Supporting Information

Photocatalysed C-H amidation of indolesenabled by tert-butyl alkyl((perfluoropyridin-4-yl)oxy)carbamate

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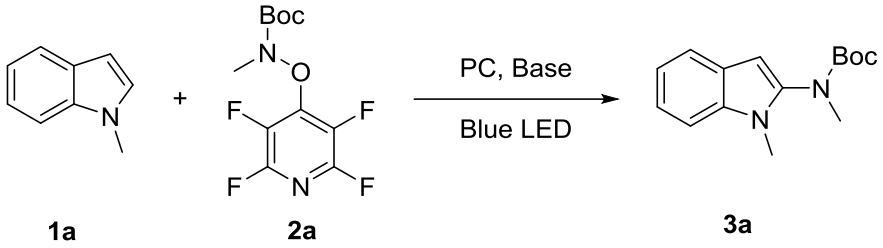
1. General Experimental Methods

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to teramethylsilane and withthe solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet; d = doublet; dd = doublet of doublet; t= triplet; q = quartet; *br* s = broad singlet; m = multiplet), coupling constants (Hz), integration. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^{+} Mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh, Petroleum PE/EtOAc solvent systems). Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

2. Optimization of reaction conditions



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

2.1. Screening of solvent

Entry[a]	Solvent	Base	PC	Yield (%)[b]
1	acetone	K_2CO_3	$Ir(ppy)_3$	83
2	DCM	K_2CO_3	$Ir(ppy)_3$	60
3	THF	K_2CO_3	$Ir(ppy)_3$	64
4	MeOH	K_2CO_3	$Ir(ppy)_3$	55
5	MeCN	K_2CO_3	$Ir(ppy)_3$	66
6	DMSO	K_2CO_3	$Ir(ppy)_3$	65
7	DMF	K_2CO_3	$Ir(ppy)_3$	63
8	toluene	K_2CO_3	$Ir(ppy)_3$	trace
9	EA	K_2CO_3	$Ir(ppy)_3$	58
10	1,4-Dioxane	K_2CO_3	$Ir(ppy)_3$	trace
11	acetone	-	$Ir(ppy)_3$	31
12	acetone	K_2CO_3	-	33
13[c]	acetone	K_2CO_3	$Ir(ppy)_3$	0
14[d]	acetone	K_2CO_3	$Ir(ppy)_3$	0

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 eq), **2a** (0.3 mmol, 1.5 eq), base (0.3 mmol, 1.5 eq), PC (5 mol %), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 12 h, 30 W blue LEDs; [b]Yield of the isolated product. [c]In the dark. [d]O_2.

2.2. Screening of PC

Entry[a]	Solvent	PC	Yield (%)[b]
1	acetone	4CZIPN	33
2	acetone	Rose bengal	25
3	acetone	Red 43	69
4	acetone	Red 94	38
5	acetone	Fluorescein Sodium	40
6	acetone	VB2	trace
7	acetone	Red 91	51
8	acetone	Eoisn Y	43

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 eq), **2a** (0.3 mmol, 1.5 eq), base (0.3 mmol, 1.5 eq), $Ir(ppy)_3$ (5 mol %), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 12 h, 30 W blue LED; [b]Yield of the isolated product.

2.3. Screening of base

Entry[a]	Solvent	Base	PC	Yield (%)[b]
1	acetone	Na_2CO_3	$Ir(ppy)_3$	52
2	acetone	K_2HPO_4	$Ir(ppy)_3$	28
3	acetone	NaOH	$Ir(ppy)_3$	48
4	acetone	NaOAc	$Ir(ppy)_3$	39
5	acetone	Et_3N	$Ir(ppy)_3$	45

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 eq), **2a** (0.3 mmol, 1.5 eq), base (0.3 mmol, 1.5 eq), $Ir(ppy)_3$ (5 mol %), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 12 h, 30 W blue LED; [b]Yield of the isolated product.

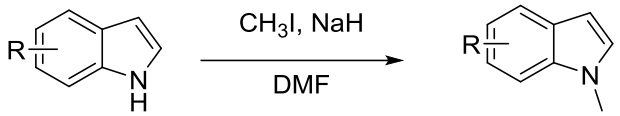
2.4. No PC screening

Entry[a]	Solvent	Base	Light	Yield (%)[b]
1	acetone	K_2CO_3	370~ nm	52
2	acetone	K_2CO_3	380~385 nm	55
3	acetone	K_2CO_3	385~390 nm	57
4	acetone	K_2CO_3	390~ nm	53
5	acetone	K_2CO_3	405~ nm	54
6	acetone	K_2CO_3	white LEDs	25
7	acetone	K_2CO_3	green LEDs	0
8	acetone	DABCO	385~390 nm	45
9	acetone	DIPEACO	385~390 nm	26
10	acetone	PMDETA	385~390 nm	trace
11	acetone	TMEDA	385~390 nm	trace
12[c]	acetone	K_2CO_3	385~390 nm	56
13[d]	acetone	K_2CO_3	385~390 nm	49
14[e]	acetone	K_2CO_3	385~390 nm	52
15[f]	acetone	K_2CO_3	385~390 nm	53

[a]Unless otherwise noted, all reactions were carried out using **1a** (0.2 mmol, 1.0 eq), **2a** (0.6 mmol, 3.0 eq), base (0.3 mmol, 1.5 eq), $Ir(ppy)_3$ (5 mol %), solvent (2.0 mL) at ambient temperature, under Ar atmosphere for 12 h, 30W blue LED; [b]Yield of the isolated product; [c]**2a** (0.6 mmol, 3.0 eq); [d]**2a** (0.6 mmol, 3.0 eq), base (0.6 mmol, 3.0 eq); [e]**1a** (0.9 mmol), base (0.45 mmol); [f]**1a** (0.9 mmol), base (0.9 mmol).

3. General Procedures for the Synthesis of Compounds 1 and 2

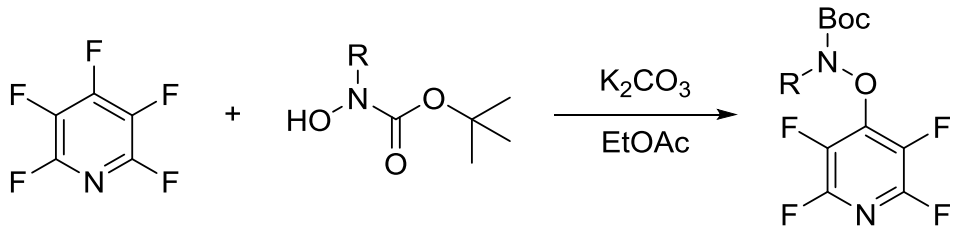
3.1 General procedure for the preparation of compounds 1



1

To a two-necked flask equipped with a magnetic stirring bar, substituted or unsubstituted indoles (5.0 mmol, 1.0 eq.) and DMF (0.25 M) were added under an Ar atmosphere. Then, the solution was cooled to 0 ℃ and NaH (5.0 mmol, 1.0 eq.) stored in coal oil was added. After the mixture was stirred for 30 minutes at room temperature, CH_3I (6 mmol, 1.2 eq.) was added dropwise, and the mixture was stirred at room temperature overnight. Thereafter, the reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc. The combined organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the residue by column chromatography (PE/EA = 19:1) afforded the desired 1-methylindoles.

3.2 General procedure for the preparation of compounds 2

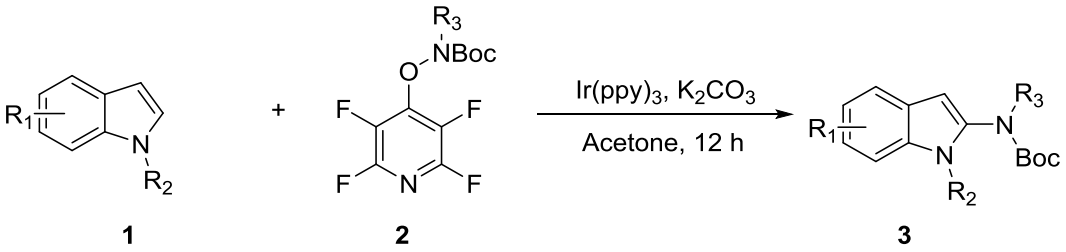


2

To a solution of oxime ester derivatives (10 mmol, 1.0 equiv.) in EtOAc was added K_2CO_3 (12 mmol, 1.2 equiv.) and pentafluoropyridine (12 mmol, 1.2 eq.). The mixture was stirred overnight. Then the reaction mixture was washed twice with water (30 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (PE/EtOAc = 19:1) to afford the corresponding *O*-aryl hydroxylamines.

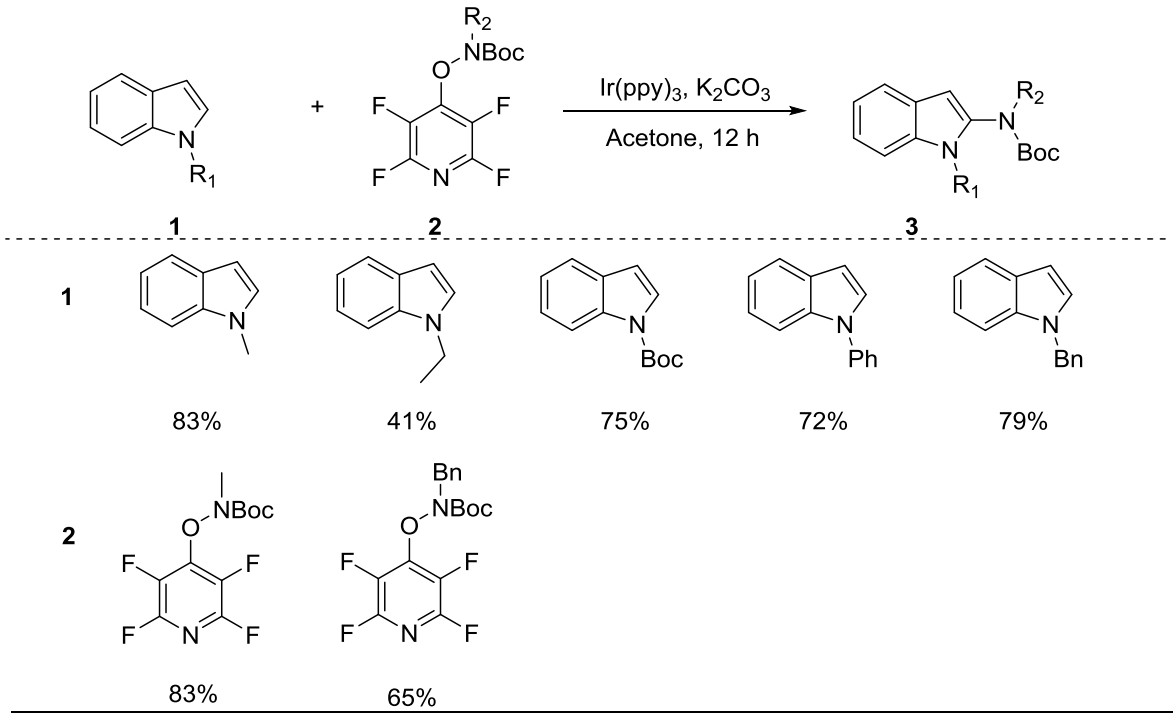
4. General Procedure for the Preparation of Products 3

4.1 Procedure for the preparation of products 3

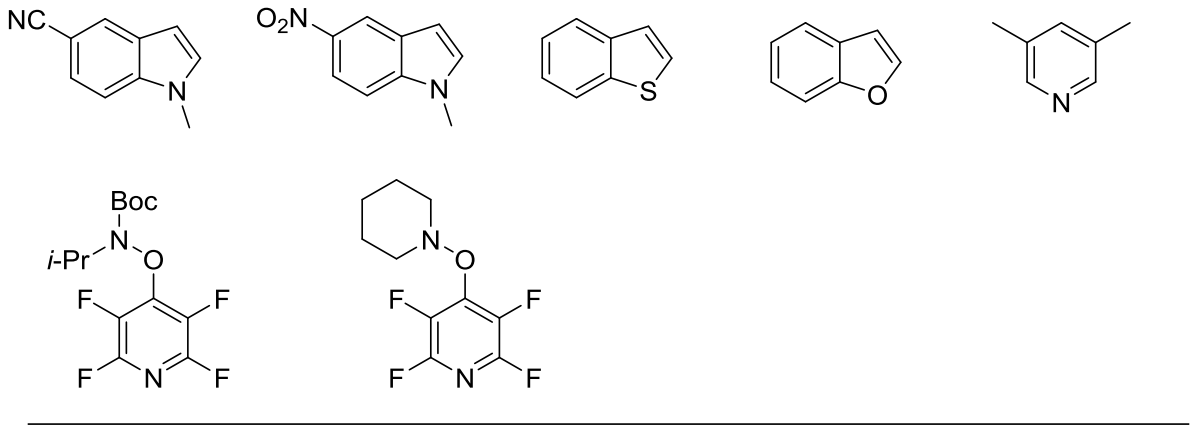


To a 15 mL Schlenk flask equipped with a magnetic stirring bar, compounds **1** (0.2 mmol, 1.0 equiv.), compounds **2** (0.3 mmol, 1.5 equiv.), K_2CO_3 (0.3 mmol, 1.5 equiv.) and acetone (2 mL) were added. The resulting mixture was charged with argon, then stirred and irradiated by a 30 W blue LED at ambient temperature for 12h. Thereafter, the solvent was removed under reduced pressure and then purified by column chromatography to afford the desired products **3**.

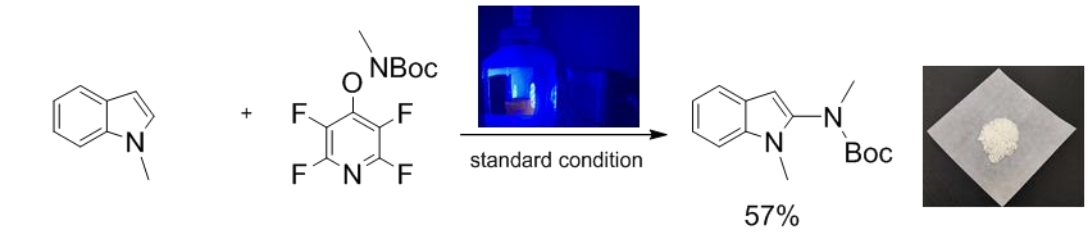
Scheme S1 Evaluation of amino substituents of starting materials 1 and 2



Scheme S2 Unsuccessful substrates



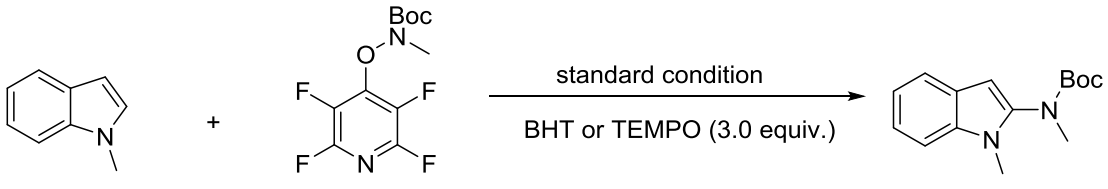
4.2 Scale-up reaction



1a (0.263 g, 2.0 mmol) **2a** (0.891 g, 3.0 mmol) **3a (0.296 g 1.138 mmol)**

5. Mechanistic Studies

5.1 Trapping Experiment



1a **2a** **3a**
BHT: trace
TEMPO: trace

Radical trapping experiments between **1a** and **2a** were conducted under standard conditions with two trapping agents (BHT and TEMPO) to determine the putative

radical. The desired product **3a** was obtained trace when BHT or TEMPO was added. The corresponding coupled product between BHT radical and the crude reaction mixture was successfully detected by HRMS (Figure S2). HRMS (EI): $C_{21}H_{35}NNaO_3^+$, $[M+Na]^+$ calcd: 372.2509, found: 372.2527 (BHT-adduct); $C_{30}H_{44}KN_2O_3^+$, $[M+K]^+$ calcd: 519.2984, found: 519.2989 (BHT-adduct). The corresponding coupled product between TEMPO radical and the crude reaction mixture was successfully detected by HRMS (Figure S3). HRMS (EI): $C_{15}H_{31}N_2O_3^+$, $[M+H]^+$ calcd: 287.2329, found: 287.2307 (TEMPO-adduct); $C_{24}H_{39}KN_3O_3^+$, $[M+K]^+$ calcd: 456.2623, found: 456.2606 (TEMPO-adduct).

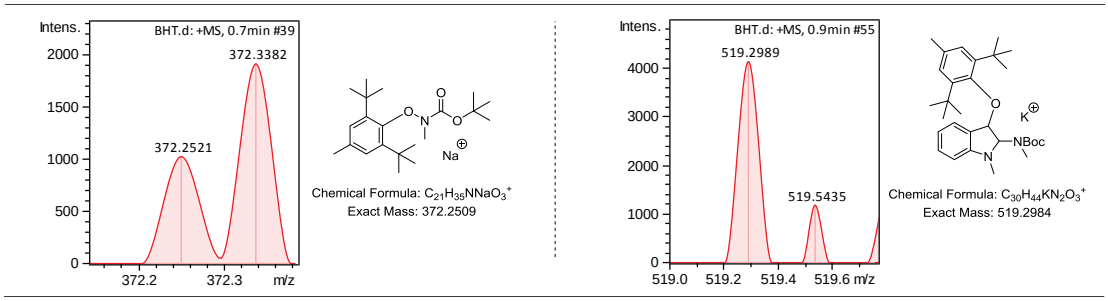


Figure S2. Crude ESI-MS of the BHT-trapping experiments

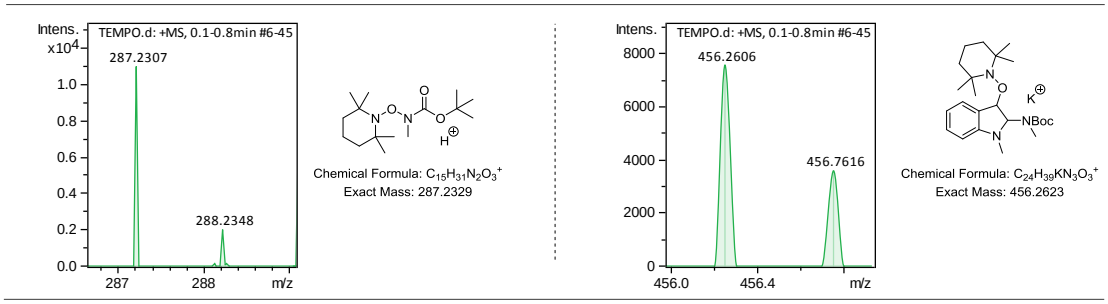
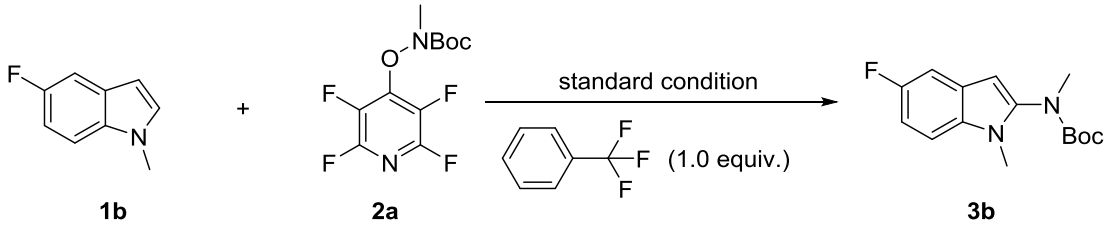


Figure S3. Crude ESI-MS of the TEMPO-trapping experiments

5.2 Light-On-Off experiment



The light on/off experiment of the model reaction was performed parallelly on a 0.40 mmol scale following the standard procedure by adding 1.0 equiv. trifluorotoluene as

internal standard. The reaction started with successive irradiation and black periods to study the influence of continuous irradiation of the visible-light for the progress photochemical reaction. After being irradiated with 30 W blue LEDs for 2 h, an aliquot (200 uL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.4 mL $CDCl_3$-d_1. The yield of the desired product **3b** was determined by ^{19}F NMR. The reaction was then stirred with light-off for 2 h and the yield was determined by ^{19}F NMR. All of the following yields were analyzed in the identical way after a 2 h light-on or light-off. These results revealed that light is a necessary component of the reaction.

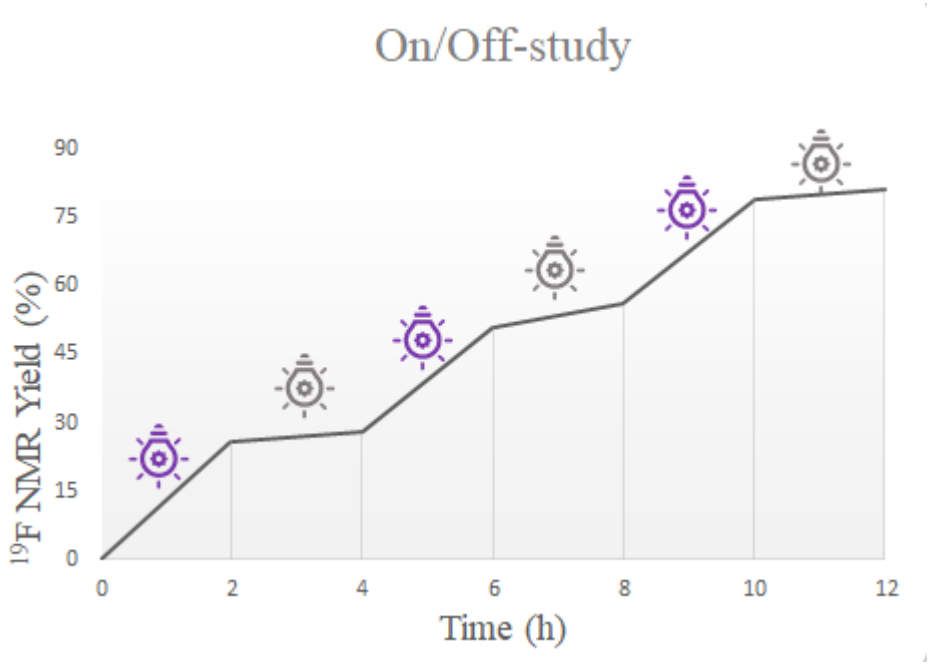
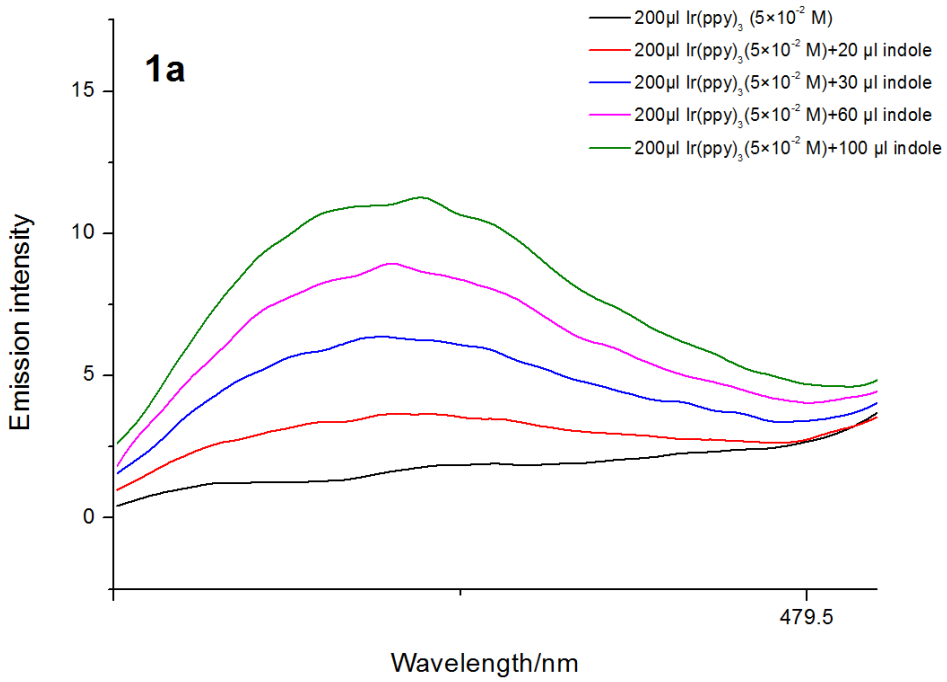
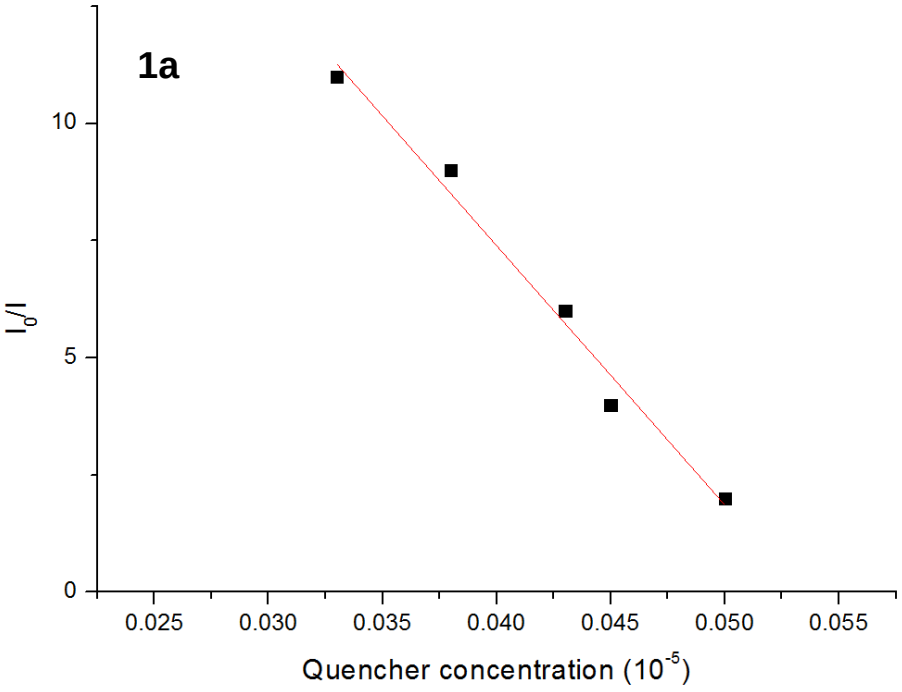


Figure S4. Time profile of the transformation with light ON/OFF over time

5.3 Emission Quenching Experiments

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in aacetone. All $Ir(ppy)_3$ solutions (concentration of 5×10^{-2} M) were excited at 492 nm and the emission intensity was collected at 560 nm.


1a
200μl Ir(ppy)3 (5×10-2 M)
200μl Ir(ppy)3(5×10-2 M)+20 μl indole
200μl Ir(ppy)3(5×10-2 M)+30 μl indole
200μl Ir(ppy)3(5×10-2 M)+60 μl indole
200μl Ir(ppy)3(5×10-2 M)+100 μl indole
Emission intensity
15
10
5
0
479.5
Wavelength/nm


1a
I0/I
10
5
0
0.025
0.030
0.035
0.040
0.045
0.050
0.055
Quencher concentration (10-5)

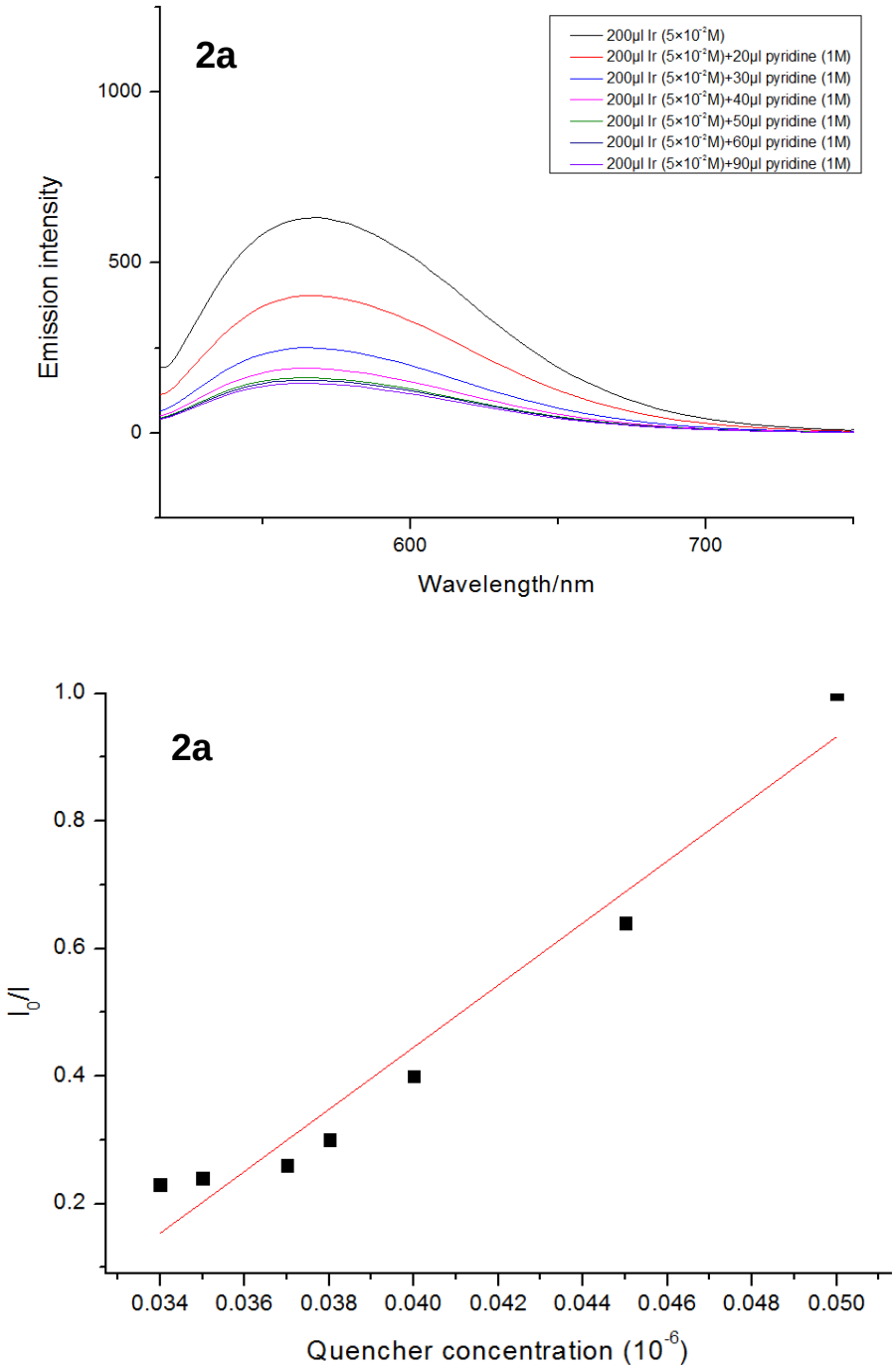
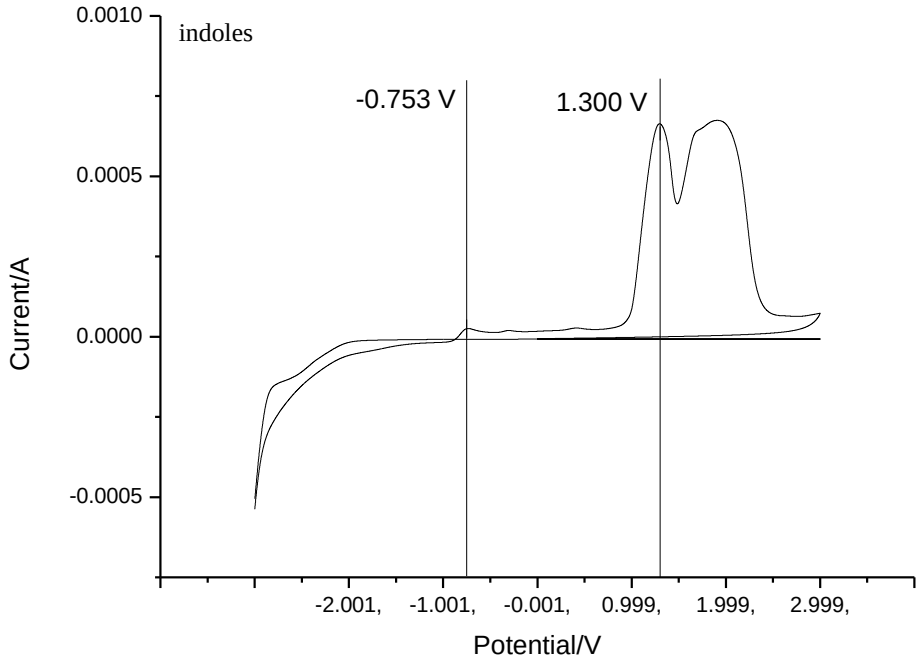


Figure S5. Quenching of the $Ir(ppy)_3$ emission (5×10-2 M in acetone) in the presence of increasing amounts of **1a**, **2a**.

5.4 Cyclic voltammetry

CV was performed using a CHI650D electrochemical workstation with a glassycarbon as the working electrode, the Ag/AgCl electrode (3 M KCl) as the reference electrode, and a platinum electrode as the counter electrode. The testing solution of **1a**, **2a** and $Ir(ppy)_3$ was prepared by dissolving the sample (0.05 mmol) into MeCN (5 mL) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The scanned potential range was typically -3.0 V and +3.0 V at a 100 mV/s.



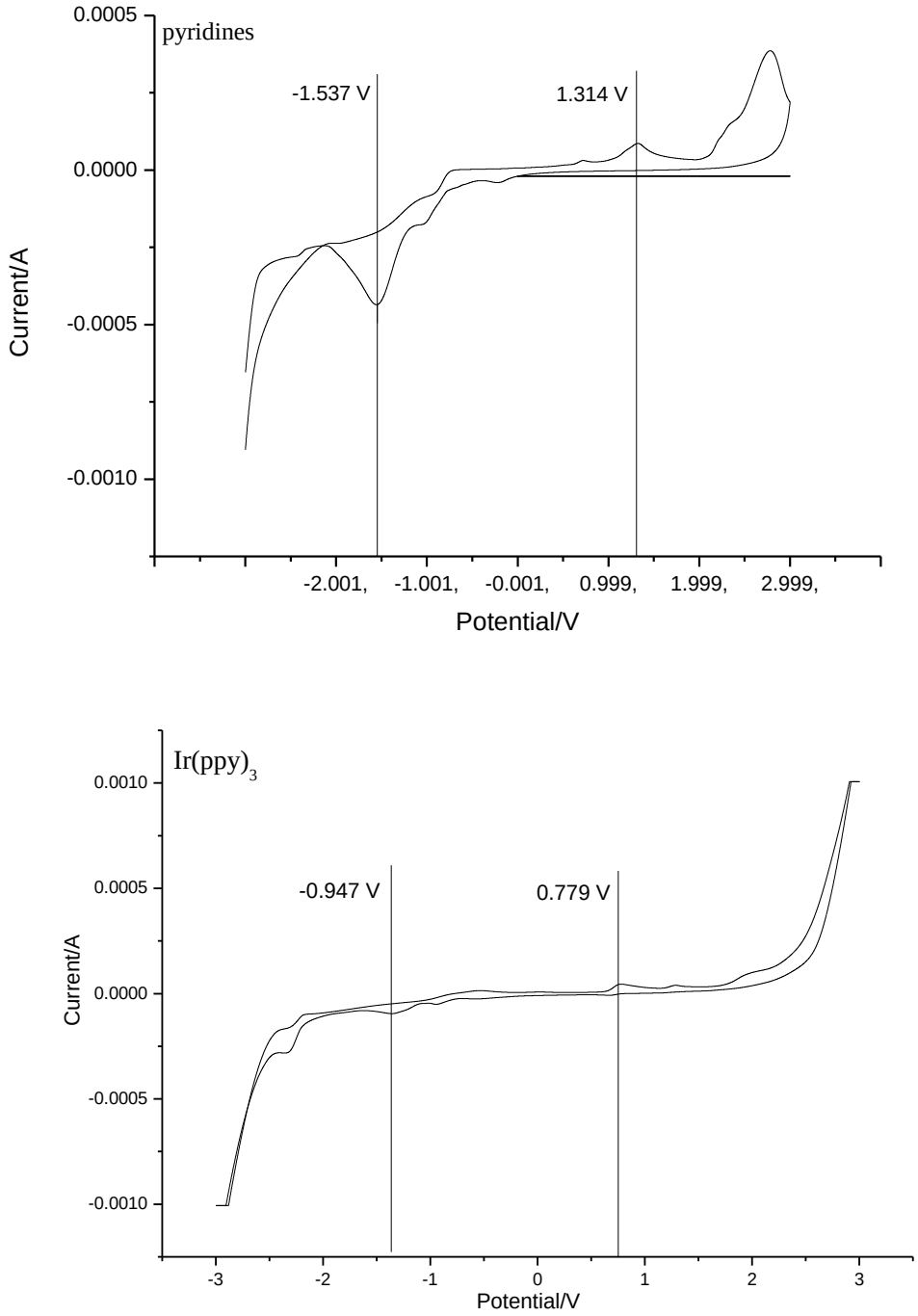


Figure S6. CV study of **1a** in MeCN, $E_{ox}^{p/2}$ = + 1.270 V vs SCE, $E_{red}^{p/2}$ = - 0.723 V vs. SCE, CV study of **2a** in MeCN, $E_{ox}^{p/2}$ = + 1.284 Vvs SCE, $E_{red}^{p/2}$ = - 1.507 V vs. SCE, CV study of $Ir(ppy)_3$ in MeCN, $E_{ox}^{p/2}$ = + 0.749 V vs SCE, $E_{red}^{p/2}$ = - 0.917 V vs. SCE. (the obtained value was referenced to Ag/AgCl and converted to SCE by substracting 0.03 V)

5.5 UV/Vis absorption spectrometry between 1a, 2a and base

UV/Vis absorption spectra between **1a** (0.1 M), **2a** (0.1 M) in 2 mL toluene were recorded in quartz cuvettes using a Shimadzu UV-2600 UV/Vis spectrometer.

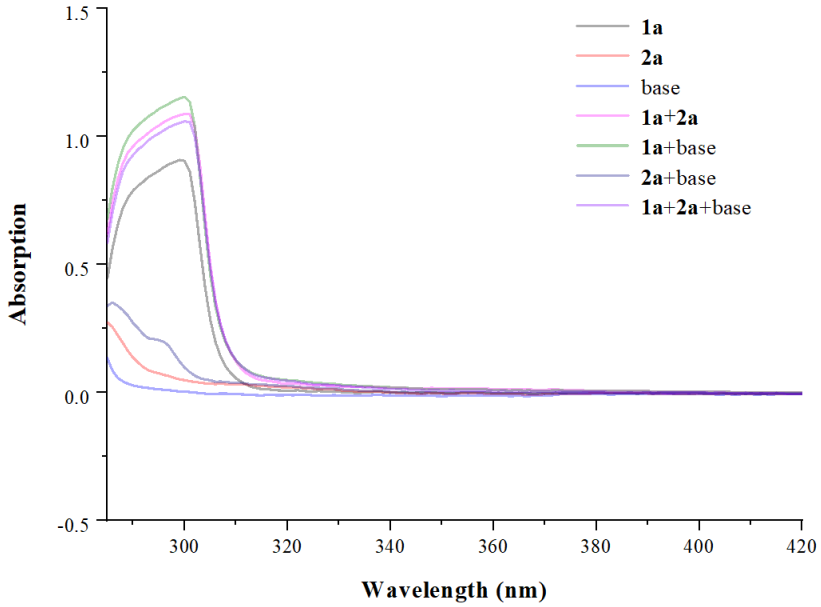
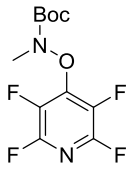


Figure S7. UV/Vis absorption spectrometry between **1a**, **2a** and base

6. Copies of NMR spectra

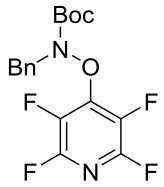
Raw material **2a** (yellow oil);



2a

IR (neat) *v* 1731, 1638, 1471, 1371, 1324, 1150, 1066, 983 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.40 (s, 3H), 1.48 (s, 9H);
^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.61 – -89.78 (m, 2F), -155.93 – -156.10 (m, 2F);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 156.7, 148.4 – 146.8 (m), 145.9 – 141.1 (m), 136.8 – 131.4 (m), 84.1, 39.3, 27.9;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{11}H_{12}F_4N_2NaO_3^+$ 319.0676; Found: 319.0651.

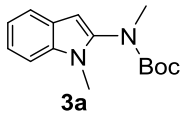
Raw material **2b** (white solid);



2b

m.p. 70-75 ℃;
IR (neat) *v* 1740, 1641, 1464, 1231, 1146, 1077, 978, 759 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 4.84 (s, 2H), 1.49 (s, 9H);
^{19}F NMR (376 MHz, Chloroform-*d*) δ -89.79 – -89.96 (m, 2F), -156.20 – -156.36 (m, 2F);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 156.0, 148.3 – 147.0 (m), 145.6 – 141.4 (m), 134.5, 135.6 – 131.7 (m), 128.9, 128.6, 128.4, 84.4, 56.4, 28.0;
HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{17}H_{16}F_4KN_2O_3^+$ 411.0729; Found: 411.0726.

Product **3a** (yellow oil);

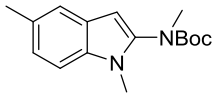


3a

IR (neat) *v* 2969, 1697, 1335, 1104, 989, 751, 734, 658 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.26 (s, 1H), 3.55 (s, 3H), 3.25 (s, 3H), 1.40 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.1, 138.9, 134.7, 126.6, 121.6, 120.6, 119.6, 109.3, 95.4, 81.0, 38.4, 28.8, 28.3;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{15}H_{20}KN_2O_2^+$ 299.1151; Found: 299.1156.

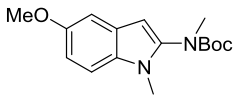
Product **3b** (white solid);



3b

m.p. 76-82 ℃;
IR (neat) *v* 2964, 1683, 1321, 1098, 993, 725, 749, 654 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.17 (s, 1H), 3.52 (s, 3H), 3.23 (s, 3H), 2.43 (s, 3H), 1.39 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.1, 138.9, 133.1, 128.8, 126.8, 123.1, 120.3, 109.0, 94.9, 80.9, 38.4, 28.8, 28.3, 21.5;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{16}H_{22}N_2NaO_2^+$ 275.1754 ; Found: 275.1724.

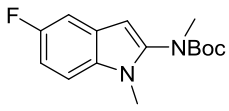
Product **3c** (purple solid);



3c

m.p. 104-105 ℃;
IR (neat) *v* 2973, 1700, 1335, 1209, 1143, 1078, 786, 725 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.19 (s, 1H), 3.83 (s, 3H), 3.52 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);
^{13}C NMR {1H} (100 MHz, Chloroform-*d*) δ 155.0, 154.2, 139.2, 129.9, 126.8, 111.7, 110.1, 102.5, 95.1, 80.9, 55.9, 38.4, 28.9, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{23}N_2O_3^+$ 291.1703; Found: 291.1720.

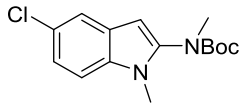
Product **3d** (brown solid);



3d

m.p. 90-94 ℃
IR (neat) *v* 1706, 1489, 1367, 1345, 1147, 1078, 952, 853 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (td, *J* = 9.5, 3.4 Hz, 2H), 6.96 (td, *J* = 9.2, 2.5 Hz, 1H), 6.23 (s, 1H), 3.55 (s, 3H), 3.25 (s, 3H), 1.41 (s, 9H);
^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.76;
^{13}C NMR {1H} (100 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 234.0 Hz), 154.9, 140.2, 131.3, 126.7 (d, *J* = 10.4 Hz), 110.0 (d, *J* = 2.8 Hz), 109.80 (d, *J* = 19.3 Hz), 105.5 (d, *J* = 23.6 Hz), 95.5 (d, *J* = 4.5 Hz), 81.1, 38.3, 29.0, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}FN_2NaO_2^+$ 301.1323 ; Found: 301.1319.

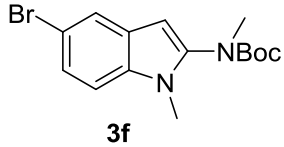
Product **3e** (white solid);



3e

mp 79-89 ℃;
IR (neat) *v* 1732, 1455, 1316, 1141, 916, 859, 821, 767 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.50 (d, *J* = 1.8 Hz, 1H), 7.18 – 7.15 (m, 2H), 6.21 (s, 1H), 3.54 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.8, 140.1, 133.1, 127.5, 125.3, 121.8, 112.0, 110.4, 95.1, 81.2, 38.3, 29.0, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{20}ClN_2O_2^+$ 295.1208 ; Found: 295.1177.

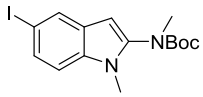
Product **3f** (yellow solid);



3f

m.p. 134-136 ℃;
IR (neat) *v* 1713, 1450, 1439, 1350, 1329, 1317, 1073, 911 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 1.9 Hz, 1H), 7.28 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.21 (s, 1H), 3.53 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.8, 139.9, 133.3, 128.1, 124.4, 123.0, 112.9, 110.9, 95.0, 81.2, 38.3, 29.0, 28.3;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{15}H_{19}BrN_2NaO_2^+$ 361.0522; Found: 361.0547.

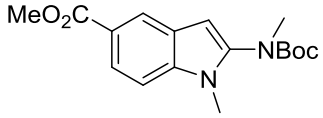
Product **3g** (purple solid);



3g

m.p. 88-90 ℃;
IR (neat) *v* 1698, 1564, 1473, 1348, 1146, 1081, 956, 826, 764 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.45 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.19 (s, 1H), 3.53 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);
^{13}C NMR {1H} (100 MHz, Chloroform-*d*) δ 160.9, 155.0, 139.2, 134.8, 134.7, 122.9, 121.5, 121.4, 108.4, 108.1, 96.0, 95.7, 95.5, 81.0, 38.4, 29.0, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{20}IN_2O_2^+$ 387.0564 ; Found: 387.0584.

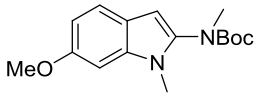
Product **3h** (pale pink oil);



3h

IR (neat) *v* 2960, 1704, 1306, 1250, 1155, 1081, 852, 769, 691 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 6.37 (s, 1H), 3.92 (s, 3H), 3.58 (s, 3H), 3.27 (s, 3H), 1.41 (s, 9H);
^{13}C NMR {1H} (100 MHz, Chloroform-*d*) δ 168.12, 154.8, 140.2, 137.2, 126.0, 123.6, 123.0, 121.7, 109.0, 96.9, 81.3, 51.9, 29.1, 28.2;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{17}H_{22}N_2NaO_4^+$ 341.1472 ; Found: 341.1479.

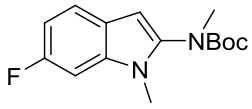
Product **3i** (white solid);



3i

m.p. 96-108 ℃;
IR (neat) *v* 1711, 1488, 1366, 1340, 1210, 1137, 843, 800 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.74 (d, *J* = 2.2 Hz, 1H), 6.19 (s, 1H), 3.87 (s, 3H), 3.50 (s, 3H), 3.23 (s, 3H), 1.44 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.0, 154.1, 139.2, 129.9, 126.8, 111.7, 110.1, 102.5, 95.0, 80.9, 55.9, 38.4, 28.9, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{16}H_{23}N_2O_3^+$ 291.1703; Found: 291.1720.

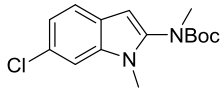
Product **3j** (yellow solid);



3j

m.p. 90-103 ℃;
IR (neat) *v* 1698, 1365, 1293, 1230, 956, 862, 771, 648 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.95 (dd, *J* = 9.8, 2.3 Hz, 1H), 6.90 – 6.81 (m, 1H), 6.24 (s, 1H), 3.50 (s, 3H), 3.24 (s, 3H), 1.50-1.33 (s, 9H);
^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.5;
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 159.7 (d, $^{1}J_{C-F}$ = 237.3 Hz), 155.0, 139.2, 134.7 (d, $^{3}J_{C-F}$ = 11.7 Hz), 122.8, 121.4 (d, $^{3}J_{C-F}$ = 9.9 Hz), 108.2 (d, $^{2}J_{C-F}$ = 24.3 Hz), 95.8 (d, $^{2}J_{C-F}$ = 26.3 Hz), 95.5, 81.1, 38.4, 29.0, 28.3;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{15}H_{19}FN_2NaO_2^+$ 301.1323; Found: 301.1337.

Product **3k** (white solid);



3k

m.p. 81-89 ℃;

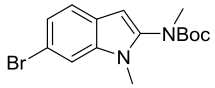
IR (neat) *v* 2971, 1708, 1455, 1366, 1323, 1148, 1077, 917, 808 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 1H), 7.09 – 7.03 (m, 1H), 6.24 (s, 1H), 3.52 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);

^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.9, 139.5, 135.1, 127.4, 125.0, 121.5, 120.3, 109.4, 95.6, 81.2, 38.3, 28.9, 28.3;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{15}H_{20}ClN_2O_2^+$ 295.1208 ; Found: 295.1231.

Product **3l** (yellow oil);



3l

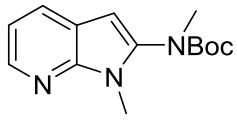
IR (neat) *v* 1705, 1471, 1452, 1365, 1338, 1319, 1089, 907 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.19 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.24 (s, 1H), 3.51 (s, 3H), 3.24 (s, 3H), 1.40 (s, 9H);

^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.8, 139.5, 135.5, 125.3, 122.9, 121.9, 115.0, 112.4, 95.6, 81.2, 38.3, 28.9, 28.3;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{15}H_{19}BrKN_2O_2^+$ 377.0261; Found: 377.0274.

Product **3m** (white solid);



3m

m.p. 126-130 ℃;

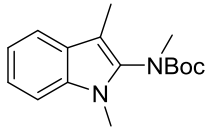
IR (neat) *v* 1680, 1493, 1348, 1146, 1081, 956, 826, 655cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 3.7 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.23 (s, 1H), 3.69 (s, 3H), 3.28 (s, 3H), 1.42 (s, 9H);

^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.7, 146.0, 142.8, 139.6, 128.3, 119.6, 116.1, 93.7, 81.3, 38.2, 28.2, 27.6;

HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{14}H_{20}N_3O_2^+$ 262.1550; Found: 262.1577.

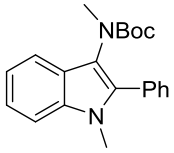
Product **3n** (white solid);



3n

m.p. 86-92 ℃;
IR (neat) *v* 2912,1700, 1335, 1209, 1143, 1078, 786, 725 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 3.53 (s, 3H), 3.19 (s, 3H), 2.19 (s, 3H), 1.35 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.5, 127.0, 121.7, 119.0, 119.0, 109.1, 103.7, 80.6, 36.9, 38.3, 28.6, 28.3;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{16}H_{22}N_2NaO_2^+$ 275.1754 ; Found: 275.1781.

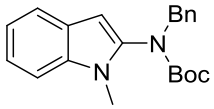
Product **3o (white solid)**;



3o

m.p. 90-96 ℃;
IR (neat) *v* 1893, 1493, 1207, 998, 858, 732, 690, 652 cm^{-1};
^{1}H NMR (400 MHz, Chloroform- *d*, *as a mixture of rotamers*) δ 7.53 – 7.46 (m, 4H), 7.42 – 7.35 (m, 3H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 3.67/3.64 (s/s, 3H), 3.13 (s, 2.28H), 2.98 (s, 0.71H), 1.49 (s, 2H), 1.18 (s, 7H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ129.8, 128.4, 122.0, 119.8, 118.1, 109.6, 79.4, 37.5, 31.1;
HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{21}H_{24}KN_2O_2^+$ 375.1469; Found: 375.1455.

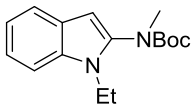
Product **3p** (white solid);



3p

m.p. 121-129 ℃;
IR (neat) *v* 1698, 1540, 1382, 1243, 1161, 872, 753, 700 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.17 (m, 7H), 7.01 – 7.05 (m, 1H), 6.17 (s, 1H), 4.78 (s, 2H), 3.27 (s, 3H), 1.41 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.8, 137.7, 134.8, 128.5, 127.6, 126.5, 121.5, 120.7, 119.5, 109.3, 96.5, 81.2, 54.8, 28.7, 28.3;
HRMS (ESI) m/z: $[M+H]^+$ Calcd for: $C_{21}H_{25}N_2O_2^+$ 337.1911; Found: 337.1912.

Product **3q** (pale oil);

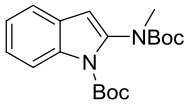


3q

IR (neat) *v* 2971, 1704, 1335, 1306, 1250, 1141, 1080, 974 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.25 (s, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.22 (s, 3H), 1.38 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.3, 138.2, 133.7, 126.9, 121.5, 120.9, 119.5, 109.7, 96.2, 80.9, 38.5, 37.2, 28.3, 15.0;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{16}H_{22}N_2NaO_2^+$ 275.1754 ; Found: 275.1724.

Product **3r** (brown oil);



3r

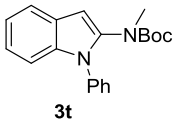
IR (neat) *v* 1710, 1453, 1325, 1228, 1149, 1076, 996, 743 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.37 (s, 1H), 3.20 (s, 3H), 1.66 (s, 9H), 1.35 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.8, 137.9, 134.6, 127.4, 124.4, 122.7, 120.6, 115.7, 115.5, 105.1, 83.8, 80.5, 37.7, 29.7, 28.3, 28.2;
HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{19}H_{26}KN_2O_4^+$ 369.1790; Found: 369.1760.

Product **3s** (white solid);

3s

m.p. 105-108 ℃;
IR (neat) *v* 1703, 1556, 1366, 1253, 1157, 858, 732, 700 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.09 (m, 6H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.33 (s, 1H), 5.19 (s, 2H), 3.01 (s, 3H), 1.36 (s, 9H);
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 155.1, 138.8, 137.6, 134.6, 128.6, 127.3, 126.8, 126.5, 121.9, 120.8, 119.8, 110.1, 96.8, 81.0, 46.1, 38.4, 28.2;
HRMS (ESI) m/z: $[M+K]^+$ Calcd for: $C_{21}H_{24}KN_2O_2^+$ 375.1469; Found: 375.1463.

Product **3t** (white solid);



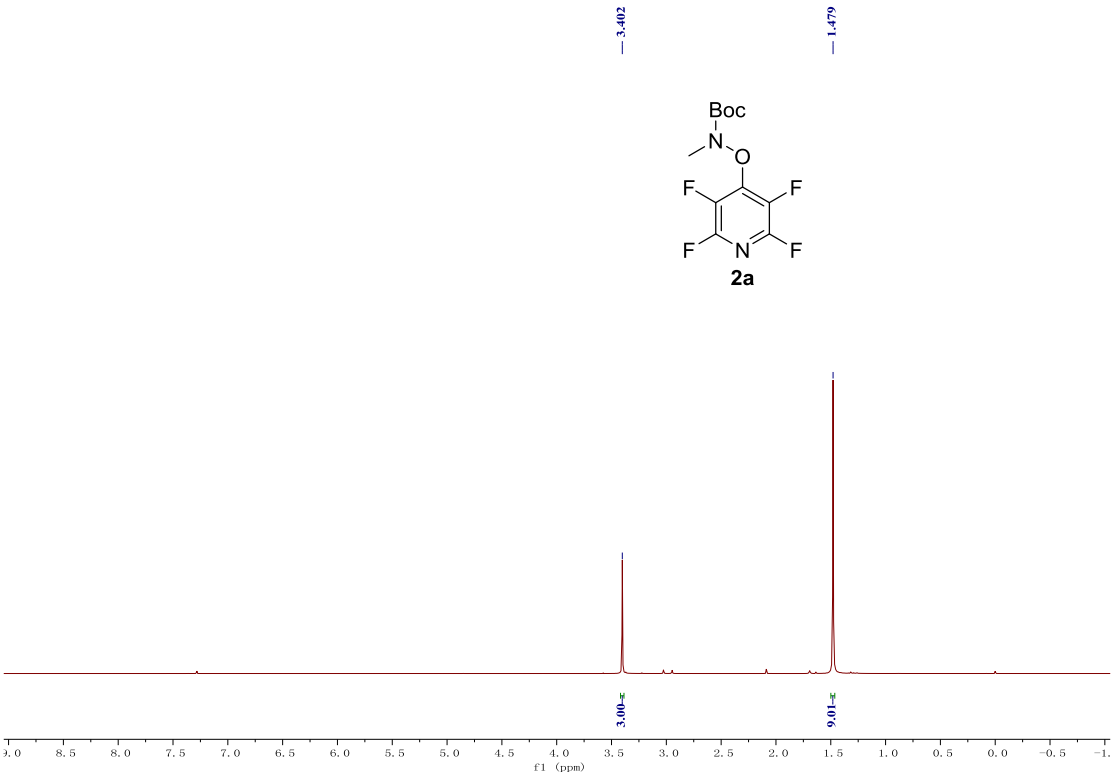
3t

m.p. 116-120 ℃;
IR (neat) *v* 2893, 1780, 1392, 1199, 980, 841, 710, 652 cm^{-1};
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.58 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 3H), 7.29 – 7.21 (s, 1H), 7.16 – 7.09 (m, 2H), 6.42 (s, 1H), 3.14 (s, 3H), 1.19 (s, 9H);

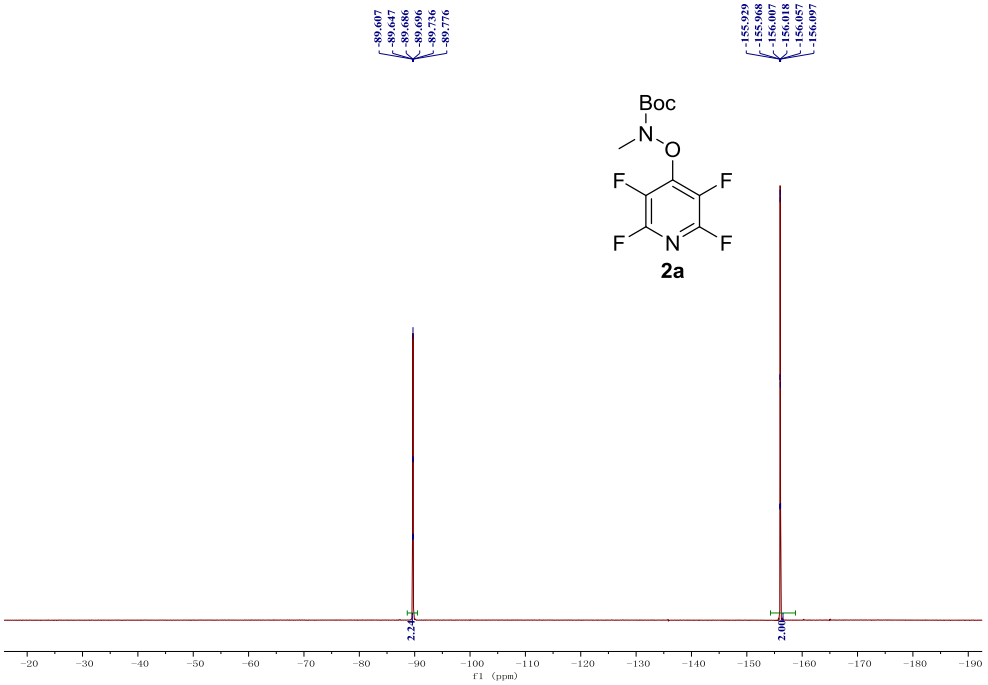
^{13}C NMR {^{1}H} (100 MHz, Chloroform-*d*) δ 154.6, 138.7, 137.1, 135.2, 129.5, 127.5, 126.9, 122.4, 120.8, 120.6, 110.5, 98.1, 80.8, 38.6, 28.1;
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for: $C_{20}H_{22}N_2NaO_2^+$ 345.1573; Found: 345.1543.

7. NMR Spectra of Compounds of 2a-2b, 3a-3t

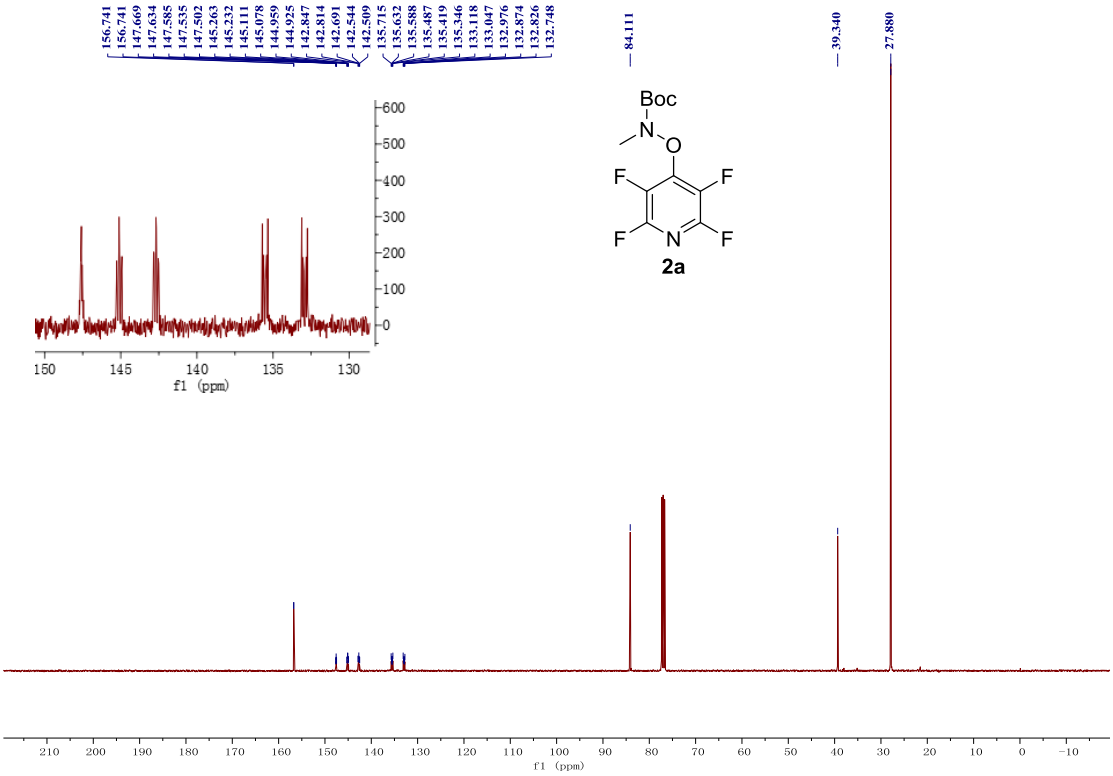
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 2a



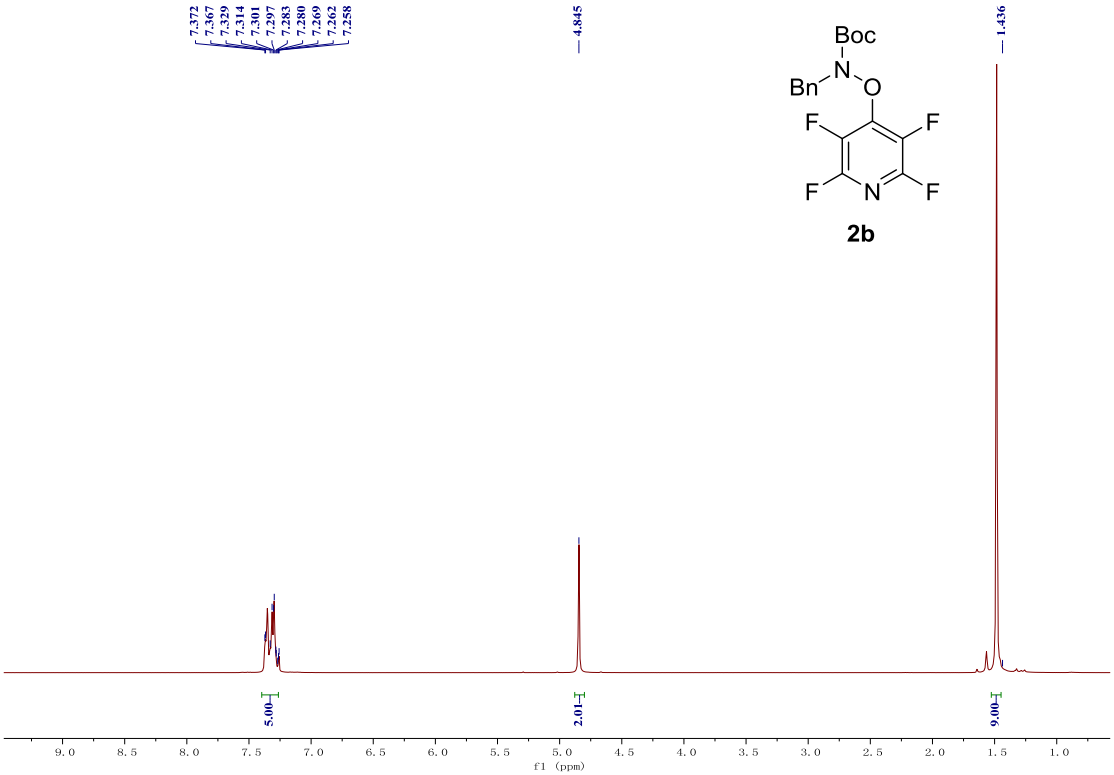
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 2a



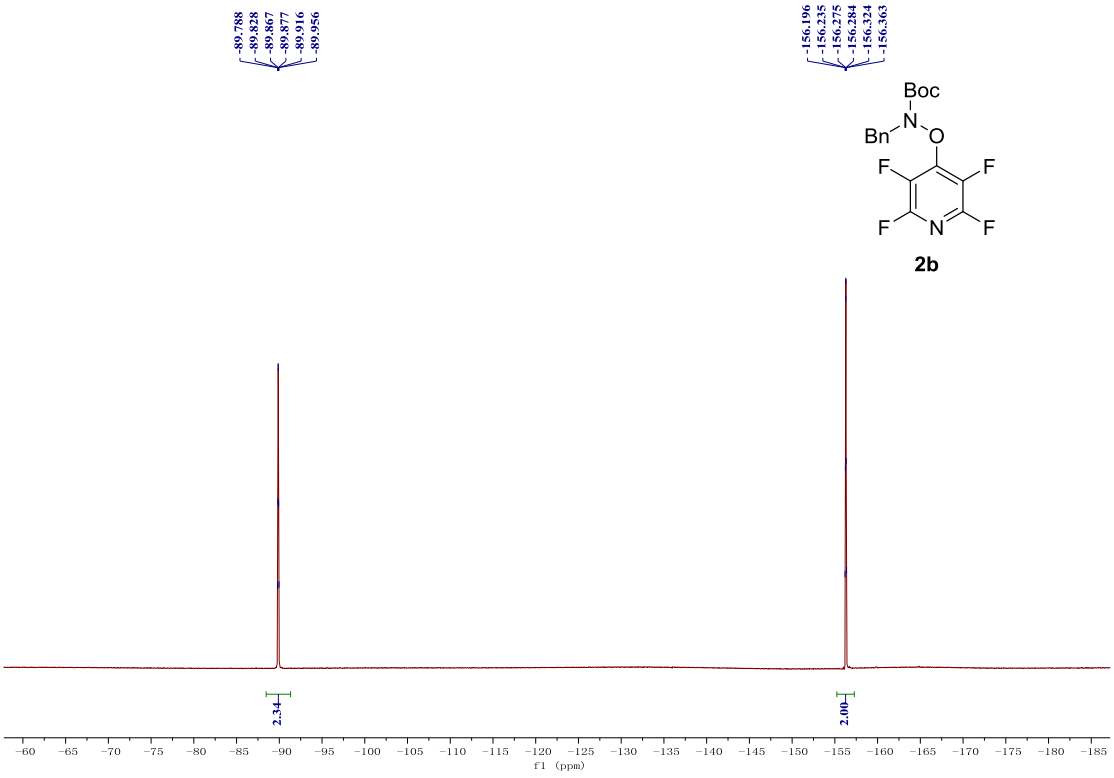
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 2a



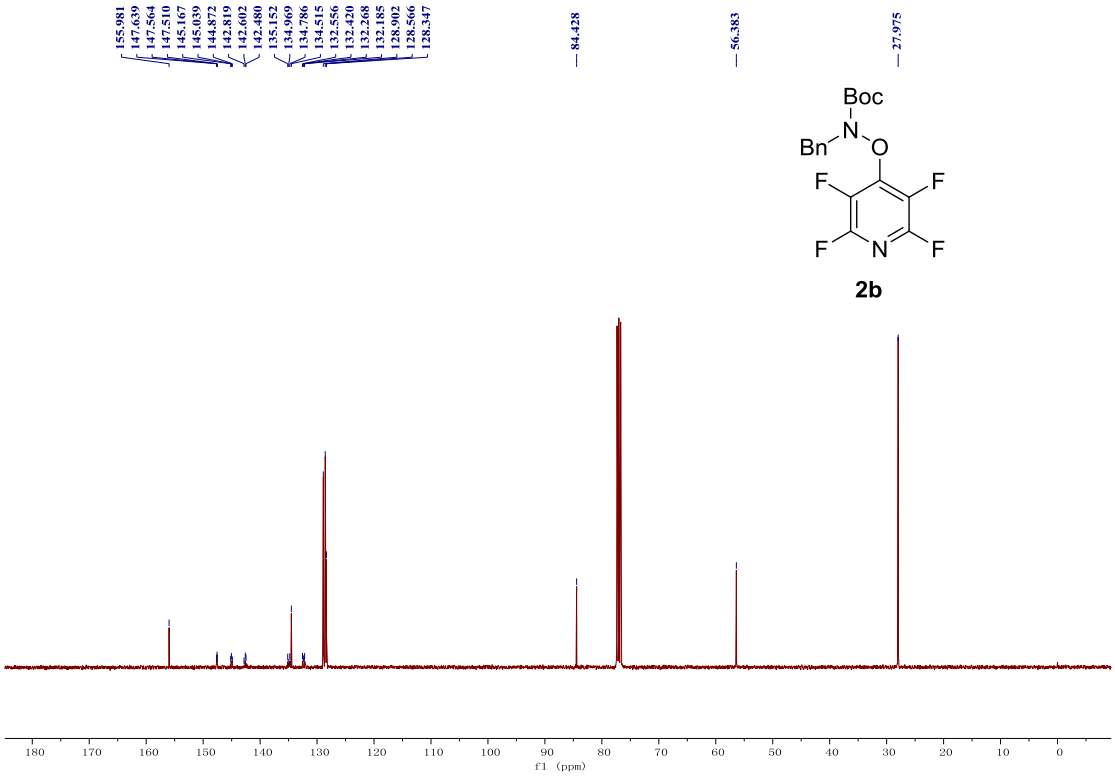
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 2b



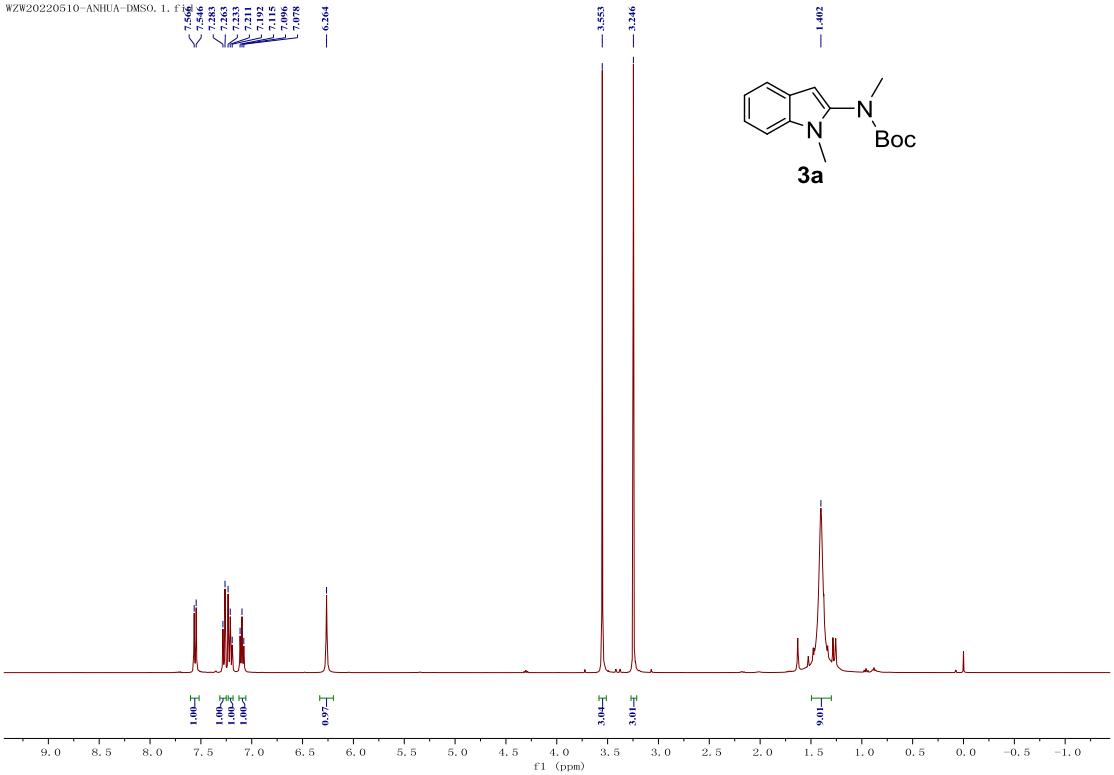
^{19}F NMR (400MHz, $CDCl_3$) spectrum of product 2b



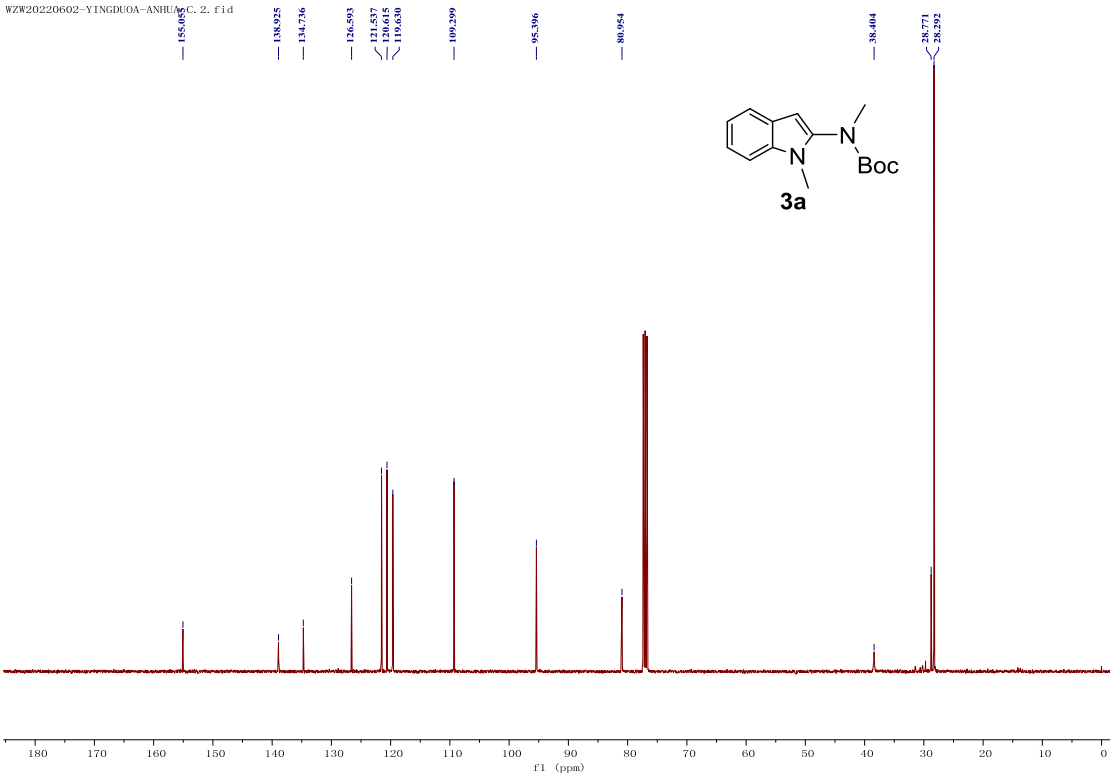
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 2b



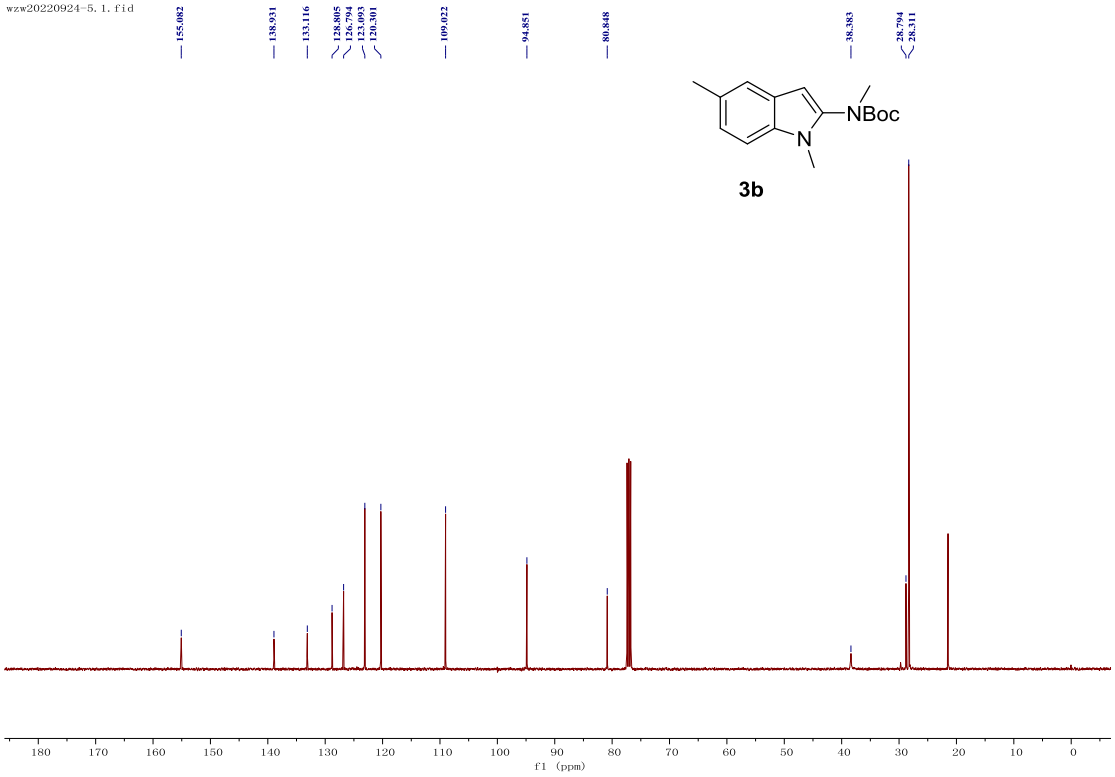
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3a



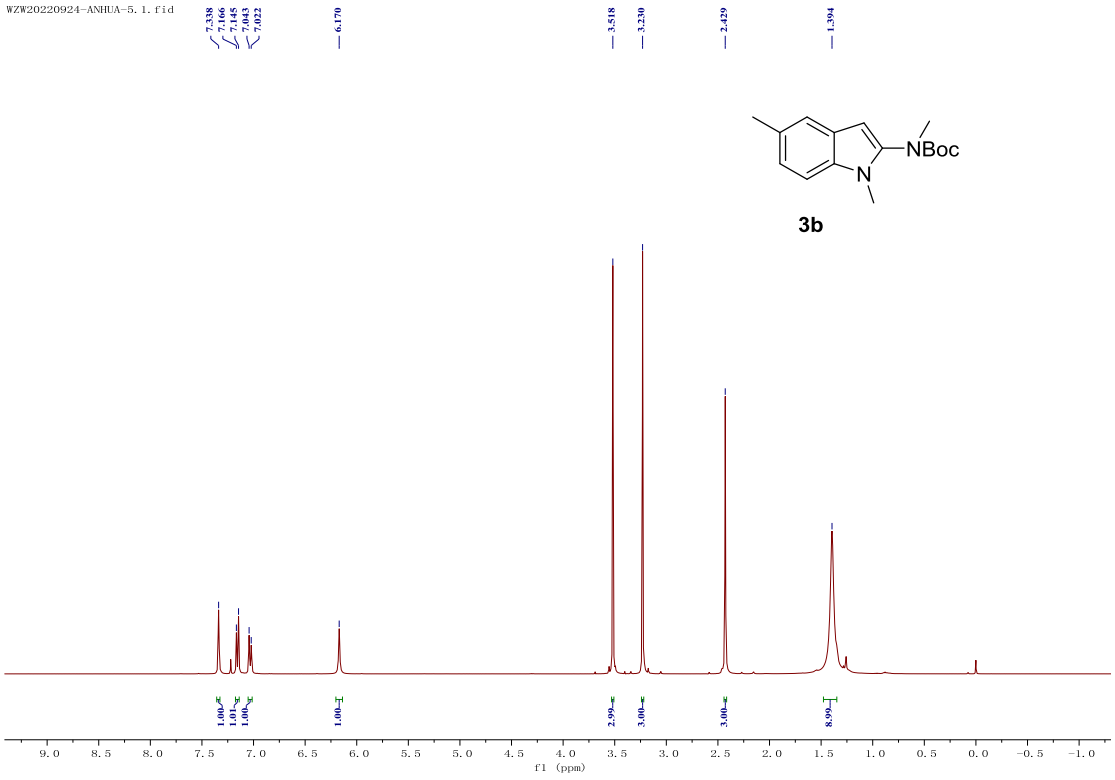
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3a



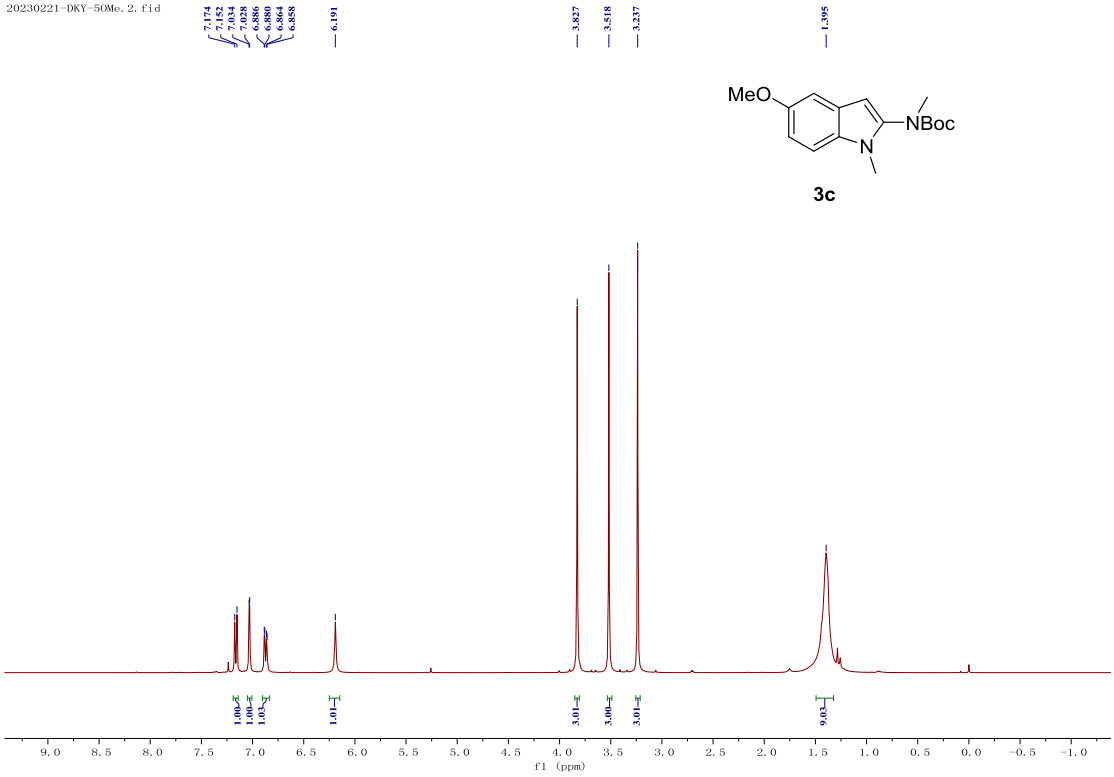
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3b



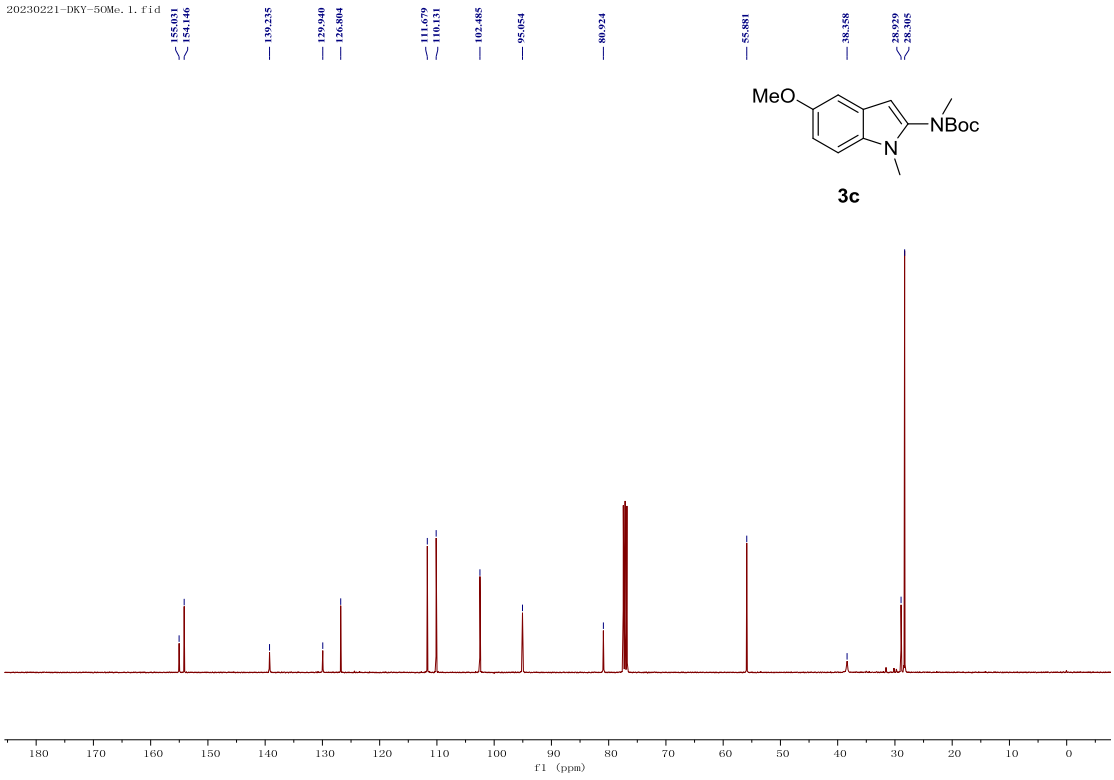
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3b



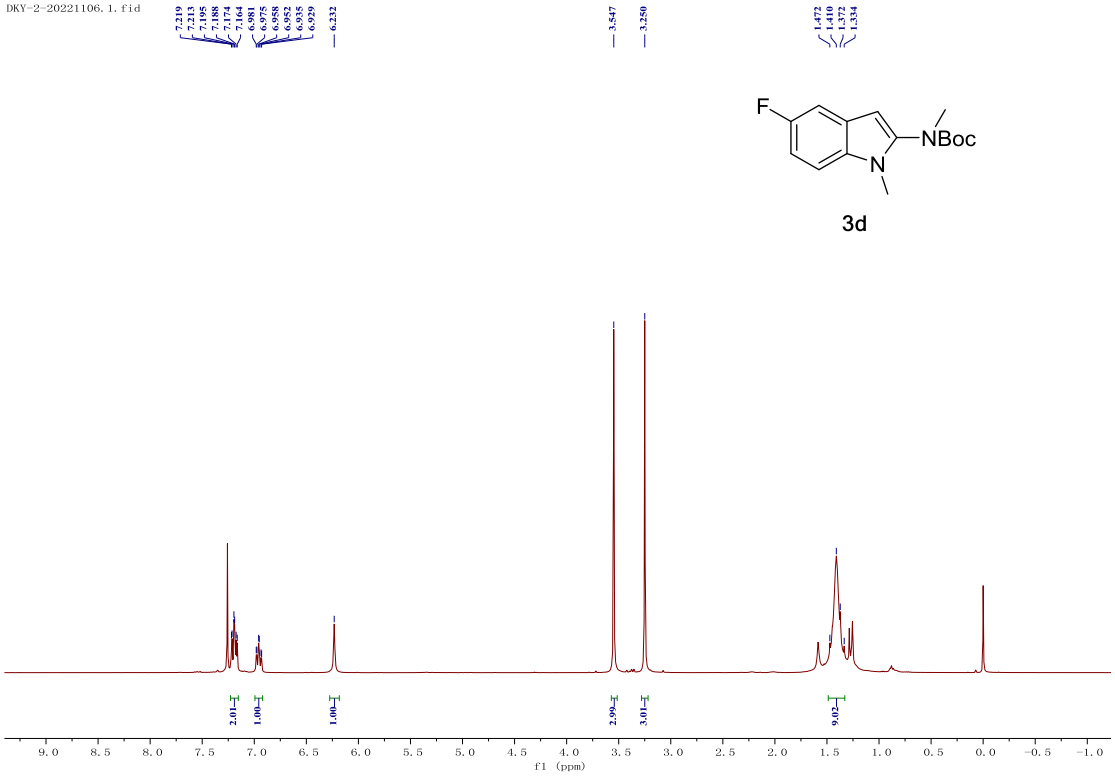
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3c



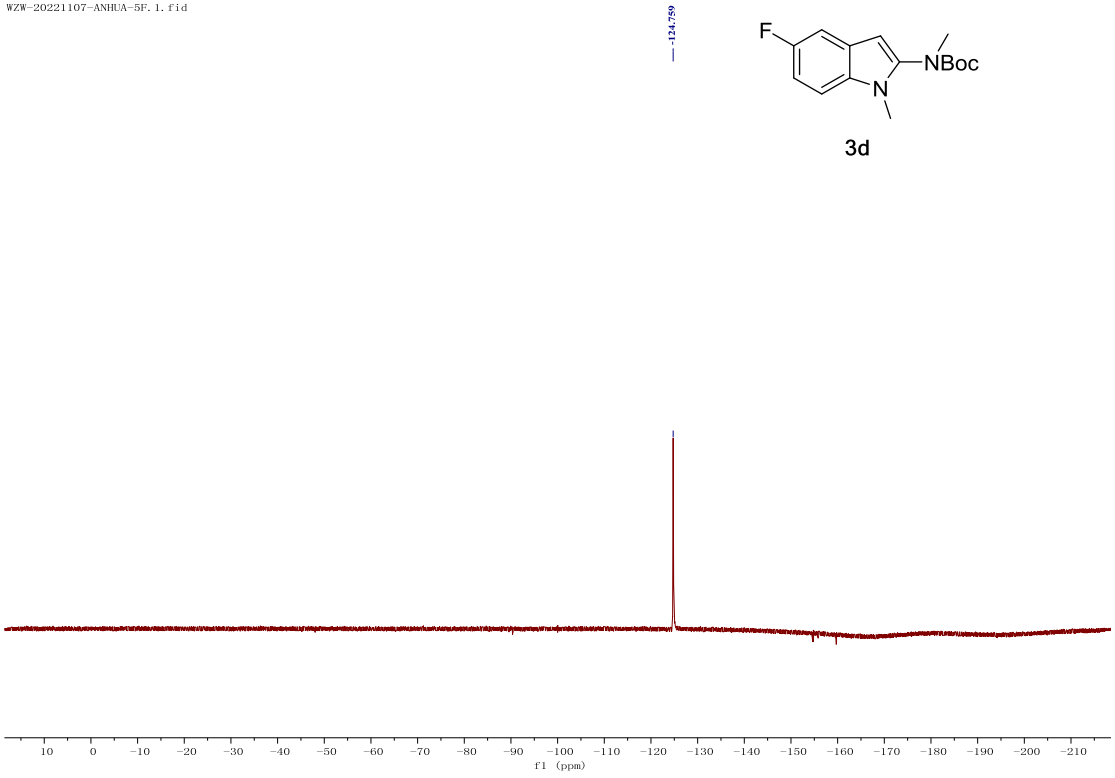
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3c



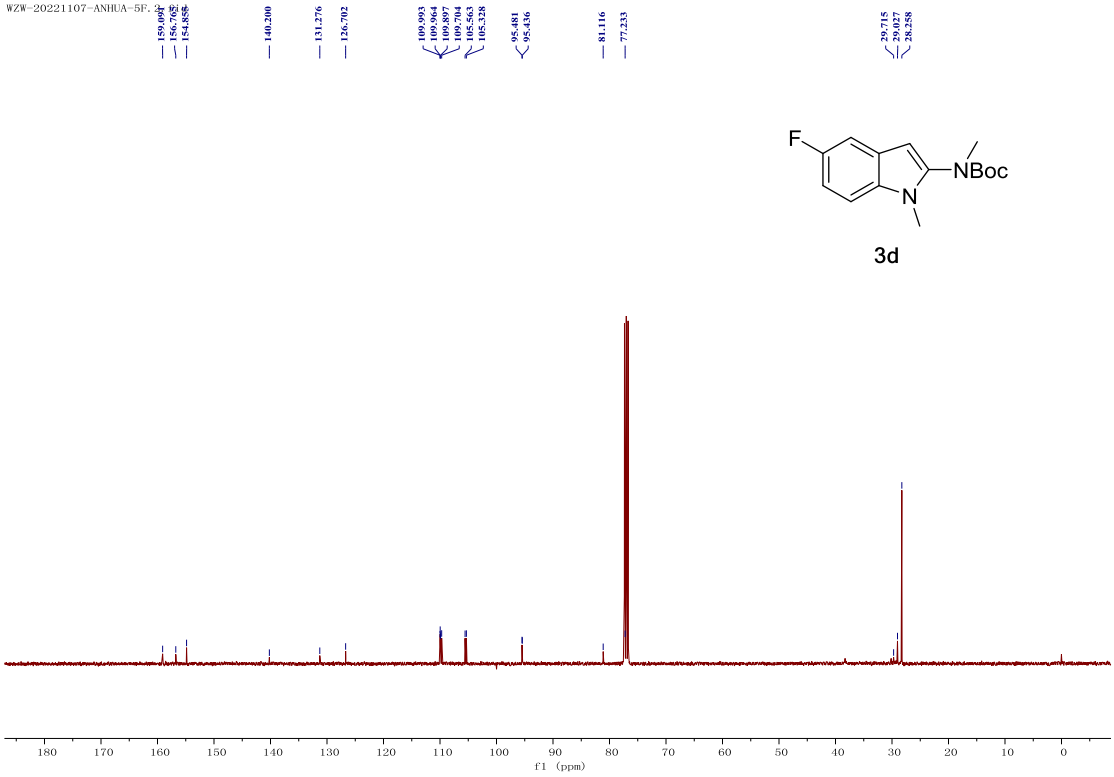
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3d



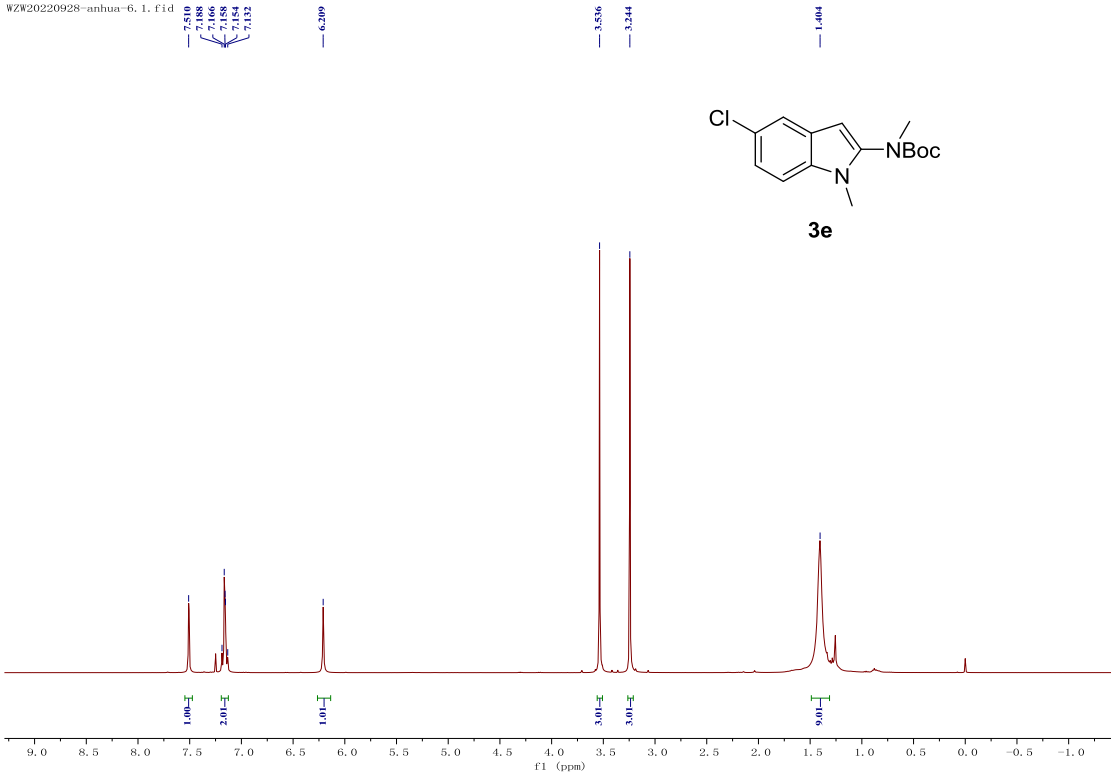
^{19}F NMR (376MHz, $CDCl_3$) spectrum of product 3d



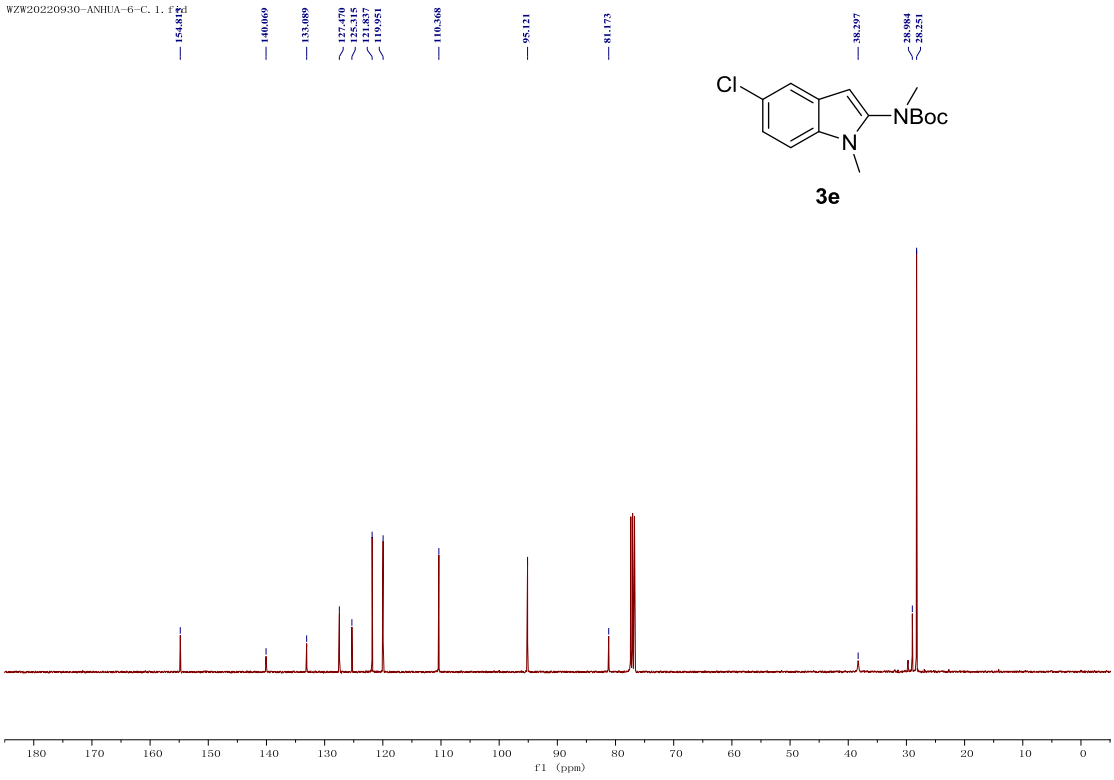
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3d



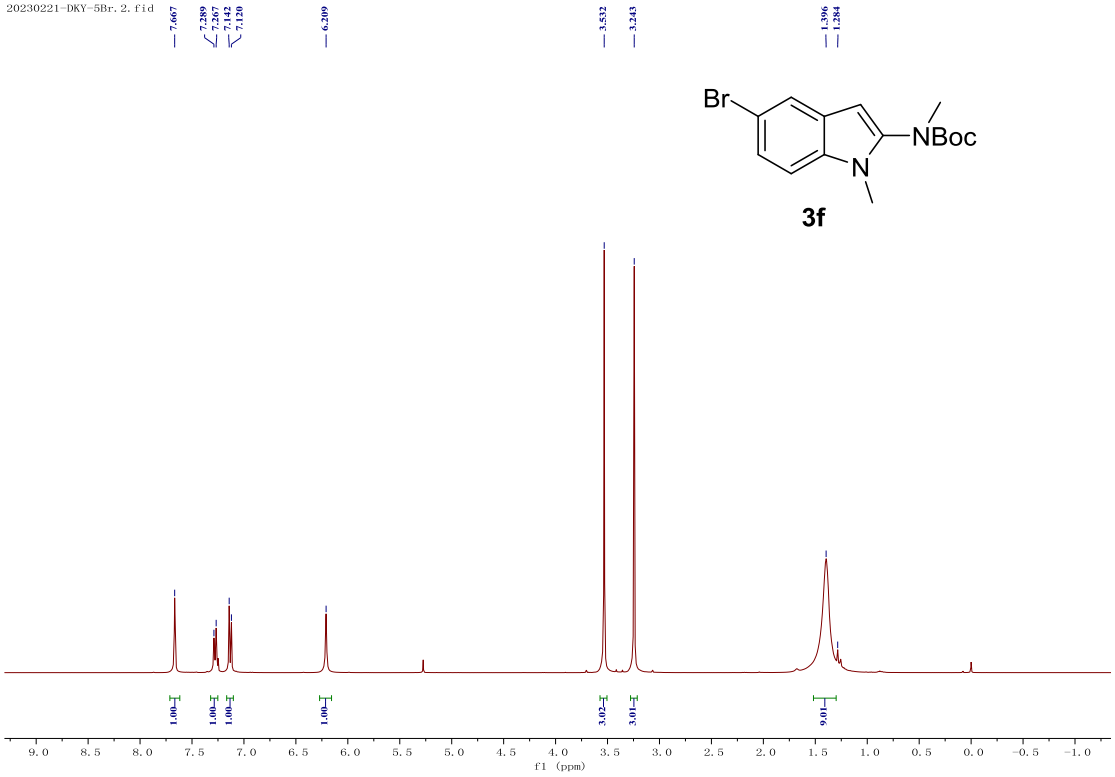
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3e



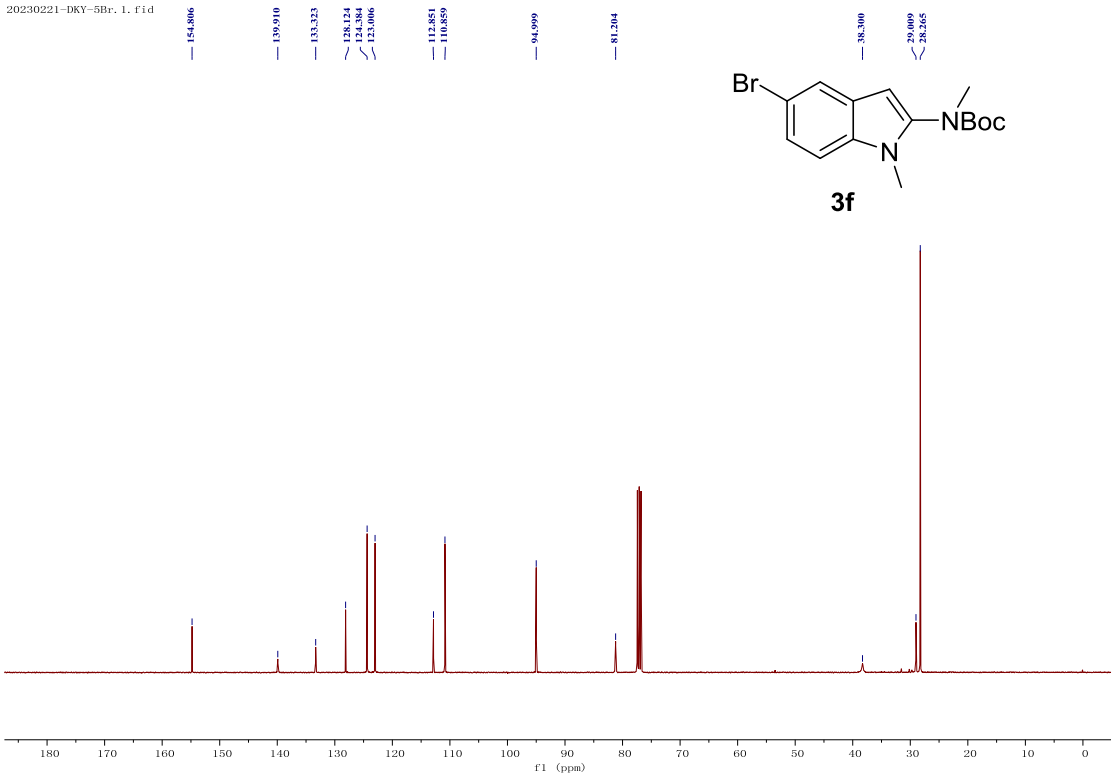
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3e



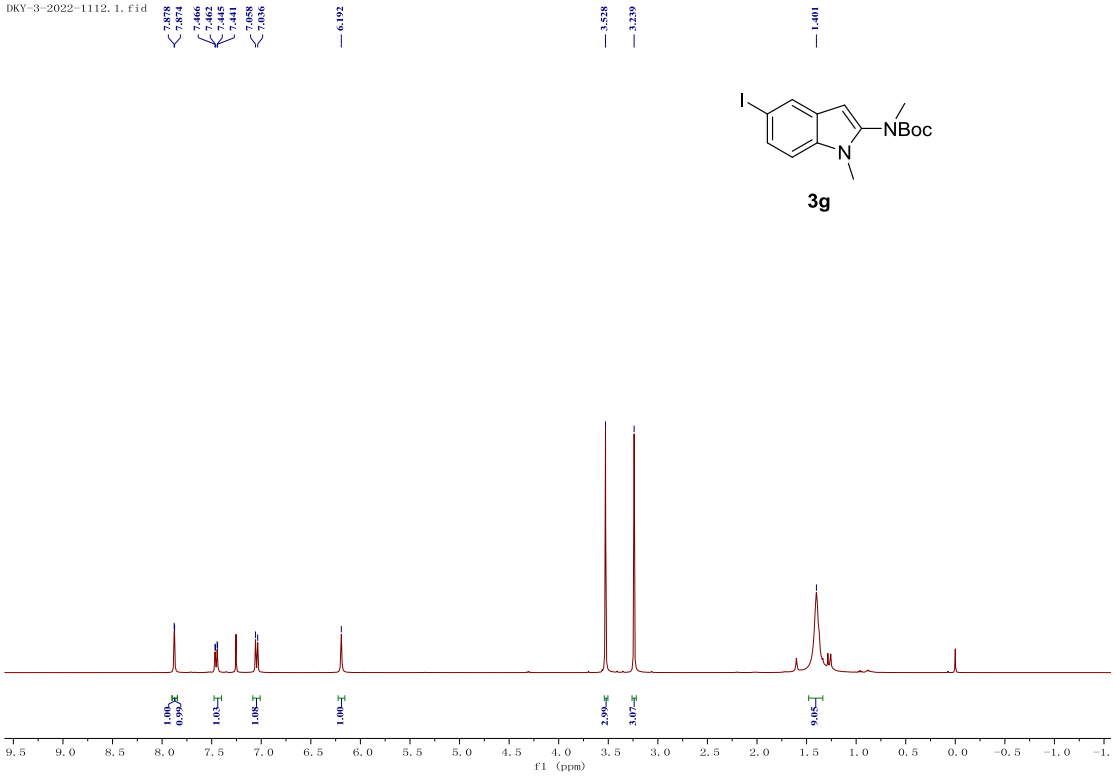
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3f



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3f

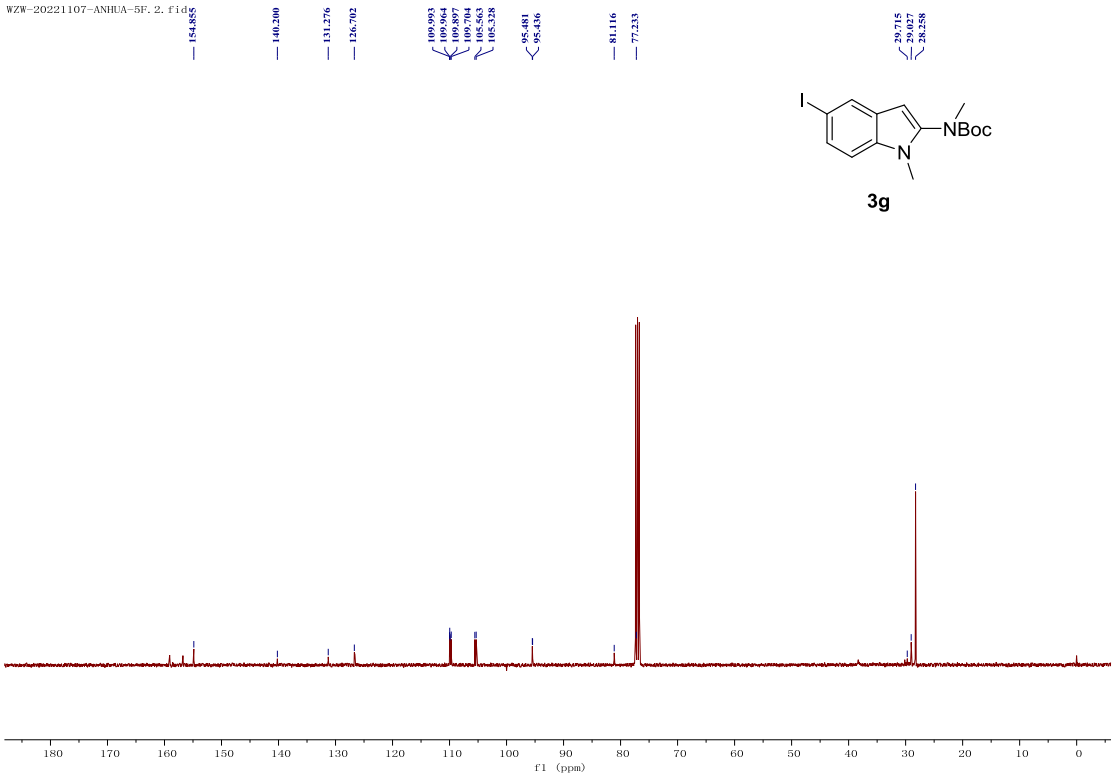


^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3g



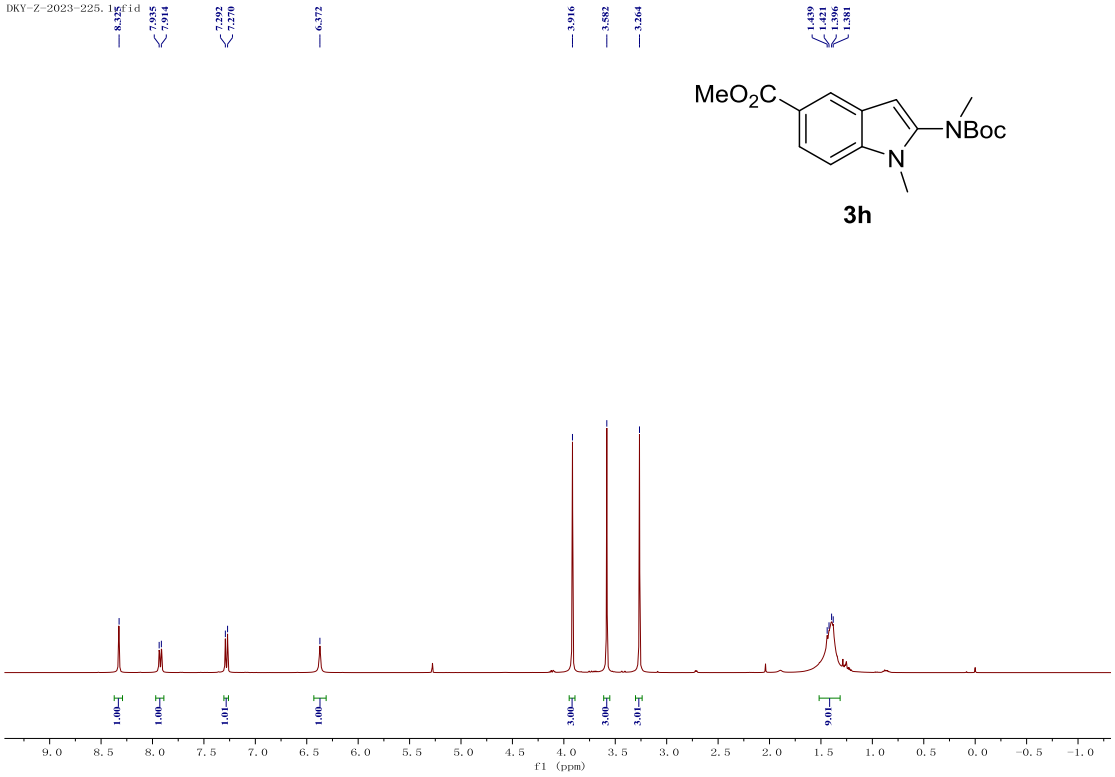
3g

^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3g



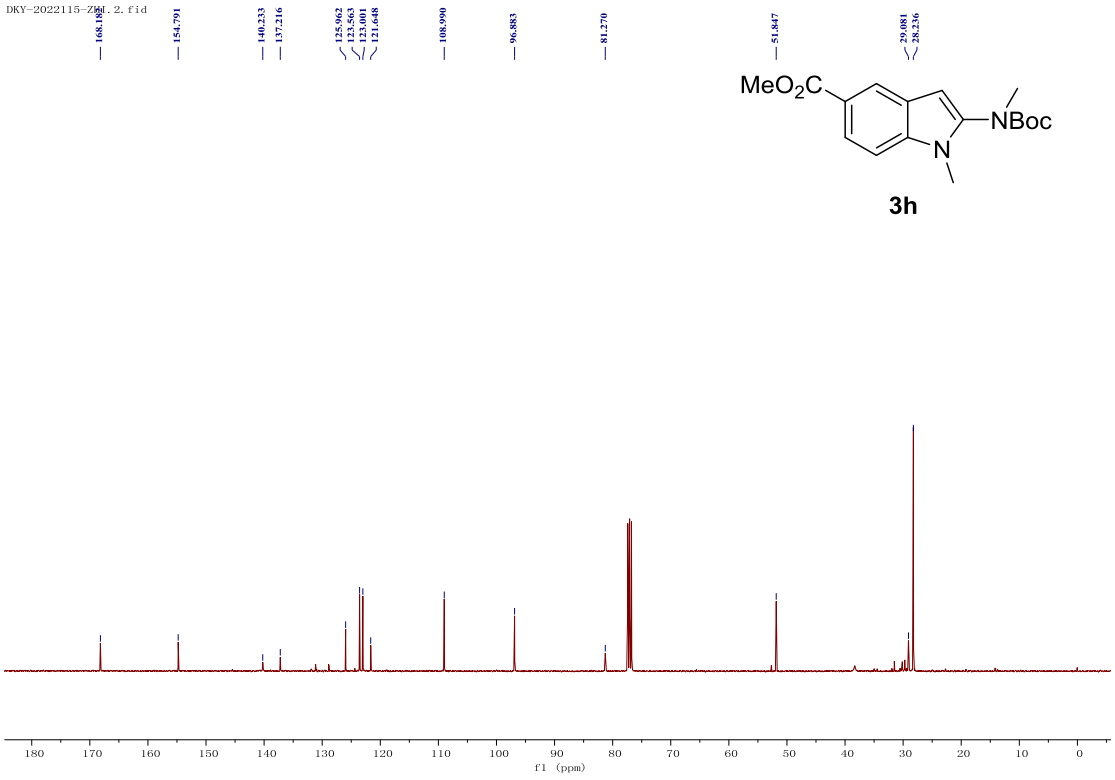
3g

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



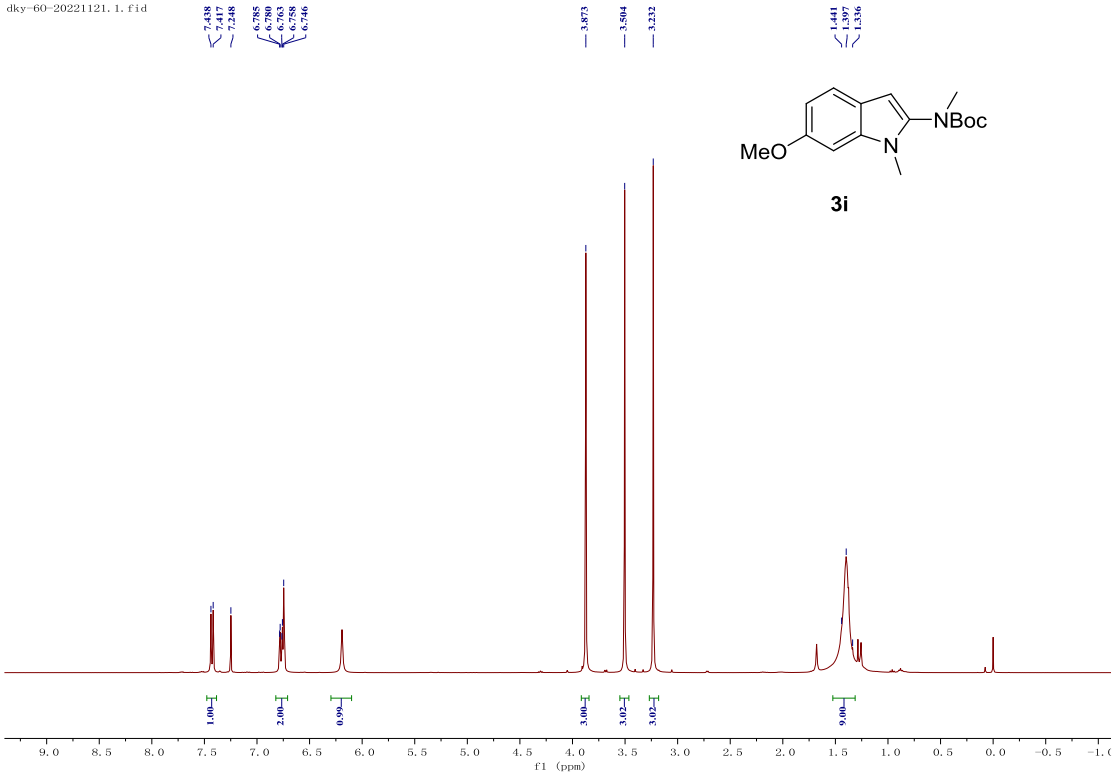
3h

^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3h



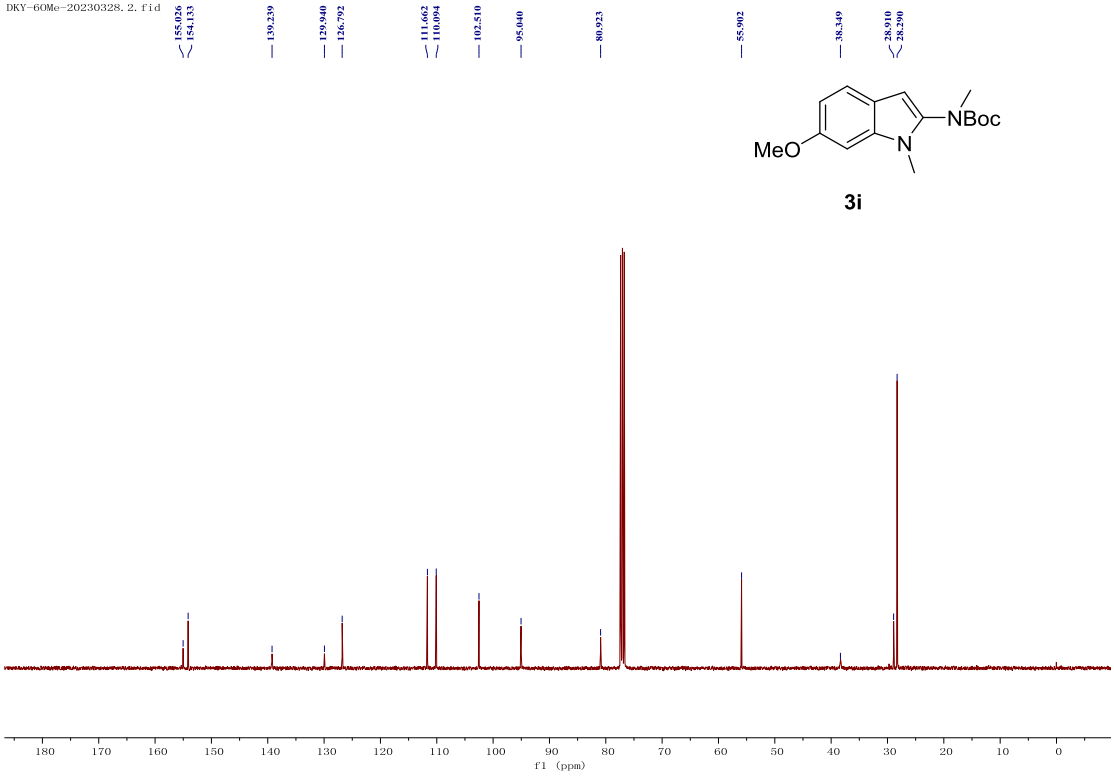
3h

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



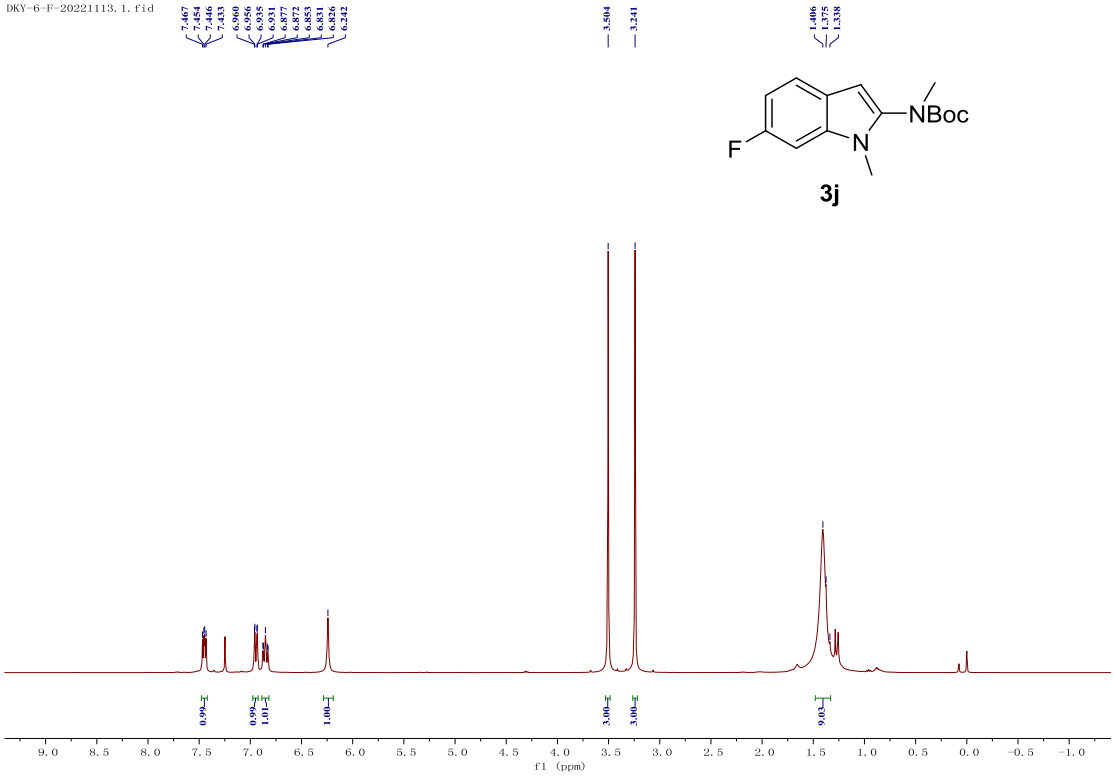
3i

^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3i

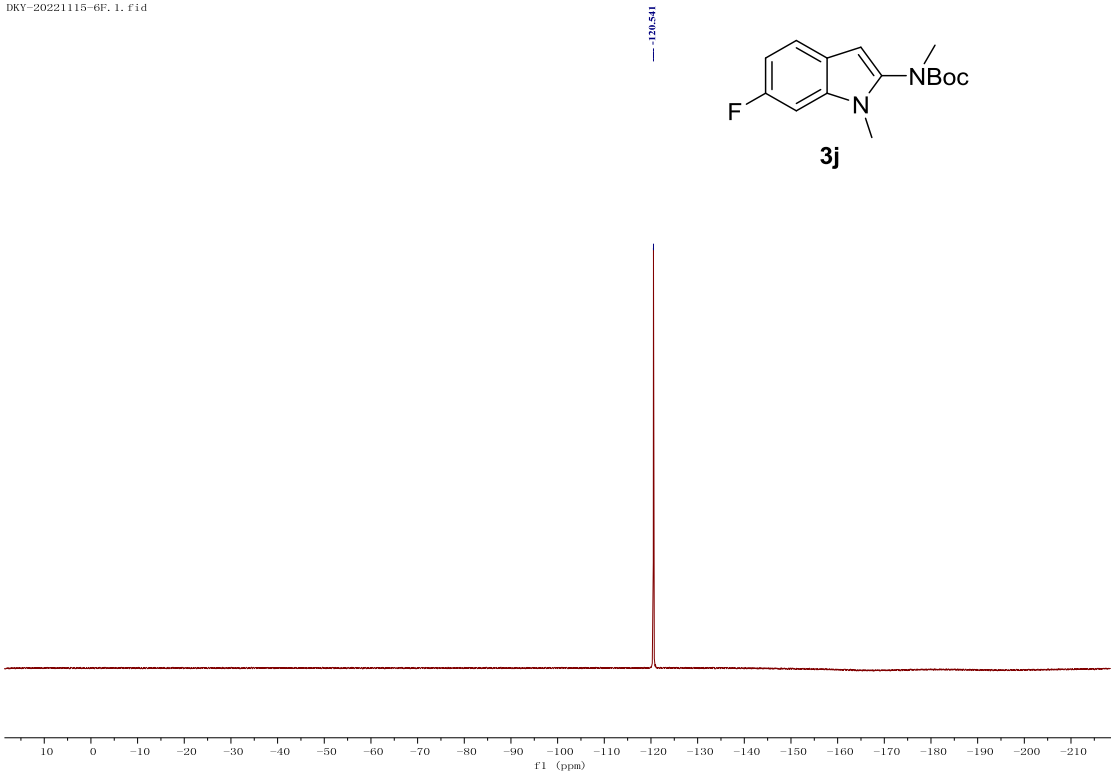


3i

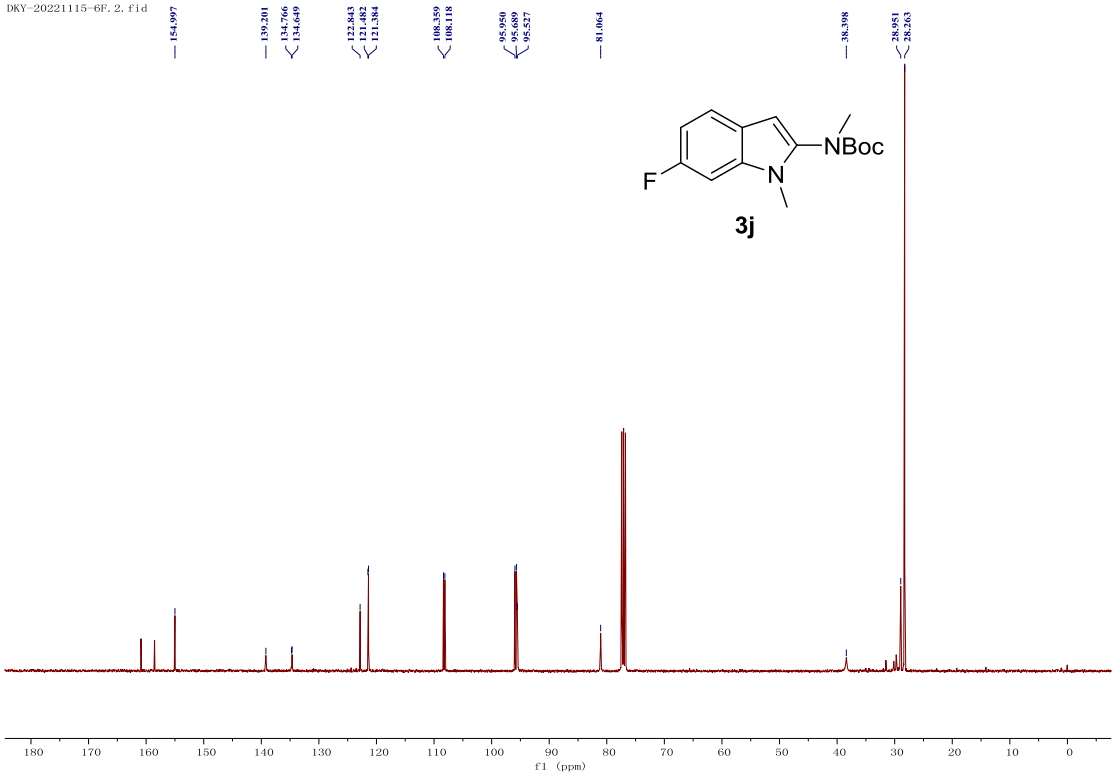
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3j



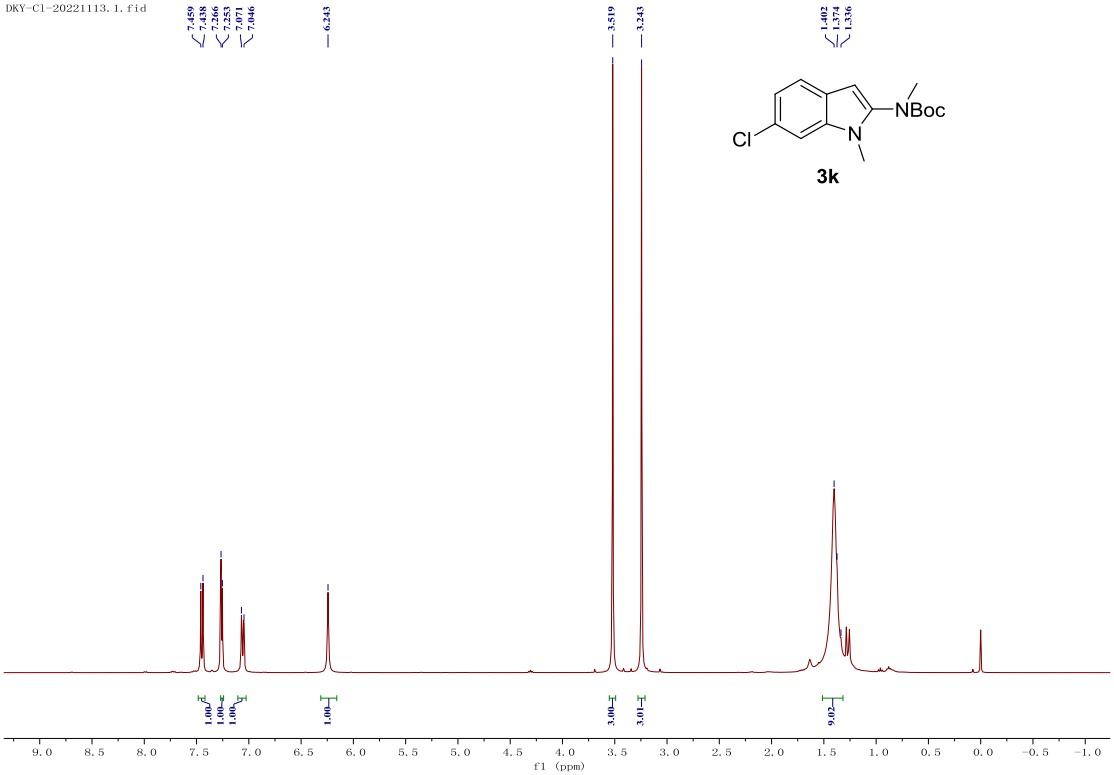
^{19}F NMR (400MHz, $CDCl_3$) spectrum of product 3j



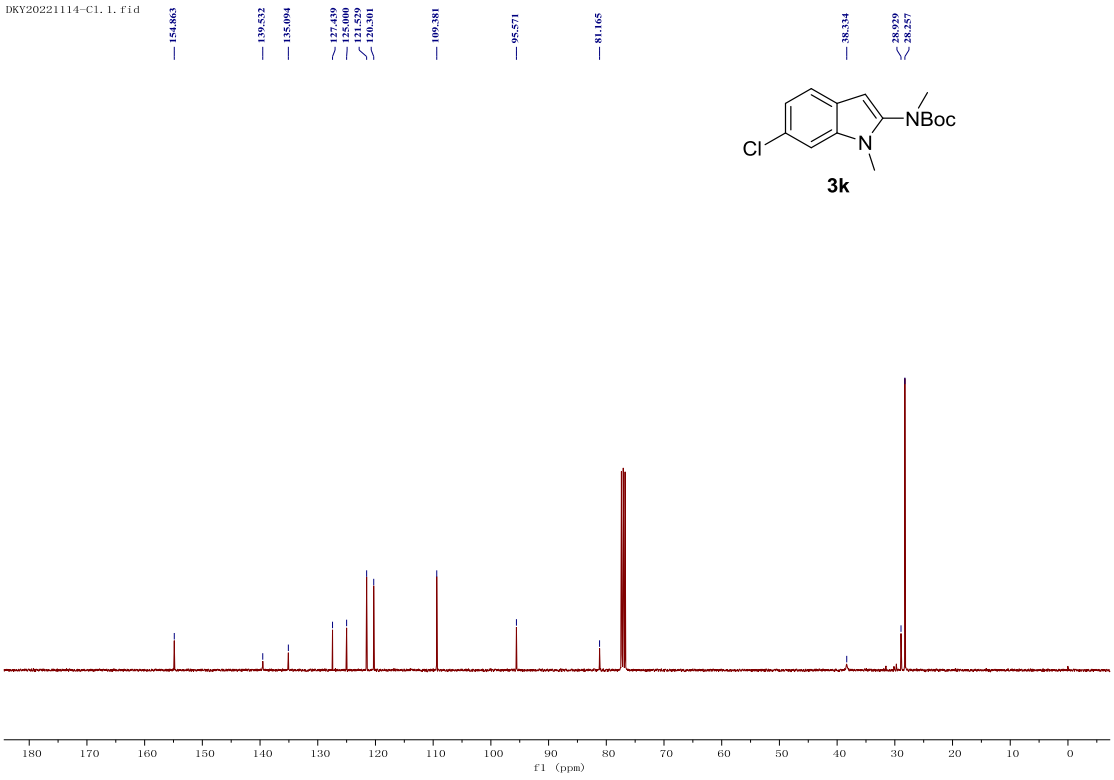
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3j



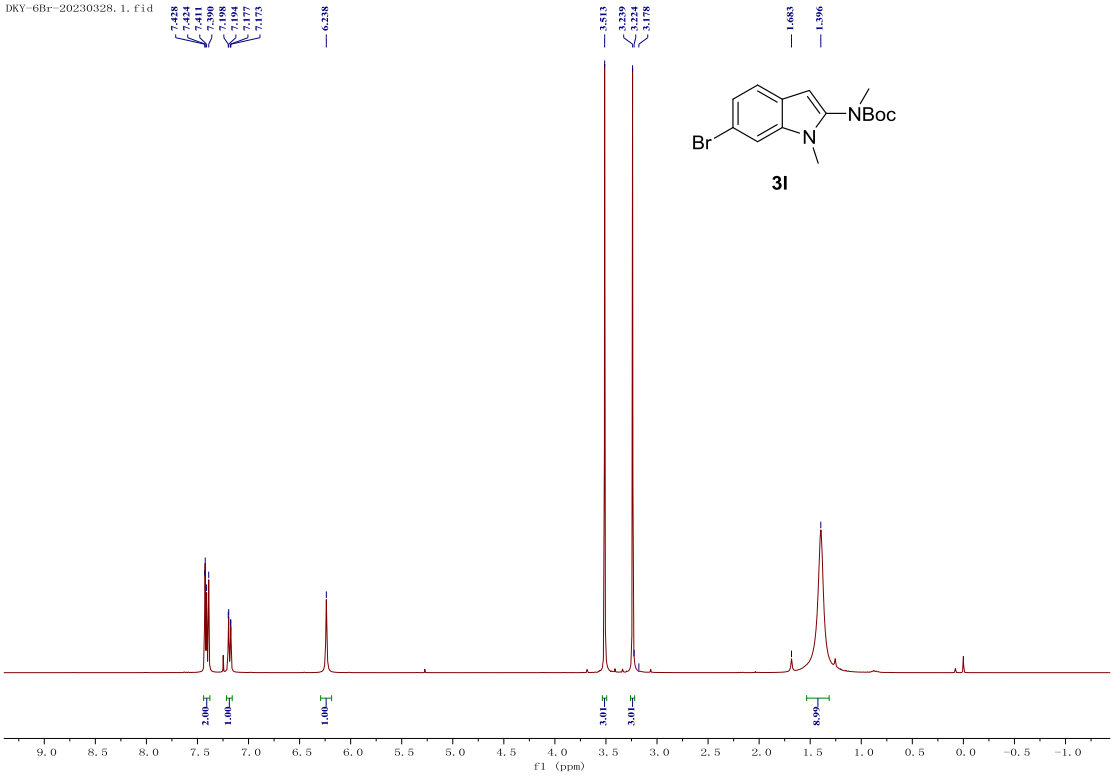
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3k



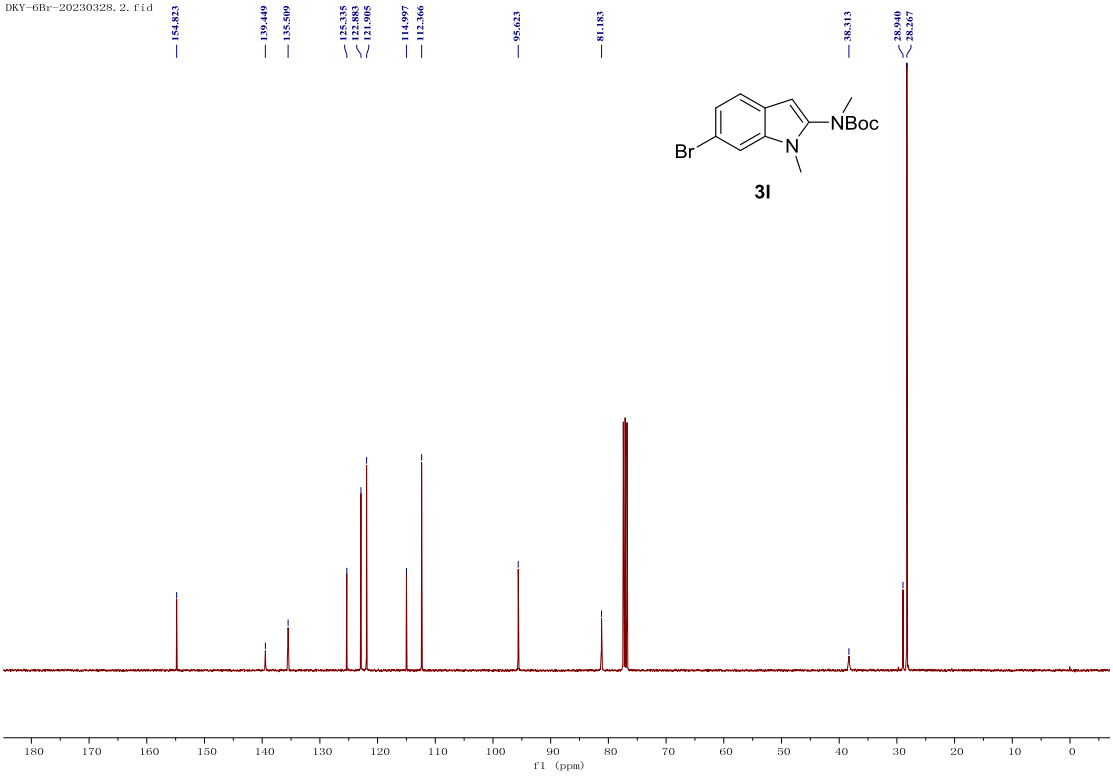
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3k



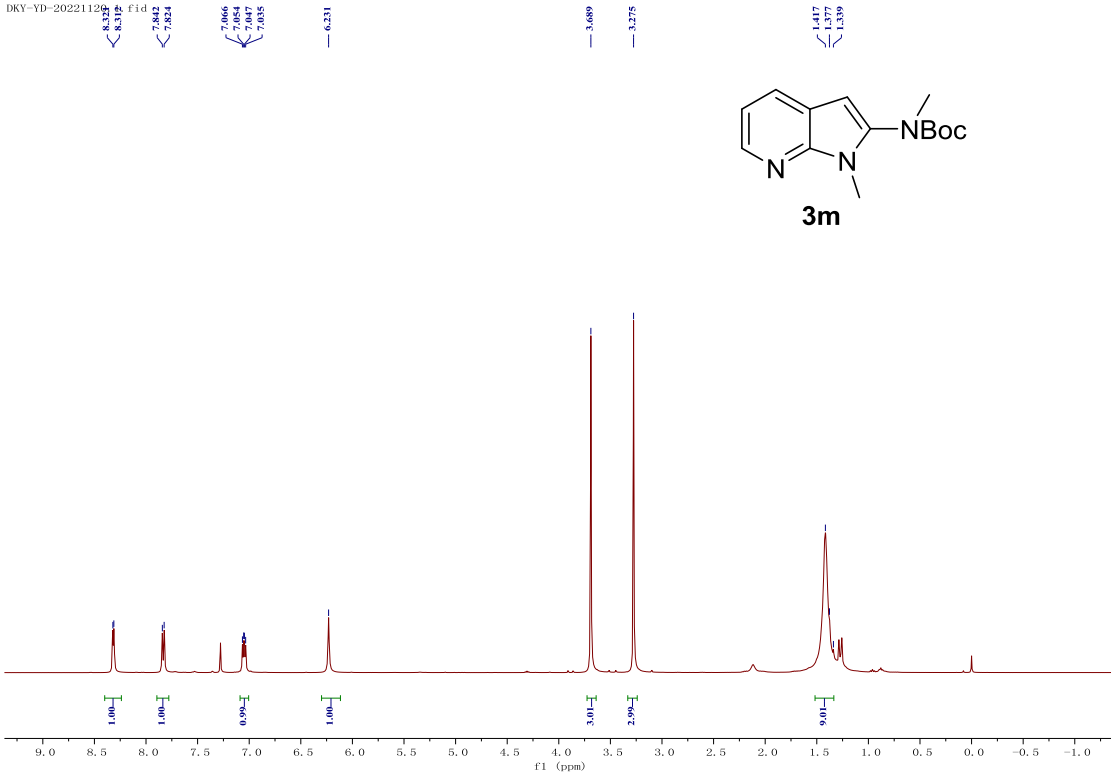
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3l



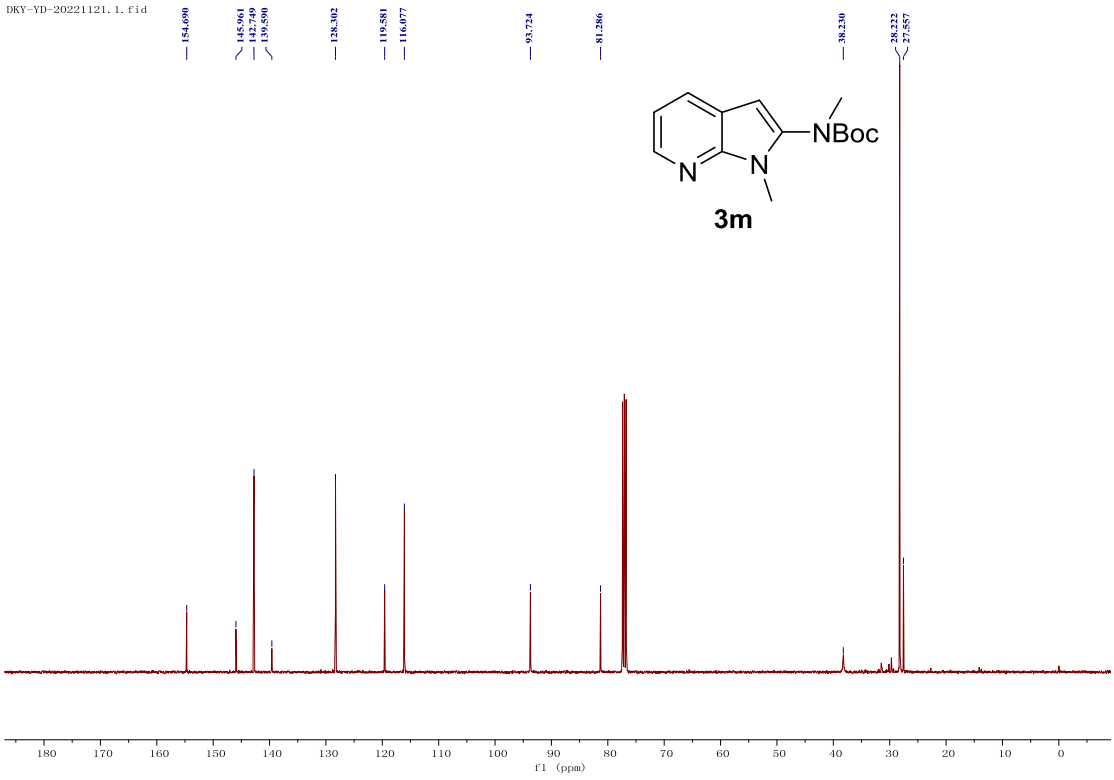
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3l



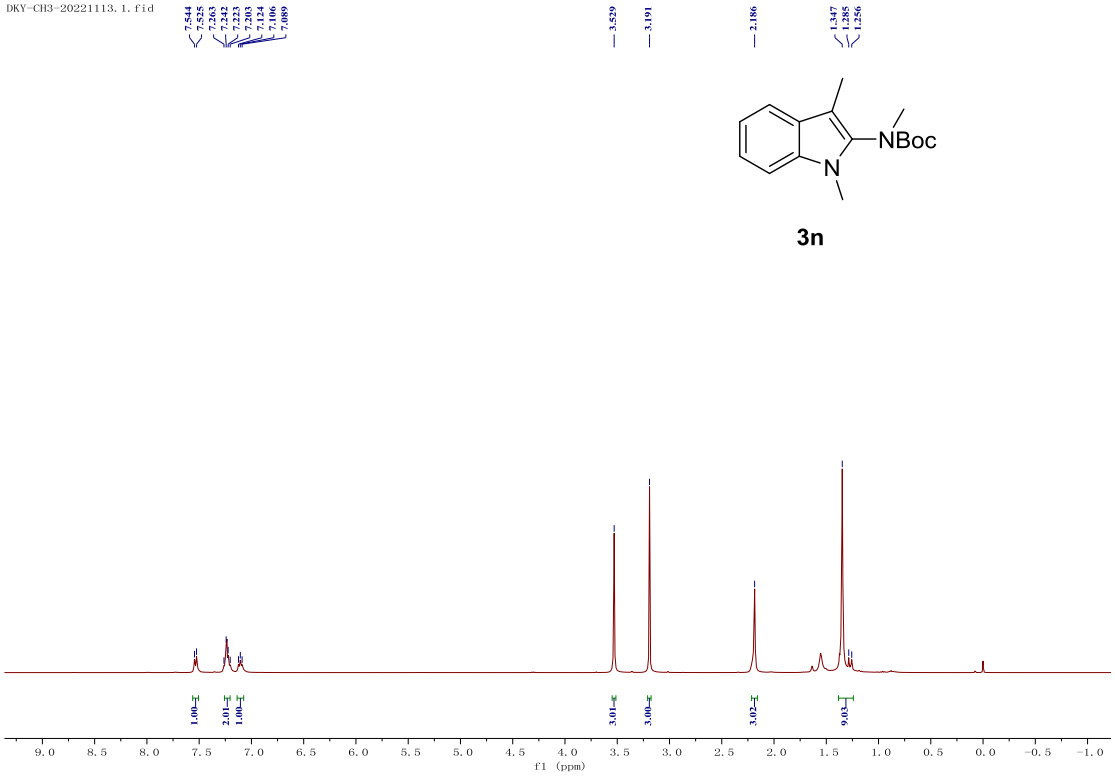
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3m



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3m

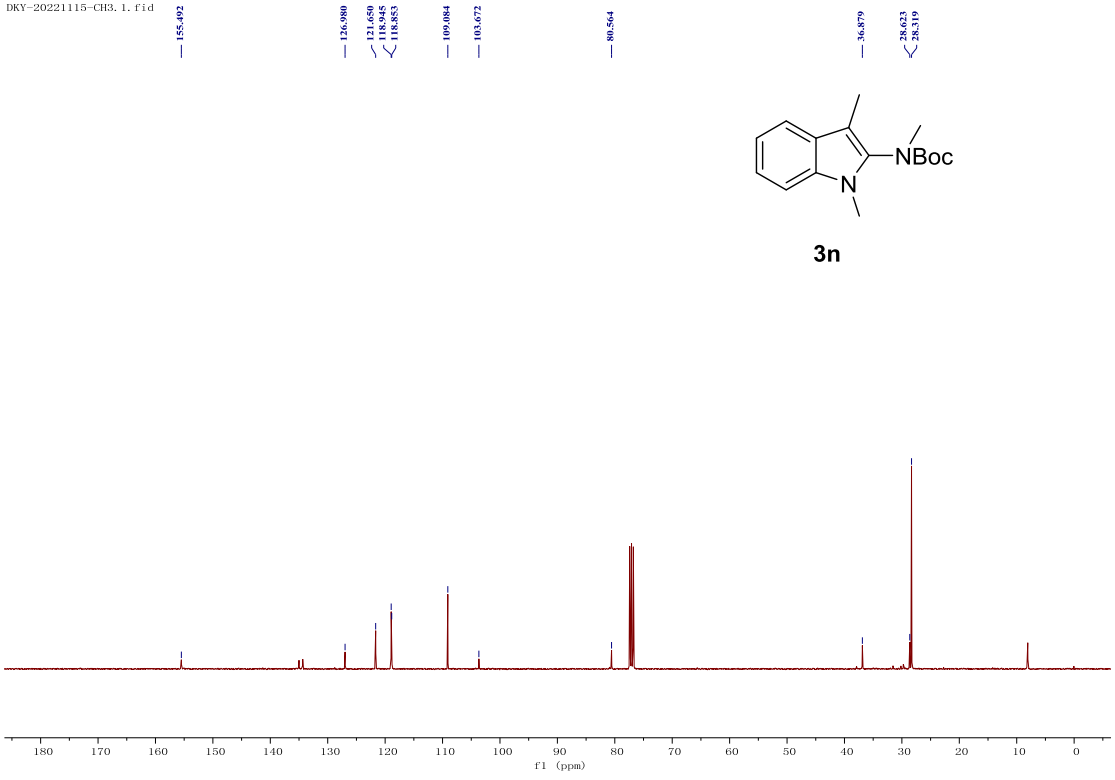


^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3n



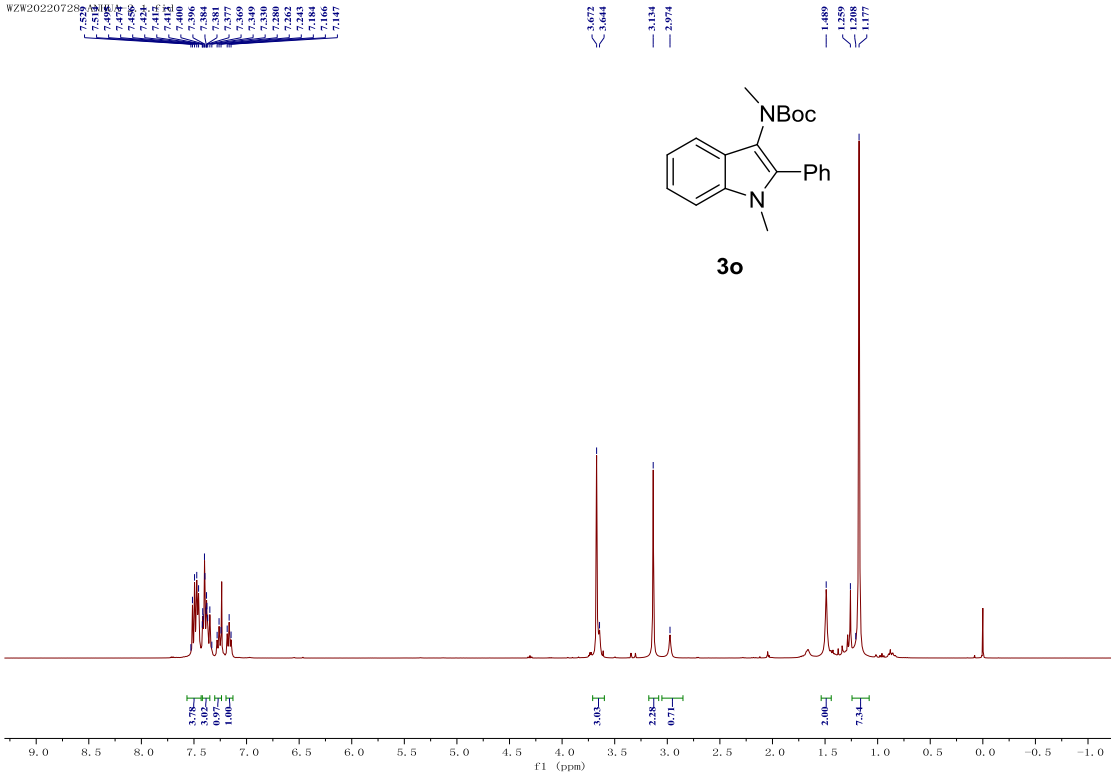
3n

^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3n

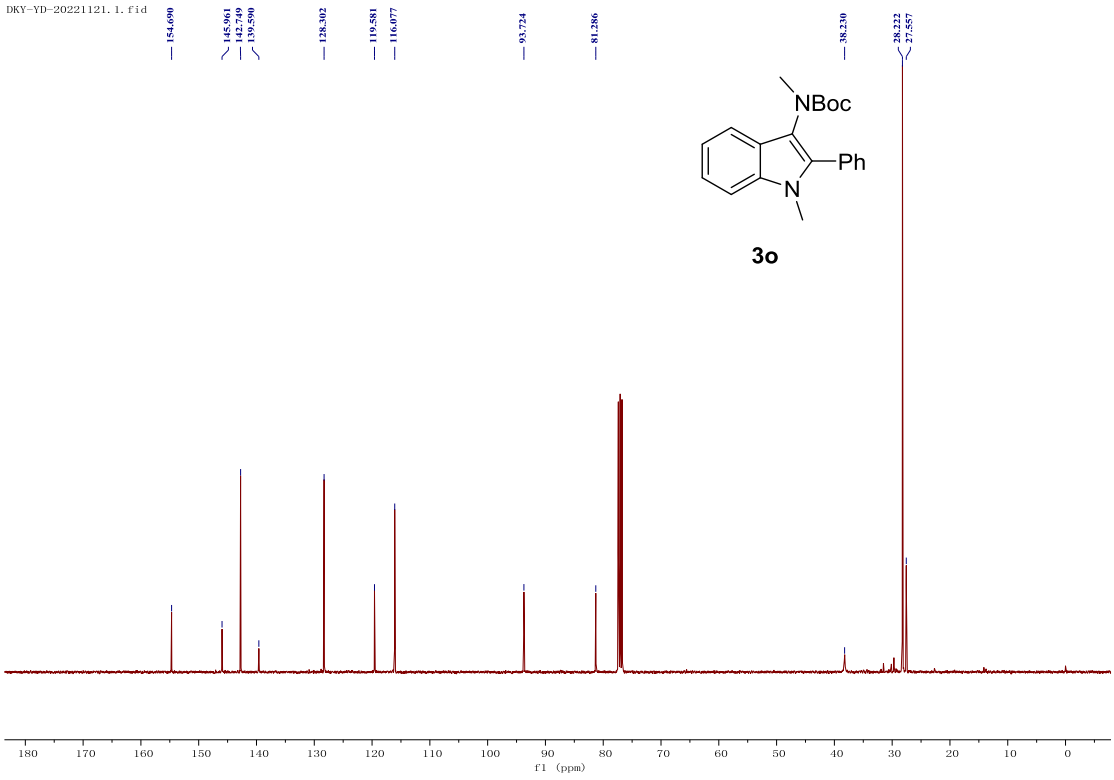


3n

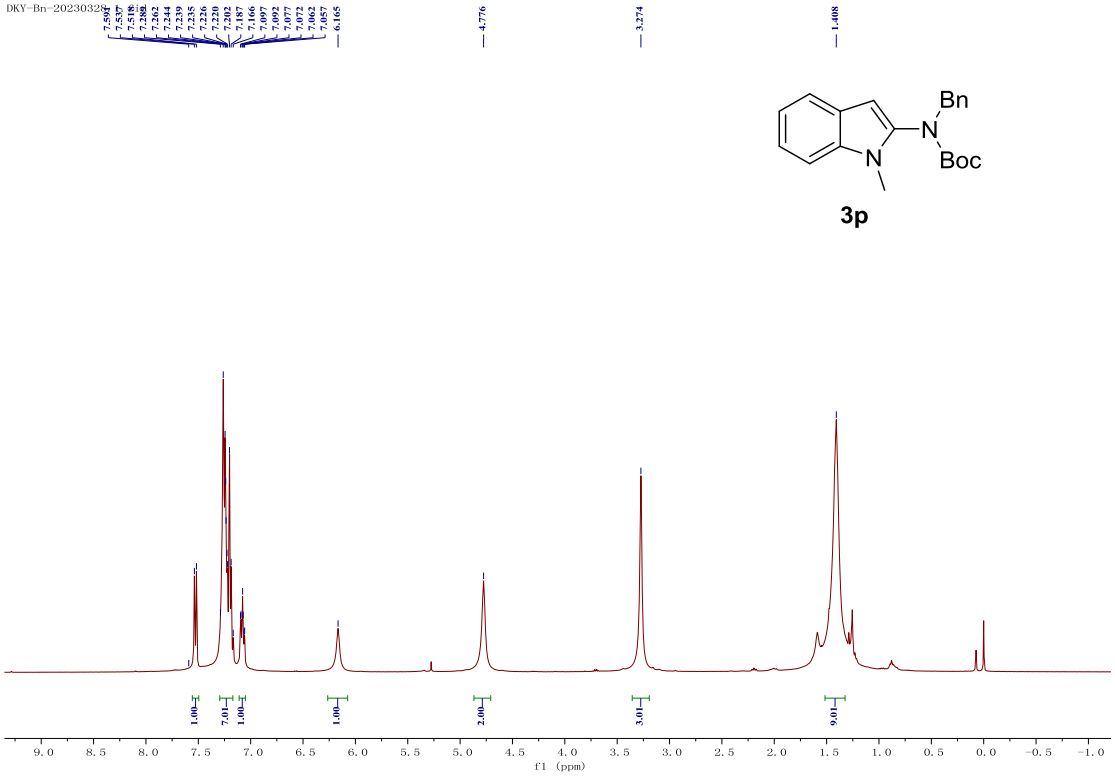
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3o



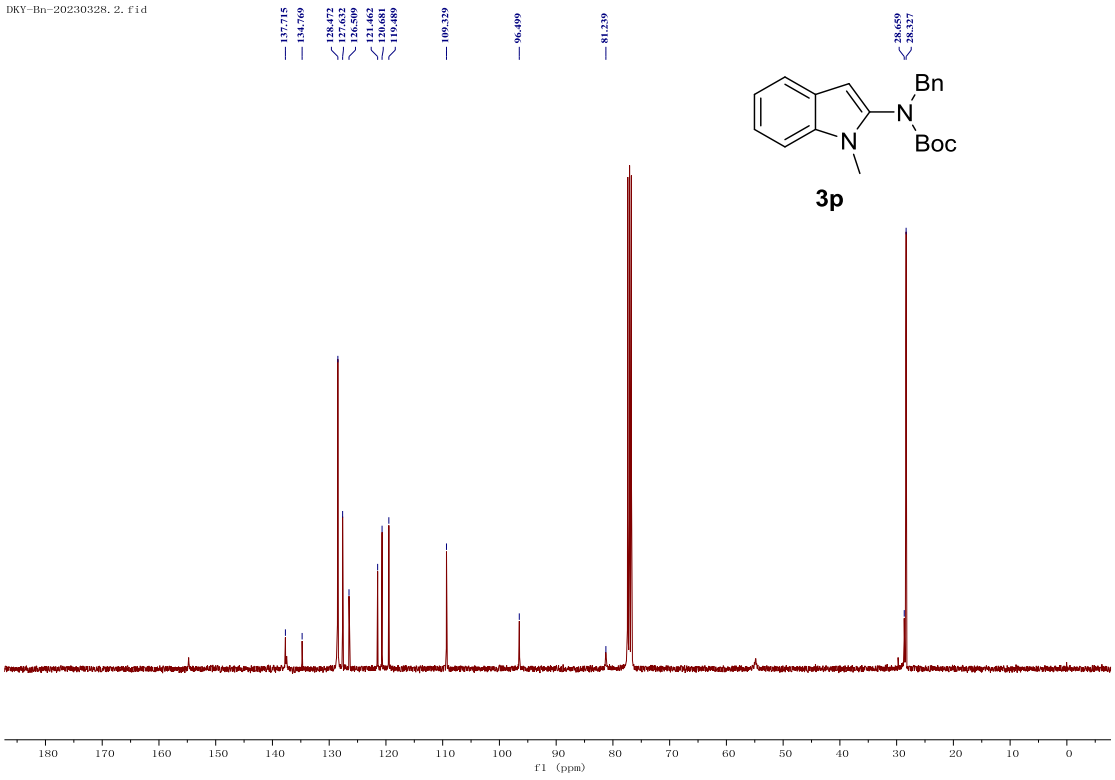
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3o



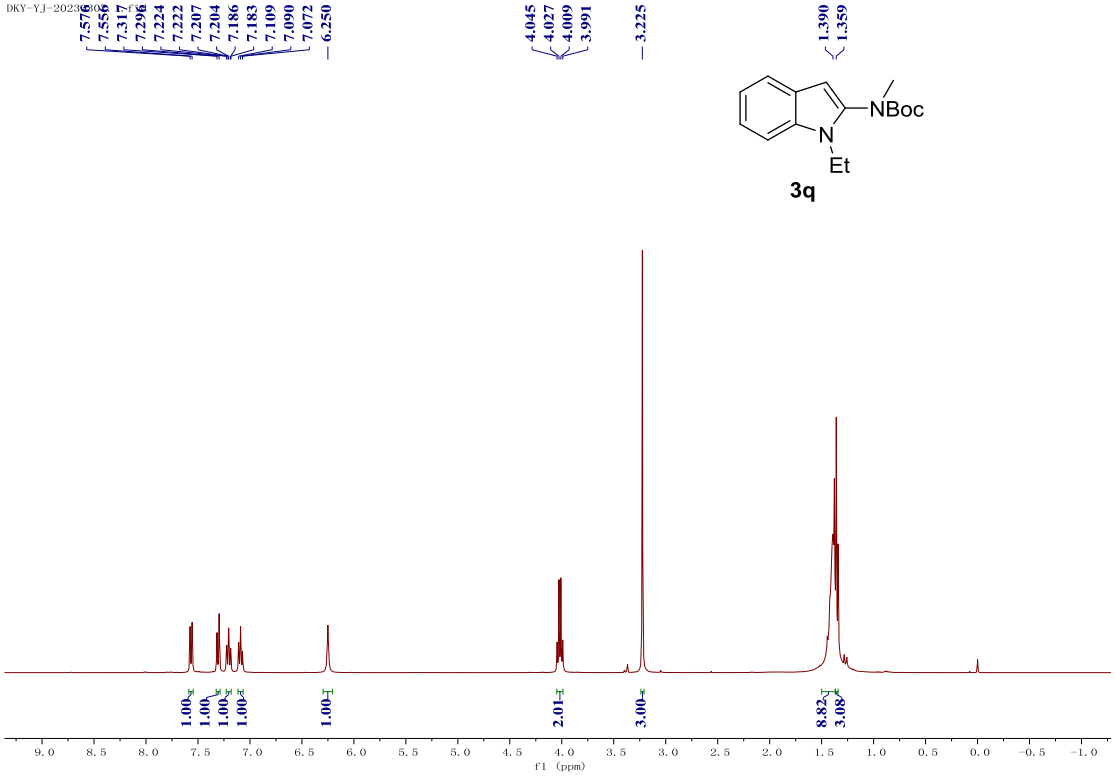
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3p



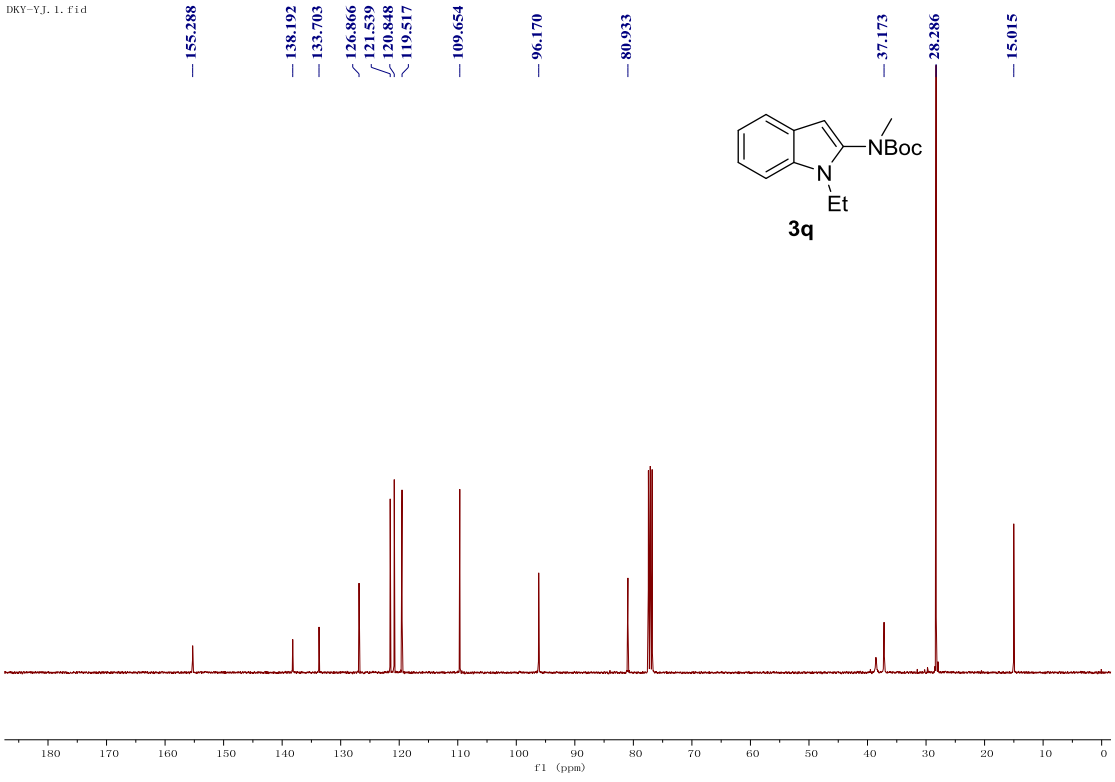
^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3p



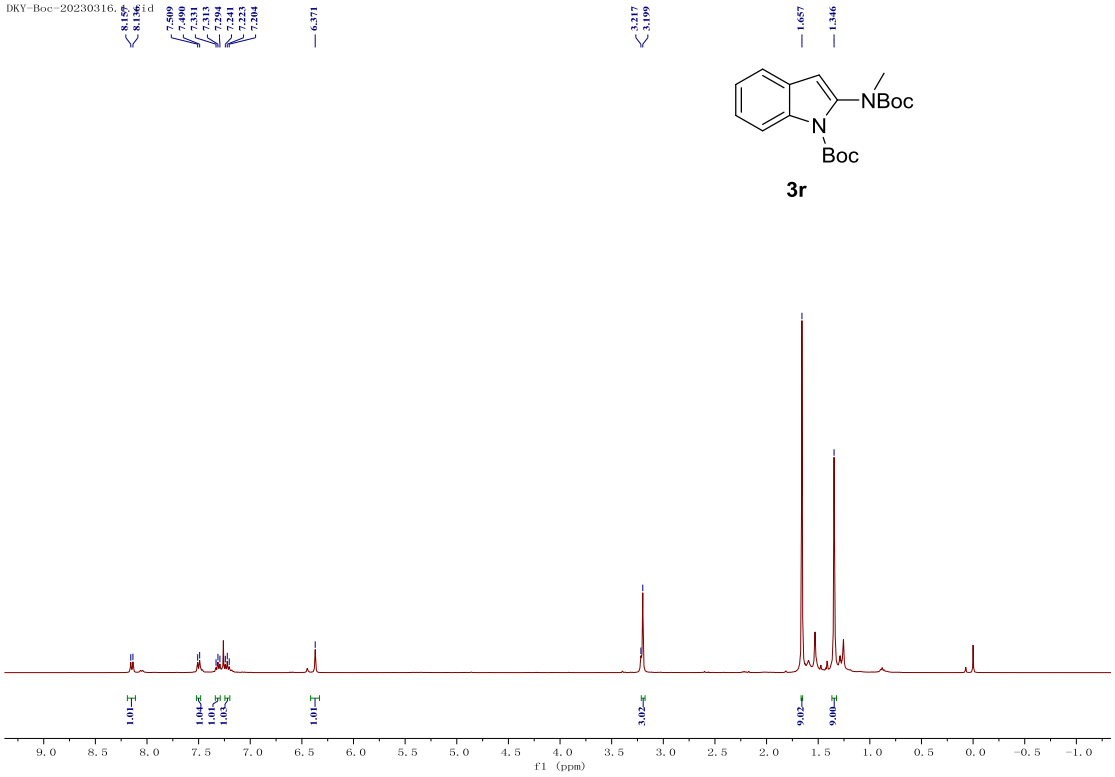
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3q



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3q

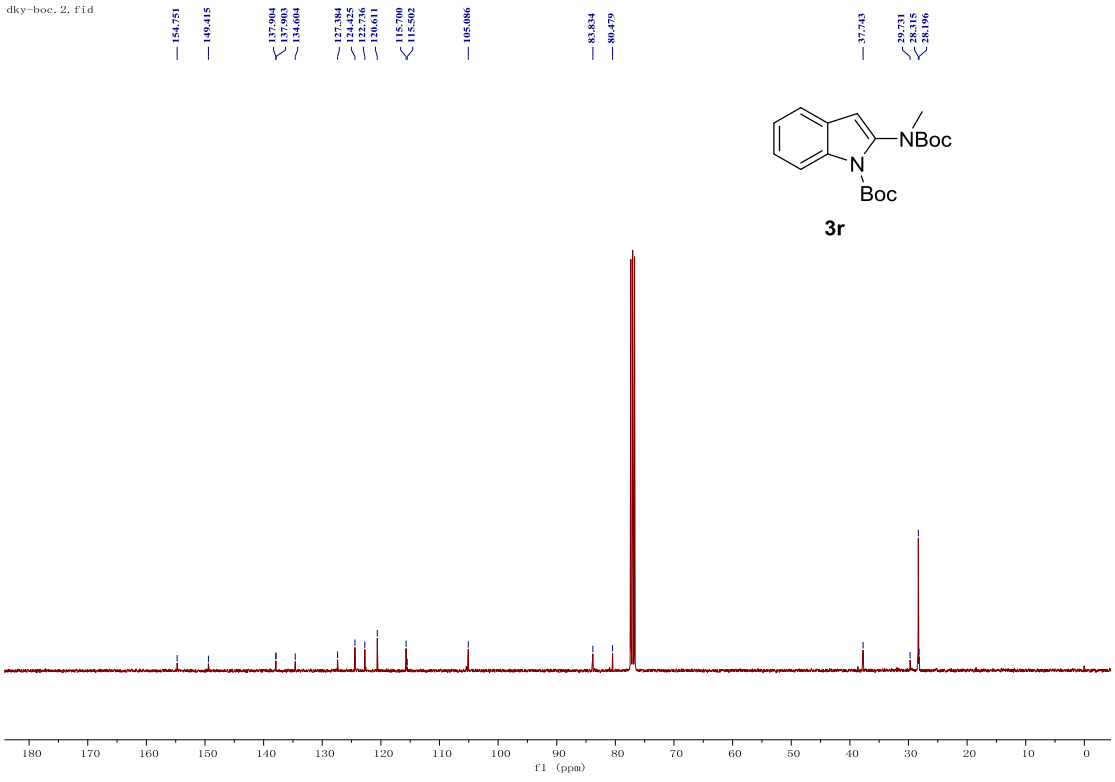


^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3r



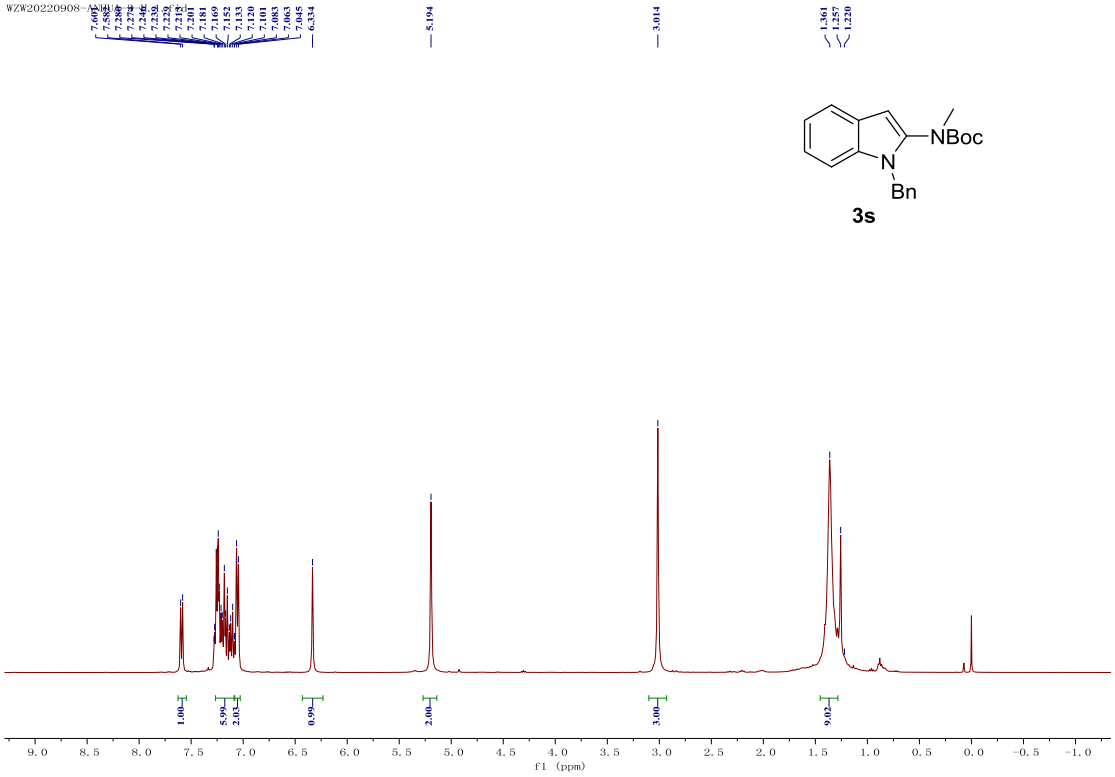
3r

^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3r

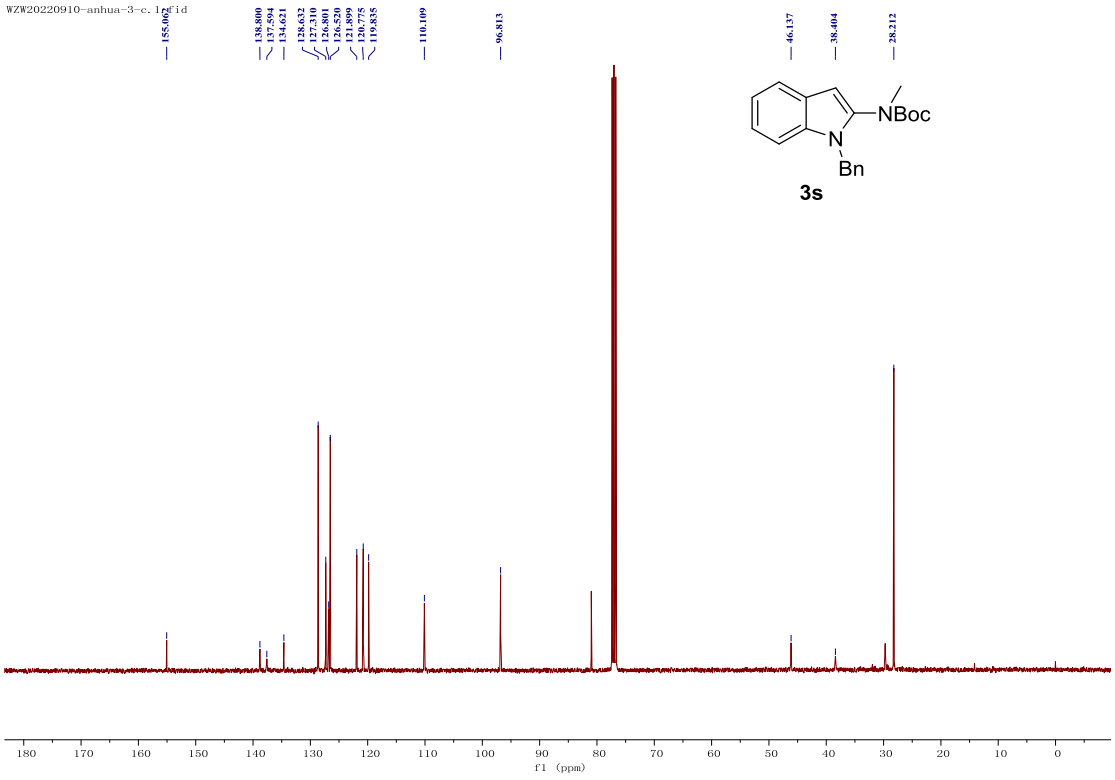


3r

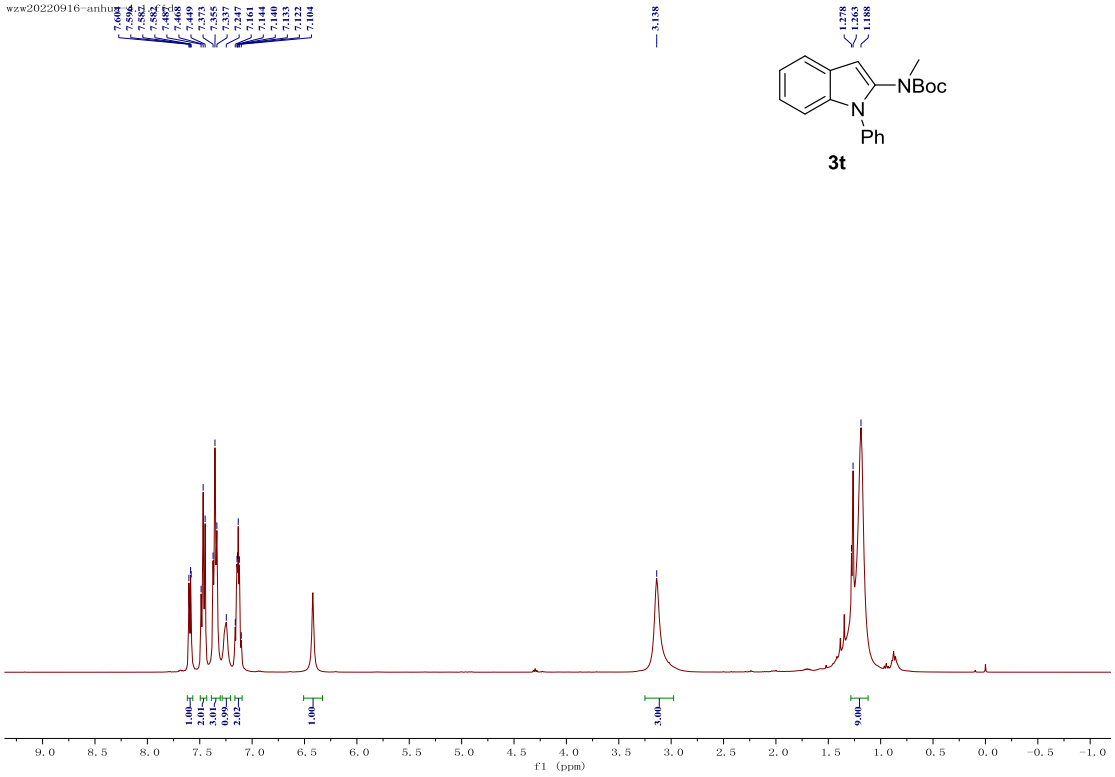
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3s



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3s



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



^{13}C NMR (400MHz, $CDCl_3$) spectrum of product 3t