SUPPORTING INFORMATION

Synthesis of 2-(α-Trifluoromethylamino)indoles via Stepwise Cascade Transformation of Imidoyl Sulfoxonium Ylides with *ortho*-Chloromethyl Anilines

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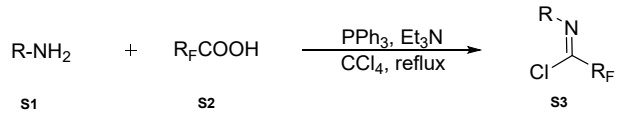
1) General information

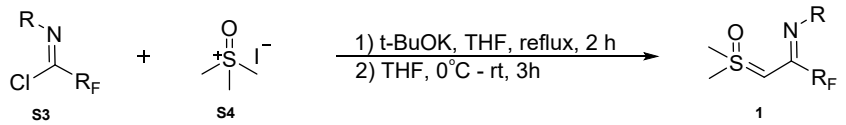
All reactions were carried out in the air. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Thin-layer chromatography was performed using silica gel GF254 precoated plates (0.20–0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm). Column chromatography was performed on silica gel 90, 200-300 mesh. ^{1}H and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded on a Bruker Advance 400 spectrometer. Melting points are uncorrected. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.16). High resolution mass spectra (HRMS) were obtained using a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer and electrospray ionization (ESI).

2) The Synthesis of Imidoyl Sulfoxonium Ylides [1]



S1 S2 S3

To a two-necked flask under a nitrogen atmosphere was added triphenylphosphine (18.8 mmol), triethylamine (7.5 mmol), carbon tetrachloride (CCl_4, 20.0 mL), and trifluoroacetic acid **S2** (7.5 mmol). The mixture was stirred in an ice bath for 20 minutes. A solution of the amine **S1** (7.5 mmol) in CCl_4 (20.0 mL) was then added, and the reaction mixture was refluxed for 3-6 hours. Upon completion, the reaction mixture was filtered, and the resulting solid was washed with petroleum ether. Then, the petroleum ether was concentrated to afford the crude product, which was purified by column chromatography on silica gel or neutral alumina to yield the desired compound **S3**.

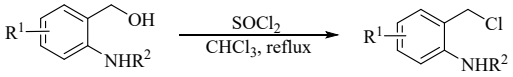


S3 S4 1

A suspension of trimethylsulfoxonium iodide **S4** (9 mmol, 3.0 equiv) in THF (100 mL)

was treated with *t*-BuOK (9 mmol, 3.0 equiv) and stirred at rt for 2 h. Fluorinated imidoyl chloride **S3** (3 mmol, 1.0 equiv) was then added, and the mixture was stirred for a further 3 h at room temperature. After filtration through Celite, the solvent was removed in vacuo. The crude residue was purified by flash chromatography to yield the product **1**.

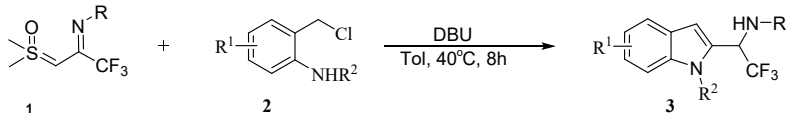
3) The Synthesis of Azadiene Precursors [2]



S5 **2**

To a solution of thionyl chloride (7 mmol) in $CHCl_3$ (5 mL), was added a solution of **S5** (3 mmol) in $CHCl_3$ (20 mL) over 5 min. The mixture was heated to 40 °C for overnight. After the reaction cooled to room temperature, then poured into ice water (10 mL). The aqueous layer was extracted with $CHCl_3$ (100 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$. Evaporation of the solvent under reduced pressure and the crude product was purified by flash column chromatography affording **2**.

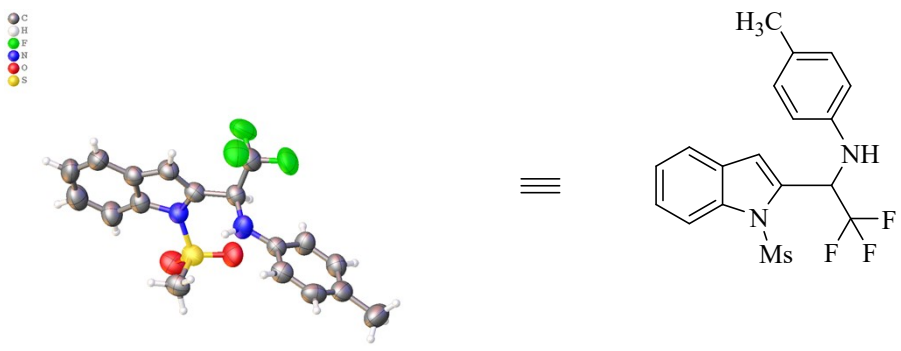
4) General Experimental Procedure



1 2 3

To a stirred solution of imidoyl sulfoxonium ylides **1** (0.2 mmol) and azadiene precursors **2** (0.1 mmol) in Tol (2 mL) at room temperature, DBU (0.15 mmol) was added. The reaction was performed at 40 °C. After the reaction completed indicated by the TLC. Then, the mixture concentrated in vacuo and the crude product was purified by flash chromatography eluting with (petroleum ether/ethyl acetate 10:1) to afford the products **3**.

5) The X-ray data



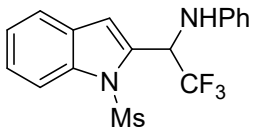
Single crystal of **3f** [$C_{18}H_{17}F_3N_2O_2S$] was obtained from the $CDCl_3$. CCDC 2504930 containing the supplementary crystallographic data can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

Identification code	251120b1_0m_a
Empirical formula	$C_{18}H_{17}F_3N_2O_2S$
Formula weight	382.39
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.219(4)
b/Å	5.4793(17)
c/Å	24.982(8)
α/°	90
β/°	99.975(14)
γ/°	90
Volume/Å3	1782.1(10)
Z	4
ρcalcg/cm^3	1.425
μ/mm^{-1}	0.226
F(000)	792.0
Crystal size/mm^3	0.4 × 0.4 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.392 to 52.742
Index ranges	$-16 \le h \le 16$, $-6 \le k \le 6$, $-31 \le l \le 31$
Reflections collected	19156
Independent reflections	3639 [R_{int} = 0.1274, R_{sigma} = 0.0917]
Data/restraints/parameters	3639/0/237

Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0686, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.1534, wR_2 = 0.1548
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.30

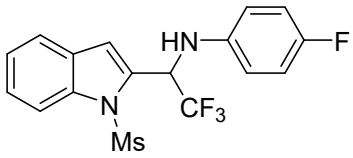
6) ^{1}H NMR and ^{13}C NMR Spectra

***N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3a**



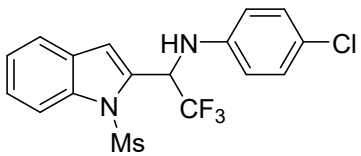
White solid, 30 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.88 (s, 1H), 6.74 (t, *J* = 7.7 Hz, 3H), 6.27 (q, *J* = 6.7 Hz, 1H), 4.02 (s, 1H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.76, 136.90, 134.35, 129.52, 128.61, 125.91, 124.20, 121.64, 120.09, 114.43, 114.37, 111.17, 53.10 (q, $J_{(C-F)}$ = 31.0 Hz), 40.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.13. HRMS (ESI) calcd for $C_{17}H_{15}F_3N_2O_2S$ $[M+Na]^+$ 391.0698, found 391.0690.

***4-fluoro-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3b**



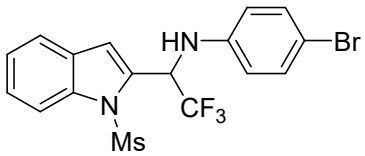
White solid, 28 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.29 (dt, *J* = 30.3, 7.5 Hz, 2H), 6.85 (dd, *J* = 14.5, 6.0 Hz, 3H), 6.74-6.64 (m, 2H), 6.17 (t, *J* = 7.4 Hz, 1H), 4.01-3.75 (m, 1H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 158.36, 155.99, 140.96, 136.83, 134.02, 128.52, 126.00, 124.25, 121.66, 116.17 (d, $J_{(C-F)}$ = 22.0 Hz), 115.86 (d, $J_{(C-F)}$ = 8.0 Hz), 114.35, 111.11, 53.54 (q, $J_{(C-F)}$ = 30.0 Hz), 40.78. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.73, -124.43. HRMS (ESI) calcd for $C_{17}H_{14}F_4N_2O_2S$ $[M+Na]^+$ 409.0604, found 409.0609.

***4-chloro-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3c**



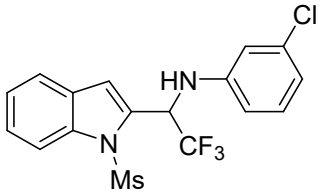
White solid, 30 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.30 (dt, *J* = 31.2, 7.5 Hz, 2H), 7.13-7.01 (m, 2H), 6.88 (s, 1H), 6.68 (d, J = 8.3 Hz, 2H), 6.27-6.14 (m, 1H), 4.03 (d, *J* = 9.1 Hz, 1H), 3.03 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.34, 136.84, 133.77, 129.41, 128.50, 126.07, 124.85, 124.29, 121.68, 115.54, 114.36, 111.24, 52.84 (q, $J_{(C-F)}$ = 31.0 Hz), 40.80. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.83. HRMS (ESI) calcd for $C_{17}H_{14}ClF_3N_2O_2S$ $[M+Na]^+$ 425.0309, found 425.0306.

***4-bromo-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3d**



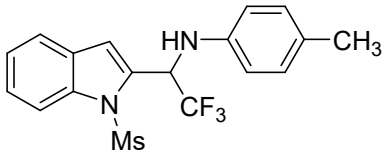
White solid, 35 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.36-7.18 (m, 4H), 6.87 (s, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.21 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.04 (d, *J* = 10.2 Hz, 1H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.80, 136.82, 133.68, 132.30, 128.49, 126.09, 124.30, 121.70, 115.94, 114.35, 111.96, 111.27, 52.67 (q, $J_{(C-F)}$ = 31.0 Hz), 40.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.81. HRMS (ESI) calcd for $C_{17}H_{14}BrF_3N_2O_2S$ $[M+Na]^+$ 468.9803, found 468.9808.

***3-chloro-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3e**



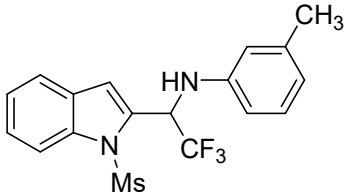
White solid, 30 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.29 (dt, *J* = 30.6, 7.6 Hz, 2H), 7.04 (t, *J* = 8.2 Hz, 1H), 6.88 (s, 1H), 6.79 – 6.65 (m, 2H), 6.62 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.23 (dd, *J* = 10.0, 6.2 Hz, 1H), 4.11 (d, *J* = 10.3 Hz, 1H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 145.95, 136.89, 135.18, 133.66, 130.58, 128.53, 126.11, 124.32, 121.72, 120.02, 114.40, 114.37, 112.29, 111.43, 52.56 (q, $J_{(C-F)}$ = 31.0 Hz), 40.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.93. HRMS (ESI) calcd for $C_{17}H_{14}ClF_3N_2O_2S$ $[M+Na]^+$ 425.0309, found 425.0304.

***4-methyl-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3f**



White solid, 28 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.26 (dt, *J* = 29.5, 7.6 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.86 (s, 1H), 6.66 (dd, *J* = 6.8, 4.6 Hz, 2H), 6.21 (q, *J* = 7.1, 6.5 Hz, 1H), 3.90 (s, 1H), 3.00 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 142.38, 136.87, 134.45, 130.02, 129.48, 128.61, 125.85, 124.16, 121.62, 114.66, 114.36, 111.03, 52.98 (q, $J_{(C-F)}$ = 31.0 Hz), 40.79, 20.45. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.78. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 405.0855, found 405.0851.

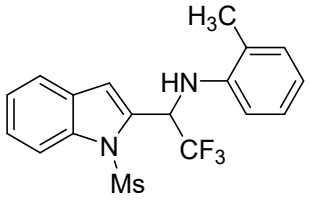
***3-methyl-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3g**



White solid, 24 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.55 (d, *J* = 6.7 Hz, 3H), 6.26 (dd, *J* = 10.7, 6.2 Hz, 1H), 3.98 (d, *J* = 10.6 Hz,

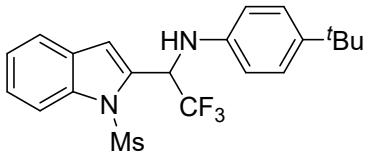
1H), 3.00 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.68, 138.35, 135.83, 133.41, 128.33, 127.57, 124.83, 123.13, 120.58, 119.95, 114.22, 113.31, 110.36, 110.07, 51.67 (q, $J_{(C-F)}$ = 31.0 Hz), 39.72, 20.52. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.93. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 405.0855, found 405.0857.

2-methyl-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline **3h**



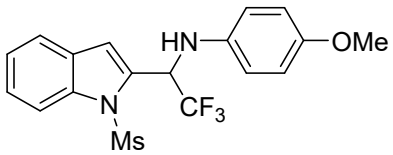
White solid, 27 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.24 (q, J = 7.4, 6.7 Hz, 1H), 7.06-6.94 (m, 2H), 6.88 (s, 1H), 6.80 (d, J = 8.1 Hz, 1H), 6.68 (t, J = 7.4 Hz, 1H), 6.31 (q, J = 7.1, 6.5 Hz, 1H), 3.97 (s, 1H), 2.99 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.78, 136.97, 134.70, 130.69, 128.61, 127.42, 125.92, 124.22, 123.04, 121.66, 119.72, 114.35, 112.35, 111.18, 52.68 (q, $J_{(C-F)}$ = 31.0 Hz), 40.73, 17.48. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.17, -75.58. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 405.0855, found 405.0858.

4-(tert-butyl)-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline 3i



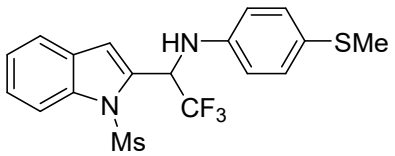
White solid, 32 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 8.6 Hz, 2H), 6.88 (s, 1H), 6.68 (d, J = 8.3 Hz, 2H), 6.24 (s, 1H), 3.95 (s, 1H), 3.01 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.88, 142.21, 136.89, 134.64, 128.64, 126.30, 125.82, 124.15, 121.60, 114.35, 114.16, 111.08, 53.46 (q, $J_{(C-F)}$ = 31.0 Hz), 40.80, 34.00, 31.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.96. HRMS (ESI) calcd for $C_{21}H_{23}F_3N_2O_2S$ $[M+Na]^+$ 447.1324, found 447.1329.

4-methoxy-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline **3j**



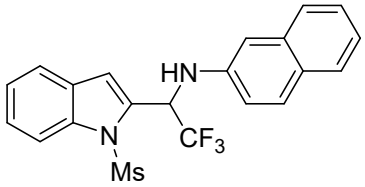
White solid, 23 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 6.87 (s, 1H), 6.72 (s, 4H), 6.14 (q, J = 7.0, 6.6 Hz, 1H), 3.84 - 3.48 (m, 4H), 3.01 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 153.87, 138.52, 136.84, 134.47, 128.59, 125.84, 124.16, 121.60, 116.39, 114.91, 114.35, 110.93, 55.60, 53.99 (q, $J_{(C-F)}$ = 31.0 Hz), 40.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.67. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_3S$ $[M+Na]^+$ 421.0804, found 421.0808.

4-(methylthio)-N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline **3k**



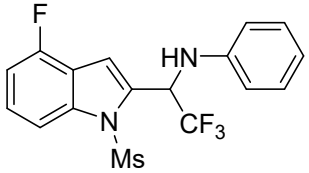
White solid, 21 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.87 (s, 1H), 6.69 (d, *J* = 8.2 Hz, 2H), 6.23 (t, *J* = 7.3 Hz, 1H), 4.02 (d, *J* = 10.0 Hz, 1H), 3.00 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.16, 136.85, 134.03, 130.34, 128.55, 127.98, 125.99, 124.25, 121.67, 115.07, 114.35, 111.21, 53.10 (q, $J_{(C-F)}$ = 31.0 Hz), 40.81, 18.00. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.81. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_2S_2$ $[M+Na]^+$ 437.0576, found 437.0573.

***N-(2,2,2-trifluoro-1-(1-(methylsulfonyl)-1H-indol-2-yl)ethyl)naphthalen-2-amine* 3l**



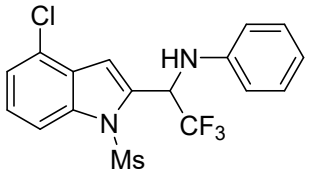
White solid, 30 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.66-7.46 (m, 4H), 7.32-7.15 (m, 4H), 7.03 (s, 1H), 6.96 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.91 (s, 1H), 6.41 (dt, *J* = 13.8, 6.5 Hz, 1H), 4.21 (d, *J* = 10.4 Hz, 1H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 142.35, 136.93, 134.59, 134.18, 129.53, 128.62, 128.59, 127.64, 126.70, 126.42, 125.98, 124.24, 123.33, 121.67, 117.38, 114.37, 111.24, 108.02, 52.75 (q, $J_{(C-F)}$ = 31.0 Hz), 40.80. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.80. HRMS (ESI) calcd for $C_{21}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 441.0855, found 441.0850.

***N-(2,2,2-trifluoro-1-(4-fluoro-1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3m**



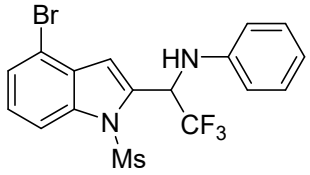
White solid, 27 mg, 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.45 (q, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.17 (p, *J* = 9.5 Hz, 3H), 6.86-6.68 (m, 4H), 6.26 (dt, *J* = 14.4, 7.0 Hz, 1H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.71 (d, $J_{(C-F)}$ = 246.0 Hz), 146.29, 138.75 (d, $J_{(C-F)}$ = 9.0 Hz), 135.13, 129.67, 127.26 (d, $J_{(C-F)}$ = 8.0 Hz), 118.94, 117.49 (d, $J_{(C-F)}$ = 23.0 Hz), 113.94, 111.14 (d, $J_{(C-F)}$ = 4.0 Hz), 109.57 (d, $J_{(C-F)}$ = 18.0 Hz), 106.49, 52.38 (q, $J_{(C-F)}$ = 30.0 Hz), 41.72. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.08 (d, $J_{(C-F)}$ = 18.0 Hz), -121.38-121.43 (m). HRMS (ESI) calcd for $C_{17}H_{14}F_4N_2O_2S$ $[M+Na]^+$ 409.0604, found 409.0606.

***N-(1-(4-chloro-1-(methylsulfonyl)-1H-indol-2-yl)-2,2,2-trifluoroethyl)aniline* 3n**



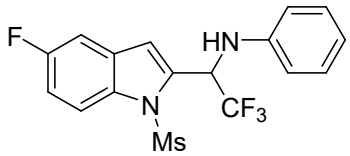
White solid, 30 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (q, J = 4.9 Hz, 1H), 7.30-7.18 (m, 2H), 7.15 (t, J = 7.8 Hz, 2H), 6.99 (s, 1H), 6.76 (dd, J = 10.9, 7.8 Hz, 3H), 6.34-6.20 (m, 1H), 4.17-3.92 (m, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.56, 137.40, 135.11, 129.58, 127.48, 126.96, 126.53, 126.17 (q, $J_{(C-F)}$ = 282.0 Hz), 123.96, 120.26, 114.43, 112.84, 109.00, 53.03 (q, $J_{(C-F)}$ = 31.0 Hz), 41.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.79. HRMS (ESI) calcd for $C_{17}H_{14}ClF_3N_2O_2S$ $[M+Na]^+$ 425.0309, found 425.0317.

***N-(1-(4-bromo-1-(methylsulfonyl)-1H-indol-2-yl)-2,2,2-trifluoroethyl)aniline* 3o**



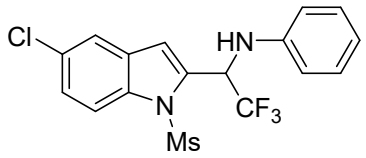
White solid, 44 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.15 (dd, J = 12.7, 5.5 Hz, 3H), 6.94 (s, 1H), 6.75 (dd, J = 8.1, 2.7 Hz, 3H), 6.27 (dt, J = 13.1, 6.4 Hz, 1H), 4.06 (d, J = 10.8 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.57, 137.00, 135.12, 129.58, 129.30, 127.13, 126.78, 126.15 (q, $J_{(C-F)}$ = 281.0 Hz), 120.25, 115.42, 114.42, 113.38, 110.72, 52.72 (q, $J_{(C-F)}$ = 31.0 Hz), 41.19. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77. HRMS (ESI) calcd for $C_{17}H_{14}BrF_3N_2O_2S$ $[M+Na]^+$ 468.9803, found 468.9807.

***N-(2,2,2-trifluoro-1-(5-fluoro-1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3p**



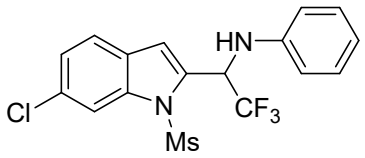
White solid, 22 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 9.4, 4.3 Hz, 1H), 7.16 (dd, J = 15.3, 7.7 Hz, 3H), 7.04 (dt, J = 9.3, 4.5 Hz, 1H), 6.85 (s, 1H), 6.76 (dd, J = 14.3, 7.6 Hz, 3H), 6.30 – 6.14 (m, 1H), 4.00 (s, 1H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.11, 158.70, 144.57, 135.94, 133.14, 129.56, 123.38 (q, $J_{(C-F)}$ = 281.0 Hz), 120.24, 115.64 (d, $J_{(C-F)}$ = 9.0 Hz), 114.42, 114.10 (d, $J_{(C-F)}$ = 26.0 Hz), 110.84, 107.17 (d, $J_{(C-F)}$ = 24.0 Hz), 52.79 (q, $J_{(C-F)}$ = 31.0 Hz), 40.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.83, -118.55. HRMS (ESI) calcd for $C_{17}H_{14}F_4N_2O_2S$ $[M+Na]^+$ 409.0604, found 409.0606.

***N-(1-(5-chloro-1-(methylsulfonyl)-1H-indol-2-yl)-2,2,2-trifluoroethyl)aniline* 3q**



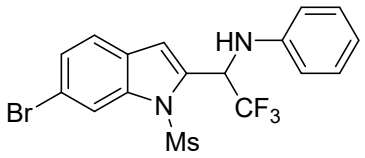
White solid, 29 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 2.1 Hz, 1H), 7.32 – 7.21 (m, 1H), 7.15 (dd, J = 15.3, 7.4 Hz, 2H), 6.86 – 6.63 (m, 4H), 6.24 (q, J = 6.4 Hz, 1H), 4.01 (s, 1H), 3.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.52, 135.65, 135.15, 130.02, 129.71, 129.57, 126.12, 126.17 (q, $J_{(C-F)}$ = 282.0 Hz), 121.14, 120.29, 115.44, 114.44, 110.30, 52.76 (q, $J_{(C-F)}$ = 31.0 Hz), 41.07. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.77. HRMS (ESI) calcd for $C_{17}H_{14}ClF_3N_2O_2S$ $[M+Na]^+$ 425.0309, found 425.0312.

***N-(1-(6-chloro-1-(methylsulfonyl)-1H-indol-2-yl)-2,2,2-trifluoroethyl)aniline* 3r**



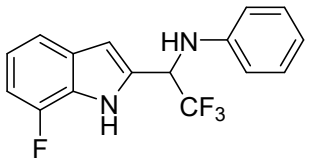
White solid, 25 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.24 – 7.06 (m, 3H), 6.84 (s, 1H), 6.74 (t, J = 7.6 Hz, 3H), 6.22 (t, J = 7.3 Hz, 1H), 4.11 – 3.91 (m, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.57, 137.13, 134.90, 131.98, 129.57, 126.99, 126.23 (q, $J_{(C-F)}$ = 282.0 Hz), 124.93, 122.36, 120.26, 114.59, 114.44, 110.65, 53.08 (q, $J_{(C-F)}$ = 31.0 Hz), 41.15. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.74. HRMS (ESI) calcd for $C_{17}H_{14}ClF_3N_2O_2S$ $[M+Na]^+$ 425.0309, found 425.0306.

N-(1-(6-bromo-1-(methylsulfonyl)-1H-indol-2-yl)-2,2,2-trifluoroethyl)aniline **3s**



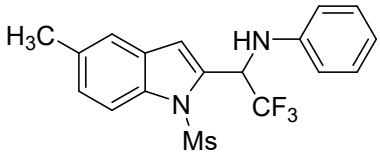
White solid, 30 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.36 (s, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.84 (s, 1H), 6.74 (t, J = 8.3 Hz, 3H), 6.22 (d, J = 6.9 Hz, 1H), 4.03 (d, J = 13.4 Hz, 1H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.55, 137.43, 134.83, 129.56, 127.62, 127.34, 126.19 (q, $J_{(C-F)}$ = 282.0 Hz), 122.66, 120.27, 119.68, 117.43, 114.44, 110.68, 52.77 (q, $J_{(C-F)}$ = 31.0 Hz), 41.20. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.76. HRMS (ESI) calcd for $C_{17}H_{14}BrF_3N_2O_2S$ $[M+Na]^+$ 468.9803, found 468.9809.

N-(2,2,2-trifluoro-1-(7-fluoro-1H-indol-2-yl)ethyl)aniline **3t**



White solid, 14 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.8 Hz, 2H), 6.96 (td, J = 7.9, 4.7 Hz, 1H), 6.82 (dq, J = 21.1, 7.6 Hz, 2H), 6.69 – 6.59 (m, 3H), 5.13 (q, J = 7.0 Hz, 1H), 4.23 (t, J = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.57 (d, $J_{(C-F)}$ = 243.0 Hz), 145.35, 131.61 (d, $J_{(C-F)}$ = 5.0 Hz), 131.28, 129.59, 125.88 (q, $J_{(C-F)}$ = 281.0 Hz), 124.63 (d, $J_{(C-F)}$ = 13.0 Hz), 120.65 (d, $J_{(C-F)}$ = 6.0 Hz), 120.26, 116.62 (d, $J_{(C-F)}$ = 4.0 Hz), 114.20, 107.70 (d, $J_{(C-F)}$ = 16.0 Hz), 103.59, 56.05 (q, $J_{(C-F)}$ = 31.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.99 (d, $J_{(C-F)}$ = 7.5 Hz) -134.71 – -134.76 (m). HRMS (ESI) calcd for $C_{16}H_{12}F_4N_2$ $[M+Na]^+$ 309.1010, found 309.1008.

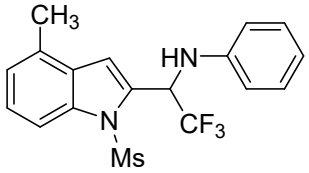
N-(2,2,2-trifluoro-1-(5-methyl-1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline **3u**



White solid, 21 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.7 Hz, 1H), 7.27 (s, 1H), 7.11 (t, J = 7.3 Hz, 3H), 6.86 – 6.63 (m, 4H), 6.22 (t, J = 6.9 Hz, 1H), 4.01 (s, 1H), 2.93 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.83, 135.16, 134.34, 134.01, 129.52, 128.91, 127.35, 126.35 (q, $J_{(C-F)}$ = 281.0 Hz), 121.45, 120.05, 114.44, 114.08, 111.13, 53.09 (q, $J_{(C-F)}$ = 31.0 Hz), 40.52, 21.18. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.92. HRMS (ESI)

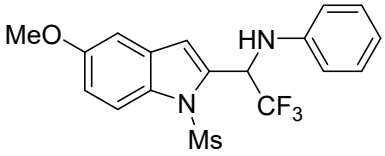
calcd for $C_{18}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 405.0855, found 405.0860.

***N-(2,2,2-trifluoro-1-(7-methyl-1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3v**



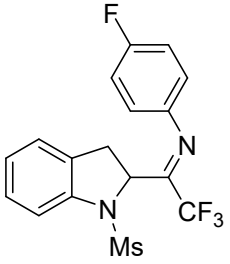
White solid, 26 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 3H), 6.28 (q, *J* = 7.5, 6.7 Hz, 1H), 4.04 (s, 1H), 2.97 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 144.82, 136.75, 133.79, 131.27, 129.52, 128.27, 126.00, 124.58, 120.03, 114.38, 111.84, 109.54, 52.75 (q, $J_{(C-F)}$ = 31.0 Hz), 40.67, 18.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.92. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_2S$ $[M+Na]^+$ 405.0855, found 405.0857.

***N-(2,2,2-trifluoro-1-(5-methoxy-1-(methylsulfonyl)-1H-indol-2-yl)ethyl)aniline* 3x**



White solid, 28 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.0 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.97 – 6.85 (m, 2H), 6.81 (s, 1H), 6.74 (t, *J* = 7.8 Hz, 3H), 6.22 (t, *J* = 7.3 Hz, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 156.96, 144.78, 134.91, 131.49, 129.65, 129.52, 126.31 (q, $J_{(C-F)}$ = 282.0 Hz), 120.07, 115.35, 115.06, 114.41, 111.32, 103.69, 55.73, 53.08 (q, $J_{(C-F)}$ = 31.0 Hz), 40.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.95. HRMS (ESI) calcd for $C_{18}H_{17}F_3N_2O_3S$ $[M+Na]^+$ 421.0804, found 421.0803.

***(E)-2,2,2-trifluoro-N-(4-fluorophenyl)-1-(1-(methylsulfonyl)indolin-2-yl)ethan-1-imine* 5**



White solid, 14 mg, 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.00 – 6.89 (m, 3H), 6.69 (dd, *J* = 8.7, 4.7 Hz, 2H), 4.93 (dd, *J* = 11.8, 7.3 Hz, 1H), 3.41 (dd, *J* = 16.5, 11.7 Hz, 1H), 3.19 (dd, *J* = 16.5, 7.2 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.44, 159.01, 158.67 (q, $J_{(C-F)}$ = 31.0 Hz), 142.93 (d, $J_{(C-F)}$ = 3.0 Hz), 141.02, 128.70, 128.07, 125.30, 124.73, 119.50 (d, $J_{(C-F)}$ = 8.0 Hz), 116.20 (d, $J_{(C-F)}$ = 23.0 Hz), 114.23, 58.31, 35.11, 34.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.32, -67.28, -118.22. HRMS (ESI) calcd for $C_{17}H_{14}F_4N_2O_2S$ $[M+Na]^+$ 409.061, found 409.058.

7) Reference

(1) Cui, J.-H.; Chen, Q.-Y.; Zhang, J.; He, Y.; Li, X.; Liu, P. N. Visible light-induced cascade annulation of sulfoxonium ylides with azides for the synthesis of 2-trifluoromethyl indoles. *Chem. Commun.* 2025, 61, 488-491.

(2) Zhang, X. K.; Pan, Y.; Liang, P.; Pang, L.; Ma, X. F.; Jiao, W.; Shao, H. W. An Effective

Method for the Synthesis of 1,3-Dihydro 2Hindazoles via N-N Bond Formation. *Adv. Synth. Catal.* 2019, 361, 5552-5557.

8) NMR spectra

Figure S1 [1]HNMR spectra of compound **3a**

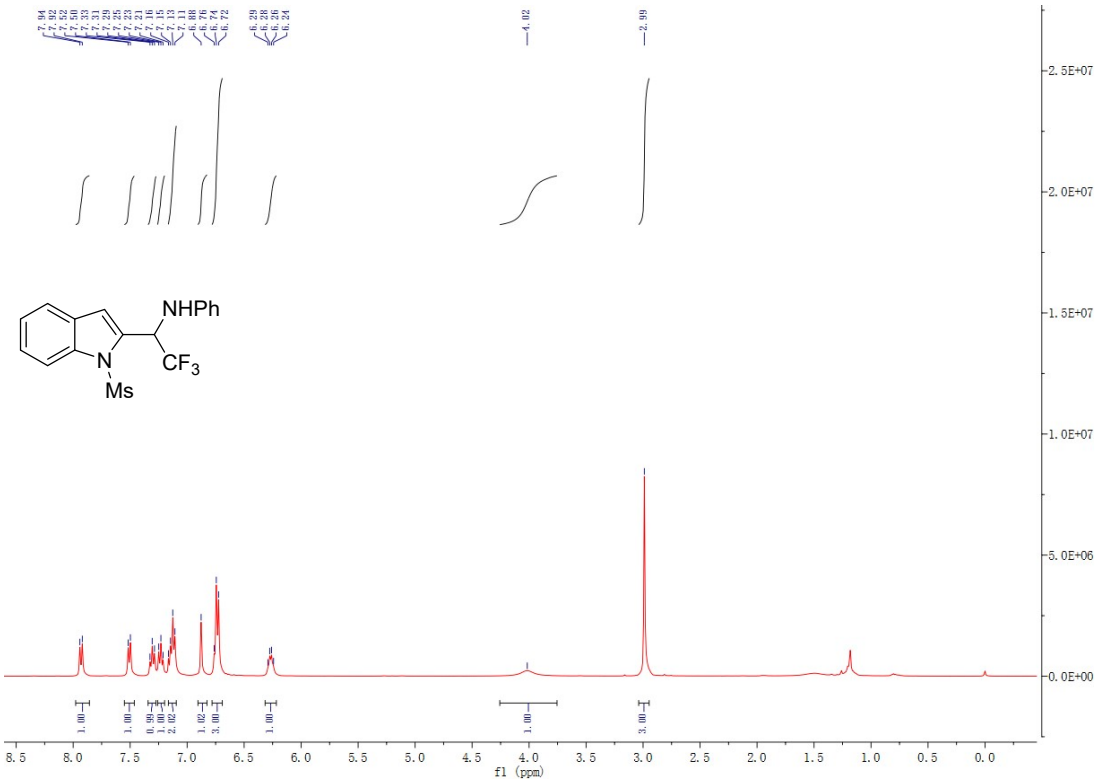


Figure S2 [13]CNMR spectra of compound **3a**

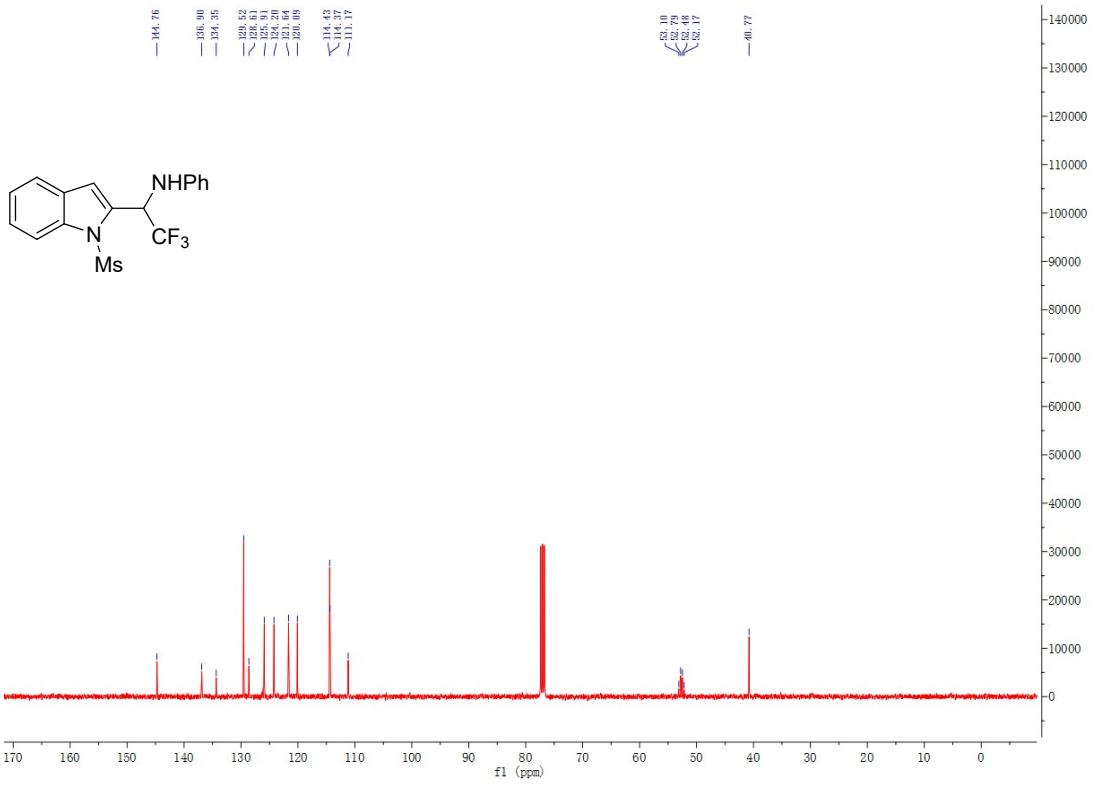


Figure S3 ^{19}FNMR spectra of compound **3a**

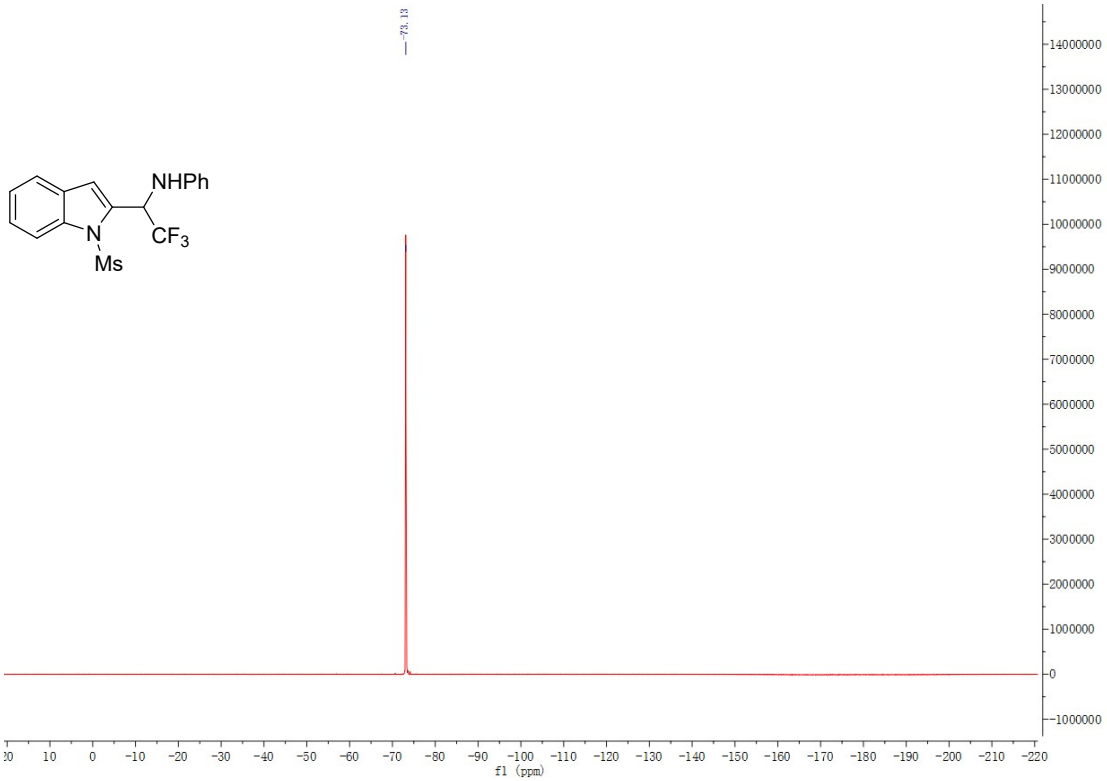


Figure S4 ^{1}HNMR spectra of compound **3b**

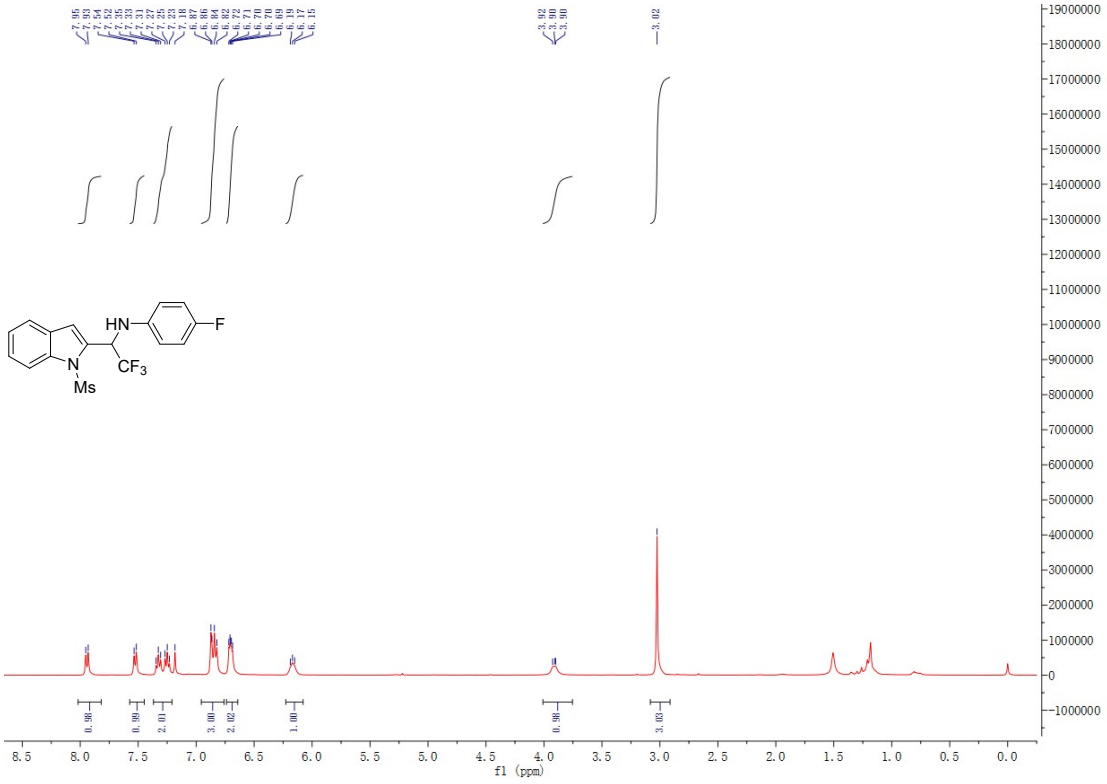


Figure S5 ^{13}CNMR spectra of compound **3b**

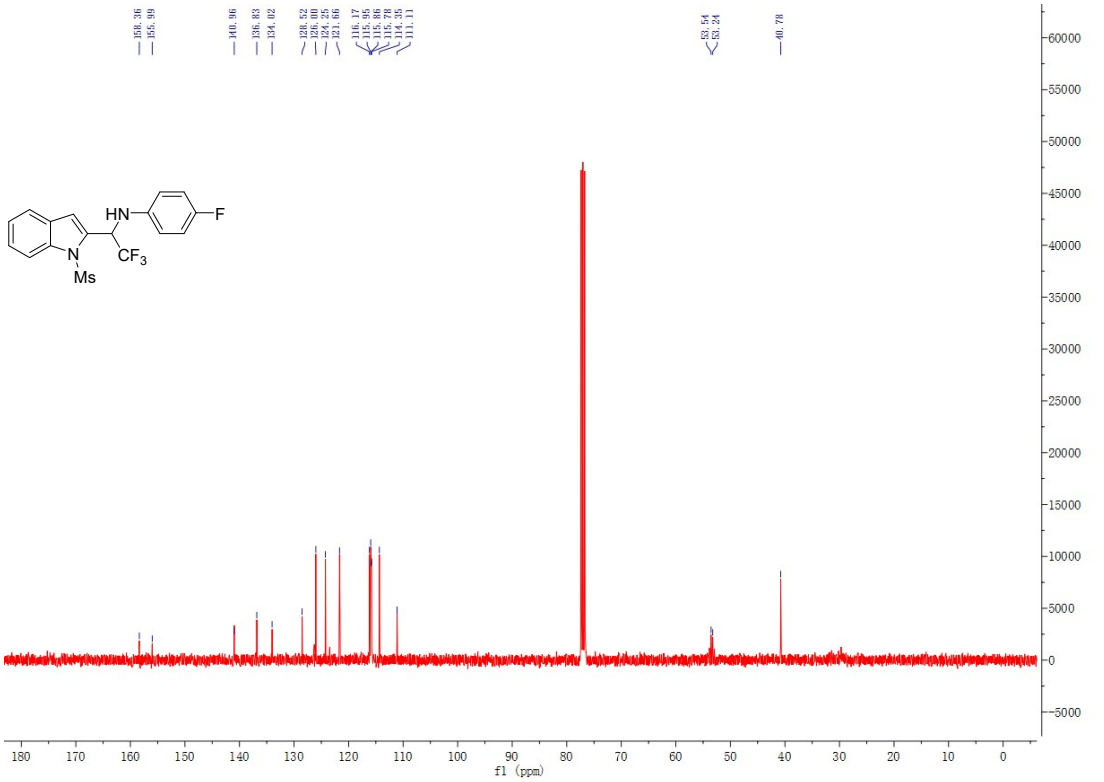


Figure S6 ^{19}FNMR spectra of compound **3b**

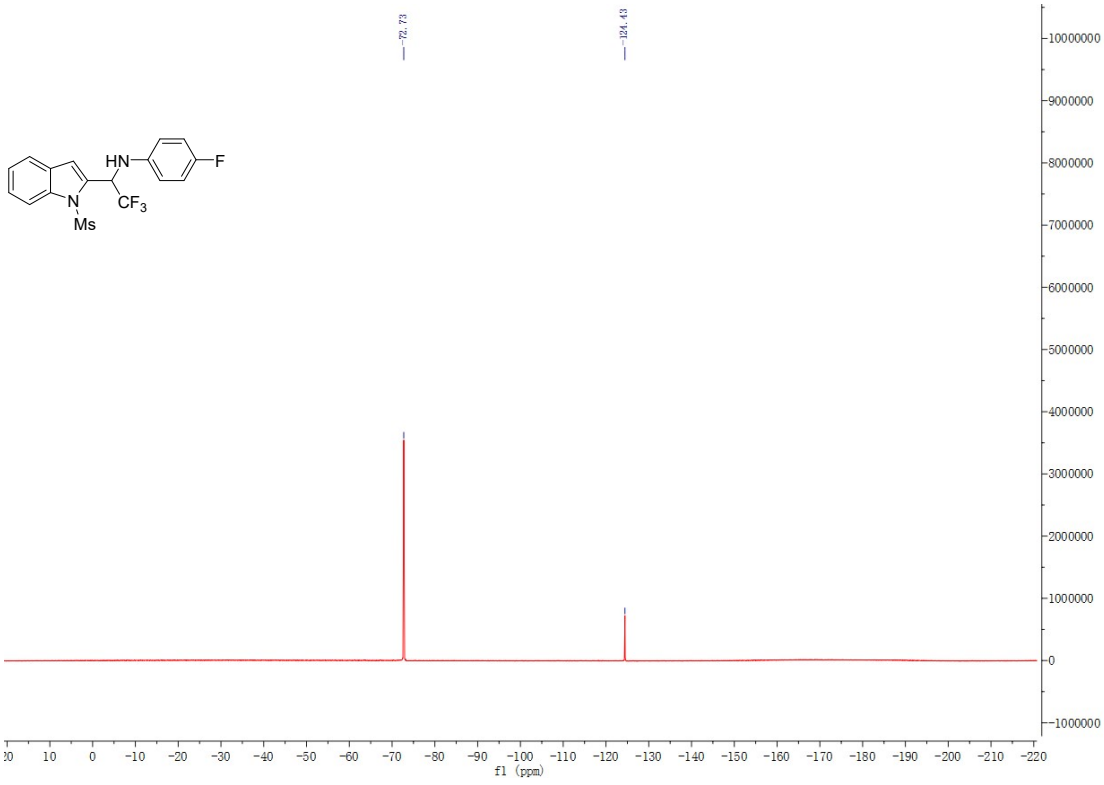


Figure S7 ^{1}HNMR spectra of compound **3c**

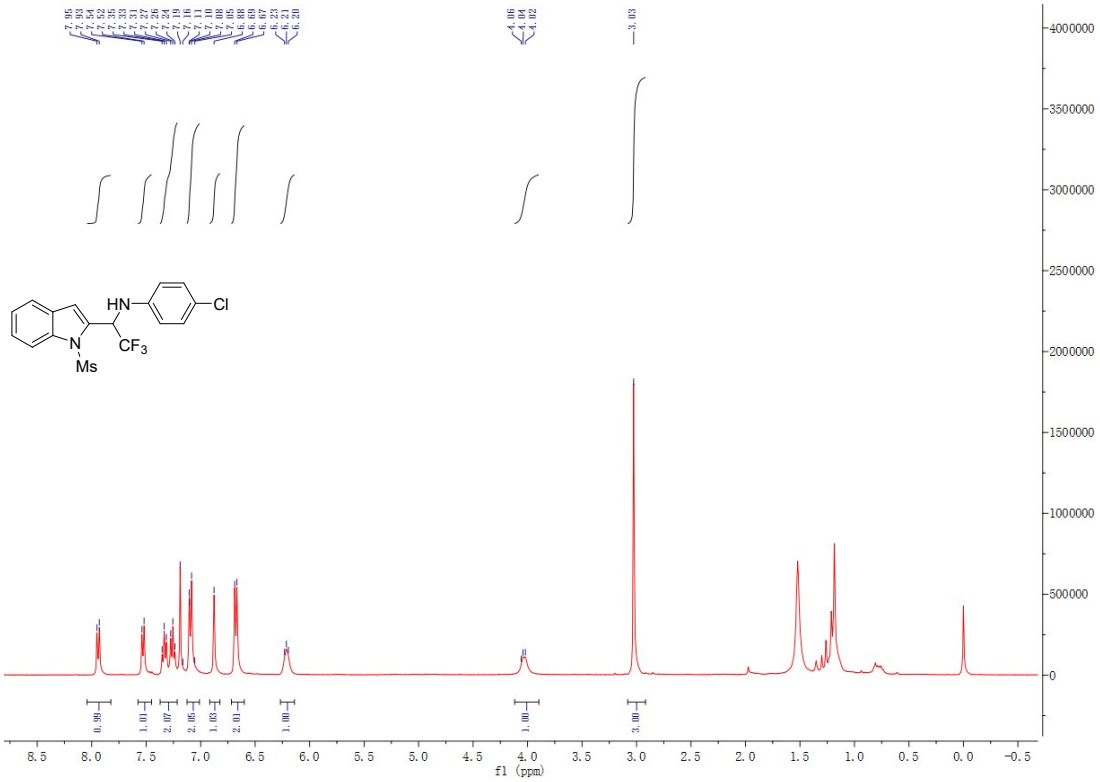


Figure S8 ^{13}CNMR spectra of compound **3c**

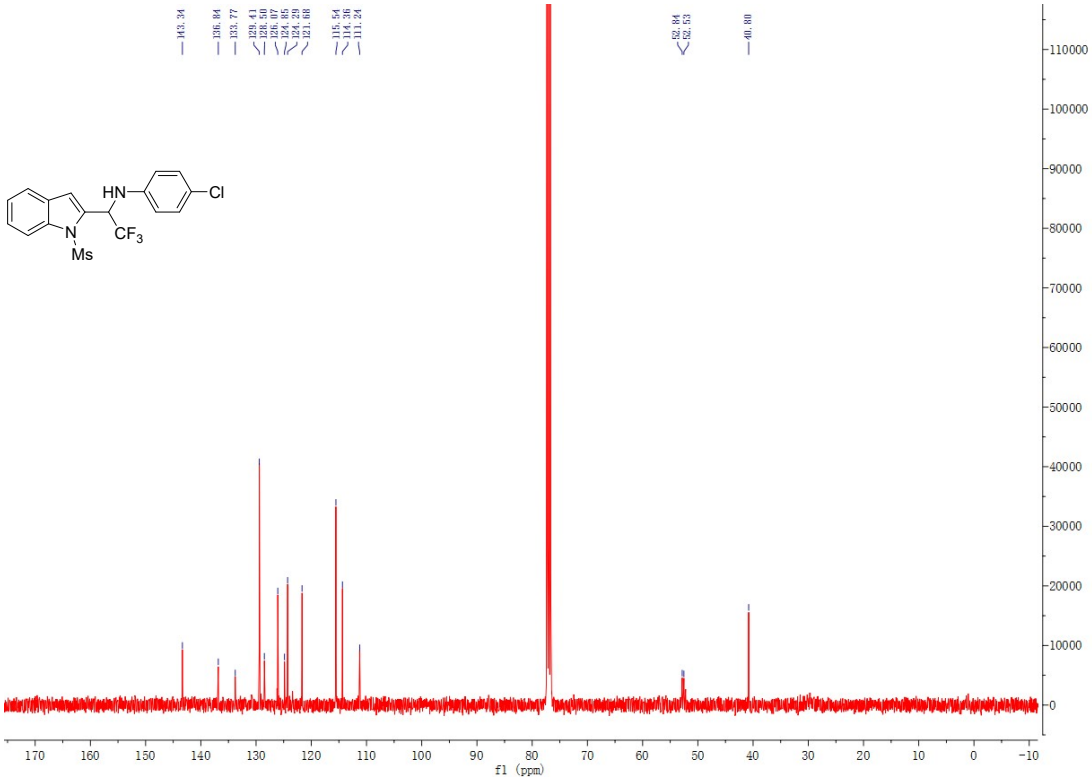


Figure S9 ^{19}FNMR spectra of compound **3c**

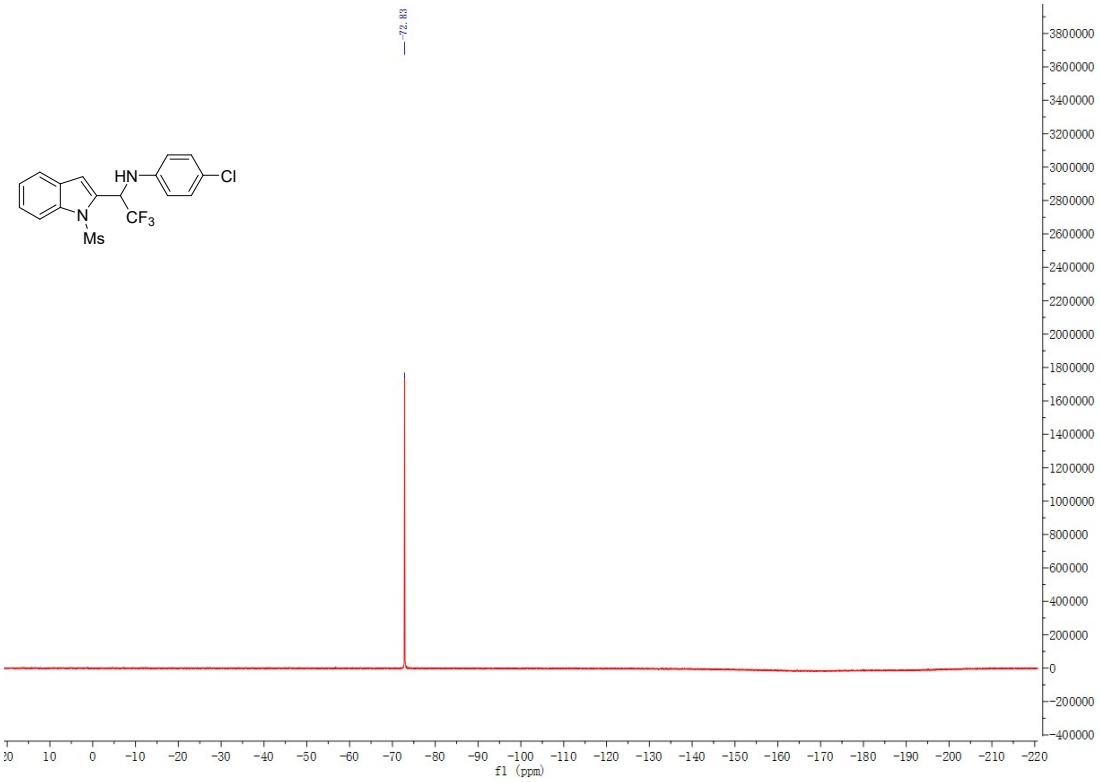


Figure S10 ^{1}HNMR spectra of compound **3d**

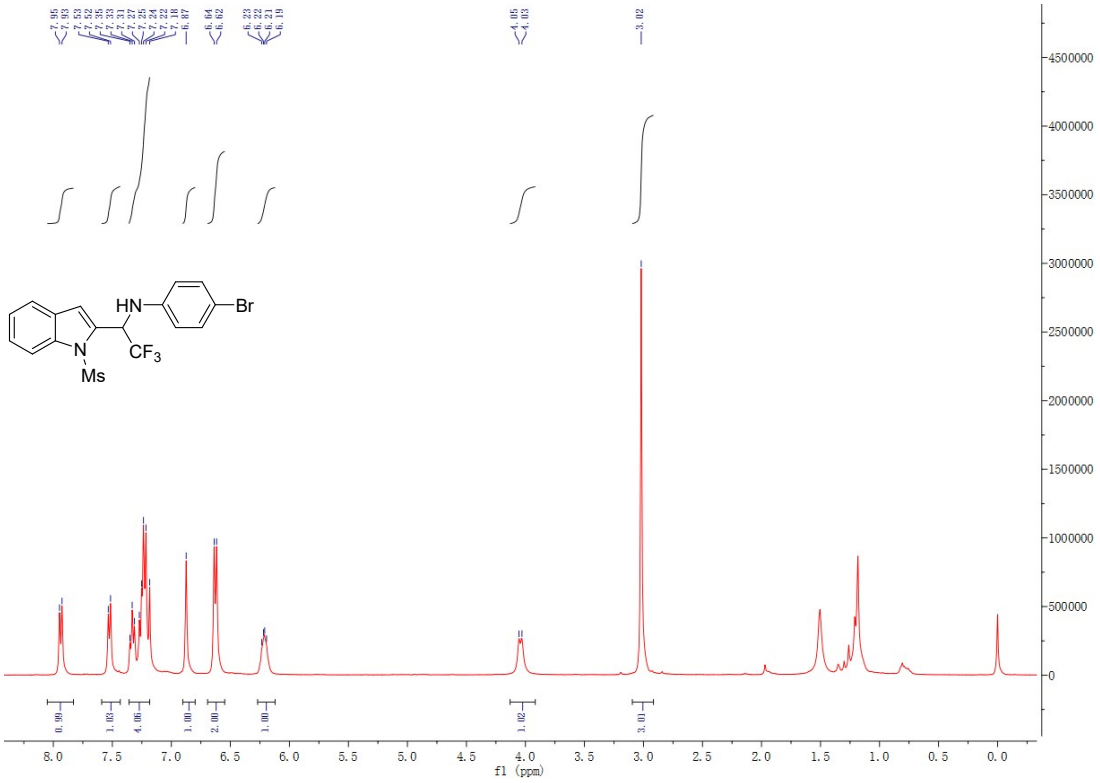


Figure S11 ^{13}CNMR spectra of compound **3d**

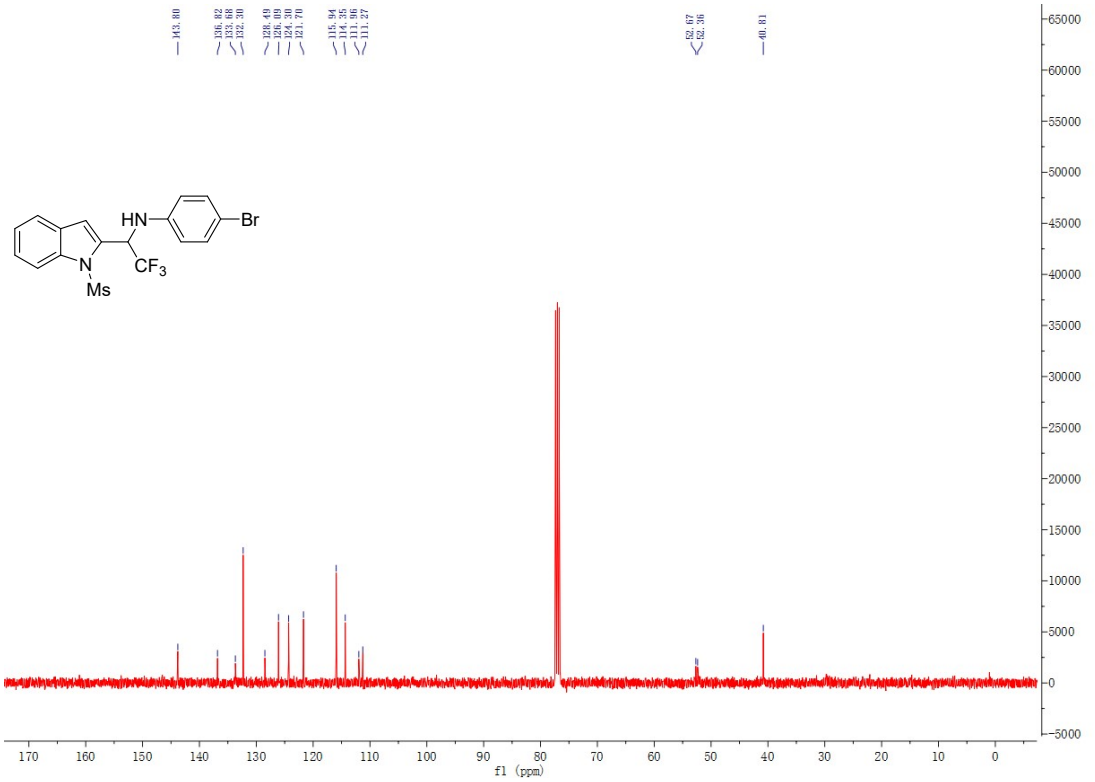


Figure S12 ^{19}FNMR spectra of compound **3d**

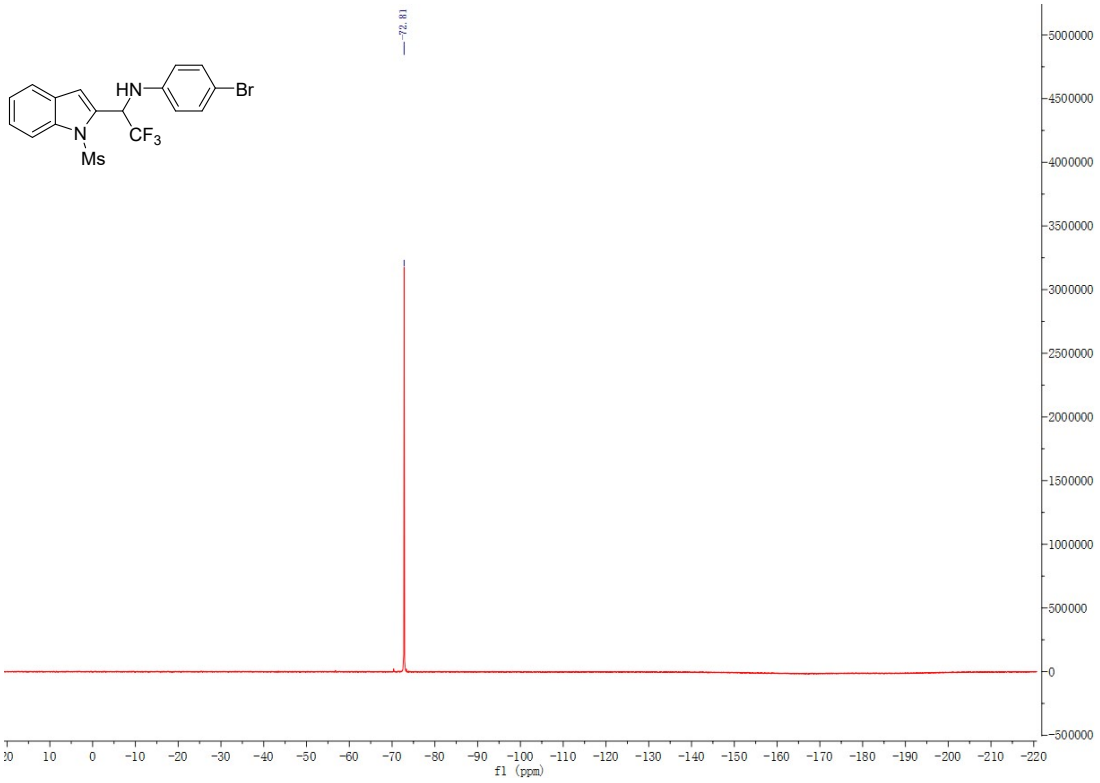


Figure S13 ^{1}HNMR spectra of compound **3e**

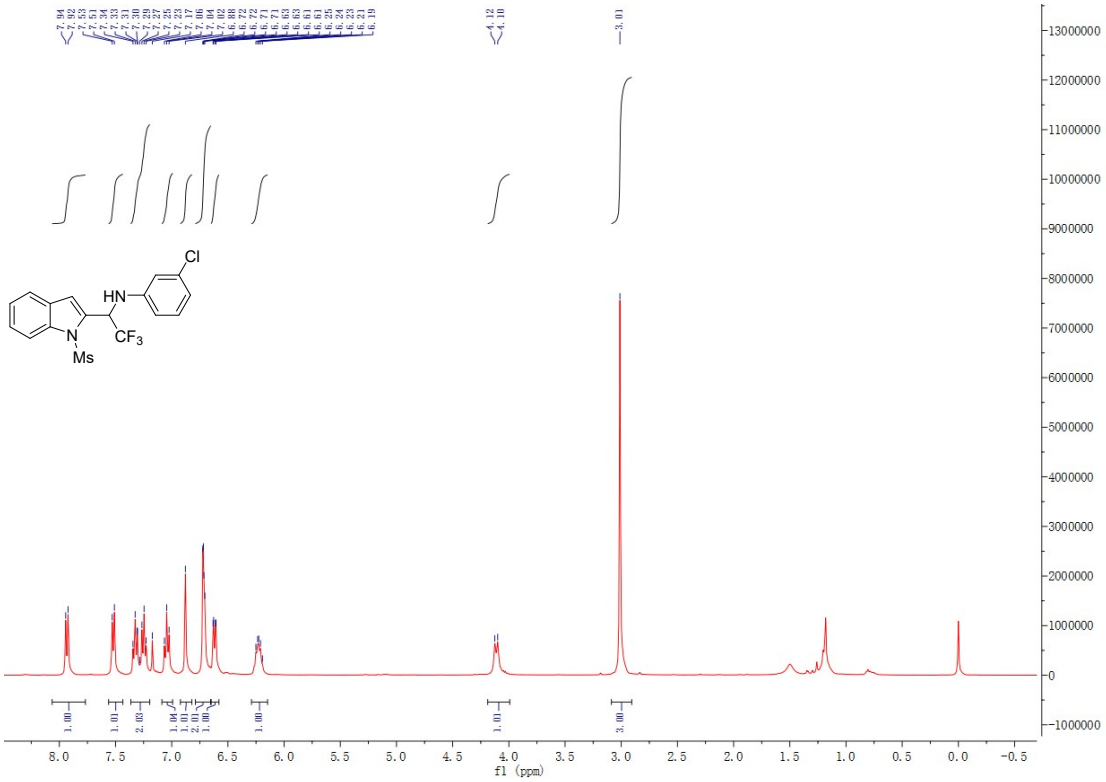


Figure S14 ^{13}CNMR spectra of compound **3e**

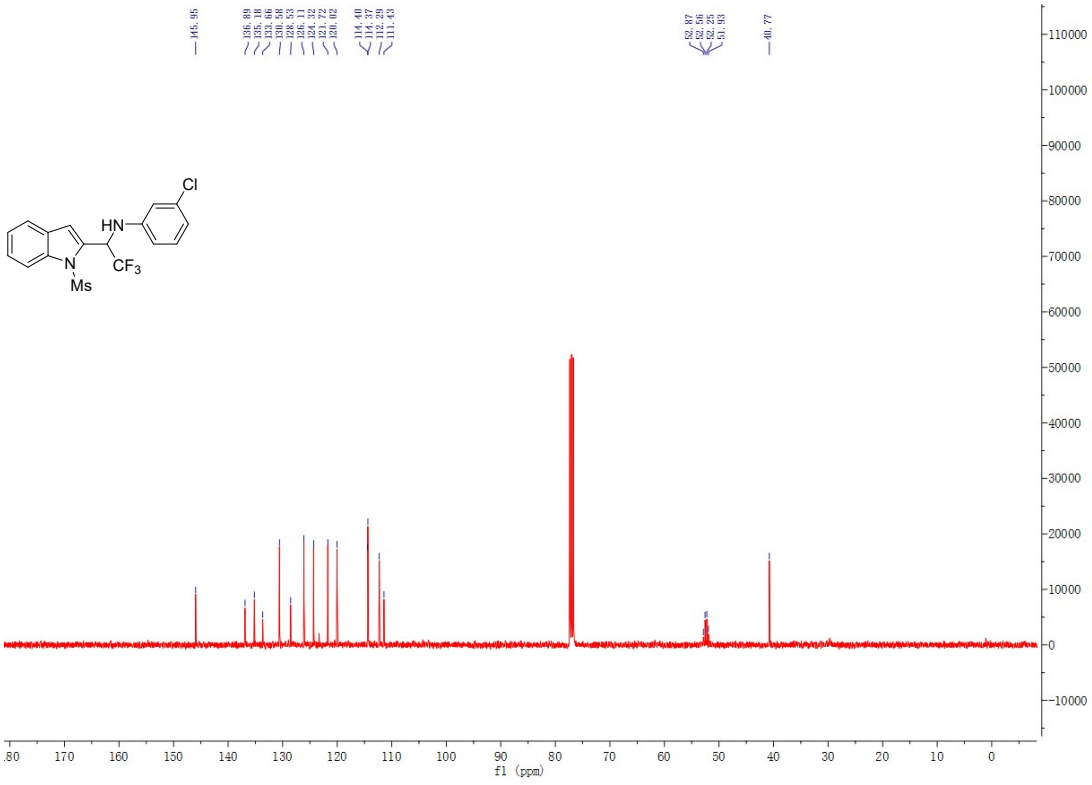


Figure S15 ^{19}FNMR spectra of compound **3e**

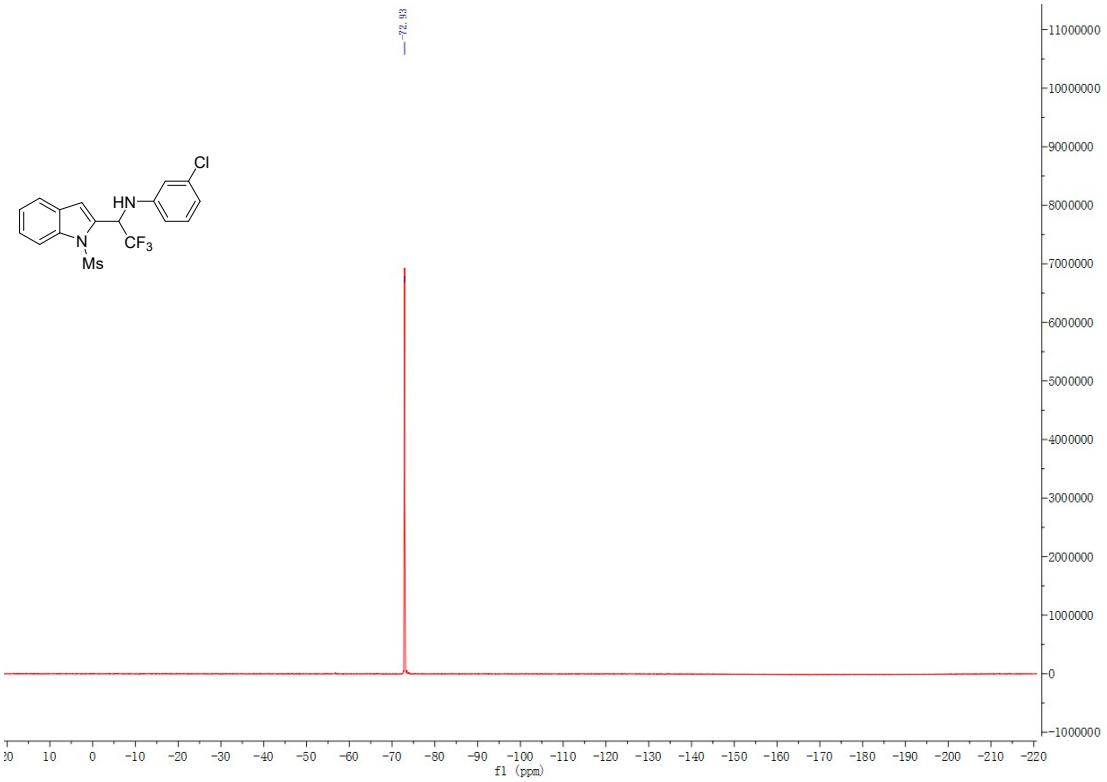


Figure S16 ^{1}HNMR spectra of compound **3f**

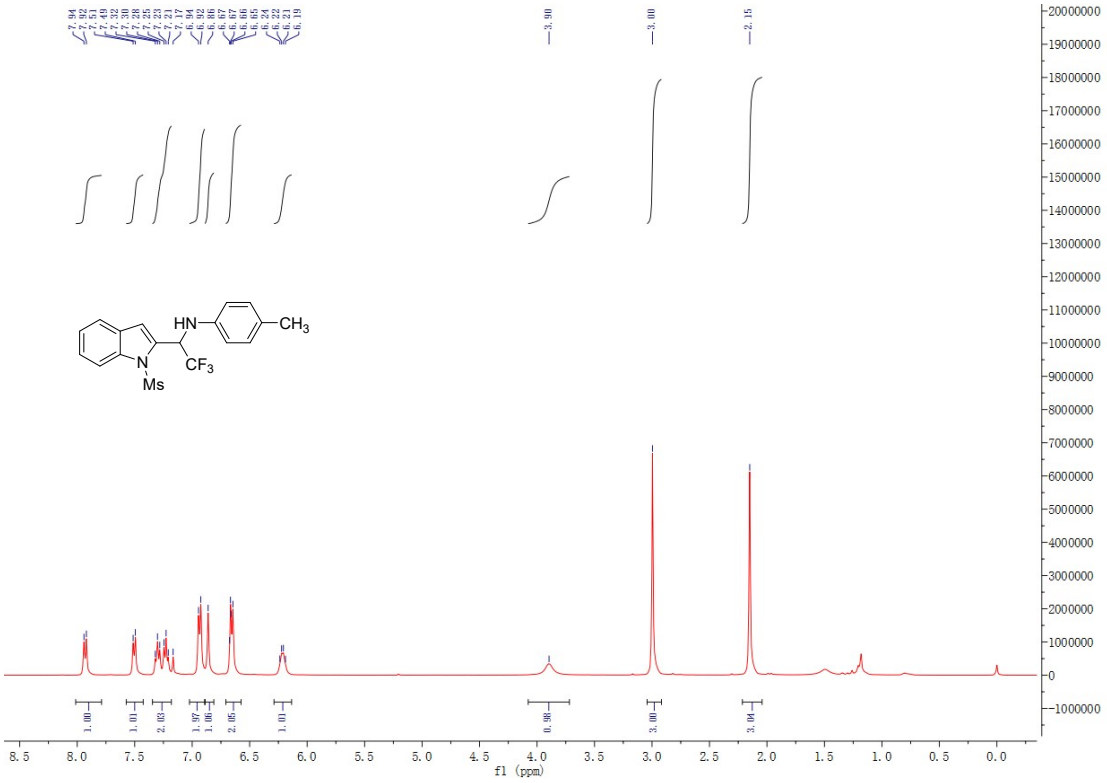


Figure S17 ^{13}CNMR spectra of compound **3f**

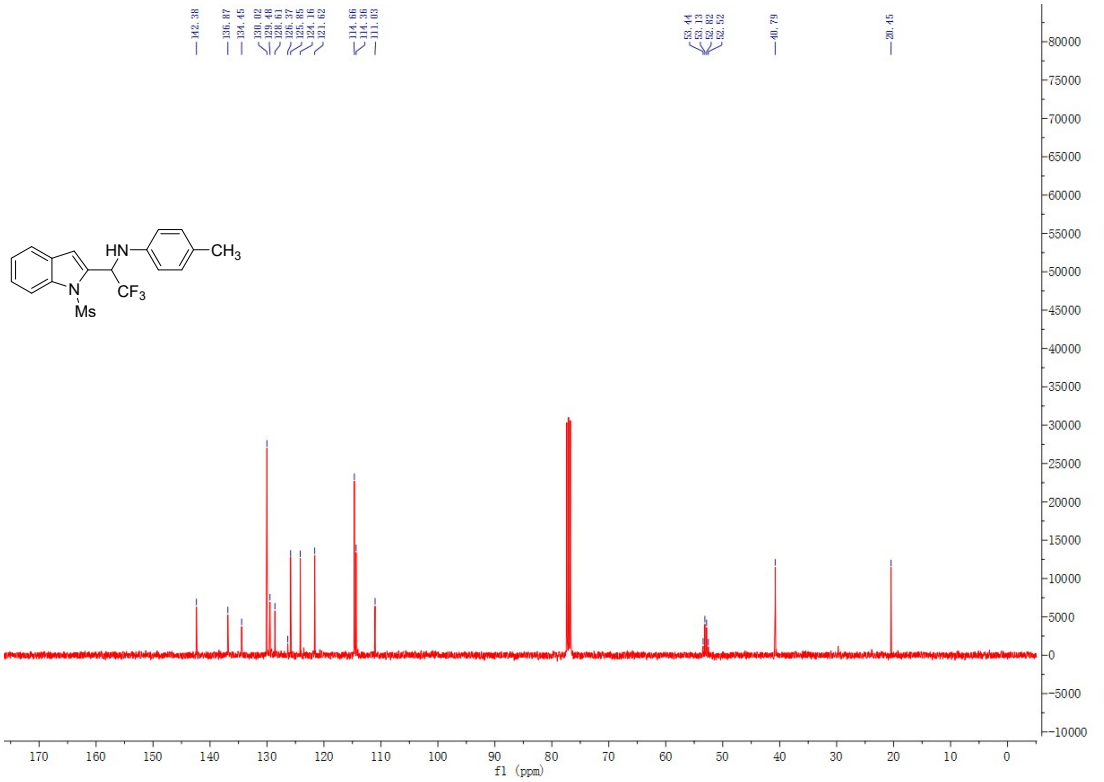


Figure S18 ^{19}FNMR spectra of compound **3f**

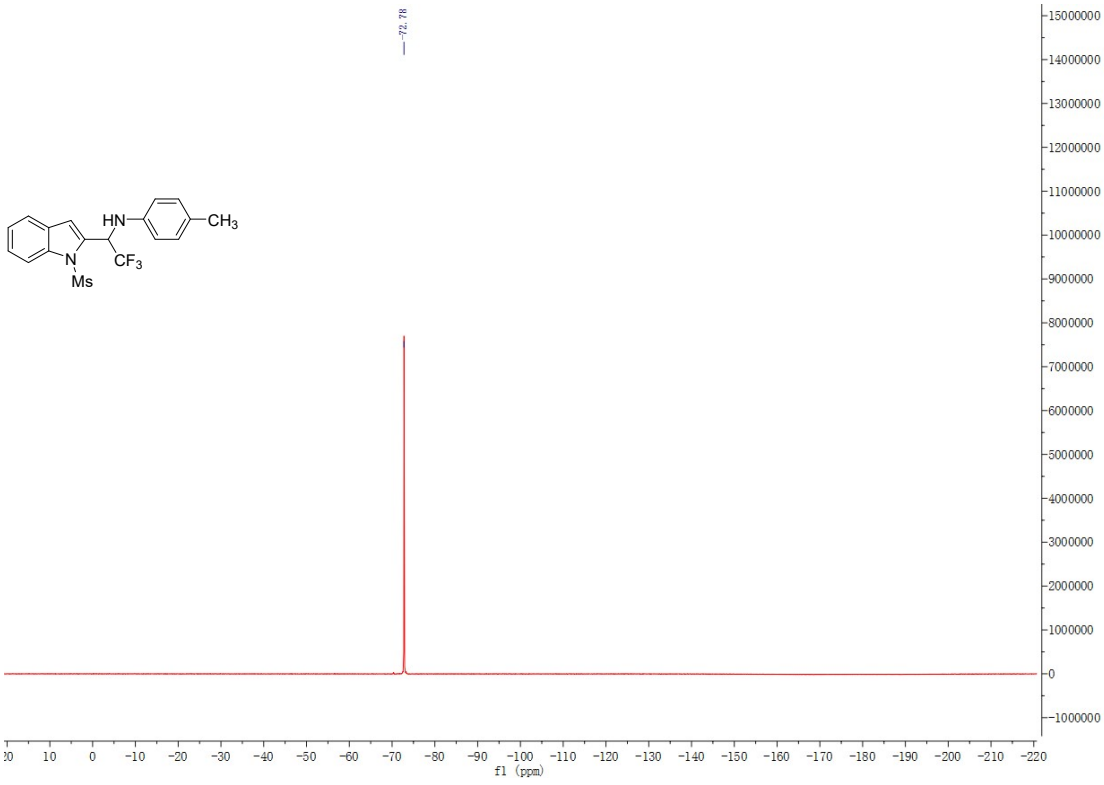


Figure S19 ^{1}HNMR spectra of compound **3g**

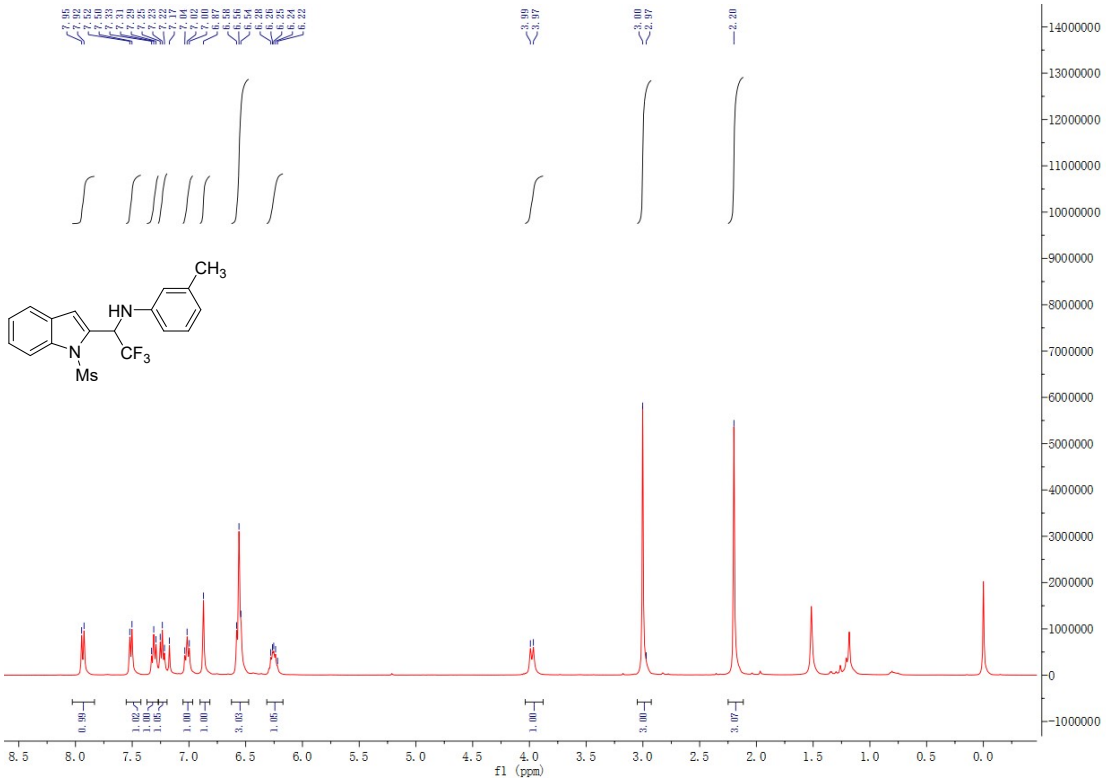


Figure S20 ^{13}CNMR spectra of compound **3g**

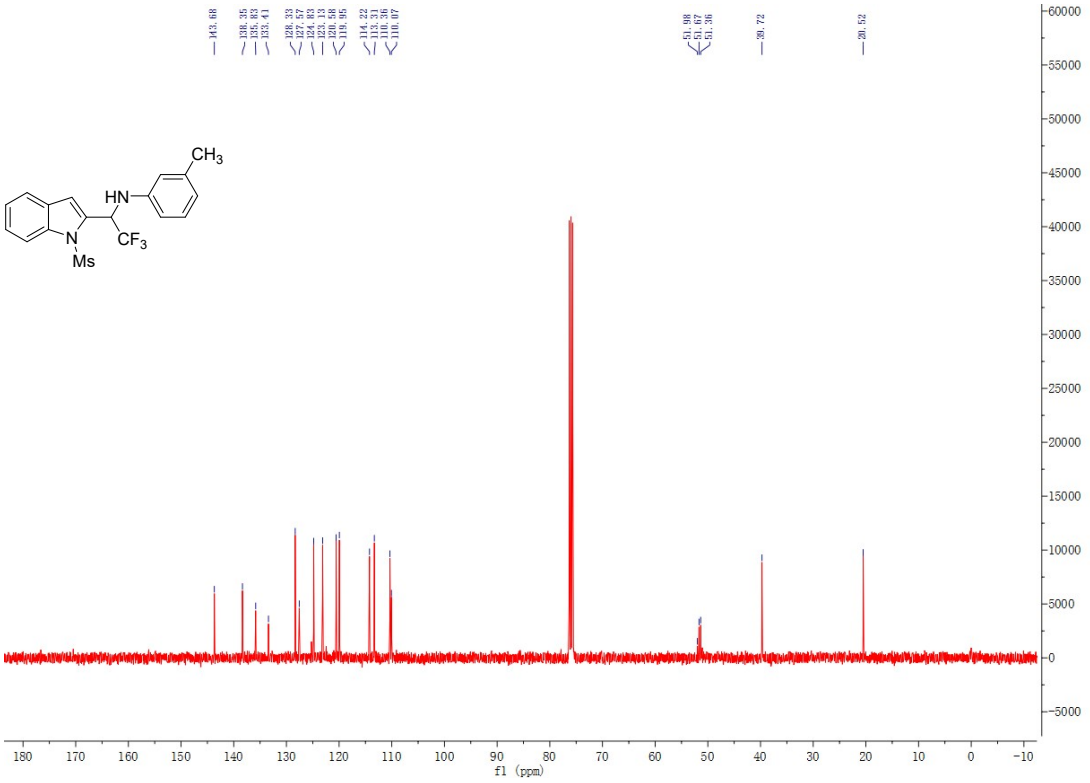


Figure S21 ^{19}FNMR spectra of compound **3g**

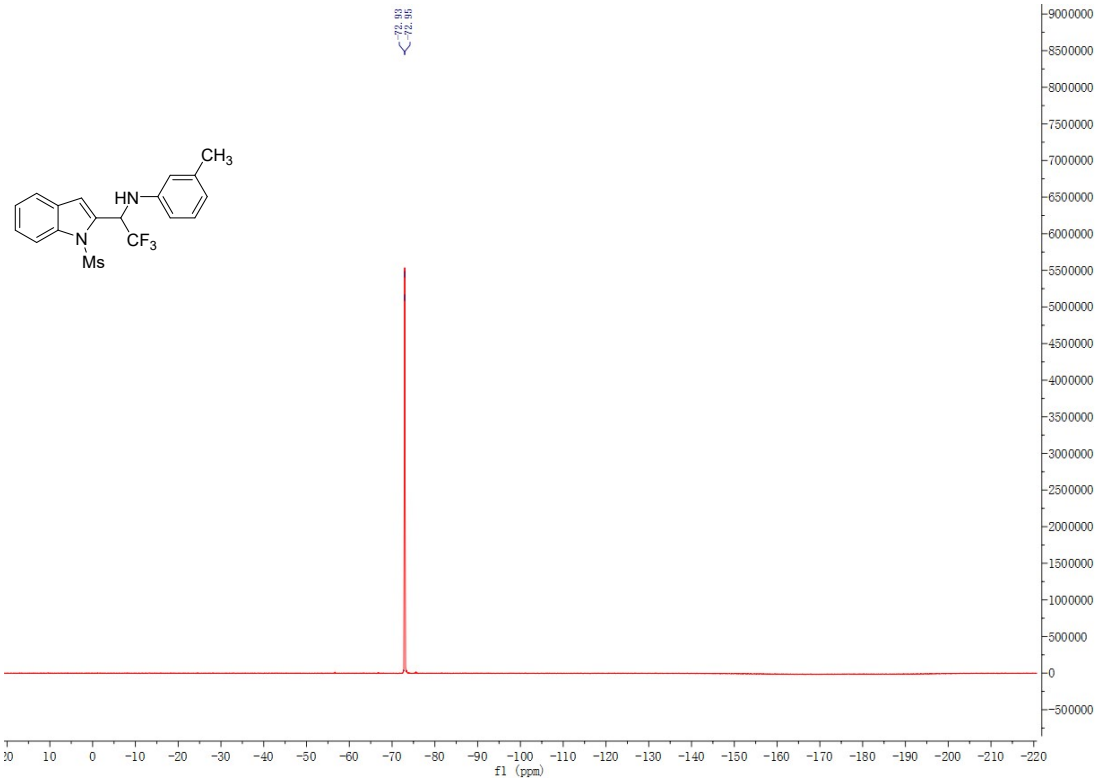


Figure S22 ^{1}HNMR spectra of compound **3h**

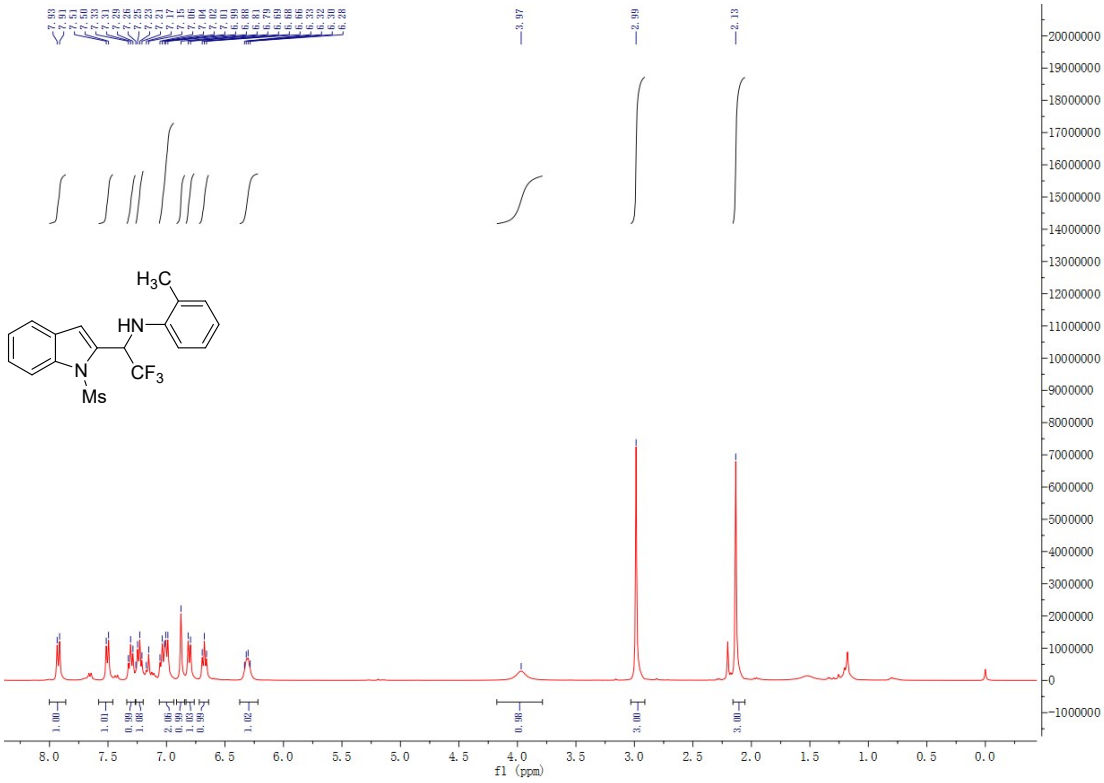


Figure S23 ^{13}CNMR spectra of compound **3h**

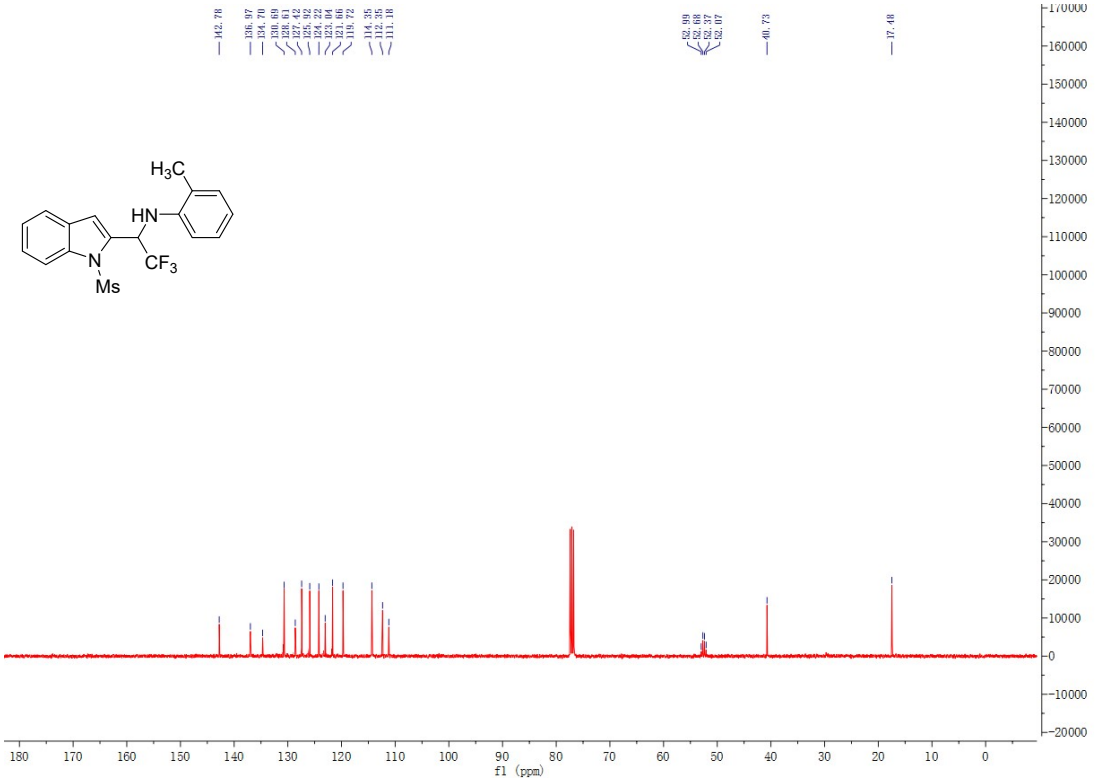


Figure S24 ^{19}FNMR spectra of compound **3h**

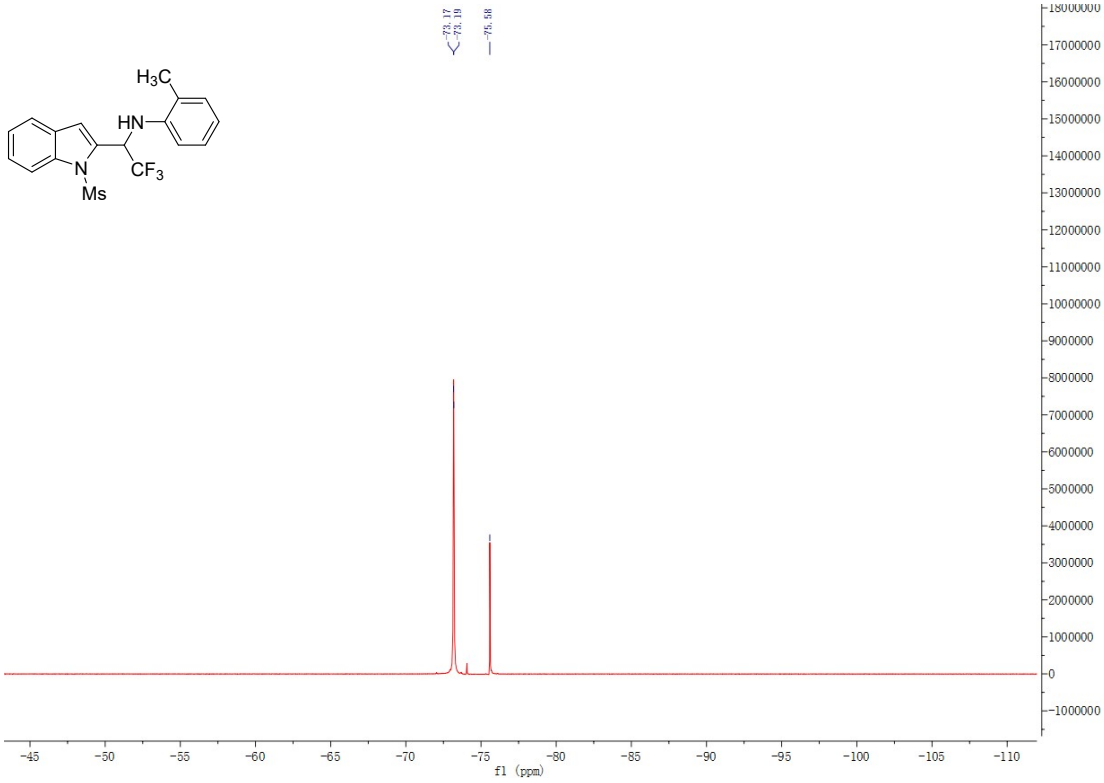


Figure S25 ^{1}HNMR spectra of compound **3i**

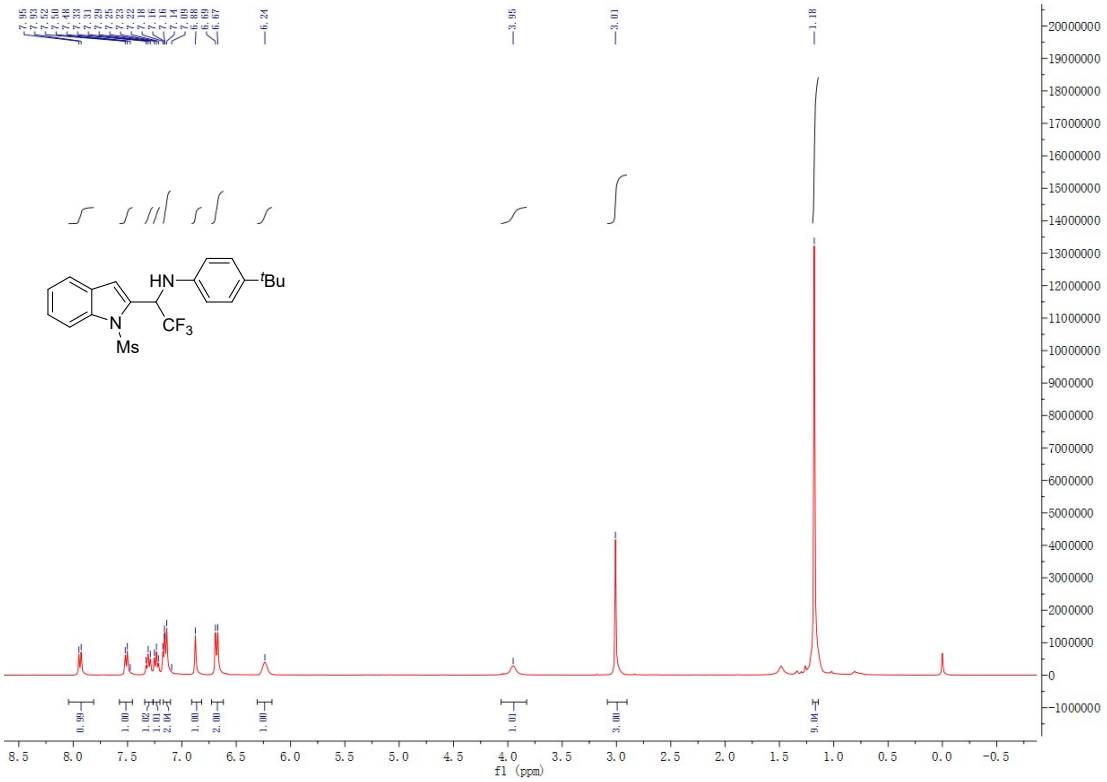


Figure S26 ^{13}CNMR spectra of compound **3i**

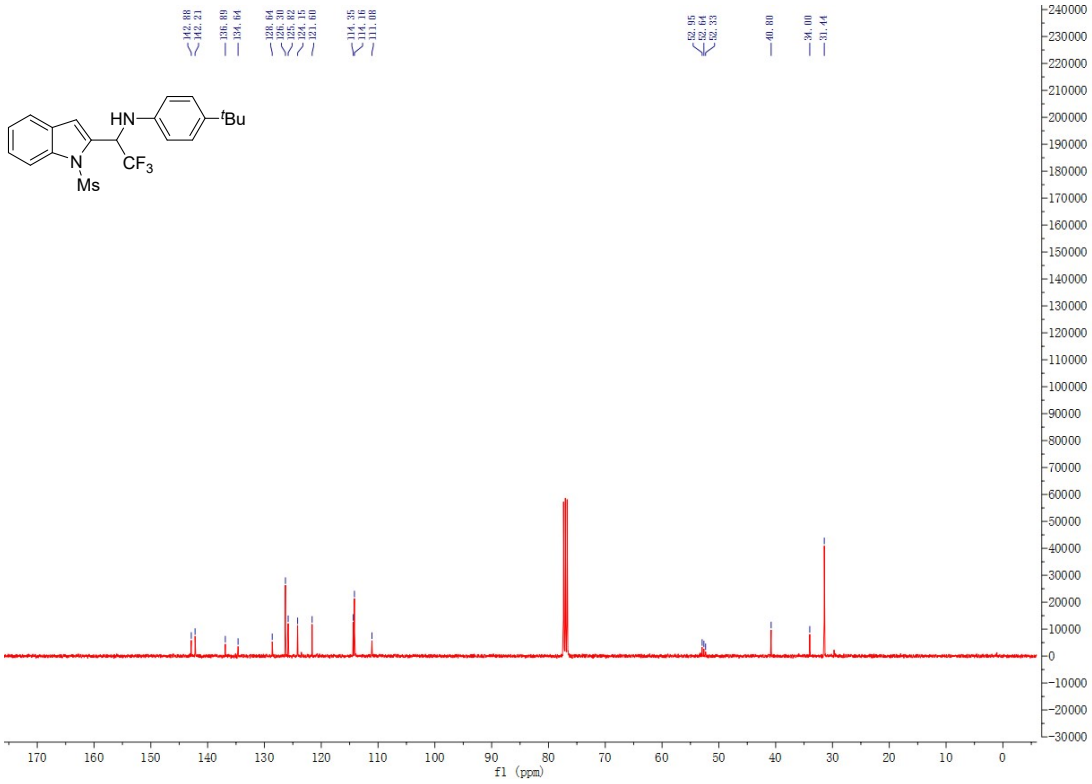


Figure S27 ^{19}FNMR spectra of compound **3i**

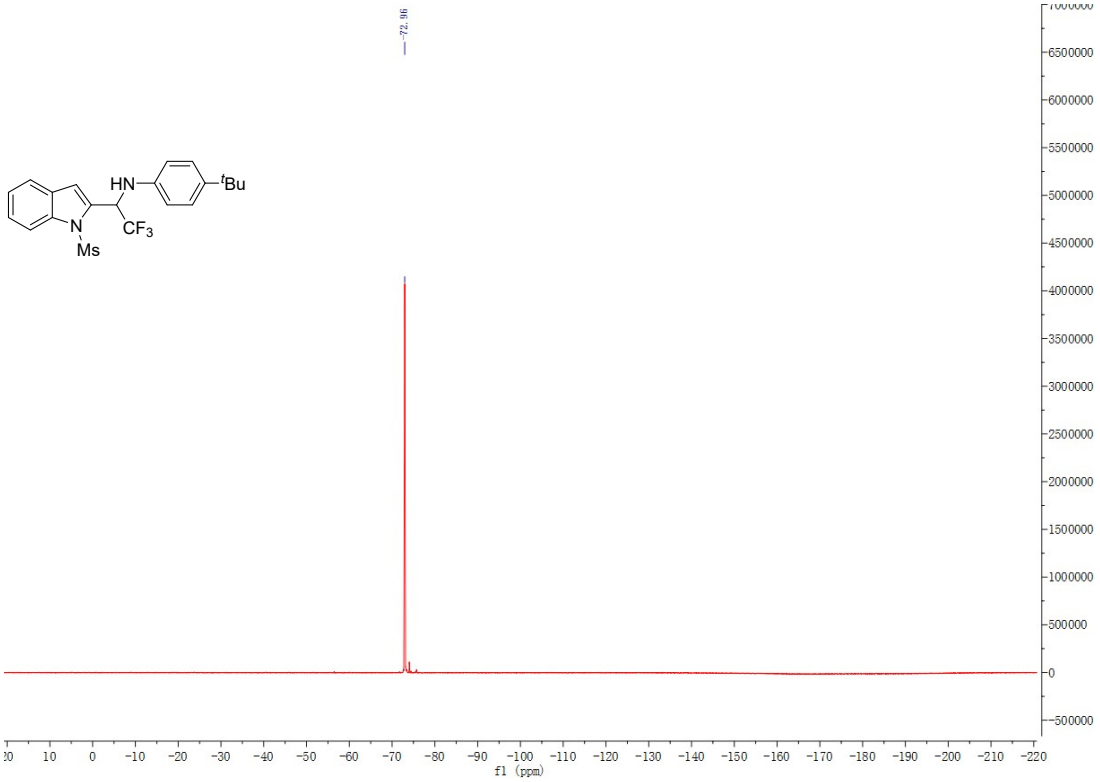


Figure S28 ^{1}HNMR spectra of compound **3j**

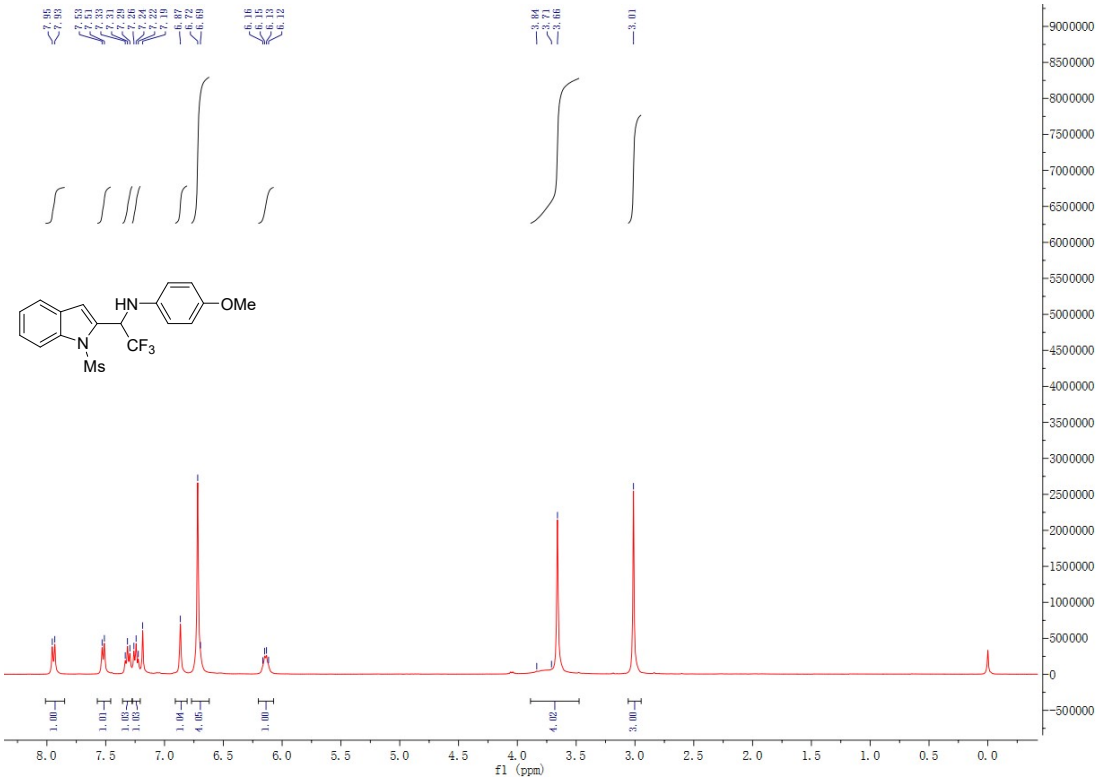


Figure S29 ^{13}CNMR spectra of compound **3j**

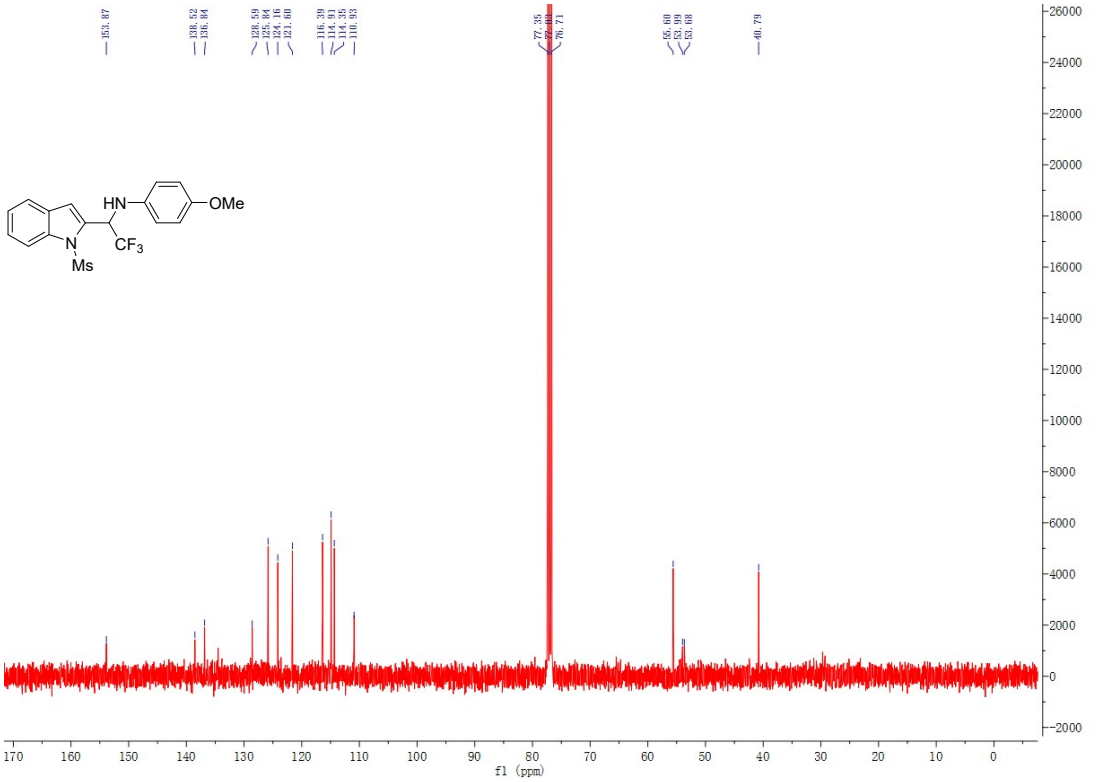


Figure S30 ^{19}FNMR spectra of compound **3j**

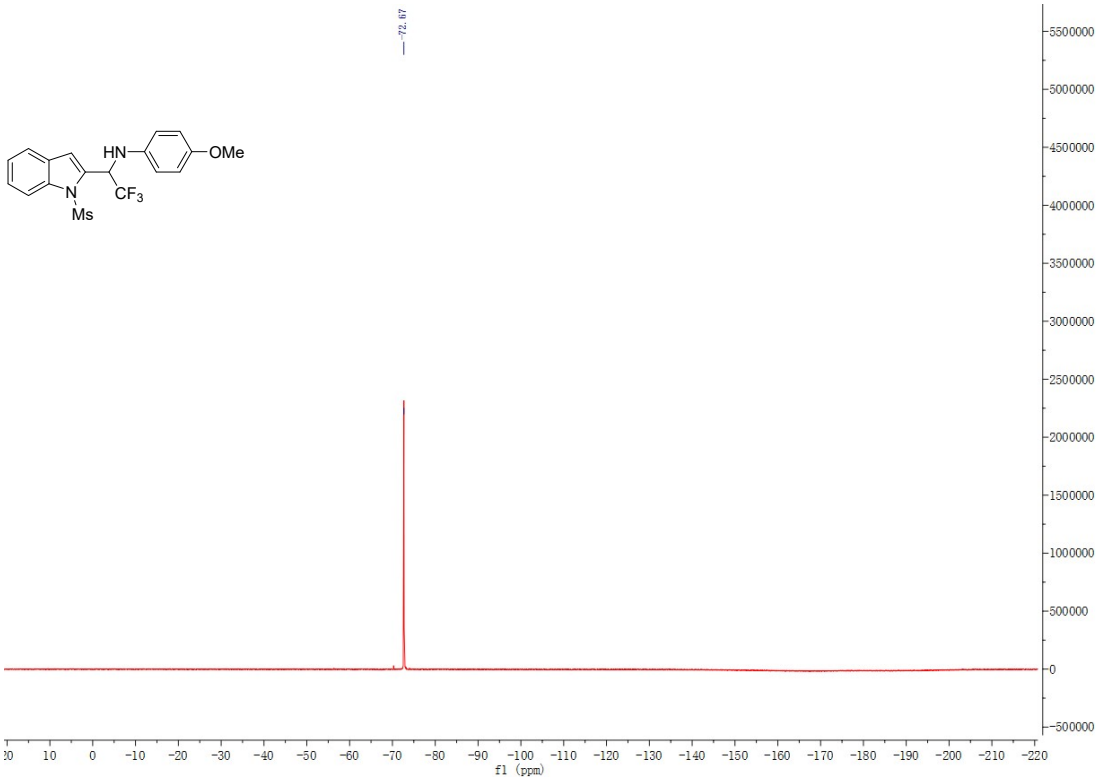


Figure S31 [1]HNMR spectra of compound **3k**

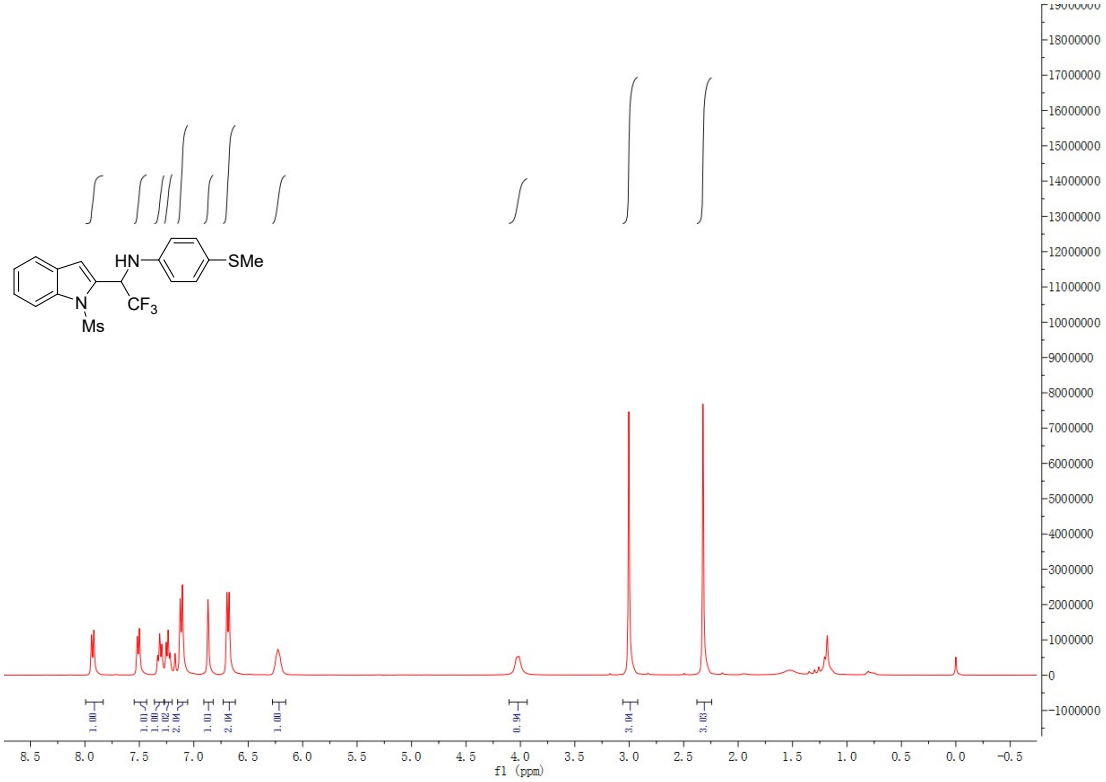


Figure S32 [13]CNMR spectra of compound **3k**

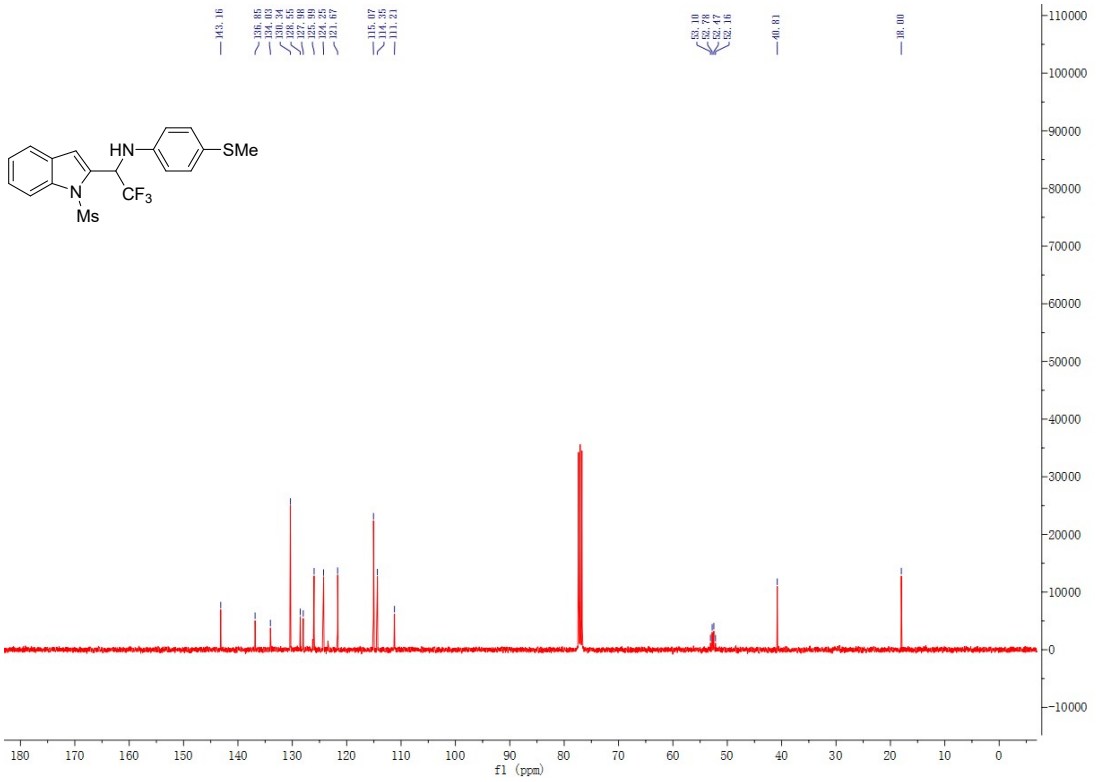


Figure S33 ^{19}FNMR spectra of compound **3k**

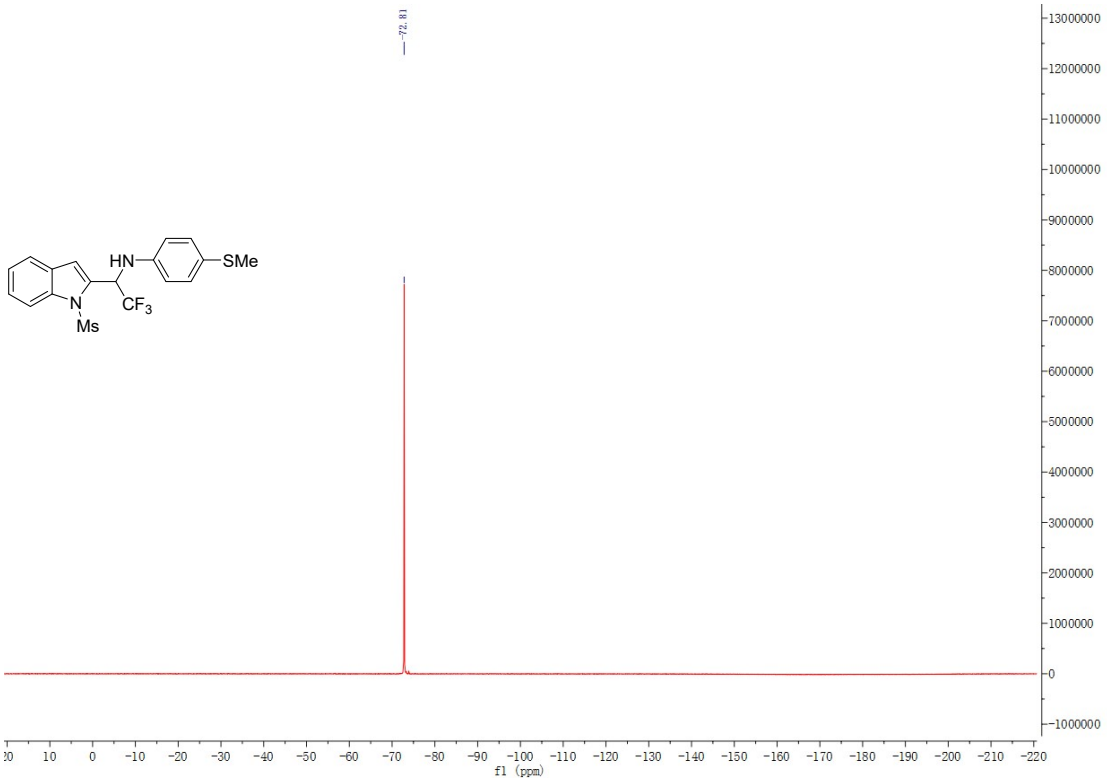


Figure S34 ^{1}HNMR spectra of compound **3l**

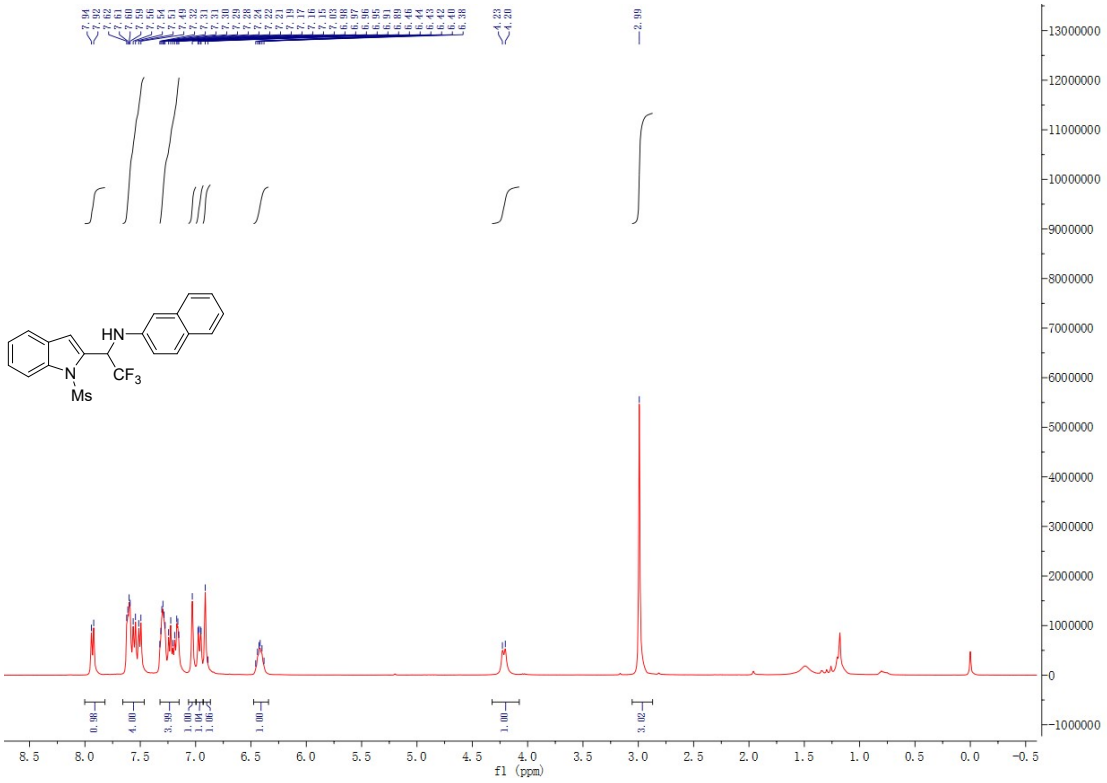


Figure S35 ^{13}CNMR spectra of compound **3l**

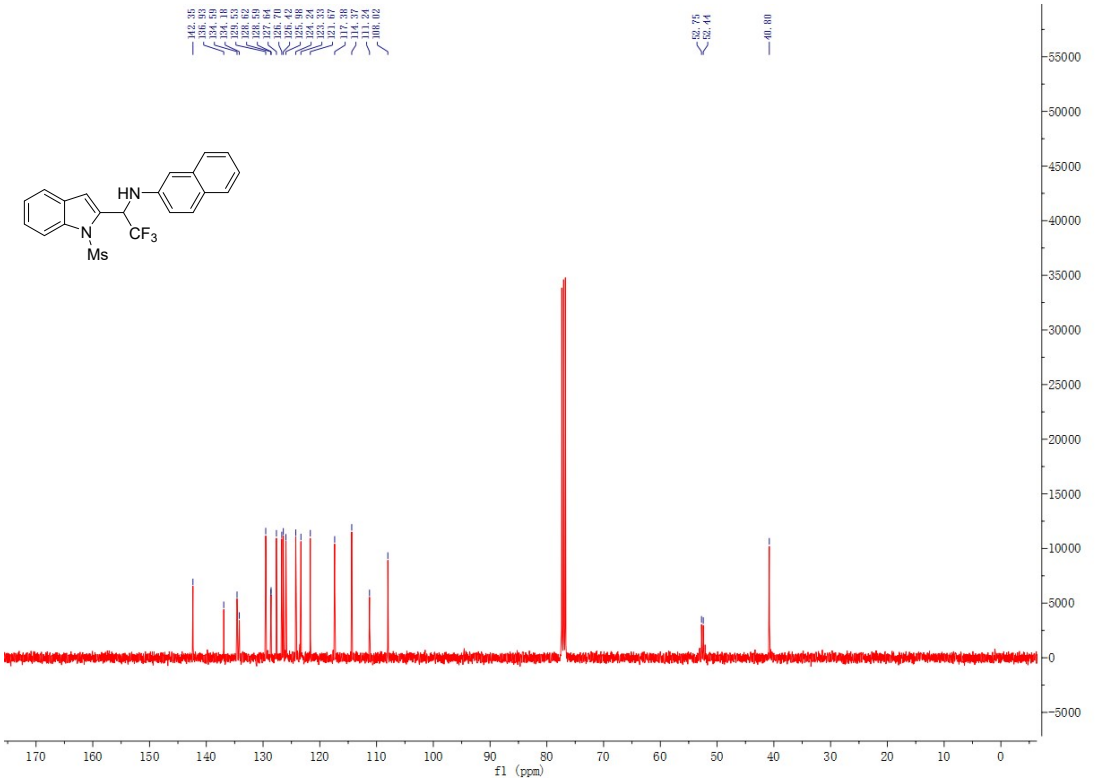


Figure S36 ^{19}FNMR spectra of compound **3l**

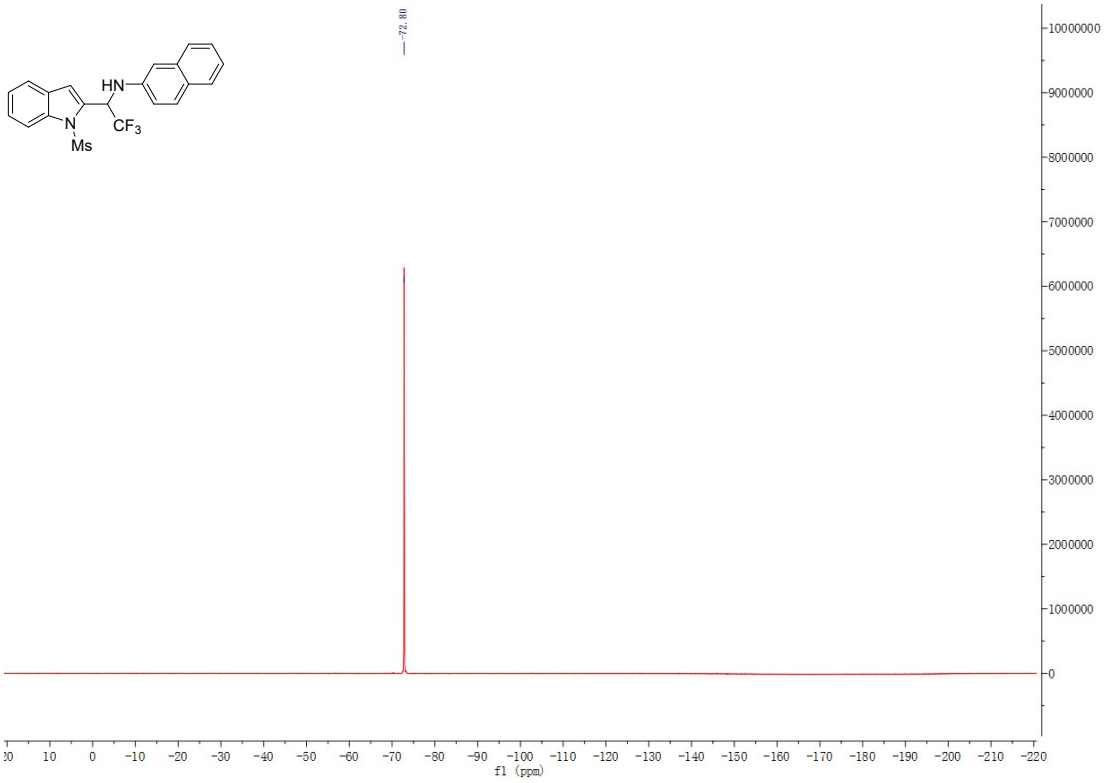


Figure S37 ^{1}HNMR spectra of compound **3m**

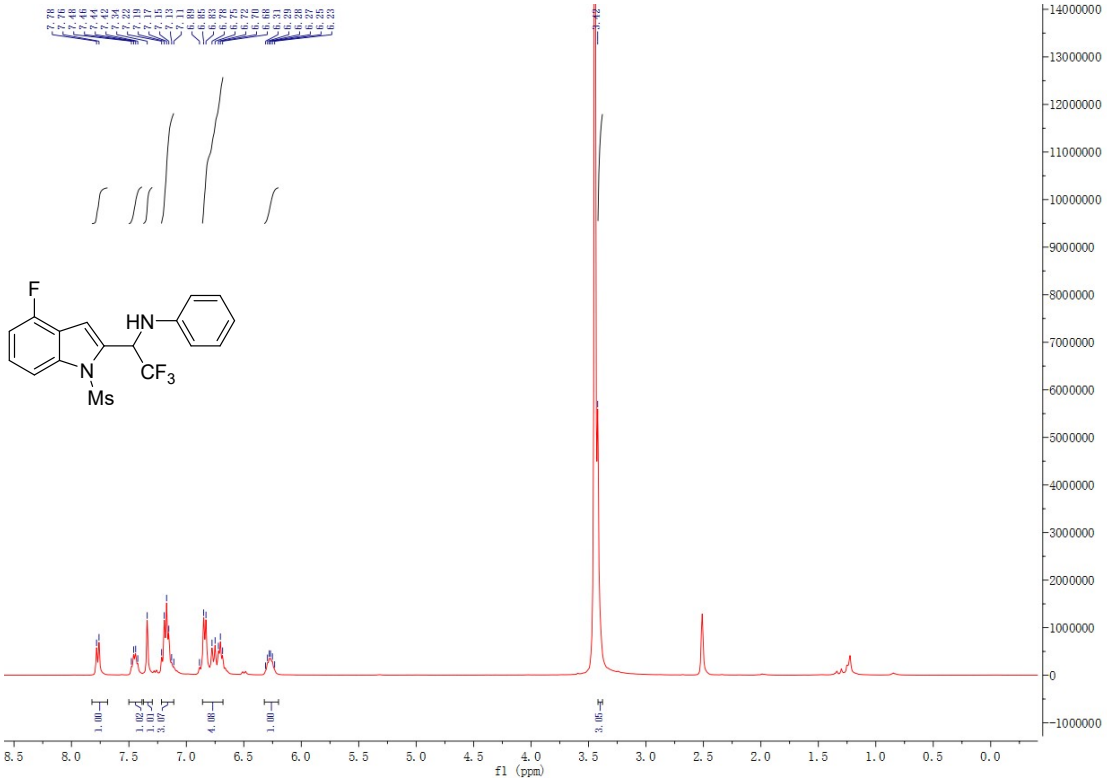


Figure S38 ^{13}CNMR spectra of compound **3m**

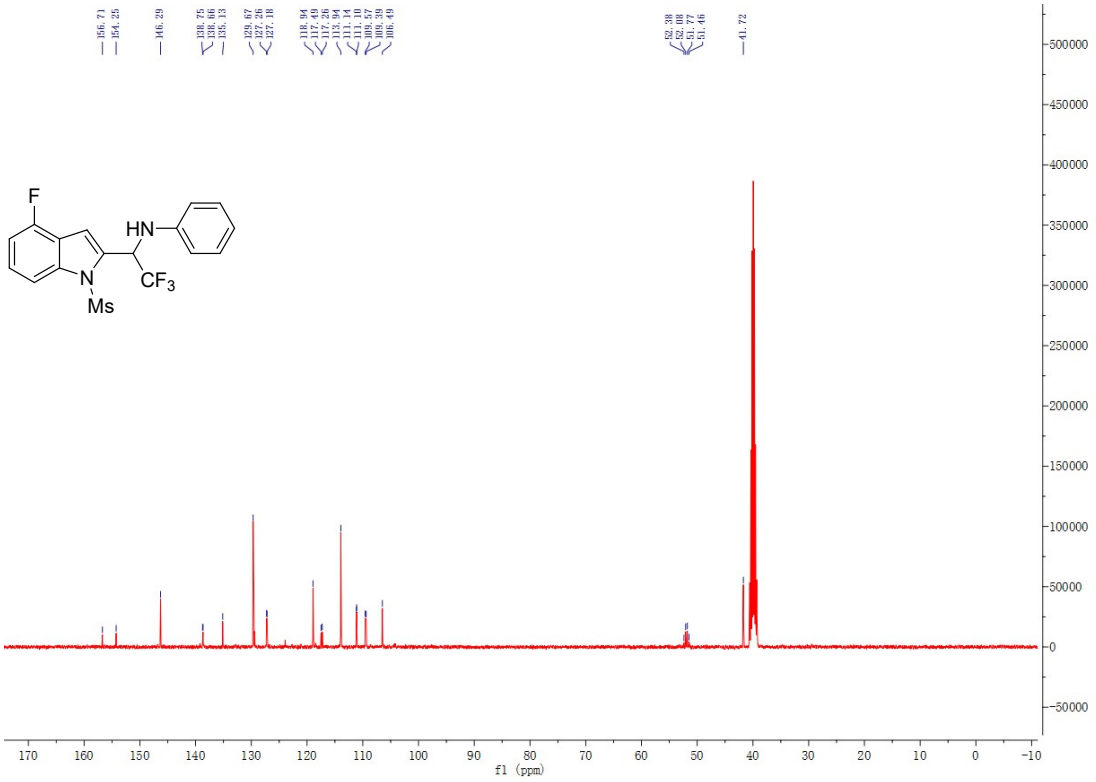


Figure S39 ^{19}FNMR spectra of compound **3m**

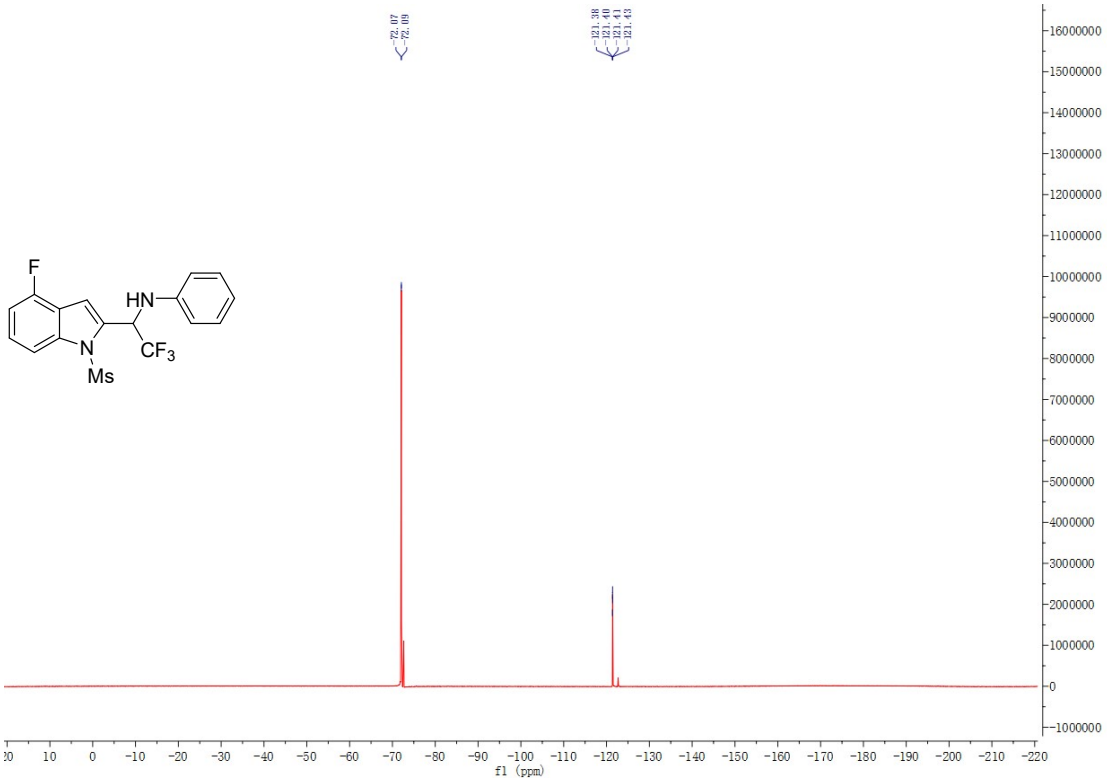


Figure S40 ^{1}HNMR spectra of compound **3n**

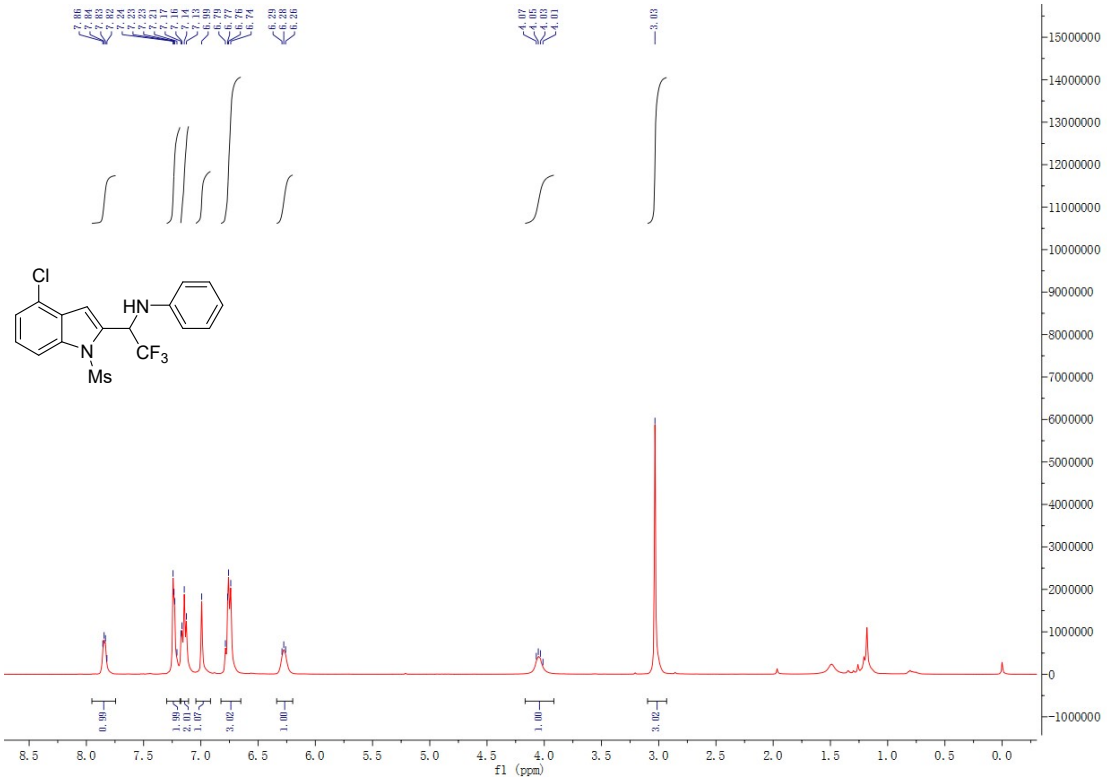


Figure S41 ^{13}CNMR spectra of compound **3n**

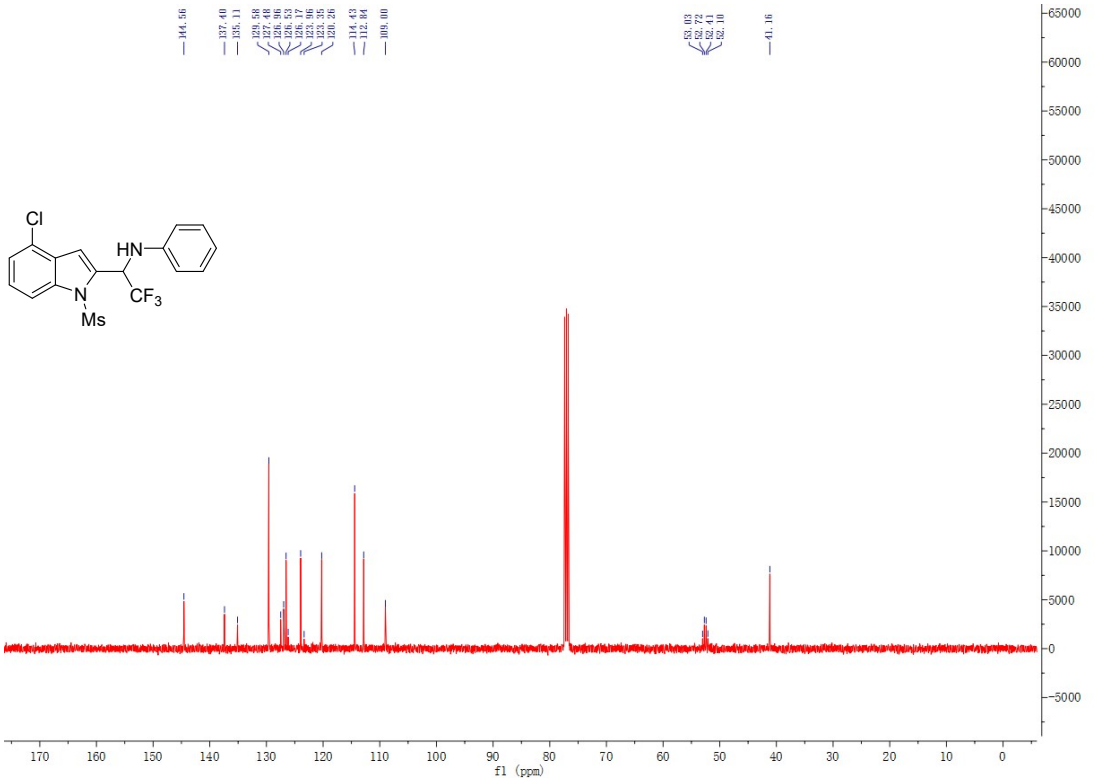


Figure S42 ^{19}FNMR spectra of compound **3n**

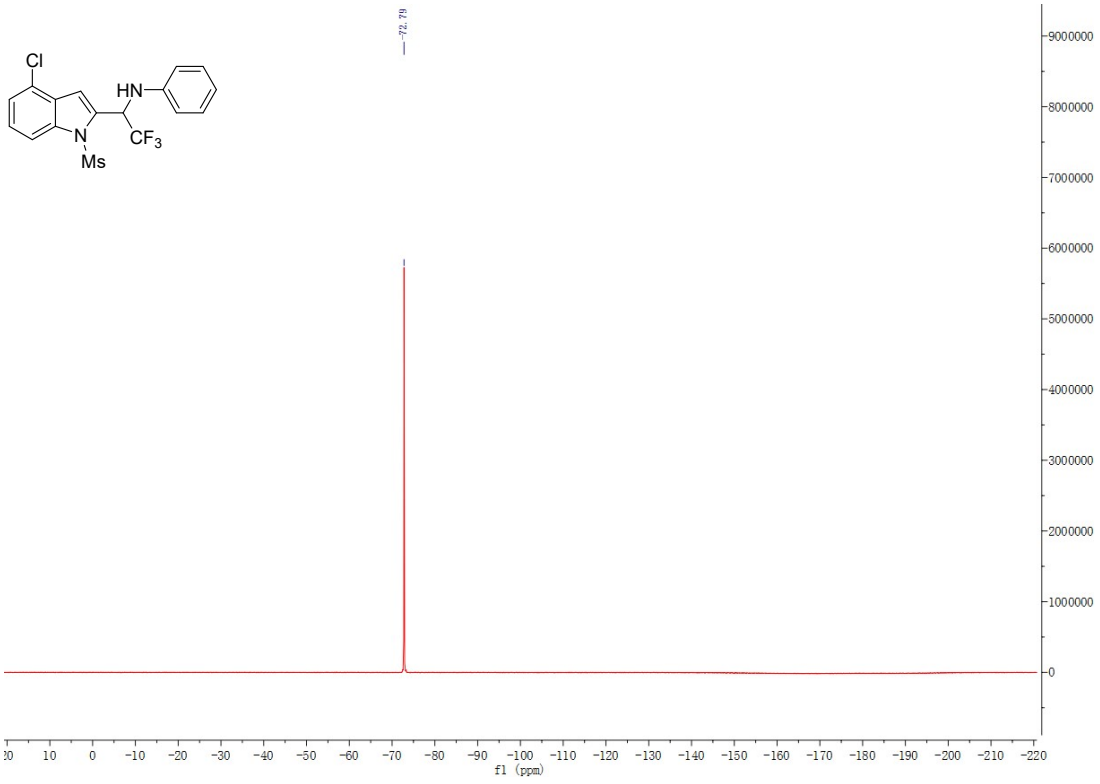


Figure S43 ^{1}HNMR spectra of compound **3o**

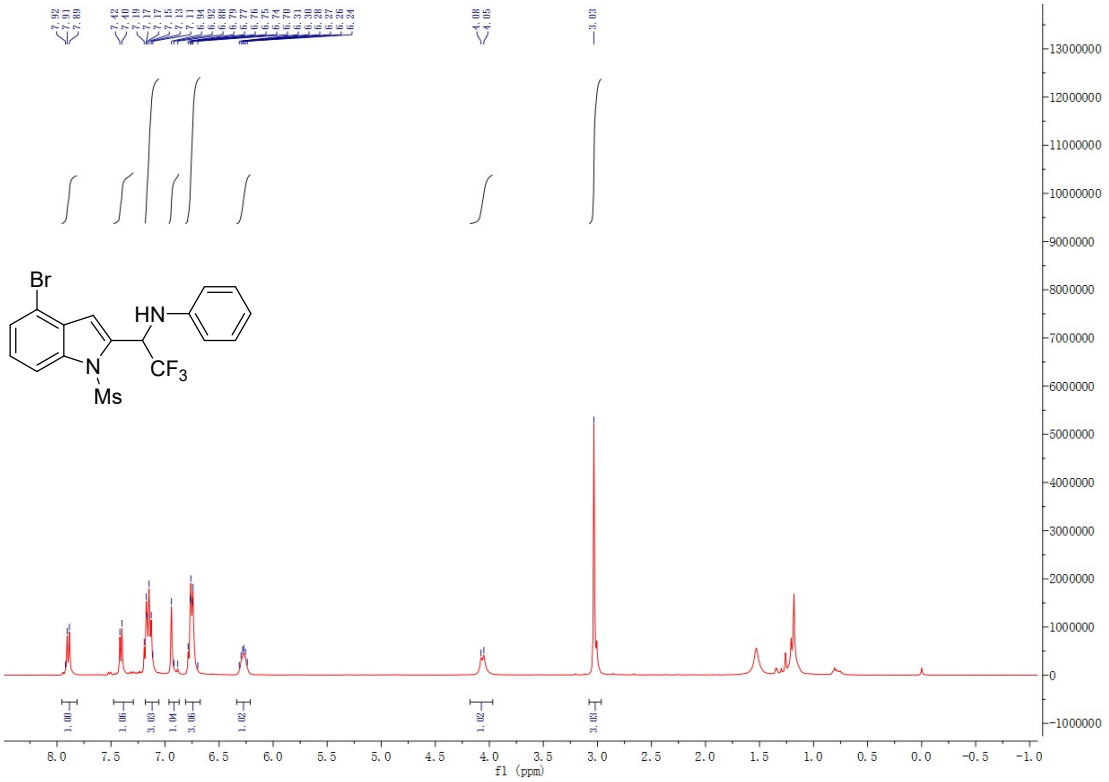


Figure S44 ^{13}CNMR spectra of compound **3o**

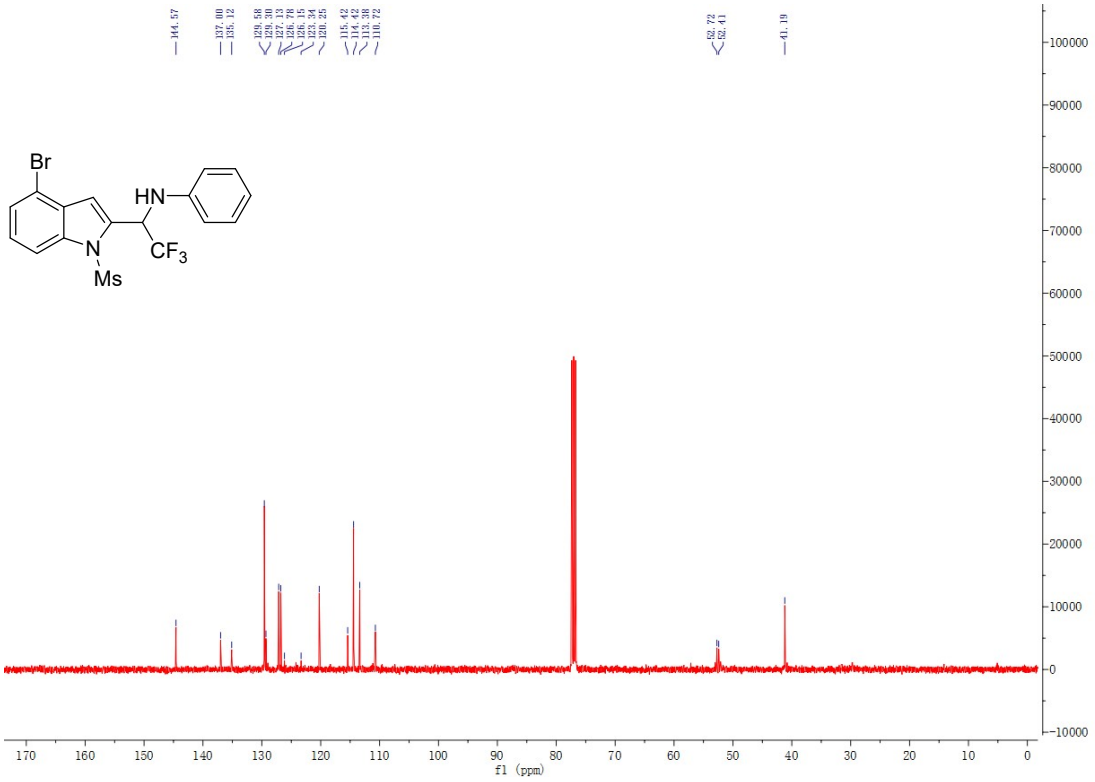


Figure S45 ^{19}FNMR spectra of compound **3o**

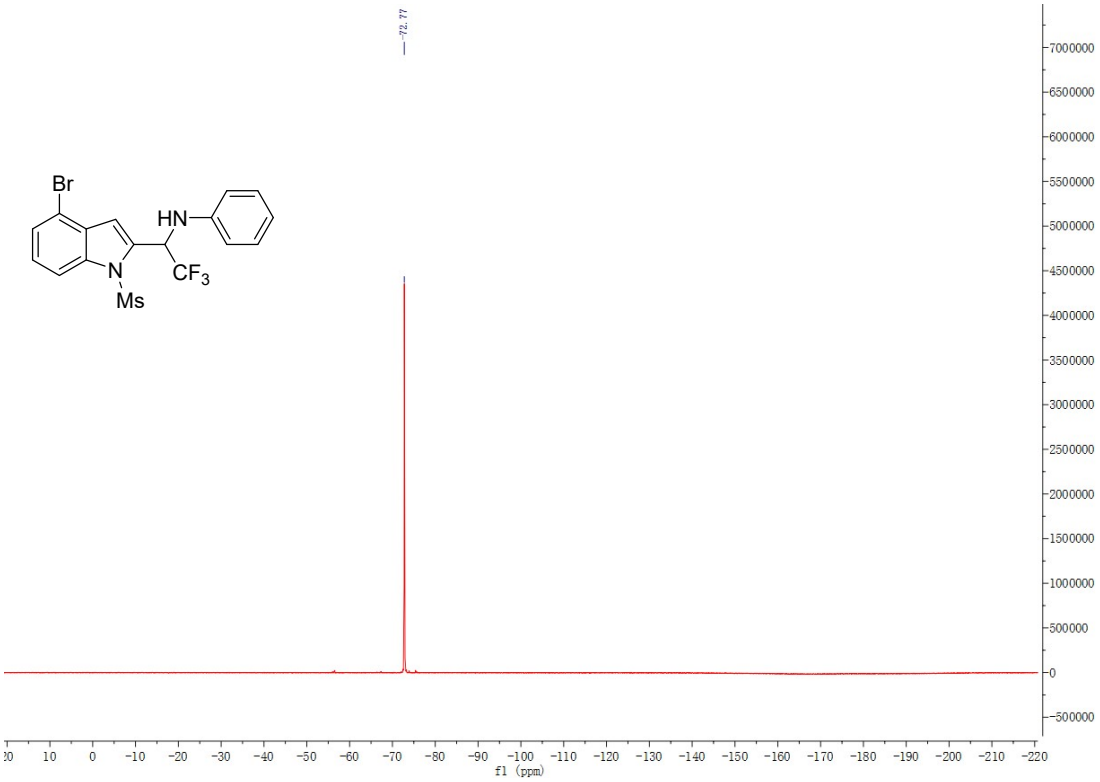


Figure S46 ^{1}HNMR spectra of compound **3p**

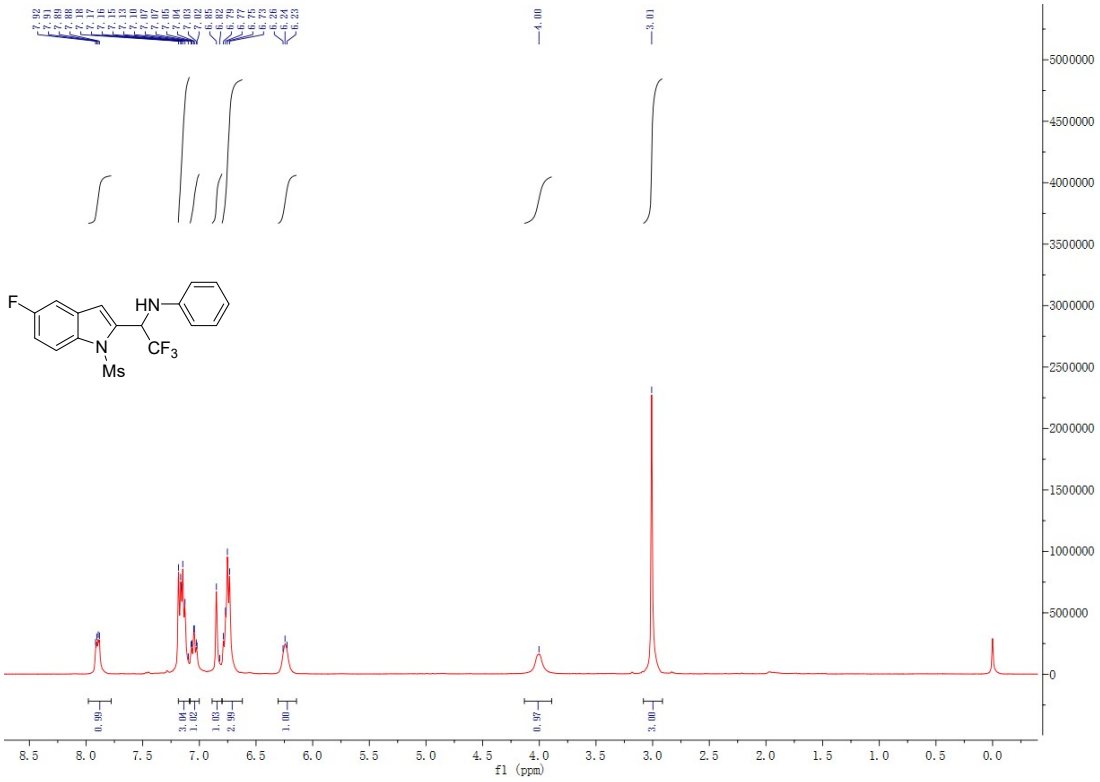


Figure S47 ^{13}CNMR spectra of compound **3p**

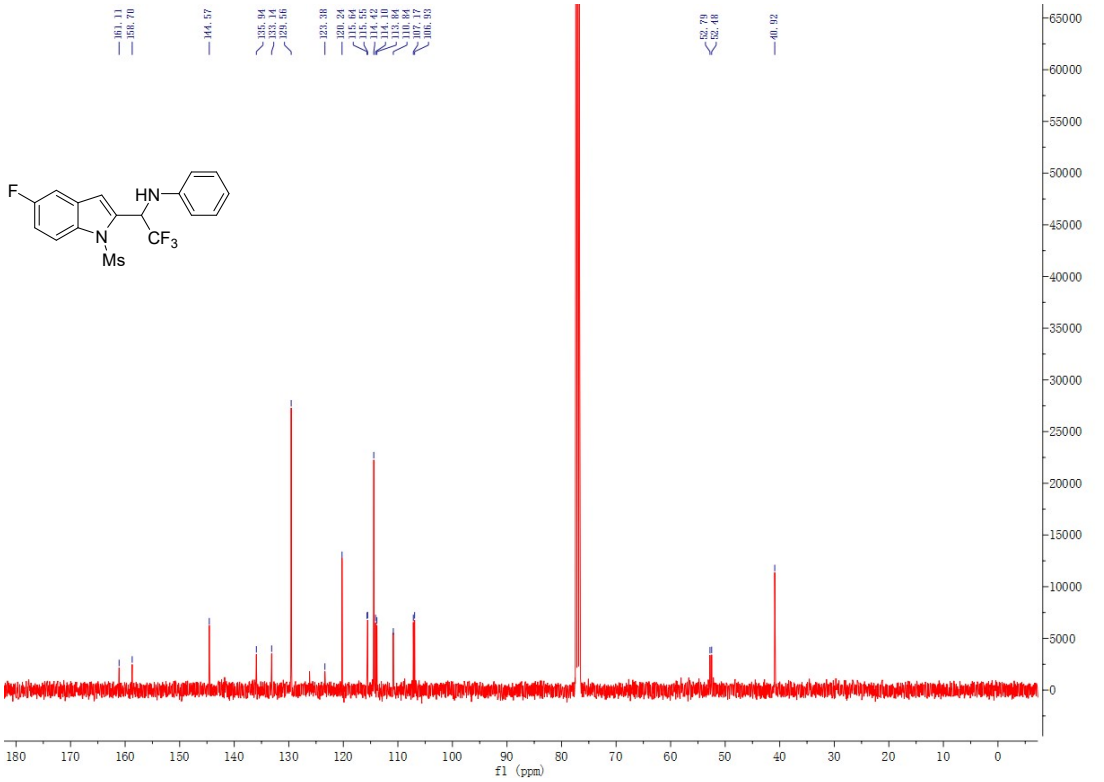


Figure S48 ^{19}FNMR spectra of compound **3p**

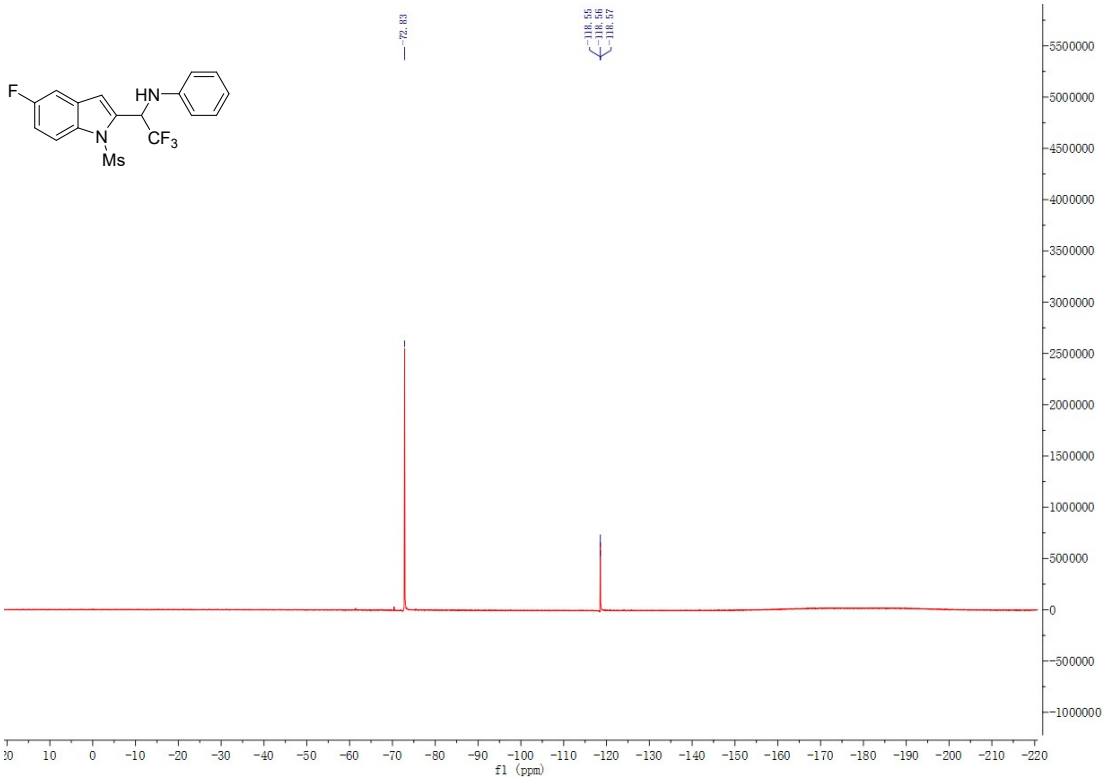


Figure S49 ^{1}HNMR spectra of compound **3q**

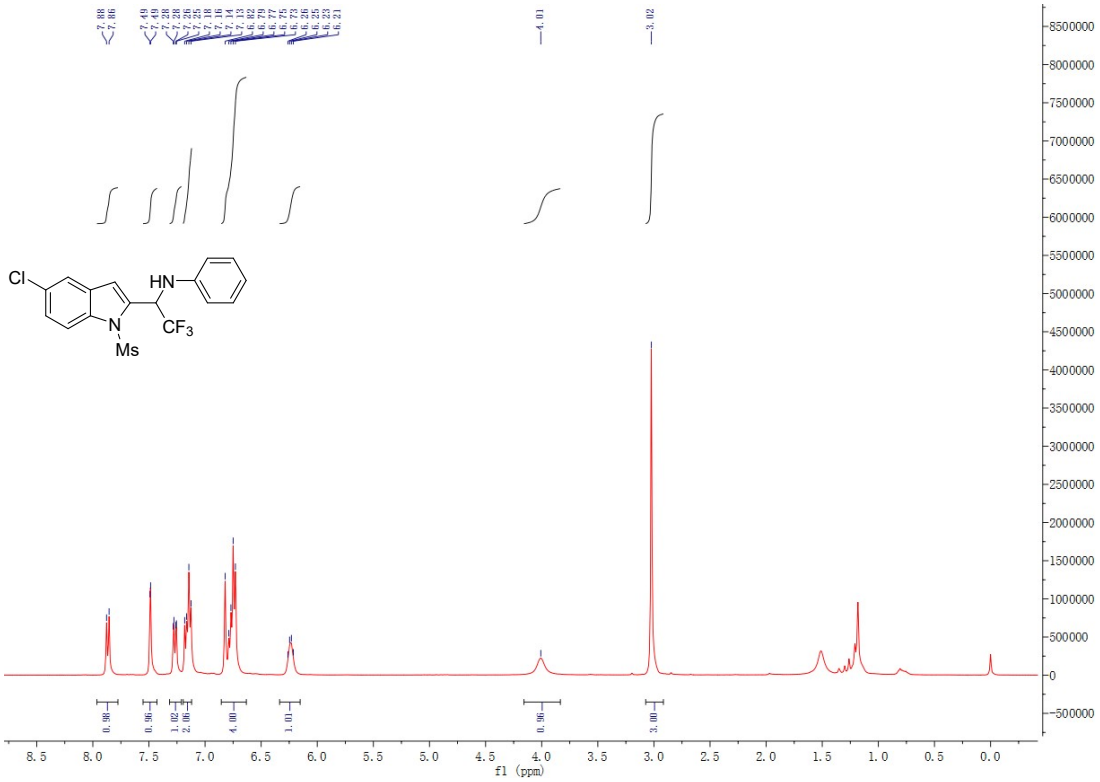


Figure S50 ^{13}CNMR spectra of compound **3q**

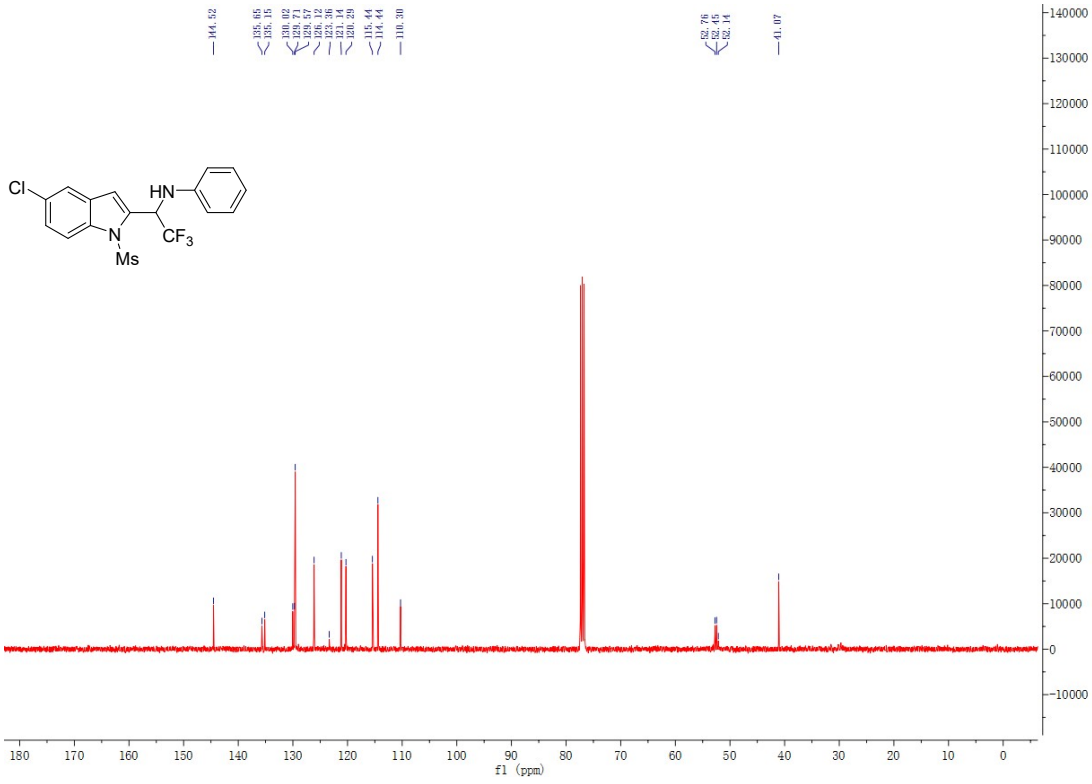


Figure S51 ^{19}FNMR spectra of compound **3q**

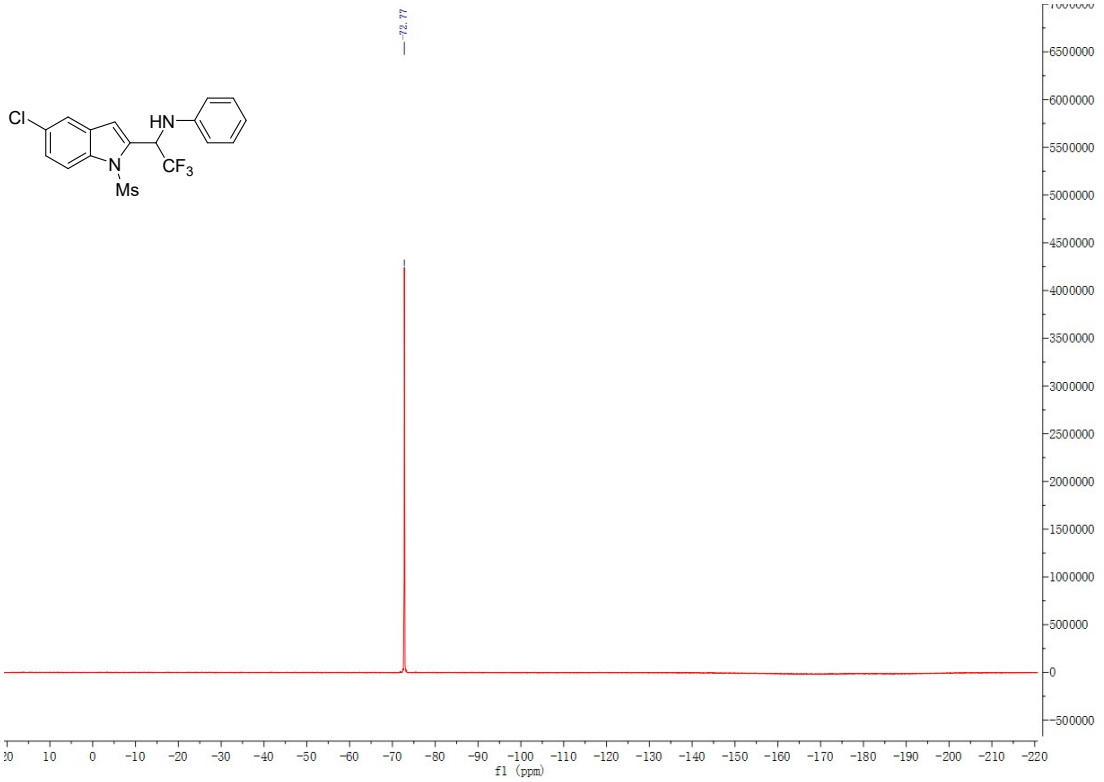


Figure S52 ^{1}HNMR spectra of compound **3r**

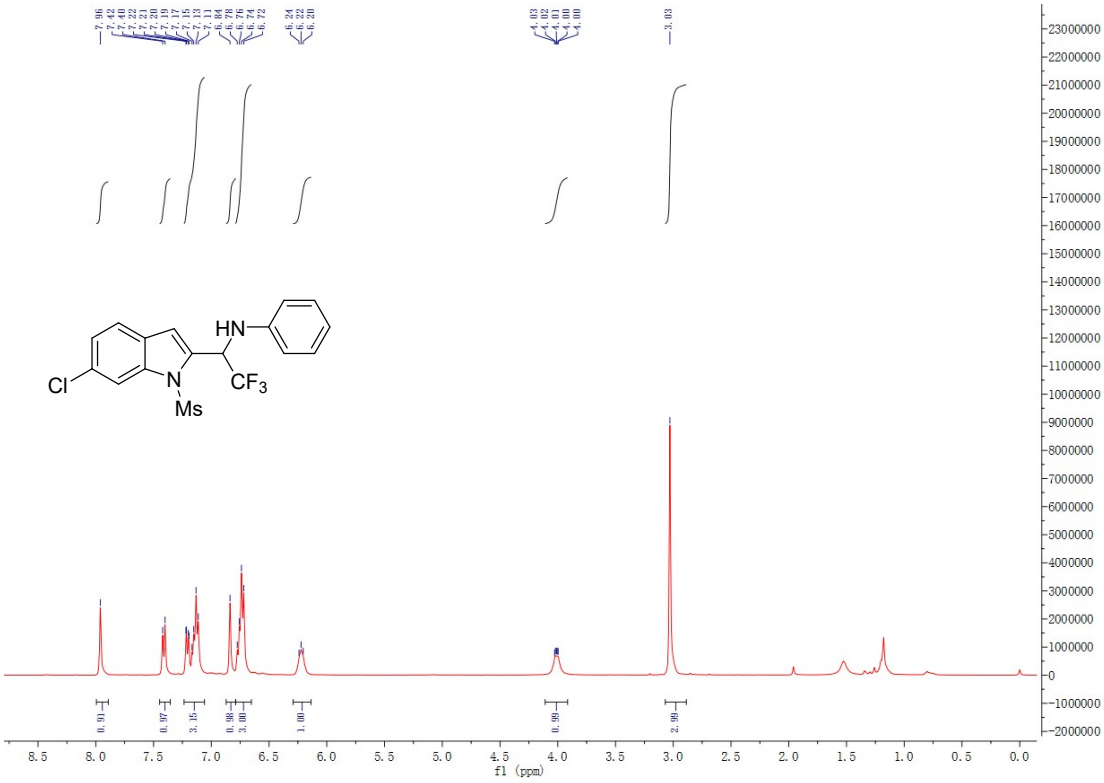


Figure S53 ^{13}CNMR spectra of compound **3r**

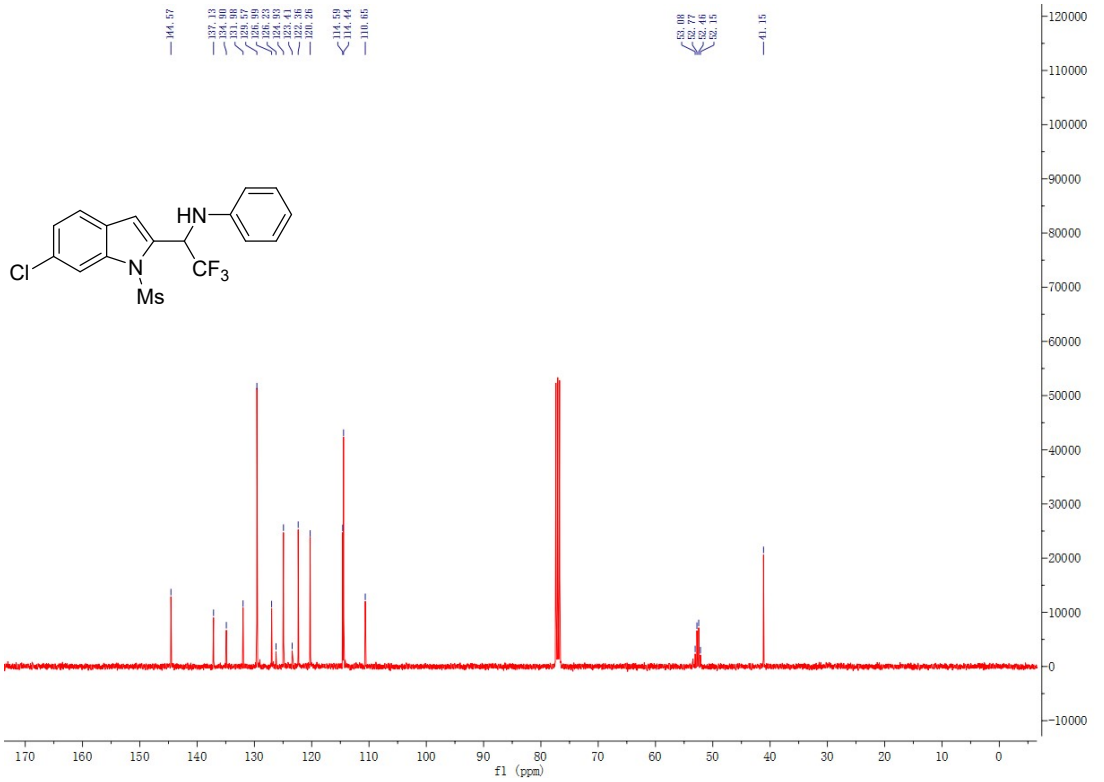


Figure S54 ^{19}FNMR spectra of compound **3r**

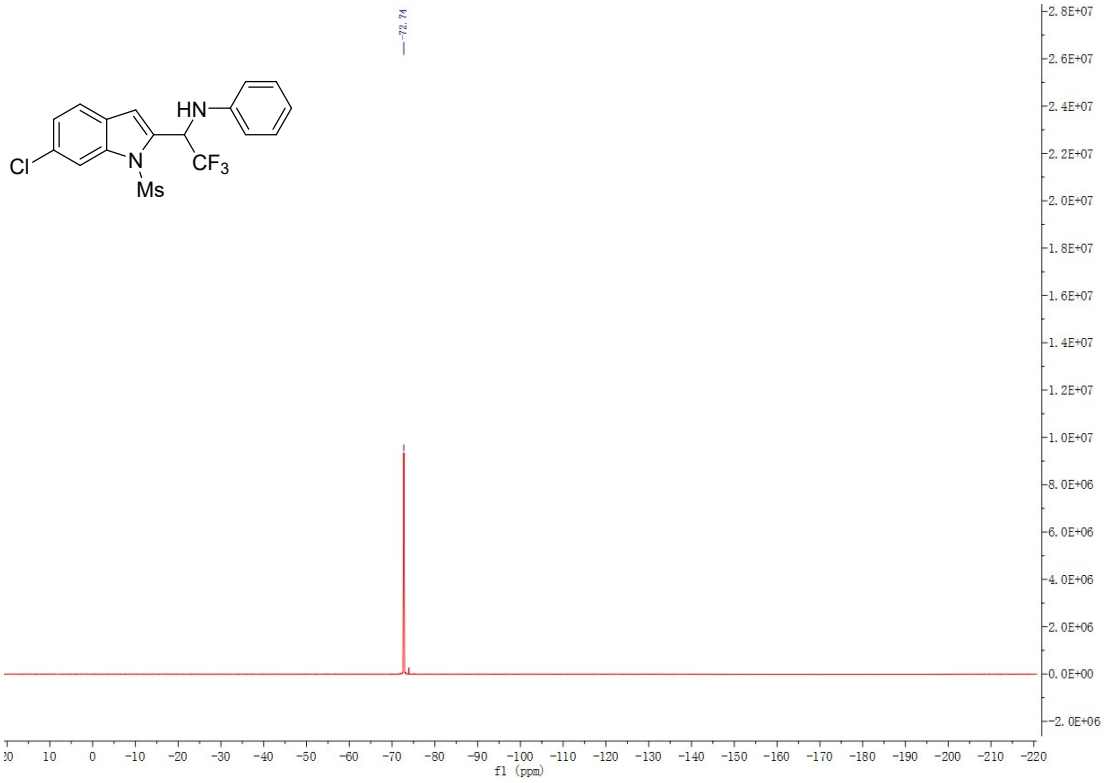


Figure S55 [1]HNMR spectra of compound **3s**

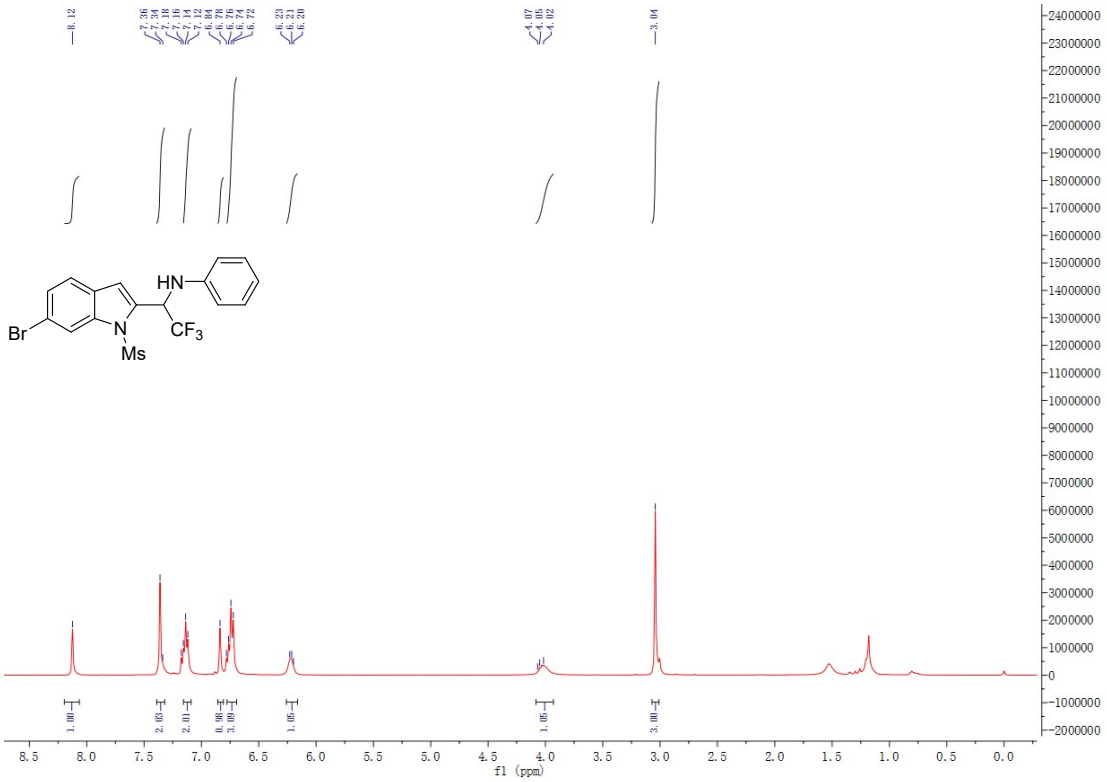


Figure S56 [13]CNMR spectra of compound **3s**

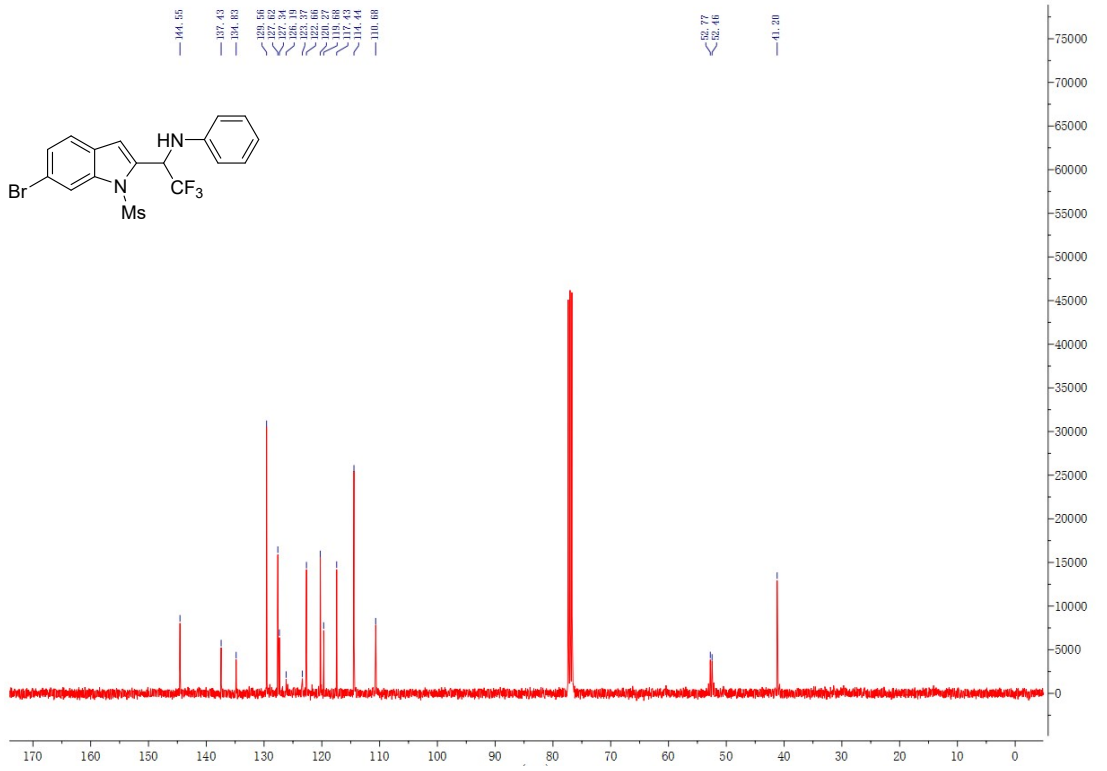


Figure S57 ^{19}FNMR spectra of compound **3s**

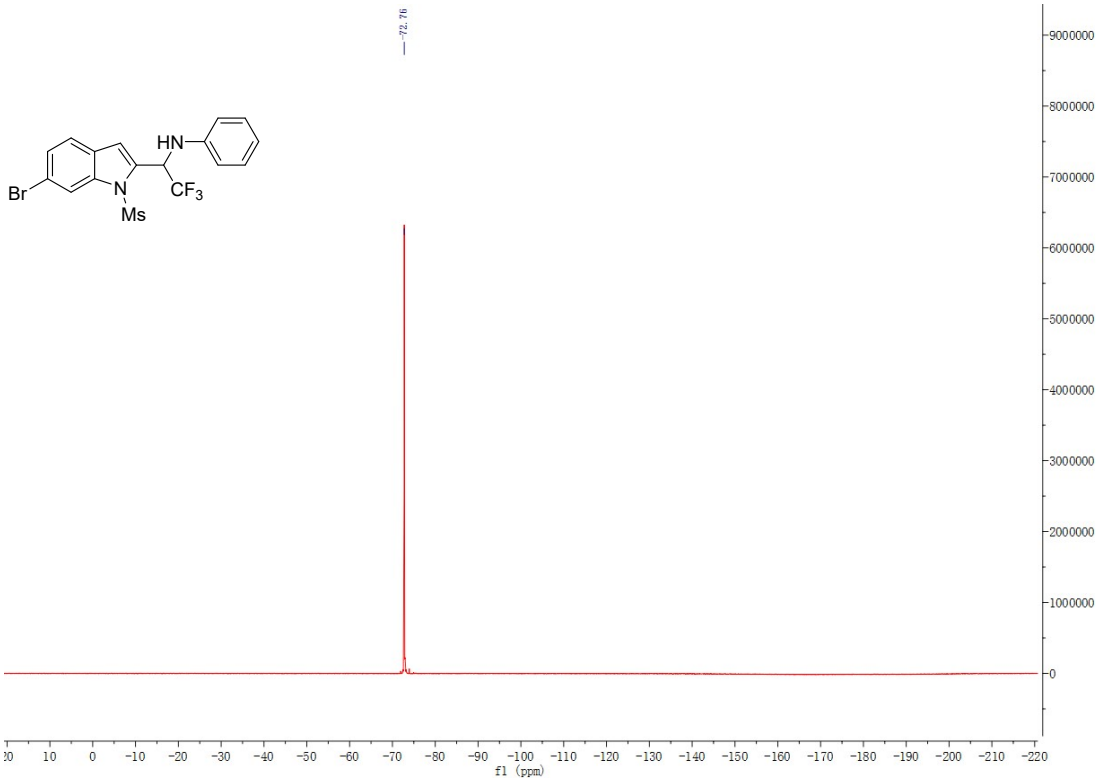


Figure S58 ^{1}HNMR spectra of compound **3t**

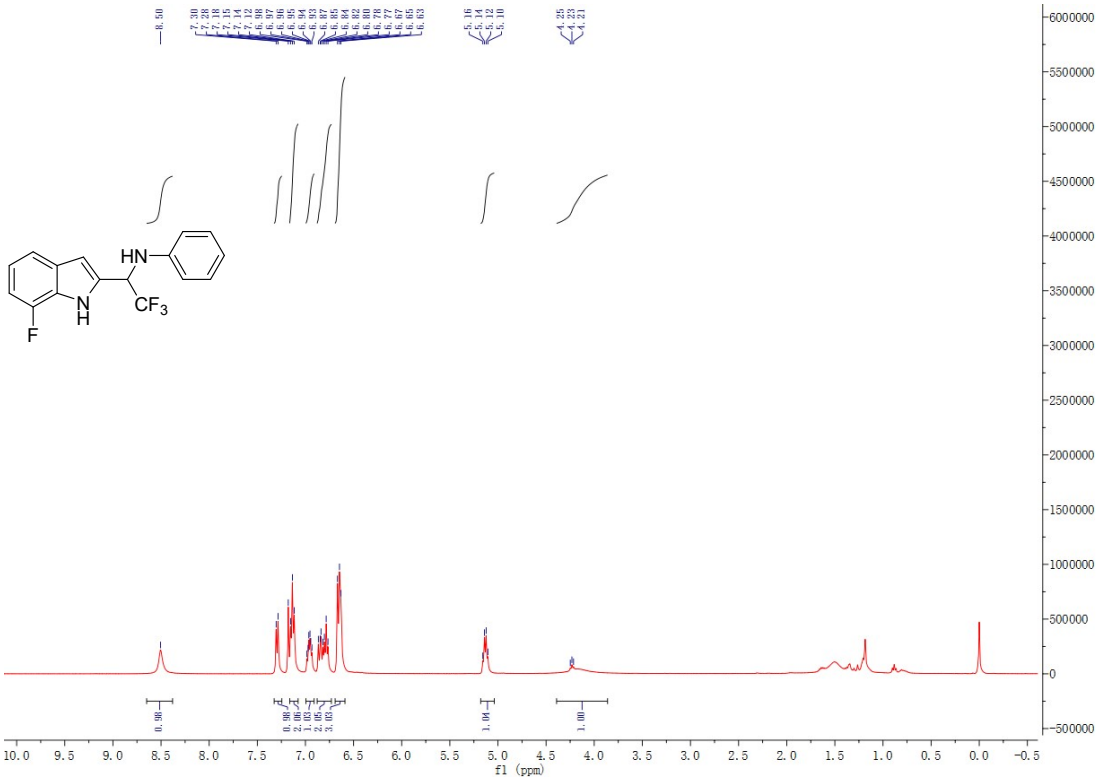


Figure S59 ^{13}CNMR spectra of compound **3t**

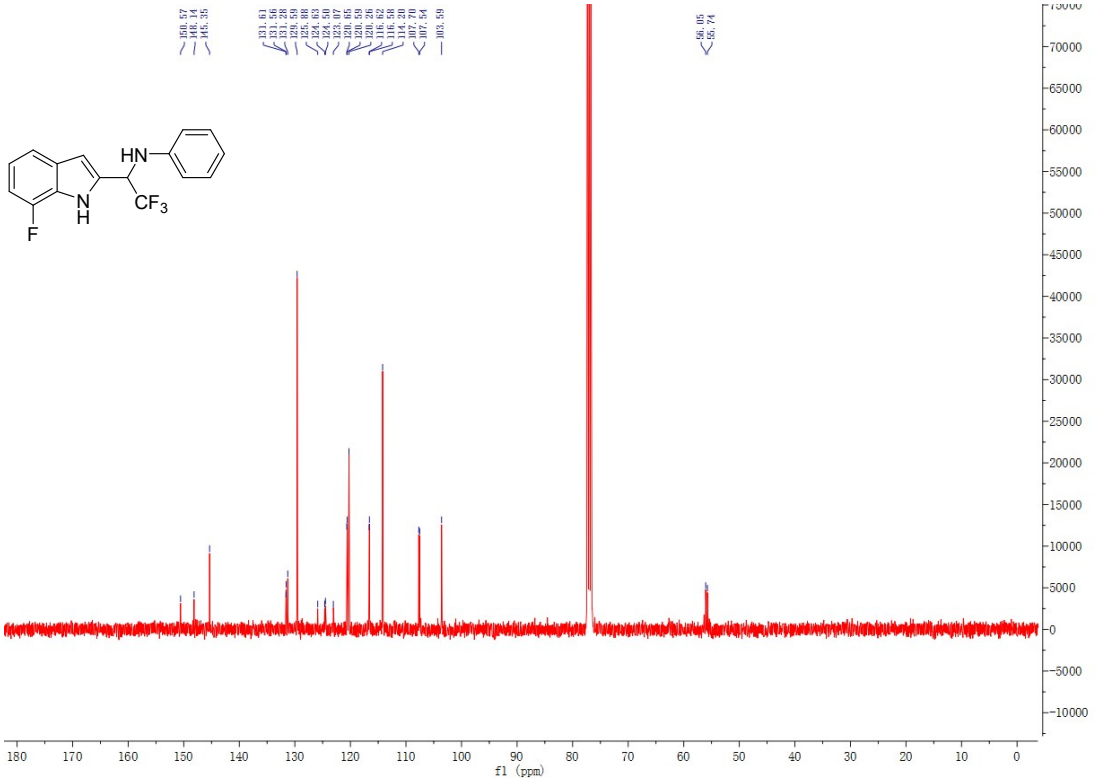


Figure S60 ^{19}FNMR spectra of compound **3t**

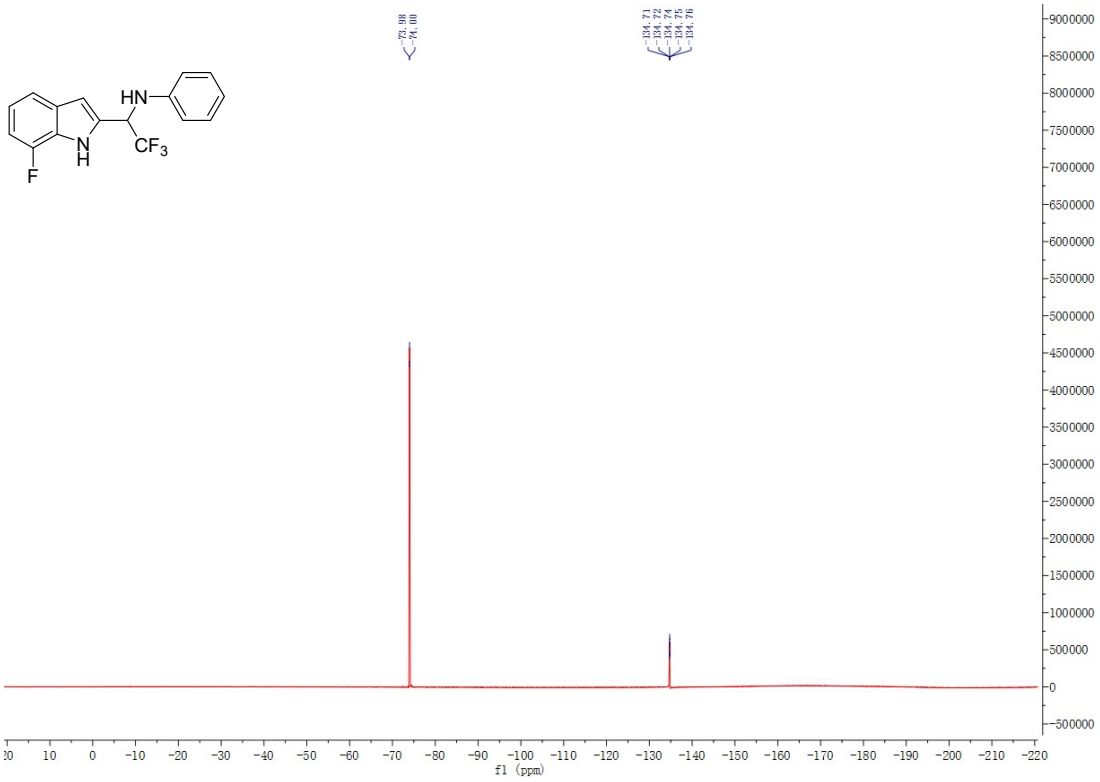


Figure S61 ^{1}HNMR spectra of compound **3u**

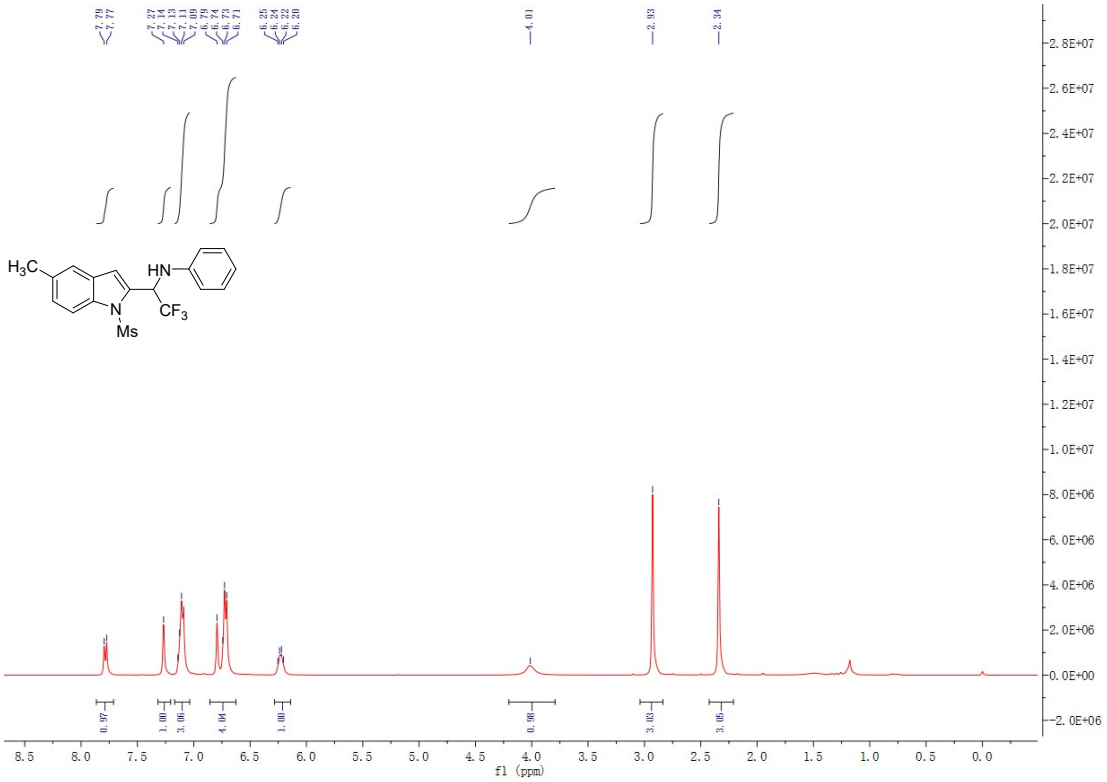
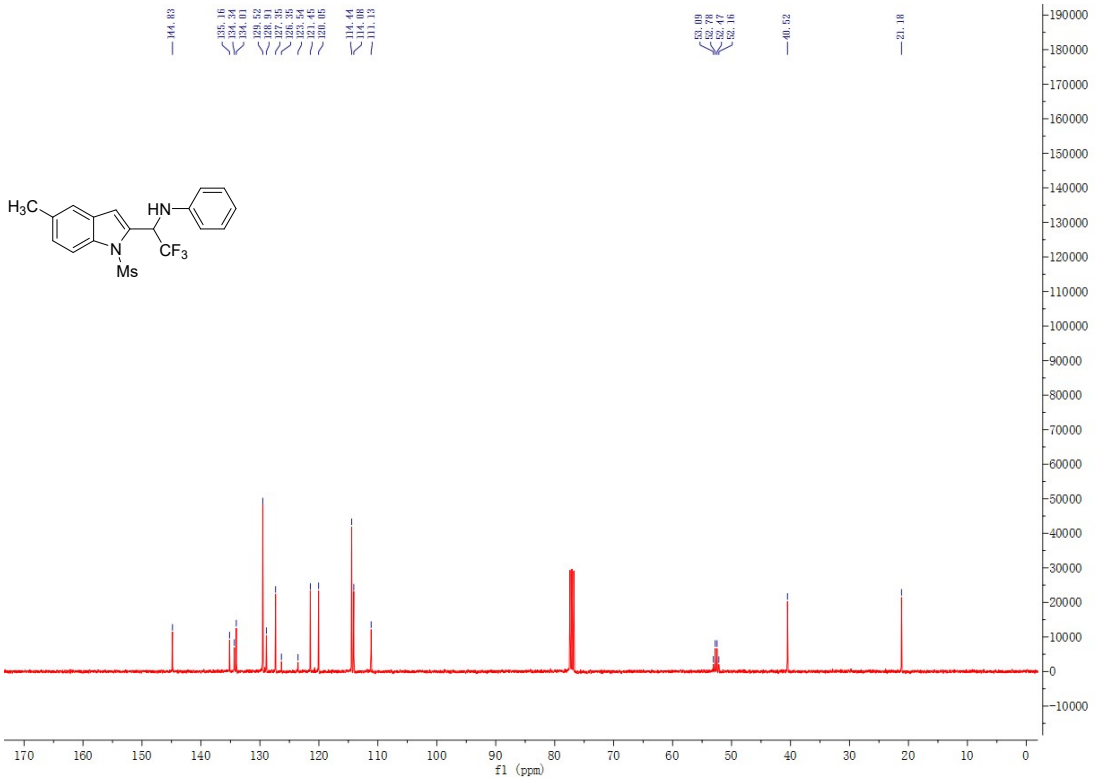


Figure S62 ^{13}CNMR spectra of compound **3u**



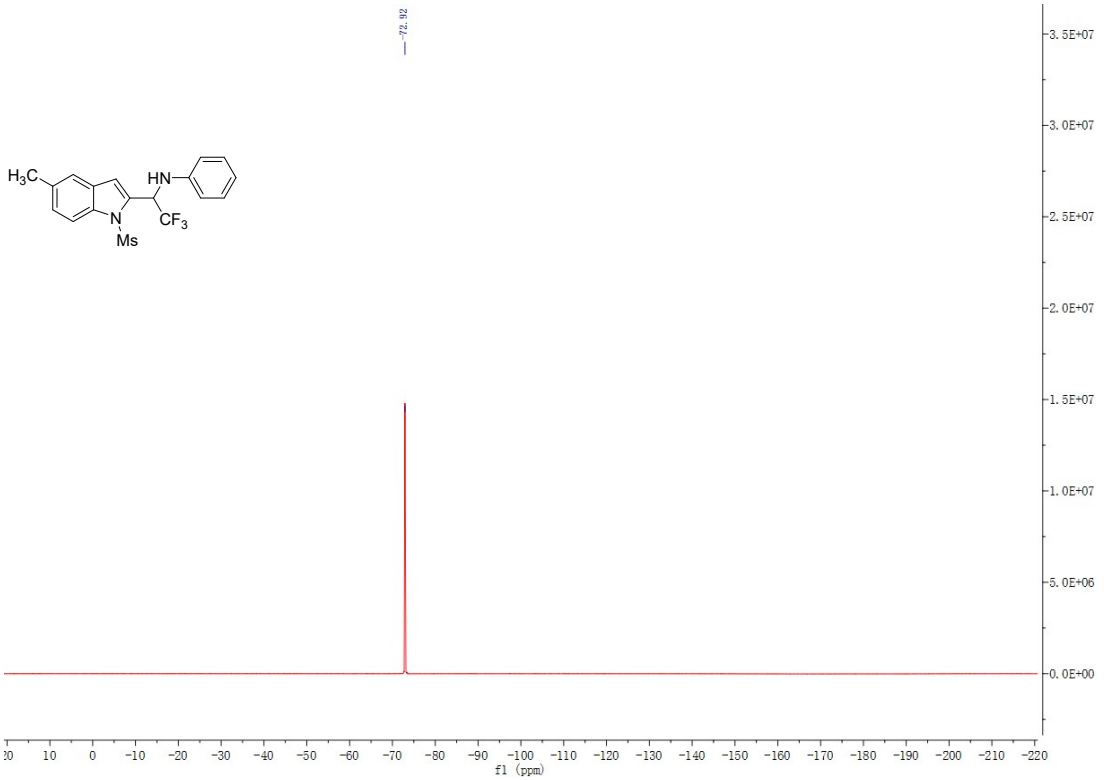


Figure S64 ^{1}HNMR spectra of compound **3v**

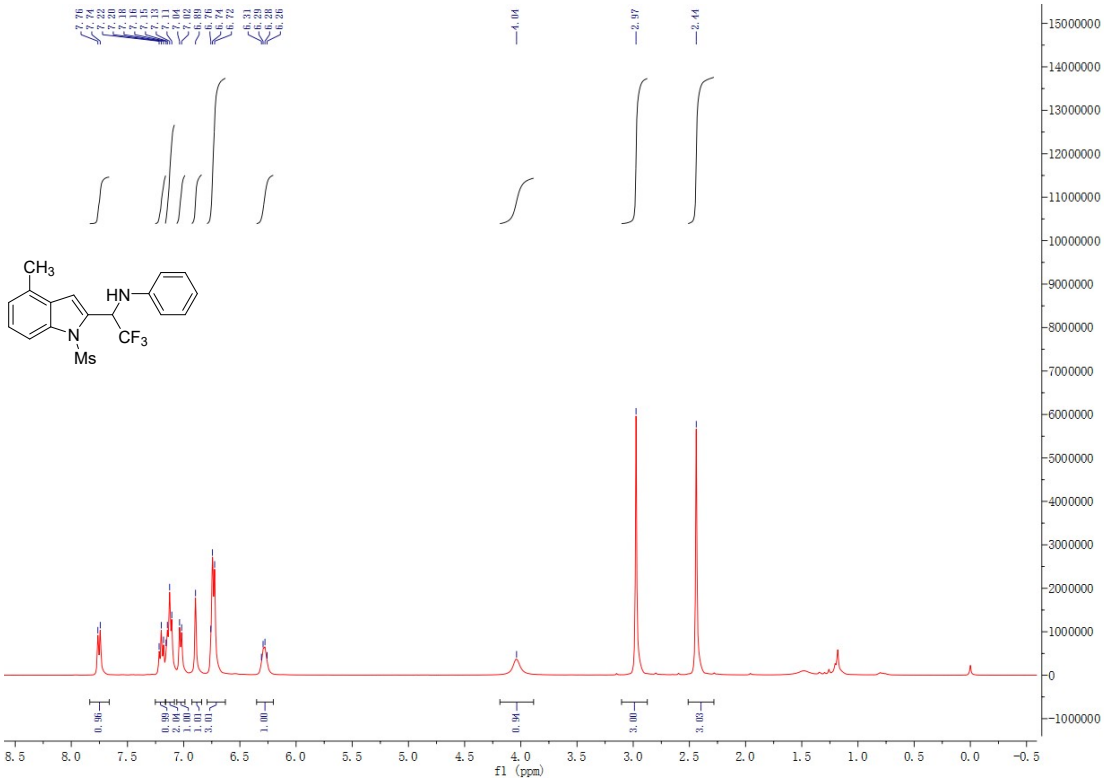


Figure S65 ^{13}CNMR spectra of compound **3v**

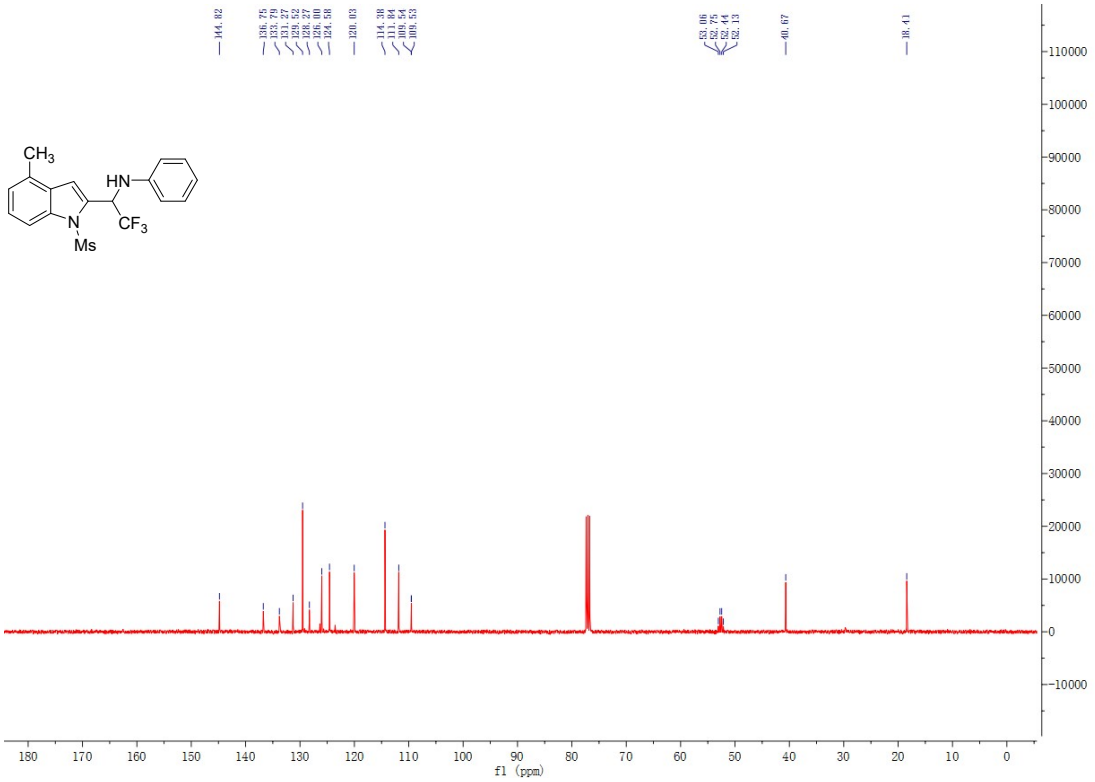


Figure S66 ^{19}FNMR spectra of compound **3v**

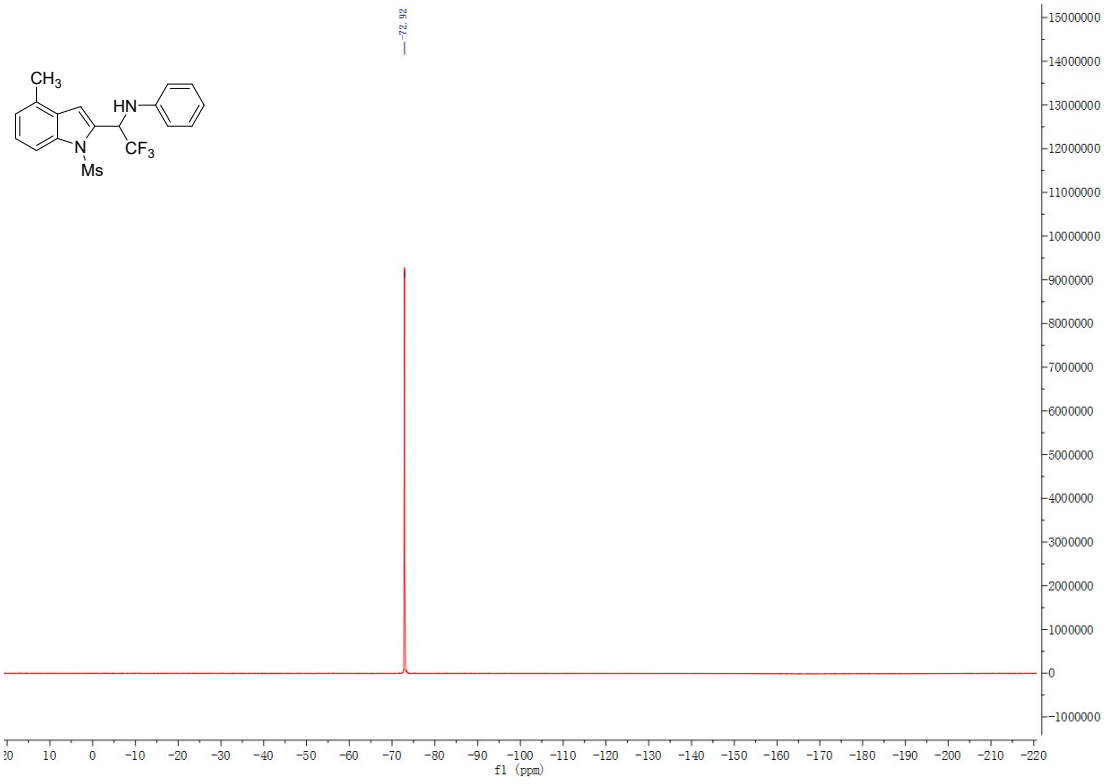


Figure S67 ^{1}HNMR spectra of compound **3x**

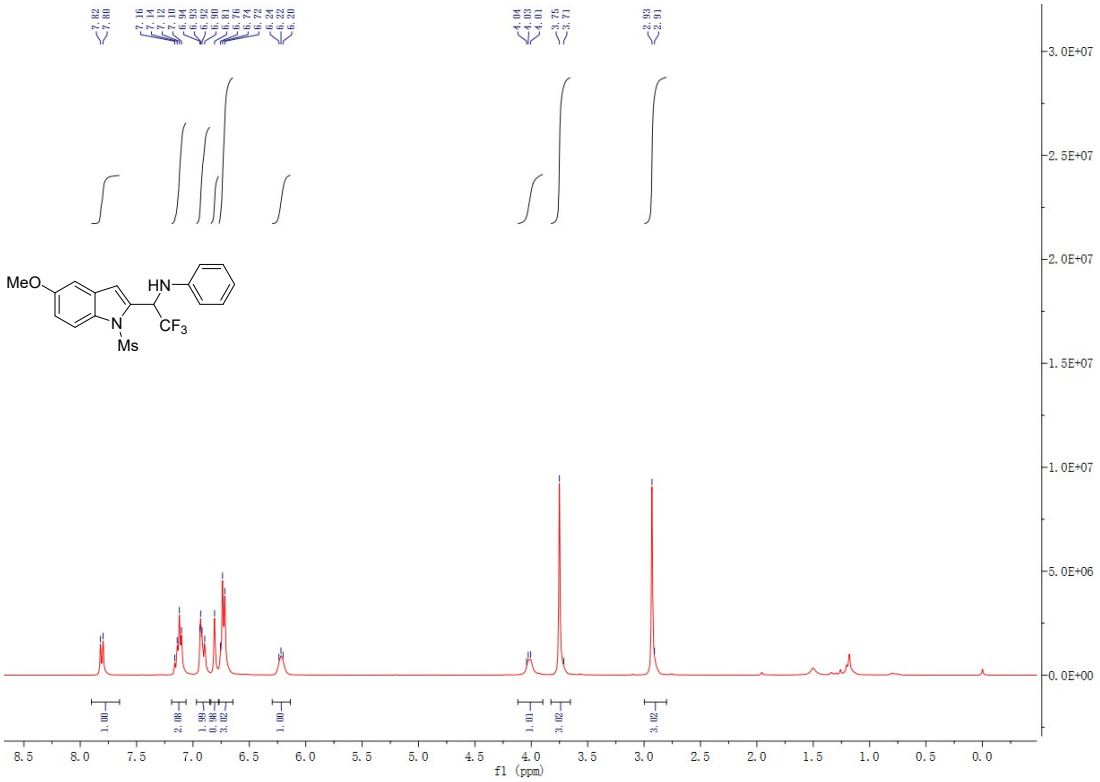


Figure S68 ^{13}CNMR spectra of compound **3x**

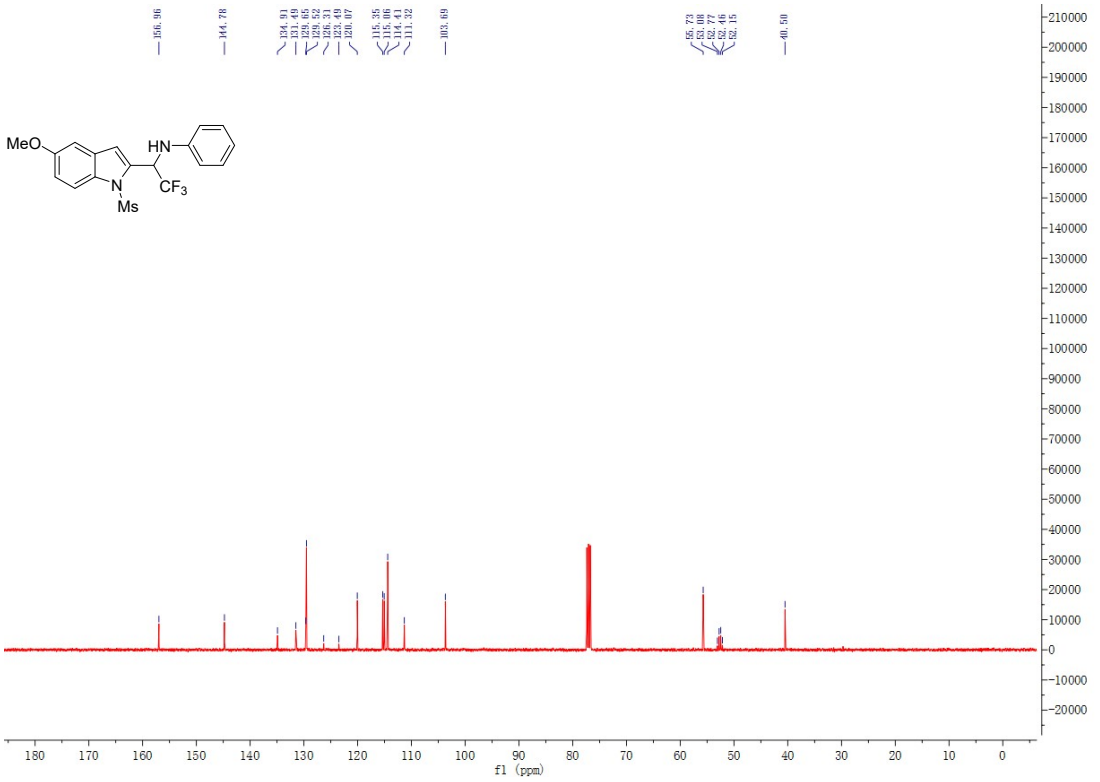


Figure S69 ^{19}FNMR spectra of compound **3x**

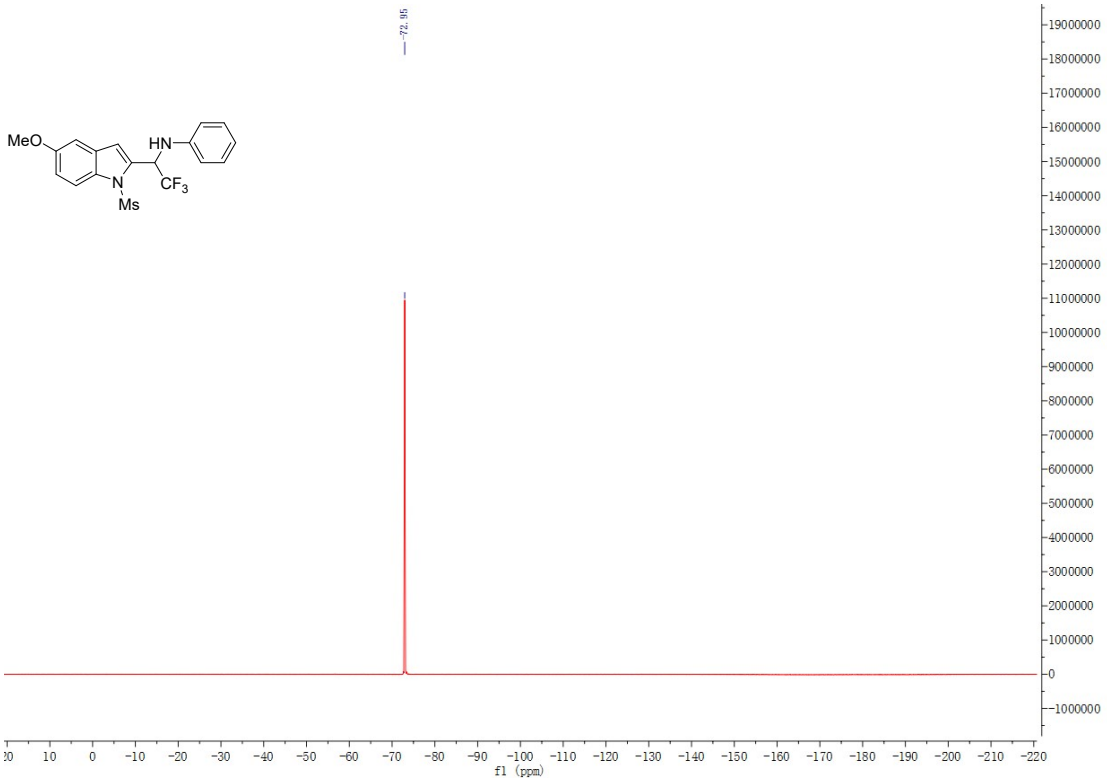


Figure S70 ^{1}HNMR spectra of compound **5**

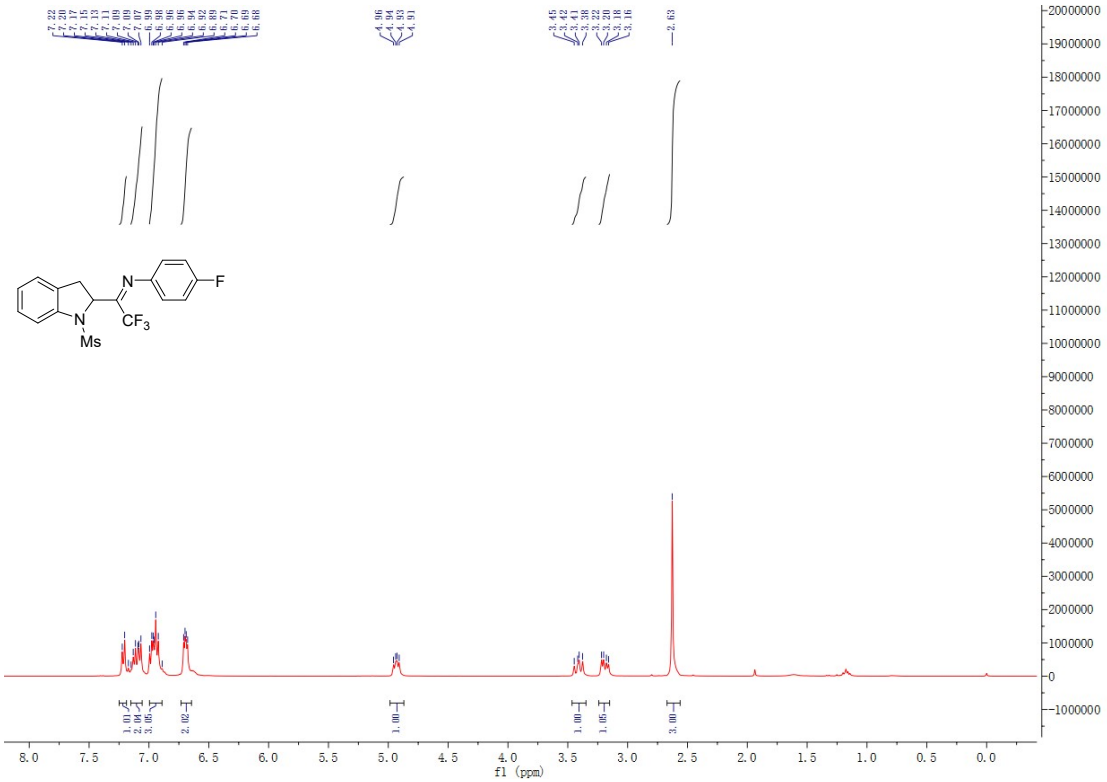


Figure S71 ^{13}CNMR spectra of compound **5**

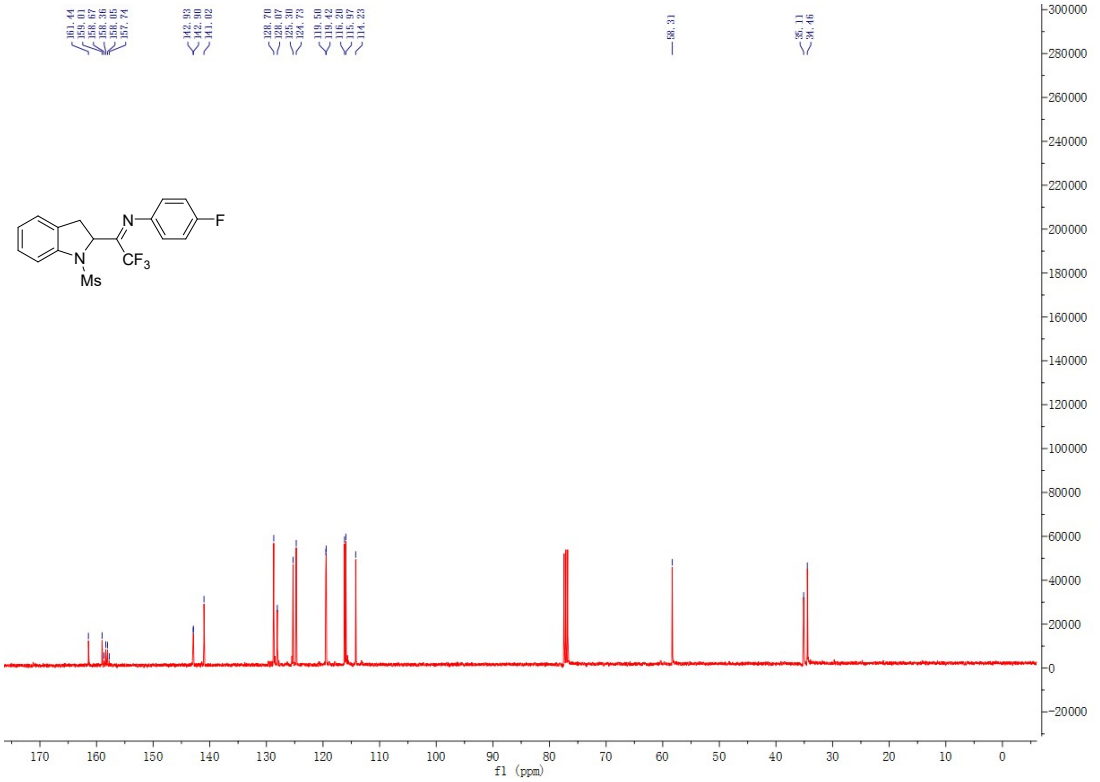


Figure S72 ^{19}FNMR spectra of compound **5**