Supporting Information

Contents

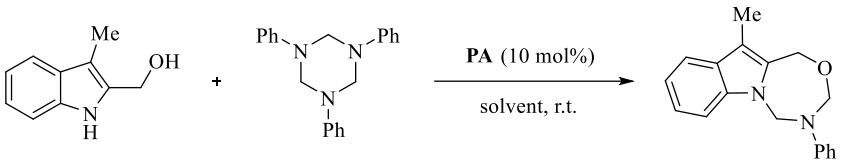
1. General Methods

Unless otherwise specified, all reactions were conducted under an atmospheric atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ or DMSO on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm). The data are reported as follows: for ^{1}H NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$ δ 7.26 ppm), (DMSO δ 2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for ^{13}C NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator ($CDCl_3$ δ 77.1 ppm), (DMSO δ 39.5 ppm), multiplicity with respect to protons. All high-resolution mass spectra were obtained on a Q-TOF Micro LC/MS System ESI spectrometer to be given in m/z. 2-Indolylmethanols **1** were either employed directly from commercial sources or prepared according to the literatures[1-4], 1,3,5-triazinanes **2** were synthesized according to modified literature reported procedure[5].

2. Representative Procedures

Optimization of the reaction conditions for 3b

1) Effect of Solvents



1b **2a** **3b**

Entry[a]	**Cat.**	Solvent	Yield (%)[b]
1	**PA**	Toluene	37
2	**PA**	CH_2Cl_2	68
3	**PA**	CH_3CN	82
4	**PA**	THF	40
5[c]	**PA**	CH_3CN	30
6[d]	**PA**	CH_3CN	81

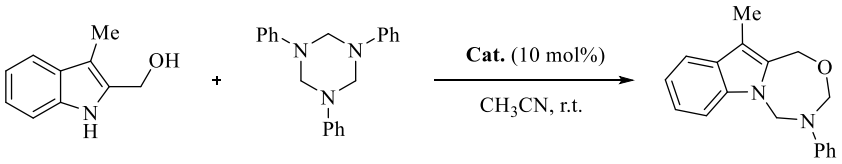
[a]Reaction conditions: **1b** (0.2 mmol), **2a** (0.12 mmol), and the **PA** (10 mol%) in the solvent specified (1 mL) at r.t. for 10 minutes.

[b]Isolated yield.

[c]**2a** (0.06 mmol)

[d]**2a** (0.2 mmol)

2) Effect of Catalysts



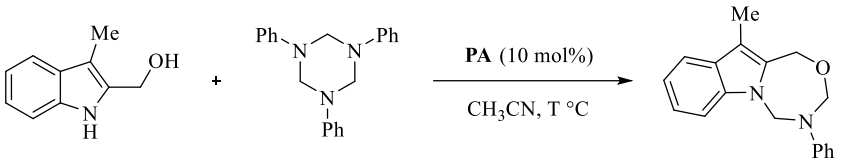
1b **2a** **3b**

Entry[a]	**Cat.**	Solvent	Yield (%)[b]
1	**PA**	CH_3CN	82
2	**TfOH**	CH_3CN	n.r.
3	***p*-TSA**	CH_3CN	69
4	**MsOH**	CH_3CN	n.r.
5	**$HNTf_2$**	CH_3CN	42
6	**PhCOOH**	CH_3CN	58
7	**CH_3COOH**	CH_3CN	50

[a]Reaction conditions: **1b** (0.2 mmol), **2a** (0.12 mmol), and the **Cat.** (10 mol%) in the CH_3CN (1 mL) at r.t. for 10 minutes. n.r.= no reaction.

[b]Isolated yield.

3) Effect of Temperatures



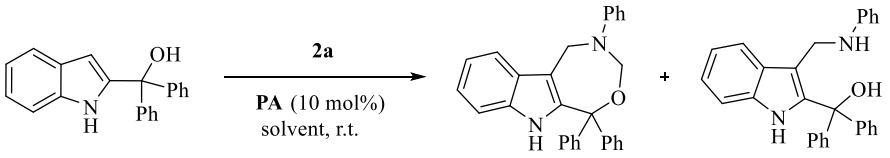
1b **2a** **3b**

Entry[a]	T (ºC)	Solvent	Yield (%)[b]
1	r.t.	CH_3CN	82
2	0	CH_3CN	78
3	-20	CH_3CN	66
4	-40	CH_3CN	63
5	50	CH_3CN	46

[a]Reaction conditions: **1b** (0.2 mmol), **2a** (0.12 mmol), and the **PA** (10 mol%) in the CH_3CN (1 mL) at T (ºC) for 10 minutes.
[b]Isolated yield.

Optimization of the reaction conditions for 4b

1) Effect of Solvents

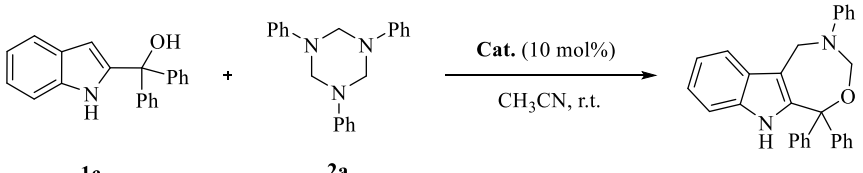


1c **4b** **Int-4b**

Entry[a]	Solvent	Yield (%)[b]	
		4b	**Int-4b**
1	Toluene	33	21
2	CH_2Cl_2	37	48
3	CH_3CN	79	-
4	THF	48	16

[a]Reaction conditions: **1c** (0.2 mmol), **2a** (0.12 mmol), and the **PA** (10 mol%) in the solvent specified (1 mL) at r.t. for 10 minutes.
[b]Isolated yield.

2) Effect of Catalysts



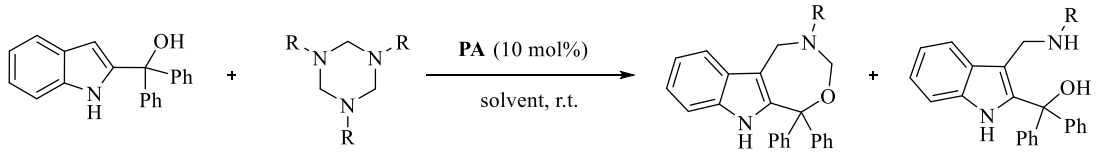
1c **2a** **4b**

Entry[a]	**Cat.**	Solvent	Yield (%)[b]
1	**TFA**	CH_3CN	trace
2	**TfOH**	CH_3CN	26
3	***p*-TSA**	CH_3CN	39
4	**MsOH**	CH_3CN	trace
5	**$HNTf_2$**	CH_3CN	trace
6	**PhCOOH**	CH_3CN	n.r.
7	**CH_3COOH**	CH_3CN	trace
8	**PA**	CH_3CN	79
9	**$Ni(OTf)_2$**	CH_3CN	32
10	**$Sc(OTf)_3$**	CH_3CN	trace
11	**$Fe(OTf)_2$**	CH_3CN	n.r.
12	**$Cu(OTf)_2$**	CH_3CN	29
13	**$Sn(OTf)_2$**	CH_3CN	n.r.
14	**$Zn(OTf)_2$**	CH_3CN	n.r.
15	**$In(OTf)_3$**	CH_3CN	n.r.
16	**$Co(OTf)_2$**	CH_3CN	n.r.

[a]Reaction conditions: **1c** (0.2 mmol), **2a** (0.12 mmol), and the **Cat.** (10 mol%) in the CH_3CN (1 mL) at r.t. for 10 minutes. n.r.= no reaction.

[b]Isolated yield.

Optimization of the reaction conditions for Int-4d



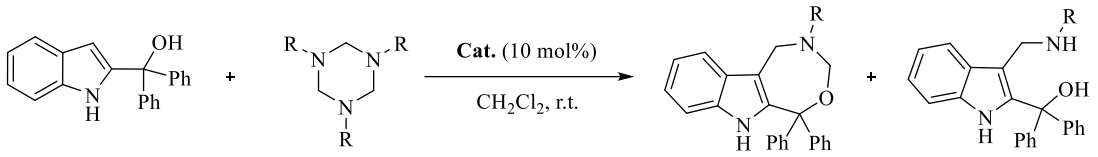
1c **2** **4d** **Int-4d**

1) Effect of Solvents

Entry[a]	Solvent	Yield (%)[b]	
		4d	**Int-4d**
1	Toluene	31	42
2	CH_2Cl_2	32	57
3	CH_3CN	71	-
4	THF	40	34
5	$CHCl_3$	30	44
6	DCE	36	40

[a]Reaction conditions: **1c** (0.2 mmol), **2** (0.06 mmol), and the **PA** (10 mol%) in the solvent specified (1 mL) at r.t. for 12 hours. R = 4-ClPh.
[b]Isolated yield.

2) Effect of Catalysts



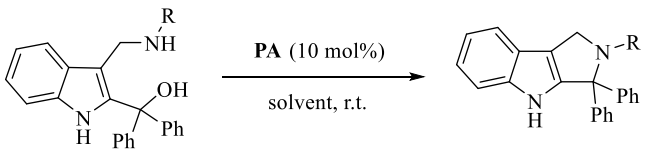
1c **2** **4d** **Int-4d**

Entry[a]	Cat.	Yield (%)[b]	
		4d	**Int-4d**
1	**TFA**	29	trace
2	**TfOH**	37	23
3	***p*-TSA**	trace	-
4	**MsOH**	trace	-
5	**$HNTf_2$**	39	42
6	**PhCOOH**	24	36
7	**CH_3COOH**	28	52
8	**PA**	32	57
9	**$Ni(OTf)_2$**	29	33
10	**$Sc(OTf)_3$**	21	38
11	**$Fe(OTf)_2$**	-	-
12	**$Co(OTf)_2$**	19	31
13	**$Cu(OTf)_2$**	40	29

[a]Reaction conditions: **1c** (0.2 mmol), **2** (0.06 mmol), and the **Cat.** (10 mol%) in the CH_2Cl_2 (1 mL) at r.t. for 12 hours. R = 4-ClPh.
[b]Isolated yield.

Optimization of the reaction conditions for 5d

1) Effect of Solvents



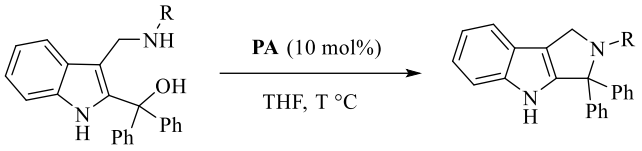
Int-4d **5d**

Entry[a]	**Cat.**	Solvent	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
1	**PA**	Toluene	24	38	36	39
2	**PA**	CH_2Cl_2	24	42	36	43
3	**PA**	CH_3CN	24	41	36	41
4	**PA**	THF	24	33	36	45

[a]Reaction conditions: **Int-4d** and the **PA** (10 mol%) in the solvent specified (1 mL) at r.t. for specific time. R = 4-ClPh.

[b]Isolated yield.

2) Effect of Temperatures



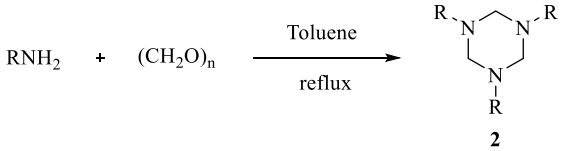
Int-4d **5d**

Entry[a]	T (°C)	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
1	r.t.	12	trace	24	33	36	45
2	40	12	25	24	55	36	54
3	60	12	messy	24	-	36	-
4	80	12	messy	24	-	36	-

[a]Reaction conditions: **Int-4d** and the **PA** (10 mol%) in the THF (1 mL) at specific T (ºC) for specific time. R = 4-ClPh.

[b]Isolated yield.

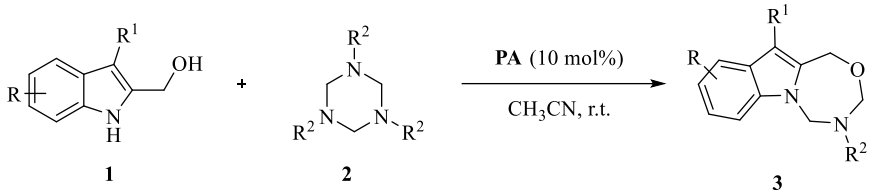
General procedure for the synthesis of triazine compounds 2



2

In a 100 mL round-bottomed flask equipped with a Dean-Stark apparatus, a mixture of aniline (30 mmol), paraformaldehyde (33 mmol), and toluene (50 mL) was heated with refluxing for 2 hours. Then the solvent was concentrated under reduced pressure at 50 °C, a precipitate came out from the mixture. The precipitate was collected by filtration, washed with *n*-hexane several times, and dried to obtain 1,3,5-triazinanes **2**.

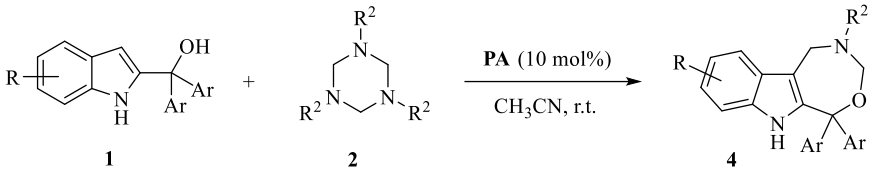
Procedure for the synthesis of compounds 3



1 2 3

Compounds **1** (0.20 mmol) and 1,3,5-triazinanes **2** (0.12 mmol) were dissolved in CH_3CN and **PA** (10 mol%) was added. The reaction mixture was stirred at room temperature for 10 minutes. The solvents were removed in vacuo and the crude products were separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford target products **3**.

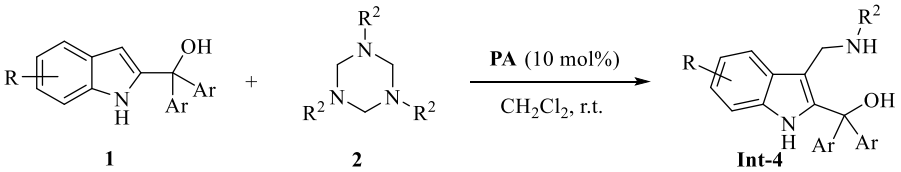
Procedure for the synthesis of compounds 4



1 2 4

Diaryl 2-indolylmethanol compounds **1** (0.20 mmol) and 1,3,5-triazinanes **2** (0.12 mmol) were dissolved in CH_3CN and **PA** (10 mol%) was added. The reaction mixture was stirred at room temperature for 10 minutes. The solvents were removed in vacuo and the crude products were separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford target products **4**.

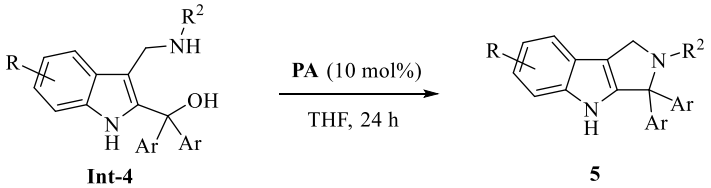
Procedure for the synthesis of compounds Int-4



1 2 Int-4

Diaryl 2-indolylmethanol compounds **1** (0.50 mmol) and 1,3,5-triazinanes **2** (0.15 mmol) were dissolved in CH_2Cl_2 and **PA** (10 mol%) was added. The reaction mixture was stirred at room temperature for 12 hours. The solvents were removed in vacuo and the crude products were separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford products **Int-4**.

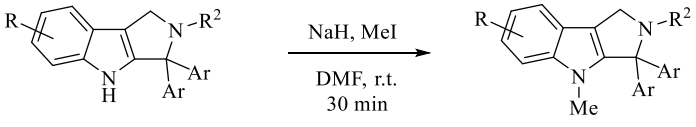
Procedure for the synthesis of compounds 5



Int-4 5

Compounds **Int-4** (0.20mmol) were dissolved in THF and **PA** (10 mol%) was added. The reaction mixture was stirred at 40 ºC for 24 hours. The solvents were removed in vacuo and the crude products were separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford target products **5** and recover compounds **Int-4**, then recovered compounds **Int-4** were repeated the above steps four times.

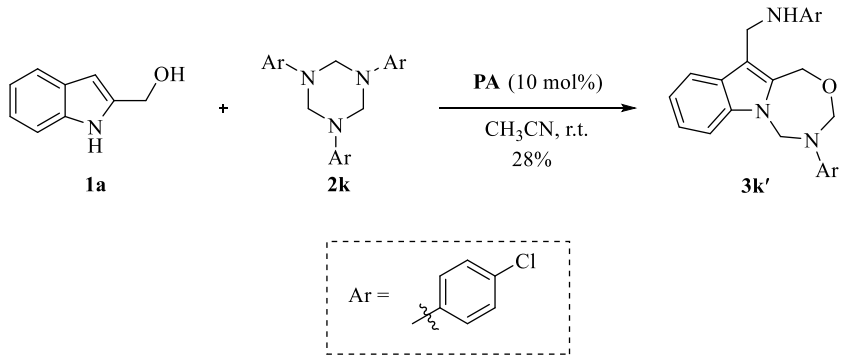
Procedure for the synthesis of compounds 5′



5 **5′**

To the solution of compounds **5** (0.1 mmol) in DMF (1 mL) were added NaH (60% suspension in mineral oil, 0.15 mmol) at 0 ºC, which was stirred at 25 ºC for 30 minutes. Then iodomethane (0.156 mmol) was added to the reaction mixture at 0 ºC, which was stirred at 25 ºC for 30 minutes. After the completion of the reaction which was indicated by TLC, the organic layer was washed with saturated NH_4Cl aqueous solution (3 × 10 mL), the combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residues were purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to afford target products **5′**.

Special substrate

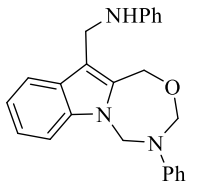


1a **2k** **3k′**

Compounds **1a** (0.20 mmol) and 1,3,5-triazinanes **2k** (0.20 mmol) were dissolved in CH_3CN and **PA** (10 mol%) was added. The reaction mixture was stirred for 10 minutes at room temperature. The solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford target products **3k′**.

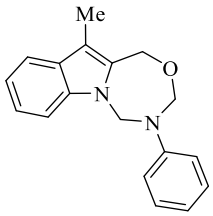
3. Characterization of products

N-((4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indol-11-yl)methyl)aniline **3a:**



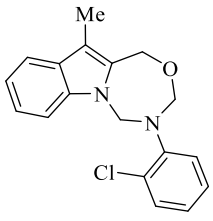
A white solid; 22.2 mg; isolated yield = 30%; m.p. 156.3 -157.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 1H), 7.38 – 7.30 (m, 1H), 7.26 – 7.16 (m, 3H), 7.14 – 7.08 (m, 2H), 7.07 – 7.01 (m, 3H), 6.87 – 6.78 (m, 1H), 6.74 – 6.69 (m, 1H), 6.66 – 6.61 (m, 2H), 5.76 (s, 2H), 5.23 (s, 2H), 4.98 (s, 2H), 4.33 (s, 2H), 3.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 145.6, 136.5, 136.1, 129.3, 126.9, 122.8, 121.9, 119.7, 119.5, 118.0, 117.5, 112.8, 111.2, 108.7, 86.8, 64.1, 61.4, 38.7. HRMS (ESI) m/z calcd for $C_{24}H_{23}N_3ONa^+$ $[M + Na]^+$ = 392.1733, found = 392.1732.

11-Methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3b:**



A white solid; 41.1 mg; isolated yield = 82%; m.p. 134.4 -135.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 1H), 7.30 – 7.24 (m, 1H), 7.21 – 7.14 (m, 1H), 7.11 – 7.03 (m, 2H), 7.03 – 6.97 (m, 3H), 6.85 – 6.68 (m, 1H), 5.66 (s, 2H), 5.19 (s, 2H), 4.89 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.4, 134.2, 129.2, 128.1, 122.4, 121.7, 119.4, 118.9, 118.0, 109.7, 108.3, 86.7, 64.3, 61.2, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_2ONa^+$ $[M + Na]^+$ = 301.1311, found = 301.1310.

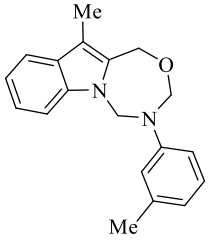
4-(2-Chlorophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3c:**



A white solid; 39.9 mg; isolated yield = 71%; m.p. 146.7 -147.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.13 (m, 1H), 7.09 – 7.01 (m, 2H), 7.00 – 6.94 (m, 1H), 6.92 – 6.79 (m, 2H), 5.72 (s, 2H), 5.06 (s, 2H), 5.01 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.5, 134.2, 130.0, 129.0,

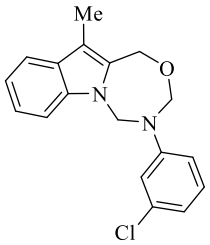
127.7, 127.7, 126.2, 126.1, 122.4, 119.1, 118.8, 109.8, 108.1, 89.5, 63.9, 61.5, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN_2ONa^+$ $[M + Na]^+$ = 335.0922, found = 335.0919.

11-Methyl-4-(*m*-tolyl)-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3d:**



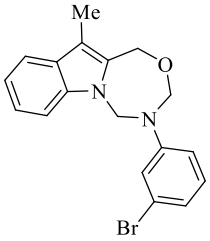
A white solid; 41.0 mg; isolated yield = 78%; m.p. 131.3 -131.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.15 (m, 1H), 7.09 – 6.94 (m, 2H), 6.87 – 6.78 (m, 2H), 6.67 – 6.55 (m, 1H), 5.72 (s, 2H), 5.23 (s, 2H), 4.93 (s, 2H), 2.23 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 138.9, 136.4, 134.1, 129.0, 128.0, 122.4, 122.4, 119.4, 118.9, 118.6, 114.8, 109.7, 108.3, 86.6, 64.3, 61.2, 21.6, 8.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2ONa^+$ $[M + Na]^+$ = 315.1468, found = 315.1465.

4-(3-Chlorophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3e:**



A white solid; 47.7 mg; isolated yield = 85%; m.p. 189.5 -190.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 1H), 7.32 – 7.26 (m, 1H), 7.24 – 7.17 (m, 1H), 7.08 – 7.02 (m, 2H), 7.01 – 6.96 (m, 1H), 6.92 – 6.85 (m, 1H), 6.79 – 6.71 (m, 1H), 5.70 (s, 2H), 5.19 (s, 2H), 4.93 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 136.4, 134.9, 133.8, 130.1, 128.0, 122.6, 121.6, 119.5, 119.1, 118.1, 115.8, 110.2, 108.1, 86.3, 64.4, 61.1, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN_2ONa^+$ $[M + Na]^+$ = 335.0922, found = 335.0928.

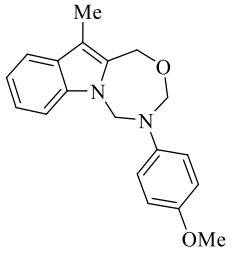
4-(3-Bromophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3f:**



A white solid; 46.8 mg; isolated yield = 73%; m.p. 185.7 -186.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 1H), 7.35 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.10 – 7.01

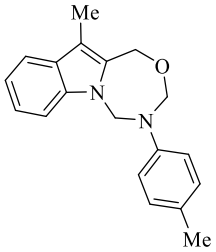
(m, 1H), 6.97 – 6.87 (m, 3H), 5.70 (s, 2H), 5.19 (s, 2H), 4.93 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 136.4, 133.8, 130.4, 128.0, 124.5, 123.1, 122.7, 121.0, 119.5, 119.1, 116.2, 110.2, 108.1, 86.3, 64.4, 61.1, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}BrN_2ONa^+$ $[M + Na]^+$ = 379.0416, found = 379.0428.

4-(4-Methoxyphenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3g:**



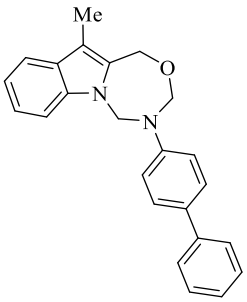
A white solid; 45.5 mg; isolated yield = 82%; m.p. 129.7-130.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 1H), 7.25 – 7.09 (m, 2H), 7.05 – 6.98 (m, 1H), 6.96 – 6.86 (m, 2H), 6.68 – 6.53 (m, 2H), 5.60 (s, 2H), 5.12 (s, 2H), 4.92 (s, 2H), 3.59 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 139.6, 136.3, 134.3, 128.0, 122.3, 121.1, 119.3, 118.8, 114.4, 109.6, 108.3, 88.0, 64.2, 62.4, 55.3, 8.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2O_2Na^+$ $[M + Na]^+$ = 331.1417, found = 331.1418.

11-Methyl-4-(*p*-tolyl)-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3h:**



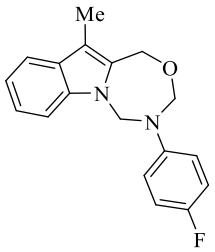
A white solid; 44.2 mg; isolated yield = 84%; m.p. 149.9 -150.6 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 1H), 7.29 – 7.22 (m, 1H), 7.21 – 7.13 (m, 1H), 7.07 – 6.98 (m, 1H), 6.94 – 6.84 (m, 4H), 5.66 (s, 2H), 5.18 (s, 2H), 4.91 (s, 2H), 2.22 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.4, 134.2, 131.2, 129.8, 128.0, 122.4, 119.4, 118.8, 118.3, 109.6, 108.3, 87.0, 64.3, 61.5, 20.5, 8.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2ONa^+$ $[M + Na]^+$ = 315.1468, found = 315.1470.

4-([1,1'-Biphenyl]-4-yl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3i:**



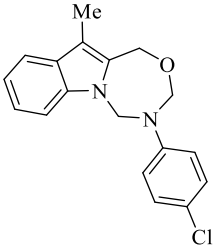
A white solid; 36.9 mg; isolated yield = 58%; m.p. 196.9 -197.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 3H), 7.38 – 7.30 (m, 4H), 7.27 – 7.18 (m, 3H), 7.12 – 7.02 (m, 3H), 5.81 (s, 2H), 5.30 (s, 2H), 4.98 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 140.6, 136.3, 134.3, 134.0, 128.6, 128.0, 127.9, 126.6, 126.6, 122.5, 119.4, 118.9, 118.0, 109.9, 108.2, 86.6, 64.4, 61.2, 8.8. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2ONa^+$ $[M + Na]^+$ = 377.1624, found = 377.1631.

4-(4-Fluorophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3j:**



A white solid; 44.8 mg; isolated yield = 84%; m.p. 139.4 -140.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 1H), 7.28 – 7.10 (m, 2H), 7.07 – 7.01 (m, 1H), 7.00 – 6.94 (m, 2H), 6.80 – 6.72 (m, 2H), 5.66 (s, 2H), 5.15 (s, 2H), 4.94 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 157.2 (*J* = 240 Hz), 142.2, 142.2, 136.3, 134.1, 127.9, 122.5, 120.8, 120.8, 119.4, 118.9, 115.8, 115.6 (*J* = 22 Hz), 109.9, 108.1, 87.6, 64.2, 62.2, 8.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.59. HRMS (ESI) m/z calcd for $C_{18}H_{17}FN_2ONa^+$ $[M + Na]^+$ = 319.1217, found = 319.1215.

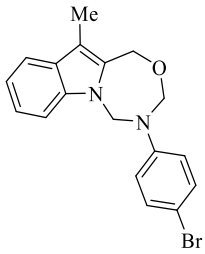
4-(4-Chlorophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3k:**



A white solid; 45.5mg; isolated yield = 81%; m.p. 175.8 -176.6 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, *J* = 7.9 Hz, 1H), 7.25 (m, *J* = 8.4 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.09 – 7.01 (m, 3H), 6.98 – 6.92 (m, 2H), 5.69 (s, 2H), 5.18 (s, 2H), 4.93 (s, 2H), 2.23 (s,

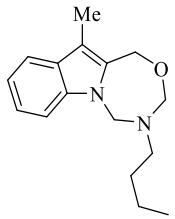
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.4, 133.9, 129.1, 127.9, 126.9, 122.6, 119.5, 119.5, 119.0, 110.1, 108.1, 86.7, 64.3, 61.4, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN_2ONa^+$ $[M + Na]^+$ = 335.0922, found = 335.0929.

4-(4-Bromophenyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3l:**



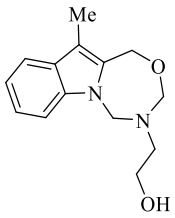
A white solid; 53.2 mg; isolated yield = 83%; m.p. 193.1 -193.6 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.15 (m, 3H), 7.10 – 7.01 (m, 1H), 6.96 – 6.84 (m, 2H), 5.72 (s, 2H), 5.20 (s, 2H), 4.95 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 136.4, 133.8, 132.0, 127.9, 122.6, 119.8, 119.5, 119.0, 114.4, 110.1, 108.0, 86.6, 64.3, 61.3, 8.7. HRMS (ESI) m/z calcd for $C_{18}H_{17}BrN_2ONa^+$ $[M + Na]^+$ = 379.0416, found = 379.0426.

4-Butyl-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3m:**



A white solid; 33.5 mg; isolated yield = 72%; m.p. 58.3 -58.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 1H), 7.30 – 7.16 (m, 2H), 7.11 – 7.02 (m, 1H), 5.22 (s, 2H), 4.82 (s, 2H), 4.71 (s, 2H), 2.36 – 2.31 (m, 2H), 2.30 (s, 3H), 1.48 – 1.34 (m, 2H), 1.28 – 1.13 (m, 2H), 0.88 – 0.74 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.6, 127.9, 122.2, 119.4, 118.8, 109.4, 108.3, 89.7, 63.8, 62.2, 46.6, 29.5, 20.2, 13.9, 8.8. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2O^+$ $[M + H]^+$ = 259.1805, found = 259.1808.

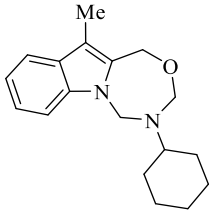
2-(11-Methyl-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indol-4(5*H*)-yl)ethan-1-ol **3n:**



A white solid; 39.9 mg; isolated yield = 90%; m.p. 112.3 -113.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 1H), 7.26 – 7.16 (m, 2H), 7.11 – 7.03 (m, 1H), 5.22 (s, 2H), 4.83 (s, 2H), 4.72 (s, 2H), 3.45 – 3.32 (t, 2H), 2.64 – 2.53 (t, 2H), 2.46 (s, 1H), 2.29 (s,

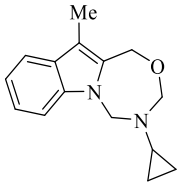
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 134.2, 127.9, 122.6, 119.6, 119.1, 110.1, 108.2, 89.8, 63.7, 62.3, 58.9, 50.1, 8.8. HRMS (ESI) m/z calcd for $C_{14}H_{18}N_2O_2Na^+$ [M + Na]$^+$ = 269.1260, found = 269.1259.

4-Cyclohexyl-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3o:**



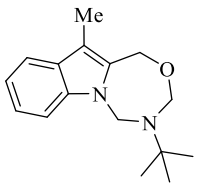
A white solid; 41.4 mg; isolated yield = 81%; m.p. 106.7 -107.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 1H), 7.32 – 7.22 (m, 1H), 7.22 – 7.15 (m, 1H), 7.11 – 7.01 (m, 1H), 5.28 (s, 2H), 4.83 (s, 2H), 4.81 (s, 2H), 2.42 – 2.31 (m, 1H), 2.29 (s, 3H), 1.86 – 1.71 (m, 2H), 1.65 – 1.54 (m, 2H), 1.49 – 1.35 (m, 1H), 1.20 – 0.92 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.9, 128.0, 122.1, 119.3, 118.7, 109.1, 108.4, 87.6, 64.1, 60.9, 55.4, 31.4, 25.8, 25.1, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{25}N_2O^+$ [M + H]$^+$ = 285.1961 found = 285.1957.

4-Cyclopropyl-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3p:**



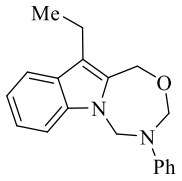
A white solid; 34.9 mg; isolated yield = 80%; m.p. 77.8 -78.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 1H), 7.35 – 7.27 (m, 1H), 7.25 – 7.16 (m, 1H), 7.11 – 7.03 (m, 1H), 5.20 (s, 2H), 4.86 (s, 2H), 4.71 (s, 2H), 2.32 (s, 3H), 1.79 – 1.64 (m, 1H), 0.49 – 0.43 (m, 2H), 0.42 – 0.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.6, 127.8, 122.2, 119.4, 118.8, 109.6, 108.5, 89.5, 63.7, 62.6, 28.6, 8.8, 7.1. HRMS (ESI) m/z calcd for $C_{15}H_{18}N_2ONa^+$ [M + Na]$^+$ = 265.1311, found = 265.1316.

4-(*T*ert-butyl)-11-methyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3q:**



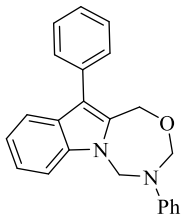
A white solid; 36.7 mg; isolated yield = 79%; m.p. 93.1 -93.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 1H), 7.33 – 7.25 (m, 1H), 7.25 – 7.15 (m, 1H), 7.11 – 7.00 (m, 1H), 5.38 (s, 2H), 4.92 (s, 2H), 4.87 (s, 2H), 2.29 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.9, 128.3, 122.0, 119.3, 118.6, 109.1, 108.8, 87.0, 63.9, 60.0, 53.8, 29.5, 8.8. HRMS (ESI) m/z calcd for $C_{16}H_{23}N_2O^+$ [M + H]$^+$ = 259.1805, found = 259.1813.

11-Ethyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3r:**



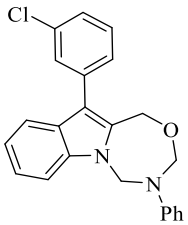
A white solid; 42.1 mg; isolated yield = 80%; m.p. 155.3 -155.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 1H), 7.32 – 7.25 (m, 1H), 7.20 – 7.14 (m, 1H), 7.12 – 7.06 (m, 2H), 7.05 – 6.98 (m, 3H), 6.83 – 6.75 (m, 1H), 5.72 (s, 2H), 5.22 (s, 2H), 4.94 (s, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 136.4, 133.7, 129.2, 127.0, 122.3, 121.8, 119.4, 118.9, 118.2, 116.7, 108.4, 86.8, 64.1, 61.4, 17.6, 16.3. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2ONa^+$ $[M + Na]^+$ = 315.1468, found = 315.1470.

4,11-Diphenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3s:**



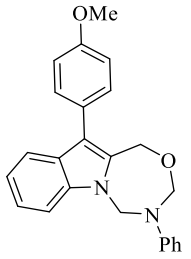
A white solid; 46.5 mg; isolated yield = 76%; m.p. 168.3 -168.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.47 – 7.35 (m, 5H), 7.34 – 7.29 (m, 1H), 7.27 – 7.20 (m, 1H), 7.17 – 7.03 (m, 5H), 6.89 – 6.80 (m, 1H), 5.86 (s, 2H), 5.27 (s, 2H), 5.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 136.3, 134.7, 134.3, 130.0, 129.2, 128.6, 126.6, 126.5, 122.8, 121.9, 120.0, 119.9, 118.3, 117.1, 108.6, 86.8, 64.9, 61.6. HRMS (ESI) m/z calcd for $C_{23}H_{20}N_2ONa^+$ $[M + Na]^+$ = 363.1468, found = 363.1463.

11-(3-Chlorophenyl)-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3t:**



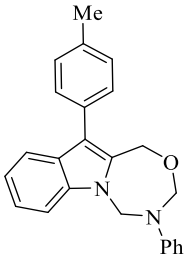
A white solid; 41.8 mg; isolated yield = 62%; m.p. 114.3 -114.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 1H), 7.43 – 7.31 (m, 3H), 7.31 – 7.21 (m, 3H), 7.19 – 7.10 (m, 2H), 7.10 – 7.04 (m, 3H), 6.88 – 6.80 (m, 1H), 5.83 (s, 2H), 5.25 (s, 2H), 5.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.3, 136.3, 135.1, 134.4, 129.8, 129.3, 128.2, 126.6, 126.4, 123.1, 122.0, 120.2, 119.8, 118.2, 115.8, 108.8, 86.8, 64.6, 61.6. HRMS (ESI) m/z calcd for $C_{23}H_{19}ClN_2ONa^+$ $[M + Na]^+$ = 397.1078, found = 397.1078.

11-(4-Methoxyphenyl)-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3u:**



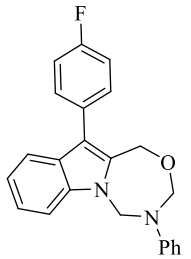
A white solid; 46.0 mg; isolated yield = 69%; m.p. 132.3 -133.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 1H), 7.41 – 7.26 (m, 3H), 7.24 – 7.19 (m, 1H), 7.17 – 7.01 (m, 5H), 6.99 – 6.93 (m, 2H), 6.90 – 6.75 (m, 1H), 5.82 (s, 2H), 5.25 (s, 2H), 5.00 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 145.8, 136.3, 134.4, 131.1, 129.2, 126.9, 126.6, 122.7, 121.9, 120.0, 119.8, 118.2, 116.8, 114.1, 108.6, 86.8, 64.9, 61.5, 55.4. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2O_2Na^+$ $[M + Na]^+$ = 393.1573, found = 393.1567.

4-Phenyl-11-(*p*-tolyl)-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3v:**



A white solid; 43.4 mg; isolated yield = 68%; m.p. 171.1 -171.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 1H), 7.43 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 7.18 – 7.00 (m, 5H), 6.90 – 6.79 (m, 1H), 5.84 (s, 2H), 5.26 (s, 2H), 5.02 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 136.3, 136.1, 134.6, 131.3, 129.9, 129.3, 129.2, 126.7, 122.7, 121.9, 120.1, 119.8, 118.2, 117.0, 108.6, 86.8, 64.9, 61.6, 21.2. HRMS (ESI) m/z calcd for $C_{24}H_{22}N_2ONa^+$ $[M + Na]^+$ = 377.1624, found = 377.1620.

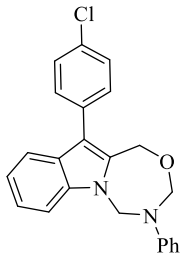
11-(4-Fluorophenyl)-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3w:**



A white solid; 38.7 mg; isolated yield = 60%; m.p. 165.1 -165.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 1H), 7.41 – 7.32 (m, 3H), 7.26 – 7.20 (m, 1H), 7.17 – 7.02

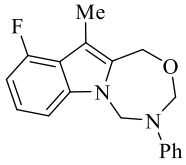
(m, 7H), 6.92 – 6.79 (m, 1H), 5.86 (s, 2H), 5.27 (s, 2H), 5.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.6 (*J* = 244 Hz), 145.7, 136.3, 134.7, 131.5, 131.4, 130.2, 130.2, 129.3, 126.6, 122.9, 122.0, 120.0, 119.8, 118.2, 116.1, 115.6, 115.4 (*J* = 22 Hz), 108.7, 86.8, 64.7, 61.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.15. HRMS (ESI) m/z calcd for $C_{23}H_{19}FN_2ONa^+$ $[M + Na]^+$ = 381.1374, found = 381.1373.

11-(4-Chlorophenyl)-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3x:**



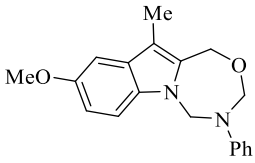
A white solid; 42.4 mg; isolated yield = 63%; m.p. 154.4 -155.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.44 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 7.17 – 7.11 (m, 2H), 7.11 – 7.03 (m, 3H), 6.89 – 6.77 (m, 1H), 5.85 (s, 2H), 5.27 (s, 2H), 4.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.3, 134.9, 132.8, 132.4, 131.2, 130.0, 129.3, 128.8, 128.6, 126.4, 123.0, 122.0, 120.1, 119.7, 118.3, 118.2, 115.9, 108.7, 86.8, 64.7, 61.6. HRMS (ESI) m/z calcd for $C_{23}H_{19}ClN_2ONa^+$ $[M + Na]^+$ = 397.1078, found = 397.1082.

10-Fluoro-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3y:**



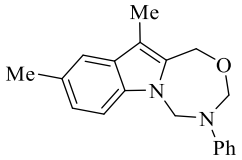
A white solid; 38.9 mg; isolated yield = 73%; m.p. 125.4 -126.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 2H), 7.06 – 6.99 (m, 4H), 6.87 – 6.78 (m, 1H), 6.68 – 6.57 (m, 1H), 5.71 (s, 2H), 5.23 (s, 2H), 4.91 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 156.5 (*J* = 246 Hz), 145.5, 139.0, 138.9, 134.1, 129.2, 122.8, 122.7, 121.9, 118.1, 116.6, 116.4 (*J* = 19 Hz), 108.5, 108.5, 104.4, 104.4, 104.3, 104.1, 63.8, 61.7, 10.5, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.67. HRMS (ESI) m/z calcd for $C_{18}H_{17}FN_2ONa^+$ $[M + Na]^+$ = 319.1217, found = 319.1227.

9-Methoxy-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3z:**



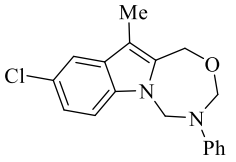
A white solid; 45.5 mg; isolated yield = 82%; m.p. 135.0 -135.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 7.04 – 6.98 (m, 2H), 6.89 – 6.77 (m, 3H), 5.69 (s, 2H), 5.23 (s, 2H), 4.93 (s, 2H), 3.82 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 145.7, 134.8, 131.6, 129.2, 128.2, 121.7, 118.0, 112.4, 109.2, 109.0, 101.2, 86.7, 64.4, 61.5, 55.9, 8.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2O_2Na^+$ $[M + Na]^+$ = 331.1417, found = 331.1412.

9,11-Dimethyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3a′:**



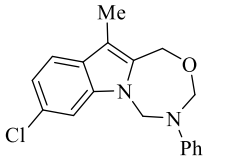
A white solid; 37.3 mg; isolated yield = 71%; m.p. 145.5 -146.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 7.12 – 7.06 (m, 2H), 7.04 – 6.97 (m, 3H), 6.83 – 6.75 (m, 1H), 5.69 (s, 2H), 5.22 (s, 2H), 4.92 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 134.8, 134.2, 129.2, 128.2, 128.0, 123.9, 121.6, 119.1, 118.0, 109.2, 108.0, 86.7, 64.4, 61.3, 21.4, 8.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2ONa^+$ $[M + Na]^+$ = 315.1468, found = 315.1467.

9-Chloro-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3 b′:**



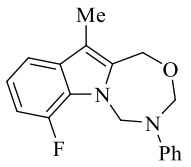
A white solid; 44.9 mg; isolated yield = 80%; m.p. 171.3 -172.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.21 – 7.05 (m, 4H), 7.03 – 6.95 (m, 2H), 6.87 – 6.75 (m, 1H), 5.68 (s, 2H), 5.21 (s, 2H), 4.91 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 135.5, 134.8, 129.2, 129.1, 124.5, 122.6, 121.9, 118.9, 118.1, 109.4, 109.3, 86.7, 64.1, 61.6, 8.7. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN_2ONa^+$ $[M + Na]^+$ = 335.0922, found = 335.0928.

8-Chloro-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3 c′:**



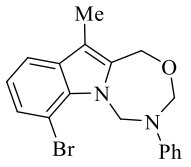
A white solid; 39.3 mg; isolated yield = 70%; m.p. 178.4 -179.2 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 1H), 7.26 – 7.23 (m, 1H), 7.16 – 7.09 (m, 2H), 7.04 – 6.95 (m, 3H), 6.87 – 6.78 (m, 1H), 5.65 (s, 2H), 5.21 (s, 2H), 4.90 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 136.7, 134.9, 129.3, 128.3, 126.6, 121.9, 120.2, 119.6, 118.1, 109.9, 108.3, 86.7, 64.1, 61.5, 8.7. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN_2ONa^+$ $[M + Na]^+$ = 335.0922, found = 335.0931.

7-Fluoro-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3d′:**



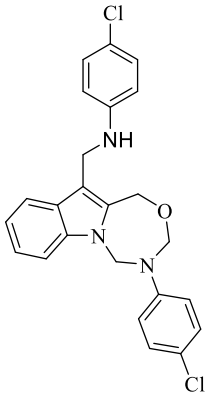
A white solid; 39.9 mg; isolated yield = 75%; m.p. 155.2 -156.0 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.08 (m, 5H), 6.96 – 6.73 (m, 3H), 6.14 – 5.94 (m, 2H), 5.22 (s, 2H), 4.92 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 148.0 (*J* = 240 Hz), 145.3, 135.6, 131.9, 131.8, 129.2, 124.3, 124.2, 121.5, 119.0, 118.9, 117.6, 117.6, 115.2, 115.1, 111.0, 108.4, 108.2 (*J* = 19 Hz), 86.5, 63.8, 63.3, 63.2, 9.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.97. HRMS (ESI) m/z calcd for $C_{18}H_{17}FN_2ONa^+$ $[M + Na]^+$ = 319.1217, found = 319.1210.

7-Bromo-11-methyl-4-phenyl-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indole **3e′:**



A white solid; 49.9 mg; isolated yield = 78%; m.p. 149.7 -150.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 1H), 7.34 – 7.25 (m, 1H), 7.23 – 7.16 (m, 1H), 7.14 – 7.07 (m, 2H), 7.06 – 7.00 (m, 2H), 6.84 – 6.75 (m, 1H), 5.74 (s, 2H), 5.24 (s, 2H), 4.95 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.3, 134.1, 129.2, 128.0, 122.4, 121.7, 119.3, 118.9, 118.0, 109.7, 108.3, 86.7, 64.3, 61.3, 8.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}BrN_2ONa^+$ $[M + Na]^+$ = 379.0416, found = 379.0415.

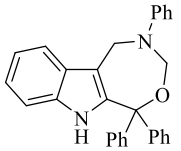
4-Chloro-*N*-((4-(4-chlorophenyl)-4,5-dihydro-1*H*,3*H*-[1,3,5]oxadiazepino[5,6-*a*]indol-11-yl)methyl)aniline **3k′**



A white solid; 24.4 mg; isolated yield = 28%; m.p. 212.3. -213.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.36 – 7.28 (m, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.06 (m, 5H), 7.01 – 6.96 (m, 2H), 6.62 – 6.53 (m, 2H), 5.78 (s, 2H), 5.22 (s, 2H), 5.01

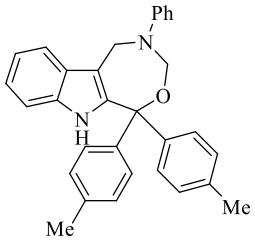
(s, 2H), 4.32 (s, 2H), 3.67 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 144.1, 136.5, 135.8, 129.2, 129.1, 129.1, 127.2, 126.6, 123.1, 122.1, 119.9, 119.6, 119.5, 116.2, 113.8, 111.1, 108.5, 86.9, 64.0, 61.6, 38.8. HRMS (ESI) m/z calcd for $C_{24}H_{21}Cl_2N_3Na^+$ [M + Na]$^+$ = 460.0954, found = 460.0959.

2,5,5-Triphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4b:**



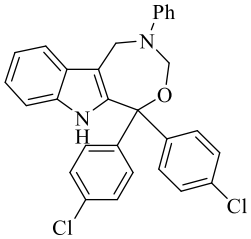
A white solid; 59.2 mg; isolated yield = 79%; m.p. 186.9 -187.6 ºC; ^{1}H NMR (400 MHz, DMSO) δ 9.65 (s, 1H), 7.80 – 7.73 (m, 1H), 7.41 – 7.29 (m, 7H), 7.21 – 7.11 (m, 4H), 7.09 – 7.03 (m, 2H), 7.02 – 6.96 (m, 4H), 6.77 – 6.69 (m, 1H), 5.23 (s, 2H), 4.73 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 148.0, 144.1, 139.1, 135.4, 129.3, 128.7, 128.6, 128.4, 128.2, 128.1, 127.4, 121.6, 119.6, 119.0, 118.4, 115.9, 113.0, 112.5, 86.3, 79.0, 45.9. HRMS (ESI) m/z calcd for $C_{29}H_{24}N_2OK^+$ [M + K]$^+$ = 455.1520, found = 455.1526.

2-Phenyl-5,5-di-*p*-tolyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4c:**



A colorless oil; 52.8 mg; isolated yield = 66%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 1H), 7.15 – 6.97 (m, 12H), 6.94 – 6.86 (m, 4H), 6.73 – 6.64 (m, 1H), 5.20 (s, 2H), 4.65 (s, 2H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.8, 138.9, 137.9, 134.3, 129.1, 128.5, 127.6, 127.4, 121.9, 119.9, 119.1, 118.2, 116.1, 113.9, 111.2, 85.9, 79.4, 46.1, 21.2. HRMS (ESI) m/z calcd for $C_{31}H_{29}N_2O^+$ [M + H]$^+$ = 445.2274, found = 445.2270.

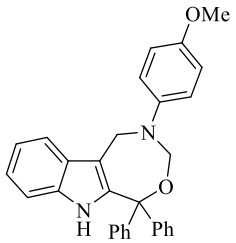
5,5-Bis(4-chlorophenyl)-2-phenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4d:**



A colorless oil; 65.4 mg; isolated yield = 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 1H), 7.22 – 7.15 (m, 5H), 7.13 – 7.07 (m, 5H), 7.01 – 6.92 (m, 6H), 6.74 – 6.67 (m, 1H), 5.19 (s, 2H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.9, 137.0, 134.6, 134.4, 129.8, 129.3, 129.1, 128.9, 128.7, 128.6, 127.3, 122.5, 120.3, 119.3,

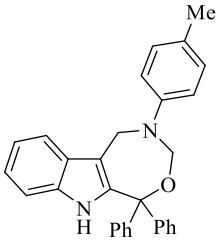
118.3, 115.7, 114.5, 111.3, 84.9, 79.5, 45.9. HRMS (ESI) m/z calcd for $C_{29}H_{23}Cl_2N_2O^+$ $[M + H]^+$ = 485.1182, found = 485.1184.

2-(4-Methoxyphenyl)-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4e:**



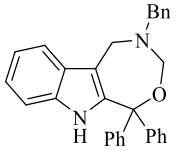
A white solid; 66.7 mg; isolated yield = 83%; m.p. 173.6 -174.0°C; ^{1}H NMR (400 MHz, DMSO) δ 9.60 (s, 1H), 7.79 – 7.65 (m, 1H), 7.39 – 7.29 (m, 7H), 7.15 – 7.09 (m, 2H), 7.07 – 7.02 (m, 2H), 7.01 – 6.95 (m, 4H), 6.86 – 6.73 (m, 2H), 5.17 (s, 2H), 4.65 (s, 2H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 152.9, 144.2, 142.0, 139.3, 135.4, 128.7, 128.6, 128.4, 127.4, 121.6, 119.5, 118.4, 117.7, 114.7, 113.1, 112.4, 86.3, 79.8, 55.6, 46.7. HRMS (ESI) m/z calcd for $C_{30}H_{27}N_2O_2^+$ $[M + H]^+$ = 447.2067, found = 447.2061.

5,5-Diphenyl-2-(*p*-tolyl)-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4f:**



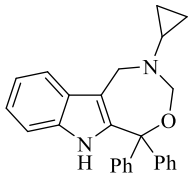
A white solid; 57.3 mg; isolated yield = 74%; m.p. 218.2 -218.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 1H), 7.35 – 7.26 (m, 6H), 7.19 – 7.05 (m, 10H), 7.03 – 6.95 (m, 2H), 5.27 (s, 2H), 4.71 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 143.8, 138.4, 134.4, 129.7, 129.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 122.0, 119.9, 118.2, 116.3, 114.3, 111.2, 86.1, 79.9, 46.4, 20.4. HRMS (ESI) m/z calcd for $C_{30}H_{27}N_2O^+$ $[M + H]^+$ = 431.2118, found = 431.2131.

2-Benzyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4g:**



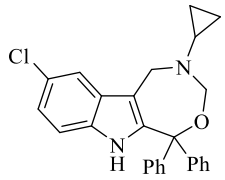
A white solid; 52.7 mg; isolated yield = 68%; m.p. 195.7 -196.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 6.96 (m, 20H), 4.72 (s, 2H), 4.01 (s, 2H), 3.97 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.2, 138.9, 134.6, 129.5, 128.7, 128.5, 128.5, 128.3, 128.2, 127.6, 127.1, 121.9, 119.7, 118.6, 112.8, 111.1, 86.2, 83.8, 53.9, 47.3. HRMS (ESI) m/z calcd for $C_{30}H_{27}N_2O^+$ $[M + H]^+$ = 431.2118, found = 431.2115.

2-Cyclopropyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4h:**



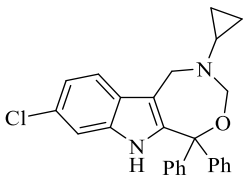
A white solid; 38.3 mg; isolated yield = 56%; m.p. 221.0 -221.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 1H), 7.39 – 7.28 (m, 6H), 7.22 – 7.09 (m, 8H), 4.74 (s, 2H), 4.18 (s, 2H), 2.78 – 2.59 (m, 1H), 0.65 – 0.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 138.5, 134.6, 128.5, 128.4, 128.4, 128.2, 121.9, 119.7, 118.6, 113.7, 111.1, 86.2, 83.3, 48.9, 30.8, 7.3. HRMS (ESI) m/z calcd for $C_{26}H_{25}N_2O^+$ $[M + H]^+$ = 381.1961, found = 381.1974.

9-Chloro-2-cyclopropyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4i:**



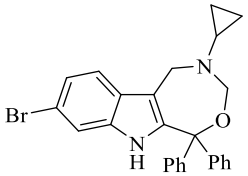
A white solid; 27.6 mg; isolated yield = 37%; m.p. 194.3 -195.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 1H), 7.31 – 7.23 (m, 6H), 7.18 – 7.07 (m, 5H), 7.05 – 6.97 (m, 2H), 4.65 (s, 2H), 4.05 (s, 2H), 2.88 – 2.34 (m, 1H), 0.60 – 0.23 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.2, 134.8, 128.5, 128.4, 128.3, 127.8, 126.9, 120.4, 119.5, 113.8, 111.0, 86.0, 83.2, 48.8, 30.7, 7.3. HRMS (ESI) m/z calcd for $C_{26}H_{24}ClN_2O^+$ $[M + H]^+$ = 415.1572, found = 415.1576.

8-Chloro-2-cyclopropyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4j:**



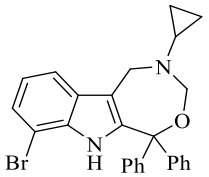
A white solid; 39.5 mg; isolated yield = 53%; m.p. 211.3 -211.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 1H), 7.30 – 7.21 (m, 6H), 7.19 – 7.06 (m, 5H), 7.05 – 6.97 (m, 2H), 4.65 (s, 2H), 4.05 (s, 2H), 2.70 – 2.44 (m, 1H), 0.55 – 0.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.2, 134.8, 128.5, 128.4, 128.3, 127.8, 126.9, 120.4, 119.5, 113.8, 111.0, 86.0, 83.2, 48.8, 30.7, 7.3. HRMS (ESI) m/z calcd for $C_{26}H_{24}ClN_2O^+$ $[M + H]^+$ = 415.1572, found = 415.1570.

8-Bromo-2-cyclopropyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4k:**



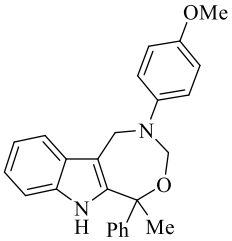
A white solid; 33.8 mg; isolated yield = 41%; m.p. 196.1 -196.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 1H), 7.28 – 7.21 (m, 7H), 7.18 – 7.04 (m, 6H), 4.65 (s, 2H), 4.05 (s, 2H), 2.69 – 2.43 (m, 1H), 0.70 – 0.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.2, 135.2, 128.5, 128.4, 128.3, 127.2, 123.0, 119.9, 115.3, 114.0, 113.8, 86.0, 83.2, 48.7, 30.7, 7.3. HRMS (ESI) m/z calcd for $C_{26}H_{24}BrN_2O^+$ $[M + H]^+$ =459.1067, found = 459.1075.

7-Bromo-2-cyclopropyl-5,5-diphenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4l:**



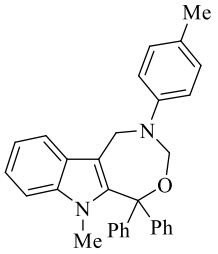
A white solid; 47.0 mg; isolated yield = 57%; m.p. 180.9 -181.6 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 1H), 7.32 – 7.24 (m, 6H), 7.23 – 7.19 (m, 1H), 7.18 – 7.10 (m, 5H), 6.98 – 6.89 (m, 1H), 4.67 (s, 2H), 4.07 (s, 2H), 2.71 – 2.29 (m, 1H), 0.73 – 0.15 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 139.2, 133.2, 129.4, 128.5, 128.4, 128.3, 124.2, 120.9, 117.8, 114.9, 104.6, 86.0, 83.2, 49.0, 30.7, 7.3. HRMS (ESI) m/z calcd for $C_{26}H_{24}BrN_2O^+$ $[M + H]^+$ =459.1067, found = 459.1074.

2-(4-Methoxyphenyl)-5-methyl-5-phenyl-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4m:**



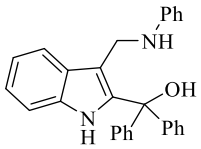
A white solid; 49.1 mg; isolated yield = 71%; m.p. 186.4 -187.2 ºC; ^{1}H NMR (400 MHz, DMSO) δ 10.99 (s, 1H), 7.77 – 7.67 (m, 1H), 7.44 – 7.24 (m, 4H), 7.16 – 6.94 (m, 6H), 6.74 – 6.68 (m, 2H), 5.39 (d, *J* = 12.5 Hz, 1H), 4.94 (d, *J* = 16.2 Hz, 1H), 4.72 (d, *J* = 12.5 Hz, 1H), 4.18 (d, *J* = 16.2 Hz, 1H), 3.61 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 152.8, 144.7, 142.1, 140.1, 135.2, 128.9, 128.1, 127.4, 126.8, 121.5, 119.5, 118.3, 117.4, 114.6, 111.9, 81.0, 79.6, 55.6, 46.2, 30.5. HRMS (ESI) m/z calcd for $C_{25}H_{25}N_2O_2^+$ $[M + H]^+$ =385.1911, found = 385.1908.

6-Methyl-5,5-diphenyl-2-(*p*-tolyl)-2,3,5,6-tetrahydro-1*H*-[1,3]oxazepino[6,5-*b*]indole **4n:**



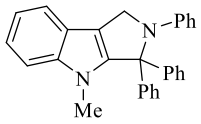
A colorless oil; 60.8 mg; isolated yield = 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.67 (m, 1H), 7.31 – 6.99 (m, 13H), 6.77 – 6.68 (m, 2H), 6.42 – 6.26 (m, 2H), 5.03 (s, 2H), 4.80 (s, 2H), 2.80 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.0, 140.8, 137.5, 129.4, 129.2, 128.2, 128.1, 128.0, 127.2, 126.1, 121.7, 119.5, 118.1, 114.8, 114.6, 109.2, 86.5, 79.2, 43.7, 31.9, 20.3. HRMS (ESI) m/z calcd for $C_{31}H_{29}N_2O^+$ $[M + H]^+$ =445.2274, found = 445.2276.

Diphenyl(3-((phenylamino)methyl)-1*H*-indol-2-yl)methanol **Int-4b:**



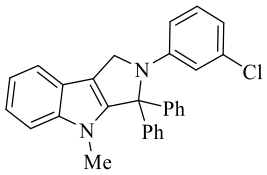
A colorless oil; 97.0 mg; isolated yield = 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.59 (m, 1H), 7.42 – 7.00 (m, 16H), 6.90 – 6.71 (m, 2H), 6.17 (d, *J* = 7.4 Hz, 1H), 4.23 (s, 2H), 3.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 144.6, 136.8, 135.7, 135.3, 128.3, 128.2, 127.5, 126.5, 124.1, 123.1, 121.8, 119.3, 118.4, 110.8, 110.6, 69.5, 29.0. HRMS (ESI) m/z calcd for $C_{28}H_{24}N_2ONa^+$ $[M + Na]^+$ =427.1781, found = 427.1781.

4-Methyl-2,3,3-triphenyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5b′:**



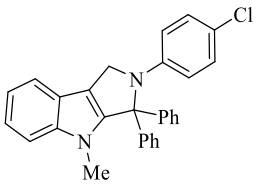
A white solid; 41.6 mg; isolated yield = 52%; m.p. 231.2 -231.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.56 – 7.50 (m, 4H), 7.34 – 7.14 (m, 9H), 7.10 – 7.00 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 4.96 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 145.2, 141.4, 139.4, 129.0, 128.4, 128.3, 127.4, 121.9, 121.3, 119.9, 119.2, 116.4, 114.3, 111.2, 109.9, 74.3, 49.4, 30.8. HRMS (ESI) m/z calcd for $C_{29}H_{25}N_2^+$ $[M + H]^+$ = 401.2012, found = 401.2020.

2-(3-Chlorophenyl)-4-methyl-3,3-diphenyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5c′:**



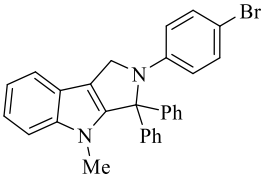
A colorless oil; 51.2 mg; isolated yield = 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.9 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.36 – 7.13 (m, 9H), 6.95 – 6.84 (m, 1H), 6.76 – 6.65 (m, 1H), 6.63 – 6.44 (m, 2H), 4.94 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.2, 141.5, 138.8, 134.4, 129.1, 128.9, 128.4, 127.7, 121.8, 121.5, 120.0, 119.2, 116.3, 113.8, 112.6, 110.7, 109.9, 74.5, 49.7, 30.9. HRMS (ESI) m/z calcd for $C_{29}H_{24}ClN_2^+$ $[M + H]^+$ = 435.1623, found = 435.1621.

2-(4-Chlorophenyl)-4-methyl-3,3-diphenyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5d′:**



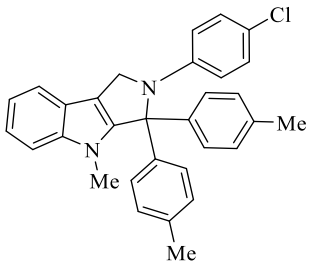
A white solid; 46.0 mg; isolated yield = 53%; m.p. 228.1 -228.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 1H), 7.54 – 7.45 (m, 4H), 7.37 – 7.14 (m, 9H), 6.98 (d, *J* = 9.1 Hz, 2H), 6.57 (d, *J* = 9.1 Hz, 2H), 4.93 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 143.7, 141.5, 139.0, 128.9, 128.4, 128.3, 127.6, 121.8, 121.4, 121.4, 120.0, 119.2, 115.3, 110.9, 109.9, 74.4, 49.6, 30.8. HRMS (ESI) m/z calcd for $C_{29}H_{24}ClN_2^+$ $[M + H]^+$ = 435.1623, found = 435.1631.

2-(4-Bromophenyl)-4-methyl-3,3-diphenyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5e′:**



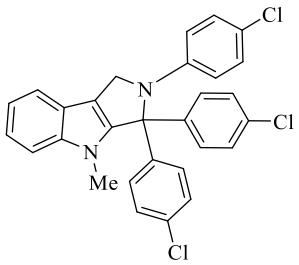
A colorless oil; 45.9 mg; isolated yield = 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 4H), 7.33 – 7.08 (m, 11H), 6.53 (d, *J* = 9.0 Hz, 2H), 4.92 (s, 2H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 144.1, 141.5, 139.0, 131.1, 128.9, 128.4, 127.7, 121.8, 121.5, 120.0, 119.2, 115.8, 110.9, 109.,9, 108.7, 74.4, 49.6, 30.9. HRMS (ESI) m/z calcd for $C_{29}H_{24}BrN_2^+$ $[M + H]^+$ = 479.1118, found = 479.1125.

2-(4-Chlorophenyl)-4-methyl-3,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5f′:**



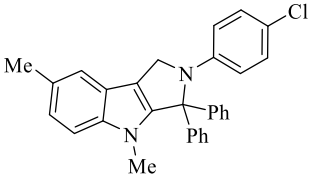
A white solid; 47.1 mg; isolated yield = 51%; m.p. 183.7 -184.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 4H), 7.25 – 7.06 (m, 7H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 4.90 (s, 2H), 3.28 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.8, 141.5, 137.3, 136.1, 129.1, 128.9, 128.2, 121.9, 121.3, 121.2, 119.9, 119.2, 115.2, 110.7, 109.9, 74.1, 49.6, 30.8, 21.1. HRMS (ESI) m/z calcd for $C_{31}H_{28}ClN_2^+$ $[M + H]^+$ = 463.1936, found = 463.1930.

2,3,3-Tris(4-chlorophenyl)-4-methyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5g′:**



A colorless oil; 54.2 mg; isolated yield = 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 4H), 7.31 – 7.15 (m, 7H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.52 (d, *J* = 9.1 Hz, 2H), 4.90 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 143.2, 141.5, 137.3, 133.8, 130.1, 128.7, 128.5, 122.2, 121.9, 121.7, 120.2, 119.3, 115.5, 111.4, 110.0, 73.6, 49.6, 30.9. HRMS (ESI) m/z calcd for $C_{29}H_{22}Cl_3N_2^+$ $[M + H]^+$ = 503.0843, found = 503.0846.

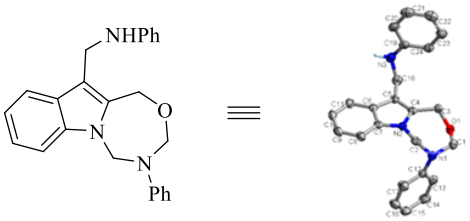
2-(4-Chlorophenyl)-4,7-dimethyl-3,3-diphenyl-1,2,3,4-tetrahydropyrrolo[3,4-*b*]indole **5h′**:



A white solid; 50.2 mg; isolated yield = 56%; m.p. 219.7 -220.3 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 4H), 7.42 – 7.20 (m, 7H), 7.16 – 7.08 (m, 1H), 7.06 – 6.94 (m, 3H), 6.69 – 6.44 (m, 2H), 4.89 (s, 2H), 3.26 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 143.7, 139.9, 139.1, 129.3, 128.9, 128.4, 128.2, 127.6, 122.9, 121.9, 121.3, 118.9, 115.2, 110.4, 109.6, 74.4, 49.6, 30.8, 21.4. HRMS (ESI) m/z calcd for $C_{30}H_{26}ClN_2^+$ $[M + H]^+$ = 449.1779, found = 449.1773.

4. X-ray single crystal data for compounds

Compound 3a:

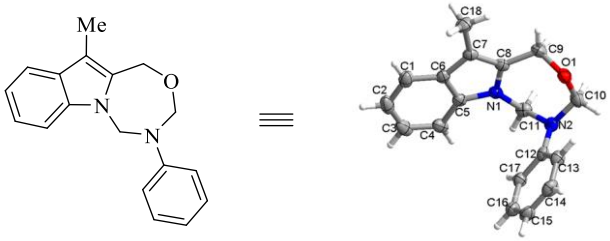


CCDC: 2312830 for **3a**

Table S1 Crystal data and structure refinement for 202305104_auto.

Identification code	202305104_auto
Empirical formula	$C_{24}H_{23}N_3O$
Formula weight	369.45
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.5178(5)
b/Å	24.0991(12)
c/Å	9.5851(5)
α/°	90
β/°	103.099(5)
γ/°	90
Volume/Å^3	1916.34(18)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	0.625
F(000)	784.0
Crystal size/mm^3	0.16 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.336 to 134.16
Index ranges	$-10 \le h \le 6$, $-28 \le k \le 28$, $-10 \le l \le 11$
Reflections collected	6618
Independent reflections	3401 [R_{int} = 0.0339, R_{sigma} = 0.0490]
Data/restraints/parameters	3401/0/257
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1210
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.1385
Largest diff. peak/hole / e Å^{-3}	0.14/-0.16

Compound 3b:

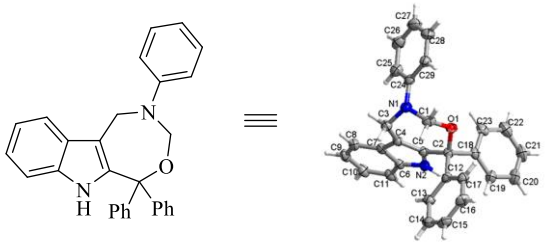


CCDC: 2312831 for **3b**

Table S2 Crystal data and structure refinement for 202305125_auto.

Identification code	202305125_auto
Empirical formula	$C_{18}H_{18}N_2O$
Formula weight	278.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	15.8575(6)
b/Å	12.2410(4)
c/Å	14.9618(6)
α/°	90
β/°	90.113(4)
γ/°	90
Volume/Å^3	2904.24(18)
Z	8
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.628
F(000)	1184.0
Crystal size/mm^3	0.18 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.126 to 134.13
Index ranges	-16 ≤ h ≤ 18, -8 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	5200
Independent reflections	2520 [R_{int}= 0.0219, R_{sigma}= 0.0288]
Data/restraints/parameters	2520/0/191
Goodness-of-fit on F^2	1.051
Final R indexes [I>= 2σ (I)]	R_1 = 0.0477, wR_2 = 0.1242
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	0.12/-0.17

Compound 4b:

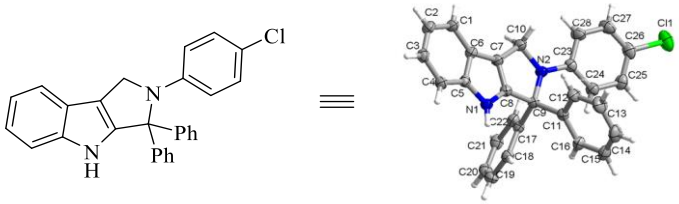


CCDC: 2312832 for **4b**

Table S3 Crystal data and structure refinement for 202308209_auto.

Identification code	202308209_auto
Empirical formula	$C_{61}H_{55}N_4O_2$
Formula weight	876.09
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.5803(4)
b/Å	12.2092(5)
c/Å	19.4505(8)
α/°	81.720(4)
β/°	79.349(4)
γ/°	73.665(4)
Volume/Å^3	2358.29(18)
Z	2
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	0.578
F(000)	930.0
Crystal size/mm^3	0.18 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.582 to 134.156
Index ranges	-9 ≤ h ≤ 12, -12 ≤ k ≤ 14, -20 ≤ l ≤ 23
Reflections collected	16507
Independent reflections	8342 [R_{int} = 0.0289, R_{sigma} = 0.0433]
Data/restraints/parameters	8342/19/605
Goodness-of-fit on F^2	1.021
Final R indexes [I > = 2σ (I)]	R_1 = 0.0531, wR_2 = 0.1386
Final R indexes [all data]	R_1 = 0.0705, wR_2 = 0.1532
Largest diff. peak/hole / e Å^{-3}	0.31/-0.26

Compound 5d:



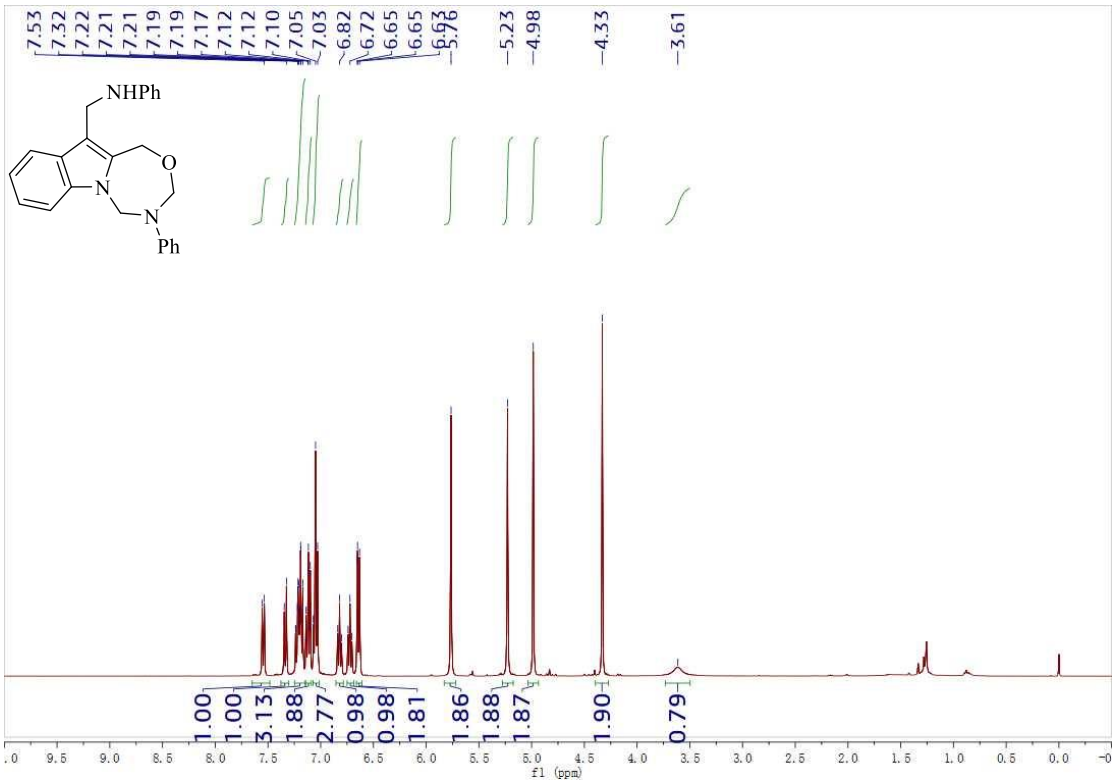
CCDC: 2312833 for **5d**

Table S4 Crystal data and structure refinement for 202309232.

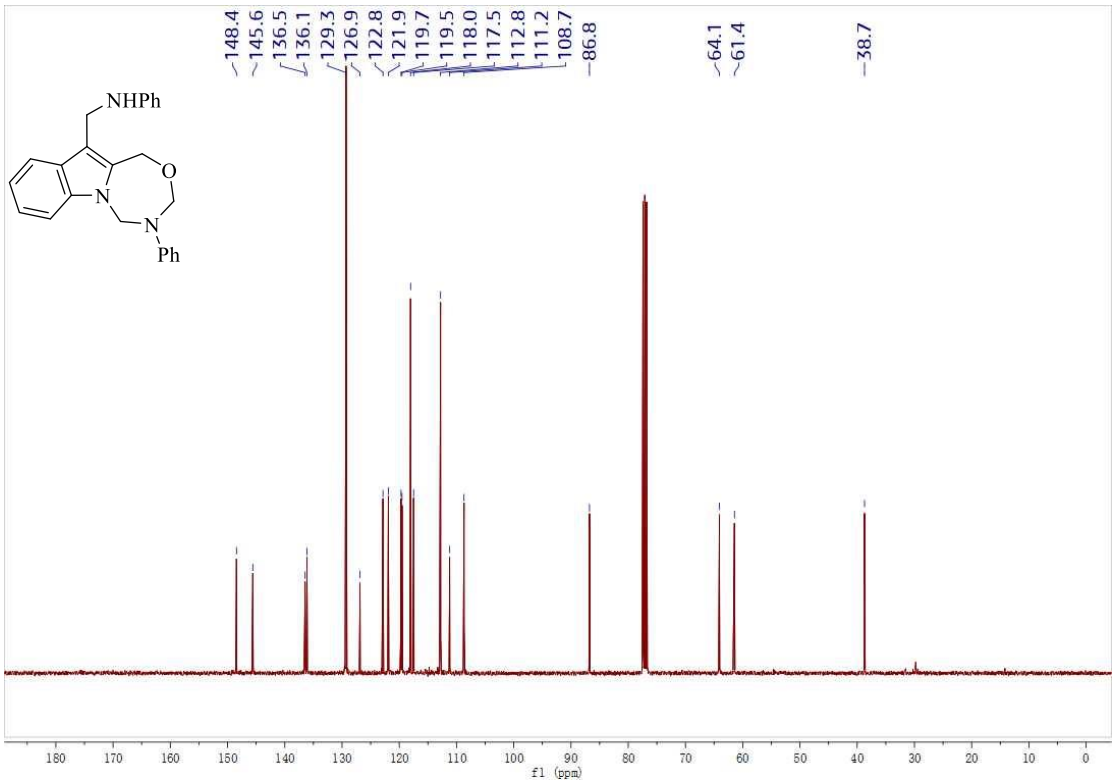
Identification code	202309232
Empirical formula	$C_{32}H_{31}ClN_2O$
Formula weight	495.04
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.9507(5)
b/Å	10.9932(4)
c/Å	13.1900(8)
α/°	87.051(4)
β/°	68.775(5)
γ/°	84.170(4)
Volume/Å^3	1337.86(12)
Z	2
ρ_{calc}g/cm^3	1.229
μ/mm^{-1}	1.463
F(000)	524.0
Crystal size/mm^3	0.15 × 0.11 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.19 to 134.158
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	9187
Independent reflections	4752 [R_{int} = 0.0255, R_{sigma} = 0.0399]
Data/restraints/parameters	4752/3/335
Goodness-of-fit on F^2	1.035
Final R indexes [I > = 2σ (I)]	R_1 = 0.0513, wR_2 = 0.1351
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1512
Largest diff. peak/hole / e Å^{-3}	0.23/-0.23

5. NMR Spectra

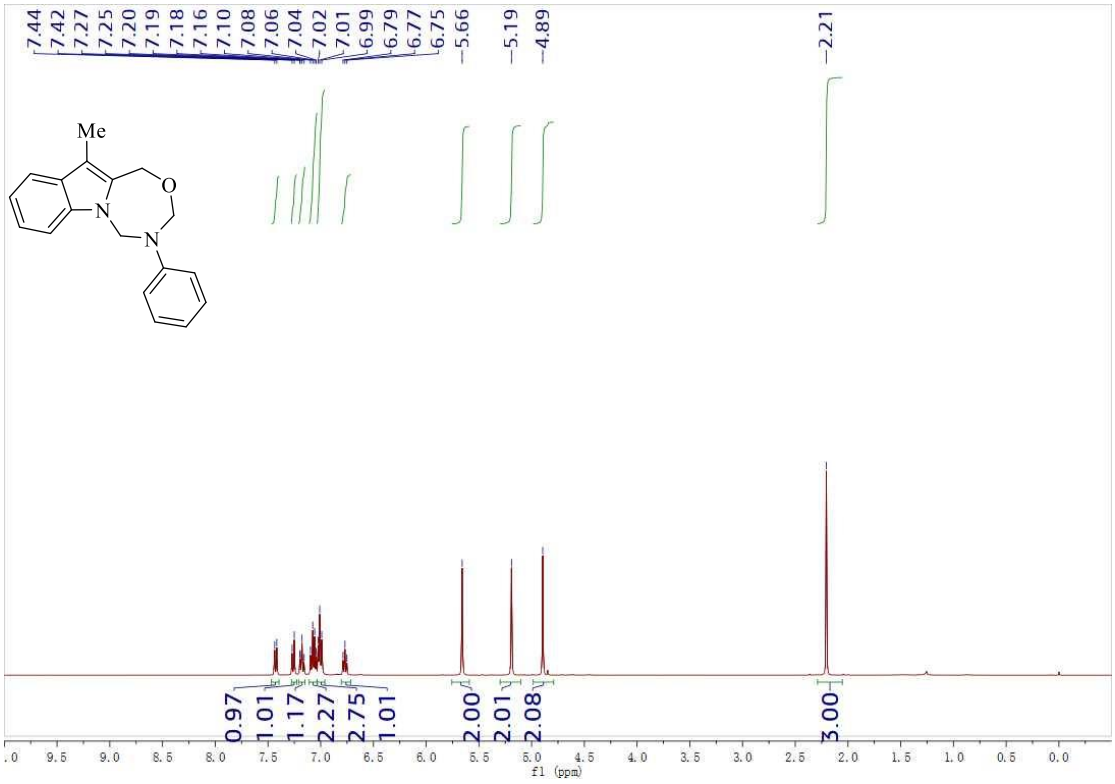
3a ^{1}H NMR (400 MHz, $CDCl_3$)



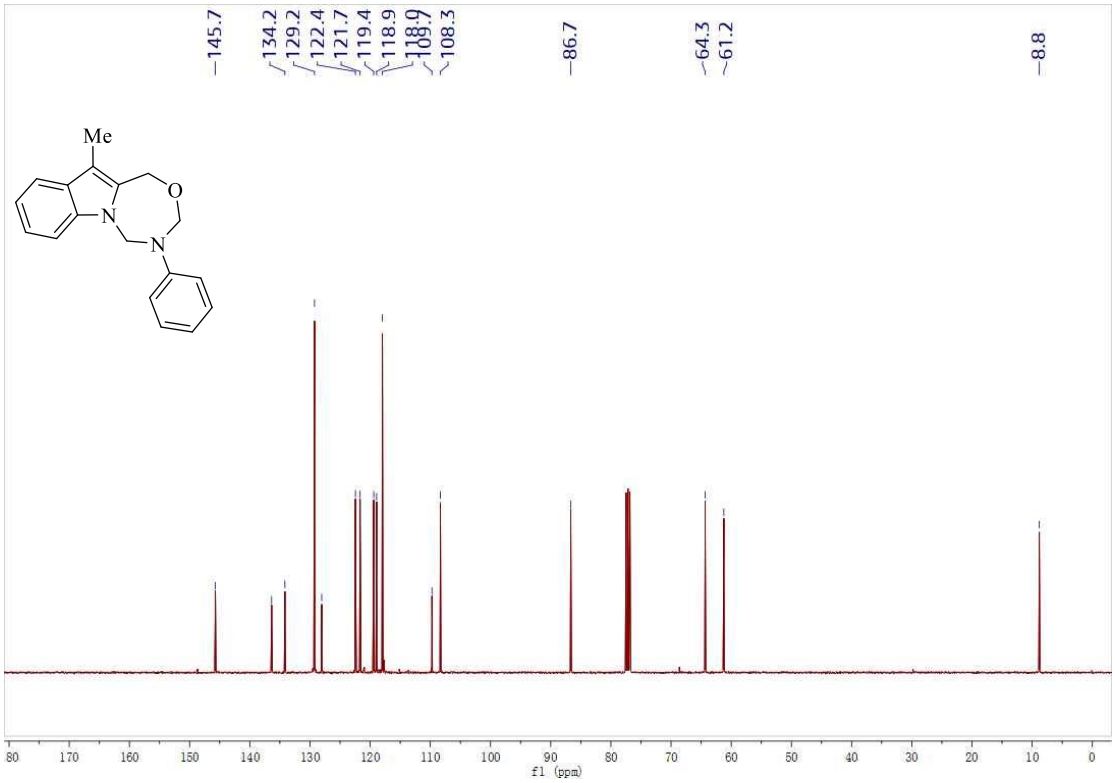
3a ^{13}C NMR (100 MHz, $CDCl_3$)



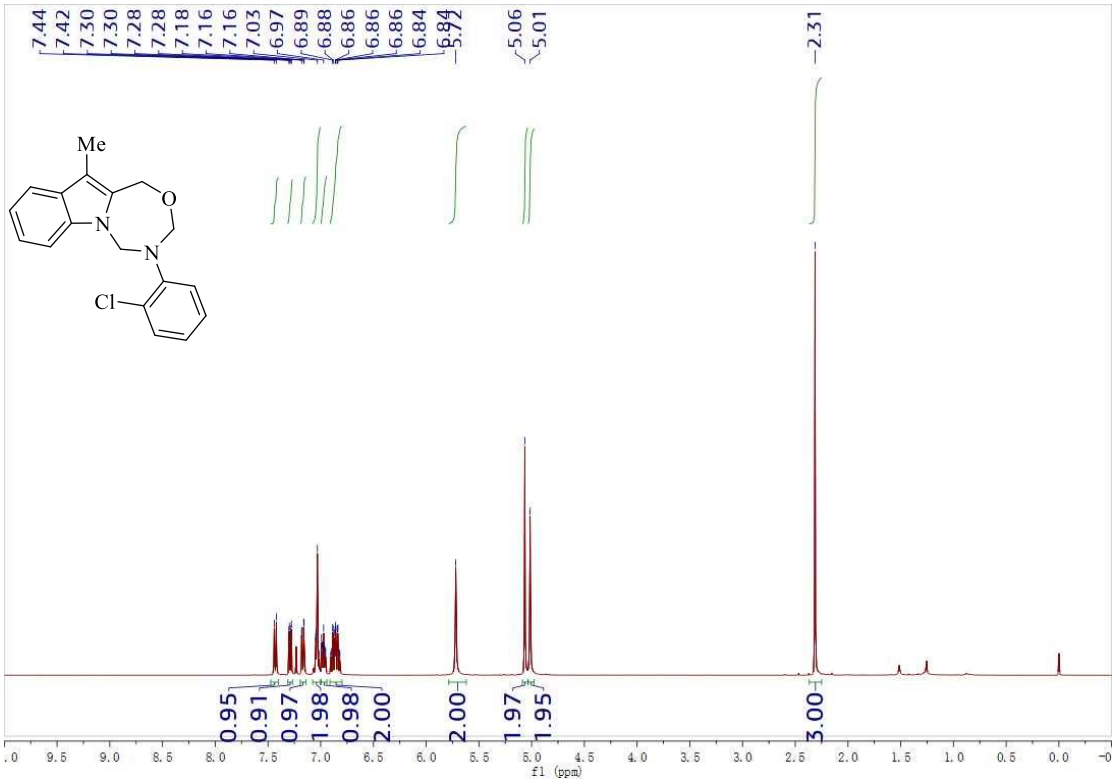
3b ^{1}H NMR (400 MHz, $CDCl_3$)



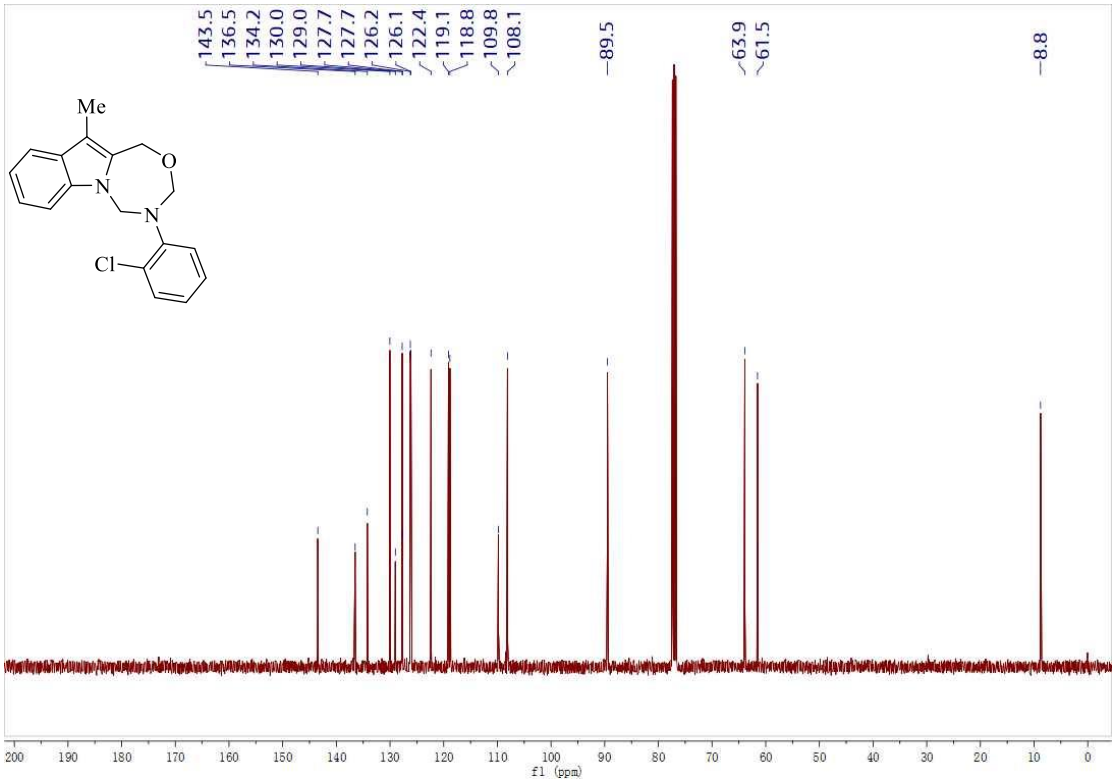
3b ^{13}C NMR (100 MHz, $CDCl_3$)



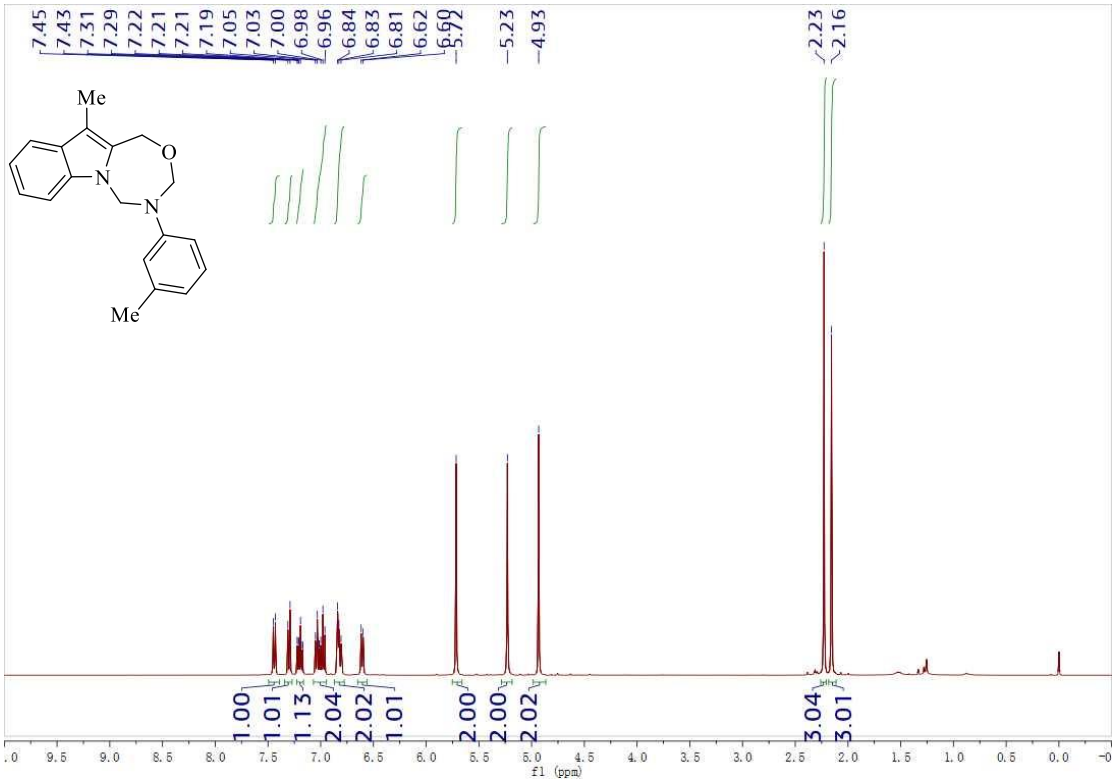
3c ^{1}H NMR (400 MHz, $CDCl_3$)



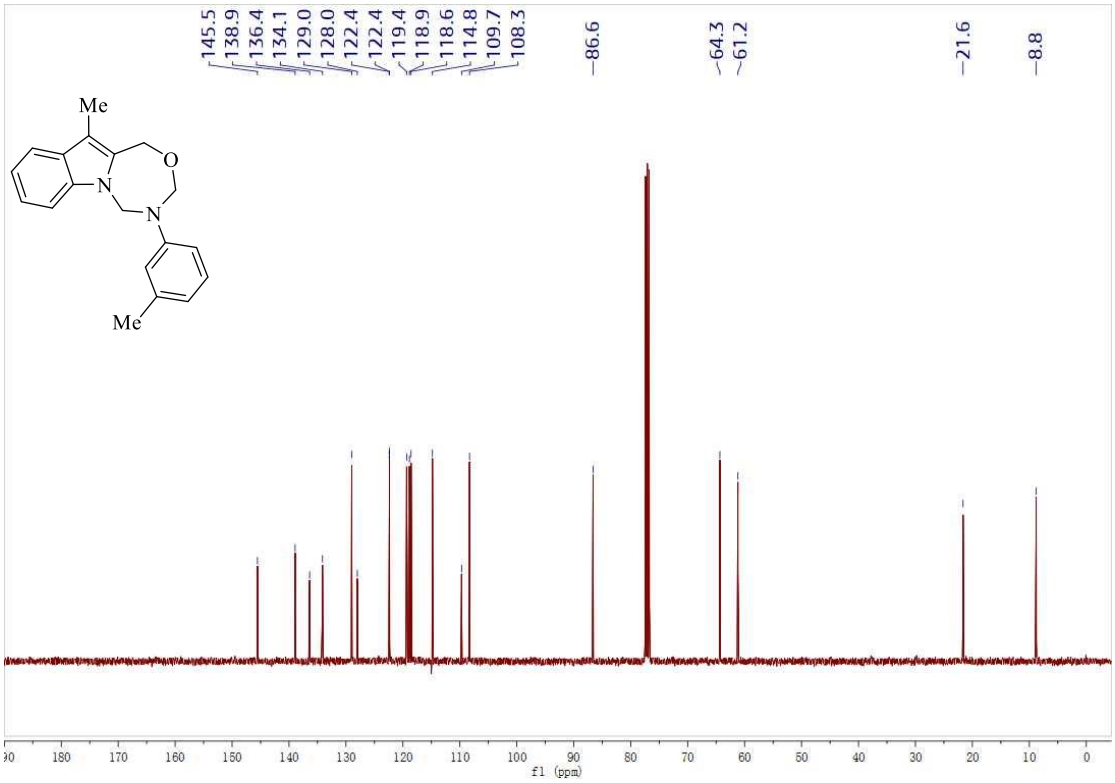
3c ^{13}C NMR (100 MHz, $CDCl_3$)



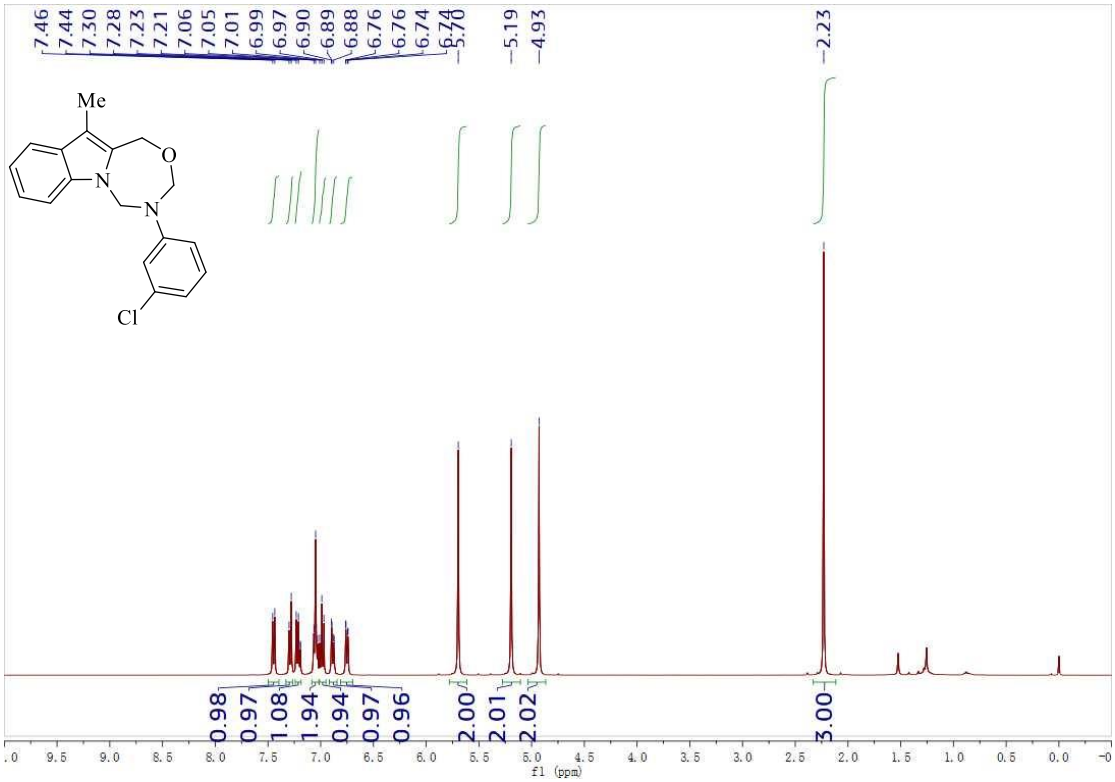
3d ^{1}H NMR (400 MHz, $CDCl_3$)



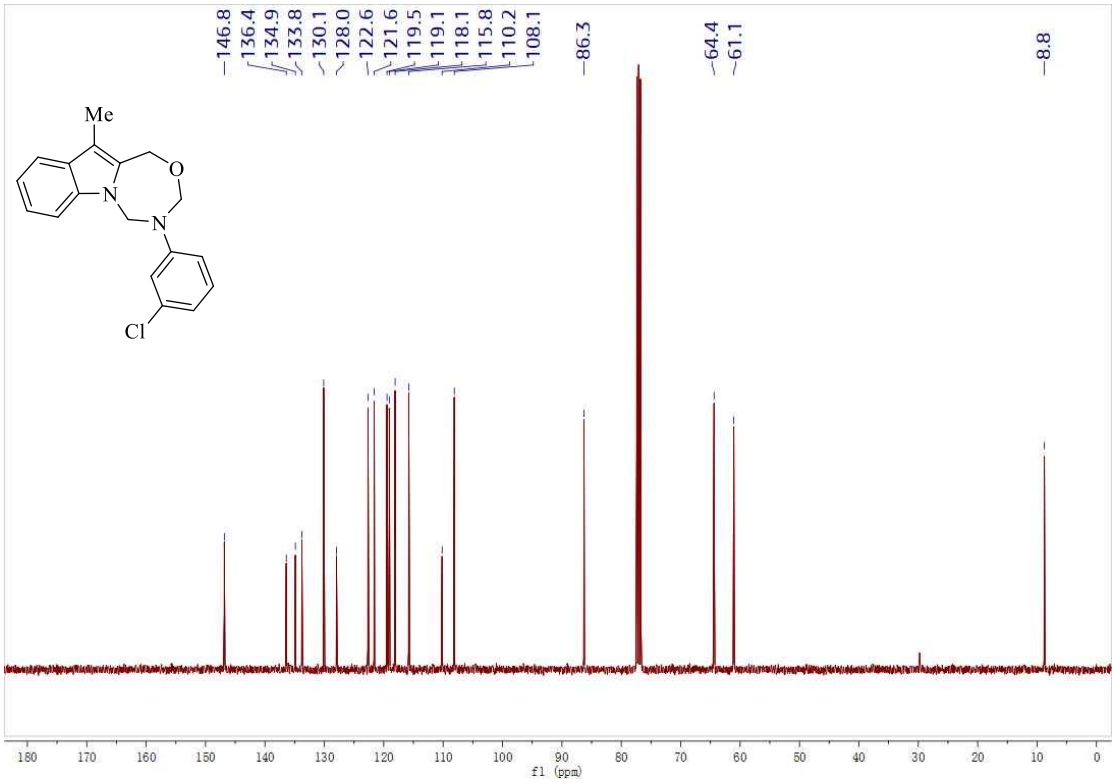
3d ^{13}C NMR (100 MHz, $CDCl_3$)



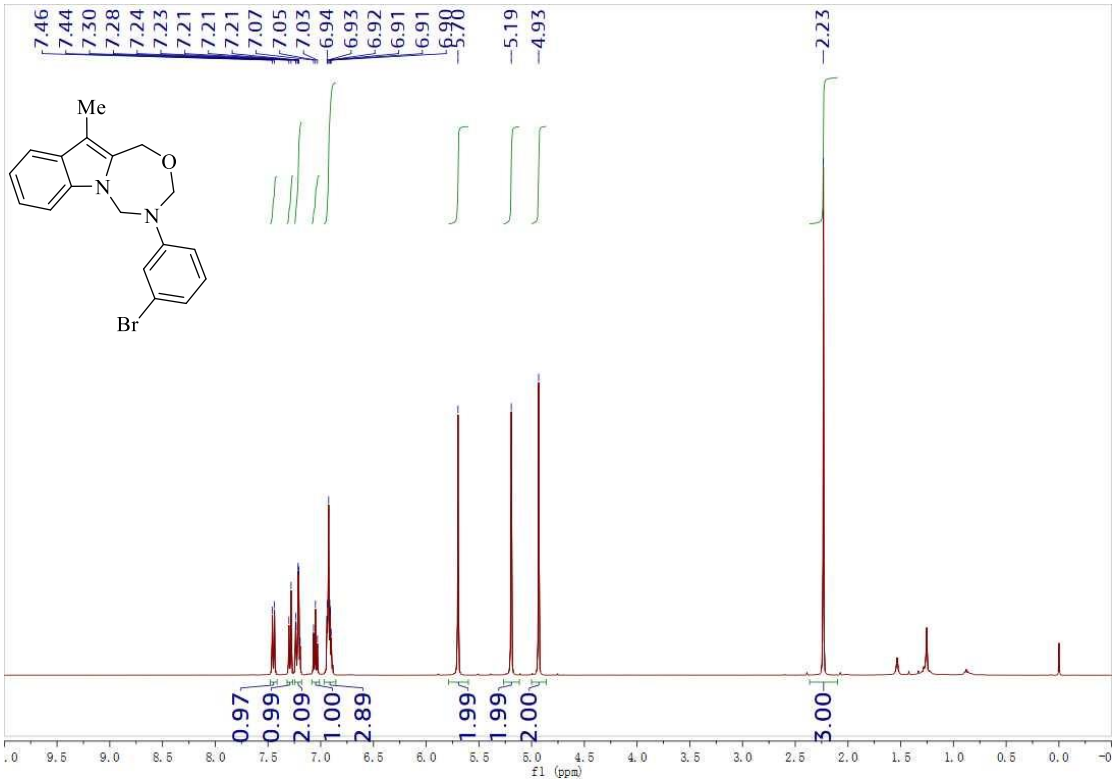
3e ^{1}H NMR (400 MHz, $CDCl_3$)



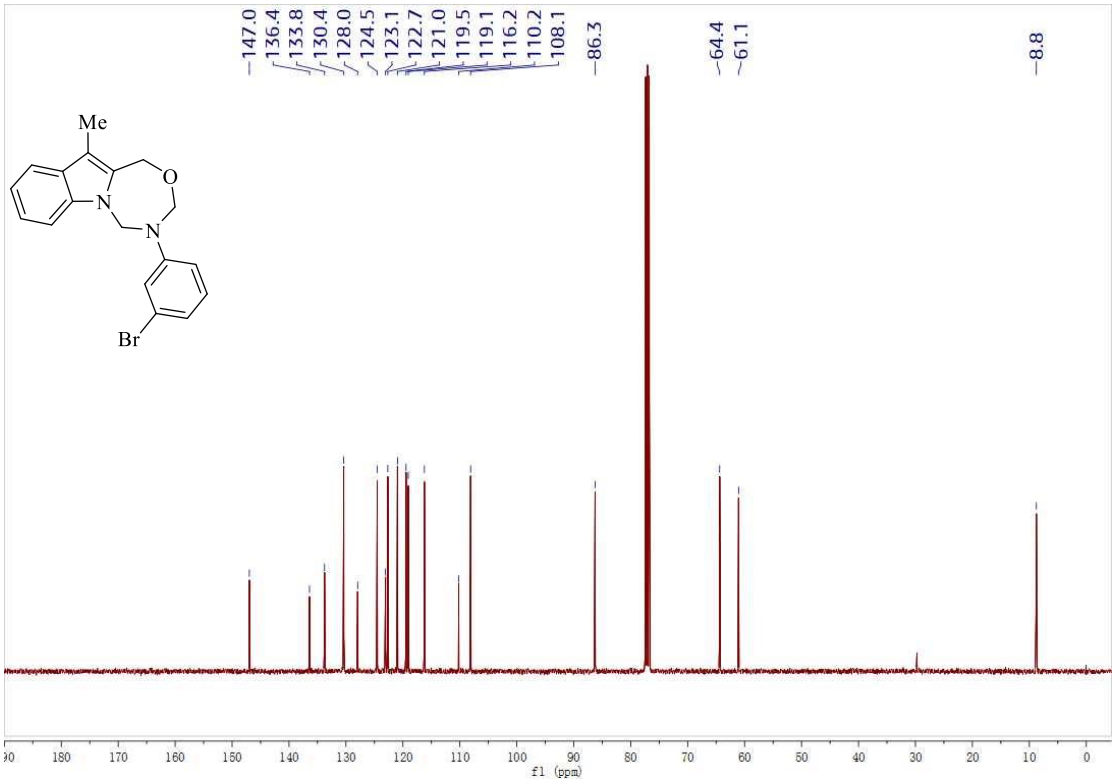
3e ^{13}C NMR (100 MHz, $CDCl_3$)



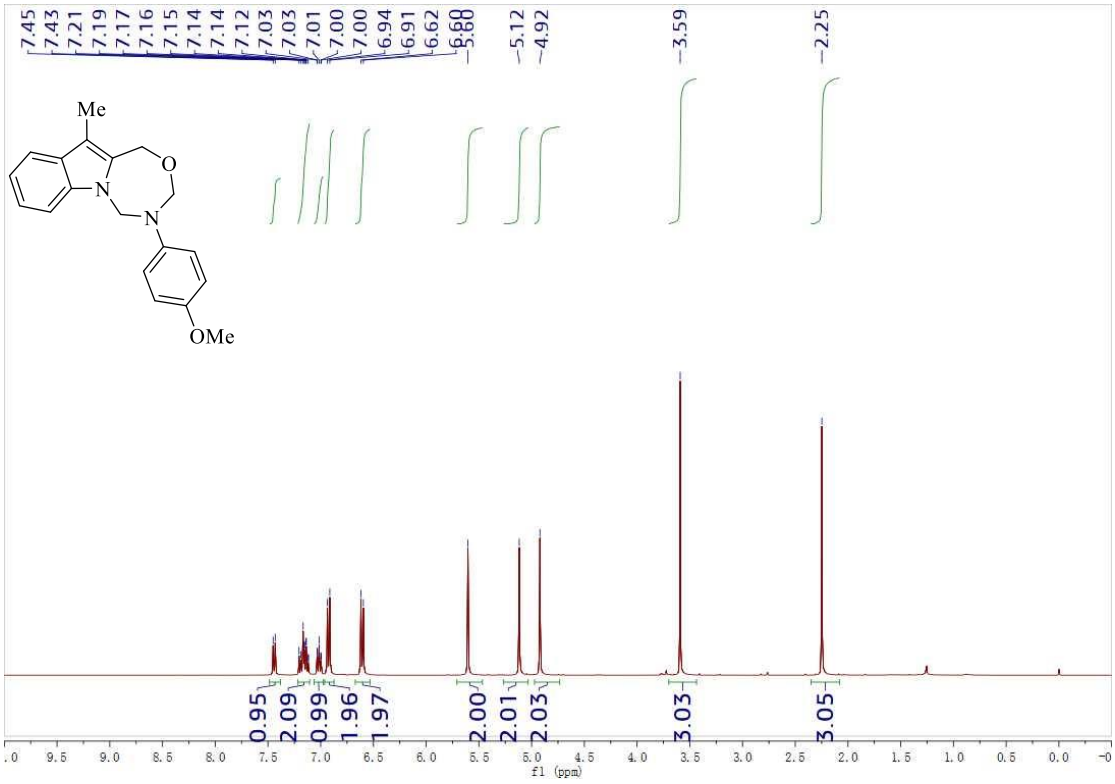
3f ^{1}H NMR (400 MHz, $CDCl_3$)



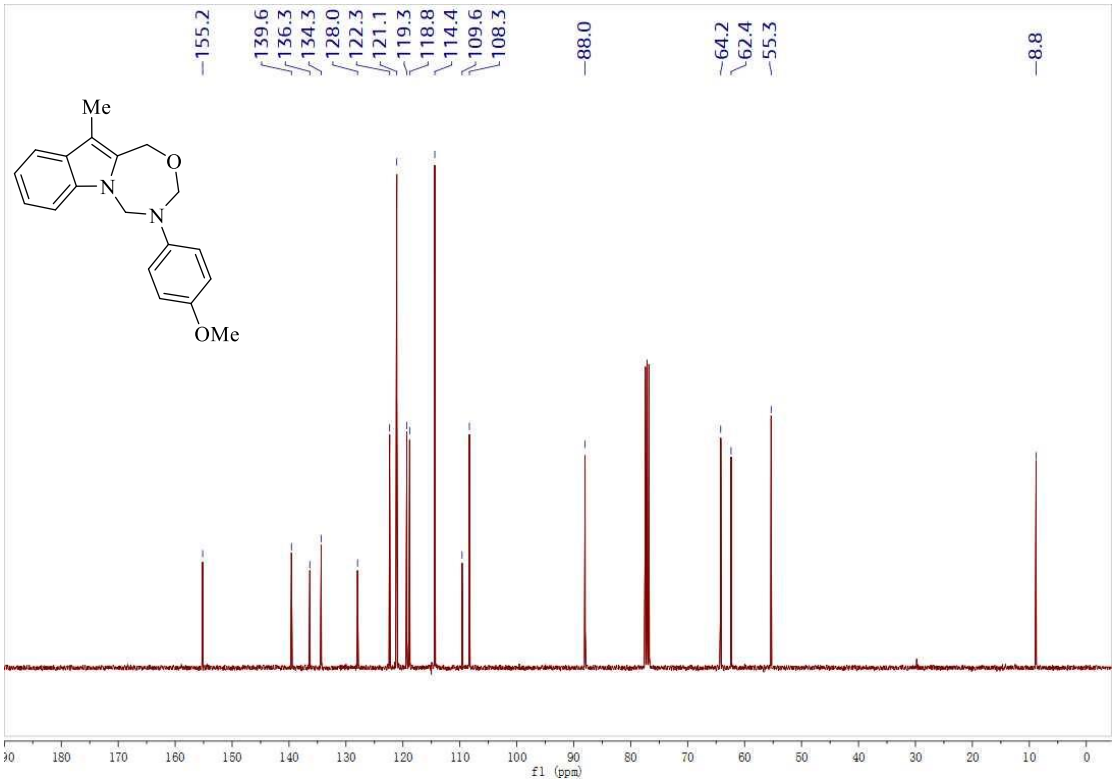
3f ^{13}C NMR (100 MHz, $CDCl_3$)



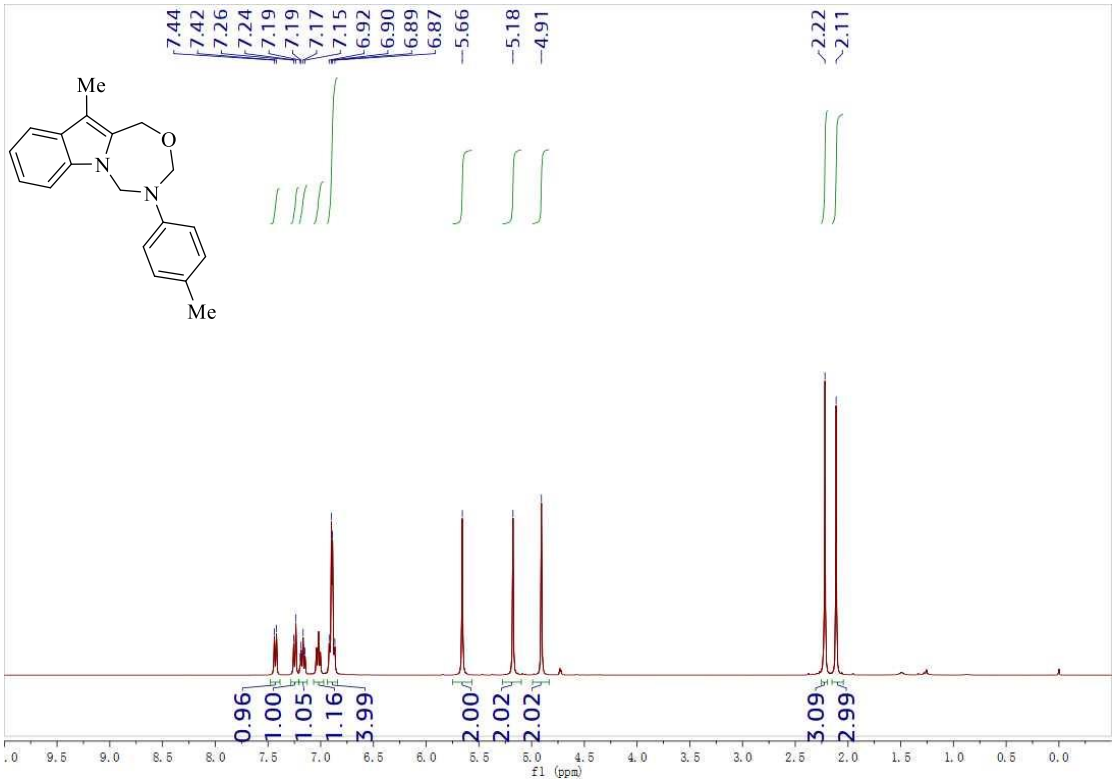
3g ^{1}H NMR (400 MHz, $CDCl_3$)



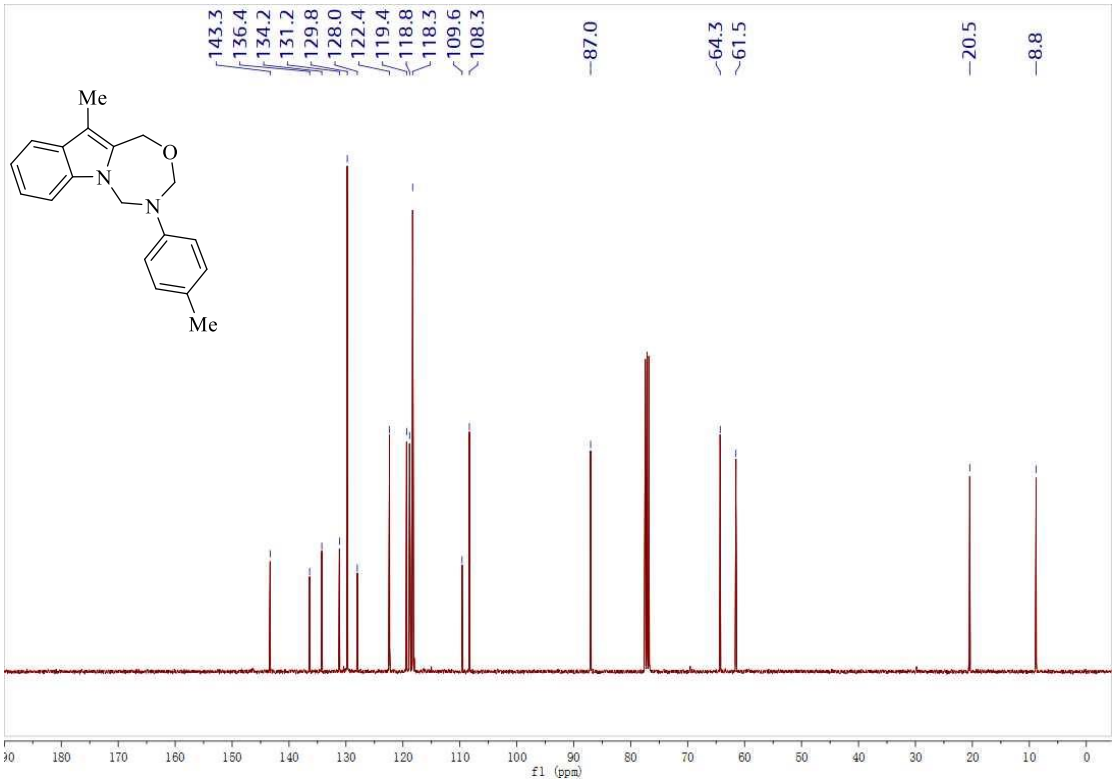
3g ^{13}C NMR (100 MHz, $CDCl_3$)



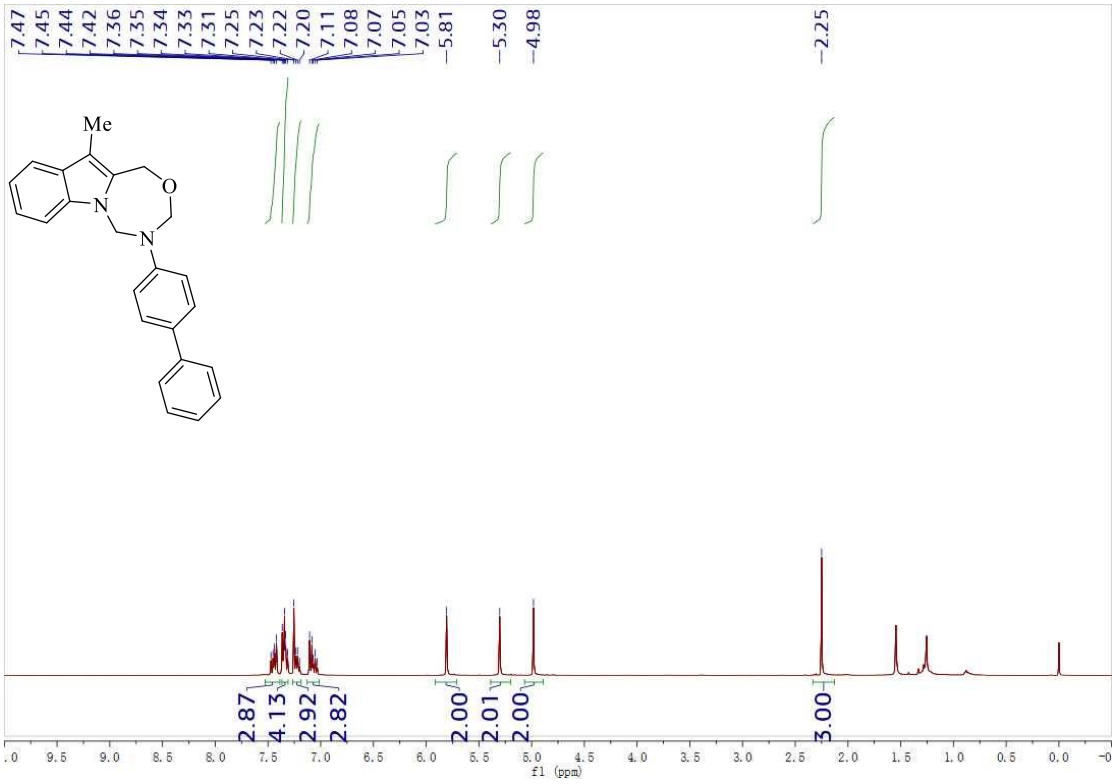
3h ^{1}H NMR (400 MHz, $CDCl_3$)



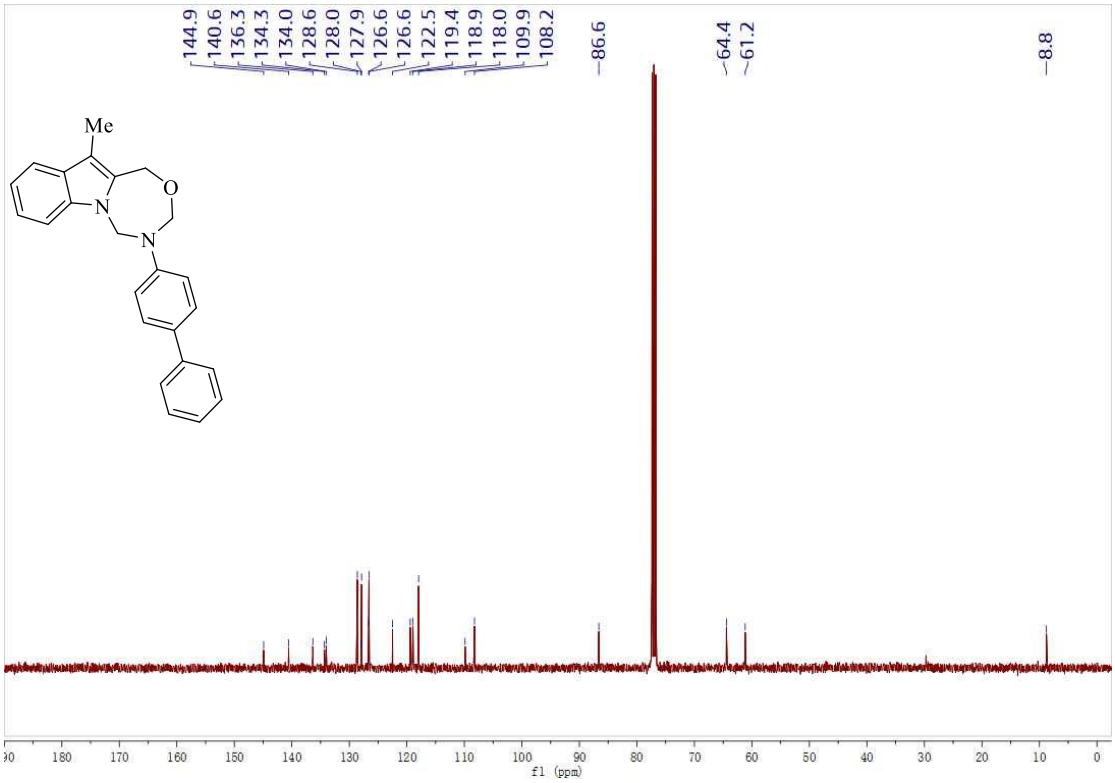
3h ^{13}C NMR (100 MHz, $CDCl_3$)



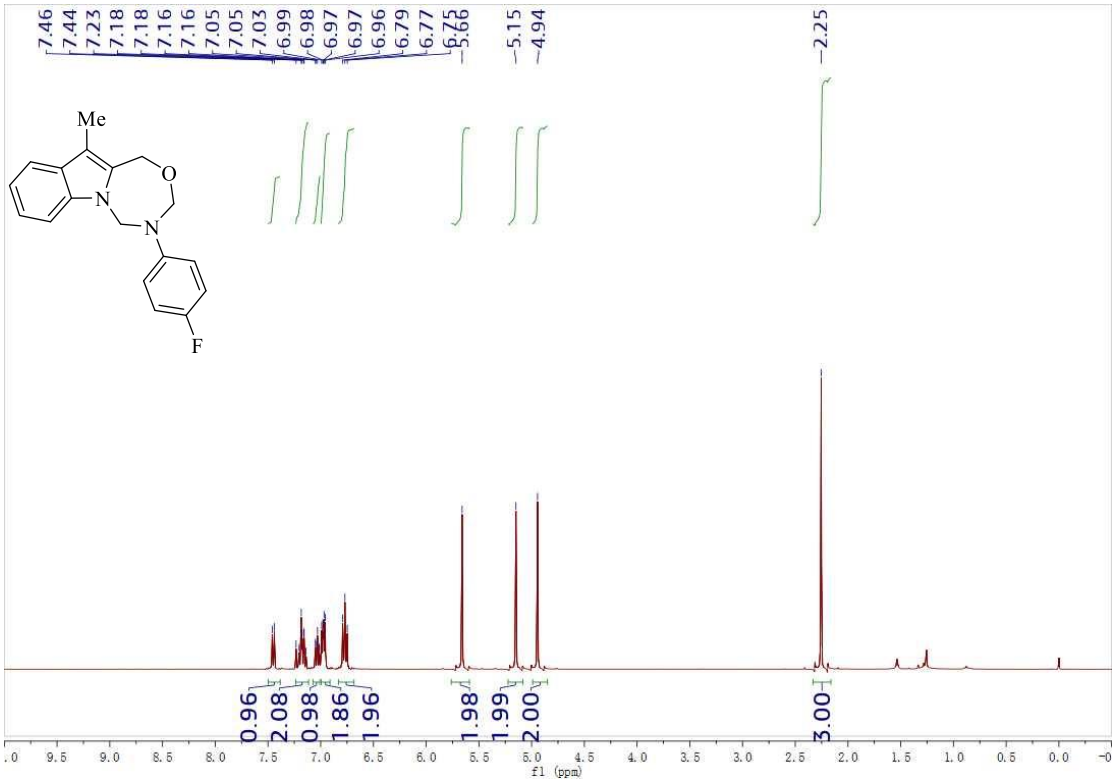
3i ^{1}H NMR (400 MHz, $CDCl_3$)



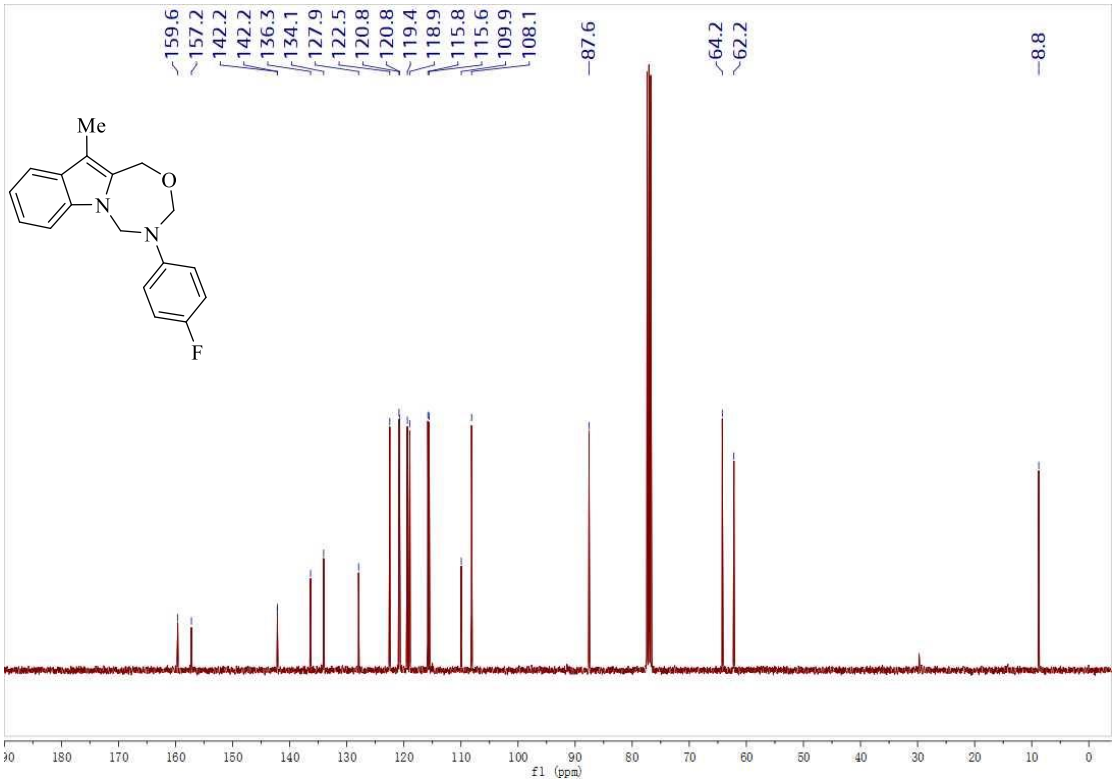
3i ^{13}C NMR (100 MHz, $CDCl_3$)



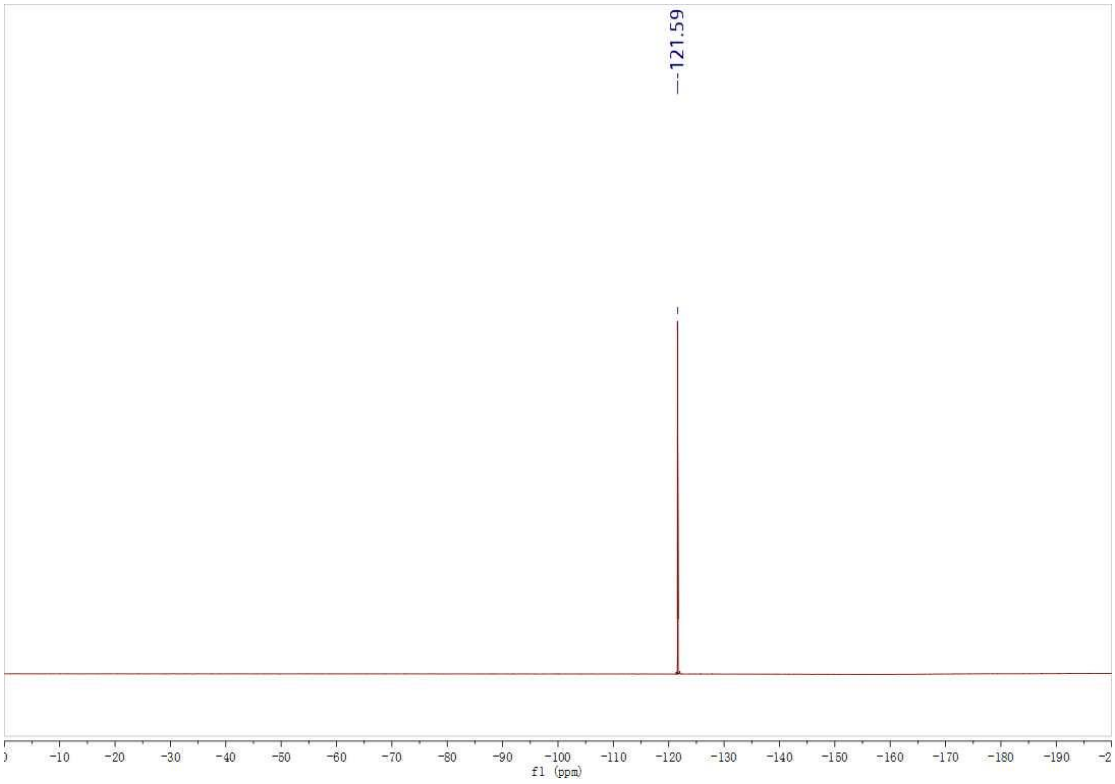
3j ^{1}H NMR (400 MHz, $CDCl_3$)



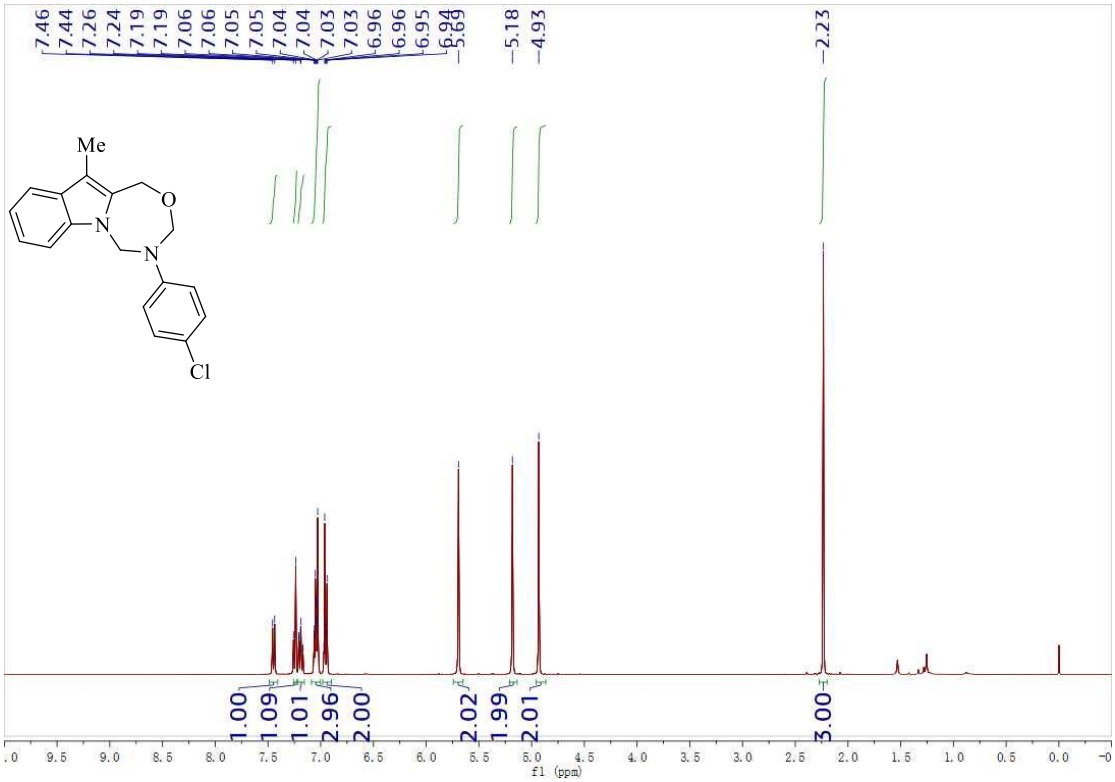
3j ^{13}C NMR (100 MHz, $CDCl_3$)



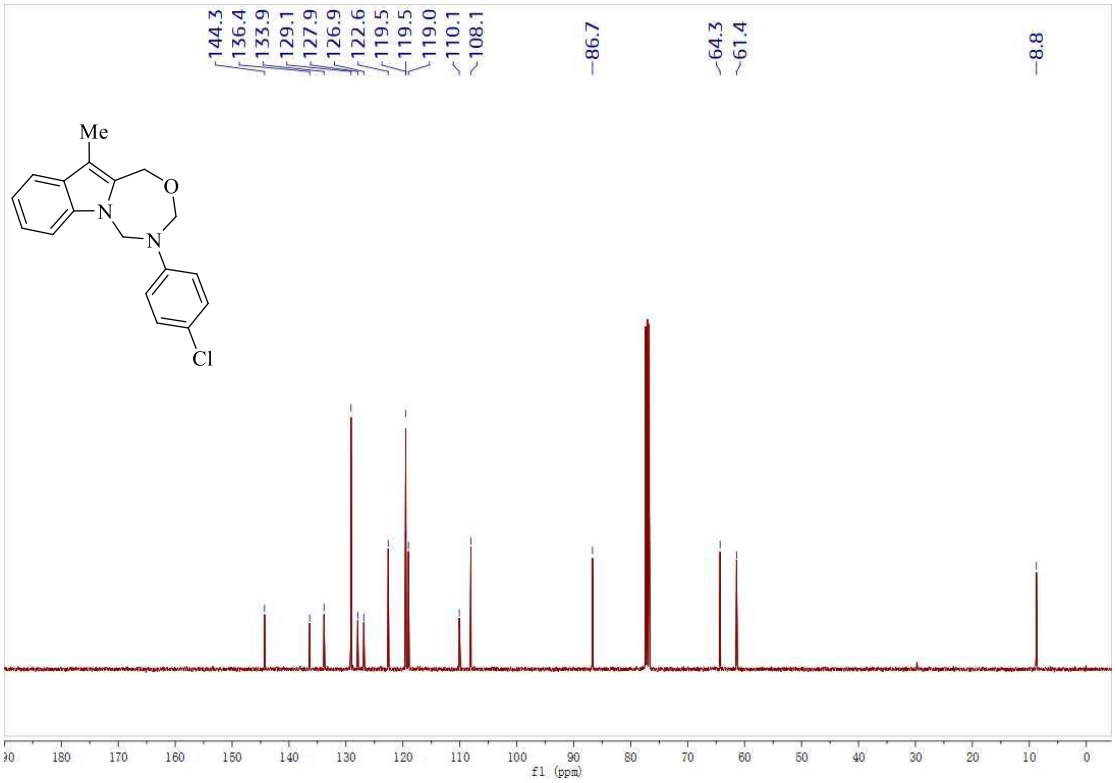
3j ^{19}F NMR (376 MHz, $CDCl_3$)



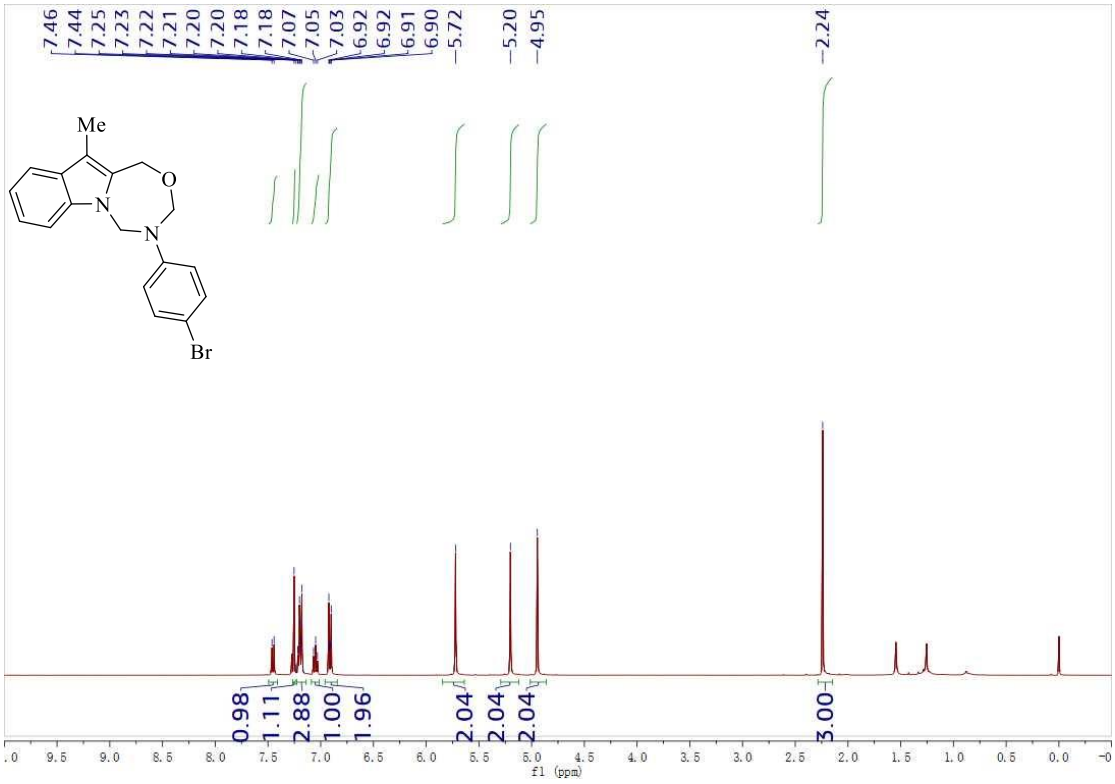
3k ^{1}H NMR (400 MHz, $CDCl_3$)



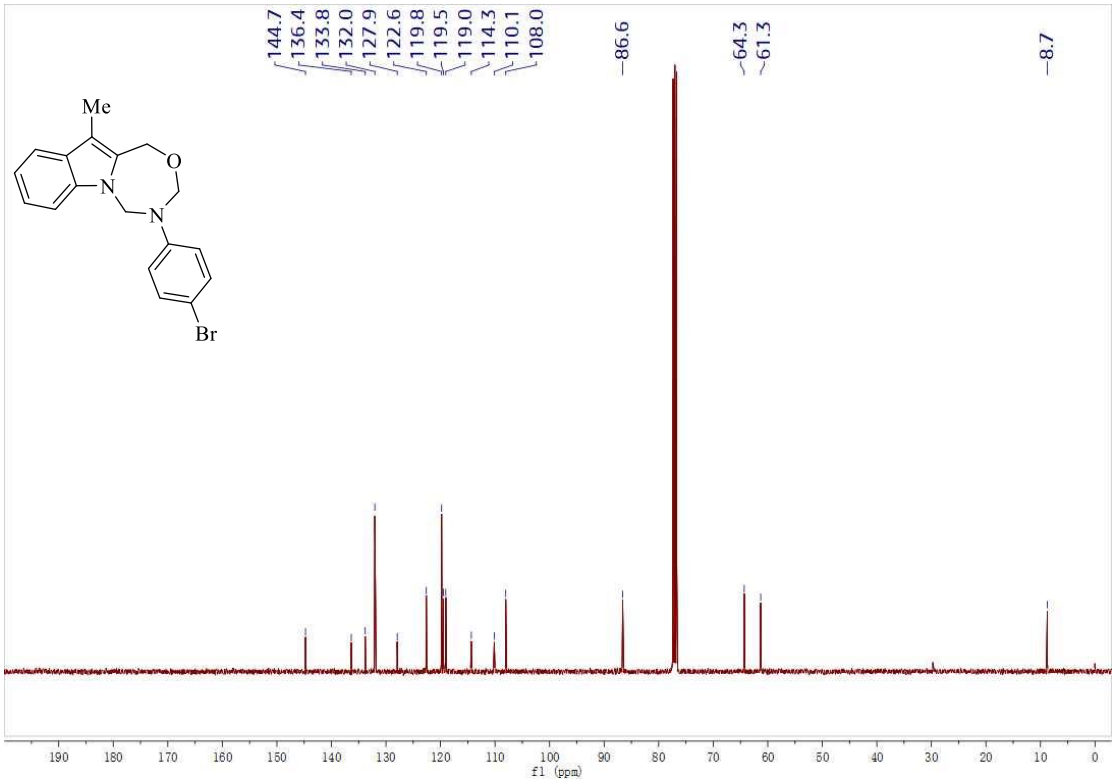
3k ^{13}C NMR (100 MHz, $CDCl_3$)



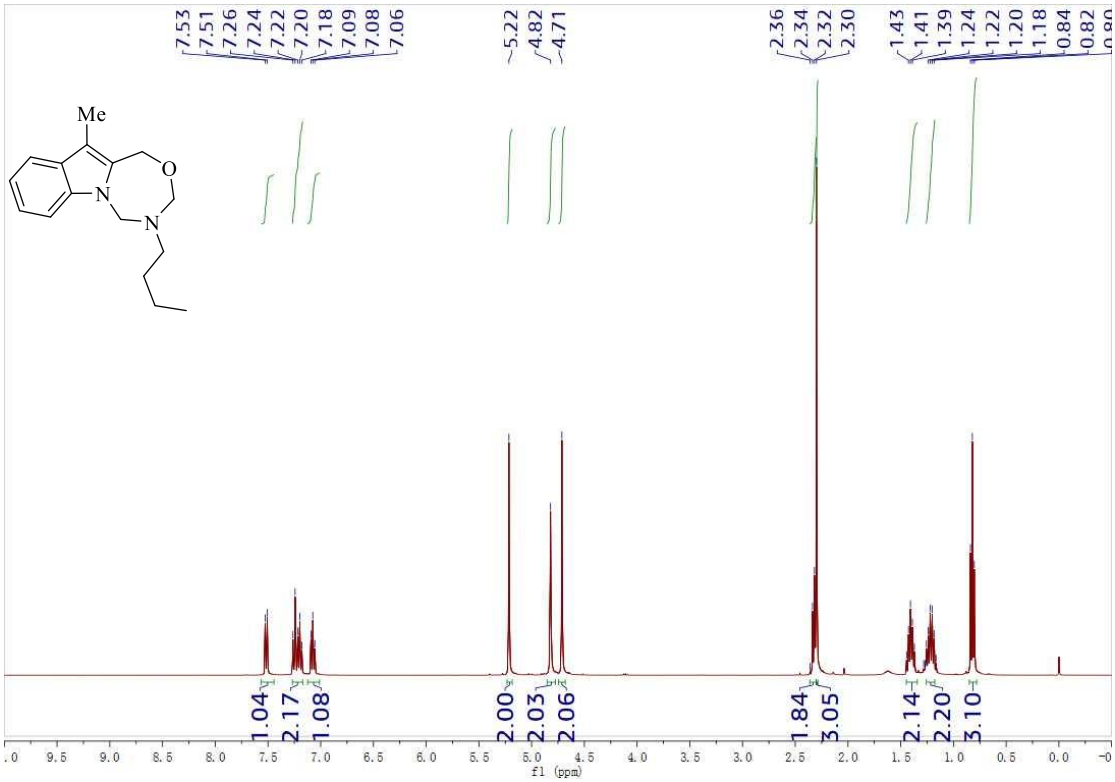
3l ^{1}H NMR (400 MHz, $CDCl_3$)



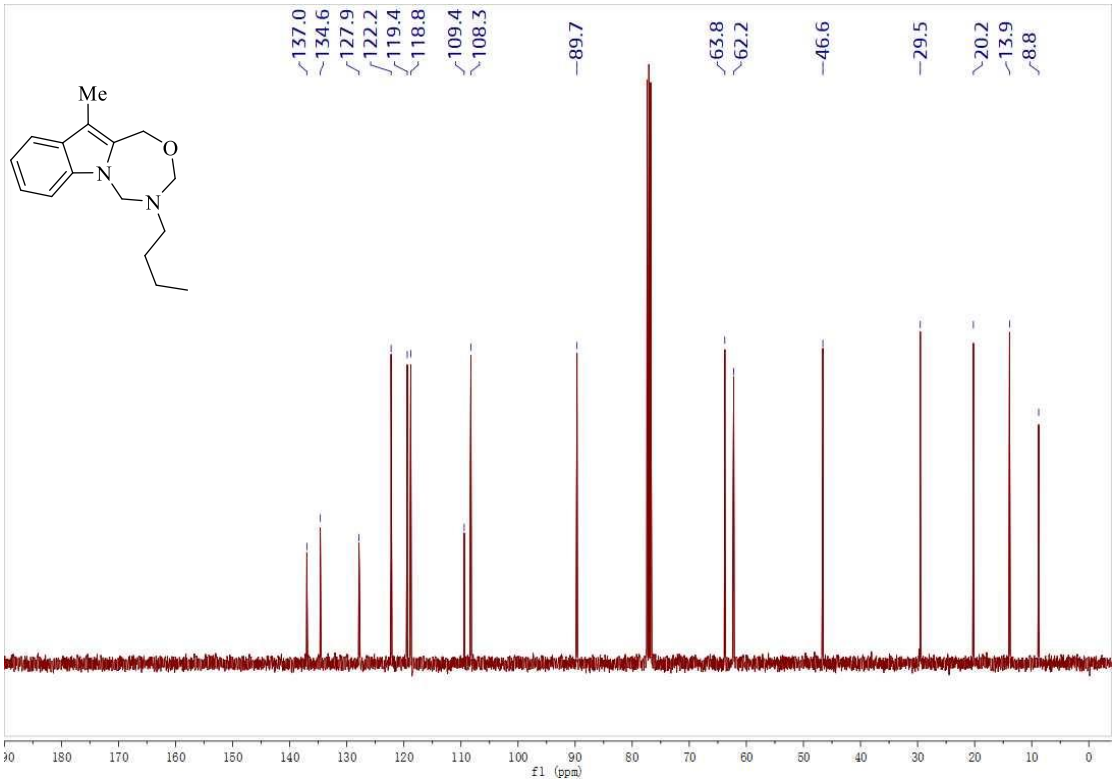
3l ^{13}C NMR (100 MHz, $CDCl_3$)



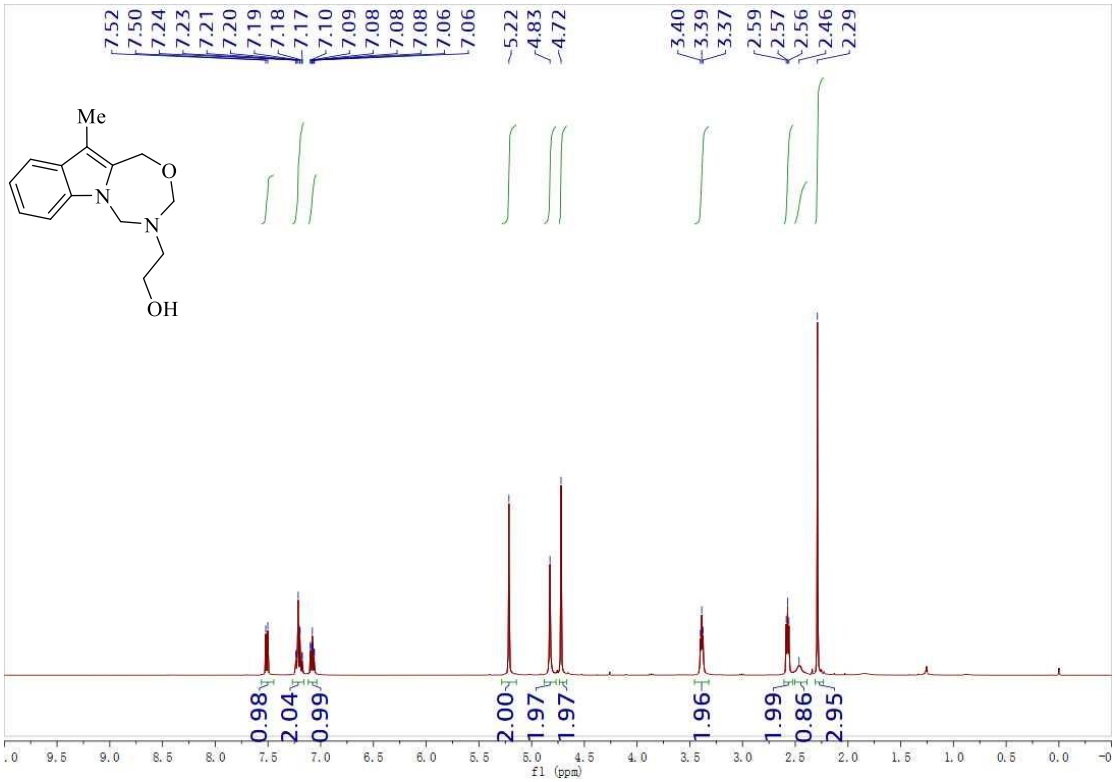
3m ^{1}H NMR (400 MHz, $CDCl_3$)



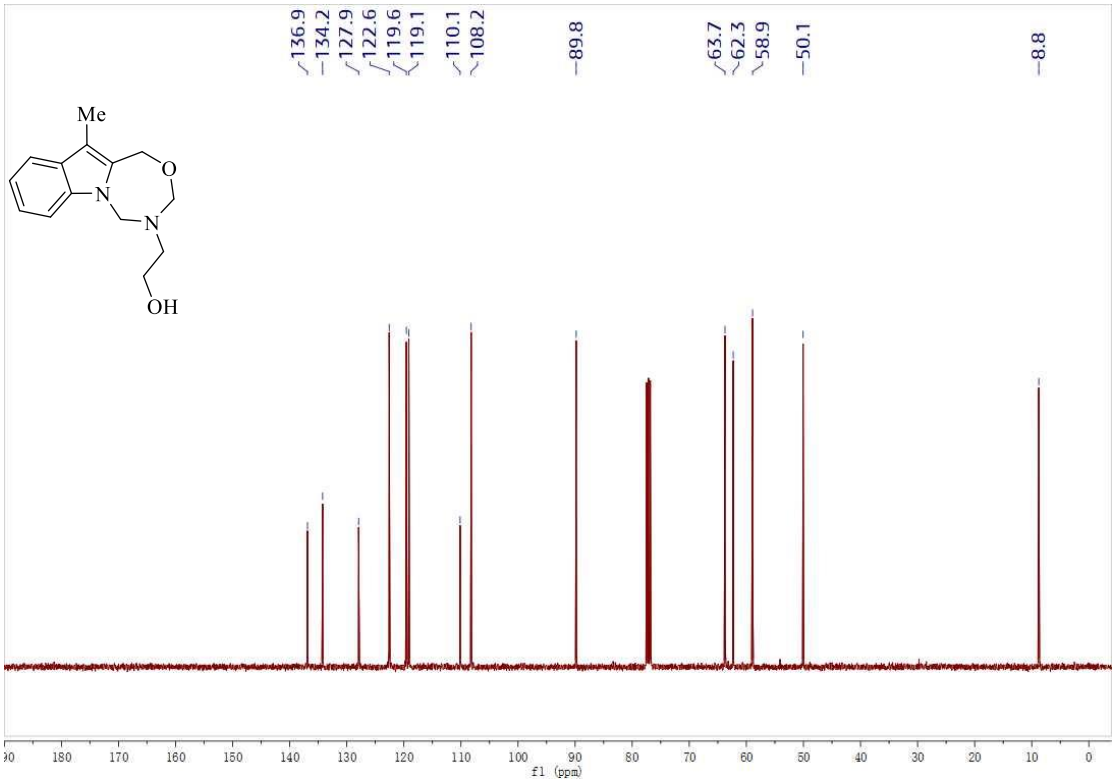
3m ^{13}C NMR (100 MHz, $CDCl_3$)



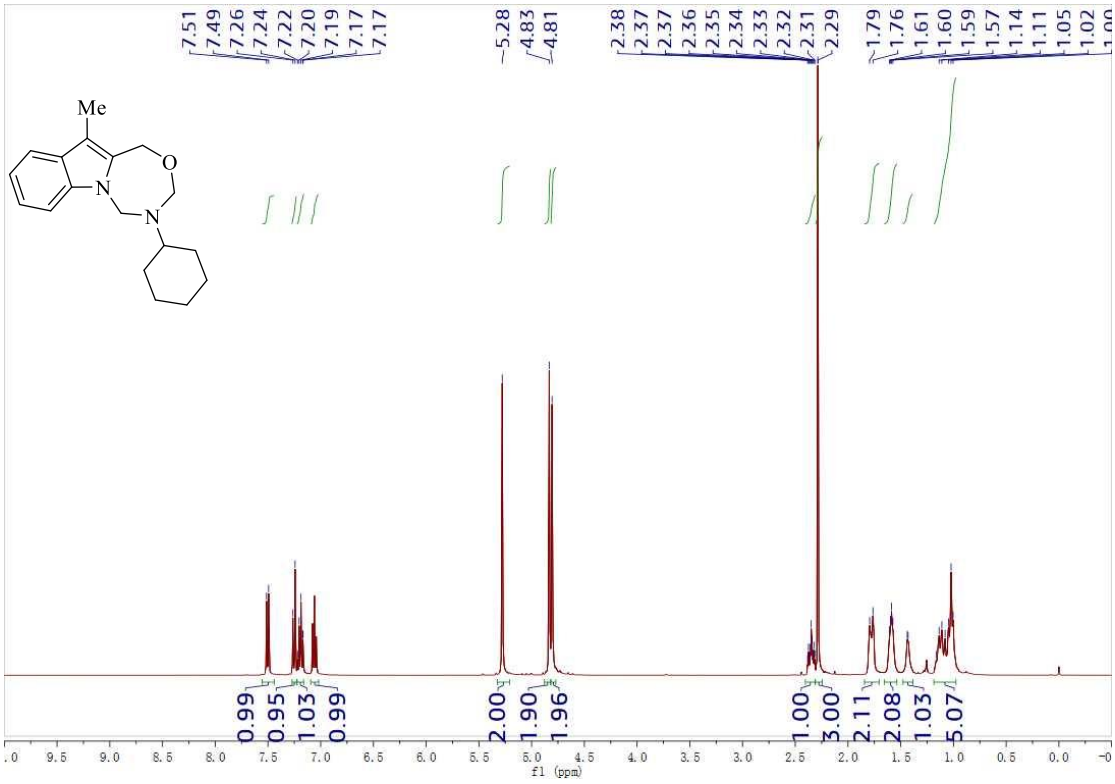
3n ^{1}H NMR (400 MHz, $CDCl_3$)



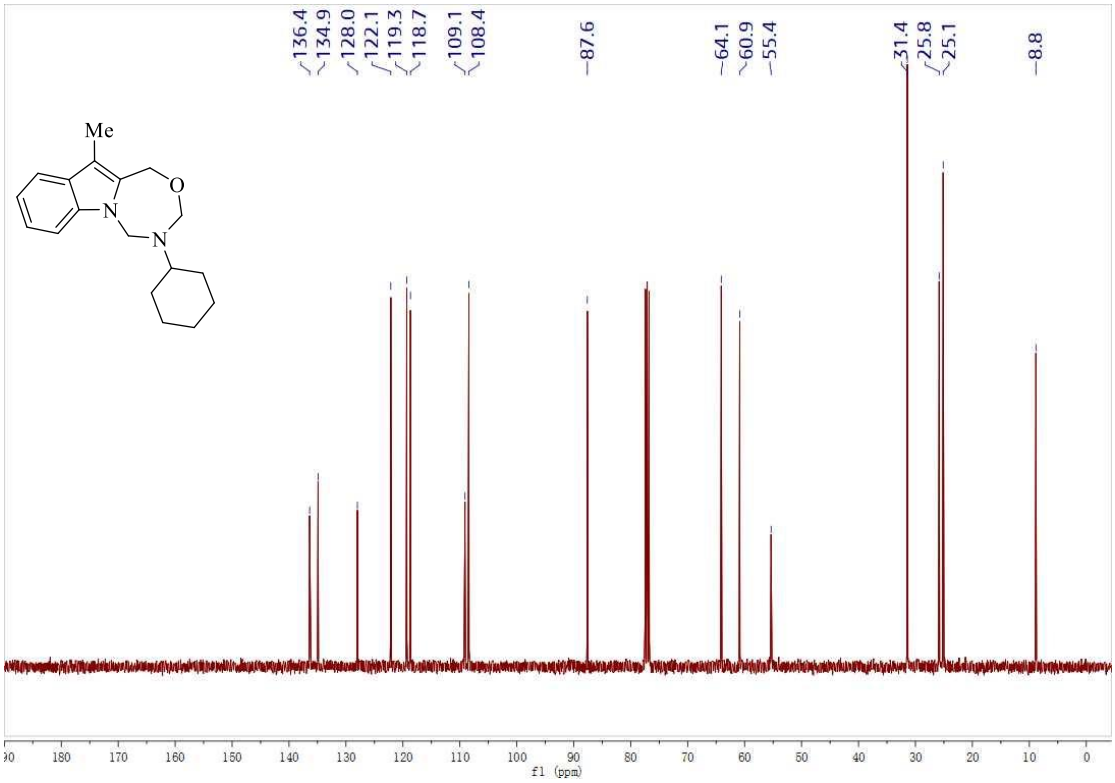
3n ^{13}C NMR (100 MHz, $CDCl_3$)



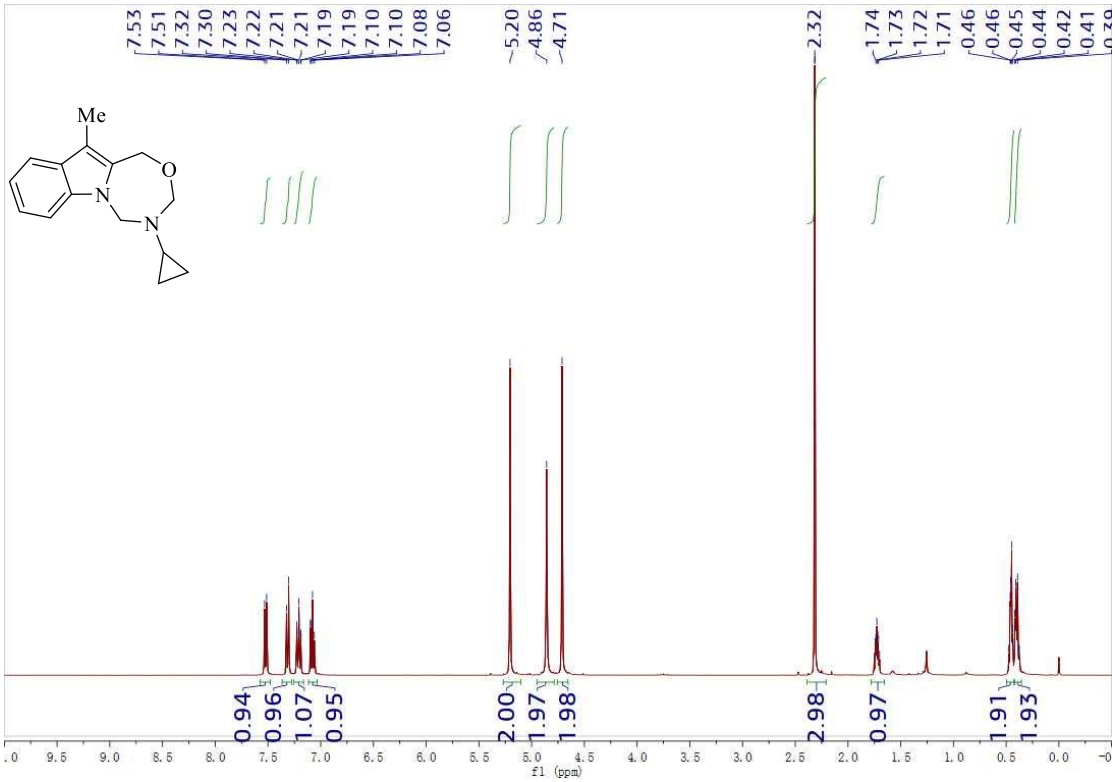
3o ^{1}H NMR (400 MHz, $CDCl_3$)



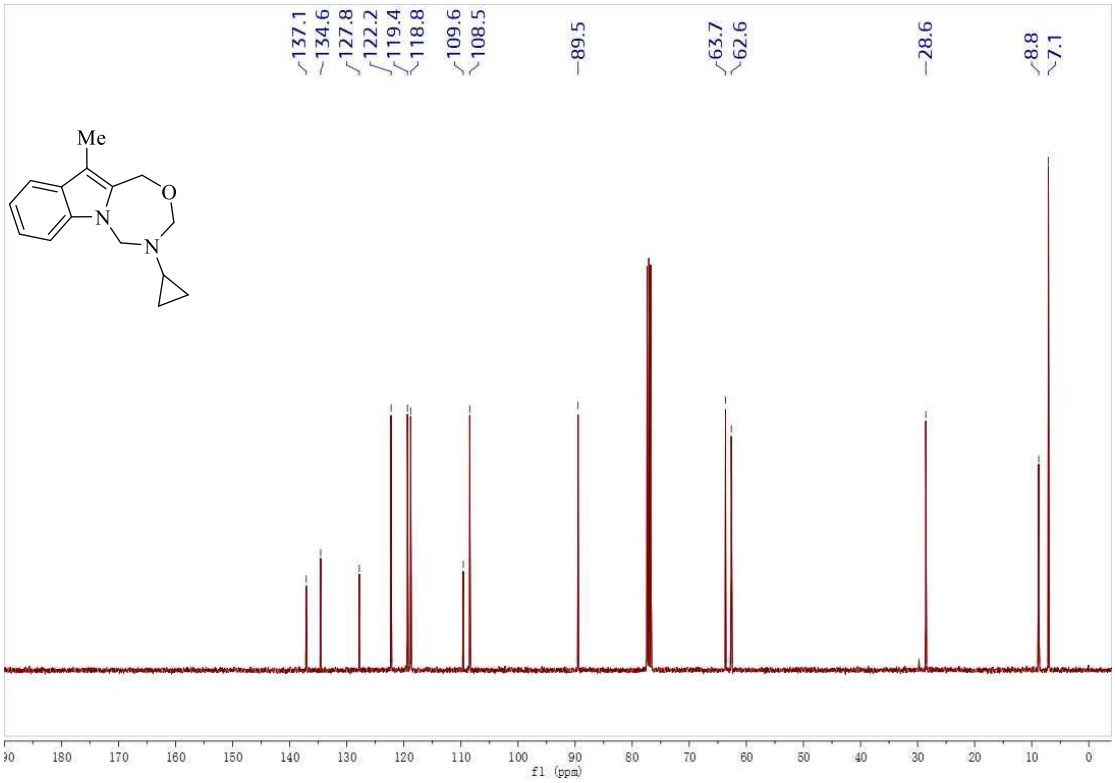
3o ^{13}C NMR (100 MHz, $CDCl_3$)



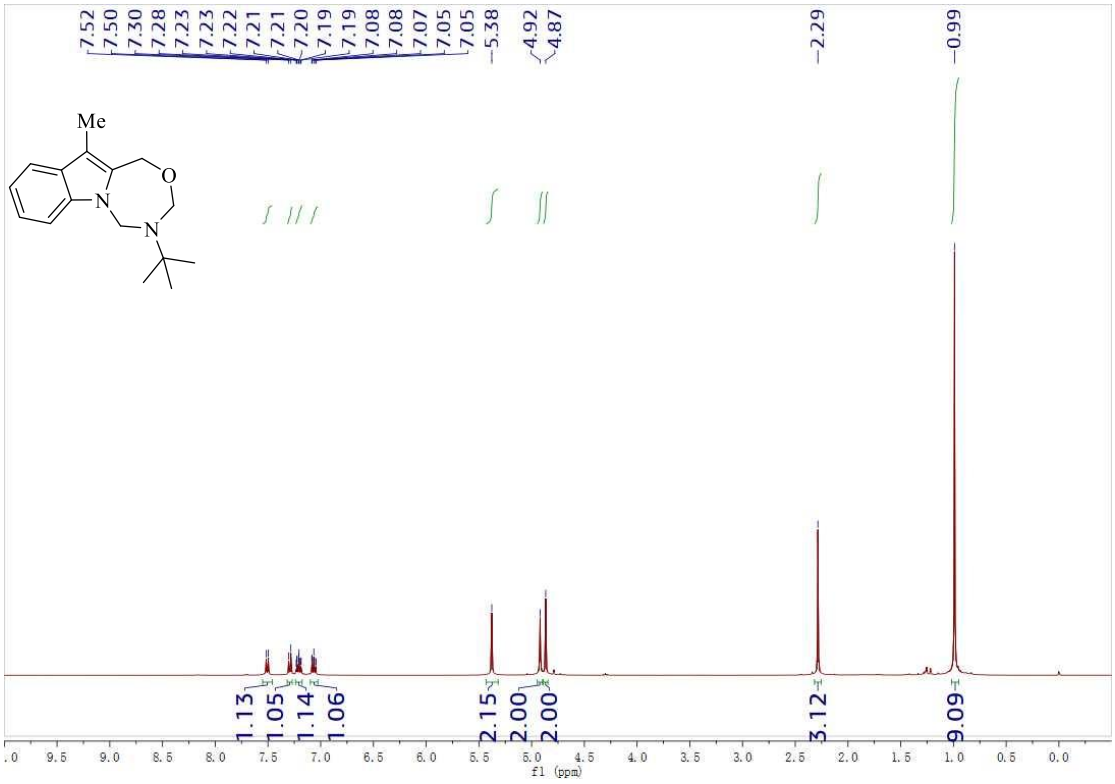
3p ^{1}H NMR (400 MHz, $CDCl_3$)



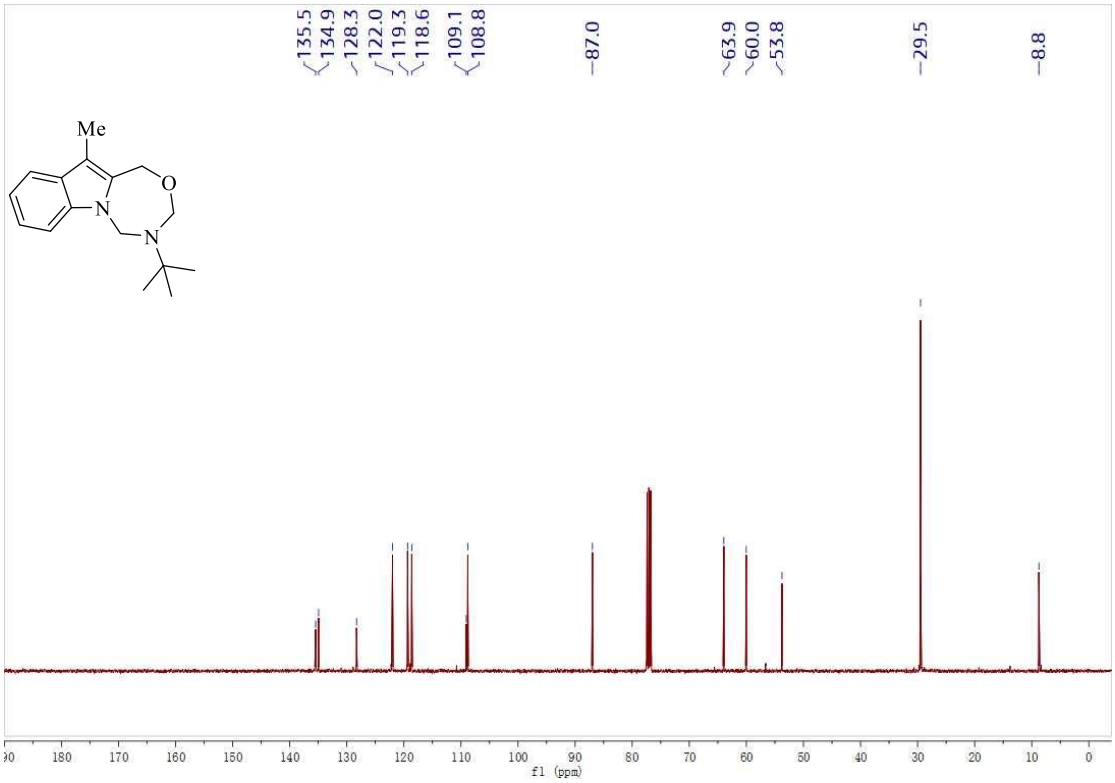
3p ^{13}C NMR (100 MHz, $CDCl_3$)



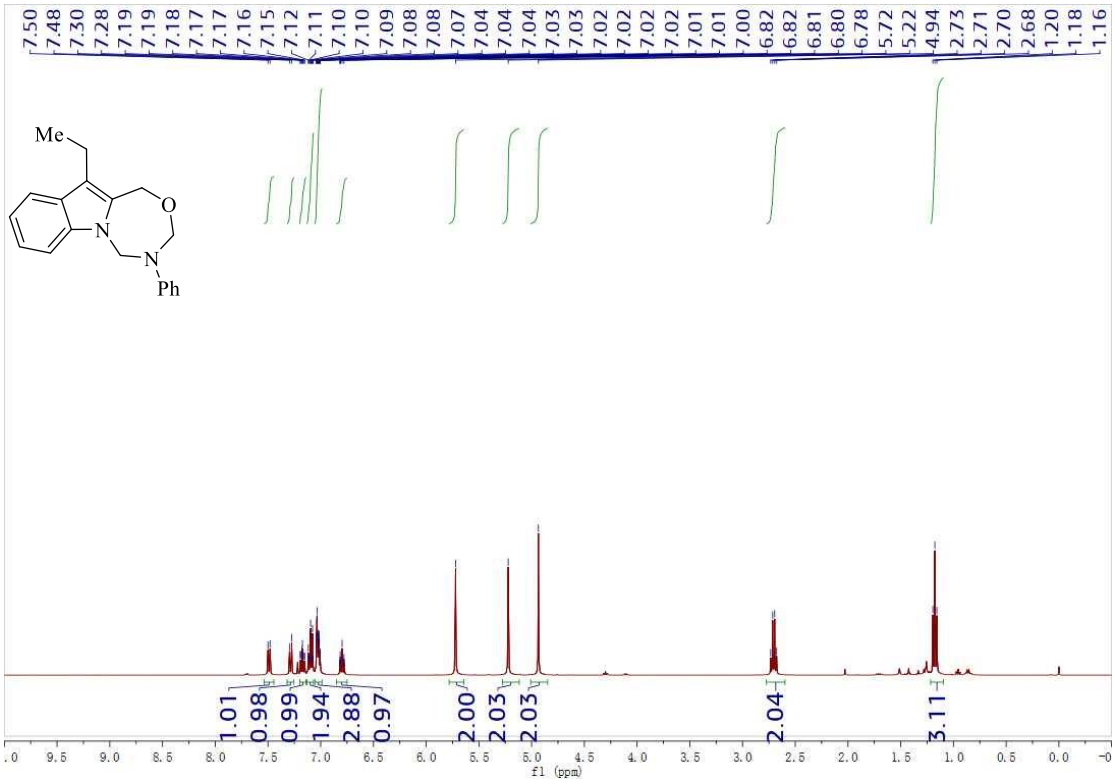
3q ^{1}H NMR (400 MHz, $CDCl_3$)



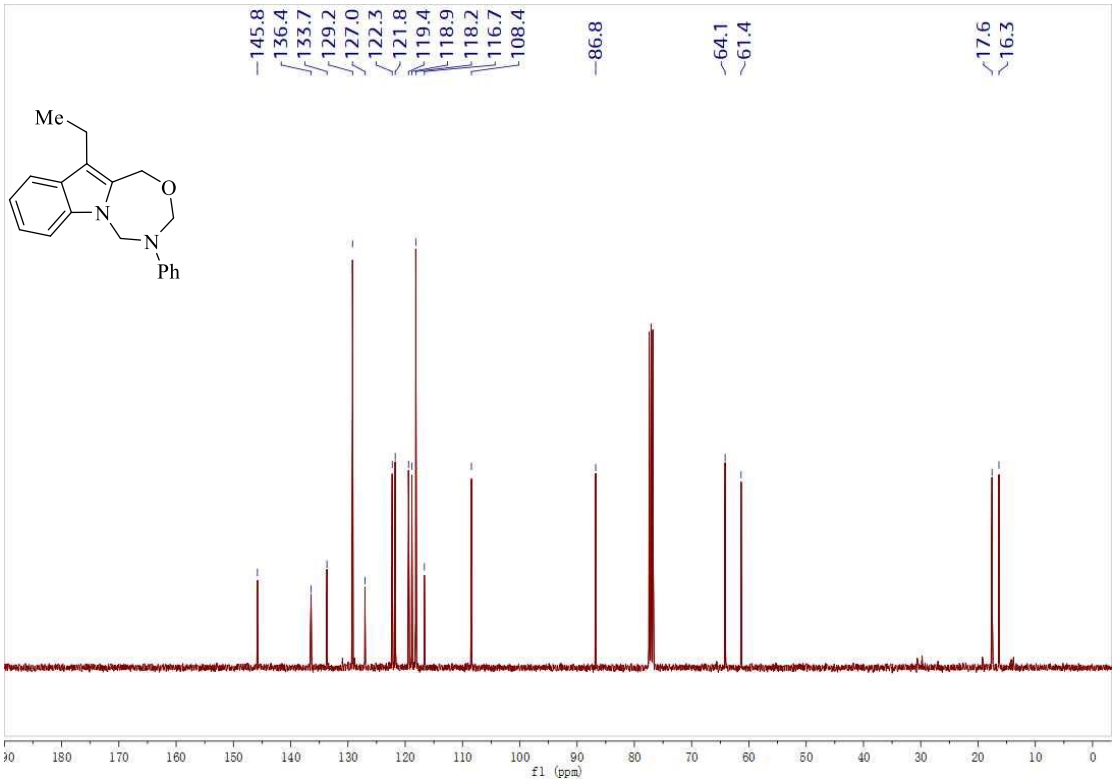
3q ^{13}C NMR (100 MHz, $CDCl_3$)



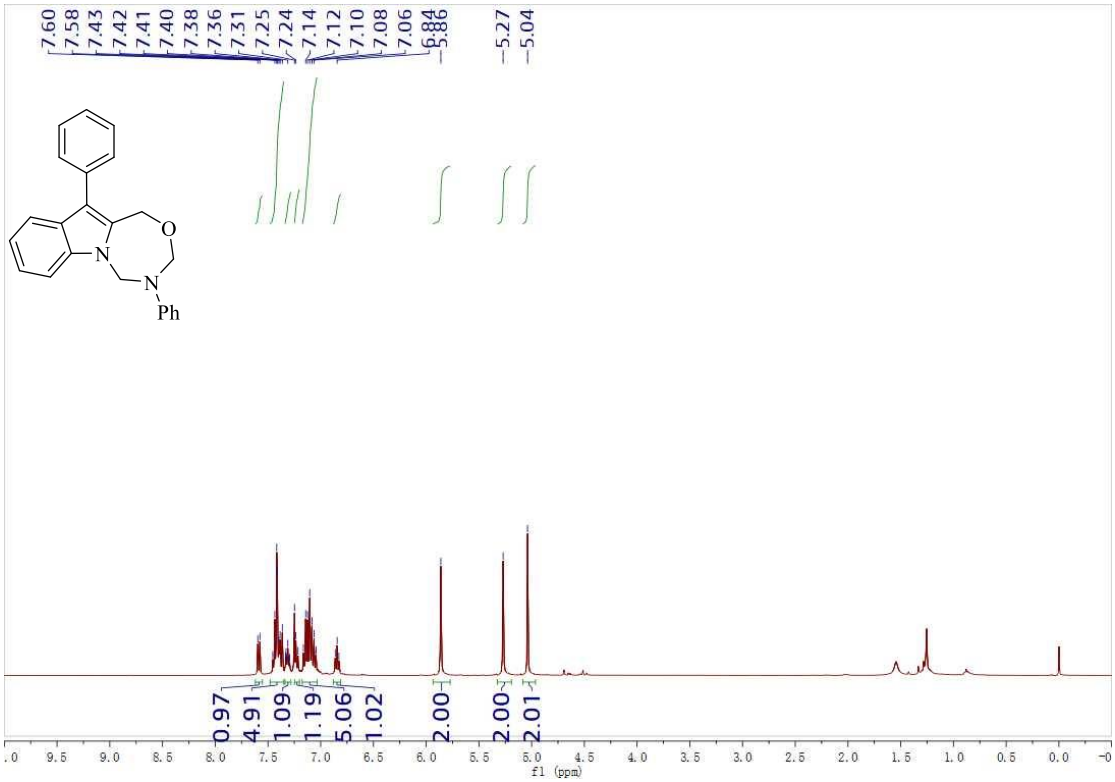
3r ^{1}H NMR (400 MHz, $CDCl_3$)



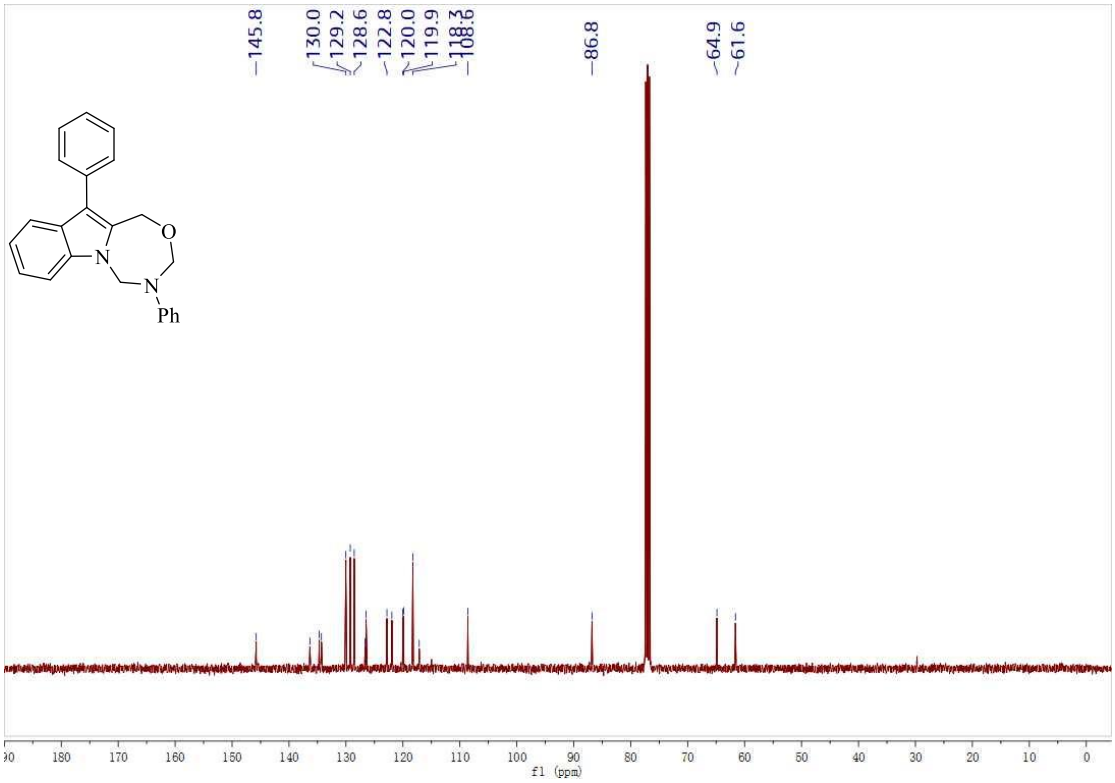
3r ^{13}C NMR (100 MHz, $CDCl_3$)



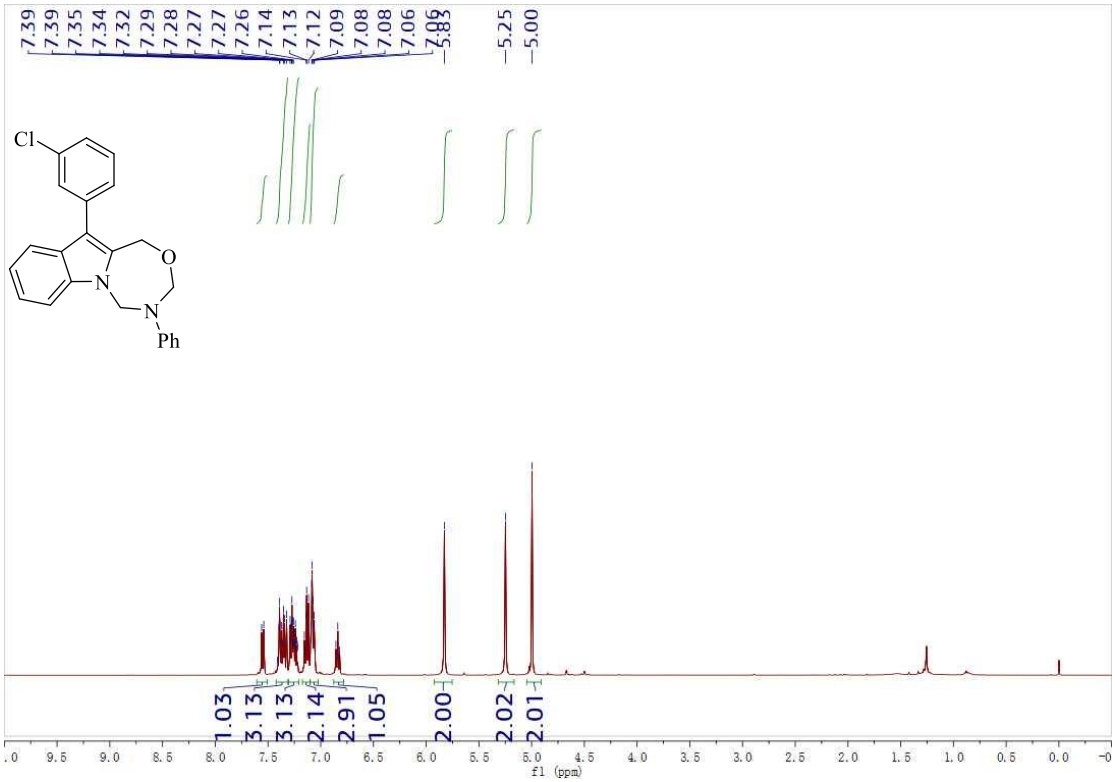
3s ^{1}H NMR (400 MHz, $CDCl_3$)



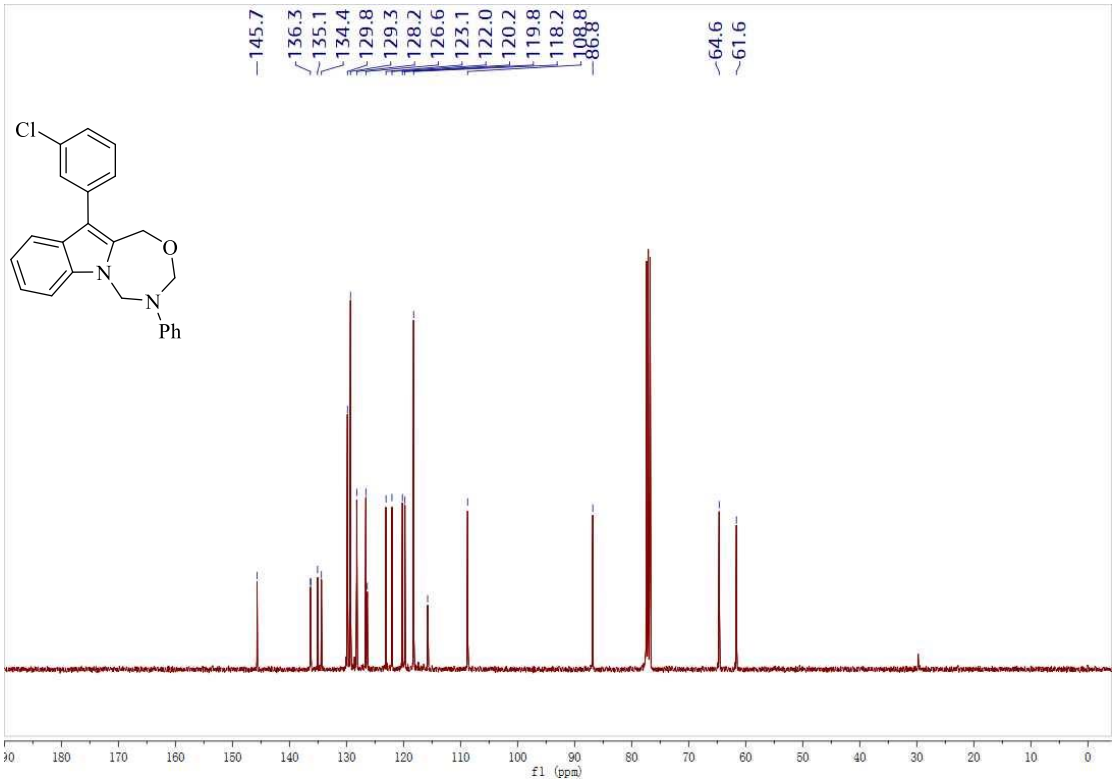
3s ^{13}C NMR (100 MHz, $CDCl_3$)



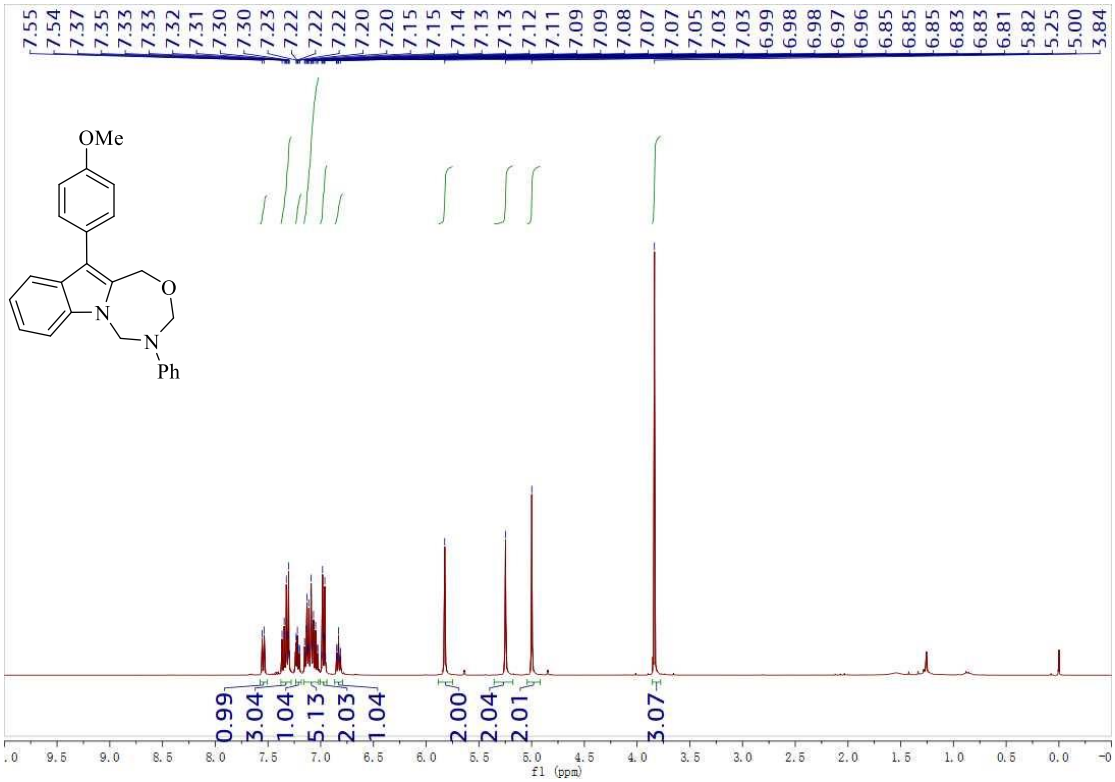
3t ^{1}H NMR (400 MHz, $CDCl_3$)



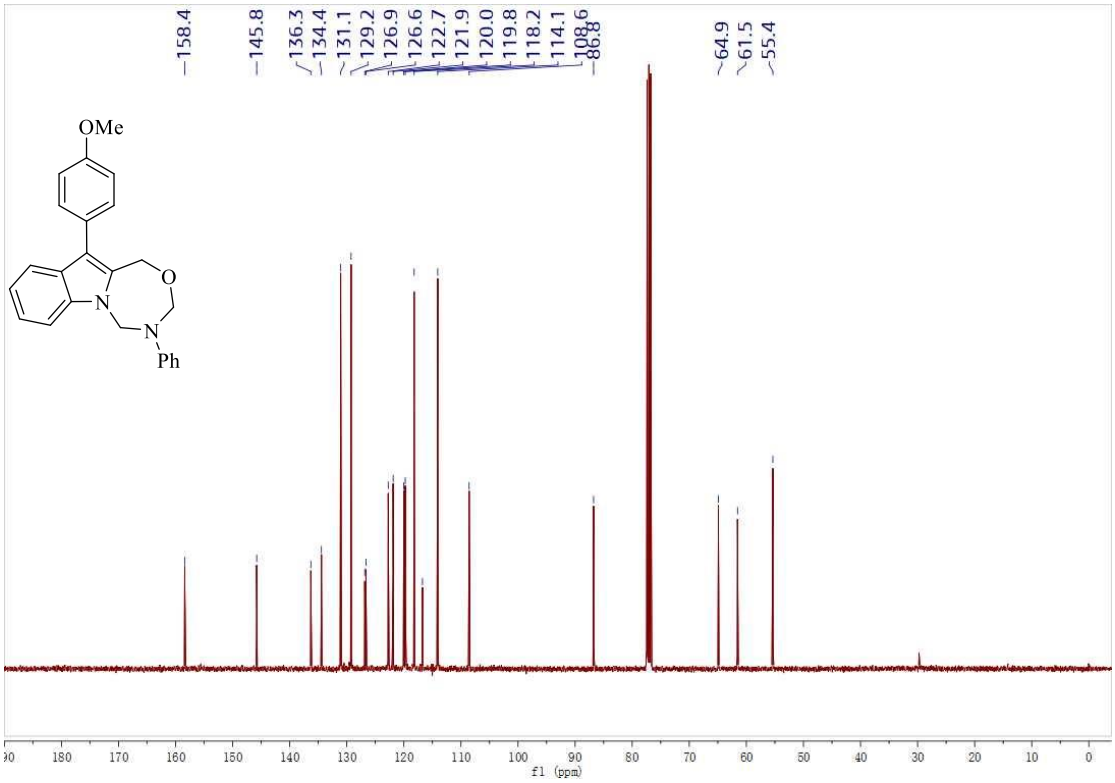
3t ^{13}C NMR (100 MHz, $CDCl_3$)



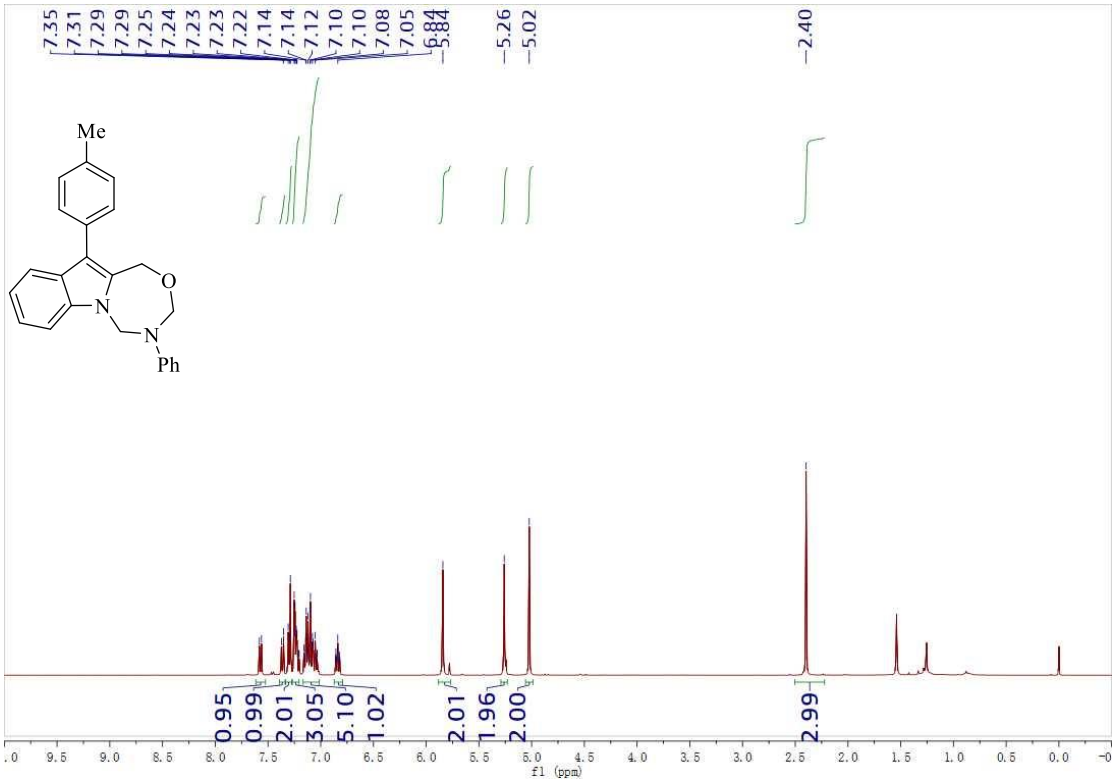
3u ^{1}H NMR (400 MHz, $CDCl_3$)



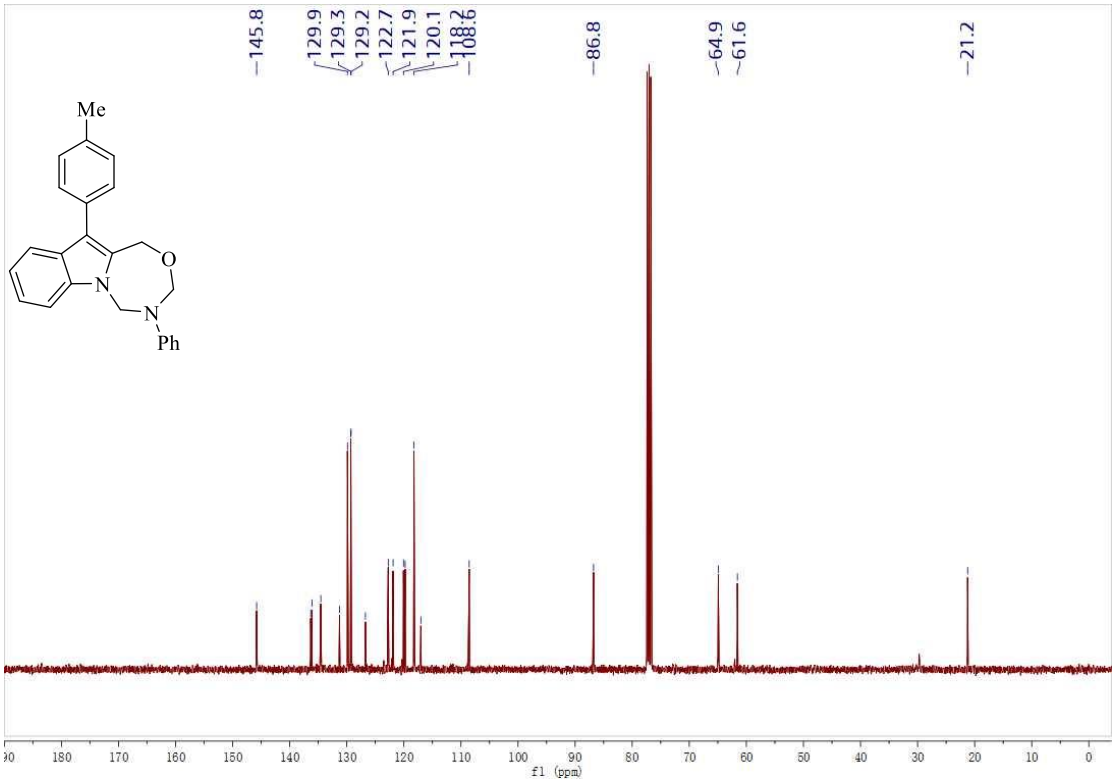
3u ^{13}C NMR (100 MHz, $CDCl_3$)



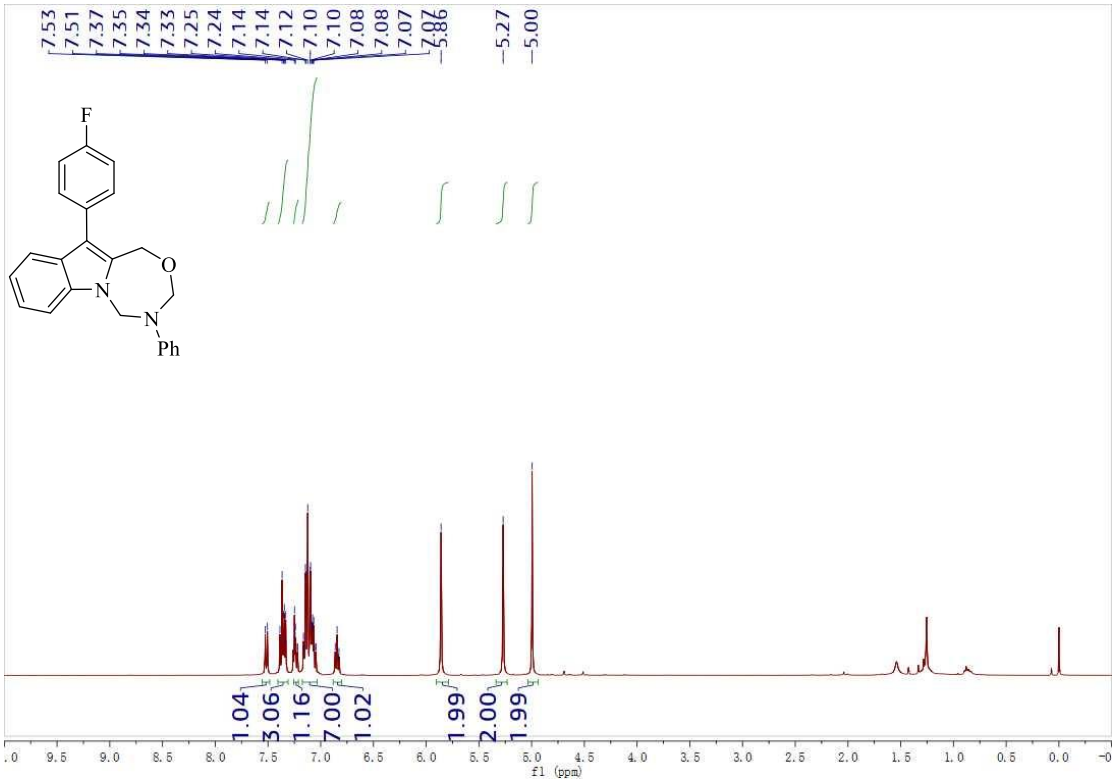
3v ^{1}H NMR (400 MHz, $CDCl_3$)



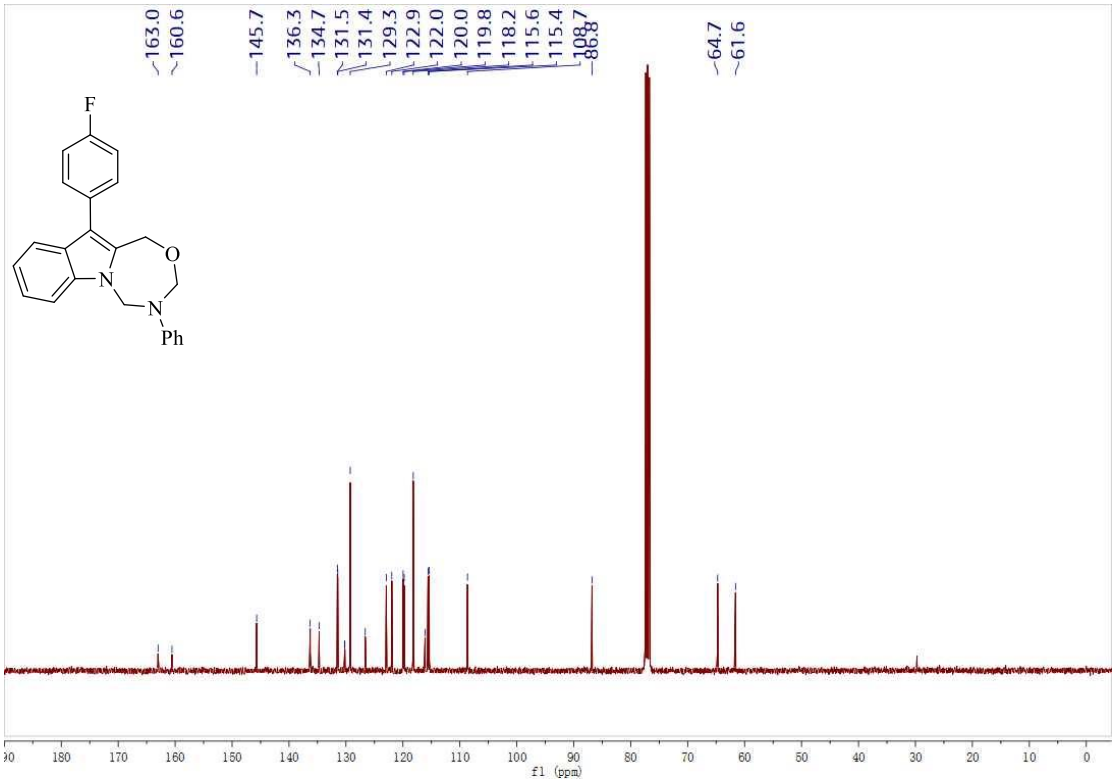
3v ^{13}C NMR (100 MHz, $CDCl_3$)



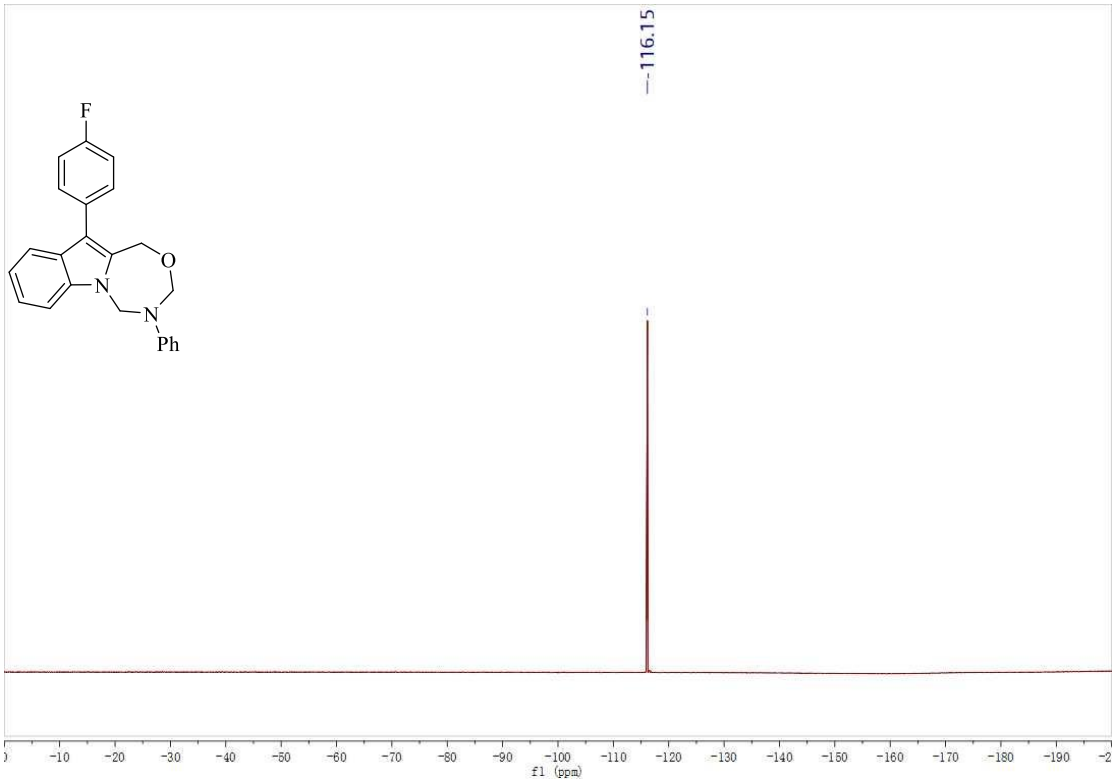
3w ^{1}H NMR (400 MHz, $CDCl_3$)



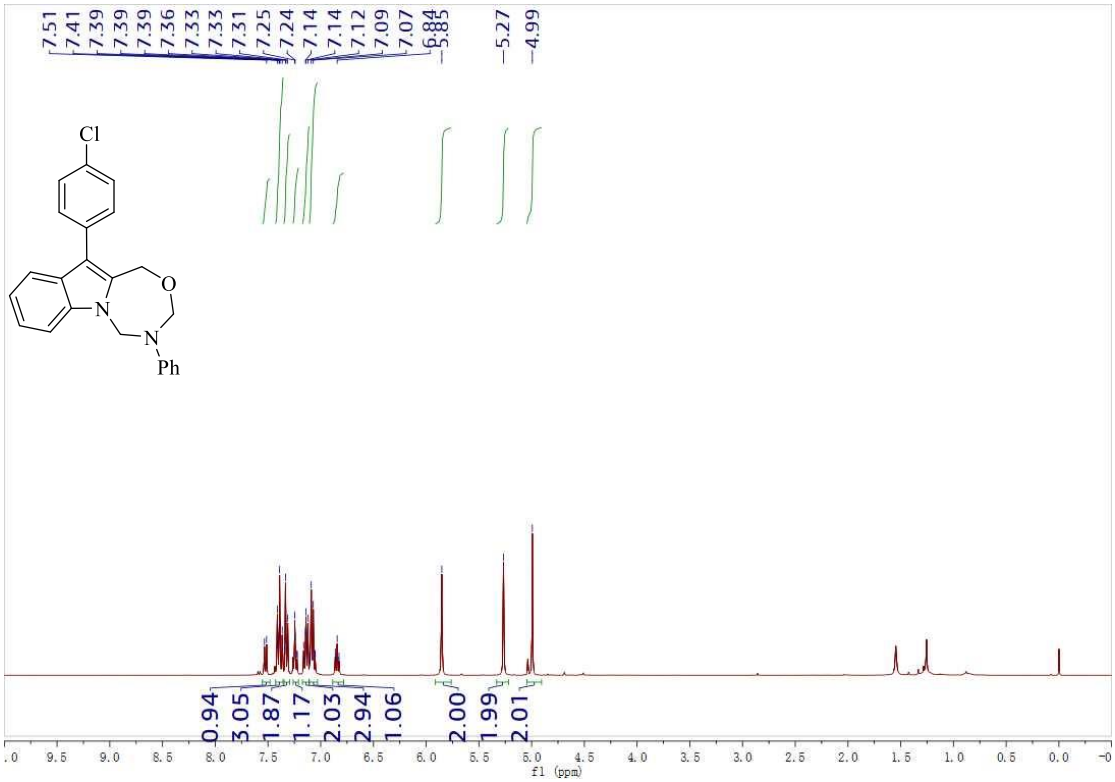
3w ^{13}C NMR (100 MHz, $CDCl_3$)



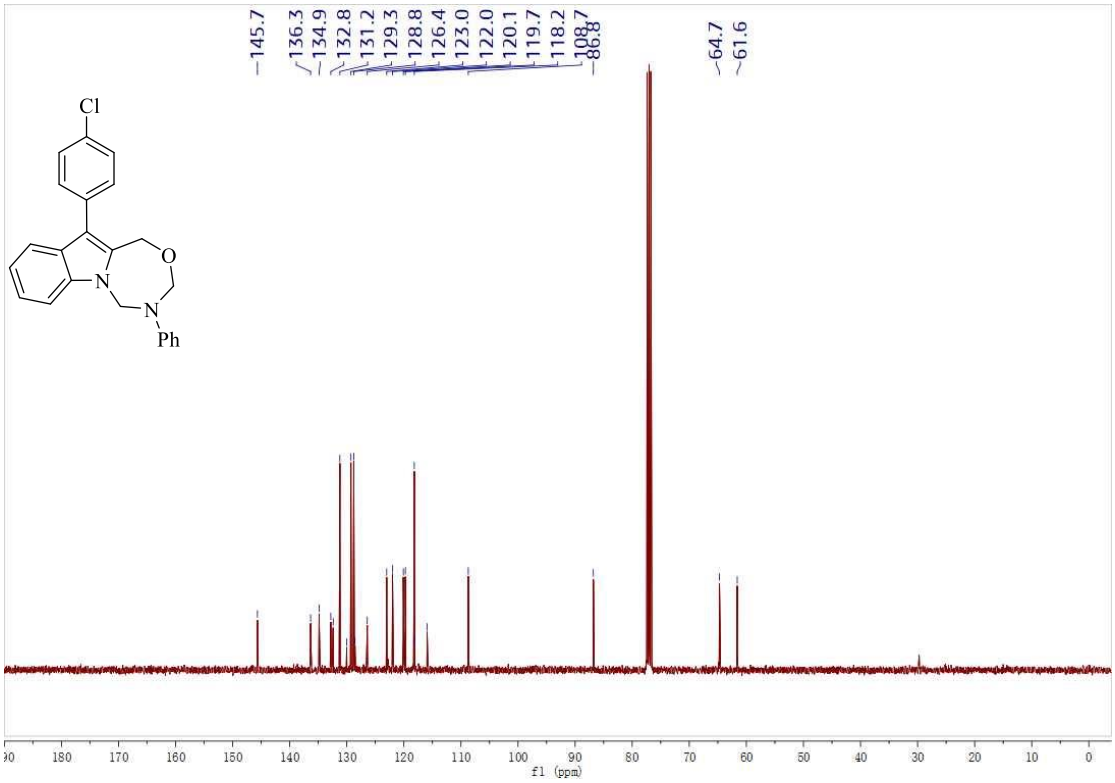
3w ^{19}F NMR (376 MHz, $CDCl_3$)



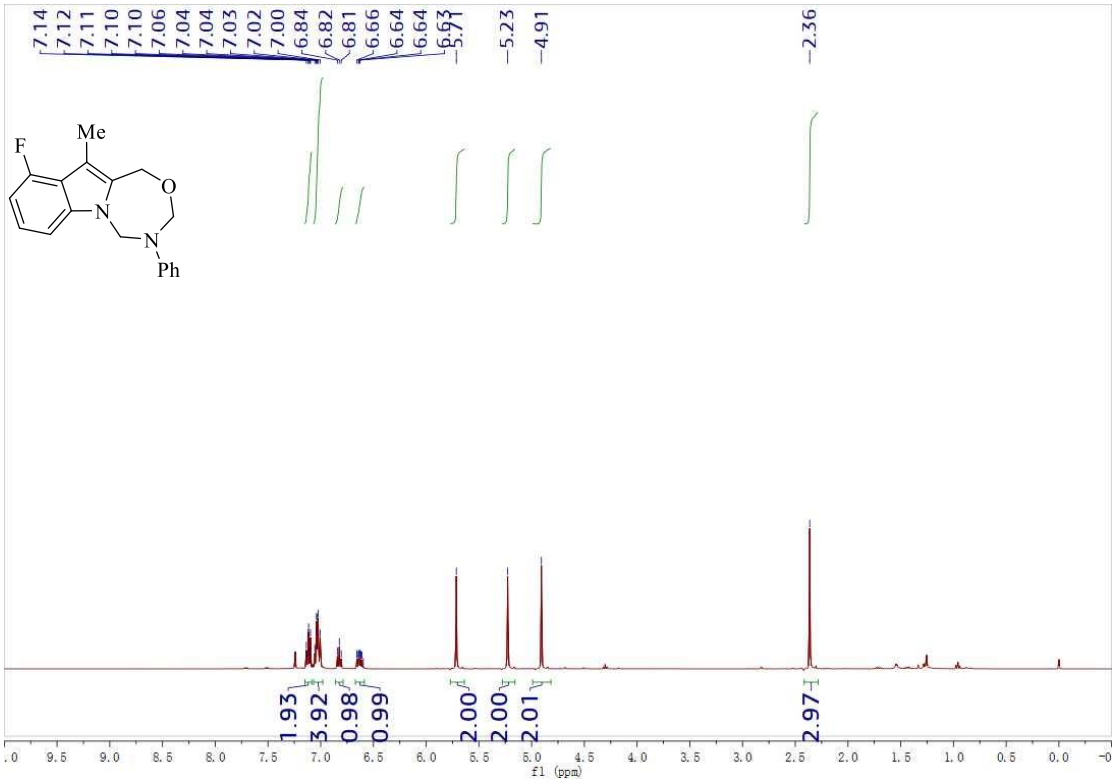
3x ^{1}H NMR (400 MHz, $CDCl_3$)



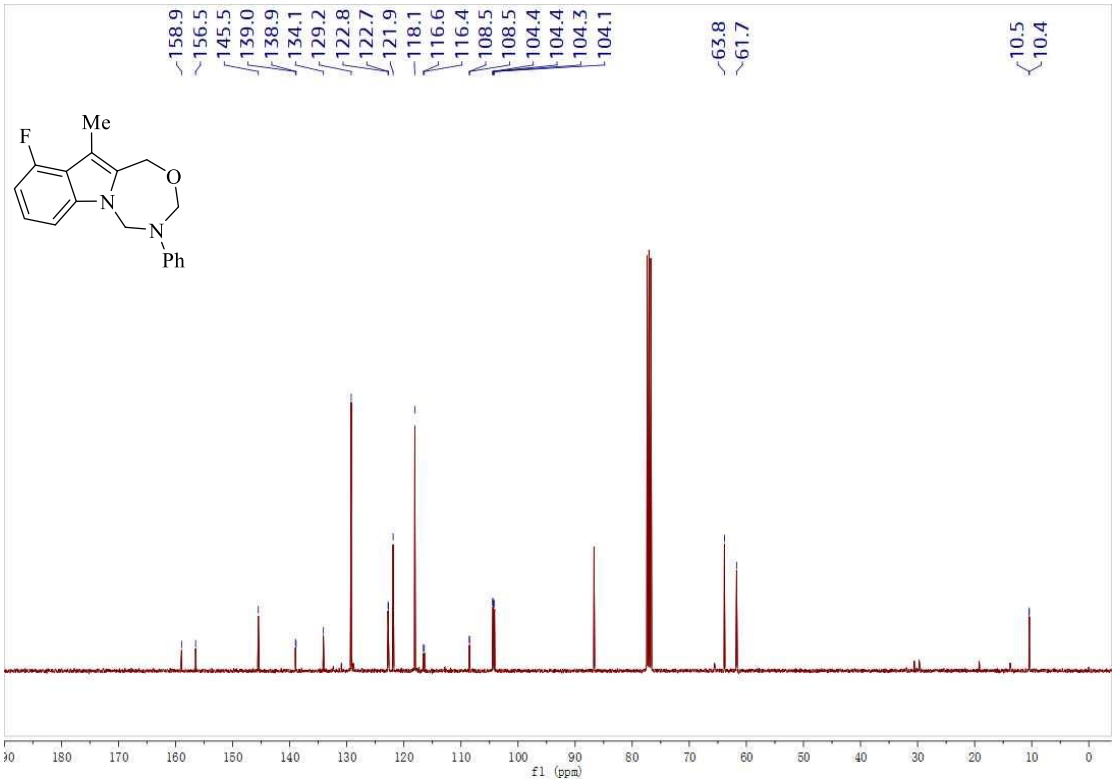
3x ^{13}C NMR (100 MHz, $CDCl_3$)



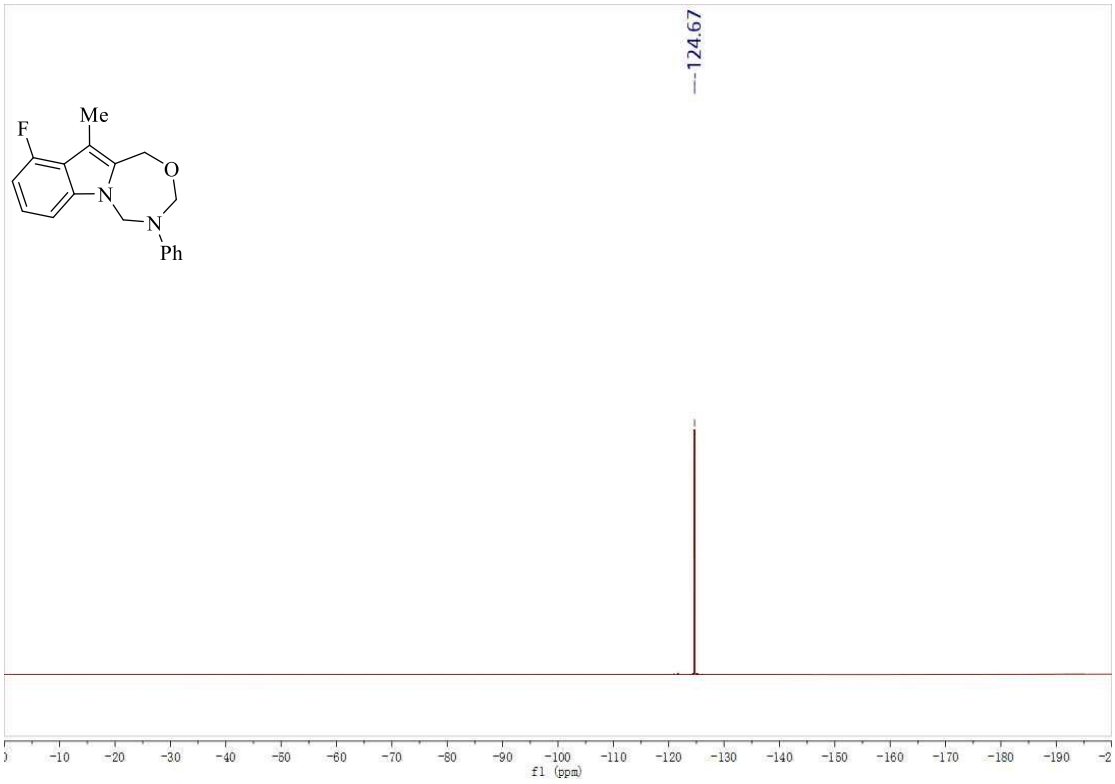
3y ^{1}H NMR (400 MHz, $CDCl_3$)



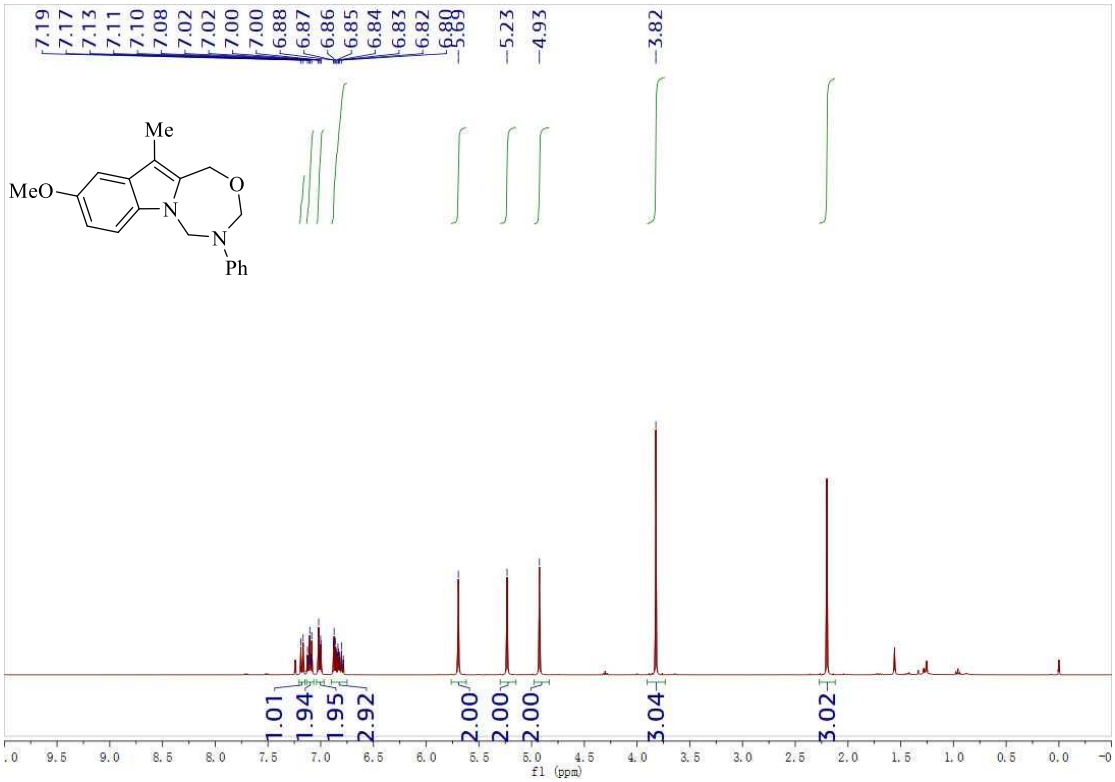
3y ^{13}C NMR (100 MHz, $CDCl_3$)



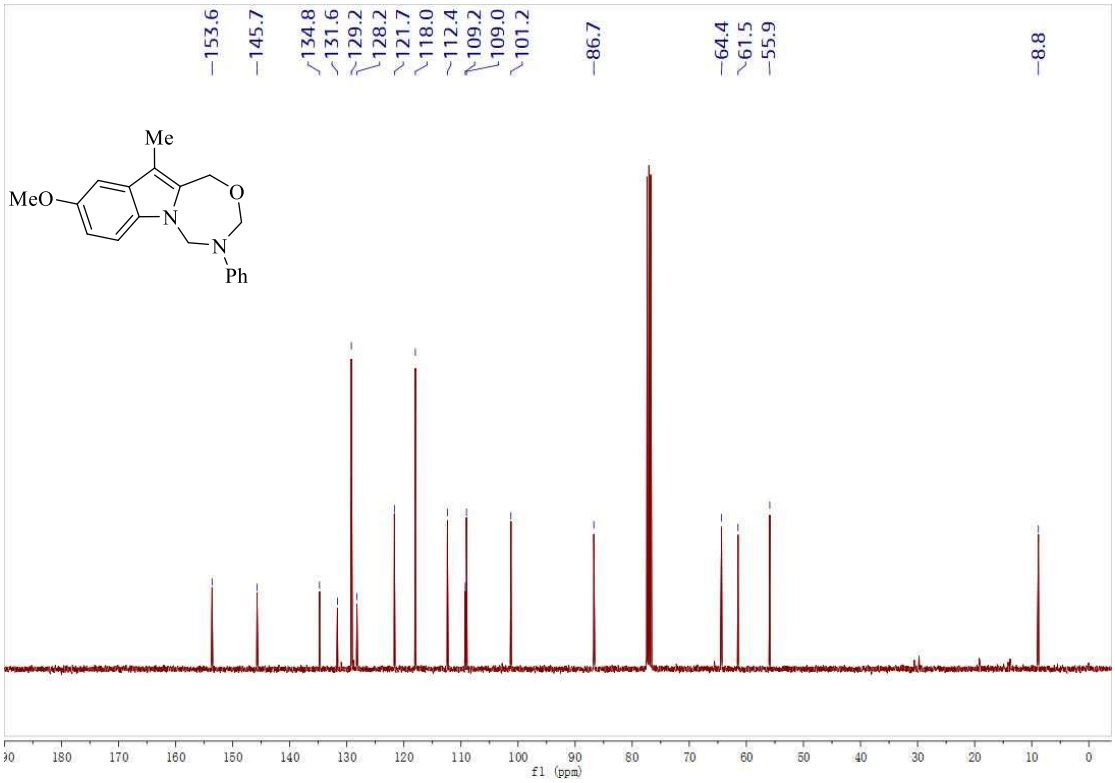
3y ^{19}F NMR (376 MHz, $CDCl_3$)



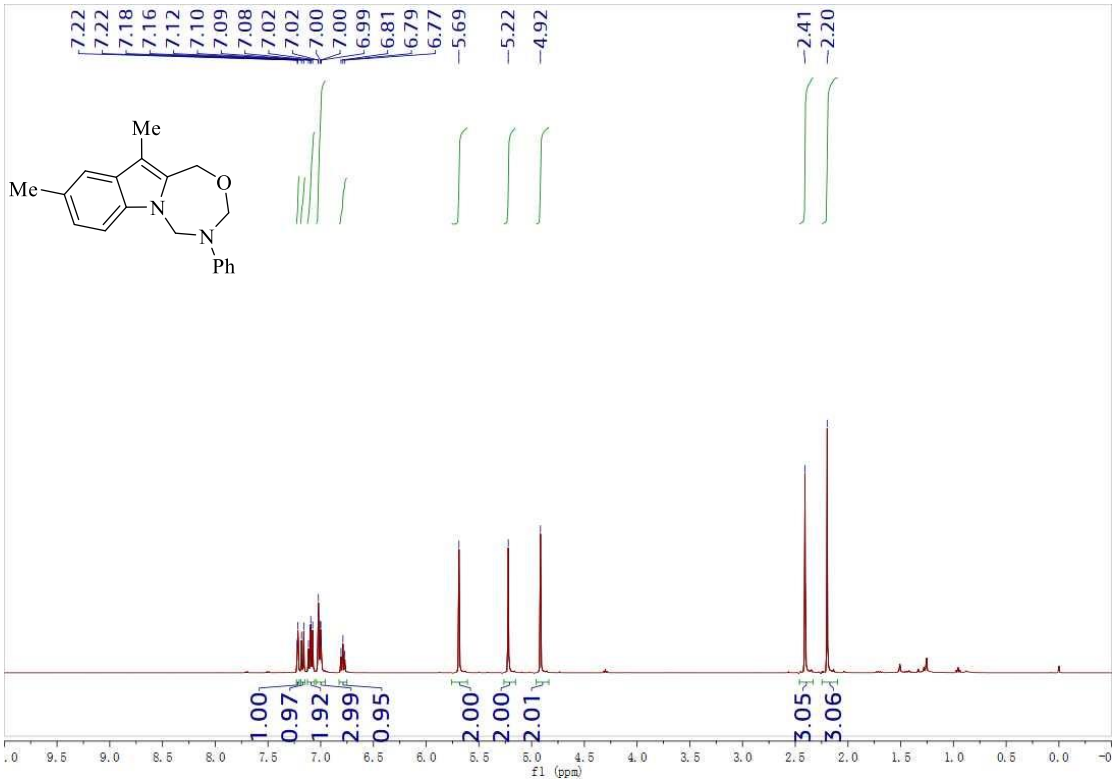
3z ^{1}H NMR (400 MHz, $CDCl_3$)



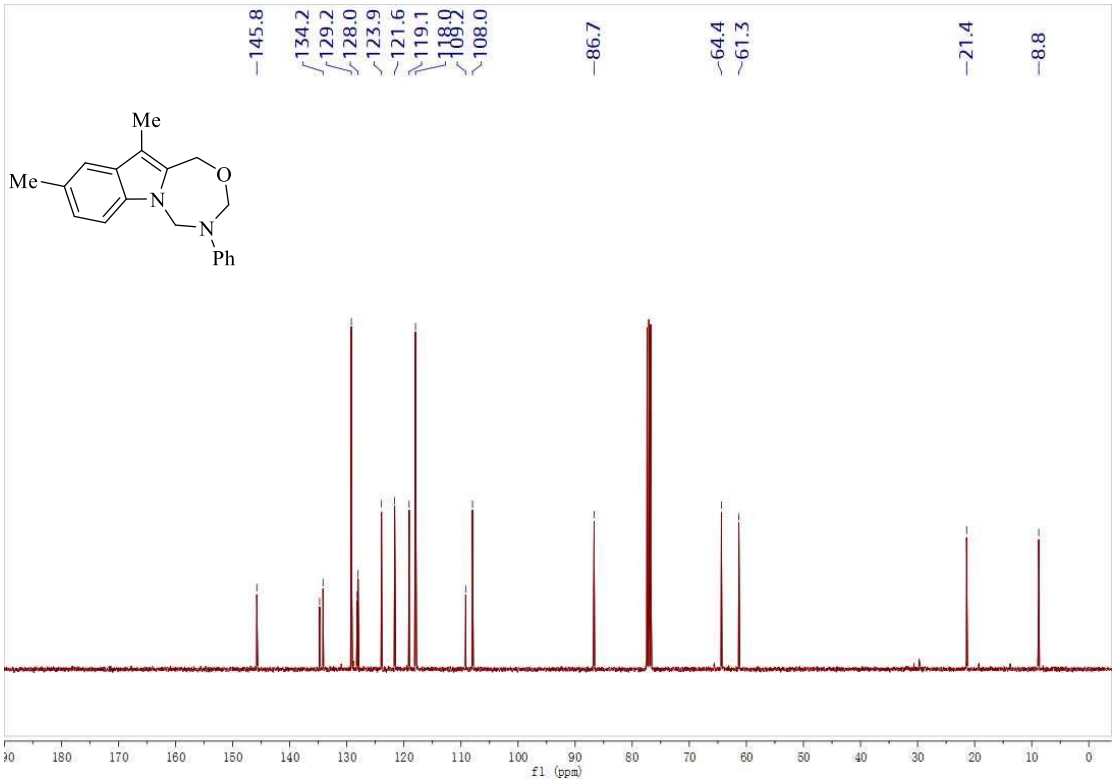
3z ^{13}C NMR (100 MHz, $CDCl_3$)



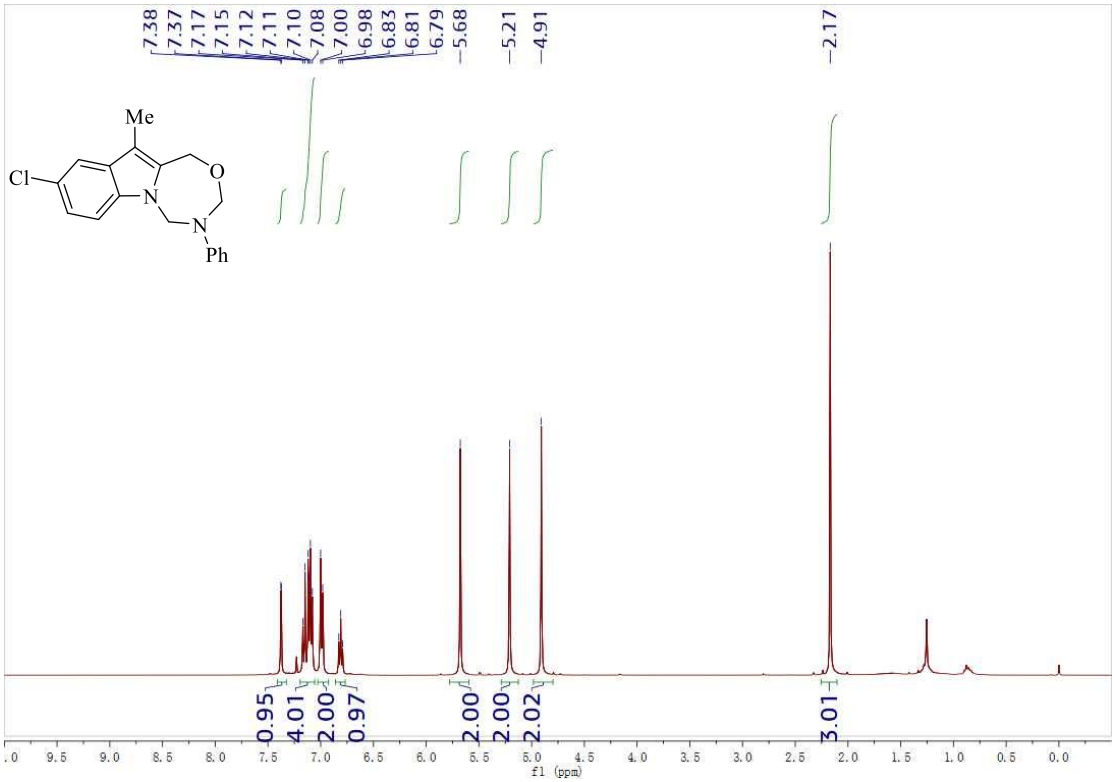
3a′ ^{1}H NMR (400 MHz, $CDCl_3$)



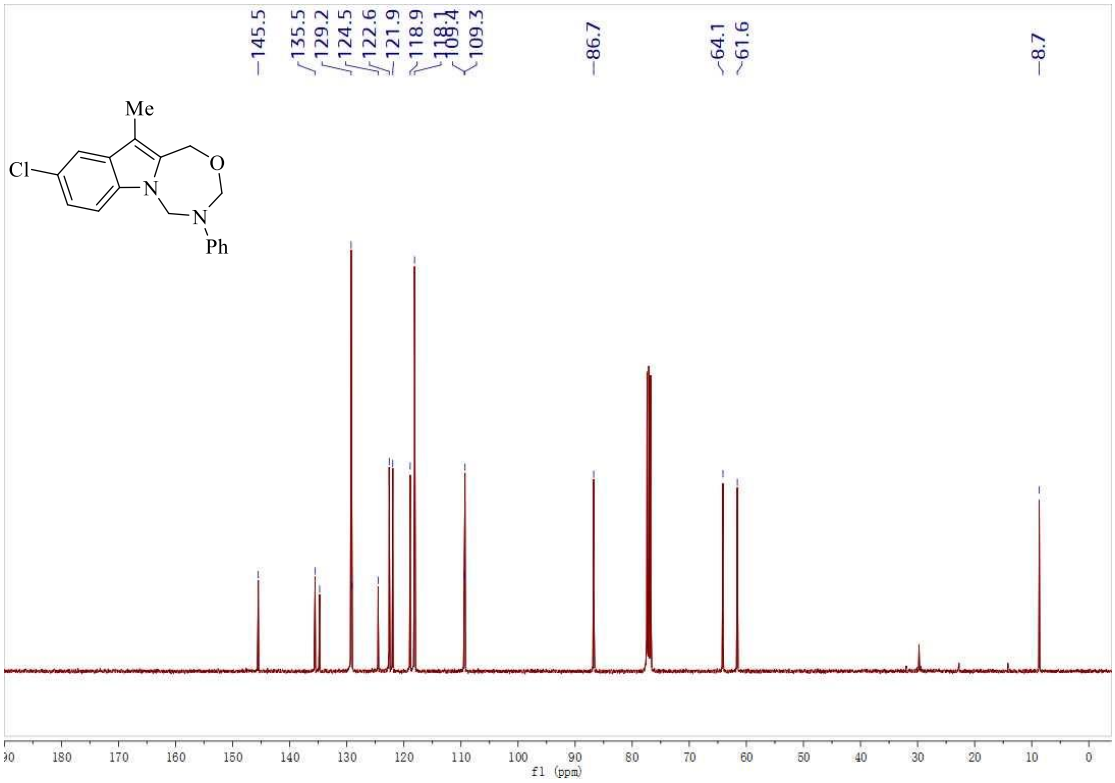
3a′ ^{13}C NMR (100 MHz, $CDCl_3$)



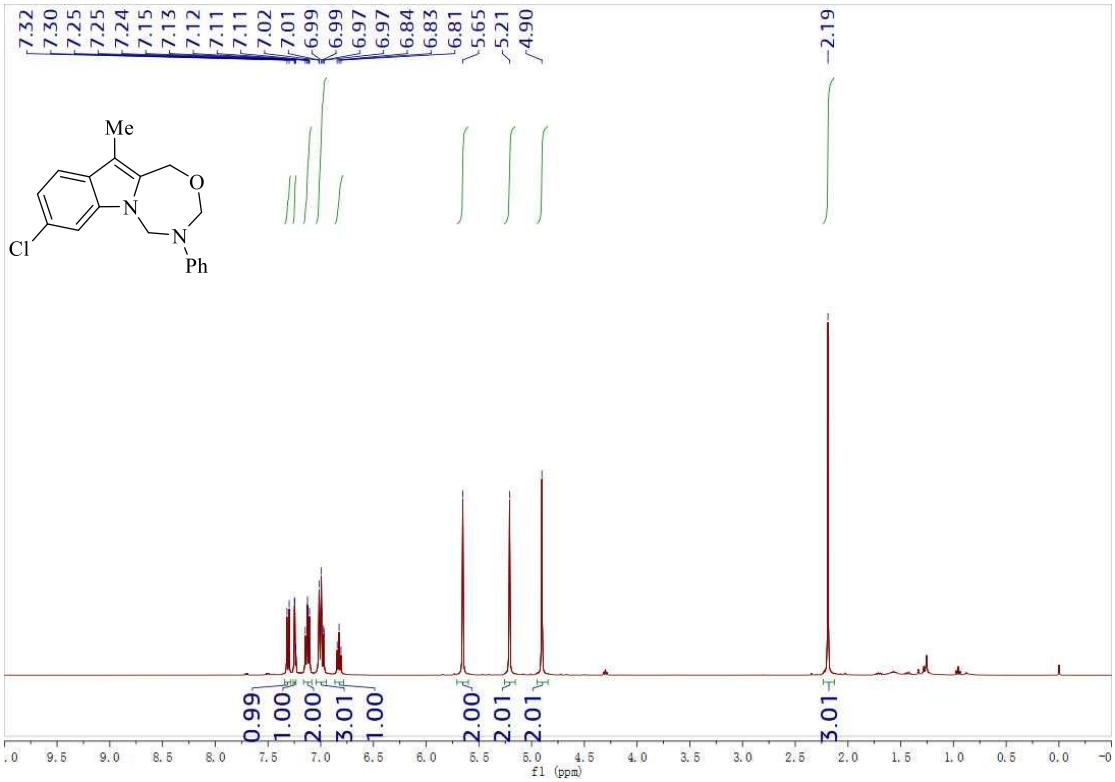
3b′ ^{1}H NMR (400 MHz, $CDCl_3$)



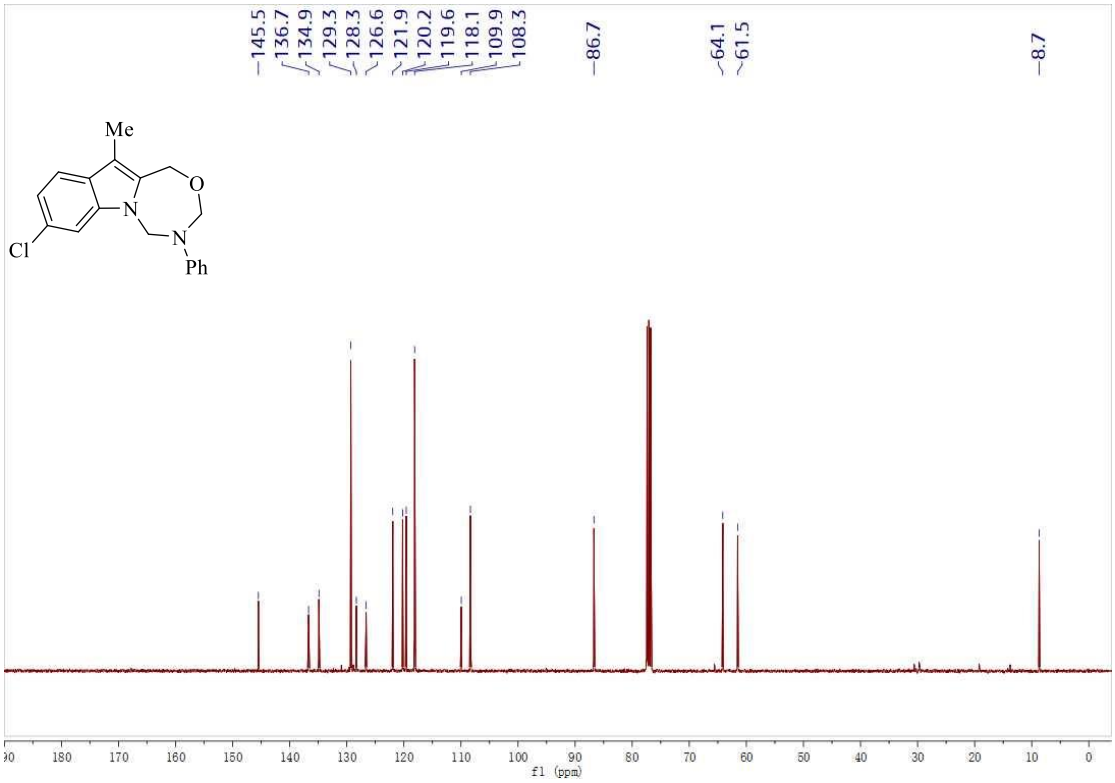
3b′ ^{13}C NMR (100 MHz, $CDCl_3$)



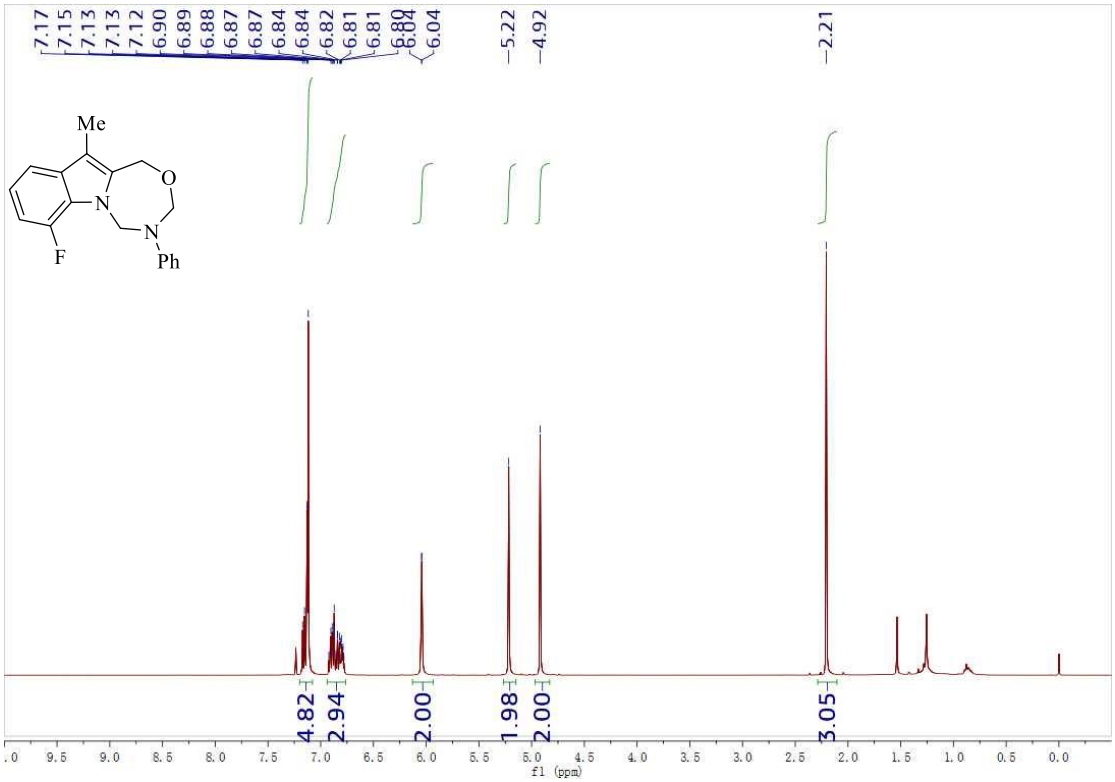
3c′ ^{1}H NMR (400 MHz, $CDCl_3$)



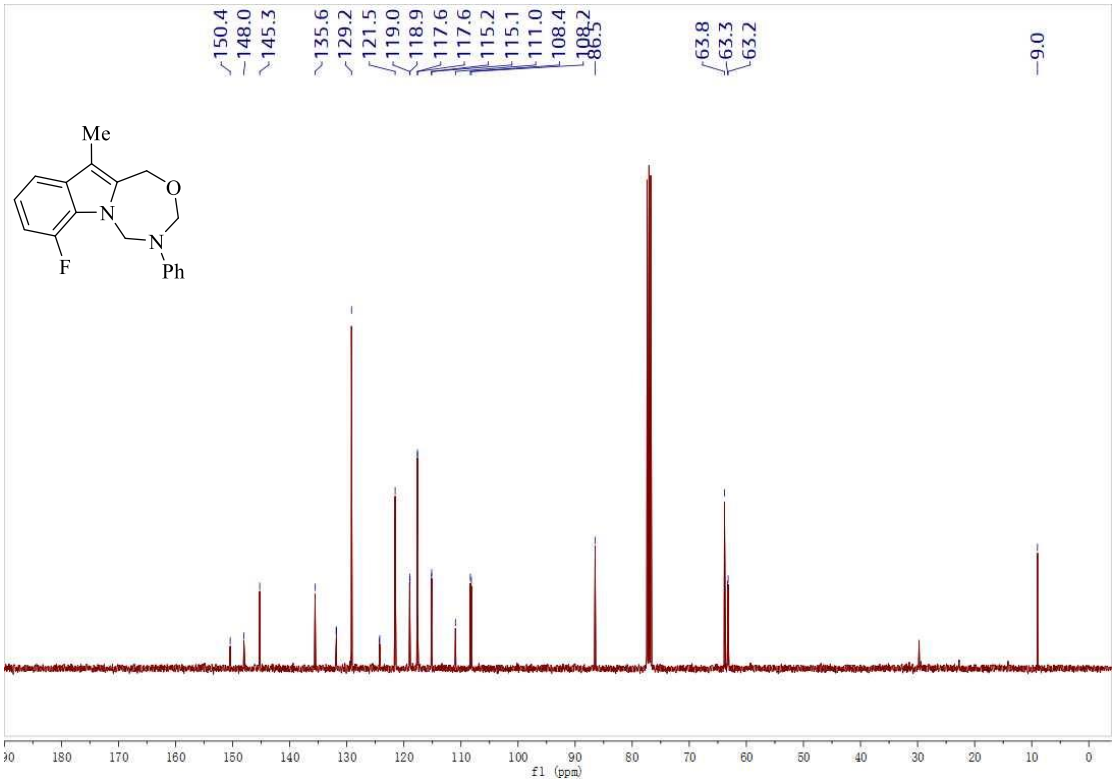
3c′ ^{13}C NMR (100 MHz, $CDCl_3$)



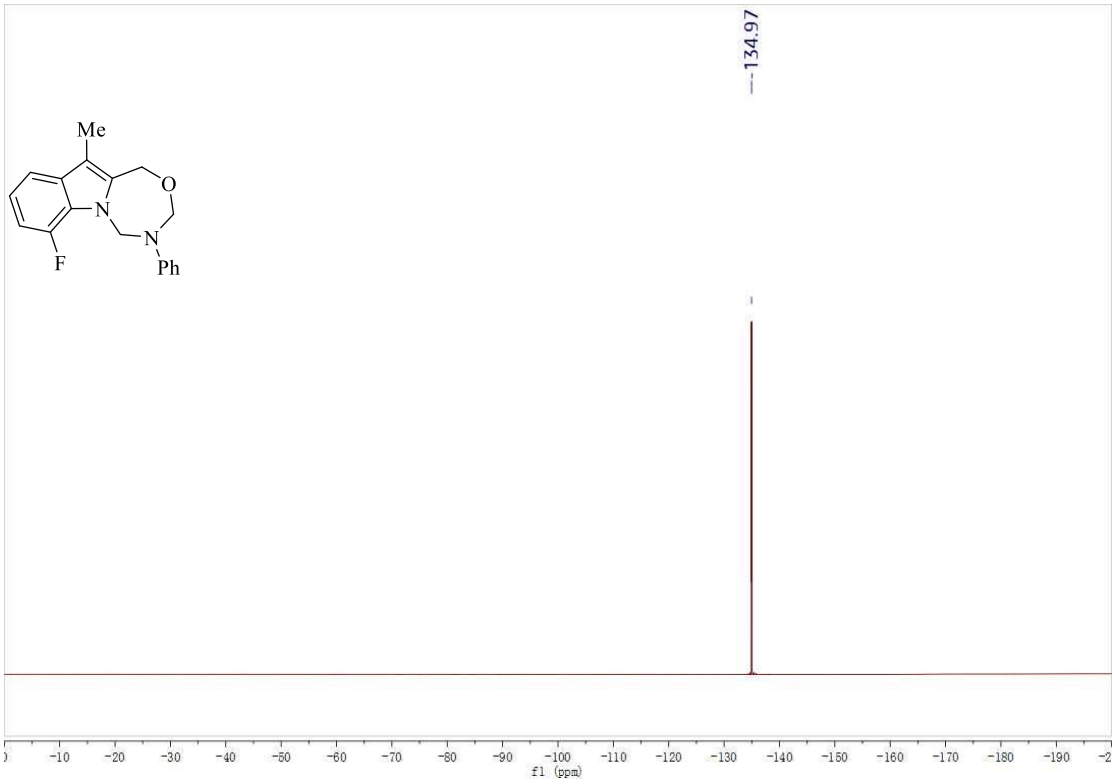
3d′ ^{1}H NMR (400 MHz, $CDCl_3$)



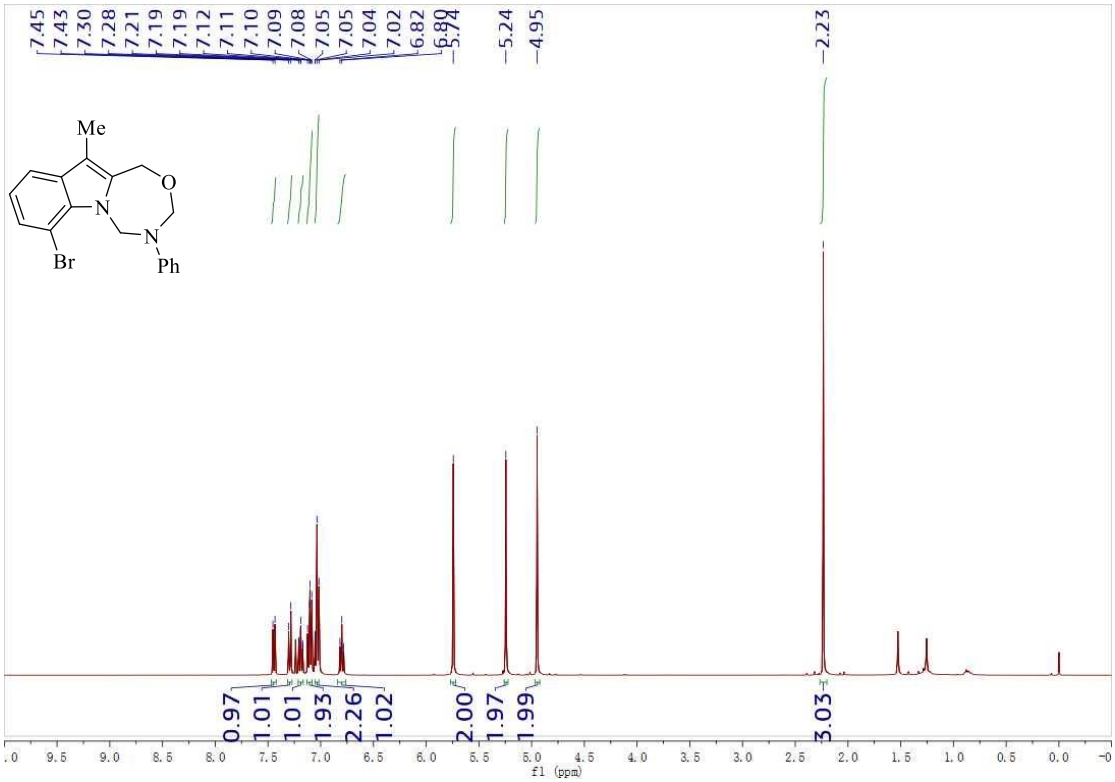
3d′ ^{13}C NMR (100 MHz, $CDCl_3$)



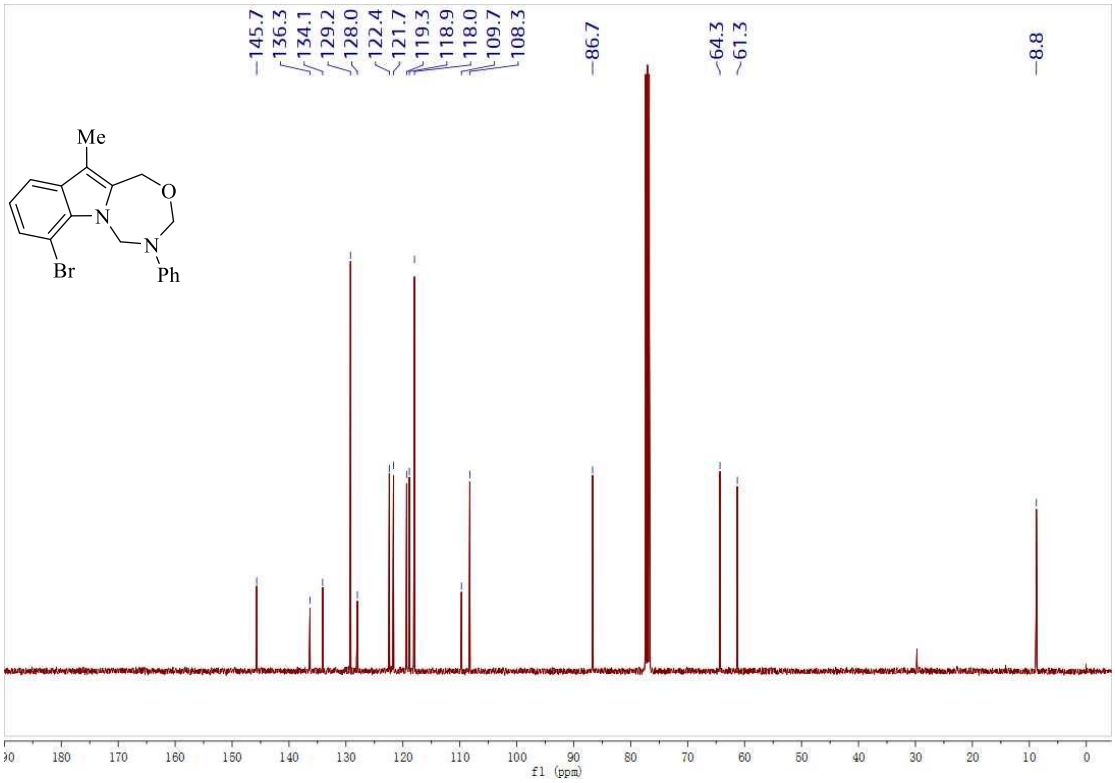
3d′ ^{19}F NMR (376 MHz, $CDCl_3$)



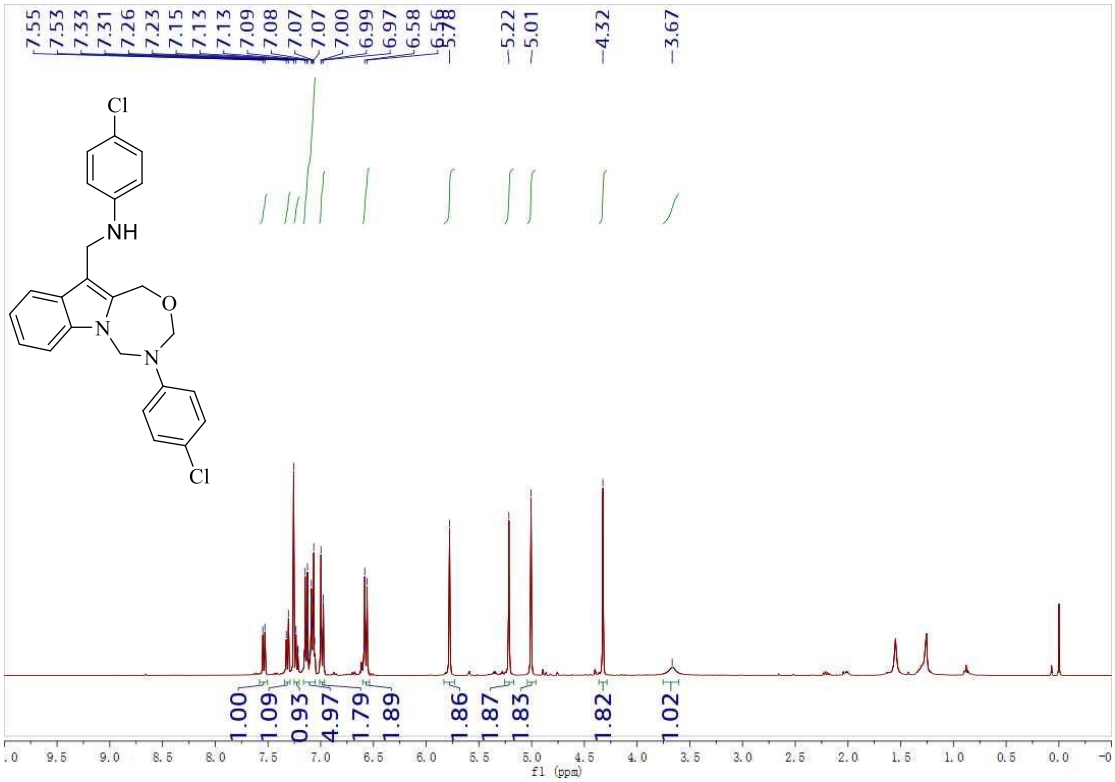
3e′ ^{1}H NMR (400 MHz, $CDCl_3$)



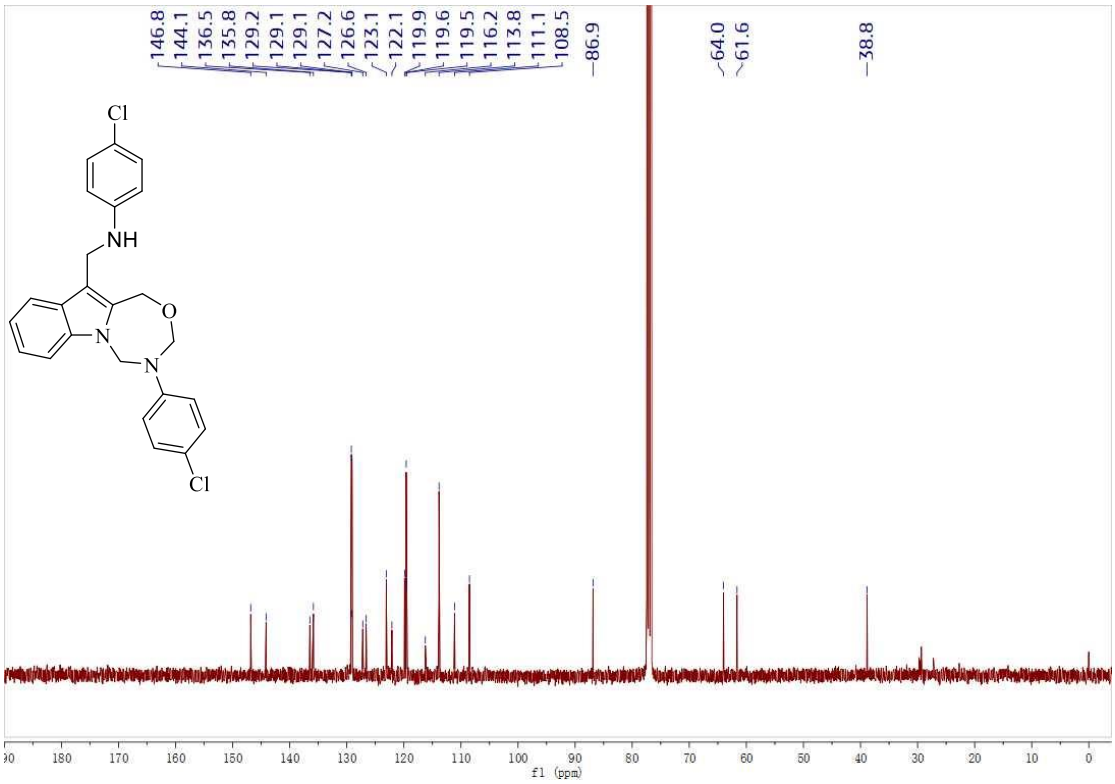
3e′ ^{13}C NMR (100 MHz, $CDCl_3$)



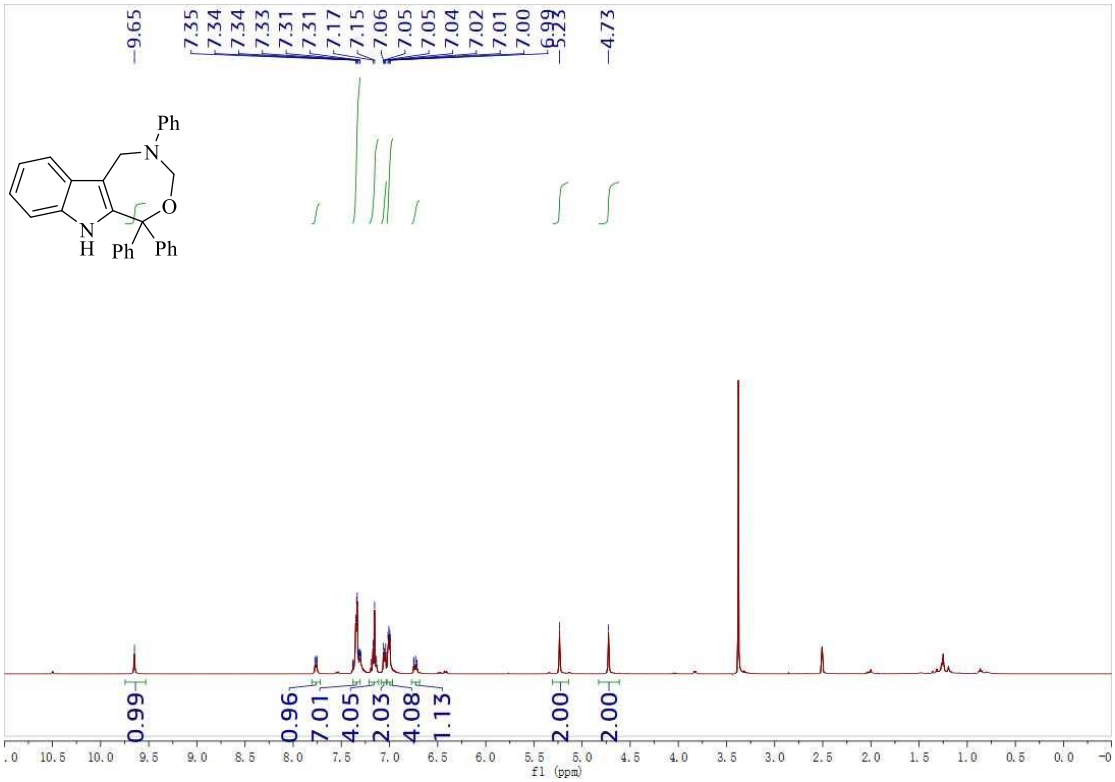
3k′ ^{1}H NMR (400 MHz, $CDCl_3$)



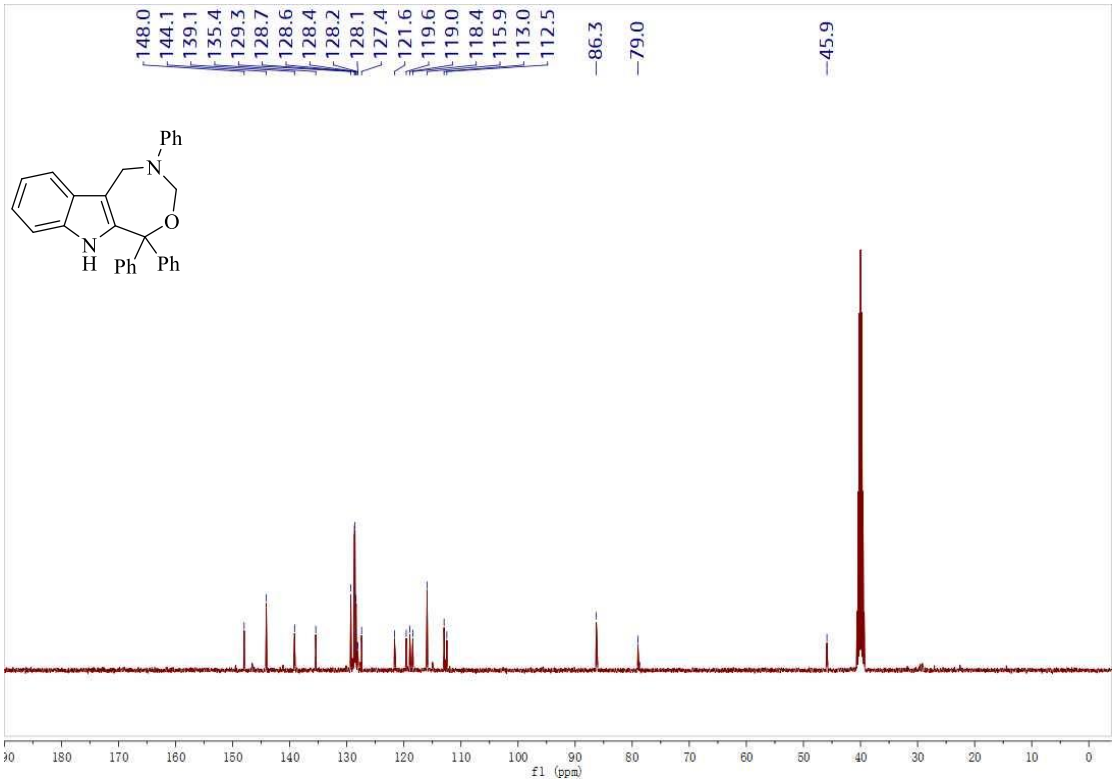
3k′ ^{13}C NMR (100 MHz, $CDCl_3$)



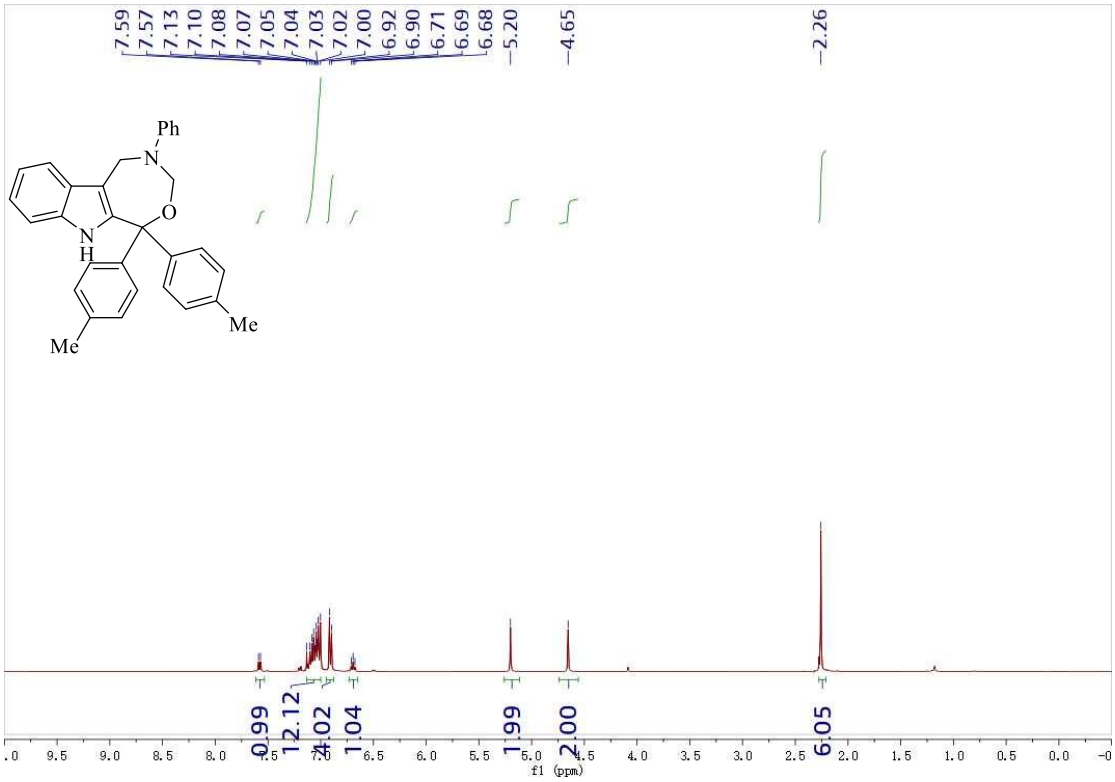
4b ^{1}H NMR (400 MHz, DMSO)



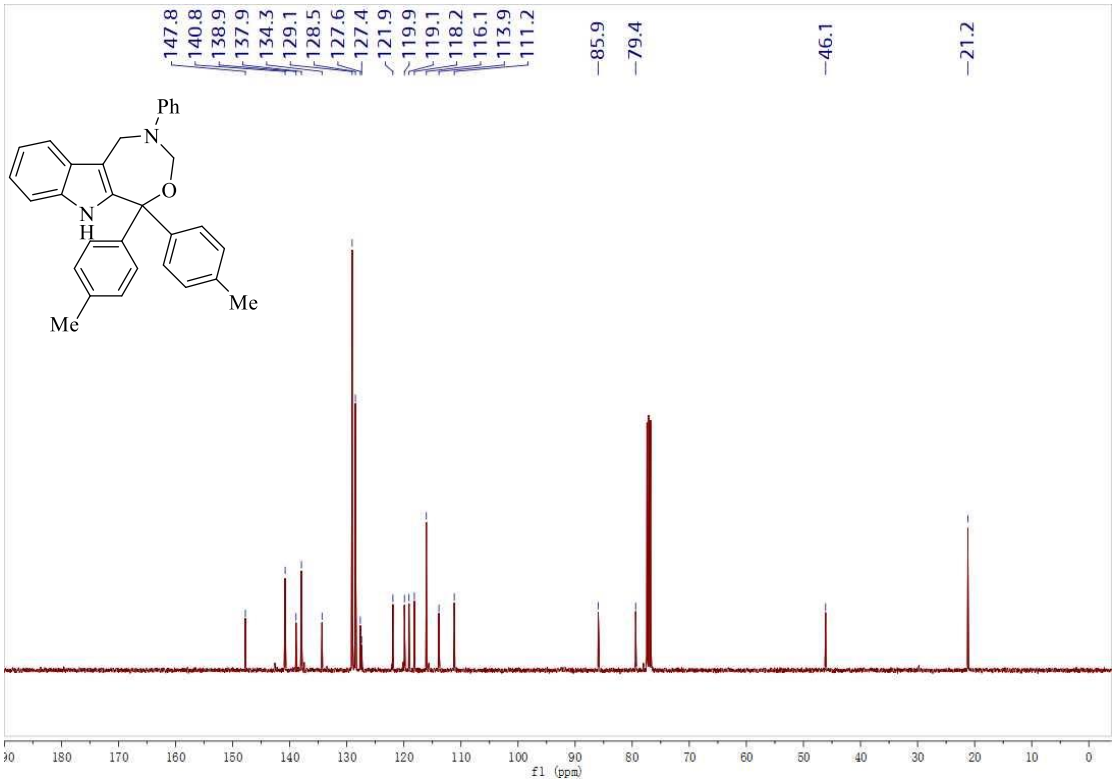
4b ^{13}C NMR (100 MHz, DMSO)



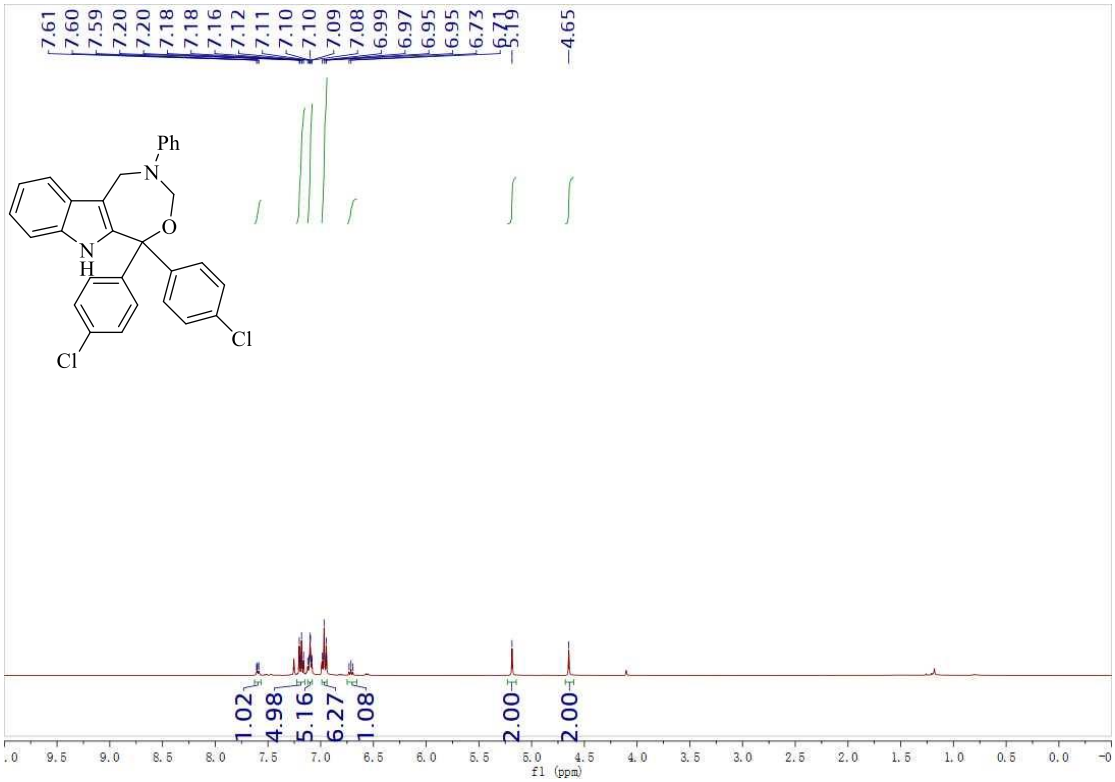
4c ^{1}H NMR (400 MHz, $CDCl_3$)



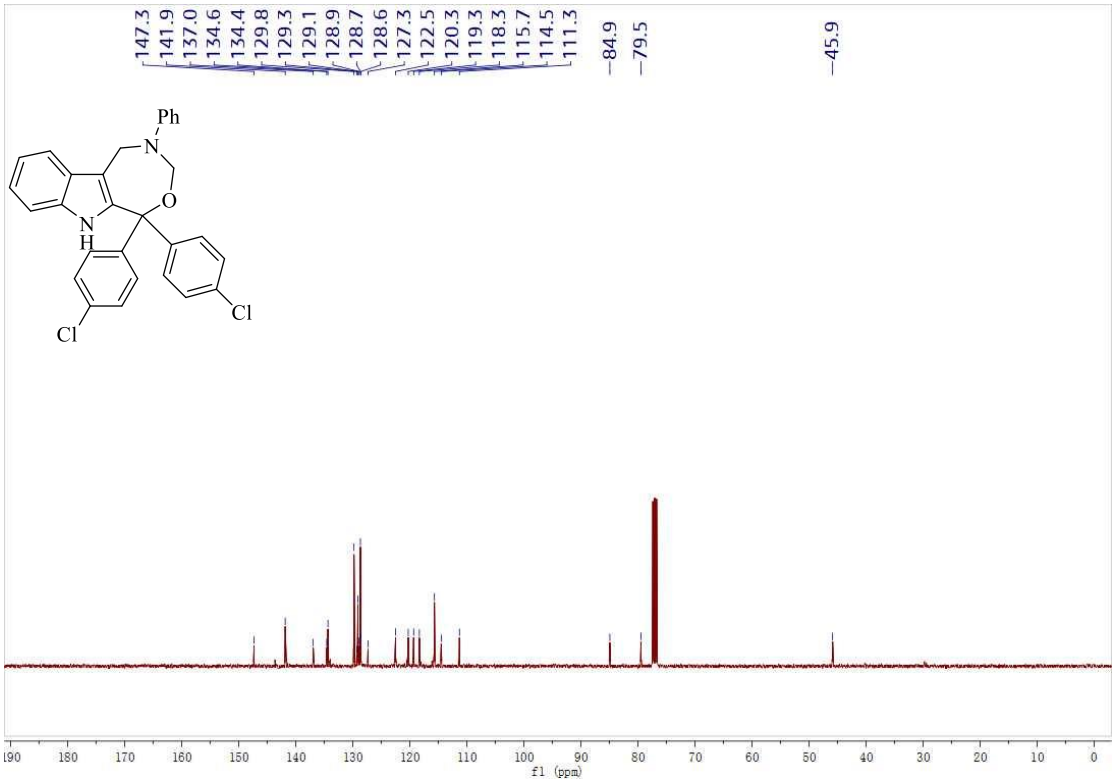
4c ^{13}C NMR (100 MHz, $CDCl_3$)



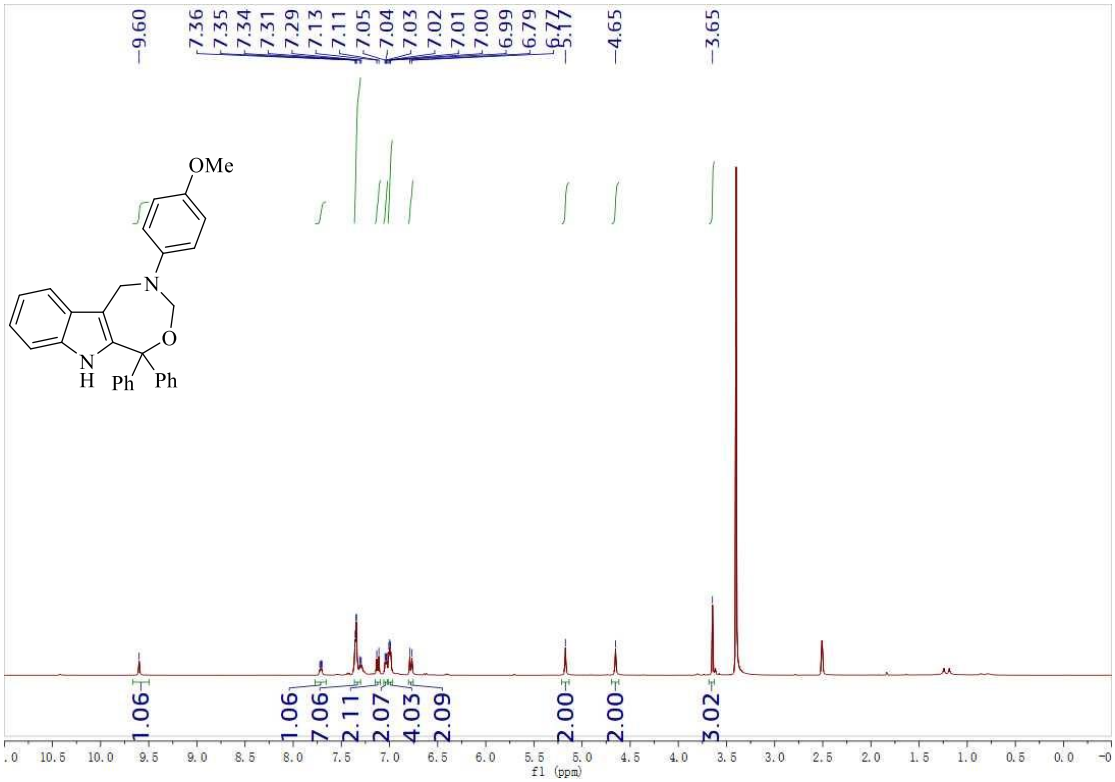
4d ^{1}H NMR (400 MHz, $CDCl_3$)



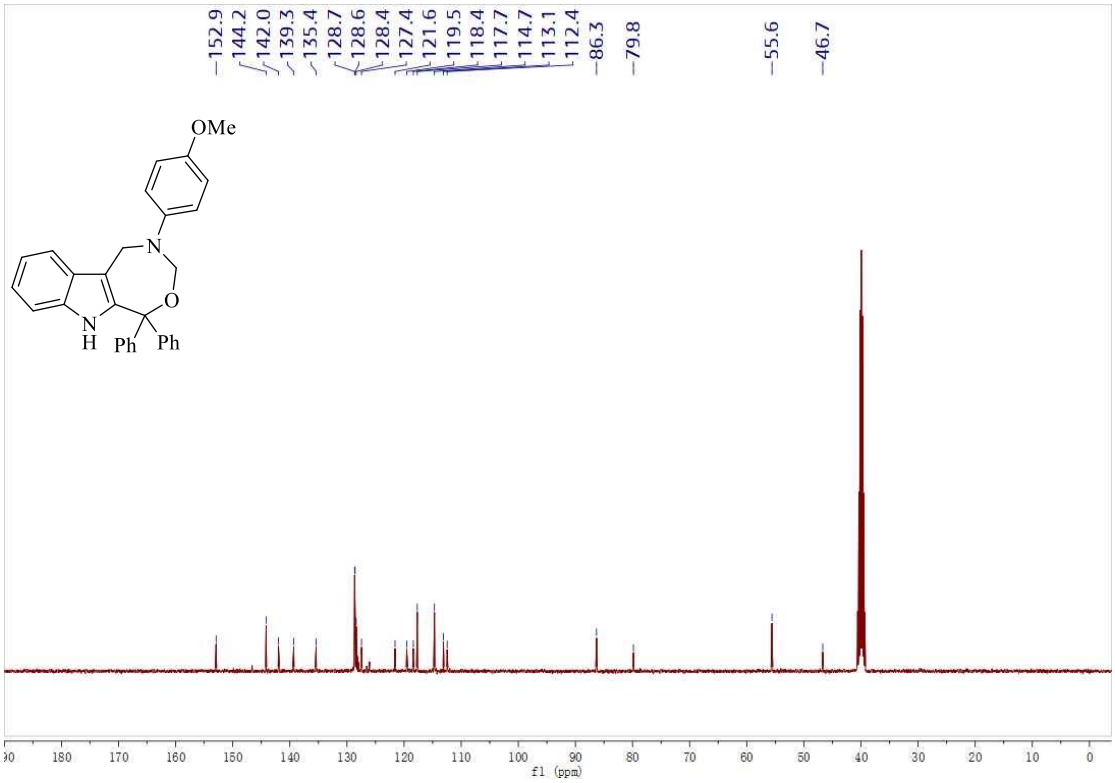
4d ^{13}C NMR (100 MHz, $CDCl_3$)



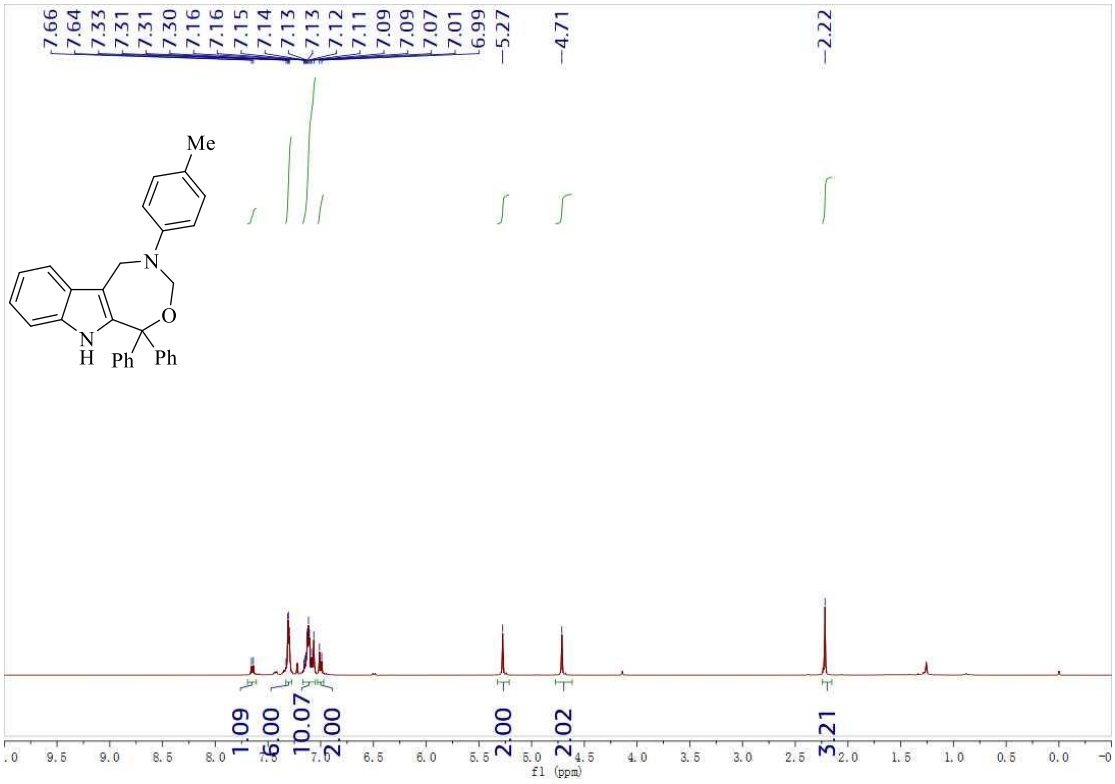
4e ^{1}H NMR (400 MHz, DMSO)



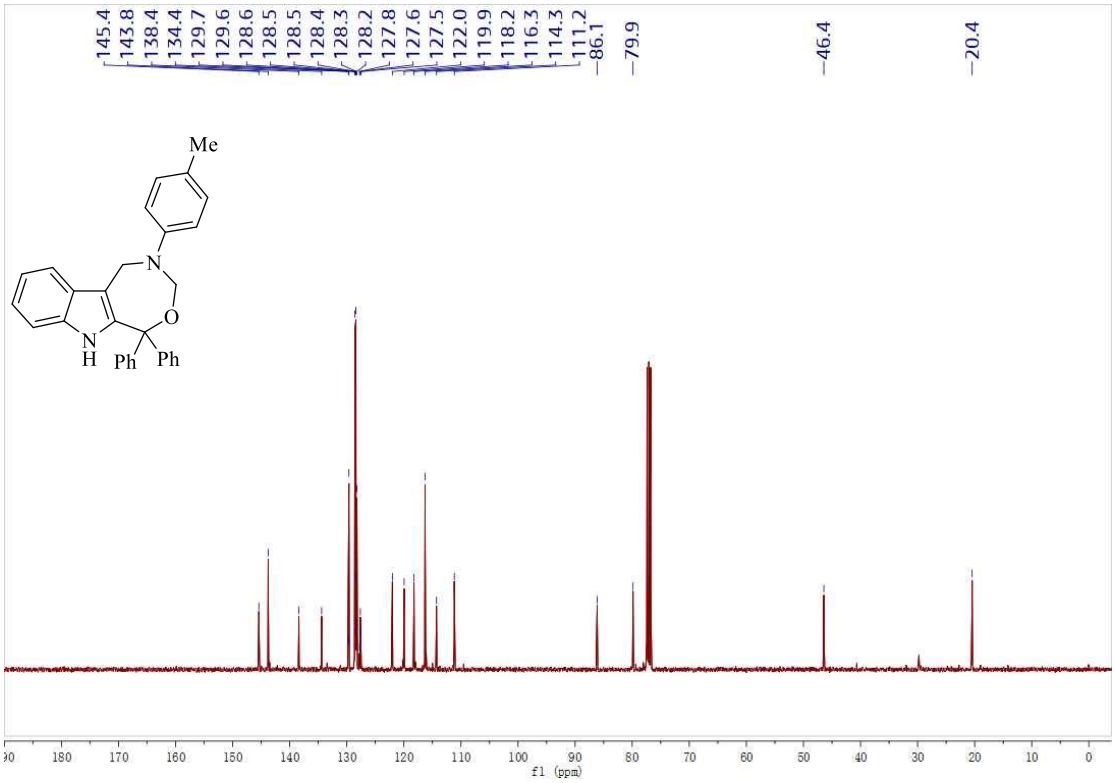
4e ^{13}C NMR (100 MHz, DMSO)



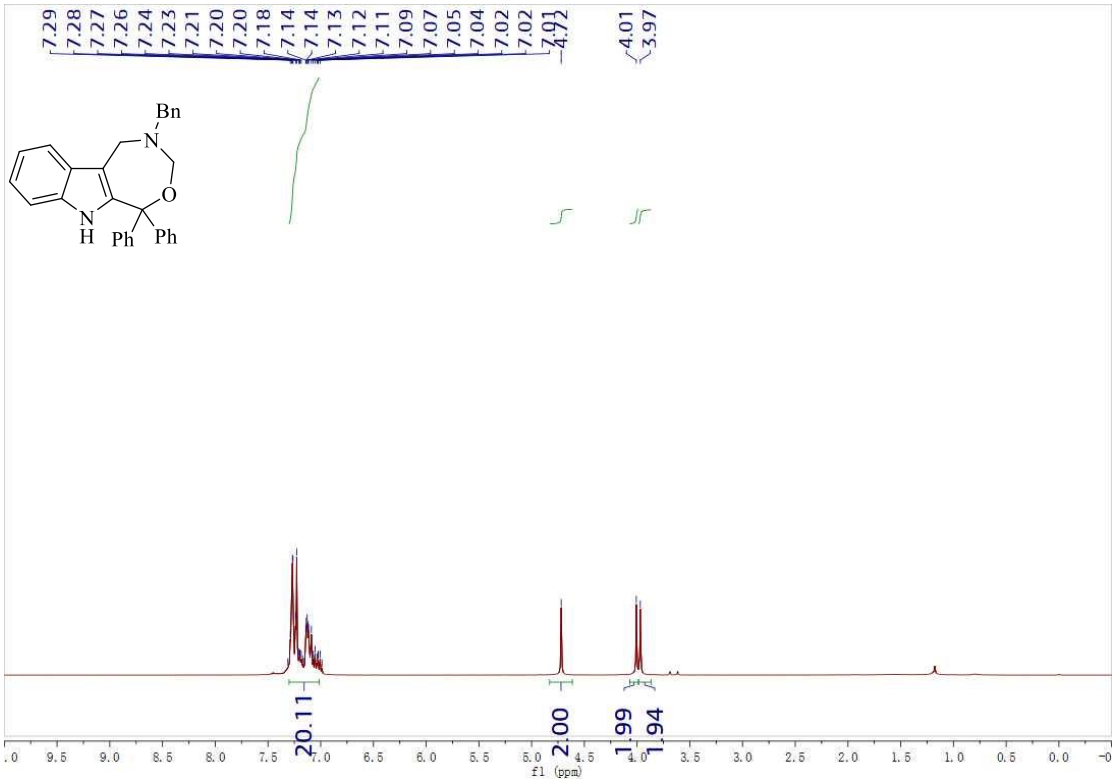
4f ^{1}H NMR (400 MHz, $CDCl_3$)



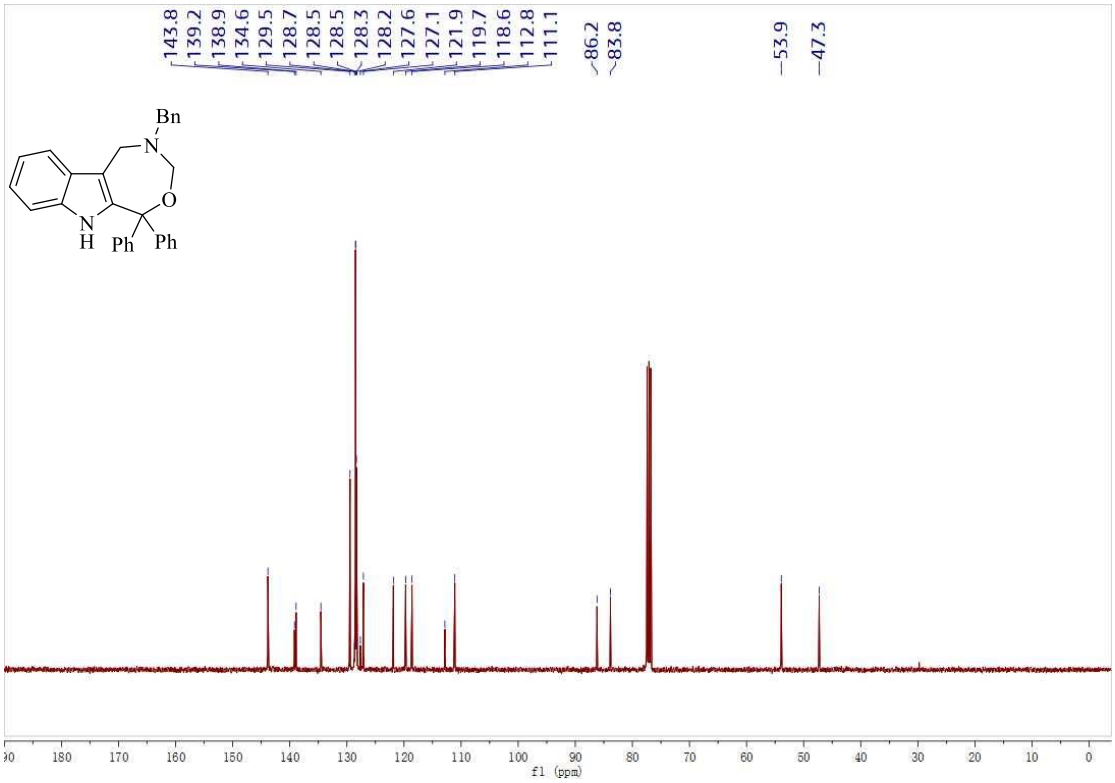
4f ^{13}C NMR (100 MHz, $CDCl_3$)



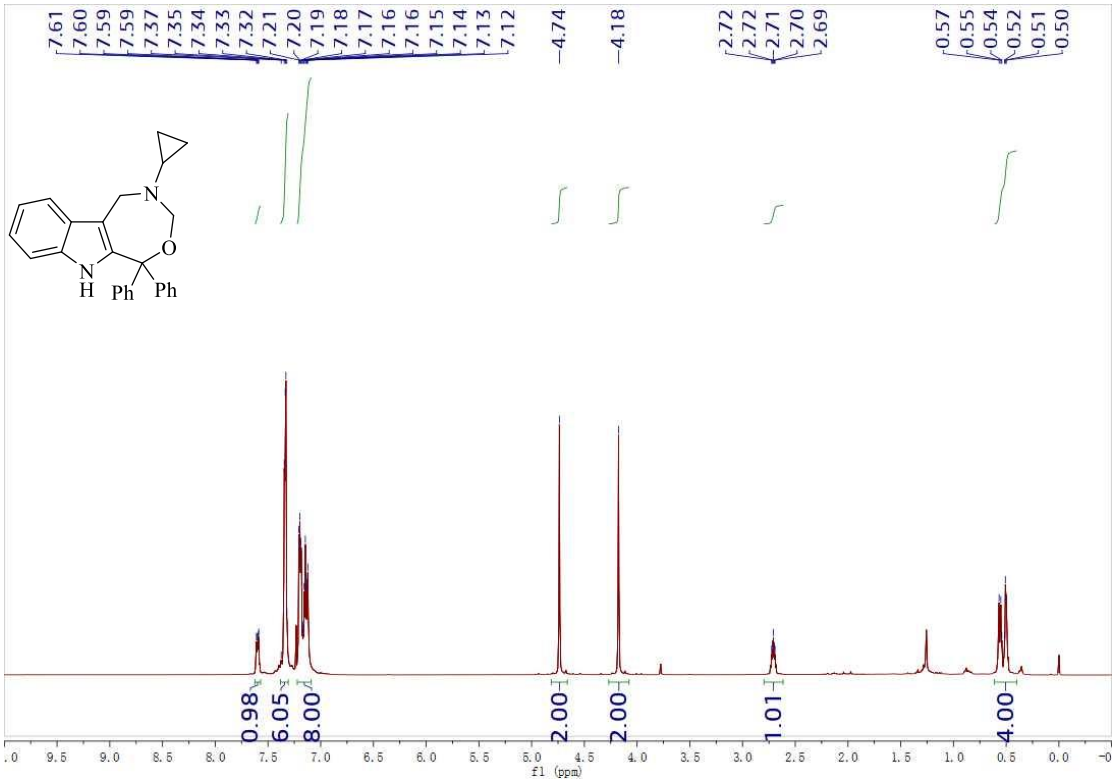
4g ^{1}H NMR (400 MHz, $CDCl_3$)



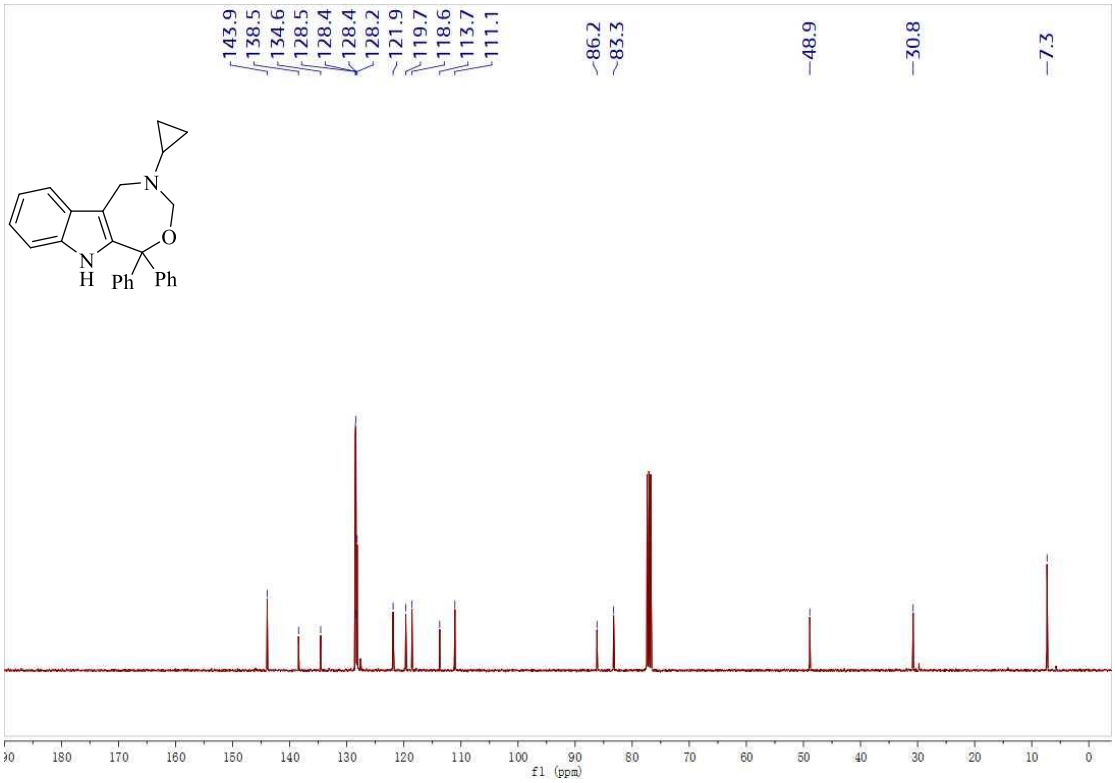
4g ^{13}C NMR (100 MHz, $CDCl_3$)



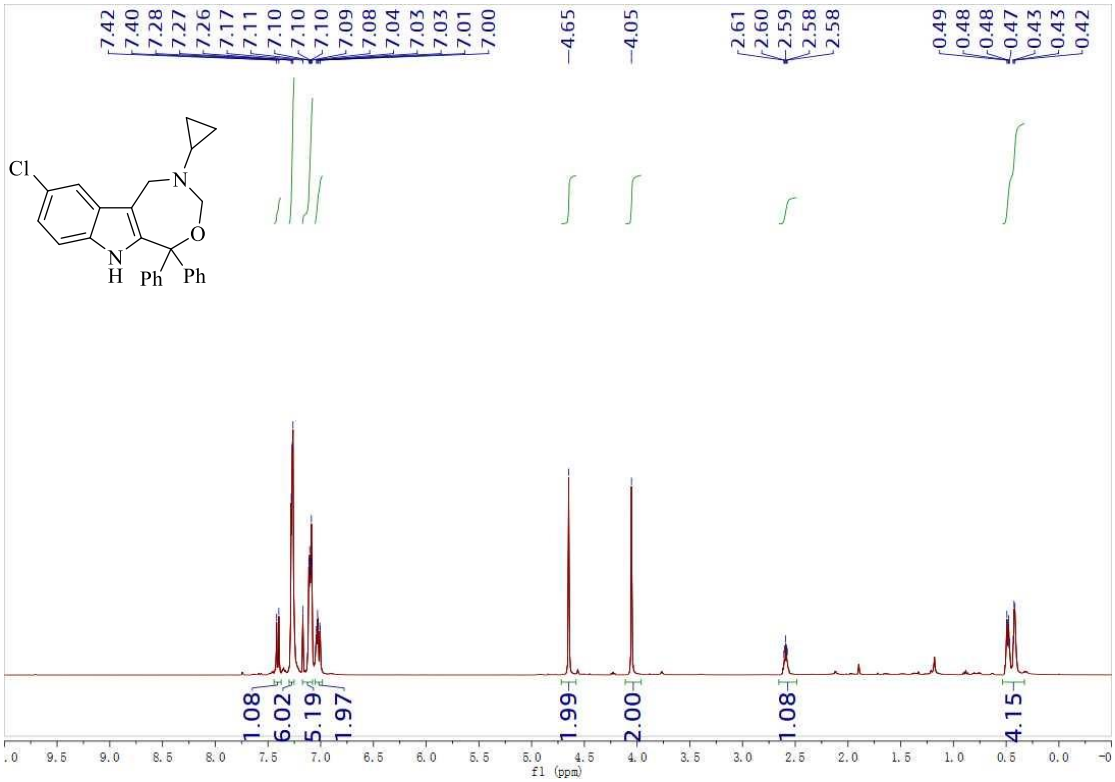
4h ^{1}H NMR (400 MHz, $CDCl_3$)



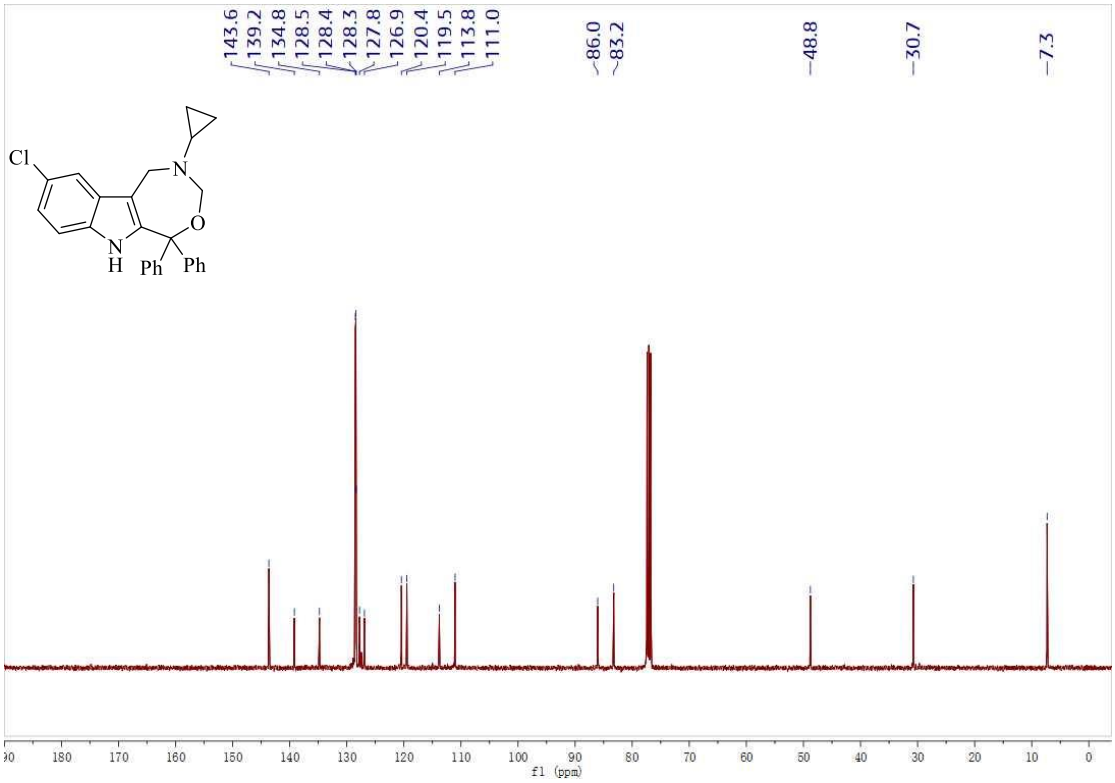
4h ^{13}C NMR (100 MHz, $CDCl_3$)



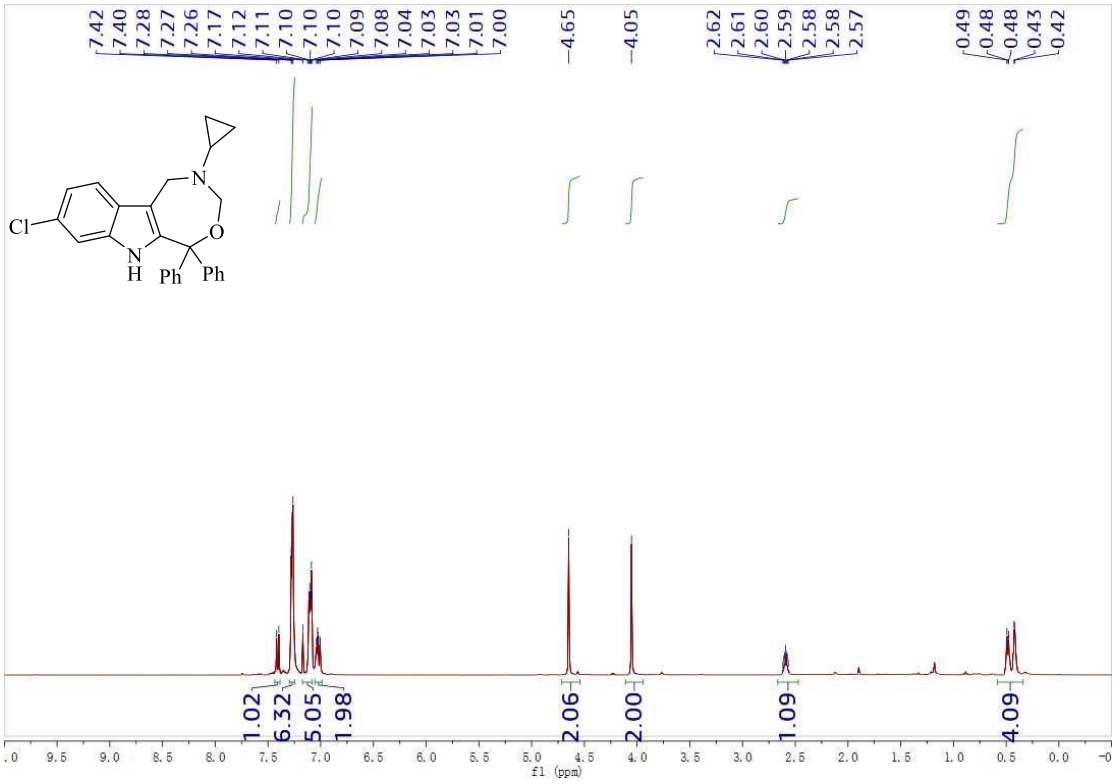
4i ^{1}H NMR (400 MHz, $CDCl_3$)



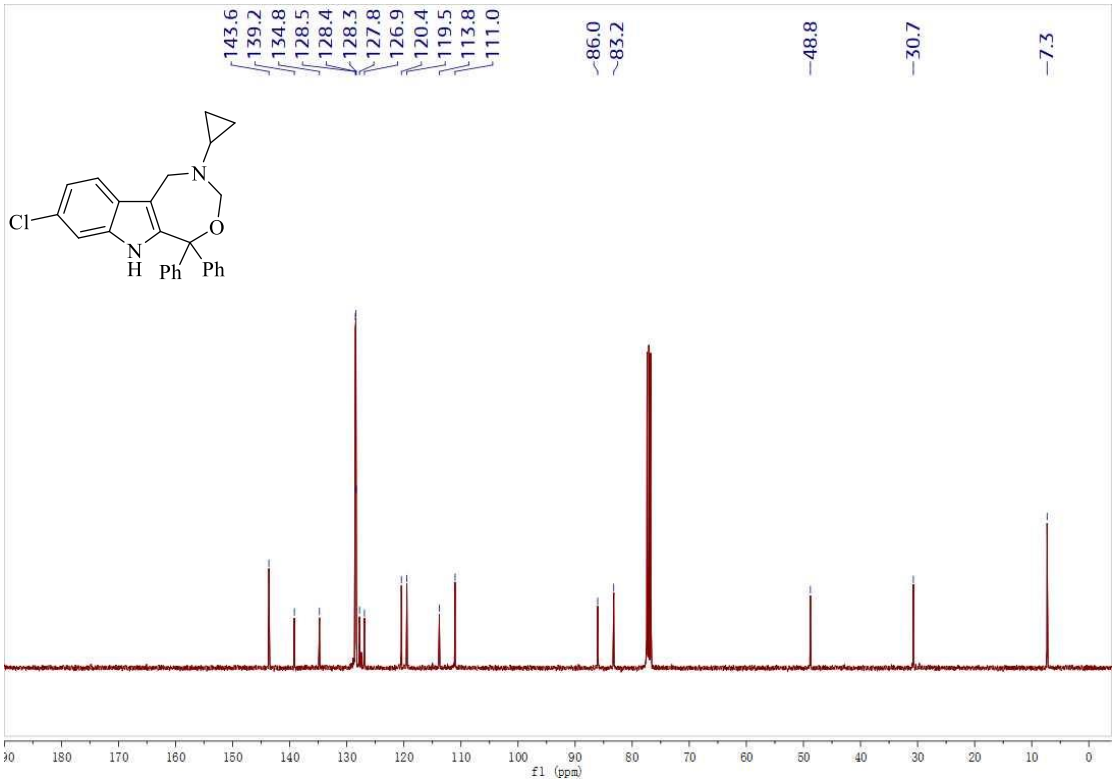
4i ^{13}C NMR (100 MHz, $CDCl_3$)



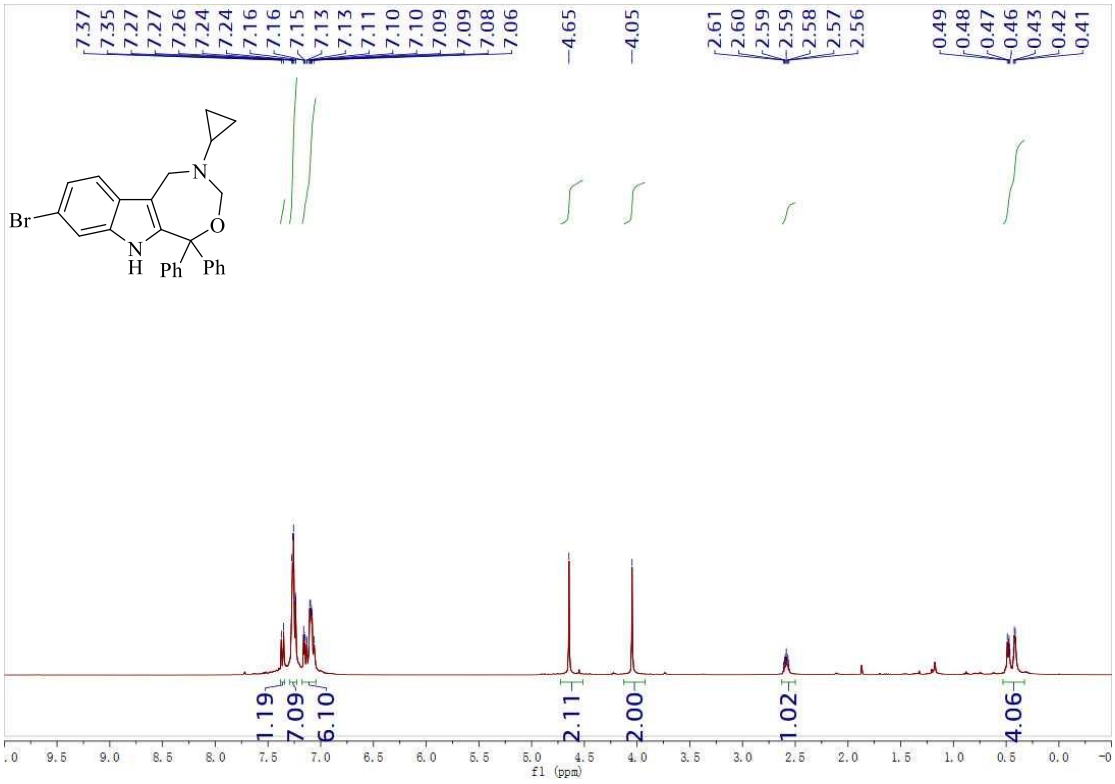
4j ^{1}H NMR (400 MHz, $CDCl_3$)



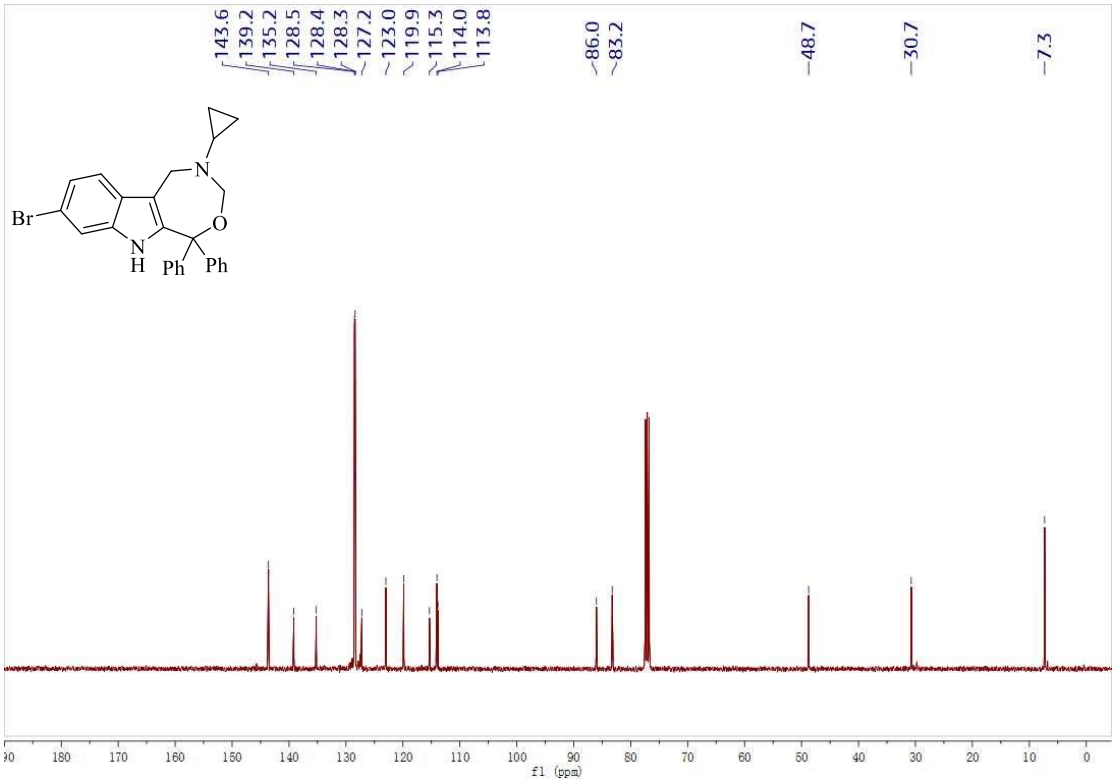
4j ^{13}C NMR (100 MHz, $CDCl_3$)



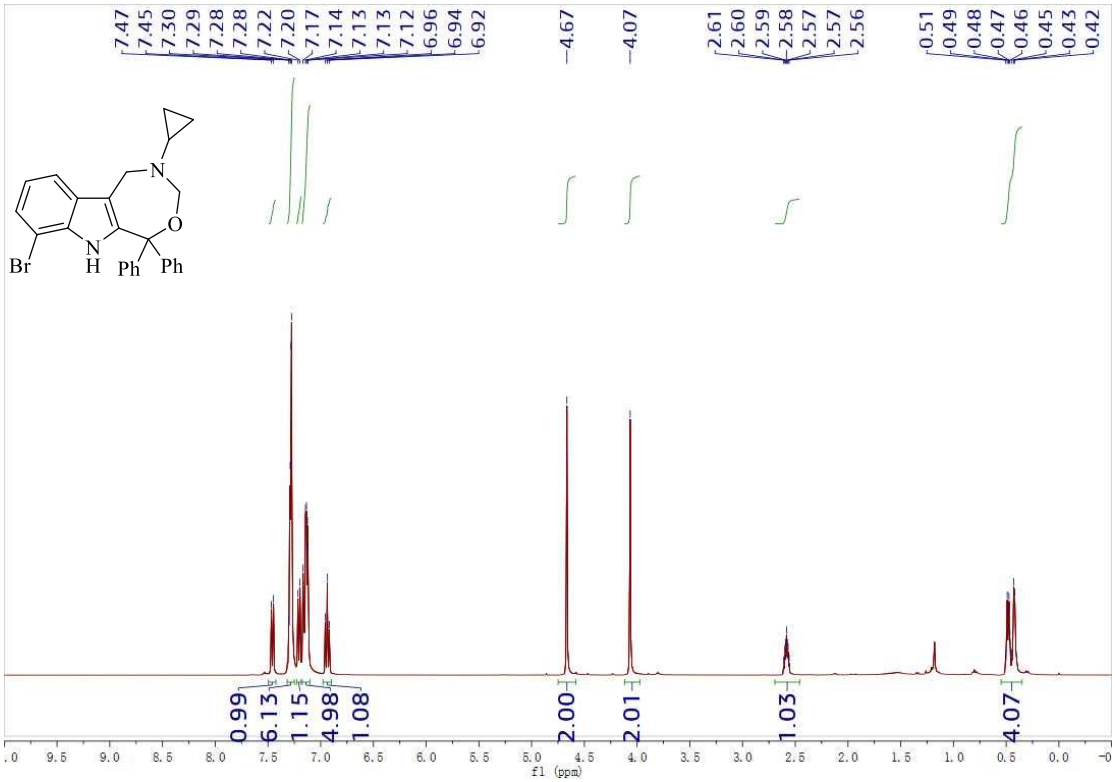
4k ^{1}H NMR (400 MHz, $CDCl_3$)



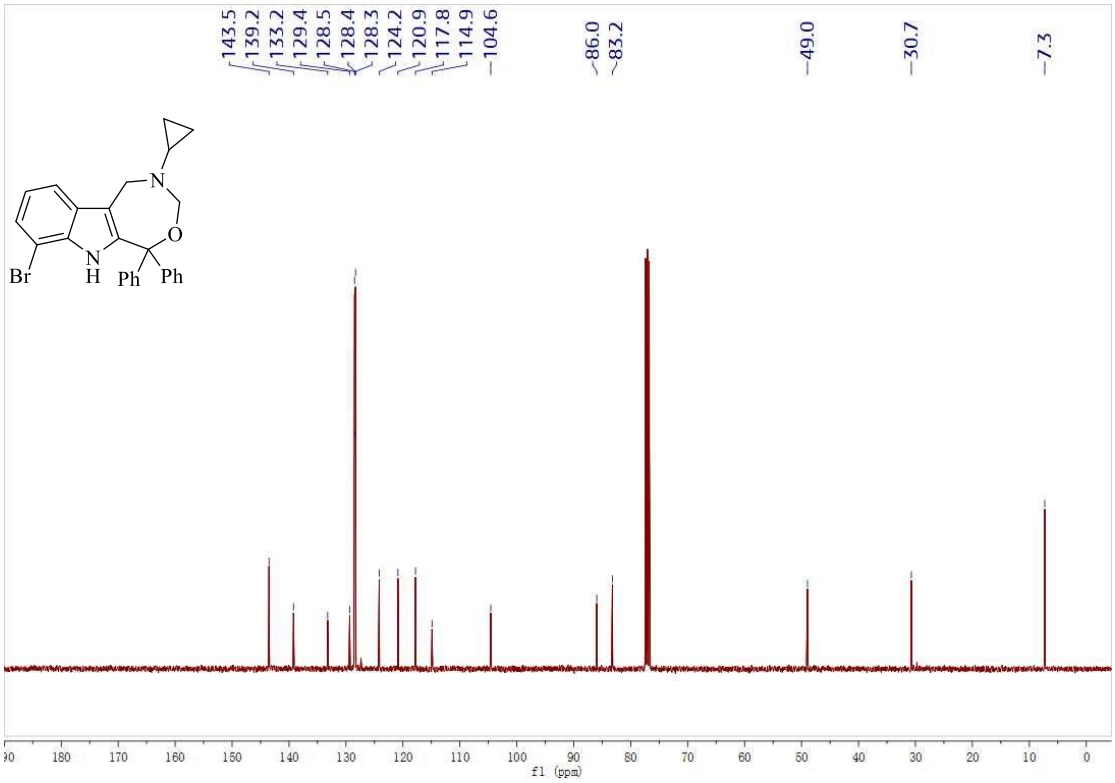
4k ^{13}C NMR (100 MHz, $CDCl_3$)



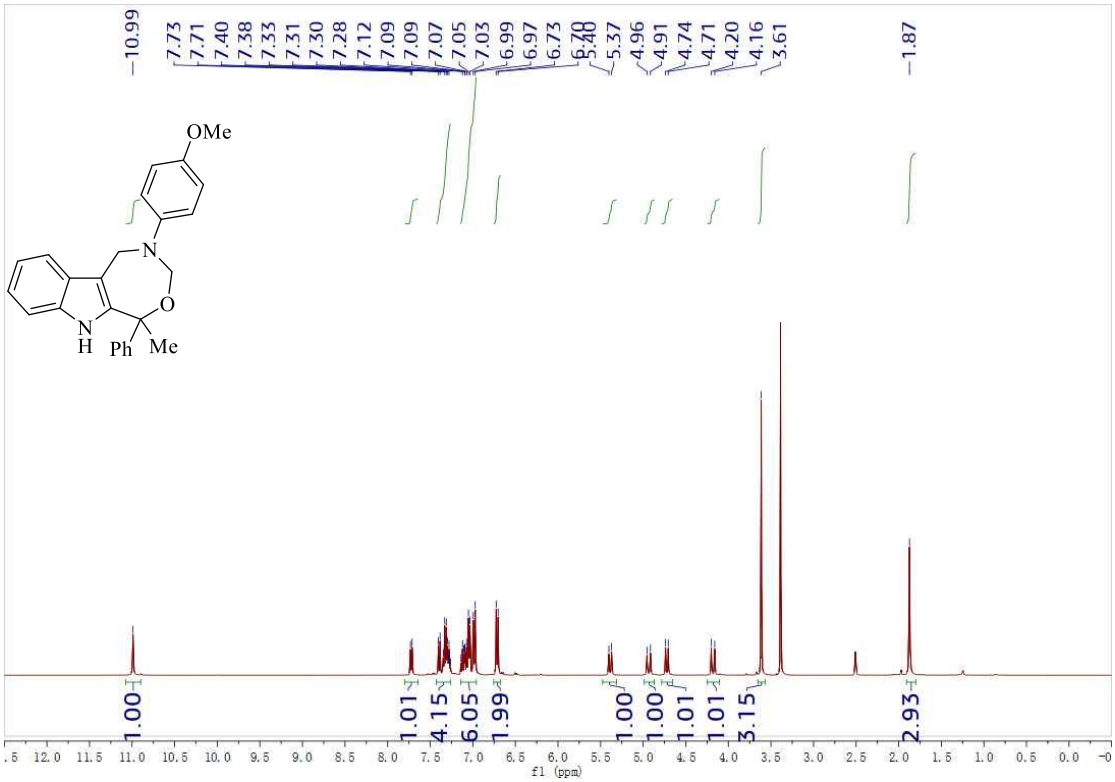
4l ^{1}H NMR (400 MHz, $CDCl_3$)



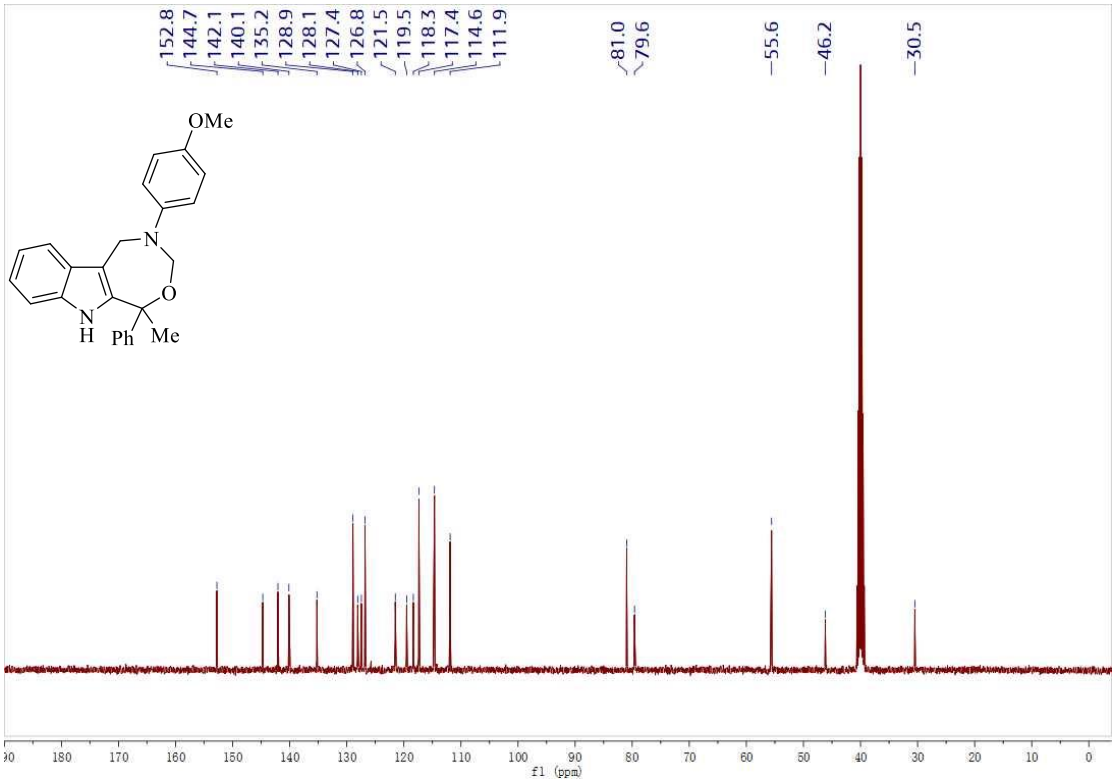
4l ^{13}C NMR (100 MHz, $CDCl_3$)



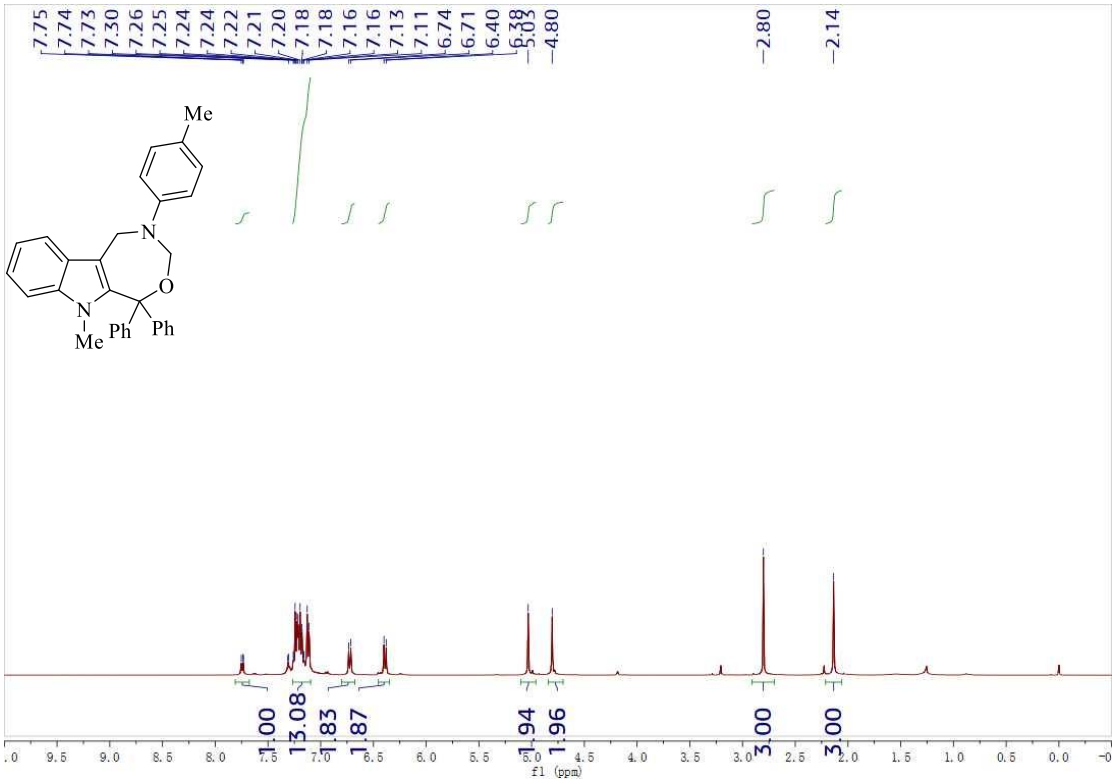
4m ^{1}H NMR (400 MHz, DMSO)



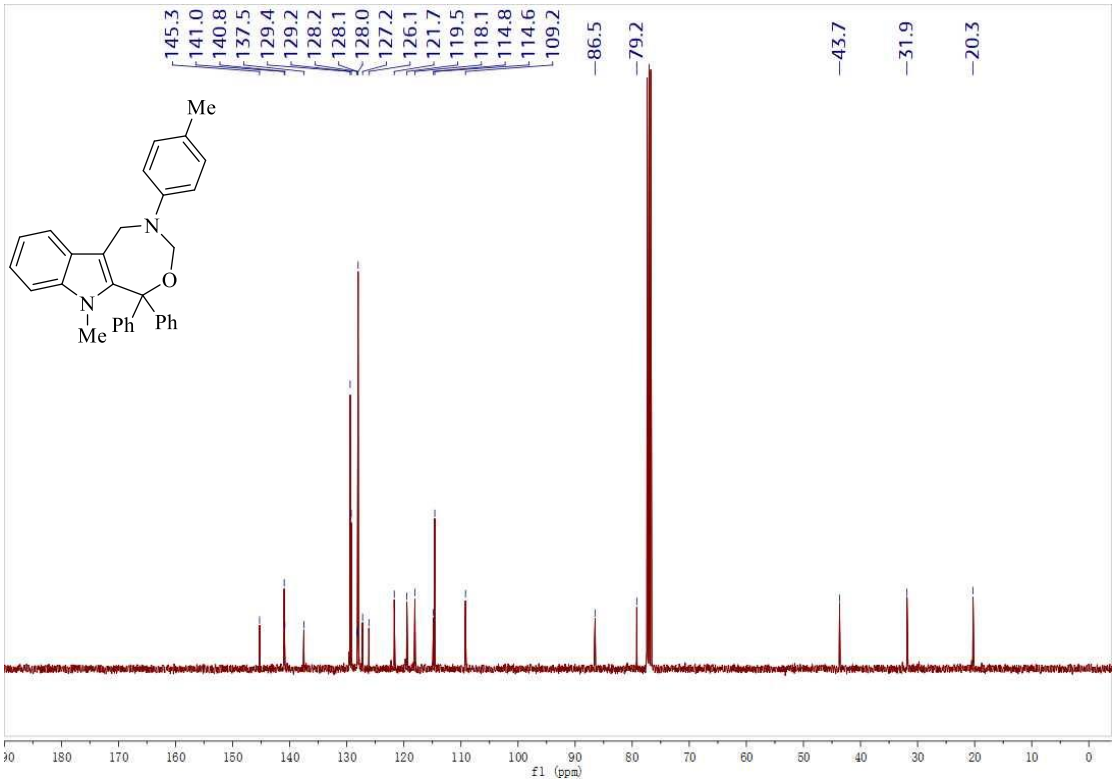
4m ^{13}C NMR (100 MHz, DMSO)



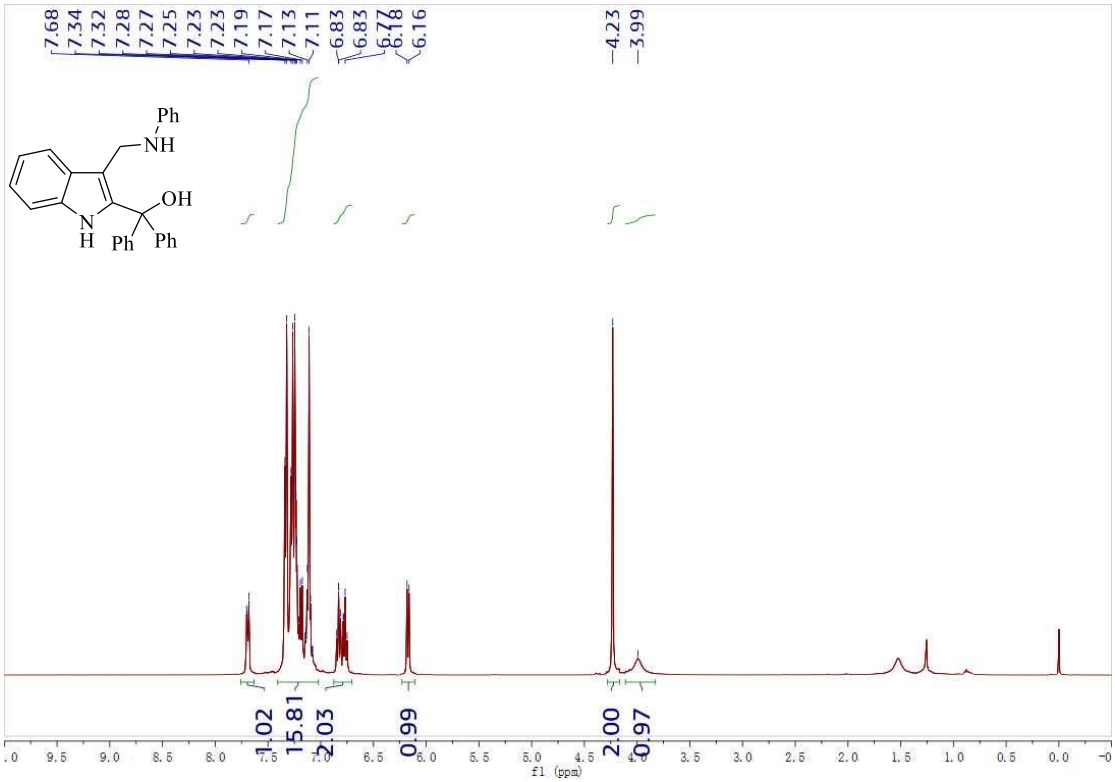
4n ^{1}H NMR (400 MHz, $CDCl_3$)



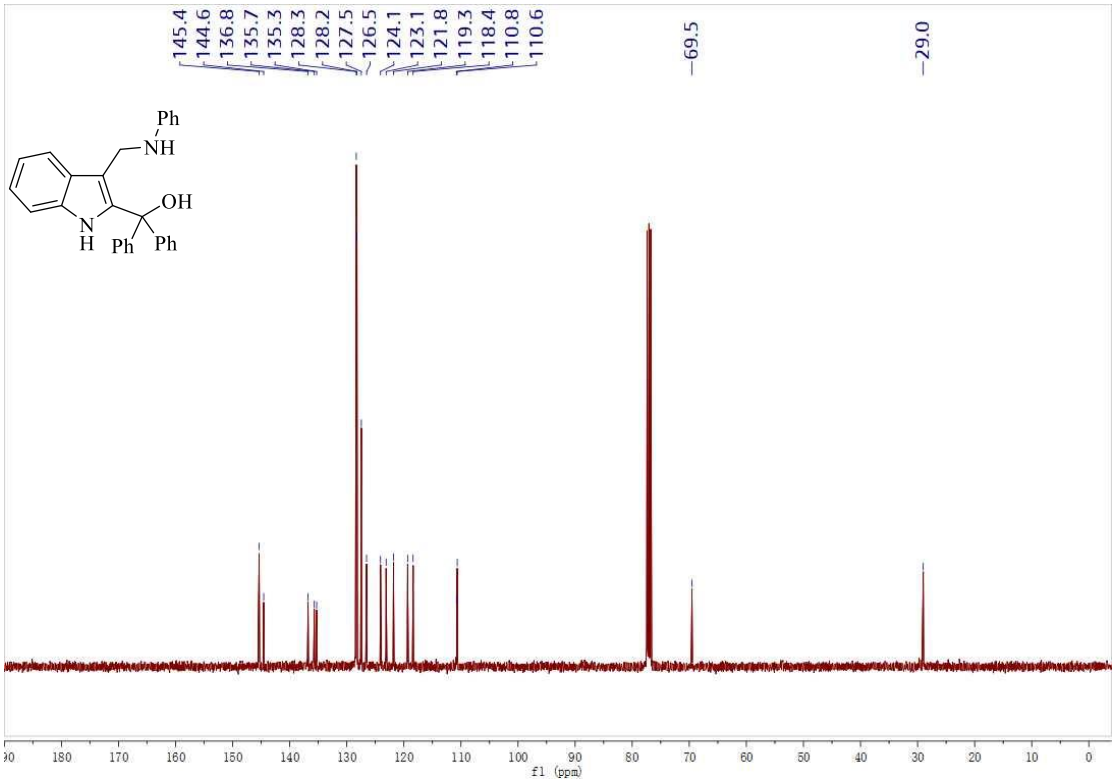
4n ^{13}C NMR (100 MHz, $CDCl_3$)



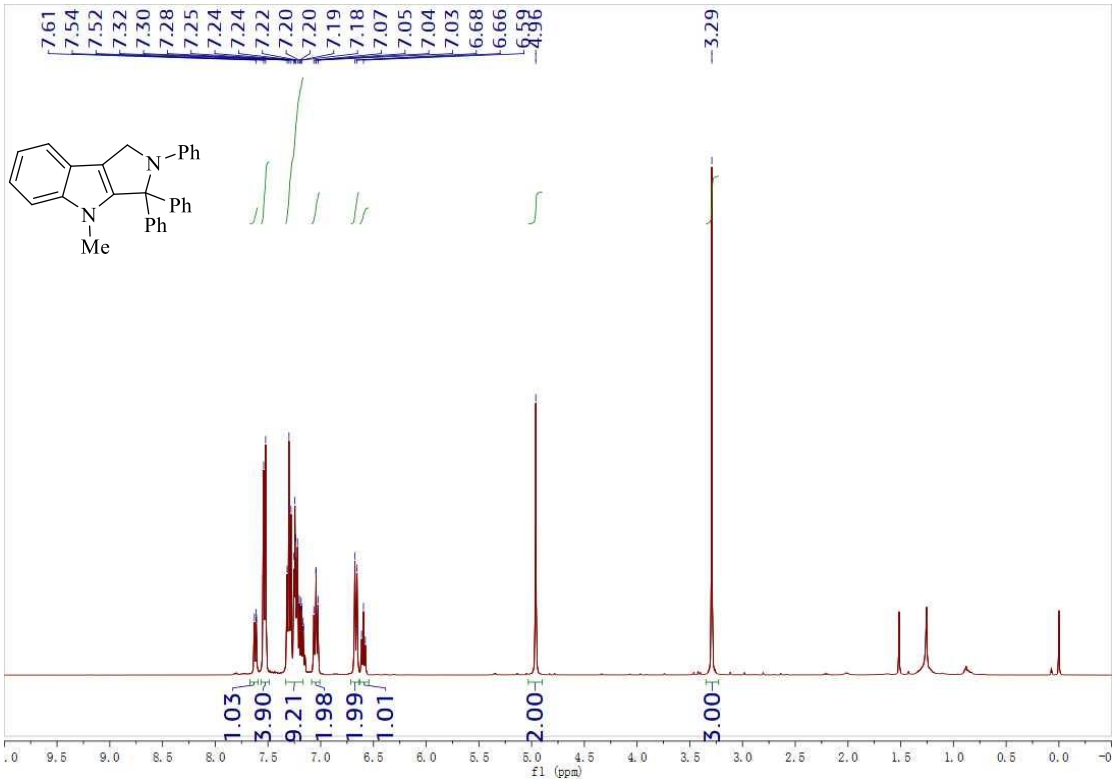
Int-4b ^{1}H NMR (400 MHz, $CDCl_3$)



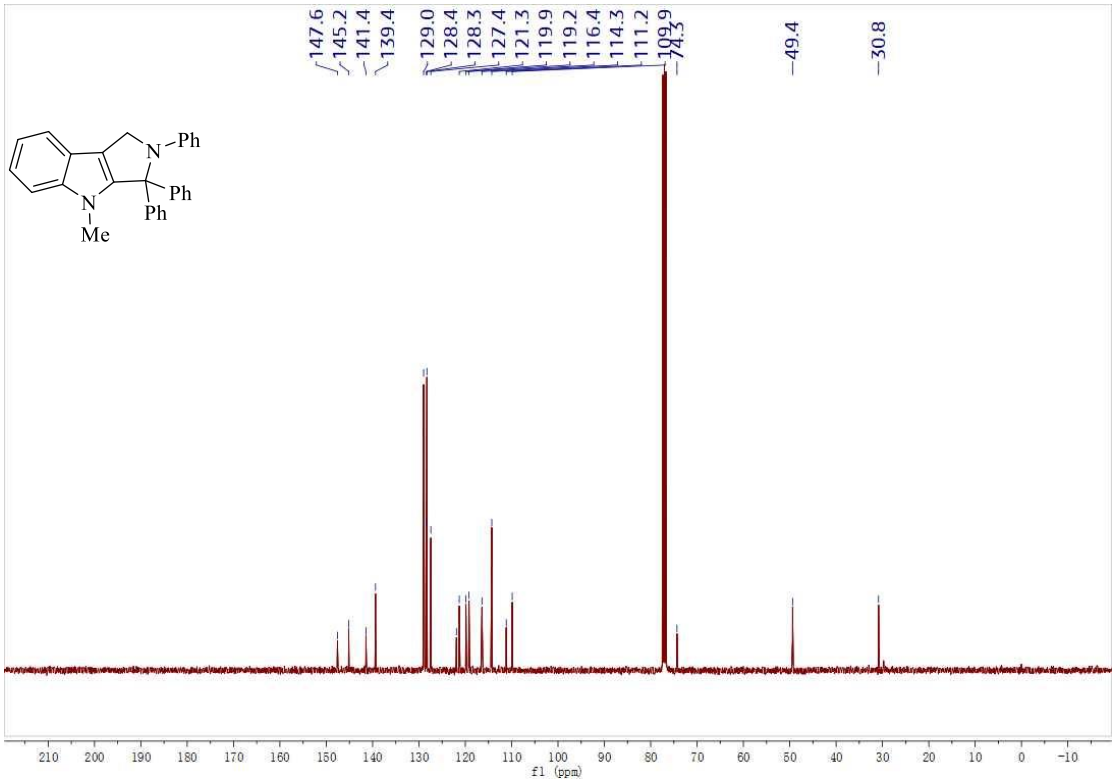
Int-4b ^{13}C NMR (100 MHz, $CDCl_3$)



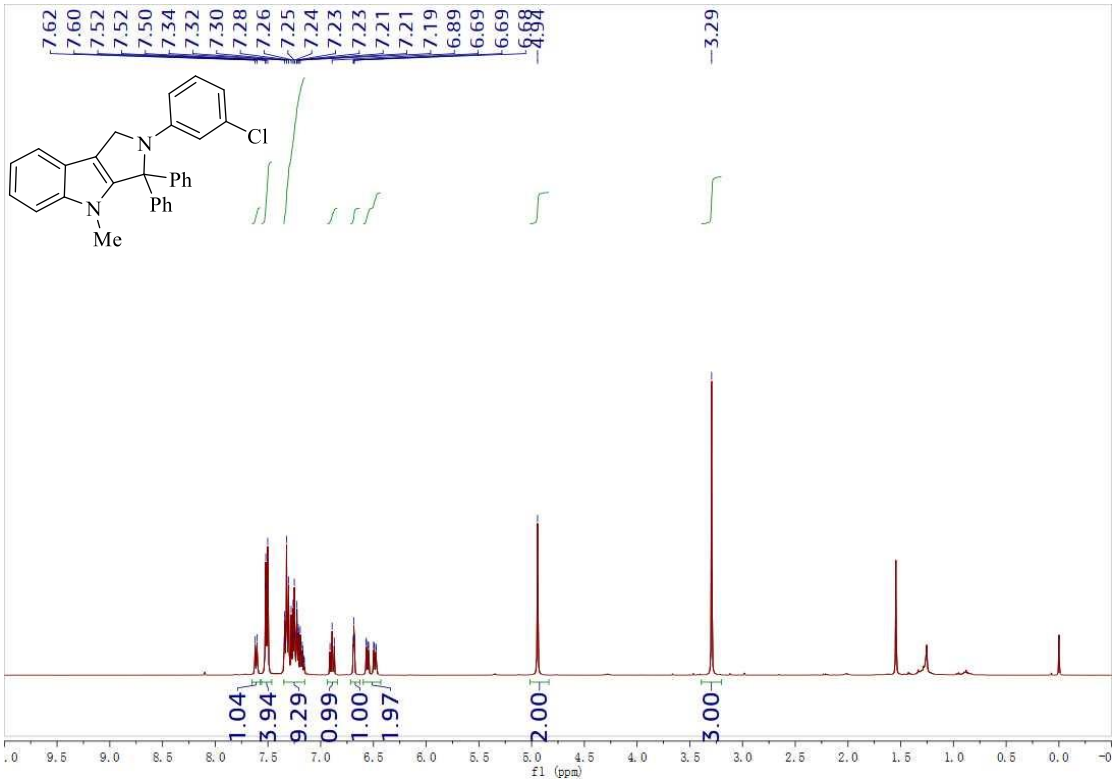
5b′ ^{1}H NMR (400 MHz, $CDCl_3$)



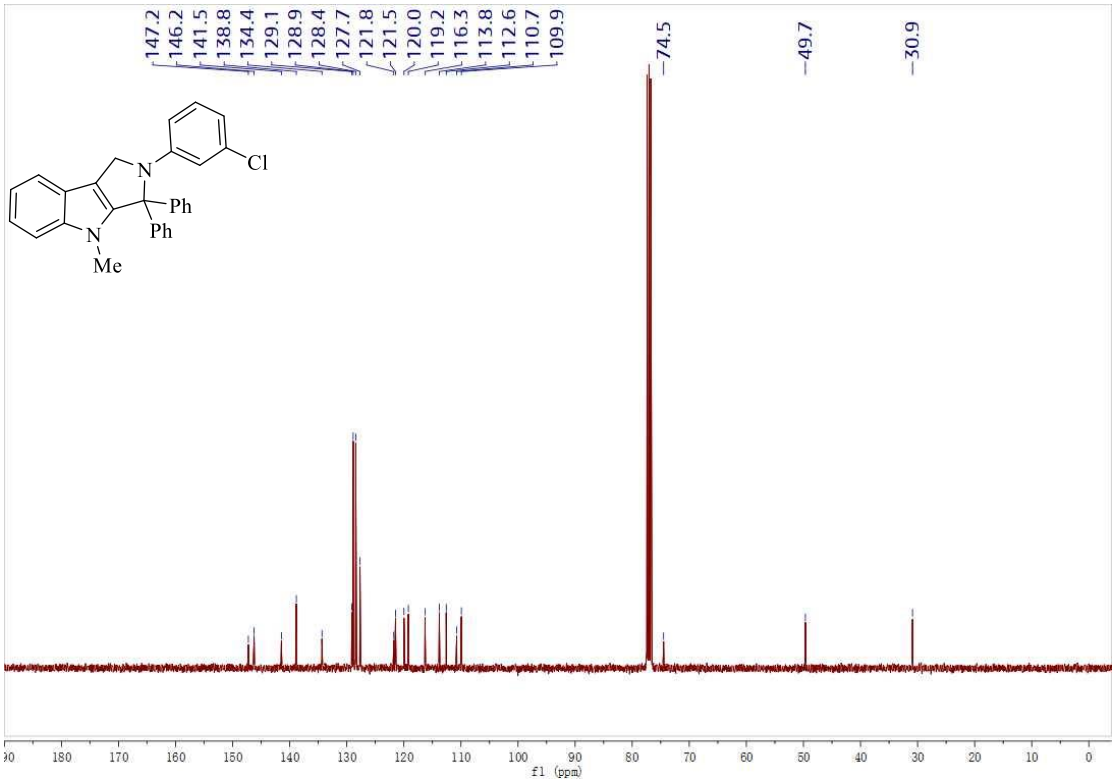
5b′ ^{13}C NMR (100 MHz, $CDCl_3$)



5c′ ^{1}H NMR (400 MHz, $CDCl_3$)



5c′ ^{13}C NMR (100 MHz, $CDCl_3$)



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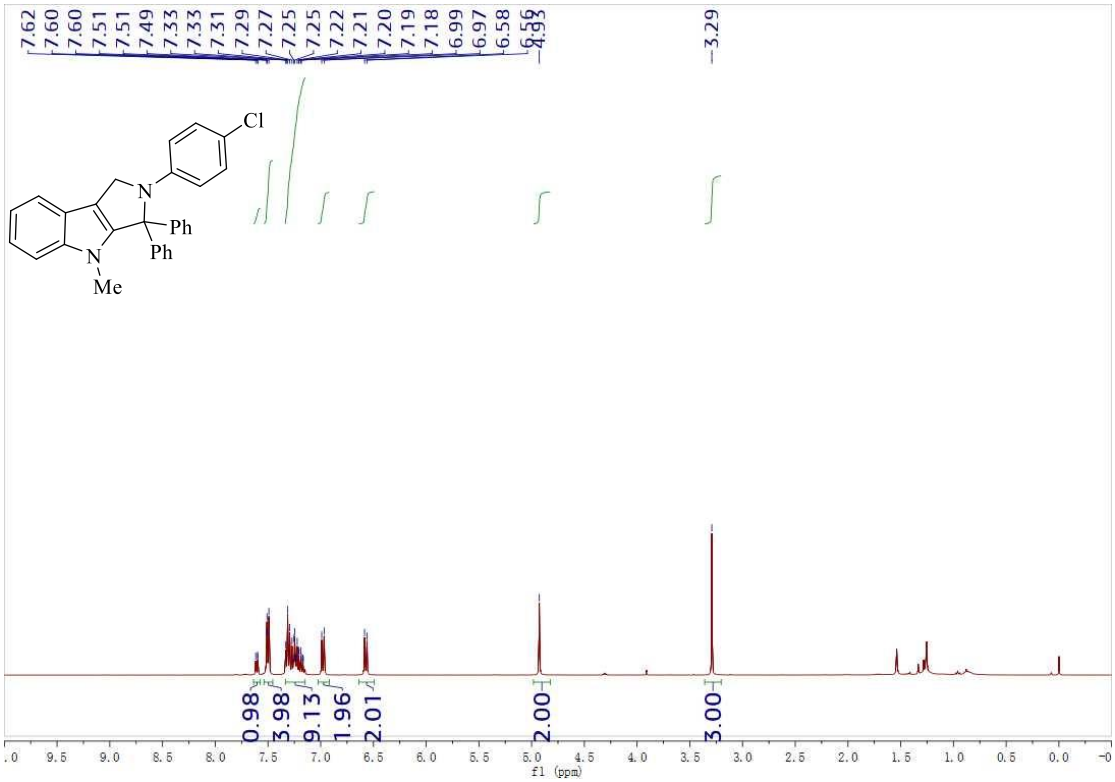
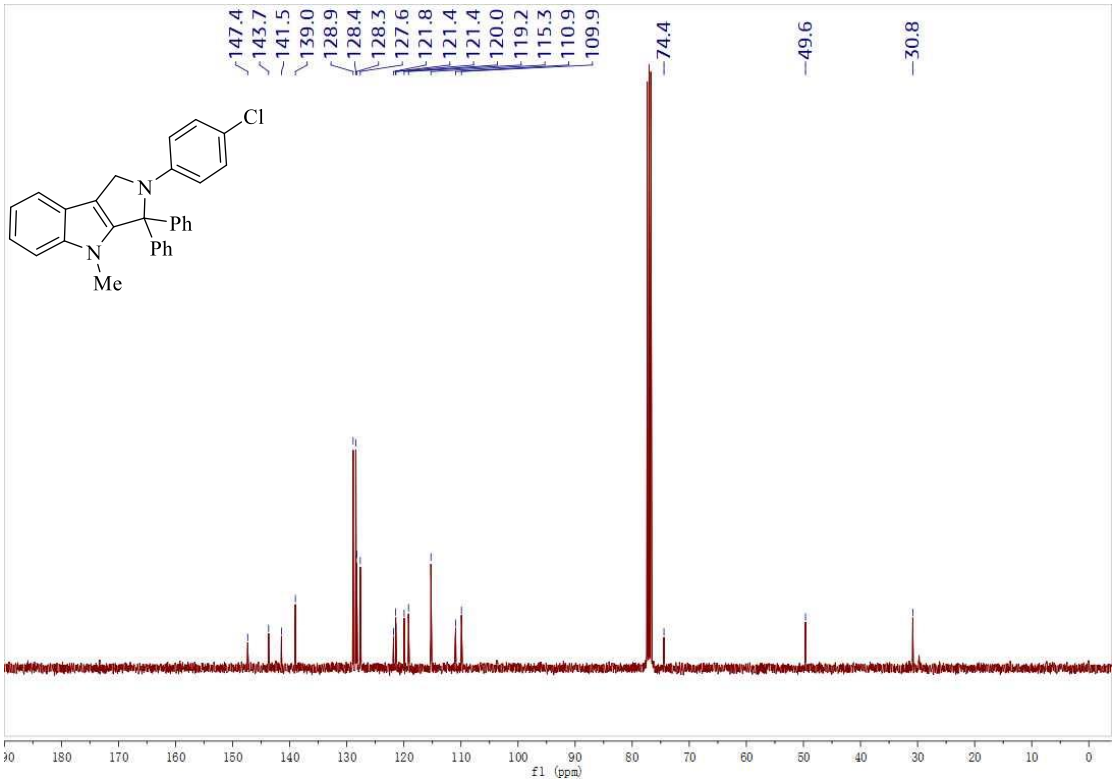


5d′ ^{13}C NMR (100 MHz, $CDCl_3$)



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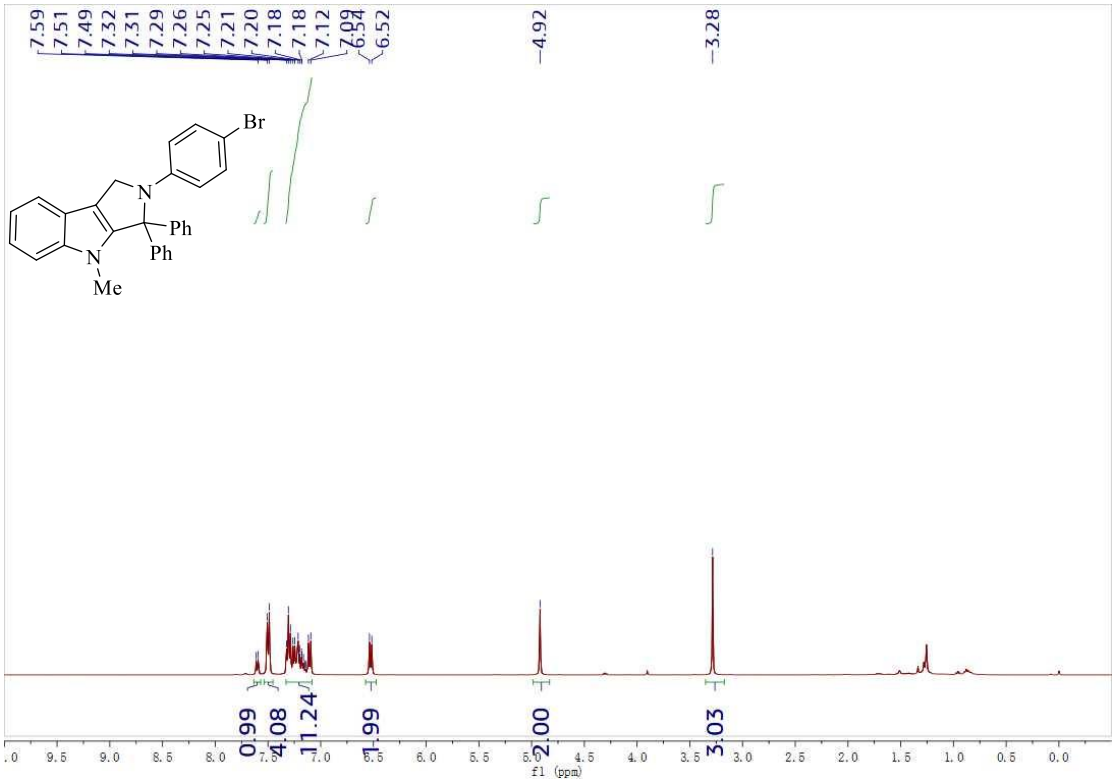

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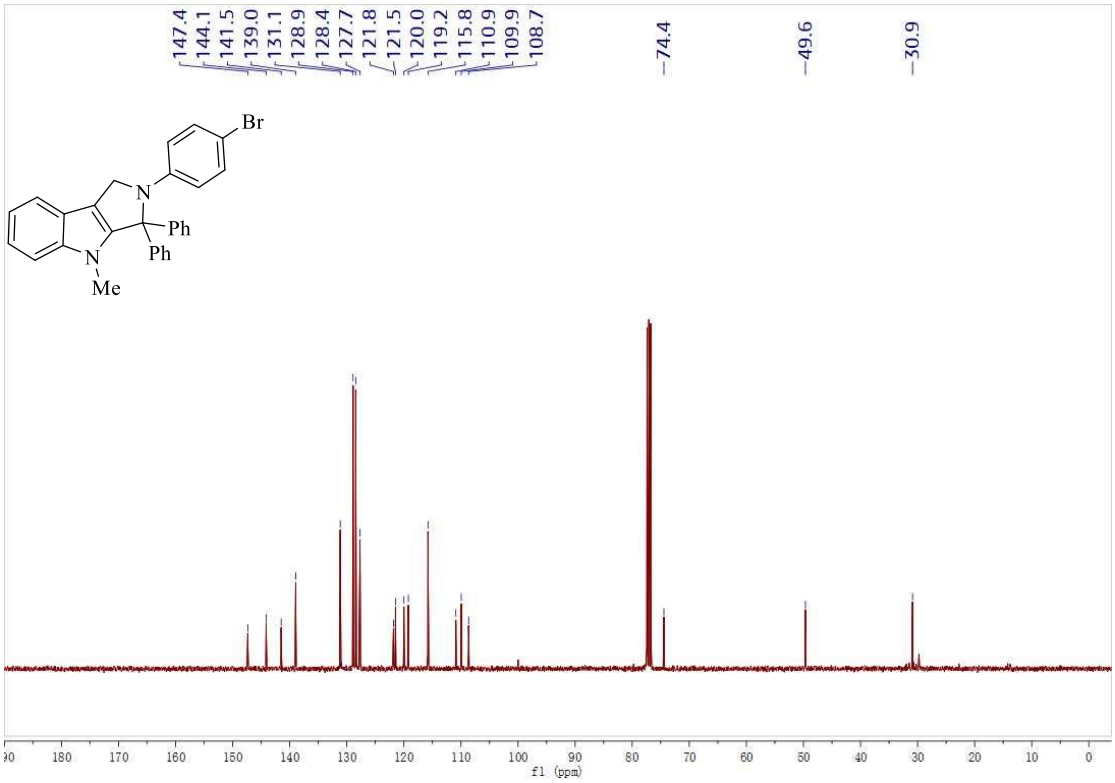

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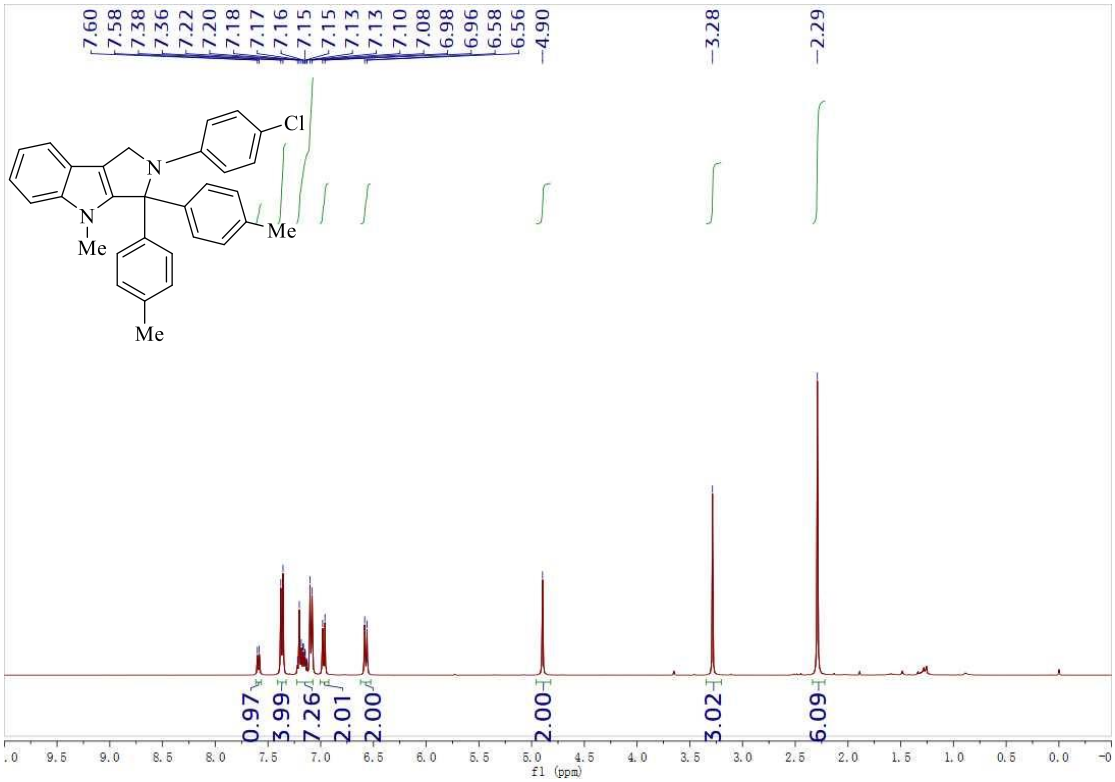

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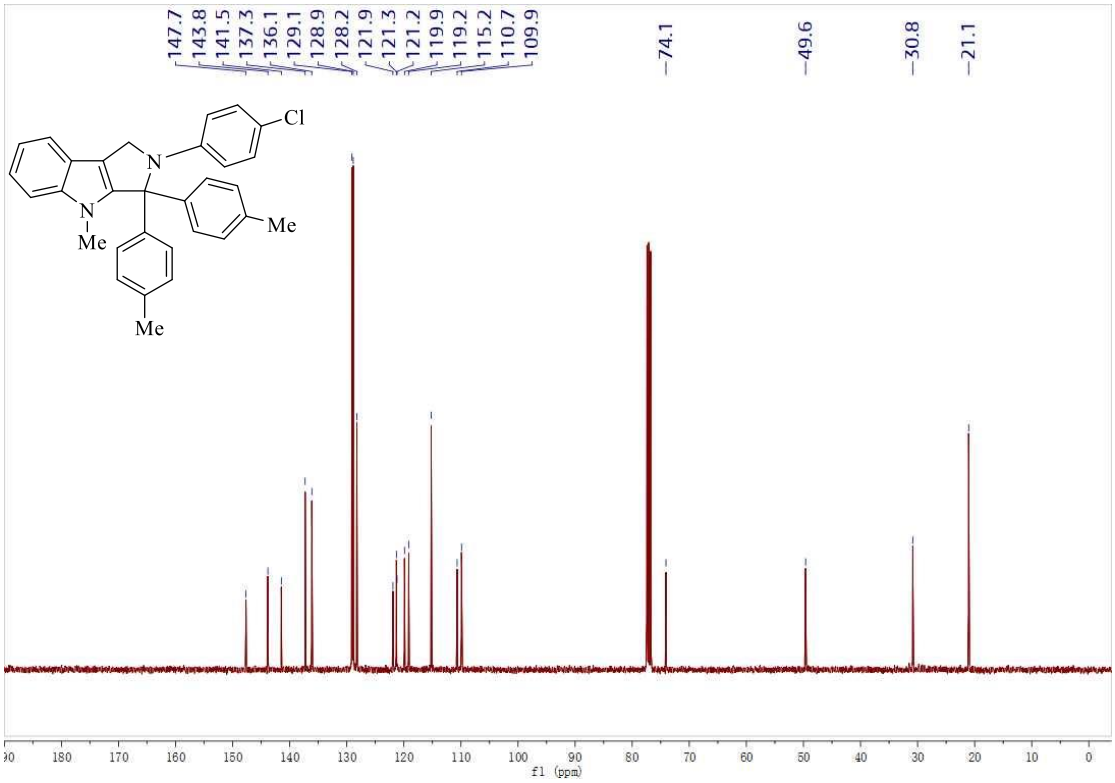

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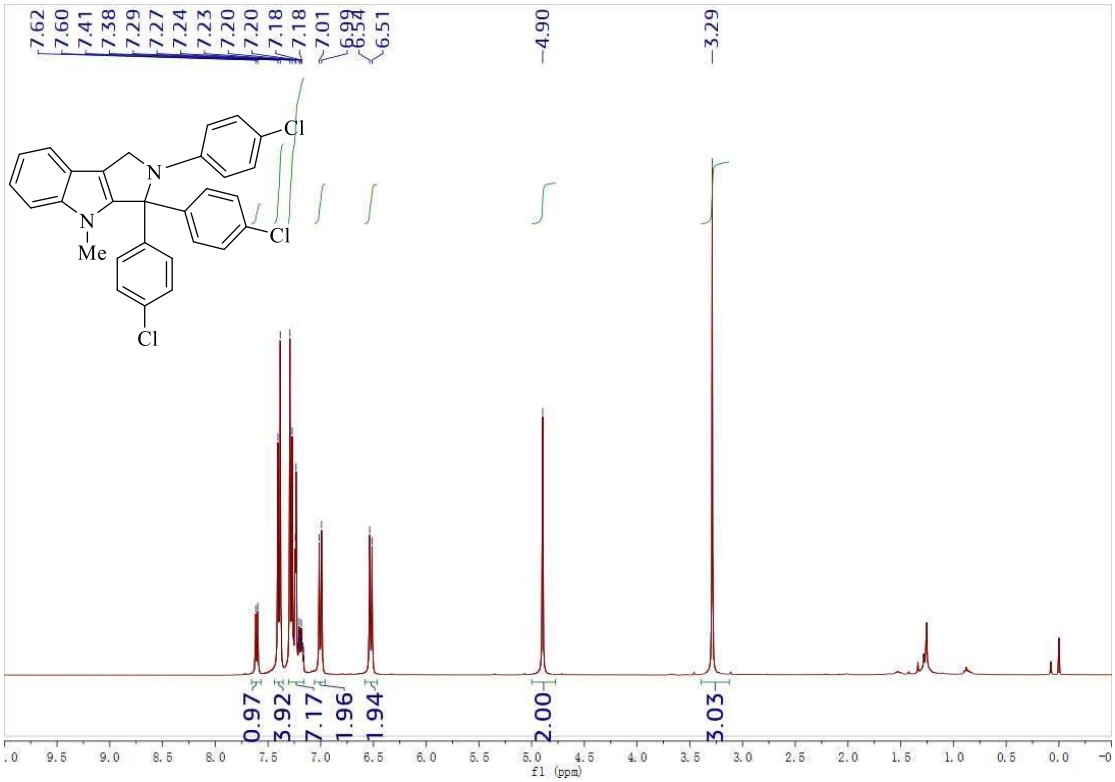

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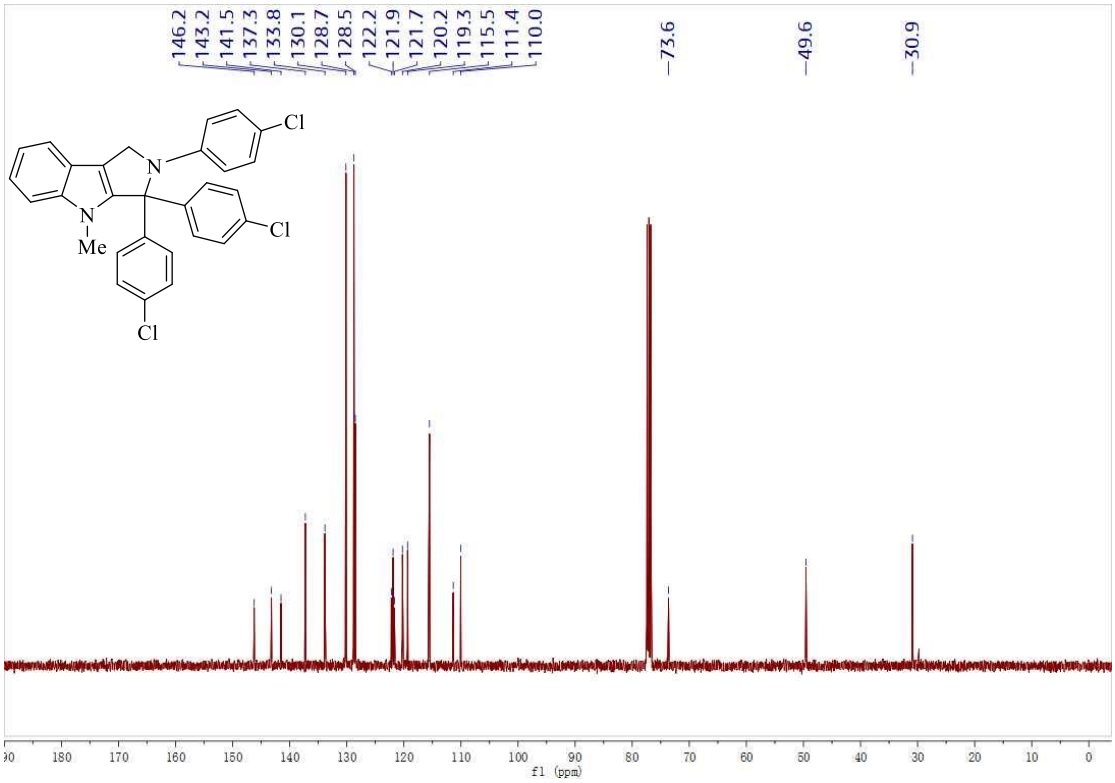

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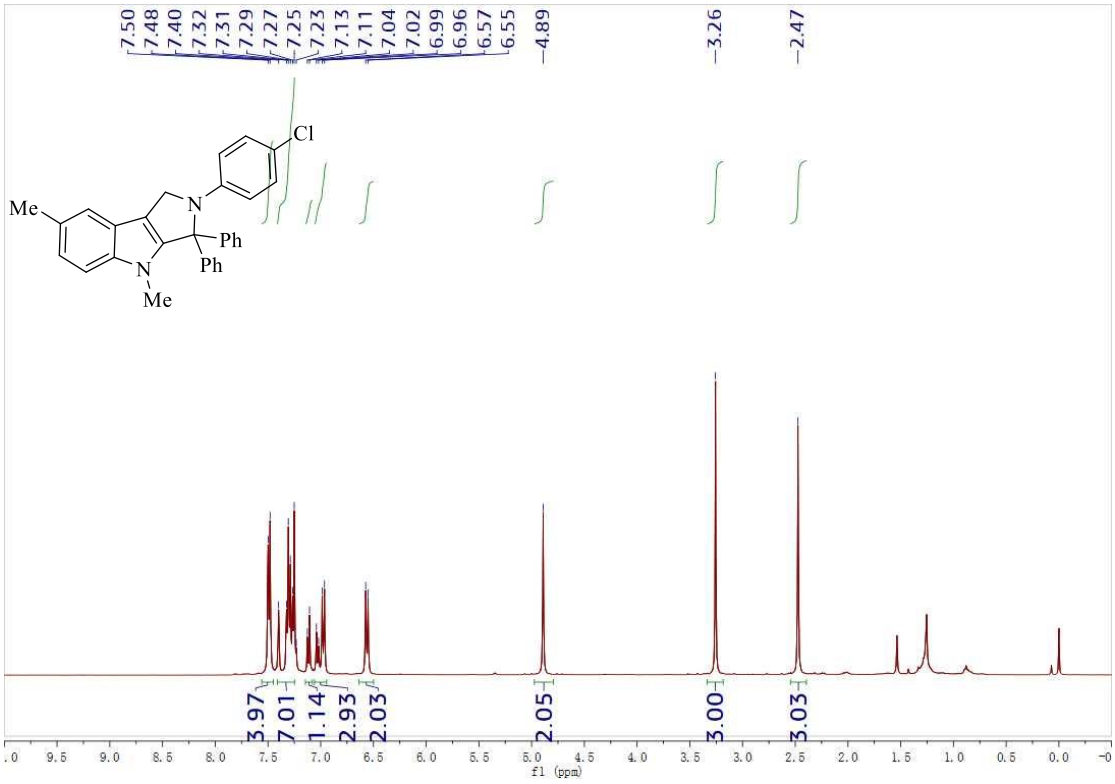
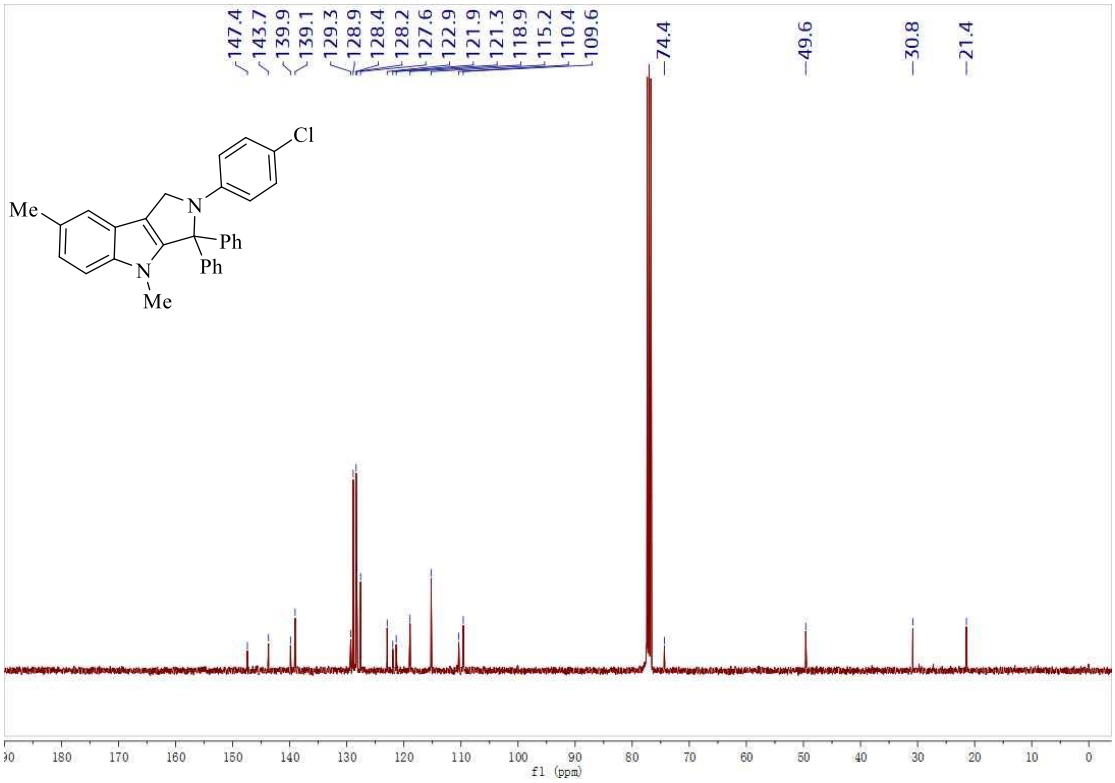


5h′ ^{13}C NMR (100 MHz, $CDCl_3$)



6. References

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