Supporting Information for

Asymmetric Fluorinative Dearomatization of Tryptamine Derivatives

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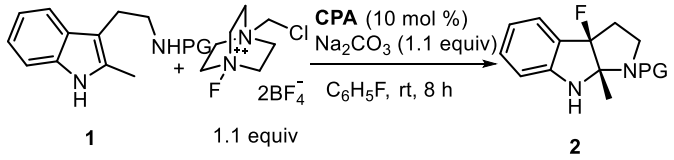
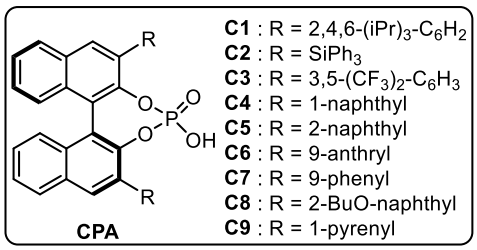
General methods.

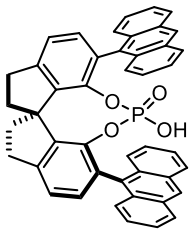
Unless stated otherwise, all solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{19}F NMR spectra were recorded on Varian or Angilent instrument (600 MHz, 400 MHz and 376 MHz, 300 MHz and 282 MHz, respectively) and referenced relative to tetramethylsilane signal or residual protio solvent signals respectively. ^{13}C NMR spectra were recorded on Varian or Agilent instrument (155 MHz, 101 MHz or 75 MHz) and referenced relative to residual solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm).

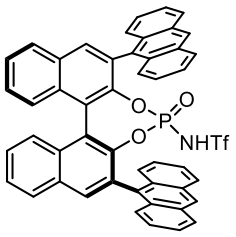
Reaction Condition Optimization Section (complete optimization data)

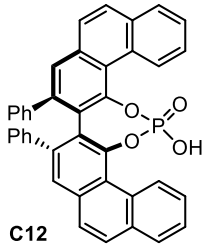
Table S1. Examination of catalysts

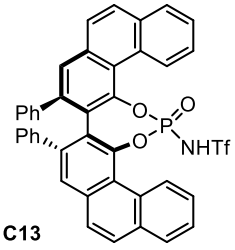


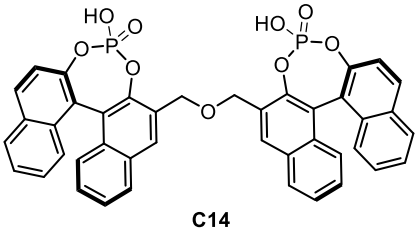








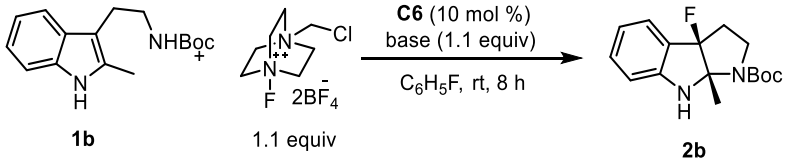




entry[a]	CPA	PG	yield (%)[b]	ee (%)[c]
1	**C1**	COOMe	48	5.5
2	**C2**	COOMe	70	4
3	**C3**	COOMe	52	0
4	**C4**	COOMe	58	13
5	**C5**	COOMe	48	3
6	**C6**	COOMe	67	37
7	**C7**	COOMe	56	22
8	**C8**	COOMe	14	19
9	**C6**	Boc	48	55
10	**C9**	Boc	93	22
11	**C10**	Boc	17	0
12	**C11**	Boc	44	28
13	**C12**	Boc	39	35
14	**C13**	Boc	35	13
15	**C14**	Boc	34	0

[a] Reaction conditions: **1** (0.2 mmol), **CPA** (0.02 mmol), Selectfluor (0.22 mmol), Na_2CO_3 (0.22 mmol) in C_6H_5F (4 mL) at rt. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S2. Examination of solvents, bases, temperature, and concentration

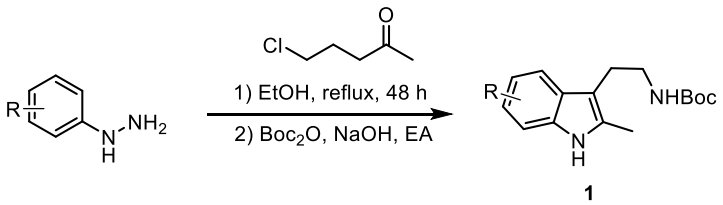


entry[a]	solvent	base	T (^{o}C)	time	yield (%)[b]	ee (%)[c]
1	C_6H_5F	Na_2CO_3	rt	8 h	48	55
2	hexane	Na_2CO_3	rt	8 h	23	0
3	toluene	Na_2CO_3	rt	8 h	47	26
4	DCM	Na_2CO_3	rt	8 h	23	49
5	EA	Na_2CO_3	rt	8 h	66	33
6	C_6H_5F	$NaHCO_3$	rt	8 h	46	40
8	C_6H_5F	K_2CO_3	rt	8 h	64	41
9	C_6H_5F	Na_3PO_4	rt	8 h	53	50
10	C_6H_5F	PS	rt	8 h	72	56
11	C_6H_5F	PS	0	8 h	60	65
12[d]	C_6H_5F	PS	0	11 h	41	5
13	C_6H_5F /c-Hexane	PS	0	11 h	69	33
14	C_6H_5F /H_2O	PS	0	1 h	42	63
15	C_6H_5F /DMA	PS	0	2 h	85	50
16	C_6H_5F /CH_3CN	PS	0	10 min	50	69
17	C_6H_5F /MeOH	PS	0	1 h	55	23
18	CH_3CN/H_2O	PS	0	10 min	41	17
19	CH_3CN	PS	0	10 min	78	47
20	C_6H_5F /CH_3CN	PS	-40	3 h	73	88
21	C_6H_5F /CH_3CN	PS	-60	16 h	64	90
22[e]	C_6H_5F/CH_3CN	PS	-60	16 h	87	90
23[f]	C_6H_5F /CH_3CN	PS	-60	10 h	84	88
24[g]	C_6H_5F /CH_3CN	PS	-60	18 h	66	90

[a] Reaction conditions: **1b** (0.2 mmol), **C6** (0.02 mmol), Selectfluor (0.22 mmol), base (0.22 mmol), Solvent (4 mL). [b] Isolated yield. [c] Determined by HPLC analysis. [d] 4 Å MS was used. [e] At 0.1 M. [f] At 0.2 M. [g] 5 mol % **C6** was used. PS: proton sponge.

General procedure for the synthesis of substrates (1a-1z)

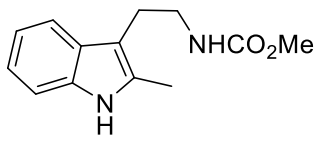
Method A



1

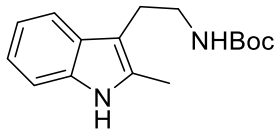
Take the synthesis of **1b** as an example. To a solution of the substituted phenylhydrazine (10 mmol, 1.0 equiv) in EtOH (30 mL) was added 5-chloropentan-2-one (1.7 mL, 20 mmol). The reaction mixture was stirred at reflux for 12-24 h. Then the solvent was removed under reduced pressure. The resulting substituted 2-(2-methyl-1H-indol-3-yl)ethanamine was directly used in the next step without further purification.

A solution of 2-(2-methyl-1H-indol-3-yl)ethanamine (1.40 g, 10.5 mmol) and NaOH in ethyl acetate (30 mL) was added dropwise to a solution of di-*tert*-butyldicarbonate (12.6 mmol, 1.2 equiv) in CH_2Cl_2 (30 mL) at 0 ^oC. The mixture was warmed to room temperature and stirred for 0.5 h. Then the reaction mixture was quenched with $NaHCO_3$ saturated solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to give tert-butyl (2-(2-methyl-1H-indol-3-yl)ethyl)carbamate **1**.



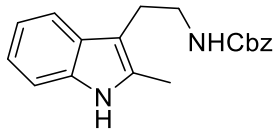
Methyl (2-(2-methyl-1H-indol-3-yl)ethyl)carbamate (**1a**) [1]

Method A. White solid. Analytical data for **1a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.14-7.06 (m, 2H), 4.71 (br s, 1H), 3.66 (s, 3H), 3.43 (q, *J* = 6.0 Hz, 2H), 2.91 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H).



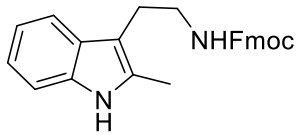
tert-Butyl (2-(2-methyl-1H-indol-3-yl)ethyl)carbamate (**1b**) [1]

Method A. White solid. Analytical data for **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.14-7.05 (m, 2H), 4.58 (br s, 1H), 3.37 (t, *J* = 6.0 Hz, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 1.44 (s, 9H).



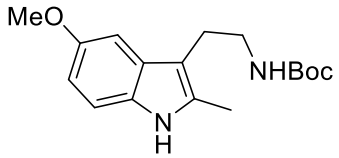
Benzyl (2-(2-methyl-1H-indol-3-yl)ethyl)carbamate (**1c**) [2]

Method A. Light red solid. Analytical data for **1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (br s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 5H), 7.28-7.26 (m, 1H), 7.14-7.05 (m, 2H), 5.10 (s, 2H), 4.77 (br s, 1H), 3.45 (q, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H).



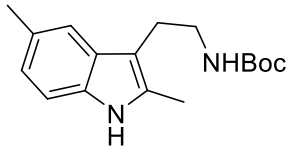
(9H-Fluoren-9-yl)methyl (2-(2-methyl-1H-indol-3-yl)ethyl)carbamate (**1d**)

Method A. White solid. Analytical data for **1d**: Mp = 132.7-133.7 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br s, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41-7.38 (m, 2H), 7.32-7.26 (m, 2H), 7.15-7.07 (m, 2H), 4.82 (br s, 1H), 4.39 (d, *J* = 6.8 Hz, 2H), 4.20 (t, *J* = 6.8 Hz, 1H), 3.48-3.43 (m, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 143.9, 141.2, 135.2, 132.0, 127.6, 127.0, 125.0, 121.1, 119.9, 119.3, 117.7, 110.3, 109.9, 108.3, 66.5, 47.2, 41.4, 24.6, 11.5. IR (film) 1695, 1515, 1461, 1447, 1237, 737 cm^{-1}.



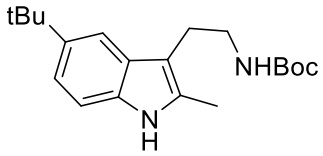
tert-Butyl (2-(5-methoxy-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1e**) [3]

Method A. White solid. Analytical data for **1e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (br s, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 6.76 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.62 (br s, 1H), 3.84 (s, 3H), 3.38-3.33 (m, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.41-2.29 (m, 3H), 1.43 (s, 9H).



tert-Butyl (2-(2,5-dimethyl-1H-indol-3-yl)ethyl)carbamate (**1f**)

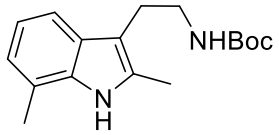
Method A. White solid. Analytical data for **1f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.27 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4, 1.6 Hz 1H), 4.58 (br s, 1H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 146.7, 133.5, 132.1, 128.3, 122.4, 117.6, 109.9, 108.1, 85.2, 41.0, 28.4, 27.4, 24.6, 21.5, 11.6. IR (film) 3392, 2927, 1687, 1366, 1161, 1051, 788 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}N_2O_2$ $[M+H]^+$: 289.1911. Found: 289.1913.



tert-Butyl (2-(5-(tert-butyl)-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1g**)

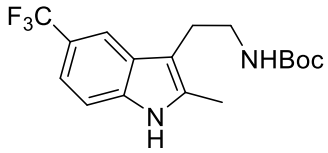
Method A. Grey solid. Analytical data for **1g**: Mp = 133.8-134.9 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br s, 1H), 7.46 (s, 1H), 7.20-7.17 (m, 2H), 4.72-4.66 (m, 1H), 3.38-3.35 (m, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 1.43 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 156.0, 141.9, 133.4, 132.2, 128.1, 118.9, 113.4, 109.7, 108.2, 79.5, 78.9, 41.0, 34.4, 31.9, 28.3, 28.1, 24.4, 11.4. IR (film) 3286, 1689,

1493, 1165, 806, 665 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{31}N_2O_2$ $[M+H]^+$: 331.2380. Found: 331.2382.



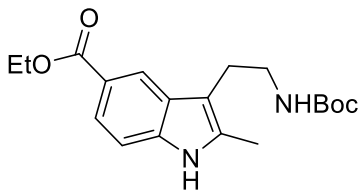
tert-Butyl (2-(2,7-dimethyl-1H-indol-3-yl)ethyl)carbamate (**1h**)

Method A. White solid. Analytical data for **1h**: Mp = 94.8-95.6 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (br s, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 4.56 (br s, 1H), 3.36 (d, *J* = 6.2 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 134.7, 131.6, 128.1, 121.8, 119.5, 119.4, 115.7, 109.1, 78.9, 41.0, 28.4, 24.7, 16.5, 11.6. IR (film) 3296, 2973, 2931, 1689, 1500, 1163, 1052, 778 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}N_2O_2$ $[M+H]^+$: 289.1911. Found: 289.1911.



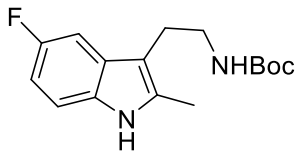
tert-Butyl (2-(2-methyl-5-(trifluoromethyl)-1H-indol-3-yl)ethyl)carbamate (**1i**)

Method A. White solid. Analytical data for **1i**: Mp = 144.8-145.2 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br s, 1H), 7.75 (s, 1H), 7.43-7.30 (m, 2H), 4.56 (br s, 1H), 3.38-3.33 (m, 2H), 2.92-2.89 (m, 2H), 2.42 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.7, 134.2, 127.9, 125.5 (q, *J* = 271.0 Hz), 121.1 (d, *J* = 31.3 Hz), 117.3, 115.0, 110.3, 109.1, 79.1, 67.7, 41.1, 28.2, 25.4, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.08 (s). IR (film) 3266, 1686, 1497, 1330, 1151, 1105, 1049, 816, 672 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}F_3N_3O_2$ $[M+NH_4]^+$: 360.1893. Found: 360.1895.



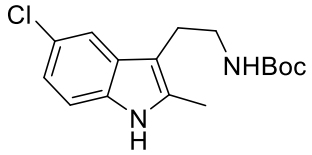
Ethyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-2-methyl-1H-indole-5-carboxylate (**1j**)

Method A. White solid. Analytical data for **1j**: Mp = 158.8-159.4 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.6 Hz, 1H), 8.10 (br s, 1H), 7.85 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 4.57 (br s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.40-3.35 (m, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.40 (d, *J* = 2.0 Hz, 3H), 1.44-1.40 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 156.0, 138.0, 133.5, 128.1, 122.6, 121.5, 120.5, 109.8, 79.1, 60.5, 41.0, 28.4, 24.5, 14.5, 11.6. IR (film) 3347, 3247, 1679, 1617, 1362, 1272, 1131, 770, 682 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{30}N_3O_4$ $[M+NH_4]^+$: 364.2231. Found: 364.2232.



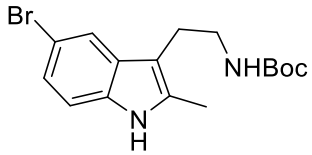
tert-Butyl (2-(5-fluoro-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1k**)

Method A. White solid. Analytical data for **1k**: Mp = 102.3-103.4 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.21-7.06 (m, 2H), 6.83 (d, *J* = 2.4 Hz, 1H), 4.62 (br s, 1H), 3.32 (t, *J* = 6.0 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 156.5, 156.0, 134.0, 131.7, 110.7, 110.6, 109.0, 108.8, 106.8, 103.0, 102.7, 79.1, 40.9, 28.4, 28.2, 24.5, 11.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.79 .IR (film) 1704, 1507, 1363, 1244, 1159, 847 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}FN_2O_2$ $[M+H]^+$: 293.166. Found: 293.1665.



tert-Butyl (2-(5-chloro-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1l**) [4]

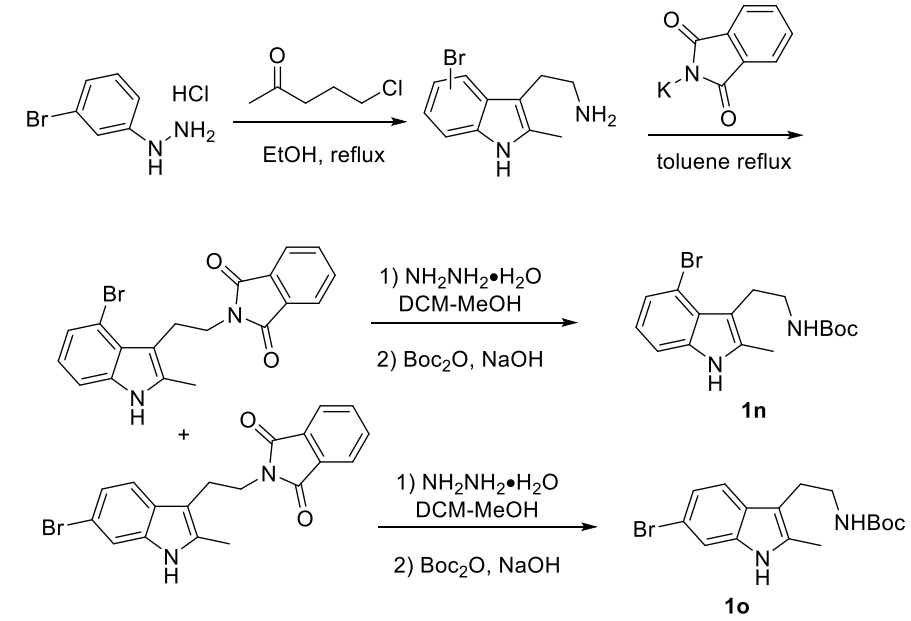
Method A. Brown solid. Analytical data for **1l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.42 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.60 (br s, 1H), 3.31 (m, 2H), 2.82 (m, 2H), 2.33 (s, 3H), 1.44 (s, 9H).



tert-Butyl (2-(5-bromo-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1m**) [5]

Method A. Light brown solid. Analytical data for **1m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 7.57 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.61 (br s, 1H), 3.31 (q, *J* = 6.0 Hz, 2H), 2.93-2.70 (m, 2H), 2.33 (s, 3H), 1.44 (s, 9H).

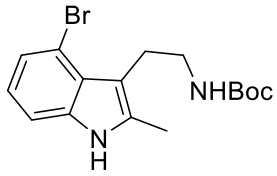
Method B



separable by silica gel chromatography

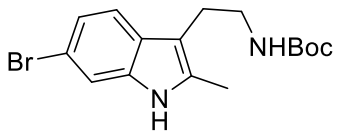
To a solution of 3-bromophenylhydrazine (10 mmol, 1.0 equiv) in EtOH (30 mL) was added 5-chloropentan-2-one (1.7 mL, 20 mmol). The reaction mixture was stirred at reflux for 24 h. Then the solvent was removed under reduced pressure. To the resulting 4- or 6-bromo-2-(2-methyl-1H-indol-3-yl)ethanamine mixture was then added toluene (50 mL) and potassium phthalimide (12 mmol, 1.2 equiv), the reaction mixture was stirred at reflux overnight. The solvent was removed under reduced pressure, giving the separated 4- or 6-bromo substituted products. Then the 4- or 6-

bromo substituted product was dissolved in DCM-MeOH (1:1), hydrazine hydrate (28 mmol, 2.8 equiv) was added. The reaction mixture was then stirred at room temperature overnight. After the reaction was complete, it was quenched with NH_4Cl saturated aqueous solution, extracted with DCM, dried with Na_2SO_4, and filtrated. The products were directly used in the next step without further purification. Then a solution of above products (10 mmol) and NaOH in ethyl acetate (30 mL) was added dropwise to a solution of di-*tert*-butyldicarbonate (12 mmol, 1.2 equiv) in DCM (30 mL) at 0 ^oC. The mixture was warmed to room temperature and stirred for 0.5 h. Then the reaction mixture was quenched with $NaHCO_3$ saturated solution and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to give **1n** or **1o**.



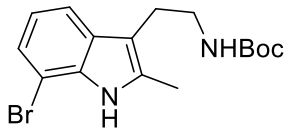
tert-Butyl (2-(4-bromo-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1n**)

Method B. Light green solid. Analytical data for **1n**: Mp = 97.6-98.8 ℃, ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 7.20-7.17 (m, 2H), 6.90-6.86 (m, 1H), 4.76 (br s, 1H), 3.40 (q, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 136.5, 134.2, 126.1, 123.6, 121.5, 112.9, 109.7, 108.7, 79.0, 42.4, 28.4, 28.0, 24.6, 11.5. IR (film) 3292, 2973, 2928, 1687, 1623, 1497, 1249, 1163, 742 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{21}N_2O_2Br$ $[M]^+$: 352.0781. Found: 352.0783.



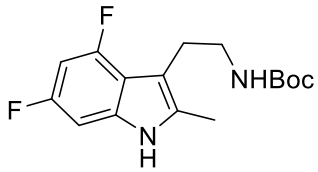
tert-Butyl (2-(6-bromo-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1o**)

Method B. Light green solid. Analytical data for **1o**: Mp = 115.1-116.8 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 7.31-7.29 (m, 2H), 7.12 (d, *J* = 8.4, 1H), 4.63 (br s, 1H), 3.30 (q, *J* = 6.8 Hz, 2H), 2.82 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 134.0, 132.8, 127.4, 122.1, 118.9, 114.1, 113.1, 108.5, 79.1, 40.9, 29.6, 28.4, 24.4, 11.5. IR (film) 3416, 3251, 2970, 2928, 2863, 1685, 1617, 1494, 1162, 1052, 850, 716 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{22}N_2O_2Br$ $[M+H]^+$: 353.0859. Found: 353.0859.



tert-Butyl (2-(7-bromo-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1p**)

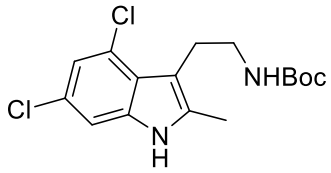
Method A. White solid. Analytical data for **1p**: Mp = 166.8-167.4 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.95 (dd, *J* = 7.6 Hz, 1H), 4.56 (br s, 1H), 3.34 (q, *J* = 6.8 Hz, 2H), 2.87 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 133.8, 132.8, 129.7, 123.3, 120.5, 117.1, 110.0, 105.0, 103.9, 79.1, 40.9, 28.4, 24.8, 11.6. IR (film) 3099, 1642, 1299, 1027, 8053274, 1689, 1488, 1164, 775 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}BrN_2O_2$ $[M+H]^+$: 353.0859. Found: 353.0861.



tert-Butyl (2-(4,6-difluoro-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1q**)

Method A. Light red solid. Analytical data for **1q**: Mp = 100.9-102.1 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (br s, 1H), 6.73 (dd, *J* = 9.2, 1.6 Hz, 1H), 6.51 (ddd, *J* = 12.0, 10.6, 2.0 Hz, 1H), 4.71 (br s, 1H), 3.36 (q, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 159.6, 157.3,

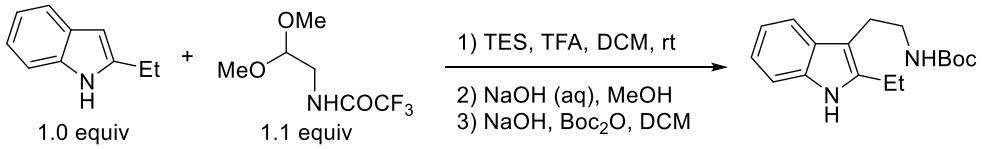
157.2, 156.8, 156.6, 156.1, 154.3, 154.2, 137.0, 136.9, 136.7, 132.4, 129.6, 113.5, 113.3, 106.8, 94.9, 94.9, 94.7, 94.6, 94.6, 94.4, 94.3, 93.2, 93.1, 92.9, 92.9, 79.1, 41.6, 28.3, 25.4, 11.1, 11.1. ^{19}F (film) 3422, 3306, 2984, 2938, 2865, 1689, 1502, 1167, 976, 825 cm^{-1}. NMR (376 MHz, $CDCl_3$) δ -120.61 (td, *J* = 12.9, 9.9, 3.5 Hz), -122.43 (d, *J* = 10.4 Hz). IR (film) 3422, 3306, 2938, 1689, 1502, 1247, 1167, 976, 825 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{20}N_2O_2F_2$ $[M+H]^+$: 310.1487. Found: 310.1488.



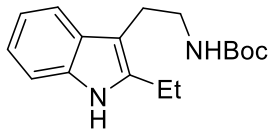
tert-Butyl (2-(4,6-dichloro-2-methyl-1H-indol-3-yl)ethyl)carbamate (**1r**)

Method A. Grey white solid. Analytical data for **1r**: Mp = 154.4-154.8 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 7.13 (s, 1H), 7.02 (d, *J* = 0.6 Hz 1H), 4.67 (br s, 1H), 3.37 (q, *J* = 6.6 Hz, 2H), 3.05 (t, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 136.6, 134.4, 126.3, 125.3, 123.8, 120.5, 109.1, 108.9, 79.1, 42.2, 28.4, 24.9, 11.5. IR (film) 3674, 3421, 3211, 2980, 2941, 2736, 1683, 1489, 1168, 905, 767 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{21}N_2O_2Cl_2$ $[M+H]^+$: 343.0975. Found: 343.0974.

Method C:



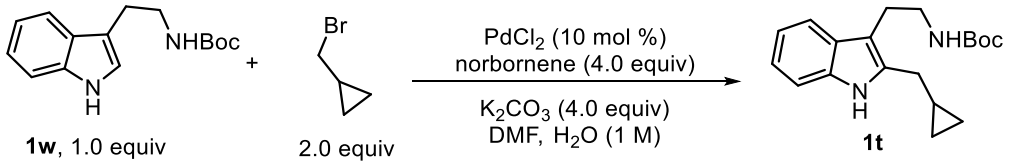
Prepared according to literature procedures. [6]



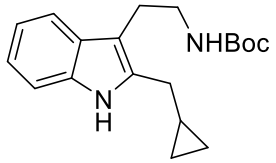
tert-Butyl (2-(2-ethyl-1H-indol-3-yl)ethyl)carbamate (**1s**)

Method C. White solid. Analytical data for **1s:** Light yellow solid, Mp = 86.3-87.5 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.16-7.02 (m, 2H), 4.63 (s, 1H), 3.36 (d, *J* = 6.1 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.43 (s, 9H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 137.9, 135.3, 128.4, 121.0, 119.1, 118.0, 110.4, 107.4, 79.0, 41.0, 28.4, 24.5, 19.2, 14.4. IR (film) 3404, 2972, 2932, 1688, 1507, 1392, 1247, 1164, 737 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{25}N_2O_2$ $[M+H]^+$: 289.1911. Found: 289.1912.

Method D:

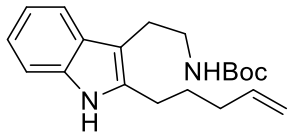


Prepared according to modified literature procedures.[7] A Schlenk flask equipped with a magnetic stirring bar was charged with **1w** (5.0 mmol, 1 equiv), norbornene (10 mmol, 2 equiv), K_2CO_3 (20 mmol, 4 equiv), and $PdCl_2$ (0.5 mmol, 0.1 equiv). A solution of water in DMF (25 mL, 1 M) was added, then the (bromomethyl)cyclopropane (20 mmol, 4 equiv) was added *via* syringe. The reaction mixture was heated at 100 ℃ and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered. The filtrate was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/4, v/v) to afford the 2-alkylindole product.



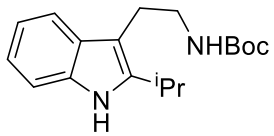
tert-Butyl (2-(2-(cyclopropylmethyl)-1H-indol-3-yl)ethyl)carbamate (**1t**)

Method D. Light yellow oil. Analytical data for **1t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.16-7.03 (m, 2H), 4.61 (s, 1H), 3.36 (q, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.65 (d, *J* = 6.8 Hz, 2H), 1.43 (s, 9H),1.04-0.94 (m, 1H), 0.62-0.57 (m, 2H), 0.28 (q, *J* = 4.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 136.1, 135.2, 128.3, 121.1, 119.2, 118.1, 110.4, 107.9, 78.9, 40.9, 30.6, 28.4, 24.5, 10.4, 4.6. IR (film) 3335, 1691, 1500, 1365, 1164, 743 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{27}N_2O_2$ $[M+H]^+$: 315.2067. Found: 315.207.



tert-Butyl (2-(2-(pent-4-en-1-yl)-1H-indol-3-yl)ethyl)carbamate (**1u**)

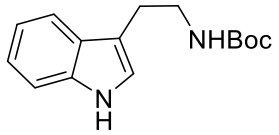
Method C. White solid. Analytical data for **1u**: Mp = 89.3-90.5 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.14-7.05 (m, 2H), 5.86-5.76 (m, 1H), 5.06–4.98 (m, 2H), 4.60 (br s, 1H), 3.38 (d, *J* = 5.8 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.74 (p, *J* = 7.6 Hz, 2H), 1.43 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 138.0, 136.2, 135.3, 128.4, 121.1, 119.1, 118.1, 115.2, 110.3, 108.3, 79.0, 40.9, 33.2, 29.0, 28.4, 25.3, 24.7. IR (film) 3420, 3286, 2973, 2932, 2866, 1685, 1495, 1455, 1167, 776 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{29}N_2O_2$ $[M+H]^+$: 329.2224. Found: 329.2222.



tert-Butyl (2-(2-isopropyl-1H-indol-3-yl)ethyl)carbamate (**1v**)

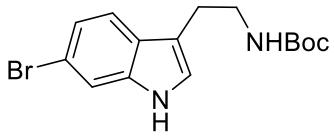
Method C. Light yellow oil. Analytical data for **1v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.14-7.05 (m, 2H), 4.63 (br s, 1H), 3.40-3.05 (m, 2H), 3.26-3.19 (m, 1H), 2.90 (t, *J* = 6.8 Hz, 2H), 1.43 (s, 9H), 1.31 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 141.8, 135.2, 128.3, 121.0, 119.2, 118.1, 110.4, 106.5, 79.0, 40.9, 28.4, 25.4, 24.6, 22.9. IR (film)

3336, 2967, 1687, 1507, 1365, 1247, 1163, 741 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{27}N_2O_2$ $[M+H]^+$: 303.2067. Found: 303.2071.



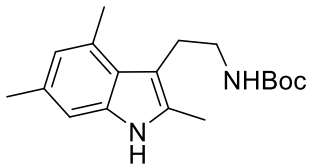
tert-Butyl (2-(1H-indol-3-yl)ethyl)carbamate (**1w**)[8]

White solid. Analytical data for **1w**: ^{1}H NMR (400 MHz, Chloroform-d) δ 8.10 (br s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.14-7.19 (m, 1H), 7.03 (s, 1H), 4.62 (br s, 1H), 3.50-3.45 (m, 2H), 2.96 (t, *J* = 6.8 Hz, 2H), 1.44 (d, *J* = 1.6 Hz, 9H).



tert-Butyl (2-(6-bromo-1H-indol-3-yl)ethyl)carbamate (**1x**)[9]

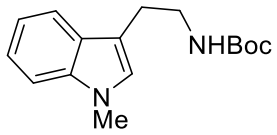
White solid. Analytical data for **1x**: 1H NMR (400 MHz, Chloroform-d) δ 8.02 (br s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.02 (s, 1H), 4.59 (br s, 1H), 3.46-3.41 (m, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 1.43 (s, 9H).



tert-Butyl (2-(2,4,6-trimethyl-1H-indol-3-yl)ethyl)carbamate (**1y**)

Method A. Grey solid. Analytical data for **1y**: Mp = 91.2-92.3 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (br s, 1H), 6.91 (s, 1H), 6.66 (s, 1H), 4.59 (s, 1H), 3.32 (d, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.62 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 136.0, 131.4, 130.6, 129.1, 124.5, 123.0, 110.0, 108.7, 108.2, 79.6, 79.0, 42.5, 28.4, 28.2, 25.9, 21.3, 20.0, 11.5. IR (film) 3443,

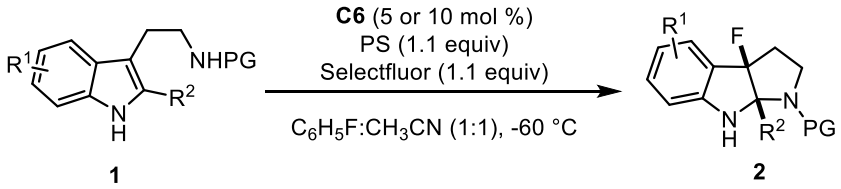
3257, 1680, 1605, 1364, 1272, 1251, 1160, 1050, 788, 702 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{27}N_2O_2$ $[M+H]^+$: 303.2067. Found: 303.2068.



tert-Butyl (2-(1-methyl-1H-indol-3-yl)ethyl)carbamate (**1z**)[10]

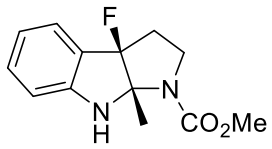
White solid. Analytical data for **1z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26-7.21 (m, 1H), 7.13-7.09 (m, 1H), 6.89 (s, 1H), 4.60 (br s, 1H), 3.76 (s, 3H), 3.45 (d, *J* = 5.6 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H), 1.44 (s, 9H).

General procedure for asymmetric fluorinative dearomatization of tryptamine derivatives



1 **2**

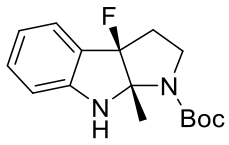
To a 25 mL Schlenk tube, substrate **1** (0.2 mmol), **C6** (7.0 mg, 0.01 mmol, 5 mol% or 14.0 mg, 0.02 mmol, 10 mol %), and Proton Sponge (PS, 47.1 mg, 0.22 mmol) were dissolved in C_6H_5F/CH_3CN (1:1, 2 mL). The vial was capped with a screw cap. The reaction mixture was stirred at room temperature for 10 min, and stirred at -60 ^oC for 15 min. Then Selectfluor (77.9 mg, 0.22 mmol) was added. After the reaction was complete (monitored by TLC), $Na_2S_2O_3$ saturated aqueous solution (2 mL) was poured into the solution, and then the mixture was allowed to warm to the room temperature. The reaction mixture was extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/ petroleum ether = 1/10, v/v) to afford the desired product **2**.



(3a*R*,8a*S*)-Methyl-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2a**)

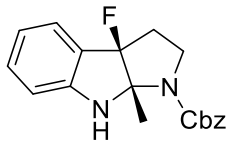
Light yellow oil, 10 mol % **C6** was used, 41.8 mg, 85% yield, 85% *ee*. Analytical data for **2a**: $[\alpha]_D^{20}$ = 248.1 (c = 1.0 Chloroform, 85% *ee*). Two rotamers exist in NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 1H), 7.24-7.20 (m, 1H), 6.83-6.80 (m, 1H), 6.66-6.62 (m, 1H), 5.75 (br s, 0.8H), 5.18 (br s, 0.2H), 3.80 (s, 0.8H), 3.65 (s, 2.2H), 3.71-3.58 (m, 1H), 3.16-3.04 (m, 1H), 2.60-2.44 (m, 2H), 1.70 (d, *J* = 4.0 Hz, 2.2H), 1.66 (d, *J* = 3.2 Hz, 0.8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.3 (d, *J* = 4.1 Hz), 131.6 (d, *J* = 3.4 Hz), 124.9, 124.4 (d, *J* = 21.7 Hz), 119.4, 119.1 (d, *J* = 2.9

Hz), 110.4 (d, *J* = 1.5 Hz), 110.2 (d, *J* = 1.8 Hz), 104.4 (d, *J* = 201.4 Hz), 84.3 (d, *J* = 26.8 Hz), 52.5, 52.0, 45.0 (d, *J* = 4.3 Hz), 44.5 (d, *J* = 4.7 Hz), 31.6 (d, *J* = 29.0 Hz), 31.2 (d, *J* = 29.0 Hz), 19.9 (d, *J* = 9.3 Hz), 18.9 (d, *J* = 8.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.81 (d, *J* = 12.8 Hz), -145.63 (d, *J* = 13.5 Hz). IR (film) 3350, 2945, 1674, 1373 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{16}FN_2O_2$ $[M+H]^+$: 251.119. Found: 251.1192. The enantiomeric excess was determined by Daicel Chiralpak IC-H (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (minor) = 7.10 min, t (major) = 7.92 min.



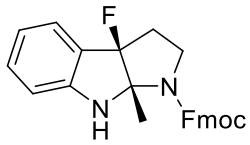
(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2b**)

Light yellow oil, 10 mol % **C6** was used, 50.2 mg, 87% yield, 90% *ee*. Analytical data for **2b**: $[\alpha]_D^{20}$ = 329.7 (c = 1.0 Chloroform, 90% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.77 (br, 0.6H), 5.13 (br, 0.4H), 3.66-3.53 (m, 1H), 3.10-3.00 (m, 1H), 2.63-2.34 (m, 2H), 1.73-1.63 (m, 3H), 1.58-1.49 (m, 3H), 1.42-1.40 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 153.4, 150.5 (d, *J* = 4.2 Hz), 150.0 (d, *J* = 4.1 Hz), 131.6 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 3.3 Hz), 124.9, 124.9, 124.7, 124.5, 119.4, 119.0 (d, *J* = 2.8 Hz), 110.4, 110.1, 105.4 (d, *J* = 201.5 Hz), 104.6 (d, *J* = 200.5 Hz), 84.1 (d, *J* = 26.6 Hz), 83.5 (d, *J* = 25.7 Hz), 80.8, 80.0, 44.8 (d, *J* = 4.5 Hz), 44.5 (d, *J* = 4.0 Hz), 31.6 (d, *J* = 28.7 Hz), 31.1 (d, *J* = 28.1 Hz), 28.5 (d, *J* = 25.2 Hz), 27.3, 20.1 (d, *J* = 9.5 Hz), 19.1 (d, *J* = 8.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.10 (d, *J* = 13.2 Hz), -145.25 (d, *J* = 14.2 Hz). IR (film) 3406, 2938, 1678, 1393 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{22}FN_2O_2$ $[M+H]^+$: 293.166. Found: 293.1667. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.86 min, t (major) = 6.68 min.



(3a*R*,8a*S*)-Benzyl-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2c**)

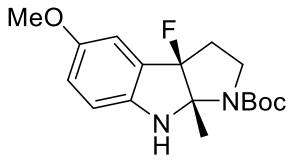
Light yellow oil, 5 mol % **C6** was used, 52.9 mg, 81% yield, 90% ee. Analytical data for **2c**: $[\alpha]_D^{26.6}$ = 255.9 (c = 1.0 Chloroform, 90% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 4.8 Hz, 5H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.17-7.02 (m, 2H), 5.11 (d, *J* = 5.6 Hz, 2H), 4.81 (s, 1H), 3.45 (dd, *J* = 11.8, 6.2 Hz, 2H), 2.92 (t, *J* = 5.8 Hz, 2H), 2.31 (d, *J* = 15.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 150.3 (d, *J* = 4.0 Hz), 136.2, 131.7 (d, *J* = 3.5 Hz), 128.8, 128.5, 128.3 (d, *J* = 24.3 Hz), 128.0, 127.7, 124.9, 119.2 (d, *J* = 3.0 Hz), 110.5, 110.1, 104.5 (d, *J* = 200.9 Hz), 84.5 (d, *J* = 26.9 Hz), 67.3, 66.6, 44.7 (d, *J* = 4.7 Hz), 31.7 (d, *J* = 28.8 Hz), 19.0 (d, *J* = 8.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.04 (d, *J* = 13.2 Hz), -145.52 (d, *J* = 13.2 Hz). IR (film) 3378, 2945, 1678, 1407, 1337, 1037, 750 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{20}FN_2O_2$ $[M+H]^+$: 327.1503. Found: 327.1505. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 48 / 2, 0.5 mL/min, λ = 254 nm, t (major) = 31.46 min, t (minor) = 33.60.



(3a*R*,8a*S*)-(9H-Fluoren-9-yl)methyl-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2d**)

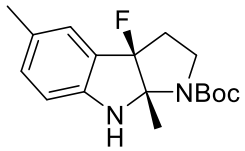
Light yellow oil, 5 mol % **C6** was used, 55.4 mg, 69% yield, 86% ee. Analytical data for **2d**: $[\alpha]_D^{26.8}$ = 189.5 (c = 1.0 Chloroform, 86% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.01 (d, *J* = 7.2 Hz, 0.5H), 7.96 (d, *J* = 7.2 Hz, 0.5H), 7.88 (d, *J* = 2.4 Hz, 0.5H), 7.86 (d, *J* = 2.8 Hz, 0.5H), 7.76 (d, *J* = 7.6 Hz, 0.5H), 7.73 (d, *J* = 7.2 Hz, 0.5H), 7.58-7.48 (m, 2H), 7.45-7.26 (m, 4H), 7.22-7.09 (m, 1H), 6.85-

6.62 (m, 2H), 6.18 (d, *J* = 7.6 Hz, 1H), 4.73 (m, 1H), 4.37-4.21 (m, 2H), 3.59-3.54 (m, 1H), 2.92-2.88 (m, 1H), 2.74-2.58 (m, 1H), 2.36-2.13 (m, 1H), 1.59 (d, *J* = 3.8 Hz, 1.5H), 0.80 (d, *J* = 3.6 Hz, 1.5H). ^{13}C NMR (151 MHz, DMSO-D_6, 80 ^{o}C) δ 152.8, 143.5, 140.5, 140.3, 130.9, 130.8, 127.1, 127.1, 126.6, 124.3, 124.2, 123.5 (d, *J* = 21.9 Hz), 119.6, 119.5, 117.7, 104.7 (d, *J* = 200.7 Hz), 65.6, 54.2, 46.4, 45.3, 43.9 (d, *J* = 4.5 Hz), 18.1 (d, *J* = 9.5 Hz). ^{19}F NMR (376 MHz, DMSO-D_6) δ -136.03 (d, *J* = 14.3 Hz), -136.55 (d, *J* = 14.1 Hz). IR (film) 3402, 2891, 1686, 1611, 1451, 1455, 745 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{24}FN_2O_2$ $[M+H]^+$: 415.1816. Found: 415.1821. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 80 / 20, 1.0 mL/min, λ = 254 nm, t (minor) = 12.52 min, t (major) = 18.51 min.



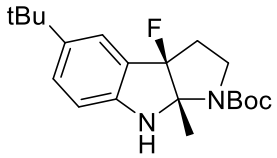
(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-5-methoxy-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2e**)

Light yellow oil, 10 mol % **C6** was used, 32.2 mg, 50% yield, 84% ee. Analytical data for **2e**: $[\alpha]_D^{28.1}$ = 281.8 (c = 1.0 Chloroform, 84% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.56 (br, 0.6H), 4.91 (br, 0.4H), 3.77 (s, 3H), 3.70-3.52 (m, 1H), 3.09-3.02 (m, 1H), 2.58-2.37 (m, 2H), 1.66 (dd, *J* = 12.0, 4.0 Hz, 3H), δ 1.54 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 154.1 (d, *J* = 3.3 Hz), 154.0, 145.2 (d, *J* = 4.5 Hz), 126.0 (d, *J* = 21.4 Hz), 118.1 (d, *J* = 3.7 Hz), 111.5, 110.8, 105.2 (d, *J* = 201.4 Hz), 85.3 (d, *J* = 26.5 Hz), 79.6, 55.5, 45.0 (d, *J* = 4.4 Hz), 31.9 (d, *J* = 28.6 Hz), 19.6 (d, *J* = 8.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.85 (s), -146.31 (d, *J* = 12.2 Hz). IR (film) 3368, 2889, 1676, 1493, 1385, 1157, 1033 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}FN_2O_3$ $[M+H]^+$: 323.1765. Found: 323.1774. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 7.38 min, t (major) = 11.79 min.



(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-5,8a-dimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2f**)

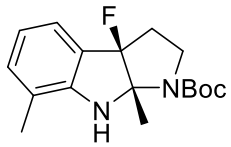
Light yellow oil, 10 mol % **C6** was used, 34.3 mg, 56% yield, 90% ee. Analytical data for **2f**: $[\alpha]_D^{28.2}$ = 278.9 (c = 1.0 Chloroform, 90% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.9 Hz, 2H), 3.66-3.53 (m, 1H), 3.08-3.01 (m, 1H), 2.55-2.46 (m, 2H), 2.27 (s, 3H), 1.65 (dd, *J* = 12.8, 4.0 Hz, 3H), 1.52 (s, 3H), 1.40 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 154.0, 149.1 (d, *J* = 4.2 Hz), 132.5 (d, *J* = 3.6 Hz), 125.5, 110.6 (d, *J* = 1.6 Hz), 105.0 (d, *J* = 201.1 Hz), 84.9 (d, *J* = 26.5 Hz), 79.6, 45.0 (d, *J* = 4.5 Hz), 31.8, 28.4 (d, *J* = 16.7 Hz), 20.7, 19.6 (d, *J* = 8.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.16, -145.39. IR (film) 3366, 2977, 1684, 1367, 1154, 1034 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}FN_2O_2$ $[M+H]^+$: 307.1816. Found: 307.1823. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.42 min, t (major) = 6.34 min.



(3a*R*,8a*S*)-*tert*-Butyl-5-(tert-butyl)-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2g**)

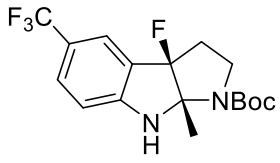
Light yellow oil, 10 mol % **C6** was used, 44.6 mg, 64% yield, 82% ee. Analytical data for **2g**: $[\alpha]_D^{25.5}$ = 169.9 (c = 1.0 Chloroform, 82% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.27 (d, *J* = 10.0 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.65 (br s, 0.7H), 5.05 (br s, 0.3H), 3.66-3.54 (m, 1H), 3.08-3.06 (m, 1H), 2.59-2.54 (m, 2H), 1.69-1.65 (m, 3H), 1.54 (s, 3H), 1.42 (s, 6H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 153.4, 148.3 (d, *J* = 4.2 Hz), 147.7 (d, *J* = 3.7 Hz), 142.3, 128.8, 128.7 (d, *J* = 3.8 Hz), 124.3 (d, *J* = 21.4 Hz), 121.4, 110.0, 109.9, 105.2 (d, *J* =

200.1 Hz), 84.5 (d, *J* = 26.7 Hz), 80.8, 80.0, 44.8 (d, *J* = 4.3 Hz), 44.6 (d, *J* = 4.6 Hz), 34.3, 31.9, 31.4 (d, *J* = 50.9 Hz), 31.0 (d, *J* = 28.9 Hz), 28.7, 28.4, 20.2 (d, *J* = 9.4 Hz), 19.2 (d, *J* = 9.2 Hz). ^{19}F NMR (376 MHz, CDCl3) δ -142.69 (d, *J* = 13.8 Hz), -144.30 (d, *J* = 14.6 Hz). IR (film) 3389, 2962, 1685, 1495, 1366, 1160, 1033 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{30}FN_2O_2$ $[M+H]^+$: 349.2286. Found: 349.2286. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 4.81 min, t (major) = 7.29 min.



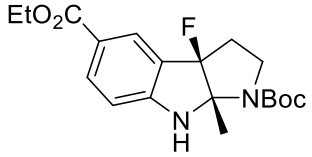
(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-7,8a-dimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2h**)

Light yellow oil, 5 mol % **C6** was used, 65% yield, 61% ee. Analytical data for **2h**: $[\alpha]_D^{25.4}$ = 152.7 (c = 1.0 Chloroform, 61% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.77 (dd, *J* = 7.6 Hz, 1H), 5.68 (br, 0.5H), 5.13 (br, 0.5H), 3.67-3.50 (m, 1H), 3.12-2.98 (m, 1H), 2.62-2.37 (m, 2H), 2.12 (s, 3H), 1.75-1.65 (m, 3H), 1.53 (s, 3H), 1.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 153.3, 149.3, 149.3, 148.8, 148.8, 132.3, 132.3, 132.2, 132.2, 124.0, 123.8, 122.4, 122.2, 119.9, 119.9, 119.7, 119.6, 119.4, 119.2, 119.2, 106.5, 106.1, 84.2, 83.9, 83.9, 83.2, 80.7, 80.1, 44.9, 44.8, 44.5, 44.5, 31.9, 31.6, 31.0, 30.7, 28.7, 28.4, 20.2, 20.1, 19.2, 19.1, 16.5, 16.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.19 (d, *J* = 13.5 Hz), -145.31 (d, *J* = 13.3 Hz). IR (film) 3437, 3392, 3315, 2967, 2921, 1718, 1657, 1525, 1264, 1095, 1051, 931, 809 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}FN_2O_2$ $[M+H]^+$: 307.1816. Found: 307.1823. The enantiomeric excess was determined by Daicel Chiralpak SFC OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.3 mL/min, λ = 214 nm, t (major) = 3.28 min, t (minor) = 3.54 min.



(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-8a-methyl-5-(trifluoromethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2i**)

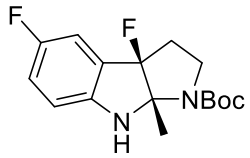
Light yellow oil, 10 mol % **C6** was used, 45.1 mg, 62% yield, 85% ee. Analytical data for **2i**: $[\alpha]_D^{26.6}$ =480.0 (c = 1.0 Chloroform, 85% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.04 (br s, 0.7H), 5.35 (br s, 0.3H), 3.70-3.56 (m, 1H), 3.12-3.07 (m, 1H), 2.56-2.45 (m, 2H), 1.70 (d, *J* = 4.0 Hz, 3H), 1.55 (s, 3H), 1.43 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ 78.90 (s), 78.79 (s), -3.38 (d, *J* = 13.1 Hz), -5.56 (d, *J* = 12.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 152.9, 152.7 (d, *J* = 93.1 Hz), 129.3, 124.8 (d, *J* = 22.2 Hz), 124.6 (q, *J* = 270.5 Hz), 122.5 (d, *J* = 3.4 Hz), 120.8 (d, *J* = 32.7 Hz), 109.6, 109.5, 104.1 (d, *J* = 201.7 Hz), 84.6 (d, *J* = 26.3 Hz), 81.2, 80.4, 31.8 (d, *J* = 28.2 Hz), 28.6, 28.4, 18.9 (d, *J* = 9.2 Hz). IR (film) 3385, 1679, 1626, 1390, 1325, 1150, 849, 654 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{21}F_4N_2O_2$ $[M+H]^+$: 361.1534. Found: 361.1535. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 4.43 min, t (major) = 5.45 min.



(3a*R*,8a*S*)-1-*tert*-Butyl-5-ethyl-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1,5(2H)-dicarboxylate (**2j**)

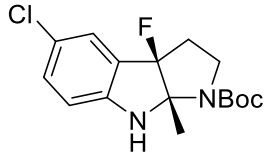
Light yellow oil, 10 mol % **C6** was used, 20.3 mg, 28% yield, 85% ee. Analytical data for **2j**: $[\alpha]_D^{27.2}$ =383.5 (c = 1.0 Chloroform, 85% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, *J* = 2.0 Hz, 1H), 8.01-7.92 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.10 (br s, 0.7H), 5.43 (br s, 0.3H), 4.38-4.30 (m, 2H), 3.69-3.56 (m, 1H), 3.13-2.97 (m, 1H), 2.63-2.44 (m, 2H), 1.71-1.67 (m, 3H), 1.55 (s, 3H), 1.43 (s, 6H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 154.0, 153.9, 134.2, 127.2, 124.6, 124.3, 121.4, 120.9, 120.9, 109.1, 108.9, 105.0, 103.0, 84.7, 84.4, 80.4, 60.5, 46.3, 44.9, 44.8, 44.6, 31.9, 31.6, 29.7, 28.6, 28.4, 20.1, 19.0, 18.9, 14.4. ^{19}F

NMR (376 MHz, $CDCl_3$) δ -142.60 (d, *J* = 19.6 Hz), -145.03 (d, *J* = 14.1 Hz). IR (film) 3380, 2988, 1688, 1616, 1365, 1156, 1029, 773 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{26}FN_2O_4$ $[M+H]^+$: 365.1871. Found: 365.1872. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 3.10 min, t (major) = 11.36 min.



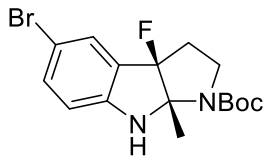
(3a*R*,8a*S*)-*tert*-Butyl-3a,5-difluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2k**)

Light yellow oil, 5 mol % **C6** was used, 28.2 mg, 46% yield, 89% ee. Two rotamers exist in NMR. Analytical data for **2k**: $[\alpha]_D^{24.9}$ =282.4 (c = 1.0 Chloroform, 89% *ee*). Two rotamers exist in NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.96-6.92 (m, 1H), 6.61-6.58 (m, 1H), 5.67 (br s, 0.6H), 5.02 (br s, 0.4H), 3.67-3.55 (m, 1H), 3.12-3.02 (m, 1H), 2.50-2.40 (m, 2H), 1.70-1.66 (m, 3H), 1.55 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 158.0, 157.9, 155.8, 155.6, 155.6, 153.8, 153.3, 146.7, 146.6, 146.1, 125.9, 125.8, 125.7, 125.6, 118.5, 118.4, 118.4, 118.3, 118.2, 118.2, 111.9, 111.8, 111.7, 111.6, 111.2, 111.1, 110.9, 110.9, 106.3, δ 104.5 (d, *J* = 201.0 Hz), 85.0, 84.8, 84.5, 84.3, 81.0, 80.2, 44.8, 44.7, 44.5, 44.5, 31.7, 31.4, 31.3, 31.0, 29.7, 28.6, 28.4, 20.2, 20.1, 19.1, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.74 (s), -125.37 (s), -144.50 (d, *J* = 11.7 Hz), -146.86 (s). IR (film) 3408, 2978, 1678, 1393, 1158, 1034, 774 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}F_2N_2O_2$ $[M+H]^+$: 311.1566. Found: 311.1576. The enantiomeric excess was determined by Daicel Chiralpak SFC OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.3 mL/min, λ = 214 nm, t (major) = 3.28 min, t (minor) = 3.65 min.



(3a*R*,8a*S*)-*tert*-Butyl-5-chloro-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2l**)

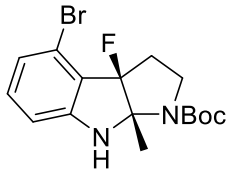
Light yellow oil, 5 mol % **C6** was used, 45.5 mg, 70% yield, 86% ee. Analytical data for **2l**: $[\alpha]_D^{25.5}$ = 269.0 (c = 1.0 Chloroform, 86% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 3.68-3.54 (m, 1H), 3.10-3.05 (m, 1H), 2.51-2.46 (m, 2H), 1.66 (m, 3H), 1.55 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 154.0, 149.5 (d, *J* = 4.1 Hz), 131.8 (d, *J* = 3.2 Hz), 126.7 (d, *J* = 22.2 Hz), 125.3, 123.6 (d, *J* = 3.2 Hz), 111.5, 104.4 (d, *J* = 202.2 Hz), 85.0 (d, *J* = 26.4 Hz), 79.82, 44.9 (d, *J* = 4.5 Hz), 31.7 (d, *J* = 28.3 Hz), 28.4 (d, *J* = 14.8 Hz), 19.3 (d, *J* = 8.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.91 (d, *J* = 13.4 Hz), -146.30 (d, *J* = 10.9 Hz). IR (film) 3370, 2979, 1681, 1479, 1367, 1157, 1035 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}ClFN_2O_2$ $[M+H]^+$: 327.127. Found: 327.1278. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.22 min, t (major) = 6.60 min.



(3a*R*,8a*S*)-*tert*-Butyl-5-bromo-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2m**)

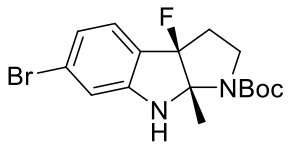
Light yellow oil, 5 mol % **C6** was used, 64.9 mg, 89% yield, 85% ee. Analytical data for **2m**: $[\alpha]_D^{25.5}$ = 270.5 (c = 1.0 Chloroform, 85% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.43 Hz, 1H), 5.80 (s, 1H), 3.61 (dt, *J* = 20.3, 9.6 Hz, 1H), 3.14-3.00 (m, 1H), 2.54-2.37 (m, 2H), 1.54 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 153.2, 149.4, 148.8, 134.3, 134.2, 127.9, 126.9, 126.7, 111.9, 111.6, 110.7, 110.2, 105.2, 103.2, 84.6, 84.3, 84.1, 83.8, 81.0, 80.2, 44.8, 44.7, 44.5, 31.7, 31.4, 31.3, 31.0, 29.6, 28.6, 28.3, 20.1, 20.0, 19.0, 18.9. IR (film) 3379, 2978, 1736, 1477, 1367, 1157, 1036 cm^{-1}. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.66 (d, *J* = 14.5 Hz), -146.05 (d, *J* = 13.0 Hz).

HRMS (ESI) calcd for $C_{16}H_{21}BrFN_2O_2$ $[M+H]^+$: 371.0765. Found: 371.0764. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.31 min, t (major) = 6.85 min.



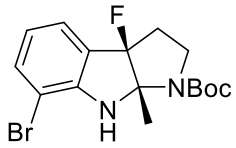
(*3aR,8aS*)-*tert*-Butyl-4-bromo-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2n**)

Light yellow oil, 10 mol % **C6** was used, 68.3 mg, 92% yield, 69% ee. Analytical data for **2n**: $[\alpha]_D^{30.3}$ = 210.2 (c = 1.0 Chloroform, 69% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.02 (m, 1H), 6.94-6.89 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.83 (br s, 0.7H), 5.14 (br s, 0.3H), 3.66-3.53 (m, 1H), 3.19-3.11 (m, 2H), 2.51-2.38 (m, 1H), 1.67 (d, *J* = 4.4 Hz, 3H), 1.55 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 152.1, 132.8, 132.8, 122.9, 122.8, 122.6, 122.4, 120.5, 109.2, 84.5, 84.3, 81.0, 80.2, 44.6, 31.0, 30.8, 29.7, 28.6, 28.4, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.96 (d, *J* = 17.2 Hz), -149.01 (d, *J* = 17.6 Hz). IR (film) 3377, 2972, 2928, 1664, 1605, 1455, 1377, 1044, 775 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2BrF$ $[M+H]^+$: 371.0765. Found: 371.0765. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (minor) = 6.03 min, t (major) = 7.02 min.



(*3aR,8aS*)-*tert*-Butyl-6-bromo-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2o**)

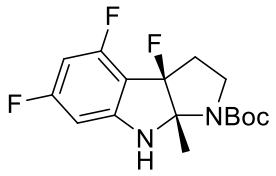
Light yellow oil, 10 mol % **C6** was used, 65.0 mg, 88% yield, 97% ee. Analytical data for **2o**: $[\alpha]_D^{30.3}$ = 188.5 (c = 1.0 Chloroform, 97% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 1H), 6.96-6.91 (m, 1H), 6.81 (s, 1H), 5.83 (br s, 0.7H), 5.16 (s, 0.3H), 3.67-3.53 (m, 1H), 3.10-3.00 (m, 1H), 2.50-2.39 (m, 2H), 1.68-1.64 (m, 3H), 1.54 (s, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 151.7, 129.0, 128.2, 126.2, 125.7, 125.3, 123.9, 123.6, 122.4, 121.9, 113.4, 113.2, 110.0, 105.0, 103.0, 84.6, 84.3, 80.3, 44.8, 31.8, 31.5, 29.7, 28.7, 28.4, 19.1, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.16 (d, *J* = 14.5 Hz), -145.45 (d, *J* = 12.9 Hz). IR (film) 3407, 2923, 2855, 1683, 1606, 1379, 1031, 768 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2BrF$ $[M+H]^+$: 371.0765. Found: 371.0765. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 6.05 min, t (minor) = 9.07 min.



(*3aR,8aS*)-*tert*-Butyl-7-bromo-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2p**)

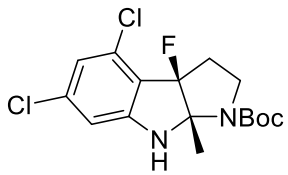
Light yellow oil, 5 mol % **C6** was used, 64.1 mg, 85% yield, 64% ee. Analytical data for **2p**: $[\alpha]_D^{29.6}$ = 194.4 (c = 1.0 Chloroform, 86% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.31-7.28 (m, 1H), 6.75-6.68 (m, 1H), 5.97 (br s, 0.5H), 5.54 (br s, 0.5H), 3.65-3.54 (m, 1H), 3.11–3.02 (m, 1H), 2.59–2.41 (m, 2H), 1.70 (dd, J = 19.3, 4.1 Hz, 3H), 1.57 (s, 5H), 1.44 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 153.2, 149.0, 148.6, 134.0, 134.0, 133.9, 133.9, 126.0, 125.8, 123.9, 123.7, 120.6, 120.5, 120.1, 106.5, 106.2, 105.1, 104.9, 103.8, 83.9, 83.8, 83.1, 82.9, 81.2, 80.4, 44.8, 44.8, 44.4, 44.4, 32.3, 32.1, 31.0, 30.9, 28.6, 28.4, 20.0, 19.9, 19.1, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.56 (d, *J* = 13.5 Hz), -145.26 (d, *J* = 10.8 Hz). HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2BrF$ $[M+H]^+$: 371.0765. Found: 371.0762. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46

cm x 25 cm), Hexanes / IPA = 50 / 1, 0.51 mL/min, λ = 254 nm, t (major) = 10.01 min, t (minor) = 11.23 min.



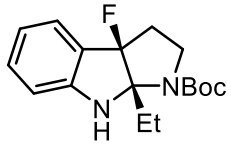
(*3aR*,*8aS*)-*tert*-Butyl-3a,4,6-trifluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2q**)

White solid, 10 mol % **C6** was used, 42.8 mg, 65% yield, 96% ee. Analytical data for **2q**: Mp = 122.1-122.5 ℃, $[\alpha]_D^{29.5}$ = 357.1 (c = 0.1 Chloroform, 96% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28-6.12 (m, 2H), 5.99 (br s, 0.7H), 5.31 (s, 0.3H), 3.70-3.56 (m, 1H), 3.19-3.10 (m, 1H), 2.84-2.76 (m, 1H), 2.51-2.38 (m, 1H), 1.67–1.66 (m, 3H), 1.55 (s, 9H), 1.44 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 167.1, 167.1, 167.0, 165.5, 165.5, 165.4, 165.4, 161.8, 161.7, 160.1, 160.0, 153.9, 153.3, 153.1, 106.8, 106.7, 106.6, 104.5, 103.7, 103.1, 102.3, 94.9, 94.7, 94.5, 94.4, 94.2, 94.1, 93.9, 93.7, 93.5, 85.2, 85.0, 84.5, 84.4, 81.2, 80.4, 45.0, 45.0, 44.7, 44.7, 31.0, 30.8, 30.5, 30.3, 28.6, 28.4, 26.9, 20.1, 20.0, 19.0, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.24 – -105.40 (m), -105.63 (qd, *J* = 9.5, 5.6 Hz), -115.14 (dt, *J* = 11.8, 5.9 Hz), -115.53 (td, *J* = 10.1, 9.4, 3.1 Hz), -143.17 (d, *J* = 15.2 Hz), -145.82 (dq, *J* = 14.8, 4.4 Hz). IR (film) 3363, 2985, 2934, 1679, 1392, 1163, 1028, 779, 675 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{20}N_2O_2F_3$ $[M+H]^+$: 329.1471. Found: 329.1470. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 4.83 min, t (minor) = 5.87 min.



(*3aR,8aS*)-*tert*-Butyl-4,6-dichloro-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2r**)

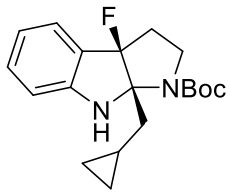
White solid, 10 mol % **C6** was used, 51.2 mg, 71% yield, 96% ee. Mp = 127.7-128.1 ℃, Analytical data for **2r**: $[\alpha]_D^{29.6}$ = 332.5 (c = 1.0 Chloroform, 96% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 6.52 (s, 1H), 5.95 (br s, 0.7H), 5.24 (br s, 0.3H), 3.68-3.54 (m, 1H), 3.20-3.03 (m, 2H), 2.51-2.38 (m, 1H), 1.67-1.66 (m, 3H), 1.55-1.43 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 153.1, 152.5, 152.4, 151.8, 138.0, 137.9, 132.9, 129.4, 129.2, 128.3, 128.2, 127.6, 119.9, 119.6, 119.5, 119.4, 108.8, 108.6, 105.3, 103.9, 84.8, 84.7, 81.2, 80.5, 44.7, 44.6, 44.5, 30.8, 30.6, 30.4, 30.2, 28.6, 28.4, 20.3, 20.2, 19.1, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.45 (d, J = 16.8 Hz), -148.55 – -149.37 (m). IR (film) 3368, 2981, 2936, 2895, 1675, 1590, 1384, 1165, 1032, 975, 846, 661 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{20}N_2O_2Cl_2F$ $[M+H]^+$: 361.0880. Found: 361.0881. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 4.74 min, t (minor) = 5.74 min.



(3a*R*,8a*S*)-*tert*-Butyl-8a-ethyl-3a-fluoro-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2s**)

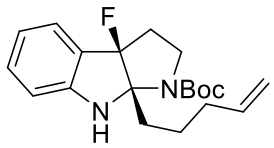
Light yellow oil, 10 mol % **C6** was used, 43.5 mg, 71% yield, 89% ee. Analytical data for **2s**: $[\alpha]_D^{26.6}$ = 376.2 (c = 1.0 Chloroform, 89% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.83-6.78 (m, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.65 (br s, 0.6H), 5.01 (br s, 0.4H), 3.65 (m, 1H), 3.14-3.07 (m, 1H), 2.56-2.50 (m, 2H), 2.41-2.25 (m, 1H), 2.04 (m, 1H), 1.54 (s, 3H), 1.43 (s, 6H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.6, 150.4 (d, *J* = 4.0 Hz), 149.9, 131.6, 131.5 (d, *J* = 3.2 Hz), 125.1 (d, *J* = 22.0 Hz), 124.8, 124.7, 119.3 (d, *J* = 1.6 Hz), 118.8 (d, *J* = 2.6 Hz), 110.2, 109.9, 106.2 (d,

J = 202.9 Hz), 105.4 (d, *J* = 201.0 Hz), 86.8 (d, *J* = 26.1 Hz), 86.2 (d, *J* = 25.8 Hz), 45.3 (d, J = 4.4 Hz), 45.0 (d, *J* = 3.5 Hz), 33.0 (d, *J* = 28.9 Hz), 32.6 (d, *J* = 28.4 Hz), 26.8 (d, *J* = 7.8 Hz), 25.7 (d, *J* = 7.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.96 (d, J = 14.0 Hz), -145.36 (s). IR (film) 3338, 2973, 1683, 1366, 1240, 1161, 742 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{24}FN_2O_2$ $[M+H]^+$: 307.1816. Found: 307.182. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.55 min, t (major) = 6.55 min.



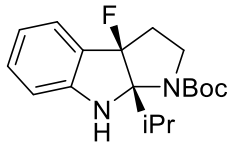
(3a*R*,8a*S*)-*tert*-Butyl-8a-(cyclopropylmethyl)-3a-fluoro-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2t**)

Light yellow oil, 10 mol % **C6** was used, 53.3 mg, 82% yield, 85% ee. Analytical data for **2t**: $[\alpha]_D^{28.4}$ = 234.7 (c = 1.0 Chloroform, 85% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 1H), 7.23 (m, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 5.58 (br s, 1H), 3.74-3.62 (m, 1H), 3.19-3.12 (m, 1H), 2.74-2.59 (m, 1H), 2.65-2.53 (m, 1H), 2.23-2.18 (m, 1H), 2.02-1.87 (m, 1H), 1.56-1.39 (m, 9H), 0.79-0.77 (m, 1H), 0.51-0.46 (m, 2H), 0.19 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 154.0, 150.3, 131.6, 131.5, 131.5, 125.5, 125.3, 124.7, 119.4, 119.0, 110.4, 110.1, 106.0, 104.0, 86.6, 86.3, 80.0, 45.3, 45.2, 45.1, 37.8, 37.7, 36.5, 36.4, 32.5, 32.3, 31.7, 31.4, 29.7, 28.7, 28.5, 6.3, 6.2, 5.3, 4.5, 3.8, 3.8. IR (film) 3391, 2929, 1681, 1381, 1160, 746 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{26}FN_2O_2$ $[M+H]^+$: 333.1973. Found: 333.1974. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.44 min, t (major) = 6.21 min.



(3aR,8aS)-*tert*-Butyl-3a-fluoro-8a-(pent-4-en-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2u**)

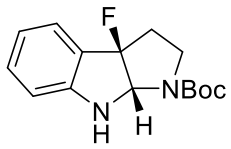
Light yellow oil, 10 mol % **C6** was used, 50.8 mg, 73% yield, 85% ee. Analytical data for **2u**: $[\alpha]_D^{29.6}$ = 281.8 (c = 1.0 Chloroform, 85% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.23-7.19 (m, 1H), 6.84-6.78 (m, 1H), 6.66-6.62 (m, 1H), 5.87-5.77 (m, 1H), 5.66 (br s, 0.7H), 5.05-4.97 (m, 2H), 4.94 (br s, 0.3H), 3.71-3.57 (m, 1H), 3.14-3.05 (m, 1H), 2.59-2.47 (m, 2H), 2.38-1.97 (m, 4H), 1.61 (s, 1H), 1.54 (s, 3H), 1.43 (s, 6H), 1.33-1.29 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.0, 153.5, 150.4, 150.4, 149.8, 147.0, 138.6, 138.3, 131.6, 131.6, 131.5, 128.8, 125.1, 125.1, 125.0, 124.9, 124.8, 124.7, 124.6, 124.4, 123.9, 119.3, 119.1, 118.9, 118.8, 115.0, 114.6, 110.2, 109.9, 106.9, 106.1, 105.5, 104.8, 86.4, 86.2, 85.9, 85.7, 80.9, 80.1, 45.2, 45.2, 44.9, 44.9, 34.8, 34.5, 33.9, 33.9, 33.5, 33.5, 33.0, 32.8, 32.6, 32.5, 32.5, 31.4, 30.2, 28.6, 28.4, 28.3, 24.0, 24.0, 23.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.38 (d, *J* = 14.5 Hz), -144.82. IR (film) 3404, 3327, 2973, 2930, 1678, 1164, 911, 747 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{28}FN_2O_2$ $[M+H]^+$: 347.2129. Found: 347.2129. The enantiomeric excess was determined by Daicel Chiralcel OJ-H (0.46 cm x 25 cm), Hexanes / IPA = 98 / 2, 1.0 mL/min, λ = 254 nm, t (major) = 5.62 min, t (minor) = 8.44 min.



(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-8a-isopropyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2v**)

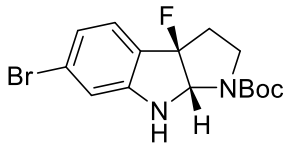
Light yellow oil, 10 mol % **C6** was used, 43.6 mg, 68% yield, 62% ee. Analytical data for **2v**: $[\alpha]_D^{25.6}$ = 47.5 (c = 1.0 Chloroform, 62% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.2 Hz, 1H), 6.97 (dd, *J* = 6.8 Hz, 1H), 6.64

(dd, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.00 (br s, 1H), 3.32-3.27 (m, 1H), 3.19-3.02 (m, 1H), 2.94-2.87 (m, 1H), 2.44-2.25 (m, 1H), 2.19-2.06 (m, 1H), 1.42-1.15 (m, 15H). ^{13}C NMR (151 MHz, cdcl3) δ 154.2, 150.4, 149.7, 149.6, 131.4, 129.9, 125.8, 124.3, 118.7, 110.1, 106.4, 105.1, 80.0, 45.6, 33.6, 33.4, 32.4, 30.9, 29.7, 28.4, 18.1, 17.2, 17.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.05 (d, *J* = 15.8 Hz). IR (film) 3389, 2921, 2852, 1690, 1462, 1376, 1161, 744 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}FN_2O_2$ $[M+H]^+$: 321.1973. Found: 321.1976. The enantiomeric excess was determined by Phenomenex Cellulose-2 (0.46 cm x 25 cm), Hexanes / IPA = 99 / 1, 1.0 mL/min, λ = 254 nm, t (minor) = 5.46 min, t (major) = 7.31 min.



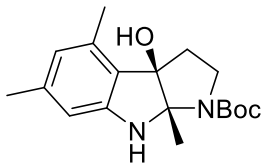
(*3aR,8aS*)-*tert*-Butyl-3a-fluoro-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2w**)

Light red oil, 10 mol % **C6** was used, 28.3 mg, 51% yield, 56% ee. Analytical data for **2w**: $[\alpha]_D^{29.8}$ = 132.0 (c = 1.0 Chloroform, 56% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 6.84 (dd, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.48 (dd, *J* = 27.0, 19.2 Hz, 1H), 5.11 (br s, 0.5H), 4.69 (br s, 0.5H), 3.86-3.71 (m, 1H), 3.27-3.17 (m, 1H), 2.72-2.57 (m, 1H), 2.51-2.43 (m, 1H), 1.53-1.47 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 153.6, 150.5, 150.4, 131.6, 131.6, 131.5, 131.5, 126.7, 124.9, 124.7, 124.6, 124.5, 124.4, 119.6, 119.6, 119.2, 119.2, 117.7, 117.5, 117.5, 117.4, 117.3, 110.4, 110.3, 109.0, 106.1, 83.5, 81.2, 80.7, 80.4, 79.9, 79.8, 79.6, 79.5, 46.3, 45.7, 45.7, 45.2, 45.2, 35.3, 35.0, 34.7, 28.5, 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.70 (td, *J* = 17.8, 5.4 Hz), -136.98 (td, *J* = 18.6, 18.2, 7.3 Hz). IR (film) 3361, 2978, 2932, 1693, 1615, 1403, 1167, 753 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}FN_2O_2$ $[M+H]^+$: 279.1503. Found: 279.151. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (minor) = 7.37 min, t (major) = 8.24 min.



(*3aR*,*8aS*)-*tert*-Butyl-6-bromo-3a-fluoro-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2x**)

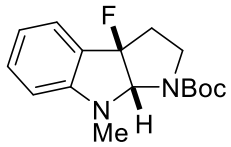
Light yellow oil, 10 mol % **C6** was used, 41.8 mg, 59% yield, 77% ee. Analytical data for **2x**: $[\alpha]_D^{29.5}$ = 111.9 (c = 1.0 Chloroform, 77% *ee*). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.2 Hz, 1H), 6.96-6.91 (m, 1H), 6.83-6.81 (m, 1H), 5.46 (dd, *J* = 23.4, 18.8 Hz, 1H), 5.27 (br s, 0.6H), 4.79 (br s, 0.4H), 3.86-3.69 (m, 1H), 3.24-3.15 (m, 1H), 2.70-2.55 (m, 1H), 2.46-2.39 (m, 1H), 1.52 (s, 4H), 1.47 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 153.4, 151.7, 151.7, 151.3, 125.8, 125.7, 125.6, 123.8, 123.6, 122.4, 122.4, 122.0, 122.0, 1133, 108.2, 107.2, 106.2, 105.2, 80.9, 80.6, 79.9, 79.8, 79.6, 79.5, 45.6, 45.1, 35.1, 34.8, 34.6, 28.5, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.55 (td, *J* = 18.2, 6.0 Hz), -139.93 (td, *J* = 18.2, 6.6 Hz). IR (film) 3351, 2925, 1692, 1609, 1405, 1168, 899, 783 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{19}FN_2O_2$ $[M+H]^+$: 357.0608. Found: 357.0609. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 7.00 min, t (minor) = 7.83 min.



(3a*R*,8a*S*)-*tert*-Butyl-3a-hydroxy-4,6,8a-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2yy**)

Light yellow oil, 10 mol % **C6** was used, 46.1 mg, 72% yield, 93% ee. Analytical data for 2m: $[\alpha]_D^{27.2}$ =201.5 (c = 1.0 Chloroform, 93% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 4.4 Hz, 1H), 6.26 (d, *J* = 6.8 Hz, 1H), 5.68 (br s, 0.6H), 5.01 (s, 0.4H), 3.52-3.41 (m, 1H), 3.01-2.95 (m, 1H), 2.64-2.57 (m, 1H),

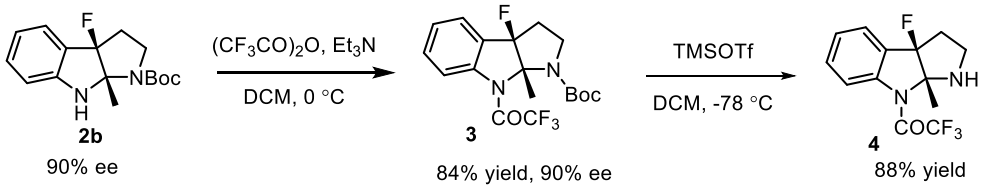
2.35 (s, 3H), 2.22 (s, 3H), 2.19-2.15 (m, 1H), 1.53 (s, 3H), 1.40 (s, 6H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.5, 150.0, 149.4, 140.2, 135.8, 123.8, 122.8, 122.3, 119.2, 108.7, 108.4, 104.9, 87.7, 86.8, 84.5, 83.9, 80.3, 79.5, 44.5, 44.2, 32.0, 31.6, 31.5, 29.6, 28.7, 28.4, 22.6, 21.4, 20.4, 19.3, 17.6. IR (film) 3371, 2926, 1675, 1596, 1383, 1166, 1046, 757 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{27}N_2O_3$ $[M+H]^+$: 319.2016. Found: 319.2018. The enantiomeric excess was determined by Daicel Chiralpak AD-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (minor) =6.70 min, t (major) = 8.98 min.



tert-Butyl-3a-fluoro-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2z**) [10]

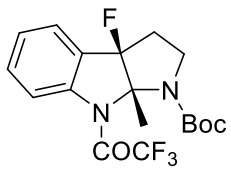
Light yellow oil, 10 mol % **C6** was used, 13.6 mg, 23% yield. Analytical data for **2z**: Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 6.77 (dd, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.46 (dd, *J* = 37.8, 21.2 Hz, 1H), 4.04-3.83 (m, 1H), 3.26-3.11 (m, 1H), 3.05-2.99 (m, 3H), 2.62-2.50 (m, 1H), 2.39-2.36 (m, 1H), 1.54-1.43 (m, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.05 – -138.20 (m), -138.20 – -140.56 (m).

Transformations of product 2b



To a solution of compound **2b** (524 mg, 1.8 mmol, 90% ee) in DCM (18 mL) was added Et_3N (0.5 mL, 3.6 mmol, 1.2 equiv). The reaction mixture was stirred at 0 ^oC for 10 min, and then $(CF_3CO)_2O$ (0.5 mL, 3.6 mmol, 1.2 equiv) was added slowly. After the reaction was complete (monitored by TLC), $NaHCO_3$ saturated solution (2 mL) was poured into the solution, and then warm to room temperature. The reaction mixture was extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/ petroleum ether = 1/20, v/v) to afford desired product **3**.

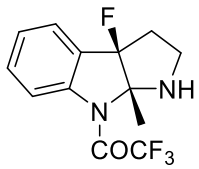
To a solution of compound **3** (155.0 mg, 0.4 mmol) in DCM (4 mL) was slowly added TMSOTf (144.8 μL, 0.8 mmol, 2.0 equiv) at -78 ^oC. After the reaction was complete (monitored by TLC), H_2O (2 mL) was poured into the solution, and then the mixture was allowed to warm to the room temperature. The reaction mixture was extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/ petroleum ether = 1/10, v/v) to afford desired product **4**.



(3a*R*,8a*S*)-*tert*-Butyl-3a-fluoro-8a-methyl-8-(2,2,2-trifluoroacetyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**3**)

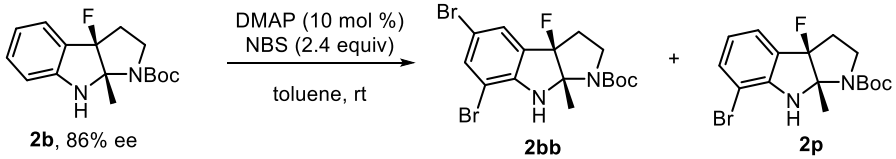
White solid. 588.0 mg, 84% yield, 90% ee. Analytical data for **3**: Mp = 91.7-92.5 ℃, Two rotamers exist in NMR. $[\alpha]_D^{25.1}$ =95.0 (c = 0.2 Chloroform, 90% ee). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.43-7.37 (m, 2H), 7.29 (m, 1H), 3.84-3.75 (m, 1H), 3.00-2.93 (m, 1H), 2.57-2.45 (m, 2H), 1.98 (d, *J* = 4.4 Hz, 3H), 1.49 (s,

9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (d, *J* = 39.3 Hz), 153.3, 139.6 (d, *J* = 4.5 Hz), 131.0 (d, *J* = 2.4 Hz), 129.3 (d, *J* = 22.6 Hz), 126.3, 124.5, 117.2 (d, *J* = 6.2 Hz), 115.9 (q, *J* = 288.7 Hz), 103.8 (d, *J* = 206.5 Hz), 92.7-91.0 (m), 81.5, 44.8, 31.7 (d, *J* = 26.8 Hz), 28.4, 19.0 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.90 (s), -151.99 (s). HRMS (ESI) calcd for $C_{18}H_{21}F_4N_2O_3$ $[M+H]^+$: 389.1483. Found: 389.1483. The enantiomeric excess was determined by Daicel Chiralpak IC-H (0.46 cm x 25 cm), Hexanes / IPA = 95 / 5, 1.0 mL/min, λ = 254 nm, t (major) = 6.77 min.



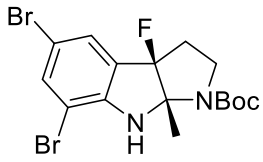
(3a*R*,8a*S*)-2,2,2-Trifluoro-1-(3a-fluoro-8a-methyl-1,3,3a,8a-tetrahydropyrrolo[2,3-b]indol-8(2H)-yl)ethanone

Light yellow oil, 101.2 mg, 88% yield. Analytical data for **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (br, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 4.16-4.01 (m, 1H), 3.75 (s, 1H), 2.69-2.47 (m, 1H), 2.43-2.34 (m, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ171.7 (d, *J* = 20.7 Hz), 155.0 (d, *J* = 37.9 Hz), 133.0, 129.8, 128.8 (d, *J* = 21.8 Hz), 126.4, 125.3 (d, *J* = 6.1 Hz), 124.5, 117.1, 114.3, 111.4, 109.5 (d, *J* = 179.7 Hz), 57.6, 45.6, 38.5 (d, J = 23.0 Hz), 15.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.22 (s), -140.30 (td, *J* = 29.3, 12.6 Hz). HRMS (ESI) calcd for $C_{13}H_{13}F_4N_2O$ $[M+H]^+$: 289.0959. Found: 289.0961.



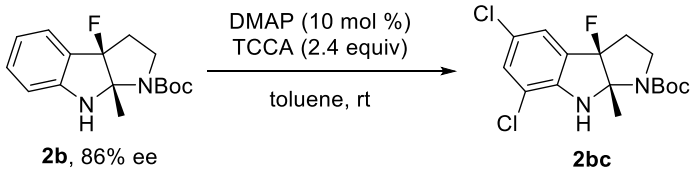
To a solution of compound **2b** (29.2 mg, 0.1 mmol, 86% ee) in toluene (2 mL) was added DMAP (1.2 mg, 0.01 mmol), and then NBS (42.7 mg, 0.24 mmol, 2.4 equiv) was added in one pot. After the reaction was complete (monitored by TLC), $Na_2S_2O_3$ saturated aqueous solution (2 mL) was poured into the solution. The reaction mixture was extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under

reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/ petroleum ether = 1/20, v/v) to afford desired products **2bb** and **2p**.



(*3aR,8aS*)-*tert*-Butyl-5,7-dibromo-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2bb**)

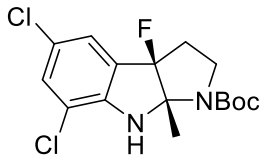
White solid, 30.6 mg, 68% yield, 87% ee. Analytical data for **2bb**: Mp = 128.5-129.1 ℃, $[\alpha]_D^{29.6}$ = 171.0 (c = 1.0 Chloroform, 87% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.39 (d, *J* = 6.4 Hz, 1H), 5.98 (br s, 0.5H), 5.51 (br s, 0.5H), 3.65-3.55 (m, 1H), 3.14-3.04 (m, 1H), 2.57-2.40 (m, 2H), 1.68 (dd, *J* = 18.2, 4.2 Hz, 3H), 1.56 (s, 3H), 1.44 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 153.0, 148.1, 147.7, 136.0, 135.9, 127.4, 127.3, 127.1, 126.9, 110.6, 110.0, 106.2, 105.8, 104.9, 104.5, 104.1, 84.3, 84.1, 83.4, 83.2, 81.4, 80.6, 44.7, 44.4, 32.2, 32.0, 31.0, 30.9, 28.6, 28.3, 19.9, 19.8, 19.0, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.96 (d, *J* = 14.6 Hz), -145.92. IR (film) 3367, 2968, 2925, 2861, 1689, 1459, 1374, 1255, 1155, 1034, 863, 783, 639 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{20}N_2O_2Br_2F$ [M+H]+: 448.9870. Found: 448.9871. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 50 / 1, 0.51 mL/min, λ = 254 nm, t (minor) = 8.41 min, t (major) = 9.11 min.



2b, 86% ee **2bc**

To a solution of compound **2b** (29.2 mg, 0.1 mmol, 86% ee) in toluene (2 mL) was added DMAP (1.2 mg, 0.01 mmol), and then TCCA (55.8 mg, 0.24 mmol, 2.4 equiv) was added in one pot. After the reaction was complete (monitored by TLC), $Na_2S_2O_3$ saturated solution (2 mL) was poured into the solution. The reaction mixture was extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under reduced

pressure. The residue was purified by silica gel column chromatography (ethyl acetate/ petroleum ether = 1/20, v/v) to afford desired product **2bc**.



(*3aR,8aS*)-*tert*-Butyl-5,7-dichloro-3a-fluoro-8a-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (**2bc**)

White solid, 23.8 mg, 66% yield, 88% ee. Analytical data for **2bc**: Mp = 73.1-74.9 ℃, $[\alpha]_D^{29.7}$ = 248.0 (c = 0.1 Chloroform, 88% ee). Two rotamers exist in NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-2.22 (m, 2H), 5.97 (br s, 0.6H), 5.48 (br s, 0.4H), 3.66-3.55 (m, 1H), 3.14-3.02 (m, 1H), 2.56-2.41 (m, 2H), 1.72-1.66 (m, 3H), 1.56 (s, 4H), 1.44 (s, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 153.1, 149.0, 146.2, 145.8, 130.8, 127.2, 127.0, 124.1, 123.7, 123.5, 115.9, 115.8, 106.1, 105.7, 104.7, 104.4, 84.7, 84.5, 83.8, 83.6, 81.4, 80.6, 44.8, 44.8, 44.4, 44.4, 42.6, 32.1, 31.9, 31.0, 30.8, 28.6, 28.4, 19.9, 19.9, 19.0, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -144.33 (d, *J* = 14.6 Hz), -146.21. IR (film) 3368, 2976, 2928, 1688, 1463, 1375, 1159, 1036, 863, 768 cm^{-1}. FTMS (ESI) calcd for $C_{16}H_{20}N_2O_2Cl_2F$ $[M+H]^+$: 361.0880. Found: 361.0882. The enantiomeric excess was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), Hexanes / IPA = 50 / 1, 0.51 mL/min, λ = 254 nm, t (minor) = 8.43 min, t (major) = 9.14 min.

X-Ray crystal structure of enantiopure 3 (CCDC 1526408)

The crystal of enantiopure **3** was obtained through slow evaporation from its solution in tetrahydrofuran and *n*-hexane. The structure and absolute configuration of **3** were then determined by X-ray crystallographic analysis.

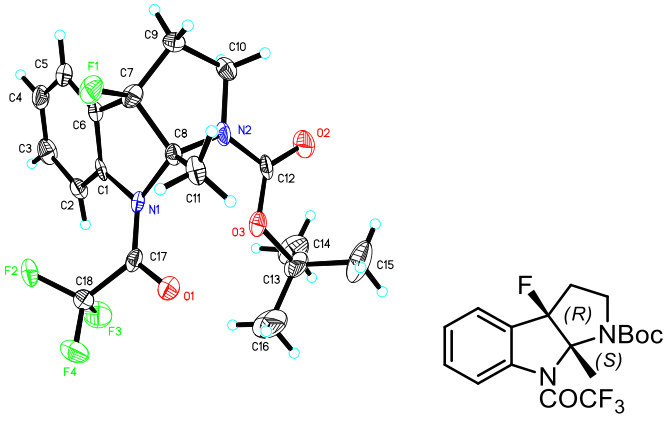


Table 1. Crystal data and structure refinement for cd214591.

Identification code	cd214591	
Empirical formula	C18 H20 F4 N2 O3	
Formula weight	388.36	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.606(4) Å	α= 90 °.
	b = 6.390(3) Å	β= 95.946(8) °.
	c = 13.828(6) Å	γ = 90 °.
Volume	932.0(7) $Å^3$	
Z	2	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.121 mm^{-1}	
F(000)	404	
Crystal size	0.112 x 0.089 x 0.075 mm^3	
Theta range for data collection	2.308 to 25.050 °.	
Index ranges	-12<=h<=12, -7<=k<=7, -14<=l<=16	
Reflections collected	4955	
Independent reflections	2965 [R(int) = 0.0582]	

Completeness to theta = 25.242 °	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4412
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2965 / 1 / 248
Goodness-of-fit on F^2	1.168
Final R indices [I>2sigma(I)]	R1 = 0.0888, wR2 = 0.2191
R indices (all data)	R1 = 0.1018, wR2 = 0.2281
Absolute structure parameter	0.1(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.507 and -0.327 e.$Å^{-3}$

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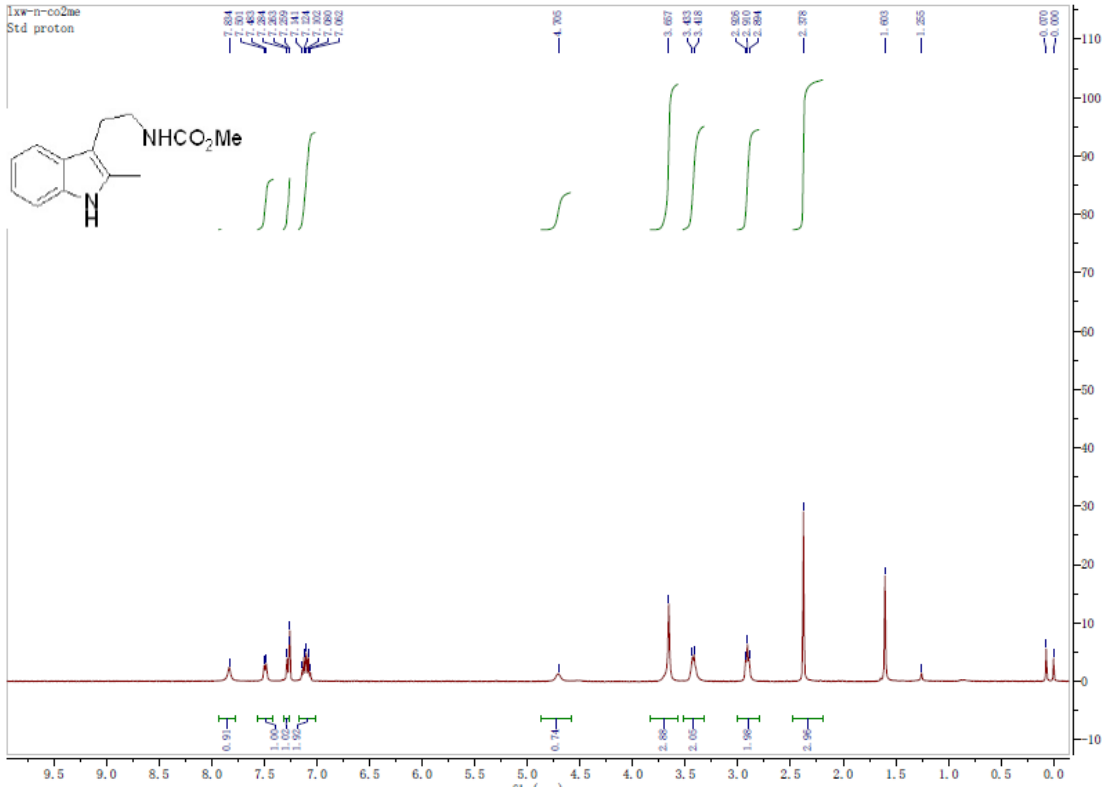
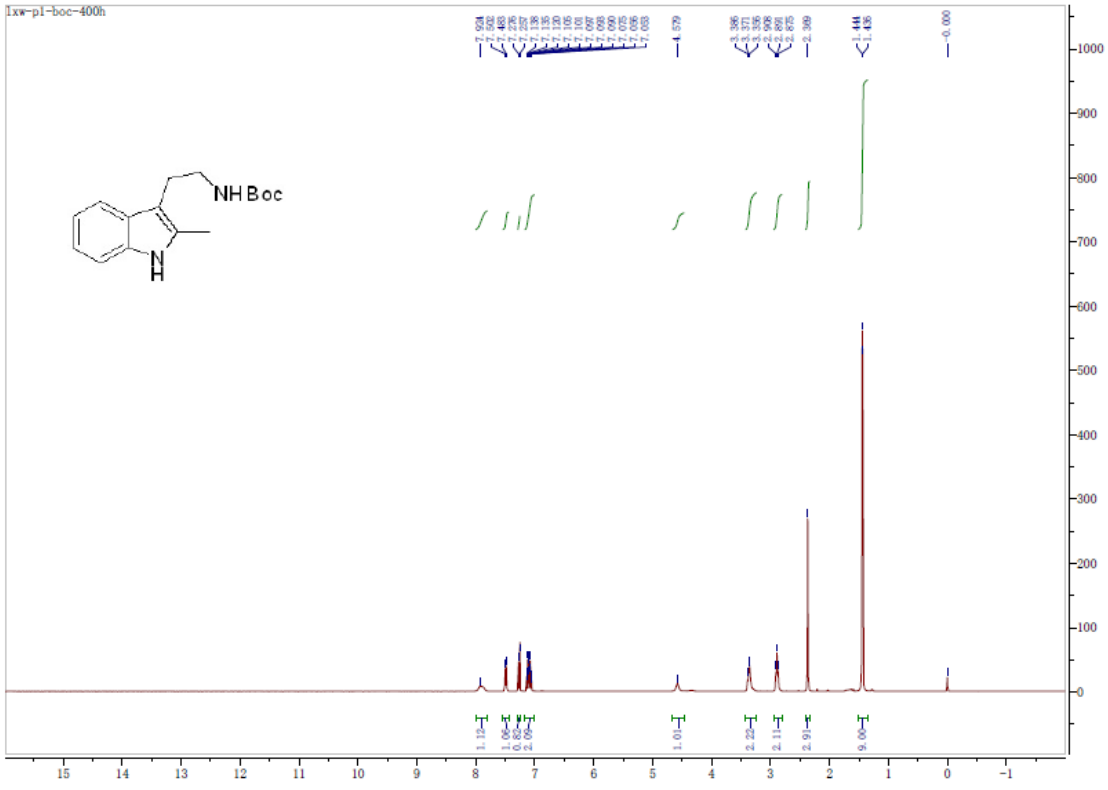
Copies of NMR Spectra and HPLC Chromatographs

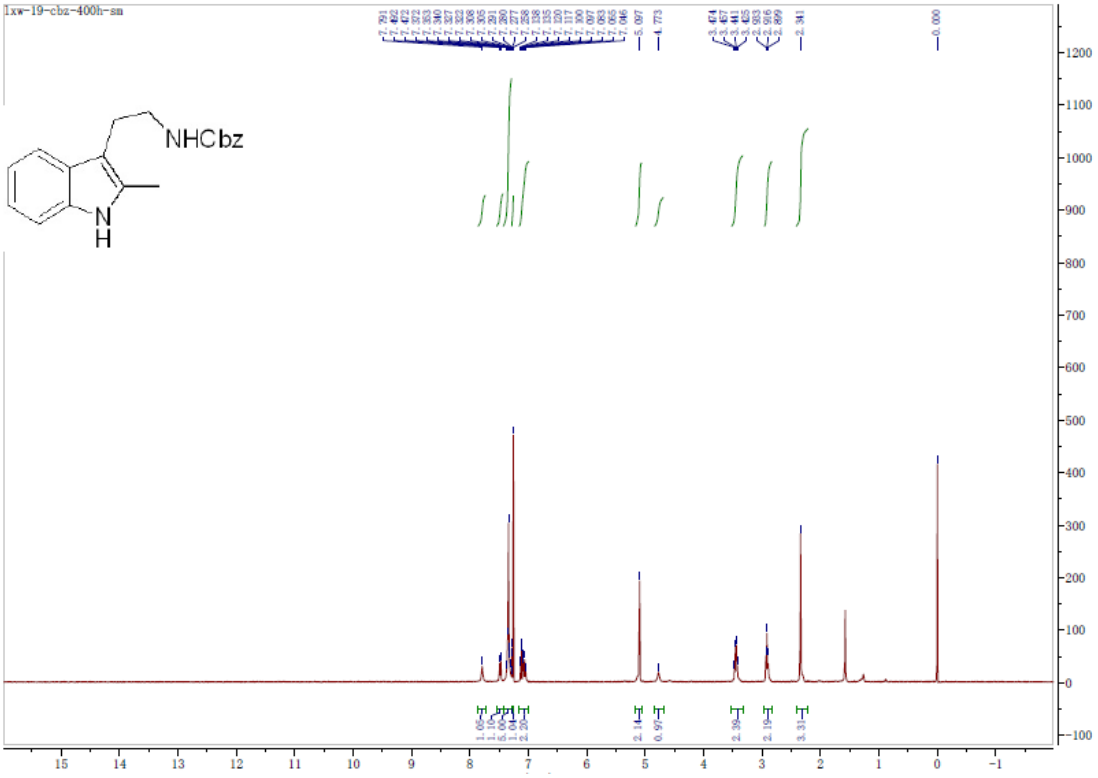
NMR Spectra of **1a**



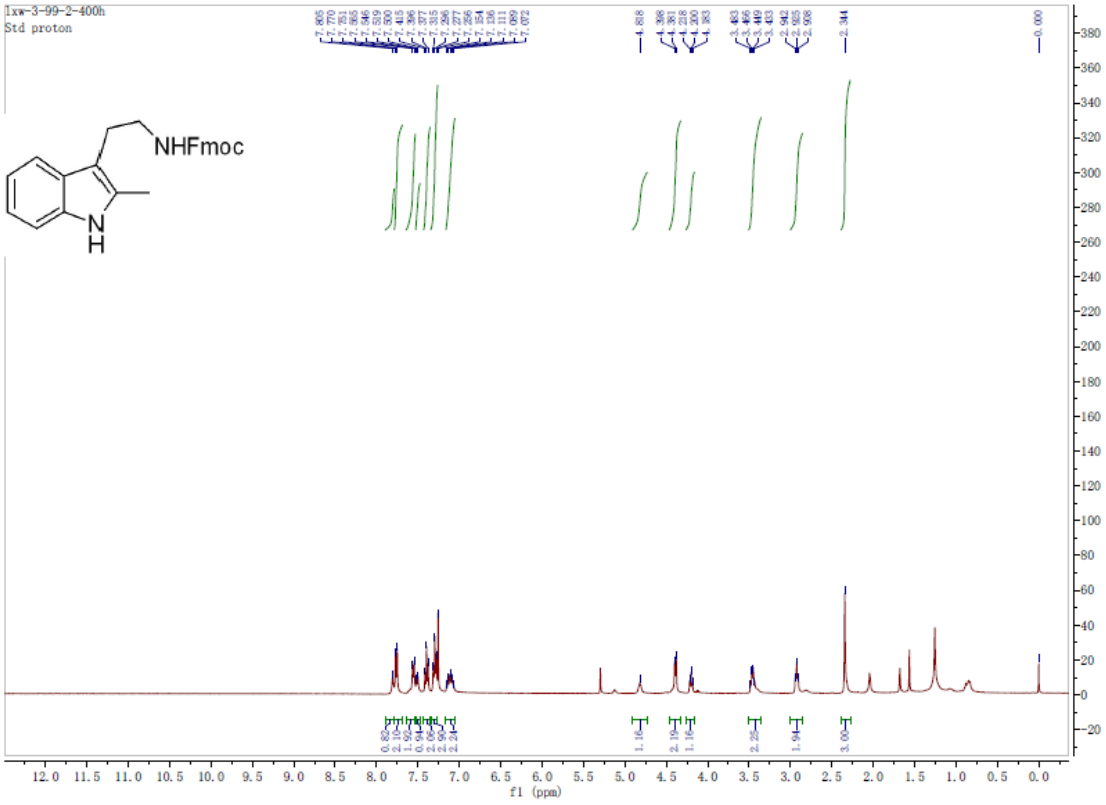
NMR Spectra of **1b**

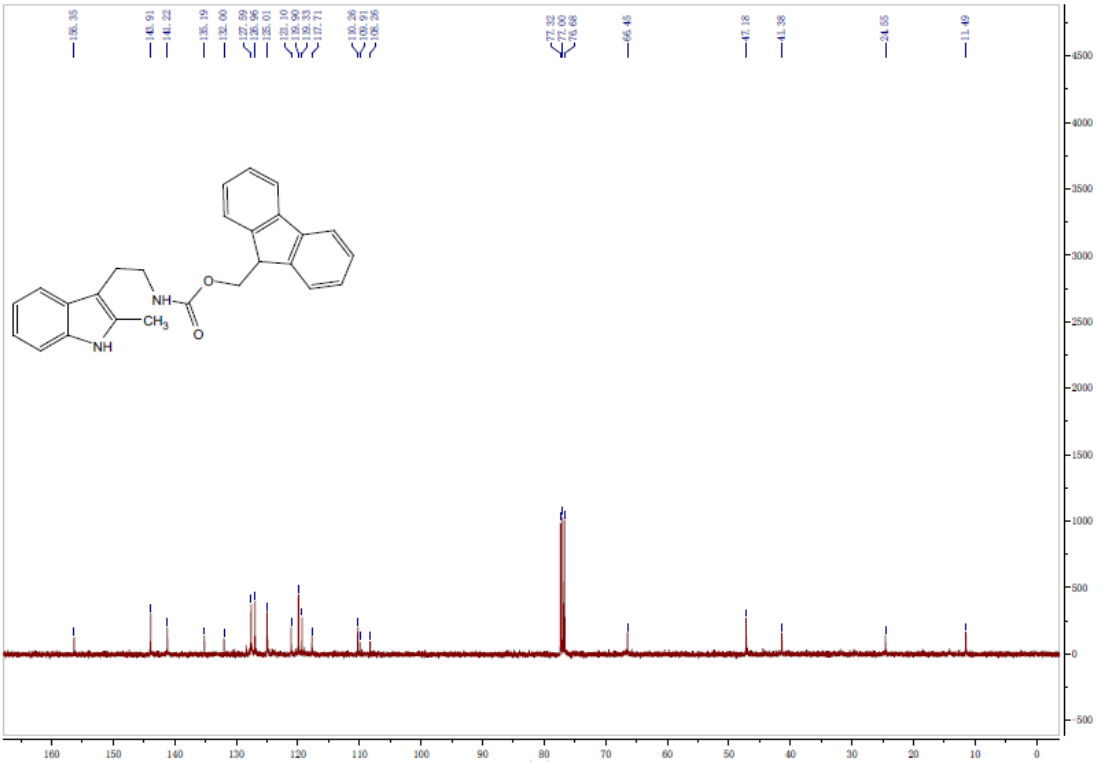


NMR Spectra of **1c**

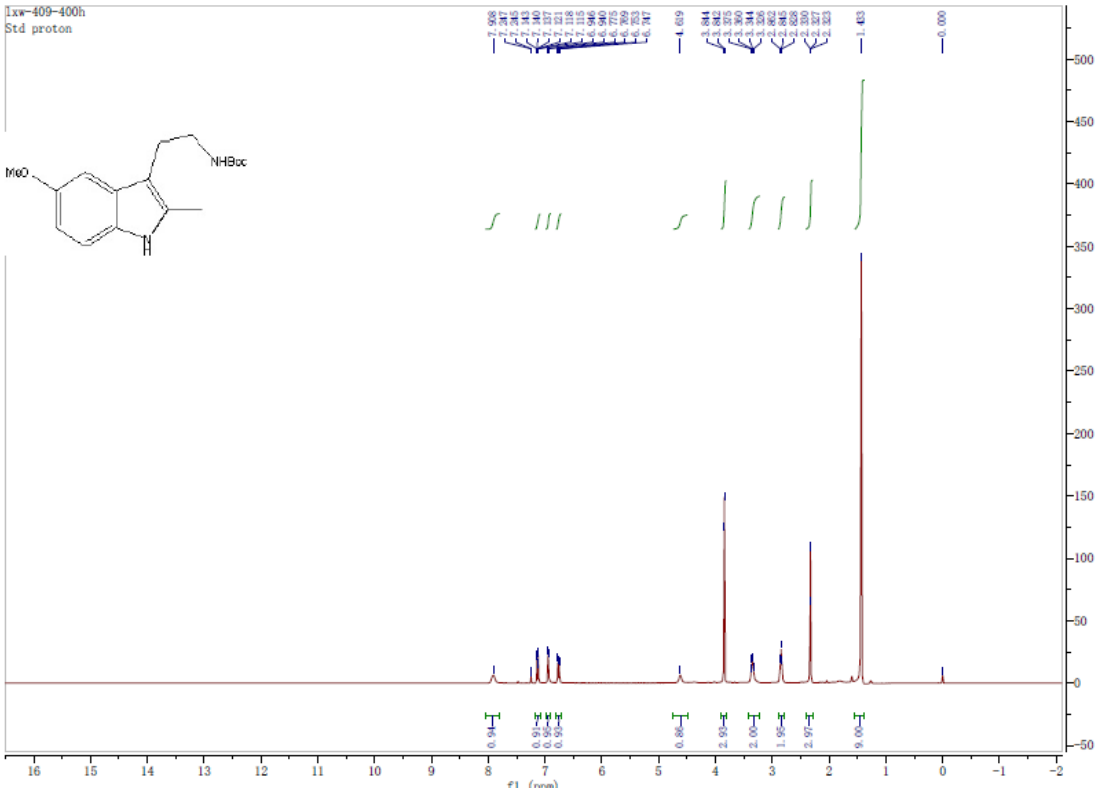


NMR Spectra of **1d**

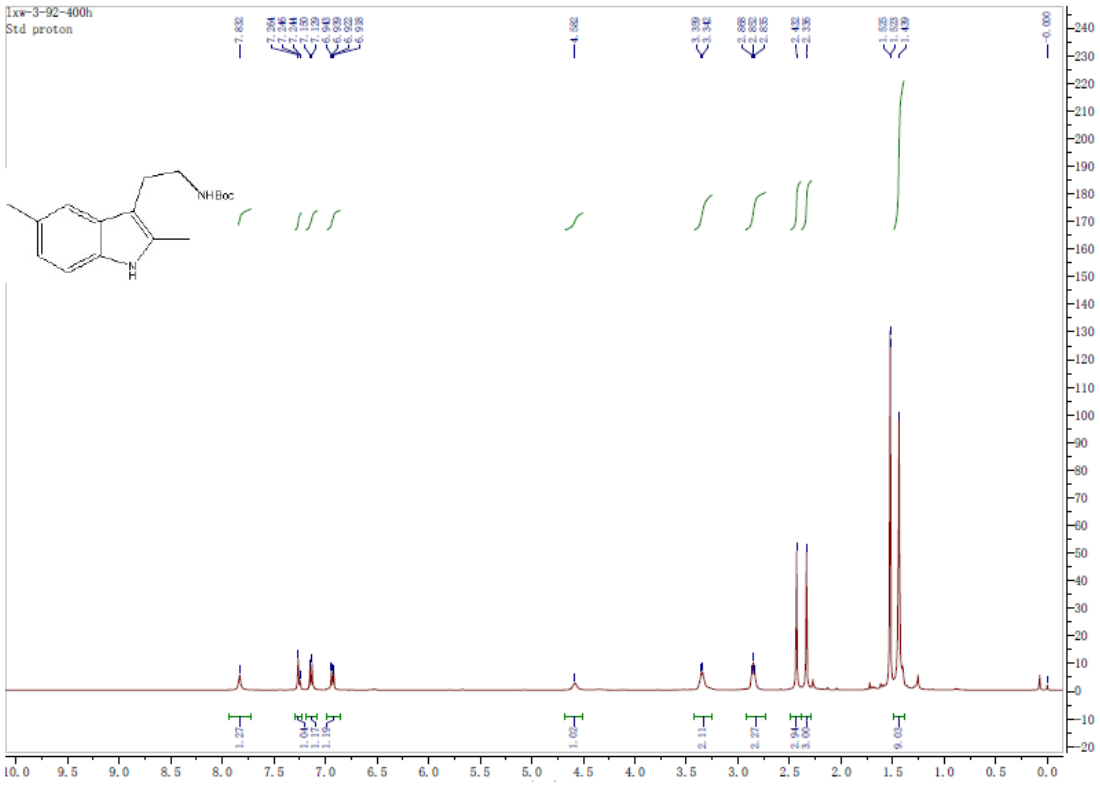


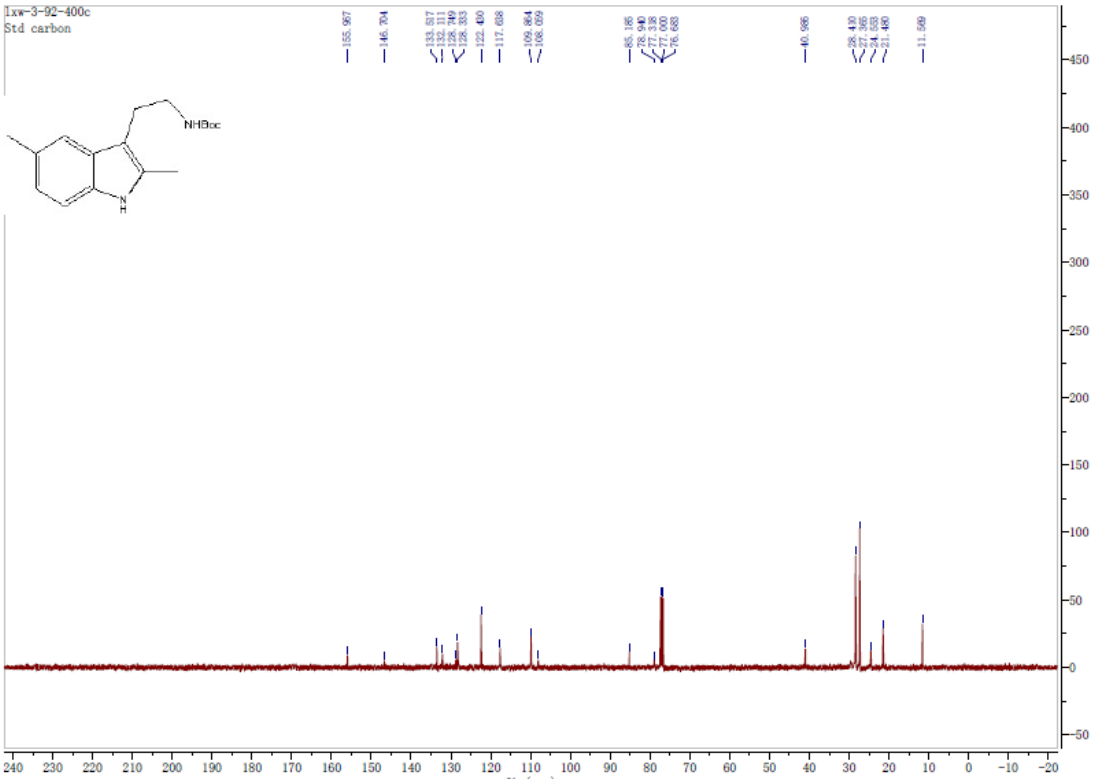


NMR Spectra of **1e**

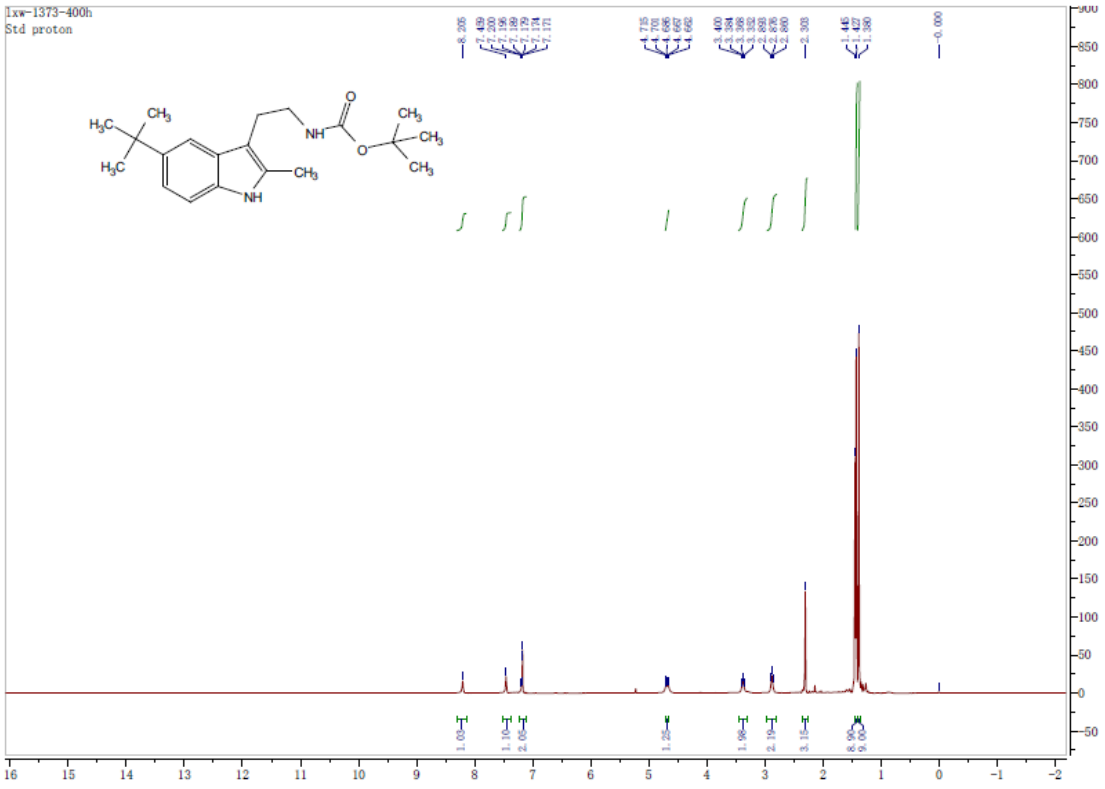


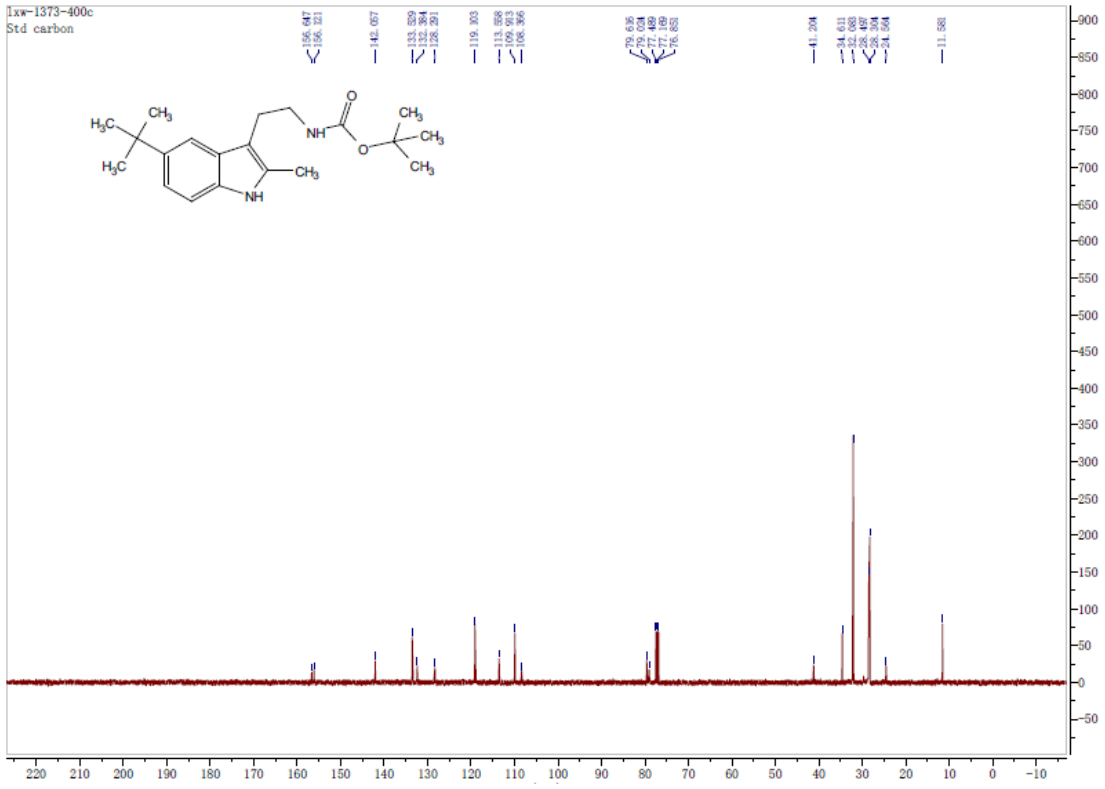
NMR Spectra of **1f**



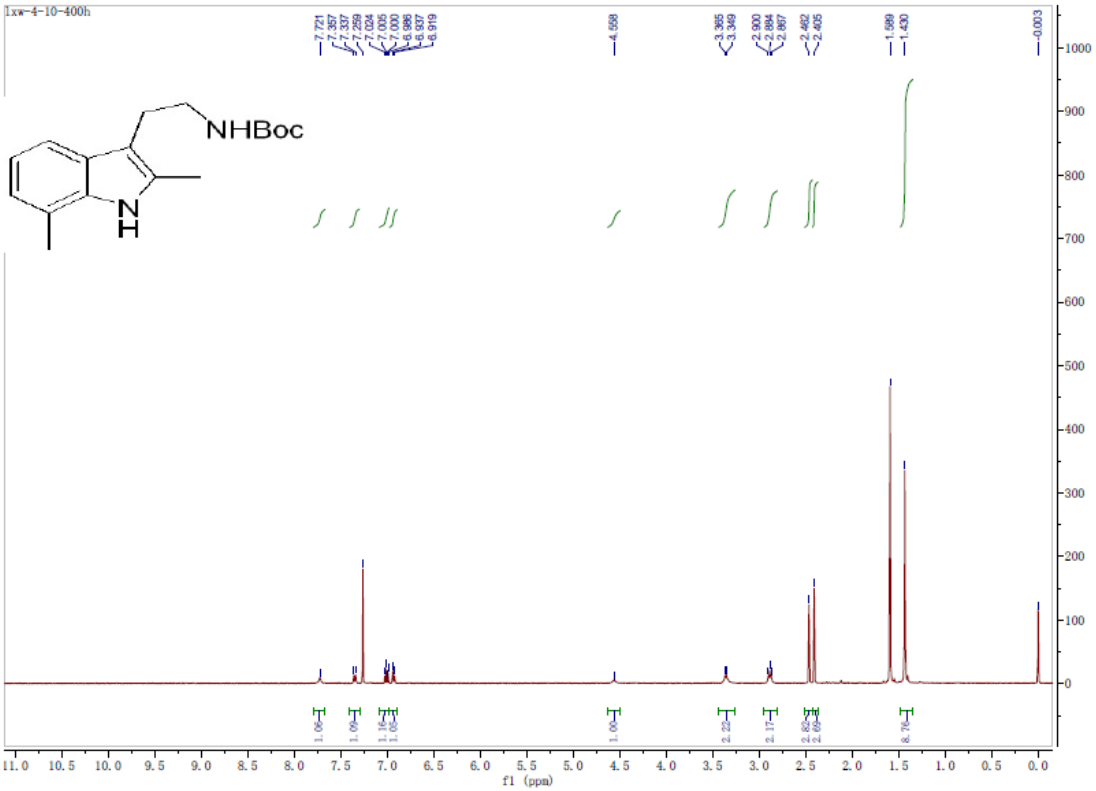


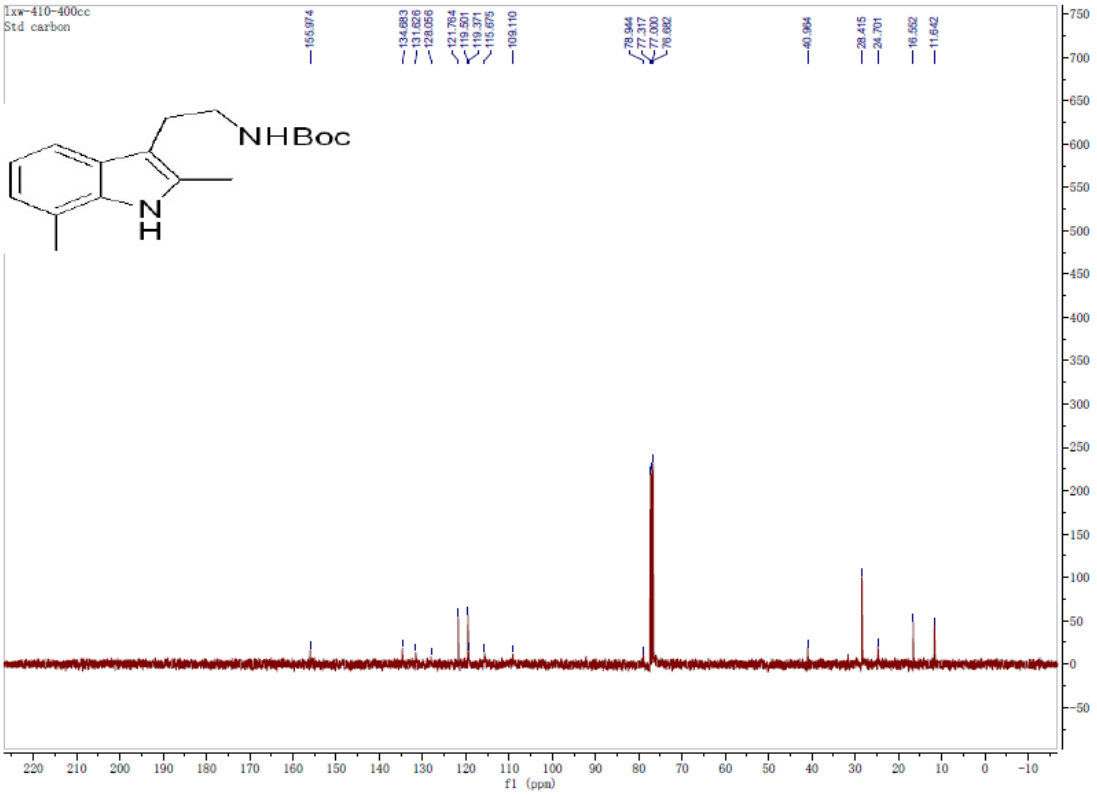
NMR Spectra of **1g**



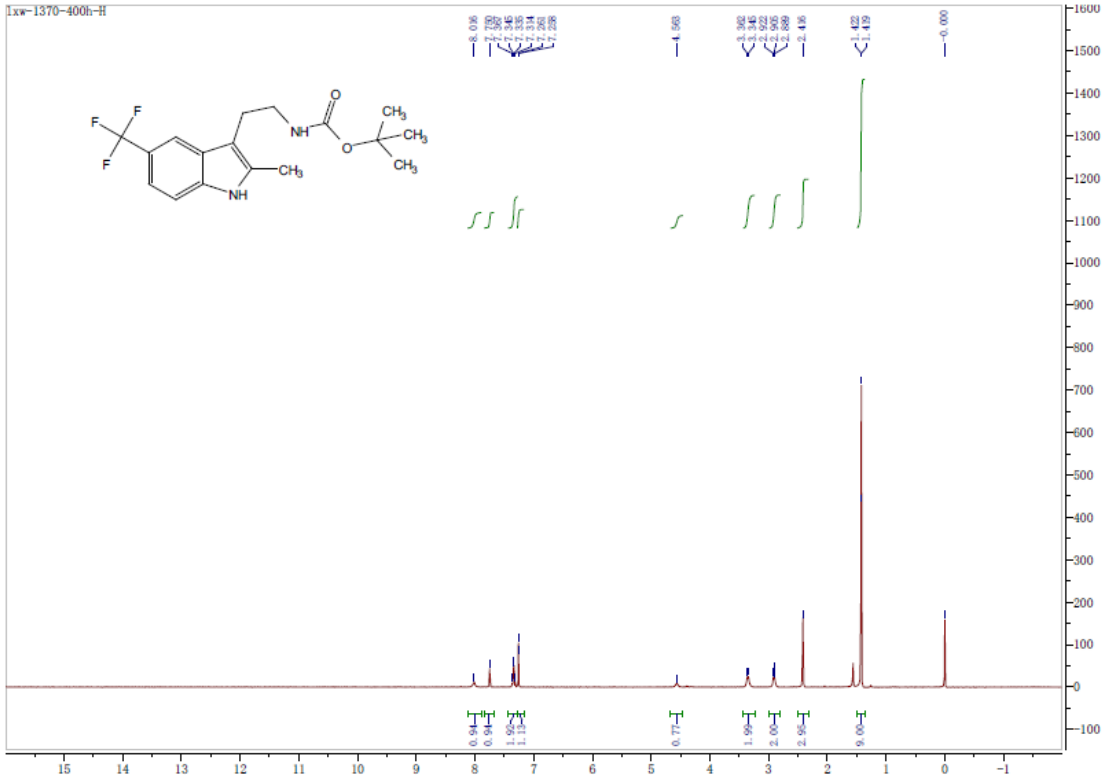


NMR Spectra of **1h**





NMR Spectra of **1i**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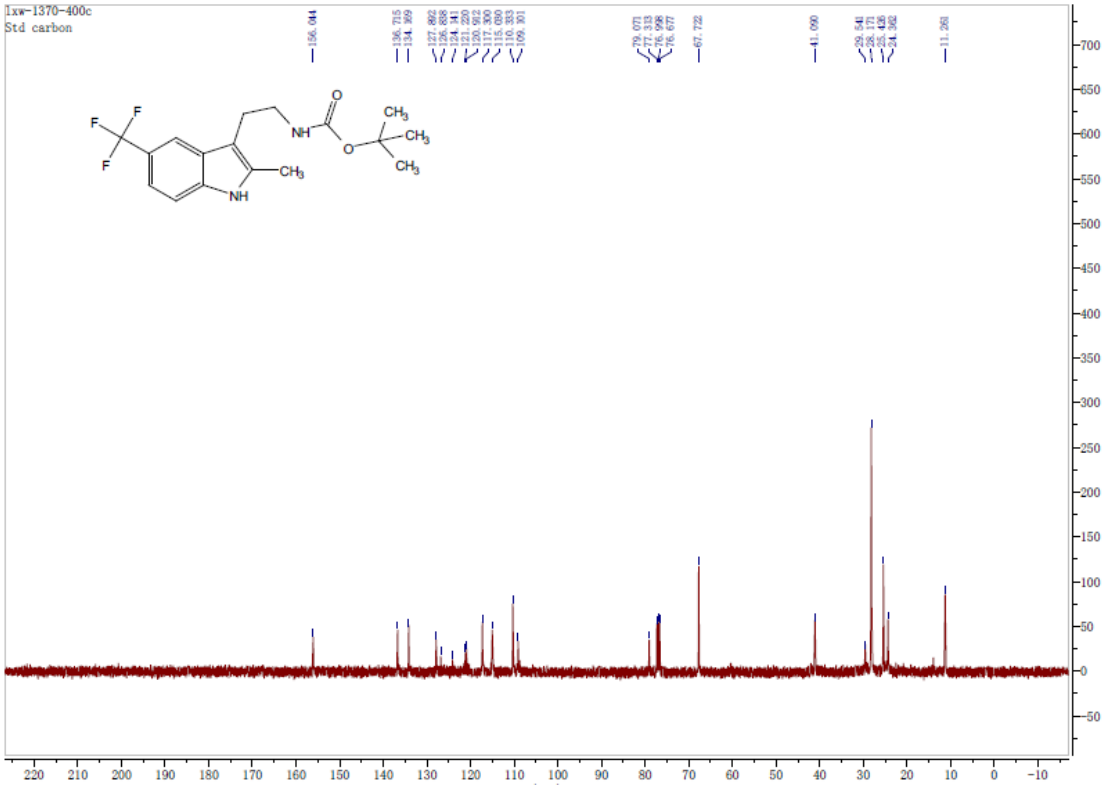
F
F
F
NH
O
O
CH3
CH3
CH3
CH3
NH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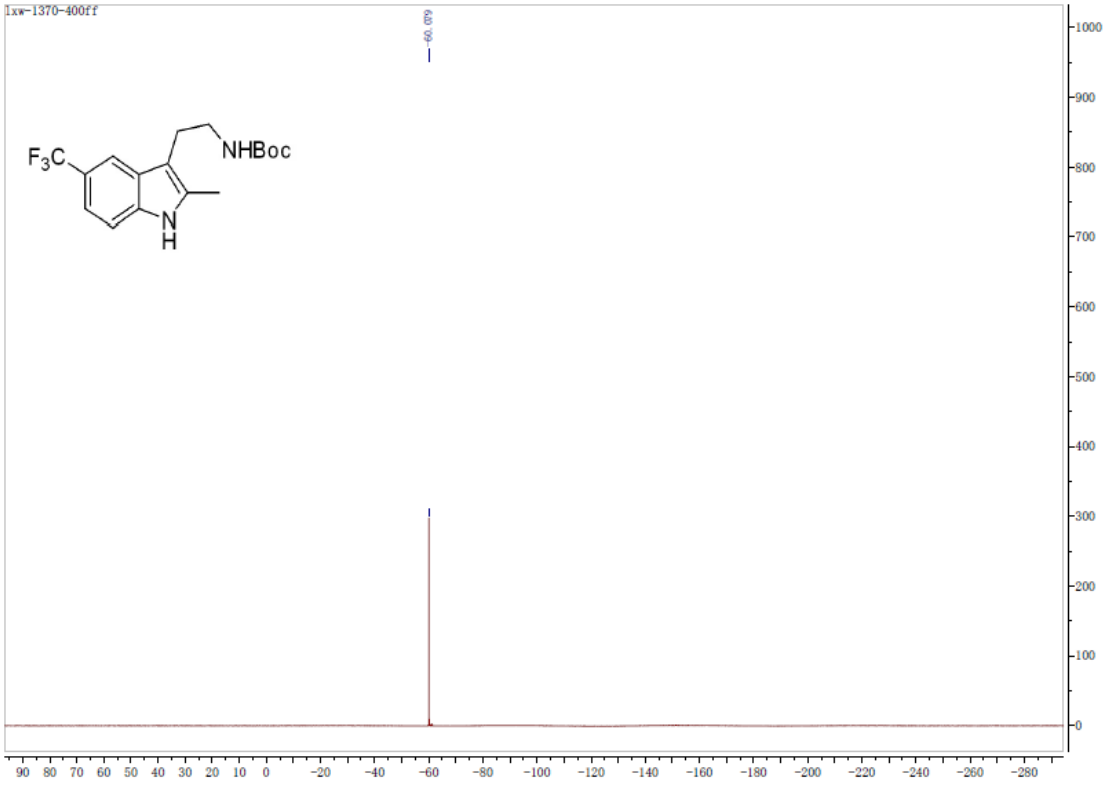
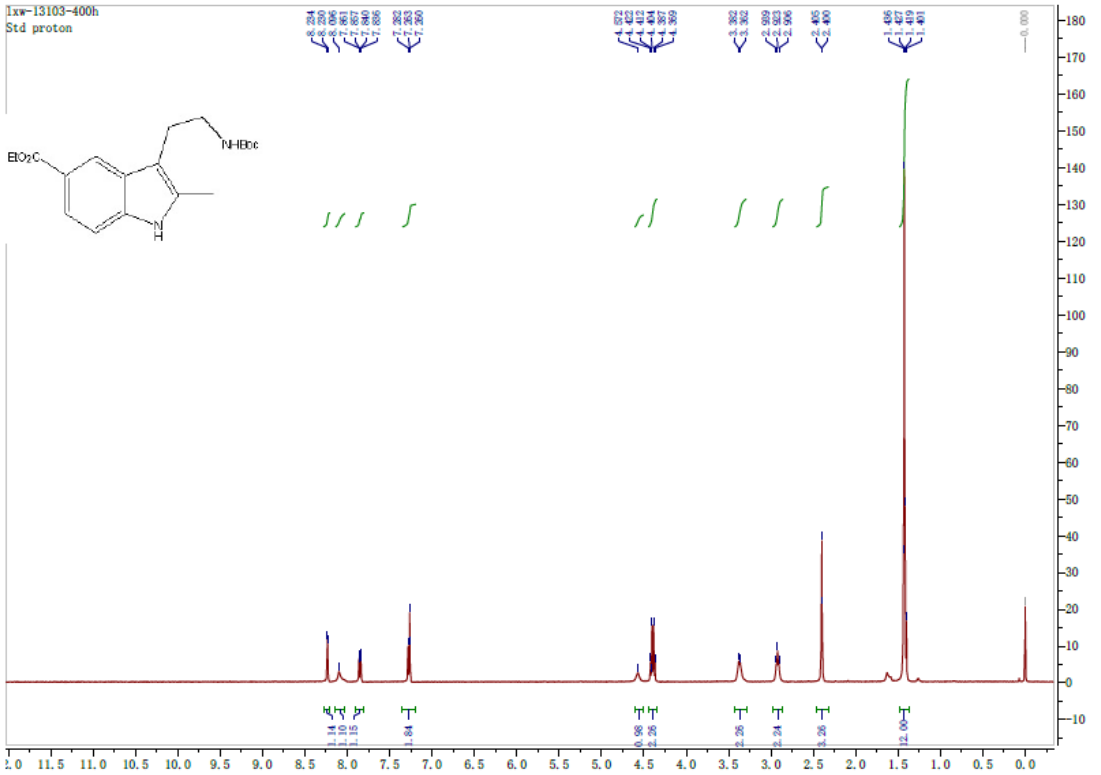
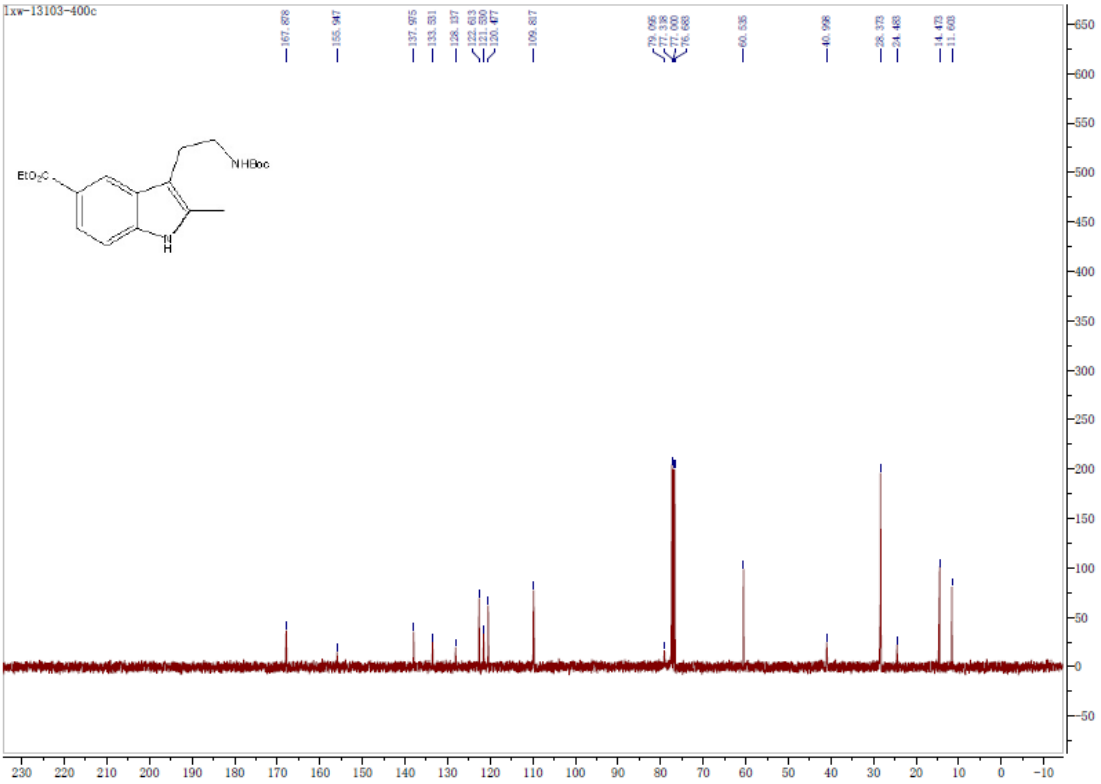
Std carbon
F
F
F
NH
O
O
CH3
CH3
CH3
CH3
NH

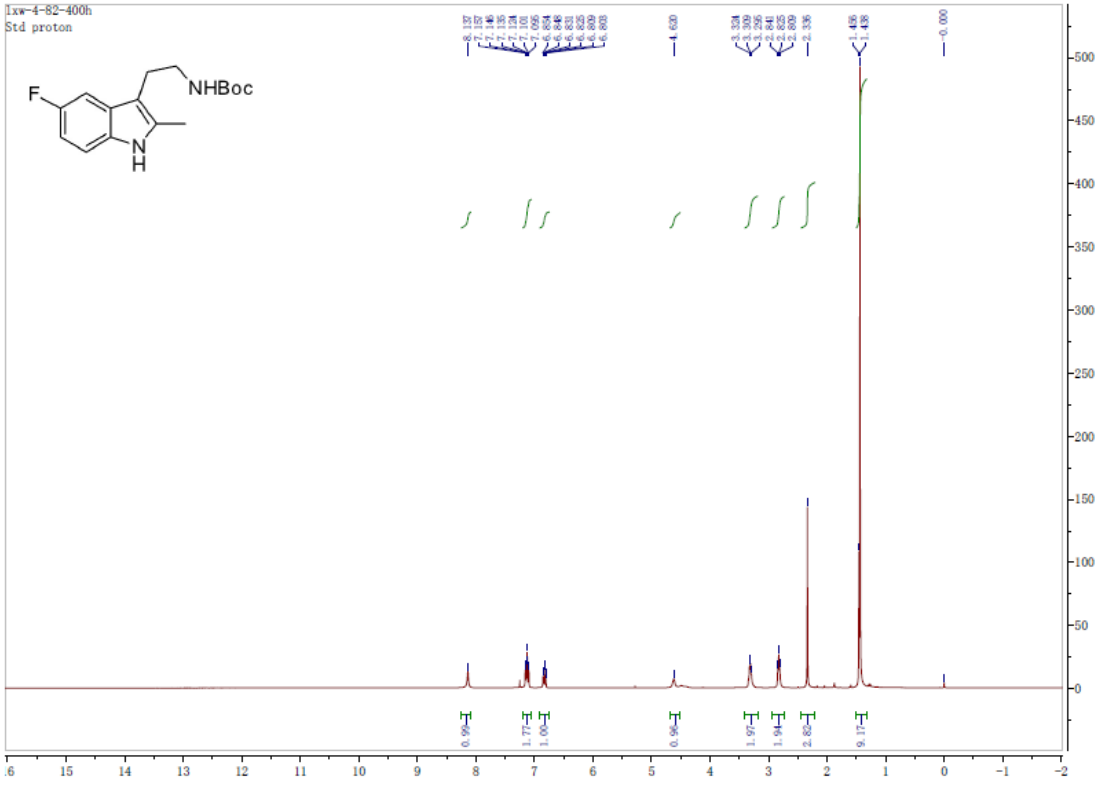


NMR Spectra of **1j**





NMR Spectra of **1k**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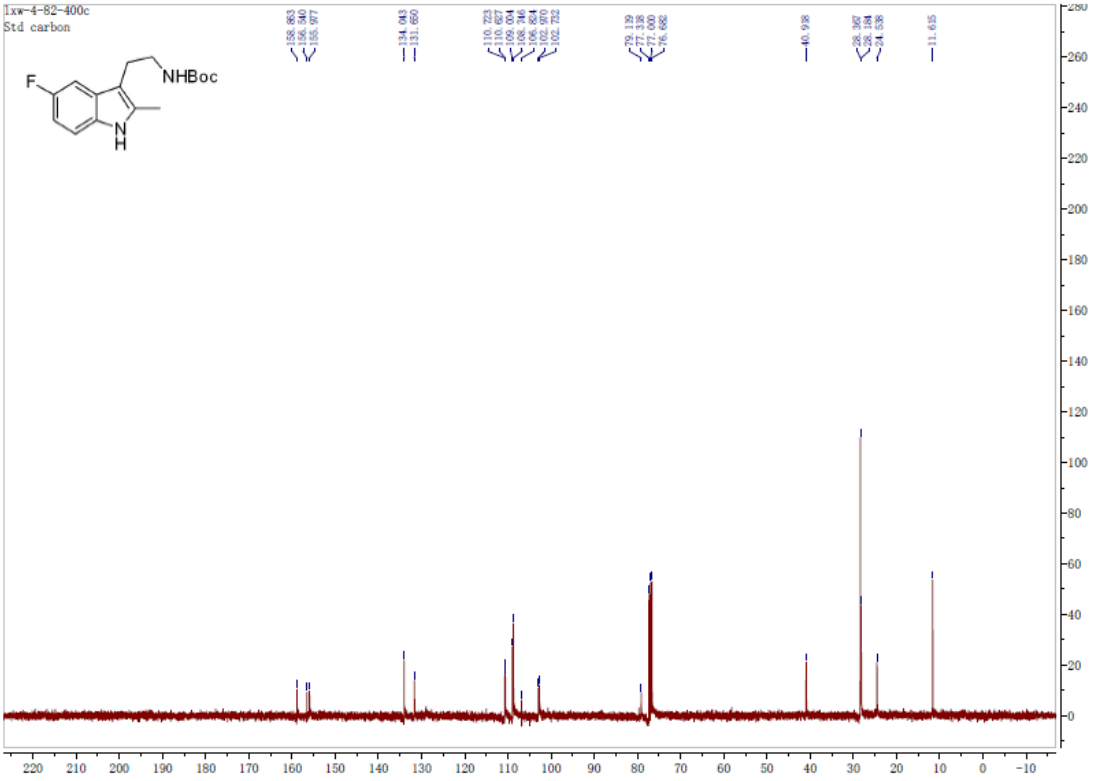
Std proton
F
NHBoc
N
H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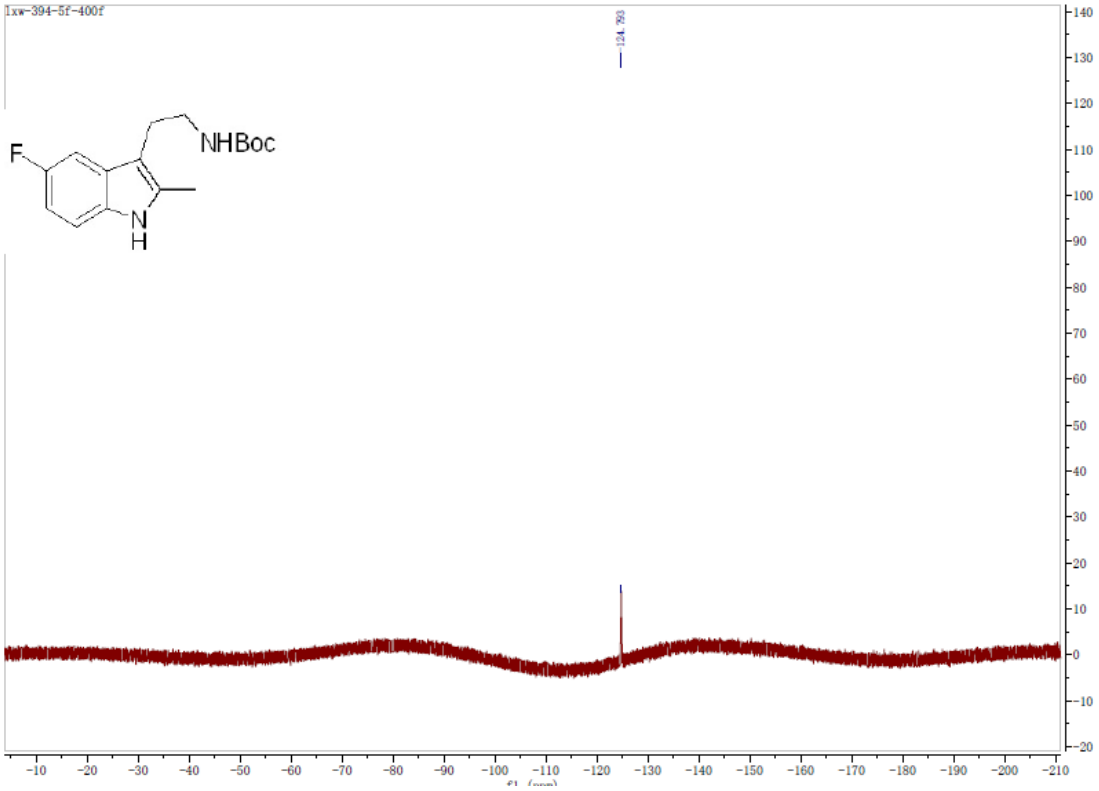
Std carbon
F
NHBoc
N
H



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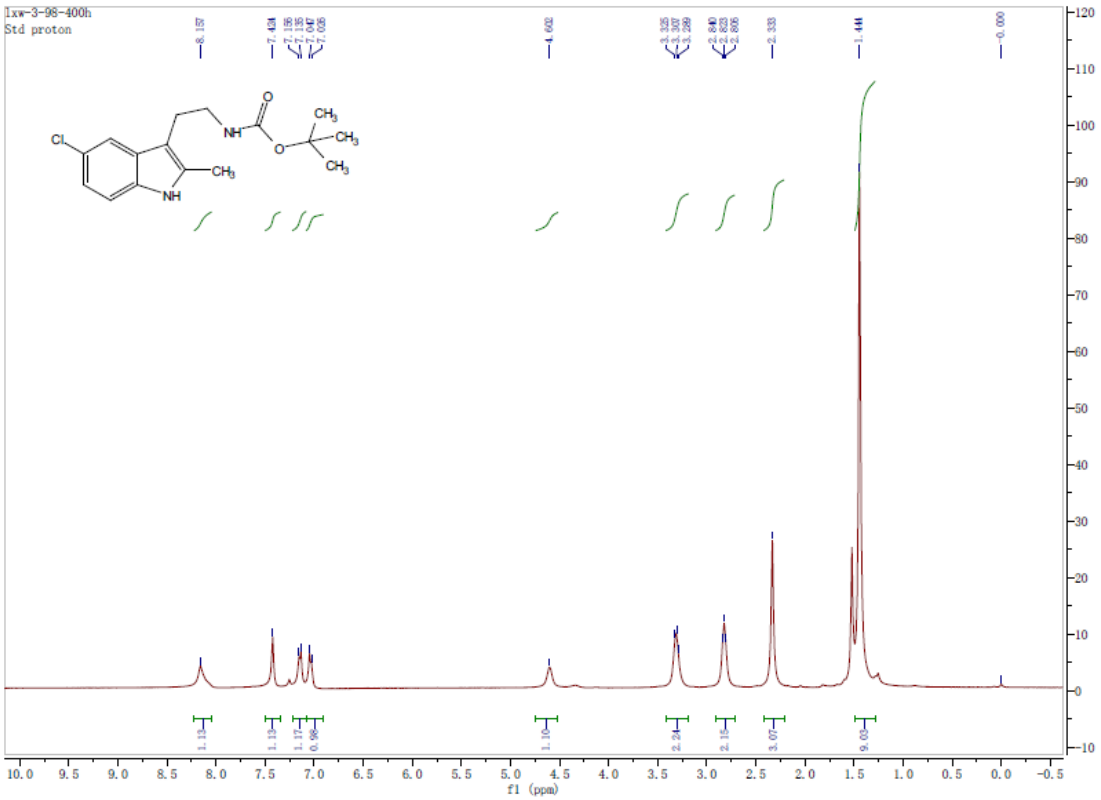
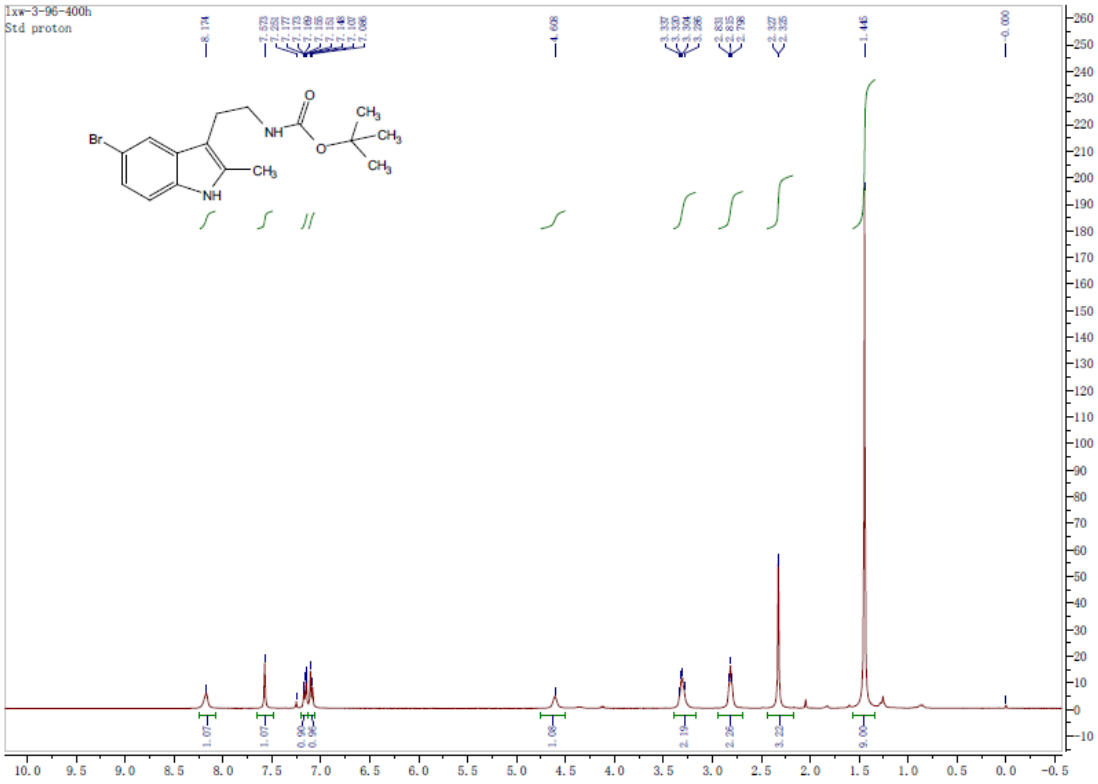
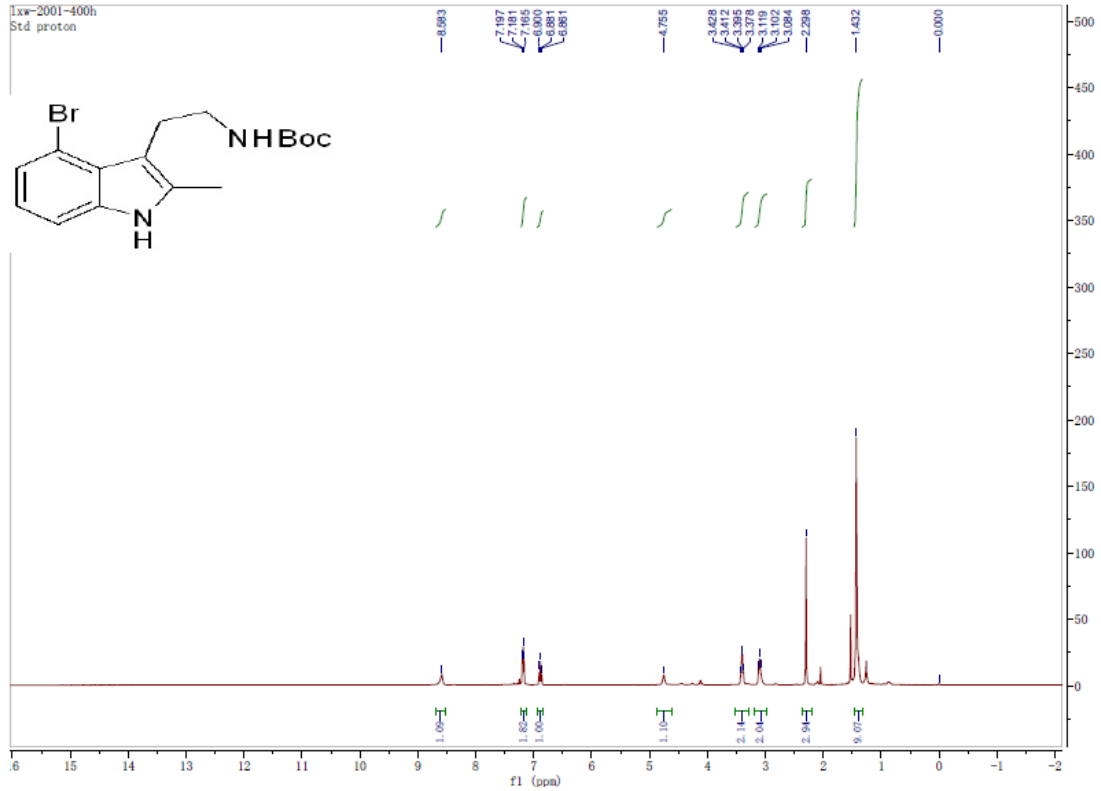
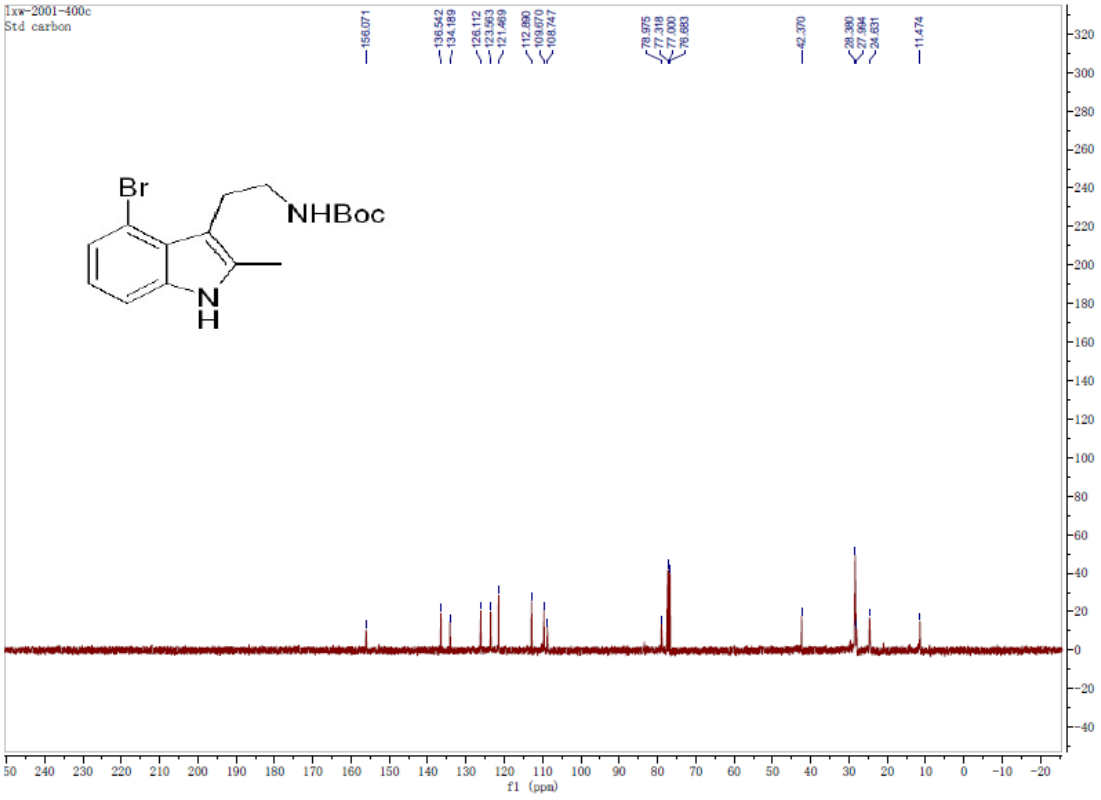


NMR Spectra of **1m**

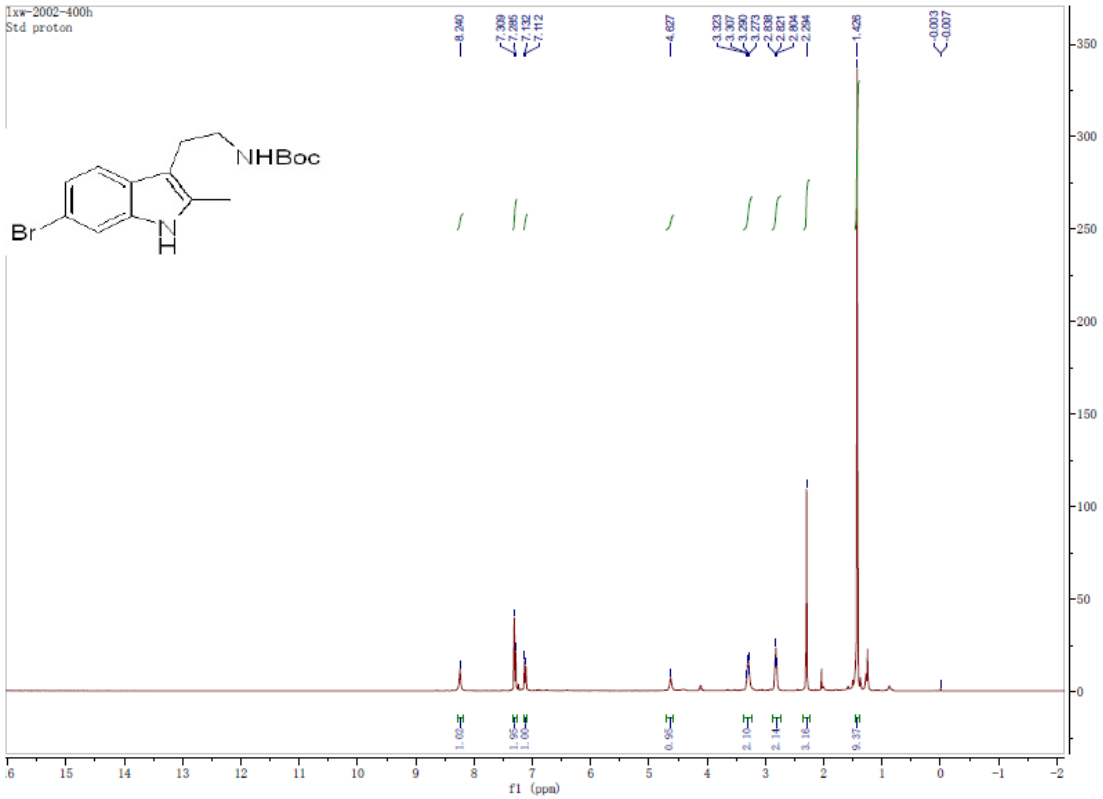


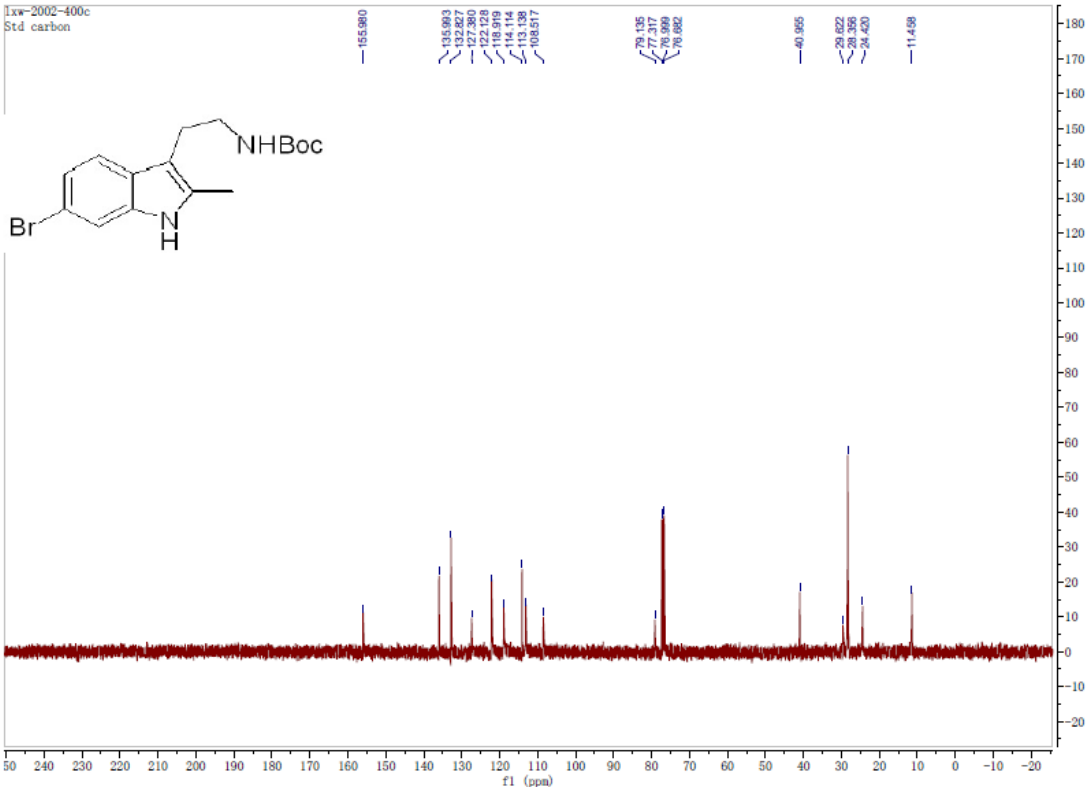
NMR Spectra of **1n**



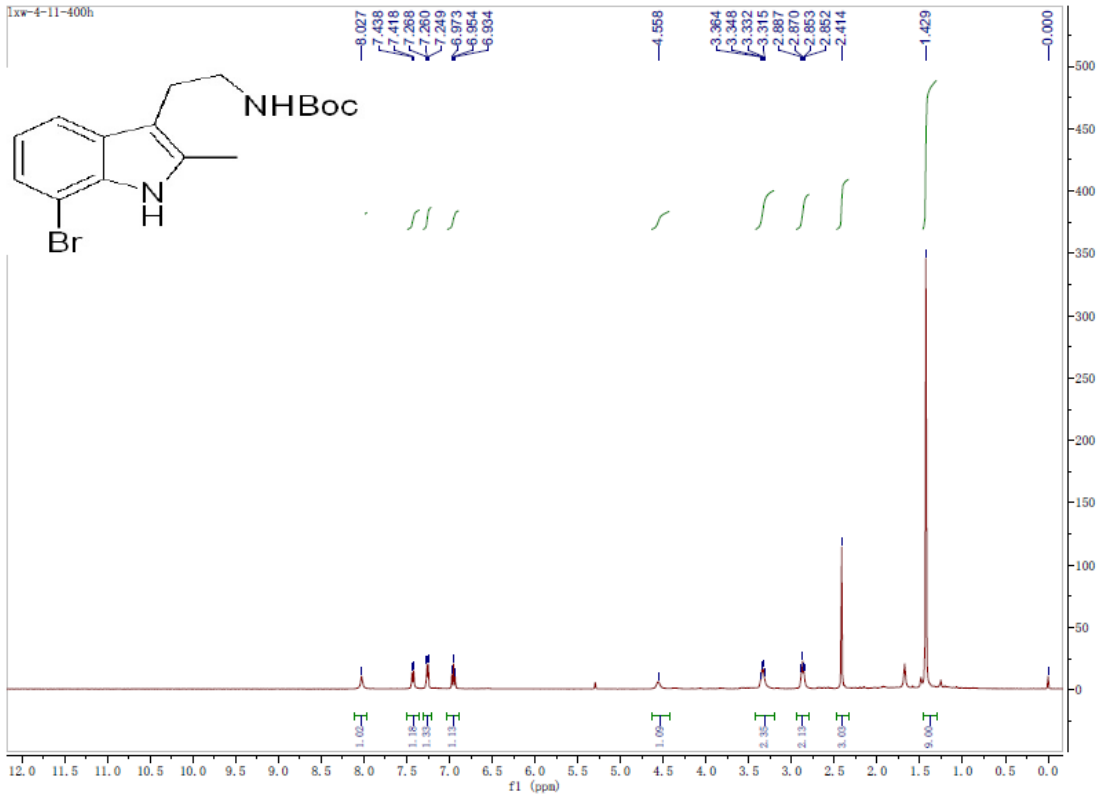


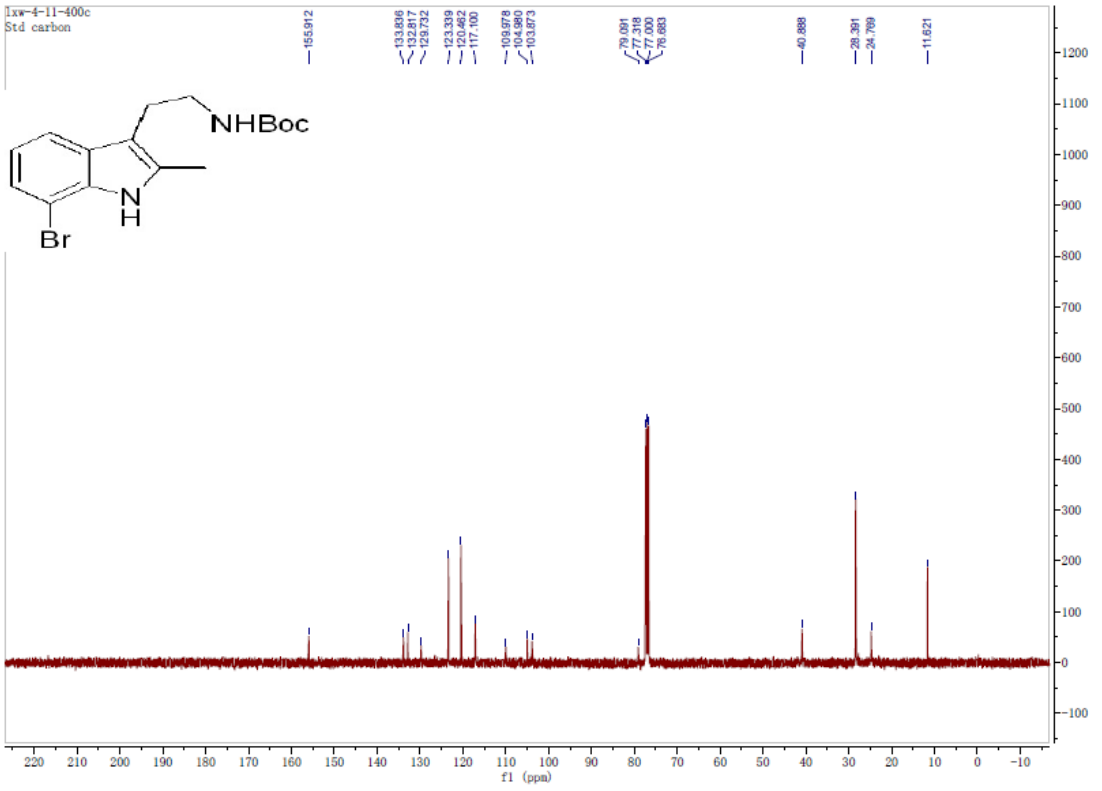
NMR Spectra of **1o**



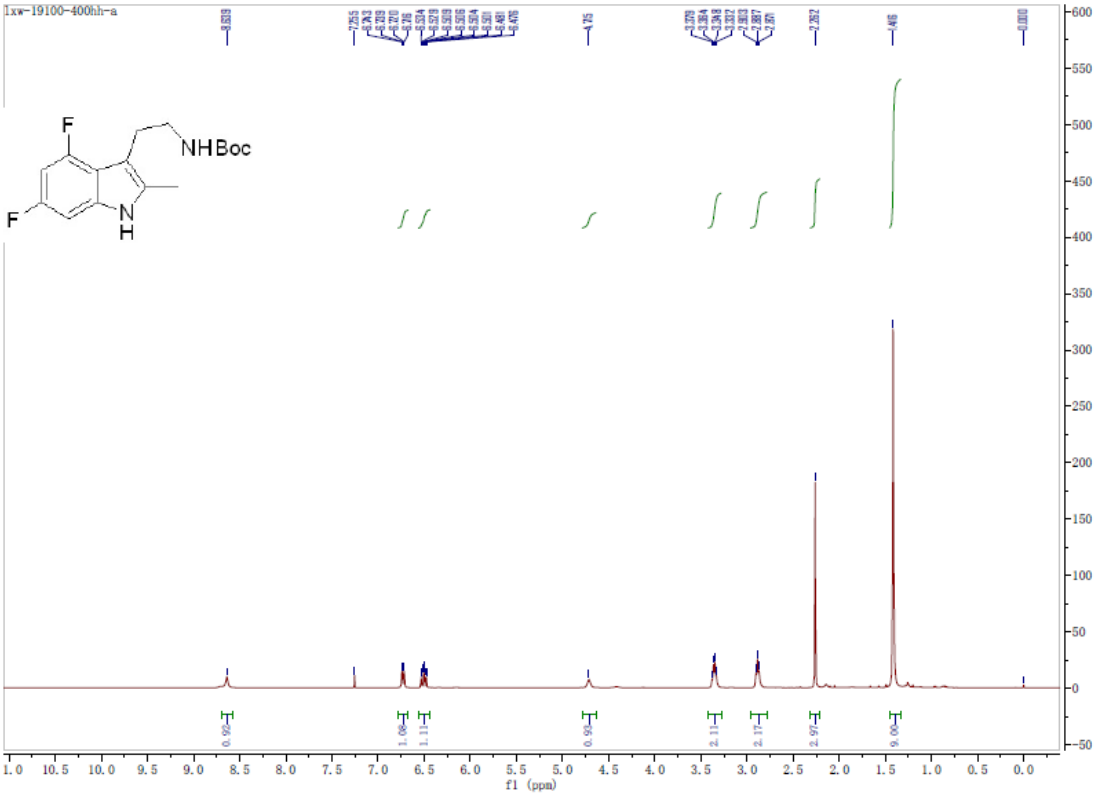


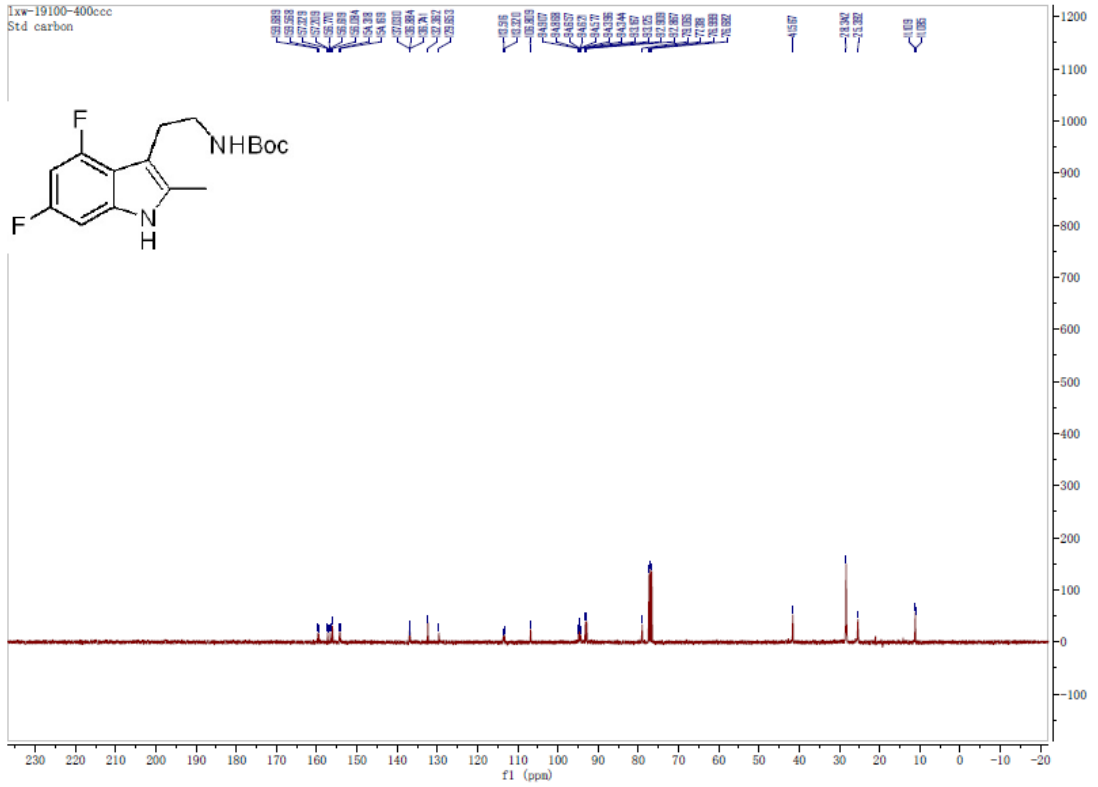
NMR Spectra of **1p**





NMR Spectra of **1q**


lxw-19100-400hh-a
F
NHBoc
F
N
H
f1 (ppm)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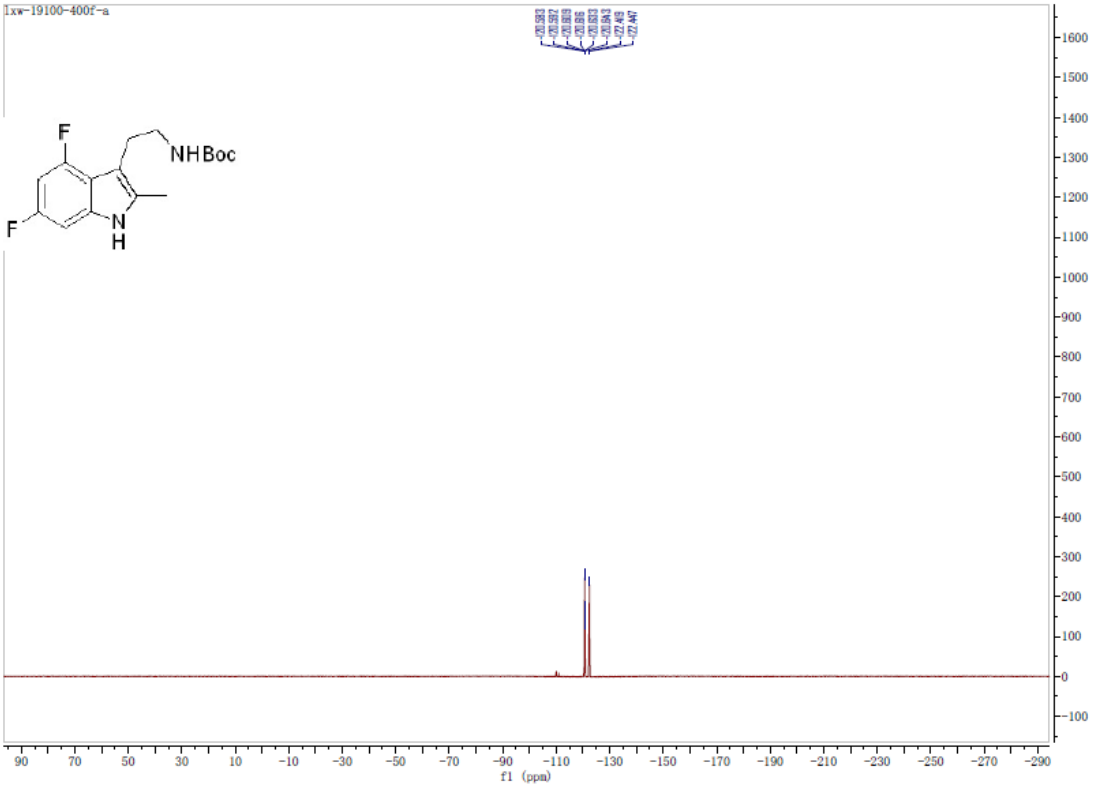
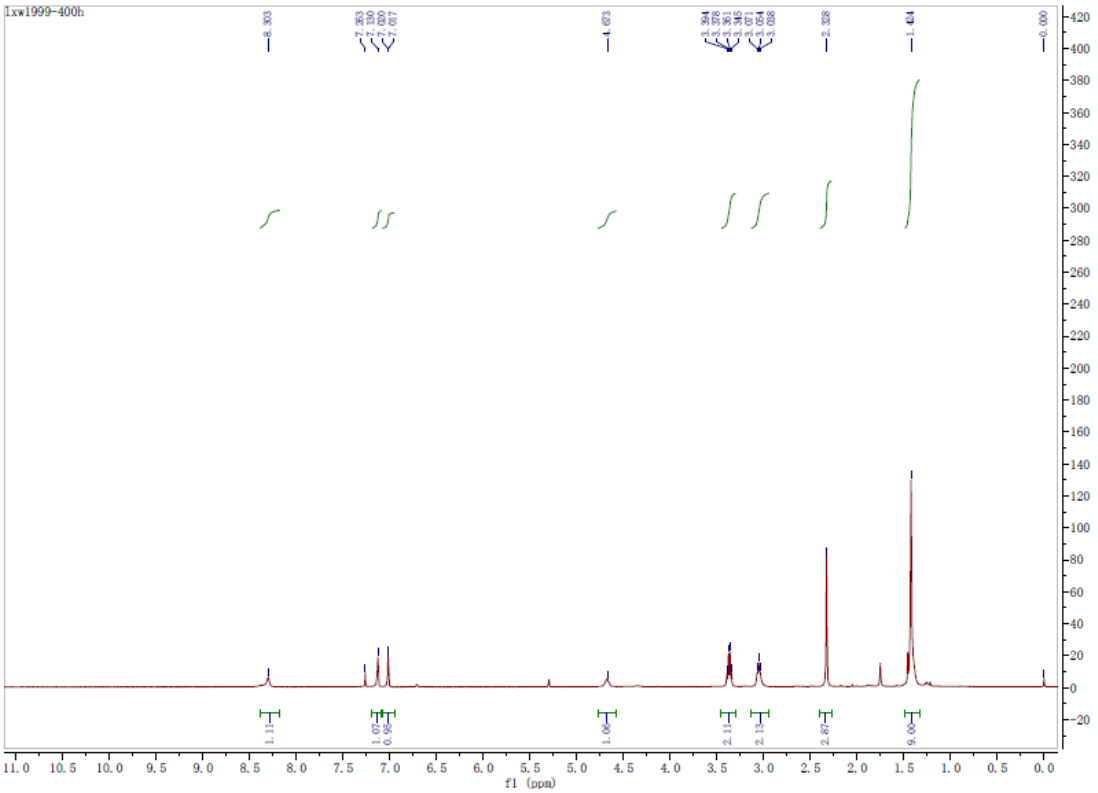
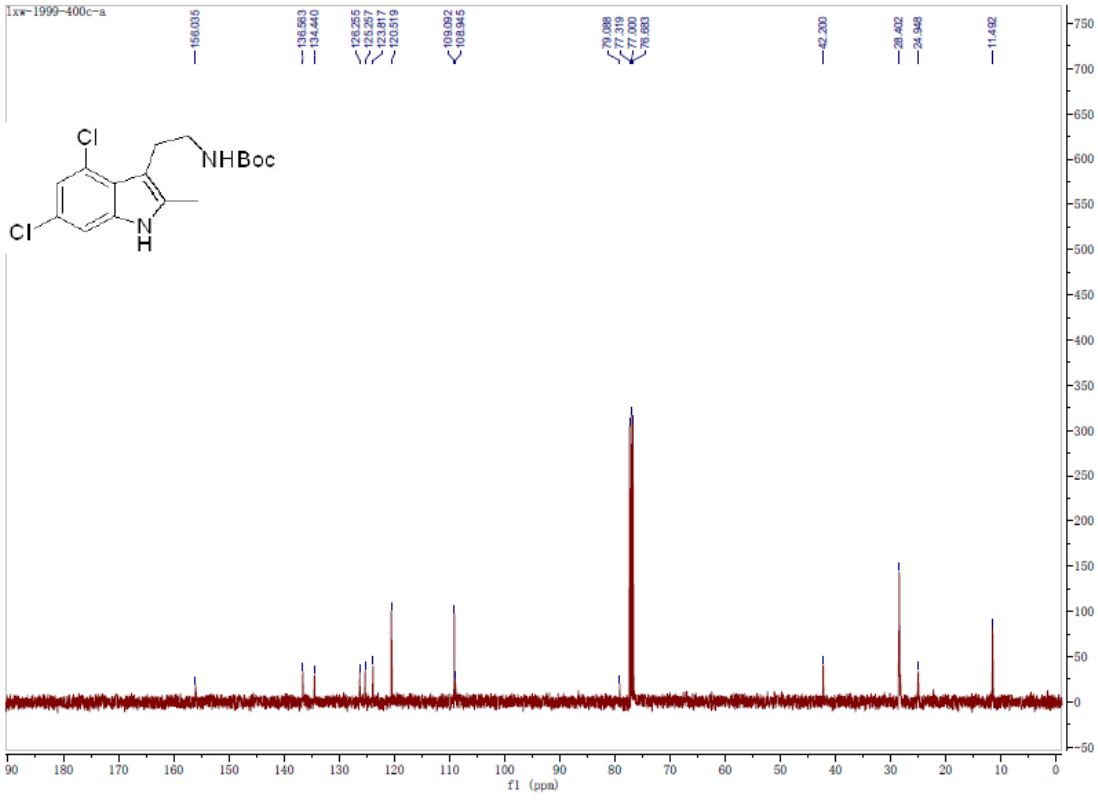
Std carbon
F
NHBoc
F
N
H
f1 (ppm)

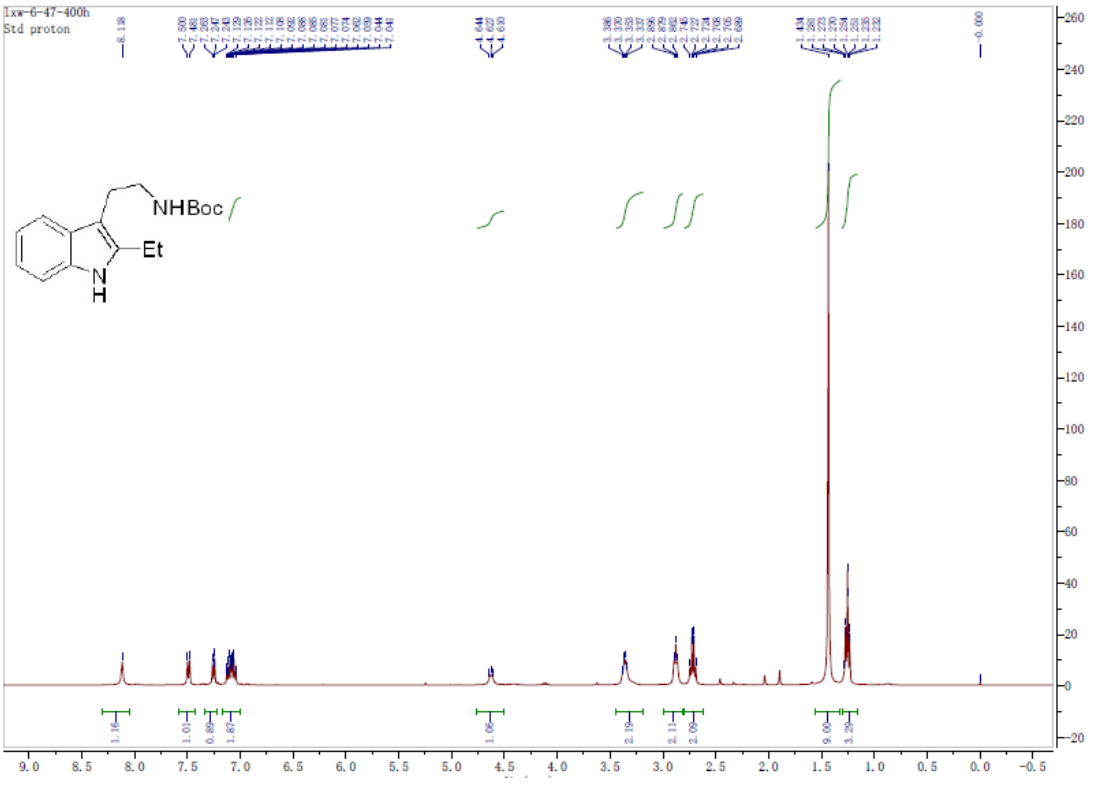


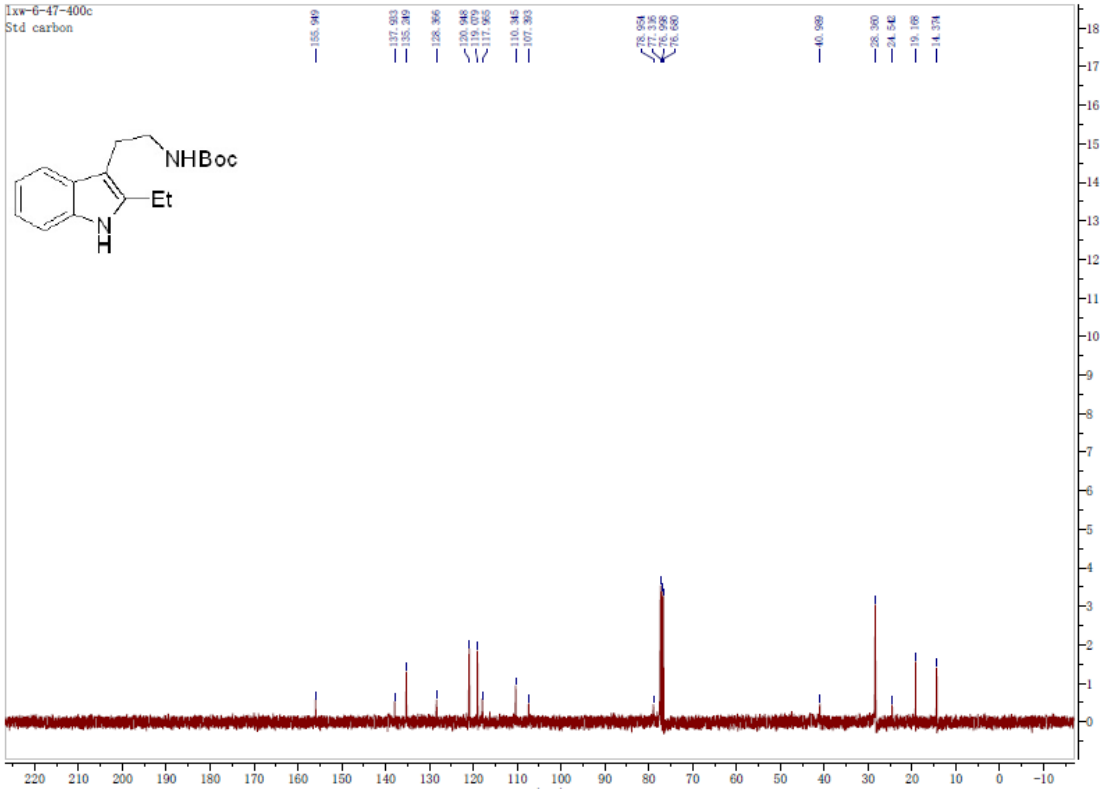
NMR Spectra of **1r**



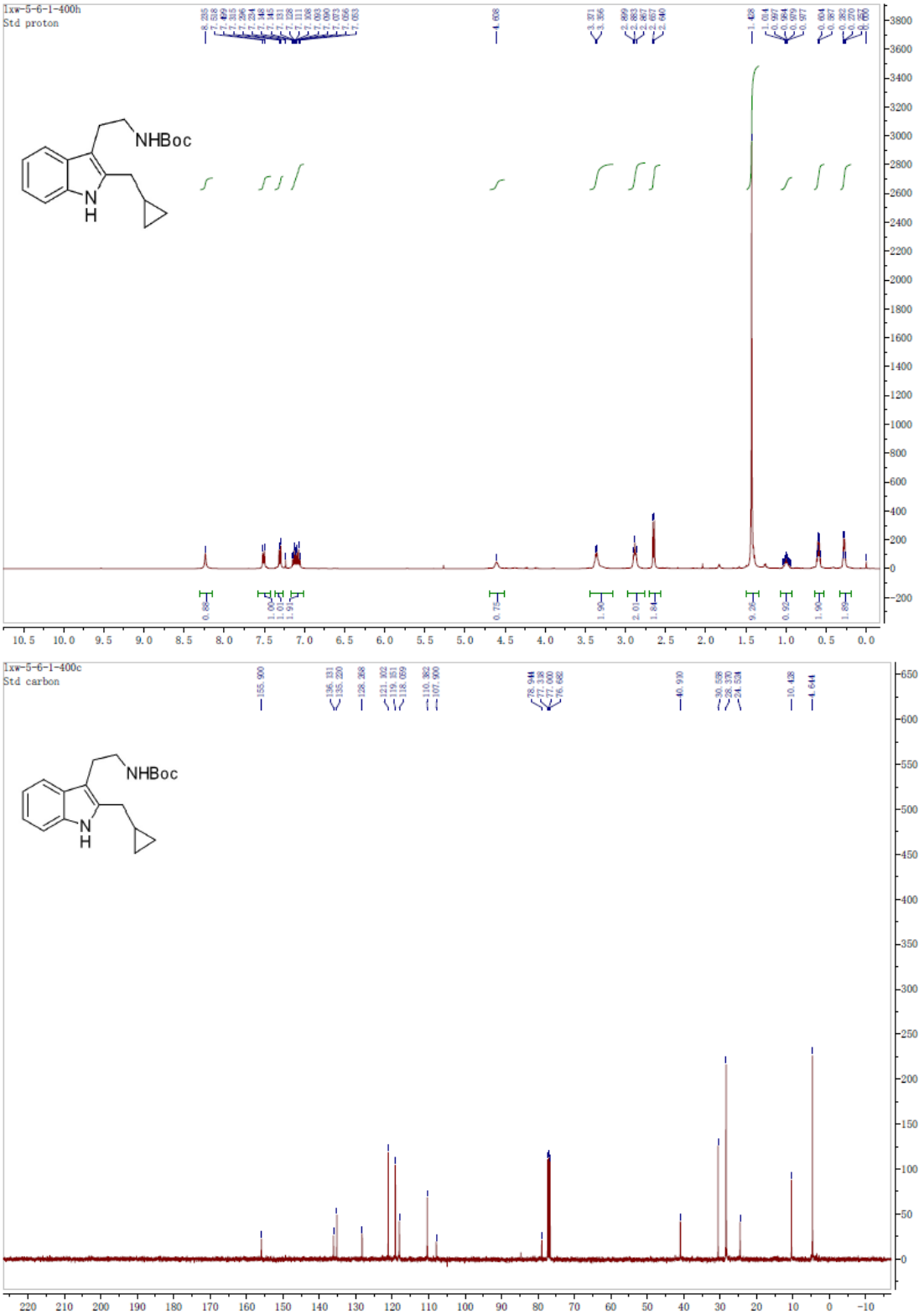


NMR Spectra of **1s**

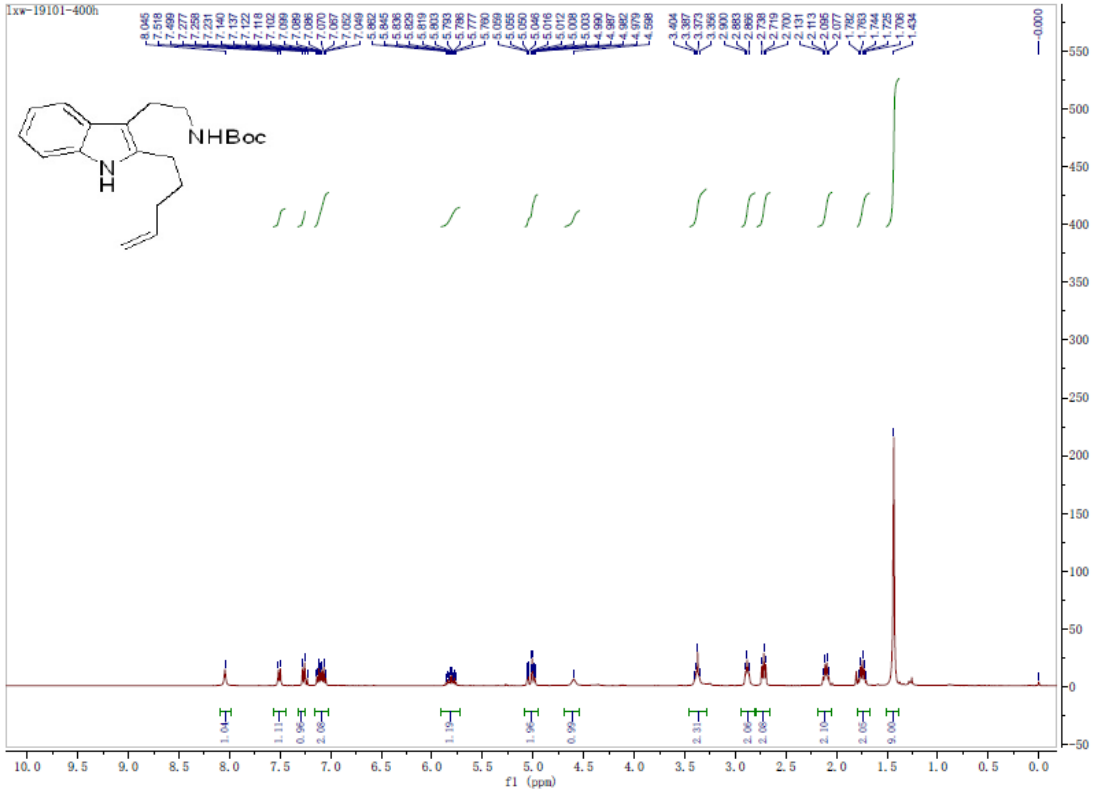


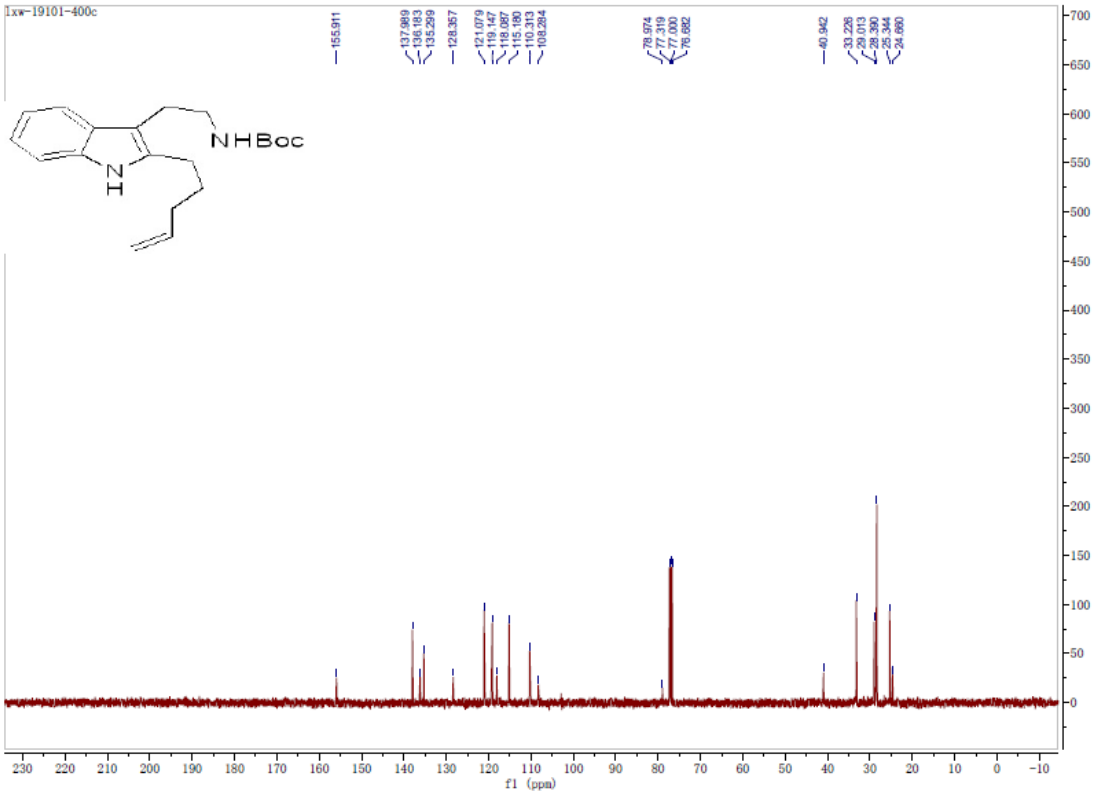


NMR Spectra of **1t**

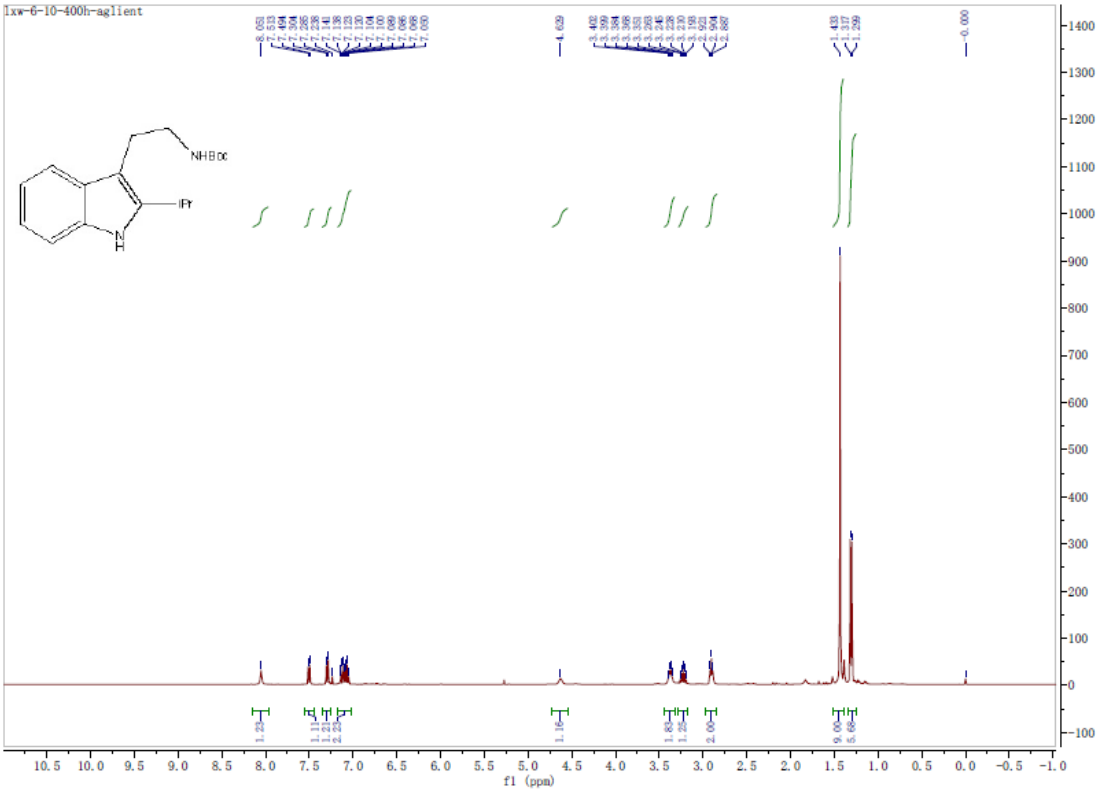


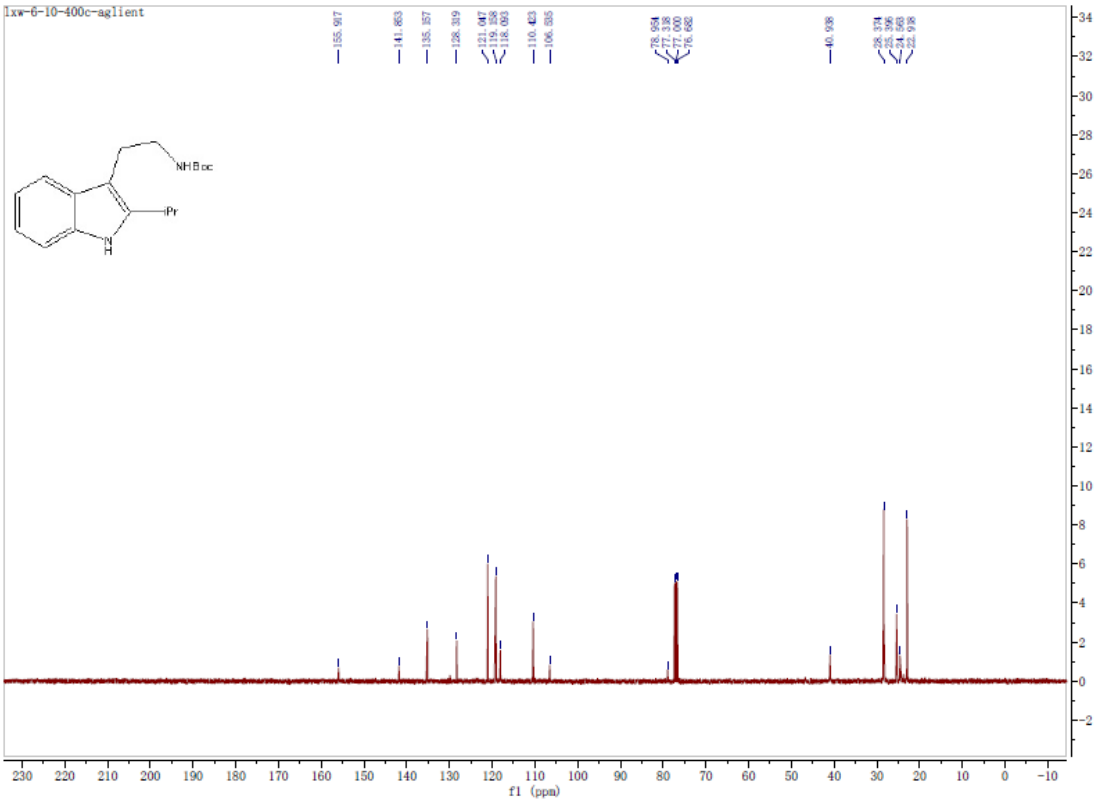
NMR Spectra of **1u**



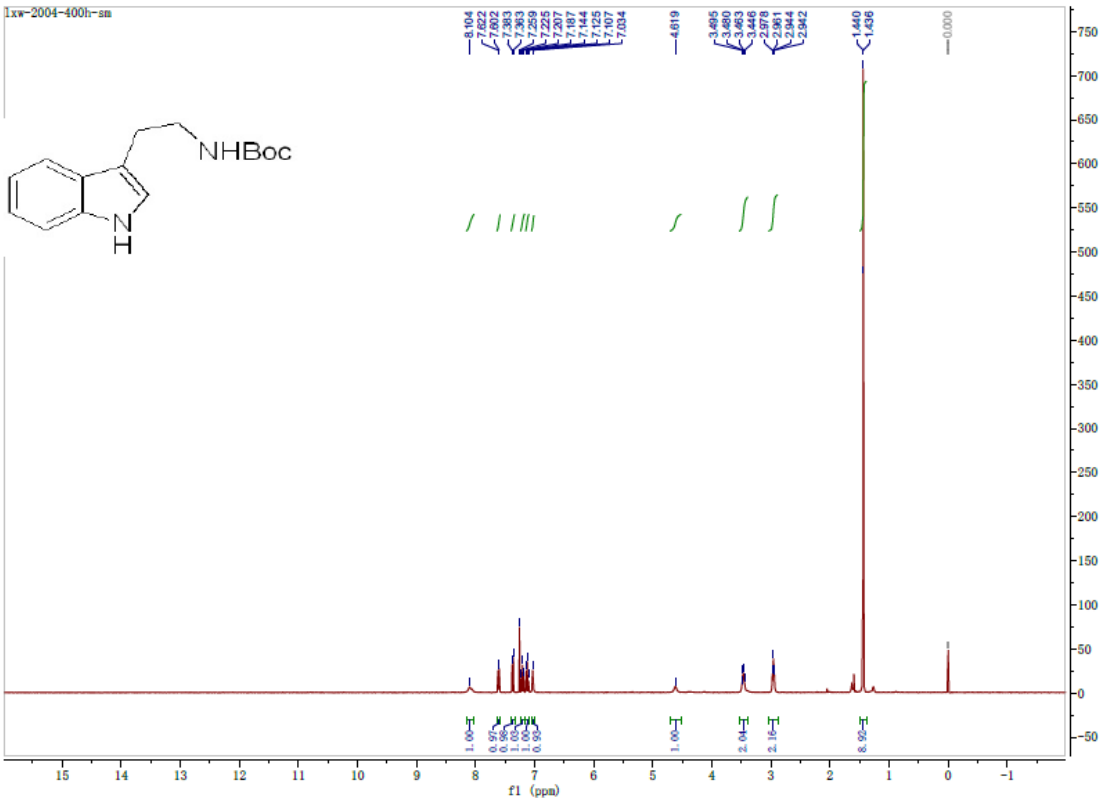


NMR Spectra of **1v**

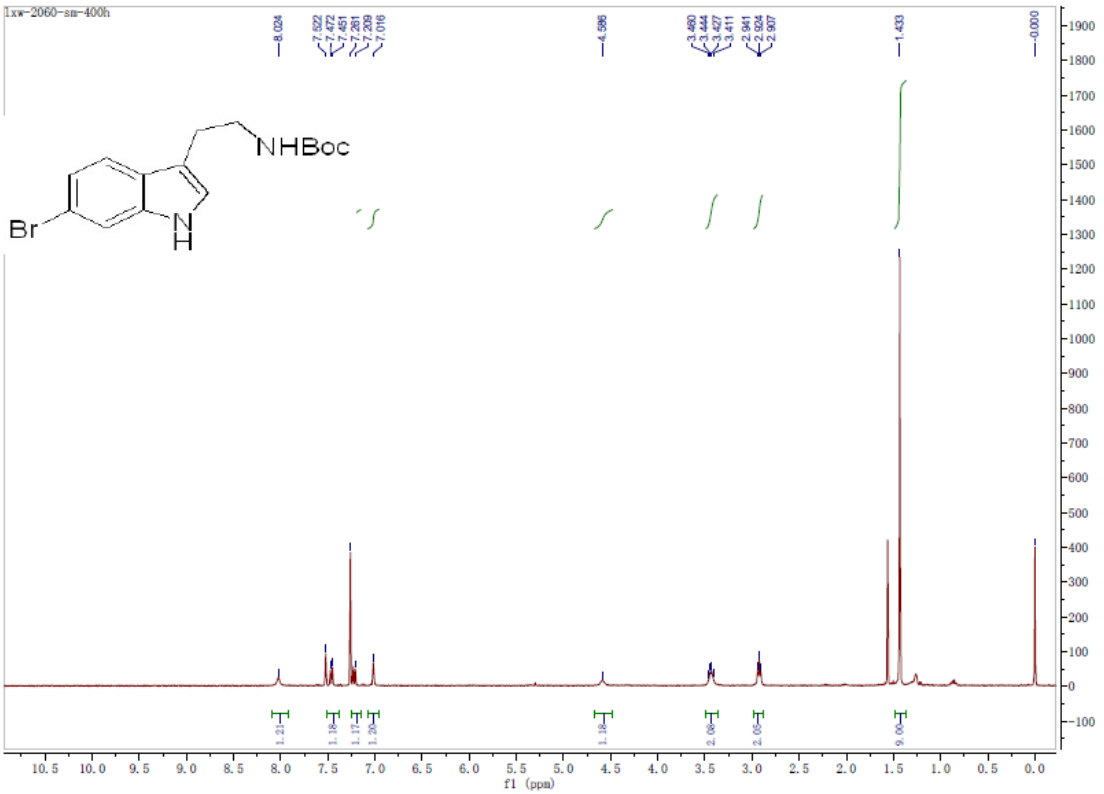




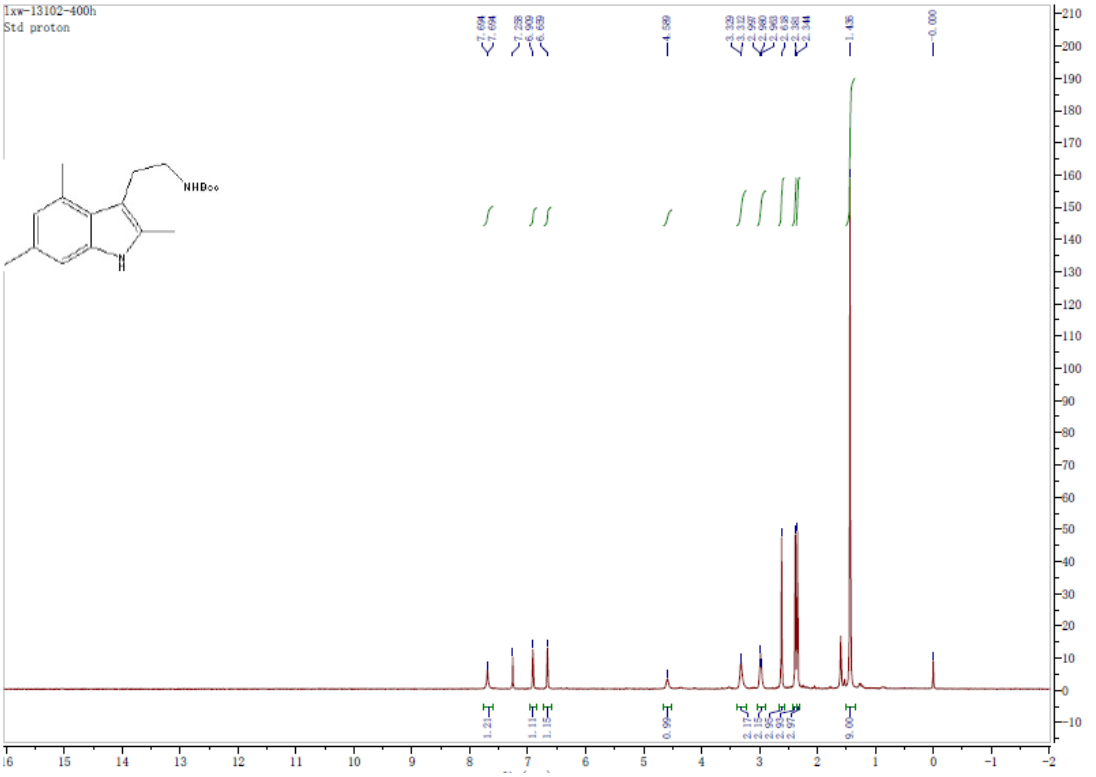
NMR Spectra of **1w**

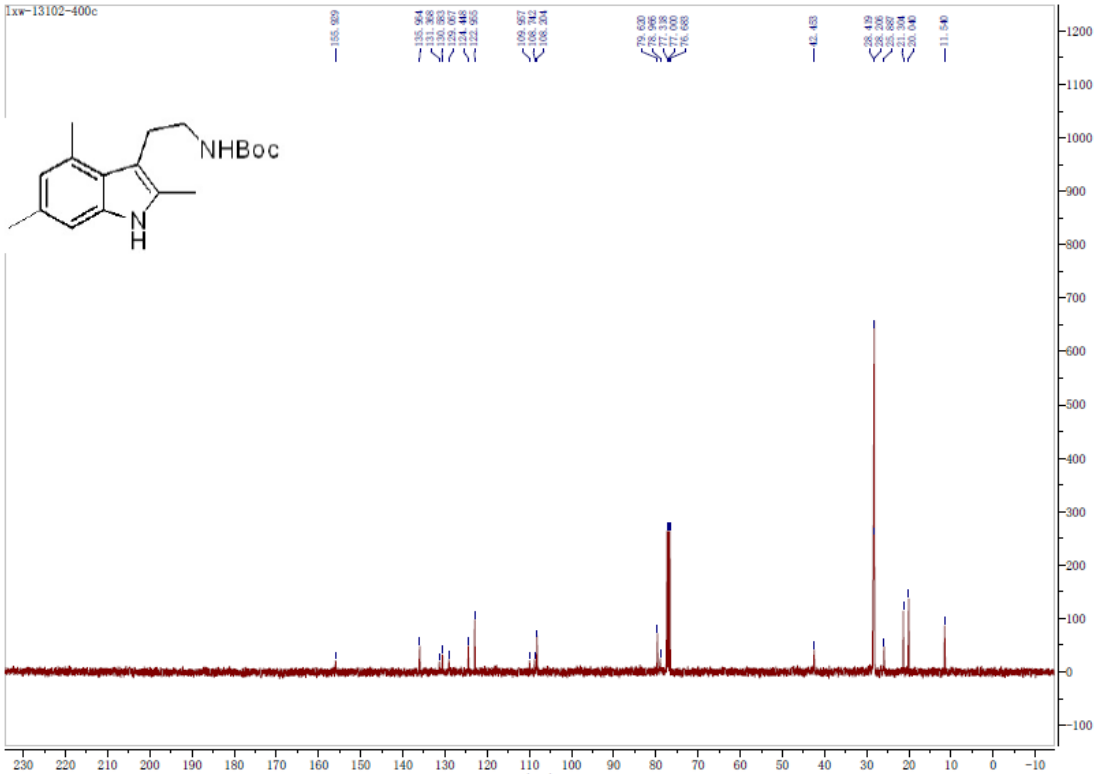


NMR Spectra of **1x**

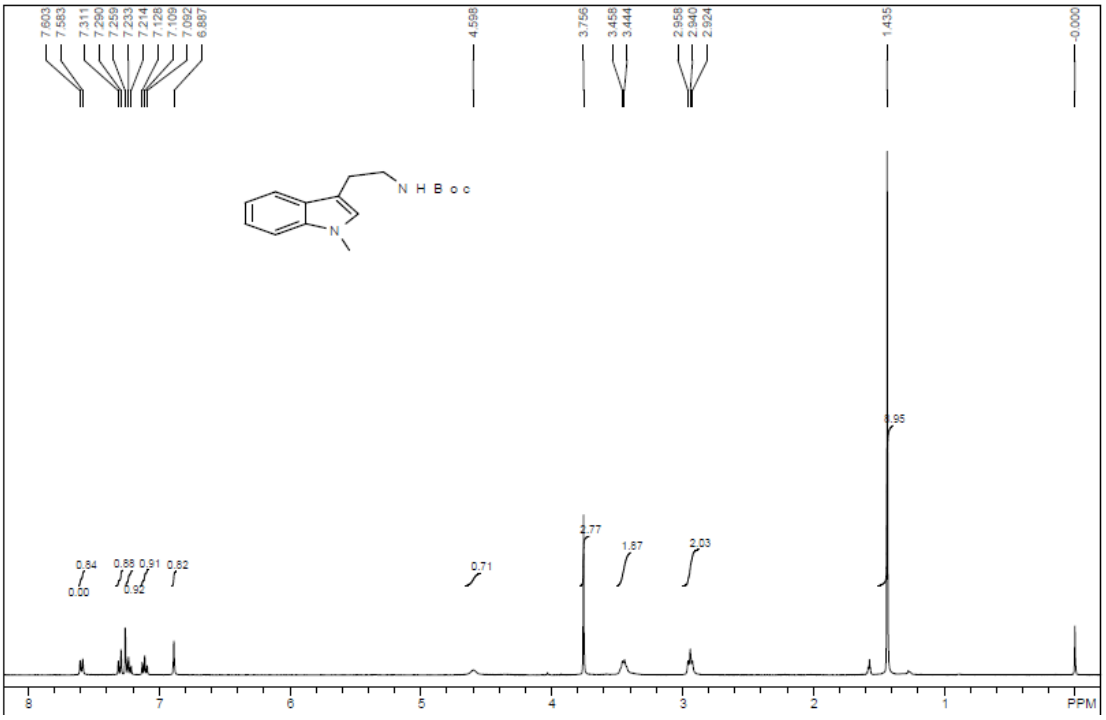


NMR Spectra of **1y**

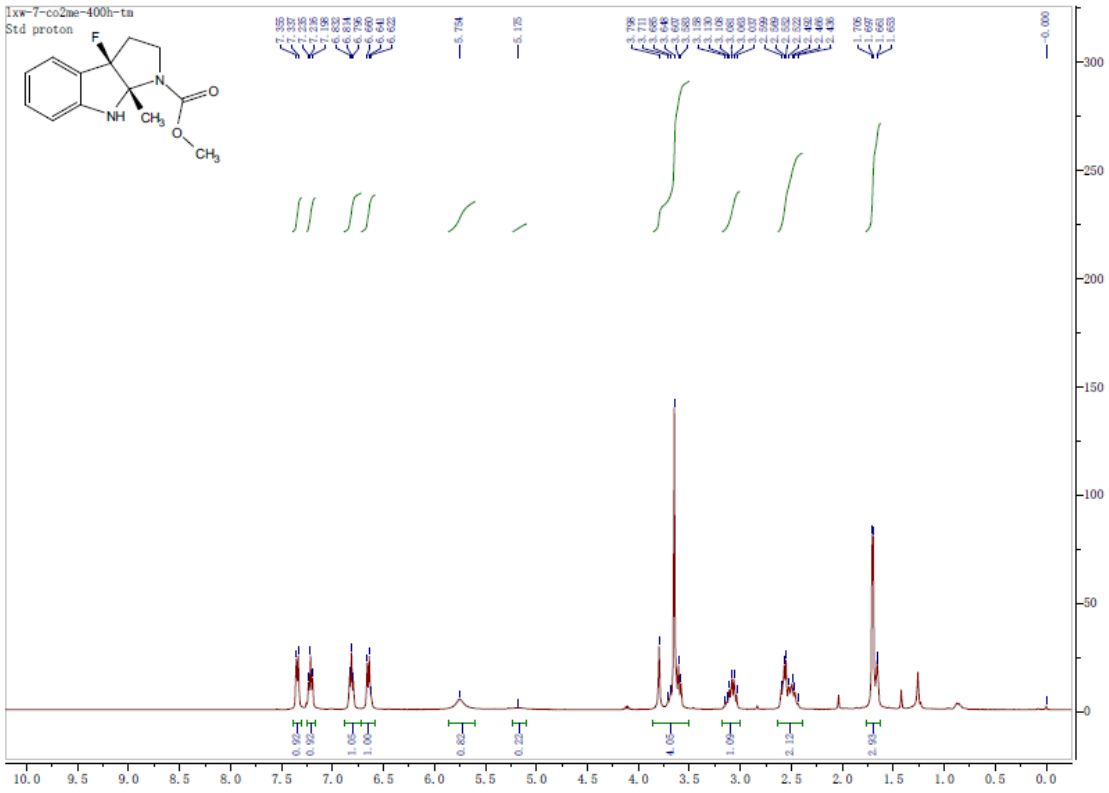


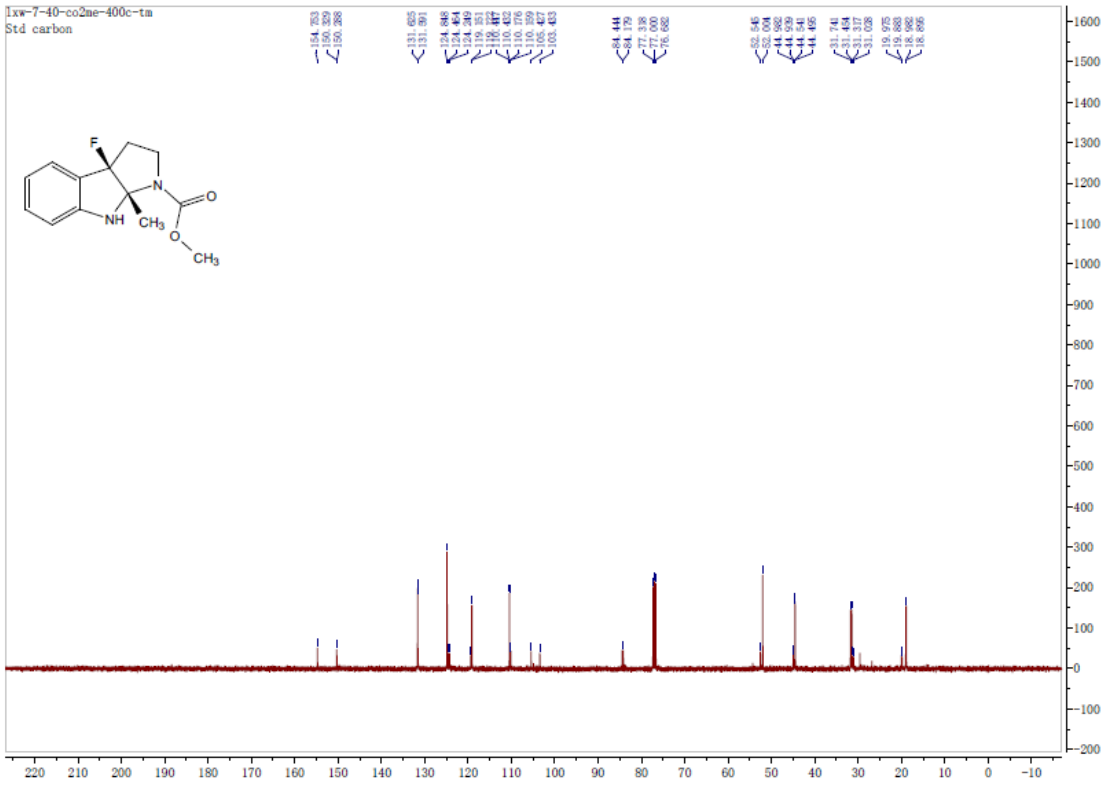


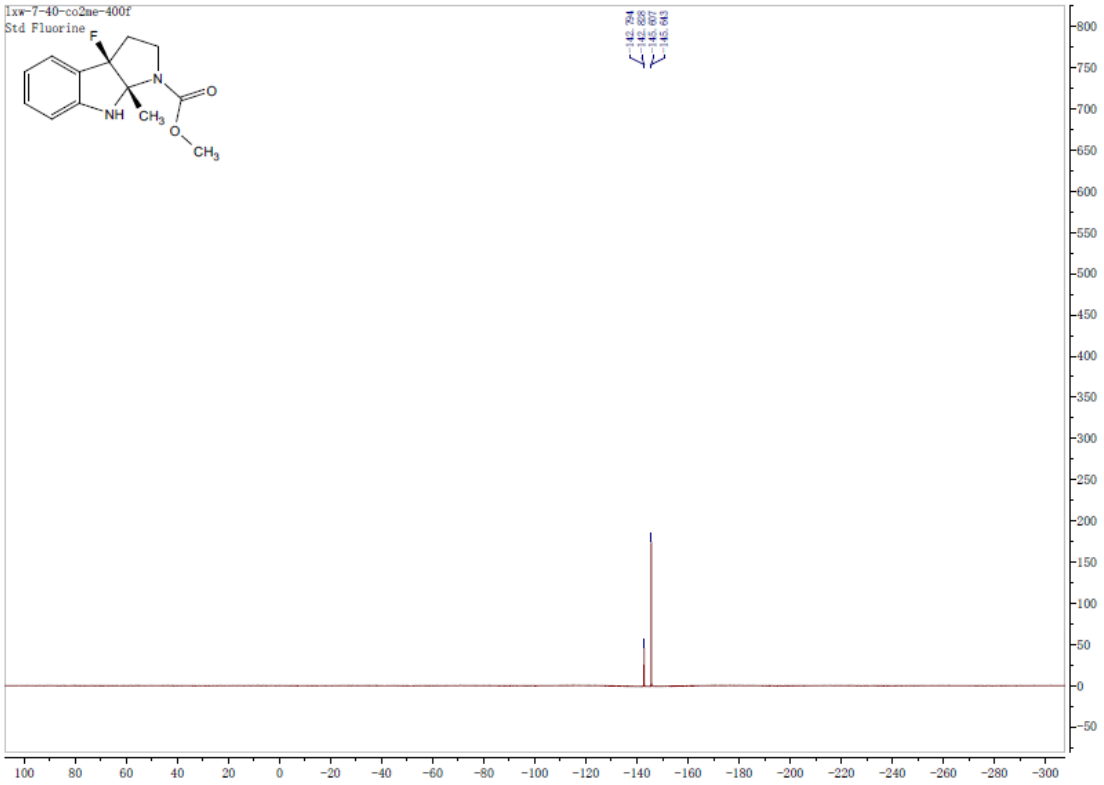
NMR Spectra of **1z**


7.603
7.583
7.311
7.290
7.259
7.233
7.214
7.128
7.109
7.092
6.887
4.598
3.756
3.458
3.444
2.958
2.940
2.924
1.435
-0.000
N H B o c
N
0.84
0.00
0.88
0.92
0.91
0.82
0.71
2.77
1.67
2.03
8.95
8
7
6
5
4
3
2
1
PPM

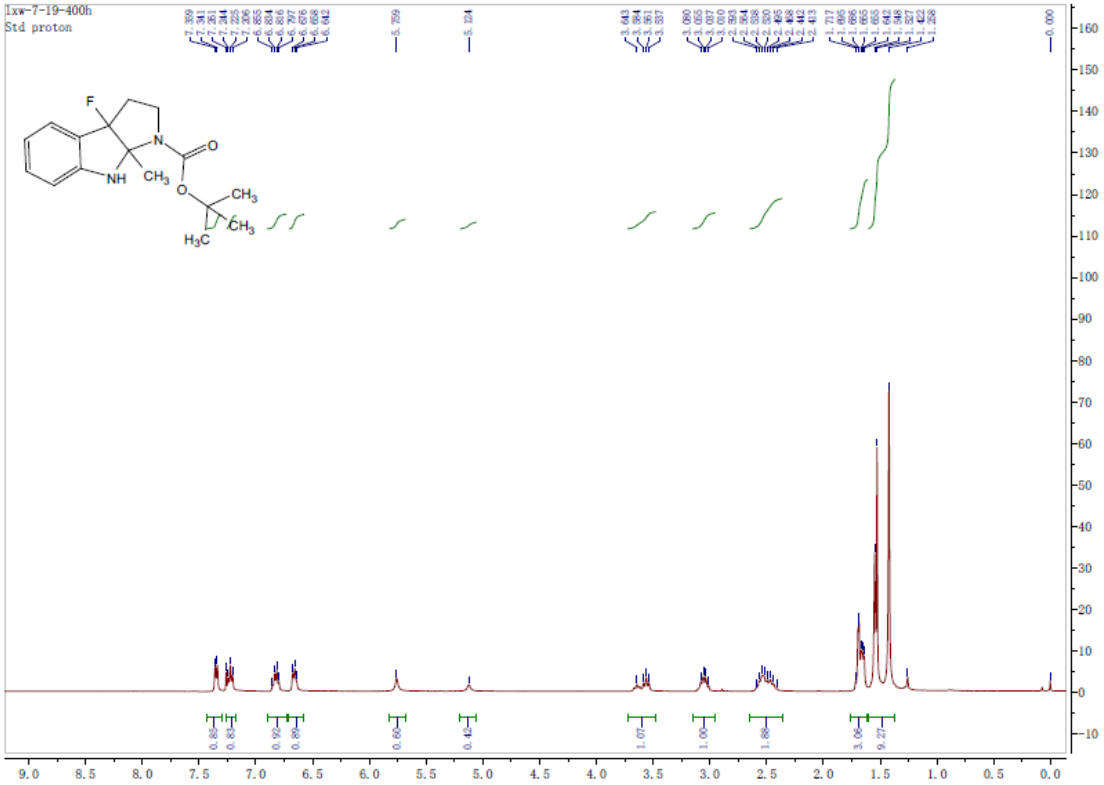
NMR Spectra of **2a**

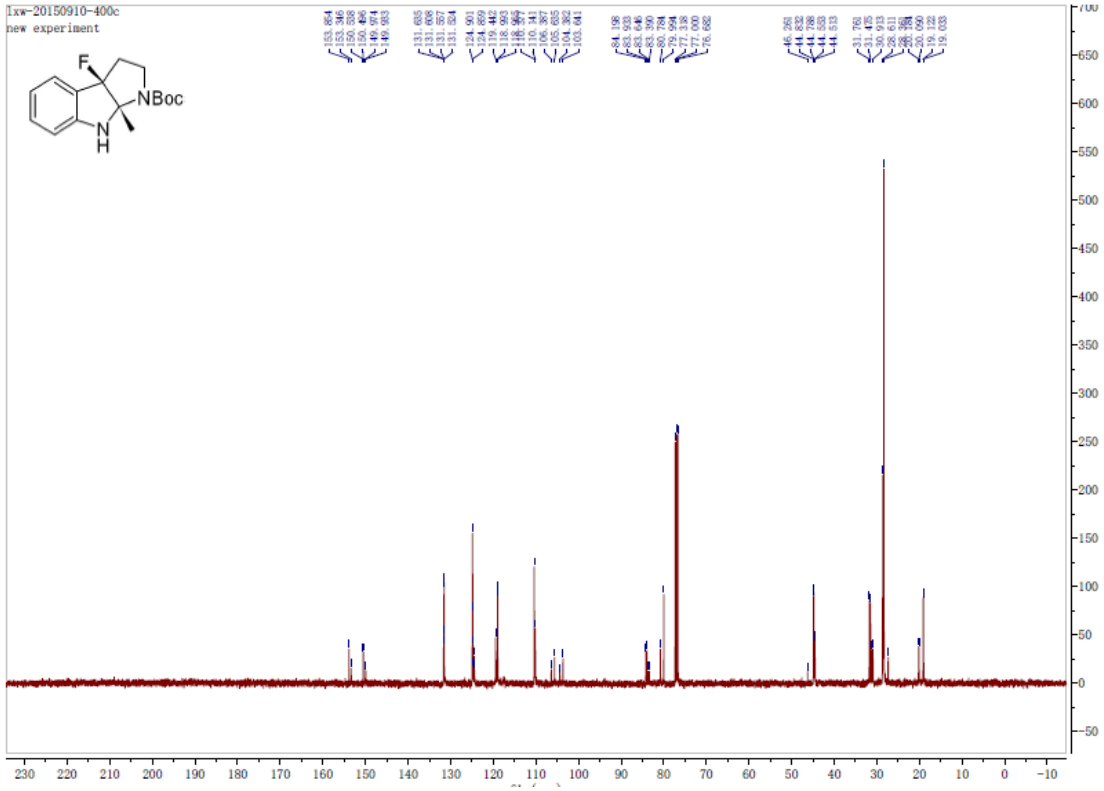

lxw-7-co2me-400h-tm
Std proton
F
N
NH
CH3
O
O
CH3

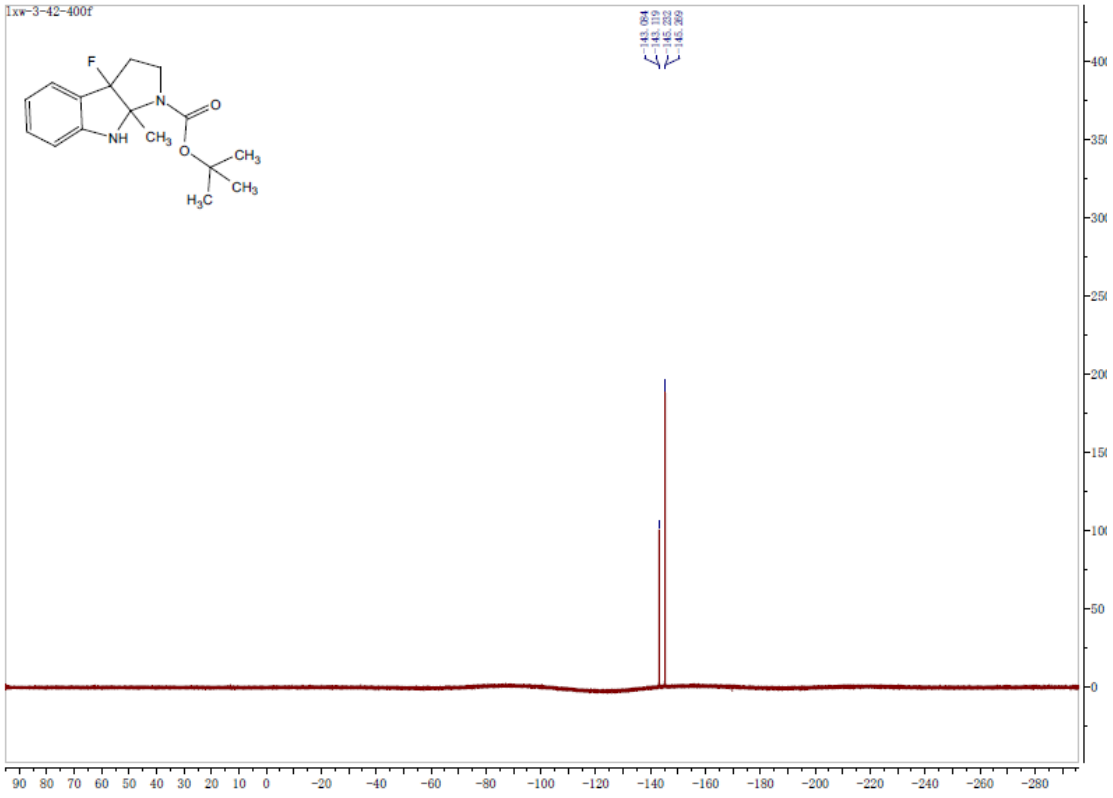

lxw-7-40-co2me-400c-tm
Std carbon
F
N
NH
CH3
O
O
CH3



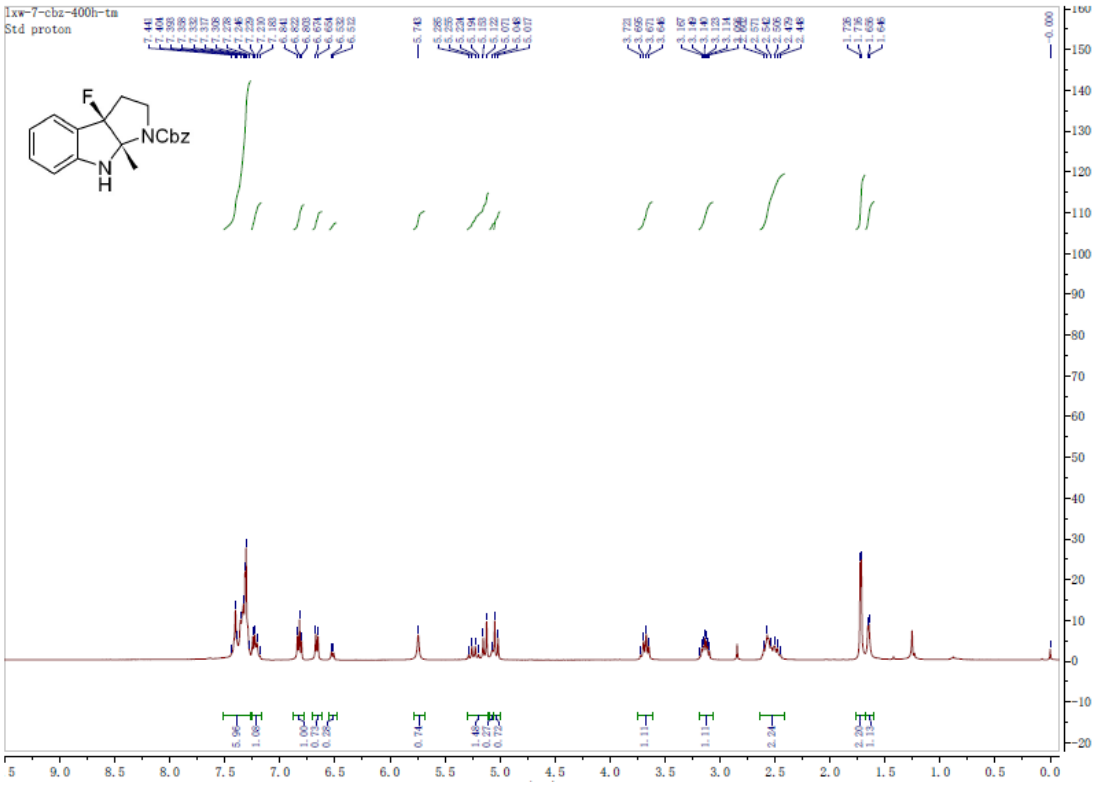
NMR Spectra of **2b**

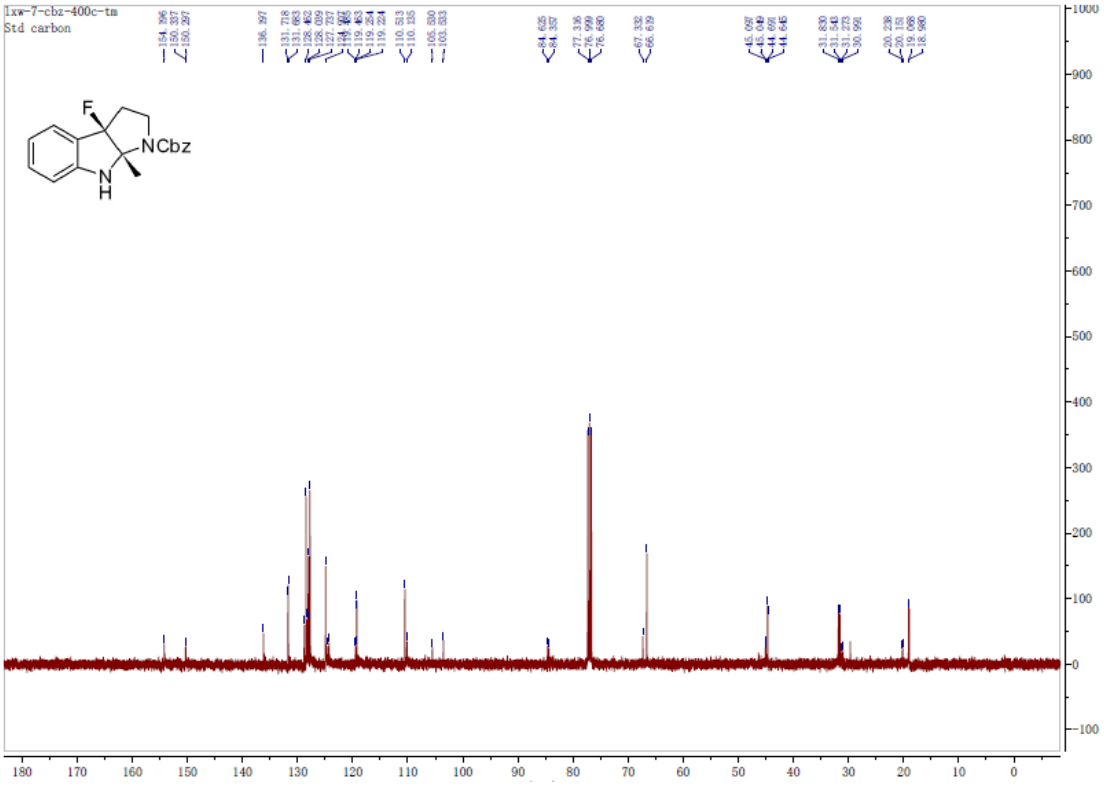

1xw-7-19-400h
Std proton
F
N
O
NH
CH3
O
CH3
CH3
H3C

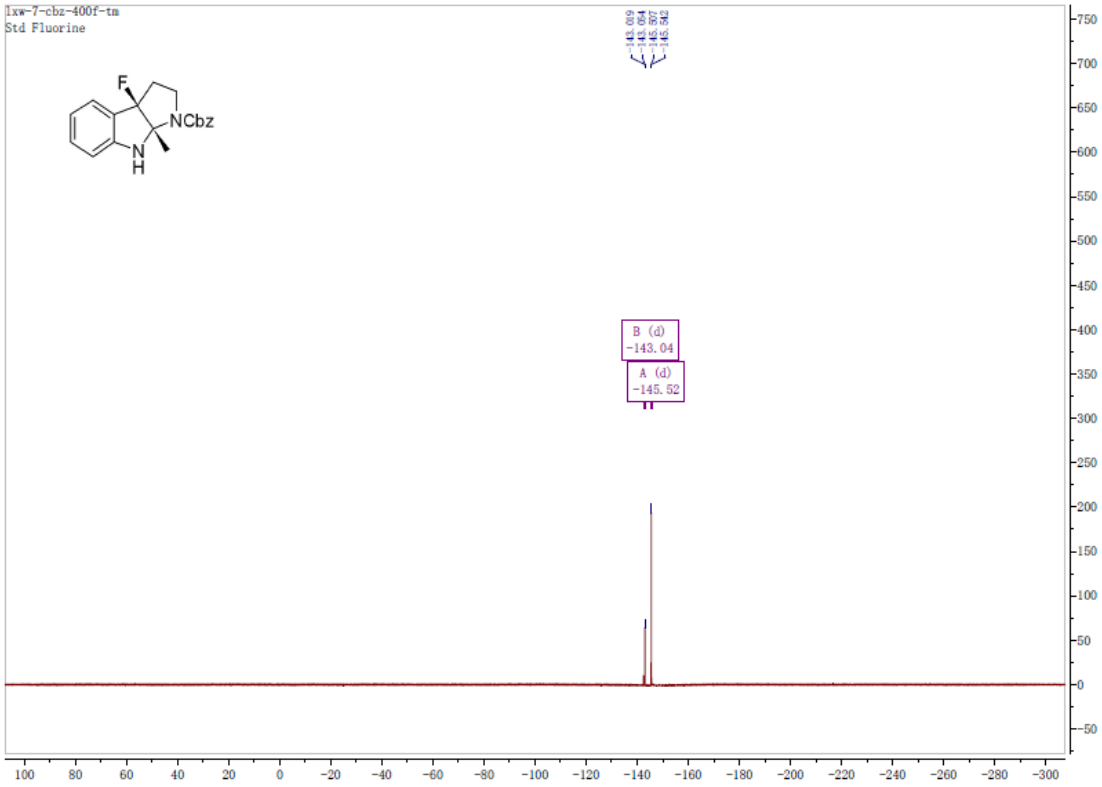

1xw-20150910-400c
new experiment
F
NBoc
N
H



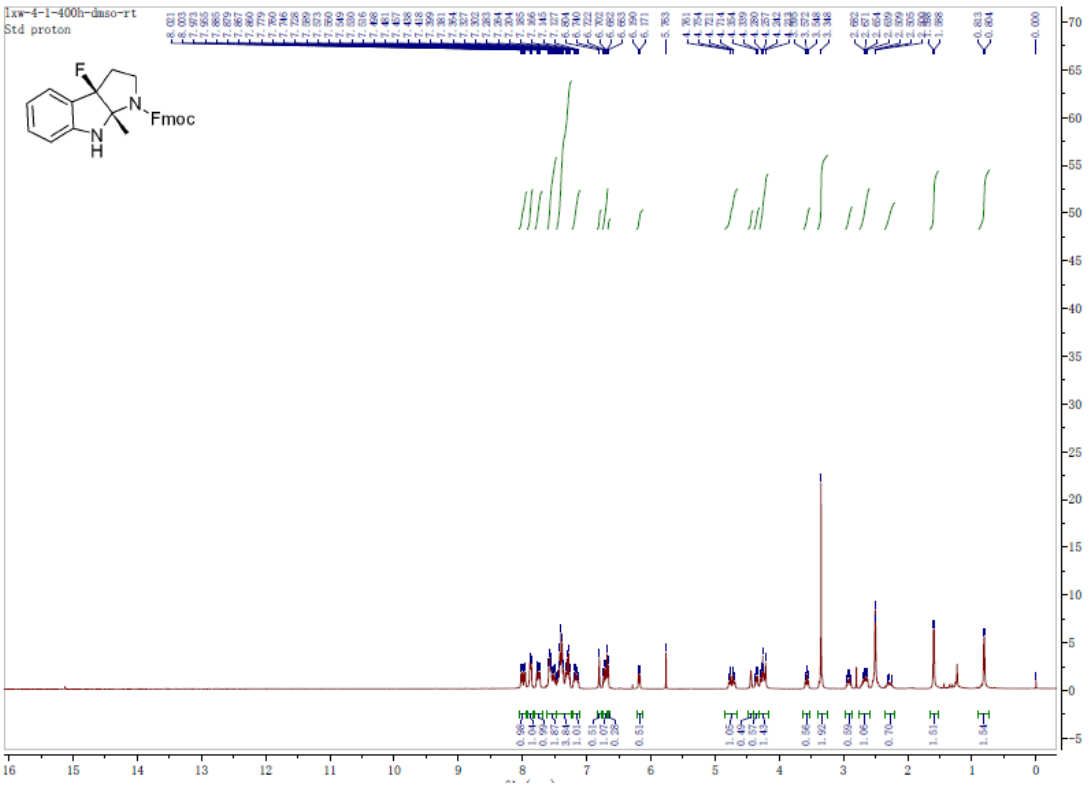
NMR Spectra of **2c**

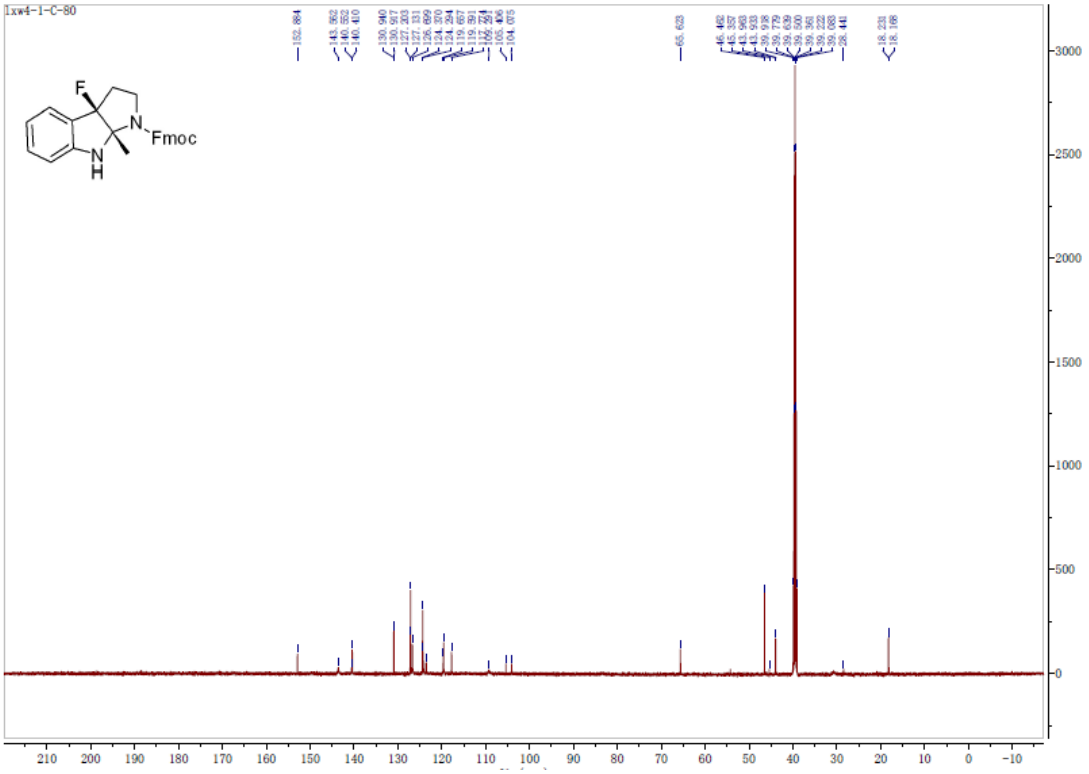

1xw-7-cbz-400h-tm
Std proton
F
NCbz
N
H

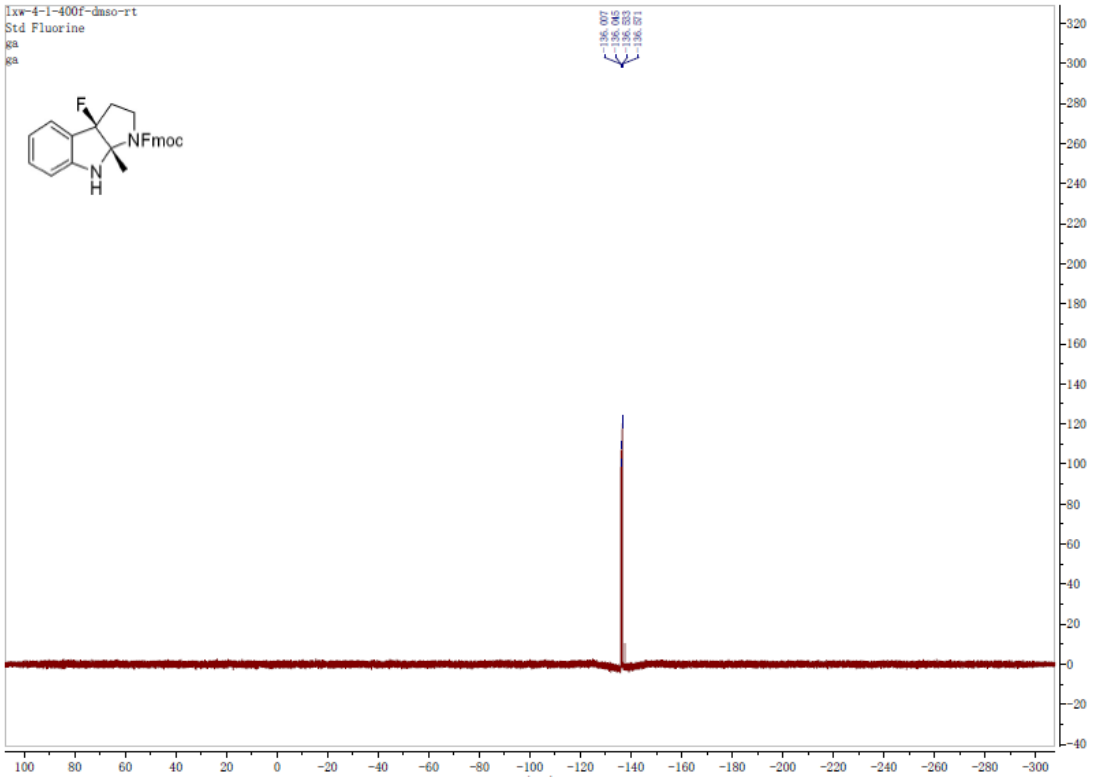

1xw-7-cbz-400c-tm
Std carbon
F
NCbz
N
H



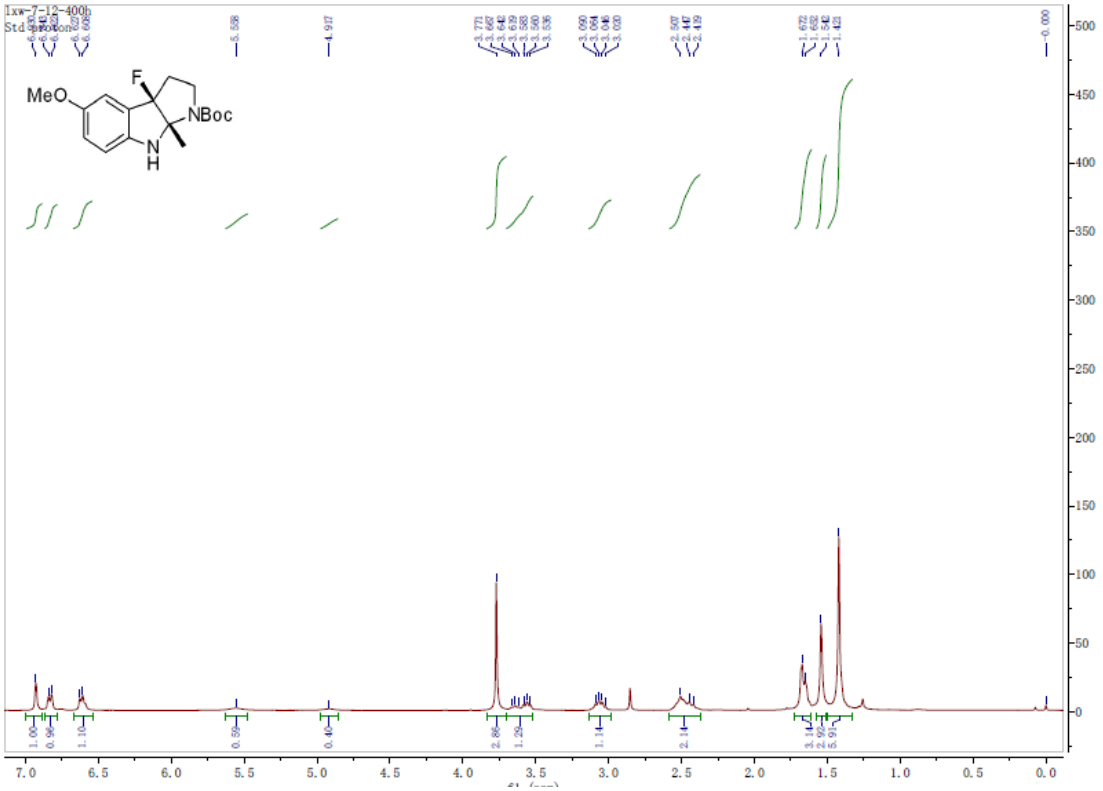
NMR Spectra of **2d**

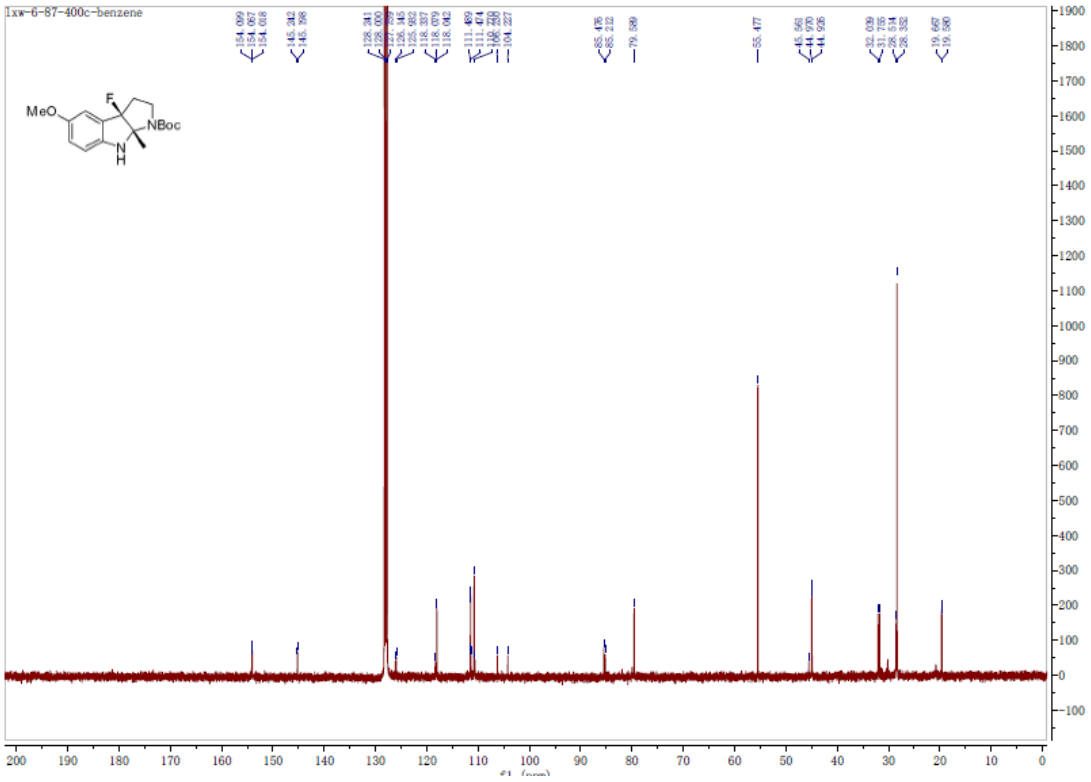

lxw-4-1-400h-dmso-rt
Std proton
F
N
Fmoc
N
H

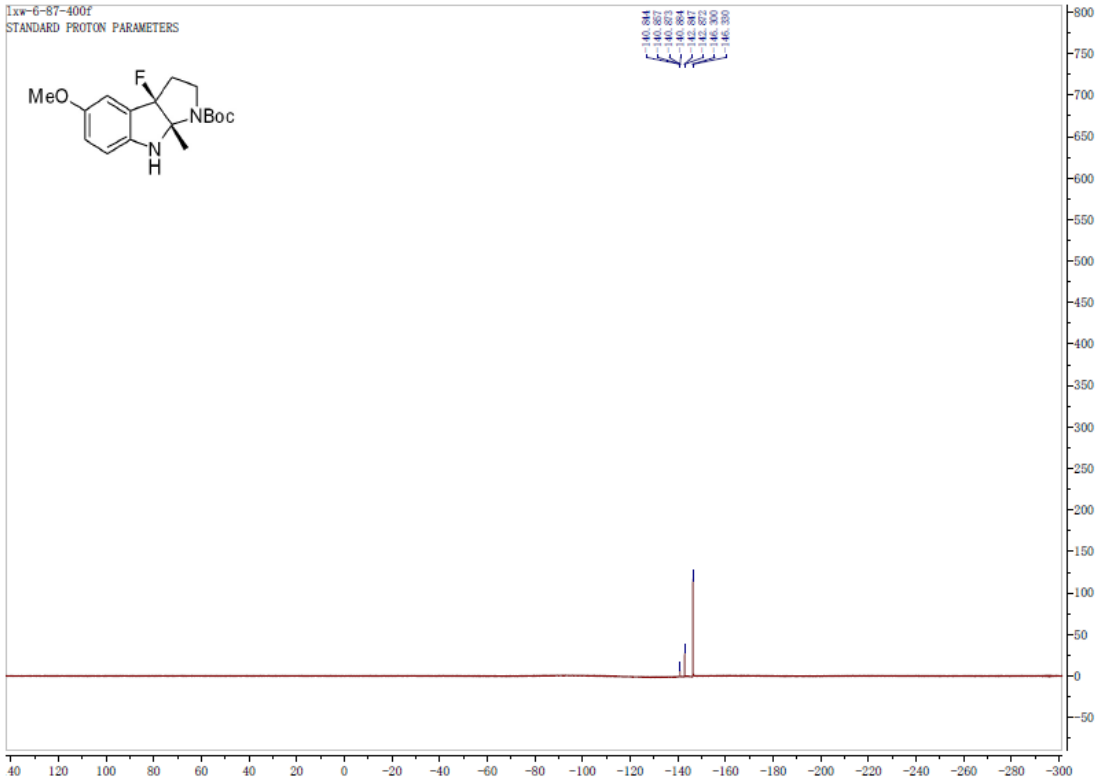

lxw4-1-C-80
F
N
Fmoc
N
H



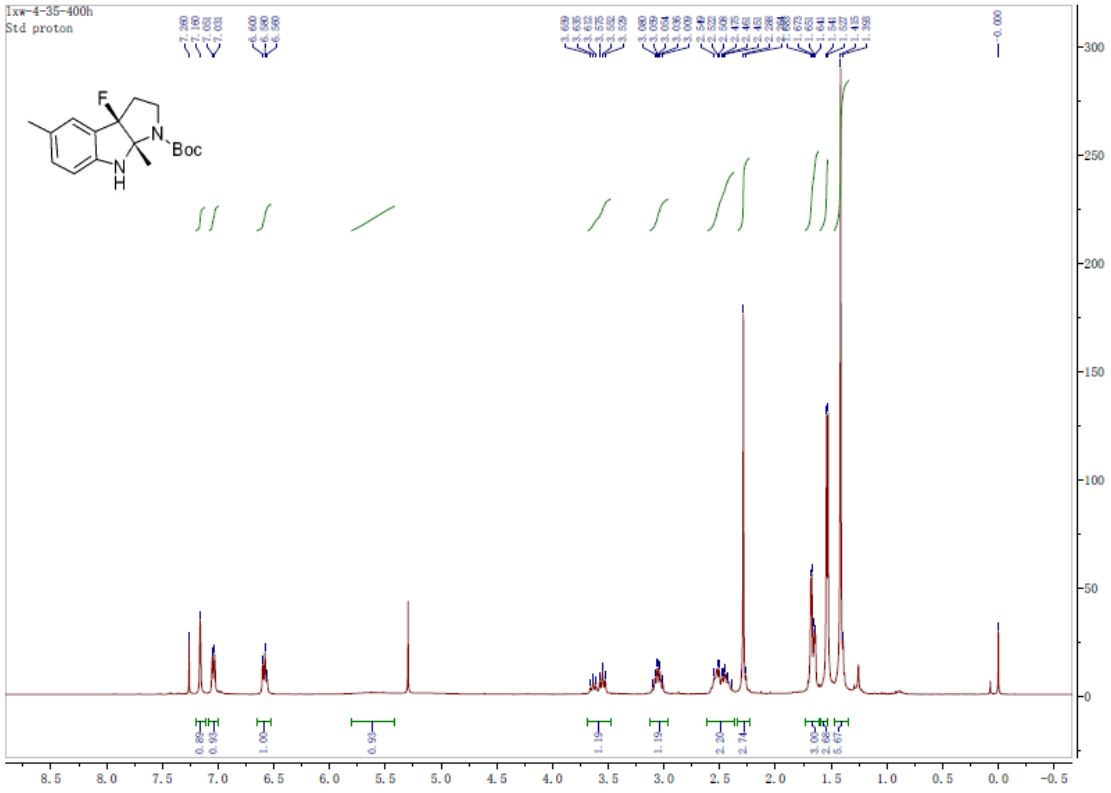
NMR Spectra of **2e**

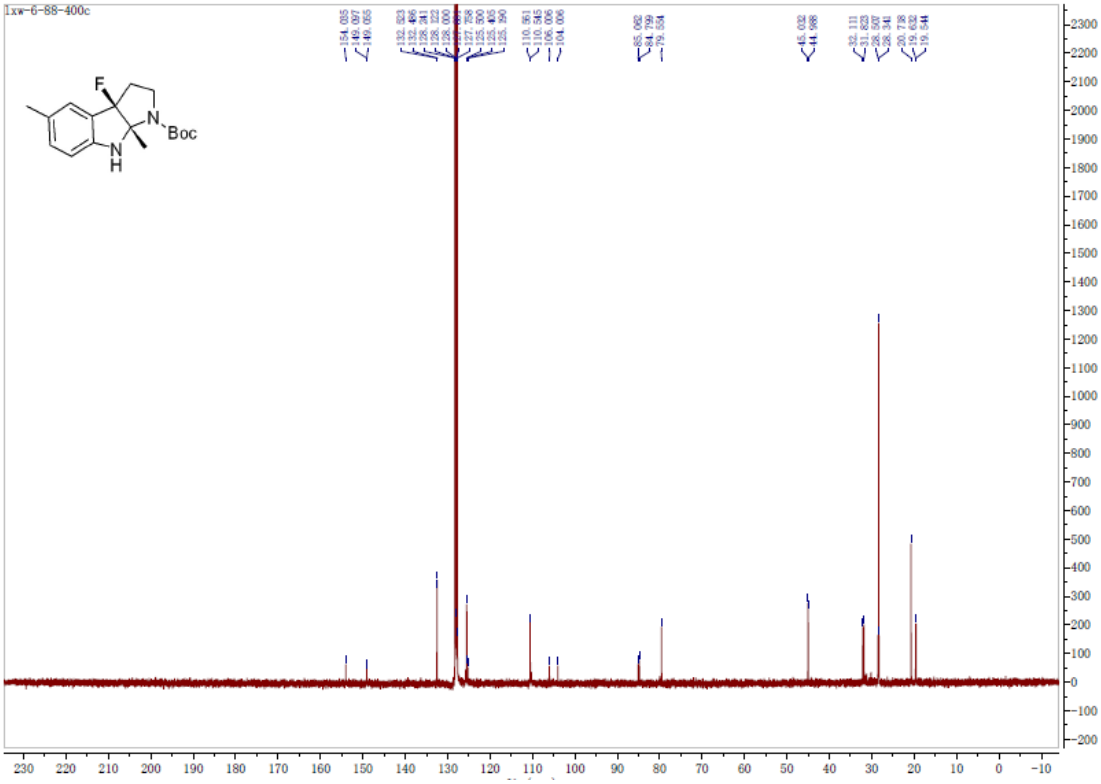

MeO
F
NBoc
N
H

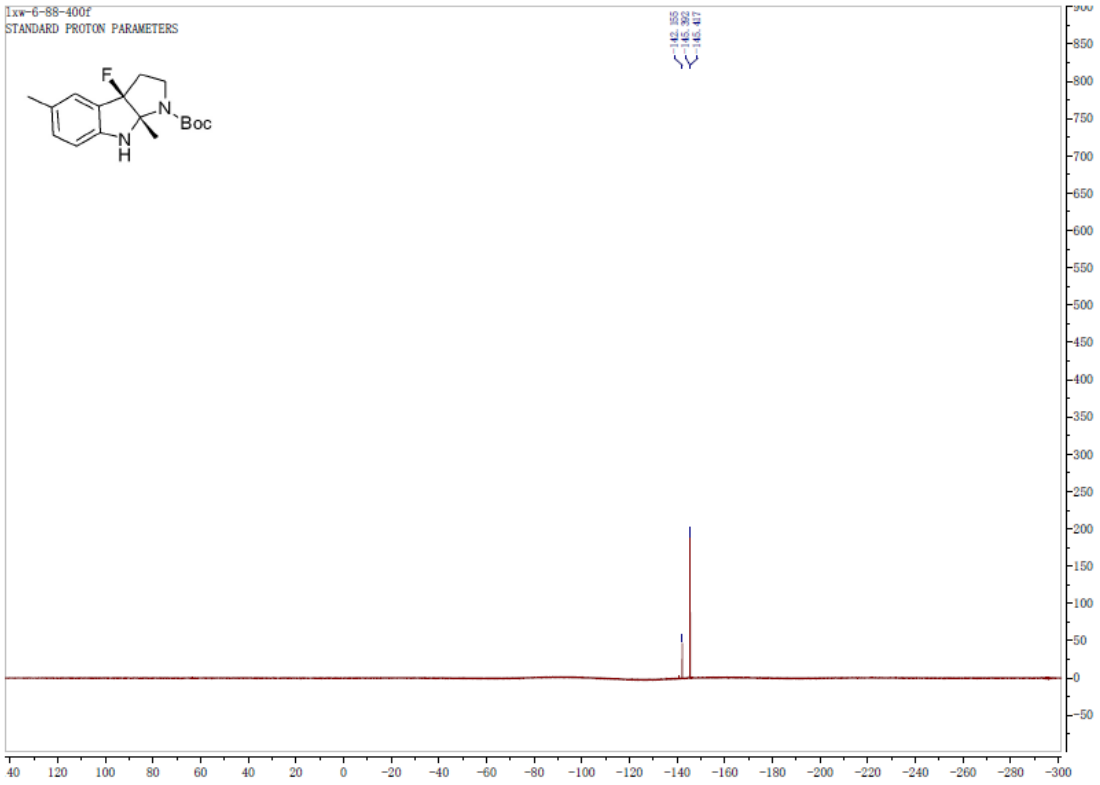




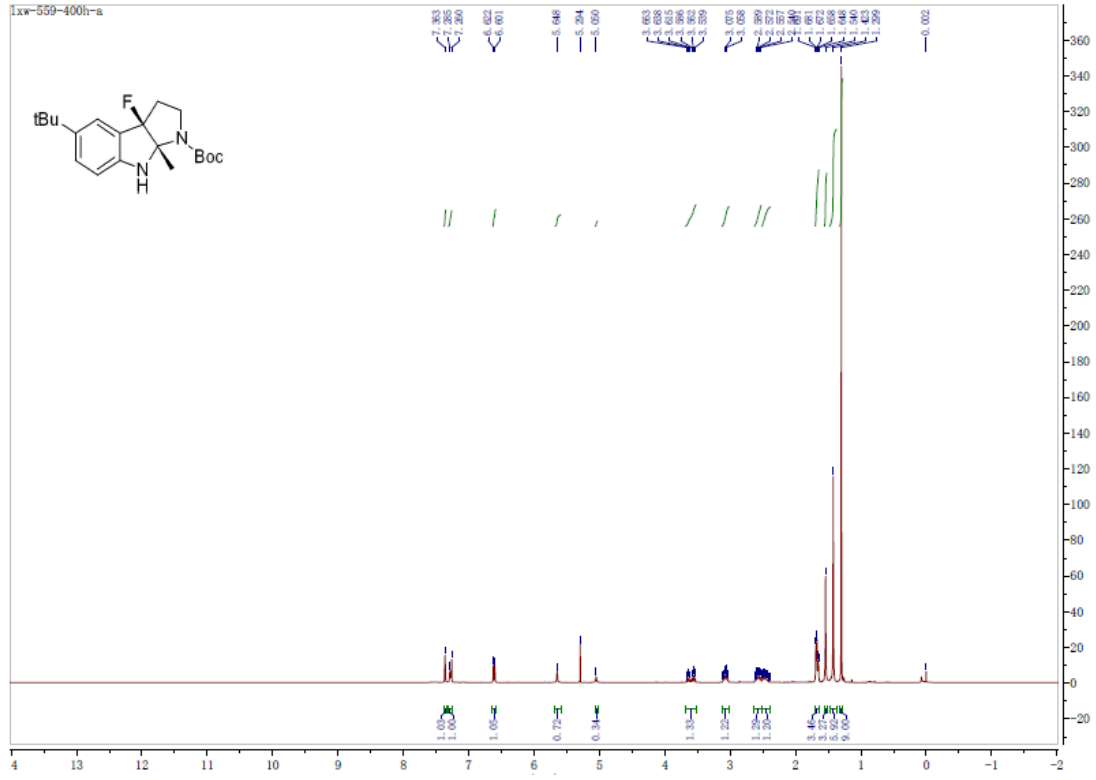
NMR Spectra of **2f**

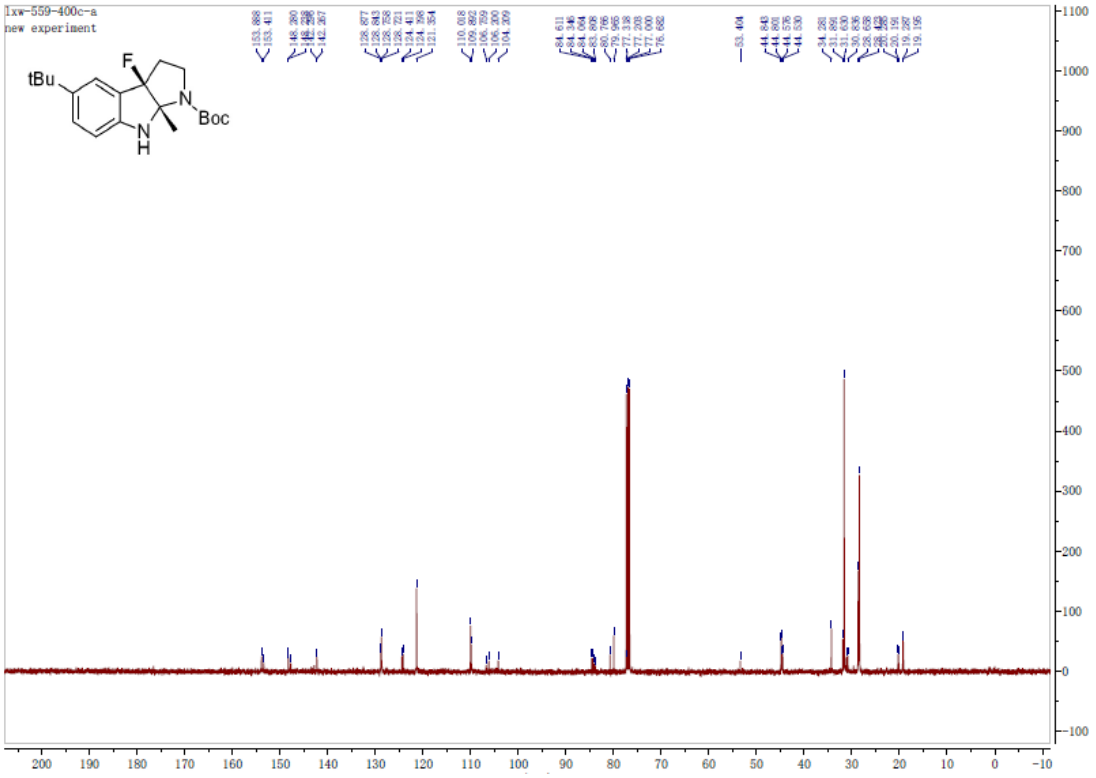

1xw-4-35-400h
Std proton
F
N
Boc
N
H

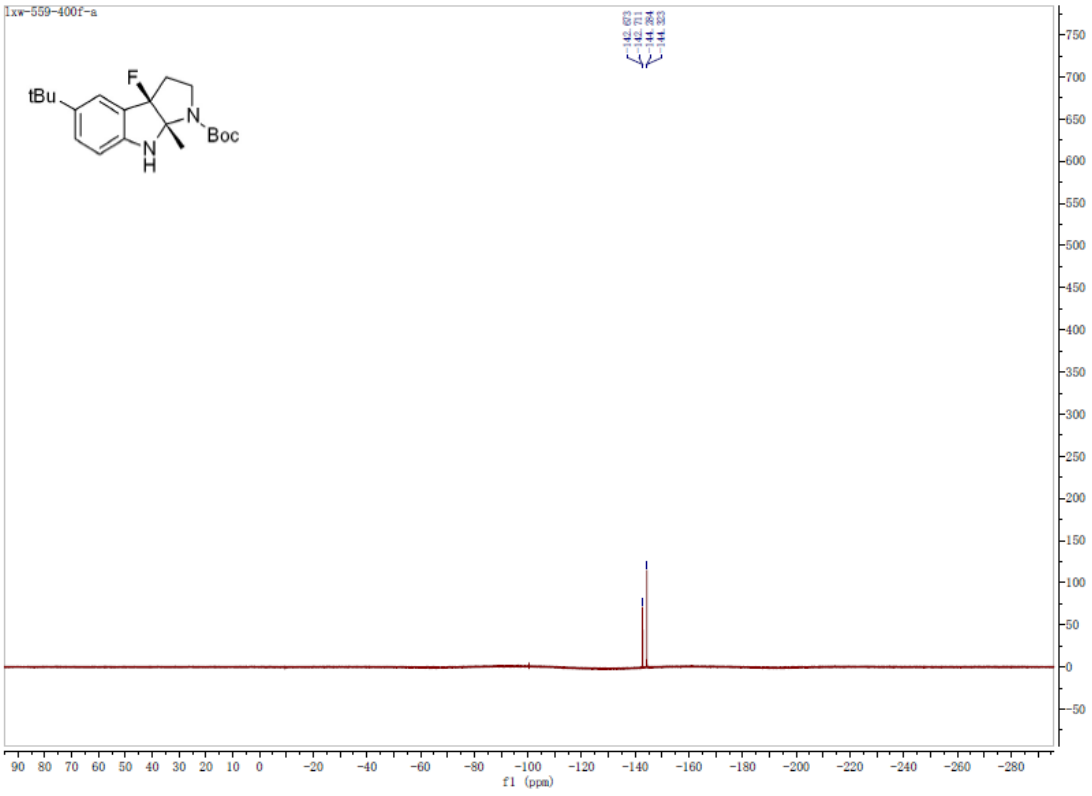

1xw-6-88-400c
F
N
Boc
N
H



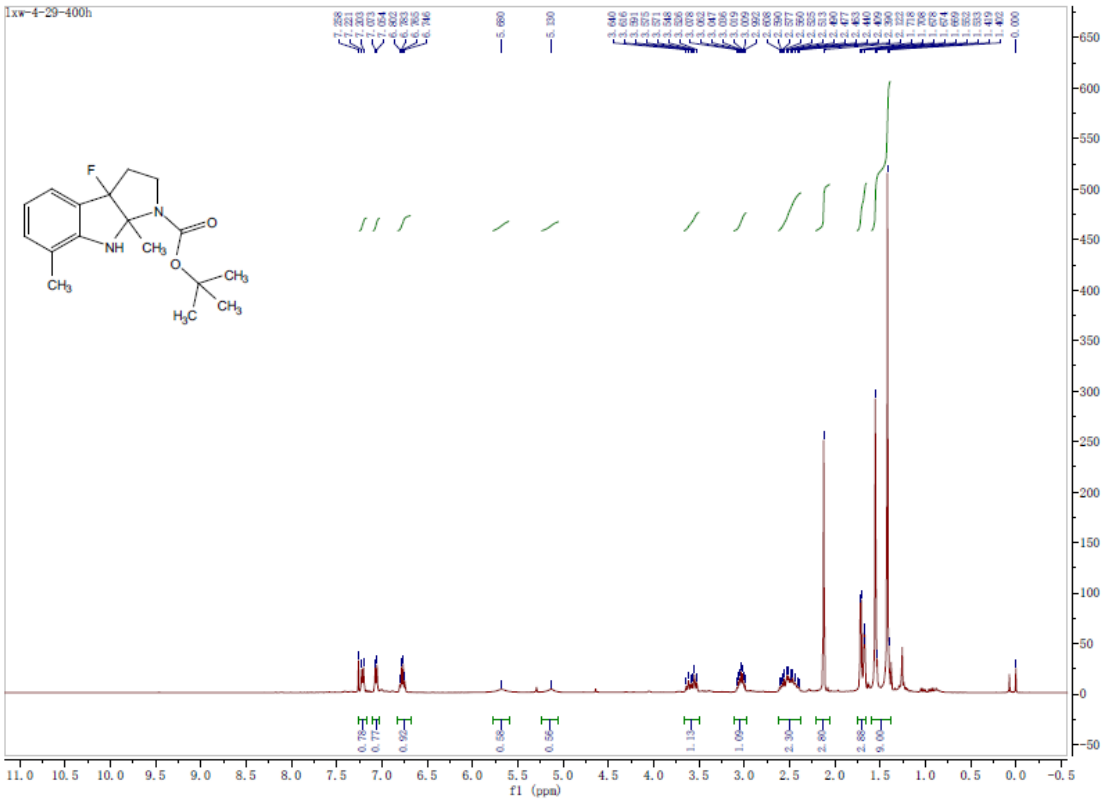
NMR Spectra of **2g**

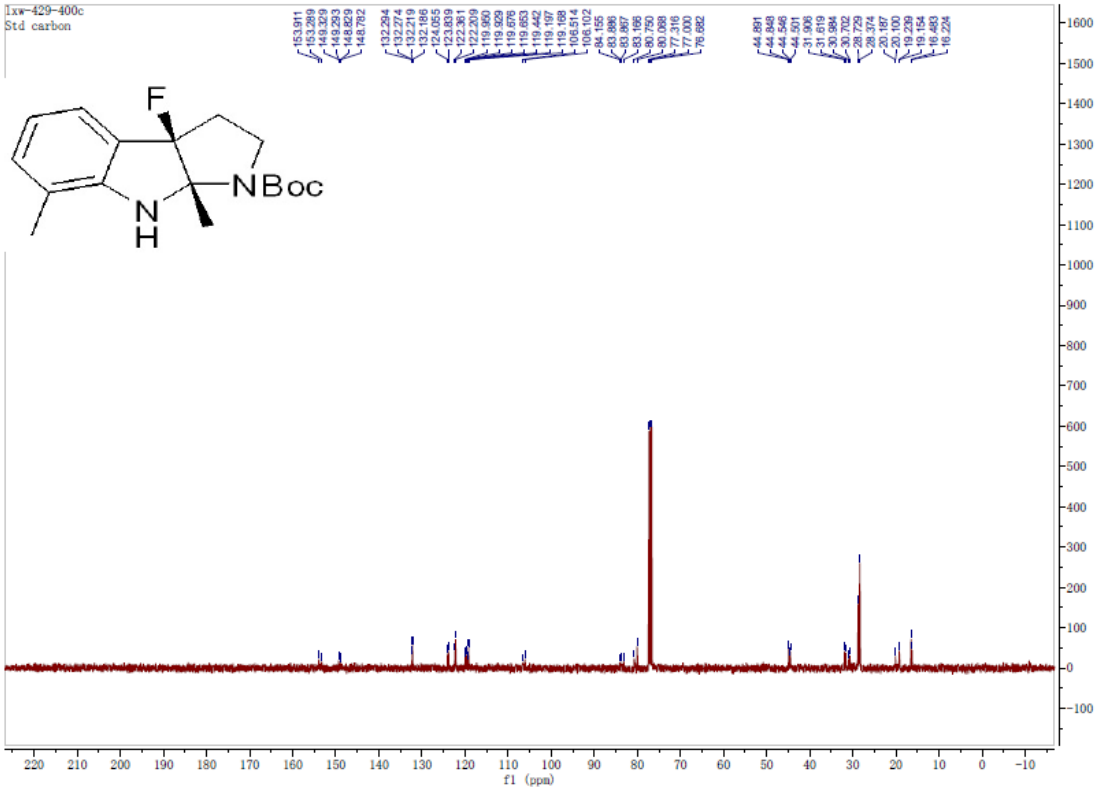

lxw-559-400h-a
tBu
F
N
Boc
N
H

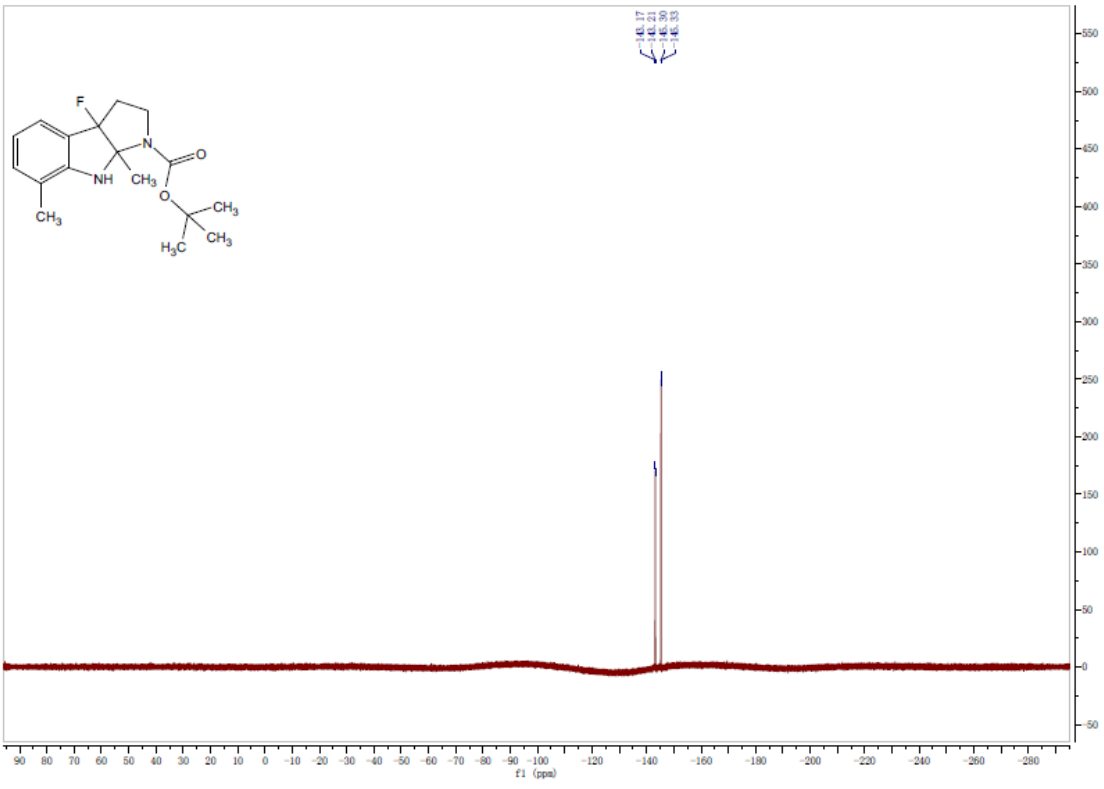

lxw-559-400c-a
new experiment
tBu
F
N
Boc
N
H



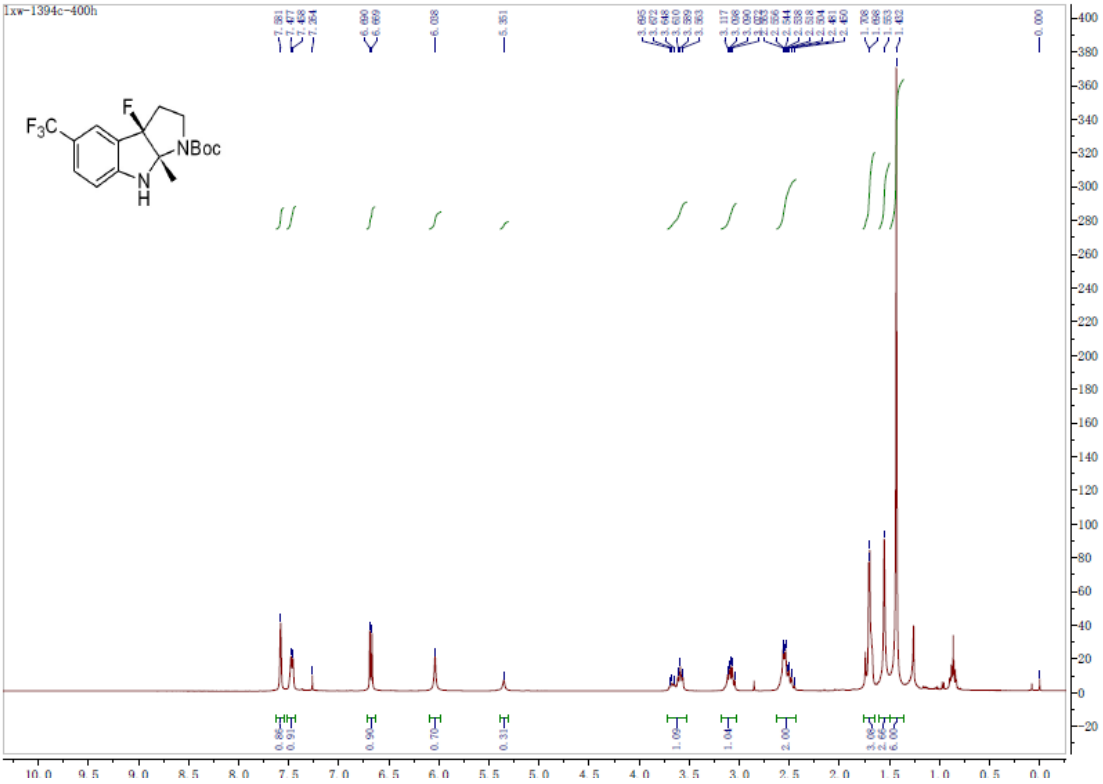
NMR Spectra of **2h**

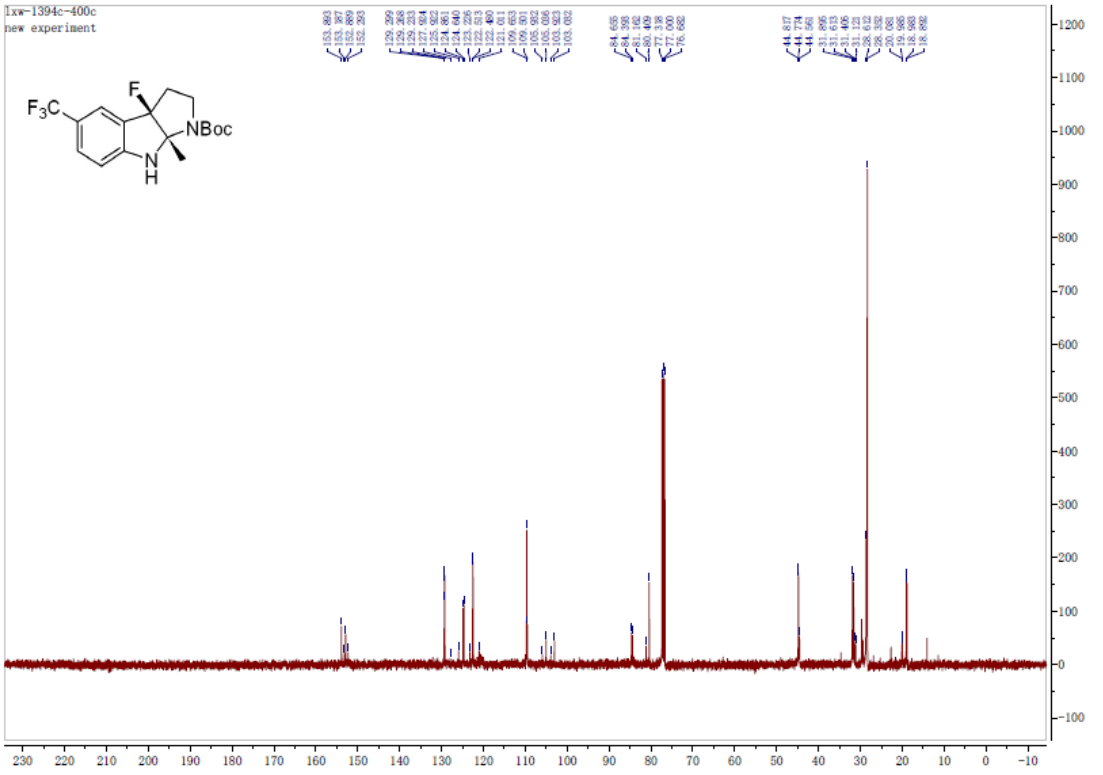

1xw-4-29-400h
F
N
O
NH
CH3
O
CH3
CH3
H3C
CH3
f1 (ppm)

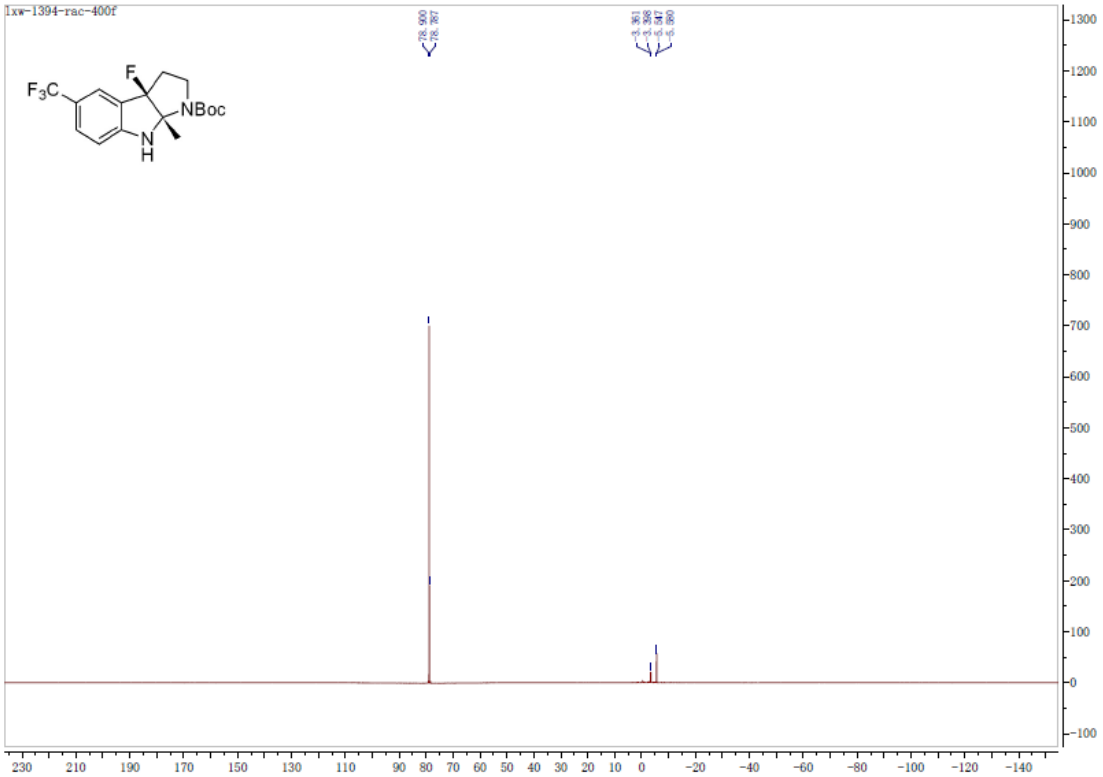

1xw-429-400c
Std carbon
F
NBoc
N
H
f1 (ppm)



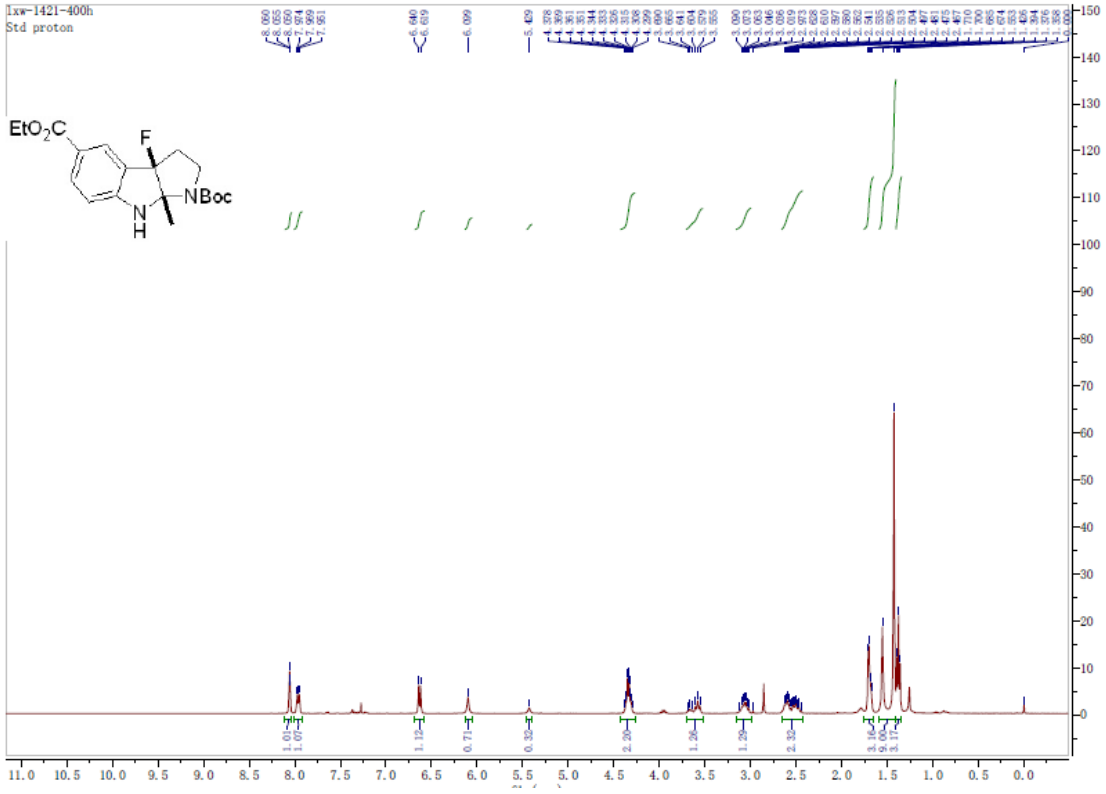
NMR Spectra of **2i**

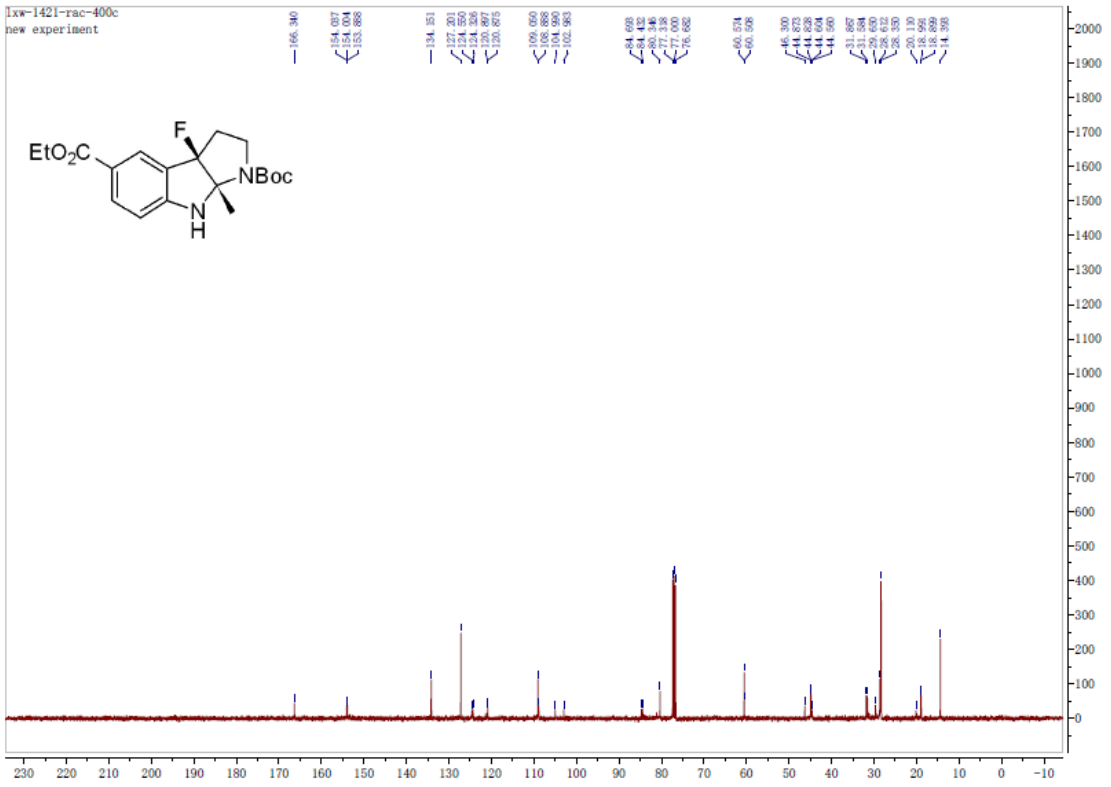

lxw-1394c-400h
F3C
F
NBoc
N
H

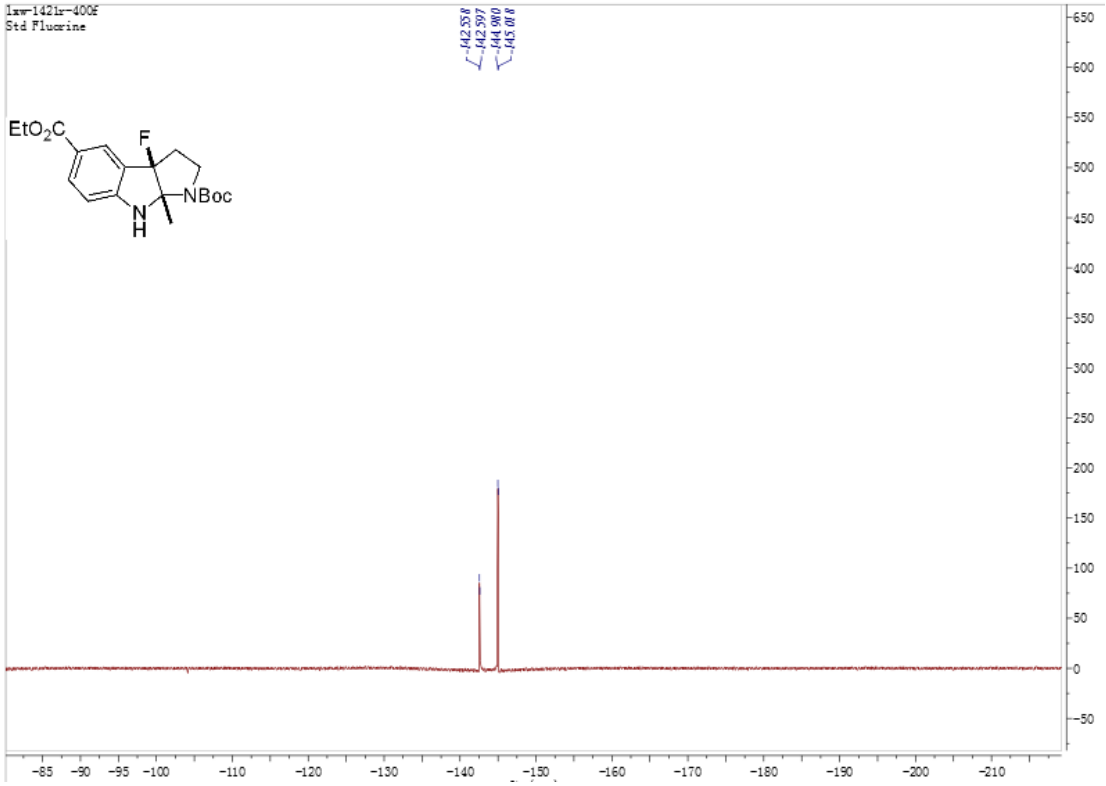

lxw-1394c-400c
new experiment
F3C
F
NBoc
N
H



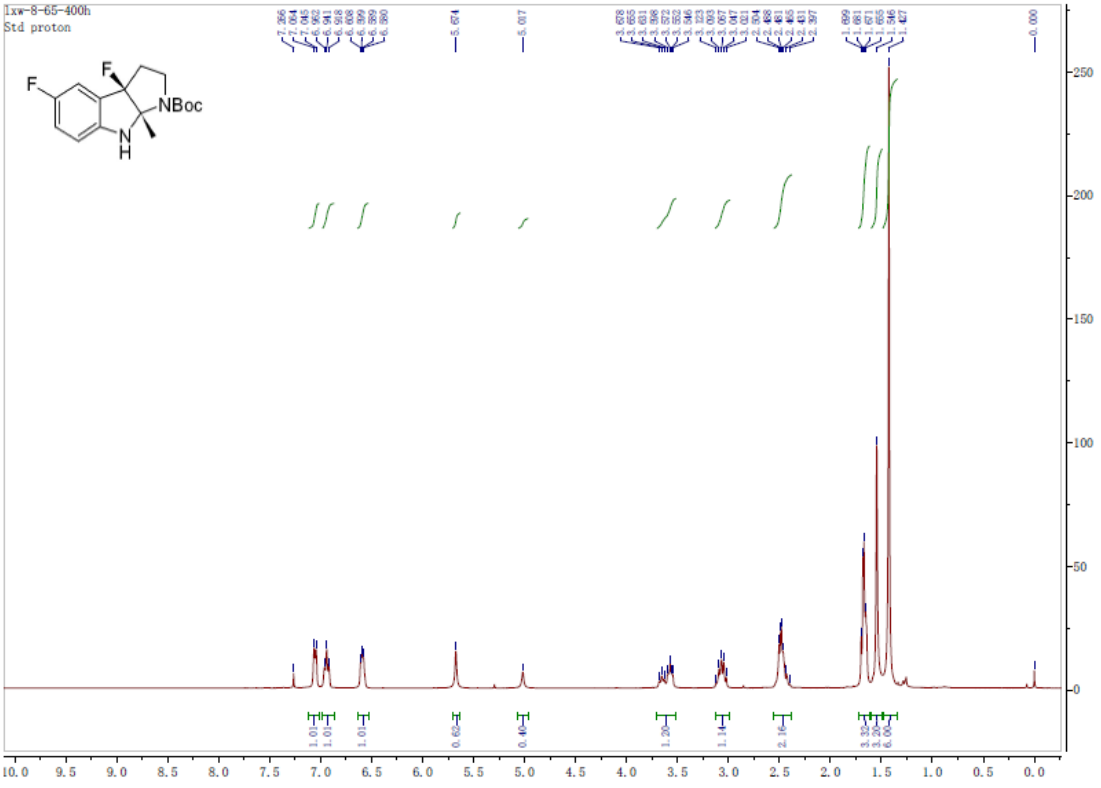
NMR Spectra of **2j**

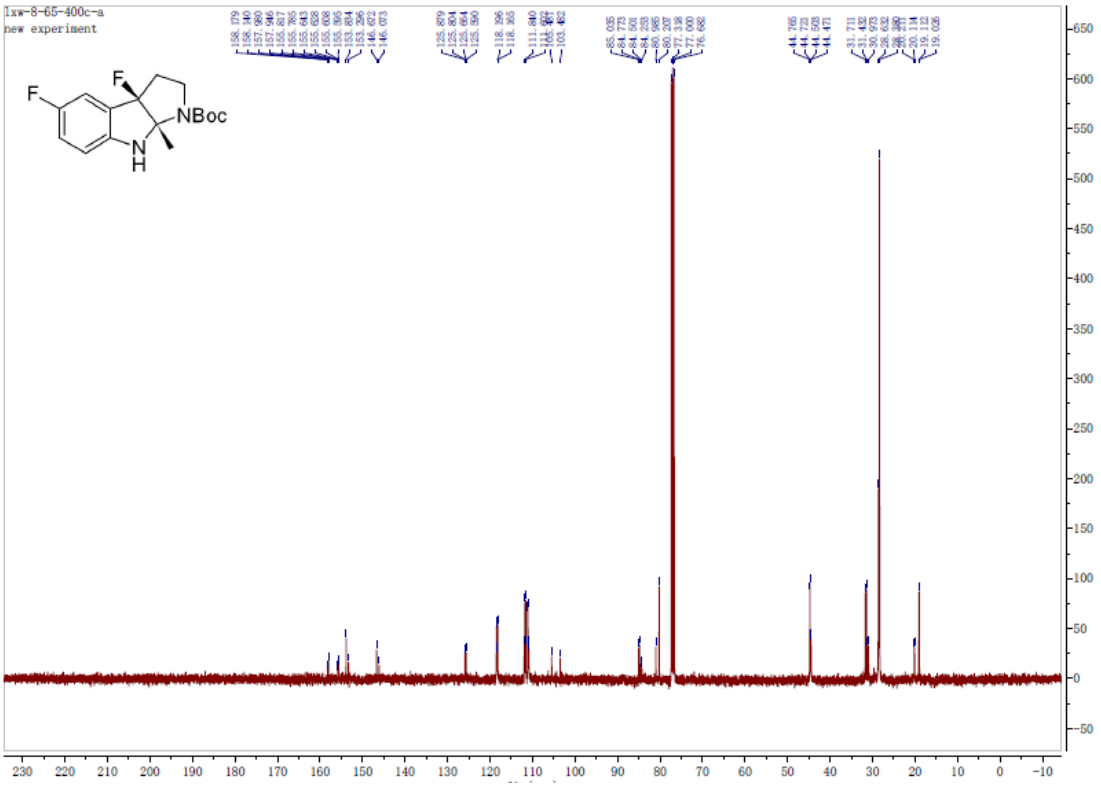


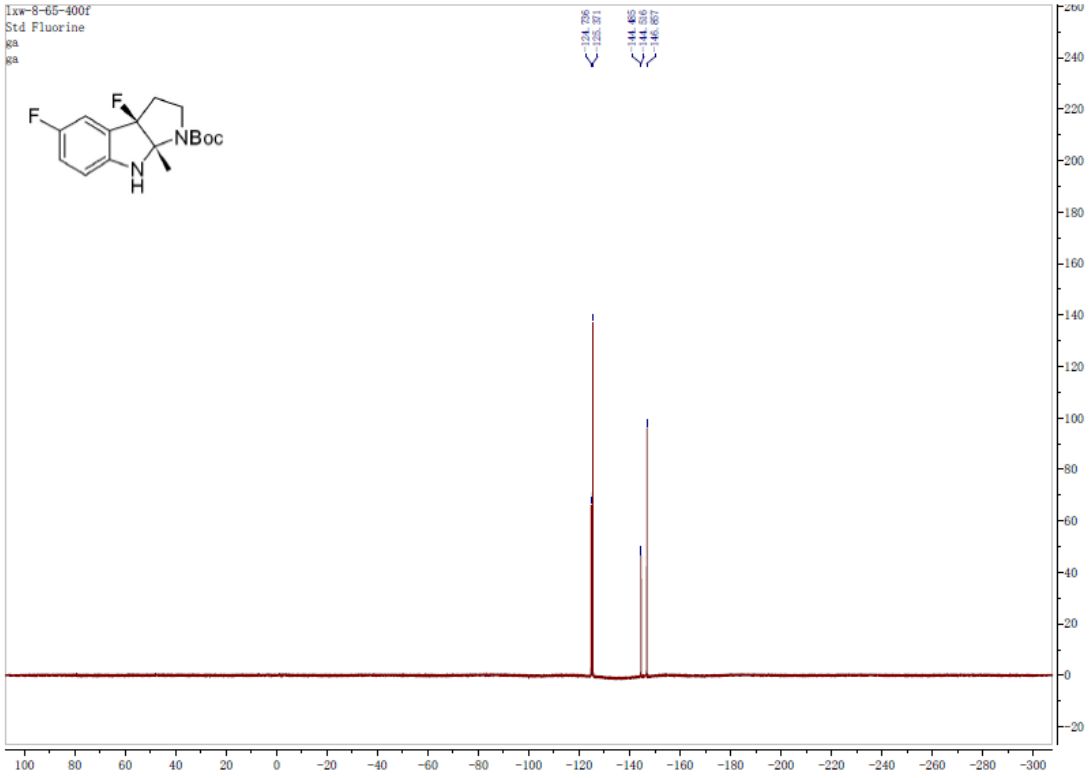

lxw-1421-rac-400c
new experiment
EtO2C
F
NBoc
N
H


lxw-1421r-400f
Std Fluorine
EtO2C
F
NBoc
N
H

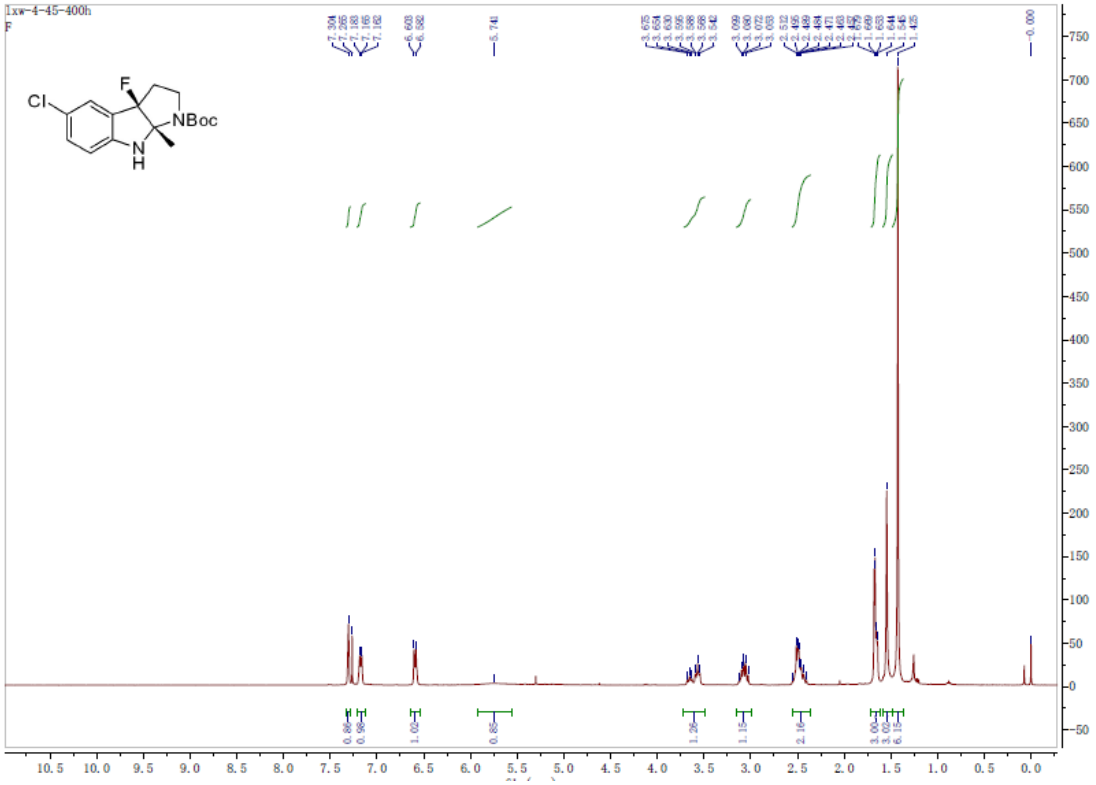
NMR Spectra of **2k**

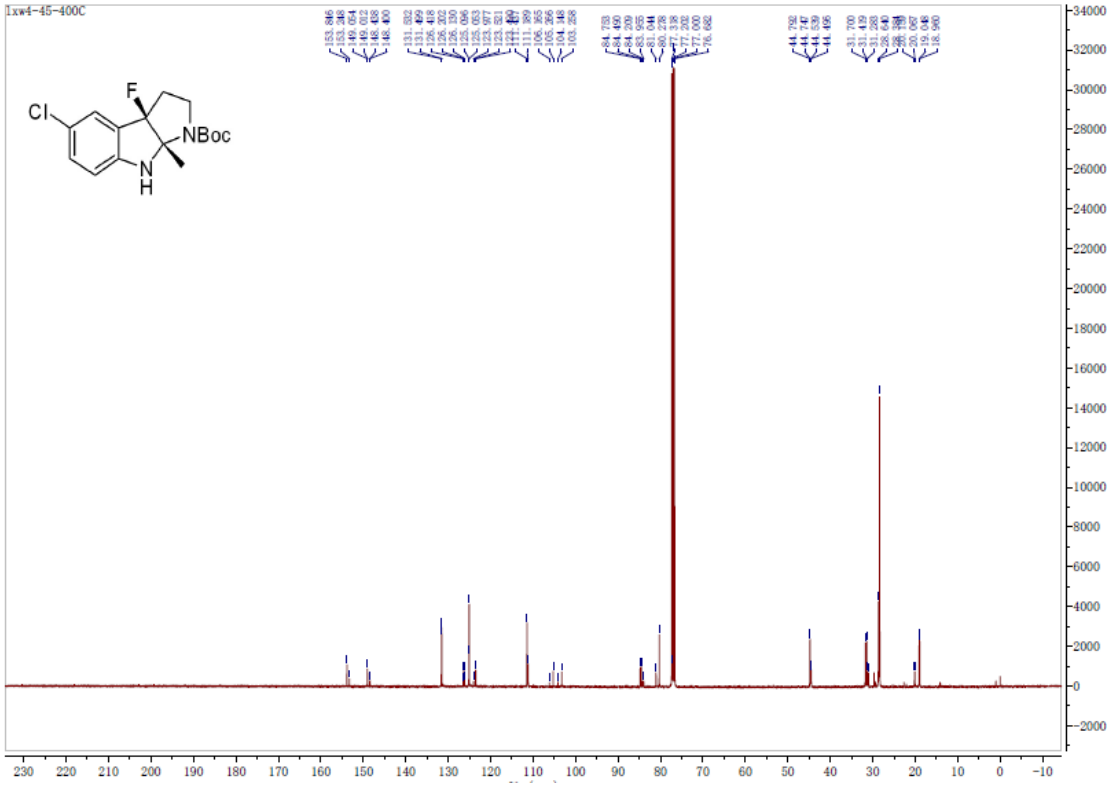

1xw-8-65-400h
Std proton
F
NBoc
N
H

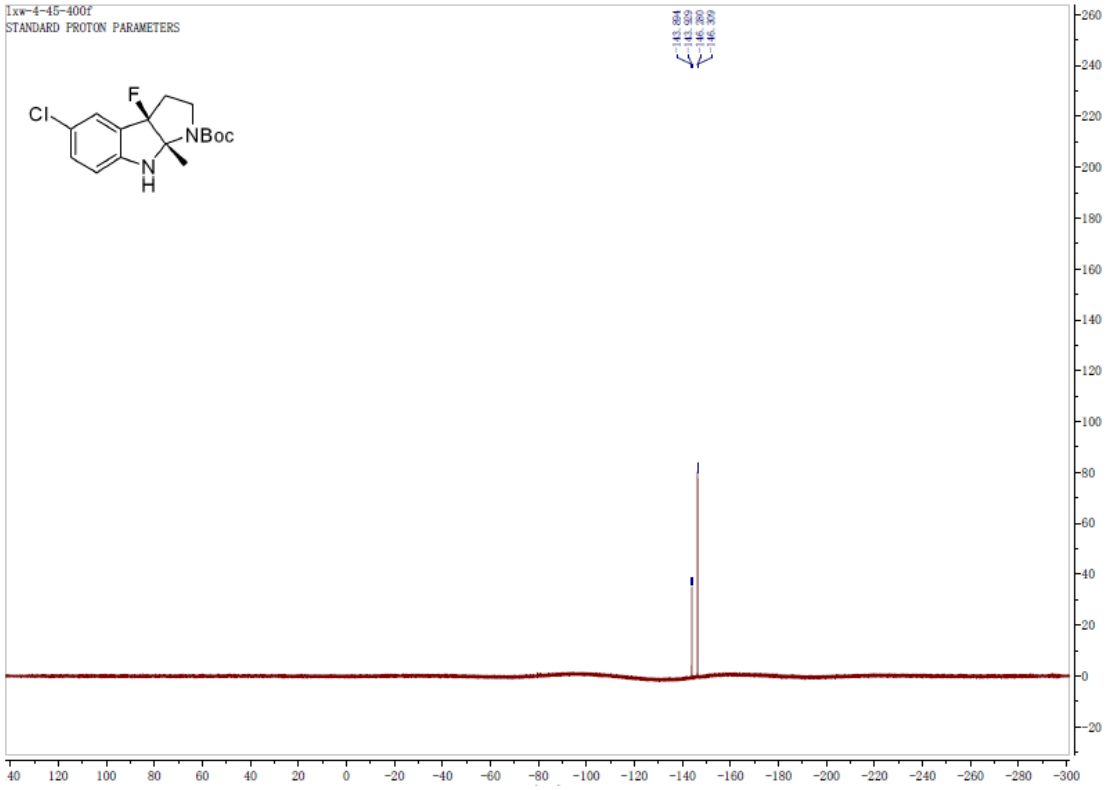

1xw-8-65-400c-a
new experiment
F
NBoc
N
H



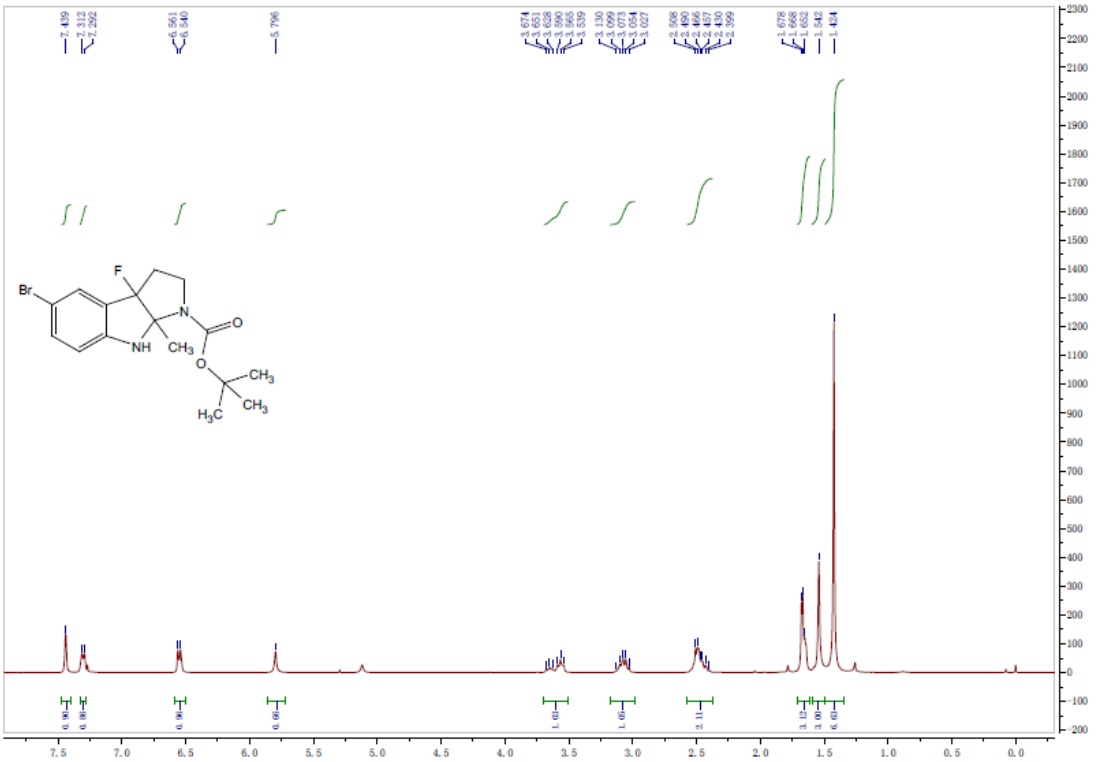
NMR Spectra of **2l**

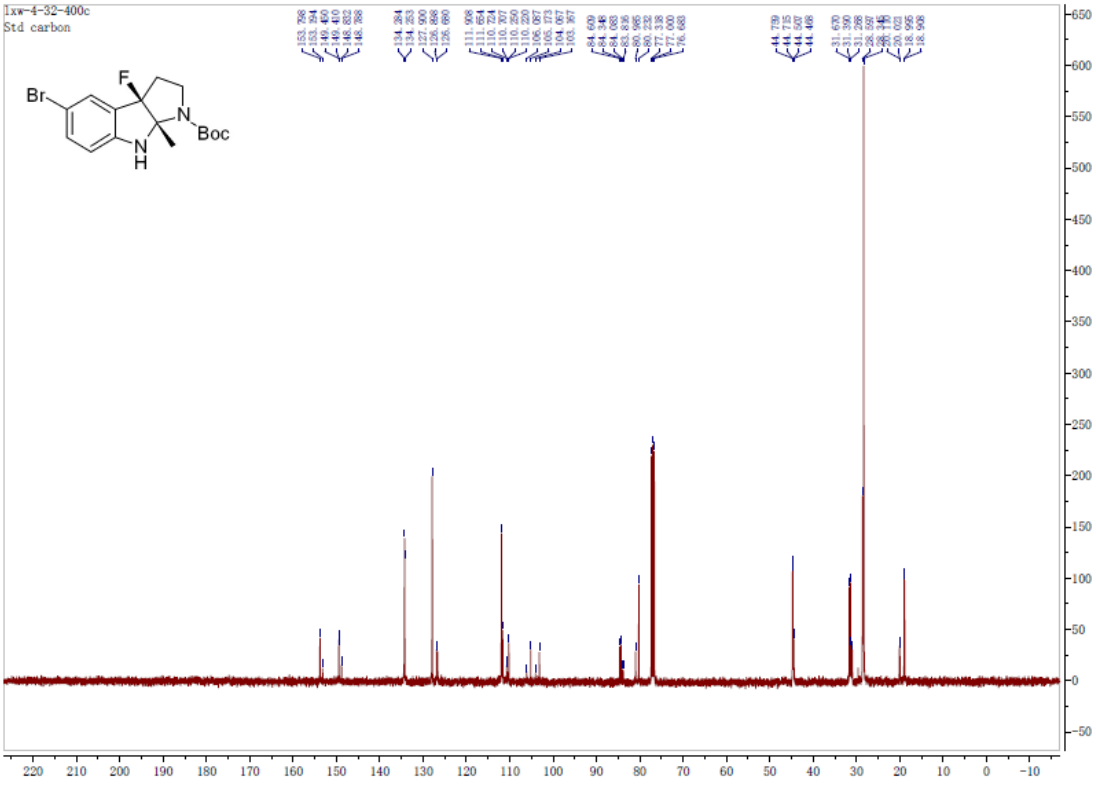

1xw-4-45-400h
F
Cl
F
NBoc
N
H

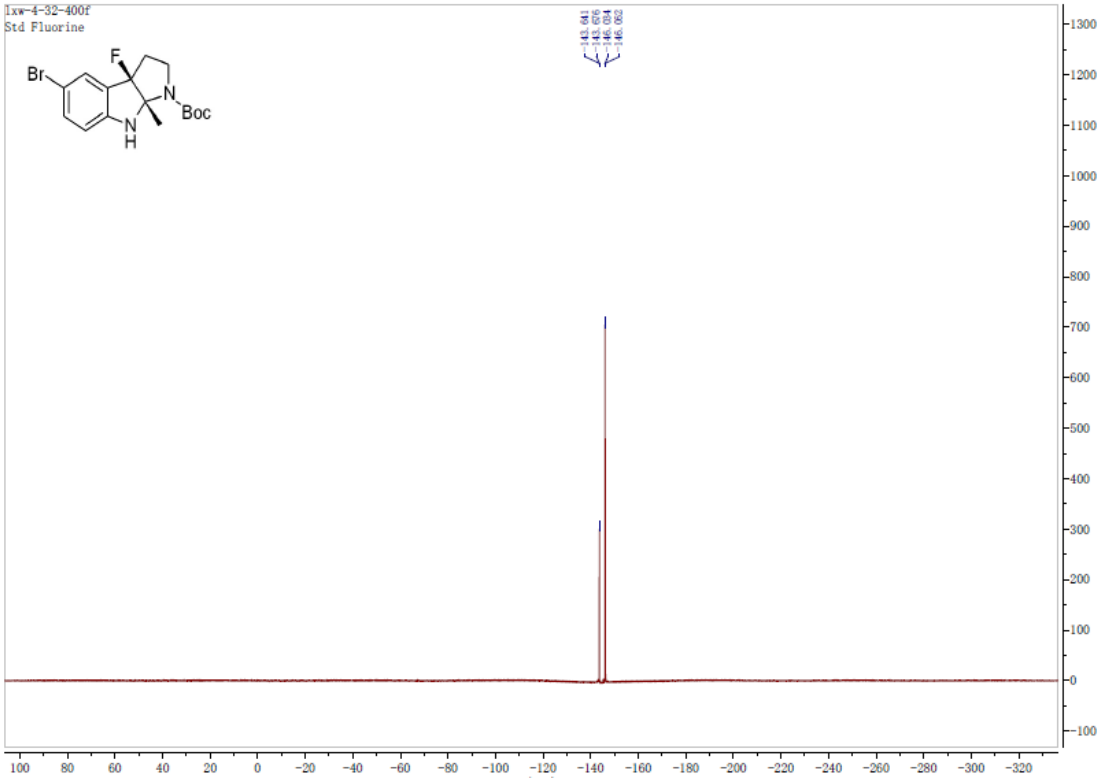

1xw4-45-400C
Cl
F
NBoc
N
H



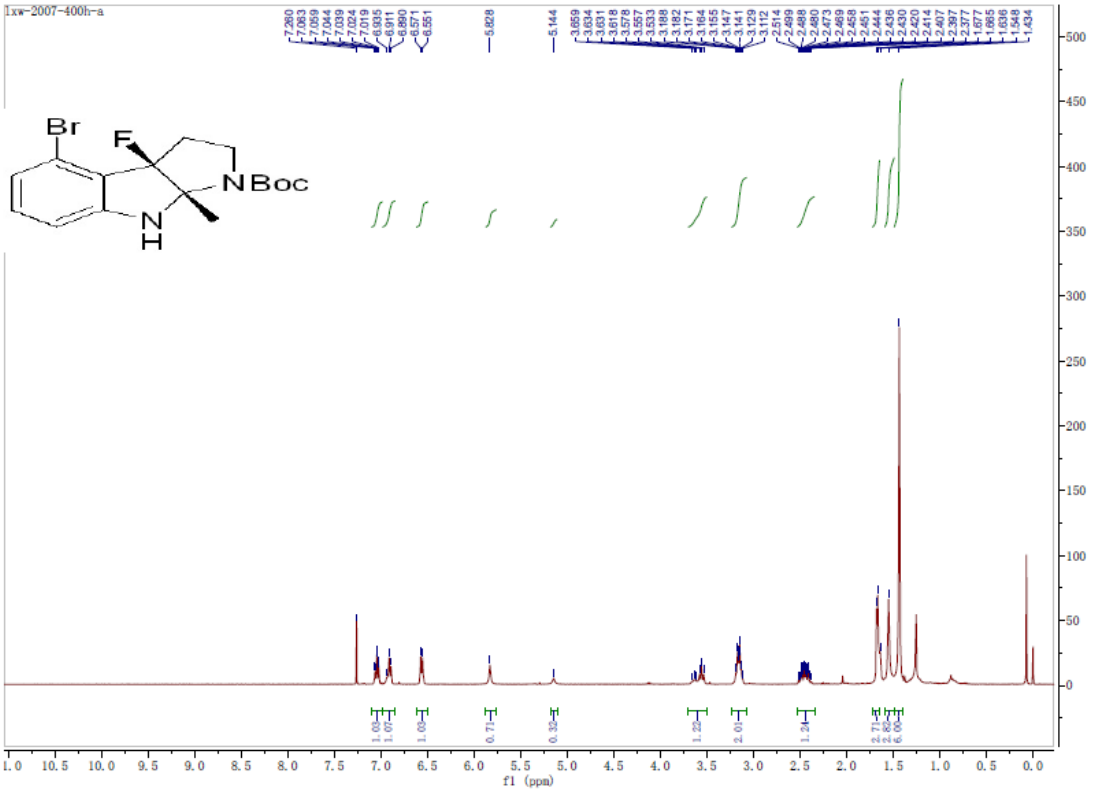
NMR Spectra of **2m**

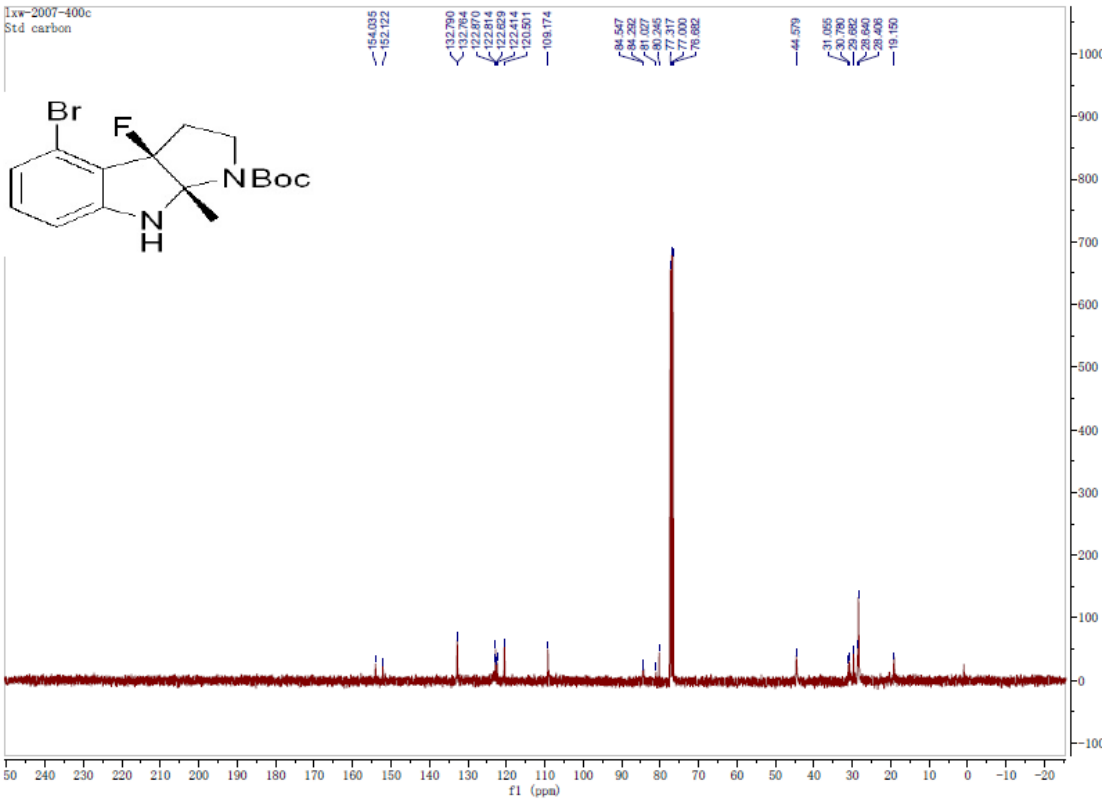

Br
F
N
O
NH
CH3
O
CH3
CH3
H3C

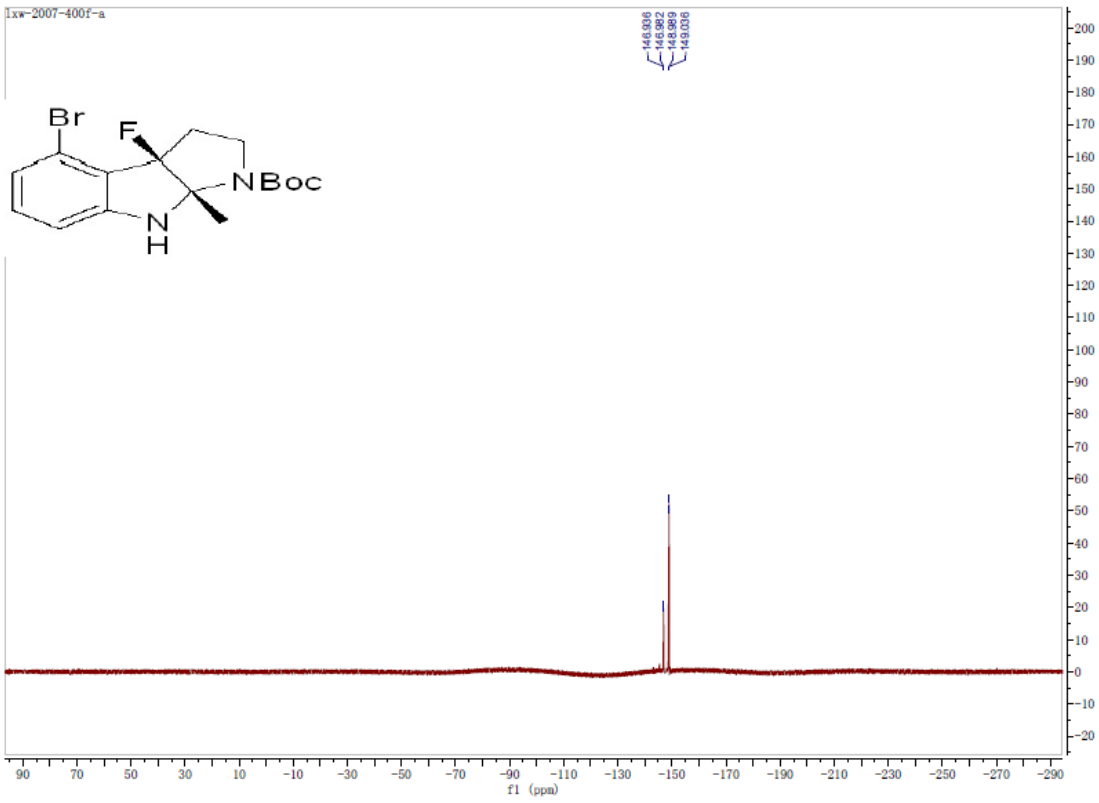

lxw-4-32-400c
Std carbon
Br
F
N
Boc
N
H



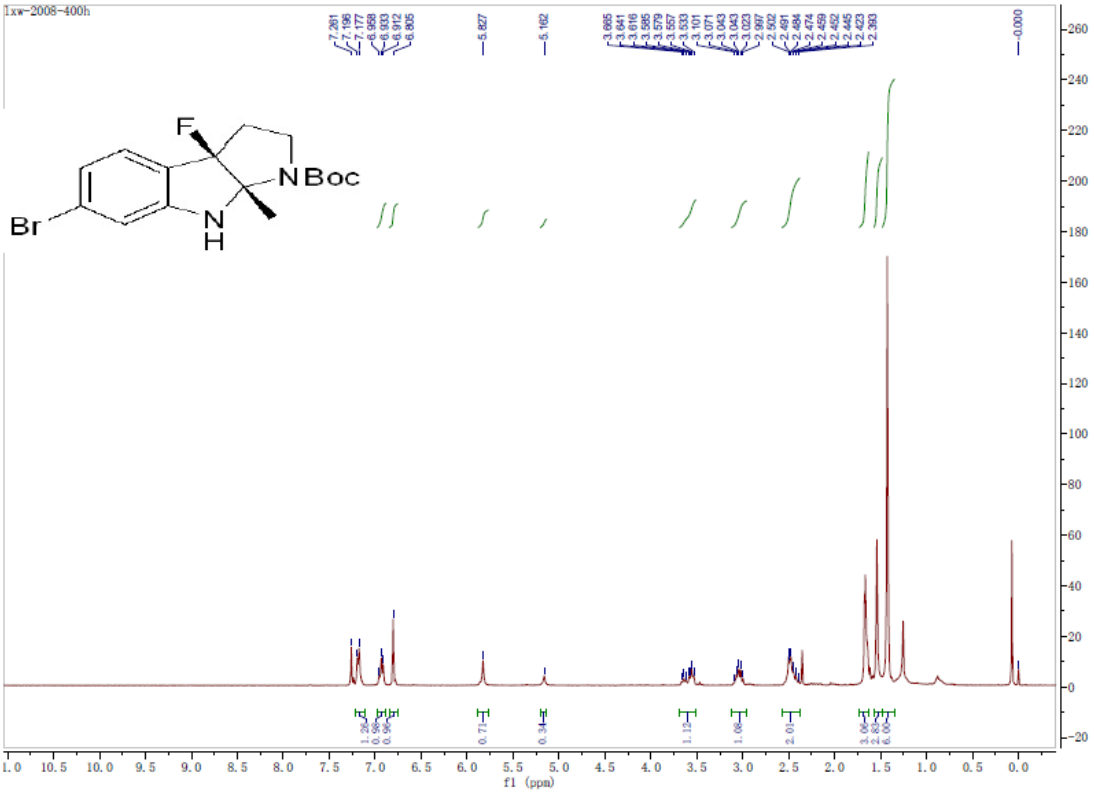
NMR Spectra of **2n**

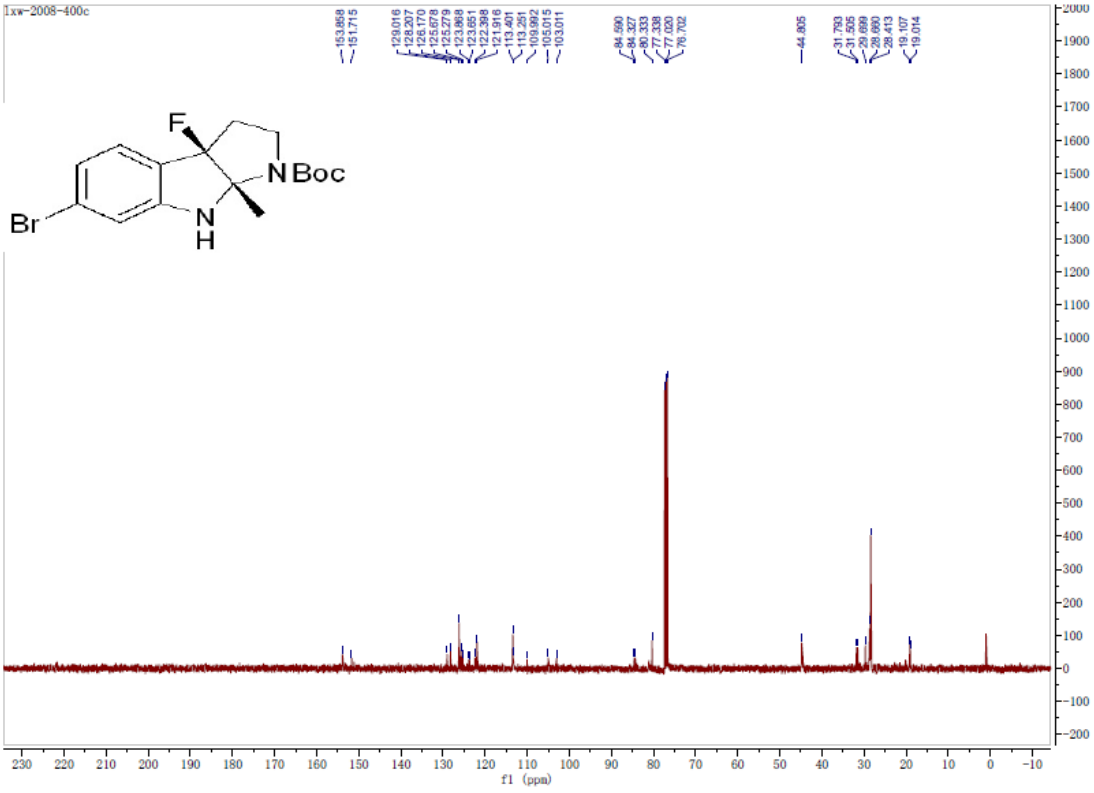

lxw-2007-400h-a
Br
F
NBoc
N
H
f1 (ppm)

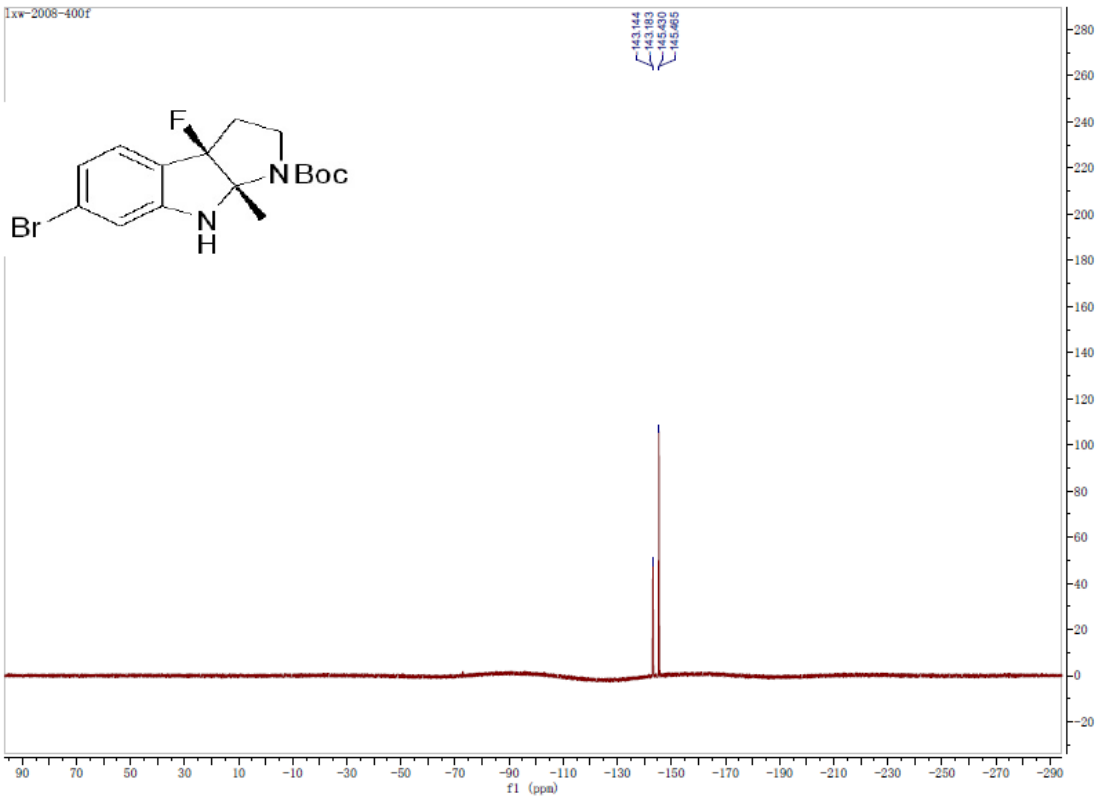

lxw-2007-400c
Std carbon
Br
F
NBoc
N
H
f1 (ppm)



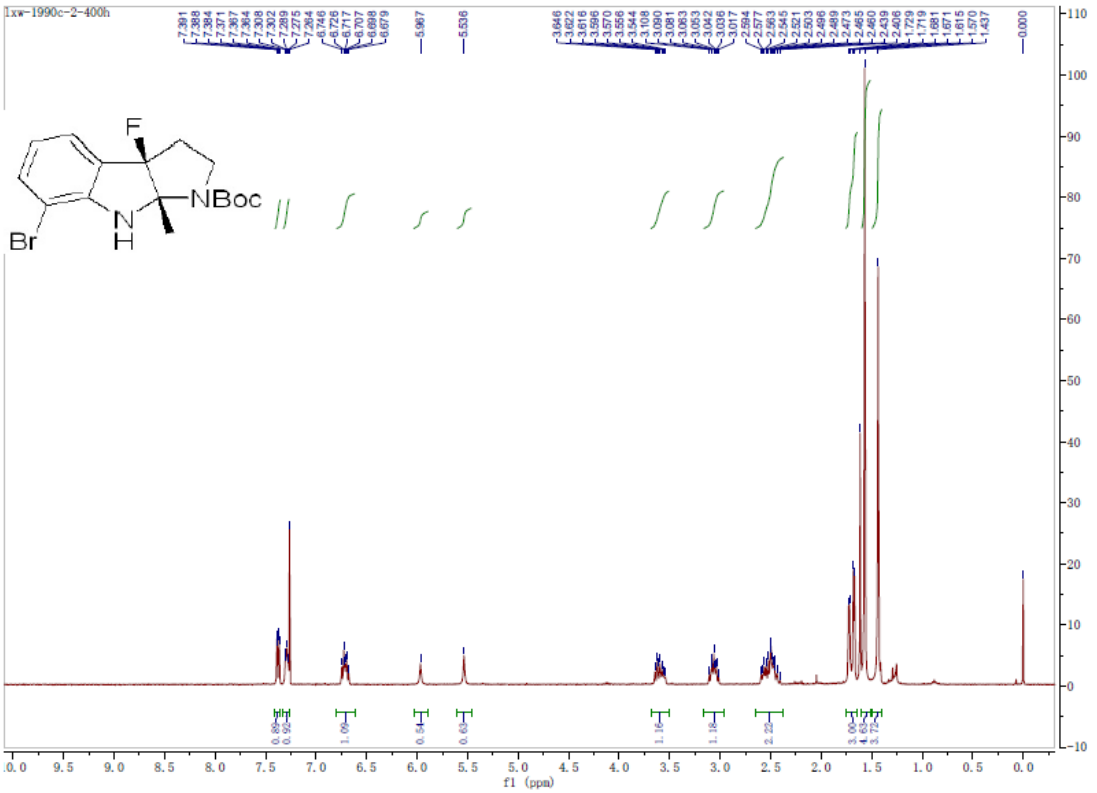
NMR Spectra of **2o**

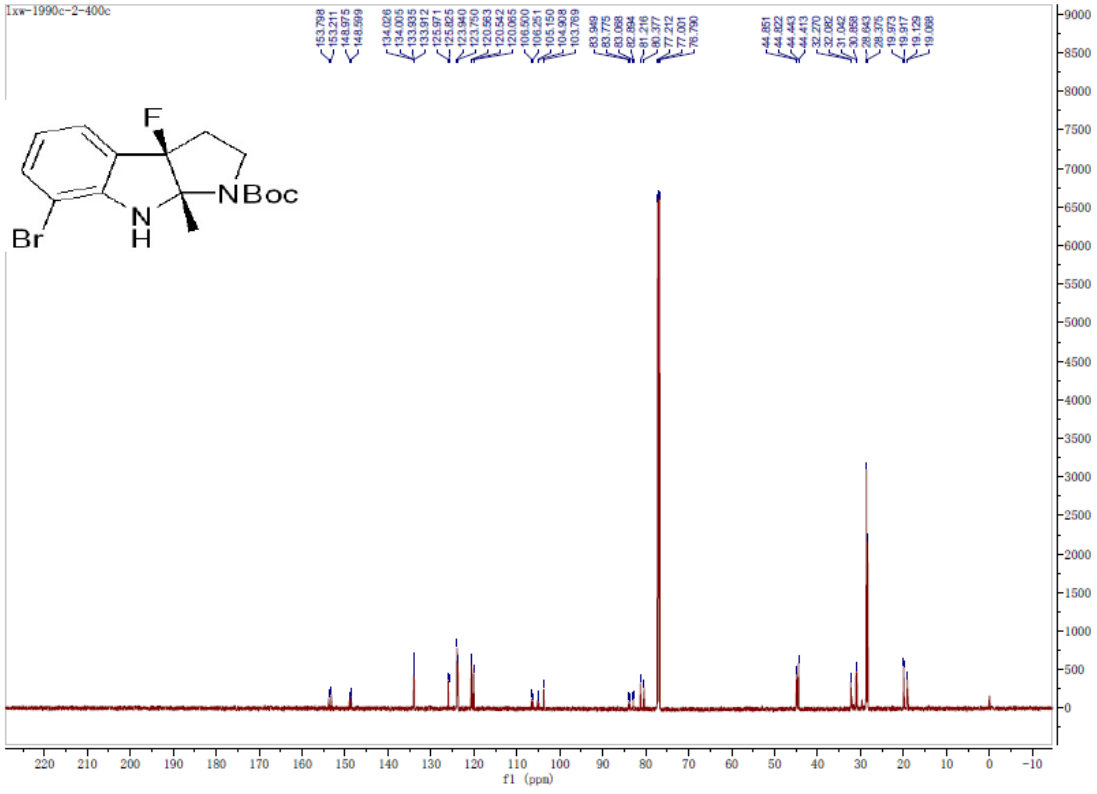

1xw-2008-400h
F
NBoc
Br
N
H
f1 (ppm)

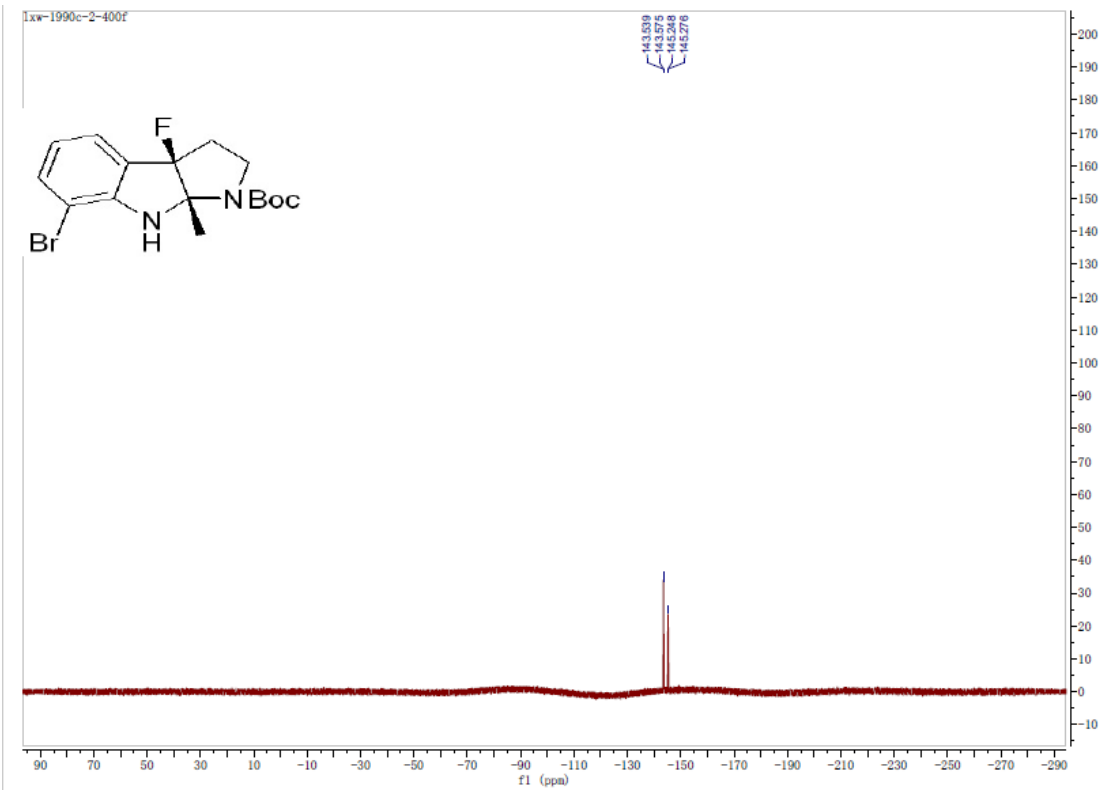

1xw-2008-400c
F
NBoc
Br
N
H
f1 (ppm)



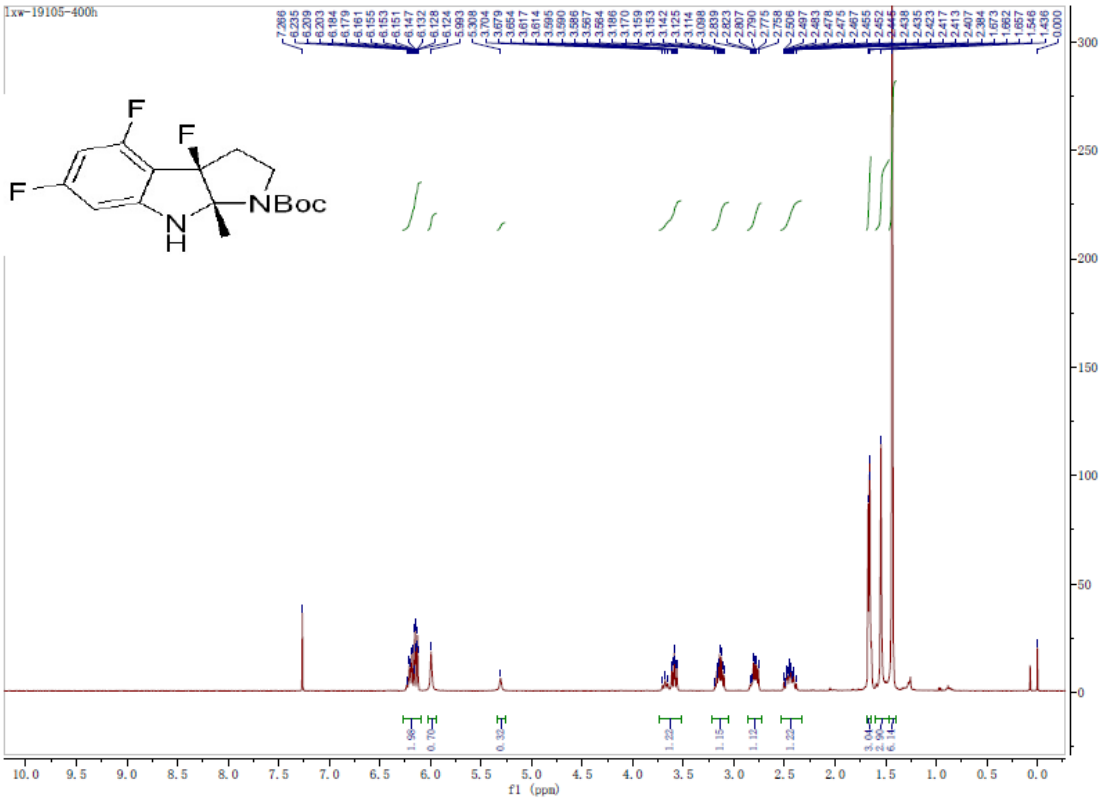
NMR Spectra of **2p**

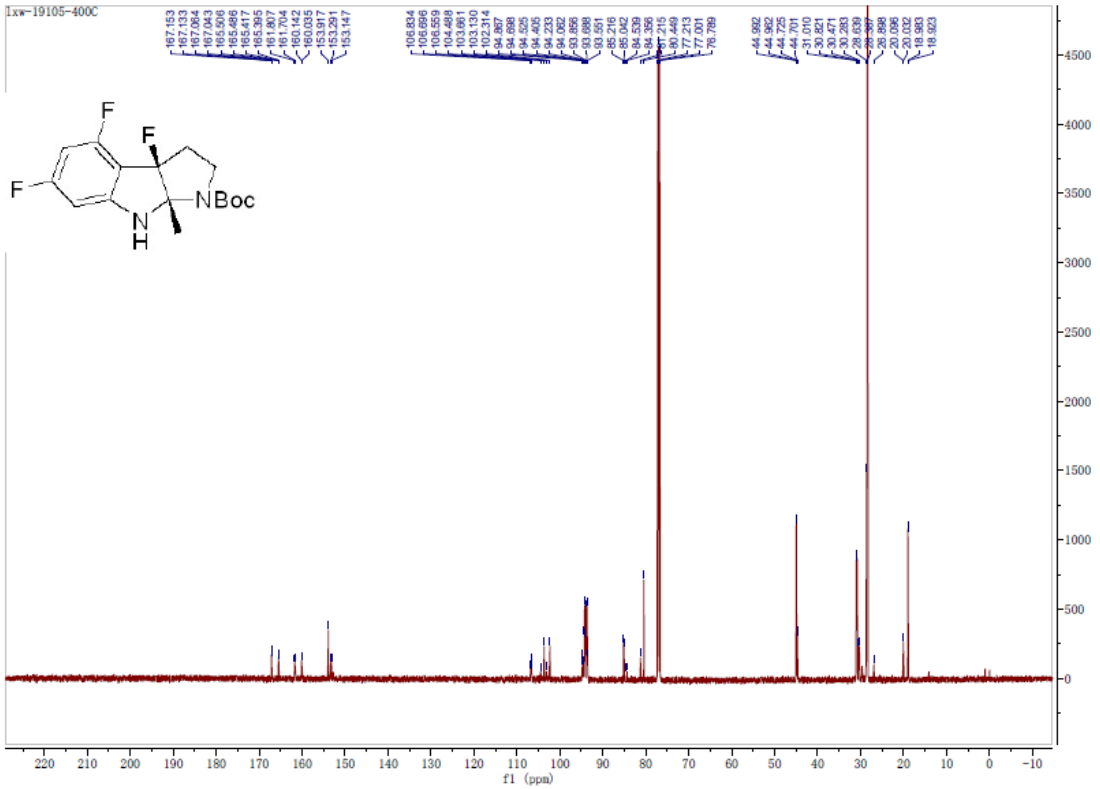

lxw-1990c-2-400h
F
NBoc
N
H
Br
f1 (ppm)

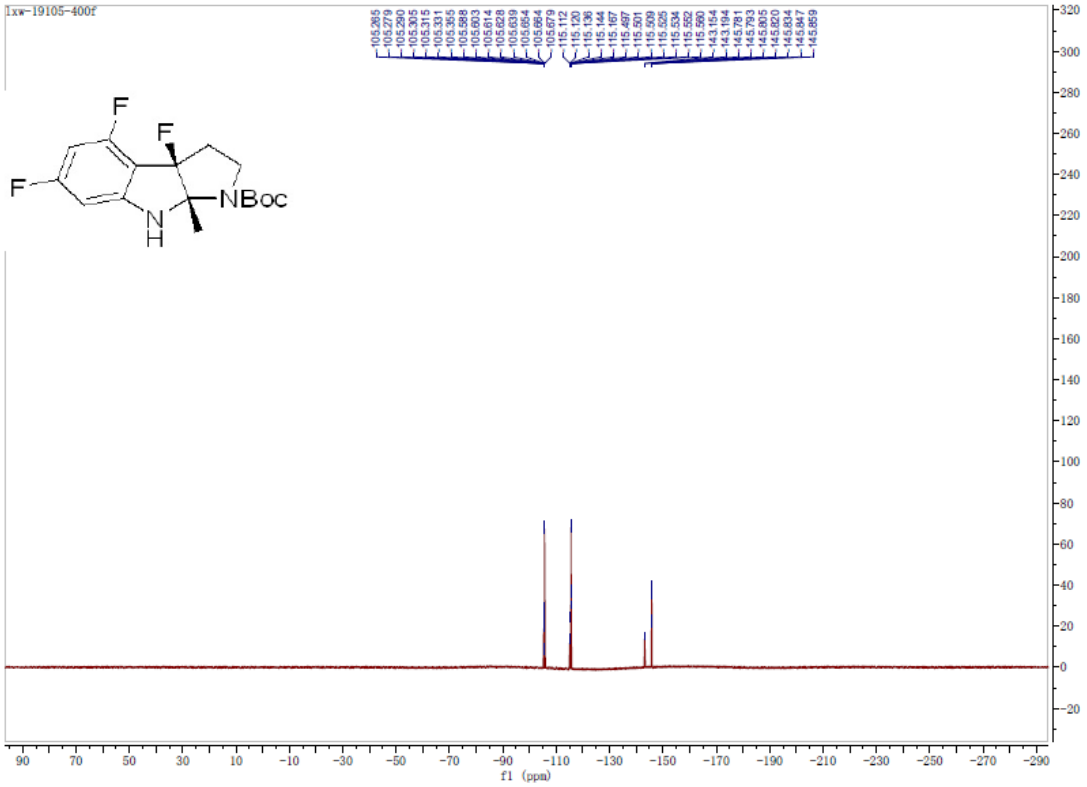

lxw-1990c-2-400c
F
NBoc
N
H
Br
f1 (ppm)



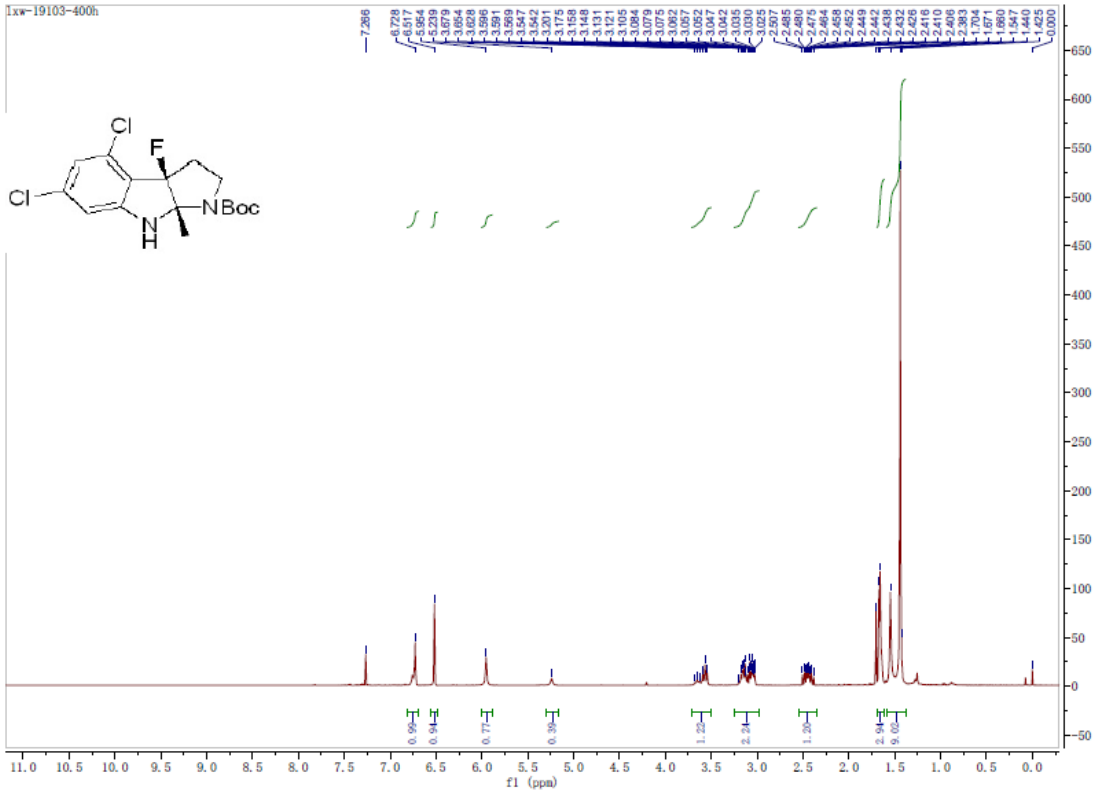
NMR Spectra of **2q**

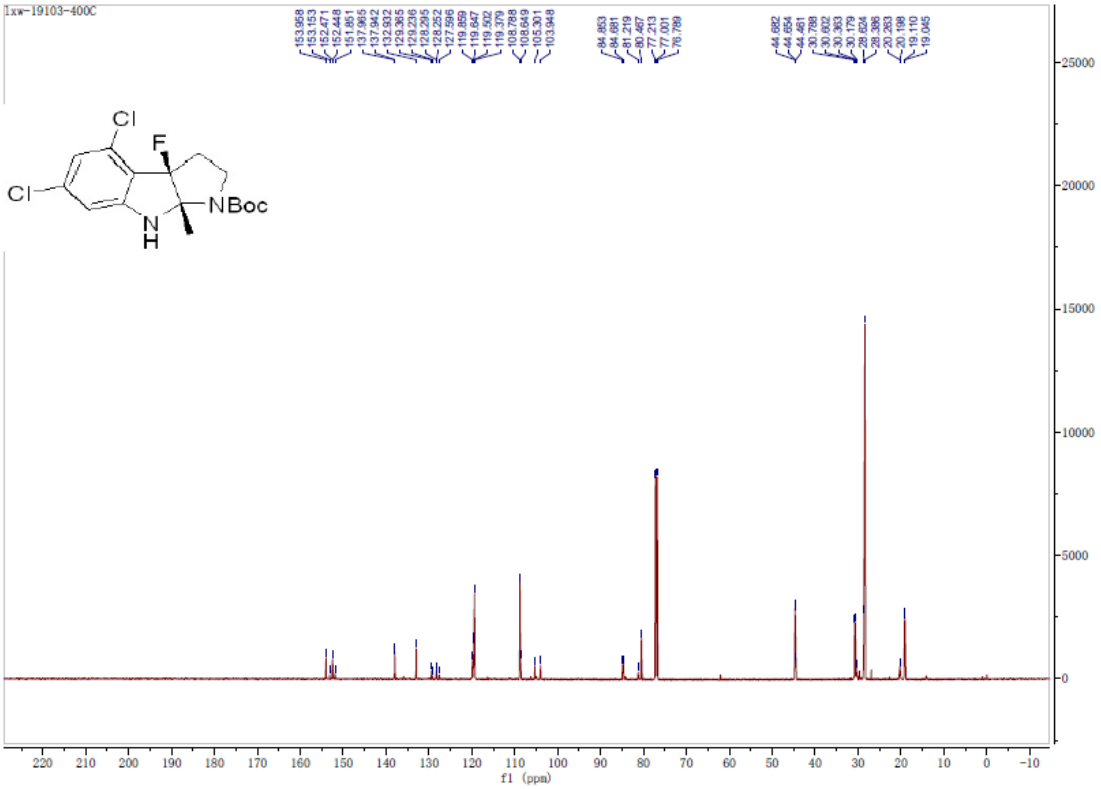

1xw-19105-400h
F
F
F
NBoc
N
H
f1 (ppm)

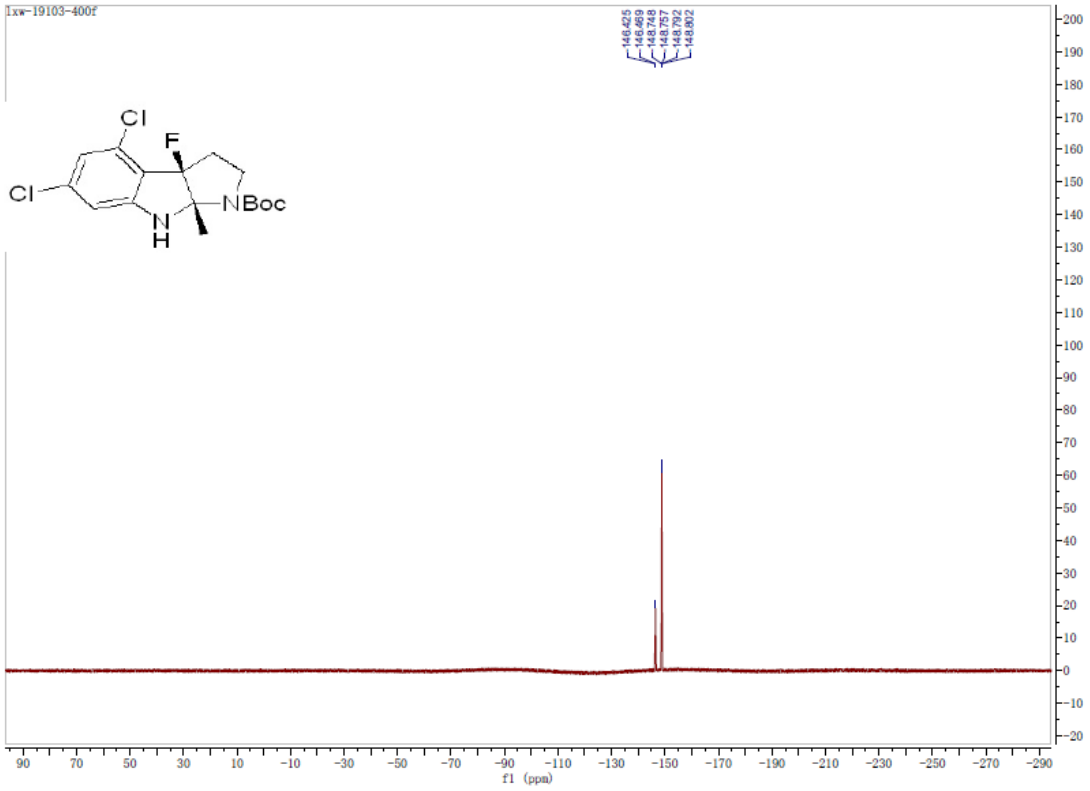

1xw-19105-400C
F
F
F
NBoc
N
H
f1 (ppm)



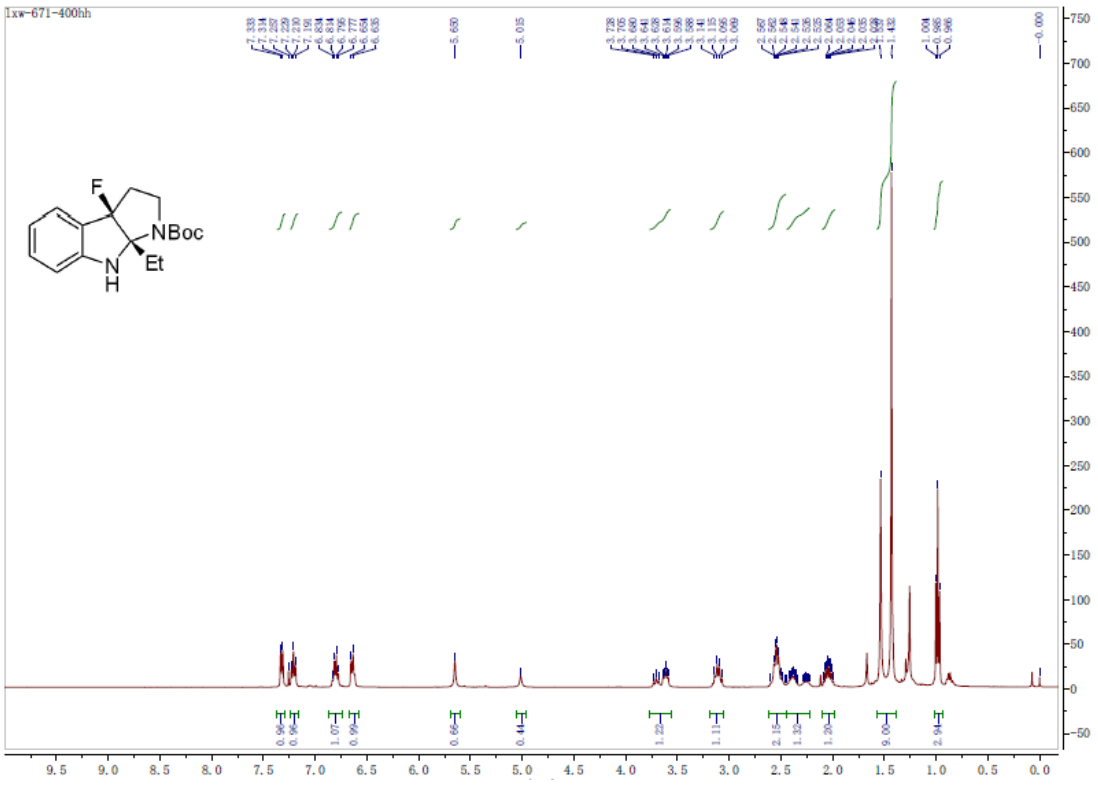
NMR Spectra of **2r**

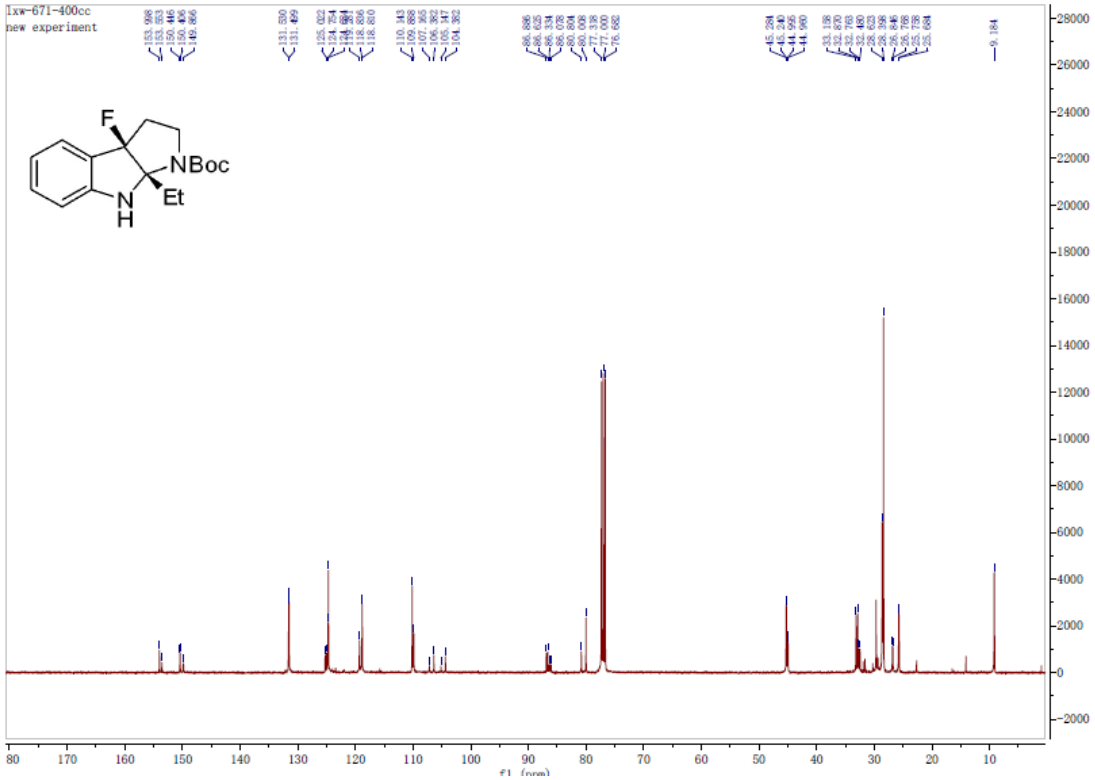

1xw-19103-400h
Cl
F
Cl
NBoc
N
H
f1 (ppm)

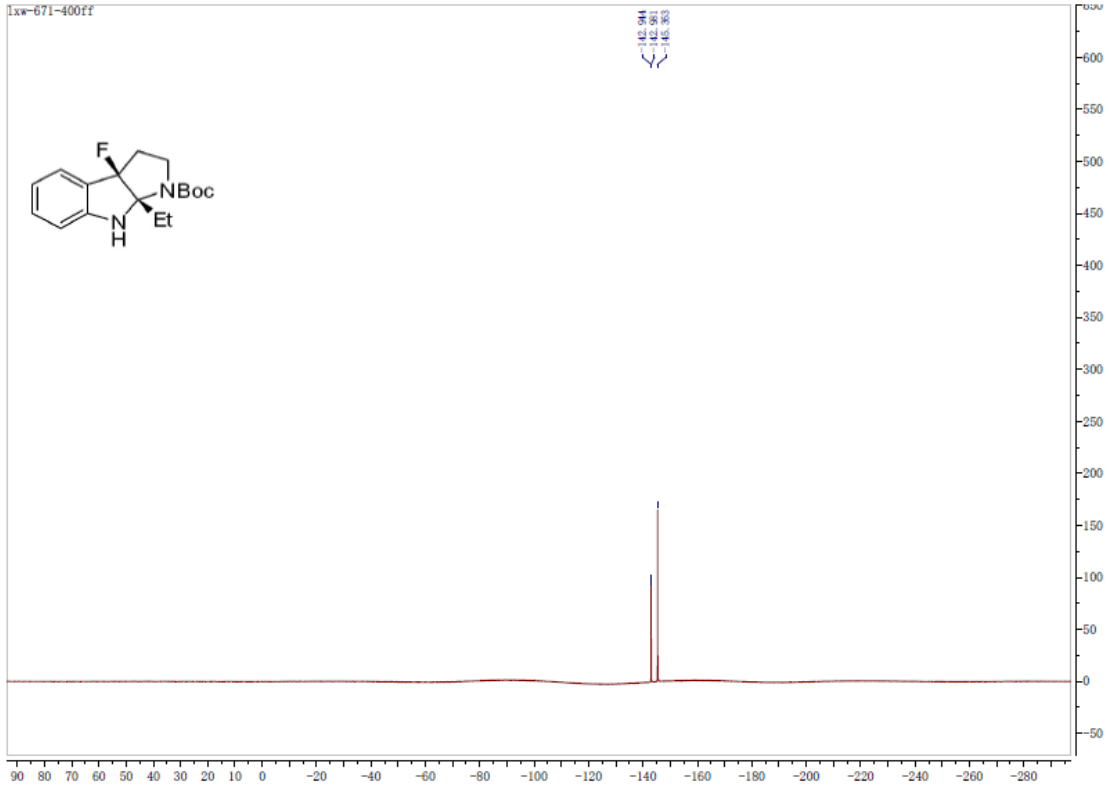

1xw-19103-400C
Cl
F
Cl
NBoc
N
H
f1 (ppm)



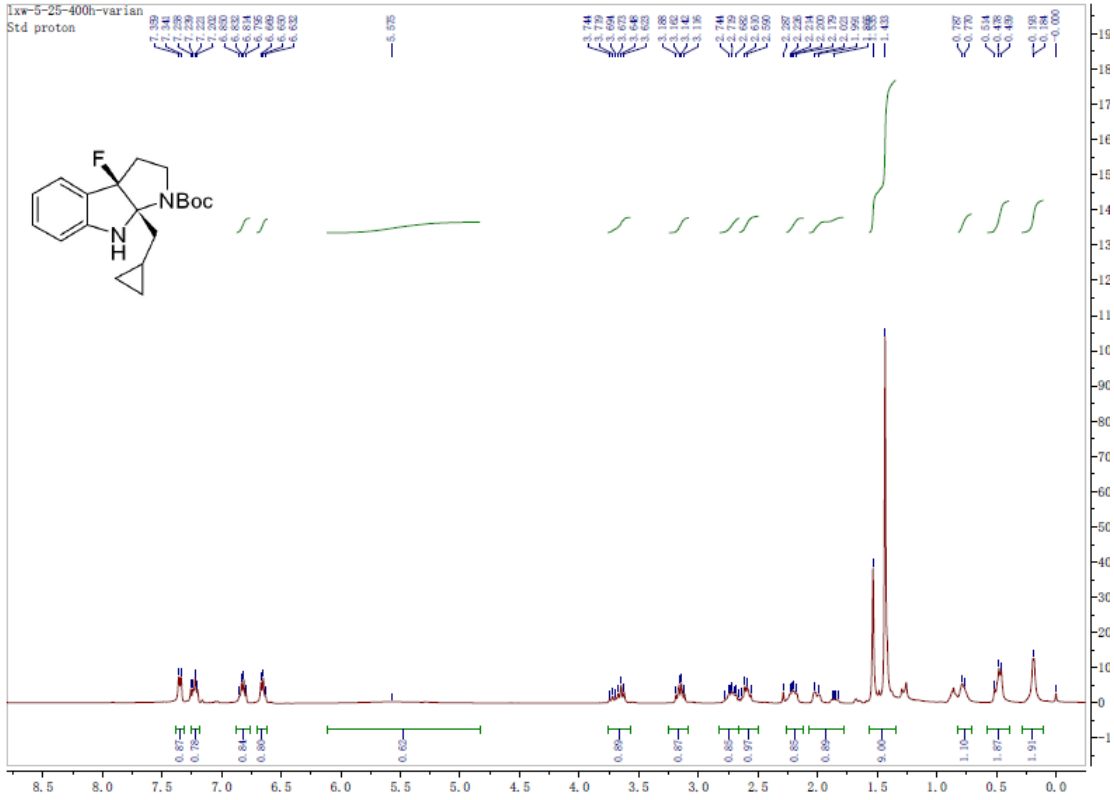
NMR Spectra of **2s**

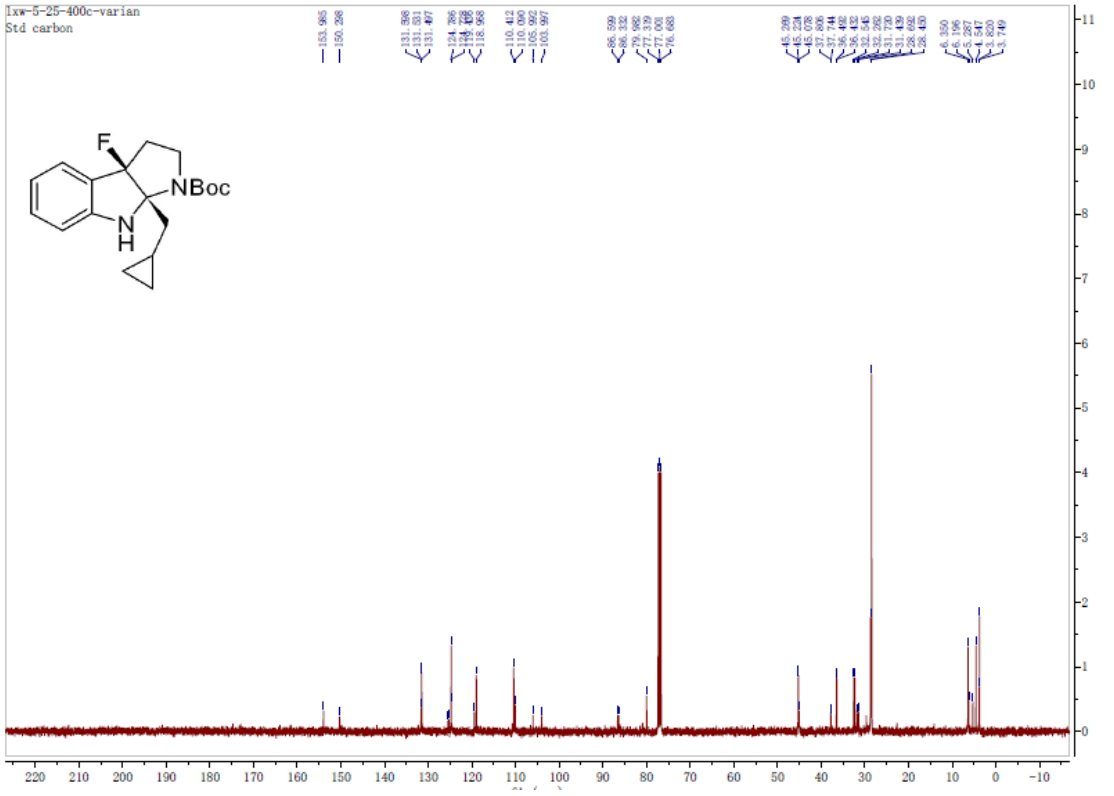

1xw-671-400hh
F
NBoc
N
H
Et

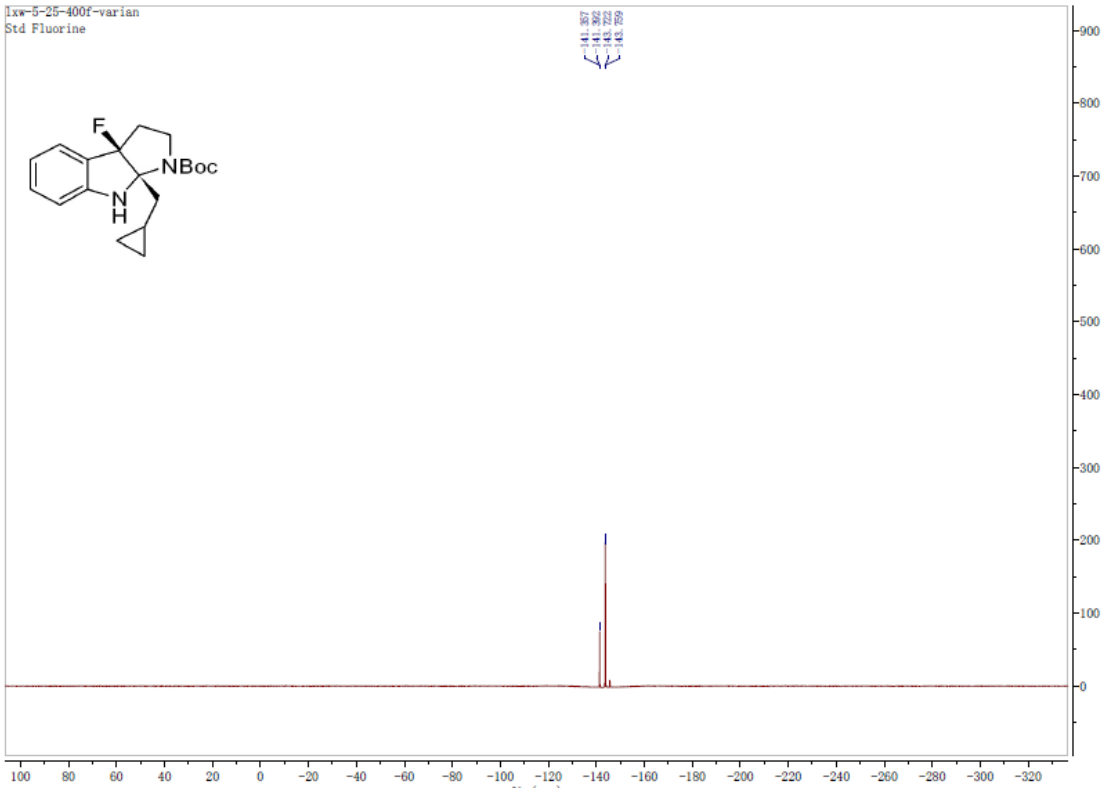

1xw-671-400cc
new experiment
F
NBoc
N
H
Et



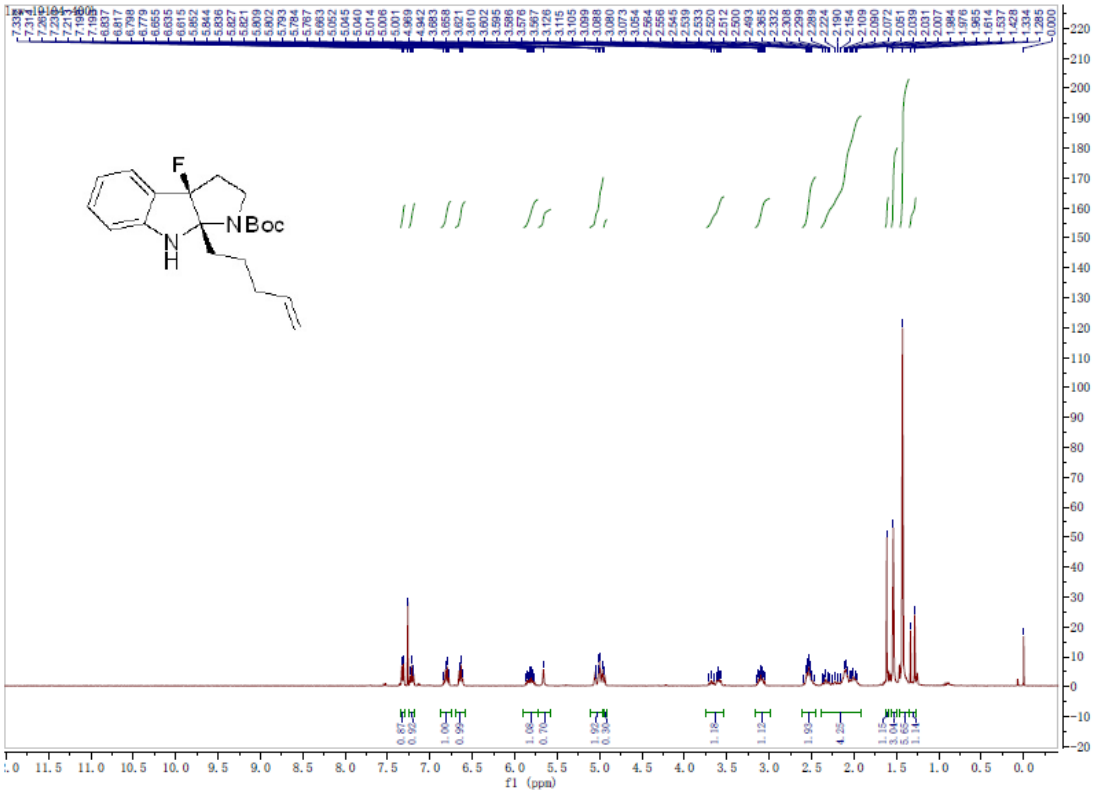
NMR Spectra of **2t**

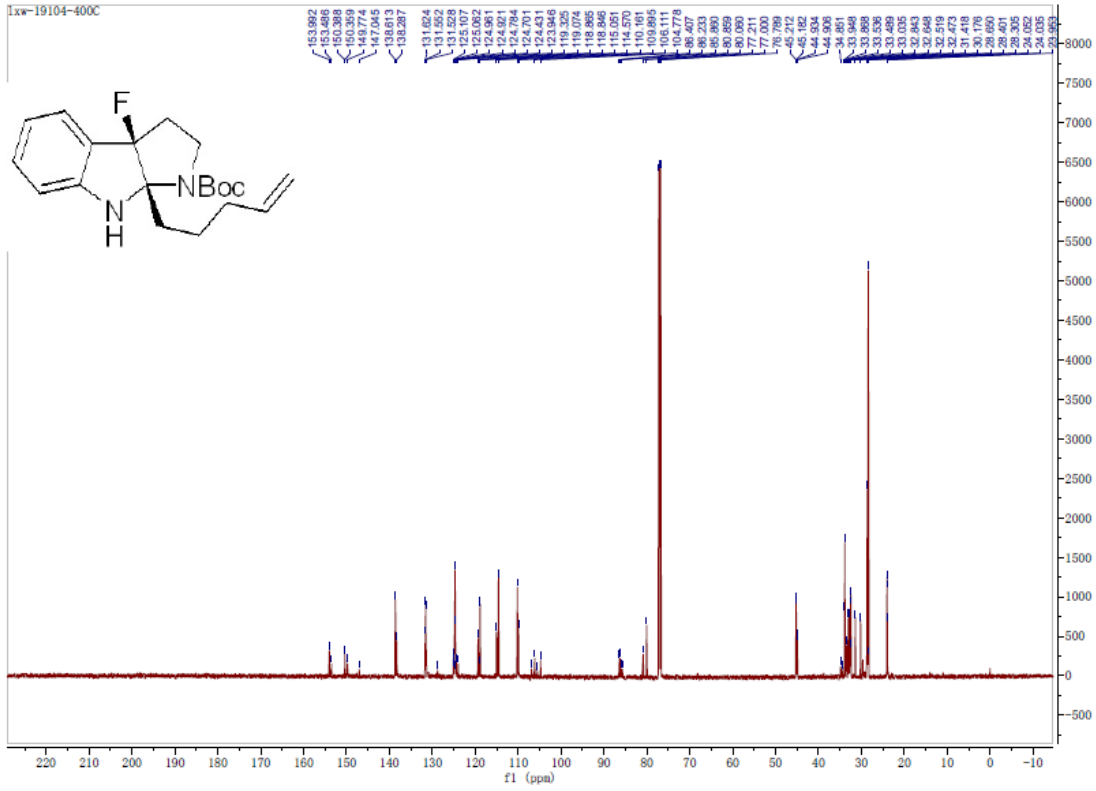

lxw-5-25-400h-varian
Std proton
F
NBoc
N
H

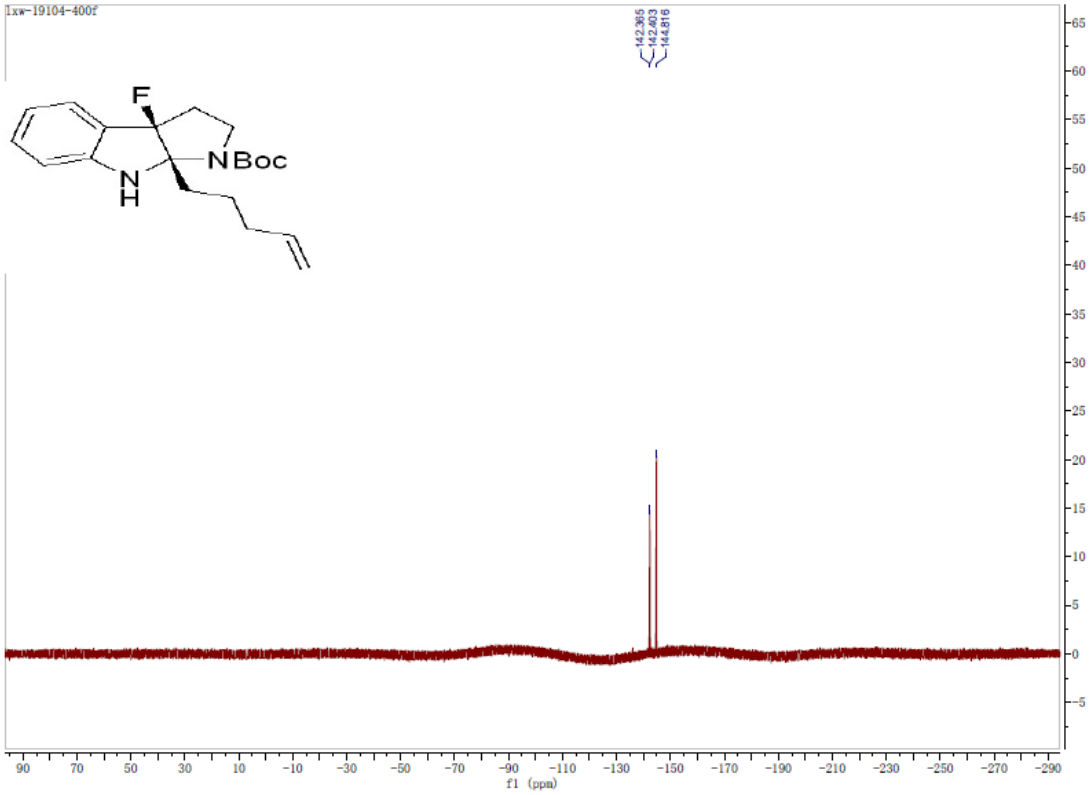

lxw-5-25-400c-varian
Std carbon
F
NBoc
N
H



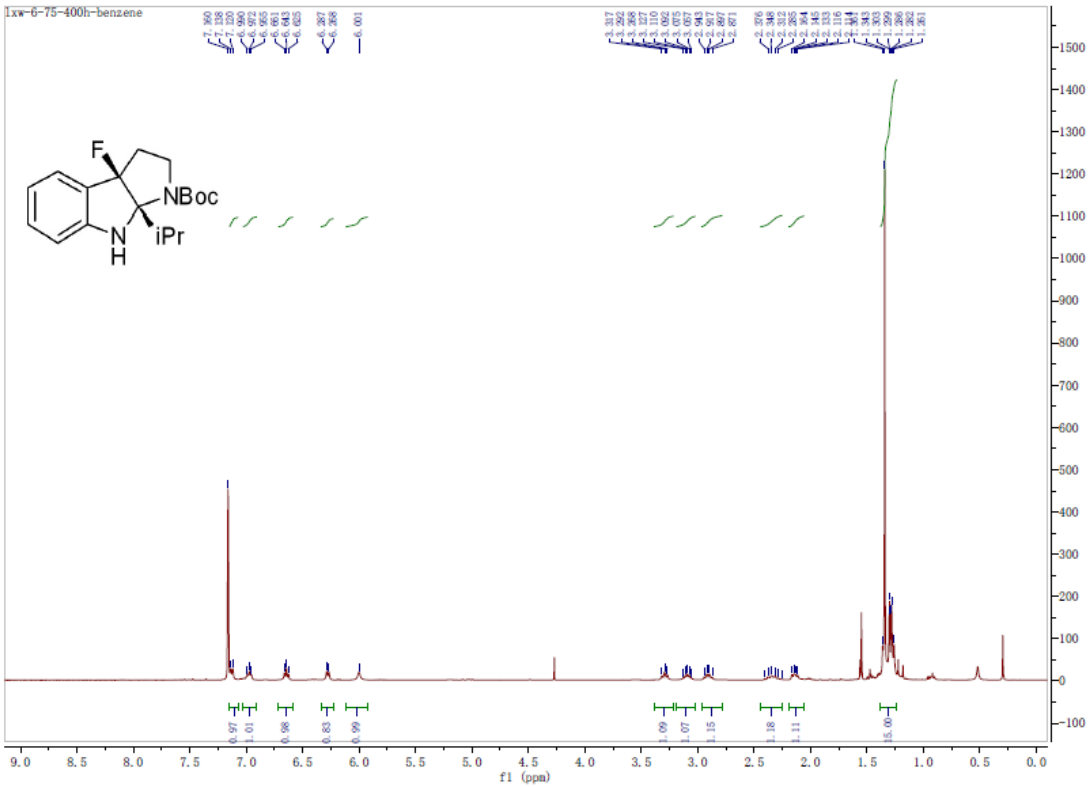
NMR Spectra of **2u**

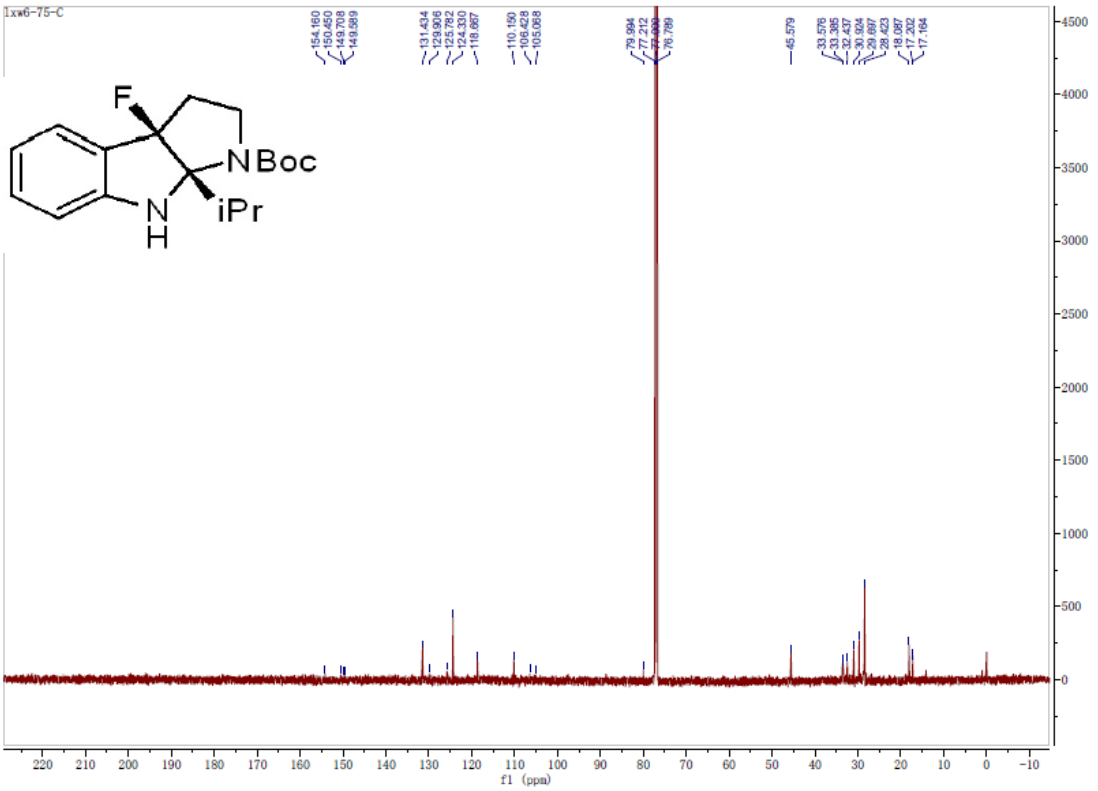

F
NBoc
N
H
f1 (ppm)

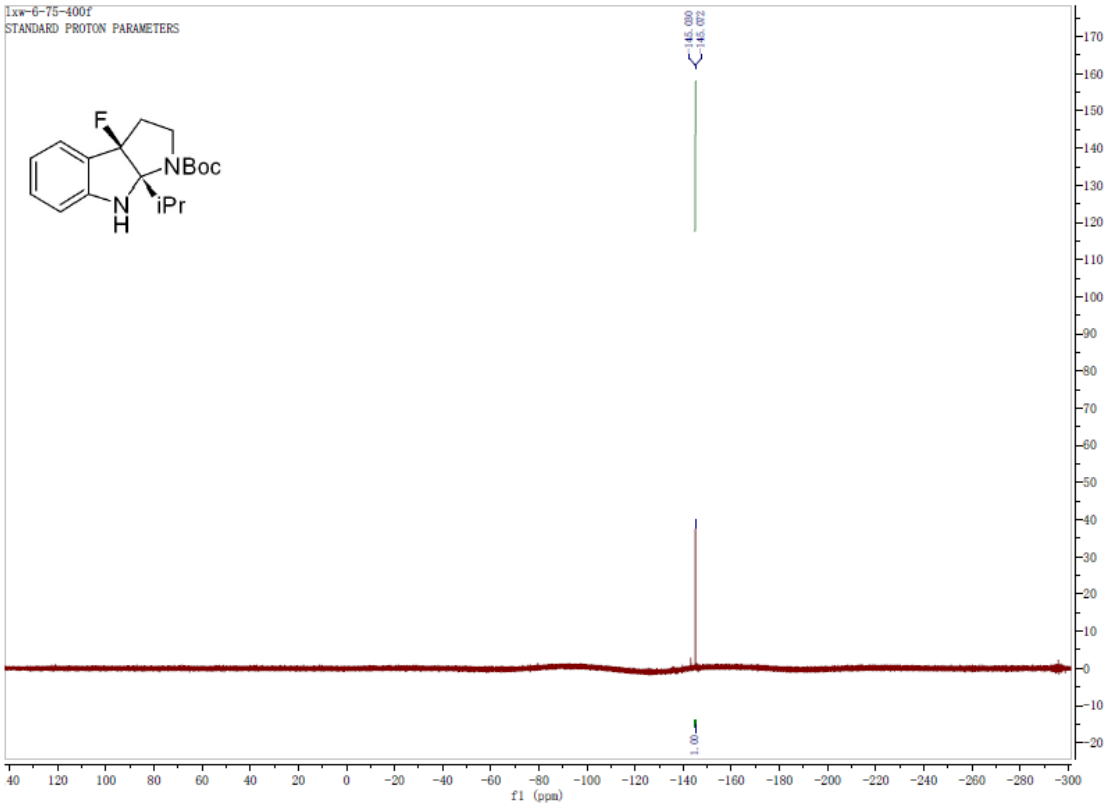

1xw-19104-400C
F
NBoc
N
H
f1 (ppm)



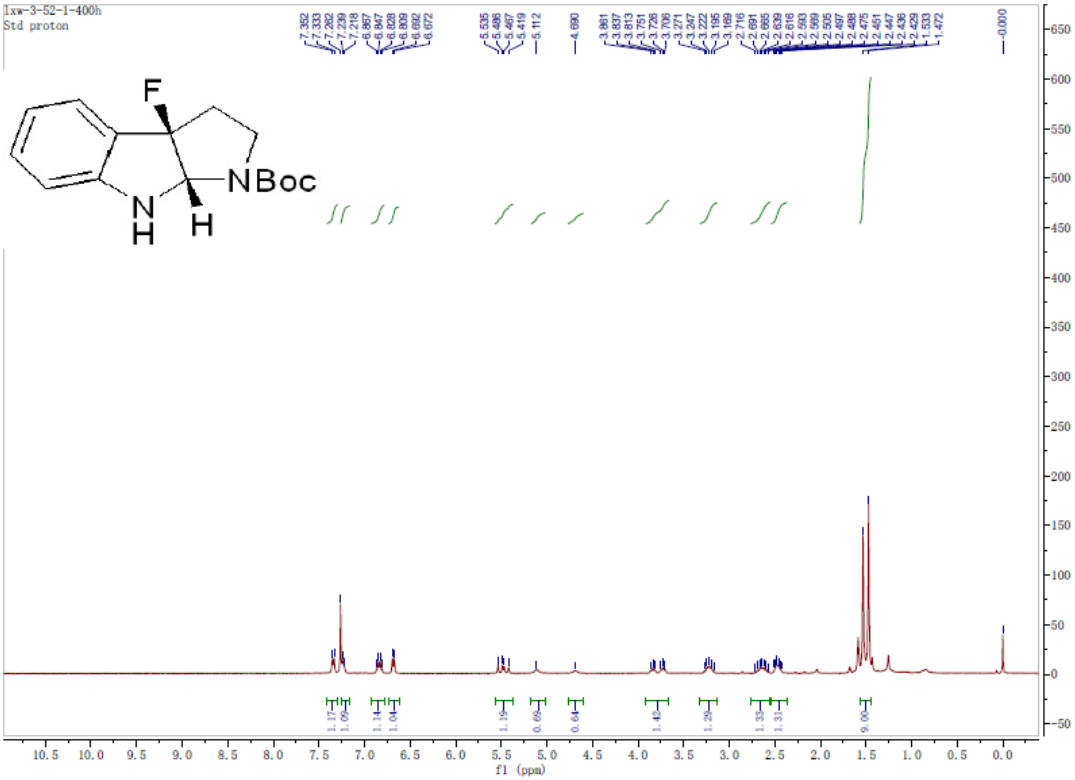
NMR Spectra of **2v**

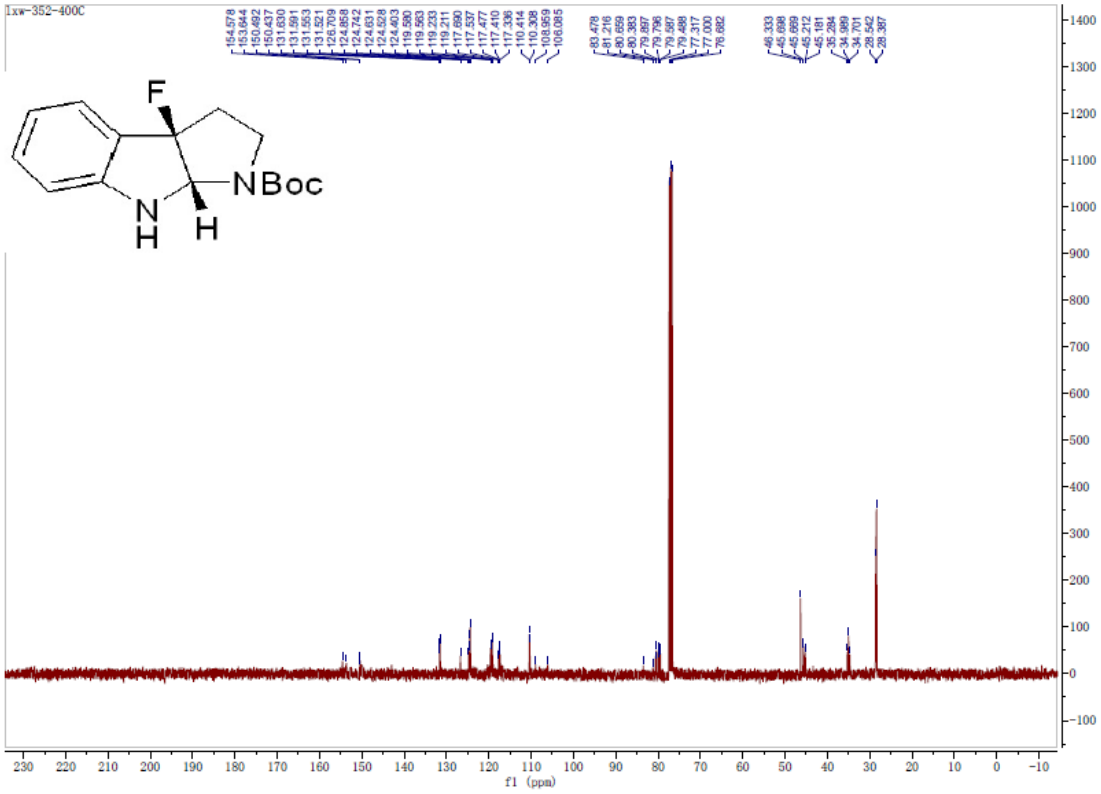


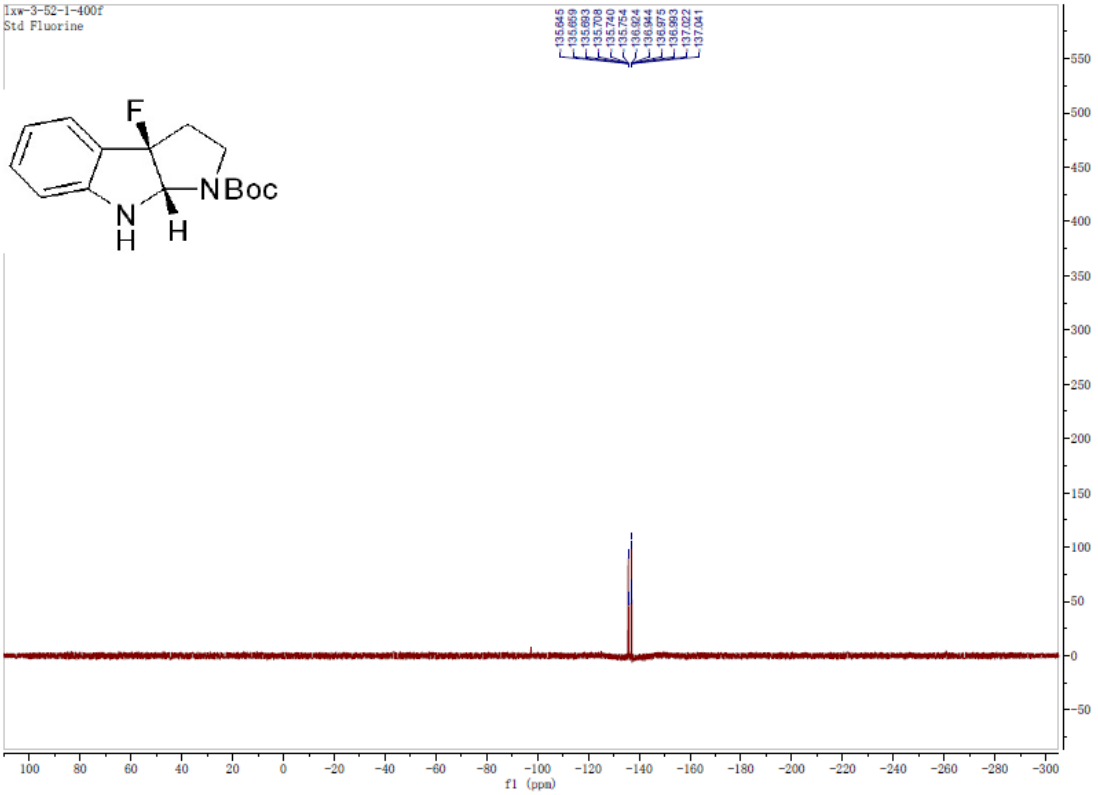

lxw6-75-C
F
NBoc
N
H
iPr
f1 (ppm)


lxw-6-75-400f
STANDARD PROTON PARAMETERS
F
NBoc
N
H
iPr
f1 (ppm)

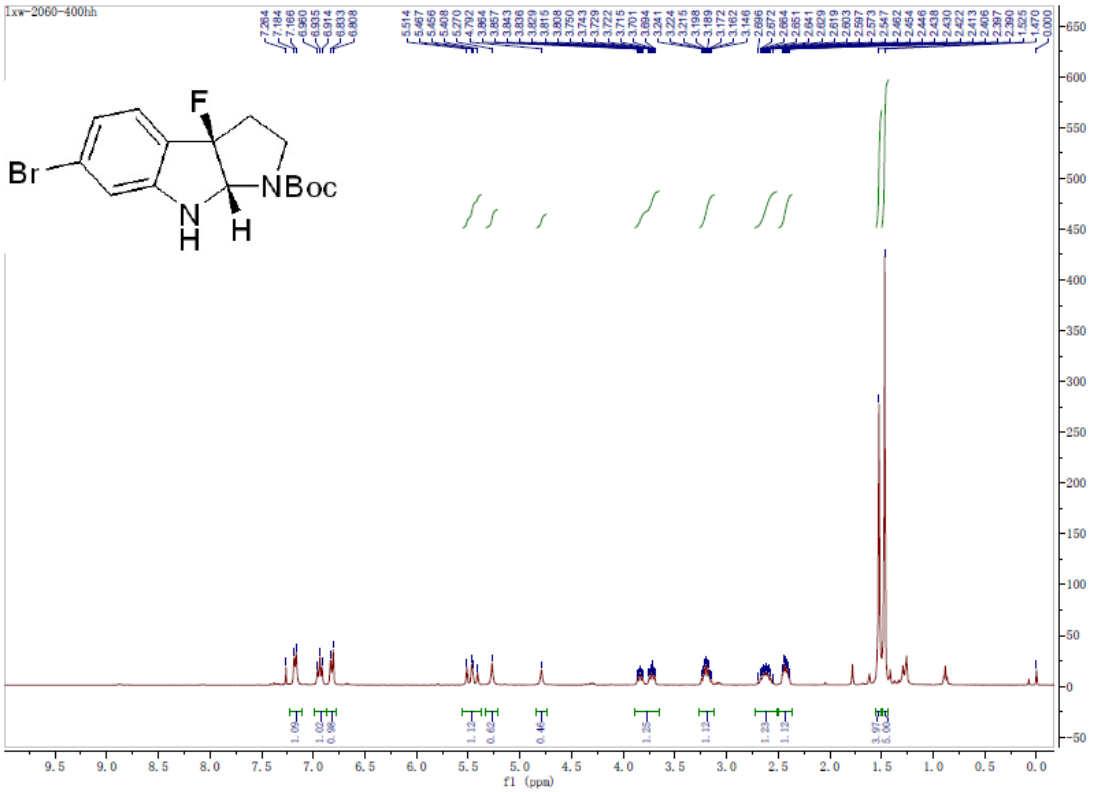
NMR Spectra of **2w**

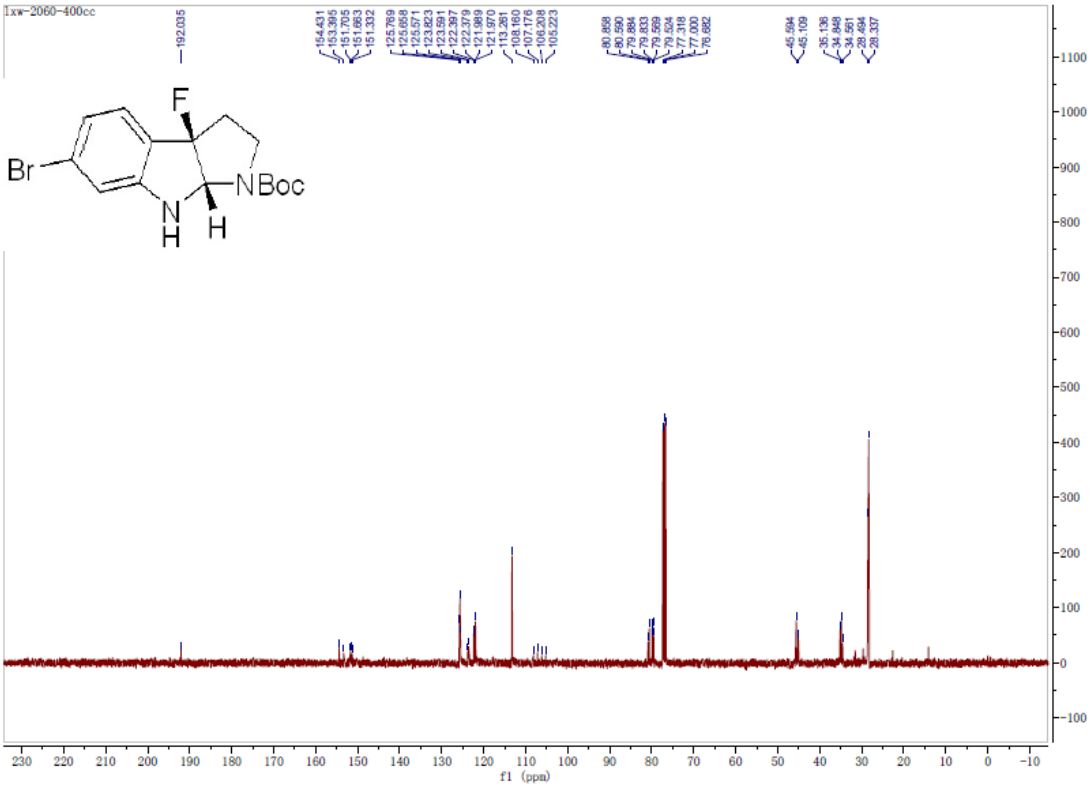

lxw-3-52-1-400h
Std proton
F
NBoc
N
H
H
f1 (ppm)

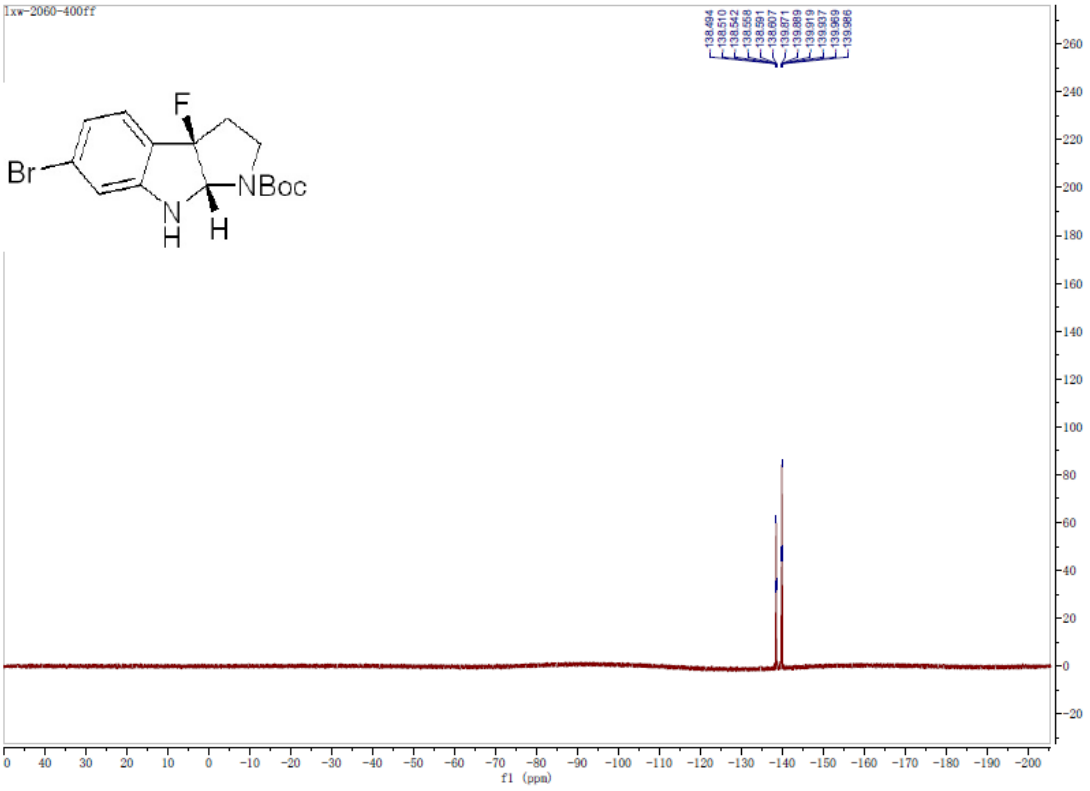

lxw-352-400C
F
NBoc
N
H
H
f1 (ppm)



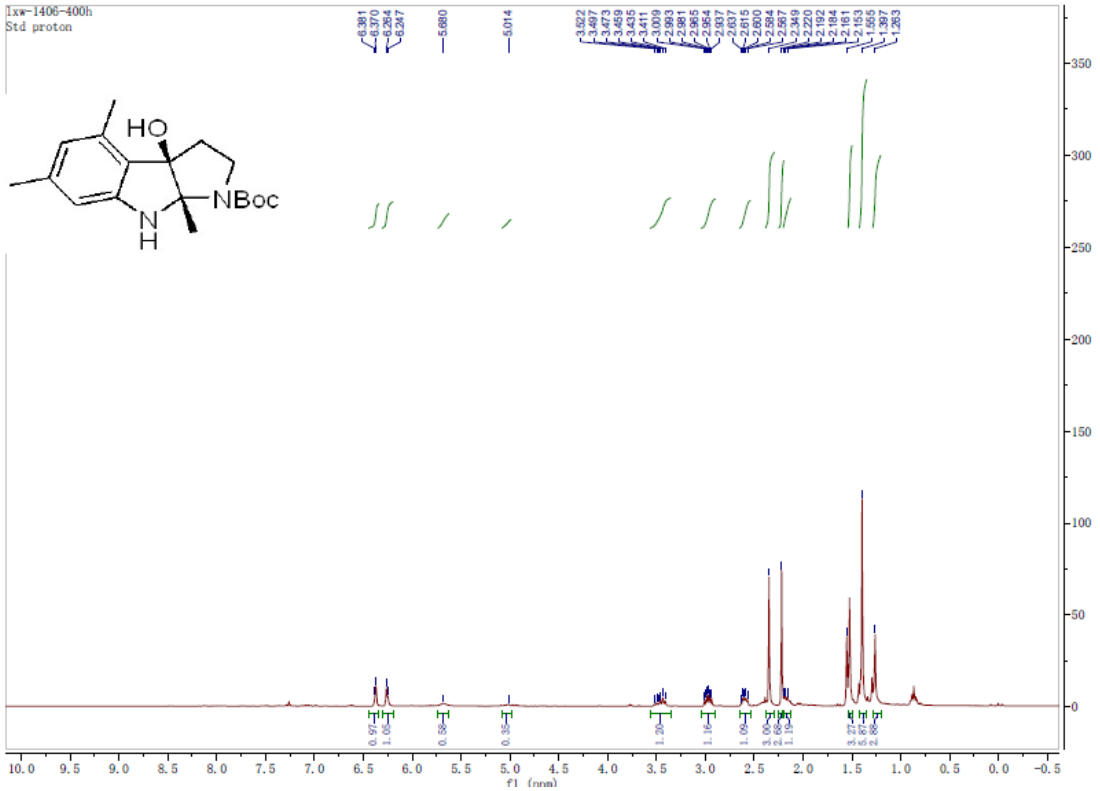
NMR Spectra of **2x**

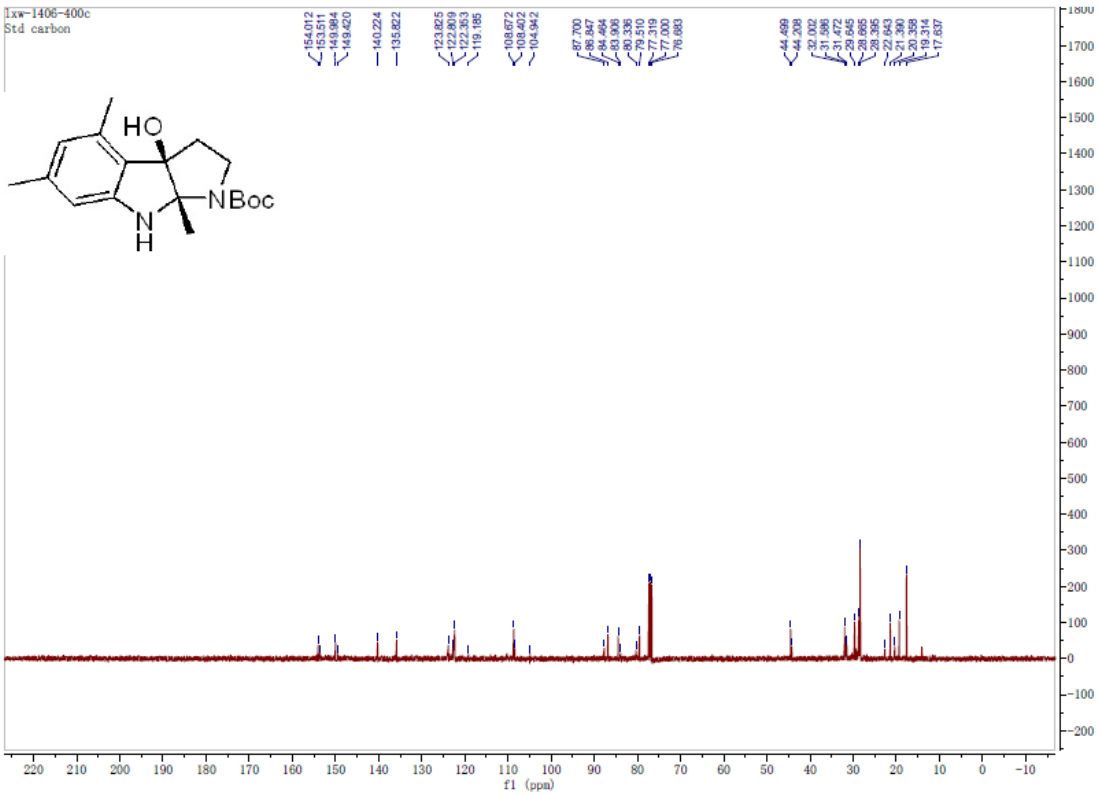

1xw-2060-400hh
F
Br
NBoc
N
H
H
f1 (ppm)


1xw-2060-400cc
F
Br
NBoc
N
H
H
f1 (ppm)

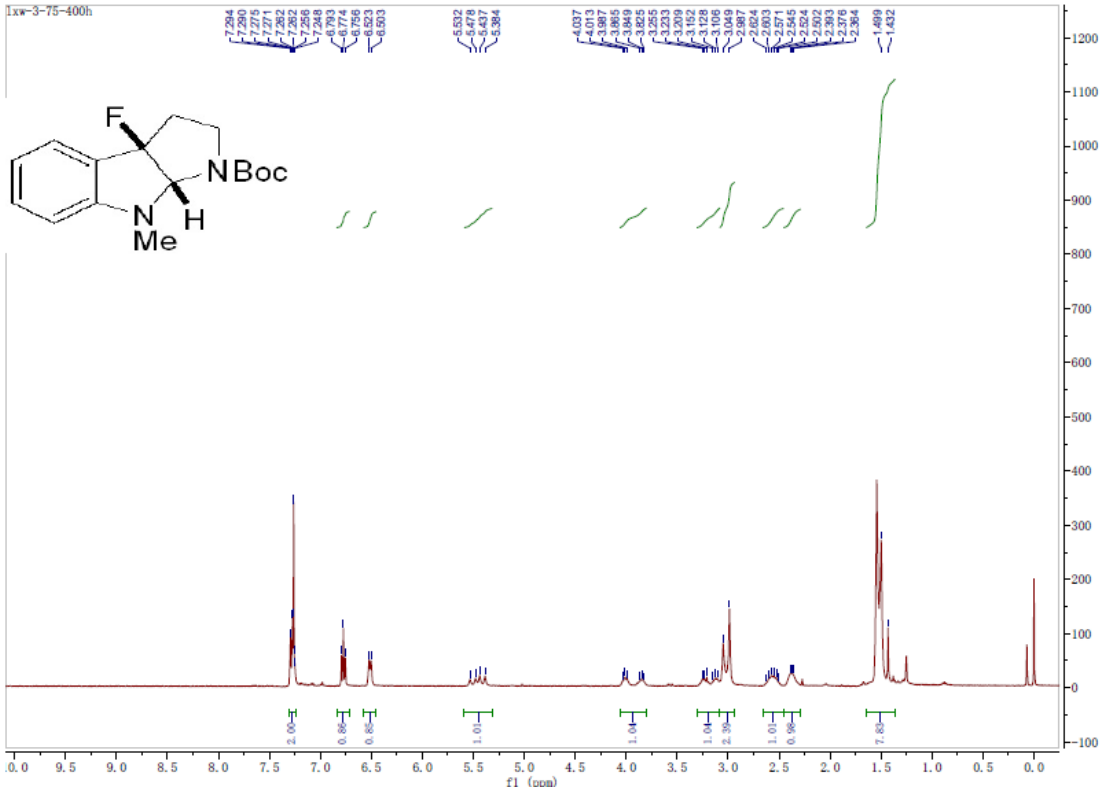


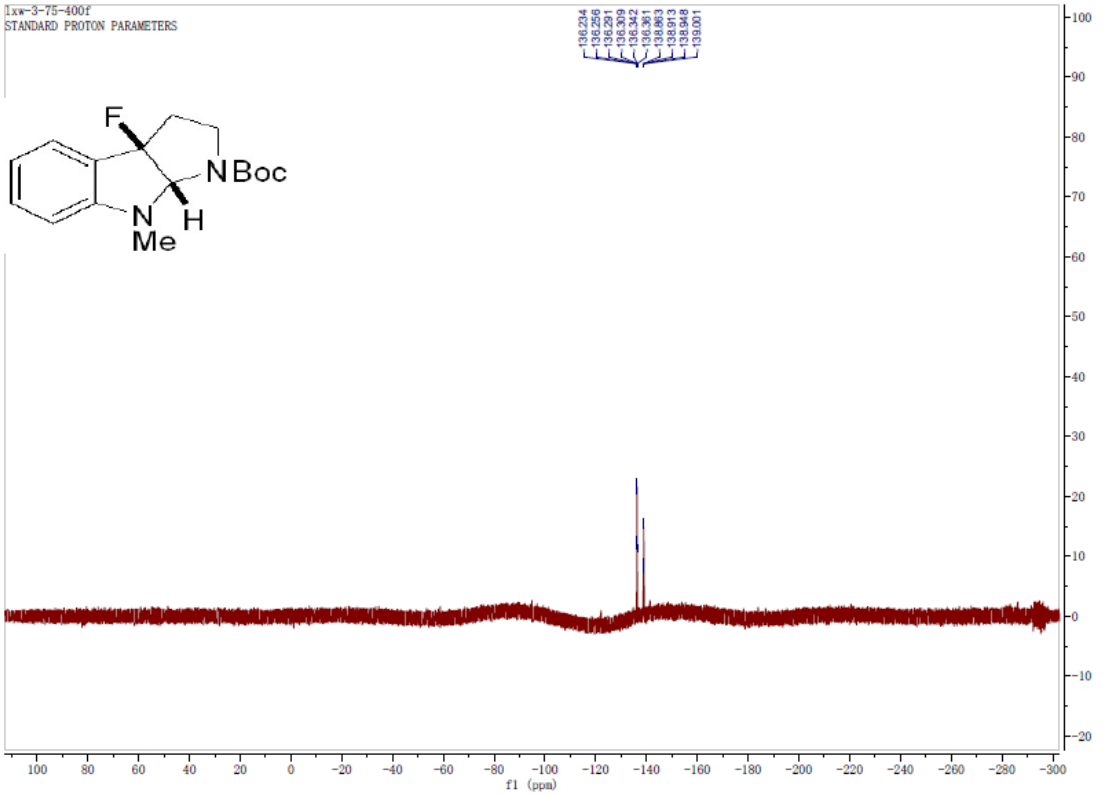
NMR Spectra of **2yy**



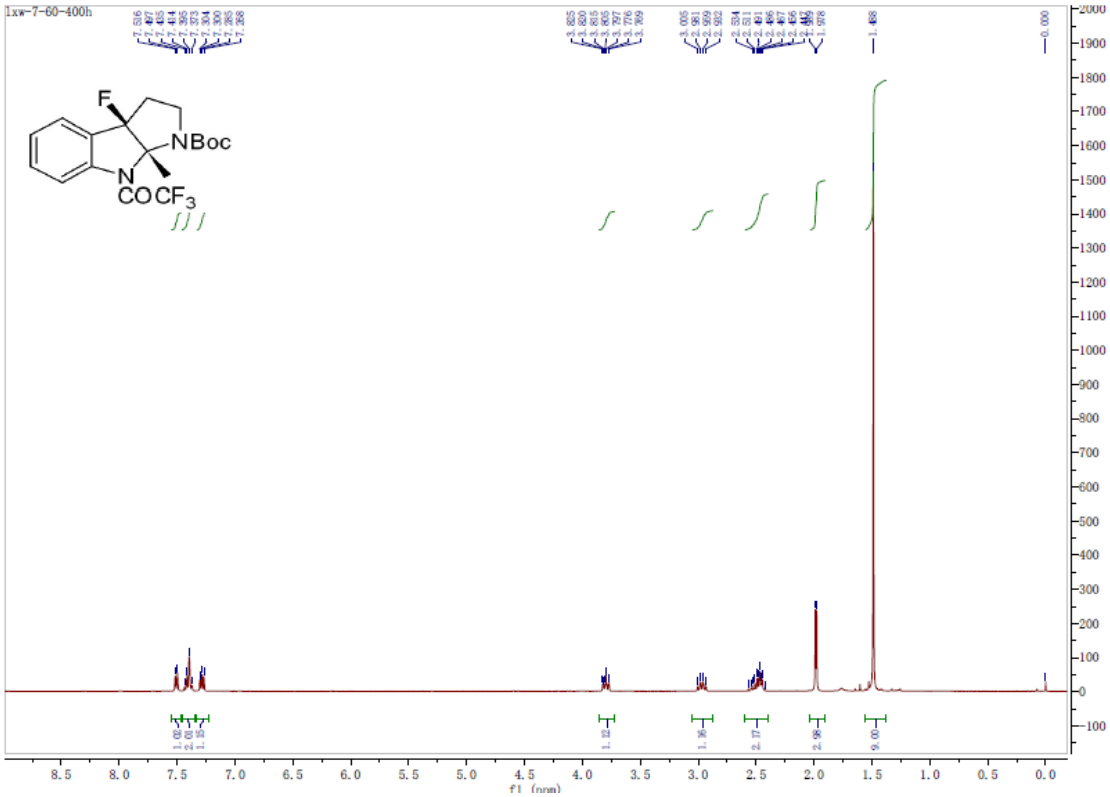


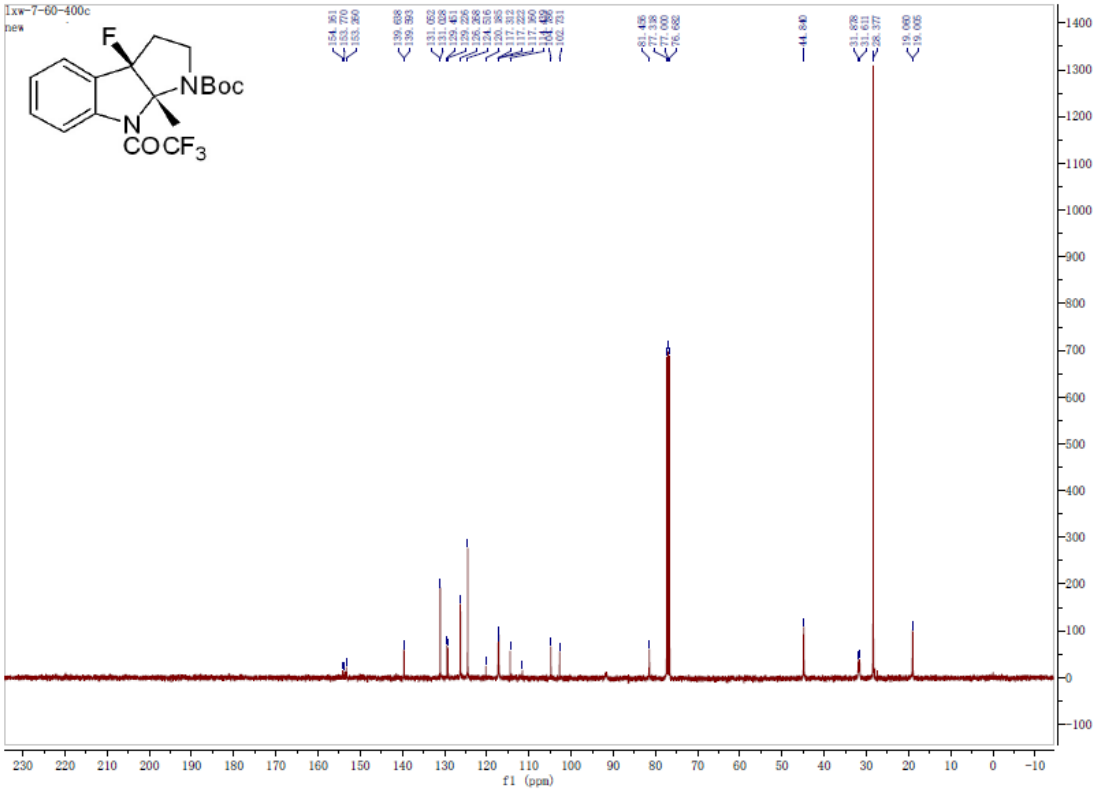
NMR Spectra of **2z**

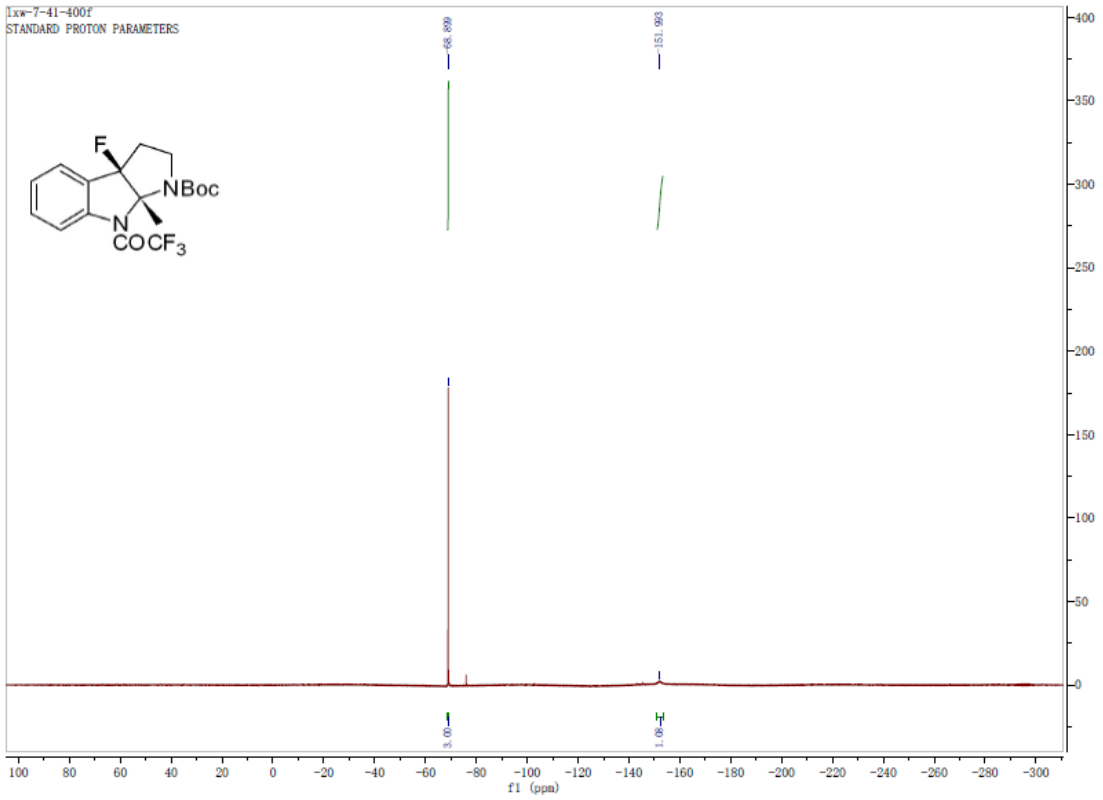




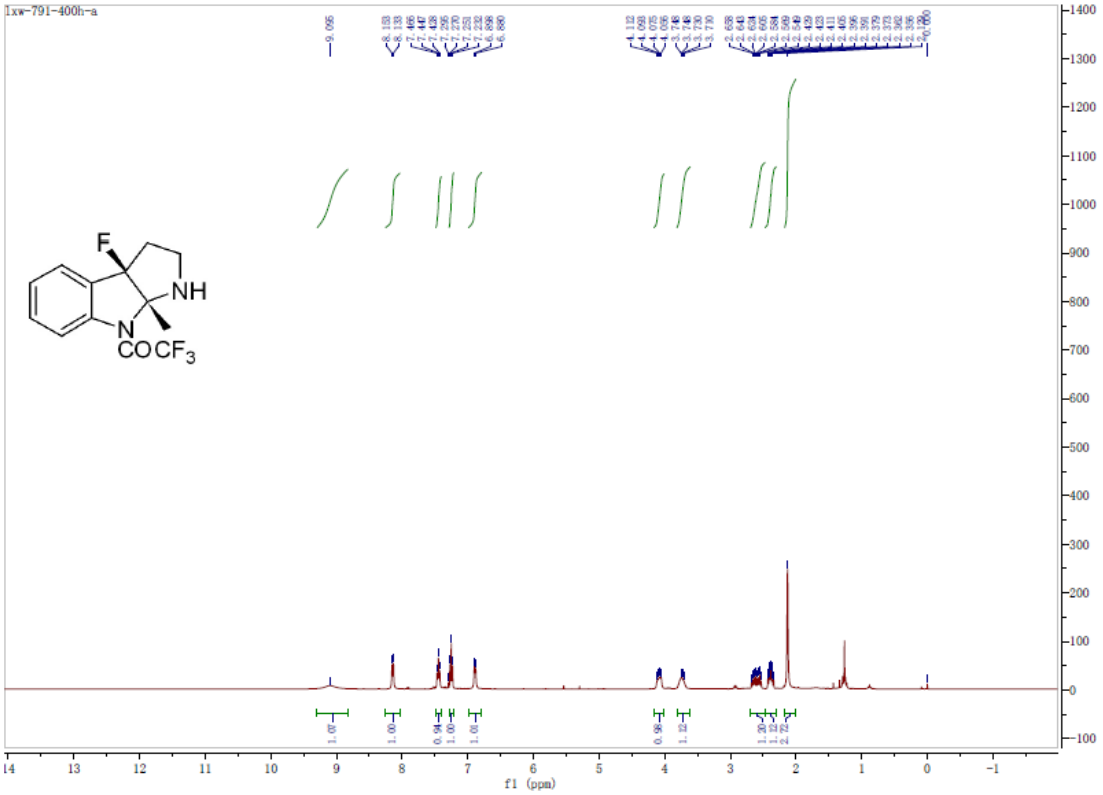
NMR Spectra of **3**

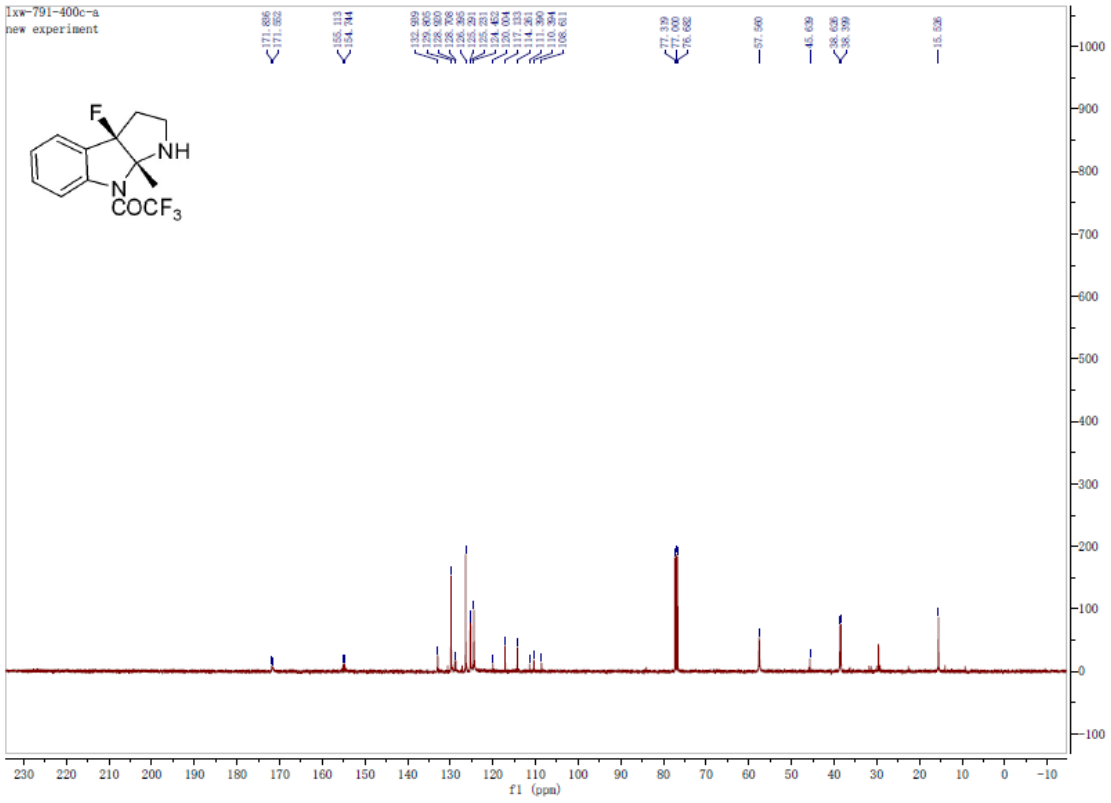

1xw-7-60-400h
F
NBoc
N
COCF3
f1 (ppm)

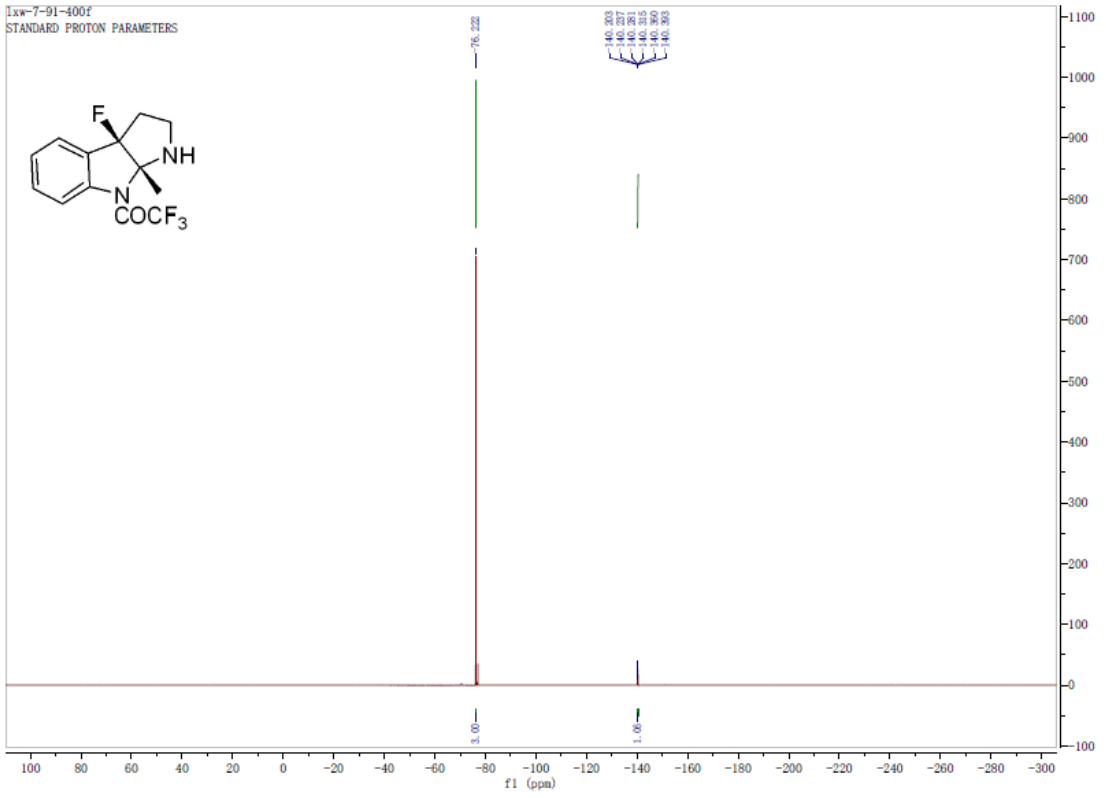

1xw-7-60-400c
new
F
NBoc
N
COCF3
f1 (ppm)



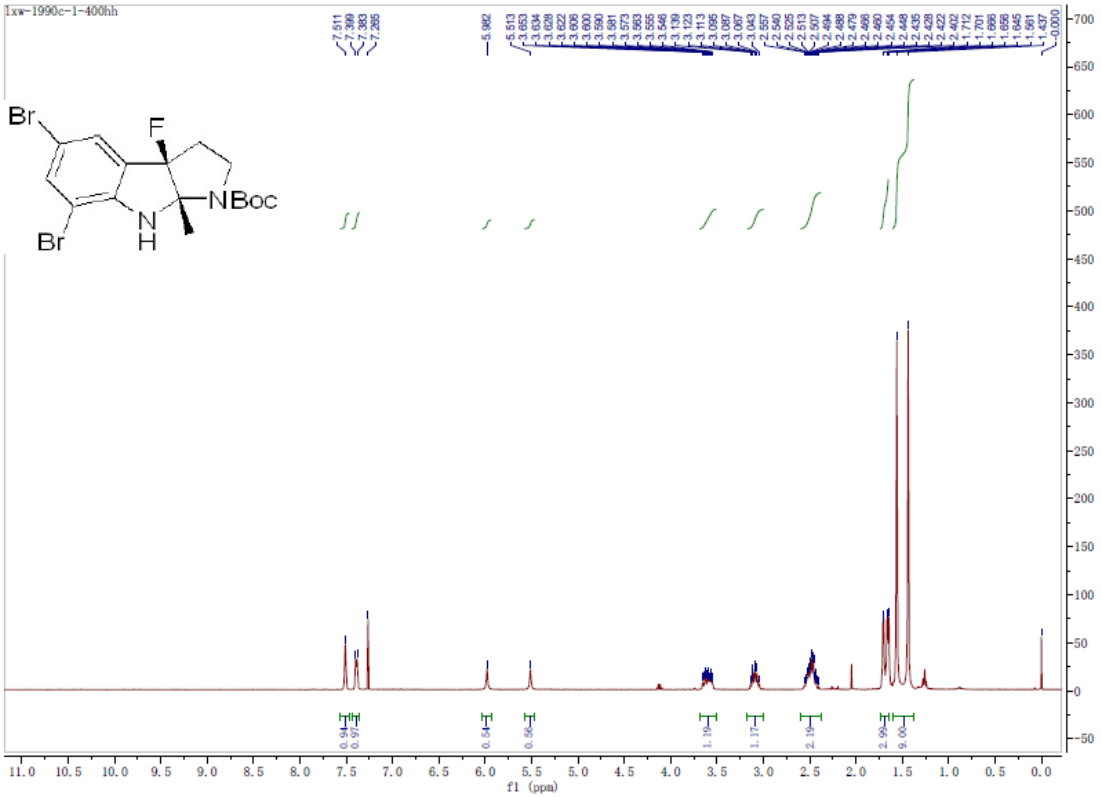
NMR Spectra of **4**

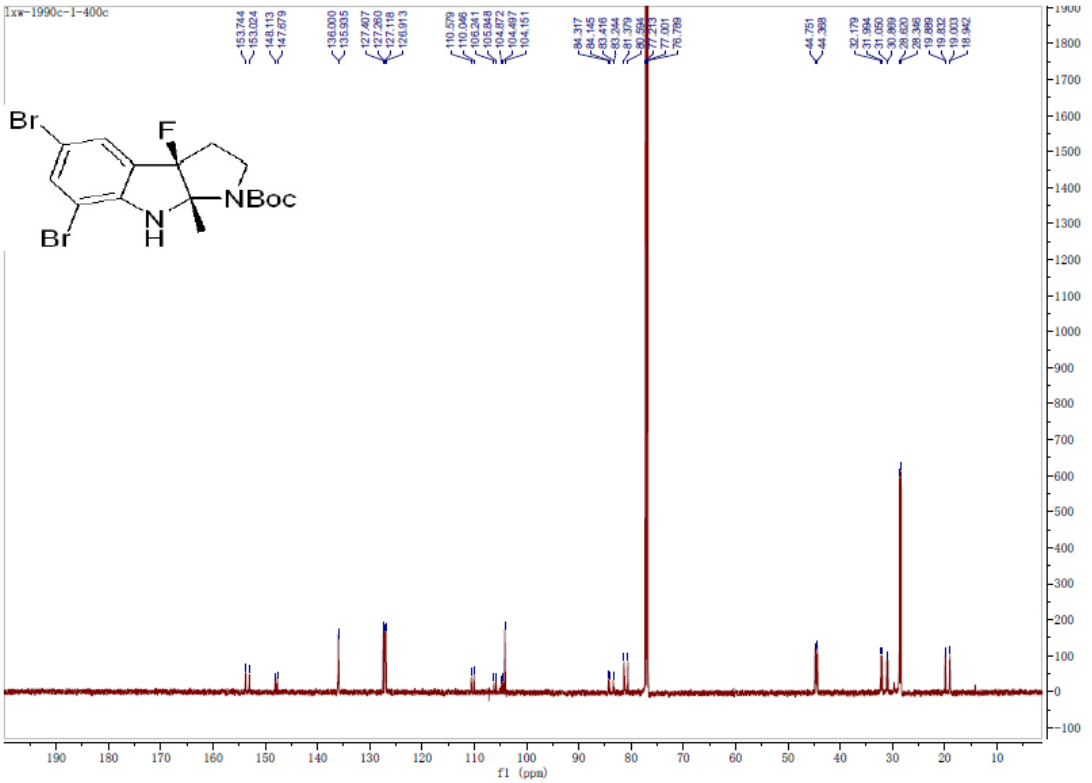


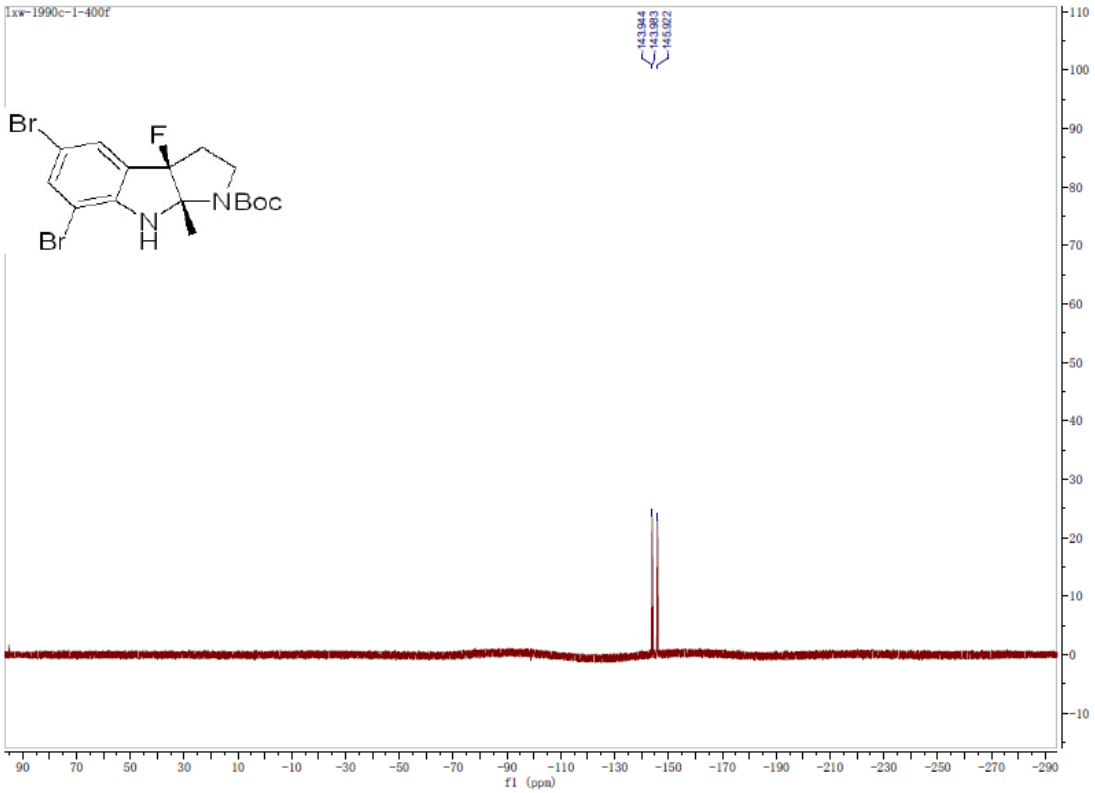

lxw-791-400c-a
new experiment
F
NH
N
COCF3
f1 (ppm)


lxw-7-91-400f
STANDARD PROTON PARAMETERS
F
NH
N
COCF3
f1 (ppm)

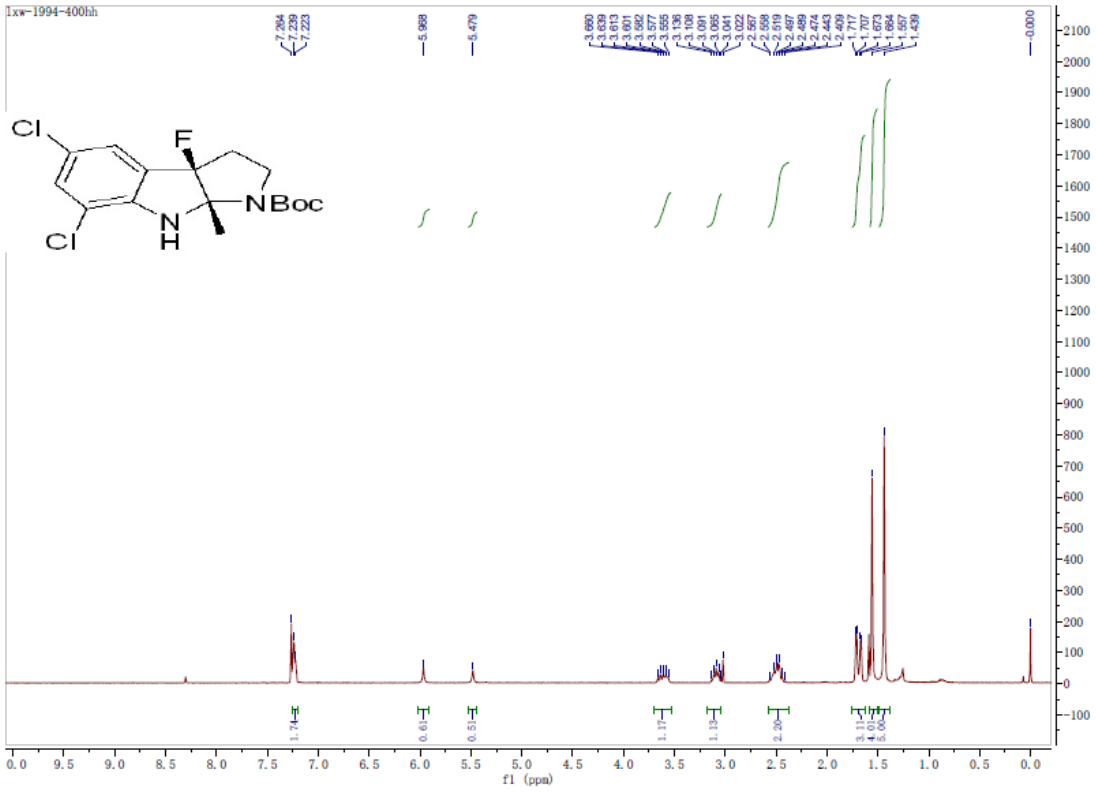
NMR Spectra of **2bb**

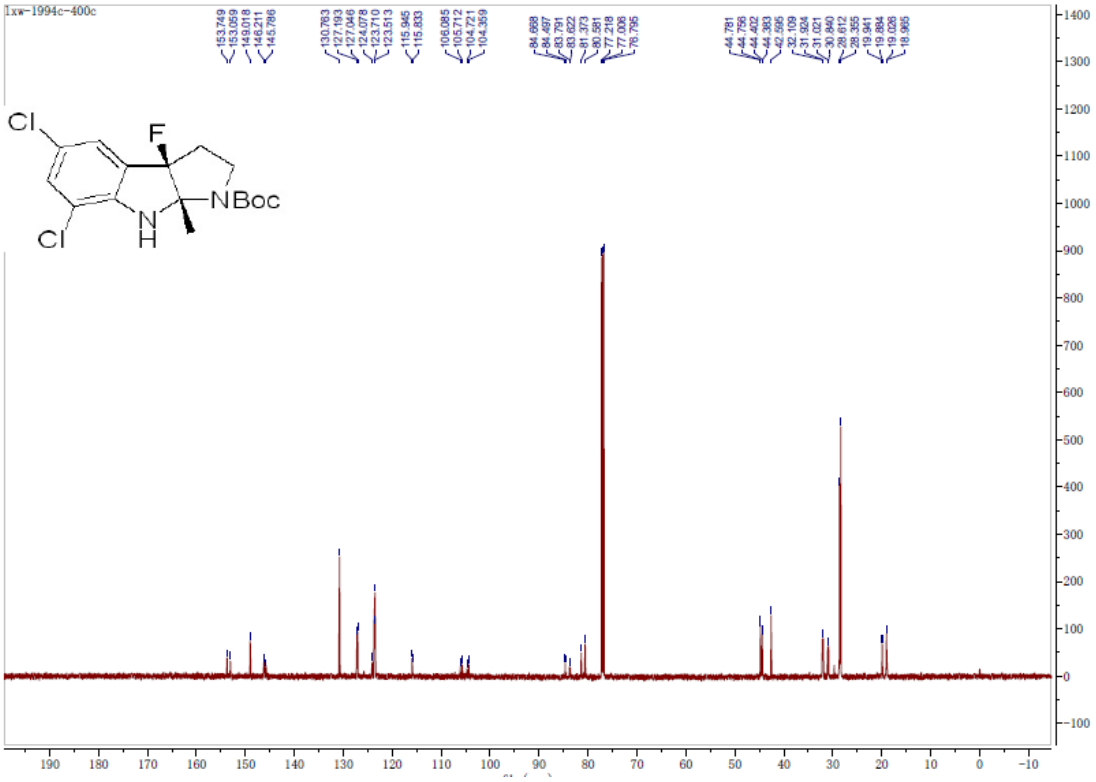

lxw-1990c-1-400hh
Br
F
NBoc
N
H
Br
f1 (ppm)

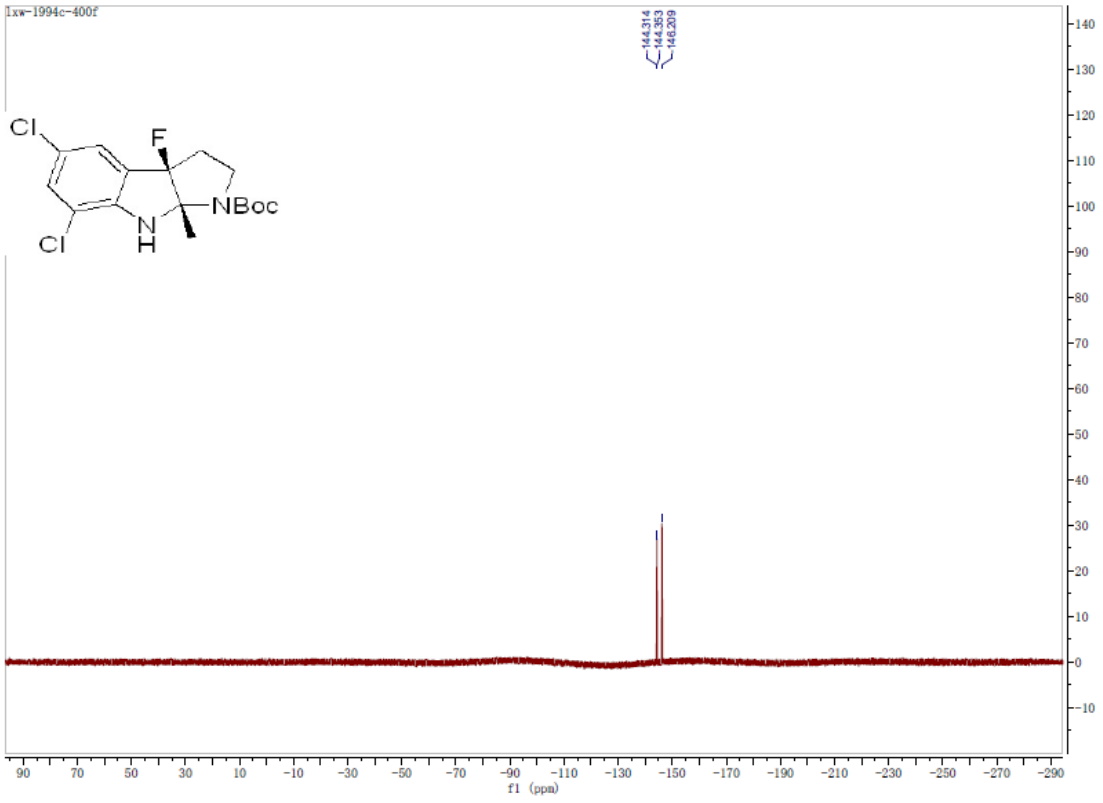

lxw-1990c-1-400c
Br
F
NBoc
N
H
Br
f1 (ppm)



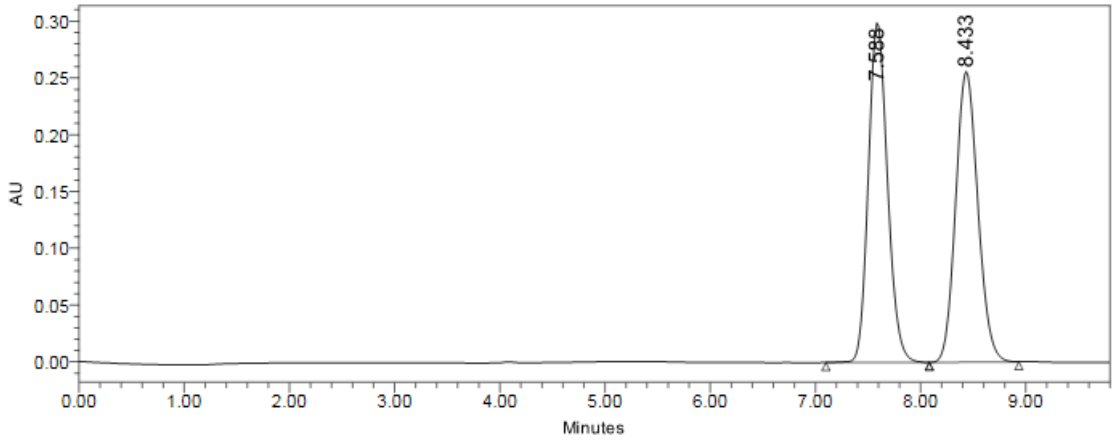
NMR Spectra of **2bc**


1xw-1994-400hh
Cl
F
NBoc
N
H
Cl
f1 (ppm)

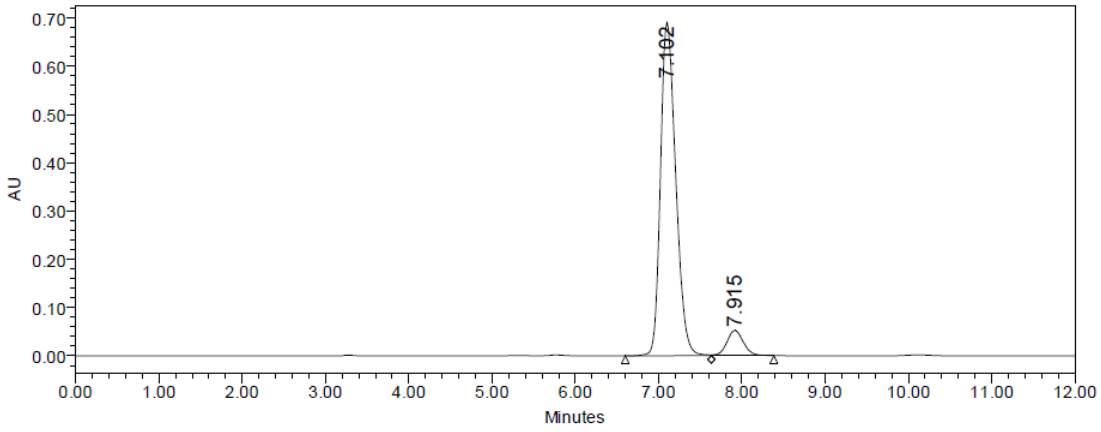

1xw-1994c-400c
Cl
F
NBoc
N
H
Cl


lxw-1994c-400f
144.314
144.353
146.209
Cl
F
NBoc
N
H
Cl
f1 (ppm)

HPLC Chromatographs of **2a**

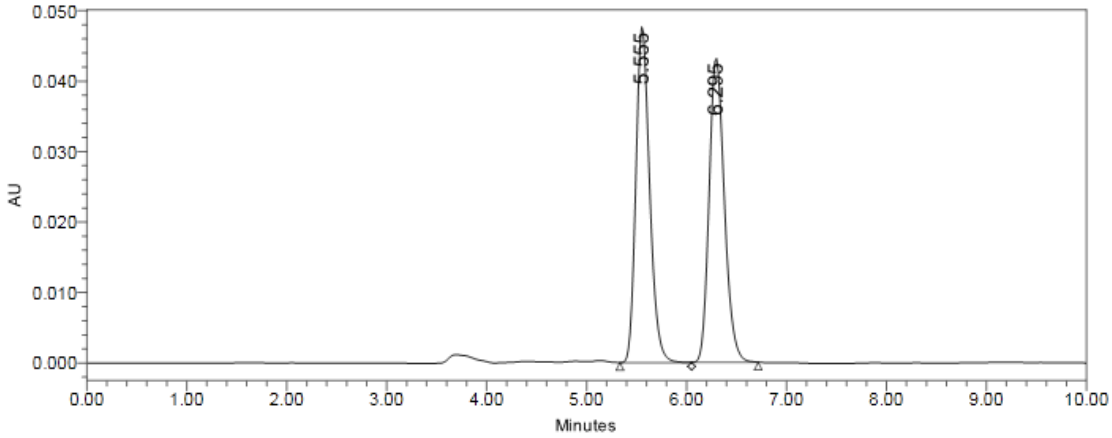


	RT	Area	% Area	Height
1	7.588	3784478	50.21	299409
2	8.433	3752654	49.79	255980

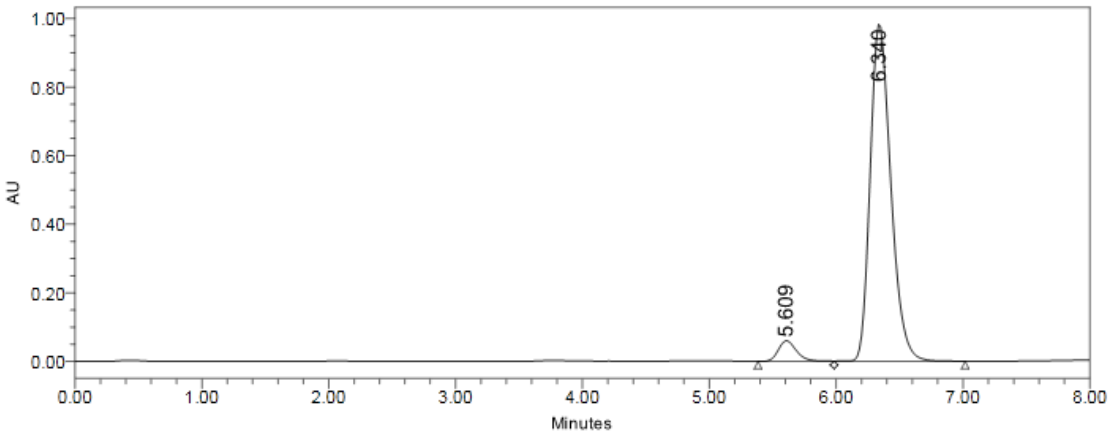


	RT	Area	% Area	Height
1	7.102	8769782	92.39	690989
2	7.915	722302	7.61	52302

HPLC Chromatographs of **2b**

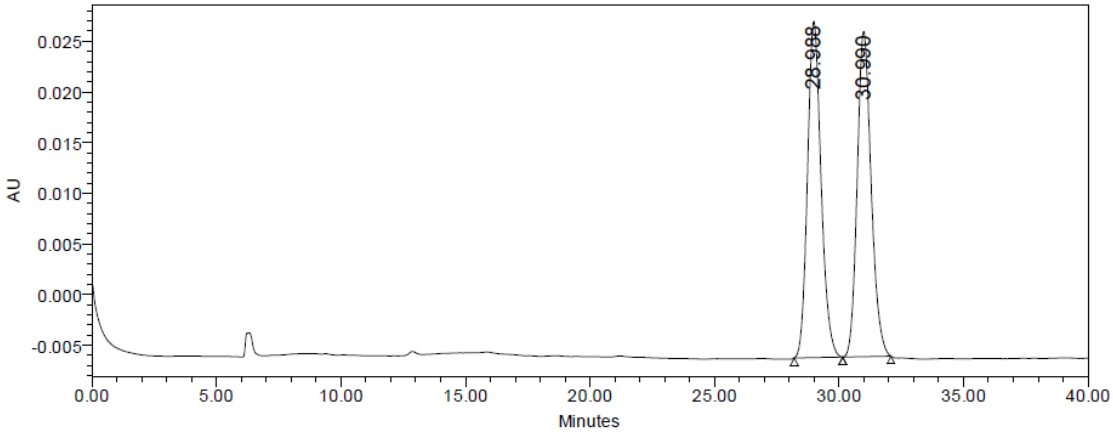


	RT	Area	% Area	Height
1	5.555	460927	50.12	47759
2	6.295	458638	49.88	43212

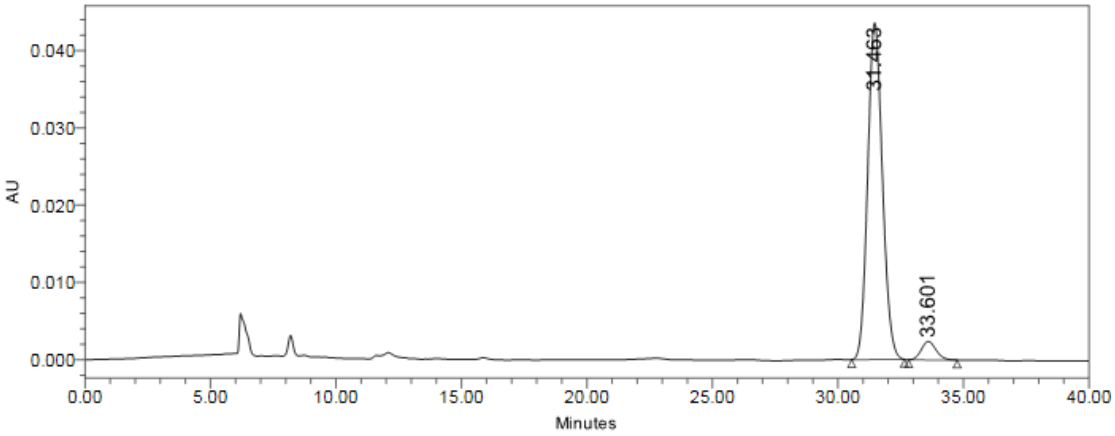


	RT	Area	% Area	Height
1	5.609	595720	5.07	60012
2	6.340	11152944	94.93	986061

HPLC Chromatographs of **2c**

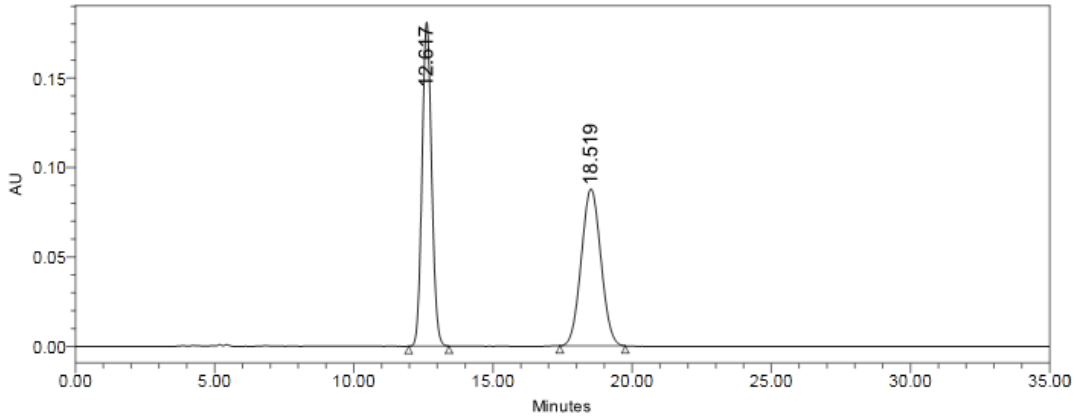


	RT	Area	% Area	Height
1	28.988	1256042	50.11	33184
2	30.990	1250610	49.89	32105

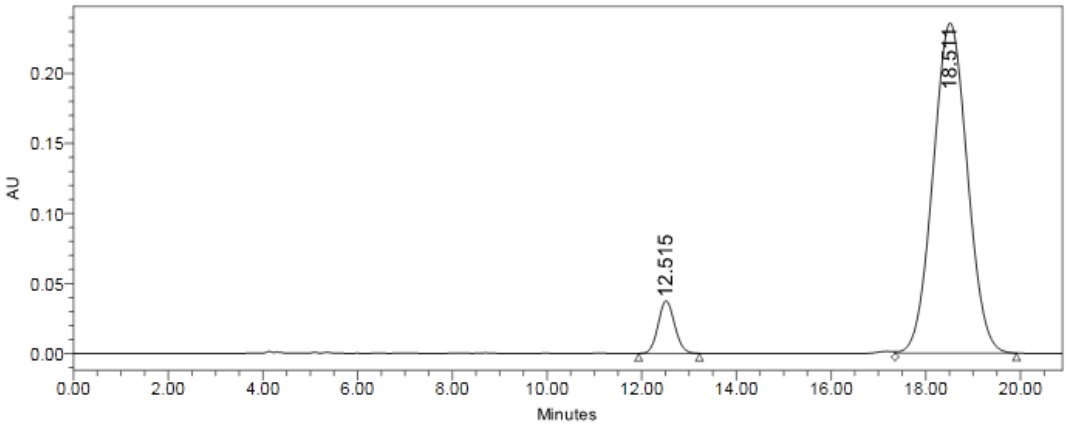


	RT	Area	% Area	Height
1	31.463	1777057	94.79	43598
2	33.601	97598	5.21	2380

HPLC Chromatographs of **2d**

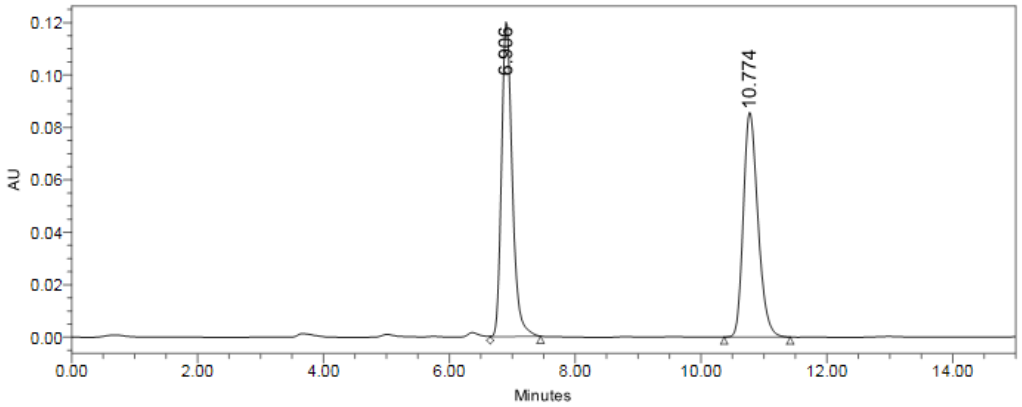


	RT	Area	% Area	Height
1	12.617	4350389	50.33	181091
2	18.519	4293347	49.67	87615

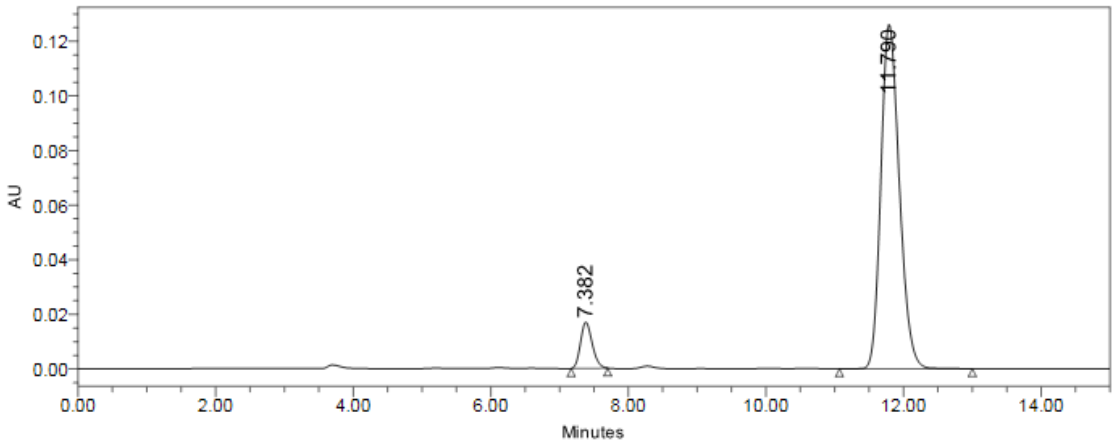


	RT	Area	% Area	Height
1	12.515	910823	7.13	37438
2	18.511	11863897	92.87	235774

HPLC Chromatographs of **2e**

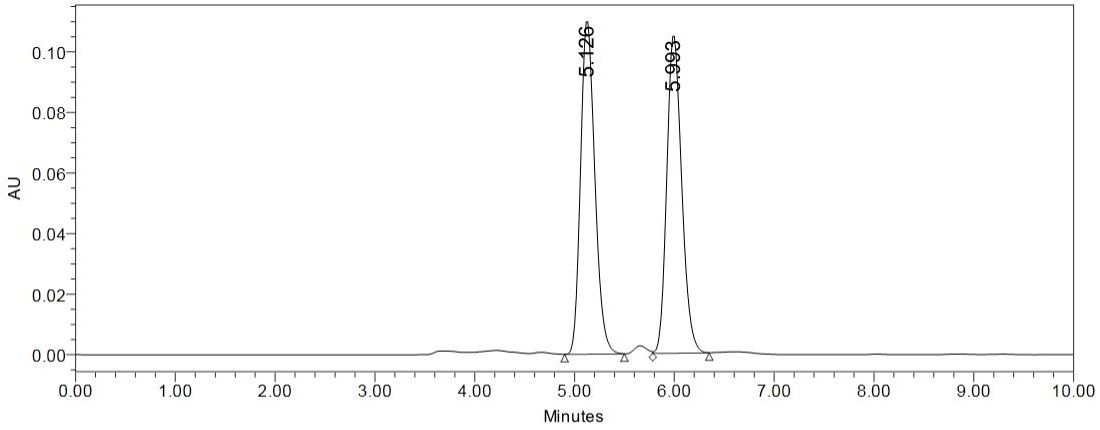


	RT	Area	% Area	Height
1	6.906	1416395	50.66	120250
2	10.774	1379214	49.34	85819

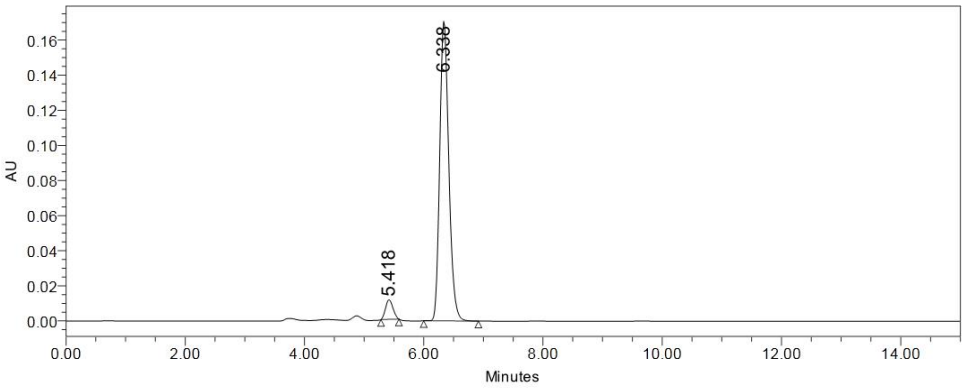


	RT	Area	% Area	Height
1	7.382	200512	7.86	16966
2	11.790	2351756	92.14	126226

HPLC Chromatographs of **2f**

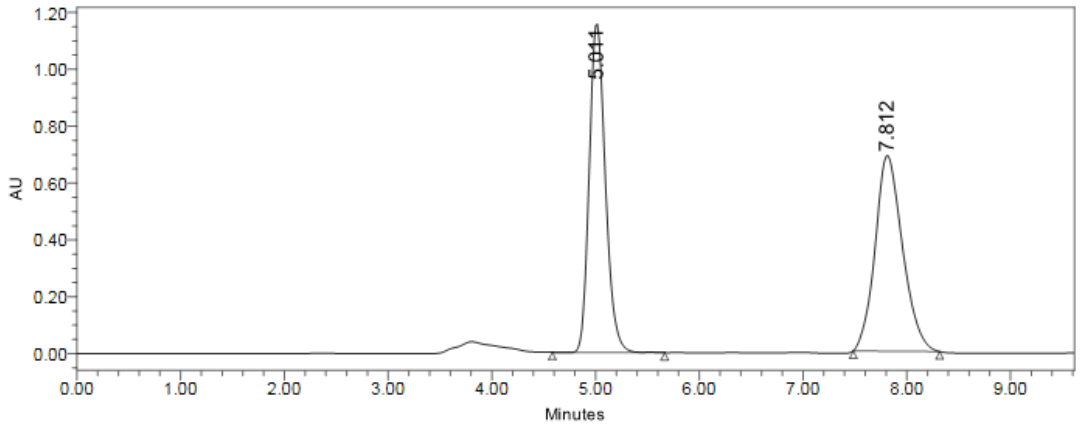


	RT	Area	% Area	Height
1	5.126	1098251	50.14	110318
2	5.993	1091914	49.86	105207

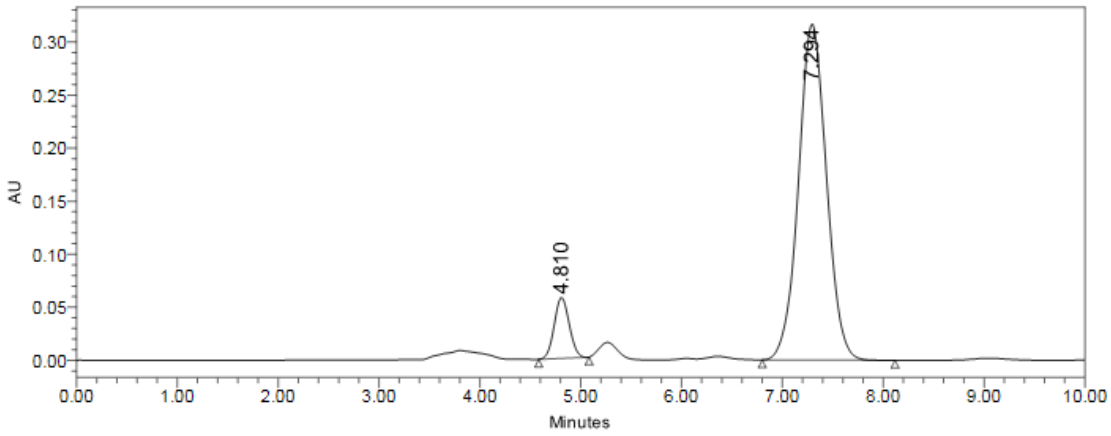


	RT	Area	% Area	Height
1	5.418	96389	5.08	11166
2	6.338	1801225	94.92	170913

HPLC Chromatographs of **2g**

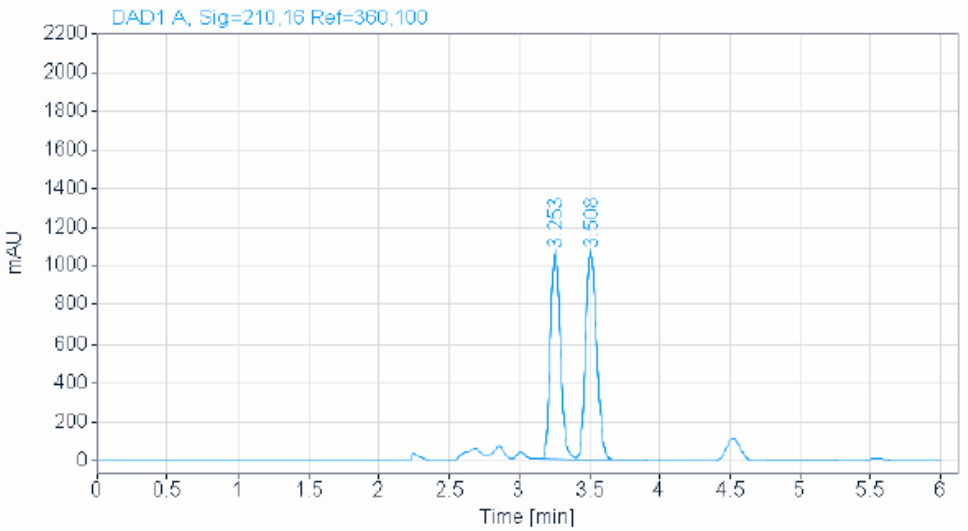


	RT	Area	% Area	Height
1	5.011	12508064	49.67	1158608
2	7.812	12672657	50.33	688624



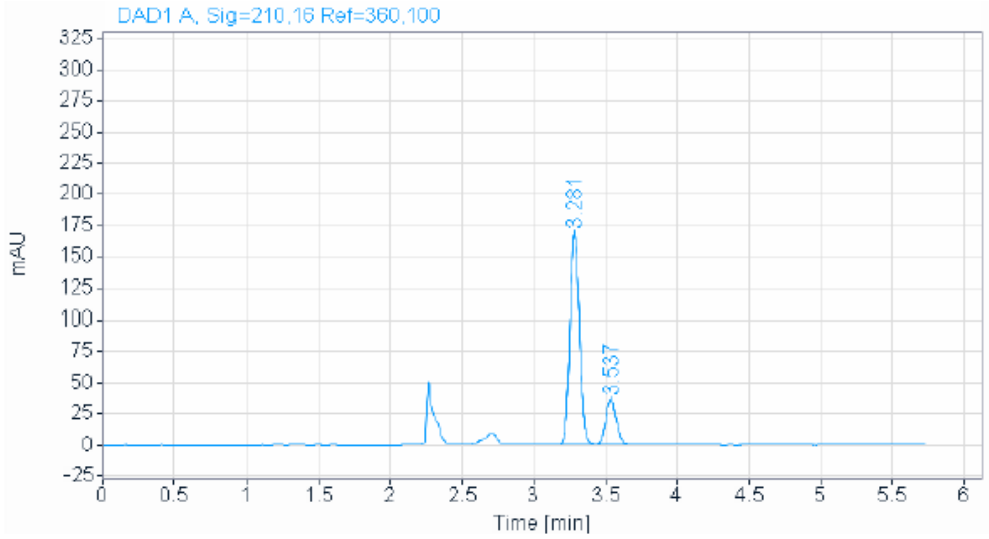
	RT	Area	% Area	Height
1	4.810	593036	8.85	57291
2	7.294	6109948	91.15	316910

HPLC Chromatographs of **2h**



Signal: DAD1 A, Sig=210, 16 Ref=360, 100

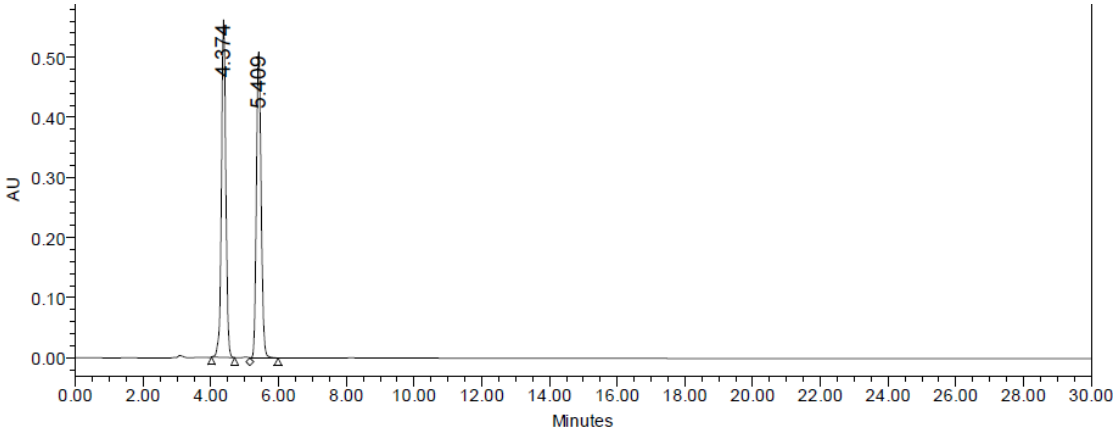
RT [min]	Type	Width [min]	Area	Height	Area%
3.253	BV	0.0770	5164.9712	1056.5814	47.0459
3.508	VB	0.0869	5813.6040	1062.0057	52.9541
		Sum	10978.5752		



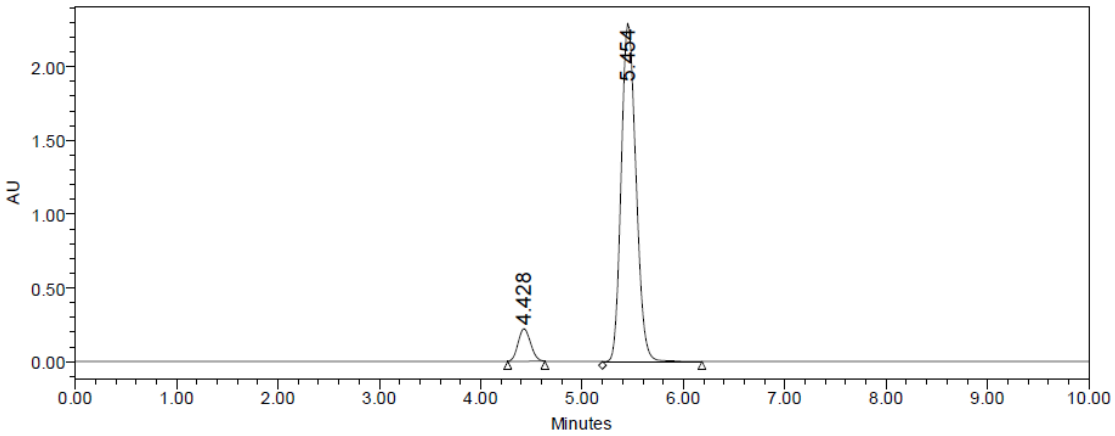
Signal: DAD1 A, Sig=210, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
3.281	BV	0.0721	780.0882	168.3072	80.5758
3.537	VB	0.0792	188.0540	36.4463	19.4242
		Sum	968.1422		

HPLC Chromatographs of **2i**

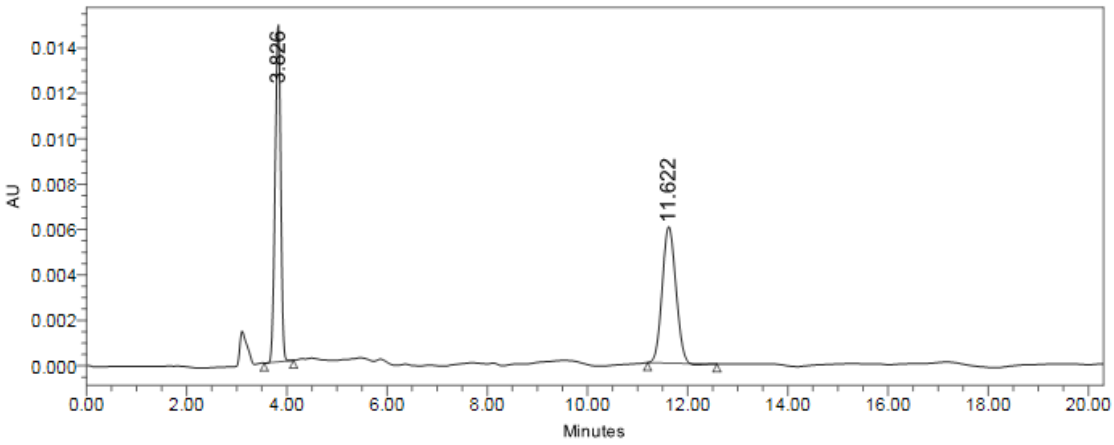


	RT	Area	% Area	Height
1	4.374	5054509	50.45	564483
2	5.409	4963749	49.55	511270

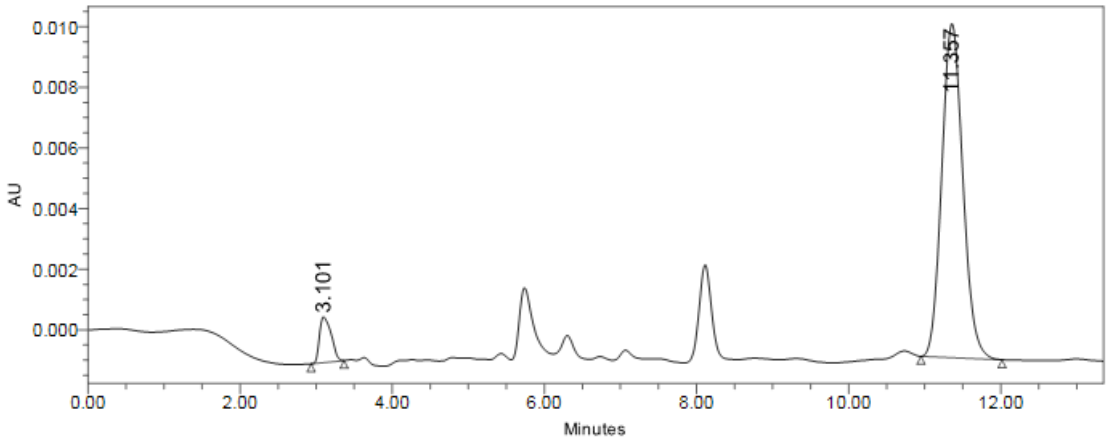


	RT	Area	% Area	Height
1	4.428	1887678	7.53	220959
2	5.454	23179645	92.47	2297261

HPLC Chromatographs of **2j**

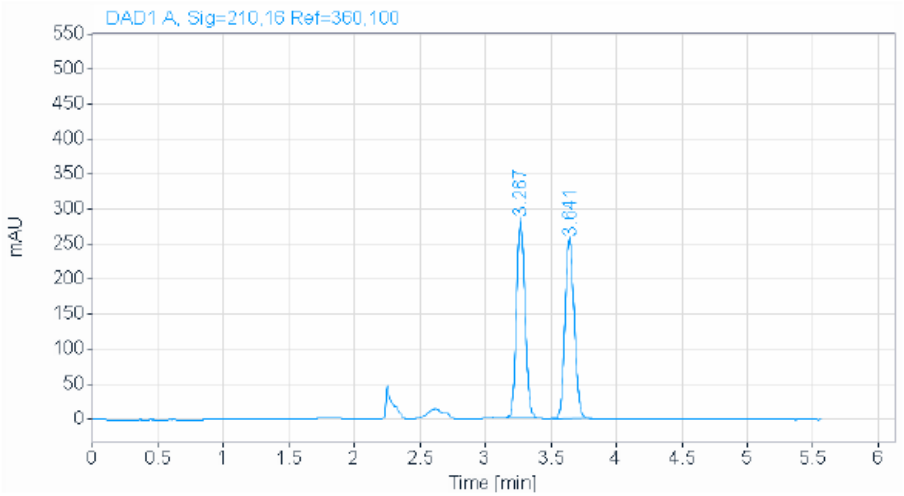


	RT	Area	% Area	Height
1	3.826	114843	49.96	14943
2	11.622	115047	50.04	6007



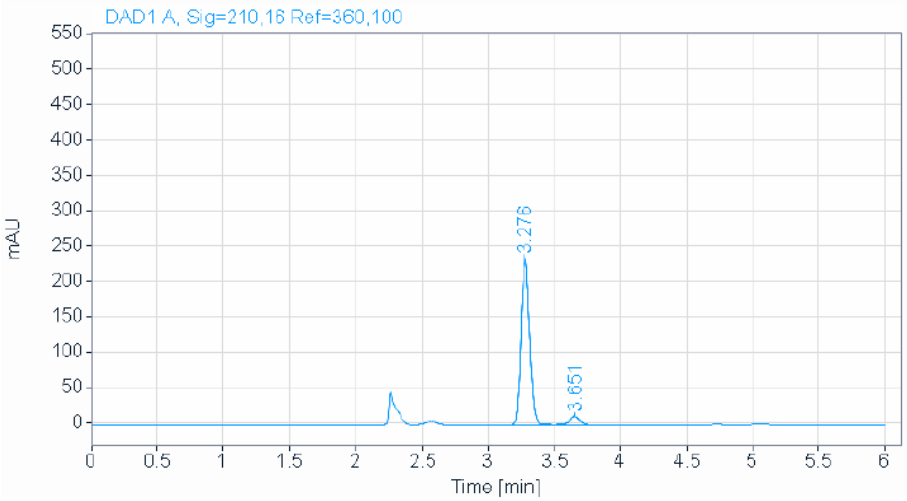
	RT	Area	% Area	Height
1	3.101	15985	7.01	1509
2	11.357	211946	92.99	11022

HPLC Chromatographs of **2k**



Signal: DAD1 A, Sig=210, 16 Ref=360, 100

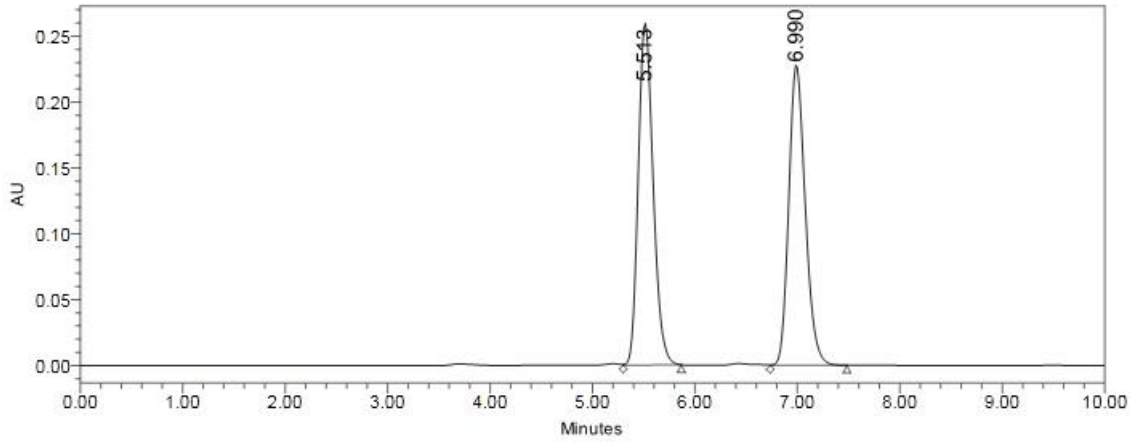
RT [min]	Type	Width [min]	Area	Height	Area%
3.267	MM	0.0757	1275.8678	280.9491	49.9846
3.641	MM	0.0836	1276.6549	254.4320	50.0154
		Sum	2552.5227		



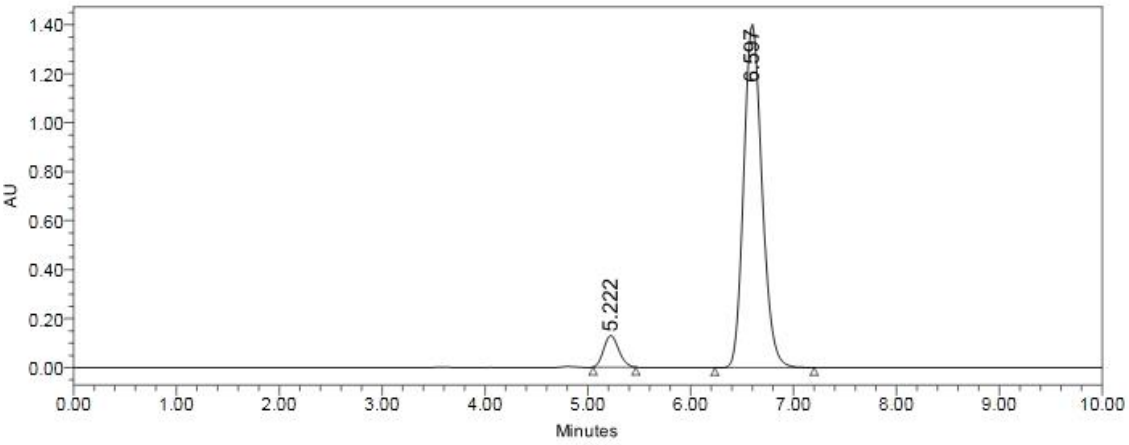
Signal: DAD1 A, Sig=210, 16 Ref=360, 100

RT [min]	Type	Width [min]	Area	Height	Area%
3.276	BV	0.0711	1072.6036	235.5274	94.2445
3.651	VV	0.0835	65.5039	12.2355	5.7555
		Sum	1138.1076		

HPLC Chromatographs of **2l**

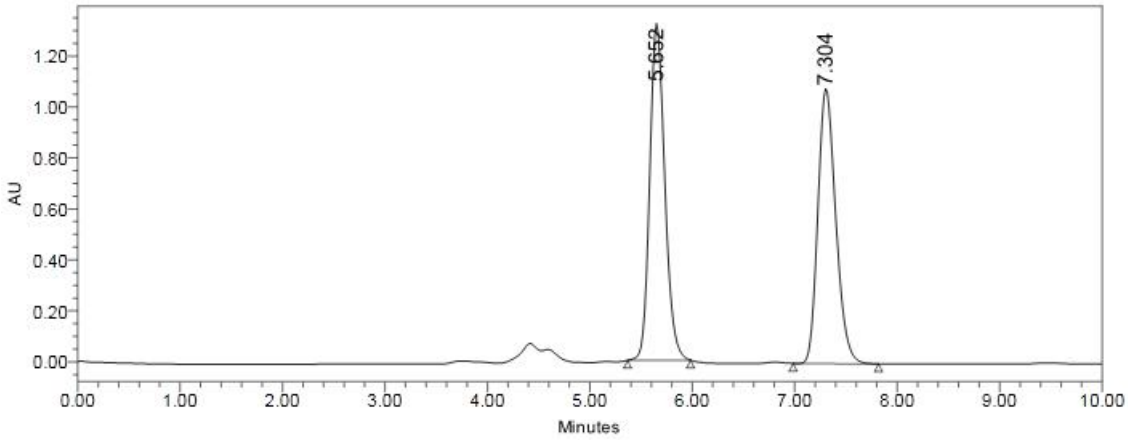


	RT	Area	% Area	Height
1	5.513	2611753	50.57	259305
2	6.990	2553104	49.43	228446

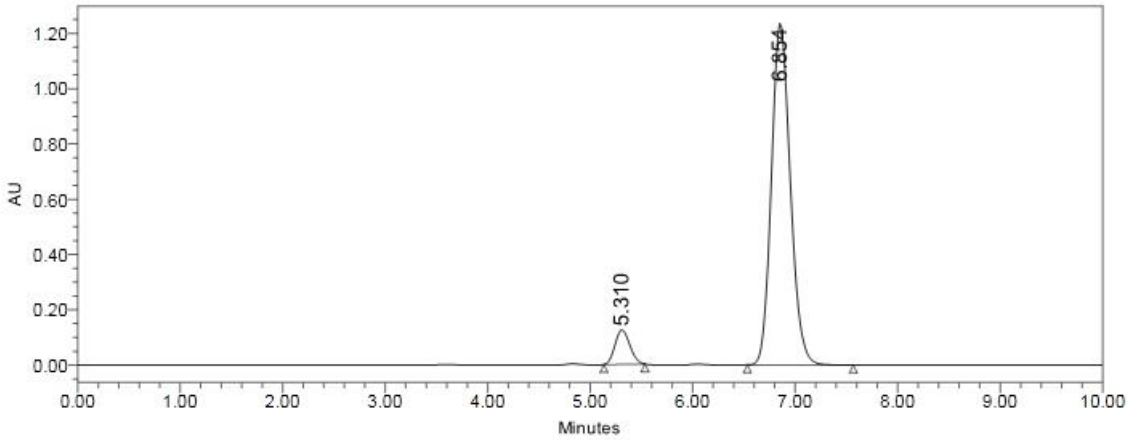


	RT	Area	% Area	Height
1	5.222	1304558	6.98	128935
2	6.597	17372872	93.02	1402025

HPLC Chromatographs of **2m**

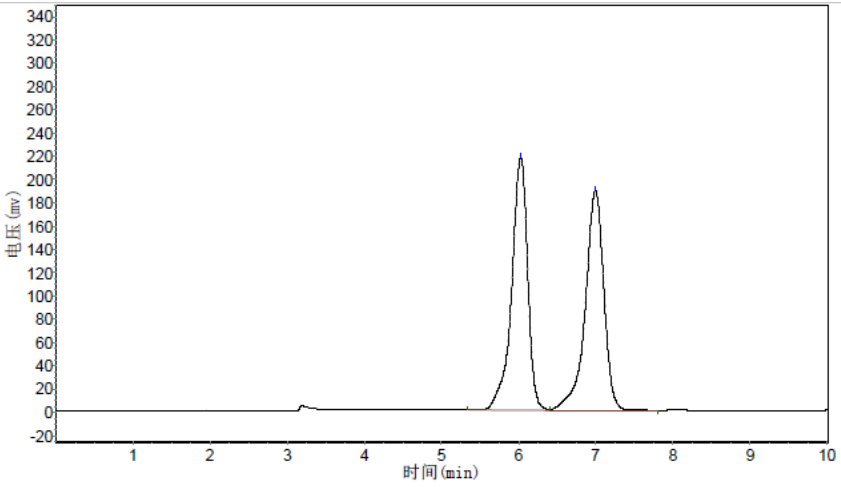


	RT	Area	% Area	Height
1	5.652	13506347	50.80	1320458
2	7.304	13079596	49.20	1080348



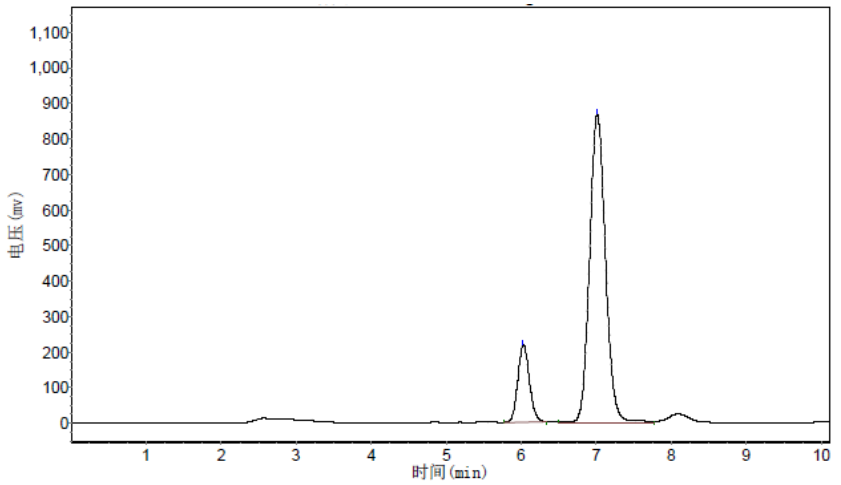
	RT	Area	% Area	Height
1	5.310	1252133	7.34	124837
2	6.854	15799941	92.66	1236208

HPLC Chromatographs of **2n**



分析结果表

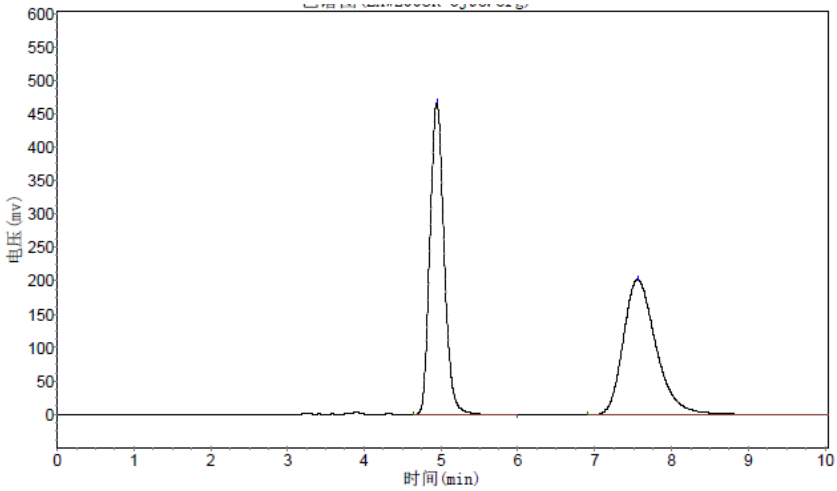
峰号	峰名	保留时间	峰高	峰面积	含量
1		6.032	217268.906	3142376.750	49.7964
2		6.998	188577.031	3168071.000	50.2036
总计			405845.938	6310447.750	100.0000



分析结果表

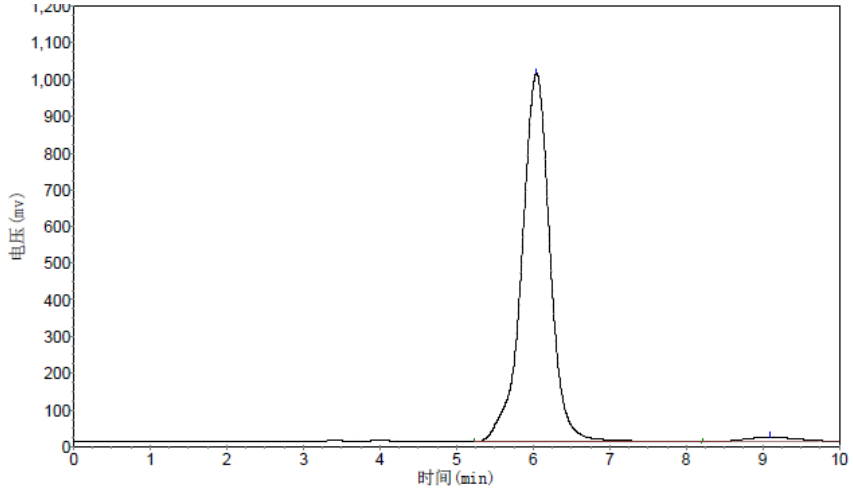
峰号	峰名	保留时间	峰高	峰面积	含量
1		6.028	217161.188	2325823.000	15.3746
2		7.015	867603.000	12801862.000	84.6254
总计			1084764.188	15127685.000	100.0000

HPLC Chromatographs of **2o**



分析结果表

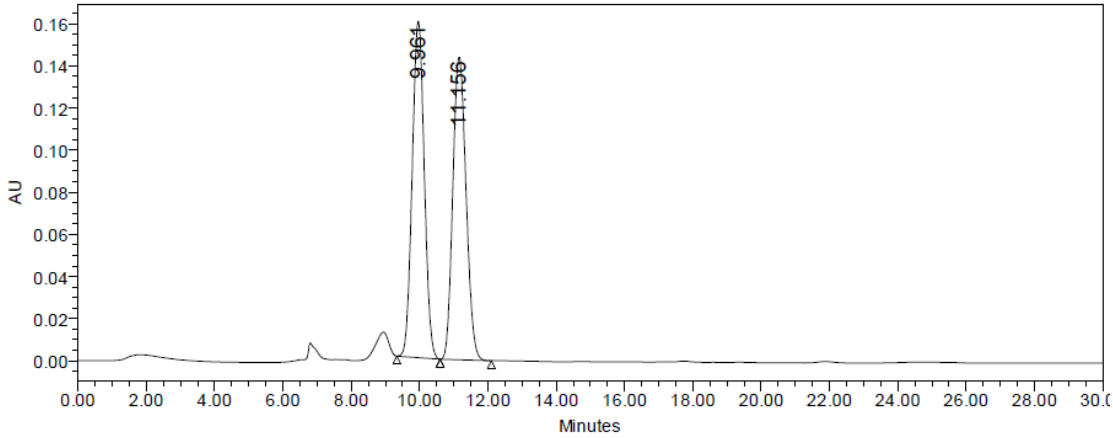
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.948	467624.063	6009539.000	49.9409
2		7.573	202489.250	6023755.500	50.0591
总计			670113.313	12033294.500	100.0000



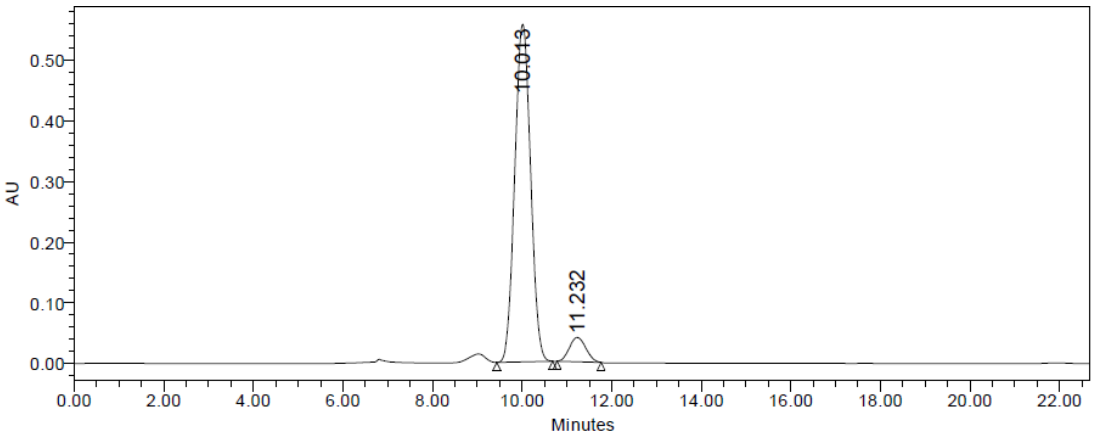
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		6.045	1003884.625	25659176.000	98.2514
2		9.088	11110.179	456666.500	1.7486
总计			1014994.804	26115842.500	100.0000

HPLC Chromatographs of **2p**

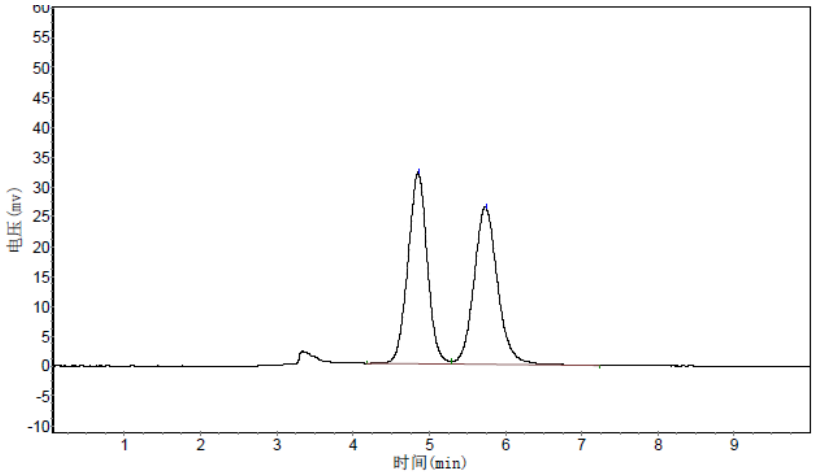


	RT	Area	% Area	Height
1	9.961	3927456	50.39	159932
2	11.156	3866600	49.61	143742



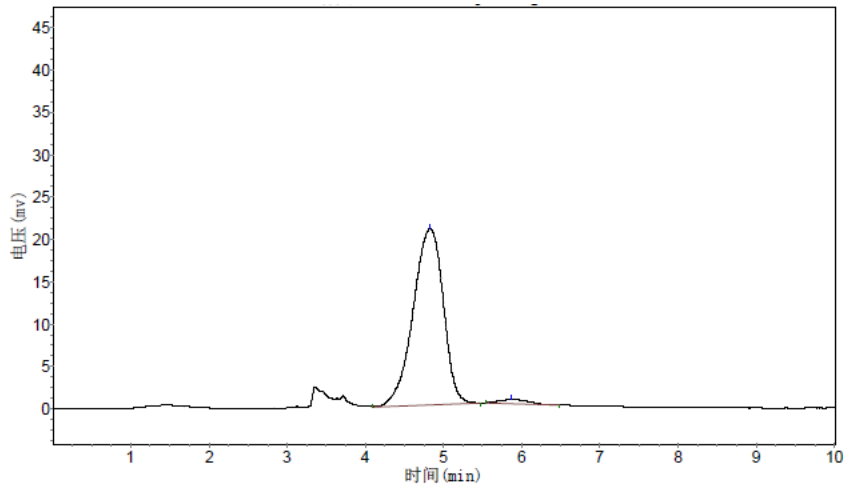
	RT	Area	% Area	Height
1	10.013	13694600	93.01	557599
2	11.232	1029104	6.99	40275

HPLC Chromatographs of **2q**



分析结果表

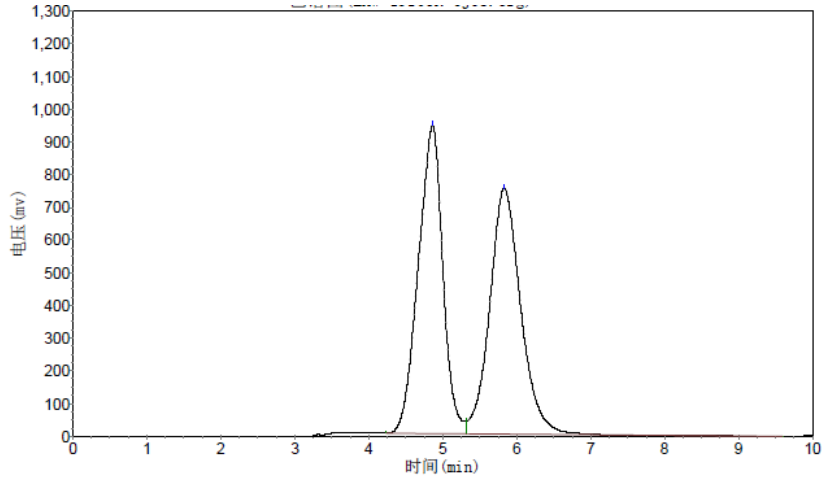
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.857	31979.967	562105.750	49.8822
2		5.748	26361.096	564760.063	50.1178
总计			58341.063	1126865.813	100.0000



分析结果表

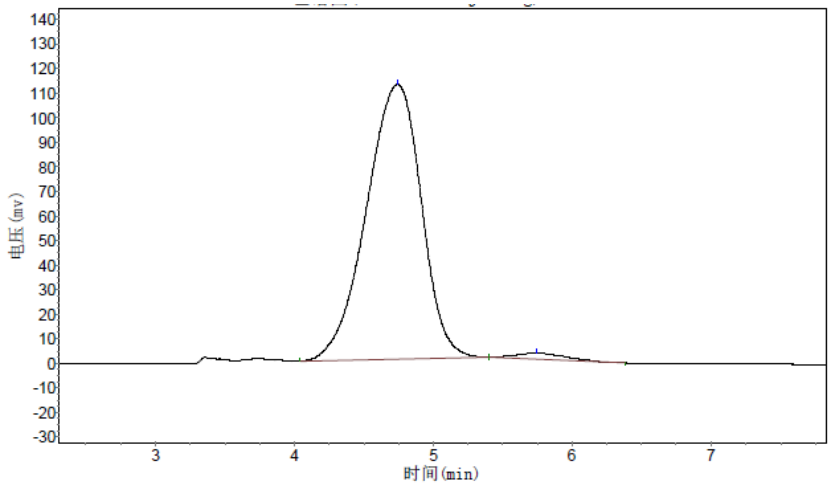
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.830	20766.449	556856.625	97.7934
2		5.868	521.211	12564.598	2.2066
总计			21287.661	569421.223	100.0000

HPLC Chromatographs of **2r**



分析结果表

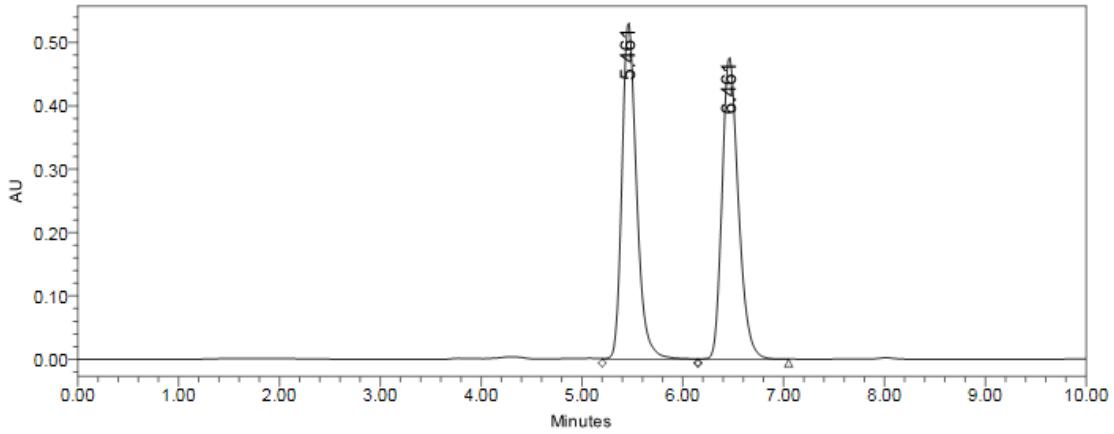
峰号	峰名	保留时间	峰高	峰面积	含量
1		4.863	942735.563	21715380.000	49.8928
2		5.832	752774.875	21808690.000	50.1072
总计			1695510.438	43524070.000	100.0000



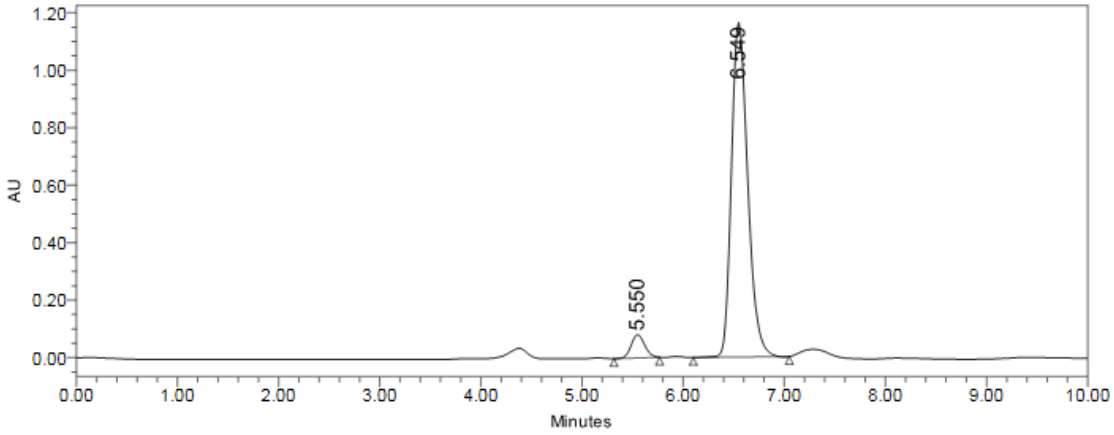
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		4.742	111909.492	3084642.500	98.0507
2		5.742	2336.747	61325.449	1.9493
总计			114246.239	3145967.949	100.0000

HPLC Chromatographs of **2s**

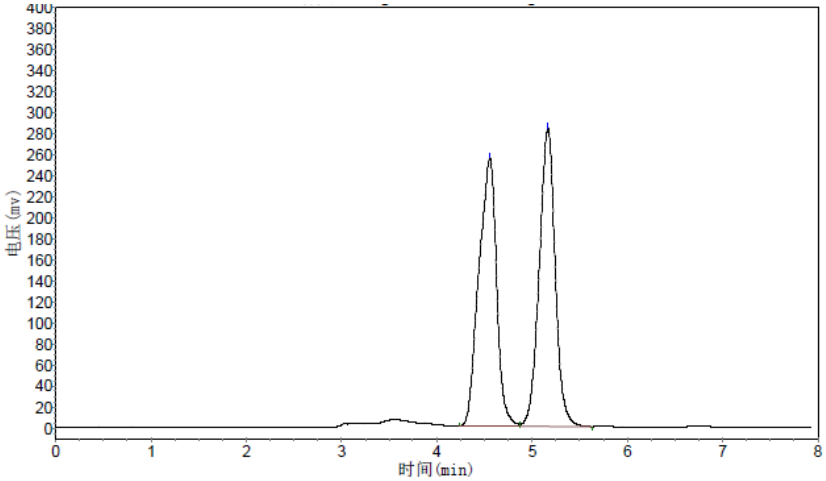


	RT	Area	% Area	Height
1	5.461	5378051	50.06	531536
2	6.461	5364275	49.94	476761



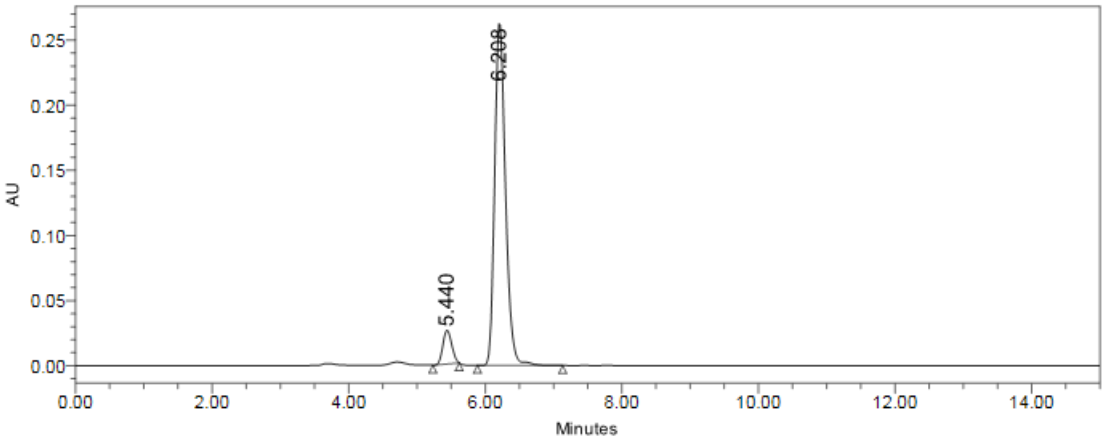
	RT	Area	% Area	Height
1	5.550	747230	5.43	81064
2	6.549	13016570	94.57	1163405

HPLC Chromatographs of **2t**



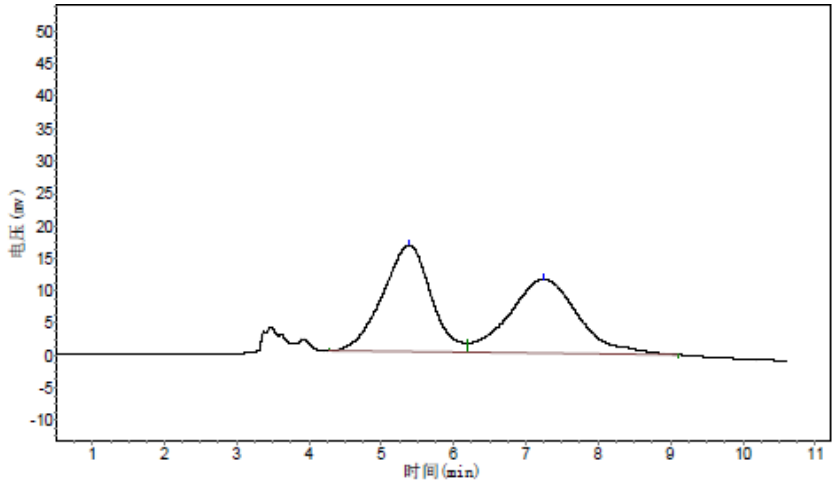
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		4.557	255738.297	3328977.000	49.9604
2		5.165	282389.813	3334260.750	50.0396
总计			538128.109	6663237.750	100.0000



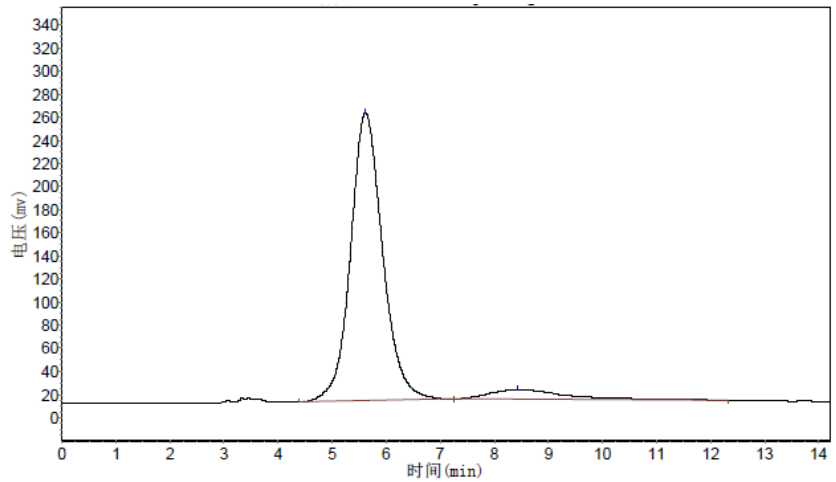
	RT	Area	% Area	Height
1	5.440	232018	7.43	25938
2	6.208	2891153	92.57	263732

HPLC Chromatographs of **2u**



分析结果表

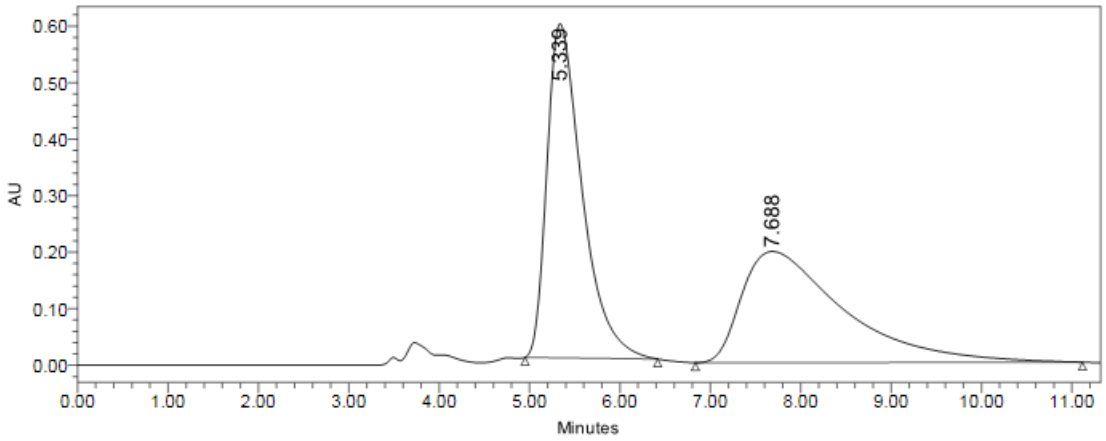
峰号	峰名	保留时间	峰高	峰面积	含量
1		5.380	16466.363	765450.375	50.2246
2		7.245	11473.976	758603.563	49.7754
总计			27940.339	1524053.938	100.0000



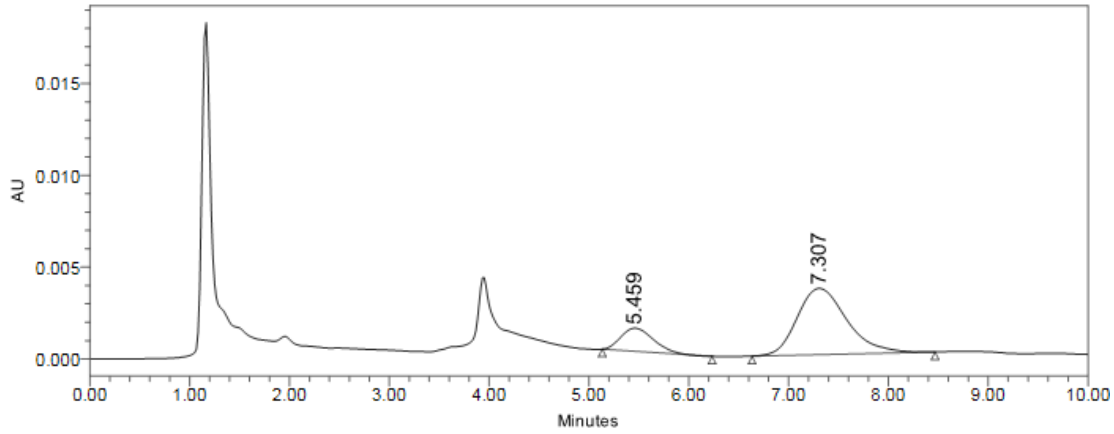
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		5.618	249267.250	10261510.000	92.4834
2		8.437	8485.041	834000.000	7.5166
总计			257752.291	11095510.000	100.0000

HPLC Chromatographs of **2v**

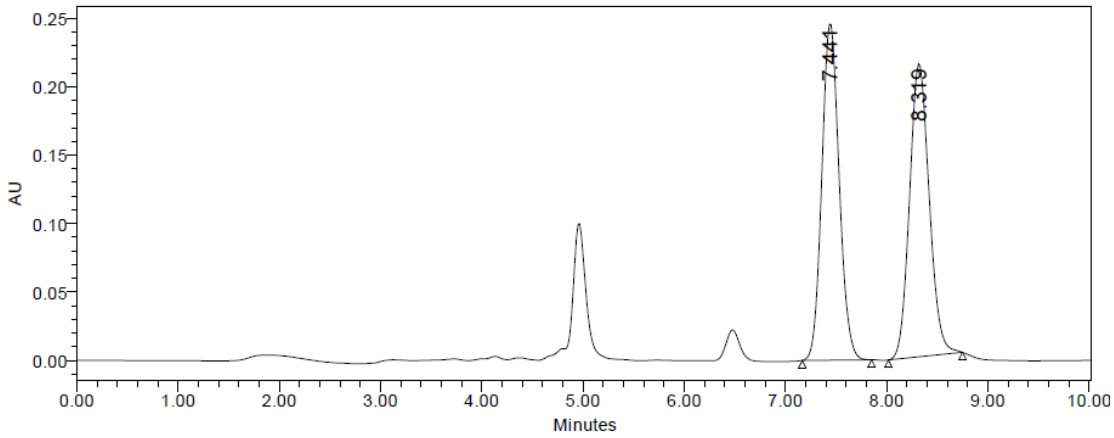


	RT	Area	% Area	Height
1	5.339	15985375	50.97	591421
2	7.688	15375692	49.03	196766

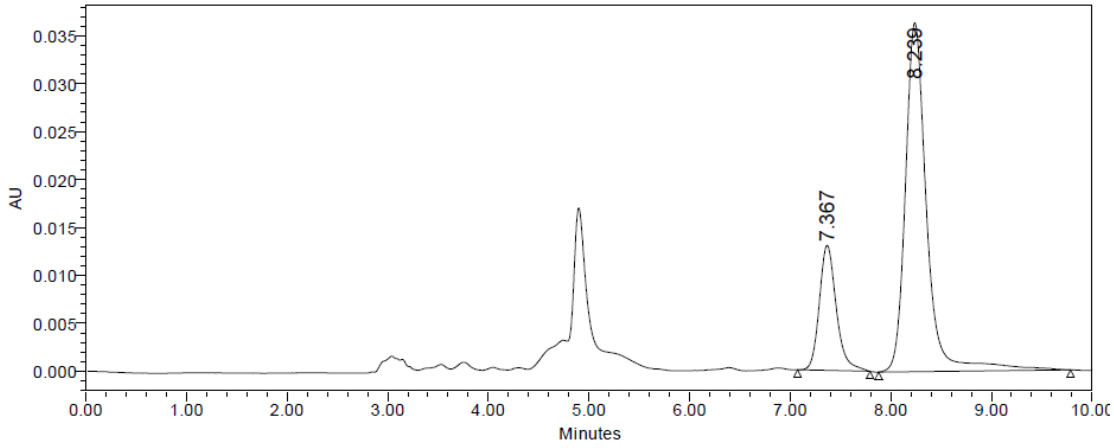


	RT	Area	% Area	Height
1	5.459	28972	18.87	1258
2	7.307	124570	81.13	3606

HPLC Chromatographs of **2w**



	RT	Area	% Area	Height
1	7.441	2924051	50.28	246766
2	8.319	2891686	49.72	214275

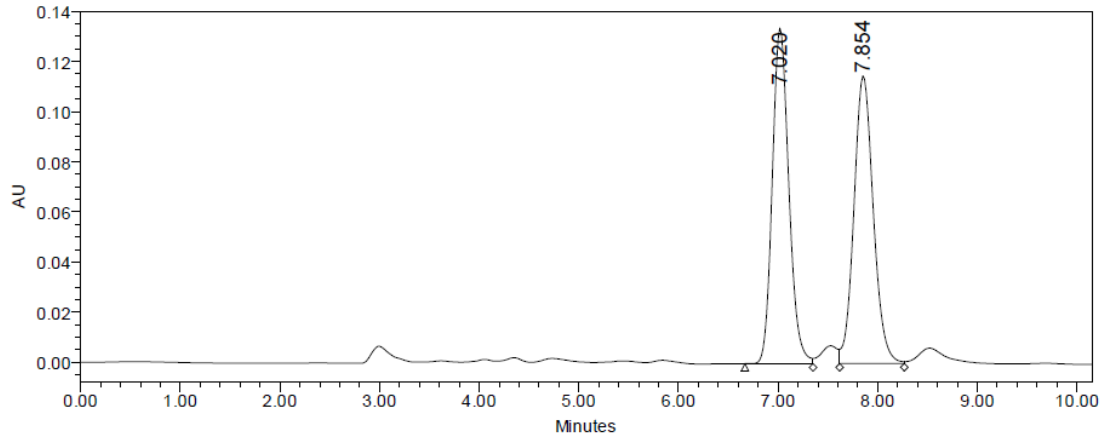


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Injection: 1; Date Acquired: 12/21/2016 6:33:26 PM CST; Result Id: 4642; Processing Method: 352

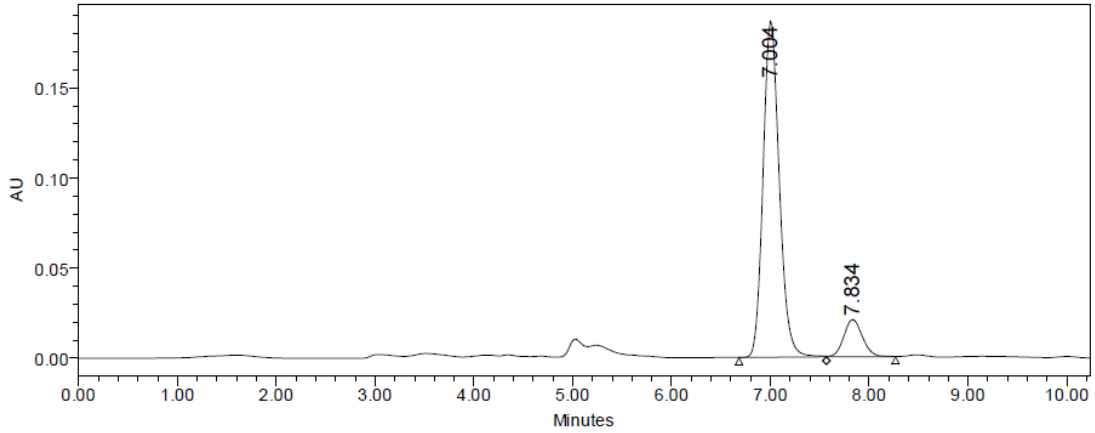
Peak Name:

	Injection	RT	Area	% Area	Height
1	1	8.239	538829	77.90	36408
2	1	7.367	152844	22.10	13049

HPLC Chromatographs of **2x**

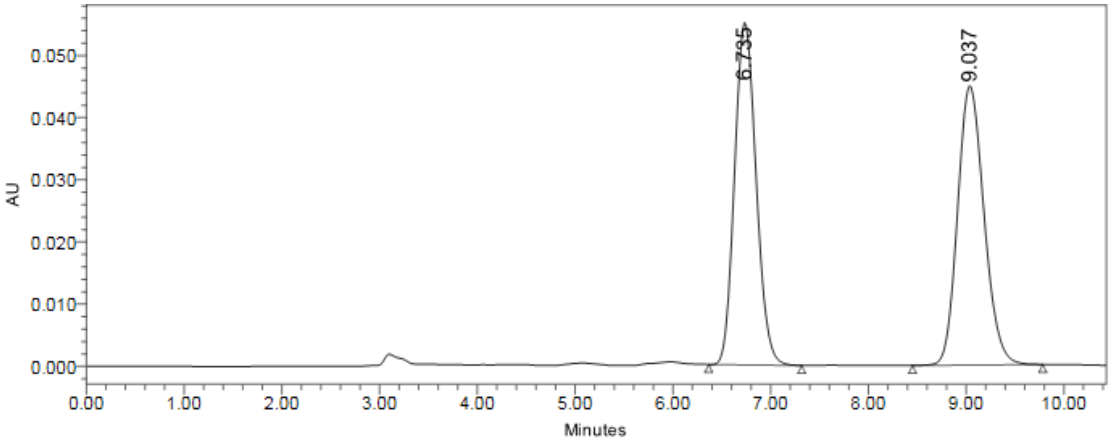


	RT	Area	% Area	Height
1	7.020	1535798	49.83	133831
2	7.854	1546454	50.17	114759

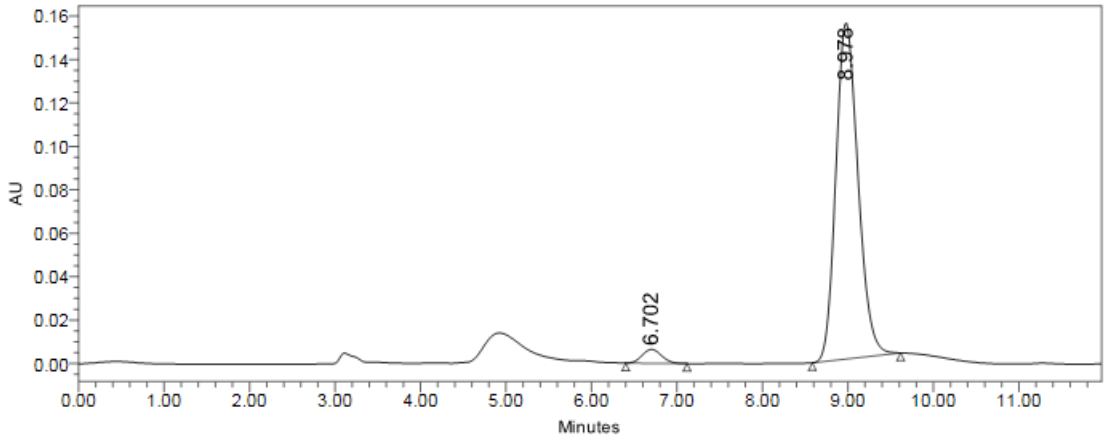


	RT	Area	% Area	Height
1	7.004	2120737	88.69	186764
2	7.834	270373	11.31	20676

HPLC Chromatographs of **2yy**

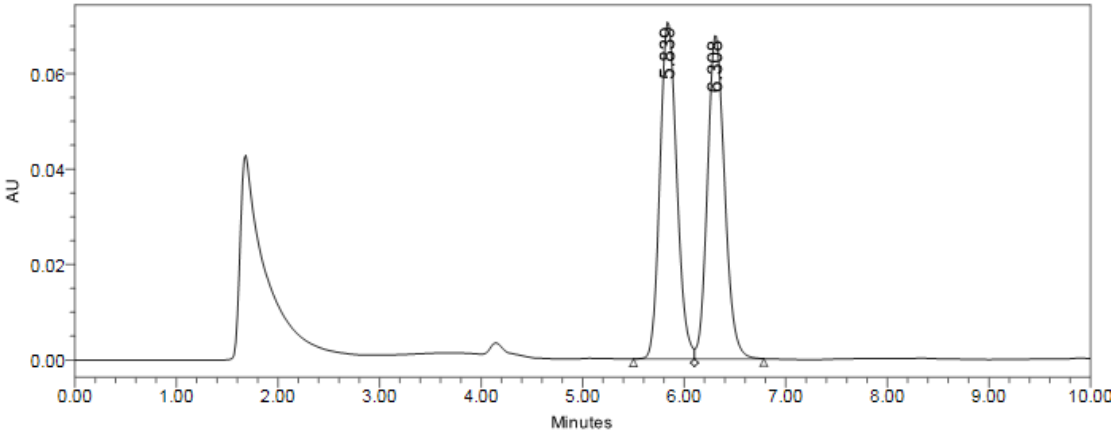


	RT	Area	% Area	Height
1	6.735	841835	49.90	55060
2	9.037	845116	50.10	44949

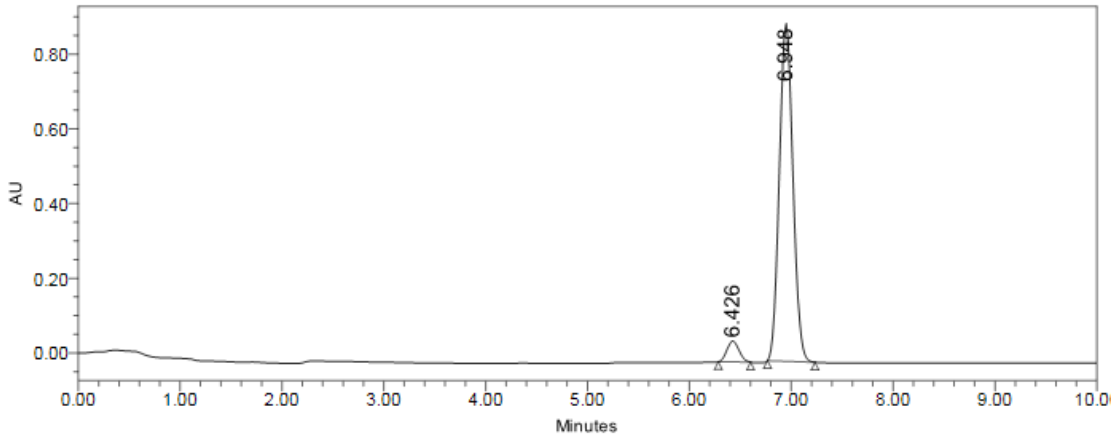


	RT	Area	% Area	Height
1	6.702	101210	3.50	6405
2	8.978	2789739	96.50	154809

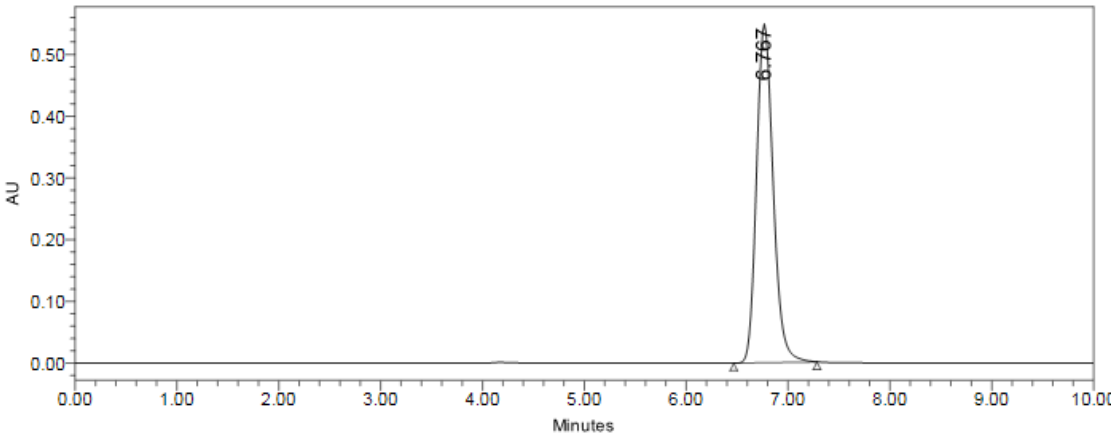
HPLC Chromatographs of **3**



	RT	Area	% Area	Height
1	5.839	810657	50.40	70739
2	6.308	797716	49.60	68025

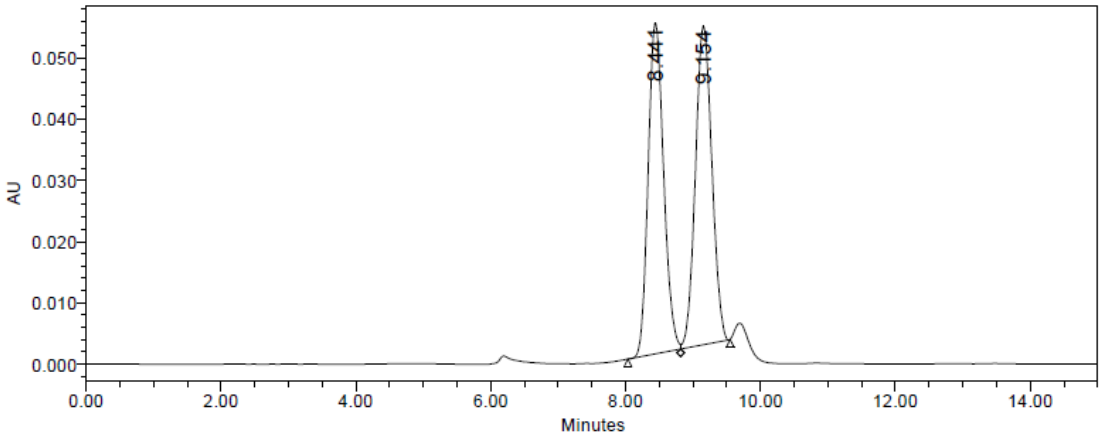


	RT	Area	% Area	Height
1	6.426	460343	5.20	55727
2	6.948	8396097	94.80	903370

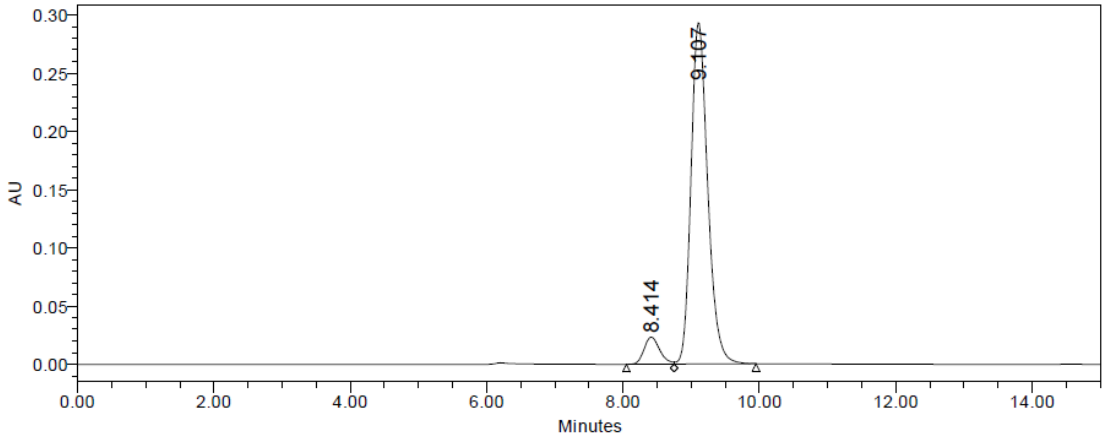


	RT	Area	% Area	Height
1	6.767	6220023	100.00	548129

HPLC Chromatographs of **2bb**

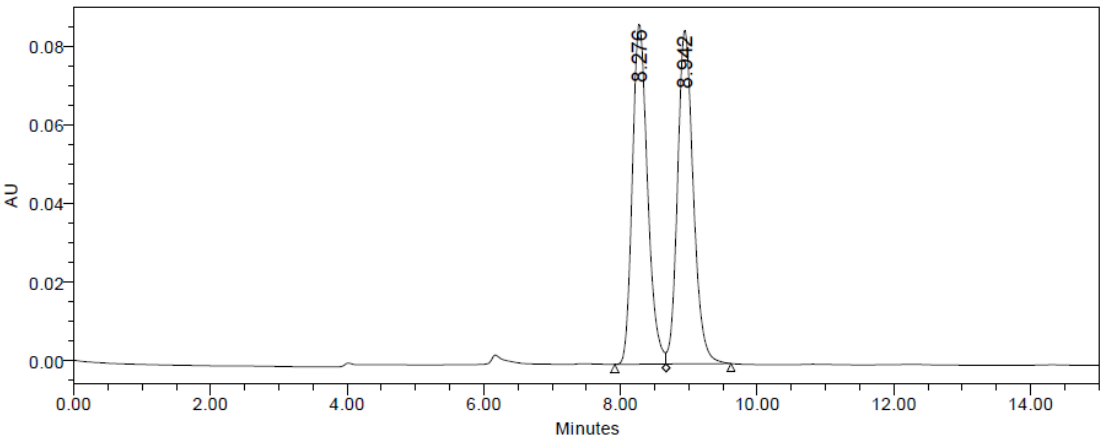


	RT	Area	% Area	Height
1	8.441	859681	49.33	54116
2	9.154	882912	50.67	52101

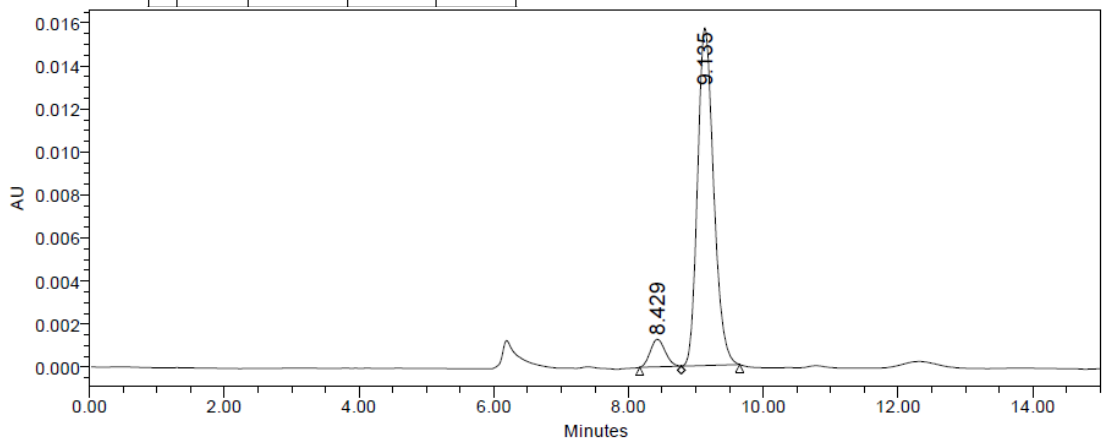


	RT	Area	% Area	Height
1	8.414	368551	6.89	23301
2	9.107	4983310	93.11	293699

HPLC Chromatographs of **2bc**



	RT	Area	% Area	Height
1	8.276	1334698	49.59	86445
2	8.942	1356945	50.41	84911



	RT	Area	% Area	Height
1	8.429	19761	7.05	1282
2	9.135	260466	92.95	15704