

## Supporting Information

### An Isothiourea-Catalyzed Asymmetric Formal [4+2] Cycloaddition of *in situ* Generated Azoalkenes with C1 Ammonium Enolates

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#### 1. General Information

##### General data:

NMR spectra were recorded on a Bruker-400 MHz spectrometer. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>:  $\delta$ H = 7.26 ppm,  $\delta$ C = 77.16 ppm).

The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker Daltonics Inc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer.

Enantiomeric excesses were performed on Waters-Breeze (2487 Dual  $\lambda$  Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). Chiralpak AD-H and OD-H columns were purchased from Daicel Chemical Industries, LTD.

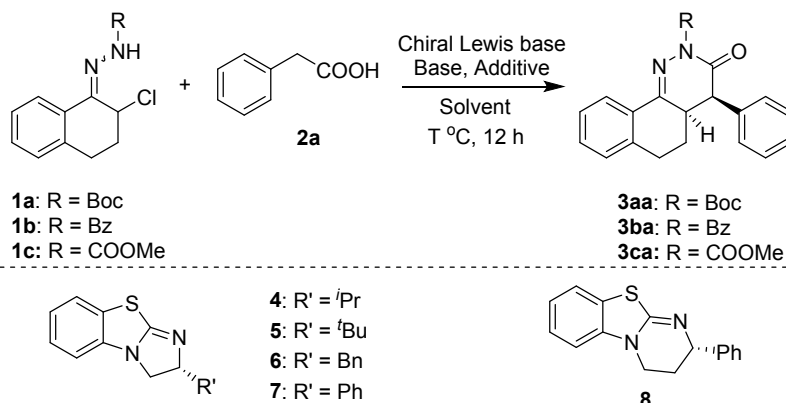
Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter.

##### Materials:

All starting materials, reagents and solvents were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas, etc.) and used as supplied unless otherwise stated. Some substrates<sup>[1]</sup> and chiral Lewis base catalysts<sup>[2]</sup> were synthesized in accordance with the similar procedures in literatures. Toluene was dried over Na and distilled prior to use.

## 2. Details for Condition Optimization

Table S1. Optimal Conditions for the Asymmetric Formal [4+2] Cycloaddition Reaction<sup>a</sup>



Entry	1	Chiral Lewis base	Base	Solvent	T/°C	Yield <sup>b</sup> (%)	dr <sup>c</sup>	ee <sup>d</sup> (%)
1 <sup>e</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	-20	79	91:9	>99
2 <sup>e</sup>	1a	4	-	THF	-20	N.R.	-	-
3 <sup>e</sup>	1a	-	<i>i</i> Pr <sub>2</sub> NEt	THF	-20	N.R.	-	-
4	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	-20	97	92:8	>99
5	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	-30	90	92:8	>99
6	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	0	99	92:8	>99
7	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	25	99	90:10	>99
8	1b	4	<i>i</i> Pr <sub>2</sub> NEt	THF	0	89	85:15	>99 (86)
9	1c	4	<i>i</i> Pr <sub>2</sub> NEt	THF	0	94	80:20	99 (55)
10	1a	4	Na <sub>2</sub> CO <sub>3</sub>	THF	0	99	89:11	>99
11	1a	4	K <sub>2</sub> CO <sub>3</sub>	THF	0	47	90:10	>99
12	1a	4	NEt <sub>3</sub>	THF	0	93	92:8	>99
13 <sup>f</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	THF	0	97	92:8	>99
14 <sup>f</sup>	1a	5	<i>i</i> Pr <sub>2</sub> NEt	THF	0	88	92:8	>99
15 <sup>f</sup>	1a	6	<i>i</i> Pr <sub>2</sub> NEt	THF	0	98	85:15	>99
16 <sup>f</sup>	1a	7	<i>i</i> Pr <sub>2</sub> NEt	THF	0	80	83:17	99
17 <sup>f</sup>	1a	8	<i>i</i> Pr <sub>2</sub> NEt	THF	0	80	72:28	99
18 <sup>f</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	DCM	0	63	91:9	>99
19 <sup>f</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	DCE	0	88	93:7	>99
20 <sup>f</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	CH <sub>3</sub> CN	0	80	82:18	99
21 <sup>f</sup>	1a	4	<i>i</i> Pr <sub>2</sub> NEt	Toluen	0	95	>95:5	>99

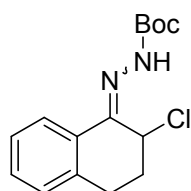
<sup>a</sup> Unless noted, reactions were performed with **1** (0.20 mmol), **2a** (0.30 mmol), *t*BuCOCl (0.40 mmol), Base (0.80 mmol), chiral Lewis base (0.04 mmol, 20 mol%), solvent (2.0 mL). <sup>b</sup> Isolated yield. <sup>c</sup> The diastereomeric ratios were determined by <sup>1</sup>H NMR spectroscopic analysis. <sup>d</sup> Determined by HPLC analysis. <sup>e</sup> Using TsCl (0.40 mmol) instead of *t*BuCOCl (0.40 mmol). <sup>f</sup> Chiral Lewis base (0.02 mmol, 10 mol%) was used. DCM = dichloromethane. DCE = 1,2-dichloroethane.

## 3. General Procedure and Characterization of Products

To a flame-dried and N<sub>2</sub>-purged Schlenk tube **A** were added requisite acid **2** (0.30 mmol), <sup>t</sup>BuCOCl (0.40 mmol), <sup>i</sup>Pr<sub>2</sub>NEt (0.40 mmol) and Toluene (1.0 mL). The suspension was stirred for 15 min at 0 °C. Meanwhile, to another flame-dried and N<sub>2</sub>-purged Schlenk tube **B** were added **1** (0.20 mmol) and Toluene (0.5 mL). The resulting solution was stirred for 10 min at 0 °C. Then the solution in Schlenk tube **A** (1.0 mL) was added to Schlenk tube **B**. Then, a solution of chiral Lewis base catalyst (0.02 mmol, 10 mol%) and <sup>i</sup>Pr<sub>2</sub>NEt (0.40 mmol) in Toluene (0.5 mL) was also added to Schlenk tube **B**. The resulting solution was stirred at 0 °C for 12 hours. After purification by column chromatography on silica gel (Petrol ether: Ethyl acetate = 10:1) the desired product **3** was obtained.

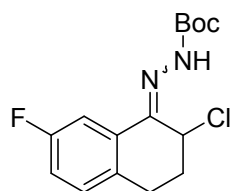
#### 4. Characterization Data of Substrates and Products

##### *tert*-butyl 2-(2-chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (**1a**)



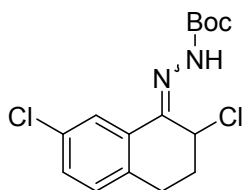
White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (s, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 7.30 - 7.19 (m, 2H), 7.13 (d, *J* = 7.0 Hz, 1H), 5.06 (t, *J* = 3.2 Hz, 1H), 3.23 (ddd, *J* = 16.4, 12.3, 4.2 Hz, 1H), 2.71 (dt, *J* = 16.3, 3.5 Hz, 1H), 2.39 - 2.21 (m, 2H), 1.57 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.55, 144.12, 137.62, 129.76, 129.43, 128.30, 126.87, 125.45, 81.95, 48.95, 31.17, 28.27, 24.08. IR (KBr, cm<sup>-1</sup>) γ 3239, 2979, 1701, 1532, 1454, 1393, 1368, 1272, 1248, 1145, 1066, 1011, 862, 814, 771; HRMS (ESI) *m/z* (M+Na)<sup>+</sup>: calculated for C<sub>15</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>2</sub>Na: 317.1033, found: 317.1024.

##### *tert*-butyl 2-(2-chloro-7-fluoro-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (**1d**)



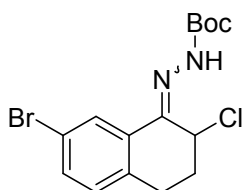
White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.10 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.96 (td, *J* = 8.3, 2.7 Hz, 1H), 5.03 (t, *J* = 3.2 Hz, 1H), 3.27 - 3.08 (m, 1H), 2.70 (dt, *J* = 16.2, 3.5 Hz, 1H), 2.41 - 2.13 (m, 2H), 1.56 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.78 (d, *J* = 244.2 Hz), 152.42, 143.02, 133.27 (d, *J* = 2.9 Hz), 131.63 (d, *J* = 8.0 Hz), 129.88 (d, *J* = 7.8 Hz), 116.77 (d, *J* = 22.2 Hz), 111.49 (d, *J* = 23.4 Hz), 82.23, 48.29, 31.13, 28.23, 23.38. IR (KBr, cm<sup>-1</sup>) γ 3192, 2978, 1733, 1703, 1539, 1492, 1393, 1368, 1275, 1249, 1226, 1147, 1063, 1015, 813, 752, 741; HRMS (ESI) *m/z* (M+Na)<sup>+</sup>: calculated for C<sub>15</sub>H<sub>18</sub>ClFN<sub>2</sub>O<sub>2</sub>Na: 335.0939, found: 335.0932.

**tert-butyl 2-(2,7-dichloro-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine-1-carboxylate (1e)**



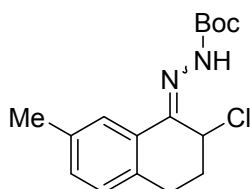
White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 8.21 (s, 1H), 7.22 (dd,  $J = 8.2, 2.2$  Hz, 1H), 7.08 (d,  $J = 8.2$  Hz, 1H), 5.03 (t,  $J = 3.3$  Hz, 1H), 3.18 (ddd,  $J = 16.4, 12.5, 4.0$  Hz, 1H), 2.70 (dt,  $J = 16.4, 3.5$  Hz, 1H), 2.41 – 2.13 (m, 2H), 1.57 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.30, 142.79, 135.83, 132.98, 131.32, 129.68, 129.43, 125.07, 82.28, 48.37, 30.96, 28.23, 23.57. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3219, 2977, 1685, 1385, 1370, 1349, 1146, 1059, 1015, 909, 817, 749; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Na}$ : 351.0643, found: 351.0638.

**tert-butyl 2-(7-bromo-2-chloro-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine-1-carboxylate (1f)**



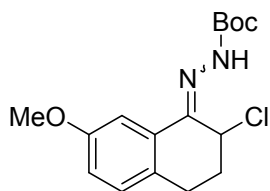
White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (s, 1H), 8.24 (s, 1H), 7.37 (dd,  $J = 8.2, 2.1$  Hz, 1H), 7.02 (d,  $J = 8.1$  Hz, 1H), 5.01 (t,  $J = 3.3$  Hz, 1H), 3.23 – 3.06 (m, 1H), 2.69 (dt,  $J = 16.3, 3.5$  Hz, 1H), 2.36 (ddd,  $J = 14.5, 7.2, 3.3$  Hz, 1H), 2.30 – 2.18 (m, 1H), 1.57 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.27, 142.62, 136.30, 132.30, 131.63, 129.92, 128.02, 120.94, 82.28, 48.37, 30.91, 28.22, 23.64. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3190, 2978, 1682, 1382, 1345, 1145, 1056, 1010, 908, 812, 747; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{15}\text{H}_{18}\text{BrClN}_2\text{O}_2\text{Na}$ : 395.0138, found: 395.0135.

**tert-butyl 2-(2-chloro-7-methyl-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine-1-carboxylate (1g)**



White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H), 8.06 (s, 1H), 7.09 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.03 (d,  $J = 7.8$  Hz, 1H), 5.04 (t,  $J = 3.3$  Hz, 1H), 3.29 – 3.07 (m, 1H), 2.68 (dt,  $J = 16.2, 3.5$  Hz, 1H), 2.36 (dd,  $J = 7.2, 3.3$  Hz, 1H), 2.32 (s, 3H), 2.30 – 2.20 (m, 1H), 1.57 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.54, 144.47, 136.52, 134.81, 130.55, 129.37, 128.20, 125.53, 81.94, 49.09, 31.33, 28.26, 23.70, 21.09. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3217, 2977, 1703, 1531, 1498, 1367, 1250, 1145, 1058, 1019, 814, 764, 750; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{16}\text{H}_{21}\text{ClN}_2\text{O}_2\text{Na}$ : 331.1189, found: 331.1180.

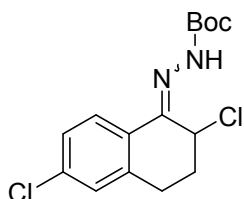
***tert*-butyl 2-(2-chloro-7-methoxy-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (1h)**



White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (s, 1H), 7.72 (d,  $J = 2.6$  Hz, 1H), 7.05 (d,  $J = 8.4$  Hz, 1H), 6.86 (dd,  $J = 8.4, 2.7$  Hz, 1H), 5.05 (t,  $J = 3.2$  Hz, 1H), 3.83 (s, 3H), 3.16 (ddd,  $J = 16.2, 12.4, 4.0$  Hz, 1H), 2.66 (dt,  $J = 16.1, 3.5$  Hz, 1H), 2.44 – 2.30 (m, 1H), 2.28 – 2.19 (m, 1H), 1.57 (s, 9H).  $^{13}\text{C}$

$\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.46, 152.54, 144.06, 130.58, 130.32, 129.46, 117.95, 107.62, 81.95, 55.42, 48.84, 31.36, 28.27, 23.29. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3223, 2978, 1736, 1701, 1533, 1495, 1368, 1290, 1272, 1240, 1149, 1065, 1036, 1013, 857, 820, 740; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{16}\text{H}_{21}\text{ClN}_2\text{O}_3\text{Na}$ : 347.1138, found: 347.1131.

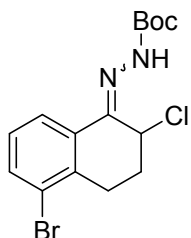
***tert*-butyl 2-(2,6-dichloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (1i)**



White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1H), 8.16 (d,  $J = 7.8$  Hz, 1H), 7.20 (dd,  $J = 28.0, 20.0$  Hz, 2H), 5.03 (s, 1H), 3.22 (t,  $J = 12.5$  Hz, 1H), 2.69 (d,  $J = 16.1$  Hz, 1H), 2.31 (dd,  $J = 32.9, 11.9$  Hz, 2H), 1.56 (s, 9H).  $^{13}\text{C}$

$\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.41, 143.19, 139.10, 135.30, 128.32, 128.10, 127.27, 127.02, 82.17, 48.45, 30.90, 28.24, 23.89. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3441, 2979, 1703, 1607, 1562, 1531, 1475, 1392, 1368, 1265, 1147, 1066, 1012, 746; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_2\text{Na}$ : 351.0643, found: 351.0633.

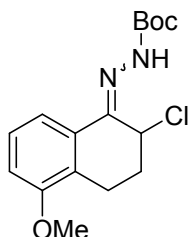
***tert*-butyl 2-(5-bromo-2-chloro-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (1j)**



White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 – 8.18 (m, 2H), 7.55 (dd,  $J = 7.8, 1.0$  Hz, 1H), 7.11 (t,  $J = 8.0$  Hz, 1H), 5.04 (t,  $J = 3.3$  Hz, 1H), 3.21 – 2.92 (m, 2H), 2.40 (ddd,  $J = 14.7, 7.0, 3.3$  Hz, 1H), 2.30 – 2.14 (m, 1H), 1.57 (s, 9H).  $^{13}\text{C}$  **NMR**

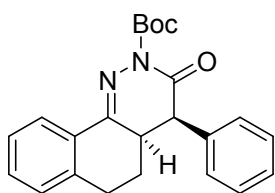
(100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.31, 143.30, 136.72, 133.39, 131.96, 127.84, 124.77, 124.40, 82.24, 47.86, 30.43, 28.23, 24.13. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3231, 2979, 1700, 1525, 1494, 1454, 1392, 1368, 1249, 1149, 1063, 740; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{15}\text{H}_{18}\text{BrClN}_2\text{O}_2\text{Na}$ : 395.0138, found: 395.0133.

**tert-butyl 2-(2-chloro-5-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine-1-carboxylate (1k)**



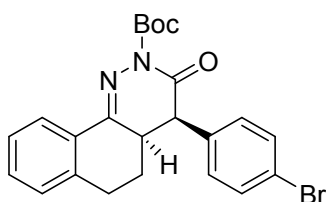
White solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (s, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.19 (t,  $J = 8.1$  Hz, 1H), 6.82 (d,  $J = 8.0$  Hz, 1H), 5.04 (t,  $J = 3.2$  Hz, 1H), 3.84 (s, 3H), 3.10 – 2.97 (m, 1H), 2.91 – 2.76 (m, 1H), 2.36 (ddd,  $J = 14.6, 7.0, 3.1$  Hz, 1H), 2.17 (ddt,  $J = 16.8, 12.4, 4.2$  Hz, 1H), 1.56 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.32, 152.53, 144.30, 130.60, 126.88, 126.86, 117.50, 110.44, 81.91, 55.50, 48.35, 30.39, 28.25, 16.85. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3210, 2960, 1732, 1705, 1537, 1470, 1438, 1368, 1261, 1148, 1019, 851, 790, 745; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{16}\text{H}_{21}\text{ClN}_2\text{O}_3\text{Na}$ : 347.1138, found: 347.1130.

**tert-butyl (4R,4aR)-3-oxo-4-phenyl-4,4a,5,6-tetrahydrobenzo[h]cinnoline-2(3H)-carboxylate (3aa)**



White solid; yield: 95%; *d.r.*: > 95:5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 – 8.24 (m, 1H), 7.35 – 7.19 (m, 5H), 7.19 – 7.04 (m, 3H), 3.88 (d,  $J = 7.0$  Hz, 1H), 3.25 (ddd,  $J = 12.4, 6.9, 5.3$  Hz, 1H), 2.86 – 2.68 (m, 2H), 2.01 – 1.89 (m, 1H), 1.62 (s, 9H), 1.48 – 1.36 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.10, 151.62, 150.61, 140.02, 134.47, 130.48, 130.33, 129.05, 128.80, 128.53, 128.02, 126.92, 125.31, 84.47, 50.33, 38.44, 28.94, 27.98, 24.67. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2935, 1772, 1721, 1454, 1369, 1309, 1272, 1249, 1151, 1093, 767, 736, 701; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}$ : 399.1685, found: 399.1677;  $[\alpha]_D^{20} = +266.1$  ( $c = 0.31$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 5.808 min,  $t_R$  (minor) = 11.550 min.

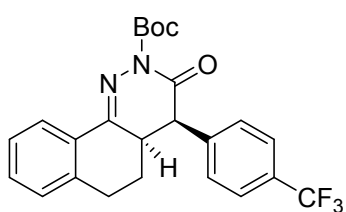
**tert-butyl (4R,4aR)-4-(4-bromophenyl)-3-oxo-4,4a,5,6-tetrahydrobenzo[h]cinnoline-2(3H)-carboxylate (3ab)**



White solid; yield: 99%; *d.r.*: 93:7;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.22 (m, 2H), 7.11 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.05 – 6.95 (m, 2H), 3.85 (d,  $J = 6.9$  Hz, 1H),

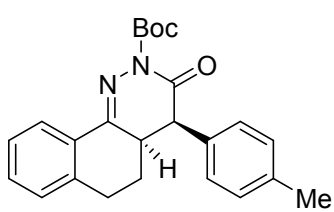
3.25 (ddd,  $J = 12.4, 6.8, 5.3$  Hz, 1H), 2.79 (dd,  $J = 8.4, 3.3$  Hz, 2H), 2.01 – 1.86 (m, 1H), 1.62 (s, 9H), 1.44 – 1.29 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.41, 151.41, 150.43, 139.91, 133.42, 132.16, 130.62, 130.40, 130.07, 128.53, 126.97, 125.23, 122.20, 84.61, 49.71, 38.23, 28.84, 27.93, 24.63. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2936, 1772, 1721, 1489, 1370, 1306, 1272, 1250, 1151, 1011, 774, 755, 734; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{23}\text{H}_{23}\text{BrN}_2\text{O}_3\text{Na}$ : 477.0790, found: 477.0789;  $[\alpha]^{20}_{\text{D}} = +151.3$  ( $c = 0.64$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_{\text{R}}$  (major) = 5.575 min,  $t_{\text{R}}$  (minor) = 12.834 min.

***tert*-butyl (4*R*,4*aR*)-3-oxo-4-(4-(trifluoromethyl)phenyl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ac)**



White solid; yield: 74%; *d.r.*: > 95:5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.51 (d,  $J = 8.2$  Hz, 2H), 7.38 – 7.23 (m, 4H), 7.12 (dd,  $J = 7.2, 1.2$  Hz, 1H), 3.96 (d,  $J = 7.0$  Hz, 1H), 3.30 (ddd,  $J = 12.5, 6.9, 5.3$  Hz, 1H), 2.86 – 2.80 (m, 2H), 1.97 (ddd,  $J = 8.9, 4.3, 2.5$  Hz, 1H), 1.62 (s, 9H), 1.47 – 1.24 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.78 (d,  $J = 1488.0$  Hz), 150.39, 139.92, 138.50, 130.76, 130.33 (d,  $J = 32.7$  Hz), 130.00, 129.84, 129.23, 128.62, 127.08, 126.03 (q,  $J = 3.7$  Hz), 125.30, 123.82 (d,  $J = 272.3$  Hz), 84.79, 50.10, 38.27, 28.87, 27.95, 24.71. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2935, 1773, 1721, 1370, 1326, 1273, 1250, 1152, 1124, 1071, 1018, 849, 832, 764, 732; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_3\text{Na}$ : 467.1558, found: 467.1561;  $[\alpha]^{20}_{\text{D}} = +179.0$  ( $c = 0.59$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_{\text{R}}$  (major) = 4.357 min,  $t_{\text{R}}$  (minor) = 9.197 min.

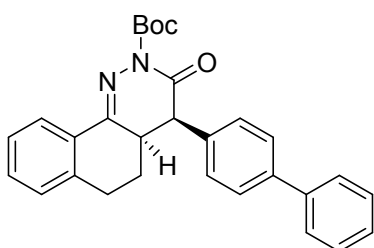
***tert*-butyl (4*R*,4*aR*)-3-oxo-4-(*p*-tolyl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ad)**



White solid; yield: 98%; *d.r.*: > 95:5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 – 8.23 (m, 1H), 7.28 (ddd,  $J = 6.6, 4.1, 2.1$  Hz, 2H), 7.09 (dd,  $J = 7.0, 1.6$  Hz, 1H), 7.06 – 6.97 (m, 4H), 3.84 (d,  $J = 6.9$  Hz, 1H), 3.26 – 3.19 (m, 1H), 2.77 (dd,  $J = 6.8, 3.4$  Hz, 2H), 2.24 (s, 3H), 1.97 – 1.82 (m, 1H),

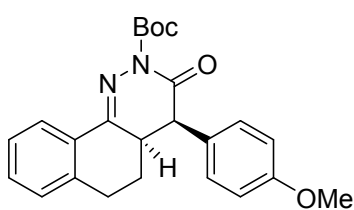
1.61 (s, 9H), 1.52 – 1.33 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.21, 151.60, 150.64, 140.00, 137.70, 131.37, 130.37, 130.36, 129.67, 128.60, 128.47, 126.84, 125.25, 84.33, 49.92, 38.44, 28.92, 27.95, 24.62, 20.97. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  2980, 2934, 1773, 1722, 1514, 1456, 1369, 1309, 1272, 1249, 1152, 1123, 1092, 850, 769, 752, 734; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ : 413.1841, found: 413.1835;  $[\alpha]_D^{20} = +195.8$  ( $c = 0.72$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 5.626 min,  $t_R$  (minor) = 10.775 min.

***tert*-butyl (4*R*,4*aR*)-4-([1,1'-biphenyl]-4-yl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ae)**



White solid; yield: 80%; *d.r.*:  $> 95:5$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 – 8.28 (m, 1H), 7.48 (ddt,  $J = 10.4, 8.6, 1.7$  Hz, 4H), 7.43 – 7.37 (m, 2H), 7.32 (ddd,  $J = 9.1, 5.0, 2.5$  Hz, 3H), 7.24 – 7.20 (m, 2H), 7.14 – 7.09 (m, 1H), 3.94 (d,  $J = 6.9$  Hz, 1H), 3.27 (ddd,  $J = 12.4, 6.8, 5.3$  Hz, 1H), 2.92 – 2.69 (m, 2H), 1.97 (ddd,  $J = 12.5, 8.7, 3.5$  Hz, 1H), 1.64 (s, 9H), 1.54 – 1.37 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.15, 151.77, 150.78, 141.00, 140.44, 140.17, 133.60, 130.65, 130.47, 129.34, 128.90, 128.70, 127.85, 127.57, 127.10, 127.07, 125.45, 84.62, 50.16, 38.60, 29.10, 28.14, 24.85. IR (KBr,  $\text{cm}^{-1}$ )  $\nu$  2981, 2935, 1772, 1721, 1487, 1369, 1307, 1272, 1249, 1151, 1092, 849, 752, 735, 699; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}$ : 475.1998, found: 475.1992;  $[\alpha]_D^{20} = +147.0$  ( $c = 0.98$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 6.027 min,  $t_R$  (minor) = 15.553 min.

***tert*-butyl (4*R*,4*aR*)-4-(4-methoxyphenyl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3af)**

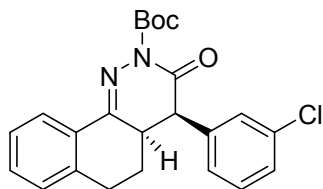


Yellow solid; yield: 99%; *d.r.*:  $> 95:5$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (dd,  $J = 7.5, 1.8$  Hz, 1H), 7.33 – 7.21 (m, 2H), 7.12 – 7.08 (m, 1H), 7.06 – 6.98 (m, 2H), 6.81 – 6.71 (m, 2H), 3.82 (d,  $J = 6.9$  Hz, 1H), 3.71 (s, 3H), 3.21 (ddd,  $J = 12.4, 6.7, 5.3$  Hz, 1H), 2.89 – 2.65 (m, 2H), 1.91



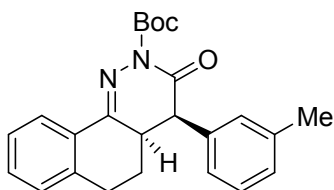
(ddd,  $J = 12.6, 6.9, 3.6$  Hz, 1H), 1.61 (s, 9H), 1.43 (tdd,  $J = 12.9, 10.1, 7.3$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.33, 159.25, 151.68, 150.66, 140.07, 130.46, 130.36, 129.86, 128.54, 126.89, 126.45, 125.27, 114.41, 84.38, 55.19, 49.50, 38.52, 28.93, 27.98, 24.60. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2980, 2934, 1772, 1721, 1513, 1369, 1271, 1251, 1182, 1151, 1027, 851, 760; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}^+$ ): calculated for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$ : 429.1790, found: 429.1780;  $[\alpha]_D^{20} = +167.3$  ( $c = 0.95$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  ee (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 7.278 min,  $t_R$  (minor) = 16.553 min.

***tert*-butyl (4*R*,4*aR*)-4-(3-chlorophenyl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ag*)**



White solid; yield: 91%; *d.r.*: 92:8;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.36 – 7.25 (m, 2H), 7.24 – 7.06 (m, 4H), 7.01 (dt,  $J = 7.3, 1.5$  Hz, 1H), 3.85 (d,  $J = 7.0$  Hz, 1H), 3.25 (ddd,  $J = 12.4, 6.9, 5.3$  Hz, 1H), 2.80 (dd,  $J = 8.4, 3.2$  Hz, 2H), 1.95 (ddt,  $J = 7.2, 5.0, 3.6$  Hz, 1H), 1.62 (s, 9H), 1.39 (tt,  $J = 12.9, 8.9$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.35, 151.50, 150.43, 139.95, 136.34, 134.75, 130.66, 130.40, 130.12, 129.31, 128.57, 128.35, 127.03, 126.55, 125.33, 84.68, 50.00, 38.30, 28.89, 27.96, 24.70. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2980, 2934, 1772, 1721, 1478, 1369, 1271, 1249, 1151, 1092, 847, 755; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}^+$ ): calculated for  $\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_3\text{Na}$ : 433.1295, found: 433.1290;  $[\alpha]_D^{20} = +191.0$  ( $c = 0.56$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  ee (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 6.519 min,  $t_R$  (minor) = 12.632 min.

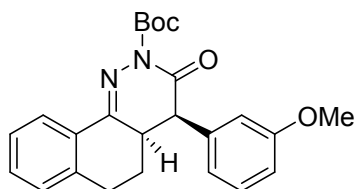
***tert*-butyl (4*R*,4*aR*)-3-oxo-4-(*m*-tolyl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ah*)**



White solid; yield: 98%; *d.r.*:  $> 95:5$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (dd,  $J = 7.4, 1.8$  Hz, 1H), 7.28 (ddd,  $J = 8.4, 5.0, 2.9$  Hz, 2H), 7.11 (dd,  $J = 8.7, 6.2$  Hz, 2H), 7.01 (d,  $J = 7.6$  Hz, 1H), 6.93 (d,  $J = 11.6$  Hz, 2H), 3.84 (d,  $J = 7.0$  Hz, 1H), 3.23 (ddd,  $J = 12.5, 6.9, 5.3$  Hz, 1H), 2.88

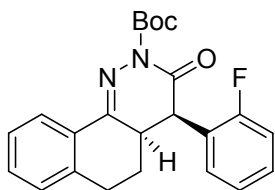
– 2.71 (m, 2H), 2.25 (s, 3H), 2.05 – 1.84 (m, 1H), 1.62 (s, 9H), 1.48 – 1.33 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.27, 151.81, 150.67, 140.05, 138.65, 134.41, 130.44, 130.40, 129.82, 128.93, 128.79, 128.52, 126.90, 125.50, 125.28, 84.40, 50.34, 38.38, 28.96, 27.99, 24.67, 21.47. IR (KBr, cm<sup>-1</sup>) γ 2980, 2934, 1773, 1721, 1369, 1306, 1271, 1249, 1151, 1092, 848, 749; HRMS (ESI) m/z (M+Na)<sup>+</sup>: calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>Na: 413.1841, found: 413.1838; [α]<sup>20</sup><sub>D</sub> = + 192.8 (c = 0.92, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t<sub>R</sub> (major) = 5.607 min, t<sub>R</sub> (minor) = 10.344 min.

***tert*-butyl (4*R*,4*aR*)-4-(3-methoxyphenyl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ai*)**



White solid; yield: 95%; *d.r.*: 95:5; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 – 8.24 (m, 1H), 7.35 – 7.23 (m, 2H), 7.12 (dt, *J* = 8.4, 7.3 Hz, 2H), 6.80 – 6.64 (m, 3H), 3.84 (d, *J* = 7.0 Hz, 1H), 3.68 (s, 3H), 3.23 (ddd, *J* = 12.4, 6.8, 5.3 Hz, 1H), 2.86 – 2.69 (m, 2H), 1.93 (ddd, *J* = 12.5, 8.6, 3.5 Hz, 1H), 1.61 (s, 9H), 1.42 (tt, *J* = 12.9, 9.4 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.95, 159.83, 151.72, 150.61, 140.05, 135.85, 130.48, 130.36, 130.04, 128.55, 126.92, 125.25, 121.02, 114.54, 113.42, 84.42, 55.11, 50.31, 38.39, 28.95, 27.98, 24.67. IR (KBr, cm<sup>-1</sup>) γ 2981, 2936, 1772, 1720, 1599, 1584, 1491, 1455, 1369, 1269, 1151, 1093, 848, 751; HRMS (ESI) m/z (M+Na)<sup>+</sup>: calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Na: 429.1790, found: 429.1784; [α]<sup>20</sup><sub>D</sub> = + 172.3 (c = 1.04, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% ee (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm), t<sub>R</sub> (major) = 6.833 min, t<sub>R</sub> (minor) = 16.082 min.

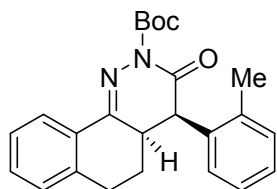
***tert*-butyl (4*R*,4*aR*)-4-(2-fluorophenyl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*aj*)**



White solid; yield: 85%; *d.r.*: > 95:5; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.22 – 7.15 (m, 1H), 7.12 – 6.97 (m, 4H), 4.41 (d, *J* = 7.1 Hz, 1H), 3.28 (ddd, *J* = 12.5, 7.0, 5.3 Hz, 1H), 2.77 (dd, *J* = 7.4, 2.8 Hz, 2H), 2.16 – 2.03 (m, 1H), 1.63 (s, 9H), 1.41 – 1.27

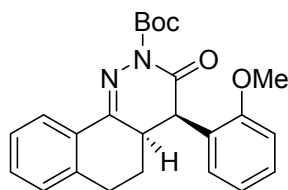
(m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.72, 160.78 (d,  $J = 246.8$  Hz), 151.70, 150.53, 140.07, 130.53, 130.21, 129.65 (d,  $J = 8.4$  Hz), 128.70 (d,  $J = 2.9$  Hz), 128.49, 126.91, 125.28, 125.06 (d,  $J = 3.7$  Hz), 121.96 (d,  $J = 14.8$  Hz), 115.55 (d,  $J = 22.8$  Hz), 84.67, 41.62 (d,  $J = 3.2$  Hz), 38.59, 28.80, 27.98, 24.28. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2934, 1774, 1721, 1492, 1456, 1370, 1271, 1250, 1151, 1099, 849, 755, 734; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{23}\text{H}_{23}\text{FN}_2\text{O}_3\text{Na}$ : 417.1590, found: 417.1585;  $[\alpha]_D^{20} = +209.7$  ( $c = 0.26$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: 98% *ee* (CHIRALPAK OD-H, hexane/*i*-PrOH = 80/20, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 7.838 min,  $t_R$  (minor) = 10.303 min.

***tert*-butyl (4*R*,4*aR*)-3-oxo-4-(*o*-tolyl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ak)**



White solid; yield: 79%; *d.r.*: > 95:5;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 – 8.25 (m, 1H), 7.34 – 7.27 (m, 2H), 7.15 (d,  $J = 7.5$  Hz, 1H), 7.11 – 7.05 (m, 2H), 7.04 – 6.98 (m, 2H), 4.32 (d,  $J = 7.5$  Hz, 1H), 3.31 (ddd,  $J = 12.8, 7.4, 5.3$  Hz, 1H), 2.86 – 2.70 (m, 2H), 2.45 (s, 3H), 1.99 – 1.88 (m, 1H), 1.61 (s, 9H), 1.48 – 1.35 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.60, 151.77, 150.76, 139.92, 137.24, 133.92, 130.95, 130.47, 130.39, 128.49, 127.71, 127.18, 127.11, 126.93, 125.36, 84.43, 44.75, 38.85, 28.89, 27.98, 24.00, 20.69. IR (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2979, 2933, 1771, 1714, 1369, 1271, 1249, 1151, 849, 766, 743; HRMS (ESI)  $m/z$  ( $\text{M}+\text{Na}$ ) $^+$ : calculated for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ : 413.1841, found: 413.1835;  $[\alpha]_D^{20} = +181.4$  ( $c = 0.69$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 4.908 min,  $t_R$  (minor) = 9.827 min.

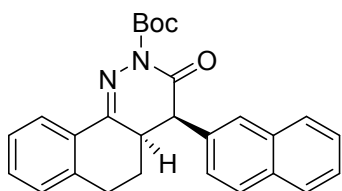
***tert*-butyl (4*R*,4*aR*)-4-(2-methoxyphenyl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3al)**



White solid; yield: 82%; *d.r.*: 95:5;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (dd,  $J = 7.4, 1.9$  Hz, 1H), 7.31 – 7.20 (m, 2H), 7.16 (td,  $J = 8.2, 1.6$  Hz, 1H), 7.11 – 7.04 (m, 1H), 7.00 (dd,  $J = 7.8, 1.6$  Hz, 1H), 6.87 – 6.72 (m, 2H), 4.57 (d,  $J = 7.7$  Hz, 1H), 3.77 (s, 3H), 3.23 (ddd,  $J = 12.8, 7.7, 5.2$  Hz, 1H), 2.73 (dd,  $J = 10.6, 4.3$  Hz, 2H), 2.10 – 1.97 (m, 1H), 1.62 (s, 9H), 1.35 – 1.16 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,

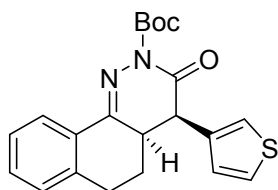
**CDCl<sub>3</sub>**)  $\delta$  168.31, 157.24, 152.08, 150.92, 140.11, 130.58, 130.22, 129.00, 128.95, 128.38, 126.77, 125.26, 123.76, 121.20, 110.70, 84.27, 55.46, 42.38, 38.71, 28.98, 28.00, 24.24. **IR** (KBr, cm<sup>-1</sup>)  $\gamma$  2980, 2935, 1772, 1716, 1494, 1460, 1369, 1271, 1248, 1151, 1110, 1024, 849, 755, 730; **HRMS** (ESI)  $m/z$  (M+Na)<sup>+</sup>: calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Na: 429.1790, found: 429.1788;  $[\alpha]_D^{20} = +226.6$  (c = 0.67, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_R$  (major) = 5.182 min,  $t_R$  (minor) = 8.966 min.

***tert*-butyl (4*R*,4*aR*)-4-(naphthalen-2-yl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3am)**



White solid; yield: 94%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.40 – 8.29 (m, 1H), 7.79 – 7.69 (m, 3H), 7.63 (d, *J* = 1.4 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.32 – 7.23 (m, 3H), 7.12 – 7.00 (m, 1H), 4.07 (d, *J* = 7.0 Hz, 1H), 3.31 (ddd, *J* = 12.5, 6.9, 5.3 Hz, 1H), 2.90 – 2.65 (m, 2H), 1.97 (ddd, *J* = 12.5, 8.6, 3.6 Hz, 1H), 1.64 (s, 9H), 1.50 – 1.36 (m, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  167.10, 151.90, 150.69, 140.03, 133.31, 132.79, 132.04, 130.55, 130.28, 128.90, 128.55, 128.18, 128.00, 127.53, 126.95, 126.37, 126.29, 125.31, 84.54, 50.51, 38.53, 28.95, 28.01, 24.79. **IR** (KBr, cm<sup>-1</sup>)  $\gamma$  2980, 2934, 1771, 1720, 1369, 1271, 1248, 1151, 1092, 849, 755, 733; **HRMS** (ESI)  $m/z$  (M+Na)<sup>+</sup>: calculated for C<sub>27</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>Na: 449.1841, found: 449.1832;  $[\alpha]_D^{20} = +144.9$  (c = 1.07, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_R$  (major) = 7.237 min,  $t_R$  (minor) = 16.740 min.

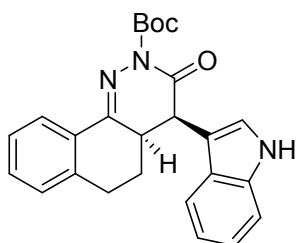
***tert*-butyl (4*R*,4*aR*)-3-oxo-4-(thiophen-3-yl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3an)**



White solid; yield: 99%; *d.r.*: 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.29 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.35 – 7.23 (m, 2H), 7.20 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.90 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.02 (d, *J* = 6.3 Hz, 1H), 3.26 – 3.11 (m, 1H), 2.80 (dd, *J* = 8.5, 3.3 Hz, 2H), 1.94 (ddt, *J* = 12.6, 5.2, 3.6 Hz, 1H), 1.61 (s, 9H), 1.56 – 1.39 (m, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  166.42, 151.79, 150.49,

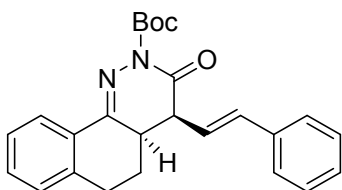
140.07, 133.35, 130.56, 130.26, 128.62, 127.52, 126.98, 126.55, 125.24, 123.71, 84.42, 46.12, 38.33, 28.86, 27.98, 24.66. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2980, 2935, 1773, 1725, 1369, 1309, 1272, 1249, 1151, 1122, 1092, 846, 749, 734; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3\text{SNa}$ : 405.1249, found: 405.1236;  $[\alpha]_{\text{D}}^{20} = +224.0$  ( $c = 0.75$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_{\text{R}}$  (major) = 5.841 min,  $t_{\text{R}}$  (minor) = 11.326 min.

***tert*-butyl (4*R*,4*aR*)-4-(1*H*-indol-3-yl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3a)**



White solid; yield: 80%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.64 (s, 1H), 8.20 (d,  $J = 7.3$  Hz, 1H), 7.67 (dd,  $J = 6.5, 2.3$  Hz, 1H), 7.33 (dd,  $J = 6.5, 2.2$  Hz, 1H), 7.24 (dd,  $J = 7.5, 1.2$  Hz, 1H), 7.18 – 7.11 (m, 3H), 7.05 (d,  $J = 7.5$  Hz, 1H), 6.90 (d,  $J = 2.5$  Hz, 1H), 4.25 (d,  $J = 5.8$  Hz, 1H), 3.27 (dt,  $J = 12.5, 5.5$  Hz, 1H), 2.90 – 2.56 (m, 2H), 2.24 – 1.88 (m, 1H), 1.70 – 1.62 (m, 1H), 1.60 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  167.30, 152.55, 151.05, 140.19, 135.65, 130.41, 130.26, 128.68, 127.73, 126.76, 125.04, 122.38, 121.99, 119.96, 118.68, 111.45, 107.72, 84.51, 41.36, 39.10, 28.81, 28.01, 24.55. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  3338, 2980, 2931, 1765, 1732, 1458, 1370, 1309, 1277, 1251, 1151, 1092, 1029, 848, 758, 744; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_3\text{Na}$ : 438.1794, found: 438.1790;  $[\alpha]_{\text{D}}^{20} = +267.2$  ( $c = 0.54$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_{\text{R}}$  (major) = 8.199 min,  $t_{\text{R}}$  (minor) = 34.141 min.

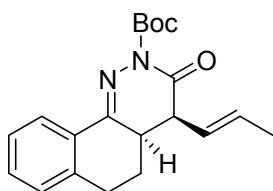
***tert*-butyl (4*S*,4*aR*)-3-oxo-4-((*E*)-styryl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ap)**



Yellow solid; yield: 79%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.28 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.40 – 7.12 (m, 8H), 6.72 (d,  $J = 15.6$  Hz, 1H), 5.89 (dd,  $J = 15.6, 9.6$  Hz, 1H), 3.46 (dd,  $J = 9.5, 5.3$  Hz, 1H), 3.09 (dt,  $J = 12.7, 5.3$  Hz, 1H), 2.96 – 2.75 (m, 2H), 2.11 – 1.95 (m, 1H), 1.90 – 1.73 (m, 1H), 1.62 (s, 9H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  166.75, 151.36, 150.30, 140.12, 136.67,

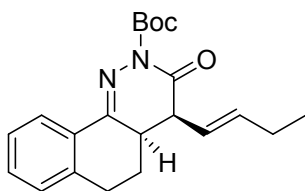
135.92, 130.58, 130.21, 128.68, 128.55, 128.18, 126.97, 126.60, 125.30, 119.51, 84.34, 49.48, 37.79, 28.91, 27.99, 25.08. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2979, 2931, 1774, 1751, 1369, 1306, 1272, 1249, 1152, 1088, 966, 850, 758, 693; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ : 425.1841, found: 425.1842;  $[\alpha]_D^{20} = +85.6$  ( $c = 0.05$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: 90% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 5.531 min,  $t_R$  (minor) = 8.245 min.

***tert*-butyl (4*S*,4*aR*)-3-oxo-4-((*E*)-prop-1-en-1-yl)-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*aq*)**



Yellow solid; yield: 99%; *d.r.*: 89:11; **<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.24 (dd,  $J = 7.8$ , 1.2 Hz, 1H), 7.39 – 7.24 (m, 2H), 7.17 (d,  $J = 7.4$  Hz, 1H), 5.81 (dq,  $J = 13.2$ , 6.5 Hz, 1H), 5.28 – 5.10 (m, 1H), 3.23 (dd,  $J = 9.3$ , 5.3 Hz, 1H), 3.02 – 2.87 (m, 2H), 2.85 – 2.71 (m, 1H), 1.92 (dtd,  $J = 7.2$ , 5.4, 4.0 Hz, 1H), 1.79 (qd,  $J = 12.9$ , 4.3 Hz, 1H), 1.62 (dd,  $J = 6.6$ , 1.6 Hz, 3H), 1.61 (s, 9H). **<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.52, 151.42, 150.40, 140.17, 133.08, 130.43, 130.36, 128.62, 126.90, 125.23, 121.22, 84.15, 48.96, 37.53, 28.91, 27.99, 24.80, 18.13. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2978, 2935, 1775, 1749, 1454, 1369, 1306, 1271, 1248, 1153, 1090, 965, 850, 769, 751, 735; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}$ : 363.1685, found: 363.1676;  $[\alpha]_D^{20} = +142.4$  ( $c = 0.51$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 4.430 min,  $t_R$  (minor) = 5.492 min.

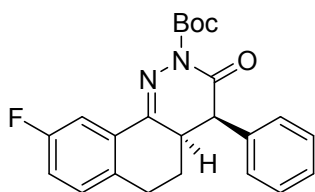
***tert*-butyl (4*S*,4*aR*)-4-((*E*)-but-1-en-1-yl)-3-oxo-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ar*)**



Yellow solid; yield: 92%; *d.r.*: 88:12; **<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.24 (dd,  $J = 7.8$ , 1.2 Hz, 1H), 7.40 – 7.22 (m, 2H), 7.17 (d,  $J = 7.4$  Hz, 1H), 5.84 (dt,  $J = 15.0$ , 6.4 Hz, 1H), 5.25 – 5.04 (m, 1H), 3.23 (dd,  $J = 9.3$ , 5.3 Hz, 1H), 3.02 – 2.91 (m, 1H), 2.88 (t,  $J = 3.5$  Hz, 1H), 2.85 – 2.75 (m, 1H), 2.03 – 1.88 (m, 3H), 1.78 (qd,  $J = 13.0$ , 4.3 Hz, 1H), 1.61 (s, 9H), 0.90 (t,  $J = 7.5$  Hz, 3H). **<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.57, 151.44, 150.41, 140.17, 140.02, 130.42, 130.38, 128.62, 126.89,

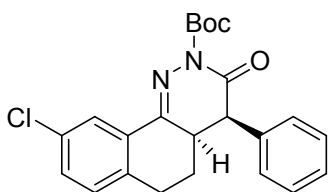
125.23, 119.02, 84.13, 48.97, 37.55, 28.92, 27.99, 25.71, 24.75, 13.34. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2977, 2934, 1775, 1751, 1456, 1369, 1308, 1271, 1249, 1153, 1090, 967, 850, 756, 735; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}^+$ ): calculated for  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ : 377.1841, found: 377.1837;  $[\alpha]^{20}_{\text{D}} = +143.9$  ( $c = 0.56$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm),  $t_{\text{R}}$  (major) = 4.208 min,  $t_{\text{R}}$  (minor) = 5.321 min.

***tert*-butyl (4*R*,4*aR*)-9-fluoro-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*da*)**



White solid; yield: 96%; *d.r.*: 94:6;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.95 (dd,  $J = 9.9, 2.7$  Hz, 1H), 7.29 – 7.19 (m, 3H), 7.16 – 7.04 (m, 3H), 7.00 (td,  $J = 8.3, 2.7$  Hz, 1H), 3.88 (d,  $J = 7.0$  Hz, 1H), 3.22 (ddd,  $J = 12.5, 6.9, 5.3$  Hz, 1H), 2.86 – 2.65 (m, 2H), 1.93 (ddd,  $J = 12.5, 8.6, 3.6$  Hz, 1H), 1.62 (s, 9H), 1.36 (ddd,  $J = 24.9, 12.8, 5.7$  Hz, 1H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.78, 161.64 (d,  $J = 244.7$  Hz), 150.61 (d,  $J = 2.8$  Hz), 150.40, 135.72 (d,  $J = 2.9$  Hz), 134.29, 132.05 (d,  $J = 7.8$  Hz), 130.15 (d,  $J = 7.7$  Hz), 129.11, 128.71, 128.13, 117.81 (d,  $J = 22.2$  Hz), 111.36 (d,  $J = 23.1$  Hz), 84.66, 50.13, 38.11, 28.22, 27.96, 24.70. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2935, 1774, 1723, 1581, 1490, 1454, 1441, 1370, 1267, 1197, 1150, 1093, 885, 850, 744, 701; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}^+$ ): calculated for  $\text{C}_{23}\text{H}_{23}\text{FN}_2\text{O}_3\text{Na}$ : 417.1590, found: 417.1586;  $[\alpha]^{20}_{\text{D}} = +195.2$  ( $c = 0.59$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess:  $> 99\%$  *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm),  $t_{\text{R}}$  (major) = 5.985 min,  $t_{\text{R}}$  (minor) = 12.425 min.

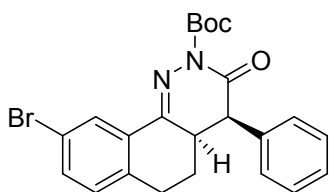
***tert*-butyl (4*R*,4*aR*)-9-chloro-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ea*)**



White solid; yield: 93%; *d.r.*:  $> 95:5$ ;  **$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.28 (d,  $J = 2.2$  Hz, 1H), 7.32 – 7.22 (m, 4H), 7.16 – 7.10 (m, 2H), 7.06 (d,  $J = 8.2$  Hz, 1H), 3.90 (d,  $J = 7.0$  Hz, 1H), 3.25 (ddd,  $J = 12.5, 6.9, 5.3$  Hz, 1H), 2.88 – 2.69 (m, 2H), 2.03 – 1.87 (m, 1H), 1.65 (s, 9H), 1.37 (tdd,  $J = 12.9, 10.7, 6.8$  Hz, 1H).  **$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.76, 150.47, 150.39, 138.27, 134.26,

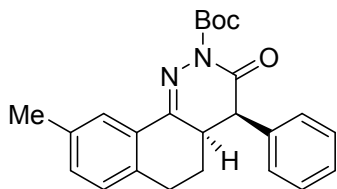
132.87, 131.82, 130.43, 129.97, 129.14, 128.69, 128.15, 124.96, 84.74, 50.10, 38.19, 28.38, 27.96, 24.48. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2981, 2935, 1774, 1723, 1477, 1454, 1370, 1281, 1263, 1248, 1151, 1090, 847, 827, 737, 700; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{23}\text{H}_{23}\text{ClN}_2\text{O}_3\text{Na}$ : 433.1295, found: 433.1289;  $[\alpha]_D^{20} = +216.6$  ( $c = 1.01$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 5.951 min,  $t_R$  (minor) = 11.805 min.

***tert*-butyl (4*R*,4*aR*)-9-bromo-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3fa)**



White solid; yield: 76%; *d.r.*: 94:6; **<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.41 (d,  $J = 2.1$  Hz, 1H), 7.39 (dd,  $J = 8.2, 2.1$  Hz, 1H), 7.32 – 7.18 (m, 3H), 7.14 – 7.06 (m, 2H), 6.97 (d,  $J = 8.2$  Hz, 1H), 3.87 (d,  $J = 7.0$  Hz, 1H), 3.22 (ddd,  $J = 12.5, 6.9, 5.3$  Hz, 1H), 2.81 – 2.60 (m, 2H), 1.92 (tt,  $J = 5.0, 3.6$  Hz, 1H), 1.62 (s, 9H), 1.49 – 1.21 (m, 1H). **<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.75, 150.47, 150.26, 138.73, 134.24, 133.29, 132.15, 130.22, 129.16, 128.69, 128.16, 127.95, 120.82, 84.77, 50.10, 38.21, 28.46, 27.96, 24.41. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2980, 2934, 1773, 1723, 1475, 1454, 1369, 1248, 1151, 1095, 735, 700; **HRMS** (ESI)  $m/z$  ( $M+\text{Na}$ )<sup>+</sup>: calculated for  $\text{C}_{23}\text{H}_{23}\text{BrN}_2\text{O}_3\text{Na}$ : 477.0790, found: 470.0792;  $[\alpha]_D^{20} = +247.9$  ( $c = 0.61$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm),  $t_R$  (major) = 6.117 min,  $t_R$  (minor) = 11.768 min.

***tert*-butyl (4*R*,4*aR*)-9-methyl-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ga)**

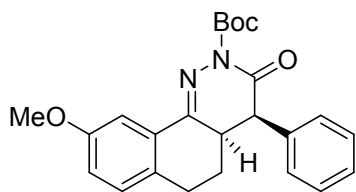


White solid; yield: 52%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.10 (s, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.09 (m, 3H), 6.99 (d,  $J = 7.8$  Hz, 1H), 3.87 (d,  $J = 7.0$  Hz, 1H), 3.23 (ddd,  $J = 12.4, 6.9, 5.2$  Hz, 1H), 2.74 (dd,  $J = 8.3, 3.2$  Hz, 2H), 2.36 (s, 3H), 1.92 (ddd,  $J = 8.9, 4.4, 2.5$  Hz, 1H), 1.62 (s, 9H), 1.39 (ddd,  $J = 12.7, 10.6, 6.2$  Hz, 1H). **<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )**  $\delta$  167.21, 152.03, 150.76, 137.23, 136.53, 134.54, 131.56, 130.01, 129.04, 128.81, 128.41, 127.99, 125.40, 84.51, 50.40, 38.49, 28.56, 27.99, 24.80, 21.16. **IR** (KBr,  $\text{cm}^{-1}$ )  $\gamma$  2979, 2932, 1772, 1720, 1496,



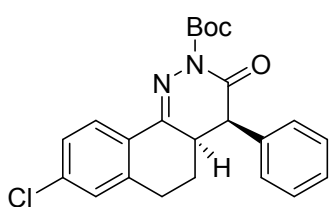
1454, 1369, 1271, 1250, 1151, 1093, 850, 742, 701; **HRMS** (ESI)  $m/z$  (M+Na)<sup>+</sup>: calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>Na: 413.1841, found: 413.1834;  $[\alpha]^{20}_D = +227.9$  (c = 0.39, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_R$  (major) = 5.066 min,  $t_R$  (minor) = 9.211 min.

***tert*-butyl (4*R*,4*aR*)-9-methoxy-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ha*)**



White solid; yield: 93%; *d.r.*: 92:8; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 2.7 Hz, 1H), 7.31 – 7.18 (m, 3H), 7.16 – 7.09 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.88 (d, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 3.21 (ddd, *J* = 12.4, 6.9, 5.2 Hz, 1H), 2.75 – 2.67 (m, 2H), 1.90 (ddd, *J* = 12.4, 8.6, 3.5 Hz, 1H), 1.62 (s, 9H), 1.44 – 1.33 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.10, 158.39, 151.50, 150.46, 134.48, 132.73, 131.15, 129.66, 129.05, 128.79, 128.02, 118.50, 107.85, 84.36, 55.42, 50.35, 38.26, 28.12, 27.98, 24.89. **IR** (KBr, cm<sup>-1</sup>) γ 2980, 2934, 1773, 1721, 1494, 1454, 1369, 1272, 1252, 1151, 1093, 1035, 850, 740, 701; **HRMS** (ESI)  $m/z$  (M+Na)<sup>+</sup>: calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Na: 429.1790, found: 429.1783;  $[\alpha]^{20}_D = +191.7$  (c = 0.78, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_R$  (major) = 6.236 min,  $t_R$  (minor) = 12.717 min.

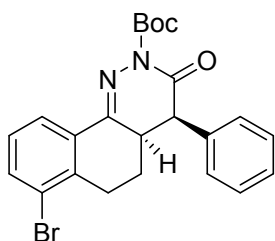
***tert*-butyl (4*R*,4*aR*)-8-chloro-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3*ia*)**



White solid; yield: 95%; *d.r.*: > 95:5; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.18 (m, 4H), 7.14 – 7.06 (m, 3H), 3.87 (d, *J* = 7.0 Hz, 1H), 3.23 (ddd, *J* = 12.5, 6.9, 5.3 Hz, 1H), 2.87 – 2.58 (m, 2H), 1.93 (ddd, *J* = 12.6, 6.9, 3.6 Hz, 1H), 1.61 (s, 9H), 1.37 (ddd, *J* = 24.7, 12.8, 5.7 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.84, 150.71, 150.52, 141.54, 136.45, 134.29, 129.11, 128.88, 128.71, 128.38, 128.14, 127.34, 126.84, 84.64, 50.16, 38.20, 28.72, 27.96, 24.46. **IR** (KBr, cm<sup>-1</sup>) γ 2981, 2936, 1773, 1723, 1586, 1479, 1455, 1370, 1307, 1271, 1250, 1152, 1098, 843,

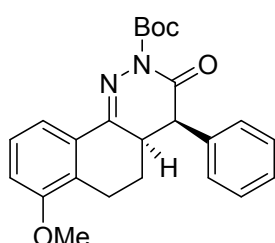
736, 700; **HRMS** (ESI)  $m/z$  ( $M+Na$ )<sup>+</sup>: calculated for  $C_{23}H_{23}ClN_2O_3Na$ : 433.1295, found: 433.1290;  $[\alpha]^{20}_D = +193.1$  ( $c = 0.90$ ,  $CHCl_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 7.056 min,  $t_R$  (minor) = 9.027 min.

***tert*-butyl (4*R*,4*aR*)-7-bromo-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ja)**



White solid; yield: 99%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.29 (dd,  $J = 8.0, 0.9$  Hz, 1H), 7.57 (dd,  $J = 7.9, 1.1$  Hz, 1H), 7.32 – 7.18 (m, 3H), 7.19 – 7.08 (m, 3H), 3.89 (d,  $J = 7.0$  Hz, 1H), 3.23 (ddd,  $J = 12.6, 7.0, 5.3$  Hz, 1H), 3.16 (dt,  $J = 16.7, 3.5$  Hz, 1H), 2.64 – 2.51 (m, 1H), 1.94 (ddd,  $J = 12.7, 8.1, 4.3$  Hz, 1H), 1.61 (s, 9H), 1.34 (qd,  $J = 13.2, 4.1$  Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  166.71, 150.74, 150.48, 139.03, 134.35, 134.27, 132.59, 129.14, 128.72, 128.17, 127.91, 124.60, 124.59, 84.66, 50.05, 37.93, 28.73, 27.97, 24.03. **IR** (KBr,  $cm^{-1}$ )  $\nu$  2980, 2936, 1774, 1724, 1455, 1369, 1308, 1269, 1251, 1151, 1026, 848, 787, 742, 700; **HRMS** (ESI)  $m/z$  ( $M+Na$ )<sup>+</sup>: calculated for  $C_{23}H_{23}BrN_2O_3Na$ : 477.0790, found: 477.0786;  $[\alpha]^{20}_D = +129.2$  ( $c = 1.45$ ,  $CHCl_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_R$  (major) = 6.594 min,  $t_R$  (minor) = 13.773 min.

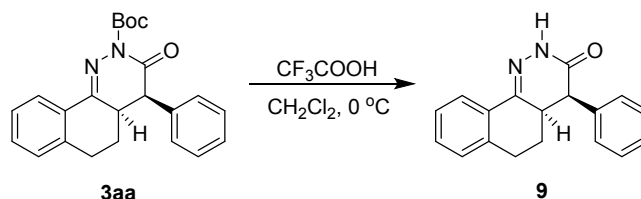
***tert*-butyl (4*R*,4*aR*)-7-methoxy-3-oxo-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (3ka)**



White solid; yield: 81%; *d.r.*: > 95:5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.97 – 7.82 (m, 1H), 7.32 – 7.17 (m, 4H), 7.18 – 7.09 (m, 2H), 6.85 (d,  $J = 7.6$  Hz, 1H), 3.87 (d,  $J = 7.0$  Hz, 1H), 3.79 (s, 3H), 3.22 (ddd,  $J = 12.5, 7.0, 5.2$  Hz, 1H), 3.14 (dt,  $J = 16.7, 3.6$  Hz, 1H), 2.44 – 2.27 (m, 1H), 1.98 – 1.82 (m, 1H), 1.61 (s, 9H), 1.30 (qd,  $J = 13.2, 4.1$  Hz, 1H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**  $\delta$  167.04, 156.45, 151.59, 150.60, 134.55, 131.38, 129.27, 129.03, 128.81, 127.99, 126.98, 117.21, 111.36, 84.40, 55.54, 50.32, 38.01, 27.98, 24.01, 21.34. **IR** (KBr,  $cm^{-1}$ )  $\nu$  2980, 2936, 1773, 1720, 1577, 1472, 1455, 1370, 1305, 1263, 1151, 1058, 847, 739, 701; **HRMS** (ESI)  $m/z$  ( $M+Na$ )<sup>+</sup>:

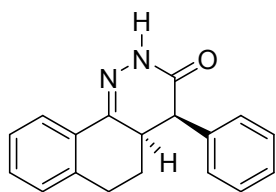
calculated for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Na: 429.1790, found: 429.1794;  $[\alpha]^{20}_{\text{D}} = + 156.2$  (c = 0.83, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK AD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_{\text{R}}$  (major) = 5.982 min,  $t_{\text{R}}$  (minor) = 13.684 min.

## 5. Synthetic Transformation of **3aa** and **3ap**

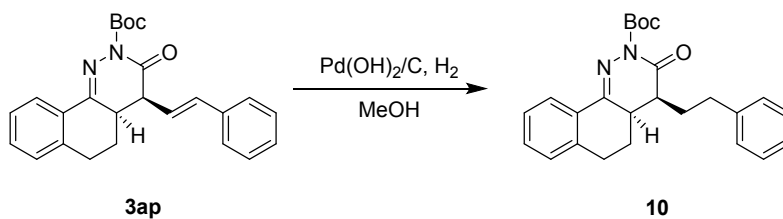


Under the optimal conditions, **3aa** was obtained in 95% yield, > 95:5 *d.r.* and > 99% *ee*. To a cooled (0 °C) solution of **3aa** (75.3 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), 4.0 equiv of CF<sub>3</sub>COOH (62 μL, 0.8 mmol) was added, and the corresponding mixture was stirred at this temperature until the reaction completed (monitoring by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired compound **9** (45.9 mg, 83% yield, > 95:5 *d.r.*, > 99% *ee*).

### (4*R*,4*aR*)-4-phenyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnolin-3(2*H*)-one (**9**)

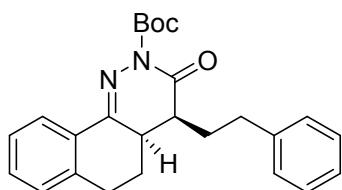


White solid; yield: 83%; *d.r.*: > 95:5; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.87 (s, 1H), 8.29 – 7.93 (m, 1H), 7.38 – 7.04 (m, 8H), 3.78 (d, *J* = 7.4 Hz, 1H), 3.22 (ddd, *J* = 12.7, 7.4, 5.1 Hz, 1H), 2.87 – 2.61 (m, 2H), 1.94 (ddd, *J* = 12.4, 8.5, 3.6 Hz, 1H), 1.37 (tdd, *J* = 13.0, 10.6, 6.9 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.82, 150.18, 139.60, 134.94, 130.64, 130.01, 129.02, 128.64, 128.56, 127.90, 126.83, 124.49, 48.03, 38.65, 29.26, 24.91. IR (KBr, cm<sup>-1</sup>) γ 3222, 2924, 2851, 1672, 1454, 1355, 1332, 1264, 1128, 1085, 765, 744, 702; HRMS (ESI) *m/z* (M+H)<sup>+</sup>: calculated for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O: 277.1341, found: 277.1331;  $[\alpha]^{20}_{\text{D}} = + 426.8$  (c = 0.51, CHCl<sub>3</sub>); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% *ee* (CHIRALPAK OD-H, hexane/*i*-PrOH = 70/30, flow rate: 1.0 mL/min, T = 30 °C, 254 nm),  $t_{\text{R}}$  (major) = 8.182 min,  $t_{\text{R}}$  (minor) = 13.424 min.



Under the optimal conditions, **3ap** was obtained in 79% yield, > 95:5 *d.r.* and 90% *ee*. To a stirring solution of **3ap** (40.3 mg, 0.1 mmol) in MeOH (5.0 mL) was slowly added palladium hydroxide-on-activated charcoal (10%; 20 mg) at room temperature. The resulting mixture was stirred at room temperature in an atmosphere of hydrogen gas for 2 h. The mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **10** (39.6 mg, 98% yield, > 95:5 *d.r.*, 90% *ee*).

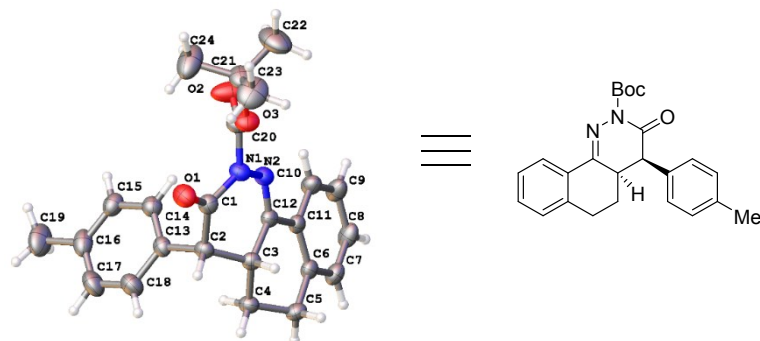
**tert-butyl (4*S*,4*aR*)-3-oxo-4-phenethyl-4,4*a*,5,6-tetrahydrobenzo[*h*]cinnoline-2(3*H*)-carboxylate (10)**



White solid; yield: 98%; *d.r.*: > 95:5;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (dd,  $J = 7.8, 1.4$  Hz, 1H), 7.37 – 7.21 (m, 4H), 7.19 – 7.13 (m, 4H), 3.20 – 2.97 (m, 1H), 2.95 – 2.86 (m, 1H), 2.82 – 2.61 (m, 4H), 1.95 – 1.78 (m, 3H), 1.75 – 1.65 (m, 1H), 1.63 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,

$\text{CDCl}_3$ )  $\delta$  169.14, 151.08, 150.63, 141.11, 139.96, 130.37, 128.51, 128.49, 128.42, 126.94, 126.10, 125.24, 84.09, 43.34, 38.26, 32.89, 29.22, 28.00, 27.18, 24.36. **IR** (KBr,  $\text{cm}^{-1}$ )  $\nu$  2980, 2931, 1771, 1455, 1369, 1271, 1249, 1152, 1096, 850, 756, 731, 701; **HRMS** (ESI)  $m/z$  ( $\text{M}+\text{Na}^+$ ): calculated for  $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}$ : 427.1998, found: 427.1991;  $[\alpha]^{20}_{\text{D}} = + 347.5$  ( $c = 0.05$ ,  $\text{CHCl}_3$ ); The product was analyzed by HPLC to determine the enantiomeric excess: 90% *ee* (CHIRALPAK OD-H, hexane/*i*-PrOH = 90/10, flow rate: 1.0 mL/min,  $T = 30$  °C, 254 nm),  $t_{\text{R}}$  (major) = 10.215 min,  $t_{\text{R}}$  (minor) = 11.356 min.

## 6. X-ray Single Crystal Data for 3ad



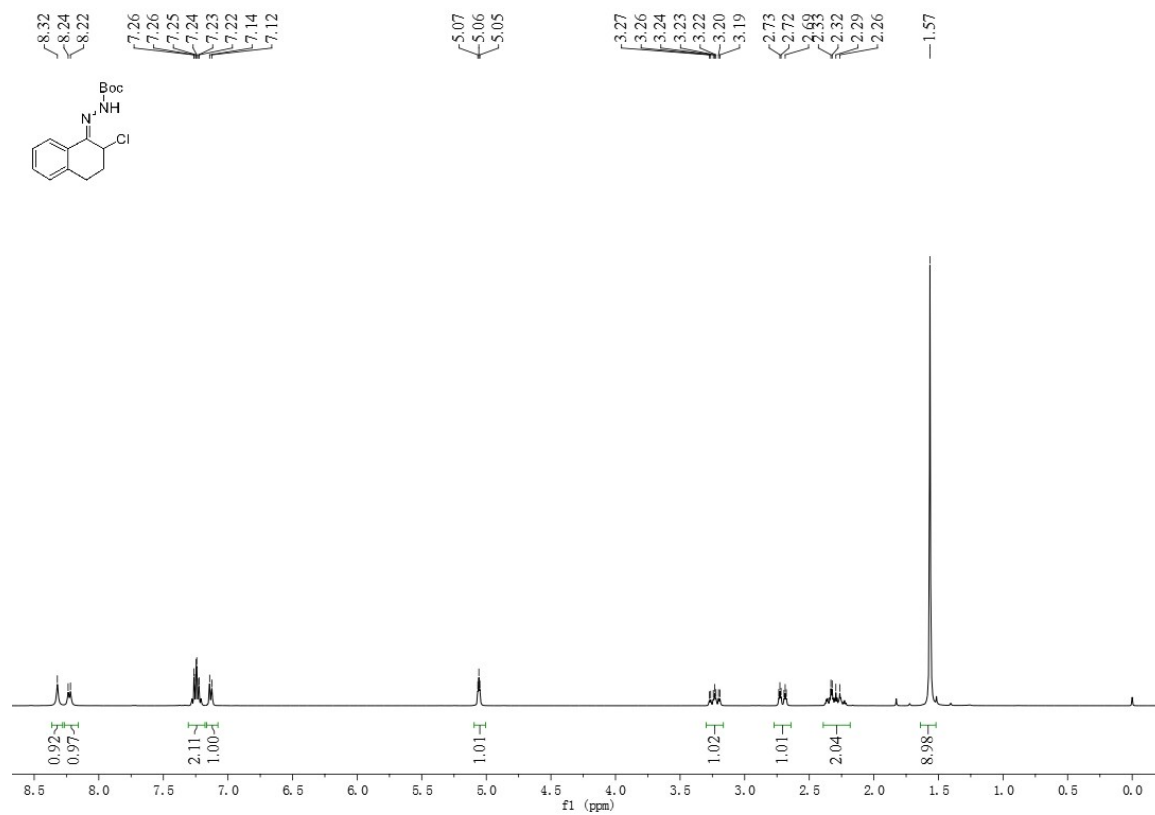
Empirical formula	$C_{24}H_{26}N_2O_3$
Formula weight	390.47
Temperature/K	170
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.2146(4)
b/Å	11.7243(5)
c/Å	10.2644(4)
$\alpha$ /°	90
$\beta$ /°	119.315(2)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	1071.84(8)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.210
$\mu/\text{mm}^{-1}$	0.412
F(000)	416.0
Crystal size/mm <sup>3</sup>	0.15 × 0.1 × 0.08
Radiation	GaK $\alpha$ ( $\lambda = 1.34139$ )
2 $\theta$ range for data collection/°	8.638 to 121.776
Index ranges	$-13 \leq h \leq 13, -15 \leq k \leq 15, -13 \leq l \leq 13$
Reflections collected	13110
Independent reflections	4904 [ $R_{\text{int}} = 0.0457, R_{\text{sigma}} = 0.0477$ ]
Data/restraints/parameters	4904/1/266
Goodness-of-fit on $F^2$	1.041
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0399, wR_2 = 0.0983$
Final R indexes [all data]	$R_1 = 0.0428, wR_2 = 0.1010$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.14
Flack parameter	0.06(12)

## 7. References:

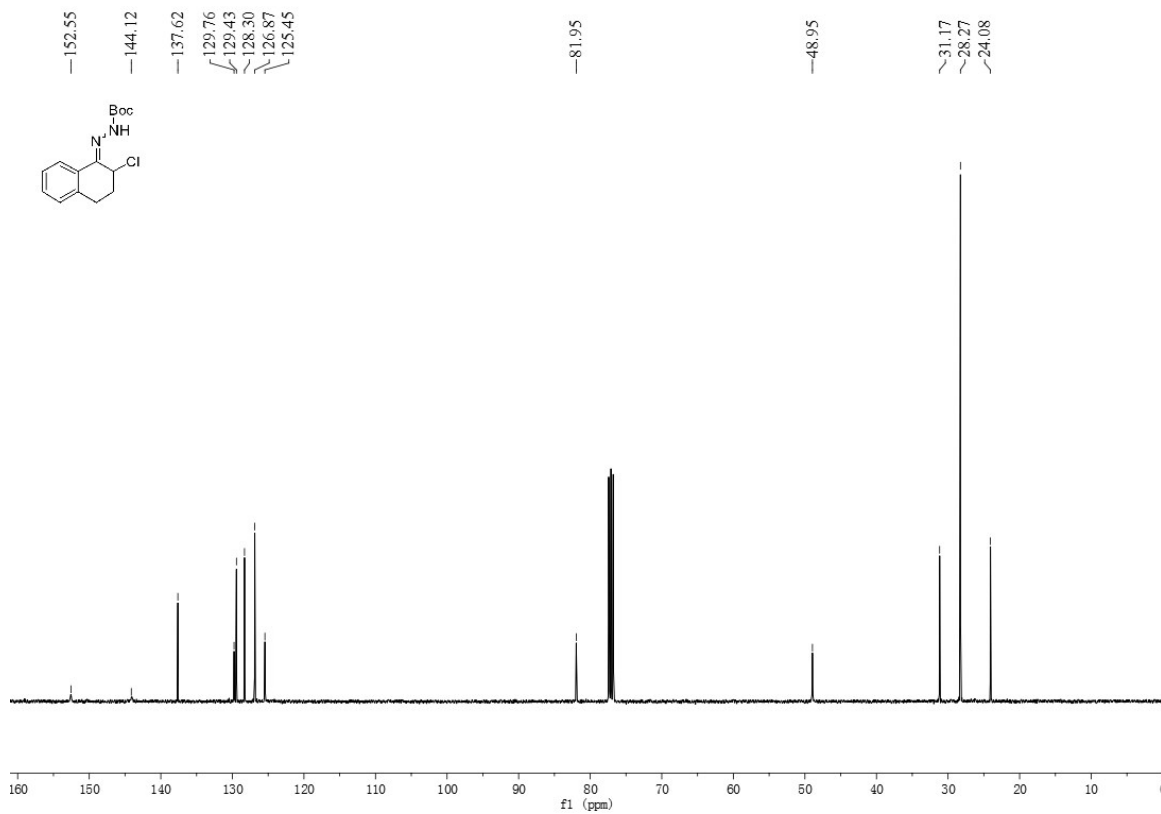
- [1] (a) Y.-J. Mei, P. A. Bentley and J. Du, *Tetrahedron Lett.*, 2008, **49**, 3802; (b) J.-R. Chen, W.-R. Dong, M. Candy, F.-F. Pan, M. Jörres and C. Bolm, *J. Am. Chem. Soc.*, 2012, **134**, 6924; (c) C. Guo, B. Sahoo, C. G. Daniliuc and F. Glorius, *J. Am. Chem. Soc.*, 2014, **136**, 17402.
- [2] (a) V. B. Birman and X. Li, *Org. Lett.*, 2006, **8**, 1351; (b) V. B. Birman and X. Li, *Org. Lett.*, 2008, **10**, 1115; (c) D. S. B. Daniels, S. R. Smith, T. Lebl, P. Shapland and A. D. Smith, *Synthesis*, 2015, **47**, 34; (d) I. Shiina, K. Nakata, K. Ono, Y.-S. Onda and M. Itagaki, *J. Am. Chem. Soc.*, 2010, **132**, 11629.

## 8. NMR Spectra of Substrates and Products

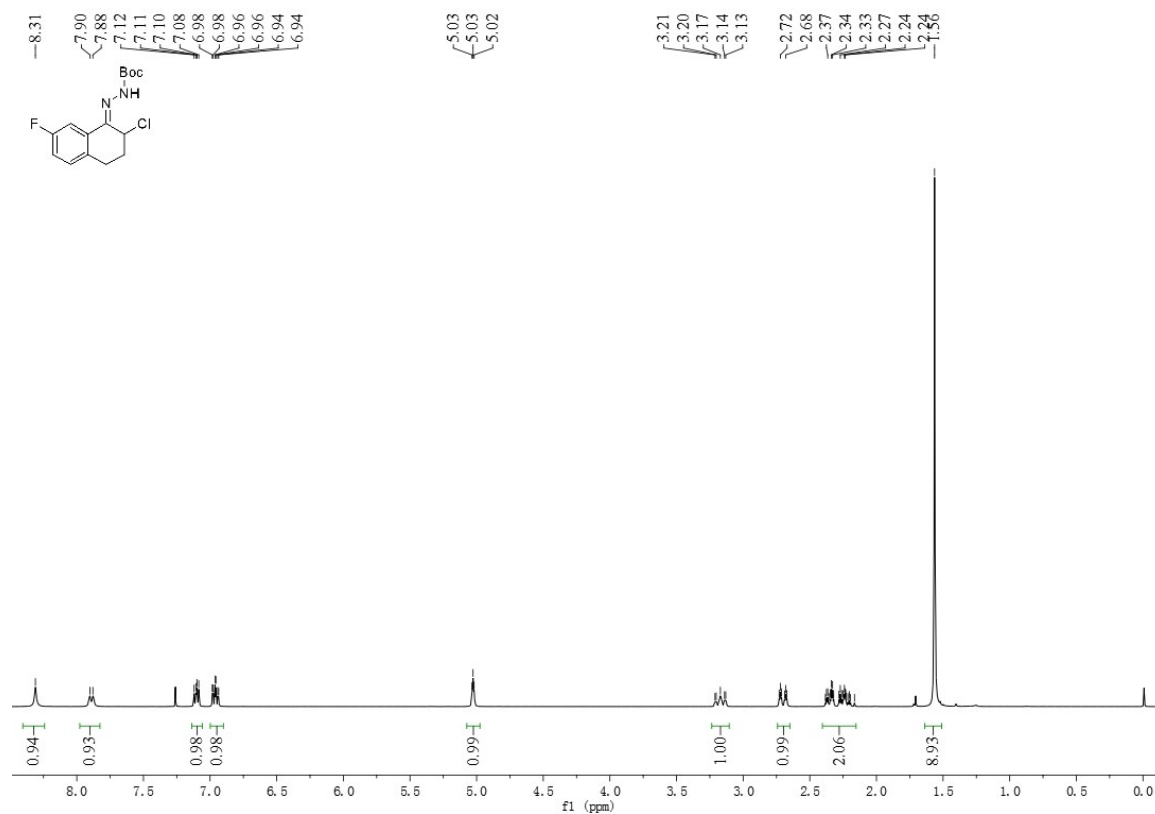
### $^1\text{H}$ NMR spectrum of **1a**



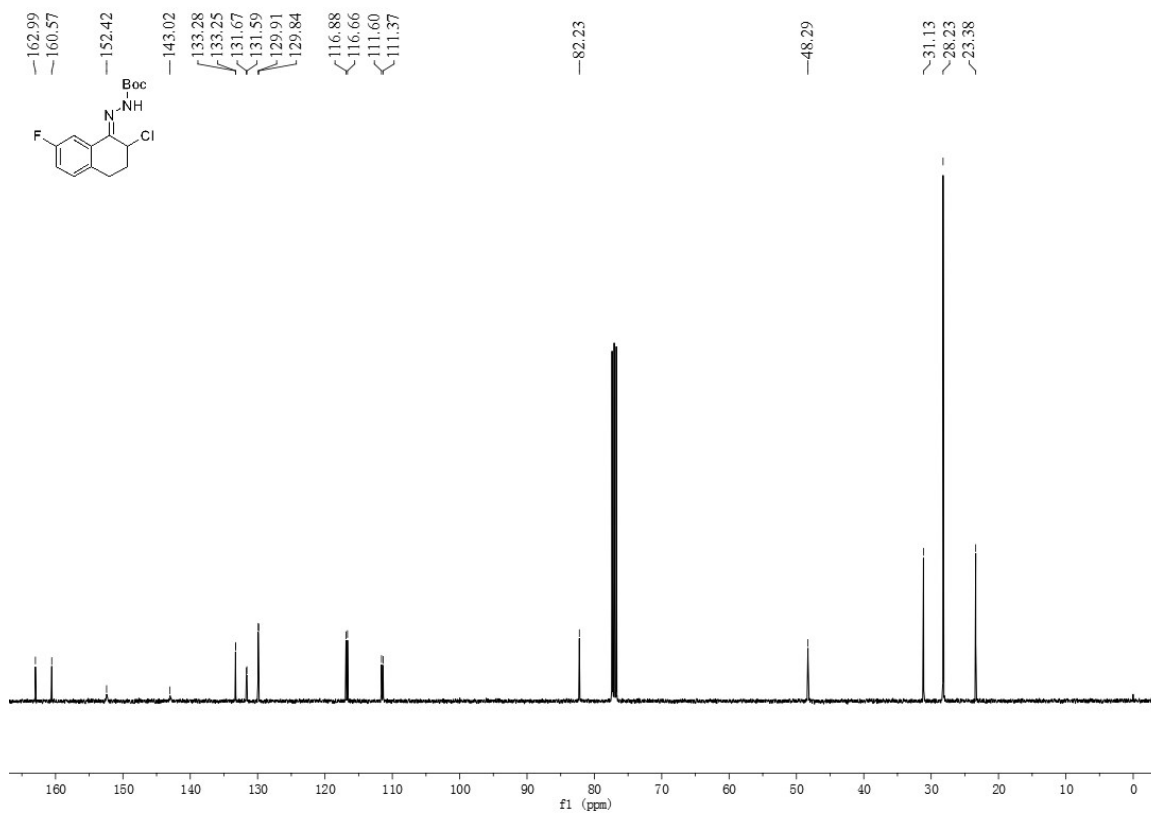
### $^{13}\text{C}$ NMR spectrum of **1a**



### $^1\text{H}$ NMR spectrum of **1d**

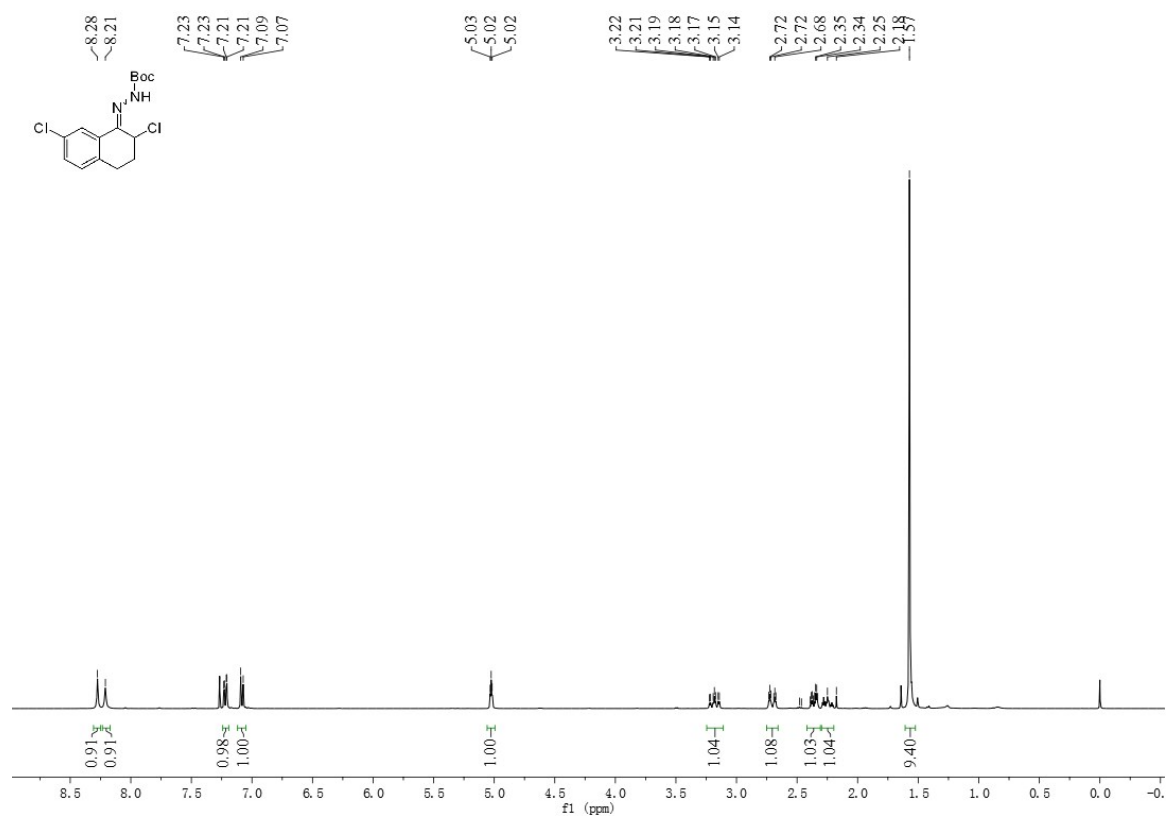


### $^{13}\text{C}$ NMR spectrum of **1d**

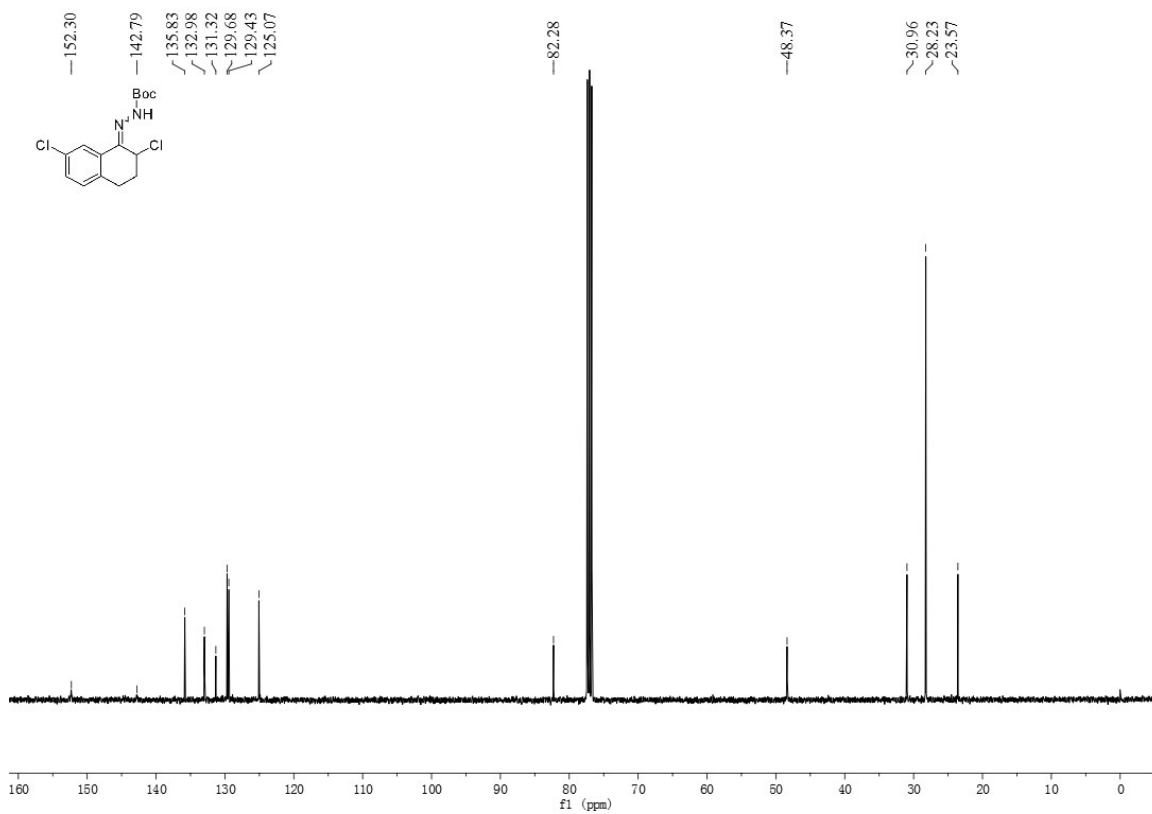




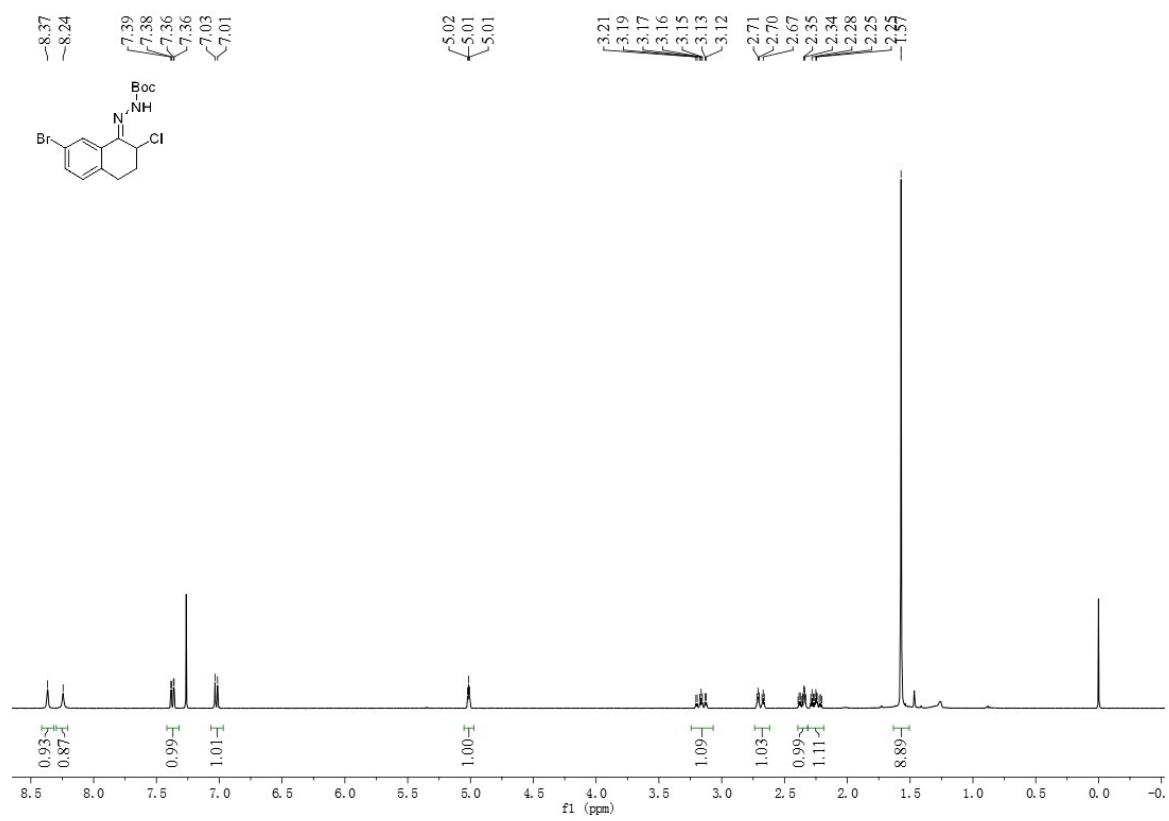
<sup>1</sup>H NMR spectrum of **1e**



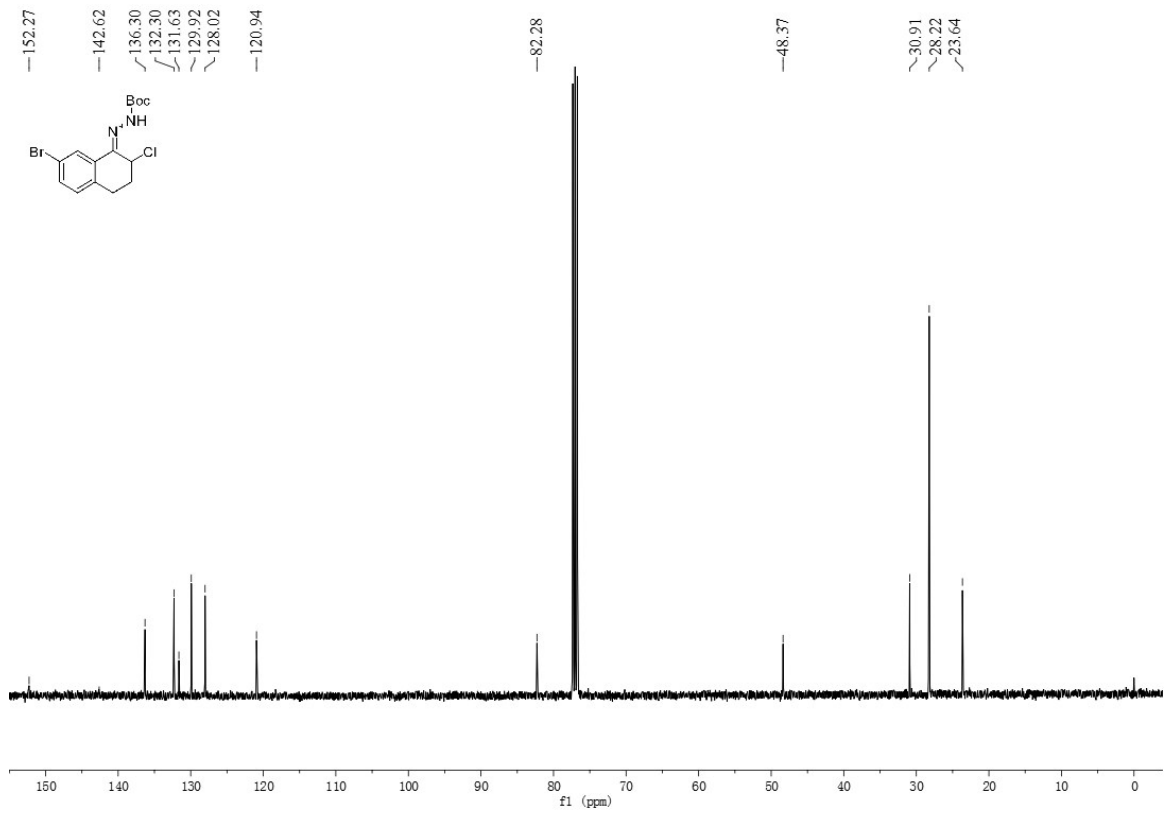
<sup>13</sup>C NMR spectrum of **1e**



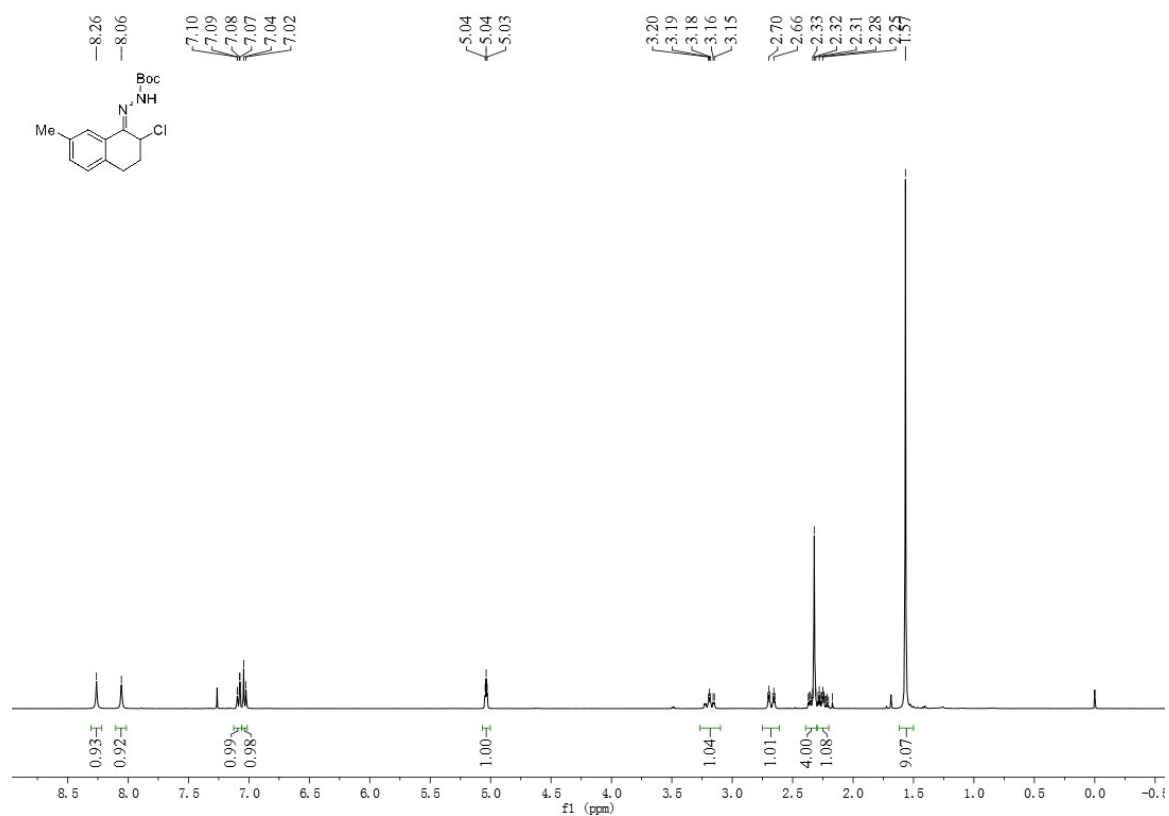
# <sup>1</sup>H NMR spectrum of **1f**



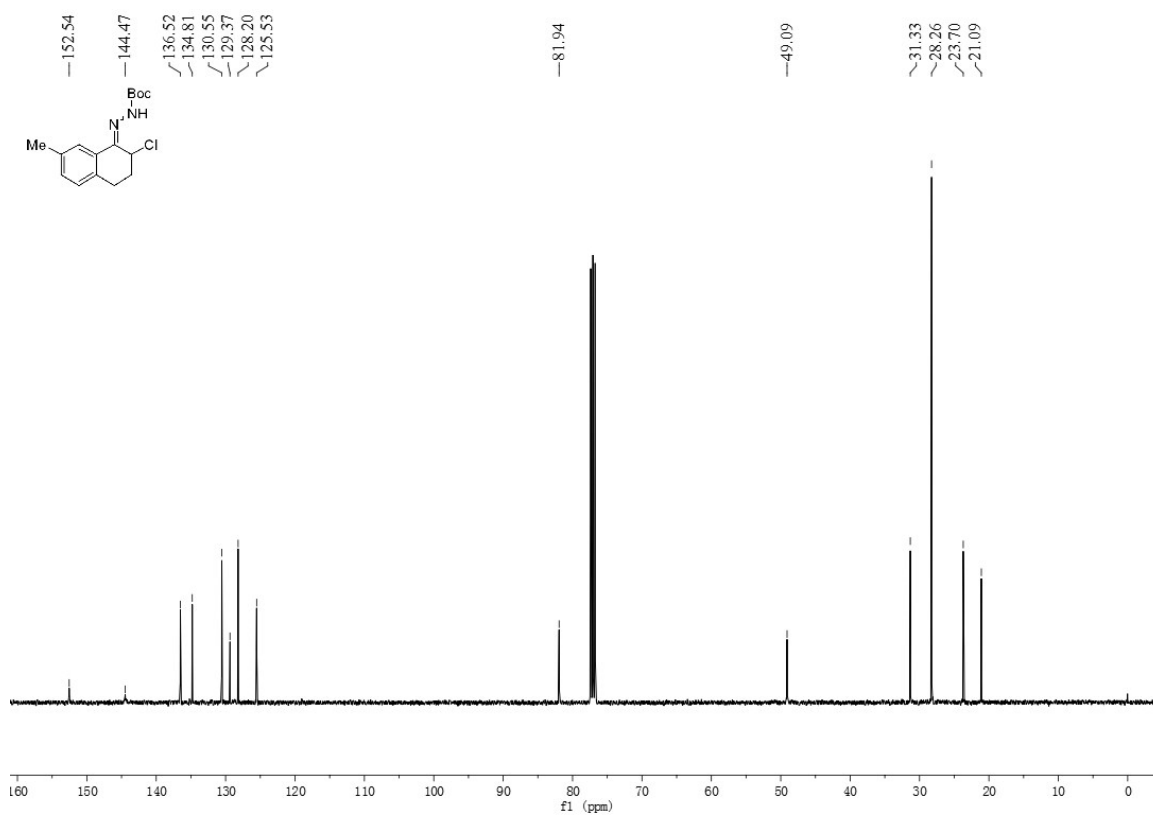
# <sup>13</sup>C NMR spectrum of **1f**



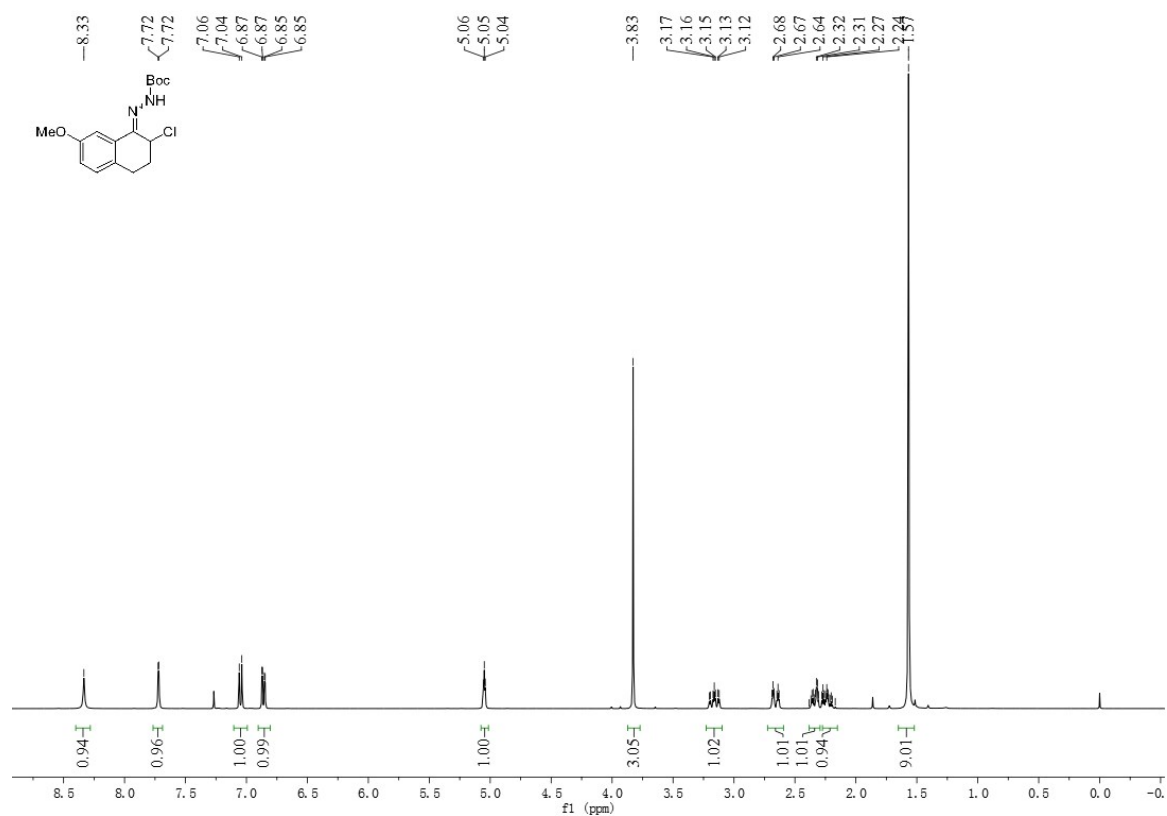
# $^1\text{H}$ NMR spectrum of **1g**



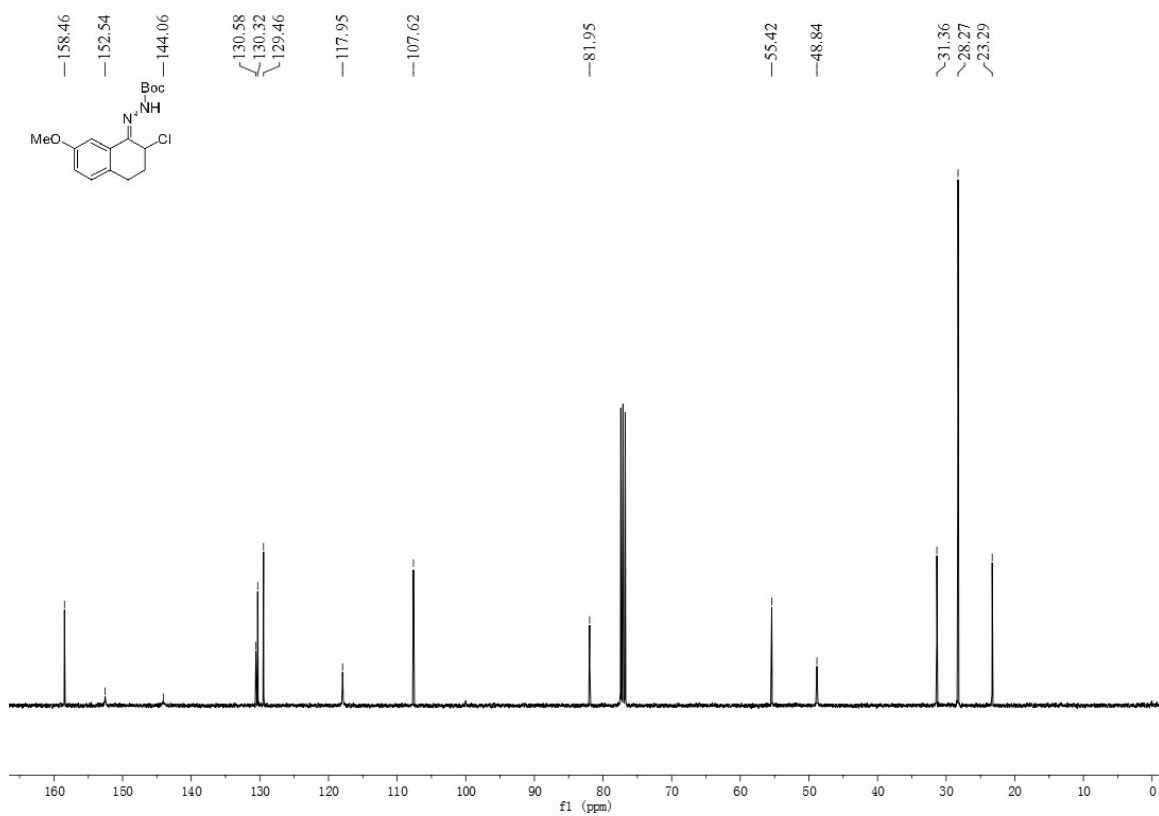
# $^{13}\text{C}$ NMR spectrum of **1g**



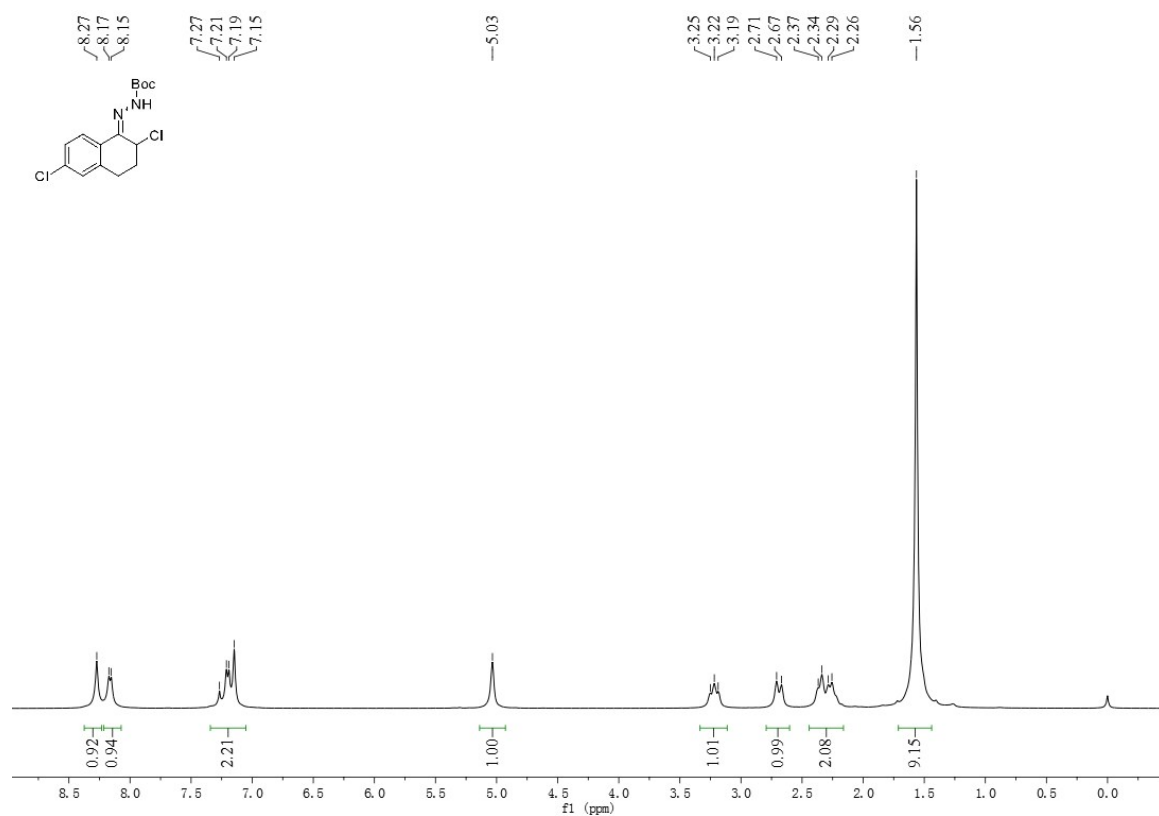
# <sup>1</sup>H NMR spectrum of **1h**



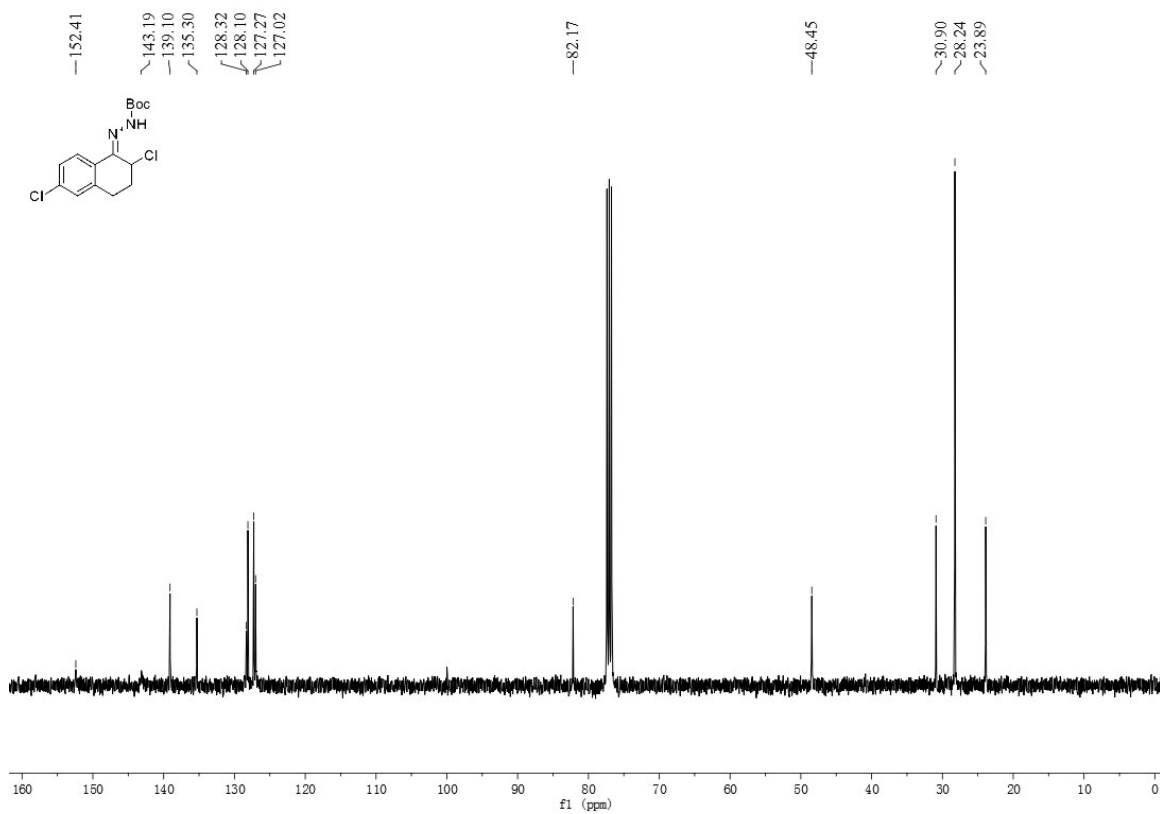
# <sup>13</sup>C NMR spectrum of **1h**



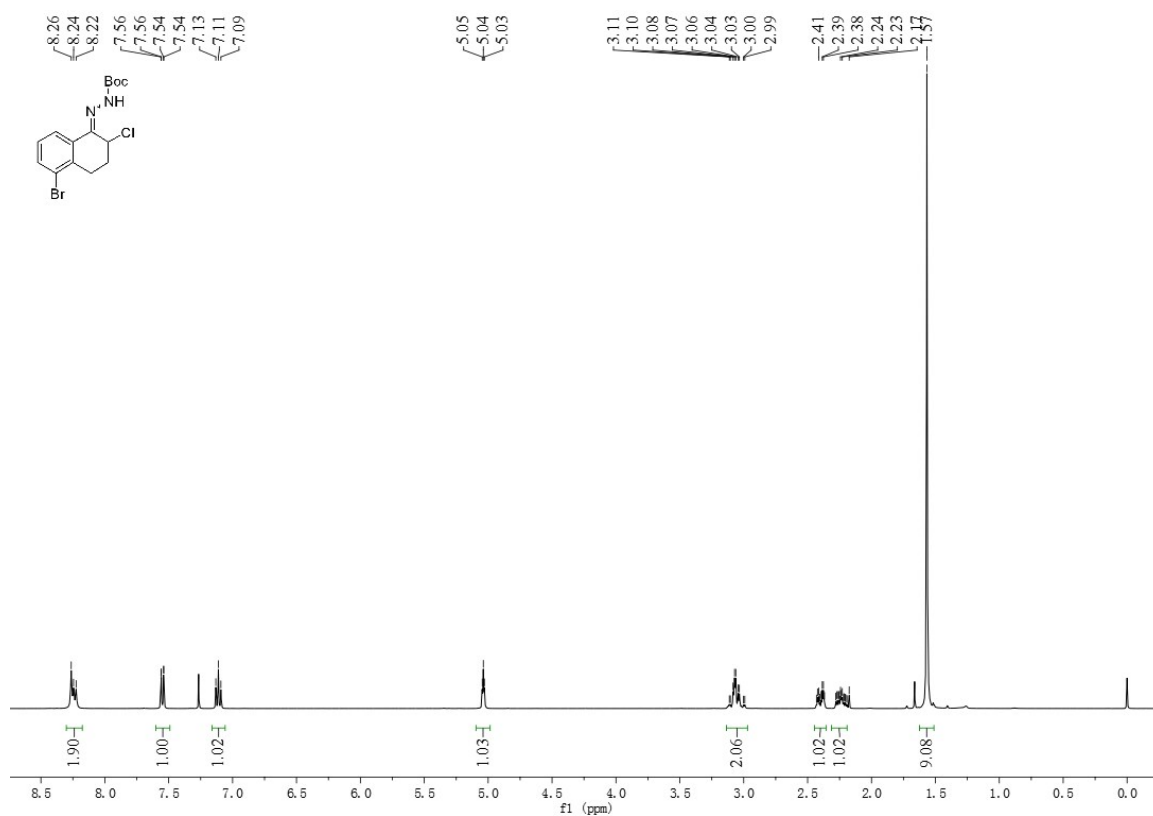
# <sup>1</sup>H NMR spectrum of **1i**



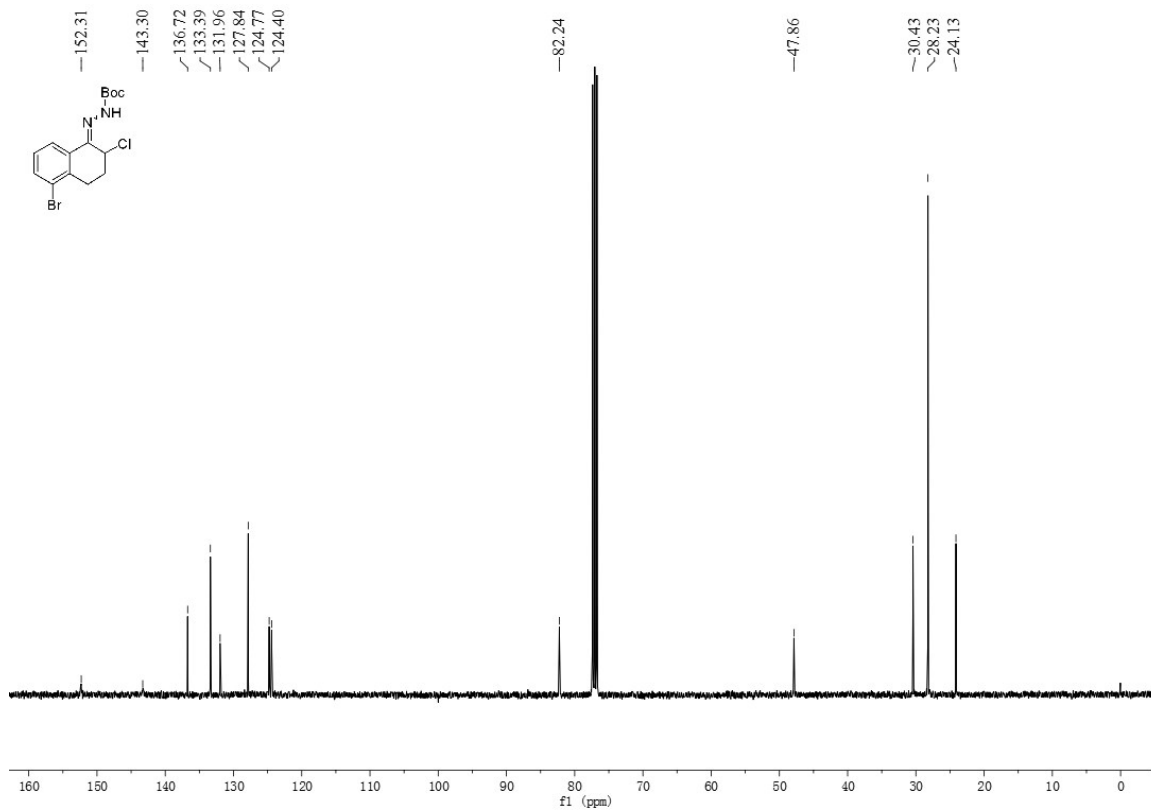
# <sup>13</sup>C NMR spectrum of **1i**



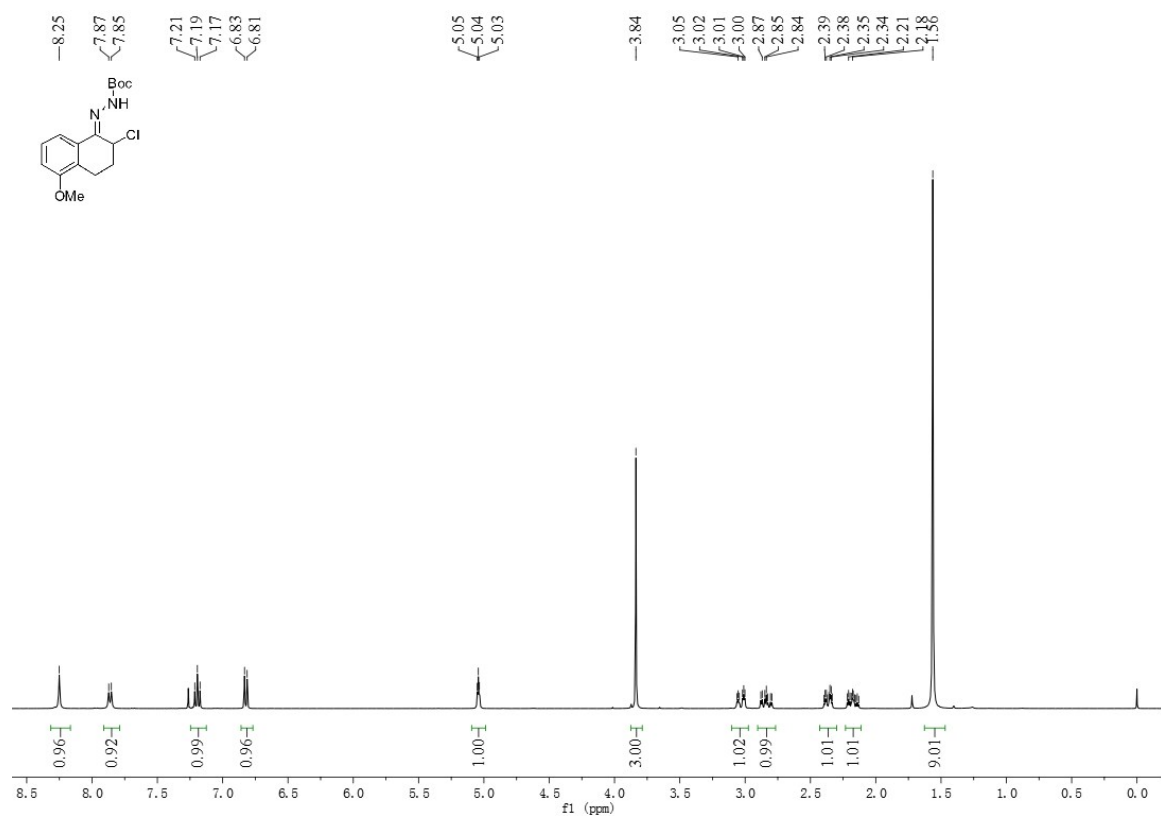
# <sup>1</sup>H NMR spectrum of **1j**



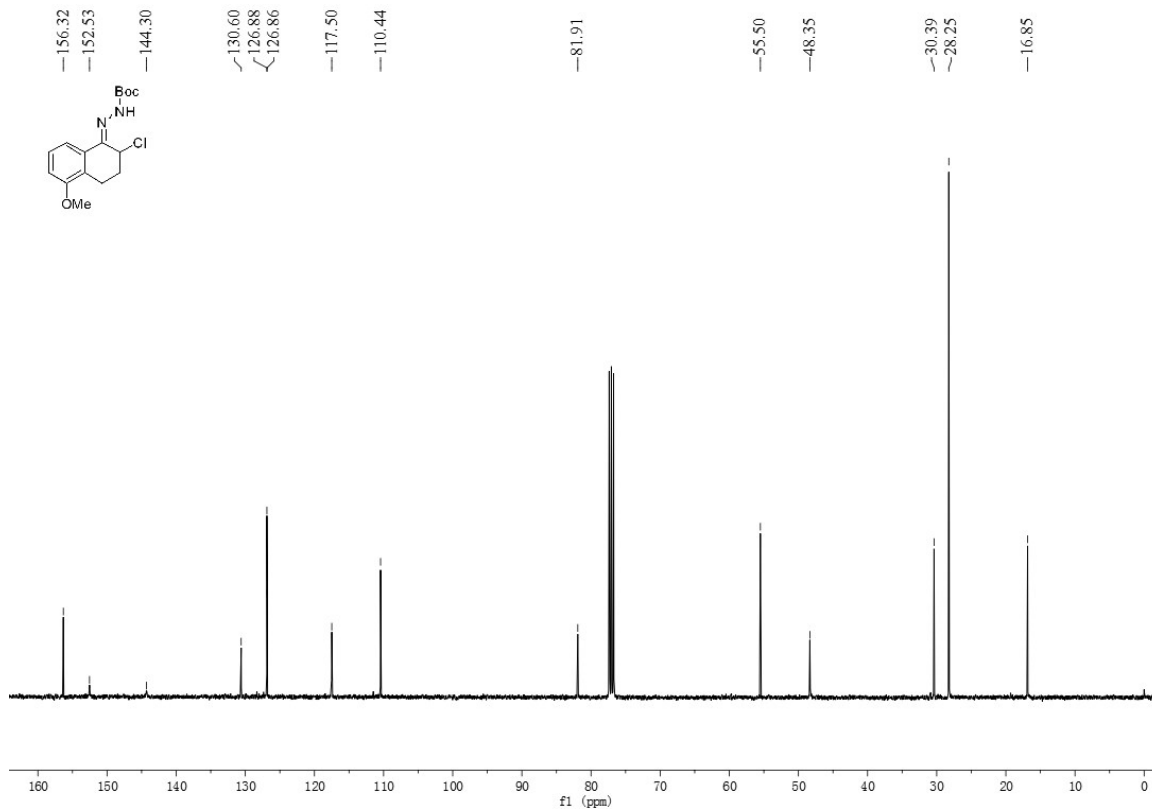
# <sup>13</sup>C NMR spectrum of **1j**



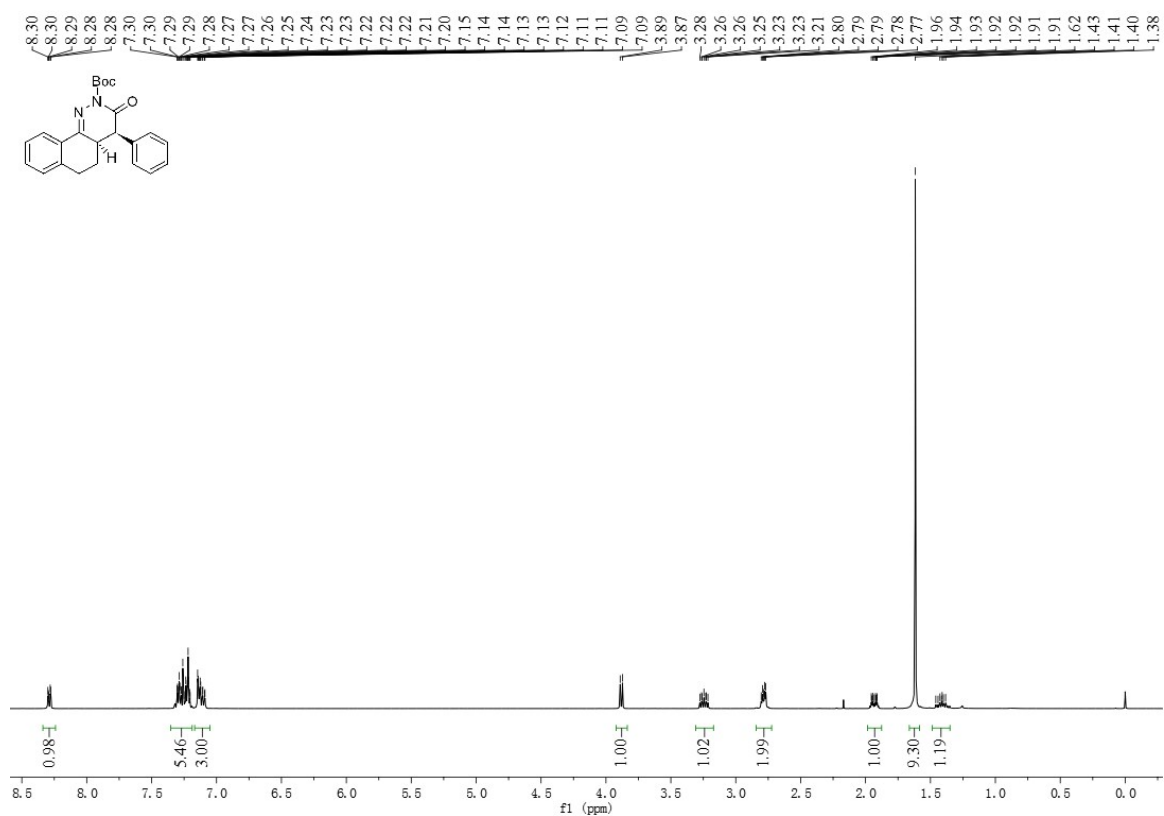
<sup>1</sup>H NMR spectrum of **1k**



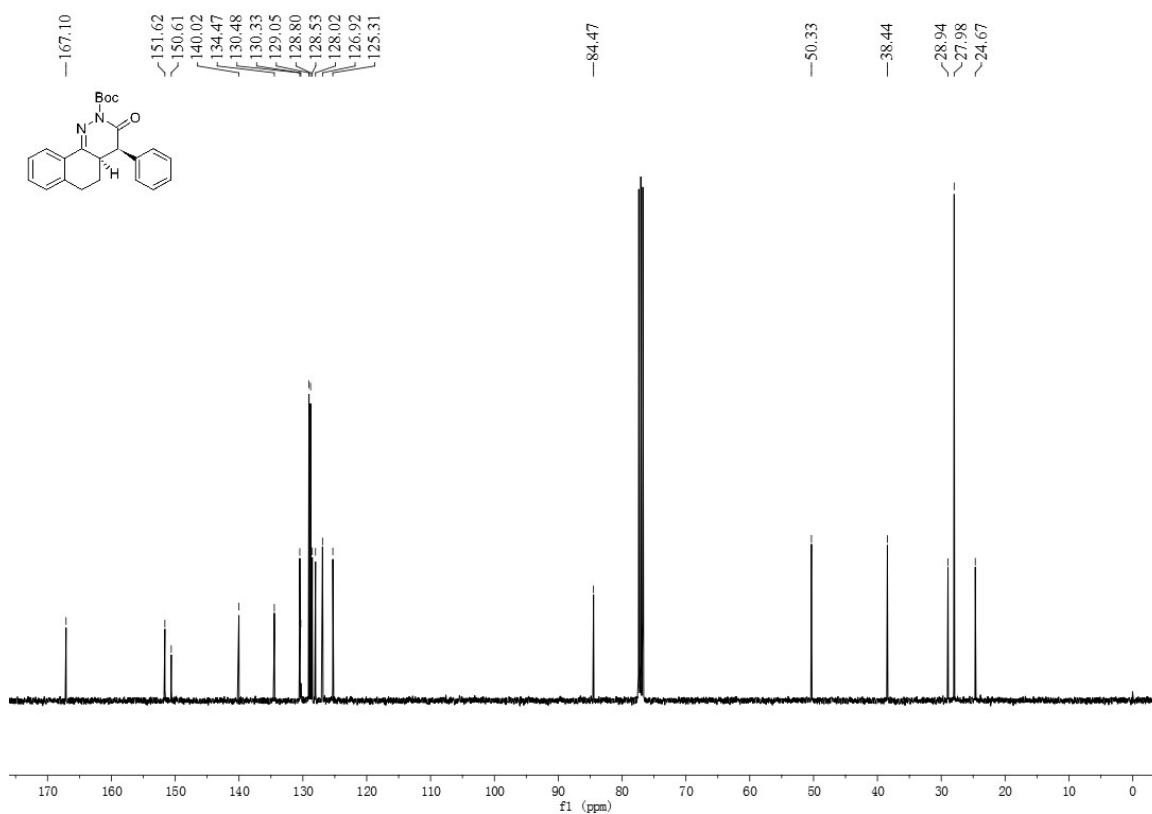
<sup>13</sup>C NMR spectrum of **1k**



### <sup>1</sup>H NMR spectrum of **3aa**

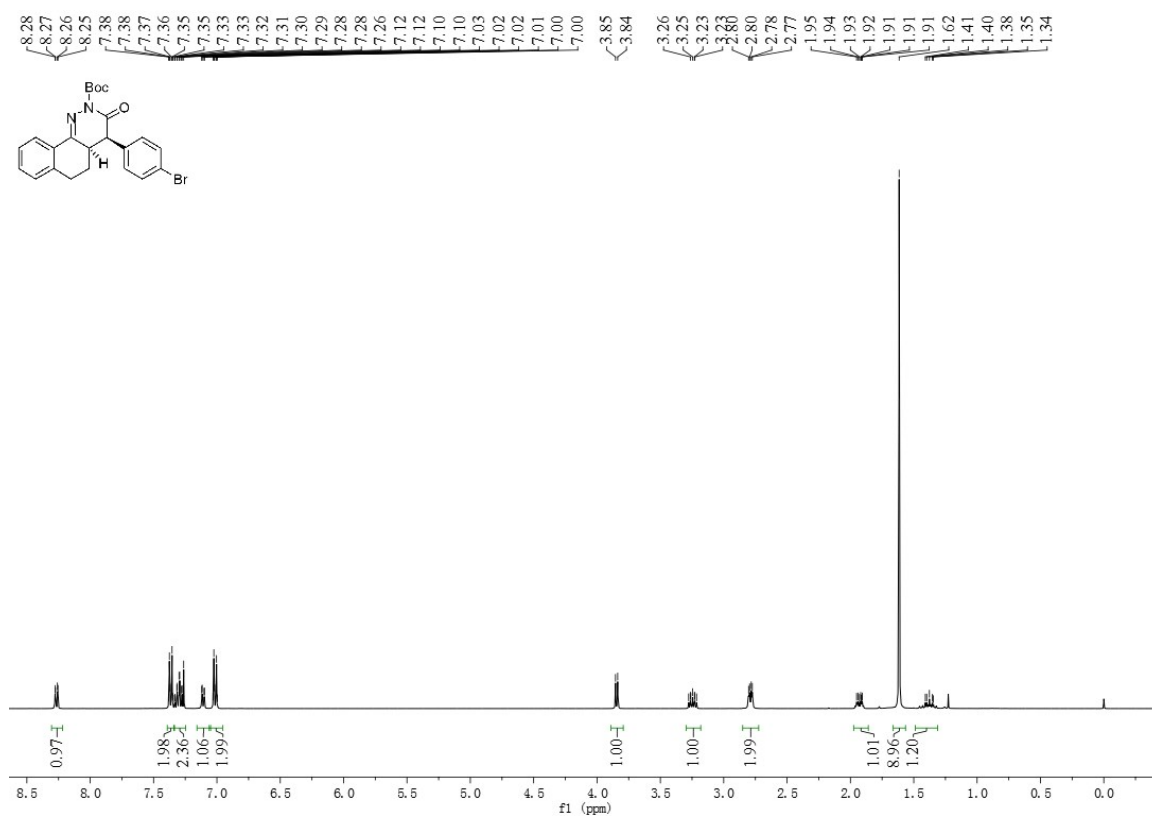


### <sup>13</sup>C NMR spectrum of **3aa**

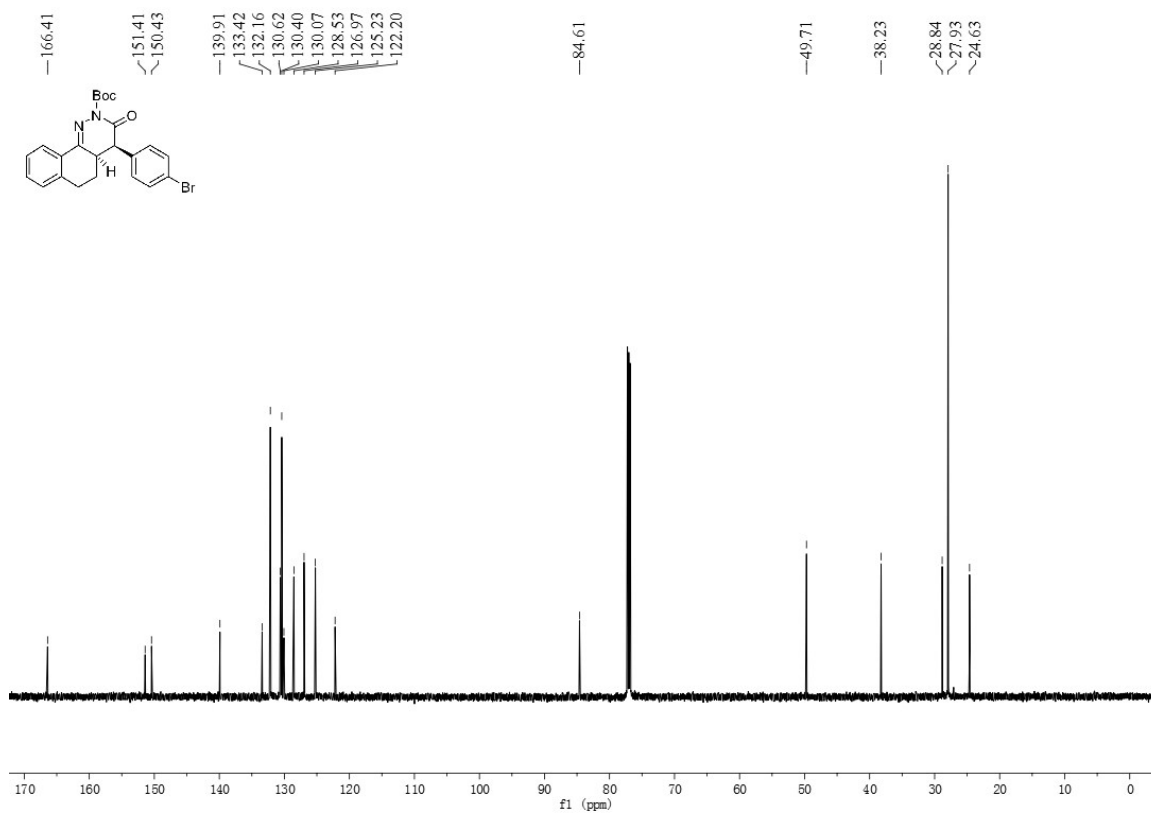




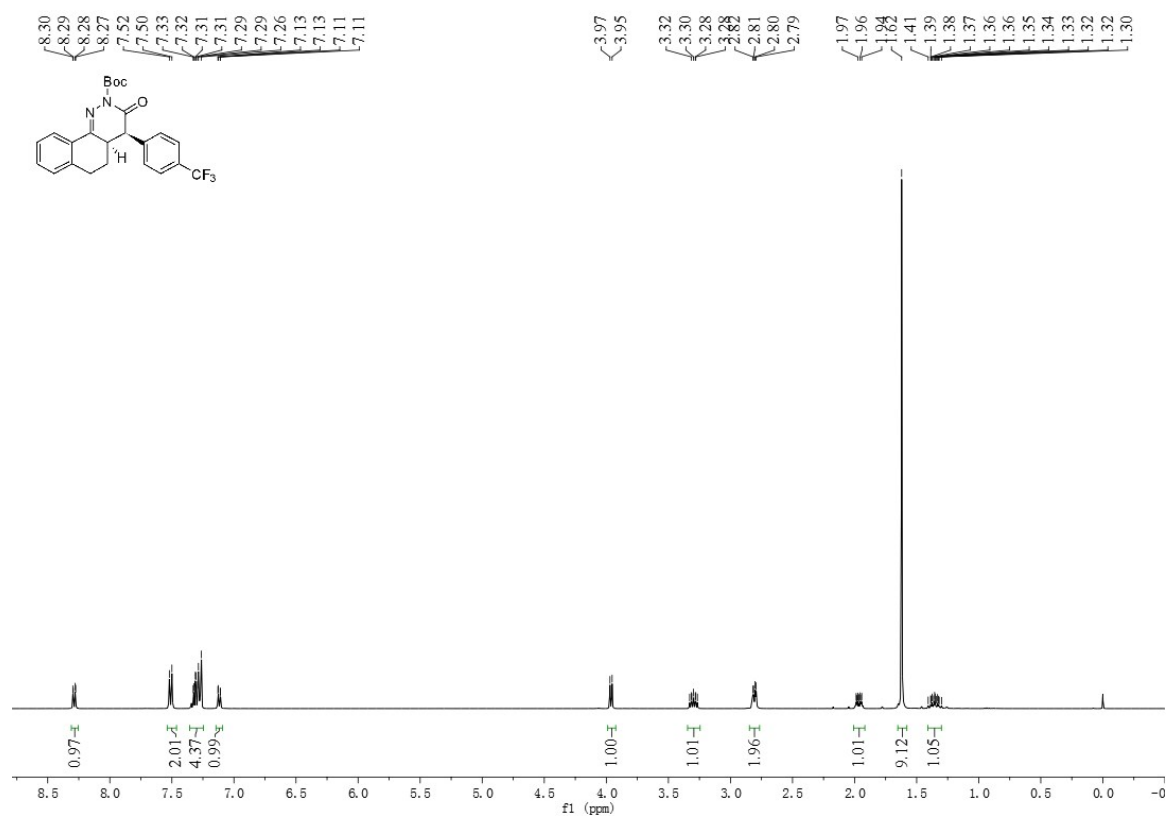
### <sup>1</sup>H NMR spectrum of **3ab**



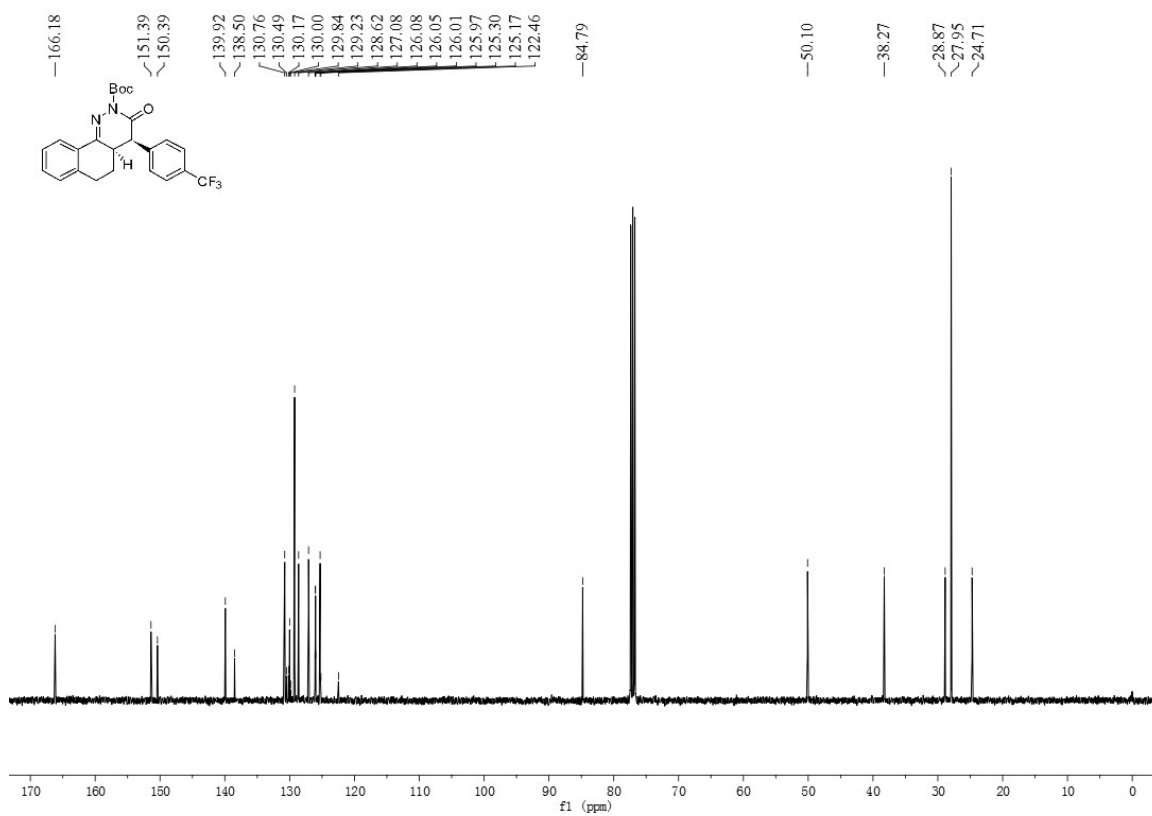
### <sup>13</sup>C NMR spectrum of **3ab**



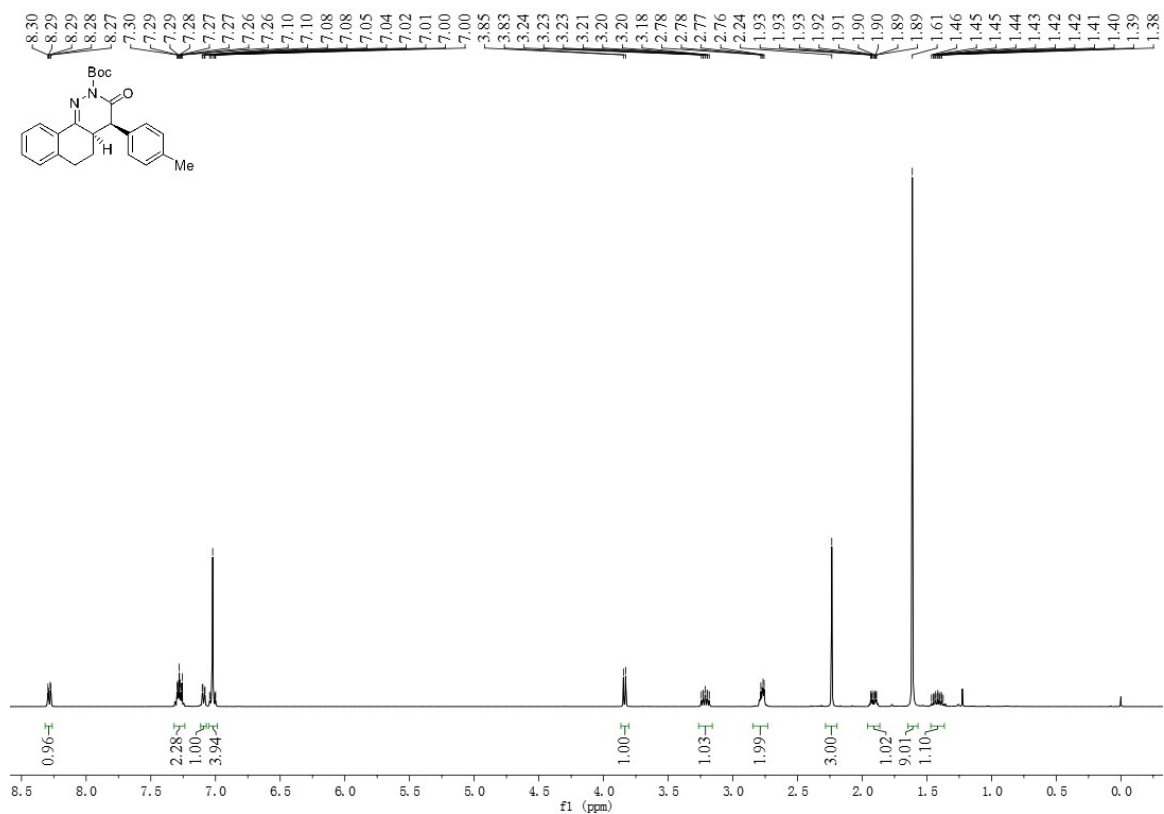
### $^1\text{H}$ NMR spectrum of **3ac**



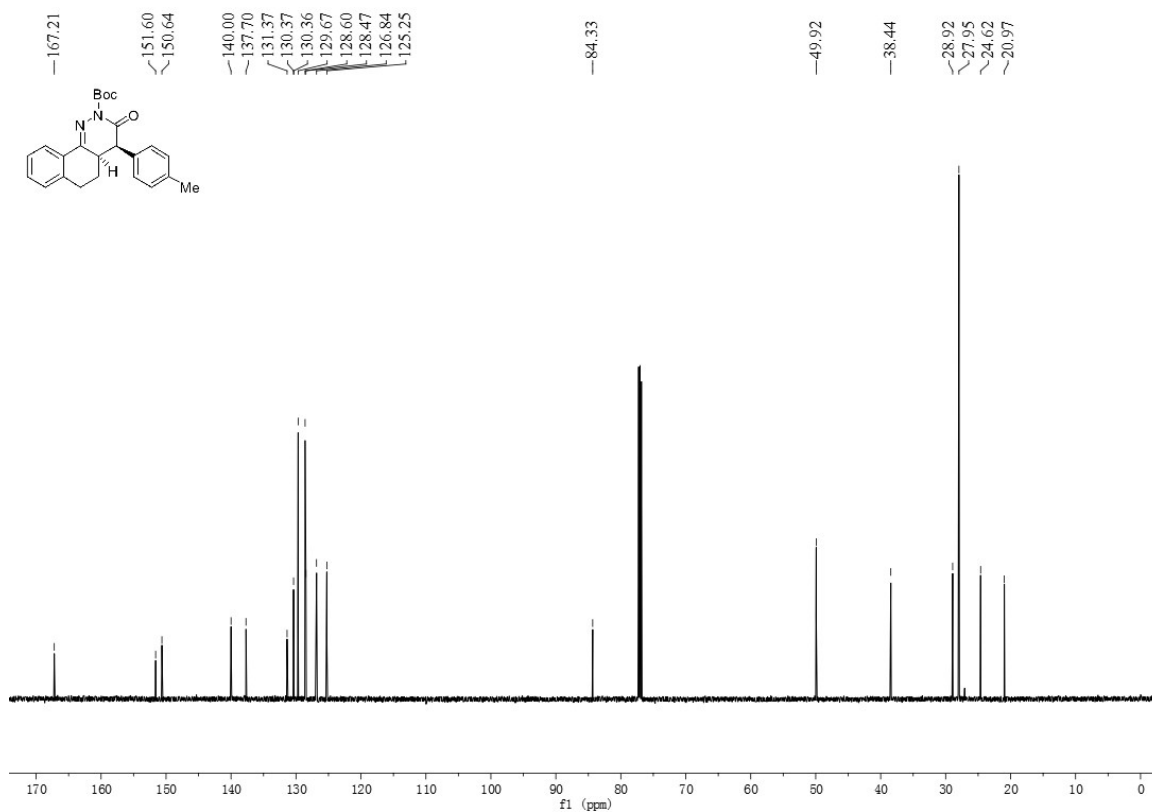
### $^{13}\text{C}$ NMR spectrum of **3ac**



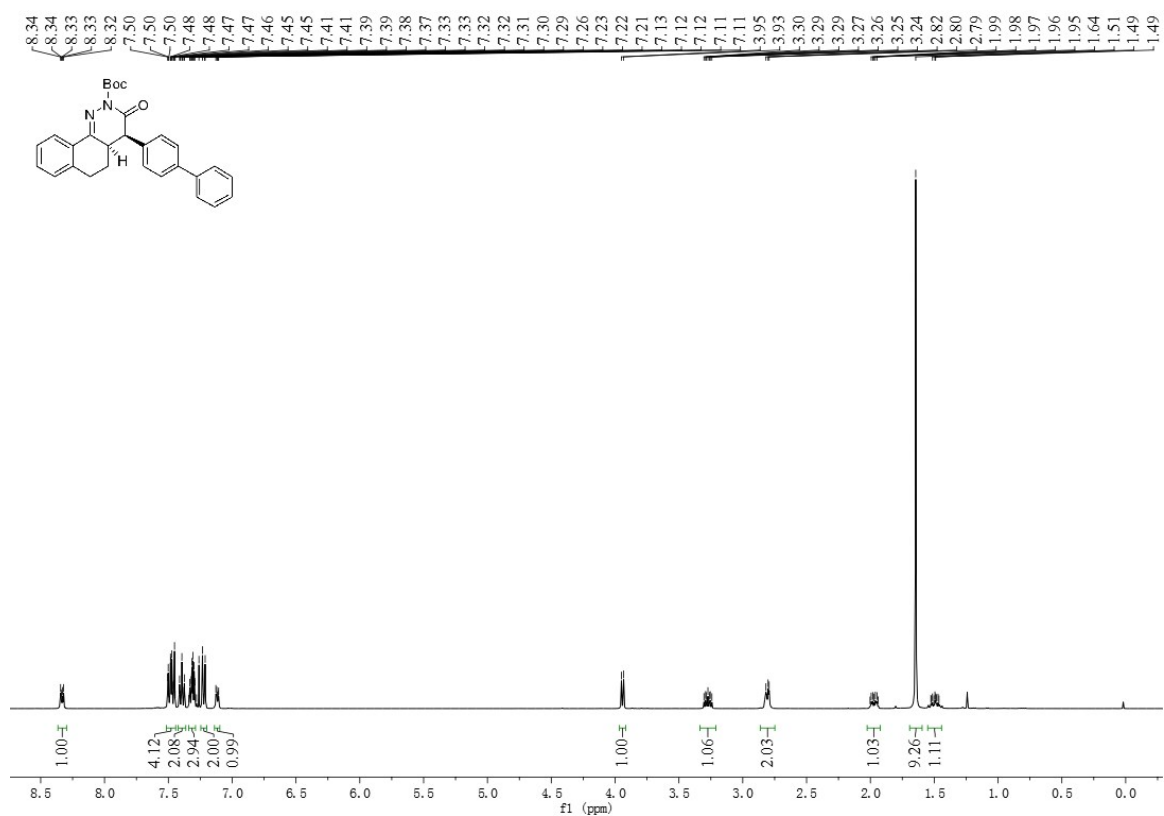
### $^1\text{H}$ NMR spectrum of **3ad**



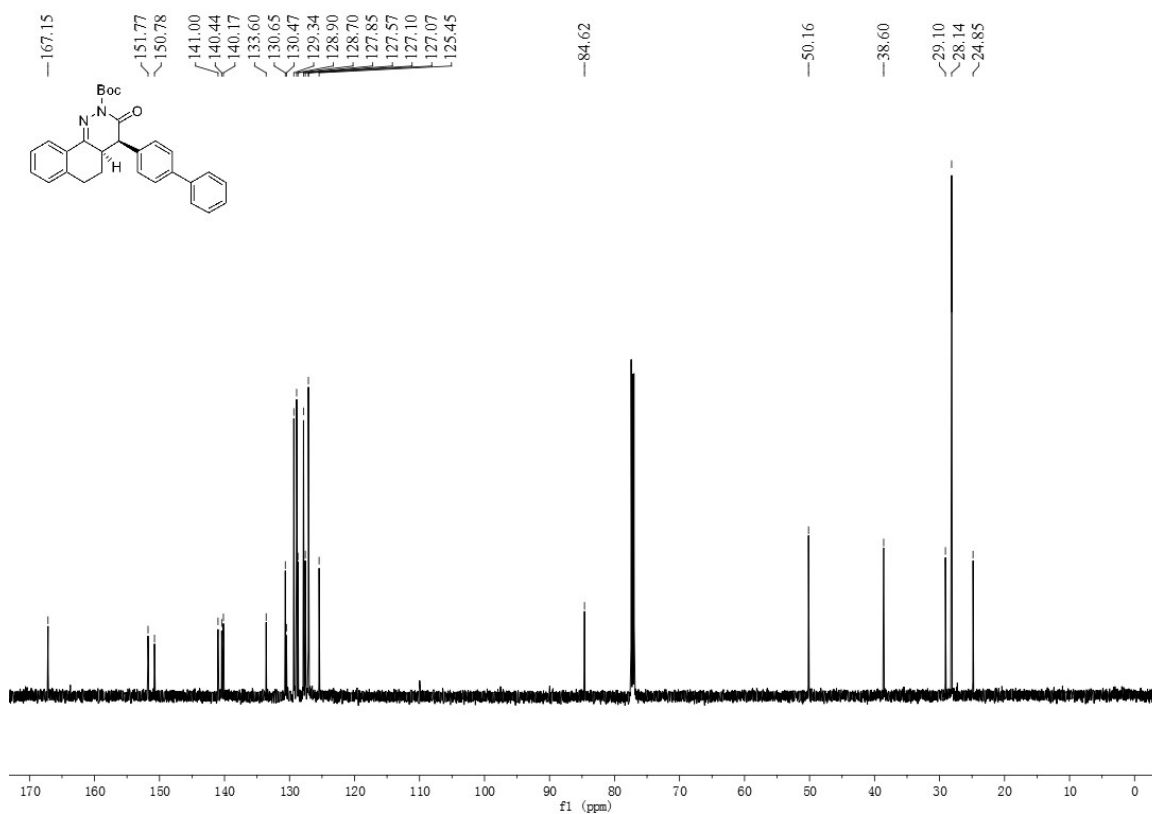
### $^{13}\text{C}$ NMR spectrum of **3ad**



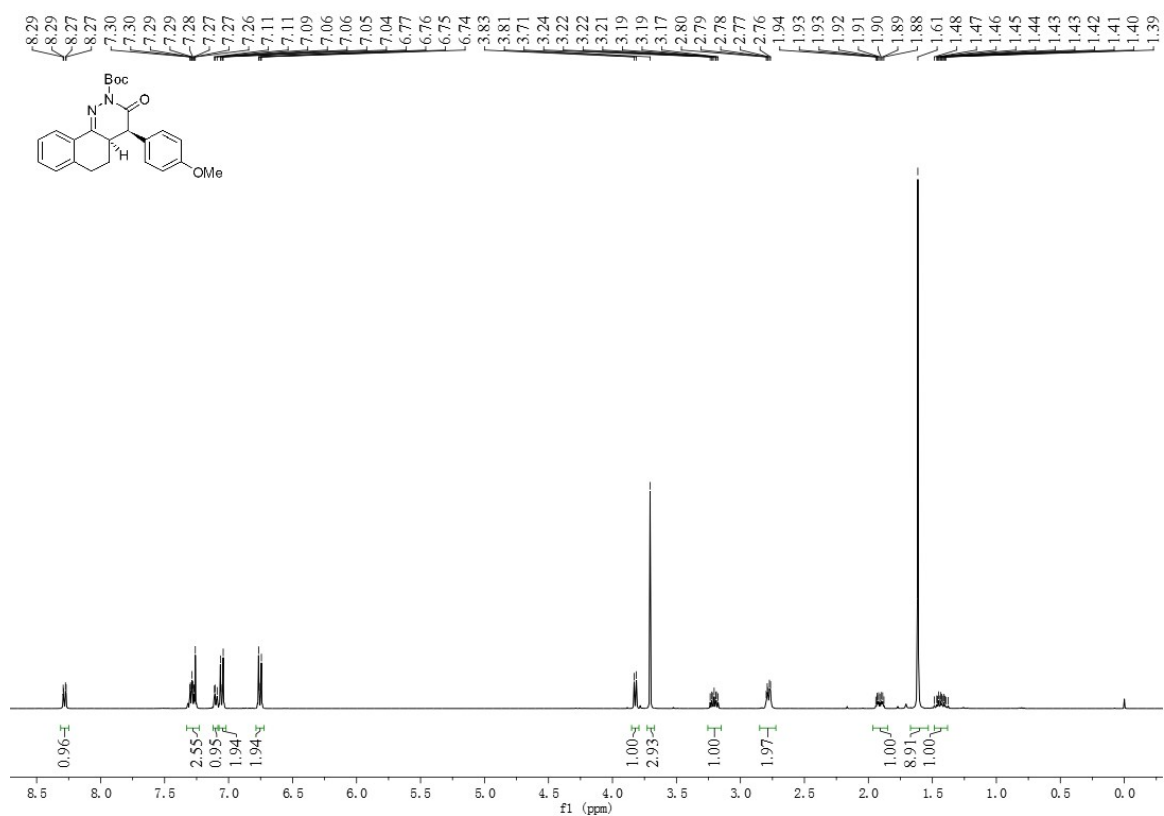
### <sup>1</sup>H NMR spectrum of 3ae



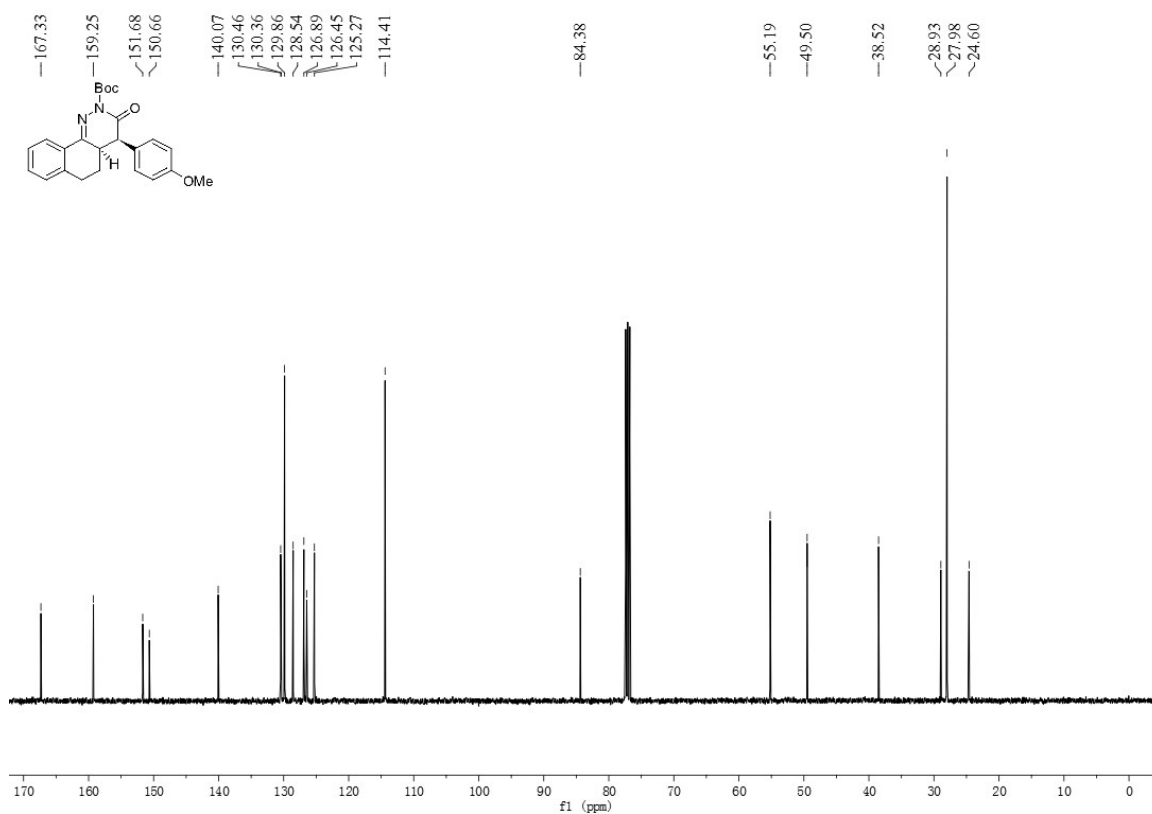
### <sup>13</sup>C NMR spectrum of 3ae



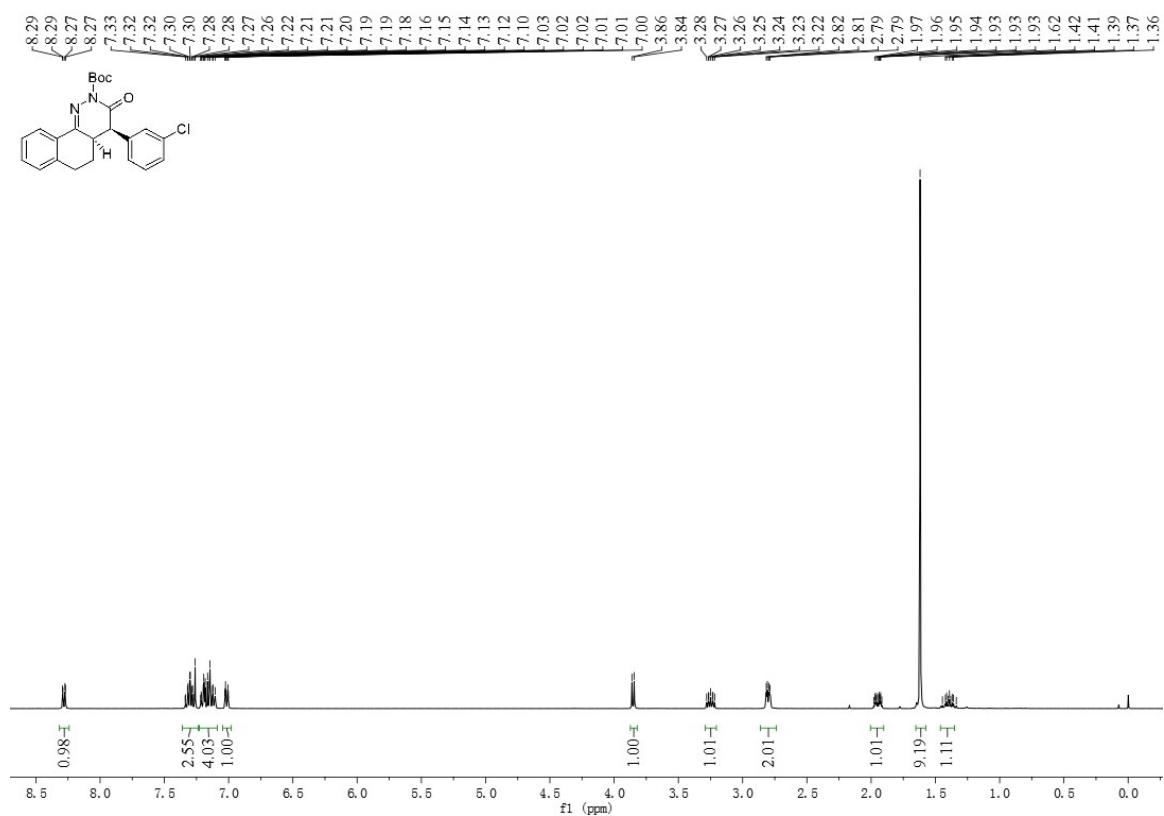
### <sup>1</sup>H NMR spectrum of **3af**



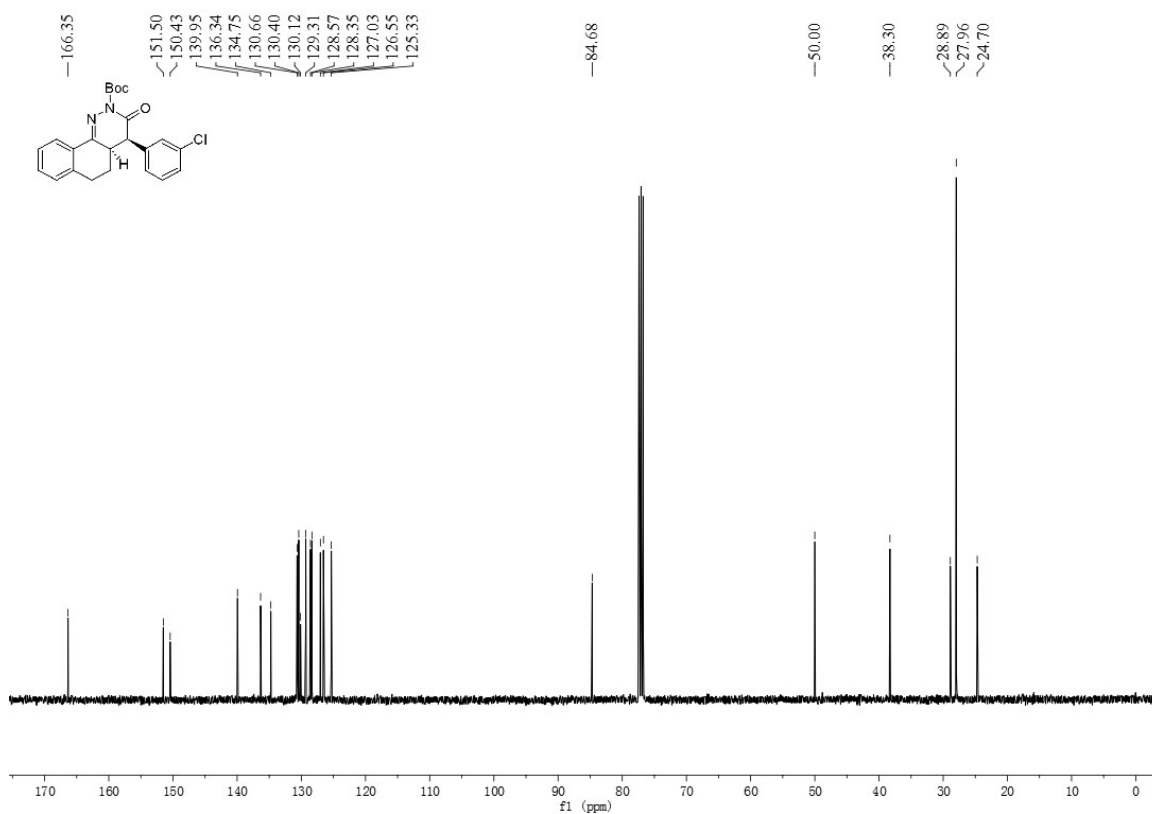
### <sup>13</sup>C NMR spectrum of **3af**



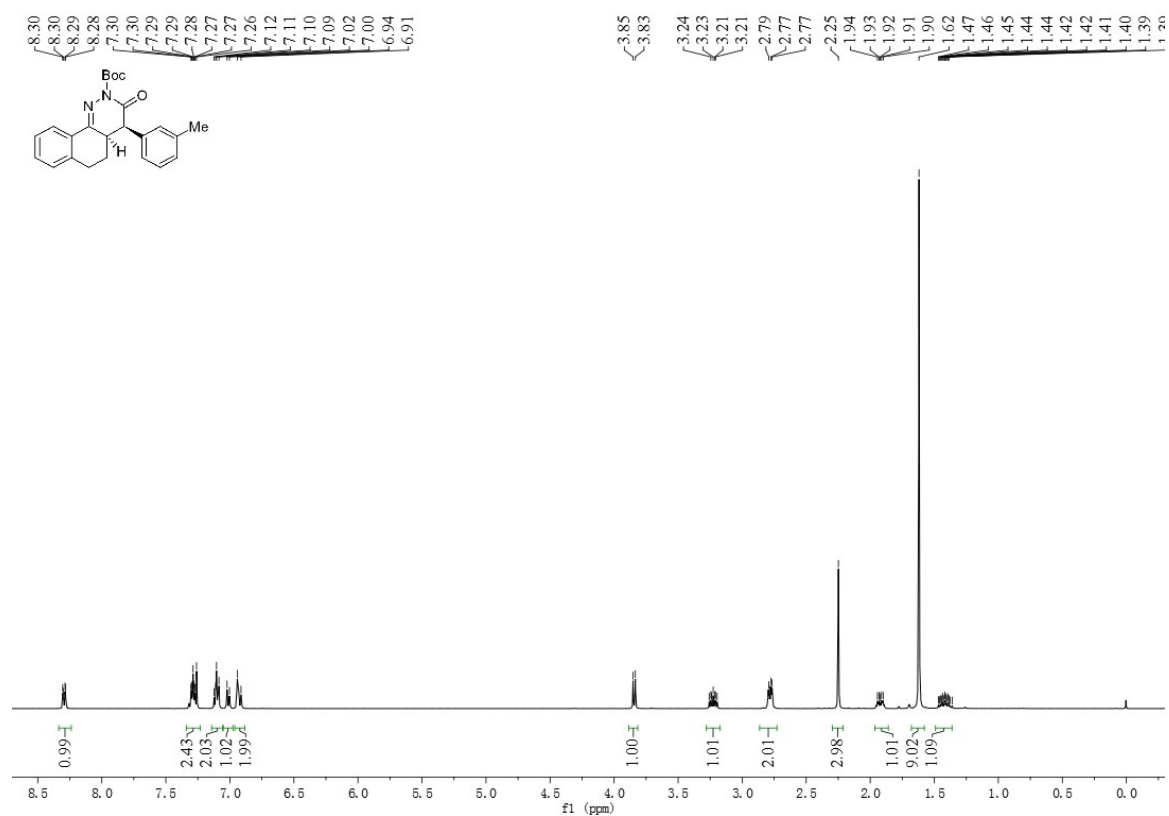
<sup>1</sup>H NMR spectrum of **3ag**



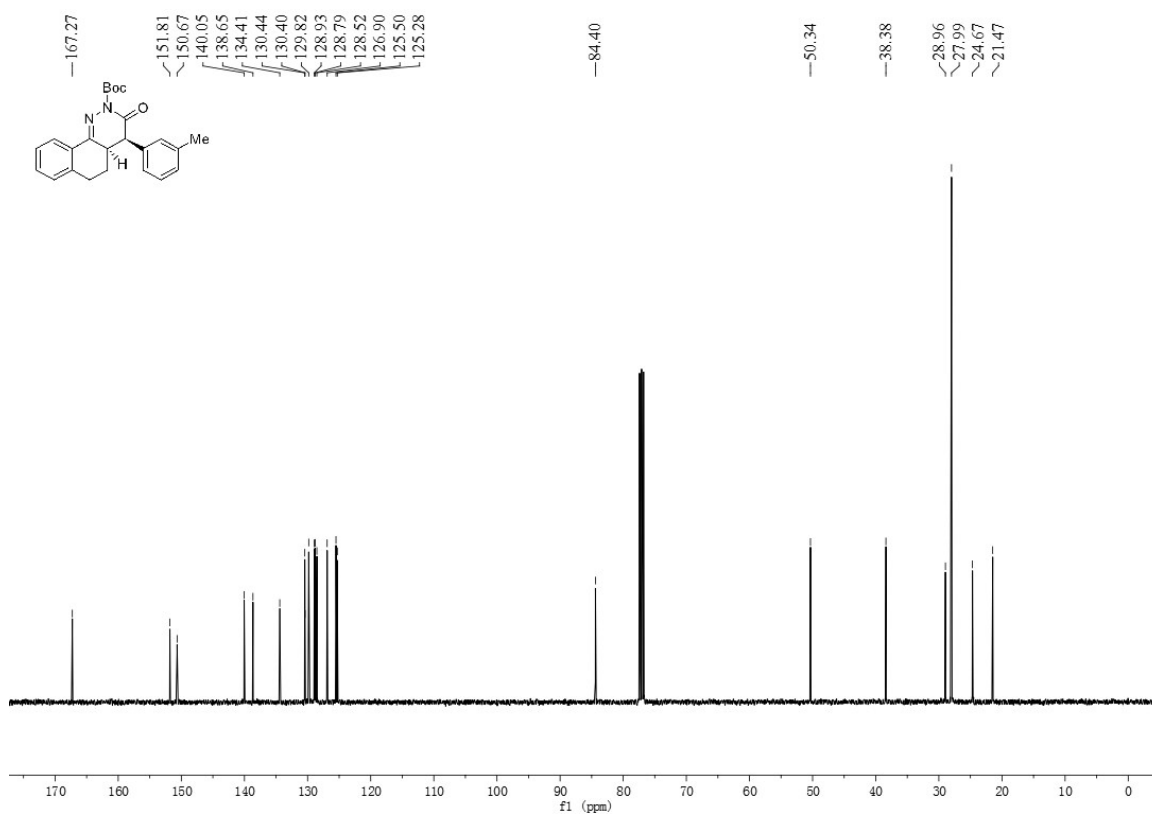
<sup>13</sup>C NMR spectrum of **3ag**



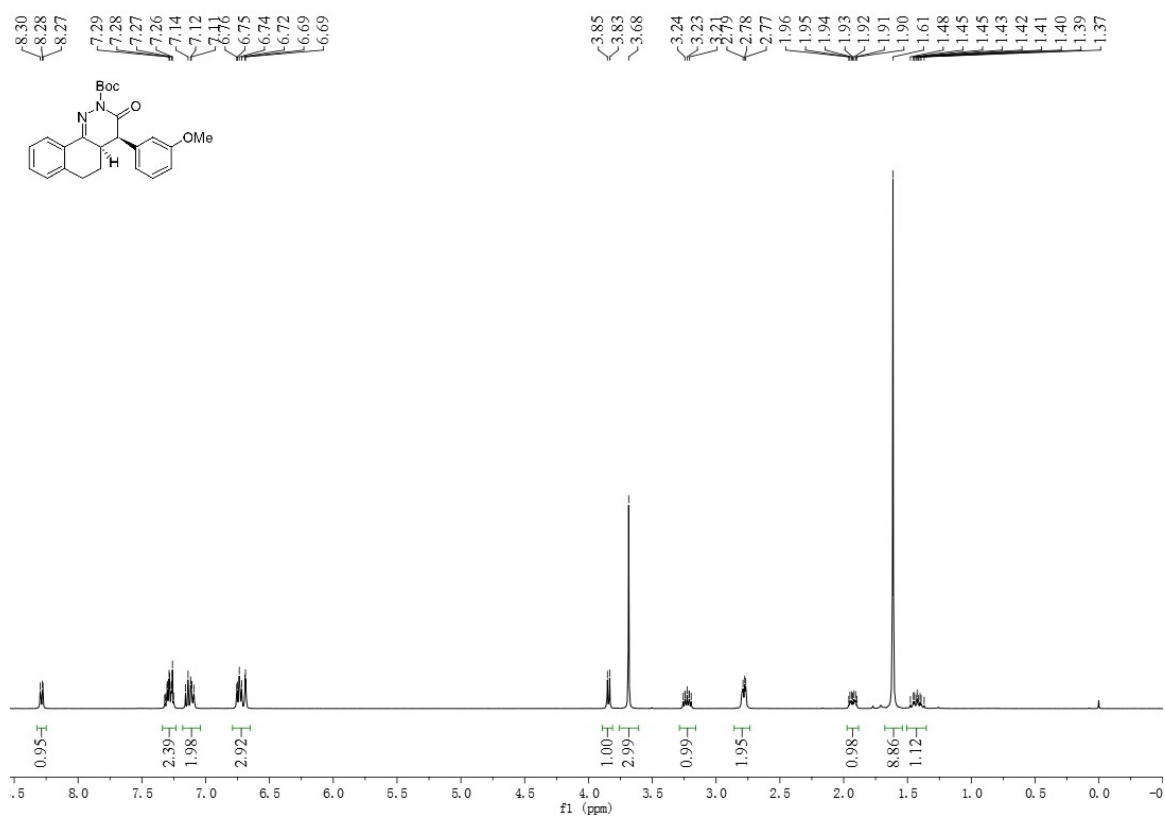
### <sup>1</sup>H NMR spectrum of **3ah**



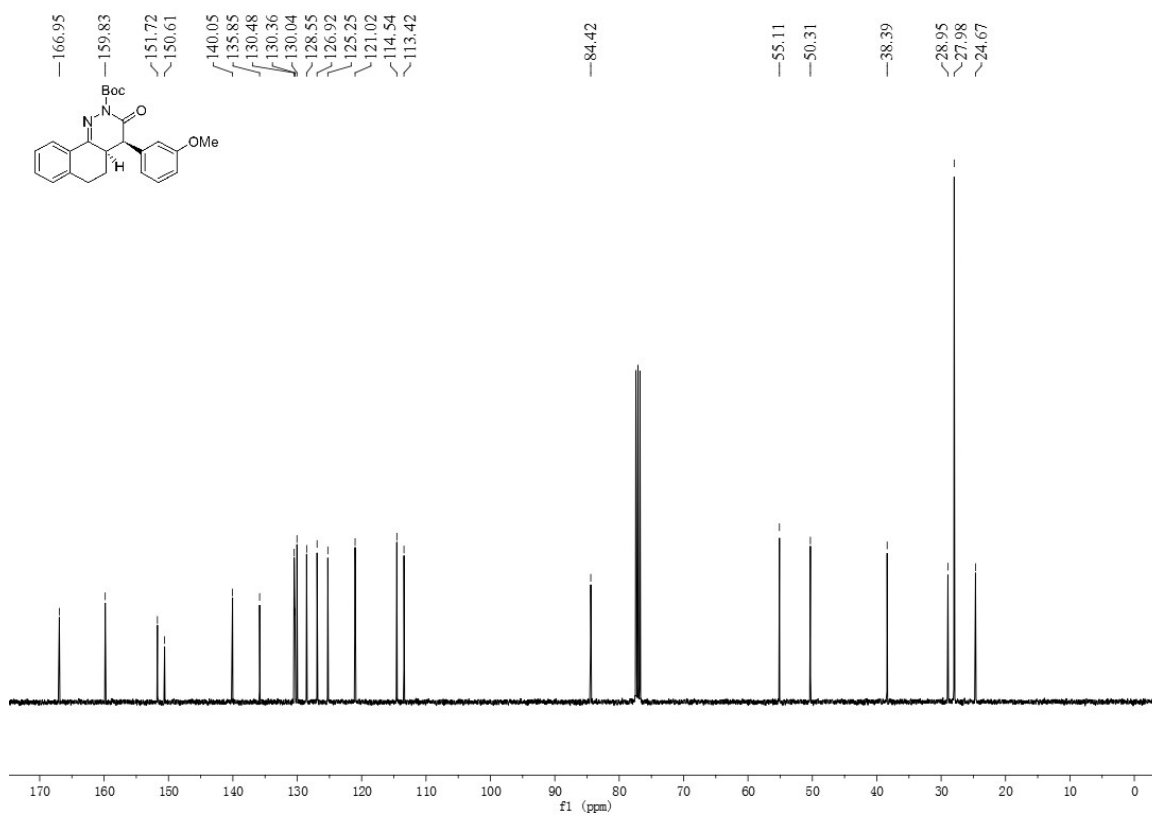
### <sup>13</sup>C NMR spectrum of **3ah**



### <sup>1</sup>H NMR spectrum of **3ai**

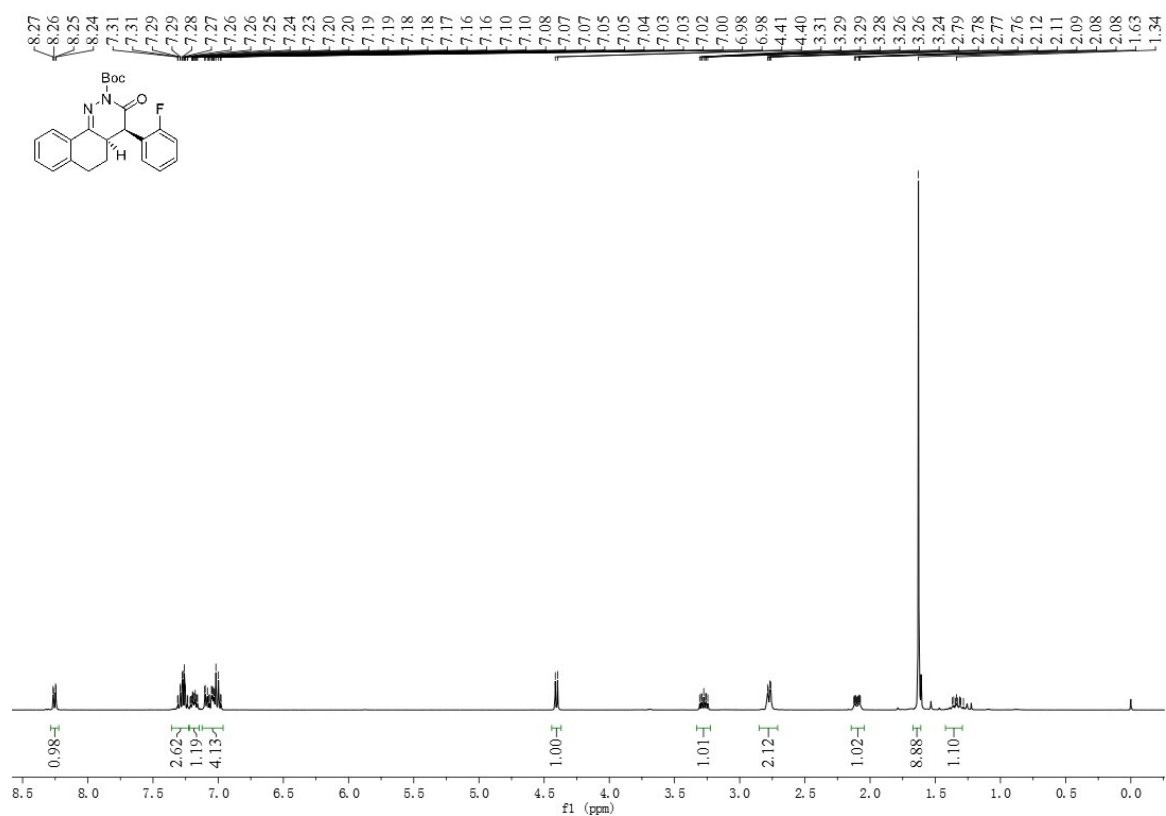


### <sup>13</sup>C NMR spectrum of **3ai**

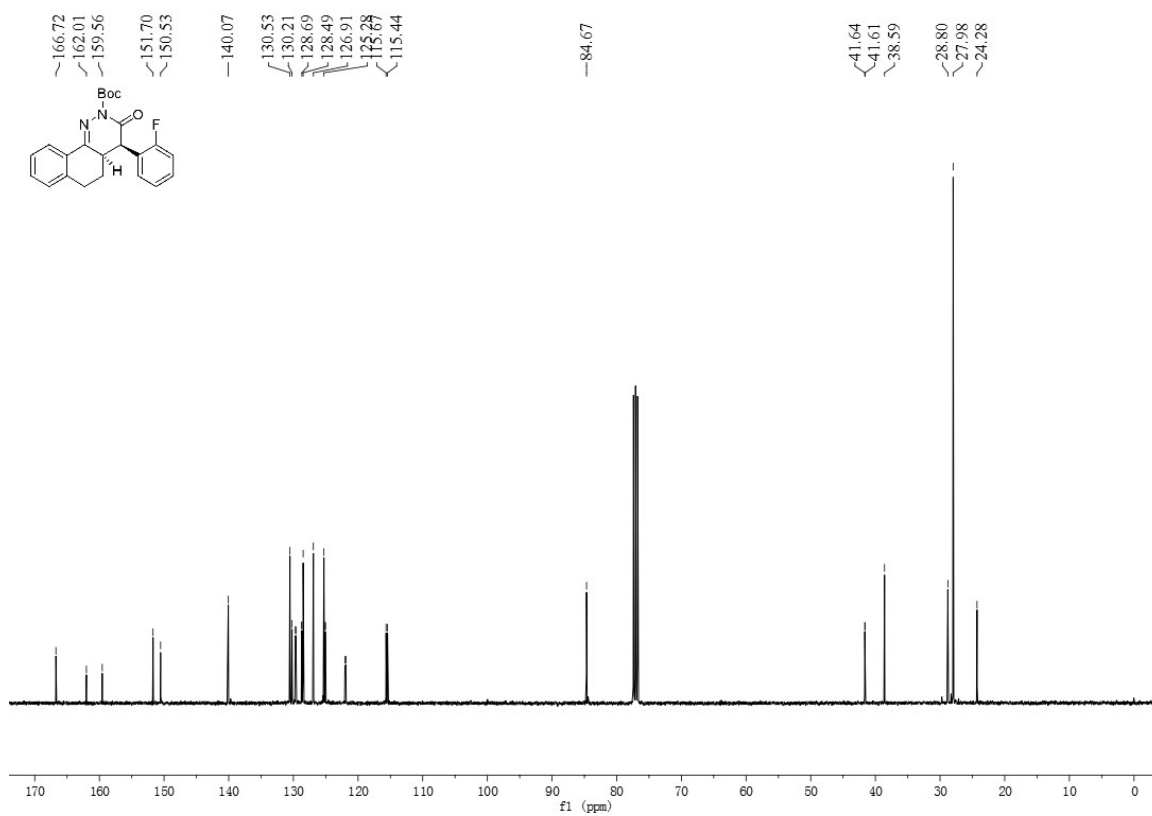




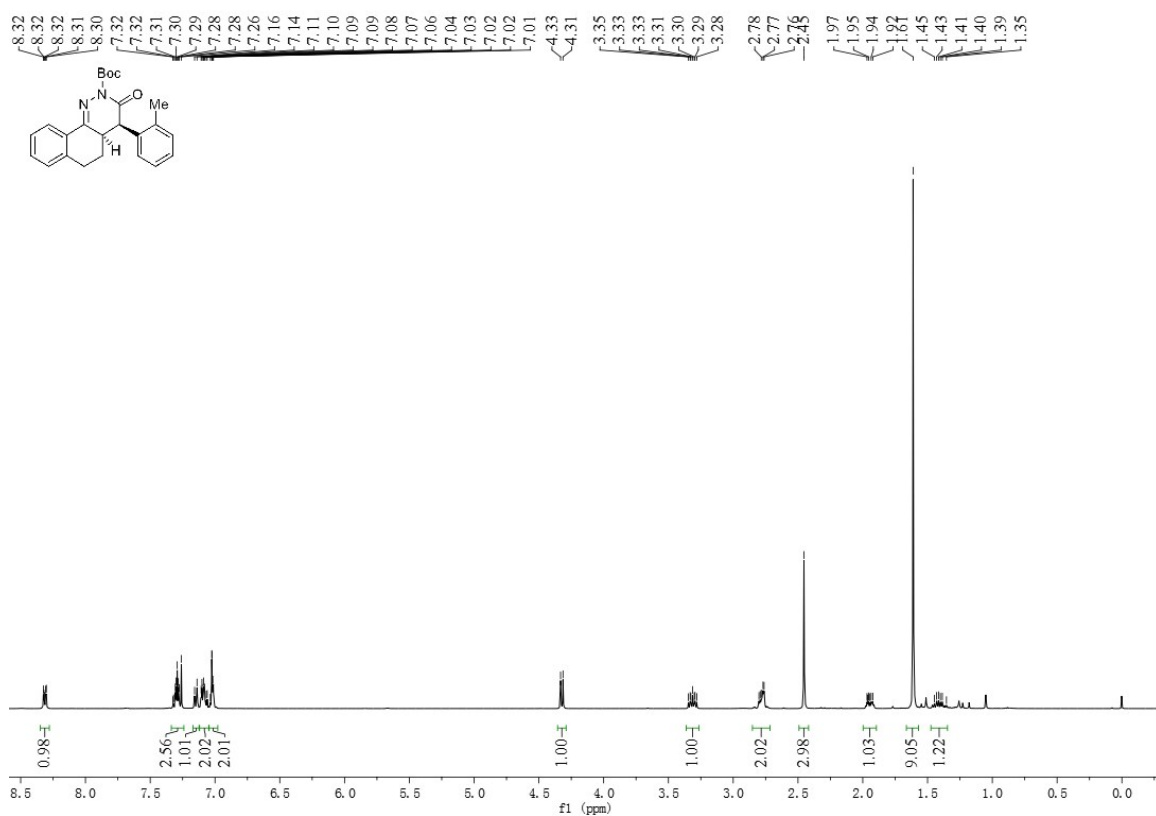
<sup>1</sup>H NMR spectrum of **3aj**



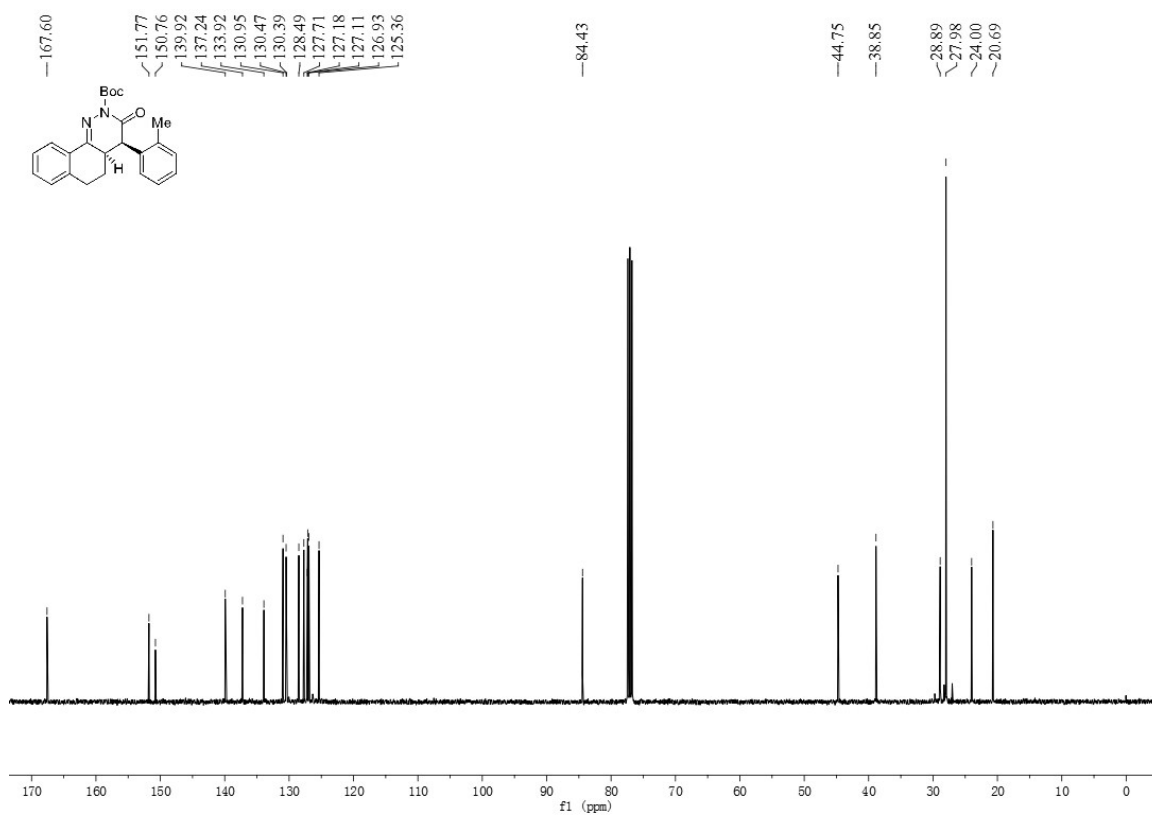
<sup>13</sup>C NMR spectrum of **3aj**



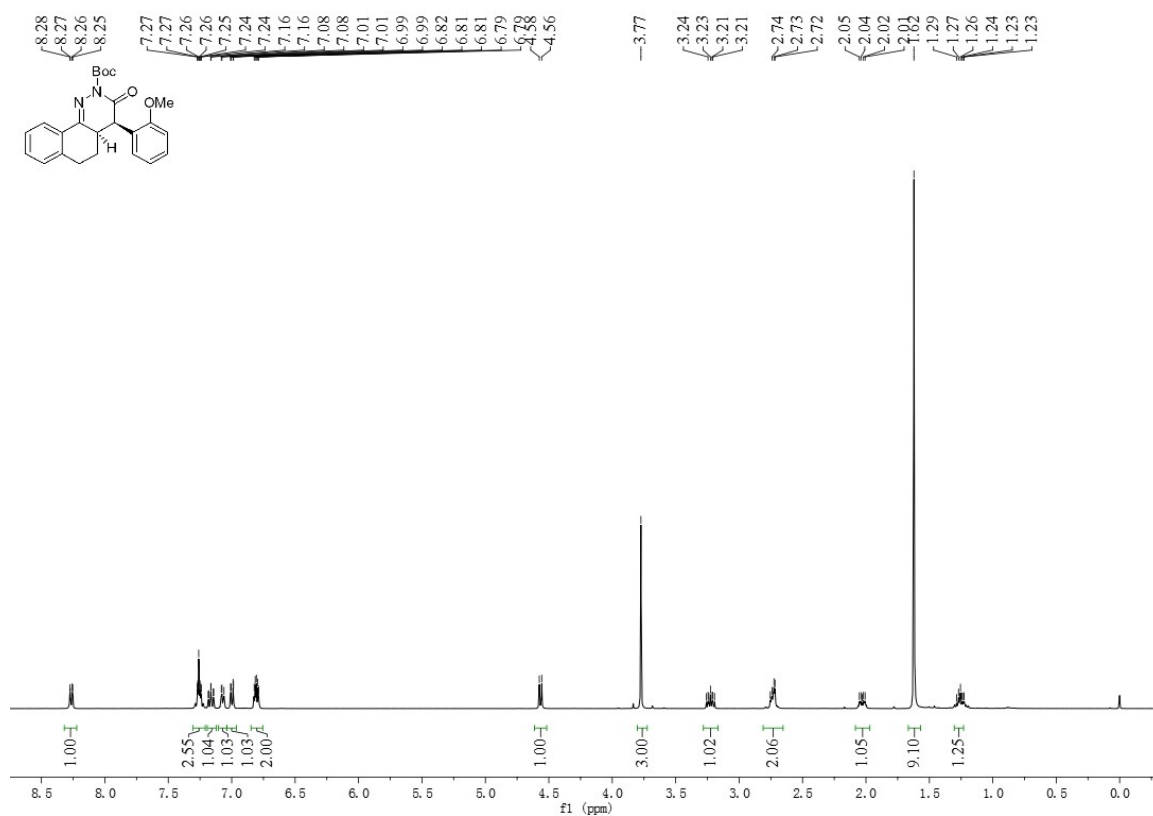
### <sup>1</sup>H NMR spectrum of **3ak**



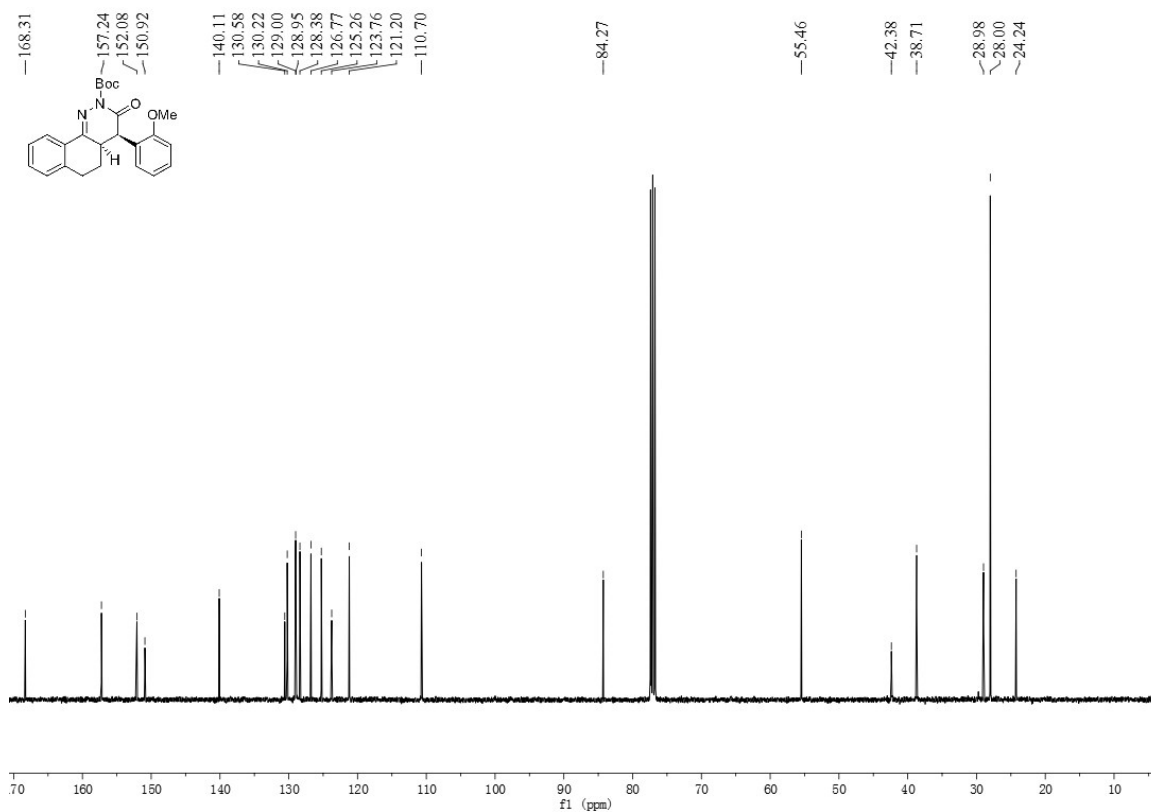
### <sup>13</sup>C NMR spectrum of **3ak**



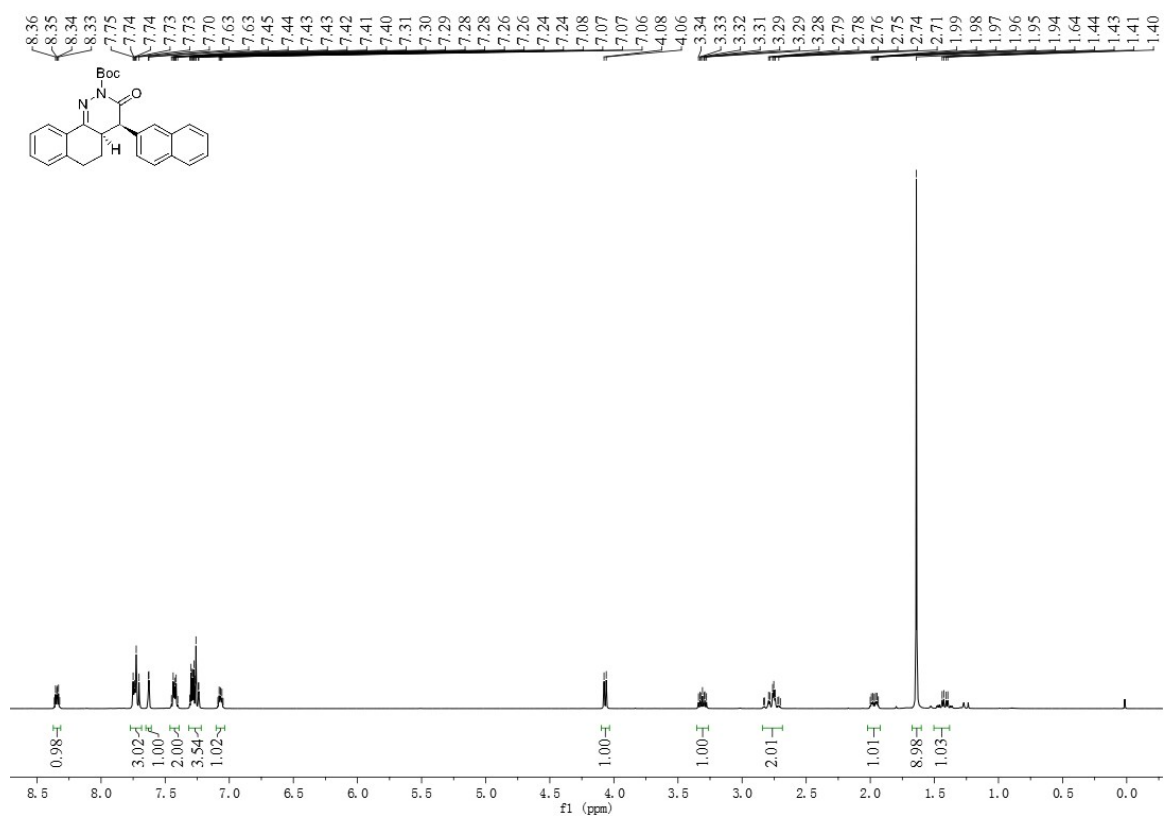
### $^1\text{H}$ NMR spectrum of **3al**



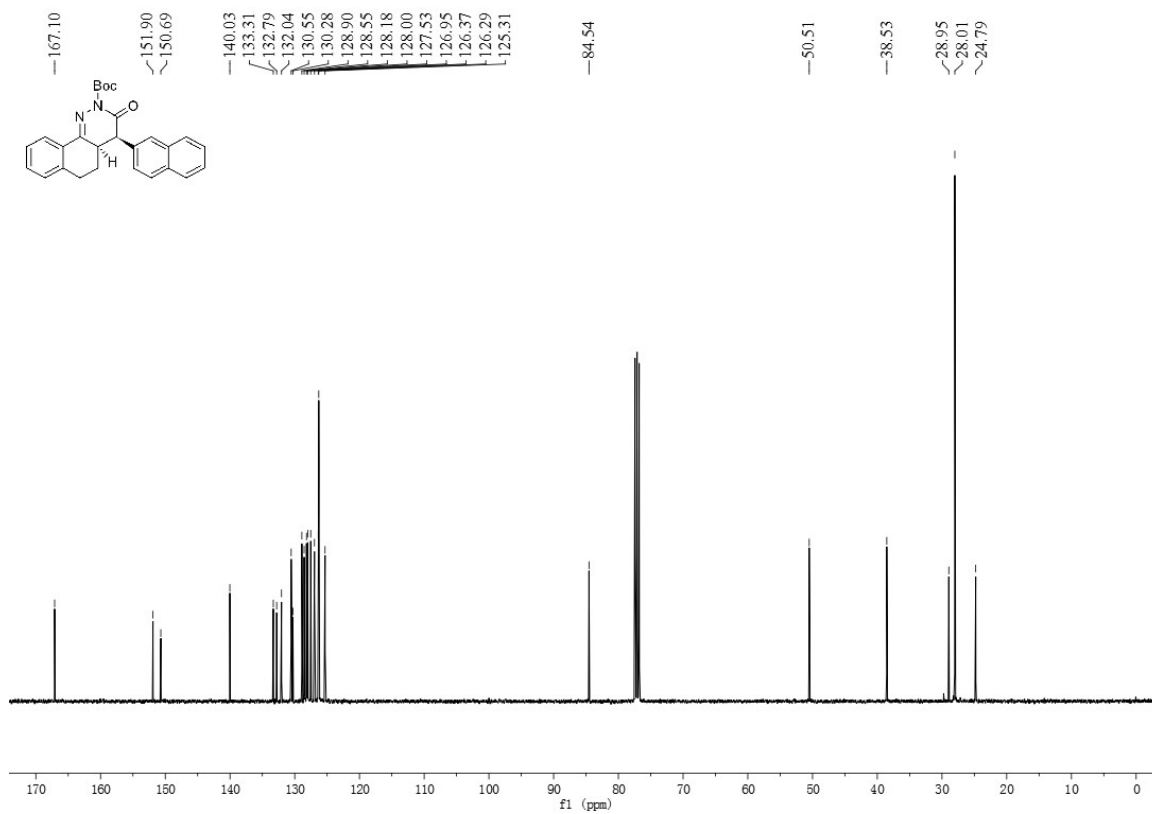
### $^{13}\text{C}$ NMR spectrum of **3al**



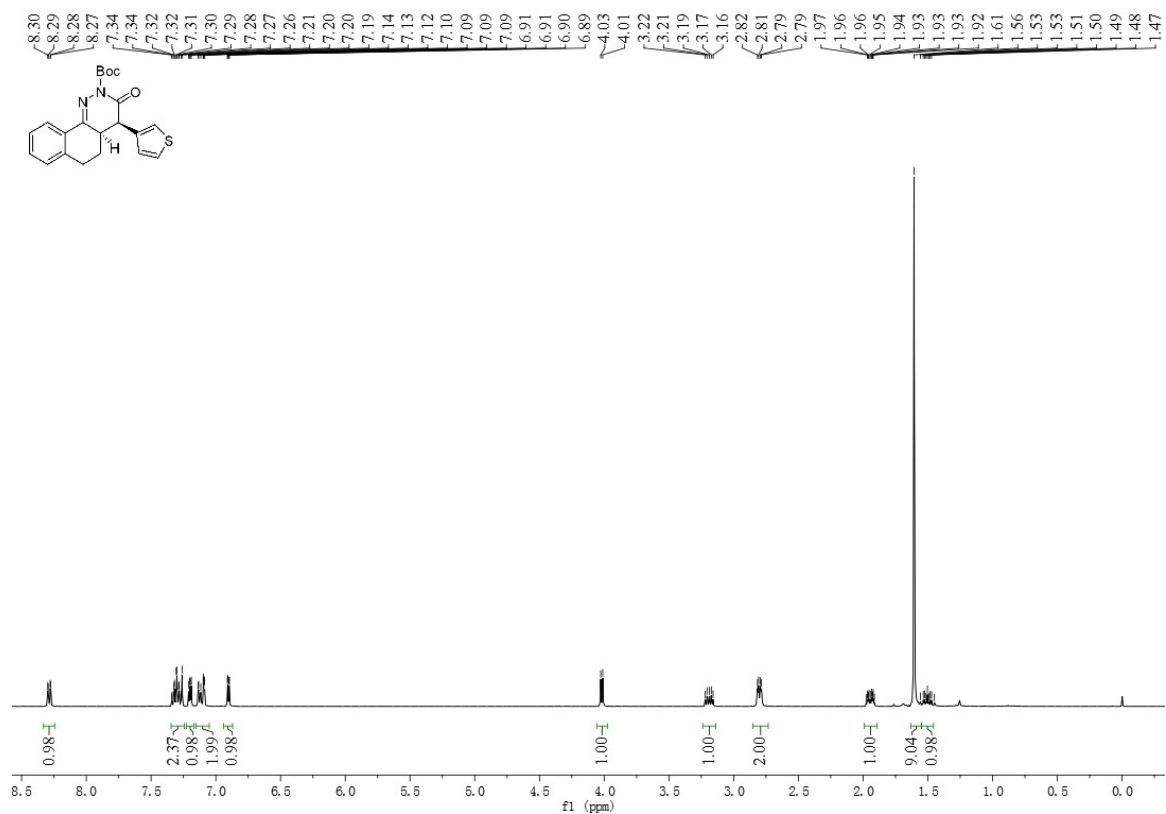
### <sup>1</sup>H NMR spectrum of **3am**



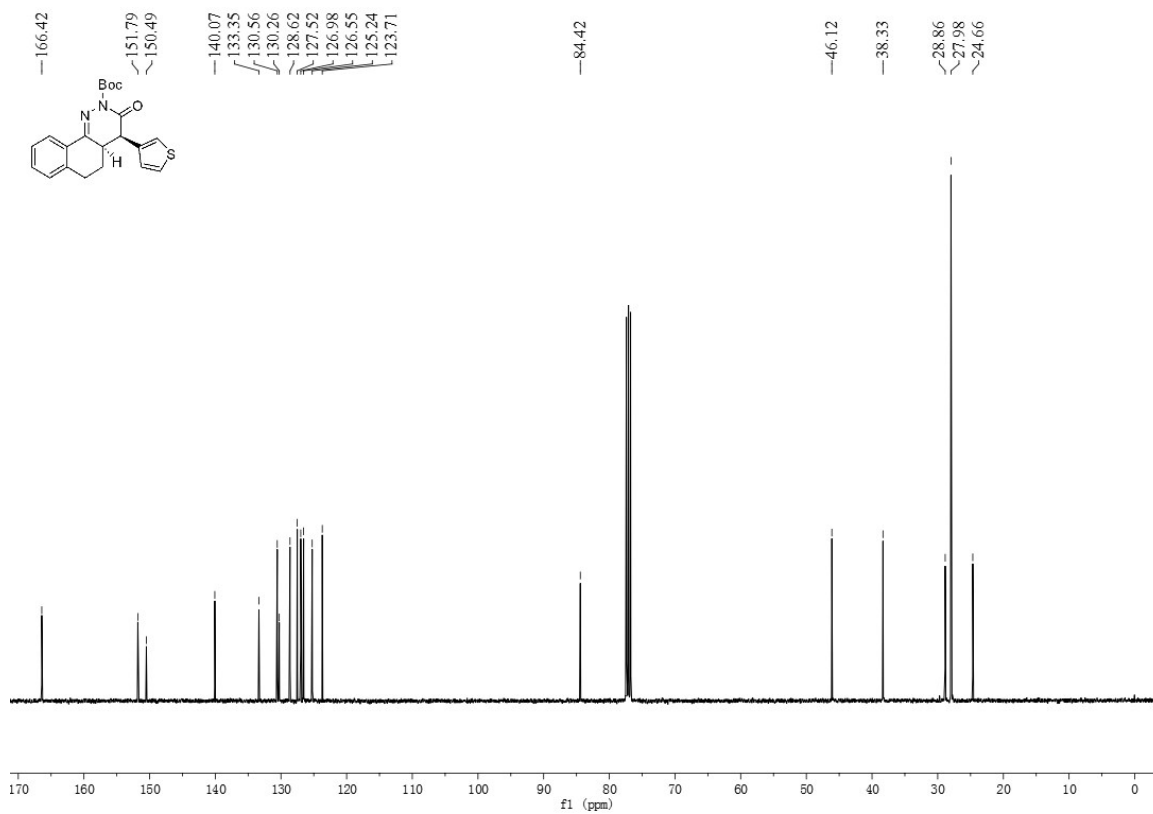
### <sup>13</sup>C NMR spectrum of **3am**



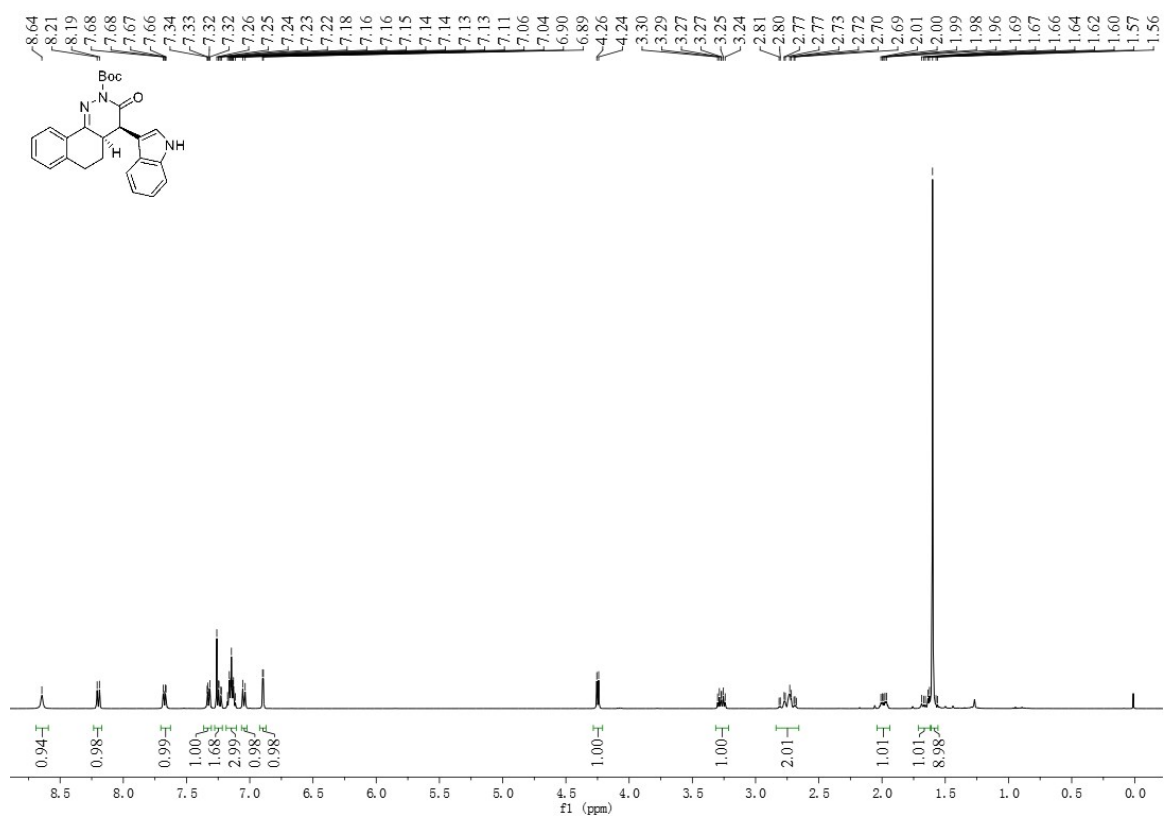
### <sup>1</sup>H NMR spectrum of **3an**



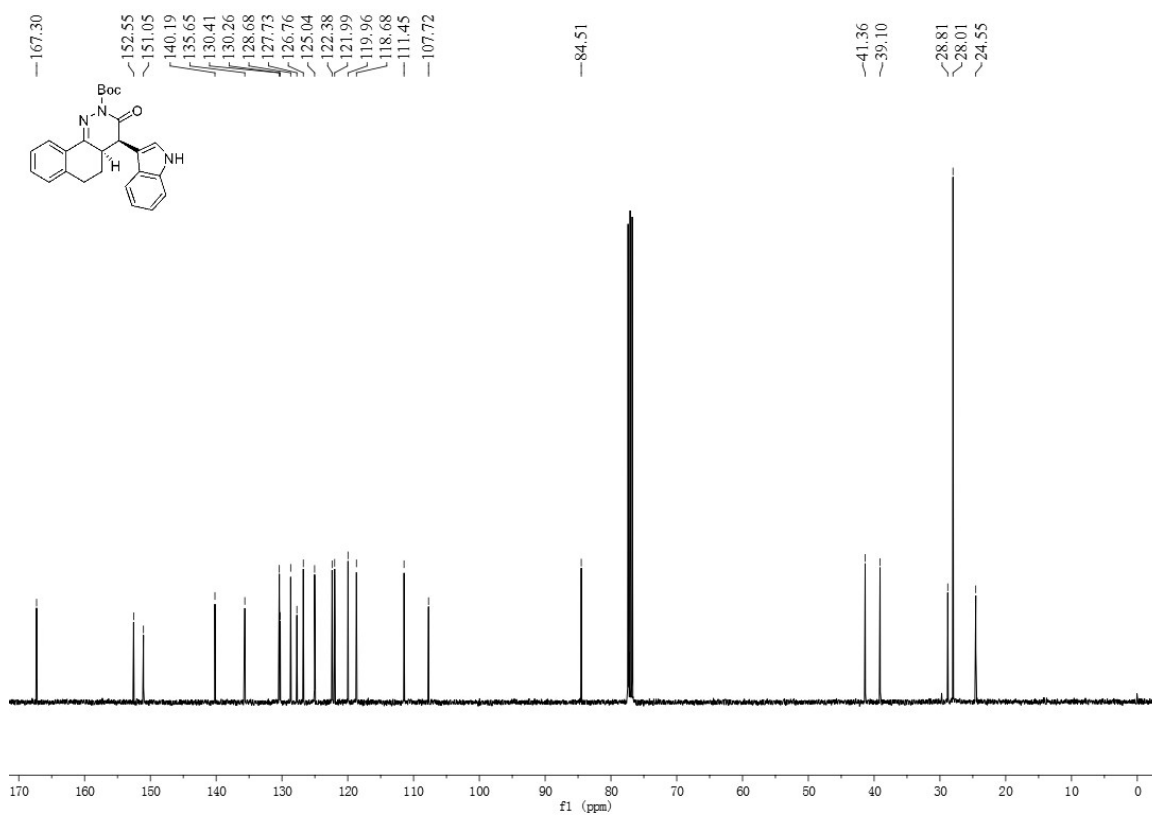
### <sup>13</sup>C NMR spectrum of **3an**



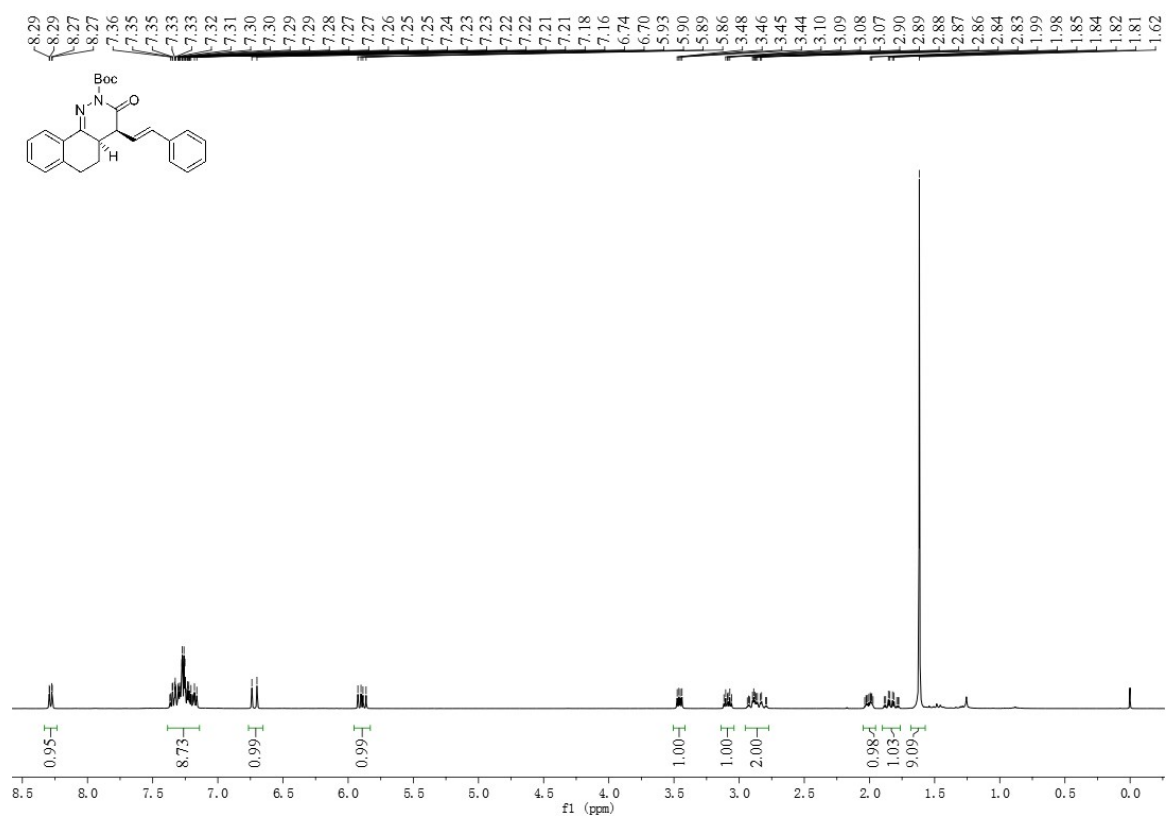
### <sup>1</sup>H NMR spectrum of **3ao**



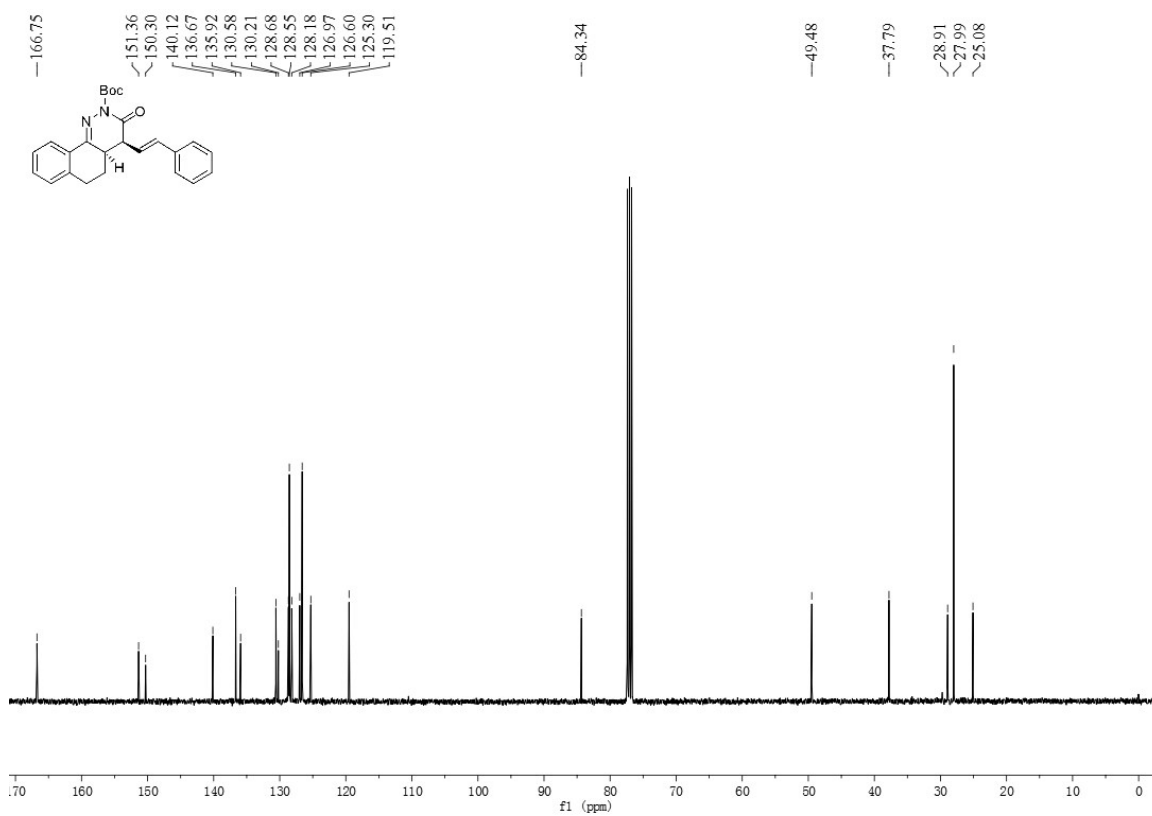
### <sup>13</sup>C NMR spectrum of **3ao**



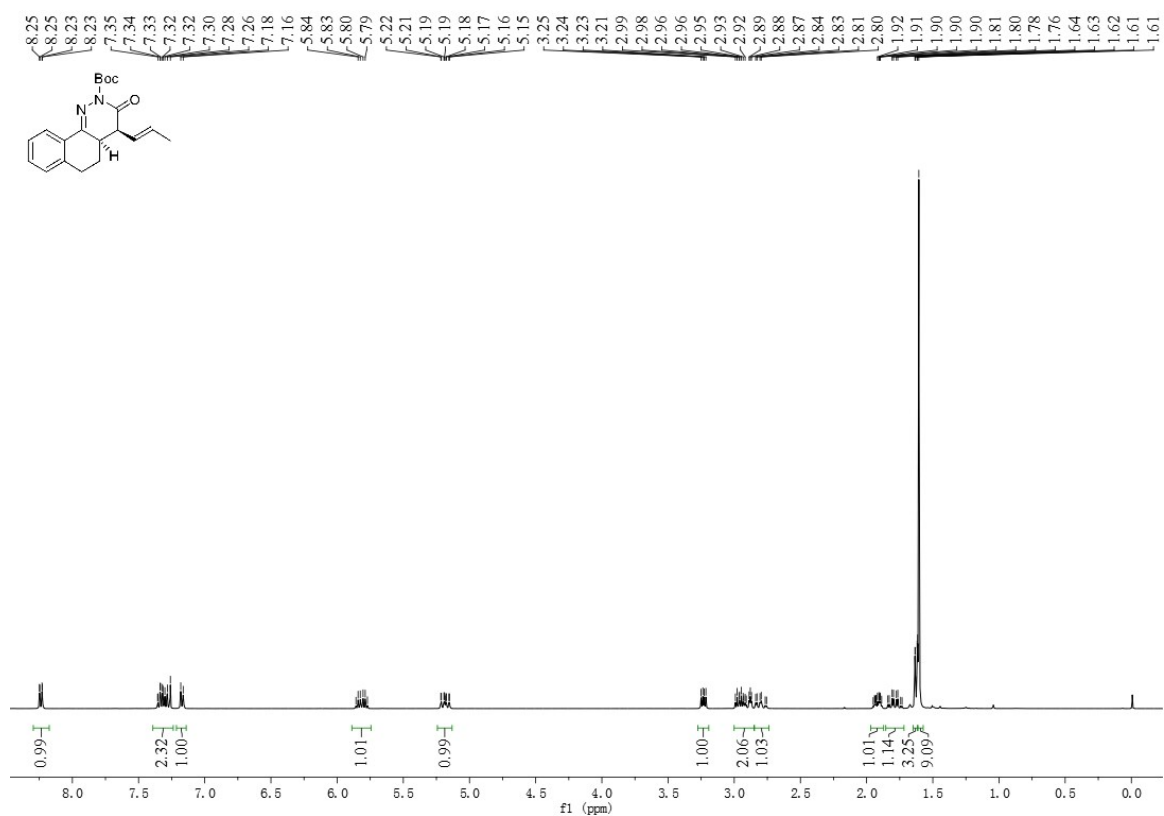
### $^1\text{H}$ NMR spectrum of **3ap**



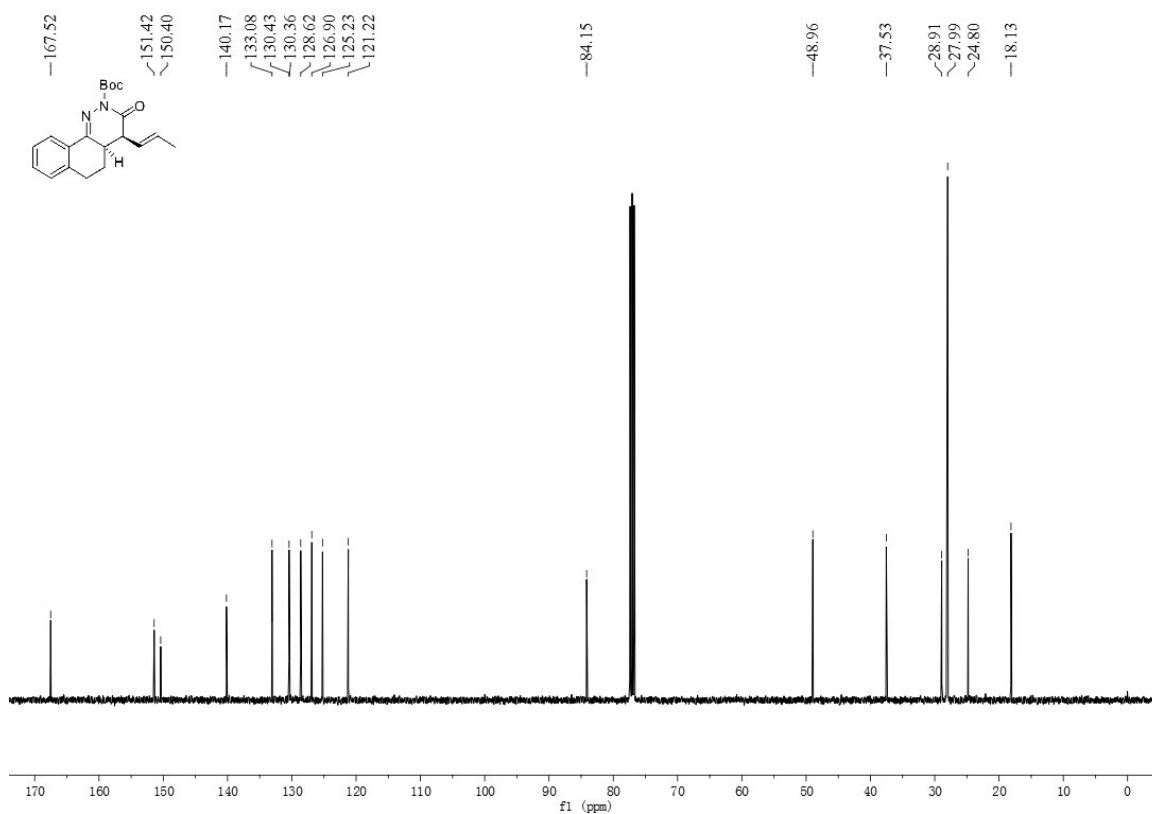
### $^{13}\text{C}$ NMR spectrum of **3ap**



### <sup>1</sup>H NMR spectrum of **3aq**

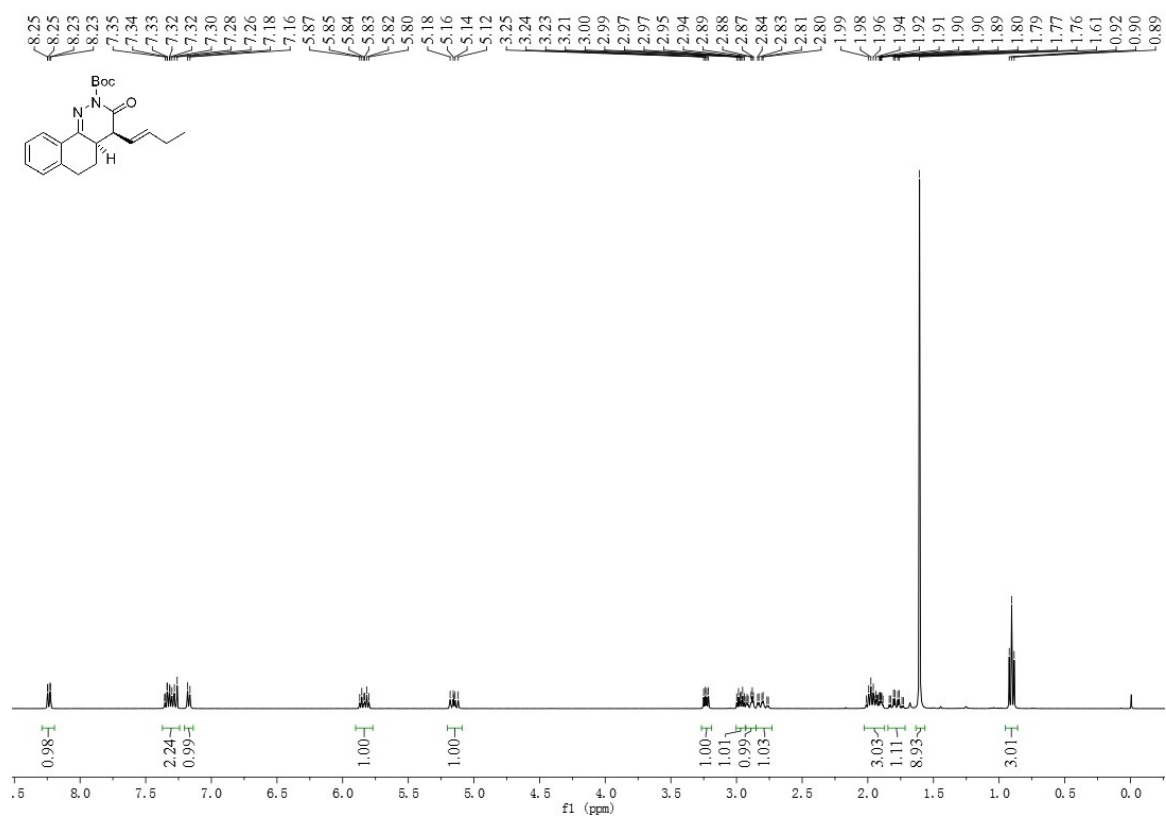


### <sup>13</sup>C NMR spectrum of **3aq**

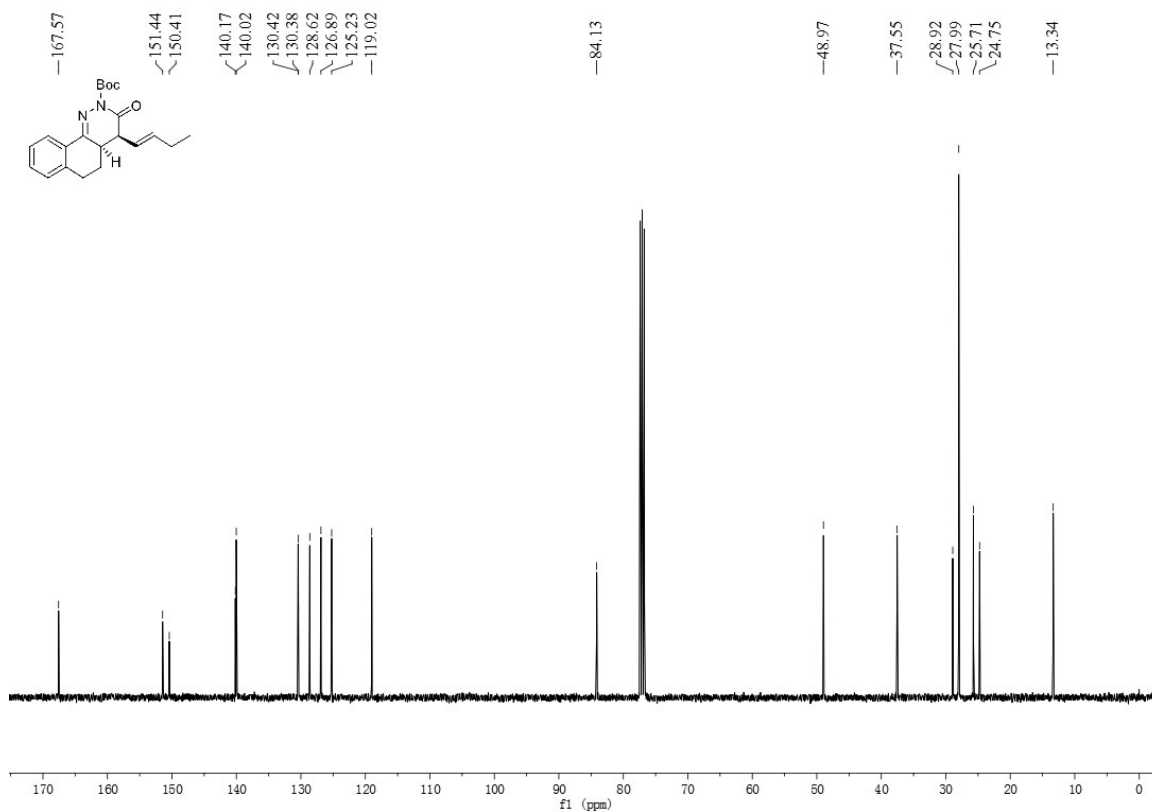




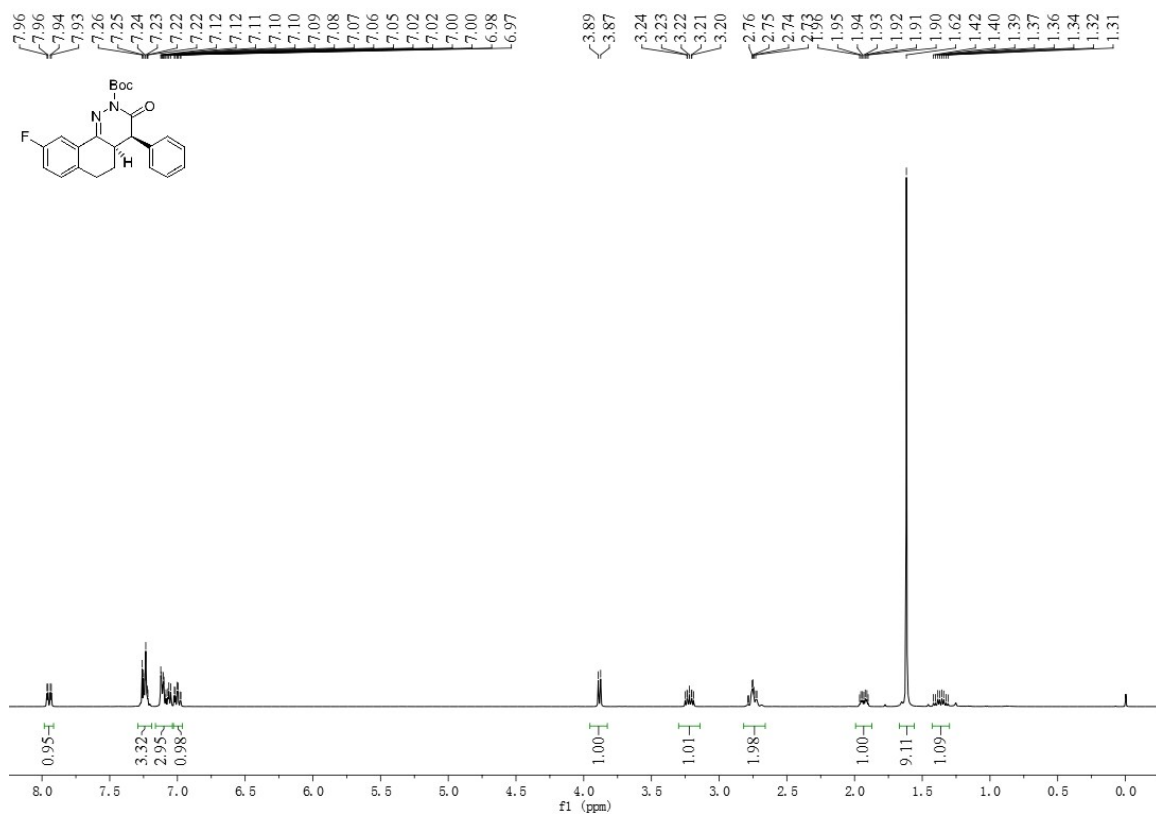
<sup>1</sup>H NMR spectrum of **3ar**



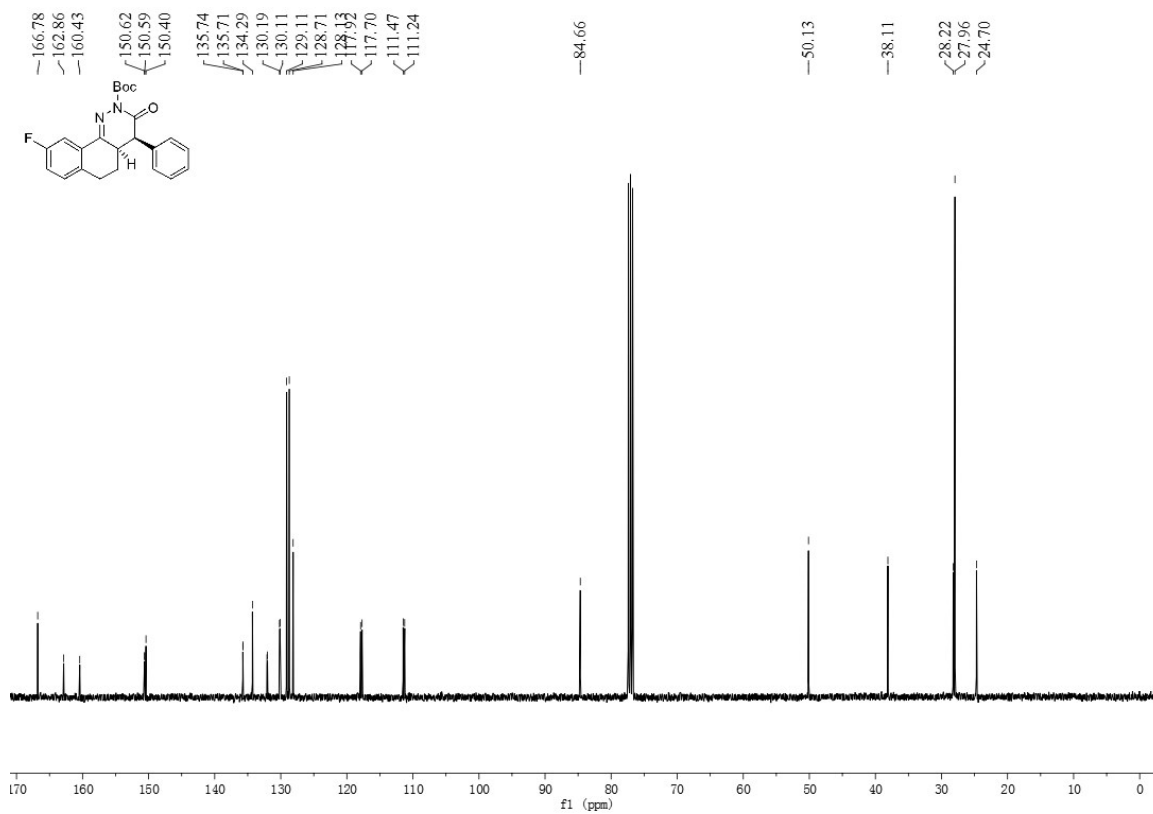
<sup>13</sup>C NMR spectrum of **3ar**



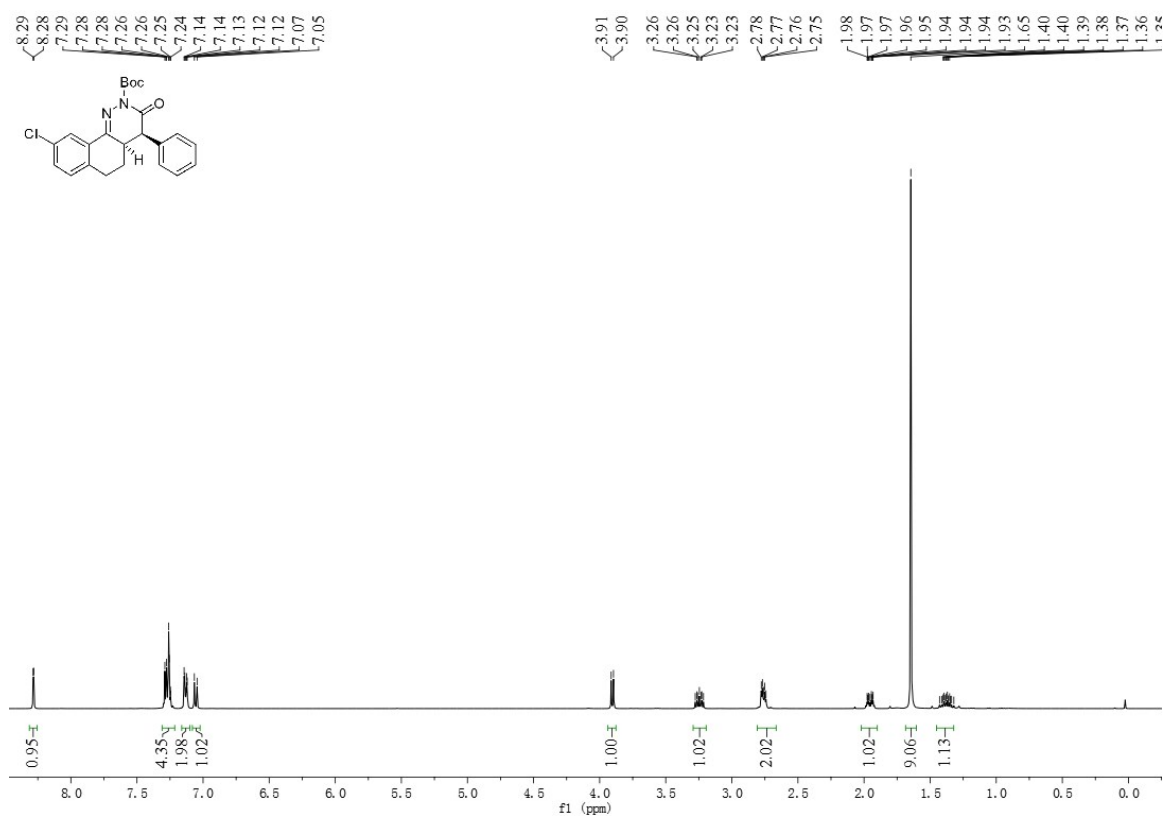
### <sup>1</sup>H NMR spectrum of **3da**



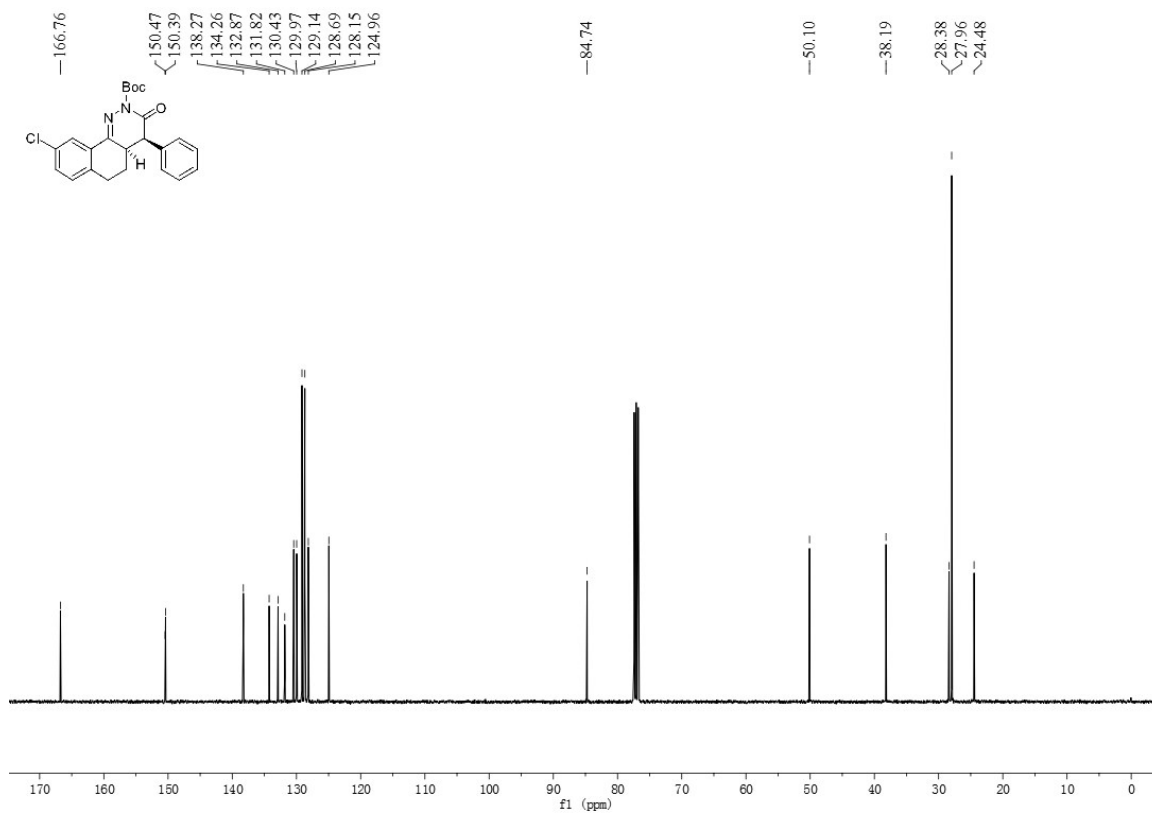
### <sup>13</sup>C NMR spectrum of **3da**



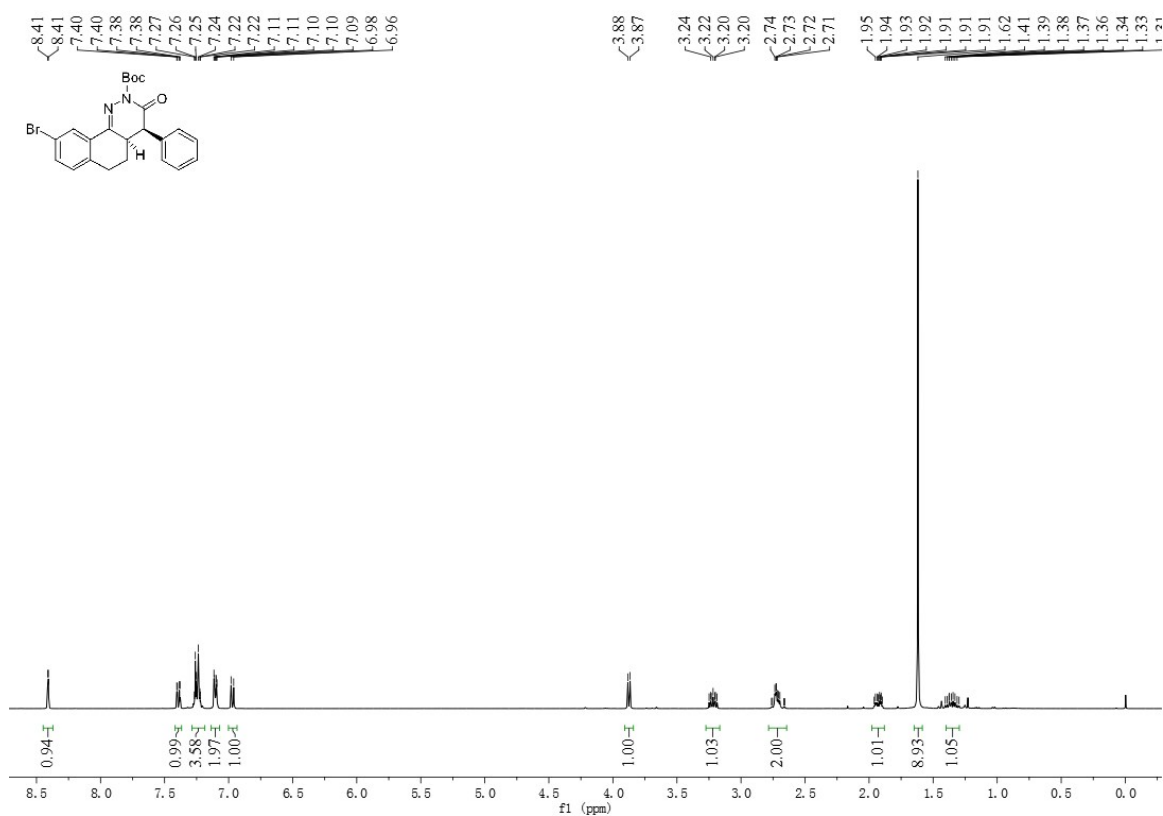
### <sup>1</sup>H NMR spectrum of **3ea**



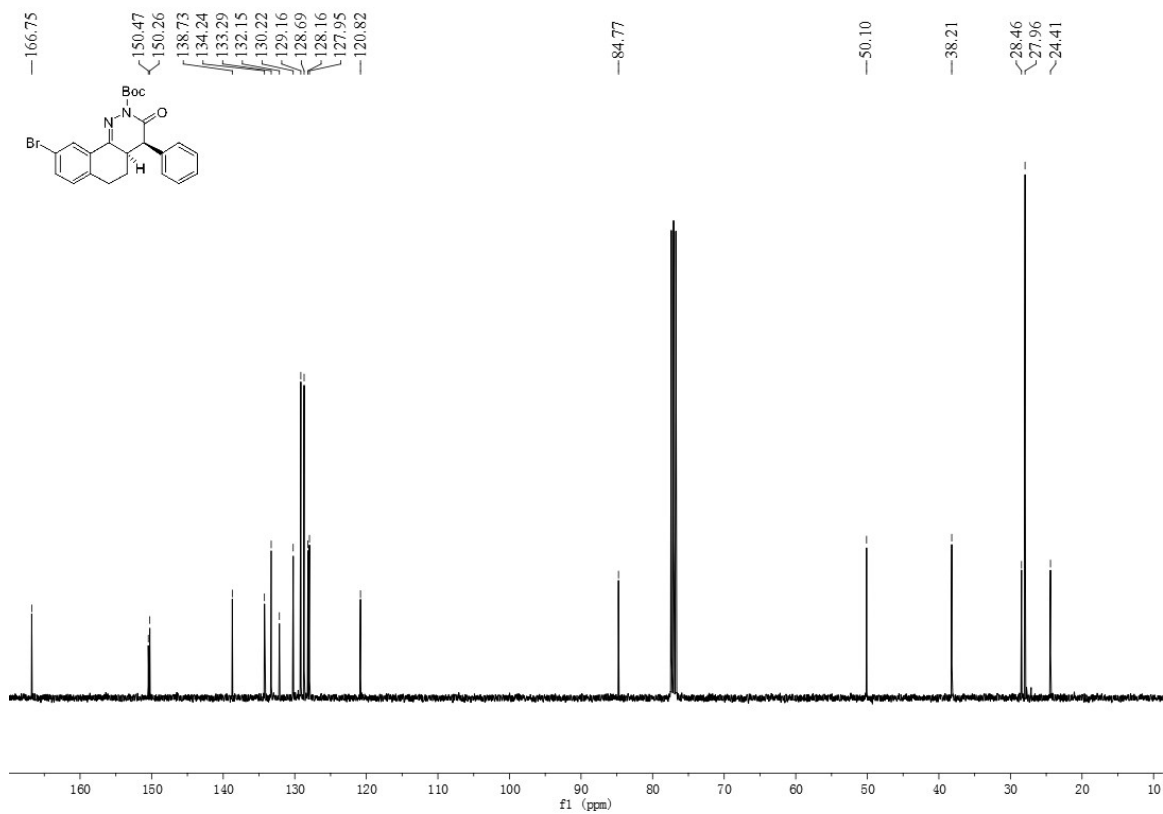
### <sup>13</sup>C NMR spectrum of **3ea**



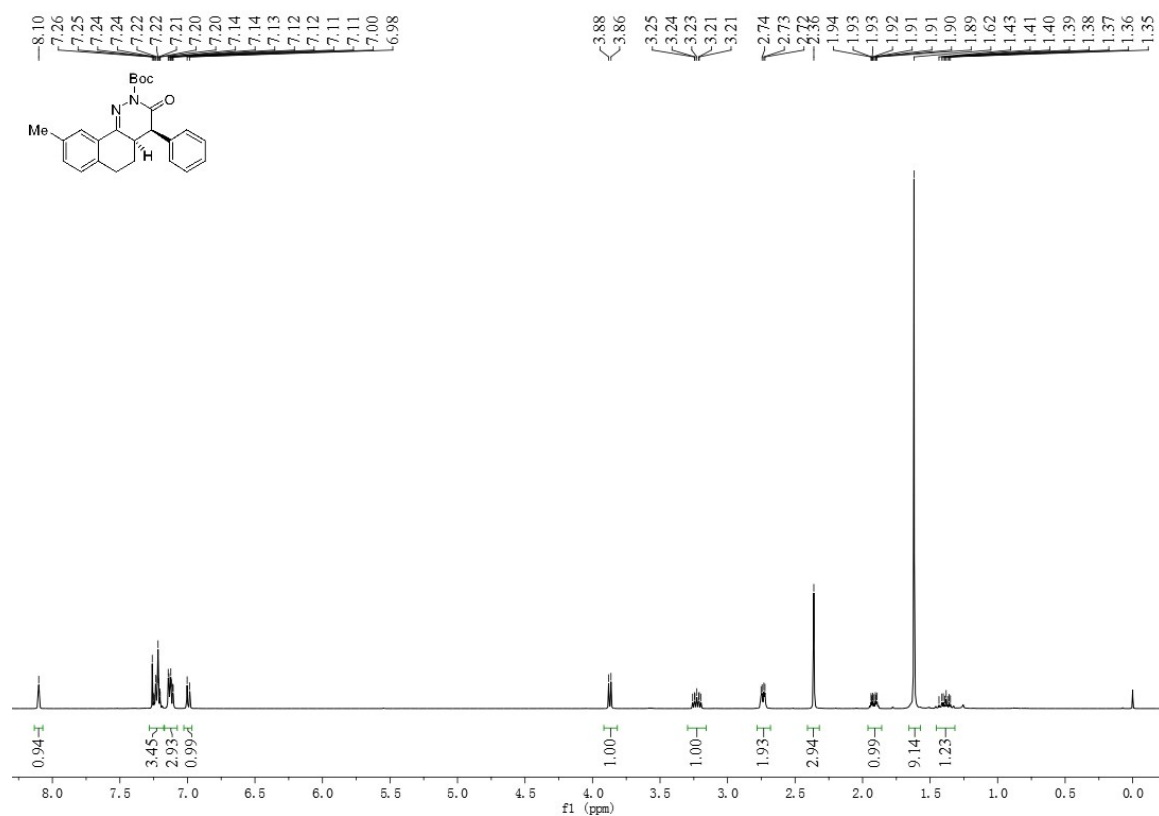
### <sup>1</sup>H NMR spectrum of **3fa**



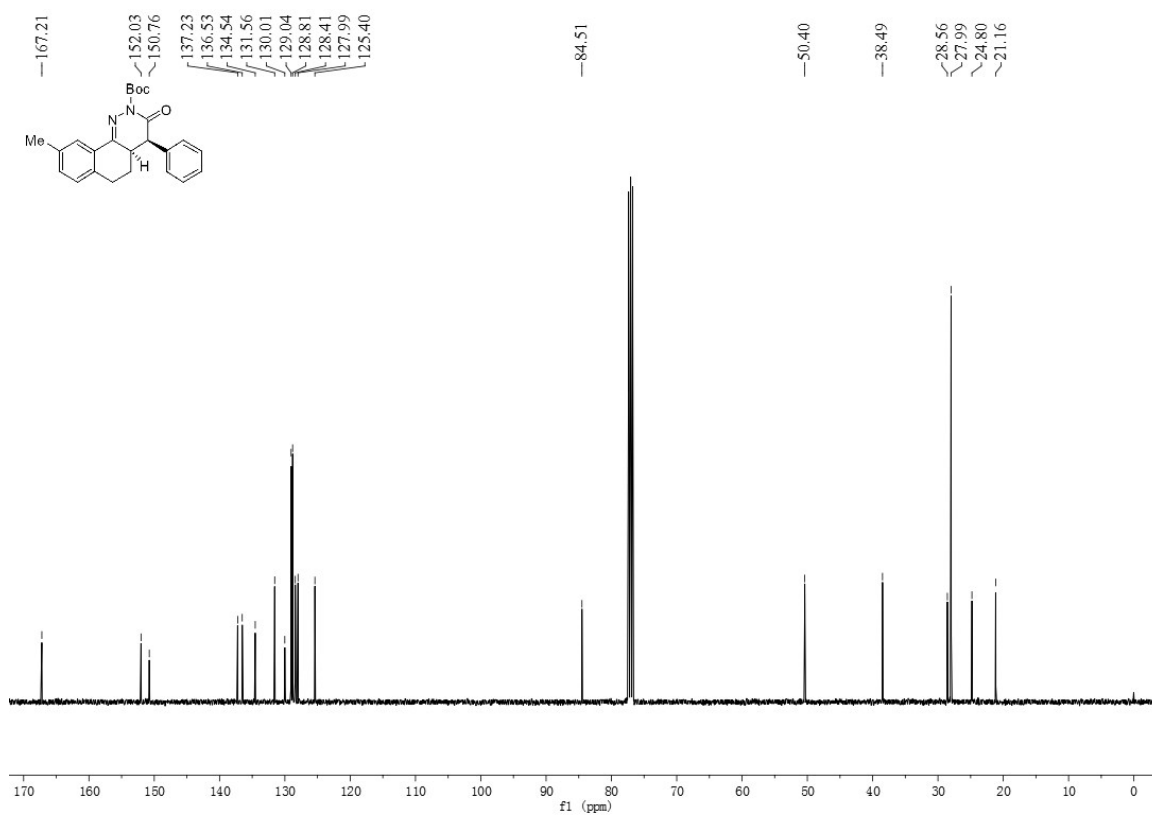
### <sup>13</sup>C NMR spectrum of **3fa**



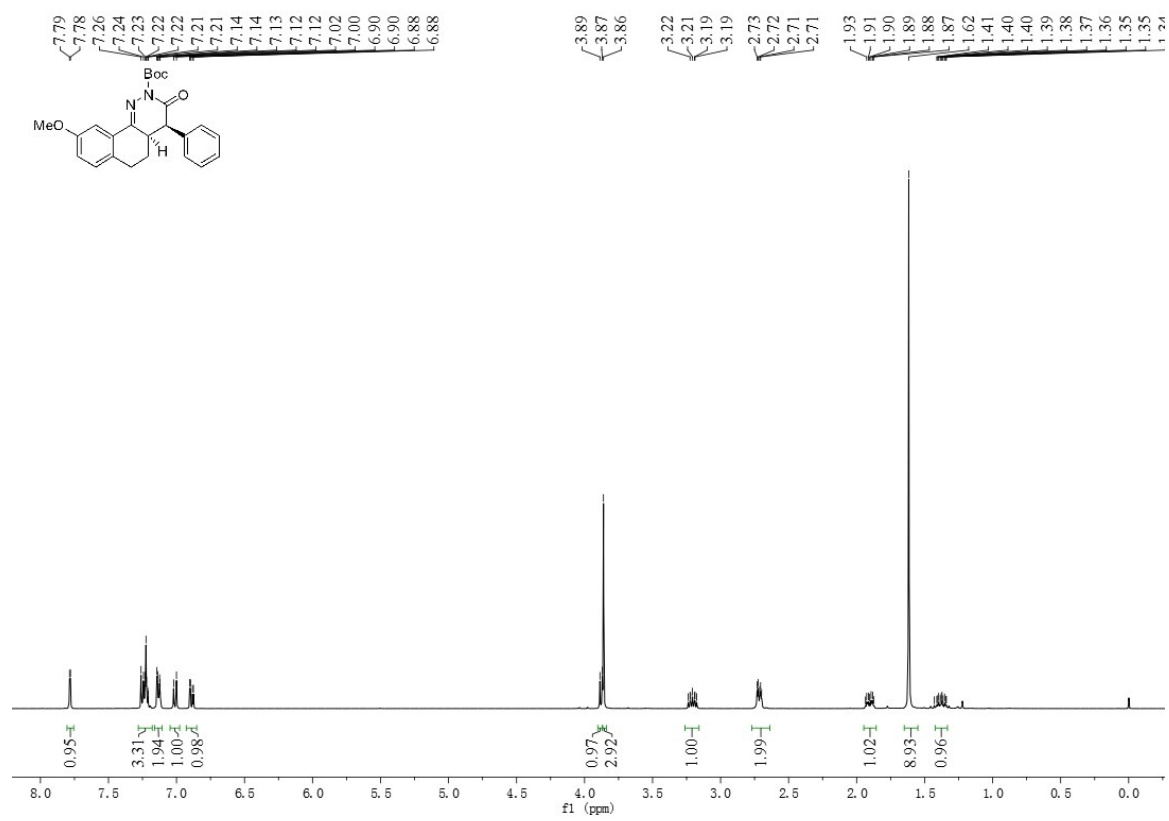
### $^1\text{H}$ NMR spectrum of **3ga**



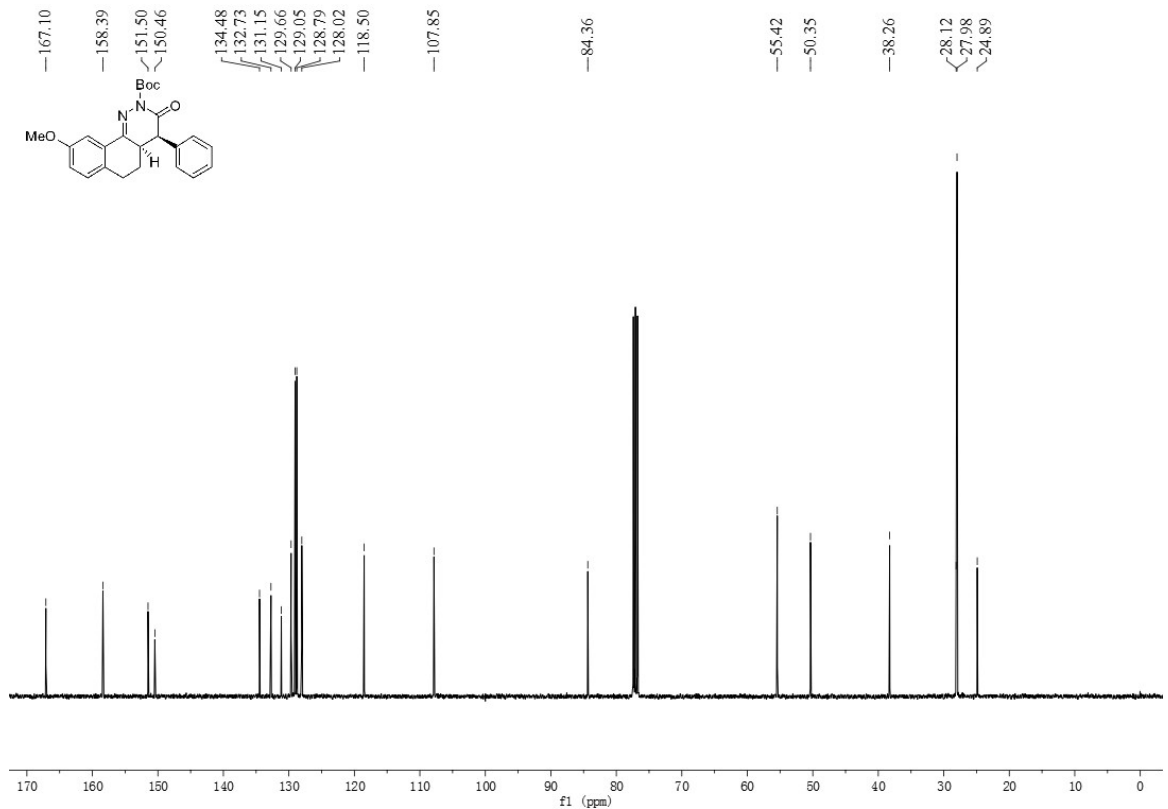
### $^{13}\text{C}$ NMR spectrum of **3ga**



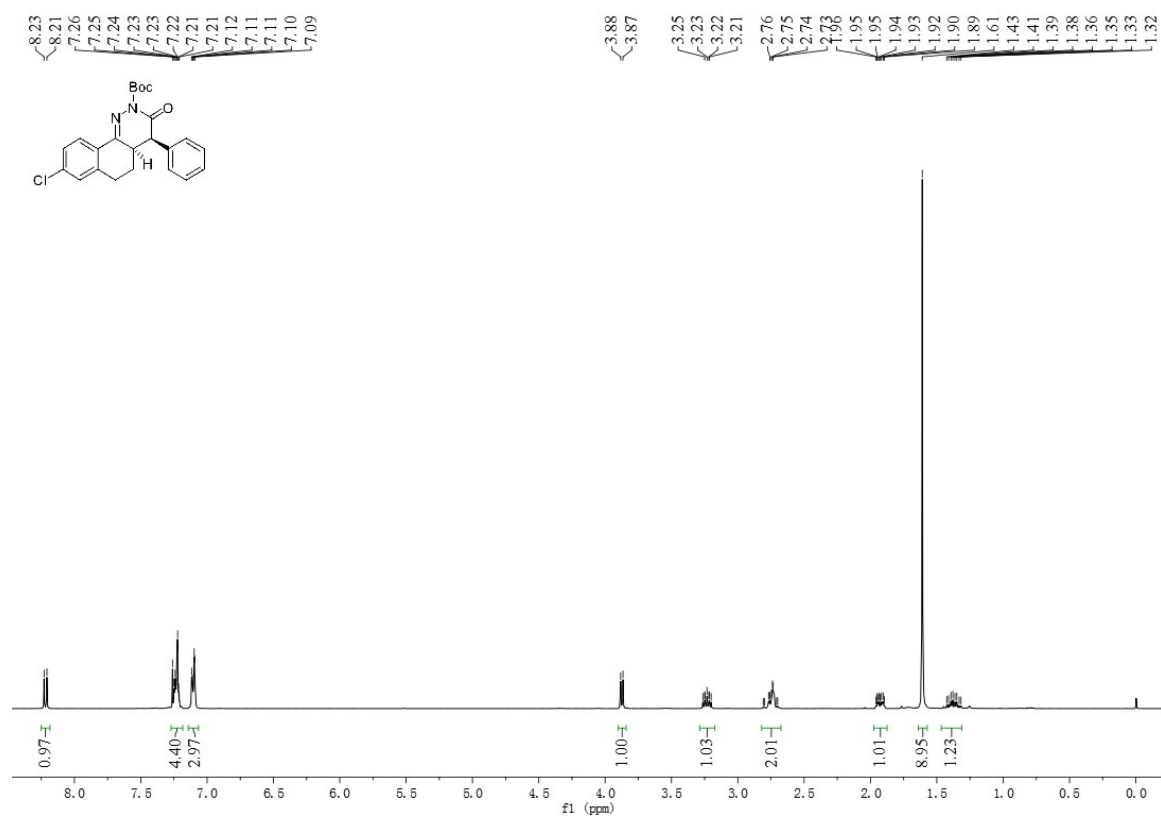
### $^1\text{H}$ NMR spectrum of **3ha**



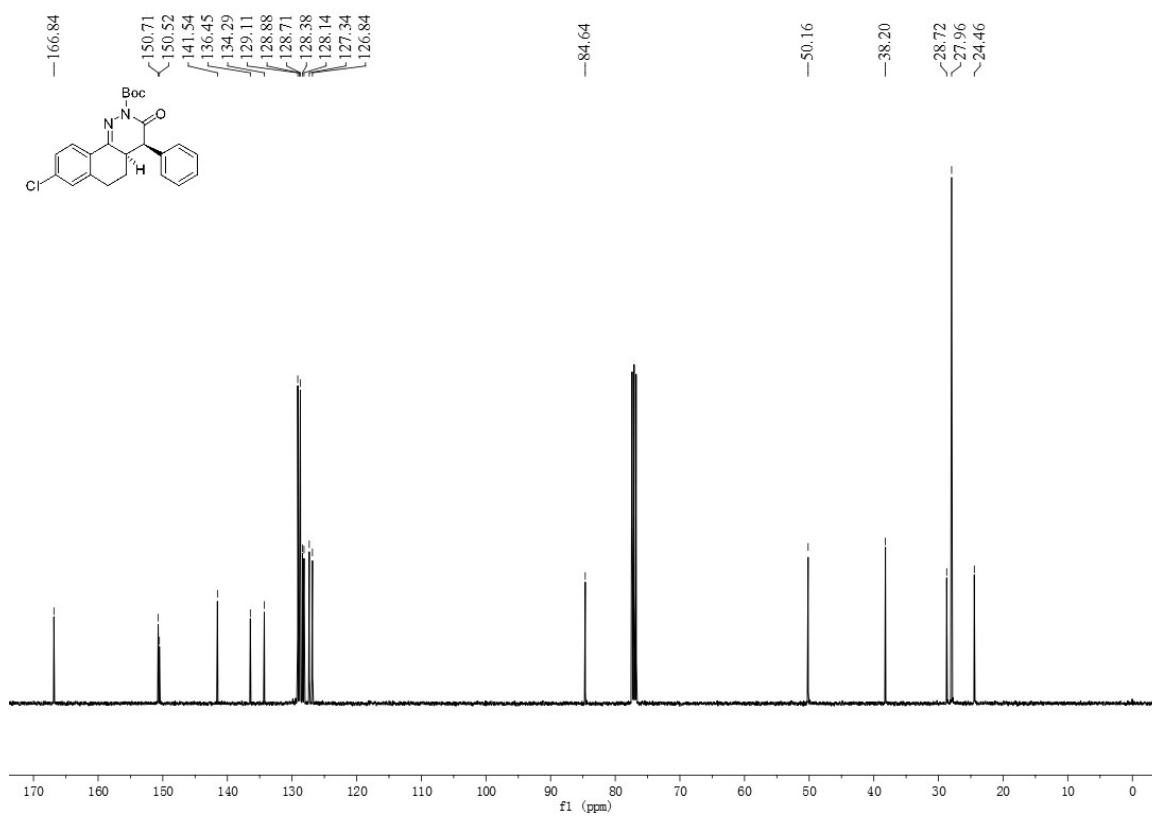
### $^{13}\text{C}$ NMR spectrum of **3ha**



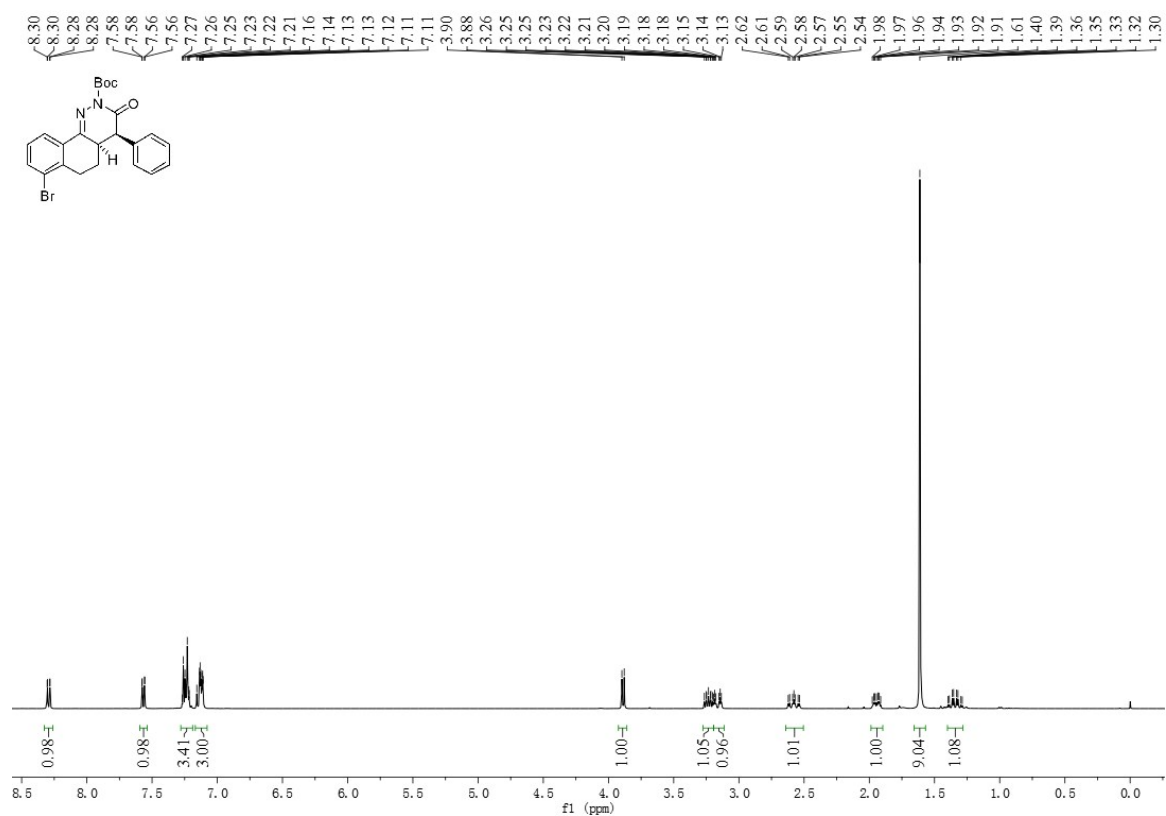
<sup>1</sup>H NMR spectrum of **3ia**



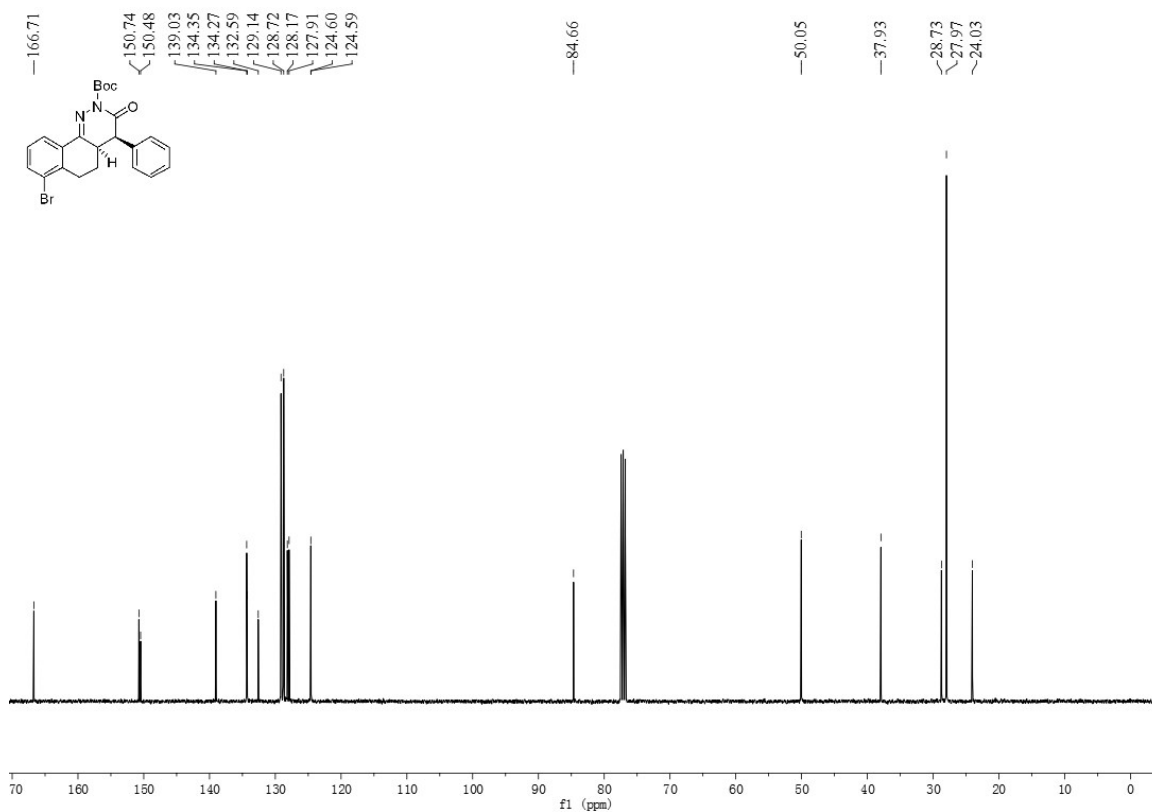
<sup>13</sup>C NMR spectrum of **3ia**



### <sup>1</sup>H NMR spectrum of **3ja**

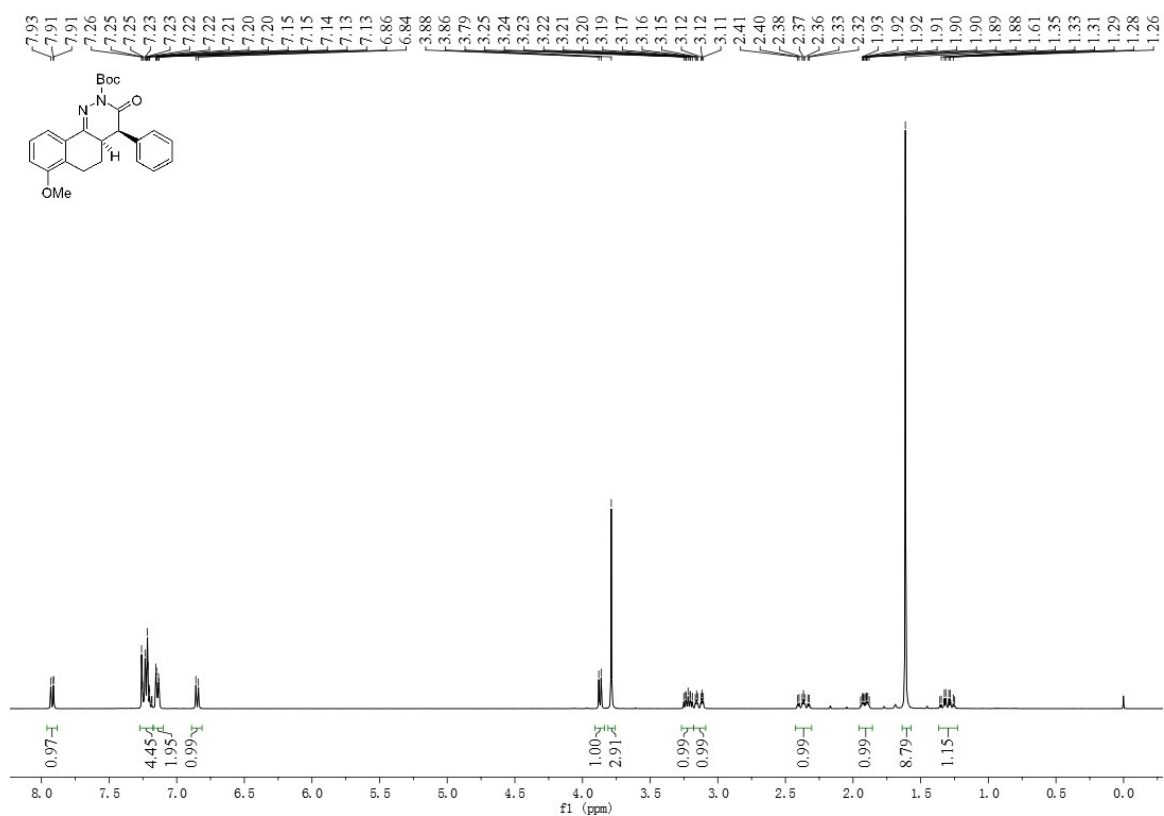


### <sup>13</sup>C NMR spectrum of **3ja**

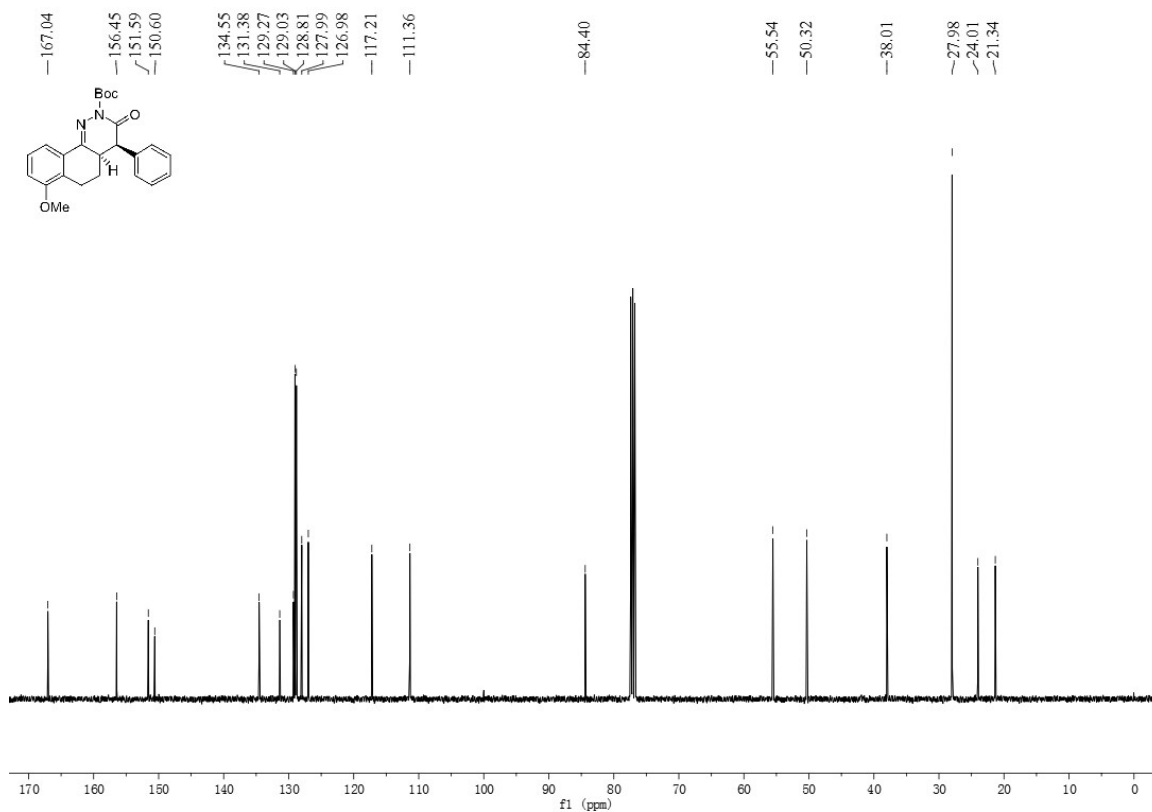




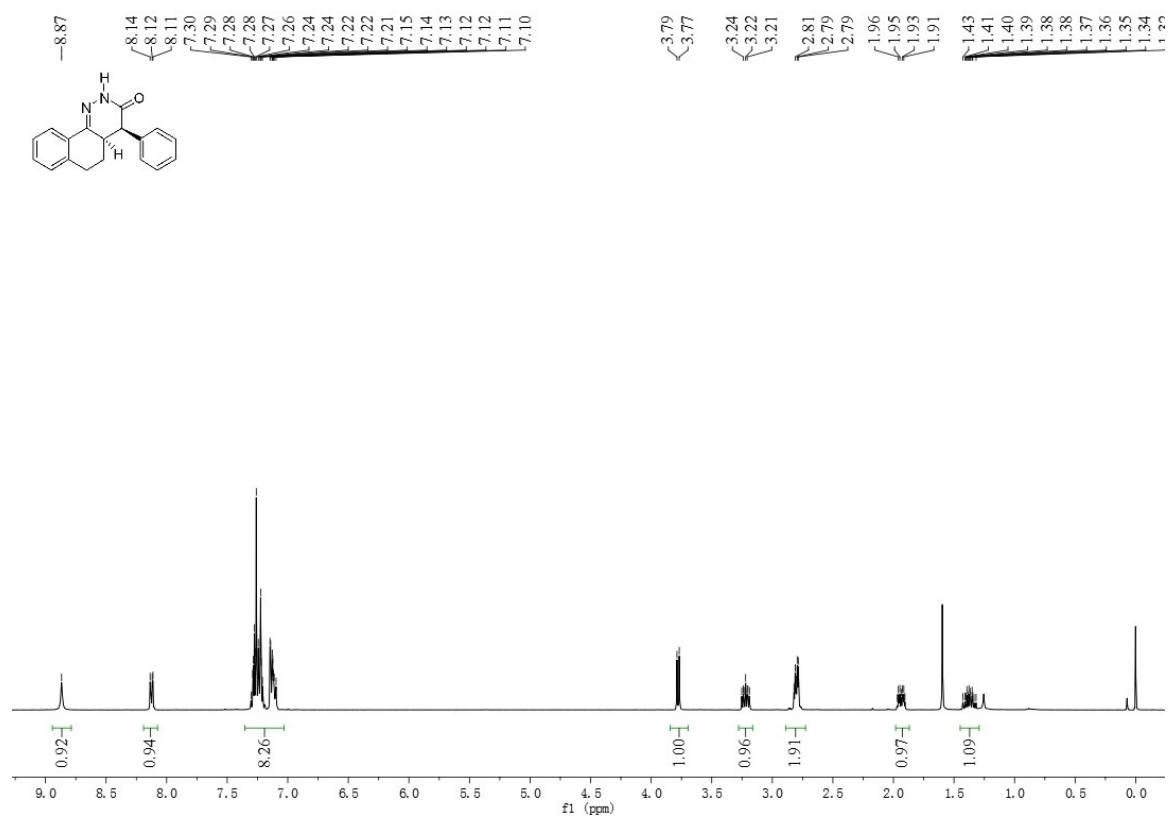
### <sup>1</sup>H NMR spectrum of **3ka**



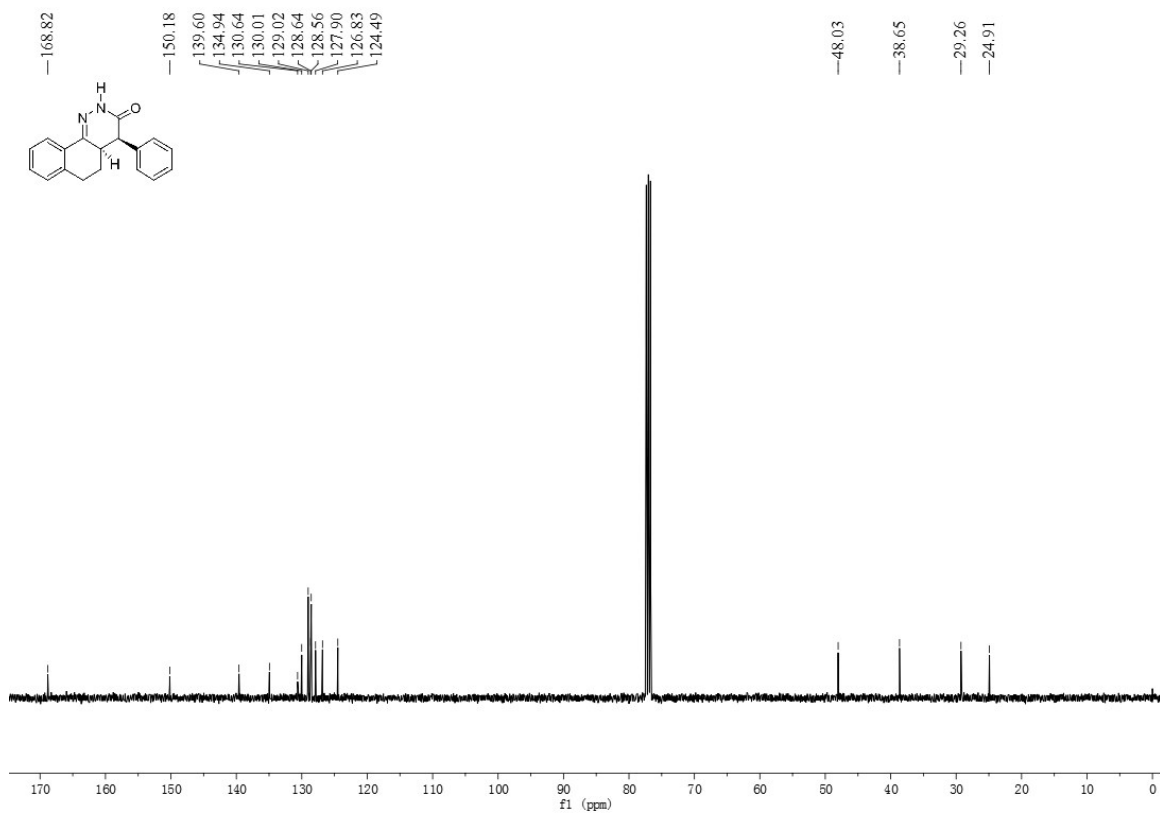
### <sup>13</sup>C NMR spectrum of **3ka**



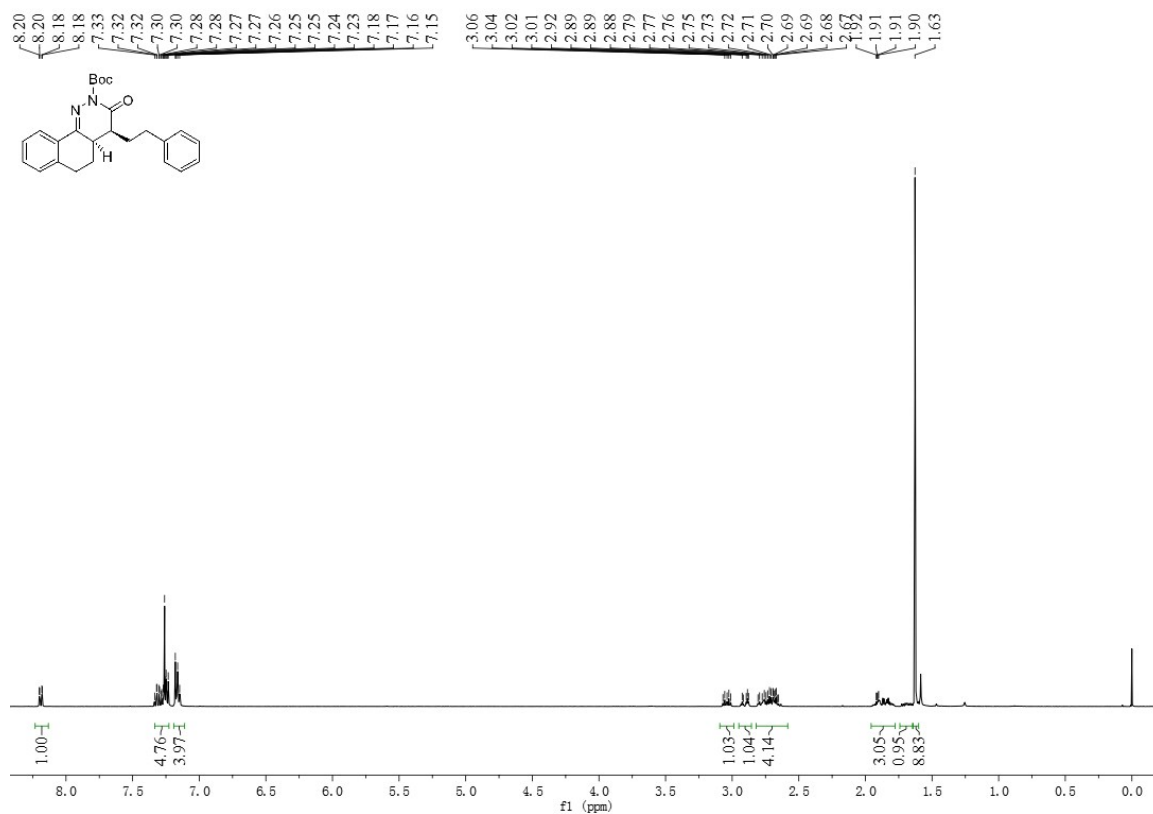
<sup>1</sup>H NMR spectrum of **9**



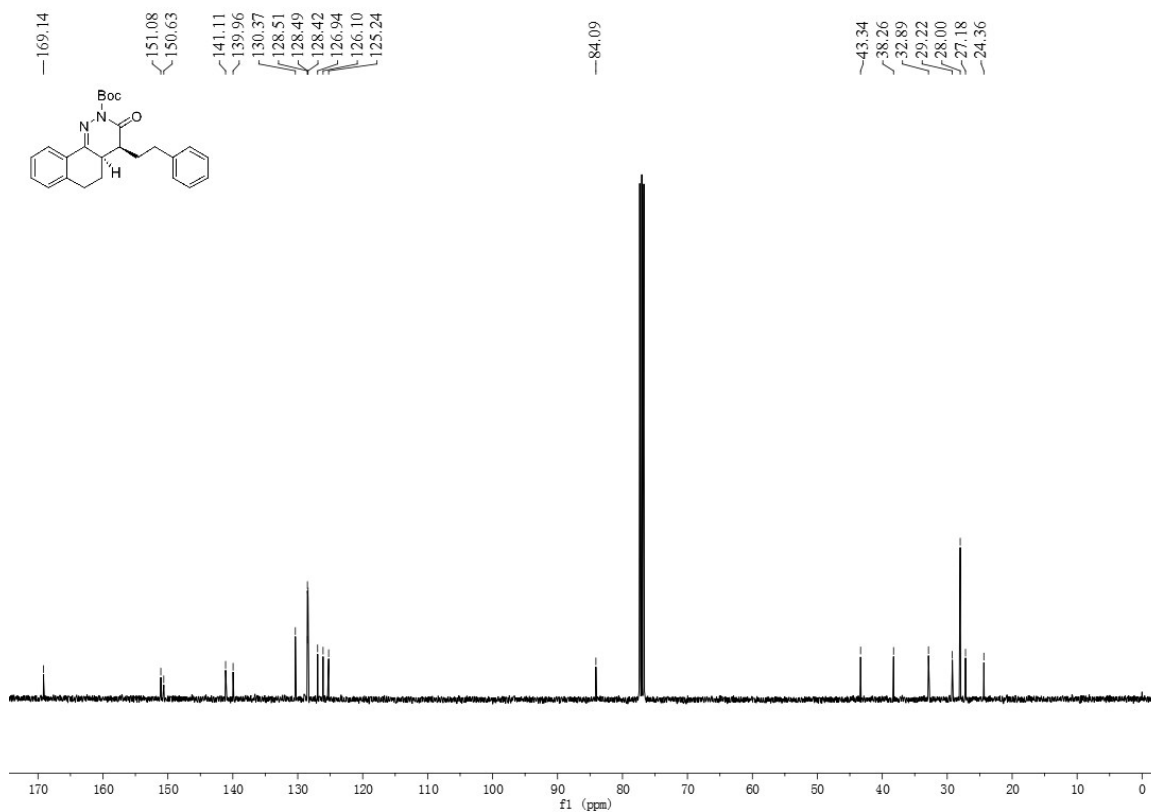
<sup>13</sup>C NMR spectrum of **9**



### <sup>1</sup>H NMR spectrum of **10**



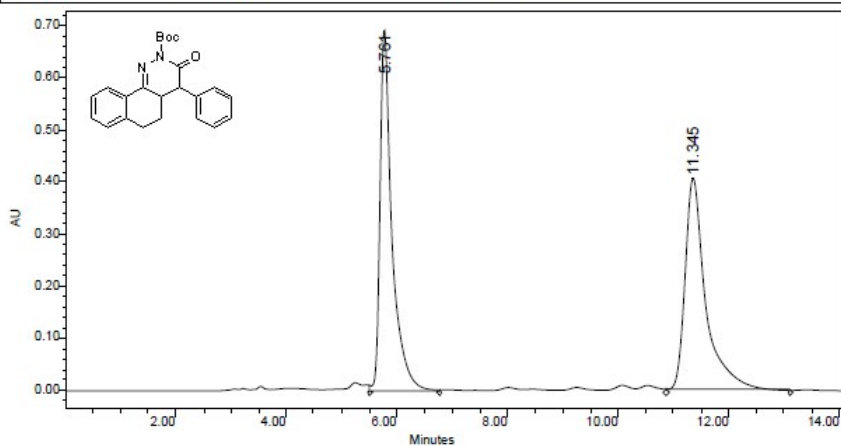
### <sup>13</sup>C NMR spectrum of **10**



## 9. HPLC of Substrates and Products

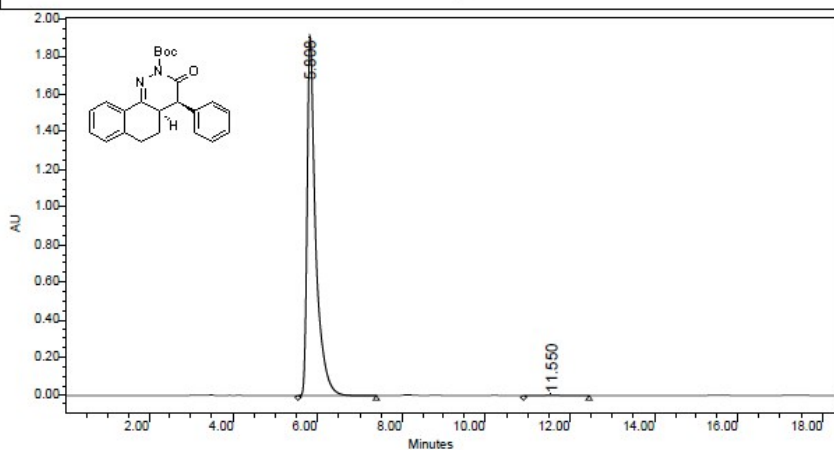
(3aa)

SAMPLE INFORMATION					
Sample Name:	ZZJ-2-184-2-AD-30%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	12/27/2017 9:23:26 AM		
Vial:	1	Acq. Method:	30% 254		
Injection #:	1	Date Processed:	1/20/2018 3:40:56 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.761	10367463	49.09	694331	62.96
2	11.345	10750985	50.91	408504	37.04

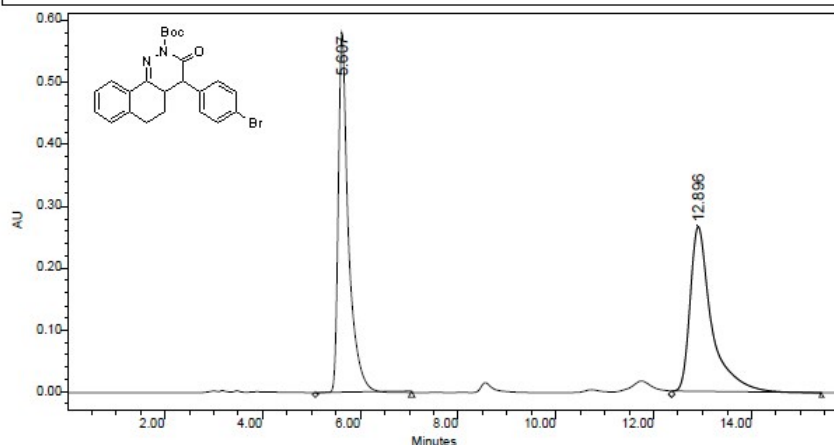
SAMPLE INFORMATION					
Sample Name:	ZZJ-3-17-4-2-AD-30%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	1/19/2018 1:59:24 PM		
Vial:	1	Acq. Method:	30% 254		
Injection #:	1	Date Processed:	1/20/2018 3:44:12 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.808	27081476	99.77	1920561	99.88
2	11.550	63280	0.23	2402	0.12

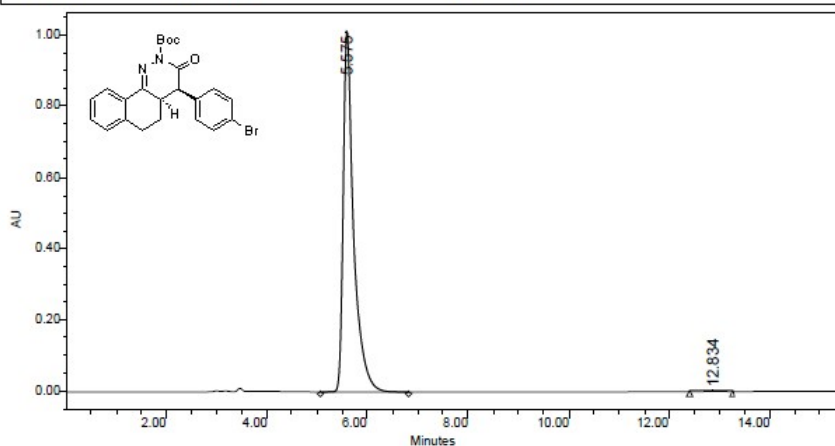
(3ab)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-1-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 3:15:30 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/20/2018 3:45:22 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.607	8396664	50.28	583397	68.51
2	12.896	8304739	49.72	268117	31.49

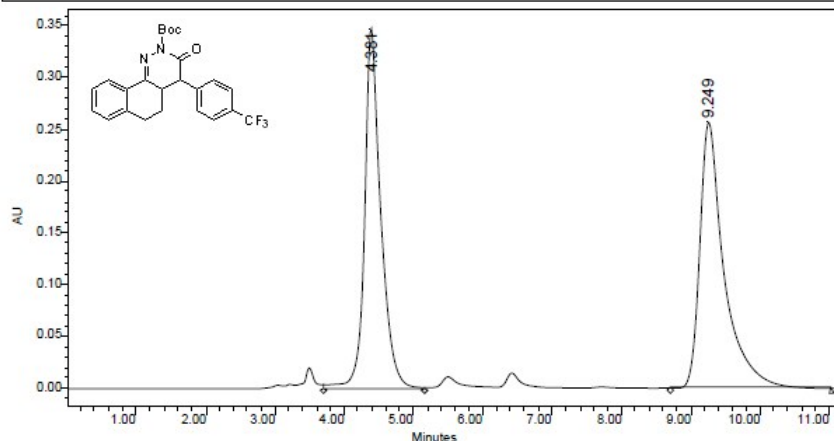
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-1-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 7:13:57 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/20/2018 7:33:03 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.575	14574149	99.87	1016634	99.92
2	12.834	18490	0.13	796	0.08

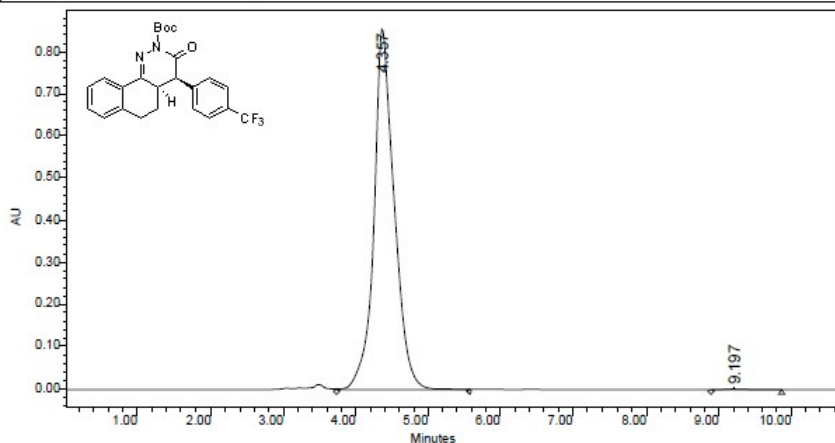
(3ac)

SAMPLE INFORMATION				
Sample Name:	ZZJ-3-28-2-RAC-AD-30%254nm	Acquired By:	System	
Sample Type:	Unknown	Date Acquired:	2/1/2018 1:37:31 PM	
Vial:	1	Acq. Method:	30% 254	
Injection #:	1	Date Processed:	2/1/2018 1:51:19 PM	
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1	
Run Time:	120.00 Minutes	Sample Set Name:		



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.361	5664787	47.44	348427	57.53
2	9.249	6275327	52.56	257234	42.47

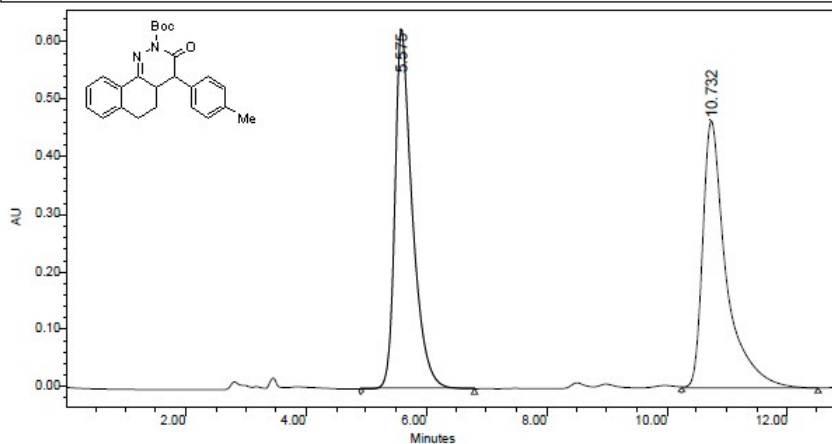
SAMPLE INFORMATION				
Sample Name:	ZZJ-3-28-1-asy-AD-30%254nm	Acquired By:	System	
Sample Type:	Unknown	Date Acquired:	2/1/2018 5:29:47 PM	
Vial:	1	Acq. Method:	30% 254	
Injection #:	1	Date Processed:	2/1/2018 5:49:45 PM	
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1	
Run Time:	120.00 Minutes	Sample Set Name:		



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.357	16650901	99.85	856875	99.85
2	9.197	25631	0.15	1323	0.15

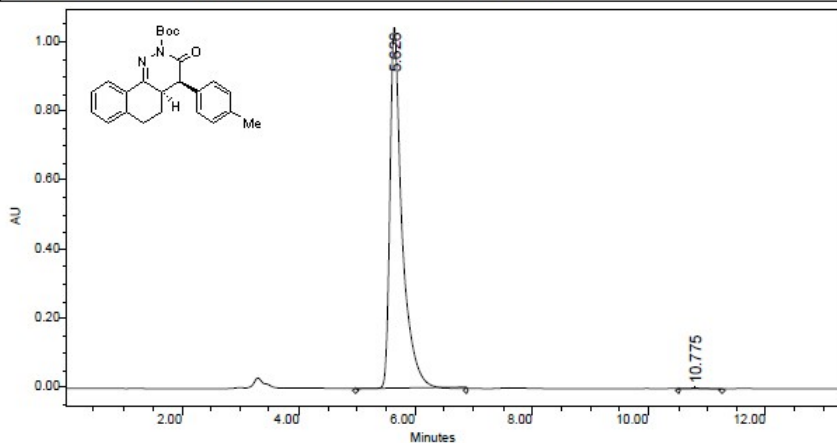
(3ad)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 3:35:03 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/20/2018 3:50:05 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.575	12618797	49.95	626629	57.41
2	10.732	12645011	50.05	464774	42.59

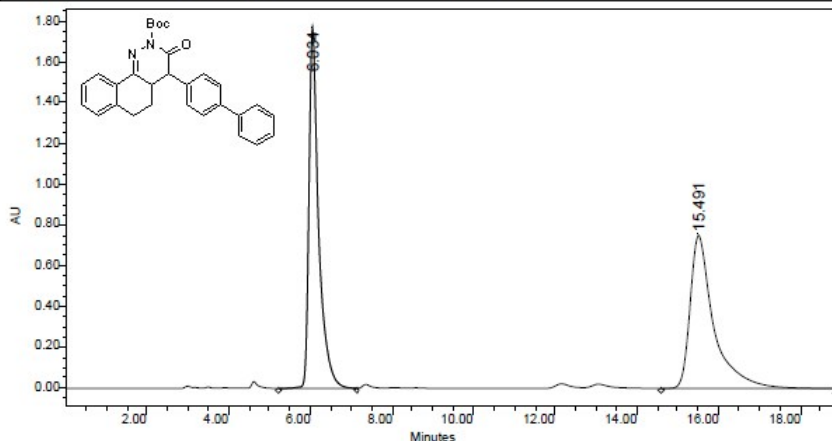
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 7:32:11 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/20/2018 7:56:28 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.626	15188205	99.70	1048353	99.82
2	10.775	44977	0.30	1842	0.18

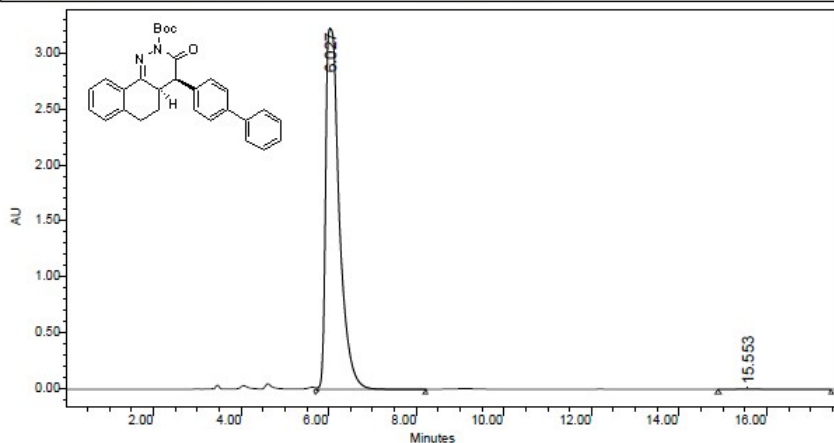
(3ae)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-4-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 3:51:26 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/20/2018 4:10:43 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.034	29275265	49.22	1770696	70.15
2	15.491	30203941	50.78	753505	29.85

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-18-4-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/20/2018 7:48:18 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	2	Date Processed:	1/20/2018 8:06:29 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	

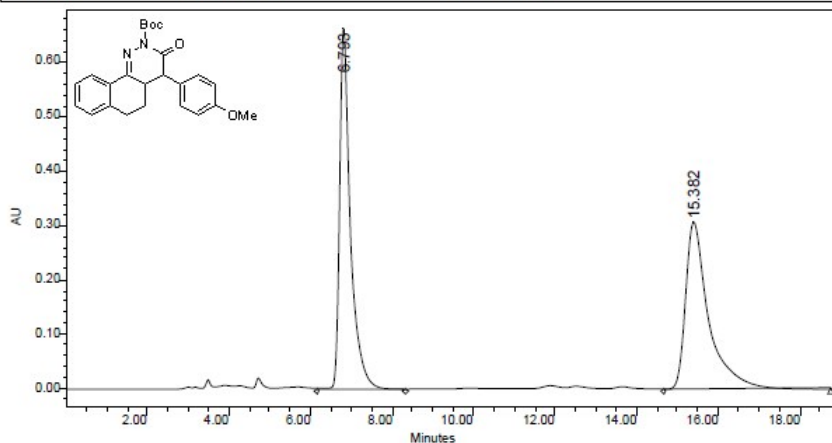


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.027	69888050	99.74	3229154	99.86
2	15.553	183377	0.26	4648	0.14



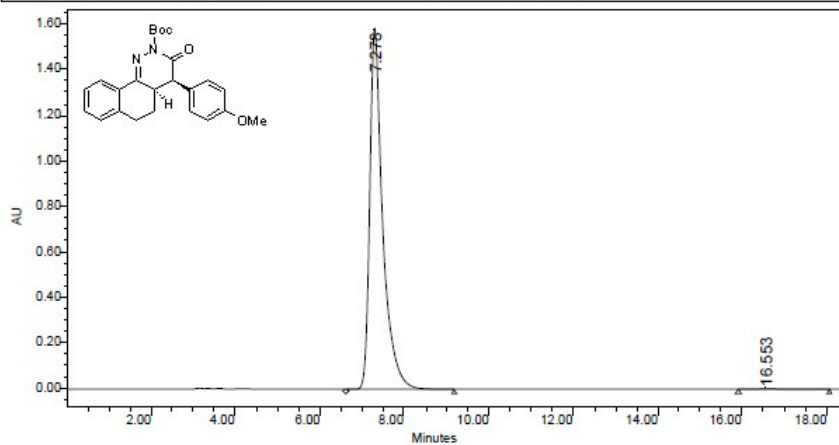
(3af)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-1-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 2:06:35 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 2:32:33 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.793	12223793	50.22	663787	68.37
2	15.382	12117069	49.78	307140	31.63

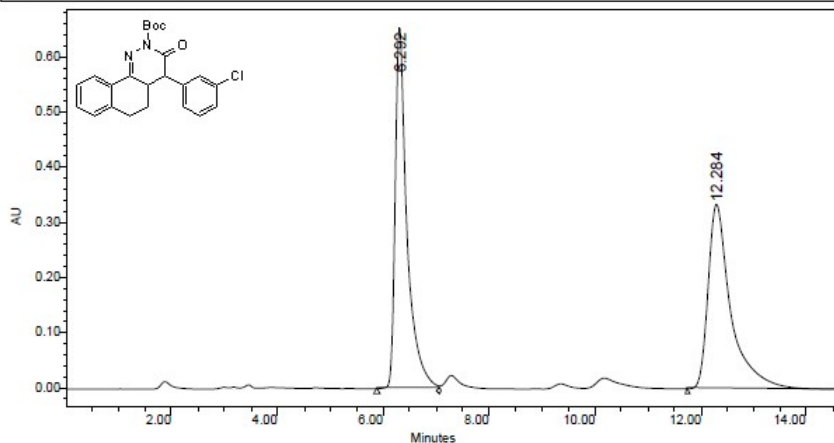
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-1-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 6:03:58 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 6:26:39 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.278	33732964	99.80	1584438	99.91
2	16.553	67358	0.20	1386	0.09

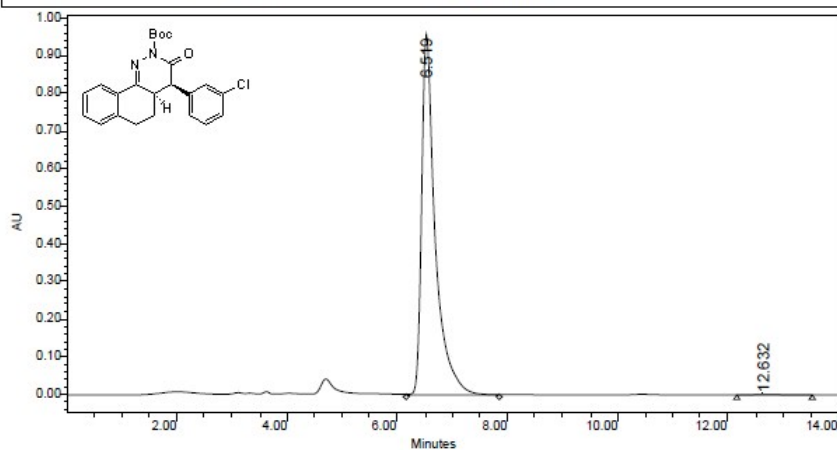
(3ag)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-2-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 2:31:36 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	2	Date Processed:	1/23/2018 2:50:24 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.292	10164539	50.34	656450	66.24
2	12.284	10027277	49.66	334498	33.76

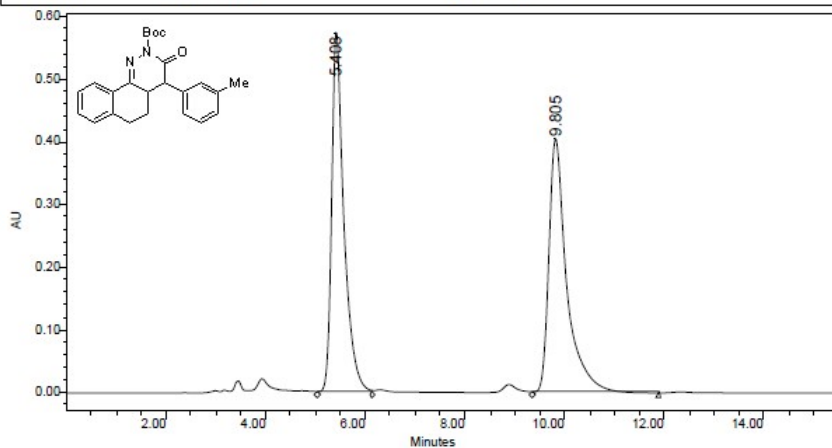
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-2-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 6:25:29 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 6:41:14 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.519	16443817	99.82	958718	99.90
2	12.632	28835	0.18	946	0.10

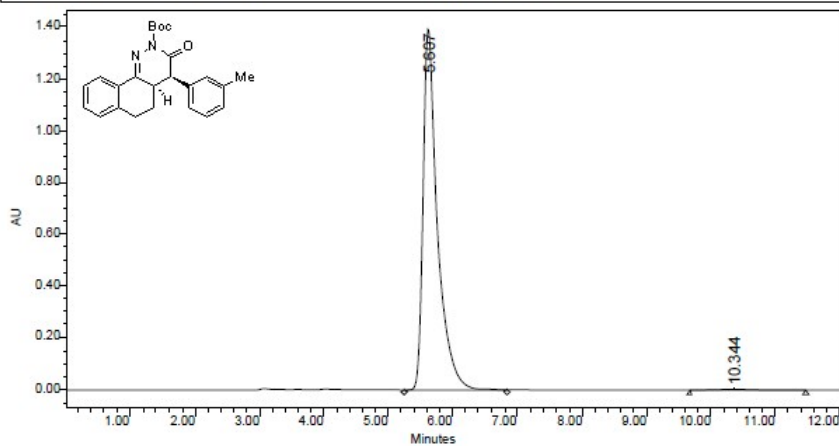
(3ah)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 2:49:19 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 3:09:40 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.408	9821192	49.32	576292	58.69
2	9.805	10093504	50.68	405613	41.31

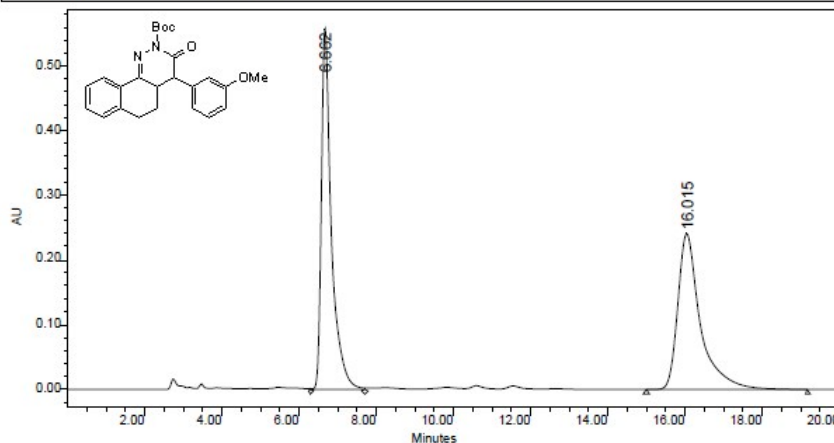
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 6:48:11 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 7:03:41 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.607	21536583	99.48	1399254	99.76
2	10.344	112507	0.52	3395	0.24

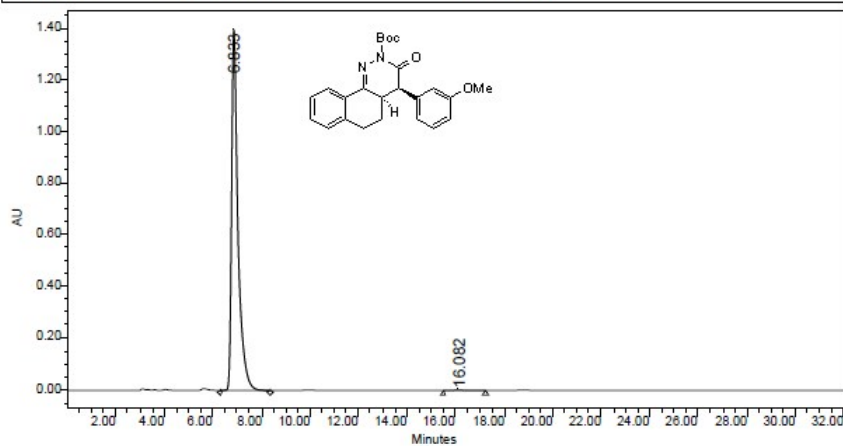
(3ai)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-4-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 3:08:26 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 3:28:48 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.662	10065323	50.66	560249	69.88
2	16.015	9803858	49.34	241470	30.12

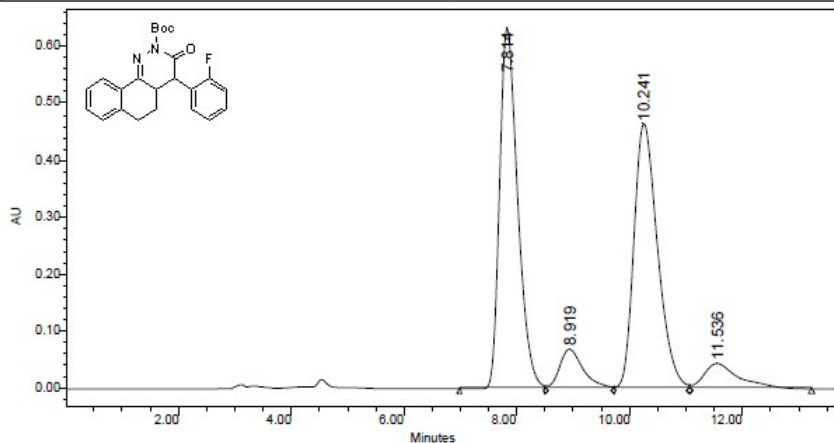
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-19-4-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/23/2018 7:08:13 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/23/2018 7:44:28 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.833	25470125	99.85	1396485	99.92
2	16.082	38247	0.15	1099	0.08

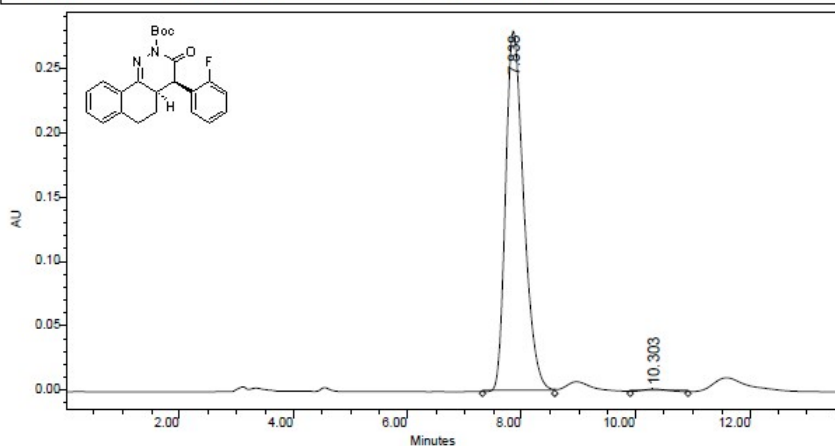
(3aj)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-1-rac-re-OD-20%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 9:01:35 PM
Vial:	1	Acq. Method:	20% 254
Injection #:	1	Date Processed:	1/27/2018 9:17:27 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14114546	44.49	632498	52.18
2	2048816	6.46	69482	5.73
3	13610043	42.90	465704	38.42
4	1953621	6.16	44502	3.67

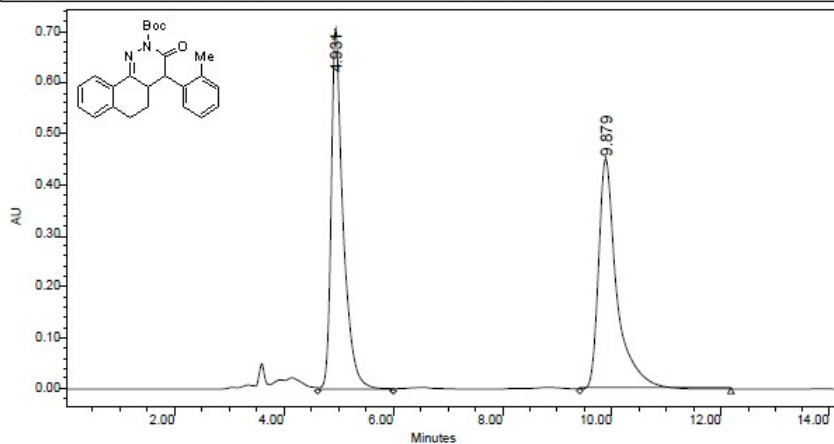
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-1-asy-OD-20%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 9:29:35 PM
Vial:	1	Acq. Method:	20% 254
Injection #:	1	Date Processed:	1/27/2018 9:43:32 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6228127	99.00	279908	99.24
2	62762	1.00	2131	0.76

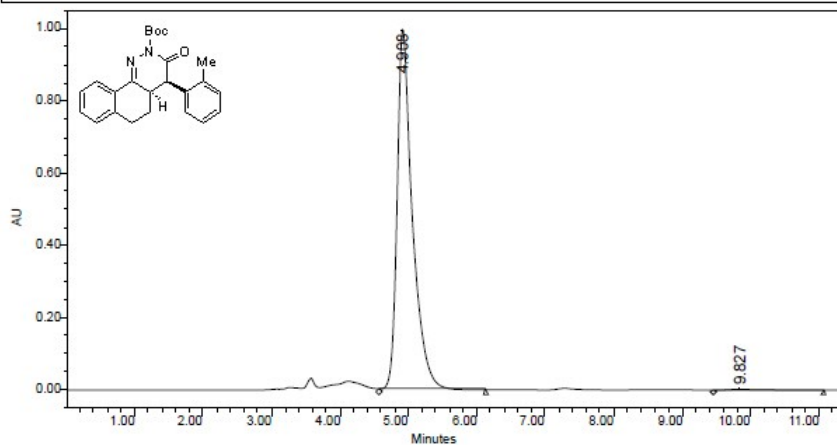
(3ak)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-2-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 2:31:34 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 2:46:21 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.931	10709804	50.32	707508	61.01
2	9.879	10574115	49.68	452151	38.99

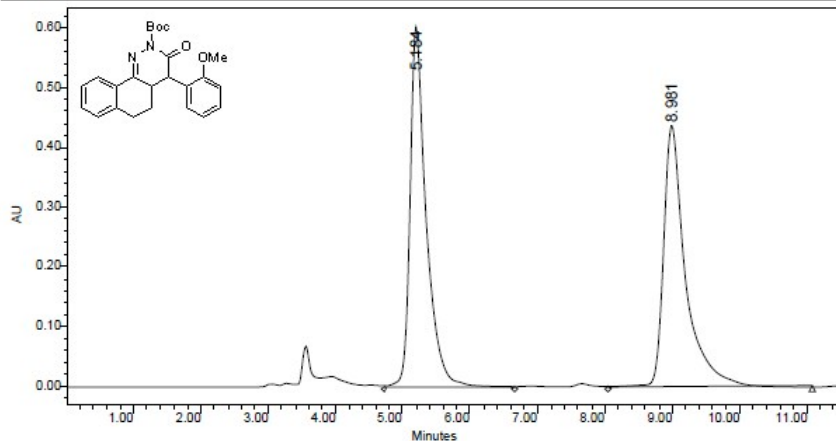
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-2-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 4:02:47 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 4:16:38 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.908	15566469	99.60	1003759	99.77
2	9.827	62565	0.40	2287	0.23

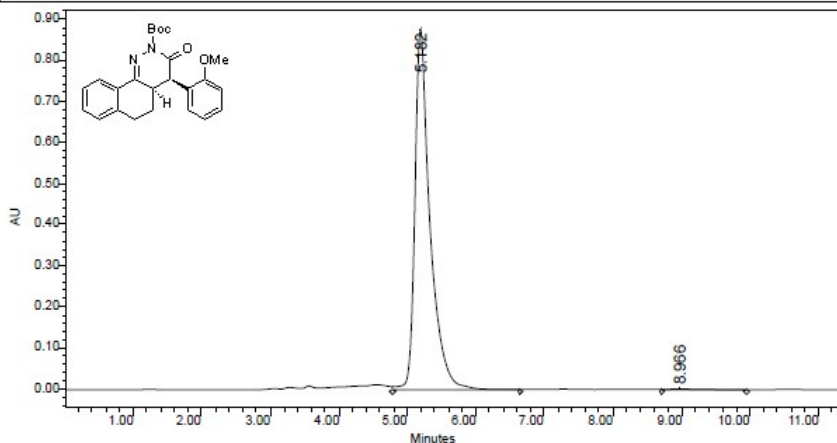
(3al)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 2:58:44 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 3:19:09 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.184	10081730	50.30	602776	57.97
2	8.981	9962893	49.70	437077	42.03

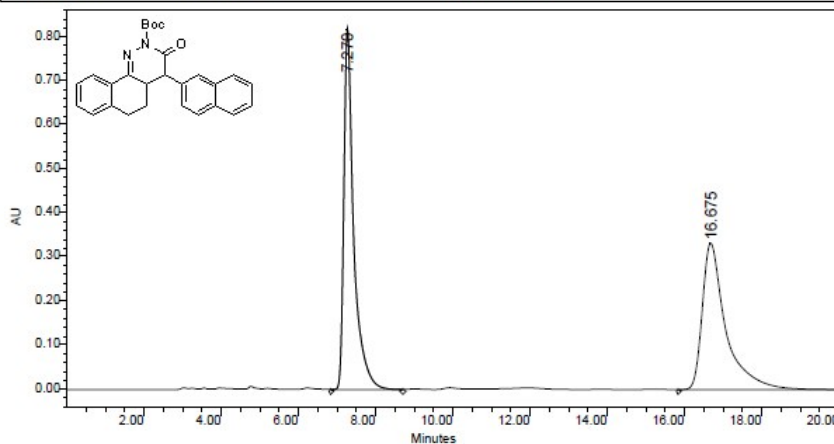
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 4:20:56 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 4:33:31 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.182	13472556	99.57	876946	99.80
2	8.966	58130	0.43	1791	0.20

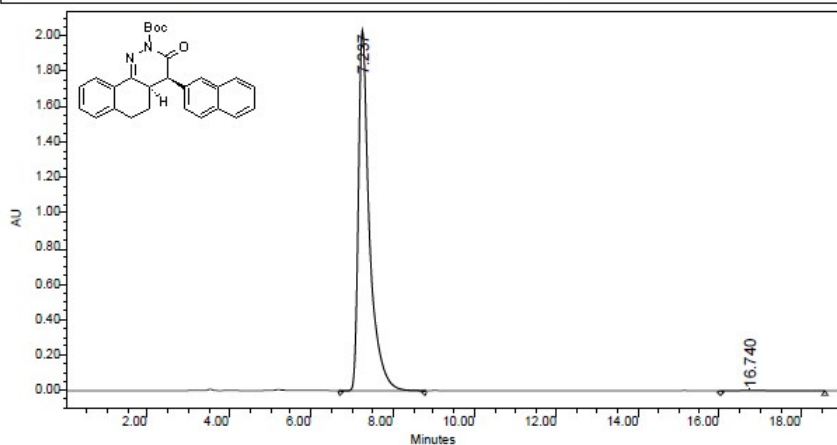
(3am)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-4-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 3:21:01 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 3:41:42 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.270	14525871	50.80	820266	71.14
2	16.675	14066109	49.20	332821	28.86

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-22-4-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/25/2018 4:38:58 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/25/2018 5:03:52 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	

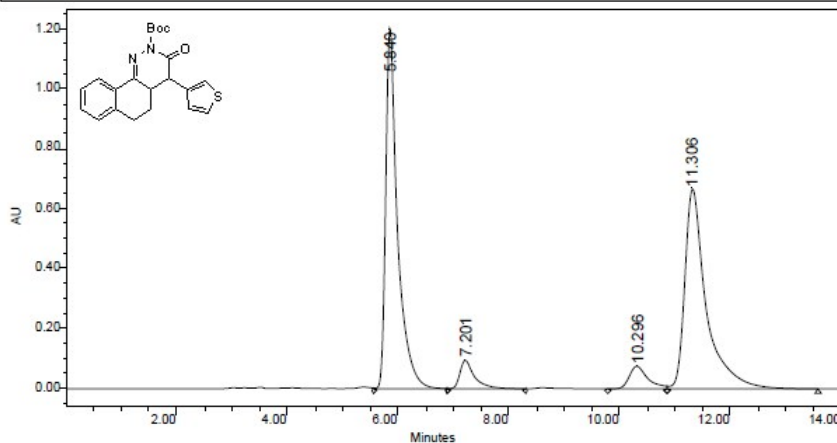


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.237	38441430	99.70	2037736	99.89
2	16.740	117179	0.30	2344	0.11



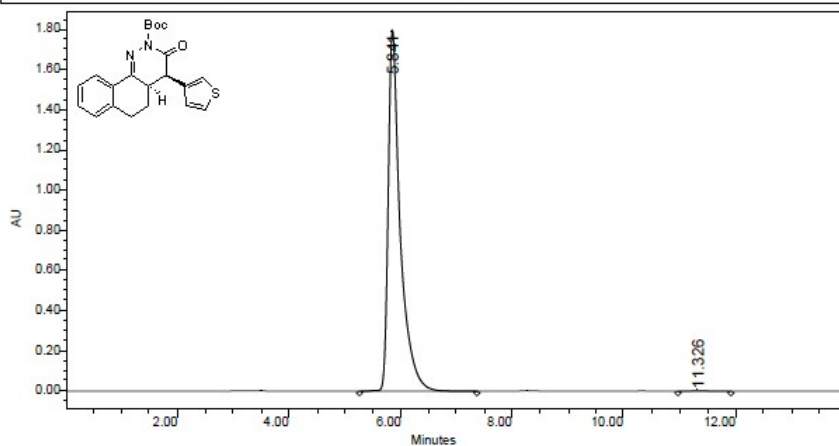
(3an)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-1-rac-new-AD-30%254nn	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 3:43:40 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/27/2018 4:00:02 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.840	18035114	45.75	1207772	59.03
2	7.201	1757545	4.46	95340	4.66
3	10.296	1758575	4.46	75512	3.69
4	11.306	17872234	45.33	667477	32.62

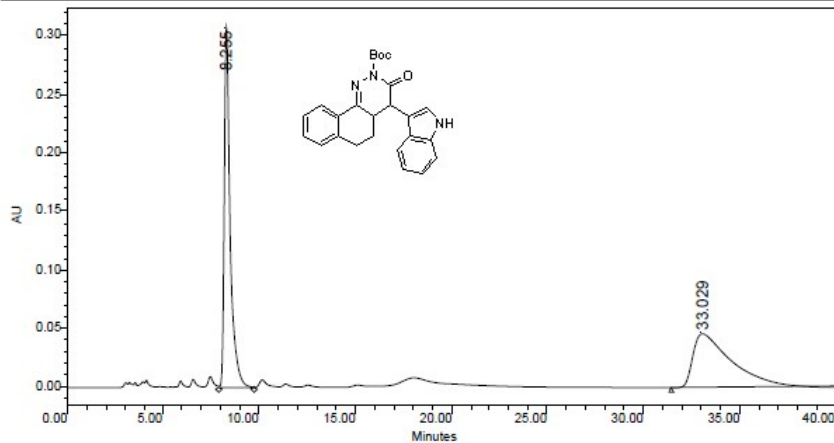
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-1-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 5:40:44 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/27/2018 5:55:25 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.841	26966775	99.82	1804878	99.89
2	11.326	48233	0.18	2005	0.11

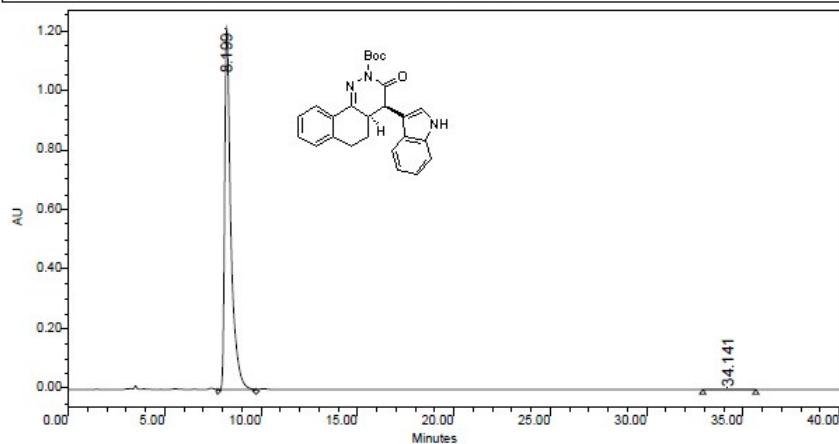
(3ao)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-2-rac-new-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 4:12:29 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/27/2018 5:02:25 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.255	6566176	50.03	308477	87.04
2	33.029	6557325	49.97	45949	12.96

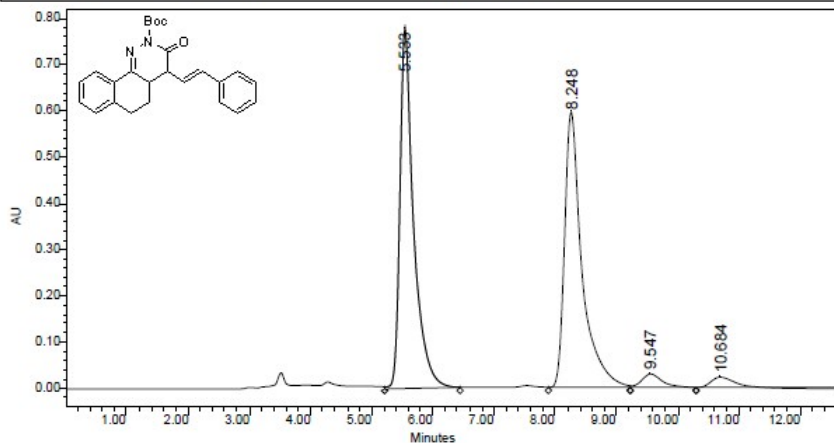
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-2-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 6:28:24 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	2	Date Processed:	1/27/2018 7:10:26 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.199	27190997	99.85	1207184	99.96
2	34.141	40697	0.15	526	0.04

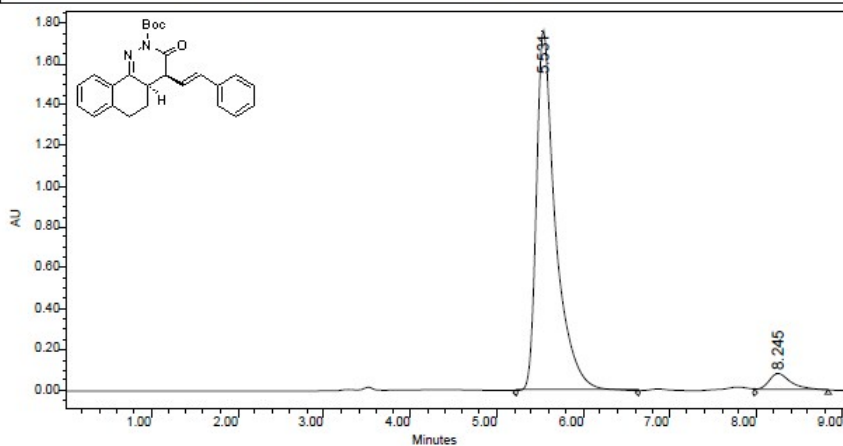
(3ap)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 5:04:11 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/27/2018 5:17:47 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.533	12176418	47.07	779133	54.30
2	8.248	12016896	46.46	598840	41.73
3	9.547	853007	3.30	31929	2.23
4	10.684	820690	3.17	25006	1.74

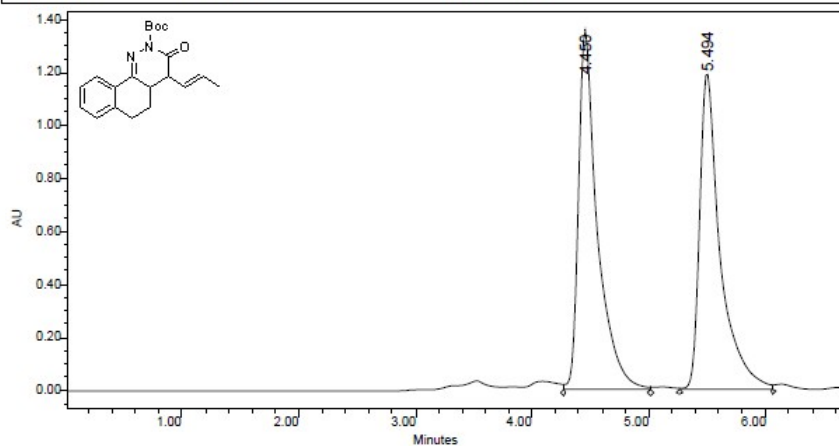
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-23-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	1/27/2018 6:07:52 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	1/27/2018 6:18:21 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.531	27126848	94.80	1764959	95.60
2	8.245	1487432	5.20	81307	4.40

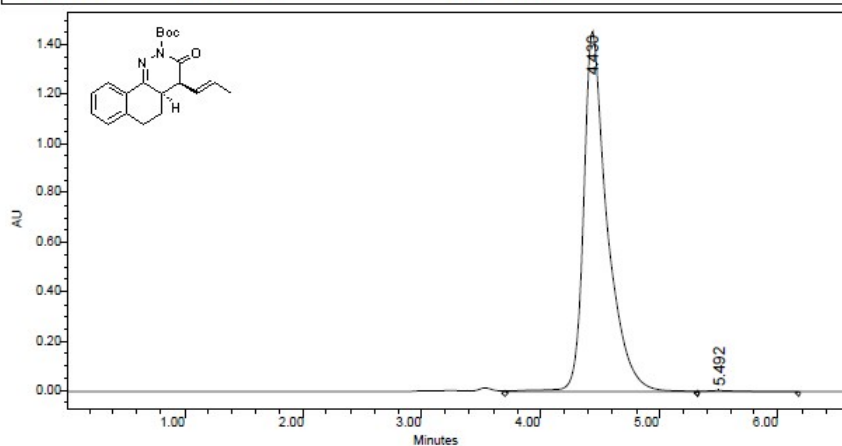
(3aq)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-28-4-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/1/2018 2:22:50 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/1/2018 2:29:39 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height	
1	4.450	15381636	51.18	1355048	53.17
2	5.494	14670879	48.82	1193488	46.83

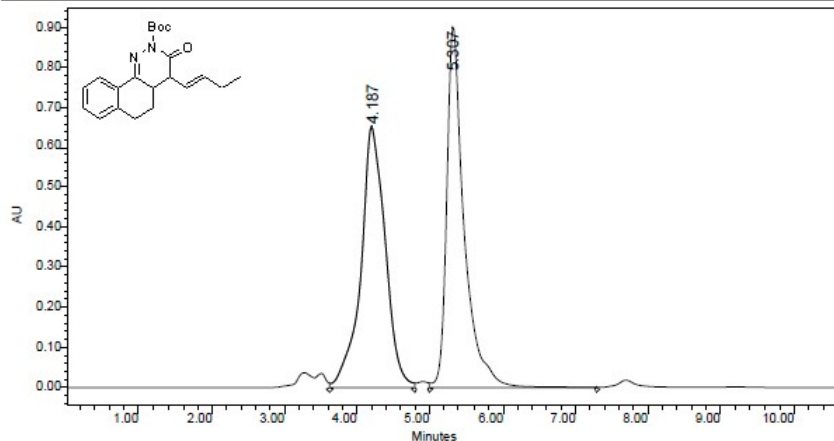
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-28-4-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/1/2018 6:03:48 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/1/2018 6:11:25 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height	
1	4.430	20107282	99.69	1456373	99.75
2	5.492	61687	0.31	3592	0.25

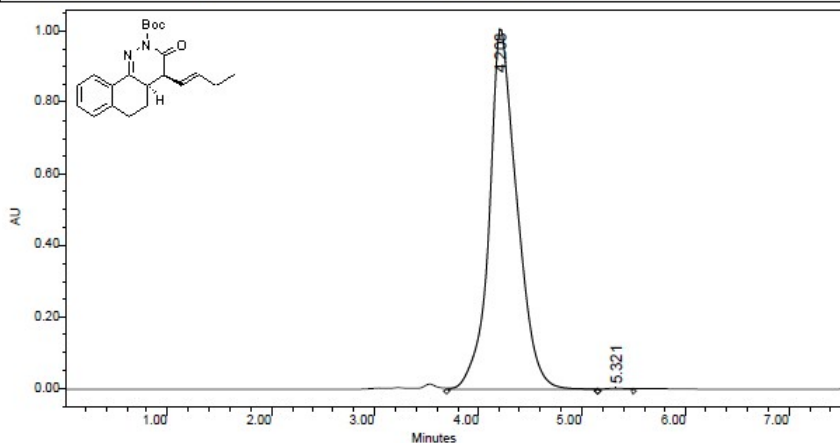
(3ar)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-28-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/1/2018 2:00:24 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/1/2018 2:23:36 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.187	15247241	50.29	653606	41.92
2	5.307	15069168	49.71	905599	58.08

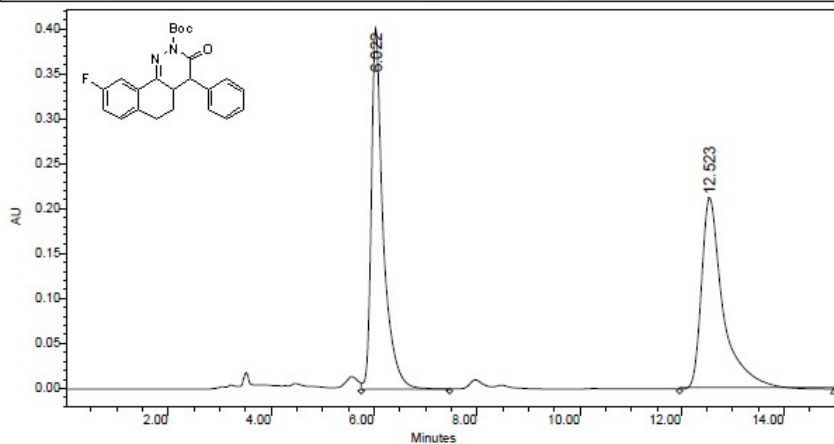
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-28-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/1/2018 5:48:04 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/1/2018 5:56:49 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.208	18783847	99.75	1010426	99.68
2	5.321	47021	0.25	3252	0.32

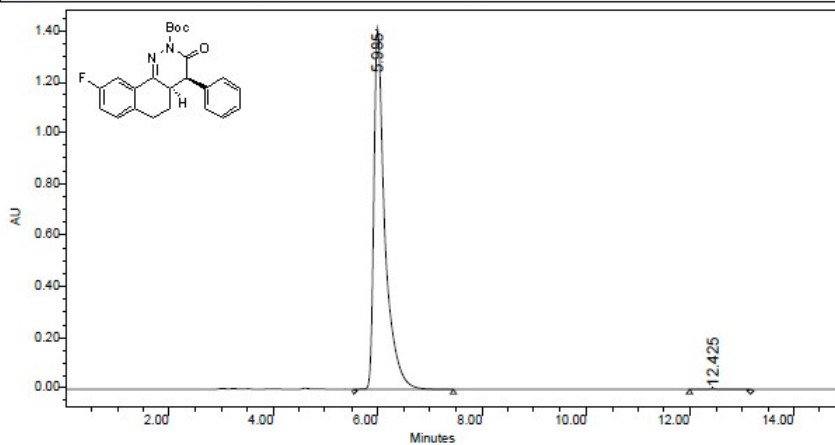
(3da)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-34-1-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/8/2018 3:12:14 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/8/2018 3:28:50 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.022	6435522	50.49	401687	65.36
2	12.523	6311290	49.51	212916	34.64

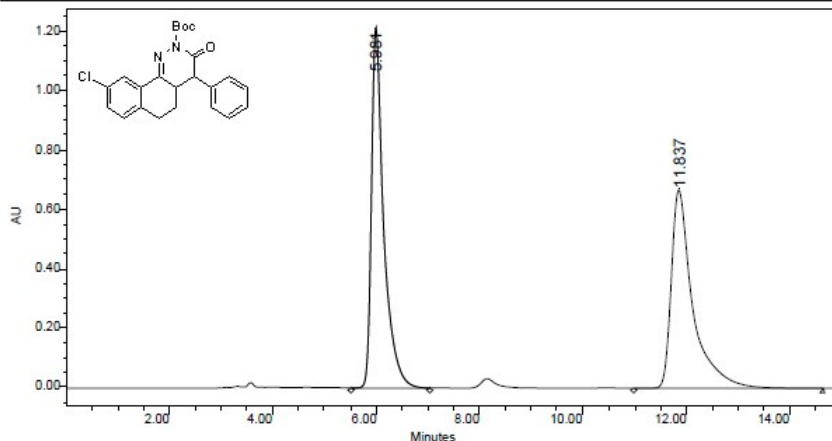
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-34-1-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/8/2018 4:13:59 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/8/2018 4:29:11 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.985	20763633	99.88	1409017	99.93
2	12.425	25663	0.12	1039	0.07

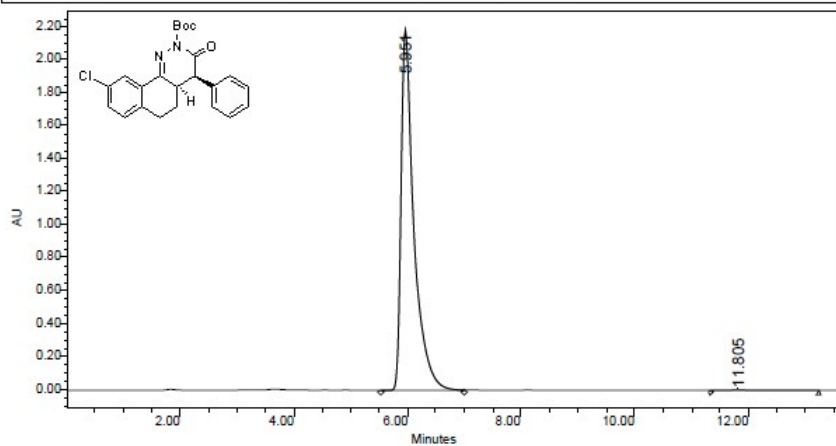
(3ea)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-1-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 3:03:44 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 3:33:37 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	19984571	50.89	1213659	64.52
2	19289293	49.11	667422	35.48

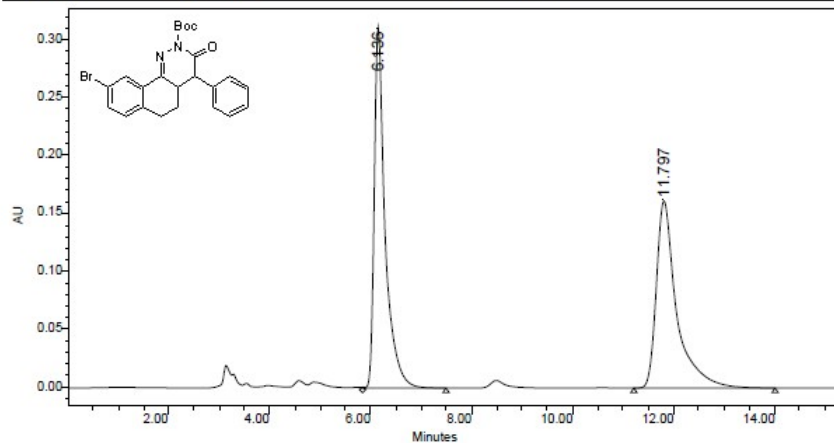
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-1-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 4:55:53 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 5:09:58 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	34217921	99.82	2185437	99.90
2	60829	0.18	2140	0.10

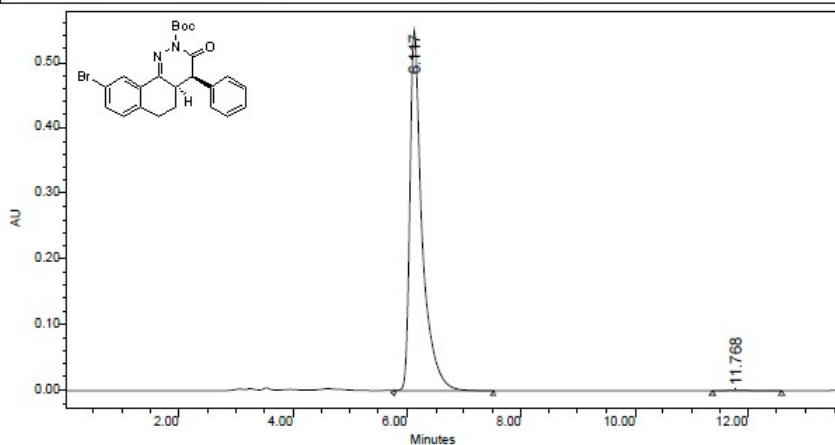
(3fa)

SAMPLE INFORMATION					
Sample Name:	ZZJ-3-33-1-rac-AD-30%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	3/6/2018 1:48:07 PM		
Vial:	1	Acq. Method:	30% 254		
Injection #:	1	Date Processed:	3/6/2018 2:05:08 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.136	4641213	50.72	310794	65.82
2	11.797	4509101	49.28	161372	34.18

SAMPLE INFORMATION					
Sample Name:	ZZJ-3-33-1-asy-AD-30%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	3/6/2018 4:04:54 PM		
Vial:	1	Acq. Method:	30% 254		
Injection #:	1	Date Processed:	3/6/2018 4:20:10 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			

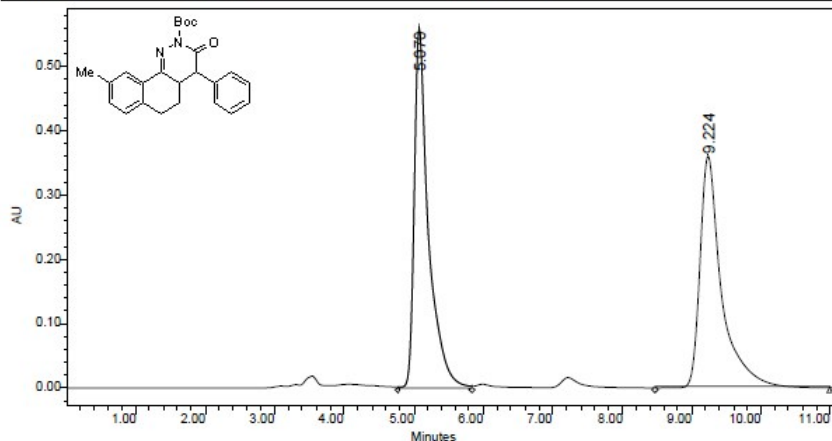


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.117	8222254	99.77	549298	99.87
2	11.768	18685	0.23	716	0.13



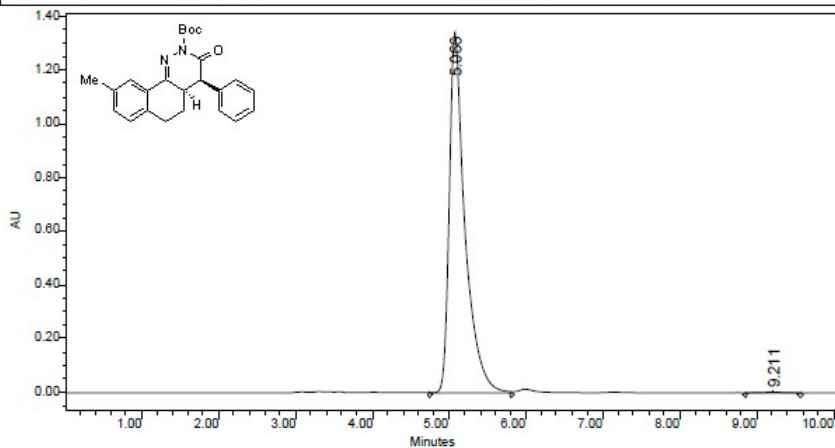
(3ga)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-2-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 3:32:32 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 3:53:07 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.070	7935775	50.37	561029	60.83
2	9.224	7820110	49.63	361289	39.17

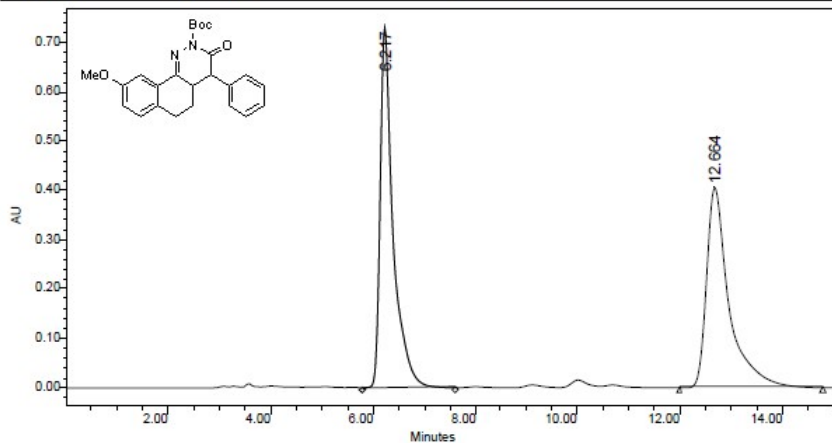
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-2-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 5:17:14 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 5:28:12 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.066	19021134	99.67	1341551	99.80
2	9.211	63848	0.33	2677	0.20

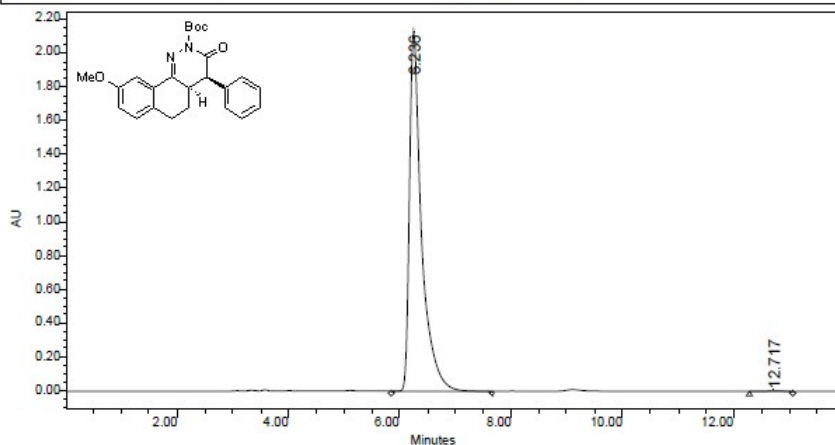
(3ha)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 3:54:48 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 4:26:49 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.217	12821304	50.76	731309	64.30
2	12.664	12437420	49.24	406028	35.70

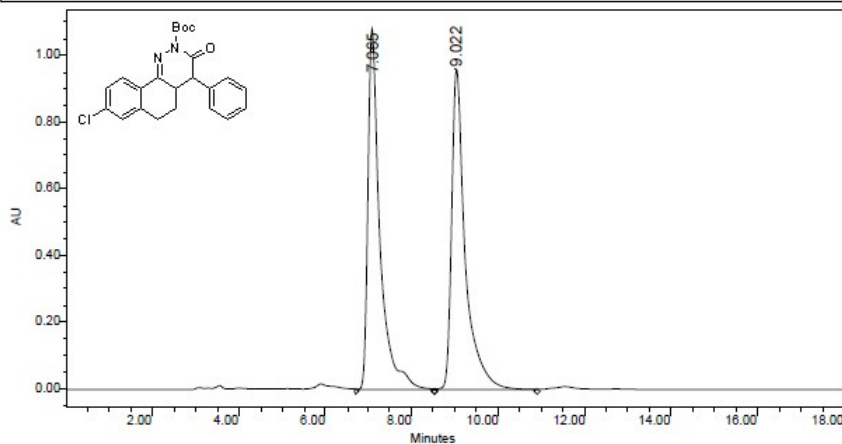
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 5:35:06 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 5:53:49 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.236	32225853	99.87	2134512	99.91
2	12.717	41269	0.13	1818	0.09

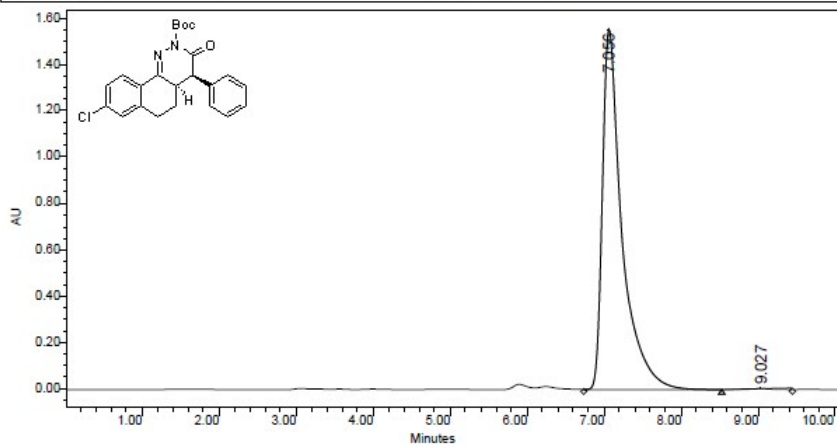
(3ia)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-4-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 4:25:46 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 4:45:49 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.065	20929387	49.92	1080836	52.93
2	9.022	20993693	50.08	961172	47.07

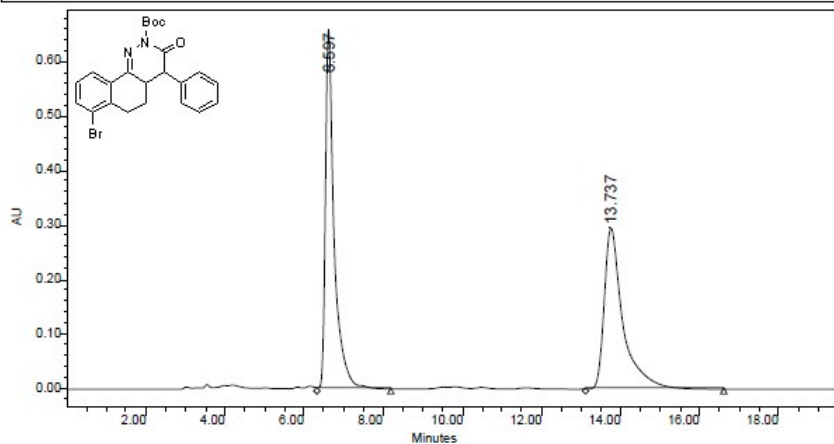
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-30-4-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	2/24/2018 5:57:15 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	2/24/2018 6:07:49 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.056	27390348	99.69	1557717	99.75
2	9.027	85383	0.31	3892	0.25

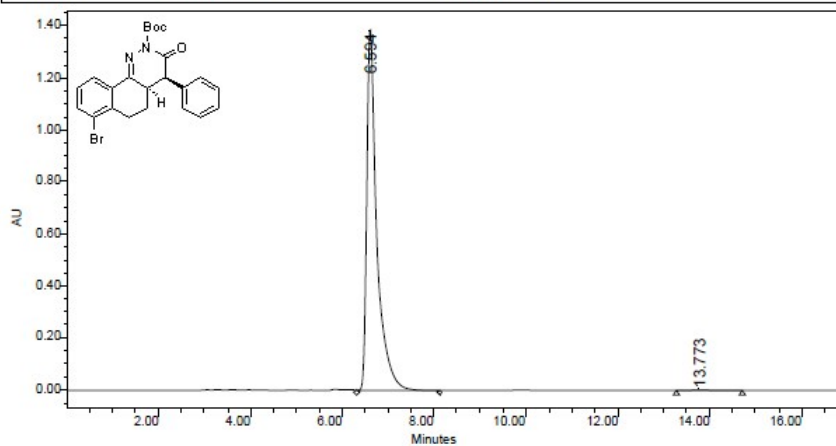
(3ja)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-33-2-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/6/2018 2:18:07 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/6/2018 2:39:16 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.597	10146410	51.07	659385	69.06
2	13.737	9722031	48.93	295369	30.94

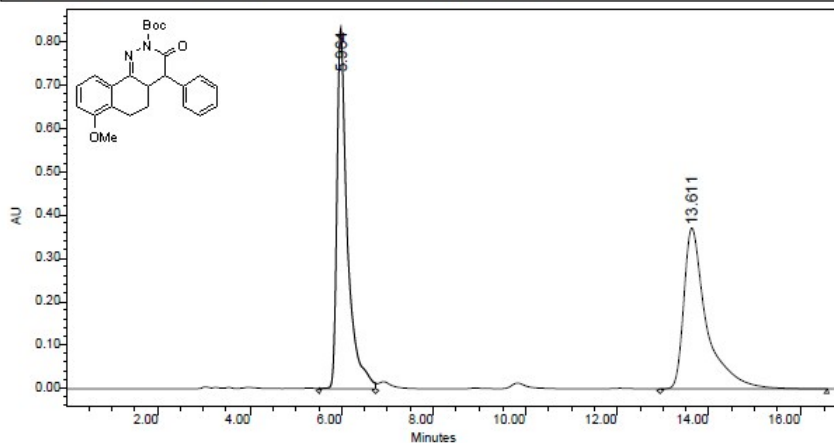
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-33-2-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/6/2018 4:27:46 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/6/2018 4:46:25 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.594	21166902	99.78	1390340	99.89
2	13.773	47250	0.22	1590	0.11

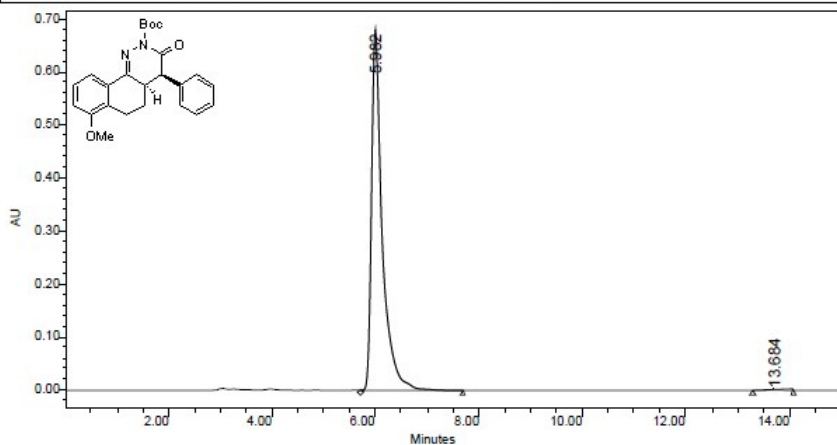
(3ka)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-33-3-rac-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/6/2018 2:54:07 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/6/2018 3:12:48 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.964	13157529	50.82	832661	69.16
2	13.611	12733544	49.18	371367	30.84

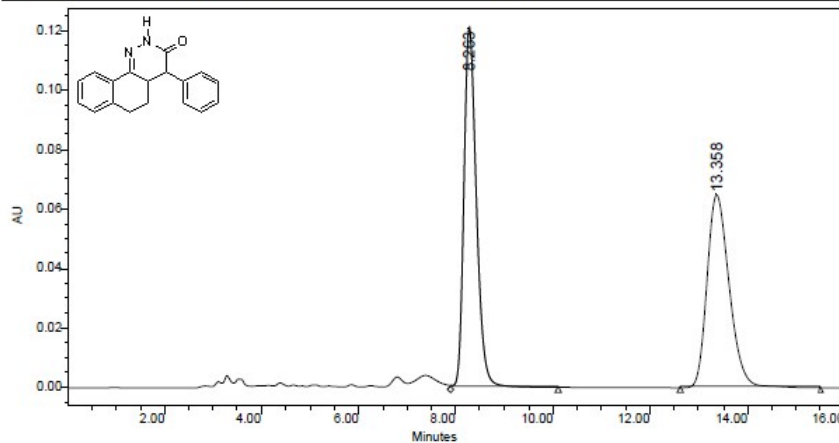
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-33-3-asy-AD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/6/2018 4:55:28 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/6/2018 5:10:59 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.982	9794836	99.88	679607	99.92
2	13.684	11844	0.12	523	0.08

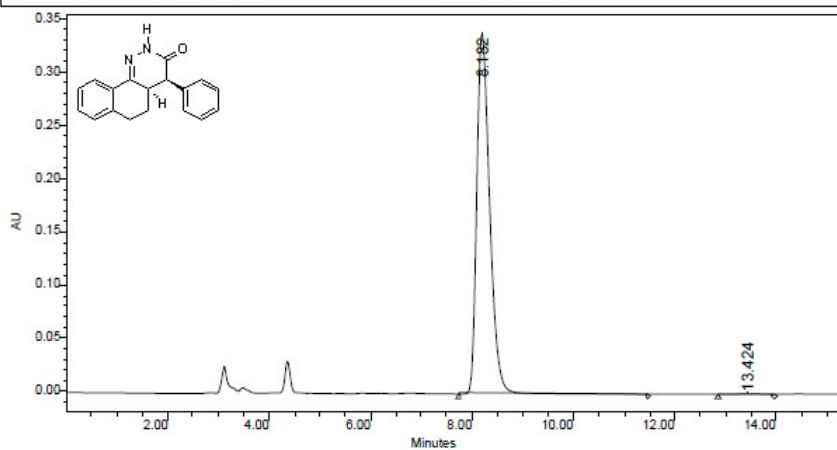
(9)

SAMPLE INFORMATION			
Sample Name:	ZZJ-3-37-rac-OD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/13/2018 4:31:55 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/13/2018 4:48:17 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.263	2163523	51.13	121146	65.11
2	13.358	2067620	48.87	64924	34.89

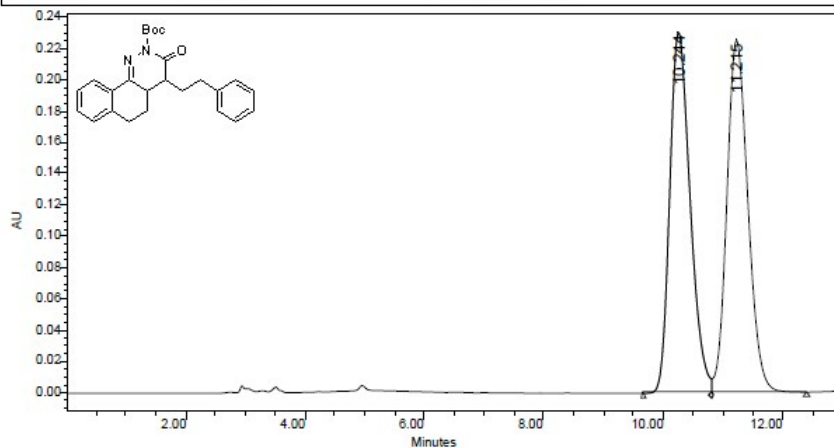
SAMPLE INFORMATION			
Sample Name:	ZZJ-3-37-asy-OD-30%254nm	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	3/13/2018 4:03:15 PM
Vial:	1	Acq. Method:	30% 254
Injection #:	1	Date Processed:	3/13/2018 4:38:01 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	120.00 Minutes	Sample Set Name:	



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.182	6018287	99.82	338285	99.89
2	13.424	10829	0.18	356	0.11

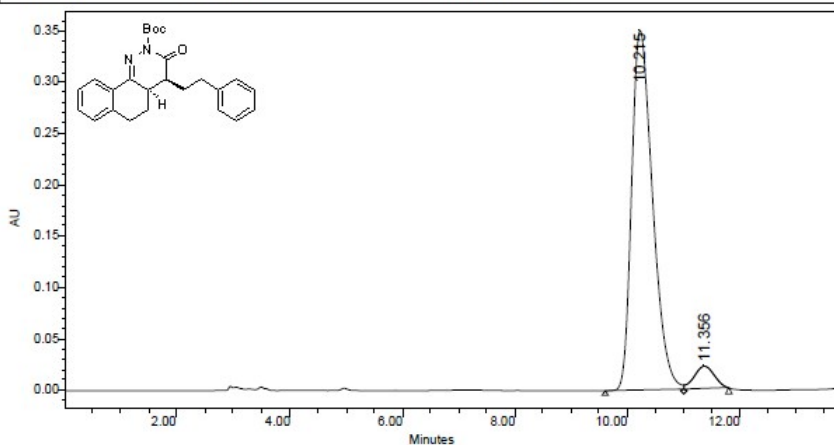
(10)

SAMPLE INFORMATION					
Sample Name:	ZZJ-3-43-rac-OD-10%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	3/19/2018 7:36:47 PM		
Vial:	1	Acq. Method:	10% 254		
Injection #:	1	Date Processed:	3/19/2018 8:39:16 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.244	5468166	49.72	230581	50.56
2	11.215	5530322	50.28	225465	49.44

SAMPLE INFORMATION					
Sample Name:	ZZJ-3-43-asy-OD-10%254nm	Acquired By:	System		
Sample Type:	Unknown	Date Acquired:	3/19/2018 8:04:14 PM		
Vial:	1	Acq. Method:	10% 254		
Injection #:	1	Date Processed:	3/19/2018 8:25:58 PM		
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1		
Run Time:	120.00 Minutes	Sample Set Name:			



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.215	9056287	94.27	350360	94.08
2	11.356	550509	5.73	22058	5.92