

## Enantioselective Synthesis of Pyrroloquinolines via Three-Component Povarov Reaction with Aminoindoles

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### Table of contents

1. General methods .....	2
2. Optimization Studies.....	2
3. General procedure for the three-component Povarov reaction .....	5
4. Procedure for the reduction of indole .....	22
5. Procedure for the protection of secondary amine and Friedel–Crafts alkylation ....	23
6. X-ray crystallographic analysis of <b>4ak</b> (CCDC 2290686) .....	24
7. Reference .....	25
8. NMR spectra and HPLC chromatograms of products .....	27

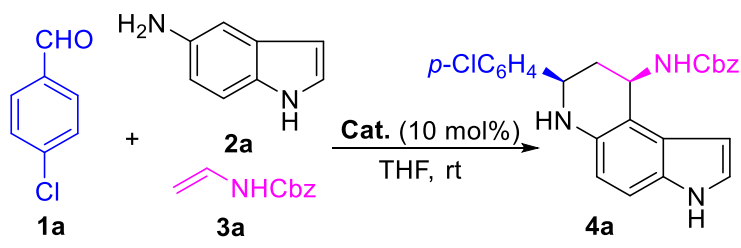
## 1. General methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian 400 MHz spectrometers. Chemical shifts ( $\delta$ ) were reported in ppm downfield from  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm) and DMSO ( $\delta = 2.50$  ppm) for  $^1\text{H}$  NMR and relative to the central  $\text{CDCl}_3$  resonance ( $\delta = 77.0$  ppm) and DMSO ( $\delta = 39.5$  ppm) for  $^{13}\text{C}$  NMR spectroscopy. Coupling constants ( $J$ ) were given in Hz. ESI-HRMS spectrometer was measured with a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Enantiomeric excess was determined by HPLC analysis on Chiralpak IE, AD and OD columns in comparison with the authentic racemates. Optical rotation data were recorded on Rudolph Autopol I automatic polarimeter. Commercially available compounds were used without further purification. Solvents were dried according to standard procedures. Column chromatography was performed with silica gel (300-400 mesh).

Chiral phosphoric acid **C1-C13** and **C15** were prepared according to the literature procedures.<sup>1</sup> Enamide **3a-3d**,  $\beta$ -substituted enecarbamate **3e** were synthesized using general procedures reported in the literature.<sup>2</sup>

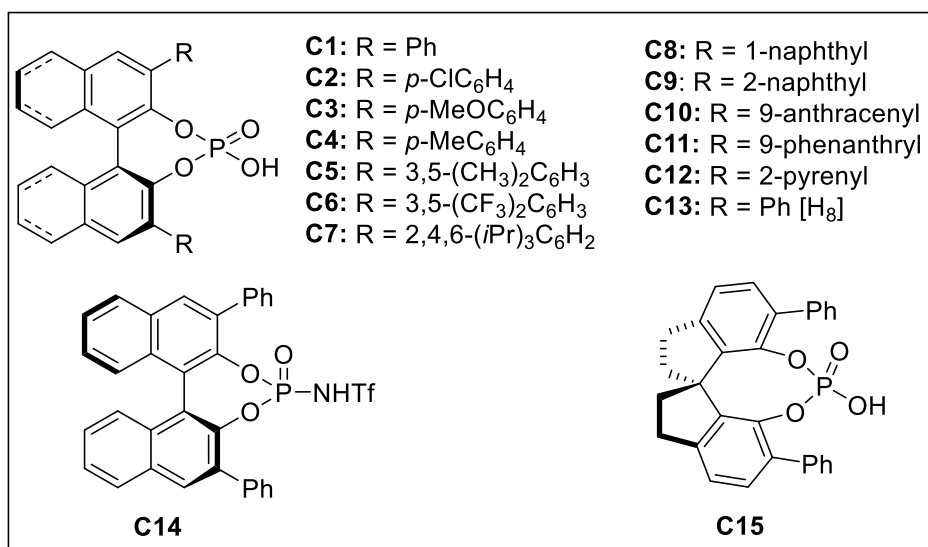
## 2. Optimization Studies

Table S1. Screening of catalysts<sup>a</sup>



Entry	Catalyst	Time (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	<b>C1</b>	4	89	94
2	<b>C2</b>	4	92	93
3	<b>C3</b>	3	73	91
4	<b>C4</b>	3	25	95
5	<b>C5</b>	24	69	36
6	<b>C6</b>	72	68	46
7	<b>C7</b>	9	70	94

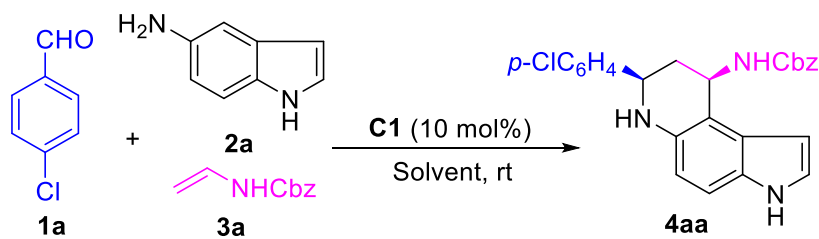
8	<b>C8</b>	3	74	94
9	<b>C9</b>	5	82	86
10	<b>C10</b>	2	81	91
11	<b>C11</b>	2	76	87
12	<b>C12</b>	7	75	82
13	<b>C13</b>	6	53	94
14	<b>C14</b>	NR		
15	<b>C15</b>	26	66	43
16 <sup>d</sup>	<b>C1</b>	24	68	88
17 <sup>e</sup>	<b>C1</b>	6	70	89
18 <sup>f</sup>	<b>C1</b>	2	79	91
19 <sup>g</sup>	<b>C1</b>	1	74	86
20 <sup>h</sup>	<b>C1</b>	120	73	92



<sup>a</sup>Unless otherwise noted, the reaction was performed with 0.12 mmol of **1a**, 0.1 mmol of **2a**, and 0.4 mmol of **3a**, 10 mol % catalyst in 1 mL of THF at rt. THF = tetrahydrofuran. <sup>b</sup>Isolated yield after flash chromatography on silica gel.

<sup>c</sup>Determined by HPLC on Daicel Chiralpak IE-H column. <sup>d</sup>Performed with 5 mol% **C1**. <sup>e</sup>Performed with 15 mol% **C1**. <sup>f</sup>Performed with 20 mol% **C1**. <sup>g</sup>Conducted at 40 °C. <sup>h</sup>Conducted at 0 °C.

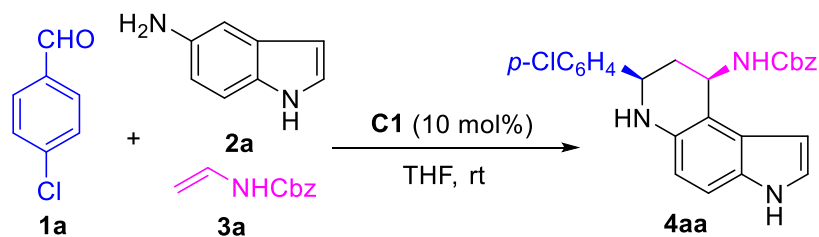
**Table S2. Screening of solvent<sup>a</sup>**



Entry	Solvent	Time (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	toluene	25	41	89
2	DCM	30	42	91
3	EA	9	55	89
4	THF	4	89	94
5	Et <sub>2</sub> O	24	61	86
6	MTBE	48	37	89
7	1,4-dioxane	24	51	94
8	ACN	10	69	87
9	EtOH	72	39	44

<sup>a</sup>Unless otherwise noted, the reaction was performed with 0.12 mmol of **1a**, 0.1 mmol of **2a**, and 0.4 mmol of **3a**, 10 mol % **C1** in 1 mL of solvent at rt. DCM = dichloromethane, EA = ethyl acetate, MTBE = methyl *tert*-butyl ether, ACN = acetonitrile. <sup>b</sup>Isolated yield after flash chromatography on silica gel. <sup>c</sup>Determined by HPLC on Daicel Chiralpak IE-H column.

**Table S3. Optimization of substrate ratio<sup>a</sup>**



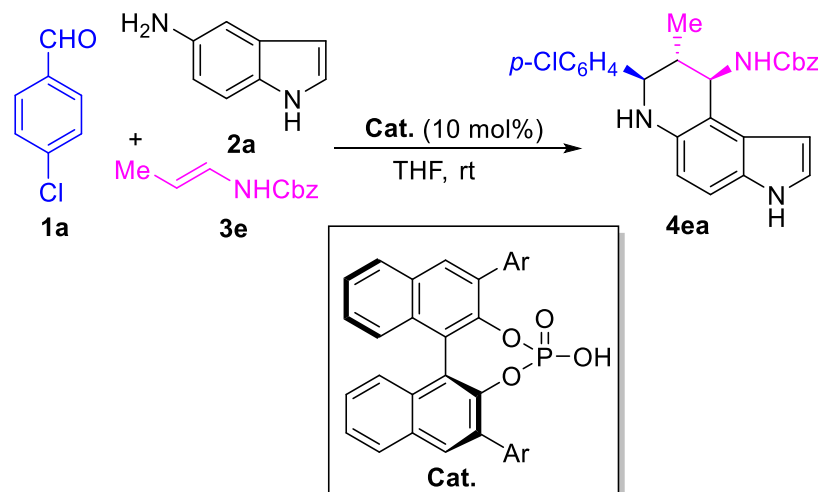
Entry	<b>3a</b> (X equiv.)	Time (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	1	72	27	94
2	2	24	58	90
3	3	24	45	88
4	4	4	89	94

<sup>a</sup>Unless otherwise noted, the reaction was performed with 0.12 mmol of **1a**, 0.1 mmol of **2a**, and X equiv. of **3a**, 10



mol % **C1** in 1 mL of THF at rt. <sup>b</sup>Isolated yield after flash chromatography on silica gel. <sup>c</sup>Determined by HPLC on Daicel Chiralpak IE-H column.

**Table S4. Optimization study for the Povarov reaction with  $\beta$ -substituted enecarbamate.**



Entry	Ar	Time (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	C <sub>6</sub> H <sub>5</sub> ( <b>C1</b> )	96	78	86
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ( <b>C2</b> )	72	56	88
3	1-naphthyl ( <b>C8</b> )	36	89	90
4	9-anthracenyl ( <b>C10</b> )	36	85	76

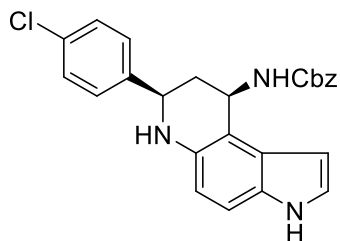
<sup>a</sup>Unless otherwise noted, the reaction was performed with 0.12 mmol of **1a**, 0.1 mmol of **2a**, and 0.4 mmol of **3e**, 10 mol % catalyst in 1 mL of THF at rt. <sup>b</sup>Isolated yield after flash chromatography on silica gel. <sup>c</sup>Determined by HPLC on Daicel Chiralpak OD-H column.

### 3. General procedure for the three-component Povarov reaction

To a solution of 4-chlorobenzaldehyde **1a** (16.9 mg, 0.12 mmol) in dried THF (1 mL), was added 5-aminoindole **2a** (13.2 mg, 0.1 mmol) and phosphoric acid **C1** (5.0 mg, 0.01 mmol). After stirring at rt for 20 minutes, benzyl *N*-vinylcarbamate **3a** (70.8 mg, 0.4 mmol) was added in one portion. The reaction mixture was stirred at RT for 4 hours. After completion of the reaction (monitored by TLC), the solvent was removed *in vacuo* and the residue was purified via flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1, v/v) to give the annulated product **4aa**.

The corresponding racemate was prepared with racemic BINOL-derived phosphoric acid under otherwise identical conditions.

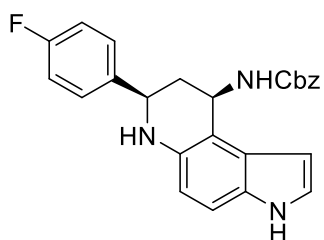
**Benzyl ((7R, 9R)-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-3H-pyrrolo[3, 2-f]quinolin-9-yl)**



**carbamate (4aa):** The product was obtained as a white solid (38.4 mg, 89% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 94% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 10.297$  min,  $t_{\text{major}} = 11.377$  min;  $[\alpha]_{\text{D}}^{25} = +41.5$  ( $c = 0.537$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.50 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.37-7.31 (m, 5H), 7.11 (t,  $J = 2.8$  Hz, 1H), 7.08 (d,  $J = 8.8$  Hz, 1H), 6.54 (d,  $J = 8.4$  Hz, 1H), 6.14 (s, 1H), 5.40 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.6$  Hz, 1H), 5.13 (d,  $J = 12.8$  Hz, 1H), 5.03 (d,  $J = 12.8$  Hz, 1H), 4.37 (d,  $J = 10.2$  Hz, 1H), 2.21 (dd,  $J = 12.0, 7.6$  Hz, 1H), 1.96 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 156.6, 155.9, 143.4, 139.4, 137.6, 137.4, 131.4, 130.2, 128.5, 128.30, 128.29, 128.2, 127.7, 127.6, 127.4, 126.4, 124.2, 112.0, 111.2, 110.9, 99.9, 65.0, 64.9, 55.1, 47.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{ClN}_3\text{NaO}_2$  454.1293, found 454.1290.

**Benzyl ((7R, 9R)-7-(4-fluorophenyl)-6, 7, 8, 9-tetrahydro-3H-pyrrolo[3, 2-f]quinolin-9-yl)**

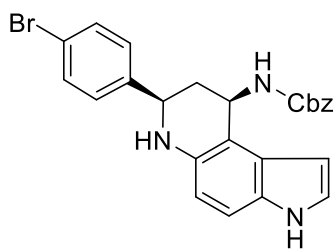


**carbamate (4ab):** The product was obtained as a white solid (34.0 mg, 82% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 98% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 21.140$  min,  $t_{\text{major}} = 24.257$  min;  $[\alpha]_{\text{D}}^{25} = +51.3$  ( $c = 0.412$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.52-7.49 (m, 2H), 7.38-7.31 (m, 5H), 7.19 (t,  $J = 8.8$  Hz, 2H), 7.08 (t,  $J = 5.2$  Hz, 1H), 7.06 (d,  $J = 8.4$  Hz, 1H), 6.54 (d,  $J = 8.6$  Hz, 1H), 6.13 (s, 1H), 5.37 (br s, 1H), 5.28 (dd,  $J = 16.8, 9.6$  Hz, 1H), 5.14 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.38 (d,  $J = 11.2$  Hz, 1H), 2.21 (dd,  $J = 12.0, 7.2$  Hz, 1H), 1.97 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 161.3 (d,  $^1J_{\text{C-F}} = 241.1$  Hz), 155.9, 140.5 (d,  $^4J_{\text{C-F}} = 2.8$  Hz), 139.5, 137.6, 130.2, 128.5 (d,  $^3J_{\text{C-F}} = 7.9$  Hz), 128.3, 127.6, 127.4, 126.4, 124.1, 115.0 (d,  $^2J_{\text{C-F}} = 20.9$  Hz), 112.0, 111.2, 110.9, 109.5, 99.9, 65.0, 55.1, 47.3, 40.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): -115.8; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{25}\text{H}_{23}\text{FN}_3\text{O}_2$  416.1769, found 416.1765.

**Benzyl ((7R, 9R)-7-(4-bromophenyl)-6, 7, 8, 9-tetrahydro-3H-pyrrolo[3, 2-f]quinolin-9-yl)**

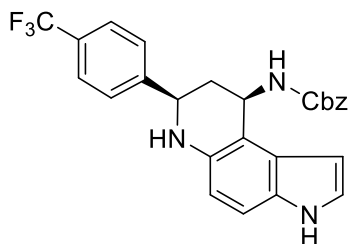
**carbamate (4ac):** The product was obtained as a white solid (33.3 mg, 70% yield) via flash



chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 92% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 14.657$  min,  $t_{\text{major}} = 15.777$  min;  $[\alpha]_{\text{D}}^{25} = +30.4$  ( $c = 0.625$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.72 (br s, 1H), 7.56 (d,  $J = 8.0$

Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.39-7.31 (m, 5H), 7.11 (t,  $J = 2.4$  Hz, 1H), 7.08 (d,  $J = 8.8$  Hz, 1H), 6.54 (d,  $J = 8.4$  Hz, 1H), 6.12 (s, 1H), 5.41 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.2$  Hz, 1H), 5.13 (d,  $J = 12.4$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.96 (br s, 1H), 4.37 (d,  $J = 11.2$  Hz, 1H), 2.21 (d,  $J = 11.6, 8.0$  Hz, 1H), 1.95 (q,  $J = 10.4$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 143.9, 139.4, 137.6, 131.2, 130.2, 128.9, 128.3, 127.7, 127.6, 127.4, 126.4, 124.2, 119.9, 112.1, 111.2, 99.9, 65.0, 64.9, 55.2, 47.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{25}\text{H}_{23}\text{BrN}_3\text{O}_2$  476.0968, found 476.0964.

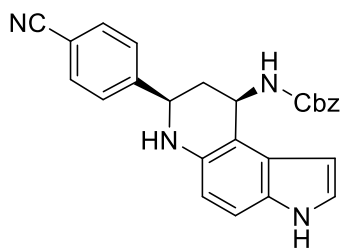
**Benzyl ((7*R*, 9*R*)-7-(4-(trifluoromethyl) phenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]**



**quinolin-9-yl)carbamate (4ad):** The product was obtained as a white solid (30.7 mg, 66% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 95% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30),

1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 13.047$  min,  $t_{\text{major}} = 14.953$  min;  $[\alpha]_{\text{D}}^{25} = +45.7$  ( $c = 0.388$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 7.73 (d,  $J = 8.4$  Hz, 2H), 7.70 (d,  $J = 8.0$  Hz, 2H), 7.38-7.30 (m, 5H), 7.11 (s, 1H), 7.10 (d,  $J = 8.8$  Hz, 2H), 6.55 (d,  $J = 8.8$  Hz, 1H), 6.15 (s, 1H), 5.50 (br s, 1H), 5.29 (dd,  $J = 16.8, 9.2$  Hz, 1H), 5.13 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.49 (d,  $J = 10.8$  Hz, 1H), 2.26 (dd,  $J = 11.6, 6.0$  Hz, 1H), 1.99 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 149.2, 137.5, 130.3, 128.30, 128.28, 127.7, 127.6, 127.5, 127.4, 126.4, 125.2 (q,  $^3J_{\text{C-F}} = 3.8$  Hz), 124.4 (q,  $^1J_{\text{C-F}} = 270.2$  Hz), 124.2, 112.1, 111.3, 99.9, 65.0, 64.9, 55.4, 47.2;  $^{19}\text{F NMR}$  (376 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): -61.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{26}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_2$  466.1737, found 466.1730.

**Benzyl ((7*R*, 9*R*)-7-(4-cyanophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate (4ae):** The product was obtained as a yellow solid (23.2 mg, 55% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 96% ee was determined



by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min,

UV 254 nm,  $t_{\text{major}} = 22.640$  min,  $t_{\text{minor}} = 26.497$  min;  $[\alpha]_{\text{D}}^{25} = +67.3$

( $c = 0.365$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm):

10.73 (br s, 1H), 7.83 (d,  $J = 8.4$  Hz, 2H), 7.68 (d,  $J = 8.4$  Hz, 2H),

7.39-7.30 (m, 5H), 7.12 (t,  $J = 2.8$  Hz, 1H), 7.09 (d,  $J = 9.6$  Hz,

1H), 6.54 (d,  $J = 8.6$  Hz, 1H), 6.13 (s, 1H), 5.53 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.6$  Hz, 1H), 5.12 (d,

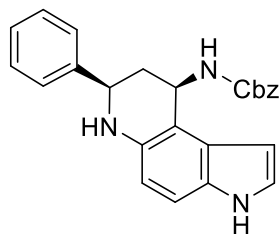
$J = 12.8$  Hz, 1H), 5.05 (d,  $J = 12.8$  Hz, 1H), 4.49 (d,  $J = 10.8$  Hz, 1H), 2.23 (dd,  $J = 12.0, 7.2$  Hz,

1H), 1.98 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 150.3, 137.5, 132.3,

128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 127.3, 126.4, 124.3, 119.0, 112.0, 111.3, 109.7, 99.8, 65.0,

55.3, 47.1, 31.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{NaO}_2$  445.1635, found 445.1628.

#### Benzyl ((7*R*, 9*R*)-7-phenyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate



**(4af):** The product was obtained as a white solid (31.3 mg, 79% yield)

via flash chromatography on a silica gel (petroleum ether/ethyl acetate

= 3:1, v/v). 94% ee was determined by HPLC on IE column, hexane/*i*-

propanol (85/15), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 23.163$  min,  $t_{\text{major}} =$

28.497 min;  $[\alpha]_{\text{D}}^{25} = +39.5$  ( $c = 0.622$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.71 (br

s, 1H), 7.48 (d,  $J = 7.6$  Hz, 2H), 7.39-7.36 (m, 6H), 7.33-7.27 (m, 2H), 7.11 (t,  $J = 2.8$  Hz, 1H), 7.09

(d,  $J = 8.8$  Hz, 1H), 6.56 (d,  $J = 8.4$  Hz, 1H), 6.16 (s, 1H), 5.37 (br s, 1H), 5.29 (dd,  $J = 16.8, 9.6$

Hz, 1H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.37 (d,  $J = 11.2$  Hz, 1H), 2.23 (dd,  $J$

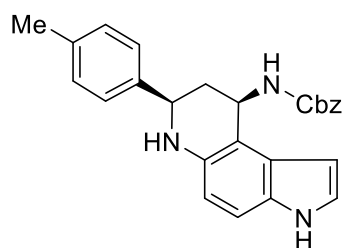
= 11.2, 6.4 Hz, 1H), 2.01 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 156.0,

144.4, 139.7, 137.6, 130.2, 128.3, 127.7, 127.6, 127.4, 126.7, 127.1, 126.7, 124.1, 112.1, 111.2,

110.8, 99.9, 65.0, 64.9, 56.0, 47.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{NaO}_2$  445.1635,

found 445.1628.

#### Benzyl ((7*R*, 9*R*)-7-(4-tolyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate



**(4ag):** The product was obtained as a white solid (37.0 mg, 90%

yield) via flash chromatography on a silica gel (petroleum

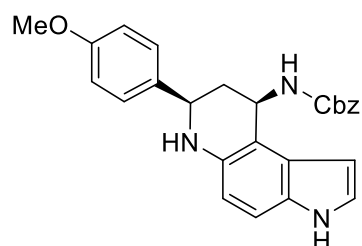
ether/ethyl acetate = 3:1, v/v). 94% ee was determined by HPLC

on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 24.563$  min,  $t_{\text{major}} = 31.300$  min;  $[\alpha]_{\text{D}}^{25} = +42.5$  ( $c = 0.741$ ,

CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 10.71 (br s, 1H), 7.37-7.31 (m, 7H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.11 (s, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 6.14 (s, 1H), 5.30-5.24 (m, 2H), 5.14 (d, *J* = 12.8 Hz, 1H), 5.07 (d, *J* = 12.8 Hz, 1H), 4.98 (br s, 1H), 4.32 (d, *J* = 11.2 Hz, 1H), 2.31 (s, 3H), 2.20 (dd, *J* = 12.0, 7.6 Hz, 1H), 1.99 (q, *J* = 11.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm): 156.0, 141.3, 137.6, 136.1, 130.2, 128.8, 128.33, 128.31, 127.7, 127.6, 127.4, 126.6, 126.5, 124.1, 112.1, 111.2, 99.9, 65.0, 64.9, 55.9, 47.4, 20.7; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub> 412.2020, found 412.2017.

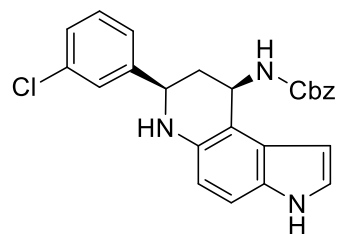
**Benzyl ((7*R*, 9*R*)-7-(4-methoxyphenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4ah):** The product was obtained as a white solid (36.0 mg, 84% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 99% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm, *t*<sub>minor</sub> = 15.477 min, *t*<sub>major</sub> = 23.837 min;

[α]<sub>D</sub><sup>25</sup> = +57.4 (*c* = 0.734, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 10.69 (br s, 1H), 7.39-7.36 (m, 7H), 7.10 (t, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.10 (s, 1H), 5.30-5.24 (m, 2H), 5.15 (d, *J* = 12.8 Hz, 1H), 5.07 (d, *J* = 12.8 Hz, 1H), 4.31 (d, *J* = 11.2 Hz, 1H), 3.70 (s, 3H), 2.19 (dd, *J* = 11.6, 8.0 Hz, 1H), 1.99 (q, *J* = 11.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm): 158.4, 155.9, 139.7, 137.6, 136.3, 130.1, 128.3, 127.7, 127.6, 127.4, 126.5, 124.1, 113.7, 112.1, 111.1, 109.5, 99.9, 65.0, 55.3, 55.1, 47.4, 40.8; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd. for C<sub>26</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub> 428.1969, found 428.1966.

**Benzyl ((7*R*, 9*R*)-7-(3-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3,2-*f*]quinolin-9-yl)**

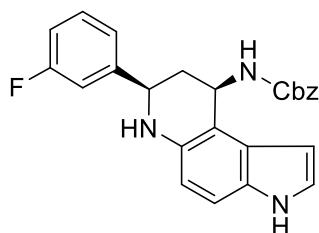


**carbamate (4ai):** The product was obtained as a white solid (37.5 mg, 87% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 94% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,

*t*<sub>minor</sub> = 21.193 min, *t*<sub>major</sub> = 23.870 min; [α]<sub>D</sub><sup>25</sup> = +40.3 (*c* = 0.561, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 10.73 (br s, 1H), 7.53 (s, 1H), 7.45-7.31 (m, 8H), 7.11 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 6.13 (s, 1H), 5.46 (br s, 1H), 5.27 (dd, *J* = 16.4, 9.2 Hz, 1H), 5.14 (d, *J* = 12.8 Hz, 1H), 5.06 (d, *J* = 12.8 Hz, 1H), 4.97 (br s, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 2.24 (dd,

$J = 11.2, 6.8$  Hz, 1H), 1.95 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.6, 155.9, 147.0, 139.4, 137.6, 137.4, 133.0, 130.2, 128.3, 127.7, 127.6, 127.4, 127.0, 126.5, 125.4, 124.2, 112.1, 111.2, 110.9, 99.9, 65.0, 64.9, 55.3, 47.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{ClN}_3\text{NaO}_2$  454.1293, found 454.1289.

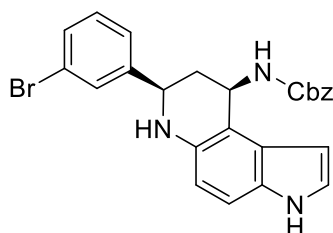
**Benzyl ((7*R*, 9*R*)-7-(3-fluorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4aj):** The product was obtained as a white solid (37.4 mg, 93% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 99% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,

$t_{\text{major}} = 10.907$  min,  $t_{\text{minor}} = 13.667$  min;  $[\alpha]_{\text{D}}^{25} = +38.5$  ( $c = 0.553$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.72 (br s, 1H), 7.44-7.27 (m, 9H), 7.11 (s, 1H), 7.08 (d,  $J = 8.4$  Hz, 1H), 6.55 (d,  $J = 8.4$  Hz, 1H), 6.14 (s, 1H), 5.44 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.2$  Hz, 1H), 5.13 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.98 (br s, 1H), 4.41 (d,  $J = 11.2$  Hz, 1H), 2.25 (dd,  $J = 11.6, 6.8$  Hz, 1H), 1.96 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 162.3 (d,  $^1J_{\text{C-F}} = 241.7$  Hz), 155.9, 147.5 (d,  $^3J_{\text{C-F}} = 7.0$  Hz), 139.4, 137.6, 130.3, 130.2 (d,  $^4J_{\text{C-F}} = 3.7$  Hz), 128.3, 127.7, 127.6, 127.4, 126.4, 124.2, 122.7 (d,  $^4J_{\text{C-F}} = 2.4$  Hz), 113.7 (d,  $^2J_{\text{C-F}} = 20.2$  Hz), 113.3 (d,  $^2J_{\text{C-F}} = 21.6$  Hz), 112.1, 111.2, 110.9, 99.9, 65.0, 64.9, 55.3, 47.2;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $D_6$ )  $\delta$  (ppm): -113.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{FN}_3\text{NaO}_2$  438.1588, found 438.1587.

**Benzyl ((7*R*, 9*R*)-7-(3-bromophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**

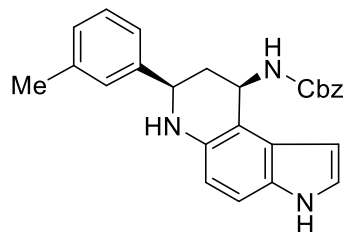


**carbamate (4ak):** The product was obtained as a white solid (40.4 mg, 85% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 94% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 13.657$  min,  $t_{\text{major}} = 15.750$  min;  $[\alpha]_{\text{D}}^{25} = +40.3$  ( $c = 0.614$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.67 (s, 1H), 7.46 (d,  $J = 8.0$  Hz, 1H), 7.37-7.30 (m, 7H), 7.10 (t,  $J = 2.4$  Hz, 1H), 7.08 (d,  $J = 8.8$  Hz, 1H), 6.52 (d,  $J = 8.8$  Hz, 1H), 6.14 (t,  $J = 2.4$  Hz, 1H), 5.45 (br s, 1H), 5.26 (dd,  $J = 17.2, 10.0$  Hz, 1H), 5.14 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.95 (br s, 1H), 4.39 (d,  $J = 11.8$  Hz, 1H), 2.23 (dd,  $J = 12.4, 7.6$  Hz, 1H), 1.95 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 155.9, 147.3, 139.3, 137.6, 130.5, 130.2, 129.9, 129.3,

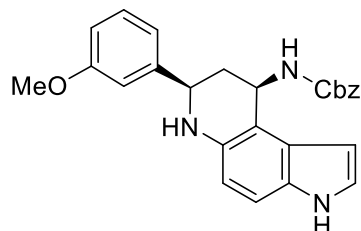
128.3, 127.7, 127.6, 127.4, 126.4, 125.8, 124.2, 121.6, 112.0, 111.2, 110.9, 99.9, 65.0, 64.9, 55.2, 47.2; HRMS (ESI) m/z:  $[M+Na]^+$  calcd. for  $C_{25}H_{22}BrN_3NaO_2$  498.0788, found 498.0790.

**Benzyl ((7*R*, 9*R*)-7-(3-tolyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*] quinolin-9-yl)carbamate**



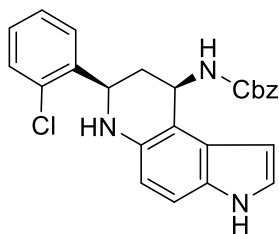
**(4al):** The product was obtained as a white solid (35.3 mg, 66% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 93% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 23.093$  min,  $t_{\text{major}} = 27.207$  min;  $[\alpha]_D^{25} = +40.6$  ( $c = 0.758$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.40-7.36 (m, 5H), 7.33-7.30 (m, 2H), 7.26 (d,  $J = 4.4$  Hz, 2H), 7.11 (t,  $J = 3.2$  Hz, 1H), 7.08 (d,  $J = 8.8$  Hz, 1H), 6.56 (d,  $J = 8.4$  Hz, 1H), 6.16 (s, 1H), 5.32-5.25 (m, 2H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.08 (d,  $J = 12.8$  Hz, 1H), 4.99 (br s, 1H), 4.33 (d,  $J = 11.2$  Hz, 1H), 2.33 (s, 3H), 2.22 (dd,  $J = 11.6, 8.0$  Hz, 1H), 2.00 (q,  $J = 11.6$  Hz, 1H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.0, 144.3, 139.7, 137.6, 137.3, 130.2, 128.3, 128.2, 127.7, 127.6, 127.4, 127.3, 126.5, 124.1, 123.8, 112.1, 111.2, 110.9, 99.9, 65.0, 64.9, 56.0, 47.5, 21.1; HRMS (ESI) m/z:  $[M+Na]^+$  calcd. for  $C_{26}H_{25}N_3NaO_2$  434.1839, found 434.1841.

**Benzyl ((7*R*, 9*R*)-7-(3-methoxyphenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate (4am):**



The product was obtained as a white solid (32.0 mg, 75% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 91% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 16.600$  min,  $t_{\text{major}} = 26.930$  min;  $[\alpha]_D^{25} = +38.3$  ( $c = 0.592$ ,  $CHCl_3$ );  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.70 (br s, 1H), 7.36-7.26 (m, 6H), 7.10-7.04 (m, 4H), 6.85 (d,  $J = 8.0$  Hz, 1H), 6.55 (d,  $J = 8.4$  Hz, 1H), 6.13 (s, 1H), 5.35 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.6$  Hz, 1H), 5.17 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.35 (d,  $J = 11.2$  Hz, 1H), 3.77 (s, 3H), 2.26 (dd,  $J = 11.6, 6.4$  Hz, 1H), 1.98 (q,  $J = 11.6$  Hz, 1H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 159.3, 156.0, 146.1, 139.6, 137.6, 130.2, 129.4, 128.4, 128.3, 127.6, 127.5, 126.5, 124.1, 118.8, 112.6, 112.15, 112.10, 111.2, 99.9, 65.0, 55.9, 55.0, 47.4, 40.7; HRMS (ESI) m/z:  $[M+Na]^+$  calcd. for  $C_{26}H_{25}N_3NaO_3$  450.1788, found 450.1787.

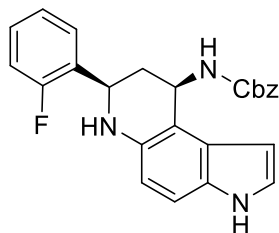
**Benzyl ((7*R*, 9*R*)-7-(2-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4an):** The product was obtained as a white solid (35.8 mg, 83% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 94% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 27.987$  min,  $t_{\text{major}} = 31.920$  min;  $[\alpha]_{\text{D}}^{25} = +46.1$  ( $c = 0.647$ ,  $\text{CHCl}_3$ );  $^1\text{H}$

NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.75 (br s, 1H), 7.73 (d,  $J = 7.6$  Hz, 1H), 7.47 (d,  $J = 8.0$  Hz, 1H), 7.42-7.30 (m, 7H), 7.13-7.09 (m, 2H), 6.56 (d,  $J = 8.4$  Hz, 1H), 6.12 (s, 1H), 5.45 (br s, 1H), 5.26 (dd,  $J = 16.4, 9.2$  Hz, 1H), 5.13 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.71 (d,  $J = 10.8$  Hz, 1H), 2.31 (dd,  $J = 12.0, 6.4$  Hz, 1H), 1.90 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 141.1, 139.5, 137.6, 131.5, 130.2, 129.3, 128.6, 128.3, 128.1, 127.6, 127.5, 127.4, 126.5, 124.3, 112.1, 111.4, 110.8, 99.8, 65.0, 52.4, 47.2, 38.5; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{25}\text{H}_{23}\text{ClN}_3\text{O}_2$  432.1473, found 432.1471.

**Benzyl ((7R, 9R)-7-(2-fluorophenyl)-6, 7, 8, 9-tetrahydro-3H-pyrrolo[3, 2-f]quinolin-9-yl)**



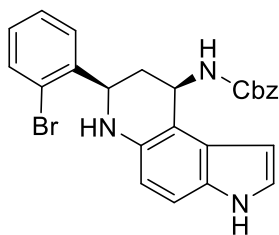
**carbamate (4ao):** The product was obtained as a white solid (29.1 mg, 70% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 92% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{major}} =$

$13.960$  min,  $t_{\text{minor}} = 17.817$  min;  $[\alpha]_{\text{D}}^{25} = +41.2$  ( $c = 0.426$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 7.64 (t,  $J = 7.2$  Hz, 1H), 7.39-7.29 (m, 6H), 7.26-7.18 (m, 2H), 7.11 (t,  $J = 2.8$  Hz, 1H), 7.10 (d,  $J = 8.8$  Hz, 1H), 6.56 (d,  $J = 8.8$  Hz, 1H), 6.14 (s, 1H), 5.41 (br s, 1H), 5.26 (dd,  $J = 16.8, 9.6$  Hz, 1H), 5.13 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.98 (br s, 1H), 4.65 (d,  $J = 10.8$  Hz, 1H), 2.27 (dd,  $J = 12.4, 6.8$  Hz, 1H), 2.03 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 159.7 (d,  $^1J_{\text{C-F}} = 242.7$  Hz), 155.9, 139.4, 137.6, 130.8 (d,  $^3J_{\text{C-F}} = 13.8$  Hz), 130.2, 128.8 (d,  $^3J_{\text{C-F}} = 8.2$  Hz), 128.3, 128.0 (d,  $^4J_{\text{C-F}} = 4.5$  Hz), 127.6, 127.4, 126.5, 124.5 (d,  $^4J_{\text{C-F}} = 3.1$  Hz), 124.2, 115.2 (d,  $^2J_{\text{C-F}} = 21.6$  Hz), 112.1, 111.3, 110.7, 99.9, 65.0, 48.8, 47.1, 38.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): -120.0; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{FN}_3\text{NaO}_2$  438.1588, found 438.1589.

**Benzyl ((7R, 9R)-7-(2-bromophenyl)-6, 7, 8, 9-tetrahydro-3H-pyrrolo[3, 2-f]quinolin-9-yl)**

**carbamate (4ap):** The product was obtained as a white solid (37.5 mg, 79% yield) via flash





chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v).

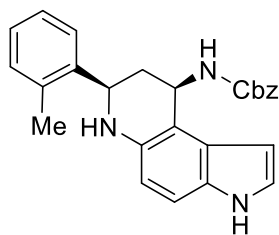
91% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 30.120$  min,  $t_{\text{major}} = 36.387$

min;  $[\alpha]_{\text{D}}^{25} = +37.4$  ( $c = 0.625$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )

$\delta$  (ppm): 10.75 (br s, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.63 (d,  $J = 8.0$  Hz,

1H), 7.44 (t,  $J = 7.6$  Hz, 1H), 7.40-7.34 (m, 5H), 7.24 (t,  $J = 7.6$  Hz, 1H), 7.12 (s, 1H), 7.10 (d,  $J = 8.8$  Hz, 1H), 6.56 (d,  $J = 8.4$  Hz, 1H), 6.15 (s, 1H), 5.47 (br s, 1H), 5.27 (dd,  $J = 16.8, 9.2$  Hz, 1H), 5.17 (d,  $J = 12.8$  Hz, 1H), 5.06 (d,  $J = 12.8$  Hz, 1H), 4.65 (d,  $J = 10.8$  Hz, 1H), 2.33 (dd,  $J = 11.2, 7.2$  Hz, 1H), 1.88 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 142.6, 139.5, 137.6, 132.6, 130.3, 129.0, 128.3, 128.1, 127.7, 127.6, 127.4, 126.5, 124.3, 122.2, 112.2, 111.4, 110.9, 99.8, 65.0, 64.9, 55.1, 47.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{25}\text{H}_{23}\text{BrN}_3\text{O}_2$  476.0968 found 476.0969.

**Benzyl ((7*R*, 9*R*)-7-(2-tolyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate**



**(4aq):** The product was obtained as a white solid (34.9 mg, 85% yield)

via flash chromatography on a silica gel (petroleum ether/ethyl acetate

= 3:1, v/v). 92% ee was determined by HPLC on IE column, hexane/*i*-

propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 19.657$  min,  $t_{\text{major}} =$

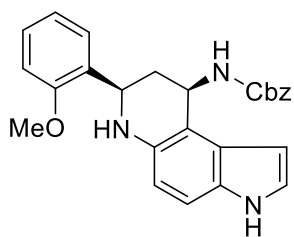
25.690 min;  $[\alpha]_{\text{D}}^{25} = +42.2$  ( $c = 0.634$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.60 (d,  $J = 7.6$  Hz, 1H), 7.42-7.31 (m, 5H), 7.25-7.18 (m, 3H), 7.12 (t,  $J = 2.8$  Hz, 1H), 7.09 (d,  $J = 8.8$  Hz), 6.57 (d,  $J = 8.4$  Hz, 1H), 6.18 (s, 1H), 5.31 (dd,  $J = 17.2, 10.0$  Hz, 1H), 5.23 (br s, 1H), 5.16 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.56 (d,  $J = 11.2$  Hz, 1H), 2.37 (s, 3H), 2.23 (dd,  $J = 11.2, 7.2$  Hz, 1H), 1.96 (q,  $J = 11.6$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 156.0, 142.1, 140.1, 137.6, 134.7, 130.22, 130.18, 128.3, 127.6, 127.4, 126.7, 126.6, 126.1, 126.0, 124.1, 112.2, 111.2, 111.0, 99.9, 65.0, 54.9, 52.2, 47.5, 18.7; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{26}\text{H}_{25}\text{N}_3\text{NaO}_2$  434.1839, found 434.1840.

**Benzyl ((7*R*, 9*R*)-7-(2-methoxyphenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**

**carbamate (4ar):** The product was obtained as a white solid (34.1 mg, 80% yield) via flash

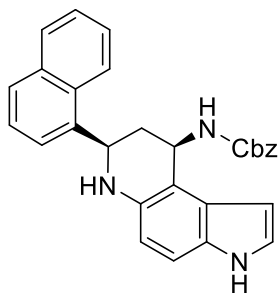
chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 94% ee was determined

by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 15.977$  min,



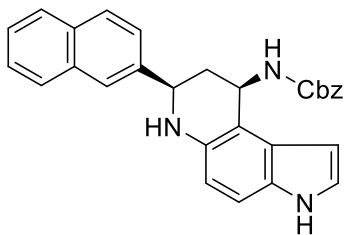
$t_{\text{major}} = 18.593$  min;  $[\alpha]_{\text{D}}^{25} = +46.7$  ( $c = 0.751$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 7.57 (d,  $J = 7.2$  Hz, 1H), 7.40-7.23 (m, 7H), 7.12 (s, 1H), 7.10 (d,  $J = 8.8$  Hz, 1H), 7.03-6.97 (m, 2H), 6.56 (d,  $J = 8.8$  Hz, 1H), 6.14 (s, 1H), 5.28-5.22 (m, 2H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.70 (d,  $J = 10.4$  Hz, 1H), 3.82 (s, 3H), 2.30 (dd,  $J = 11.6, 7.2$  Hz, 1H), 1.93 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 156.2, 155.9, 139.9, 137.6, 131.9, 130.1, 128.3, 127.9, 127.6, 127.4, 126.6, 126.5, 124.1, 120.4, 112.2, 111.2, 110.8, 110.7, 99.8, 79.2, 65.0, 55.5, 49.0, 47.2; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_3$  428.1969, found 428.1966.

**Benzyl ((7*R*, 9*R*)-7-(naphthalen-1-yl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4as):** The product was obtained as a white solid (34.0 mg, 76% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 89% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 36.037$  min,  $t_{\text{major}} = 43.743$  min;  $[\alpha]_{\text{D}}^{25} = +40.1$  ( $c = 0.591$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 8.33 (d,  $J = 8.4$  Hz, 1H), 7.97 (d,  $J = 8.0$  Hz, 1H), 7.89-7.77 (m, 2H), 7.59-7.52 (m, 3H), 7.34-7.28 (m, 5H), 7.12 (s, 1H), 7.11 (d,  $J = 9.2$  Hz, 1H), 6.60 (d,  $J = 8.4$  Hz, 1H), 6.16 (s, 1H), 5.47-5.41 (m, 2H), 5.19 (d,  $J = 10.8$  Hz, 1H), 5.11 (d,  $J = 12.8$  Hz, 1H), 5.03 (d,  $J = 12.8$  Hz, 1H), 2.41 (dd,  $J = 12.0, 6.8$  Hz, 1H), 2.10 (q,  $J = 10.8$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.9, 140.0, 139.9, 137.6, 133.5, 130.3, 130.2, 128.8, 128.3, 127.6, 127.4, 126.6, 126.1, 125.7, 125.6, 124.2, 123.1, 112.3, 111.2, 111.1, 99.9, 64.94, 64.87, 54.9, 47.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{29}\text{H}_{25}\text{N}_3\text{NaO}_2$  470.1839, found 470.1843.

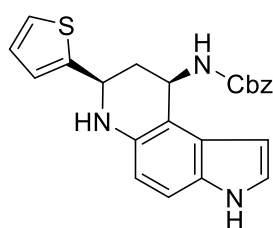
**Benzyl ((7*R*, 9*R*)-7-(naphthalen-2-yl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4at):** The product was obtained as a white solid (39.8 mg, 89% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 93% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 18.020$  min,  $t_{\text{major}} = 21.403$  min;  $[\alpha]_{\text{D}}^{25} = +43.0$  ( $c = 0.540$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.74 (br s, 1H), 8.00 (s, 1H), 7.94-7.92 (m, 3H), 7.64 (d,  $J = 8.4$

Hz, 1H), 7.54-7.48 (m, 2H), 7.43 (d,  $J = 9.2$  Hz, 1H), 7.36-7.30 (m, 4H), 7.13 (s, 1H), 7.11 (d,  $J = 8.8$  Hz, 1H), 6.61 (d,  $J = 8.8$  Hz, 1H), 6.18 (s, 1H), 5.50 (br s, 1H), 5.35 (dd,  $J = 17.2, 9.6$  Hz, 1H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.55 (d,  $J = 11.6$  Hz, 1H), 2.33 (dd,  $J = 11.6, 6.8$  Hz, 1H), 2.10 (q,  $J = 12.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.0, 142.0, 139.7, 137.6, 133.1, 132.5, 130.2, 128.33, 128.30, 127.8, 127.7, 127.6, 127.5, 127.4, 126.5, 126.1, 125.6, 125.4, 124.9, 124.2, 112.1, 111.2, 111.0, 99.9, 65.0, 64.9, 56.0, 47.5; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{29}\text{H}_{26}\text{N}_3\text{O}_2$  448.2020, found 448.2017.

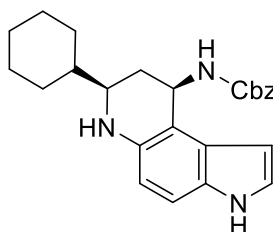
**Benzyl ((7*R*, 9*R*)-7-(thiophen-2-yl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4au):** The product was obtained as a white solid (31.0 mg, 77% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 95% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} =$

12.177 min,  $t_{\text{major}} = 14.360$  min;  $[\alpha]_{\text{D}}^{25} = +35.7$  ( $c = 0.531$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 7.43-7.31 (m, 7 Hz), 7.12 (t,  $J = 3.2$  Hz, 1H), 7.09 (d,  $J = 8.8$  Hz, 1H), 7.02-7.00 (m, 1H), 6.55 (d,  $J = 8.4$  Hz, 1H), 6.15 (s, 1H), 5.55 (br s, 1H), 5.28 (dd,  $J = 17.2, 10.0$  Hz, 1H), 5.16 (d,  $J = 12.8$  Hz, 1H), 5.08 (d,  $J = 12.8$  Hz, 1H), 4.98 (br s, 1H), 4.70 (d,  $J = 10.8$  Hz, 1H), 2.33 (dd,  $J = 12.0, 6.8$  Hz, 1H), 2.04 (q,  $J = 11.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.0, 148.5, 139.1, 137.6, 130.4, 128.4, 127.8, 127.7, 127.5, 126.6, 126.4, 124.3, 124.2, 123.8, 112.2, 111.3, 111.2, 100.0, 65.1, 64.9, 51.8, 47.1; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{23}\text{H}_{21}\text{N}_3\text{NaO}_2\text{S}$  426.1247, found 426.1245.

**Benzyl ((7*R*, 9*R*)-7-cyclohexyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo [3, 2-*f*]quinolin-9-yl)**

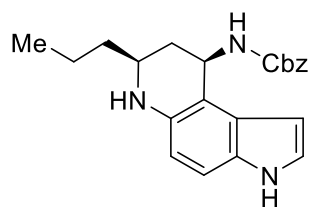


**carbamate (4av):** The product was obtained as a white solid (29.4 mg, 73% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 93% ee was determined by HPLC on IE column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} =$

18.223 min,  $t_{\text{major}} = 25.733$  min;  $[\alpha]_{\text{D}}^{25} = +44.7$  ( $c = 0.837$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.64 (br s, 1H), 7.44-7.31 (m, 5H), 7.06 (t,  $J = 2.8$  Hz, 1H), 7.02 (d,  $J = 8.4$  Hz, 2H), 6.50 (d,  $J = 8.8$  Hz, 1H), 6.09 (s, 1H), 5.17-5.06 (m, 3H), 4.73 (br s, 1H), 3.01 (dd,  $J = 12.0, 3.2$  Hz, 1H), 2.07 (dd,  $J = 11.6, 7.2$  Hz, 1H), 1.81-1.64 (m, 5H), 1.47-1.42 (m, 1H), 1.24-1.06 (m, 6H);  $^{13}\text{C}$  NMR

(100 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 156.0, 137.6, 129.9, 128.3, 127.6, 127.5, 126.5, 123.9, 112.0, 111.0, 99.8, 64.9, 56.2, 47.4, 41.7, 33.8, 28.8, 27.9, 26.3, 26.14, 26.07; HRMS (ESI)  $m/z$ : [M+Na]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>30</sub>N<sub>3</sub>O<sub>2</sub> 404.2338, found 404.2331.

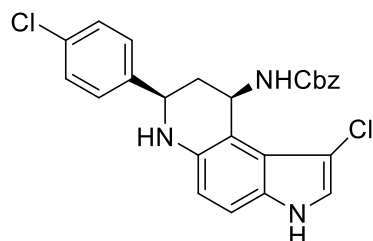
**Benzyl ((7*R*, 9*R*)-7-propyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate**



**(4aw):** The product was obtained as a white solid (22.1 mg, 61% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 90% ee was determined by HPLC on IE column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 9.587$  min,  $t_{\text{major}} =$

10.490 min;  $[\alpha]_{\text{D}}^{25} = +35.5$  ( $c = 0.494$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 10.63 (br s, 1H), 7.43-7.32 (m, 5H), 7.06 (t,  $J = 2.8$  Hz, 1H), 7.02 (d,  $J = 8.8$  Hz, 1H), 6.46 (d,  $J = 8.4$  Hz, 1H), 6.08 (s, 1H), 5.17-5.02 (m, 3H), 4.84 (br s, 1H), 3.18-3.12 (m, 1H), 2.13 (dd,  $J = 12.0, 7.6$  Hz, 1H), 1.64-1.41 (m, 5H), 0.92 (t,  $J = 6.4$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 155.9, 139.4, 137.6, 129.9, 128.3, 127.6, 127.5, 126.6, 123.9, 111.8, 111.0, 110.9, 99.8, 64.9, 51.0, 47.0, 37.9, 37.5, 18.2, 14.2; HRMS (ESI)  $m/z$ : [M+Na]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>NaO<sub>2</sub> 386.1839, found 386.1837.

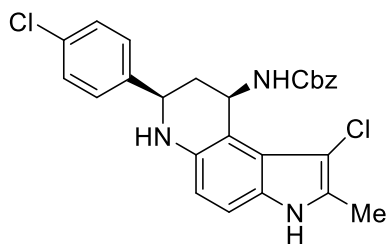
**Benzyl ((7*R*, 9*R*)-1-chloro-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate (4ax):**



The product was obtained as a yellow solid (33.9 mg, 73% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 90% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30),

1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 11.087$  min,  $t_{\text{major}} = 12.150$  min;  $[\alpha]_{\text{D}}^{25} = +23.7$  ( $c = 0.276$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 11.03 (br s, 1H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.37-7.31 (m, 4H), 7.28 (d,  $J = 7.2$  Hz, 1H), 7.24 (d,  $J = 2.4$  Hz, 1H), 7.19 (d,  $J = 7.2$  Hz, 1H), 7.15 (d,  $J = 8.8$  Hz, 1H), 6.67 (d,  $J = 8.4$  Hz, 1H), 6.26 (d,  $J = 6.4$  Hz, 1H), 5.95 (br s, 1H), 5.36 (dd,  $J = 11.6, 5.6$  Hz, 1H), 4.90 (t,  $J = 13.6$  Hz, 2H), 4.48 (s, 1H), 2.34-2.23 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 154.8, 144.2, 139.9, 137.5, 130.7, 129.2, 128.3, 128.2, 128.1, 128.0, 127.4, 127.1, 122.4, 122.3, 113.1, 107.2, 102.2, 64.5, 52.1, 43.9, 36.7; HRMS (ESI)  $m/z$ : [M+Na]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>NaO<sub>2</sub> 488.0903, found 488.0901.

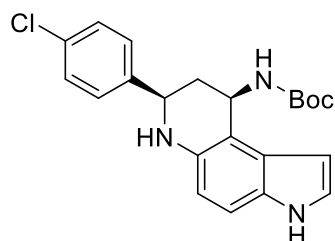
**Benzyl ((7*R*, 9*R*)-1-chloro-7-(4-chlorophenyl)-2-methyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-**



**7-quinolin-9-yl)carbamate (4ay):** The product was obtained as a light yellow solid (34.5 mg, 72% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 68% ee was determined by HPLC on AD column, hexane/*i*-propanol (80/20), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} =$

21.333 min,  $t_{\text{major}} = 23.007$  min;  $[\alpha]_{\text{D}}^{25} = +38.7$  ( $c = 0.729$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.96 (br s, 1H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.37-7.26 (m, 5H), 7.20 (d,  $J = 7.2$  Hz, 1H), 7.07 (d,  $J = 8.6$  Hz, 1H), 6.60 (d,  $J = 8.6$  Hz, 1H), 6.16 (d,  $J = 6.8$  Hz, 1H), 5.88 (br s, 1H), 5.38 (dd,  $J = 11.6, 5.6$  Hz, 1H), 4.95 (d,  $J = 12.8$  Hz, 1H), 4.88 (d,  $J = 12.8$  Hz, 1H), 4.47 (t,  $J = 5.8$  Hz, 1H), 2.37-2.24 (m, 5H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 154.8, 144.3, 139.8, 137.5, 130.9, 130.8, 128.4, 128.2, 128.1, 128.0, 127.8, 127.4, 127.1, 123.0, 112.3, 111.6, 107.0, 100.0, 64.6, 52.2, 43.9, 36.9, 11.1; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{22}\text{H}_{25}\text{N}_3\text{NaO}_2$  502.1060, found 502.1059.

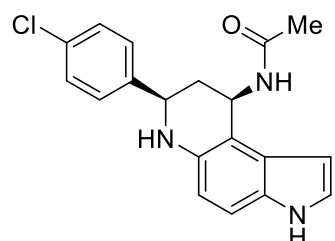
**Tert-butyl ((7*R*, 9*R*)-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo [3, 2-*f*]quinolin-9-yl)**



**carbamate (4ba):** The product was obtained as a white solid (39.3 mg, >99% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 91% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min,

UV 254 nm,  $t_{\text{major}} = 7.503$  min,  $t_{\text{minor}} = 10.833$  min;  $[\alpha]_{\text{D}}^{25} = +48.3$  ( $c = 0.647$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.69 (br s, 1H), 7.49 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.13 (s, 1H), 7.07 (d,  $J = 8.4$  Hz, 1H), 6.74 (d,  $J = 9.6$  Hz, 1H), 6.53 (d,  $J = 8.4$  Hz, 1H), 6.20 (s, 1H), 5.37 (br s, 1H), 5.19 (dd,  $J = 16.4, 9.6$  Hz, 1H), 4.37 (d,  $J = 10.4$  Hz, 1H), 2.16 (dd,  $J = 11.6, 7.6$  Hz, 1H), 1.94 (q,  $J = 11.2$  Hz, 1H), 1.42 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 155.4, 143.5, 139.3, 131.3, 130.2, 128.5, 128.2, 126.5, 124.1, 112.0, 111.3, 111.0, 99.8, 77.4, 55.1, 46.5, 40.5, 28.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{22}\text{H}_{24}\text{ClN}_3\text{NaO}_2$  420.1455, found 420.1455.

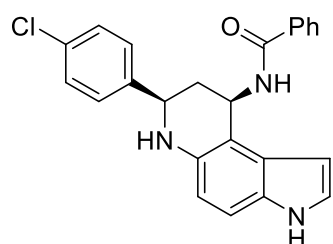
***N*-((7*R*, 9*R*)-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**acetamide (4ca):** The product was obtained as a white solid (25.4 mg, 75% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 90% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 10.267$  min,  $t_{\text{major}} = 25.233$  min;  $[\alpha]_{\text{D}}^{25} = +35.7$  ( $c = 0.483$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.73 (br s, 1H), 8.01 (d,  $J = 8.8$  Hz, 1H), 7.49 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.14 (s, 1H), 7.09 (d,  $J = 8.8$  Hz, 1H), 6.55 (d,  $J = 8.8$  Hz, 1H), 6.10 (s, 1H), 5.46 (dd,  $J = 16.8, 8.8$  Hz, 1H), 5.42 (br s, 1H), 4.34 (d,  $J = 10.8$  Hz, 1H), 2.21 (dd,  $J = 11.2, 8.0$  Hz, 1H), 1.86-1.76 (m, 4H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 168.5, 143.4, 139.6, 131.4, 130.1, 128.5, 128.2, 126.5, 124.3, 112.0, 111.2, 110.7, 99.7, 55.0, 44.6, 39.9, 22.6; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{19}\text{ClN}_3\text{O}$  340.1217, found 340.1207.

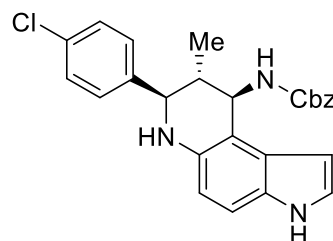
***N*-((7*R*, 9*R*)-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**benzamide (4da):** The product was obtained as a white solid (21.3 mg, 53% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v). 92% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,

$t_{\text{minor}} = 15.350$  min,  $t_{\text{major}} = 18.283$  min;  $[\alpha]_{\text{D}}^{25} = +27.4$  ( $c = 0.158$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.72 (br s, 1H), 8.48 (d,  $J = 8.8$  Hz, 1H), 7.88 (d,  $J = 7.2$  Hz, 2H), 7.81 (d,  $J = 7.2$  Hz, 2H), 7.47 (d,  $J = 8.4$  Hz, 2H), 7.48-7.38 (m, 5H), 7.11 (d,  $J = 8.4$  Hz, 1H), 7.08 (s, 1H), 6.59 (d,  $J = 8.4$  Hz, 1H), 6.07 (s, 1H), 5.78 (dd,  $J = 16.4, 9.2$  Hz, 1H), 5.49 (br s, 1H), 4.46 (d,  $J = 10.8$  Hz, 1H), 2.27 (dd,  $J = 12.0, 7.2$  Hz, 1H), 2.09 (q,  $J = 10.8$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 165.6, 143.5, 139.5, 134.6, 131.4, 130.9, 128.6, 128.3, 128.2, 128.1, 127.4, 127.3, 126.6, 124.4, 112.0, 111.3, 110.8, 99.5, 54.9, 45.2, 22.7; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{24}\text{H}_{21}\text{ClN}_3\text{O}$  402.1373, found 402.1364.

**Benzyl ((7*R*, 8*S*, 9*R*)-7-(4-chlorophenyl)-8-methyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**

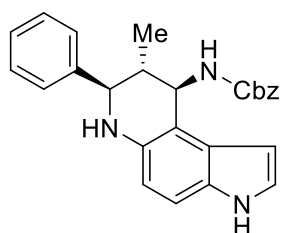


**carbamate (4ea):** The product was obtained as a white solid (39.6 mg, 89% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 4:1, v/v). 90% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30),

1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 13.810$  min,  $t_{\text{major}} = 19.760$  min;  $[\alpha]_{\text{D}}^{25} = +45.7$  ( $c = 0.627$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.71 (br s, 1H), 7.44-7.43 (m, 3H), 7.37-7.29 (m, 6H), 7.10 (s, 1H), 7.07 (d,  $J = 8.8$  Hz, 1H), 6.52 (d,  $J = 8.4$  Hz, 1H), 6.11 (s, 1H), 5.37 (br s, 1H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.09 (d,  $J = 12.8$  Hz, 1H), 4.82 (t,  $J = 9.6$  Hz, 1H), 3.98 (d,  $J = 10.0$  Hz, 1H),

2.05 (dd,  $J = 15.2, 8.4$  Hz, 1H), 0.69 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.7, 141.9, 137.7, 131.7, 130.3, 129.7, 128.33, 128.30, 128.2, 127.71, 127.70, 127.6, 127.4, 126.6, 124.2, 111.6, 111.1, 99.7, 79.2, 65.0, 61.9, 53.7, 15.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{26}\text{H}_{25}\text{ClN}_3\text{O}_2$  446.1630, found 446.1625.

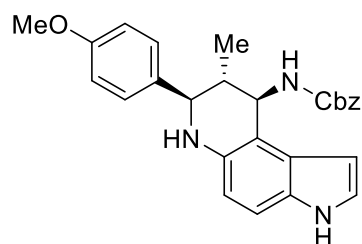
**Benzyl ((7*R*, 8*S*, 9*R*)-8-methyl-7-phenyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)**



**carbamate (4ef):** The product was obtained as a white solid (33.7 mg, 82% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 4:1, v/v). 92% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} =$

12.097 min,  $t_{\text{major}} = 15.510$  min;  $[\alpha]_{\text{D}}^{25} = +37.4$  ( $c = 0.735$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.67 (br s, 1H), 7.42-7.30 (m, 9H), 7.08 (s, 1H), 7.05(d,  $J = 8.4$  Hz, 1H), 6.52 (d,  $J = 8.4$  Hz, 1H), 6.10 (s, 1H), 5.32 (br s, 1H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.09 (d,  $J = 12.8$  Hz, 1H), 4.97 (br s, 1H), 4.82 (t,  $J = 9.6$  Hz, 1H), 3.94 (d,  $J = 10.0$  Hz, 1H), 2.08 (dd,  $J = 16.4, 9.6$  Hz, 1H), 0.68 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 156.7, 156.6, 142.8, 139.7, 137.7, 137.4, 130.2, 129.1, 128.32, 128.29, 128.2, 127.8, 127.7, 127.6, 127.4, 126.6, 124.1, 111.6, 111.2, 111.0, 99.7, 64.9, 62.7, 53.8, 42.5, 15.5; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_2$  412.2025, found 412.2018.

**Benzyl ((7*R*, 8*S*, 9*R*)-7-(4-methoxyphenyl)- 8-methyl-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl) carbamate (4eh):**

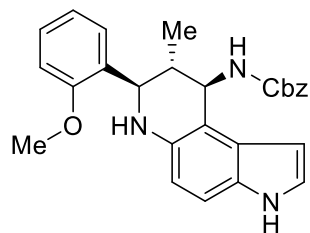


The product was obtained as a white solid (33.1 mg, 75% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 98% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30),

1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 14.543$  min,  $t_{\text{major}} = 18.040$  min;  $[\alpha]_{\text{D}}^{25} = +51.7$  ( $c = 0.672$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 10.67 (br s, 1H), 7.38-7.30 (m, 8H), 7.08 (s, 1H), 7.04 (d,  $J = 8.4$  Hz, 1H), 6.94 (d,  $J = 8.4$  Hz, 2H), 6.51 (d,  $J = 8.8$  Hz, 1H), 6.10 (s, 1H), 5.21 (br s, 1H), 5.15 (d,  $J = 12.8$  Hz, 1H), 5.09 (d,  $J = 12.8$  Hz, 1H), 4.80 (t,  $J = 9.6$  Hz, 1H), 3.88 (d,  $J = 10.4$  Hz, 1H), 3.76 (s, 3H), 2.03 (dd,  $J = 16.4, 9.6$  Hz, 1H), 0.67 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 158.5, 156.7, 139.7, 137.7, 134.8, 130.1, 128.8, 128.3, 127.6, 127.3, 126.6, 124.0, 113.6, 111.6, 111.2, 111.0, 99.7, 64.9, 62.1, 55.1, 53.9, 42.6, 15.5; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$

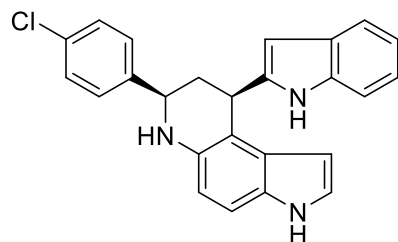
calcd. for C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>3</sub> 442.2125, found 442.2121.

**Benzyl ((7*R*, 8*S*, 9*R*)-8-methyl-7-(2-tolyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate (4er):**



The product was obtained as a white solid (29.5 mg, 67% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 90% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 27.313$  min,  $t_{\text{major}} = 31.087$  min;  $[\alpha]_{\text{D}}^{25} = +39.1$  ( $c = 0.359$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 10.68 (br s, 1H), 7.46 (d,  $J = 7.6$  Hz, 1H), 7.38-7.27 (m, 5H), 7.08-6.97 (m, 4H), 6.51 (d,  $J = 8.4$  Hz, 1H), 6.09 (s, 1H), 5.18 (br s, 1H), 5.12 (d,  $J = 12.8$  Hz, 1H), 5.07 (d,  $J = 12.8$  Hz, 1H), 4.78 (t,  $J = 9.2$  Hz, 1H), 4.46 (d,  $J = 9.6$  Hz, 1H), 3.79 (s, 3H), 2.11 (dd,  $J = 16.0, 8.8$  Hz, 1H), 0.73 (d,  $J = 6.8$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 157.1, 156.5, 139.8, 137.7, 130.8, 130.0, 128.30, 128.25, 128.0, 127.7, 127.6, 127.4, 127.3, 126.8, 124.0, 120.6, 111.6, 111.1, 111.0, 110.8, 99.6, 64.9, 55.5, 53.7, 42.0, 15.2; HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>28</sub>N<sub>3</sub>O<sub>3</sub> 442.2125, found 442.2121.

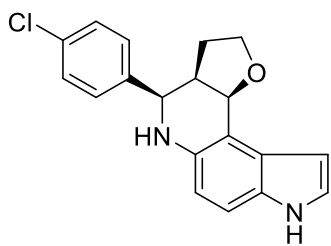
**(7*R*, 9*R*)-7-(4-chlorophenyl)-9-(1*H*-indol-2-yl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolone (4fa):**



The product was obtained as a white solid (36.6 mg, 92% yield) via flash chromatography on a silica gel (hexane /ethyl acetate = 4:1, v/v). 86% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 17.930$  min,  $t_{\text{major}} = 21.940$  min;  $[\alpha]_{\text{D}}^{25} = +43.7$  ( $c = 0.791$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 10.77 (br s, 1H), 10.60 (br s, 1H), 7.53 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 3H), 7.22 (d,  $J = 7.6$  Hz, 1H), 7.11 (d,  $J = 8.4$  Hz, 1H), 6.97-6.89 (m, 2H), 6.85 (t,  $J = 2.8$  Hz, 1H), 6.66 (d,  $J = 8.8$  Hz, 1H), 6.28 (s, 1H), 5.47 (s, 1H), 4.78 (dd,  $J = 11.2, 6.4$  Hz, 1H), 4.47 (d,  $J = 10.0$  Hz, 1H), 2.27 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 144.0, 143.7, 139.1, 136.1, 131.4, 130.1, 128.6, 128.2, 128.0, 127.4, 123.7, 119.7, 119.1, 118.3, 112.3, 111.0, 110.9, 110.6, 99.7, 98.9, 55.7, 42.3, 36.9; HRMS (ESI)  $m/z$ : [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>21</sub>ClN<sub>3</sub> 398.1419, found 398.1416.

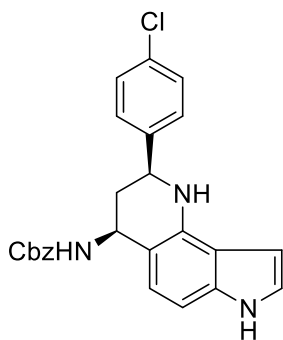
**4(3*aR*, 4*R*, 10*cR*)-4-(4-chlorophenyl)-3, 3*a*, 4, 5, 8, 10*c*-hexahydro-2*H*-furo[3, 2-*c*]pyrrolo[3, 2-*f*]quinoline (4ga):** The product was obtained as a white solid (26.9 mg, 83% yield) via flash





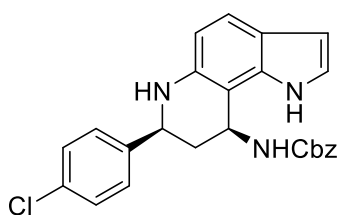
chromatography on a silica gel (petroleum ether/ethyl acetate = 4:1, v/v). 55% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{major}} = 8.597$  min,  $t_{\text{minor}} = 15.153$  min;  $[\alpha]_{\text{D}}^{25} = +33.7$  ( $c = 0.865$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.74 (br s, 1H), 8.25 (d,  $J = 8.0$  Hz, 2H), 7.80 (d,  $J = 8.0$  Hz, 2H), 7.18 (s, 1H), 7.14 (d,  $J = 8.8$  Hz, 1H), 6.59 (d,  $J = 8.4$  Hz, 1H), 6.32 (s, 1H), 5.82 (br s, 1H), 4.72 (d,  $J = 4.4$  Hz, 1H), 3.93 (dd,  $J = 14.0, 7.6$  Hz, 1H), 3.81 (d,  $J = 10.8$  Hz, 1H), 3.73 (dd,  $J = 14.4, 7.6$  Hz, 1H), 2.41-2.35 (m, 1H), 1.98-1.90 (m, 1H), 1.58-1.51 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 150.8, 147.0, 138.6, 129.8, 129.7, 128.5, 124.6, 123.3, 112.0, 111.2, 109.2, 99.4, 74.4, 64.4, 57.4, 42.9, 28.3; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{18}\text{ClN}_2\text{O}$  325.1102, found 325.1098.

**Benzyl ((2*R*, 4*R*)-2-(4-chlorophenyl)-2, 3, 4, 7-tetrahydro-1*H*-pyrrolo[2, 3-*h*]quinolin-4-yl)**



**carbamate (5a):** The product was obtained as a white solid (26.4 mg, 61% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 4:1, v/v). 86% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{major}} = 21.270$  min,  $t_{\text{minor}} = 30.780$  min;  $[\alpha]_{\text{D}}^{25} = +31.8$  ( $c = 0.613$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.00 (br s, 1H), 7.38-7.23 (m, 10H), 6.92 (s, 1H), 6.45 (d,  $J = 8.0$  Hz, 1H), 6.40 (s, 1H), 5.34 (dd,  $J = 16.4, 7.2$  Hz, 1H), 5.15-5.09 (m, 3H), 4.79 (d,  $J = 9.6$  Hz, 1H), 4.46 (dd,  $J = 8.8, 2.0$  Hz, 1H), 2.60-2.54 (m, 1H), 2.14-2.07 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 157.1, 141.6, 140.3, 136.2, 135.2, 133.3, 128.9, 128.53, 128.50, 128.3, 128.1, 127.9, 127.8, 122.3, 121.4, 109.9, 102.4, 67.0, 54.6, 44.9, 38.8; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{ClN}_3\text{NaO}_2$  454.1293, found 454.1294.

**Benzyl ((7*R*, 9*R*)-7-(4-chlorophenyl)-6, 7, 8, 9-tetrahydro-1*H*-pyrrolo[2, 3-*f*]quinolin-9-yl)**



**carbamate (5b):** The product was obtained as a white solid (36.7 mg, 85% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 7:1, v/v). 92% ee was determined by HPLC on OD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 17.823$  min,  $t_{\text{major}} = 22.043$  min;  $[\alpha]_{\text{D}}^{25} = +41.8$  ( $c = 0.865$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,

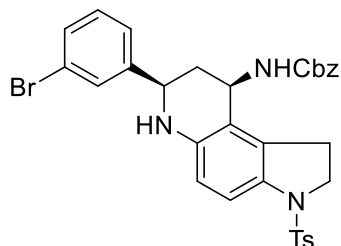
DMSO-d<sub>6</sub>)  $\delta$  (ppm): 9.72 (br s, 1H), 7.48 (d,  $J$  = 8.4 Hz, 2H), 7.42 (d,  $J$  = 8.4 Hz, 2H), 7.39-7.30 (m, 5H), 7.20 (d,  $J$  = 8.4 Hz, 1H), 6.99 (s, 1H), 6.49 (d,  $J$  = 8.4 Hz, 1H), 6.26 (s, 1H), 5.70 (br s, 1H), 5.20 (dd,  $J$  = 16.4, 8.4 Hz, 1H), 5.12 (d,  $J$  = 12.8 Hz, 1H), 5.06 (d,  $J$  = 12.8 Hz, 1H), 4.39 (d,  $J$  = 10.4 Hz, 1H), 2.31 (dd,  $J$  = 11.6, 6.4 Hz, 1H), 2.03 (q,  $J$  = 11.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 156.7, 143.1, 142.0, 137.1, 134.7, 131.5, 128.5, 128.32, 128.27, 127.72, 127.66, 122.2, 120.3, 119.8, 110.1, 103.7, 101.4, 65.5, 54.9, 46.0, 39.3; HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd. for C<sub>25</sub>H<sub>23</sub>ClN<sub>3</sub>O<sub>2</sub> 432.1473, found 432.1468.

#### 4. Procedure for the reduction of indole

To a solution of pyrroloquinolines **4ak** (47.5 mg, 0.1 mmol) in AcOH (1 mL), was added NaCNBH<sub>3</sub> (10 mg, 0.2 mmol) portionwise. The mixture was allowed to stir at rt until the reaction was complete by thin layer chromatography (TLC) analysis. Then the reaction mixture was diluted with water (1 mL) and the aqueous layer was extracted with ethyl acetate (5 mL x 3). The combined organic layer was washed with a saturated aqueous NaHCO<sub>3</sub> solution (5 mL x 2), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated in vacuum. The resulting residue was directly used in the next step without further purification.

To a stirred solution of the crude product in chloroform (2 mL), was added pyridine (9.7  $\mu$ L, 0.12 mmol) and TsCl (20.9 mg, 0.11 mmol) at room temperature. The resulting mixture was continued to stir at room temperature for 30 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was poured into water. The aqueous layer was extracted with DCM (5 mL x 3). The combined organic layers were rinsed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (petroleum ether/ ethyl acetate = 4:1, v/v) to give the desired product **6**.

**Benzyl ((7*R*, 9*R*)-7-(3-bromophenyl)-3-tosyl-2,3,6,7,8,9-hexahydro-1*H*-pyrrolo[3,2-*f*]quinolin-9-yl) carbamate (**6**):** The product was obtained as a bright yellow solid (60.6 mg, 96%



yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1, v/v). 95% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{major}}$  = 26.773 min,  $t_{\text{minor}}$  = 30.553 min;  $[\alpha]_D^{25}$  = +47.3 ( $c$  = 0.792, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 7.61-7.59 (m, 3H), 7.47 (d,  $J$  = 8.0 Hz,

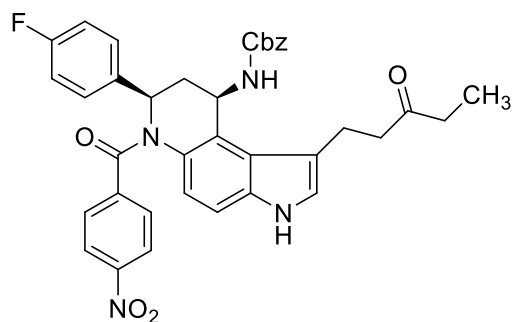
1H), 7.40-7.27 (m, 9H), 7.22-7.17 (m, 2H), 6.53 (d,  $J = 8.8$  Hz, 1H), 5.98 (br s, 1H), 5.02 (d,  $J = 12.8$  Hz, 1H), 4.96 (d,  $J = 12.8$  Hz, 1H), 4.86 (dd,  $J = 16.4, 9.6$  Hz, 1H), 4.39 (d,  $J = 10.8$  Hz, 1H), 3.82-3.76 (m, 1H), 3.59 (dd,  $J = 19.6, 9.6$  Hz, 1H), 2.68-2.59 (m, 1H), 2.50-2.42 (m, 1H), 2.32 (s, 3H), 2.06 (dd,  $J = 11.6, 6.8$  Hz, 1H), 1.91-1.82 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 155.9, 147.0, 144.3, 144.1, 137.7, 133.5, 132.6, 132.2, 131.0, 130.5, 130.2, 129.6, 128.7, 128.2, 128.1, 127.7, 126.1, 122.1, 118.8, 115.3, 114.4, 65.6, 54.7, 50.5, 47.1, 39.5, 27.3, 21.4; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{32}\text{H}_{30}\text{BrN}_3\text{NaO}_4\text{S}$  654.1033, found 654.1030.

### 5. Procedure for the protection of secondary amine and Friedel–Crafts alkylation

A round-bottom flask was charged with pyrroloquinolines **4ab** (41.5 mg, 0.1 mmol), pyridine (48.2  $\mu\text{L}$ , 0.6 mmol) and dry  $\text{CH}_2\text{Cl}_2$  (3 mL). Then the resulting solution was cooled down to 0  $^\circ\text{C}$ , and 4-nitrobenzoyl chloride (111.3 mg, 0.6 mmol) was added slowly. Stirring was continued at 0  $^\circ\text{C}$  for 30 minutes, then warmed up to room temperature and stirred for 6 hours. After completion of the reaction, the reaction was quenched with aqueous NaOH solution (3 mL, 1N) at 0  $^\circ\text{C}$ . Next, the organic layer was separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (5 mL X 3). The combined organic layers were rinsed with dilute HCl (4 mL, 1 N) and brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum and the residue was purified via column chromatography (petroleum ether/ ethyl acetate = 3:1, v/v) to afford the desired product **4ab'**.

4-Nitrobenzoyl-protected pyrroloquinolines **4ab'** (46.2 mg, 0.1 mmol) and racemic 1,1-binaphthyl-2,2-diyl hydrogenphosphate (3.4 mg, 0.01 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  in 4 mL vial. After stirring for 10 minutes, ethyl vinyl ketone (9.8  $\mu\text{L}$ , 0.12 mmol) was added. The mixture was stirred at room temperature for 24 hours. Then the reaction mixture was diluted with water and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (5 mL x 3). The combined organic layers were washed with brine, and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1, v/v) furnished the desired C3-alkylation product **7**.

**Benzyl ((7*R*, 9*R*)-7-(4-fluorophenyl)-6-(4-nitrobenzoyl)-1-(3-oxopentyl)-6, 7, 8, 9-tetrahydro-3*H*-pyrrolo[3, 2-*f*]quinolin-9-yl)carbamate (7):** The product was obtained as a bright yellow solid (40.4 mg, 76% yield) via flash chromatography on a silica gel (petroleum ether/ethyl acetate = 2:1,

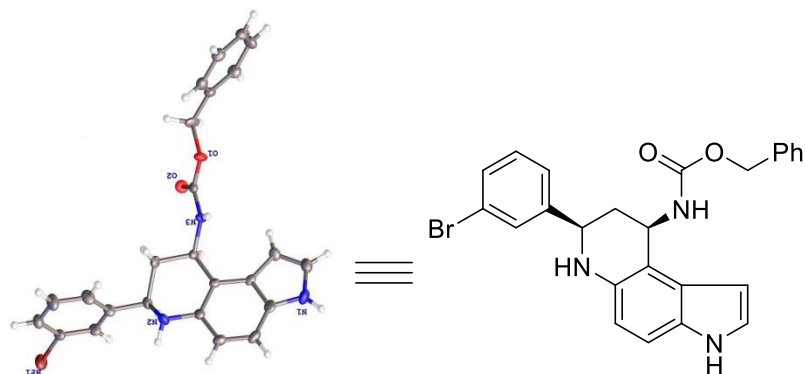


v/v). 94% ee was determined by HPLC on AD column, hexane/*i*-propanol (70/30), 1.0 mL/min, UV 254 nm,  $t_{\text{minor}} = 39.640$  min,  $t_{\text{major}} = 43.620$  min;  $[\alpha]_{\text{D}}^{25} = +47.6$  ( $c = 0.815$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.94 (br s, 1H), 8.14 (d,  $J = 8.4$  Hz, 2H), 7.67 (d,  $J = 8.0$  Hz, 2H), 7.47-7.24

(m, 8H), 7.07-7.00 (m, 2H), 6.96-6.91 (m, 2H), 5.86-5.72 (m, 2H), 5.25-5.22 (t,  $J = 7.0$  Hz, 1H), 5.03 (d,  $J = 12.8$  Hz, 1H), 4.89 (d,  $J = 12.8$  Hz, 1H), 3.04 (d,  $J = 14.0$  Hz, 1H), 2.93-2.61 (m, 5H), 2.45-2.33 (m, 2H), 0.90 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 210.4, 160.7 (d,  $^1J_{\text{C-F}} = 240.6$  Hz), 154.2, 147.9, 143.4, 137.2, 136.2, 134.3, 128.2, 128.1 (d,  $^3J_{\text{C-F}} = 8.4$  Hz), 127.6, 127.4, 124.4, 124.2, 123.4, 120.6, 119.2, 115.0, 114.8 (d,  $^2J_{\text{C-F}} = 20.7$  Hz), 111.3, 65.0, 43.9, 42.7, 39.7, 34.6, 34.1, 19.9, 7.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): -112.6; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{37}\text{H}_{33}\text{FN}_4\text{NaO}_6$  671.2276, found 671.2275.

## 6. X-ray crystallographic analysis of 4ak (CCDC 2290686)

Single crystals of  $\text{C}_{25}\text{H}_{22}\text{BrN}_3\text{O}_2$  were obtained via slow volatilization in a mixed solution of dichloromethane/*i*-Propanol. A suitable crystal was selected and measured on a New Gemini Dual-sourced diffractometer (Cu  $K\alpha$   $\lambda = 1.54184$  Å). The crystal was kept at 170 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. The ellipsoid contour percent probability level of **4ak** is 50%.



Identification code	exp_4381
Empirical formula	$\text{C}_{25}\text{H}_{22}\text{BrN}_3\text{O}_2$
Formula weight	476.36

Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	5.1550(3)
b/Å	8.0069(4)
c/Å	50.226(3)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2073.11(19)
Z	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.526
$\mu$ /mm <sup>-1</sup>	2.931
F(000)	976.0
Crystal size/mm <sup>3</sup>	0.14 × 0.12 × 0.1
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
2 $\Theta$ range for data collection/°	7.04 to 147.668
Index ranges	-5 ≤ h ≤ 6, -9 ≤ k ≤ 6, -62 ≤ l ≤ 61
Reflections collected	11527
Independent reflections	4112 [R <sub>int</sub> = 0.0427, R <sub>sigma</sub> = 0.0423]
Data/restraints/parameters	4112/0/284
Goodness-of-fit on F <sup>2</sup>	1.032
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0550, wR <sub>2</sub> = 0.1300
Final R indexes [all data]	R <sub>1</sub> = 0.0604, wR <sub>2</sub> = 0.1362
Largest diff. peak/hole / e Å <sup>-3</sup>	1.10/-0.89
Flack/Hoof parameter	-0.002(16)/0.009(9)

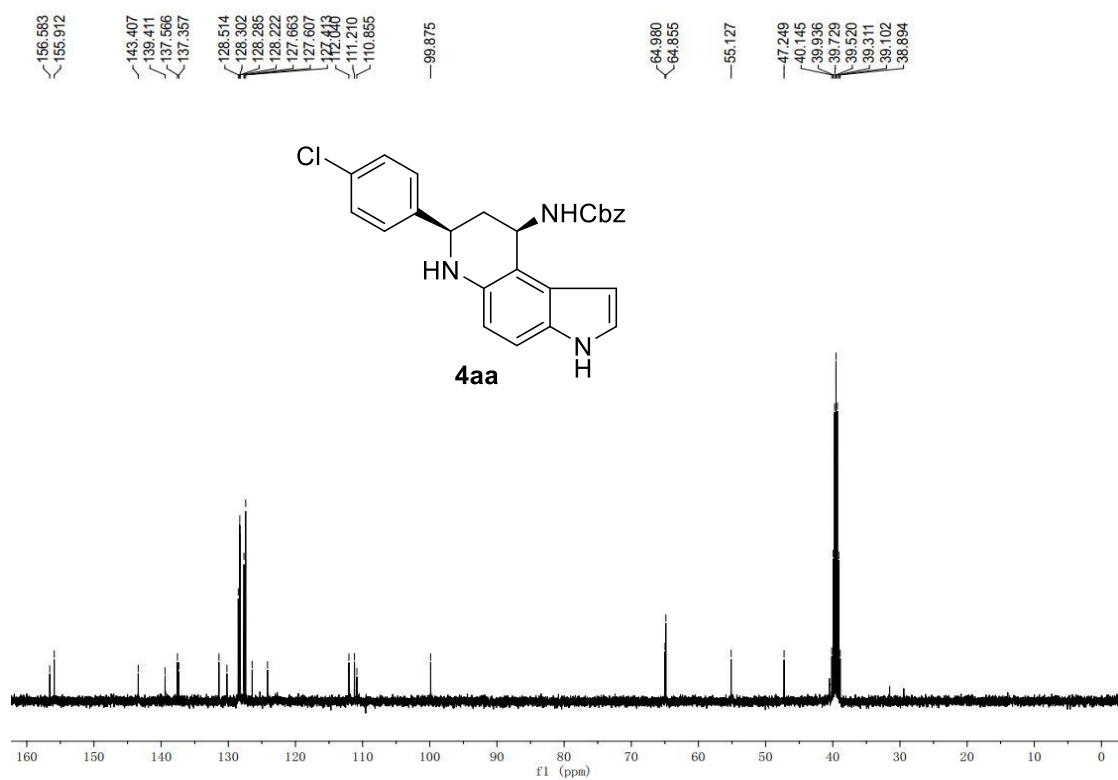
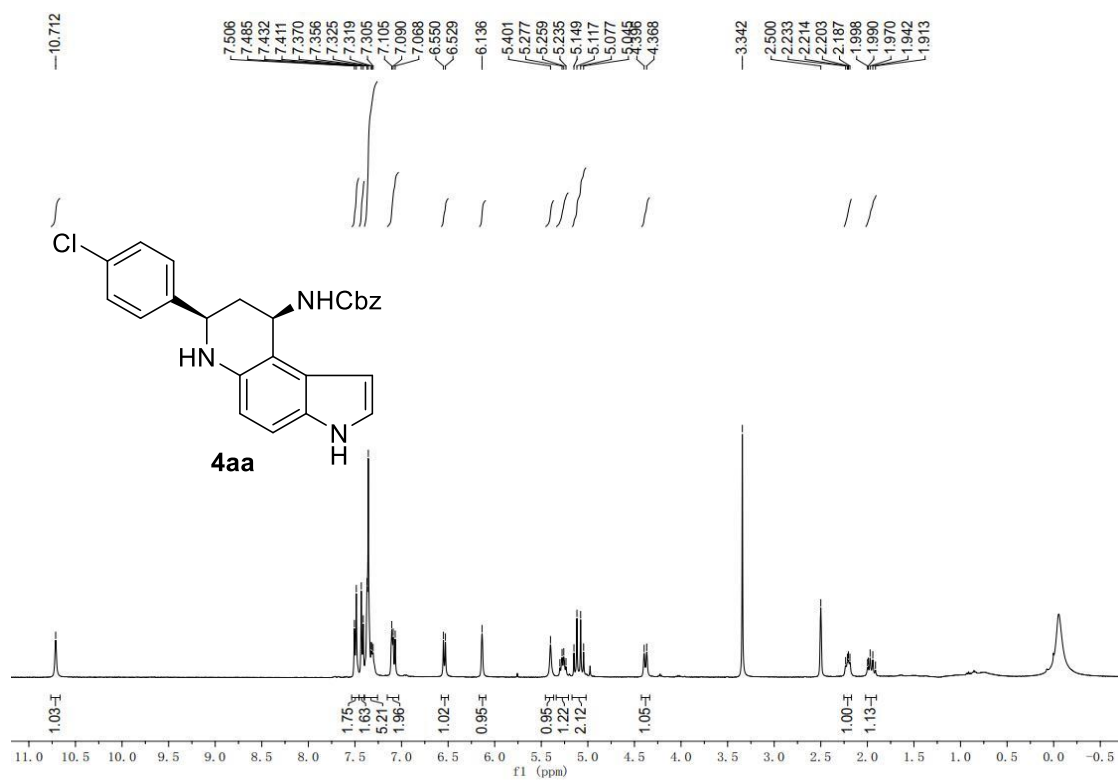
## 7. Reference

(1) (a) Wu, T. R.; Shen, L.; Chong, J. M. Asymmetric Allylboration of Aldehydes and Ketones Using

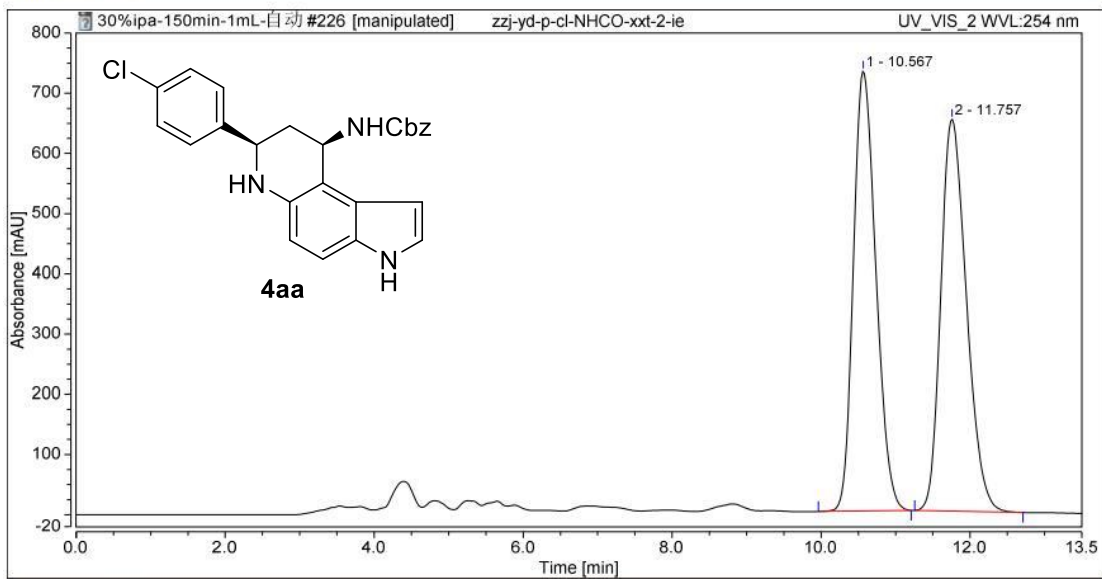
3,3'-Disubstitutedbinaphthol-Modified Boronates. *Org. Lett.* **2004**, *6*, 2701-2704. (b) Shen, K.; Liu, X.; Cai, Y.; Lin, L.; Feng, X. Facile and Efficient Enantioselective Strecker Reaction of Ketimines by Chiral Sodium Phosphate. *Chem. Eur. J.* **2009**, *15*, 6008-6014. (c) Xu, B.; Zhu, S.-F.; Xie, X.-L.; Shen, J.-J.; Zhou, Q.-L. Asymmetric N-H Insertion Reaction Cooperatively Catalyzed by Rhodium and Chiral Spiro Phosphoric Acids. *Angew. Chem. Int. Ed.* **2011**, *50*, 11483-11486. (d) Gicquiaud, J.; Abadie, B.; Dhara, K.; Berlande, M.; Hermange, P.; Sotiropoulos, J.-M.; Toullec, P. Y. Brønsted Acid-Catalyzed Enantioselective Cycloisomerization of Arylalkynes. *Chem. Eur. J.* **2020**, *26*, 16266-16271.

(2) (a) Hoang, T. T.; Smith, T. P.; Raines, R. T. A Boronic Acid Conjugate of Angiogenin that Shows ROS-Responsive Neuroprotective Activity. *Angew. Chem. Int. Ed.* **2017**, *56*, 2619-2622. (b) Carboni, A.; Dagousset, G.; Magnier, E.; Masson, G. Photoredox-Induced Three-Component Oxy-, Amino-, and Carbotrifluoromethylation of Encarbamates. *Org. Lett.* **2014**, *16*, 1240-1243.

## 8. NMR spectra and HPLC chromatograms of products



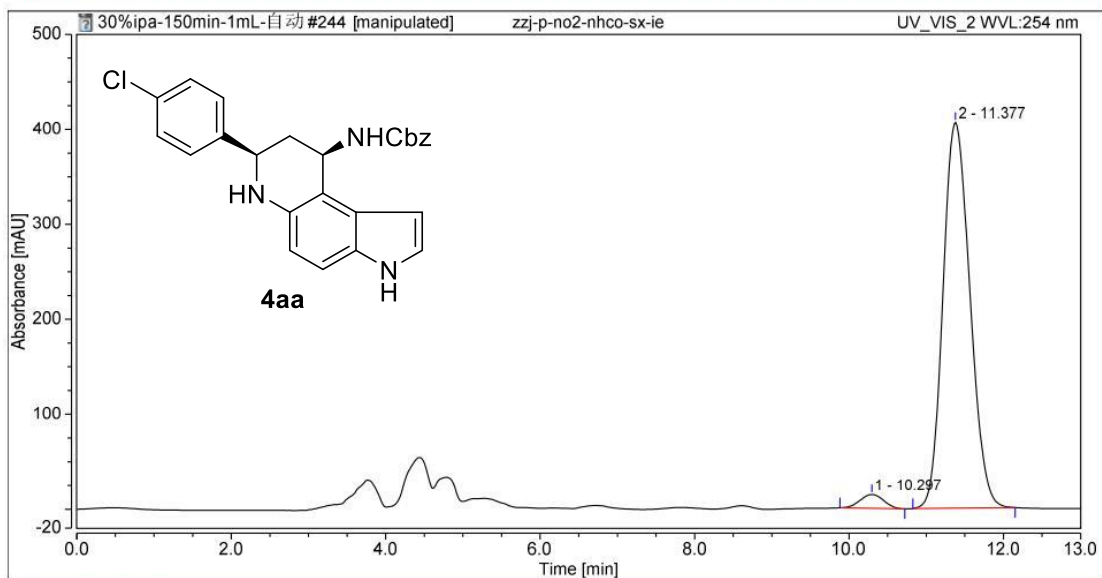
### Chromatogram



### Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.567	255.738	730.757	49.64	52.89	n.a.
2		11.757	259.439	650.827	50.36	47.11	n.a.
<b>Total:</b>			<b>515.178</b>	<b>1381.584</b>	<b>100.00</b>	<b>100.00</b>	

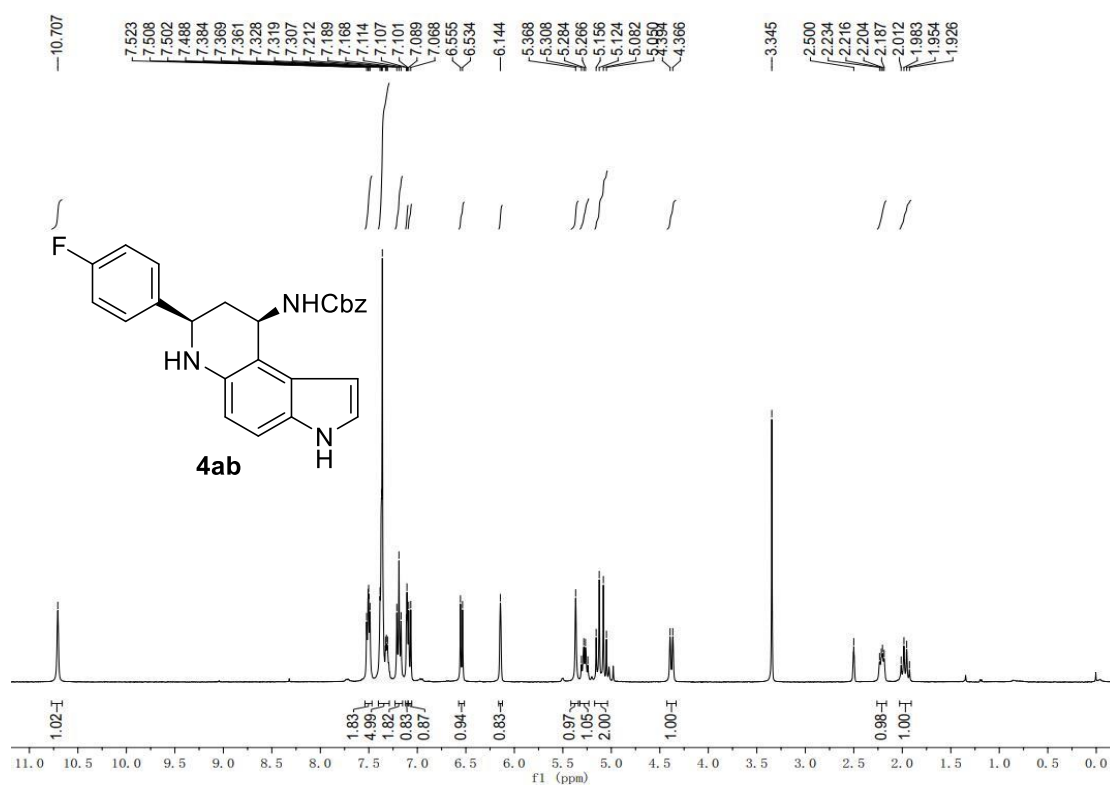
### Chromatogram



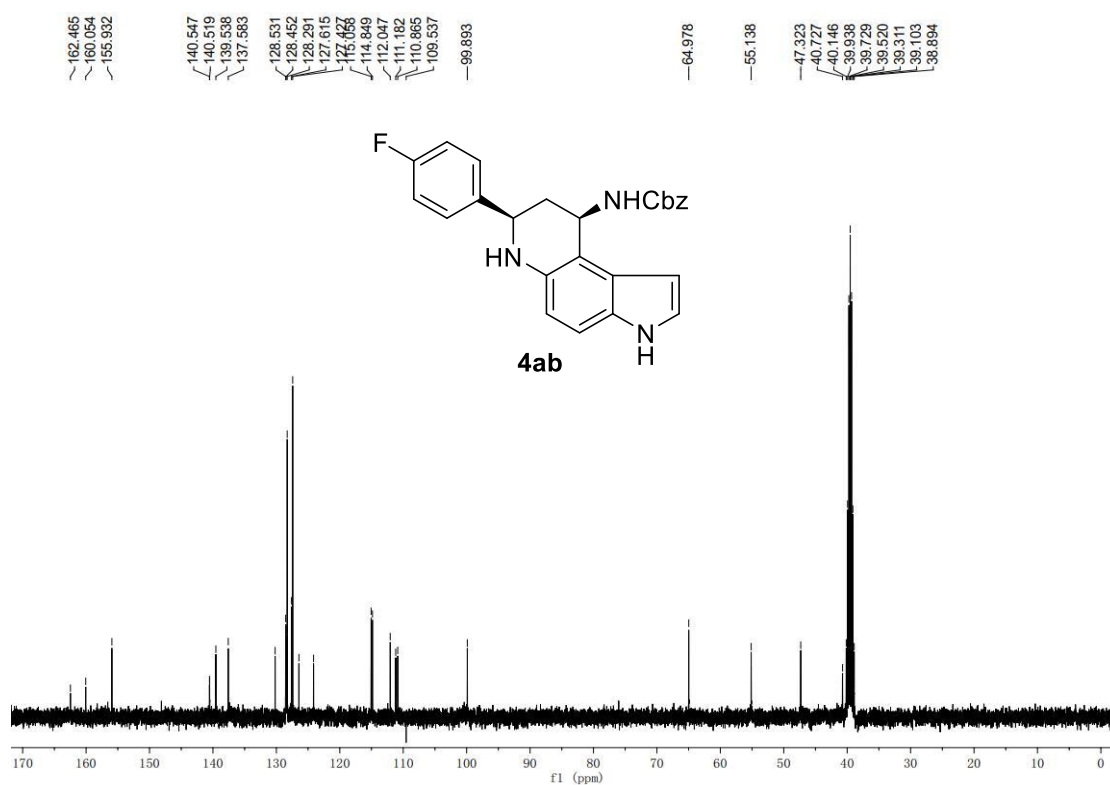
### Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.297	5.144	14.593	3.04	3.47	n.a.
2		11.377	163.918	406.154	96.96	96.53	n.a.
<b>Total:</b>			<b>169.062</b>	<b>420.747</b>	<b>100.00</b>	<b>100.00</b>	

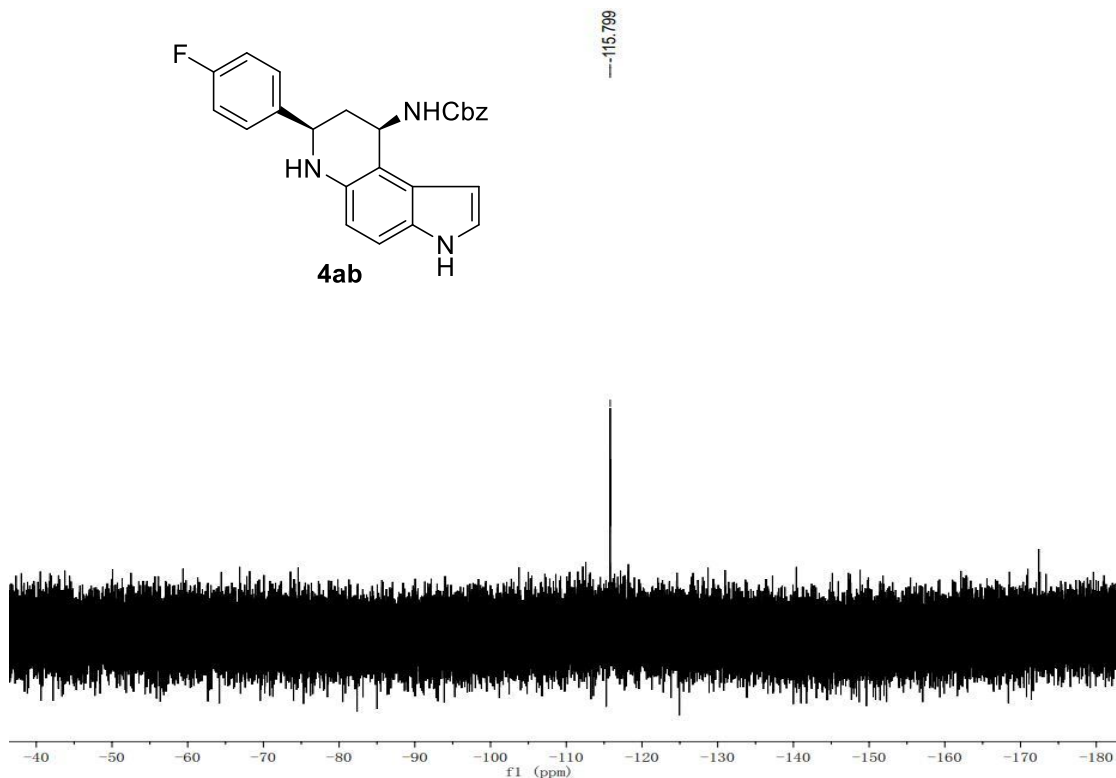
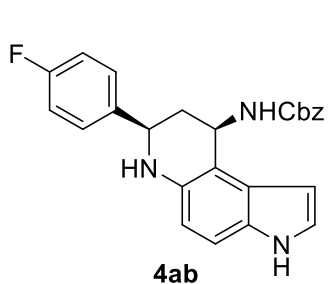




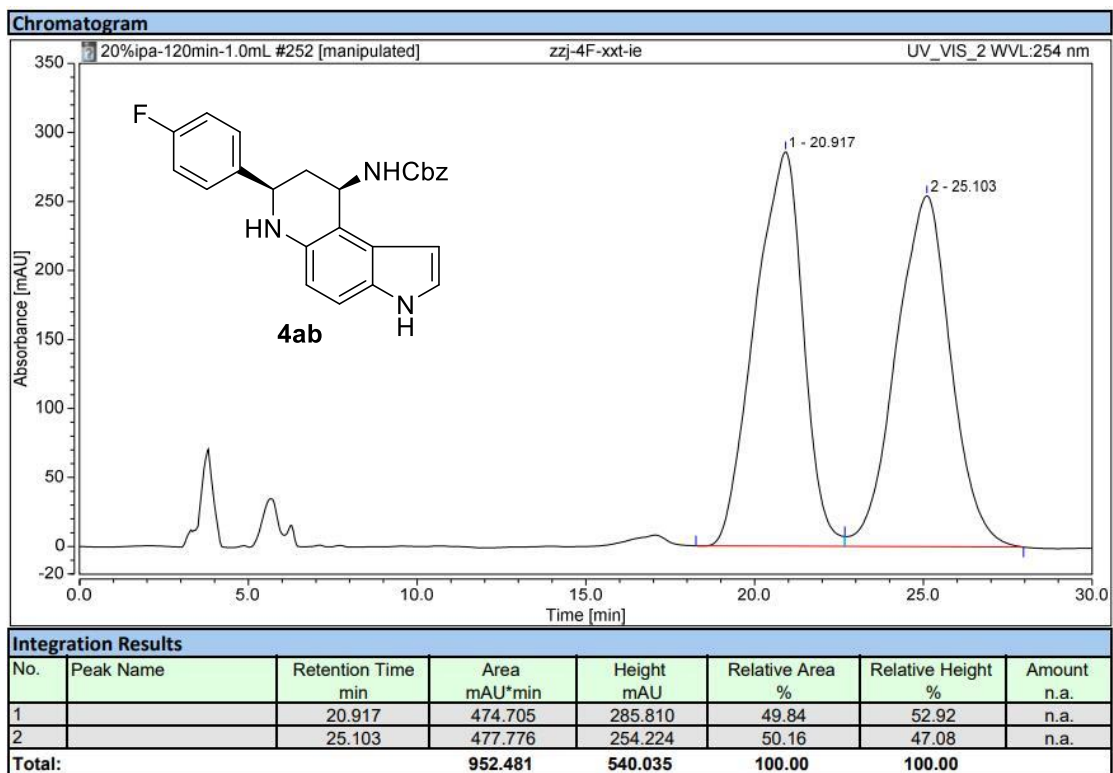
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ab**

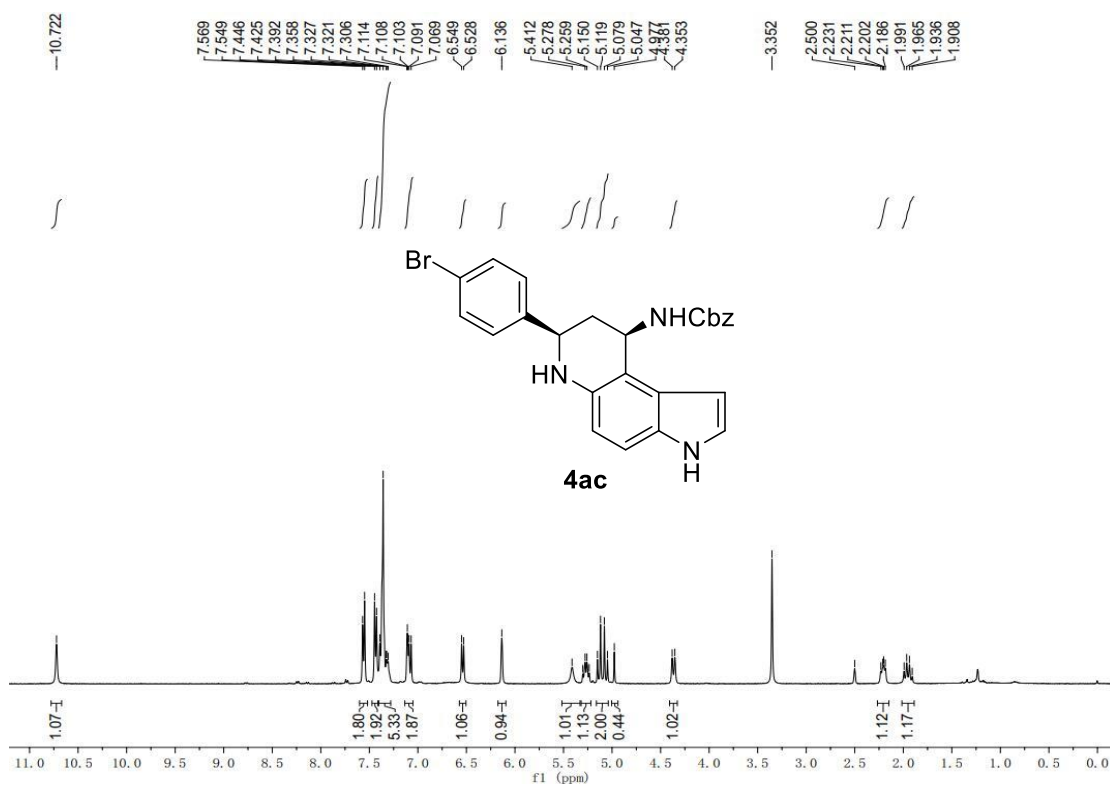
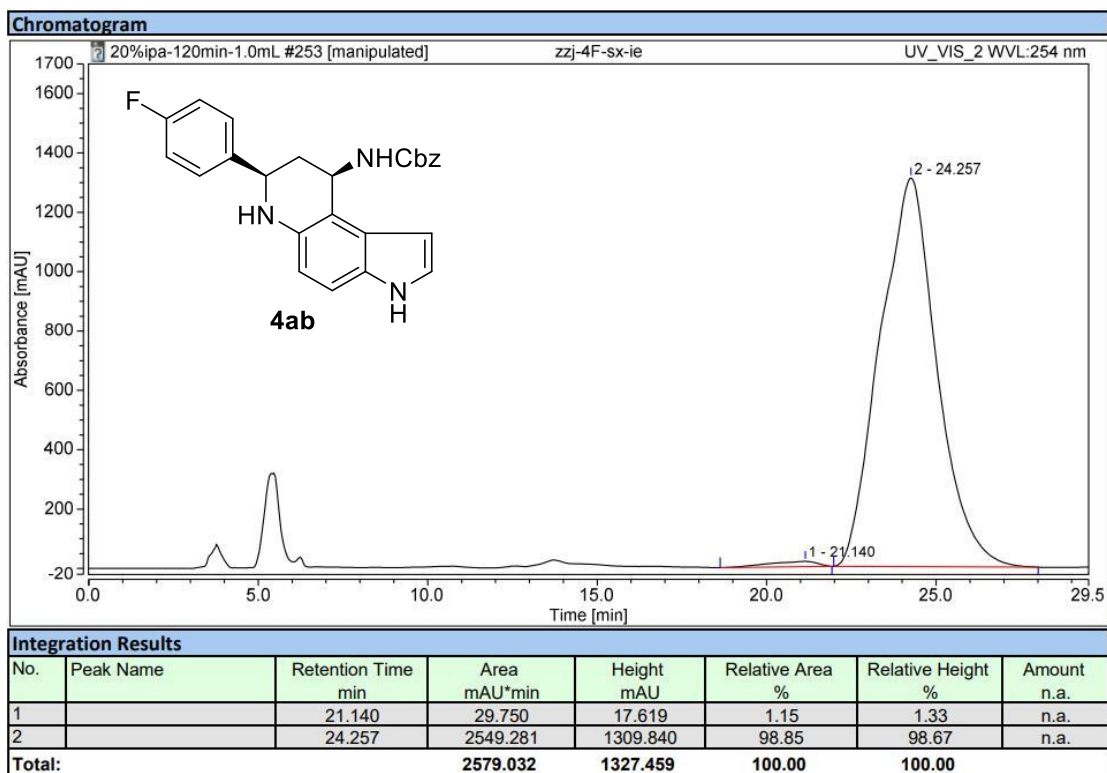


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ab**

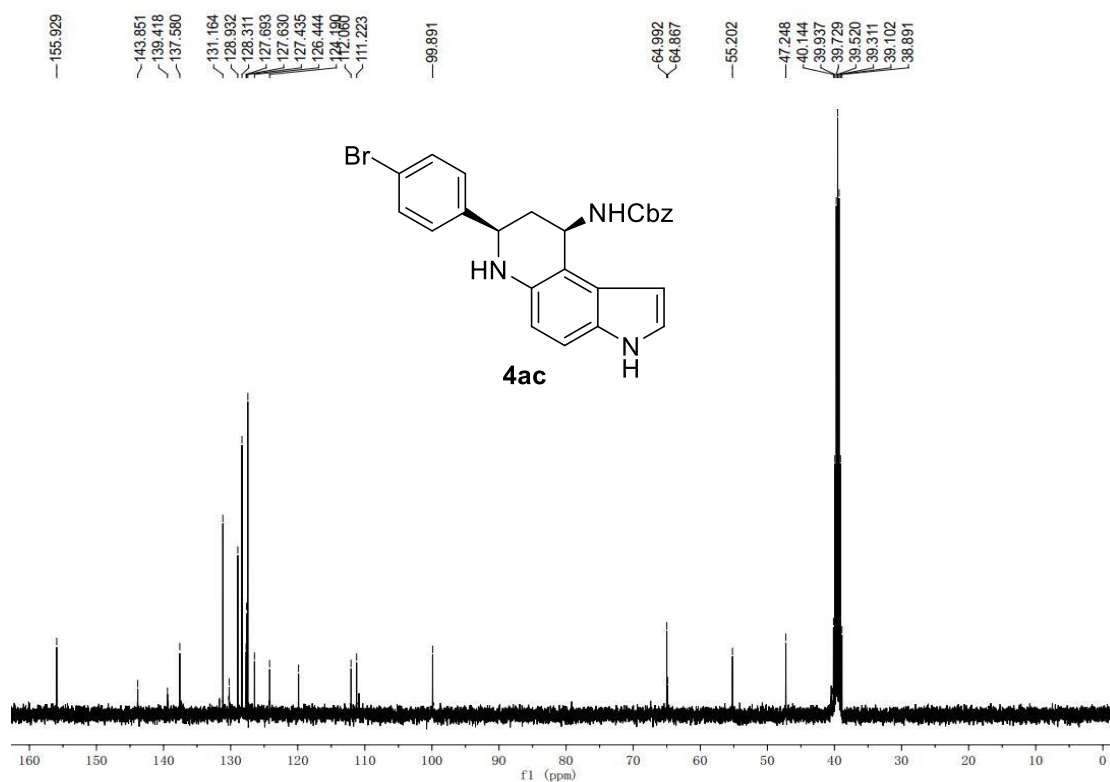


$^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ ) of **4ab**

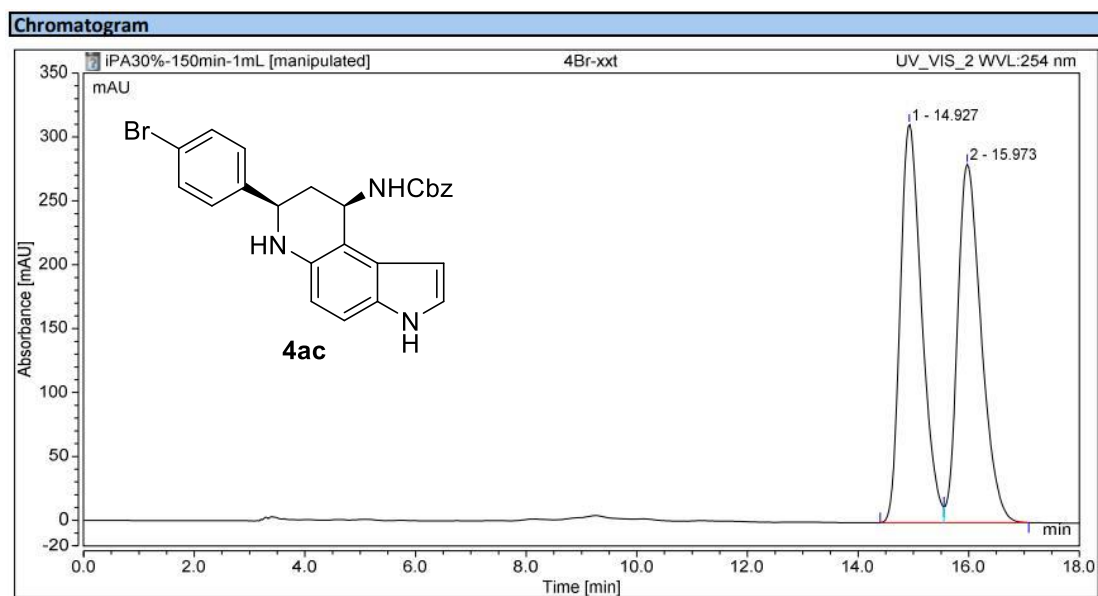




<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ac

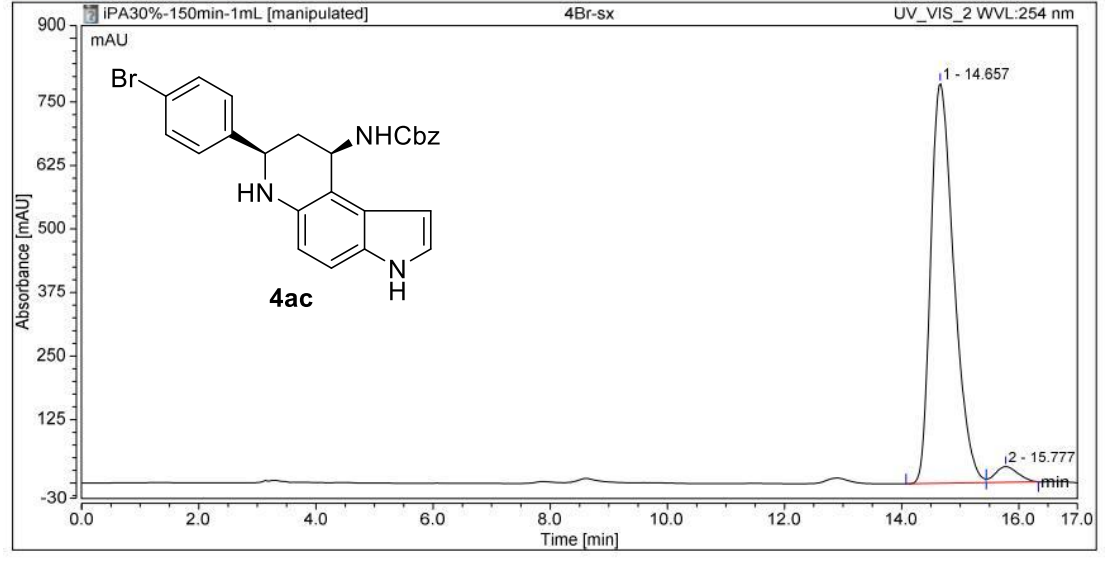


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ac**



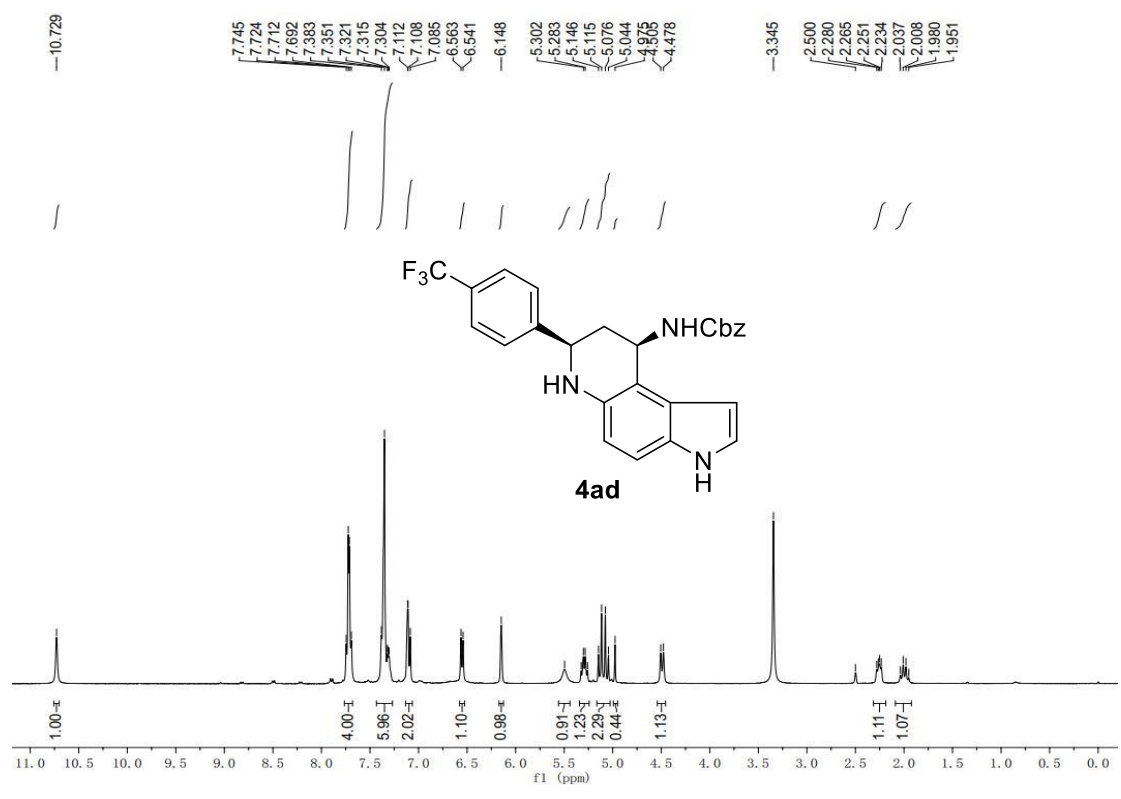
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		14.927	139.924	311.658	50.21	52.63	n.a.
2		15.973	138.762	280.454	49.79	47.37	n.a.
<b>Total:</b>			<b>278.685</b>	<b>592.112</b>	<b>100.00</b>	<b>100.00</b>	

**Chromatogram**

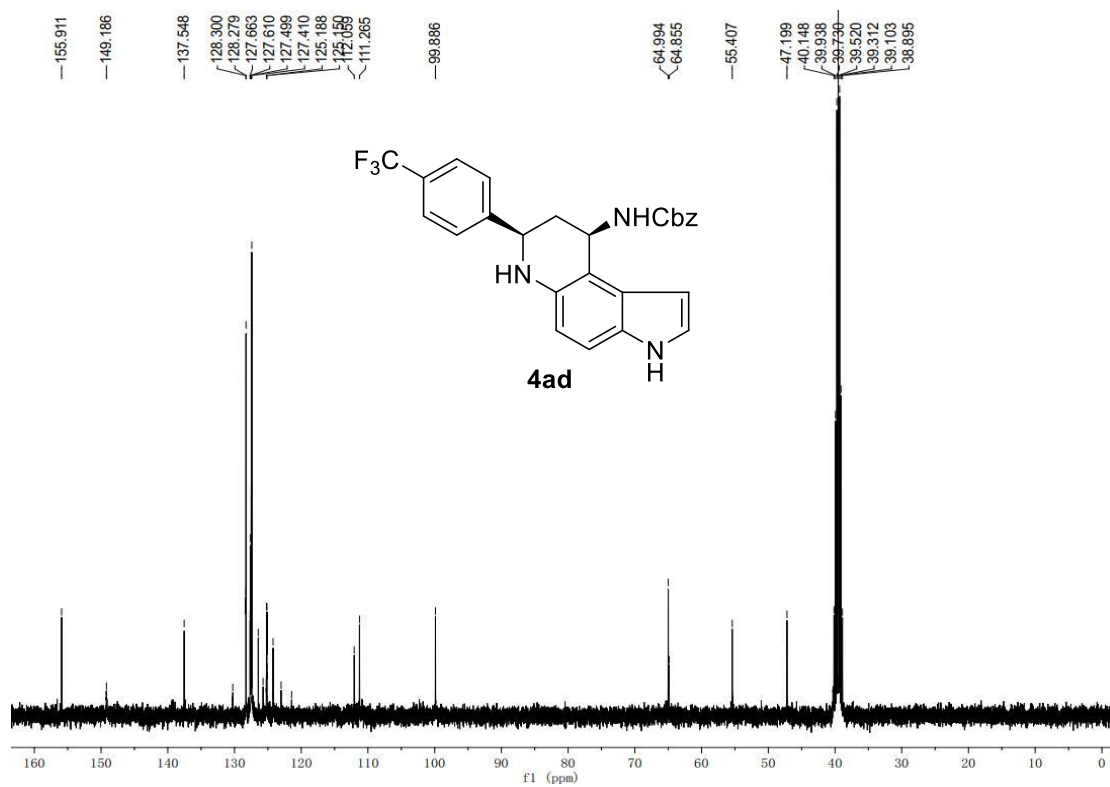


**Integration Results**

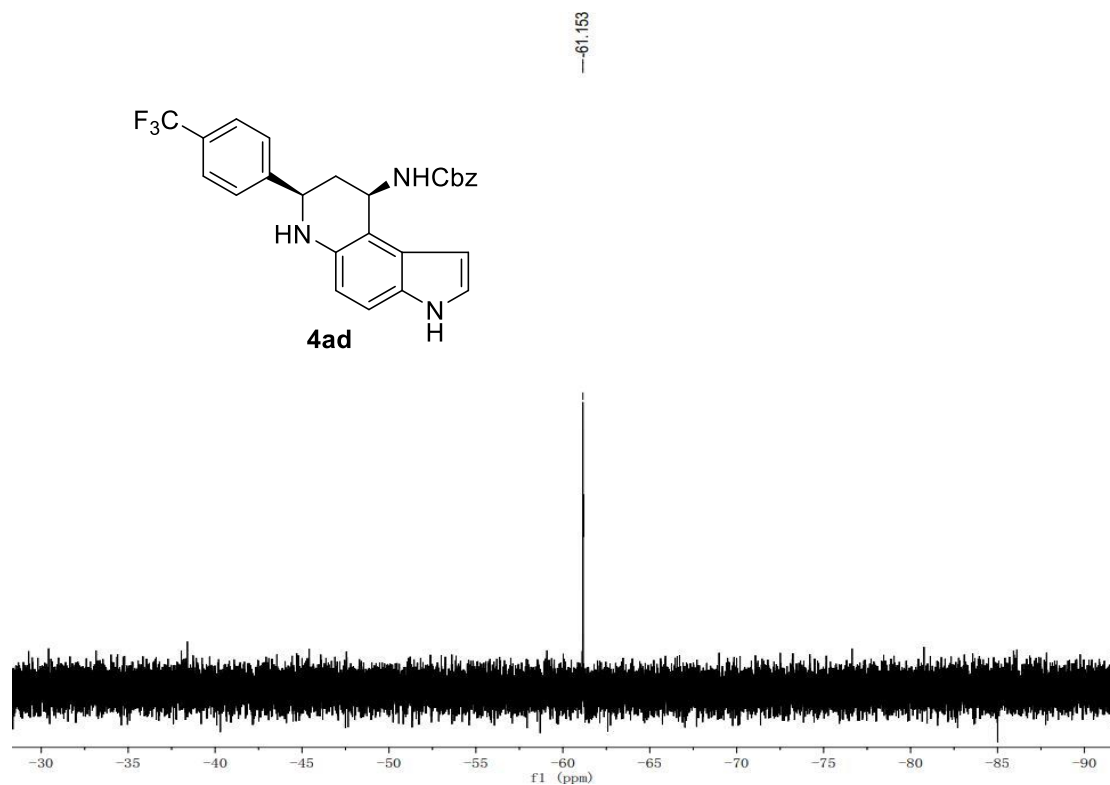
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.657	360.395	787.012	96.27	96.20	n.a.
2		15.777	13.953	31.070	3.73	3.80	n.a.
<b>Total:</b>			<b>374.349</b>	<b>818.082</b>	<b>100.00</b>	<b>100.00</b>	



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ad

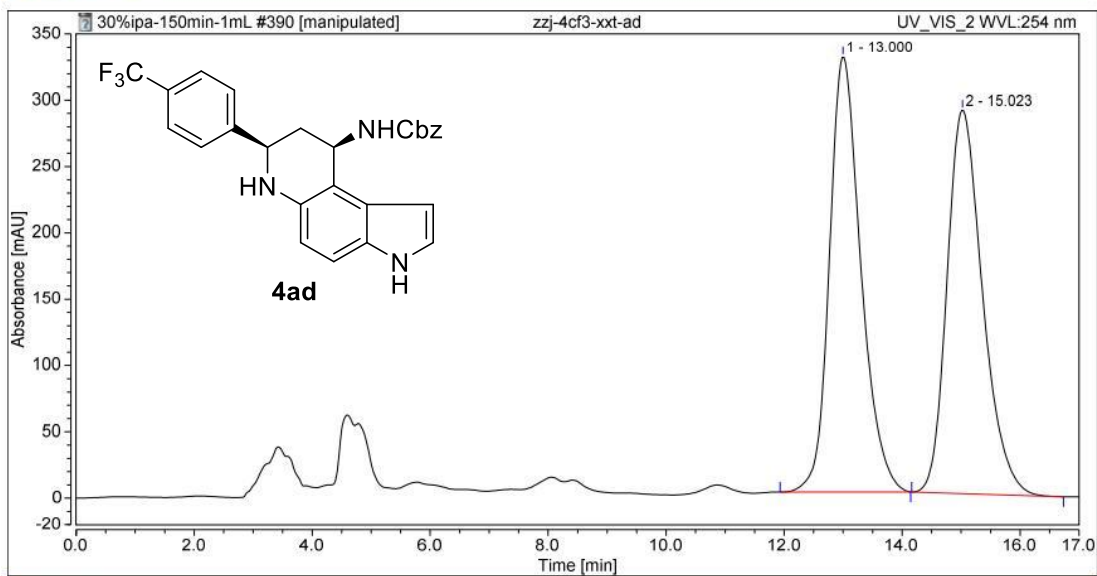


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ad**



<sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) of **4ad**

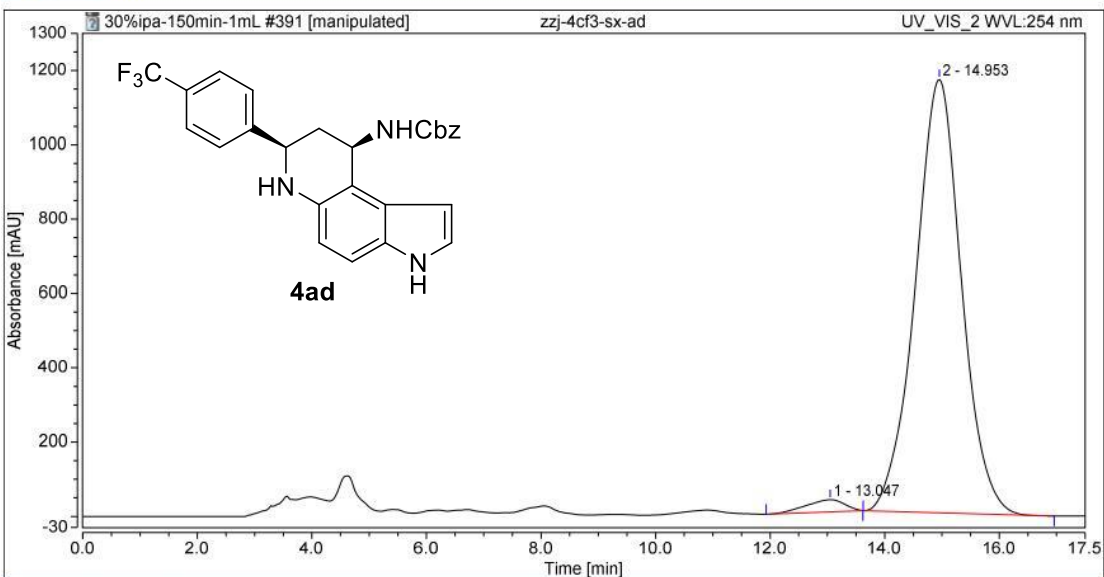
### Chromatogram



### Integration Results

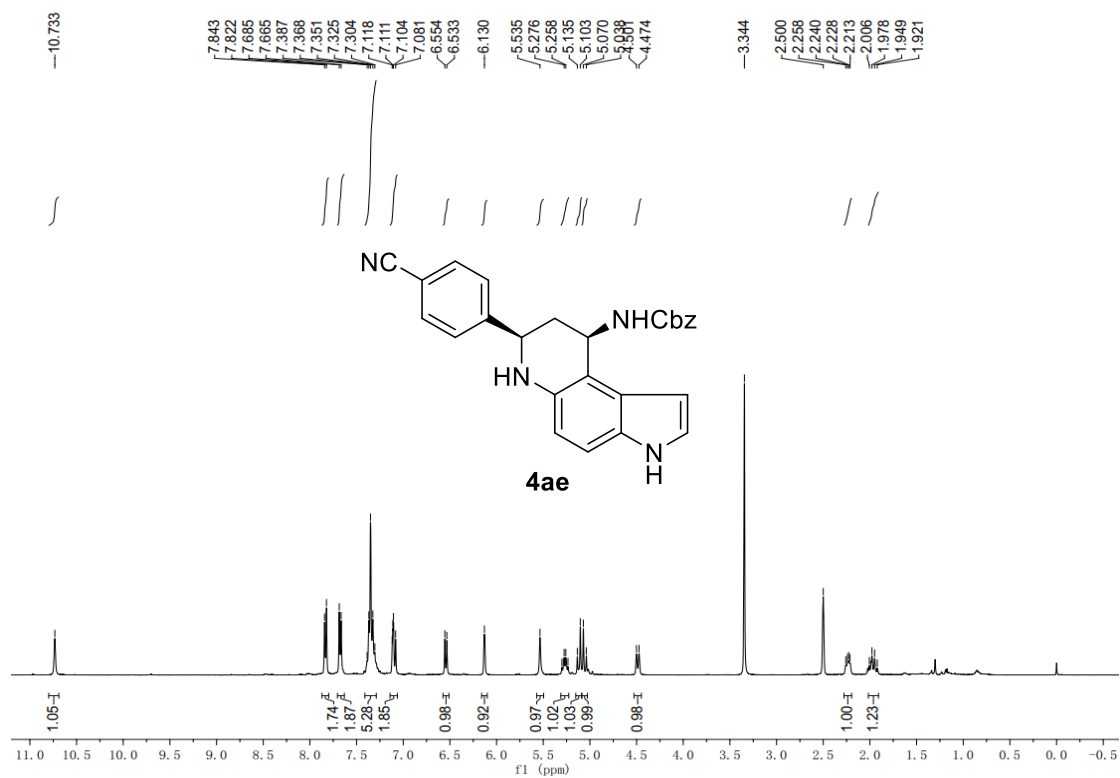
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.000	202.652	328.199	50.14	53.16	n.a.
2		15.023	201.528	289.157	49.86	46.84	n.a.
<b>Total:</b>			<b>404.179</b>	<b>617.356</b>	<b>100.00</b>	<b>100.00</b>	

### Chromatogram

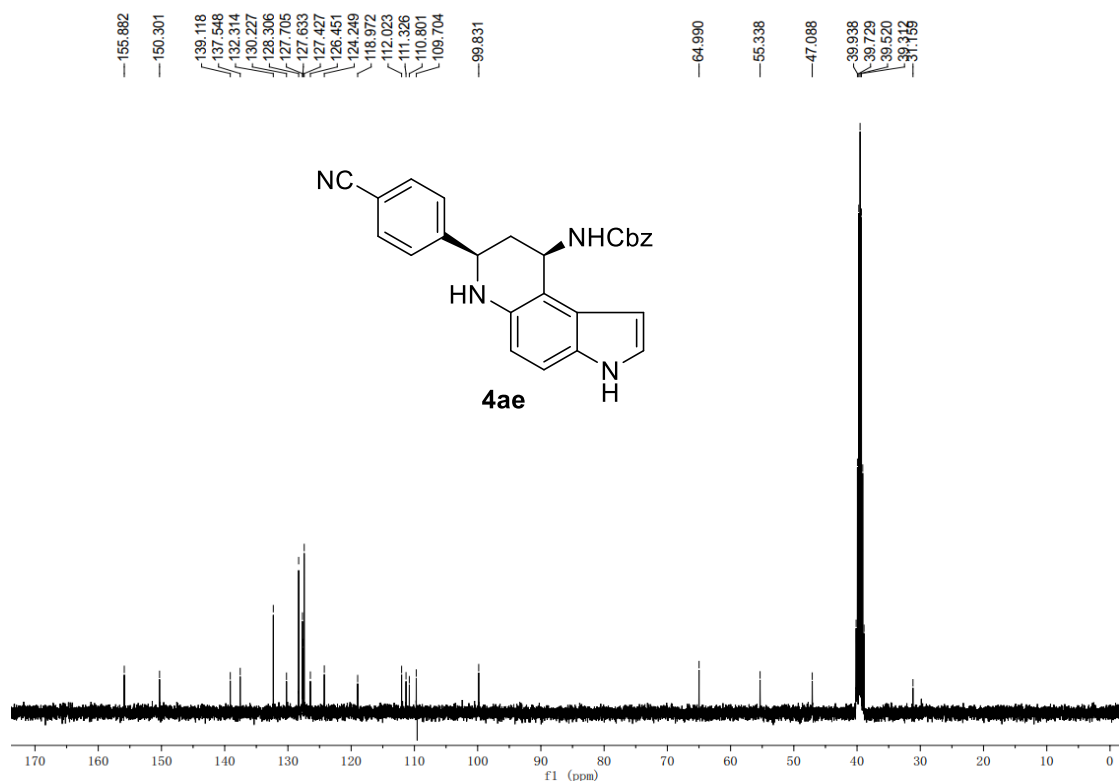


### Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		13.047	25.629	32.567	2.31	2.72	n.a.
2		14.953	1085.351	1166.049	97.69	97.28	n.a.
<b>Total:</b>			<b>1110.981</b>	<b>1198.616</b>	<b>100.00</b>	<b>100.00</b>	

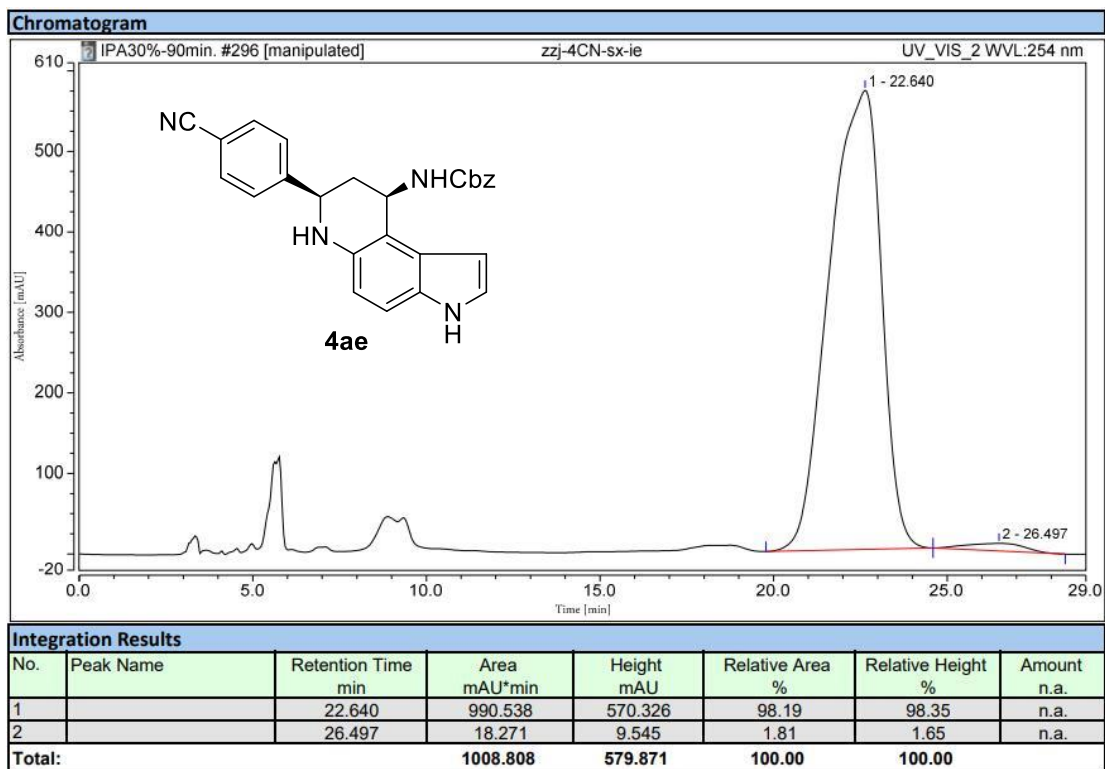
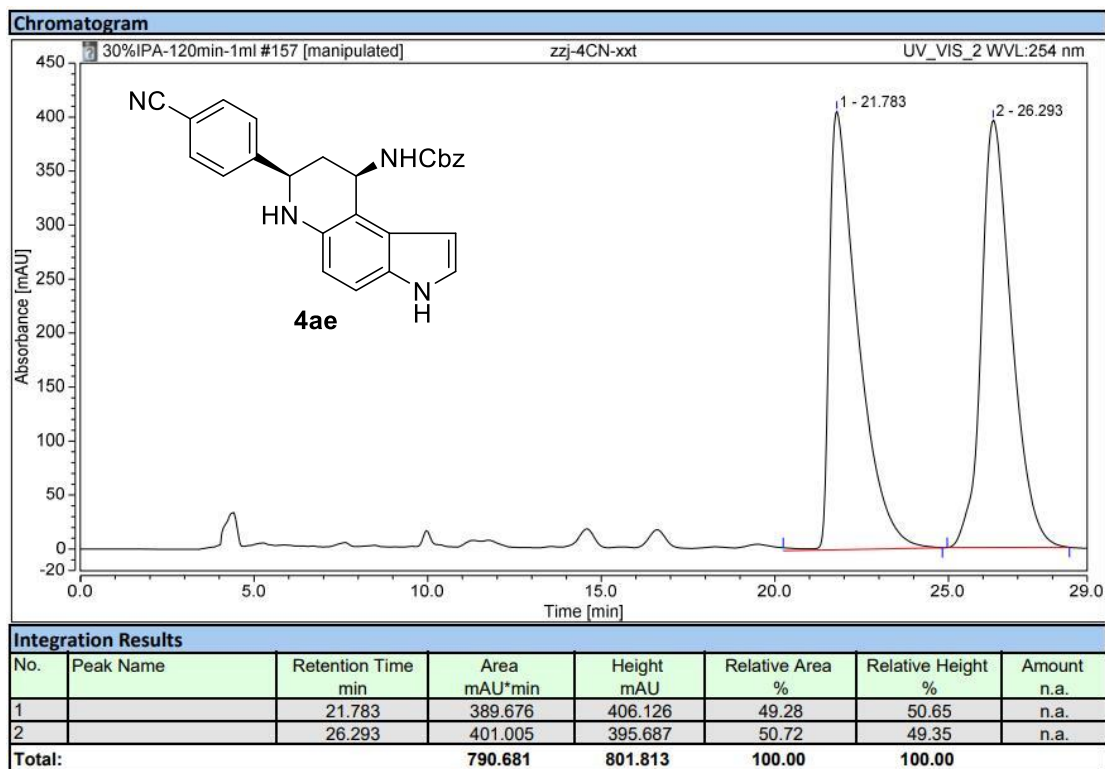


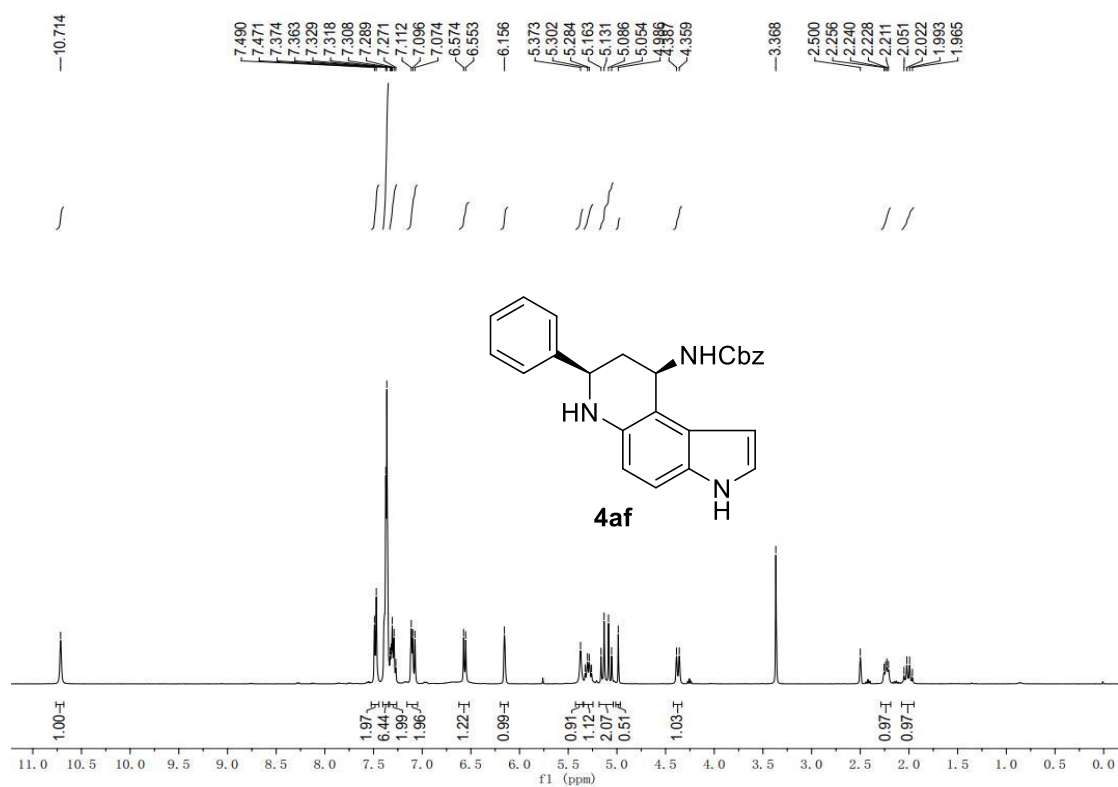
**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ae**



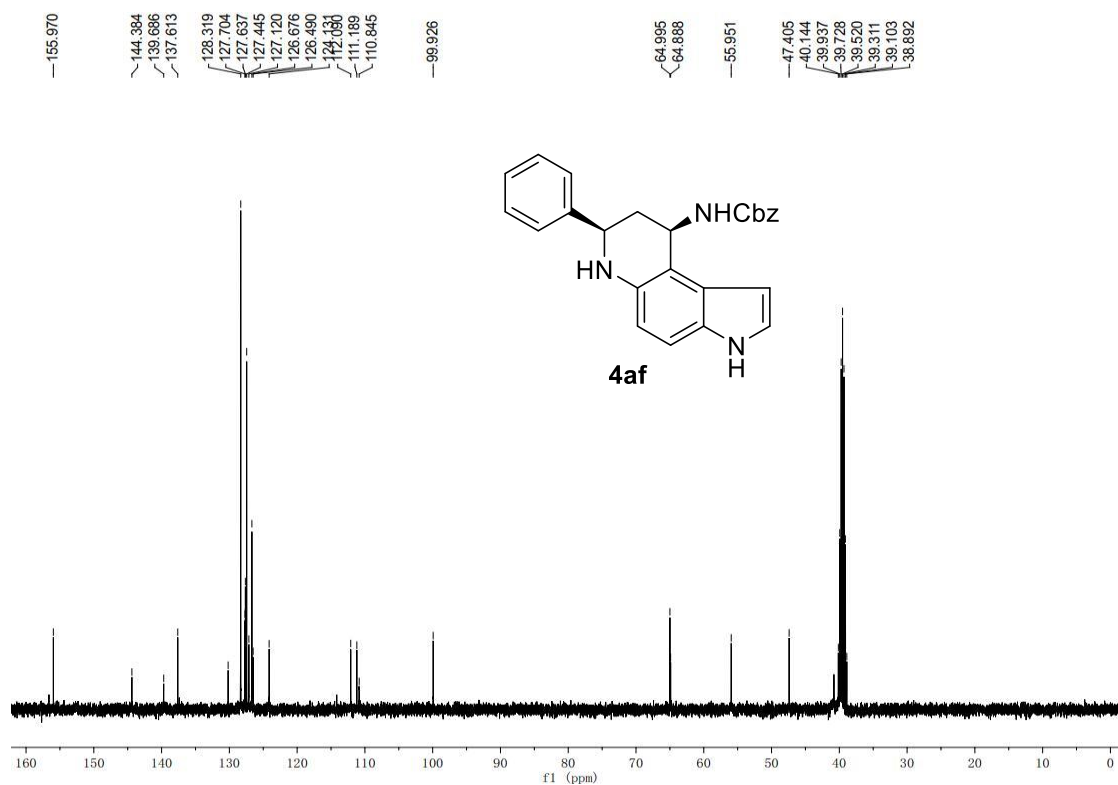
**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ae**



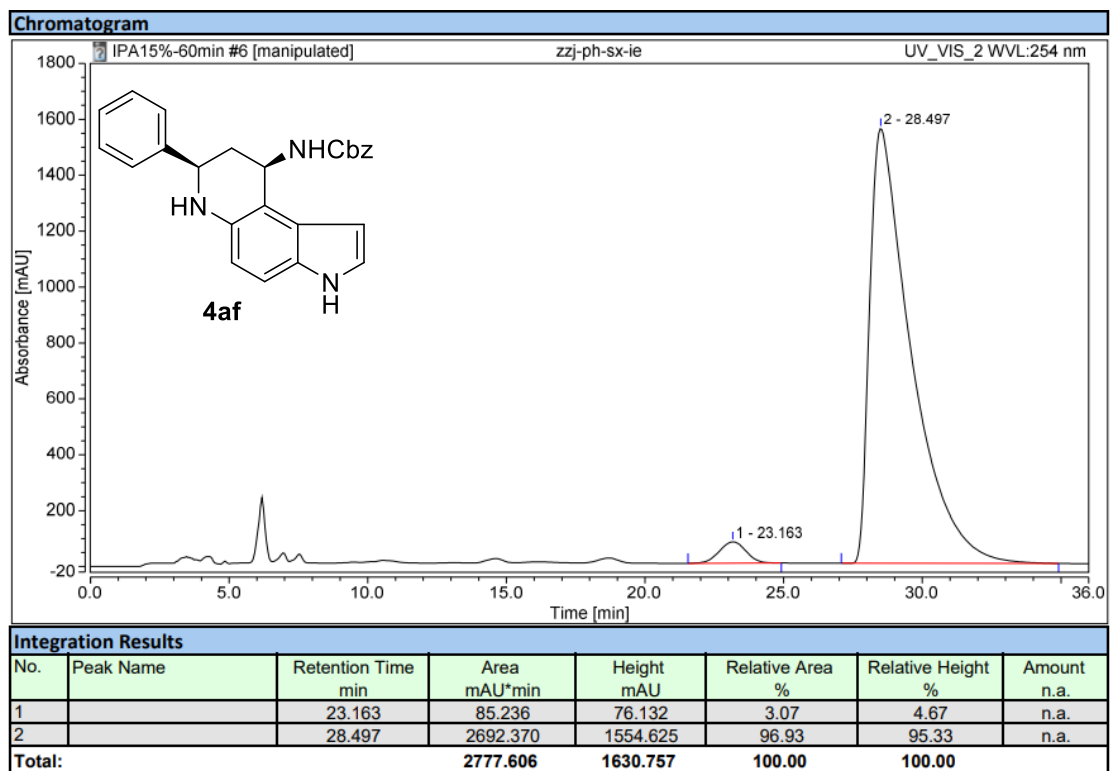
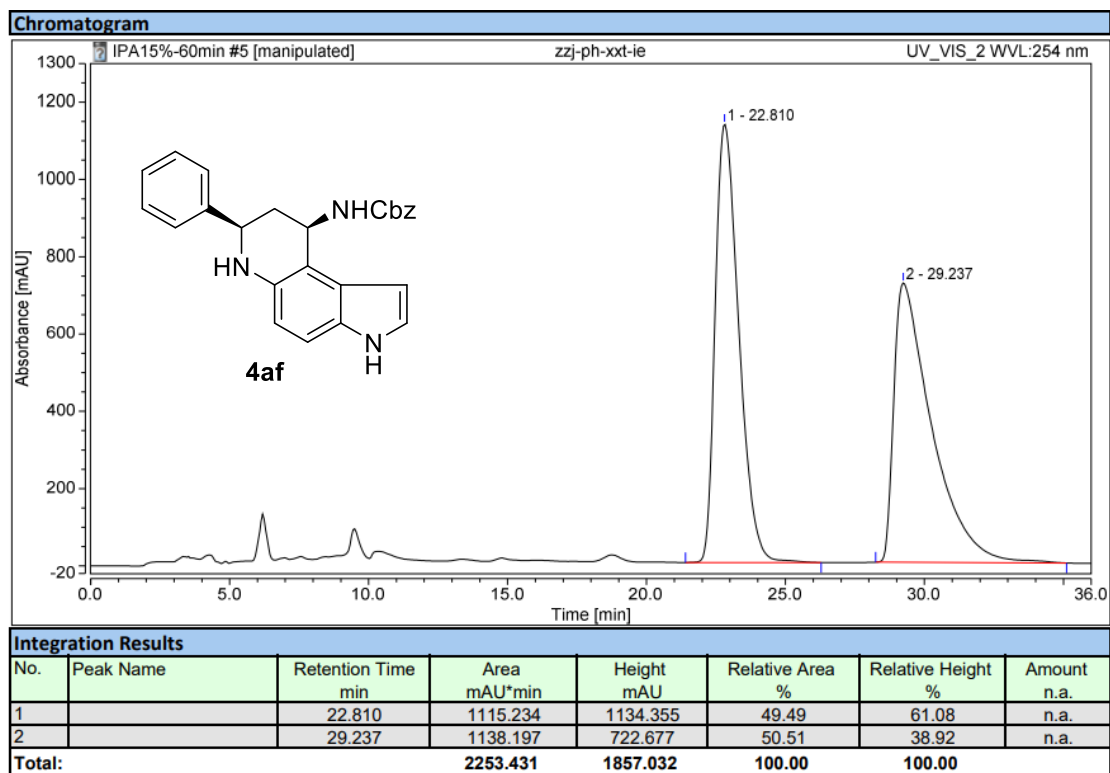


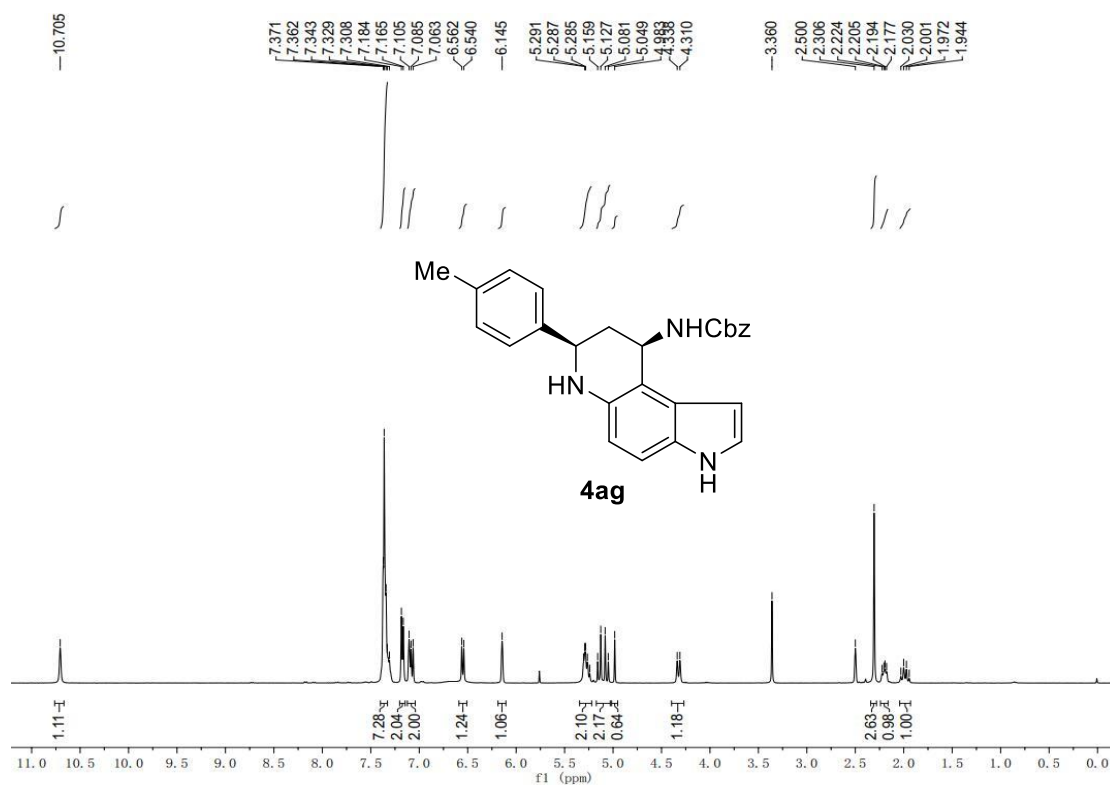


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4af**

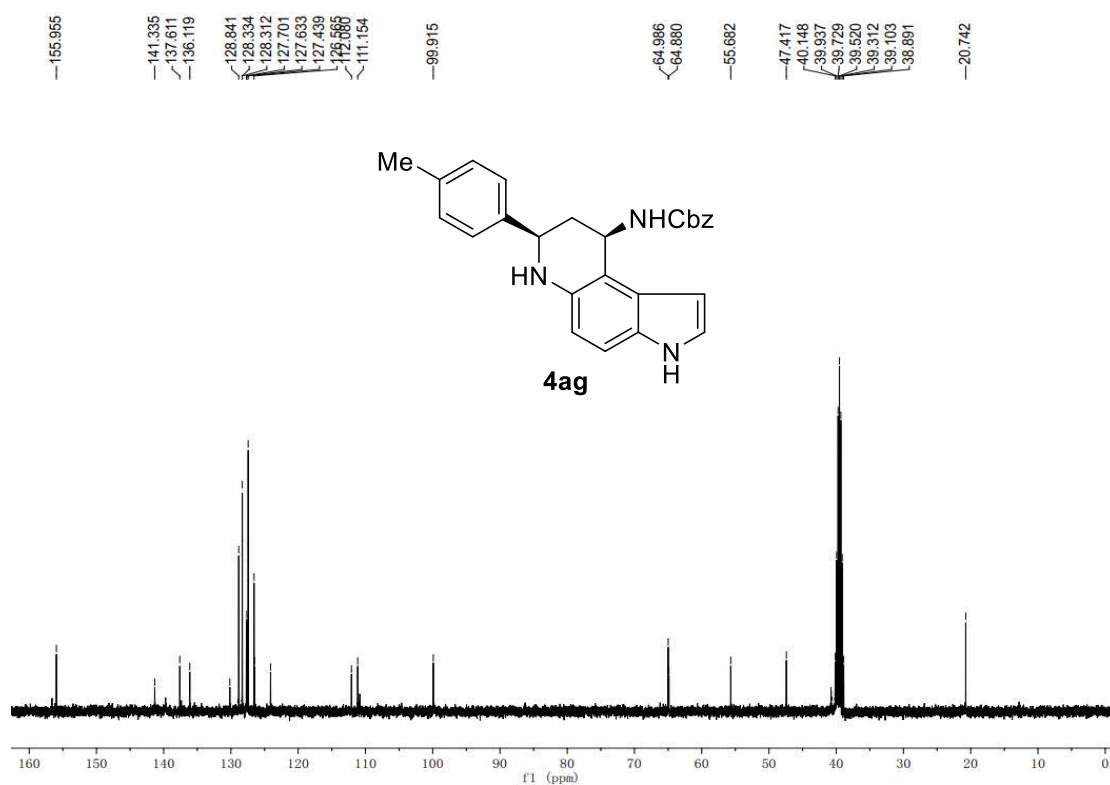


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4af**

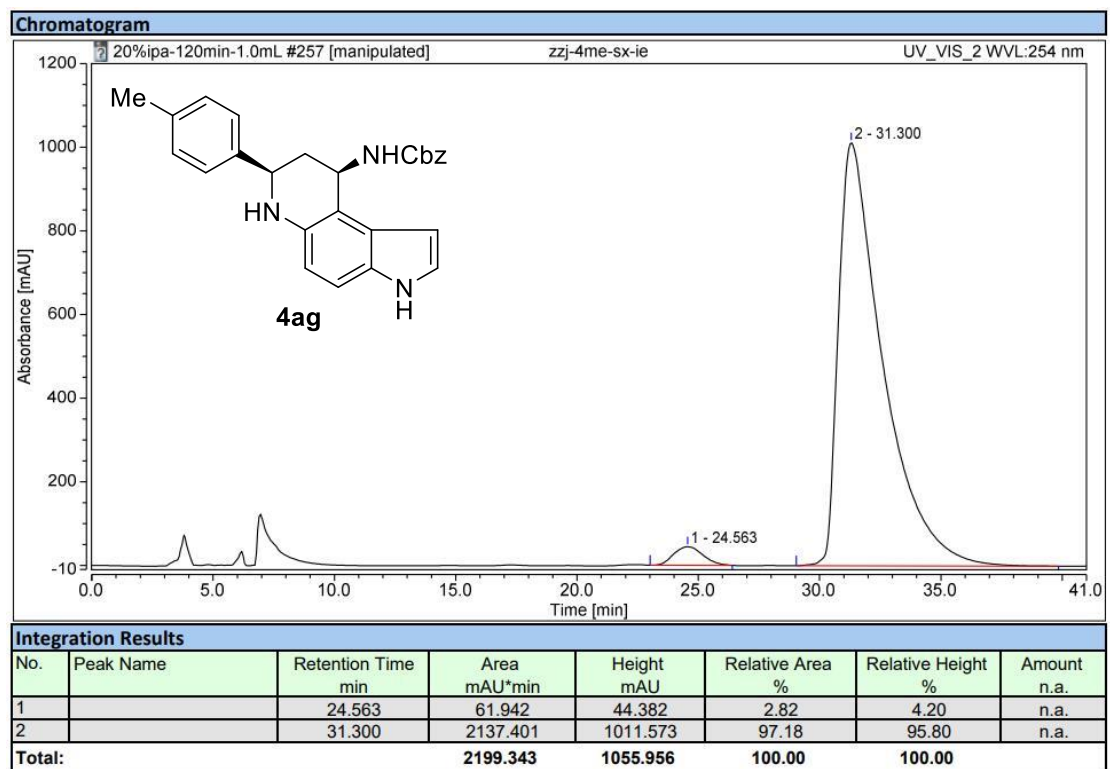
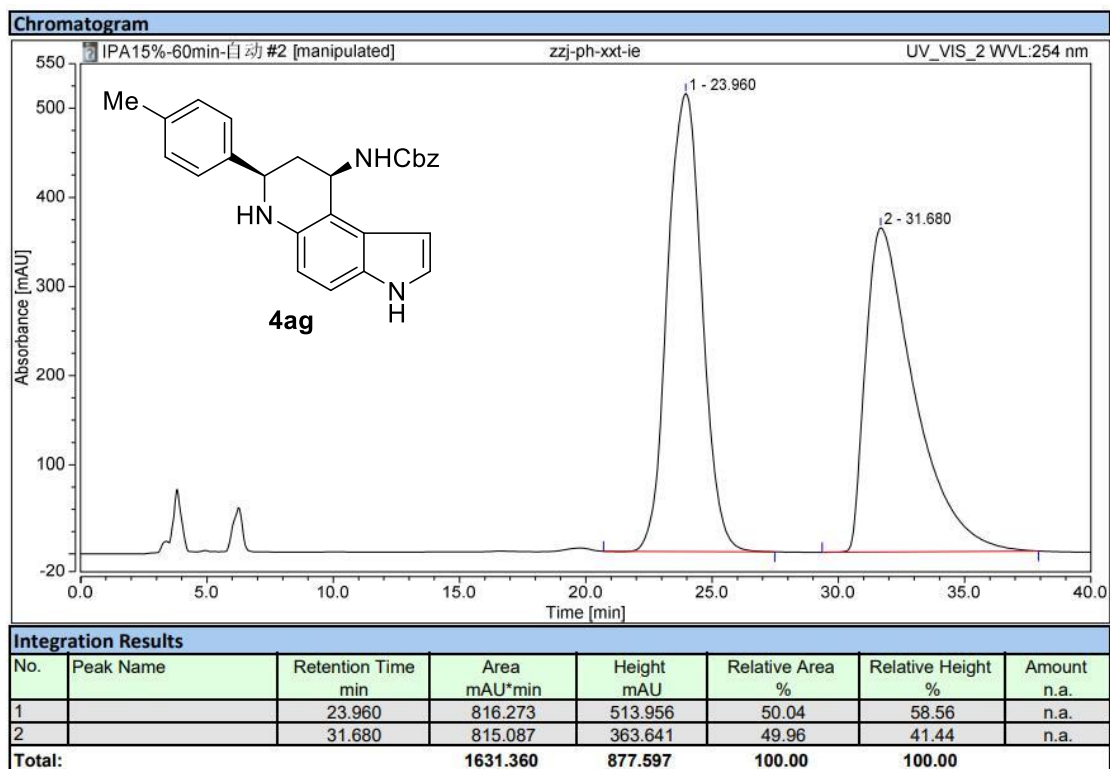


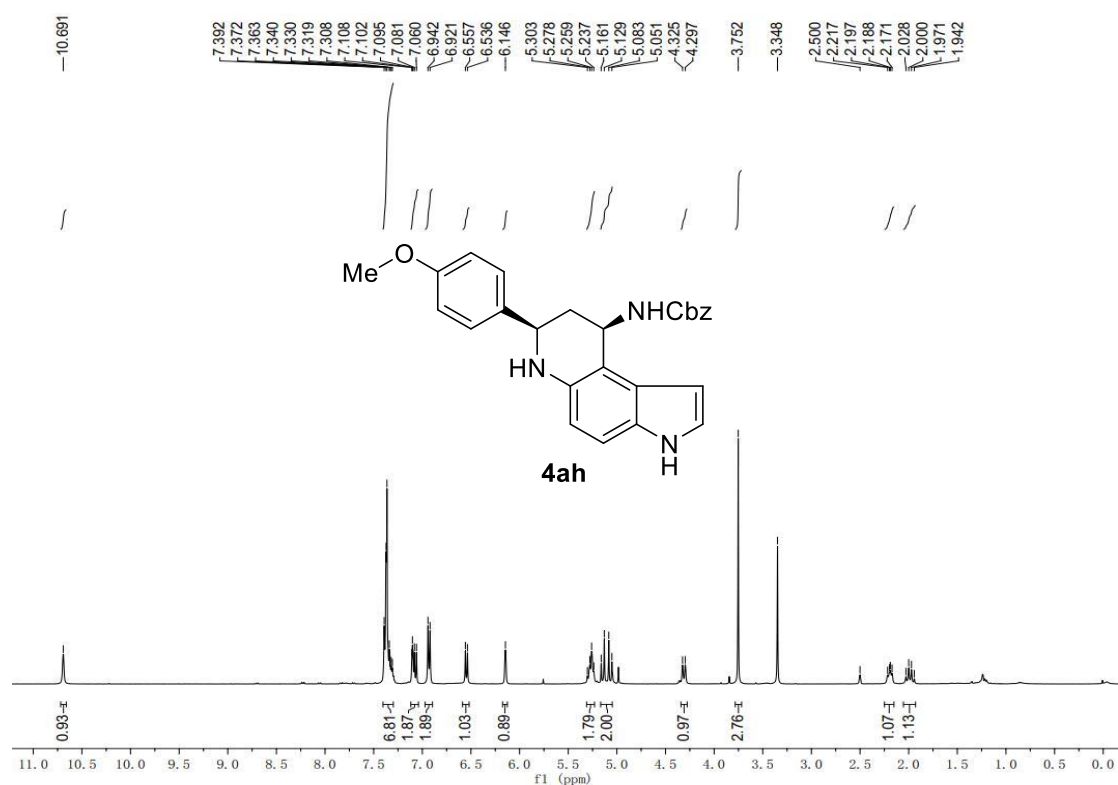


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ag**

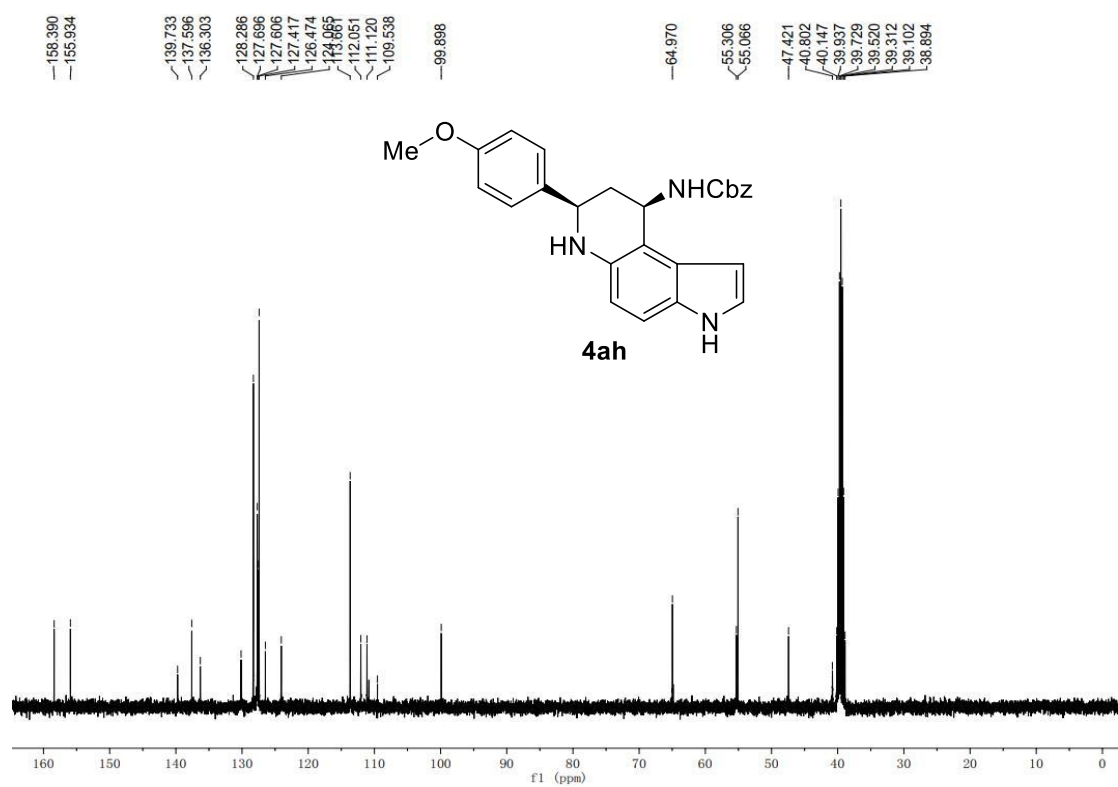


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ag**

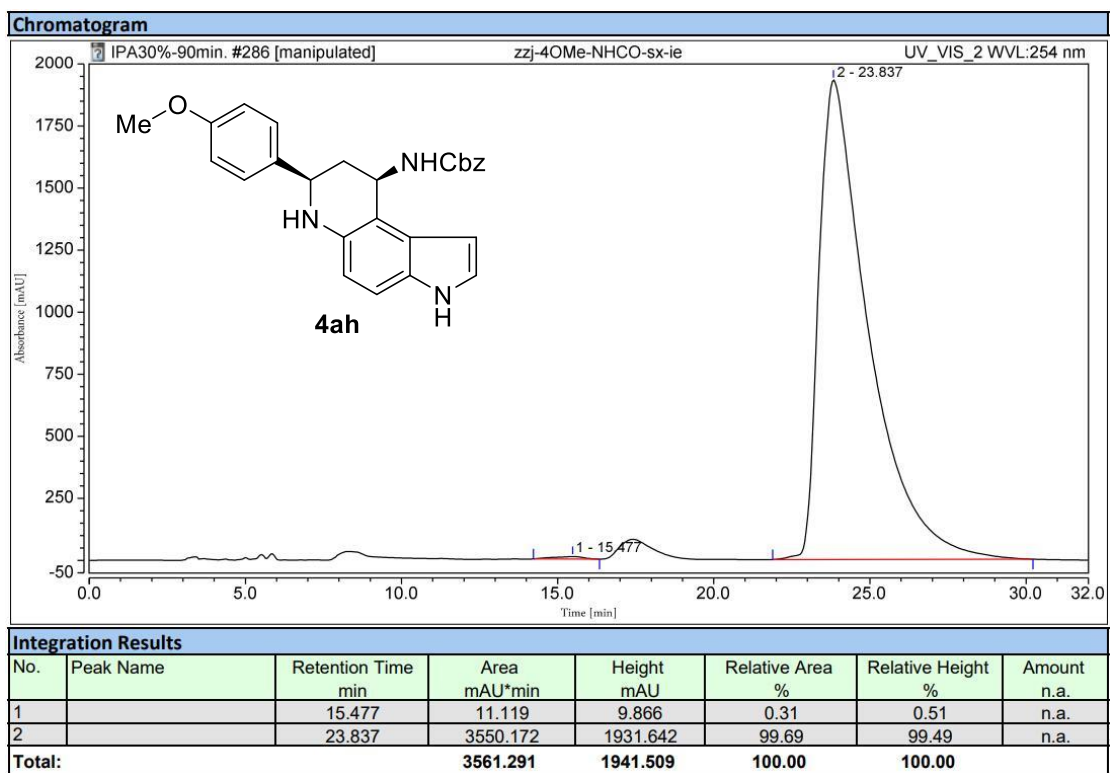
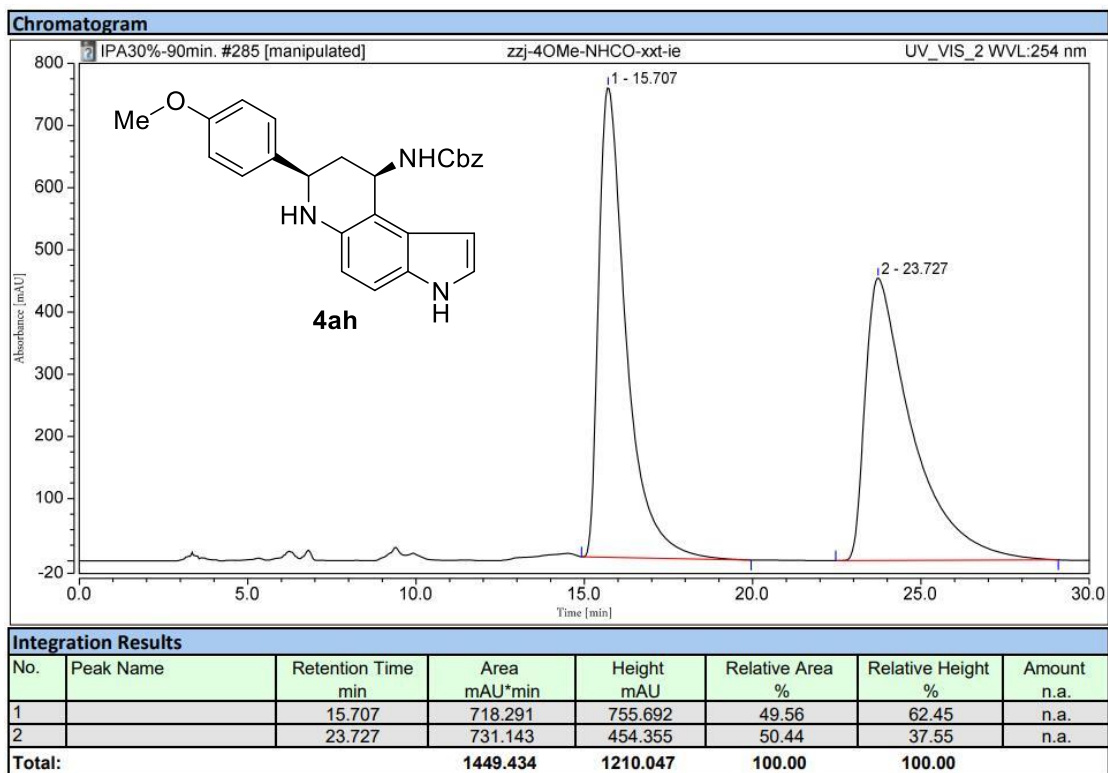


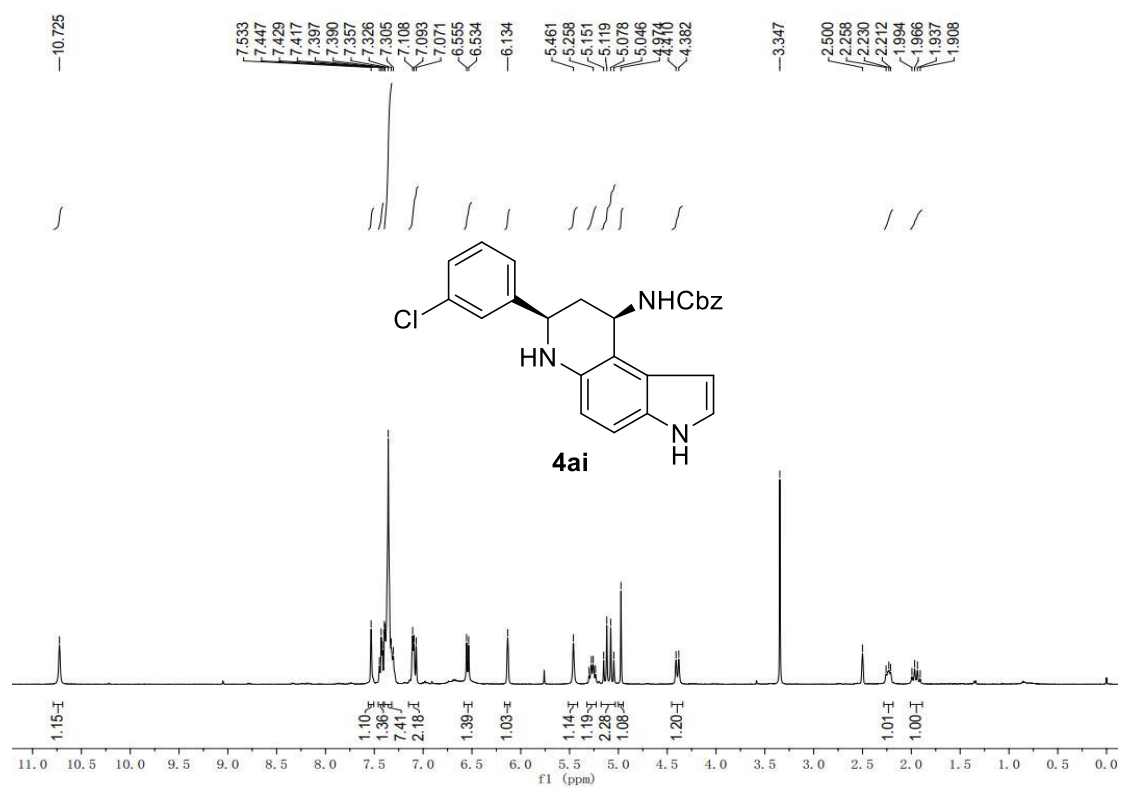


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ah**

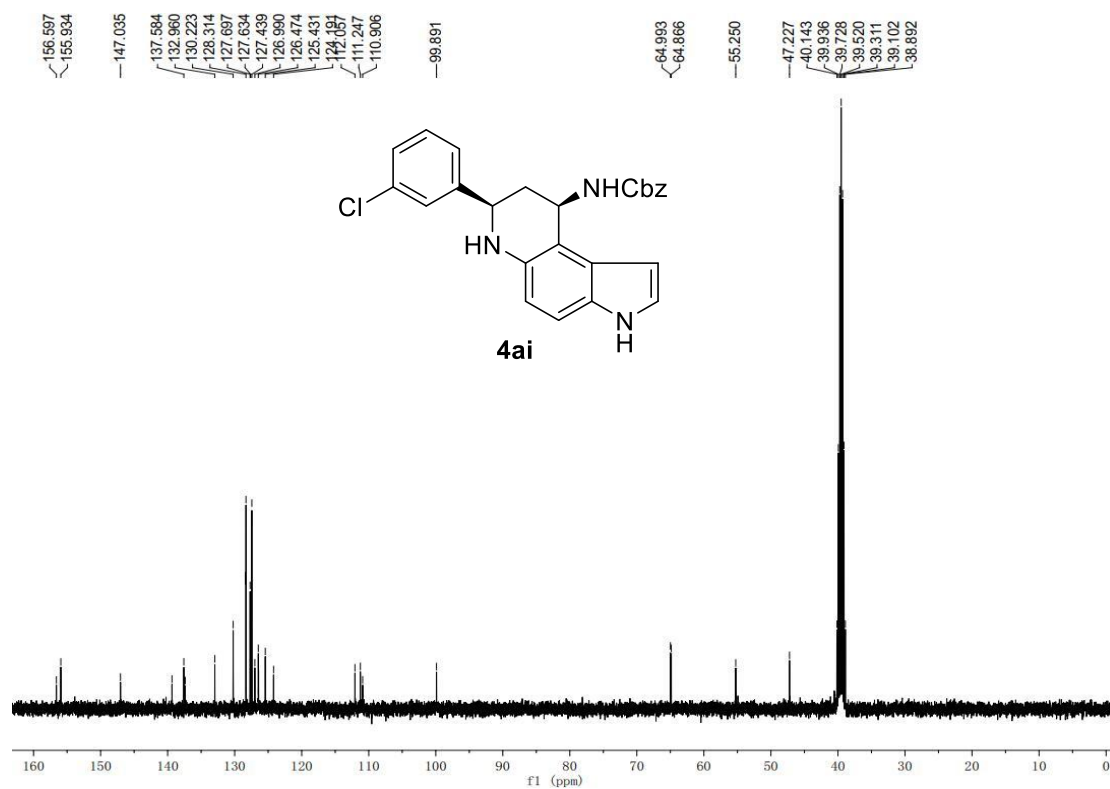


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ah**



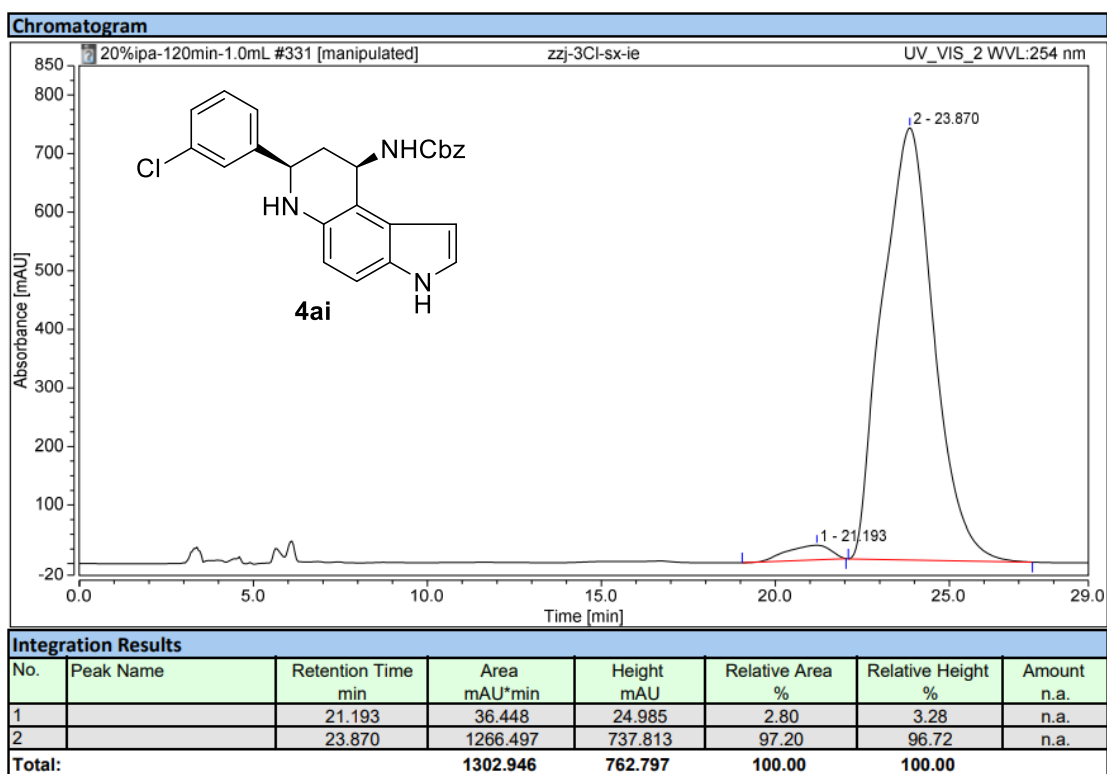
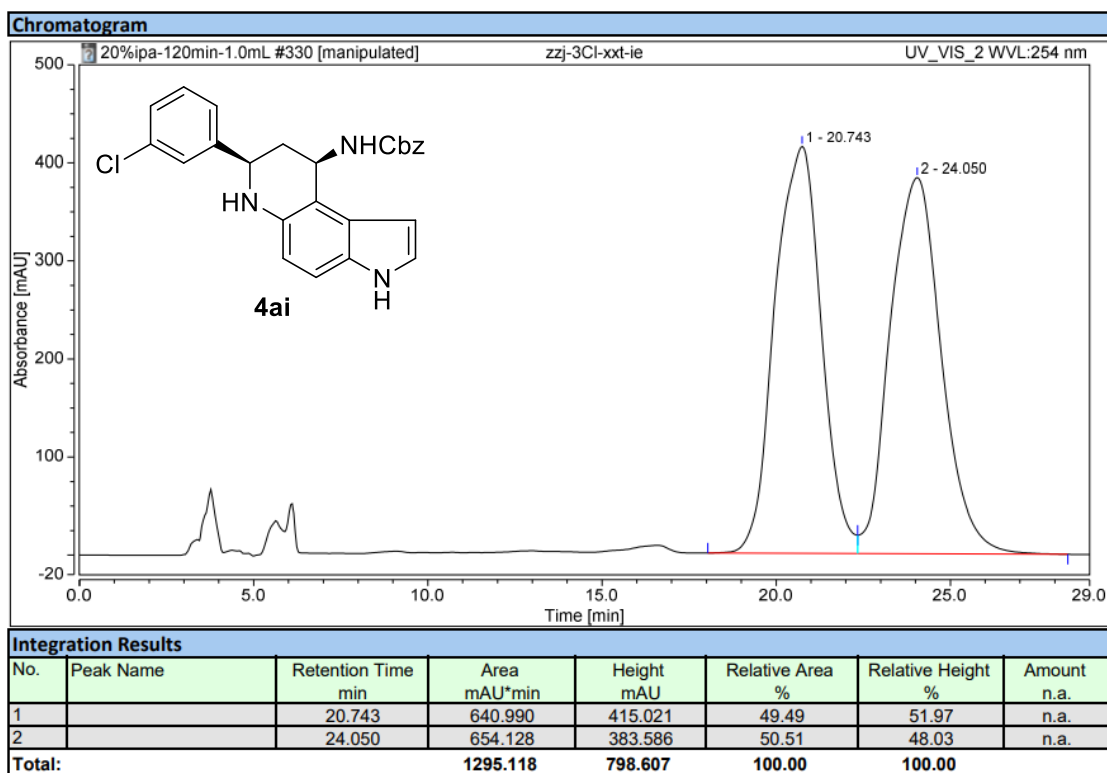


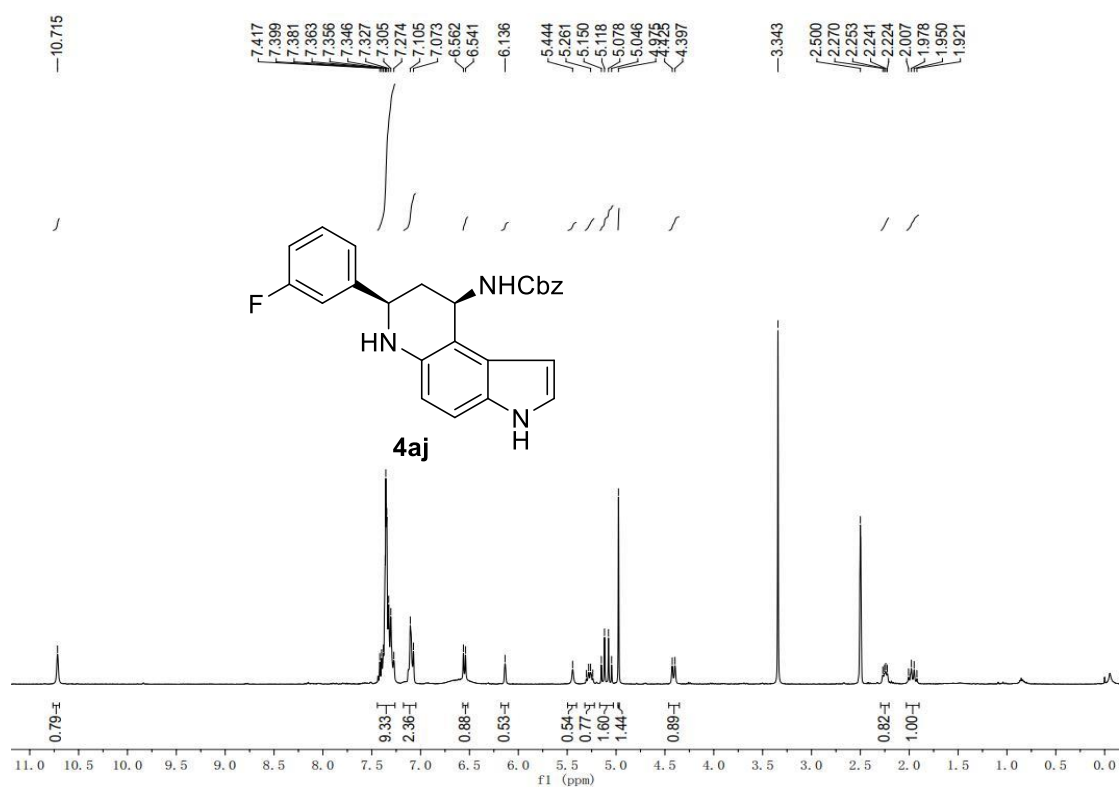
**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ai**



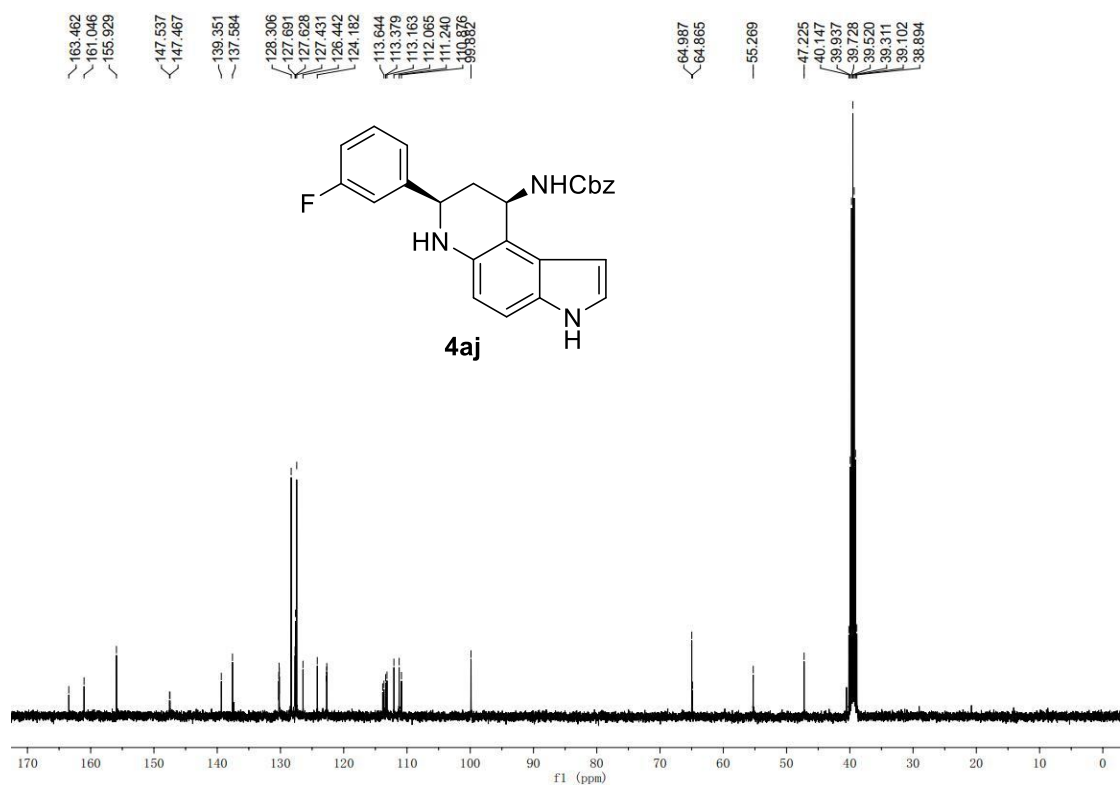
**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ai**



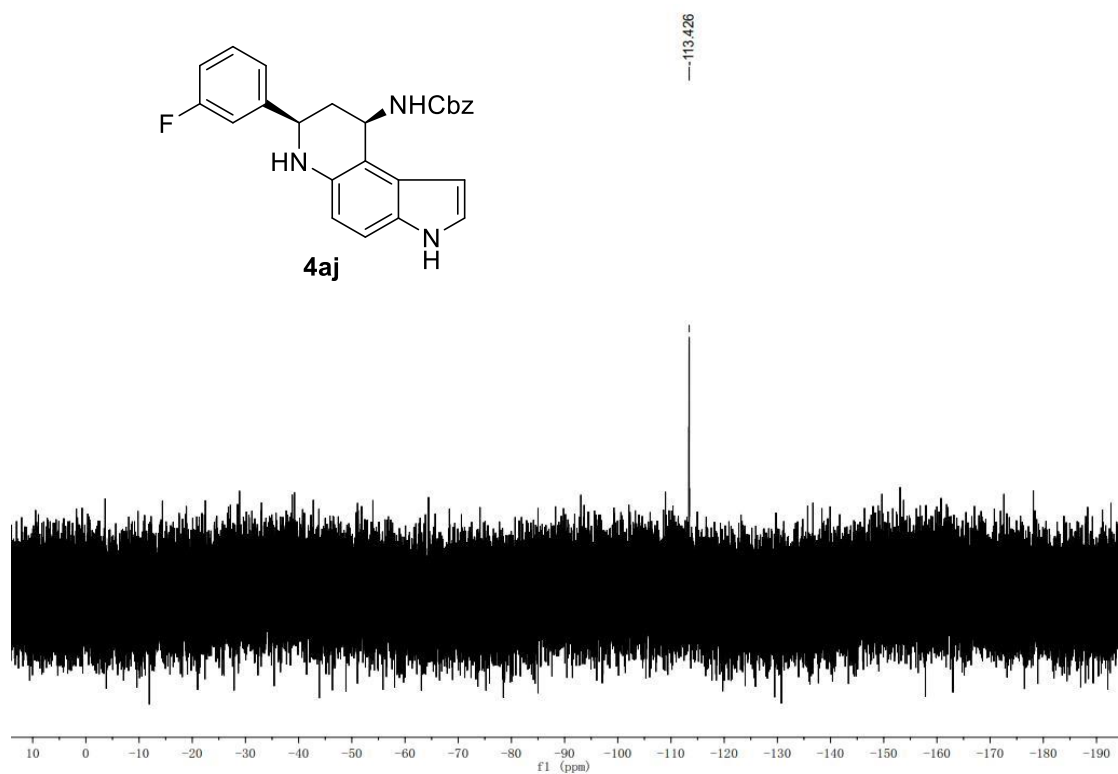




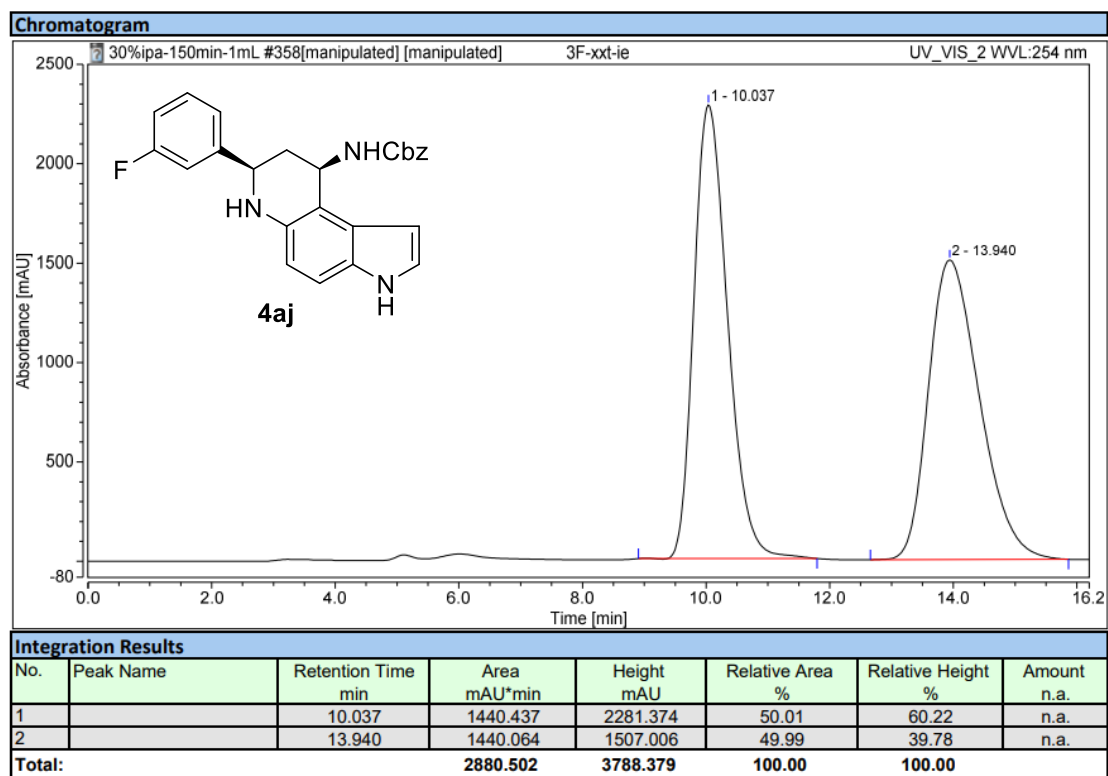
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4aj

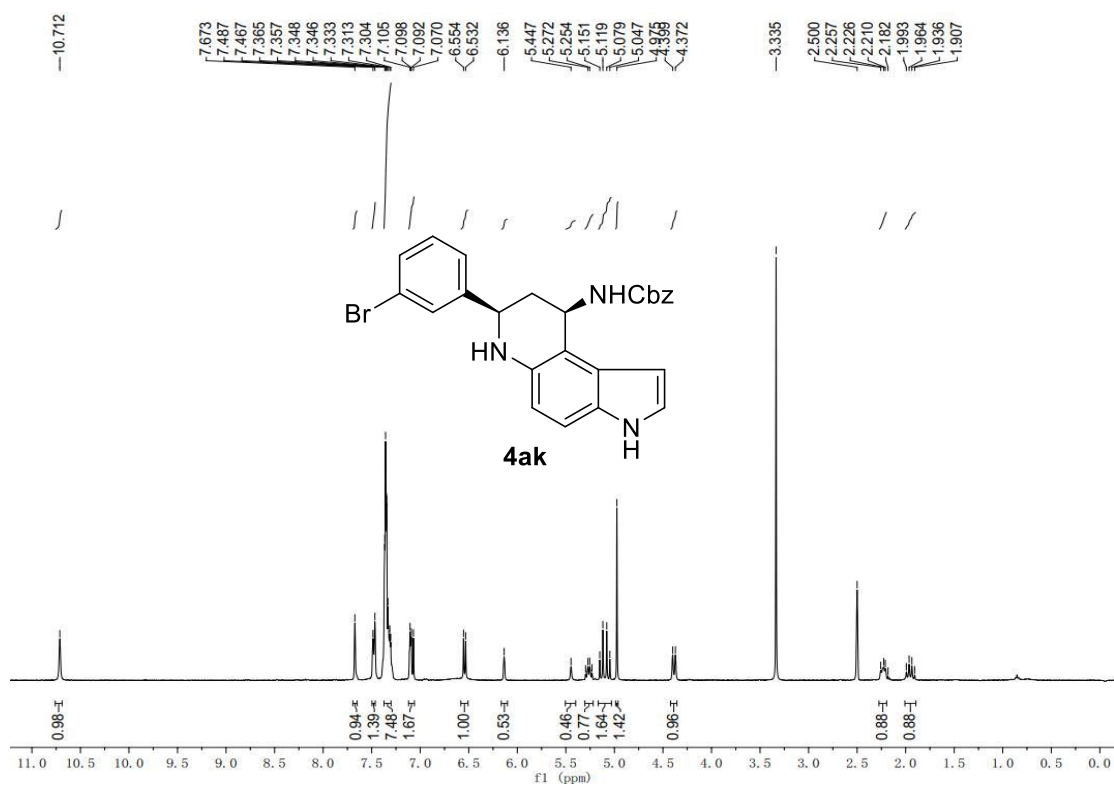
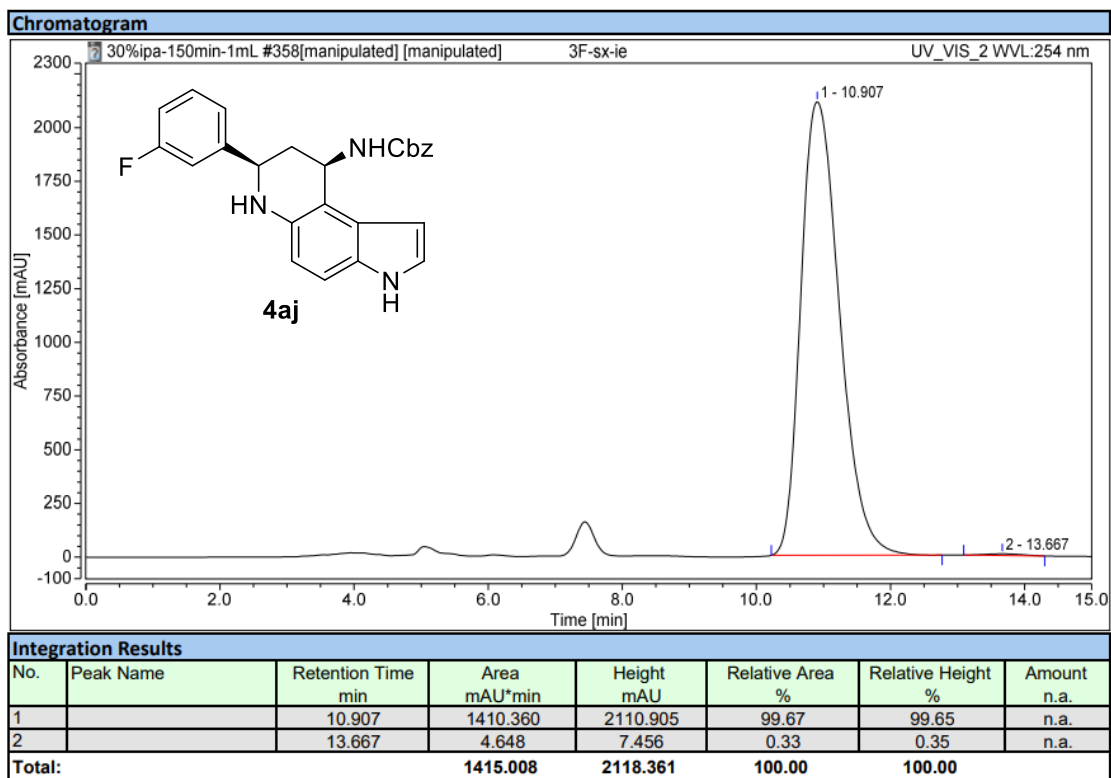


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4aj

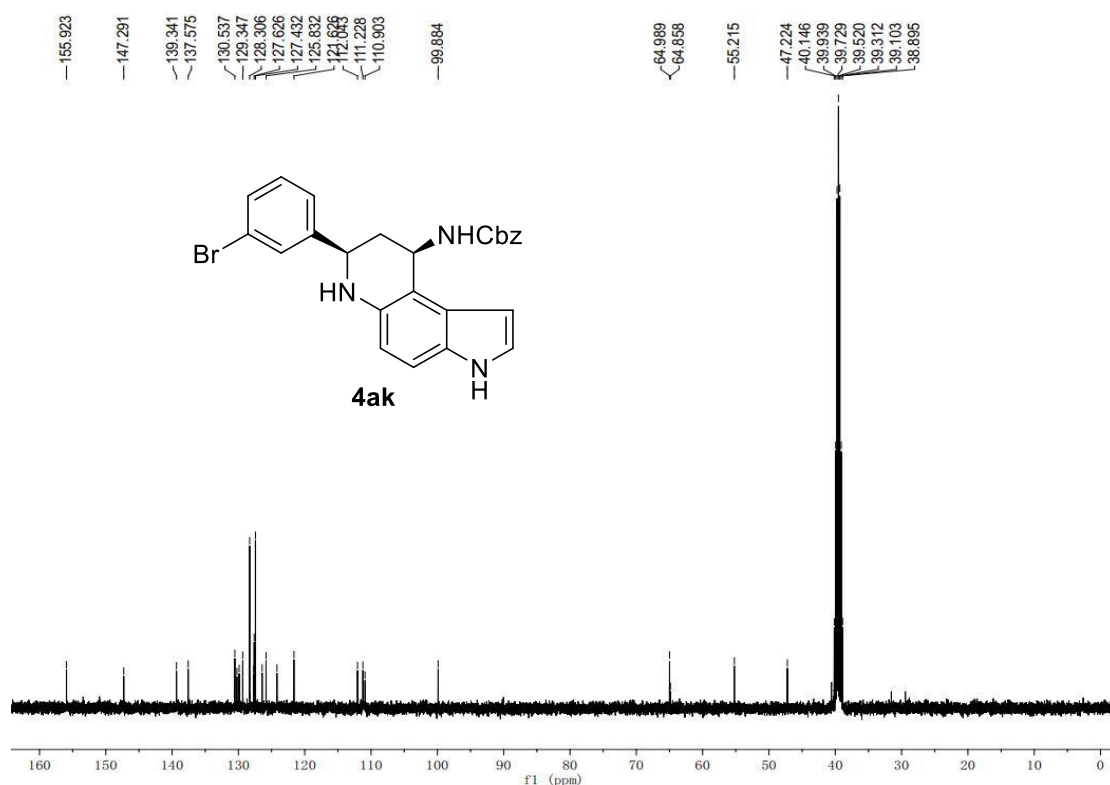


<sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) of **4aj**

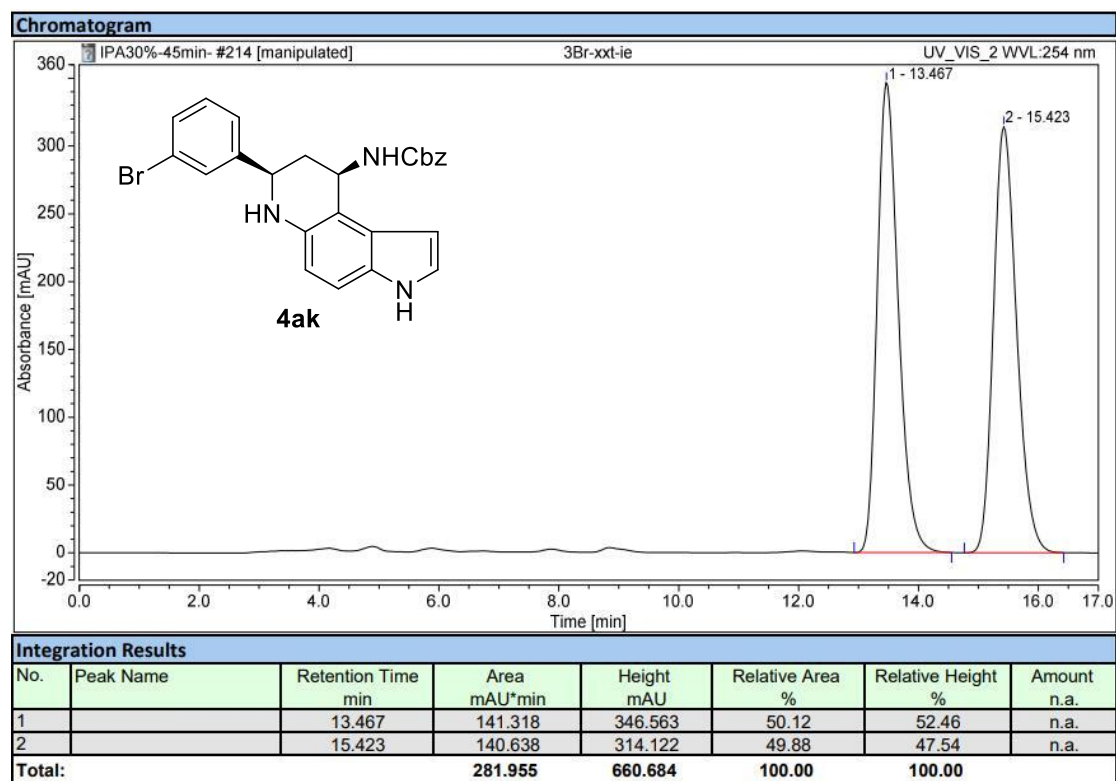


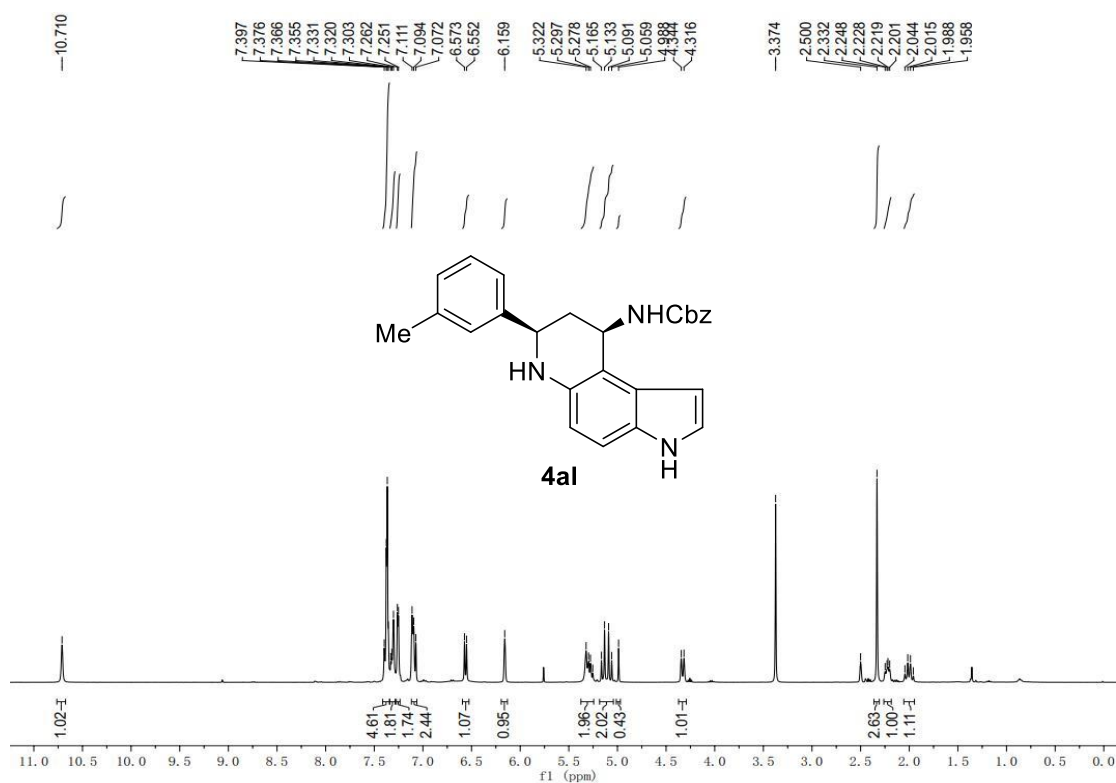
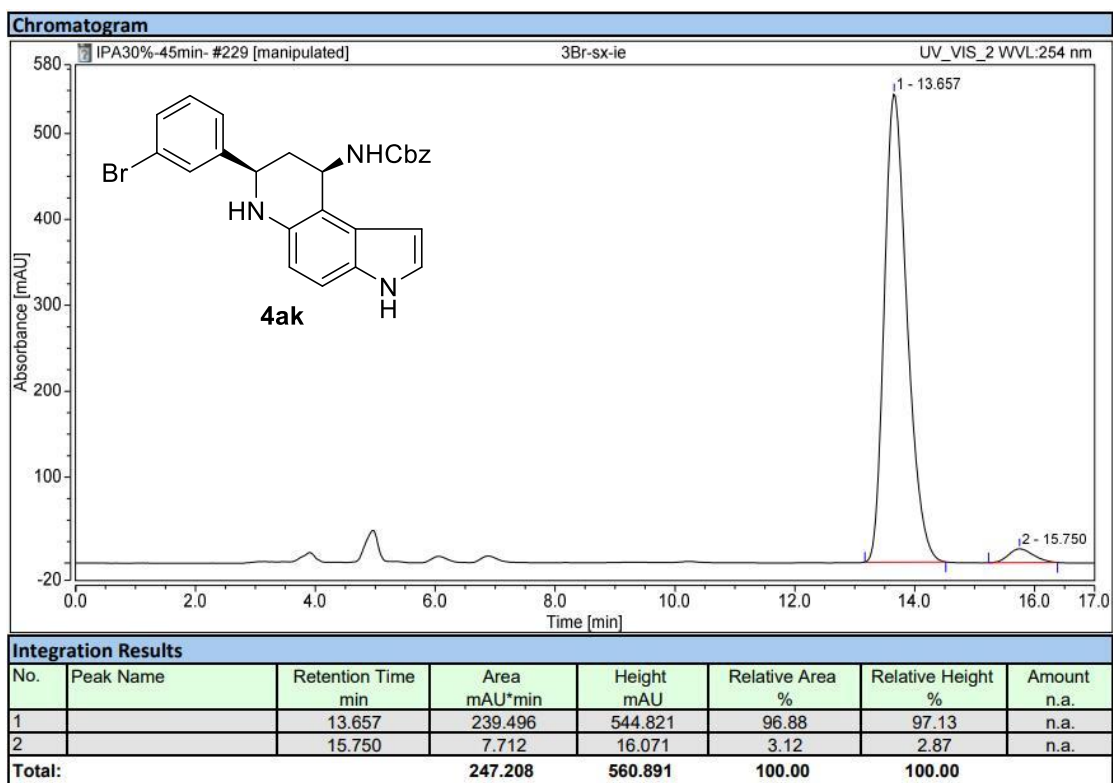


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ak

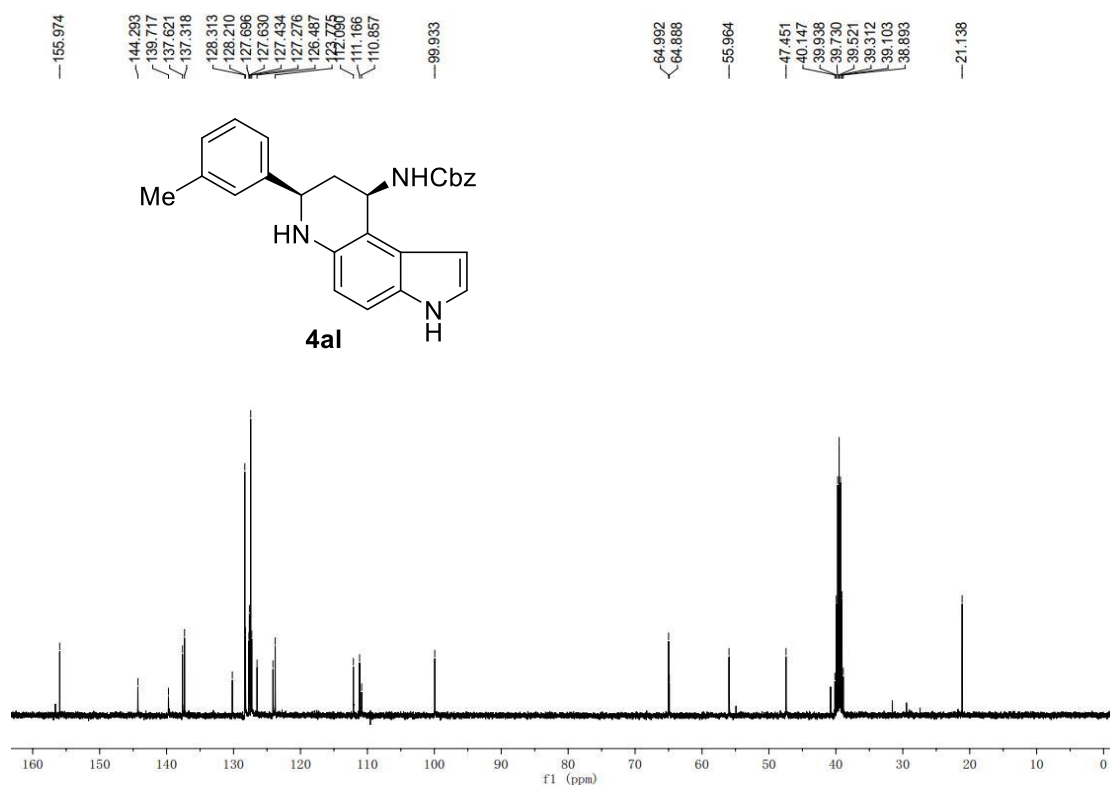


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ak**

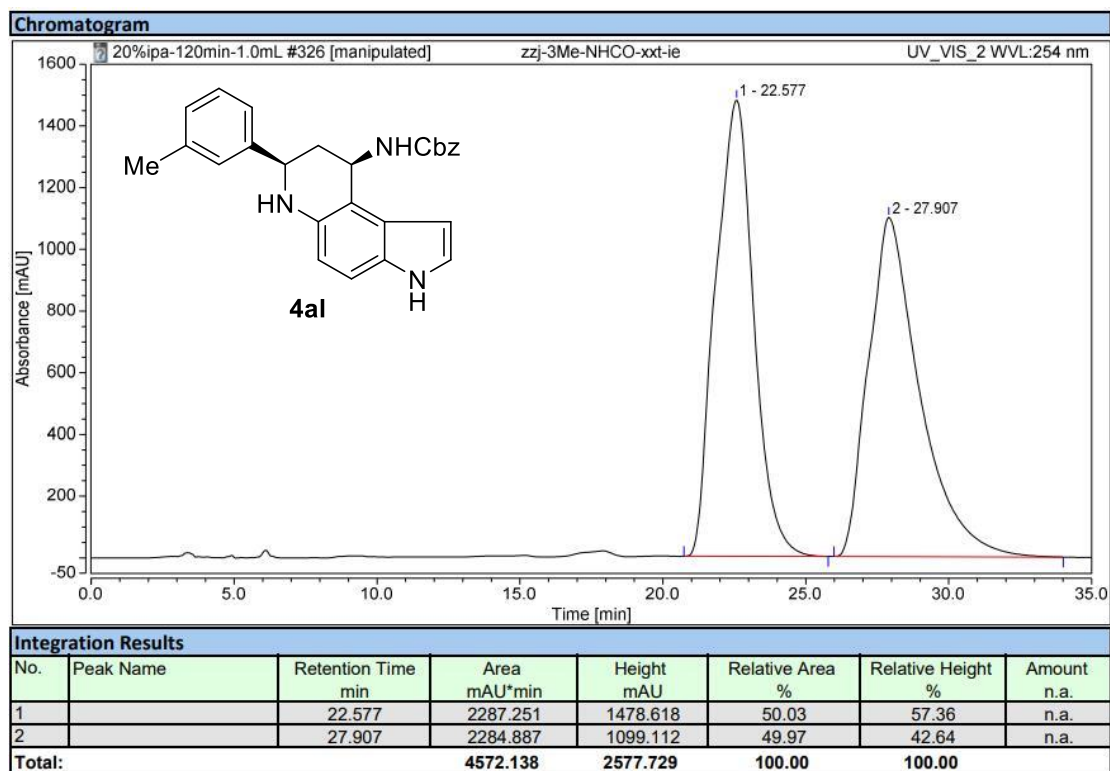


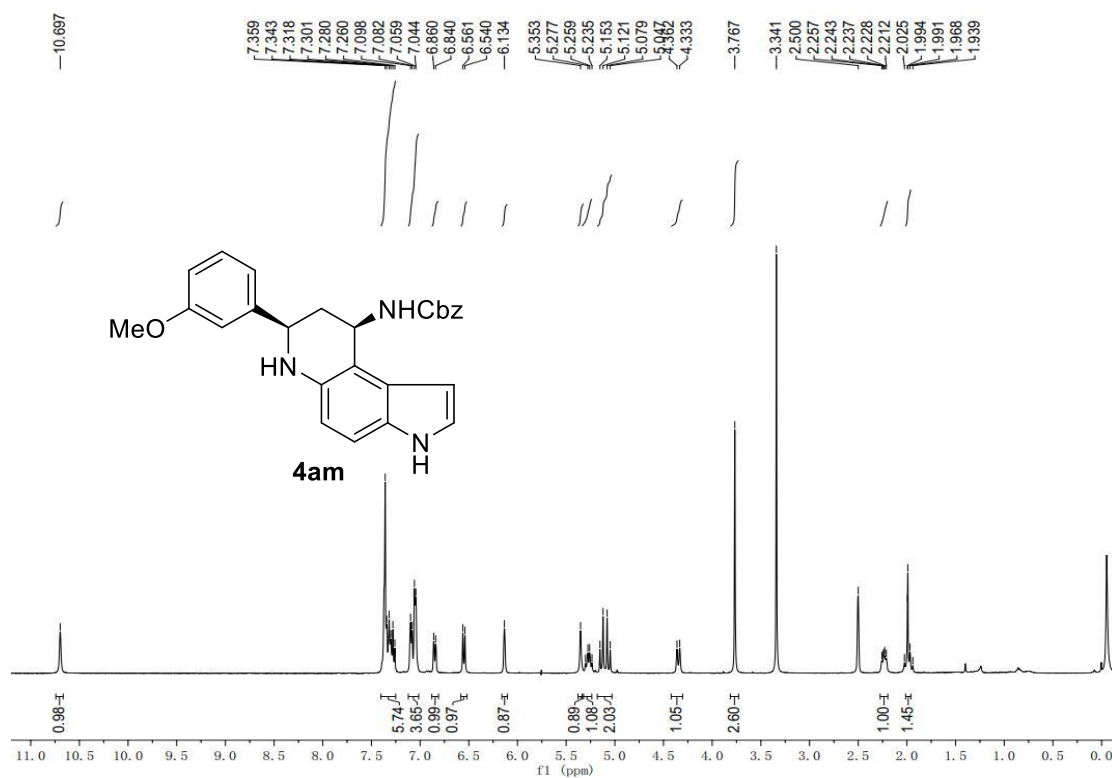
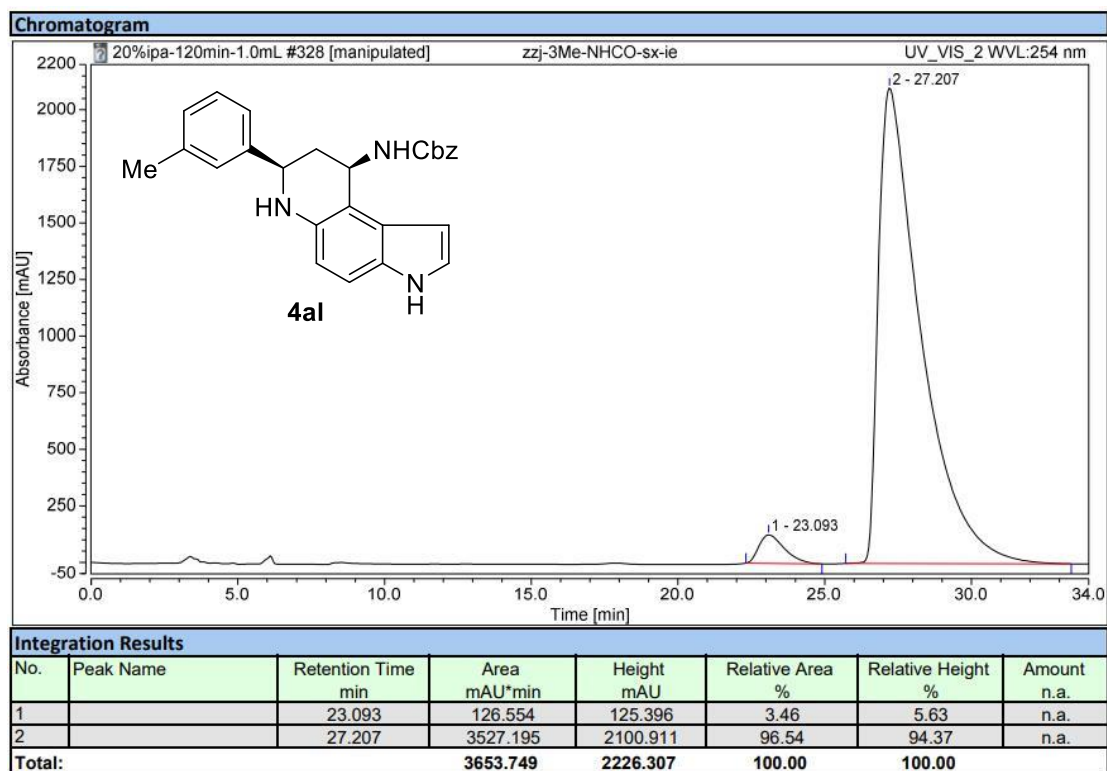


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4al



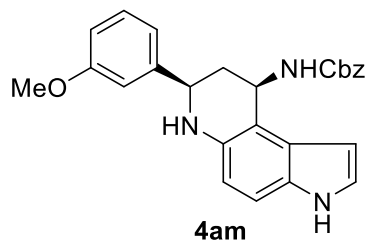
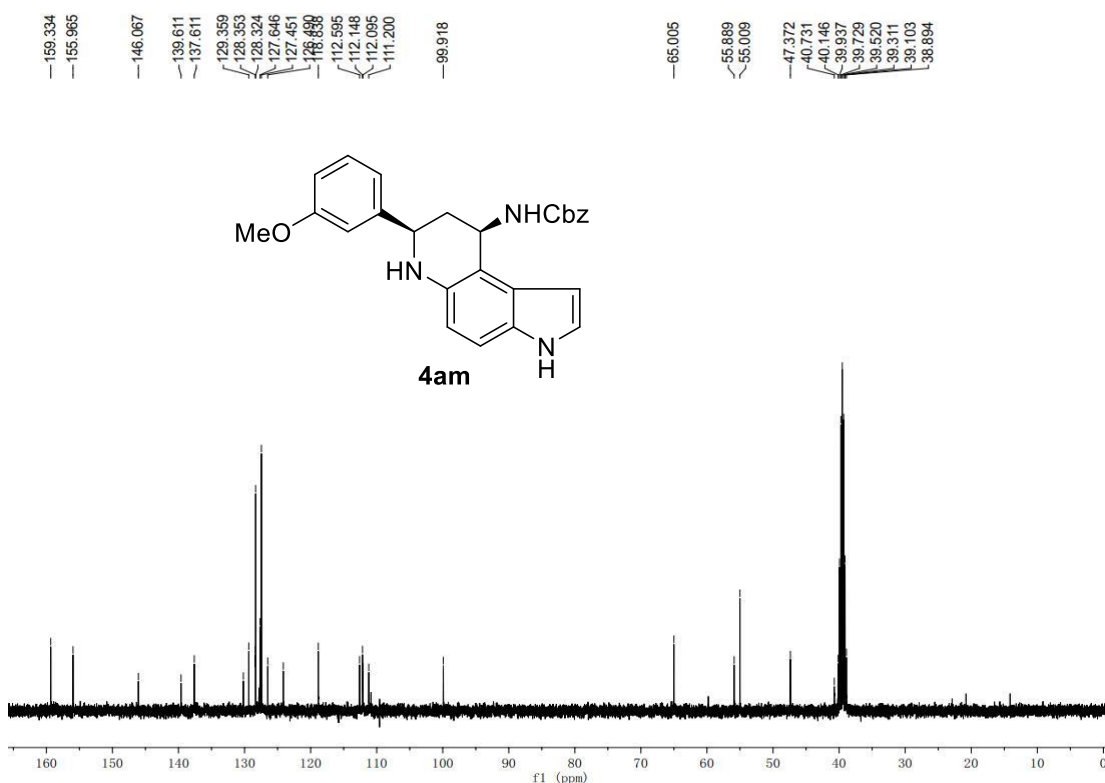
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4a1**



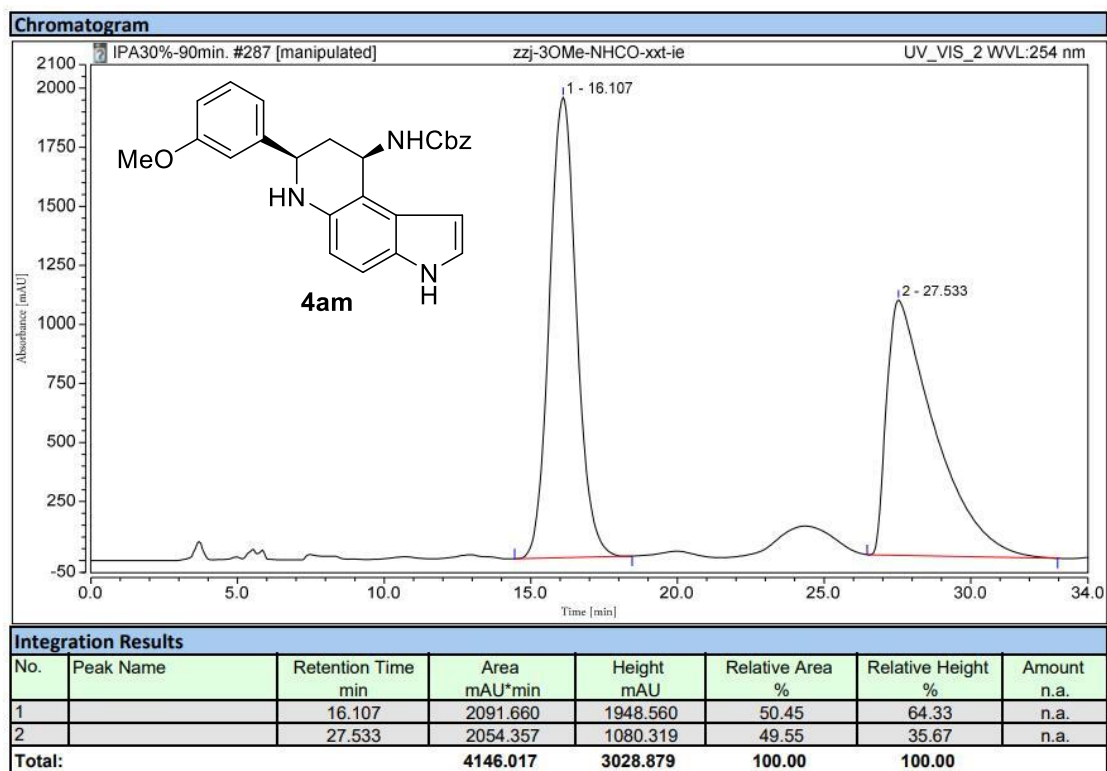


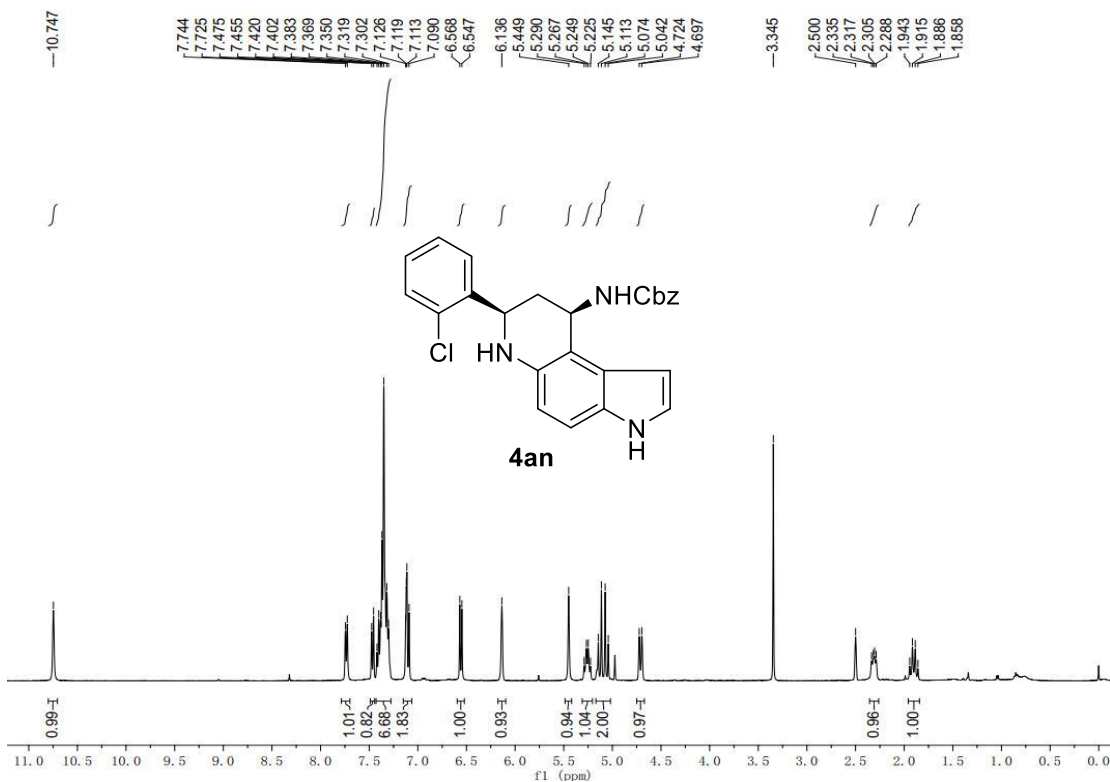
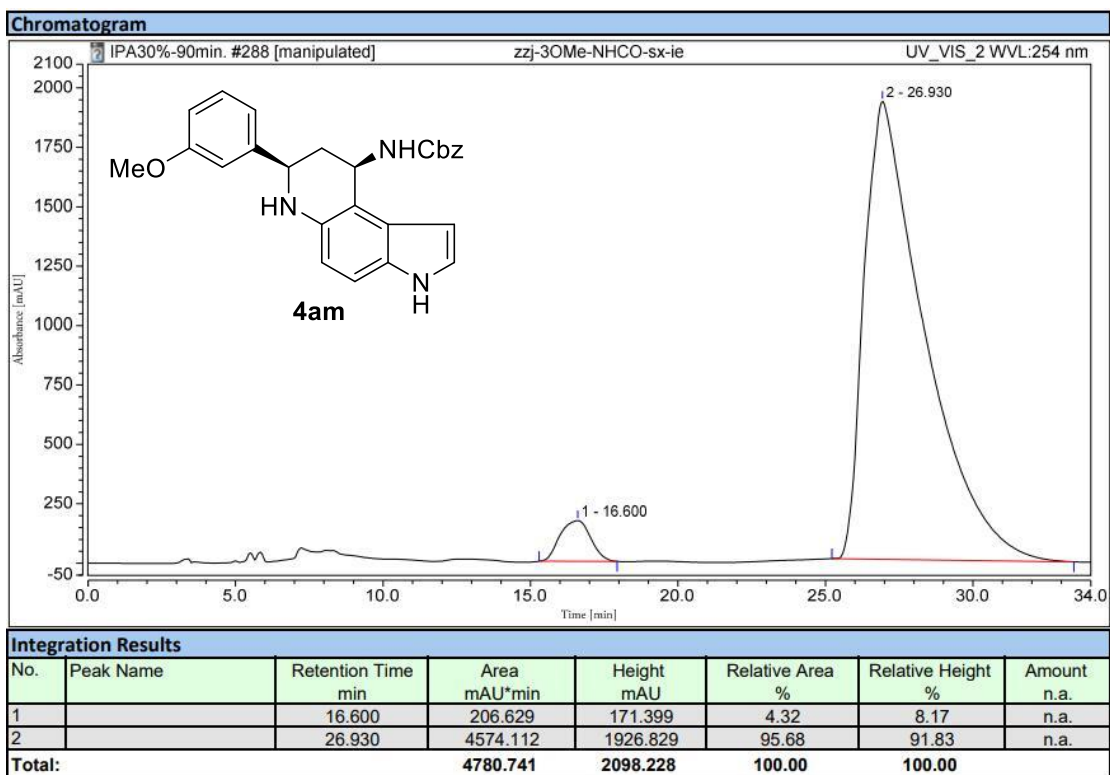
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4am

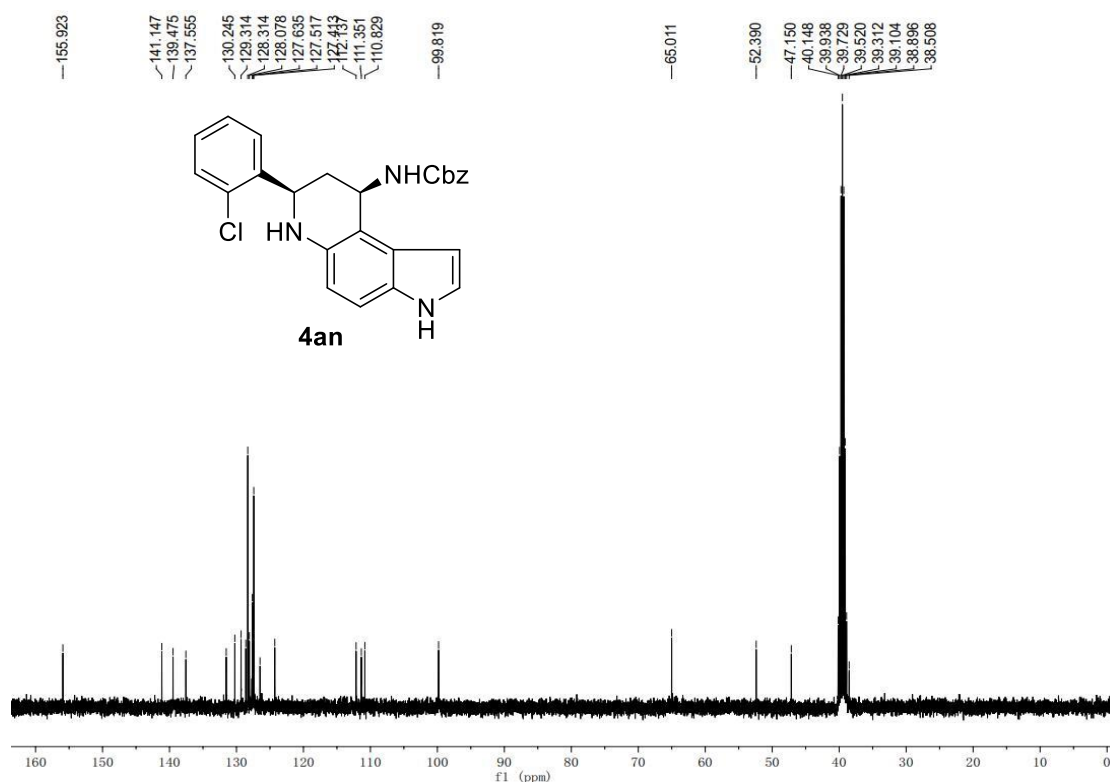




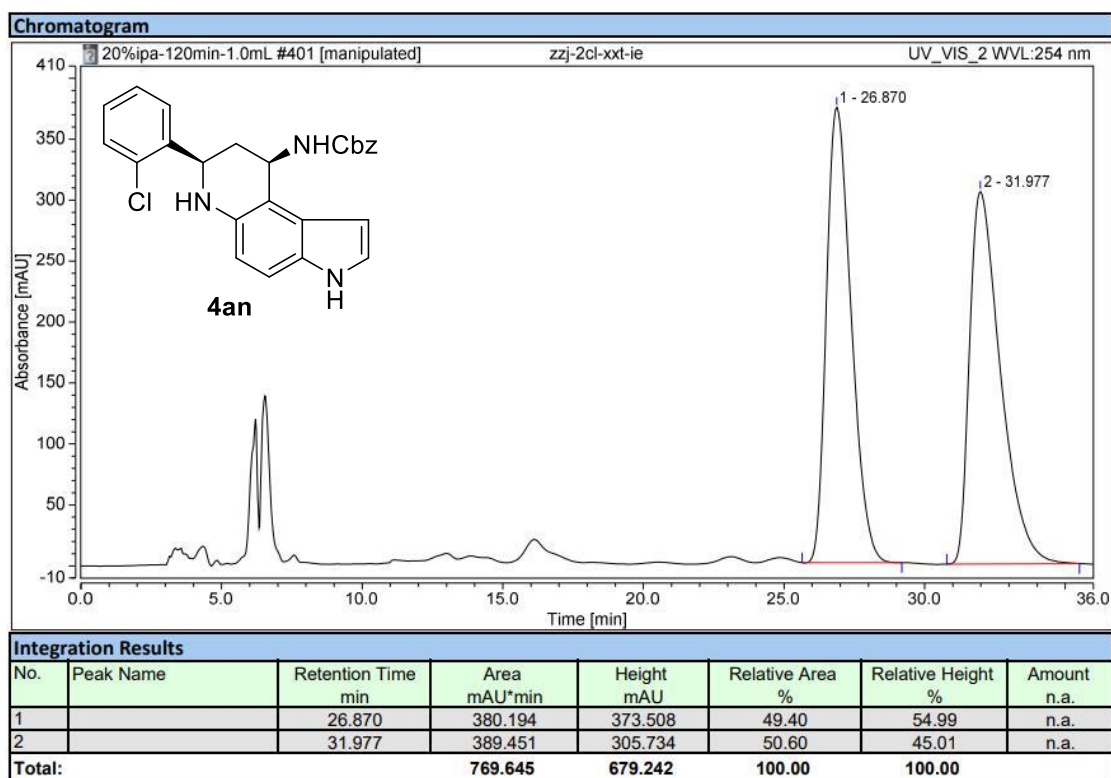
$^{13}\text{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>) of **4am**

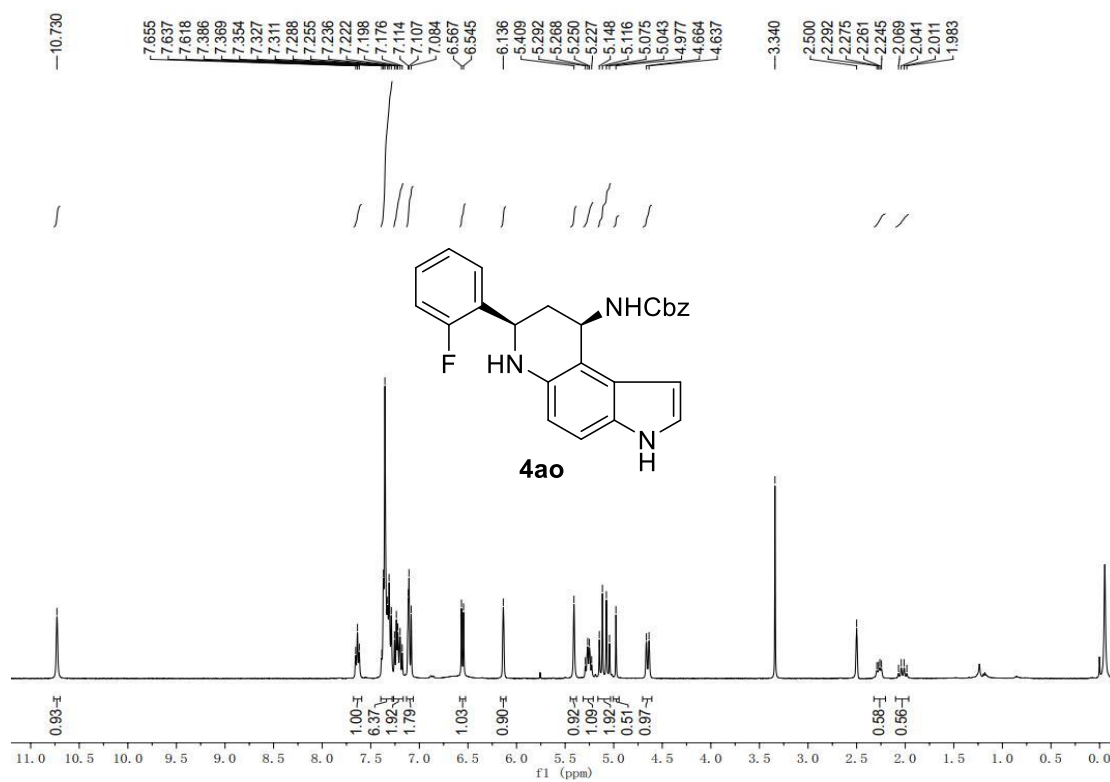
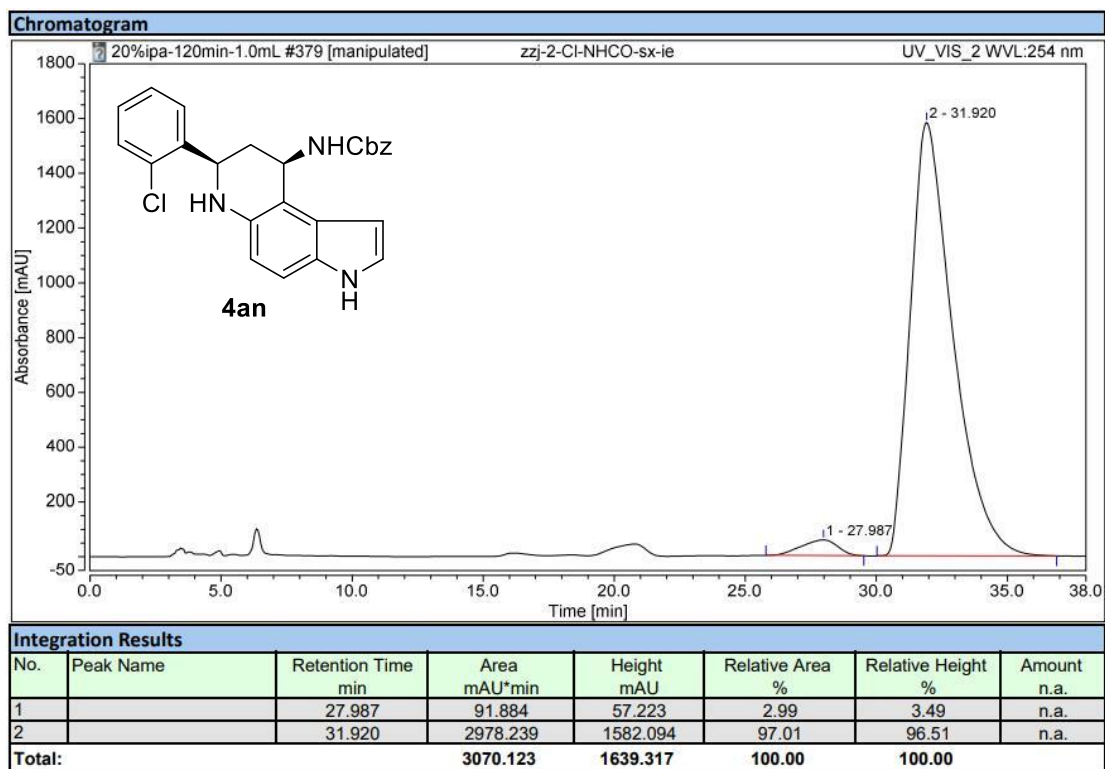




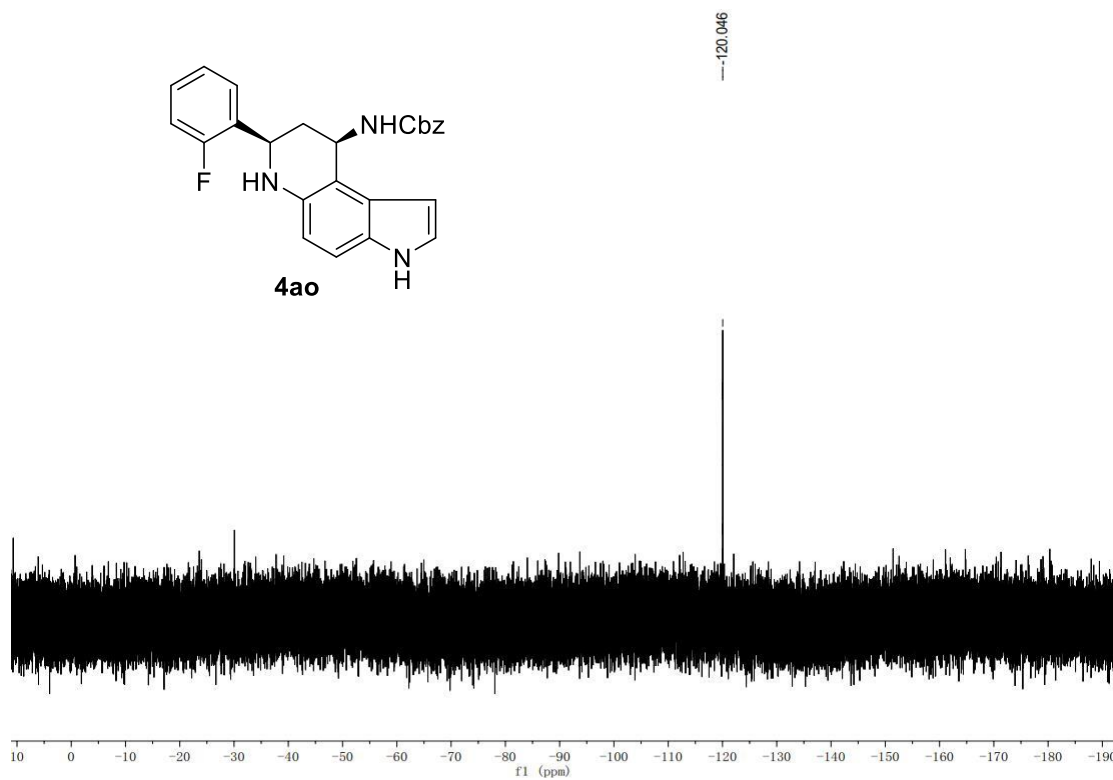
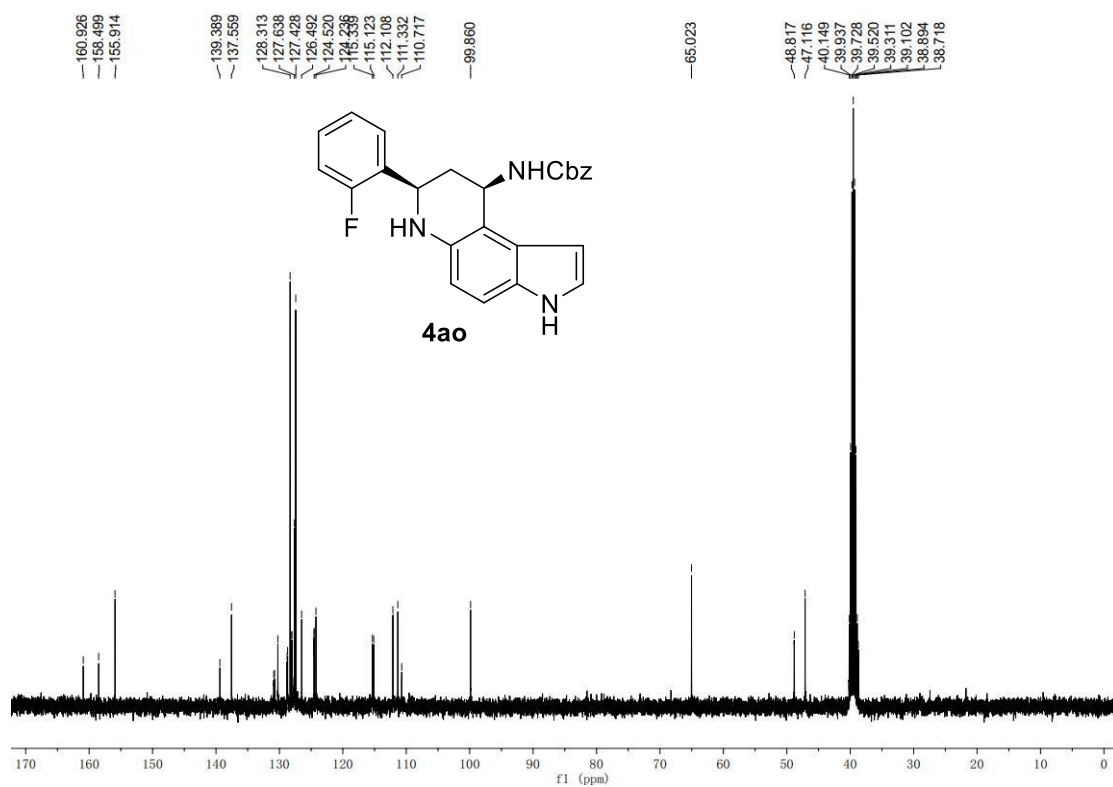


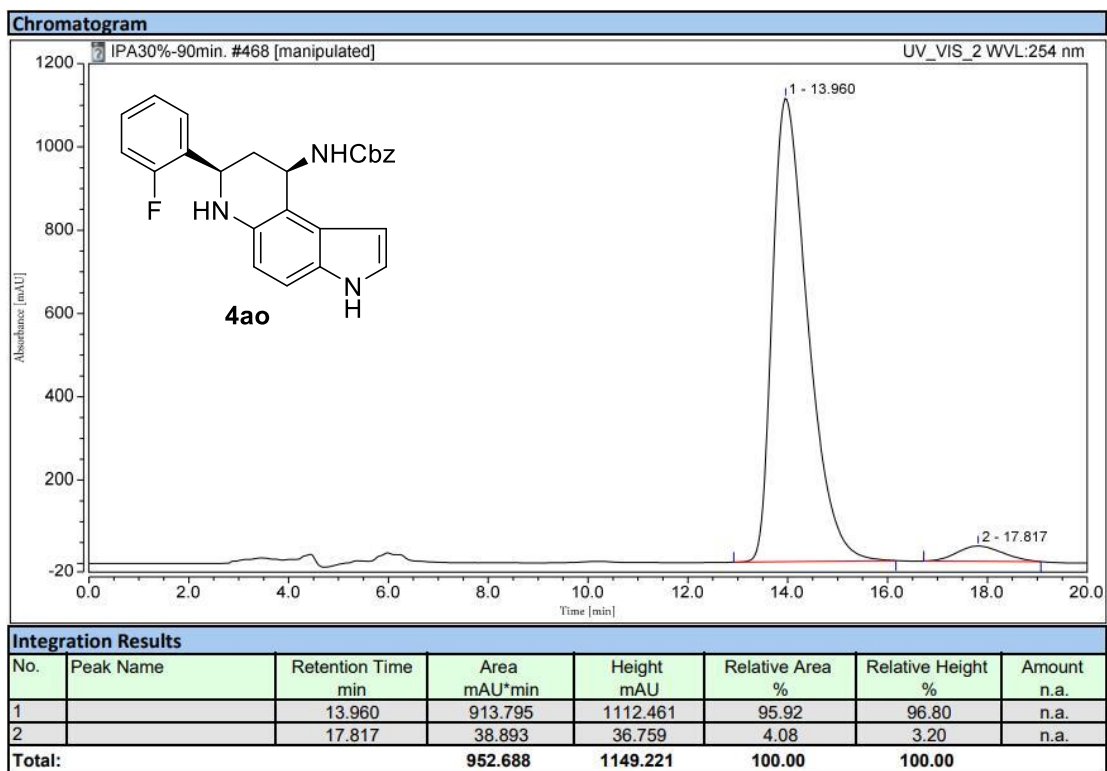
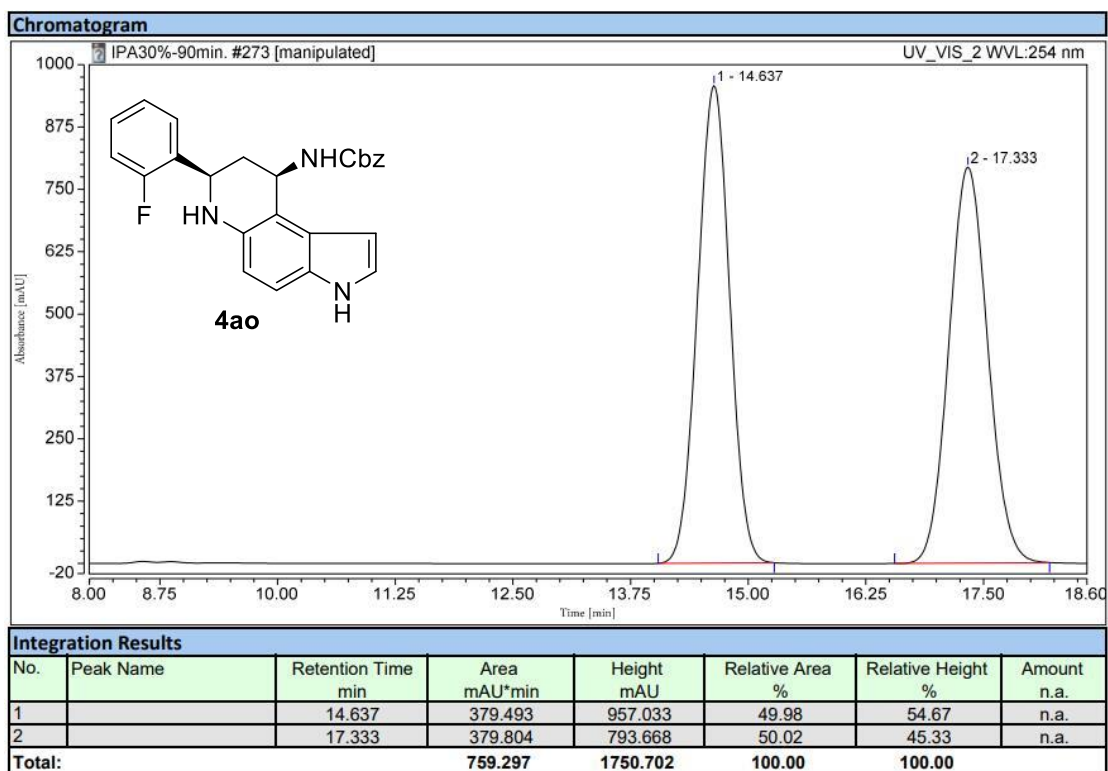
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4an

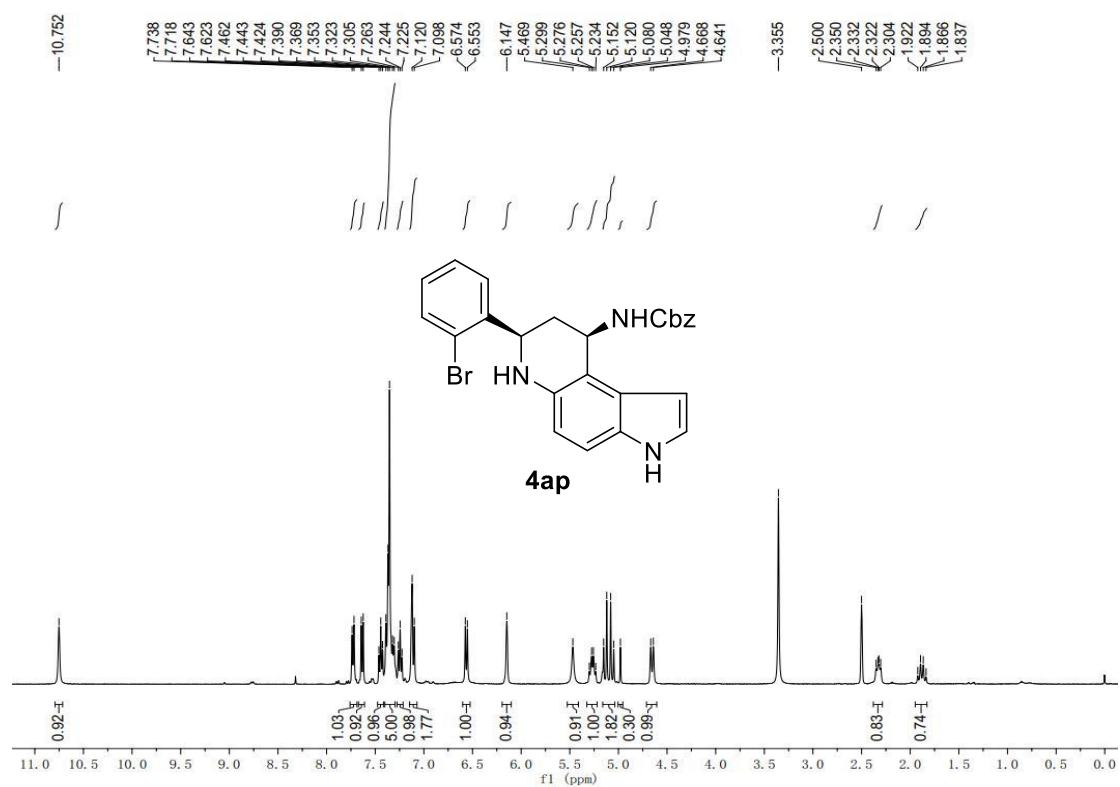




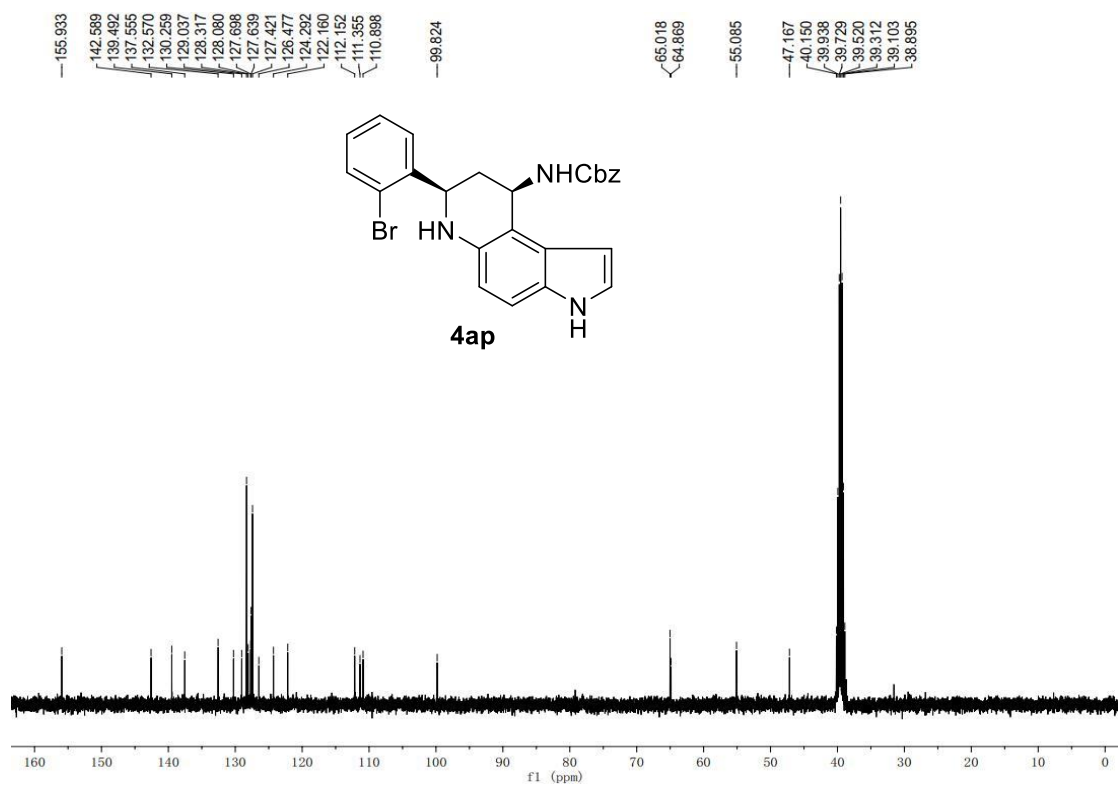
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ao



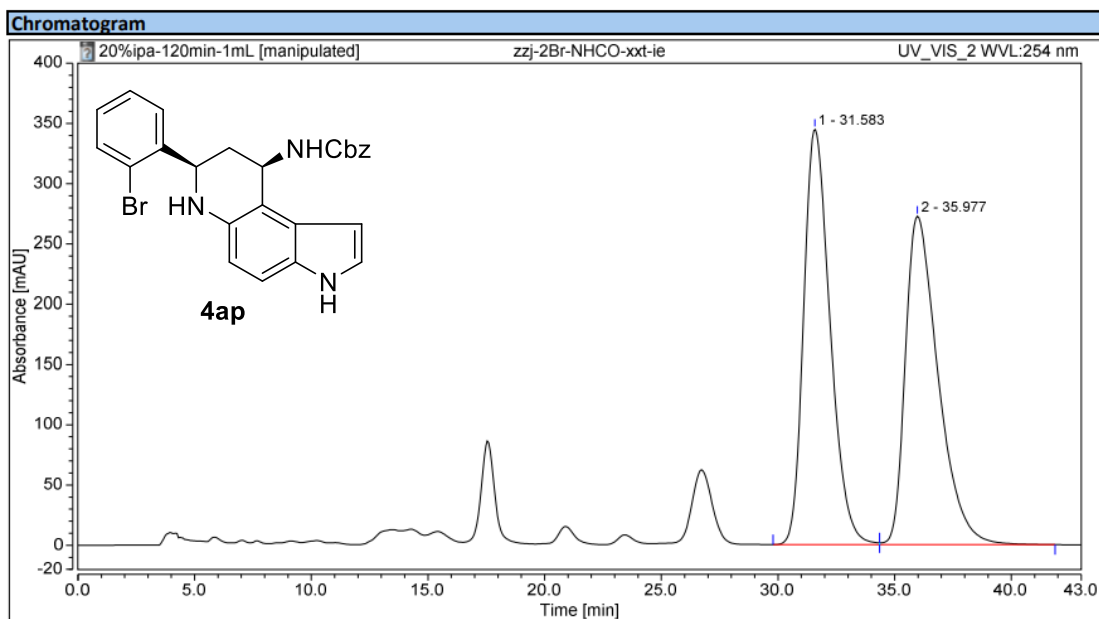




**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ap**

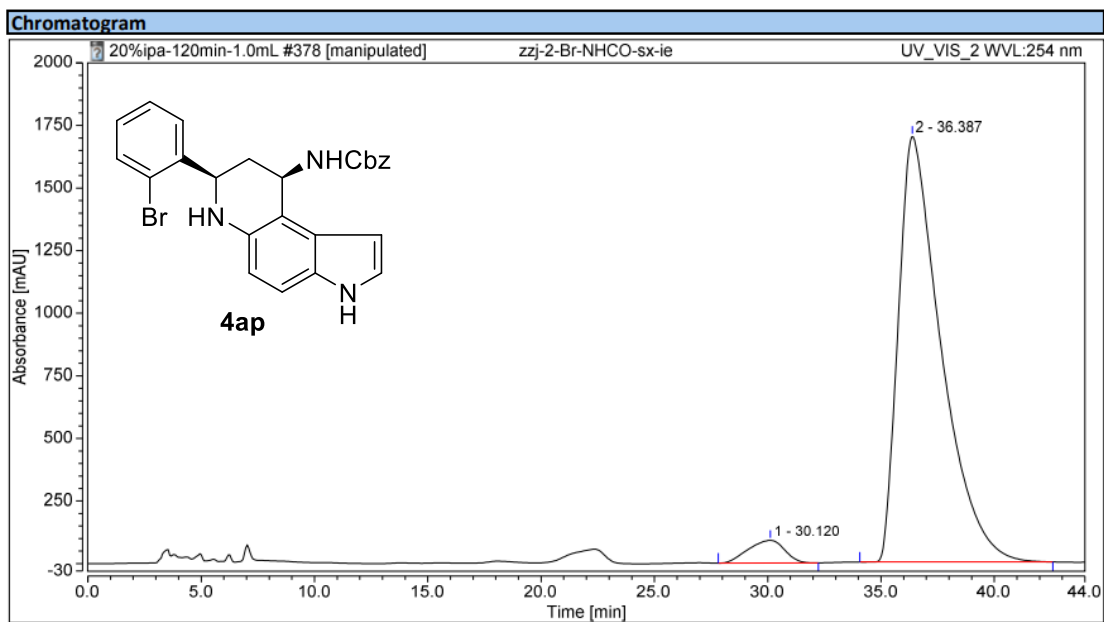


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ap**



**Integration Results**

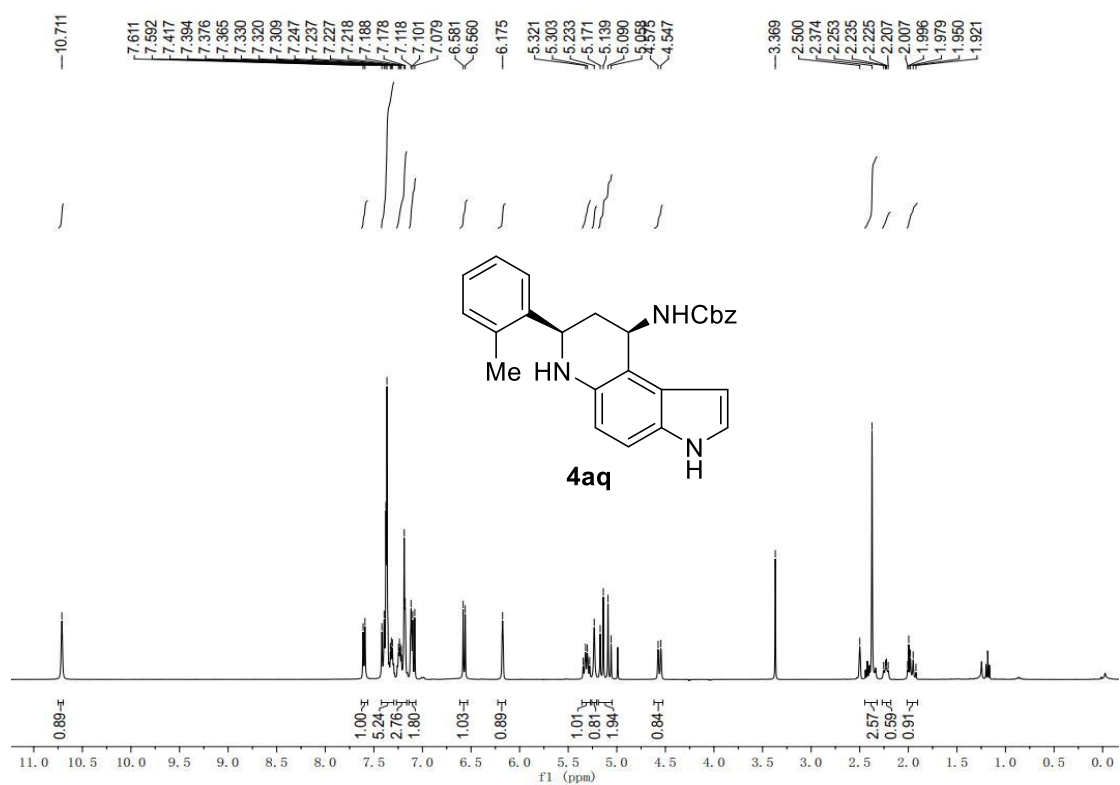
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		31.583	452.312	344.799	50.49	55.85	n.a.
2		35.977	443.461	272.558	49.51	44.15	n.a.
<b>Total:</b>			<b>895.773</b>	<b>617.357</b>	<b>100.00</b>	<b>100.00</b>	



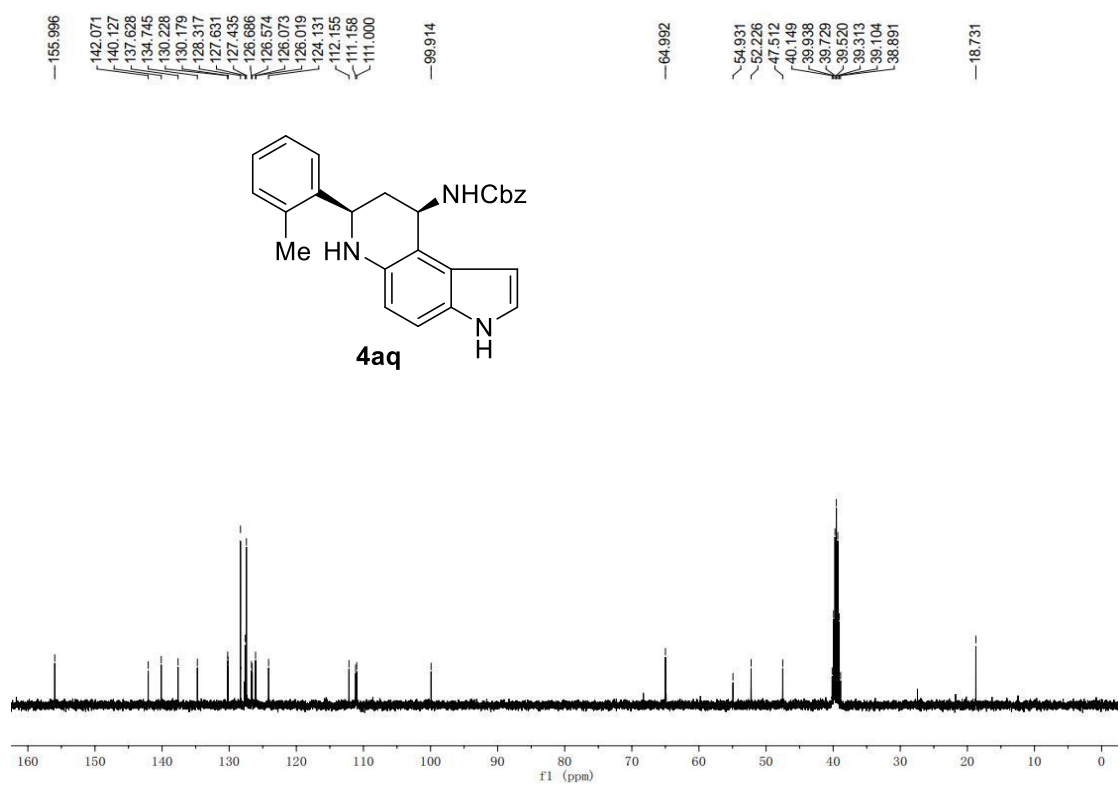
**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		30.120	168.598	90.741	4.35	5.07	n.a.
2		36.387	3707.007	1700.558	95.65	94.93	n.a.
<b>Total:</b>			<b>3875.605</b>	<b>1791.299</b>	<b>100.00</b>	<b>100.00</b>	

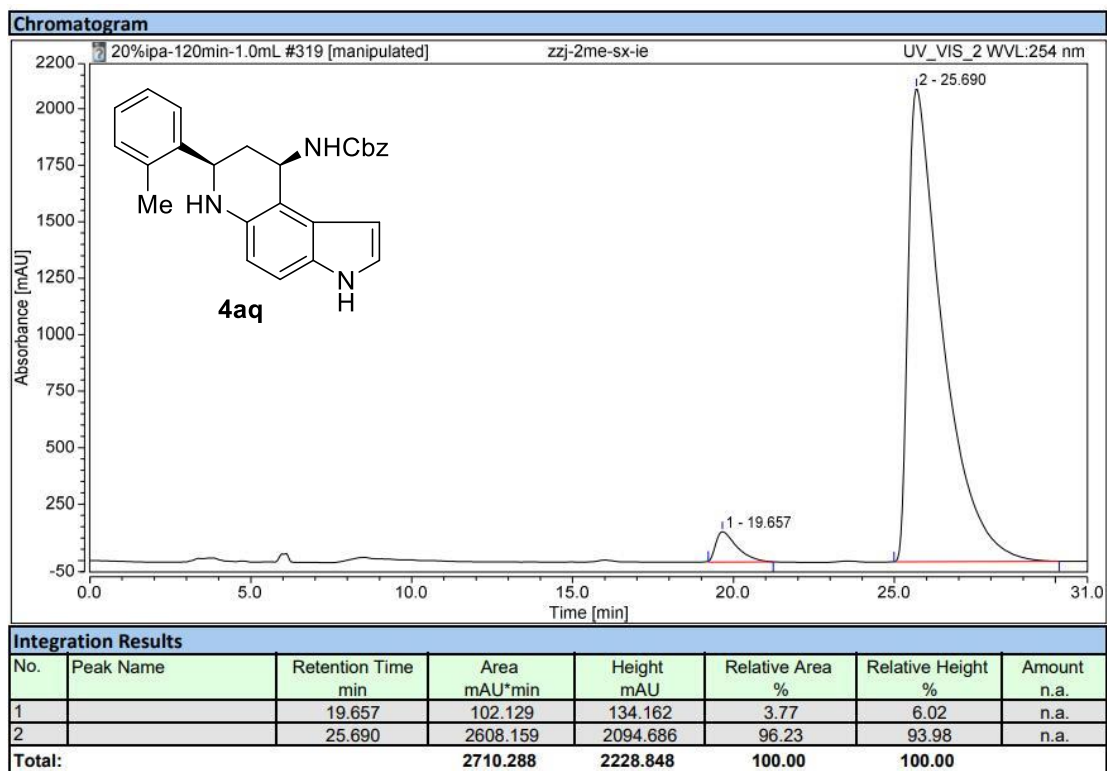
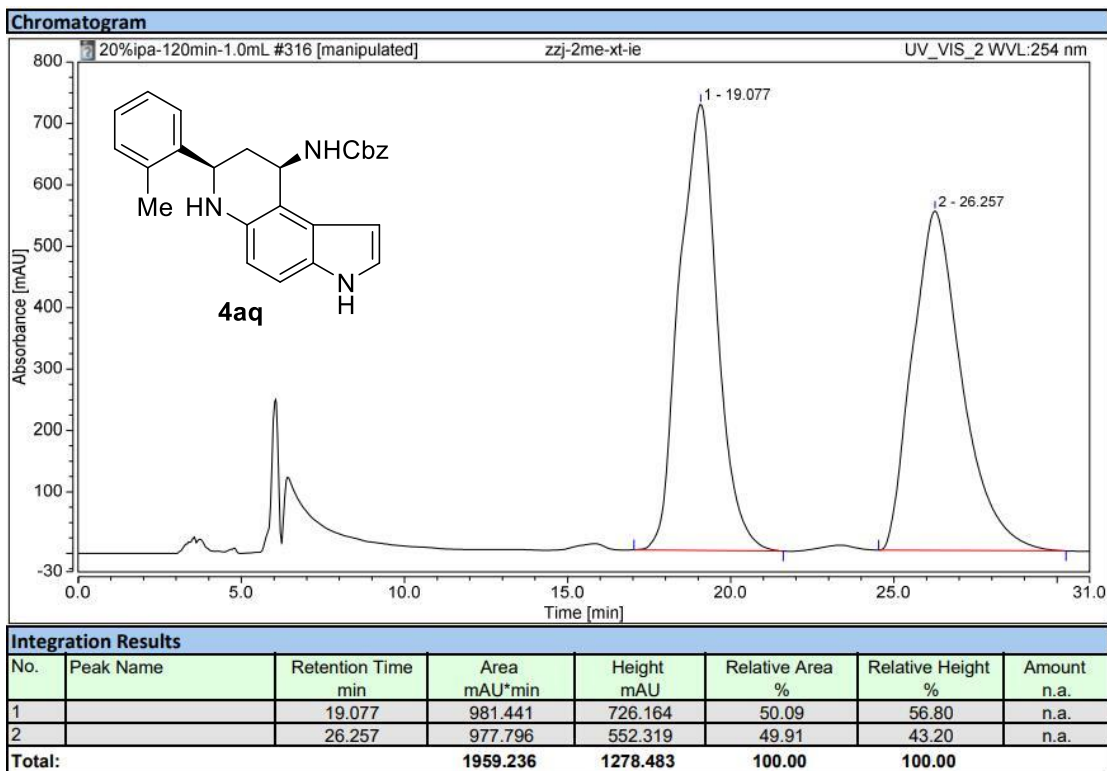


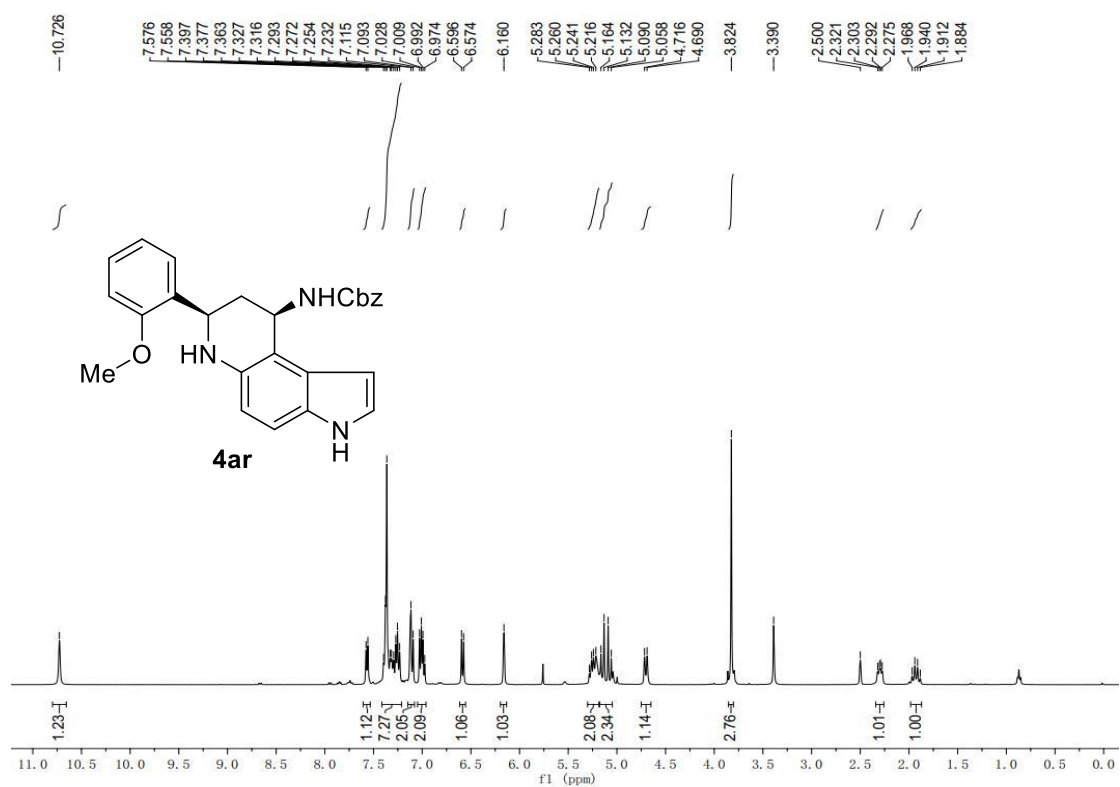


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4aq**

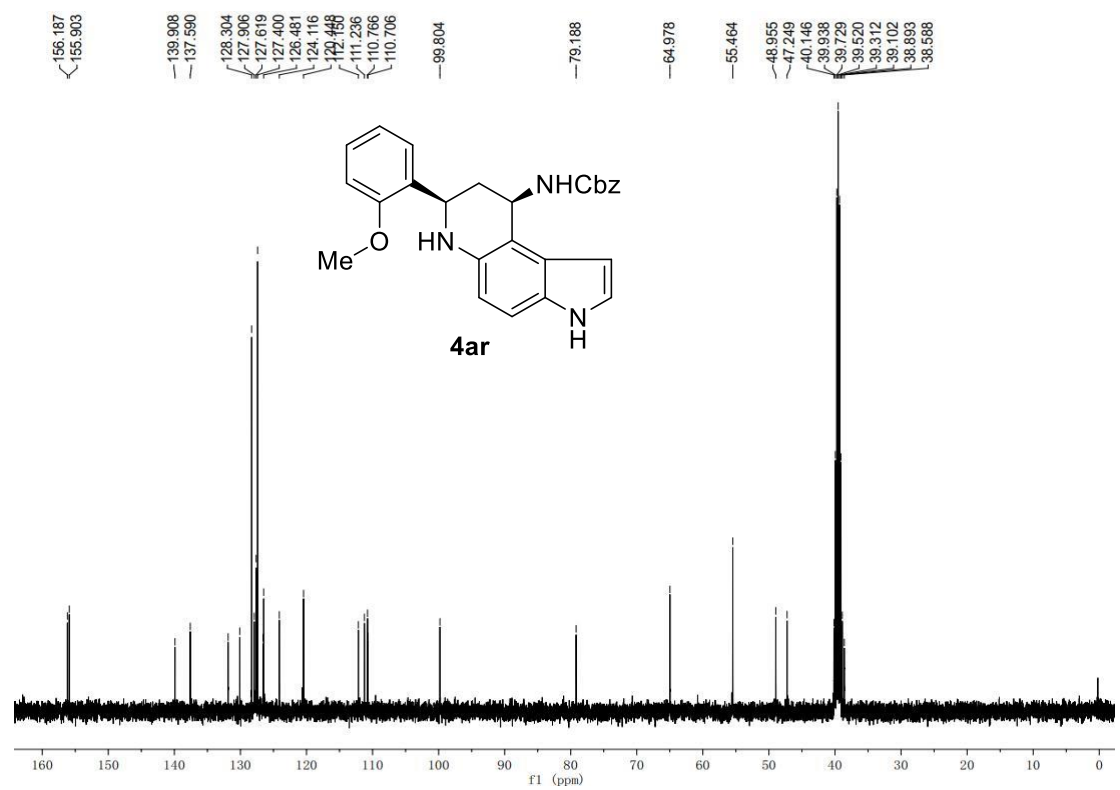


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4aq**

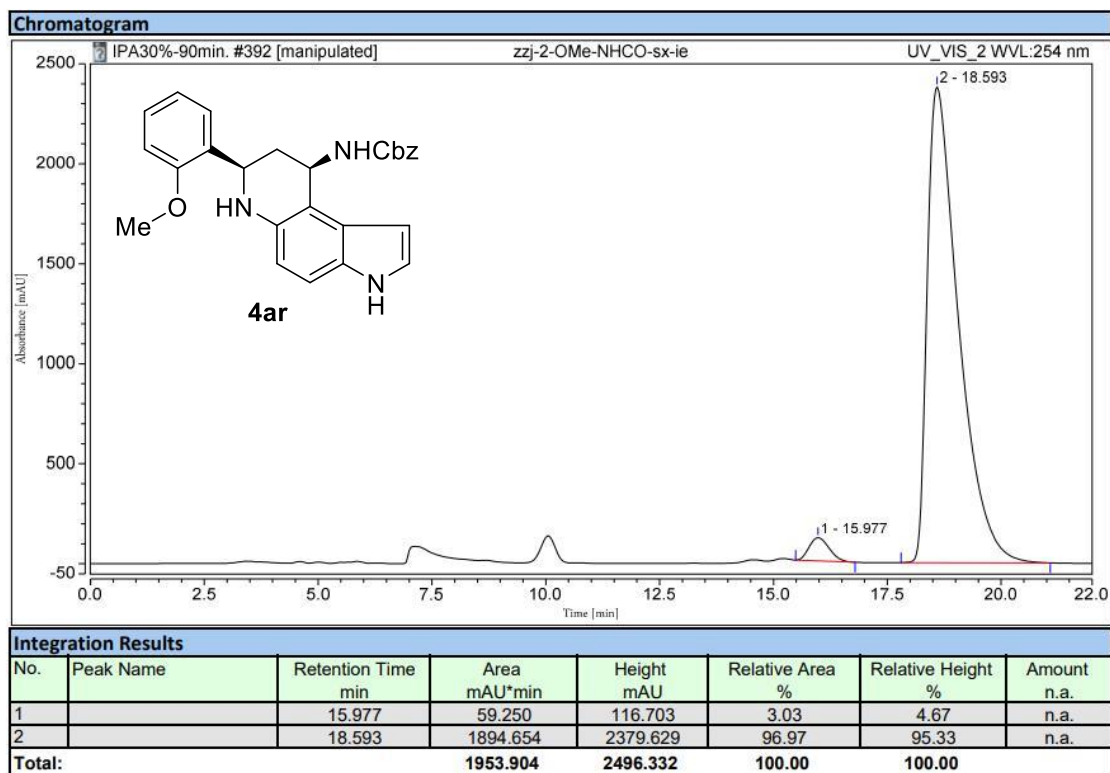
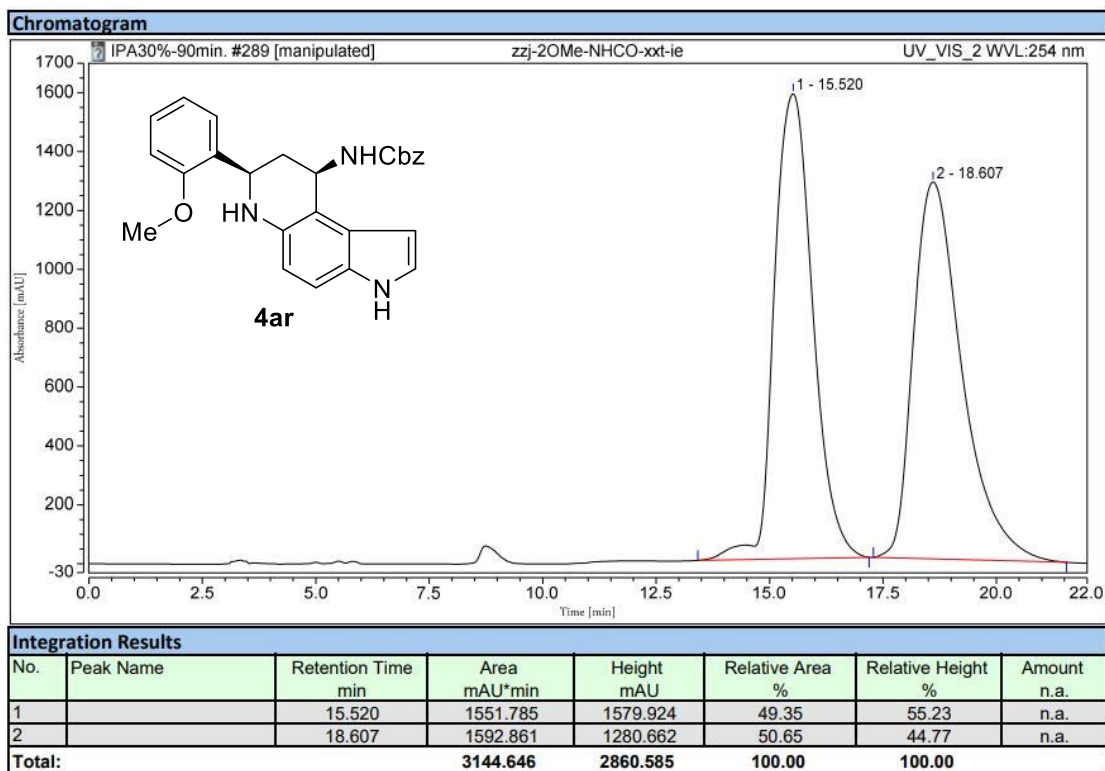


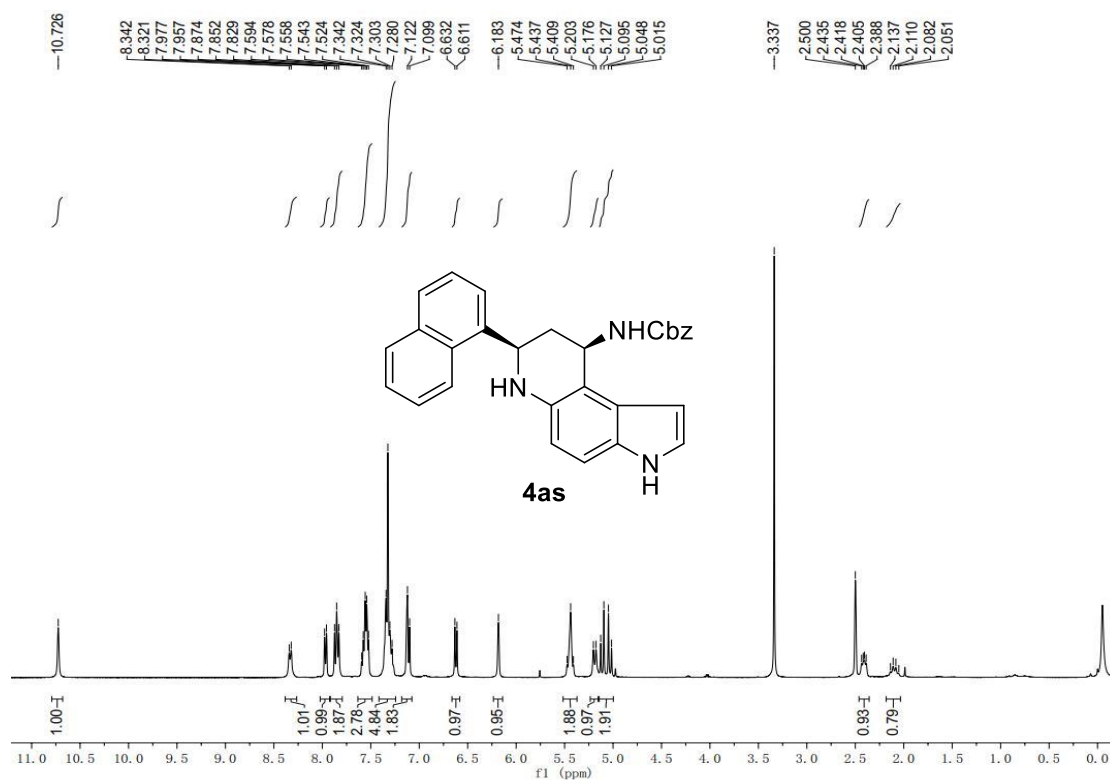


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ar**

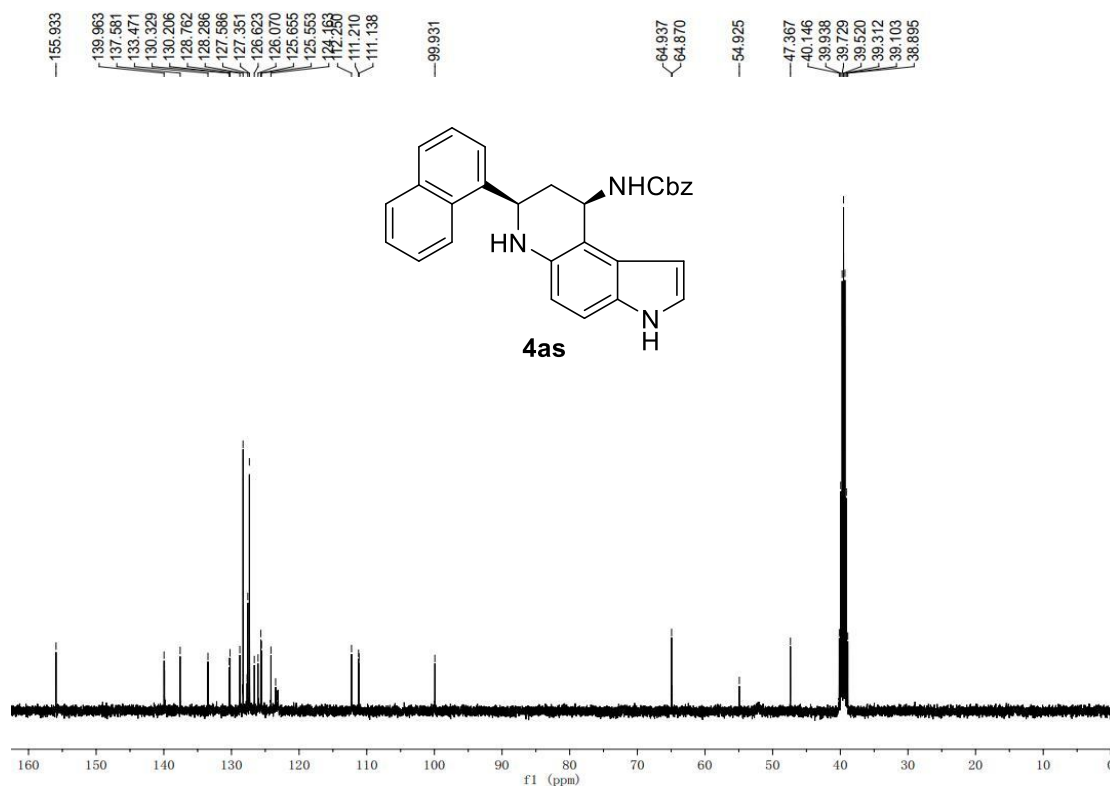


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ar**

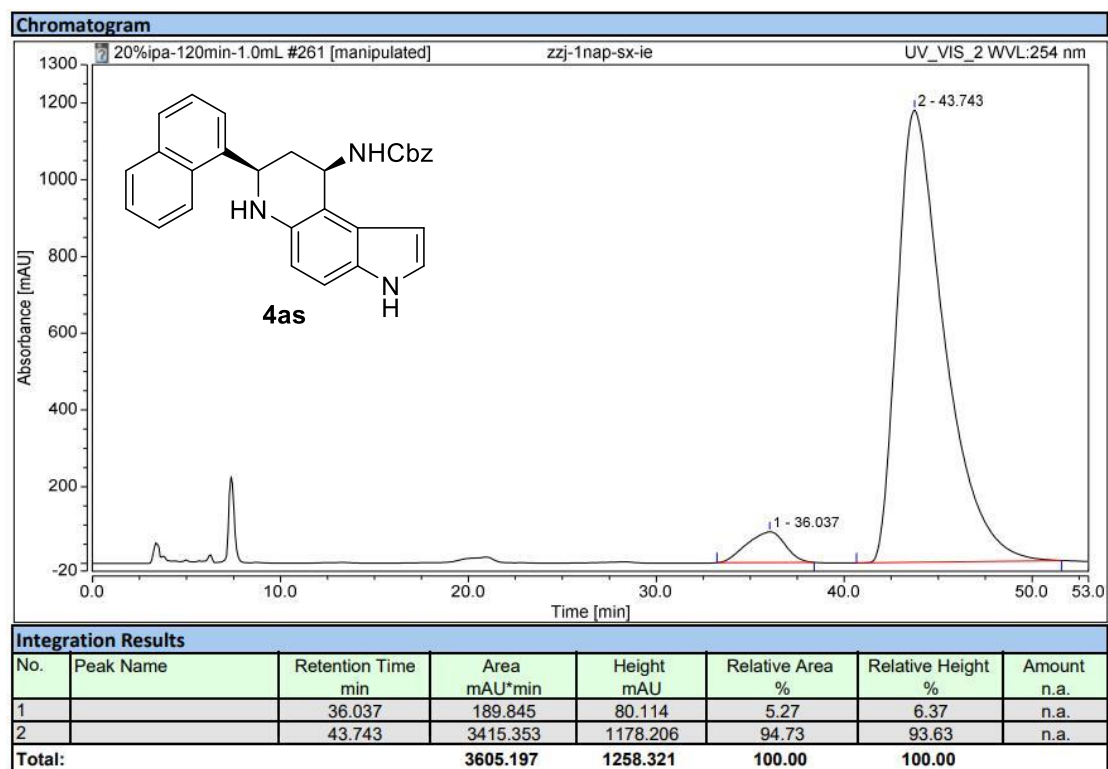
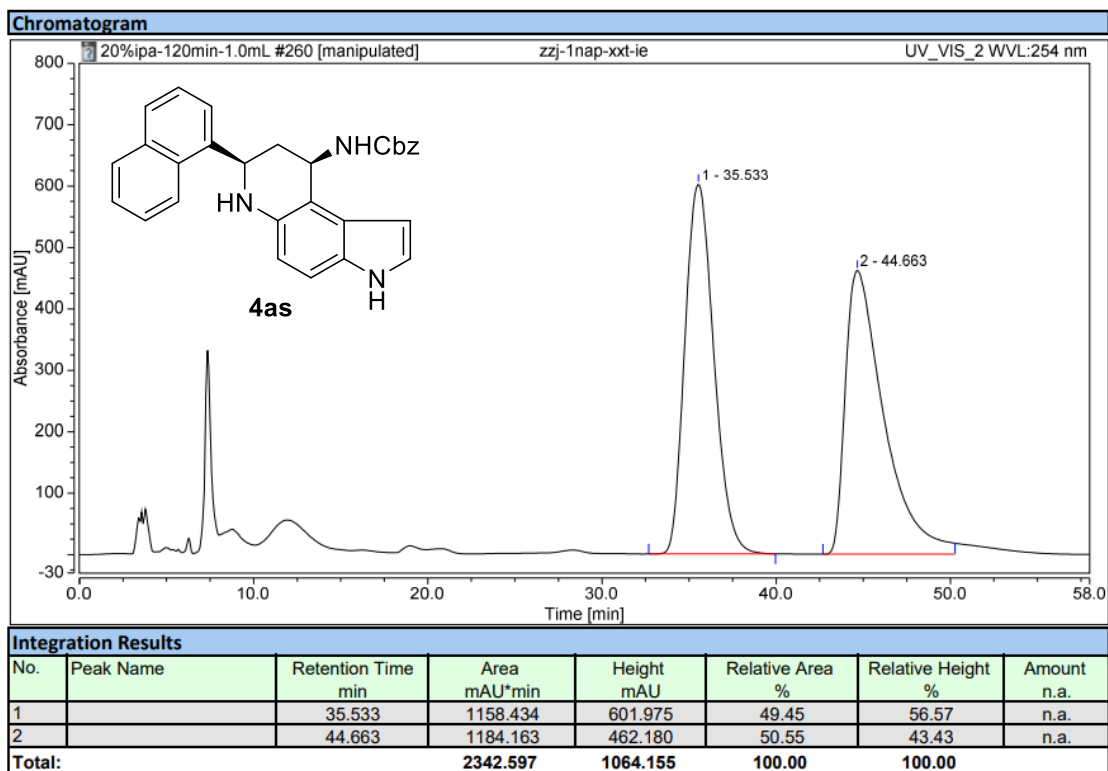


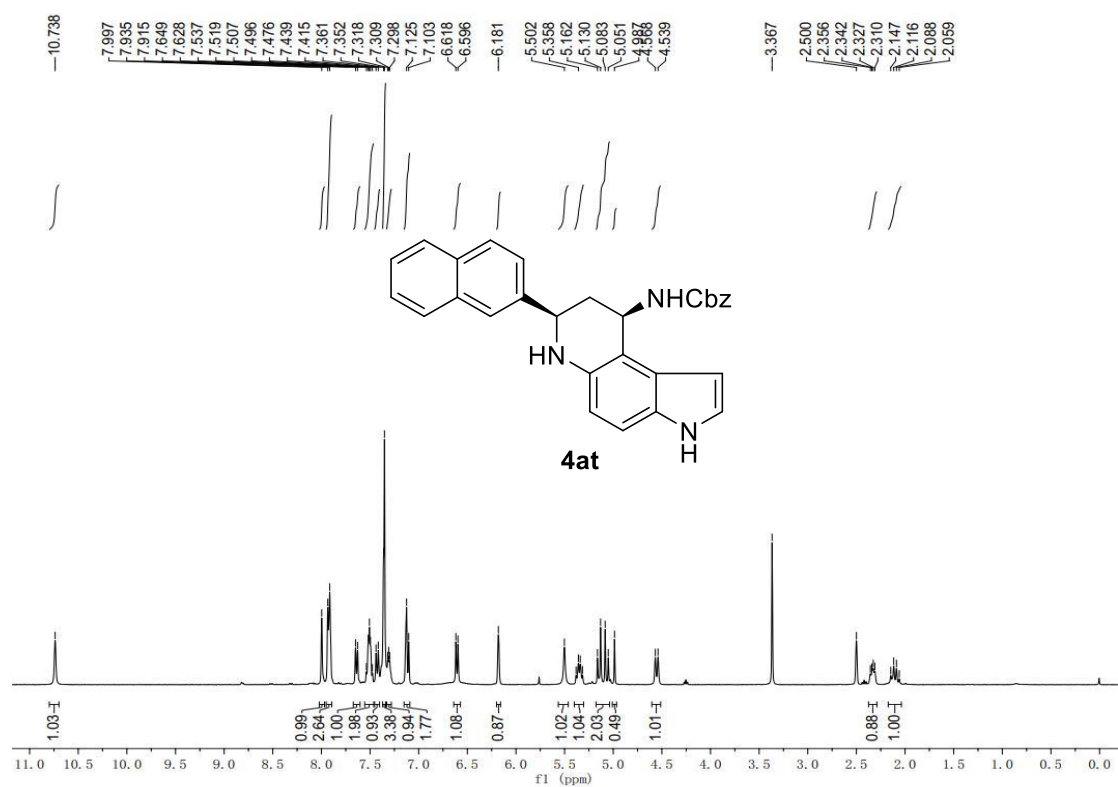


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4as**

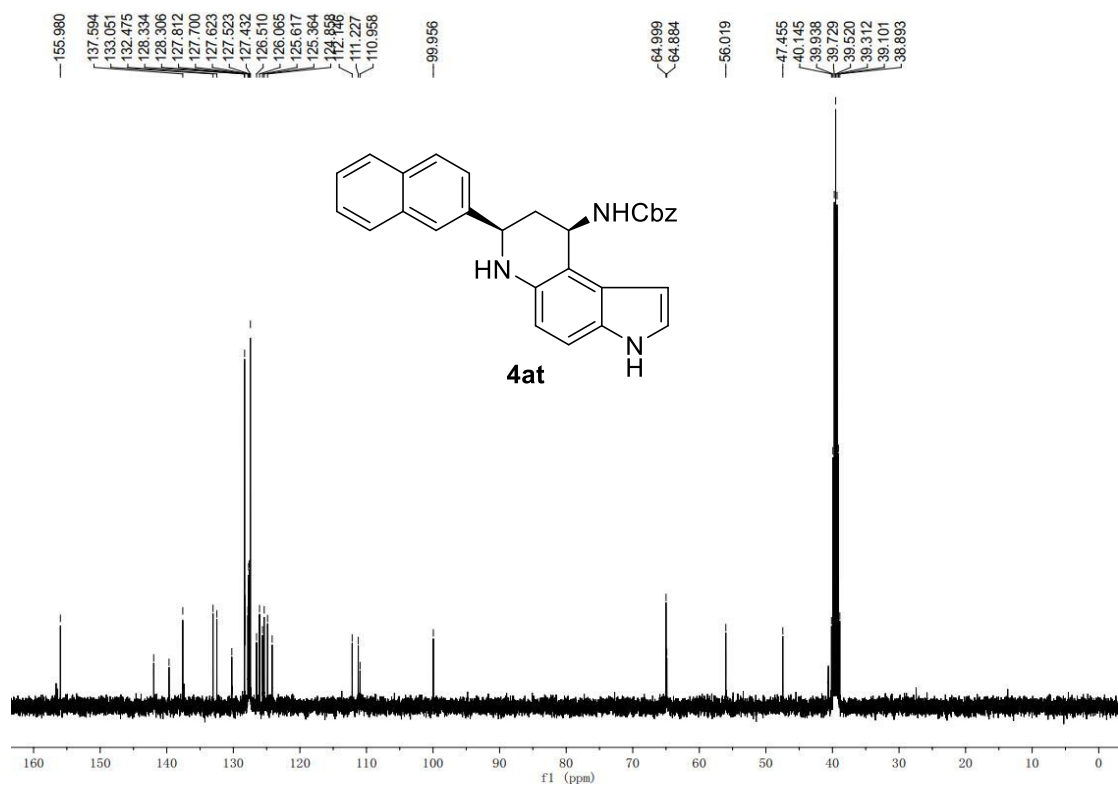


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4as**





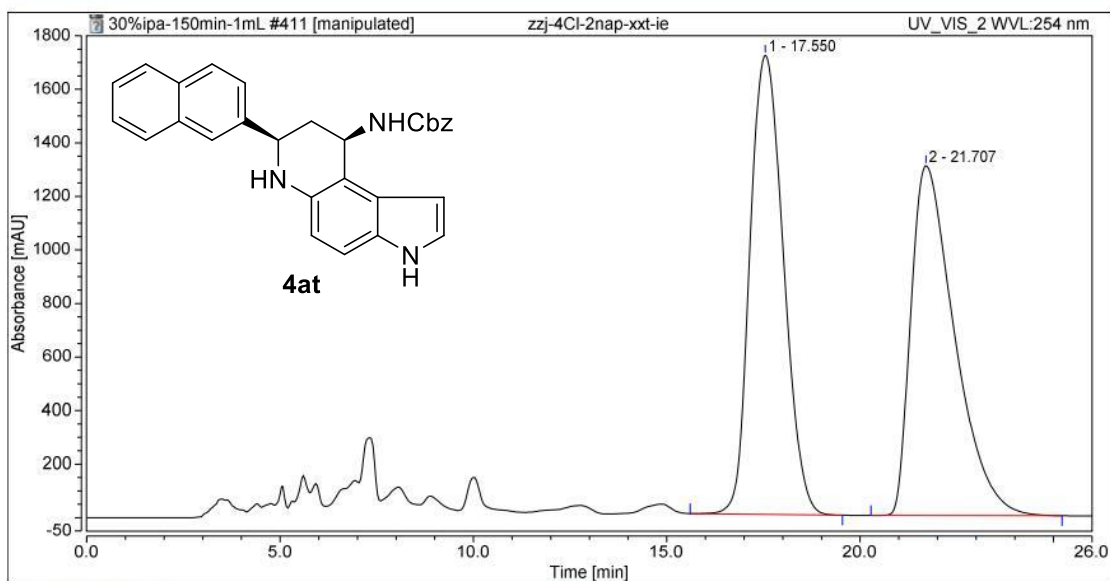
**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4at**



**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4at**



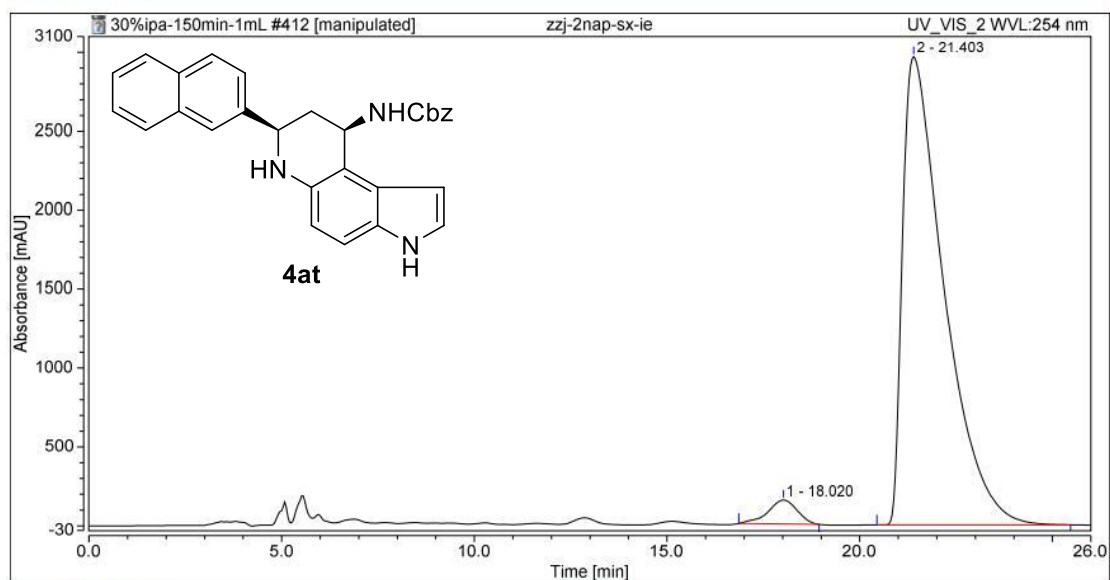
**Chromatogram**



**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.550	1720.961	1715.432	50.23	56.77	n.a.
2		21.707	1705.313	1306.368	49.77	43.23	n.a.
<b>Total:</b>			<b>3426.274</b>	<b>3021.800</b>	<b>100.00</b>	<b>100.00</b>	

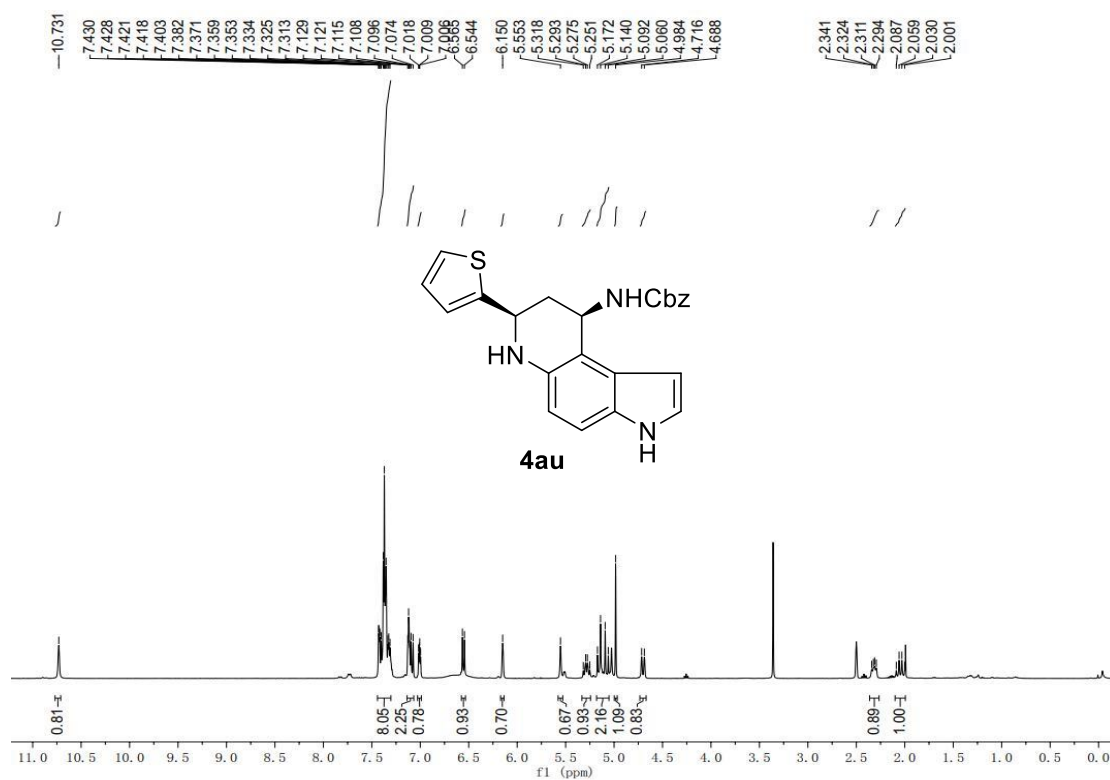
**Chromatogram**



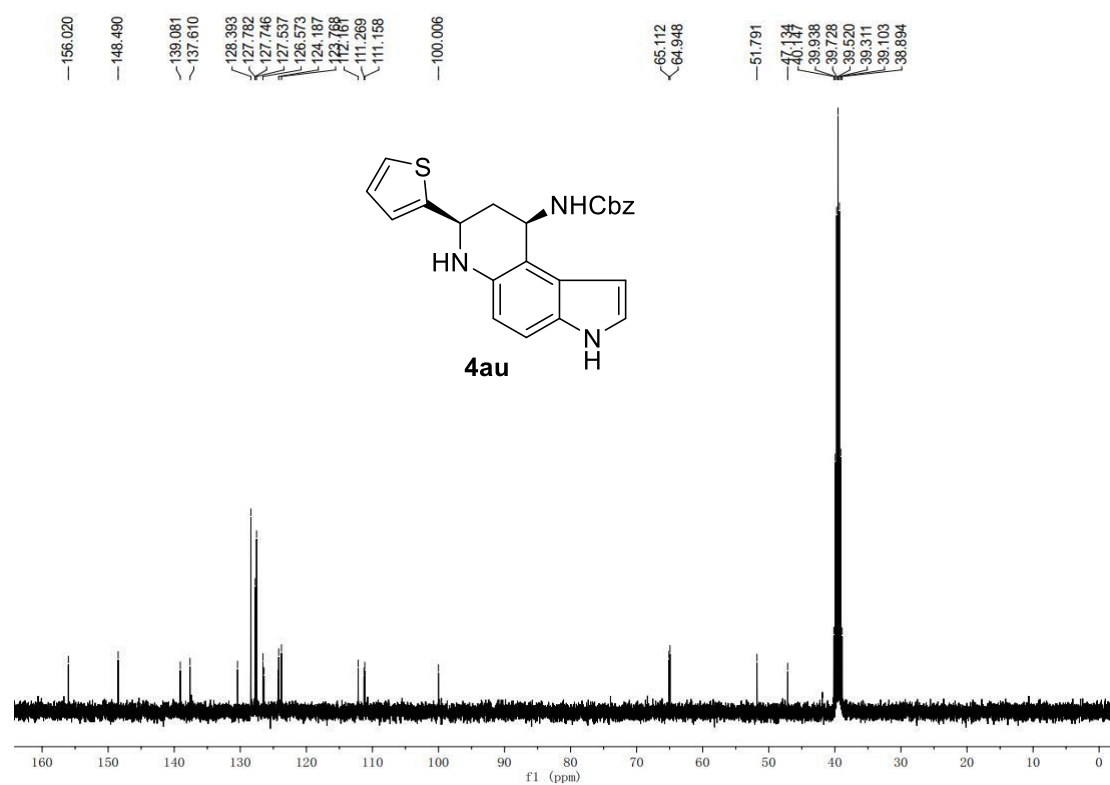
**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.020	132.259	151.036	3.45	4.84	n.a.
2		21.403	3701.505	2967.218	96.55	95.16	n.a.
<b>Total:</b>			<b>3833.765</b>	<b>3118.255</b>	<b>100.00</b>	<b>100.00</b>	

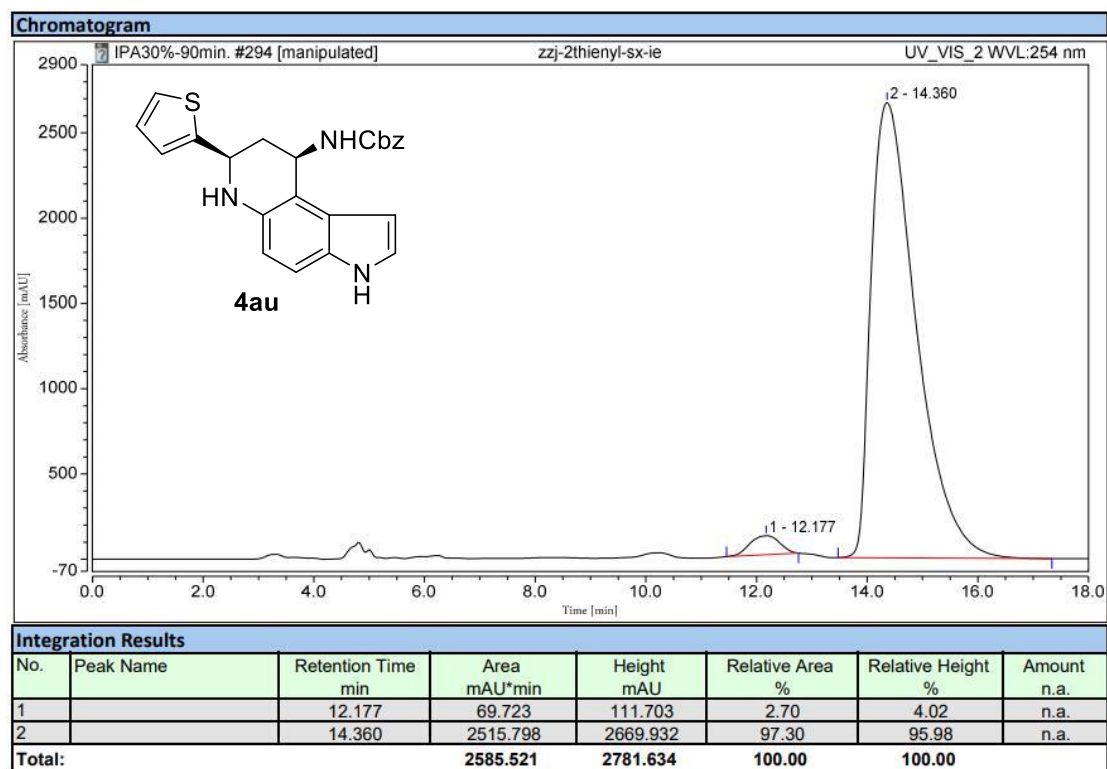
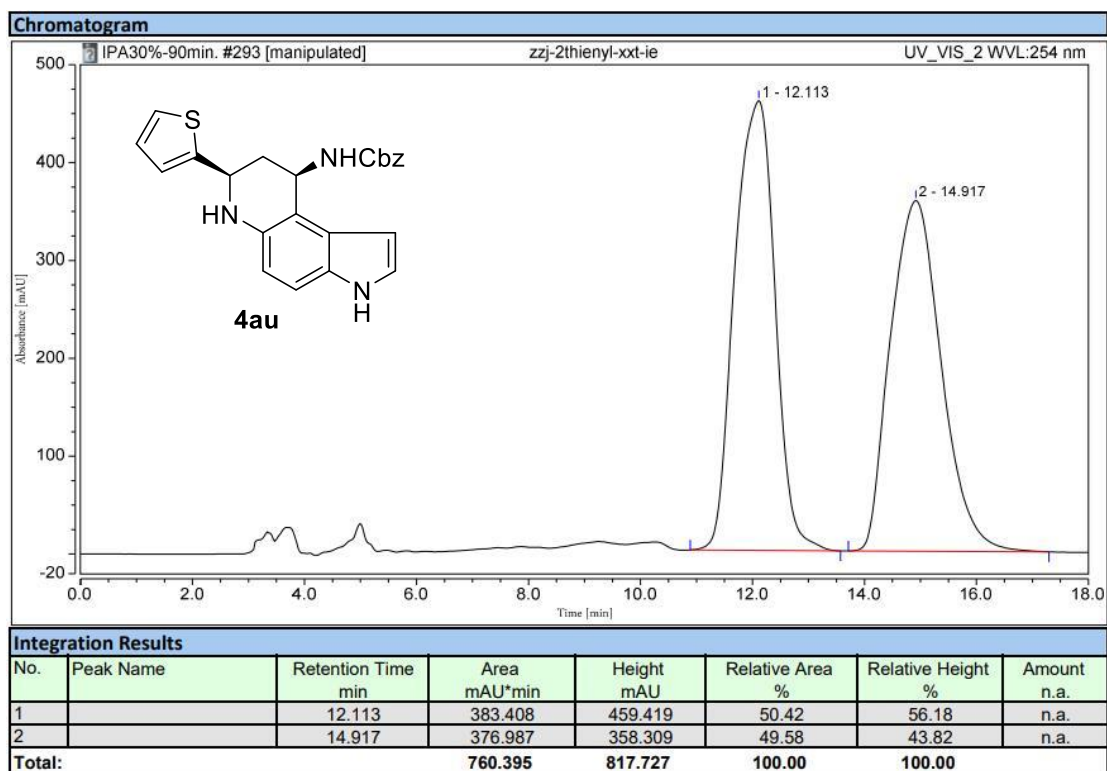


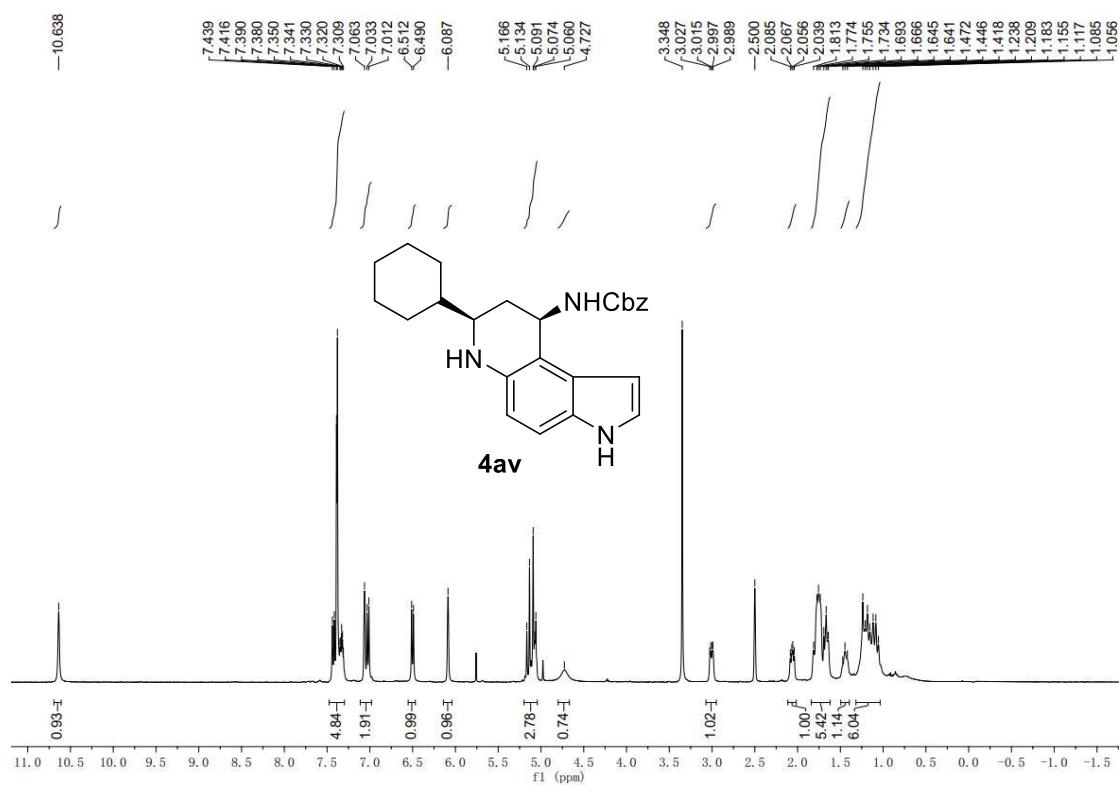


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4au**

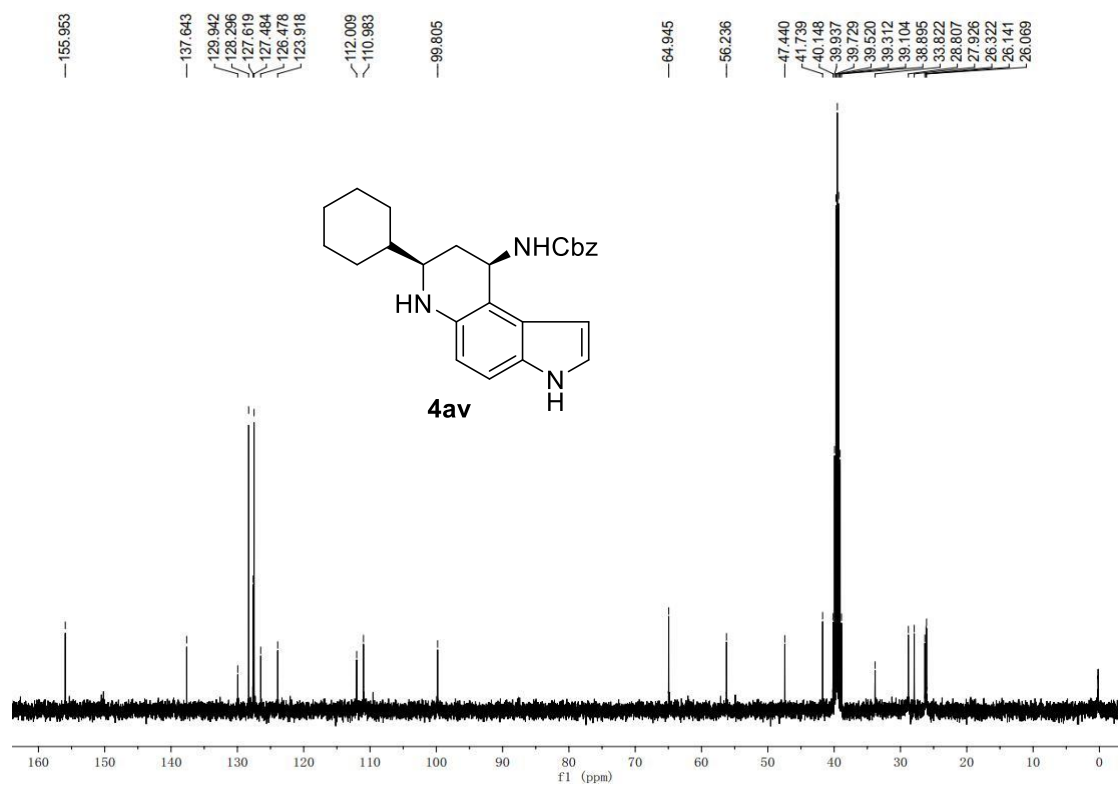


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4au**

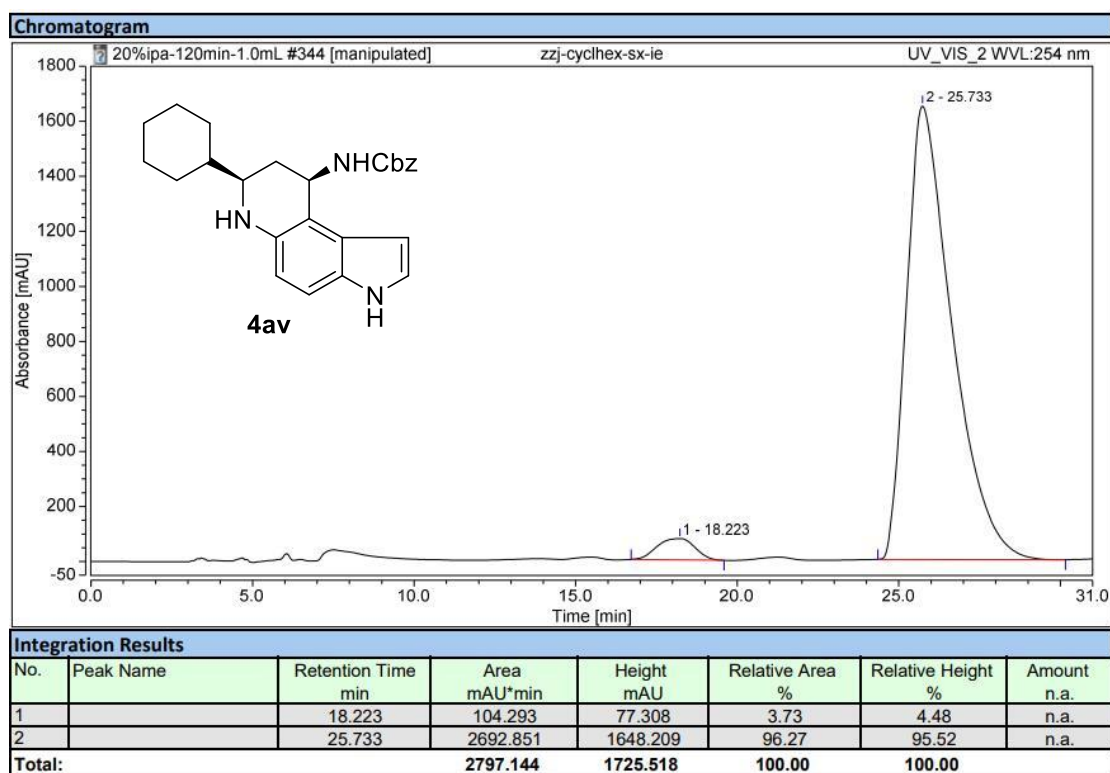
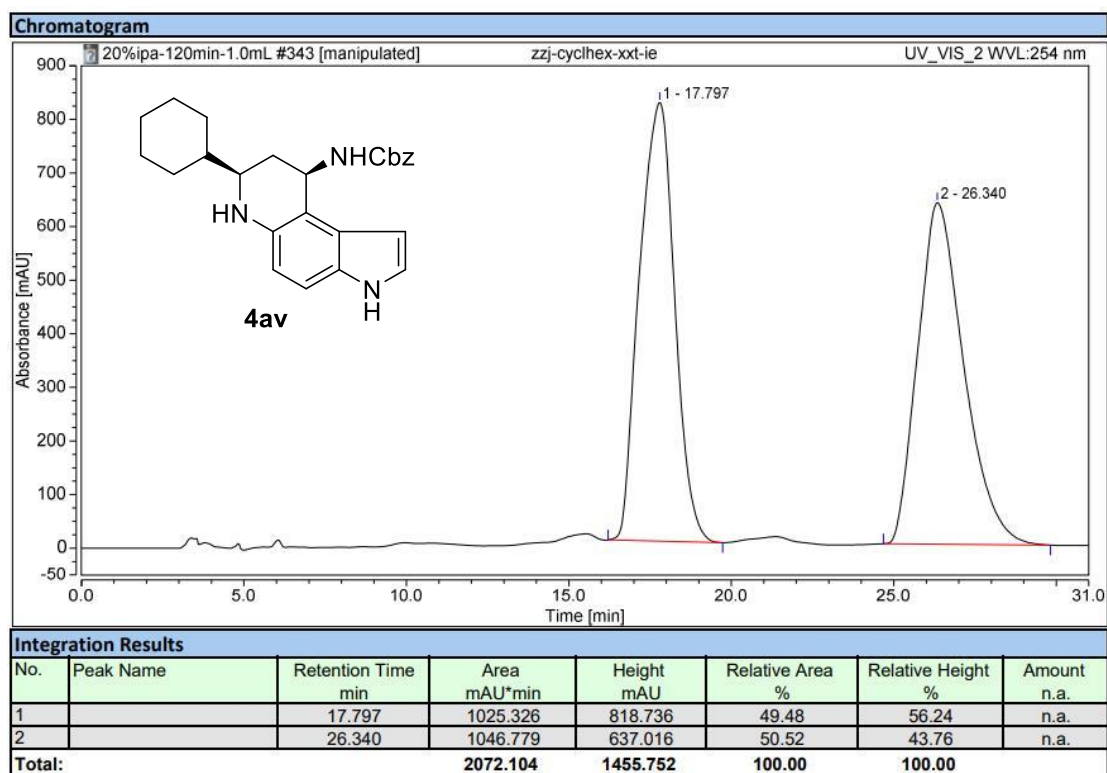


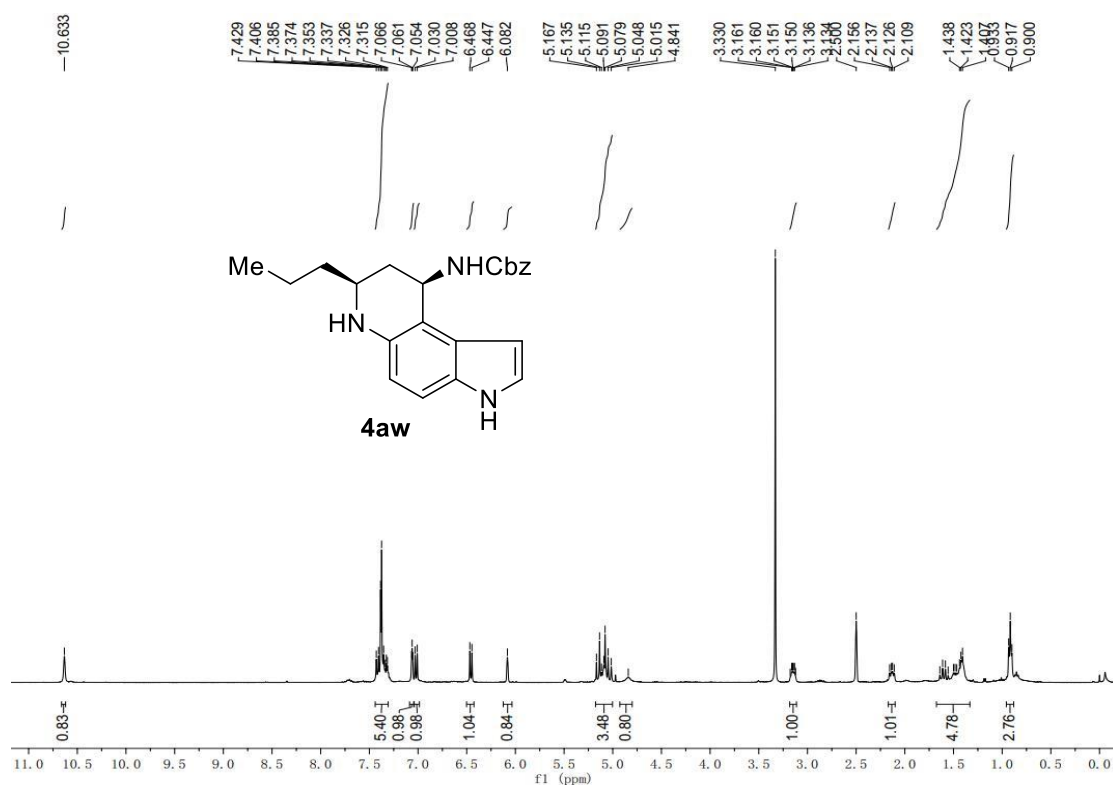


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4av**

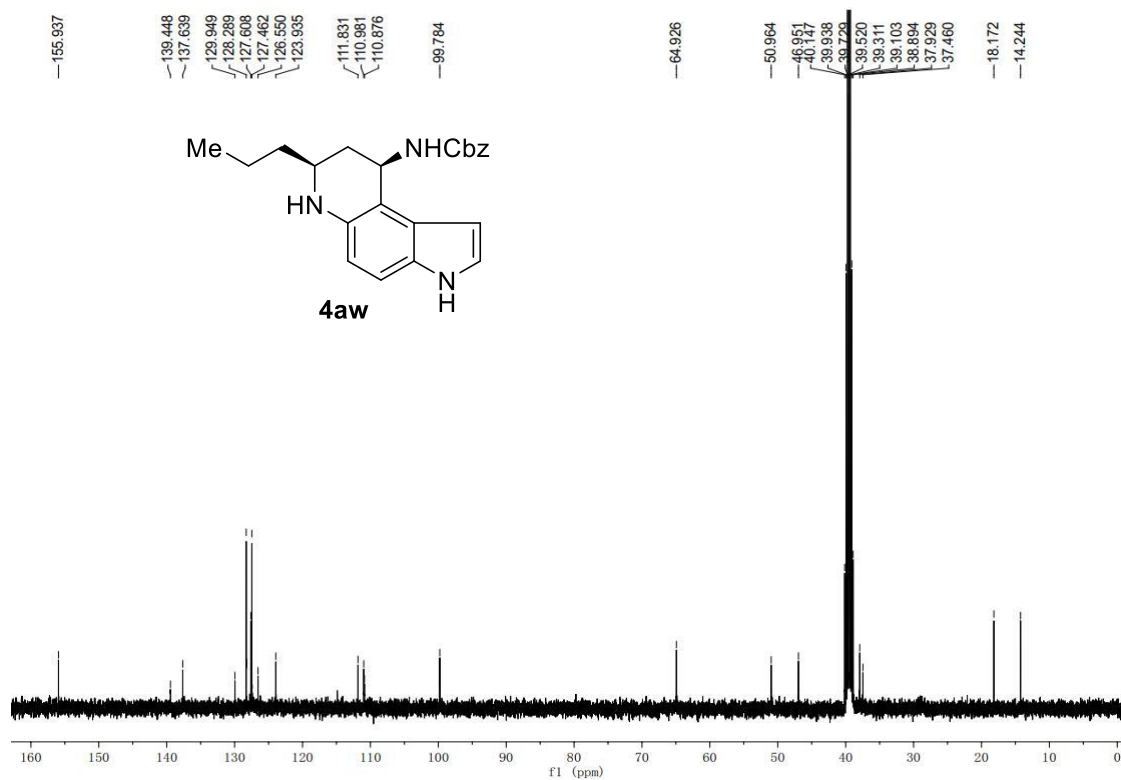


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4av**



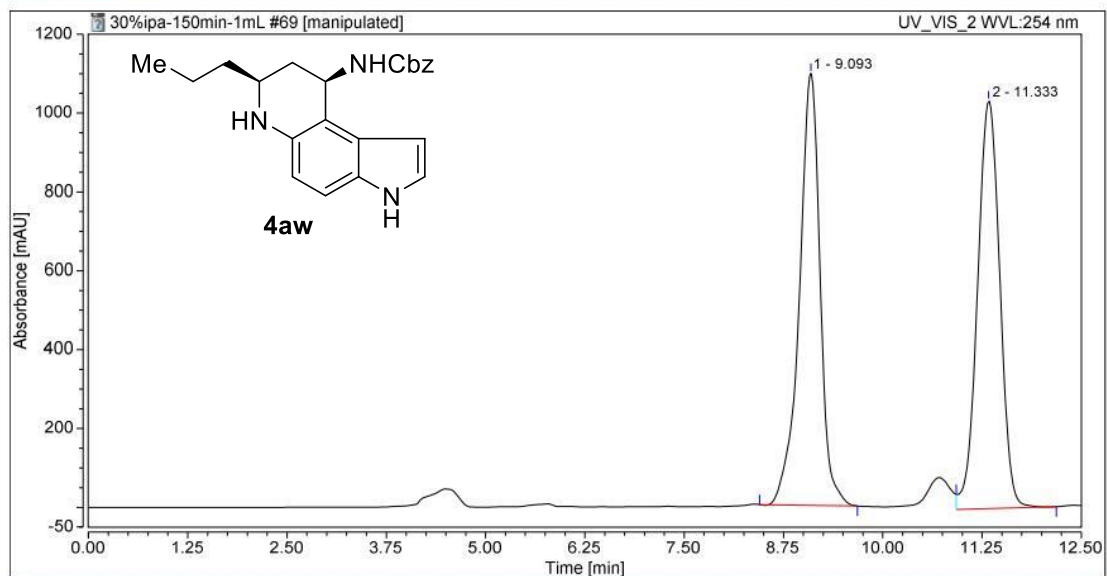


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4aw**



**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4aw**

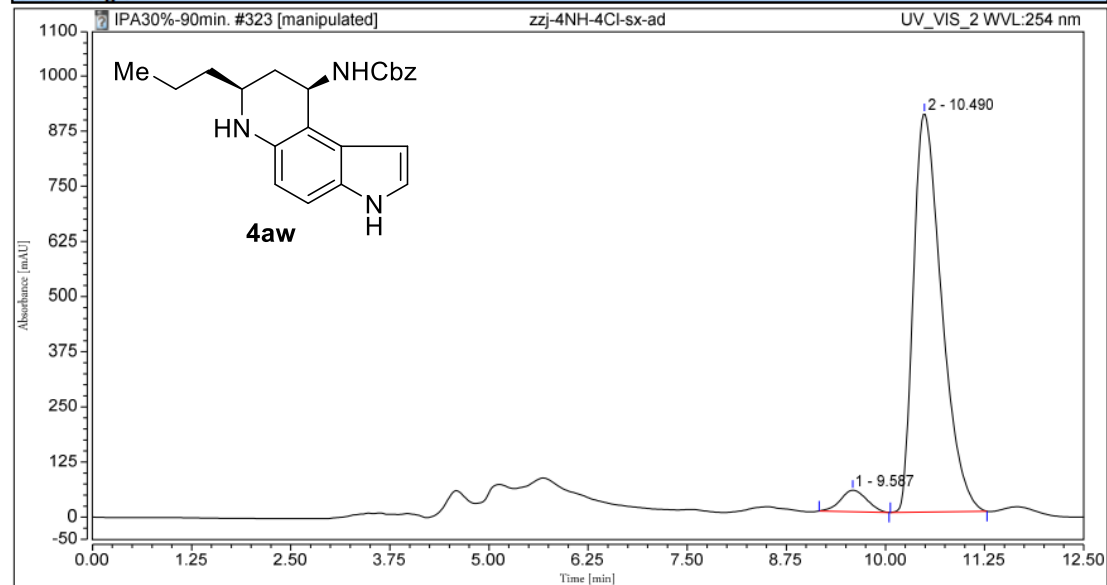
**Chromatogram**



**Integration Results**

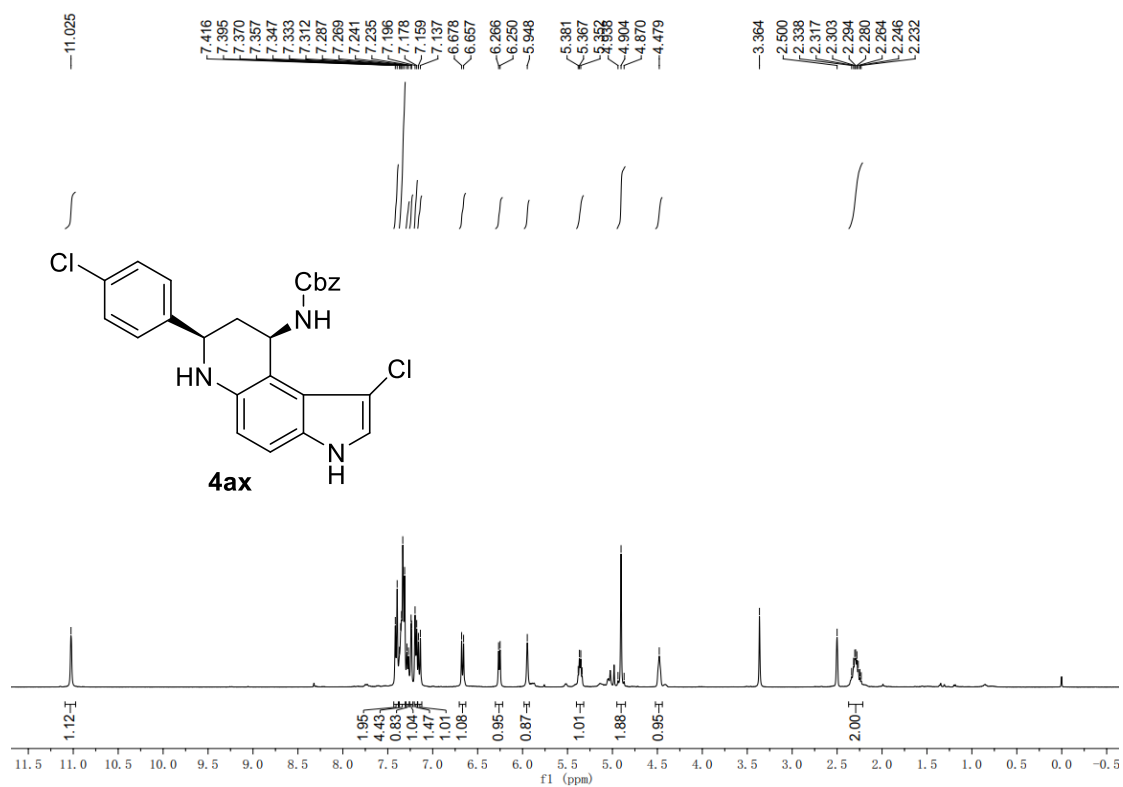
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.093	330.411	1095.493	49.56	51.46	n.a.
2		11.333	336.290	1033.457	50.44	48.54	n.a.
<b>Total:</b>			<b>666.701</b>	<b>2128.950</b>	<b>100.00</b>	<b>100.00</b>	

**Chromatogram**

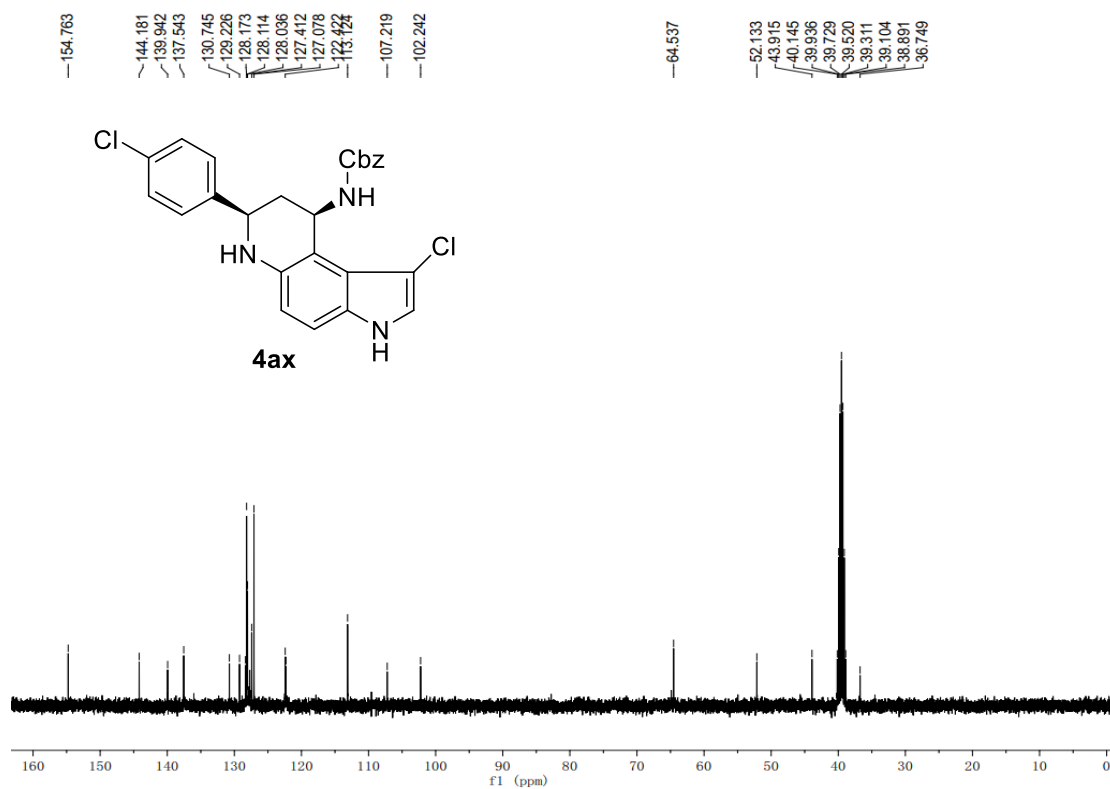


**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.587	18.648	48.601	4.77	5.11	n.a.
2		10.490	372.303	902.973	95.23	94.89	n.a.
<b>Total:</b>			<b>390.951</b>	<b>951.574</b>	<b>100.00</b>	<b>100.00</b>	

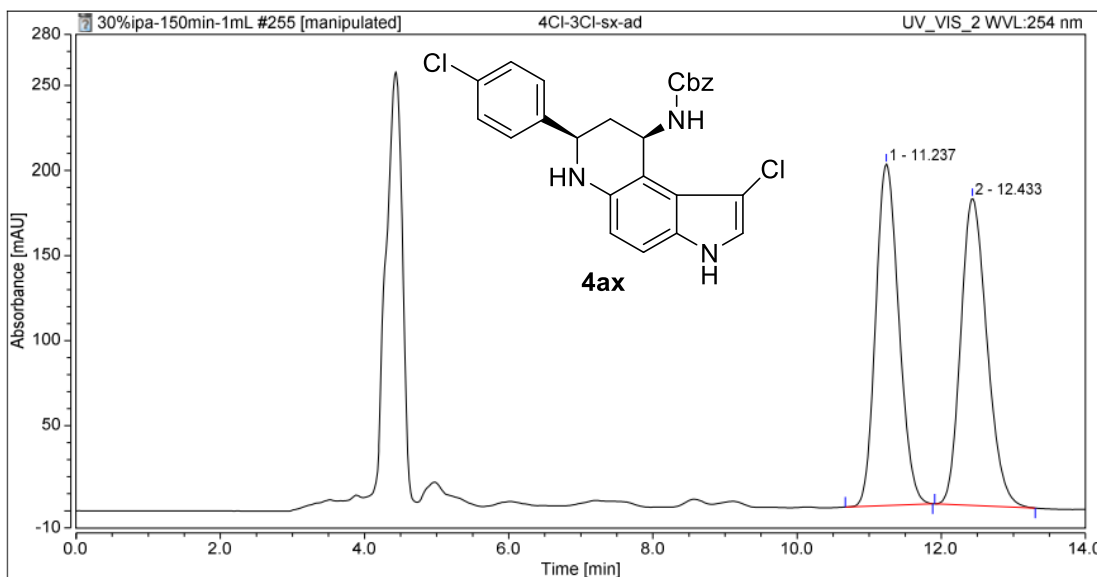


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ax**



**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ax**

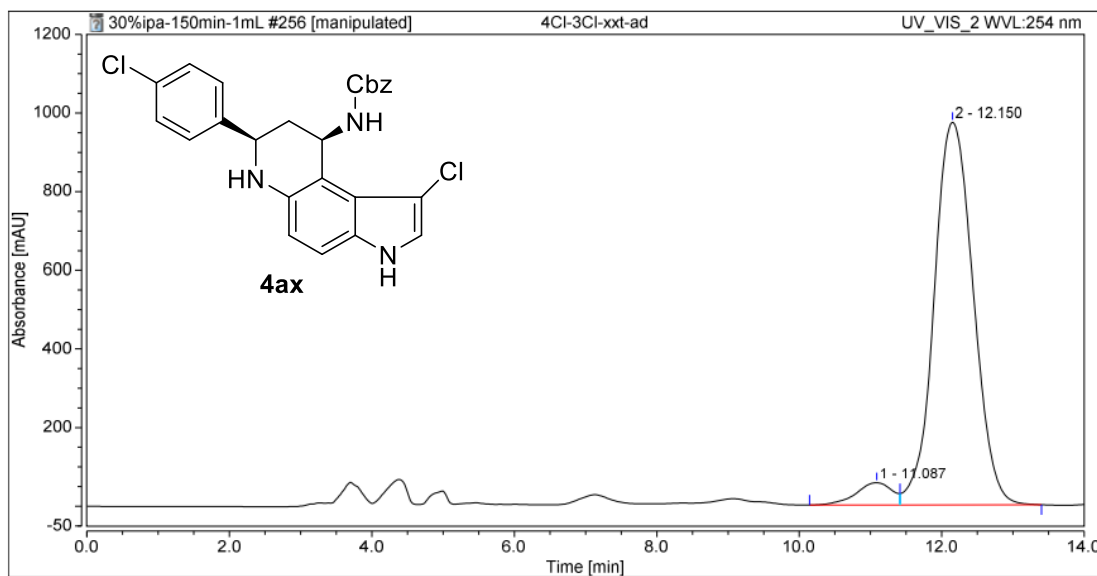
**Chromatogram**



**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.237	74.633	200.786	49.52	52.67	n.a.
2		12.433	76.079	180.457	50.48	47.33	n.a.
<b>Total:</b>			<b>150.712</b>	<b>381.243</b>	<b>100.00</b>	<b>100.00</b>	

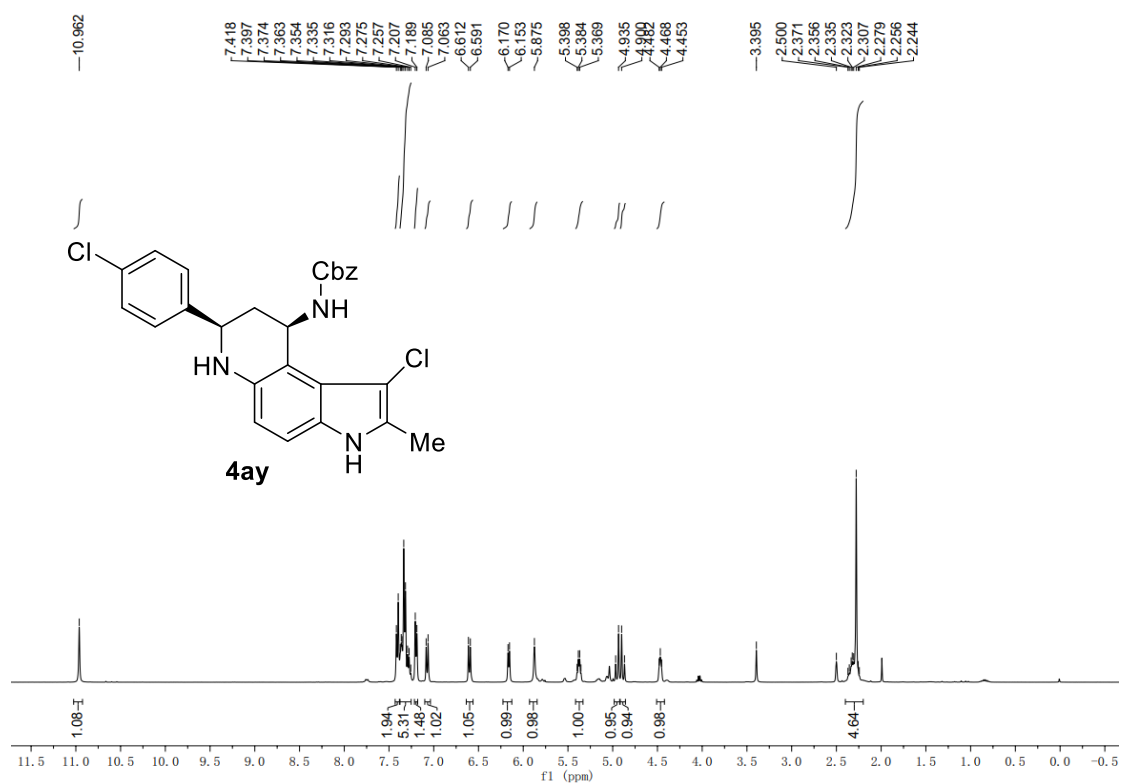
**Chromatogram**



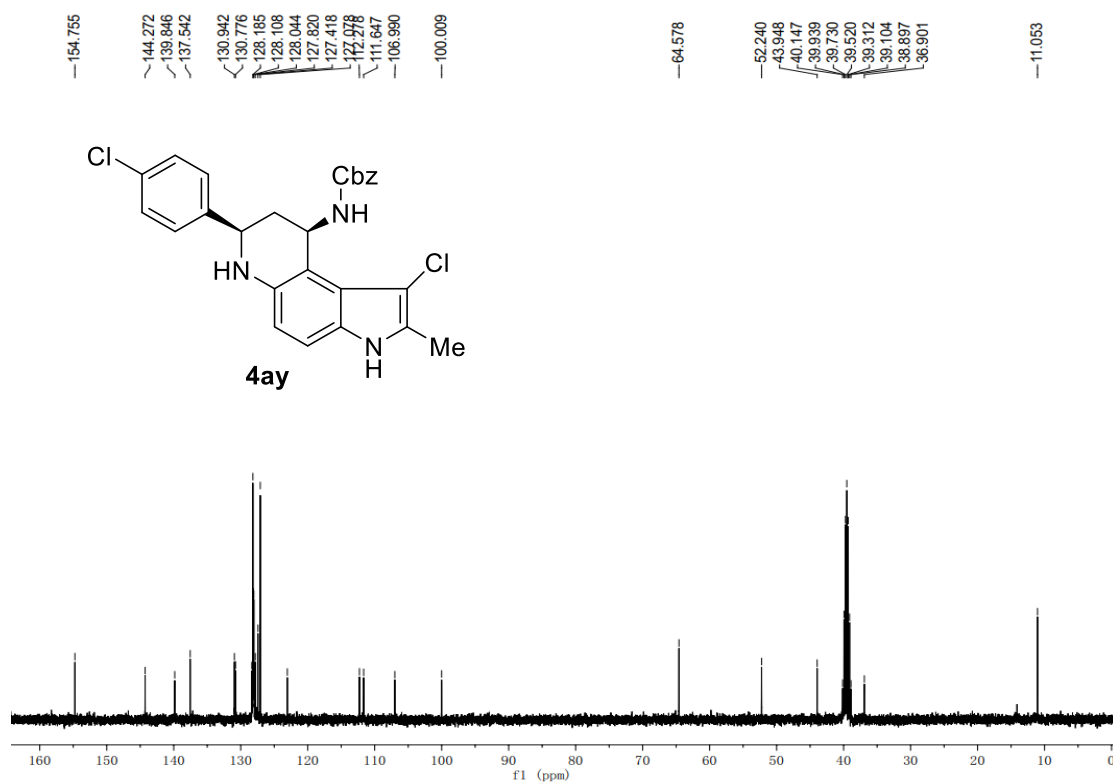
**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.087	32.989	56.462	5.06	5.48	n.a.
2		12.150	618.945	973.059	94.94	94.52	n.a.
<b>Total:</b>			<b>651.934</b>	<b>1029.521</b>	<b>100.00</b>	<b>100.00</b>	

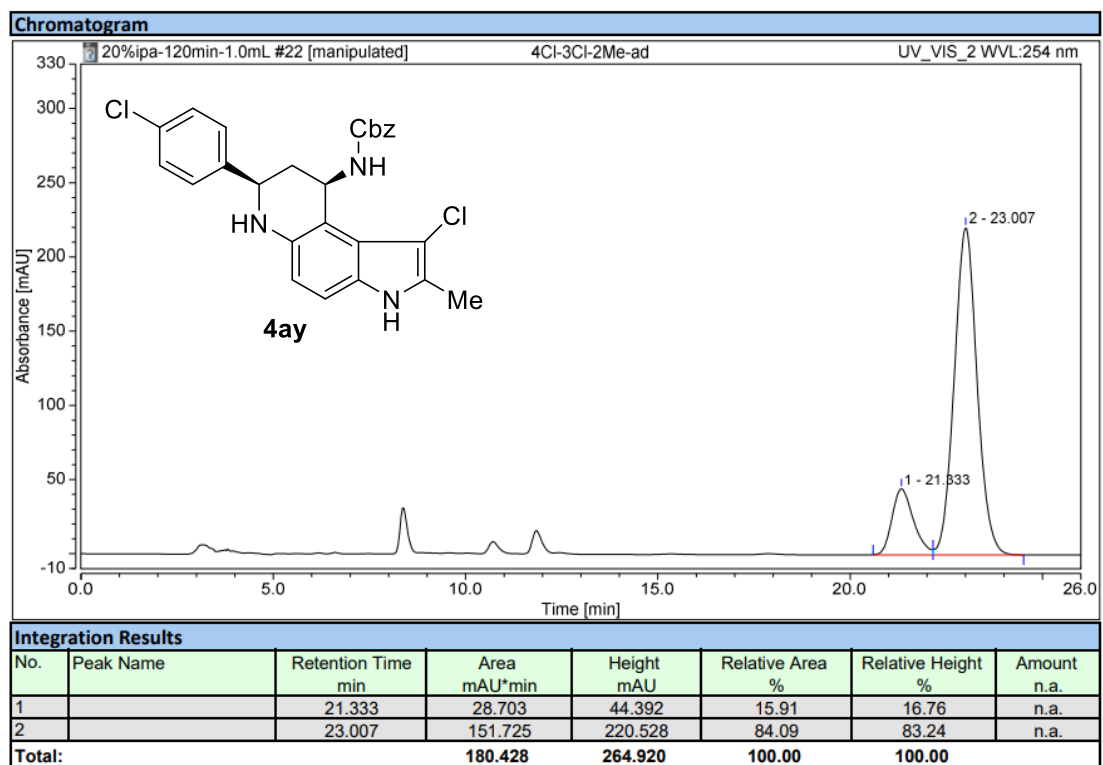
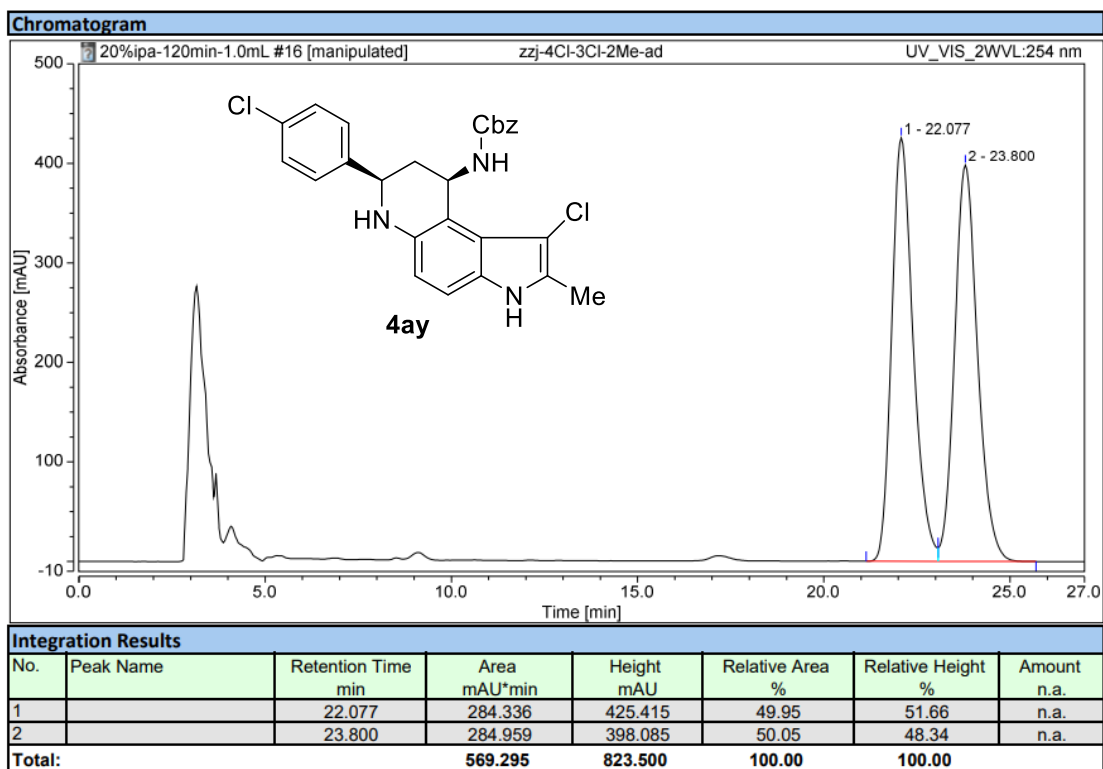


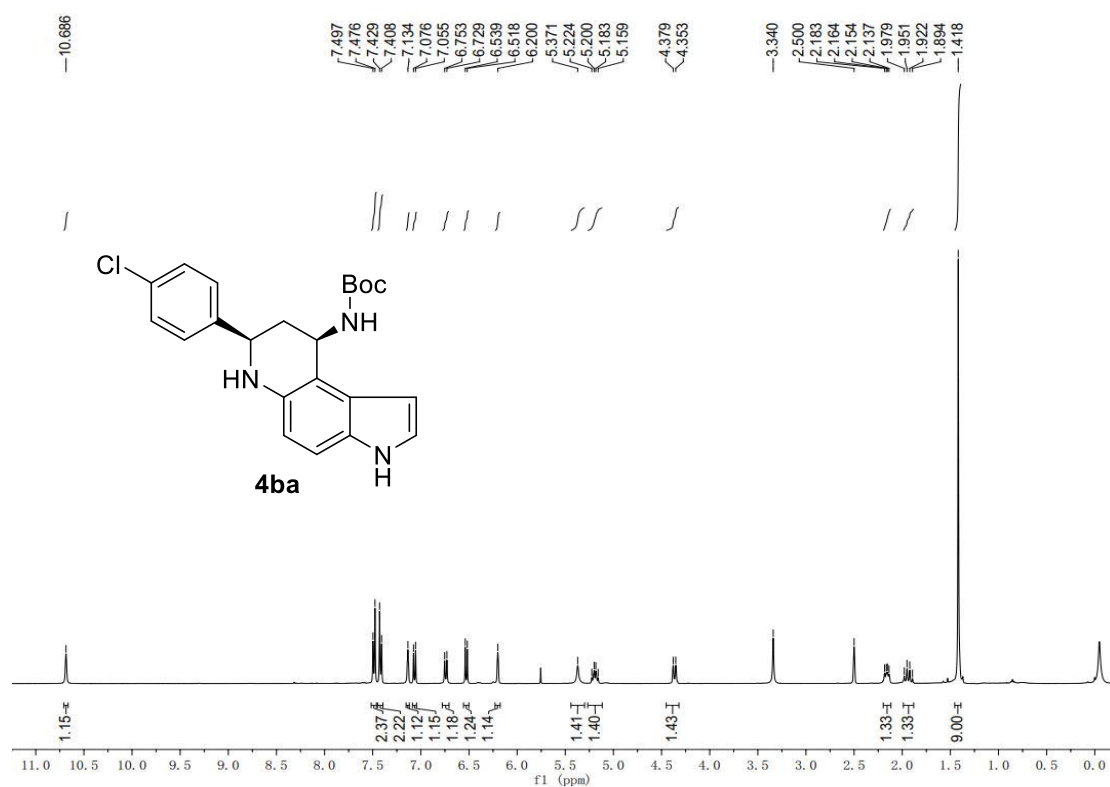


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4ay**

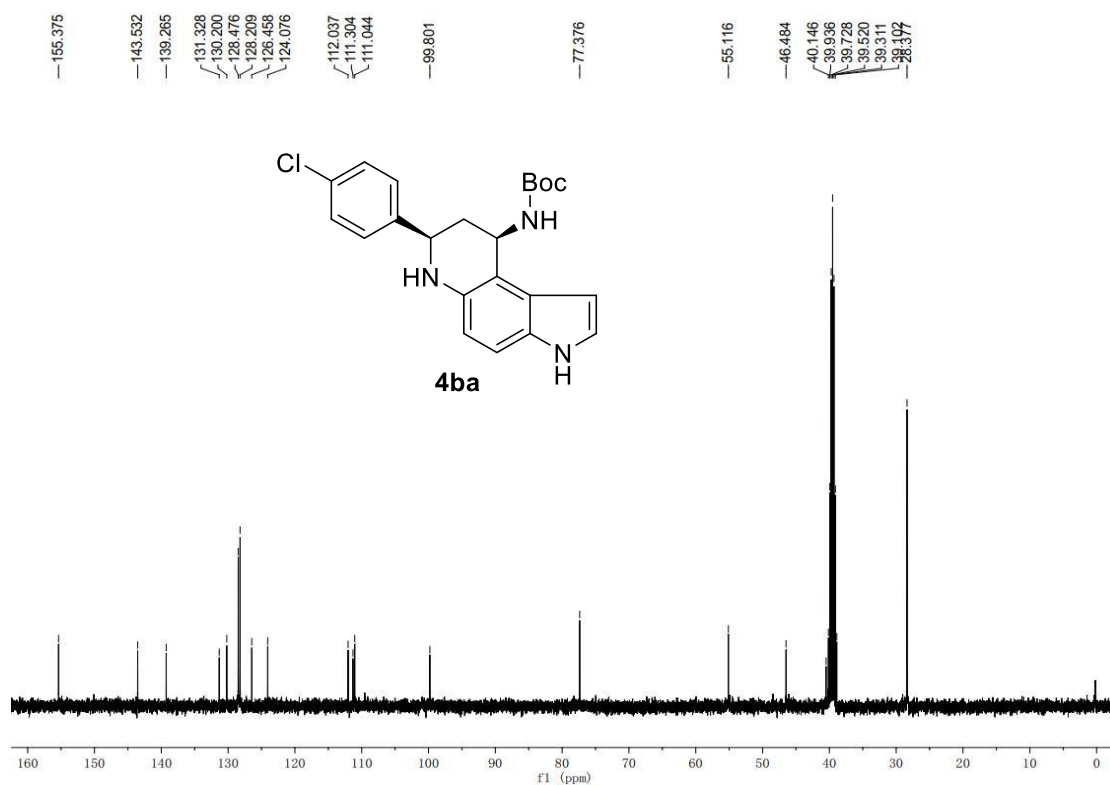


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4ay**

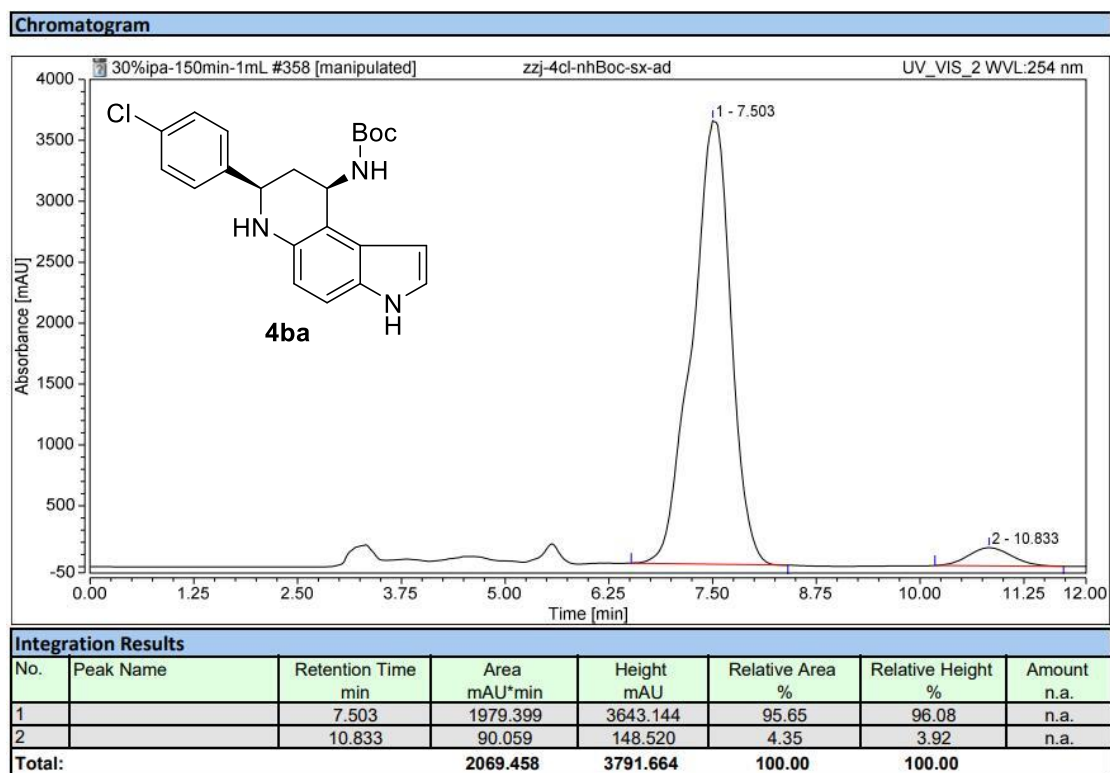
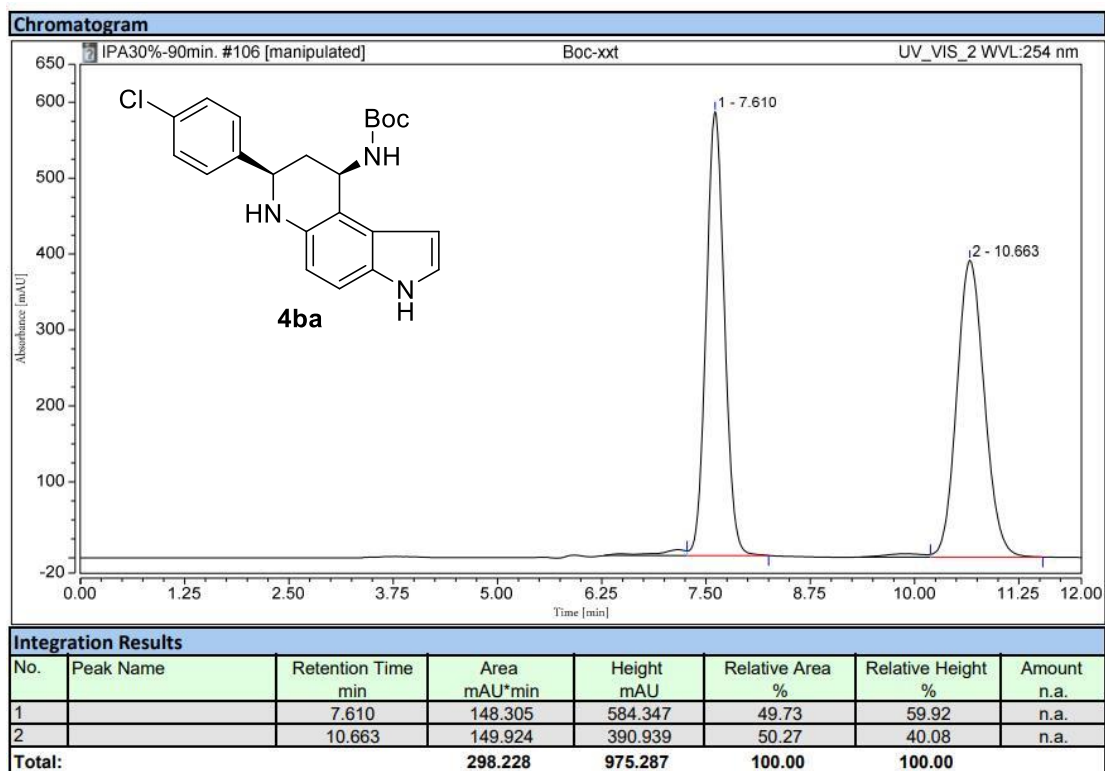


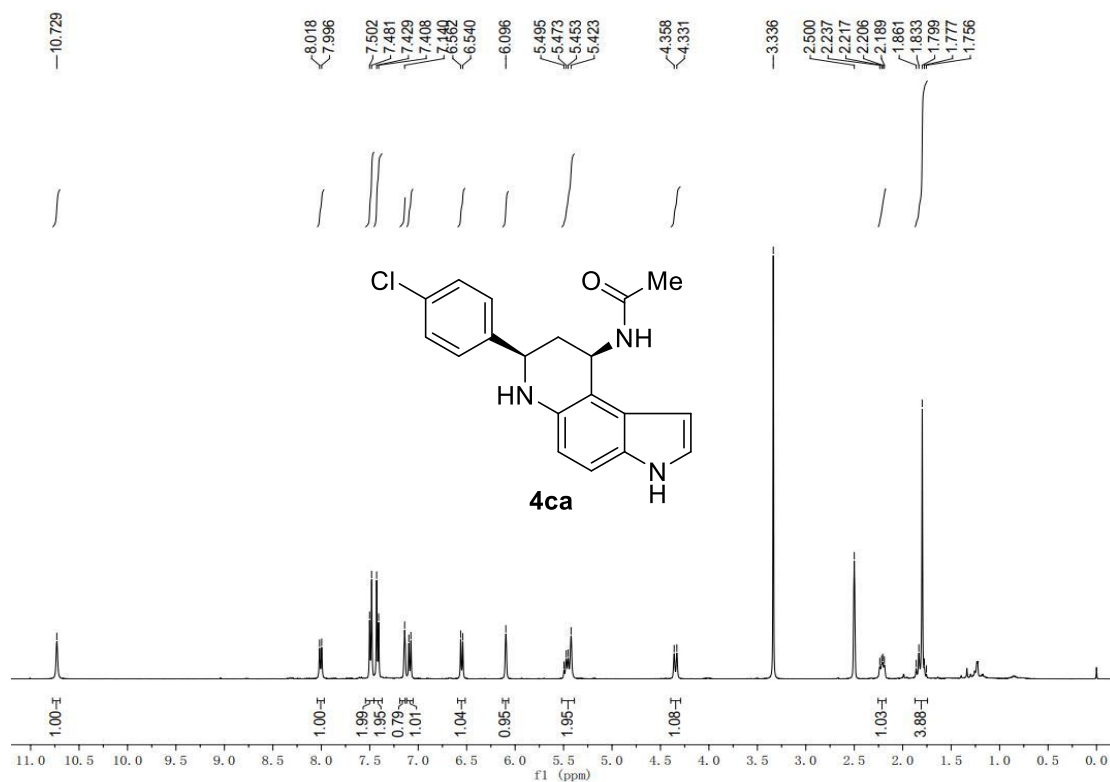


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ba**

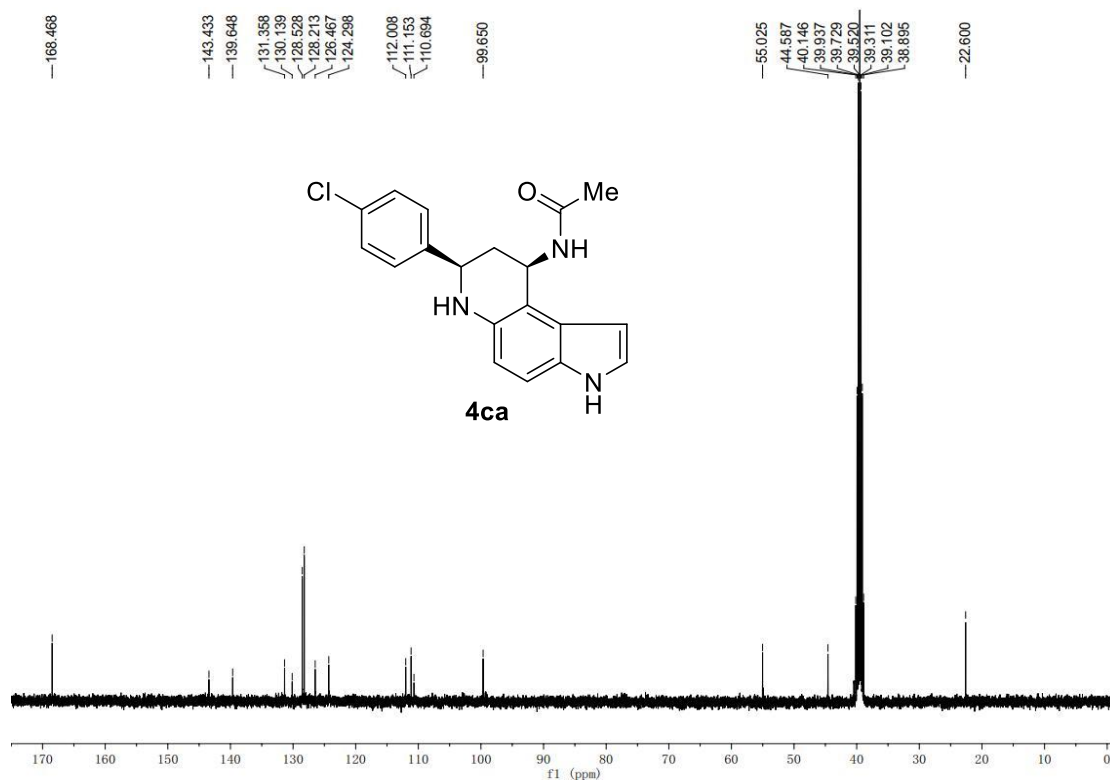


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ba**

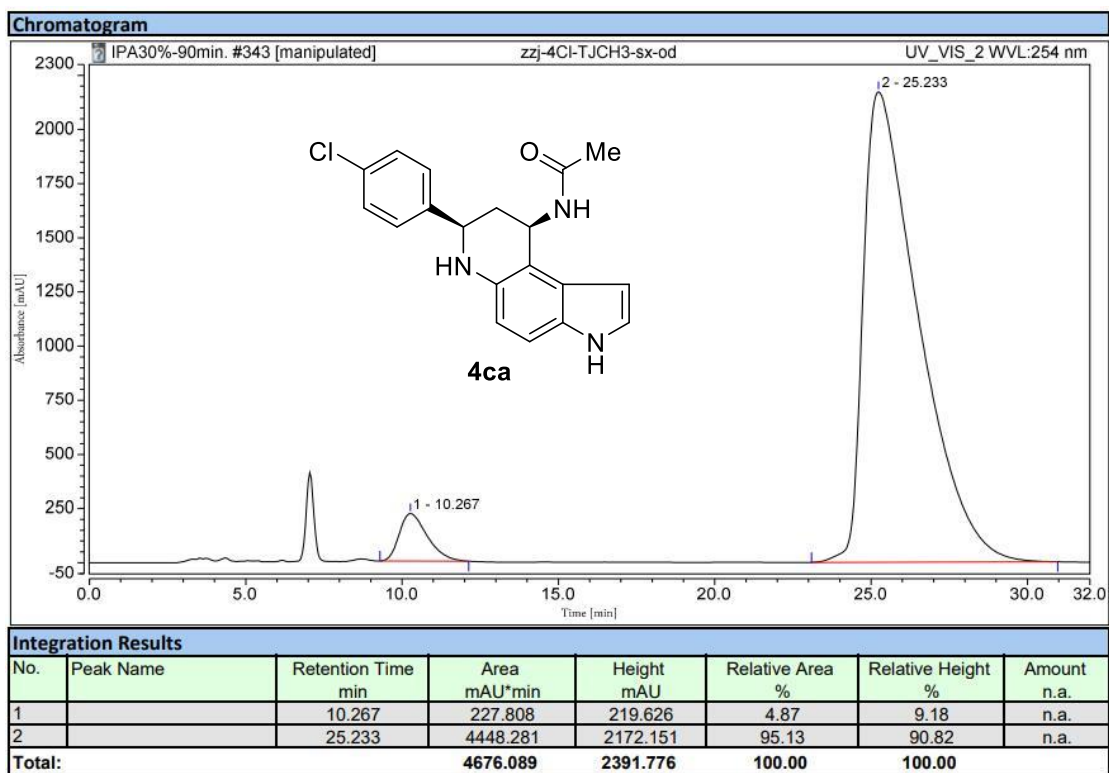
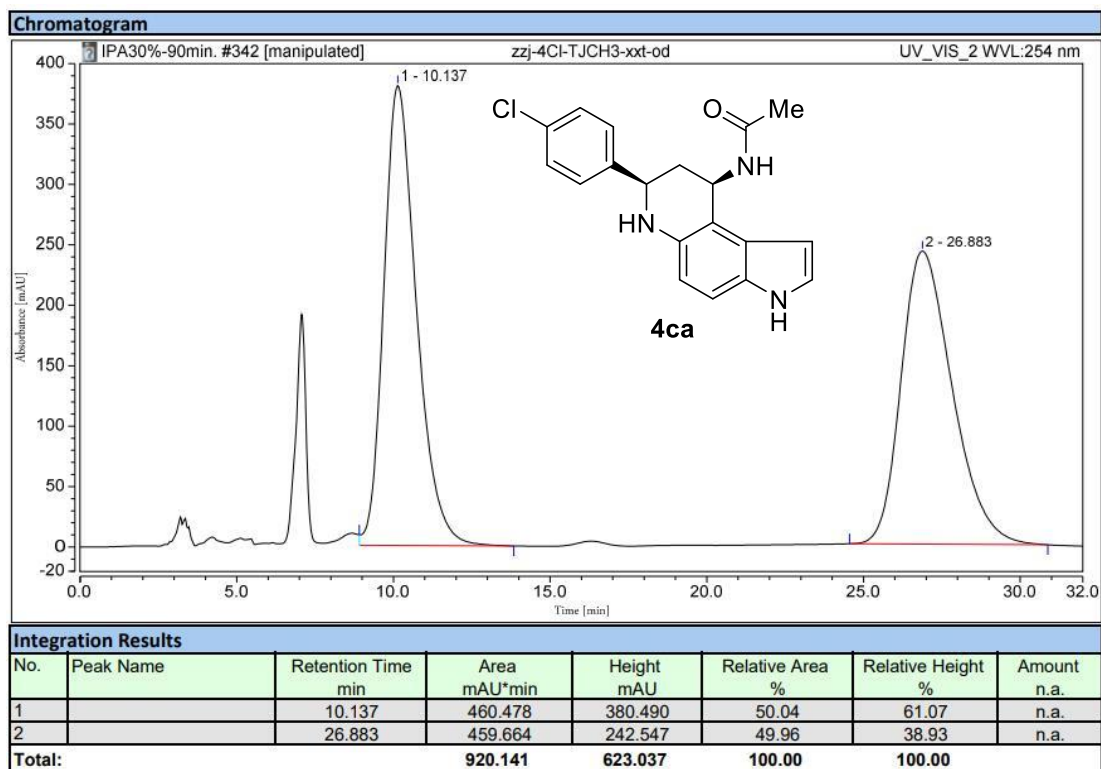


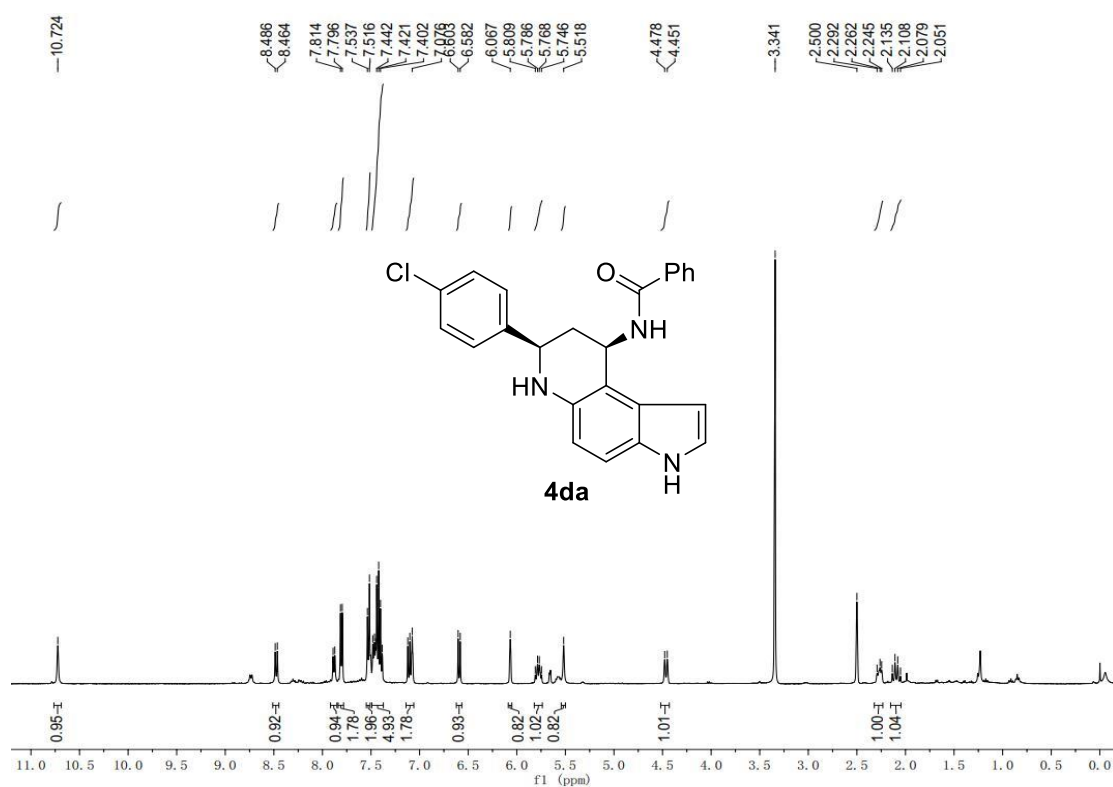


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ba**

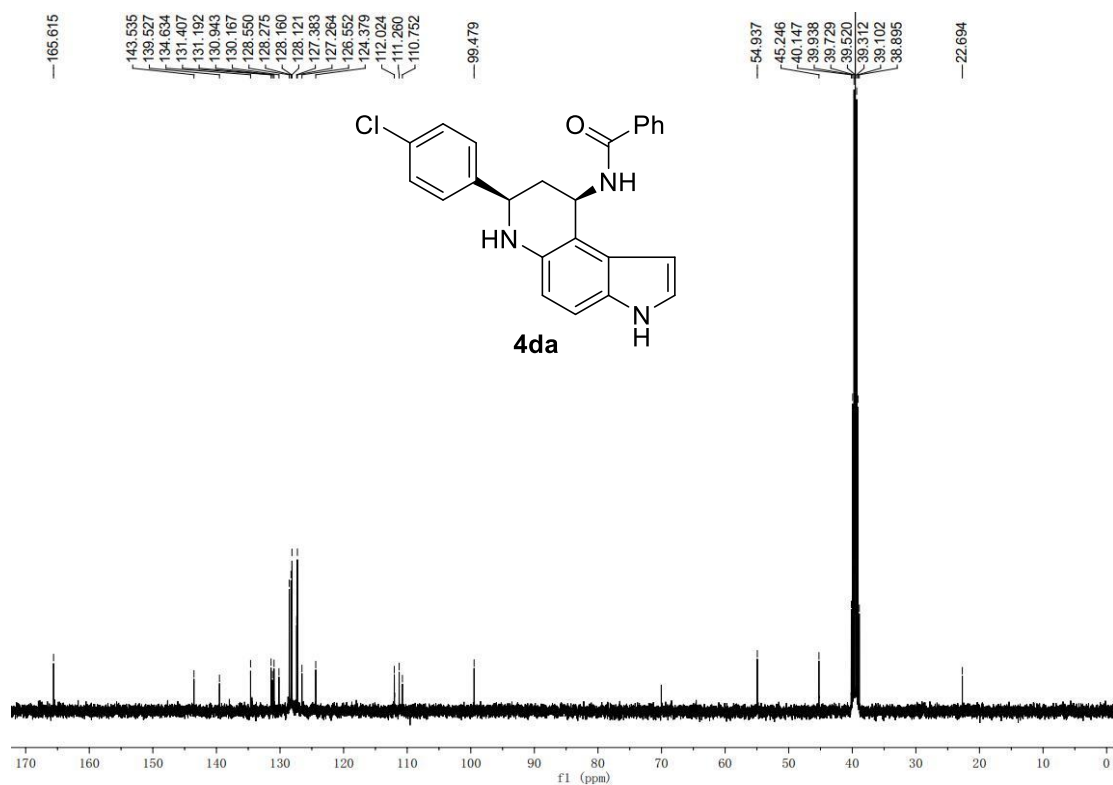


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ba**

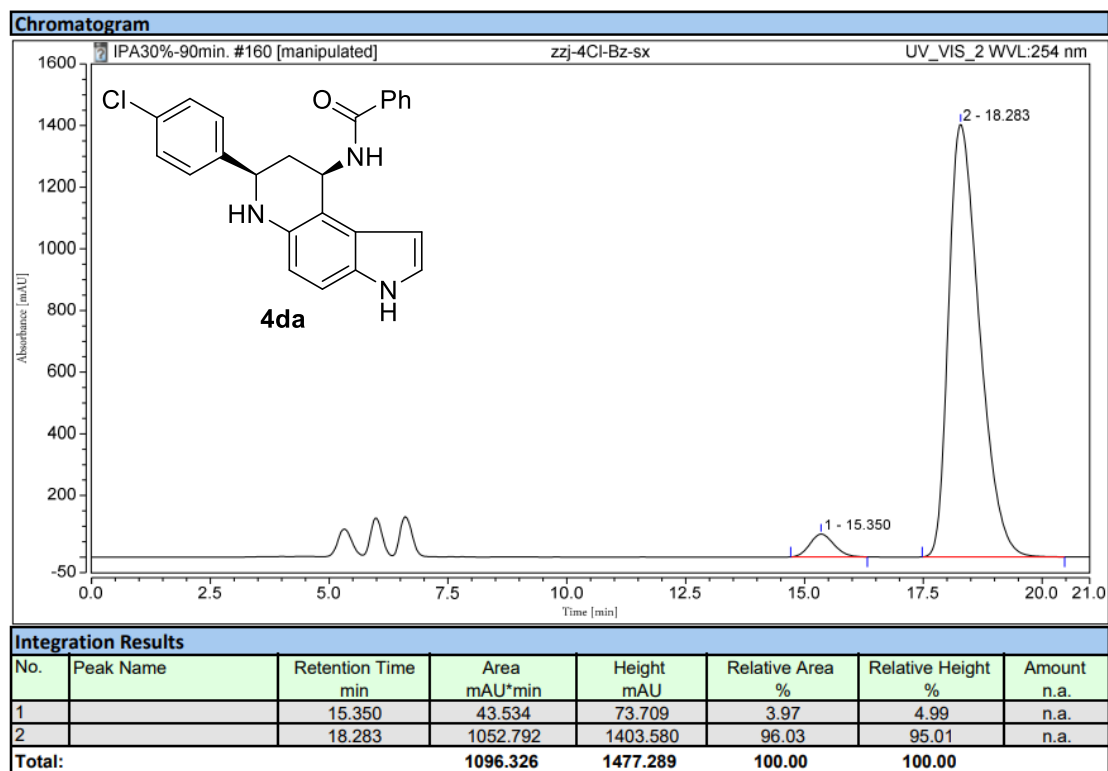
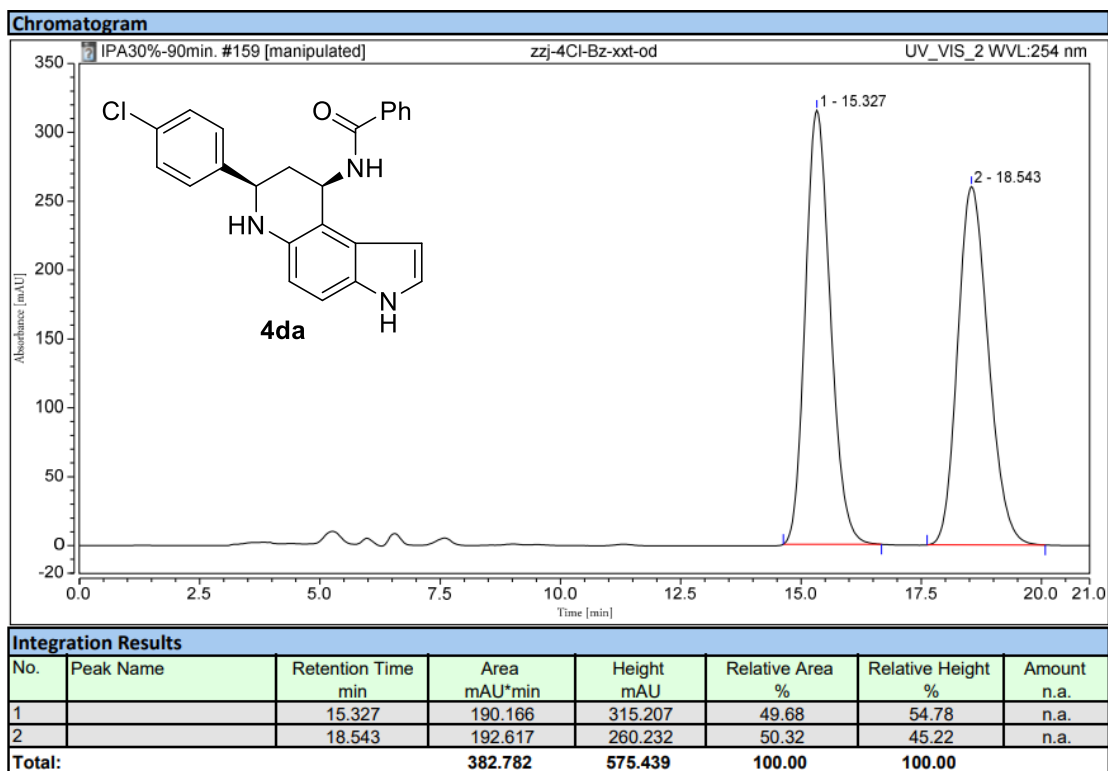




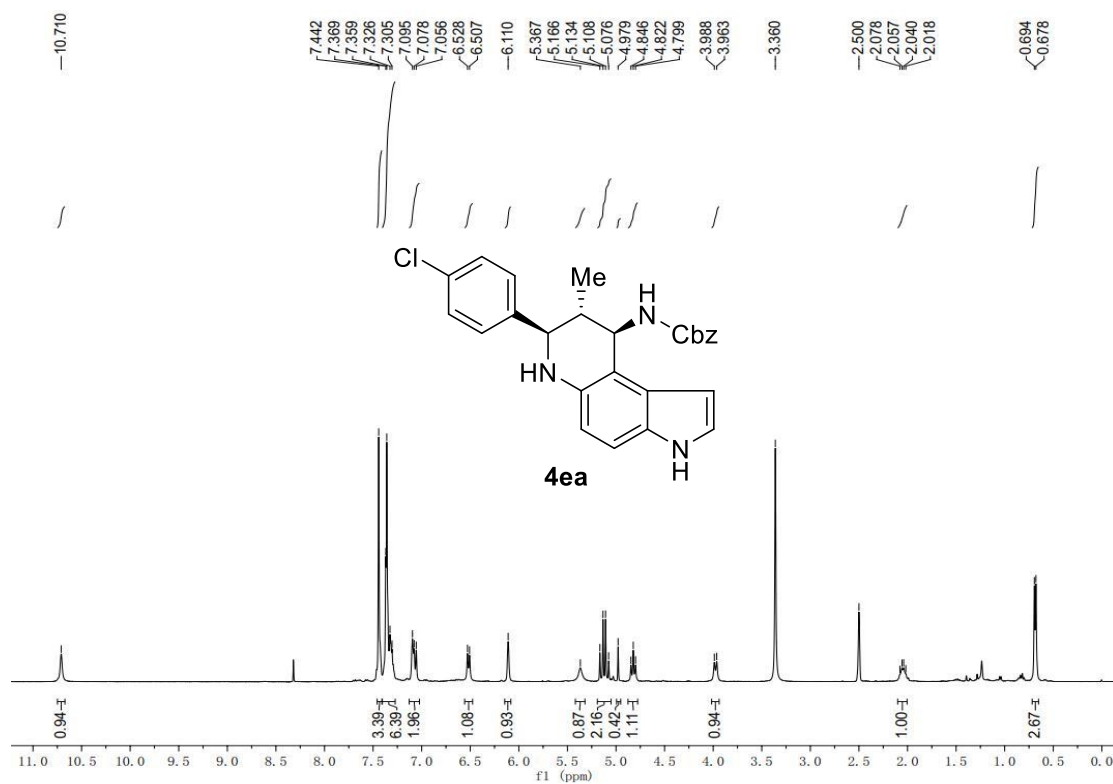
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4da**



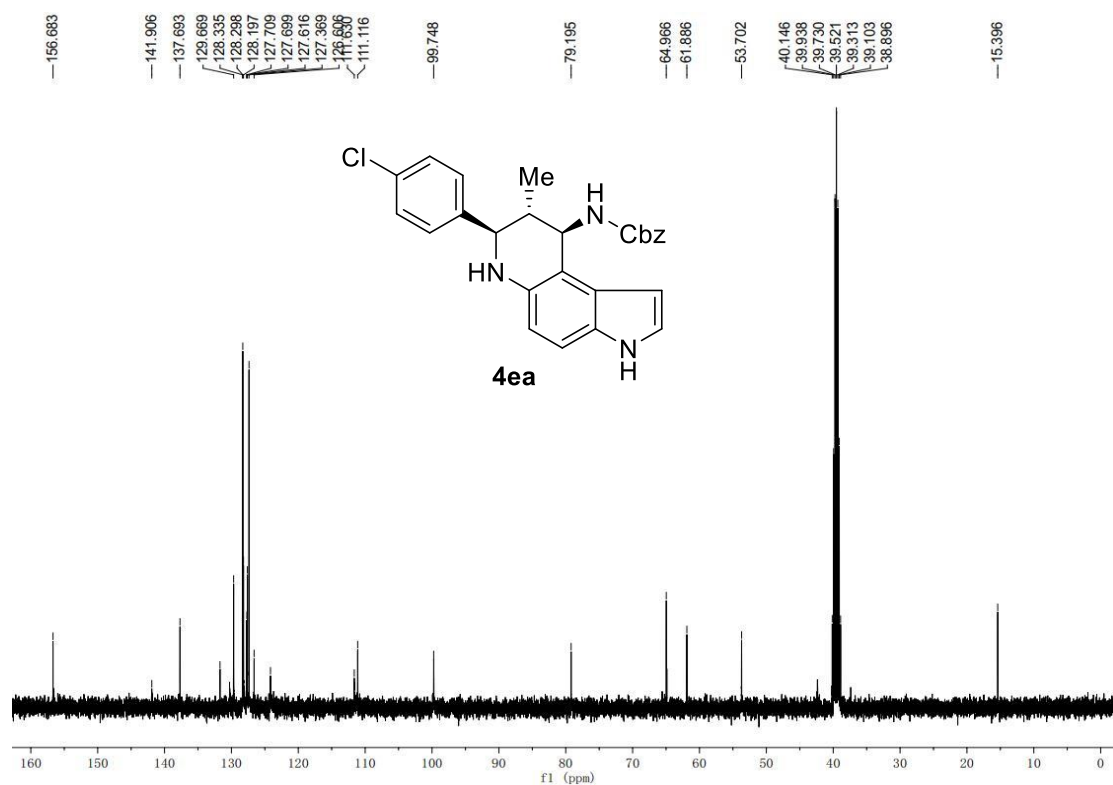
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4da**



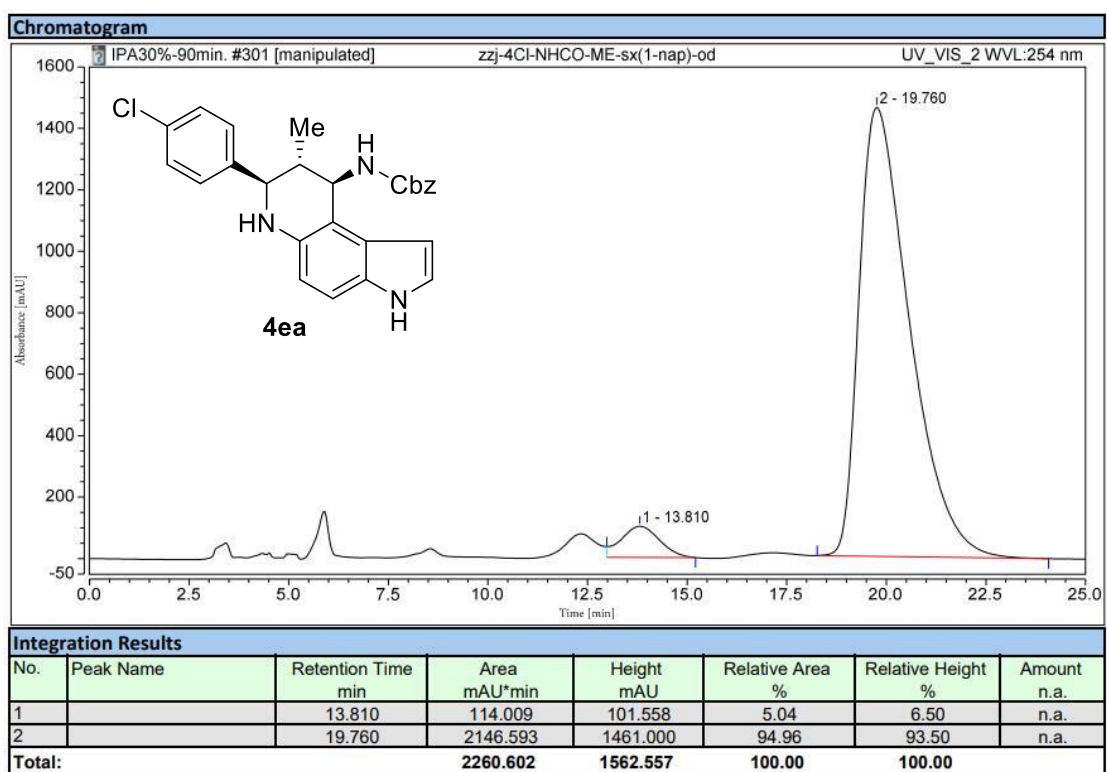
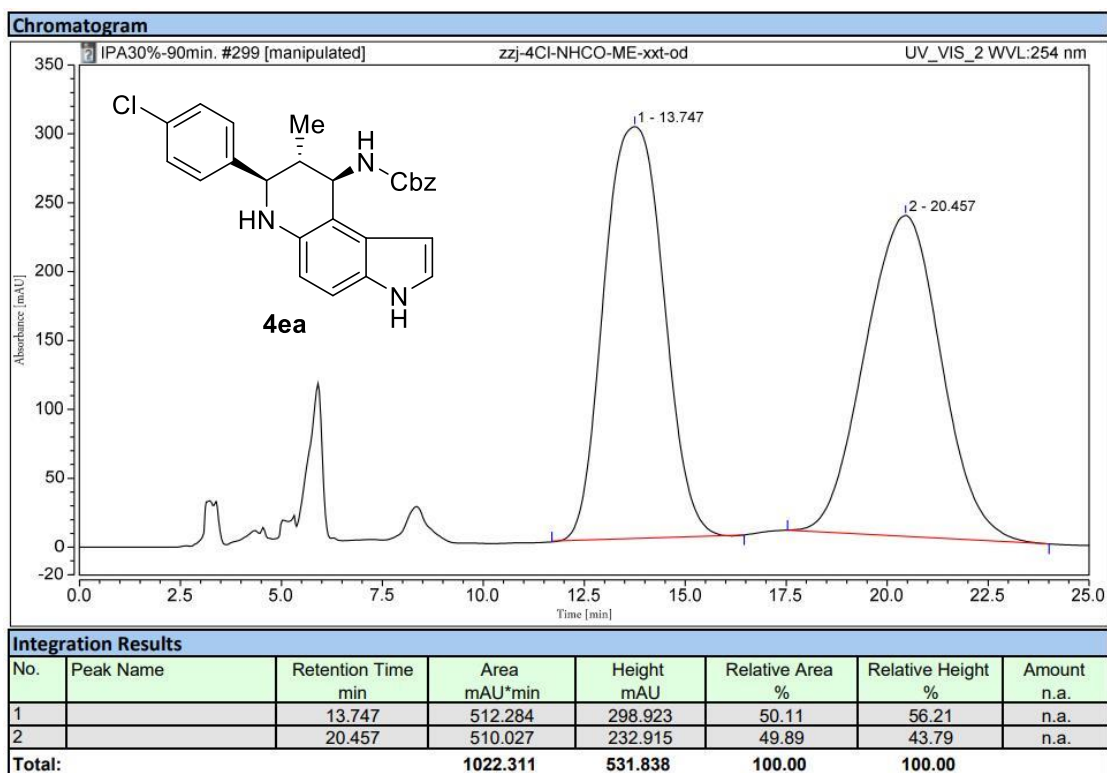


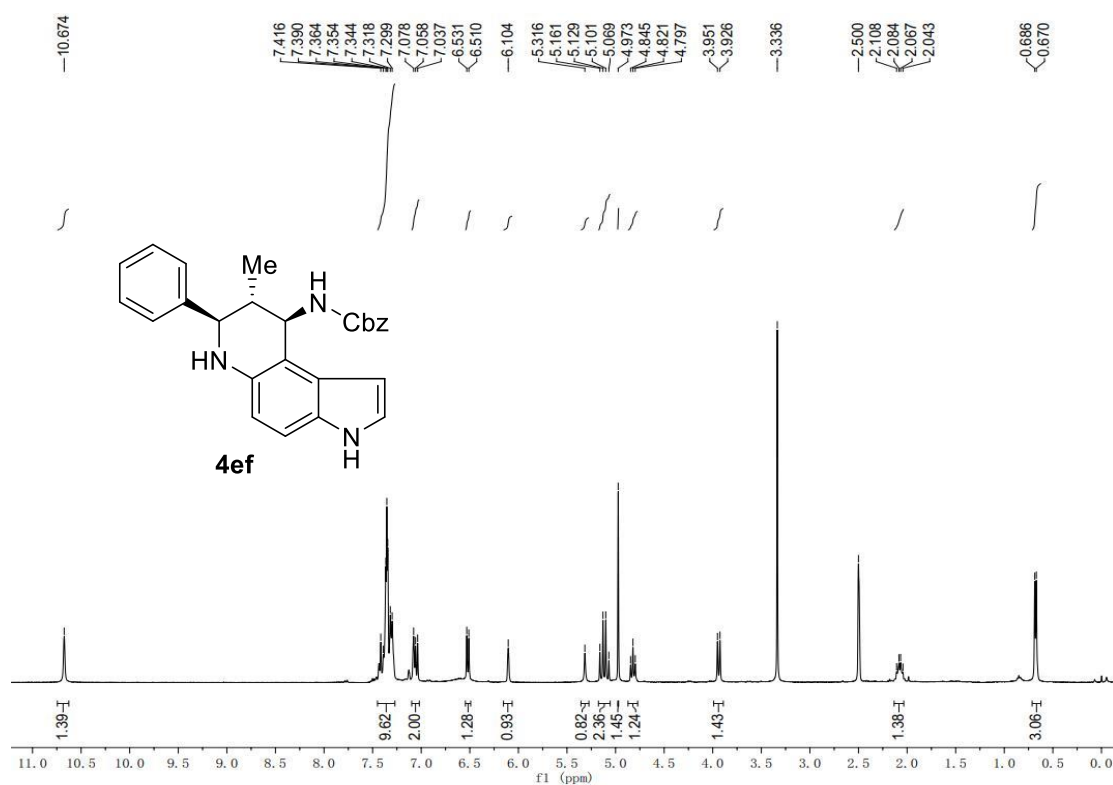


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ea**

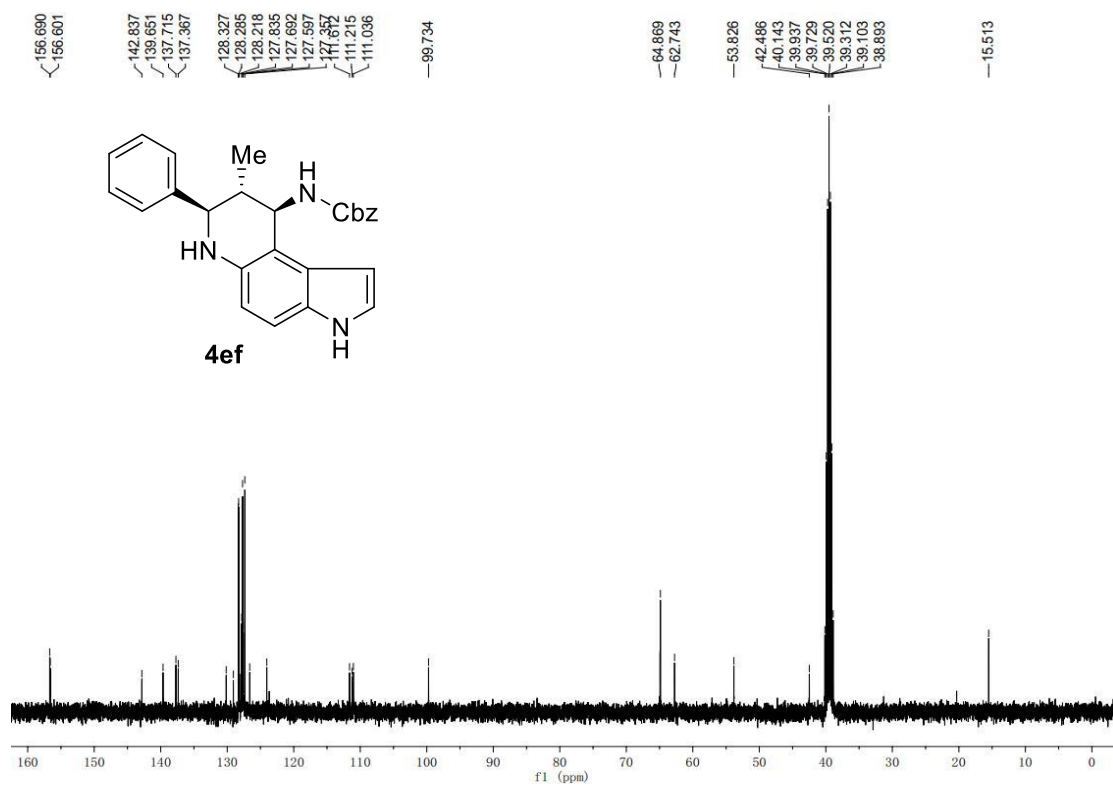


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ea**

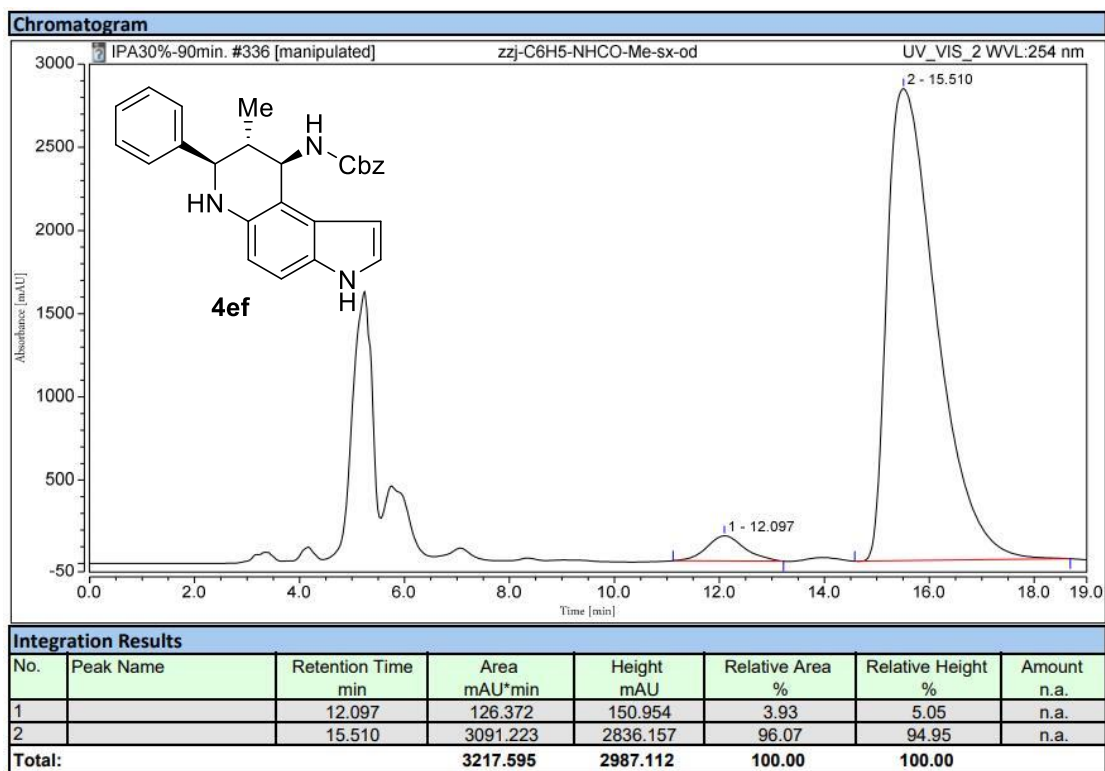
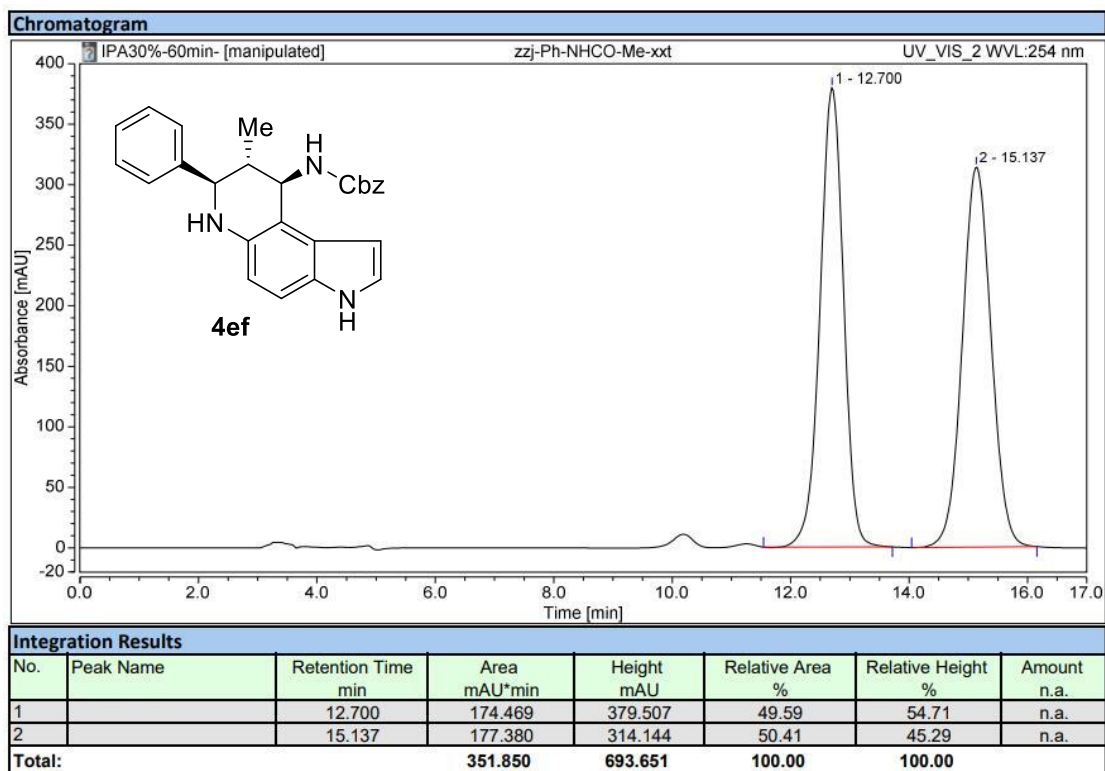


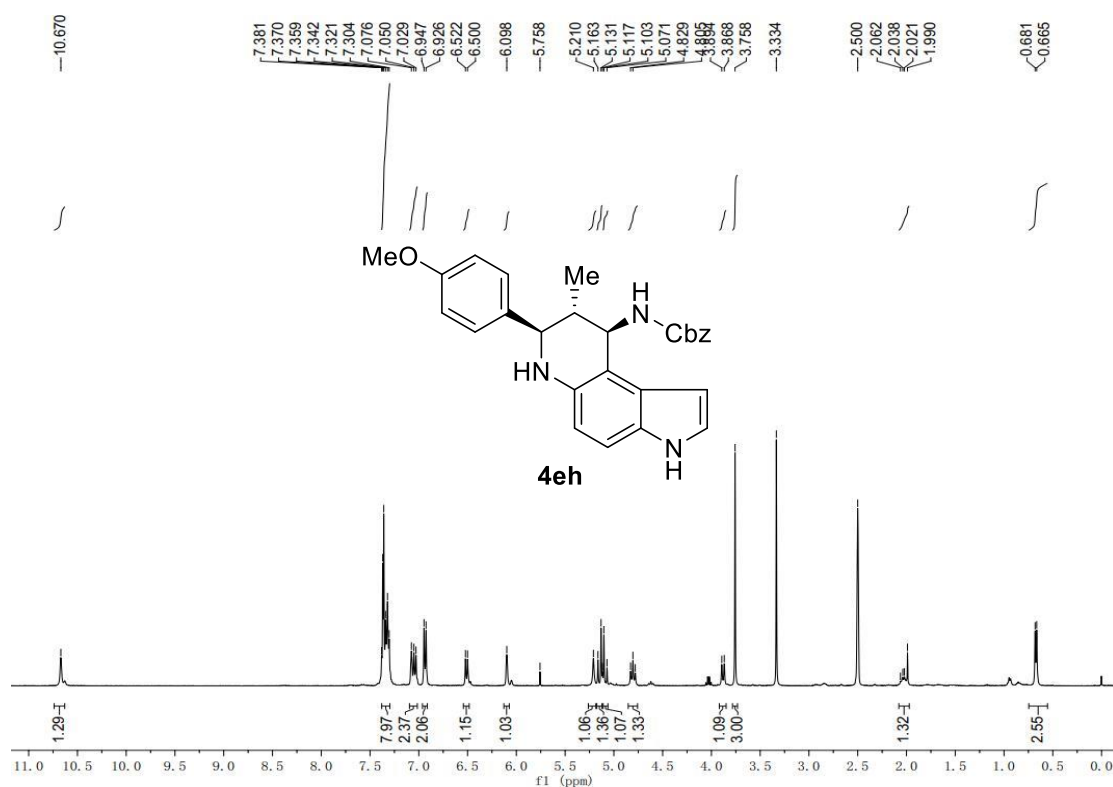


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ef**

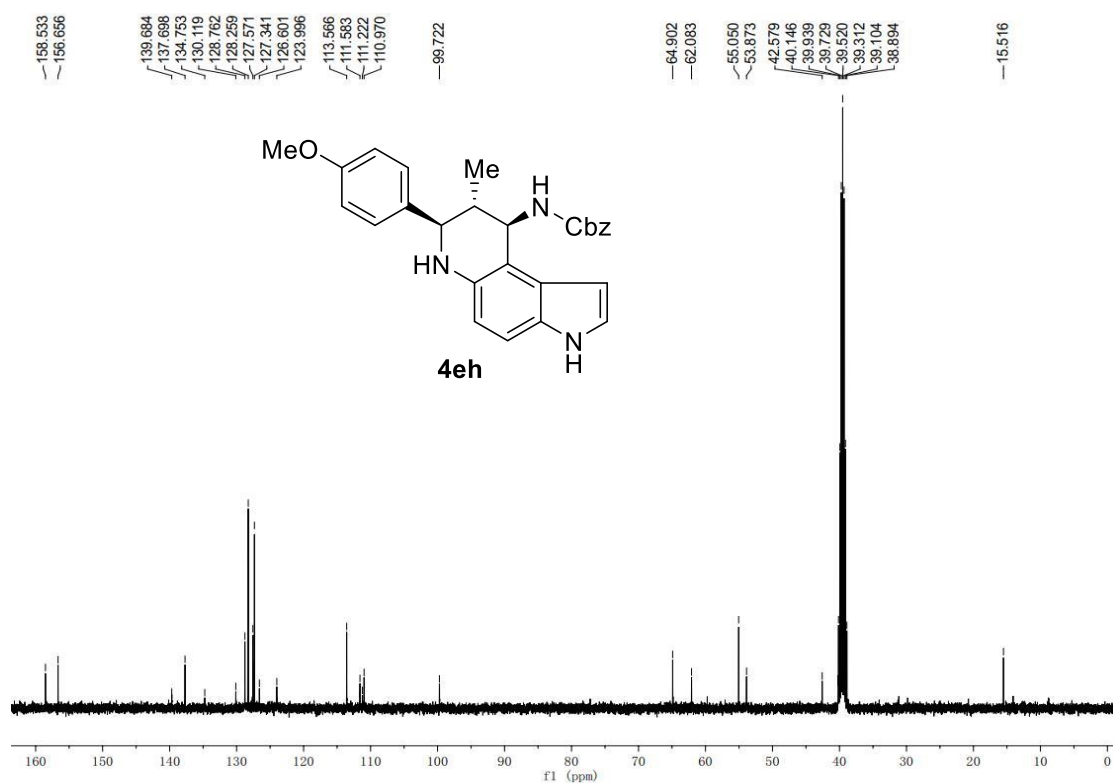


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ef**



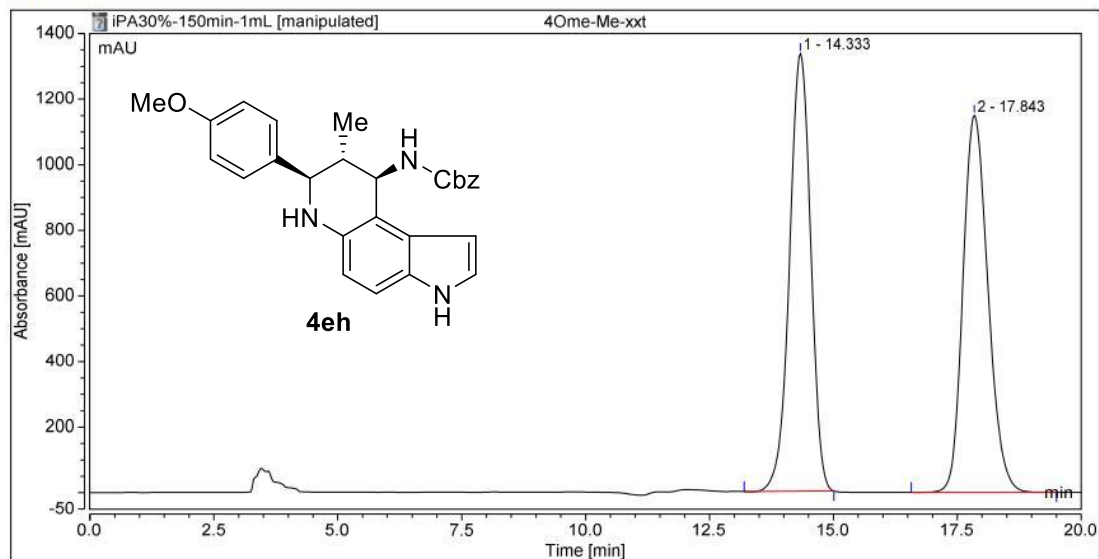


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4eh**



**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4eh**

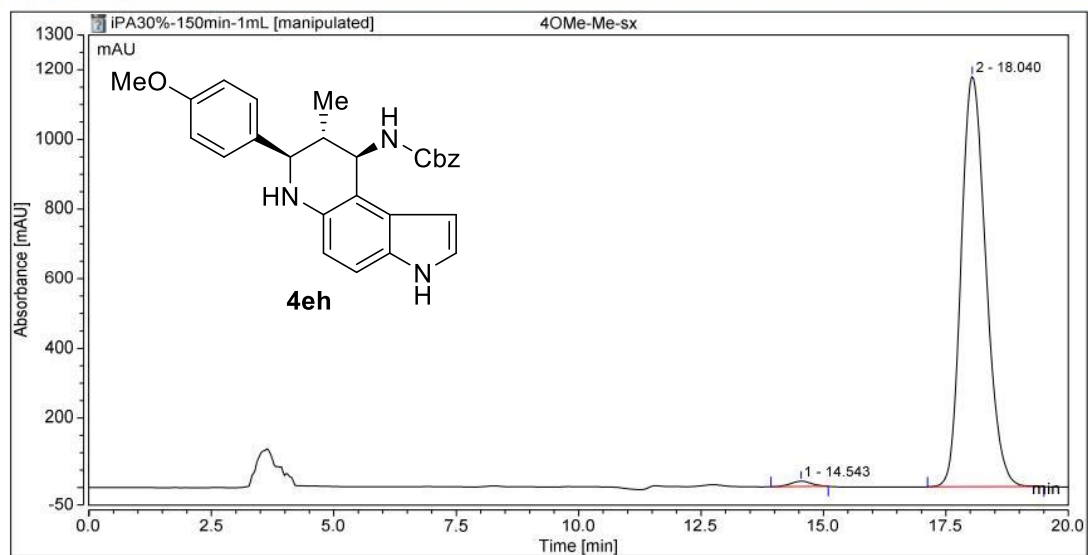
### Chromatogram



### Integration Results

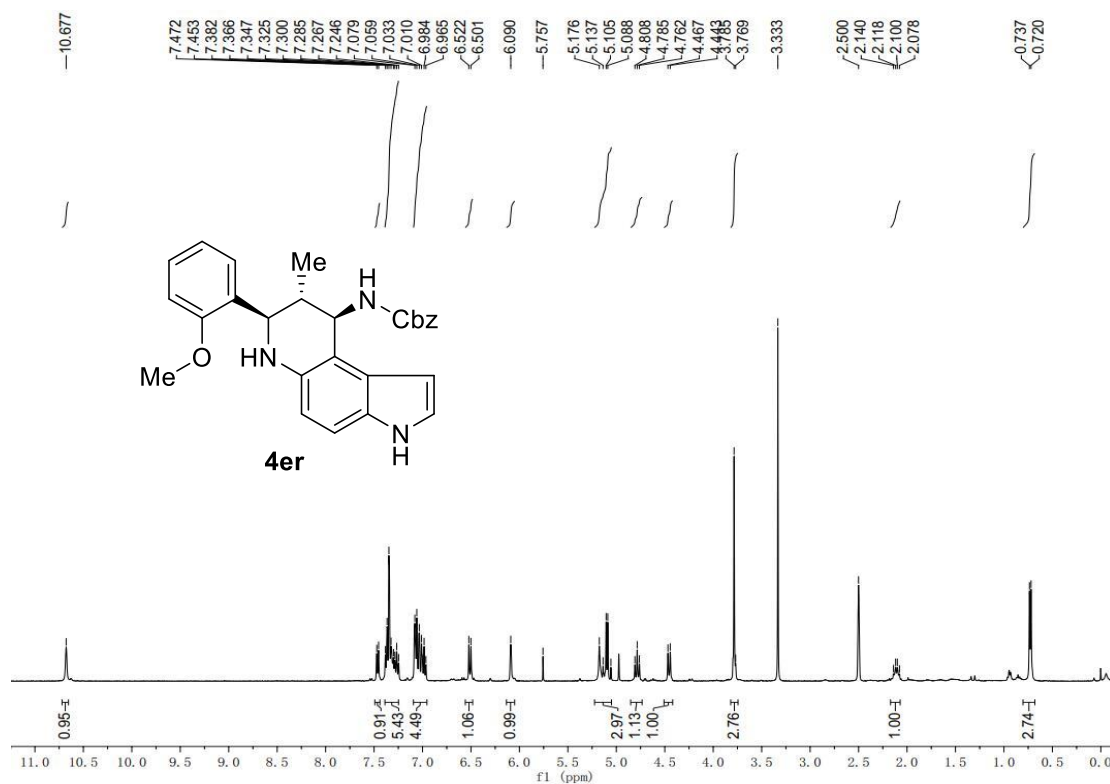
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.333	661.020	1334.524	49.59	53.72	n.a.
2		17.843	671.893	1149.899	50.41	46.28	n.a.
<b>Total:</b>			<b>1332.912</b>	<b>2484.423</b>	<b>100.00</b>	<b>100.00</b>	

### Chromatogram

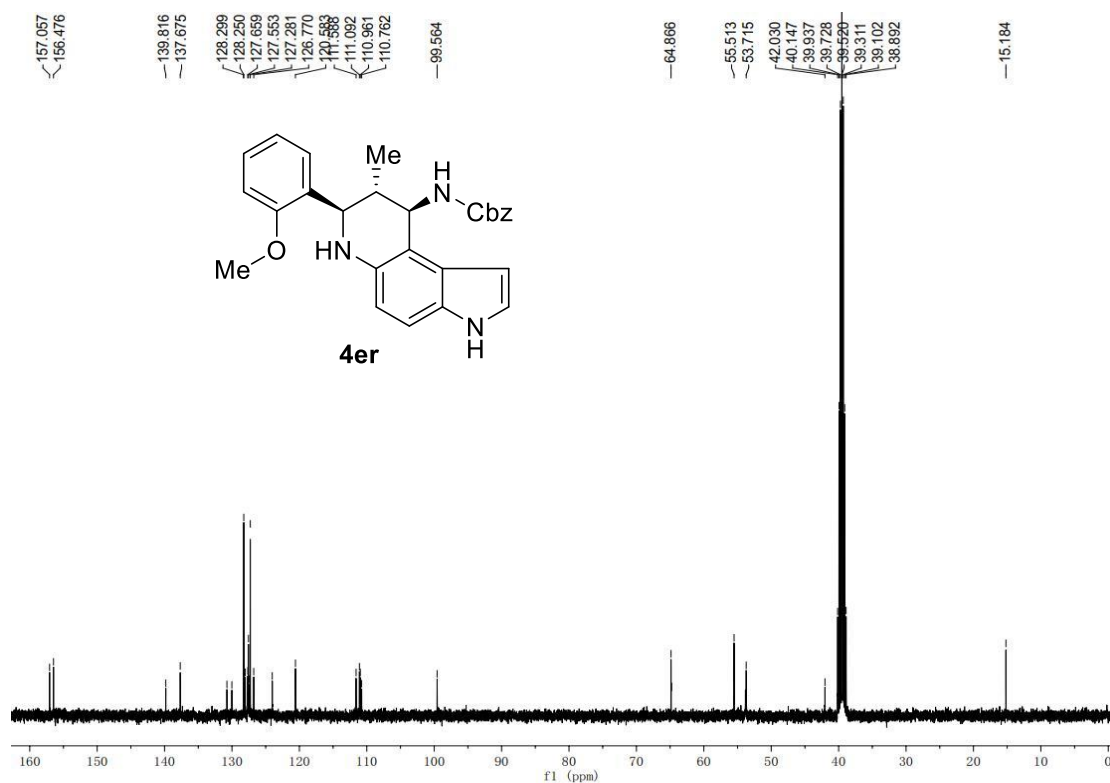


### Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.543	7.740	15.495	1.11	1.30	n.a.
2		18.040	689.368	1178.354	98.89	98.70	n.a.
<b>Total:</b>			<b>697.108</b>	<b>1193.849</b>	<b>100.00</b>	<b>100.00</b>	

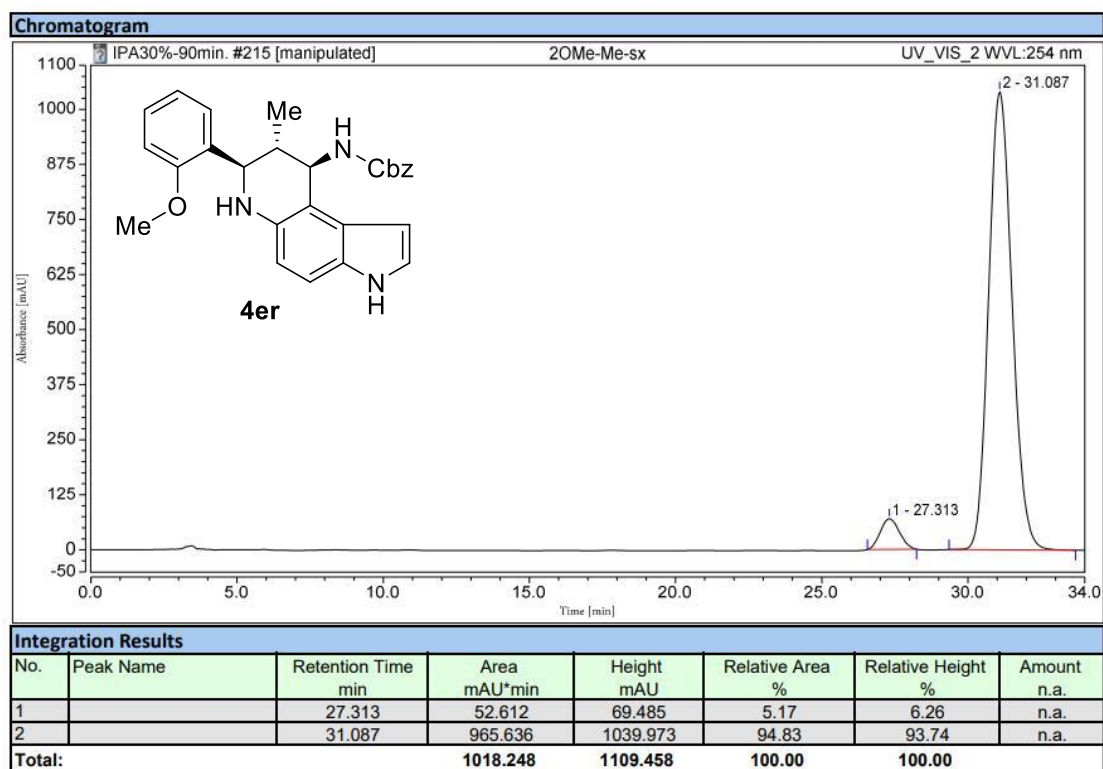
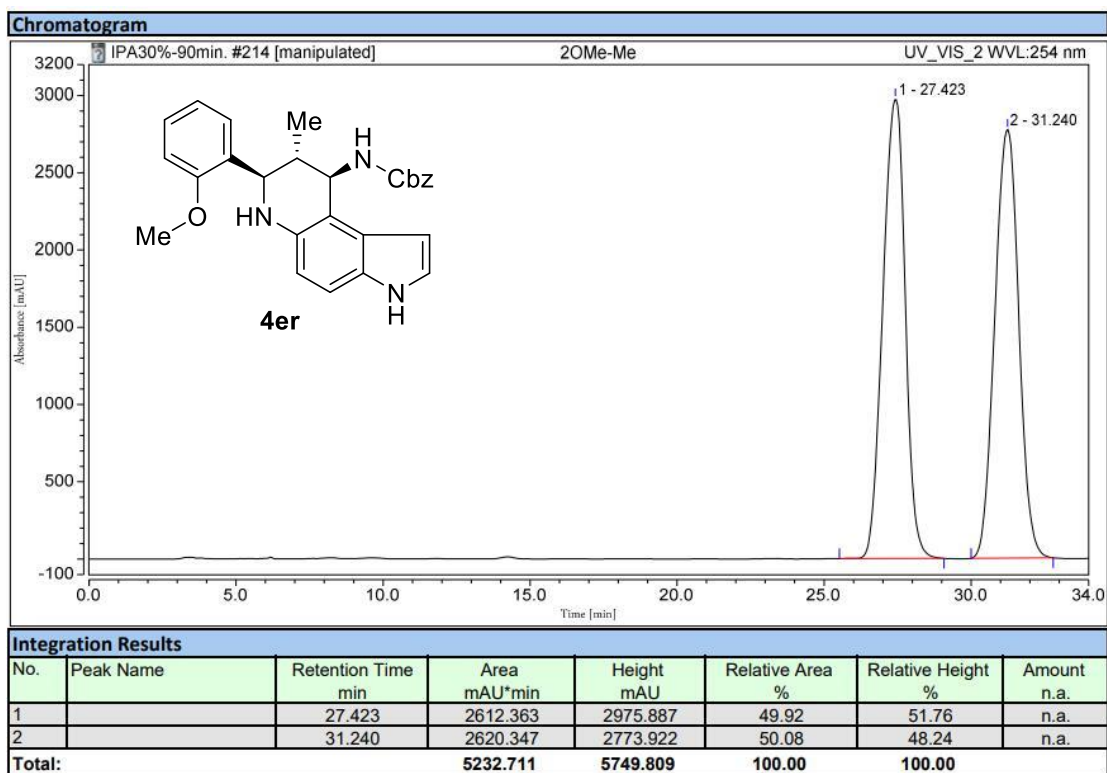


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 4er**

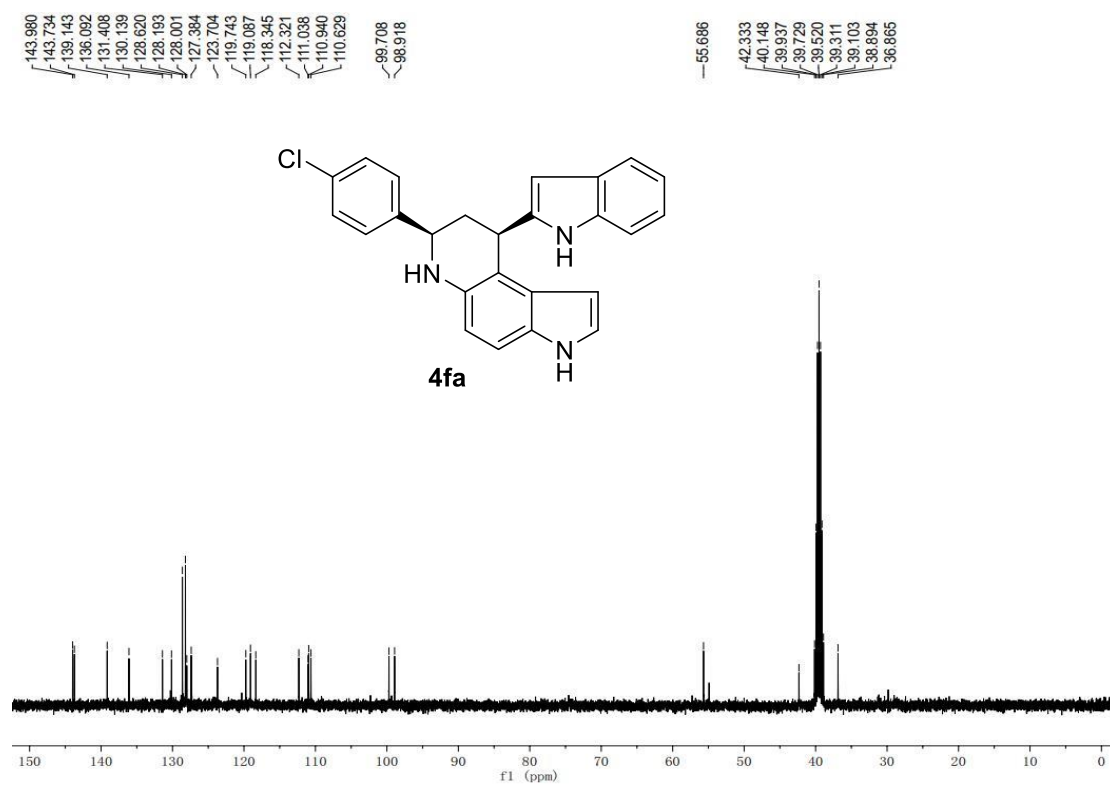
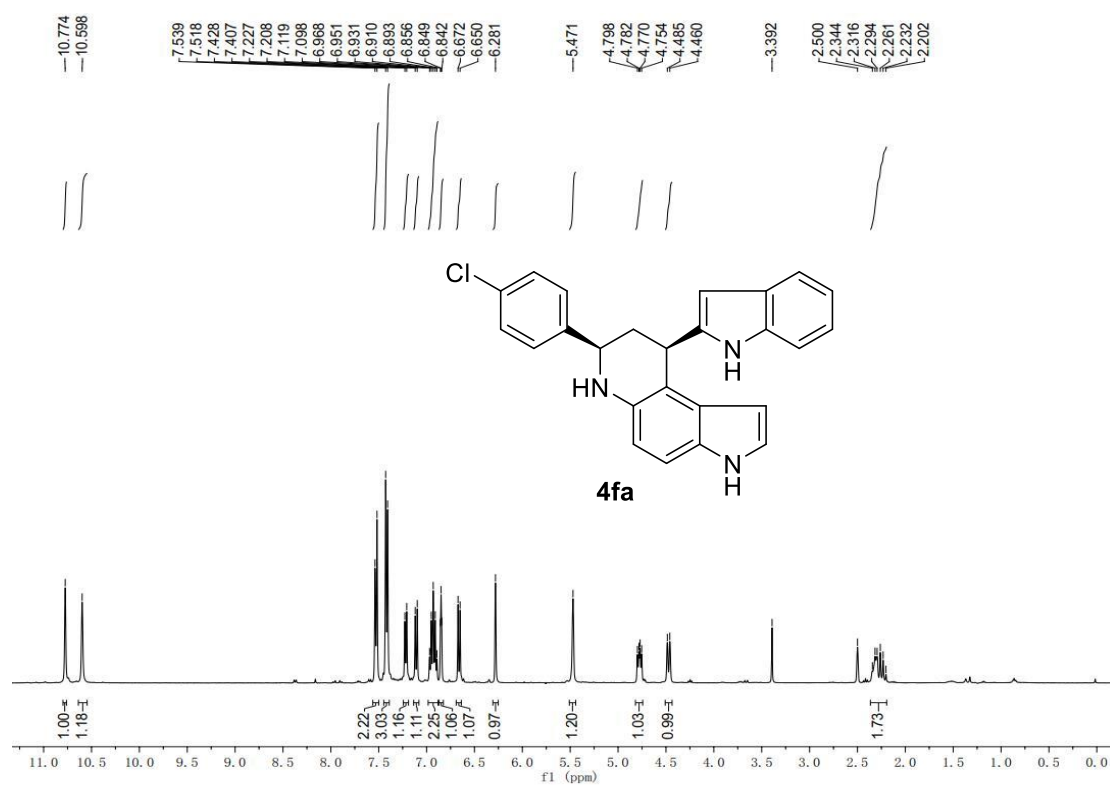


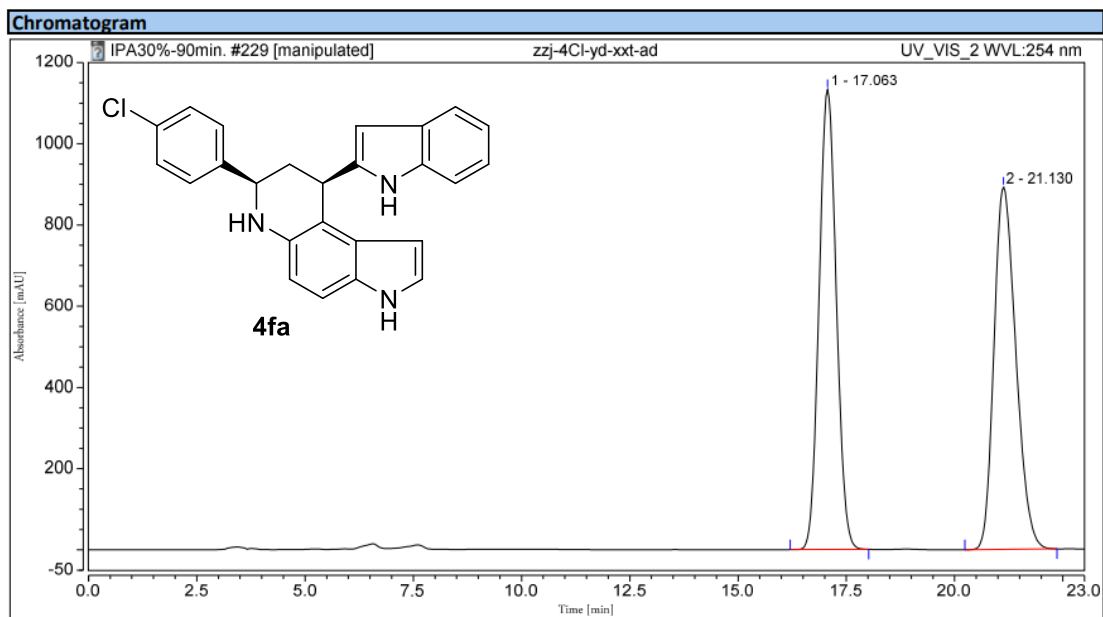
**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 4er**





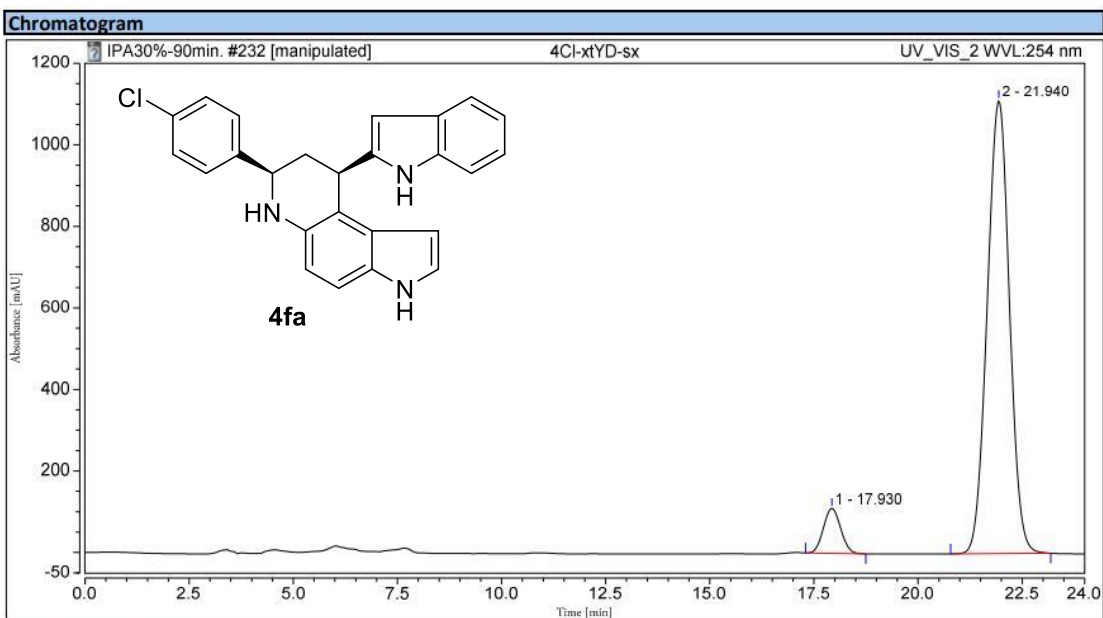






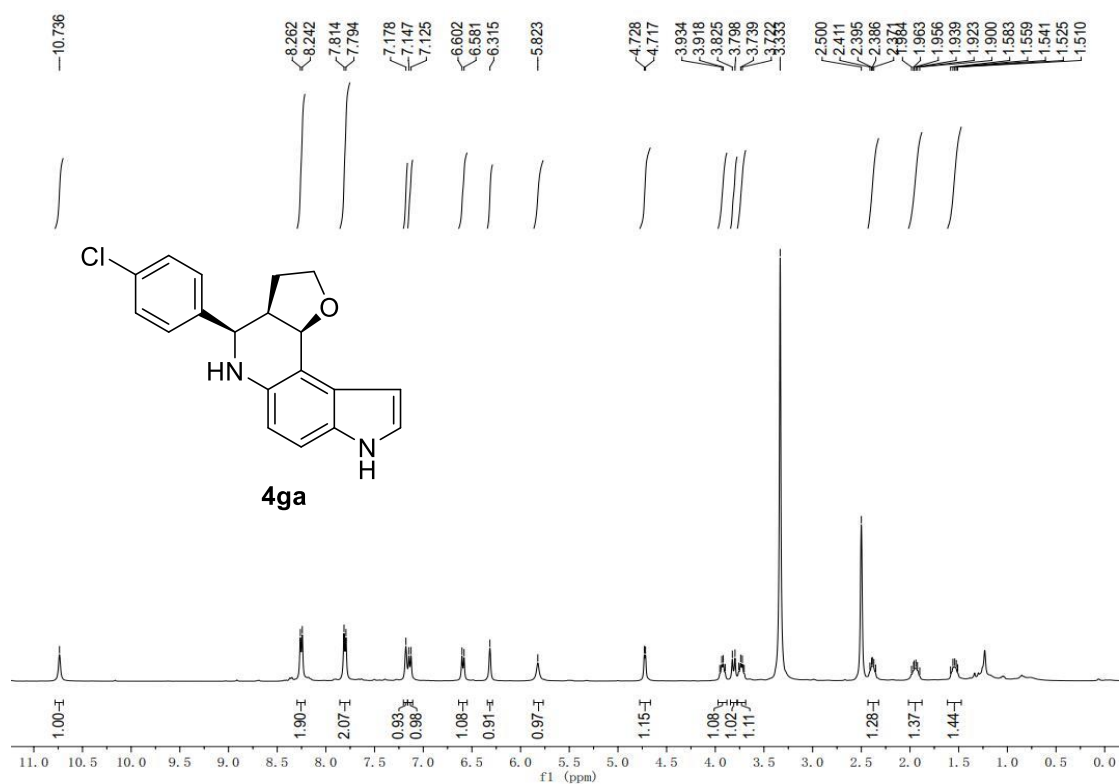
**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.063	523.040	1132.433	50.04	55.94	n.a.
2		21.130	522.271	892.033	49.96	44.06	n.a.
<b>Total:</b>			<b>1045.311</b>	<b>2024.466</b>	<b>100.00</b>	<b>100.00</b>	

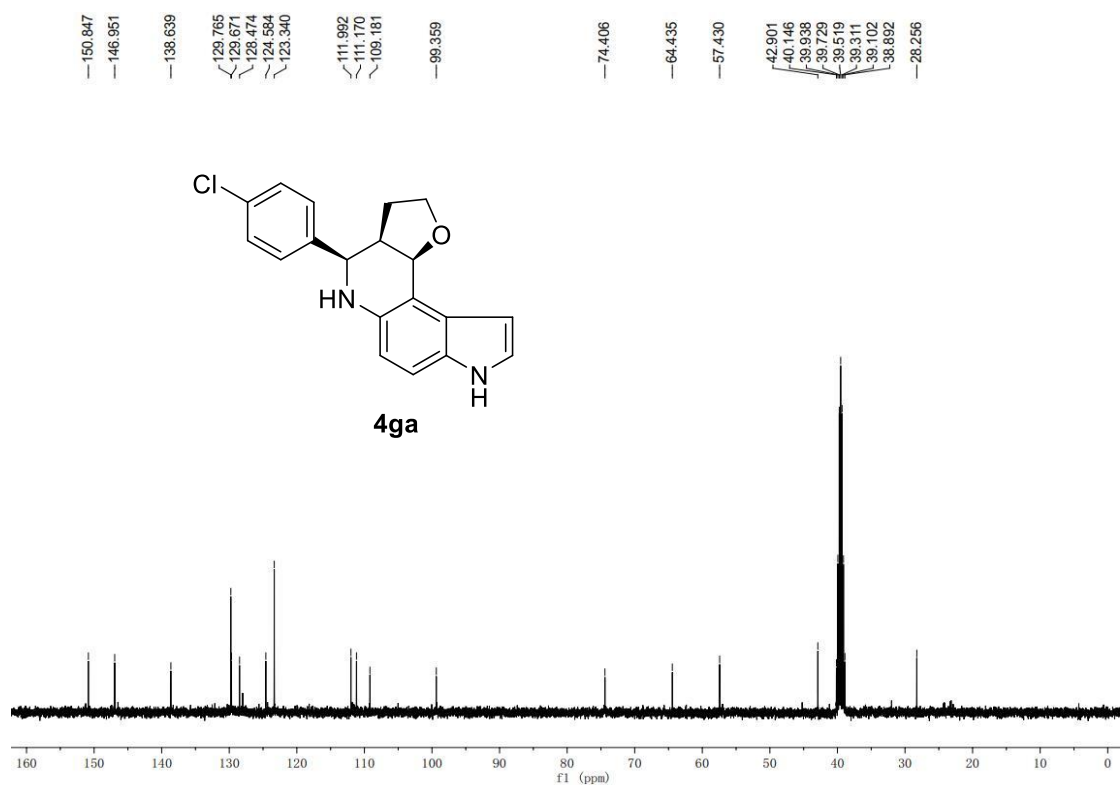


**Integration Results**

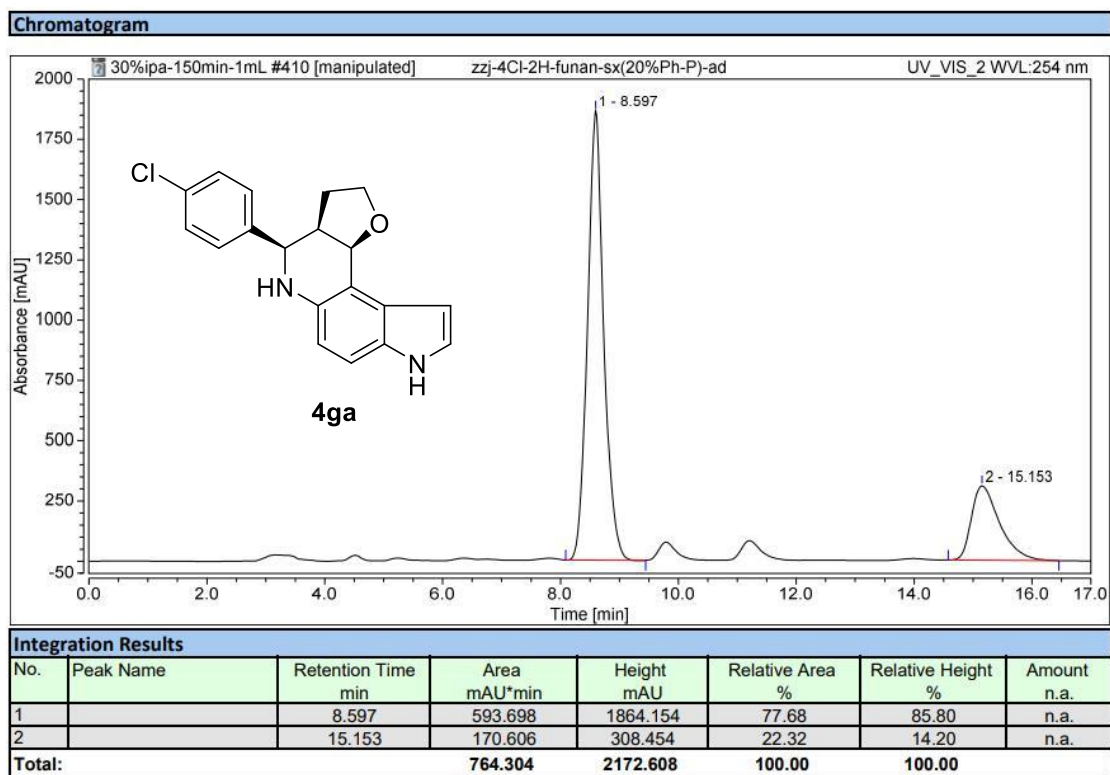
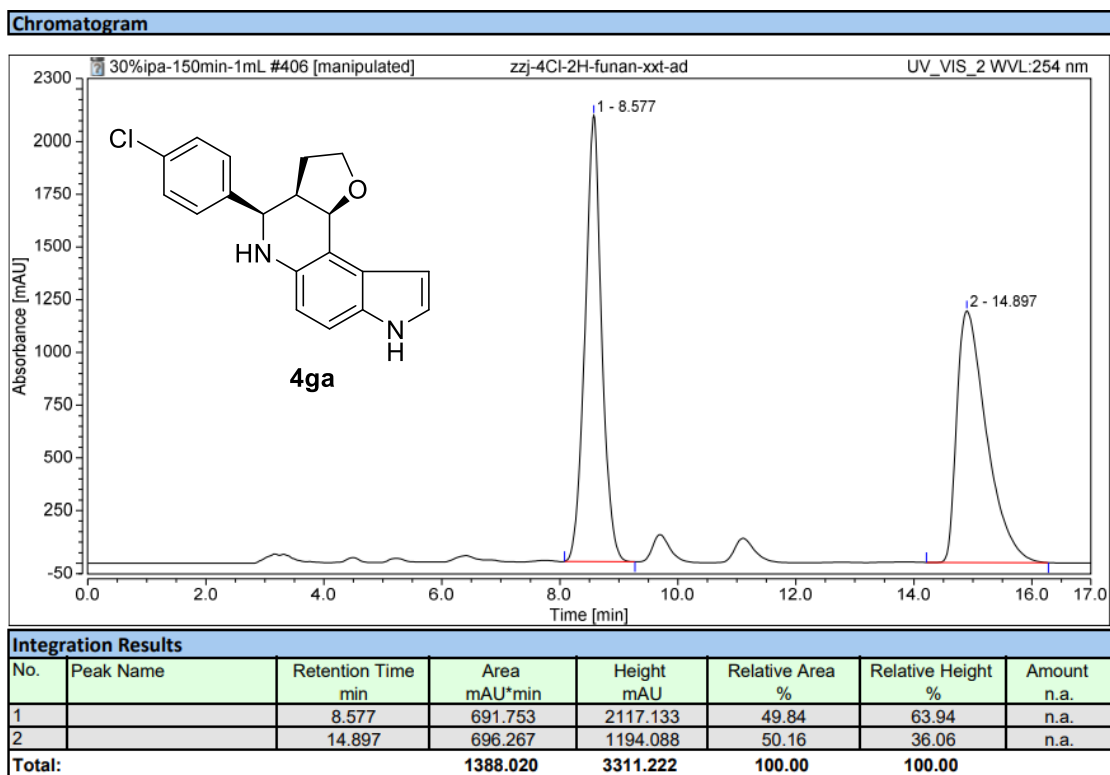
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		17.930	53.109	110.314	7.18	9.03	n.a.
2		21.940	686.310	1111.575	92.82	90.97	n.a.
<b>Total:</b>			<b>739.419</b>	<b>1221.888</b>	<b>100.00</b>	<b>100.00</b>	

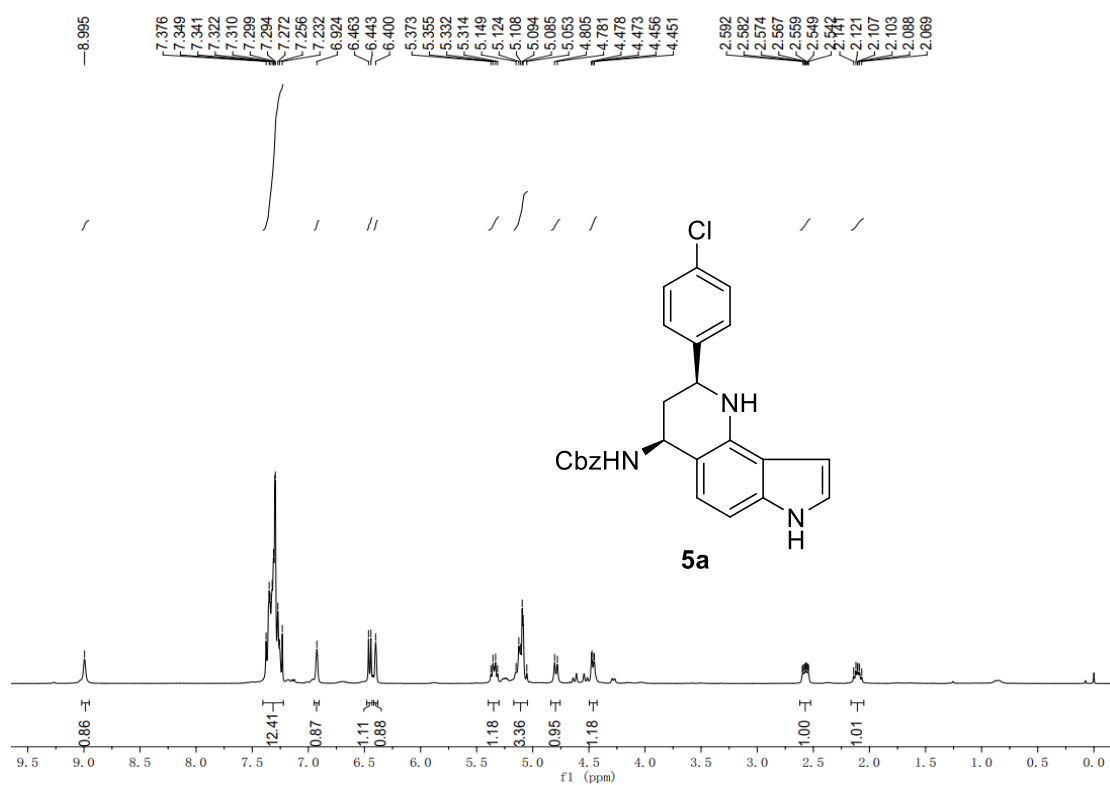


<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **4ga**

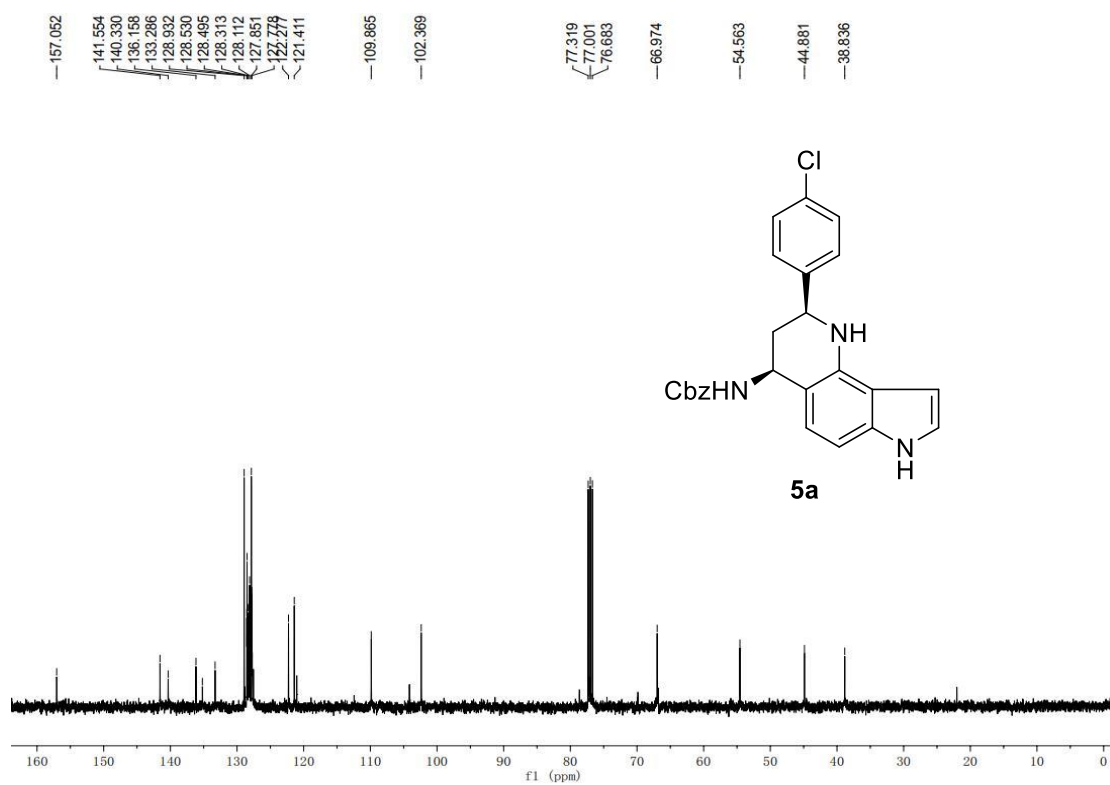


<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **4ga**



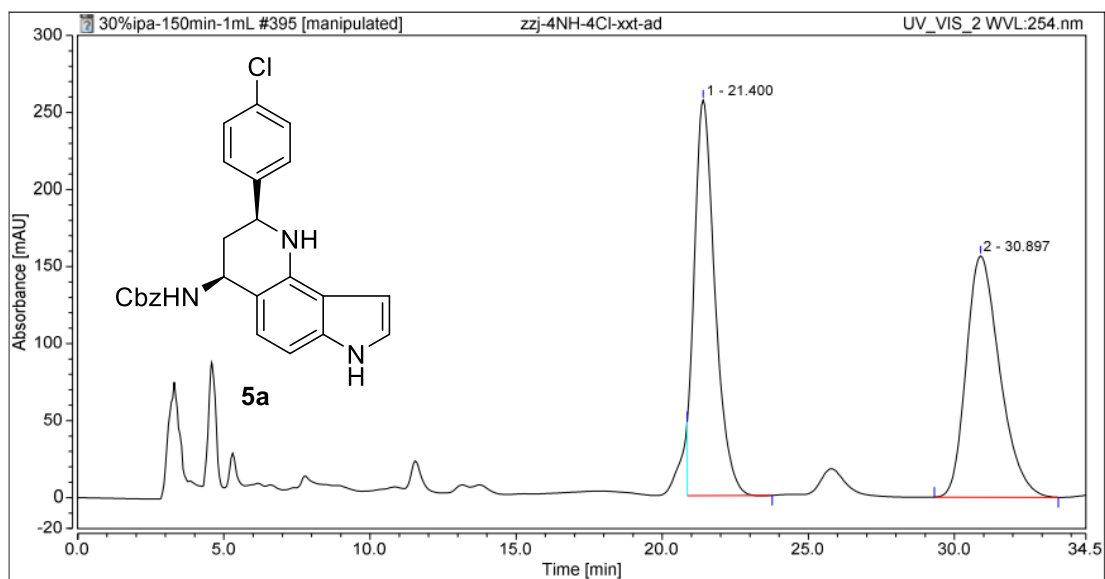


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **5a**



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **5a**

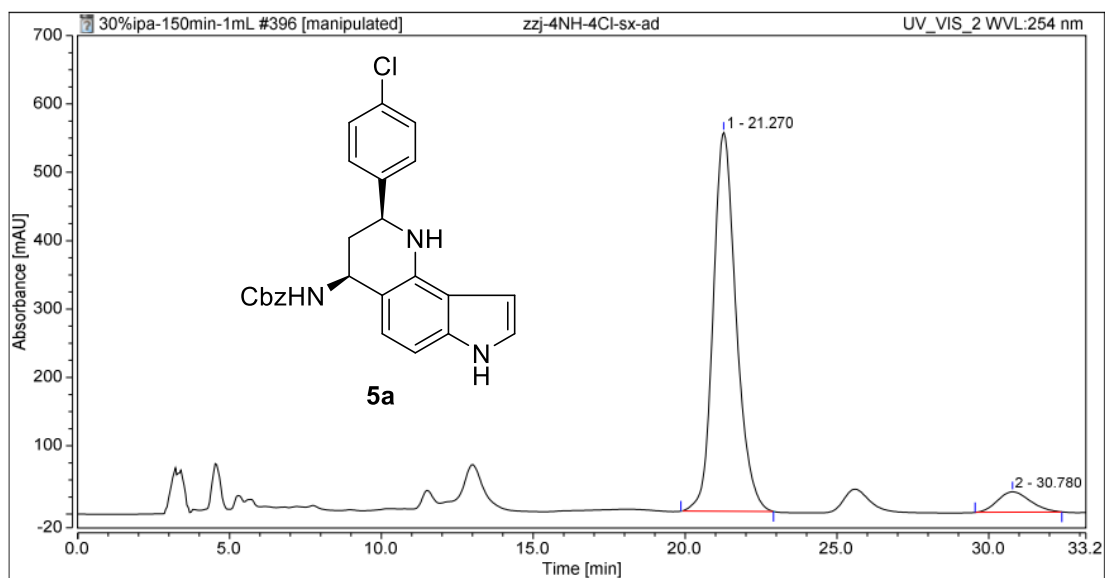
### Chromatogram



### Integration Results

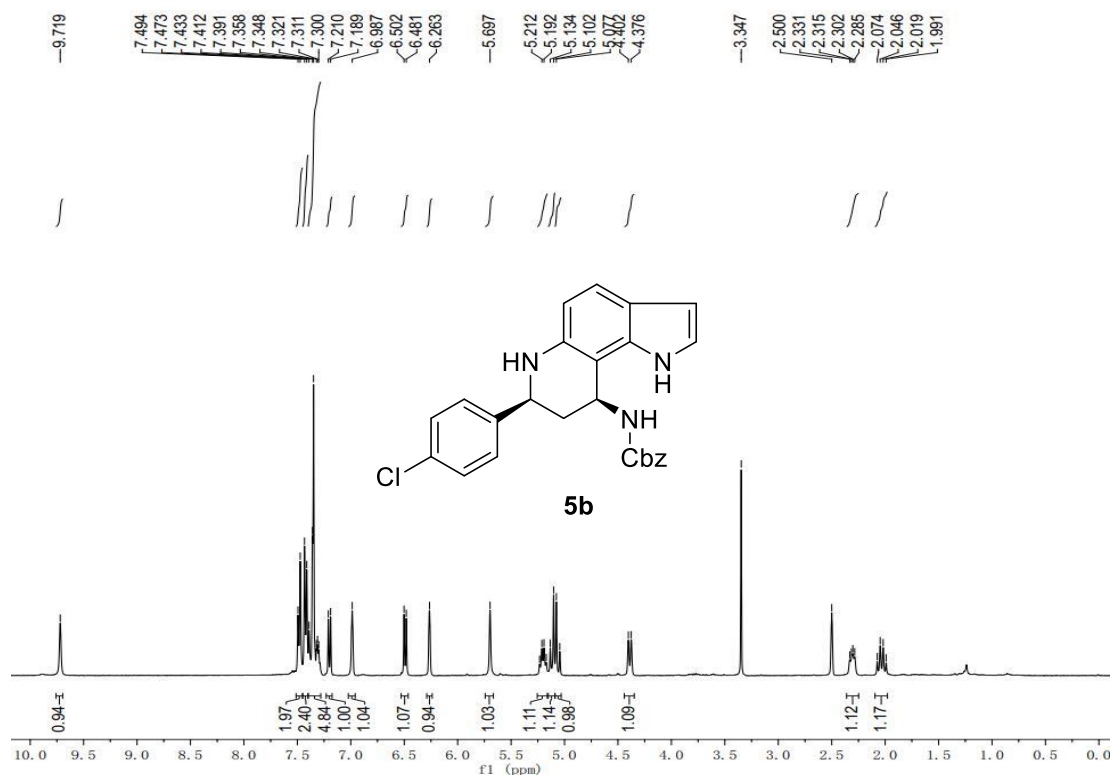
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.400	210.763	256.706	50.29	62.11	n.a.
2		30.897	208.306	156.597	49.71	37.89	n.a.
<b>Total:</b>			<b>419.068</b>	<b>413.303</b>	<b>100.00</b>	<b>100.00</b>	

### Chromatogram

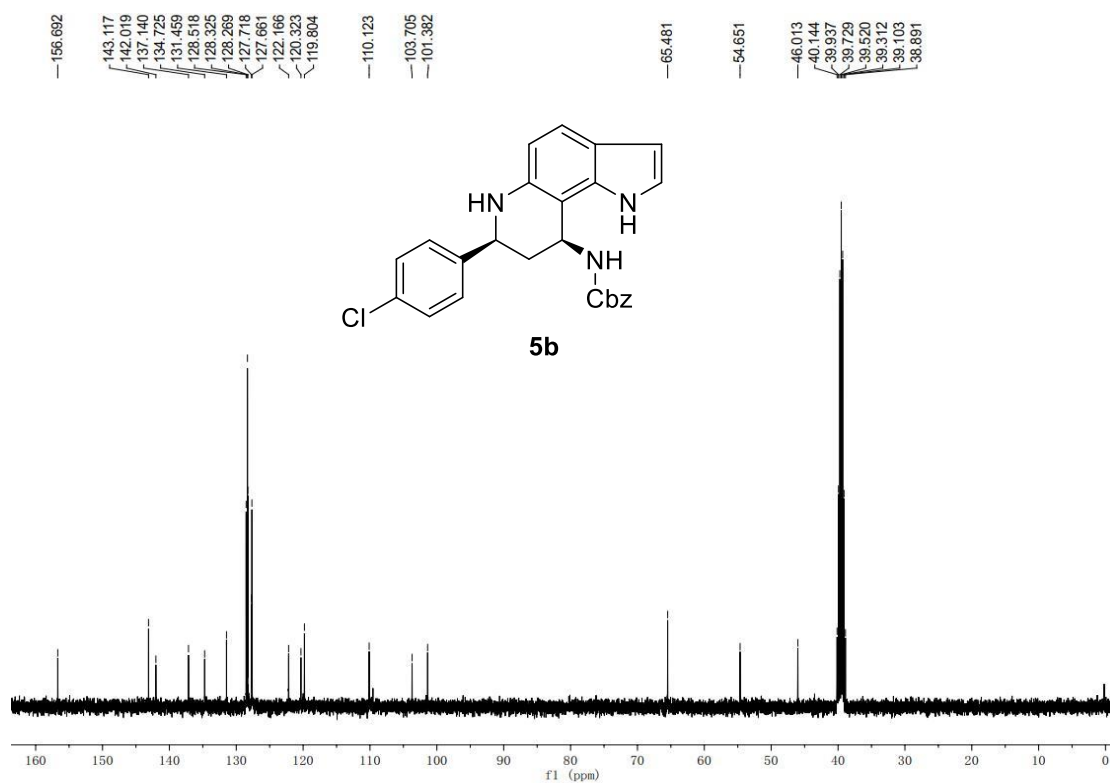


### Integration Results

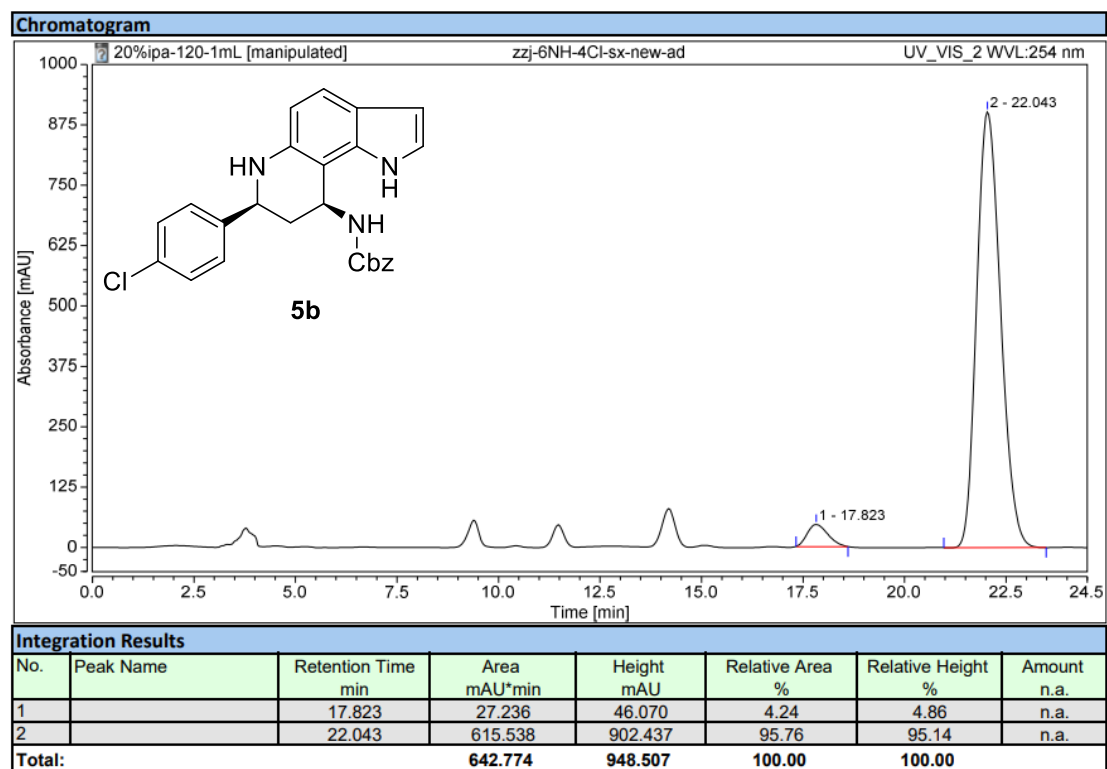
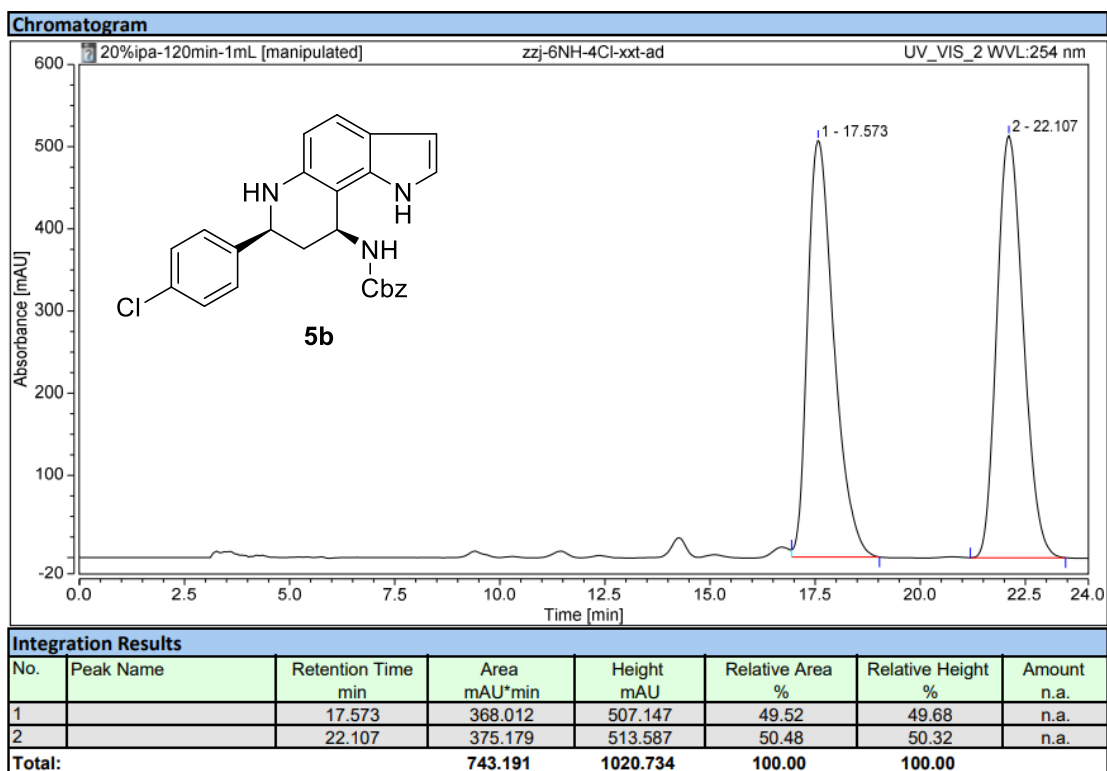
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.270	485.621	554.561	92.87	94.90	n.a.
2		30.780	37.263	29.807	7.13	5.10	n.a.
<b>Total:</b>			<b>522.884</b>	<b>584.368</b>	<b>100.00</b>	<b>100.00</b>	



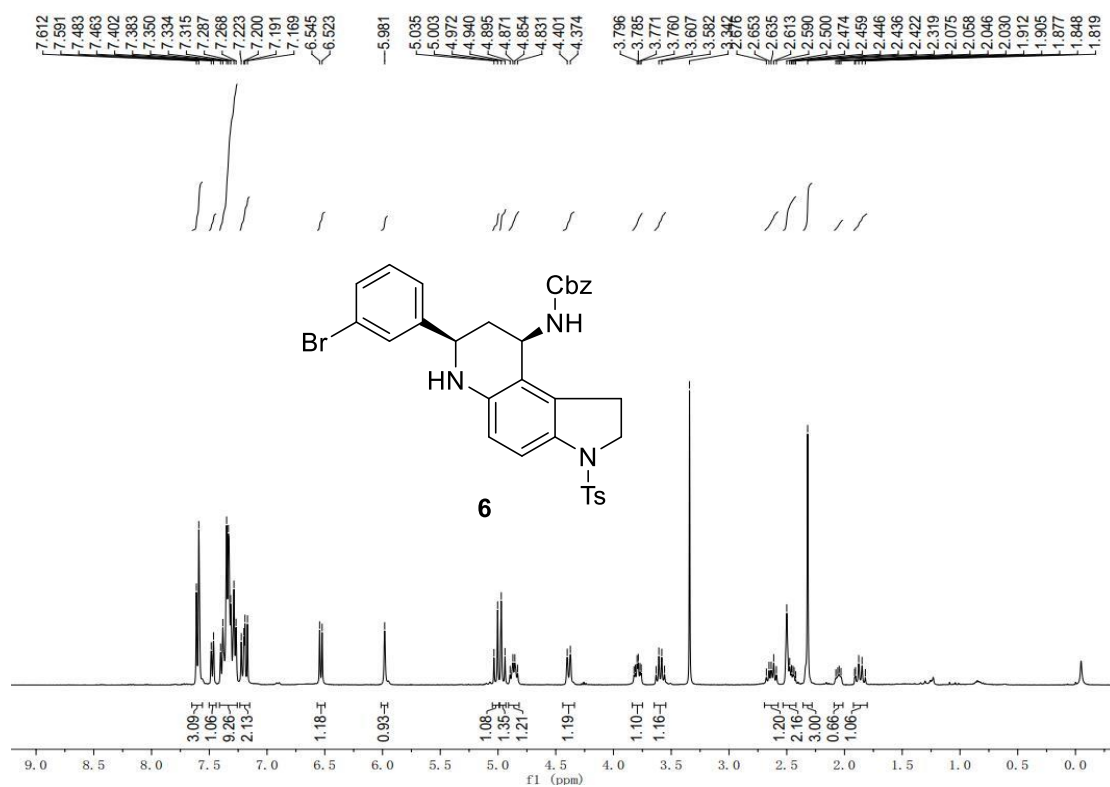
<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of **5b**



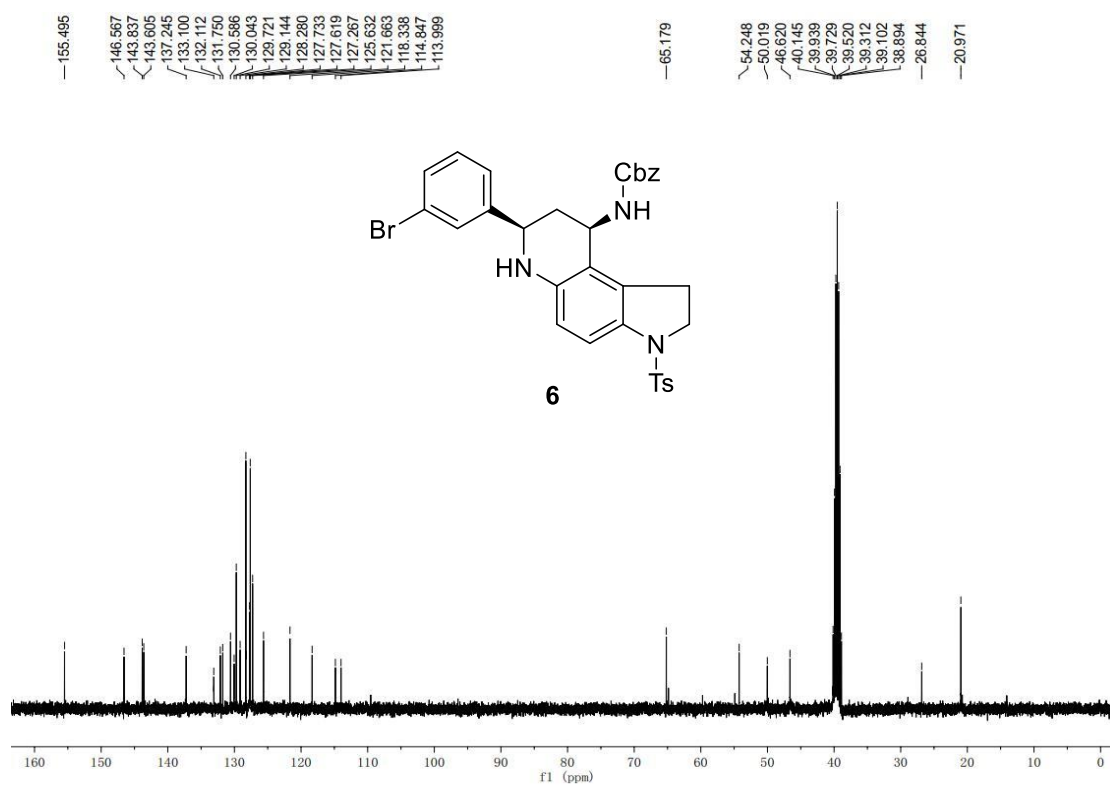
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of **5b**



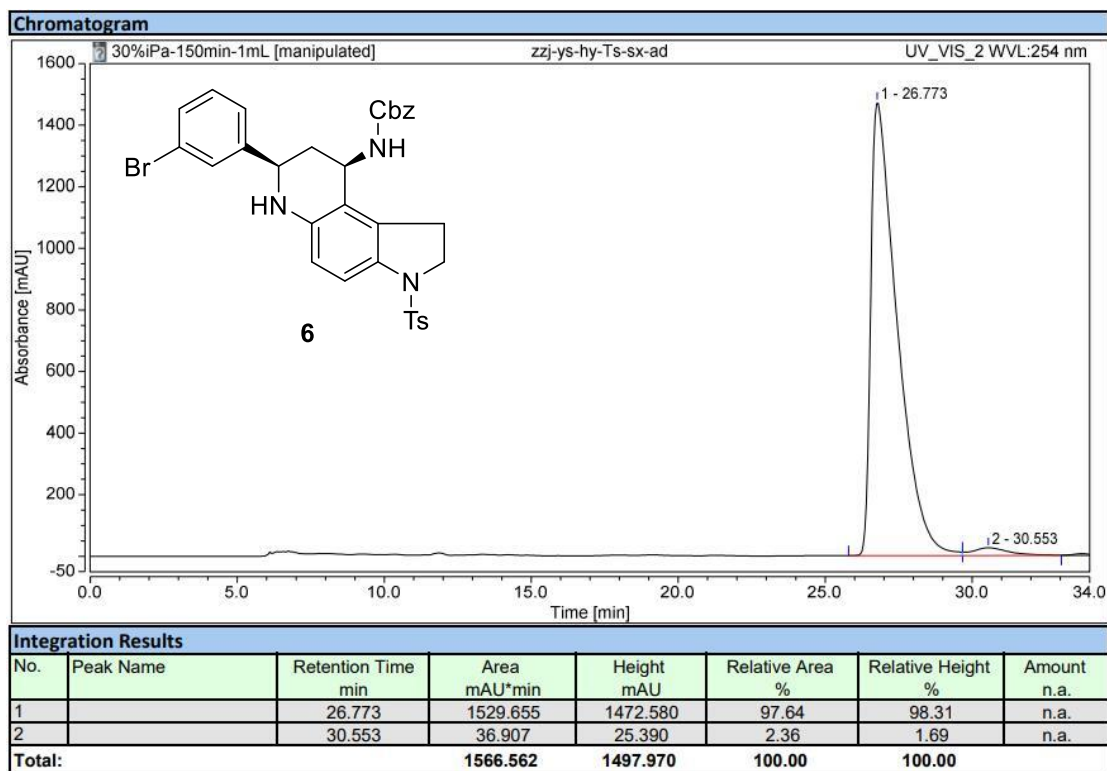
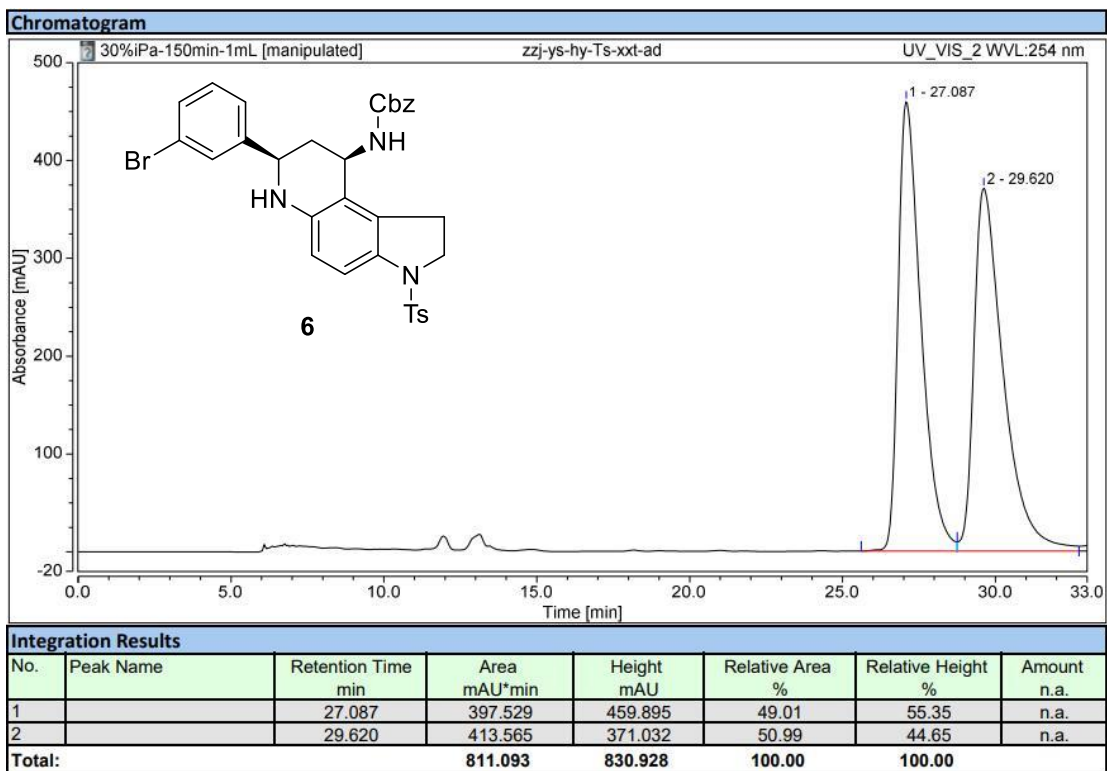


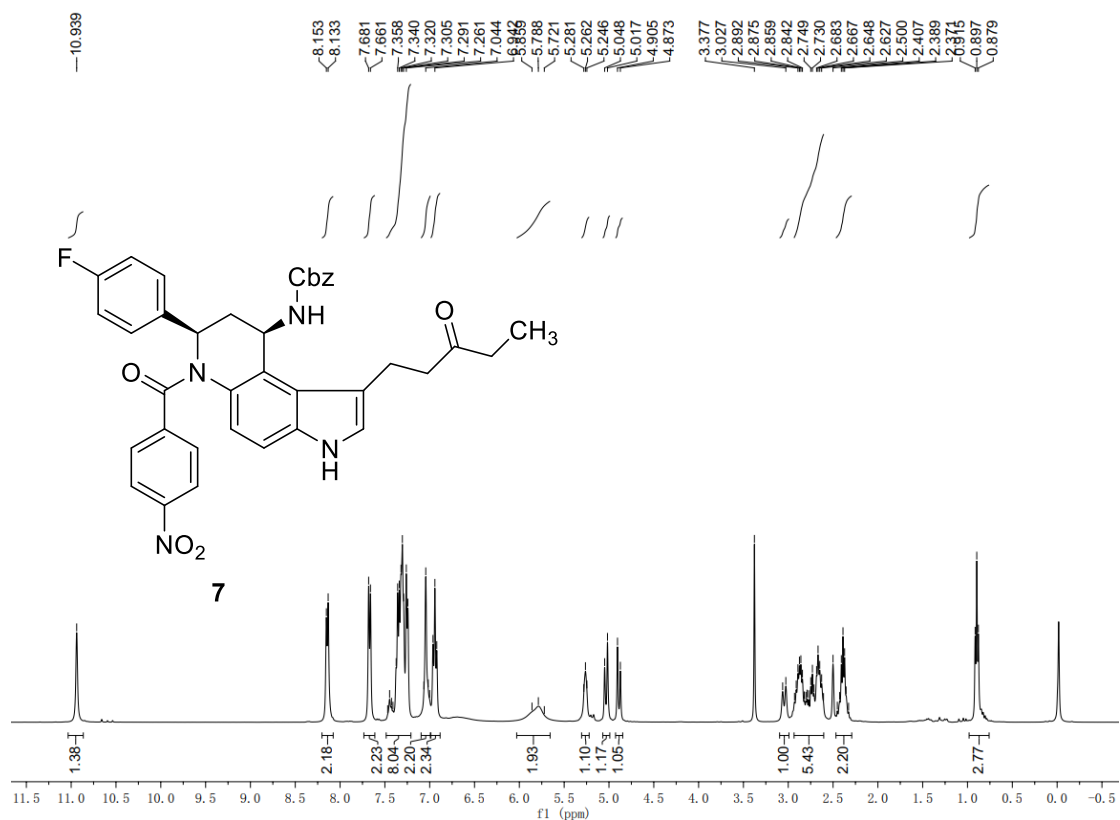


**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 6**

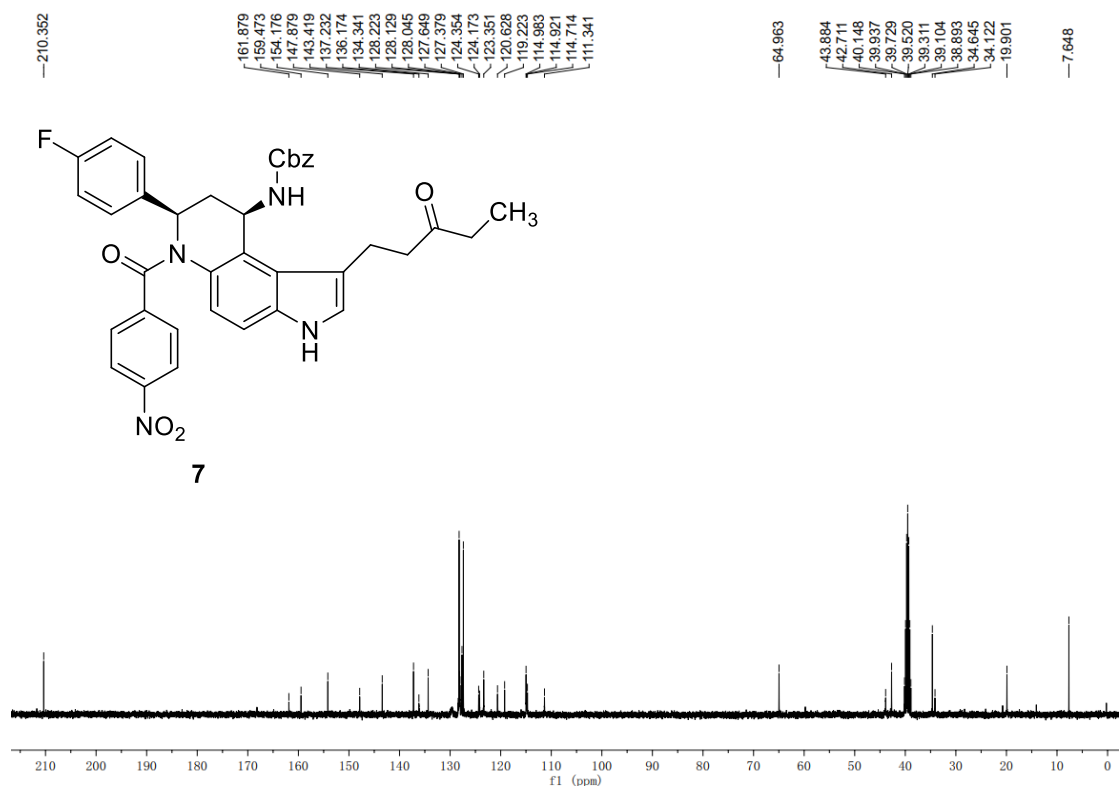


**<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) of 6**

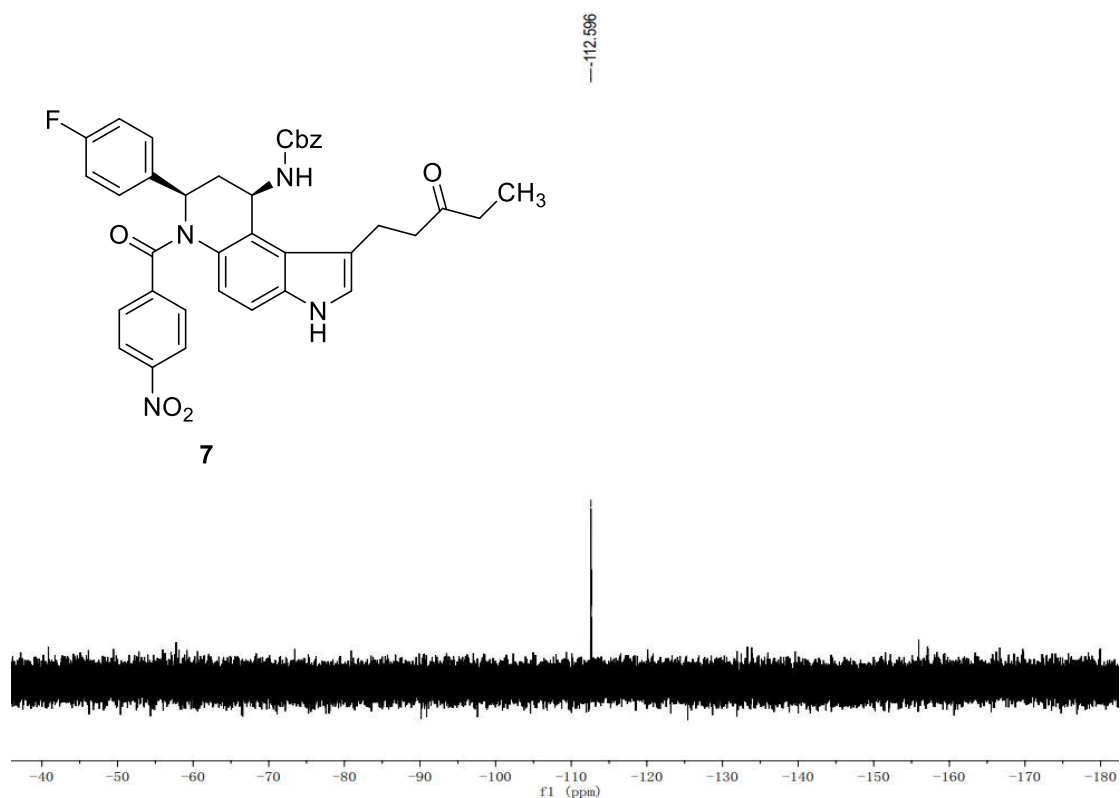




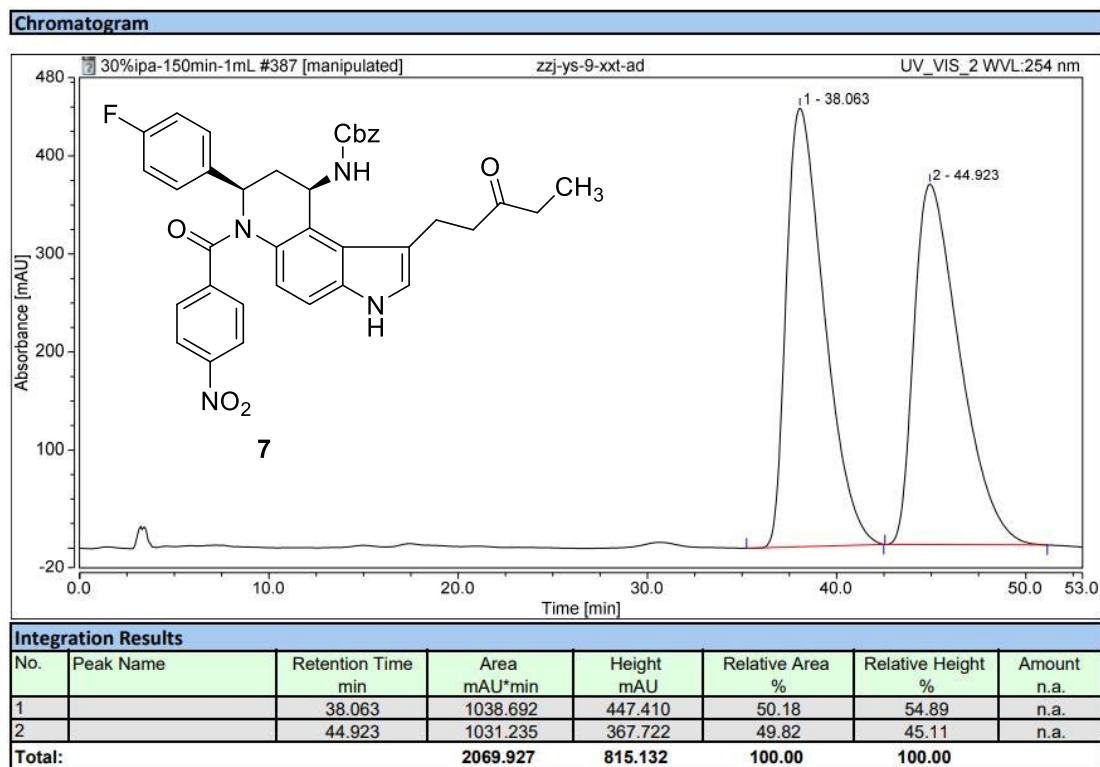
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) of 7



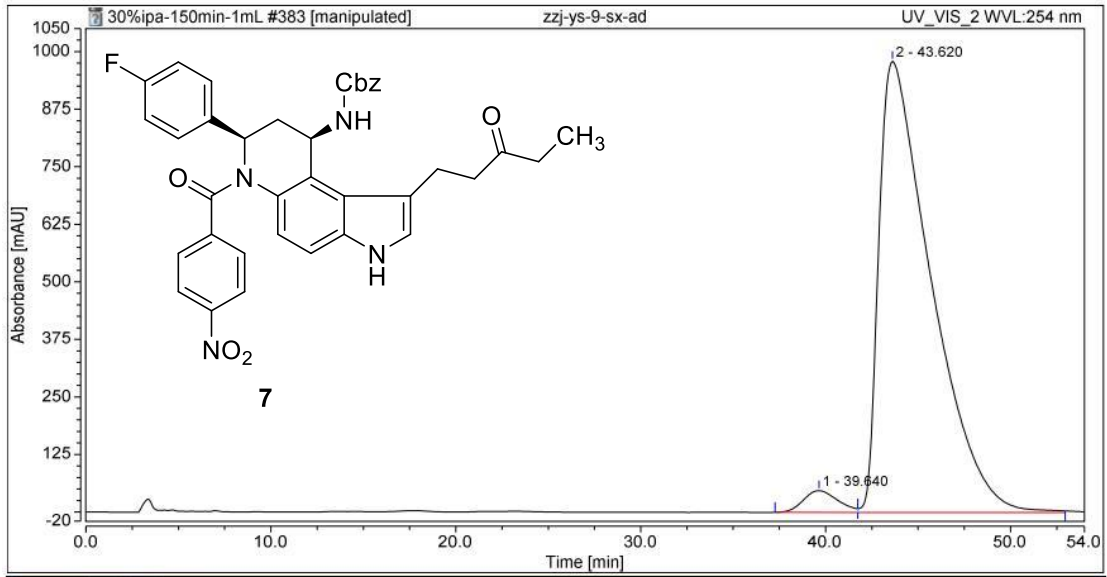
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) of 7



<sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) of 7



**Chromatogram**



**Integration Results**

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		39.640	101.121	47.067	3.06	4.58	n.a.
2		43.620	3201.766	980.117	96.94	95.42	n.a.
<b>Total:</b>			<b>3302.887</b>	<b>1027.184</b>	<b>100.00</b>	<b>100.00</b>	