Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Divergent Synthesis of Difluoromethylated Indole-3-carbinols and Bisindolylmethanes

Yifei Qu,[§] Xiaojia Cai,[§] Yuzhuang Guan,[§]Jiamin Tan, Zhangping Cai, Mingyun Liu, Yasi Huang, Jinhui Hu,* Wen-Hua Chen * and Jia-Qiang Wu *

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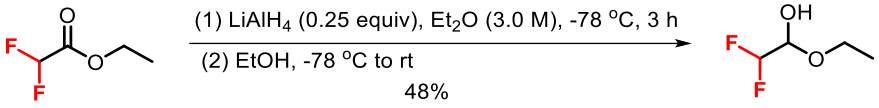
General Information

The solvents were dried by distillation over the drying agents indicated in parentheses: THF and diethyl ether (Na-benzophenone). Trifluoroethanol, Anhydrous dichloromethane were purchased from Adamas-beta. Commercially available chemicals were obtained from commercial suppliers and used without further purfication unless otherwise stated.

NMR-spectra were recorded on Bruker AvanceIII-500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3OD: δ_H = 3.31 ppm, δ_C = 49.00 ppm; $(CD_3)_2SO$: δ_H = 2.49 ppm, δ_C = 39.52 ppm). The following abbreviations were used to describe peak splitting patterns: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), td (triplet of doublets), ddd (doublet of doublet of doublets). Coupling constants (*J*) were reported in hertz unit (Hz). High-resolution mass spectra (HRMS) were produced by Thermo Fisher Scientific. Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

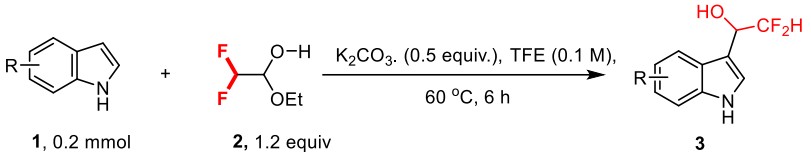
1 Synthesis of difluoroacetaldehyde hemiethanol



The title compound was prepared according to as known procedure.[1]

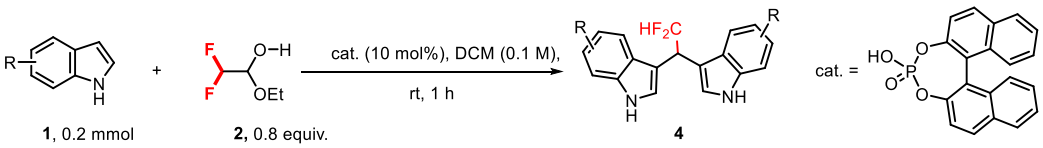
2 General Procedure for Synthesis of Harmonic difluoro compound

General procedure A:



In an oven-dried pressure tube, a mixture of Indoles **1** (0.2 mmol, 1 equiv), difluoroacetaldehyde hemiethanol **2** (0.24 mmol, 1.2 equiv), K_2CO_3 (0.5 equiv) in TFE (2mL) was stirred at 60℃ for 8h. The reaction mixture was then diluted with Ethyl acetate (10 mL) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA) to afford the desired product **3**.

General procedure B:

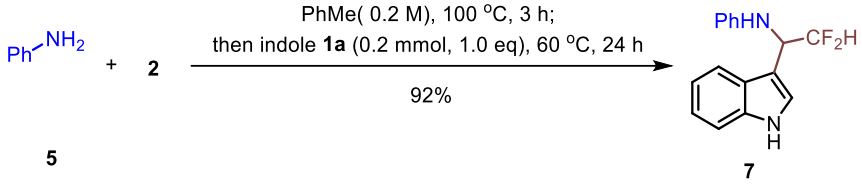


In an oven-dried pressure tube, a mixture of Indoles **1** (0.2 mmol, 1 equiv), difluoroacetaldehyde hemiethanol **2** (0.16 mmol, 0.8 equiv), 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (10 mol%) in DCM (2mL) was stirred at room temperature for 8h. The reaction mixture was then diluted with Ethyl acetate (10 mL) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA) to afford the desired product **4**.

General procedure C:

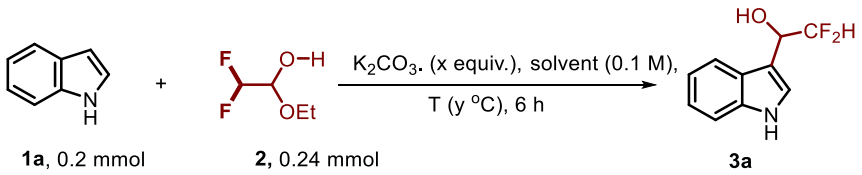
In an oven-dried pressure tube, a mixture of anilines **5** (0.2 mmol, 1 equiv),

difluoroacetaldehyde hemiethanol **2** (0.16 mmol, 0.8 equiv), in PhMe (2mL) was stirred at 100 °C for 3h. Then the reaction mixture was cooled to 60 °C, followed indoles (0.2 mmol) was added. The reaction mixture was stirred for 24 h, then diluted with ethyl acetate (10 mL) and washed with brine. The aqueous phase was extracted with ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA) to afford the desired product **7**.



5 7

3 Optimization of the reaction conditions



1a, 0.2 mmol **2,** 0.24 mmol **3a**

Table 1. Optimization of the solvent and temperature.

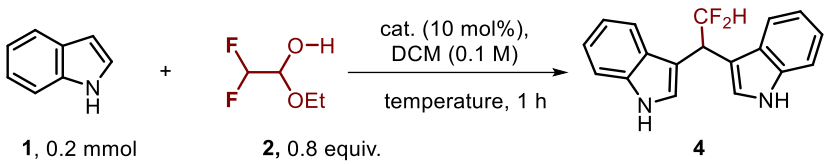
Entry	Solvent	x / equiv.	y / °C	yield [a]
1	TFE (0.1 M)	0.5	60	93%
2	DCM (0.1 M)	0.5	60	82%
3	MeOH (0.1 M)	0.5	60	< 10%
4	EtOH (0.1 M)	0.5	60	43%
5	TFE (0.1 M)	0	60	< 20%
6	TFE (0.1 M)	1.0	60	88%
7	TFE (0.1 M)	0.5	rt	40%
8	TFE (0.1 M)	0.5	90	76%

[a] NMR yield by using 4-Iodoanisole as an internal standard.

Table 2. Optimization of the base

Entry	Base	x / equiv.	y / °C	yield [a]
1	Na_2CO_3	0.5	60	90%
2	$NaHCO_3$	0.5	60	88%
3	Na_3PO_4	0.5	60	88%
4	Na_2HPO_4	0.5	60	91%
5	NaOH	0.5	60	90%
6	KOH	0.5	60	90%
7	LiOH	0.5	60	86%
8	KOAc	0.5	60	90%
9	K_2CO_3	0.5	60	93%

[a] NMR yield by using 4-Iodoanisole as an internal standard.



1, 0.2 mmol **2,** 0.8 equiv. **4**

Table 1. Optimization of the solvent and temperature.

cat. = 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate

Entry	Solvent	temperature / °C	yield [a]
1	TFE (0.1 M)	rt	51%
2	DCM (0.1 M)	rt	92%
3	DCM (dry, 0.1 M)	rt	90%
4	EtOH (0.1 M)	rt	33%
5	MeOH (0.1 M)	rt	28%
6	DCM (0.1 M)	0	18%
7	DCE	0	15%

[a] NMR yield by using 4-Iodoanisole as an internal standard.

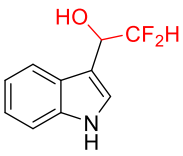
Table 2. Optimization of the catalyst.

Entry	catalyst	equiv.	temperature / °C	yield [a]
1	1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate	10%	60	95%
2	$CuCl_2$	10%	60	32%
3	$InCl_3$	10%	60	32%
4	$InBr_3$	10%	60	93%
5	$RuCl_3$	10%	60	88%
6	HCl	10%	60	28%
7	AcOH	10%	60	12%

[a] NMR yield by using 4-Iodoanisole as an internal standard.

4 Characterization of Products

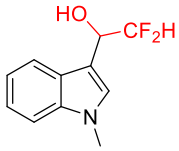
2,2-Difluoro-1-(1H-indol-3-yl)ethan-1-ol (3a)



Following general procedure A the title compound was afforded as a brown oil (35.5 mg, 90%). TLC (PE: EA, 2:1 *v*/*v*): R_f = 0.5; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.25 (s, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.00 (td, *J* = 56.0, 4.3Hz, 1H), 5.17- 5.11 (m, 1H), 2.45 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.2, 128.0, 125.5, 122.5, 120.1, 119.5, 115.8 (t, *J* = 245.0 Hz), 109.8, 68.3 (t, *J* = 25.4 Hz), 33.0. ^{19}F NMR (470 MHz,

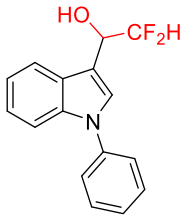
Chloroform-*d*) δ -125.10 (ddd, *J* = 282.3, 55.8, 10.0 Hz), -127.32 (ddd, *J* = 281.6, 56.4, 11.6 Hz). **HRMS (ESI):** calcd for $C_{10}H_8F_2NO$ $[M - H]^-$: 196.0568, found: 196.0559.

2,2-Difluoro-1-(1-methyl-1H-indol-3-yl)ethan-1-ol (3b)



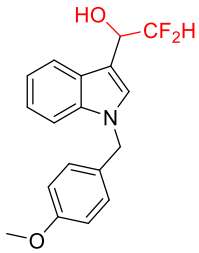
Following general procedure A to afford the title compound as a yellow oil (37.6 mg, 89%). TLC (PE: EA, 4:1 *v*/*v*): R_f = 0.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.27 (td, *J* = 7.5, 1.0Hz, 1H), 7.16 (td, *J* = 7.4, 1.0Hz, 1H), 7.16 (s, 1H), 5.98 (td, *J* = 56.1, 4.5Hz, 1H), 5.15-5.10 (m, 1H), 3.78 (s, 3H), 2.34 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.0, 127.9, 125.4, 122.3, 119.9, 119.4, 115.7 (t, *J* = 244.7 Hz), 109.6, 109.6 (t, *J* = 3.4 Hz), 68.1 (t, *J* = 25.2 Hz), 32.9. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.17 (ddd, *J* = 282.5, 56.7, 10.0 Hz), -127.21 (ddd, *J* = 282.5, 57.4, 12.1 Hz). **HRMS (ESI):** calcd for $C_{11}H_{12}F_2NO$ $[M + H]^+$: 212.0881, found: 212.0878.

2,2-difluoro-1-(1-phenyl-1H-indol-3-yl)ethan-1-ol (3c)



Following general procedure A to afford the title compound as a yellow oil (47.0 mg, 86%). TLC (PE: EA, 8:1 *v*/*v*): R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.46 (s, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.55 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.06 (td, *J* = 56.1, 4.4 Hz, 1H), 5.22 (td, *J* = 10.8, 4.4 Hz, 1H), 2.47 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 136.5, 129.8, 127.3, 127.1, 124.6, 123.3, 121.0, 119.8, 115.8 (t, *J* = 245.2 Hz), 112.3 (t, *J* = 3.8 Hz), 111.04, 68.31 (t, *J* = 25.1 Hz). ^{19}F NMR (377 MHz, CDCl3) δ -126.03 (d, *J* = 281.6 Hz), -127.09 (d, *J* = 281.6 Hz). HRMS (ESI) calculated for $C_{22}H_{17}F_2N_2$ $[M-H]^-$: 347.1354, found 347.1321

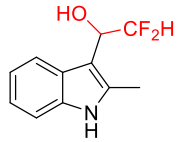
2,2-difluoro-1-(1-(4-methoxybenzyl)-1H-indol-3-yl)ethan-1-ol (3d)



Following general procedure A to afford the title compound as a yellow oil (47.0 mg, 74%). TLC (PE: EA, 8:1 *v*/*v*): R_f = 0.2; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.00 (td, *J* =

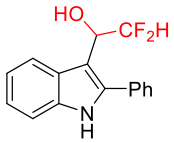
56.2, 4.5 Hz, 1H), 5.22 (s, 2H), 5.13 (td, J = 11.8, 9.7, 4.4 Hz, 1H), 3.78 (s, 3H), 2.18 (br, 1H) .^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 136.8, 128.9, 128.5, 127.2, 126.8, 122.6, 120.2, 119.7, 115.8 (t, *J* = 245.2 Hz), 114.4, 110.4 (t, *J* = 3.8 Hz), 110.3, 68.4 (t, *J* = 25.6 Hz), 55.4, 49.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.96 (d, *J* = 285.8 Hz), -127.18 (d, *J* = 281.6 Hz).

2,2-Difluoro-1-(2-methyl-1H-indol-3-yl)ethan-1-ol (3e)



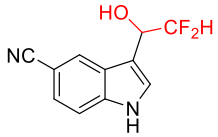
Following general procedure A to afford the title compound as a brown oil (32.9 mg, 78%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.6; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.15 (td, *J* = 7.5, 1.1 Hz, 1H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 6.05 (td, *J* = 56.5, 5.8 Hz, 1H), 5.09-5.03 (m, 1H), 2.43 (s, 3H), 2.32 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.3, 134.3, 125.7, 121.8, 120.2, 119.1, 115.5 (t, *J* = 244.5 Hz), 110.6, 106.6z (t, *J* = 3.6 Hz), 68.8 (t, *J* = 26.5 Hz), 12.1. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.72 (d, *J* = 10.1 Hz), -125.84 (d, *J* = 10.2 Hz). **HRMS (ESI):** calcd for $C_{11}H_{10}F_2NO$ [M - H]$^-$: 210.0724, found: 210.0720.

2,2-Difluoro-1-(2-phenyl-1H-indol-3-yl)ethan-1-ol (3f)



Following general procedure A to afford the title compound as a yellow oil (53.5 mg, 98%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 6.7 Hz, 2H), 7.47 - 7.40 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.21 (td, *J* = 56.5, 5.7 Hz, 1H), 5.13-5.08 (m, 1H), 2.35 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.4, 136.0, 131.7, 129.1, 129.1, 128.9, 125.6, 123.0, 120.8, 120.5, 115.6 (t, *J* = 244.5 Hz), 111.4, 107.7 (d, *J* = 6.6 Hz), 68.7 (t, *J* = 26.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -123.67 (ddd, *J* = 283.1, 55.8, 8.7 Hz), -124.95 (ddd, *J* = 283.1, 57.1, 10.5 Hz). **HRMS (ESI):** calcd for $C_{16}H_{12}F_2NO$ [M - H]$^-$: 272.0881, found: 272.0883.

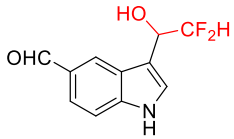
3-(2,2-Difluoro-1-hydroxyethyl)-1H-indole-5-carbonitrile (3g)



Following general procedure A to afford the title compound as a yellow oil (35.9 mg, 81%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.2; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.12 (s, 1H), 7.45-7.43 (m, 3H), 6.95 (td, *J* = 56.0, 4.4 Hz, 1H), 5.19 – 5.13 (m, 1H), 2.59 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.1, 125.0, 125.8, 125.8, 125.5, 120.5, 115.6 (t, *J* = 245.5 Hz), 112.5, 112.4 (t, *J* = 3.7 Hz), 103.7, 68.3 (t, *J* = 25.9 Hz). ^{19}F

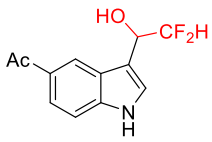
NMR (470 MHz, Chloroform-*d*) δ -125.42 (ddd, *J* = 285.2, 56.7, 10.8 Hz), -127.18 (ddd, *J* = 284.0, 55.6, 9.9 Hz). **HRMS (ESI):** calcd for $C_{11}H_7F_2N_2O$ [M - H]$^-$: 221.0520, found: 221.0520.

3-(2,2-Difluoro-1-hydroxyethyl)-1H-indole-5-carbaldehyde (3h)



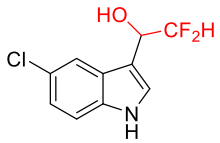
Following general procedure A to afford the title compound as a white solid (44.1 mg, 98%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.2; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.65 (s, 1H), 9.99 (s, 1H), 8.32 (s, 1H), 7.66 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.55 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.18 (td, *J* = 56.5, 4.5 Hz, 1H), 6.09 (s, 1H), 5.10 (t, *J* = 9.9 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 192.7, 139.8, 128.8, 125.5, 125.0, 125.5, 121.2, 116.4 (t, *J* = 243.6 Hz), 113.8 (t, *J* = 7.1 Hz), 112.4, 66.6 (t, *J* = 24.7 Hz). ^{19}F NMR (470 MHz, DMSO-d_6) δ -125.13 (ddd, *J* = 276.5, 56.3, 12.2 Hz), -125.10 (ddd, *J* = 276.2, 55.7, 11.4 Hz). **HRMS (ESI):** calcd for $C_{11}H_8F_2NO_2$ [M - H]$^-$: 224.0517, found: 224.0521.

1-(3-(2,2-Difluoro-1-hydroxyethyl)-1H-indol-5-yl)ethan-1-one (3i)



Following general procedure A to afford the title compound as a yellow oil (42.1 mg, 88%). TLC (PE: EA, 1:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.51 (s, 1H), 8.40 (s, 1H), 7.76 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 6.18 (td, *J* = 55.9, 4.3 Hz, 1H), 6.04 (d, *J* = 5.2 Hz, 1H), 5.13- 5.07 (m, 1H), 2.61 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.6, 138.9, 128.8, 125.1, 125.7, 122.0, 121.4, 116.4 (t, *J* = 243.7 Hz), 113.6 (t, *J* = 3.5 Hz), 111.5, 66.5 (t, *J* = 24.6 Hz), 26.7. ^{19}F NMR (470 MHz, DMSO-d_6) δ -125.20 (ddd, *J* = 276.7, 56.6, 12.8 Hz), -125.32 (ddd, *J* = 275.1,55.6, 11.3 Hz). **HRMS (ESI):** calcd for $C_{12}H_{12}F_2NO_2$ [M + H]$^+$: 240.0830, found: 240.0829.

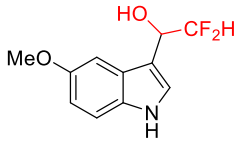
1-(5-chloro-1H-indol-3-yl)-2,2-Difluoroethan-1-ol (3j)



Following general procedure A to afford the title compound as a yellow oil (45.3 mg, 98%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.0 Hz, 1H), 5.93 (td, *J* = 56.0, 4.2 Hz, 1H), 5.07 – 5.01 (m, 1H), 2.62 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 134.6, 125.9, 125.1, 124.7,

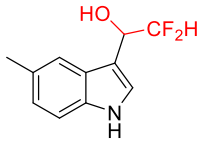
123.1, 118.9, 115.5 (t, J = 245.0 Hz), 112.5, 110.9 (t, J = 3.6 Hz), 68.1 (t, J = 25.4 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.23 (ddd, J = 282.6, 55.8, 10.0 Hz), -127.20 (ddd, J = 282.5, 56.8, 11.8 Hz). **HRMS (ESI):** calcd for $C_{10}H_7ClF_2NO$ [M - H]$^-$: 230.0178, found: 230.0179.

2,2-Difluoro-1-(5-methoxy-1H-indol-3-yl)ethan-1-ol (3k)



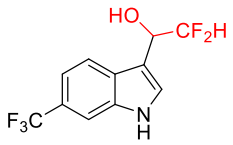
Following general procedure A to afford the title compound as a white solid (39.5 mg, 87%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.17 (s, 1H), 7.29 (d, J = 8.9 Hz, 2H), 7.17 (d, J = 2.3 Hz, 1H), 6.90 (dd, J = 8.8, 2.4 Hz, 1H), 6.03 (td, J = 56.3, 3.9 Hz, 1H), 5.13 (td, J = 11.6, 4.3 Hz, 1H), 3.86 (s, 3H), 2.31 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 154.7, 131.4, 125.5, 124.0, 115.8 (t, J = 245.1 Hz), 113.4, 112.3, 111.3 – 111.3 (m), 101.1, 68.5 (t, J = 25.8 Hz), 56.0. ^{19}F NMR (470 MHz, Chloroform-d) δ -125.55 – -127.80 (m). **HRMS (ESI):** calcd for $C_{11}H_{10}F_2NO_2$ [M - H]$^-$: 226.0674, found: 226.0673.

2,2-Difluoro-1-(5-methyl-1H-indol-3-yl)ethan-1-ol (3l)



Following general procedure A to afford the title compound as a yellow solid (40.9 mg, 97%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.53 (s, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.25 (s, 1H), 7.08 (d, J = 9.1 Hz, 1H), 6.02 (td, J = 56.1, 4.3 Hz, 1H), 5.16-5.10 (m, 1H), 2.47 (s, 3H), 2.28 (d, J = 4.3 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 134.7, 129.9, 125.2, 124.6, 123.5, 119.1, 115.8 (t, J = 245.0 Hz), 111.2, 111.1 (t, J = 3.7 Hz), 68.5 (t, J = 25.4 Hz), 21.6. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.08 (ddd, J = 281.3, 55.7, 9.1 Hz), -127.38 (ddd, J = 281.7, 55.6, 12.1 Hz). **HRMS (ESI):** calcd for $C_{11}H_{10}F_2NO$ [M - H]$^-$: 210.0724, found: 210.0725.

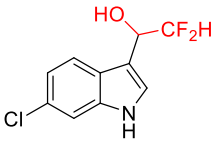
2,2-Difluoro-1-(6-(trifluoromethyl)-1H-indol-3-yl)ethan-1-ol (3m)



Following general procedure A to afford the title compound as a brown oil (37.1 mg, 70%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.68 (s, 1H), 7.44 (s, 1H), 7.41 (d, J = 8.4 Hz, 1H), 5.98 (td, J = 56.1, 4.4 Hz, 1H), 5.21-5.15 (m, 1H), 2.48 (d, J = 3.7 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 135.1, 128.2, 125.9, 124.9 (q, J = 271.8 Hz), 125.0 (q, J = 32.1

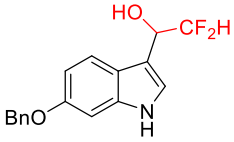
Hz), 120.0, 117.1 (q, J = 3.6 Hz), 115.6 (t, J = 245.5 Hz), 111.7 (t, J = 3.6 Hz), 109.1 (q, J = 4.5 Hz), 68.2 (t, J = 25.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -60.81, -125.77 (t, J = 10.3 Hz), -125.89 (t, J = 9.9 Hz). **HRMS (ESI):** calcd for $C_{11}H_7F_5NO$ [M - H]$^-$: 264.0442, found: 264.0443.

1-(6-chloro-1H-indol-3-yl)-2,2-Difluoroethan-1-ol (3n)



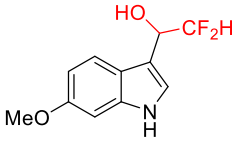
Following general procedure A to afford the title compound as a yellow solid (41.6 mg, 90%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 1.7 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 8.5, 1.7 Hz, 1H), 5.96 (td, J = 56.1, 4.3 Hz, 1H), 5.15-5.09 (m, 1H), 2.38 (d, J = 4.3 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 136.6, 128.8, 124.5, 123.9, 121.2, 120.4, 115.6 (t, J = 245.0 Hz), 111.6 (t, J = 3.6 Hz), 111.4, 68.2 (t, J = 25.0 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.41 (ddd, J = 282.2, 56.9, 10.1 Hz), -127.18 (ddd, J = 283.5, 56.4, 11.1 Hz). **HRMS (ESI):** calcd for $C_{10}H_7ClF_2NO$ [M - H]$^-$: 230.0178, found: 230.0179.

1-(6-(benzyloxy)-1H-indol-3-yl)-2,2-Difluoroethan-1-ol (3o)



Following general procedure A to afford the title compound as a yellow solid (45.2 mg, 75%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 6.90 (dd, J = 8.7, 2.2 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H), 5.94 (td, J = 56.1, 4.3 Hz, 1H), 5.05 (s, 3H), 2.51 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 155.9, 137.2, 136.9, 128.6, 127.9, 127.5, 122.3, 120.3, 120.0, 115.6 (t, J = 245.1 Hz), 111.2 (t, J = 3.6 Hz), 111.1, 96.2, 70.6, 68.3 (t, J = 25.3 Hz).
^{19}F NMR (377 MHz, DMSO-d6) δ -125.1 (d, J = 275.1 Hz), 125.2 (d, J = 275.1 Hz). **HRMS (ESI):** calcd for $C_{17}H_{14}F_2NO_2$ [M - H]$^-$: 302.0987, found: 302.0988.

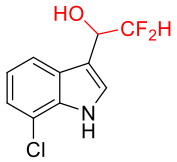
2,2-Difluoro-1-(6-methoxy-1H-indol-3-yl)ethan-1-ol (3p)



Following general procedure A to afford the title compound as a white solid (39.5 mg, 87%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.53 (d, J = 8.7 Hz, 1H), 7.18 (s, 1H), 6.90 (d, J = 2.2 Hz, 1H), 6.71 (dd, J = 8.7, 2.3 Hz, 1H), 5.98 (td, J = 55.9, 4.5 Hz, 1H), 5.01 (td, J = 9.1, 4.8 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, Methanol-d_4) δ 157.8, 138.8, 123.6, 121.9, 120.8, 117.6 (t, J = 243.7 Hz), 112.4-112.4 (m),

110.6, 95.4, 69.2-68.8 (m), 55.9. ^{19}F NMR (470 MHz, Methanol-d_4) δ -125.94 (ddd, J = 279.3, 55.7, 9.1 Hz), -128.30 (ddd, J = 280.4, 57.1, 13.1 Hz). **HRMS (ESI):** calcd for $C_{11}H_{10}F_2NO_2$ [M - H]$^-$: 226.0674, found: 226.0672.

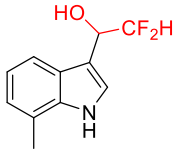
1-(7-chloro-1H-indol-3-yl)-2,2-Difluoroethan-1-ol (3q)



Following general procedure A to afford the title compound as a yellow oil (29.6 mg, 64%). TLC (PE: EA, 2:1 *v*/*v*): R$_f$= 0.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 2.5 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 5.97 (td, J = 56.1, 4.4 Hz, 1H), 5.13 (td, J = 10.6, 4.3 Hz, 1H), 2.51 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 133.6, 127.3, 123.9, 122.1, 121.2, 118.2, 116.9, 115.5 (t, J = 245.3 Hz), 112.5 (t, J = 3.6 Hz), 68.3 (t, J = 25.7 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -126.7 (d, J = 283.2 Hz), -126.8 (d, J =283.2 Hz).
HRMS (ESI): calcd for $C_{10}H_7ClF_2NO$ [M - H]$^-$: 230.0178, found: 230.0179.

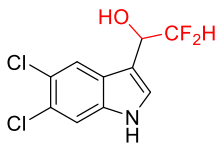
2,2-Difluoro-1-(7-methyl-1H-indol-3-yl)ethan-1-ol (3r)

^{19}F NMR (377 MHz, Chloroform-*d*) δ -126.07 (d, J = 281.7 Hz), -127.37 (d, J = 281.7 Hz).



Following general procedure A to afford the title compound as a yellow oil (35.4 mg, 84%). TLC (PE: EA, 2:1 *v*/*v*): R$_f$= 0.4; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.26 (s, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 6.9 Hz, 1H), 5.98 (td, J = 55.6, 3.0 Hz, 1H), 5.15-5.10 (m, 1H), 2.47 (s, 3H), 2.37 (d, J = 3.4 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 136.0, 125.5, 123.4, 123.1, 120.8, 120.7, 117.1, 115.8 (t, J = 244.7 Hz), 112.0 (t, J = 3.7 Hz), 68.5 (t, J = 25.4 Hz), 16.7. ^{19}F NMR (377 MHz, Chloroform-d) δ -126.0 (d, J = 281.7 Hz), -127.4 (d, J = 281.7 Hz).
HRMS (ESI): calcd for $C_{11}H_{10}F_2NO$ [M - H]$^-$:210.0724, found: 210.0715.

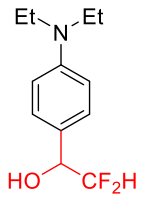
1-(5,6-dichloro-1H-indol-3-yl)-2,2-difluoroethan-1-ol (3s)



Following general procedure A to afford the title compound as a yellow oil (47.5 mg, 90%). TLC (PE: EA, 2:1 *v*/*v*): R$_f$= 0.4; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.78 (s, 1H), 7.43 (s, 1H), 7.26 (s, 1H), 5.93 (td, J = 56.1, 4.3 Hz, 1H), 5.06 (td, J = 10.7, 4.2 Hz, 1H), 2.76 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 134.9, 125.6, 125.5, 125.2, 124.4, 120.6, 115.4 (t, J = 245.3 Hz), 112.9, 110.9 (t, J = 3.6 Hz), 68.0 (t, J = 25.5 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -125.39 (ddd, J = 282.8, 55.6,

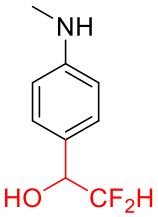
10.3 Hz), -127.27 (ddd, *J* = 282.2, 55.3, 10.2 Hz). **HRMS (ESI):** calcd for $C_{10}H_6Cl_2F_2NO$ $[M - H]^-$: 263.9789, found: 263.9789.

1-(4-(diethylamino)phenyl)-2,2-Difluoroethan-1-ol (3t)



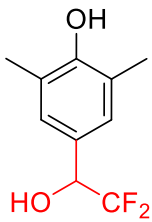
Following general procedure A to afford the title compound as a yellow oil (41.3 mg, 90%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.76 (td, *J* = 56.2, 4.8 Hz, 1H), 4.68 (td, *J* = 10.3, 4.8 Hz, 1H), 3.36 (q, *J* = 7.1 Hz, 4H), 2.33 (s, 1H), 1.17 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 148.4, 128.5, 122.3 (t, *J* = 3.2 Hz), 116.2 (t, *J* = 244.5 Hz), 111.6, 73.9 – 73.5 (m), 44.5, 12.6. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -126.88 (ddd, *J* = 281.8, 56.4, 9.6 Hz), -127.65 (ddd, *J* = 281.8, 55.9, 10.6 Hz). **HRMS (ESI):** calcd for $C_{12}H_{18}F_2NO$ $[M + H]^+$: 230.1350, found: 230.1347.

2,2-Difluoro-1-(4-(methylamino)phenyl)ethan-1-ol (3u)



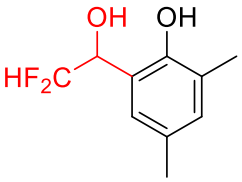
Following general procedure A to afford the title compound as a white solid (21 mg, 56%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.73 (td, *J* = 56.2, 4.8 Hz, 1H), 4.68 (td, *J* = 10.2, 4.8 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 150.0, 128.4, 124.4 (t, *J* = 3.3 Hz), 116.2 (t, *J* = 244.3 Hz), 112.5, 73.7 (t, *J* = 24.6 Hz), 30.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -127.00 (ddd, *J* = 282.1, 56.3, 9.6 Hz), -127.67 (ddd, *J* = 281.2, 55.3,10.4 Hz). **HRMS (ESI):** calcd for $C_9H_{12}F_2NO$ $[M + H]^+$: 188.0881, found:188.0878.

4-(2,2-Difluoro-1-hydroxyethyl)-2,6-dimethylphenol (3v)



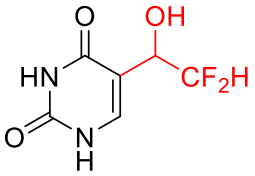
Following general procedure A to afford the title compound as a white solid (20.3 mg, 50%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Methanol-d_4) δ 6.97 (s, 2H), 5.75 (td, *J* = 56.2, 4.7 Hz, 1H), 4.58-4.52 (m, 1H), 2.21 (s, 6H). ^{13}C NMR (125 MHz, Methanol-d_4) δ 154.6, 129.5 (t, *J* = 3.2 Hz), 128.5, 125.5, 117.8 (t, *J* = 243.8 Hz), 74.2 (t, *J* = 24.3 Hz), 16.7. ^{19}F NMR (470 MHz, Methanol-d_4) δ -128.26 (ddd, *J* = 281.0, 55.6, 9.6 Hz), -129.11 (ddd, *J* = 281.2, 55.5, 12.0 Hz). **HRMS (ESI):** calcd for $C_{10}H_{11}F_2O_2$ $[M - H]^-$: 201.0721, found:201.0721.

2-(2,2-Difluoro-1-hydroxyethyl)-4,6-dimethylphenol (3w)



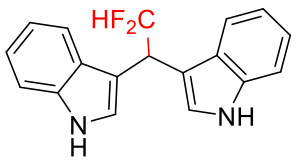
Following general procedure A to afford the title compound as a white solid (29 mg, 72%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.8; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.36 (s, 1H), 6.97 (s, 1H), 6.85 (s, 1H), 6.13 (d, J = 5.4 Hz, 1H), 5.98 (td, J = 55.8, 3.6 Hz, 1H), 5.11-5.04 (m, 1H), 2.17 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.3, 130.8, 127.8, 126.1, 124.5, 124.3 (t, J = 3.3 Hz), 116.1(t, J = 243.3 Hz), 67.4 (t, J = 22.9 Hz), 20.3, 16.5. ^{19}F NMR (470 MHz, DMSO-d_6) δ -125.43 (ddd, J = 275.4, 55.4, 8.2 Hz), -129.51 (ddd, J = 275.6, 56.3, 16.9 Hz). **HRMS (ESI):** calcd for $C_{10}H_{11}F_2O_2$ [M - H]$^-$: 201.0721, found:201.0721.

5-(2,2-Difluoro-1-hydroxyethyl)pyrimidine-2,4(1H,3H)-dione (3x)



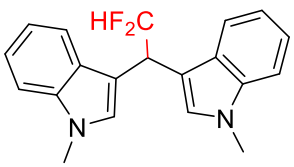
Following general procedure A to afford the title compound as a white solid (26.3 mg, 69%). TLC (PE: EA, 1:2 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.48 (s, 1H), 5.97 (td, J = 56.0, 3.3 Hz, 1H), 4.76-4.70 (m, 1H). ^{13}C NMR (125 MHz, Methanol-d_4) δ 165.5, 153.1, 142.1, 116.2 (t, J = 243.4 Hz), 110.0 (t, J = 3.6 Hz), 67.6 (t, J = 24.3 Hz). ^{19}F NMR (470 MHz, Methanol-d_4) δ -129.88 (ddd, J = 281.2, 55.6, 7.7 Hz), -133.04 (ddd, J = 281.3, 56.2, 15.5 Hz). **HRMS (ESI):** calcd for $C_6H_5F_2N_2O_3$ [M - H]$^-$: 191.0262, found:191.0260.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(1H-indole) (4a)



Following general procedure B to afford the title compound as a colourless oil (27.2 mg, 92%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.7;^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (s, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.20 – 7.07 (m, 6H), 6.37 (td, J = 56.6, 3.4 Hz, 1H), 5.03 (td, J = 16.1, 3.4 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.3, 127.2, 123.5, 122.3, 119.8 , 119.4, 117.3 (t, J = 245.0 Hz), 111.9 (t, J = 3.7 Hz), 111.4, 38.8 (t, J = 22.0 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -117.69 (dd, J = 57.0, 15.8 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{13}F_2N_2$ [M - H]$^-$: 295.1041, found: 295.1046.

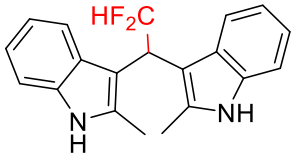
3,3'-(2,2-Difluoroethane-1,1-diyl)bis(1-methyl-1H-indole) (4b)



Following general procedure B to afford the title compound as a yellow solid (22.7 mg, 70%). TLC (PE: EA, 16:1 *v*/*v*):

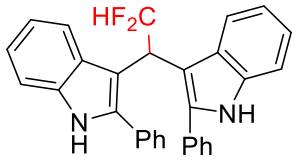
R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.15 – 7.11 (m, 2H), 7.06 (s, 2H), 6.38 (td, *J* = 56.7, 3.3 Hz, 1H), 5.06 (td, *J* = 16.4, 3.1 Hz, 1H), 3.76 (s, 6H).^{13}C NMR (125 MHz, Chloroform-d) δ 137.1, 128.1, 127.7, 121.9, 119.5, 119.3, 1I7.4 (t, J = 247.5 Hz), 110.4 (t, *J* = 3.7 Hz), 109.5, 38.6 (t, *J* = 21.8 Hz), 33.0. ^{19}F NMR (470 MHz, Chloroform-d) δ -117.68 (dd, *J* = 56.8, 16.3 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{18}F_2N_2Na$ $[M + Na]^+$:347.1330, found: 347.1321.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(2-methyl-1H-indole) (4c)



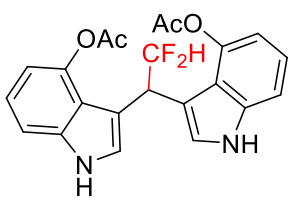
Following general procedure B to afford the title compound as a yellow oil (26.9 mg, 83%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, DMSO-d6) δ 10.89 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 – 6.87 (m, 3H), 6.84 (t, *J* = 7.3 Hz, 2H), 4.87 (td, *J* = 16.5, 5.8 Hz, 1H), 2.34 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d6) δ 135.0., 132.9., 127.6, 119.9, 118.5, 118.4, 117.4 (t, *J* = 240.5 Hz), 110.5, 106.8 (t, *J* = 4.1 Hz), 12.2. ^{19}F NMR (470 MHz, DMSO-d6) δ -114.58 (dd, *J* = 56.0, 16.8 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{17}F_2N_2$ $[M - H]^-$:323.1354, found: 323.1360.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(2-phenyl-1H-indole) (4d)



Following general procedure B to afford the title compound as a yellow oil (41.2 mg, 92%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (s, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.30 – 6.77 (m, 16H), 5.26 (td, *J* = 15.3, 5.8 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.9, 135.7, 133.0, 129.2, 128.6, 128.3, 127.8, 122.1, 121.0, 120.2, 117.1 (t, *J* = 243.3 Hz), 110.9, 109.7 (t, *J* = 4.4 Hz), 40.4 (t, *J* = 22.6 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -113.77 (dd, *J* = 56.2, 15.3 Hz). **HRMS (ESI)**: calcd for $C_{30}H_{21}F_2N_2$ $[M - H]^-$:447.1667, found: 447.1669.

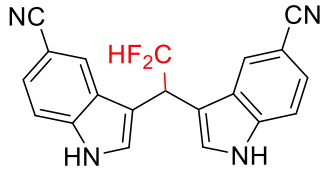
(2,2-Difluoroethane-1,1-diyl)bis(1H-indole-3,4-diyl)diacetate (4e)



Following general procedure B to afford the title compound as a yellow solid (31.3 mg, 76%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.30 (d, *J* = 2.0 Hz, 2H), 7.09 – 7.00 (m, 4H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.45 (d, *J* = 1.9 Hz, 2H), 6.30 (td, *J* =56.5, 3.2Hz, 1H), 5.33

(td, J = 15.0, 2.8 Hz, 1H), 2.00 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 170.3, 143.7, 138.7, 124.8, 122.2, 119.2, 117.9 (t, J = 245.1 Hz), 113.1, 110.1 (t, J = 3.7 Hz), 109.6, 39.6 (t, J = 21.1 Hz), 20.9. ^{19}F NMR (470 MHz, Chloroform-d) δ -119.90 (dd, J = 56.4, 15.1 Hz). **HRMS (ESI)**: calcd for $C_{22}H_{17}F_2N_2O_4$ [M - H]$^-$:411.1150, found: 411.1157.

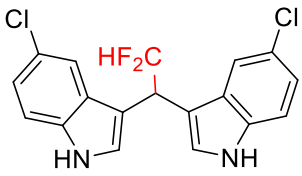
3,3'-(2,2-Difluoroethane-1,1-diyl)bis(1H-indole-5-carbonitrile) (4f)



Following general procedure B to afford the title compound as a yellow solid (24 mg, 69%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, DMSO-d6) δ 11.69 (d, J = 1.1 Hz, 2H), 8.18 (s, 2H), 7.67 (d, J = 2.3 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.42 (dd, J = 8.4, 1.4 Hz, 2H), 6.70 (td, J = 56.2, 4.5 Hz, 1H), 5.25 (td, J = 15.5, 4.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d6) δ 137.9, 125.8, 125.6, 124.8, 123.9, 120.8, 117.2 (t, J = 242.7 Hz), 113.0, 111.7 (t, J = 3.7 Hz), 100.9, 37.3 (t, J = 22.5 Hz). ^{13}C NMR (101 MHz, DMSO-d6) δ 138.2, 127.2, 127.0, 125.2, 124.4, 121.2, 117.6 (t, J = 243.1Hz), 113.4, 112.1 (t, J = 3.7 Hz), 101.2, 37.7 (t, J = 22.5 Hz).

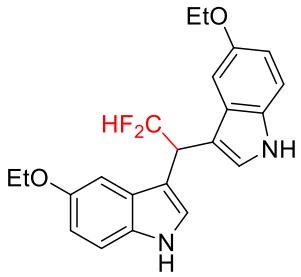
^{19}F NMR (470 MHz, DMSO-d6) δ -117.4 (dd, J = 56.1, 15.7 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{11}F_2N_4$ [M - H]$^-$:345.0946, found: 345.0954.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(5-chloro-1H-indole) (4g)



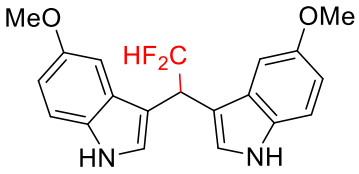
Following general procedure B to afford the title compound as a red brown oil (30.6 mg, 84%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.16 (s, 2H), 7.49 (d, J = 1.5 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 7.16 – 7.12 (m, 4H), 6.32 (td, J = 56.4, 3.3 Hz, 1H), 4.87 (td, J = 16.2, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 134.7, 128.1, 125.7, 124.9, 122.9, 118.9, 116.9 (t, J = 245.2 Hz), 112.5, 111.2 (t, J = 3.6 Hz), 38.8 (t, J = 22.2 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -117.64 (dd, J = 56.4, 16.2 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{11}Cl_2F_2N_2$ [M - H]$^-$:363.0261, found: 363.0269.

3,3'-(2,2-difluoroethane-1,1-diyl)bis(5-ethoxy-1H-indole) (4h)



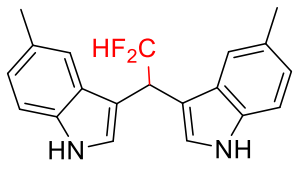
Following general procedure B to afford the title compound as a yellow oil (33 mg, 86%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.5; 1H NMR (500 MHz, Chloroform-d) δ 8.00 (s, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.06 (dd, J = 9.8, 2.2 Hz, 4H), 6.88 (dd, J = 8.8, 2.4 Hz, 2H), 6.36 (td, J = 56.7, 3.4 Hz, 1H), 4.91 (td, J = 16.0, 3.4 Hz, 1H), 4.09 – 3.95 (m, 4H), 1.41 (t, J = 7.0 Hz, 6H). 13C NMR (125 MHz, Chloroform-d) δ 153.3 , 131.4 , 127.6 , 124.1 , 117.3 (t, J = 245.0 Hz), 112.8 , 111.9 , 111.4 (t, J = 3.7 Hz), 102.5 , 64.3 , 38.8 (t, J = 21.9 Hz), 15.0 . 19F NMR (470 MHz, Chloroform-d) δ -117.32 (dd, J = 56.9, 15.9 Hz). **HRMS (ESI)**: calcd for $C_{22}H_{21}F_2N_2O_2$ $[M - H]^-$:383.1565, found: 383.1569.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(5-methoxy-1H-indole) (4i)



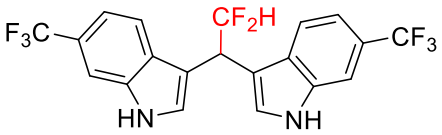
Following general procedure B to afford the title compound as a white solid(34.9 mg, 98%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.00 (s, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 2.4 Hz, 2H), 7.02 (d, J = 2.3 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 2H), 6.35 (td, *J* = 56.6, 3.5 Hz, 1H), 4.91 (td, *J* = 16.1, 3.4 Hz, 1H), 3.78 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 154.2, 131.5, 127.7, 124.3, 117.4 (t, *J* = 245.1 Hz), 112.3 (d, *J* = 39.9 Hz), 111.5 (t, *J* = 3.8 Hz), 101.4, 56.0, 38.9 (t, *J* = 22.0 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -117.38 (dd, *J* = 56.5, 16.2 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{17}F_2N_2O_2$ $[M - H]^-$:355.1252, found: 355.1258.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(5-methyl-1H-indole)(4j)



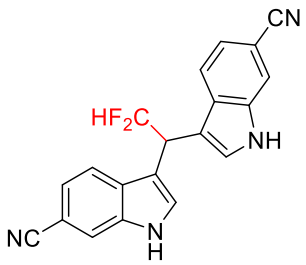
Following general procedure B to afford the title compound as a yellow solid (26.9 mg, 83%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.6; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.91 (s, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.13 (s, 2H), 7.01 (s, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.35 (t, *J* = 56.7 Hz, 1H), 4.97 (t, *J* = 15.5 Hz, 1H), 2.45 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.8, 132.2, 125.1, 122.8, 121.6, 119.1, 117.4 (t, *J* = 244.9 Hz), 111.8 (t, *J* = 3.8 Hz), 111.3, 38.9 (t, *J* = 22.1 Hz), 21.8. ^{19}F NMR (470 MHz, Chloroform-d) δ -119.90 (dd, *J* = 56.4, 15.1 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{17}F_2N_2$ $[M - H]^-$:323.1354, found: 323.1360.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(6-(trifluoromethyl)-1H-indole)(4k)



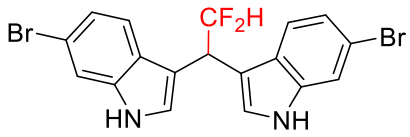
Following general procedure B to afford the title compound as a white solid (21.6 mg, 50%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.38 (s, 2H), 7.66 (s, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.32 (d, J = 9.3 Hz, 4H), 6.37 (td, *J* = 56.3, 3.2 Hz, 1H), 5.04 (td, *J* = 16.0, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.2, 129.3, 125.1, 125.2 (q, *J* = 271.6 Hz), 124.8 (q, *J* = 32.3 Hz), 119.8, 116.9 (t, *J* = 245.2 Hz), 116.8 (q, *J* = 3.1 Hz), 111.9 (t, *J* = 3.6 Hz), 109.1 (q, *J* = 4.4 Hz), 38.8 (t, *J* = 22.3 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -60.69 , -117.87 (dd, J = 56.6, 16.0 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{11}F_8N_2$ $[M - H]^-$:431.0789, found: 431.0792.

3,3'-(2,2-difluoroethane-1,1-diyl)bis(1H-indole-6-carbonitrile) (4l)



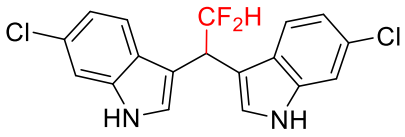
Following general procedure B to afford the title compound as a white solid (31.8 mg, 92%). TLC (PE: EA, 2:1 *v*/*v*): R_f= 0.4; 1H NMR (500 MHz, DMSO-d6) δ 11.68 (s, 2H), 7.88 (s, 2H), 7.77 – 7.66 (m, 4H), 7.28 (dd, J = 8.3, 1.4 Hz, 2H), 6.69 (td, J = 56.2, 4.2 Hz, 1H), 5.20 (td, J = 15.7, 4.1 Hz, 1H). 13C NMR (125 MHz, DMSO-d6) δ 135.3 , 130.2 , 129.0 , 121.8 , 121.0 , 120.5 , 117.7 (t, J = 242.4 Hz), 117.0 , 112.0 , 103.0 , 37.8 (t, J = 22.2 Hz). 19F NMR (470 MHz, DMSO-d6) δ -117.38 (dd, J = 56.1, 15.9 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{11}F_2N_4$ $[M - H]^-$:345.0946, found: 345.0950.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(6-bromo-1H-indole) (4m)



Following general procedure B to afford the title compound as a white solid (40.6 mg, 90%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.13 (s, 1H), 7.52 (d, *J* = 1.4 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.16 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 6.32 (td, *J* = 56.4, 3.3 Hz, 1H), 4.93 (td, *J* = 15.9, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.1, 125.0, 124.0, 123.3, 120.7, 117.0 (t, *J* = 245.5 Hz), 116.1, 114.4, 111.9 (t, *J* = 3.6 Hz), 38.8 (t, *J* = 22.5 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -117.83 (dd, *J* = 56.2, 15.9 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{11}Br_2F_2N_2$ $[M - H]^-$:450.9251, found: 450.9255.

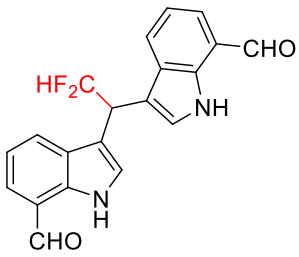
3,3'-(2,2-Difluoroethane-1,1-diyl)bis(6-chloro-1H-indole) (4n)



Following general procedure B to afford the title compound as a white solid (30.6 mg, 84%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.10 (s, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 1.6 Hz, 2H), 7.10 (d, *J* = 2.1 Hz, 2H), 7.04 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.32 (td, *J* = 56.5, 3.3 Hz, 1H), 4.93 (td, *J* = 16.0, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.7, 128.4, 125.7, 124.1, 120.7, 120.3, 117.0 (t, *J* = 245.2 Hz), 111.8 (t, *J* = 3.7 Hz), 111.4, 38.7 (t, *J* = 22.2 Hz). ^{13}C NMR (101 MHz, Chloroform-d) δ 136.5, 128.3, 125.6, 123.9, 120.6, 120.1, 116.9 (t, *J* = 245.5 Hz), 111.7 (t, *J* = 3.9 Hz), 111.2, 38.6 (t, *J* = 22.2 Hz).

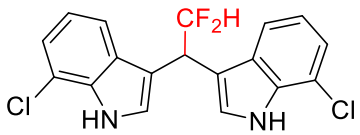
^{19}F NMR (470 MHz, Chloroform-d) δ -117.70 (dd, *J* = 56.7, 15.9 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{11}Cl_2F_2N_2$ $[M - H]^-$:363.0261, found: 363.0270.

3,3'-(2,2-difluoroethane-1,1-diyl)bis(1H-indole-7-carbaldehyde) (4o)



Following general procedure B to afford the title compound as a white solid (6.4 mg, 18%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.6; 1H NMR (500 MHz, Chloroform-d) δ 10.14 (s, 4H), 7.84 (d, J = 7.9 Hz, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 2.1 Hz, 2H), 7.24 (t, J = 7.6 Hz, 2H), 6.40 (td, J = 56.4, 3.4 Hz, 1H), 5.10 (td, J = 15.8, 3.3 Hz, 1H). 13C NMR (125 MHz, Chloroform-d) δ 193.5 , 134.1 , 129.2 , 128.2 , 126.7 , 125.0 , 120.6 , 119.6 , 116.8 (t, J = 245.2 Hz), 111.8 (t, J = 3.7 Hz), 38.6 (t, J = 22.4 Hz). 19F NMR (470 MHz, Chloroform-d) δ -117.61 (dd, J = 56.6, 15.8 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{13}F_2N_2O_2$ $[M - H]^-$:351.0939, found: 351.0945.

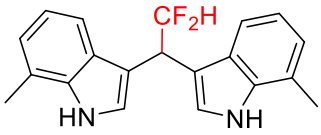
3,3'-(2,2-Difluoroethane-1,1-diyl)bis(7-chloro-1H-indole) (4p)



Following general procedure B to afford the title compound as a white solid (31.3 mg, 86%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.6; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.35 (s, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 4H),7.02 (t, *J* = 7.8 Hz, 2H), 6.35 (td, *J* = 56.4, 3.3 Hz, 1H), 4.98 (td, *J* = 15.9, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 133.6, 128.6, 124.1, 121.9, 120.8, 118.0, 116.9 (t, *J* = 245.4 Hz), 112.8 (t, J = 3.6 Hz), 39.1 (t, *J* = 22.3 Hz). ^{19}F NMR (470 MHz, Chloroform-d) δ -117.86 (dd, *J* = 56.3, 16.0 Hz). **HRMS (ESI)**: calcd for

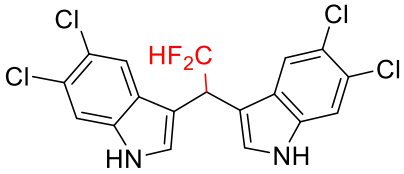
$C_{18}H_{11}Cl_2F_2N_2$ [M - H]$^-$:363.0261, found: 363.0270.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(7-methyl-1H-indole) (4q)



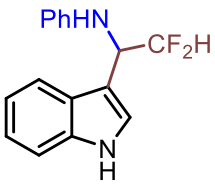
Following general procedure B to afford the title compound as a white solid (27.9 mg, 86%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.09 (s, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 2.3 Hz, 2H), 7.04 – 6.99 (m, 4H), 6.36 (td, *J* = 56.6, 3.5 Hz, 1H), 5.01 (td, *J* = 16.1, 3.4 Hz, 1H), 2.47 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.9, 125.8, 123.2, 122.8, 120.6, 120.0, 117.3 (t, *J* = 245.0 Hz), 117.1, 112.4 (t, *J* = 3.7 Hz), 39.0 (t, *J* = 22.0 Hz), 16.7. ^{19}F NMR (470 MHz, Chloroform-d) δ -117.74 (dd, *J* = 56.5, 16.2 Hz). **HRMS (ESI)**: calcd for $C_{20}H_{18}F_2N_2Na$ [M + Na]$^+$:347.1330, found: 347.1319.

3,3'-(2,2-Difluoroethane-1,1-diyl)bis(5,6-dichloro-1H-indole)(4r)



Following general procedure B to afford the title compound as a white solid (17.2 mg, 40%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-d) δ 8.23 (s, 2H), 7.53 (s, 2H), 7.46 (s, 2H), 7.18 (d, *J* = 2.4 Hz, 2H), 6.30 (td, *J* = 56.3, 3.2 Hz, 1H), 4.82 (td, *J* = 16.0, 3.1 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.2, 125.8, 125.6, 125.4, 124.2, 120.4, 116.7 (t, *J* = 245.4 Hz), 113.0, 111.0 (t, *J* = 3.5 Hz), 38.8. ^{19}F NMR (470 MHz, Chloroform-d) δ -117.76 (dd, *J*= 56.6, 16.0 Hz). **HRMS (ESI)**: calcd for $C_{18}H_9Cl_4F_2N_2$ [M - H]$^-$:430.9482, found: 430.9486.

N-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)aniline (7aa)



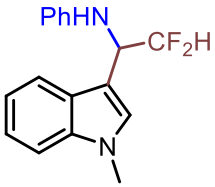
Following general procedure C to afford the title compound as a yellow oil (38.6 mg, 63%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.48; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.59 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.50 (td, *J* = 56.0, 3.0 Hz, 1H), 5.42 (t, *J* = 12.9 Hz, 1H), 4.53 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.8, 136.5, 129.5, 126.2, 123.4, 122.8, 120.3, 119.1, 118.7, 115.9 (t, *J* = 246.2 Hz), 113.9, 111.6, 110.7 (dd, *J* = 4.1, 2.1 Hz), 53.9 (t, *J* = 23.2 Hz).

^{19}F NMR (377 MHz, Chloroform-d) δ -124.07 (d, *J* = 277.3 Hz), -125.68 (d, *J* = 276.6

Hz).

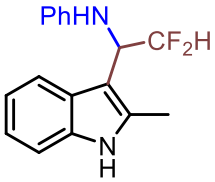
HRMS (ESI) calculated for $C_{16}H_{15}F_2N_2$ $[M+H]^+$: 273.1197; found: 273.1192.

***N*-(2,2-difluoro-1-(1-methyl-1H-indol-3-yl)ethyl)aniline (7ba)**



Following general procedure C to afford the title compound as a yellow oil (37.4 mg, 65%). TLC (PE : EA = 16:1 *v*/*v*): R_f = 0.35; ^{1}H NMR (600 MHz, Chloroform-d)δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.18 (q, J = 7.8 Hz, 3H), 7.14 (s, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.16 (td, *J* = 56.1, 2.9 Hz, 1H), 5.07 (td, *J* = 13.0, 2.8 Hz, 1H), 4.18 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 146.9, 137.3, 129.4, 127.9, 126.7, 122.3, 119.9, 119.1, 118.7, 115.9 (t, *J* = 246.7 Hz), 113.9, 109.8, 109.0 (d, J = 2.9 Hz), 53.9 (t, J = 23.1 Hz), 33.0. ^{19}F NMR (377 MHz, Chloroform-d) δ -124.10 (d, *J* = 276.2 Hz), -125.70 (d, *J* = 276.6 Hz). HRMS (ESI) calculated for $C_{17}H_{17}F_2N_2$ $[M+H]^+$: 287.1354; found: 287.1359.

***N*-(2,2-difluoro-1-(2-methyl-1H-indol-3-yl)ethyl)aniline (7ca)**



Following general procedure C to afford the title compound as a yellow oil (37.4 mg, 65%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.42; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.07 (s, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 2.6 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 7.1 Hz, 1H), 6.78 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 8.0 Hz, 2H), 6.17 (td, J = 56.0, 3.0 Hz, 1H), 5.08 (td, J = 12.8, 3.0 Hz, 1H), 4.22 (s, 1H), 2.49 (s, 3H).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (s, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.19 – 7.11 (m, 4H), 6.75 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.3 Hz, 2H), 6.13 (td, J = 56.4, 3.9 Hz, 1H), 4.92 (t, J = 12.0 Hz, 1H), 4.34 (s, 1H), 2.46 (s, 3H).

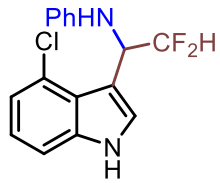
^{13}C NMR (151 MHz, Chloroform-d) δ 147.6, 135.5, 130.1, 130.4, 130.1, 127.0, 125.1, 124.2, 119.4, 119.3, 116.9 (t, *J* = 246.4 Hz), 115.0, 114.6, 112.0, 110.8 (d, J = 3.4 Hz), 54.6 (t, J = 23.0 Hz), 22.4.

^{13}C NMR (101 MHz, Chloroform-d) δ 147.0, 135.3, 133.7, 129.3, 126.9, 121.6, 120.1, 118.6, 118.5, 116.1(t, *J* = 246.7 Hz), 113.8, 110.7, 105.8 (t, *J* = 3.5 Hz), 54.5 (t, *J* = 24.0 Hz), 12.39.

^{19}F NMR (377 MHz, Chloroform-d) δ -122.56 (d, J = 275.1 Hz), -124.26 (d, J = 275.1 Hz).

HRMS (ESI) calculated for $C_{17}H_{17}F_2N_2$ ($[M+H]^+$): 287.1354; found 287.1357.

***N*-(1-(4-chloro-1H-indol-3-yl)-2,2-difluoroethyl)aniline (7da)**

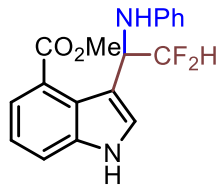


Following general procedure C to afford the title compound as a yellow oil (38.6 mg, 63%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.26; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.26 (s, 1H), 7.31 – 7.26 (m, 2H), 7.20 – 7.09 (m, 4H), 6.78 – 6.66 (m, 3H), 6.32 (td, *J* = 55.6, 2.0 Hz, 1H), 5.81 (dt, *J* = 16.1, 7.7 Hz, 1H), 4.42 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.5, 138.0, 129.4, 125.6, 125.2 (d, *J* = 2.4 Hz), 123.5, 123.2, 121.4, 118.5, 115.9 (t, *J* = 247.6 Hz), 113.9, 111.4 (d, *J* = 6.7 Hz), 110.5, 53.0 (t, *J* = 21.0 Hz).

^{19}F NMR (377 MHz, Chloroform-d) δ -123.78 (d, *J* = 272.0 Hz), -132.72 (d, *J* = 272.0 Hz).

HRMS (ESI) calculated for $C_{16}H_{14}ClF_2N_2$ ([M+H]$^+$): 307.0808; found 307.0809.

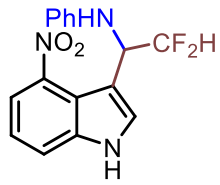
methyl 3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-4-carboxylate (7ea)



Following general procedure C to afford the title compound as a yellow oil (35.2 mg, 54%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.26; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.38 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.80 – 6.58 (m, 3H), 6.21 (td, *J* = 56.0, 1.8 Hz, 1H), 5.92 (t, *J* = 13.0 Hz, 1H), 4.41 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 168.9, 146.6, 138.0, 129.3, 126.8, 124.0, 123.9, 123.6, 121.4, 118.2, 116.3 (dd, *J* = 247.5, 244.7 Hz), 116.26, 113.9, 111.66 (d, J = 6.4 Hz), 53.5 (t, *J* = 21.3 Hz), 52.4. ^{19}F NMR (377 MHz, Chloroform-d) δ -124.76 (d, *J* = 273.2 Hz), -131.33 (d, *J* = 273.2 Hz).

HRMS (ESI) calculated for $C_{18}H_{17}F_2N_2O_2$ ([M+H]$^+$): 331.1252; found 331.1255.

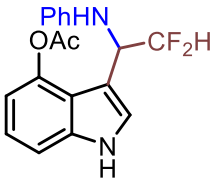
***N*-(2,2-difluoro-1-(4-nitro-1H-indol-3-yl)ethyl)aniline (7fa)**



Following general procedure C to afford the title compound as a yellow oil (32.4 mg, 32%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.18; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.69 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.53 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 2H), 6.74 (s, 1H), 6.71 (d, *J* = 8.3 Hz, 2H), 6.12 (td, *J* = 56.2, 2.1 Hz, 1H), 5.73 (t, *J* = 12.8 Hz, 1H), 4.40 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 146.0, 143.1, 139.3, 129.5, 129.0, 121.4, 119.0, 118.8, 118.7, 118.0, 115.7 (t, *J* = 245.1 Hz), 114.0, 110.7 (d, *J* = 4.8 Hz), 53.25 (t, *J* = 21.8 Hz). ^{19}F NMR

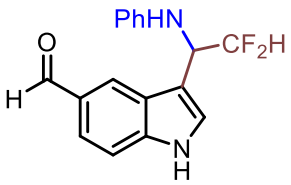
(377 MHz, Chloroform-d) δ -127.01 (d, *J* = 277.7 Hz), -129.05 (d, *J* = 278.2 Hz). **HRMS (ESI)**: calcd for $C_{16}H_{14}F_2N_3O_2$ $[M+H]^+$: 318.1049, found: 318.1046.

3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indol-4-yl acetate (7ga)



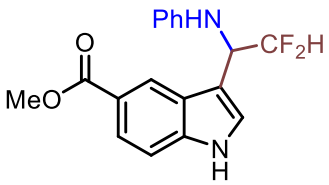
Following general procedure C to afford the title compound as a yellow oil (63.4 mg, 96%). TLC (PE: EA, 4:1 *v*/*v*): R_f = 0.28; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.26 (s, 1H), 7.25 (t, *J* = 8.2 Hz, 1H), 7.22 – 7.12 (m, 4H), 6.93 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 6.20 (td, *J* = 55.9, 2.7 Hz, 1H), 5.17-5.19 (m, 1H), 4.34 (d, *J* = 6.0 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 170.0, 146.7, 143.7, 138.8, 129.5, 124.5, 123.0, 118.7, 118.6, 116.0(t, *J* = 245.1 Hz), 113.83, 113.6, 109.6, 53.9 (dd, *J* = 23.7, 21.4 Hz), 21.2. ^{19}F NMR (377 MHz, Chloroform-d) δ -122.95 (d, *J* = 275.2 Hz), -129.49 (d, *J* = 275.2 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{17}F_2N_2O_2$ $[M+H]^+$: 331.1252, found: 331.1253.

3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-5-carbaldehyde (7ha)



Following general procedure C to afford the title compound as a yellow oil (40.0 mg, 67%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.18; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 8.75 (s, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.16 (td, *J* = 56.0, 2.7 Hz, 1H), 5.11 (t, *J* = 12.6 Hz, 1H), 4.23 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 192.6, 146.4, 136.1, 131.7, 131.4, 129.6, 128.1, 121.6, 119.6, 119.1, 115.6 (d, J = 246.7 Hz), 114.4, 114.0, 111.5, 53.6 (t, *J* = 23.3 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.65 (d, *J* = 278.9 Hz), -125.72 (d, *J* = 278.9 Hz). HRMS (ESI) calculated for $C_{17}H_{15}F_2N_2O$ $[M+H]^+$: 301.1146; found: 301.1139.

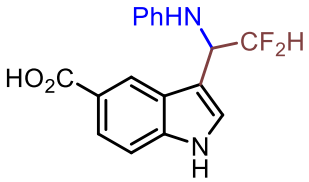
methyl 3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-5-carboxylate (7ia)



Following general procedure C to afford the title compound as a yellow oil (51.3 mg, 63%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.18; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.63 (s, 1H), 8.46 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 2H), 6.15 (td, *J* = 56.0, 2.7 Hz, 1H), 5.11 (t, *J* = 12.3 Hz,

1H), 4.28 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 168.3, 146.5, 139.1, 129.5, 125.9, 125.1, 124.0, 122.3, 122.0, 118.9, 115.6 (d, *J* = 246.6 Hz), 114.0, 112.0, 111.4, 53.7 (t, *J* = 23.1 Hz), 52.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -125.15. HRMS (ESI) calculated for $C_{18}H_{17}F_2N_2O_2$ ([M+H] $^+$): 331.1252; found 331.1252.

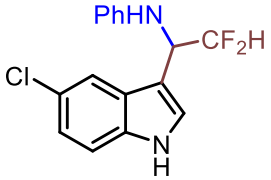
3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-5-carboxylic acid (7ja)



Following general procedure C to afford the title compound as a yellow oil (42.5 mg, 67%). TLC (PE: EA = 2:1 *v*/*v*): R_f = 0.40;

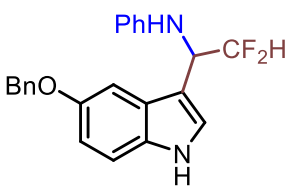
^{1}H NMR (600 MHz, DMSO-d6) δ 12.44 (s, 1H), 11.45 (s, 1H), 8.44 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.05 (t, J = 7.8 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.55 (t, *J* = 7.2 Hz, 1H), 6.37 (dd, *J* = 56.0, 3.0 Hz, 1H), 6.21 (d, *J* = 8.7 Hz, 1H), 5.28 (q, *J* = 14.0, 12.7 Hz, 1H), 3.40 (s, 3H). 13C NMR (151 MHz, DMSO-d6) δ 148.0, 139.2, 129.2, 126.8, 126.5, 123.0, 122.5, 122.0, 117.1, 116.7 (t, *J* = 244.4 Hz), 113.6, 111.8, 111.7, 52.2 (t, *J* = 23.3 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -117.48 (d, *J* = 273.8 Hz), -119.05 (d, *J* = 273.8 Hz). HRMS (ESI) calculated for $C_{17}H_{15}F_2N_2O_2$ [M+H] $^+$: 317.1096; found: 317.1089

***N*-(1-(5-chloro-1H-indol-3-yl)-2,2-difluoroethyl)aniline (7ka)**



Following general procedure C to afford the title compound as a yellow oil (42.8 mg, 70%). TLC (PE: EA= 8:1 *v*/*v*): R_f = 0.42; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.26 (s, 1H), 7.17 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.12 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 2H), 6.13 (td, *J* = 56.0, 3.0 Hz, 1H), 5.09-5.00 (m, 1H), 4.16 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.5, 134.8, 129.5, 127.4, 126.2, 124.9, 123.2, 119.0, 118.7, 115.6 (t, *J* = 246.7 Hz), 114.0, 112.6, 110.5, 53.7 (t, *J* = 23.3 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ 123.76 (d, *J* = 276.2 Hz), 122.16 (d, *J* = 276.6 Hz). **HRMS (ESI)**: calcd for $C_{16}H_{14}F_2N_2Cl$ $[M+H]^+$: 307.0808, found: 307.0804.

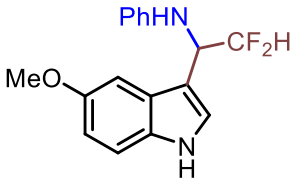
***N*-(1-(5-(benzyloxy)-1H-indol-3-yl)-2,2-difluoroethyl)aniline (7la)**



Following general procedure C to afford the title compound as a yellow oil (59.7 mg, 79%). TLC (PE: EA = 8:1 *v*/*v*): R_f=

0.45; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 1H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.12 (d, *J* = 2.2 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 6.14 (td, *J* = 56.0, 3.0 Hz, 1H), 5.03 (s, 2H), 4.98 (t, *J* = 12.4 Hz, 1H), 4.13 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.7, 147.0, 137.6, 131.7, 129.5, 128.7, 128.0, 127.8, 126.7, 123.9, 118.8, 117.1 (t, *J* = 246.6 Hz), 114.0, 113.8, 112.3, 110.6, 102.6, 70.9, 54.1 (t, *J* = 23.4Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.08 (d, *J* = 277.4 Hz), -125.47 (d, *J* = 277.4 Hz). **HRMS (ESI)**: calcd for $C_{24}H_{21}F_2N_2O$ $[M+H]^+$: 391.1616, found: 391.1611.

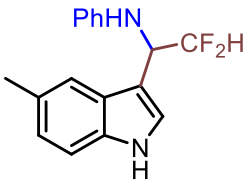
***N*-(2,2-difluoro-1-(5-methoxy-1H-indol-3-yl)ethyl)aniline (7ma)**



Following general procedure C to afford the title compound as a yellow oil (46.5 mg, 77%). TLC (PE: EA = 8:1 *v*/*v*): R_f = 0.44;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.08 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.18 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.04 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 6.16 (td, *J* = 56.1, 3.1 Hz, 1H), 5.02 (t, *J* = 12.6 Hz, 1H), 4.16 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 154.6, 147.0, 131.5, 129.5, 126.7, 123.9, 118.8, 115.9 (t, *J* = 246.7 Hz), 114.0, 113.0, 112.3, 110.6, 101.0, 56.0, 54.1 (t, *J* = 23.4Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.09 (d, *J* = 277.3 Hz), -125.46 (d, *J* = 277.3 Hz). **HRMS (ESI)**: calcd for $C_{18}H_{17}F_2N_2O$ $[M+H]^+$: 315.1303, found: 315.1295.

***N*-(2,2-difluoro-1-(5-methyl-1H-indol-3-yl)ethyl)aniline (7na)**

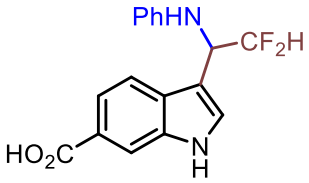


Following general procedure C to afford the title compound as a yellow oil (35.2 mg, 62%). TLC (PE: EA = 8:1 *v*/*v*): R_f = 0.3;

^{1}H NMR (600 MHz, Chloroform-d) δ 8.03 (s, 1H), 7.48 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.19 (td, *J* = 56.0, 3.0 Hz, 1H), 5.09 (td, J = 12.8, 2.9 Hz, 1H), 4.23 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 146.9, 134.8, 129.7, 129.4, 126.4, 124.4, 123.5, 118.7, 118.6, 115.9 (t, *J* = 246.7 Hz), 113.9, 111.3, 110.1 (dd, *J* = 3.9, 1.8 Hz), 53.9 (t, *J* = 23.0 Hz), 21.7. ^{19}F NMR (377 MHz, Chloroform-d) δ -123.81 (d,

J = 276.8 Hz), -125.77 (d, *J* = 276.7 Hz). HRMS (ESI) calculated for $C_{17}H_{17}F_2N_2$ ([M+H] $^+$: 287.1354; found: 287.1350.

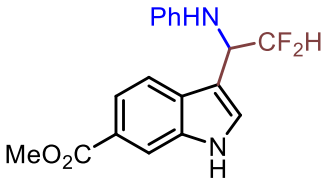
3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-6-carboxylic acid (7oa)



Following general procedure C to afford the title compound as a yellow oil (10.2 mg, 16%). TLC (PE: EA = 2:1 *v*/*v*): R_f = 0.40;

^{1}H NMR (600 MHz, Chloroform-d) δ 8.49 (s, 1H), 8.21 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 2H), 6.16 (td, *J* = 56.0, 2.7 Hz, 1H), 5.14 – 5.07 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 146.3, 135.7, 130.3, 129.4, 127.0, 123.3, 121.8, 118.9, 118.8, 115.5 (t, *J* = 245.7 Hz), 114.5, 114.1, 113.8, 53.6 (t, *J* = 23.7Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -125.26 (d, *J* = 33.3 Hz). HRMS (ESI) calculated for $C_{17}H_{15}F_2N_2O_2$ $[M+H]^+$: 317.1096; found: 317.1093

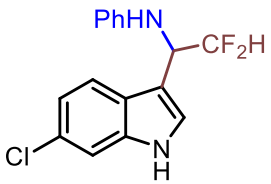
methyl 3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-6-carboxylate (7pa)



Following general procedure C to afford the title compound as a yellow oil (48.2 mg, 73%). TLC (PE: EA = 4:1 *v*/*v*): R_f = 0.19;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.15 (s, 1H), 7.84 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.17 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.15 (td, *J* = 56.0, 2.9 Hz, 1H), 5.09-5.00 (m, 1H), 4.19 (d, *J* = 6.8 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.0, 146.5, 135.8, 129.9, 129.5, 126.7, 124.6, 121.4, 119.0, 118.8, 115.6 (t, *J* = 247.0 Hz), 114.0 , 113.9 , 111.2, 53.7 (t, *J* = 23.4Hz), 52.2. ^{19}F NMR (377 MHz, Chloroform-d) δ -125.11 – -125.31 (m). **HRMS (ESI)**: calcd for $C_{18}H_{17}F_2N_2O_2$ $[M+H]^+$: 331.1253, found: 331.1254.

***N*-(1-(6-chloro-1H-indol-3-yl)-2,2-difluoroethyl)aniline (7qa)**

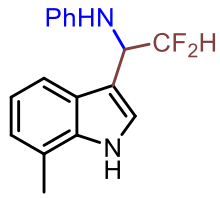


Following general procedure C to afford the title compound as a yellow oil (52.0 mg, 85%). TLC (PE: EA = 8:1 *v*/*v*): R_f = 0.42;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.26 (s, 1H), 7.17 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.11

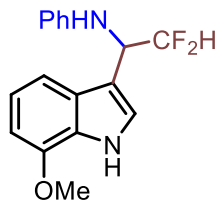
(d, *J* = 1.8 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 2H), 6.13 (td, *J* = 56.0, 3.0 Hz, 1H), 5.09-5.00 (m, 1H), 4.16 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.6, 136.8, 129.5, 128.8, 125.0, 124.0, 121.2, 120.1, 119.0, 115.7 (t, *J* = 246.9 Hz), 113.9, 111.6, 111.0, 53.8(t, *J* = 23.4Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.50 (d, *J* = 279.2 Hz), -125.84 (d, *J* = 279.5 Hz). **HRMS (ESI)**: calcd for $C_{16}H_{14}F_2N_2Cl$ [M + H]$^+$: 307.0808, found: 307.0804.

***N*-(2,2-difluoro-1-(7-methyl-1H-indol-3-yl)ethyl)aniline (7ra)**



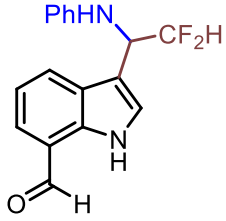
Following general procedure C to afford the title compound as a yellow oil (35.2 mg, 57%). TLC (PE: EA = 8:1 *v*/*v*): R_f = 0.3; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.07 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.17 (td, *J* = 56.0, 2.9 Hz, 1H), 5.08 (td, *J* = 12.8, 2.3 Hz, 1H), 4.20 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 146.9, 136.1, 129.4, 125.8, 123.3, 123.1, 120.9, 120.6, 118.7, 116.8, 115.9 (t, *J* = 246.7 Hz), 113.9, 111.24 (dd, *J* = 3.9, 1.8 Hz), 54.0 (t, *J* = 23.0 Hz), 16.7. ^{19}F NMR (377 MHz, Chloroform-d) δ -124.00 (d, *J* = 277.2 Hz), -125.80 (d, *J* = 276.4 Hz). HRMS (ESI) calculated for $C_{17}H_{17}F_2N_2$ [M+H]$^+$: 287.1354; found: 287.1350

***N*-(2,2-difluoro-1-(7-methoxy-1H-indol-3-yl)ethyl)aniline (7sa)**



Following general procedure C to afford the title compound as a yellow oil (50.1 mg, 82%). TLC (PE: EA, 8:1 *v*/*v*): R_f = 0.4; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.44 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.20 (td, *J* = 56.0, 3.1 Hz, 1H), 5.10 (t, *J* = 12.4 Hz, 1H), 4.26 (s, 1H), 4.00 (s, 3H).. ^{13}C NMR (151 MHz, Chloroform-d) δ 146.9, 146.4, 129.4, 127.5, 127.1, 122.9, 120.8, 118.7, 115.9 (t, *J* = 246.7 Hz), 113.9, 111.7, 111.1 (dd, *J* = 3.9, 1.8 Hz), 102.5, 55.5, 54.0 (t, *J* = 23.1 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -123.90 (d, *J* = 277.3 Hz), -125.74 (d, *J* = 277.2 Hz). **HRMS (ESI)**: calcd for $C_{17}H_{17}F_2N_2O$ [M+ H]$^+$: 303.1303, found: 303.1308.

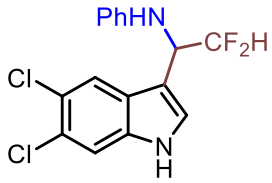
3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-7-carbaldehyde (7ta)



Following general procedure C to afford the title

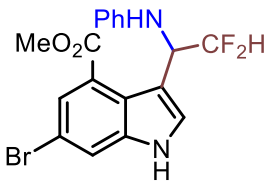
compound as a yellow oil (32.4 mg, 57%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (600 MHz, Chloroform-d) δ 10.16 (s, 1H), 10.12 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.42 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.15 (td, *J* = 56.0, 2.6 Hz, 1H), 5.16 – 5.06 (m, 1H), 4.19 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 193.6, 146.5, 134.3, 129.5, 129.5, 127.6, 126.7, 125.2, 120.8, 120.0, 119.0, 115.7 (t, *J* = 246.8 Hz), 114.0, 111.0, 53.8 (t, *J* = 23.4 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.45 (d, *J* = 279.2 Hz), -125.42 (d, *J* = 278.9 Hz). **HRMS (ESI)**: calcd for $C_{17}H_{15}F_2N_2O$ $[M+H]^+$: 300.1068, found: 300.1066.

N-(1-(5,6-dichloro-1H-indol-3-yl)-2,2-difluoroethyl)aniline (7ua)



Following general procedure C to afford the title compound as a yellow oil (51.0 mg, 75%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.42; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.54 (s, 1H), 8.09 (s, 1H), 7.83 (s, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.45 (td, *J* = 56.0, 2.9 Hz, 1H), 5.41 – 5.25 (m, 1H), 4.50 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.3, 135.2, 129.6, 126.9, 126.1, 125.5, 124.7, 120.4, 119.2, 115.5 (t, *J* = 246.7 Hz), 114.0, 113.1, 110.6, 53.7 (t, *J* = 23.6 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -124.52 (d, *J* = 279.6 Hz), -125.87 (d, *J* = 279.6 Hz). HRMS (ESI): calcd for $C_{16}H_{13}F_2N_2Cl$ $[M+ H]^+$: 341.0418, found: 341.0413.

methyl 6-bromo-3-(2,2-difluoro-1-(phenylamino)ethyl)-1H-indole-4-carboxylate (7va)

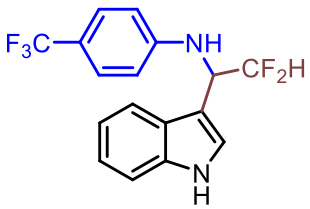


Following general procedure C to afford the title compound as a yellow oil (51.3 mg, 63%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.26; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.43 (s, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 2H), 6.20 (td, *J* = 56.0, 1.6 Hz, 1H), 5.89 (td, *J* = 13.0, 5.7 Hz, 1H), 4.39 (d, *J* = 6.7 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 146.4, 138.7, 129.4, 127.4, 126.8, 124.9, 123.2, 118.7, 118.4, 116.10(t, *J* = 247.5 Hz), 114.54, 113.9, 112.0 (d, *J* = 5.1 Hz), 53.2(t, *J* = 23.8 Hz), 52.7.

^{19}F NMR (377 MHz, Chloroform-d) δ -125.56 (d, *J* = 274.5 Hz), -130.63 (d, *J* = 274.5 Hz).

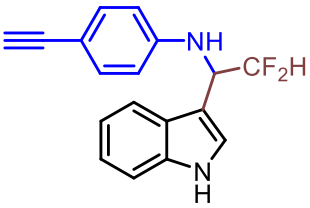
HRMS(ESI) calculated for $C_{18}H_{16}BrF_2N_2O_2$ ([M+H] $^+$): 409.0357; found 409.0355.

N-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)-4-(trifluoromethyl)aniline (7ab)



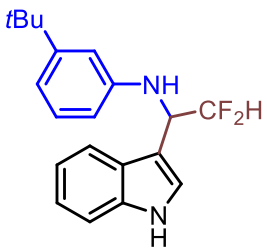
Following general procedure C to afford the title compound as a yellow oil (38.4 mg, 56%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.21; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.26 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 9.0 Hz, 3H), 7.33 – 7.27 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.20 (td, *J* = 55.7, 2.8 Hz, 1H), 5.21 – 5.08 (m, 1H), 4.54 (d, *J* = 6.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 149.4, 136.5, 126.8 (q, *J* = 3.8 Hz), 126.0, 124.9 (q, *J* = 270.5 Hz), 123.4, 123.1, 120.6, 120.3 (q, *J* = 32.7 Hz), 118.8, 115.6 (t, *J* = 247.0 Hz), 113.0, 111.8, 110.1 (d, *J* = 4.9 Hz), 53.44 (t, *J* = 22.9 Hz). ^{19}F NMR (471 MHz, Chloroform-d) δ -61.19, -123.02 (d, *J* = 277.6 Hz), -126.65 (d, *J* = 277.6 Hz). HRMS (ESI): calcd for $C_{17}H_{12}F_5N_2$ [M - H]$^-$: 340.0993, found: 340.0984.

N-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)-4-ethynylaniline (7ac)



Following general procedure C to afford the title compound as a yellow oil (35.3 mg, 60%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.16; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.26 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.18 (td, *J* = 55.8, 2.9 Hz, 1H), 5.17 – 5.06 (m, 1H), 4.39 (d, *J* = 6.6 Hz, 1H), 2.98 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 147.1, 136.3, 133.5, 130.8, 126.0, 123.2, 122.9, 120.4, 118.8, 115.5(t, *J* = 246.9 Hz), 113.3, 111.6, 111.4, 84.3, 75.1, 53.4 (t, *J* = 23.0 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -123.49 (d, *J* = 277.5 Hz), -126.32 (d, *J* = 277.5 Hz). HRMS (ESI): calcd for $C_{18}H_{15}F_2N_2$ [M + H]$^+$: 297.1198, found: 297.1194.

3-(tert-butyl)-N-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)aniline (7ad)

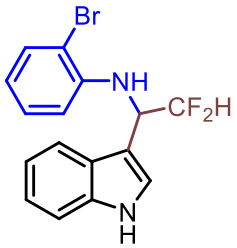


Following general procedure C to afford the title compound as a yellow oil (35.0 mg, 53%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.21;

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H),

6.87 (d, *J* = 7.8 Hz, 1H), 6.81 (s, 1H), 6.60 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.21 (td, *J* = 56.1, 3.0 Hz, 1H), 5.12 (t, *J* = 12.6 Hz, 1H), 4.25 – 4.20 (m, 1H), 1.31 (s, 8H). ^{13}C NMR (151 MHz, Chloroform-d) δ 152.6, 146.6 , 136.4, 129.1, 126.2, 123.4, 122.8, 120.3, 119.1, 116.1, 116.0 (t, J = 246.6 Hz), 111.9, 111.6, 110.9, 110.5, 54.0 (t, *J* = 23.1 Hz), 34.7, 31.4 . ^{19}F NMR (377 MHz, Chloroform-d) δ -123.99 (d, *J* = 276.7 Hz), -125.32 (d, *J* = 276.7 Hz). HRMS (ESI): calcd for $C_{20}H_{23}F_2N_2$ $[M + H]^+$: 329.1823, found: 329.1824.

2-bromo-*N*-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)aniline (7ae)



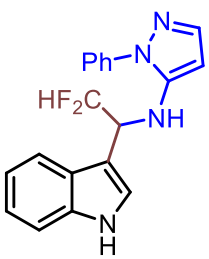
Following general procedure C to afford the title compound as a yellow oil (22.4 mg, 32%). TLC (PE : EA = 8:1 *v*/*v*): R_f = 0.29; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.24 (s, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 2.9 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.19 (td, *J* = 55.9, 3.0 Hz, 1H), 5.20 – 5.09 (m, 1H), 5.01 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.5, 136.4 , 132.6 , 128.5 , 126.0 , 123.4 , 122.8 , 120.4 , 119.0 , 118.9 , 115.5(t, *J* = 247.5 Hz),, 112.5 , 111.6 , 110.6 , 110.1 , 53.8(t, *J* = 23.2 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -123.92 (d, *J* = 277.5 Hz), -125.84 (d, *J* = 277.5 Hz).

HRMS (ESI) calculated for $C_{16}H_{14}BrF_2N_2$ ($[M+H]^+$): 351.0302; found 351.0304

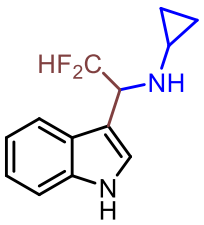
***N*-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)-1-phenyl-1H-pyrazol-5-amine (7af)**



Following general procedure C to afford the title compound as a yellow oil (38.6 mg, 57%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.20; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.35 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.51 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 6.28 (td, J = 56.6, 3.3 Hz, 1H), 4.56 (ddd, J = 18.0, 13.8, 3.3 Hz, 1H), 3.65 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 142.9, 140.3, 138.5, 136.3, 129.5, 127.6, 126.7, 124.1, 123.0, 122.7, 120.0, 119.2, 117.2 (t, *J* = 244.9 Hz), 111.4, 110.3 (dd, *J* = 5.5, 2.4 Hz), 99.1 (t, *J* = 3.1 Hz), 37.7 (t, *J* = 22.1 Hz). ^{19}F NMR (377 MHz, Chloroform-d) δ -116.58 (d, *J* = 274.5 Hz), -118.83 (d, *J* = 273.9 Hz). HRMS (ESI): calcd for $C_{19}H_{17}F_2N_4$ $[M + H]^+$: 339.1416,

found: 339.1410.

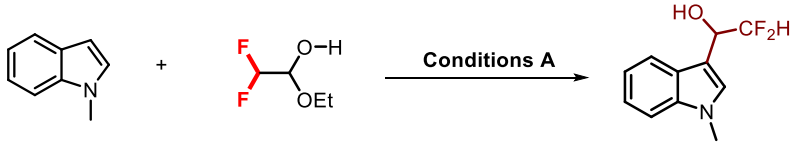
***N*-(2,2-difluoro-1-(1H-indol-3-yl)ethyl)cyclopropanamine (7ag)**



Following general procedure C to afford the title compound as a yellow oil (29.3 mg, 62%). TLC (PE : EA = 4:1 *v*/*v*): R_f = 0.20; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.28 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.19 (td, *J* = 8.1, 1.1 Hz, 1H), 6.07 (td, *J* = 56.6, 3.4 Hz, 1H), 4.40 (ddd, *J* = 14.6, 13.3, 3.3 Hz, 1H), 2.33 – 2.22 (m, 1H), 0.54 – 0.38 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 136.3, 126.9, 123.3, 122.6, 120.1, 119.3, 1196.7 (t, *J* = 245.2 Hz), 111.8 (t, *J* = 3.5 Hz), 111.5, 57.8 (t, *J* = 22.4 Hz), 29.6, 7.0, 6.8. ^{19}F NMR (377 MHz, Chloroform-d) δ -123.50 (d, *J* = 277.8 Hz), -124.4(d, *J* = 277.8 Hz).

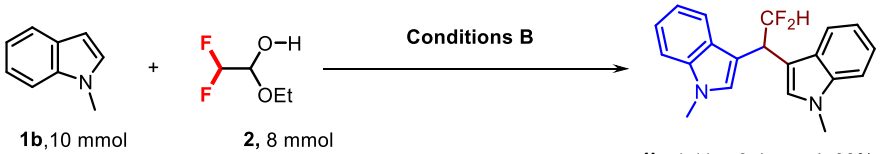
HRMS (ESI) calculated for $C_{13}H_{15}F_2N_2$ ([M+H] $^+$): 237.1197; found 237.1194.

4 Gram-scale Synthesis of product 3b and 4b



1b 7.6 mmol **2** 9.12 mmol **3b** 1.44g, 6.84 mmol, 90% yield

In an oven-dried 100 ml round bottom flask, a mixture of 1-methylindole **1b** (7.6 mmol, 1.0 equiv), 1-ethoxy-2,2-difluoroethan-1-ol **2** (1.15g, 9.12 mmol, 1.2 equiv), K_2CO_3 (525.2 mg, 3.8 mmol, 0.5 equiv) in TFE (20 mL) was stirred at 60 ℃ for 6 h. The reaction mixture was then diluted with Ethyl acetate (30 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 1.44 g of product **3b**, yield 90%.



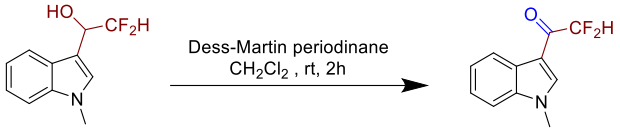
1b,10 mmol **2,** 8 mmol **4b,** 1.11g, 3.4 mmol, 68% yield

In an oven-dried pressure tube, a mixture of 1-methylindole **1b** (7.6 mmol, 1.0 equiv), 1-ethoxy-2,2-difluoroethan-1-ol **2** (1.15g, 9.12 mmol, 1.2 equiv), (S)-(+)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (10 mol%) in DCM (20mL) was

stirred at room temperature for 1h. The reaction mixture was then diluted with Ethyl acetate (30 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 1.11 g of product **4b**, yield 68%.

5 Derivatization of product 3b and Characterization Data of Compounds 9-13 and 4b.

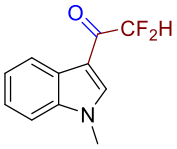
5.1 Compound 9



3b **9**

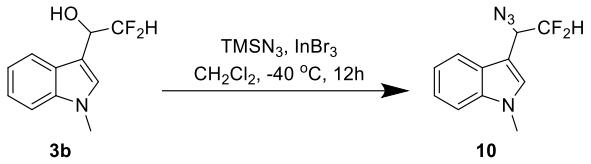
In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), Dess-Martin periodinane (313.8 mg, 0.74 mmol, 3.7 equiv), in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. The reaction mixture was then diluted with ethyl acetate (10 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 14 mg of product **9**, yield 53%.[2]

2,2-Difluoro-1-(1-methyl-1H-indol-3-yl)ethan-1-one (9)



According to the above procedure and provide the title compound as a yellow oil (22.2 mg, 53%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.4; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 – 8.39 (m, 1H), 8.00 (s, 1H), 7.39 – 7.35 (m, 3H), 6.10 (t, *J* = 54.3 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 182.8 (t, *J* = 25.3 Hz), 137.9 (t, *J* = 7.1 Hz), 137.2, 126.9, 124.3, 123.6, 122.6, 112.2 (t, *J* = 254.0 Hz), 110.4 (t, *J* = 2.1 Hz), 109.9, 33.9. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -112.25- -120.00 (m), -120.11- -126.03 (m).

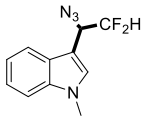
5.2 Compound 10



3b 10

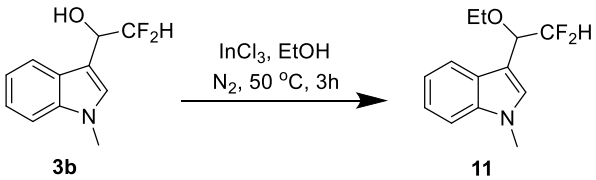
In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), $TMSN_3$ (34.6 mg, 0.3 mmol, 1.5 equiv), $InBr_3$ (35.5mg, 0.1 mmol, 0.5 equiv) in CH_2Cl_2 (1 ml) was stirred at – 40℃ for 12 h. The reaction mixture was then diluted with ethyl acetate (10 ml). The aqueous phase was extracted with Ethyl acetate. The organic layers were combined and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 19 mg of product **10**, yield 57%.

3-(1-azido-2,2-Difluoroethyl)-1-methyl-1H-indole (10)



According to the above procedure and provide the title compound as a yellow oil (26.9 mg, 57%). TLC (PE: EA, 4:1 *v*/*v*): R_f= 0.7; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 7.19 (t, *J* = 7.3 Hz, H), 6.00 (td, *J* = 55.6, 3.8 Hz, 1H), 4.97 (td, *J* = 12.5, 3.7 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.0, 128.7, 126.6, 122.6, 120.3, 118.9, 114.9 (t, *J* = 246.3 Hz), 109.8, 104.7 (t, *J* = 3.1 Hz), 59.6 (t, *J* = 24.0 Hz), 33.1. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -122.32 (ddd, *J* = 279.3, 55.5, 12.0 Hz), -123.78 (ddd, *J* = 279.4, 55.5, 13.3 Hz).

5.3 Compound 11

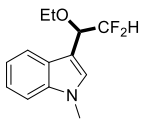


3b 11

In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), $InCl_3$ (8.4 mg, 0.04 mmol, 0.2 equiv) in EtOH (1 ml) was stirred at 50℃ with nitrogen protection for 3h. The reaction

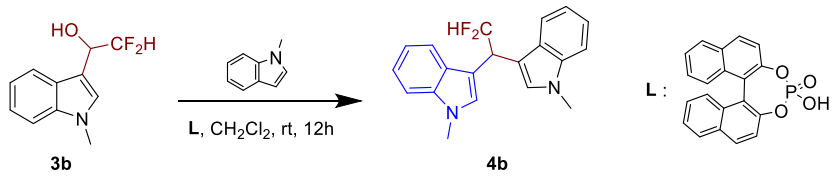
mixture was then diluted with ethyl acetate (10 ml). The aqueous phase was extracted with Ethyl acetate. The organic layers were combined and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 32/1) to afford the desired 26.3 mg of product **11**, yield 75%.

3-(1-ethoxy-2,2-Difluoroethyl)-1-methyl-1H-indole (11)



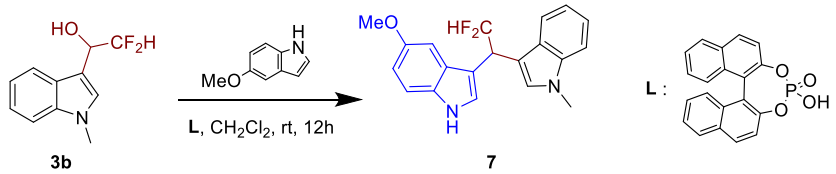
According to the above procedure and provide the title compound as a yellow oil (33.9 mg, 75%). TLC (PE: EA, 32:1 *v*/*v*): R_f= 0.3; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 5.98 (td, *J* = 56.1, 4.5 Hz, 1H), 4.76 (td, *J* = 10.8, 4.5 Hz, 1H), 3.80 (s, 3H), 3.61 – 3.49 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.2, 128.8, 127.0, 122.1, 119.8, 117.1-113.2 (m), 109.5, 108.2-108.1 (m), 77.2, 75.4-75.0 (m), 64.7, 32.9, 15.2. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -124.78 (ddd, *J* = 282.3, 56.8, 10.6 Hz), -125.95 (ddd, *J* = 282.3, 56.8, 12.1 Hz).

5.4 Compound 4b



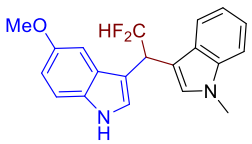
In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), 1-Methyl-1H-indole (26.2 mg, 0.2 mmol, 1 equiv), 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (6.9mg, 0.02 mmol, 0.1 equiv) in CH_2Cl_2 (1 ml) was stirred at room temperature for 12 h. The reaction mixture was then diluted with ethyl acetate (10 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 35.7 mg of product **4b**, yield 55%.[2]

5.5 Compound 12



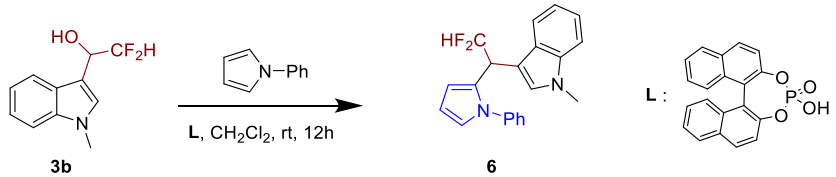
In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), 5-methoxy-1H-indole (29.4 mg, 0.2 mmol, 1 equiv), 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (6.9mg, 0.02 mmol, 0.1 equiv) in CH_2Cl_2 (1 ml) was stirred at room temperature for 12 h. The reaction mixture was then diluted with ethyl acetate (10 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 4/1) to afford the desired 58.3 mg of product **7**, yield 86%.

3-(2,2-difluoro-1-(1-methyl-1H-indol-3-yl)ethyl)-5-methoxy-1H-indole (12)



According to the above procedure and provide the title compound as a white solid (58.3 mg, 86%). TLC (PE: EA, 4:1 *v/v*): R_f = 0.3; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.27 (t, J = 8.1 Hz, 2H), 7.16 – 7.12 (m, 2H), 7.07 (d, J = 1.8 Hz, 1H), 7.05 (s, 1H), 6.90 (dd, J = 8.8, 2.1 Hz, 1H), 6.39 (td, J = 56.7, 3.3 Hz, 1H), 5.01 (td, J = 16.2, 3.1 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 154.1 , 137.0 , 131.3 , 128.1 , 127.6 , 124.1 , 121.8 , 119.4 , 119.2 , 116.3 (t, J = 245.1 Hz), 112.4 , 111.9 , 111.7 (t, J = 3.6 Hz), 110.1 (t, J = 3.7 Hz), 109.4 , 101.2 , 55.9 , 38.6 (t, J = 21.9 Hz), 32.8 . ^{19}F NMR (471 MHz, Chloroform-d) δ -117.54 (dd, J = 56.7, 16.4 Hz). **HRMS (ESI):** calcd for $C_{20}H_{18}F_2N_2ONa$ $[M + Na]^+$: 363.1279, found:363.1266.

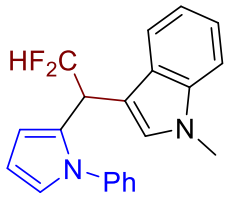
5.6 Compound 13



In an oven-dried Pressure tube, a mixture of 2,2-Difluoro-1-(1-methyl-1H-indol -3-yl)ethan-1-ol **3b** (0.2 mmol, 1.0 equiv), 1-phenyl-1H-pyrrole (28.6 mg, 0.2 mmol, 1 equiv), 1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate (6.9mg, 0.02

mmol, 0.1 equiv) in CH_2Cl_2 (1 ml) was stirred at room temperature for 12 h. The reaction mixture was then diluted with ethyl acetate (10 ml) and washed with brine. The aqueous phase was extracted with Ethyl acetate. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography (PE/EA= 8/1) to afford the desired 25 mg of product **6**, yield 37%.[2]

3-(2,2-difluoro-1-(1-phenyl-1H-pyrrol-2-yl)ethyl)-1-methyl-1H-indole (13)



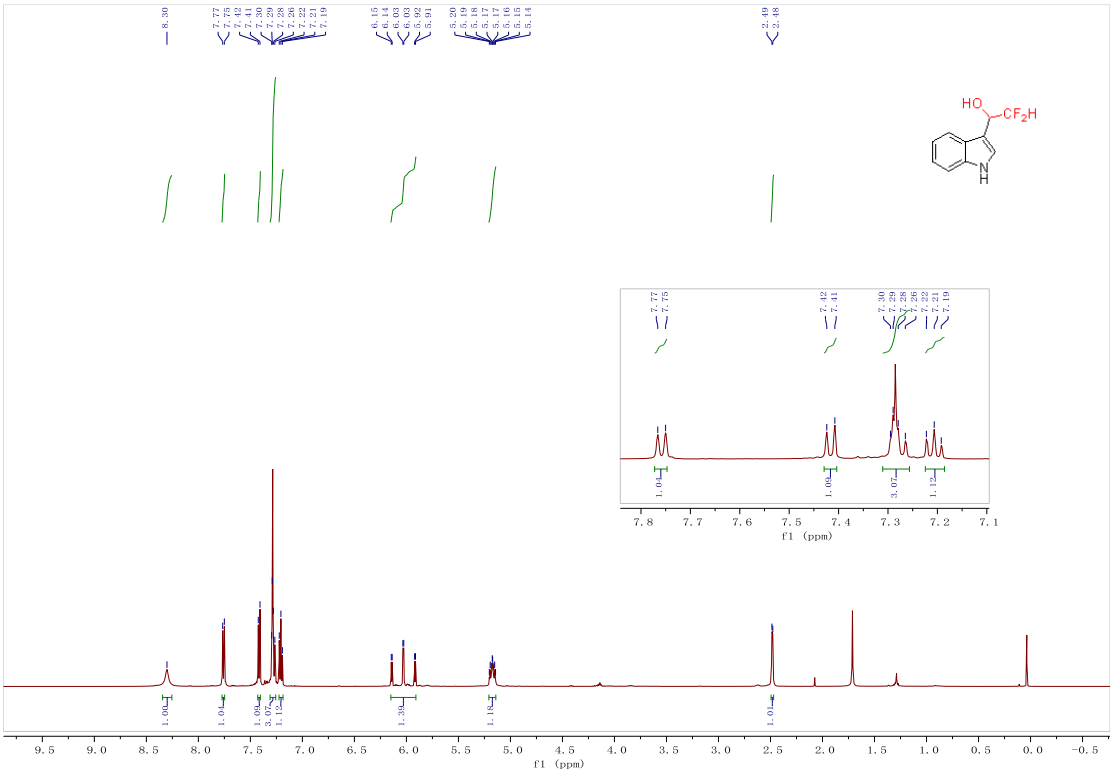
According to the above procedure and provide the title compound as a yellow oil (25 mg, 37%). TLC (PE: EA, 8:1 *v*/*v*): R_f= 0.5; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.31 (m, 5H), 7.29 – 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 7.00 (s, 1H), 6.86 (dd, J = 2.6, 1.8 Hz, 1H), 6.53 (s, 1H), 6.38 (t, J = 3.2 Hz, 1H), 6.15 (td, J = 56.7, 4.0 Hz, 1H), 4.66 (td, J = 15.1, 4.0 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 139.6 , 137.0 , 129.2 , 129.0 , 128.9 (t, J = 4.3 Hz), 127.6 , 127.1 , 126.5 , 122.3 , 121.8 , 119.3 , 119.0 , 116.6 (t, J = 245.4 Hz), 109.6 (t, J = 3.2 Hz), 109.3 , 108.6 , 108.5 , 38.8 (t, J = 22.6 Hz), 32.9 . ^{19}F NMR (470 MHz, Chloroform-d) δ -115.78 – -119.11 (m). **HRMS (ESI):** calcd for $C_{21}H_{19}F_2N_2$ $[M + H]^+$: 337.1510, found:337.1503.

6 References

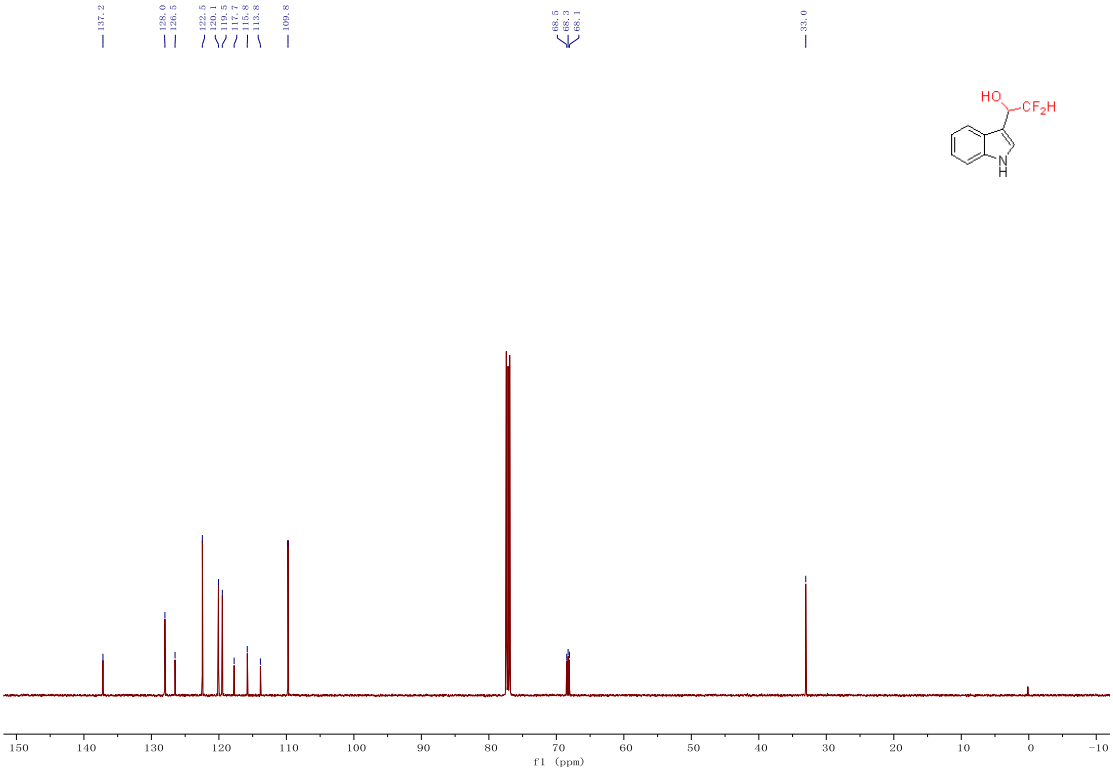
1. S. Kaneko, T. Yamazaki, T. Kitazume, *J. Org. Chem.* **1993**, *58*, 2302-2312.
2. X. Cai, J. Xu, X. Cui, J. Qu, W. Sun, J. Hu, S. Zhao, W.-H. Chen, H. Li, J.-Q. Wu, *Org. Chem. Front.*, **2022**, *9*, 6273−6280.

7 ^{1}H,^{13}C and ^{19}F NMR Spectra of Synthesized Compounds

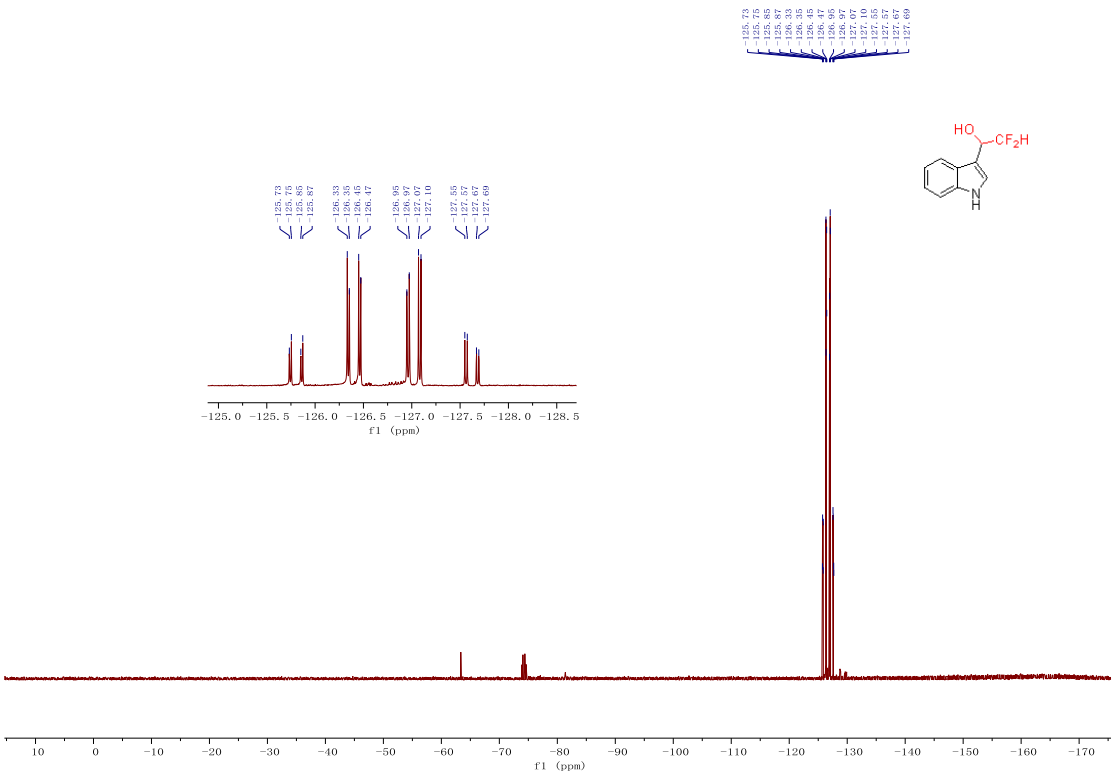
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3a**



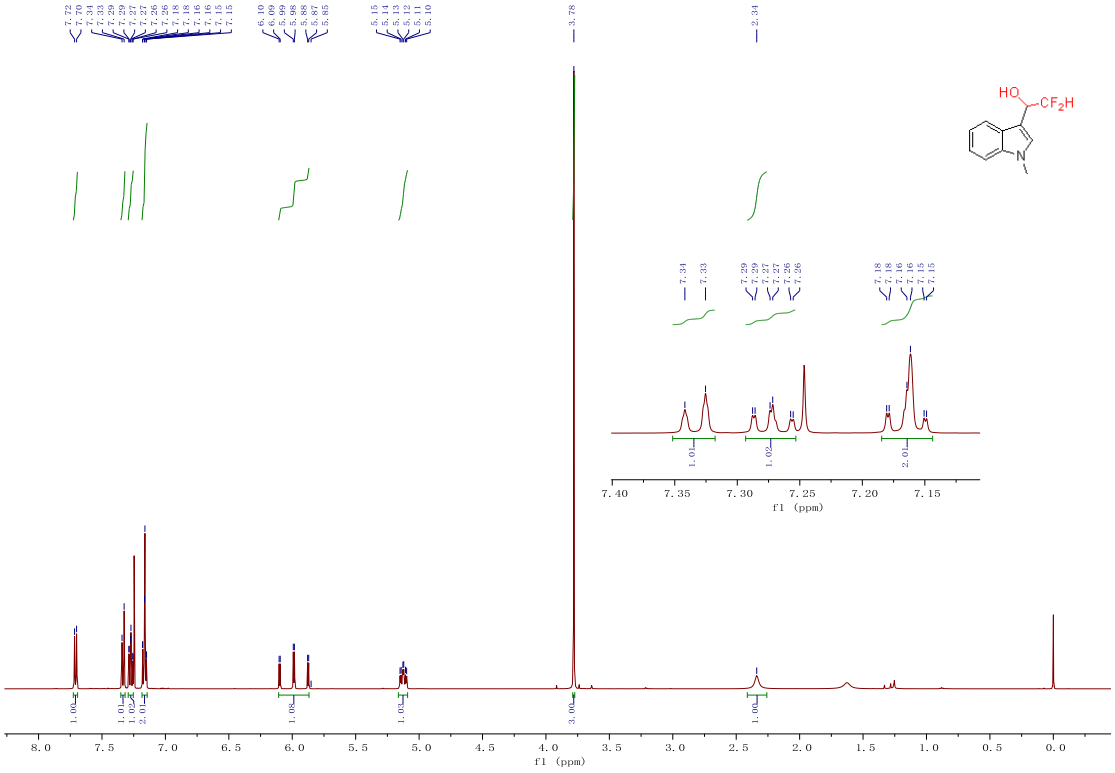
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3a**



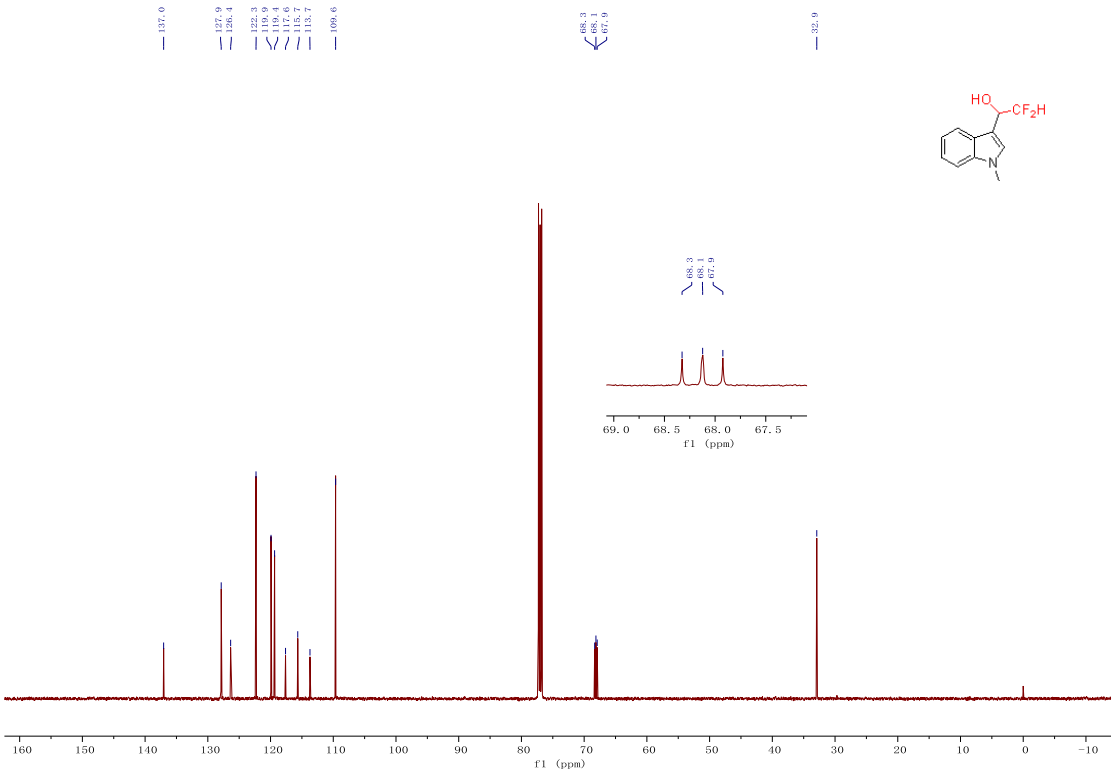
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3a**



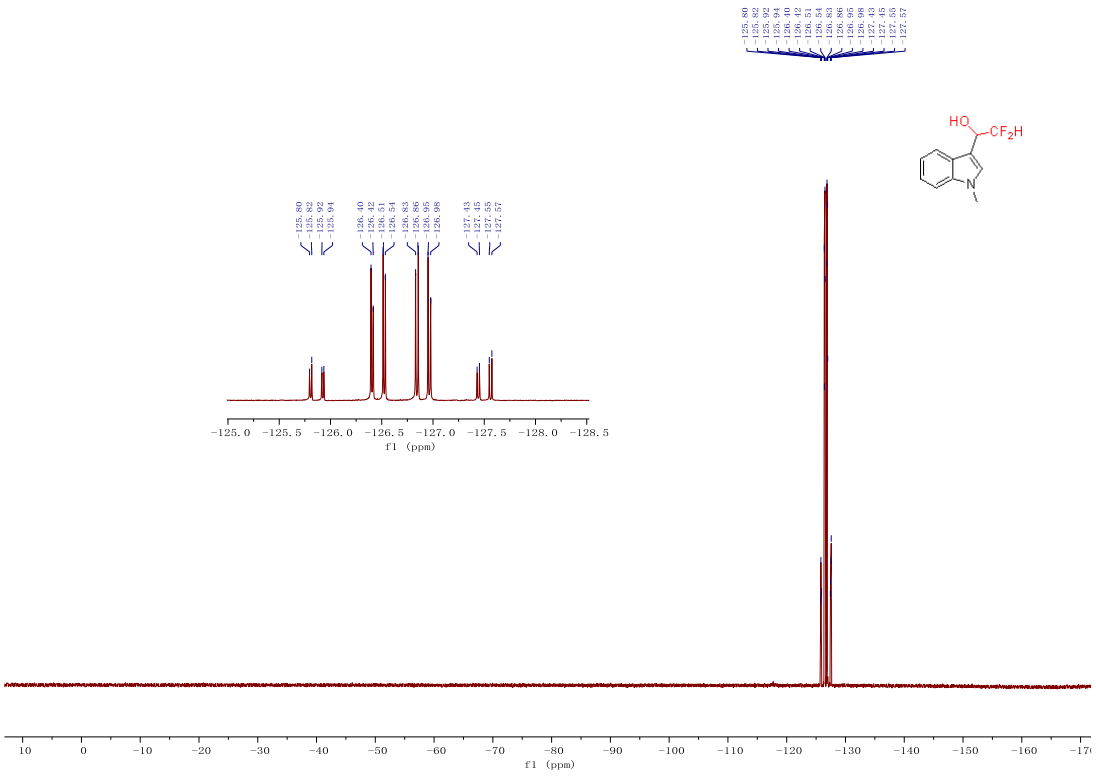
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3b**



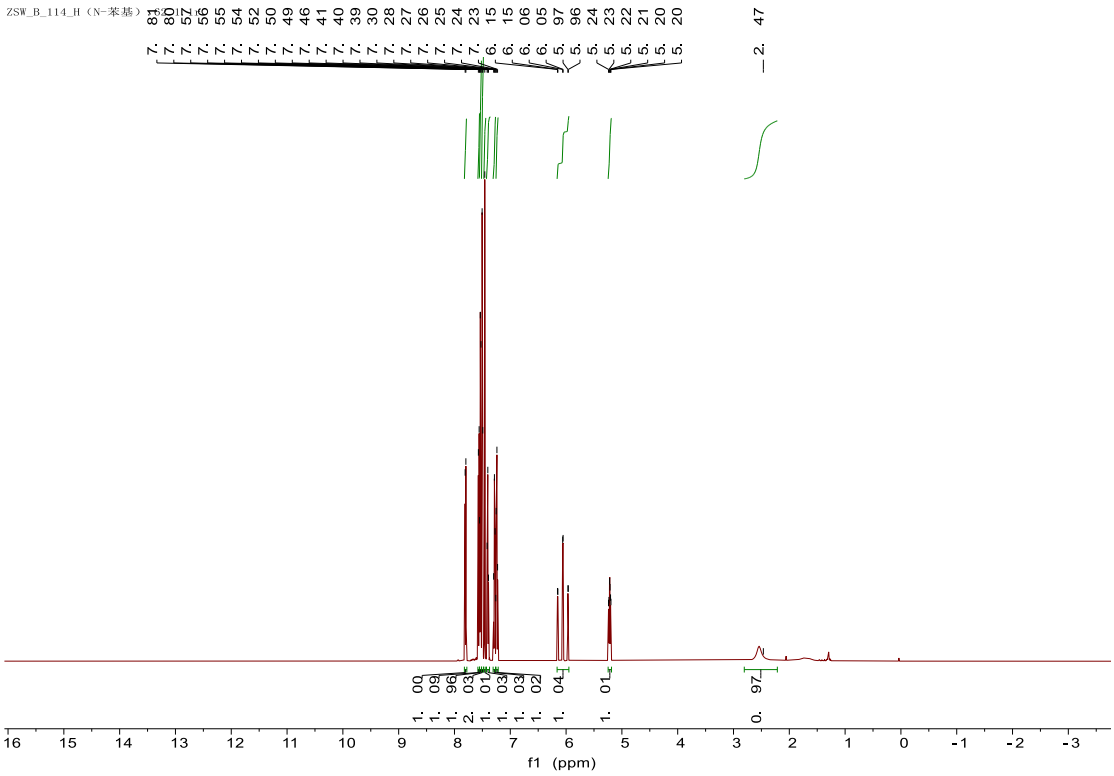
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3b**



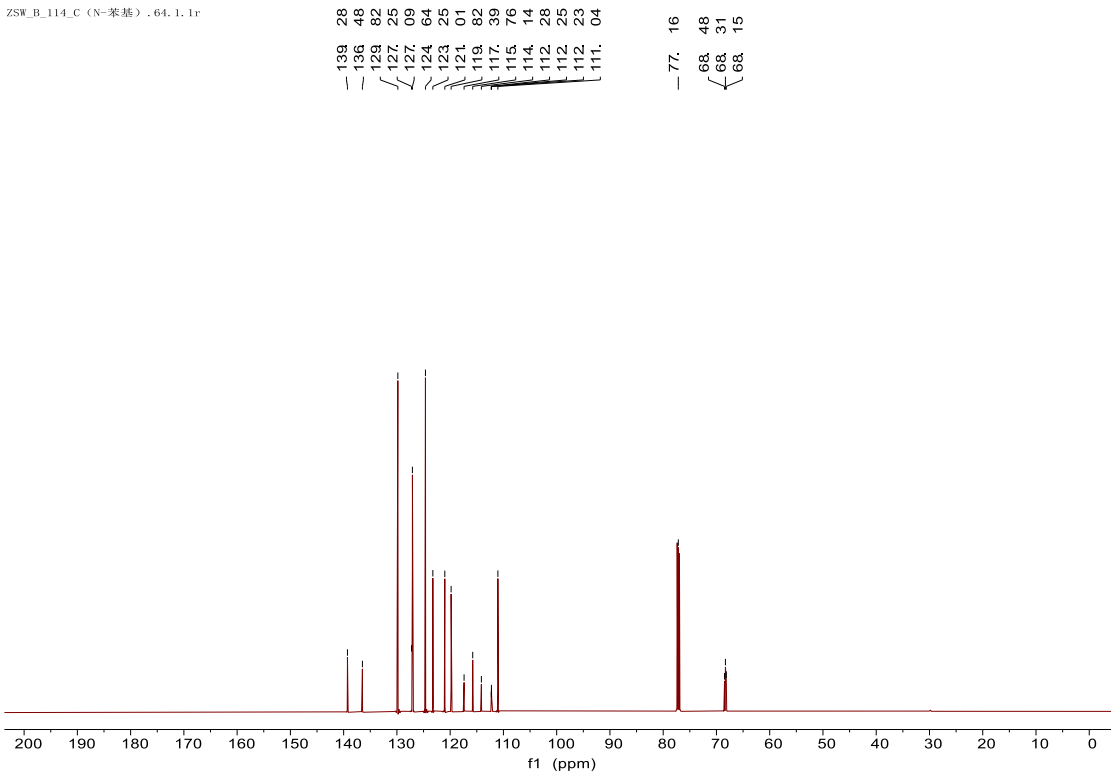
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3b**



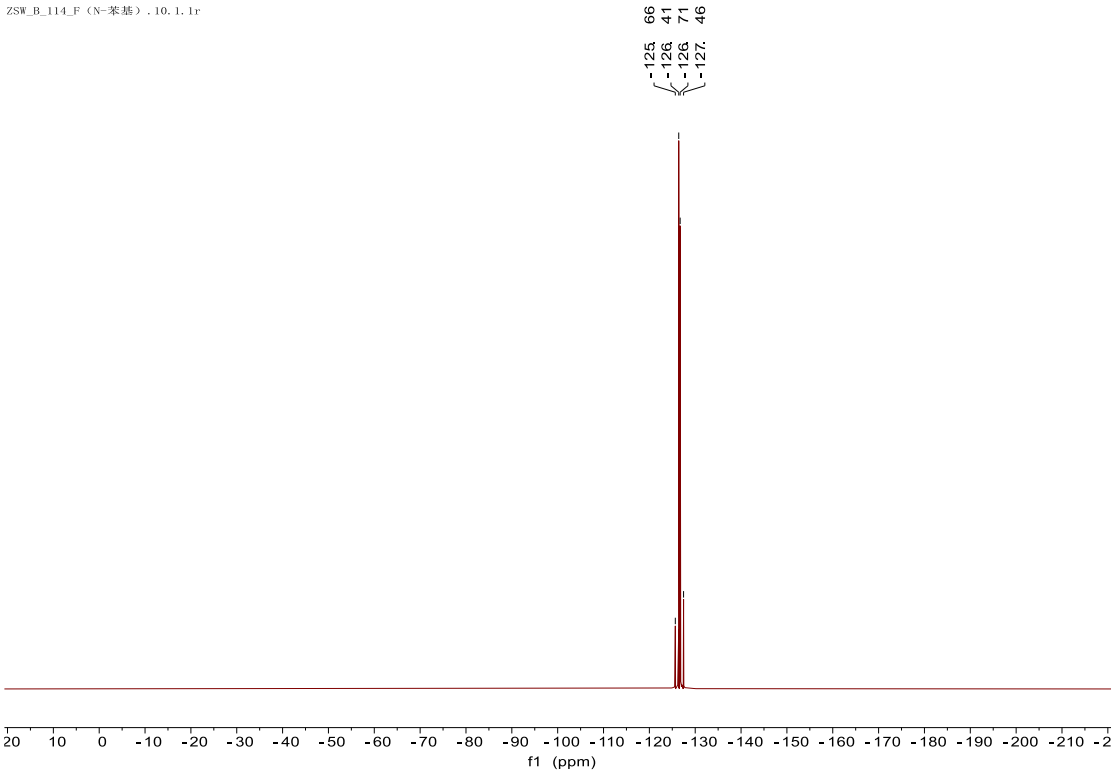
^{1}H NMR (600 MHz, Chloroform-*d*) spectra of **3c**



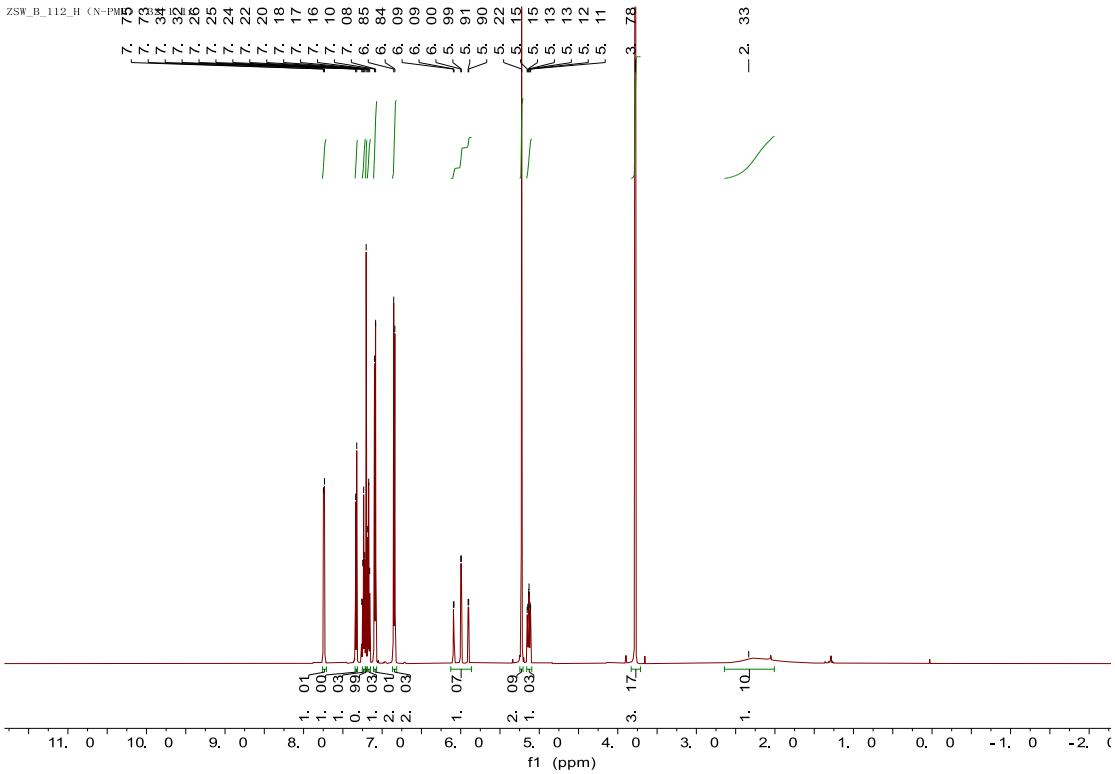
^{13}C NMR (151 MHz, Chloroform-*d*) spectra of **3c**



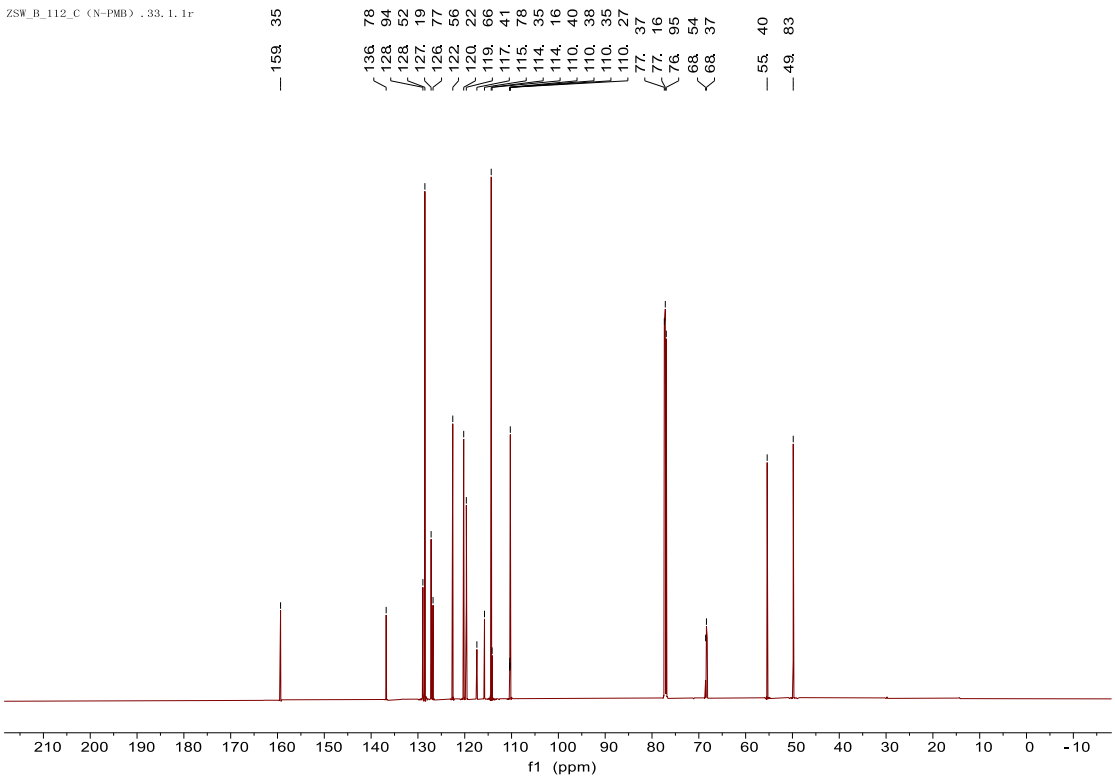
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3c**



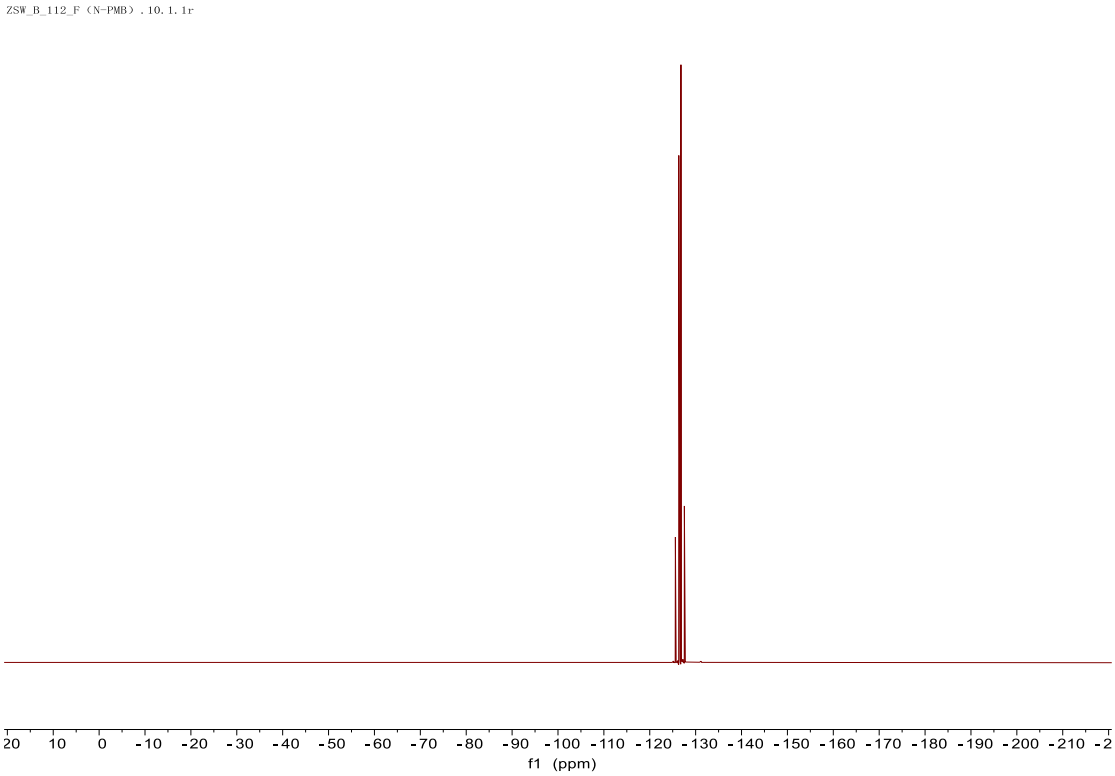
^{1}H NMR (600 MHz, Chloroform-*d*) spectra of **3d**



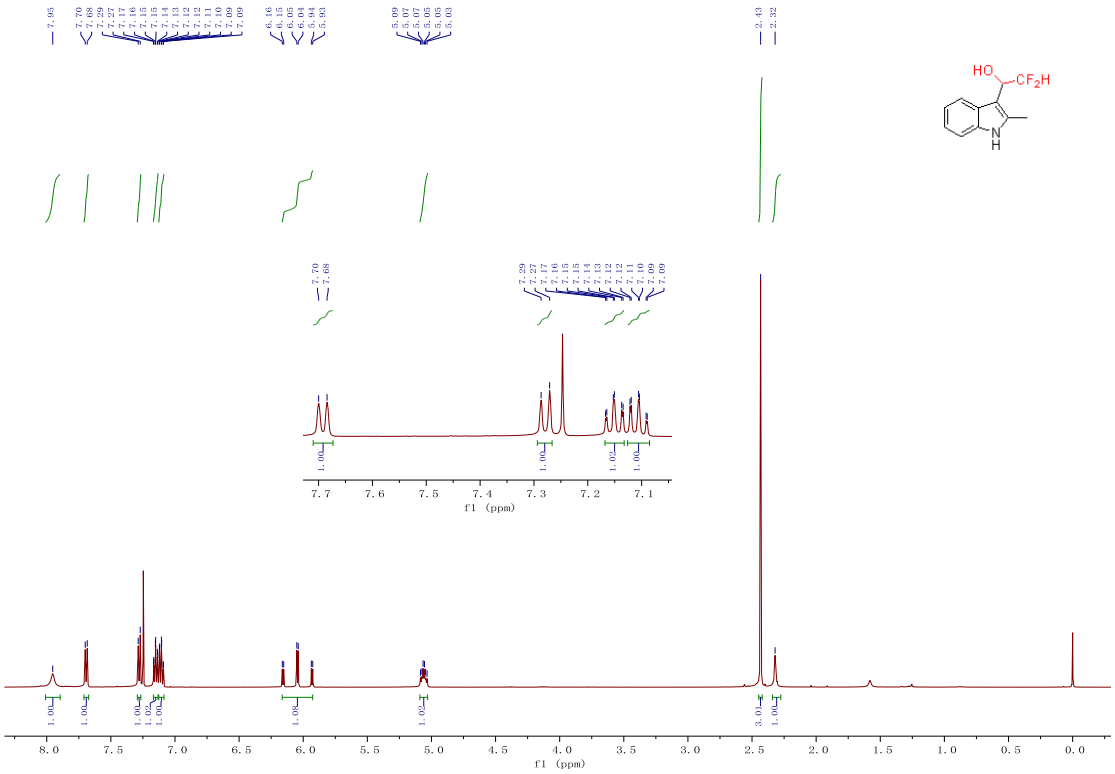
^{13}C NMR (151 MHz, Chloroform-*d*) spectra of **3d**



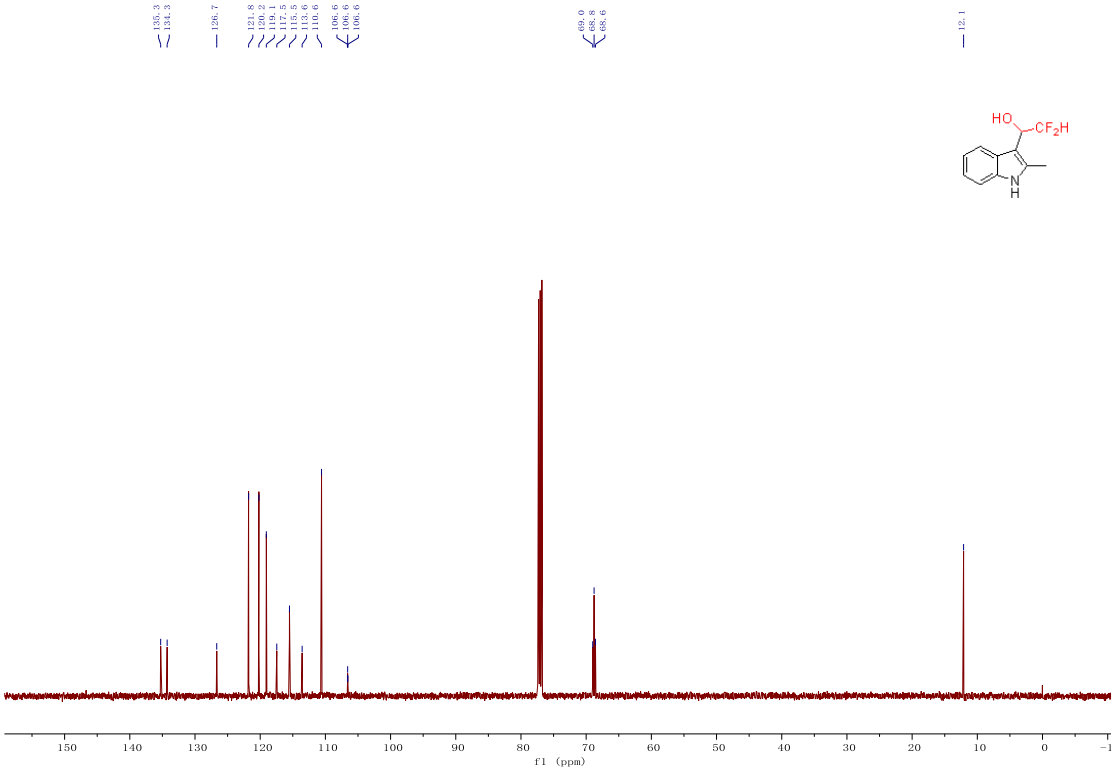
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3d**



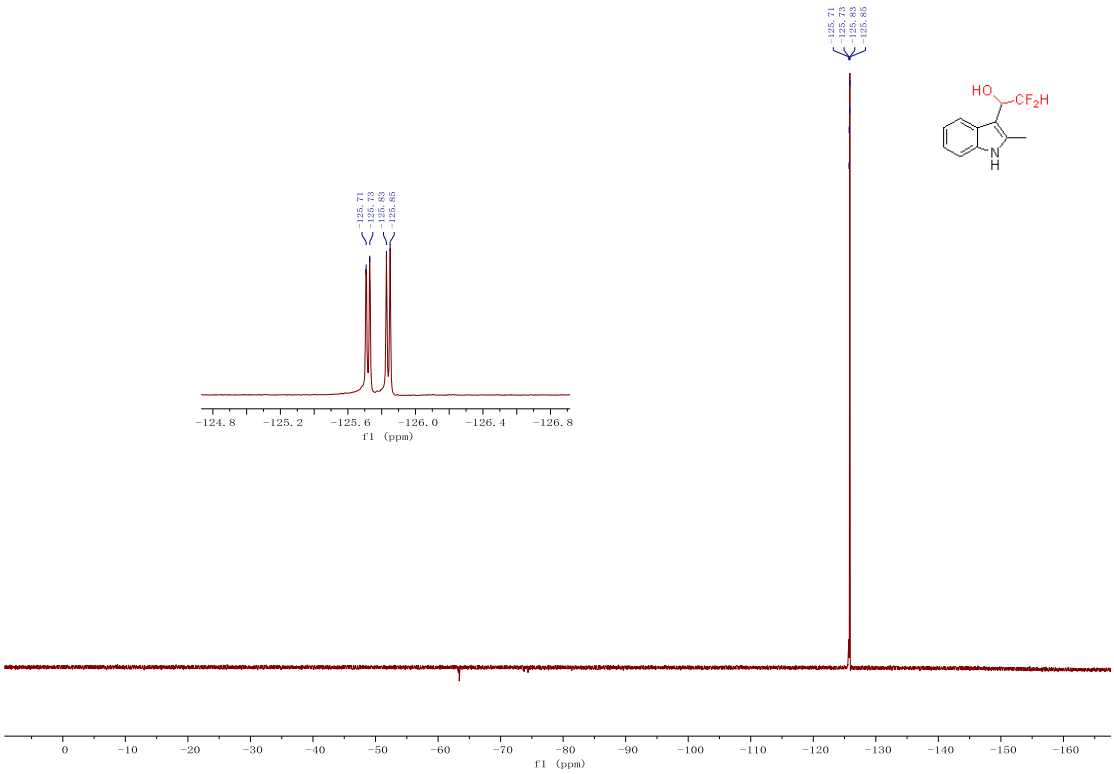
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3e**



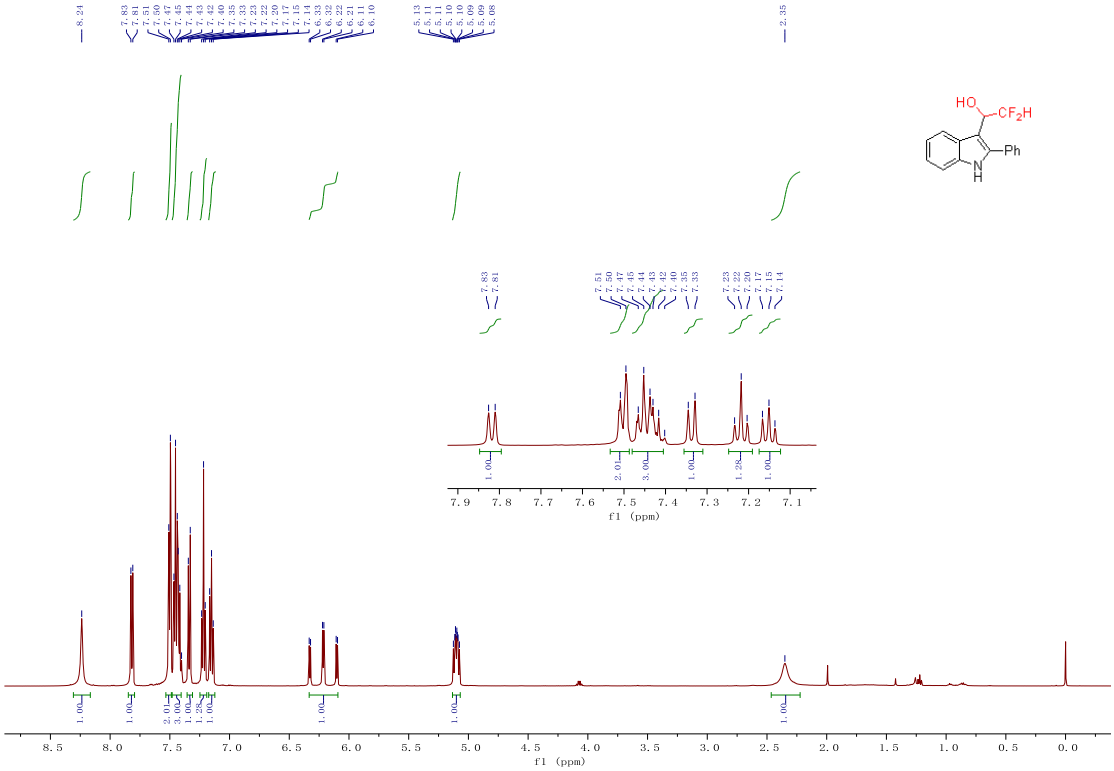
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3e**



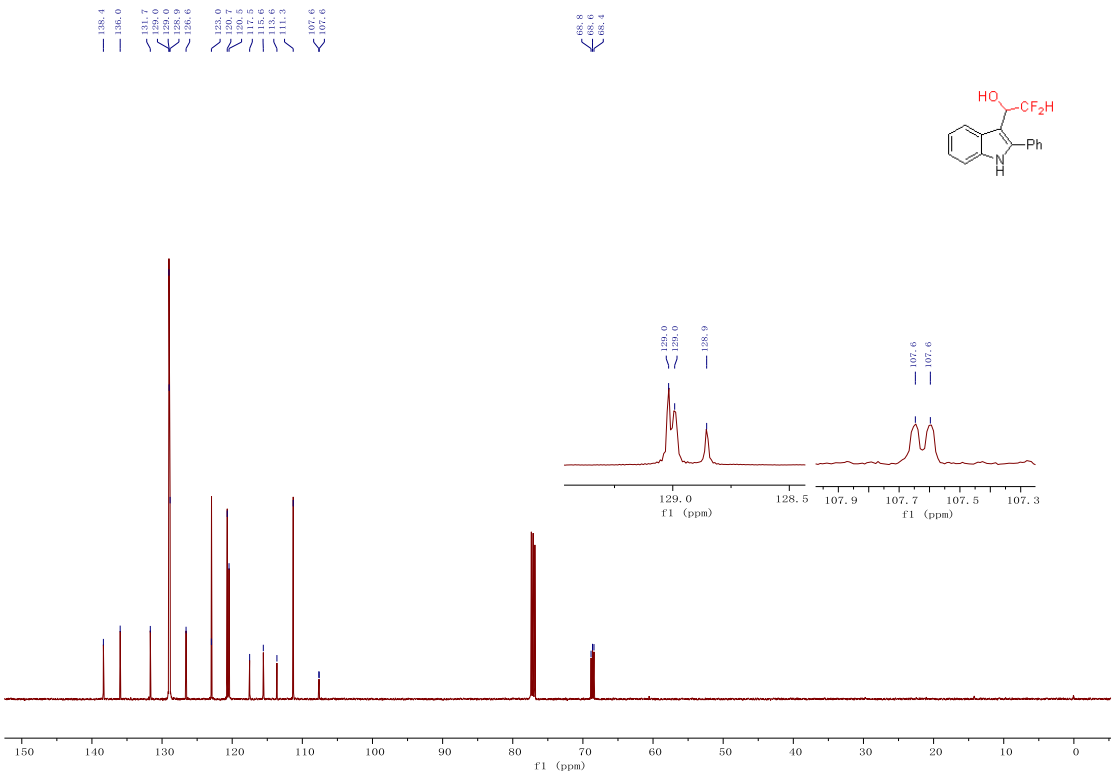
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3e**



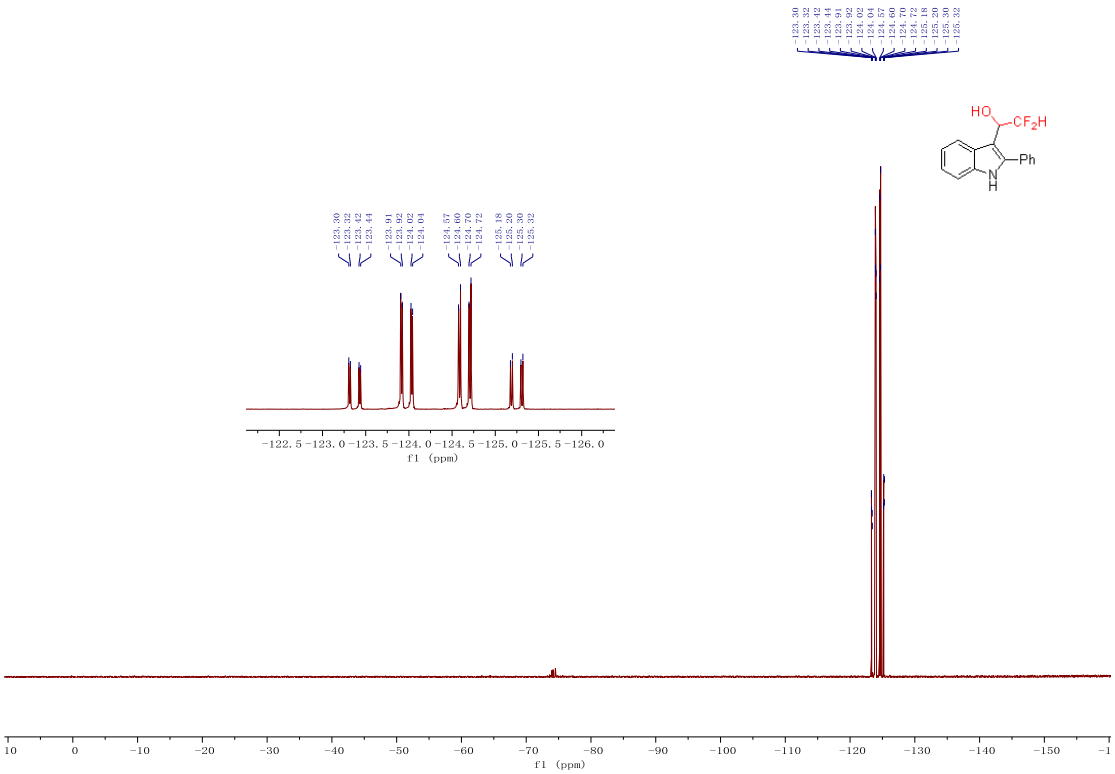
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3f**



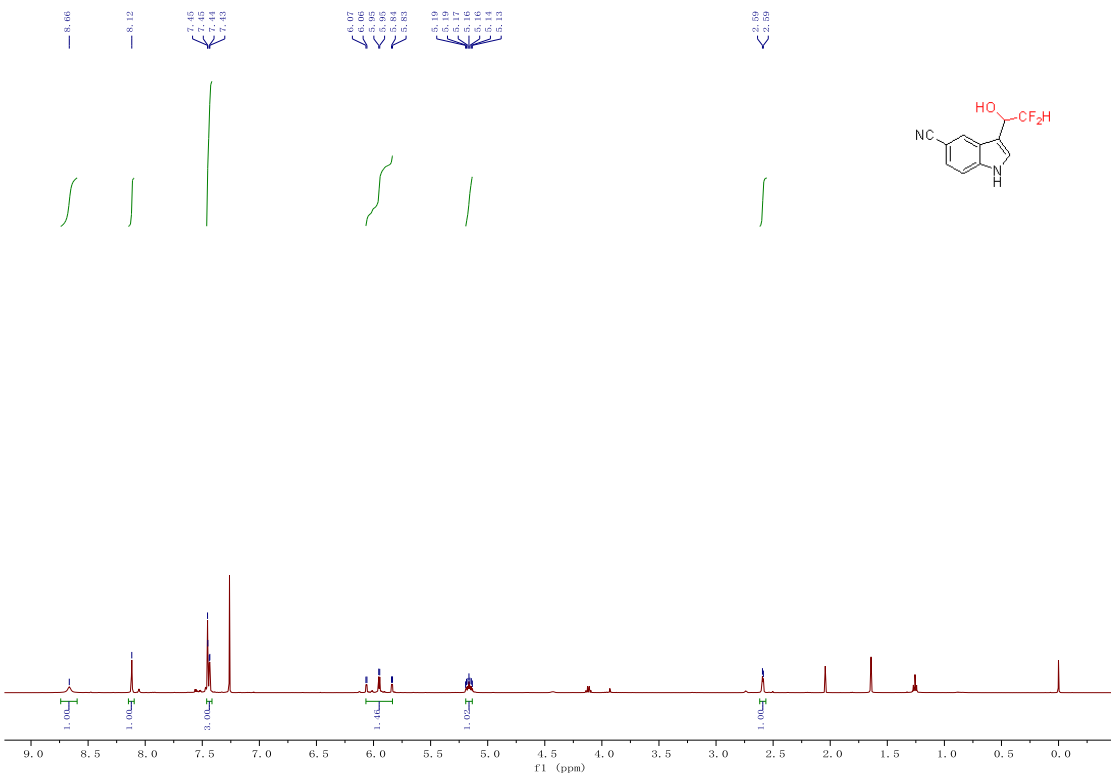
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3f**



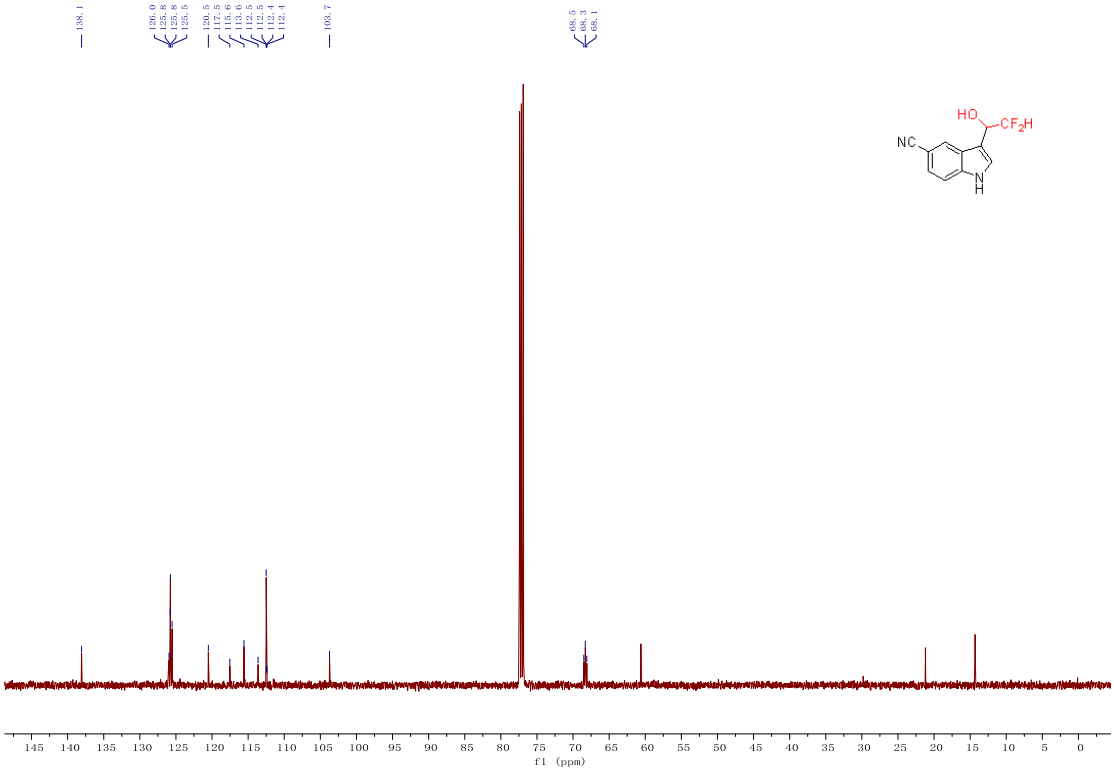
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3f**



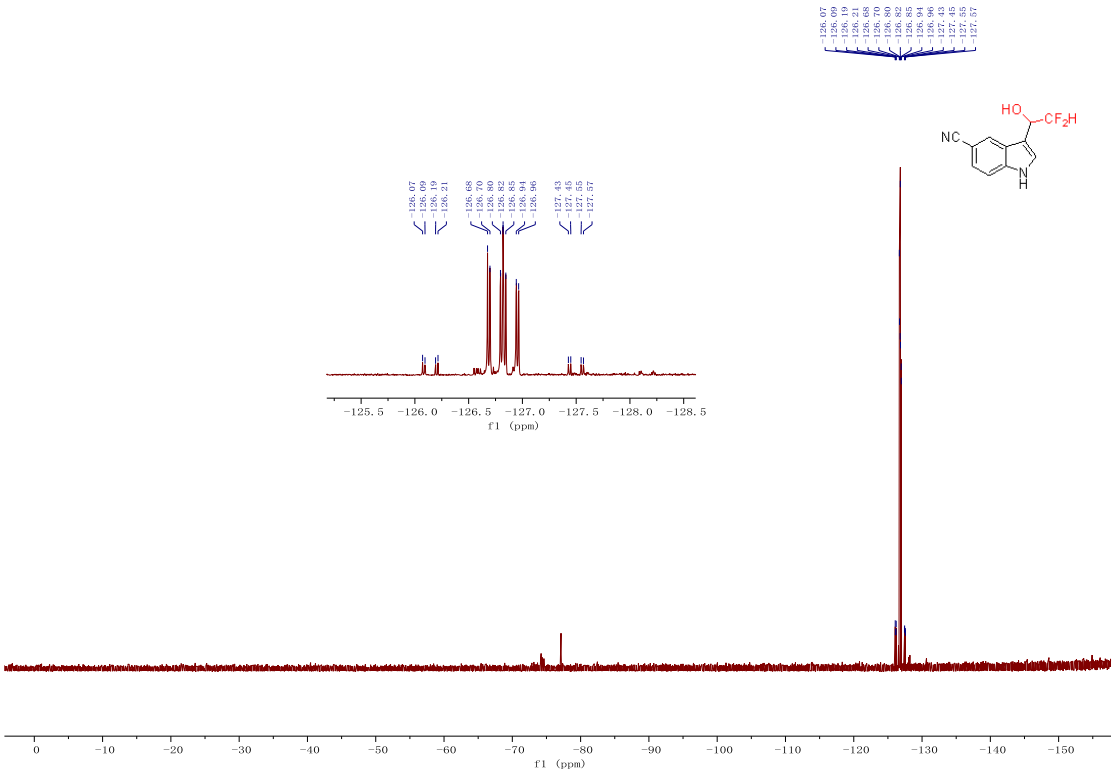
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3g**



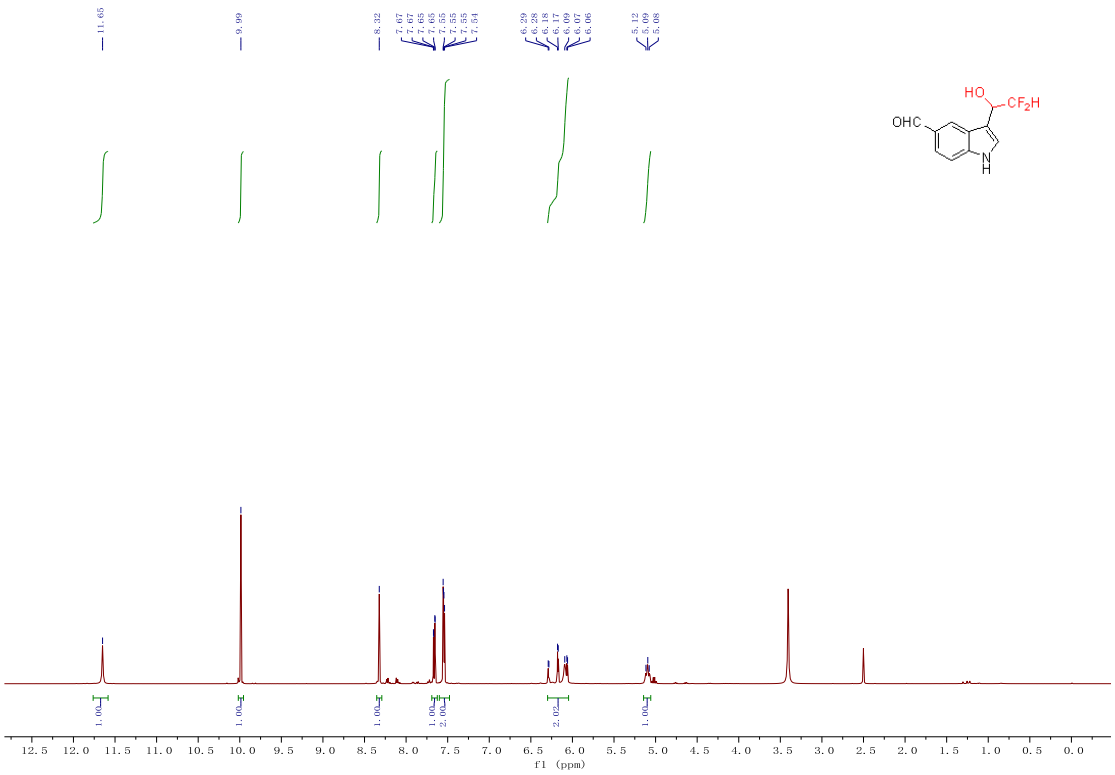
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3g**



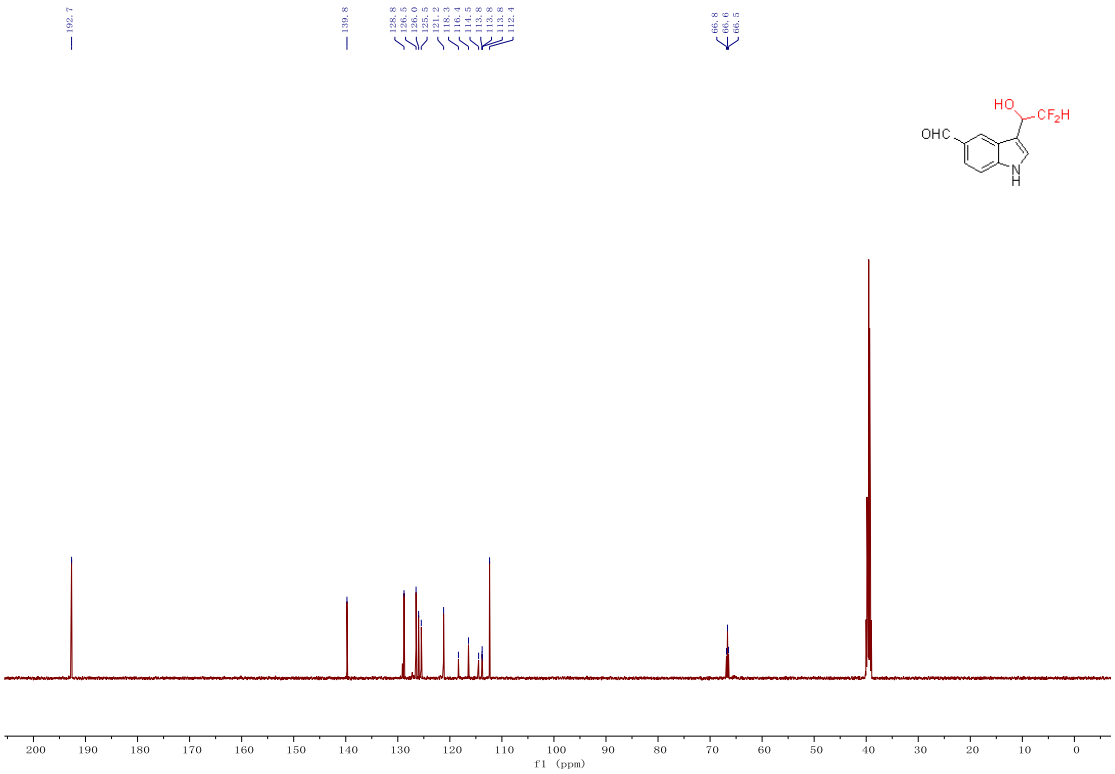
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3g**



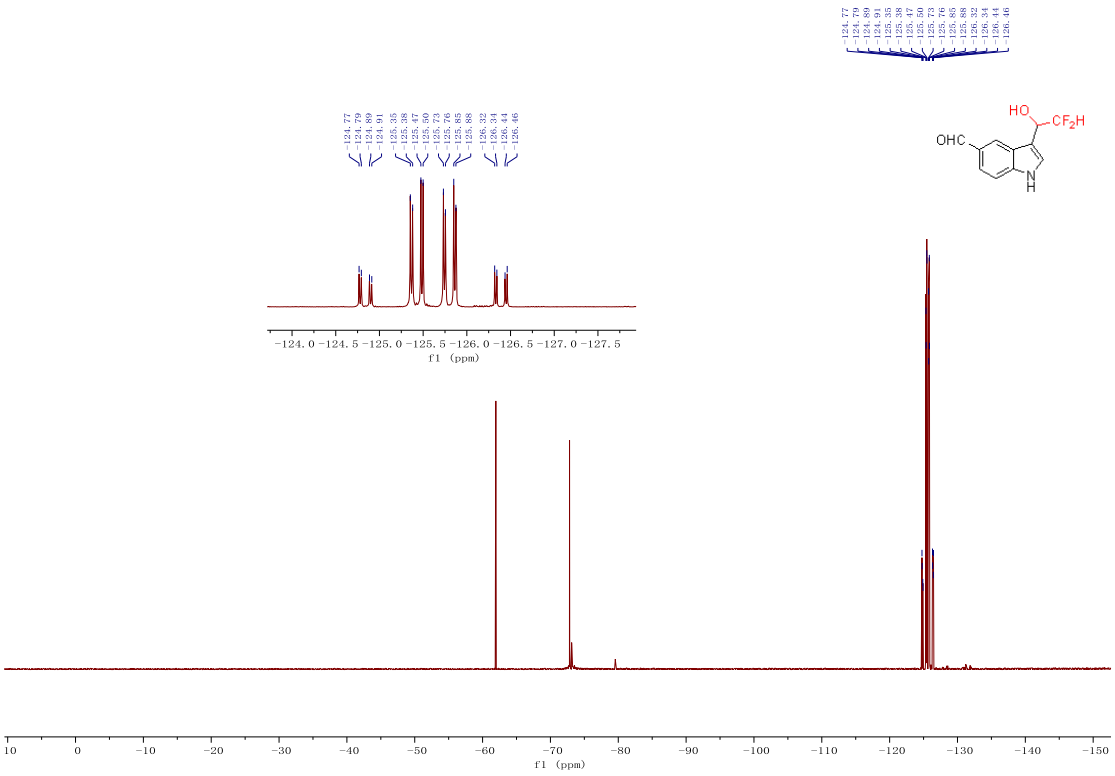
^{1}H NMR (500 MHz, DMSO-d_6) spectra of **3h**



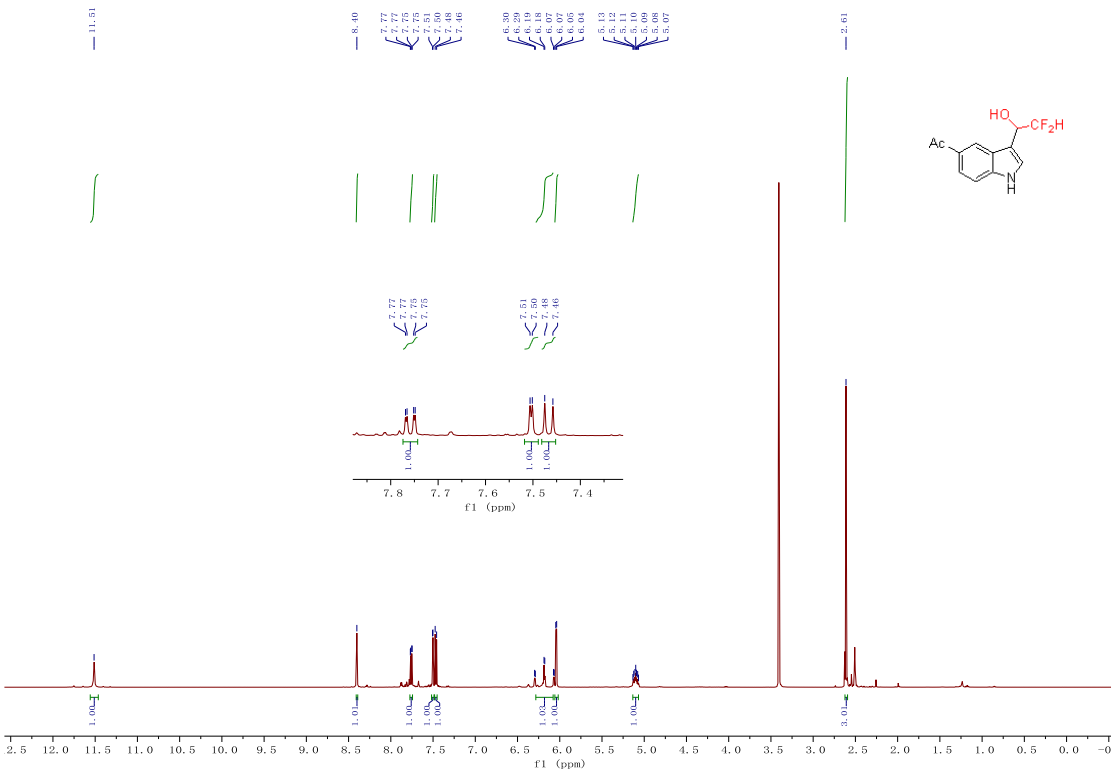
^{13}C NMR (125 MHz, DMSO-d_6) spectra of **3h**



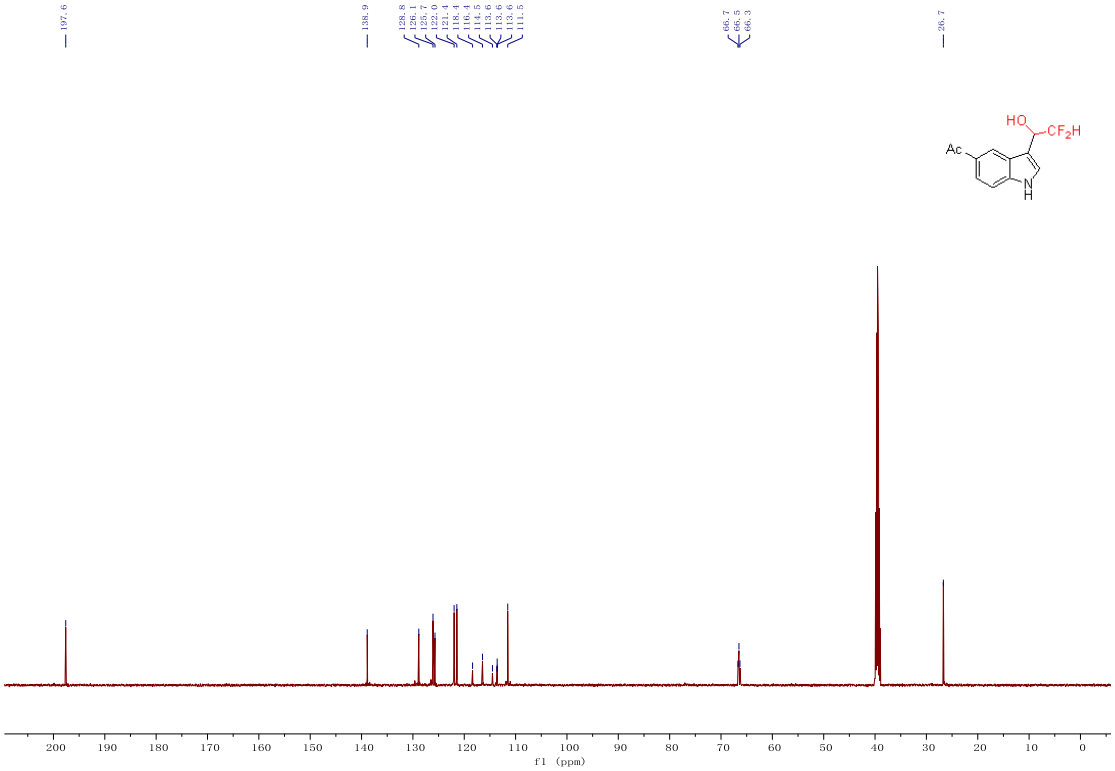
^{19}F NMR (470 MHz, DMSO-d_6) spectra of **3h**



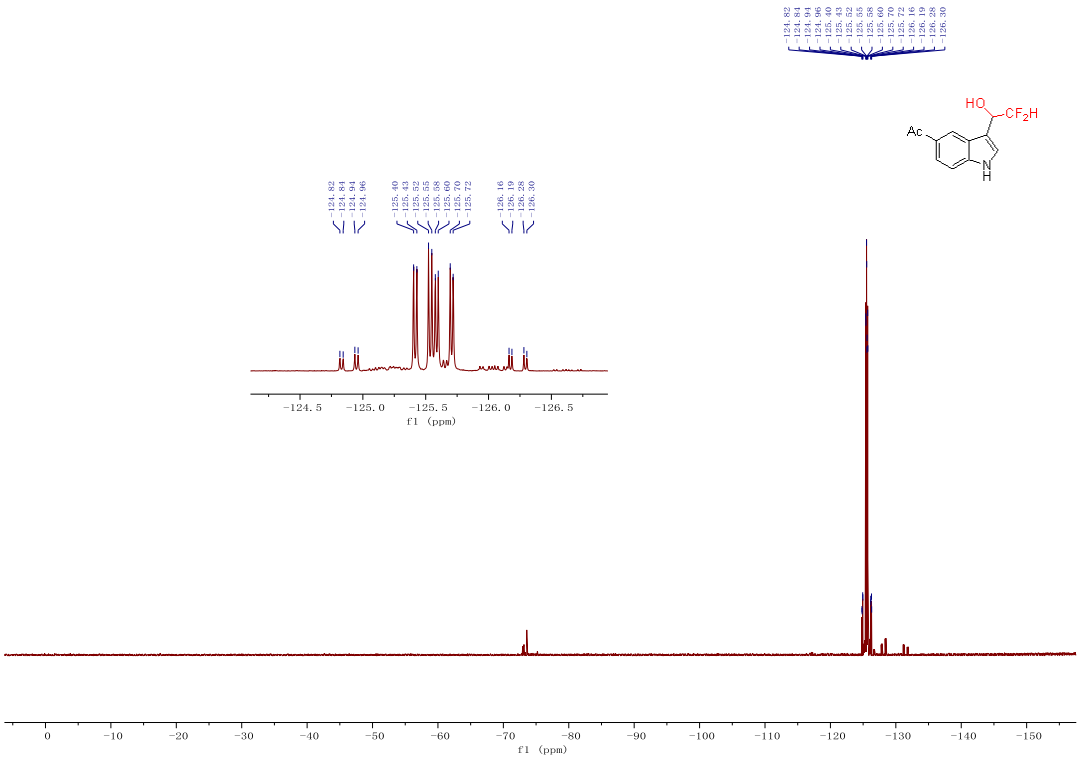
^{1}H NMR (500 MHz, DMSO-d_6) spectra of **3i**



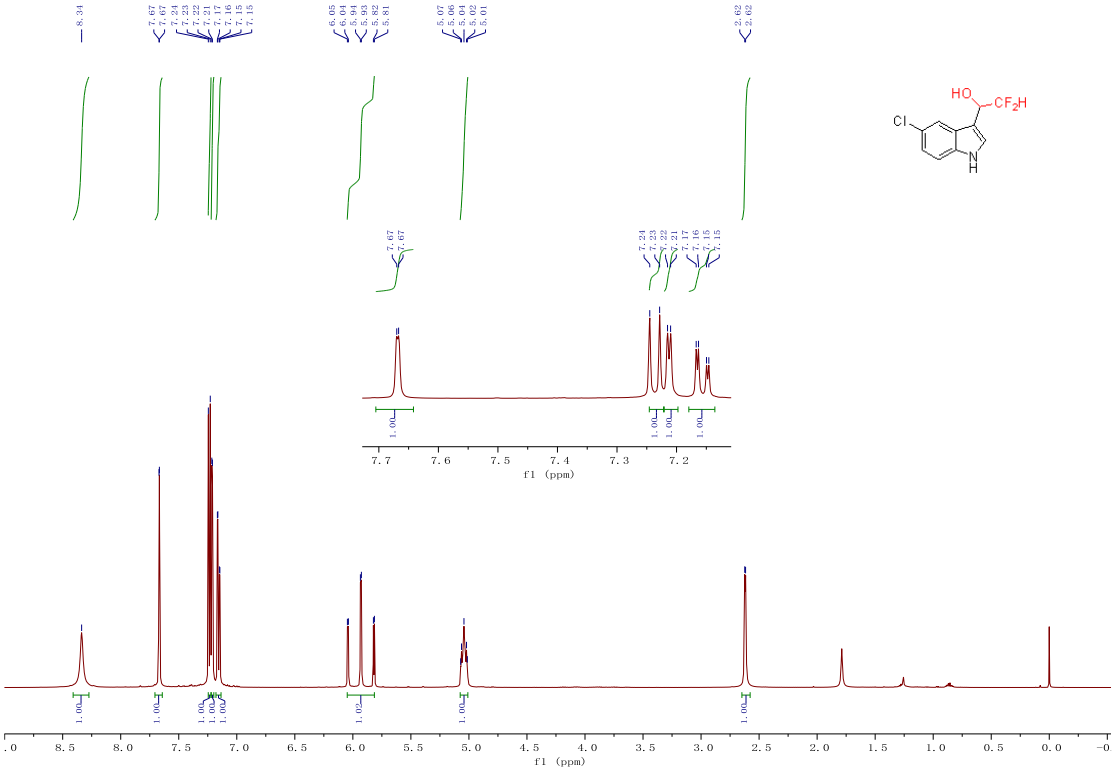
^{13}C NMR (125 MHz, DMSO-d_6) spectra of **3i**



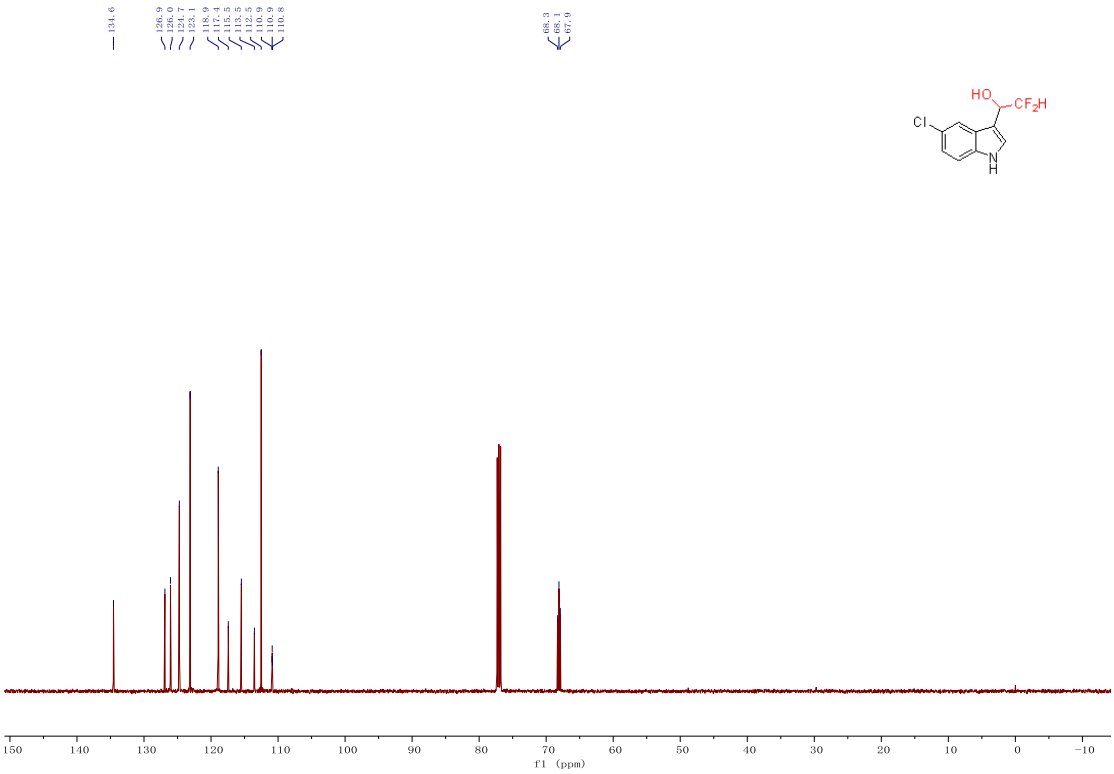
^{19}F NMR (470 MHz, DMSO-d_6) spectra of **3i**



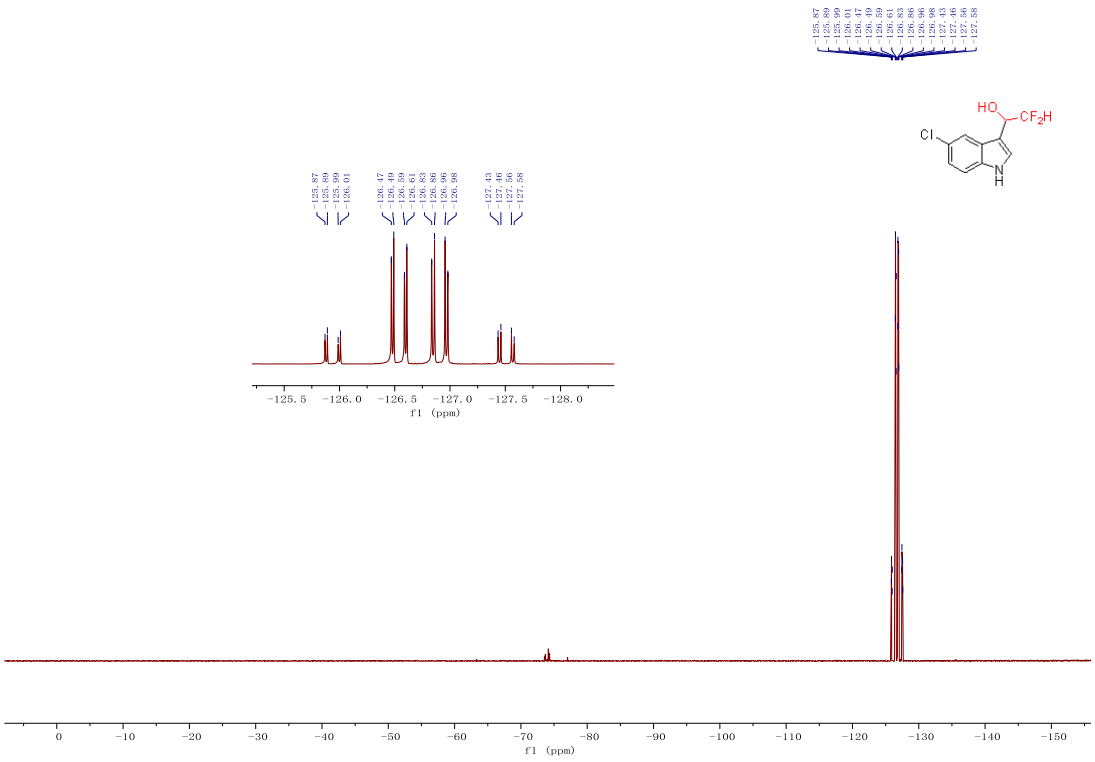
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3j**



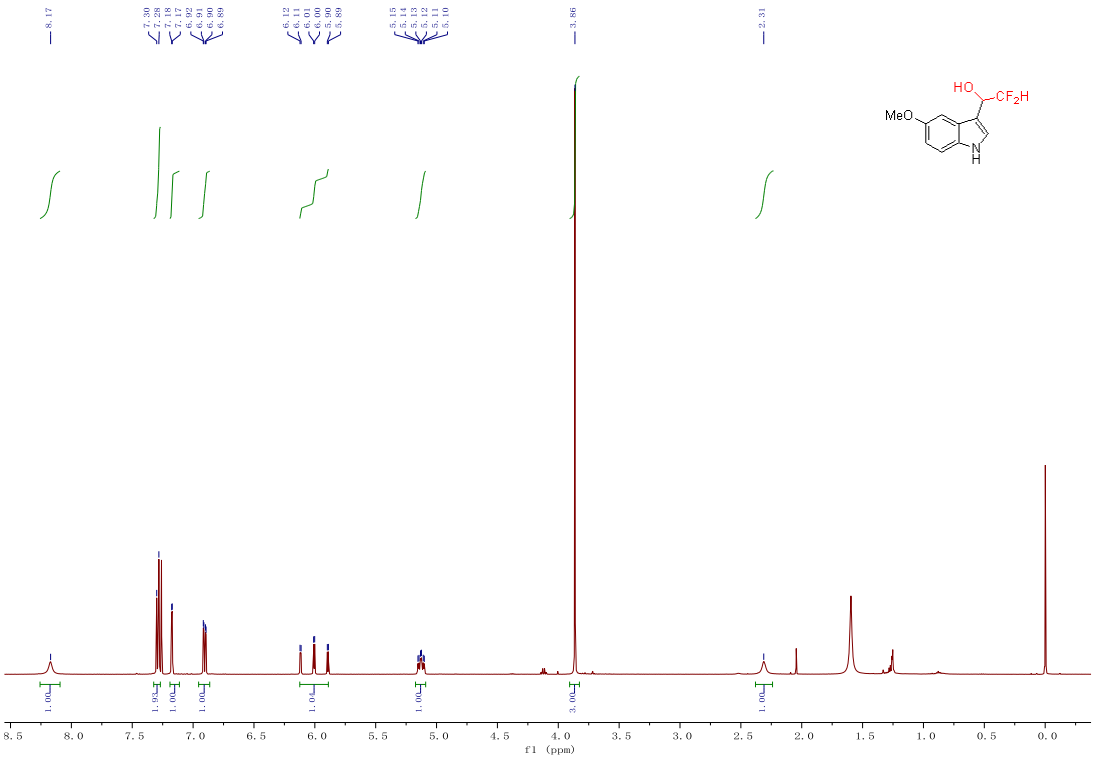
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3j**



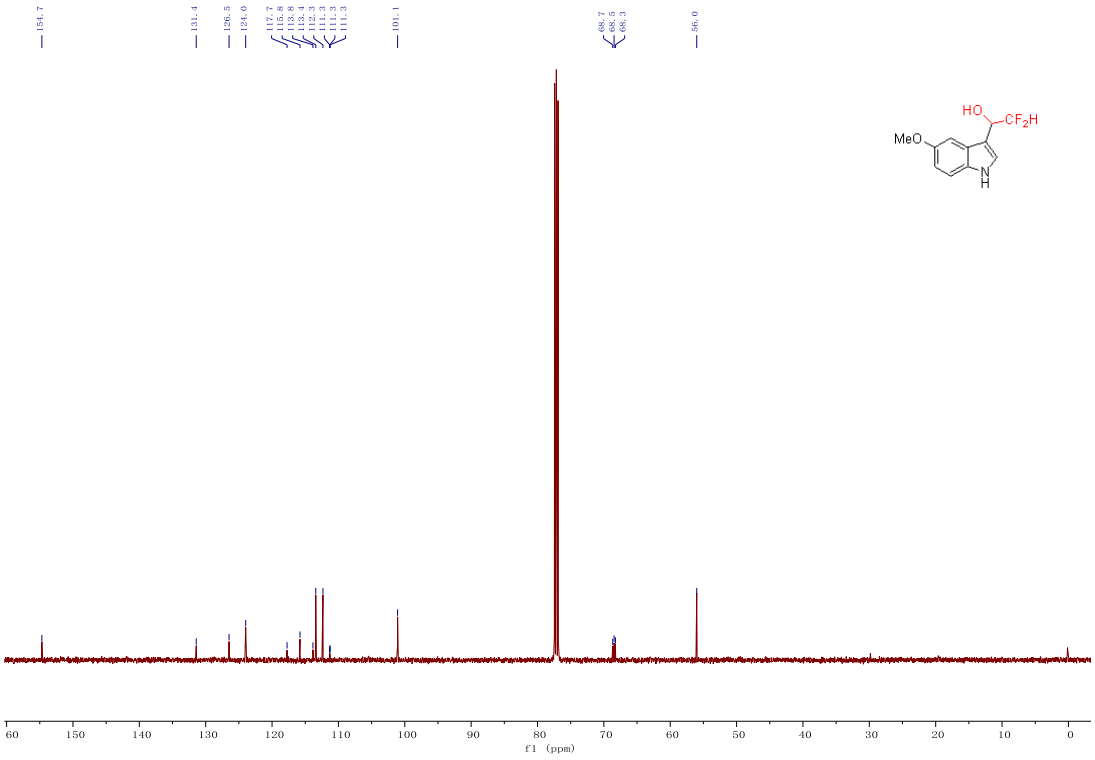
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3j**



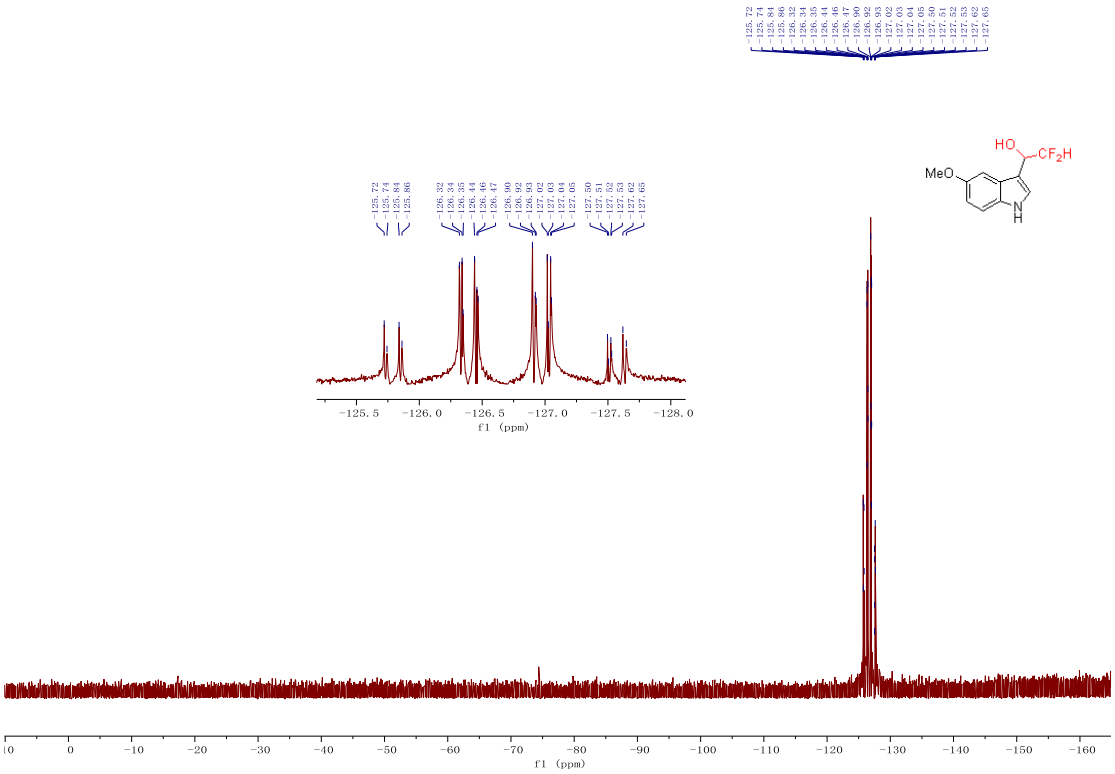
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3k**



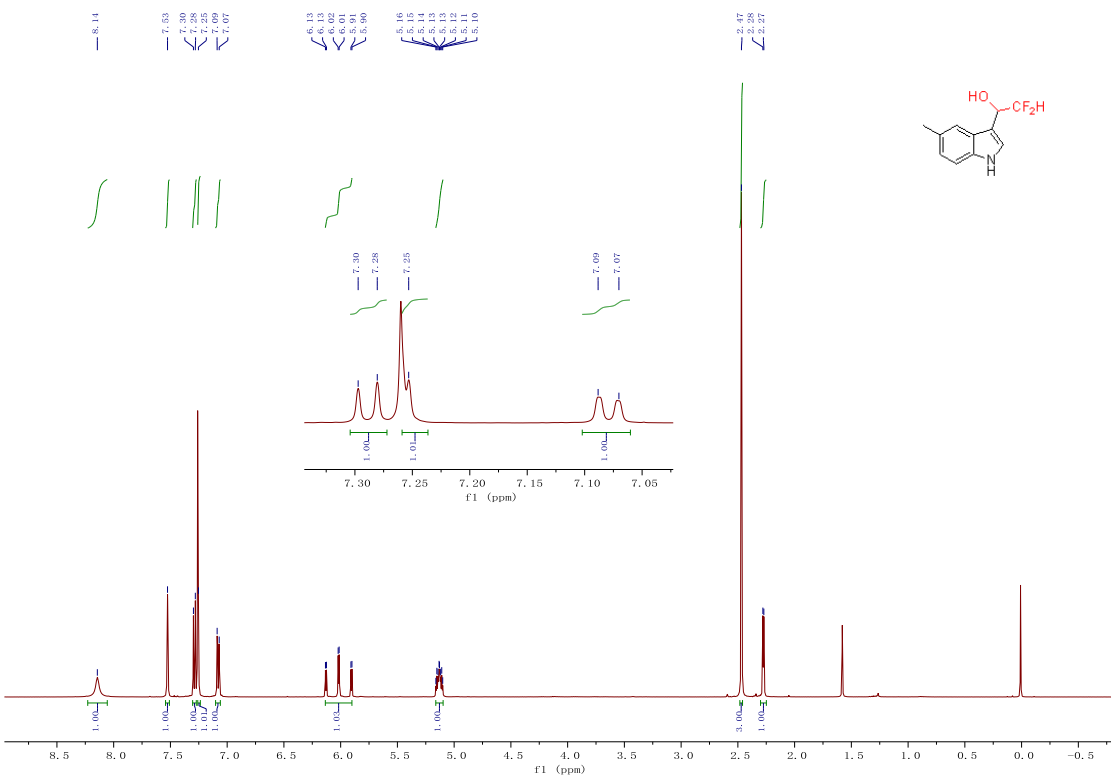
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3k**



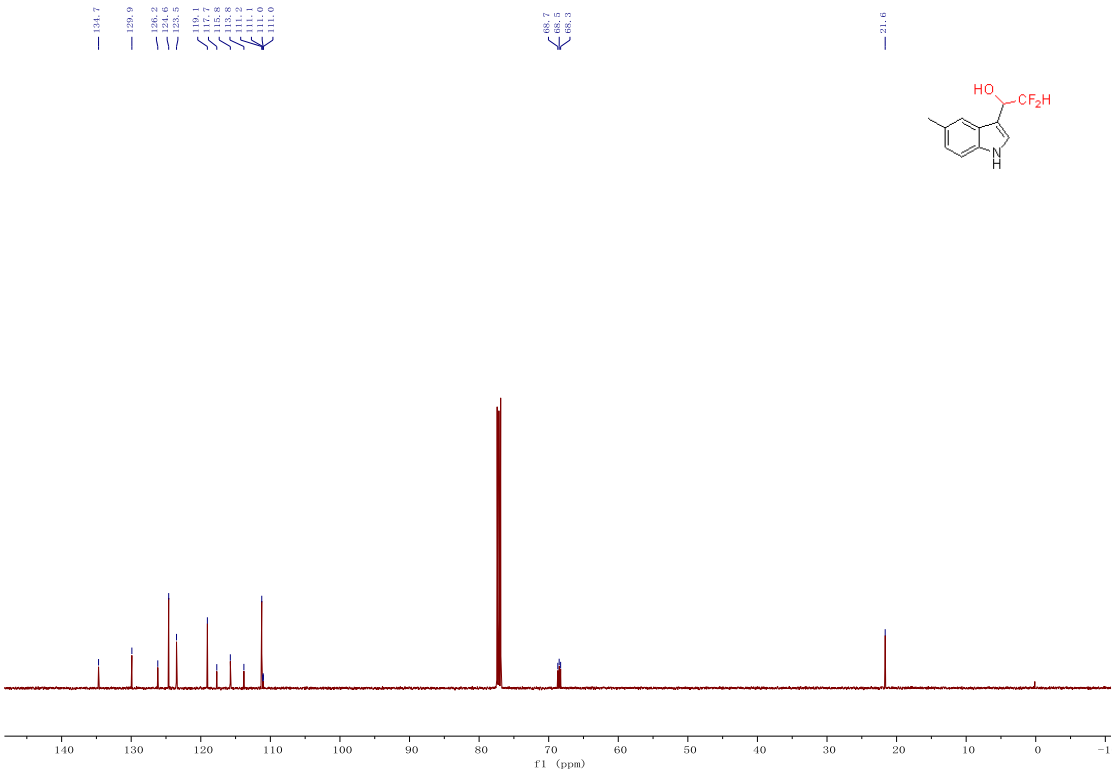
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3k**



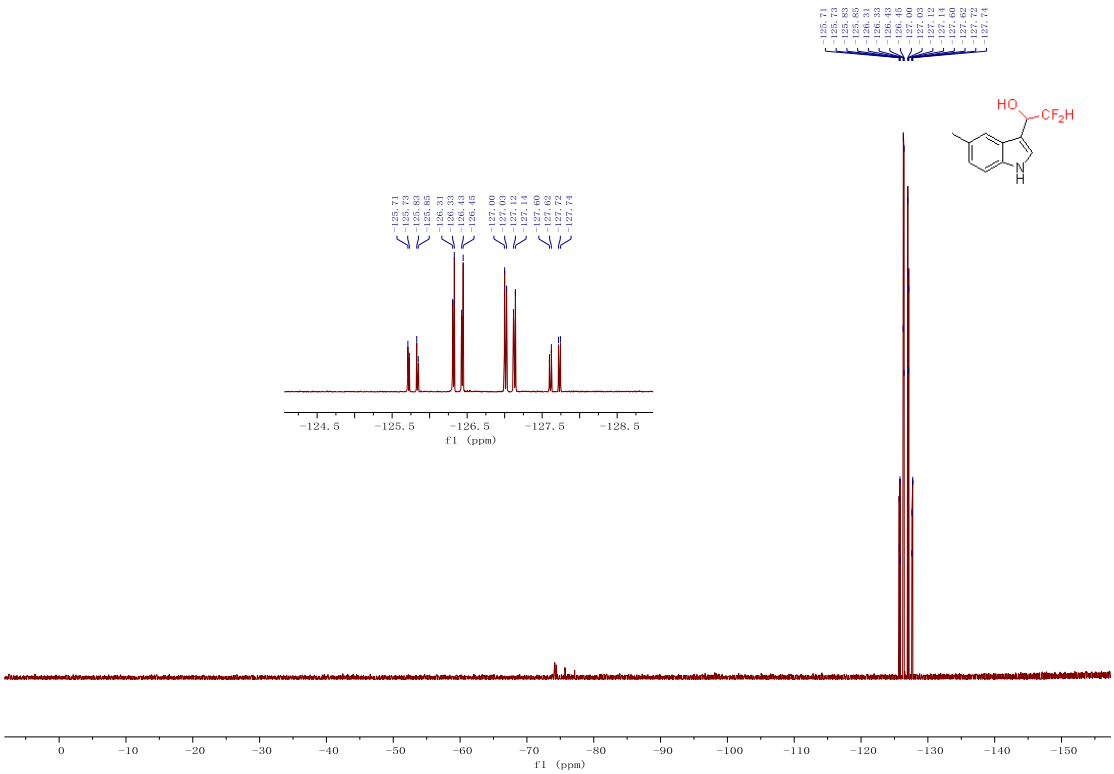
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3l**



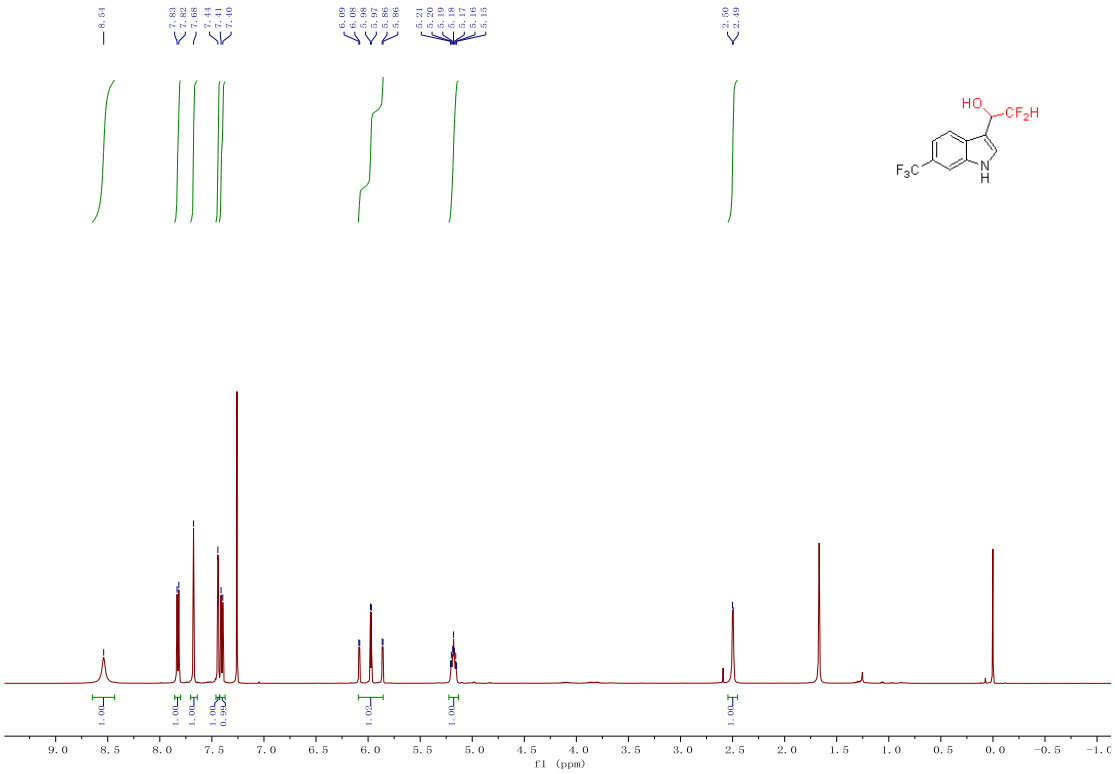
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3l**



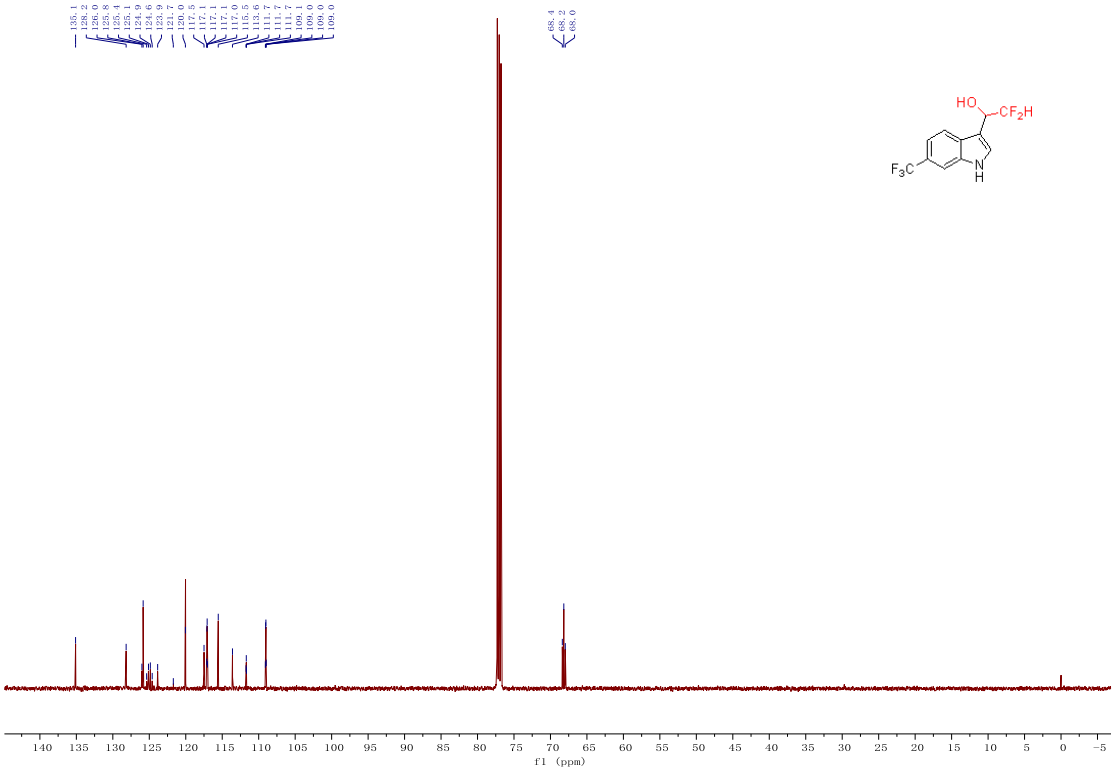
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3l**



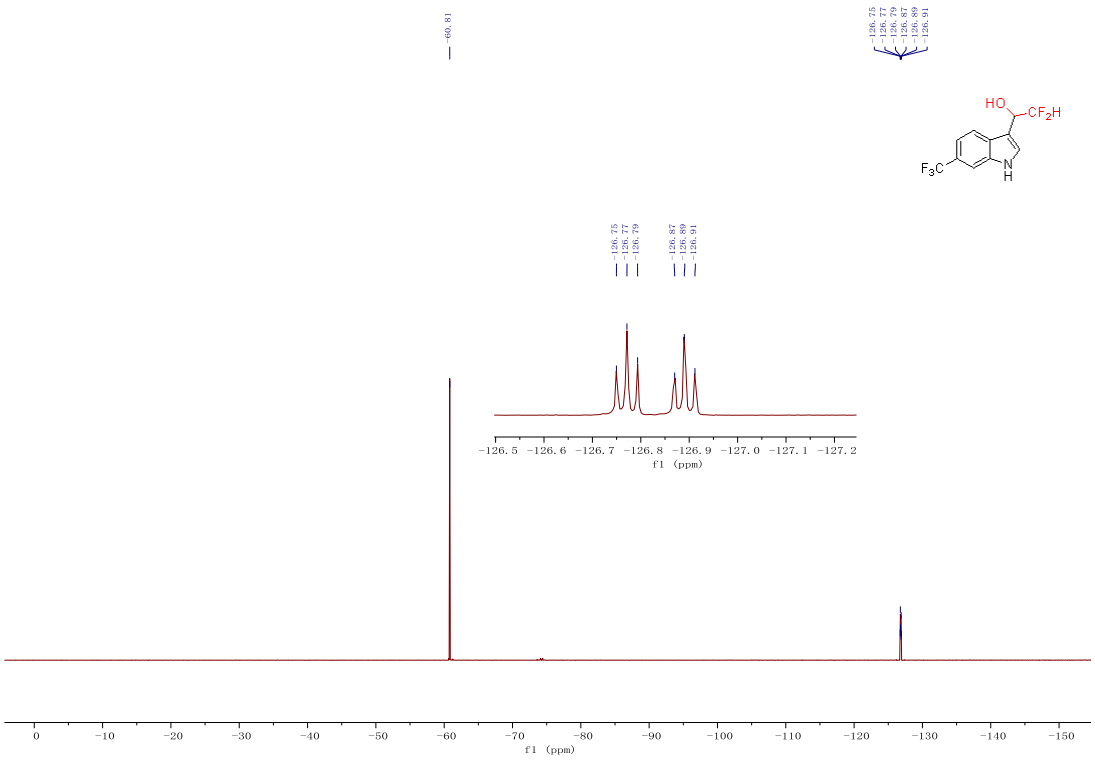
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3m**



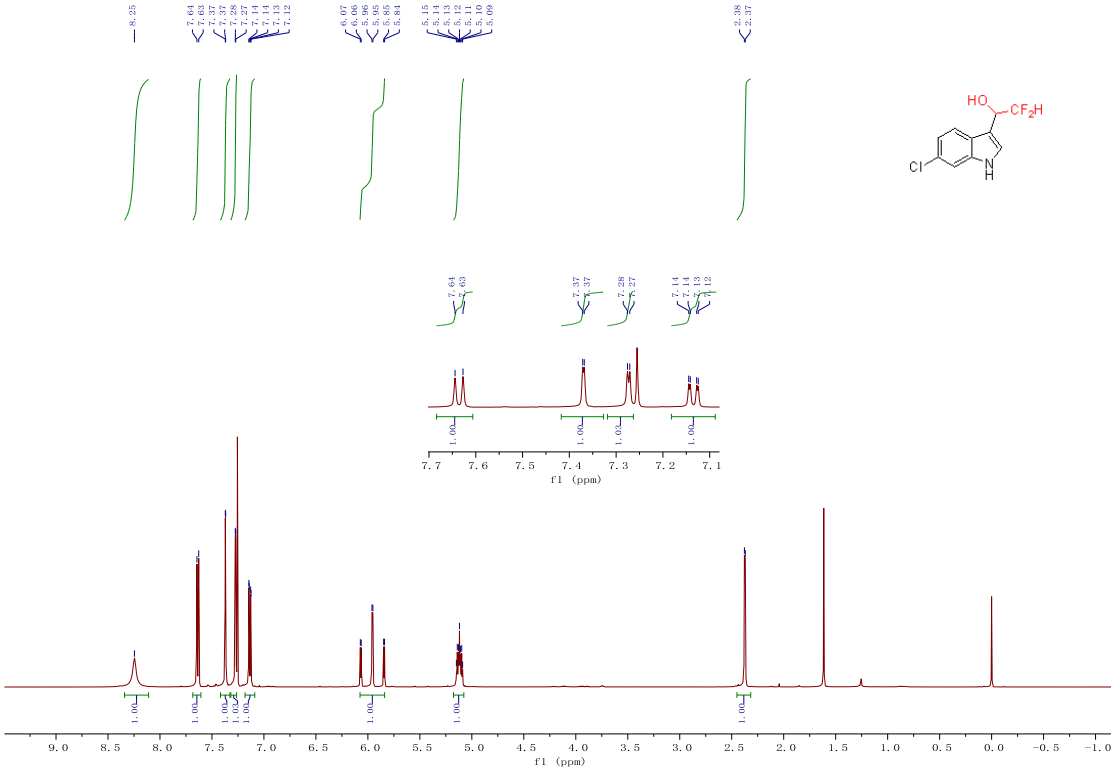
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3m**



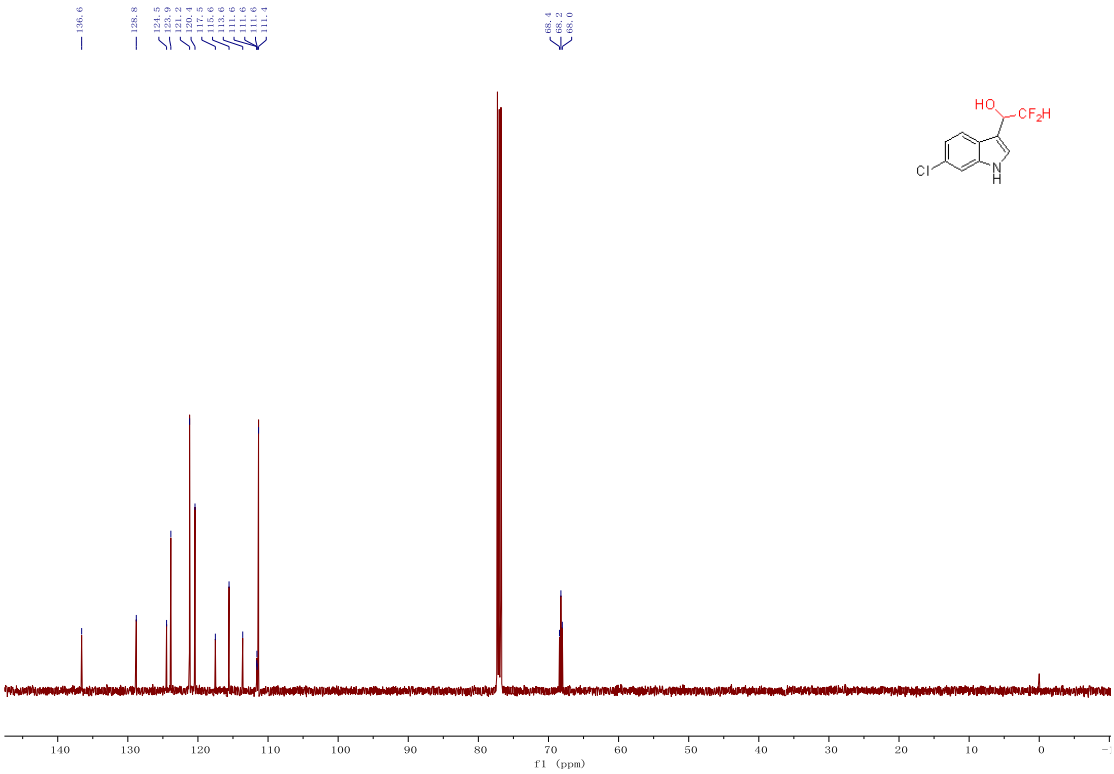
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3m**



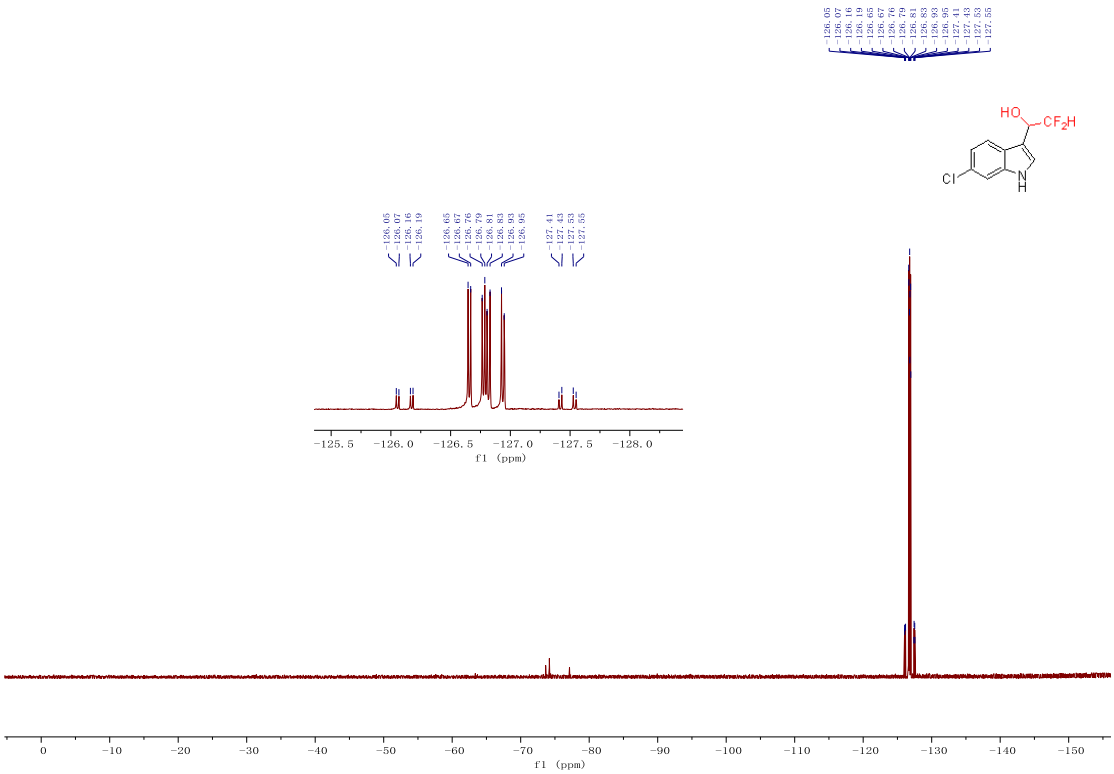
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3n**



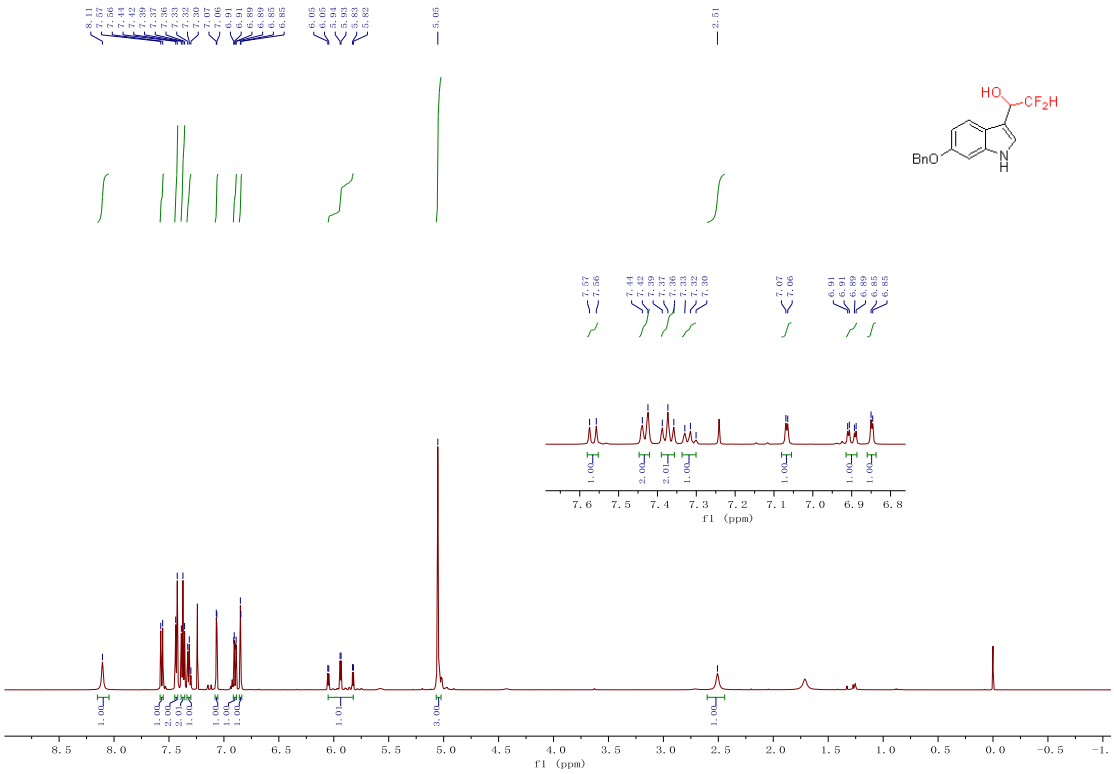
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3n**



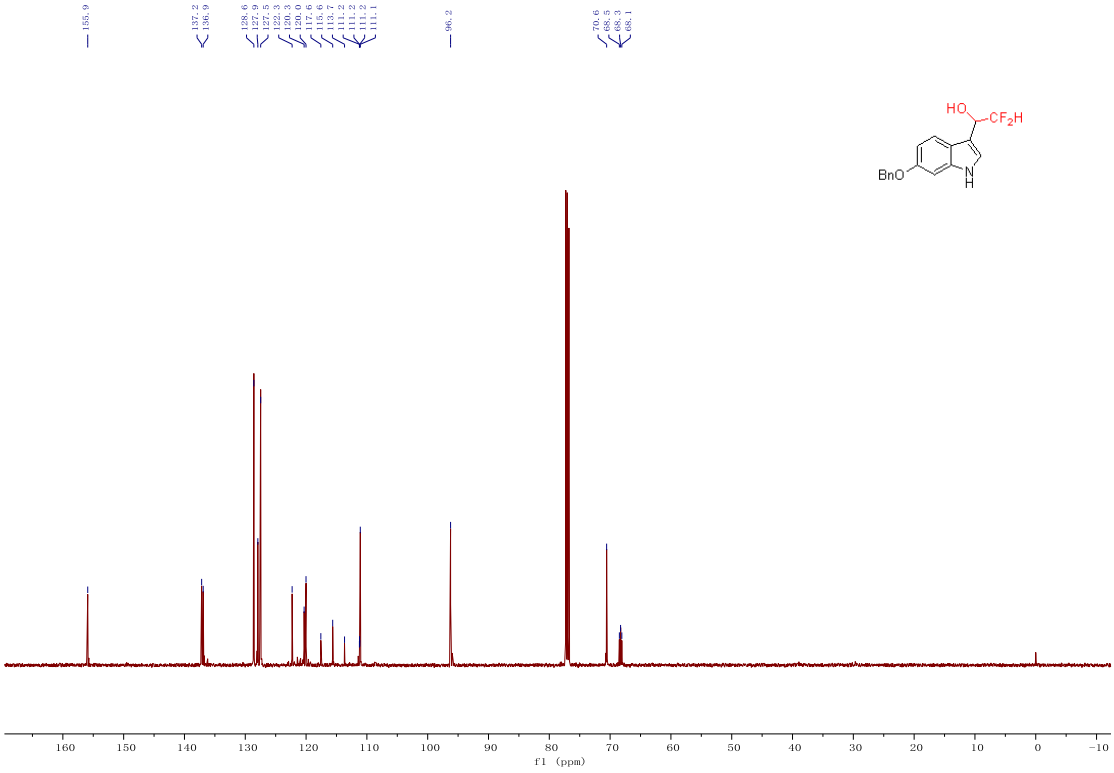
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3n**



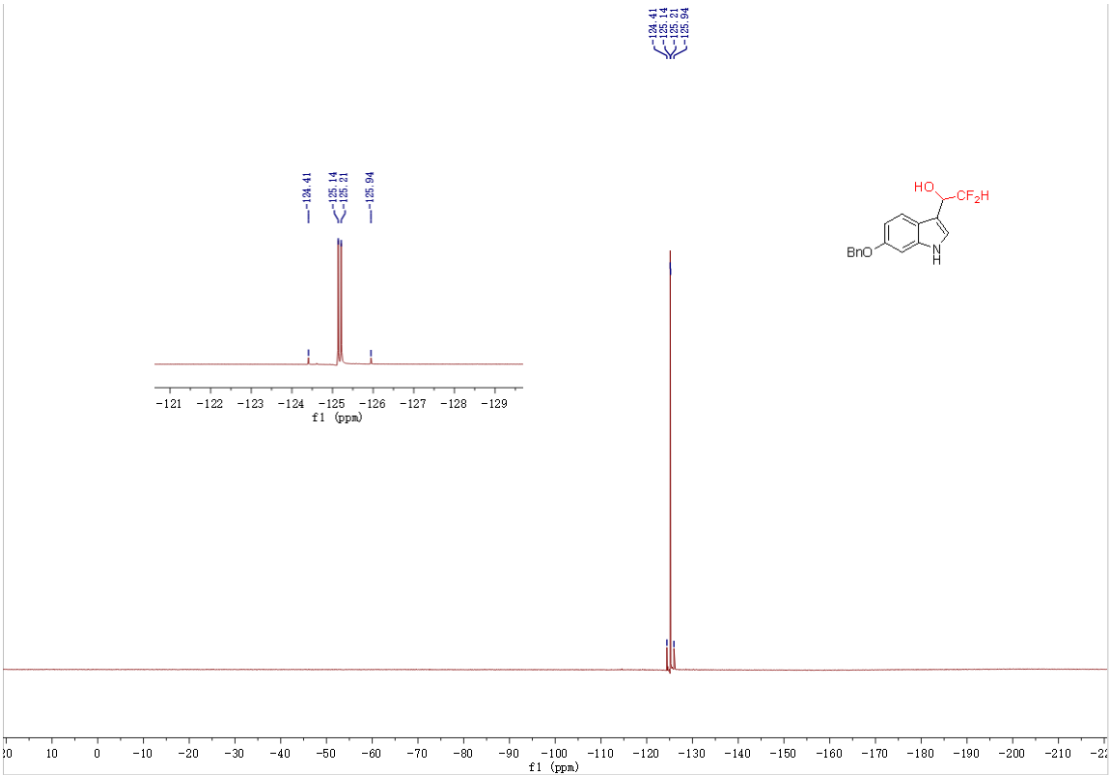
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3o**



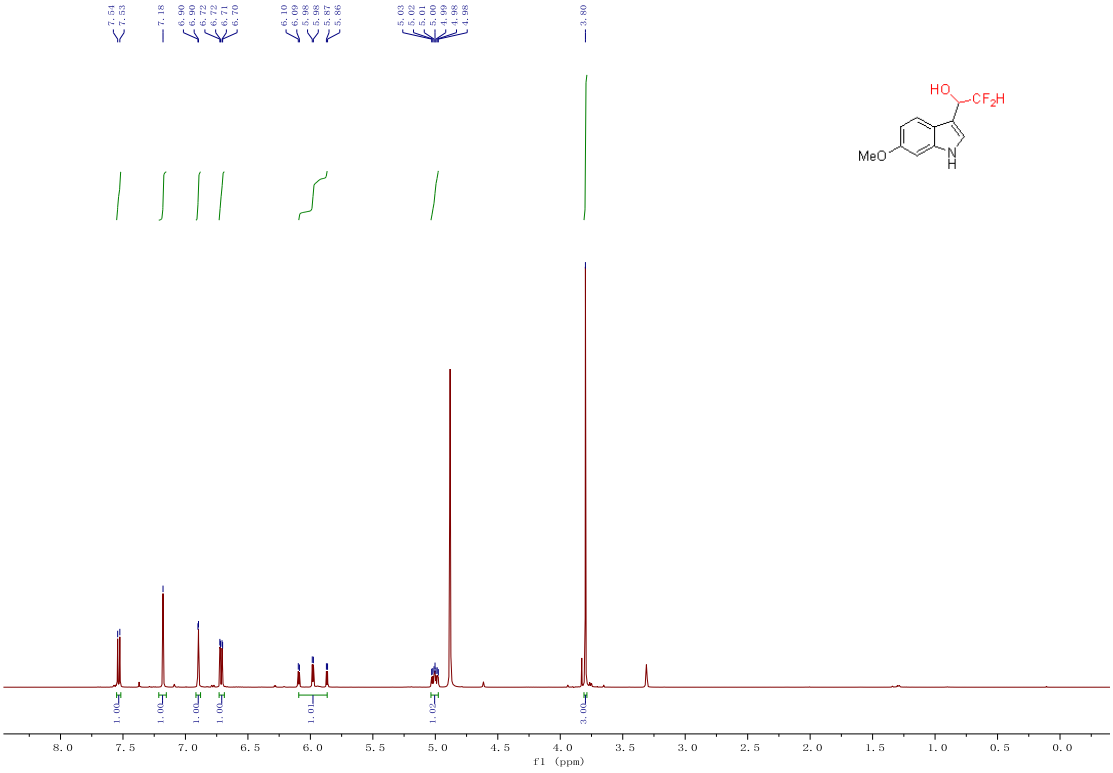
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3o**



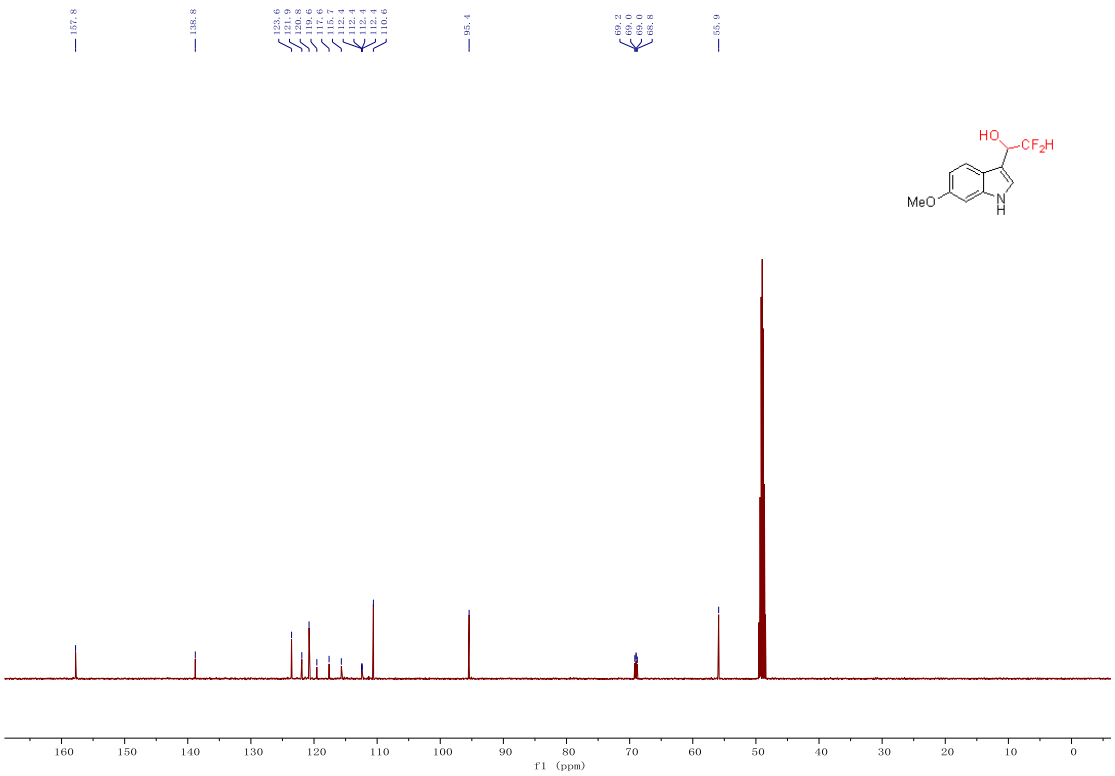
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3o**



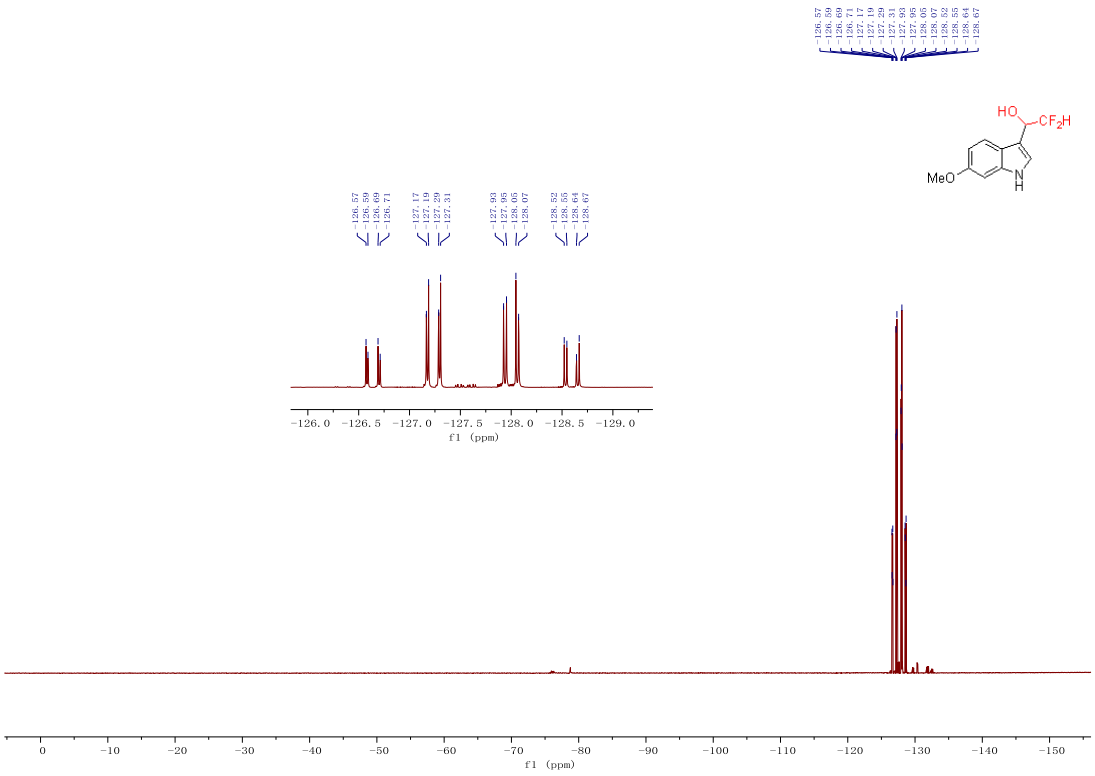
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **3p**



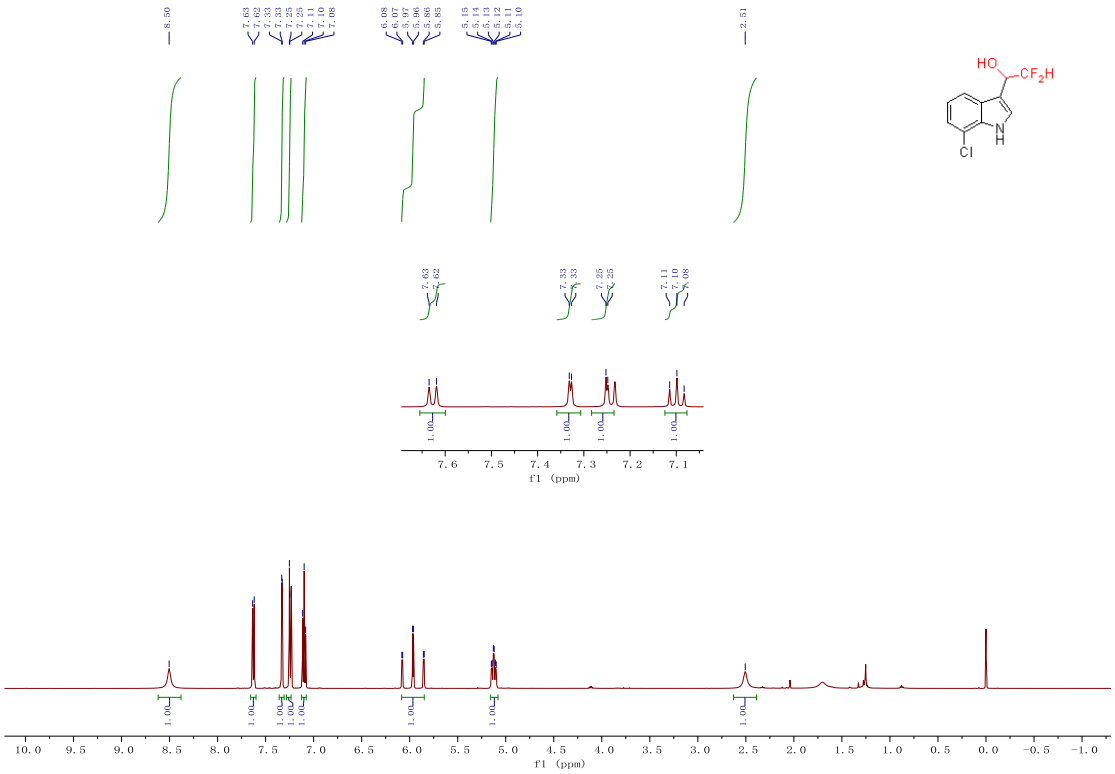
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **3p**



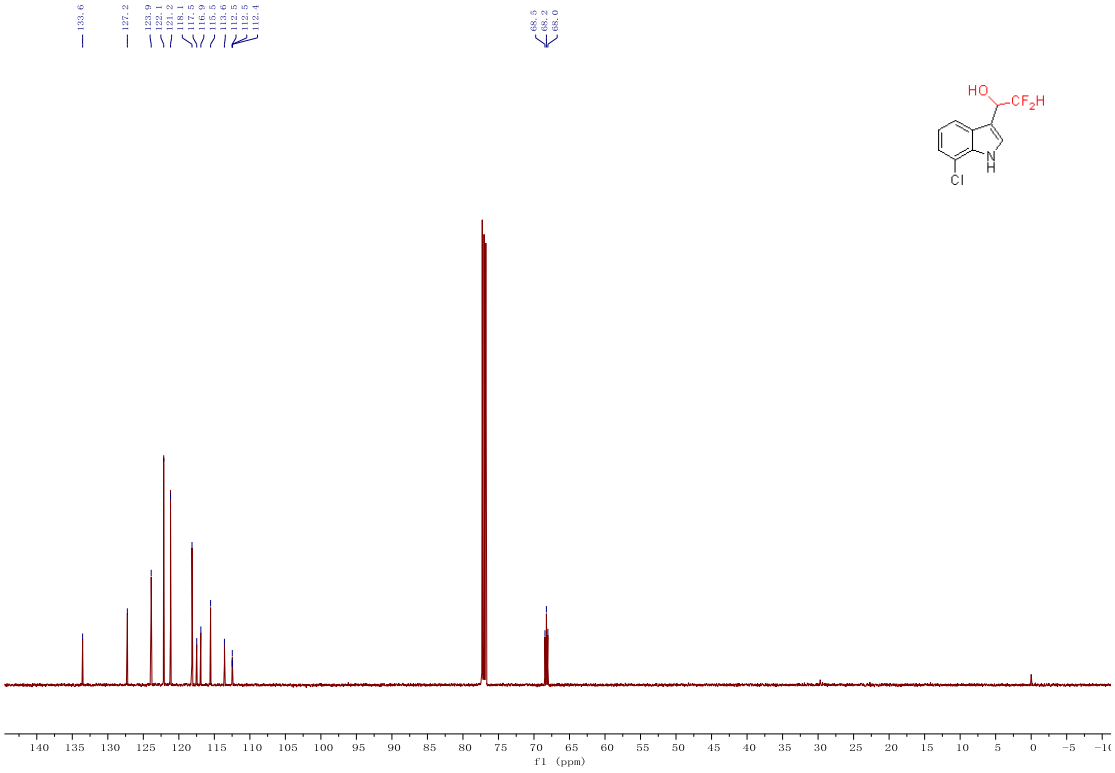
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **3p**



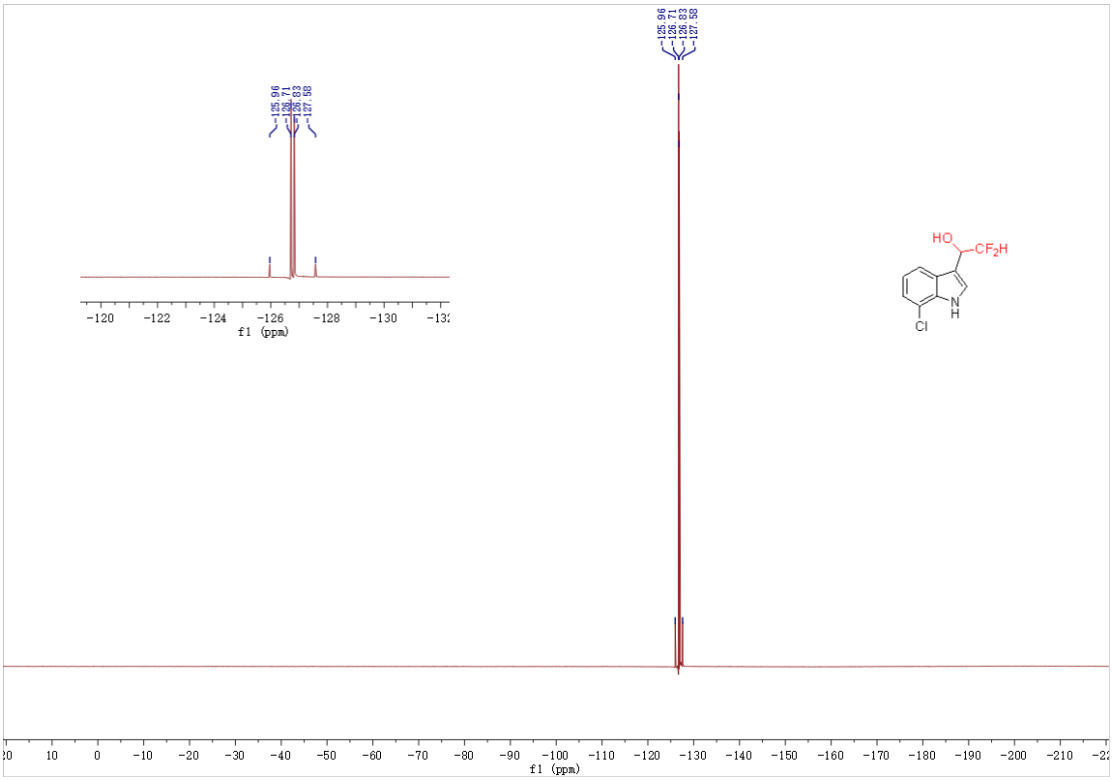
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3q**



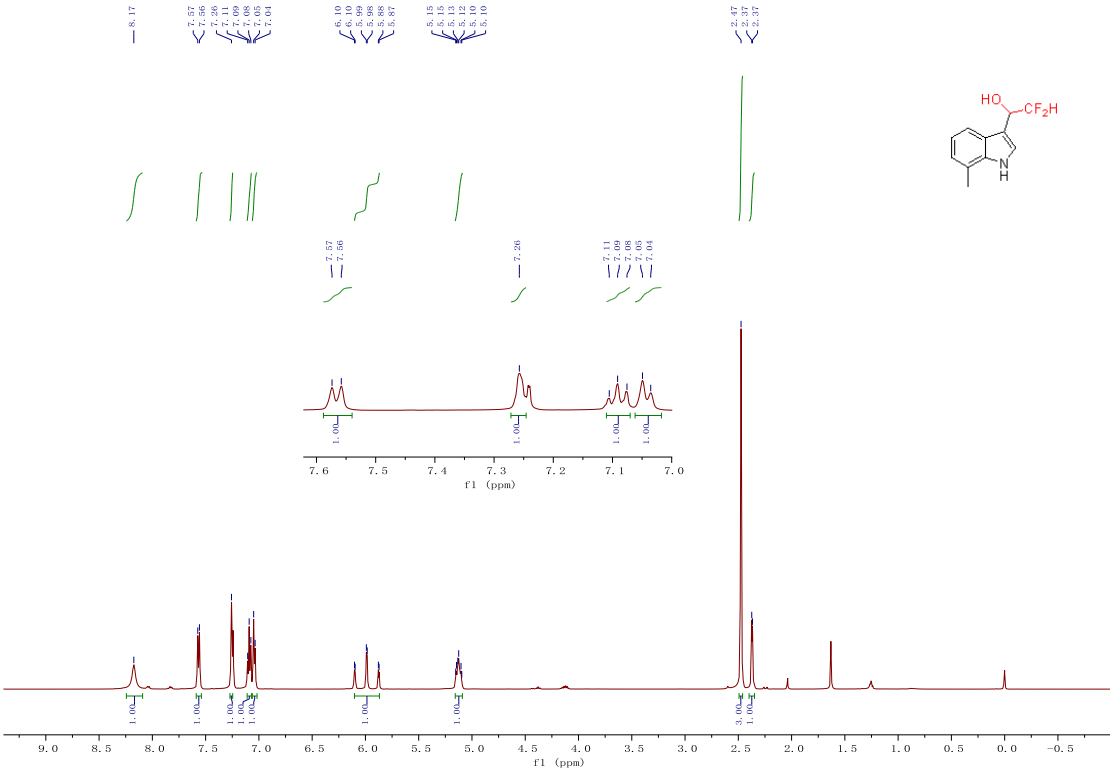
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3q**



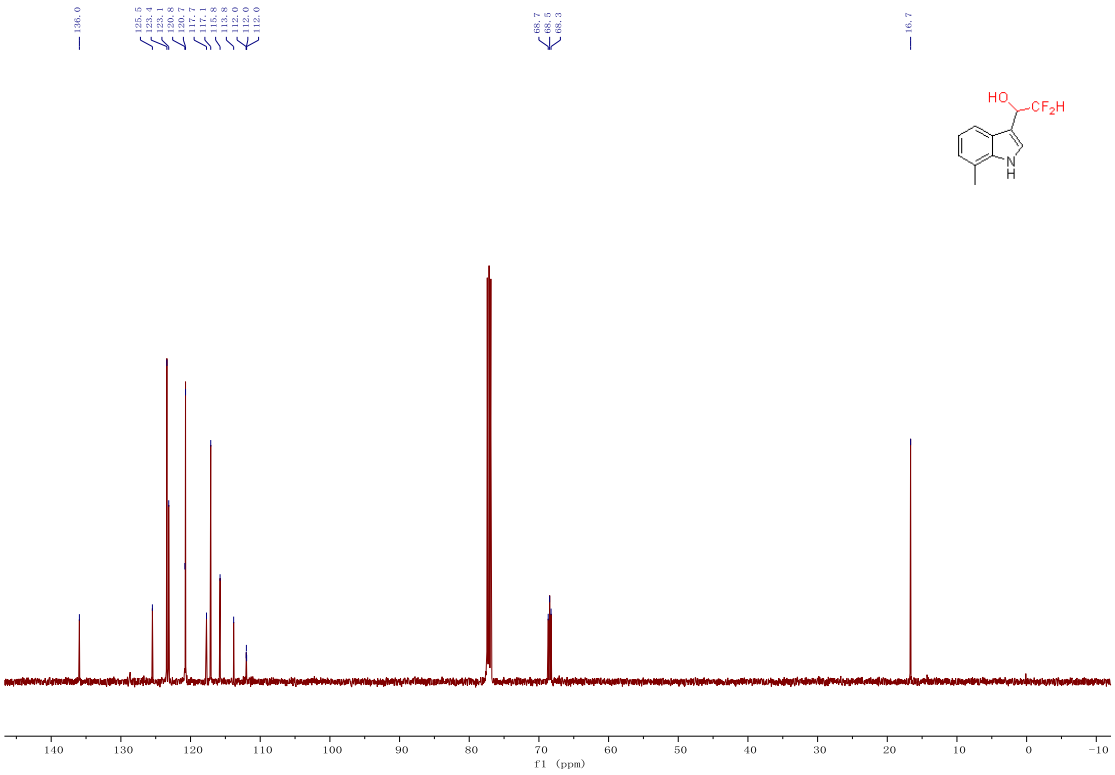
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3q**



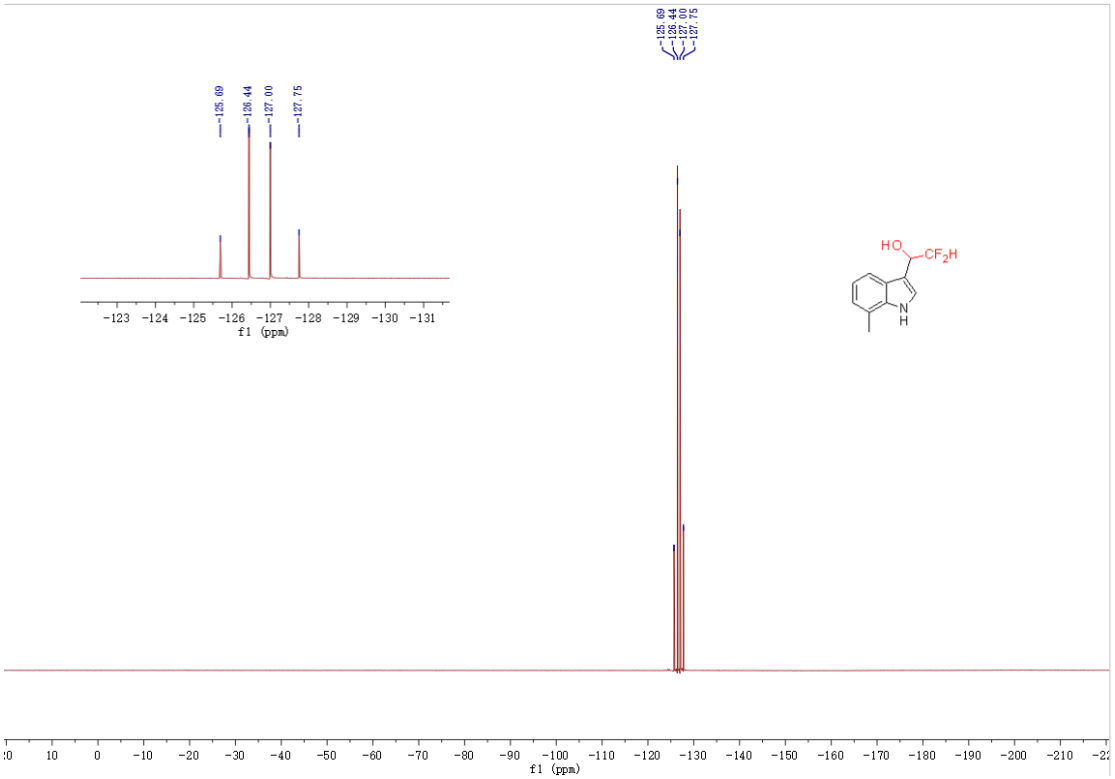
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3r**



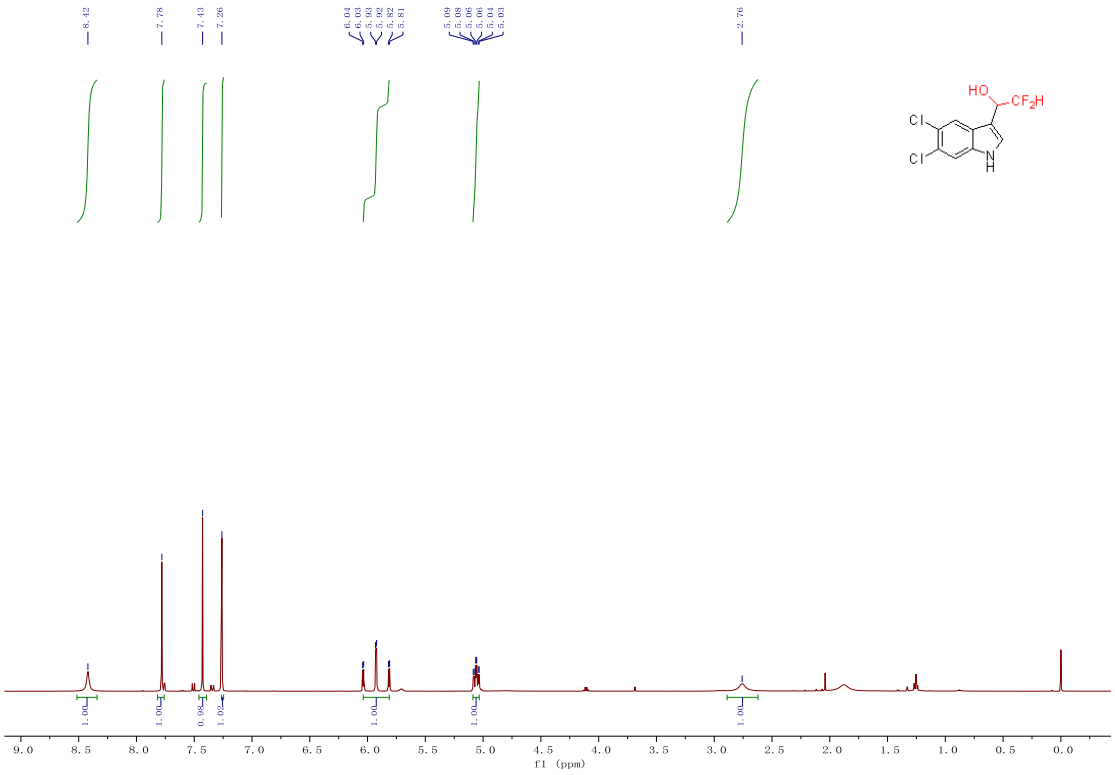
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3r**



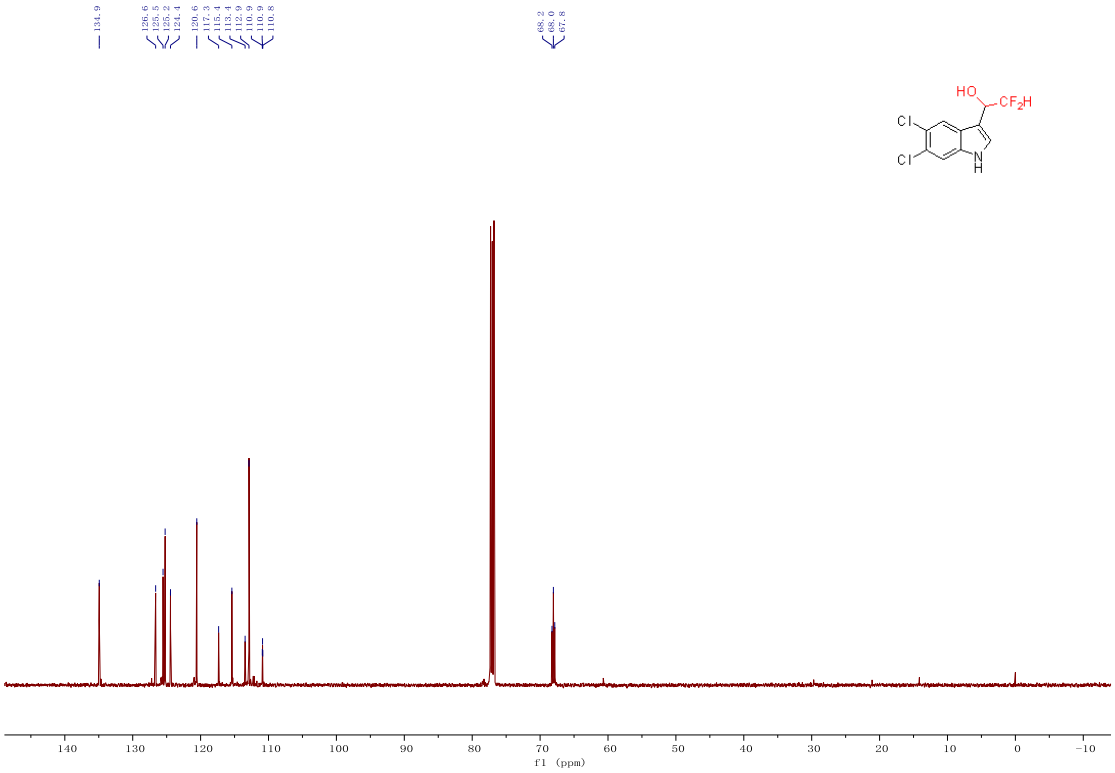
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3r**



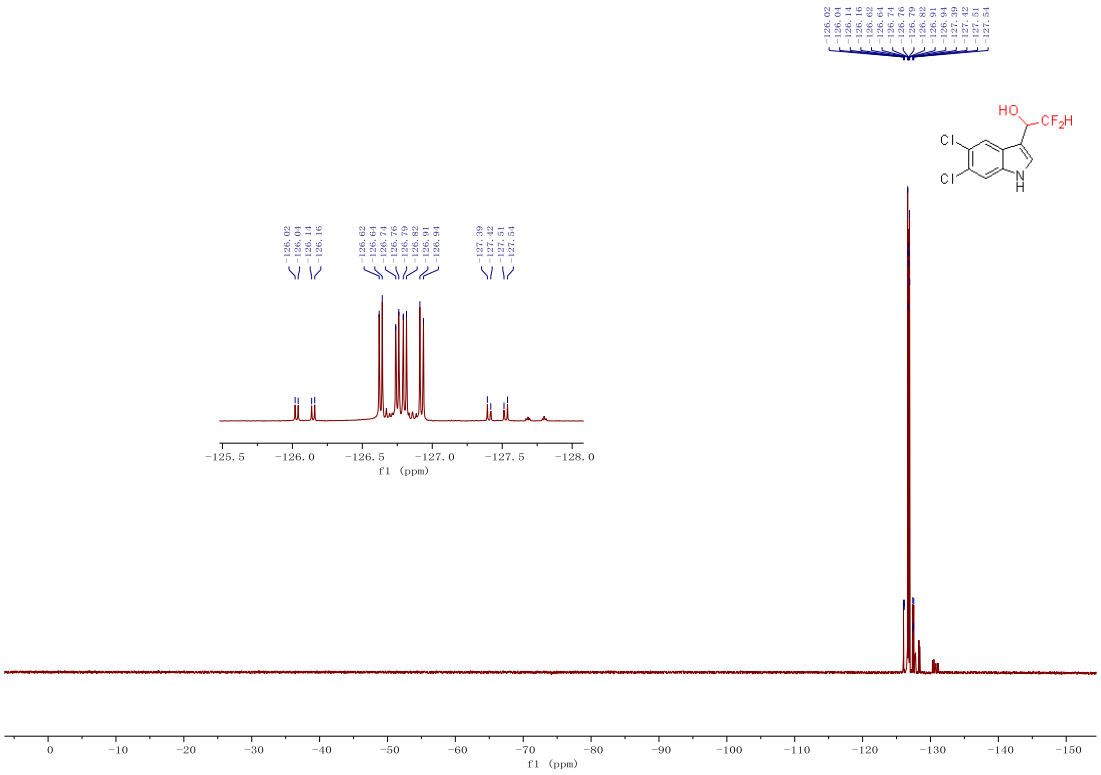
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3s**



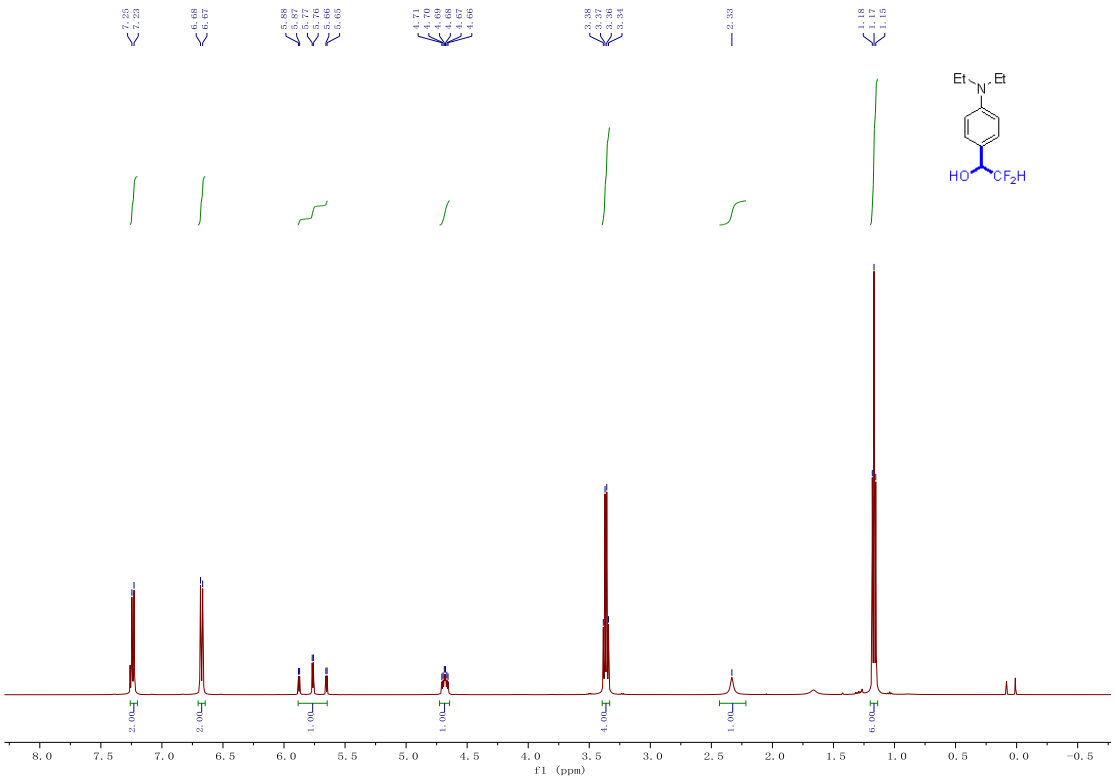
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3s**



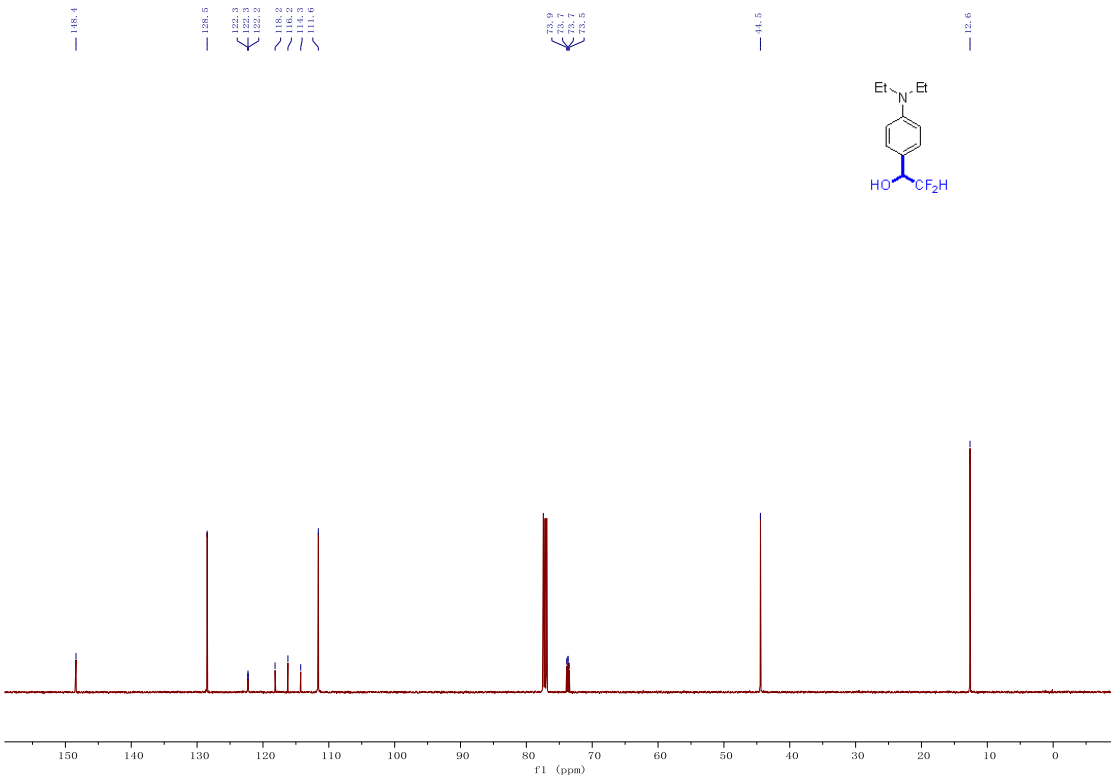
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3s**



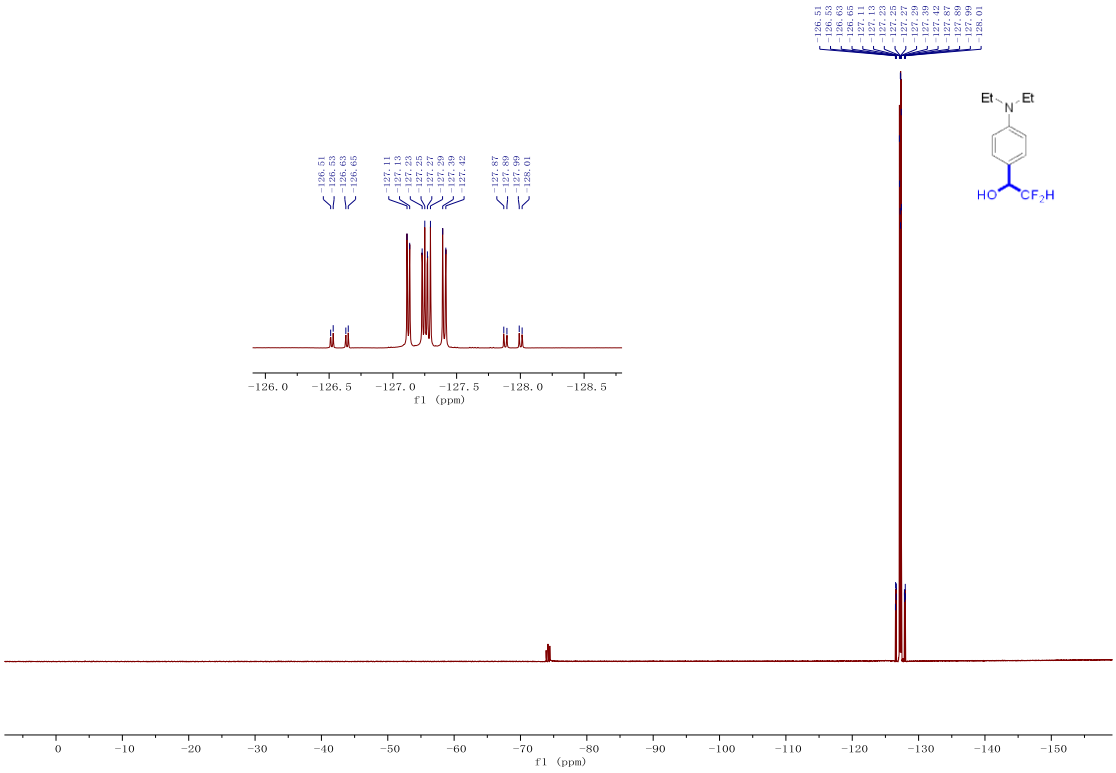
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3t**



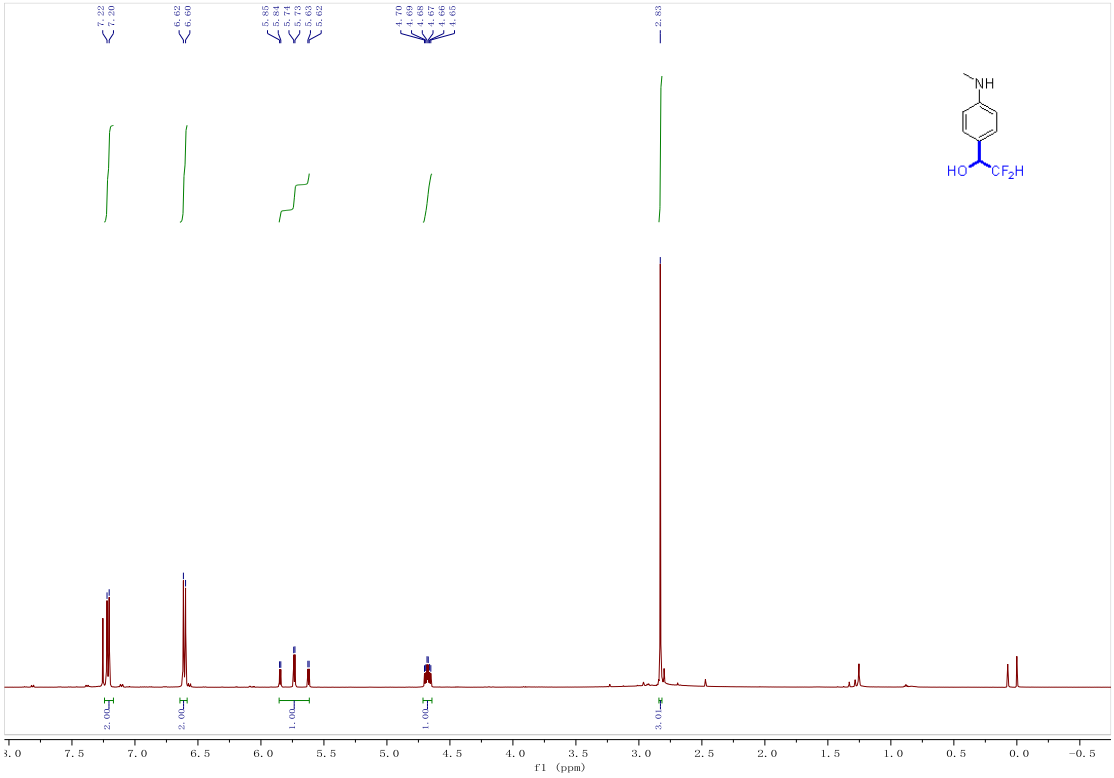
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3t**



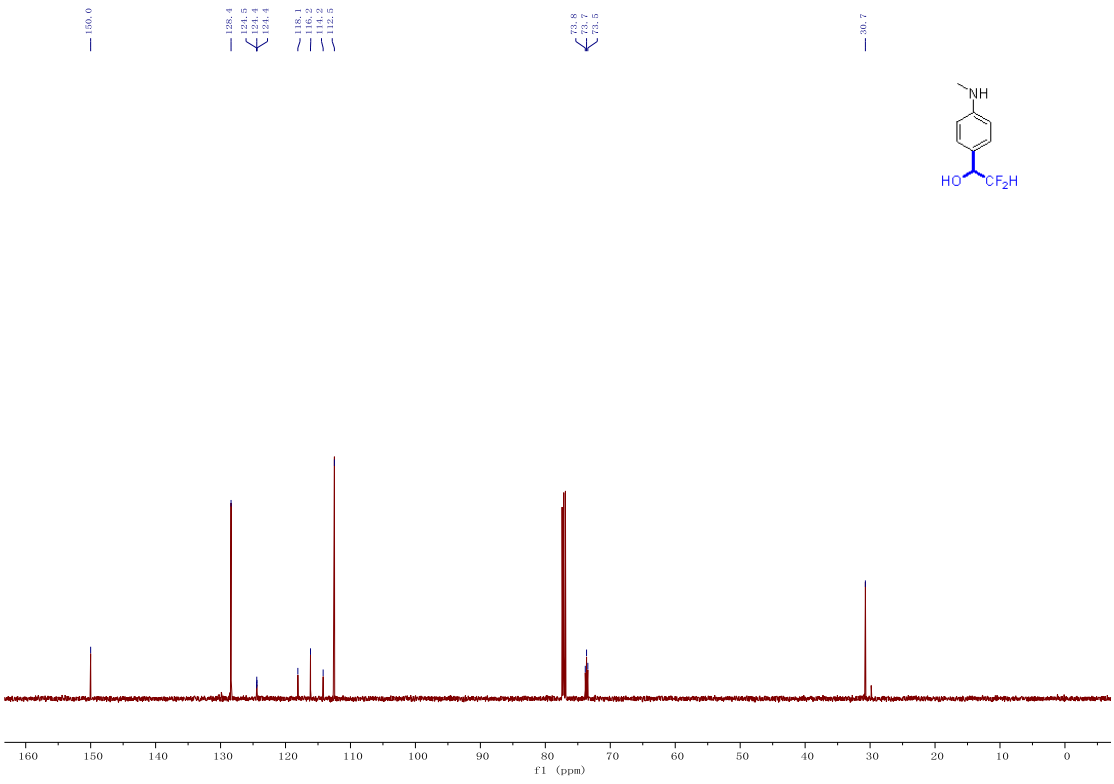
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3t**



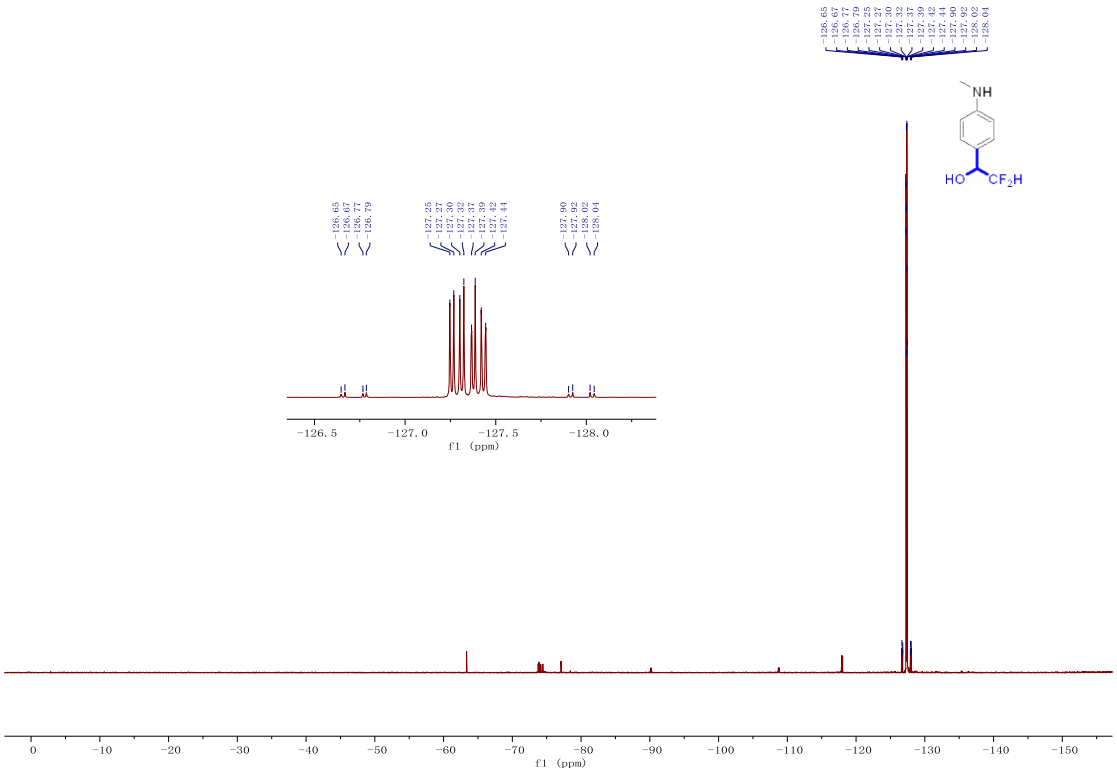
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **3u**



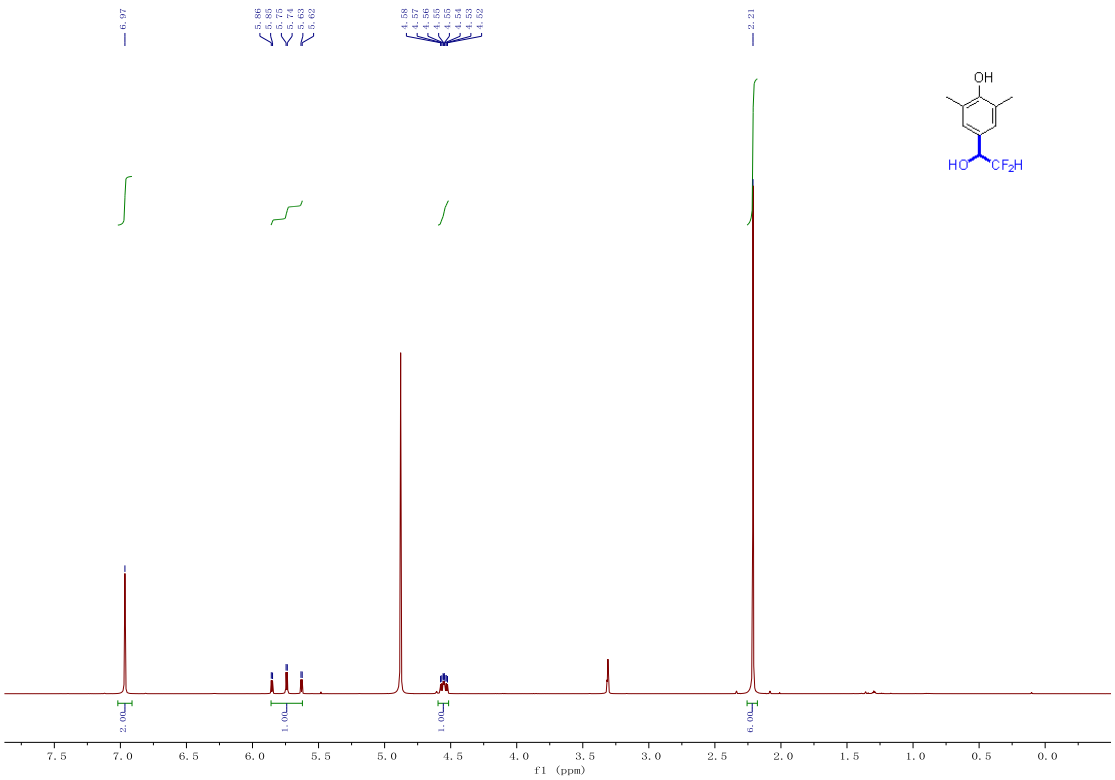
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **3u**



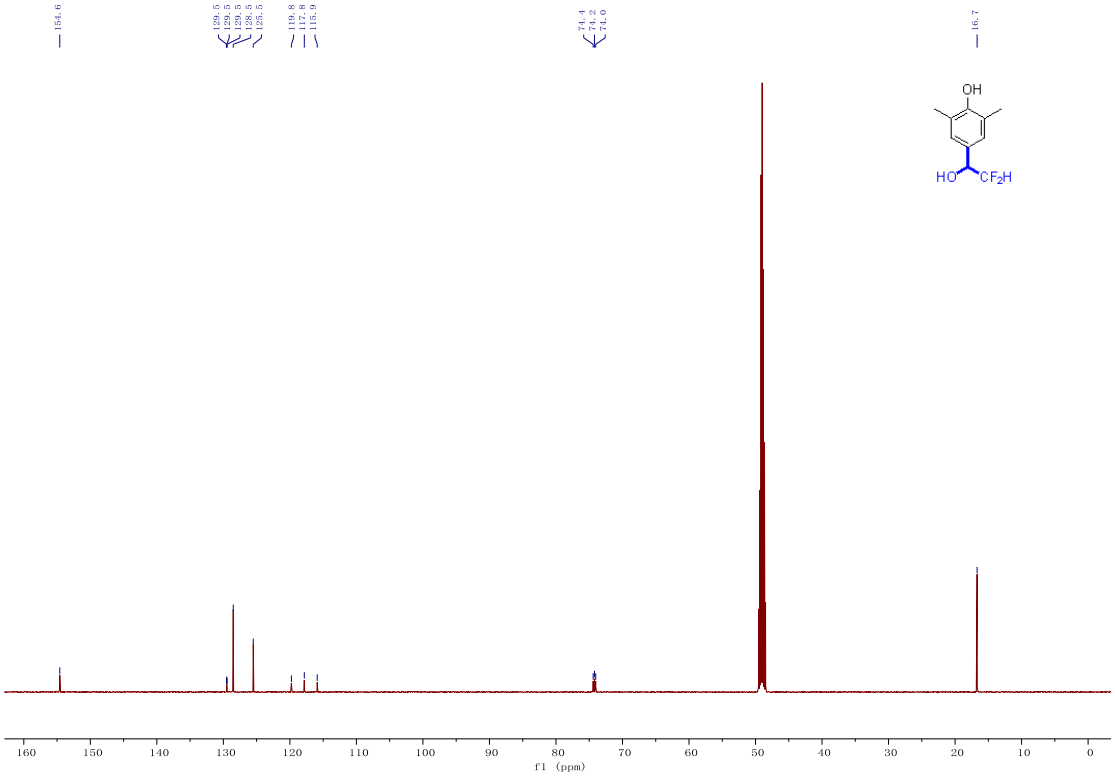
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **3u**



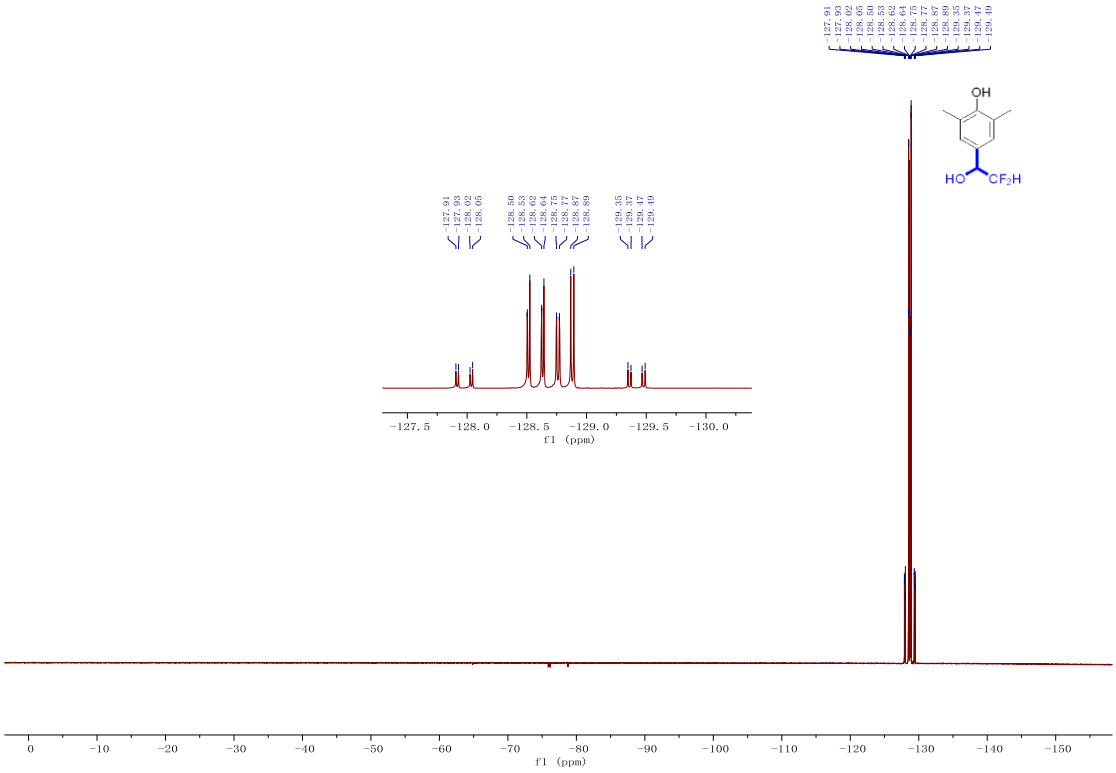
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **3v**



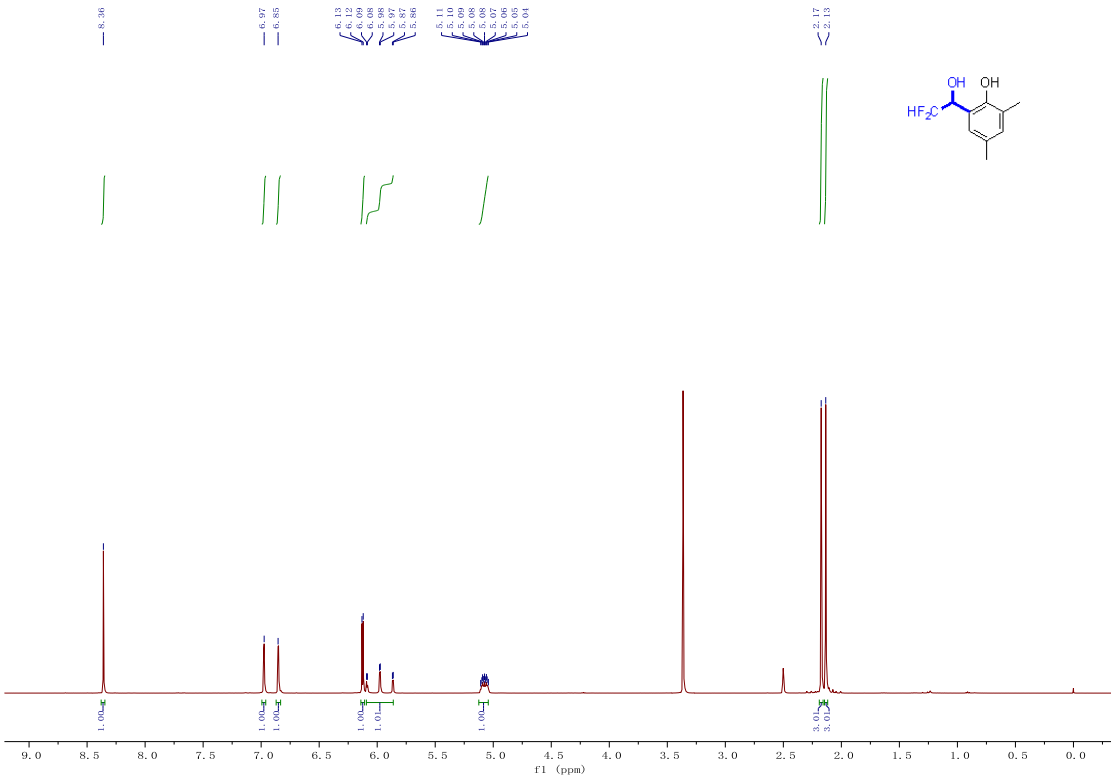
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **3v**



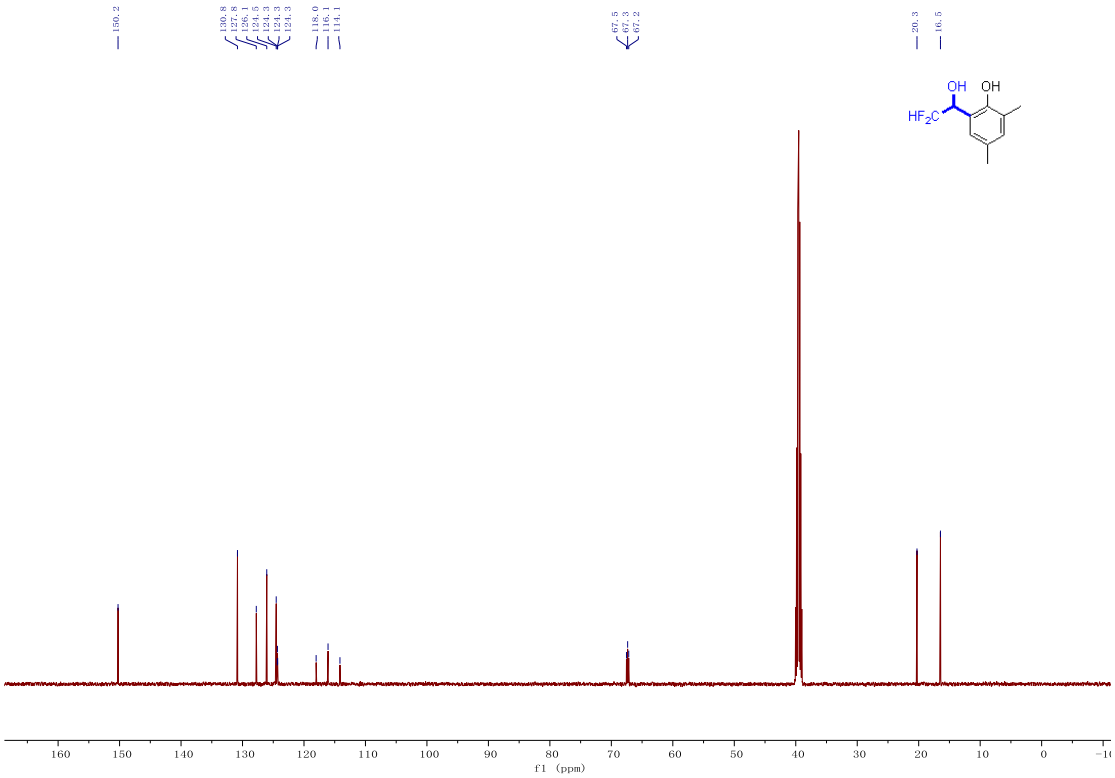
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **3v**



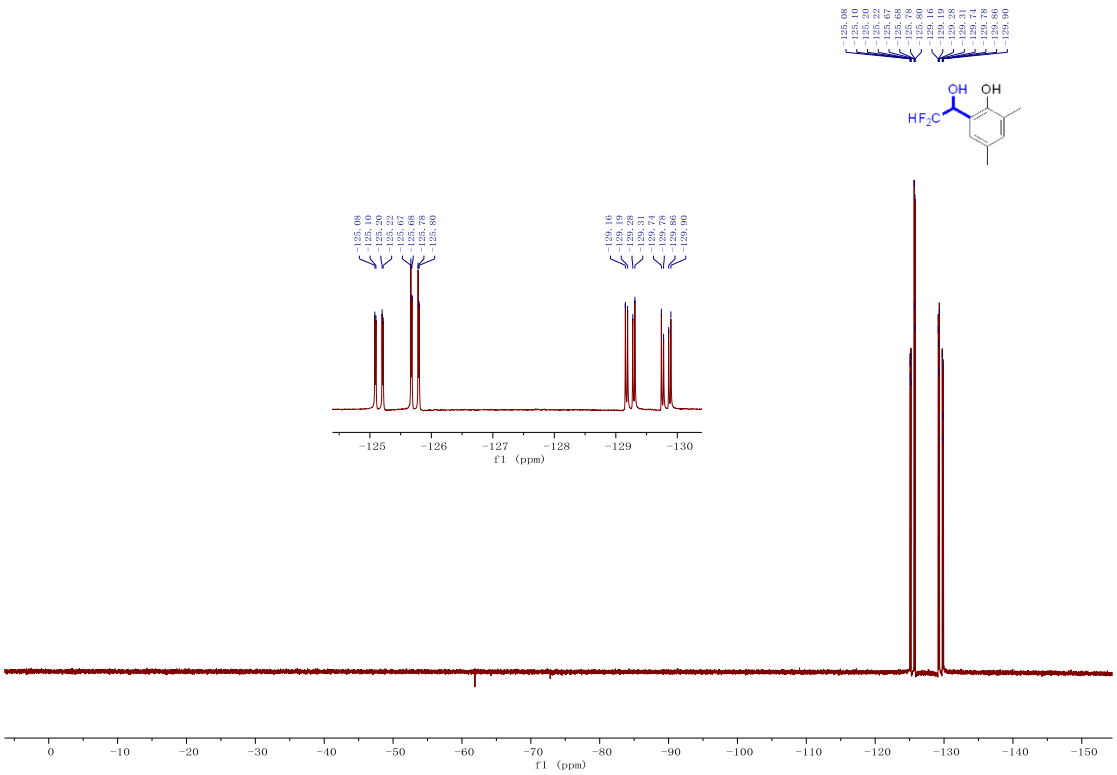
^{1}H NMR (500 MHz, DMSO-d_6) spectra of **3w**



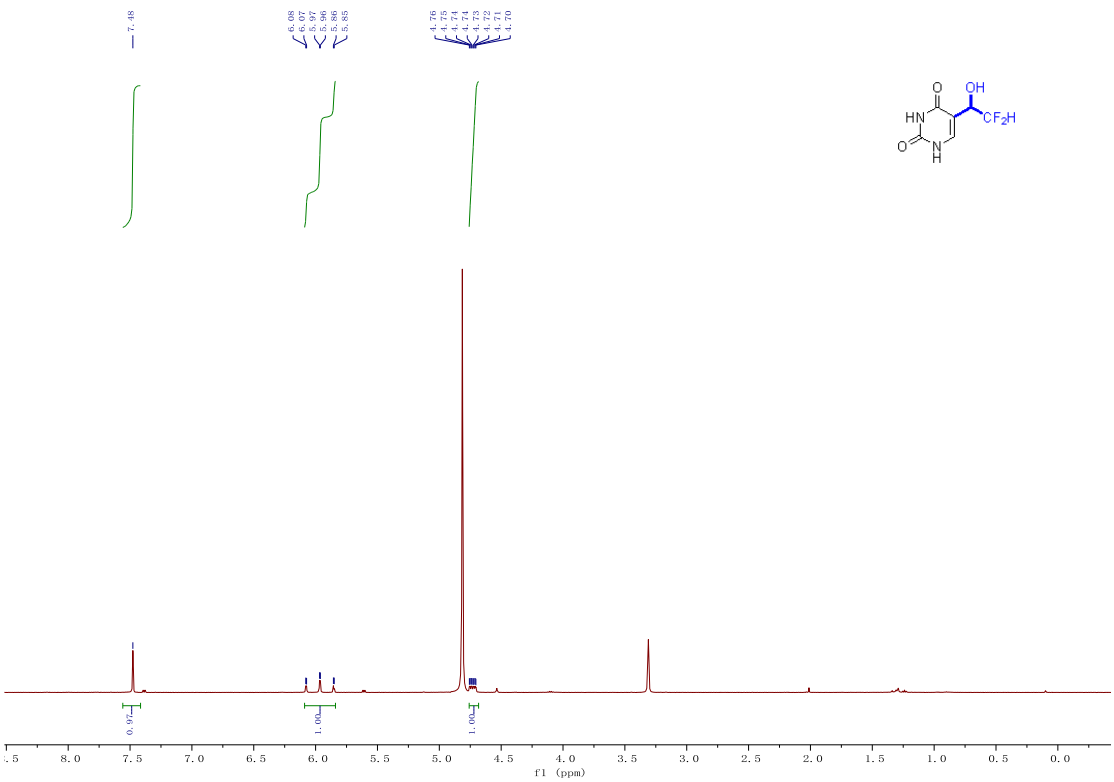
^{13}C NMR (125 MHz, DMSO-d_6) spectra of **3w**



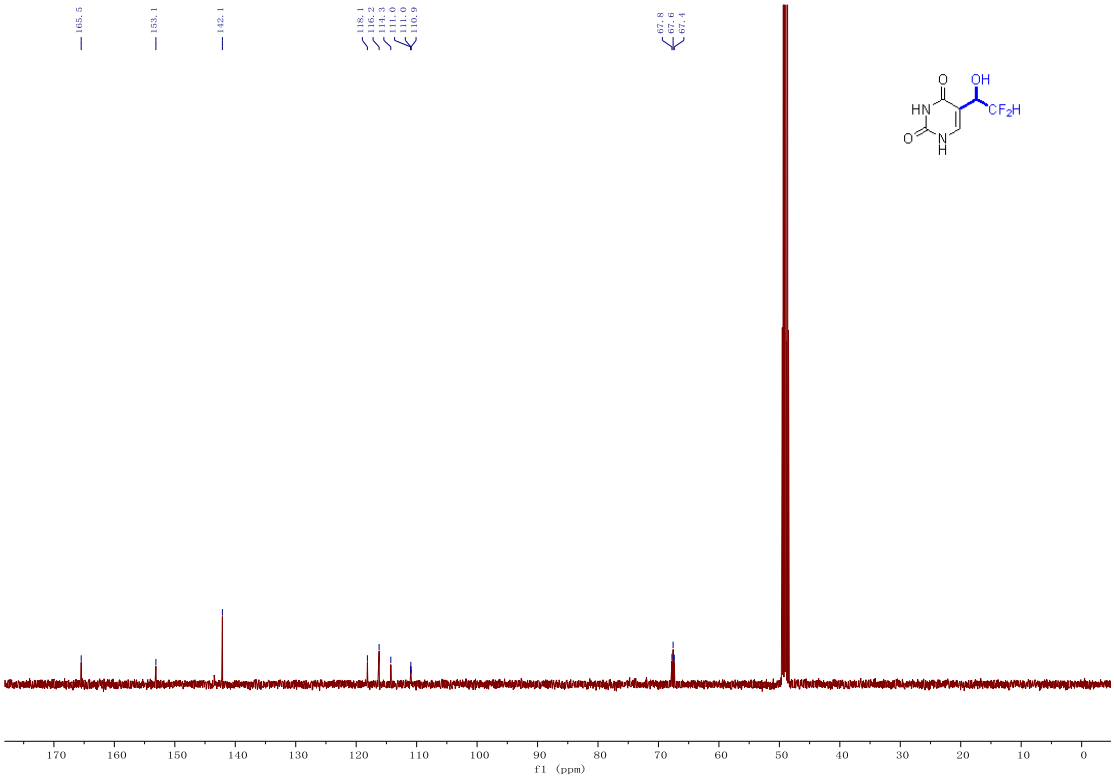
^{19}F NMR (470 MHz, DMSO-d_6) spectra of **3w**



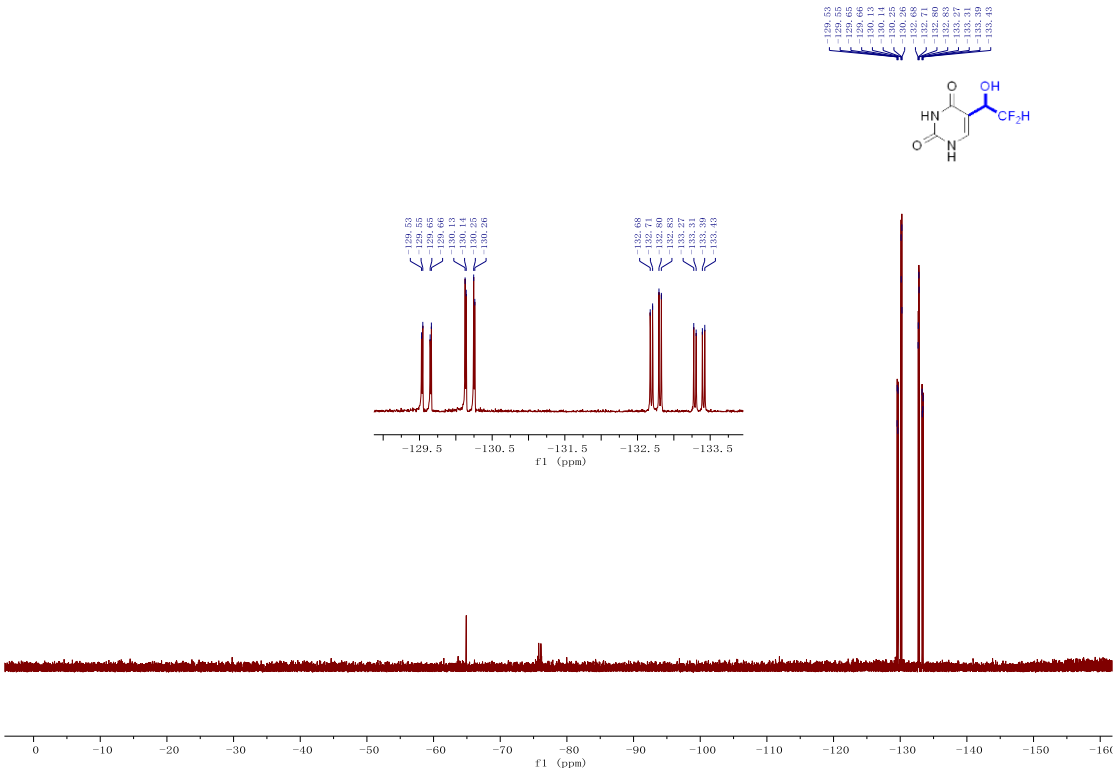
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **3x**



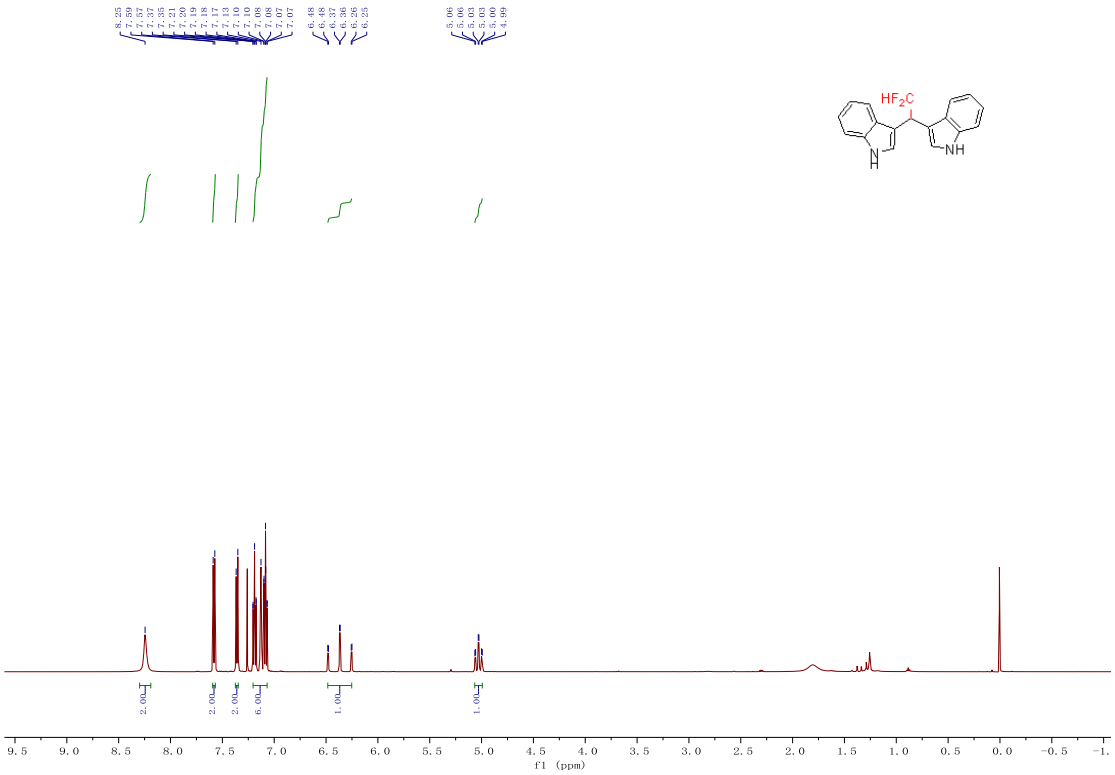
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **3x**



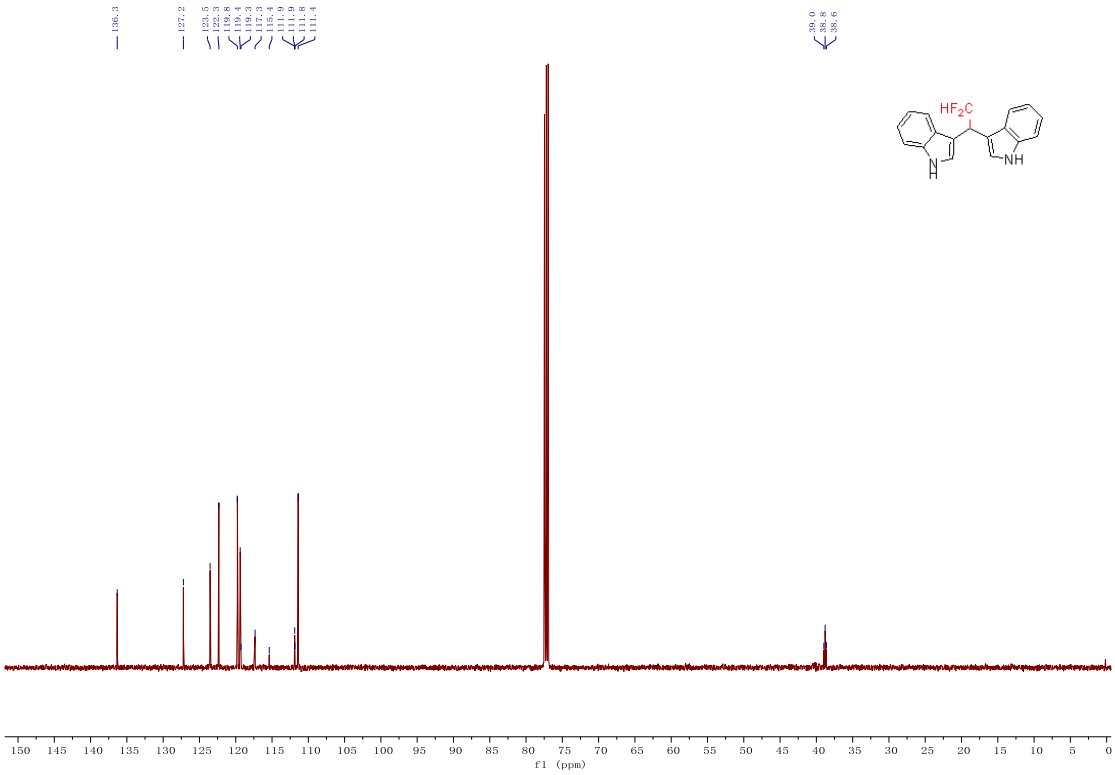
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **3x**



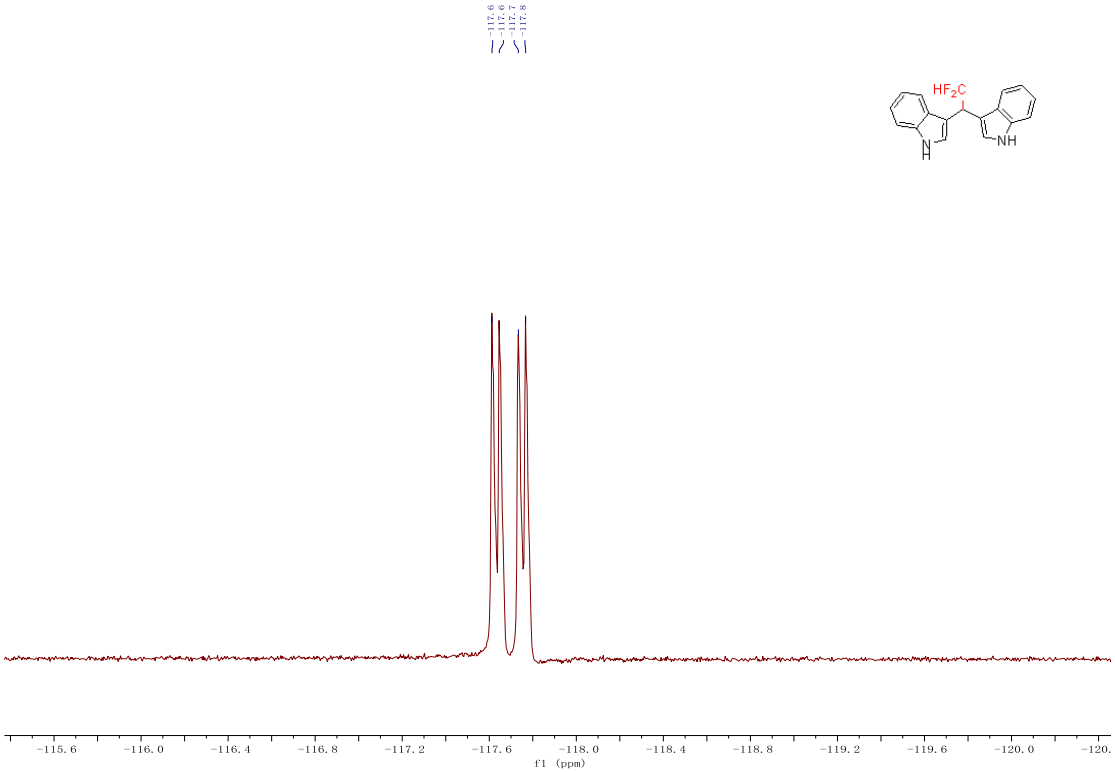
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4a**



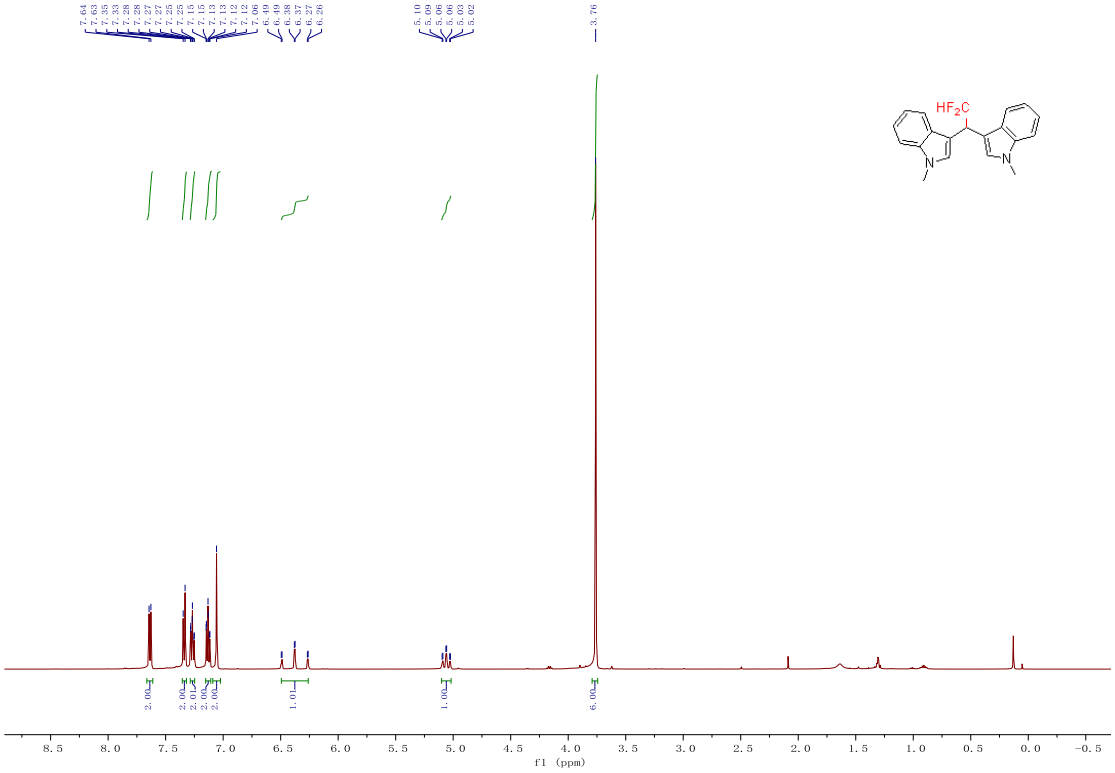
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4a**



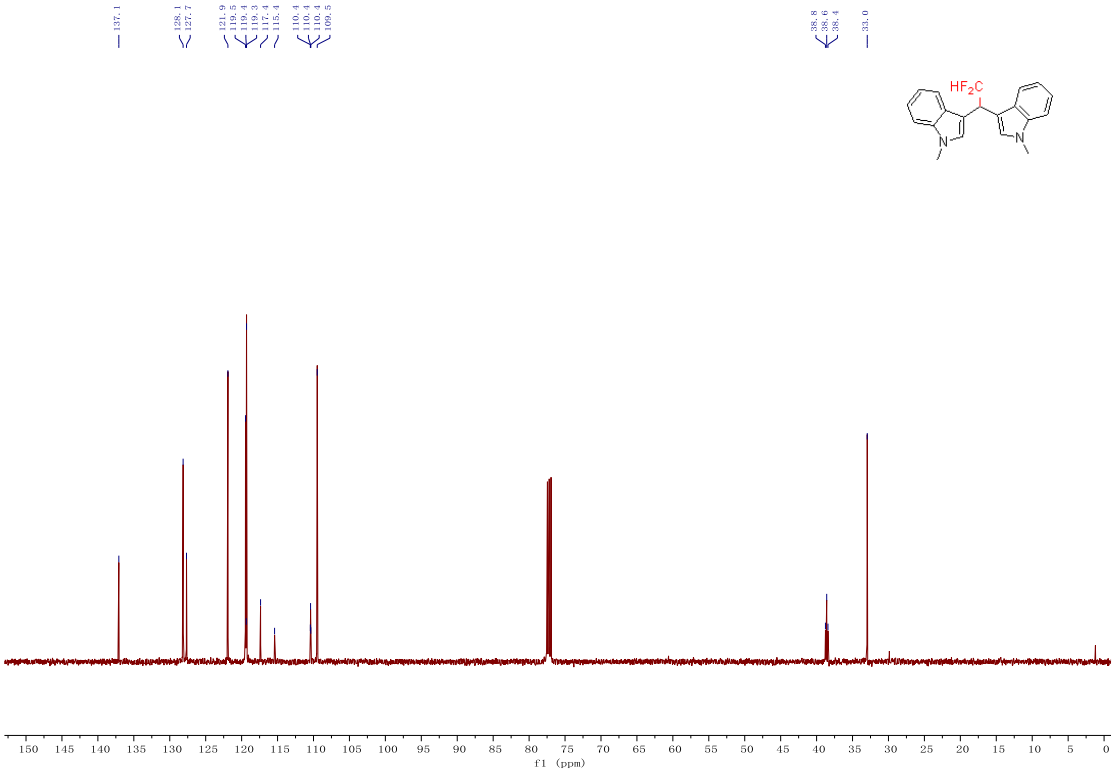
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4a**



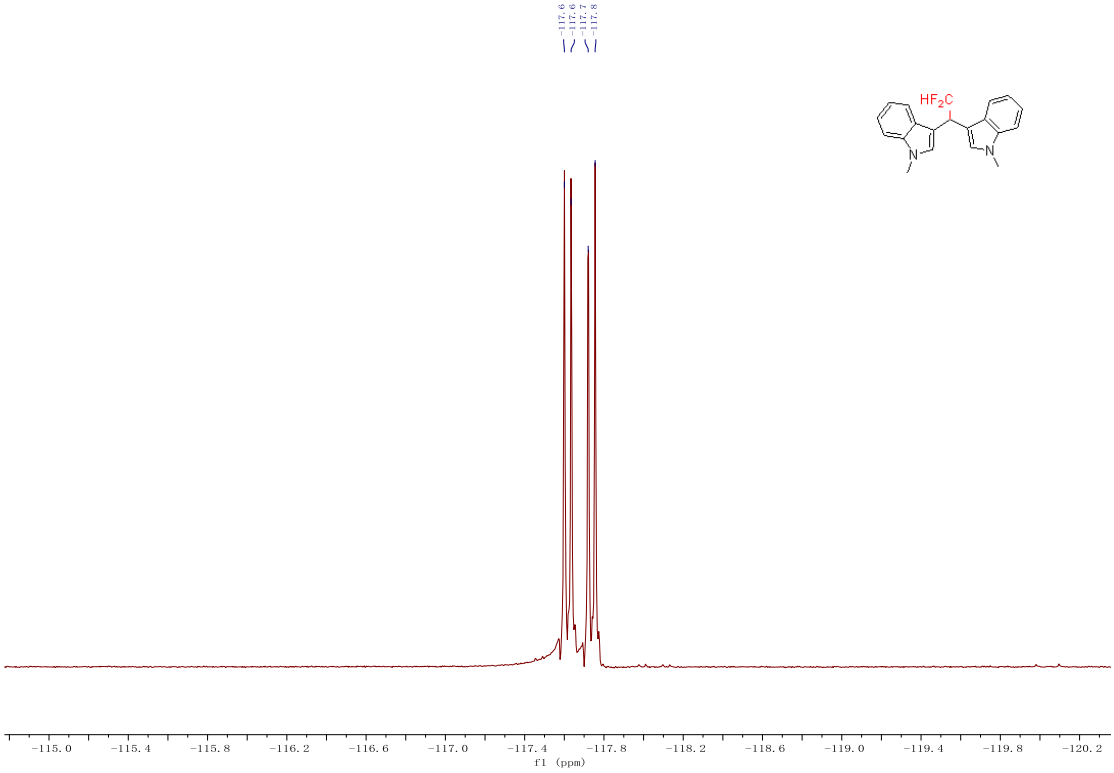
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4b**



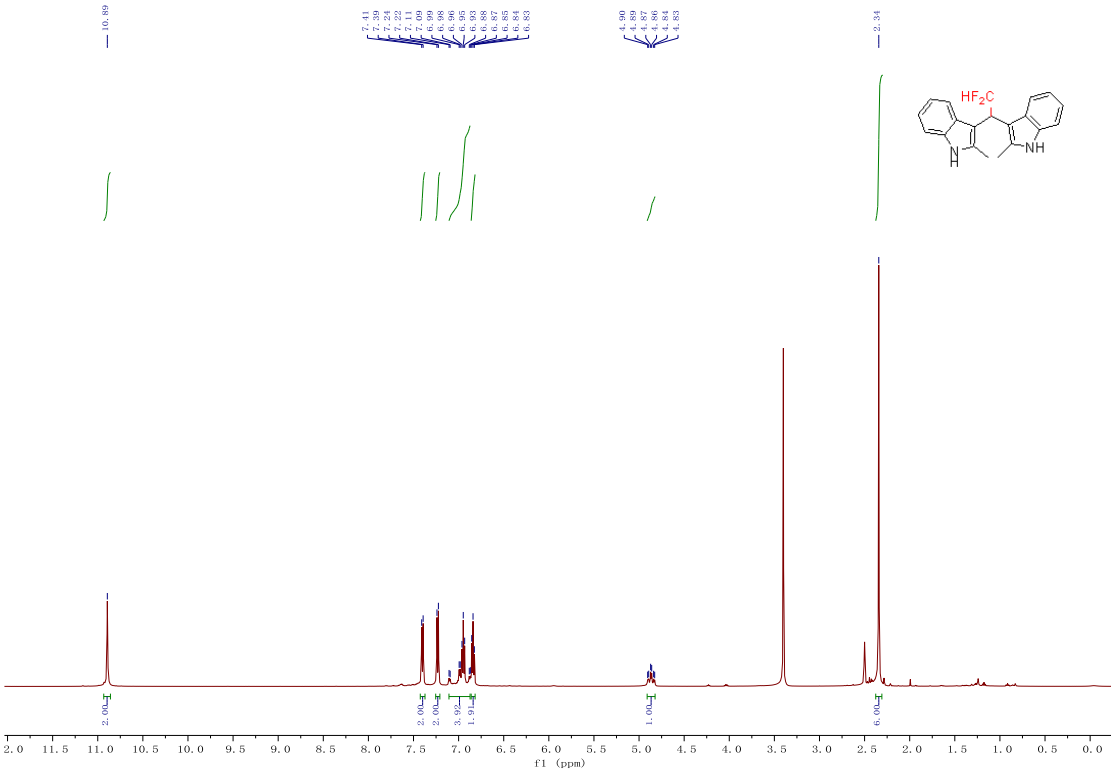
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4b**



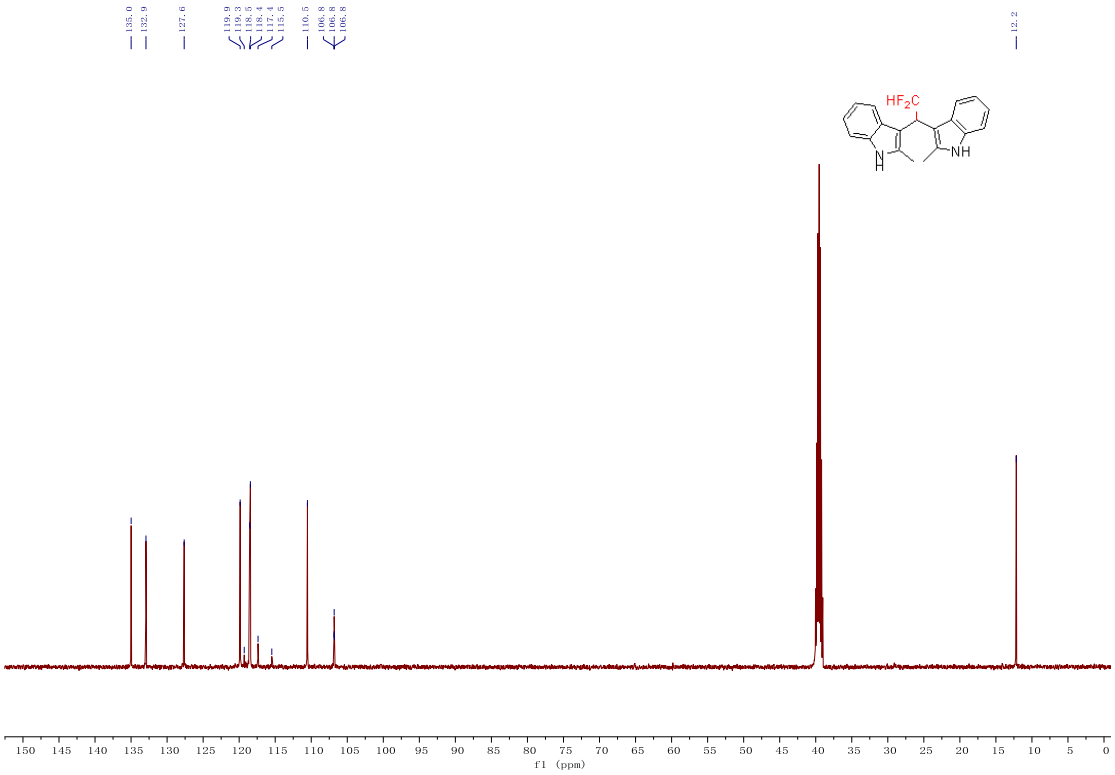
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4b**



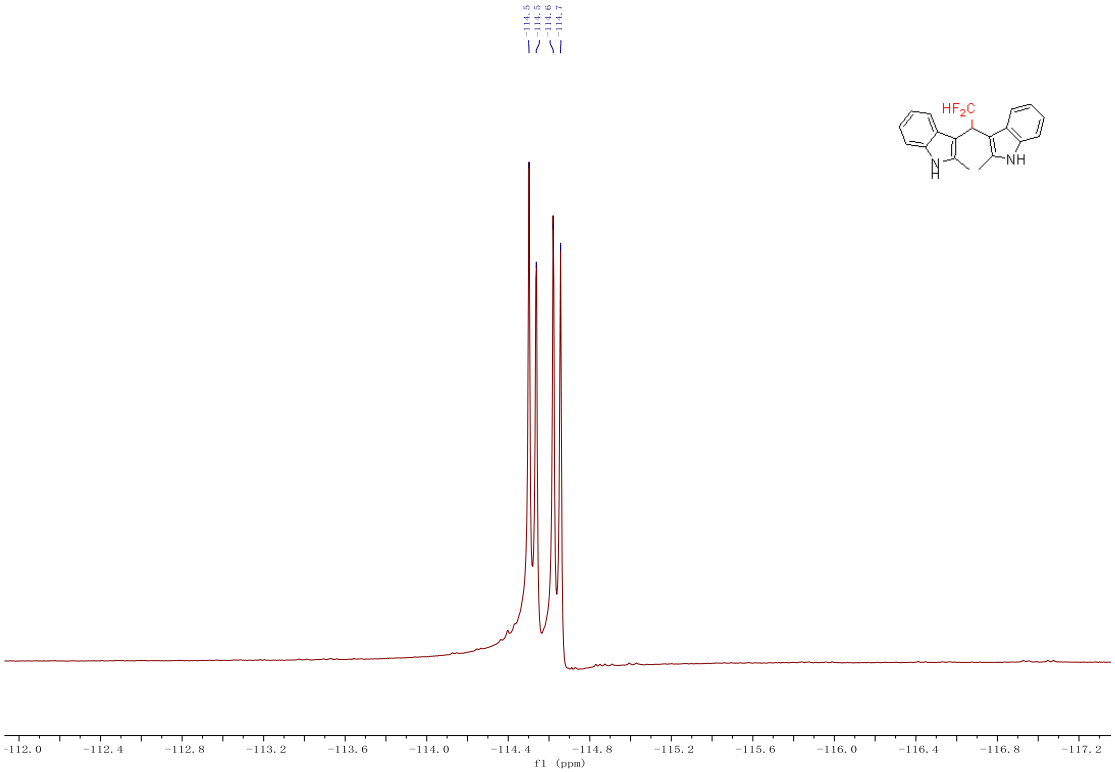
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4c**



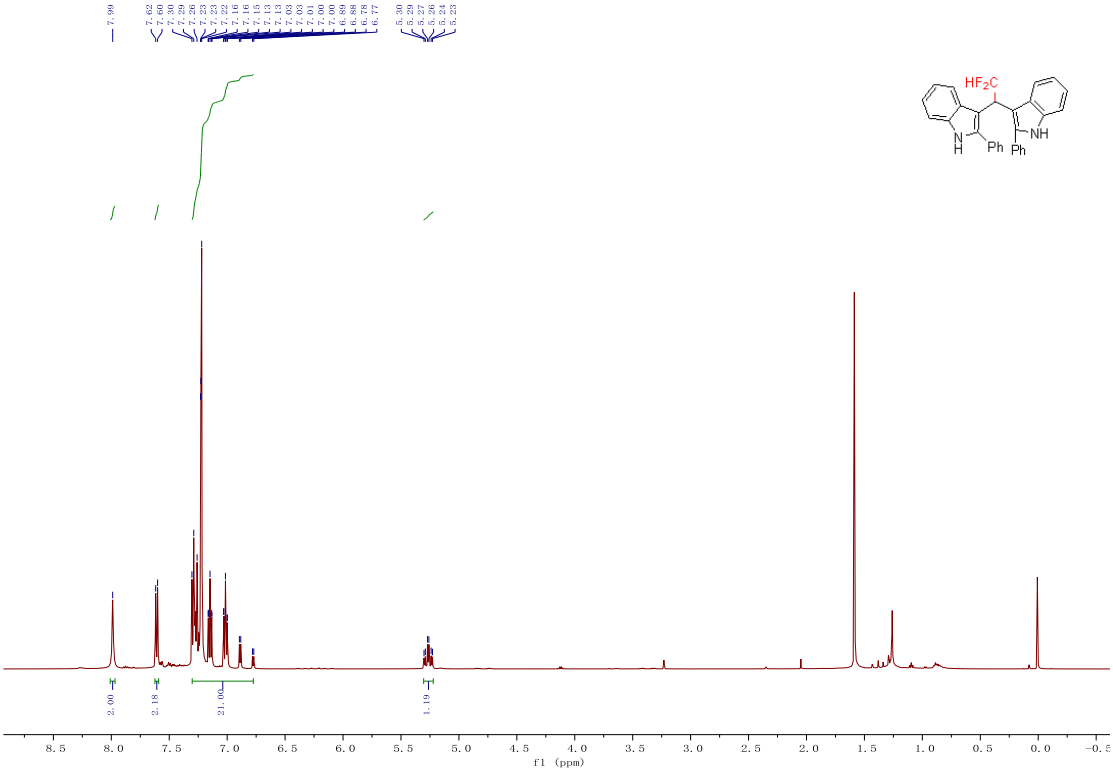
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4c**



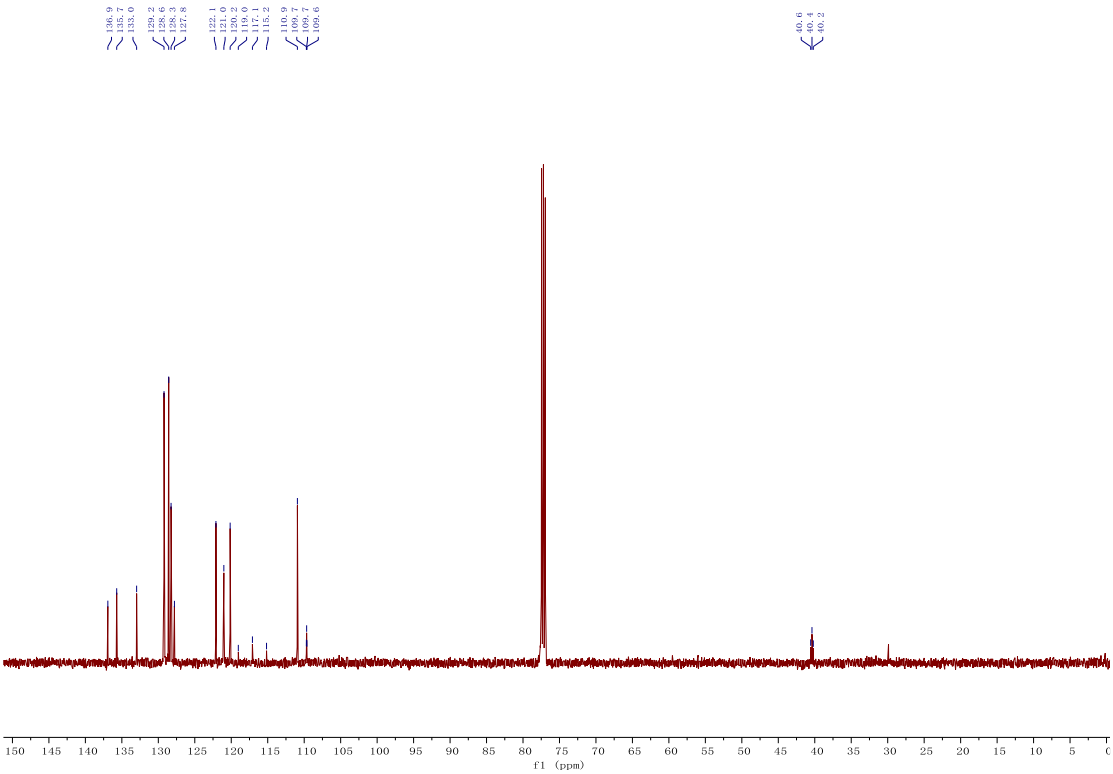
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4c**



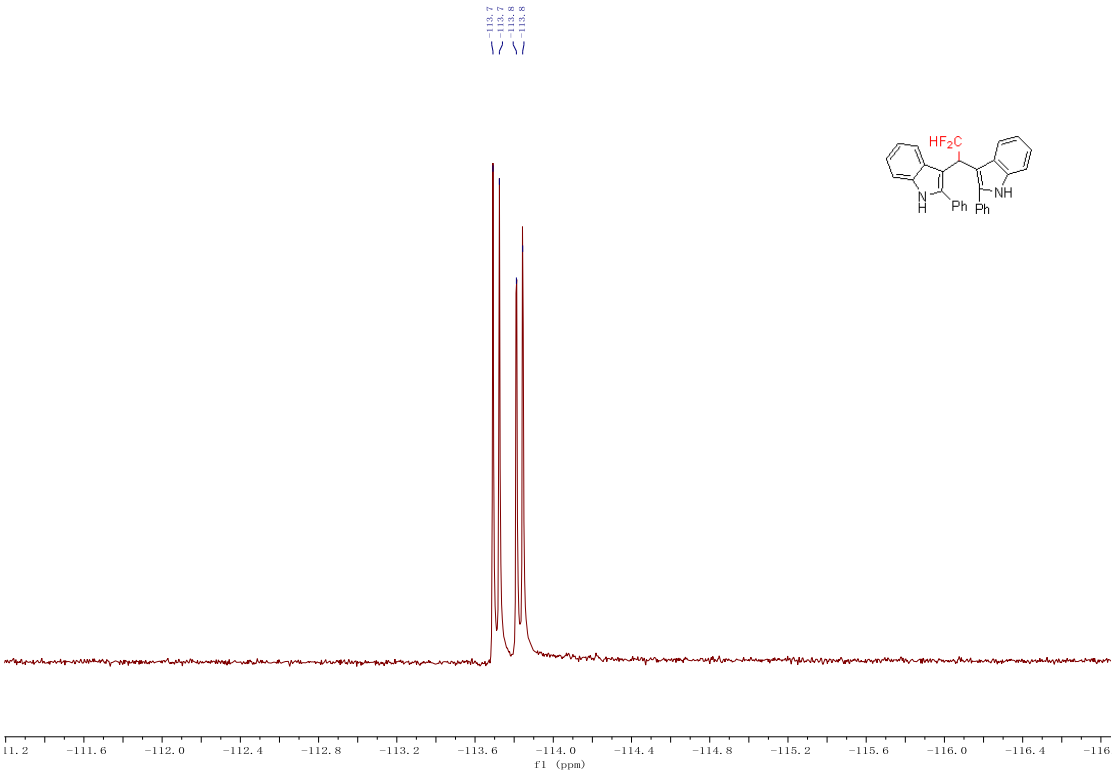
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4d**



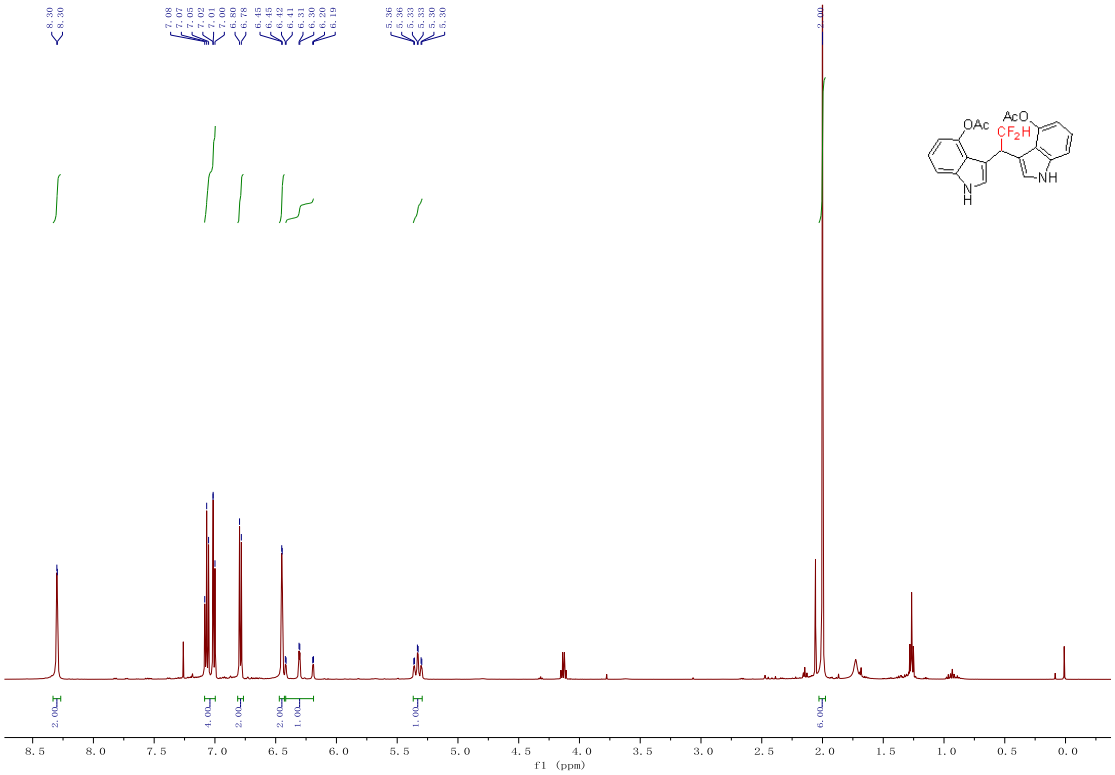
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4d**



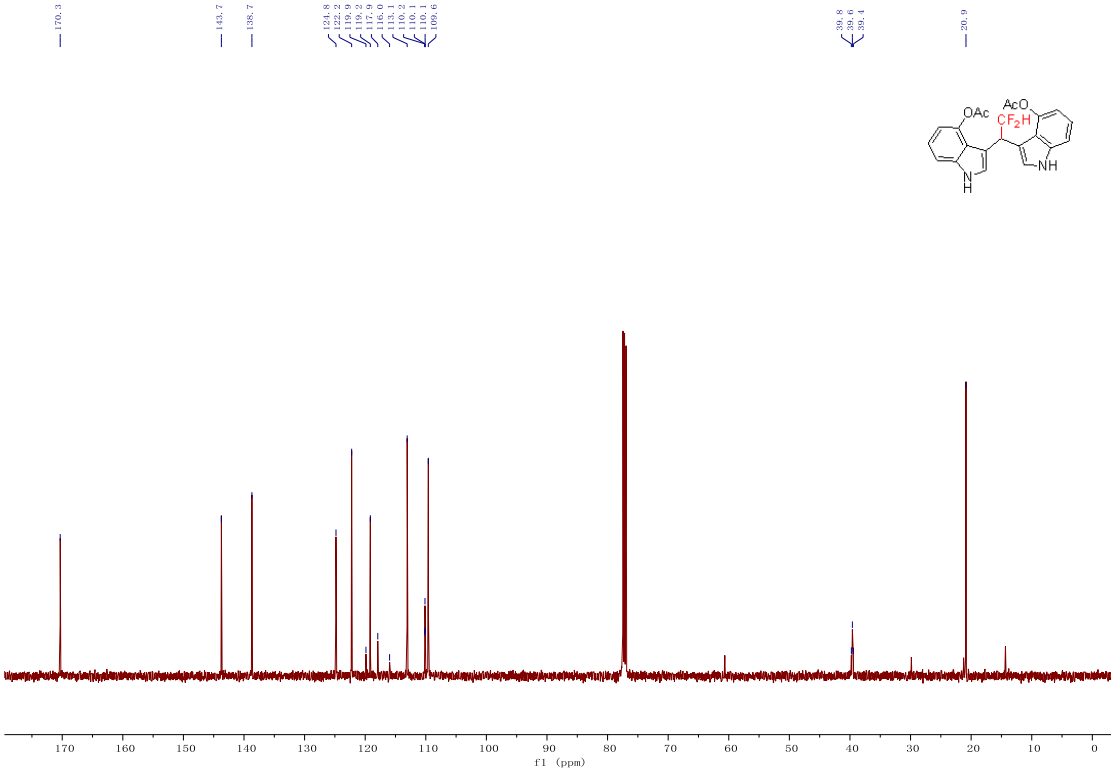
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4d**



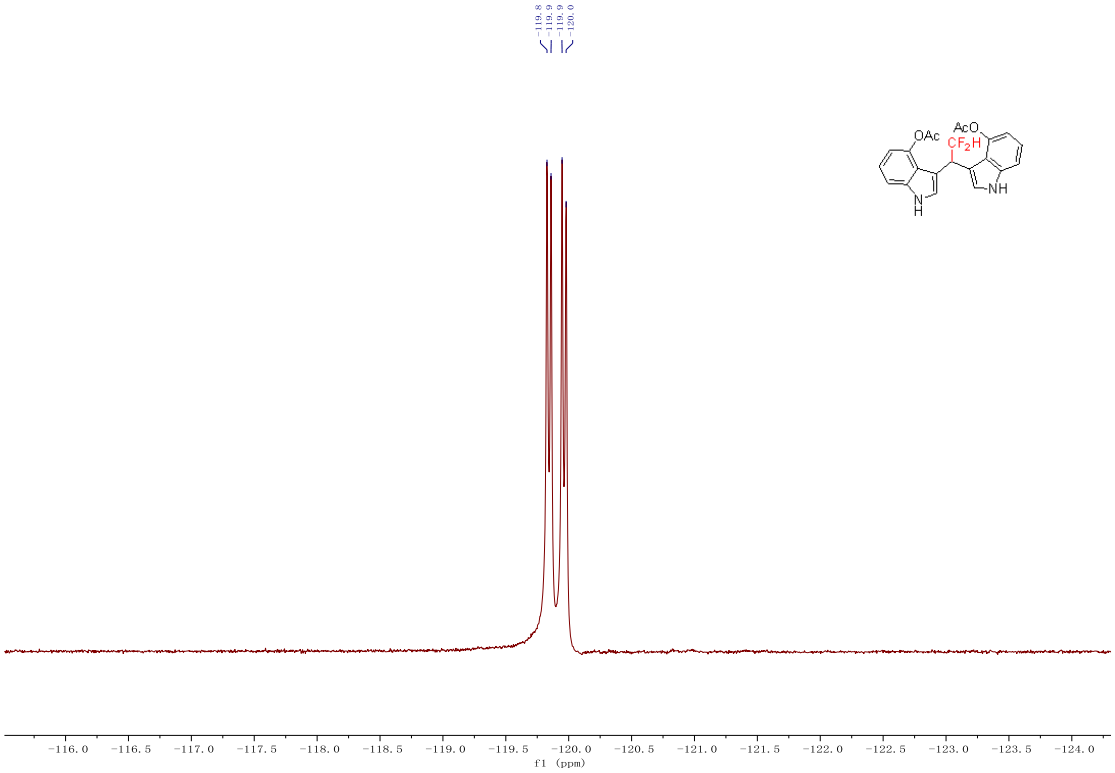
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4e**



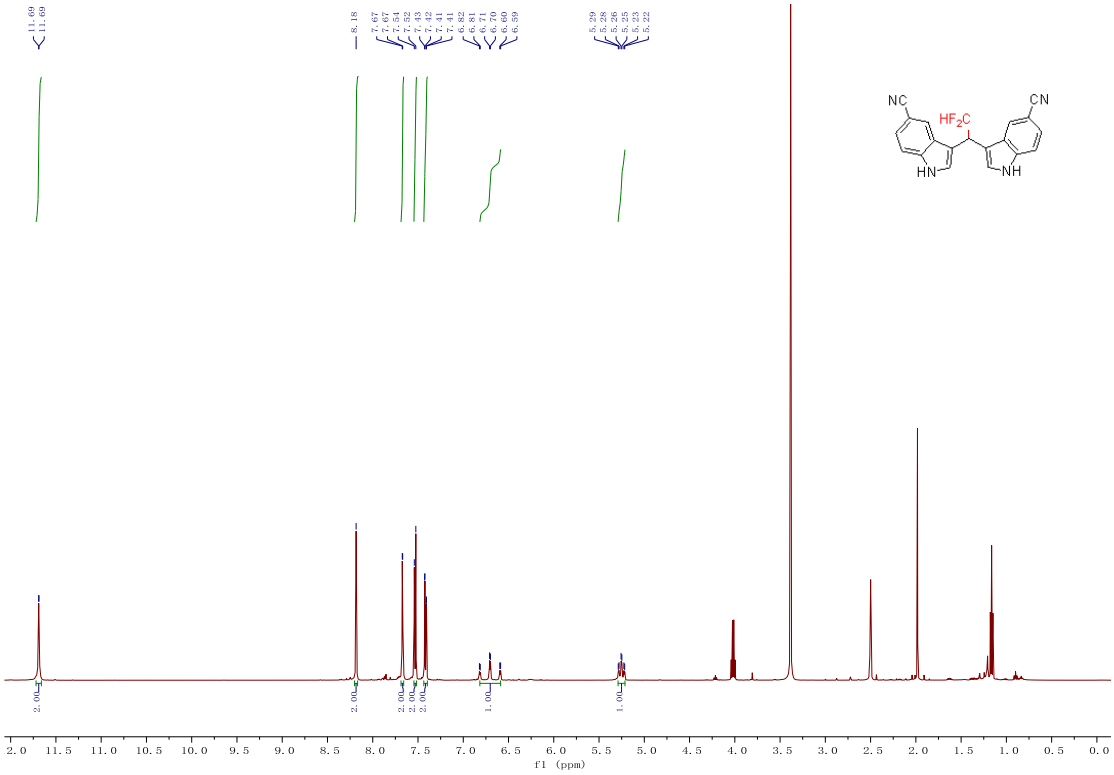
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4e**



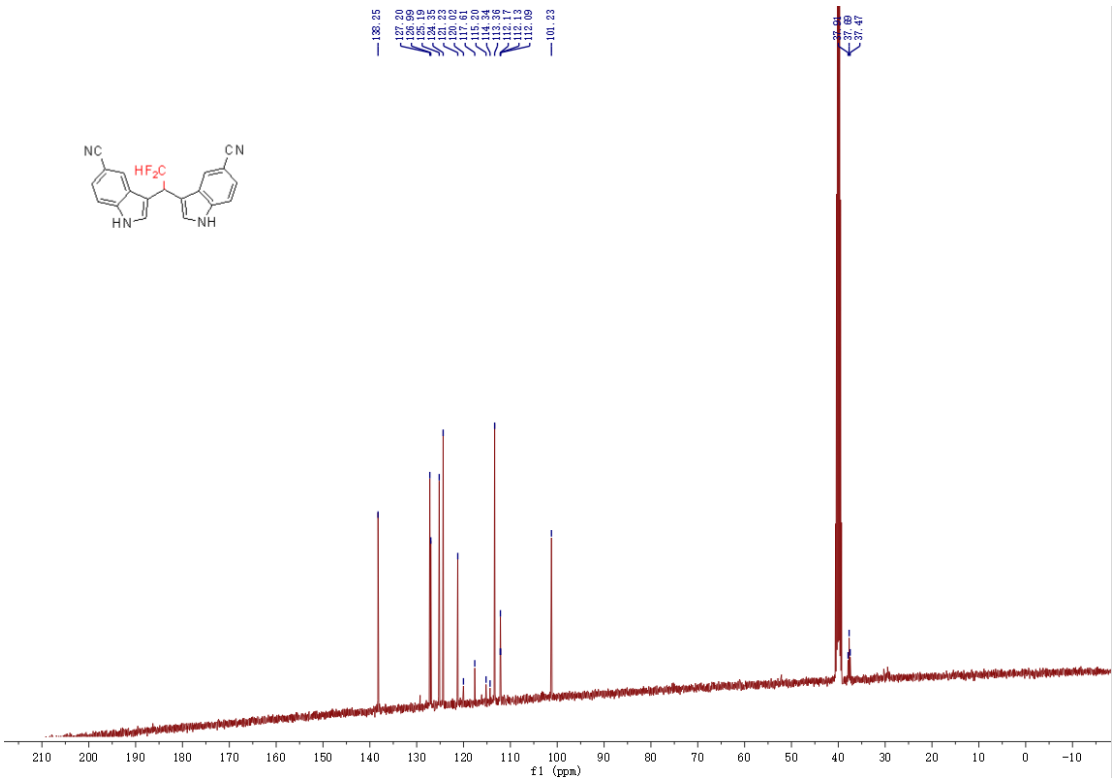
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4e**



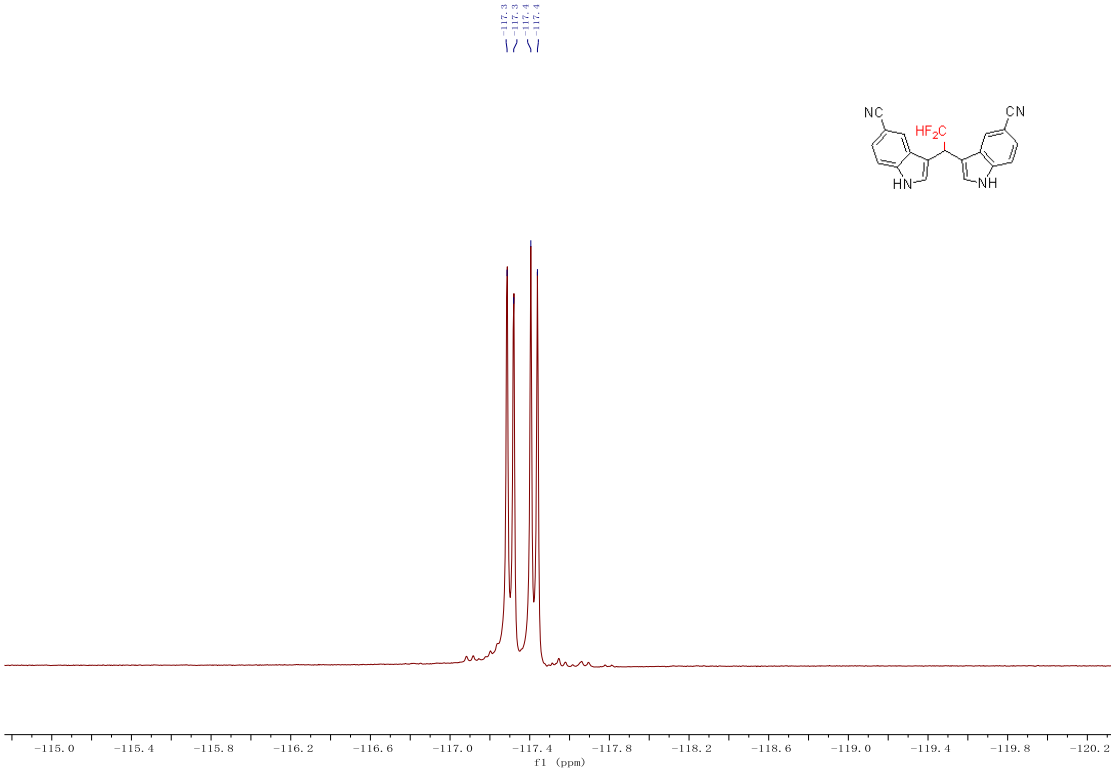
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4f**



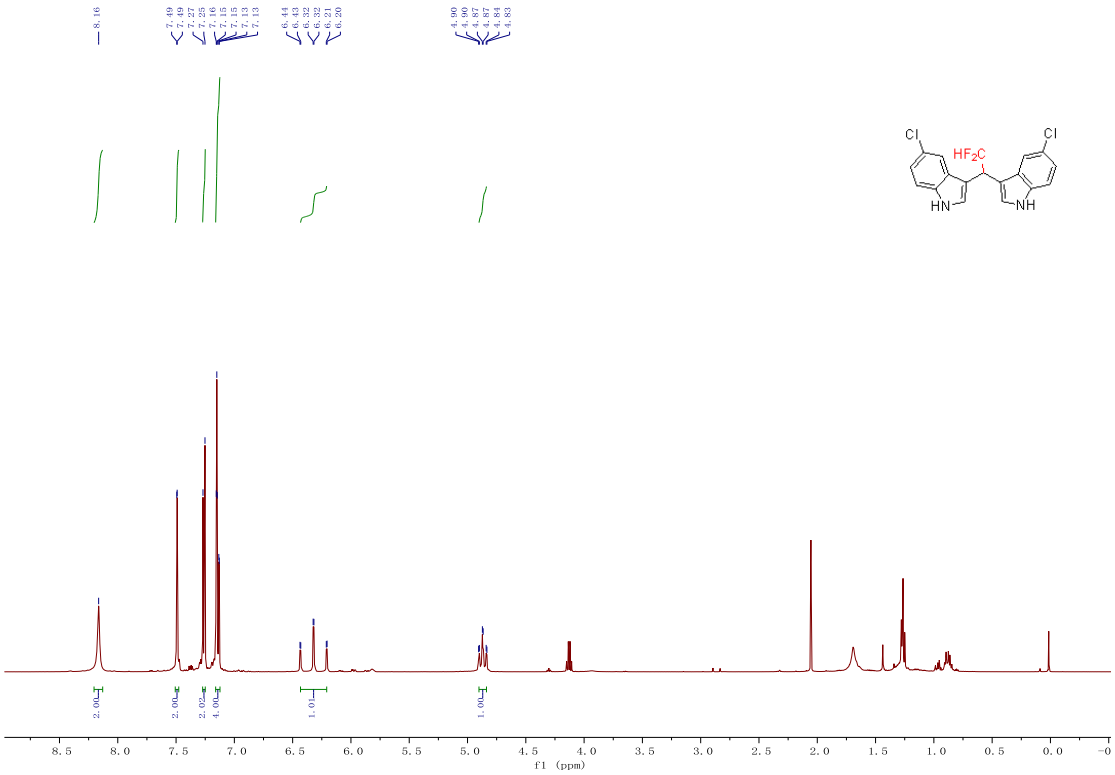
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4f**



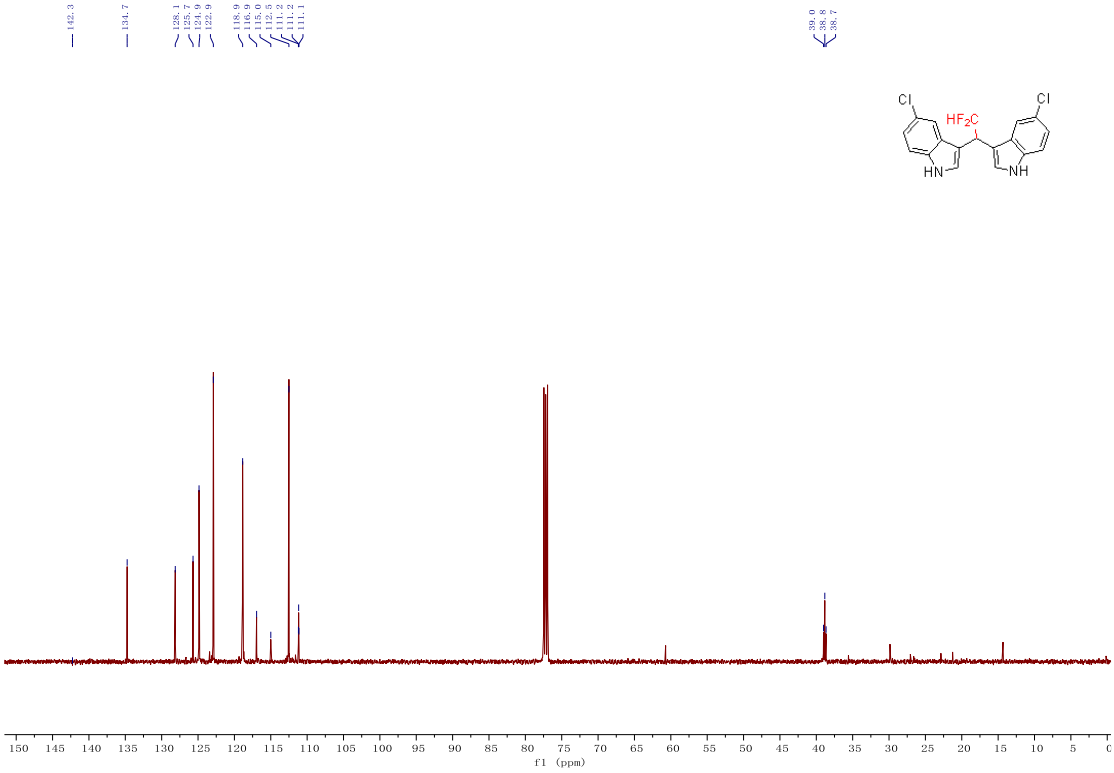
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4f**



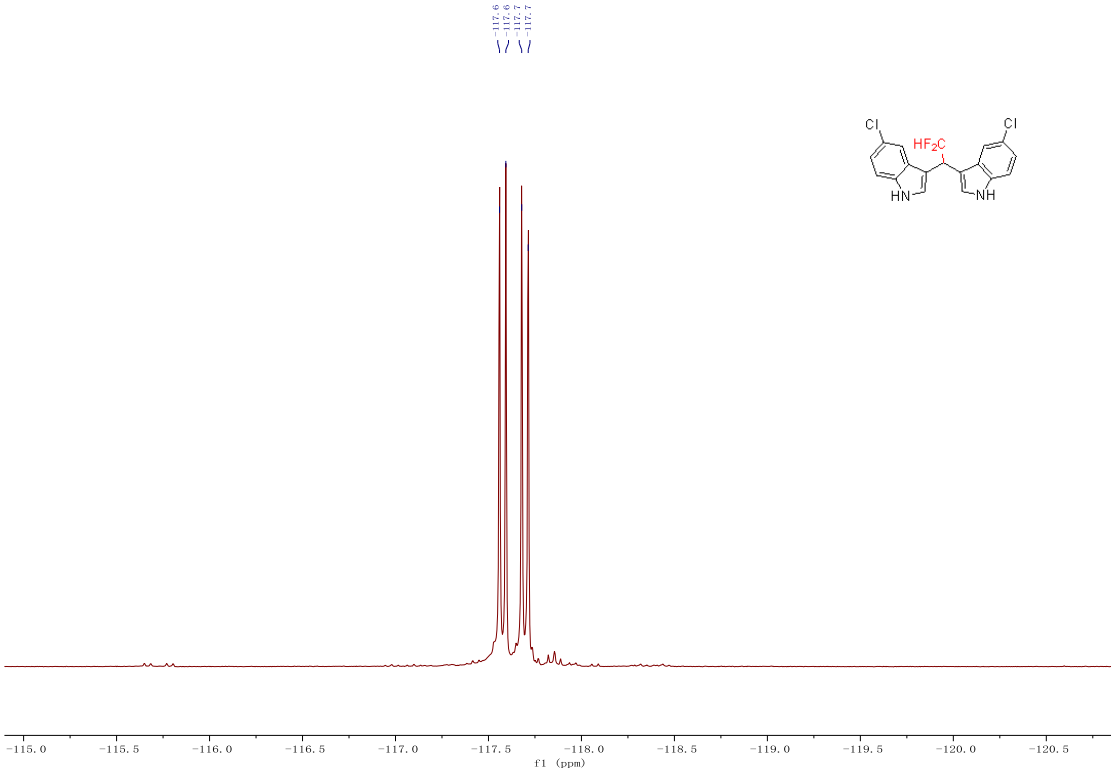
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4g**



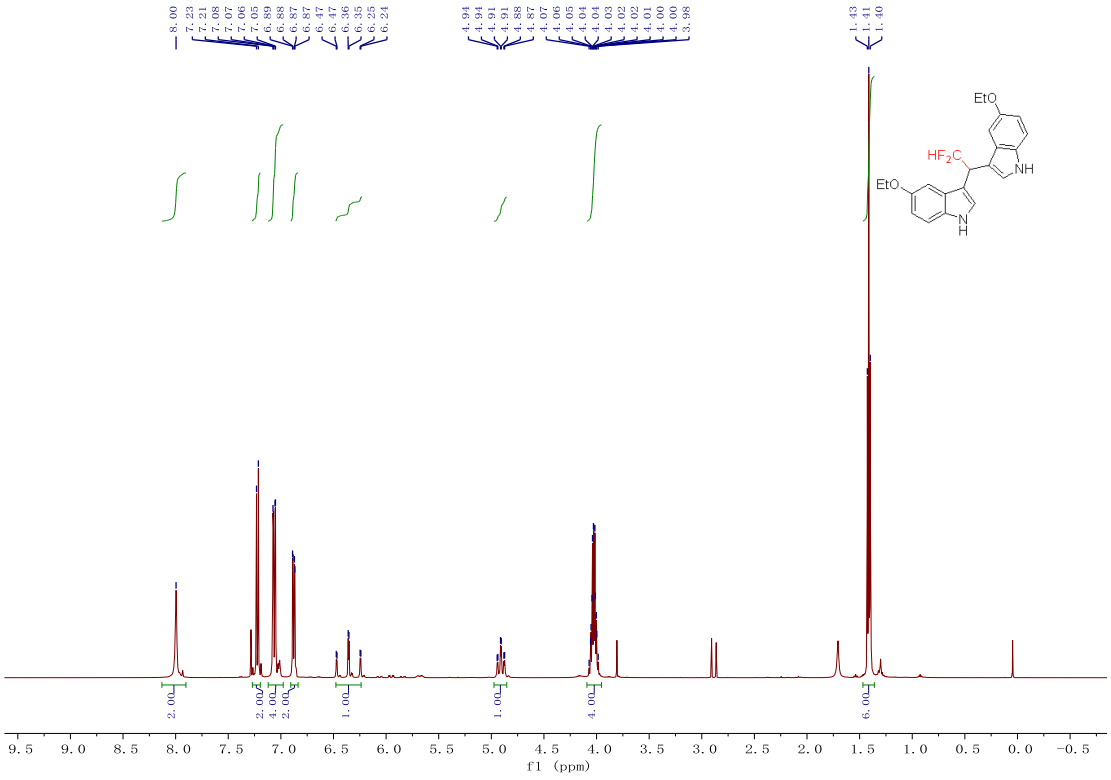
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4g**



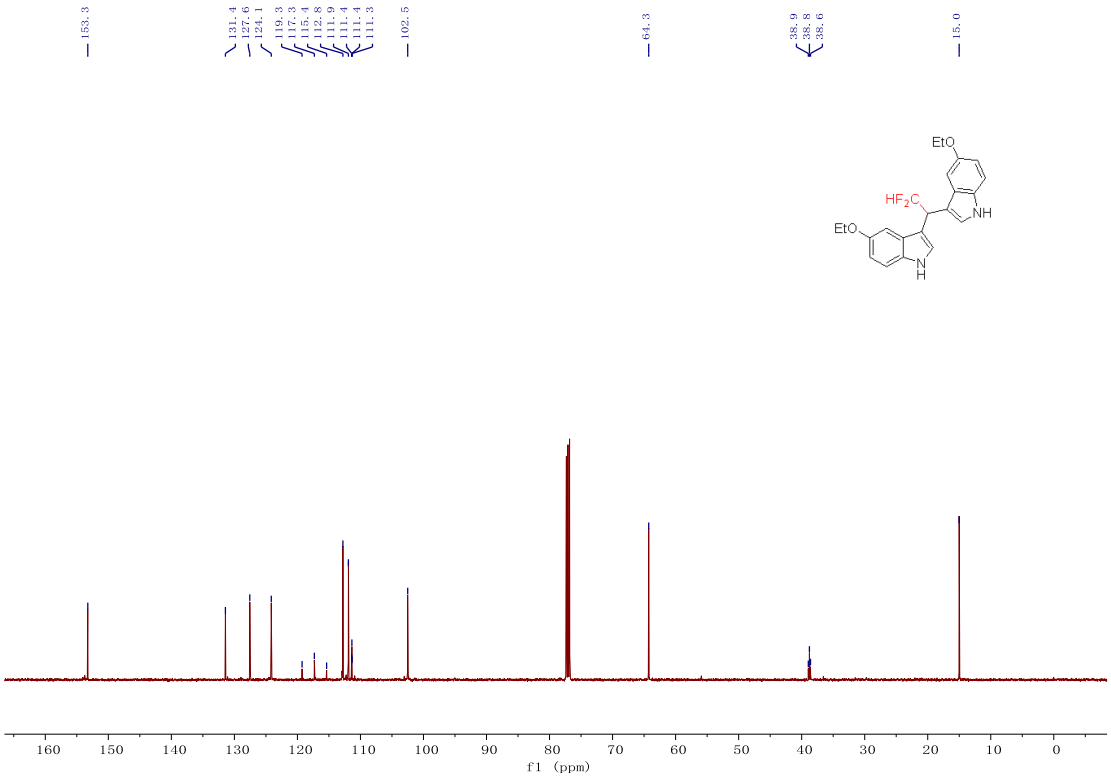
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4g**



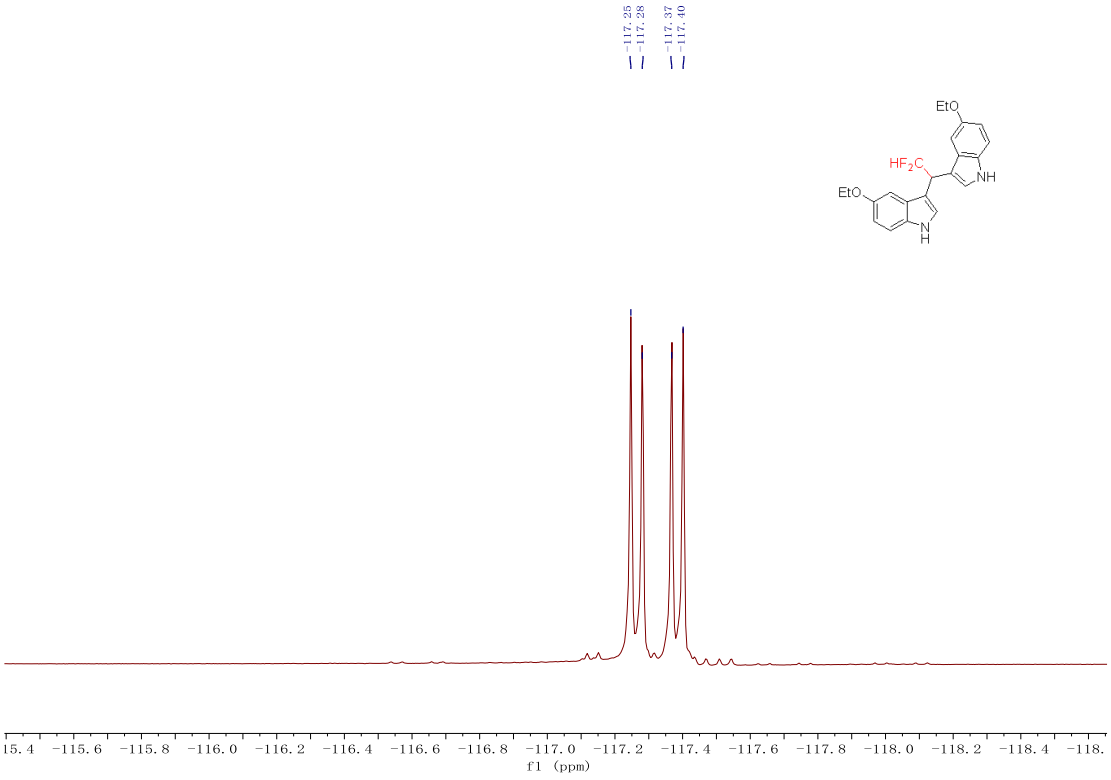
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4h**



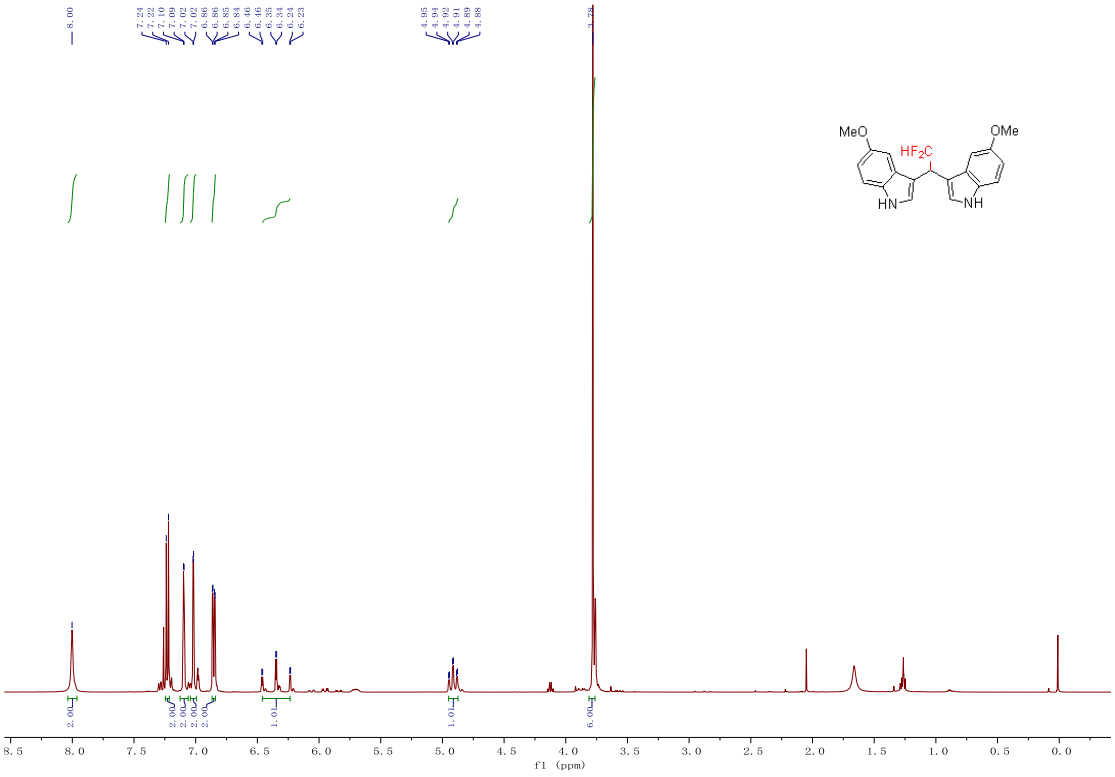
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4h**



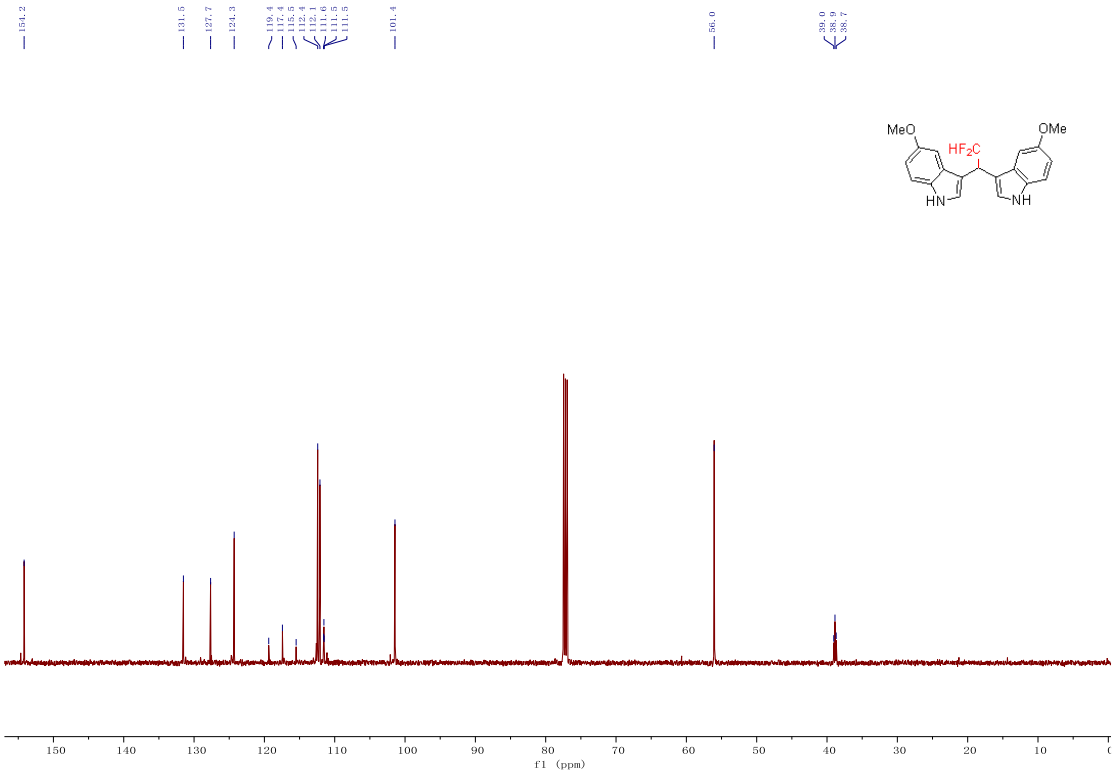
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4h**



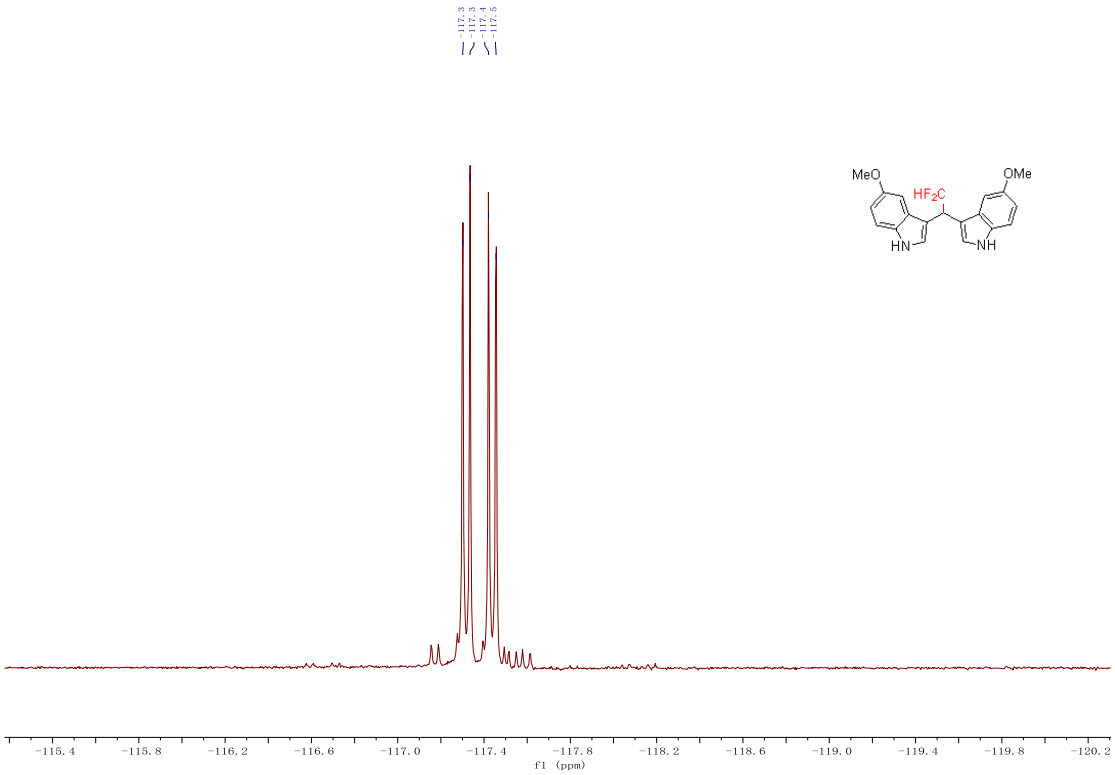
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4i**



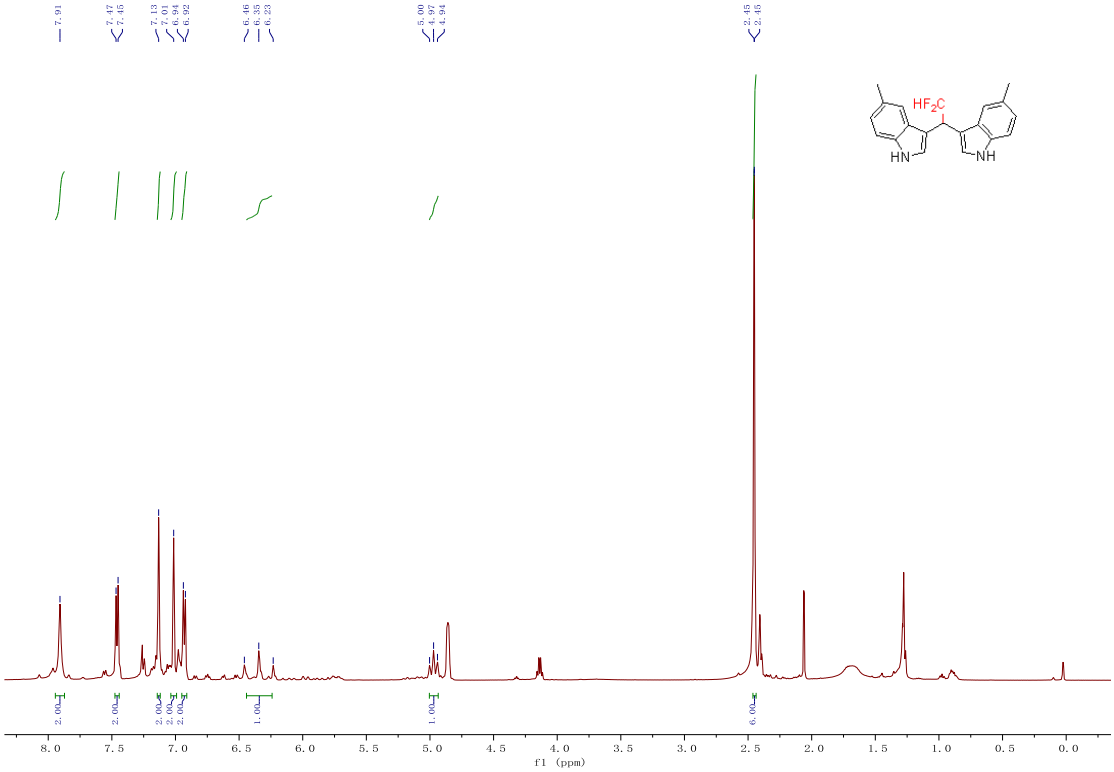
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4i**



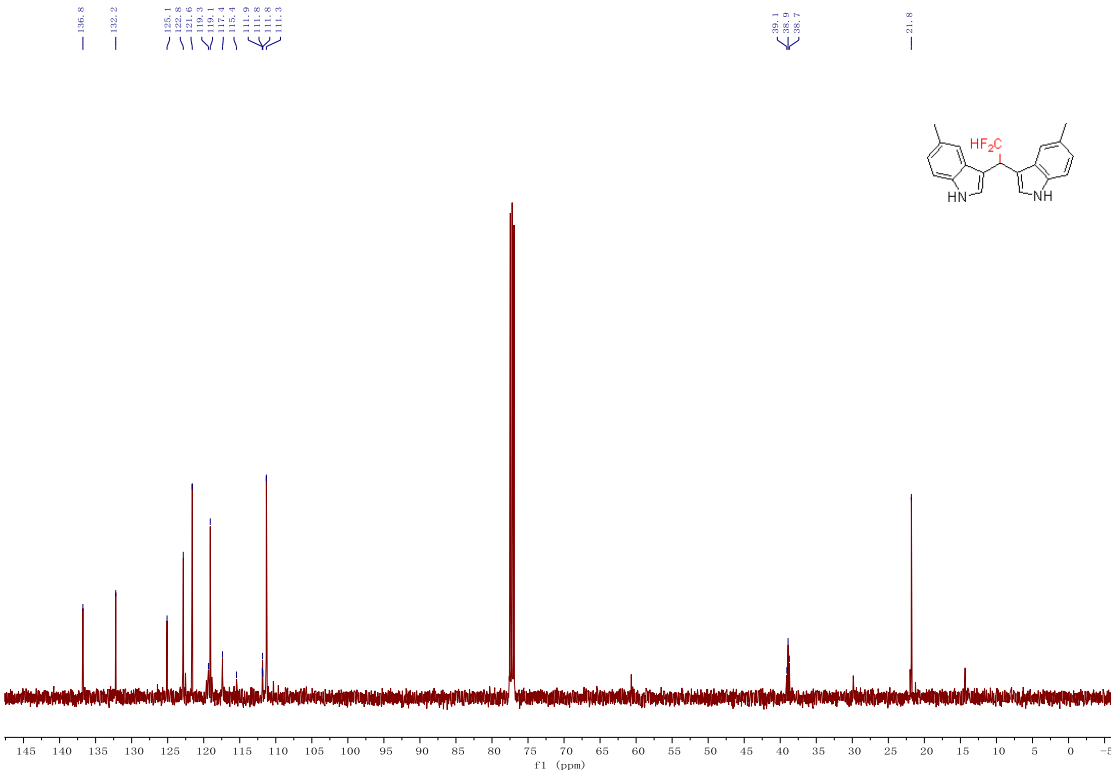
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4i**



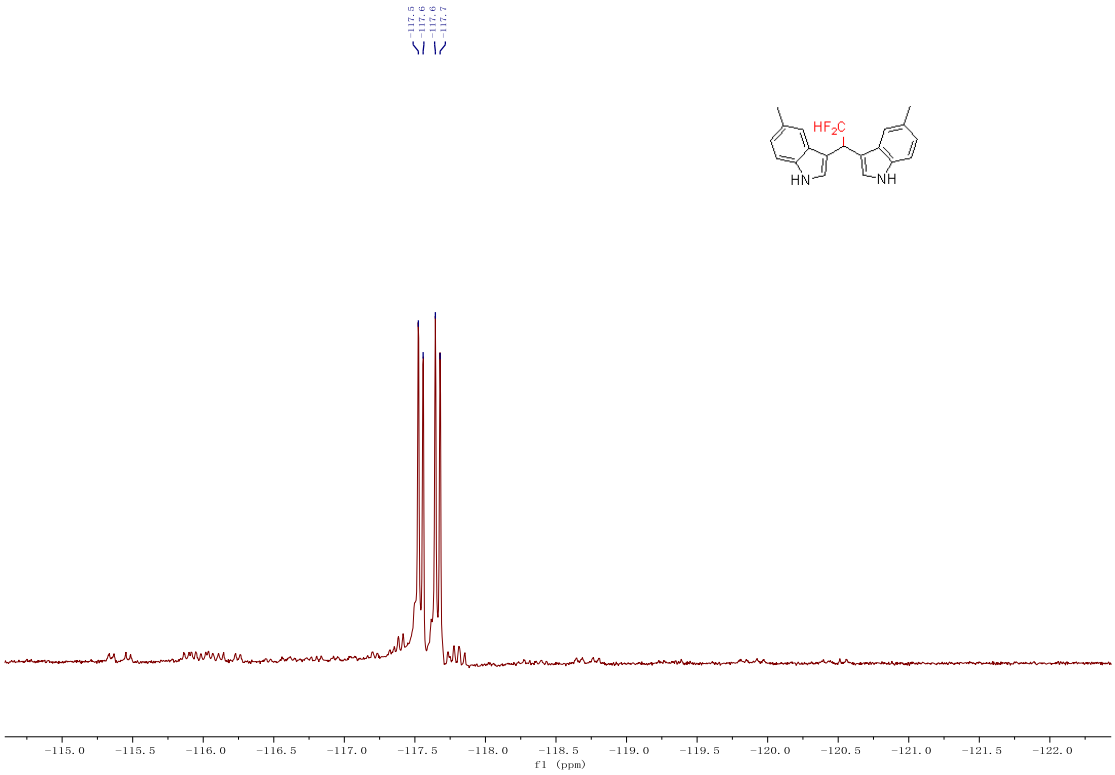
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4j**



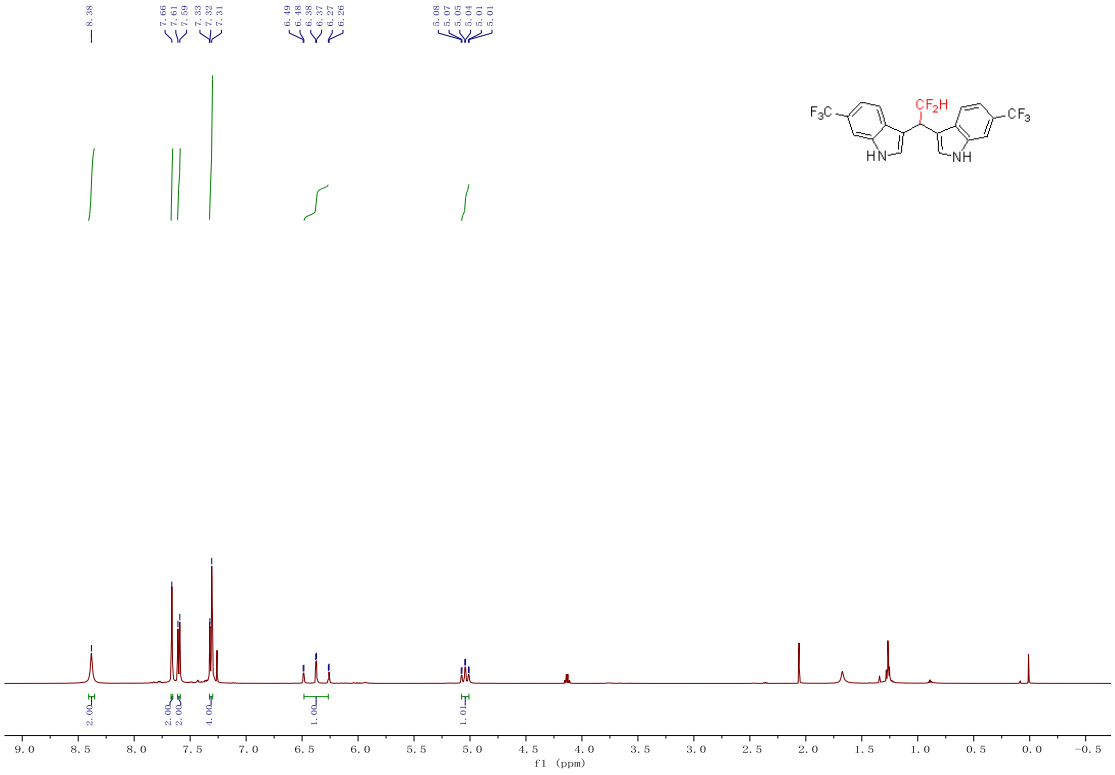
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4j**



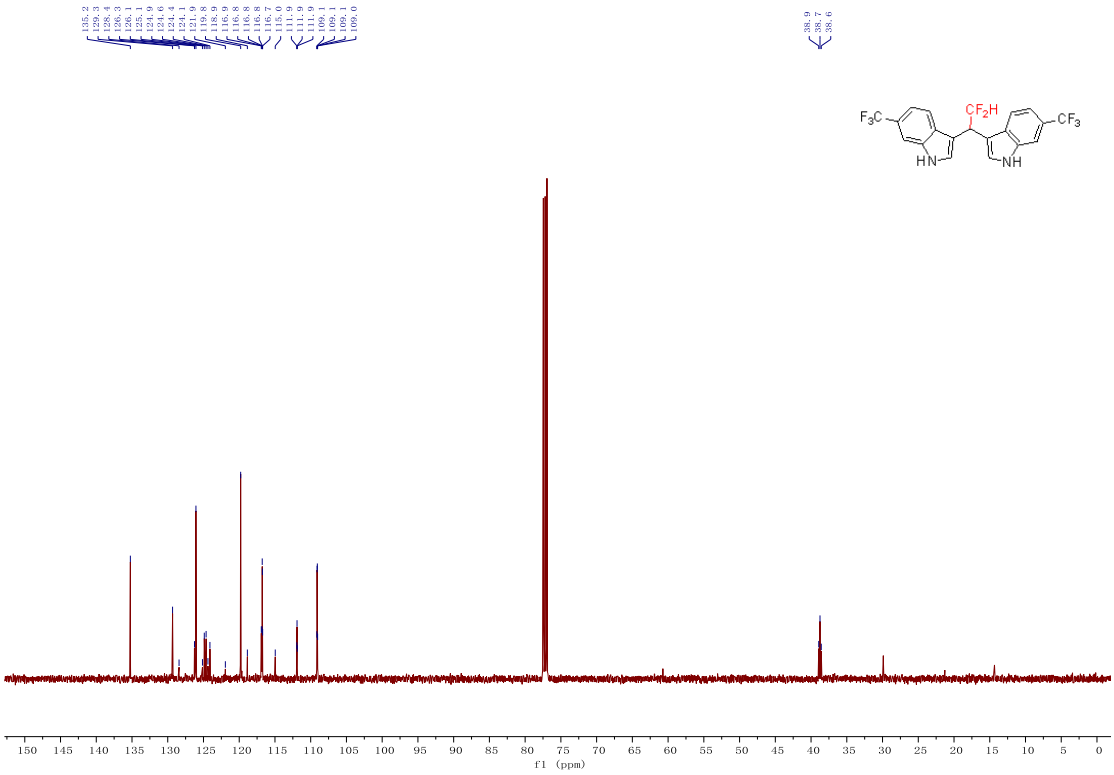
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4j**



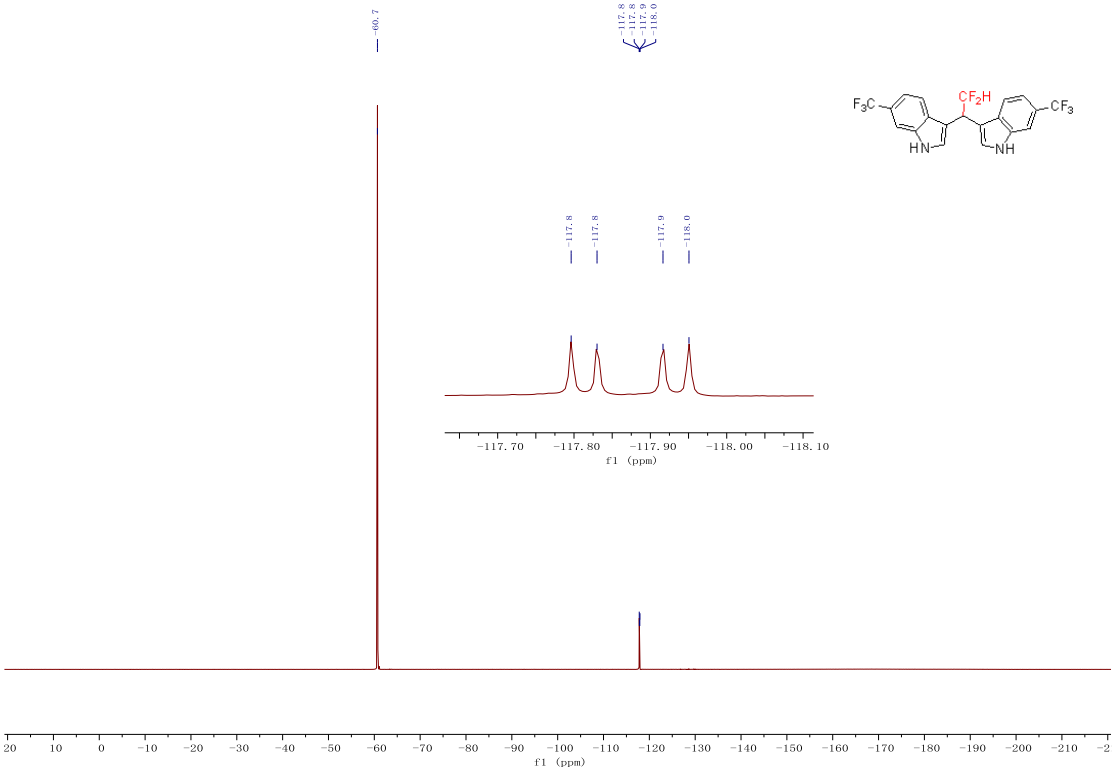
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4k**



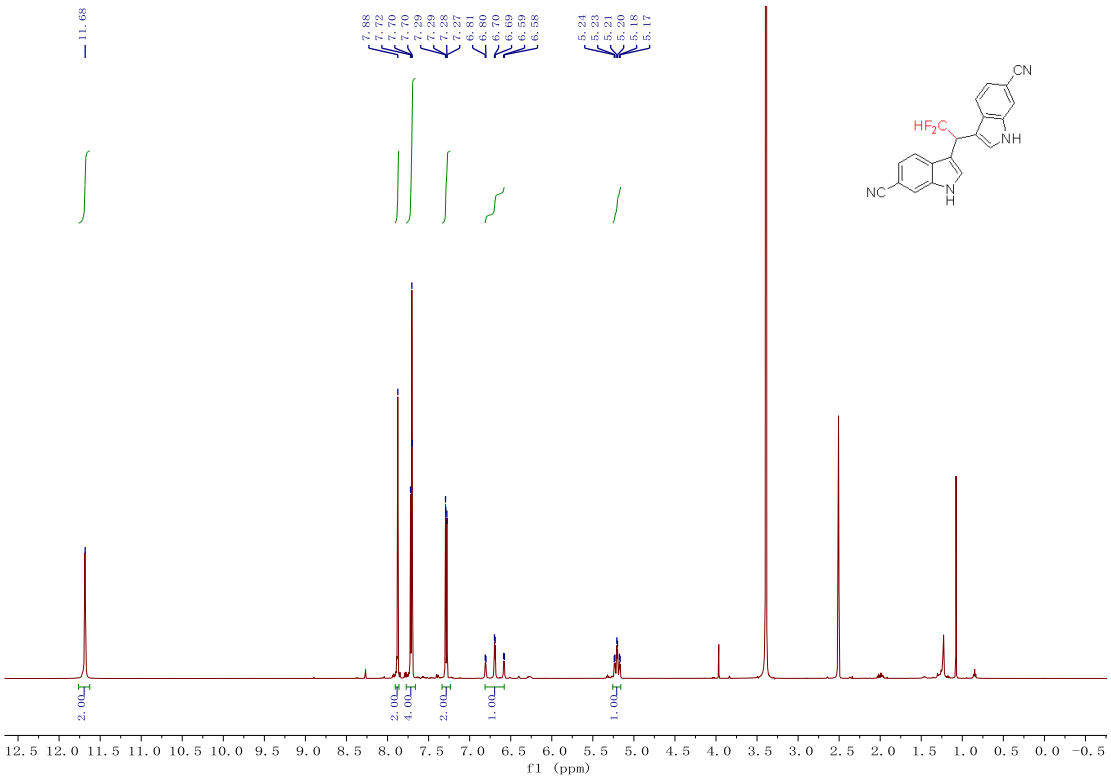
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4k**



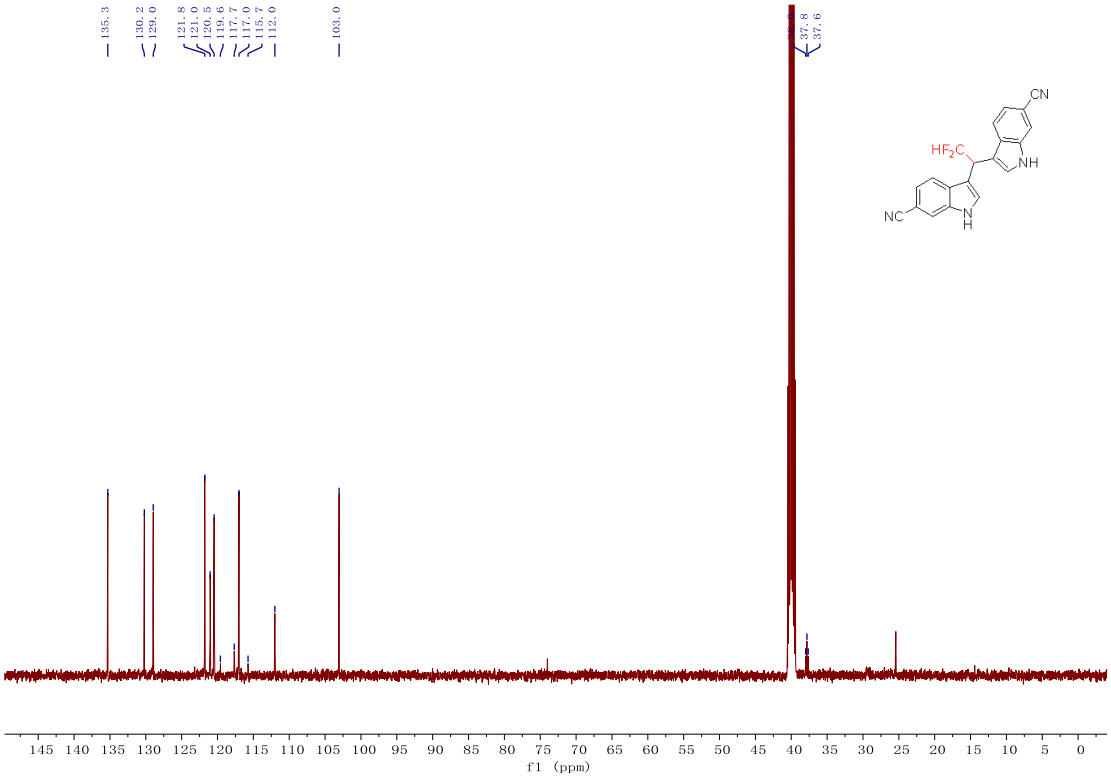
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4k**



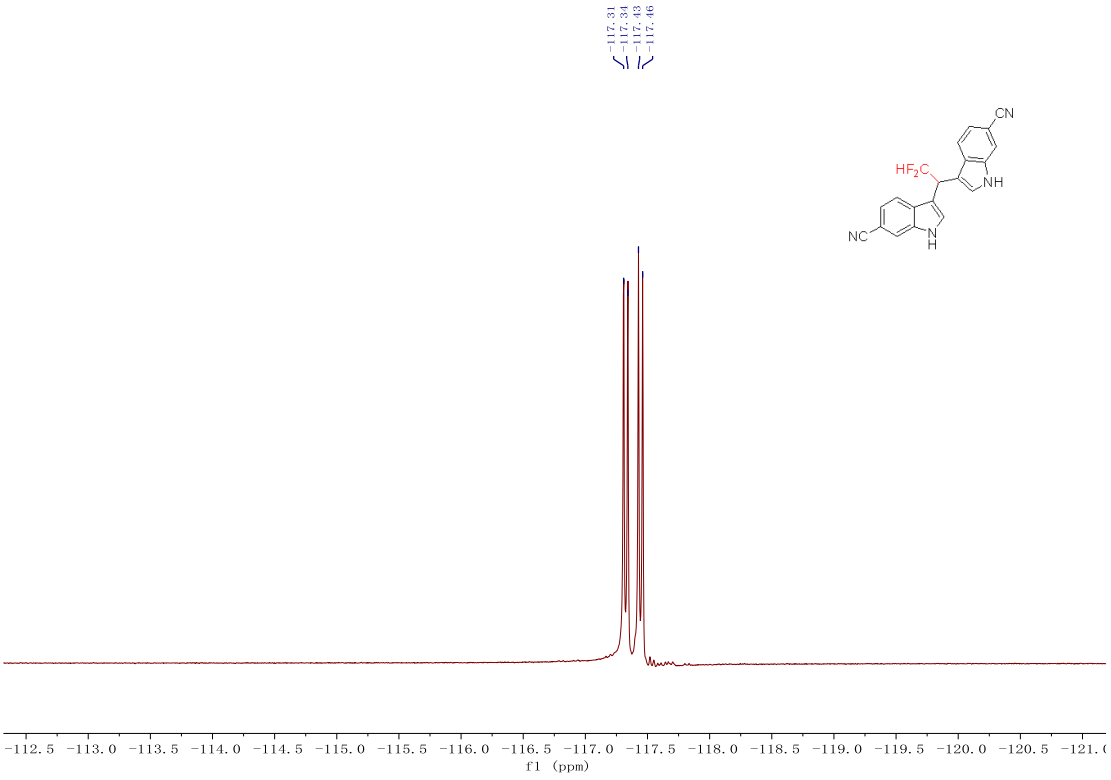
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4l**



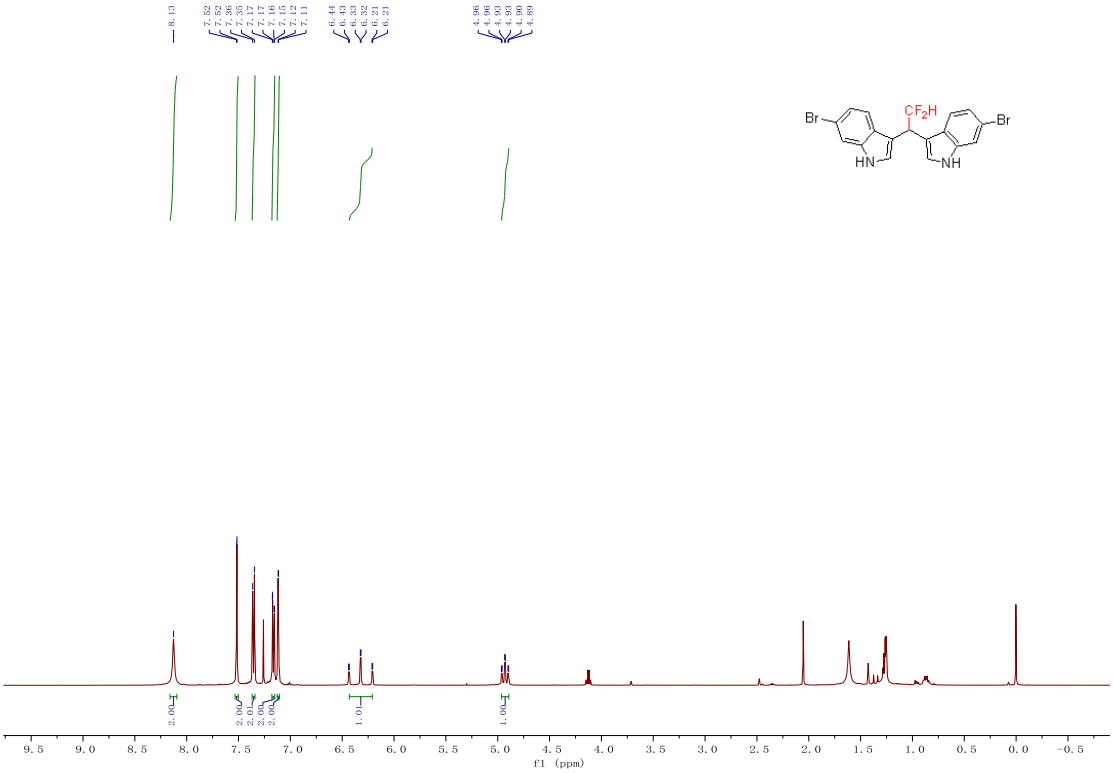
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4l**



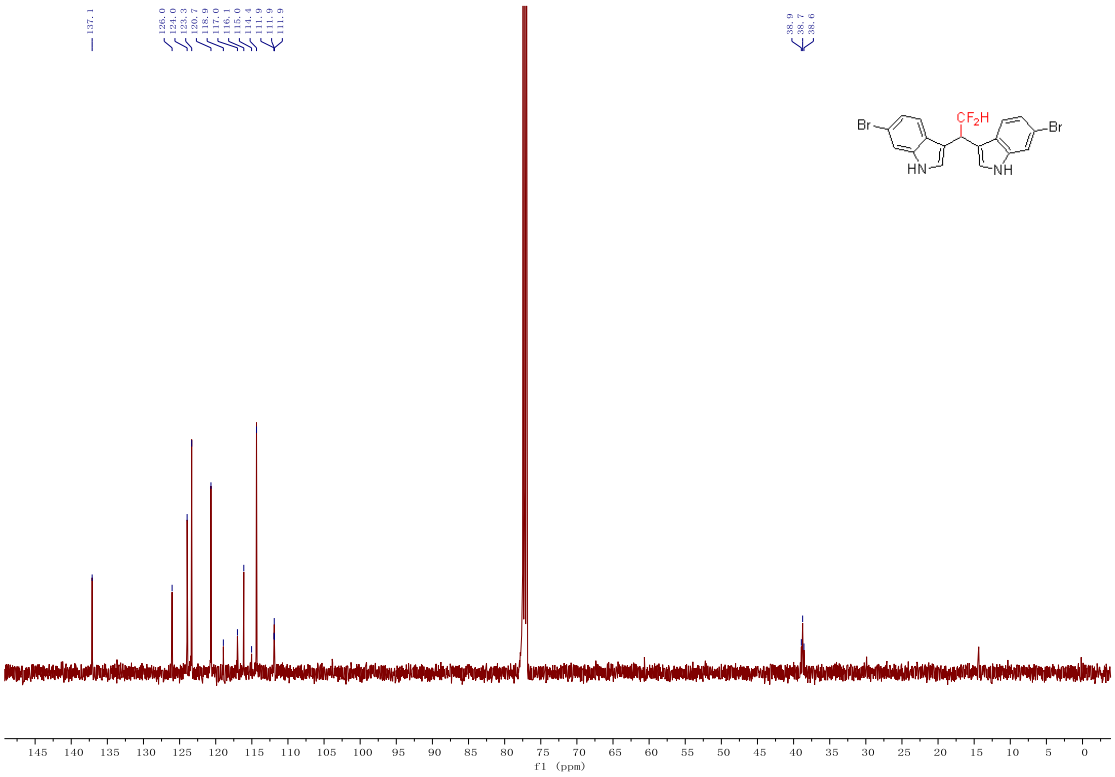
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4l**



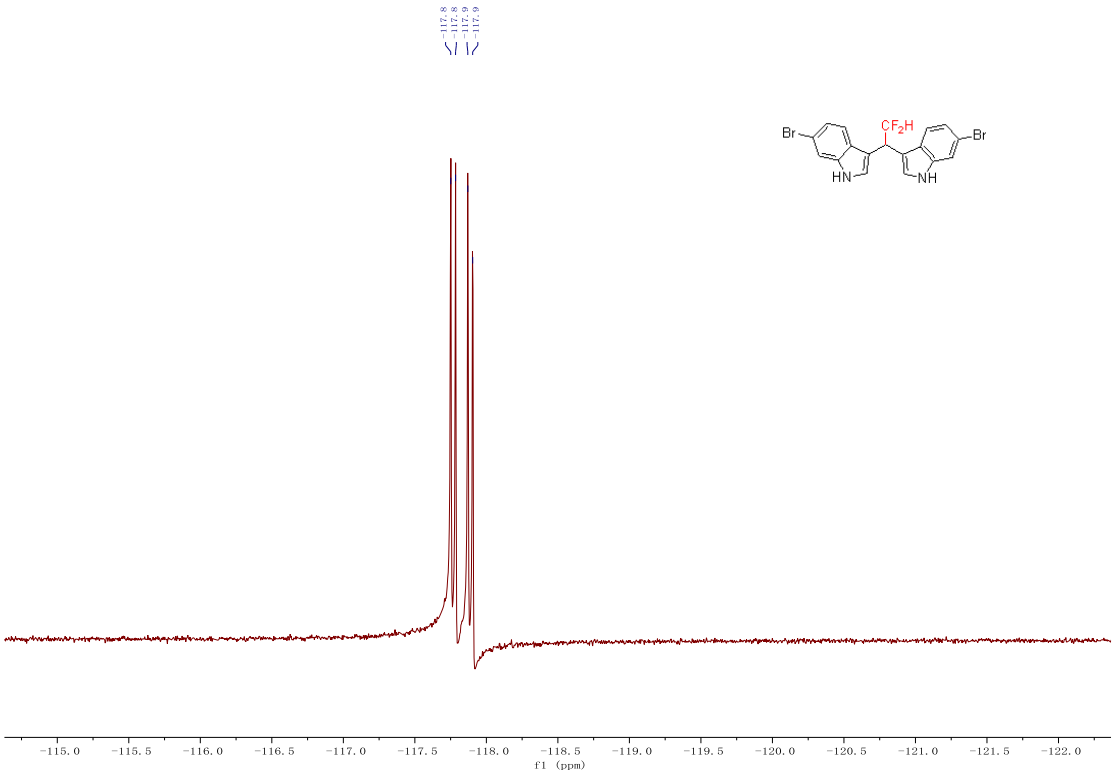
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4m**



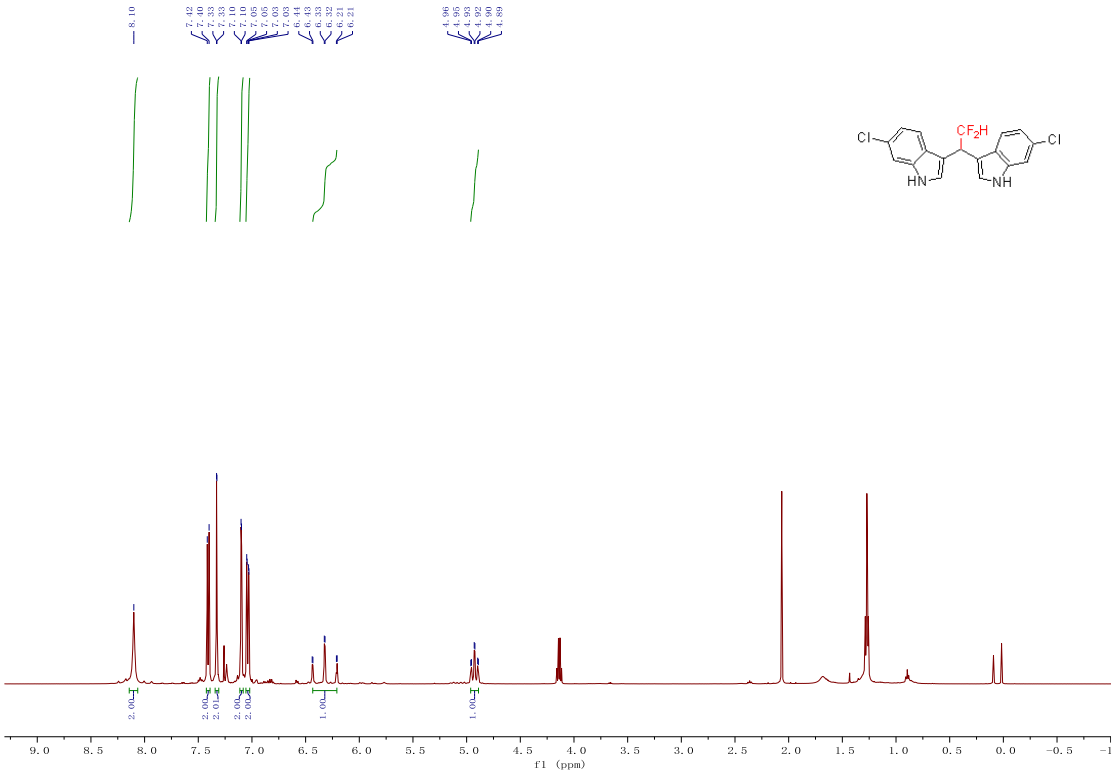
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4m**



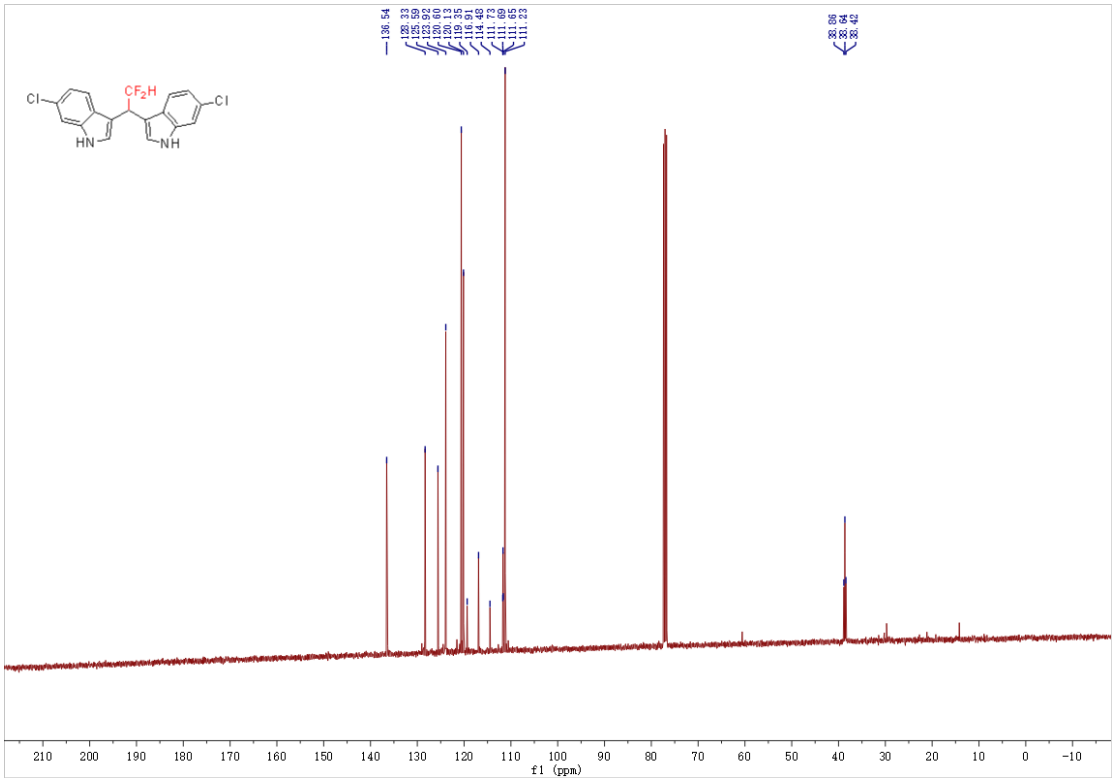
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4m**



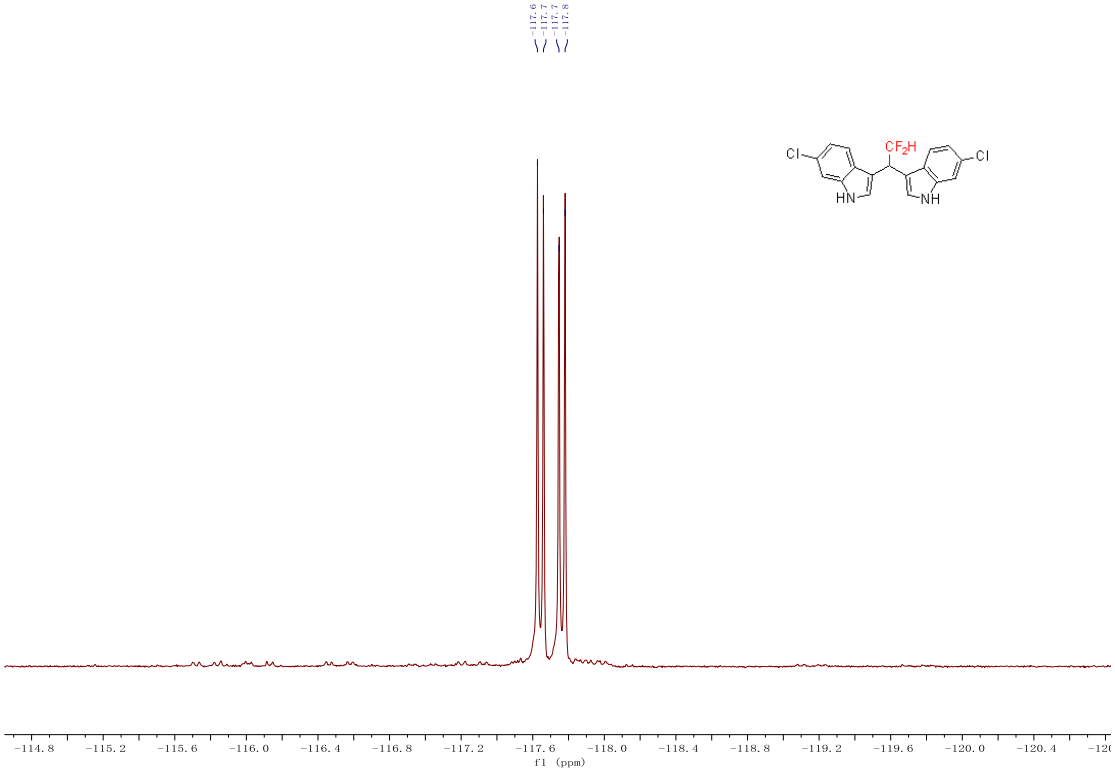
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4n**



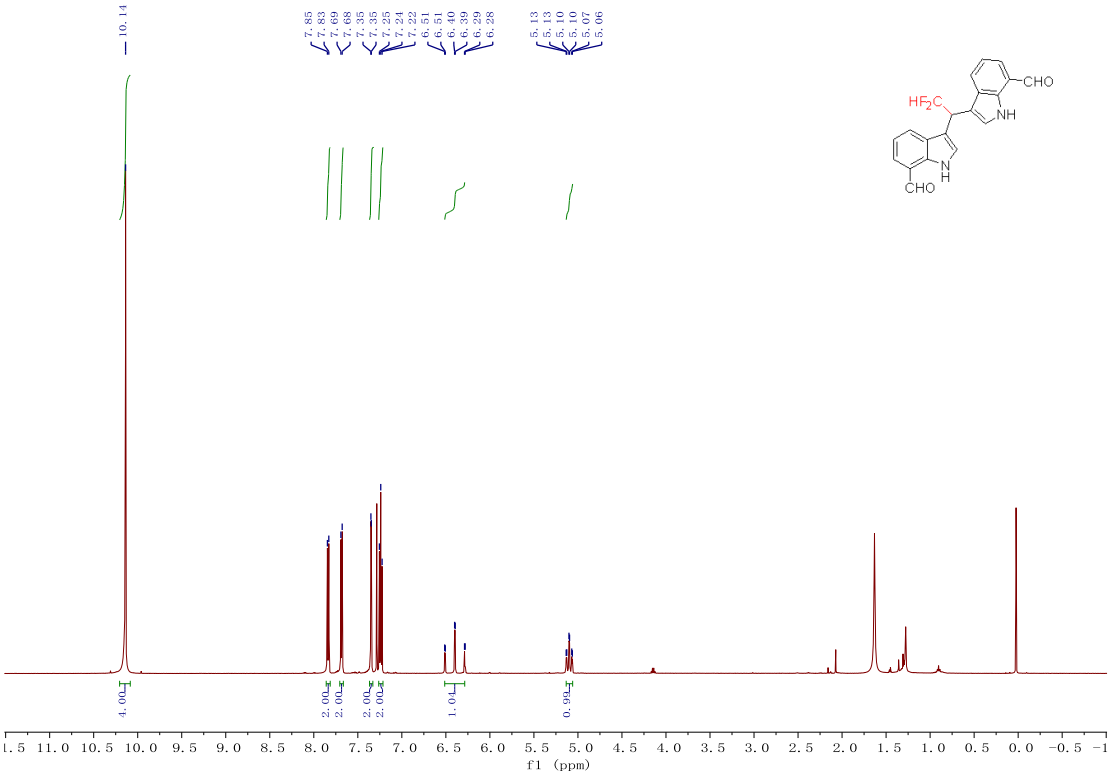
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4n**



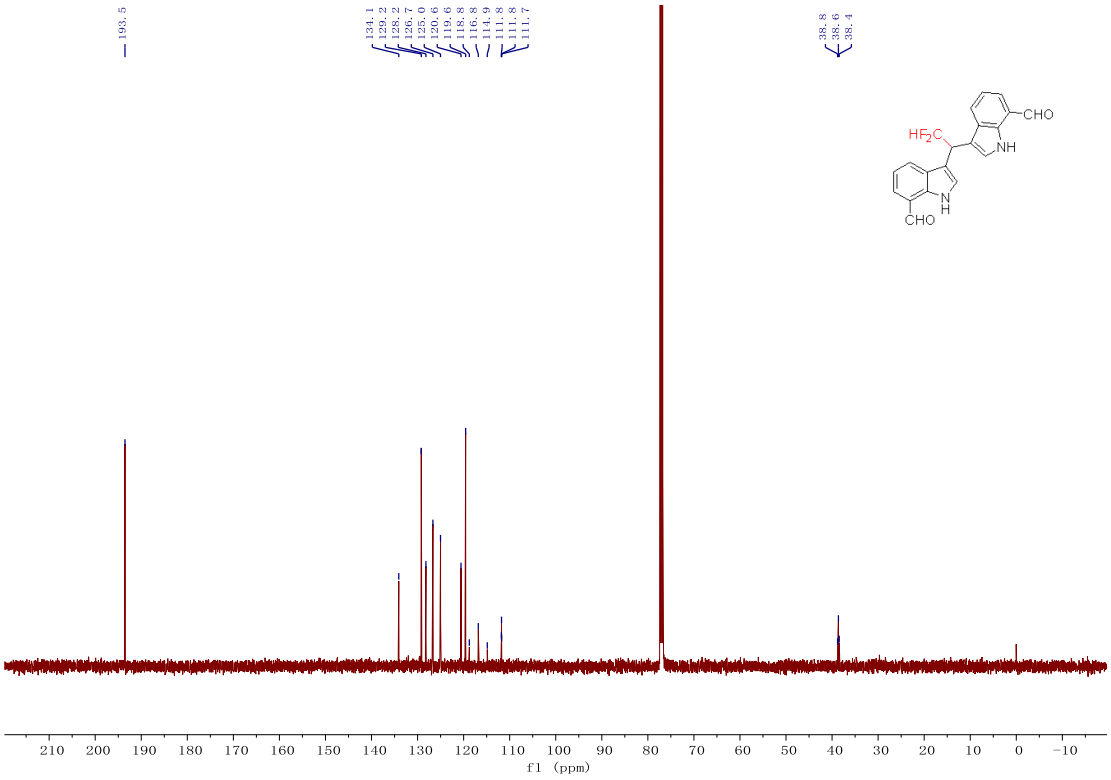
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4n**



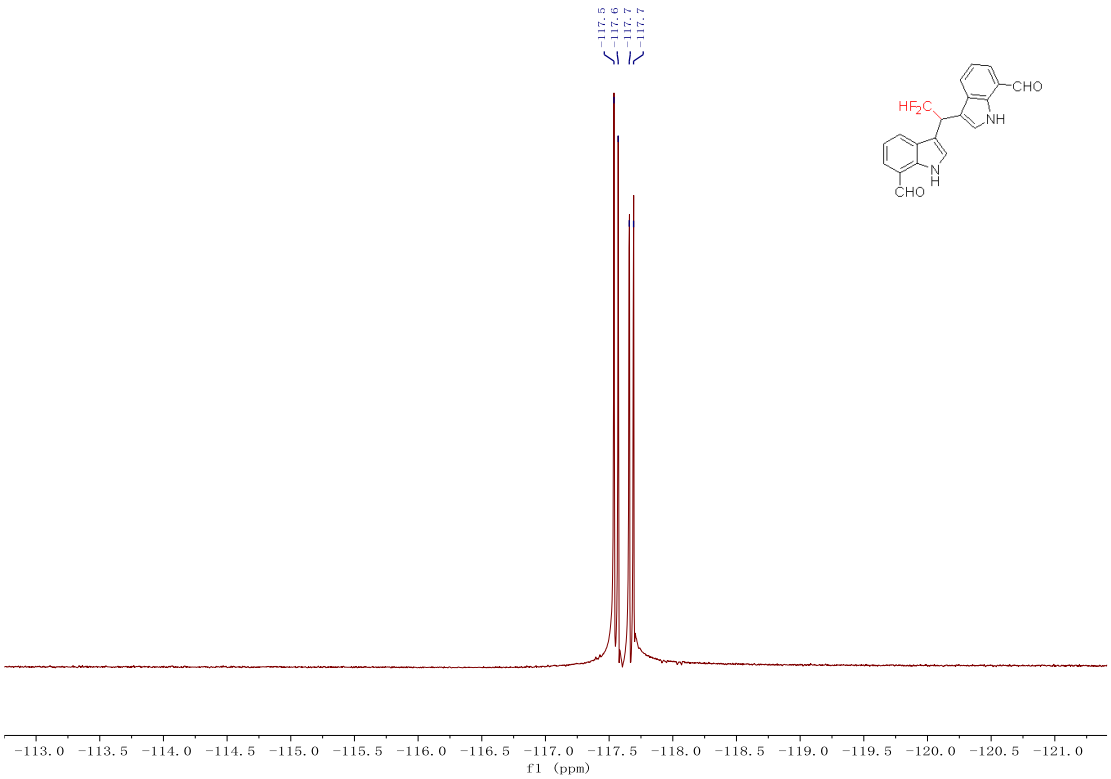
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4o**



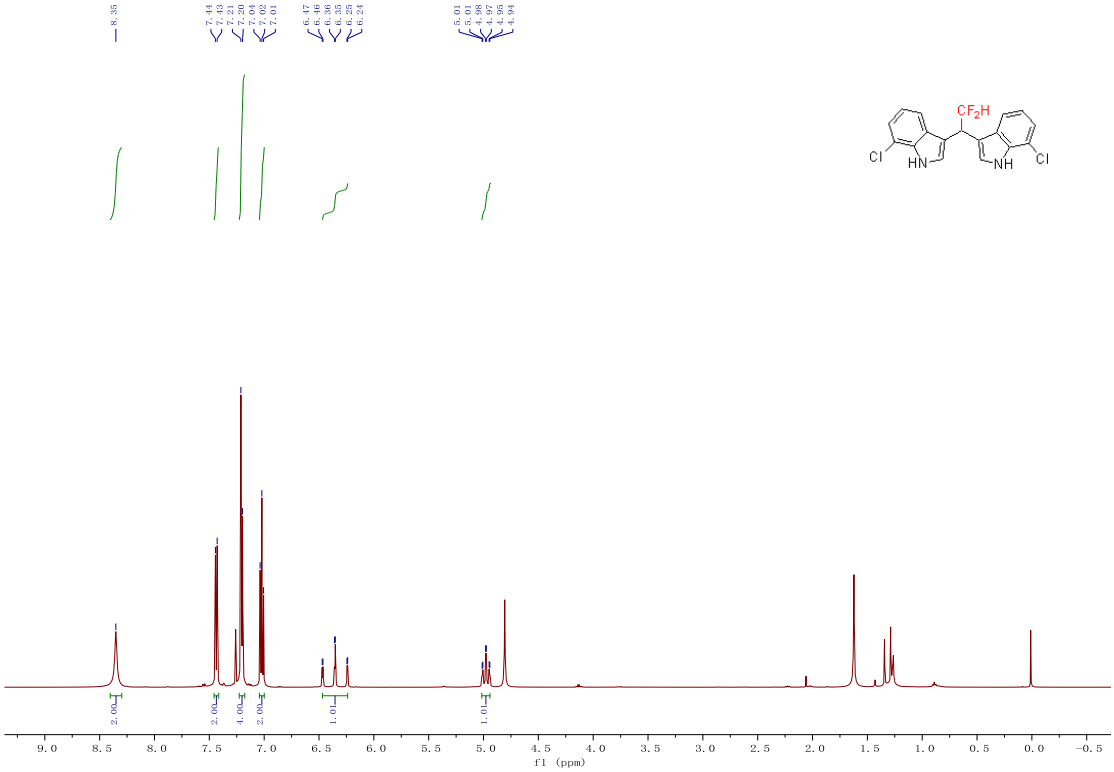
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4o**



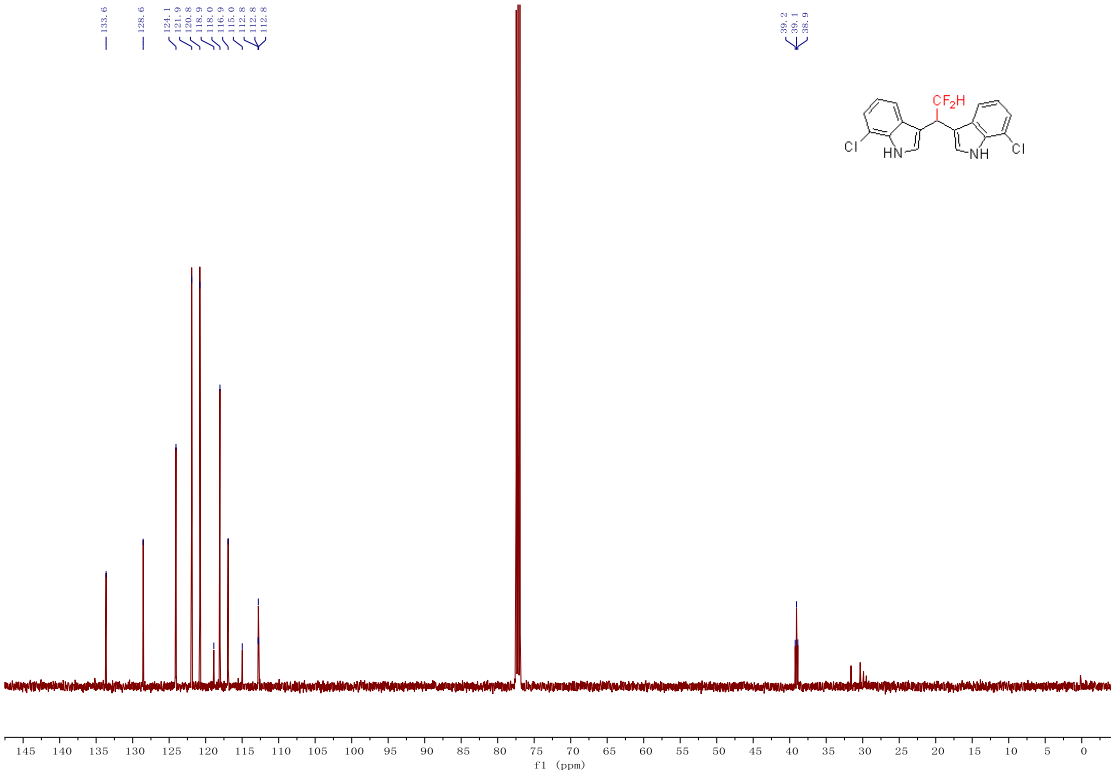
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4o**



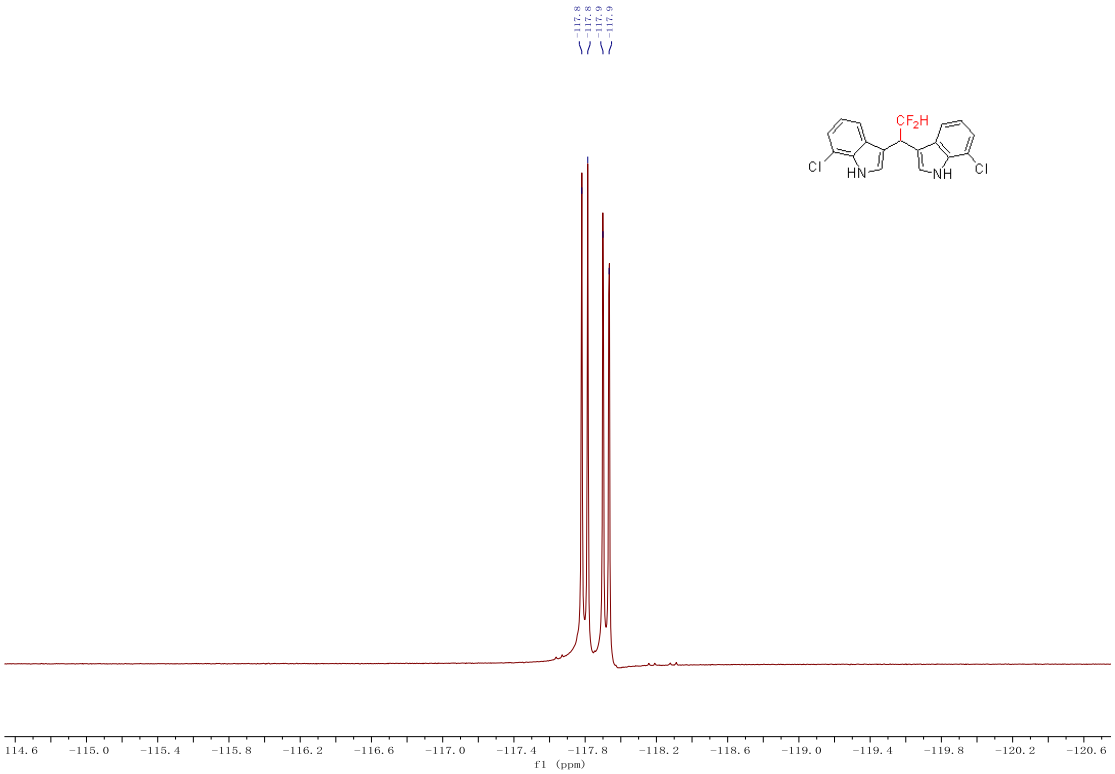
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4p**



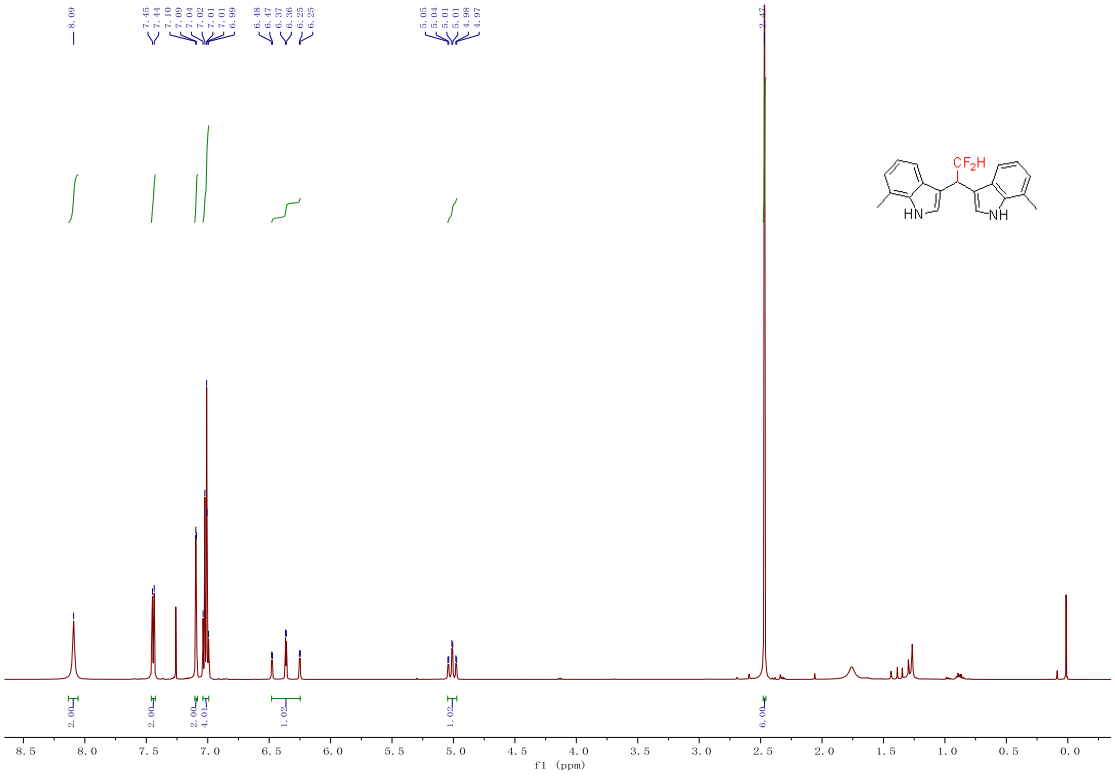
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4p**



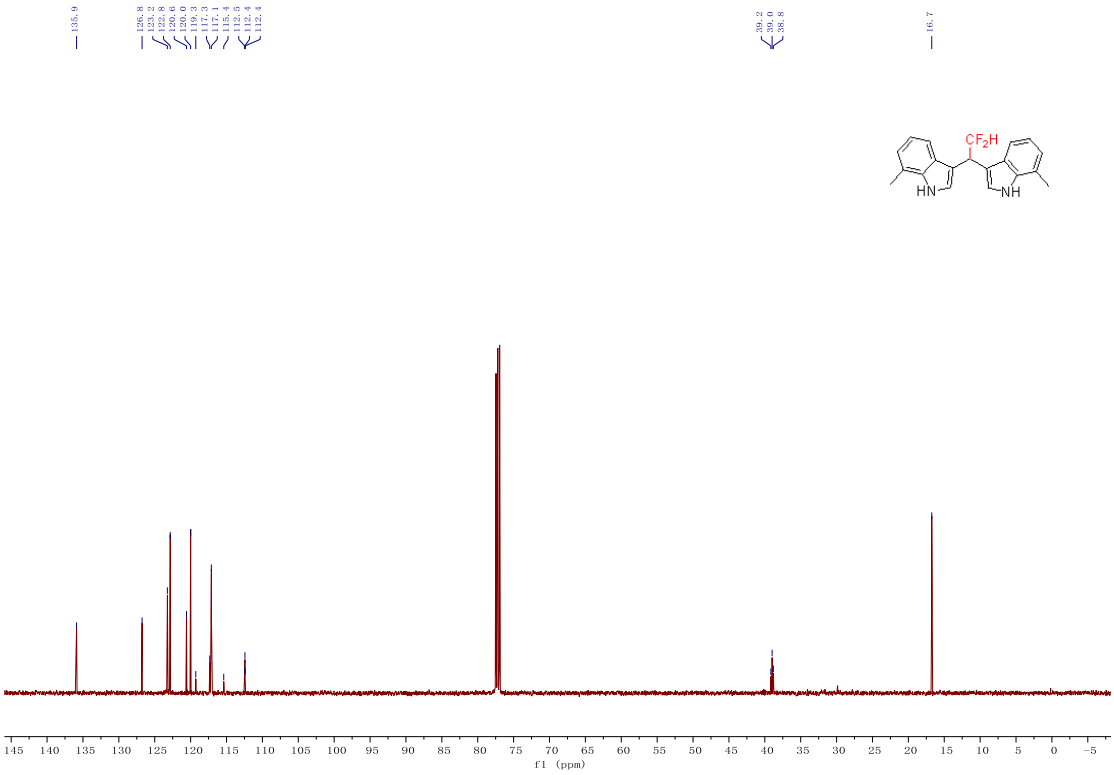
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4p**



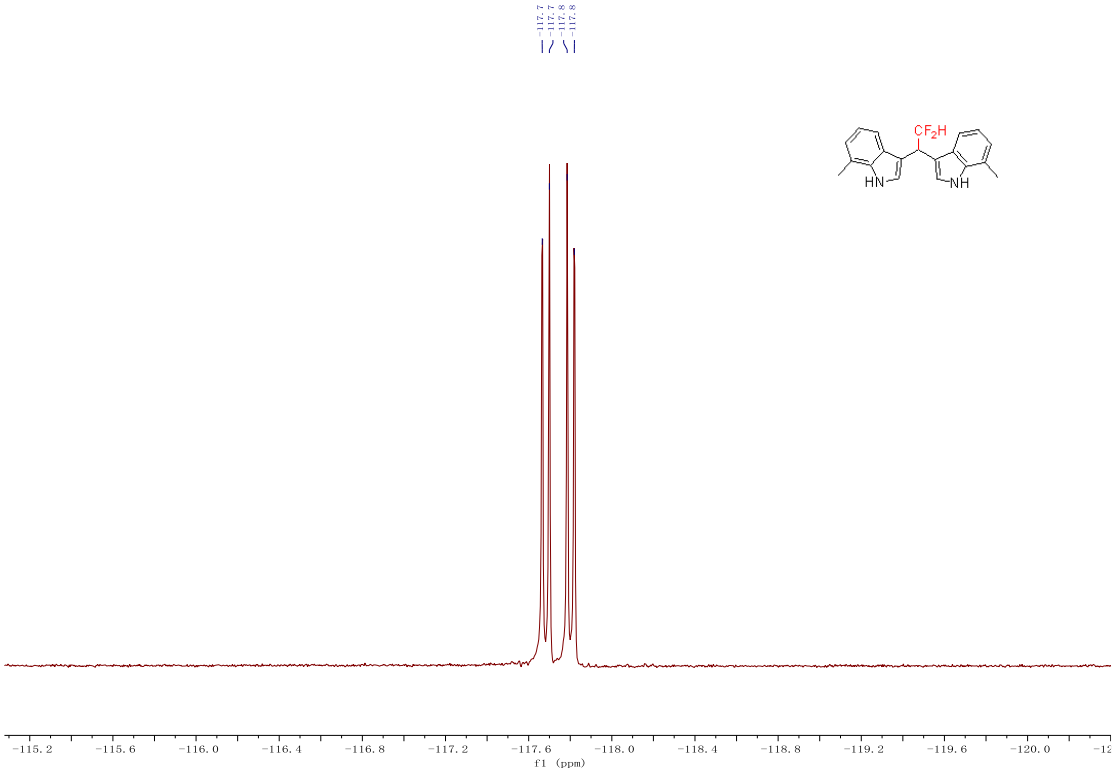
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4q**



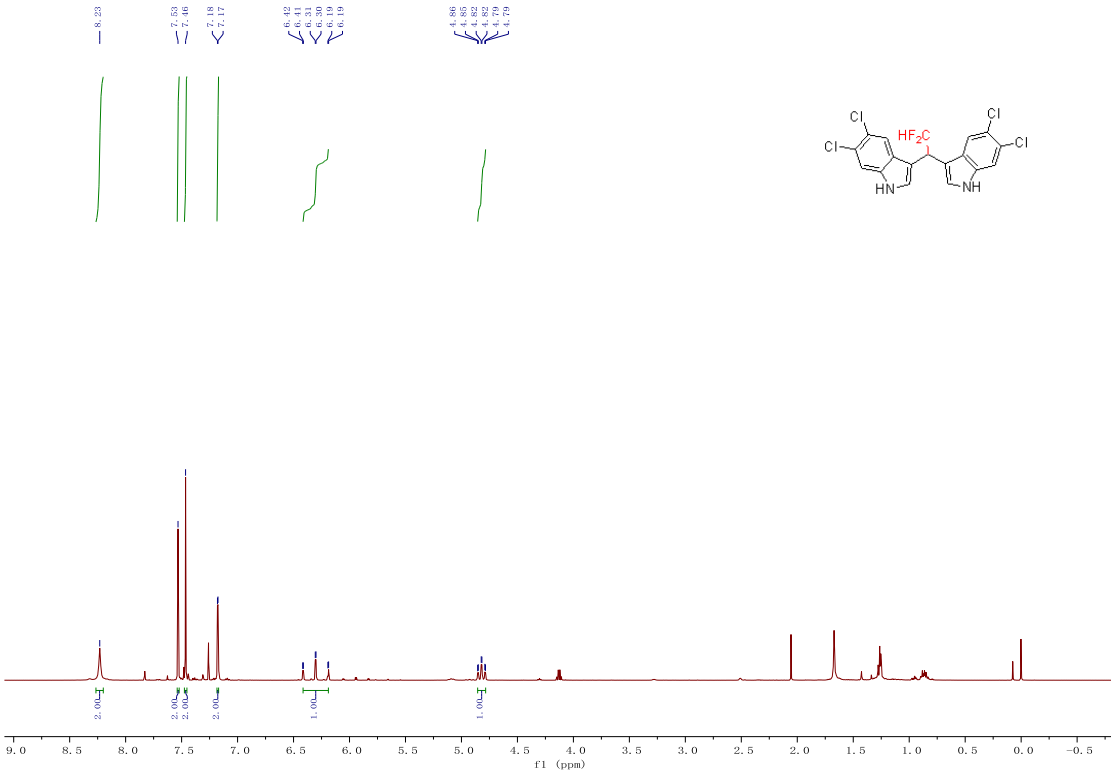
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4q**



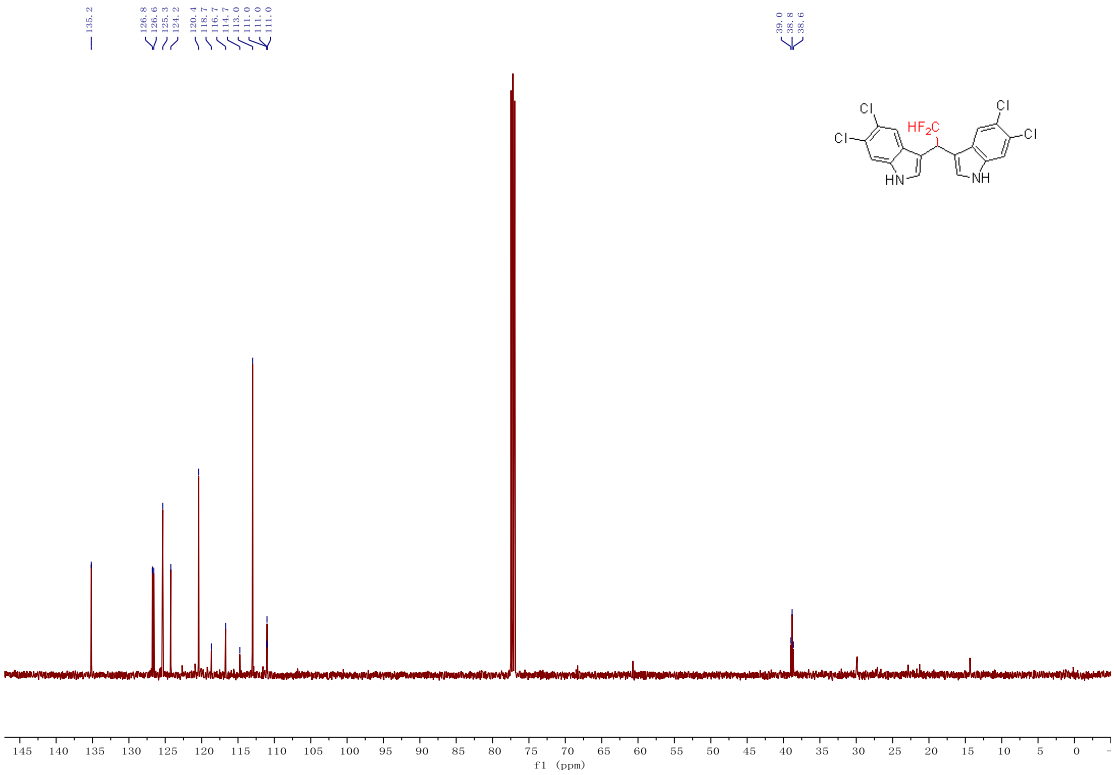
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4q**



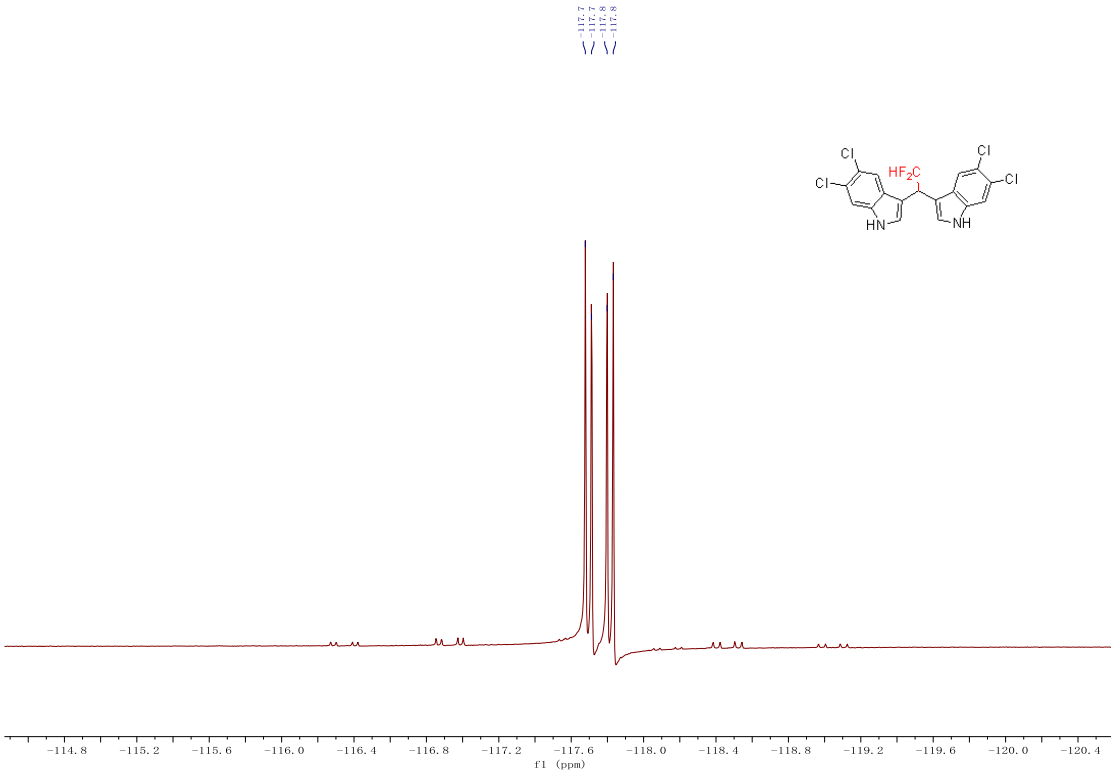
^{1}H NMR (500 MHz, Methanol-d_4) spectra of **4r**



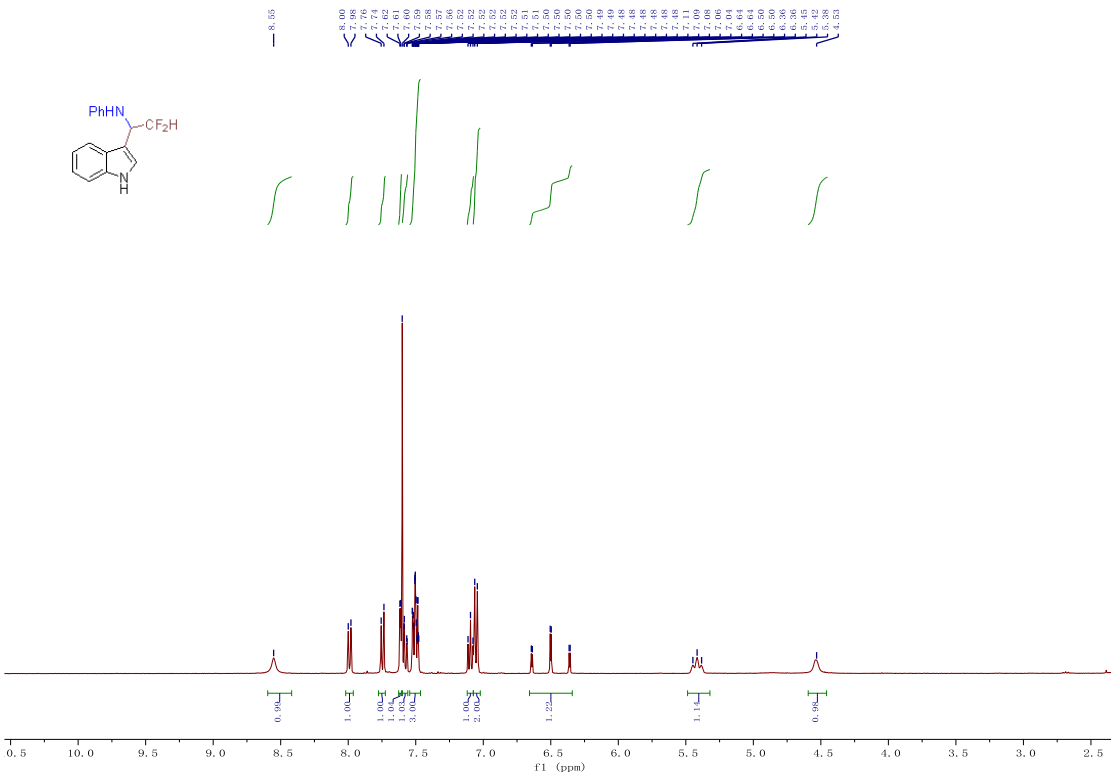
^{13}C NMR (125 MHz, Methanol-d_4) spectra of **4r**



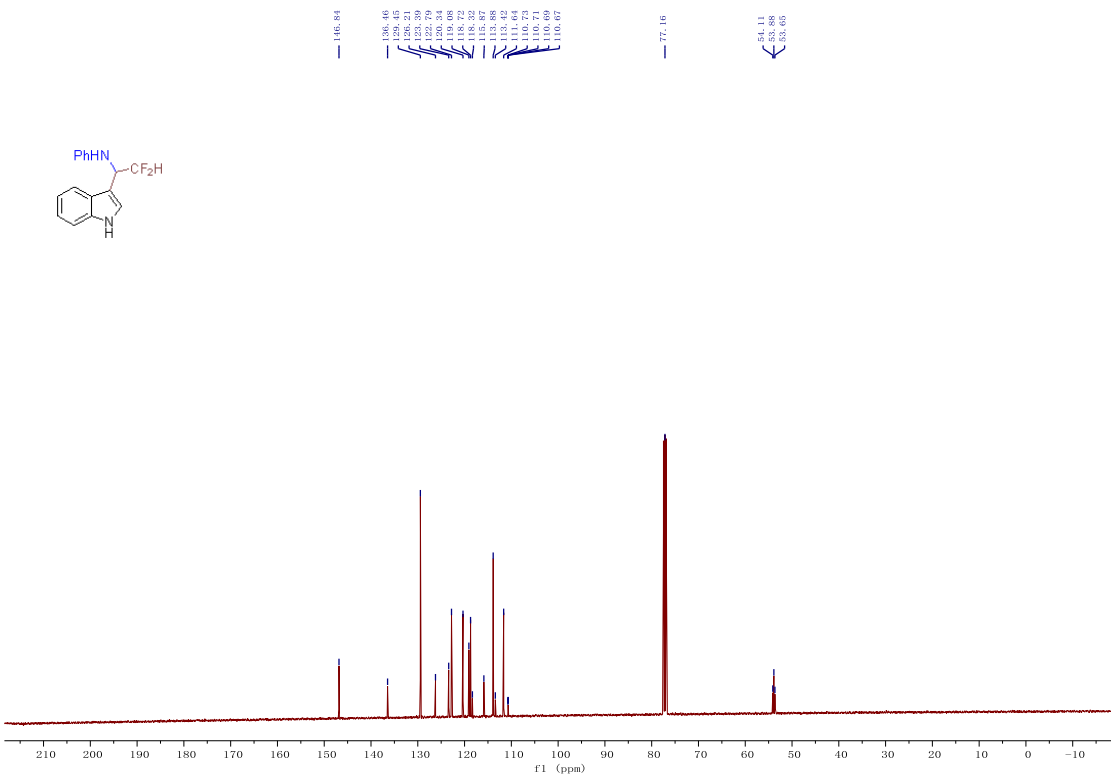
^{19}F NMR (470 MHz, Methanol-d_4) spectra of **4r**



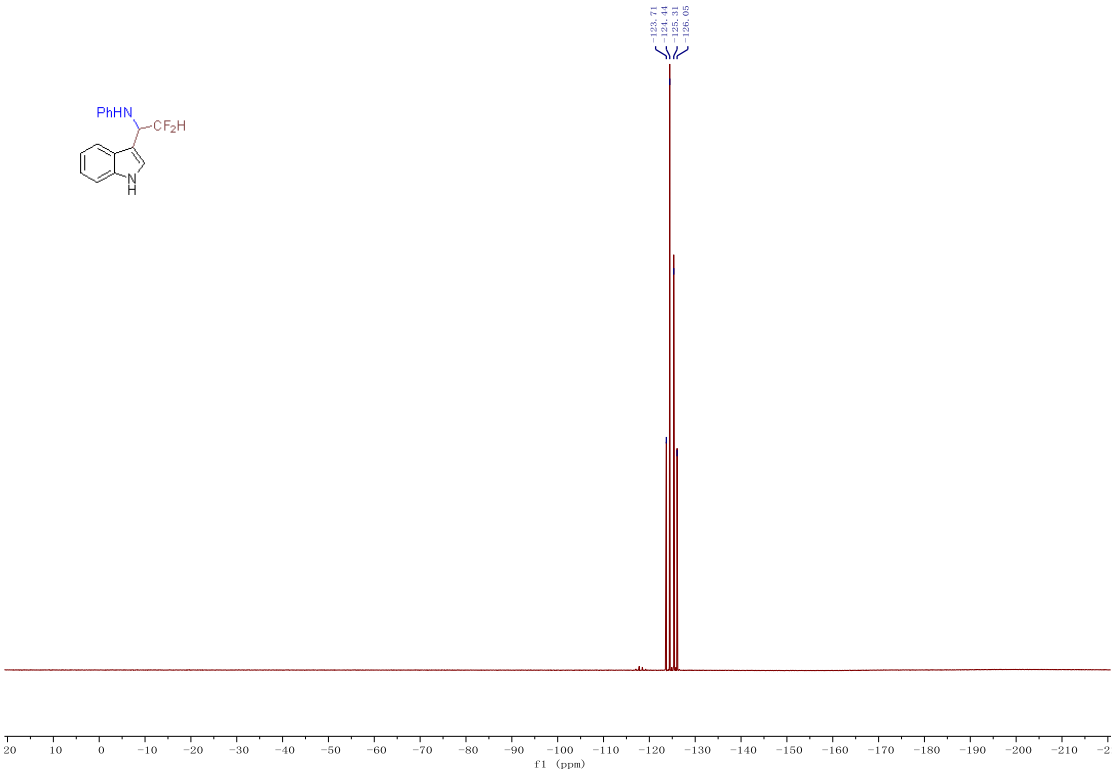
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7aa**



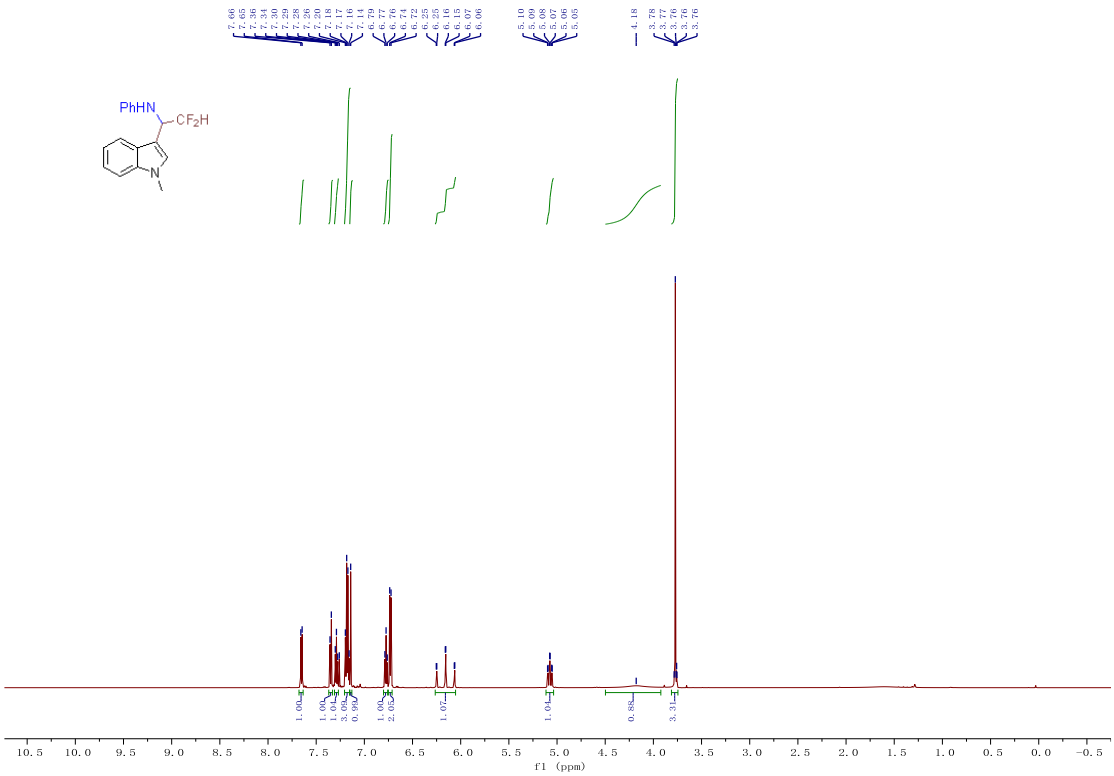
^{13}C NMR (101 MHz, Chloroform-*d*) spectra of **7aa**



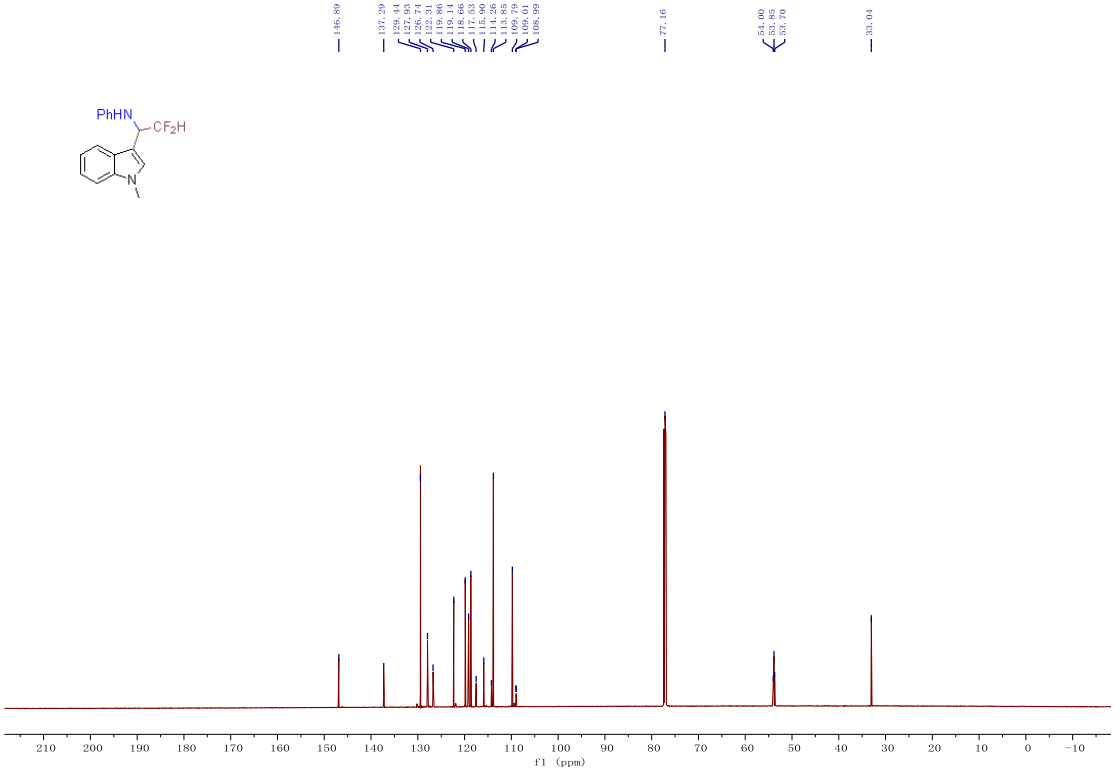
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7aa**



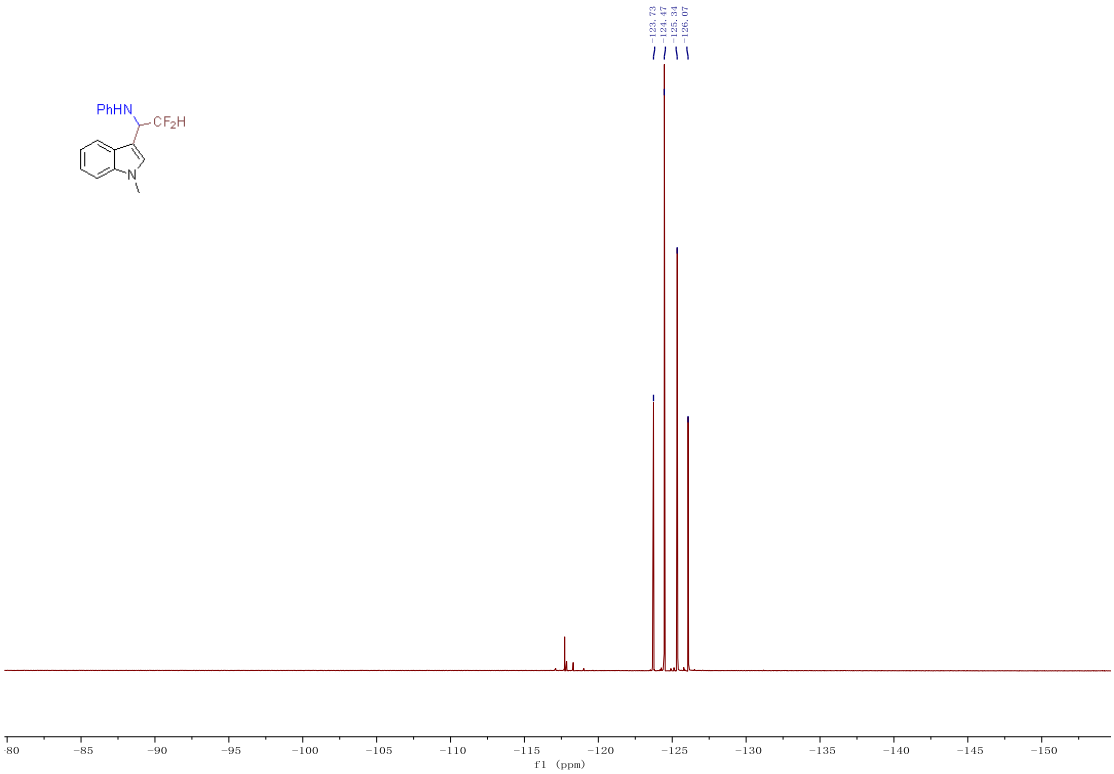
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ba**



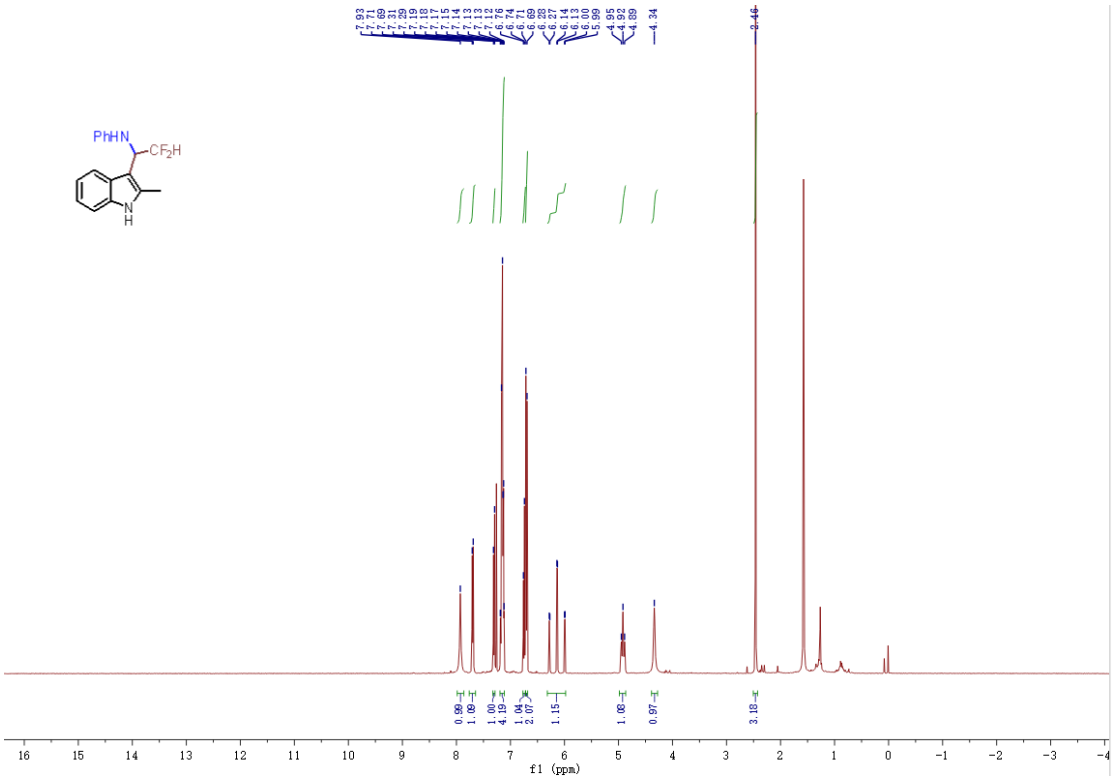
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7ba**



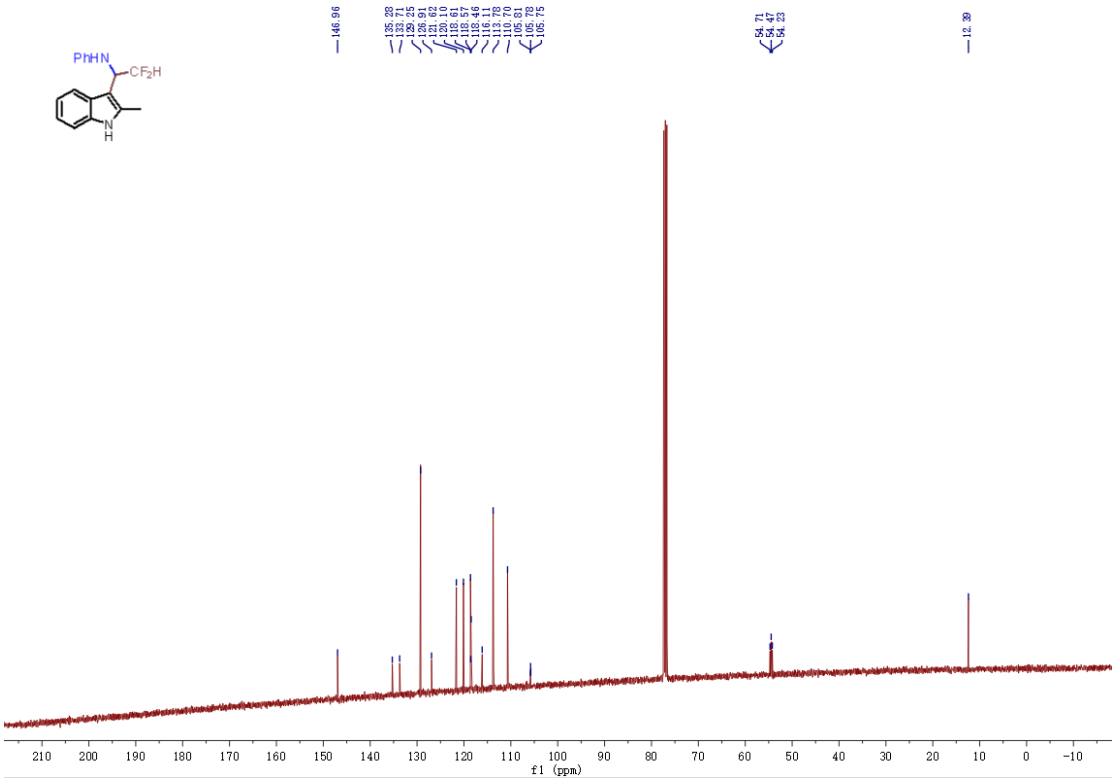
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ba**



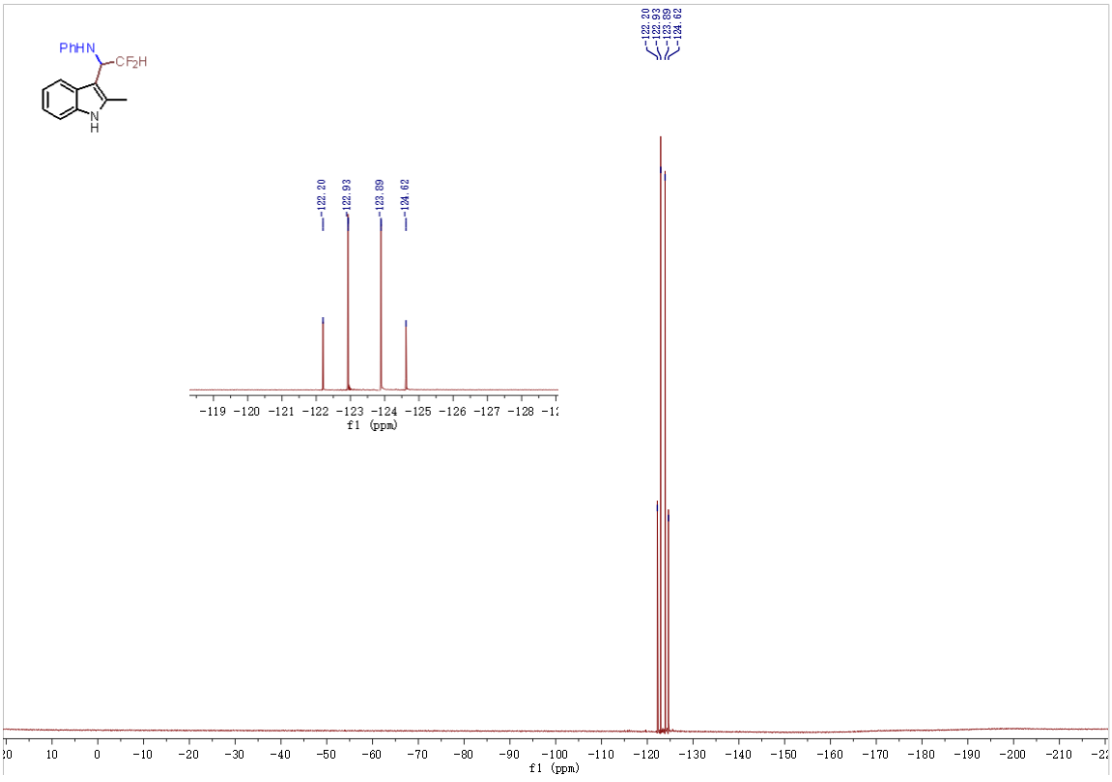
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ca**



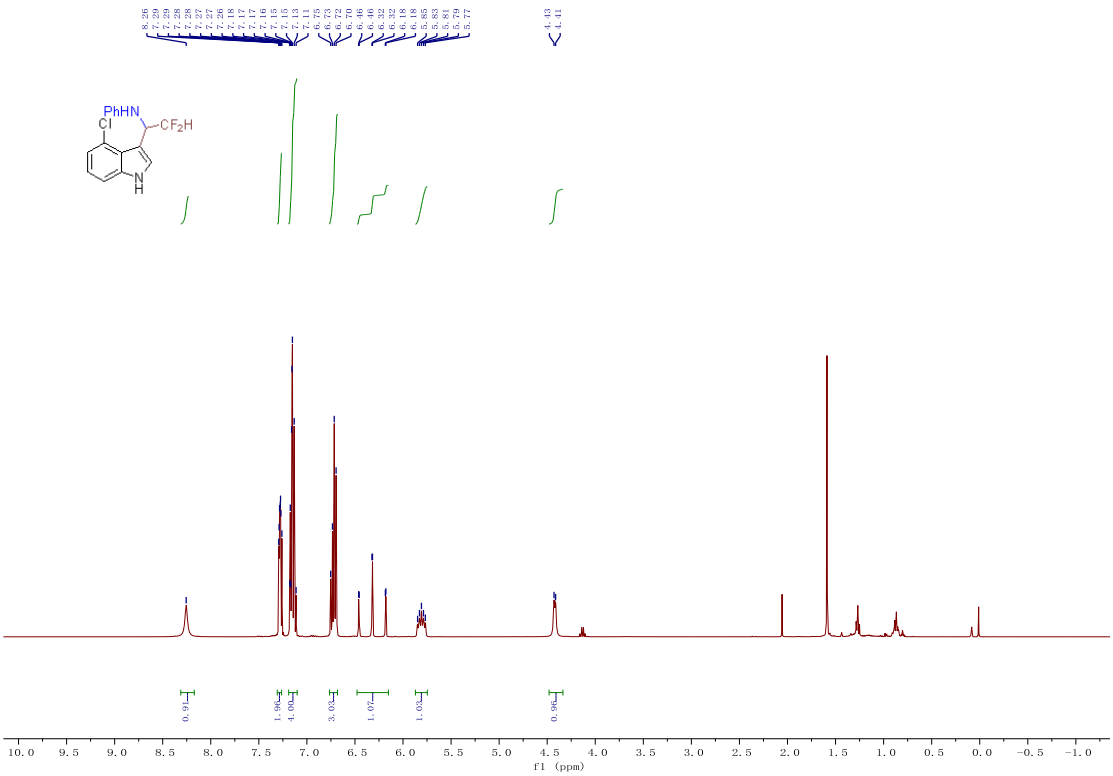
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7ca**



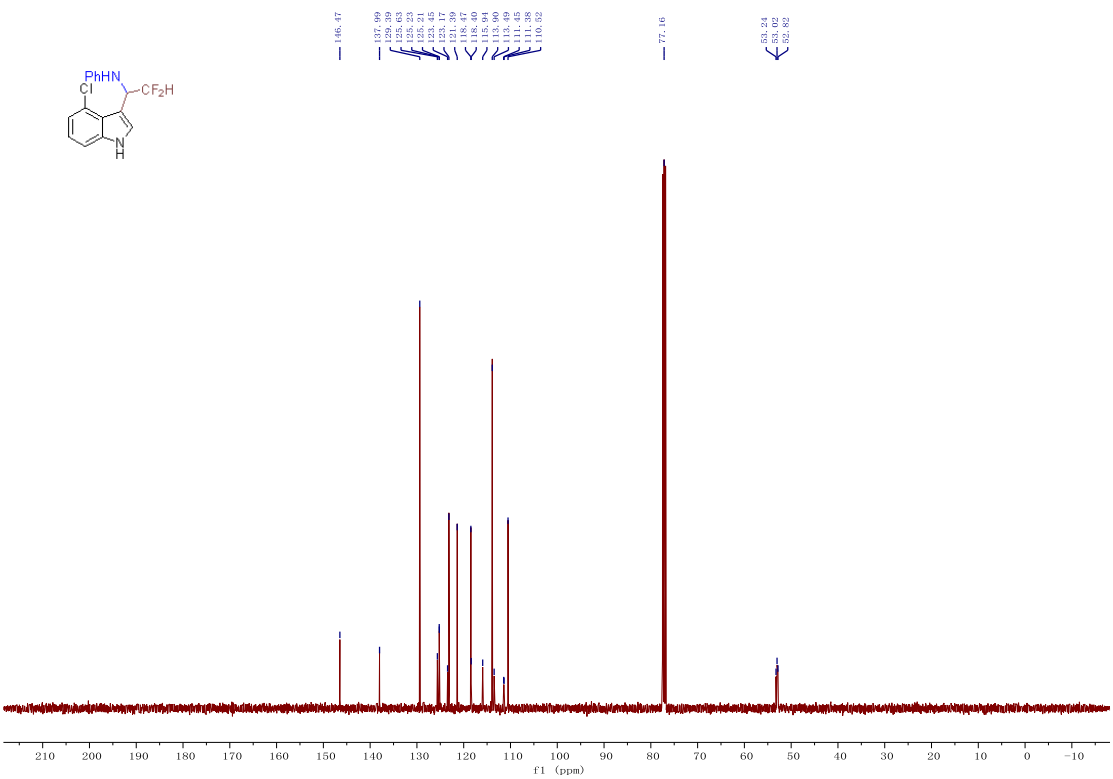
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ca**



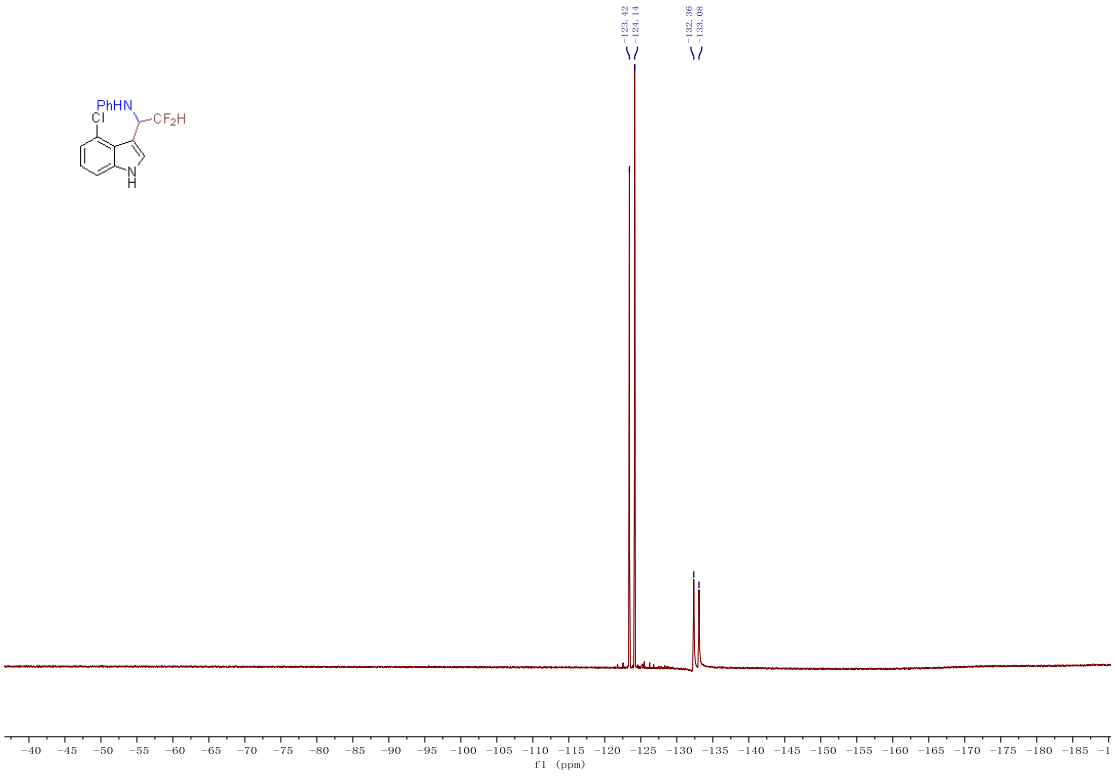
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7da**



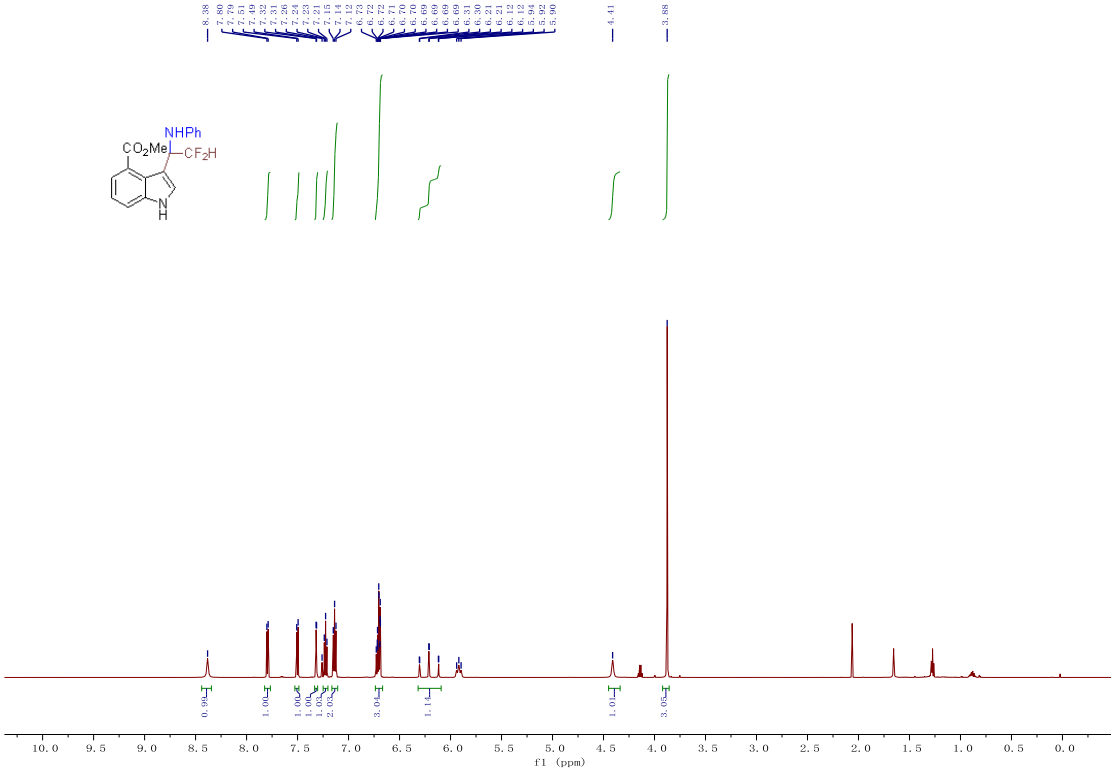
^{13}C NMR (101 MHz, Chloroform-d) spectra of **7da**



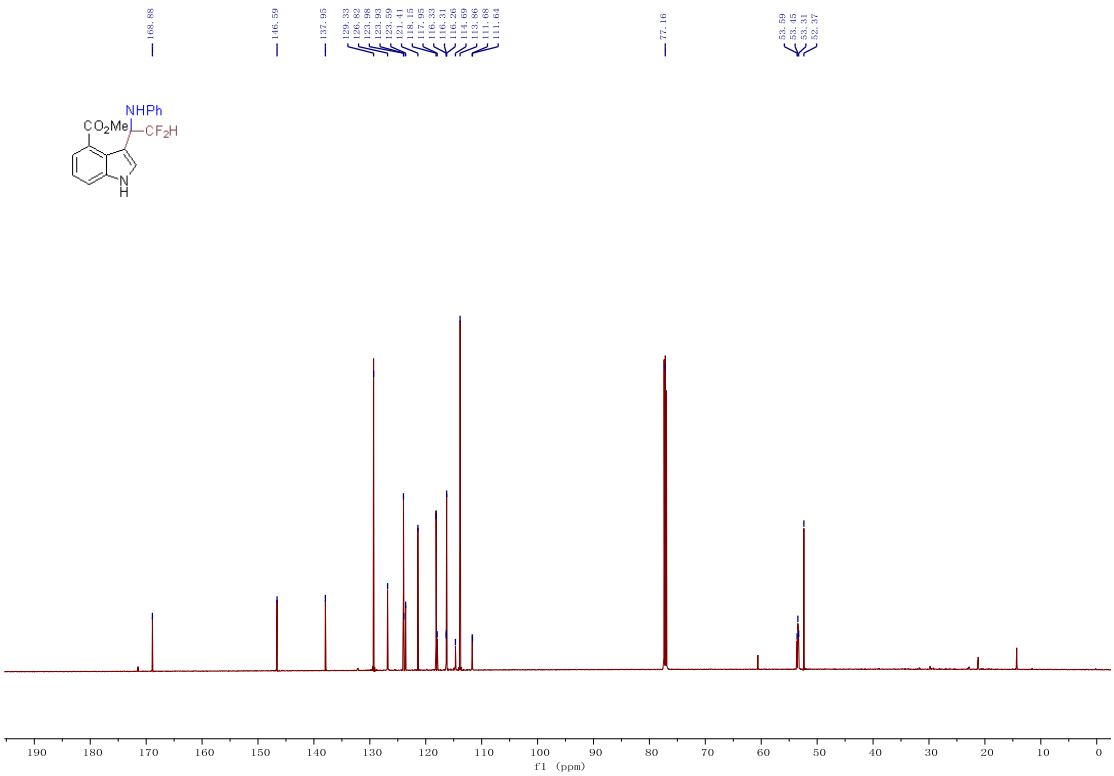
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7da**



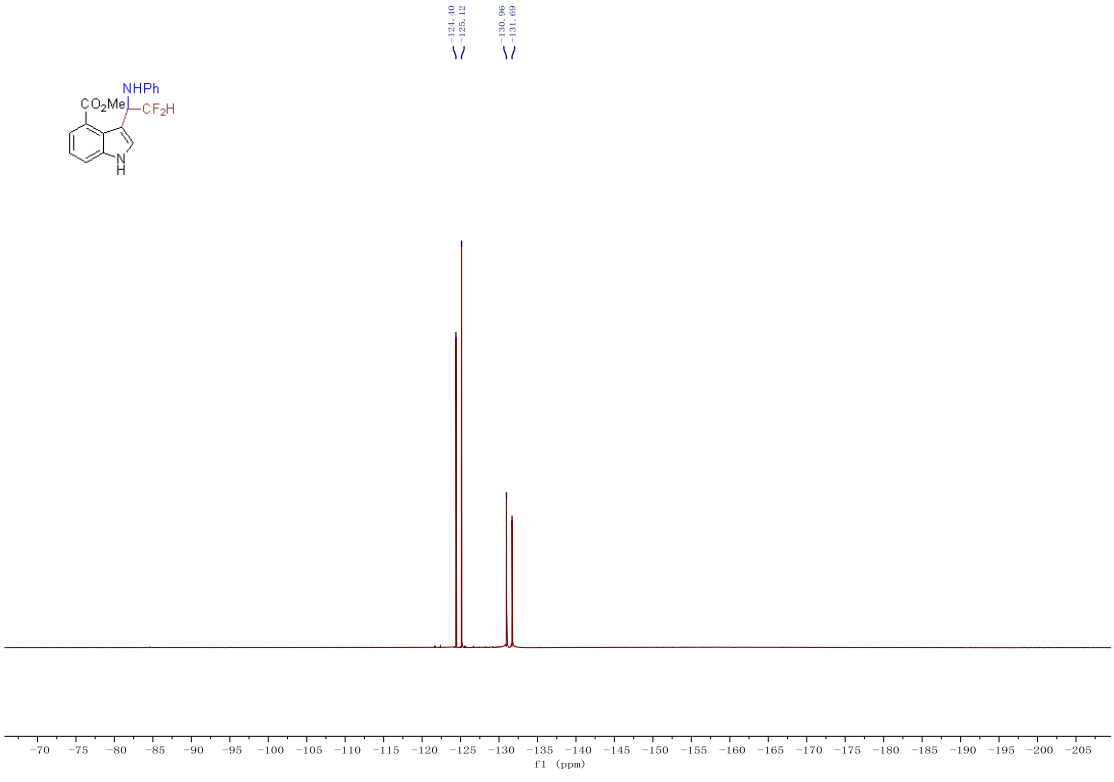
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ea**



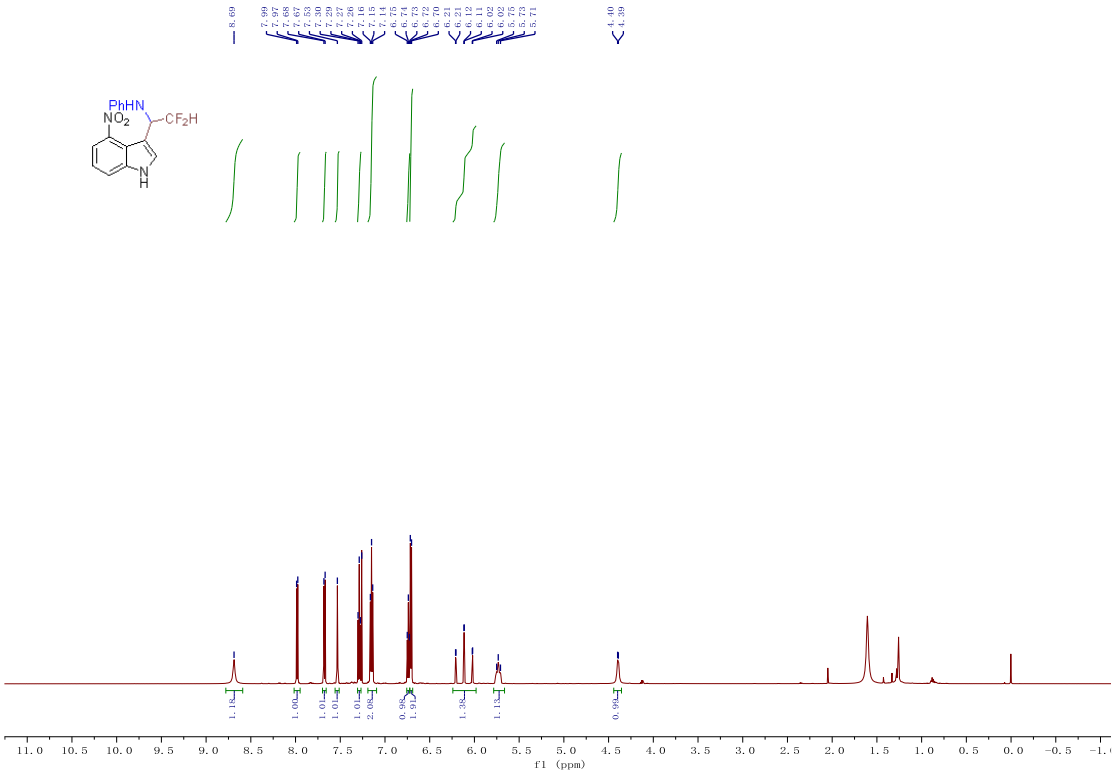
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7ea**



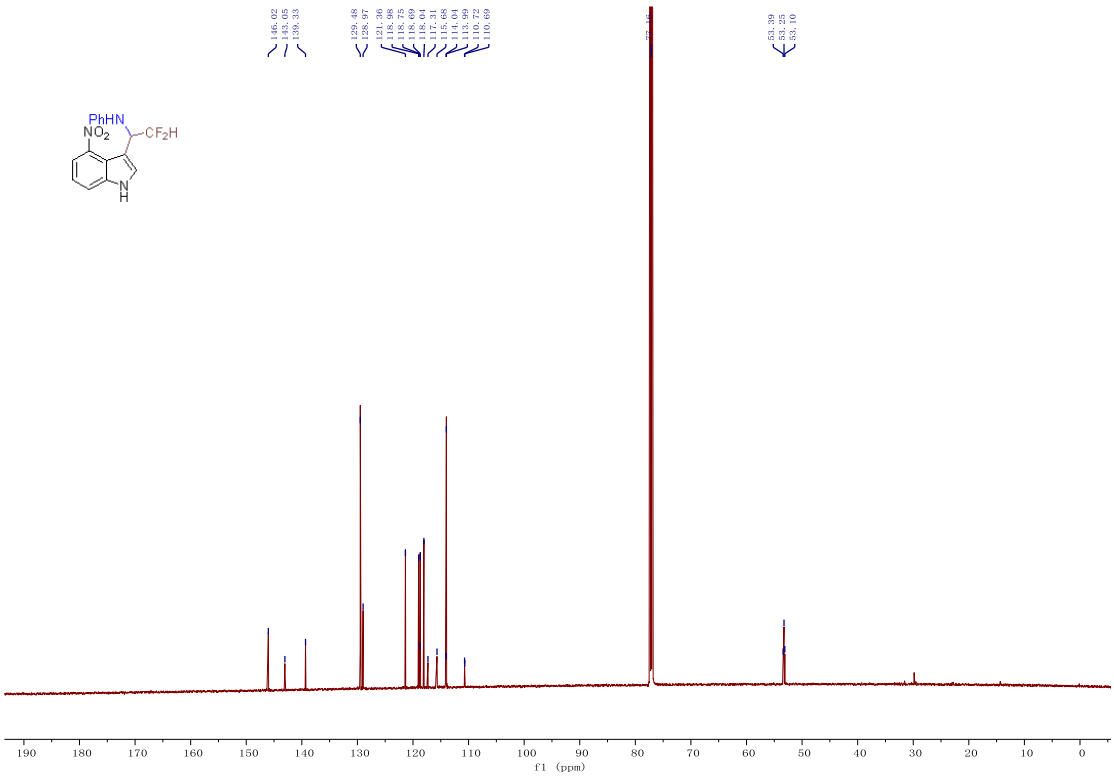
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ea**



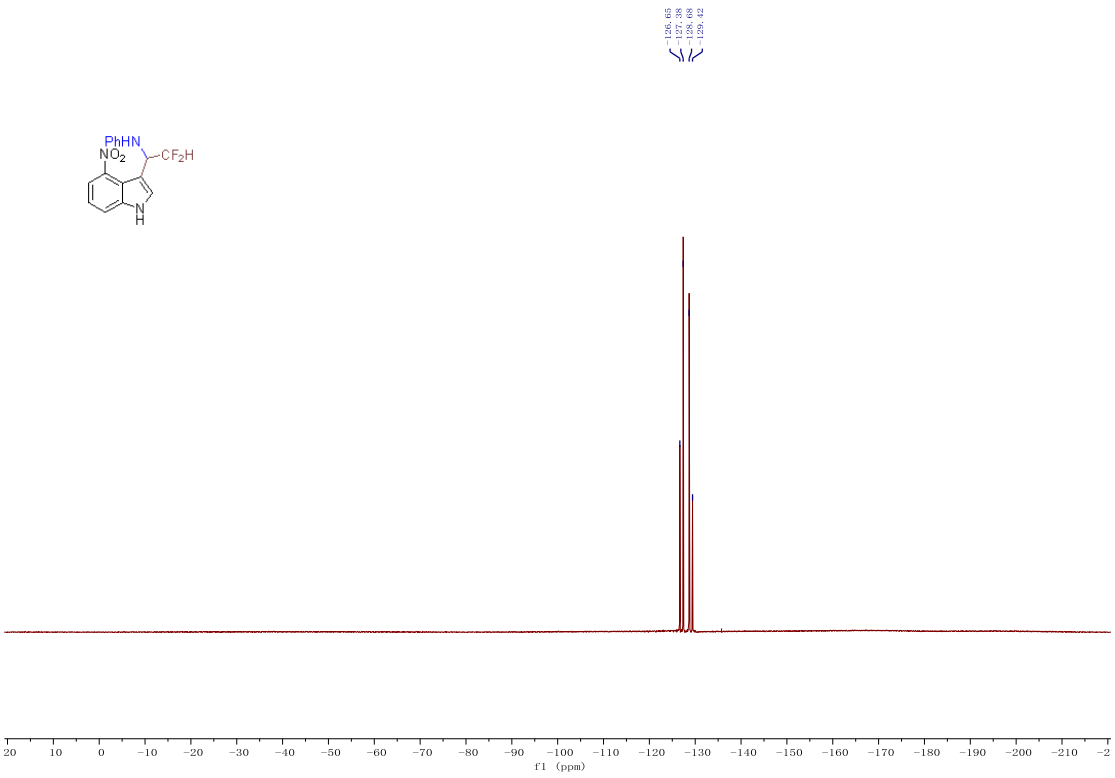
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7fa**



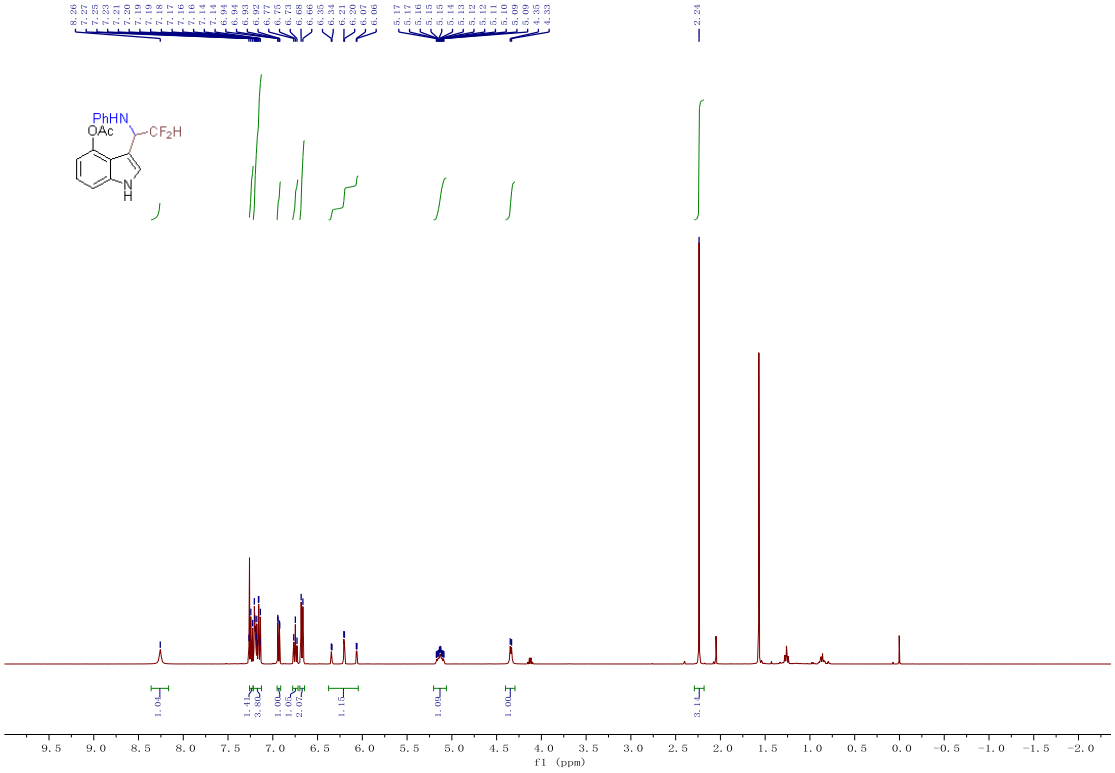
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7fa**



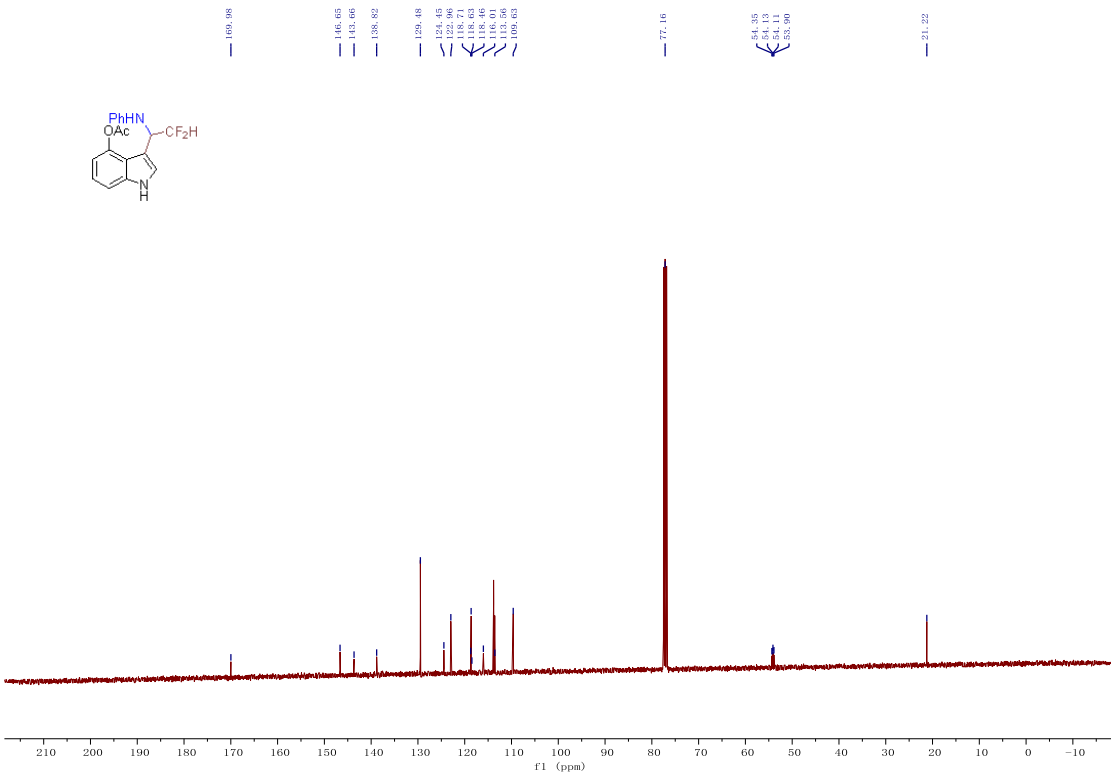
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7fa**



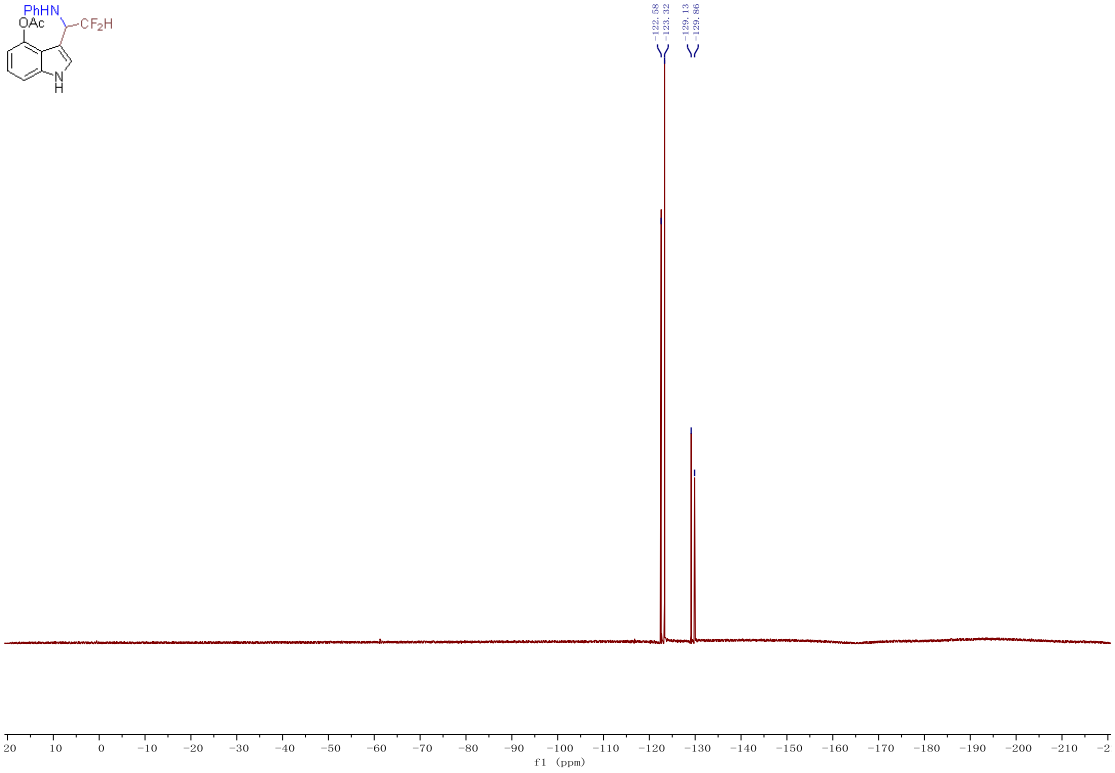
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ga**



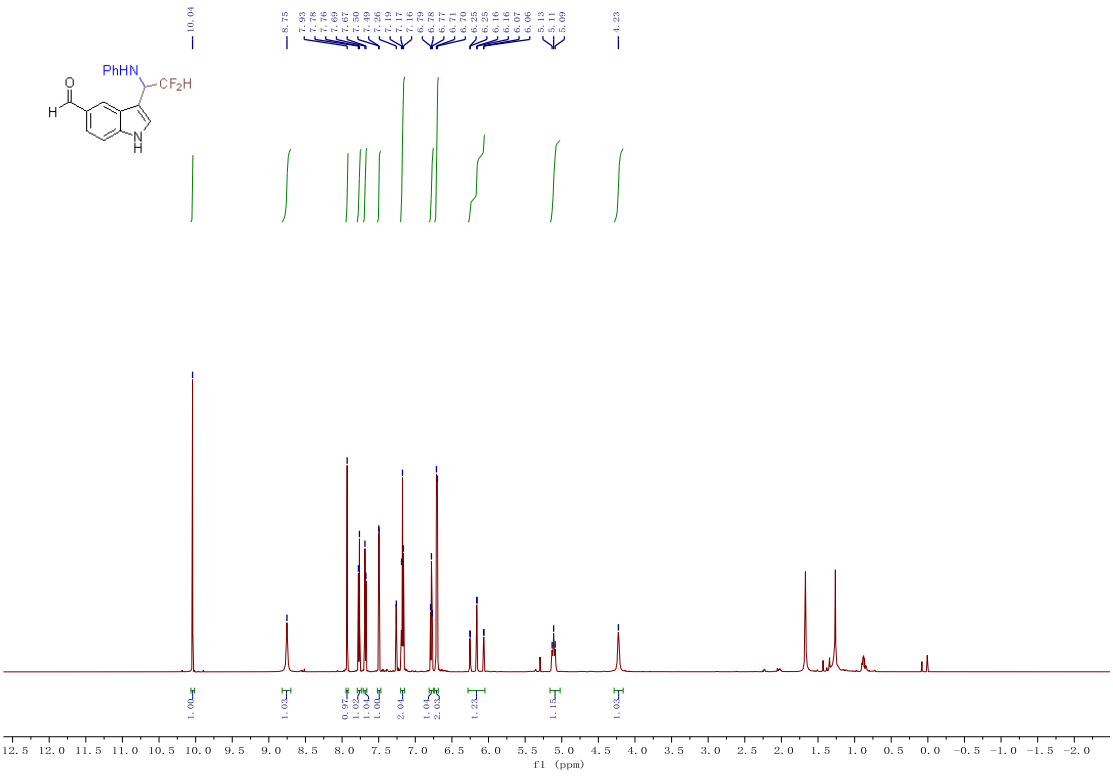
^{13}C NMR (101 MHz, Chloroform-d) spectra of **7ga**



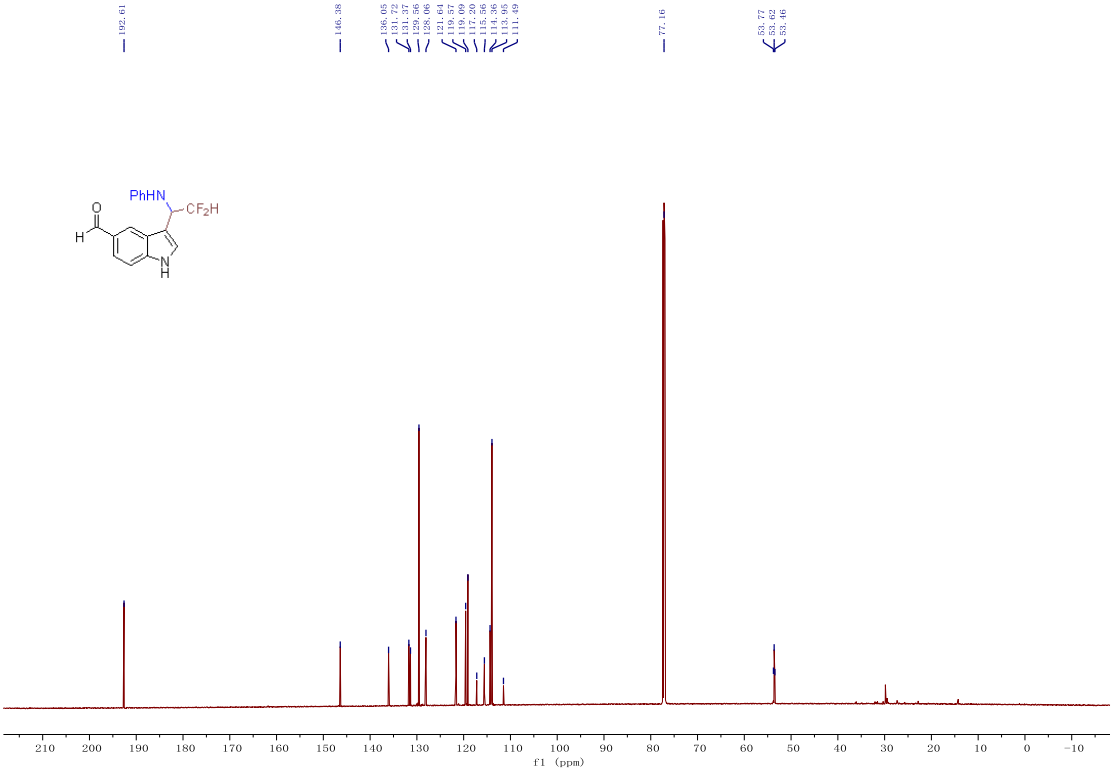
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ga**



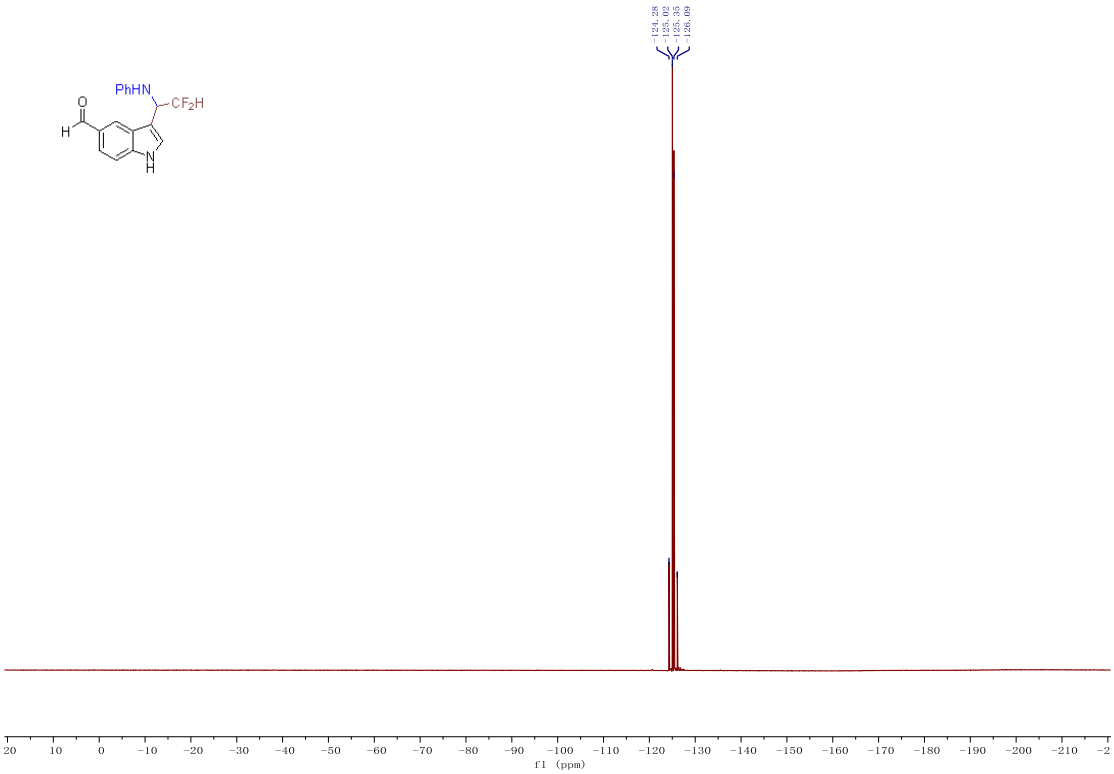
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ha**



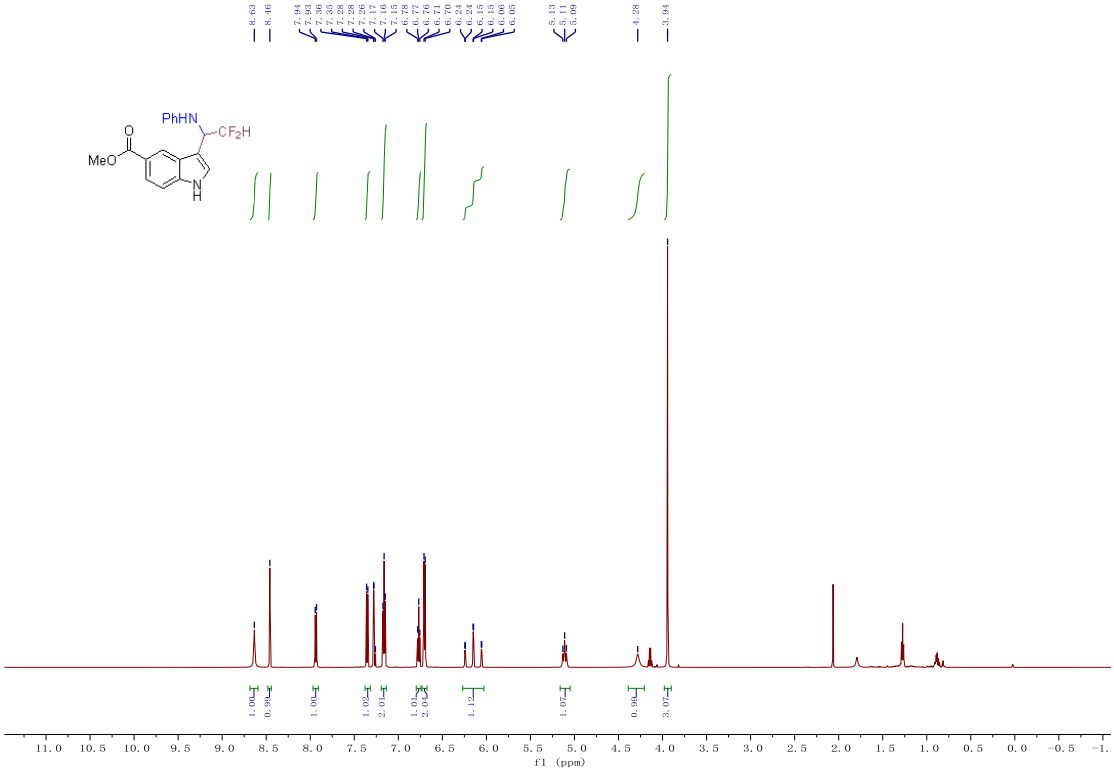
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7ha**



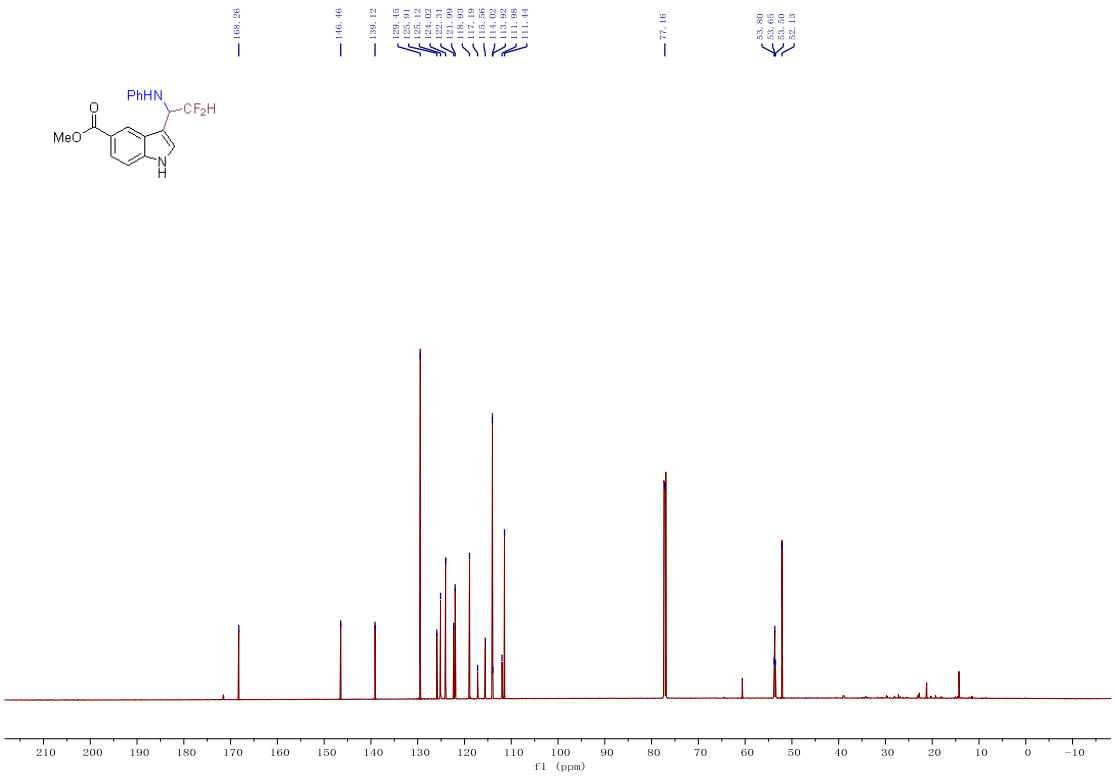
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ha**



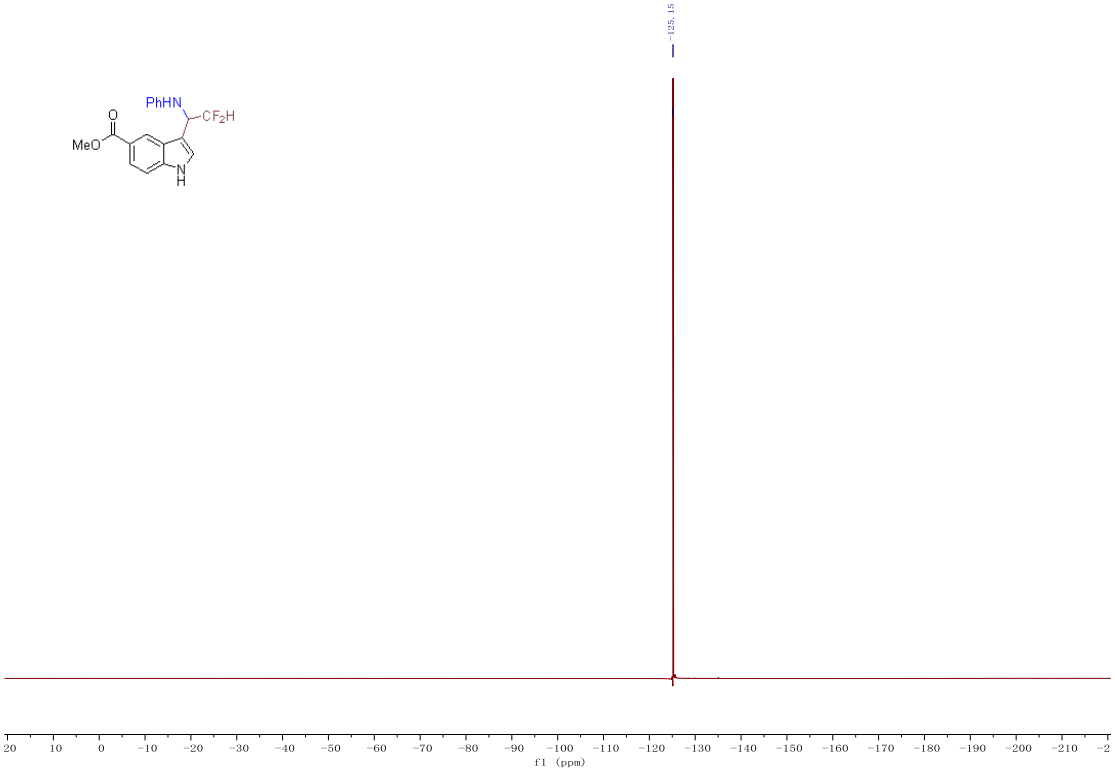
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ia**



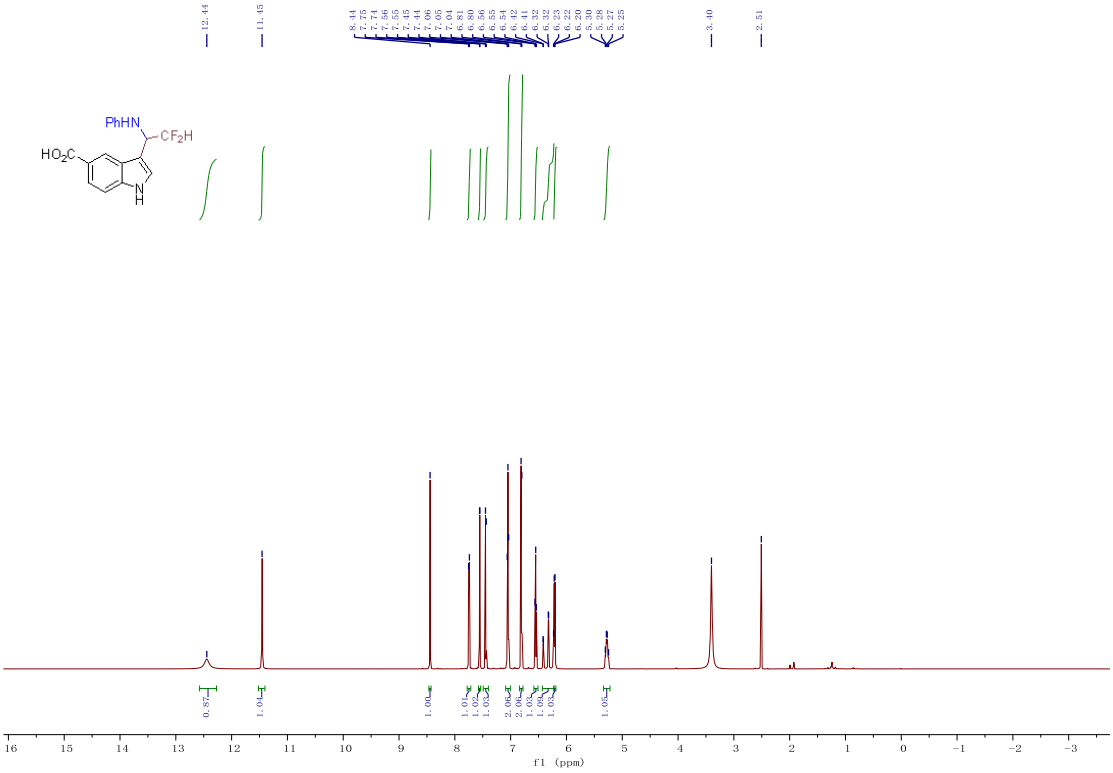
^{13}C NMR (151 MHz, Chloroform-d) spectra of **7ia**



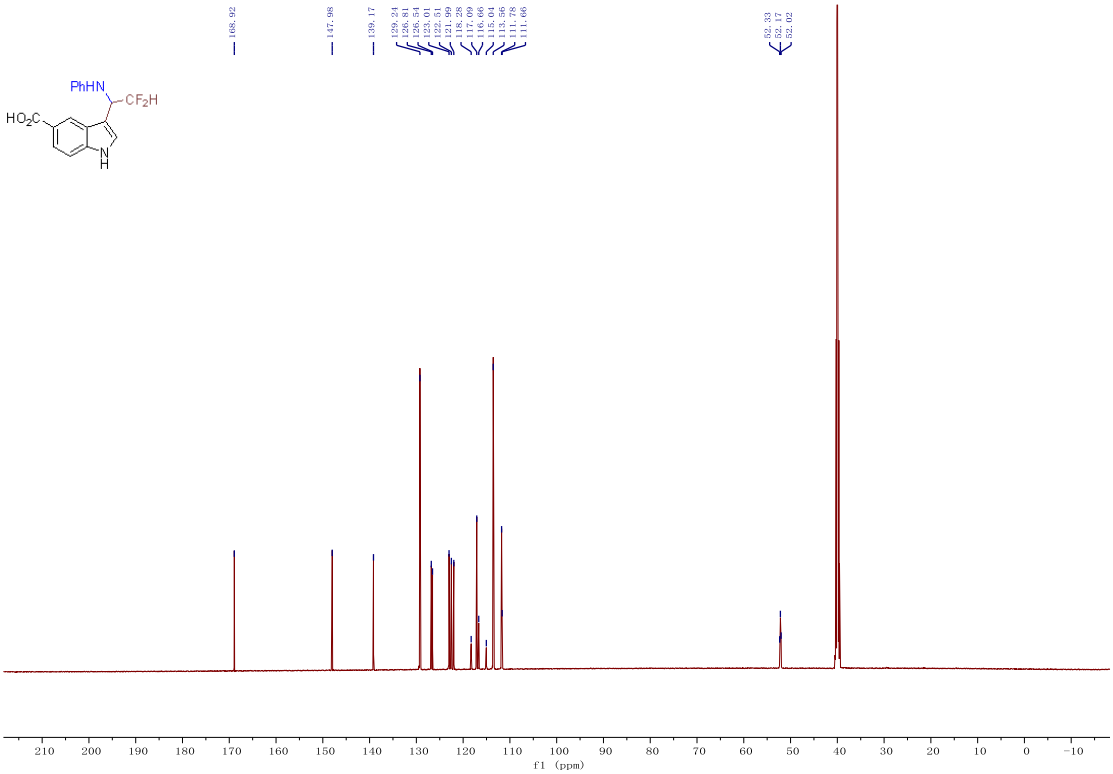
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ia**



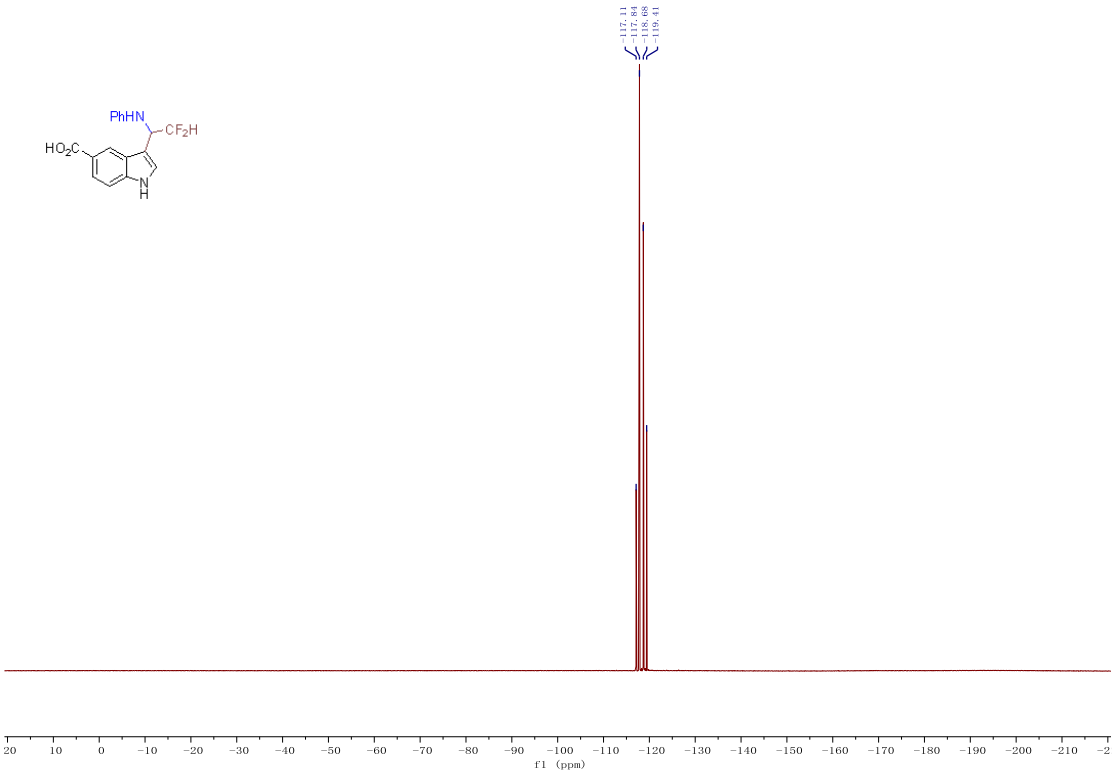
^{1}H NMR (600 MHz, DMSO-d6) spectra of **7ja**



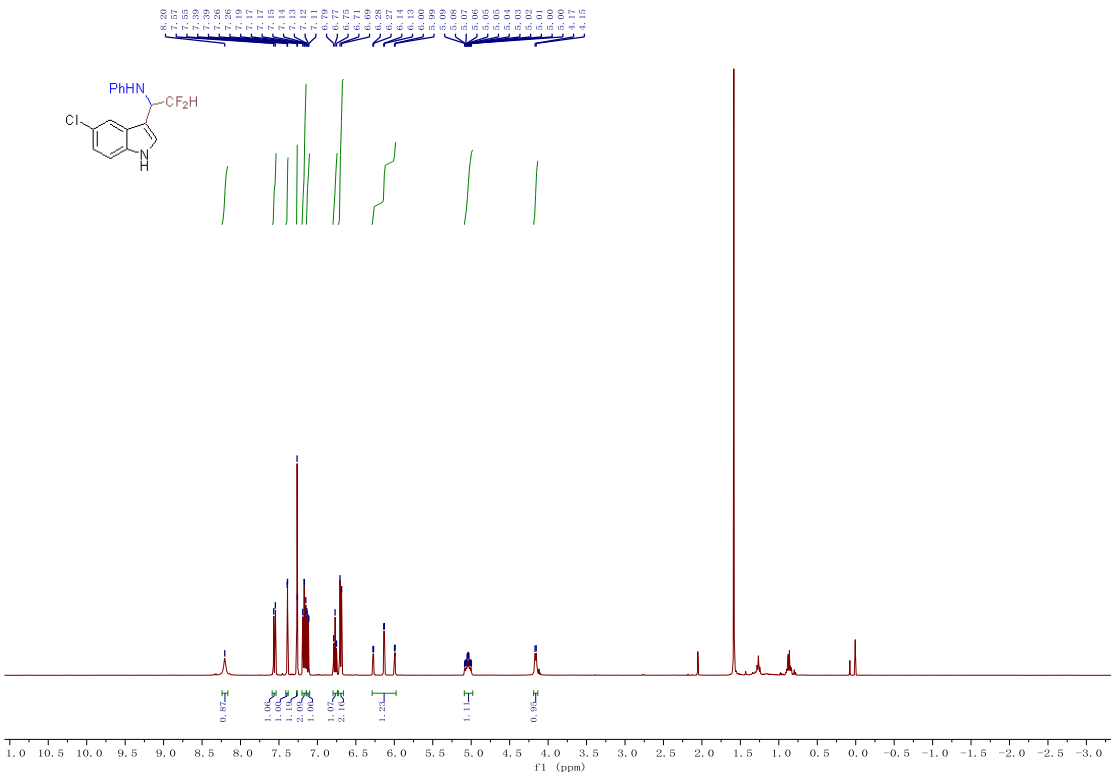
^{13}C NMR (151 MHz, DMSO-d6) spectra of **7ja**



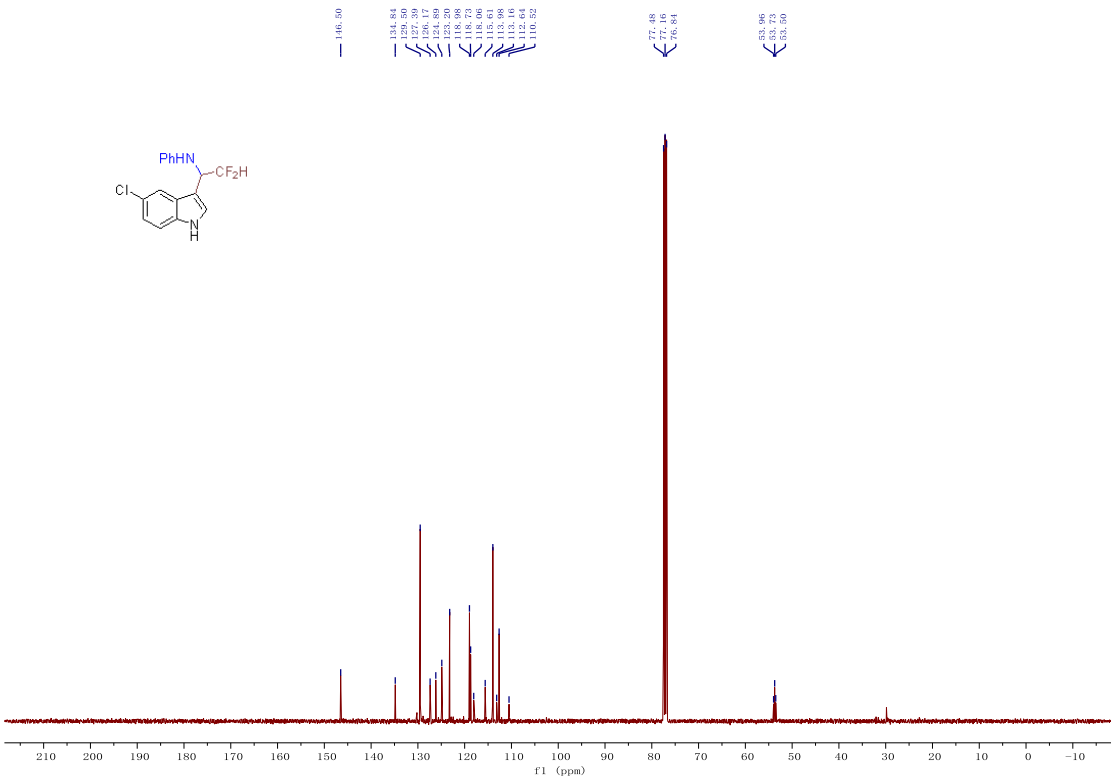
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ja**



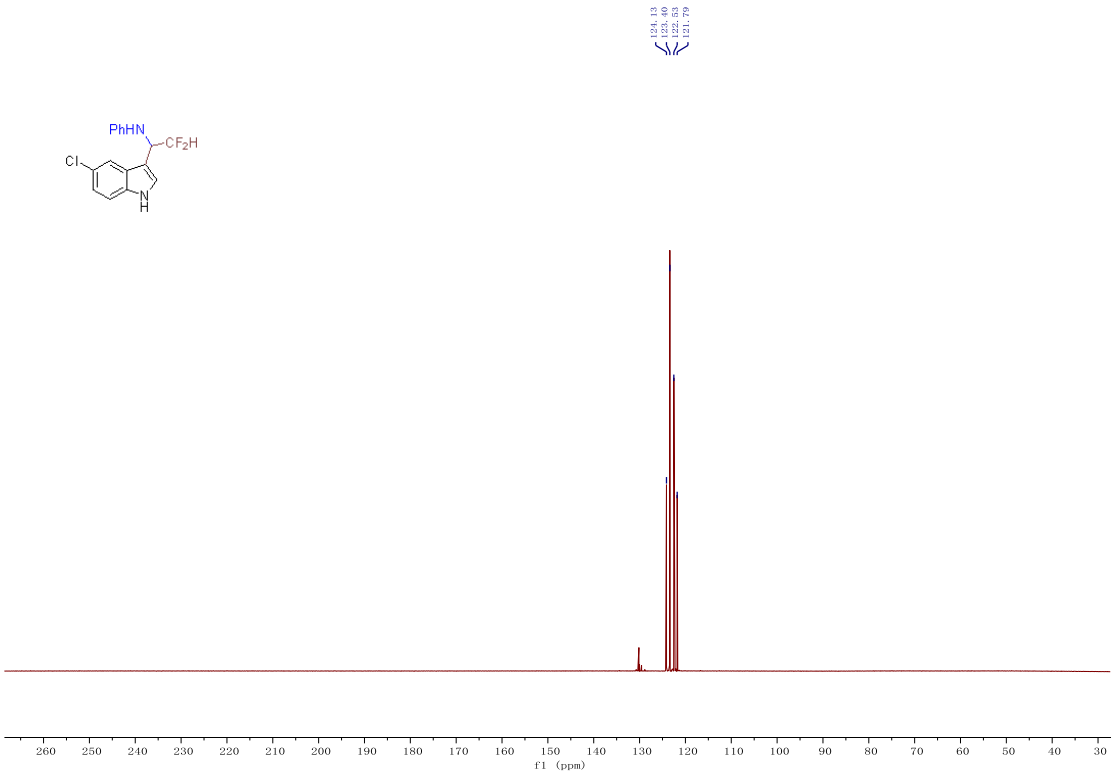
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ka**



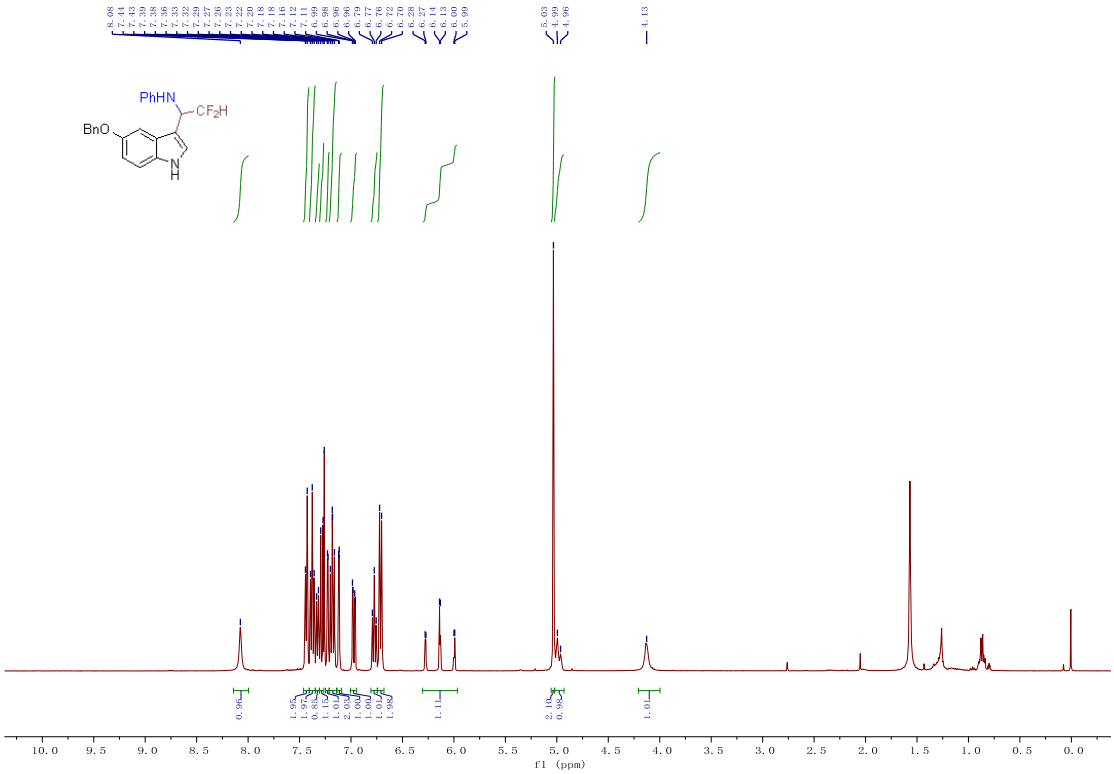
^{13}C NMR (101 MHz, DMSO-d6) spectra of **7ka**



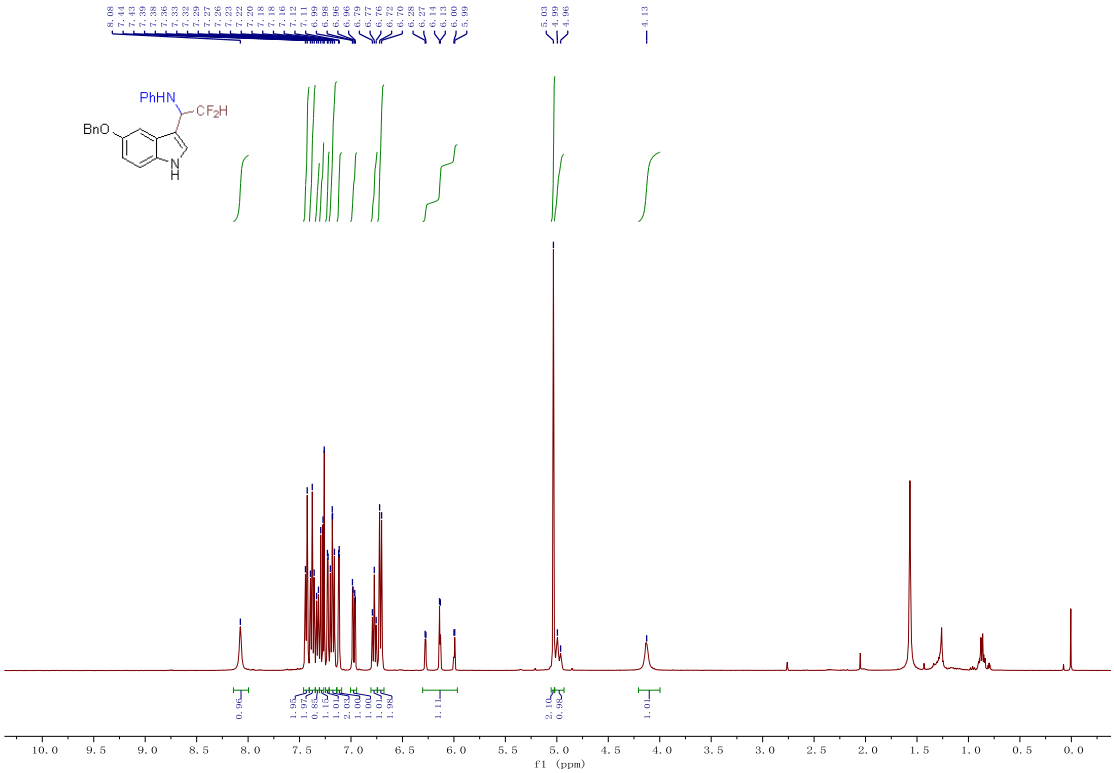
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ka**



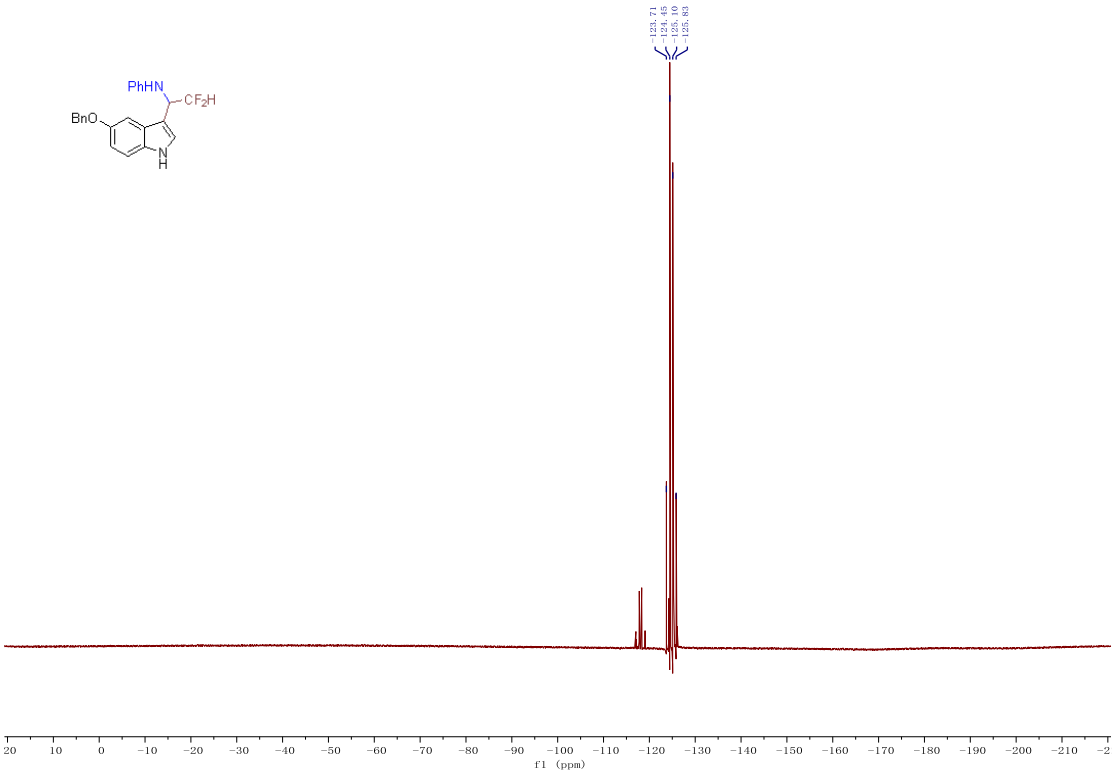
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7la**



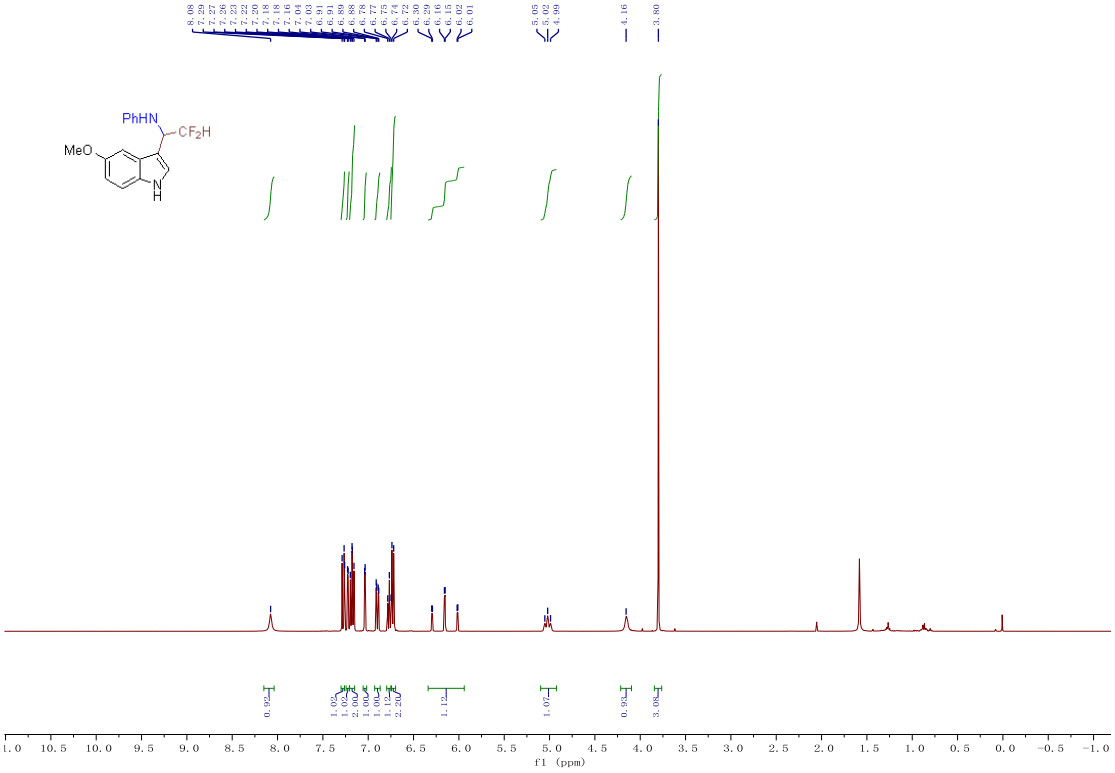
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7la**



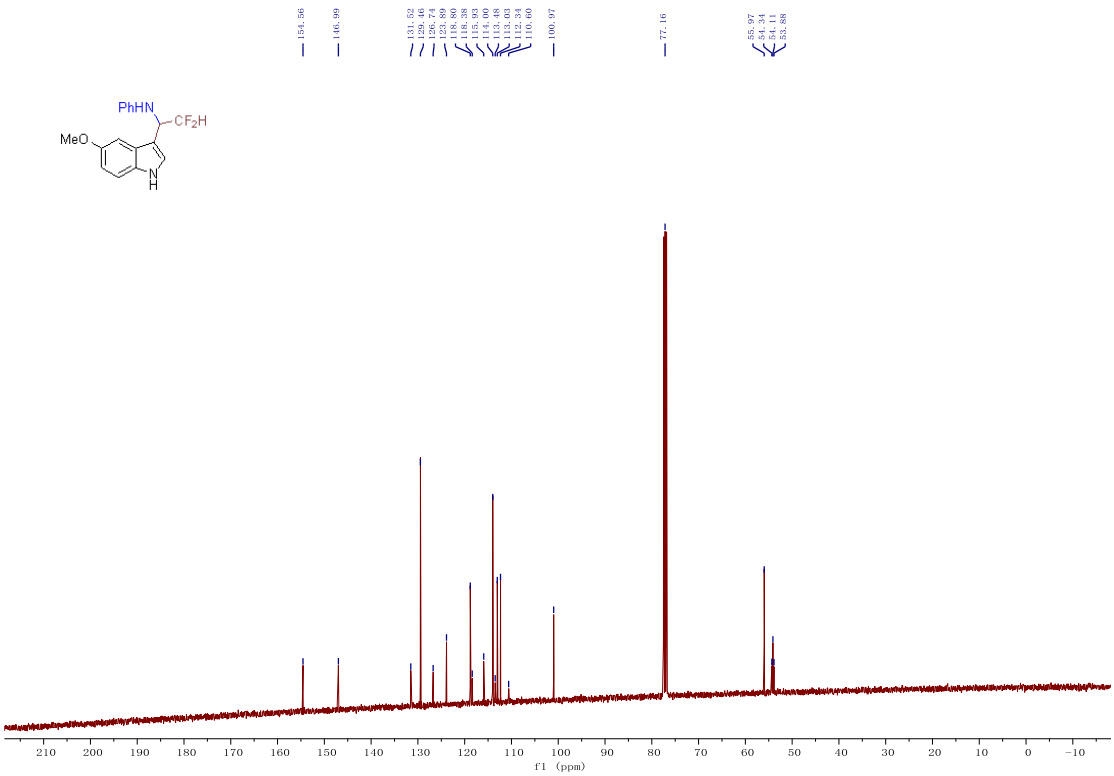
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7la**



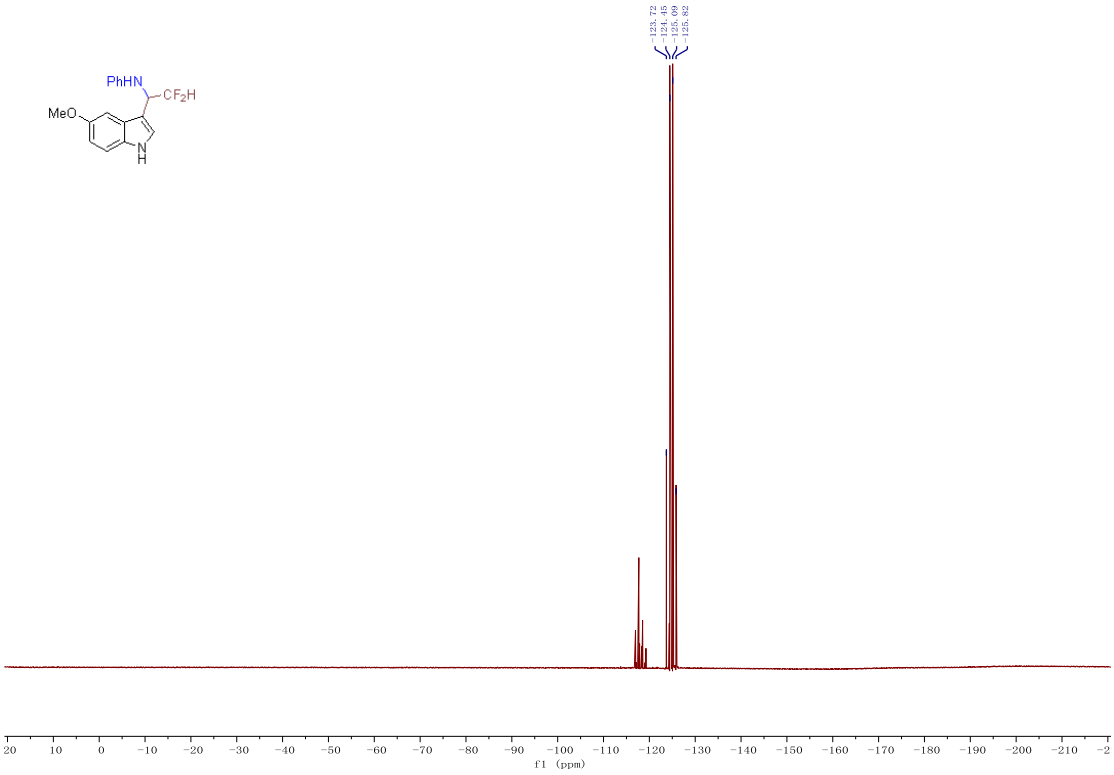
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ma**



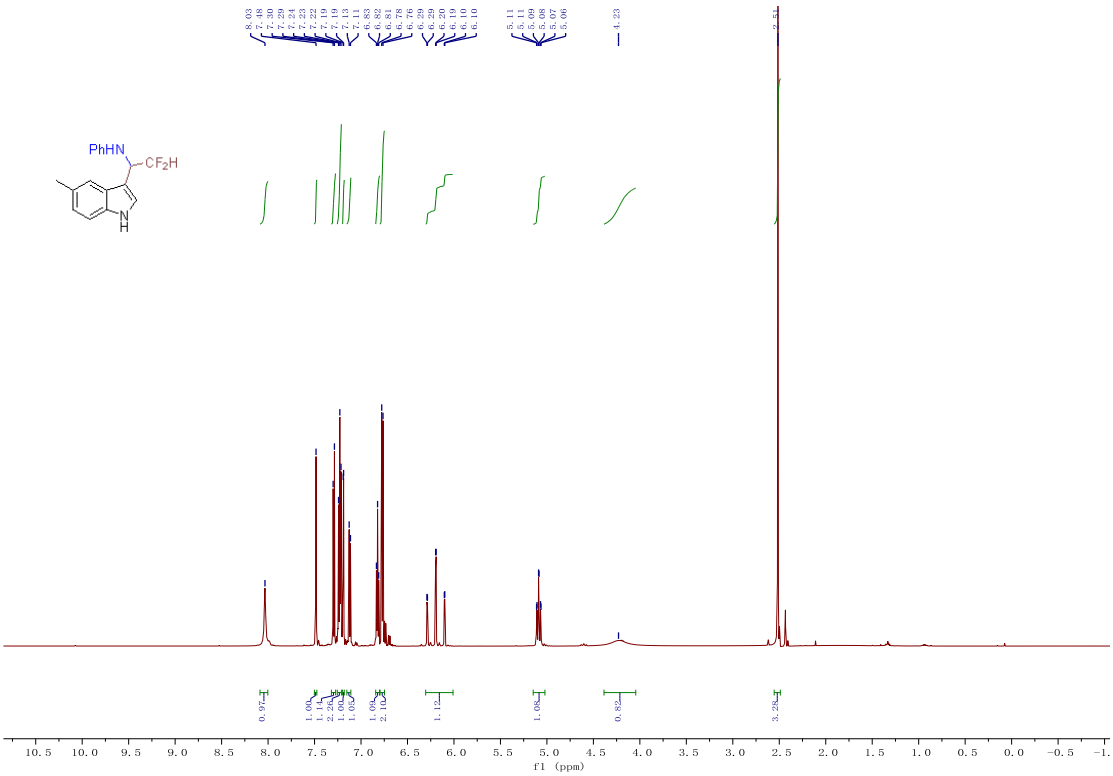
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ma**



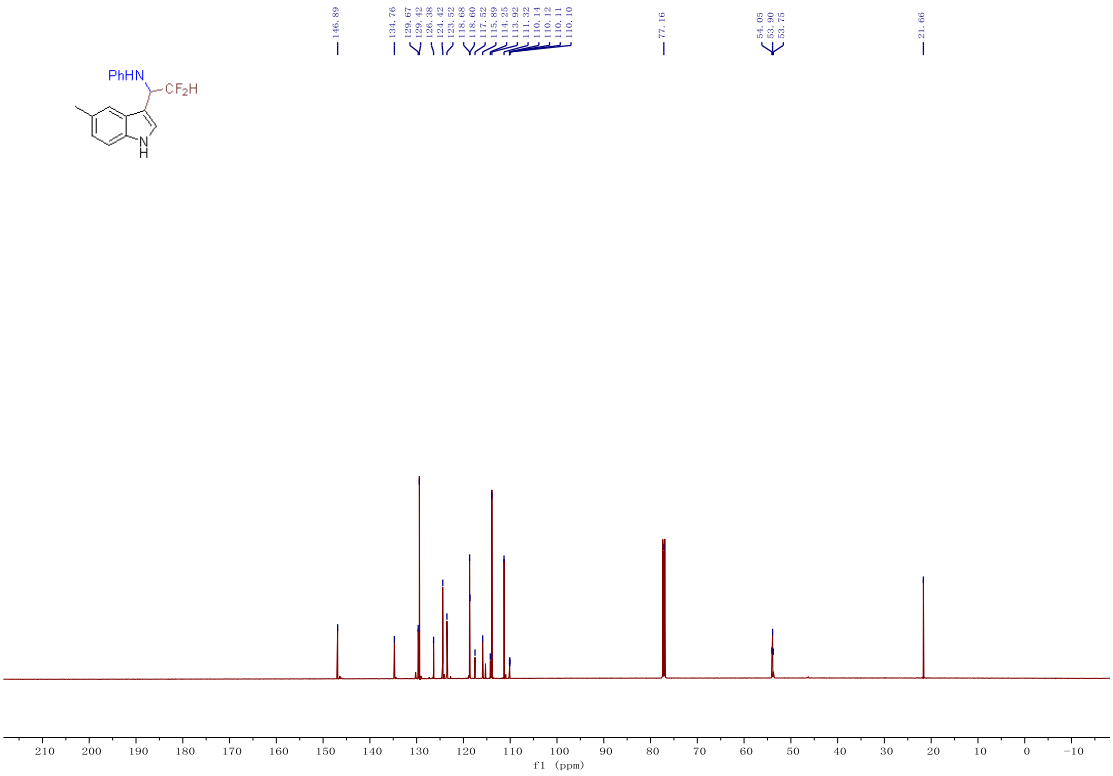
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ma**



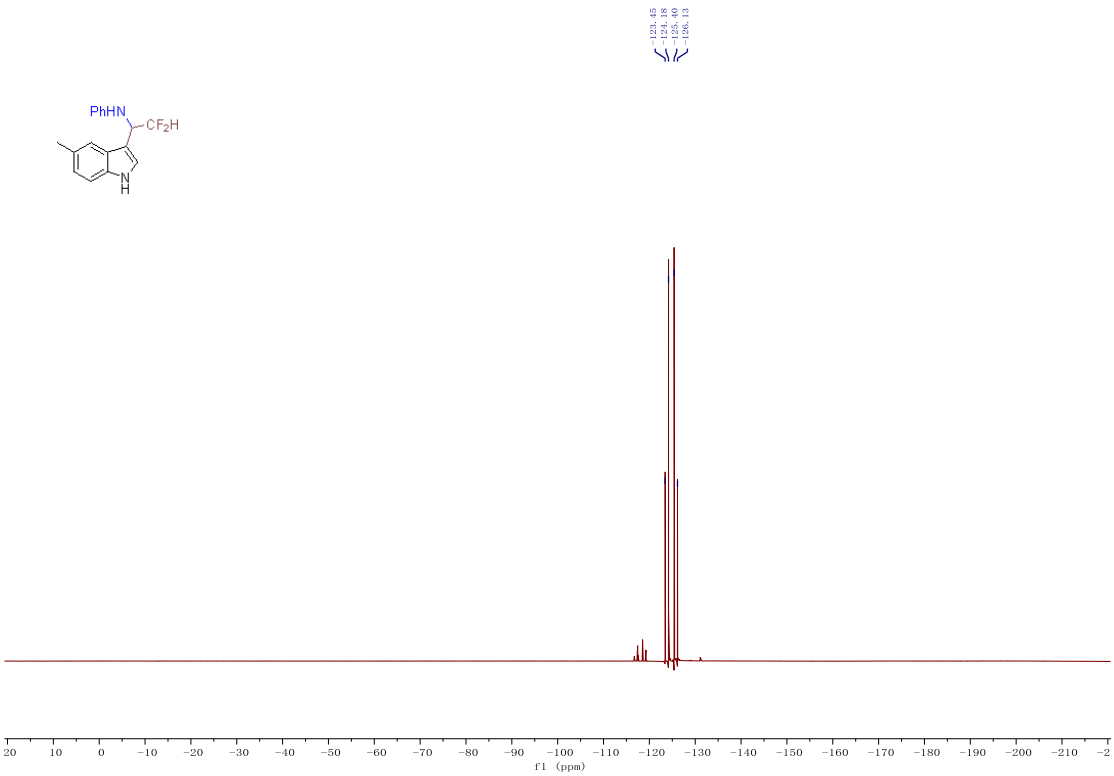
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7na**



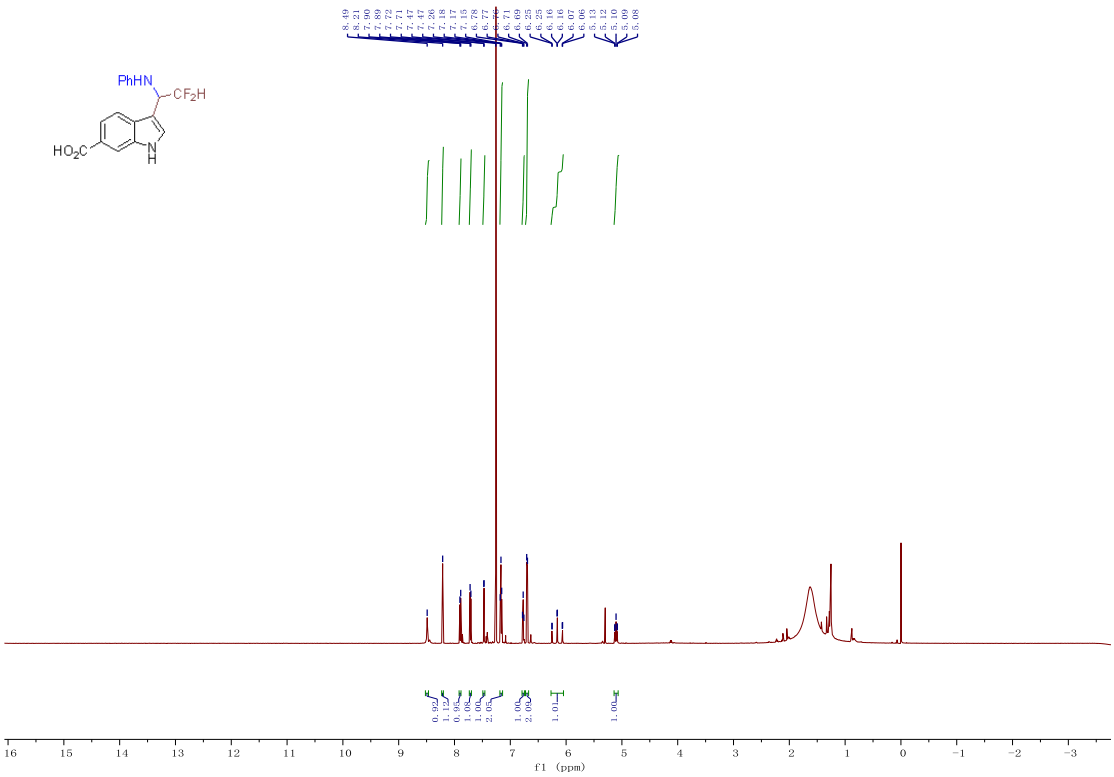
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7na**



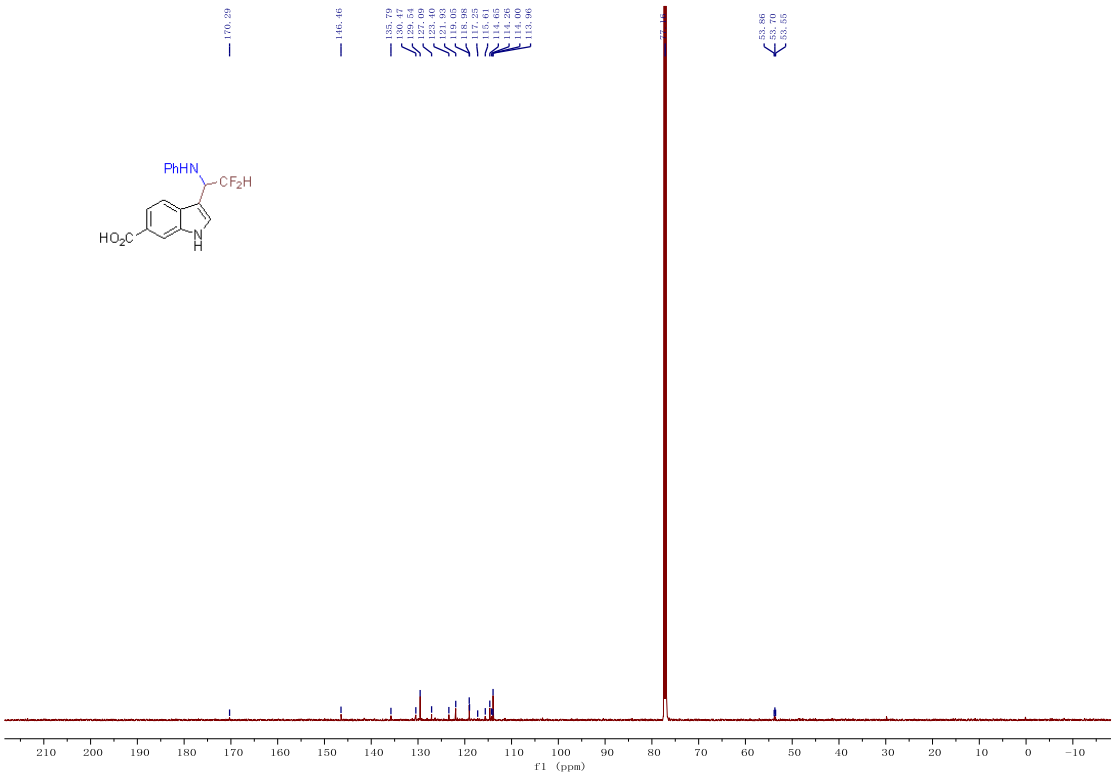
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7na**



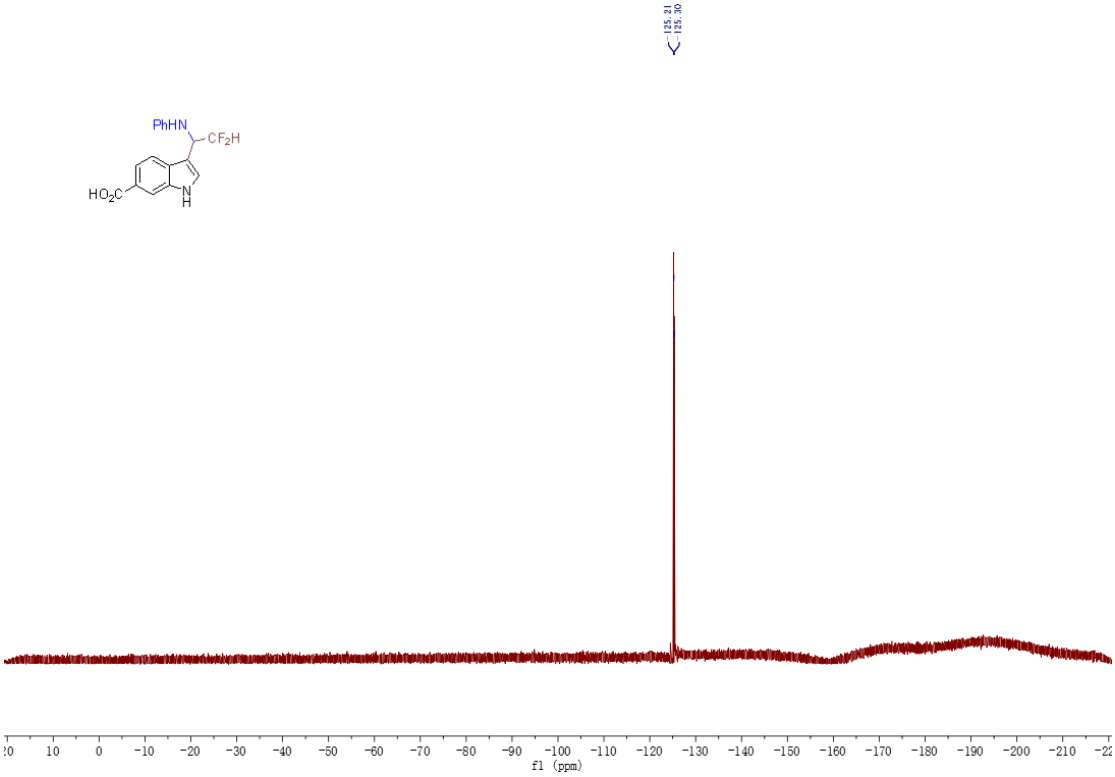
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7oa**



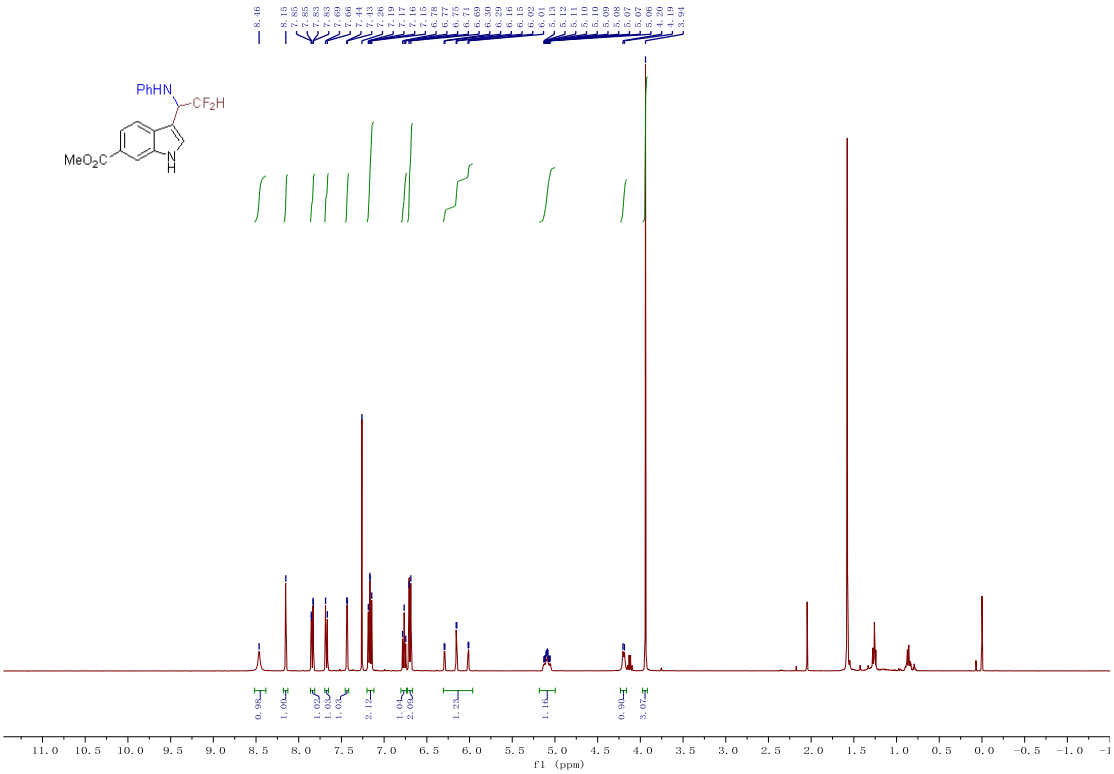
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7oa**



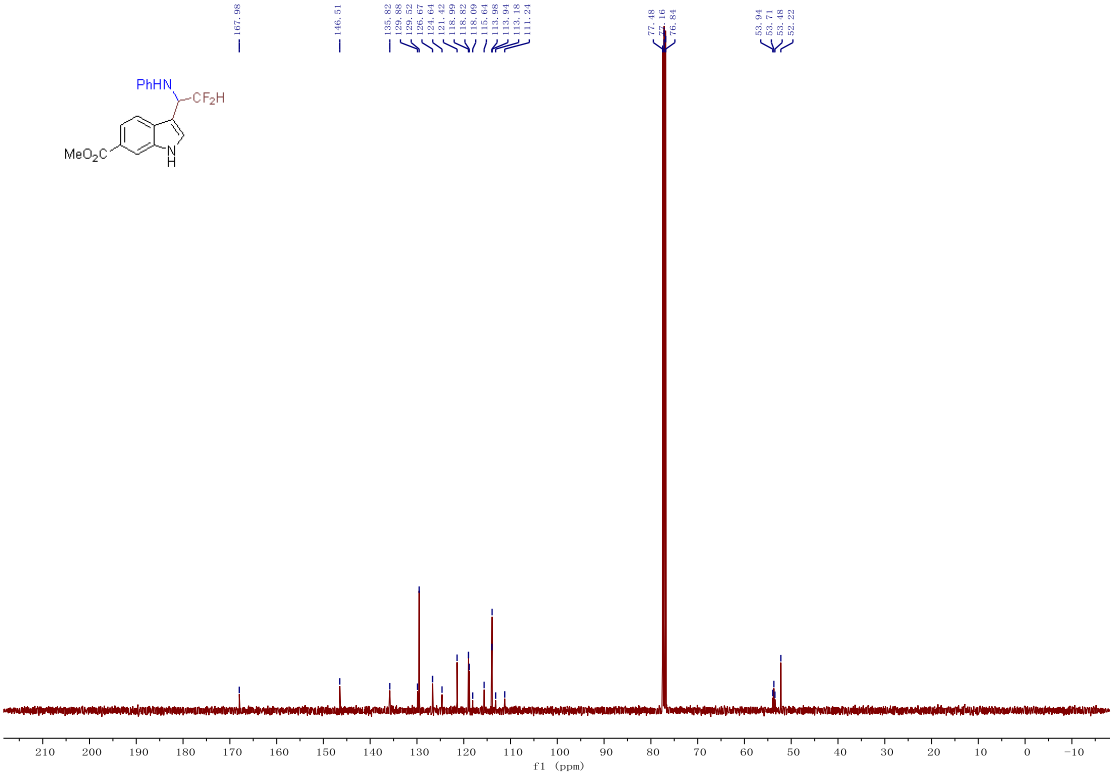
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7oa**



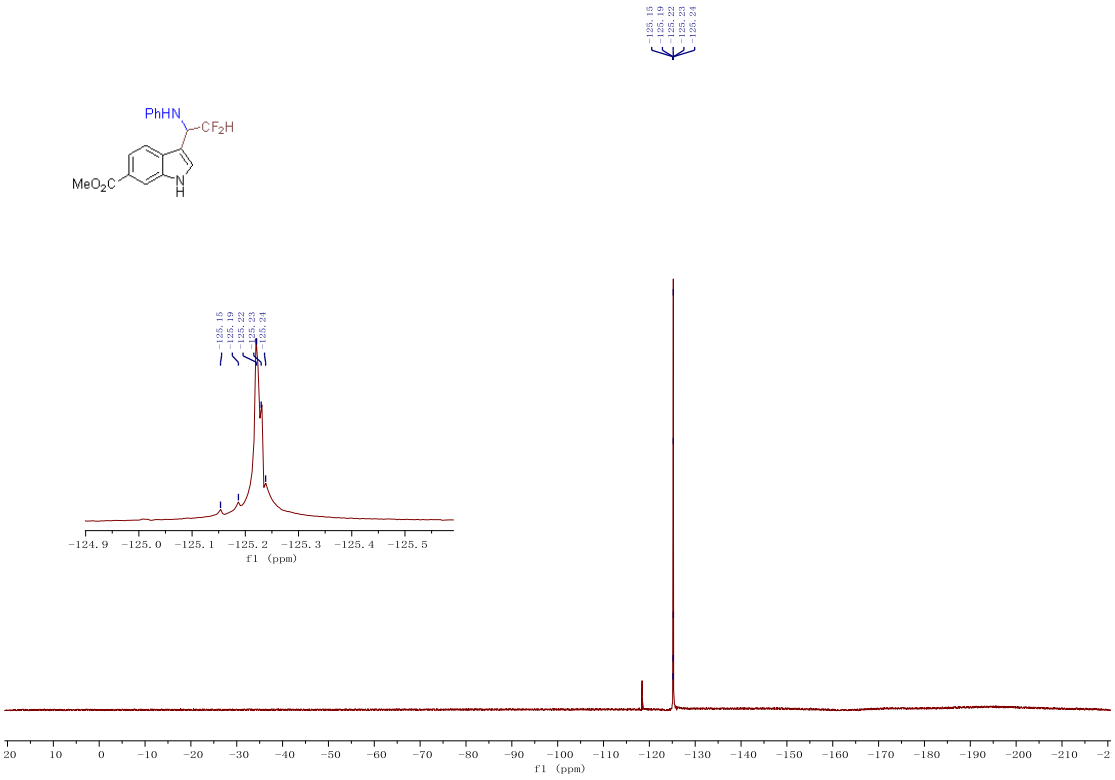
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7pa**



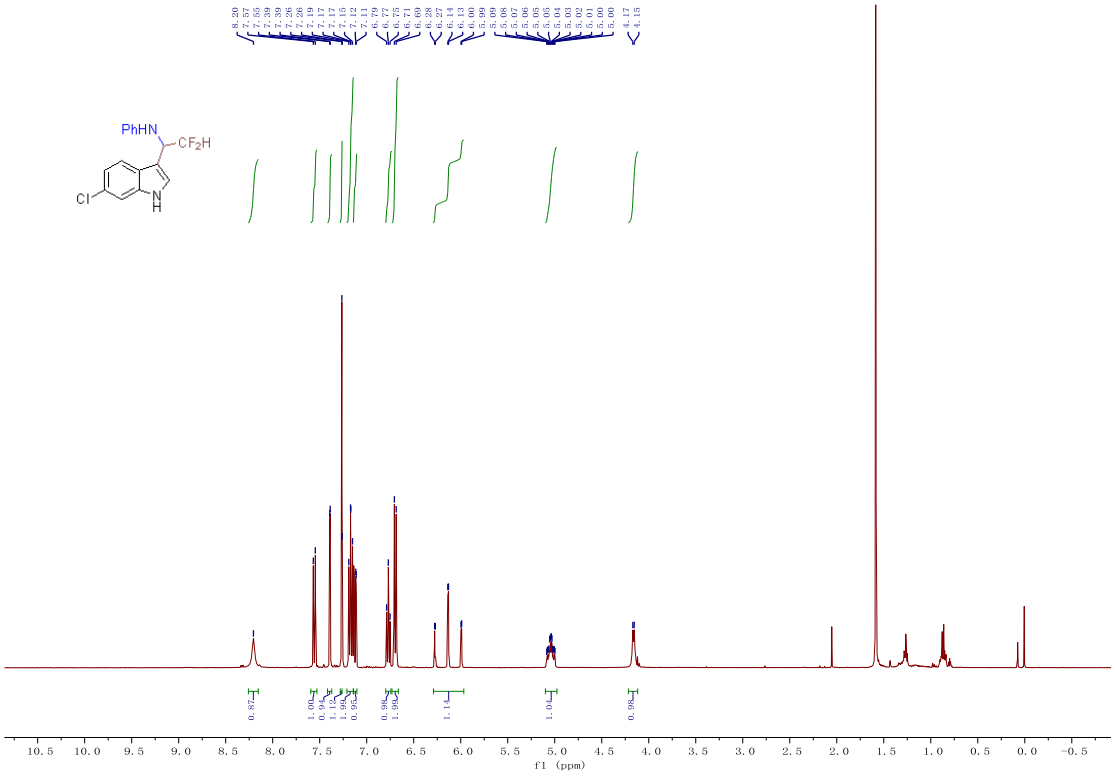
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7pa**



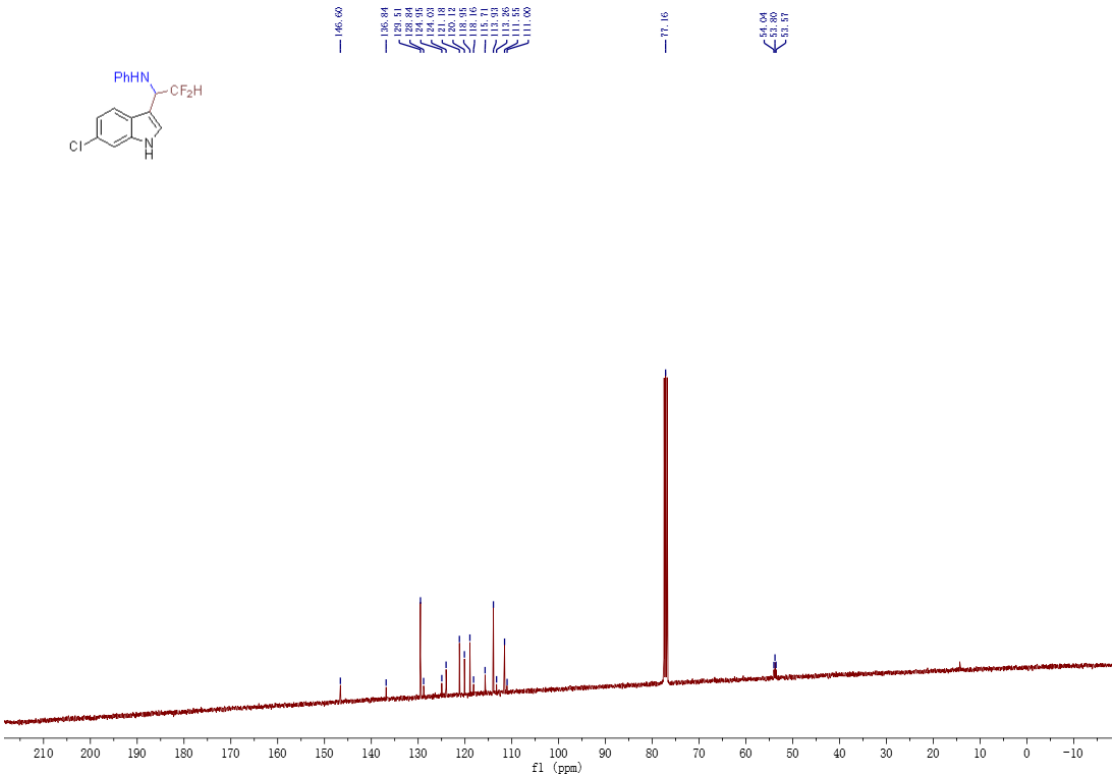
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7pa**



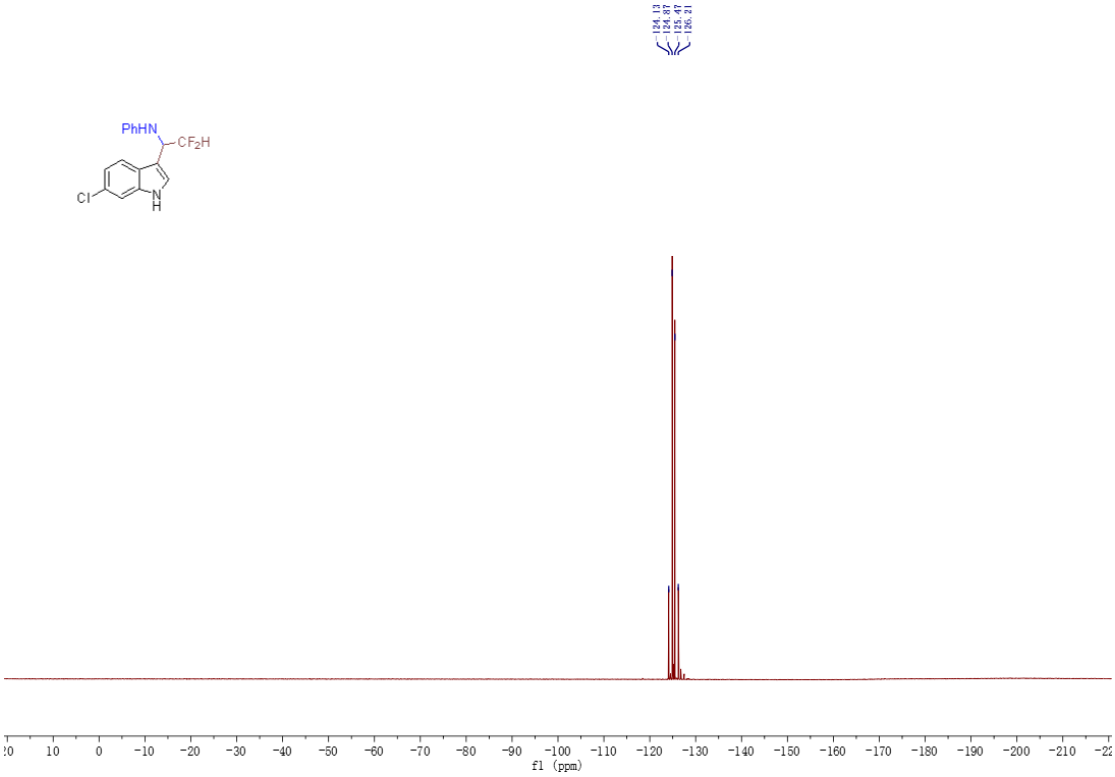
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7qa**



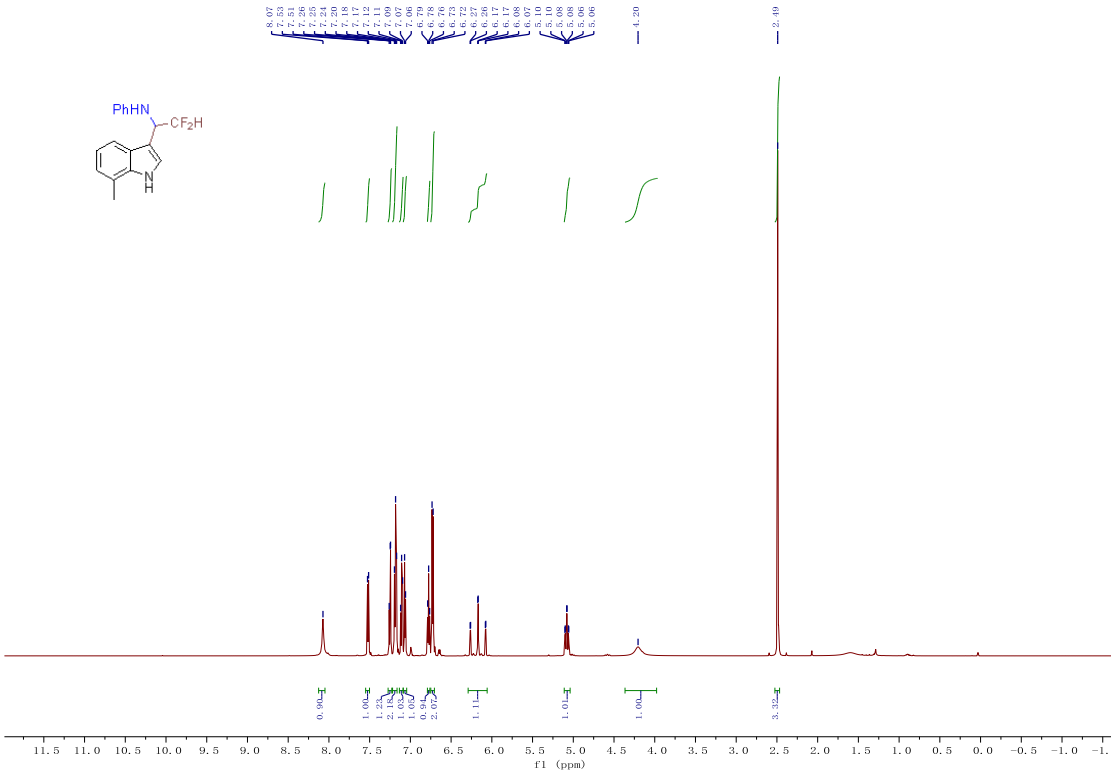
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7qa**



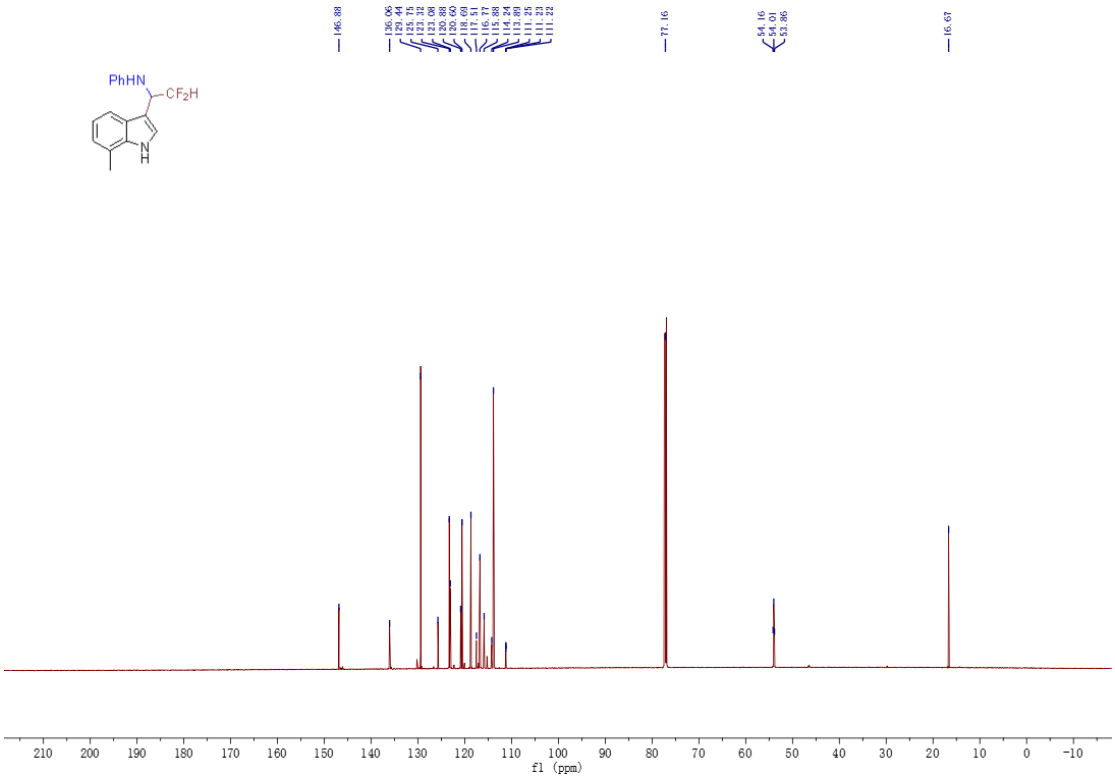
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7qa**



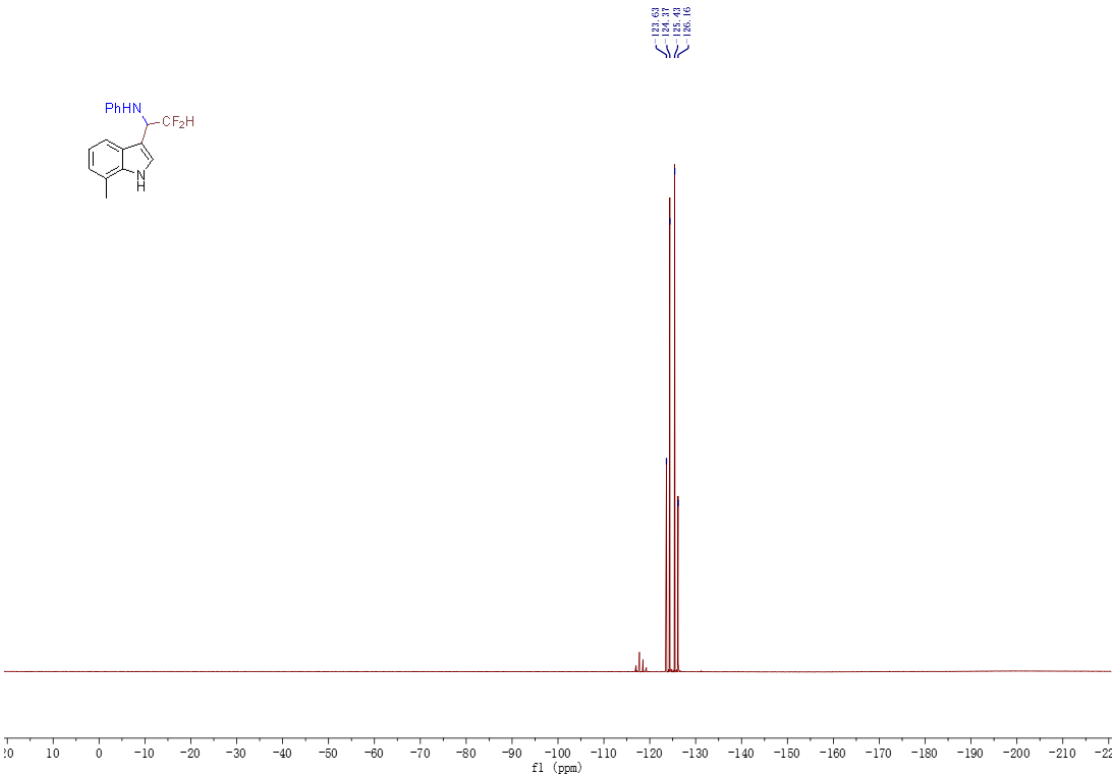
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ra**



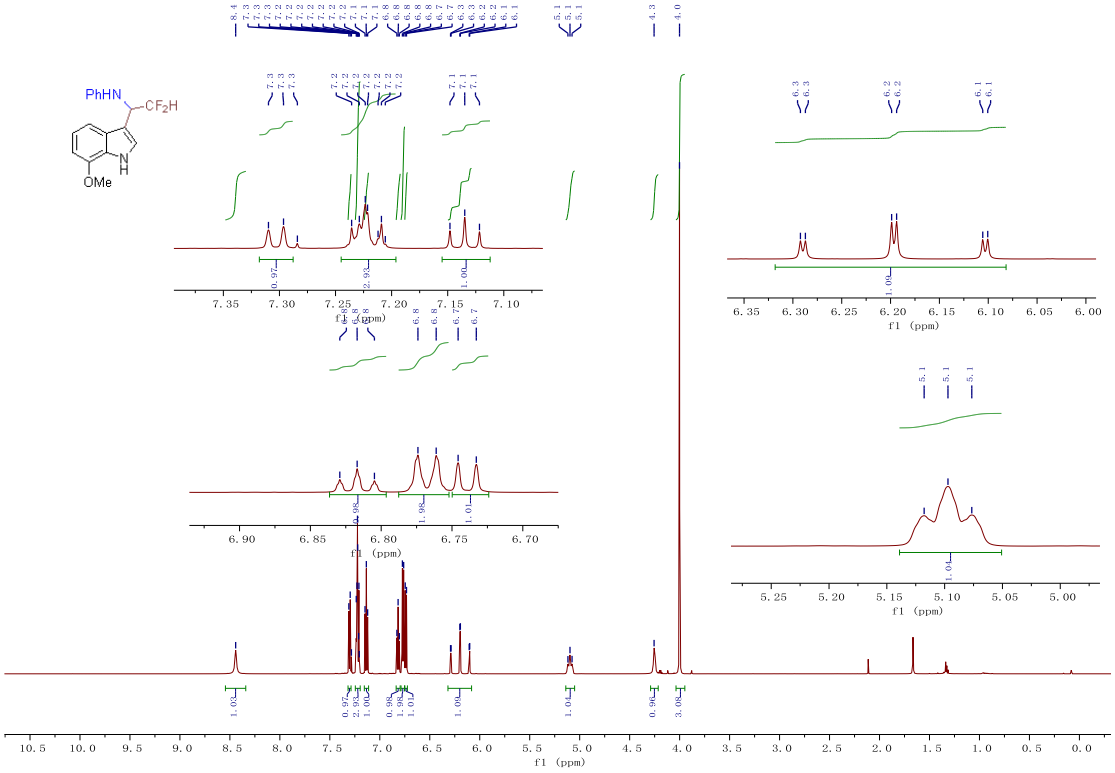
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ra**



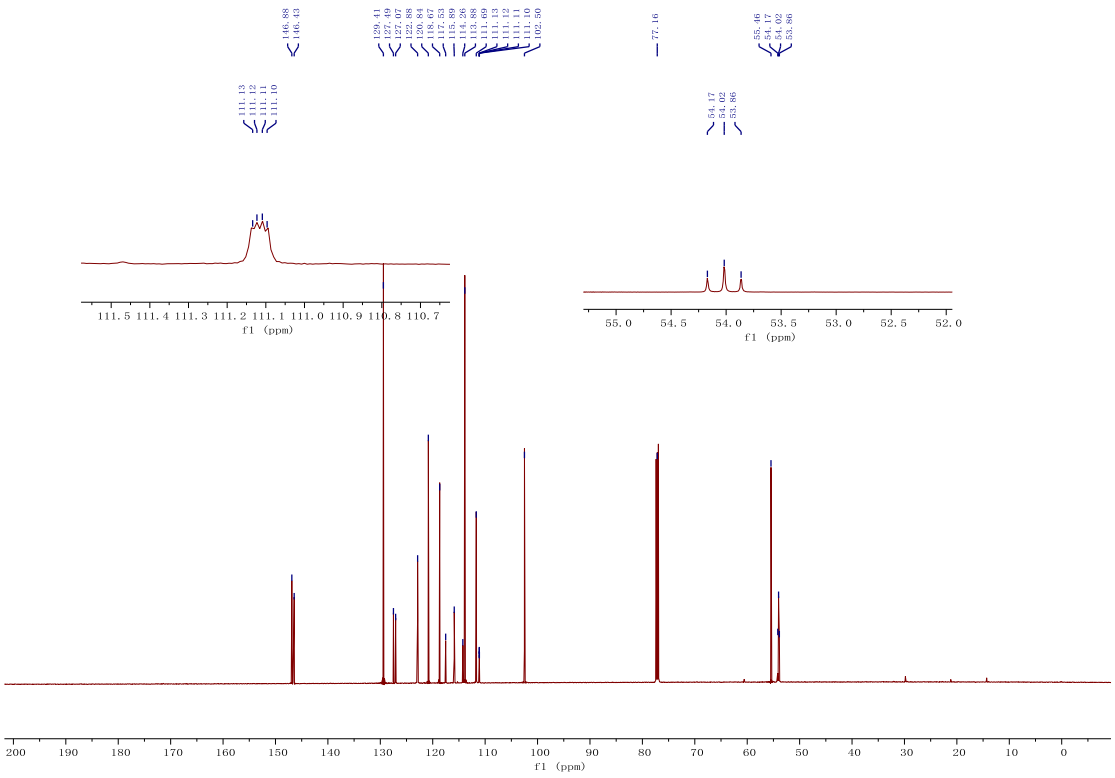
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ra**



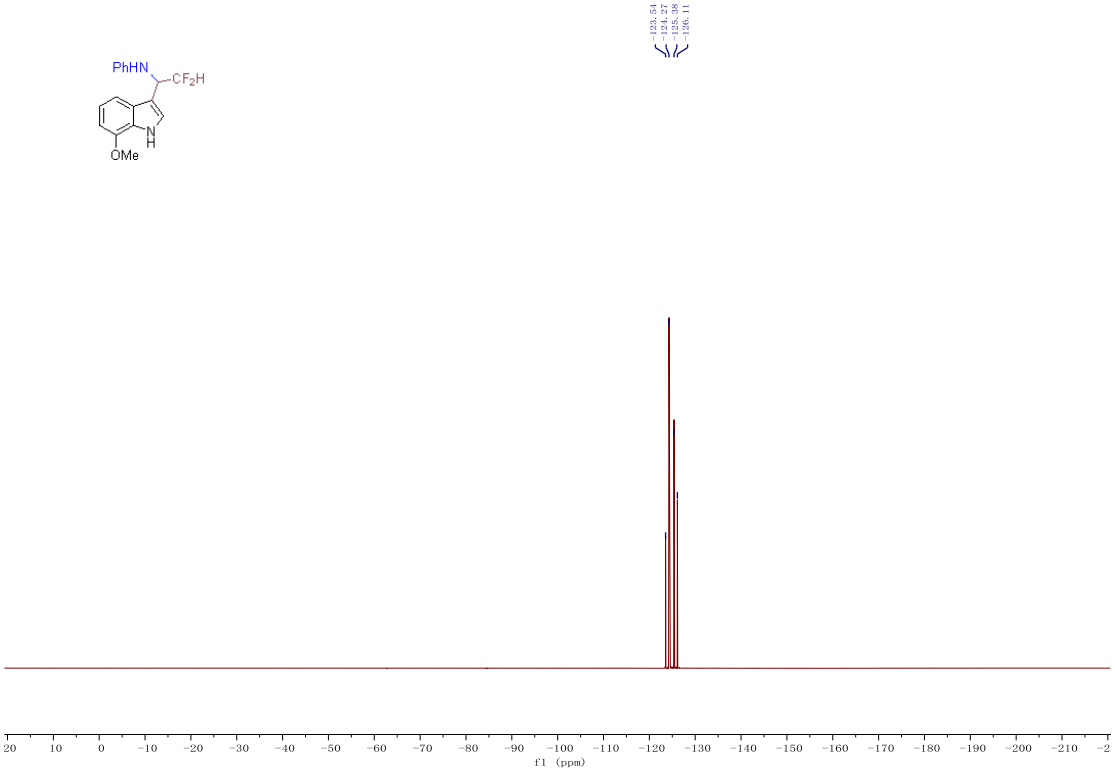
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7sa**



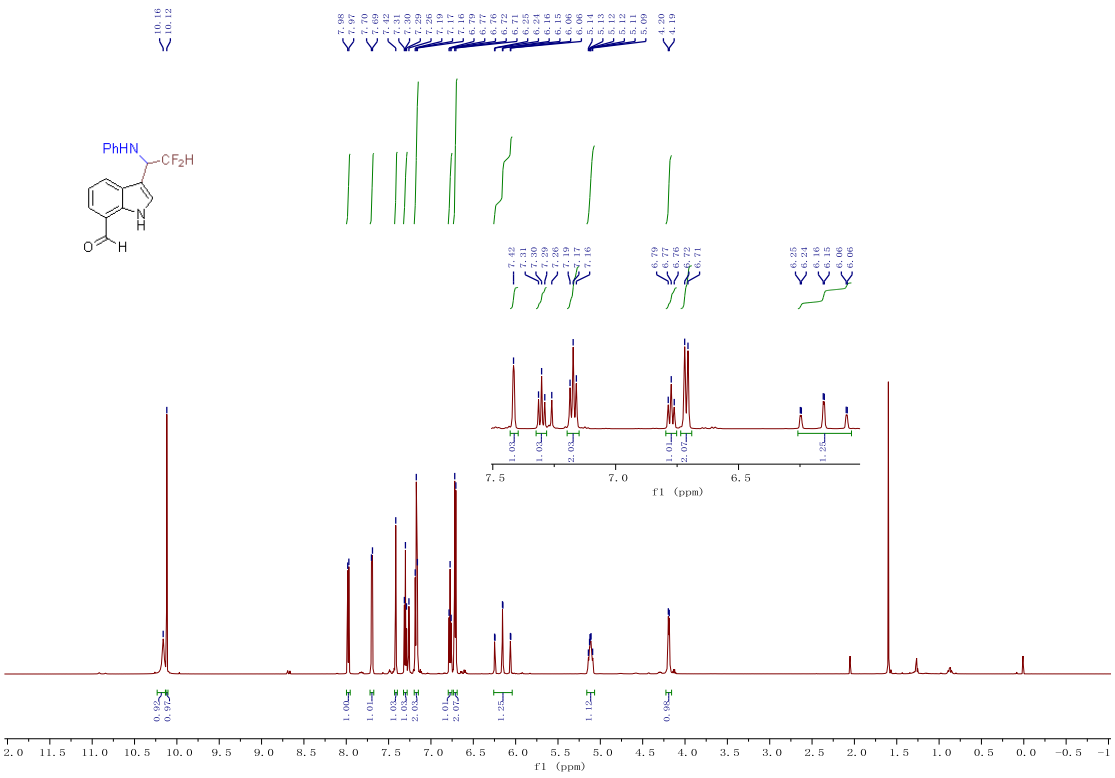
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7sa**



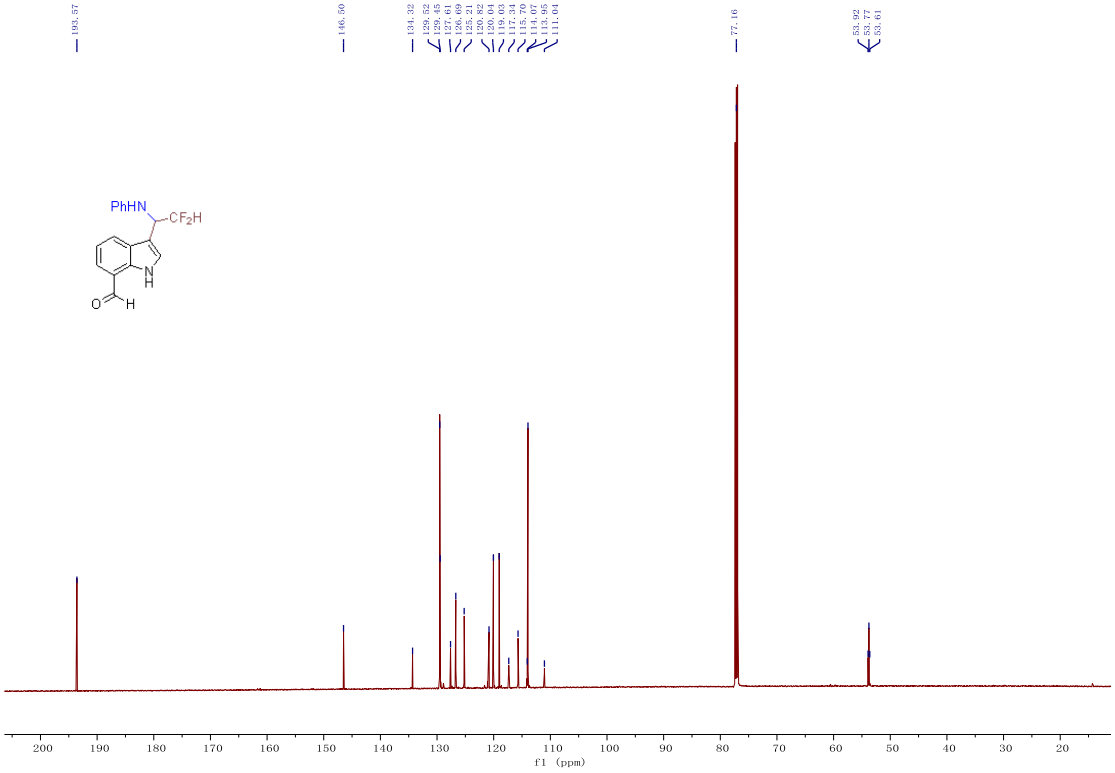
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7sa**



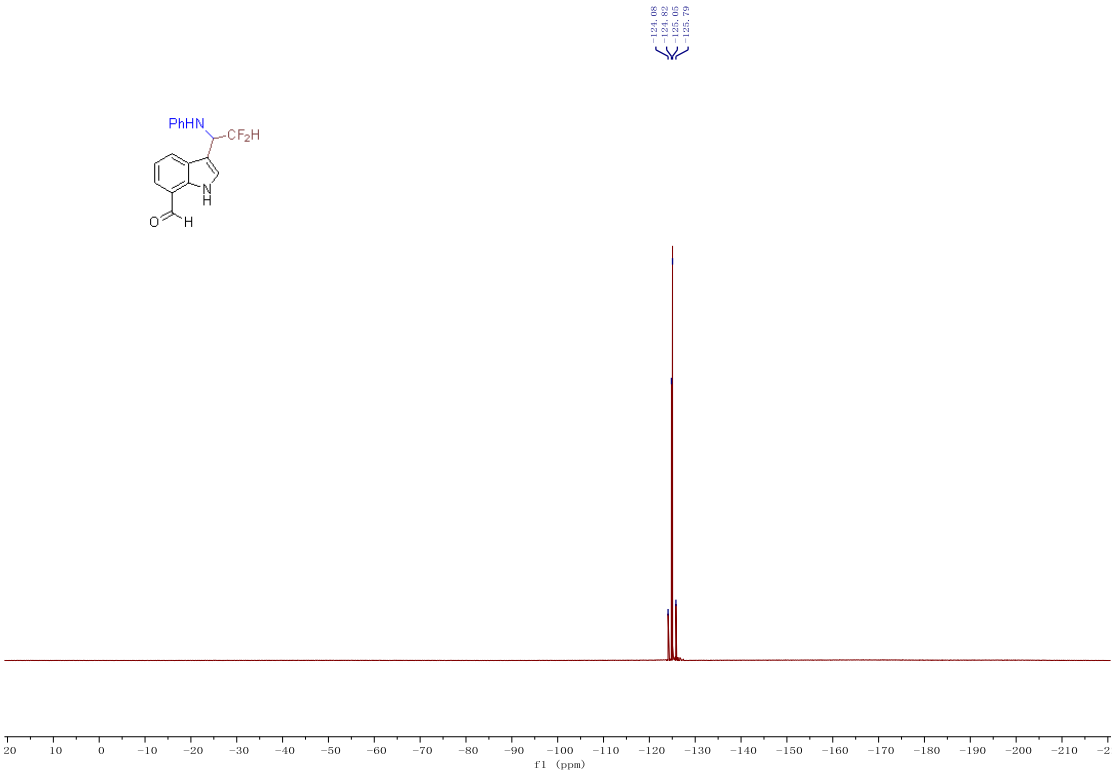
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ta**



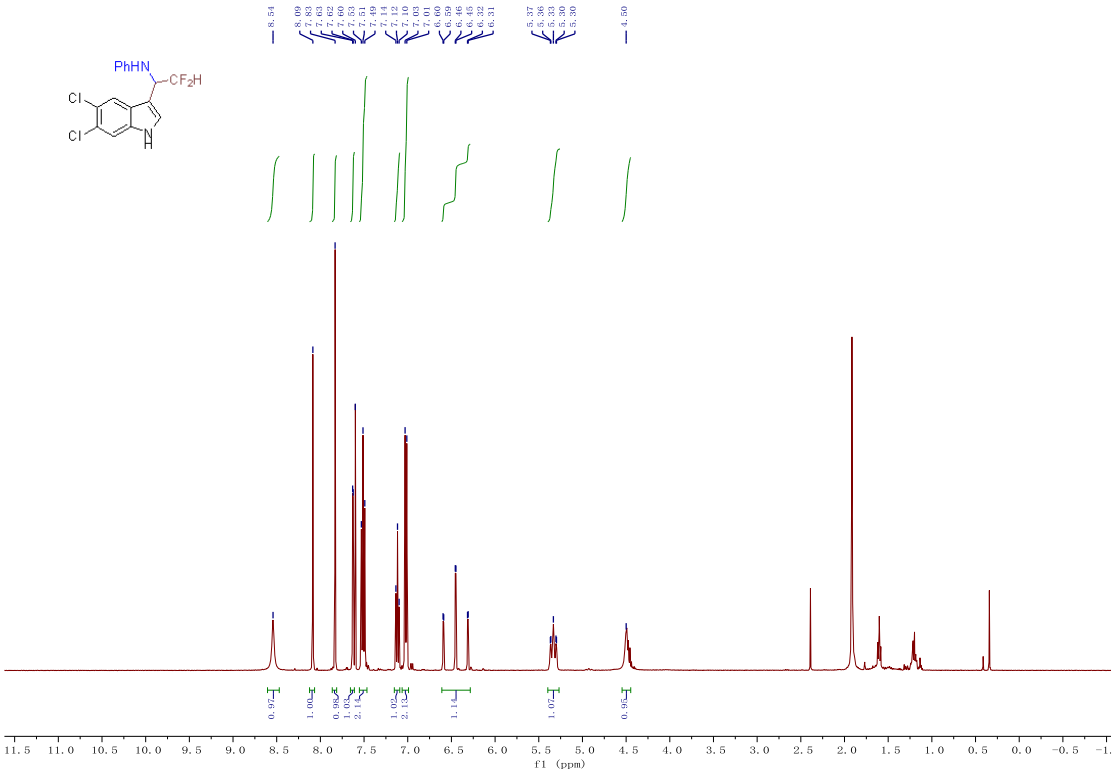
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ta**



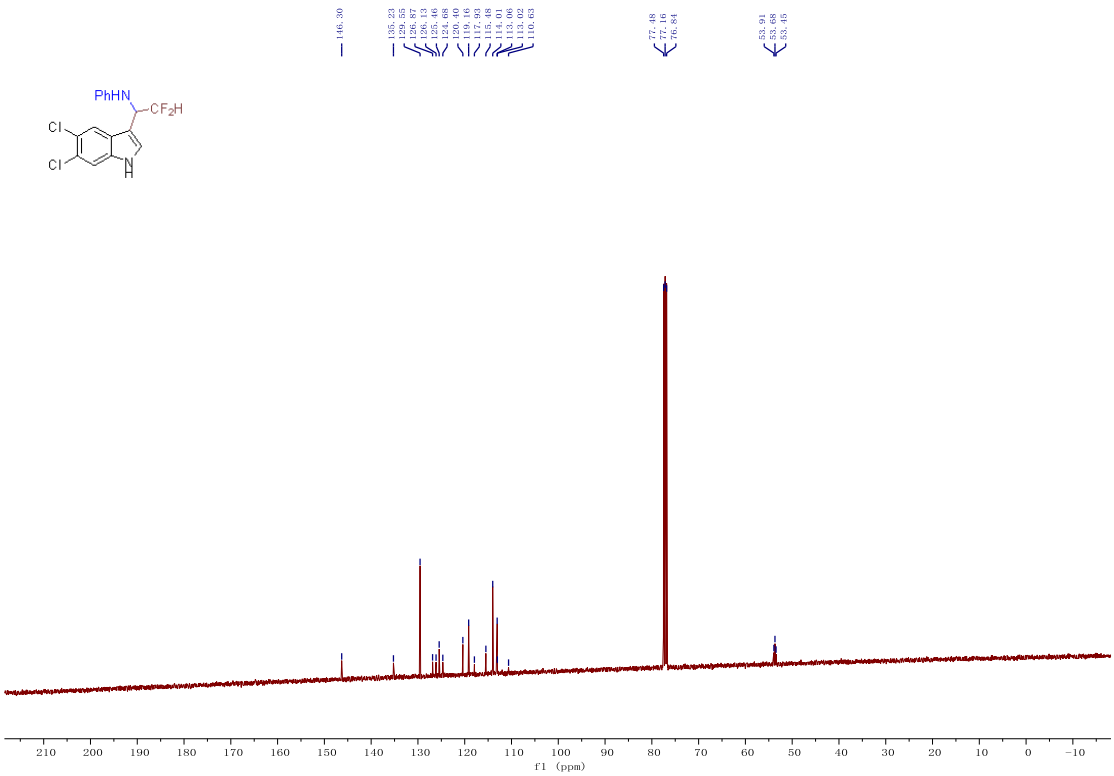
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ta**



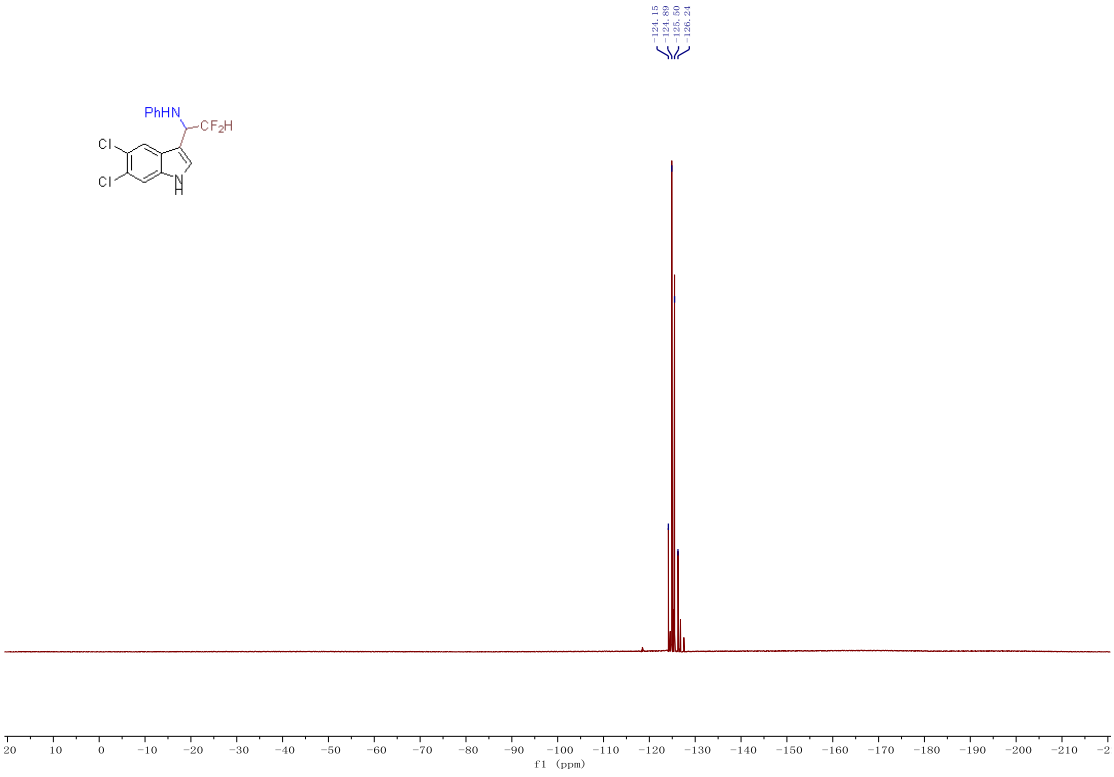
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ua**



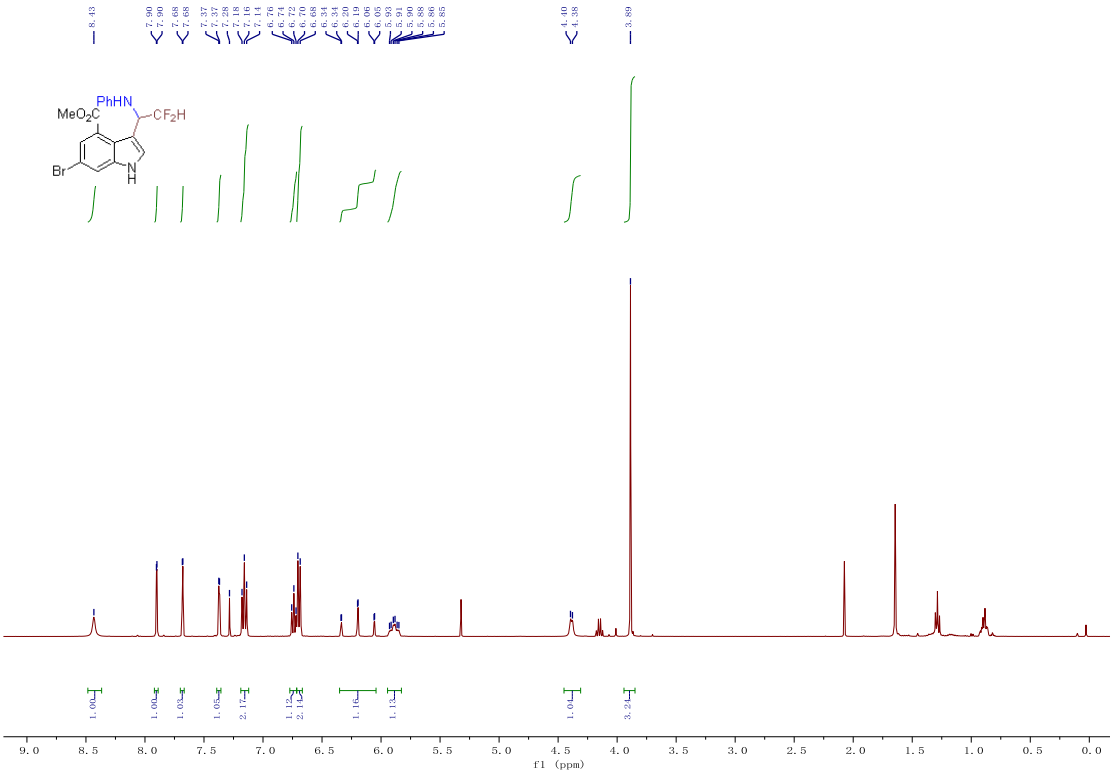
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ua**



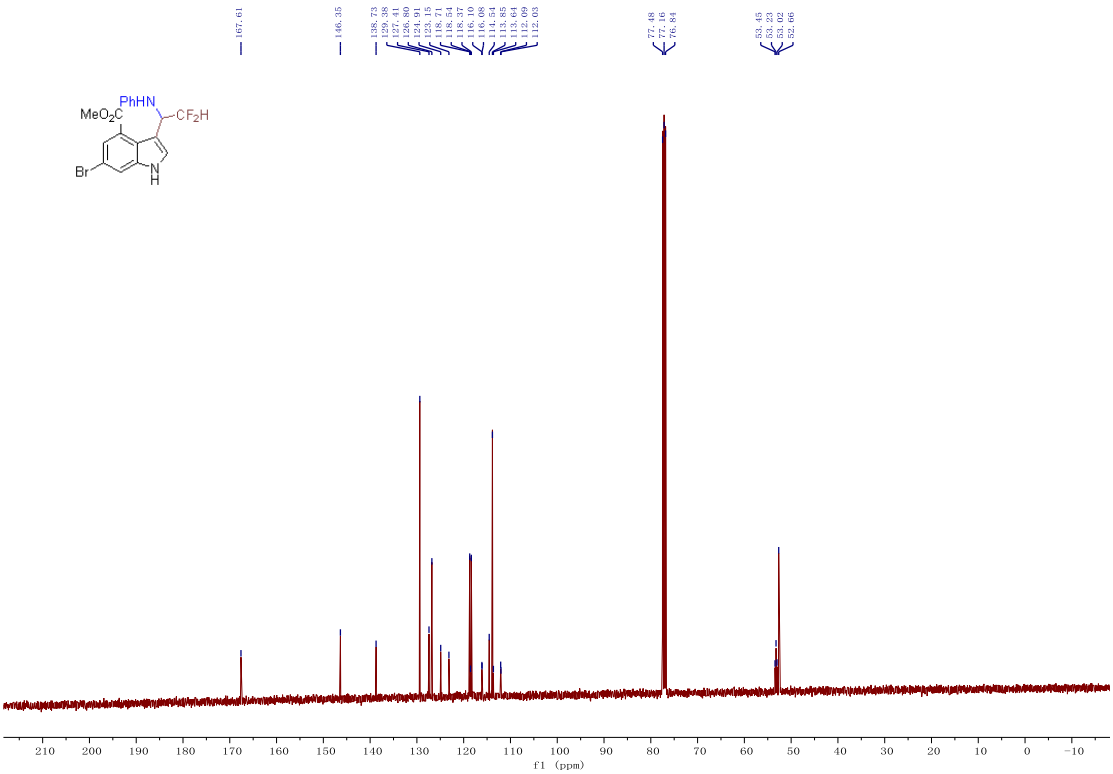
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ua**



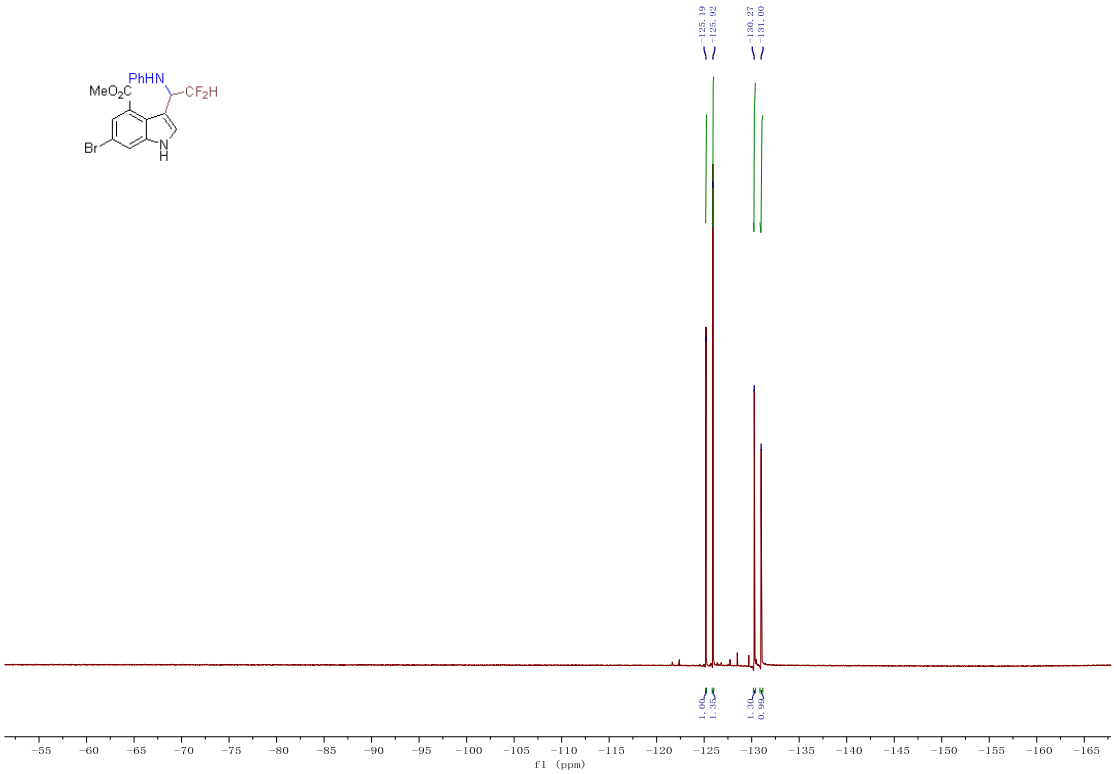
^{1}H NMR (400 MHz, CDCl3) spectra of **7va**



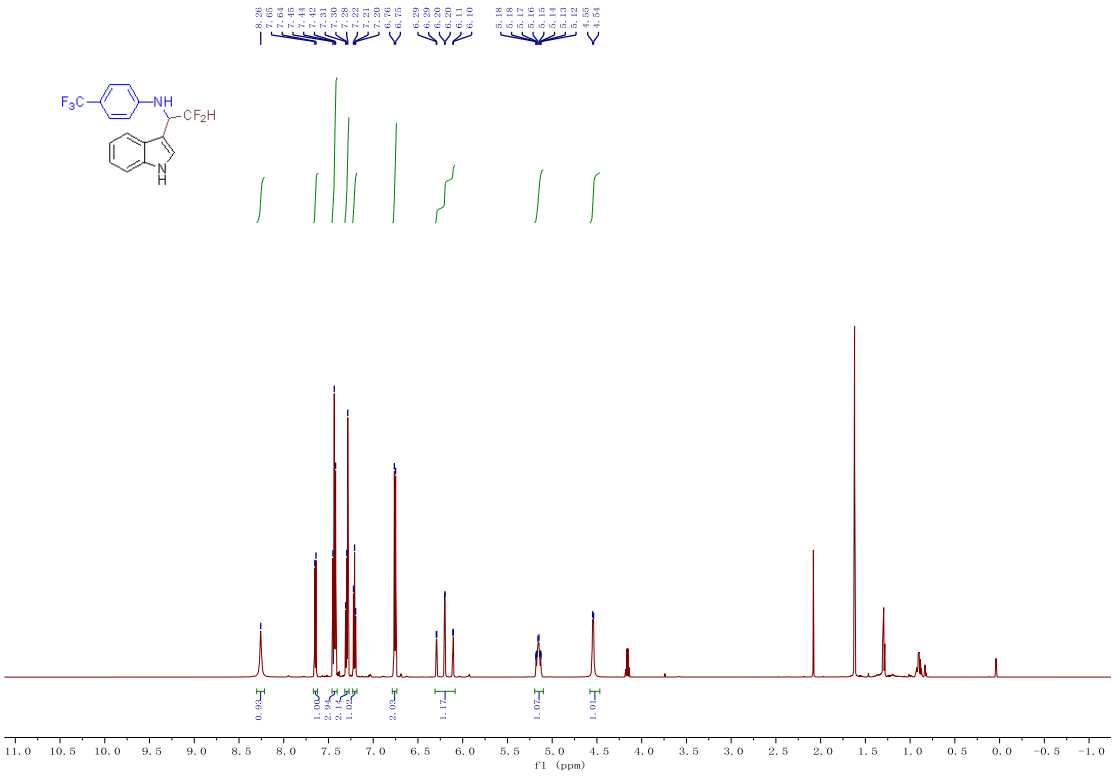
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7va**



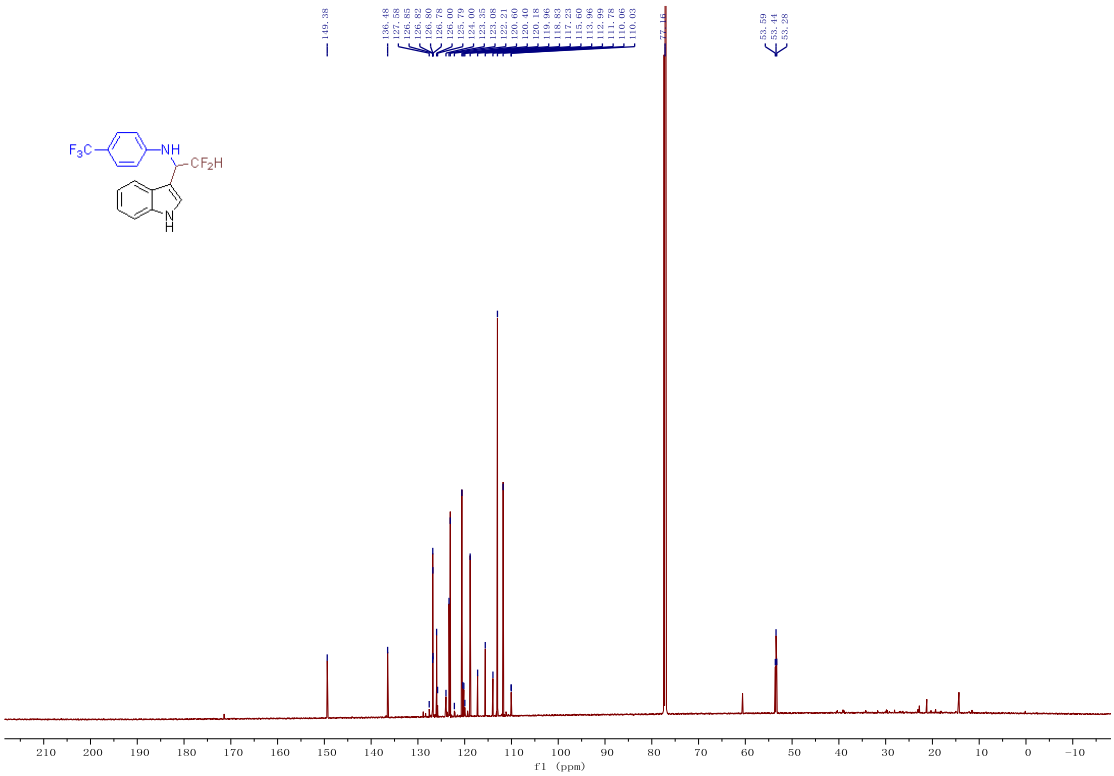
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7va**



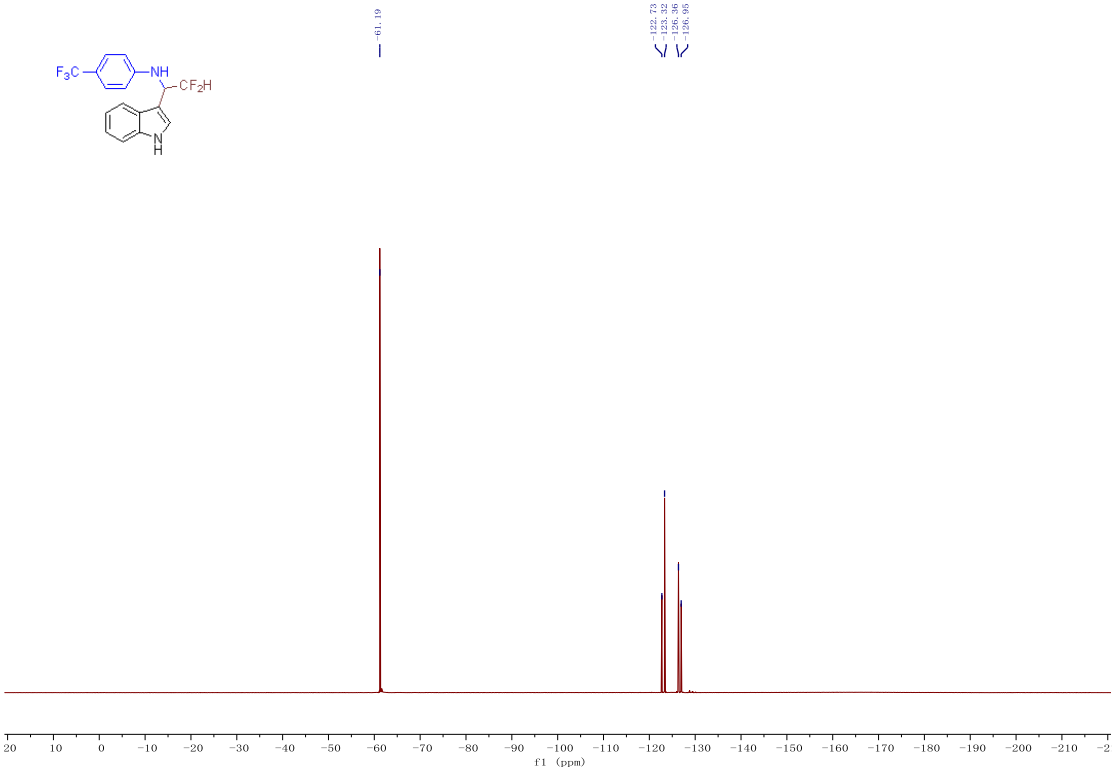
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ab**



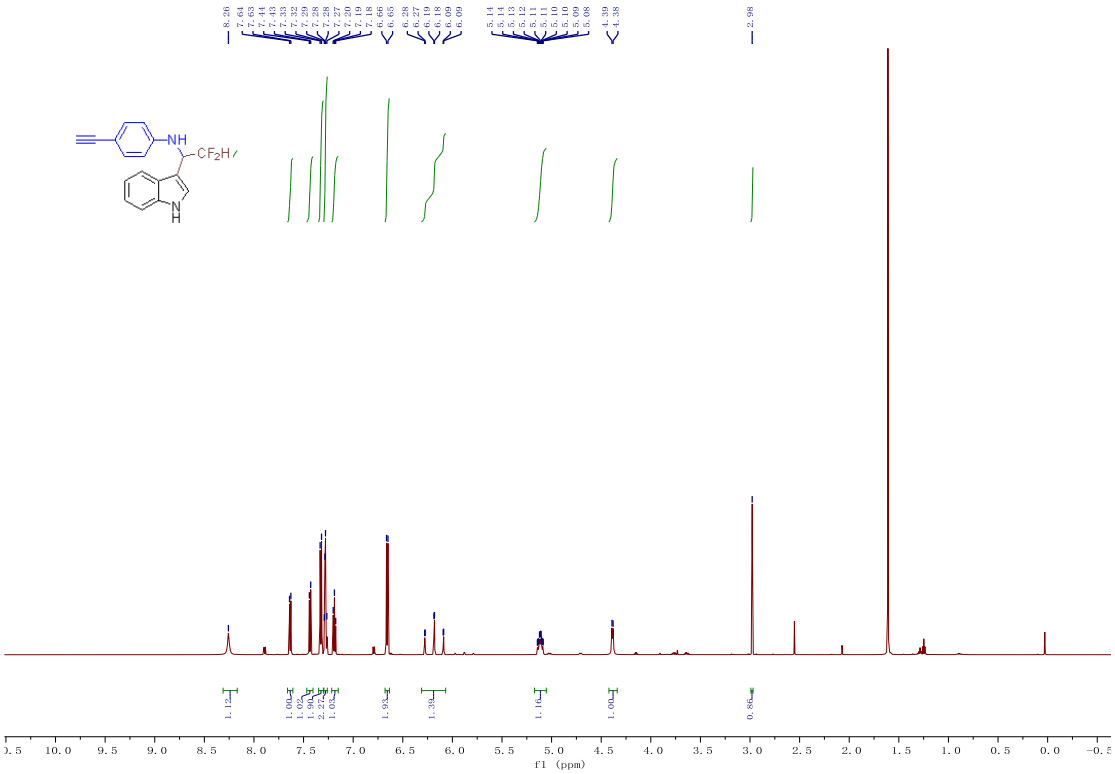
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ab**



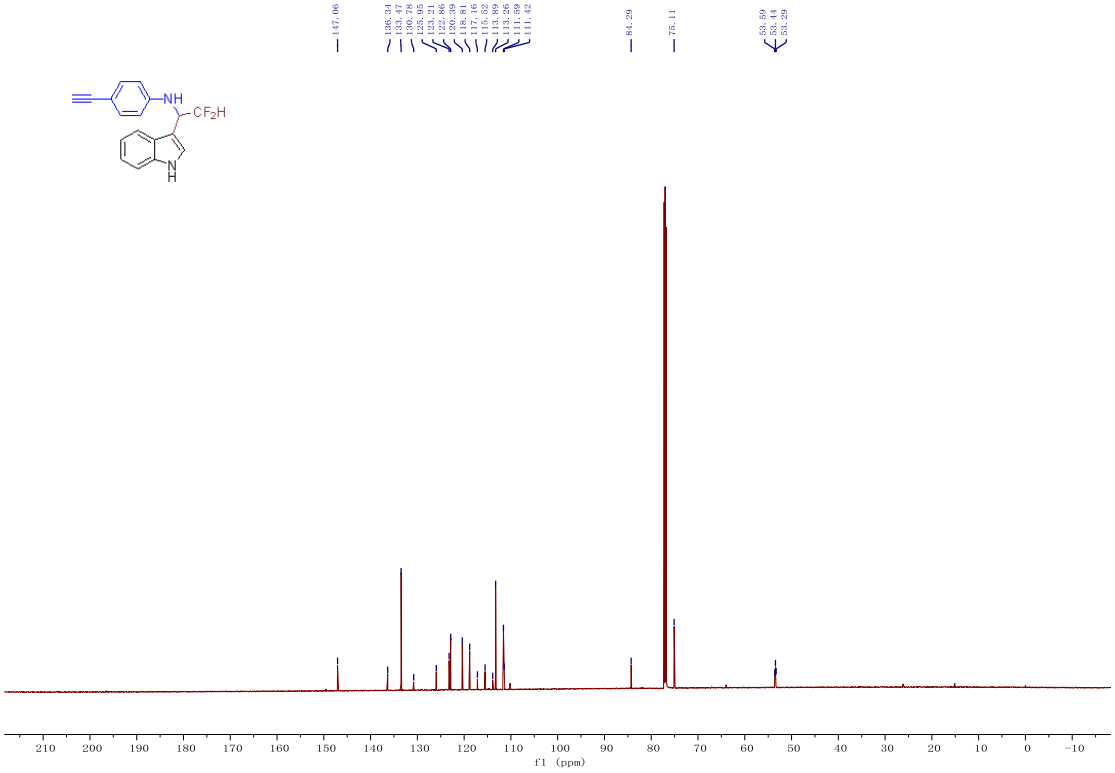
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ab**



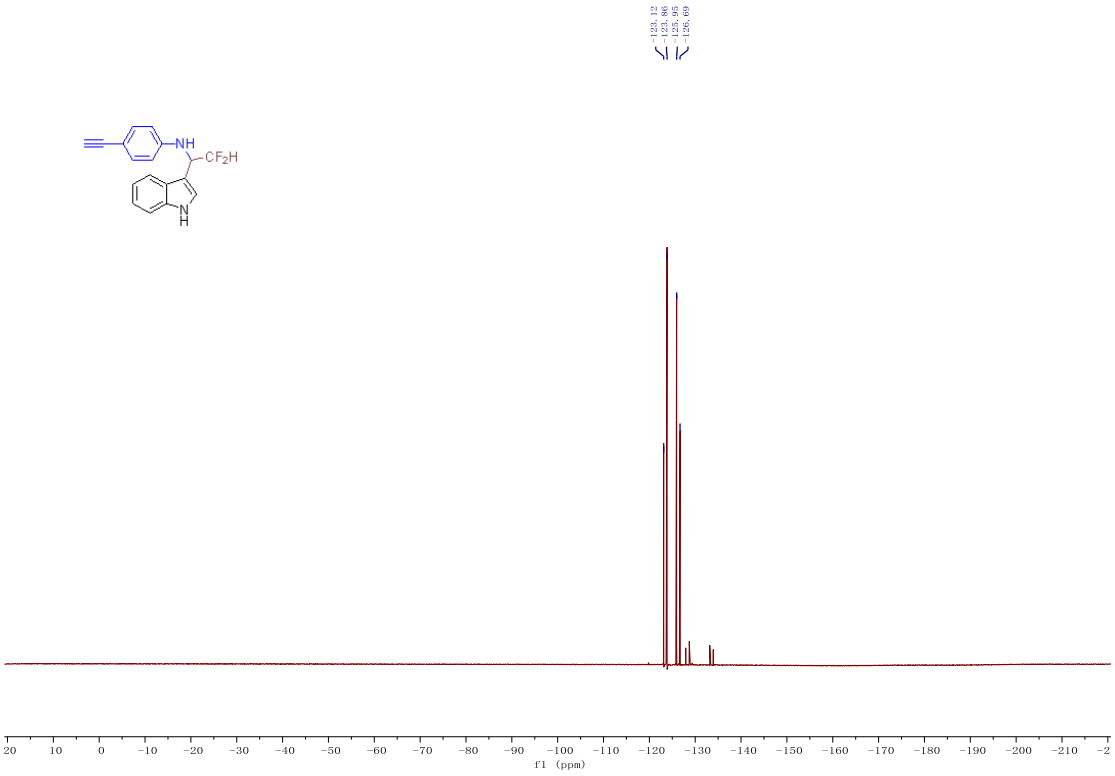
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ac**



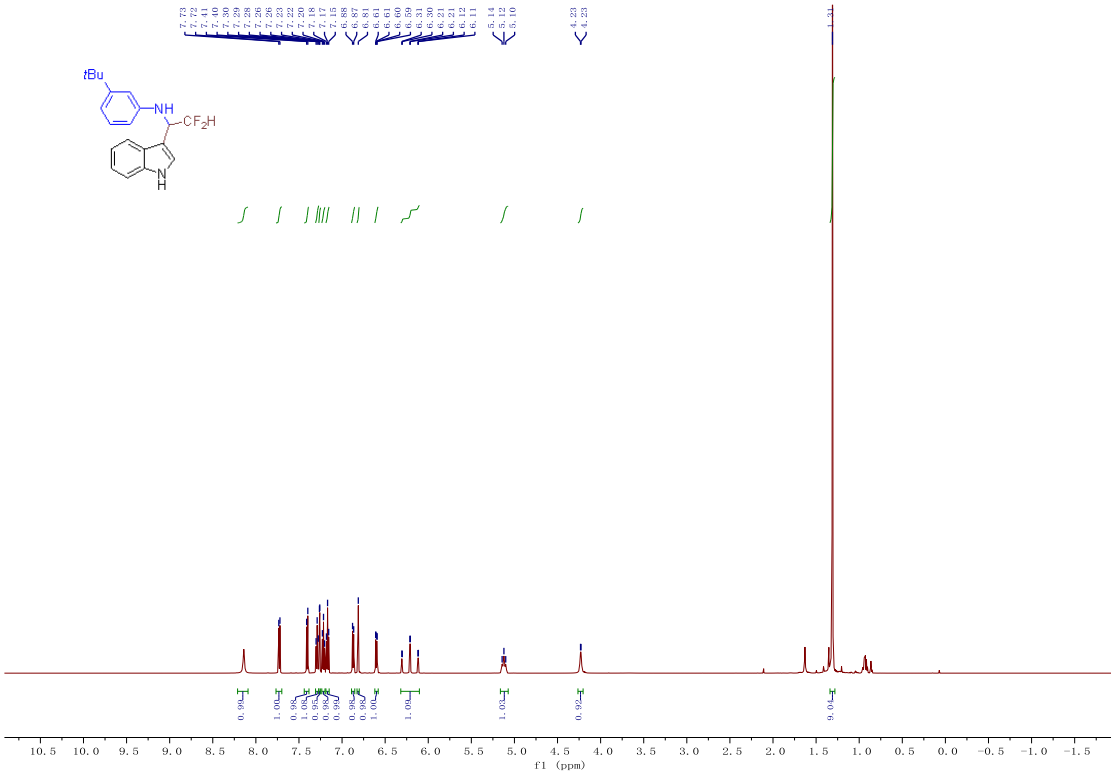
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ac**



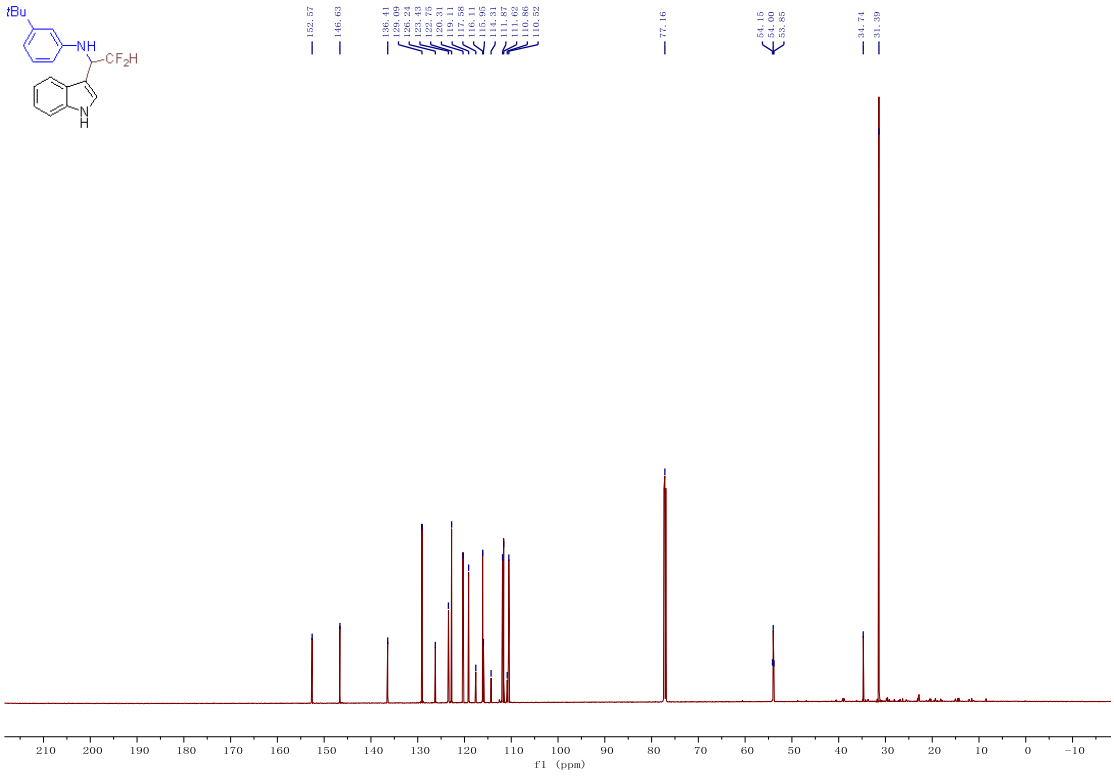
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ac**



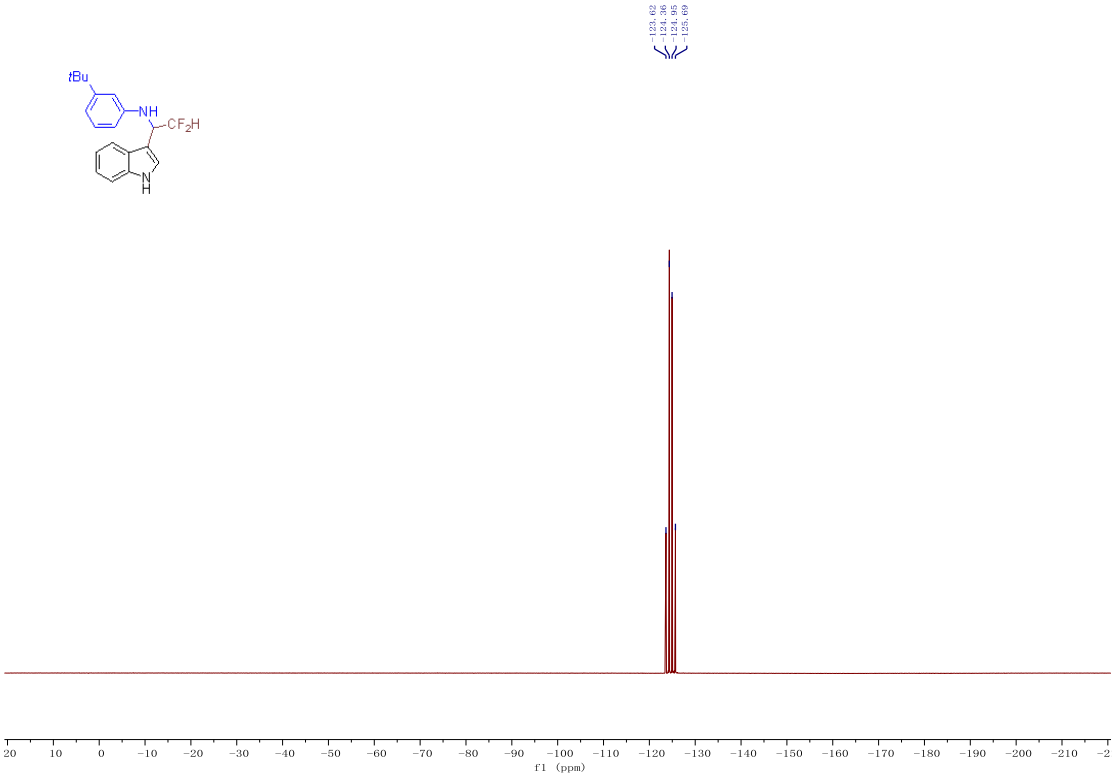
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7ad**



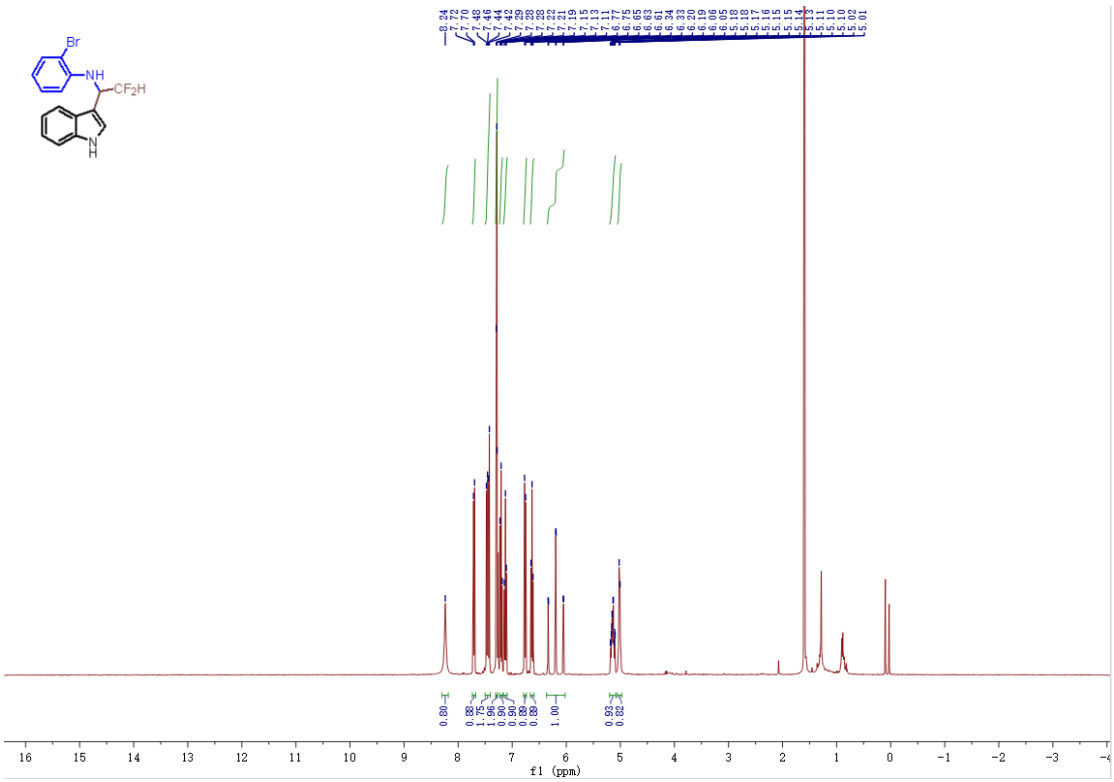
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ad**



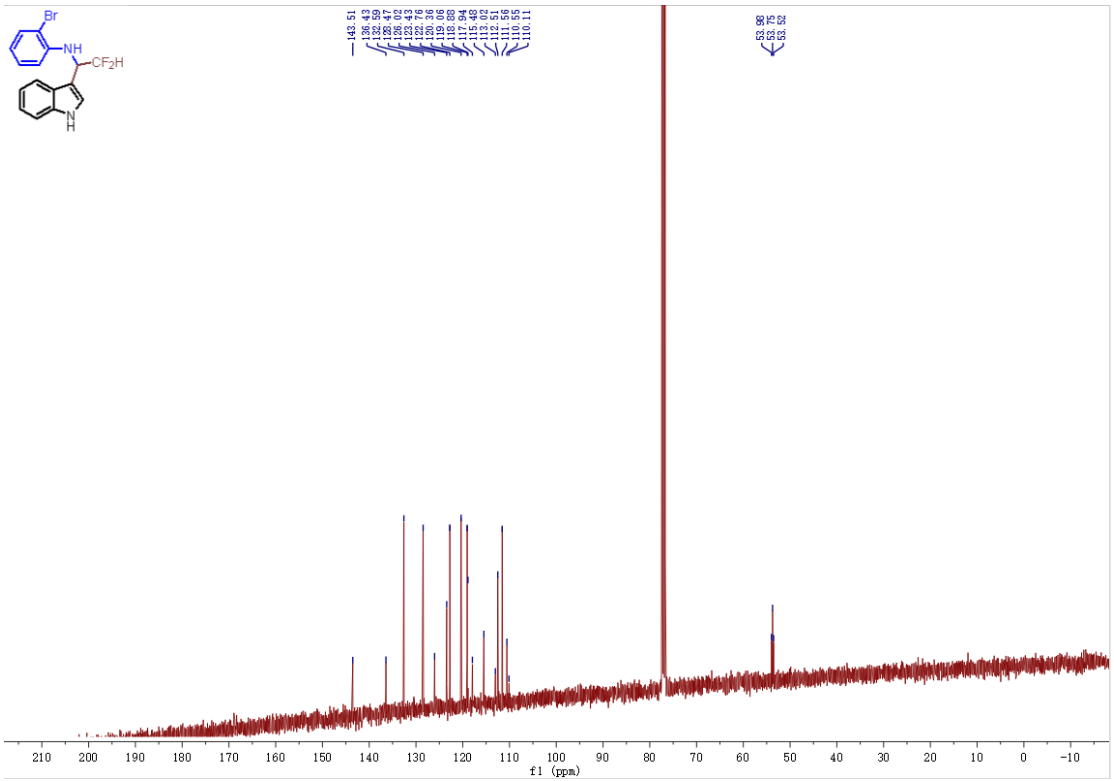
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ad**



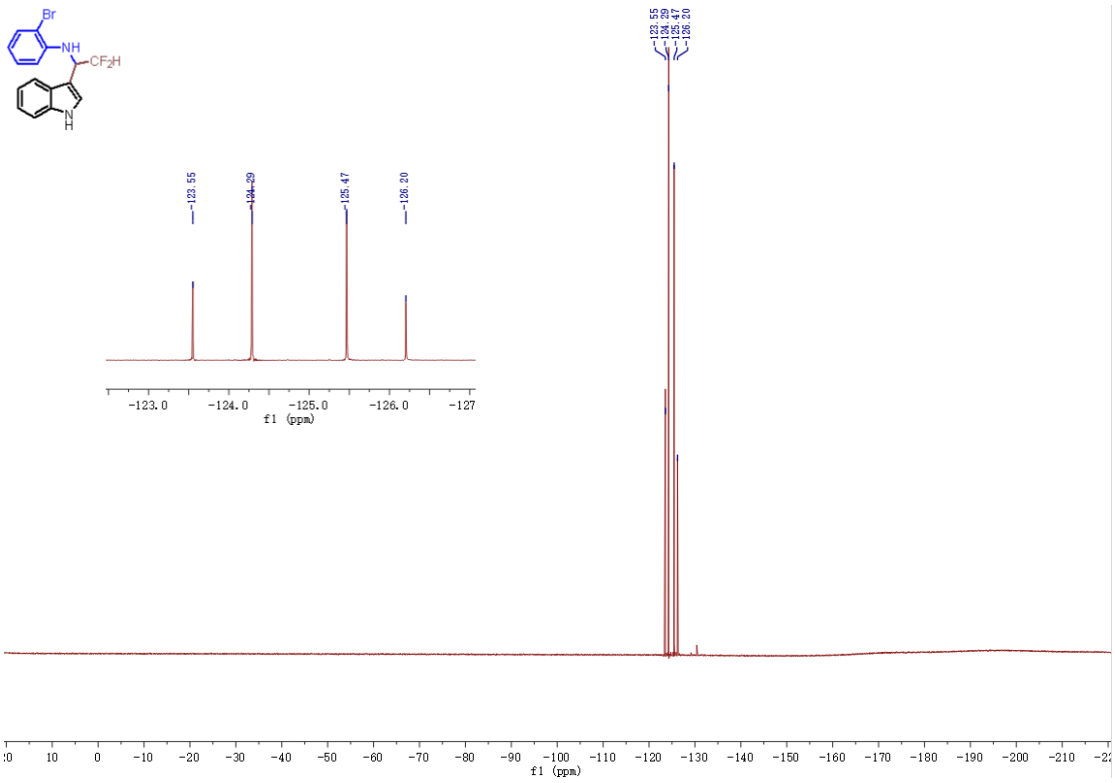
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ae**



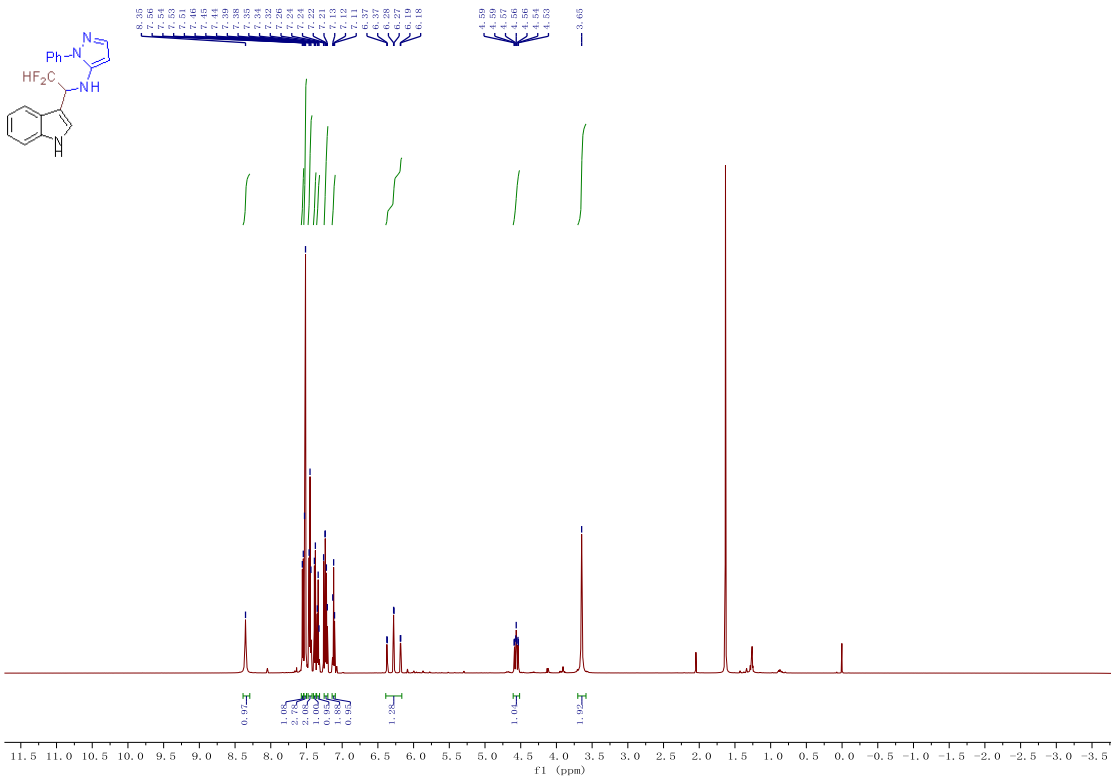
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7ae**



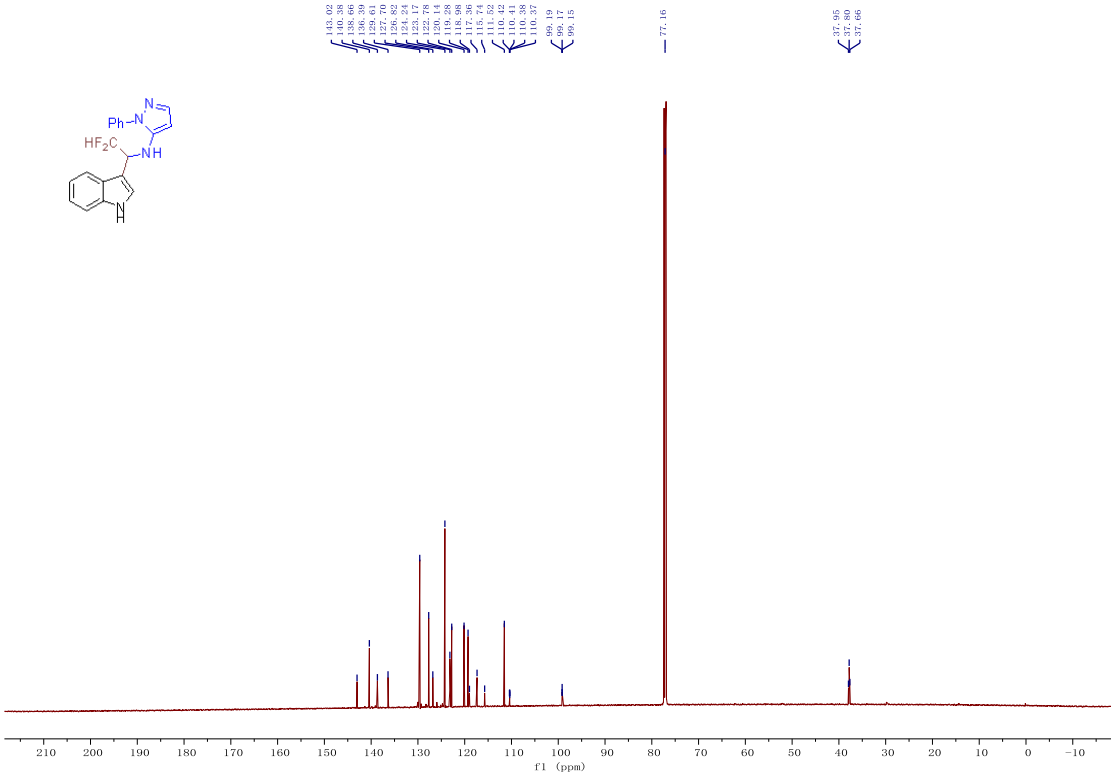
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ae**



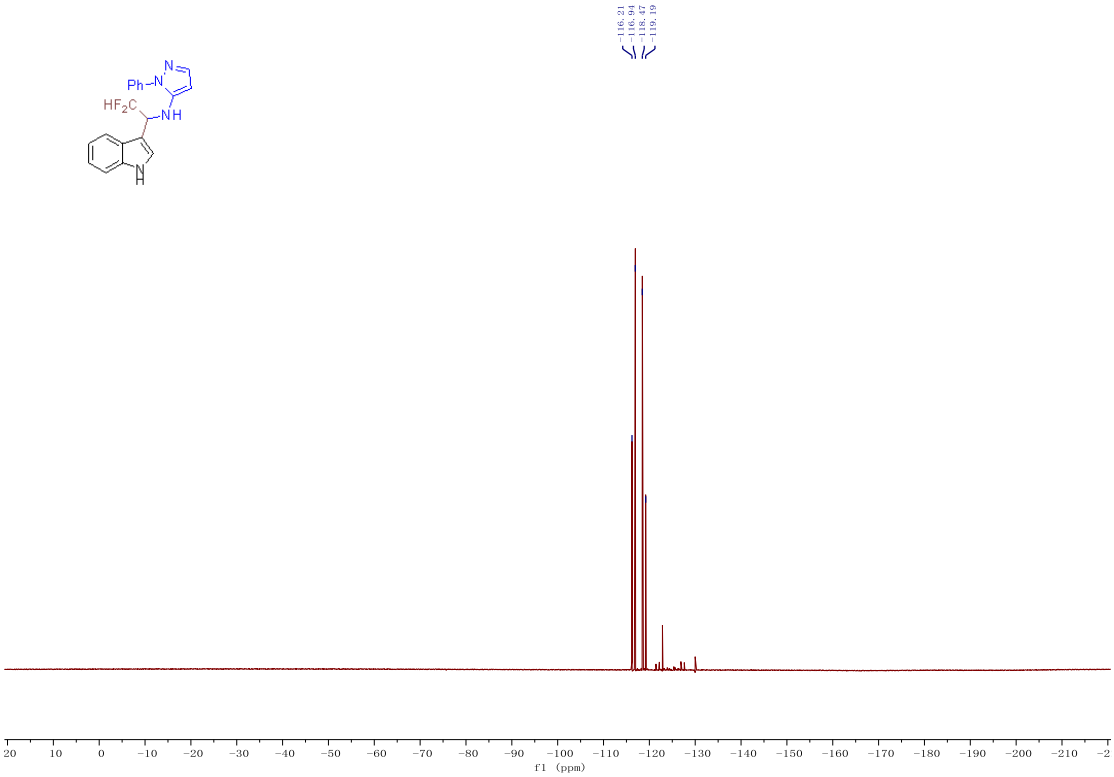
^{1}H NMR (600 MHz, $CDCl_3$) spectra of **7af**



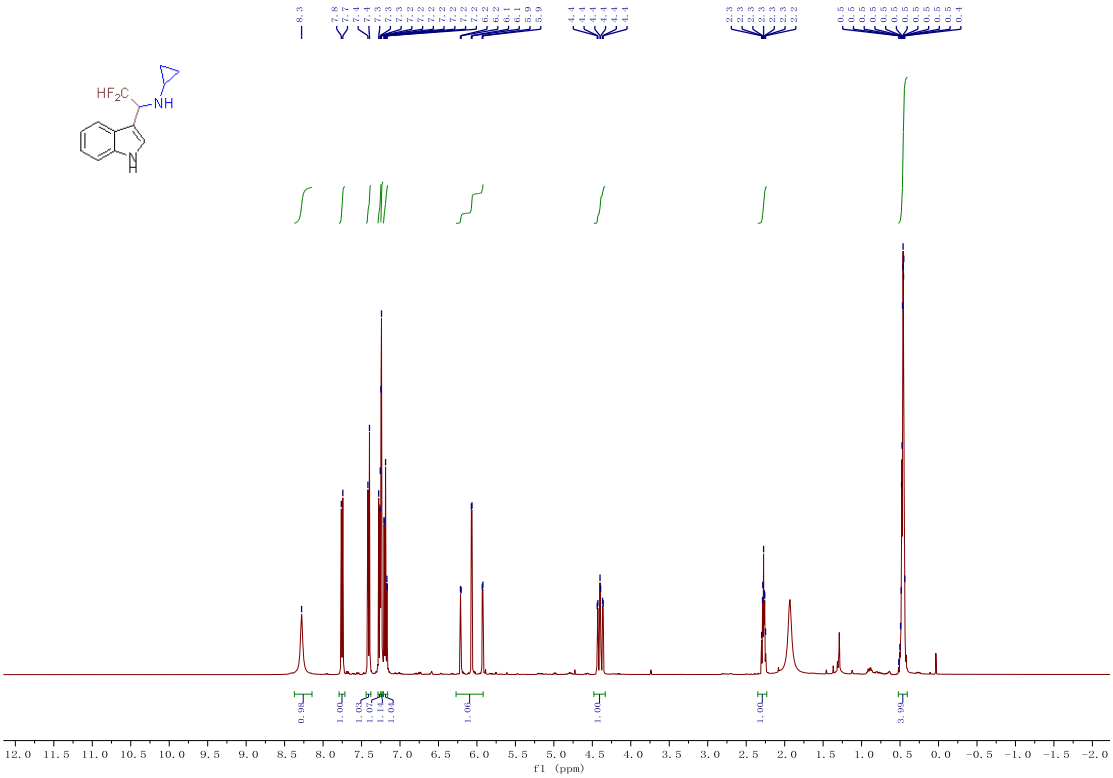
^{13}C NMR (151 MHz, $CDCl_3$) spectra of **7af**



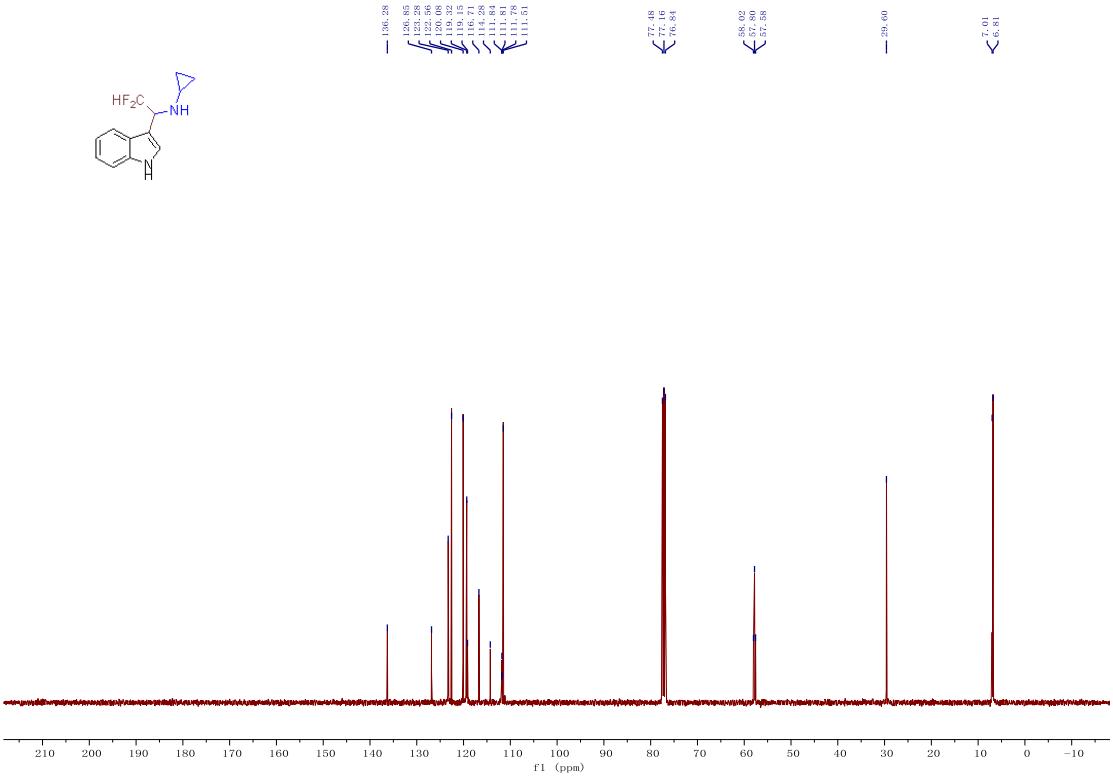
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7af**



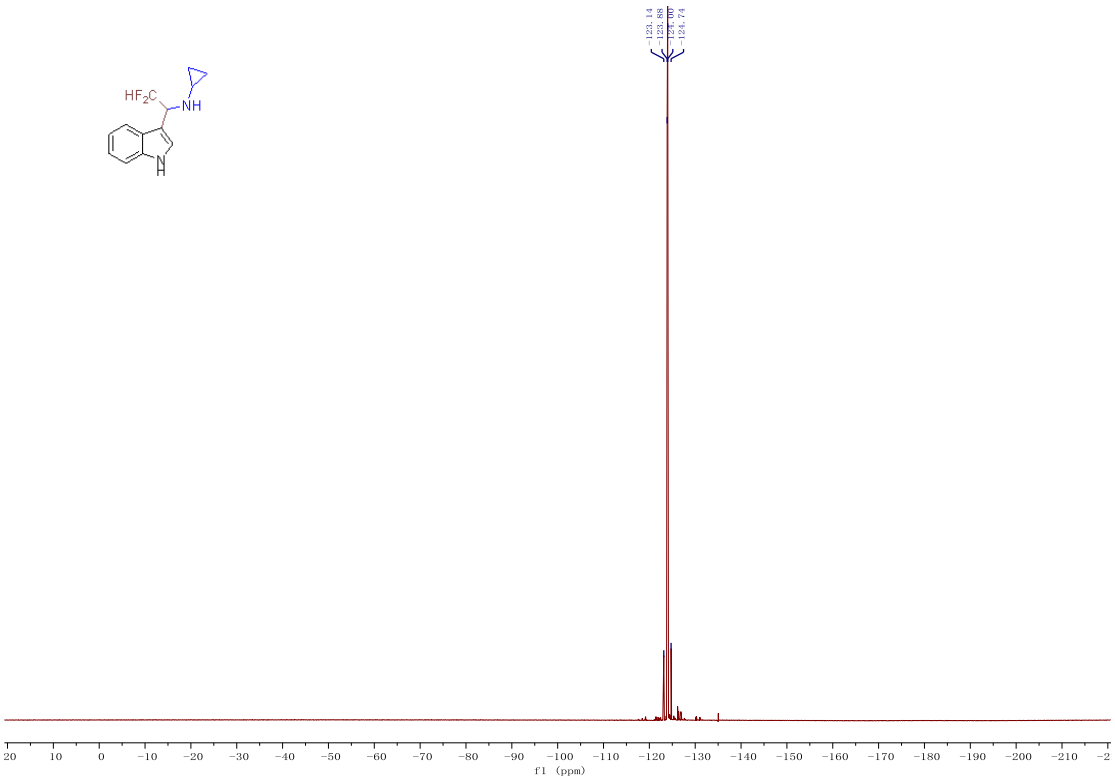
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ag**



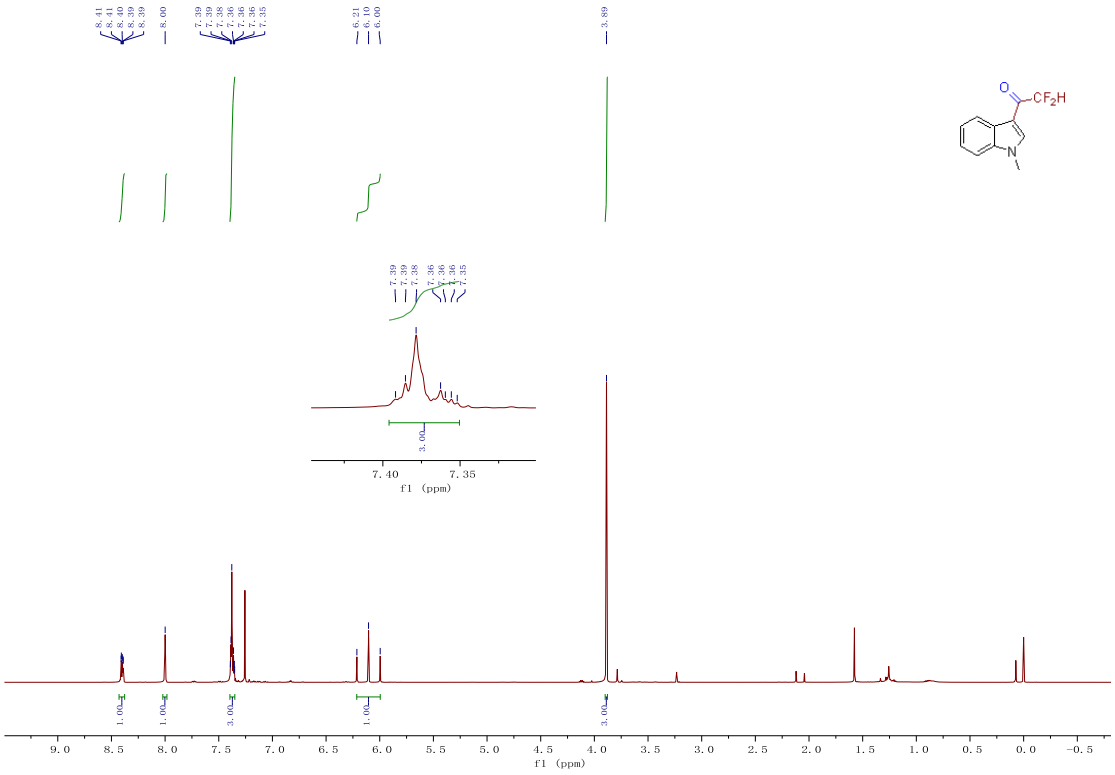
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ag**



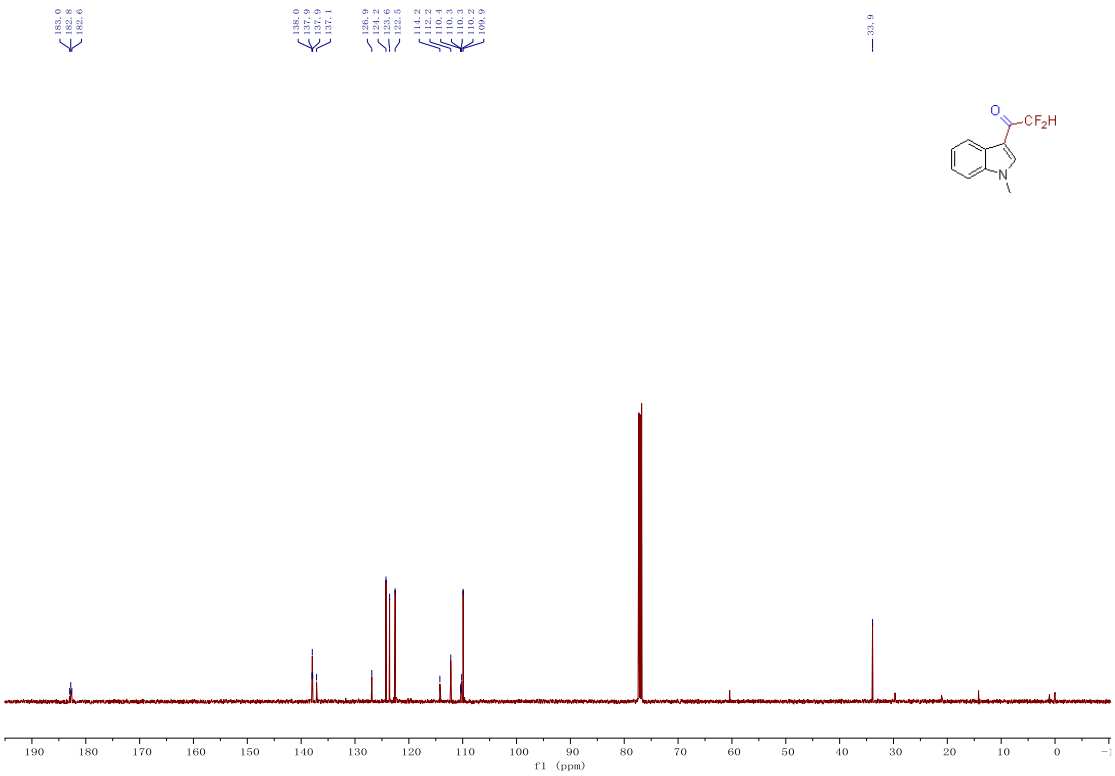
^{19}F NMR (377 MHz, Chloroform-*d*) spectra of **7ag**



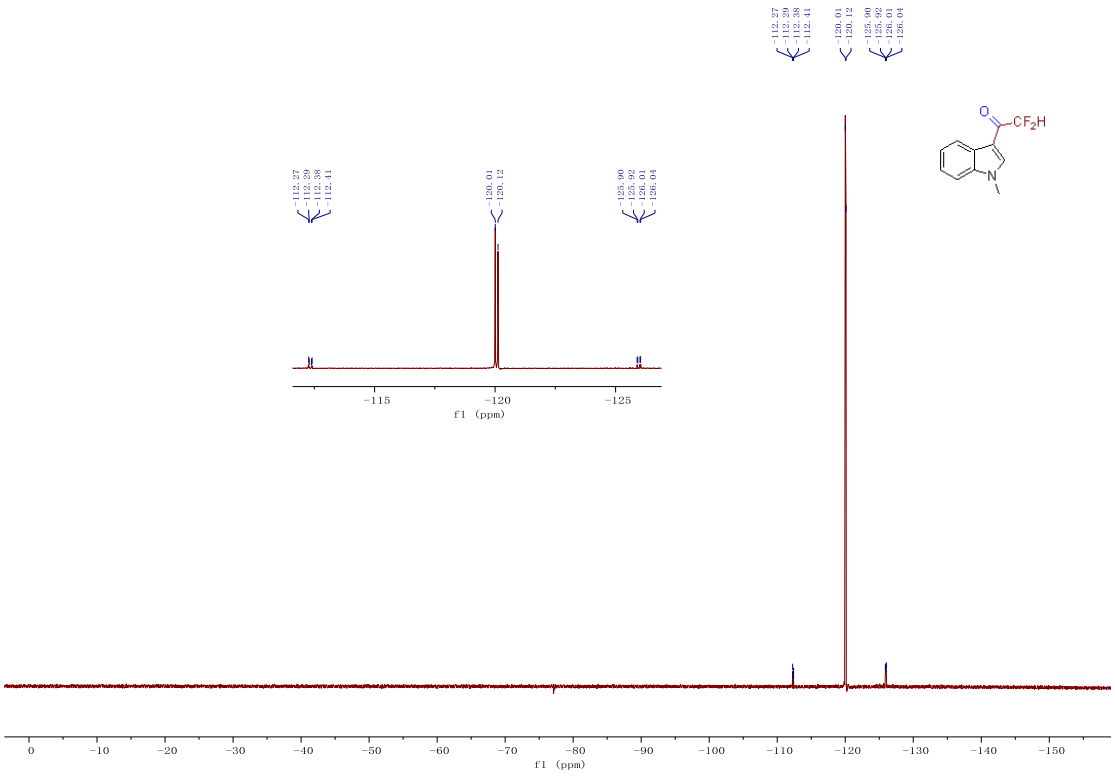
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **9**



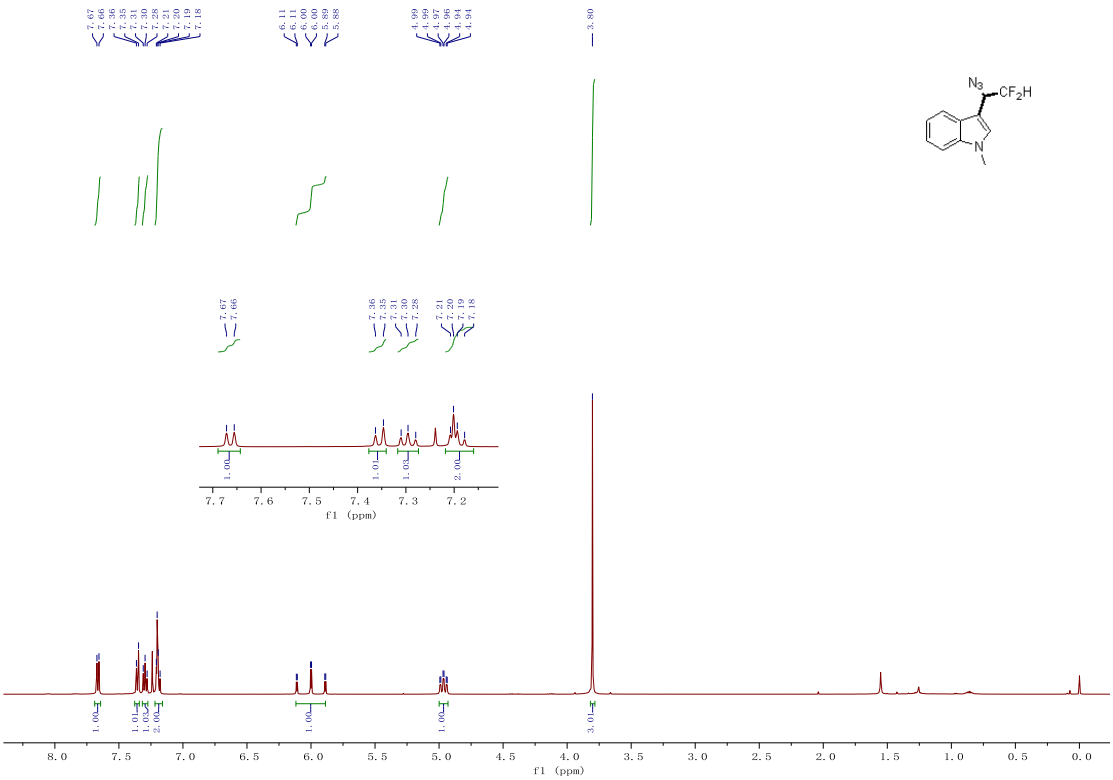
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **9**



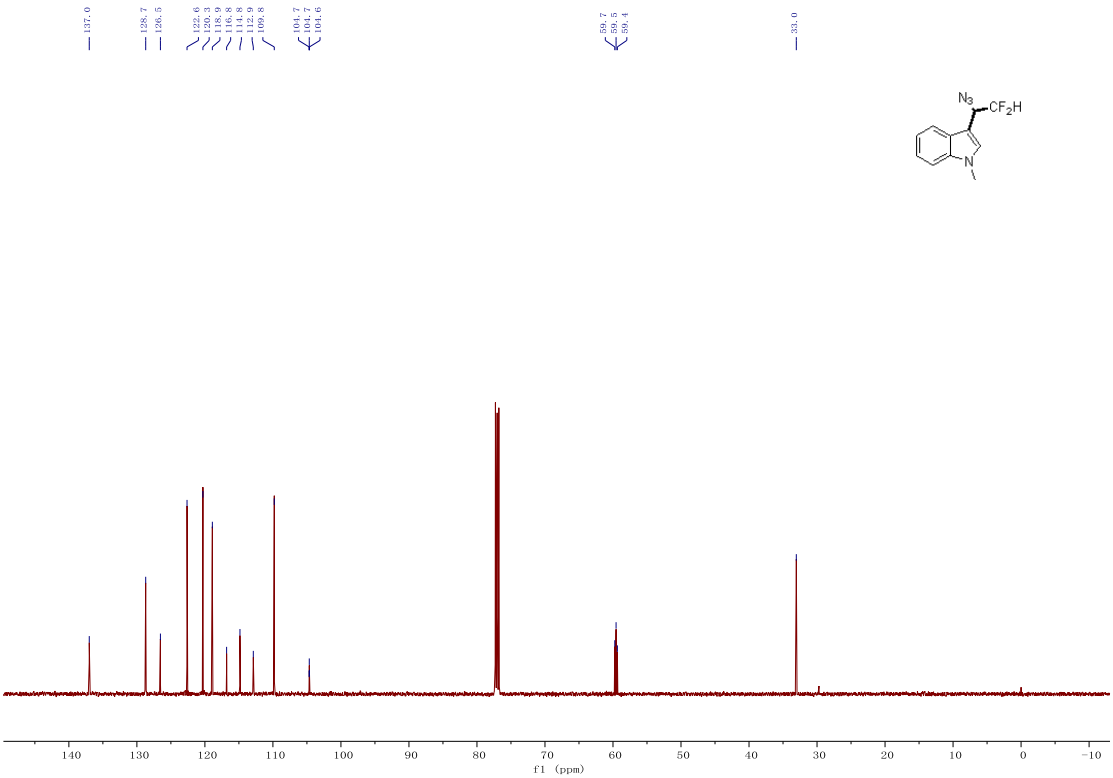
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **9**



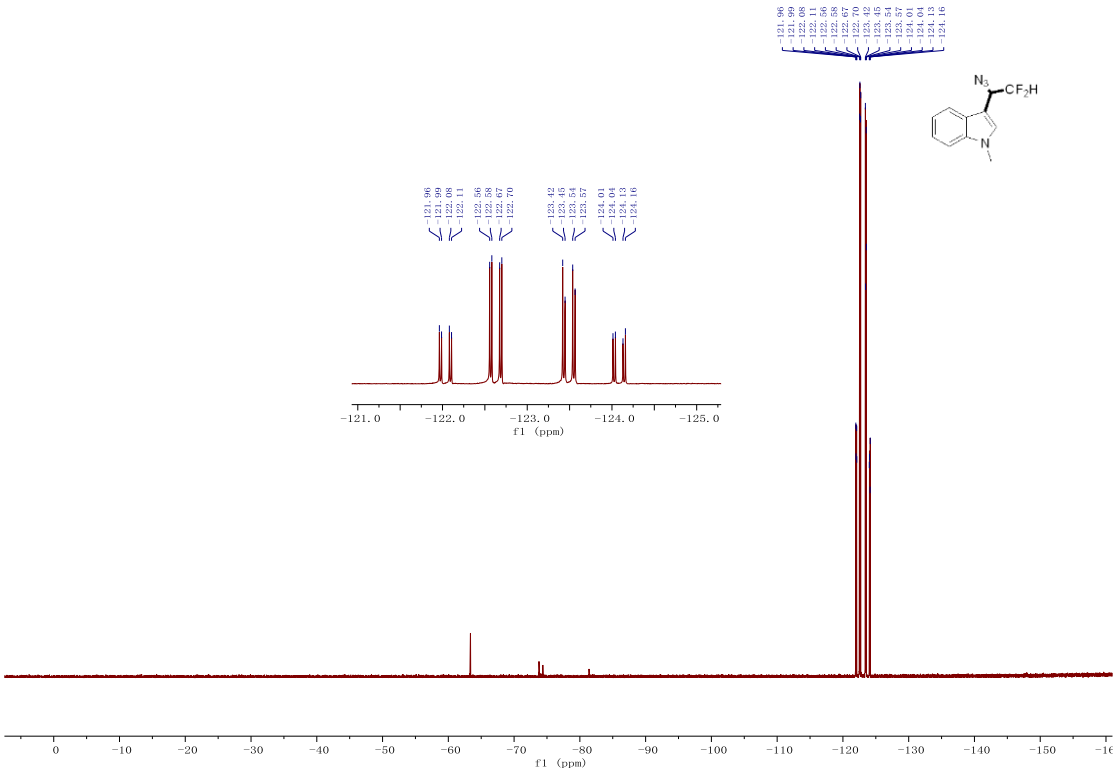
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **10**



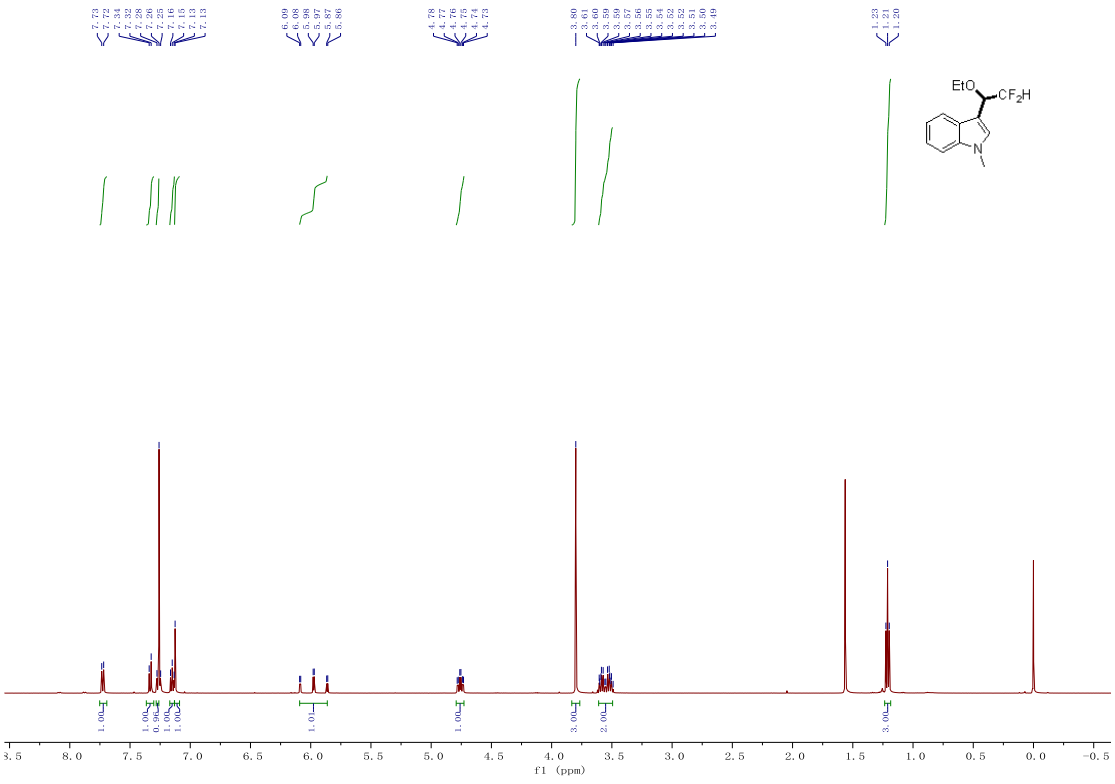
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **10**



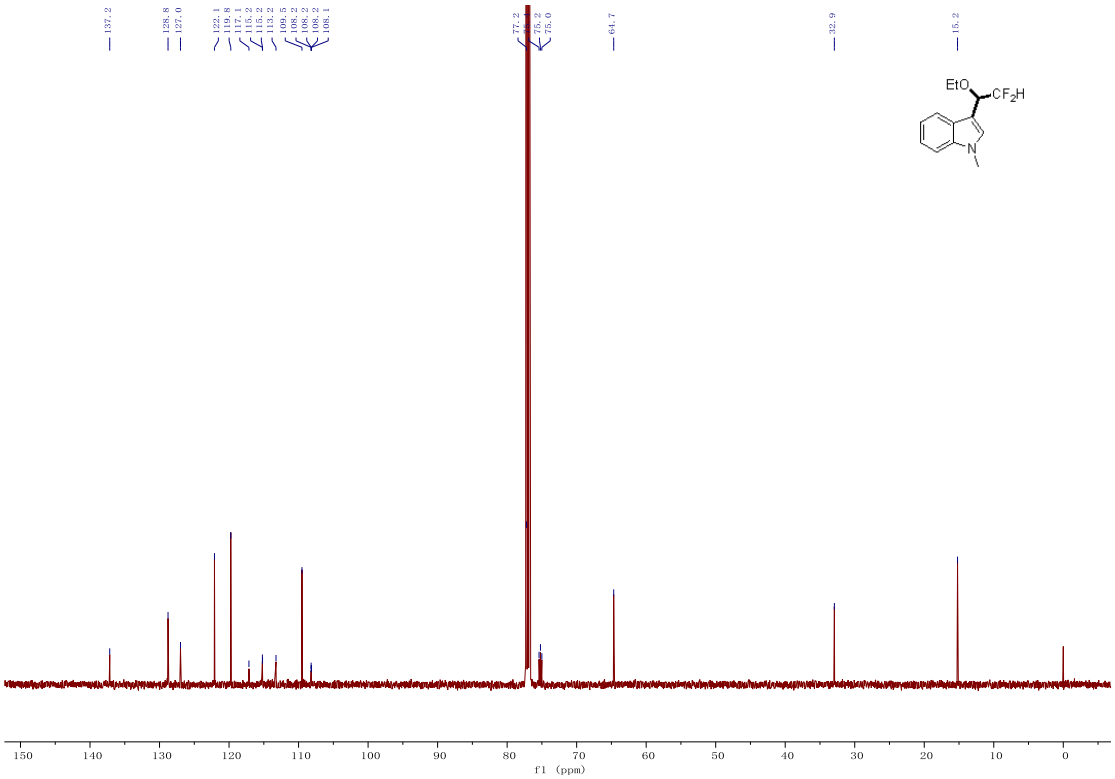
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **10**



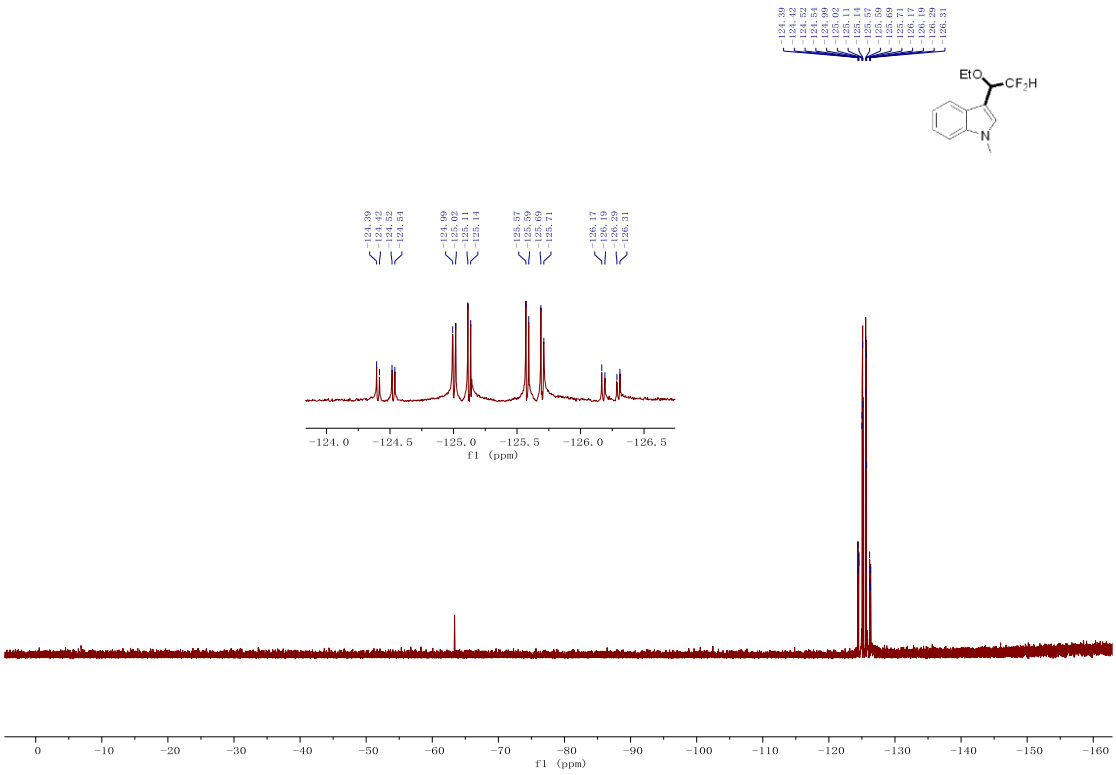
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **11**



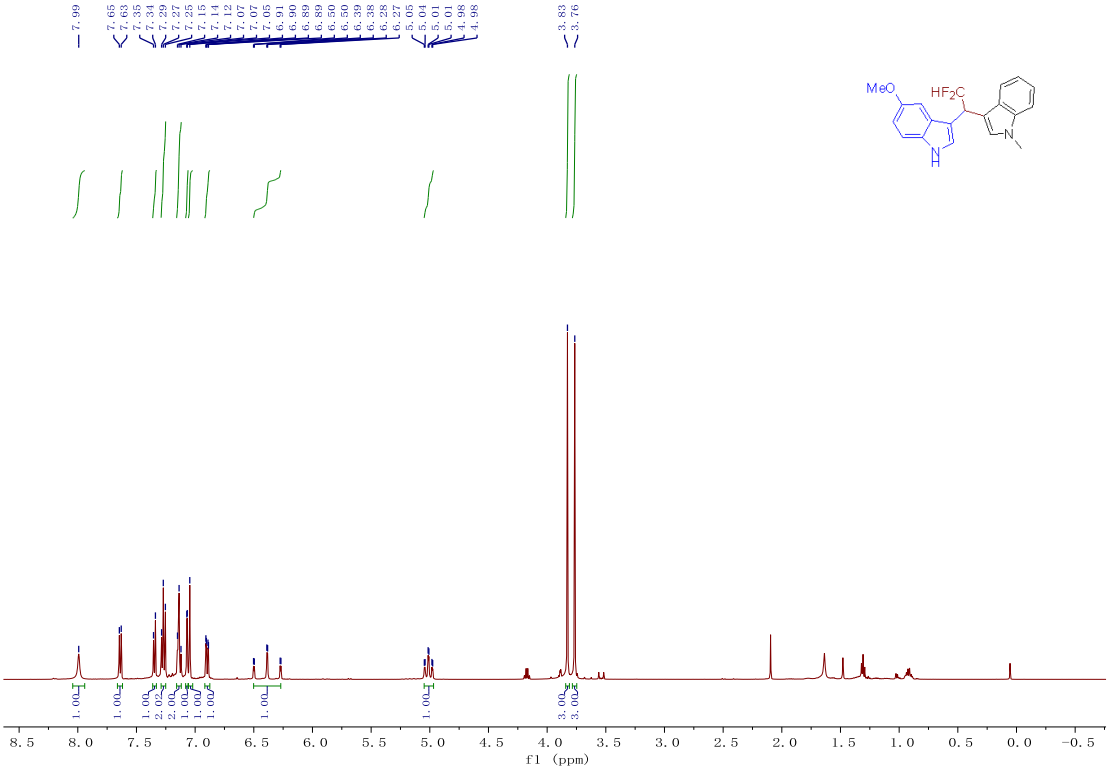
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **11**



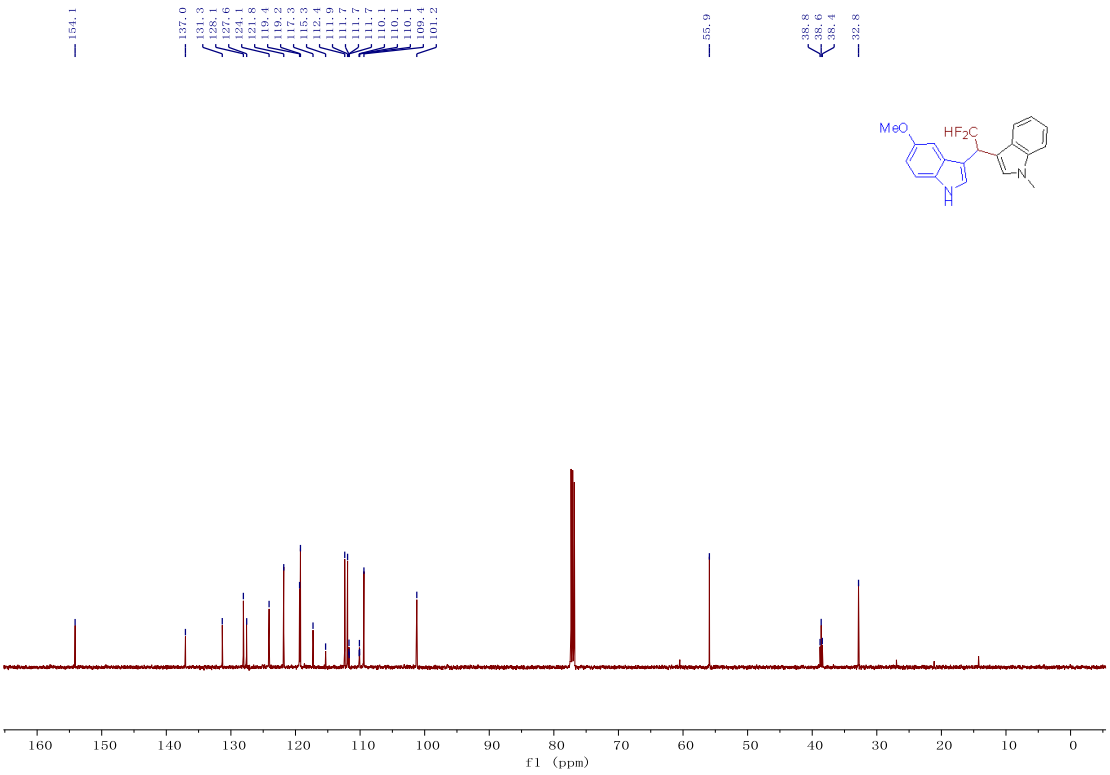
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **11**



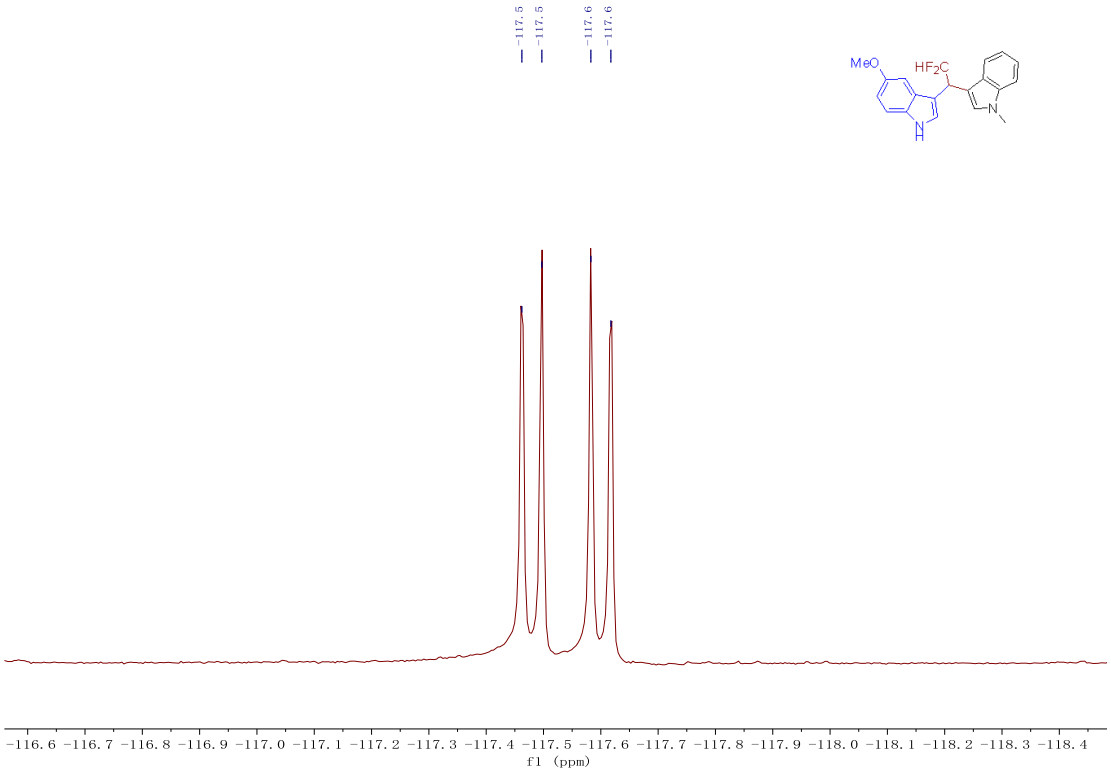
^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **12**



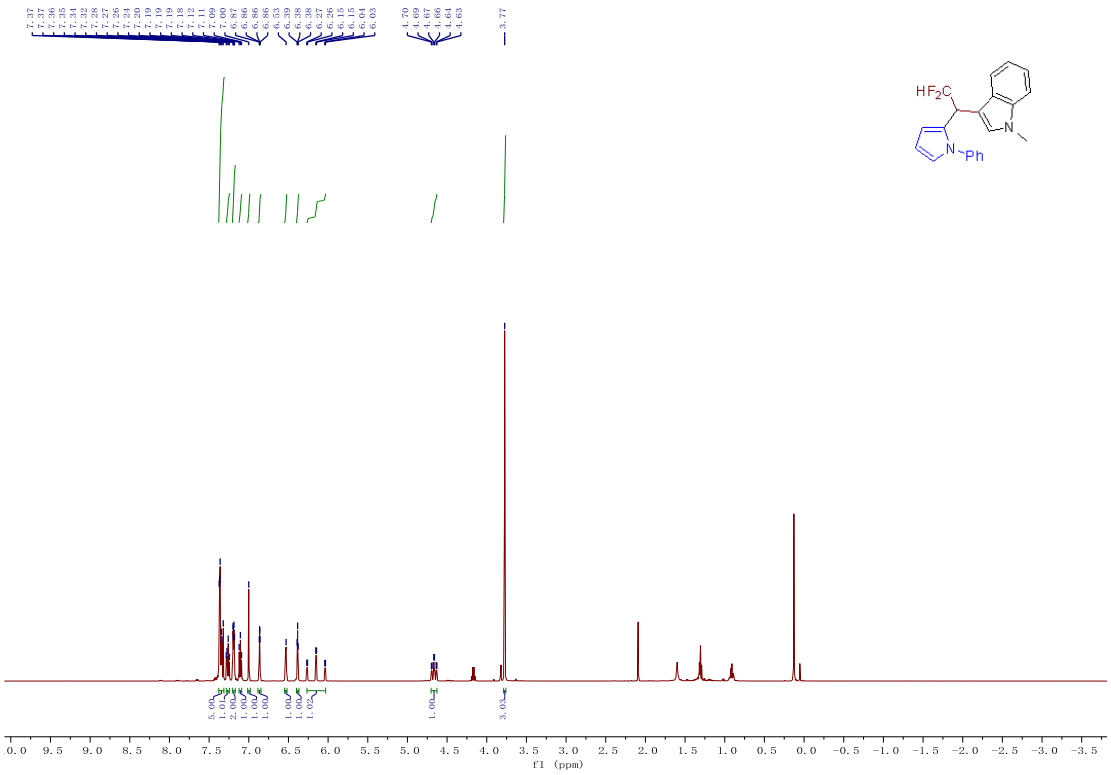
^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **12**



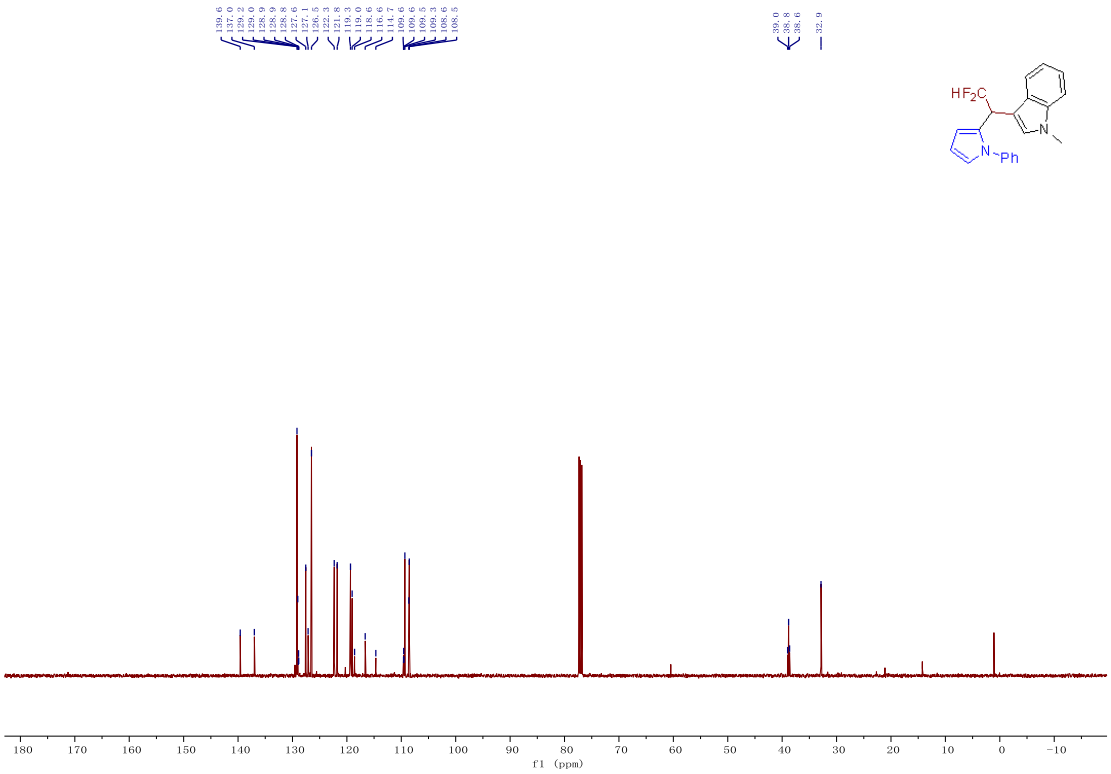
^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **12**



^{1}H NMR (500 MHz, Chloroform-*d*) spectra of **13**



^{13}C NMR (125 MHz, Chloroform-*d*) spectra of **6**



^{19}F NMR (470 MHz, Chloroform-*d*) spectra of **13**