131.9, 131.4, 131.1, 129.2, 124.9, 117.7, 112.8, 112.2, 107.6, 105.3, 102.7, 80.3, 66.8, 59.0, 55.8, 55.7, 39.8, 28.3; IR (KBr): 2976, 1723, 1597, 1513, 1232, 1161, 1026, 765 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}ClN_3O_7+Na)^+$ requires m/z 660.2452, 661.2486, found m/z 660.2449, 661.2507; The enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.373 (major), t_R = 10.627 (minor).

di-*tert*-butyl (((3a*R*,8a*R*)-6-bromo-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3ka):



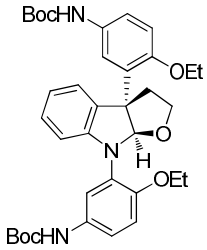
3ka

Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1k** (23.9 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ka** (46.6 mg) in 68% yield as white solid.

m.p. 86–89 °C; $[\alpha]_D^{20}$ = -98.1 (c 0.5, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41 (d, *J* = 2.6 Hz, 1H), 7.39 – 7.26 (m, 2H), 7.26 – 7.13 (m, 1H), 7.12 – 7.05 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.42 (s, 1H), 6.40 (s, 1H), 6.24 (d, *J* = 8.2 Hz, 1H), 6.12 (s, 1H), 4.08 (t, *J* = 7.8 Hz, 1H), 3.76 – 3.70 (m, 4H), 3.69 (s, 3H), 2.86 – 2.74 (m, 1H), 2.52 – 2.41 (m, 1H), 1.51 (s, 9H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.2, 153.00, 151.0, 149.9, 132.0, 131.9, 131.9, 131.1, 129.1, 125.4, 121.5, 120.6, 112.8, 112.2, 110.4, 102.7, 80.2,

66.7, 59.1, 55.7, 55.7, 39.8, 28.3; IR (KBr): 2952, 1718, 1654, 1522, 1248, 1159, 1023, 819, 789, 726 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{40}BrN_3O_7+Na)^+$ requires m/z 704.1947, 706.1927, found m/z 704.1943, 706.1936; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 30.547 (minor), t_R = 34.123 (major).

di-*tert*-butyl (((3a*R*,8a*R*)-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-ethoxy-3,1-phenylene))dicarbamate (3ab):



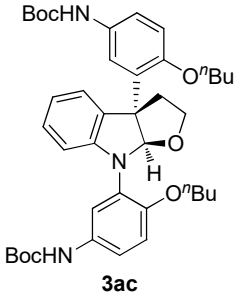
3ab

Following the general procedure, the solution of quinone imine ketal **2b** (70.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1a** (16.1 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ab** (62.6 mg) in 99% yield as white solid.

m.p. 113–115 °C; $[\alpha]_D^{20}$ = -84.6 (c 0.6, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 – 7.27 (m, 3H), 7.13 – 7.08 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 6.34 (s, 1H), 6.19 (s, 1H), 4.12 – 4.01 (m, 2H), 3.96 – 3.89 (m, 2H), 3.89 – 3.83 (m, 1H), 3.77 – 3.69 (m, 1H), 2.96 – 2.86 (m, 1H), 2.52 – 2.43 (m, 1H), 1.50 (s, 9H), 1.49 (s, 9H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.2, 153.1, 149.9, 148.3, 133.1, 132.1, 131.7, 130.7, 130.4, 127.6, 124.6, 118.1, 114.1, 112.6, 108.1, 102.1, 80.1, 67.4, 64.2, 64.0, 59.4, 39.5, 28.4, 28.3, 14.7, 14.5; IR (KBr): 2977, 1717, 1596, 1521, 1226, 1161, 806, 741, 789, 668 cm^{-1}; ESI FTMS exact mass calcd for $(C_{36}H_{45}N_3O_7+H)^+$ requires m/z 632.3336, found m/z 632.3337; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.200 (major), t_R = 19.237 (minor).

di-*tert*-butyl

(((3a*R*,8a*R*)-2,3-dihydro-8*H*-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-butoxy-3,1-phenylene))di carbamate (3ac):



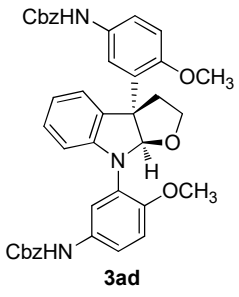
3ac

Following the general procedure, the solution of quinone imine ketal **2c** (84.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1a** (16.1 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ac** (51.5 mg) in 75% yield as white solid.

m.p. 92–94 °C; $[\alpha]_D^{20}$ = +56.9 (c 0.6, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 1H), 7.41 – 7.27 (m, 2H), 7.18 – 7.14 (m, 1H), 7.08 – 7.02 (m, 1H), 6.94 (d, *J* = 1.8 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.78 – 6.70 (m, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.24 (s, 1H), 6.10 (s, 1H), 4.12 (t, *J* = 7.6 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.89 – 3.68 (m, 4H), 3.04 – 2.93 (m, 1H), 2.48 – 2.40 (m, 1H), 1.80 – 1.68 (m, 2H), 1.50 (s, 9H), 1.47 (s, 9H), 1.47 – 1.38 (m, 4H), 1.21 – 1.12 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.1, 150.0, 148.3, 132.6, 131.6, 131.4, 130.7, 130.2, 127.7, 125.0, 118.2, 113.7, 112.3, 108.4, 102.1, 80.1, 68.2, 68.1, 67.9, 59.6, 39.5, 31.3, 31.2, 28.4, 28.3, 19.3, 18.9, 13.9, 13.8; IR (KBr): 2956, 1718, 1647, 1575, 1466, 1201, 1120, 973, 860, 785 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{53}N_3O_7+Na)^+$ requires m/z 710.3782, found m/z 710.3793; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.567 (major), t_R = 13.367 (minor).

dibenzyl

(((3a*R*,8a*R*)-2,3-dihydro-8H-furo[2,3-b]indole-3a,8(8a*H*)-diyl)bis(4-me thoxy-3,1-phenylene))dicarbamate (3ad):



3ad

Following the general procedure, the solution of quinone imine ketal **2d** (71.8 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptophol **1a** (16.1 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and

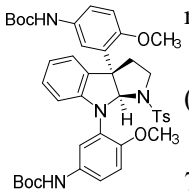
3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3ad** (54.6 mg) in 81% yield as white solid.

m.p. 98–100 °C; $[\alpha]_D^{20}$ = -77.3 (c 0.3, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, *J* = 2.0 Hz, 1H), 7.42 – 7.28 (m, 13H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.75 – 6.68 (m, 2H), 6.45 (d, *J* = 7.9 Hz, 1H), 6.14 (s, 1H), 5.17 (s, 4H), 4.08 (t, *J* = 7.8 Hz, 1H), 3.75 – 3.67 (m, 7H), 2.88 – 2.75 (m, 1H), 2.51 – 2.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.7, 154.1, 151.1, 148.3, 136.2, 132.8, 132.4, 131.2, 130.5, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 124.5, 120.1, 119.2, 118.4, 117.7, 116.9, 112.7, 112.2, 108.2, 102.2, 67.1, 66.9, 66.8, 59.5, 55.8, 55.6, 39.7; IR (KBr): 2949, 1651, 1574, 1440, 1206, 1083, 975, 860, 750 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{37}N_3O_7+H)^+$ requires m/z 672.2710, found m/z 672.2715; The enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 28.040 (major), t_R = 38.327 (minor).

di-*tert*-butyl

(((3a*R*,8a*R*)-1-tosyl-1,2,3,8a-tetrahydropyrrolo[2,3-b]indole-3a,8-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3na):

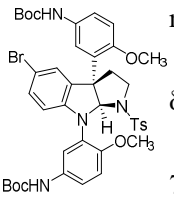
Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptamine **1n** (31.4 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3na** (58.4 mg) in 77% yield as white solid.



m.p. 97–100 °C; $[\alpha]_D^{20}$ = -96.1 (c 1.2, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (s, 1H), 7.40 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.04 – 7.00 (m, 3H), 6.91 (s, 1H), 6.90 – 6.85 (m, 2H), 6.73 – 6.67 (m, 2H), 6.50 (s, 1H), 6.36 (s, 1H), 6.30 (s, 1H), 3.82 (s, 3H), 3.80 – 3.76 (m, 1H), 3.65 (s, 3H), 3.09 – 2.99 (m, 1H), 2.81 – 2.69 (m, 1H), 2.32 (s, 3H), 2.29 – 2.24 (m, 1H), 1.52 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.6, 147.9, 147.6, 146.6, 143.3, 137.2, 133.1, 126.2, 125.8, 125.7, 124.3, 123.9, 123.1, 121.6, 119.9, 112.9, 107.5, 106.9, 102.3, 82.0, 74.9, 54.8, 50.5, 50.4, 42.7, 34.2, 23.3, 23.2, 16.2; IR (KBr): 2949, 1645, 1575, 1440, 1185, 1010, 974, 858, 756 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{48}N_4O_8S+Na)^+$ requires m/z 779.3091, found m/z 779.3119; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.183 (minor), t_R = 8.410 (major).

di-*tert*-butyl (((3a*R*,8a*R*)-5-bromo-1-tosyl-1,2,3,8a-tetrahydropyrrolo[2,3-b]indole-3a,8-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3oa):

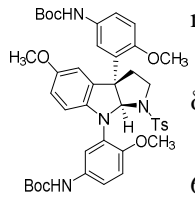
Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptamine **1o** (39.2 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3na** (57.9 mg) in 69% yield as white solid.



m.p. 117–120 °C; $[\alpha]_D^{20}$ = -340.3 (c 1.1, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 1H), 7.41 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.06 (m, 2H), 7.04 – 7.02 (m, 2H), 6.93 – 6.84 (m, 3H), 6.75 – 6.67 (m, 2H), 6.50 (s, 1H), 6.25 (s, 1H), 6.21 (s, 1H), 3.83 (s, 3H), 3.81 – 3.76 (m, 1H), 3.65 (s, 3H), 3.09 – 3.01 (m, 1H), 2.80 – 2.72 (m, 1H), 2.32 (s, 3H), 2.30 – 2.25 (m, 1H), 1.52 (s, 9H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.5, 147.6, 142.6, 137.8, 133.8, 131.5, 131.1, 130.8, 129.2, 128.8, 127.4, 126.8, 112.7, 112.3, 108.7, 80.3, 59.8, 55.6, 39.3, 29.7, 28.5, 28.4, 21.4; IR (KBr): 3169, 2950, 1647, 1576, 1438, 1200, 1095, 974, 859, 787 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{47}BrN_4O_8S+Na)^+$ requires m/z 857.2196, 859.2175 , found m/z 857.2201, 859.2224; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.060 (minor), t_R = 6.670 (major).

di-*tert*-butyl (((3a*R*,8a*R*)-5-methoxy-1-tosyl-1,2,3,8a-tetrahydropyrrolo[2,3-b]indole-3a,8-diyl)bis(4-methoxy-3,1-phenylene))dicarbamate (3pa):

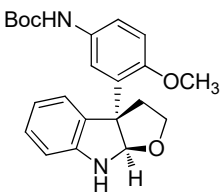
Following the general procedure, the solution of quinone imine ketal **2a** (63.3 mg, 0.25 mmol) in toluene (1 mL) was added to the mixture of tryptamine **1p** (34.4 mg, 0.1 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg). Then, the reaction mixture was stirred at 30 °C for 12 h, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =2:1) on silica gel to afford pure compound **3pa** (57 mg) in 73% yield as white solid.



m.p. 117–120 °C; $[\alpha]_D^{20}$ = -48.1 (c 1.1, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (s, 1H), 7.36 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.12 (s, 1H), 7.06 – 6.98 (m, 3H), 6.86 (t, *J* = 9.4 Hz, 2H), 6.78 – 6.70 (m, 2H), 6.64 – 6.58 (m, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 6.32 (s, 1H), 6.29 (s, 1H), 3.84 (s, 3H), 3.81 – 3.76 (m, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 3.07 – 2.99 (m, 1H), 2.79 – 2.70 (m, 1H), 2.32 (s, 3H), 2.30 – 2.25 (m, 1H), 1.52 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.1, 152.8, 151.7, 142.8, 142.3, 138.4, 132.4, 131.3, 131.1, 130.9, 130.3, 129.2, 126.9, 113.1, 112.7, 112.2, 112.1, 107.9, 87.5, 80.2, 60.3, 56.1, 55.6, 55.5, 48.0, 39.3, 28.5, 28.4, 21.4; IR (KBr): 3031, 2948, 1646, 1569, 1438, 1215, 1095, 975, 862, 771 cm^{-1}; ESI FTMS exact mass calcd for $(C_{42}H_{50}N_4O_9S+H)^+$ requires m/z 787.3376, found m/z 787.3377; The enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.590 (minor), t_R = 17.110 (major).

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7aa):**

Following the general procedure, to the mixture of tryptophol **1a** (64.4 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7aa** (23.1 mg) in 60% yield as white solid.

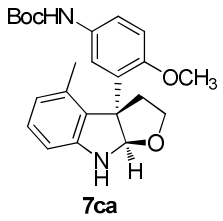


7aa

m.p. 88–89 °C; $[\alpha]_D^{20}$ = +123.6 (c 1.5, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 (s,

1H), 7.11 – 7.05 (m, 2H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.38 (s, 1H), 5.80 (s, 1H), 4.67 (s, 1H), 4.10 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.68 – 3.60 (m, 1H), 2.90 – 2.80 (m, 1H), 2.44 – 2.36 (m, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.1, 149.7, 132.3, 131.8, 131.2, 128.2, 125.1, 119.0, 112.4, 108.8, 98.4, 80.2, 67.5, 60.7, 55.8, 39.5, 28.3; IR (KBr): 2950, 1643, 1573, 1438, 1201, 1097, 973, 859, 758 cm^{-1}; ESI FTMS exact mass calcd for $(C_{22}H_{26}N_2O_4+Na)^+$ requires m/z 405.1791, found m/z 405.1795; The enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.663 (major), t_R = 16.277 (minor).

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-4-methyl-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7ca):**



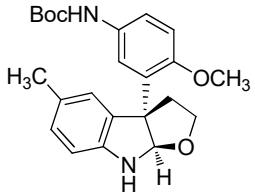
7ca

Following the general procedure, to the mixture of tryptophol **1c** (70 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ca** (27.8 mg) in 70% yield as white solid.

m.p. 120–123 °C; $[\alpha]_D^{20}$ = +126.3 (c 0.1, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (s, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.79 (s, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 5.55 (s, 1H), 4.65 (s, 1H), 4.18 – 4.09 (m, 1H), 3.81 – 3.75 (m, 1H), 3.67 (s, 3H), 2.95 – 2.85 (m, 1H), 2.42 – 2.34 (m, 1H), 2.08 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.9, 153.0, 149.8, 134.8, 131.2, 130.3, 128.2, 121.4, 112.6, 106.7, 99.3, 80.2, 66.9, 60.6, 55.8, 37.1, 28.3, 18.7; IR (KBr): 2949, 1643, 1573, 1435, 1201, 1097, 973, 859, 786 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{28}N_2O_4+Na)^+$ requires m/z 419.1947, found m/z 419.1950; The enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak IA,

hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.893 (major), t_R = 15.617 (minor).

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-5-methyl-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7ea):**

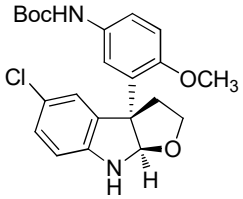


7ea

Following the general procedure, to the mixture of tryptophol **1e** (70 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ea** (29 mg) in 73% yield as white solid.

m.p. 92–94 °C; $[\alpha]_D^{20}$ = +426.4 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38 (s, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 5.78 (s, 1H), 4.56 (s, 1H), 4.09 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 3.67 – 3.61 (m, 1H), 2.88 – 2.79 (m, 1H), 2.42 – 2.35 (m, 1H), 2.25 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.5, 147.9, 142.3, 127.4, 126.8, 126.0, 123.4, 123.2, 120.5, 113.7, 107.2, 103.7, 93.6, 75.0, 62.2, 55.6, 50.6, 34.3, 23.1, 15.7; IR (KBr): 2949, 1641, 1573, 1435, 1201, 1097, 973, 859, 786 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{28}N_2O_4+Na)^+$ requires m/z 419.1947, found m/z 419.1946; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.917 (major), t_R = 15.700 (minor).

***tert*-butyl (3-((3a*R*,8a*R*)-5-chloro-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)-4-methoxyphenyl)carbamate (7ga):**

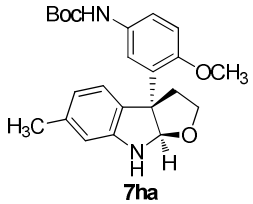


7ga

Following the general procedure, to the mixture of tryptophol **1g** (78 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ga** (41 mg) in 99% yield as white solid.

m.p. 130–133 °C; $[\alpha]_D^{20}$ = -180.2 (c 0.5, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.01 (s, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.56 – 6.51 (m, 1H), 6.37 (s, 1H), 5.82 (s, 1H), 4.72 (s, 1H), 4.32 – 3.87 (m, 1H), 3.70 (s, 3H), 3.67 – 3.62 (m, 1H), 2.85 – 2.77 (m, 1H), 2.44 – 2.38 (m, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.4, 147.9, 143.1, 129.3, 126.2, 126.1, 122.8, 119.8, 118.2, 113.9, 107.2, 104.2, 93.6, 75.1, 61.9, 55.5, 50.6, 34.2, 23.1; IR (KBr): 2950, 1641, 1573, 1435, 1201, 1097, 973, 859, 786 cm^{-1}; ESI FTMS exact mass calcd for $(C_{22}H_{25}ClN_2O_4+Na)^+$ requires m/z 439.1401, 441.1371, found m/z 439.1396, 441.1383; The enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.353 (major), t_R = 16.103 (minor).

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-6-methyl-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7ha):**



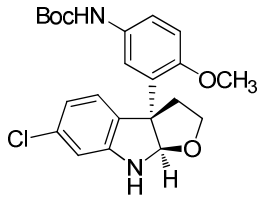
7ha

Following the general procedure, to the mixture of tryptophol **1h** (70 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the

reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ha** (29.9 mg) in 76% yield as white solid.

m.p. 90–93 °C; $[\alpha]_D^{20}$ = +129.1 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (s, 1H), 6.98 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 6.33 (s, 1H), 5.78 (s, 1H), 4.61 (s, 1H), 4.09 (t, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.68 – 3.62 (m, 1H), 2.89 – 2.80 (m, 1H), 2.40 – 2.34 (m, 1H), 2.28 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.7, 153.1, 149.8, 138.2, 131.8, 131.2, 129.3, 124.9, 119.9, 112.3, 109.7, 98.6, 80.1, 67.6, 60.4, 55.7, 39.5, 28.3, 21.5; IR (KBr): 2950, 1641, 1573, 1439, 1201, 1097, 973, 860, 787 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{28}N_2O_4+Na)^+$ requires m/z 419.1947, found m/z 419.1945; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.093 (major), t_R = 18.787 (minor).

***tert*-butyl (3-((3a*R*,8a*R*)-6-chloro-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)-4-methoxyphenyl)carbamate (7ja):**



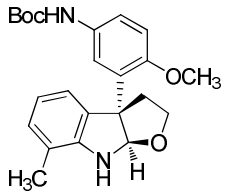
7ja

Following the general procedure, to the mixture of tryptophol **1j** (78 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ja** (29.4 mg) in 71% yield as white solid.

m.p. 93–95 °C; $[\alpha]_D^{20}$ = -22.2 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 6.39 (s, 1H), 5.81 (s, 1H), 4.75 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.71 (s, 3H), 3.67 – 3.61 (m, 1H), 2.86 – 2.77 (m, 1H), 2.38 – 2.31 (m, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.6, 153.1, 150.8, 133.7, 131.5, 131.3, 131.0, 125.7, 118.7, 112.4, 108.5, 98.6, 80.3, 67.2, 60.1, 55.7, 39.4, 28.3; IR (KBr): 2950, 1640, 1573, 1443, 1201, 1097, 973, 820, 788

cm^{-1}; ESI FTMS exact mass calcd for $(C_{22}H_{25}ClN_2O_4+Na)^+$ requires m/z 439.1401, 441.1371, found m/z 439.1393, 441.1378; The enantiomeric excess: 91%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.653 (major), t_R = 12.990 (minor).

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-7-methyl-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7la):**



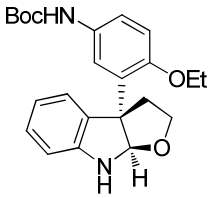
7la

Following the general procedure, to the mixture of tryptophol **1l** (70 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2a** (25.3 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7la** (24.4 mg) in 62% yield as white solid.

m.p. 110–111 °C; $[\alpha]_D^{20}$ = +132.5 (c 0.9, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (s, 1H), 6.98 – 6.90 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 5.81 (s, 1H), 4.47 (s, 1H), 4.12 – 4.07 (m, 1H), 3.73 (s, 3H), 3.68 – 3.61 (m, 1H), 2.91 – 2.83 (m, 1H), 2.43 – 2.35 (m, 1H), 2.17 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.5, 147.9, 143.1, 126.6, 126.3, 126.0, 123.8, 117.5, 114.1, 113.1, 107.2, 93.1, 74.9, 62.5, 55.9, 50.6, 34.2, 23.1, 11.6; IR (KBr): 2983, 1699, 1541, 1473, 1163, 1027, 951, 747, 668 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{28}N_2O_4+Na)^+$ requires m/z 419.1947, found m/z 419.1942; The enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.770 (major), t_R = 13.047 (minor).

***tert*-butyl (4-ethoxy-3-((3a*R*,8a*R*)-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate (7ab):**

Following the general procedure, to the mixture of tryptophol **1a** (64.4 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2b** (28.1 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ab** (20.1 mg) in 51% yield as white solid.



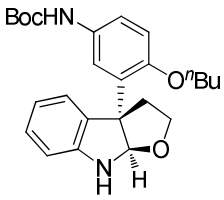
7ab

m.p. 98–100 °C; $[\alpha]_D^{20}$ = +155.5 (c 0.7, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35 (s, 1H), 7.09 – 7.02 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.32 (s, 1H), 5.86 (s, 1H), 4.67 (s, 1H), 4.10 (t, *J* = 7.8 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.87 – 3.79 (m, 1H), 3.71 – 3.62 (m, 1H), 2.91 – 2.82 (m, 1H), 2.45 – 2.37 (m, 1H), 1.49 (s, 9H), 1.31 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.0, 149.8, 132.6, 131.9, 130.9, 128.1, 124.9, 118.9, 112.6, 108.7, 98.5, 80.1, 67.1, 63.9, 60.7, 39.5, 28.3, 14.5; IR (KBr): 2949, 1641, 1572, 1434, 1201, 1097, 973, 860, 759 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{28}N_2O_4+Na)^+$ requires m/z 419.1947, found m/z 419.1945; The enantiomeric excess: 97%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.410 (major), t_R = 16.233 (minor).

***tert*-butyl**

(4-butoxy-3-((3a*R*,8a*R*)-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)phenyl)carbamate

(7ac):



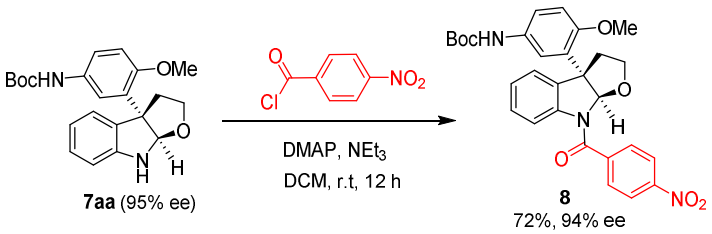
7ac

Following the general procedure, to the mixture of tryptophol **1a** (64.4 mg, 0.4 mmol), catalyst **6a** (3.4 mg, 0.005 mmol) and 3 Å MS (100 mg), was added toluene (2 mL). Then, the solution of quinone imine ketal **2c** (33.7 mg, 0.1 mmol) in toluene (3 mL) was added to the above mentioned reaction mixture over 1 h by a syringe pump. During the procedure, the reaction mixture was stirred at room temperature. Next, the resultant reaction mixture was further stirred at room temperature for 10 min, which indicated the completion of the reaction. Subsequently, the reaction

mixture was directly purified through preparative thin layer chromatography (PE:EA =4:1) on silica gel to afford pure compound **7ac** (23.9 mg) in 56% yield as white solid.

m.p. 100–102 °C; $[\alpha]_D^{20}$ = +51.6 (c 0.3, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (s, 1H), 7.16 – 7.05 (m, 2H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.85 (s, 1H), 4.63 (s, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.85 – 3.75 (m, 1H), 3.71 – 3.60 (m, 1H), 2.96 – 2.83 (m, 1H), 2.43 – 2.32 (m, 1H), 1.76 – 1.66 (m, 2H), 1.47 (s, 9H), 1.45 – 1.38 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 153.2, 149.8, 132.4, 131.5, 130.8, 128.1, 125.1, 118.9, 112.3, 108.7, 98.5, 80.2, 68.1, 67.4, 60.7, 39.6, 31.3, 28.3, 19.3, 13.9; IR (KBr): 2951, 1642, 1572, 1434, 1201, 1096, 974, 860, 762 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{32}N_2O_4+Na)^+$ requires m/z 447.2260, found m/z 447.2265; The enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.653 (major), t_R = 11.307 (minor).

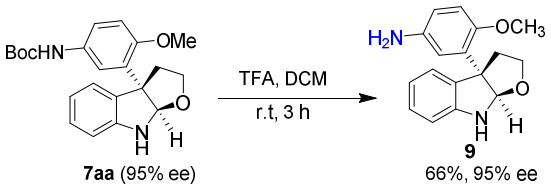
5. Synthetic procedure and characterization data of products 8-9



To the mixture of **7aa** (38.2 mg, 0.1 mmol), 4-nitrobenzoyl chloride (18.9 mg, 0.102 mmol) and DMAP (2.5 mg, 0.02 mmol) was added newly distilled dichloromethane (1 mL). In an ice-water bath, trimethylamine (17 μL,0.12 mmol) was added to the reaction mixture. Then, the reaction mixture was stirred at room temperature for 4 h and was monitored by TLC, which indicated the incompletion of the reaction. Subsequently, another parts of 4-nitrobenzoyl chloride (74.3 mg, 0.4 mmol) and trimethylamine (56 μL, 0.4 mmol) were added to the reaction mixture, which was further stirred at room temperature for another 8 h. After the completion of the reaction indicated by TLC, the reaction mixture was quenched by the saturated aqueous solution of $NaHCO_3$, which was extracted by dichloromethane. The organic layer was washed with brine and combined together, which was dried by anhydrous sodium sulfate. Finally, the organic layer was

evaporated under the reduced pressure to give a residue, which was further purified through preparative thin layer chromatography on silica gel to give pure product **8** (38.3 mg) in 72% yield as white solid.

***tert*-butyl (4-methoxy-3-((3a*R*,8a*R*)-8-(4-nitrobenzoyl)-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl) phenyl)carbamate (8):** Preparative thin layer chromatography, petroleum ether/ethyl acetate = 2/1; Reaction time = 12 h; yield: 72% (38.3 mg); white solid; m.p. 94–97 °C; $[\alpha]_D^{20}$ = +160.1 (c 0.6, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (d, *J* = 8.9 Hz, 2H), 8.20 – 8.11 (m, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.42 (s, 1H), 7.34 – 7.28 (m, 1H), 7.16 – 7.05 (m, 3H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.43 (s, 1H), 5.84 (s, 1H), 4.10 (t, *J* = 7.9 Hz, 1H), 3.63 – 3.56 (m, 1H), 3.48 (s, 3H), 2.81 – 2.71 (m, 1H), 2.53 – 2.47 (m, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.4, 153.3, 153.1, 148.7, 142.7, 142.3, 135.0, 131.8, 131.1, 129.4, 128.2, 125.3, 124.1, 123.4, 117.3, 112.6, 98.9, 80.4, 67.0, 59.4, 56.2, 39.2, 28.3; IR (KBr): 3169, 1648, 1571, 1437, 1201, 1097, 973, 860, 750 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{29}N_3O_7+Na)^+$ requires m/z 554.1904, found m/z 554.1923; The enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.163 (major), t_R = 18.120 (minor).

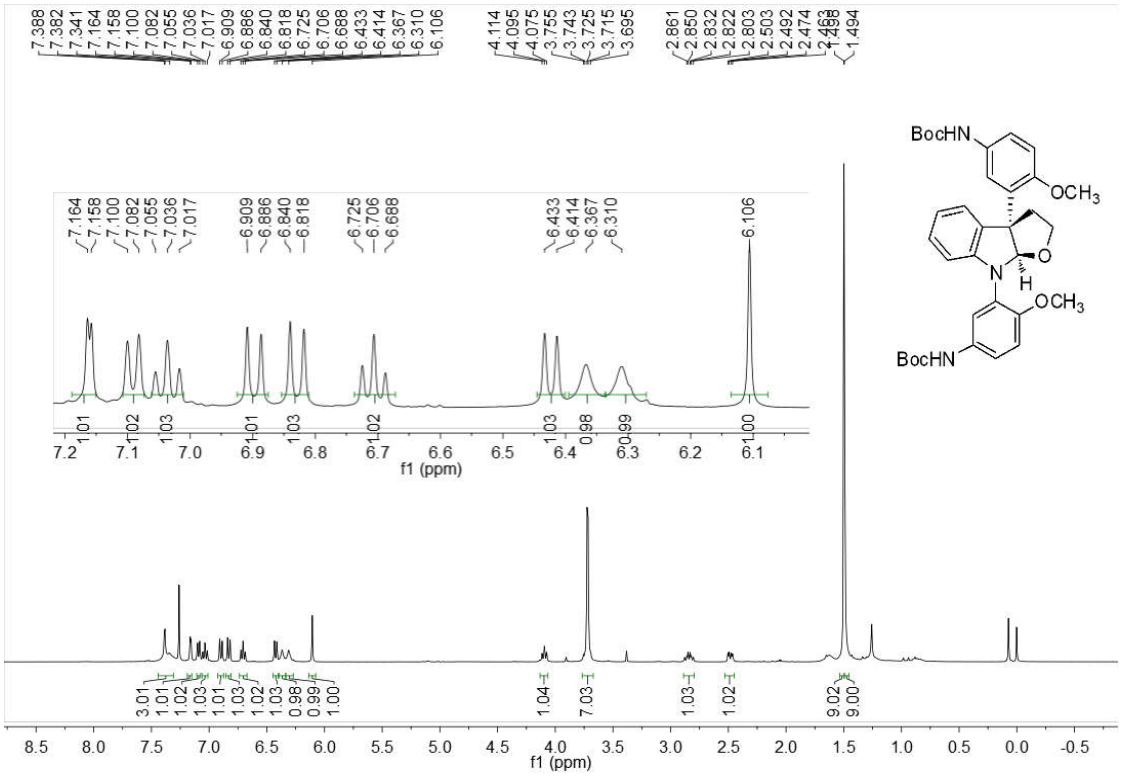


To the solution of **7aa** (38.2 mg, 0.1 mmol) in dichloromethane was slowly added TFA (150 mg, 1.3 mmol), which was stirred at room temperature for 3 h. After the completion of the reaction indicated by TLC, the reaction mixture was quenched by the saturated aqueous solution of $NaHCO_3$ and modulated to pH = 7-8. Then, the mixture was extracted by dichloromethane, and the organic layer was combined together, which was dried by anhydrous sodium sulfate. Finally, the organic layer was evaporated under the reduced pressure to give a residue, which was further purified through column chromatography on silica gel (washed by Et_3N in advance) to give pure product **9** (18.7 mg) in 66% yield as brown solid.

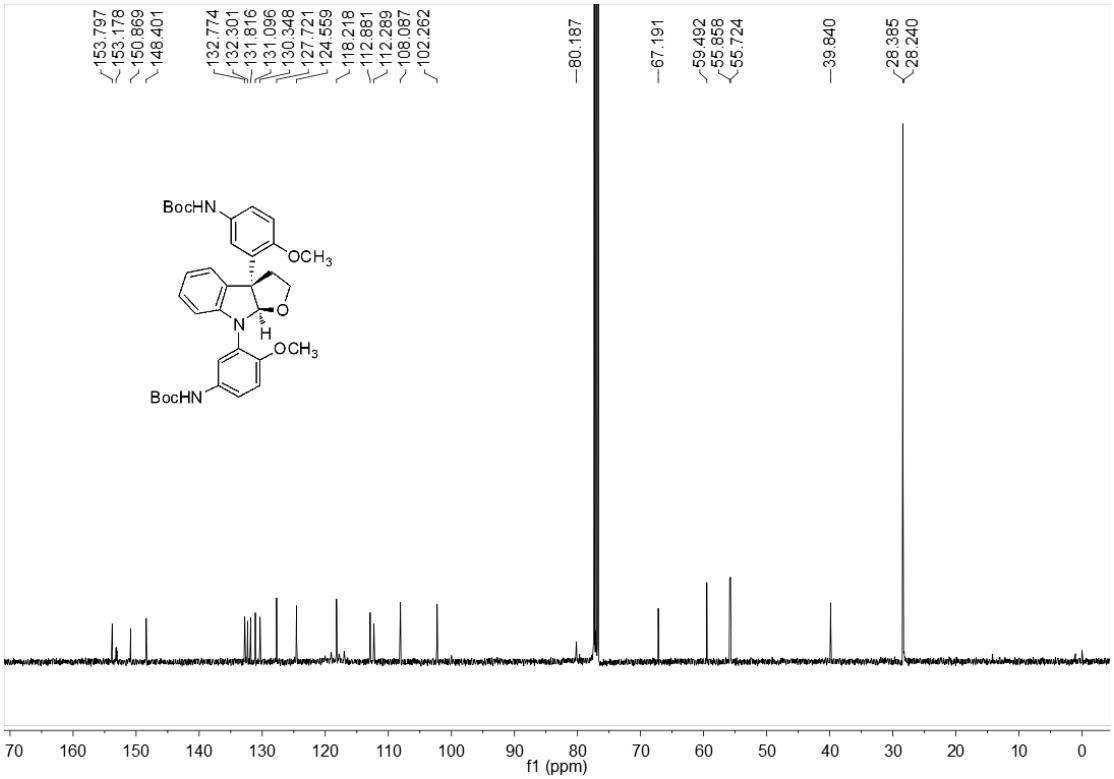
4-methoxy-3-((3a*R*,8a*R*)-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-b]indol-3a-yl)aniline (9): Flash chromatography, dichloromethane/ethyl acetate = 1/1; Reaction time = 3 h; yield: 66% (18.7 mg); brown solid; m.p. 83–85 °C; $[\alpha]_D^{20}$ = +189.9 (c 0.4, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26 – 7.12 (m, 1H), 7.12 – 7.06 (m, 2H), 6.79 – 6.72 (m, 2H), 6.64 (d, J = 7.8 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 6.58 – 6.52 (m, 1H), 5.81 – 5.76 (m, 1H), 4.13 – 4.08 (m, 1H), 3.77 – 3.50 (m, 5H), 2.89 – 2.82 (m, 1H), 2.41 – 2.36 (m, 1H), 2.34 – 2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.0, 149.7, 139.7, 132.6, 132.4, 128.1, 125.3, 119.1, 116.1, 114.3, 113.4, 108.9, 98.6, 67.6, 60.8, 56.1, 39.6; IR (KBr): 3358, 2947, 2360, 1655, 1454, 1114, 1042, 952, 668 cm^{-1}; ESI FTMS exact mass calcd for $(C_{17}H_{18}N_2O_2+Na)^+$ requires m/z 305.1266, found m/z 305.1267; The enantiomeric excess: 95%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 21.873 (major), t_R = 72.047 (minor).

6. NMR spectra of products 3, 7 and 8-9

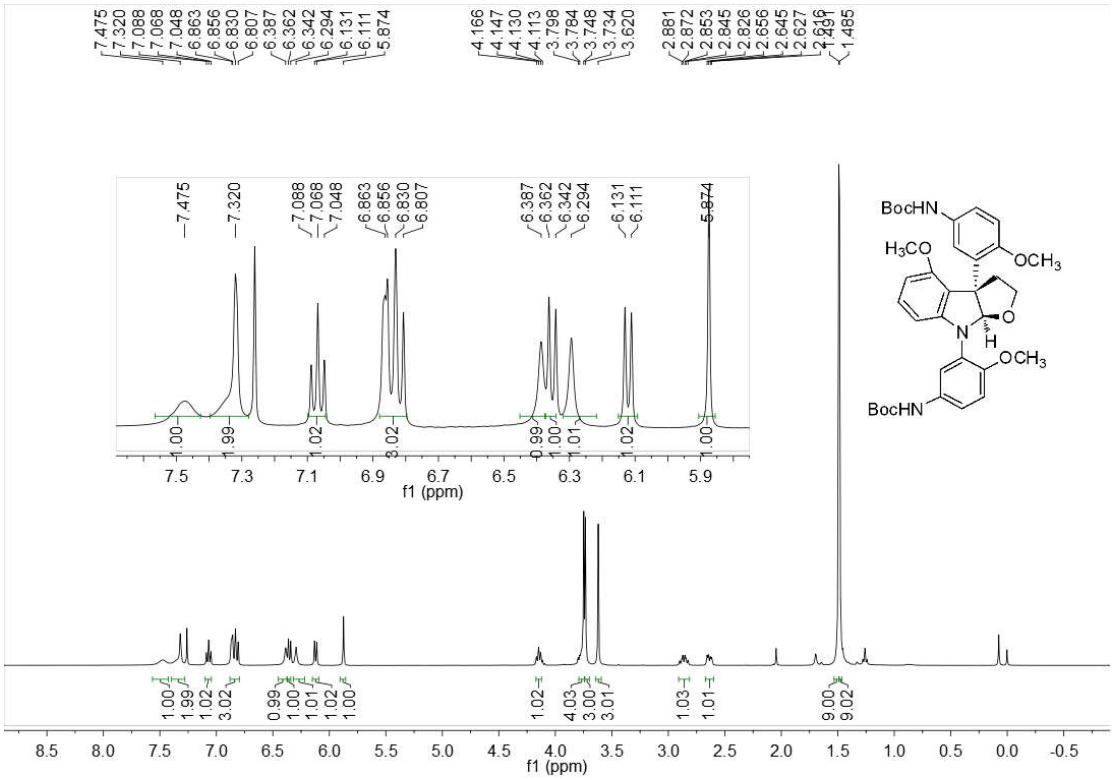
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**



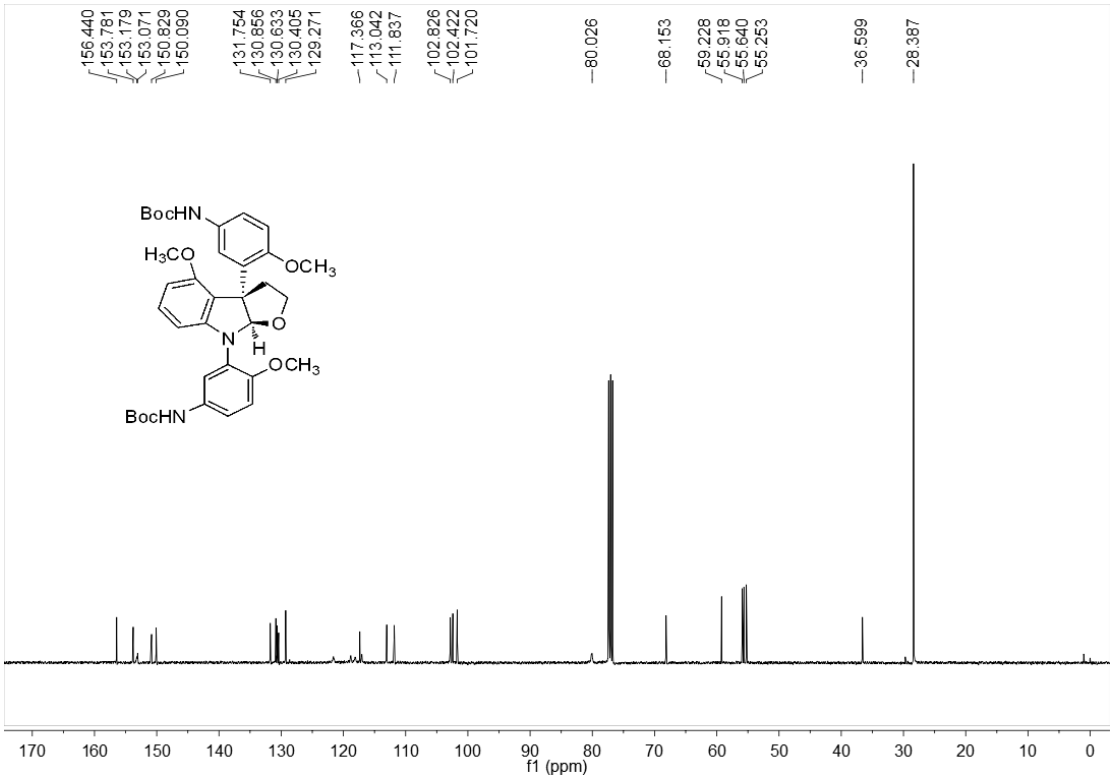
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**



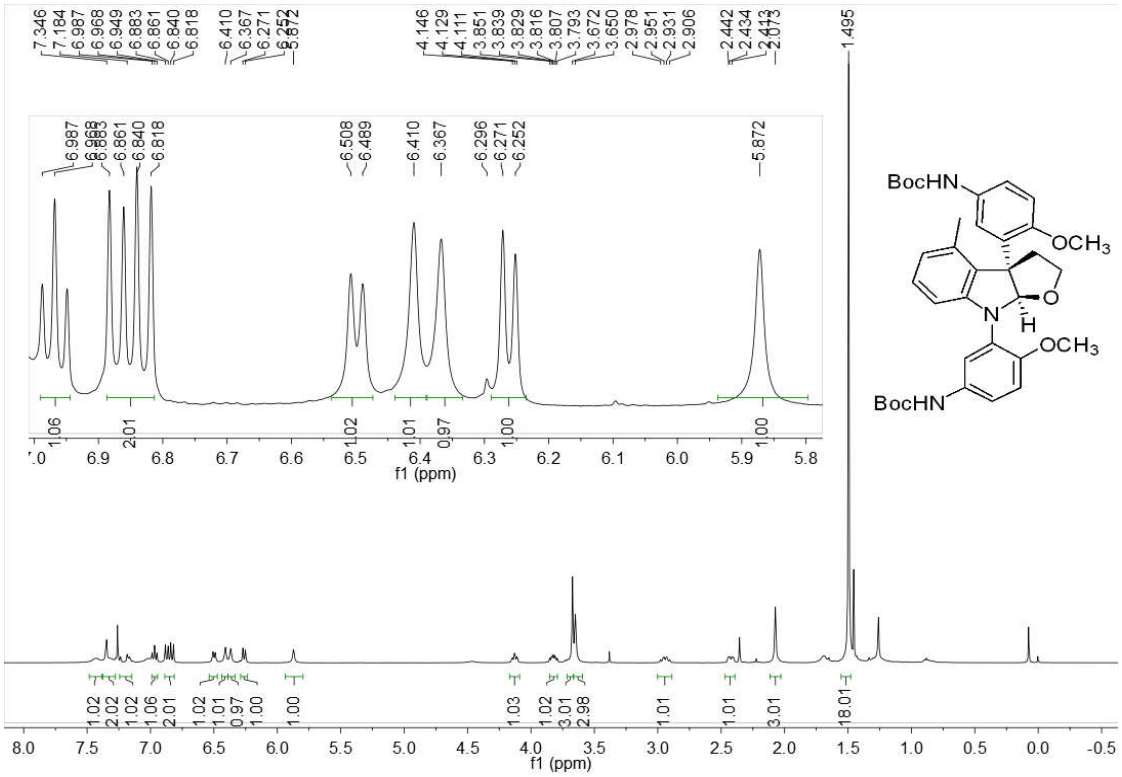
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba**



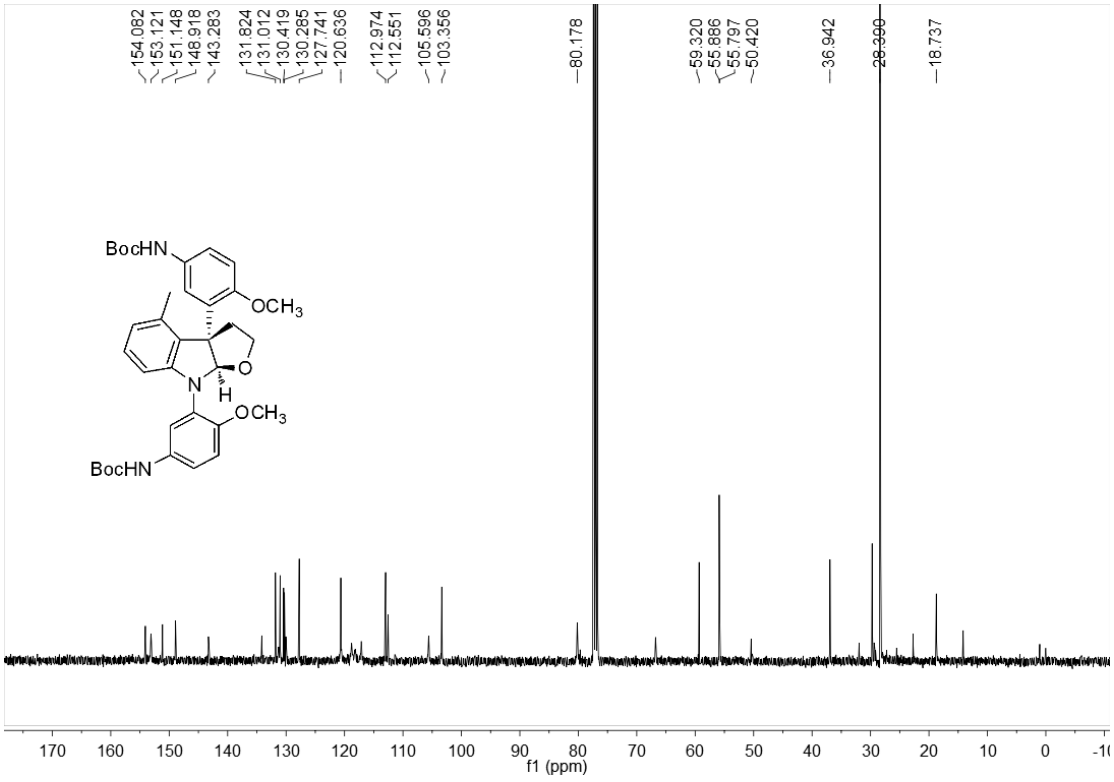
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba**



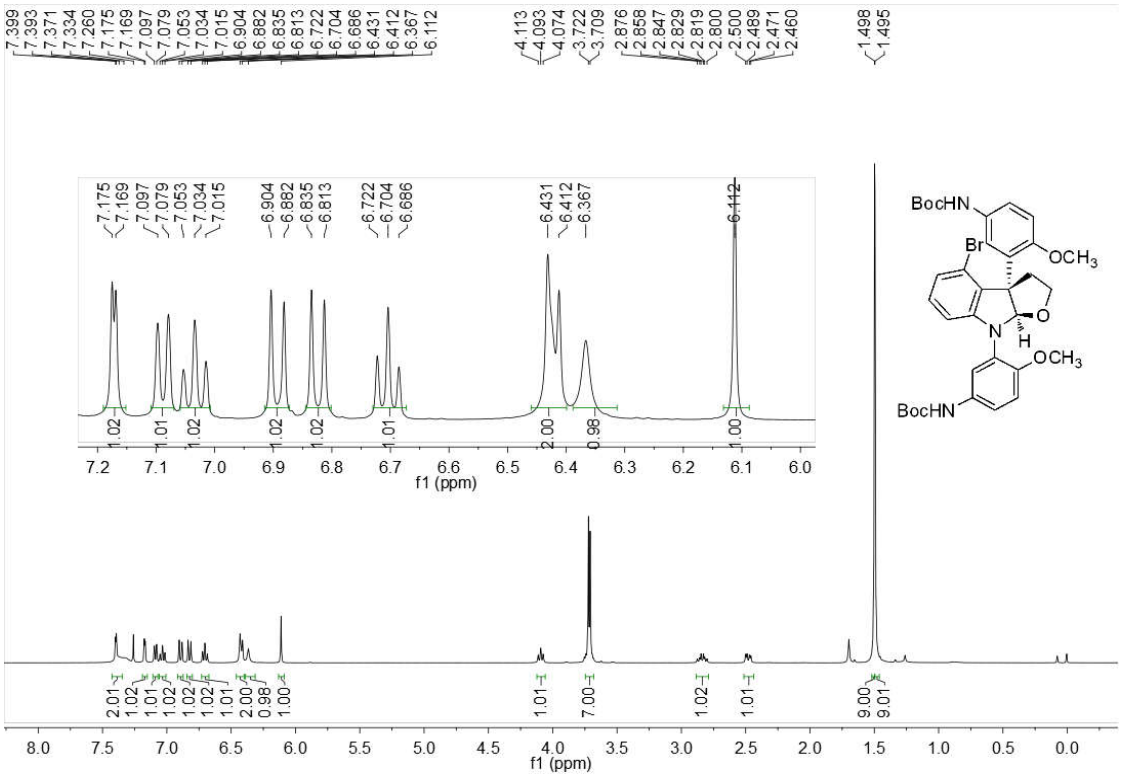
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ca**



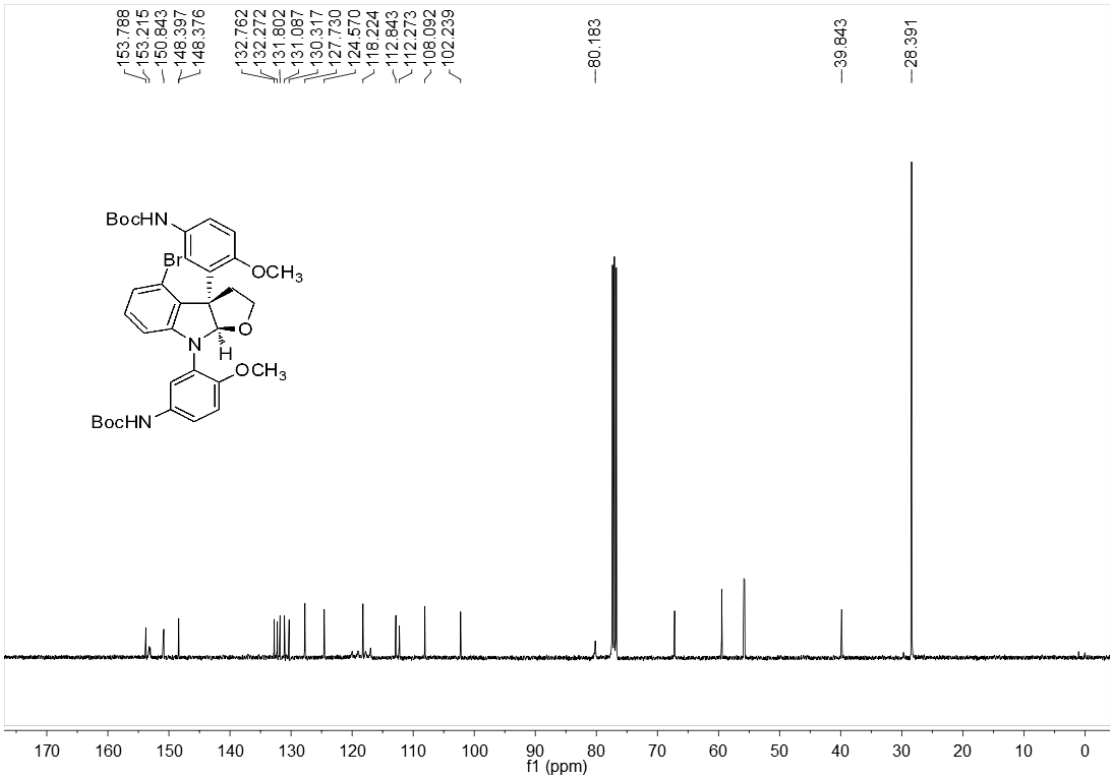
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ca**



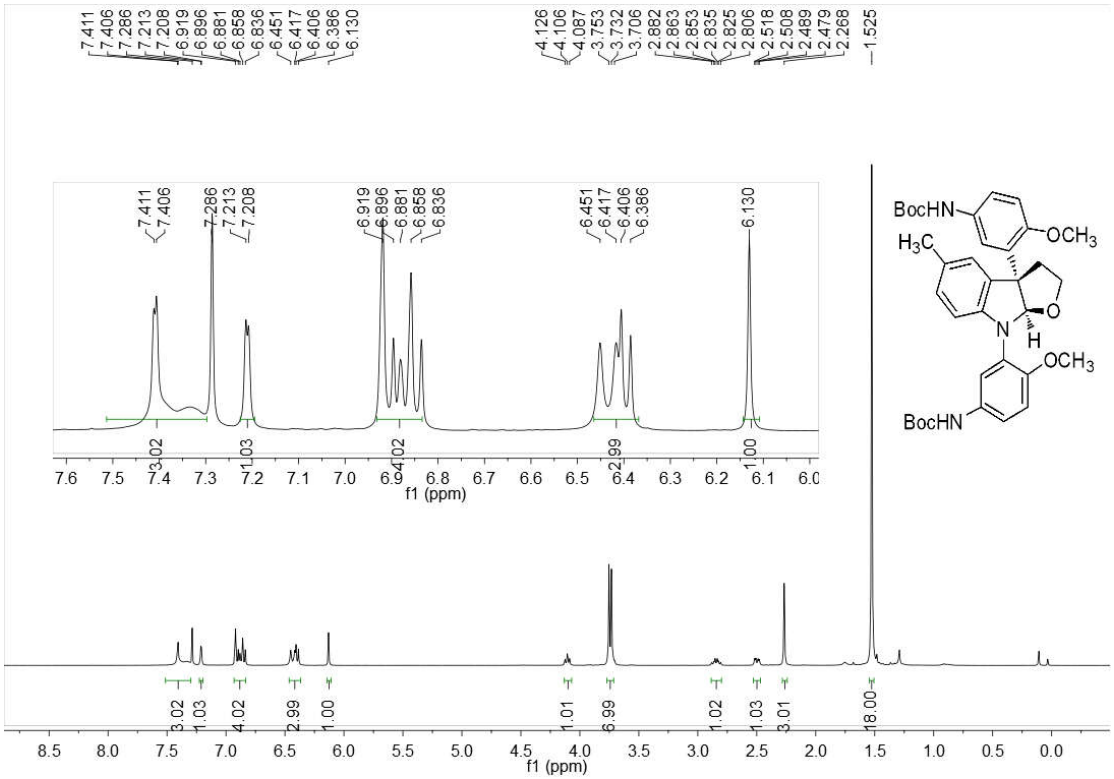
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da**



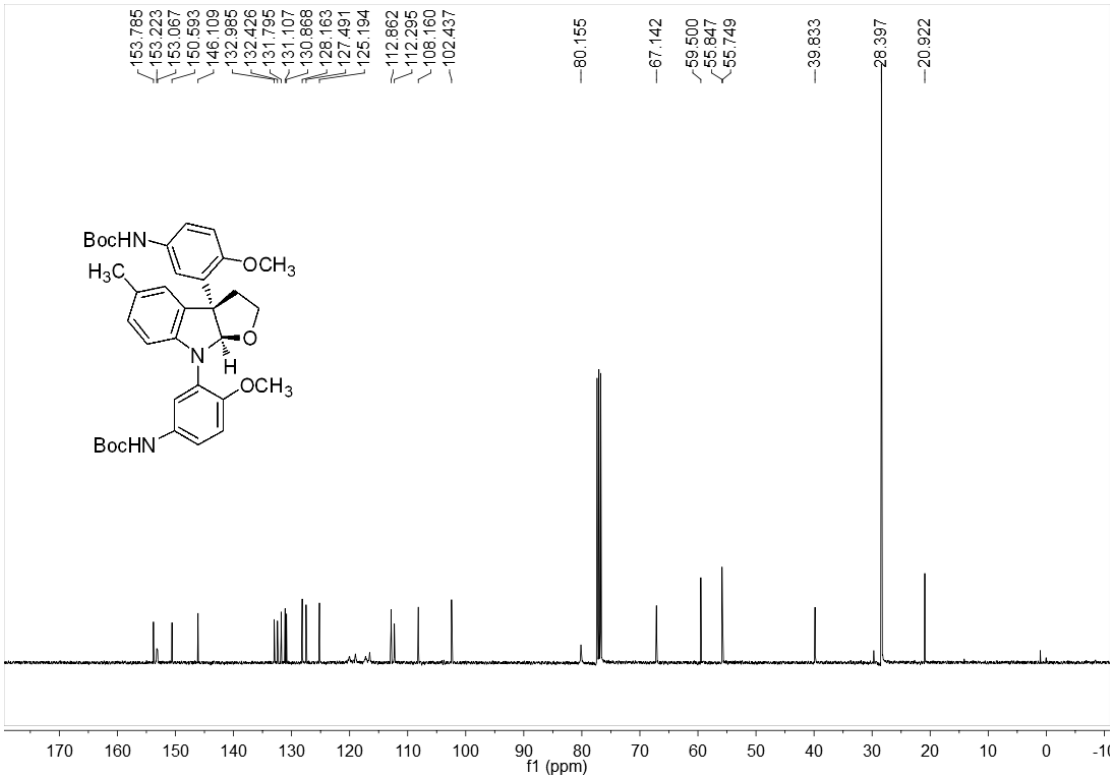
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da**



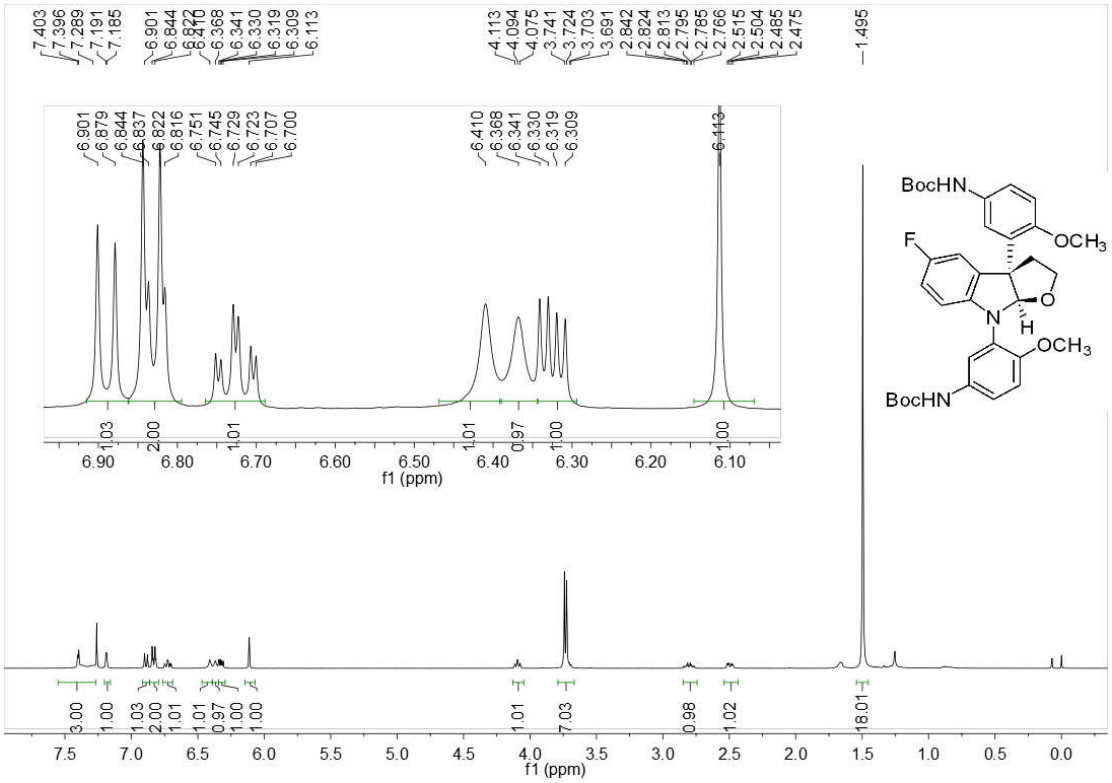
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ea**



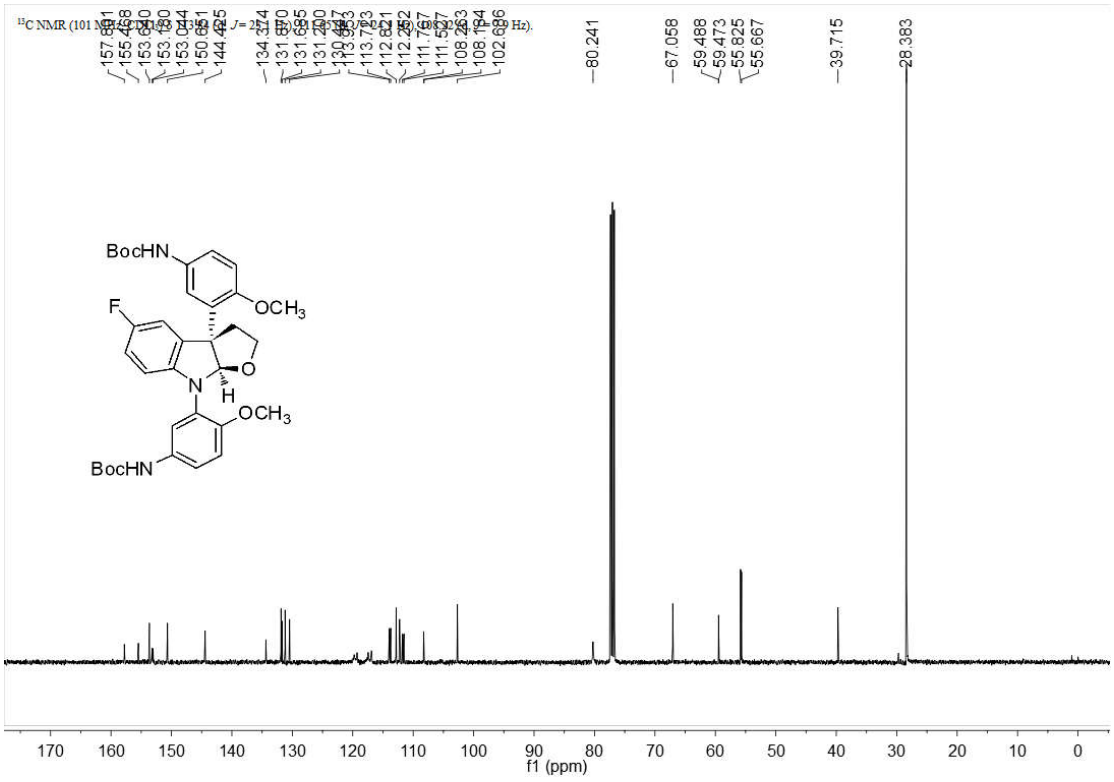
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea**



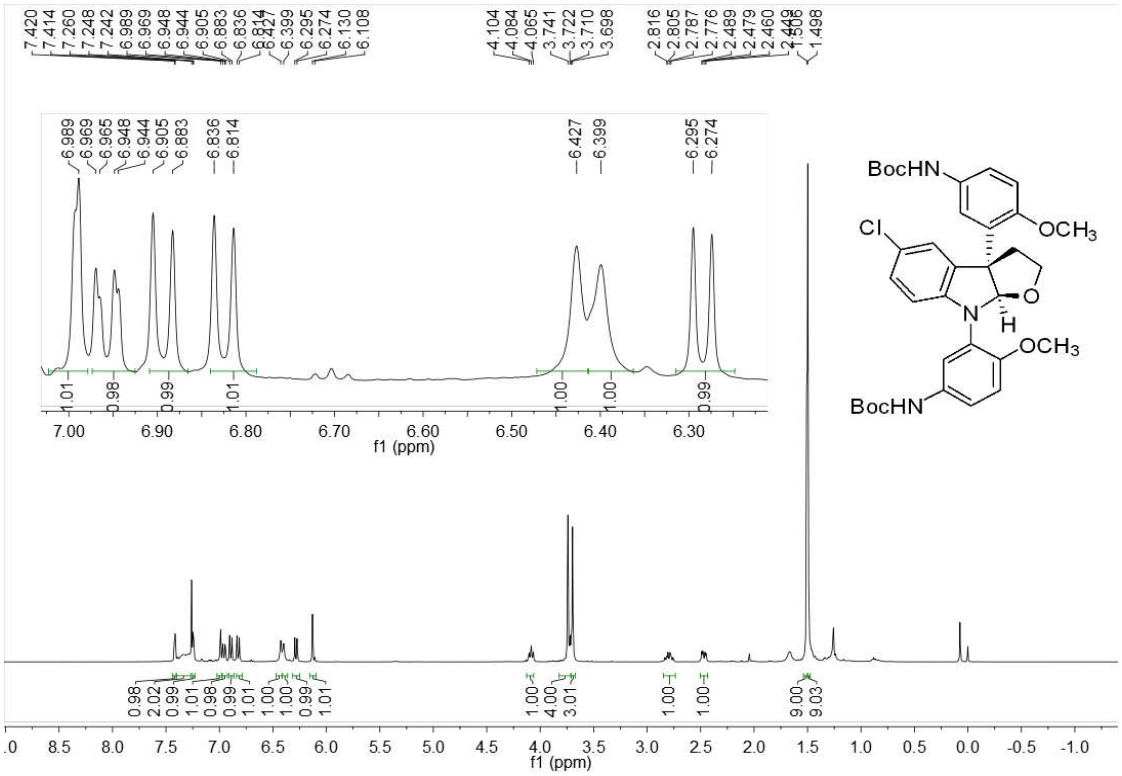
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3fa**



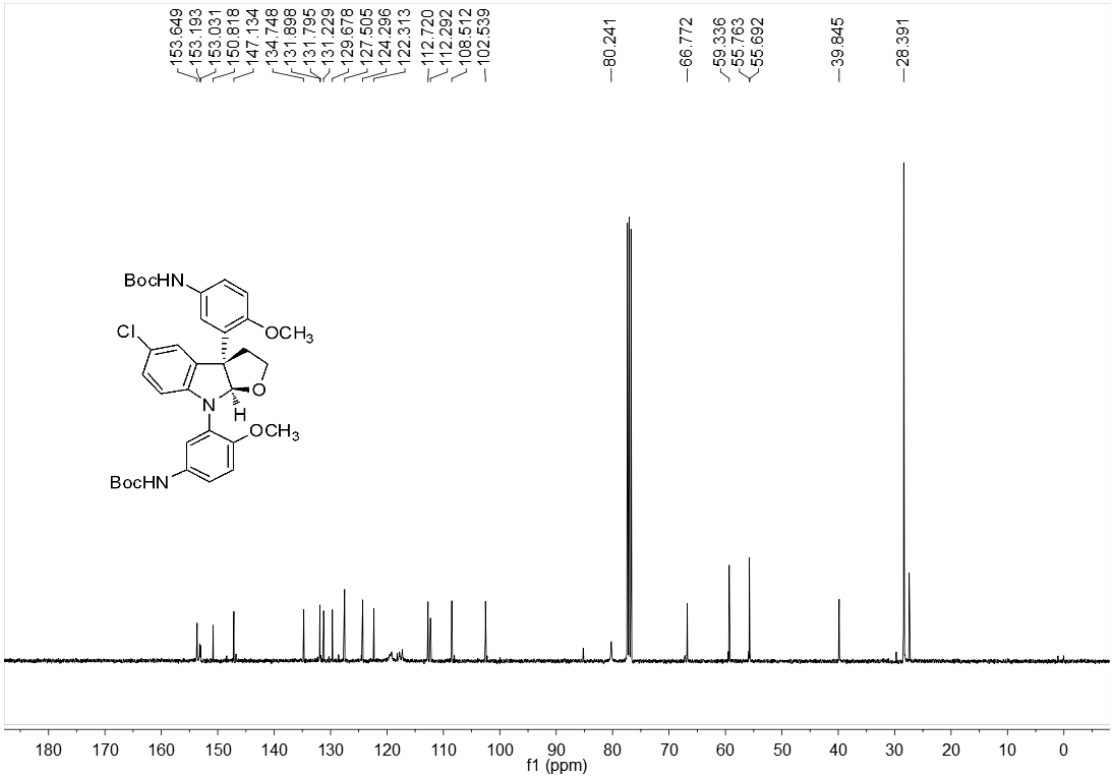
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3fa**



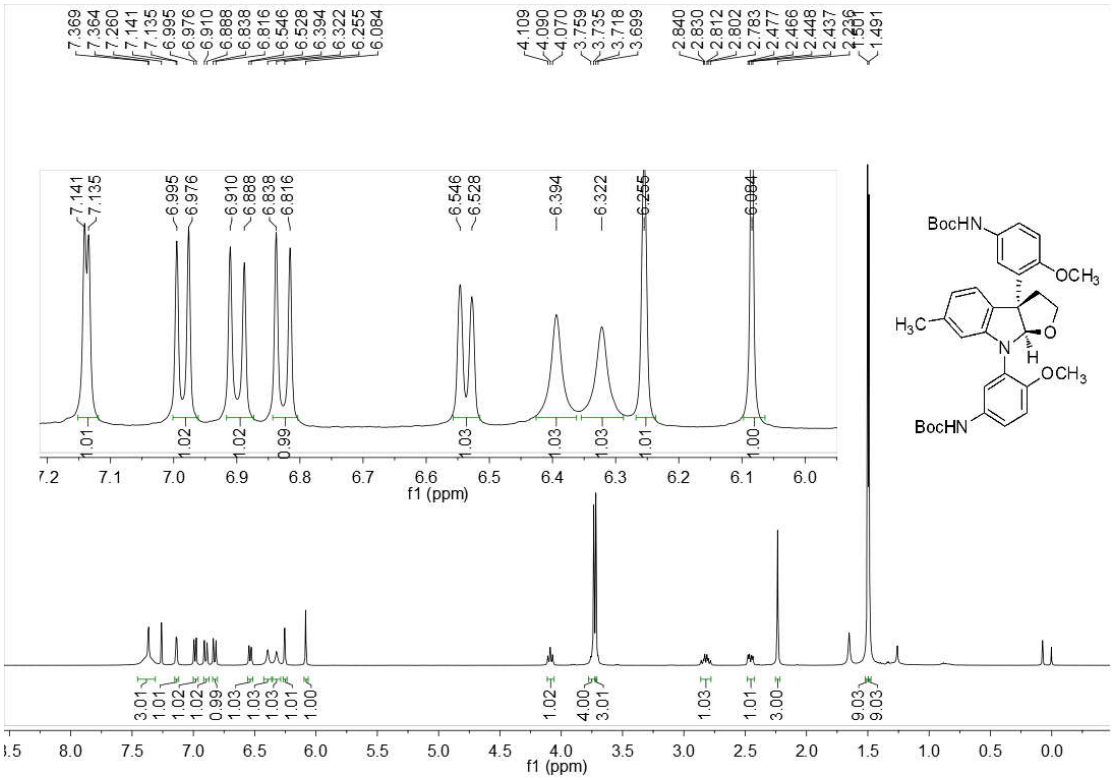
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga**



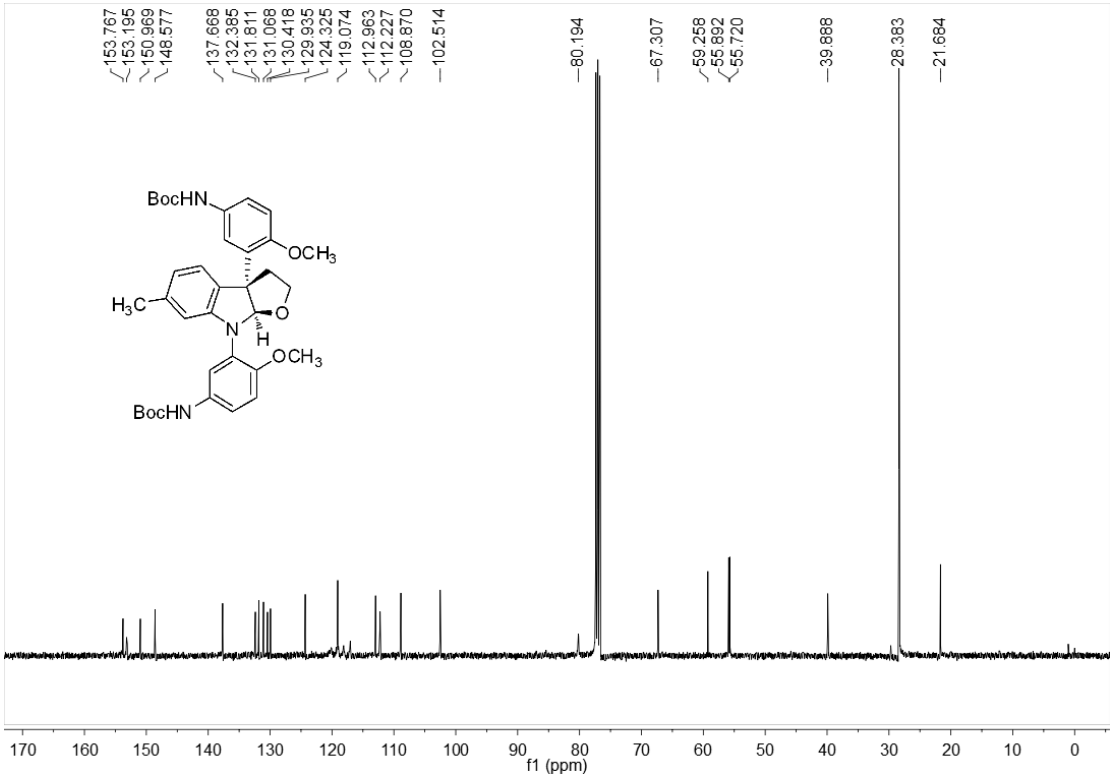
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**



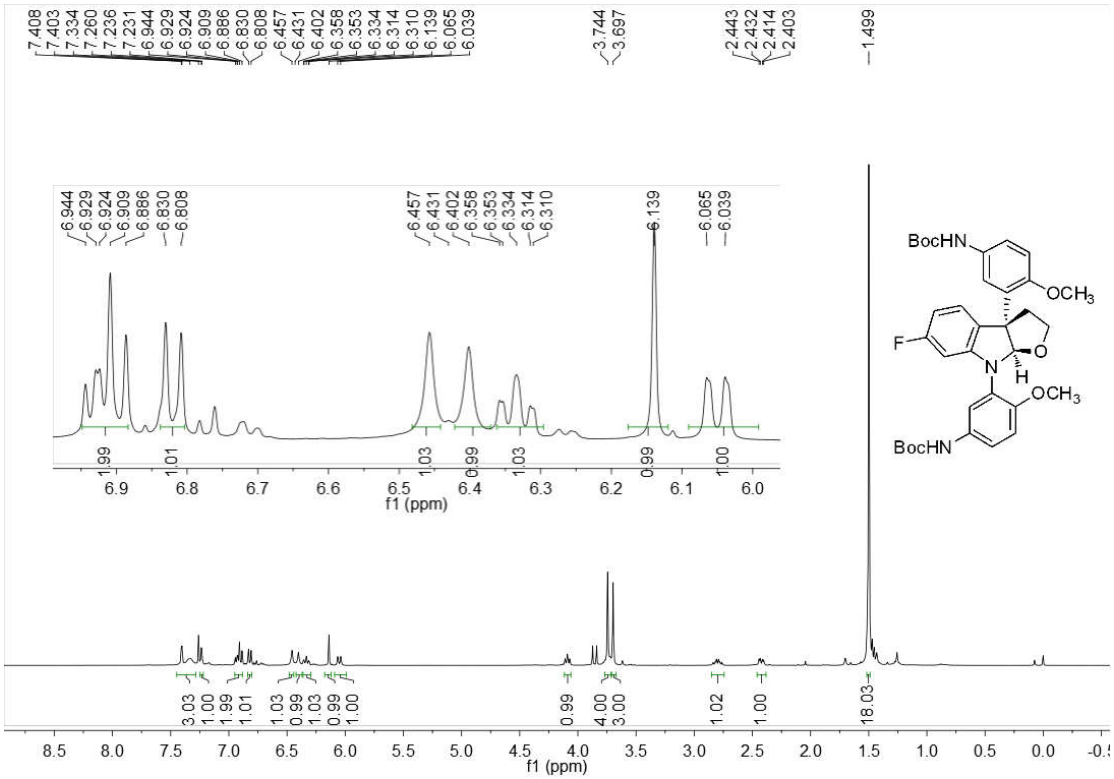
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ha**



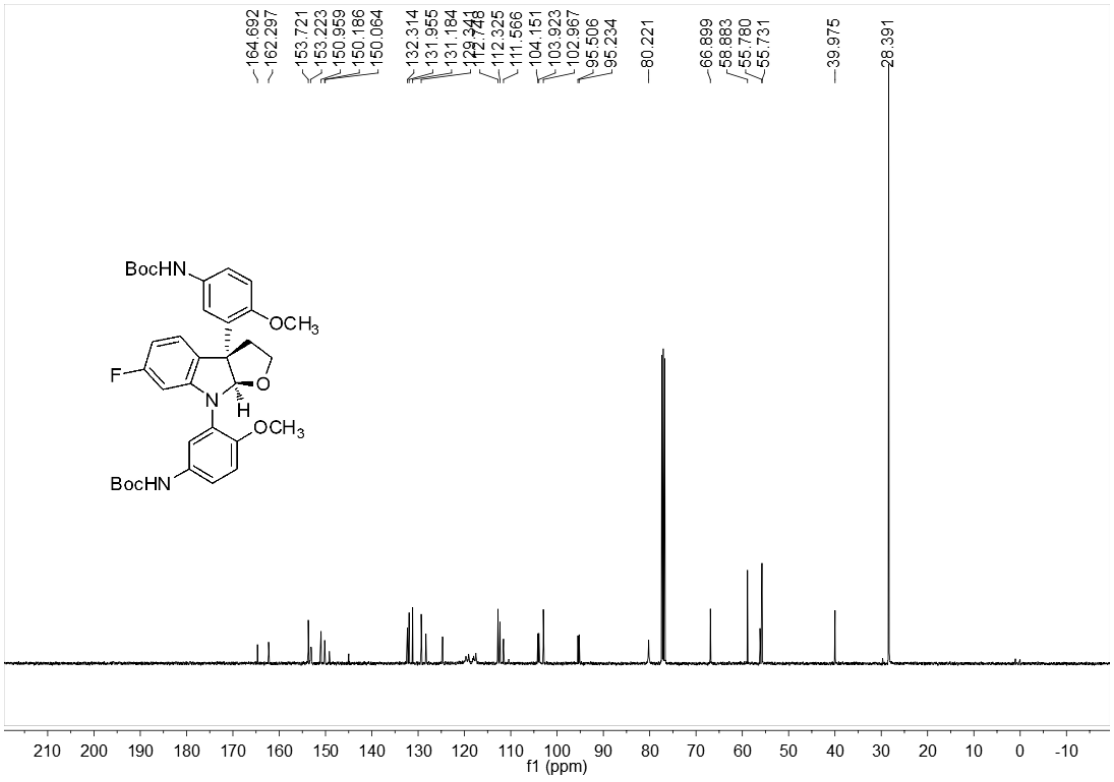
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha**



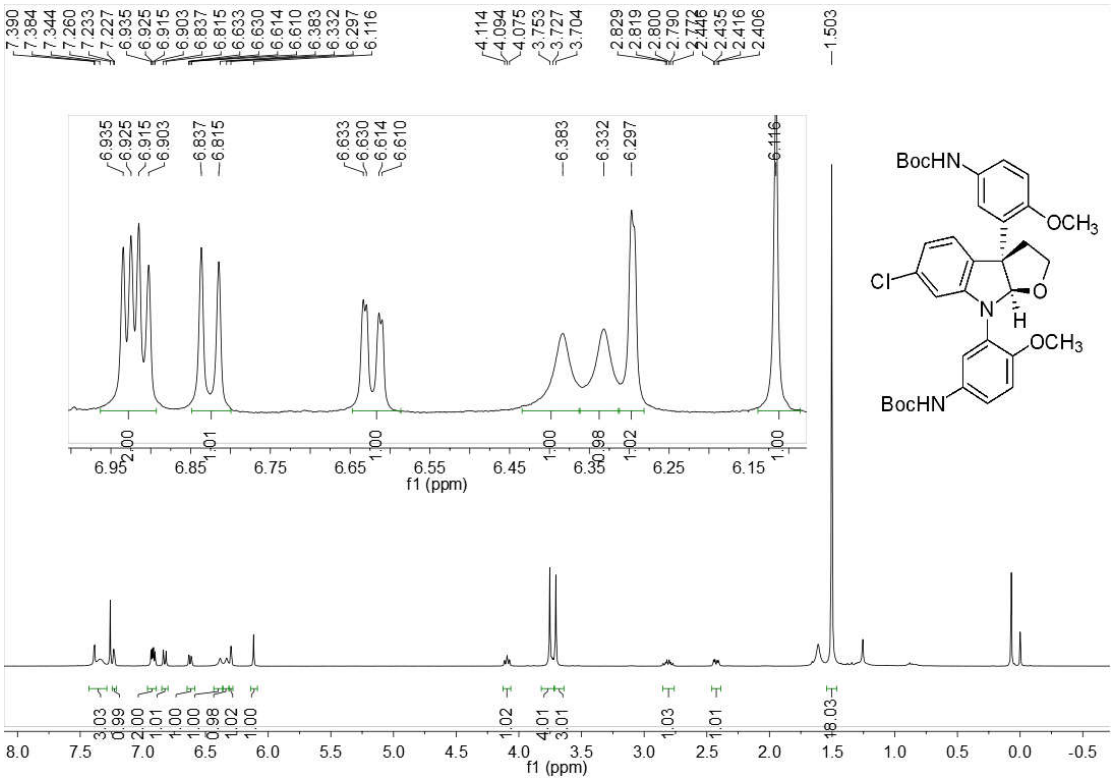
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ia**



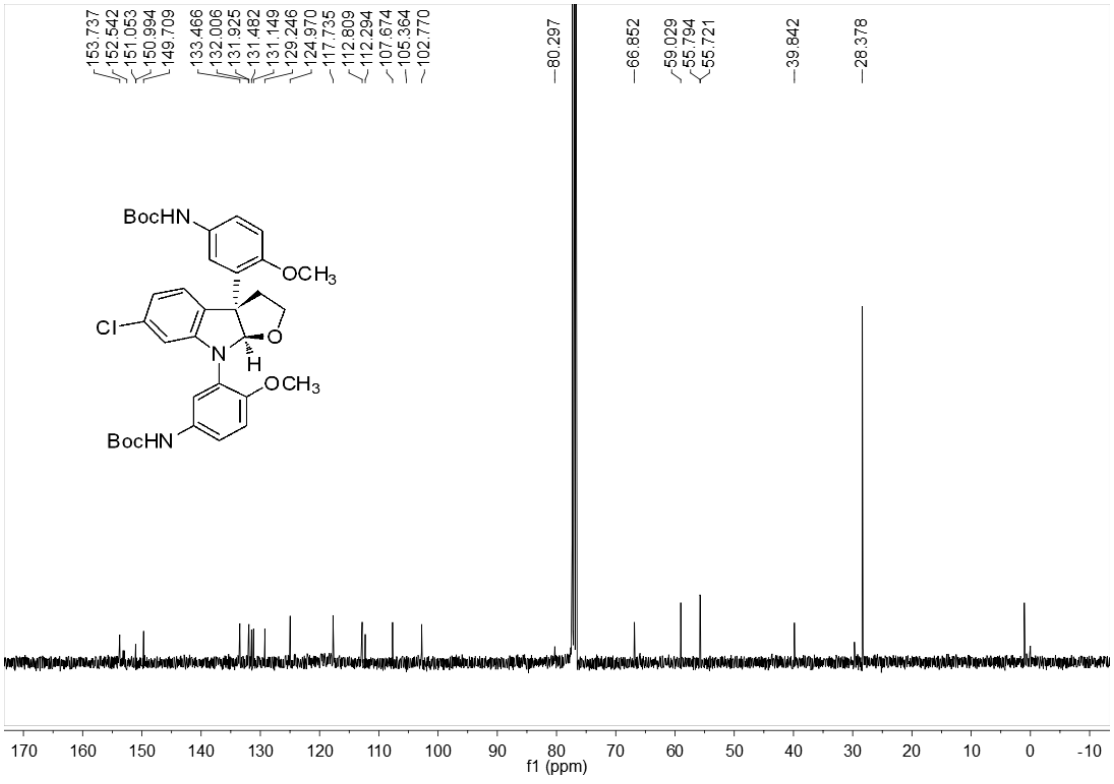
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ia**



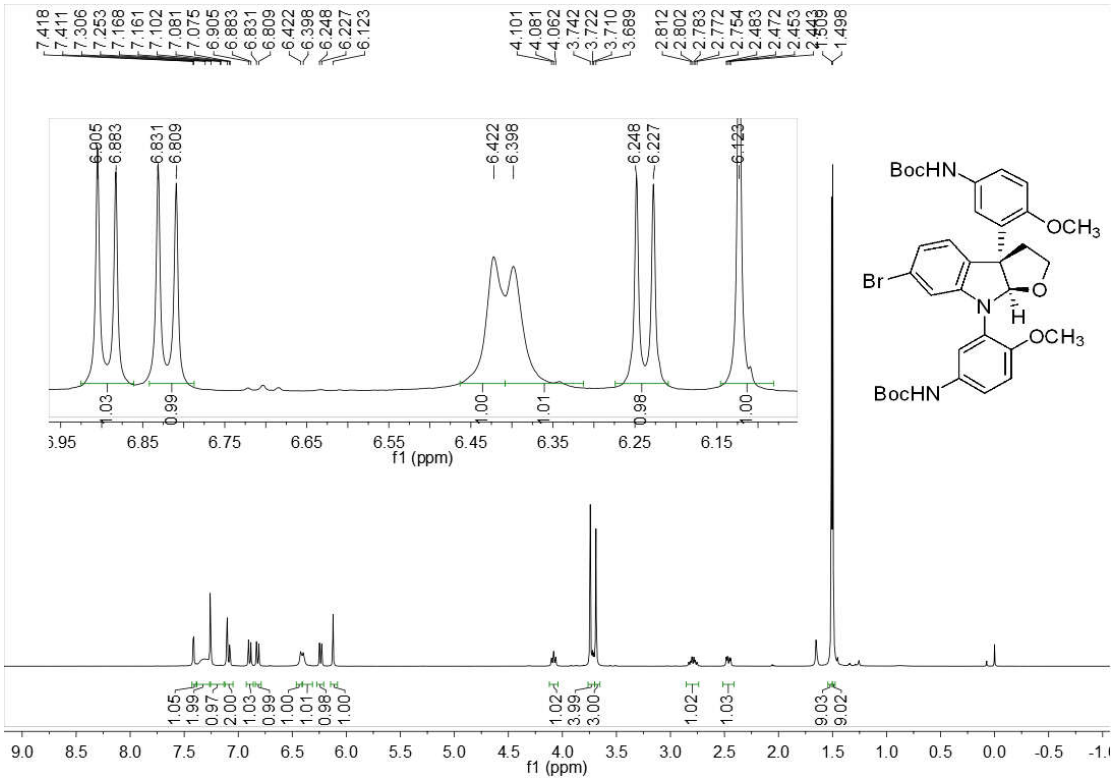
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ja**



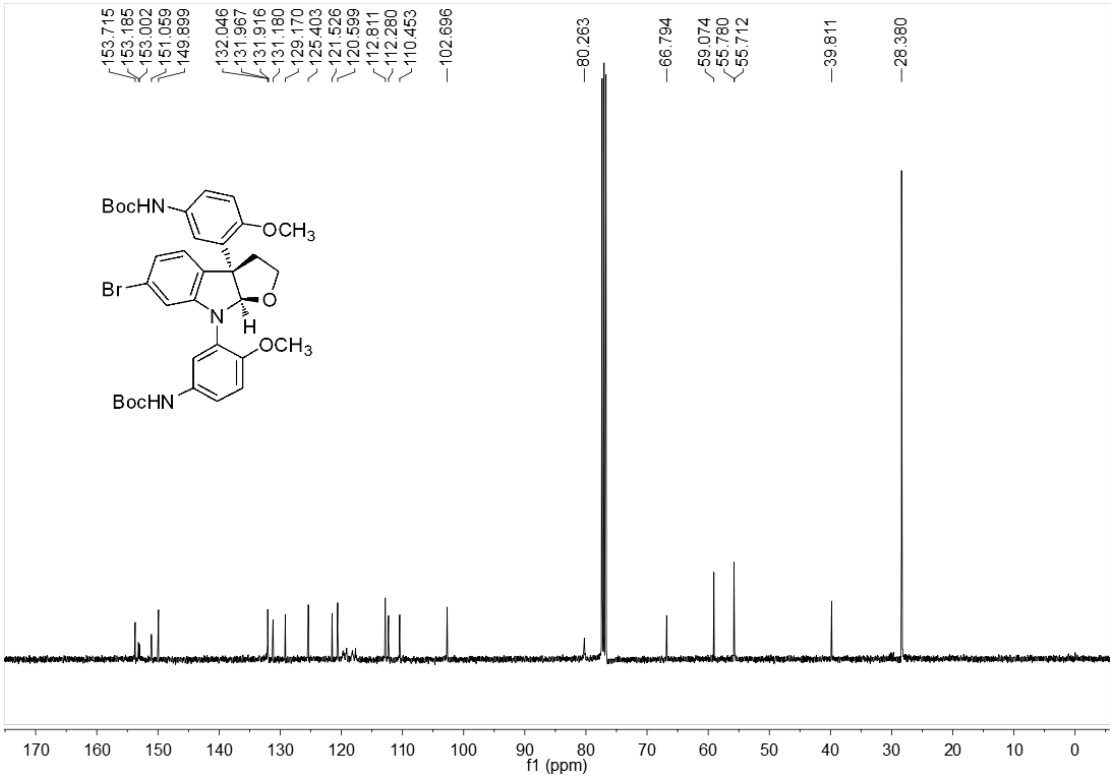
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ja**



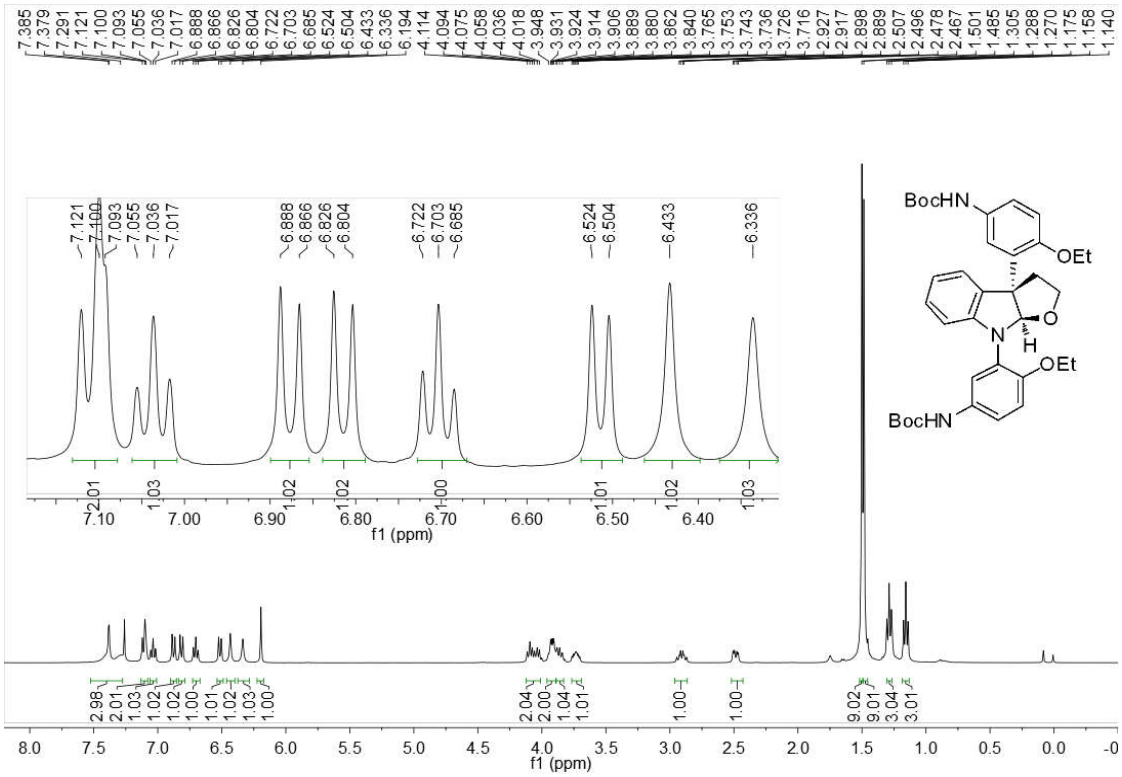
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ka**



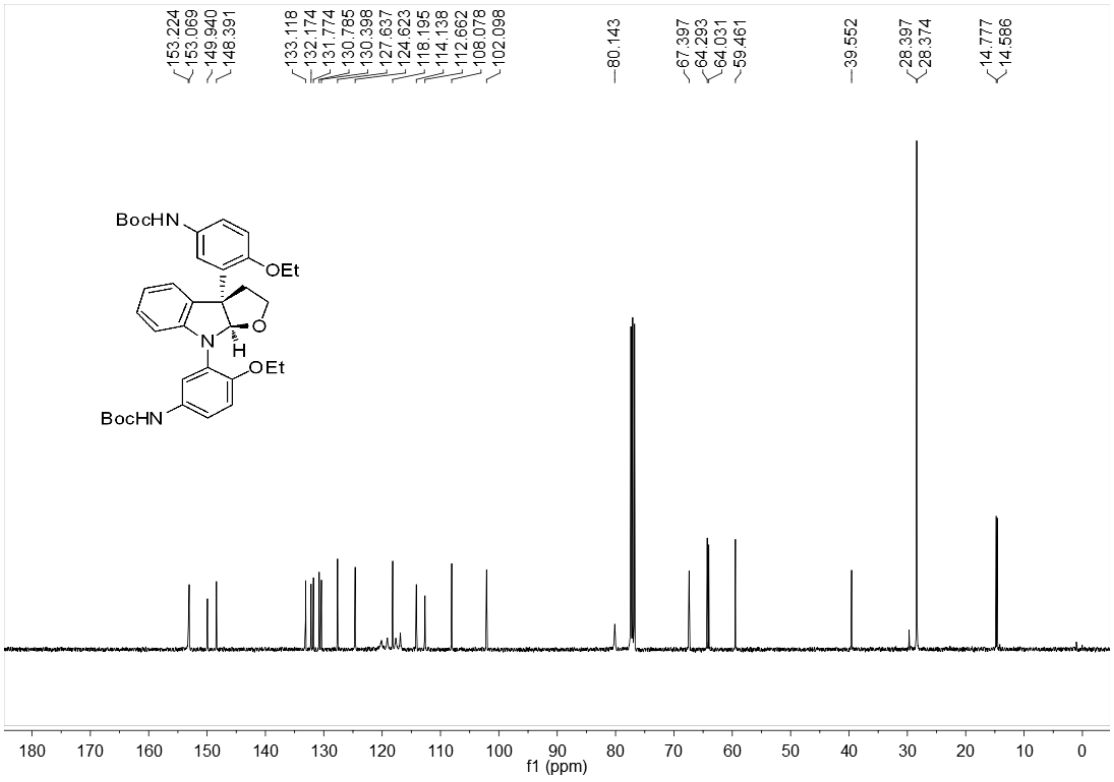
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ka**



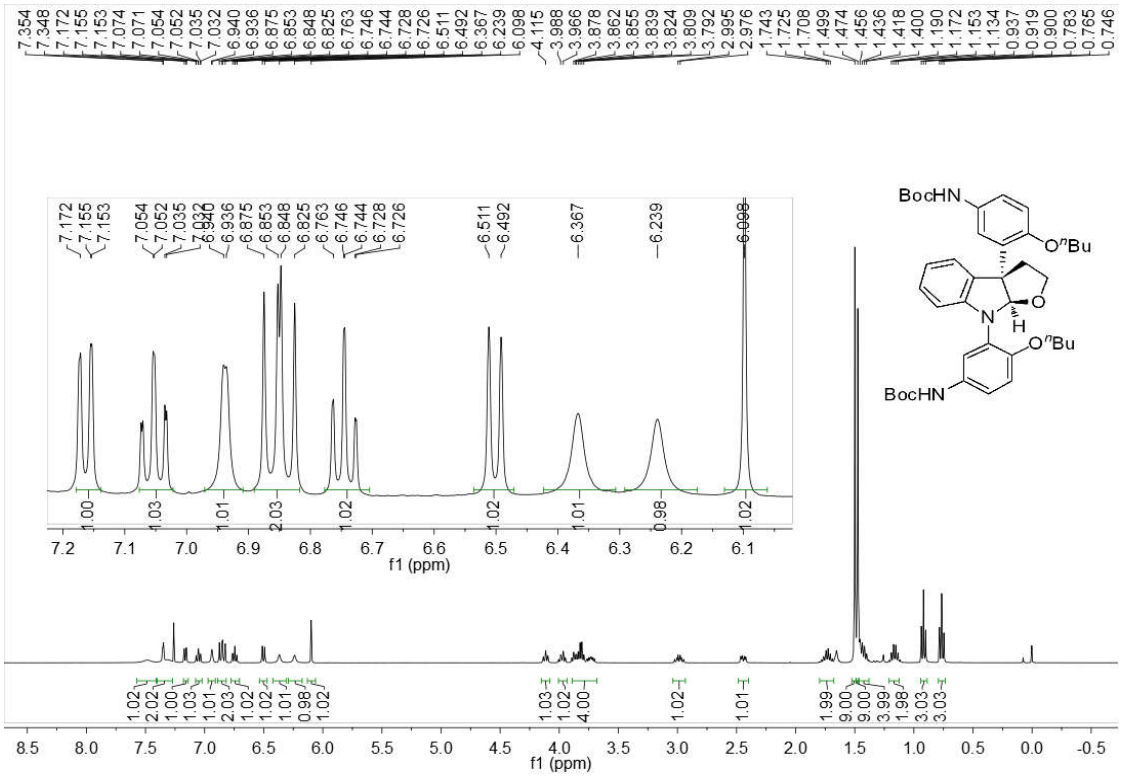
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab**



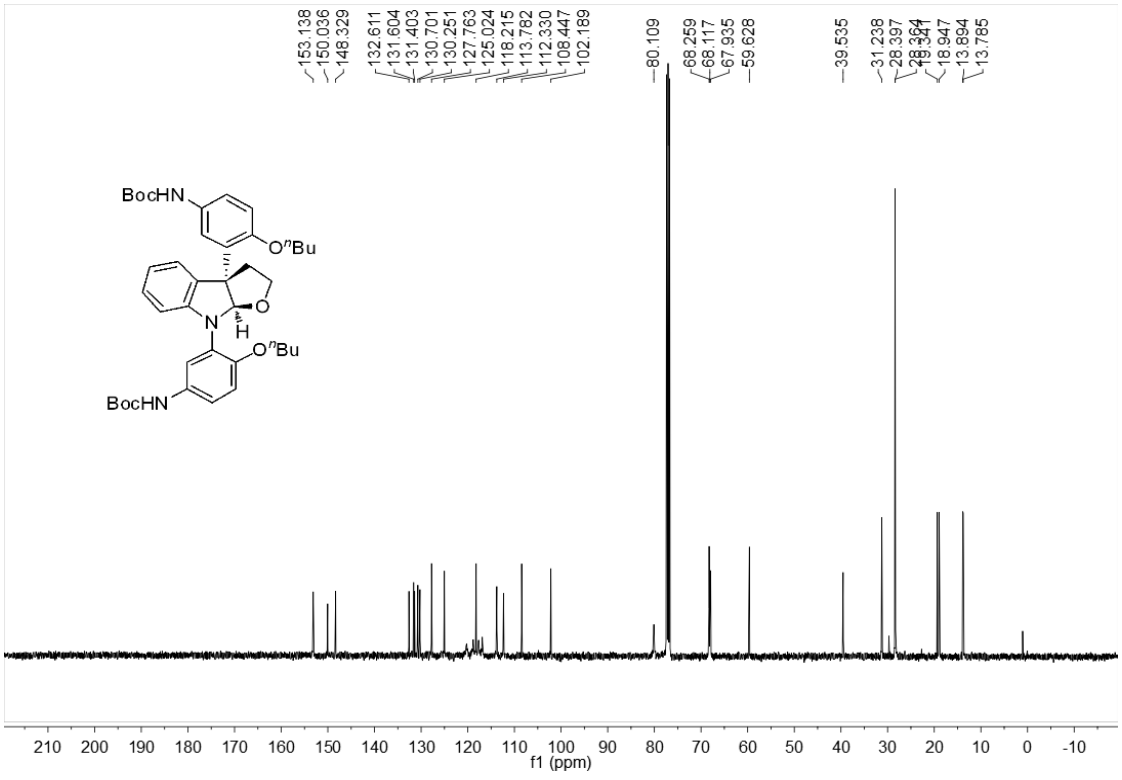
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ab**



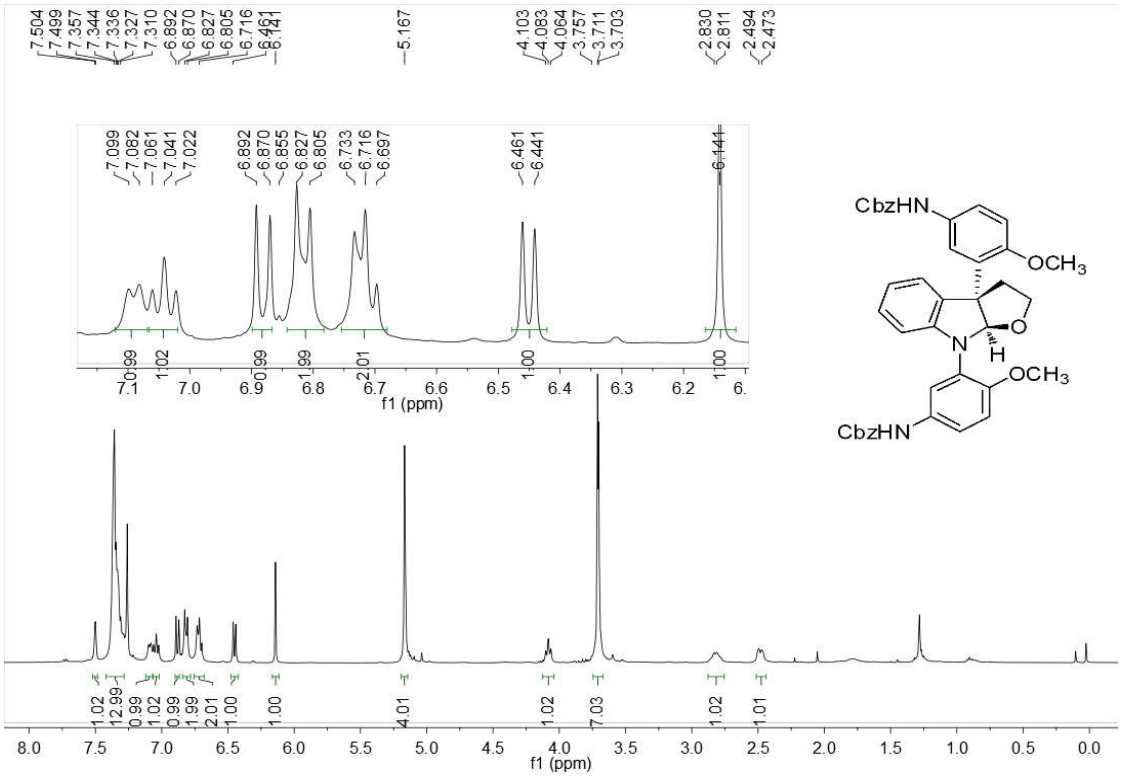
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac**



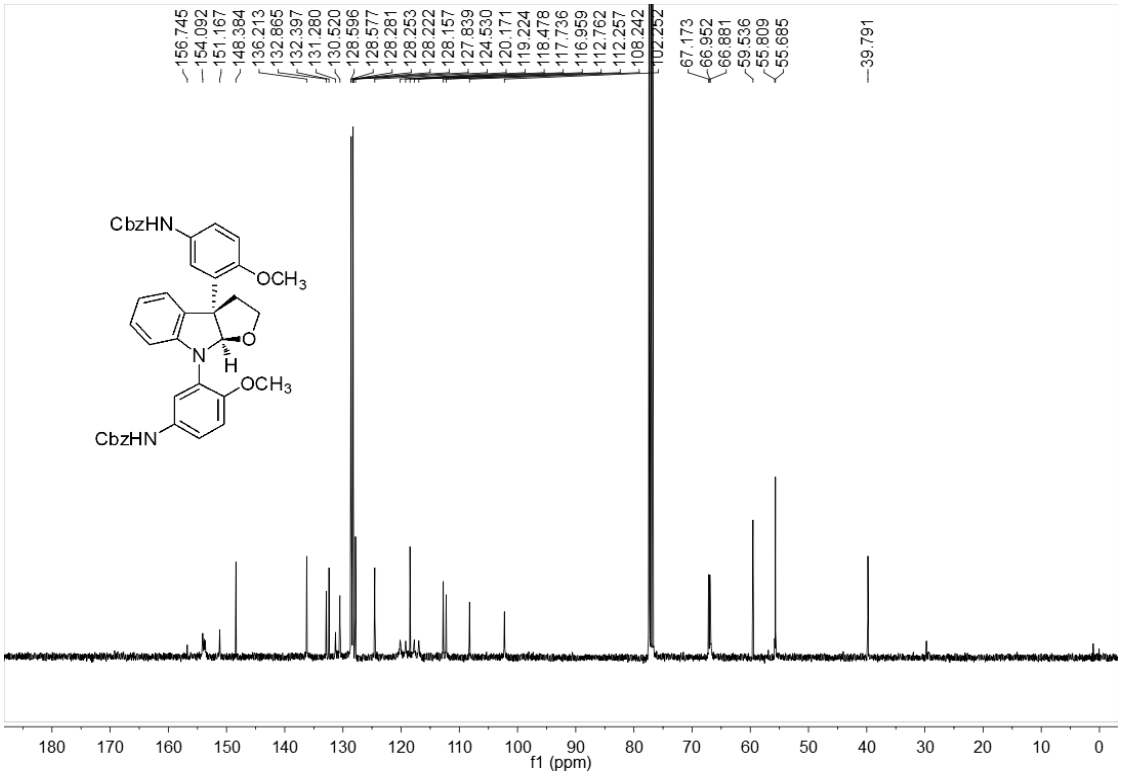
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ac**



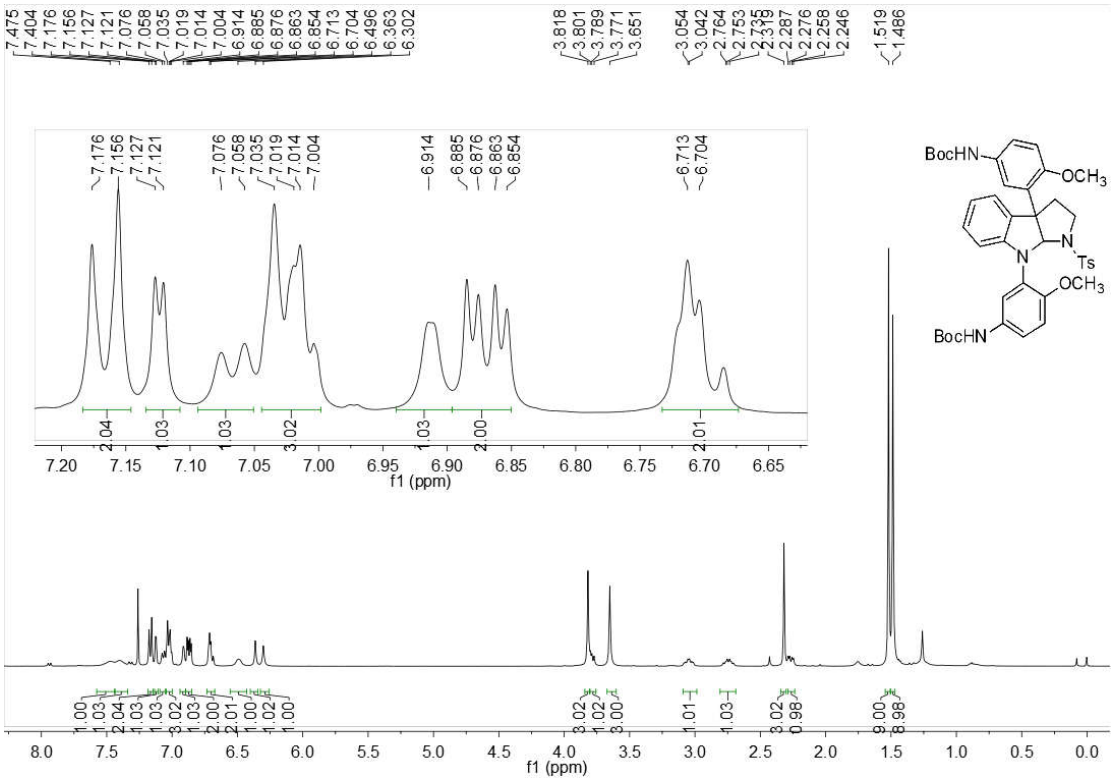
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad**



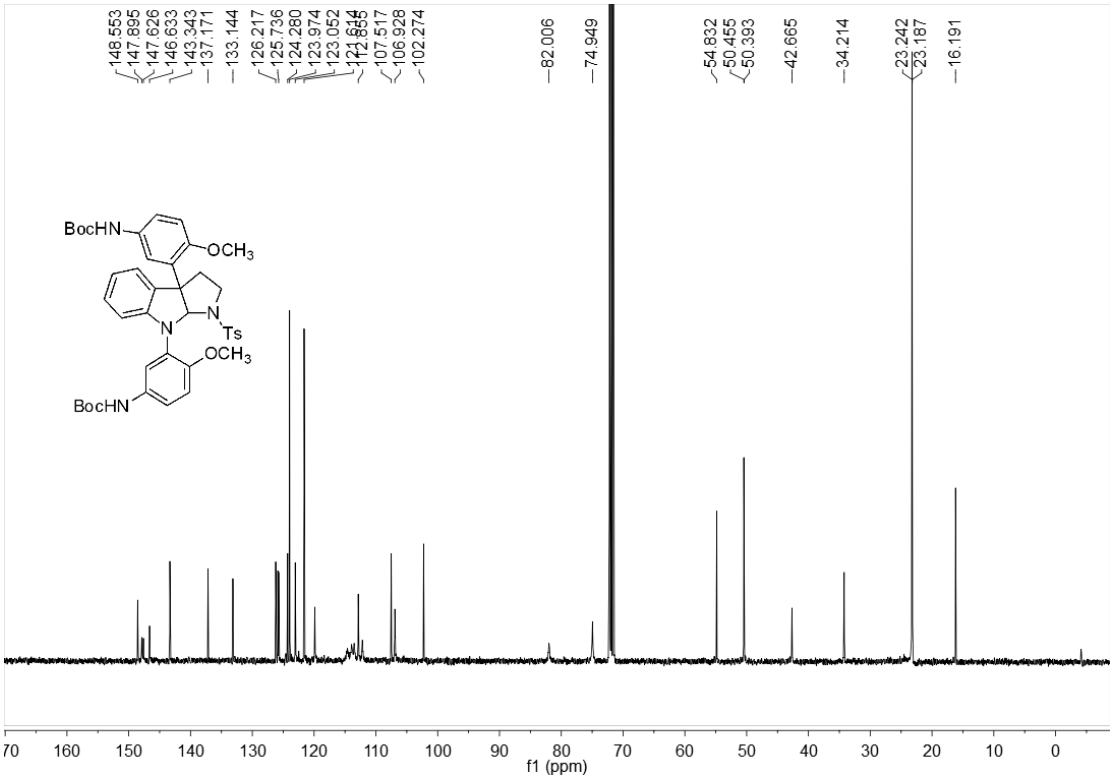
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ad**



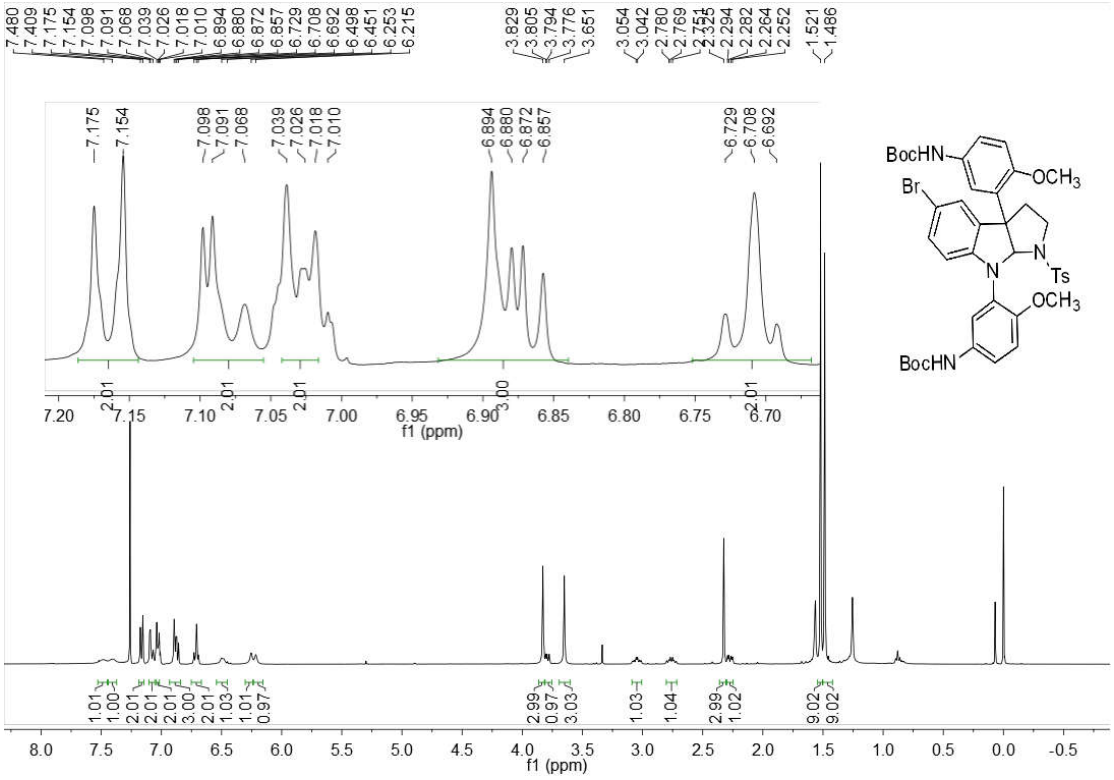
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3na**



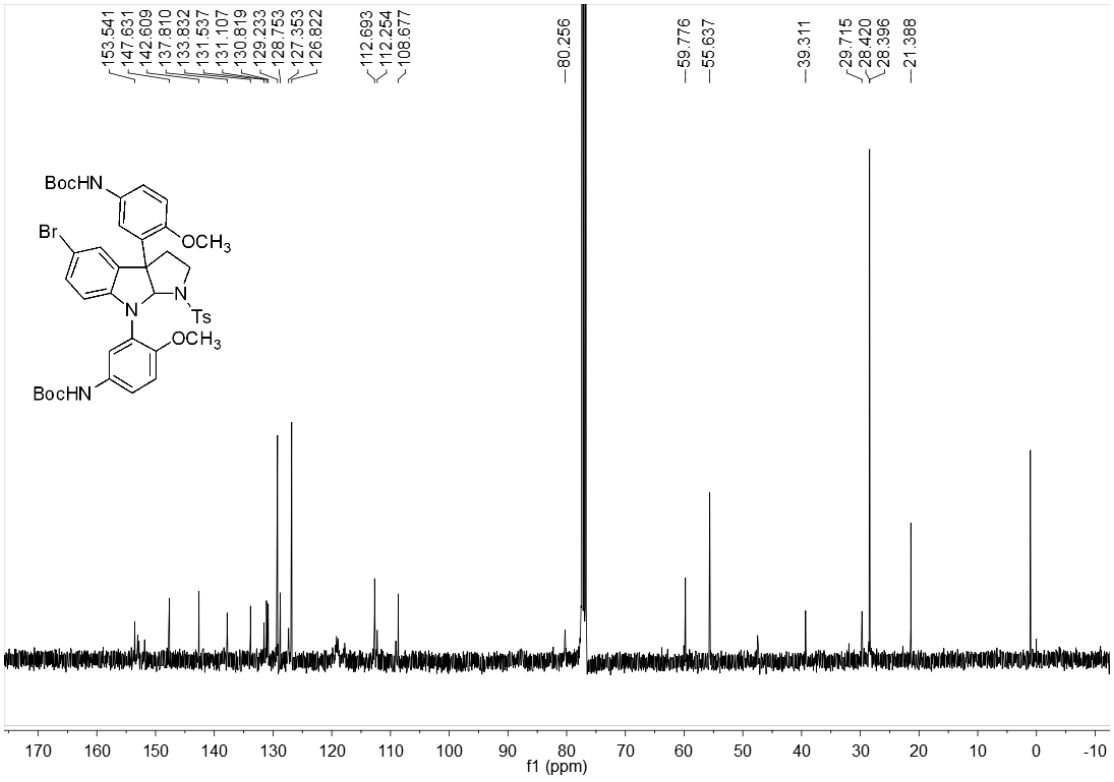
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3na**



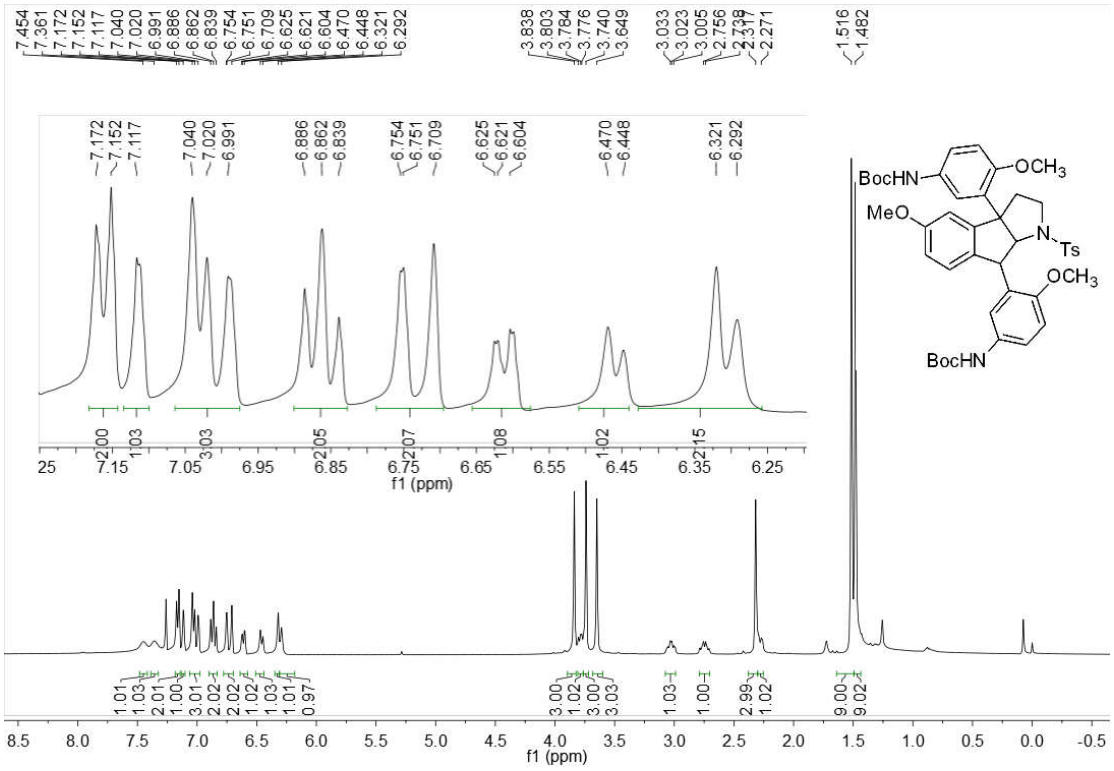
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3oa**



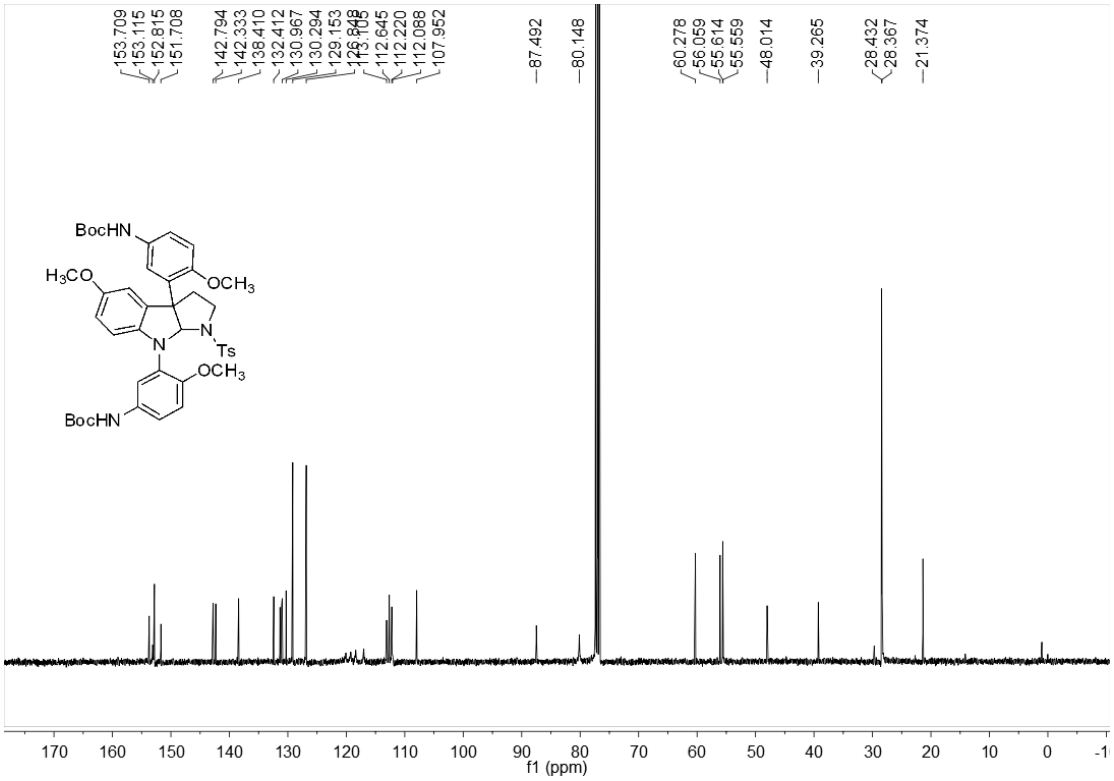
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3oa**



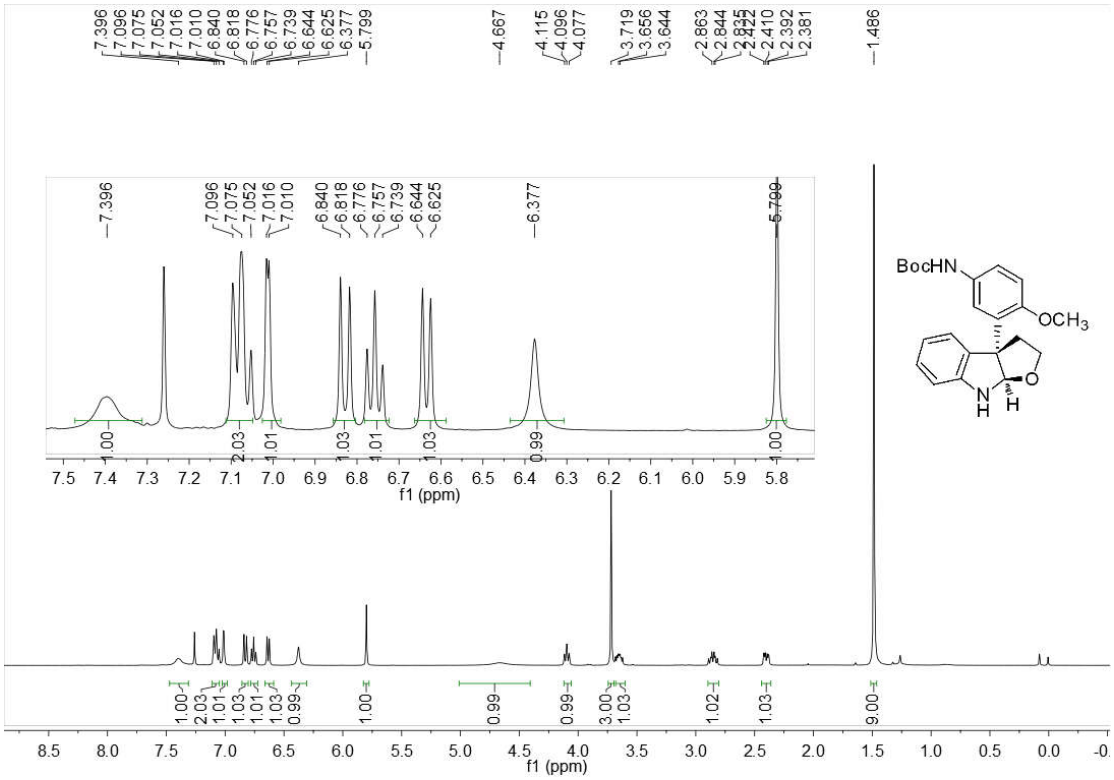
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3pa**



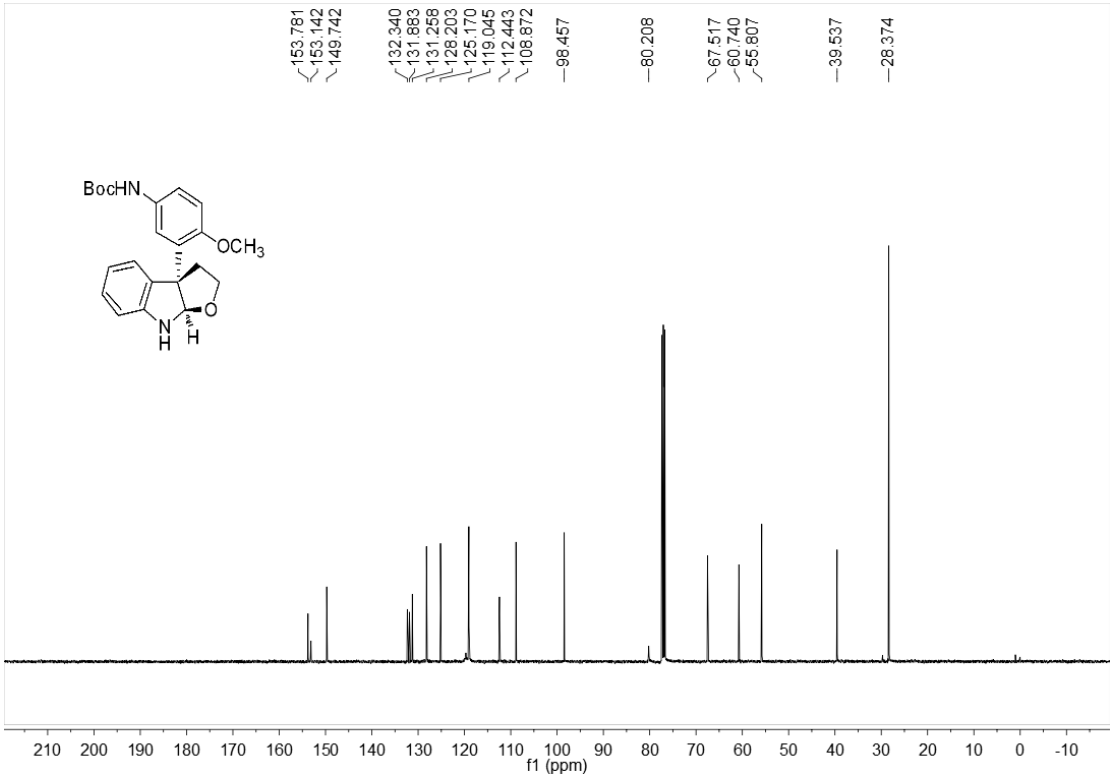
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3pa**



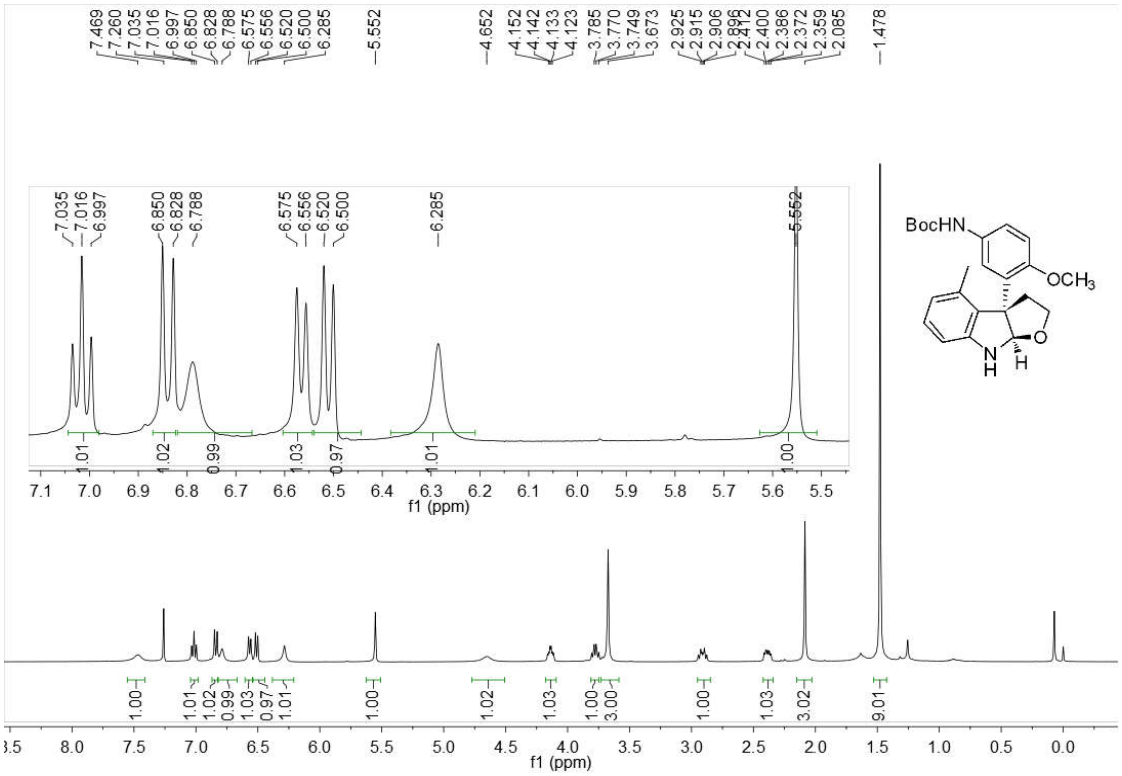
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7aa**



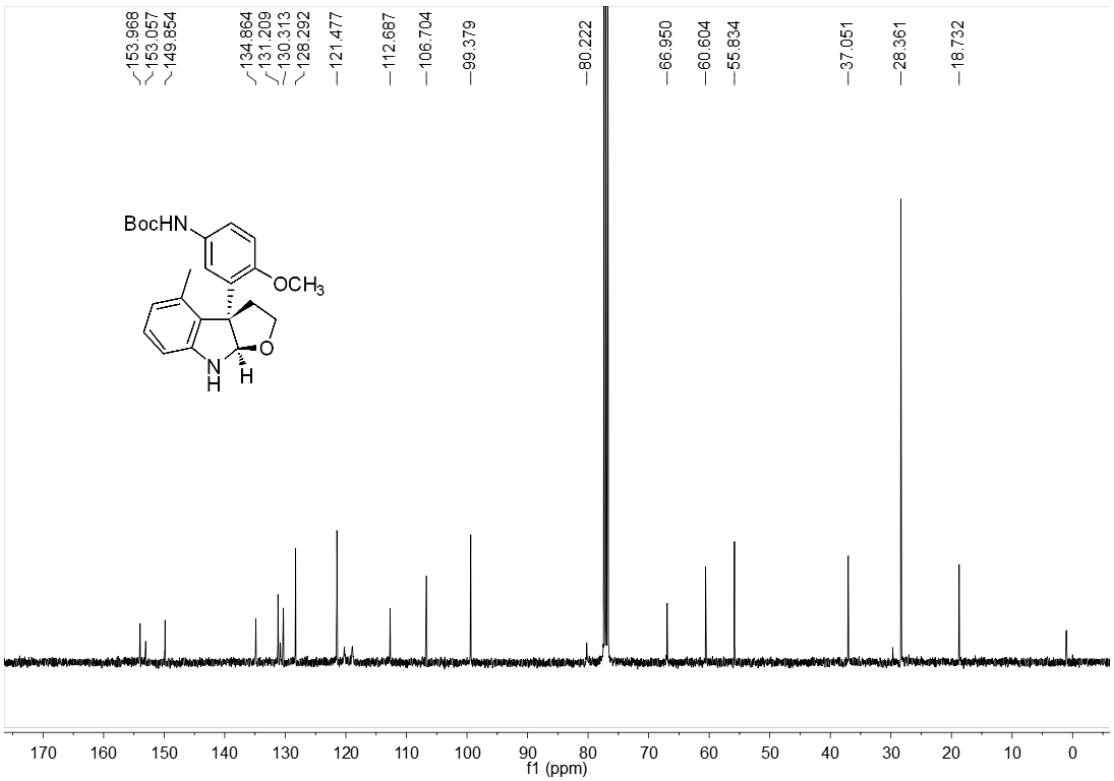
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7aa**



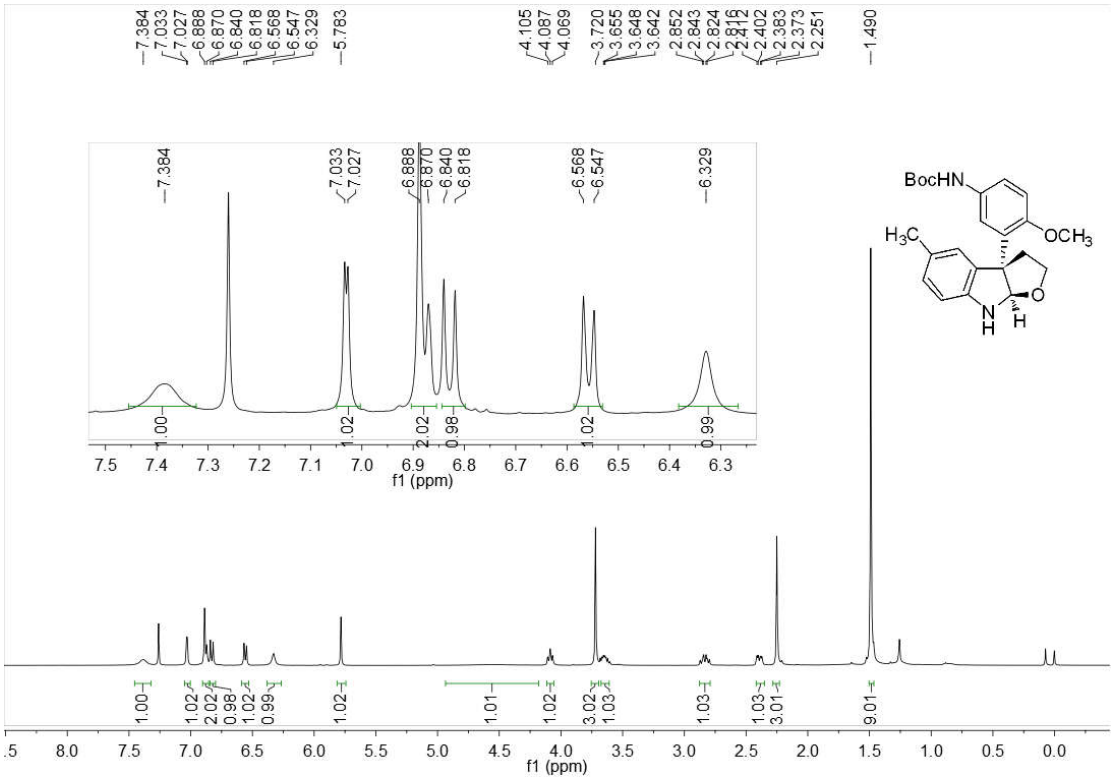
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ca**



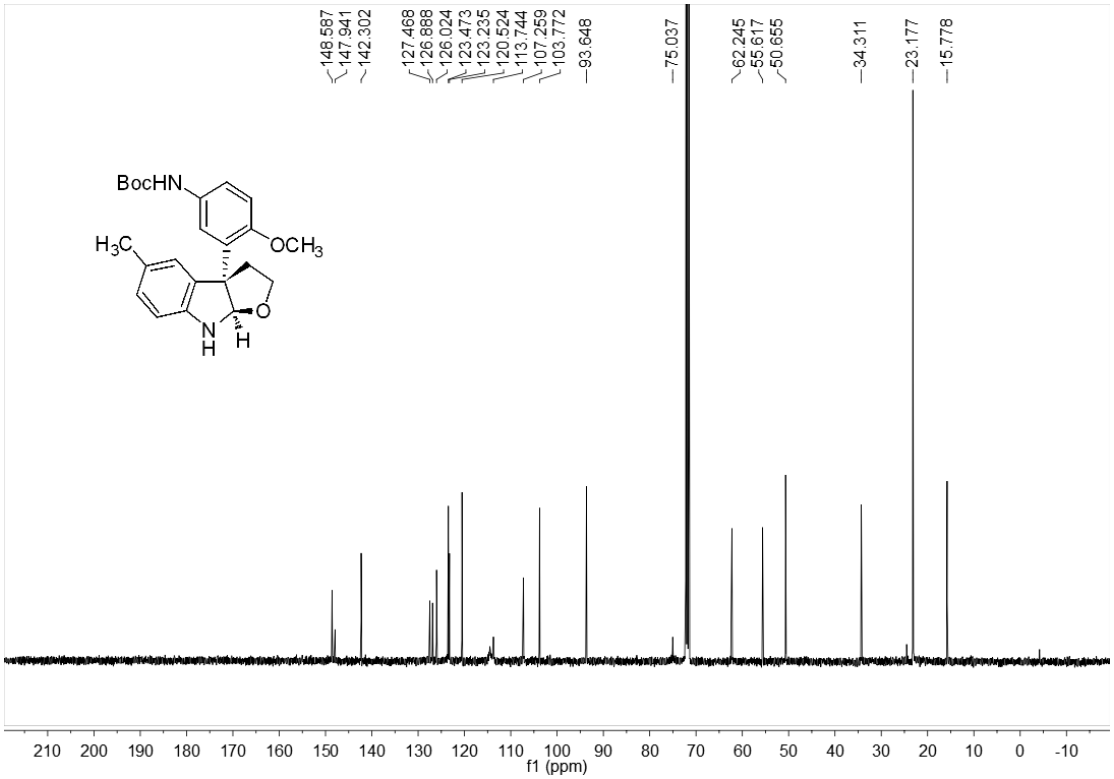
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ca**



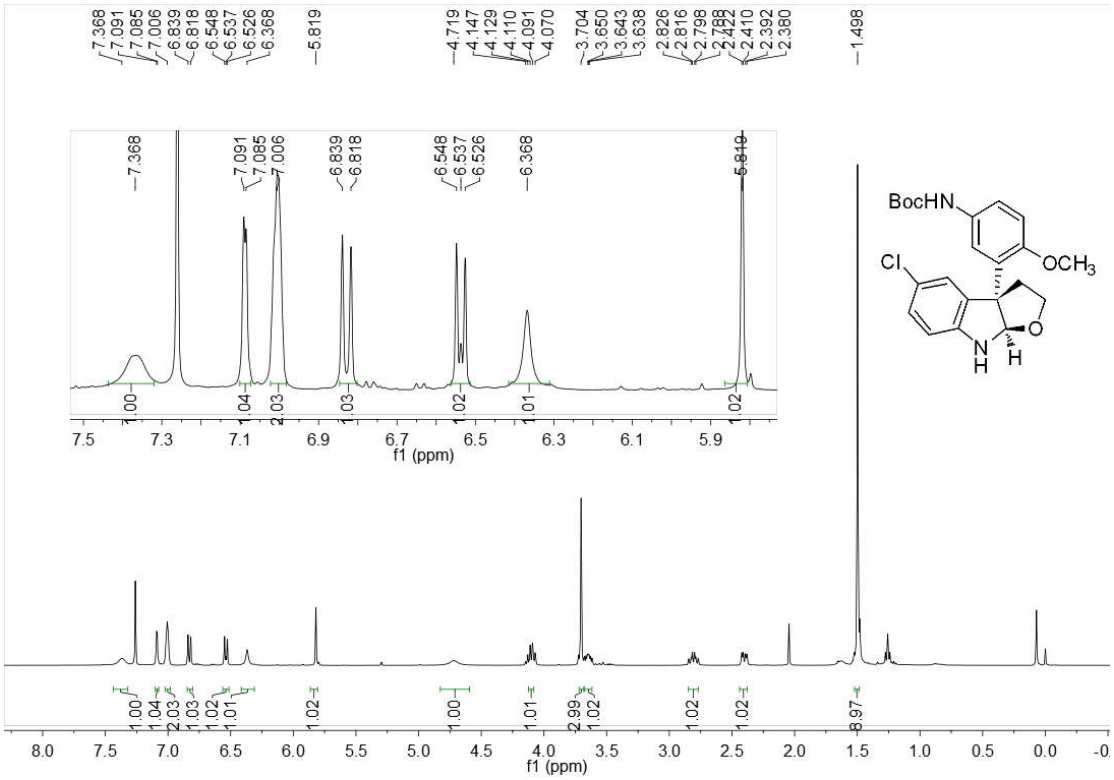
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ea**



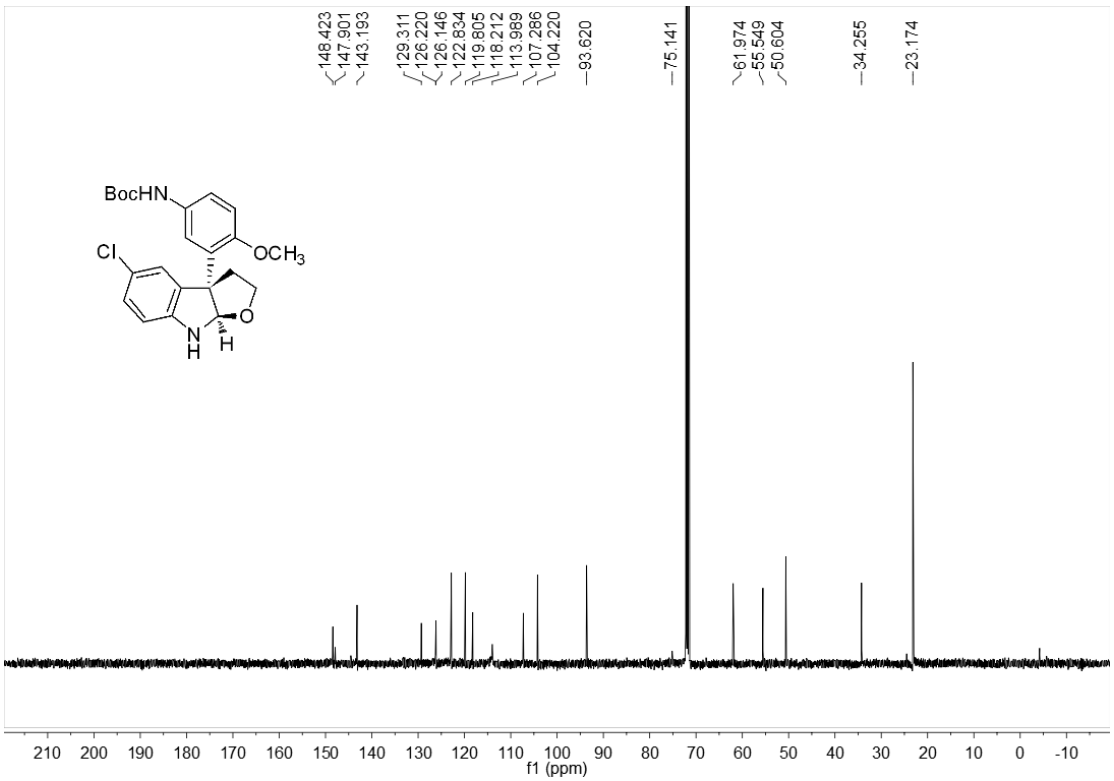
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ea**



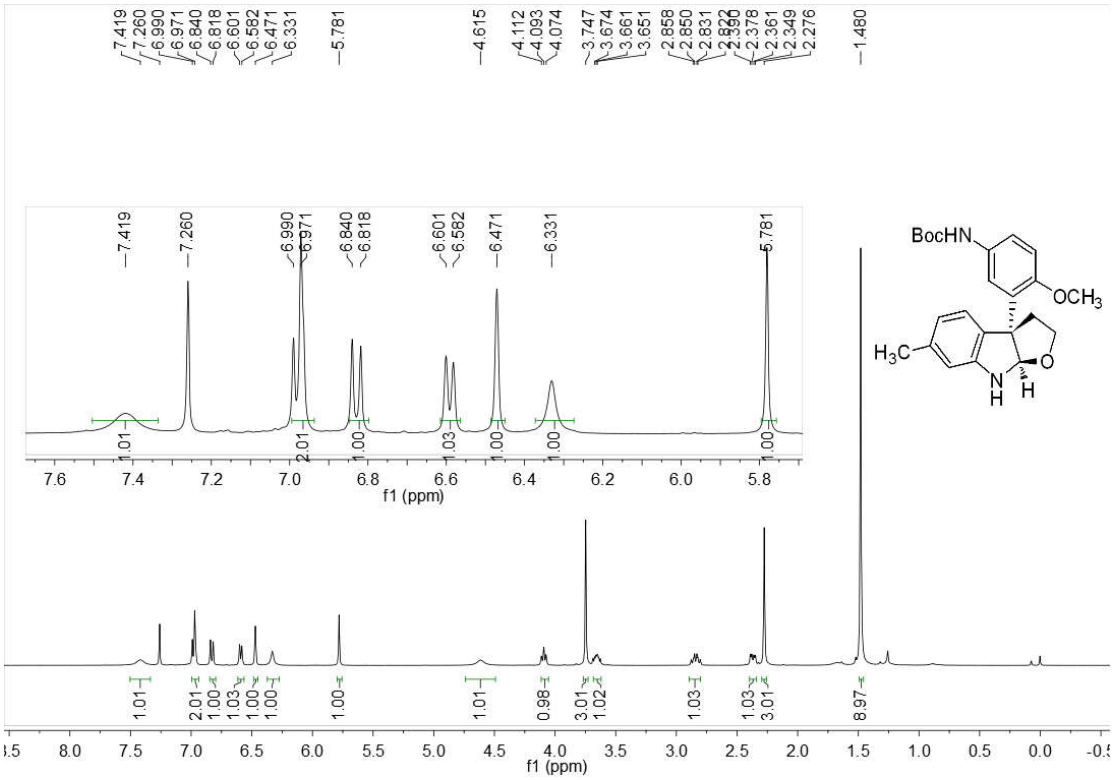
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ga**



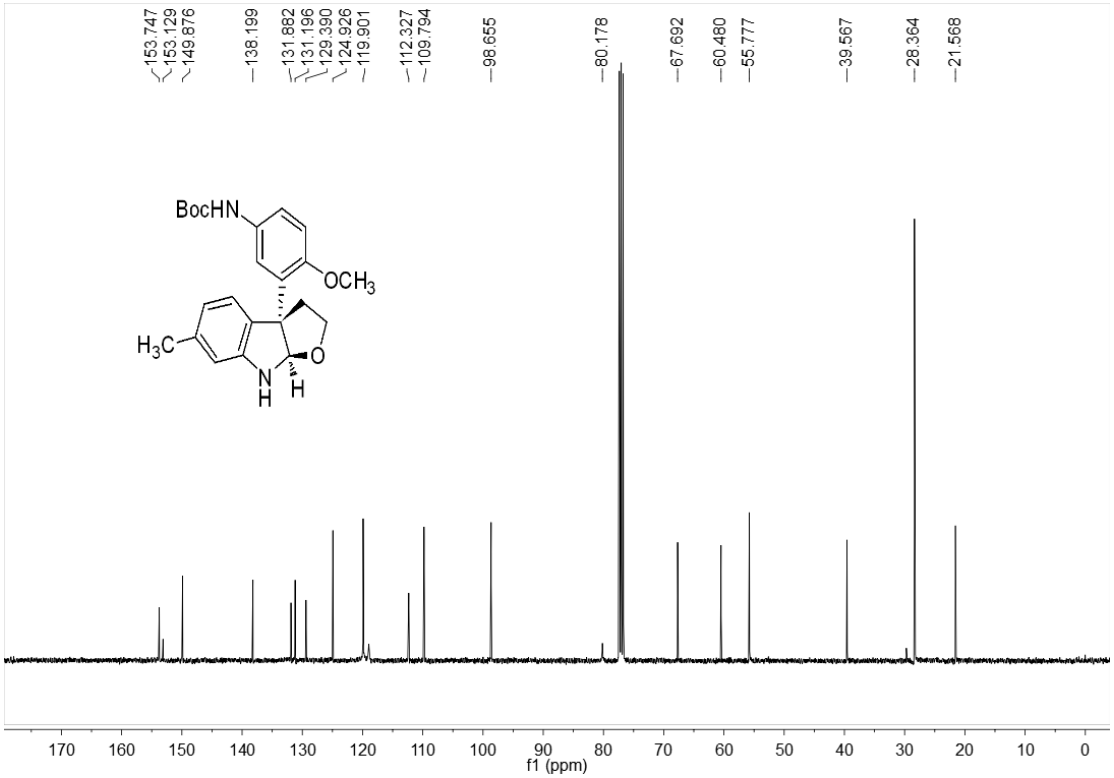
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ga**



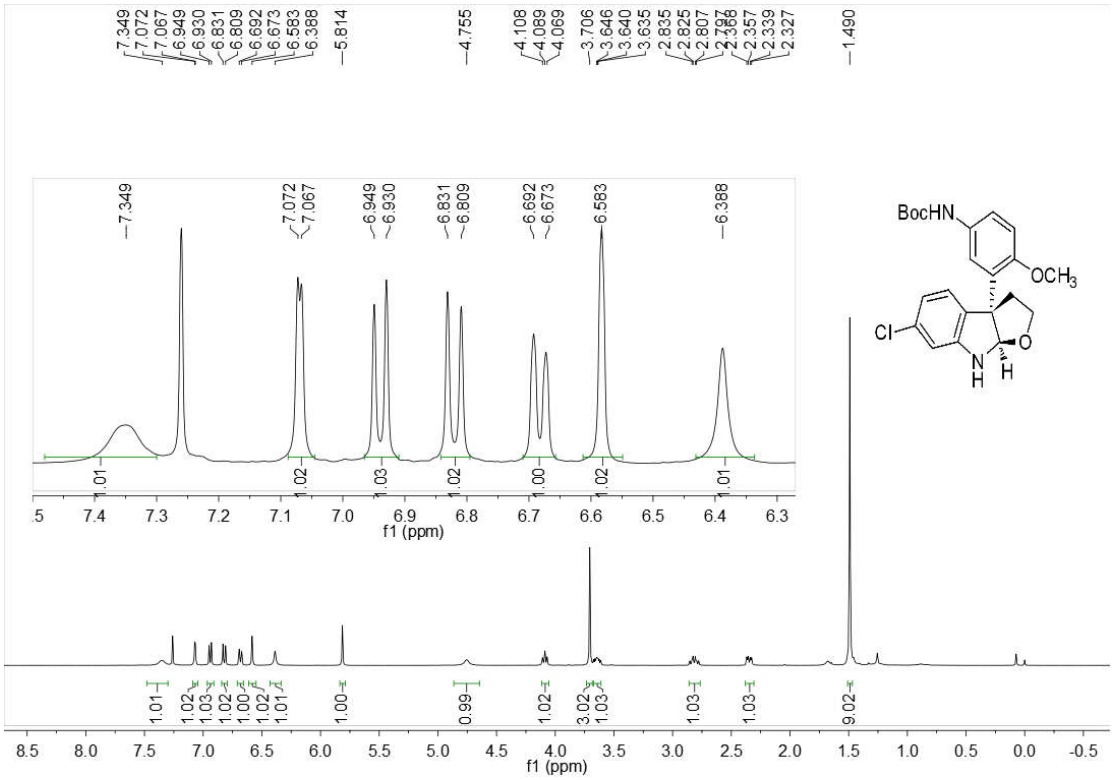
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ha**



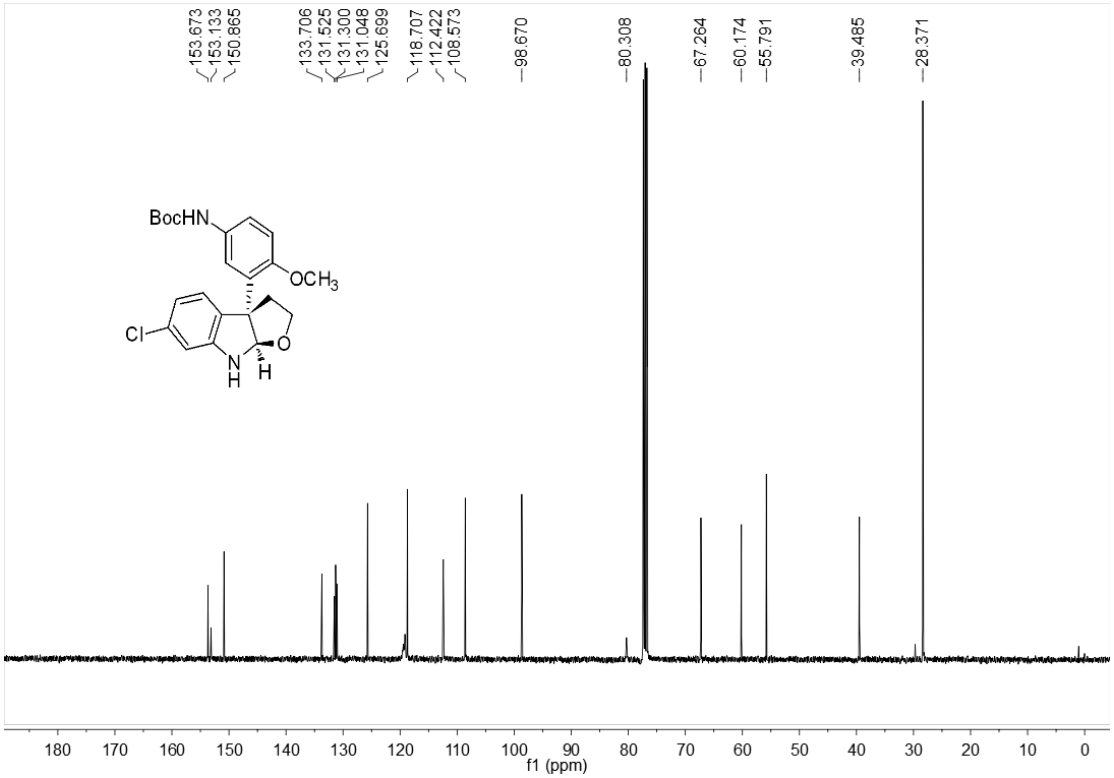
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ha**



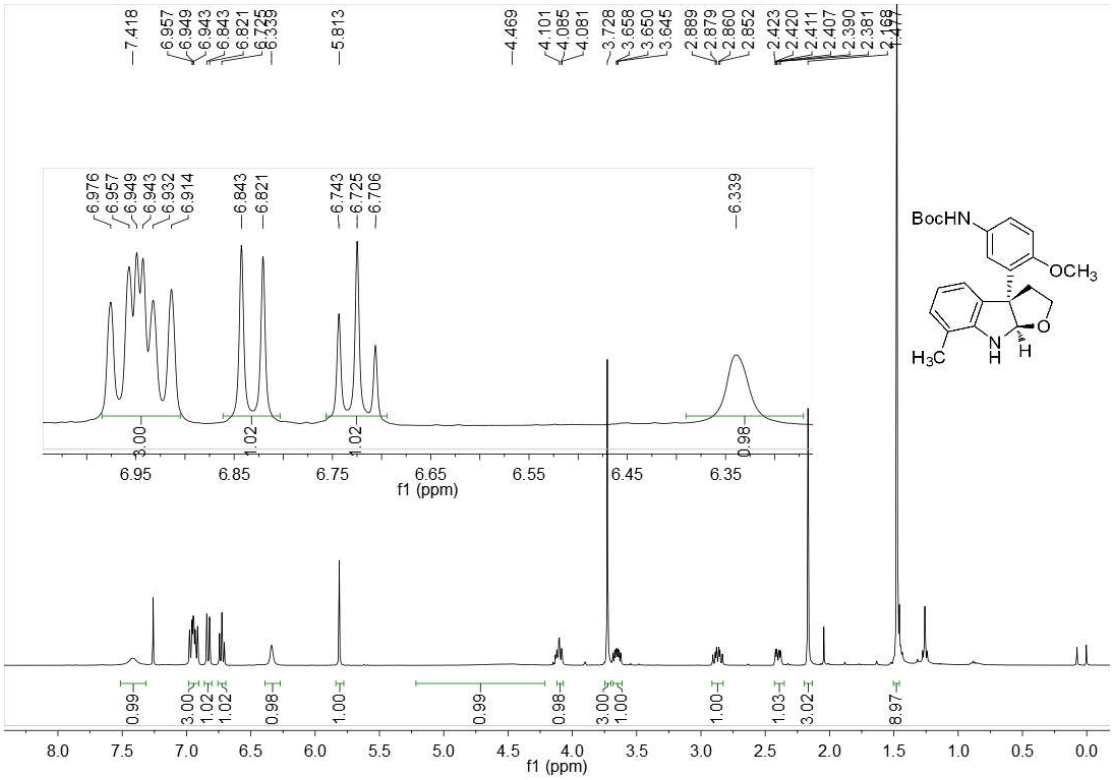
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ja**



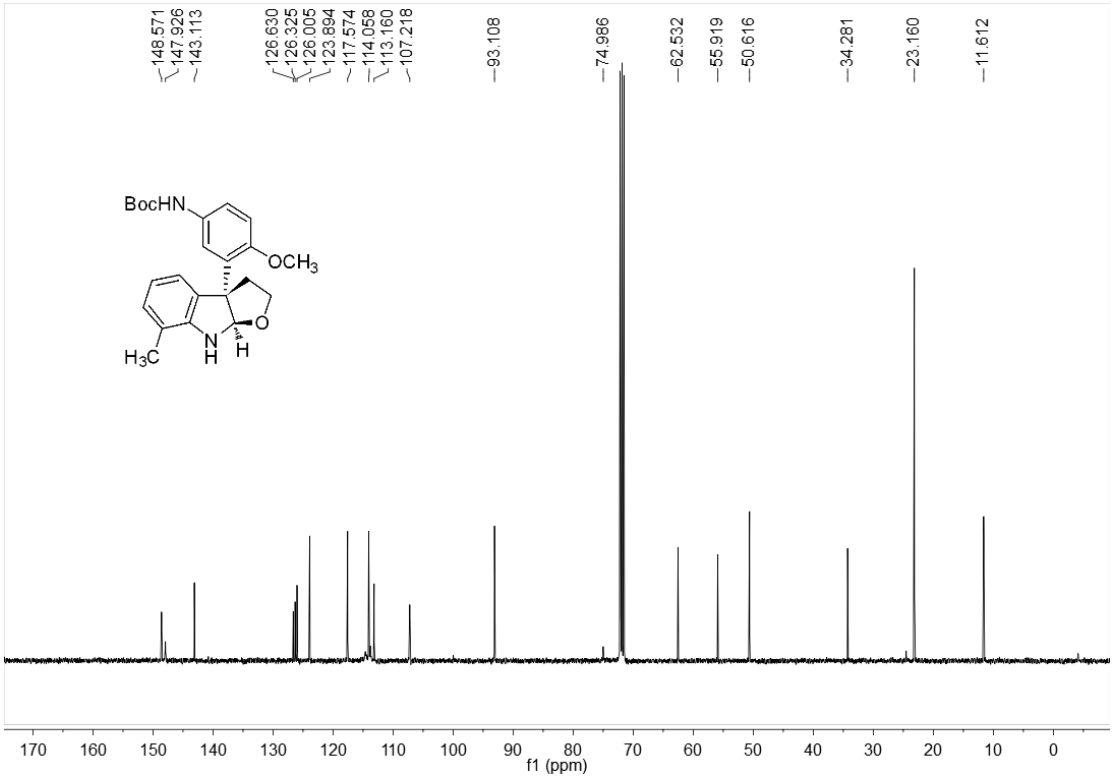
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ja**



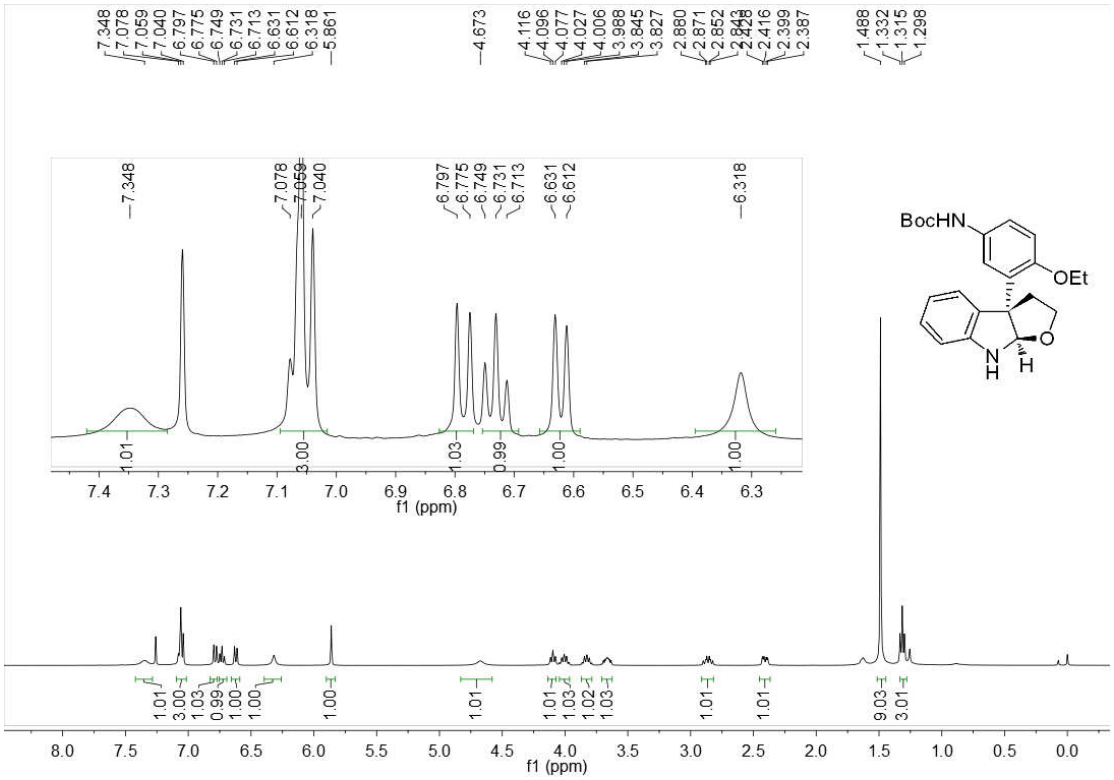
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7la**



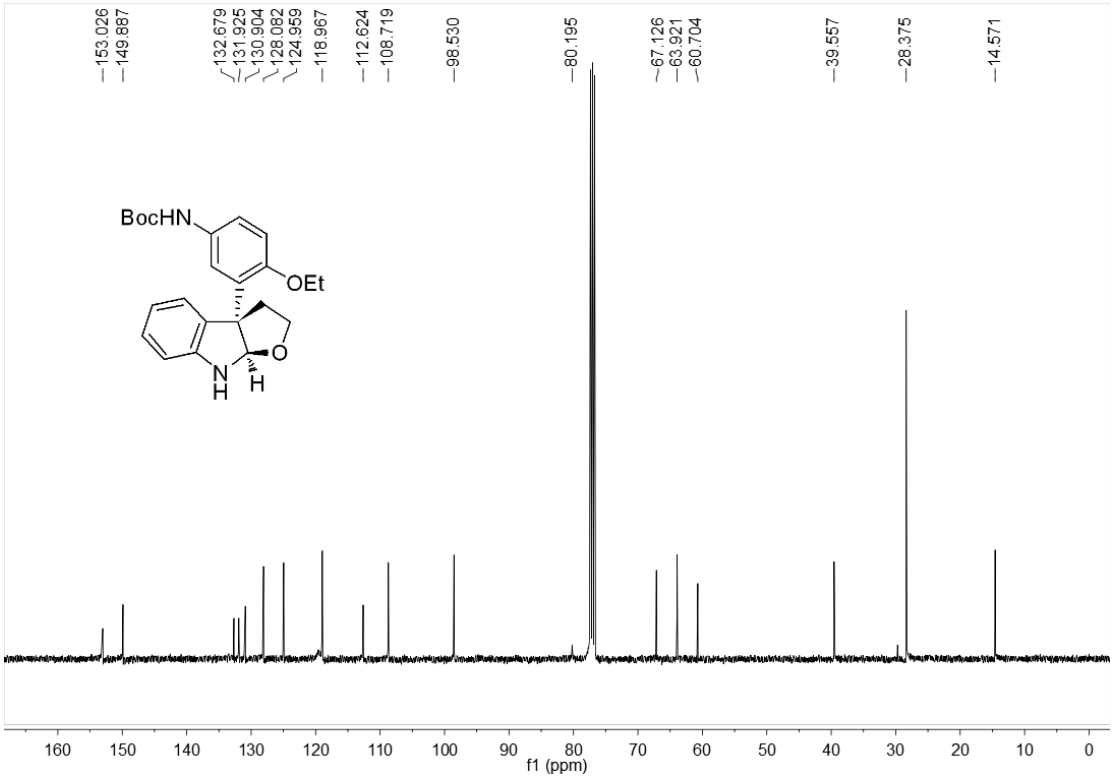
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7la**



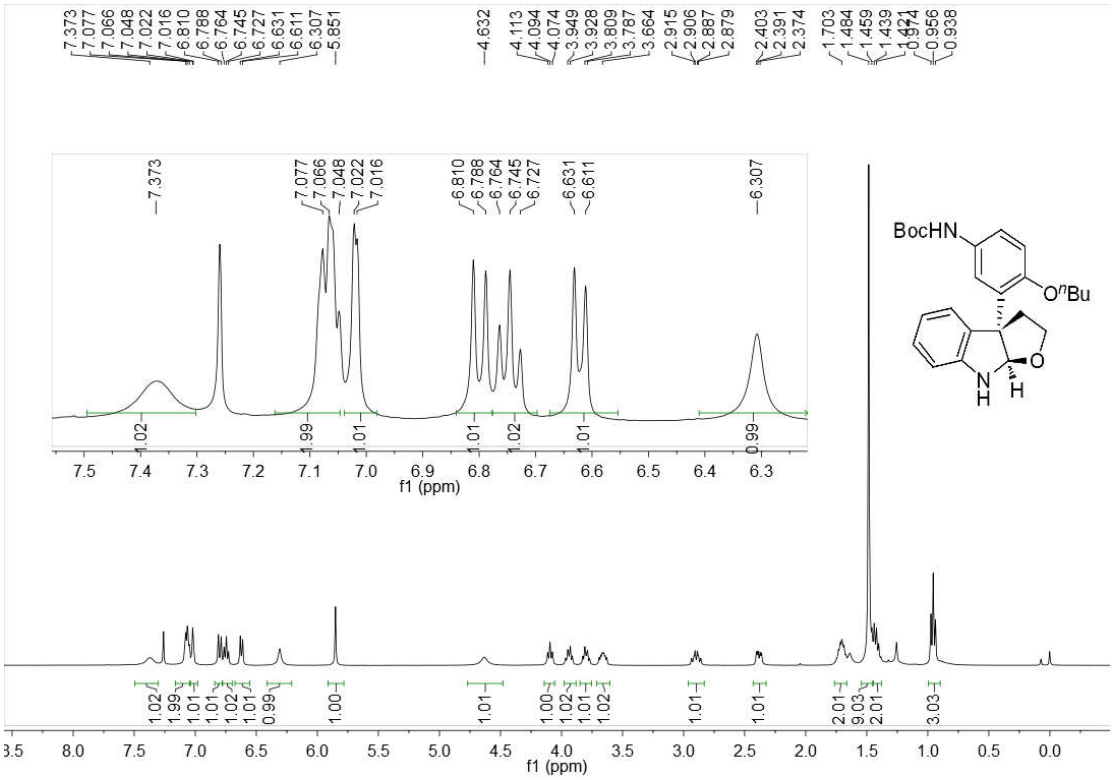
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ab**



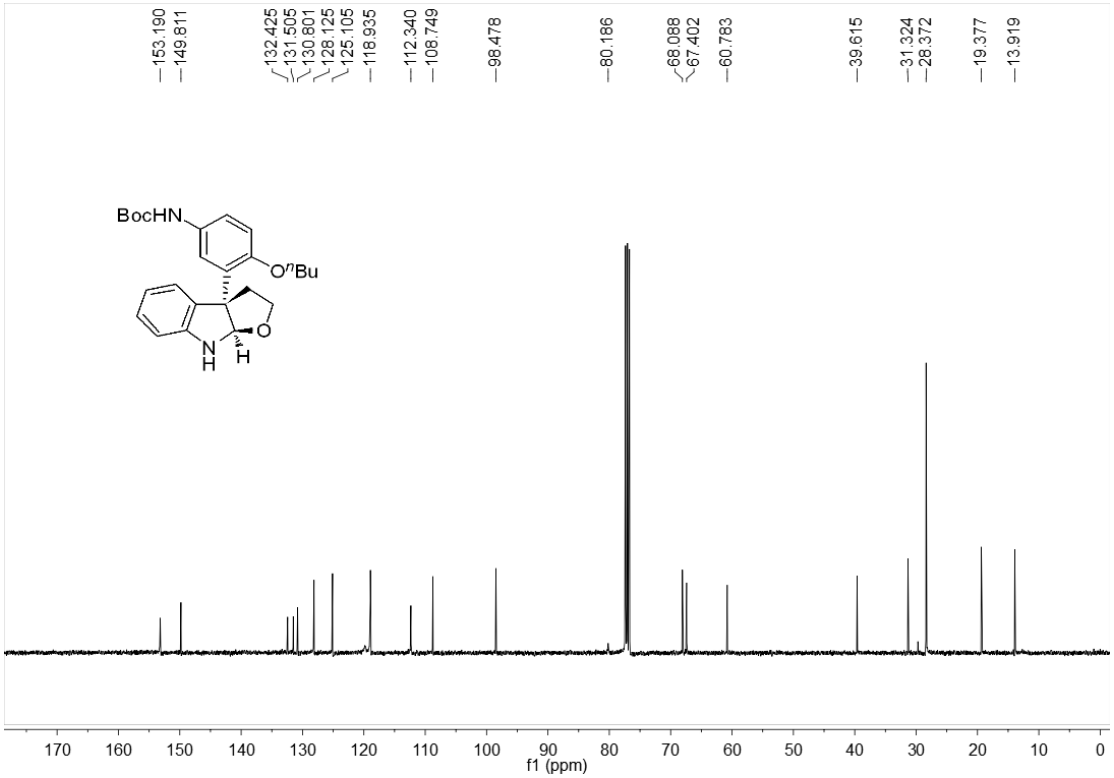
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ab**



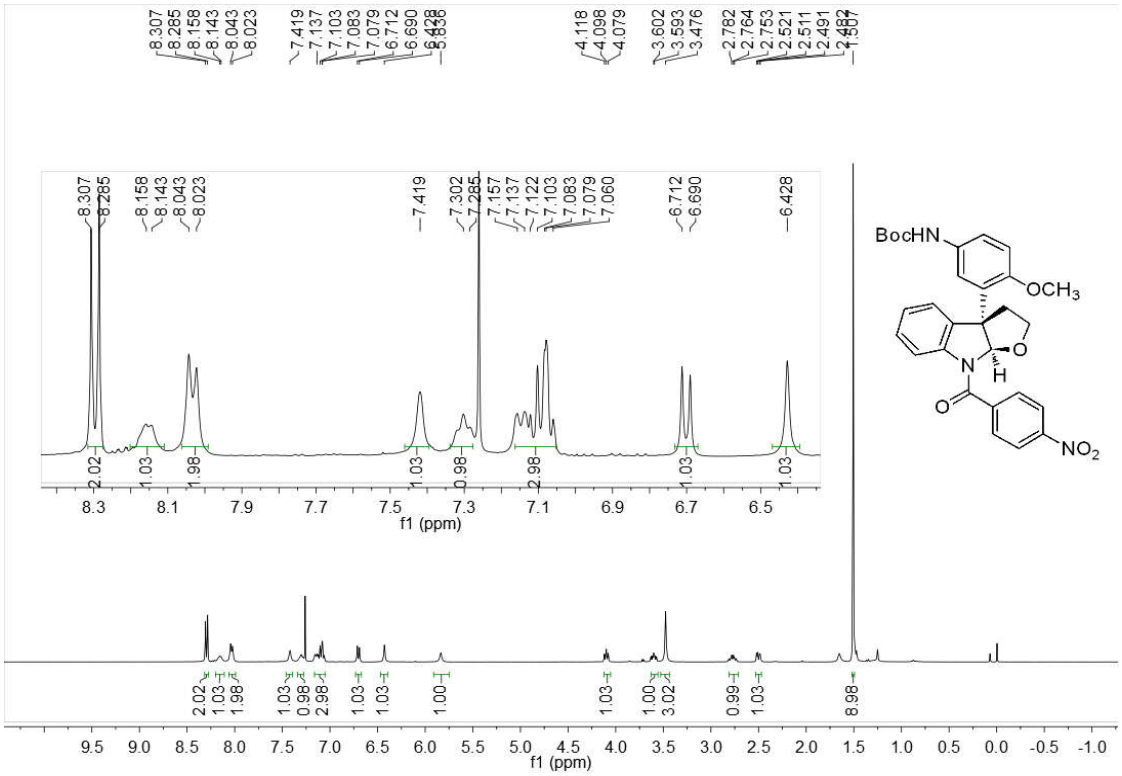
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7ac**



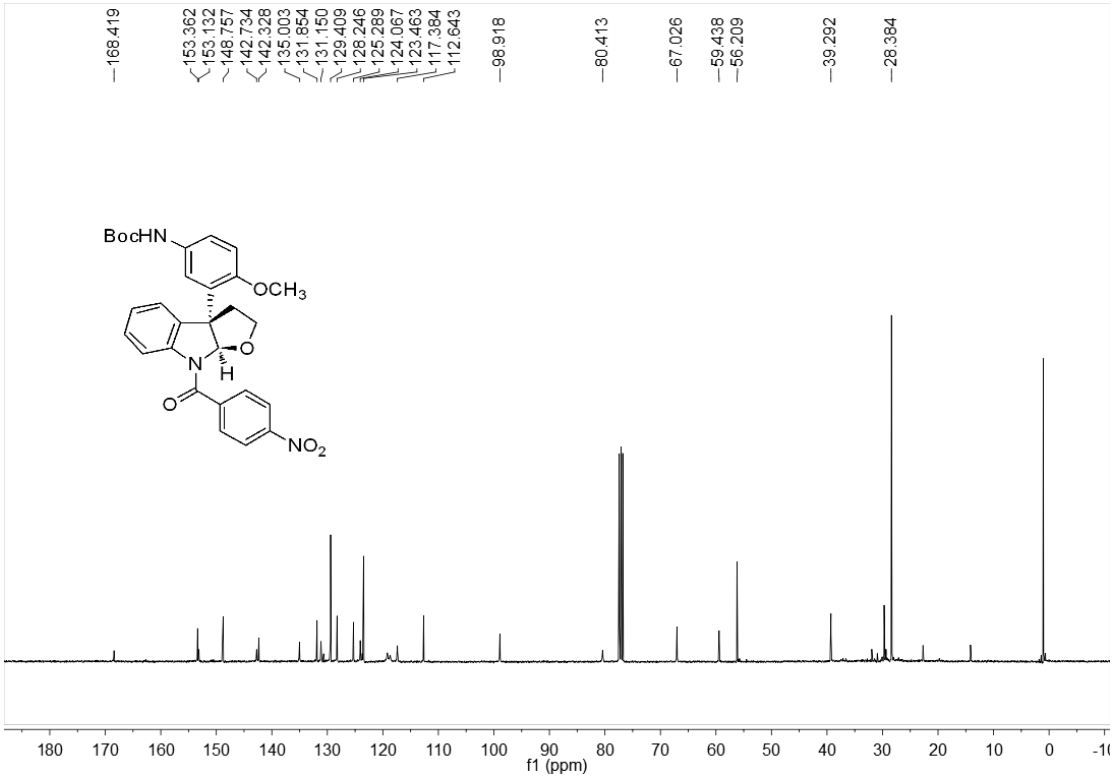
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7ac**



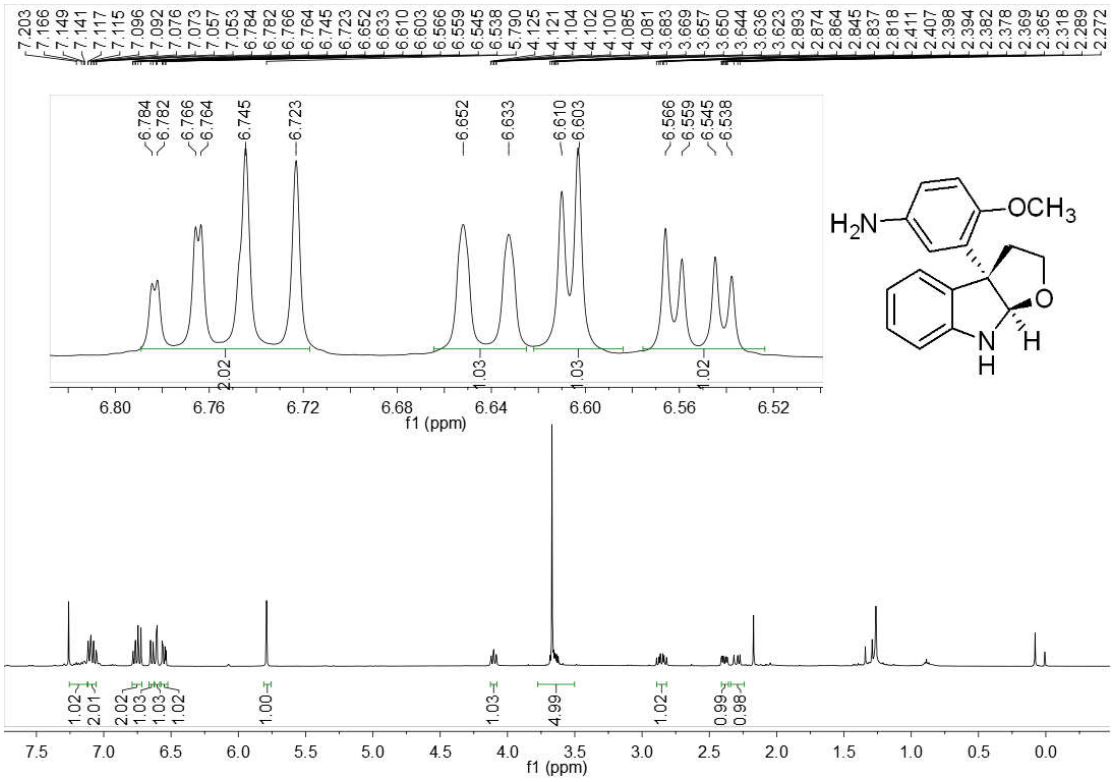
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8**



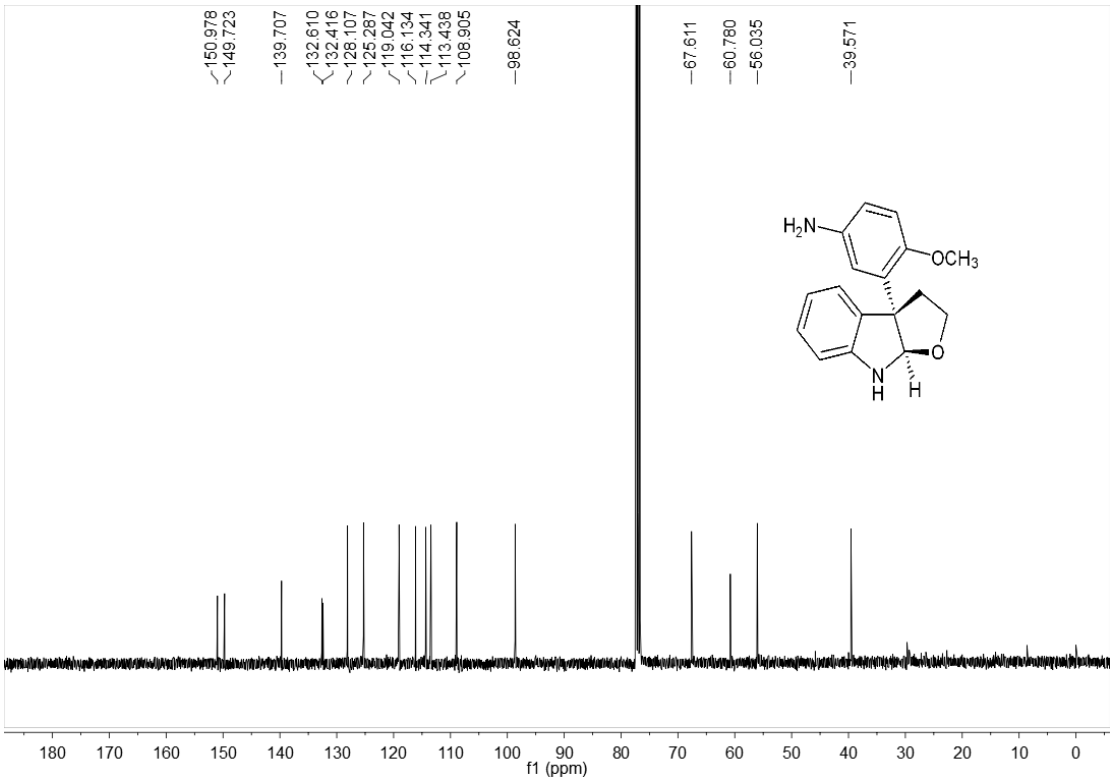
^{13}C NMR (100 MHz, $CDCl_3$) of compound **8**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**

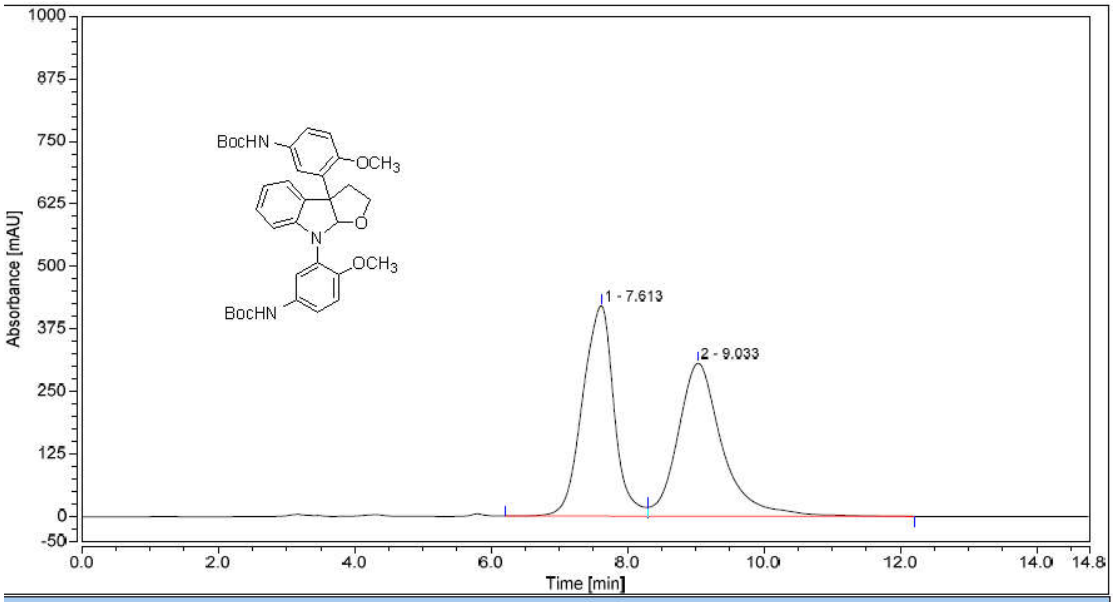


^{13}C NMR (100 MHz, $CDCl_3$) of compound **9**



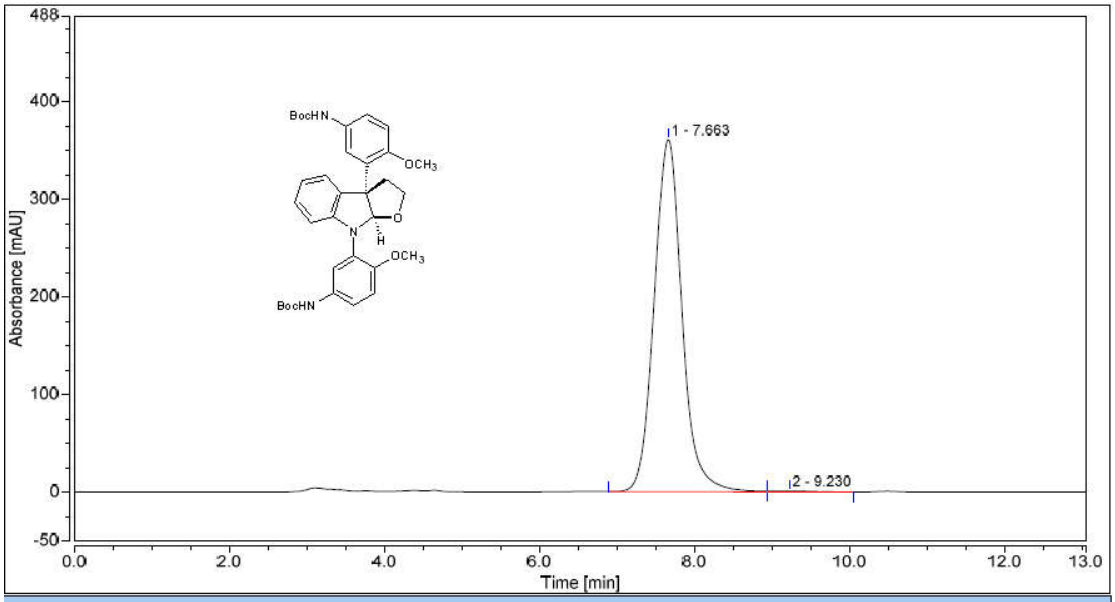
7. HPLC copies of products 3, 7 and 8-9

3aa



Integration Results

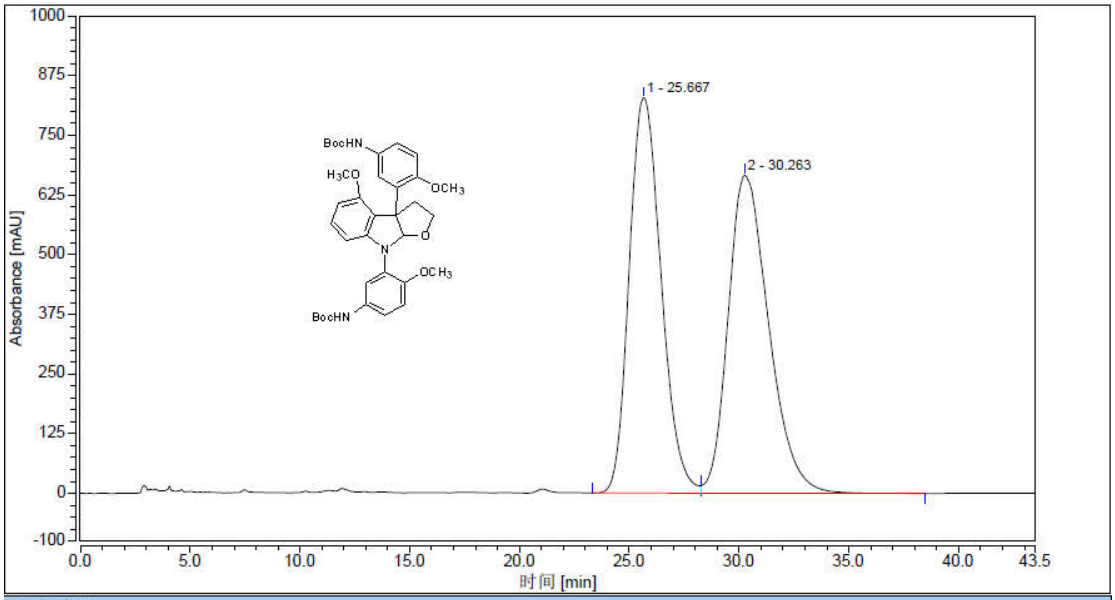
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.613	224.182	420.695	49.28	57.91	n.a.
2		9.033	230.731	305.768	50.72	42.09	n.a.
Total:			**454.913**	**726.463**	**100.00**	**100.00**	



Integration Results

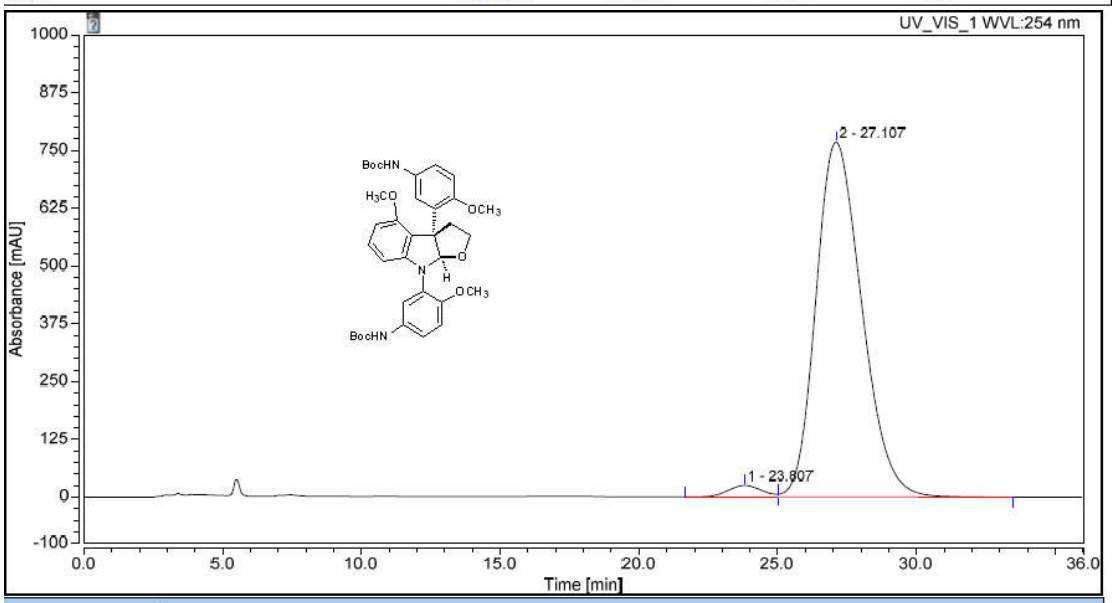
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.663	149.917	360.812	99.68	99.78	n.a.
2		9.230	0.483	0.795	0.32	0.22	n.a.
Total:			**150.401**	**361.606**	**100.00**	**100.00**	

3ba



积分结果

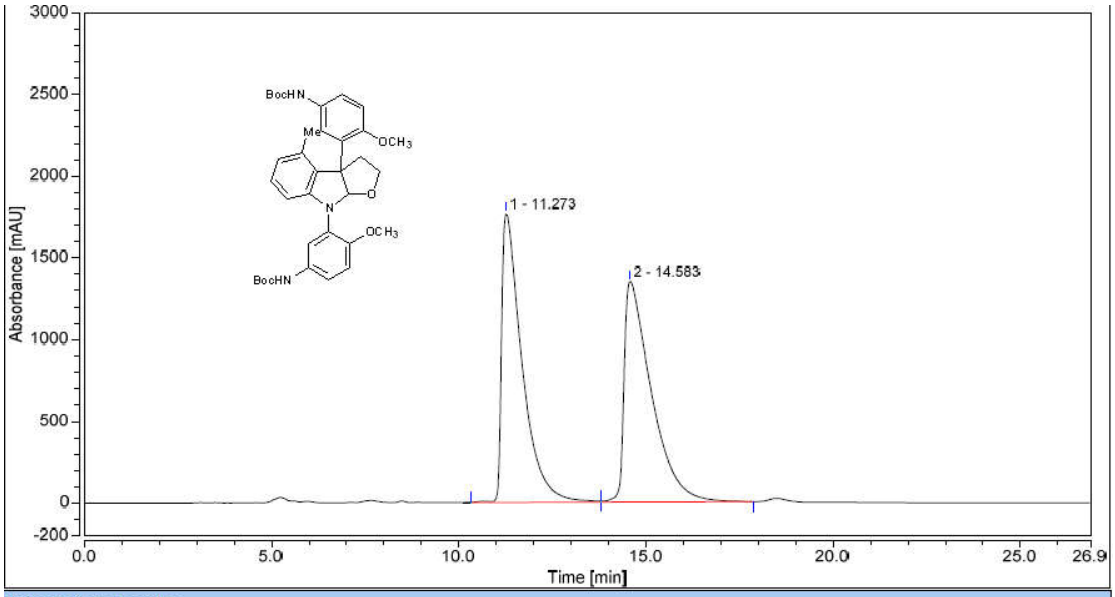
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		25.667	1394.768	828.592	49.45	55.42	n.a.
2		30.263	1425.932	666.502	50.55	44.58	n.a.
总和:			**2820.700**	**1495.094**	**100.00**	**100.00**	



Integration Results

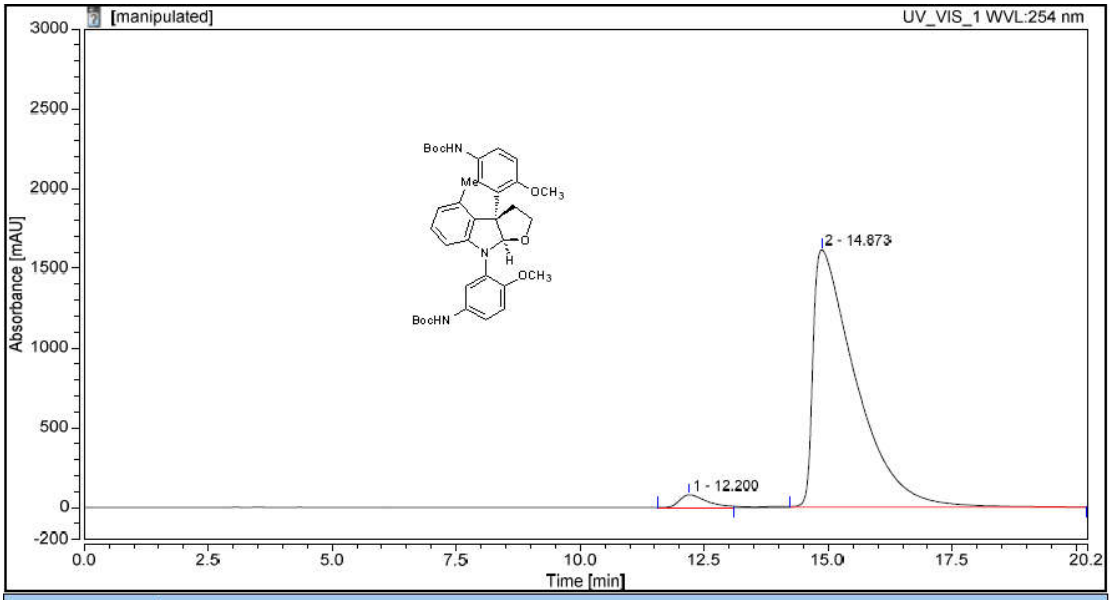
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.807	35.108	24.774	2.33	3.13	n.a.
2		27.107	1468.861	767.945	97.67	96.87	n.a.
Total:			**1503.969**	**792.719**	**100.00**	**100.00**	

3ca



Integration Results

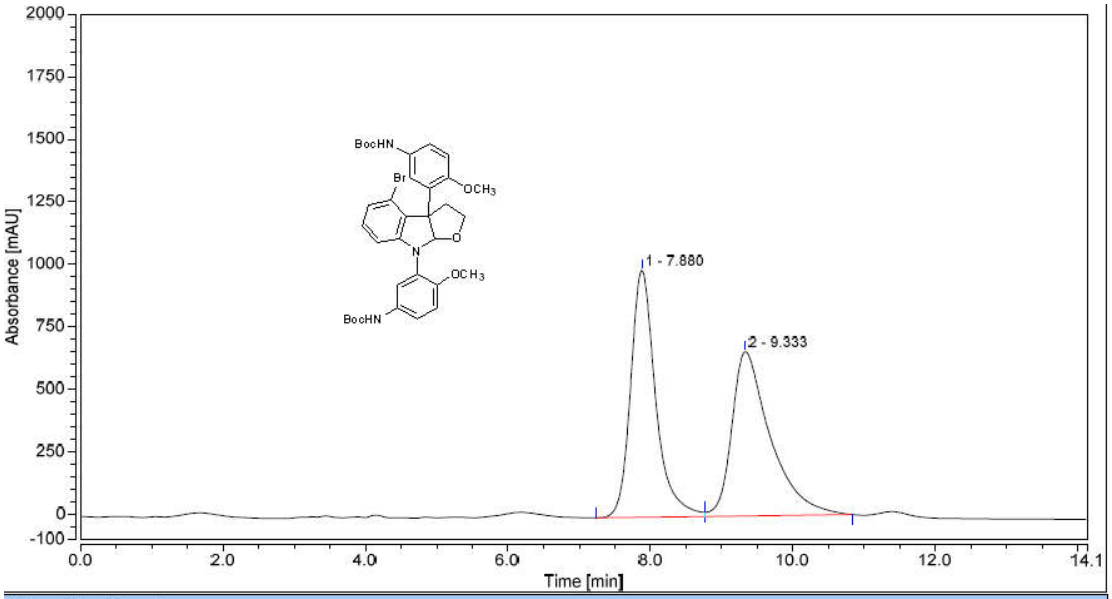
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.273	1114.086	1769.100	49.52	56.69	n.a.
2		14.583	1135.838	1351.301	50.48	43.31	n.a.
Total:			**2249.923**	**3120.400**	**100.00**	**100.00**	



Integration Results

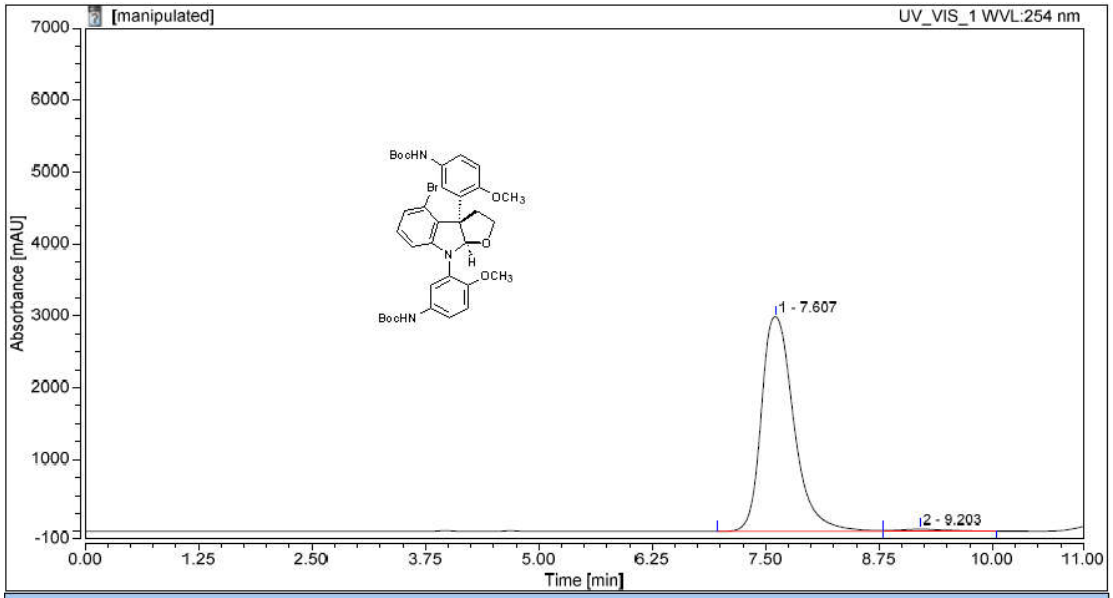
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.200	49.993	80.090	2.99	4.72	n.a.
2		14.873	1623.421	1615.325	97.01	95.28	n.a.
Total:			**1673.413**	**1695.415**	**100.00**	**100.00**	

3da



Integration Results

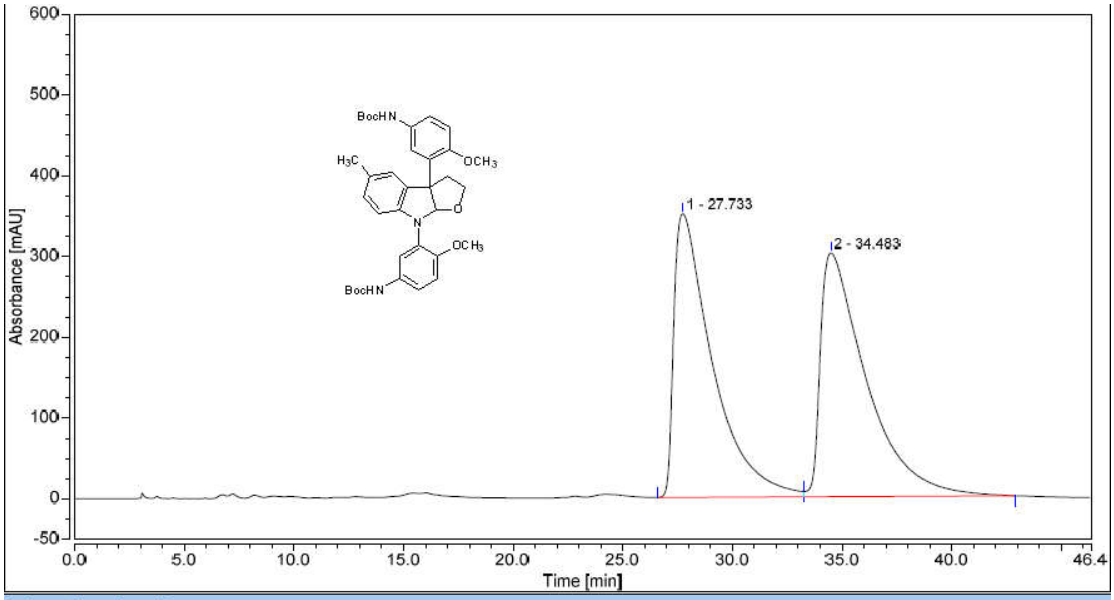
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.880	401.890	986.928	49.40	60.06	n.a.
2		9.333	411.641	656.422	50.60	39.94	n.a.
Total:			**813.531**	**1643.349**	**100.00**	**100.00**	



Integration Results

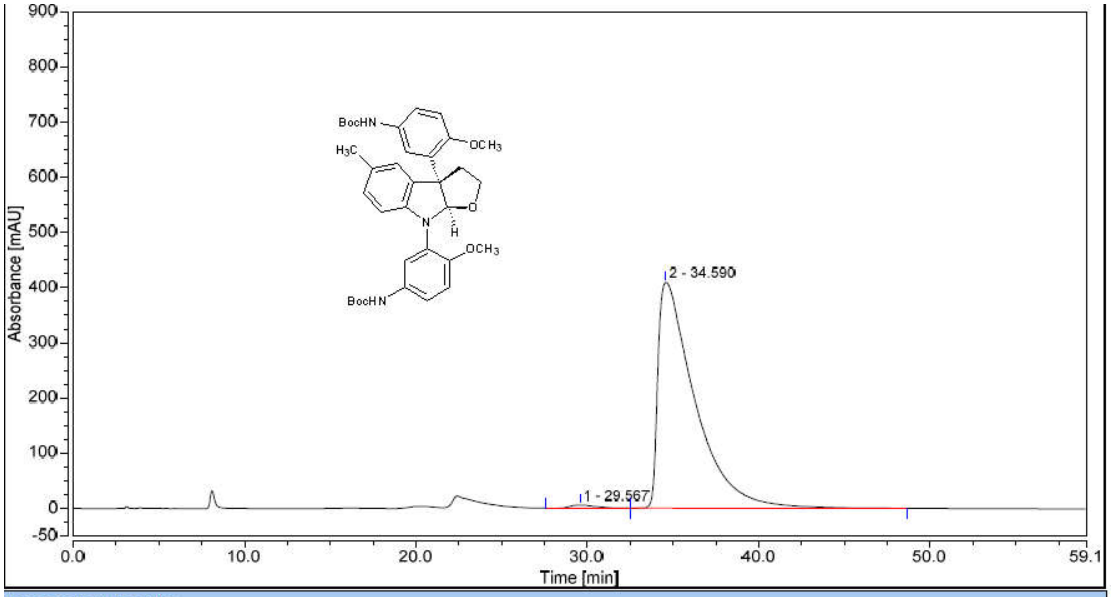
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.607	1239.358	2986.863	98.55	99.04	n.a.
2		9.203	18.297	28.891	1.45	0.96	n.a.
Total:			**1257.656**	**3015.754**	**100.00**	**100.00**	

3ea:



Integration Results

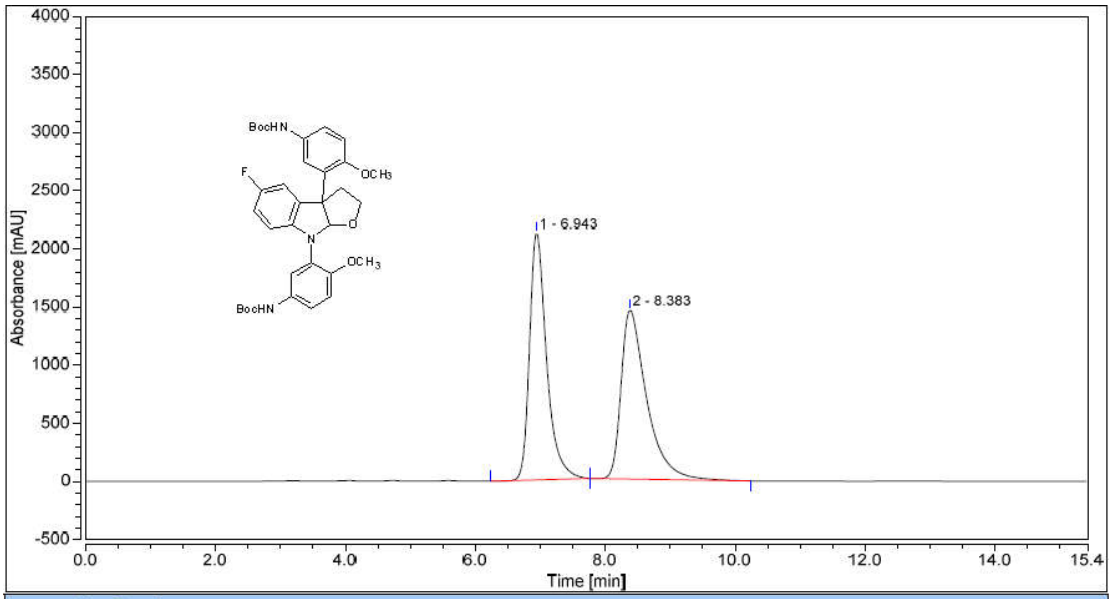
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.733	714.011	351.288	49.44	53.78	n.a.
2		34.483	730.250	301.854	50.56	46.22	n.a.
Total:			**1444.261**	**653.142**	**100.00**	**100.00**	



Integration Results

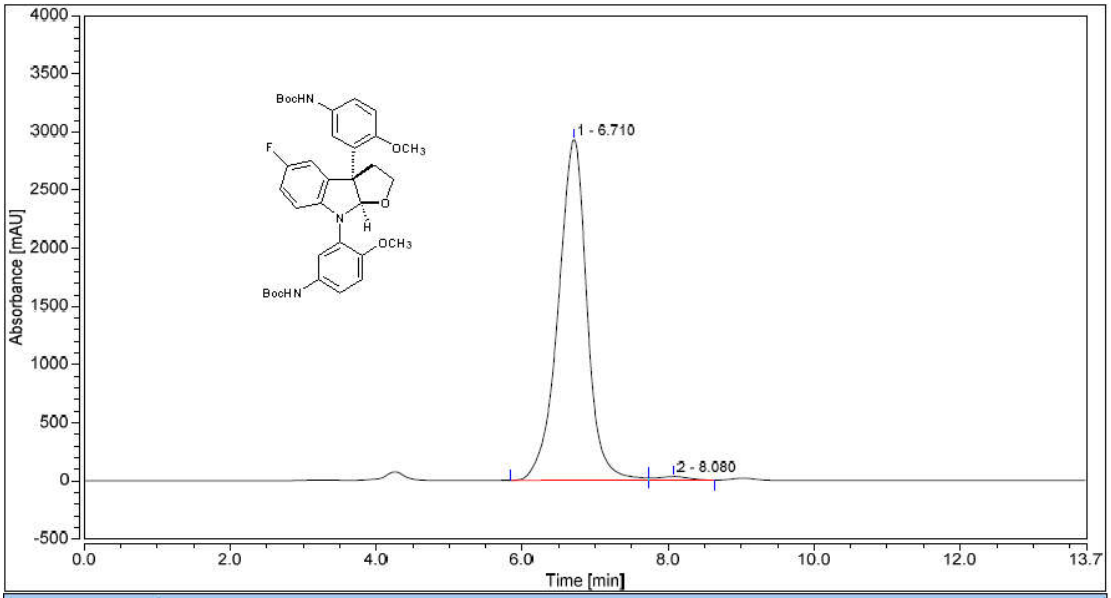
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.567	10.141	5.814	0.98	1.40	n.a.
2		34.590	1025.719	409.405	99.02	98.60	n.a.
Total:			**1035.860**	**415.219**	**100.00**	**100.00**	

3fa:



Integration Results

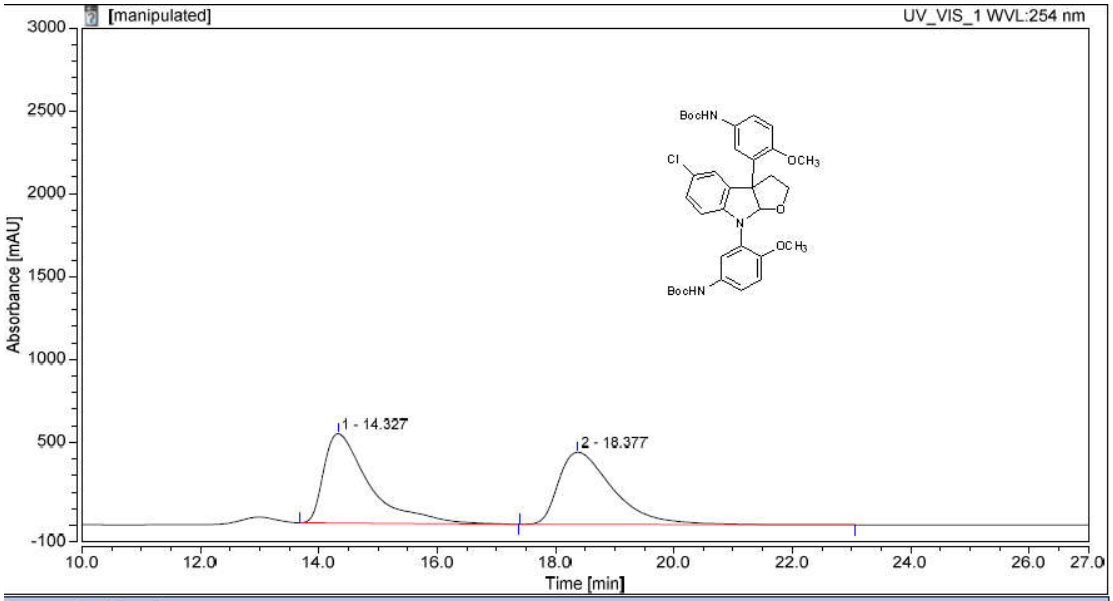
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.943	644.151	2122.637	49.42	59.40	n.a.
2		8.383	659.273	1450.997	50.58	40.60	n.a.
Total:			**1303.424**	**3573.635**	**100.00**	**100.00**	



Integration Results

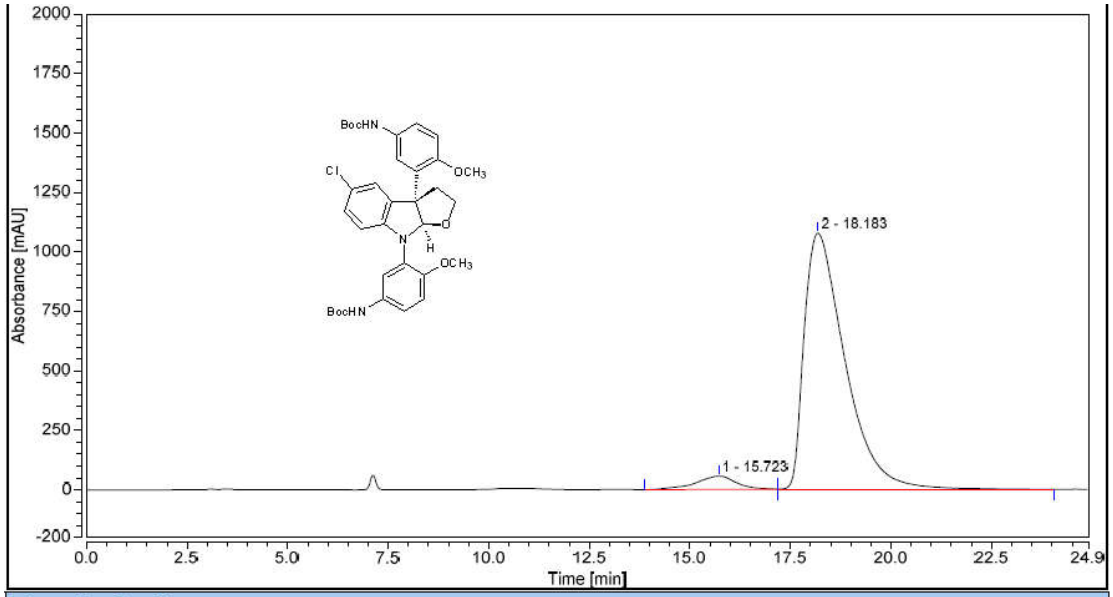
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.710	1336.316	2929.723	98.87	98.98	n.a.
2		8.080	15.286	30.200	1.13	1.02	n.a.
Total:			**1351.602**	**2959.923**	**100.00**	**100.00**	

3ga



Integration Results

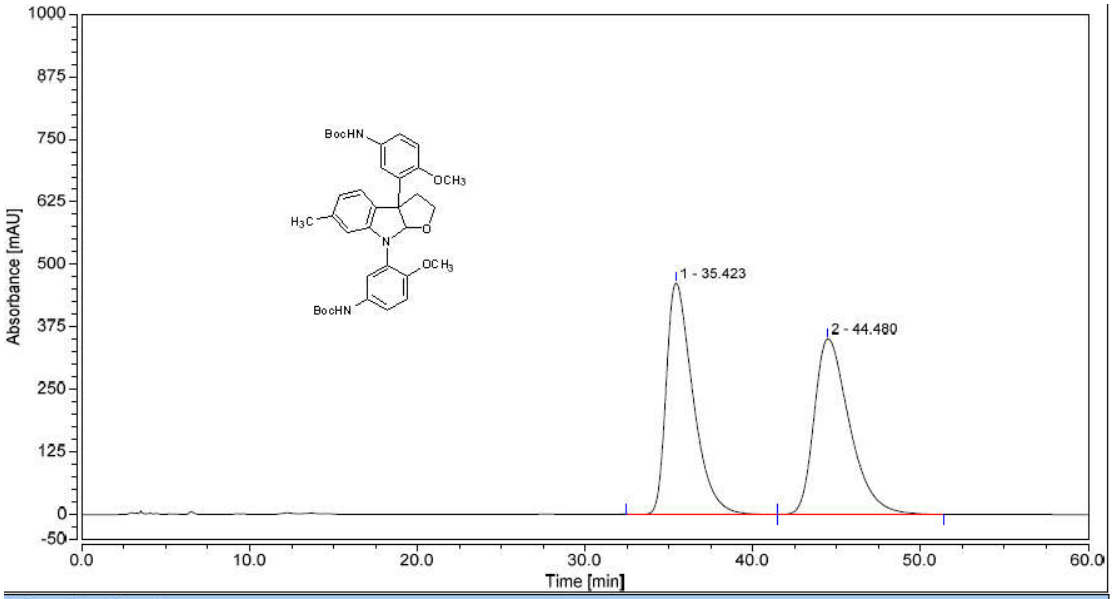
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.327	481.381	539.349	50.96	55.31	n.a.
2		18.377	463.326	435.727	49.04	44.69	n.a.
Total:			**944.707**	**975.075**	**100.00**	**100.00**	



Integration Results

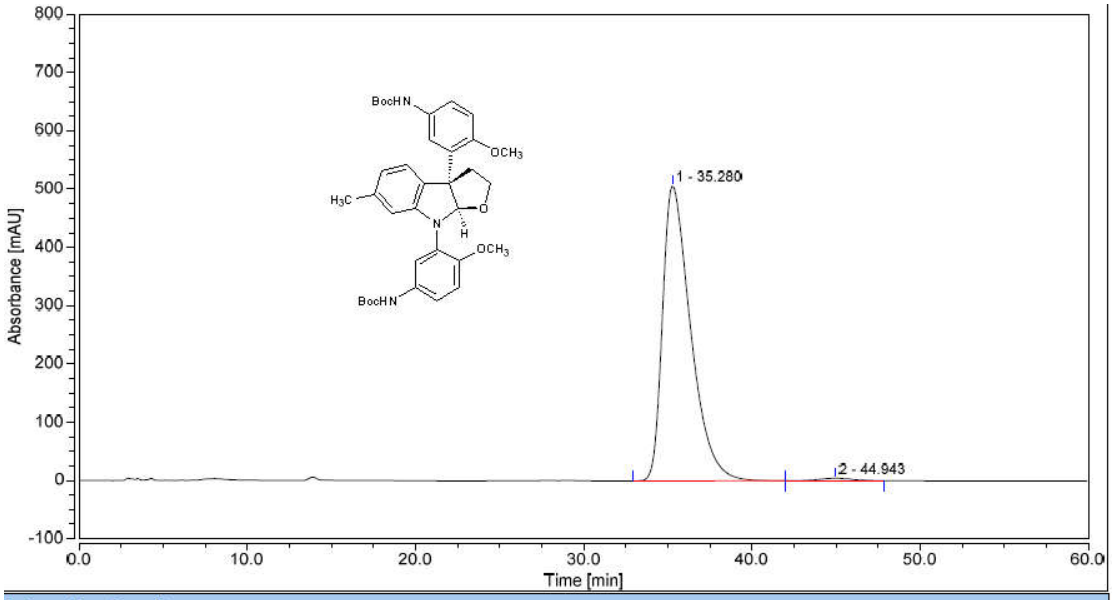
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.723	66.598	56.633	4.99	4.99	n.a.
2		18.183	1269.047	1078.661	95.01	95.01	n.a.
Total:			**1335.646**	**1135.295**	**100.00**	**100.00**	

3ha



Integration Results

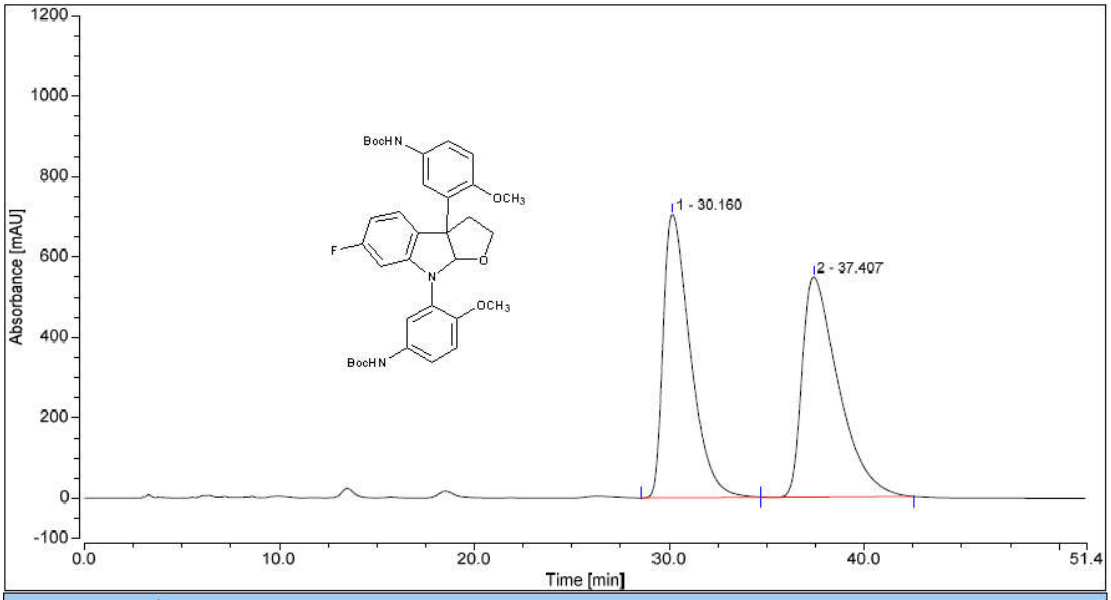
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.423	853.851	462.698	49.87	56.86	n.a.
2		44.480	858.437	351.060	50.13	43.14	n.a.
Total:			**1712.289**	**813.758**	**100.00**	**100.00**	



Integration Results

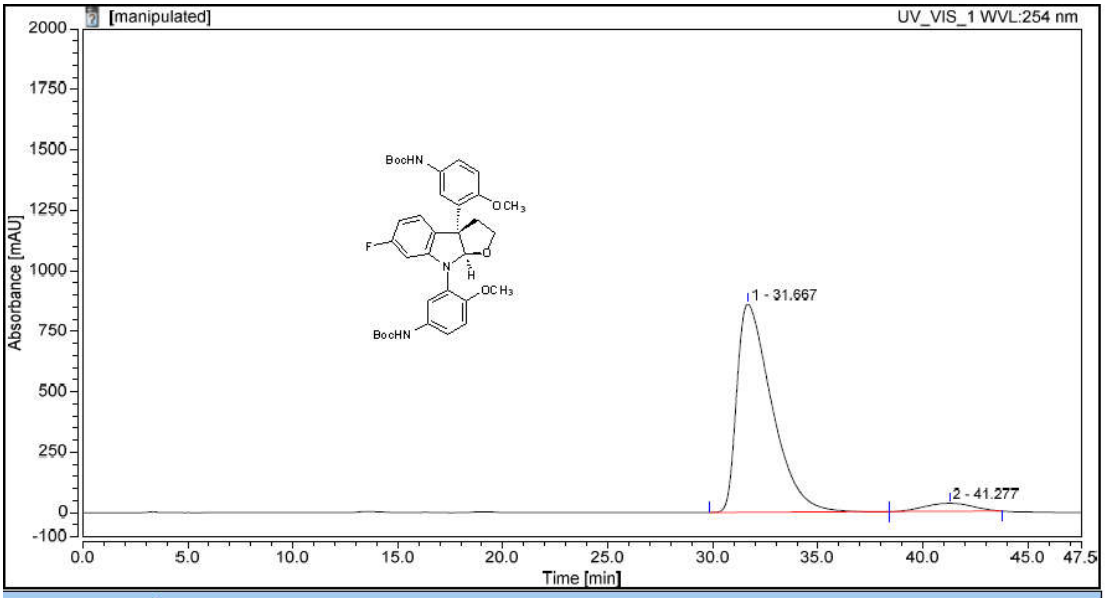
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.280	979.876	506.070	99.00	99.15	n.a.
2		44.943	9.856	4.358	1.00	0.85	n.a.
Total:			**989.732**	**510.428**	**100.00**	**100.00**	

3ia:



Integration Results

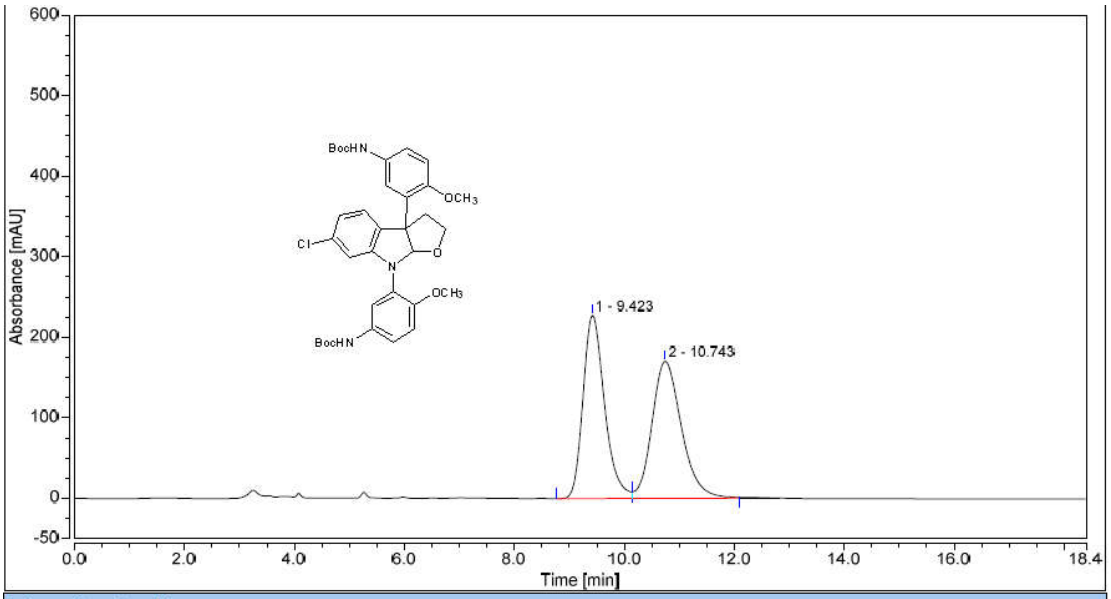
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.160	1136.892	704.920	49.06	56.29	n.a.
2		37.407	1180.414	547.469	50.94	43.71	n.a.
Total:			**2317.306**	**1252.389**	**100.00**	**100.00**	



Integration Results

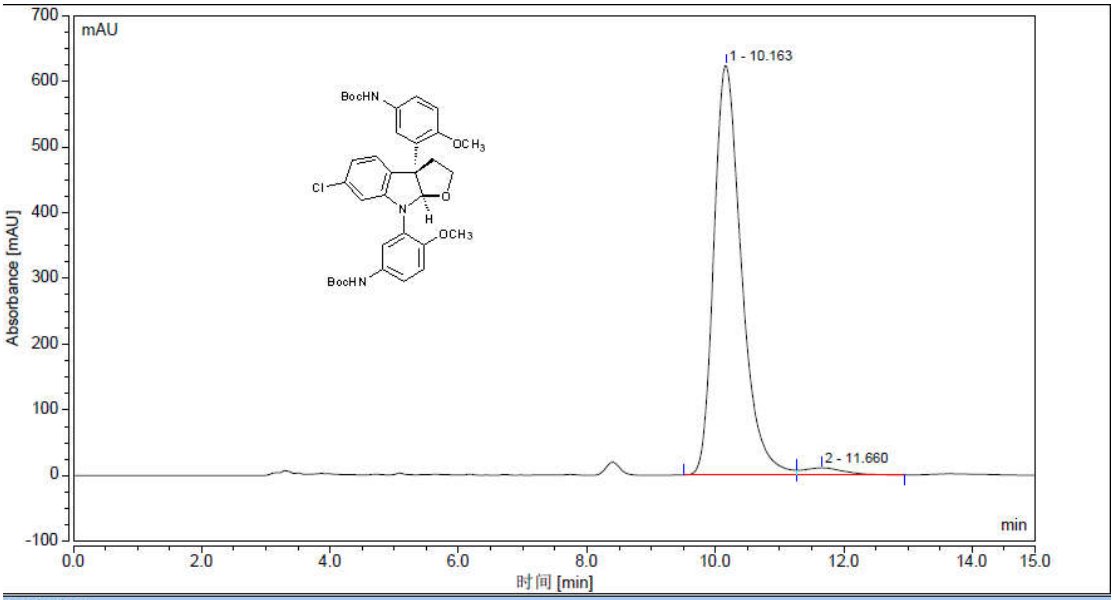
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.667	1654.583	860.228	94.98	96.28	n.a.
2		41.277	87.409	33.254	5.02	3.72	n.a.
Total:			**1741.992**	**893.482**	**100.00**	**100.00**	

3ja:



Integration Results

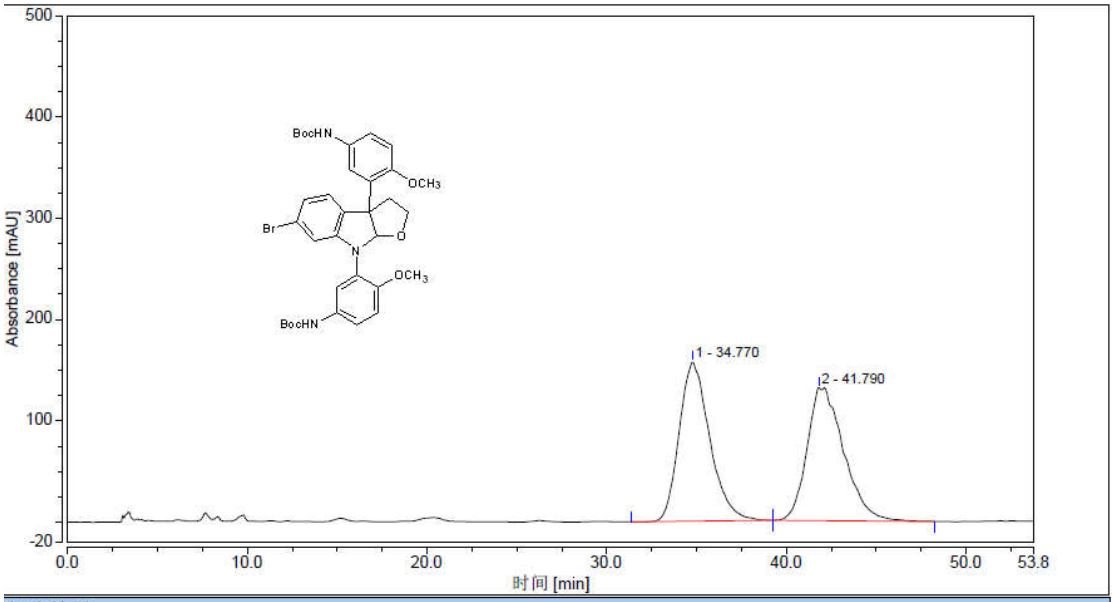
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.423	103.146	227.559	49.35	57.20	n.a.
2		10.743	105.877	170.265	50.65	42.80	n.a.
Total:			**209.023**	**397.825**	**100.00**	**100.00**	



积分结果

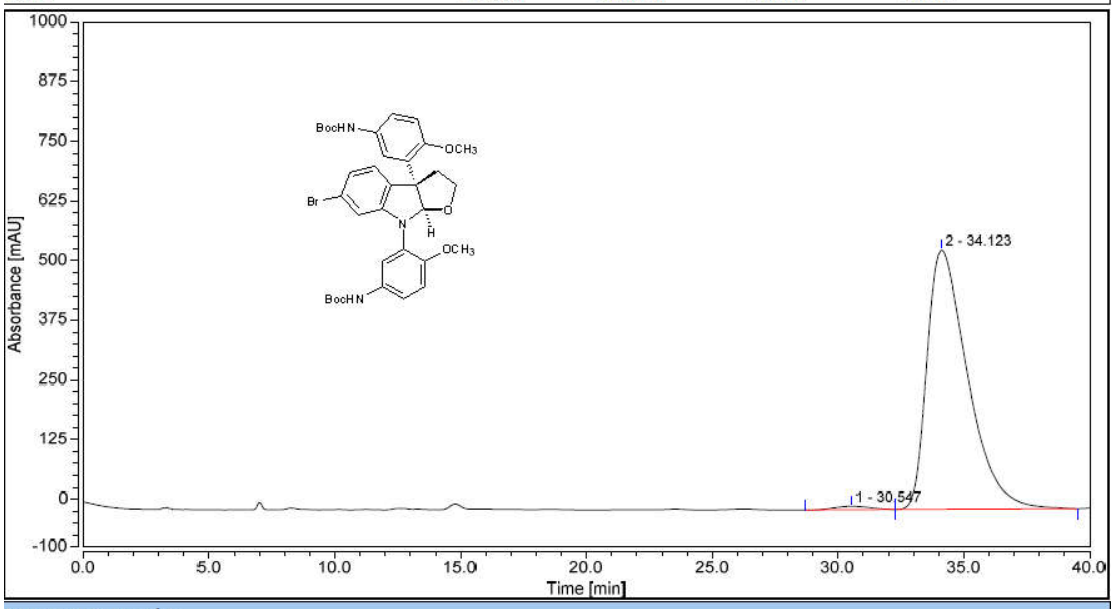
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		10.163	309.689	623.534	97.53	98.30	n.a.
2		11.660	7.832	10.796	2.47	1.70	n.a.
总和:			**317.521**	**634.330**	**100.00**	**100.00**	

3ka:



积分结果

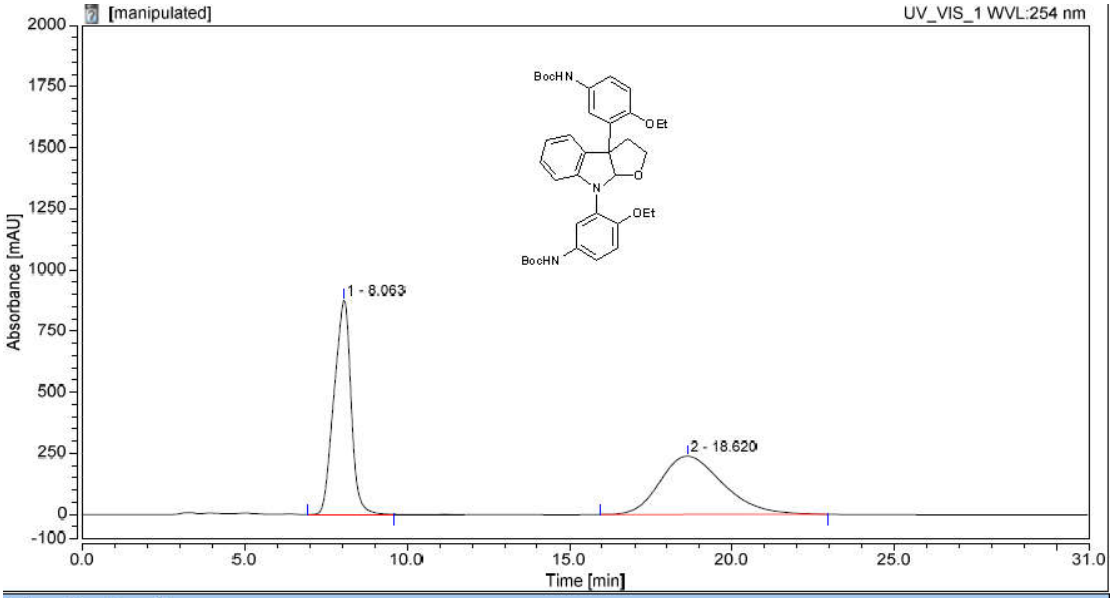
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		34.770	309.381	157.433	49.96	54.49	n.a.
2		41.790	309.840	131.480	50.04	45.51	n.a.
总和:			**619.221**	**288.913**	**100.00**	**100.00**	



Integration Results

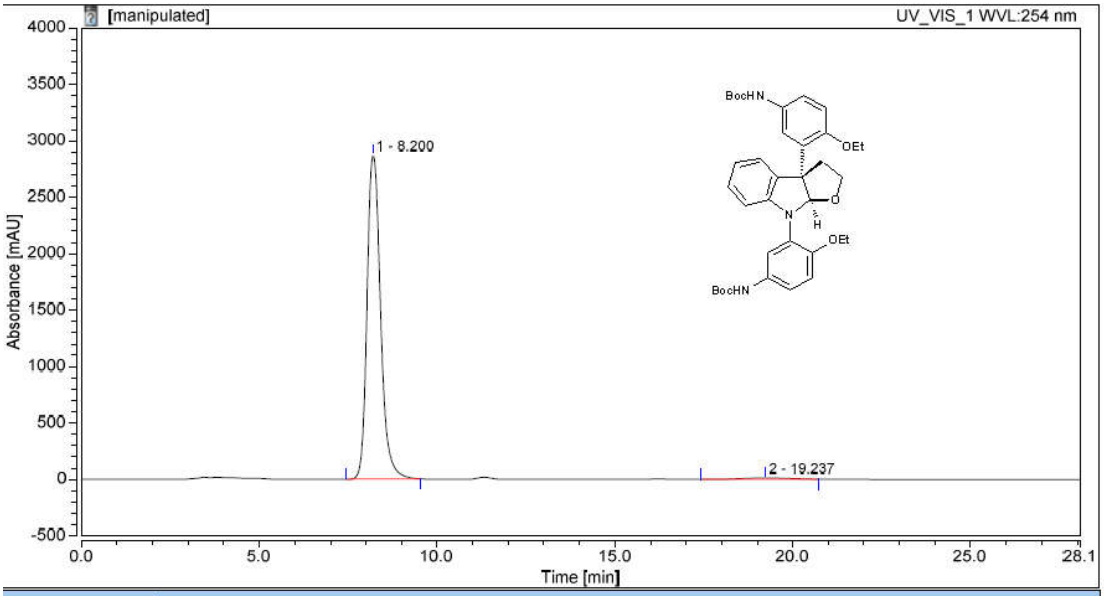
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.547	11.875	7.188	1.16	1.31	n.a.
2		34.123	1014.926	543.030	98.84	98.69	n.a.
Total:			**1026.801**	**550.218**	**100.00**	**100.00**	

3ab:



Integration Results

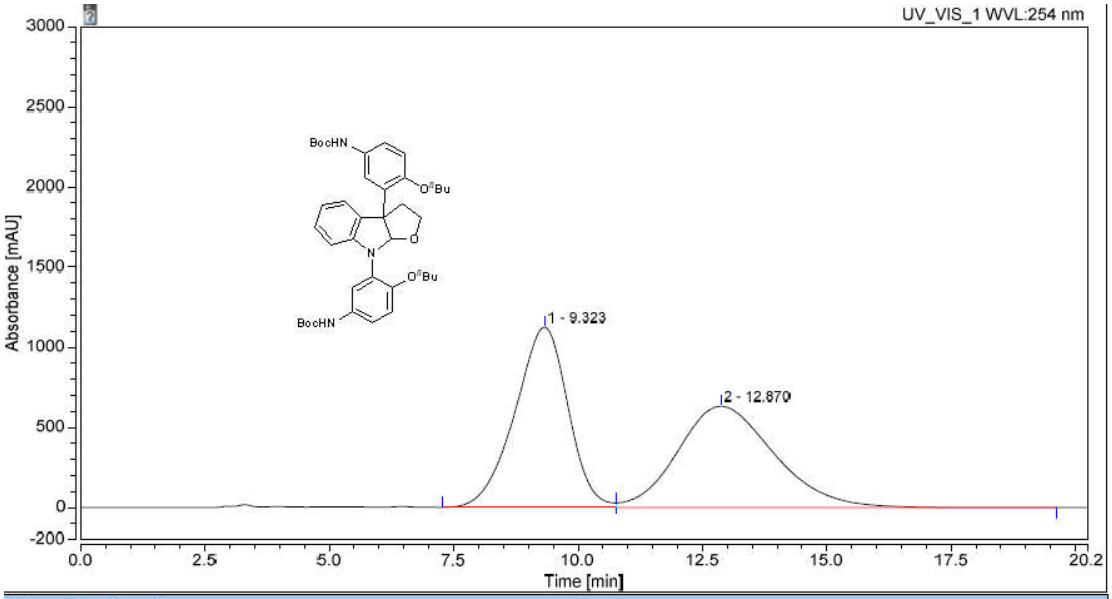
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.063	533.354	877.354	49.99	78.65	n.a.
2		18.620	533.532	238.228	50.01	21.35	n.a.
Total:			**1066.885**	**1115.582**	**100.00**	**100.00**	



Integration Results

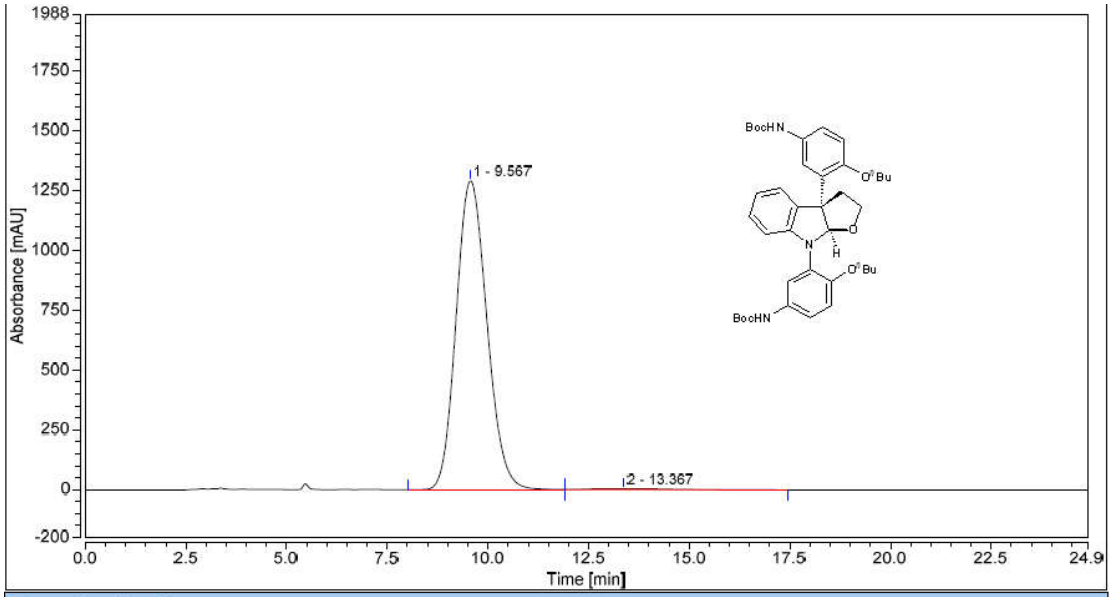
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.200	1263.439	2868.452	98.57	99.62	n.a.
2		19.237	18.273	11.029	1.43	0.38	n.a.
Total:			**1281.712**	**2879.481**	**100.00**	**100.00**	

3ac:



Integration Results

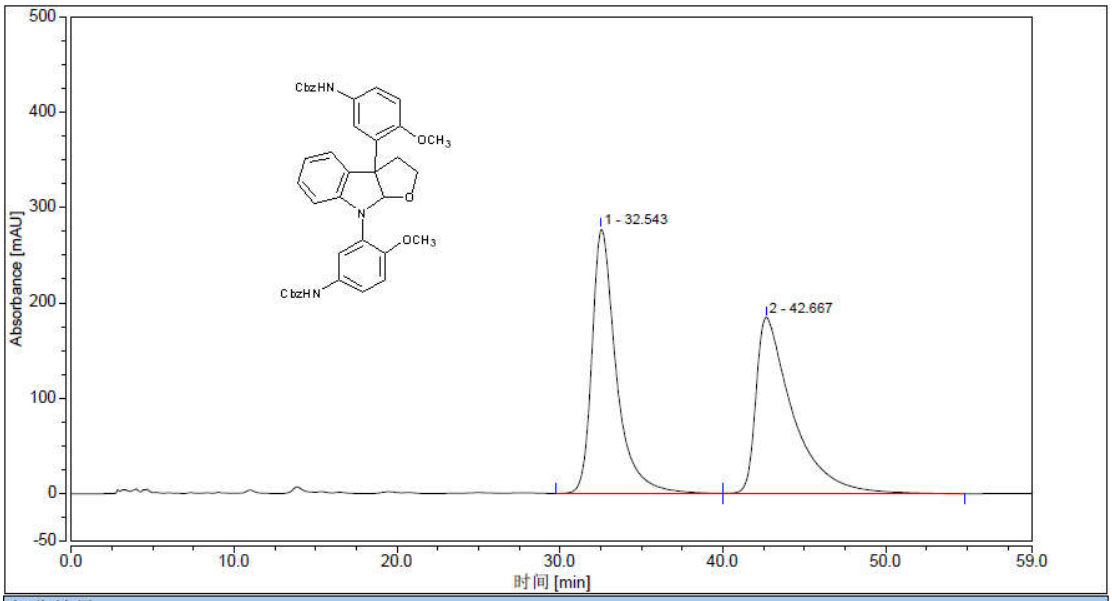
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.323	1388.720	1123.481	49.55	64.04	n.a.
2		12.870	1414.024	630.846	50.45	35.96	n.a.
Total:			**2802.744**	**1754.327**	**100.00**	**100.00**	



Integration Results

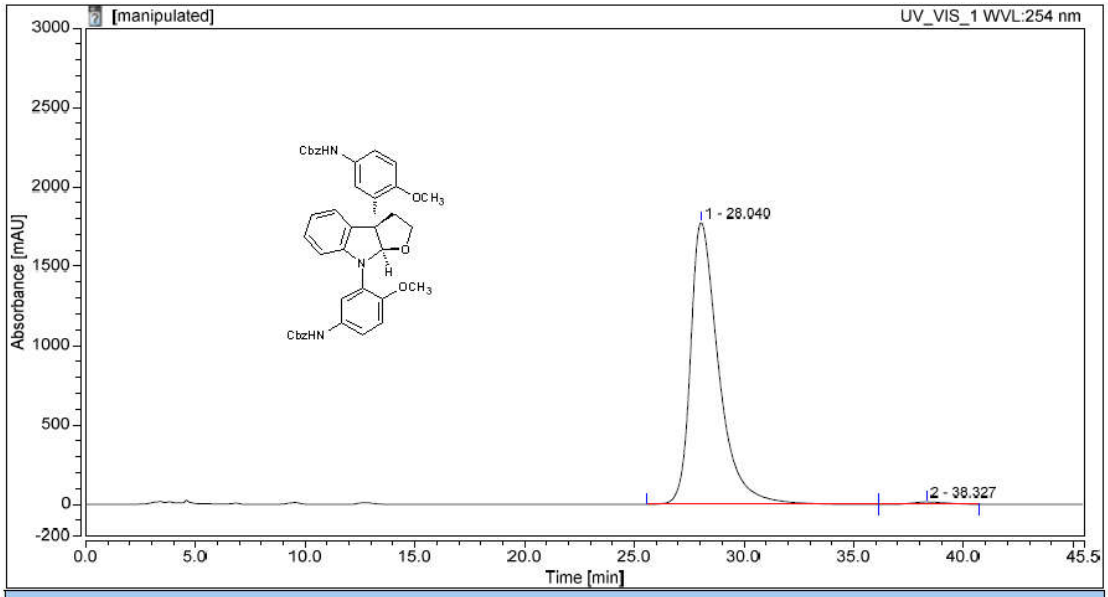
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.567	1145.121	1291.771	99.08	99.61	n.a.
2		13.367	10.577	5.007	0.92	0.39	n.a.
Total:			**1155.697**	**1296.778**	**100.00**	**100.00**	

3ad:



积分结果

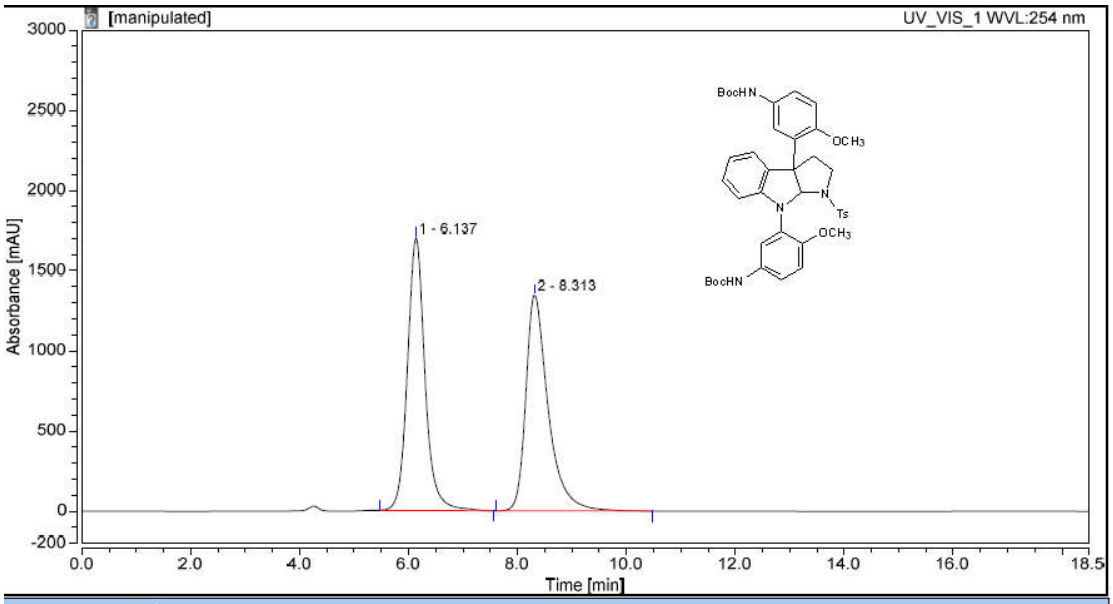
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		32.543	477.699	277.244	49.78	60.01	n.a.
2		42.667	481.938	184.766	50.22	39.99	n.a.
总和:			**959.637**	**462.010**	**100.00**	**100.00**	



Integration Results

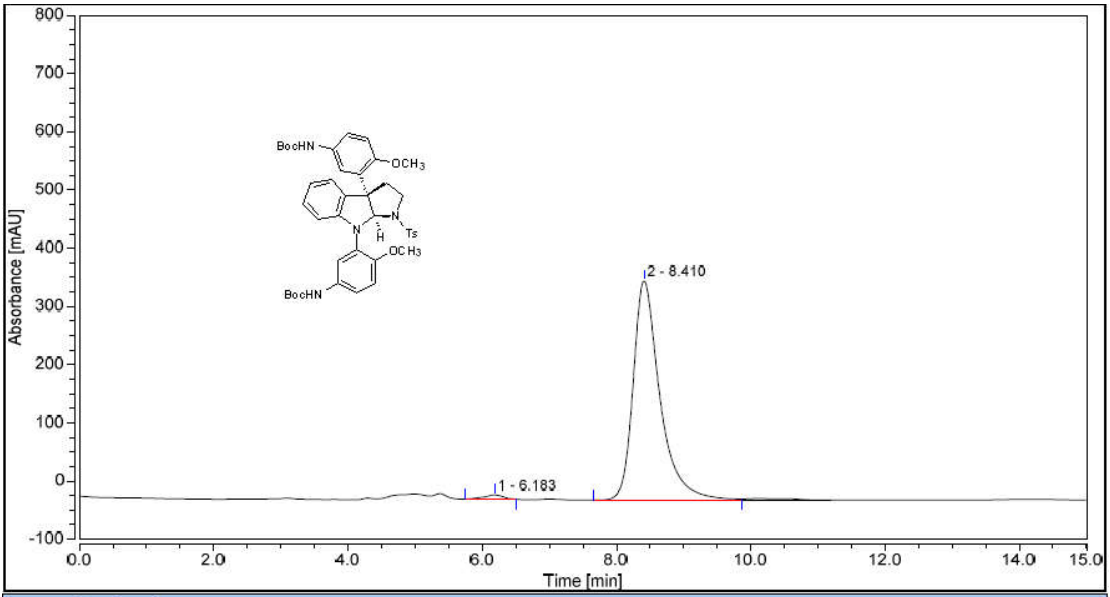
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.040	2635.902	1774.441	99.07	99.20	n.a.
2		38.327	24.845	14.285	0.93	0.80	n.a.
Total:			**2660.747**	**1788.725**	**100.00**	**100.00**	

3na:



Integration Results

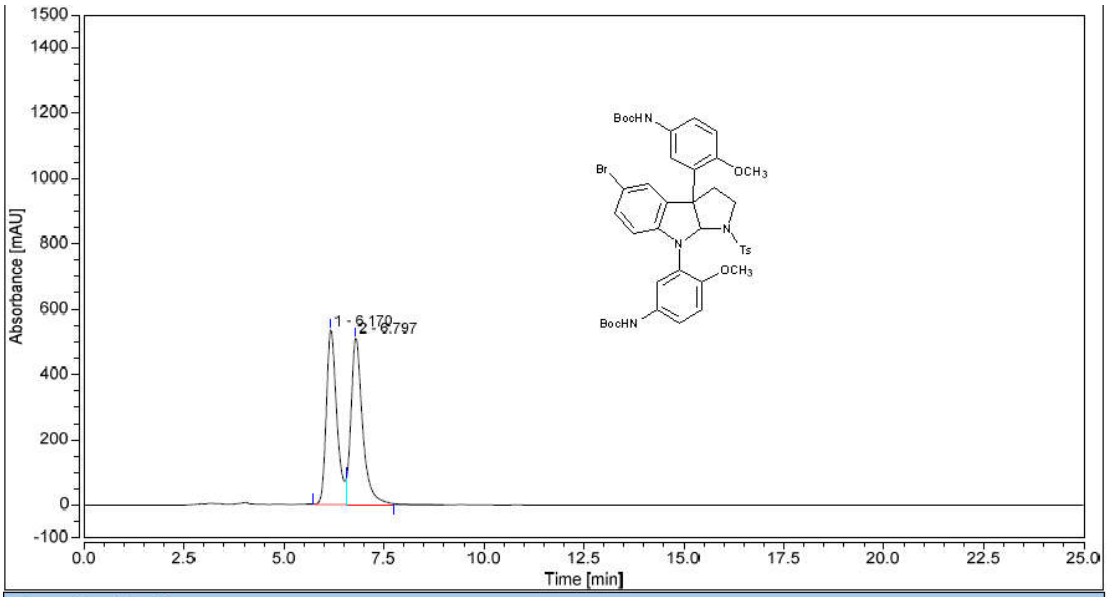
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.137	636.676	1698.305	49.86	55.77	n.a.
2		8.313	640.332	1346.637	50.14	44.23	n.a.
Total:			**1277.008**	**3044.942**	**100.00**	**100.00**	



Integration Results

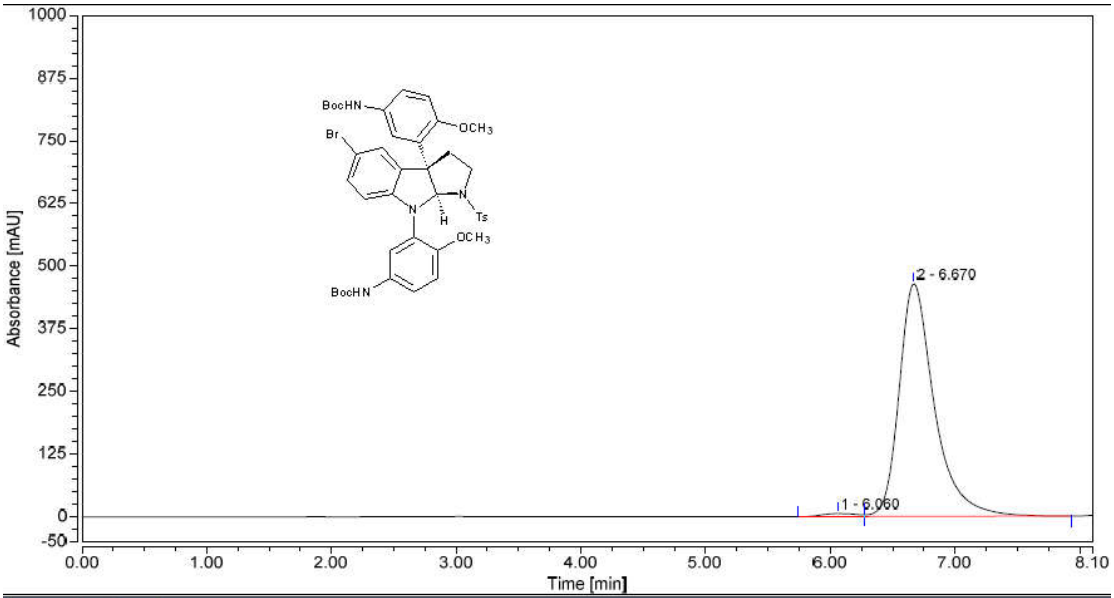
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.183	2.513	7.481	1.42	1.95	n.a.
2		8.410	174.283	376.692	98.58	98.05	n.a.
Total:			**176.795**	**384.173**	**100.00**	**100.00**	

3oa:



Integration Results

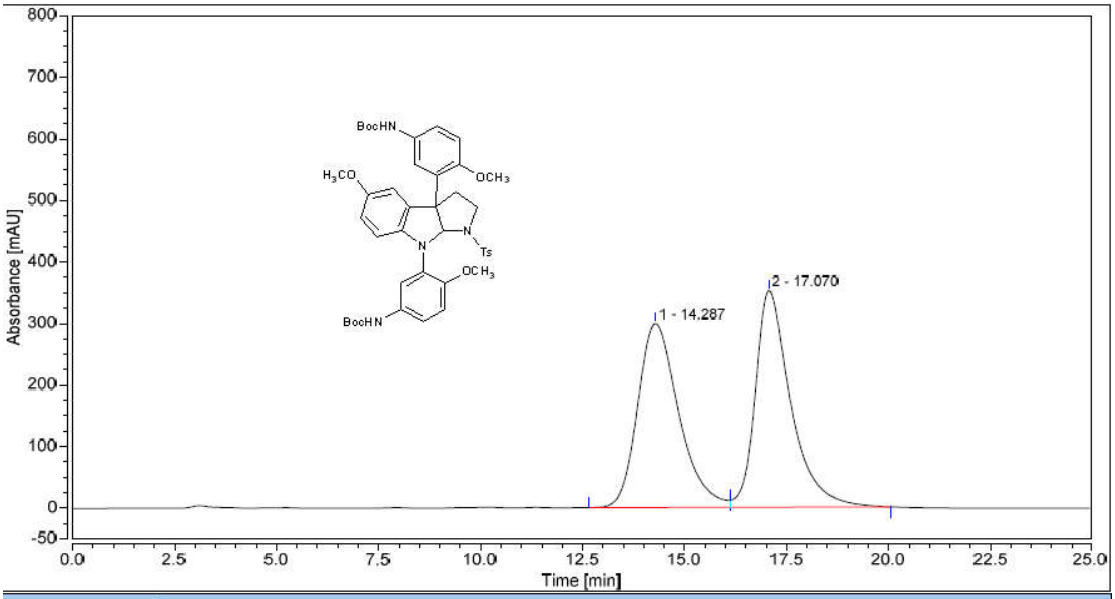
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.170	162.602	534.106	48.65	51.16	n.a.
2		6.797	171.641	509.980	51.35	48.84	n.a.
Total:			**334.243**	**1044.086**	**100.00**	**100.00**	



Integration Results

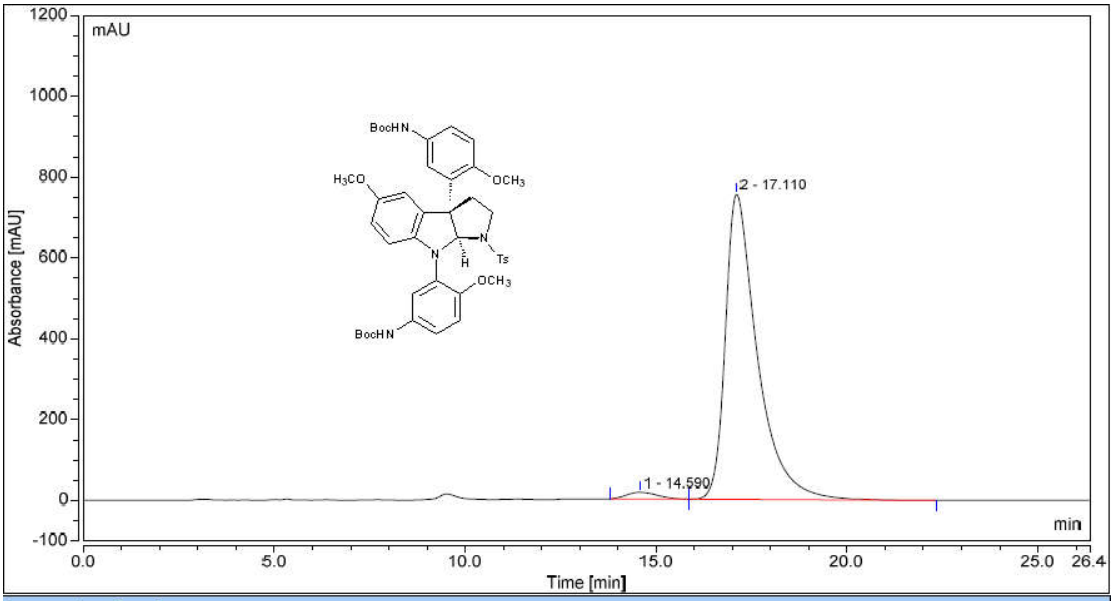
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.060	1.889	6.142	1.23	1.31	n.a.
2		6.670	151.931	463.875	98.77	98.69	n.a.
Total:			**153.820**	**470.017**	**100.00**	**100.00**	

3pa:



Integration Results

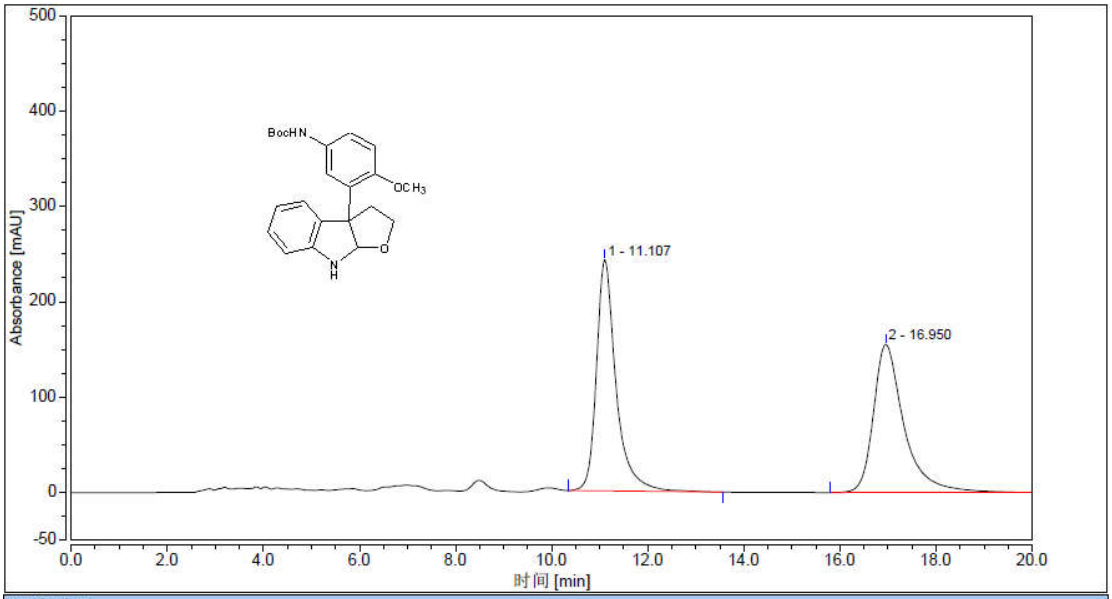
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.287	347.992	298.743	49.61	45.91	n.a.
2		17.070	353.522	351.926	50.39	54.09	n.a.
Total:			**701.513**	**650.670**	**100.00**	**100.00**	



Integration Results

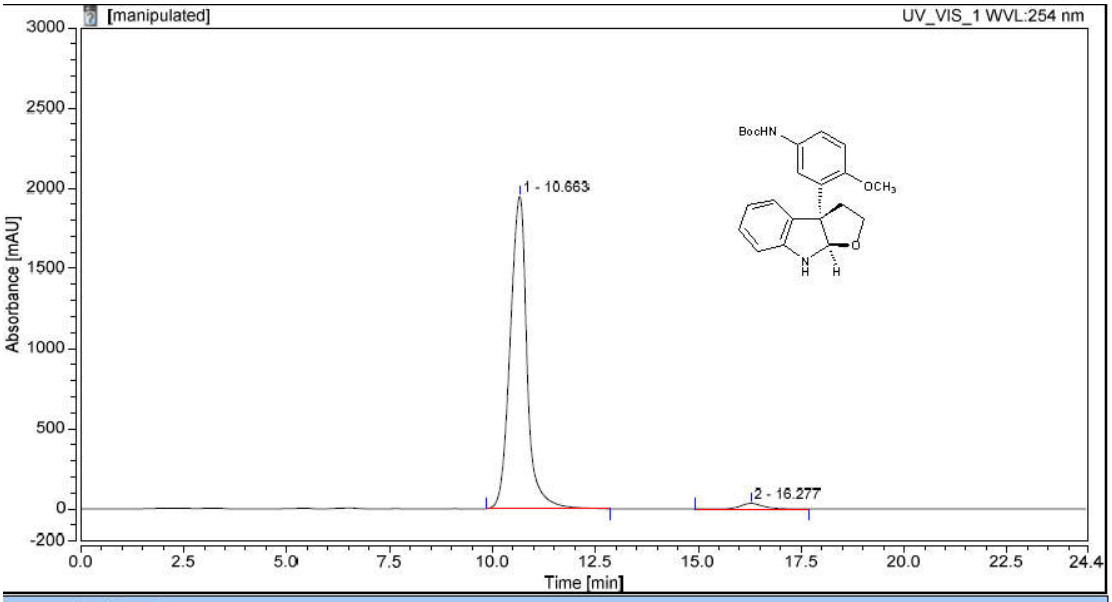
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.590	15.568	16.602	2.07	2.15	n.a.
2		17.110	735.690	755.446	97.93	97.85	n.a.
Total:			**751.258**	**772.048**	**100.00**	**100.00**	

7aa:



积分结果

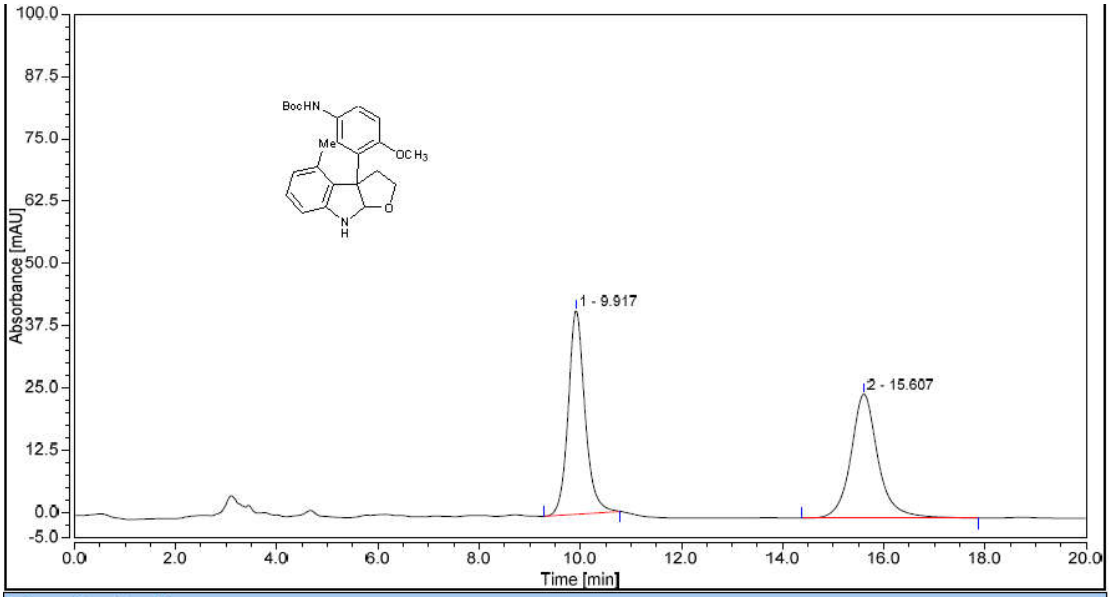
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.107	114.772	242.605	50.11	60.97	n.a.
2		16.950	114.254	155.323	49.89	39.03	n.a.
总和:			**229.026**	**397.928**	**100.00**	**100.00**	



Integration Results

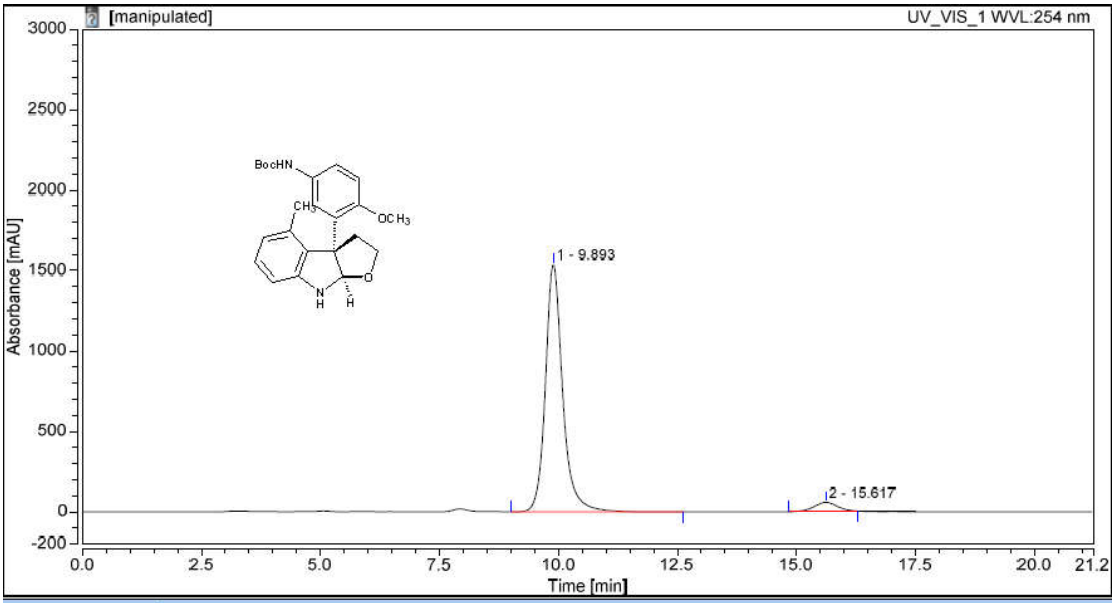
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.663	927.380	1949.062	97.65	98.26	n.a.
2		16.277	22.338	34.609	2.35	1.74	n.a.
Total:			**949.718**	**1983.671**	**100.00**	**100.00**	

7ca:



Integration Results

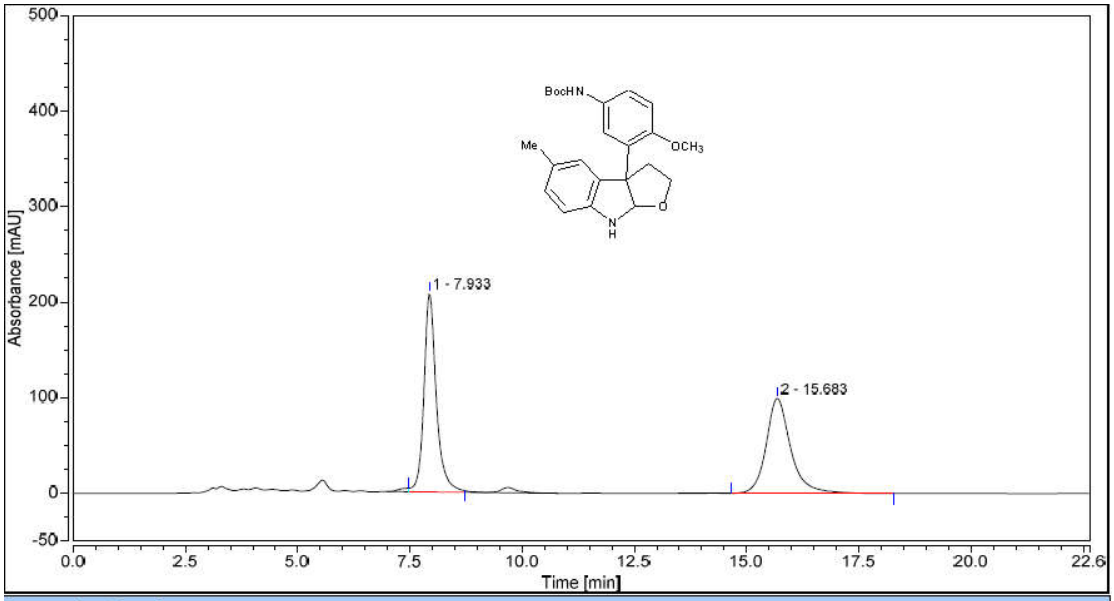
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.917	15.685	40.852	50.20	62.14	n.a.
2		15.607	15.563	24.894	49.80	37.86	n.a.
Total:			**31.248**	**65.746**	**100.00**	**100.00**	



Integration Results

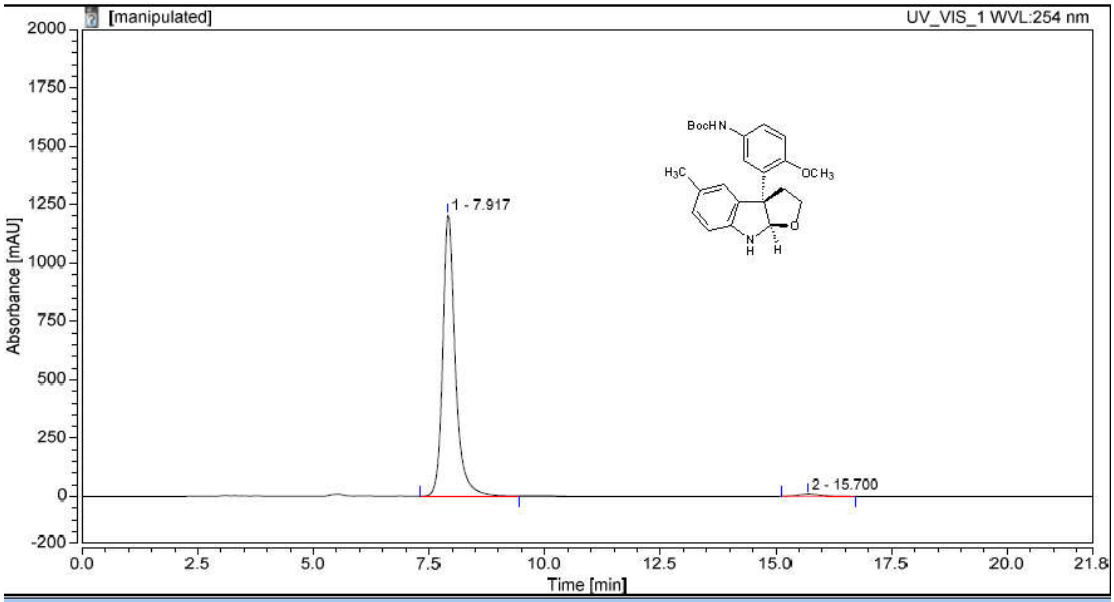
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.893	648.156	1537.684	94.91	96.33	n.a.
2		15.617	34.787	58.660	5.09	3.67	n.a.
Total:			**682.944**	**1596.344**	**100.00**	**100.00**	

7ea:



Integration Results

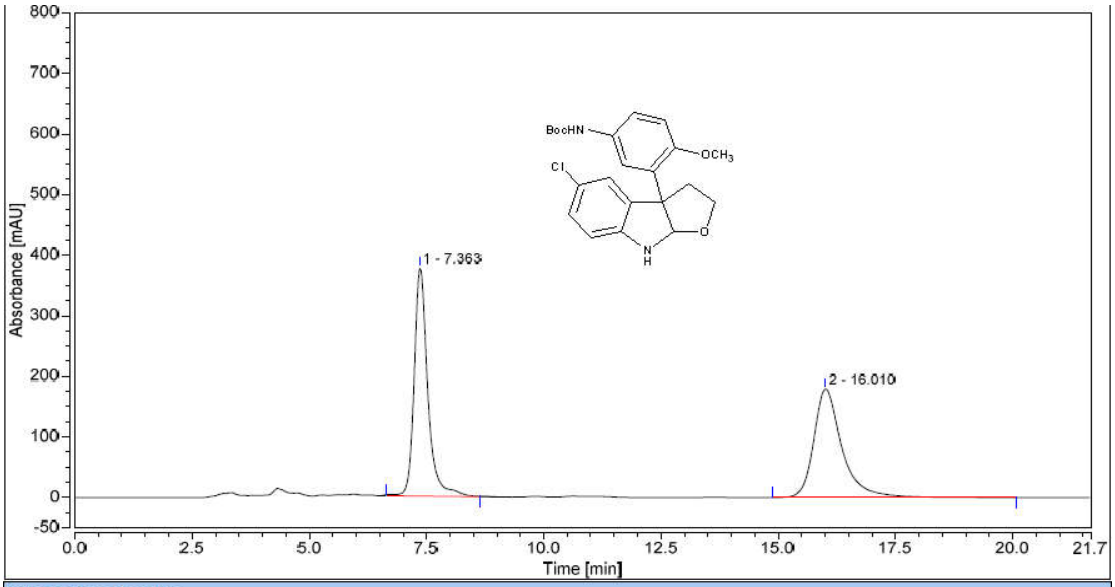
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.933	66.700	208.011	51.30	67.64	n.a.
2		15.683	63.328	99.537	48.70	32.36	n.a.
Total:			**130.028**	**307.548**	**100.00**	**100.00**	



Integration Results

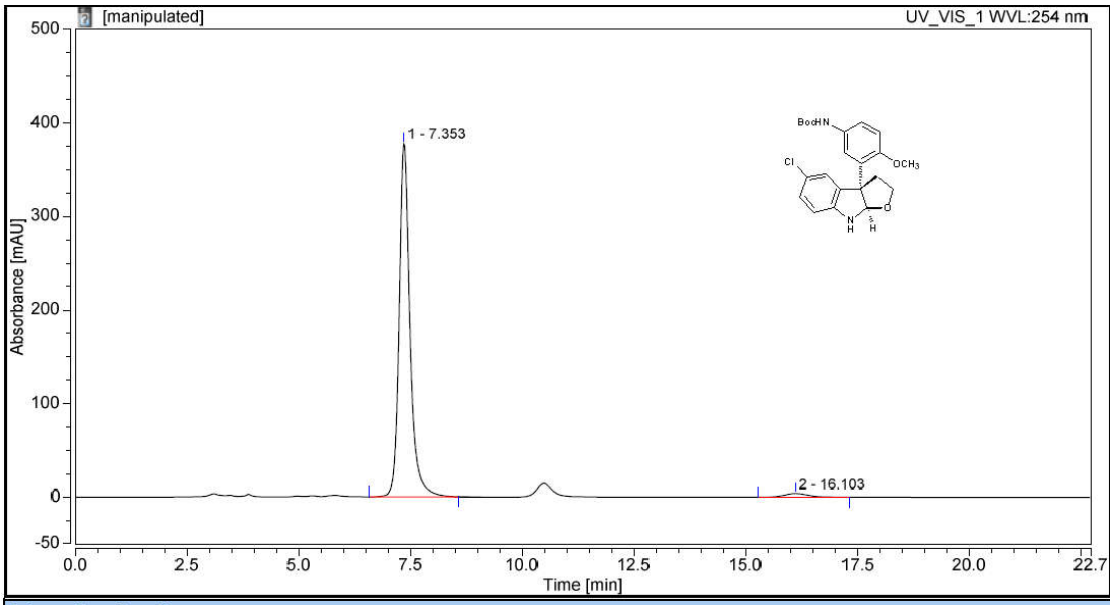
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.917	380.827	1205.902	98.64	99.25	n.a.
2		15.700	5.236	9.107	1.36	0.75	n.a.
Total:			**386.063**	**1215.009**	**100.00**	**100.00**	

7ga:



Integration Results

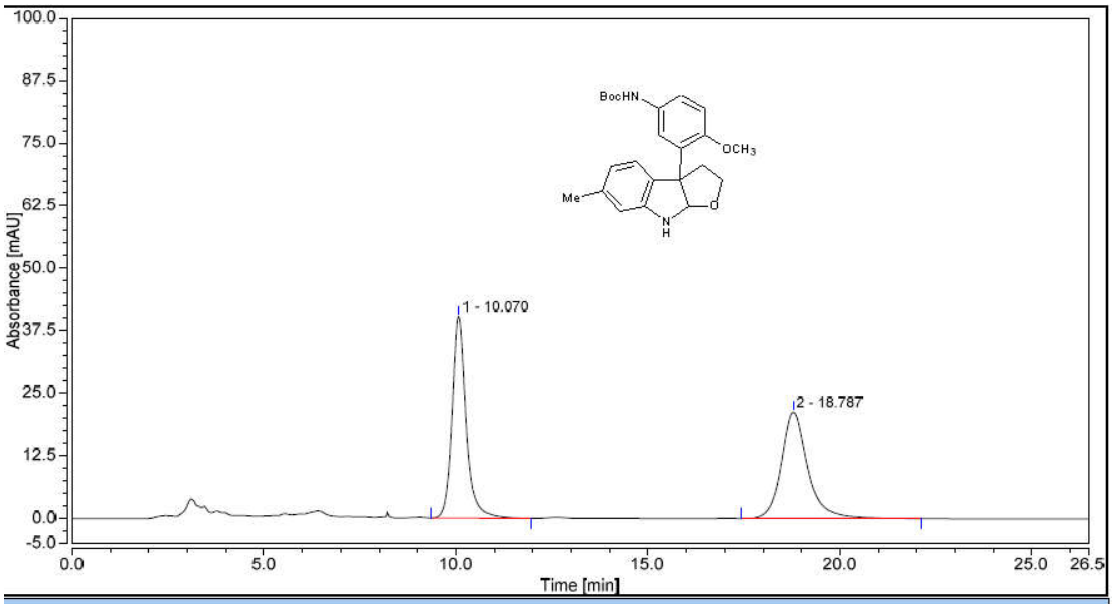
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.363	126.643	376.689	50.37	67.80	n.a.
2		16.010	124.789	178.903	49.63	32.20	n.a.
Total:			**251.433**	**555.592**	**100.00**	**100.00**	



Integration Results

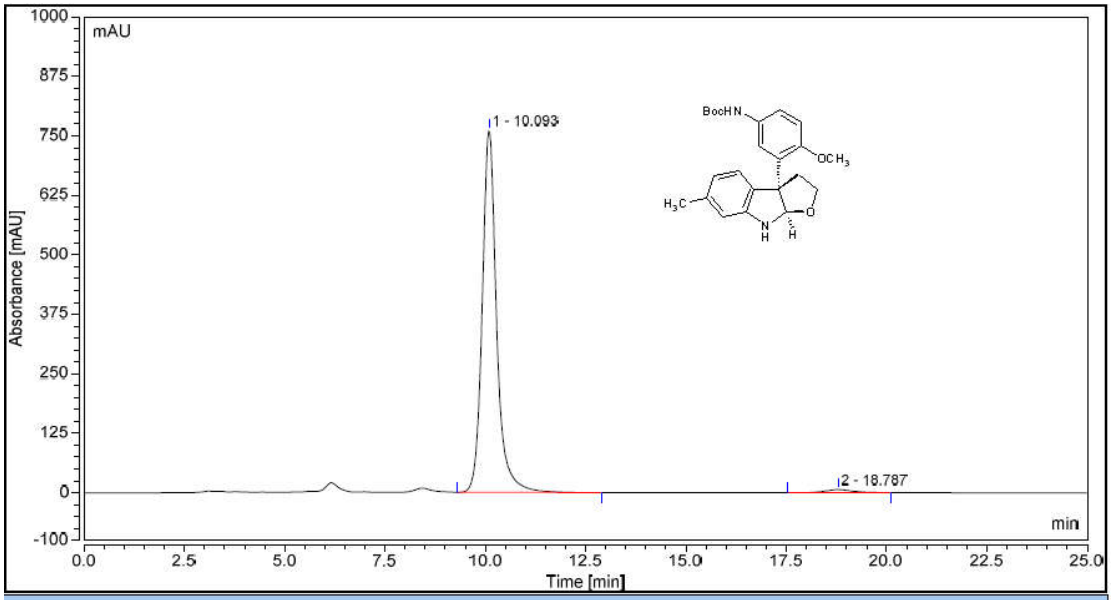
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.353	106.445	378.016	97.87	99.02	n.a.
2		16.103	2.315	3.729	2.13	0.98	n.a.
Total:			**108.760**	**381.745**	**100.00**	**100.00**	

7ha:



Integration Results

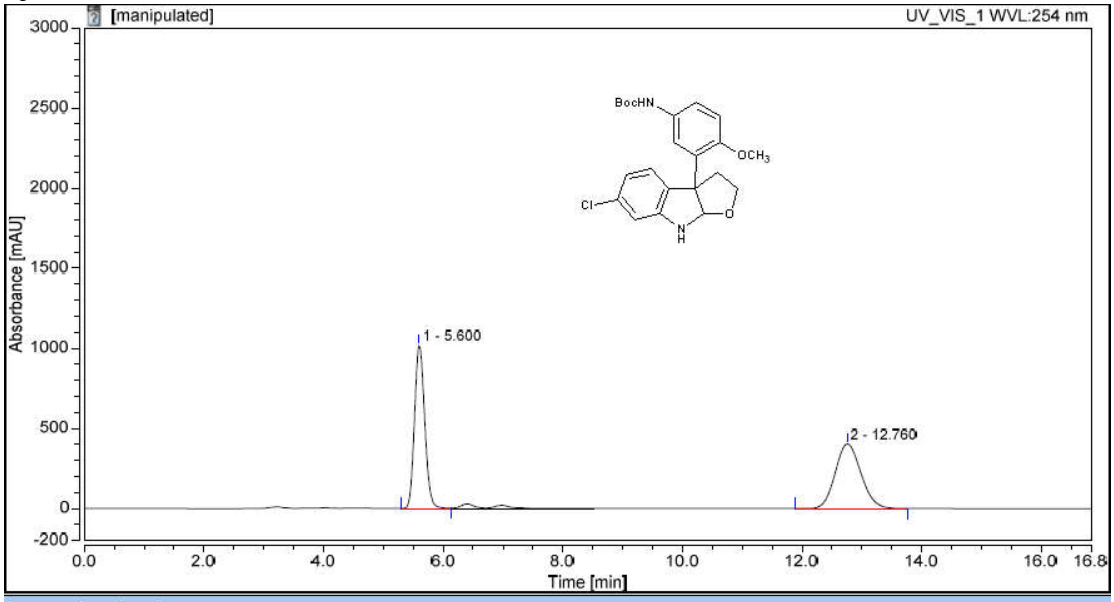
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.070	17.069	40.330	50.06	65.45	n.a.
2		18.787	17.030	21.289	49.94	34.55	n.a.
Total:			**34.100**	**61.619**	**100.00**	**100.00**	



Integration Results

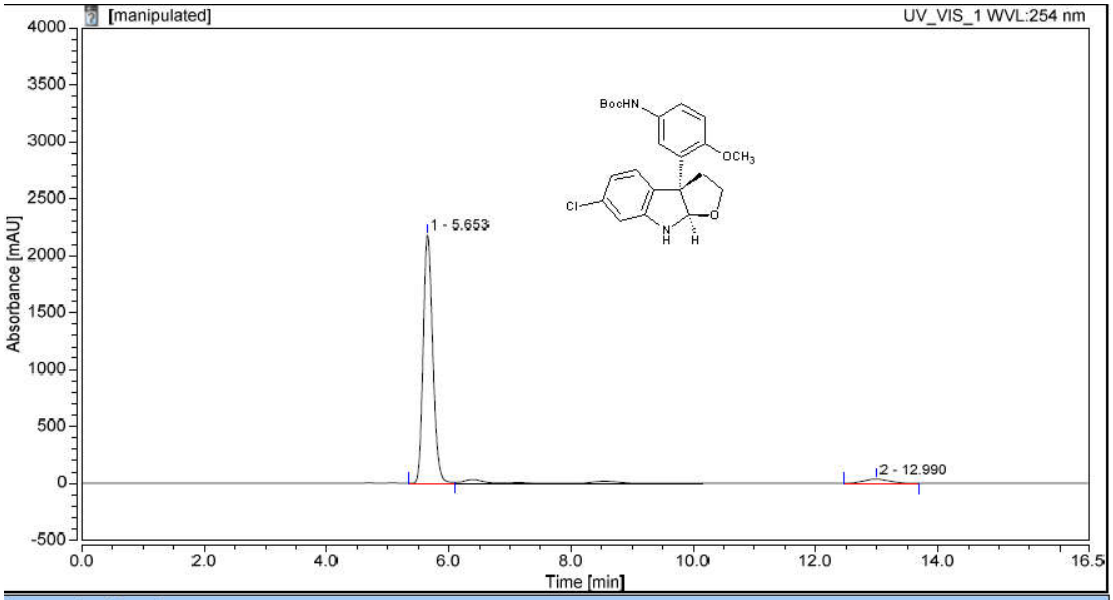
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.093	317.056	761.370	98.50	99.17	n.a.
2		18.787	4.837	6.378	1.50	0.83	n.a.
Total:			**321.893**	**767.748**	**100.00**	**100.00**	

7ja:



Integration Results

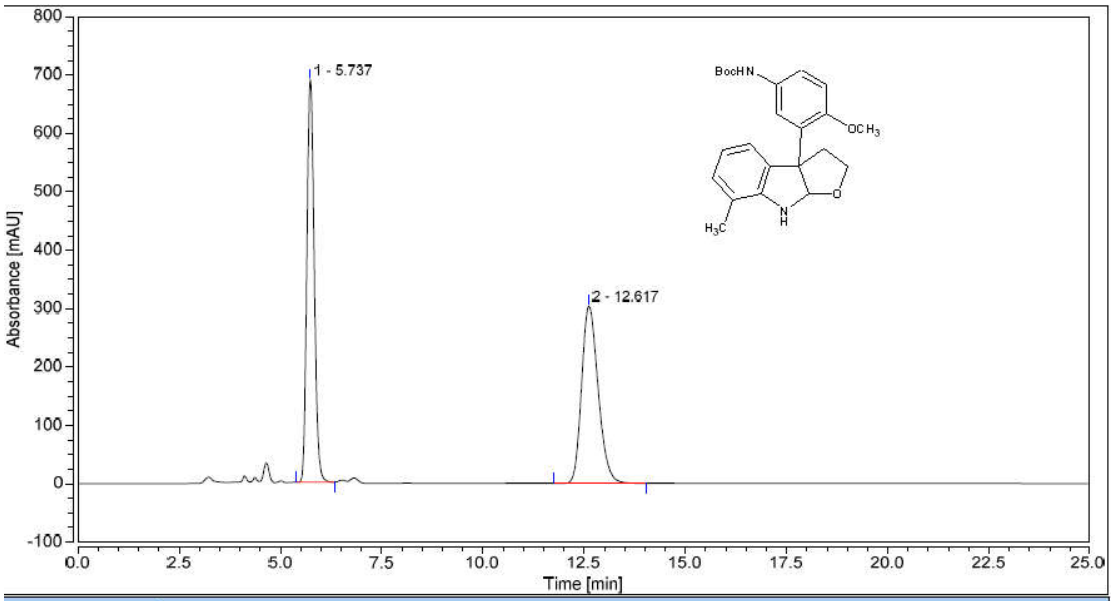
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.600	201.541	1019.788	50.06	71.62	n.a.
2		12.760	201.070	404.131	49.94	28.38	n.a.
Total:			**402.611**	**1423.920**	**100.00**	**100.00**	



Integration Results

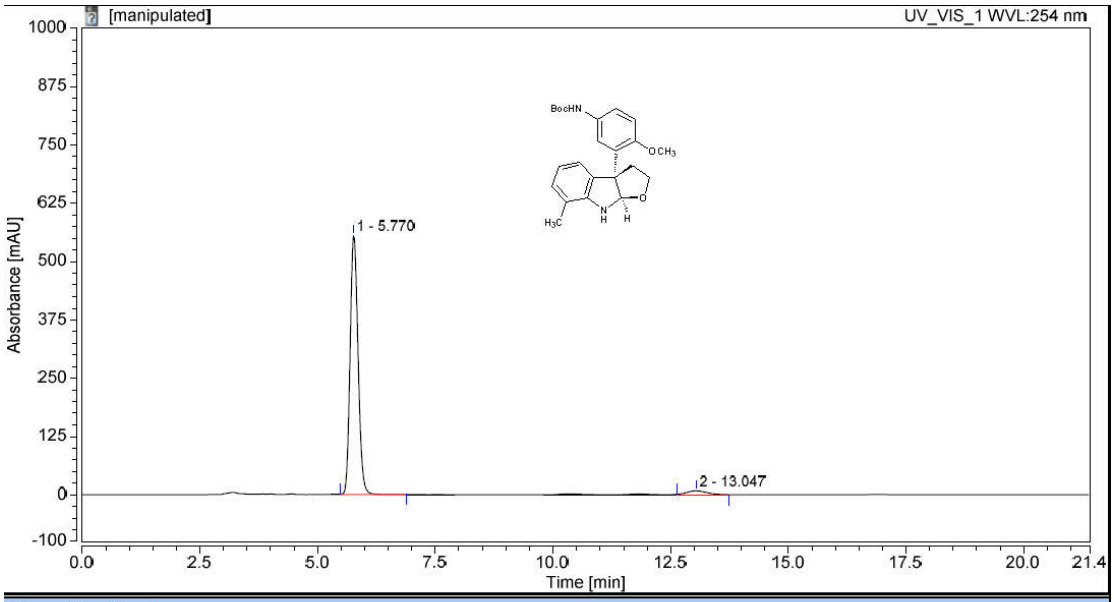
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.653	395.436	2184.209	95.70	98.34	n.a.
2		12.990	17.765	36.949	4.30	1.66	n.a.
Total:			**413.201**	**2221.158**	**100.00**	**100.00**	

7la:



Integration Results

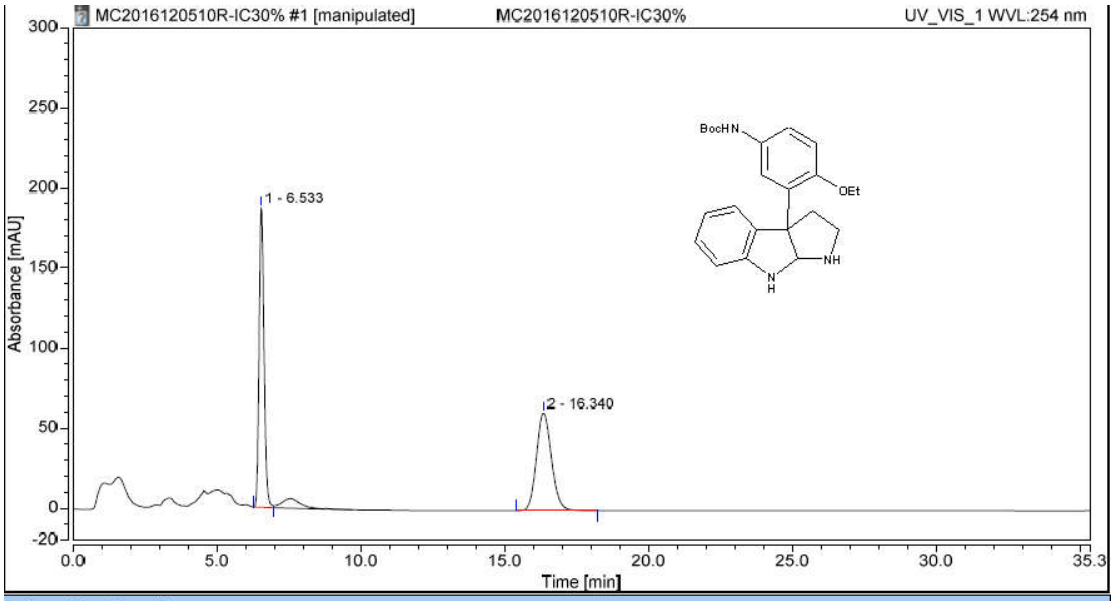
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.737	144.721	688.702	50.03	69.36	n.a.
2		12.617	144.537	304.284	49.97	30.64	n.a.
Total:			**289.258**	**992.986**	**100.00**	**100.00**	



Integration Results

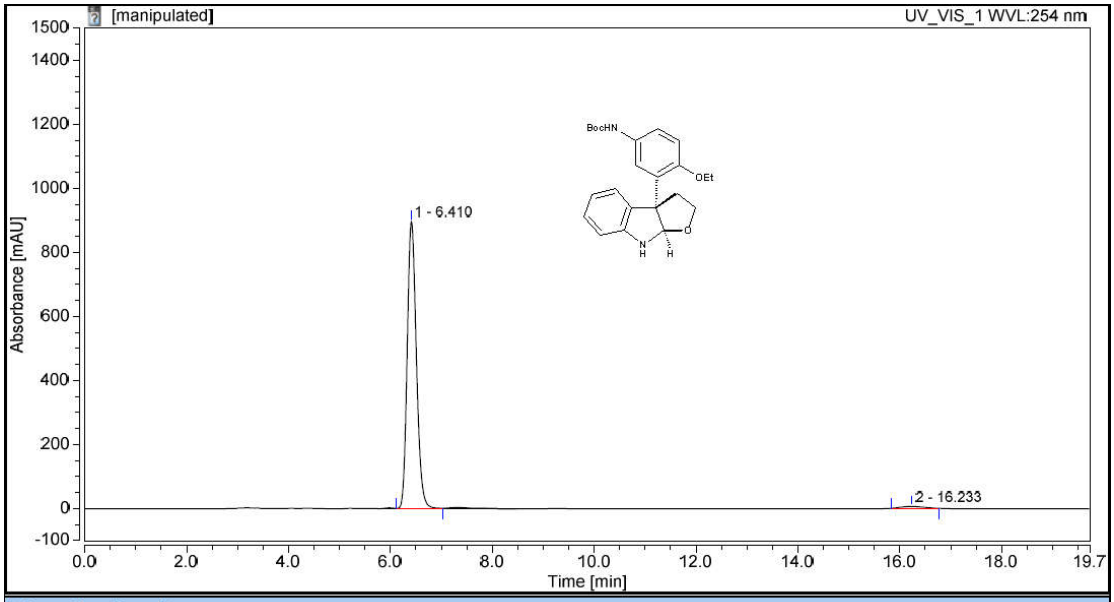
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.770	107.963	555.707	96.58	98.60	n.a.
2		13.047	3.824	7.891	3.42	1.40	n.a.
Total:			**111.788**	**563.598**	**100.00**	**100.00**	

7ab:



Integration Results

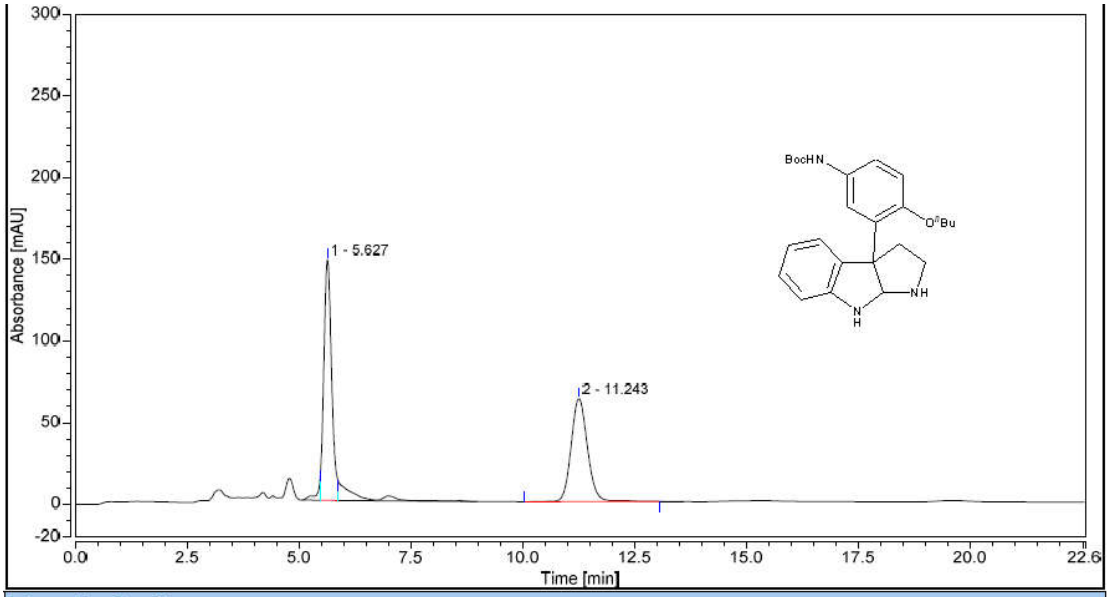
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.533	37.052	187.120	50.10	75.42	n.a.
2		16.340	36.898	60.978	49.90	24.58	n.a.
Total:			**73.950**	**248.098**	**100.00**	**100.00**	



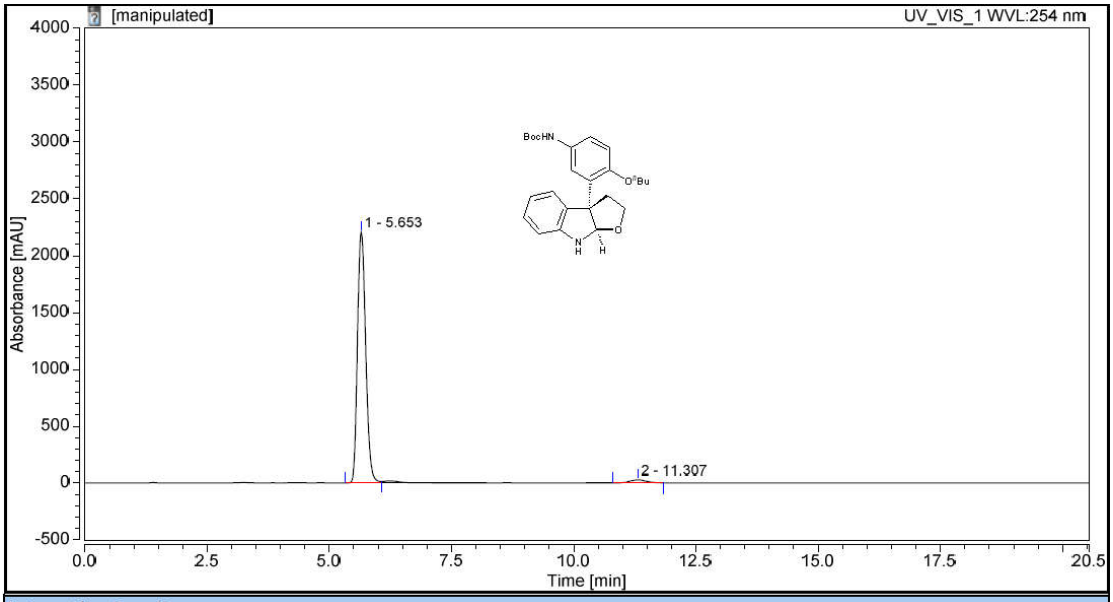
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.410	186.720	896.283	98.44	99.35	n.a.
2		16.233	2.957	5.878	1.56	0.65	n.a.
Total:			**189.677**	**902.161**	**100.00**	**100.00**	

7ac:

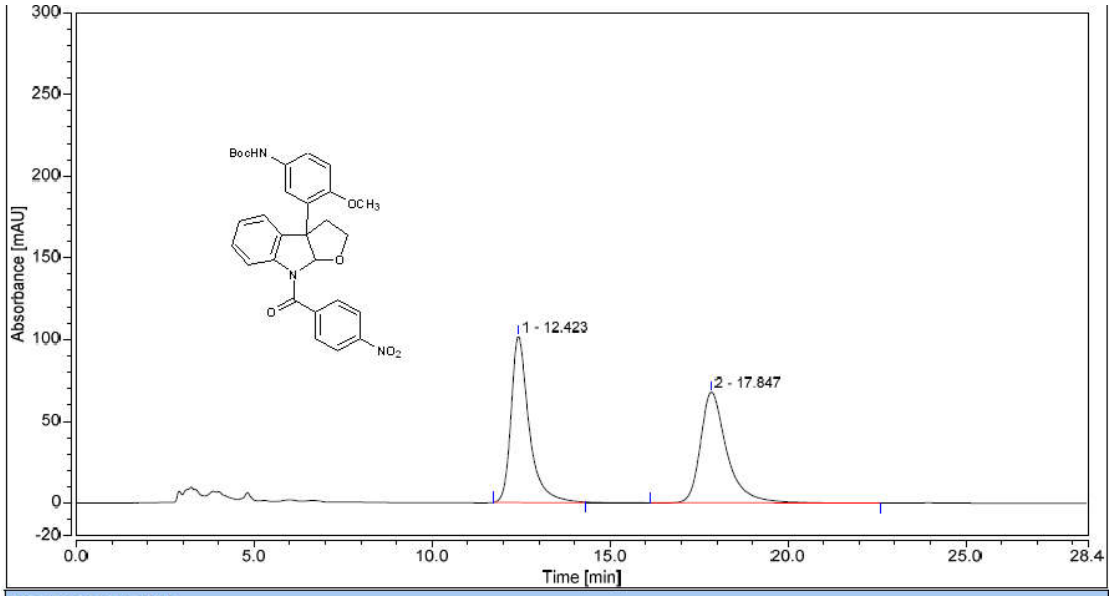


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.627	29.440	147.296	52.35	69.98	n.a.
2		11.243	26.799	63.172	47.65	30.02	n.a.
Total:			**56.239**	**210.468**	**100.00**	**100.00**	



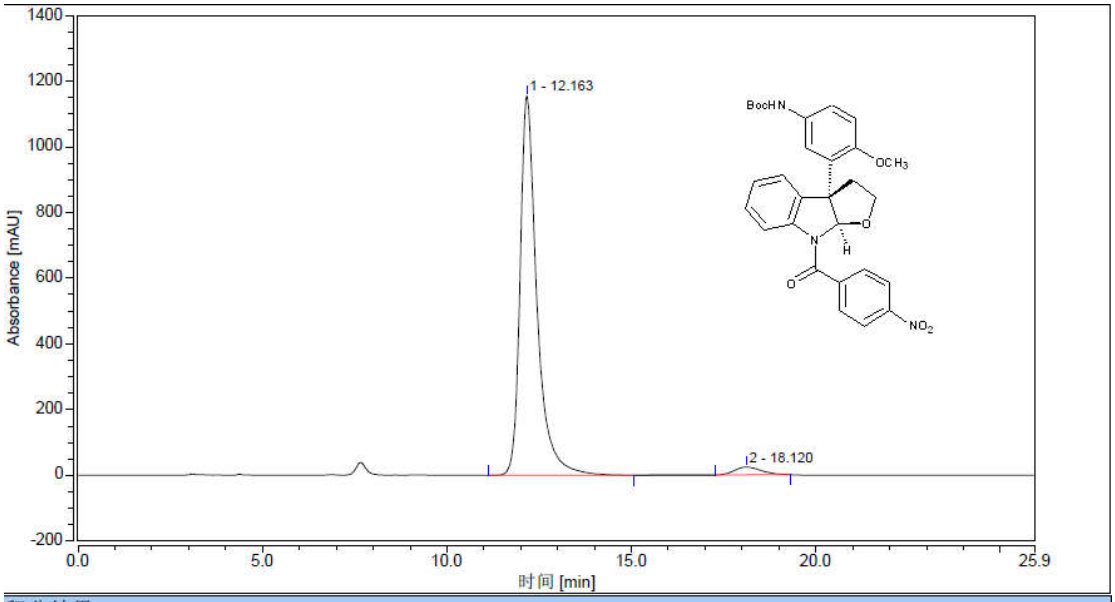
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.653	429.889	2207.367	97.49	98.77	n.a.
2		11.307	11.071	27.490	2.51	1.23	n.a.
Total:			**440.959**	**2234.857**	**100.00**	**100.00**	

Compound 8



Integration Results

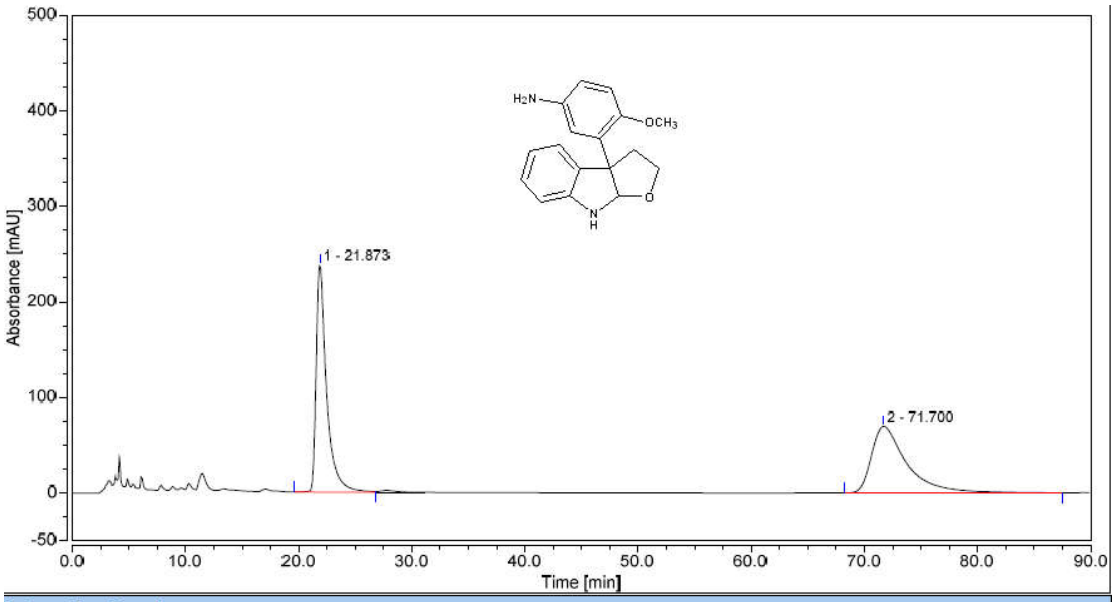
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.423	59.692	101.684	50.69	60.00	n.a.
2		17.847	58.077	67.779	49.31	40.00	n.a.
Total:			**117.770**	**169.463**	**100.00**	**100.00**	



积分结果

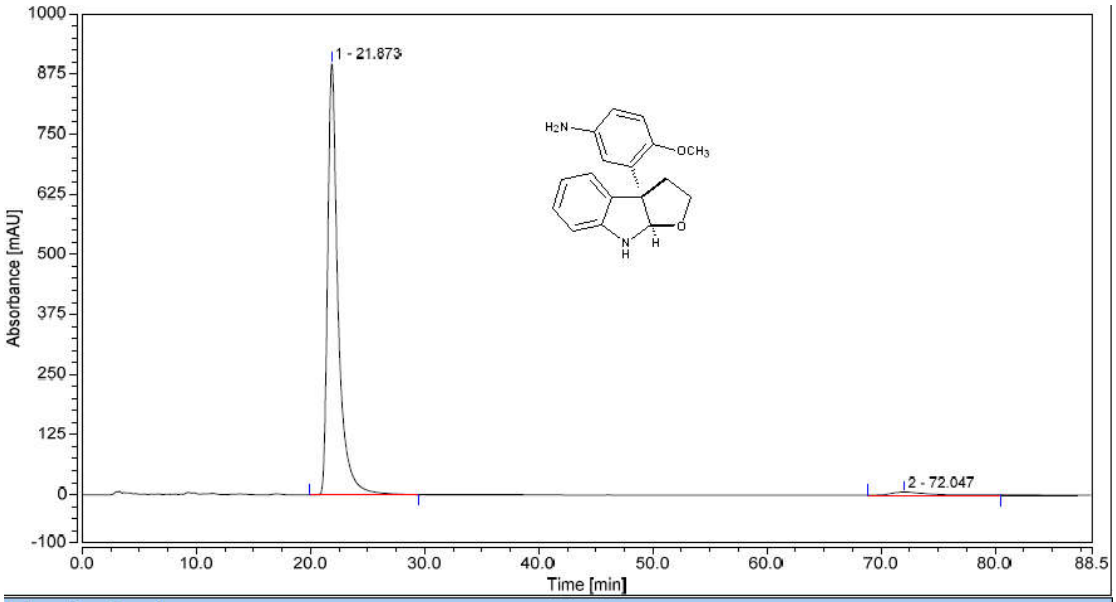
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.163	611.734	1155.461	96.90	98.01	n.a.
2		18.120	19.598	23.454	3.10	1.99	n.a.
总和:			**631.332**	**1178.915**	**100.00**	**100.00**	

Compound 9:



Integration Results

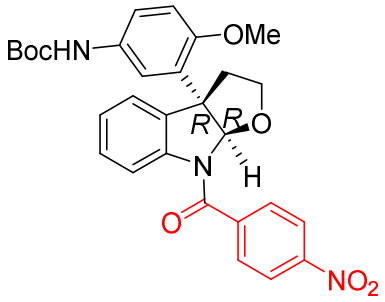
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.873	253.870	238.000	50.42	77.37	n.a.
2		71.700	249.595	69.608	49.58	22.63	n.a.
Total:			**503.464**	**307.608**	**100.00**	**100.00**	



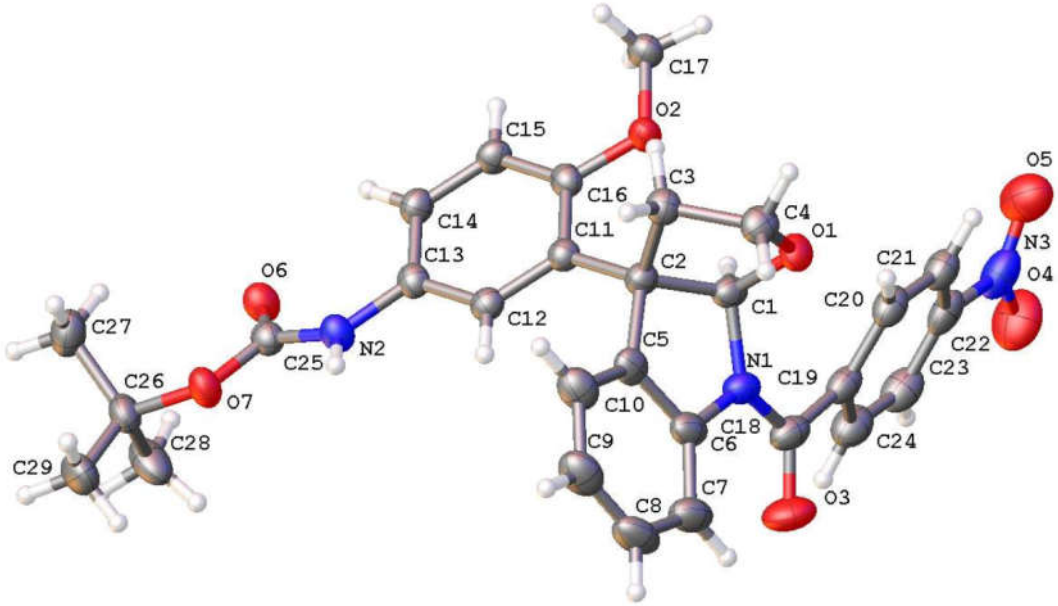
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.873	959.379	898.862	97.71	99.29	n.a.
2		72.047	22.441	6.440	2.29	0.71	n.a.
Total:			**981.820**	**905.302**	**100.00**	**100.00**	

8. X-ray single crystal data for compound 8



(*R*,*R*)-8



The thermal ellipsoid was drawn at the 30% probability level.

Identification code	cu_d8v17103_0m	
Empirical formula	C29 H31 N3 O8	
Formula weight	549.57	
Temperature	293.15 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 13.172(3) Å	α= 90°.
	b = 6.6186(8) Å	β= 112.481(18)°.
	c = 16.673(3) Å	γ = 90°.
Volume	1343.1(4) $Å^3$	
Z	2	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	0.831 mm^{-1}	

F(000)	580
Crystal size	0.2 x 0.1 x 0.02 mm^3
Theta range for data collection	2.868 to 68.274°.
Index ranges	-15<=h<=14, -7<=k<=7, -20<=l<=19
Reflections collected	17501
Independent reflections	4854 [R(int) = 0.0620]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5524
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4854 / 1 / 373
Goodness-of-fit on F^2	1.113
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0846
R indices (all data)	R1 = 0.0498, wR2 = 0.0912
Absolute structure parameter	0.00(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.150 and -0.197 $e.Å^{-3}$