Supporting Information

Photocatalytic Redox-Neutral Selective Single C(sp3)–F Bond Activation of Perfluoroalkyl Imines under Redox-Neutral Conditions

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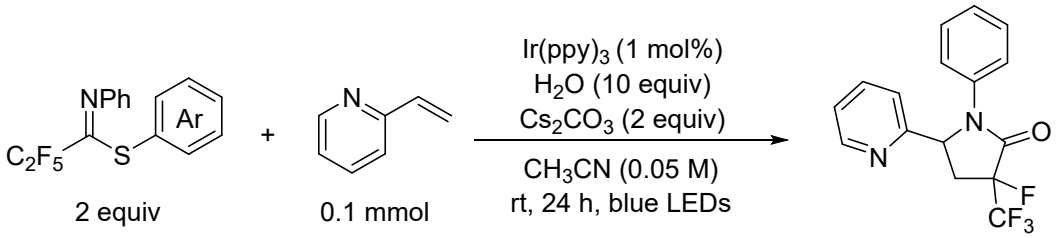
I. General Information

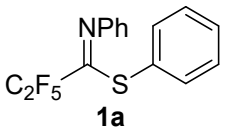
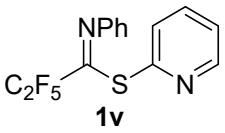
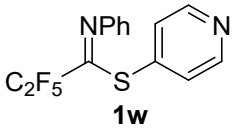
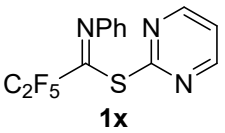
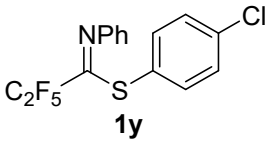
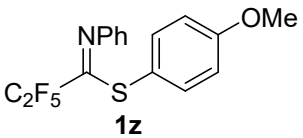
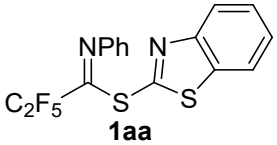
Unless otherwise stated, all reactions were set up in a clear Pyrex glass tube and were stirred with a Teflon-coated magnetic stir bar. Analytical grade solvents and commercially available reagents were used to conduct the reactions. All other reagents were purchased from TCI, Innochem, J&K, Adamas, and Energy chemicals, and were directly used without further purifications. TLC was performed on silica HSGF254 plates and visualized by quenching of UV fluorescence (λmax= 254 nm). Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. All reaction glassware was flame- or oven-dried before use. Reactions were monitored by thin-layer chromatography (TLC), and the products were obtained by column chromatography on silica gel.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Bruker AM-400 MHz spectrometer (400MHz, 101MHz and 376MHz). ^{1}H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and internally referenced to TMS (0.00 ppm) or the residual protic-solvent peak in $CDCl_3$ (7.26 ppm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.0 ppm). In reporting spectral data the format (δ) chemical shift (multiplicity, *J* values in Hz, integration) was used with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were measured on a TOF by ESI and performed on Bruker Daltonics APEXII 47e Specifications. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer. The melting point was measured by WRX® X-4B.

II. Detailed Reaction Optimizations

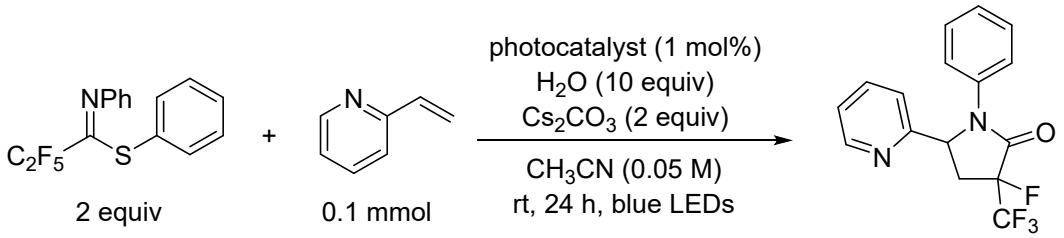
Table S1. Screening of substrates[a]



Substrate	Yield (%)[b]	dr[c]
 **1a**	83	12:1
 **1v**	72	11:1
 **1w**	71	12:1
 **1x**	68	10:1
 **1y**	62	11:1
 **1z**	62	12:1
 **1aa**	N.D.	

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), H_2O (1 mmol), $Ir(ppy)_3$ (0.001 mmol) in 2.0 mL of dry CH_3CN with 6 W blue LED irradiation at rt for 24 h, unless otherwise noted. [b] Isolated yield; N.D. = not detected. [c] Detected by ^{19}F NMR.

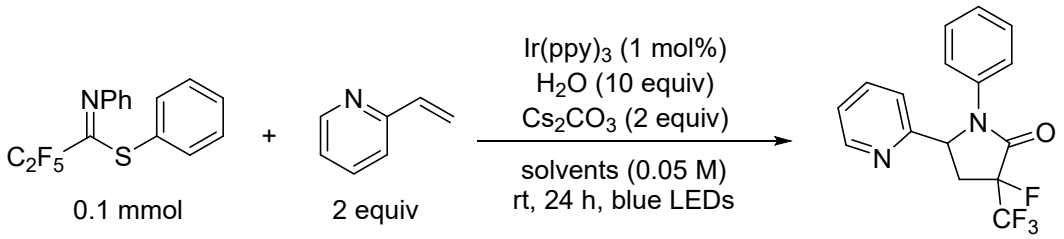
Table S2. Screening of catalyst screening and control experiments[a]



Entry	PC	Yield (%)[b]	dr[c]
1	$Ir(ppy)_3$	83	12:1
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	N.D	
3	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	N.D	
4	$[Ru(bpy)_3]Cl_2$	N.D	
5	$Ir(dFppy)_3$	68	16:1
6	$Ir(t\text{-}Buppy)_3$	65	8:1
7	Mes-$Acr^+ClO_4^-$	N.D.	
8	4-CzIPN	N.D	
9	Eosin-Y	N.D	
10	no catalyst	N.D	
11	no light	N.D	

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), H_2O (1 mmol) and photocatalyst (0.001 mmol) in 2.0 mL of dry CH_3CN with 6 W blue LED irradiation at rt for 24 h, unless otherwise noted. [b] Isolated yield; N.D. = not detected. [c] Detected by ^{19}F NMR.

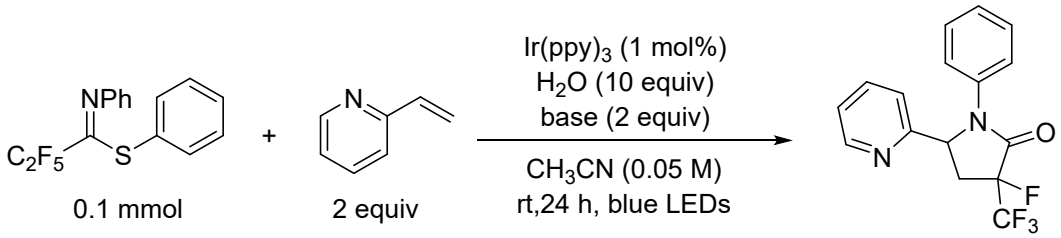
Table S3. Screening of solvents[a]



Entry	solvents	Yield (%)[b]	dr[c]
1	CH_3CN	72	12:1
2	AcOEt	N.D	
3	DMF	67	11:1
4	DMSO	45	5:1
5	TFE	N.D	
6	DCM	60	17:1
7	Acetone	69	10:1
8	Dioxane	N.D	
9	Toluene	N.D	
10	THF	N.D	

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), H_2O (1 mmol), $Ir(ppy)_3$ (0.001 mmol) in 2.0 mL of dry solvent with 6 W blue LED irradiation at rt for 24 h, unless otherwise noted. [b] Isolated yield; N.D. = not detected. [c] Detected by ^{19}F NMR.

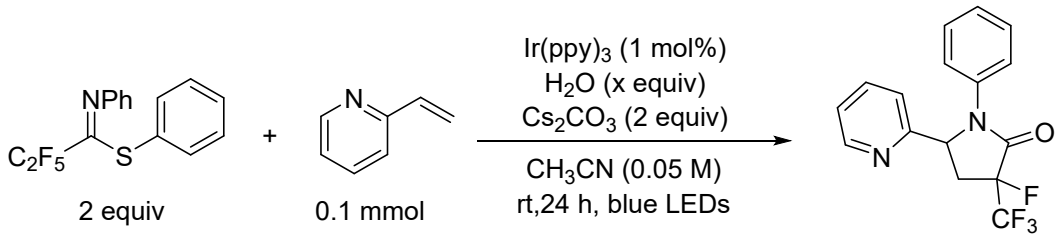
Table S4. Screening of bases[a]



Entry	bases	Yield (%)[b]	dr[c]
1	Cs_2CO_3	75	12:1
2	K_2HPO_4	65	11:1
3	Na_2CO_3	67	13:1
4	K_2CO_3	67	9:1
5	$NaHCO_3$	54	10:1
6	Li_2CO_3	60	11:1
7	Na_2HPO_4	63	10:1
8	NaOH	66	12:1
9	KOH	60	11:1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), bases (0.2 mmol), H_2O (1 mmol), $Ir(ppy)_3$ (0.001 mmol) in 2.0 mL of dry CH_3CN with 6 W blue LED irradiation at rt for 24 h, unless otherwise noted. [b] Isolated yield; N.D. = not detected. [c] Detected by ^{19}F NMR.

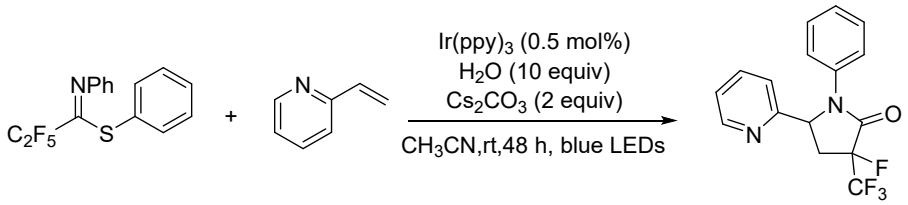
Table S5. Screening of water[a]



Entry	H_2O (equiv)	Yield (%)[b]	dr[c]
1	5	78	9:1
2	10	82	12:1
3	25	69	10:1
4	50	55	9:1
5	100	25	11:1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), H_2O (x equiv), $Ir(ppy)_3$ (0.001 mmol) in 2.0 mL of dry CH_3CN with 6 W blue LED irradiation at rt for 24 h, unless otherwise noted. [b] Isolated yield; N.D. = not detected. [c] Detected by ^{19}F NMR.

III. Gram-Scale Synthesis of 3a



1a, 8.0 mmol **2a**, 4.0 mmol **3a**, 0.93g, 72%

To a 100 mL round-bottom flask equipped with a magnetic stir-bar were added phenyl 2,2,3,3,3-pentafluoro-N-phenylpropanimidothioate **1a** (8.0 mmol, 2.0 equiv), 2-vinylpyridine **2a** (4.0 mmol, 1.0 equiv), cesium carbonate (8.0 mmol, 2.0 equiv), and $Ir(ppy)_3$ (0.02 mmol, 0.5 mol%). Then, acetonitrile (40.0 mL) and water (0.72 ml, 10 equiv) were added. The vessel was bubbled with a stream of argon for 20 min via a syringe needle, and the tightly sealed tube was irradiated with a 36 W blue LED at about 20 ℃ for 48 h. The solvent was removed under reduced pressure by a rotary evaporator. Then, the residue was purified by silica gel column chromatography to give the desired product **3a** with a 72% yield.

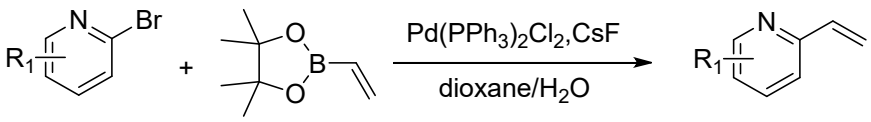
IV. General Synthetic Procedures

1. General Procedure for Single C(sp^3)-F Bond Cleavage

Polyfluorinated Iminosulfide **1** (0.2 mmol, 2.0 equiv), cesium carbonate (0.2 mmol, 2.0 equiv) and $Ir(ppy)_3$ (0.002 mmol, 1.4 mg, 2.0 mol%) were added into a 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar. Then anhydrous MeCN (2 ml, 0.05 M), distilled water (18 ul, 10 equiv) and the alkene (0.1 mmol, 1 equiv) were added sequentially by syringes. The vessel was bubbled with a stream of argon for 20 min via a syringe needle, and the tightly sealed tube was irradiated with 6 W blue LEDs at about 20 ℃. After 24 h, the solvent was removed, and the crude products were purified by column chromatography over silica gel as indicated.

2. Synthesis of Alkenylpyridines

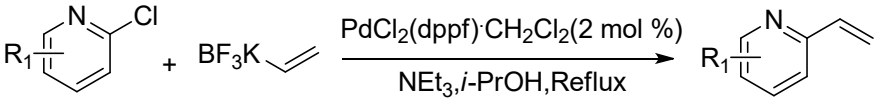
Procedure A:



Following the modified procedure of reported literature,[1] to a solution of bromo-substituted azaarene (10.0 mmol, 1.0 equiv.), CsF (4.6 g, 30.0 mmol) and pinacol vinylboronate (2.3 g, 15.0

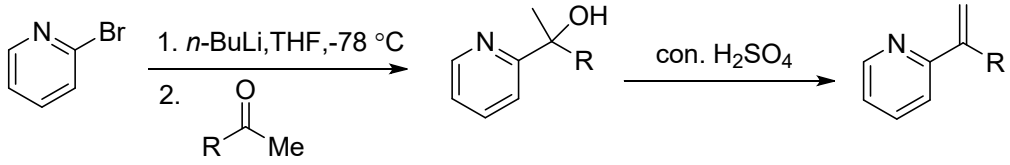
mmol) in dioxane/H_2O (20 mL/10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.7 g, 1.0 mmol). After stirring for 16 h at 80 °C under Ar, the mixture was concentrated in vacuo. The crude product was further purified by column chromatography (petroleum ether/ethyl acetate = 40/1 - 10/1) on silica gel to yield the corresponding alkenylpyridines.

Procedure B:



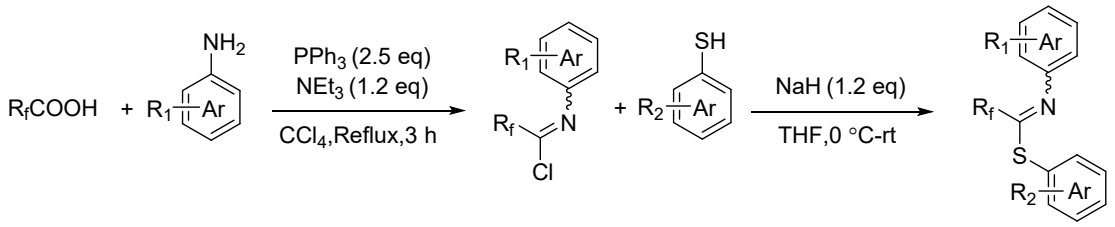
Following the modified procedure of reported literature,[2] a solution of chloro-substituted azaarene (8.0 mmol, 1.0 equiv.), potassium vinyltrifluoroborate (1.29 g, 9.6 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (131 mg, 0.16 mmol), and Et_3N (1.12 mL, 8.0 mmol) in iPrOH (125 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature and partitioned between CH_2Cl_2 (100 mL) and H_2O (40 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried (MgSO4), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (petroleum ether/ethyl acetate = 40/1 - 10/1) gave the vinylpyridines.

Procedure C:



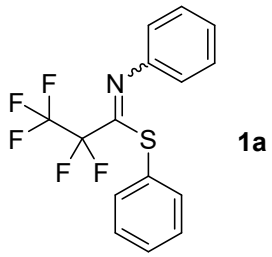
Following the modified procedure of reported literature,[3] a solution of 2-bromopyridine (2.37 g, 1.43 mL, 15.0 mmol, 1.0 equiv.) in THF (19 mL, 0.8 M) was cooled to -78 °C. n-Butyllithium (15.8 mmol, 1.1 equiv.) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, the corresponding ketone (15.0 mmol, 1.0 equiv.) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. NH_4Cl (aq) (20 mL) and EtOAc (20 mL) was added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried (MgSO4), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes/ EtOAc (9:1 to 4:2 (v/v)), to afford the title compound pyridine alcohol. Concentrated H_2SO_4 (5 mL) was added to the above alcohol and stirred at 100 °C for 1 h. Crashed ice was added and neutralized with NaOH solution to PH = 7 - 8. The reaction mixture was extracted with ethyl ether (20 mL×3) then washed with brine and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and purified by silica gel column chromatography to afford the pure products.

3. Synthesis of Perfluoroalkyl Group Substituted Iminosulfides



A 200 mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with PPh_3 (34.5 g, 132 mmol), Et_3N (7.3 mL, 53 mmol), CCl_4 (21.1 mL, 220 mmol), and TFA (3.4 mL, 44 mmol). After the solution was stirred for about 10 min (ice bath), an amine (53 mmol) dissolved in CCl_4 (21.1 mL, 220 mmol) was added. The mixture was then refluxed with stirring (3 h). After the reaction was completed, residual solid Ph3PO, PPh3, and Et_3N-HCl were washed with hexane several times. Then the hexane was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding fluorinated imidoyl chlorides.

To a solution of thiophenol (2.37 g, 1.43 mL, 15.0 mmol, 1.0 equiv.) in THF (19 mL, 0.8 M) was cooled to 0 °C. Sodium hydride (15.8 mmol, 1.1 equiv.) was then slowly added and the reaction mixture was stirred at 0 °C for 10 min. After that time, the corresponding fluorinated imidoyl chlorides (15.0 mmol, 1.0 equiv.) was added to the above solution, and the reaction mixture was stirred for 3 h at room temperature, diluted with diethyl ether (60 mL), and washed with aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the corresponding product.



1a

Chemical Formula: $C_{15}H_{10}F_5NS$

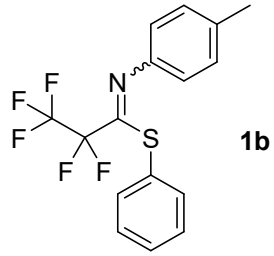
phenyl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.30 – 7.25 (m, 2H), 7.24 – 7.12 (m, 5H), 7.07 – 7.00 (m, 1H), 6.81 – 6.74 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 151.7 (t, *J* = 29.6 Hz), 146.3, 134.7, 129.3, 129.0, 128.7, 126.9, 125.5, 119.0, 118.4 (qt, *J* = 287.2, 35.7 Hz), 110.2 (tq, *J* = 259.6, 36.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.70 (s, 3F), -111.18 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}F_5NS$ 332.0527; Found 332.0526.



1b

Chemical Formula: $C_{16}H_{12}F_5NS$

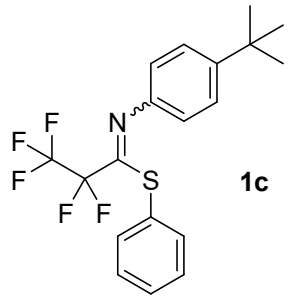
phenyl 2,2,3,3,3-pentafluoro-*N*-(p-tolyl)propanimidothioate (1b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.31 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.14 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 150.9 (t, *J* = 29.6 Hz), 143.8, 135.5, 134.6, 129.2, 129.1, 128.9, 127.2, 119.4, 118.4 (qt, *J* = 287.4, 35.8 Hz), 110.3 (tq, *J* = 259.7, 36.3 Hz), 20.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.67 (s, 3F), -110.62 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}F_5NS$ 346.0683; Found 346.0682.



1c

Chemical Formula: $C_{19}H_{18}F_5NS$

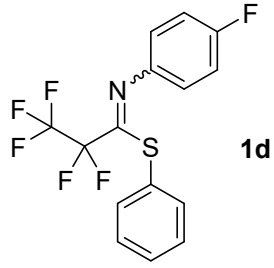
phenyl *N*-(4-(tert-butyl)phenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1c)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 3H), 7.15 – 7.09 (m, 2H), 6.76 – 6.70 (m, 2H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 150.5 (t, *J* = 29.8 Hz), 148.7, 143.5, 134.5, 129.1, 128.9, 127.2, 125.4, 119.1, 118.5 (qt, *J* = 287.3, 36.3 Hz), 110.2 (tq, *J* = 259.6, 36.4 Hz), 34.4, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.70 (s, 3F), -111.29 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}F_5NS$ 388.1153; Found 388.1151.



1d

Chemical Formula: $C_{15}H_9F_6NS$

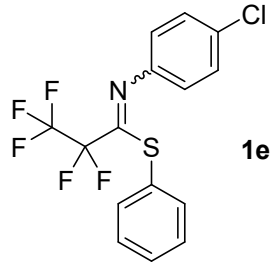
phenyl 2,2,3,3,3-pentafluoro-*N*-(4-fluorophenyl)propanimidothioate (1d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.21 (m, 3H), 7.19 – 7.11 (m, 2H), 6.89 – 6.82 (m, 2H), 6.80 – 6.72 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 160.5 (d, *J* = 245.4 Hz), 152.0 (t, *J* = 29.5 Hz), 142.2 (d, *J* = 3.1 Hz), 134.4, 129.4, 129.1, 126.8, 121.0 (d, *J* = 8.3 Hz), 118.4 (qt, *J* = 287.3, 35.7 Hz), 115.5 (d, *J* = 22.8 Hz), 110.4 (tq, *J* = 259.6, 36.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.74 (s, 3F), -111.57 (s, 2F), -117.11 (s, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}F_6NS$ 350.0433; Found 350.0432.



Chemical Formula: $C_{15}H_9ClF_5NS$

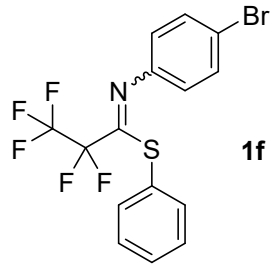
phenyl *N*-(4-chlorophenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1e)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.21 (m, 3H), 7.19 – 7.09 (m, 4H), 6.70 – 6.66 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 152.8 (t, *J* = 29.2 Hz), 144.7, 134.7, 130.9, 129.5, 129.1, 128.7, 127.5, 120.4, 118.4 (qt, *J* = 287.4, 35.8 Hz), 110.0 (tq, *J* = 259.9, 36.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.75 (s, 3F), -111.73 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}ClF_5NS$ 366.0137; Found 366.0136.



Chemical Formula: $C_{15}H_9BrF_5NS$

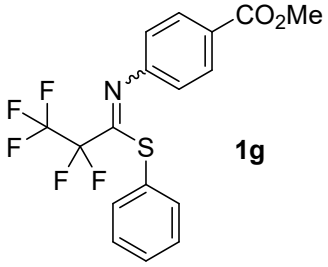
phenyl *N*-(4-bromophenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1f)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.28 – 7.20 (m, 5H), 7.19 – 7.13 (m, 2H), 6.64 – 6.59 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 152.9 (t, *J* = 29.3 Hz), 145.2, 134.8, 131.7, 129.5, 129.1, 127.5, 120.7, 118.6, 118.3 (qt, *J* = 287.4, 35.7 Hz), 110.0 (tq, *J* = 260.0, 36.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.7 (s, 3F), -111.8 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}BrF_5NS$ 409.9632; Found 409.9631.



Chemical Formula: $C_{17}H_{12}F_5NO_2S$

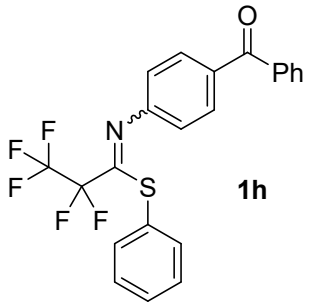
methyl 4-((2,2,3,3,3-pentafluoro-1-(phenylthio)propylidene)amino)benzoate (1g)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.86 – 7.79 (m, 2H), 7.25 – 7.20 (m, 3H), 7.16 – 7.08 (m, 2H), 6.78 – 6.71 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 166.4, 153.4 (t, *J* = 29.3 Hz), 150.2, 135.0, 130.3, 129.7, 129.1, 126.6, 126.2, 118.4, 118.3 (qt, *J* = 287.6, 35.7 Hz), 109.9 (tq, *J* = 261.1, 37.0 Hz), 52.04.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.83 (s, 3F), -112.09 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_5NO_2S$ 390.0582; Found 390.0581.



1h

Chemical Formula: $C_{22}H_{14}F_5NOS$

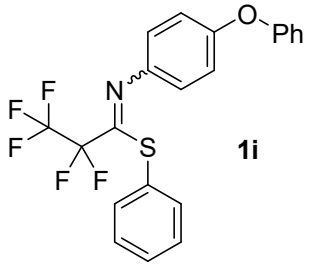
phenyl *N*-(4-benzoylphenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1h)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.75 – 7.69 (m, 2H), 7.64 – 7.55 (m, 3H), 7.52 – 7.44 (m, 2H), 7.29 – 7.21 (m, 3H), 7.19 – 7.11 (m, 2H), 6.81 – 6.75 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 195.4, 153.2 (t, *J* = 29.1 Hz), 149.7, 137.6, 134.9, 134.1, 132.3, 131.0, 129.8, 129.6, 129.2, 128.3, 126.3, 118.3, 118.3 (qt, *J* = 287.7, 35.7 Hz), 109.9 (tq, *J* = 261.2, 37.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.80 (s, 3F), -112.24 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{15}F_5NOS$ 436.0789; Found 436.0785.



1i

Chemical Formula: $C_{21}H_{14}F_5NOS$

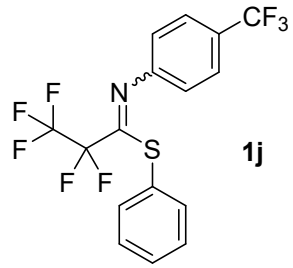
phenyl 2,2,3,3,3-pentafluoro-*N*-(4-phenoxyphenyl)propanimidothioate (1i)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.37 – 7.30 (m, 2H), 7.29 – 7.16 (m, 5H), 7.10 (td, *J* = 7.5, 1.1 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.87 – 6.79 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 157.2, 155.0, 150.5 (t, *J* = 29.3 Hz), 141.3, 134.2, 129.7, 129.1, 129.1, 127.2, 123.3, 121.3, 119.1, 118.6, 118.5 (qt, *J* = 287.4, 35.9 Hz), 110.2 (tq, *J* = 259.5, 36.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.65 (s, 3F), -111.41 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}F_5NOS$ 424.0789; Found 424.0788.



1j

Chemical Formula: $C_{16}H_9F_8NS$

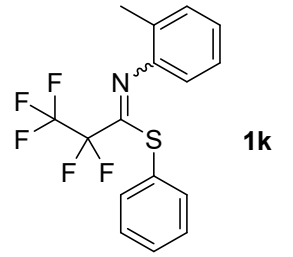
phenyl 2,2,3,3,3-pentafluoro-*N*-(4-(trifluoromethyl)phenyl)propanimidothioate (1j)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.14 – 7.07 (m, 2H), 6.73 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 153.9 (t, *J* = 29.2 Hz), 149.1, 135.0, 129.7, 129.2, 127.0 (q, *J* = 32.6 Hz), 126.2, 125.8 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 271.7 Hz), 118.7, 118.4 (qt, *J* = 287.3, 35.6 Hz), 109.9 (tq, *J* = 260.2, 37.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -62.39 (s, 3F), -80.87 (s, 3F), -112.57 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}F_8NS$ 400.0401; Found 400.0399.



1k

Chemical Formula: $C_{16}H_{12}F_5NS$

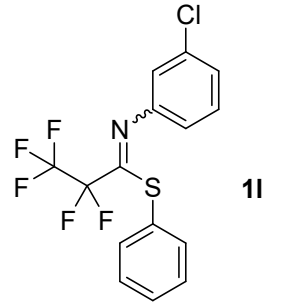
phenyl 2,2,3,3,3-pentafluoro-*N*-(o-tolyl)propanimidothioate (1k)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.27 – 7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 7.06 – 7.02 (m, 1H), 6.98 – 6.91 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 151.3 (t, *J* = 29.4 Hz), 145.1, 134.7, 130.2, 129.4, 128.9, 127.8, 126.7, 126.0, 125.7, 117.1, 118.5 (qt, *J* = 287.3, 35.3 Hz), 110.0 (tq, *J* = 259.6, 36.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.7 (s, 3F), -111.5 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}F_5NS$ 346.0683; Found 346.0684.



1l

Chemical Formula: $C_{15}H_9ClF_5NS$

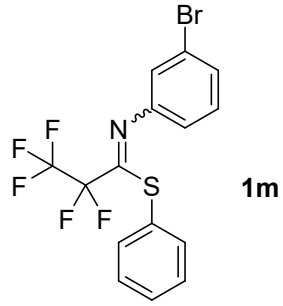
phenyl *N*-(3-chlorophenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1l)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.94 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.61 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 153.3 (t, *J* = 29.0 Hz), 147.1, 134.8, 134.4, 129.7, 129.6, 129.1, 126.2, 125.2, 119.0, 118.4 (qt, *J* = 287.3, 35.6 Hz), 117.1, 110.0 (tq, *J* = 260.0, 36.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.80 (s, 3F), -112.11 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}ClF_5NS$ 366.0137; Found 366.0136.



1m

Chemical Formula: $C_{15}H_9BrF_5NS$

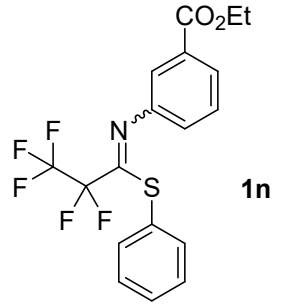
phenyl *N*-(3-bromophenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1m)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.23 (dtd, *J* = 6.9, 3.2, 1.2 Hz, 3H), 7.18 – 7.13 (m, 2H), 7.09 (ddd, *J* = 8.0, 1.9, 1.1 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.83 (t, *J* = 1.9 Hz, 1H), 6.66 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 153.3 (t, *J* = 29.2 Hz), 147.1, 134.8, 130.0, 129.6, 129.1, 128.0, 126.1, 122.4, 121.8, 118.3 (qt, *J* = 287.4, 35.7 Hz), 117.5, 110.4 (tq, *J* = 260.0, 36.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.80 (s, 3F), -112.21 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}BrF_5NS$ 409.9632; Found 409.9633.



1n

Chemical Formula: $C_{18}H_{14}F_5NO_2S$

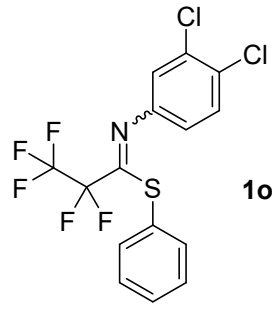
ethyl 3-((2,2,3,3,3-pentafluoro-1-(phenylthio)propylidene)amino)benzoate (1n)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.68 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.20 – 7.09 (m, 3H), 6.93 (ddd, *J* = 7.9, 2.2, 1.1 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 165.8, 153.0 (t, *J* = 29.3 Hz), 146.1, 134.7, 131.0, 129.4, 129.1, 128.7, 126.4, 126.3, 123.2, 112.0, 118.5 (qt, *J* = 288.6, 35.4 Hz), 110.4 (tq, *J* = 260.3, 36.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.74 (s, 3F), -111.91 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_5NO_2S$ 404.0738; Found 404.0735.



1o

Chemical Formula: $C_{15}H_8Cl_2F_5NS$

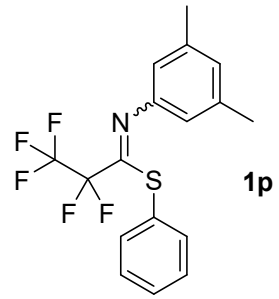
phenyl *N*-(3,4-dichlorophenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1o)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.29 – 7.14 (m, 6H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.5, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 154.1 (t, *J* = 29.0 Hz), 145.2, 134.8, 132.5, 130.2, 129.7, 129.2, 128.7, 126.0, 120.8, 118.5, 118.3 (qt, *J* = 287.5, 35.6 Hz), 109.8 (tq, *J* = 261.2, 37.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.85 (s, 3F), -112.48 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_9Cl_2F_5NS$ 399.9747; Found 399.9745.



1p

Chemical Formula: $C_{17}H_{14}F_5NS$

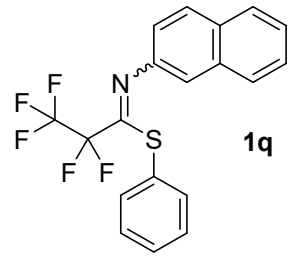
phenyl *N*-(3,5-dimethylphenyl)-2,2,3,3,3-pentafluoropropanimidothioate (1p)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.29 – 7.24 (m, 2H), 7.22 – 7.12 (m, 3H), 6.64 (s, 1H), 6.37 (s, 2H), 2.20 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 150.9 (t, *J* = 29.6 Hz), 146.2, 138.4, 134.7, 129.1, 128.8, 127.1, 127.0, 118.5 (qt, *J* = 287.4, 35.9 Hz), 116.6, 110.2 (tq, *J* = 259.7, 36.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.71 (s, 3F), -111.14 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_5NS$ 360.0840; Found 360.0837.



1q

Chemical Formula: $C_{19}H_{12}F_5NS$

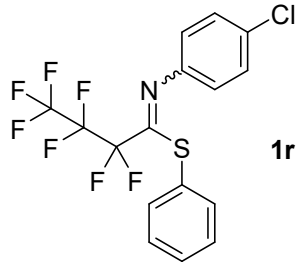
phenyl 2,2,3,3,3-pentafluoro-*N*-(naphthalen-2-yl)propanimidothioate (1q)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.75 – 7.61 (m, 3H), 7.47 – 7.36 (m, 2H), 7.25 – 7.19 (m, 2H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.09 – 6.94 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 152.0 (t, *J* = 29.5 Hz), 143.8, 134.7, 133.2, 131.3, 129.2, 128.8, 128.7, 127.7, 127.6, 126.7, 126.5, 125.5, 119.2, 118.5 (qt, *J* = 287.3, 35.7 Hz), 116.0, 110.2 (tq, *J* = 259.8, 36.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.64 (s, 3F), -111.14 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}F_5NS$ 382.0683; Found 382.0682.



1r

Chemical Formula: $C_{16}H_9ClF_7NS$

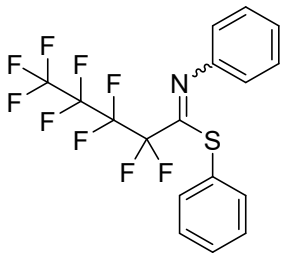
phenyl *N*-(4-chlorophenyl)-2,2,3,3,4,4,4-heptafluorobutanimidothioate (1r)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.24 – 7.19 (m, 1H), 7.18 – 7.09 (m, 4H), 7.08 – 7.01 (m, 2H), 6.66 – 6.58 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 152.4 (t, *J* = 27.7 Hz), 144.6, 134.3, 130.7, 129.3, 129.1, 128.6, 126.7, 120.2. carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.87 (t, *J* = 9.3 Hz, 3F), -109.77 (q, *J* = 9.4 Hz, 2F), -123.50 – -124.37 (m, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}ClF_7NS$ 416.0105; Found 416.0104.



1s

Chemical Formula: $C_{17}H_{10}F_9NS$

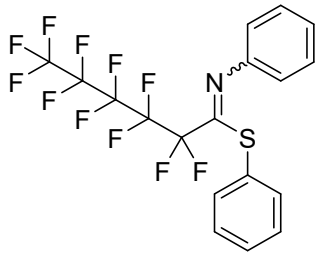
phenyl 2,2,3,3,4,4,5,5,5-nonafluoro-*N*-phenylpentanimidothioate (1s)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.21 – 7.07 (m, 7H), 7.01 – 6.95 (m, 1H), 6.75 – 6.69 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 151.4 (t, *J* = 28.0 Hz), 146.1, 134.3, 129.1, 129.0, 128.6, 127.1, 125.4, 118.9. carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.94 (t, *J* = 9.8 Hz, 3F), -108.53 (t, *J* = 12.8 Hz, 2F), -120.66 (dddt, *J* = 13.3, 9.9, 6.5, 3.5 Hz, 2F), -124.77 (tt, *J* = 12.9, 4.1 Hz, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}F_9NS$ 432.0463; Found 432.0460.



1t

Chemical Formula: $C_{18}H_{10}F_{11}NS$

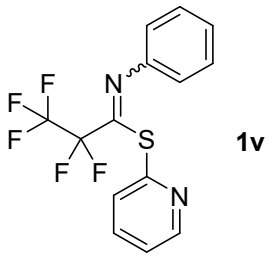
phenyl 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-*N*-phenylhexanimidothioate (1t)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.20 – 7.05 (m, 7H), 7.00 – 6.94 (m, 1H), 6.71 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 151.4 (t, *J* = 27.9 Hz), 146.2, 134.2, 129.1, 129.0, 128.6, 127.1, 125.3, 118.9. carbons corresponding to the C_5F_{11} group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.76 (t, *J* = 10.3 Hz, 3F), -108.38 (t, *J* = 13.9 Hz, 2F), -119.99 (p, *J* = 8.4 Hz, 2F), -121.49 – -121.65 (m, 2F), -126.19 (tt, *J* = 13.7, 3.9 Hz, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{10}F_{11}NS$ 482.0431; Found 482.0428.



1v

Chemical Formula: $C_{14}H_9F_5N_2S$

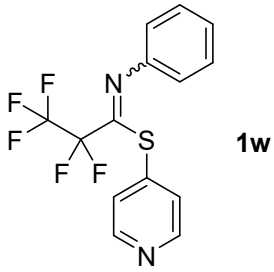
pyridin-2-yl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1v)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.36 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.41 (td, *J* = 7.7, 1.9 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.13 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.91 – 6.85 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 152.1, 150.2, 148.6 (t, *J* = 29.9 Hz), 136.8, 128.6, 126.9, 126.0, 122.3, 119.3, 118.5 (qt, *J* = 287.5, 36.0 Hz), 109.7 (tq, *J* = 259.5, 36.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.91 (s, 3F), -112.59 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}F_5N_2S$ 333.0479; Found 333.0478.



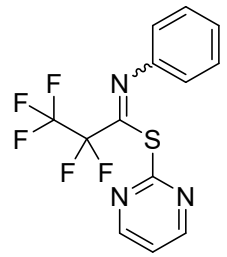
1w

Chemical Formula: $C_{14}H_9F_5N_2S$

pyridin-4-yl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1w)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.38 – 8.31 (m, 2H), 7.23 – 7.16 (m, 2H), 7.10 – 7.03 (m, 3H), 6.86 – 6.80 (m, 2H).

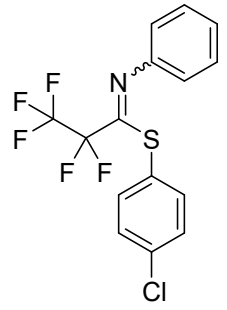
^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 149.9, 148.1 (t, *J* = 30.0 Hz), 145.7, 138.6, 128.8, 126.9, 126.4, 119.3, 118.3 (qt, *J* = 287.4, 35.8 Hz), 109.4 (tq, *J* = 259.3, 37 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.74 (s, 3F), -112.04 (s, 2F).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{10}F_5N_2S$ 333.0479; Found 333.0478.



1x

Chemical Formula: $C_{13}H_8F_5N_3S$

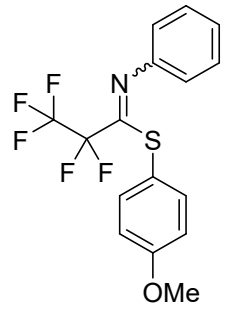
pyrimidin-2-yl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1x)
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.45 (d, *J* = 4.9 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.16 – 7.11 (m, 1H), 7.03 – 6.96 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 167.8, 157.8, 146.6, 145.9 (t, *J* = 30.2 Hz), 128.7, 126.6, 119.5, 118.6 (qt, *J* = 287.6, 36.3 Hz), 118.3, 109.3 (tq, *J* = 259.1, 36.8 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -81.06 (s, 3F), -113.32 (d, *J* = 2.0 Hz, 2F).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_9F_5N_3S$ 334.0432; Found 334.0430.



1y

Chemical Formula: $C_{15}H_9ClF_5NS$

4-chlorophenyl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1y)
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.16 (m, 4H), 7.15 – 7.05 (m, 3H), 6.78 – 6.73 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 151.2 (t, *J* = 29.7 Hz), 146.2, 136.0, 135.9, 129.2, 128.8, 125.6, 125.2, 118.9, 118.3 (qt, *J* = 287.2, 35.6 Hz), 110.1 (tq, *J* = 259.7, 36.7 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.70 (s, 3F), -111.21 (s, 2F).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}ClF_5NS$ 336.0137; Found 336.0135.



1z

Chemical Formula: $C_{16}H_{12}F_5NOS$

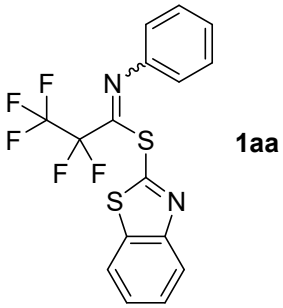
4-methoxyphenyl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1z)

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.26 – 7.19 (m, 4H), 7.09 – 7.03 (m, 1H), 6.81 – 6.76 (m, 2H), 6.73 – 6.67 (m, 2H), 3.75 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 159.7, 151.9 (t, *J* = 29.6 Hz), 145.4, 135.9, 127.7, 124.3, 117.9, 117.4 (qt, *J* = 287.4, 35.6 Hz), 109.4 (tq, *J* = 260.0, 36.4 Hz), 115.9, 113.6, 54.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.67 (s, 3F), -110.84 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}F_5NOS$ 362.0633; Found 362.0631.



1aa

Chemical Formula: $C_{16}H_9F_5N_2S_2$

benzo[d]thiazol-2-yl 2,2,3,3,3-pentafluoro-*N*-phenylpropanimidothioate (1aa)

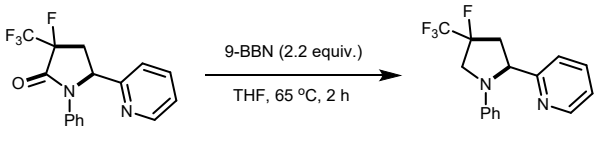
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.91 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.04 – 6.98 (m, 1H), 6.97 – 6.91 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 155.3, 152.8, 145.8 (t, *J* = 30.7 Hz), 145.8, 137.4, 128.7, 126.5, 125.9, 123.3, 121.1, 119.2, 118.3 (qt, *J* = 287.6, 35.8 Hz), 109.6 (tq, *J* = 260.2, 37.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.84 (s, 3F), -112.01 (s, 2F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{10}F_5N_2S_2$ 389.0200; Found 389.0199.

4. Derivatization of Products

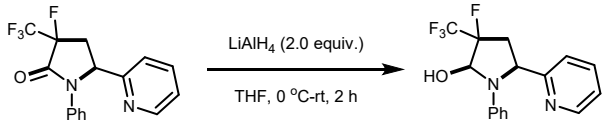


3a **5a, 70%**

To a reaction vial was added **3a** (33.0 mg, 0.1 mmol, 1.0 equiv.) under N_2. Subsequently, 9-BBN (0.5 M in THF, 0.5 mL, 2.2 equiv.) was added via syringe, and the reaction mixture was stirred at 65 °C for 2 hours. After completion, 1 M HCl and EtOAc were added. The two-phase mixture was separated, and then the aqueous phase was basified to pH > 10 with Na_2CO_3 and extracted with EtOAc. The resulting organic layer was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product **5a** (21.6 mg, 70%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.64 – 8.58 (m, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 – 7.14 (m, 4H), 6.83 – 6.75 (m, 1H), 6.51 (dd, *J* = 8.8, 1.1 Hz, 2H), 5.13 (dd, *J* = 9.7, 1.8 Hz, 1H), 4.16 – 4.03 (m, 1H), 4.02 – 3.88 (m, 1H), 3.08 – 2.88 (m, 1H), 2.75 – 2.60 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 161.5, 149.6, 145.6, 137.0, 129.4, 122.3, 120.3, 118.0, 112.6, 63.9, 54.6 (d, *J* = 24.2 Hz), 38.7 (d, *J* = 21.0 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.34 (d, *J* = 6.2 Hz, 3F), -162.44 (q, *J* = 6.4 Hz, 1F).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}F_4N_2$ 311.1166; Found 311.1164.

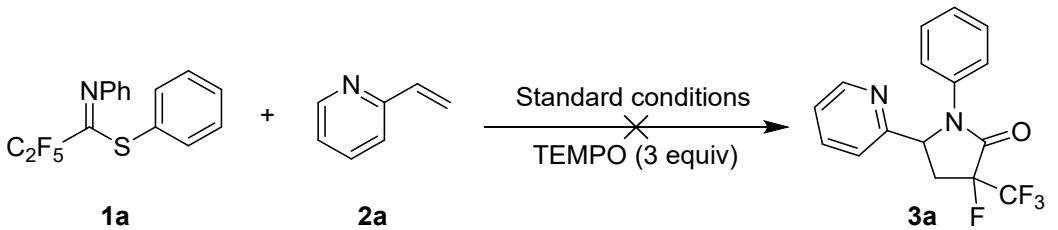


3a **5b, 55%**

To a solution of **3a** (33.0 mg, 0.1 mmol, 1.0 equiv.) in THF (1.0 mL, 0.1 M) was slowly added lithium aluminum hydride (8.0 mg, 0.2 mmol, 2.0 equiv.), and the reaction mixture was stirred at r.t. for 2 hours. When the reaction was completed, the reaction was quenched with 1 M NaOH, H_2O and extracted with EtOAc. The separated organic layer was washed twice with water and once with brine, then dried over anhydrous Na_2SO_4, the resulting organic layer was concentrated under reduced pressure, and the crude product was purified by chromatography on silica gel to afford the desired product **5b** (18.0 mg, 55%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.49 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.72 (td, *J* = 7.6, 1.8 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.11 (m, 3H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.80 – 6.74 (m, 1H), 6.55 (d, *J* = 9.9 Hz, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 5.17 (dt, *J* = 8.9, 3.2 Hz, 1H), 3.07 (td, *J* = 14.7, 8.9 Hz, 1H), 2.51 – 2.36 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 159.8, 149.9, 142.8, 137.6, 129.2, 123.0, 122.5, 119.3, 114.2, 80.9 (d, *J* = 20.3 Hz), 61.0, 37.0 (d, *J* = 22.7 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.30 (d, *J* = 9.5 Hz, 3F), -172.66 (q, *J* = 9.2 Hz, 1F).
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}F_4N_2O$ 327.1115; Found 327.1113.

V. Mechanistic Studies

1. The Radical Trapping Experiments



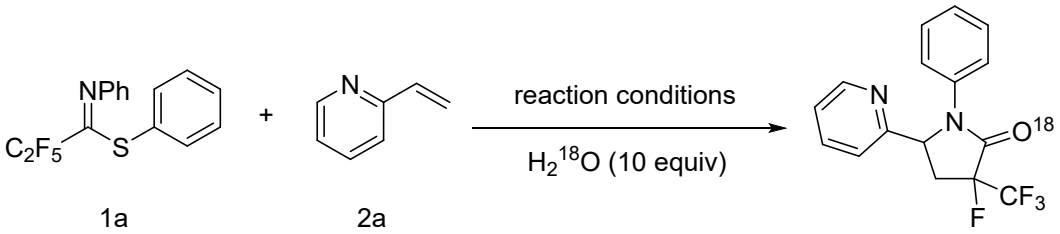
1a **2a** **3a**

To a 10 mL pyrex glass tube which equipped with a magnetic stirring bar were added **1a** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), H_2O (10 equiv), $Ir(ppy)_3$ (0.001 mmol) followed by TEMPO (3.0 equiv) in dry CH_3CN (2 mL). The reaction mixture was stirred at rt and irradiated by

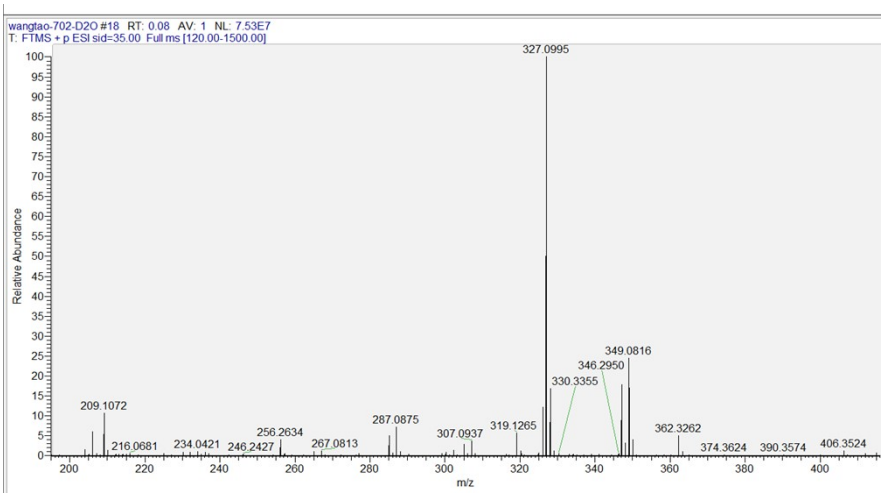
6W blue LEDs for 24 hours. The reaction was monitored by TLC. No desired product **3a** was observed.

2. For the Labeling experiments:

Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), Cs_2CO_3 (0.2 mmol), $H_2{}^{18}O$ (1 mmol), $Ir(ppy)_3$ (0.001 mmol), 6 W blue LEDs, rt, 24 h. Isolated yields.
The ^{18}O was determined by HRMS.



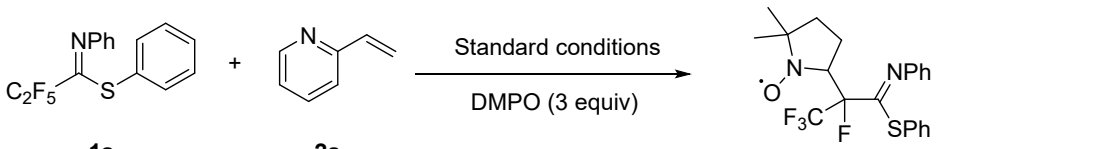
$(M+H)^+$ Calcd: 327.1002
Found: 327.0995



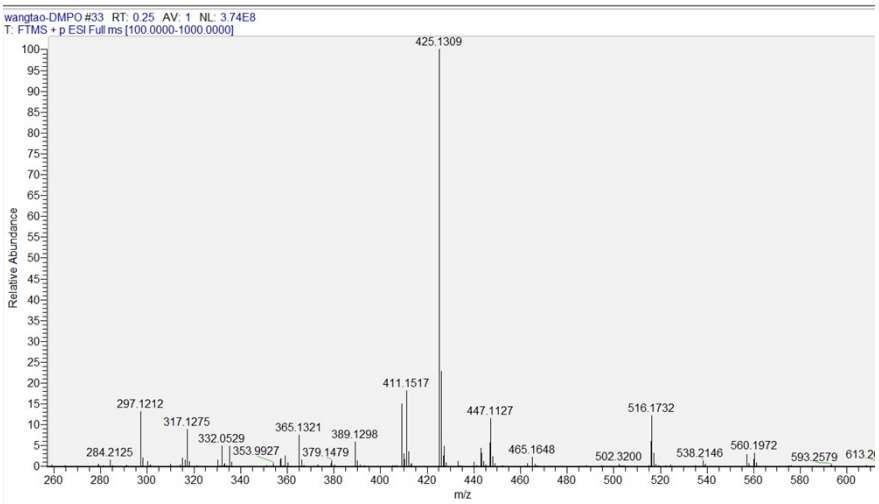
3. General procedure of the ESR experiments

EPR spectra were recorded at 300K using a Bruker A300 EPR spectrometer at 9.4447 GHz. The EPR parameters were set as the following: sweep width 120 G, center field 3362 G, time constant 81.92 ms, sweep time 60.00 s, microwave power 23.49 mW, modulation amplitude 1.00 G, modulation frequency 100 kHz, and receiver gain 1.00×10^4.

To gain more insight into the possible radical intermediates, EPR trapping experiments were conducted in the presence of a spin trapping agent, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) (33.9 mg). As a result, the formation of the DMPO spin adduct of radical was observed (α_N = 13.61 G, α_H = 24.18 G, and g = 2.0069) by EPR and HRMS (ESI+) (Figure S1).



determined by HRMS and EPR
calcd m/z for $[C_{21}H_{21}F_4N_2OS]^+$ 425.1305
Found: 425.1309



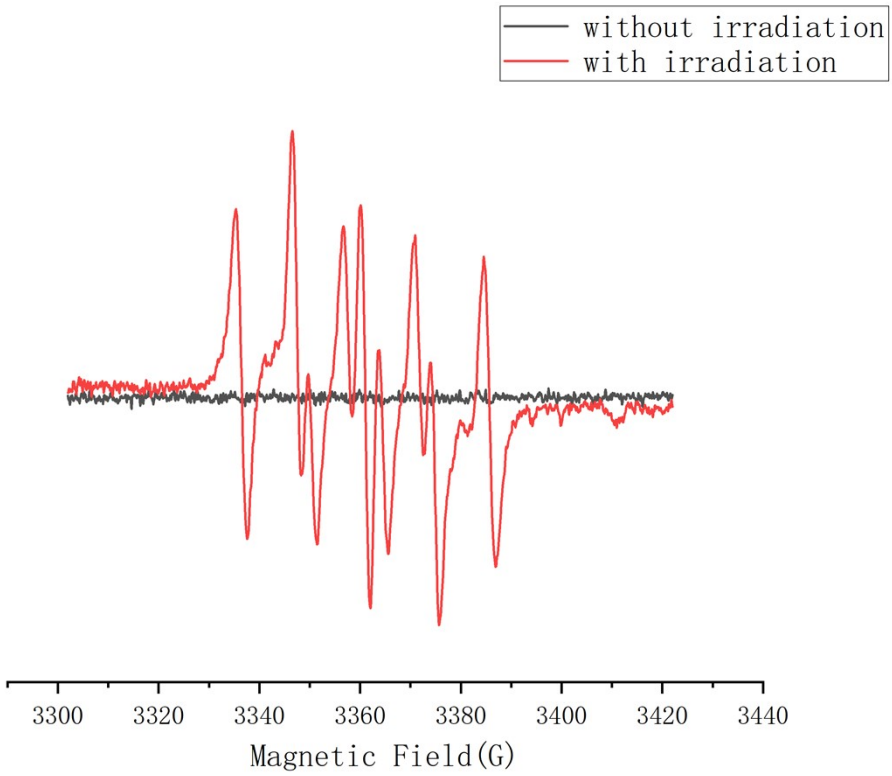


Figure S1. EPR spectra in the absence and presence of irradiation.

4. The Cyclic Voltammetry Experiments

Cyclovoltammetry experiments were carried out on a CH electrochemical workstation using a glassy carbon working electrode, $Hg/HgCl_2$ reference electrode, and Pt wire counter electrode. The measurements were taken at room temperature in dry CH_3CN containing 0.1 M Bu_4NPF_6 as electrolyte. Scan Rate (V/s) = 0.05.

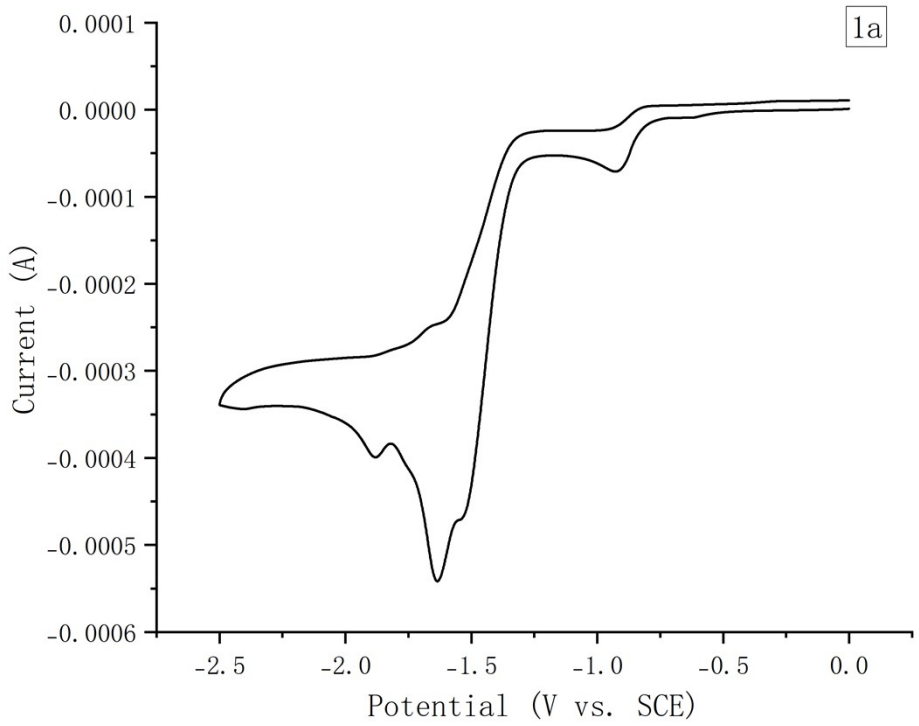


Figure S2. CV of **1a**

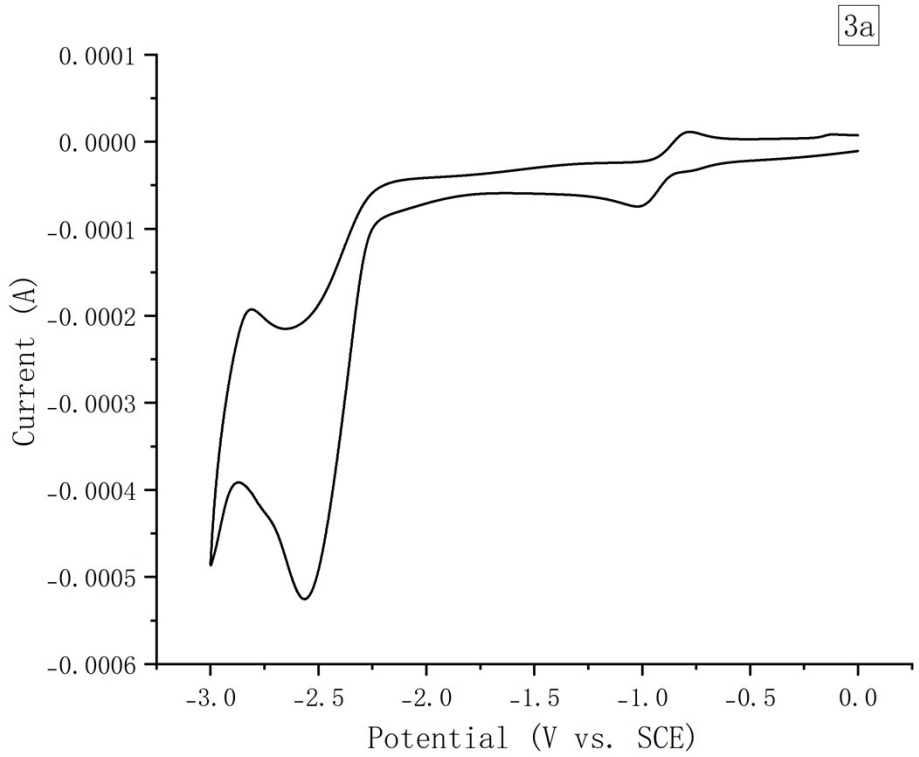


Figure S3. CV of **3a**

5. Quenching studies of $Ir(ppy)_3$ with 1a and 2a

Fluorescence quenching experiments were performed for a combination of $Ir(ppy)_3$ with **1a** or **2a** involved in the model reaction, and the results are depicted in respectively Figure S4 and Figure S5.

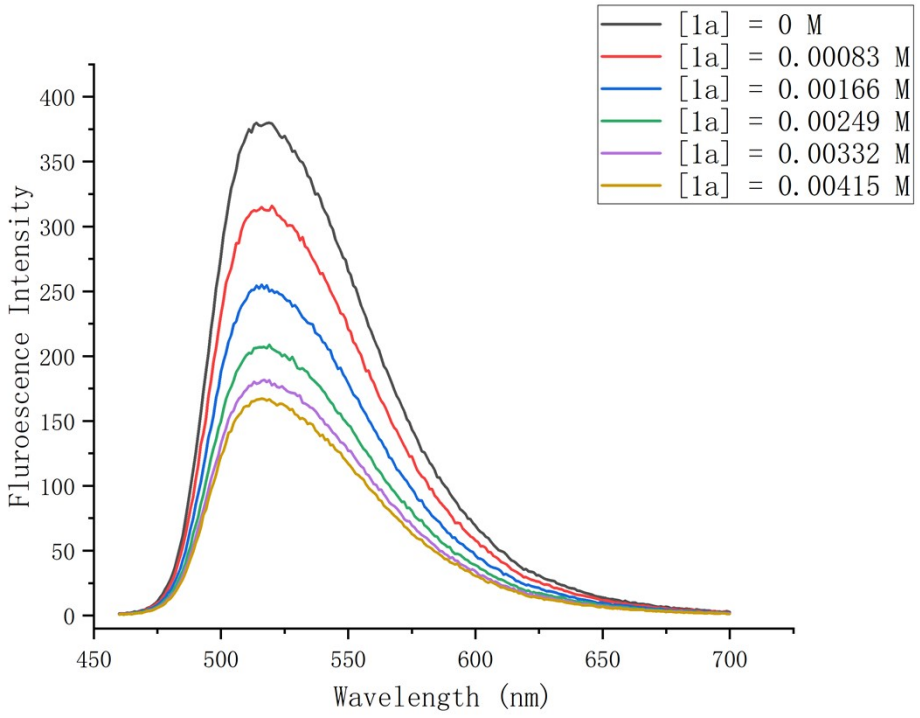


Figure S4. Fluorescence emission spectra of $Ir(ppy)_3$ in acetonitrile in the absence and presence of **1a**.

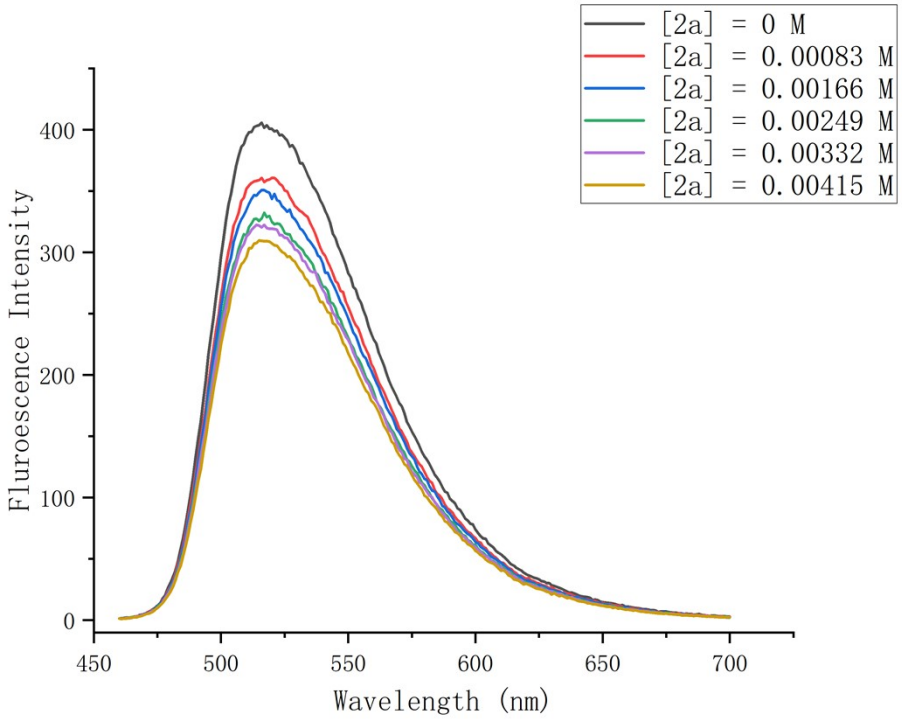


Figure S5. Fluorescence emission spectra of $Ir(ppy)_3$ in acetonitrile in the absence and presence of **2a**.

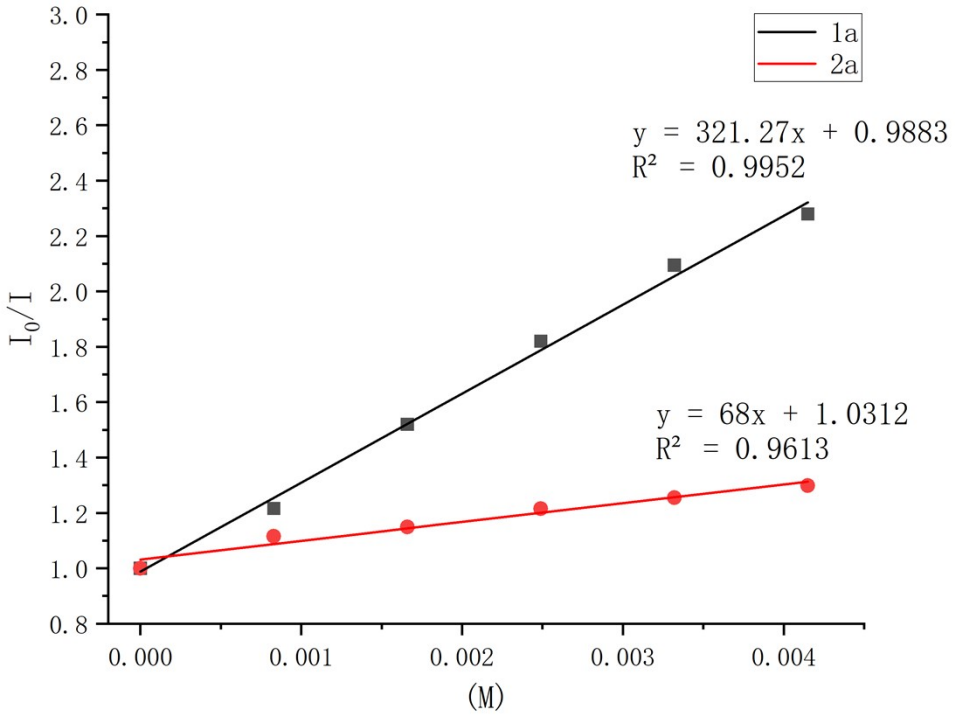
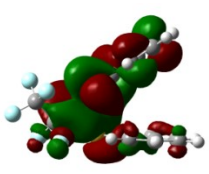


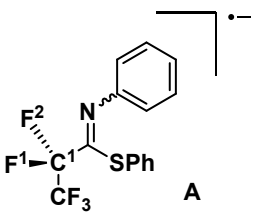
Figure S6. Stern-Volmer plot for the fluorescence quenching

6. Theoretical Calculations

Computational Details All calculations were performed using density functional theory as implemented within the Gaussian 16 (revision A.03) suite of programs[4]. Geometry optimizations were performed at the (U)M06-2X[5-6] level of theory with 6-311+ G(d,p) basis set, and vibrational frequencies of all the intermediates and transition states were performed at the (U)M06-2X/6-31+G(d,p). For modeling reactions conducted in solvent, solvation effects were incorporated using the SMD[7] model in geometry optimization, and frequency analysis (Acetonitrile, Eps= 35.688). All stationary points were confirmed to have no imaginary frequencies. Reported Gibbs free energies and enthalpies include thermal corrections computed at 298.15 K and 1 atm, and are reported in kcal/mol using the conversion of 1 Hartree = 627.5095kcal/mol. Molecular visualizations were created using CYLview[8].

(A)





A

(B)

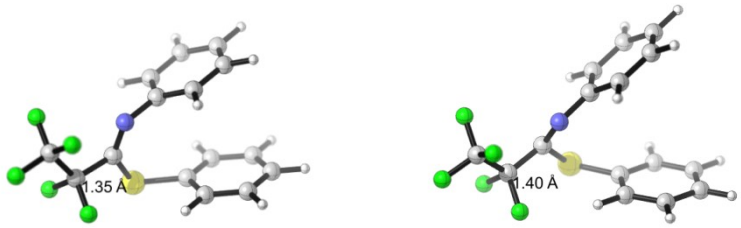


Figure S7. (A) SOMO of radical anion **A**. (B) The bond length of **1a** and radical anion **A**.

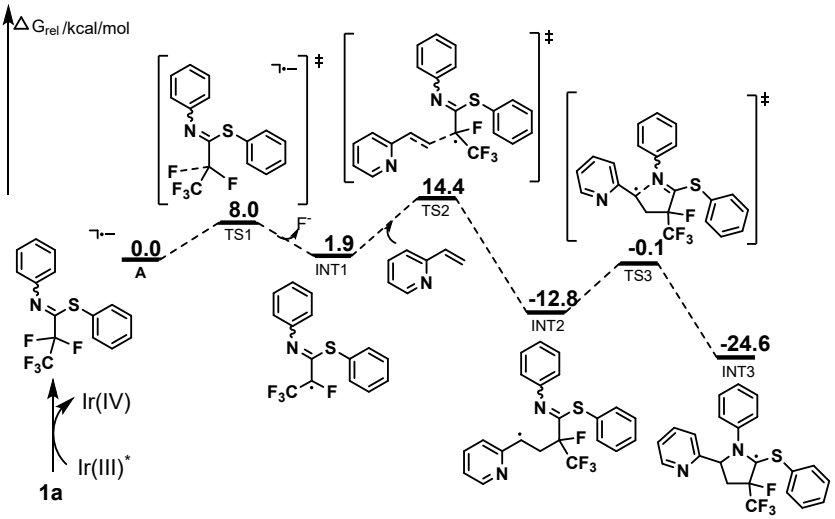


Figure S8. DFT calculated reaction energy profiles. Calculations were performed at the (U)M06-2X/6-31+G(d,p)/SMD(CH_3CN) level of theory. Free energies are in kcal·mol^{-1}.

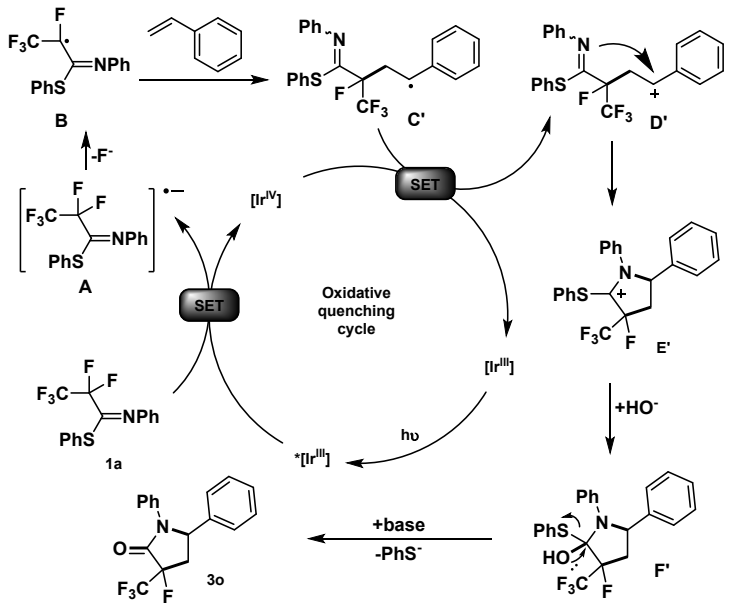


Figure S9. An alternative mechanism for styrene**.**

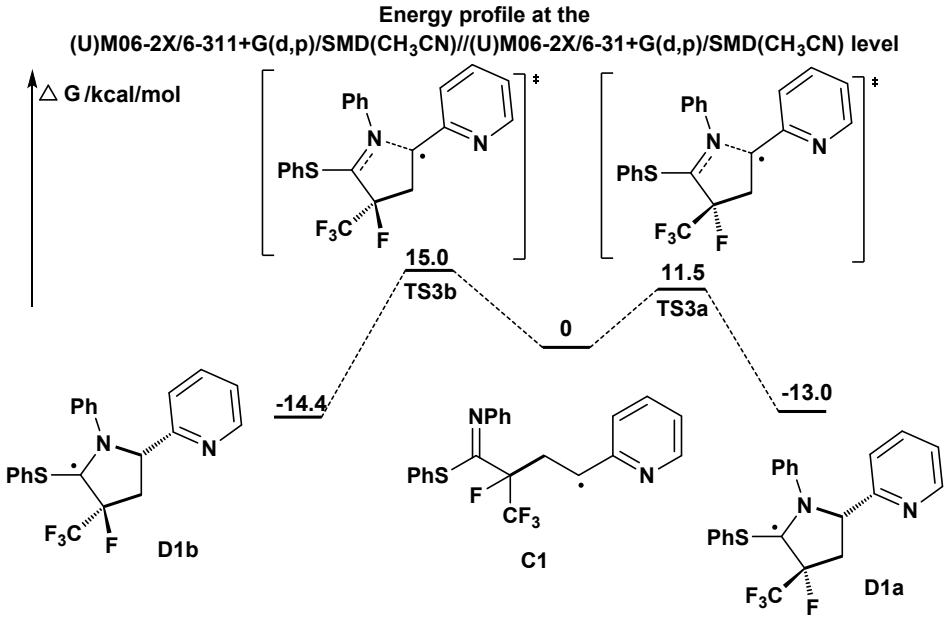


Figure S10. DFT-computed free energy changes of vinylpyridine to form **D1a** and **D1b.**

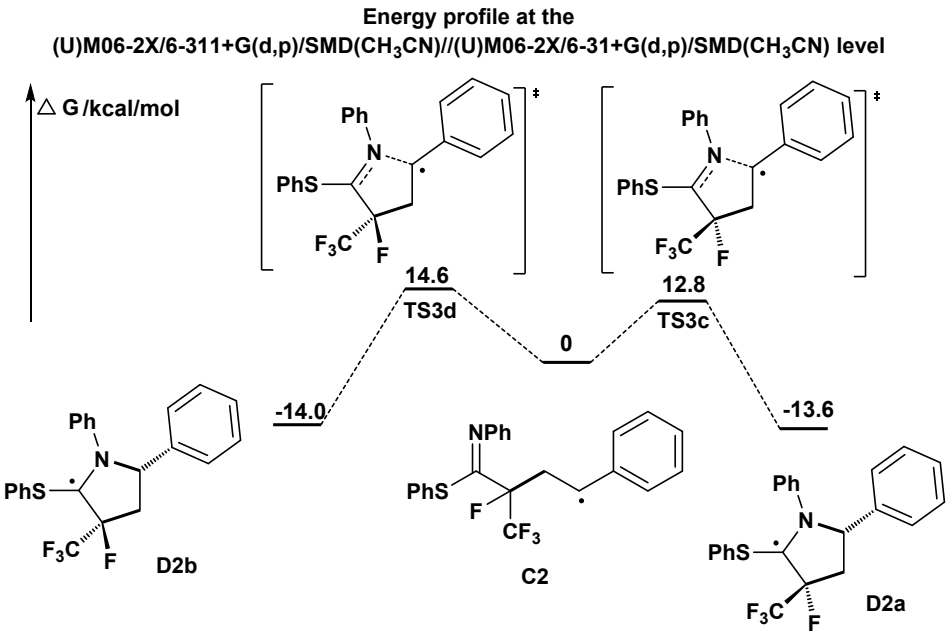


Figure S11. DFT-computed free energy changes of styrene to form **D2a** and **D2b**.

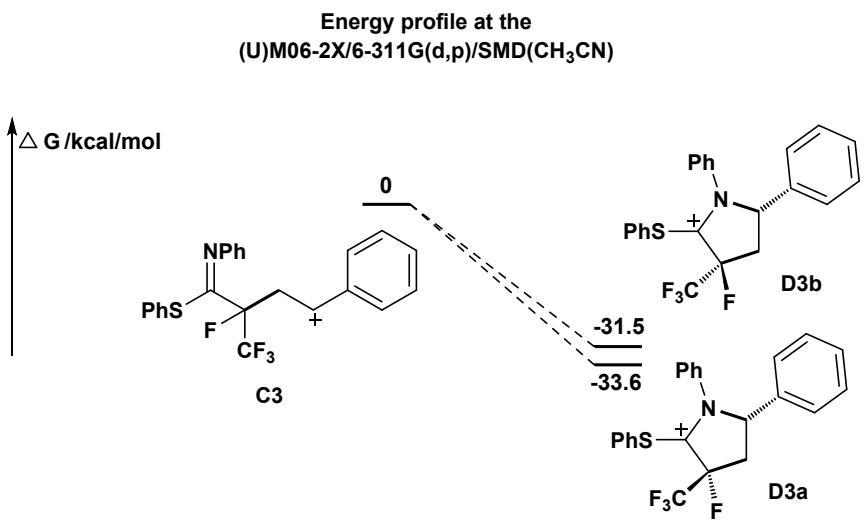
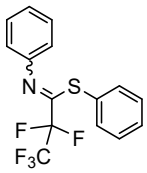
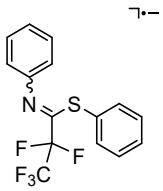


Figure S12. DFT-computed free energy changes of to form **D3a** and **D3b**.



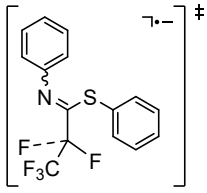
C	-0.53302800	3.75714000	0.51900300
C	-0.23133900	2.41160300	0.34143800
C	1.06195100	2.00529700	-0.06806300
C	2.02580300	3.02334100	-0.26325900
C	1.70957600	4.36199200	-0.09263600
C	0.42349100	4.74713400	0.29680400
N	1.46635200	0.70378200	-0.22599300
C	0.60733700	-0.30356000	-0.46534800
C	1.20198800	-1.65233800	-0.41557400
S	-0.81401300	-0.20266500	-1.54297900
C	-2.23542500	-0.42532600	-0.48032800
C	-2.14102400	-0.74265600	0.87432700
C	-3.29919000	-0.90194600	1.63209300
C	-4.55448500	-0.75270000	1.04933000
C	-4.64569400	-0.43916400	-0.30575200
C	-3.49508400	-0.27531700	-1.06906200
F	0.26207400	-2.62158800	-0.19850500
F	1.83159100	-2.06414800	-1.59304800
C	2.28122200	-1.86073600	0.67041000
F	3.43405800	-1.26828200	0.37173900
F	2.53904600	-3.17181300	0.79922000
F	1.87025800	-1.42073300	1.86035200
H	-1.53095600	4.03503700	0.84319200
H	-0.98610800	1.66511900	0.55397600
H	3.02664700	2.72885400	-0.56190000

H	2.47282100	5.11486100	-0.26037500
H	0.17745900	5.79364900	0.43284600
H	-1.16536100	-0.85928200	1.33369900
H	-3.21444200	-1.14610400	2.68538500
H	-5.45233900	-0.87851800	1.64303800
H	-5.61667000	-0.31776900	-0.77301100
H	-3.57503700	-0.02776200	-2.12292600



C	-4.31002500	-1.67081100	-0.77659500
C	-3.13812600	-0.93978500	-0.98764200
C	-2.66027900	-0.08344000	0.01898800
C	-3.38191100	0.05826900	1.21763400
C	-4.53259500	-0.70023500	1.42950600
C	-5.00244700	-1.56558100	0.43340500
N	-1.52382800	0.72566900	-0.15017100
C	-0.37885900	0.34816400	-0.55009500
C	0.61057100	1.50859000	-0.77370500
S	0.08382900	-1.33493400	-1.01916100
C	1.67119100	-1.60782400	-0.20858100
C	1.78252400	-1.53809000	1.18650000
C	3.00370400	-1.84130400	1.79487800
C	4.09878500	-2.23752700	1.02003000
C	3.97434500	-2.32560400	-0.37024500
C	2.76338400	-2.00545900	-0.99059100
F	1.84520200	1.07366600	-1.13754700
F	0.14968100	2.28886300	-1.80472200
C	0.81767200	2.46207300	0.44584600
F	-0.26686200	3.21191000	0.68788900
F	1.84812100	3.29497000	0.19731300
F	1.10900200	1.75672700	1.55380100
H	-4.67956900	-2.32313000	-1.56261700
H	-2.62412800	-1.00121800	-1.94147900
H	-3.02200800	0.74828500	1.97483100
H	-5.07199600	-0.60393800	2.36737000
H	-5.90903000	-2.14141200	0.59482900
H	0.92830900	-1.25303400	1.79249400
H	3.09260000	-1.77794400	2.87564400
H	5.04340200	-2.48016800	1.49819100
H	4.82084000	-2.63443200	-0.97683700

H	2.67321500	-2.05760000	-2.07126900



Ts1

C	-0.38594200	-0.71496600	0.18278000
C	0.70794700	0.14537100	0.20031800
C	1.29153900	0.58820600	-1.00114200
C	0.71381700	0.18104400	-2.21944100
C	-0.39091400	-0.66706500	-2.22740200
C	-0.94129900	-1.12994800	-1.03032700
N	2.35504300	1.47990200	-0.92533800
C	3.41589800	1.40695100	-1.70704700
C	4.29419800	2.50698700	-1.74226400
S	3.85338400	0.00223300	-2.75590300
C	5.30821200	-0.58501100	-1.89604200
C	5.39790100	-0.56400700	-0.50039200
C	6.53255700	-1.07556600	0.12684800
C	7.57022400	-1.62683100	-0.62738400
C	7.47019300	-1.65782600	-2.01793700
C	6.34625800	-1.13134900	-2.65569900
F	5.53204000	2.32491400	-2.22297400
F	3.79243900	3.72548600	-3.03481500
C	4.29905500	3.53879700	-0.63006200
F	3.14632000	4.19446300	-0.48799600
F	5.26355600	4.44812900	-0.83577300
F	4.57216300	2.95908700	0.56147400
H	-0.81114800	-1.05829800	1.12163300
H	1.13729000	0.47849600	1.14119300
H	1.11180400	0.56229800	-3.15573200
H	-0.82752600	-0.96337100	-3.17708200
H	-1.80018400	-1.79384100	-1.04235400
H	4.58744000	-0.14923800	0.09362300
H	6.59941400	-1.05033400	1.21055700
H	8.44997000	-2.02818200	-0.13391600
H	8.27329900	-2.08032600	-2.61452000
H	6.28212600	-1.13840300	-3.74031300

F^-

F	0.00000000	0.00000000	0.00000000

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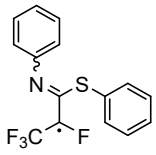
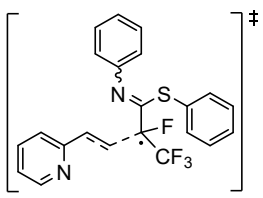


INT1

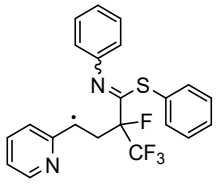
C	-3.99886	-1.99792	-0.81941
C	-2.84358	-1.22559	-0.923
C	-2.5443	-0.25987	0.06918
C	-3.45964	-0.06999	1.13383
C	-4.59281	-0.86867	1.24224
C	-4.8679	-1.83793	0.26698
N	-1.45451	0.58688	0.04109
C	-0.25752	0.33006	-0.44096
C	0.61711	1.42624	-0.51708
S	0.33554	-1.30042	-0.99206
C	1.93374	-1.42906	-0.16988
C	2.05012	-1.26236	1.21749
C	3.29158	-1.44478	1.83197
C	4.40707	-1.81878	1.0743
C	4.28089	-2.00185	-0.30597
C	3.04784	-1.79956	-0.93408
F	1.79856	1.32543	-1.13793
C	0.33899	2.81147	0.01498
F	-0.67954	3.4313	-0.63584
F	1.43053	3.5948	-0.12558
F	0.01498	2.80473	1.32982
H	-4.22584	-2.72332	-1.59527
H	-2.21232	-1.32779	-1.79834
H	-3.24415	0.69593	1.87254
H	-5.27216	-0.72866	2.07797
H	-5.76225	-2.44931	0.34266
H	1.1832	-0.99437	1.81383
H	3.38144	-1.30662	2.90574
H	5.36794	-1.96846	1.55816
H	5.1428	-2.29075	-0.90068
H	2.95715	-1.92302	-2.0091



Ts2

C	2.99522500	2.75969000	0.26928600
C	2.10219400	1.71194400	0.07102700
C	1.38053100	1.19340000	1.15244700

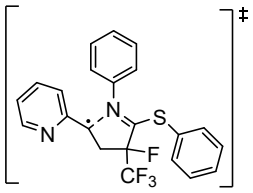
C	1.58956000	1.72106000	2.43429700
C	2.46030100	2.78602000	2.61836700
C	3.16871600	3.30939600	1.53633200
N	0.51279800	0.10388600	1.04835500
C	-0.35460000	-0.06855300	0.12009000
C	-1.10452200	-1.30601900	0.18542300
S	-0.70231500	1.03363200	-1.26029400
C	-2.46457000	1.20984800	-1.02768700
C	-3.01015500	1.39346600	0.24429400
C	-4.38498700	1.55343700	0.38678300
C	-5.21256800	1.56080900	-0.73351300
C	-4.66139800	1.39468200	-2.00136600
C	-3.29053200	1.20720300	-2.15157600
C	0.32879500	-2.94815300	-0.57006600
F	-2.06314500	-1.52315200	-0.71317000
C	1.55543300	-2.59555100	-0.11469300
C	2.43447900	-1.68592600	-0.84839200
C	3.68949000	-1.33394200	-0.33102300
C	4.51633400	-0.49981400	-1.07102300
C	4.07036800	-0.03630300	-2.30468700
C	2.79680700	-0.42057700	-2.72844000
N	1.99204700	-1.21471600	-2.02953900
C	-1.45168300	-1.92393200	1.52327000
F	-2.23513600	-2.99174500	1.33062400
F	-2.13129000	-1.05742300	2.29283900
F	-0.38423400	-2.31910300	2.21315300
H	3.55924500	3.14365400	-0.57565300
H	1.99535700	1.26272600	-0.91047000
H	1.04730200	1.28374000	3.26638900
H	2.59949900	3.20076700	3.61193200
H	3.86148000	4.13169000	1.68468200
H	-2.36309900	1.40743600	1.11676400
H	-4.80745100	1.68439600	1.37812600
H	-6.28346800	1.69417900	-0.61843700
H	-5.30133400	1.39394000	-2.87830700
H	-2.86045700	1.04666900	-3.13544300
H	0.02917600	-2.66923100	-1.57553300
H	-0.25962900	-3.70276600	-0.05771600
H	1.90327800	-2.93893800	0.85561800
H	3.99748700	-1.71355700	0.63808700
H	5.49119900	-0.21268100	-0.68928400
H	4.68188900	0.61215200	-2.92257100
H	2.40298700	-0.06363500	-3.67810200



INT2

C	2.74278400	3.02663400	0.08812100
C	2.03322600	1.83113500	0.00639700
C	1.14180700	1.48490000	1.02558400
C	0.98357100	2.32504000	2.13275100
C	1.67463700	3.53080500	2.19068300
C	2.55964100	3.88434900	1.17120500
N	0.44906800	0.26080800	1.03274800
C	-0.29780400	-0.16022700	0.10495600
C	-0.82730900	-1.58647900	0.26725400
S	-0.66829100	0.68421500	-1.44292000
C	-2.42778500	0.91177300	-1.21168400
C	-2.92944700	1.44591700	-0.02346600
C	-4.30054100	1.64724800	0.11665600
C	-5.16615500	1.34464900	-0.93322900
C	-4.65764400	0.82825400	-2.12411400
C	-3.29057100	0.60006900	-2.26325100
C	0.19994500	-2.62169700	-0.24669300
F	-1.98084300	-1.76084400	-0.46680200
C	1.59123900	-2.41662100	0.24750900
C	2.56602700	-1.71482300	-0.51964800
C	3.85122900	-1.44584900	0.01148200
C	4.76849900	-0.75075400	-0.75651700
C	4.40274900	-0.33896300	-2.04056700
C	3.11291400	-0.64237400	-2.48597100
N	2.21223200	-1.29678400	-1.76212600
C	-1.25209800	-1.88152300	1.71864000
F	-1.95816900	-3.02263700	1.75256600
F	-2.02908500	-0.91338300	2.21651900
F	-0.20679700	-2.04468600	2.53677800
H	3.43831300	3.28729600	-0.70377900
H	2.17777700	1.15741800	-0.83189400
H	0.31347400	2.02002600	2.93047700
H	1.53334200	4.18950700	3.04172100
H	3.10927400	4.81837500	1.22637000
H	-2.25084400	1.70031100	0.78617400
H	-4.68981900	2.05028100	1.04624700
H	-6.23315800	1.50924300	-0.82322700
H	-5.32736100	0.58617000	-2.94331200
H	-2.89275800	0.16745300	-3.17586800

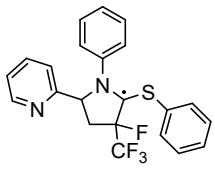
H	0.17924400	-2.52397700	-1.33557400
H	-0.18148200	-3.61097700	0.02868700
H	1.86082900	-2.75146100	1.24252800
H	4.09433000	-1.77732000	1.01598300
H	5.75541900	-0.52673900	-0.36396900
H	5.08976300	0.20356500	-2.68008900
H	2.78776900	-0.32959900	-3.47624200



Ts3

C	2.56957600	3.21190100	-0.34346200
C	1.91829800	1.98030500	-0.45792000
C	1.27000000	1.42805600	0.65740200
C	1.29918600	2.10332100	1.88767400
C	1.93997100	3.33970500	1.99007000
C	2.57789500	3.89696300	0.87566900
N	0.62960500	0.16499600	0.61716200
C	-0.44222100	-0.13918800	-0.07293900
C	-0.74540200	-1.61782100	0.09419900
S	-1.12262400	0.82703900	-1.42519900
C	-2.88064000	0.90596600	-1.02634700
C	-3.32326600	1.58301700	0.11900100
C	-4.69305300	1.70325800	0.36555200
C	-5.62153800	1.16895800	-0.53547800
C	-5.17653400	0.50719700	-1.68365000
C	-3.80624800	0.36896300	-1.93010000
C	0.62642300	-2.34765100	0.01467800
F	-1.58692200	-2.09804200	-0.91525200
C	1.72349200	-1.50564000	0.59941600
C	2.94567600	-1.26591300	-0.14875500
C	4.12520400	-0.87888900	0.53061100
C	5.28369700	-0.63326700	-0.19676300
C	5.25046500	-0.77077100	-1.58947900
C	4.04267900	-1.15188200	-2.18461100
N	2.91877700	-1.39418000	-1.50255500
C	-1.51406900	-1.95084900	1.39513600
F	-1.77860300	-3.27835700	1.47515800
F	-2.70296200	-1.31244700	1.46322300
F	-0.80999500	-1.61706400	2.49817600
H	3.06981800	3.63427700	-1.21041200
H	1.92280600	1.44570900	-1.40182000

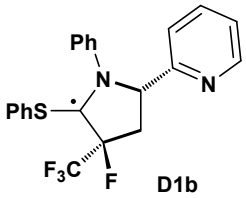
H	0.81055500	1.65755200	2.74902200
H	1.94618000	3.86364300	2.94165200
H	3.08289000	4.85502200	0.95923200
H	-2.60487400	2.01131700	0.81134000
H	-5.03339800	2.22358400	1.25650900
H	-6.68591800	1.27090200	-0.34371700
H	-5.89196100	0.08994800	-2.38667100
H	-3.46164800	-0.15590800	-2.81589400
H	0.80615400	-2.51027200	-1.05054600
H	0.56718900	-3.32167500	0.50908300
H	1.85986500	-1.56555500	1.67414500
H	4.11473000	-0.78623700	1.61253700
H	6.19917500	-0.34206100	0.31046200
H	6.12958700	-0.59144000	-2.19995500
H	3.98094000	-1.26837900	-3.26521400



INT3

C	0.21936600	-3.62049900	0.76244200
C	0.59272100	-2.29621300	0.99513800
C	0.25455500	-1.31729900	0.06674200
C	-0.44109200	-1.64864100	-1.09799700
C	-0.80921700	-2.97029500	-1.32676700
C	-0.48060900	-3.95661200	-0.39447600
N	0.62646100	0.04260900	0.31514800
C	-0.32592600	0.99687100	0.65031300
C	0.23665200	2.36024700	0.40189700
S	-1.63076700	0.68629600	1.76273400
C	-2.71491400	-0.33710000	0.75587000
C	-3.03036300	-1.62134300	1.19756700
C	-3.86290500	-2.43347300	0.42769400
C	-4.37135700	-1.96719500	-0.78264900
C	-4.05790900	-0.67811100	-1.21748600
C	-3.23834700	0.14250900	-0.44692900
C	1.67655600	2.09907200	-0.05118000
F	0.21263700	3.16661700	1.53543700
C	1.67538000	0.64446200	-0.52465200
C	2.98665600	-0.09088500	-0.34144700
C	3.42717400	-0.99435800	-1.30884800
C	4.60939200	-1.69404100	-1.08320500
C	5.30498500	-1.46316800	0.09811200

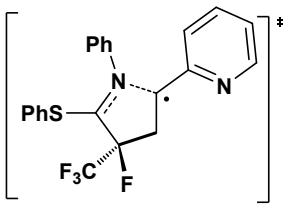
C	4.78172500	-0.53881200	1.00294100
N	3.65017000	0.13367300	0.79607300
C	-0.55857500	3.14998100	-0.64134800
F	-0.02682900	4.36283300	-0.85045200
F	-1.83634700	3.32261400	-0.29160800
F	-0.54161800	2.49891300	-1.82300800
H	0.47458400	-4.38737900	1.48692300
H	1.13300200	-2.00375600	1.89018800
H	-0.71807600	-0.86199200	-1.79576000
H	-1.36825300	-3.22782400	-2.22086100
H	-0.77552100	-4.98649900	-0.56995000
H	-2.59974600	-1.99044100	2.12377600
H	-4.09640000	-3.43788900	0.76754000
H	-5.01210200	-2.60339700	-1.38535600
H	-4.46098400	-0.30643700	-2.15475500
H	-2.99239100	1.14768000	-0.77619400
H	2.30942000	2.18385400	0.83557900
H	2.02346100	2.79520800	-0.81665800
H	1.37576500	0.58227700	-1.58214600
H	2.84389100	-1.15038400	-2.21122700
H	4.97676200	-2.40669400	-1.81485900
H	6.23091500	-1.98181800	0.32086700
H	5.29725100	-0.32858900	1.93688200



D1b

C	0.27893600	-0.52107700	0.07950200
C	-0.30137700	-1.77159200	-0.12110200
C	-1.68819600	-1.92477500	0.01128000
C	-2.48166200	-0.82148200	0.35251500
C	-1.89023700	0.42447400	0.53996000
C	-0.50965700	0.58262100	0.40536000
N	-2.26968400	-3.19591000	-0.16188400
C	-3.48129400	-3.45805600	-0.78034300
C	-3.66502900	-4.93990200	-0.83339400
S	-4.14094100	-2.40509100	-2.01319400
C	-5.63169800	-1.73754500	-1.27617100
C	-5.97459000	-1.90261500	0.06685700
C	-7.15628400	-1.33990900	0.55158200
C	-7.99352600	-0.61105200	-0.29208500
C	-7.64277200	-0.44646600	-1.63336700
C	-6.46853600	-1.00894800	-2.12890300

C	-2.65490500	-5.49032000	0.16178000
F	-3.38338800	-5.43618600	-2.12504300
C	-1.54162200	-4.43124400	0.18464000
C	-5.08526400	-5.43773300	-0.56832800
F	-5.13618000	-6.77956600	-0.63503300
F	-5.96581700	-4.96400800	-1.45967300
F	-5.51185000	-5.08304500	0.65221100
H	1.35395300	-0.41202700	-0.02704100
H	0.32078500	-2.62066600	-0.38729700
H	-3.55070400	-0.94358600	0.49192800
H	-2.51346200	1.27280500	0.80629200
H	-0.05282500	1.55509100	0.55946800
H	-5.32645400	-2.46652900	0.73215300
H	-7.41739800	-1.47422200	1.59726200
H	-8.91120400	-0.17557500	0.09058600
H	-8.28650500	0.11794800	-2.30146500
H	-6.20673800	-0.88365500	-3.17677200
H	-2.29643600	-6.47520900	-0.13940100
H	-3.11868300	-5.56180900	1.15003600
H	-0.79101500	-4.64501600	-0.58551000
C	-0.84659900	-4.34310900	1.52660800
C	-1.50271500	-3.80821100	2.63820400
C	-0.82854600	-3.76997400	3.85288100
H	-2.51660300	-3.42751400	2.54244300
C	1.03508500	-4.79251900	2.75470000
C	0.47010100	-4.27359600	3.91569300
H	-1.30616000	-3.35482400	4.73504100
H	2.04484400	-5.19456600	2.76445600
H	1.03635400	-4.26404900	4.84068300
N	0.39783800	-4.82493700	1.57667100



TS3b

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C	-0.50893900	-2.06192400	0.07585300
C	-1.33236900	-2.47844800	1.12698200
C	-1.23930900	-1.86945600	2.38155500
C	-0.35172800	-0.81192500	2.57034900
C	0.46352600	-0.38355400	1.52096800

N	-2.19904900	-3.58653800	0.99409700
C	-3.16717800	-3.68906900	0.14012700
C	-3.73150300	-5.09537100	0.17428200
S	-3.50107100	-2.57321100	-1.20754400
C	-5.28066300	-2.41112400	-1.06530100
C	-5.82021200	-1.66457600	-0.01436000
C	-7.20152200	-1.50800400	0.07916800
C	-8.03768900	-2.08252300	-0.88019200
C	-7.49218200	-2.81408500	-1.93518000
C	-6.11026700	-2.98275600	-2.03073900
C	-2.53005000	-6.08559600	0.36753900
F	-4.41052400	-5.39854100	-0.99126800
C	-1.27084100	-5.37198000	0.75920000
C	-4.78545500	-5.28605700	1.27274400
F	-5.21817100	-6.55881400	1.30007800
F	-5.86196600	-4.51531500	1.07118800
F	-4.29550800	-4.99764000	2.48373900
H	1.02997600	-0.69399700	-0.53664800
H	-0.55451000	-2.57283700	-0.88239200
H	-1.86649700	-2.22915500	3.19243000
H	-0.28841500	-0.33076500	3.54152700
H	1.16311300	0.43239800	1.67391900
H	-5.16341300	-1.21766300	0.72711900
H	-7.62331900	-0.93351700	0.89828400
H	-9.11363400	-1.95617900	-0.80689500
H	-8.14038200	-3.25996500	-2.68340200
H	-5.68084500	-3.56147400	-2.84296900
H	-2.40423100	-6.56454600	-0.60709900
H	-2.80169200	-6.86543400	1.08225000
H	-0.62372800	-5.05208300	-0.05370400
C	-0.57880300	-5.56311100	2.01865500
C	-1.20456400	-6.08812400	3.16563700
C	-0.49218300	-6.14960200	4.35592700
H	-2.22975100	-6.43966400	3.12228400
C	1.36387200	-5.17674500	3.20459300
C	0.82279700	-5.68623300	4.38580900
H	-0.95779400	-6.55234400	5.25053400
H	2.38608900	-4.80525500	3.18748400
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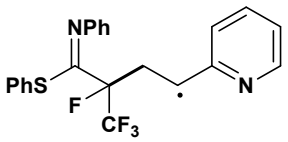
N	0.69640800	-5.10789700	2.05293000



C1

C	0.59417000	-1.81708700	0.02316700
C	0.84995400	-2.67086500	1.09502400
C	0.83553700	-2.16503000	2.39858800
C	0.59267200	-0.80718500	2.62763500
C	0.31667100	0.03226200	1.55080600
C	0.31885200	-0.46777600	0.24691700
N	1.14364600	-2.98682700	3.50330400
C	0.46485000	-4.00140600	3.83159000
C	1.04994300	-4.85378800	4.96681100
S	-0.99596800	-4.59877900	2.96529700
C	-2.17293800	-4.68347800	4.31227500
C	-2.42319600	-3.55644900	5.09804700
C	-3.37757600	-3.62623400	6.11246100
C	-4.09664700	-4.80371000	6.32022200
C	-3.85663900	-5.91815200	5.51509100
C	-2.88855400	-5.86554100	4.51324600
C	2.26923600	-5.63228200	4.44283800
F	0.11453800	-5.75960400	5.42741000
C	2.83651900	-6.58668300	5.43816000
C	4.13002700	-6.50403500	6.02658700
C	5.63944600	-7.49481700	7.47444600
C	6.60116100	-6.50116800	7.26016100
C	6.28626500	-5.46526300	6.38078700
C	1.38258000	-3.98028900	6.19430800
F	1.54963900	-4.74456400	7.28342500
F	0.39143300	-3.11863300	6.46941600
F	2.50399600	-3.27343400	6.02361800
H	0.60873700	-2.21092600	-0.98858200
H	1.07919500	-3.71990900	0.92632000
H	0.60953500	-0.42737200	3.64500300
H	0.10933200	1.08269100	1.73135000
H	0.11540300	0.19276900	-0.59011400
H	-1.87700200	-2.63343600	4.92104400
H	-3.56540100	-2.75423200	6.73156400
H	-4.84433000	-4.85221800	7.10595000
H	-4.41461900	-6.83613700	5.67261900
H	-2.68302300	-6.73902500	3.90144100
H	2.99861300	-4.90593900	4.07975900
H	1.90109500	-6.19043400	3.57116700

H	2.21937000	-7.42565300	5.74367700
H	5.85089800	-8.31683000	8.15505600
H	7.55725300	-6.54607100	7.76960400
H	6.99879500	-4.66978000	6.18464400
C	5.04793700	-5.45863600	5.75734900
H	4.78831000	-4.65709000	5.07498900
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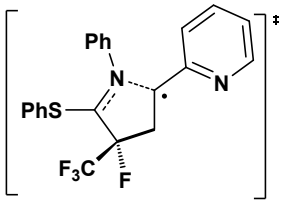
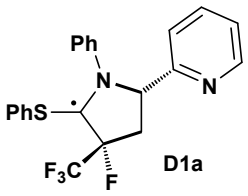


TS3a

C	2.96383900	2.77963100	-0.28158600
C	2.07770000	1.70982300	-0.39642000
C	1.46547700	1.19162100	0.75042900
C	1.76352100	1.72555000	2.00793200
C	2.64010200	2.80317100	2.11331200
C	3.24215900	3.33159400	0.96958400
N	0.61729300	0.06086400	0.71031600
C	-0.41834600	-0.08959100	-0.05903300
C	-0.93283400	-1.50686400	0.06357800
S	-0.93972600	0.97292400	-1.38674400
C	-2.68695400	1.10830600	-1.00487000
C	-3.09482400	1.82572000	0.12288000
C	-4.45419200	1.96347800	0.39576700
C	-5.40140600	1.40047900	-0.46193300
C	-4.98858800	0.69662600	-1.59318500
C	-3.62865400	0.54508700	-1.86716600
C	0.32050800	-2.42383900	0.01473100
F	-1.80493400	-1.83555000	-0.95504300
C	1.50963600	-1.73313000	0.60930700
C	2.67565900	-1.44843300	-0.20030000
C	3.90067000	-1.11674400	0.41743000
C	4.97650600	-0.74298300	-0.37184300
C	4.81543100	-0.70540800	-1.75993000
C	3.57165100	-1.05367200	-2.28671400
N	2.52294100	-1.41252500	-1.54398300
C	-1.74500600	-1.74243400	1.34391200
F	-2.22628000	-2.99672800	1.37255500
F	-2.79716300	-0.91751900	1.43142200
F	-0.99761900	-1.57311200	2.44156900
H	3.44175900	3.17619000	-1.17234800

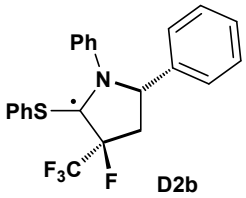
H	1.88721800	1.25934600	-1.36614900
H	1.30065700	1.29056400	2.88917600
H	2.85999100	3.22391900	3.08970000
H	3.93344800	4.16447300	1.05442000
H	-2.35280600	2.26455000	0.78477400
H	-4.77252600	2.51529800	1.27504000
H	-6.46022300	1.51258500	-0.24898100
H	-5.72272900	0.25764100	-2.26188900
H	-3.30148200	-0.01452300	-2.73839700
H	0.48952900	-2.62208000	-1.04630700
H	0.11131700	-3.36907200	0.52320300
H	1.69349600	-1.87240800	1.67029500
H	3.98089400	-1.15403800	1.50001700
H	5.92754000	-0.48203900	0.08302900
H	5.62773200	-0.41924900	-2.41900400
H	3.41179400	-1.03805800	-3.36281400



D1a

C	0.01726100	-3.54869000	1.16097500
C	0.39553800	-2.21018300	1.27566800
C	0.25939100	-1.36245000	0.17808100
C	-0.23096500	-1.84273100	-1.03860400
C	-0.60149800	-3.18141500	-1.14841400
C	-0.48261300	-4.03371300	-0.04772600
N	0.60906300	0.01673000	0.31632600
C	-0.31357800	0.97775300	0.70221700
C	0.26251500	2.33156600	0.47782500
S	-1.66360500	0.64562000	1.74815600
C	-2.72208700	-0.34769300	0.68008300
C	-3.17609600	-1.57877400	1.15518600
C	-3.99696800	-2.37062300	0.34933800
C	-4.35485500	-1.93776200	-0.92691100
C	-3.90102700	-0.70178000	-1.39415100
C	-3.09103800	0.09883300	-0.59132000
C	1.66178300	2.06527900	-0.08438700
F	0.34195200	3.08355000	1.66789800
C	1.61869500	0.61216800	-0.57359200
C	2.93854200	-0.12021500	-0.46409700
C	3.51150400	-0.72030500	-1.58360700
C	4.72256300	-1.39509600	-1.43488000
C	5.30714000	-1.44810800	-0.17448300

C	4.65334100	-0.81911400	0.88633700
N	3.49650000	-0.16718700	0.75203100
C	-0.57532900	3.22492300	-0.43905100
F	-0.01841300	4.44004900	-0.58130100
F	-1.81923100	3.41597300	0.02192600
F	-0.67283900	2.68581900	-1.66555800
H	0.11484100	-4.21062700	2.01603600
H	0.78665600	-1.81361600	2.20805500
H	-0.33889000	-1.16505400	-1.88172100
H	-0.99233100	-3.55639500	-2.08966700
H	-0.77886100	-5.07481600	-0.13408100
H	-2.87384400	-1.92660600	2.13935700
H	-4.34118100	-3.33285900	0.71703200
H	-4.98409400	-2.55952300	-1.55651600
H	-4.18170200	-0.35692600	-2.38503500
H	-2.73626500	1.05839800	-0.95636400
H	2.35759300	2.14674500	0.75524700
H	1.95824600	2.76295100	-0.86898500
H	1.26832300	0.56783300	-1.61348300
H	3.01272600	-0.65992500	-2.54608800
H	5.19506200	-1.87301500	-2.28753300
H	6.24669400	-1.96335400	-0.00610700
H	5.08061600	-0.84106200	1.88593200



D2b

C	-0.16790500	-1.03882200	0.00106800
C	0.14856900	0.31622500	0.06682900
C	-0.76635100	1.21859000	0.62505600
C	-1.99734700	0.75468800	1.10676500
C	-2.29749400	-0.60318400	1.04455100
C	-1.38735300	-1.50629800	0.49219900
N	-0.45427800	2.59121700	0.66897000
C	-0.72839600	3.44903700	1.72063100
C	-0.14026300	4.78349100	1.40043100
S	-0.88835600	2.88124000	3.36783100
C	0.14094400	4.73256700	-0.09342200
F	1.06486100	4.98876300	2.10943100
C	0.34893500	3.23860300	-0.39056500
C	-0.99159500	5.98835700	1.79746600
F	-0.38537900	7.13524900	1.44363800
F	-1.20876700	6.04782200	3.11810500

F	-2.18686200	5.96581300	1.18985700
H	0.54812100	-1.73111700	-0.43132600
H	1.10547800	0.66976200	-0.30433100
H	-2.72139200	1.45649200	1.50770200
H	-3.25499800	-0.95300700	1.41852700
H	-1.62902500	-2.56321300	0.43999300
H	1.00859500	5.34007600	-0.35380000
H	-0.73167800	5.10038800	-0.64115800
C	-2.61210000	3.16227700	3.77037400
C	-3.57159600	3.55817700	2.83703200
C	-2.97686900	2.95486100	5.10543300
C	-4.89320700	3.74807100	3.24354200
H	-3.29219300	3.71928500	1.79951800
C	-4.29998900	3.14188500	5.49950800
H	-2.23060100	2.65105400	5.83557200
C	-5.26380400	3.54131900	4.57164200
H	-5.63352400	4.05816400	2.51178400
H	-4.57511800	2.97855000	6.53726900
H	-6.29322900	3.69018500	4.88213600
C	-0.09570500	2.84588700	-1.78141700
C	0.84775900	2.49753800	-2.74769500
C	-1.45448500	2.85163200	-2.11532200
C	0.44102900	2.16321400	-4.04132700
H	1.90301000	2.48154300	-2.48532200
C	-1.86225600	2.51084400	-3.40245400
H	-2.19322200	3.11706900	-1.36062700
C	-0.91360700	2.16680600	-4.36946200
H	1.18257900	1.89322600	-4.78723200
H	-2.91900700	2.51173800	-3.65242400
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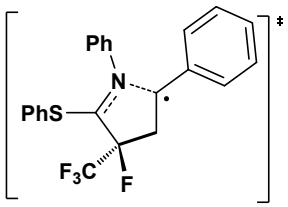
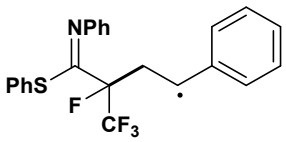


TS3d

C	0.59976400	-0.48845900	0.25085800
C	-0.29847500	-1.53711500	0.06004800
C	-1.11329000	-1.95228400	1.11939500
C	-1.00686600	-1.33855900	2.37120600
C	-0.11868400	-0.27951100	2.54875000
C	0.68650000	0.14666400	1.49083500

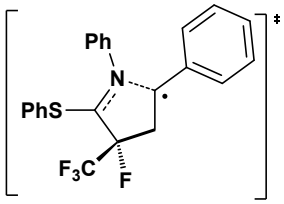
N	-1.97520100	-3.06359800	1.00063200
C	-2.93491400	-3.18609700	0.13865300
C	-3.47858100	-4.59925800	0.18005700
S	-3.27587400	-2.09445300	-1.22880200
C	-5.05365800	-1.92806400	-1.06750000
C	-5.58236900	-1.18753200	-0.00666200
C	-6.96245200	-1.03046000	0.10215300
C	-7.80922200	-1.59847600	-0.85191700
C	-7.27507800	-2.32458000	-1.91633900
C	-5.89420700	-2.49410900	-2.02673400
C	-2.26232800	-5.57535600	0.35738900
F	-4.16877500	-4.91446300	-0.97665400
C	-1.01306500	-4.85703000	0.77352900
C	-4.51767800	-4.80316700	1.28994100
F	-4.93699100	-6.08083000	1.32037700
F	-5.60530800	-4.04406800	1.09978700
F	-4.02049200	-4.51122000	2.49675800
H	1.23458600	-0.17059400	-0.57070200
H	-0.35180600	-2.05060500	-0.89649200
H	-1.62506500	-1.69705000	3.18950400
H	-0.04630600	0.20388800	3.51821300
H	1.38694400	0.96350700	1.63491300
H	-4.91777100	-0.74554200	0.73090900
H	-7.37523500	-0.46052000	0.92904200
H	-8.88425400	-1.47177100	-0.76668600
H	-7.93127800	-2.76621200	-2.66012800
H	-5.47381600	-3.06995700	-2.84579000
H	-2.12703000	-6.02812100	-0.62864200
H	-2.52828400	-6.37566200	1.05133500
H	-0.37772200	-4.51010400	-0.03875400
C	-0.33146200	-5.06276500	2.03433900
C	-0.95426200	-5.63884600	3.16073500
C	-0.27709200	-5.73687800	4.37283300
H	-1.97055800	-6.01455700	3.08893600
C	1.65791900	-4.67616900	3.39261700
C	1.02991900	-5.25817000	4.49750400
H	-0.77258200	-6.18840400	5.22753300
H	2.67302900	-4.29951400	3.47877700
H	1.55311900	-5.33802000	5.44548200
C	0.98614500	-4.57751600	2.17907100
H	1.47622500	-4.12261100	1.32091200



C2

C	0.30217800	-2.11639400	0.03090500
C	0.54632600	-2.97908300	1.09831900
C	0.52886500	-2.48200600	2.40526400
C	0.29445800	-1.12399100	2.64206700
C	0.03016000	-0.27537100	1.56947900
C	0.03547700	-0.76663300	0.26226900
N	0.82587000	-3.31371800	3.50543400
C	0.13823900	-4.32572400	3.82354900
C	0.71363300	-5.19300900	4.95197100
S	-1.32570600	-4.90401900	2.94883200
C	-2.50630300	-4.98008100	4.29320500
C	-2.73827000	-3.85600100	5.08886800
C	-3.69445400	-3.91850100	6.10203100
C	-4.43368900	-5.08530100	6.29894200
C	-4.21211700	-6.19631200	5.48387800
C	-3.24226900	-6.15141900	4.48331500
C	1.92290400	-5.98284100	4.42098400
F	-0.23317600	-6.09104300	5.40658900
C	2.50003300	-6.93420400	5.41567100
C	3.78925000	-6.83469200	6.00663100
C	4.20308000	-7.83834900	6.92527200
C	5.44989300	-7.79190500	7.52889800
C	6.33507400	-6.74472100	7.24368900
C	5.94911200	-5.74499000	6.34432600
C	1.05804000	-4.33219500	6.18526500
F	1.19524400	-5.10189800	7.27454200
F	0.08897600	-3.44358300	6.45595600
F	2.19982500	-3.65581500	6.02483500
H	0.31919200	-2.50359900	-0.98336600
H	0.76913900	-4.02857400	0.92385800
H	0.30882400	-0.75106000	3.66201500
H	-0.17046900	0.77532000	1.75601000
H	-0.15875500	-0.09898100	-0.57130400
H	-2.17666600	-2.94065800	4.92055900
H	-3.86776400	-3.04890200	6.72871200
H	-5.18268600	-5.12802700	7.08375400
H	-4.78593000	-7.10595900	5.63268400
H	-3.05138400	-7.02293000	3.86398800
H	2.65248600	-5.26126100	4.04822400

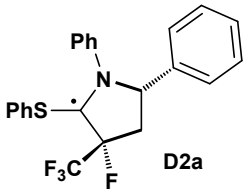
H	1.54115400	-6.53879400	3.55380900
H	1.87870800	-7.77526900	5.71030200
H	3.51921200	-8.65318400	7.14928300
H	5.73923000	-8.57286800	8.22611500
H	7.31145800	-6.70845100	7.71655600
H	6.62896900	-4.92825400	6.11945000
C	4.70233500	-5.78102200	5.73402400
H	4.43090900	-4.98767000	5.04491800



TS3c

C	-0.78891500	-1.04609400	0.04456400
C	-1.69879400	-2.09717000	-0.05917200
C	-2.27155900	-2.63706900	1.09886700
C	-1.90793400	-2.13890300	2.35488400
C	-1.00899900	-1.07932700	2.45047600
C	-0.44651600	-0.53152100	1.29564600
N	-3.13077700	-3.75653500	1.07694300
C	-4.17023600	-3.92063400	0.31326300
C	-4.67758700	-5.33707400	0.46240100
S	-4.70154600	-2.89260400	-1.03961300
C	-6.44278600	-2.73482000	-0.63985900
C	-6.83245300	-2.01067600	0.49013600
C	-8.18756200	-1.85710800	0.77537800
C	-9.14936500	-2.41098700	-0.07215700
C	-8.75493500	-3.12200100	-1.20537400
C	-7.39923900	-3.28965700	-1.49130100
C	-3.42620900	-6.26265100	0.40636300
F	-5.56767200	-5.68269200	-0.53581200
C	-2.21518000	-5.57019800	0.95583900
C	-1.04655600	-5.29076600	0.15117400
C	0.16223800	-4.94749400	0.79931300
C	1.28171200	-4.56293000	0.07278100
C	1.22930500	-4.50662500	-1.32466800
C	0.04309300	-4.84269200	-1.98160200
C	-5.46811000	-5.55774300	1.75931400
F	-5.95323600	-6.81045600	1.80809500
F	-6.51662000	-4.72900000	1.85606200
F	-4.70344700	-5.38127600	2.84366400
H	-0.34176400	-0.63551700	-0.85583900

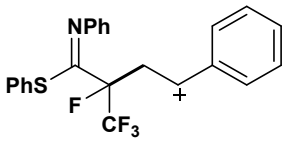
H	-1.93472600	-2.51735500	-1.03153600
H	-2.33862700	-2.59026400	3.24427800
H	-0.73936500	-0.68889800	3.42700800
H	0.26333600	0.28654600	1.37137200
H	-6.07947000	-1.57887400	1.14427500
H	-8.49136200	-1.29978600	1.65636200
H	-10.20478900	-2.28635200	0.15043100
H	-9.50010900	-3.55448900	-1.86610200
H	-7.08660800	-3.85527700	-2.36407400
H	-3.30986900	-6.51829800	-0.64918600
H	-3.62799000	-7.18878000	0.95226900
H	-2.03111500	-5.69442200	2.01944800
H	0.20341800	-4.98289600	1.88560300
H	2.19900400	-4.30370900	0.59375800
H	2.10380400	-4.20608800	-1.89360600
H	-0.00704700	-4.79916000	-3.06586700
C	-1.08297900	-5.22769400	-1.25917000
H	-1.99680200	-5.46485200	-1.79662700



D2a

C	0.08578700	-0.92396000	0.15227000
C	0.60105800	0.36913000	0.06583400
C	0.14322000	1.22792700	-0.93505800
C	-0.82995000	0.80278100	-1.84295300
C	-1.34722000	-0.48757600	-1.74506800
C	-0.88977300	-1.35249300	-0.74889000
N	0.67440000	2.55269500	-1.02568400
C	-0.15722200	3.65099400	-1.13697500
C	0.60528100	4.82135300	-1.65643700
S	-1.68197600	3.75649600	-0.29996200
C	2.03064600	4.29726300	-1.84760700
F	0.59479100	5.90871700	-0.76842700
C	1.91267700	2.76663600	-1.81193000
C	3.10410400	2.05846700	-1.20973300
C	3.78054200	1.08230200	-1.94170300
C	4.87120100	0.40912200	-1.38507300
C	5.28495700	0.70622600	-0.08829400
C	4.60830800	1.68119000	0.65108900
C	0.00189100	5.40581000	-2.93461600
F	0.68237700	6.48262500	-3.35887000
F	-1.27290200	5.78686600	-2.75770100

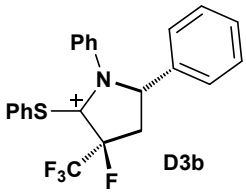
F	0.02071400	4.50147100	-3.92658100
H	0.43929300	-1.59098900	0.93263300
H	1.34187800	0.72205200	0.77747700
H	-1.17563200	1.48751100	-2.61351000
H	-2.10595400	-0.81800000	-2.44801000
H	-1.29500300	-2.35702500	-0.67390100
H	2.60657900	4.65814400	-0.99131800
H	2.50904000	4.64923000	-2.76350300
H	1.74148600	2.37943700	-2.82595700
H	3.44983100	0.84435500	-2.94988400
H	5.39051900	-0.34890600	-1.96380600
H	6.12966100	0.18189000	0.34849000
H	4.92488600	1.91357400	1.66360000
C	3.52540700	2.35396100	0.09235100
H	2.99382500	3.10374100	0.67521600
C	-1.24391900	3.10167100	1.31545700
C	-2.09754100	2.16703500	1.90400300
C	-0.06986000	3.49553900	1.96341500
C	-1.77752500	1.62995000	3.15201400
H	-2.99704400	1.84801100	1.38394200
C	0.25274400	2.93863800	3.19904700
H	0.59038700	4.22327800	1.49801200
C	-0.59973900	2.00661000	3.79679400
H	-2.44267500	0.90338700	3.60907300
H	1.16975100	3.23746500	3.69868100
H	-0.34443700	1.57609500	4.76023800



C3

C	0.91567500	-0.44080800	-0.02094400
C	1.17314700	-1.27948500	1.05838100
C	1.16224800	-0.75776900	2.35242300
C	0.91863900	0.59986700	2.56446300
C	0.63933200	1.42322000	1.48084300
C	0.63915700	0.90725100	0.18661500
N	1.46278300	-1.55998700	3.47267000
C	0.80519000	-2.58440300	3.79572300
C	1.36787700	-3.38018400	4.98267700
S	-0.60336400	-3.25412100	2.90324100
C	-1.80007500	-3.40110800	4.22864400
C	-2.15007500	-2.27916200	4.97601900
C	-3.11594800	-2.39636100	5.97069900

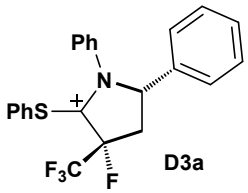
C	-3.74749700	-3.61656800	6.19224400
C	-3.40730400	-4.72733900	5.42407300
C	-2.42571100	-4.62720400	4.44427700
C	2.70812200	-4.01654000	4.58778100
F	0.50434300	-4.37429200	5.36968100
C	3.21000200	-4.95936800	5.60589100
C	4.51122000	-5.10148100	6.04734800
C	4.77067900	-6.13944800	6.99499100
C	6.04237600	-6.32558300	7.48171100
C	7.06930100	-5.48520500	7.03868300
C	6.84170200	-4.45660700	6.11098100
C	1.54042800	-2.49524000	6.22917200
F	1.84116000	-3.27376000	7.27839000
F	0.42260300	-1.83584300	6.52160300
F	2.52622600	-1.61521700	6.08965000
H	0.92906300	-0.84583100	-1.02597800
H	1.40566200	-2.32728200	0.90166500
H	0.94033800	0.98913000	3.57573600
H	0.43131500	2.47356800	1.64783500
H	0.43295800	1.55551500	-0.65661900
H	-1.66920300	-1.32597500	4.78520500
H	-3.38190300	-1.52831200	6.56231900
H	-4.50597800	-3.70218500	6.96143800
H	-3.89832600	-5.67832200	5.59392400
H	-2.14082000	-5.49419500	3.85982900
H	3.41438000	-3.24214400	4.29784200
H	2.50296600	-4.64156100	3.70256800
H	2.47356000	-5.64341800	6.02423000
H	3.94782200	-6.76828400	7.31614400
H	6.25140100	-7.10805200	8.19894800
H	8.07231300	-5.62972900	7.42470000
H	7.66212800	-3.82541300	5.79595500
C	5.57864200	-4.25695700	5.61381000
H	5.39252900	-3.46233800	4.90303000



D3b

C	0.96610500	-1.20501900	0.07379900
C	1.05524700	0.14342700	0.40177000
C	0.05698100	0.99579500	-0.05041400
C	-1.01347500	0.55829800	-0.82087700
C	-1.08467600	-0.79246400	-1.13998100

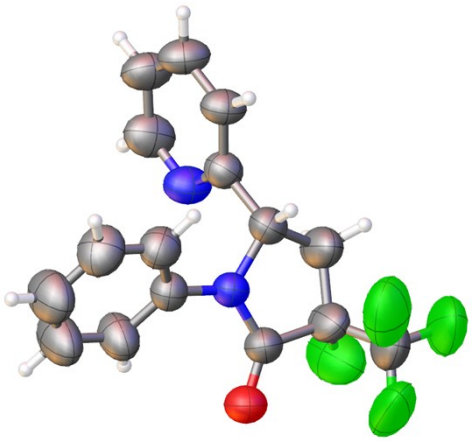
C	-0.09880300	-1.66894200	-0.69355800
N	0.15249800	2.39888200	0.26658900
C	-0.50308700	2.97330400	1.22069100
C	-0.14812600	4.46772700	1.28020700
S	-1.49488300	2.03506800	2.27133700
C	0.92563200	4.63093500	0.19620400
F	0.36650500	4.73873100	2.52025600
C	1.07013100	3.27952200	-0.51594200
C	-1.39067700	5.39108600	1.09209600
F	-1.11408200	6.43776800	0.31768300
F	-1.82257500	5.86558700	2.25201900
F	-2.38840800	4.71383200	0.50995000
H	1.73040800	-1.89050000	0.41844700
H	1.87377500	0.53096700	0.99742800
H	-1.76348200	1.26479700	-1.15865000
H	-1.90870900	-1.15734100	-1.74054500
H	-0.16030500	-2.72053500	-0.94689700
H	1.85019100	4.89063300	0.71064800
H	0.68367700	5.42447700	-0.50410900
C	-2.23444500	3.23950100	3.36740800
C	-3.56171100	3.59868300	3.14469600
C	-1.52507800	3.70047100	4.47394100
C	-4.17561600	4.47522000	4.03191400
H	-4.10061500	3.21111500	2.28844100
C	-2.14966800	4.58360600	5.34568700
H	-0.50335400	3.38438800	4.64329900
C	-3.46836800	4.97197300	5.12257800
H	-5.20492500	4.76960300	3.86742100
H	-1.60711600	4.96160000	6.20364200
H	-3.94987400	5.65848100	5.80896800
C	0.69000800	3.22940700	-1.97778500
C	1.49802400	2.52807900	-2.86899300
C	-0.49087900	3.82021200	-2.43069600
C	1.13469200	2.42353400	-4.20924000
H	2.41068800	2.06276800	-2.51158600
C	-0.85473700	3.71221600	-3.76704100
H	-1.13098400	4.36356900	-1.74313000
C	-0.04158400	3.01369100	-4.65789800
H	1.76952600	1.87987400	-4.89881200
H	-1.77195100	4.17289200	-4.11426900
H	-0.32673100	2.93166800	-5.70026200
H	2.06822900	2.85924700	-0.38350200



C	-0.17366000	-0.25066000	0.06915800
C	0.11493600	1.05971300	0.43294900
C	-0.39014300	2.08587400	-0.35556000
C	-1.16189200	1.85240500	-1.48673500
C	-1.43728300	0.53535200	-1.83660700
C	-0.94419500	-0.51039000	-1.06122000
N	-0.09471000	3.45580700	-0.01556000
C	-0.77313900	4.15687300	0.83651100
C	-0.30898400	5.61399200	0.75575100
S	-2.03884400	3.44744900	1.75841100
C	1.05646000	5.50405900	0.08783800
F	-0.25707800	6.22844600	1.96887100
C	0.98836300	4.21357300	-0.73331700
C	2.24932700	3.39212300	-0.79807700
C	2.71264500	2.94728800	-2.03369000
C	3.85968600	2.16162500	-2.10773400
C	4.53735700	1.81078900	-0.94520200
C	4.06924800	2.24550300	0.29376400
C	-1.29892600	6.42070600	-0.10157400
F	-0.85951700	7.66449500	-0.25264600
F	-2.50705200	6.47354200	0.45148400
F	-1.41653200	5.86028600	-1.30839500
H	0.20830600	-1.06756200	0.66884600
H	0.71376500	1.28727700	1.30710100
H	-1.53499100	2.68652700	-2.07073600
H	-2.03691200	0.32926300	-2.71459700
H	-1.16153400	-1.53467900	-1.33935200
H	1.79129300	5.41684100	0.88923900
H	1.29185200	6.37082400	-0.52655000
H	0.61372000	4.39878000	-1.74188200
H	2.17410000	3.21719400	-2.93604900
H	4.21929000	1.82230500	-3.07185900
H	5.42862800	1.19674200	-1.00107100
H	4.59307000	1.96797000	1.20078800
C	2.92900900	3.03515900	0.36846600
H	2.56060100	3.36144800	1.33658600
C	-2.47466000	4.69200600	2.97312700
C	-3.68225300	5.36843500	2.83294700
C	-1.67685600	4.84218300	4.10533400

C	-4.07938600	6.24405100	3.83826000
H	-4.29757300	5.22115300	1.95399300
C	-2.08176500	5.72776000	5.09560100
H	-0.75330600	4.28455700	4.20480300
C	-3.27942400	6.42668500	4.96159300
H	-5.01489400	6.78094400	3.73967100
H	-1.46519000	5.86426200	5.97563200
H	-3.59340300	7.11074200	5.74105100

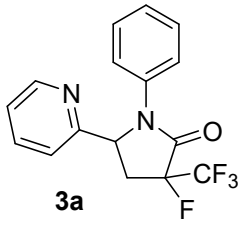
VI. X-Ray Crystal Structure Determinations



Single crystal of **3a** (CCDC 2209201) was obtained by recrystallization from a mixed solvent of acetone/ petroleum ether at room temperature (evaporation in air). The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer.

```
Bond precision:   C-C = 0.0059 A          Wavelength=1.54184

Cell:             a=15.5988(5)     b=8.2297(4)          c=12.1249(6)
                  alpha=90         beta=101.812(4)      gamma=90
Temperature:      295 K

                 Calculated                Reported
Volume           1523.56(12)               1523.56(12)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C16 H12 F4 N2 O           C16 H12 F4 N2 O
Sum formula      C16 H12 F4 N2 O           C16 H12 F4 N2 O
Mr               324.28                    324.28
Dx,g cm-3        1.414                     1.414
Z                4                         4
Mu (mm-1)        1.073                     1.073
F000             664.0                     664.0
F000'            666.66
h,k,lmax         19,10,15                  19,10,15
Nref             3216                      3031
Tmin,Tmax        0.975,0.979               0.809,1.000
Tmin'            0.968

Correction method= # Reported T Limits: Tmin=0.809 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.942           Theta(max)= 76.552

R(reflections)= 0.0722( 1541)                    wR2(reflections)=
                                                 0.2354( 3031)
S = 1.307                  Npar= 208
```

VII. Characterization Data of the Products



3a

Chemical Formula: $C_{16}H_{12}F_4N_2O$

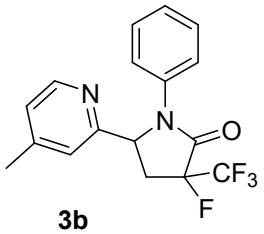
3-fluoro-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3a): yellow solid (mp = 118.3-118.8 ℃), 26.8 mg, (Yield: 83%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.60 – 8.54 (m, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.26 (m, 2H), 7.22 – 7.13 (m, 3H), 5.40 (ddd, *J* = 7.7, 5.6, 3.8 Hz, 1H), 3.22 (td, *J* = 14.8, 7.7 Hz, 1H), 2.77 – 2.62 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.3 Hz), 157.5, 150.1, 137.3, 136.3, 129.0, 126.7, 123.5, 122.9, 121.4, 121.1 (qd, *J* = 282.0, 31.8 Hz), 92.3 (dq, *J* = 199.8, 34.4 Hz), 60.6, 34.1 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.88 (d, *J* = 10.5 Hz, 3F), -167.16 (q, *J* = 10.6 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}F_4N_2O$ 325.0959; Found 325.0958.



3b

Chemical Formula: $C_{17}H_{14}F_4N_2O$

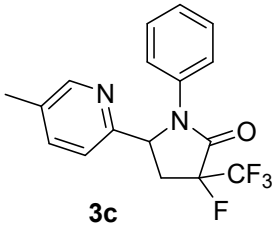
3-fluoro-5-(4-methylpyridin-2-yl)-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3b): yellow solid (mp = 125.6-126.6 ℃), 27.6 mg, (Yield: 81%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.41 (d, *J* = 5.0 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.32 – 7.25 (m, 2H), 7.20 – 7.11 (m, 1H), 7.04 – 6.95 (m, 2H), 5.35 (ddd, *J* = 7.8, 5.5, 3.9 Hz, 1H), 3.19 (td, *J* = 14.9, 7.8 Hz, 1H), 2.66 (dddd, *J* = 25.7, 15.0, 5.5, 1.2 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.1 Hz), 157.4, 149.7, 136.4, 129.0, 126.6, 124.5, 122.7, 122.0 (qd, *J* = 283.3, 32.3 Hz), 92.4 (dq, *J* = 201.0, 34.3 Hz), 60.6, 34.1 (d, *J* = 20.3 Hz), 21.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.91 (d, *J* = 10.4 Hz, 3F), -167.10 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O$ 339.1115; Found 339.1112.



3c

Chemical Formula: $C_{17}H_{14}F_4N_2O$

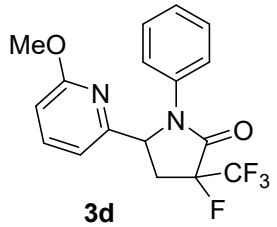
3-fluoro-5-(5-methylpyridin-2-yl)-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3c): white solid (mp = 105.6-127.3 ℃), 27.6 mg, (Yield: 81%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.42 – 8.35 (m, 1H), 7.45 – 7.37 (m, 3H), 7.32 – 7.23 (m, 2H), 7.19 – 7.11 (m, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 5.36 (ddd, *J* = 7.7, 5.7, 3.9 Hz, 1H), 3.19 (td, *J* = 14.6, 7.7 Hz, 1H), 2.67 (dddd, *J* = 25.6, 15.0, 5.7, 1.3 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.3 Hz), 154.6, 150.5, 137.7, 136.4, 133.2, 129.0, 126.7, 122.9, 121.9 (qd, *J* = 284.7, 31.8 Hz), 120.8, 92.4 (dq, *J* = 200.0, 34.2 Hz), 60.4, 34.2 (d, *J* = 20.2 Hz), 18.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.89 (d, *J* = 10.7 Hz, 3F), -167.21 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O$ 339.1115; Found 339.1114.



3d

Chemical Formula: $C_{17}H_{14}F_4N_2O_2$

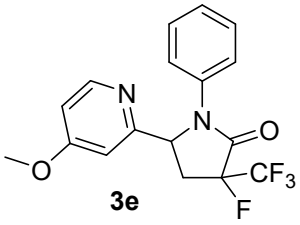
3-fluoro-5-(6-methoxypyridin-2-yl)-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3d): yellow dense oil, 25.3 mg, (Yield: 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.44 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.32 – 7.24 (m, 2H), 7.19 – 7.12 (m, 1H), 6.72 (dd, *J* = 7.2, 0.7 Hz, 1H), 6.61 (dd, *J* = 8.3, 0.7 Hz, 1H), 5.22 (ddd, *J* = 7.8, 5.2, 4.2 Hz, 1H), 3.89 (s, 3H), 3.13 (td, *J* = 14.8, 7.7 Hz, 1H), 2.72 (dddd, *J* = 26.2, 15.0, 5.3, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.4, 163.2 (d, *J* = 22.5 Hz), 154.4, 139.2, 136.5, 128.9, 126.8, 123.4, 122.0 (qd, *J* = 283.5, 32.0 Hz), 114.8, 111.1, 92.2 (dq, *J* = 200.1, 34.0 Hz), 60.3, 53.5, 33.5 (d, *J* = 20.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.01 (d, *J* = 10.7 Hz, 3F), -167.27 (q, *J* = 10.6 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O_2$ 355.1064; Found 355.1063.



3e

Chemical Formula: $C_{17}H_{14}F_4N_2O_2$

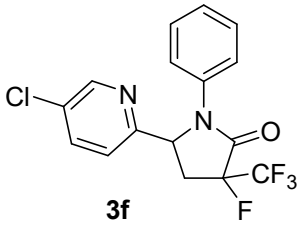
3-fluoro-5-(4-methoxypyridin-2-yl)-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3e): yellow solid (mp = 104.2-124.7 °C), 27.5 mg, (Yield: 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.38 (d, *J* = 5.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.74 – 6.63 (m, 2H), 5.35 (dt, *J* = 8.4, 4.7 Hz, 1H), 3.74 (s, 3H), 3.20 (td, *J* = 15.1, 7.8 Hz, 1H), 2.66 (ddd, *J* = 25.7, 15.1, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 166.6, 163.1 (d, *J* = 22.3 Hz), 159.3, 151.3, 136.4, 129.0, 126.7, 122.7, 121.8 (qd, *J* = 283.4, 31.8 Hz), 109.2, 107.7 (d, *J* = 1.3 Hz), 92.3 (dq, *J* = 199.8, 34.3 Hz), 60.5, 55.2, 34.0 (d, *J* = 20.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.89 (d, *J* = 10.8 Hz, 3F), -166.93 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O_2$ 355.1064; Found 355.1063.



3f

Chemical Formula: $C_{16}H_{11}ClF_4N_2O$

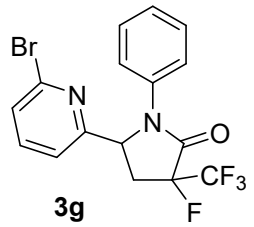
5-(5-chloropyridin-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3f): white solid (mp = 143.9-144.7 ℃), 22.9 mg, (Yield: 64%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.53 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.22 – 7.14 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.39 (ddd, *J* = 7.8, 5.5, 3.8 Hz, 1H), 3.21 (td, *J* = 15.0, 7.7 Hz, 1H), 2.66 (dddd, *J* = 25.5, 15.1, 5.5, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 22.3 Hz), 155.6, 149.1, 137.0, 136.1, 131.9, 129.2, 126.9, 122.9, 122.2, 121.8 (qd, *J* = 283.4, 31.8 Hz), 92.2 (dq, *J* = 200.2, 34.2 Hz), 60.0, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.86 (d, *J* = 10.6 Hz, 3F), -167.02 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_4N_2O$ 359.0569; Found 359.0566.



3g

Chemical Formula: $C_{16}H_{11}BrF_4N_2O$

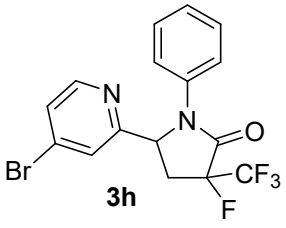
5-(6-bromopyridin-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3g): dense yellow oil, 26.3 mg, (Yield: 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.50 – 7.42 (m, 3H), 7.41 – 7.36 (m, 1H), 7.32 (dd, *J* = 8.7, 7.2 Hz, 2H), 7.22 – 7.15 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 5.40 (td, *J* = 4.9, 2.5 Hz, 1H), 3.22 (ddd, *J* = 17.0, 15.1, 7.9 Hz, 1H), 2.72 – 2.57 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 22.5 Hz), 159.2, 142.3, 139.6, 136.1, 129.2, 128.0, 126.9, 122.6, 121.7 (qd, *J* = 283.3, 31.5 Hz), 119.8, 92.3 (dq, *J* = 199.9, 34.3 Hz), 60.0, 34.0 (d, *J* = 20.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.79 (d, *J* = 10.3 Hz, 3F), -166.94 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrF_4N_2O$ 403.0064; Found 403.0062.



3h

Chemical Formula: $C_{16}H_{11}BrF_4N_2O$

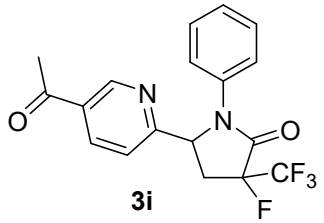
5-(4-bromopyridin-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3h): yellow solid (mp = 82.1-82.7 ℃), 33.2 mg, (Yield: 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.38 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.44 – 7.27 (m, 6H), 7.22 – 7.12 (m, 1H), 5.36 (ddd, *J* = 7.7, 5.4, 3.8 Hz, 1H), 3.20 (td, *J* = 15.0, 7.8 Hz, 1H), 2.67 (dddd, *J* = 25.4, 15.1, 5.5, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 22.2 Hz), 159.0, 150.8, 136.0, 133.9, 129.2, 127.0, 126.9, 125.0, 122.9, 121.8 (qd, *J* = 283.4, 31.8 Hz), 92.1 (dq, *J* = 200.3, 34.2 Hz), 60.1, 33.8 (d, *J* = 20.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.88 (d, *J* = 10.7 Hz, 3F), -166.98 (dt, *J* = 13.2, 10.6 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrF_4N_2O$ 403.0064; Found 403.0062.



3i

Chemical Formula: $C_{18}H_{14}F_4N_2O_2$

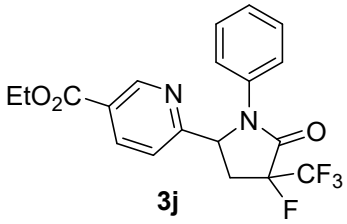
5-(5-acetylpyridin-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3i): yellow solid (mp = 96.9-98.7 ℃), 23.9 mg, (Yield: 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 9.11 (d, *J* = 2.2 Hz, 1H), 8.14 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.34 – 7.25 (m, 3H), 7.22 – 7.13 (m, 1H), 5.49 (ddd, *J* = 8.5, 5.3, 3.7 Hz, 1H), 3.24 (td, *J* = 15.4, 7.9 Hz, 1H), 2.74 – 2.55 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 195.9, 163.0 (d, *J* = 22.2 Hz), 161.8, 150.2, 136.9, 136.1, 129.2, 126.9, 122.6, 121.7 (qd, *J* = 283.4, 31.6 Hz), 121.2, 92.2 (dq, *J* = 200.1, 34.3 Hz), 60.3, 33.8 (d, *J* = 20.7 Hz), 26.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.84 (d, *J* = 10.7 Hz, 3F), -166.85 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_4N_2O_2$ 367.1064; Found 367.1062.



3j

Chemical Formula: $C_{19}H_{16}F_4N_2O_3$

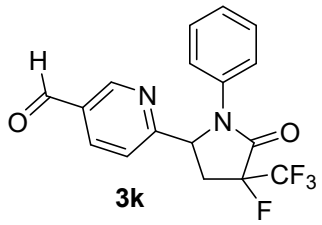
ethyl 6-(4-fluoro-5-oxo-1-phenyl-4-(trifluoromethyl)pyrrolidin-2-yl)nicotinate (3j): dense yellow oil, 25.9 mg, (Yield: 64%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 9.17 (d, *J* = 2.1 Hz, 1H), 8.21 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.33 – 7.22 (m, 3H), 7.20 – 7.13 (m, 1H), 5.52 – 5.44 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.24 (td, *J* = 15.3, 7.8 Hz, 1H), 2.67 (ddd, *J* = 25.3, 15.1, 5.4 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.5, 163.0 (d, *J* = 22.2 Hz), 161.7, 151.2, 138.4, 136.1, 129.2, 126.9, 126.1, 122.6, 121.8 (qd, *J* = 283.3, 31.7 Hz), 120.9, 92.2 (dq, *J* = 200.2, 34.2 Hz), 61.6, 60.4, 33.9 (d, *J* = 20.7 Hz), 14.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.84 (d, *J* = 10.6 Hz, 3F), -166.91 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_4N_2O_3$ 397.1170; Found 397.1168.



3k

Chemical Formula: $C_{17}H_{12}F_4N_2O_2$

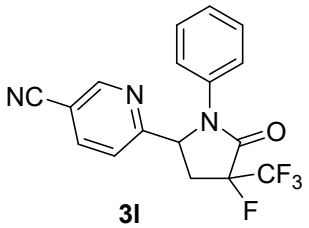
6-(4-fluoro-5-oxo-1-phenyl-4-(trifluoromethyl)pyrrolidin-2-yl)nicotinaldehyde (3k): dense brown oil, 15.9 mg, (Yield: 45%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 10.06 (s, 1H), 9.04 (dd, *J* = 2.2, 0.8 Hz, 1H), 8.09 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.21 – 7.13 (m, 1H), 5.51 (ddd, *J* = 8.0, 5.3, 3.6 Hz, 1H), 3.26 (ddd, *J* = 16.1, 15.1, 7.9 Hz, 1H), 2.75 – 2.61 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 189.7, 163.3, 163.0 (d, *J* = 22.5 Hz), 152.1, 137.4, 136.1, 131.0, 129.2, 127.0, 122.6, 121.7, 121.7 (qd, *J* = 284.4, 31.8 Hz), 92.2 (dq, *J* = 200.0, 34.3 Hz), 60.4, 33.8 (d, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.81 (d, *J* = 10.5 Hz, 3F), -166.82 (q, *J* = 10.4 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}F_4N_2O_2$ 353.0908; Found 353.0907.



3l

Chemical Formula: $C_{17}H_{11}F_4N_3O$

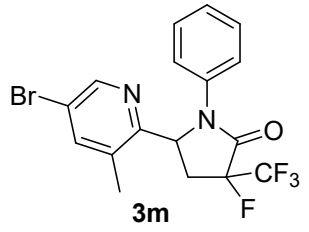
6-(4-fluoro-5-oxo-1-phenyl-4-(trifluoromethyl)pyrrolidin-2-yl)nicotinonitrile (3l): yellow solid (mp = 157.1-157.9 °C), 22.9 mg, (Yield: 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.85 (d, *J* = 2.0 Hz, 1H), 7.89 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 7.23 – 7.16 (m, 1H), 5.49 (ddd, *J* = 8.3, 5.1, 3.6 Hz, 1H), 3.25 (ddd, *J* = 16.8, 15.1, 8.0 Hz, 1H), 2.72 – 2.57 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 162.9 (d, *J* = 22.0 Hz), 161.9, 152.7, 140.6, 135.9, 129.3, 127.1, 122.5, 121.6 (qd, *J* = 283.2, 31.5 Hz), 121.3, 115.9, 109.8, 92.1 (dq, *J* = 200.1, 34.5 Hz), 60.2, 33.7 (d, *J* = 20.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.79 (d, *J* = 10.4 Hz, 3F), -166.60 (q, *J* = 10.6 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}F_4N_3O$ 350.0911; Found 350.0908.



3m

Chemical Formula: $C_{17}H_{13}BrF_4N_2O$

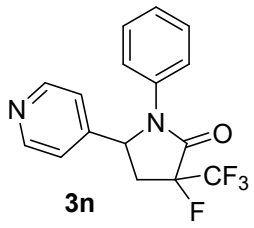
5-(5-bromo-3-methylpyridin-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3m): yellow solid (mp = 110.6-111.1 ℃), 26.8 mg, (Yield: 63%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.47 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.30 – 7.14 (m, 5H), 5.46 (td, *J* = 6.9, 4.2 Hz, 1H), 3.12 (ddd, *J* = 14.7, 9.3, 7.3 Hz, 1H), 2.84 – 2.69 (m, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 22.6 Hz), 152.8, 149.0, 140.9, 136.3, 133.1, 129.0, 127.3, 124.1, 122.1 (qd, *J* = 283.9, 32.3 Hz), 120.2, 91.9 (dq, *J* = 201.5, 33.8 Hz), 56.5, 32.8 (d, *J* = 20.8 Hz), 17.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.06 (d, *J* = 10.9 Hz, 3F), -168.42 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}BrF_4N_2O$ 417.0220; Found 417.0219.



3n

Chemical Formula: $C_{16}H_{12}F_4N_2O$

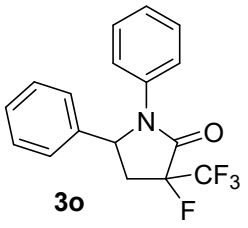
3-fluoro-1-phenyl-5-(pyridin-4-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3n): yellow solid (mp = 156.9-157.7 ℃), 24.4 mg, (Yield: 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.60 – 8.55 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.27 (m, 2H), 7.21 – 7.14 (m, 3H), 5.31 – 5.24 (m, 1H), 3.26 (td, *J* = 15.3, 7.9 Hz, 1H), 2.50 – 2.36 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 162.9 (d, *J* = 22.2 Hz), 150.8, 147.6, 135.7, 129.2, 127.1, 122.7, 121.6 (qd, *J* = 283.5, 31.6 Hz), 121.2, 92.0 (dq, *J* = 200.1, 34.4 Hz), 58.3, 35.3 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.78 (d, *J* = 10.4 Hz, 3F), -165.85 (q, *J* = 10.5 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}F_4N_2O$ 325.0959; Found 325.0956.



3o

Chemical Formula: $C_{17}H_{13}F_4NO$

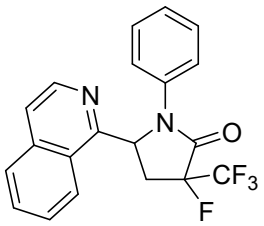
3-fluoro-1,5-diphenyl-3-(trifluoromethyl)pyrrolidin-2-one (3o): white solid (mp = 106.9-107.6 ℃), 16.5 mg, (Yield: 51%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.39 – 7.34 (m, 2H), 7.34 – 7.21 (m, 7H), 7.16 – 7.11 (m, 1H), 5.23 (ddd, *J* = 7.6, 6.1, 4.1 Hz, 1H), 3.23 (ddd, *J* = 15.2, 12.8, 7.6 Hz, 1H), 2.47 (dddd, *J* = 26.0, 15.2, 6.1, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.3 Hz), 138.6, 136.2, 129.2, 128.9, 128.7, 126.7, 126.5, 123.3, 121.9 (qd, *J* = 283.6, 31.9 Hz), 92.2 (dq, *J* = 199.8, 34.2 Hz), 59.5 (d, *J* = 2.4 Hz), 36.2 (d, *J* = 20.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.85 (d, *J* = 10.7 Hz, 3F), -166.37 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}F_4NO$ 324.1006; Found 324.1005.



3p

Chemical Formula: $C_{20}H_{14}F_4N_2O$

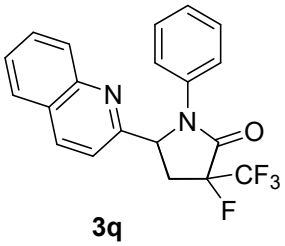
3-fluoro-5-(isoquinolin-1-yl)-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3p): white solid (mp = 101.4-102.6 ℃), 15.9 mg, (Yield: 42%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.47 (d, *J* = 5.6 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.69 (dddd, *J* = 21.8, 8.3, 6.9, 1.3 Hz, 2H), 7.59 (d, *J* = 5.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.09 – 7.01 (m, 1H), 6.20 (q, *J* = 6.6, 5.9 Hz, 1H), 3.32 (ddd, *J* = 14.9, 11.3, 7.6 Hz, 1H), 2.96 – 2.80 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.6 Hz), 155.2, 141.9, 136.7, 136.6, 130.5, 128.8, 128.3, 128.2, 126.7, 126.0, 123.3, 122.5, 122.1 (qd, *J* = 283.9, 30.9 Hz), 121.5, 92.1 (dq, *J* = 200.5, 34.0 Hz), 58.4, 33.7 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.92 (d, *J* = 10.7 Hz, 3F), -167.98 (s, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}F_4N_2O$ 375.1115; Found 375.1114.



3q

Chemical Formula: $C_{20}H_{14}F_4N_2O$

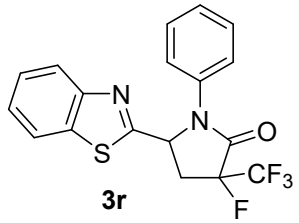
3-fluoro-1-phenyl-5-(quinolin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3q): brown solid (mp = 151.3-152.1 ℃), 27.9 mg, (Yield: 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.13 – 8.02 (m, 2H), 7.80 – 7.69 (m, 2H), 7.58 – 7.48 (m, 3H), 7.31 – 7.21 (m, 3H), 7.14 – 7.06 (m, 1H), 5.62 (ddd, *J* = 7.8, 5.8, 3.8 Hz, 1H), 3.34 (td, *J* = 14.8, 7.8 Hz, 1H), 2.69 (dddd, *J* = 25.7, 15.2, 5.9, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.2 (d, *J* = 22.1 Hz), 158.1, 147.7, 138.0, 136.4, 130.3, 129.1, 127.7, 127.5, 127.2, 126.7, 122.6, 121.9 (qd, *J* = 283.6, 31.7 Hz), 117.6, 117.6, 92.3 (dq, *J* = 199.9, 34.3 Hz), 61.2, 34.2 (d, *J* = 20.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.77 (d, *J* = 10.8 Hz, 3F), -166.55 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}F_4N_2O$ 375.1115; Found 375.1111.



3r

Chemical Formula: $C_{18}H_{12}F_4N_2OS$

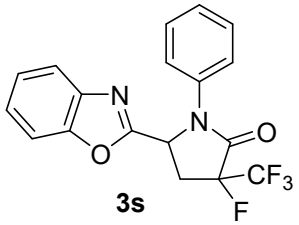
5-(benzo[d]thiazol-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3r): white solid (mp = 140.3-141.2 ℃), 21.3 mg, (Yield: 56%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.99 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.57 – 7.45 (m, 3H), 7.43 – 7.30 (m, 3H), 7.24 – 7.17 (m, 1H), 5.81 (ddd, *J* = 8.0, 5.4, 3.6 Hz, 1H), 3.38 (td, *J* = 15.2, 7.9 Hz, 1H), 2.85 (dddd, *J* = 24.9, 15.3, 5.4, 1.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 169.0, 162.6 (d, *J* = 22.1 Hz), 152.4, 135.8, 135.0, 129.3, 127.3, 126.6, 126.0, 123.5, 123.0, 122.0, 121.7 (qd, *J* = 283.5, 31.6 Hz), 91.7 (dq, *J* = 201.9, 34.4 Hz), 57.8, 34.2 (d, *J* = 21.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.80 (d, *J* = 10.6 Hz, 3F), -166.09 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_4N_2OS$ 381.0679; Found 381.0678.



3s

Chemical Formula:
$C_{18}H_{12}F_4N_2O_2$

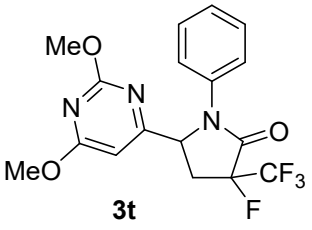
5-(benzo[d]oxazol-2-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3s): white solid (mp = 154.7-155.4 ℃), 19.0 mg, (Yield: 52%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.71 – 7.65 (m, 1H), 7.51 – 7.44 (m, 3H), 7.38 – 7.30 (m, 4H), 7.24 – 7.17 (m, 1H), 5.59 (ddd, *J* = 7.9, 5.8, 3.5 Hz, 1H), 3.29 (ddd, *J* = 15.1, 13.3, 7.9 Hz, 1H), 3.02 – 2.86 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 162.4 (d, *J* = 22.2 Hz), 161.3, 150.9, 140.4, 135.7, 129.3, 127.6, 126.2, 125.0, 123.2, 121.7 (qd, *J* = 283.7, 31.8 Hz), 120.6, 111.1, 91.3 (dq, *J* = 202.2, 34.5 Hz), 53.7, 31.8 (d, *J* = 21.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.92 (d, *J* = 10.7 Hz, 3F), -168.06 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_4N_2O_2$ 365.0908; Found 365.0907.



3t

Chemical Formula: $C_{17}H_{15}F_4N_3O_3$

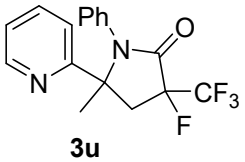
5-(2,6-dimethoxypyrimidin-4-yl)-3-fluoro-1-phenyl-3-(trifluoromethyl)pyrrolidin-2-one (3t): dense yellow oil, 28.2 mg, (Yield: 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.50 – 7.43 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.16 (m, 1H), 6.23 (s, 1H), 5.18 (dt, *J* = 8.3, 4.3 Hz, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.14 (ddd, *J* = 17.7, 15.2, 8.1 Hz, 1H), 2.71 – 2.54 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 172.4, 167.9, 165.9, 163.0 (d, *J* = 22.1 Hz), 136.3, 129.2, 126.9, 122.5, 121.7 (qd, *J* = 283.3, 31.7 Hz), 99.5, 92.0 (dq, *J* = 200.4, 34.3 Hz), 59.3, 55.1, 54.1, 33.0 (d, *J* = 21.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.94 (d, *J* = 10.3 Hz, 3F), -166.74 (q, *J* = 10.5 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}F_4N_3O_3$ 386.1122; Found 386.1121.



3u

Chemical Formula: $C_{17}H_{14}F_4N_2O$

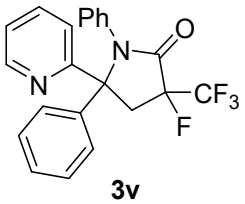
3-fluoro-5-methyl-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3u): yellow solid (mp = 138.4-139.7 ℃), 24.4 mg, (Yield: 72%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.69 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.68 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.30 – 7.22 (m, 4H), 6.92 – 6.83 (m, 2H), 3.08 (ddd, *J* = 27.3, 15.8, 1.0 Hz, 1H), 2.73 (dd, *J* = 23.0, 15.7 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.9 (d, *J* = 22.0 Hz), 161.3, 149.7, 136.8, 134.9, 129.0, 128.1, 127.2, 123.0, 122.0 (qd, *J* = 284.0, 31.7 Hz), 120.4, 92.0 (dq, *J* = 198.4, 33.8 Hz), 65.5, 42.0 (d, *J* = 20.8 Hz), 24.7 (d, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.91 (d, *J* = 10.1 Hz, 3F), -166.69 (q, *J* = 9.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O$ 339.1115; Found 339.1114.



3v

Chemical Formula: $C_{22}H_{16}F_4N_2O$

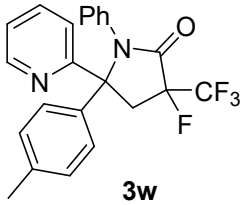
3-fluoro-1,5-diphenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3v): dense yellow oil, 30.1 mg, (Yield: 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.75 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.59 (td, *J* = 7.8, 1.8 Hz, 1H), 7.32 – 7.24 (m, 6H), 7.23 – 7.18 (m, 1H), 7.14 – 7.03 (m, 5H), 3.91 (dd, *J* = 26.3, 15.5 Hz, 1H), 3.17 (dd, *J* = 25.7, 15.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.4 (d, *J* = 21.9 Hz), 159.5, 149.2, 140.2, 136.3, 136.0, 128.5, 128.4, 128.3, 128.2, 127.1, 126.6, 123.9, 123.0, 121.8 (qd, *J* = 284.8, 31.6 Hz), 92.0 (dq, *J* = 198.1, 34.3 Hz), 73.6, 44.5 (d, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.24 (d, *J* = 10.1 Hz, 3F), -167.89 (q, *J* = 10.1 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}F_4N_2O$ 401.1272; Found 401.1269.



3w

Chemical Formula: $C_{23}H_{18}F_4N_2O$

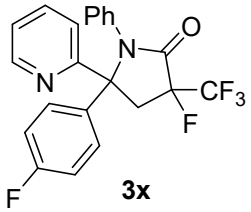
3-fluoro-1-phenyl-5-(pyridin-2-yl)-5-(p-tolyl)-3-(trifluoromethyl)pyrrolidin-2-one (3w): white solid (mp = 102.0-103.1 ℃), 30.3 mg, (Yield: 73%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.76 – 8.70 (m, 1H), 7.58 (td, *J* = 7.8, 1.9 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.03 (m, 10H), 3.87 (dd, *J* = 26.4, 15.5 Hz, 1H), 3.15 (dd, *J* = 25.7, 15.5 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.4 (d, *J* = 22.3 Hz), 159.7, 149.1, 138.2, 137.2, 136.2, 136.0, 129.1, 128.4, 128.1, 127.1, 126.7, 123.9, 122.9, 121.8 (qd, *J* = 282.8, 31.6 Hz), 92.0 (dq, *J* = 197.2, 34.2 Hz), 73.5, 44.4 (d, *J* = 20.8 Hz), 20.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.24 (d, *J* = 10.0 Hz, 3F), -167.86 (q, *J* = 9.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}F_4N_2O$ 425.1428; Found 425.1427.



3x

Chemical Formula: $C_{22}H_{15}F_5N_2O$

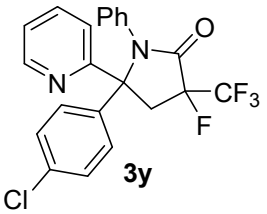
3-fluoro-5-(4-fluorophenyl)-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3x): dense yellow oil, 29.8 mg, (Yield: 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.75 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.64 (td, *J* = 7.8, 1.9 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.15 – 7.09 (m, 3H), 7.07 – 7.02 (m, 2H), 7.00 – 6.94 (m, 2H), 3.82 (dd, *J* = 25.3, 15.5 Hz, 1H), 3.14 (dd, *J* = 26.6, 15.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.2 (d, *J* = 21.9 Hz), 162.2 (d, *J* = 249.1 Hz), 159.5, 149.3, 136.6, 135.7, 130.2 (d, *J* = 8.2 Hz), 128.5, 127.1, 126.3, 123.6, 123.1, 121.8 (qd, *J* = 282.6, 31.5 Hz), 115.4 (d, *J* = 21.7 Hz), 91.9 (dq, *J* = 197.8, 34.2 Hz), 73.0, 44.9 (d, *J* = 20.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.28 (d, *J* = 9.7 Hz, 3F), -113.08 (s, 1F), -168.53 (q, *J* = 9.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}F_5N_2O$ 419.1177; Found 419.1175.



3y

Chemical Formula: $C_{22}H_{15}ClF_4N_2O$

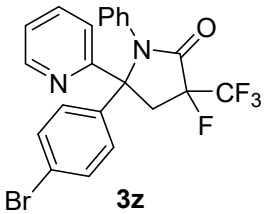
5-(4-chlorophenyl)-3-fluoro-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3y): dense colorless oil, 30.9 mg, (Yield: 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.75 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.62 (td, *J* = 7.8, 1.8 Hz, 1H), 7.31 – 7.25 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.07 – 7.01 (m, 2H), 3.88 (dd, *J* = 25.8, 15.5 Hz, 1H), 3.09 (dd, *J* = 25.6, 15.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.2 (d, *J* = 21.9 Hz), 159.1, 149.3, 138.7, 136.6, 135.7, 134.3, 129.6, 128.6, 128.6, 127.2, 126.3, 123.7, 123.2, 121.7 (qd, *J* = 282.6, 31.4 Hz), 91.8 (dq, *J* = 197.8, 34.3 Hz), 73.0, 44.7 (d, *J* = 20.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.25 (d, *J* = 10.1 Hz, 3F), -168.13 (q, *J* = 10.1 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}ClF_4N_2O$ 435.0882; Found 435.0878.



3z

Chemical Formula: $C_{22}H_{15}BrF_4N_2O$

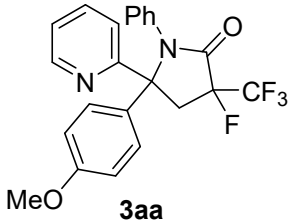
5-(4-bromophenyl)-3-fluoro-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3z): white solid (mp = 107.6-108.5 ℃), 31.8 mg, (Yield: 66%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.75 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.61 (td, *J* = 7.8, 1.9 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.29 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.16 – 7.10 (m, 3H), 7.07 – 7.00 (m, 2H), 3.89 (dd, *J* = 26.0, 15.5 Hz, 1H), 3.08 (dd, *J* = 25.3, 15.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.3 (d, *J* = 22.1 Hz), 159.0, 149.3, 139.4, 136.5, 135.7, 131.6, 129.9, 128.6, 127.2, 126.3, 123.8, 123.2, 122.5, 121.7 (qd, *J* = 282.7, 31.4 Hz), 91.8 (dq, *J* = 197.8, 34.3 Hz), 73.1, 44.6 (d, *J* = 20.9 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.25 (d, *J* = 9.8 Hz, 3F), -168.01 (q, *J* = 10.1 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}BrF_4N_2O$ 479.0377; Found 479.0375.



3aa

Chemical Formula: $C_{23}H_{18}F_4N_2O_2$

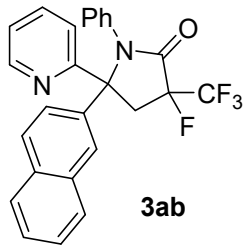
3-fluoro-5-(4-methoxyphenyl)-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3aa): dense brown oil, 33.3 mg, (Yield: 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.73 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H), 7.61 (td, *J* = 7.8, 1.8 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.19 – 7.04 (m, 7H), 6.83 – 6.77 (m, 2H), 3.84 – 3.73 (m, 4H), 3.17 (dd, *J* = 26.9, 15.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 164.2 (d, *J* = 21.7 Hz), 160.0, 159.3, 149.1, 136.4, 136.0, 131.7, 131.7, 129.6, 128.4, 127.0, 126.6, 123.6, 122.9, 121.8 (qd, *J* = 284.0, 31.2 Hz), 113.7, 92.0 (dq, *J* = 197.4, 34.1 Hz), 55.2, 44.5 (d, *J* = 20.6 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.25 (d, *J* = 9.9 Hz, 3F), -168.47 (q, *J* = 10.0 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}F_4N_2O_2$ 434.1377; Found 434.1374.



3ab

Chemical Formula: $C_{26}H_{18}F_4N_2O$

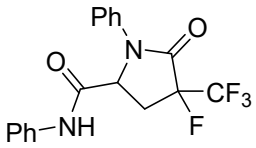
3-fluoro-5-(naphthalen-2-yl)-1-phenyl-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (3ab): brown solid (mp = 248.5-249.3 °C), 15.6 mg, (Yield: 34%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.77 – 8.68 (m, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.25 – 7.19 (m, 1H), 7.17 – 7.00 (m, 8H), 6.49 (d, *J* = 7.5 Hz, 1H), 4.85 (dd, *J* = 34.4, 15.1 Hz, 1H), 3.32 (dd, *J* = 15.0, 9.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 165.6 (d, *J* = 22.7 Hz), 157.8, 149.3, 137.5, 136.5, 135.5, 134.9, 129.9, 129.6, 129.6, 128.5, 127.8, 127.6, 126.5, 126.0, 125.9, 125.6, 124.4, 123.1, 121.5 (qd, *J* = 284.3, 32.8 Hz), 92.1 (dq, *J* = 194.9, 33.5 Hz), 74.4 (d, *J* = 3.0 Hz), 41.4 (d, *J* = 22.0 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -78.82 (d, *J* = 11.5 Hz, 3F), -161.79 (s, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{19}F_4N_2O$ 451.1428; Found 451.1425.



3ac

Chemical Formula: $C_{18}H_{14}F_4N_2O_2$

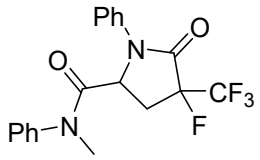
4-fluoro-5-oxo-*N*,1-diphenyl-4-(trifluoromethyl)pyrrolidine-2-carboxamide (3ac): dense yellow oil, 18.7 mg, (Yield: 51%).

^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm) = 9.76 (s, 1H), 7.67 – 7.60 (m, 2H), 7.61 – 7.54 (m, 2H), 7.48 – 7.38 (m, 2H), 7.32 – 7.24 (m, 3H), 7.14 – 7.05 (m, 1H), 5.20 (dt, *J* = 8.2, 4.1 Hz, 1H), 3.33 (ddd, *J* = 19.8, 15.4, 8.2 Hz, 1H), 2.88 – 2.74 (m, 1H).

^{13}C NMR (101 MHz, Acetone-d_6) δ (ppm) = 167.8, 163.5 (d, *J* = 22.4 Hz), 139.1, 138.0, 129.9, 129.6, 127.7, 125.1, 124.6, 124.3, 123.5, 121.8, 121.5, 120.4, 94.2, 93.8, 92.2, 91.8, 59.6, 31.2 (d, *J* = 21.5 Hz).

^{19}F NMR (376 MHz, Acetone-d_6) δ (ppm) = -80.67 (d, J = 10.1 Hz, 3F), -167.55 (q, J = 10.1 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_4N_2O_2$ 367.1064; Found 367.1061.



3ad

Chemical Formula: $C_{19}H_{16}F_4N_2O_2$

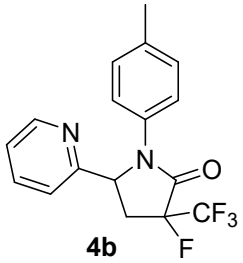
4-fluoro-*N*-methyl-5-oxo-*N*,1-diphenyl-4-(trifluoromethyl)pyrrolidine-2-carboxamide (3ad): dense yellow oil, 22.4 mg, (Yield: 59%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 7.55 – 7.47 (m, 3H), 7.46 – 7.39 (m, 2H), 7.35 – 7.27 (m, 3H), 7.06 (dd, J = 8.0, 1.6 Hz, 2H), 4.62 (ddd, J = 7.9, 5.3, 4.1 Hz, 1H), 3.21 (s, 3H), 2.76 – 2.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 168.0, 162.7 (d, J = 22.4 Hz), 141.7, 136.2, 130.5, 129.2, 129.2, 127.6, 126.9, 123.6, 123.3, 122.9, 120.4, 120.1, 92.5, 92.2, 90.5, 90.2, 54.8, 38.0, 30.6 (d, J = 21.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.25 (d, J = 10.8 Hz, 3F), -167.30 (q, J = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_4N_2O_2$ 381.1221; Found 381.1220.



4b

Chemical Formula: $C_{17}H_{14}F_4N_2O$

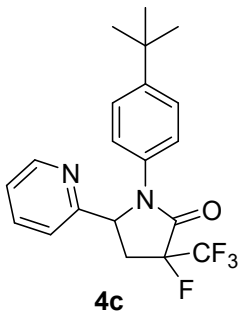
3-fluoro-5-(pyridin-2-yl)-1-(p-tolyl)-3-(trifluoromethyl)pyrrolidin-2-one (4b): yellow solid (mp = 85.6-86.8 ℃), 26.2 mg, (Yield: 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.62 – 8.54 (m, 1H), 7.60 (td, J = 7.7, 1.8 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.22 – 7.12 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 5.35 (ddd, J = 7.8, 5.6, 4.0 Hz, 1H), 3.20 (td, J = 14.9, 7.7 Hz, 1H), 2.68 (dddd, J = 25.8, 15.1, 5.7, 1.3 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, J = 22.0 Hz), 157.7, 150.0, 137.2, 136.7, 133.8, 129.6, 123.4, 122.8, 121.9 (qd, J = 284.5, 32.1 Hz), 121.4, 92.3 (dq, J = 199.6, 34.2 Hz), 60.7, 34.0 (d, J = 20.5 Hz), 20.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.90 (d, J = 10.8 Hz, 3F), -167.06 (q, J = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O$ 339.1115; Found 339.1112.



4c

Chemical Formula: $C_{20}H_{20}F_4N_2O$

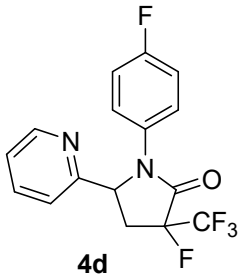
1-(4-(tert-butyl)phenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4c): white solid (mp = 121.9-123.4 ℃), 28.3 mg, (Yield: 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.59 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 2H), 5.39 (ddd, *J* = 7.9, 5.2, 3.8 Hz, 1H), 3.20 (ddd, *J* = 16.0, 15.1, 7.8 Hz, 1H), 2.66 (dddd, *J* = 25.4, 15.1, 5.2, 1.2 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.1 Hz), 157.9, 150.0, 149.7, 137.3, 133.7, 125.9, 123.4, 122.2, 121.9 (qd, *J* = 284.8, 31.9 Hz), 121.2, 92.4 (dq, *J* = 199.5, 34.1 Hz), 60.6, 34.4, 34.1 (d, *J* = 20.5 Hz), 31.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.89 (d, *J* = 10.6 Hz, 3F), -166.98 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}F_4N_2O$ 351.1585; Found 351.1581.



4d

Chemical Formula: $C_{16}H_{11}F_5N_2O$

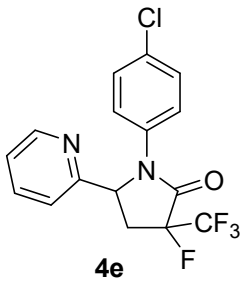
3-fluoro-1-(4-fluorophenyl)-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4d): white solid (mp = 88.4-89.1 ℃), 25.8 mg, (Yield: 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.62 – 8.54 (m, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.22 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.00 – 6.93 (m, 2H), 5.32 (ddd, *J* = 7.6, 6.0, 3.9 Hz, 1H), 3.22 (ddd, *J* = 15.0, 12.9, 7.6 Hz, 1H), 2.74 (dddd, *J* = 25.9, 15.1, 5.9, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.2 (d, *J* = 22.4 Hz), 160.7 (d, *J* = 247.5 Hz), 156.9, 150.2, 137.3, 132.2 (d, *J* = 3.1 Hz), 125.1 (d, *J* = 8.4 Hz), 123.7, 121.9 (qd, *J* = 283.6, 31.9 Hz), 121.7, 115.9 (d, *J* = 22.8 Hz), 92.2 (dq, *J* = 200.3, 34.2 Hz), 60.8, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.92 (d, *J* = 10.7 Hz, 3F), -114.00 (s, 1F), -167.48 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}F_5N_2O$ 343.0864; Found 343.0863.



4e

Chemical Formula: $C_{16}H_{11}ClF_4N_2O$

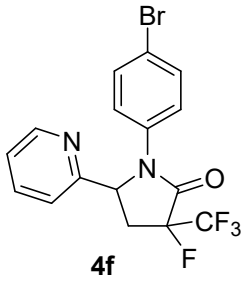
1-(4-chlorophenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4e): white solid (mp = 112.4-113.2 ℃), 24.9 mg, (Yield: 69%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.61 – 8.55 (m, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.27 – 7.19 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 5.35 (ddd, *J* = 7.7, 5.7, 3.8 Hz, 1H), 3.22 (td, *J* = 14.6, 7.7 Hz, 1H), 2.70 (dddd, *J* = 25.7, 15.0, 5.7, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.4 Hz), 157.1, 150.2, 137.3, 134.9, 132.2, 129.2, 124.1, 123.7, 121.8 (qd, *J* = 283.5, 31.8 Hz), 121.4, 92.2 (dq, *J* = 200.3, 34.3 Hz), 60.6, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.88 (d, *J* = 10.4 Hz, 3F), -167.19 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_4N_2O$ 359.0569; Found 359.0568.



4f

Chemical Formula: $C_{16}H_{11}BrF_4N_2O$

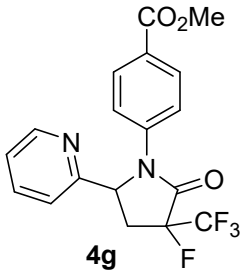
1-(4-bromophenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4f): white solid (mp = 115.6-116.8 ℃), 22.7 mg, (Yield: 56%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.58 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.63 (td, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.22 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.35 (ddd, *J* = 7.8, 5.7, 3.8 Hz, 1H), 3.22 (ddd, *J* = 15.1, 14.2, 7.7 Hz, 1H), 2.69 (dddd, *J* = 25.6, 15.1, 5.7, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.4 Hz), 157.0, 150.2, 137.4, 135.4, 132.1, 124.3, 123.7, 121.8 (qd, *J* = 283.6, 31.8 Hz), 121.4, 120.0, 92.2 (dq, *J* = 200.4, 34.3 Hz), 60.5, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.86 (d, *J* = 10.8 Hz, 3F), -167.17 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrF_4N_2O$ 403.0064; Found 403.0062.



4g

Chemical Formula: $C_{18}H_{14}F_4N_2O_3$

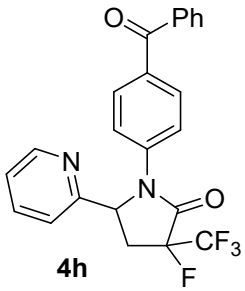
methyl 4-(3-fluoro-2-oxo-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate (4g): white solid (mp = 149.9-150.6 ℃), 25.1 mg, (Yield: 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.60 – 8.54 (m, 1H), 8.00 – 7.92 (m, 2H), 7.67 – 7.55 (m, 3H), 7.21 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 5.46 (ddd, *J* = 7.8, 5.4, 3.5 Hz, 1H), 3.87 (s, 3H), 3.24 (td, *J* = 15.3, 7.8 Hz, 1H), 2.76 – 2.61 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 166.1, 163.3 (d, *J* = 22.6 Hz), 157.2, 150.2, 140.3, 137.4, 130.5, 127.9, 123.6, 121.8, 121.7 (qd, *J* = 284.4, 31.6 Hz), 121.1, 92.3 (dq, *J* = 201.0, 34.3 Hz), 60.4, 52.2, 34.1 (d, *J* = 20.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.83 (d, *J* = 10.5 Hz, 3F), -166.95 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}F_4N_2O_3$ 383.1013; Found 383.1011.



4h

Chemical Formula: $C_{23}H_{16}F_4N_2O_2$

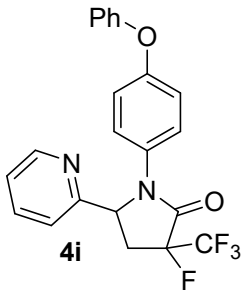
1-(4-benzoylphenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4h): brown solid (mp = 129.5-130.3 ℃), 24.6 mg, (Yield: 57%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.59 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.78 – 7.70 (m, 4H), 7.65 – 7.54 (m, 4H), 7.49 – 7.43 (m, 2H), 7.25 – 7.17 (m, 2H), 5.48 (ddd, *J* = 7.8, 5.6, 3.5 Hz, 1H), 3.26 (td, *J* = 15.1, 7.8 Hz, 1H), 2.70 (dddd, *J* = 25.5, 15.3, 5.6, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 195.4, 163.4 (d, *J* = 22.1 Hz), 157.2, 150.3, 139.9, 137.5, 137.2, 135.2, 132.6, 131.0, 129.9, 128.3, 123.7, 121.8, 121.1, 118.9 (qd, *J* = 283.8, 32.1 Hz), 92.3 (dq, *J* = 201.3, 34.4 Hz), 60.4, 34.1 (d, *J* = 20.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.80 (d, *J* = 10.5 Hz, 3F), -167.01 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}F_4N_2O_2$ 429.1221; Found 429.1214.



4i

Chemical Formula: $C_{22}H_{16}F_4N_2O_2$

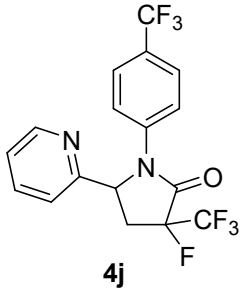
3-fluoro-1-(4-phenoxyphenyl)-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4i): yellow solid (mp = 109.4-110.2 ℃), 32.3 mg, (Yield: 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.64 – 8.54 (m, 1H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.23 – 7.15 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.32 (ddd, *J* = 7.7, 5.7, 4.0 Hz, 1H), 3.20 (td, *J* = 14.4, 7.6 Hz, 1H), 2.72 (ddd, *J* = 25.8, 15.0, 5.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.3 Hz), 157.3, 156.4, 155.8, 150.1, 137.2, 131.2, 129.8, 124.7, 123.8, 123.6, 121.9 (qd, *J* = 284.6, 31.8 Hz), 121.6, 119.2, 118.7, 92.2 (dq, *J* = 200.1, 34.3 Hz), 60.9, 34.0 (d, *J* = 20.4 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.88 (d, *J* = 10.8 Hz, 3F), -167.23 (q, *J* = 10.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}F_4N_2O_2$ 417.1221; Found 417.1216.



4j

Chemical Formula: $C_{17}H_{11}F_7N_2O$

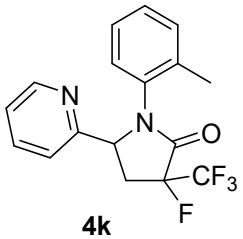
3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (4j): white solid (mp = 100.5-101.6 ℃), 21.7 mg, (Yield: 55%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.59 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.23 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 5.44 (ddd, *J* = 7.9, 5.6, 3.6 Hz, 1H), 3.25 (td, *J* = 15.1, 7.8 Hz, 1H), 2.69 (dddd, *J* = 25.3, 15.1, 5.6, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.4 (d, *J* = 22.2 Hz), 157.0, 150.3, 139.4, 137.5, 128.3 (q, *J* = 33.1 Hz), 126.2 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.0 Hz), 123.7, 122.3, 121.7 (qd, *J* = 283.4, 31.5 Hz), 121.1, 92.2 (dq, *J* = 200.5, 34.3 Hz), 60.4, 34.1 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -62.62 (s, 3F), -79.85 (d, *J* = 10.2 Hz, 3F), -167.14 (q, *J* = 10.3 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}F_7N_2O$ 393.0832; Found 393.0827.



4k

Chemical Formula: $C_{17}H_{14}F_4N_2O$

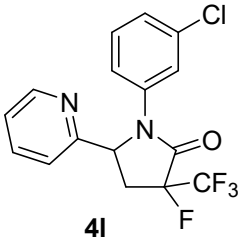
3-fluoro-5-(pyridin-2-yl)-1-(o-tolyl)-3-(trifluoromethyl)pyrrolidin-2-one (4k): yellow solid (mp = 105.2-106.0 ℃), 19.6 mg, (Yield: 57%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.65 – 8.56 (m, 1H), 7.52 (td, *J* = 7.6, 1.8 Hz, 1H), 7.19 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H), 7.15 – 7.08 (m, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.09 (td, *J* = 6.9, 4.4 Hz, 1H), 3.27 – 3.11 (m, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 162.8 (d, *J* = 22.3 Hz), 155.3, 150.1, 136.7, 136.1, 134.3, 131.2, 128.6, 126.4, 123.9, 123.7, 122.3 (qd, *J* = 284.9, 32.2 Hz), 91.8 (dq, *J* = 200.4, 34.0 Hz), 61.4, 33.2 (d, *J* = 20.9 Hz), 17.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.97 (d, *J* = 11.2 Hz, 3F), -168.19 (q, *J* = 11.0 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_4N_2O_2$ 339.1115; Found 339.1116.



4l

Chemical Formula: $C_{16}H_{11}ClF_4N_2O$

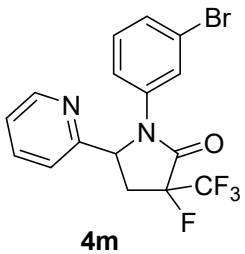
1-(3-chlorophenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4l): white solid (mp = 101.4-102.2 ℃), 26.8 mg, (Yield: 74%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.62 – 8.55 (m, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.57 (t, *J* = 2.0 Hz, 1H), 7.29 – 7.11 (m, 5H), 5.37 (ddd, *J* = 7.8, 5.7, 3.7 Hz, 1H), 3.22 (td, *J* = 14.8, 7.7 Hz, 1H), 2.70 (dddd, *J* = 25.4, 15.0, 5.6, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.2 (d, *J* = 22.5 Hz), 157.0, 150.3, 137.42, 137.37, 134.7, 130.0, 126.8, 123.7, 123.0, 121.8 (qd, *J* = 284.5, 31.8 Hz), 121.3, 120.7, 92.2 (dq, *J* = 200.3, 34.3 Hz), 60.5, 34.0 (d, *J* = 20.4 Hz).

^{19}F NMR (376 MHz,Chloroform-*d*) δ (ppm) = -79.87 (d, *J* = 10.4 Hz, 3F), -167.24 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}ClF_4N_2O$ 359.0569; Found 359.0562.



4m

Chemical Formula: $C_{16}H_{11}BrF_4N_2O$

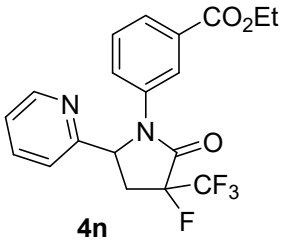
1-(3-bromophenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4m): yellow solid (mp = 80.5-81.6 ℃), 23.7 mg, (Yield: 58%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.62 – 8.56 (m, 1H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.64 (td, *J* = 7.8, 1.8 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H), 7.19 – 7.11 (m, 2H), 5.36 (ddd, *J* = 7.8, 5.6, 3.7 Hz, 1H), 3.21 (td, *J* = 14.8, 7.7 Hz, 1H), 2.70 (dddd, *J* = 25.6, 15.1, 5.6, 1.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.2 (d, *J* = 22.4 Hz), 157.0, 150.3, 137.6, 137.4, 130.2, 129.8, 125.9, 123.7, 122.6, 121.8 (qd, *J* = 283.5, 31.7 Hz), 121.3, 121.2, 92.2 (dq, *J* = 200.5, 34.3 Hz), 60.5, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.87 (d, *J* = 10.8 Hz, 3F), -167.20 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrF_4N_2O$ 403.0064; Found 403.0060.



4n

Chemical Formula: $C_{19}H_{16}F_4N_2O_3$

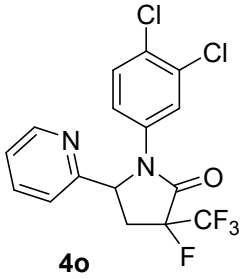
ethyl 3-(3-fluoro-2-oxo-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-1-yl)benzoate (4n): brown solid (mp = 81.6-82.3 ℃), 33.9 mg, (Yield: 85%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.58 (dd, *J* = 5.3, 1.9 Hz, 1H), 8.03 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.16 (m, 2H), 5.43 (ddd, *J* = 7.7, 5.8, 3.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.24 (ddd, *J* = 15.0, 13.5, 7.6 Hz, 1H), 2.75 (ddd, *J* = 25.8, 15.0, 5.9 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 165.5, 163.2 (d, *J* = 22.6 Hz), 156.9, 150.3, 137.3, 136.5, 131.4, 129.1, 127.7, 127.4, 123.7, 123.6, 121.8 (qd, *J* = 283.5, 31.7 Hz), 121.7, 92.2 (dq, *J* = 200.4, 34.2 Hz), 61.3, 60.5, 34.0 (d, *J* = 20.5 Hz), 14.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.88 (d, *J* = 10.8 Hz, 3F), -167.33 (q, *J* = 11.0 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_4N_2O_3$ 397.1170; Found 397.1167.



4o

Chemical Formula: $C_{16}H_{10}Cl_2F_4N_2O$

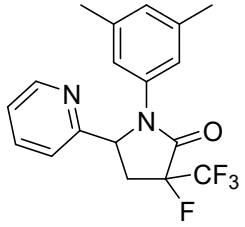
1-(3,4-dichlorophenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4o): white solid (mp = 127.7-128.5 °C), 24.3 mg, (Yield: 61%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.63 – 8.56 (m, 1H), 7.72 – 7.63 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 5.34 (ddd, *J* = 7.9, 5.7, 3.6 Hz, 1H), 3.22 (td, *J* = 14.8, 7.7 Hz, 1H), 2.69 (dddd, *J* = 25.4, 15.2, 5.6, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.2 (d, *J* = 22.6 Hz), 156.7, 150.4, 137.5, 135.7, 133.1, 130.6, 130.5, 124.6, 123.8, 121.8, 121.7 (qd, *J* = 283.6, 31.7 Hz), 121.3, 92.1 (dq, *J* = 200.6, 34.3 Hz), 60.4, 34.0 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.86 (d, *J* = 10.7 Hz, 3F), -167.17 (q, *J* = 10.8 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}Cl_2F_4N_2O$ 393.0179; Found 393.0178.



4p

Chemical Formula: $C_{18}H_{16}F_4N_2O$

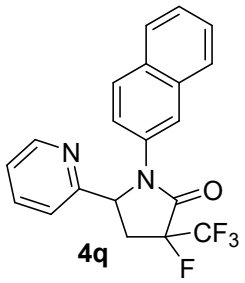
1-(3,5-dimethylphenyl)-3-fluoro-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4p): white solid (mp = 138.4-139.0 °C), 26.6 mg, (Yield: 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.61 – 8.55 (m, 1H), 7.61 (td, *J* = 7.8, 1.8 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.03 (s, 2H), 6.79 (s, 1H), 5.36 (ddd, *J* = 7.8, 5.5, 3.9 Hz, 1H), 3.19 (td, *J* = 15.0, 7.7 Hz, 1H), 2.67 (dddd, *J* = 25.6, 15.0, 5.6, 1.3 Hz, 1H), 2.22 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.1 (d, *J* = 22.2 Hz), 157.7, 149.9, 138.3, 137.2, 136.1, 128.6, 123.4, 121.3, 120.7, 119.2 (qd, *J* = 284.8, 32.3 Hz), 92.3 (dq, *J* = 199.6, 34.1 Hz), 60.7, 34.0 (d, *J* = 20.5 Hz), 21.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.90 (d, *J* = 10.6 Hz, 3F), -167.08 (q, *J* = 10.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}F_4N_2O$ 353.1272; Found 353.1270.



4q

Chemical Formula: $C_{20}H_{14}F_4N_2O$

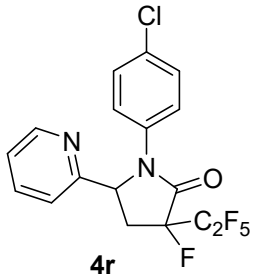
3-fluoro-1-(naphthalen-2-yl)-5-(pyridin-2-yl)-3-(trifluoromethyl)pyrrolidin-2-one (4q): white solid (mp = 157.9-158.3 ℃), 24.4 mg, (Yield: 65%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.56 (d, *J* = 4.6 Hz, 1H), 7.91 (s, 1H), 7.77 – 7.70 (m, 3H), 7.59 – 7.50 (m, 2H), 7.47 – 7.39 (m, 2H), 7.22 – 7.11 (m, 2H), 5.57 – 5.47 (m, 1H), 3.27 (tdd, *J* = 14.8, 7.7, 1.4 Hz, 1H), 2.74 (ddd, *J* = 25.7, 15.0, 5.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.3 (d, *J* = 22.3 Hz), 157.4, 150.1, 137.3, 133.8, 133.0, 131.6, 129.0, 127.9, 127.5, 126.6, 126.3, 123.5, 121.9 (qd, *J* = 284.6, 31.9 Hz), 121.5, 121.4, 121.0, 92.4 (dq, *J* = 199.9, 34.1 Hz), 60.7, 34.1 (d, *J* = 20.3 Hz).

^{19}F NMR (376 MHz,Chloroform-*d*) δ (ppm) = -79.79 (d, *J* = 11.0 Hz, 3F), -166.94 (q, *J* = 11.2 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}F_4N_2O$ 375.1115; Found 375.1113.



4r

Chemical Formula: $C_{17}H_{11}ClF_6N_2O$

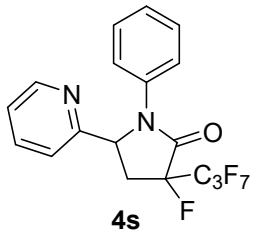
1-(4-chlorophenyl)-3-fluoro-3-(perfluoroethyl)-5-(pyridin-2-yl)pyrrolidin-2-one (4r): yellow solid (mp = 97.3-98.6 ℃), 26.2 mg, (Yield: 64%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.59 – 8.57 (m, 1H), 7.62 (td, *J* = 7.8, 1.8 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.27 – 7.20 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 5.35 (ddd, *J* = 7.6, 5.8, 3.6 Hz, 1H), 3.33 (td, *J* = 14.9, 7.5 Hz, 1H), 2.73 (ddd, *J* = 25.8, 15.1, 5.9 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 23.2 Hz), 157.0, 150.2, 137.3, 134.9, 132.2, 129.2, 124.1, 123.7, 121.5, 92.9 (dt, *J* = 201.3, 28.9 Hz), 60.7, 34.5 (d, *J* = 20.9 Hz). Carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -79.82 (d, *J* = 10.4 Hz, 3F), -123.91 – -127.22 (m, 2F), -165.66 (h, *J* = 9.7 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}ClF_6N_2O$ 409.0537; Found 409.0535.



4s

Chemical Formula: $C_{18}H_{12}F_8N_2O$

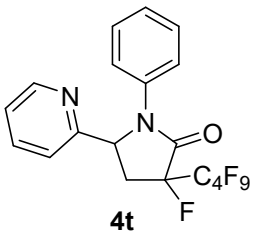
3-fluoro-3-(perfluoropropyl)-1-phenyl-5-(pyridin-2-yl)pyrrolidin-2-one (4s): white solid (mp = 93.6-94.2 ℃), 30.3 mg, (Yield: 71%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.60 – 8.55 (m, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.32 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 5.41 (ddd, *J* = 7.7, 5.4, 3.7 Hz, 1H), 3.34 (dddd, *J* = 16.4, 15.2, 7.7, 1.2 Hz, 1H), 2.75 (ddd, *J* = 25.6, 15.1, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 21.8 Hz), 157.5, 150.0, 137.2, 136.3, 129.0, 126.7, 123.5, 122.8, 121.3, 93.5 (dt, *J* = 197.1, 28.3 Hz), 60.7, 34.5 (d, *J* = 20.8 Hz). Carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.83 (td, *J* = 10.2, 3.9 Hz, 3F), -121.18 – -123.71 (m, 2F), -124.41 (dt, *J* = 10.3, 6.2 Hz, 2F), -164.45 (ttt, *J* = 13.2, 6.7, 3.9 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{13}F_8N_2O$ 425.0895; Found 425.0891.



4t

Chemical Formula: $C_{19}H_{12}F_{10}N_2O$

3-fluoro-3-(perfluorobutyl)-1-phenyl-5-(pyridin-2-yl)pyrrolidin-2-one (4t): white solid (mp = 90.3-91.6 ℃), 33.4 mg, (Yield: 70%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) = 8.58 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.13 (m, 3H), 5.41 (ddd, *J* = 7.7, 5.5, 3.7 Hz, 1H), 3.35 (td, *J* = 15.9, 8.1 Hz, 1H), 2.75 (ddd, *J* = 25.6, 15.1, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) = 163.0 (d, *J* = 22.6 Hz), 157.5, 150.1, 137.2, 136.4, 129.0, 126.7, 123.5, 122.8, 121.4, 93.7 (dt, *J* = 203.1, 28.8 Hz), 60.7, 34.6 (d, *J* = 20.6 Hz). Carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) = -80.77 (tt, *J* = 11.3, 2.8 Hz, 3F), -120.40 – -122.99 (m, 4F), -126.06 – -126.27 (m, 2F), -164.27 (tdq, *J* = 14.5, 10.4, 5.2 Hz, 1F).

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{13}F_{10}N_2O$ 475.0863; Found 475.0860.

VIII. References

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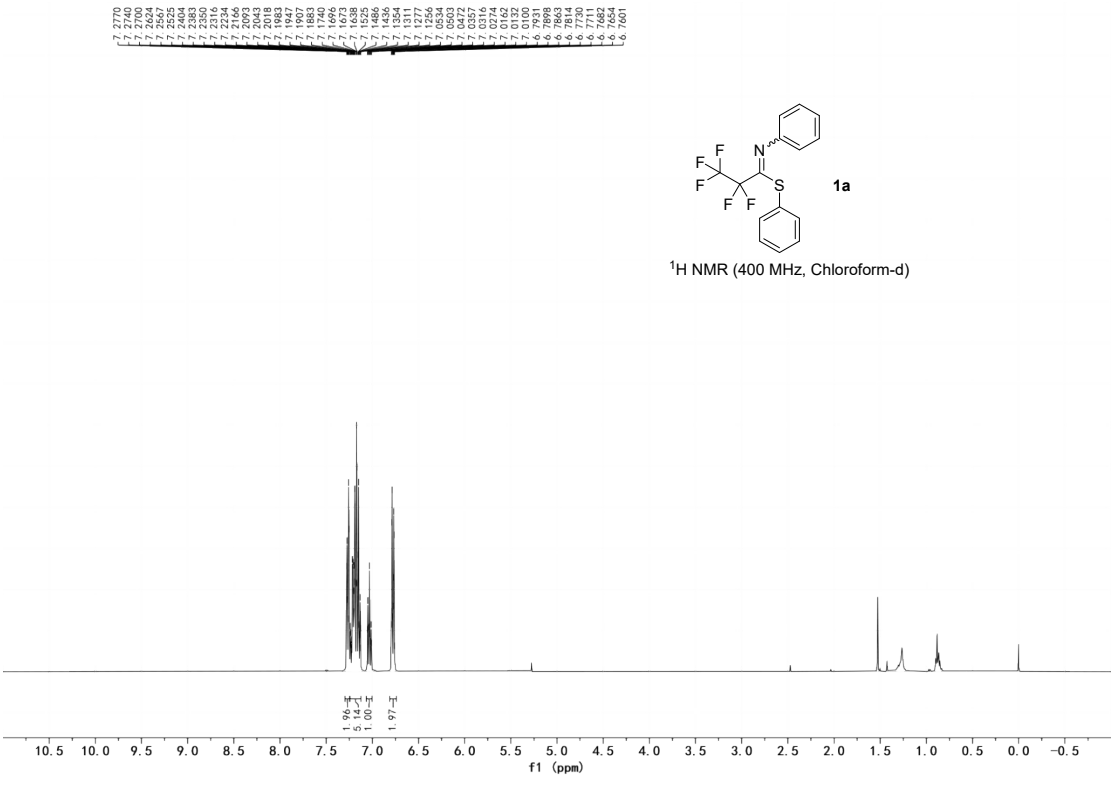
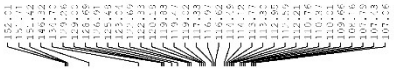
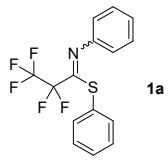
NMR Spectra of the Substrates

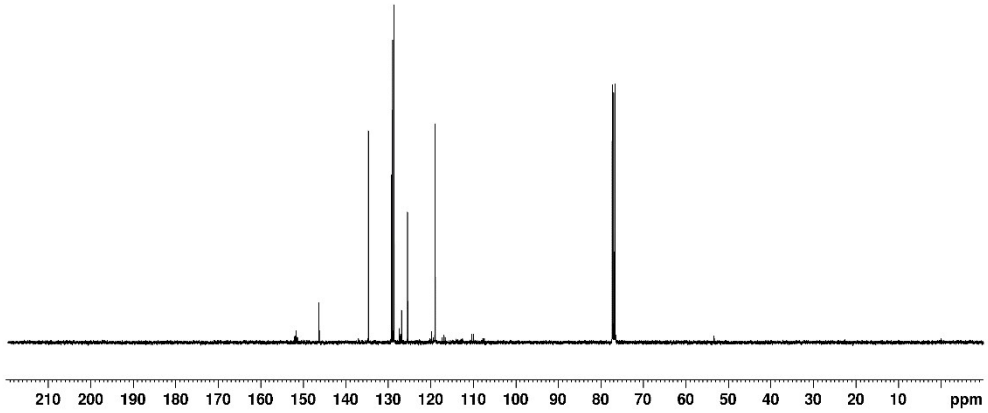






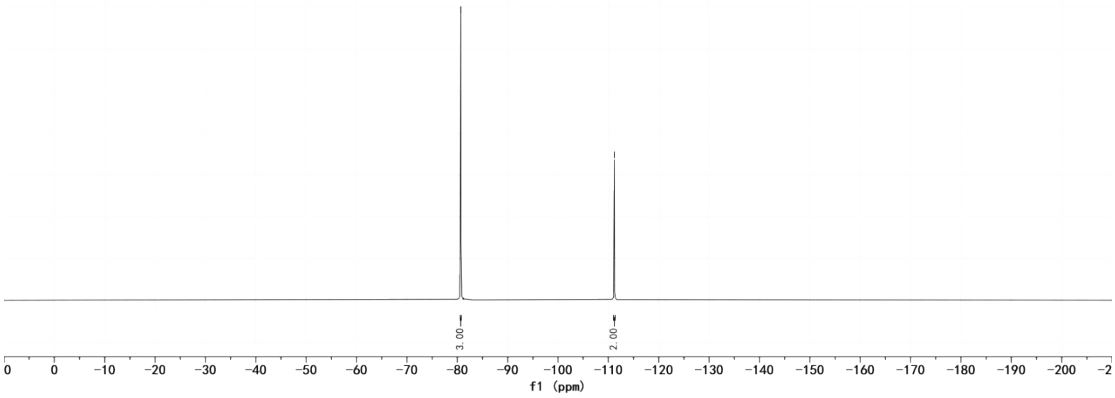
1a

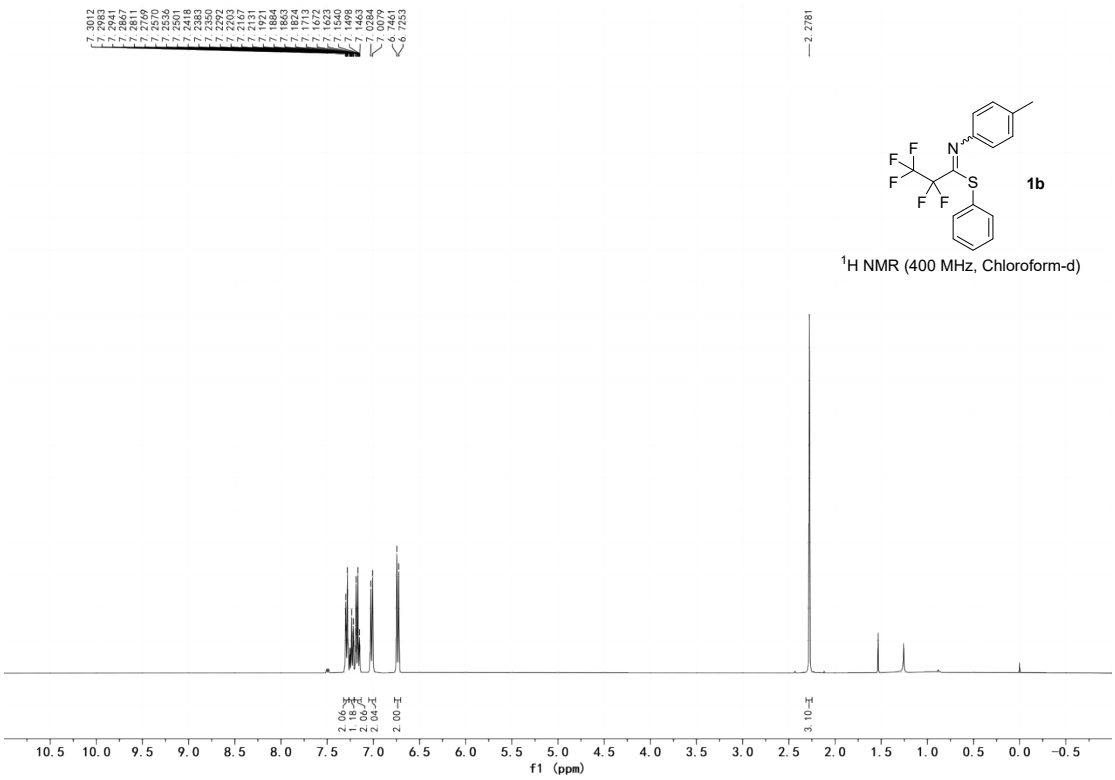
^{13}C NMR (101 MHz, Chloroform-d)



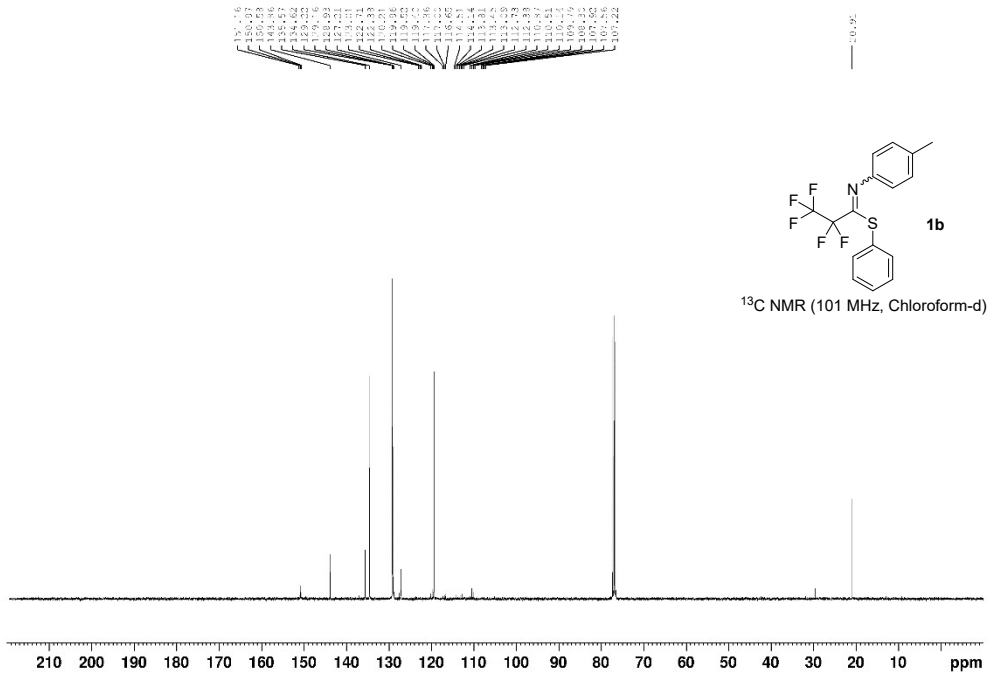
1a

^{19}F NMR (376 MHz, Chloroform-d)





^{1}H NMR (400 MHz, Chloroform-d)



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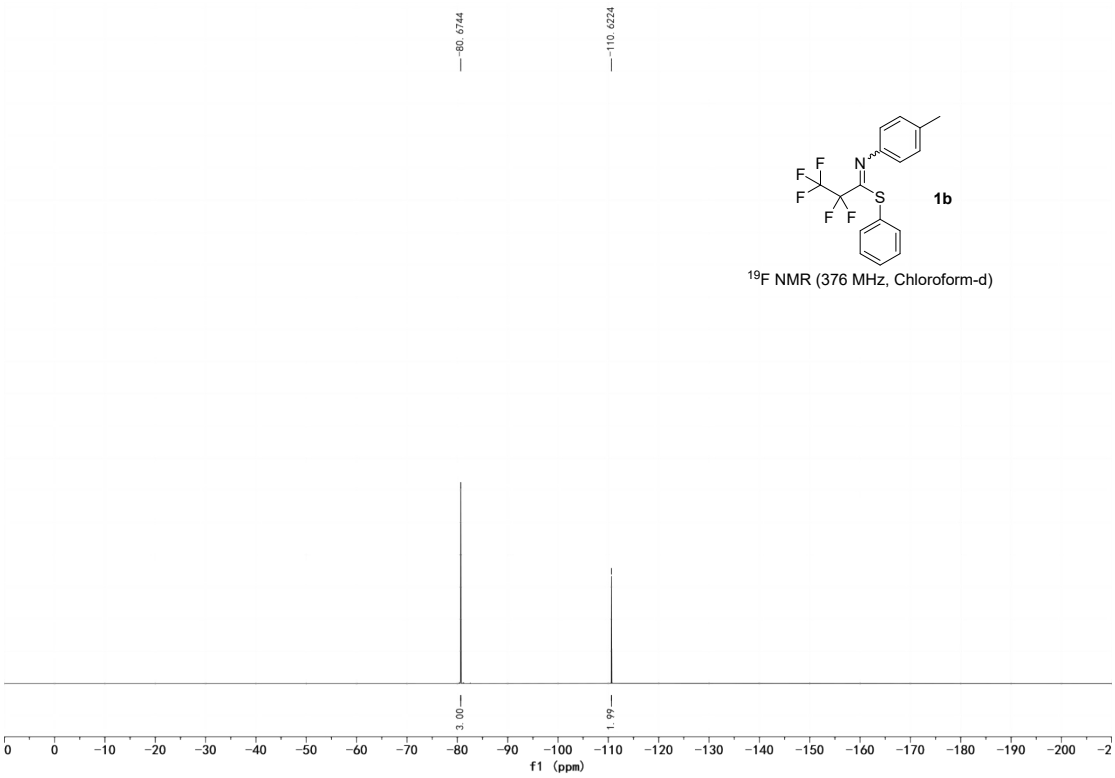

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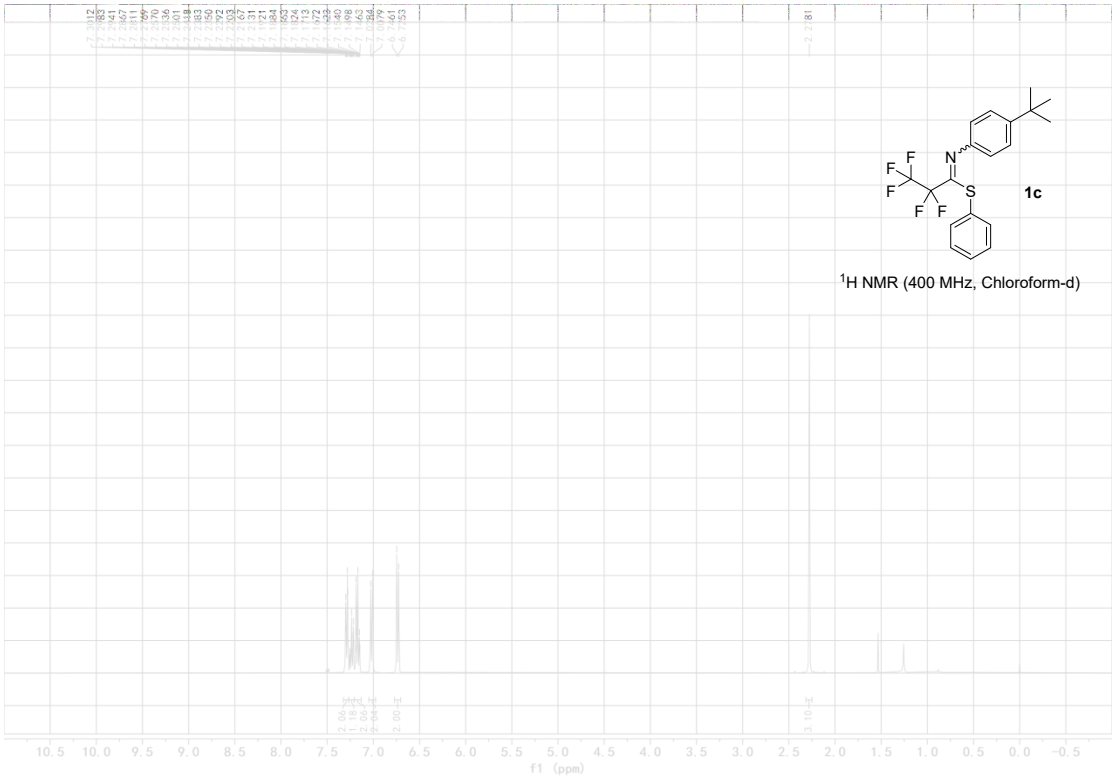

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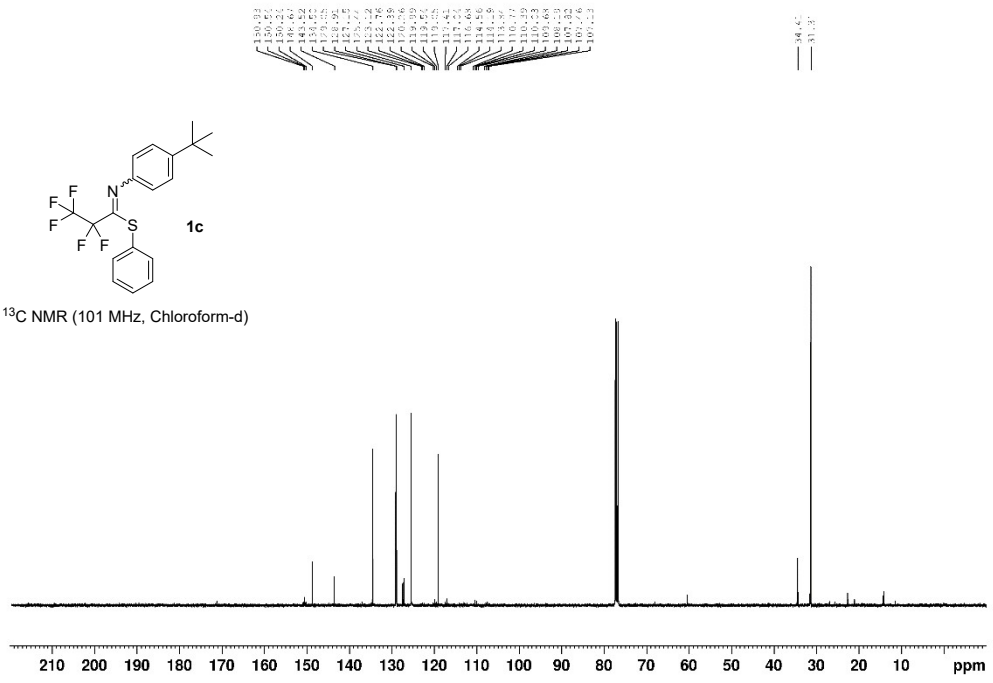

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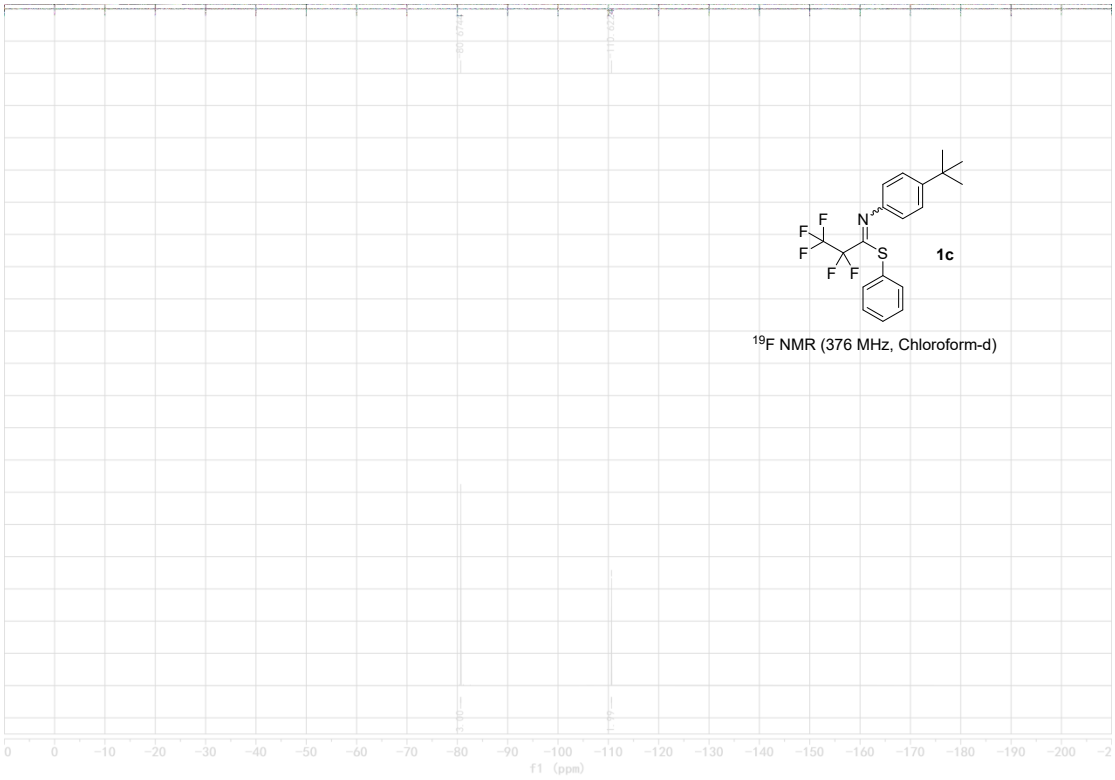

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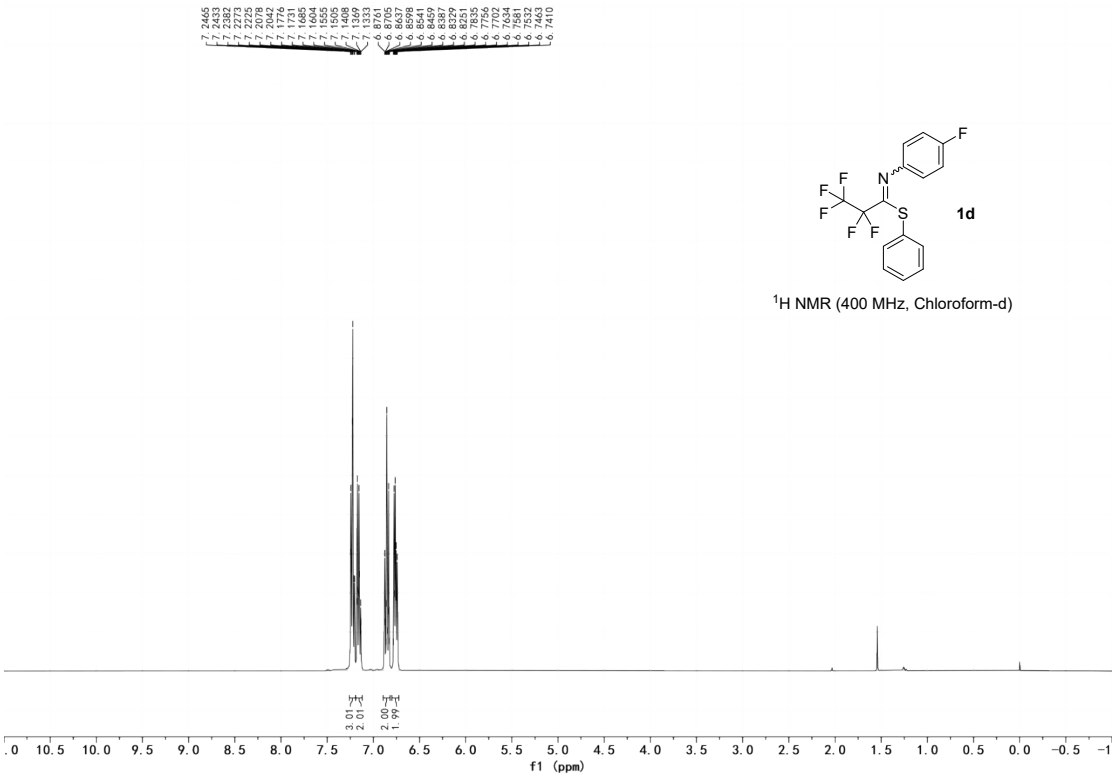
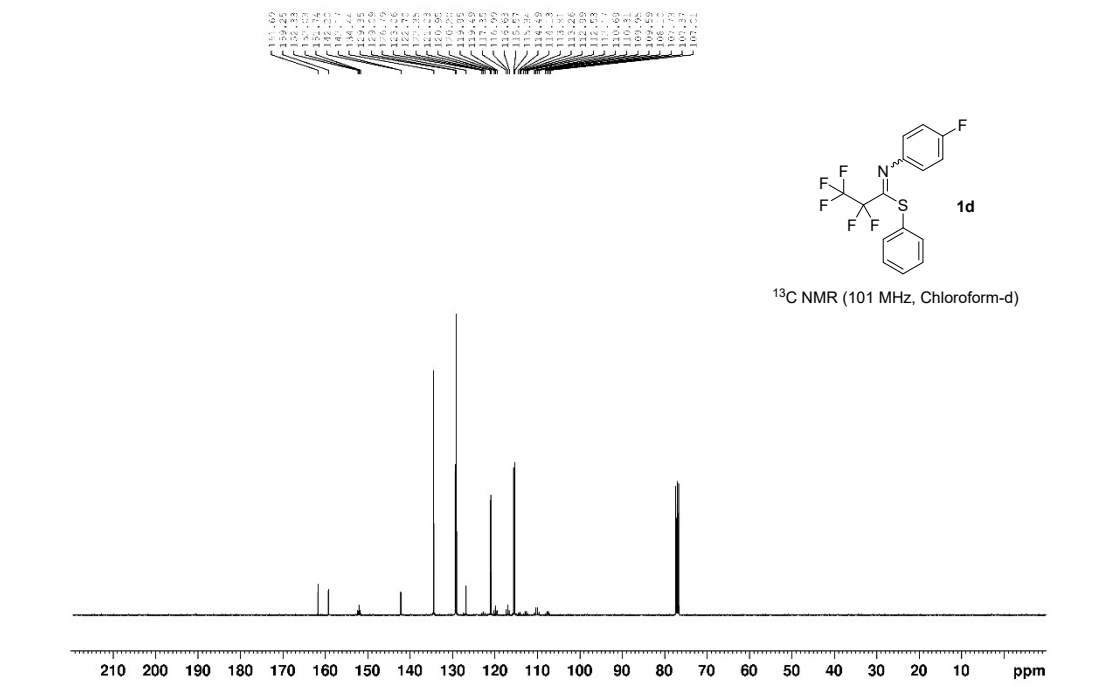
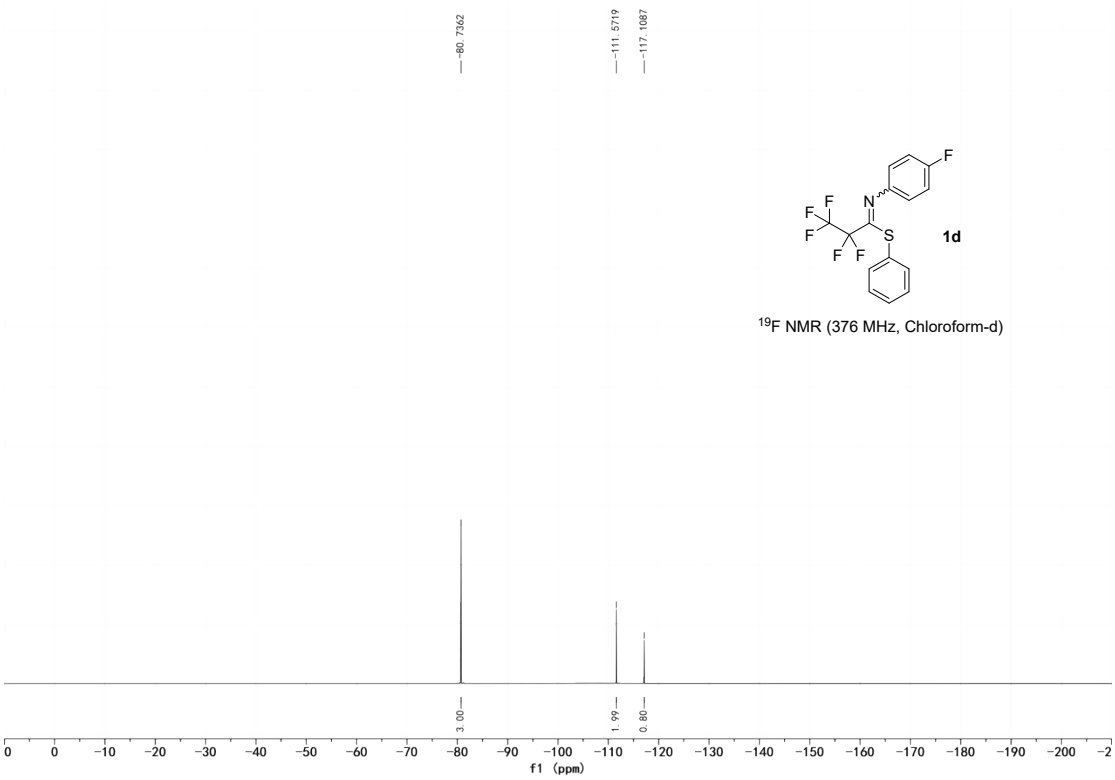

1d
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)


1d
13C NMR (101 MHz, Chloroform-d)
ppm



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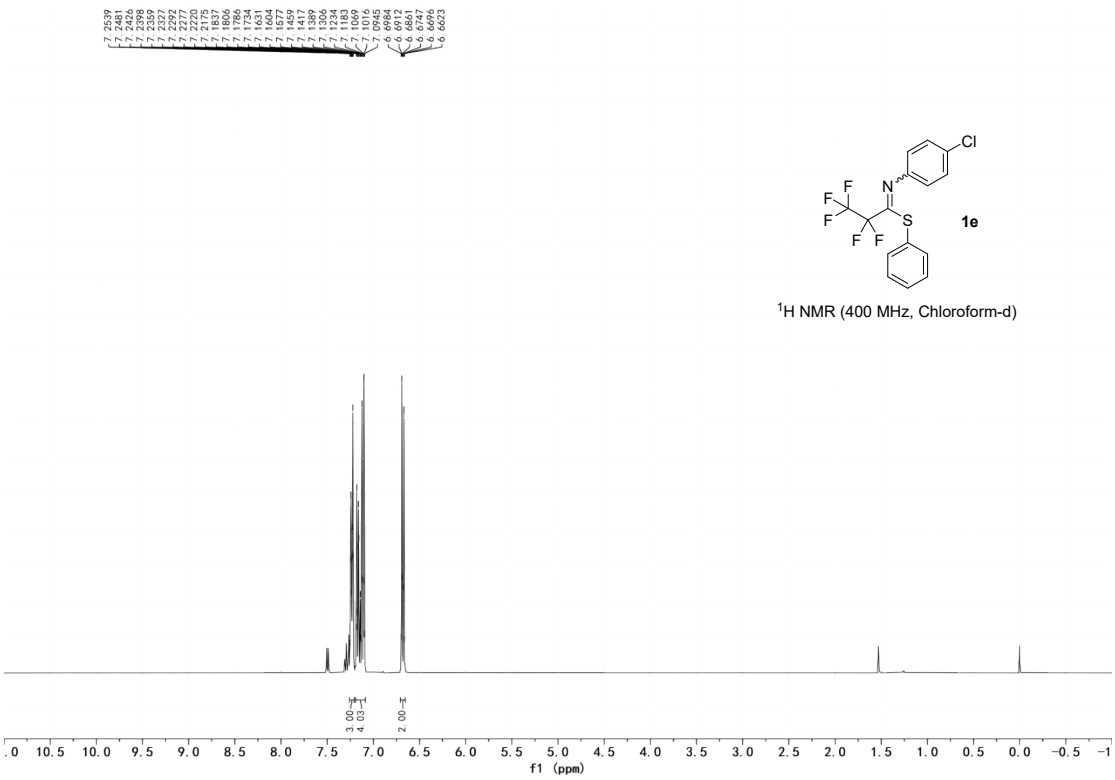
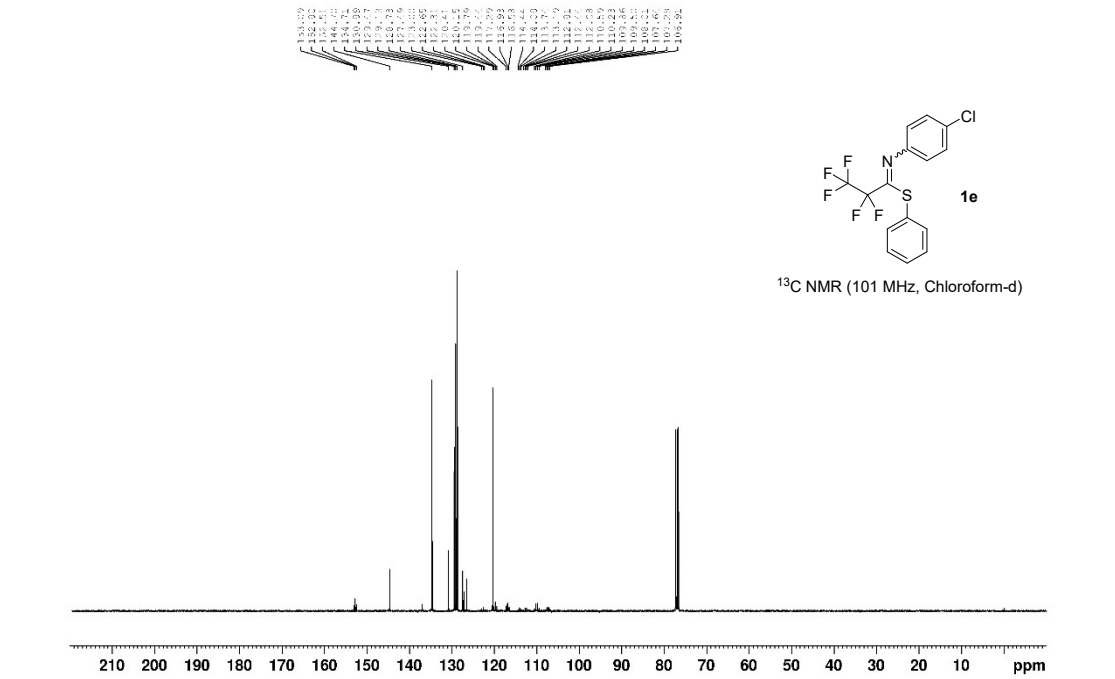


^{1}H NMR (400 MHz, Chloroform-d)



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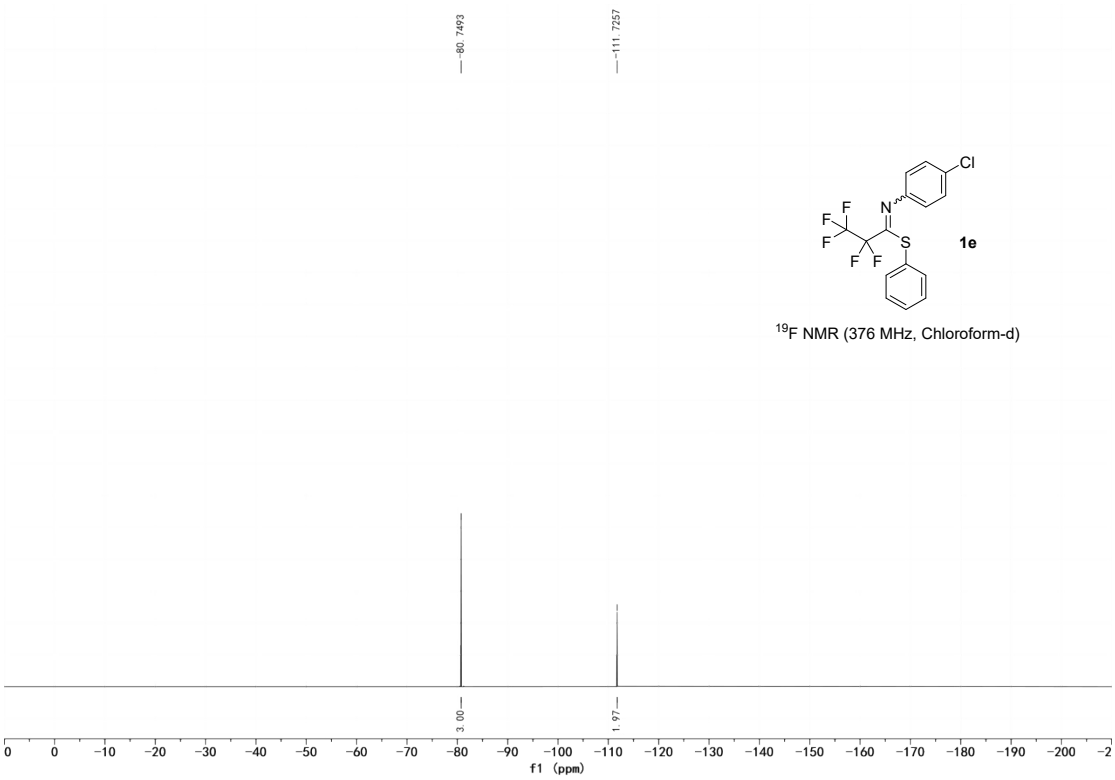

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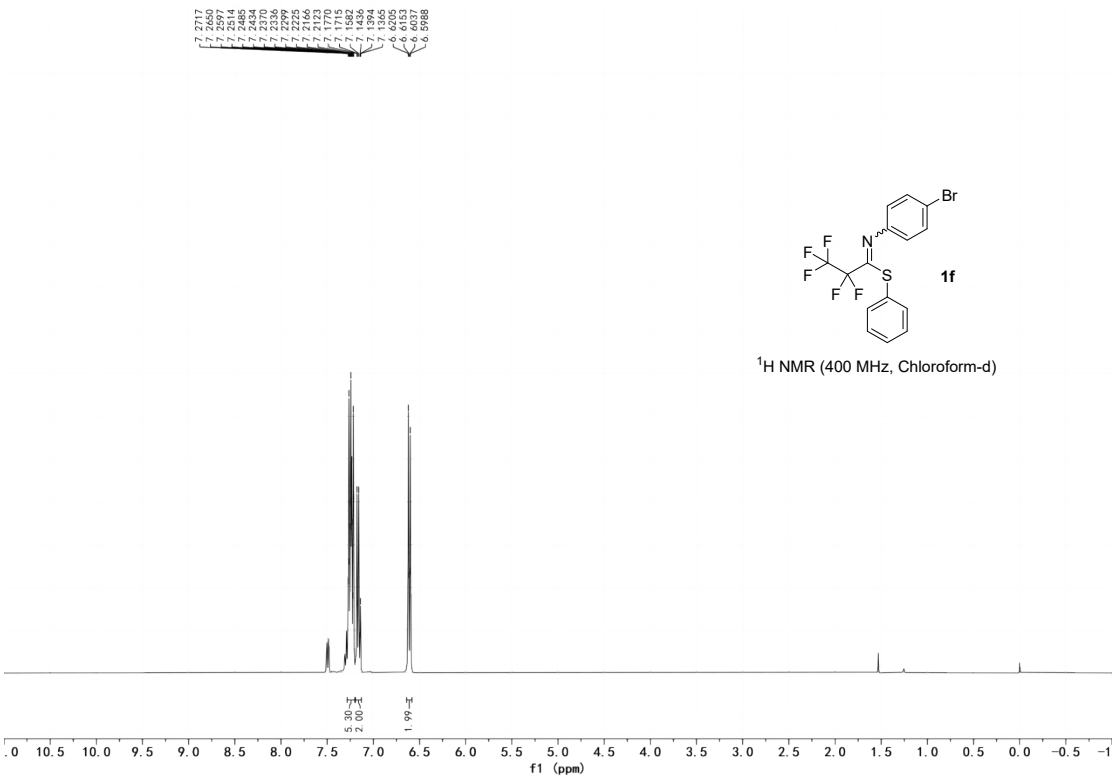

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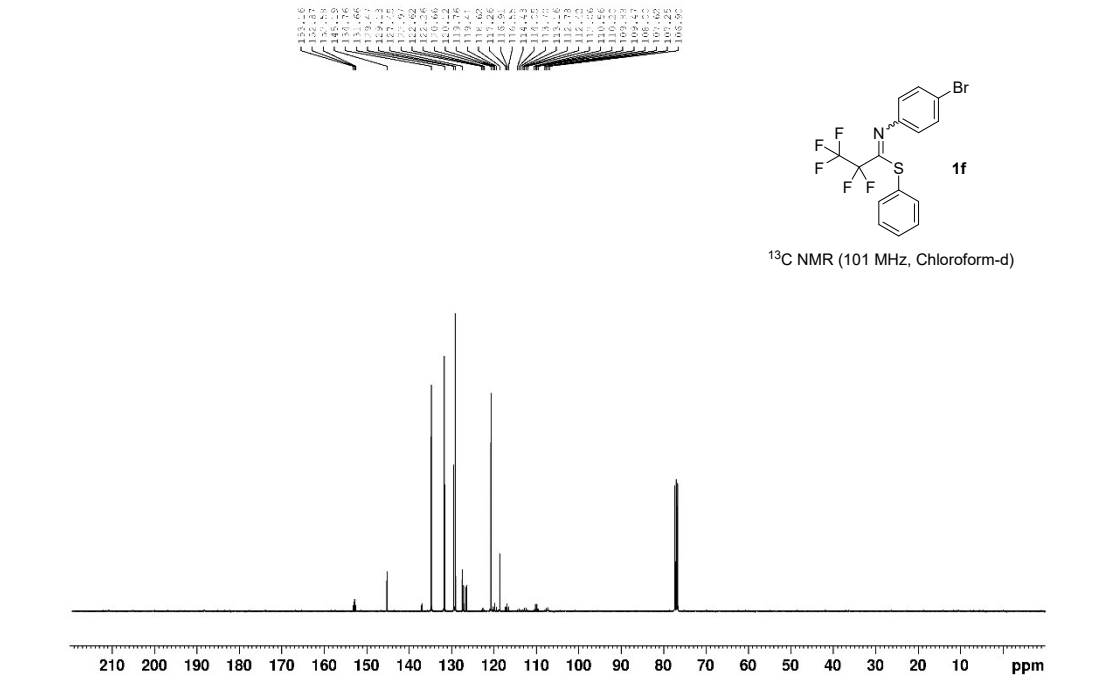

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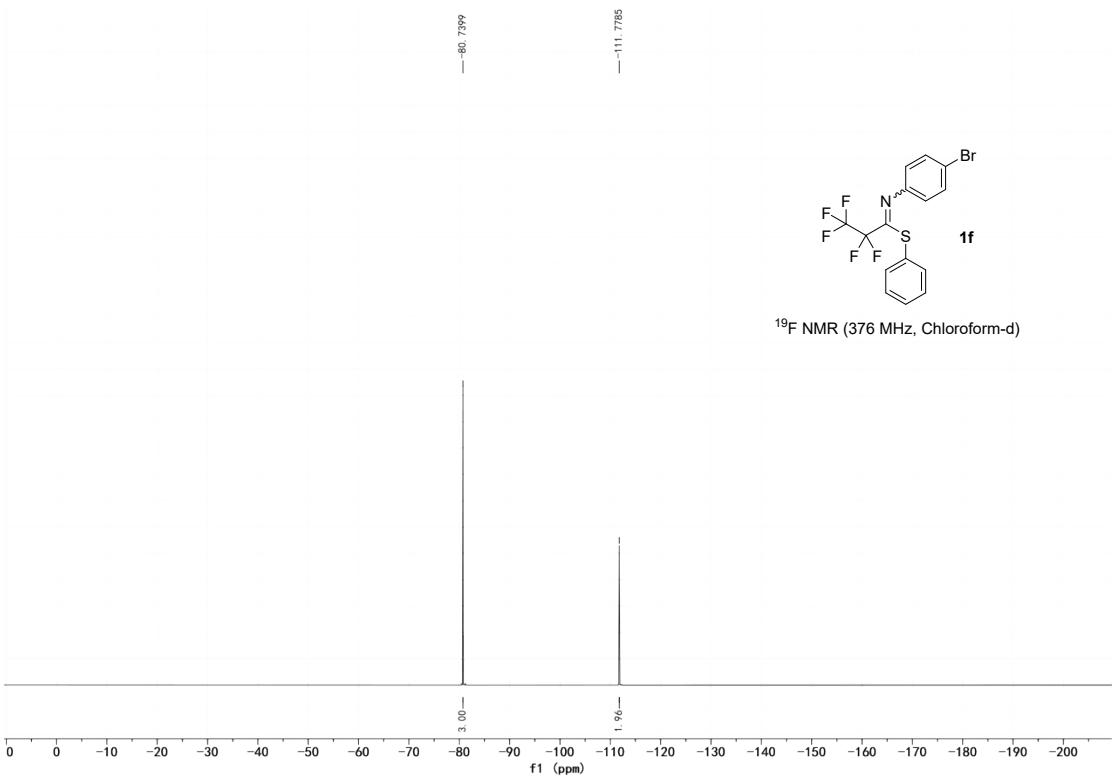

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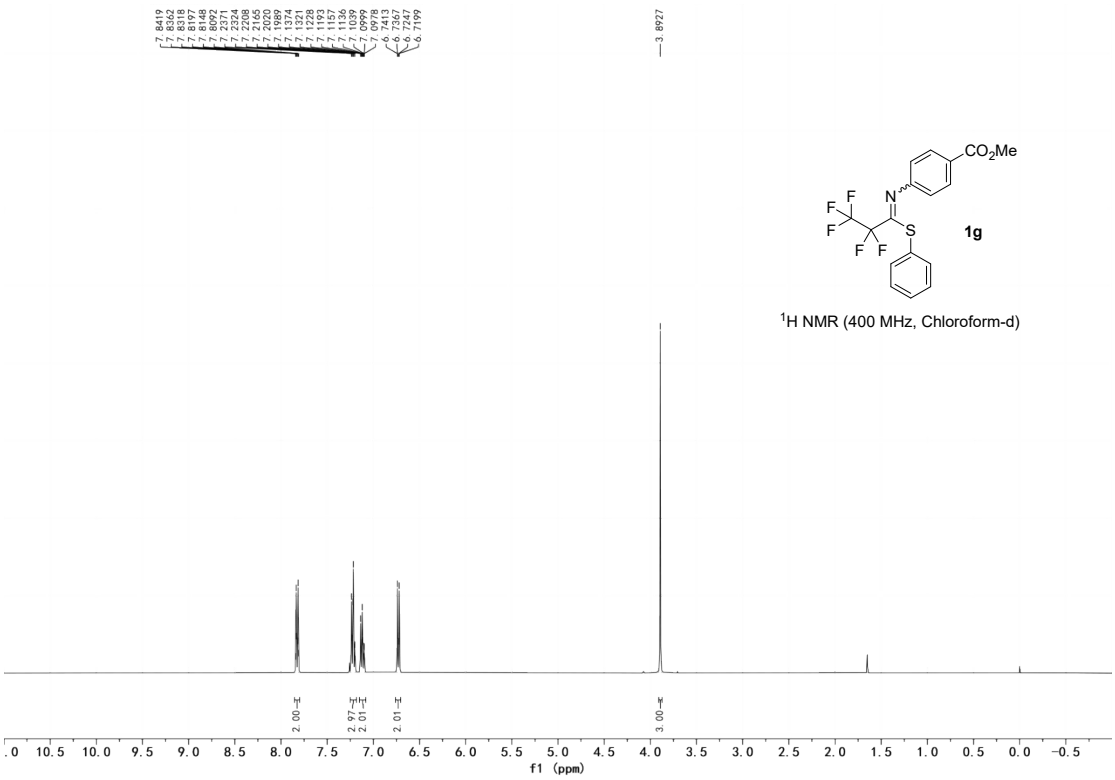

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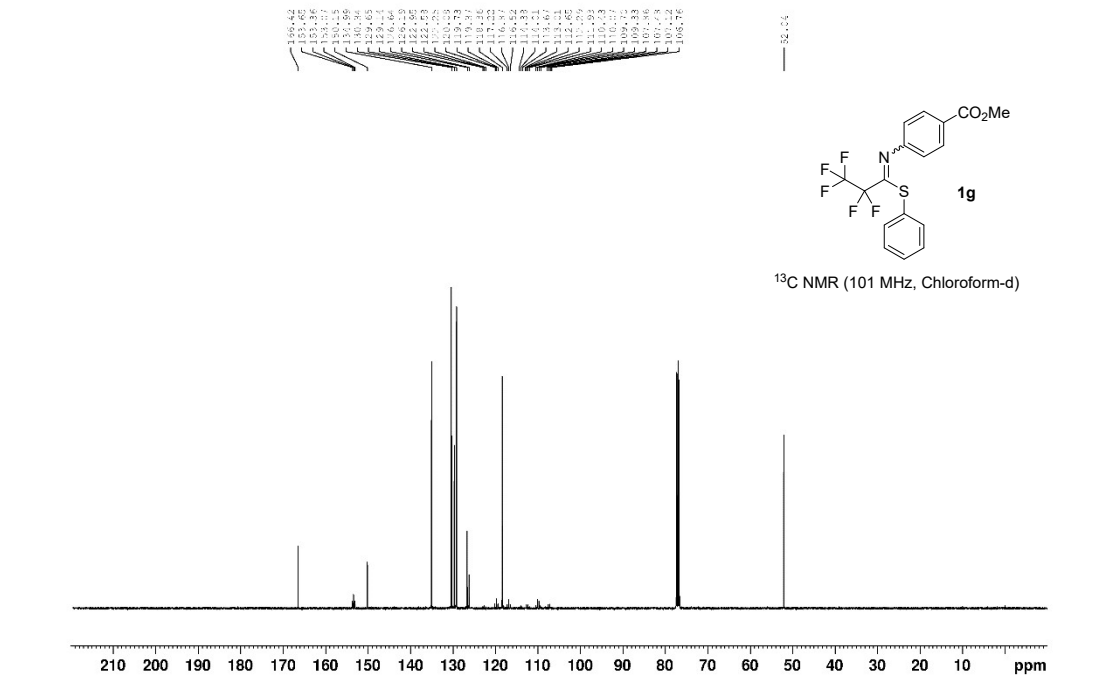
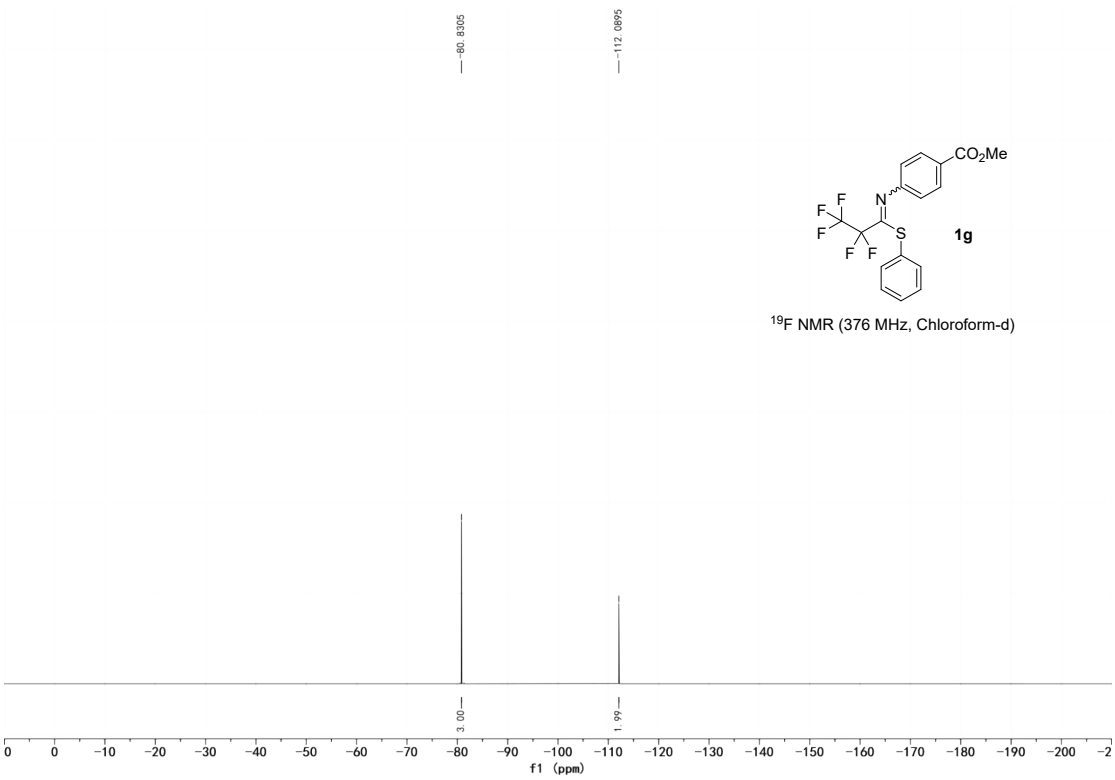


^{13}C NMR (101 MHz, Chloroform-d)



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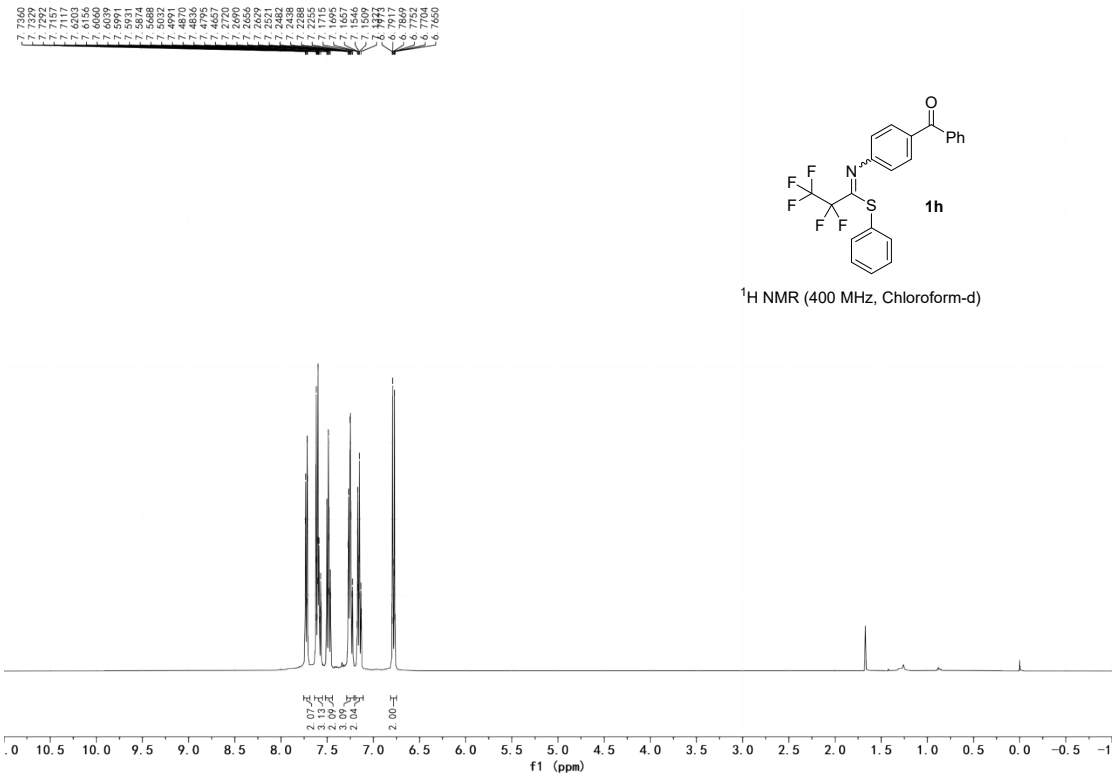
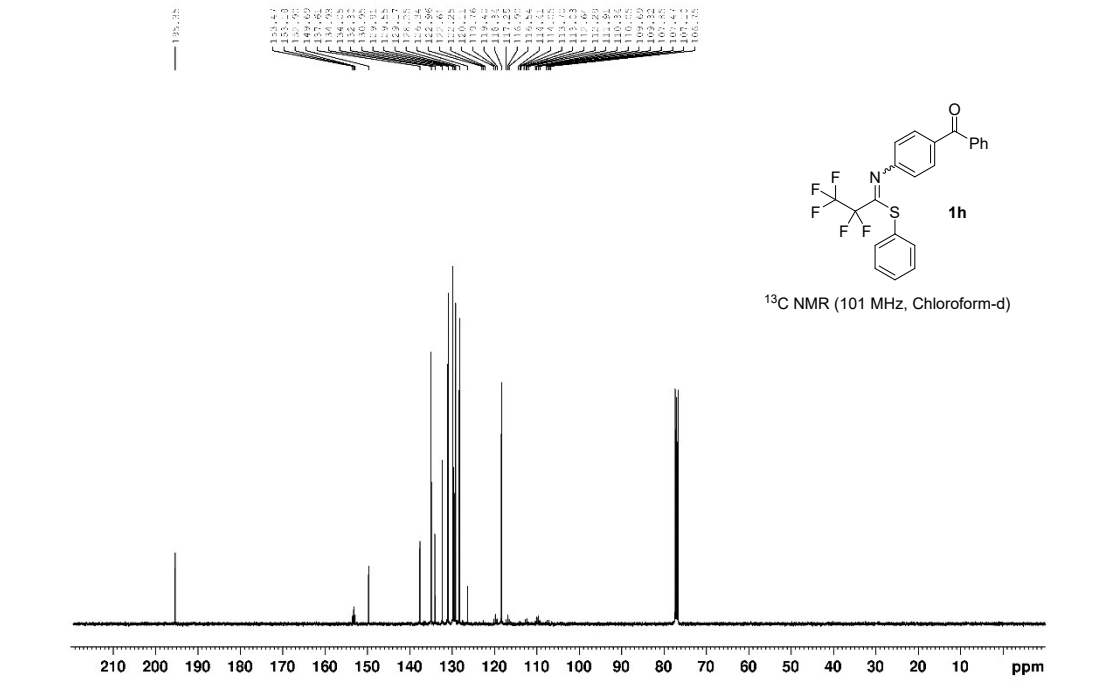

1h
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)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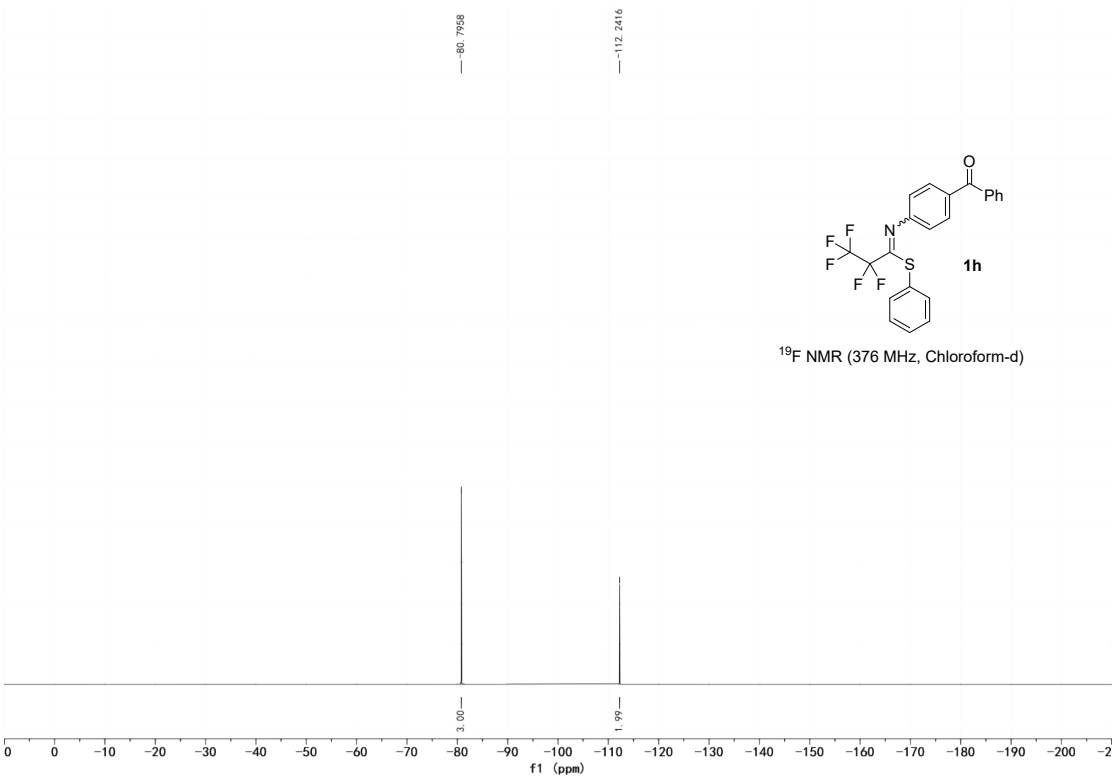
13C NMR (101 MHz, Chloroform-d)
ppm



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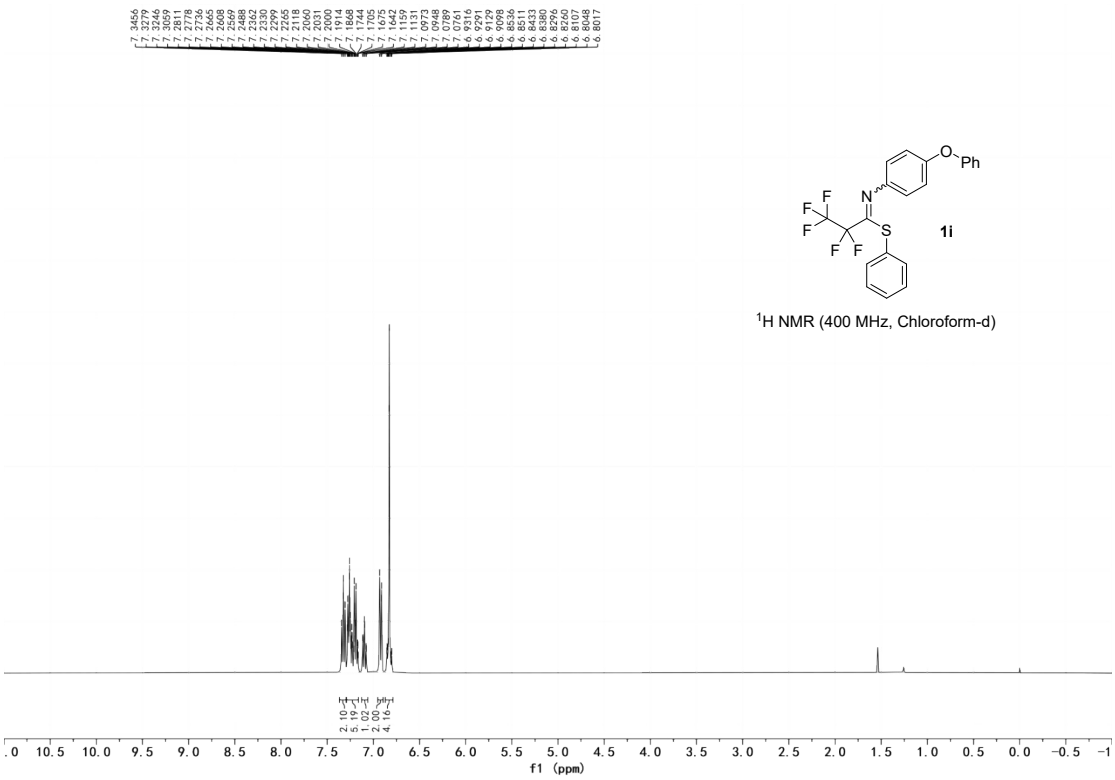
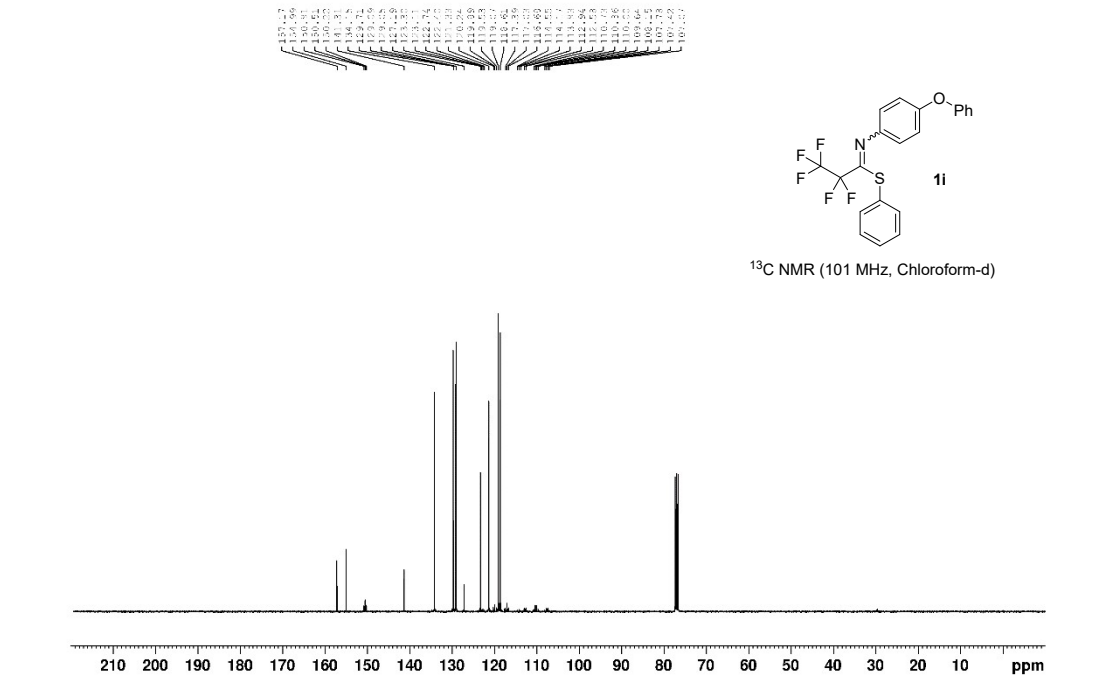

1i
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)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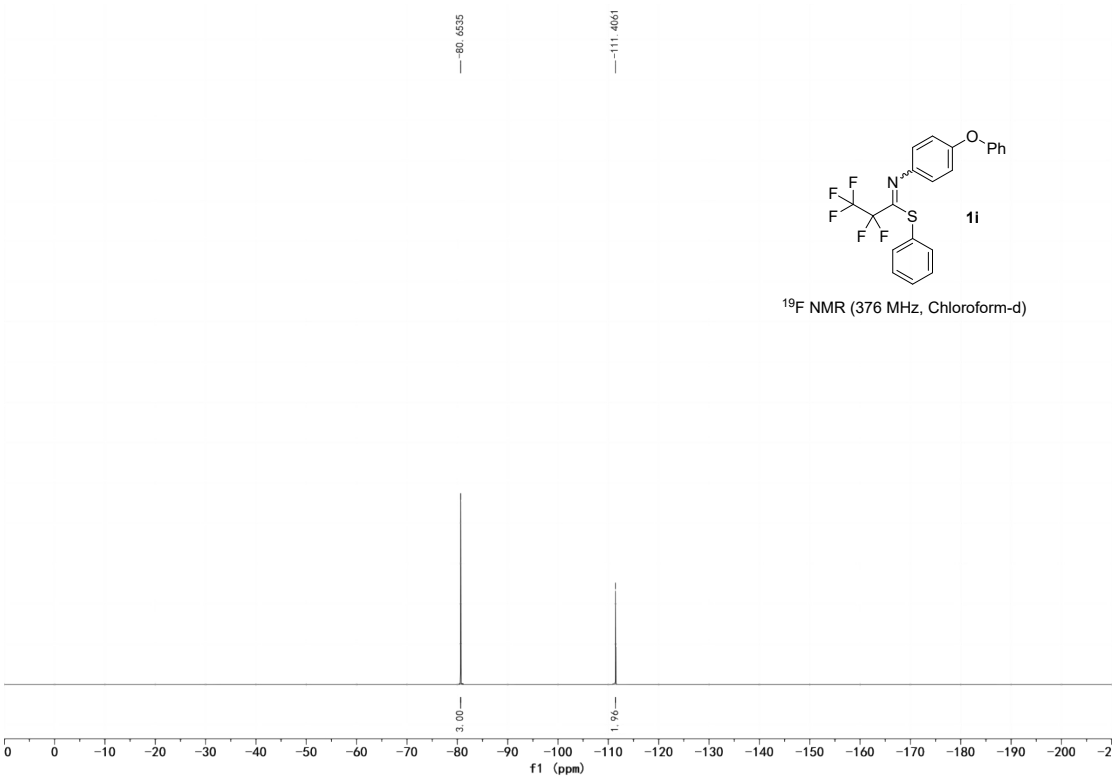
ppm



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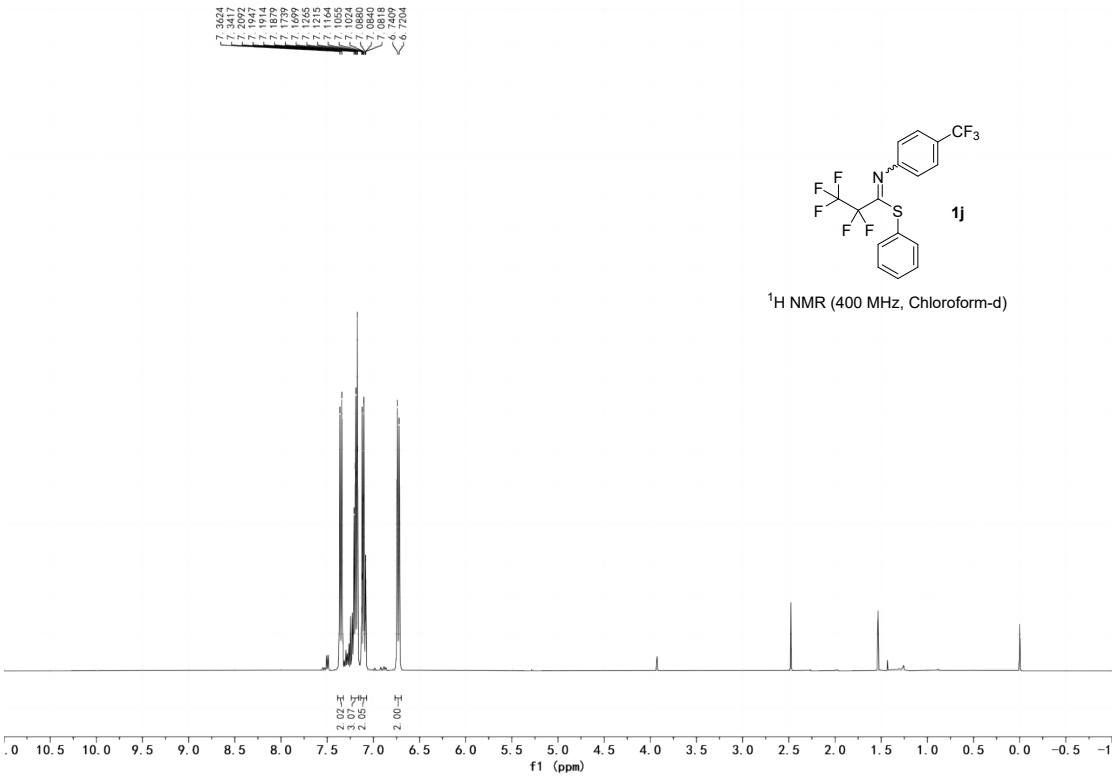
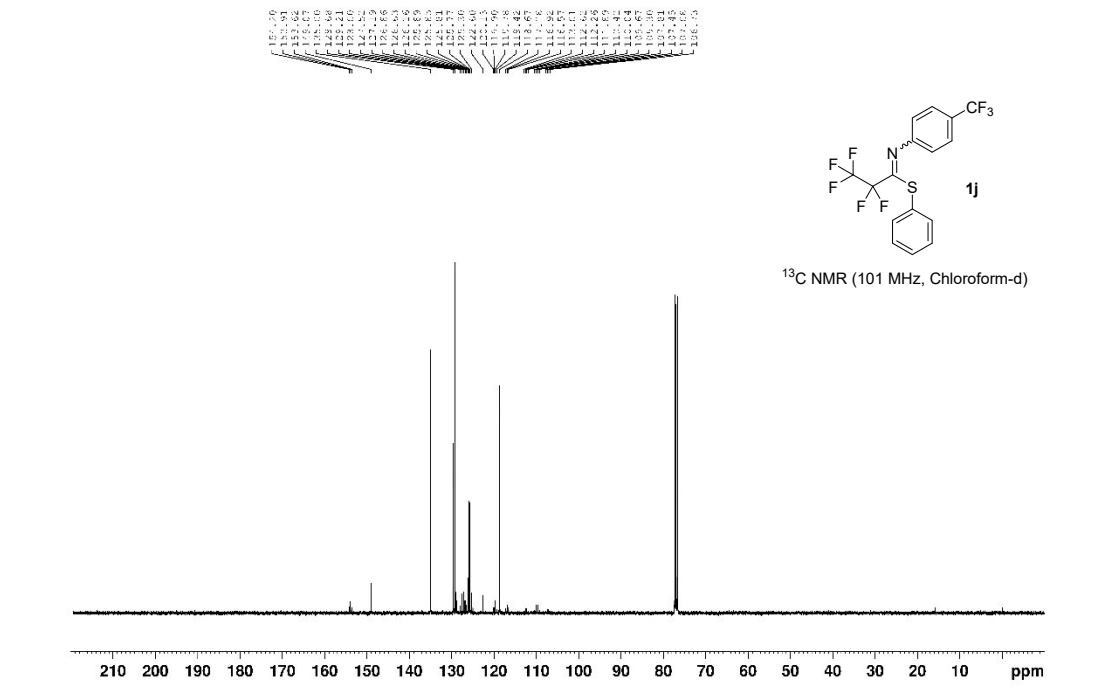


^{1}H NMR (400 MHz, Chloroform-d)



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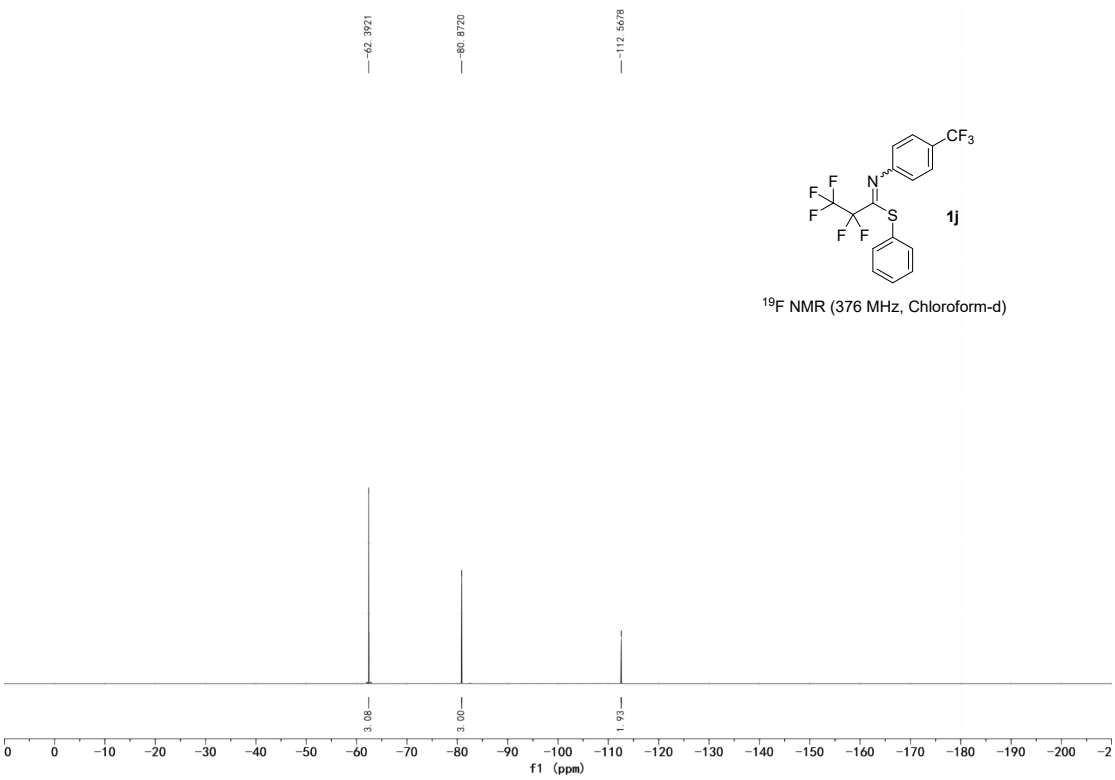

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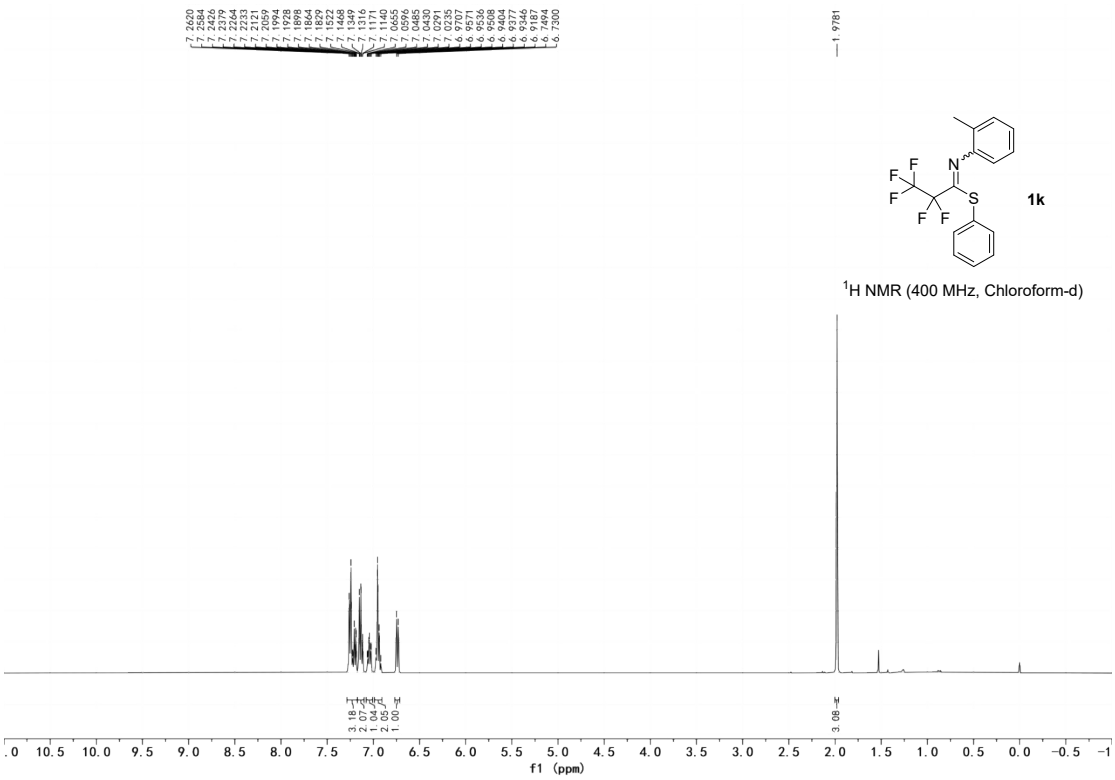
1.9781
1k
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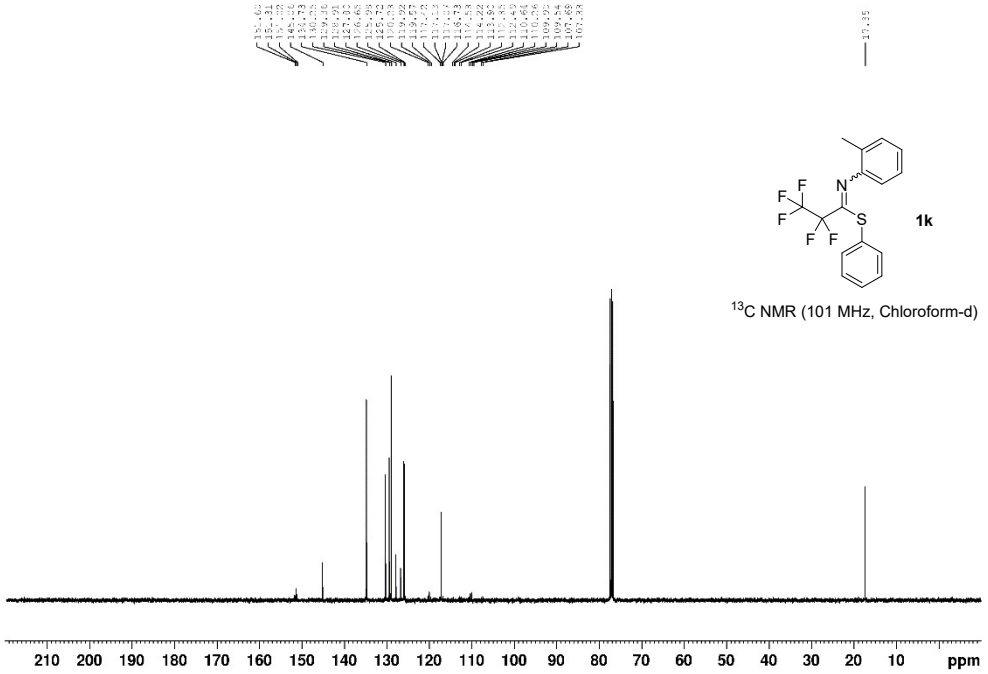
3.18
2.07
1.04
2.05
1.00
3.06
f1 (ppm)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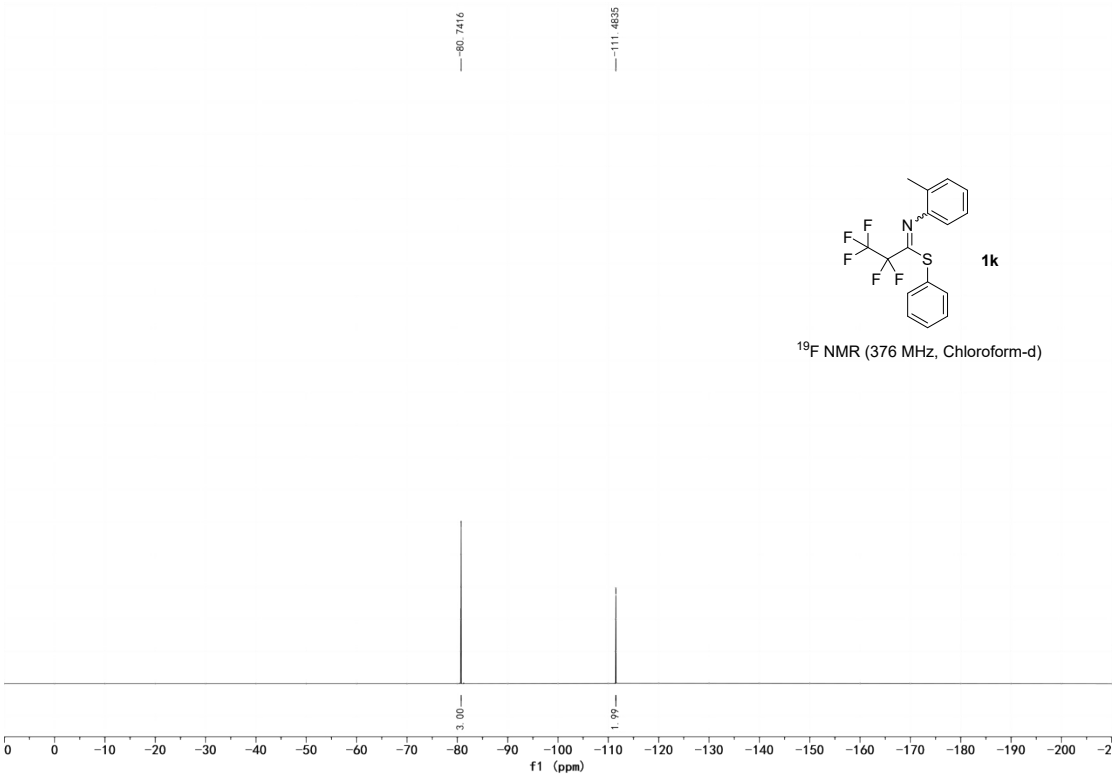

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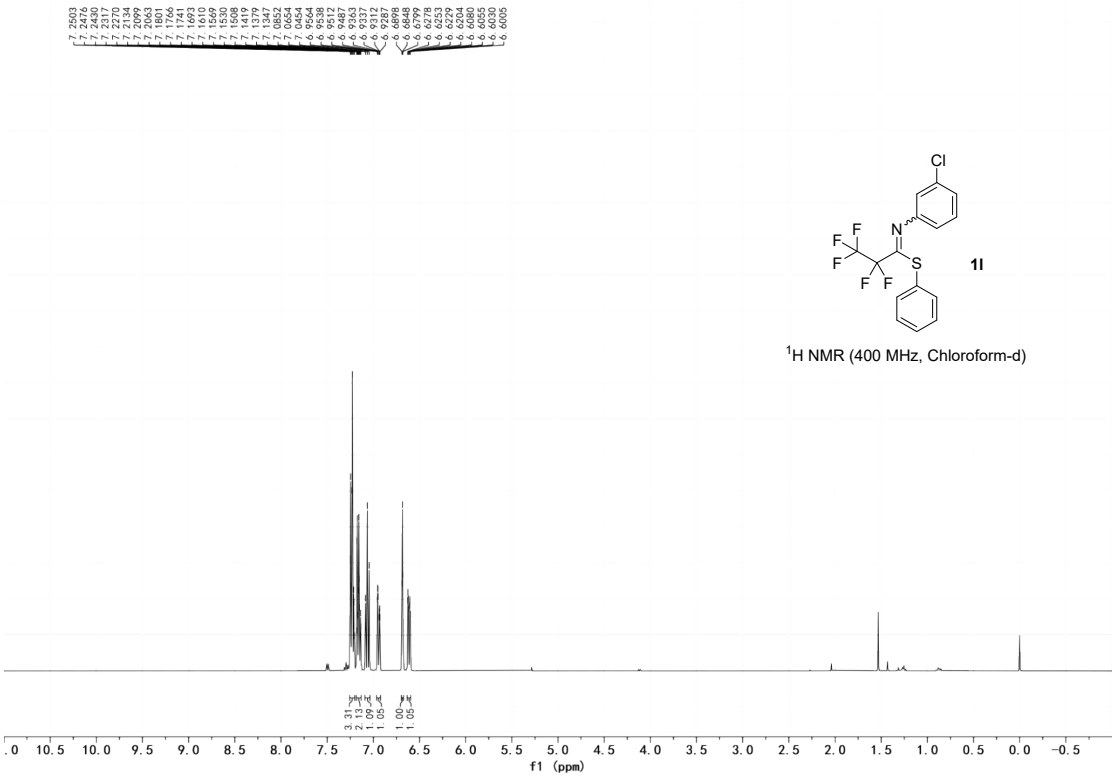
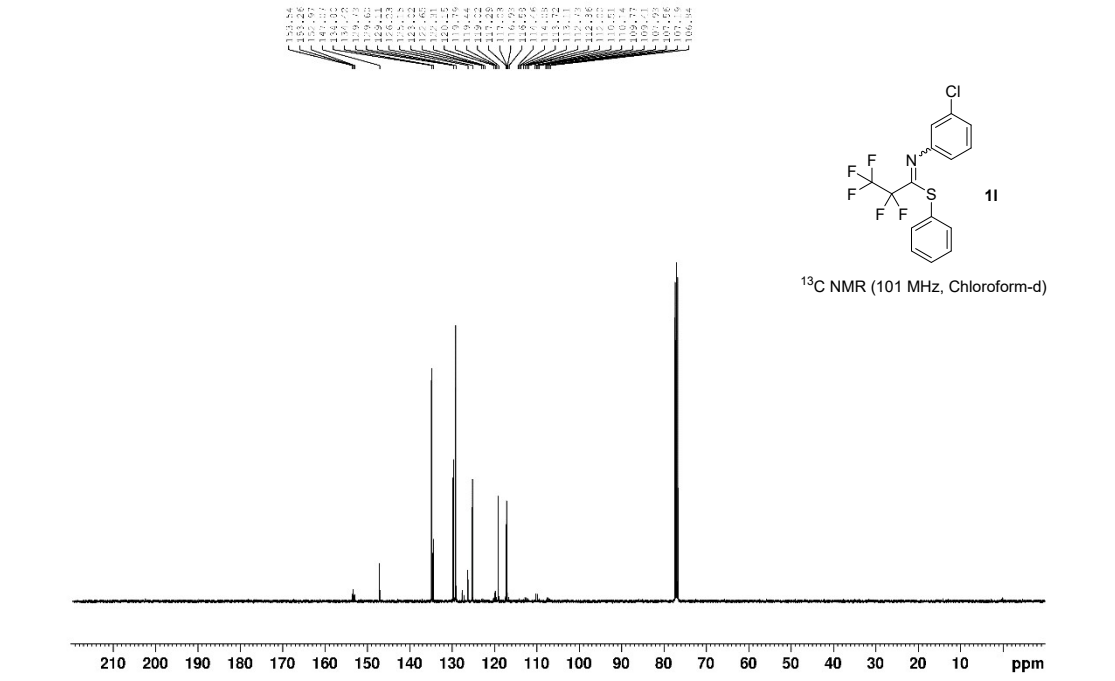
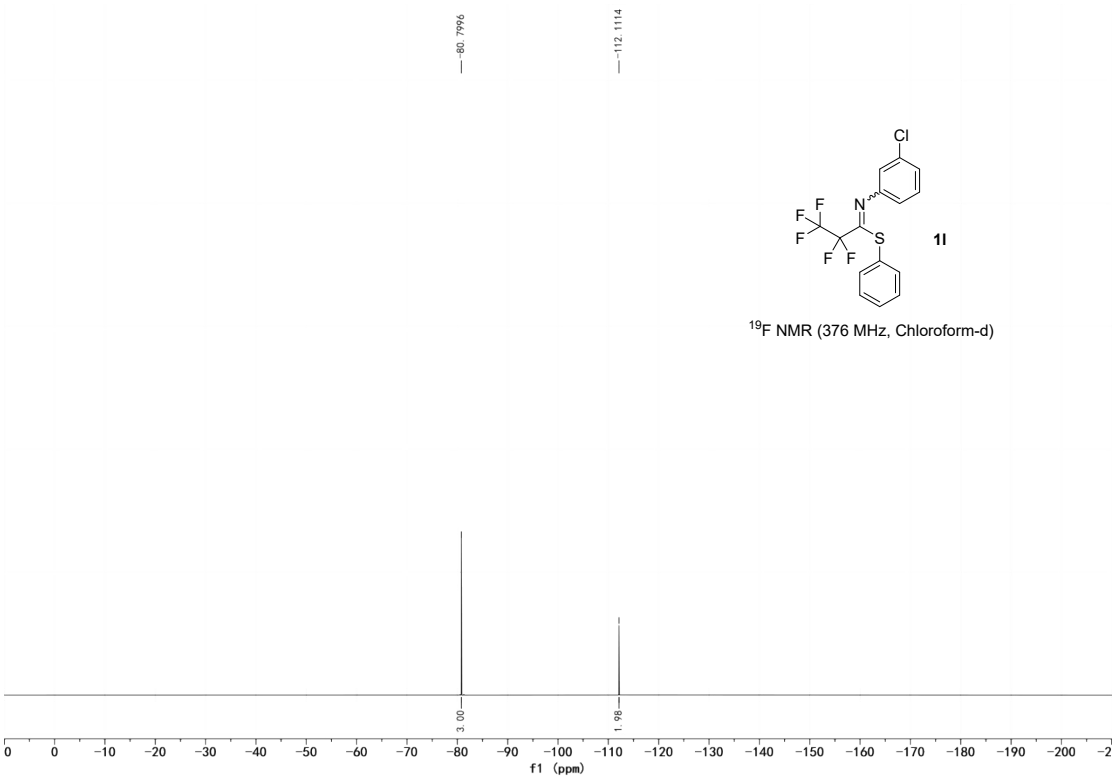
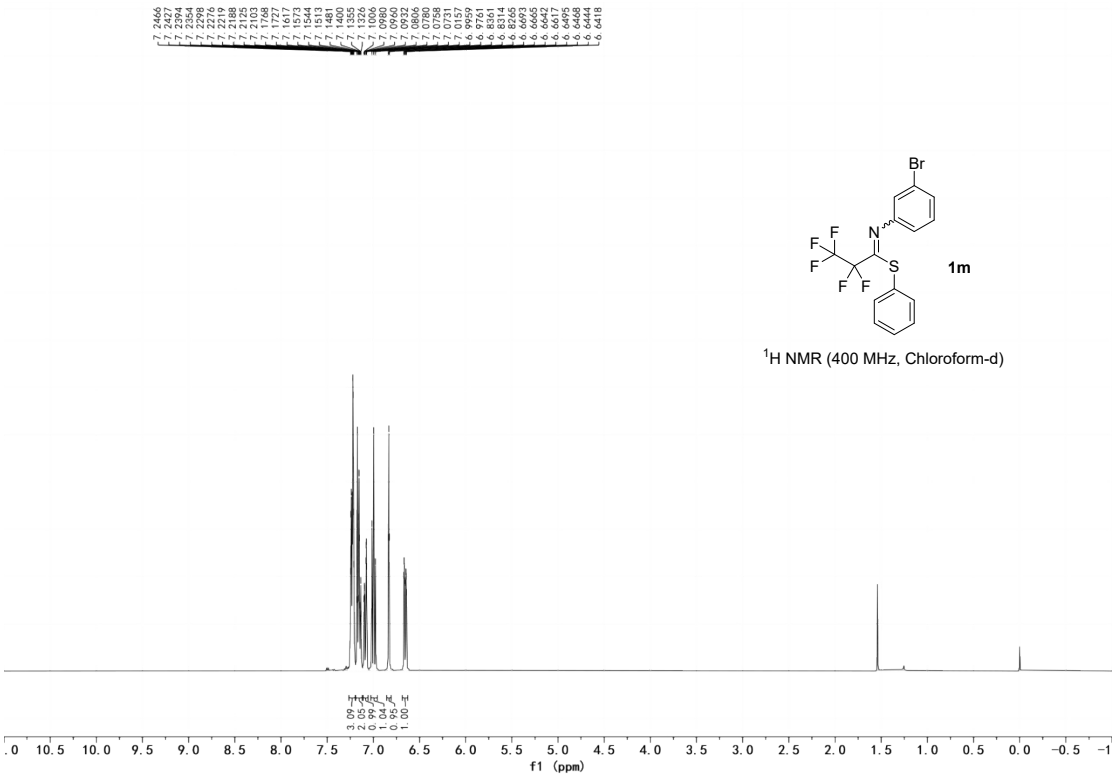

Cl
F
F
F
N
F
F
S
1l
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

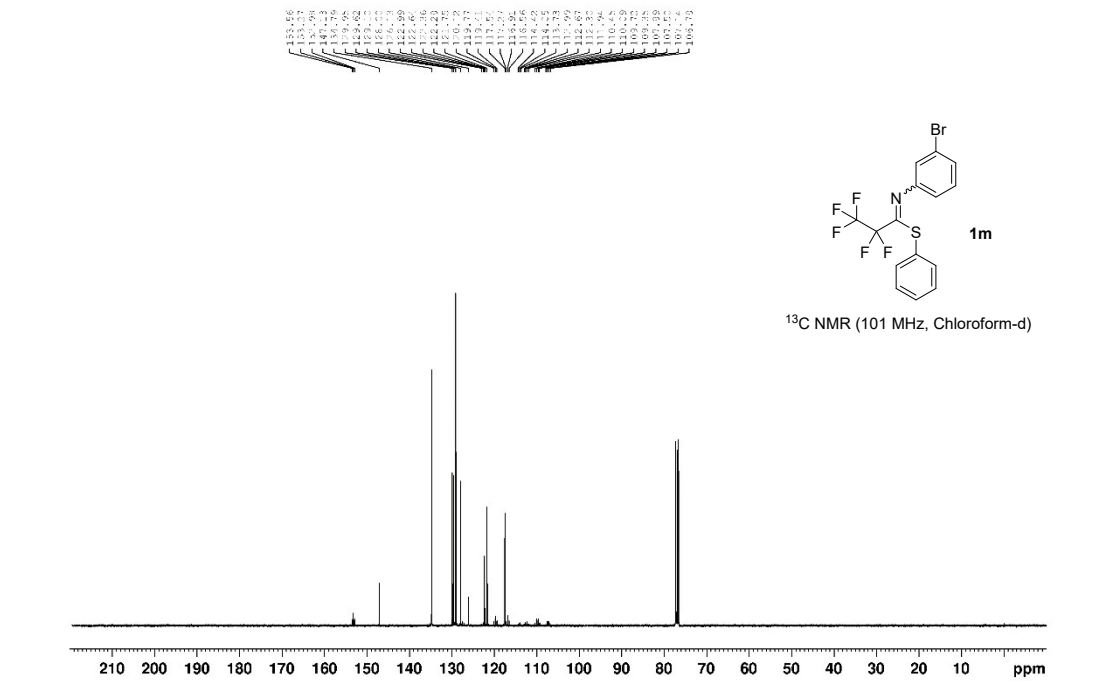

Cl
F
F
F
N
F
F
S
1l
13C NMR (101 MHz, Chloroform-d)
ppm



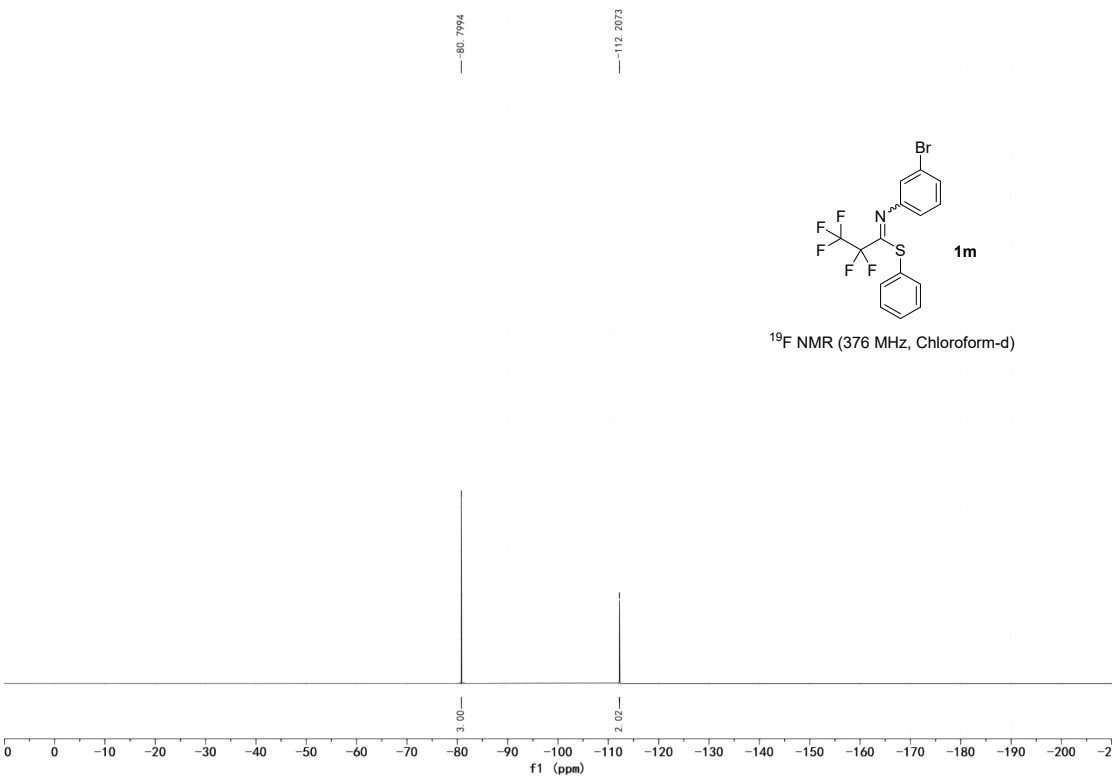
^{19}F NMR (376 MHz, Chloroform-d)



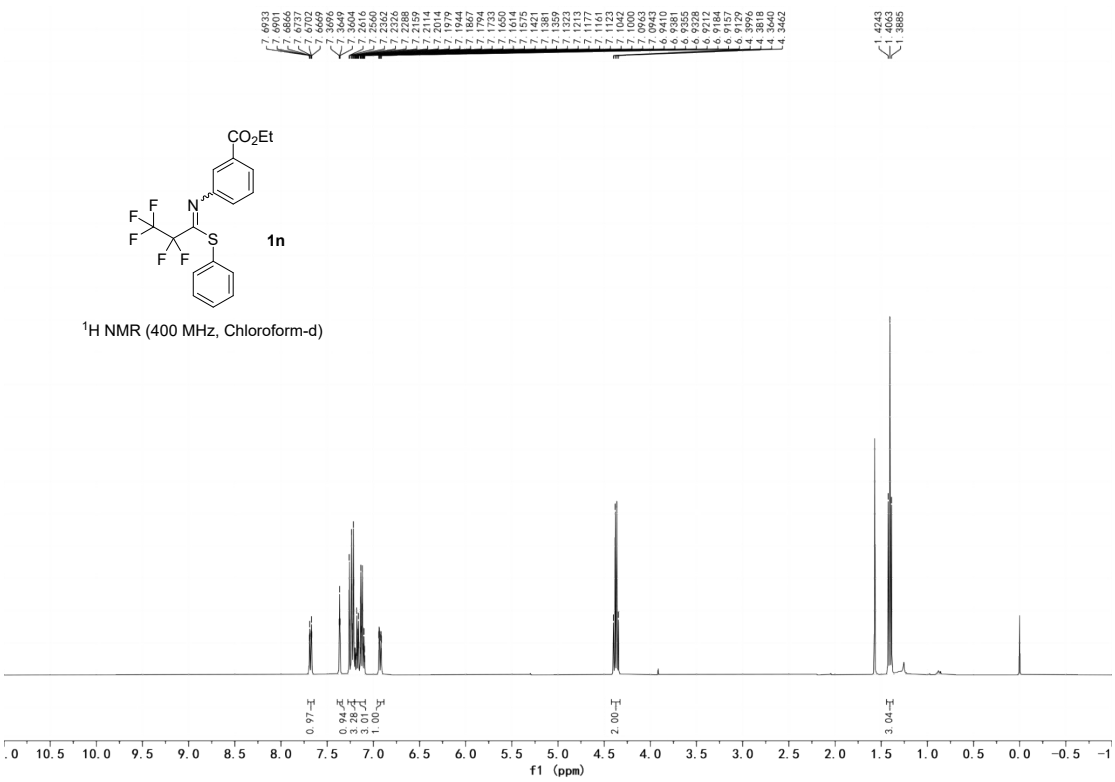
^{1}H NMR (400 MHz, Chloroform-d)

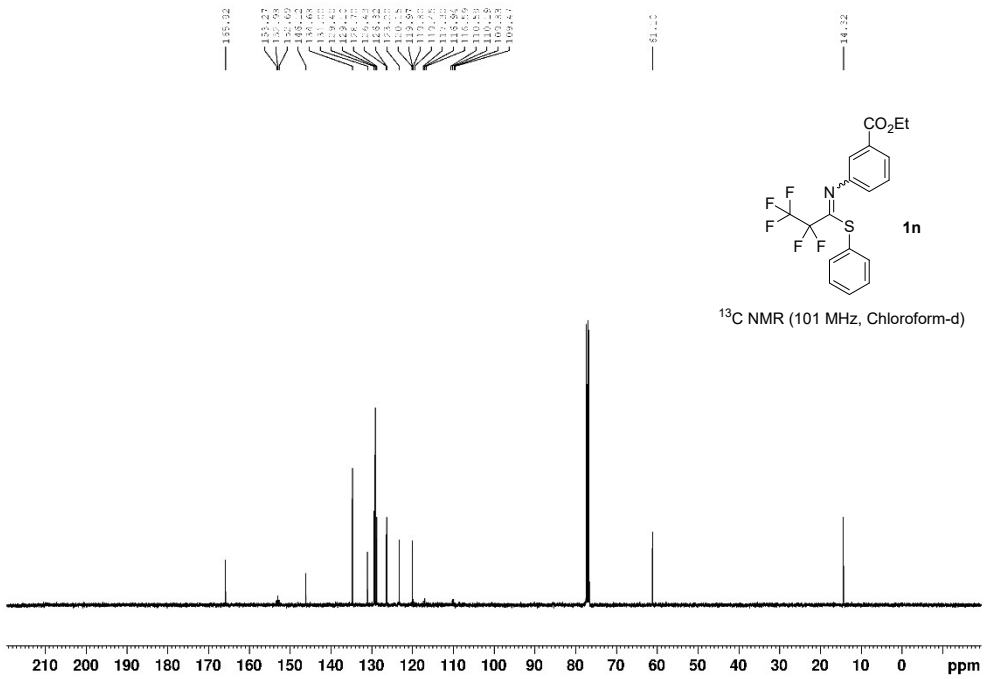


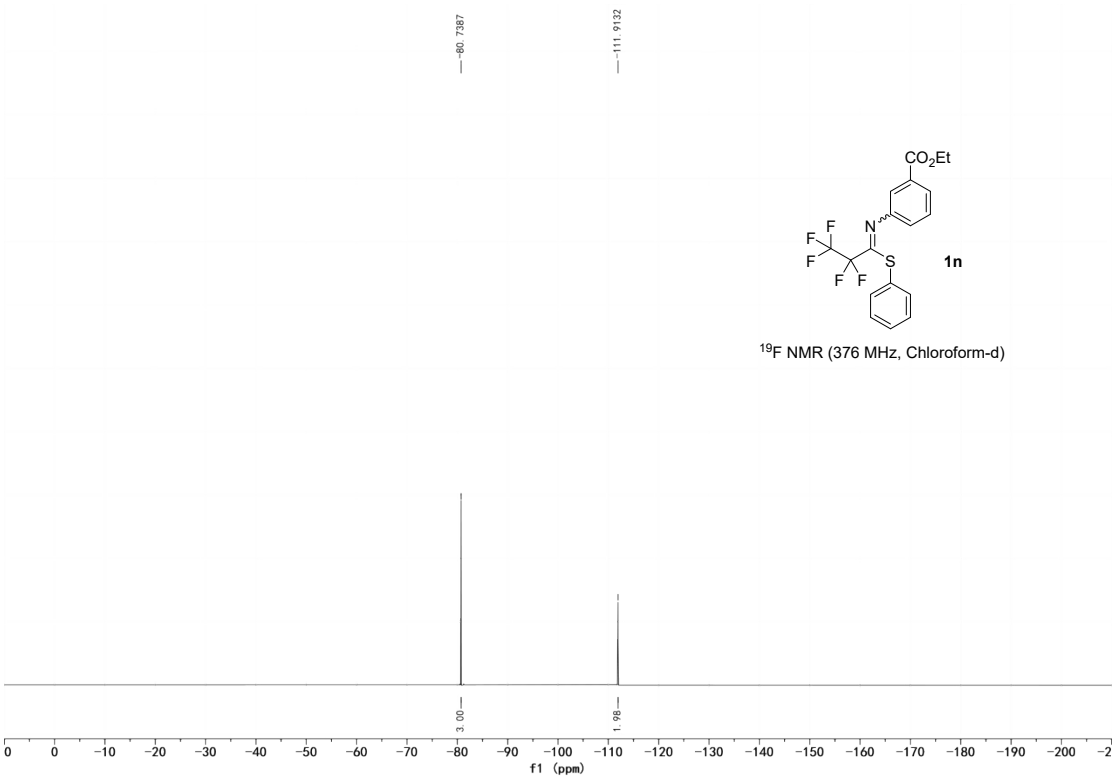
^{13}C NMR (101 MHz, Chloroform-d)



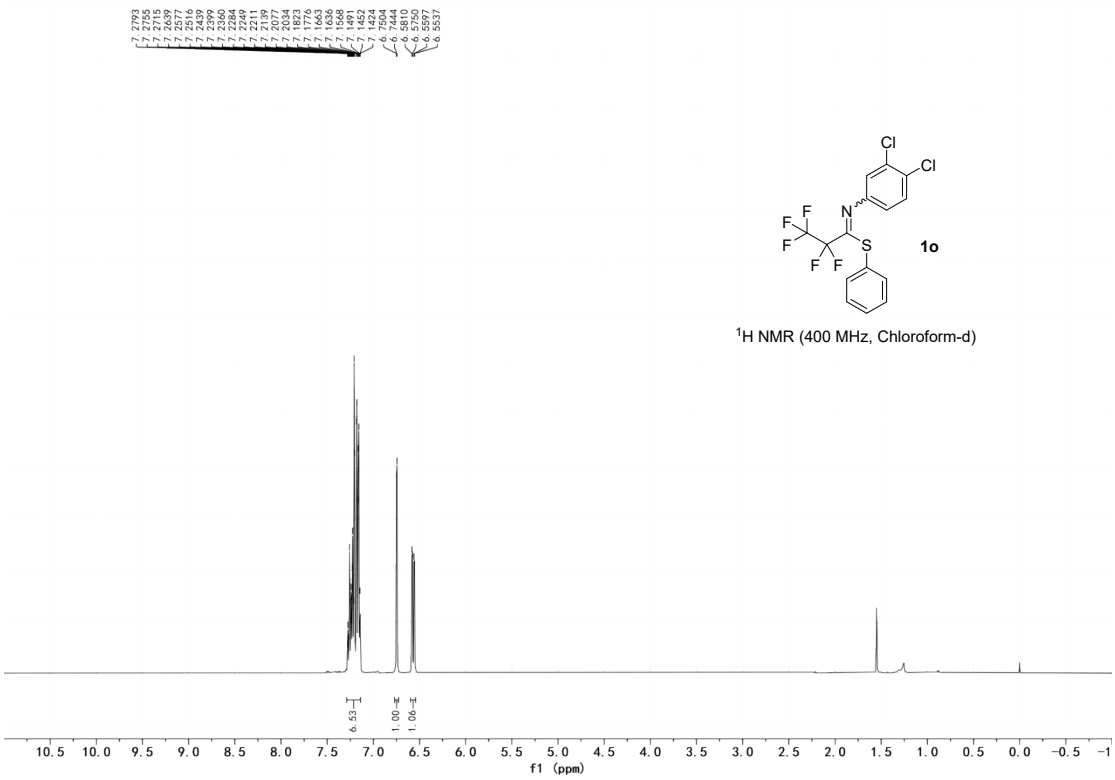
^{19}F NMR (376 MHz, Chloroform-d)


CO2Et
F
F
F
N
S
F
F
1n
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

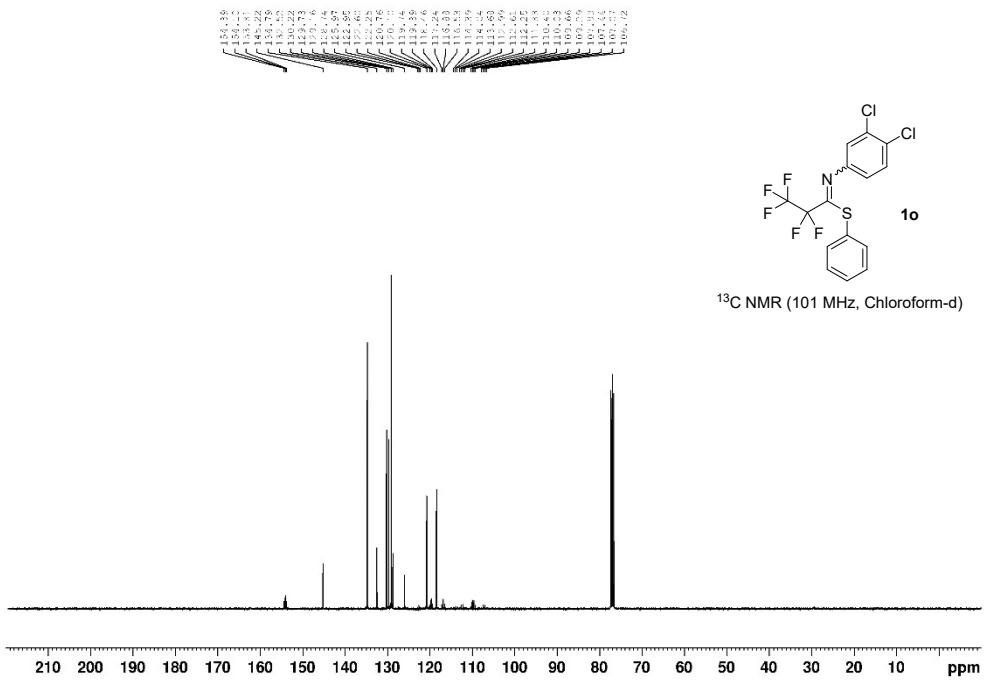

CO2Et
F
F
F
N
S
F
F
1n
13C NMR (101 MHz, Chloroform-d)
ppm



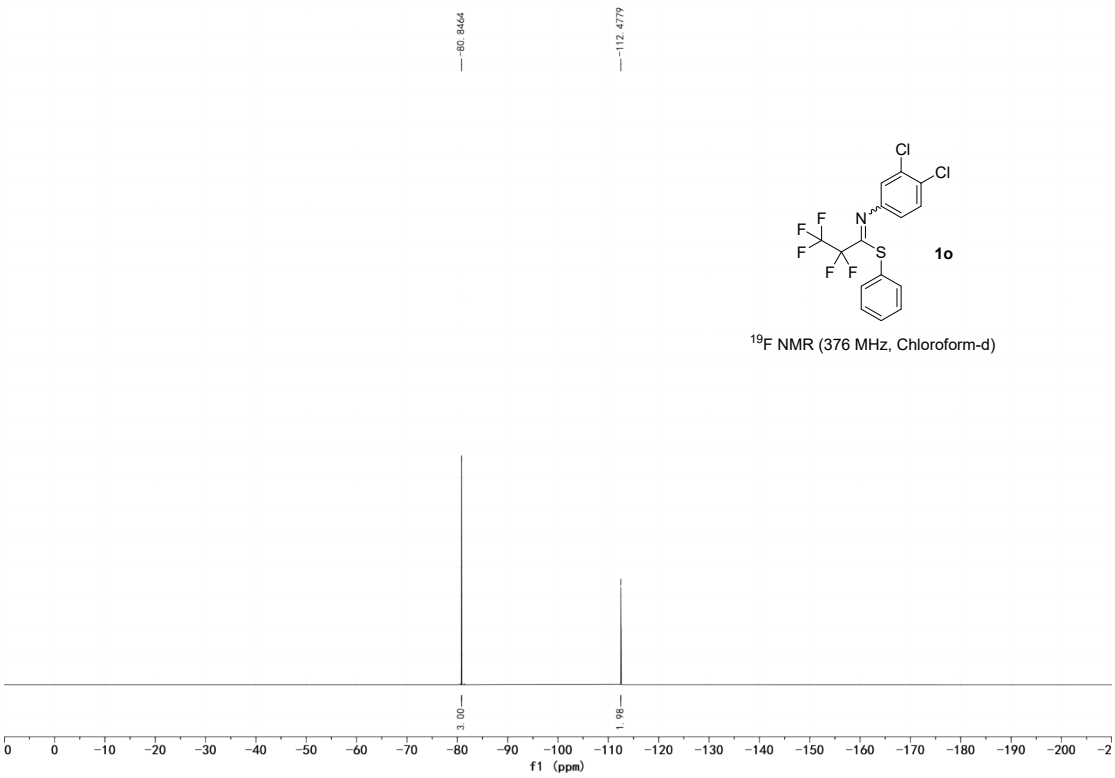
^{19}F NMR (376 MHz, Chloroform-d)



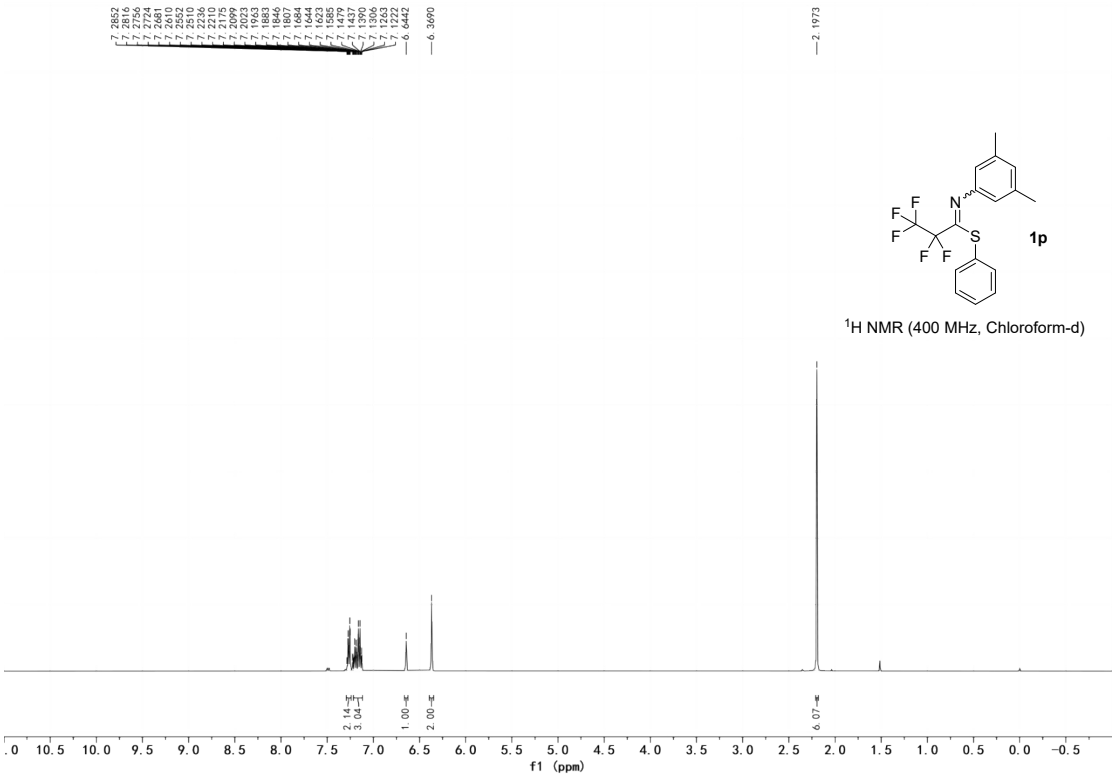
^{1}H NMR (400 MHz, Chloroform-d)



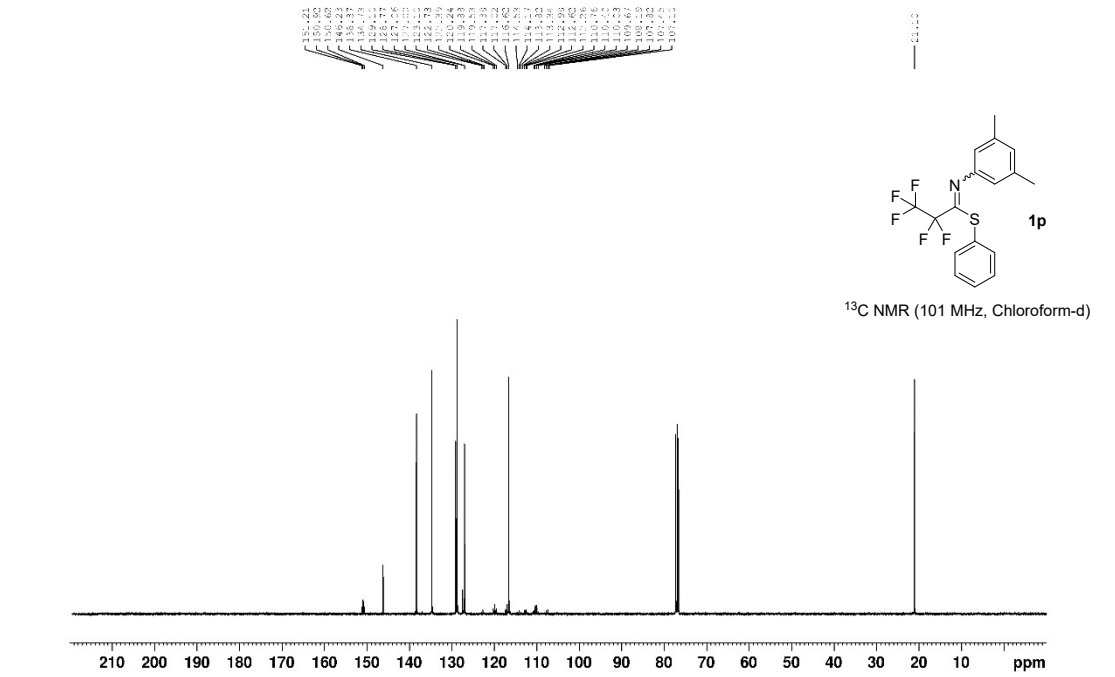
^{13}C NMR (101 MHz, Chloroform-d)



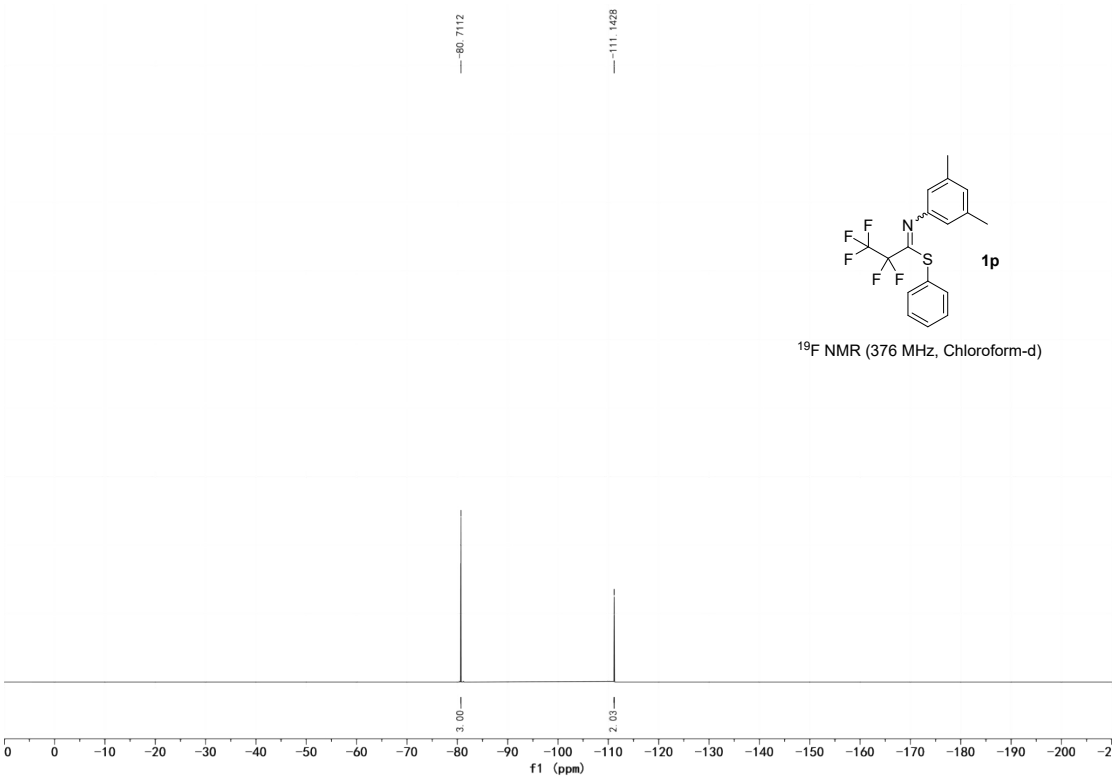
^{19}F NMR (376 MHz, Chloroform-d)



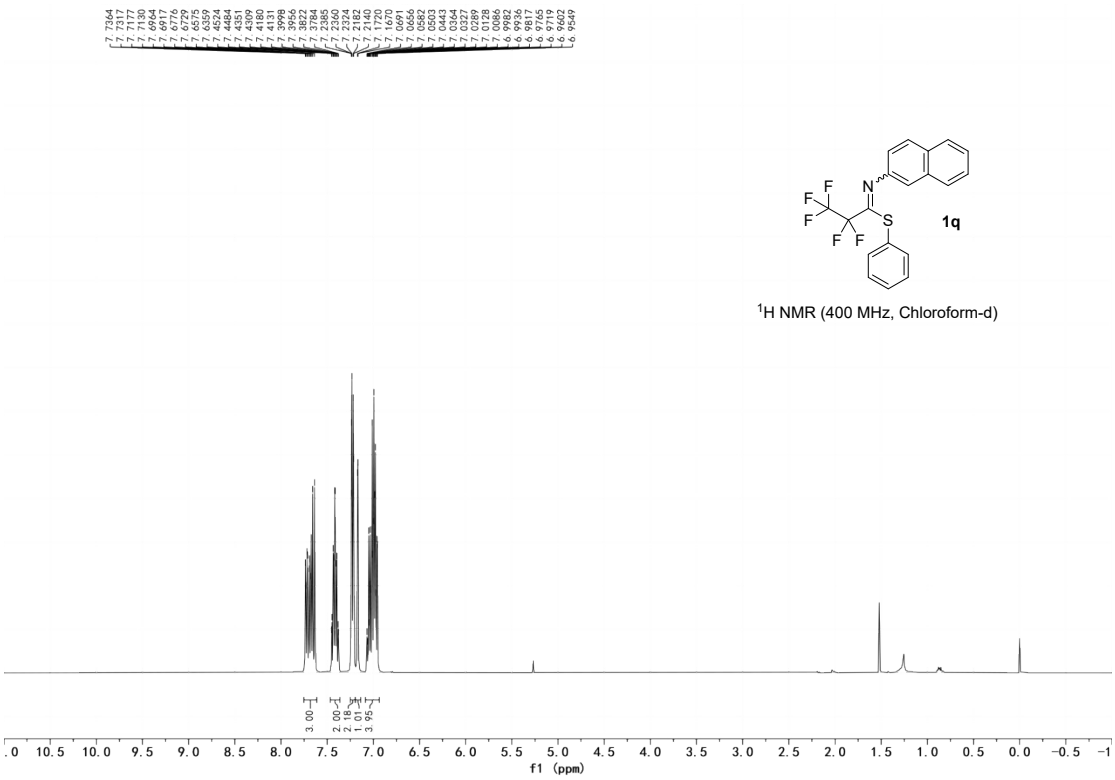
^{1}H NMR (400 MHz, Chloroform-d)

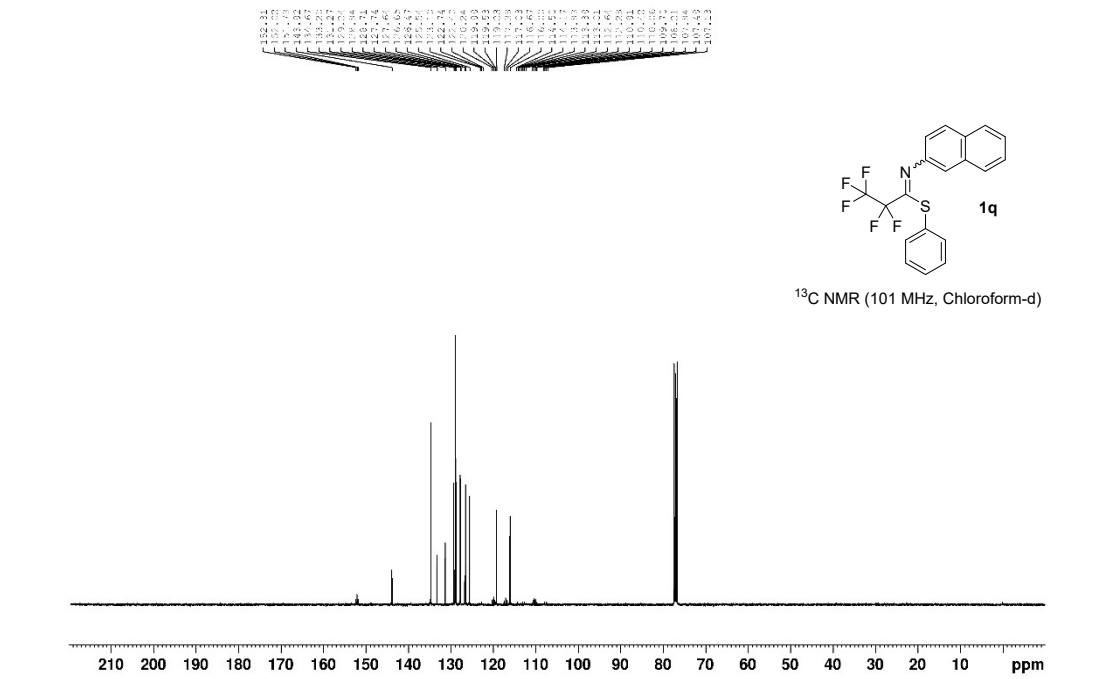


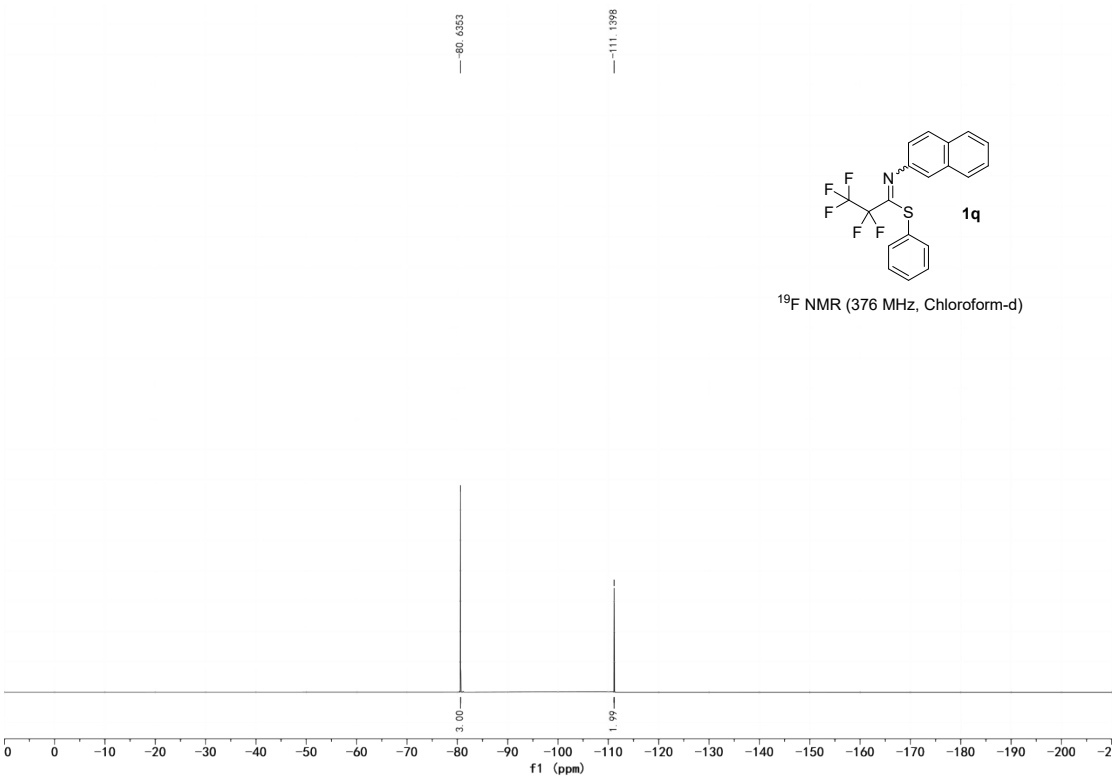
^{13}C NMR (101 MHz, Chloroform-d)



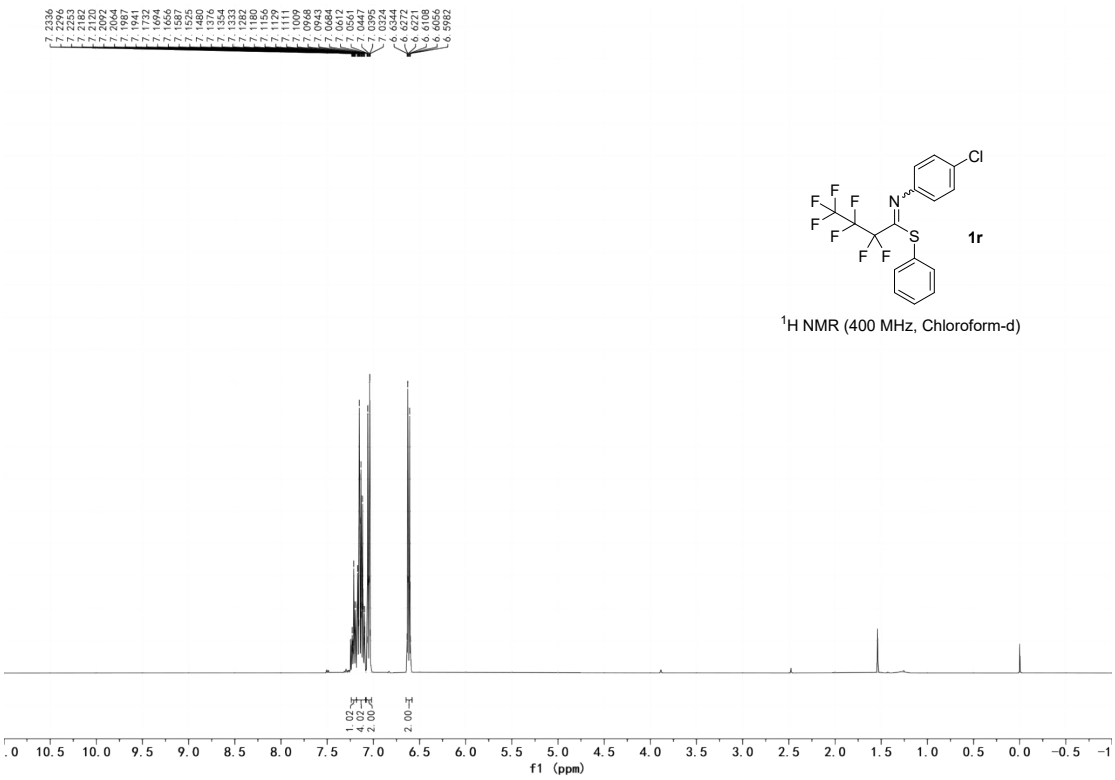
^{19}F NMR (376 MHz, Chloroform-d)


1q
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

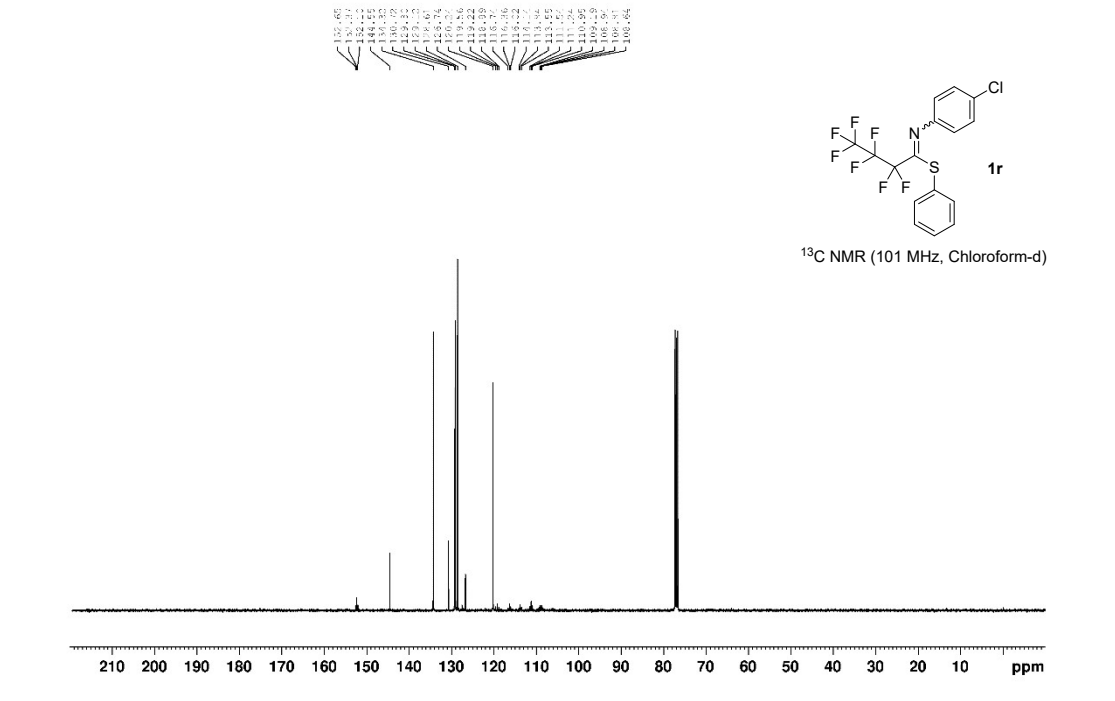

1q
13C NMR (101 MHz, Chloroform-d)
ppm



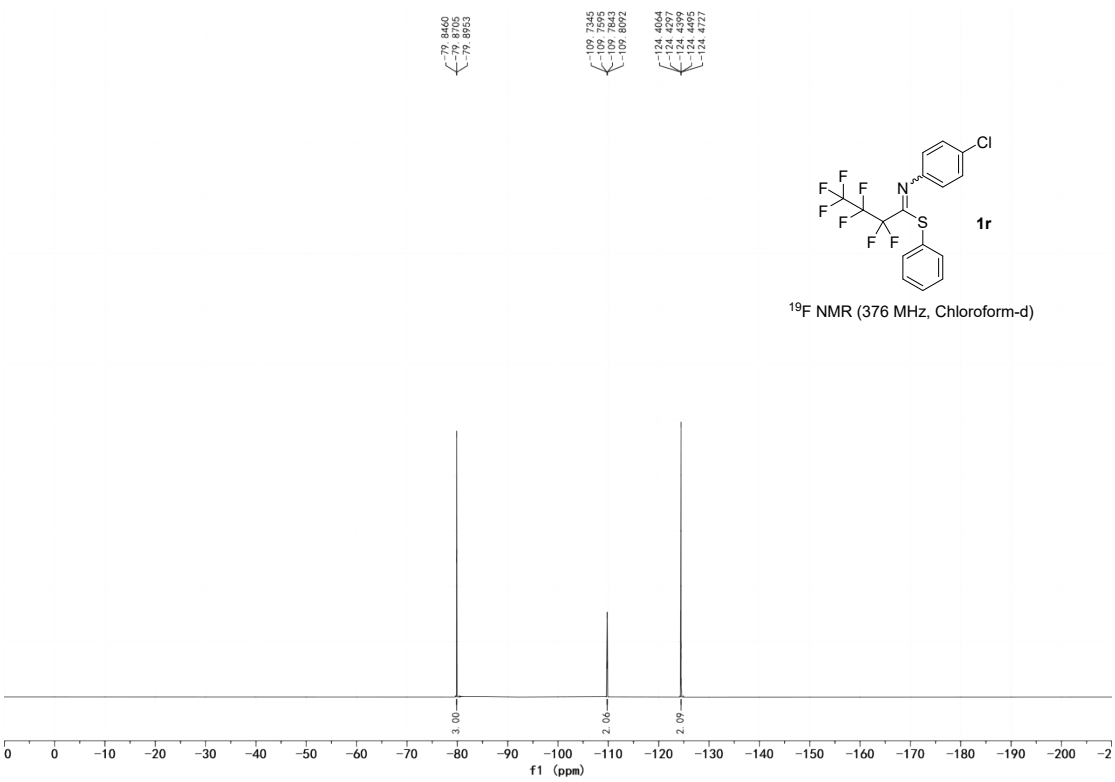
^{19}F NMR (376 MHz, Chloroform-d)



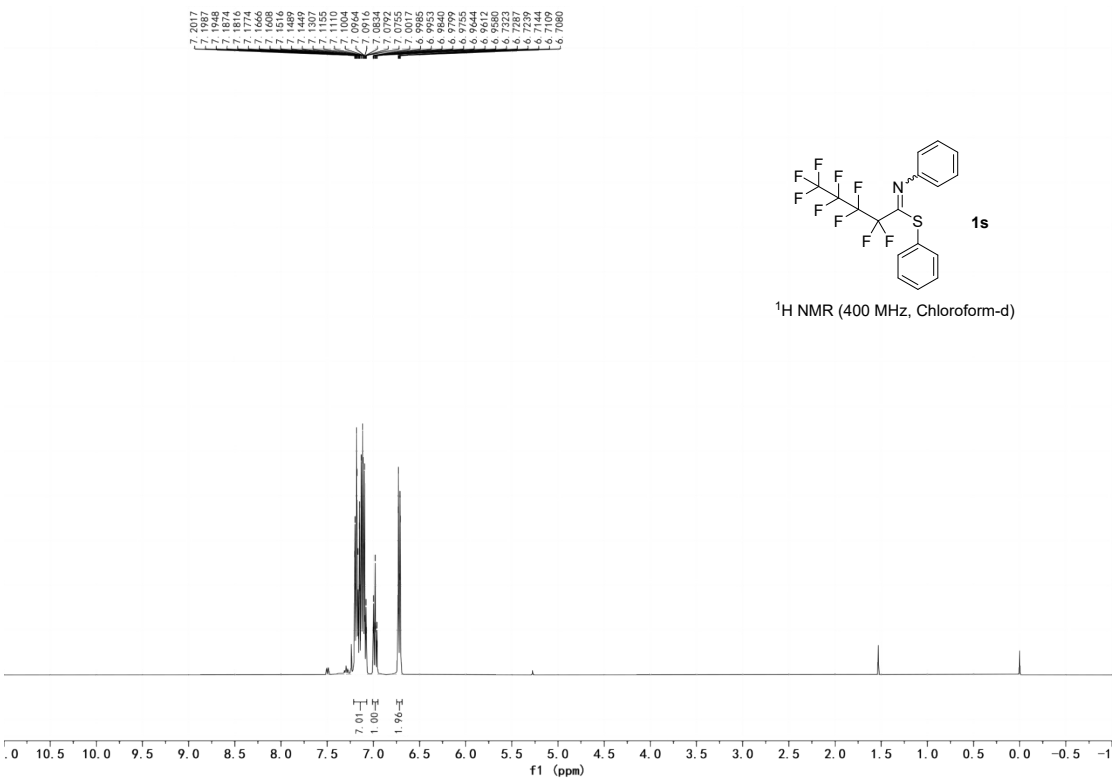
^{1}H NMR (400 MHz, Chloroform-d)

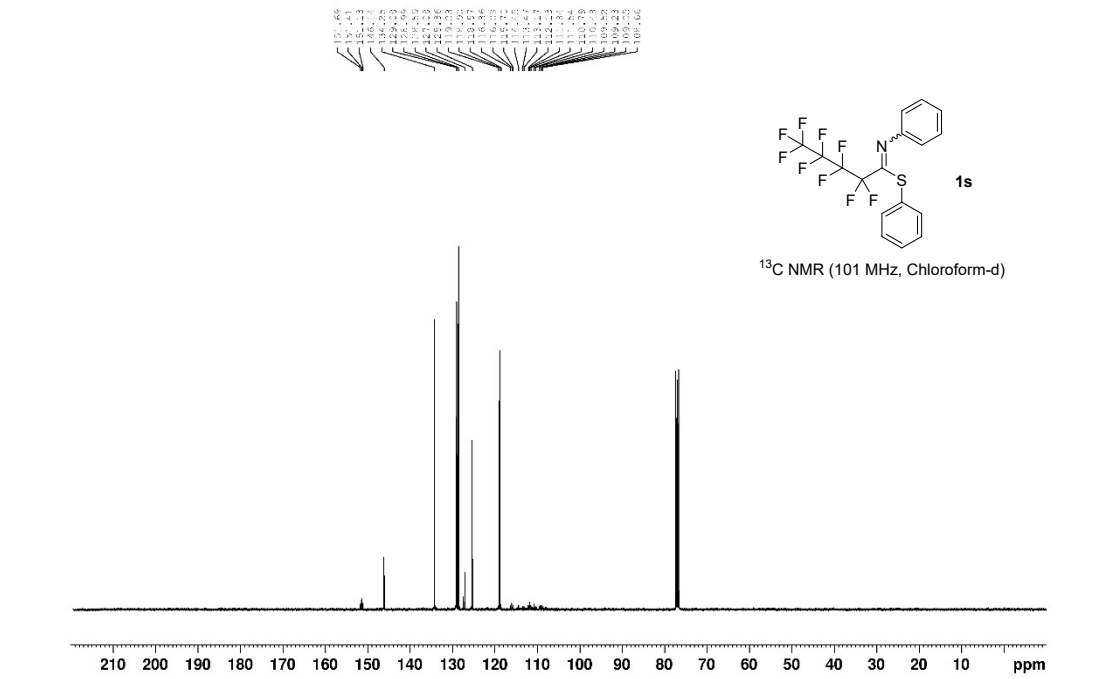


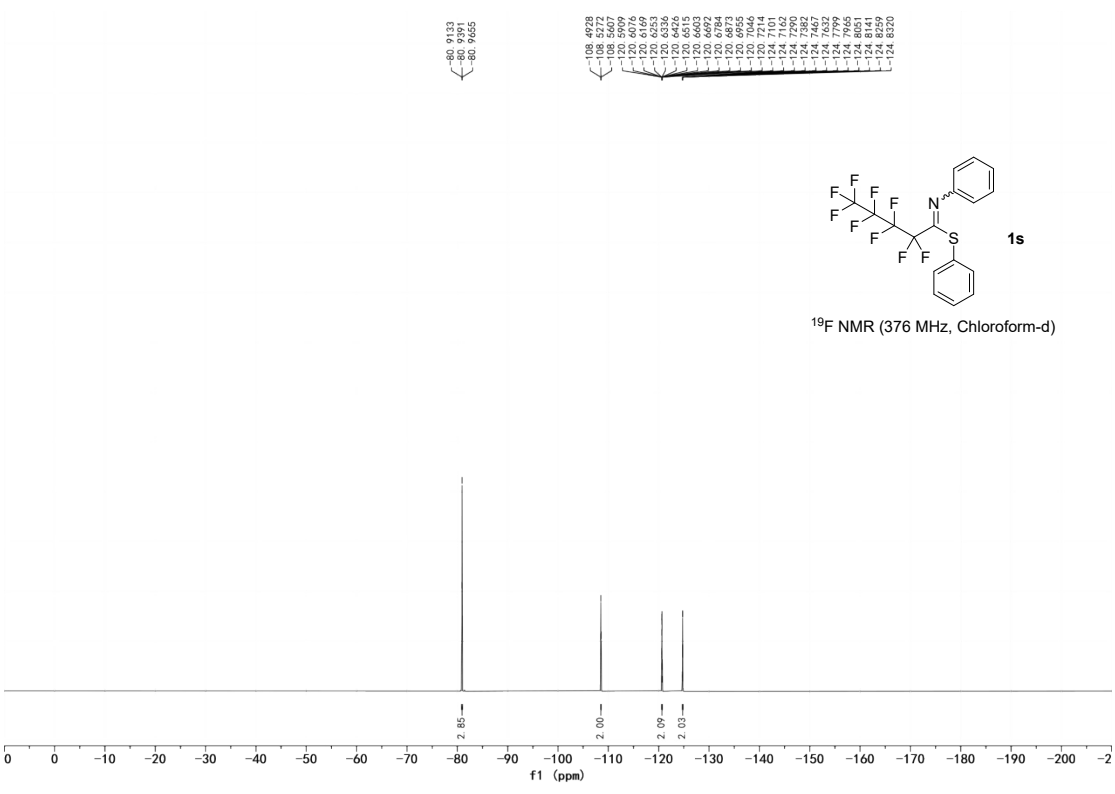
^{13}C NMR (101 MHz, Chloroform-d)



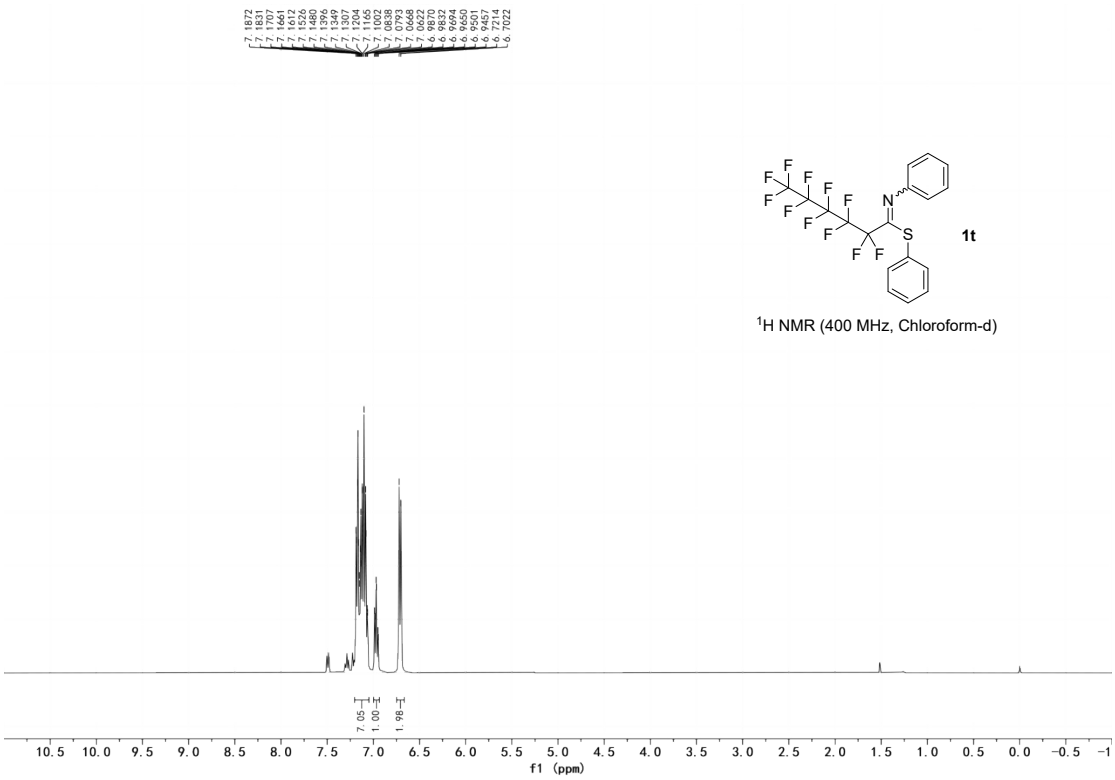
^{19}F NMR (376 MHz, Chloroform-d)

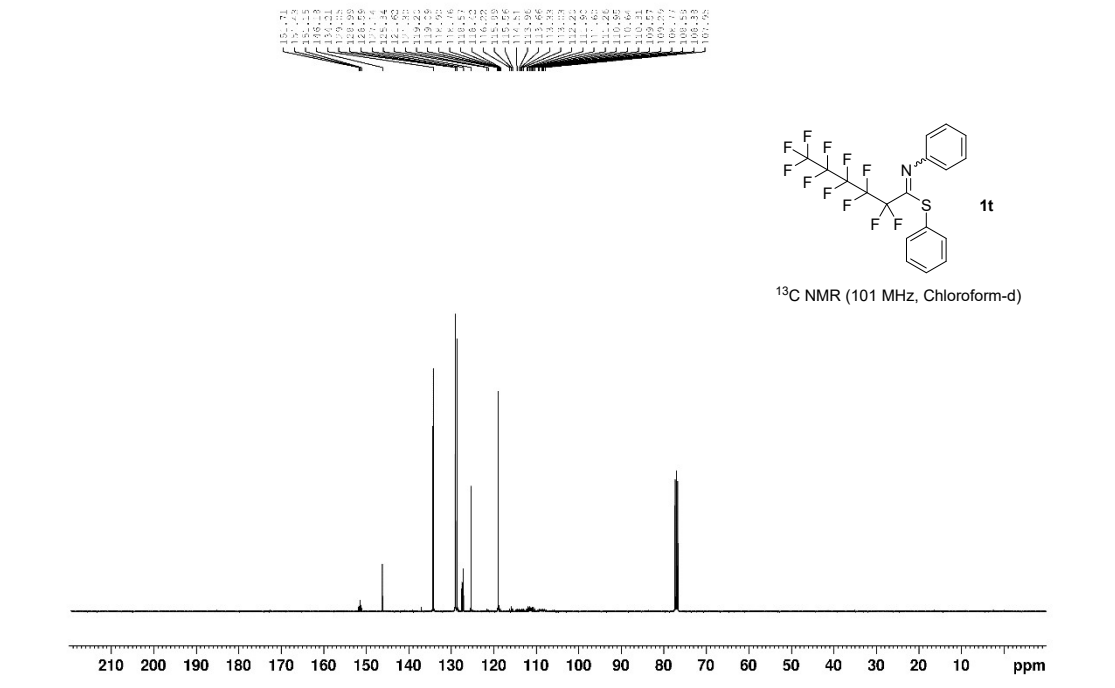

1s
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

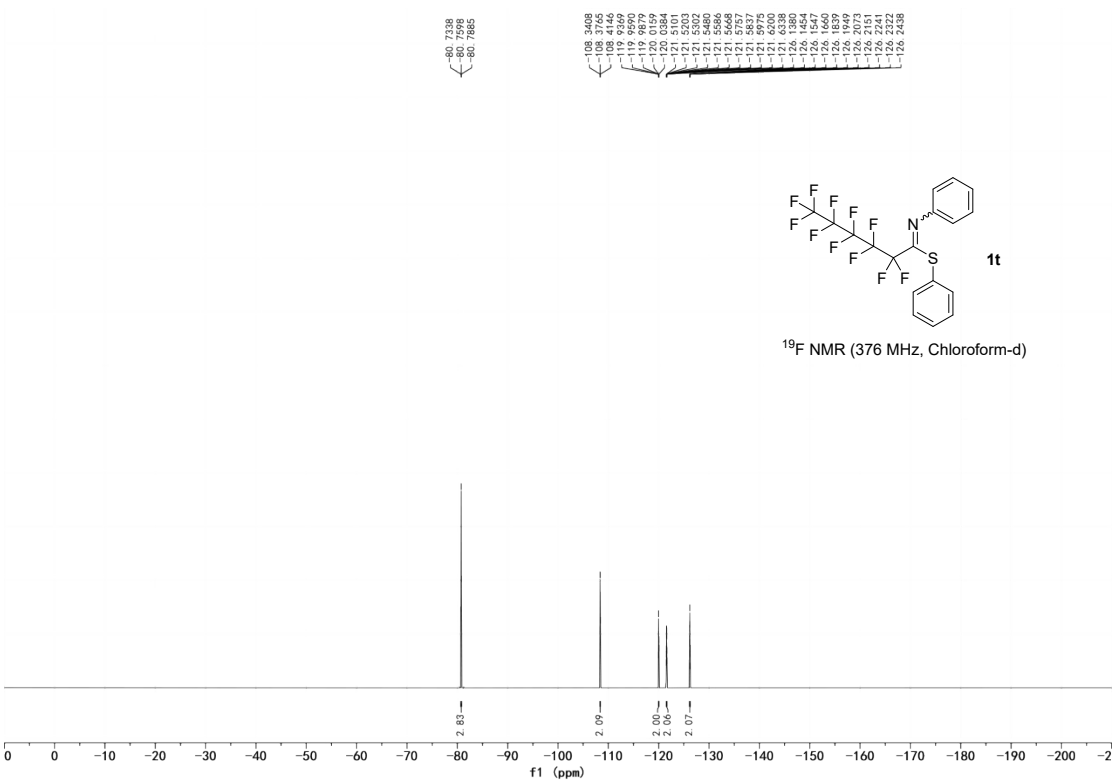

1s
13C NMR (101 MHz, Chloroform-d)
ppm



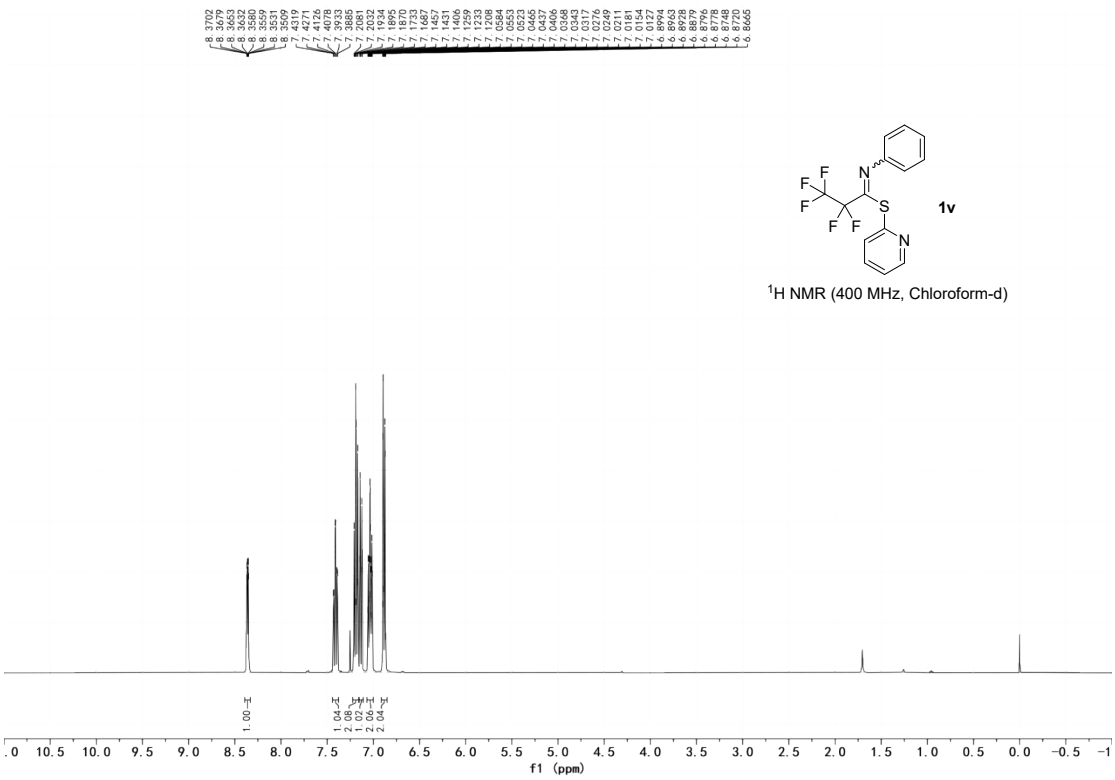
^{19}F NMR (376 MHz, Chloroform-d)

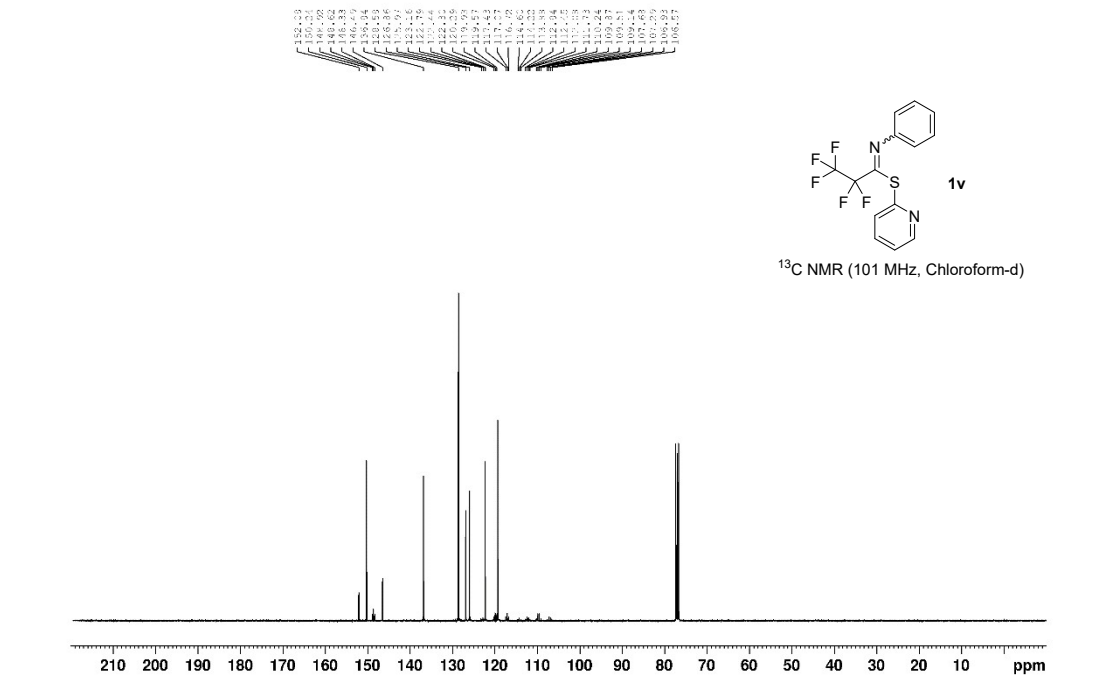

7.1872
7.1831
7.1707
7.1647
7.1612
7.1526
7.1480
7.1396
7.1349
7.1307
7.1204
7.1145
7.1002
7.0838
7.0793
7.0668
7.0622
6.9870
6.9832
6.9694
6.9650
6.9501
6.9457
6.7214
6.7022
F
F
F
F
F
F
F
F
F
F
F
N
S
1t
1H NMR (400 MHz, Chloroform-d)
7.05
1.00
1.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

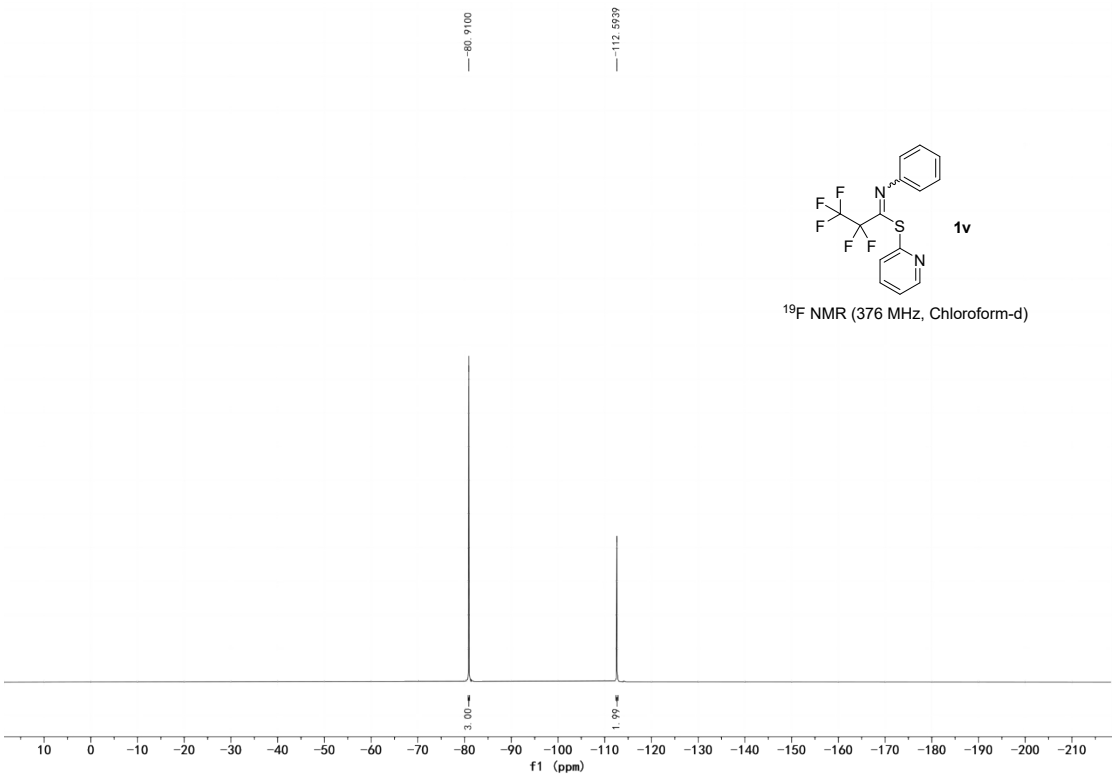

F
F
F
F
F
F
F
F
F
F
F
N
S
1t
13C NMR (101 MHz, Chloroform-d)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



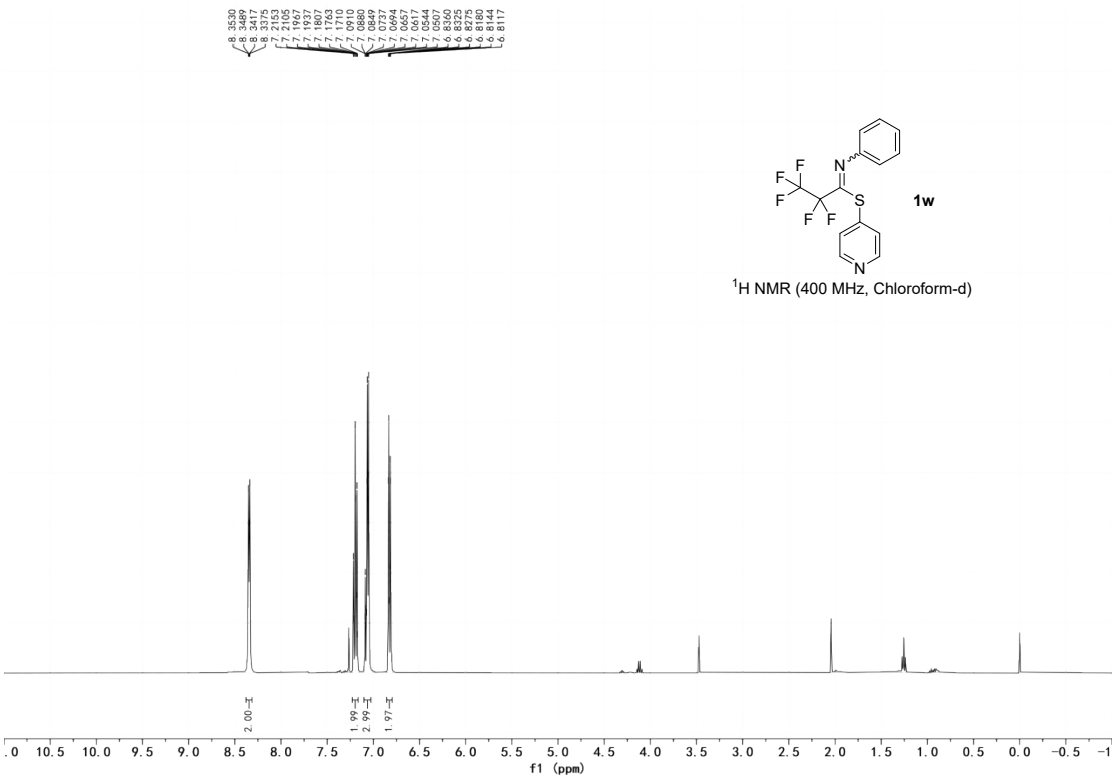
^{19}F NMR (376 MHz, Chloroform-d)

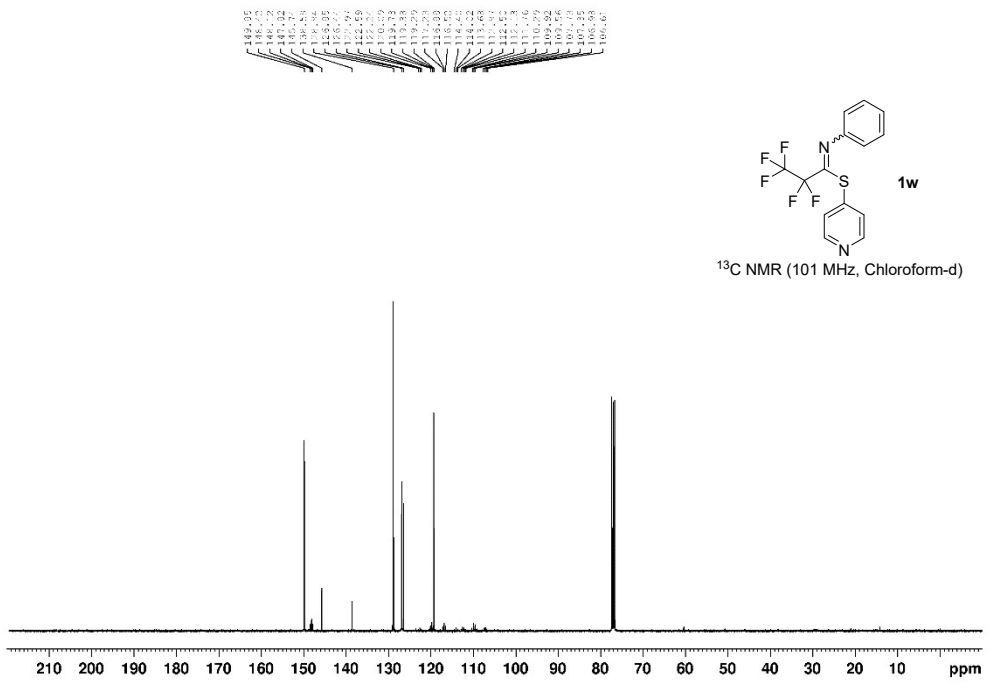

1v
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

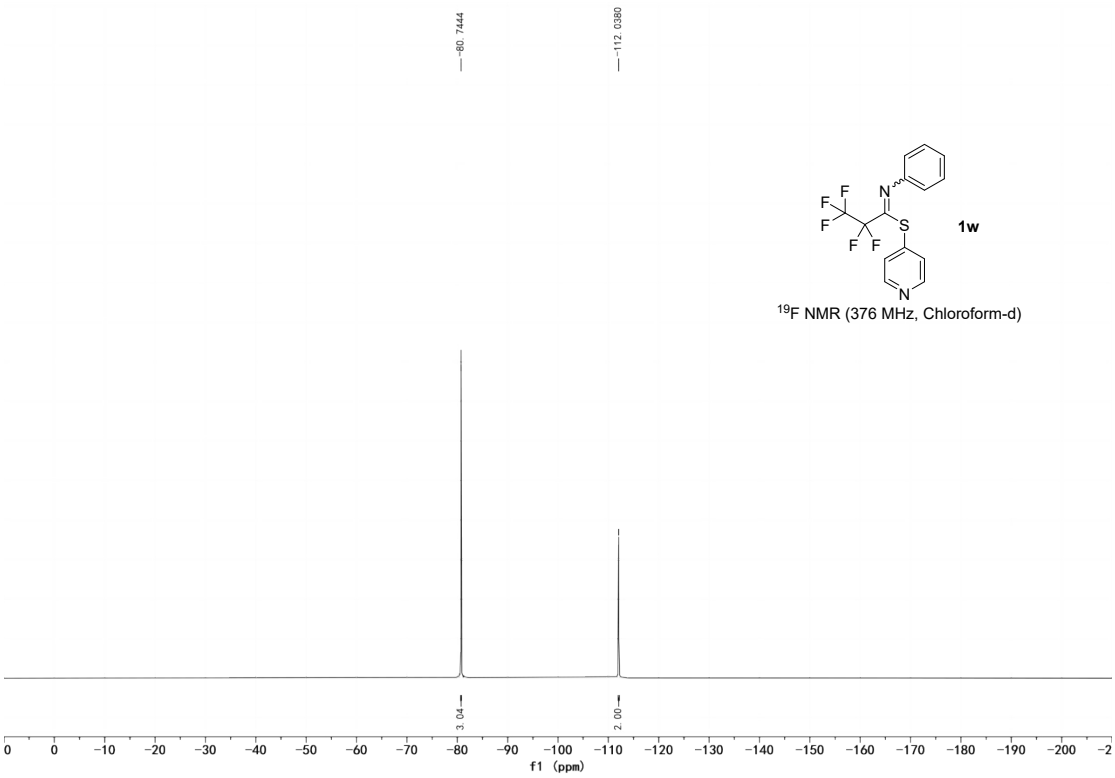

1v
13C NMR (101 MHz, Chloroform-d)
ppm



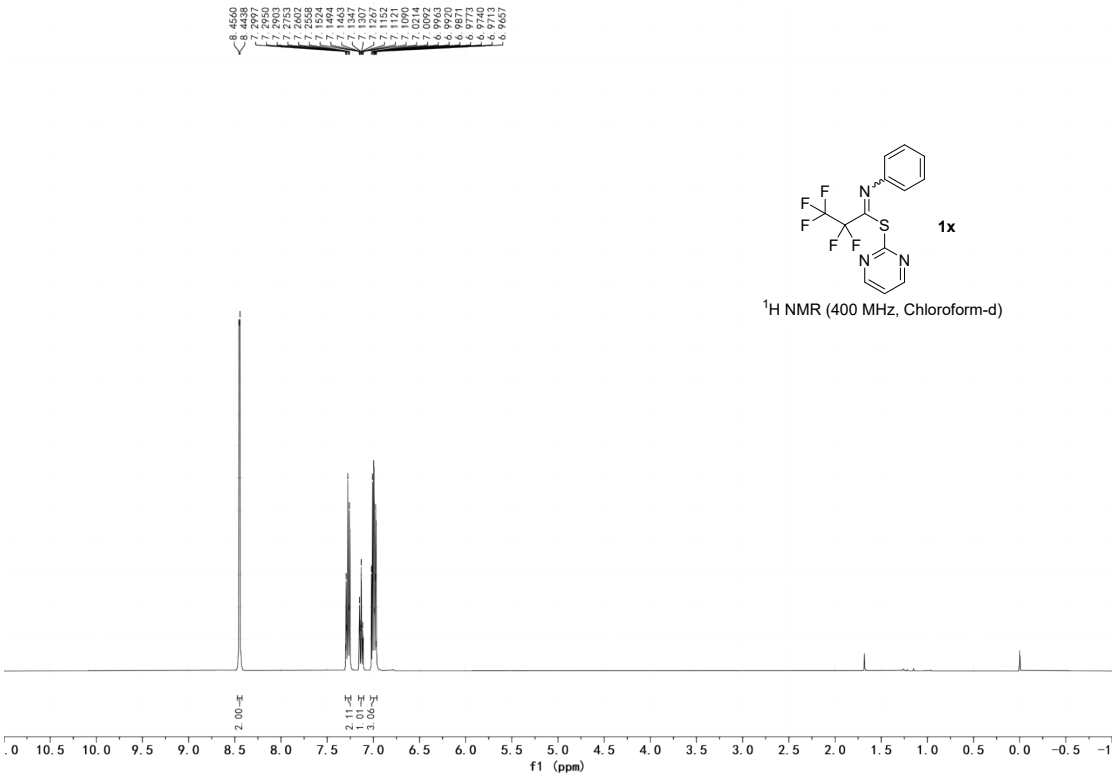
^{19}F NMR (376 MHz, Chloroform-d)

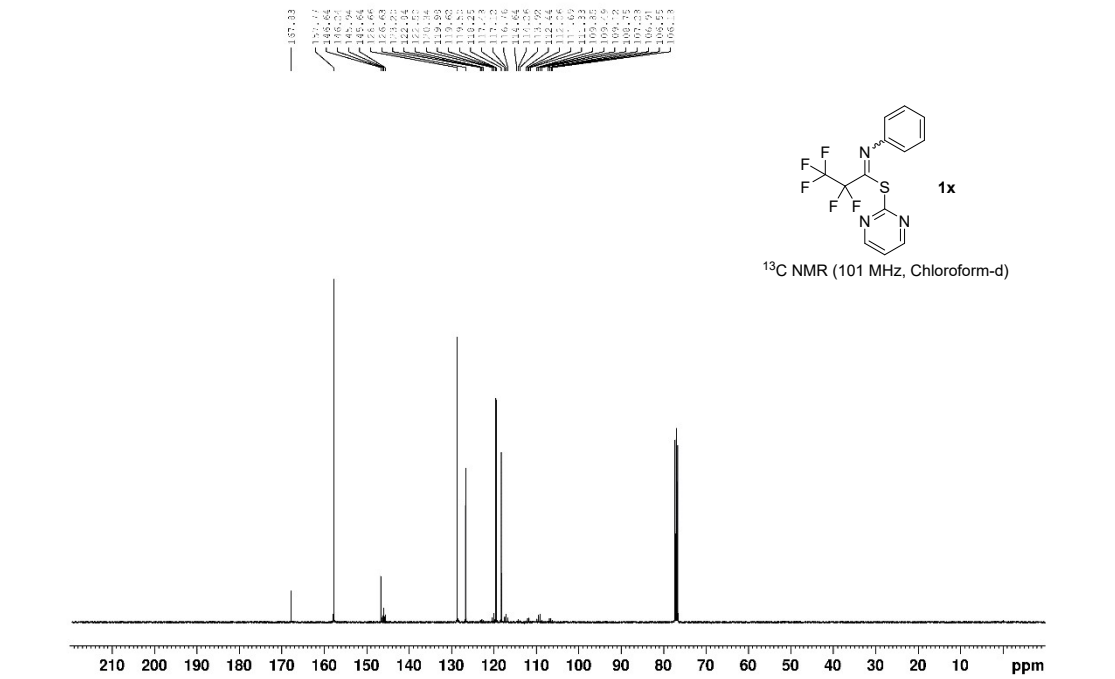

1w
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

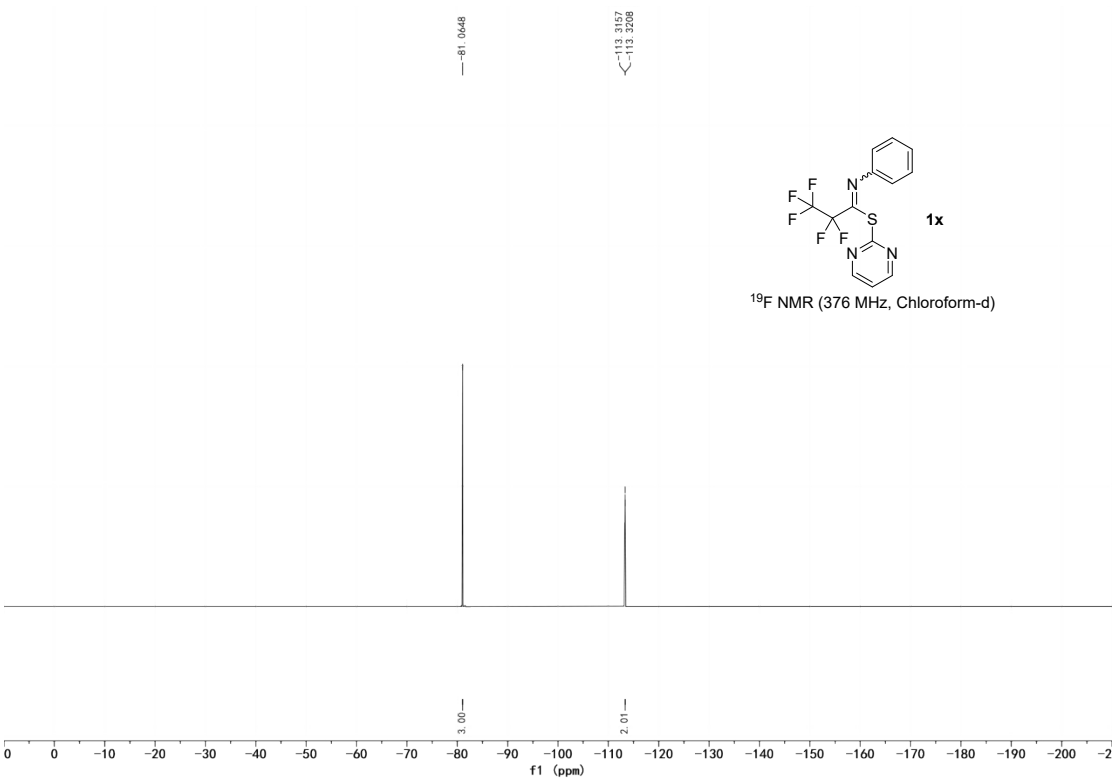

1w
13C NMR (101 MHz, Chloroform-d)
ppm



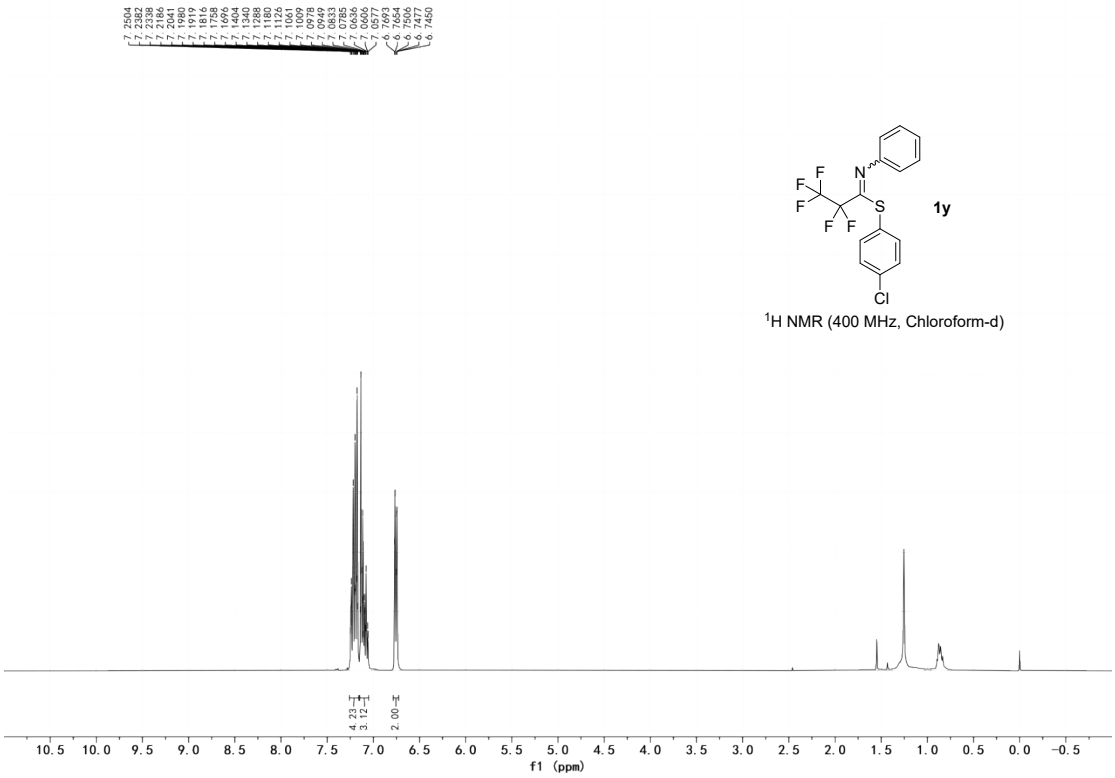
^{19}F NMR (376 MHz, Chloroform-d)

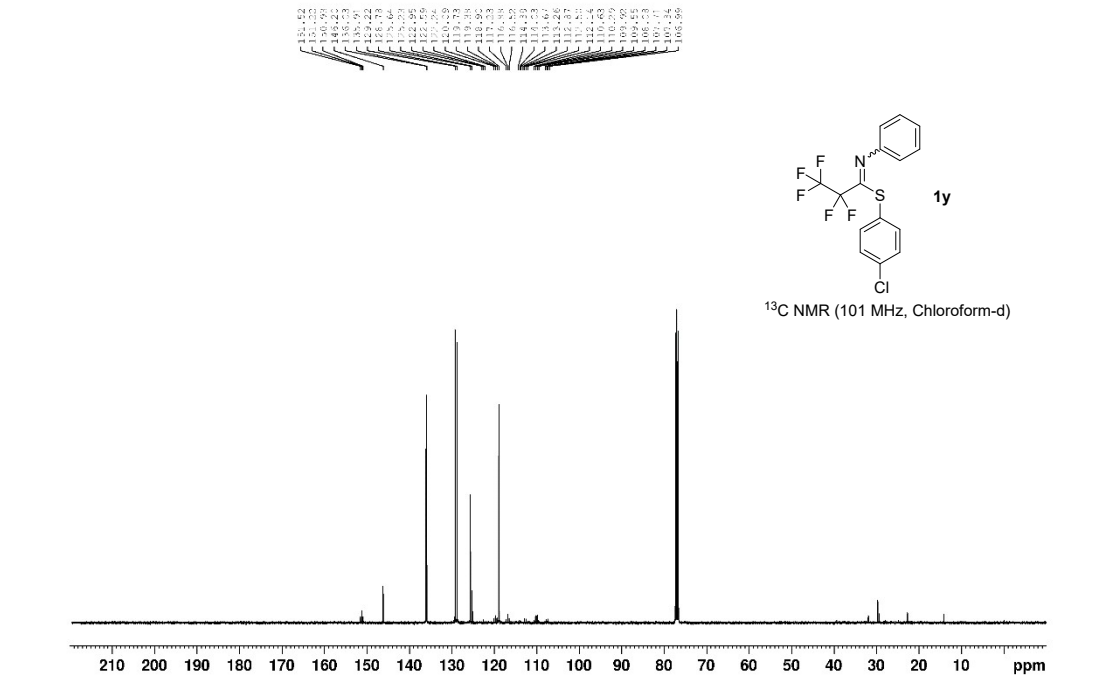

1x
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

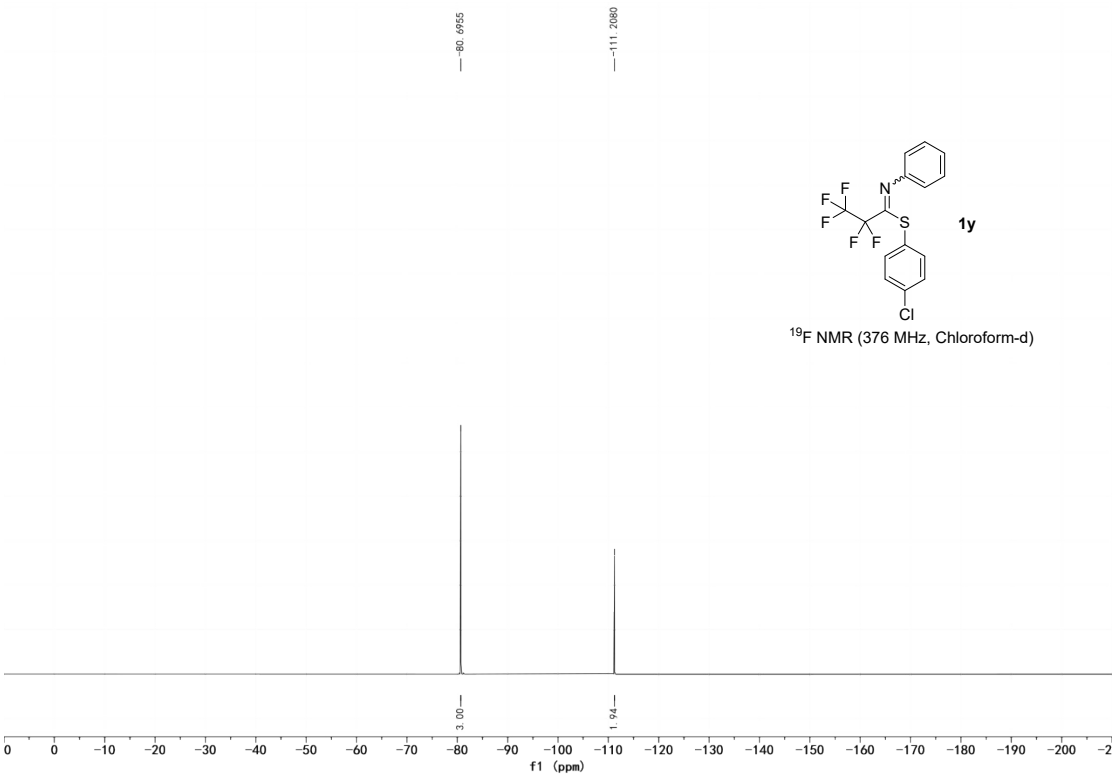

1x
13C NMR (101 MHz, Chloroform-d)
ppm



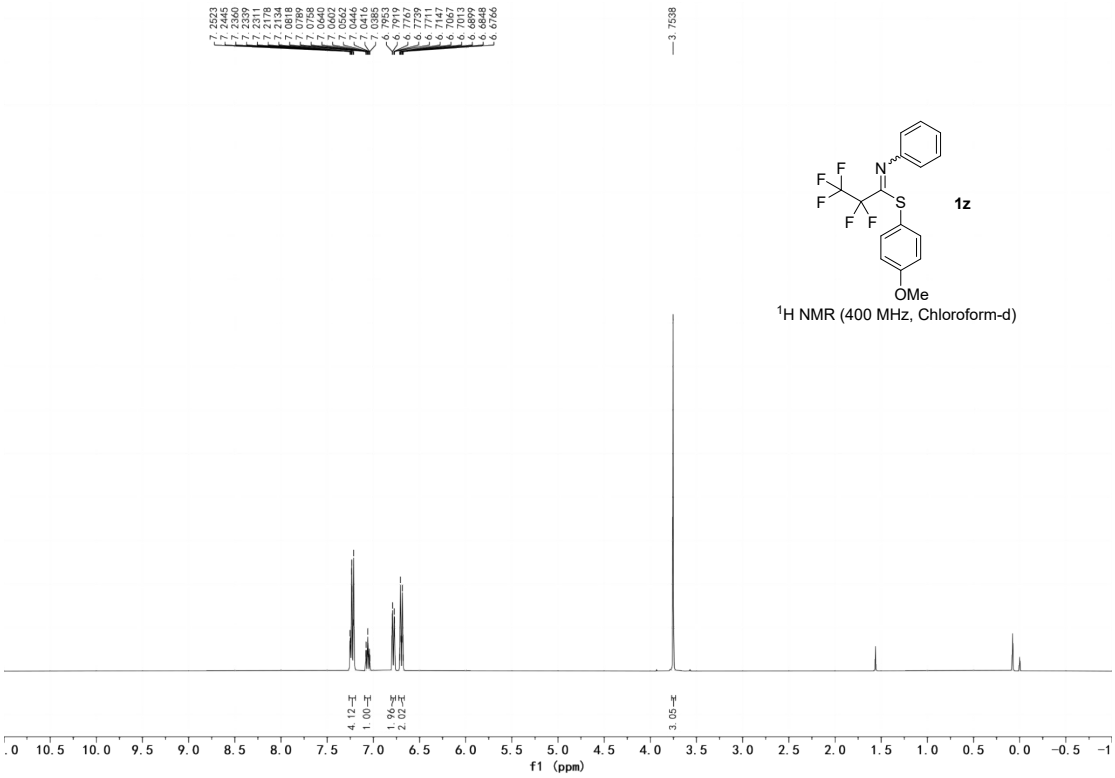
^{19}F NMR (376 MHz, Chloroform-d)

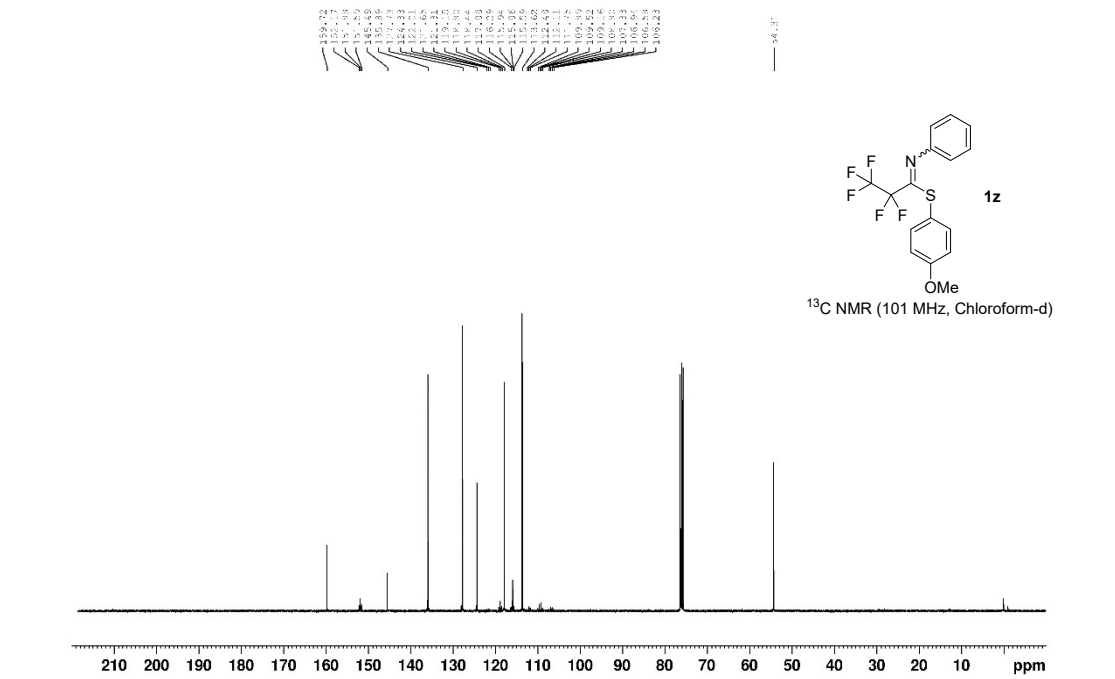

1y
1H NMR (400 MHz, Chloroform-d)
4.23
3.12
2.00
f1 (ppm)

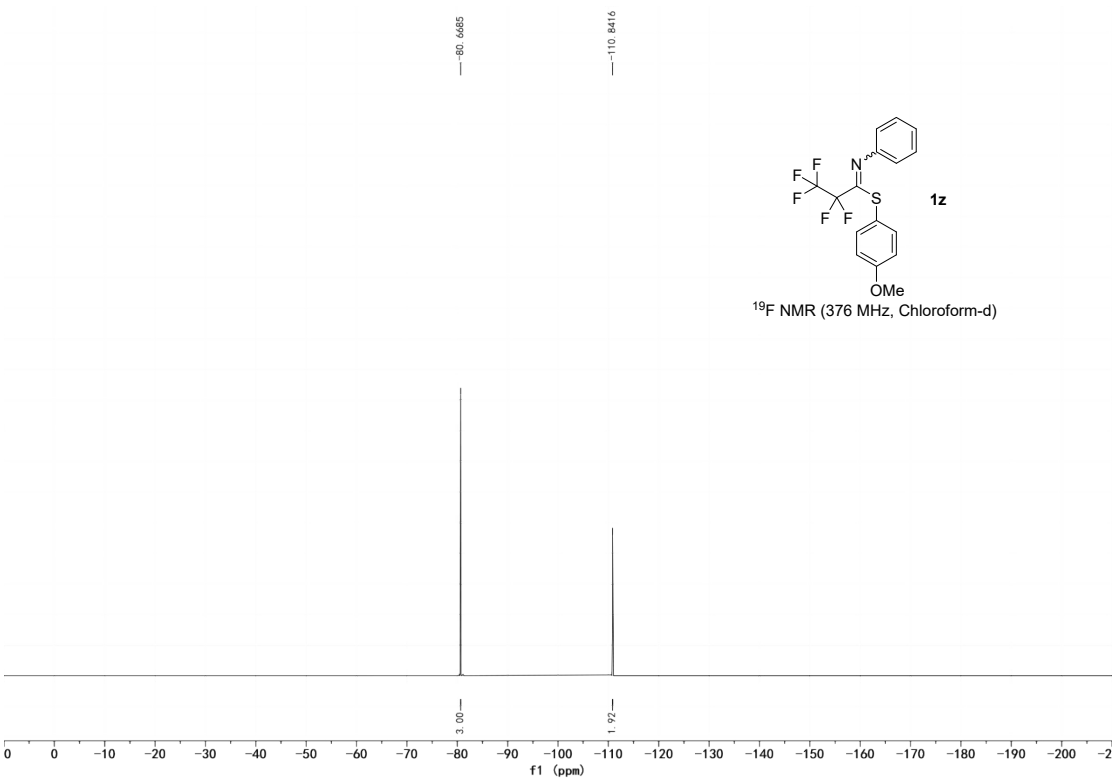

1y
13C NMR (101 MHz, Chloroform-d)
ppm



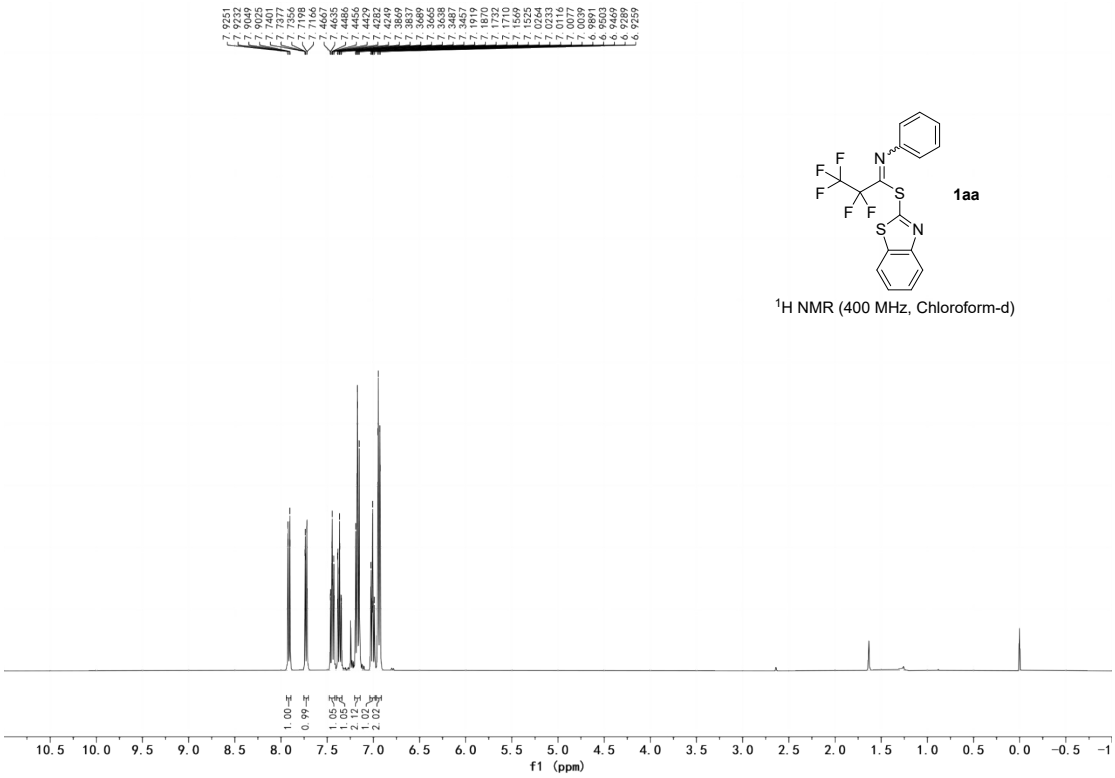
^{19}F NMR (376 MHz, Chloroform-d)

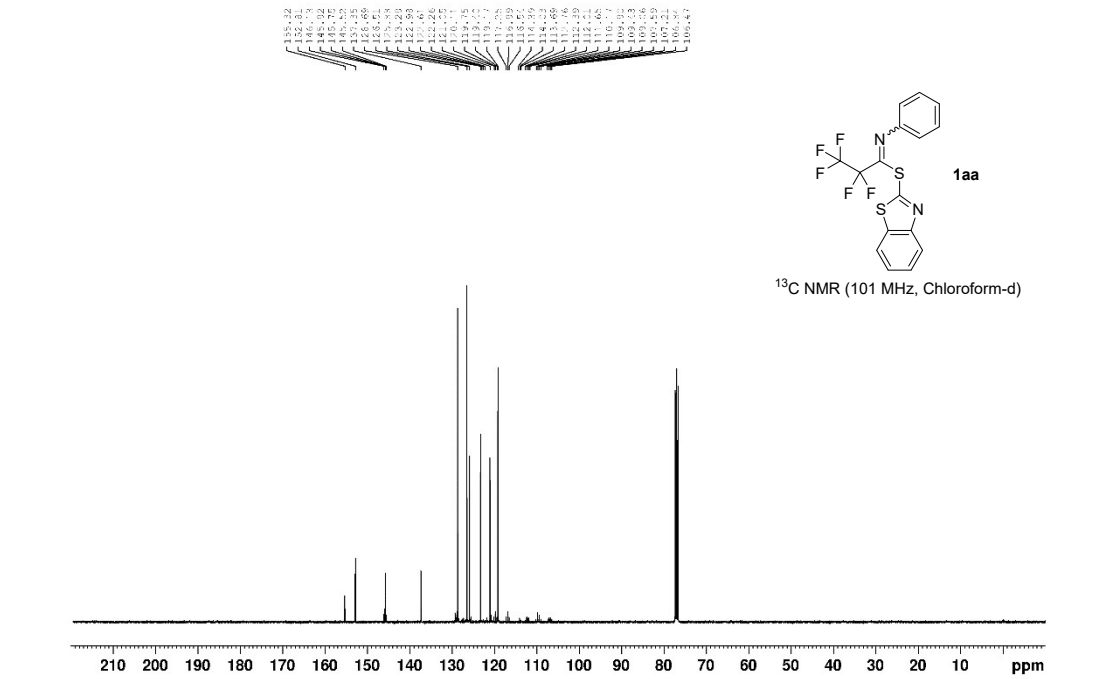

1z
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

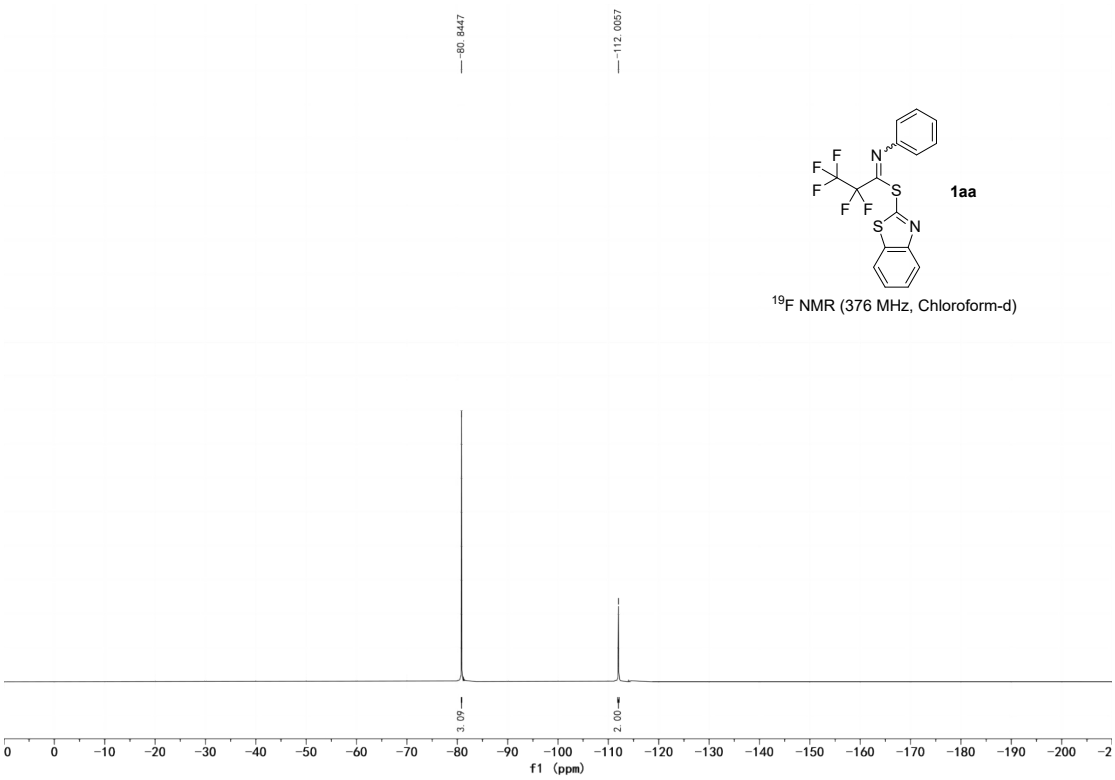

1z
13C NMR (101 MHz, Chloroform-d)
ppm



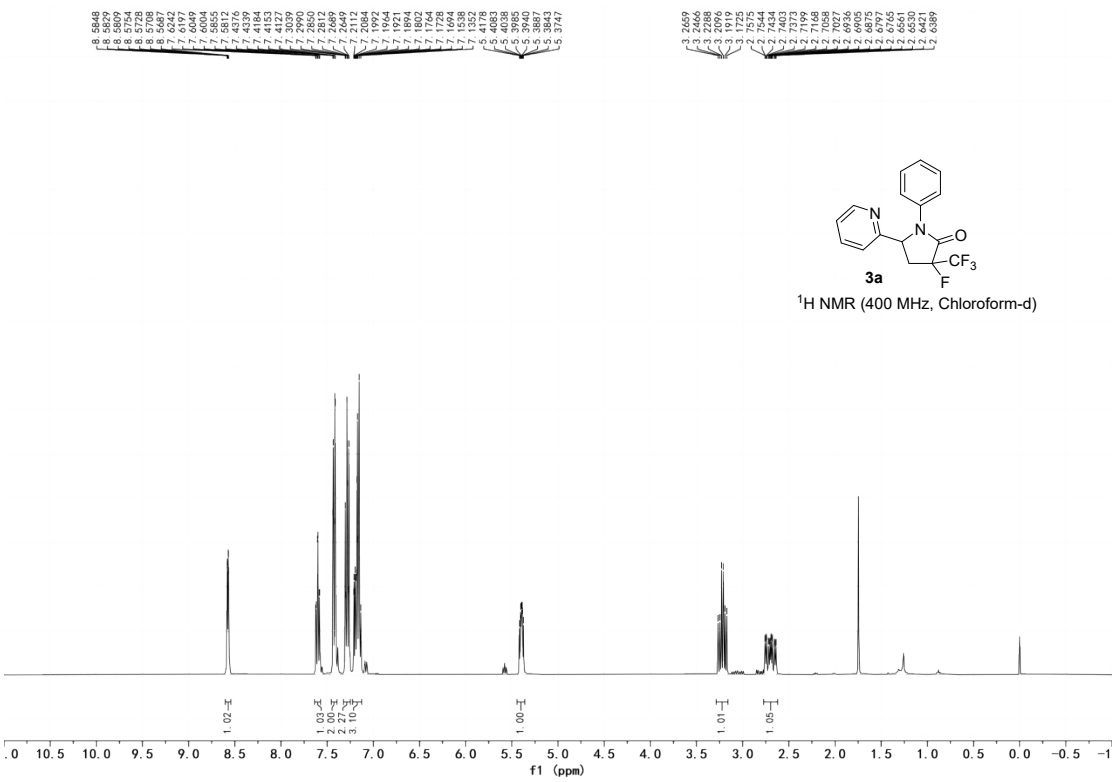
^{19}F NMR (376 MHz, Chloroform-d)

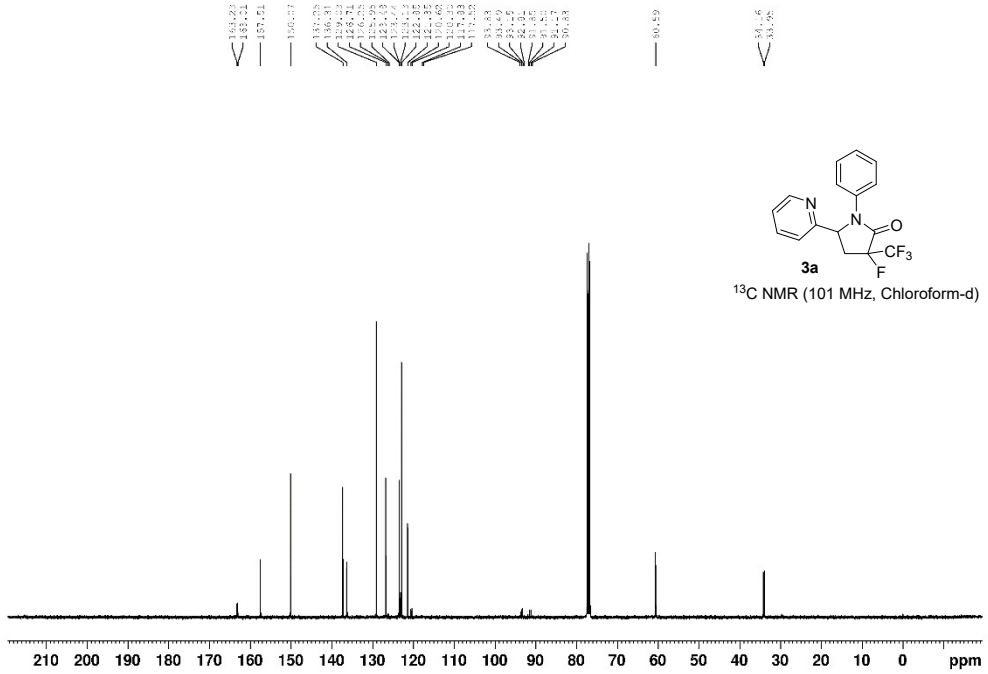

1aa
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

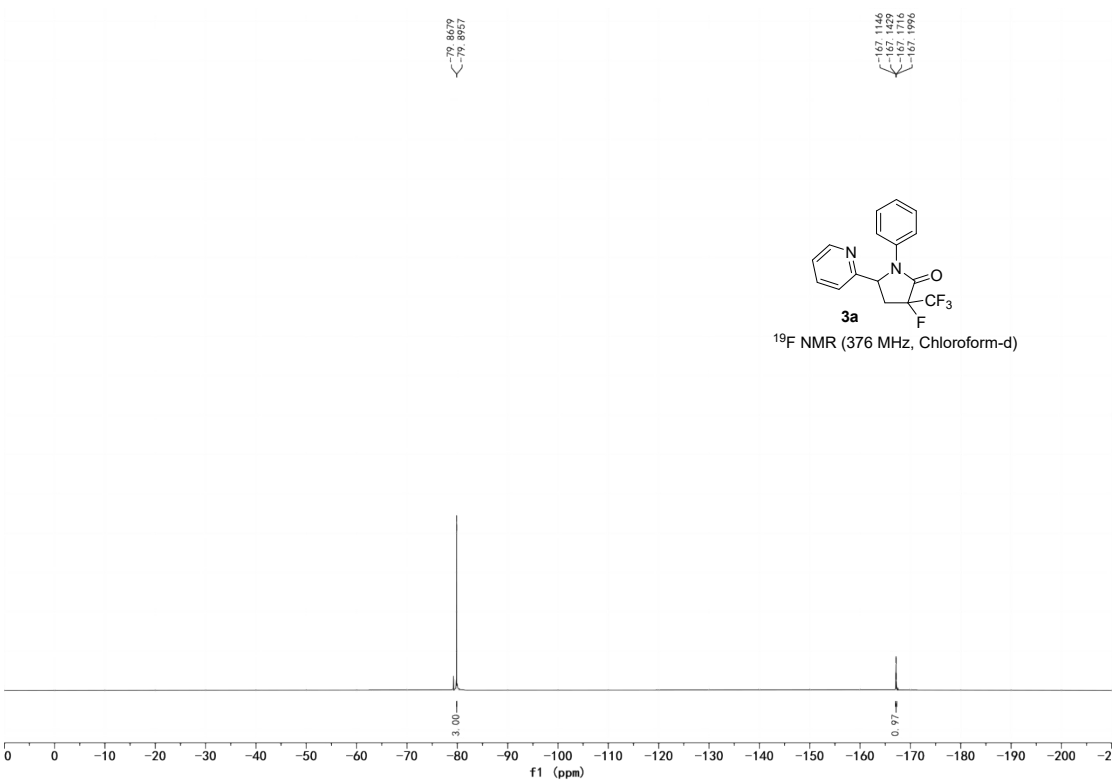

1aa
13C NMR (101 MHz, Chloroform-d)
ppm



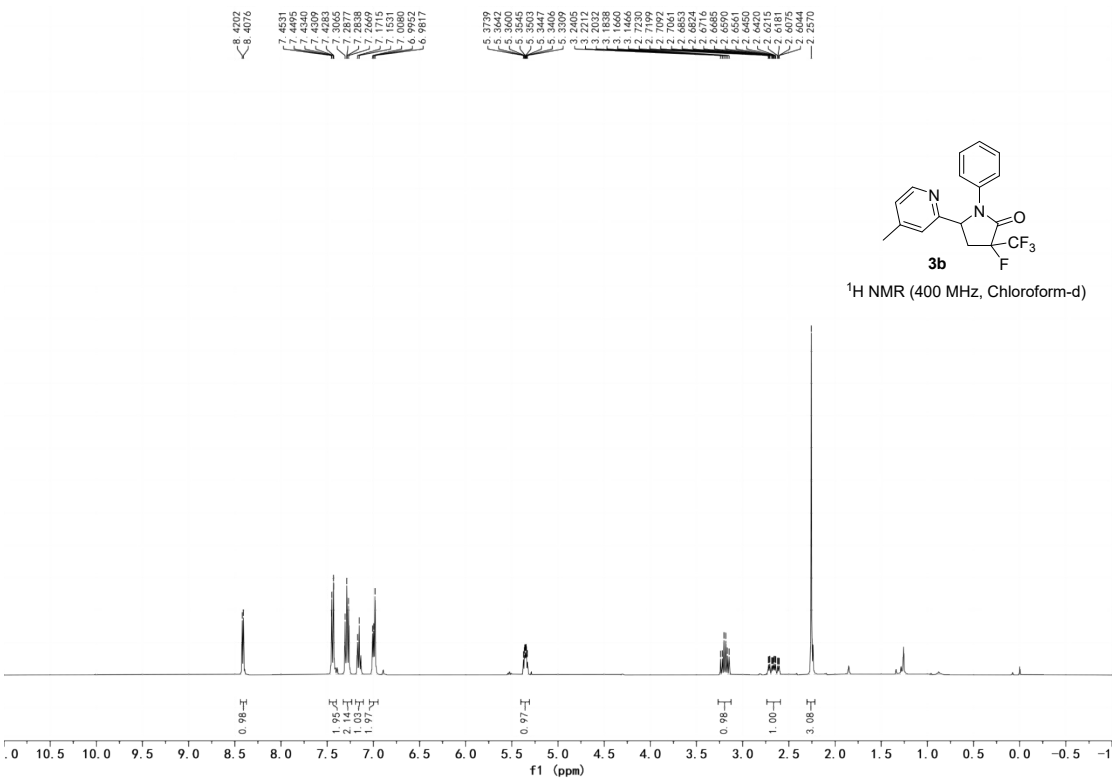
NMR Spectra of the Products


3a
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

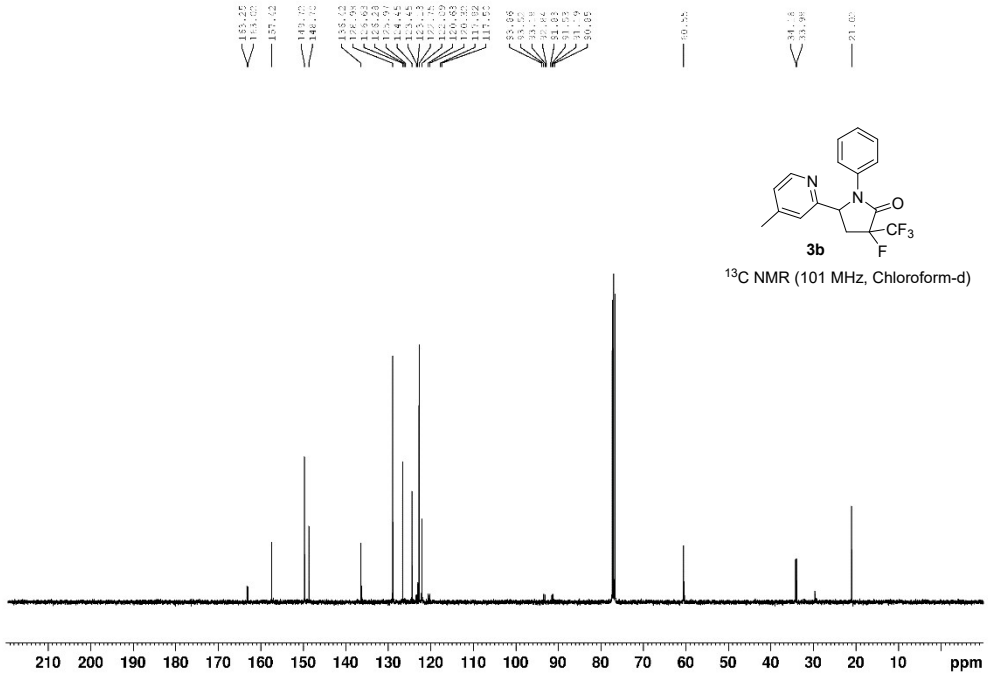

3a
13C NMR (101 MHz, Chloroform-d)
ppm



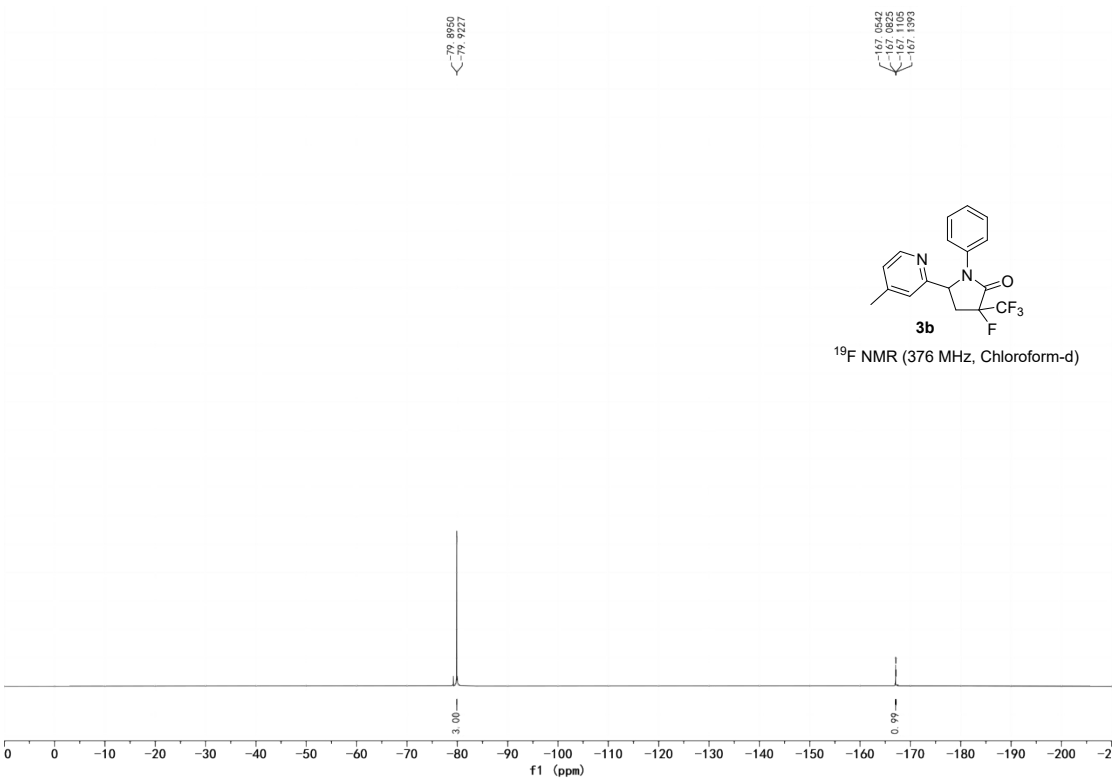
^{19}F NMR (376 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-d)

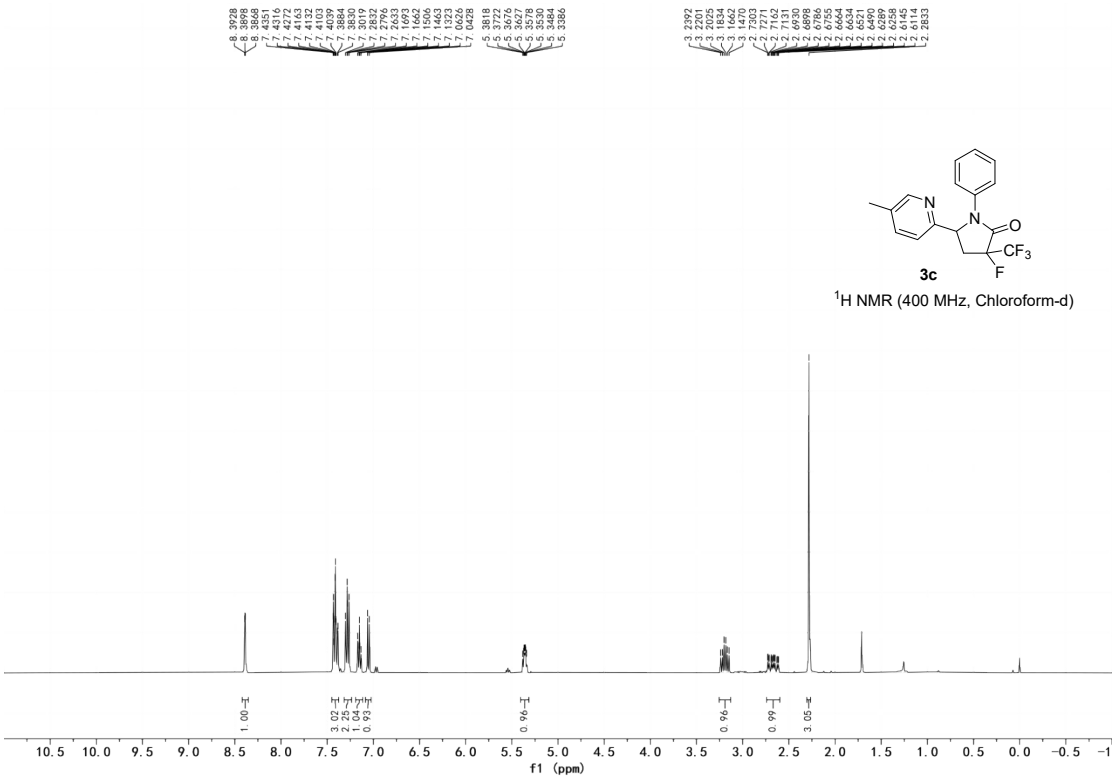


^{13}C NMR (101 MHz, Chloroform-d)



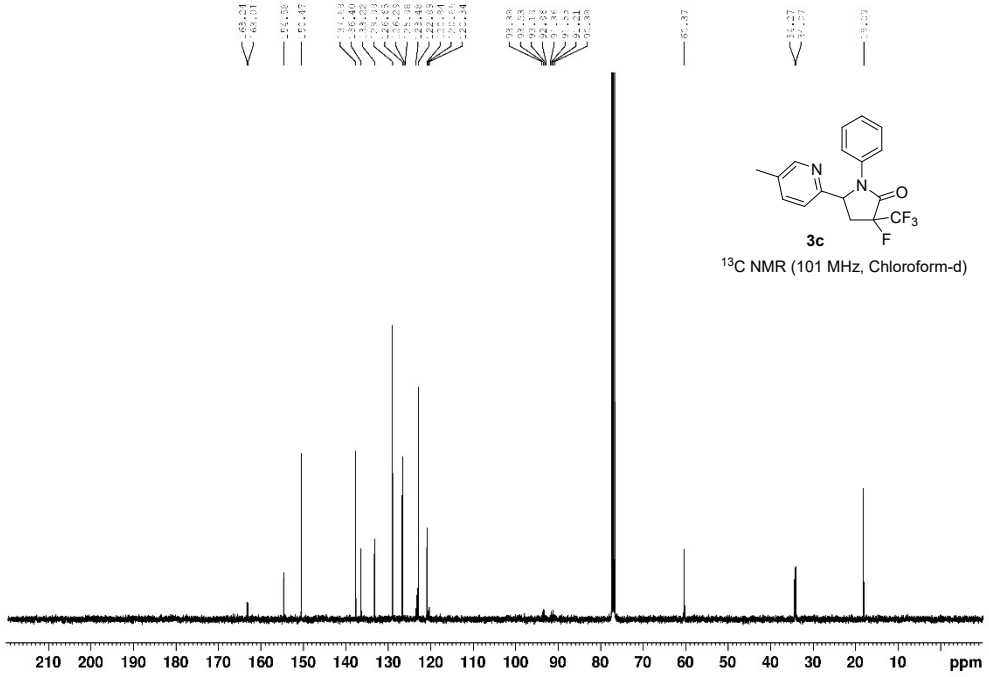
3b

^{19}F NMR (376 MHz, Chloroform-d)



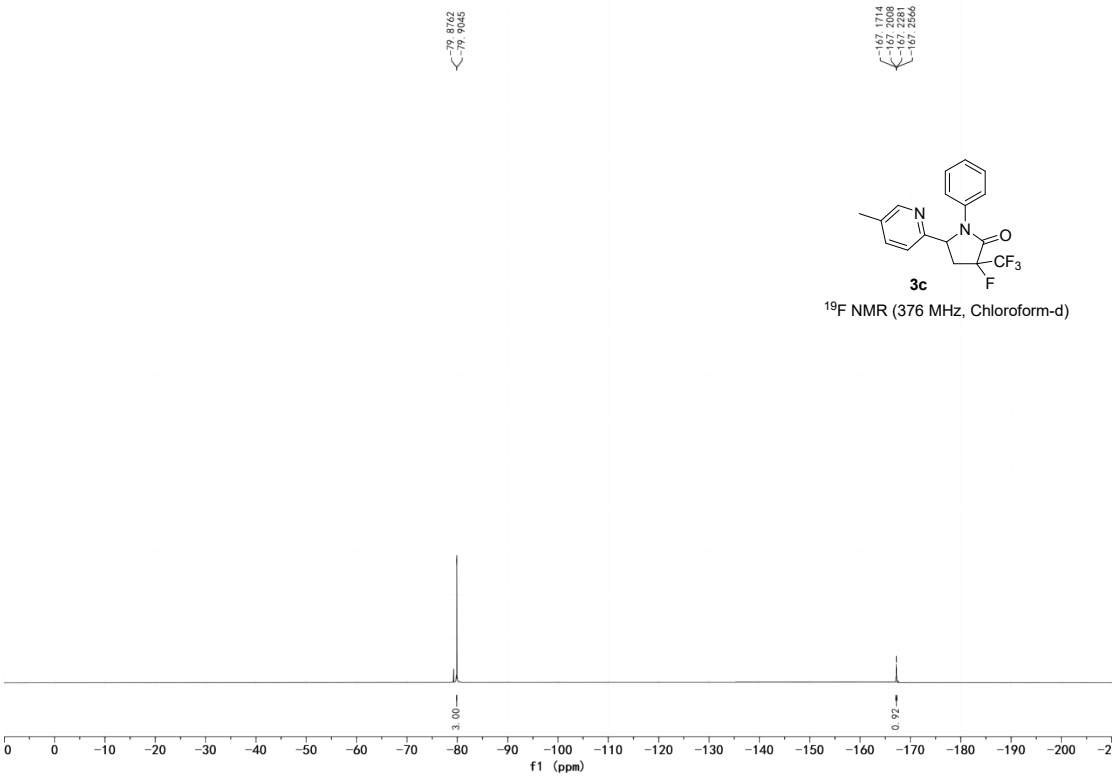
3c

^{1}H NMR (400 MHz, Chloroform-d)



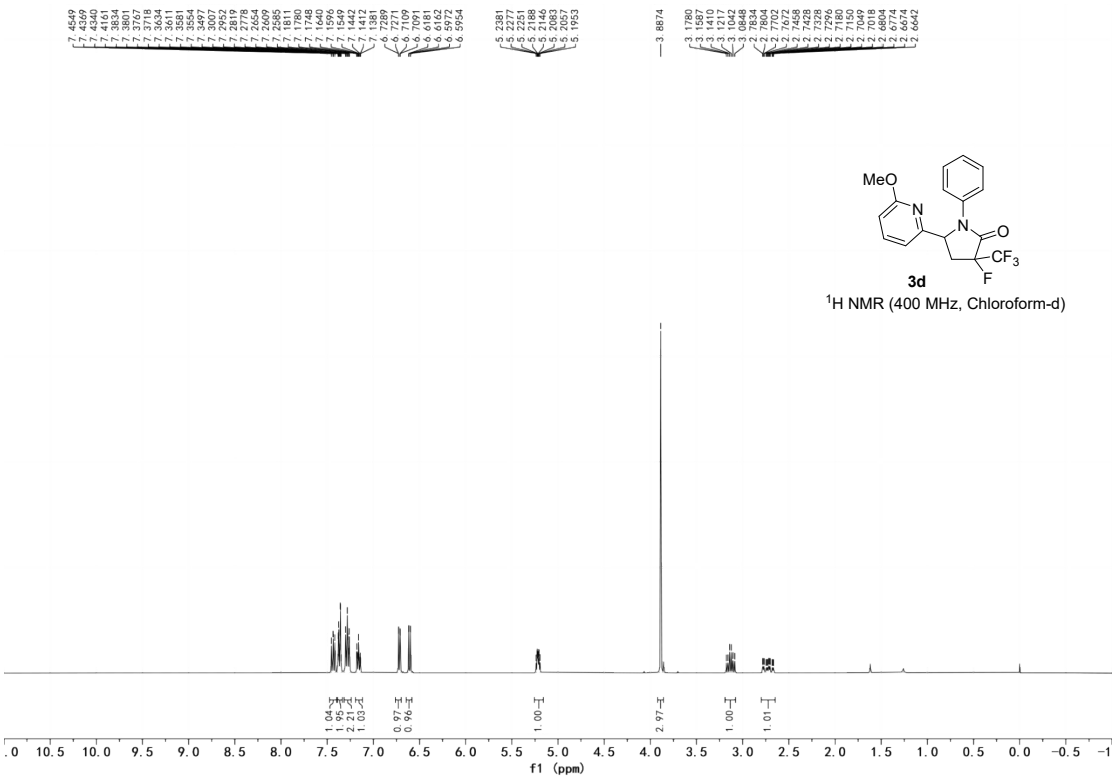
3c

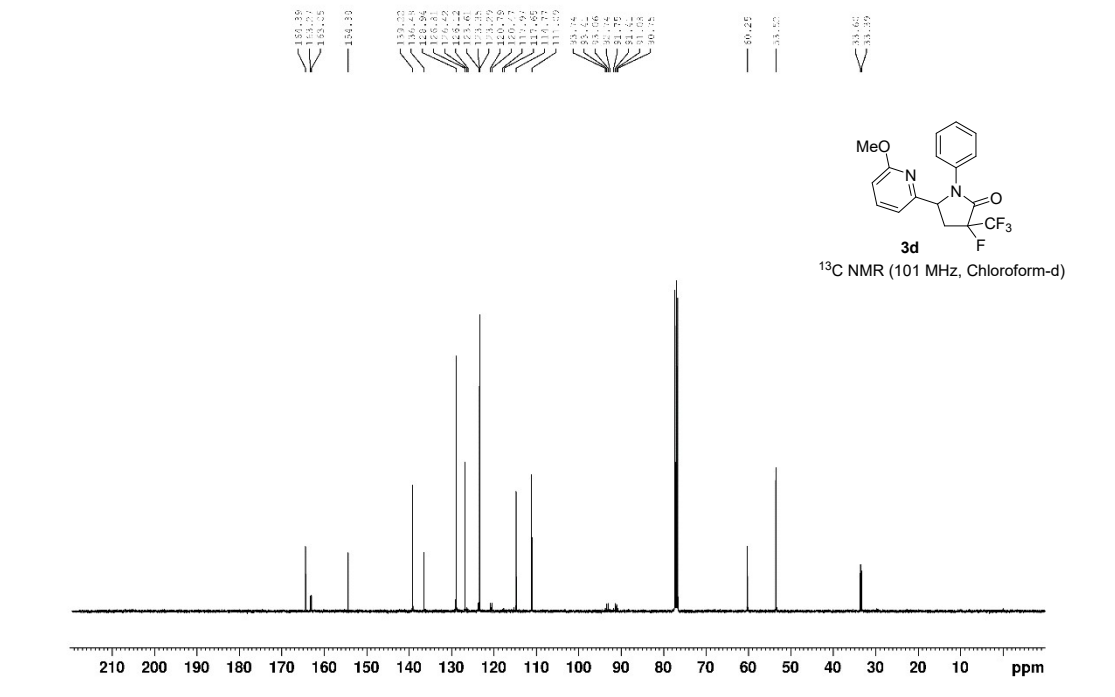
^{13}C NMR (101 MHz, Chloroform-d)

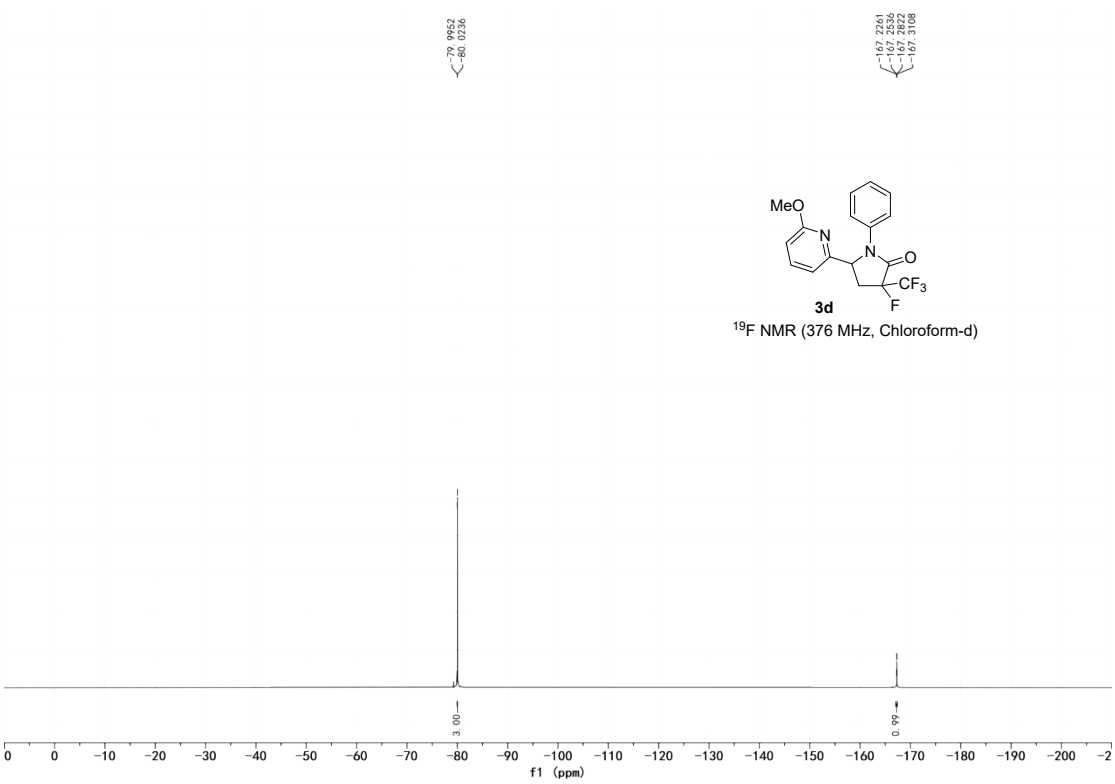


3c

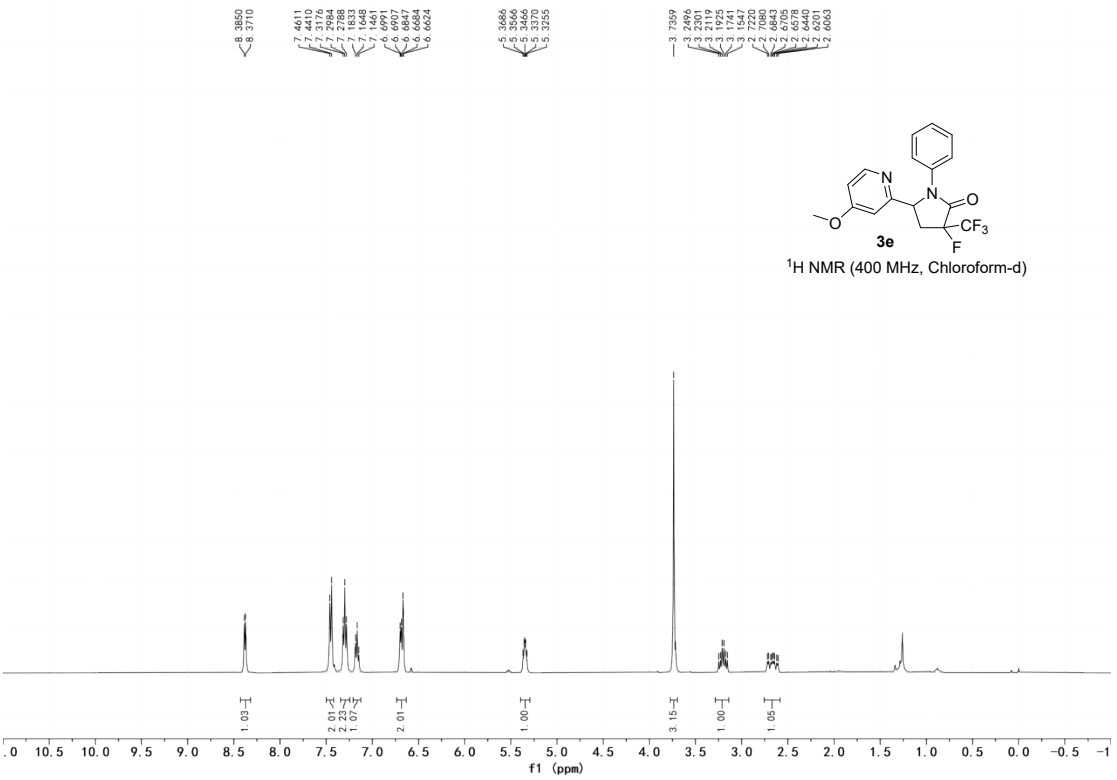
^{19}F NMR (376 MHz, Chloroform-d)

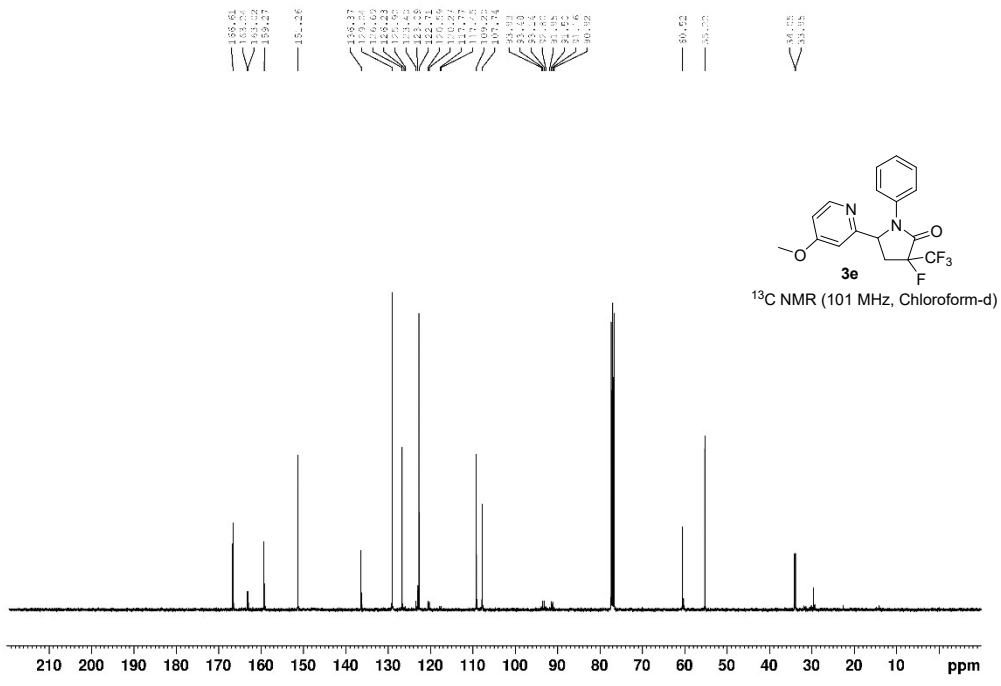

MeO
N
N
O
CF3
F
3d
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

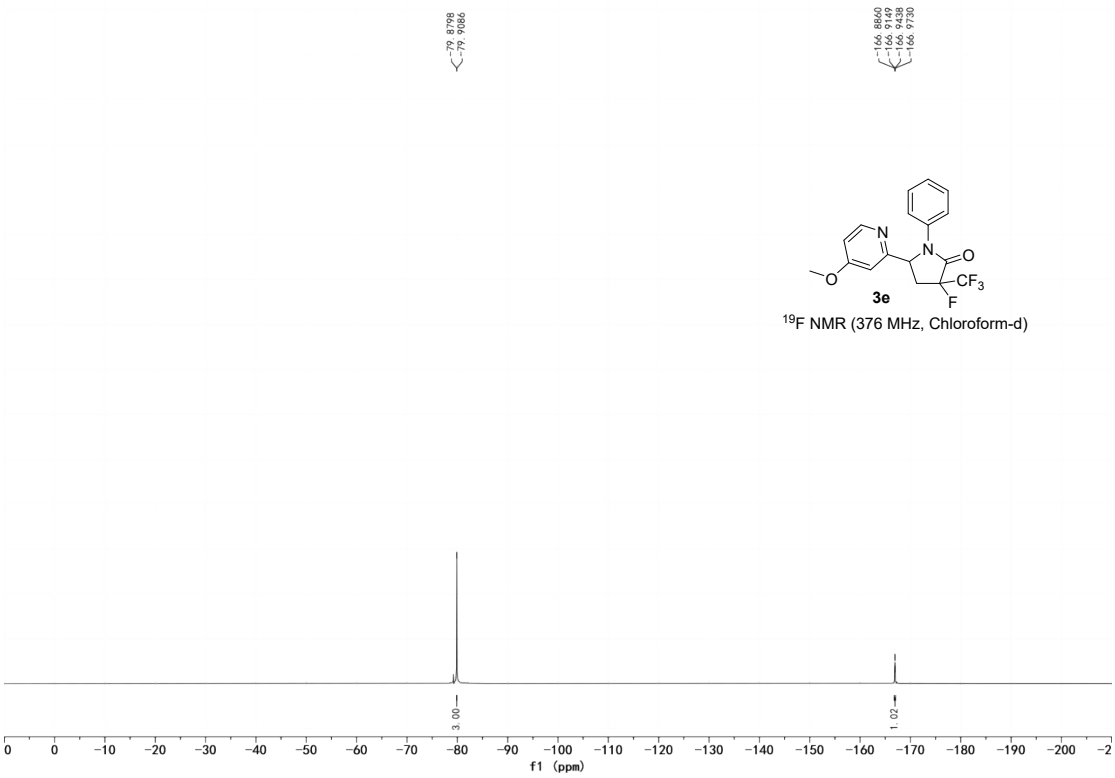

MeO
N
N
O
CF3
F
3d
13C NMR (101 MHz, Chloroform-d)
ppm



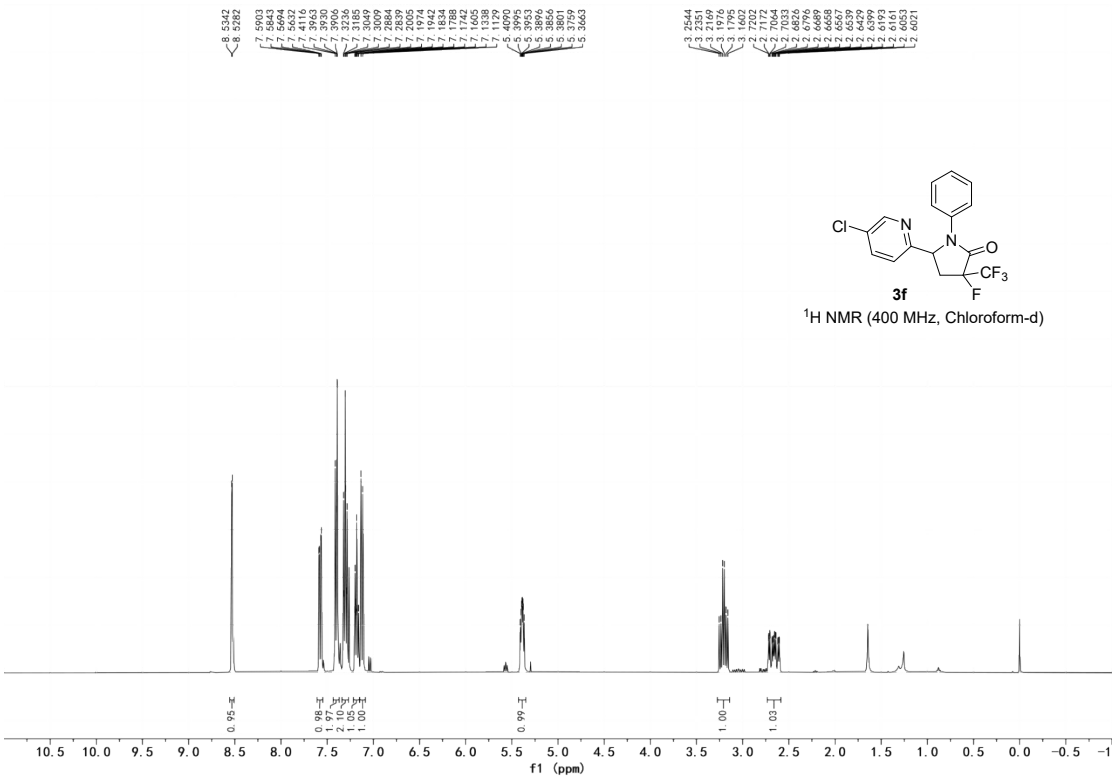
^{19}F NMR (376 MHz, Chloroform-d)

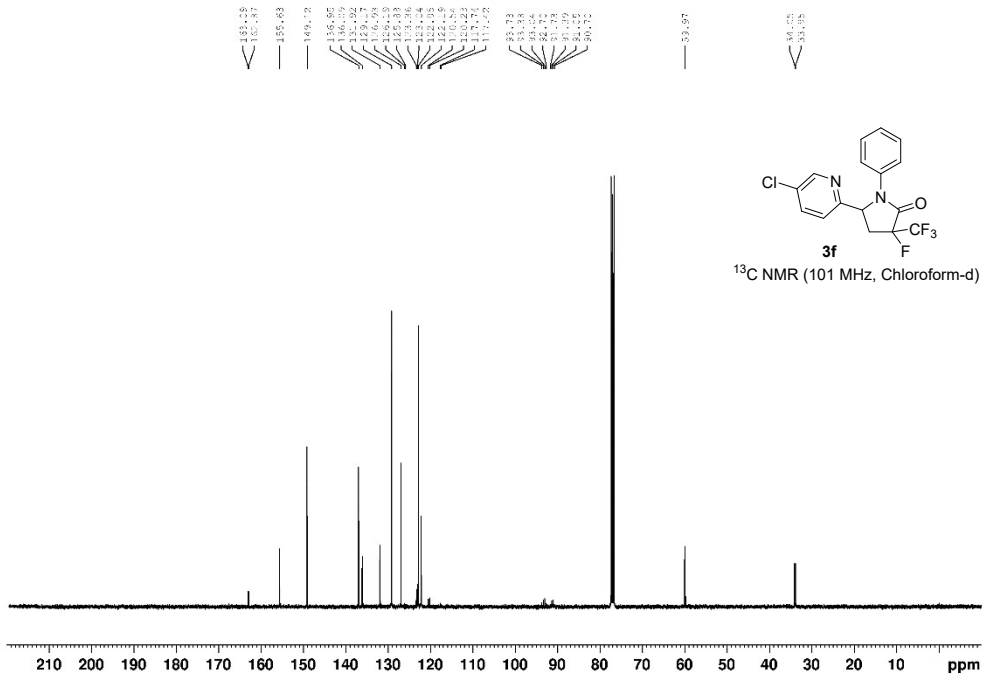

3e
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

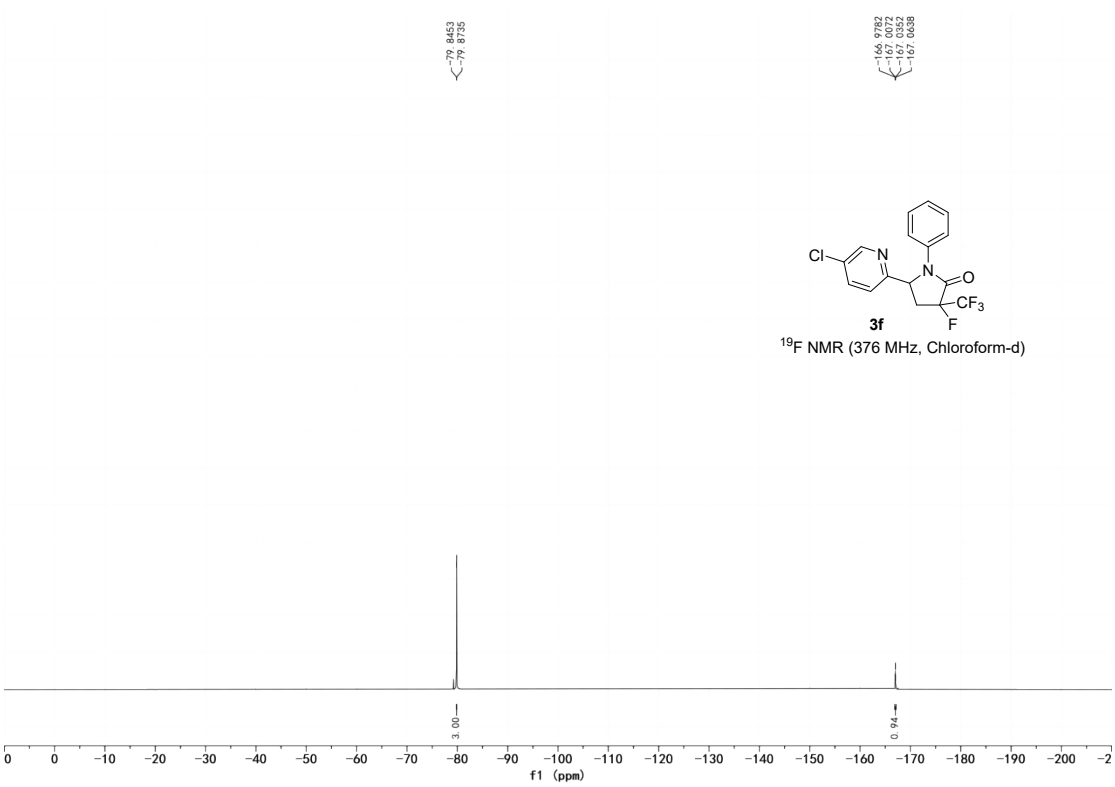

3e
13C NMR (101 MHz, Chloroform-d)
ppm



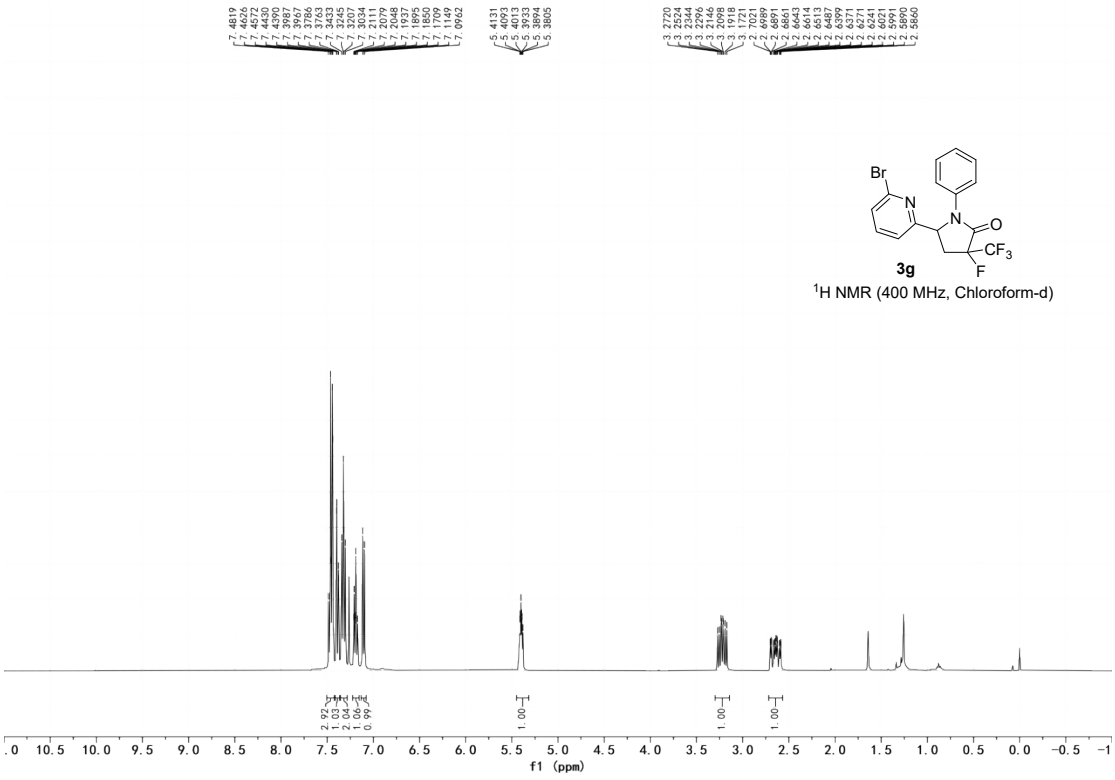
^{19}F NMR (376 MHz, Chloroform-d)


Cl
N
O
CF3
F
3f
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

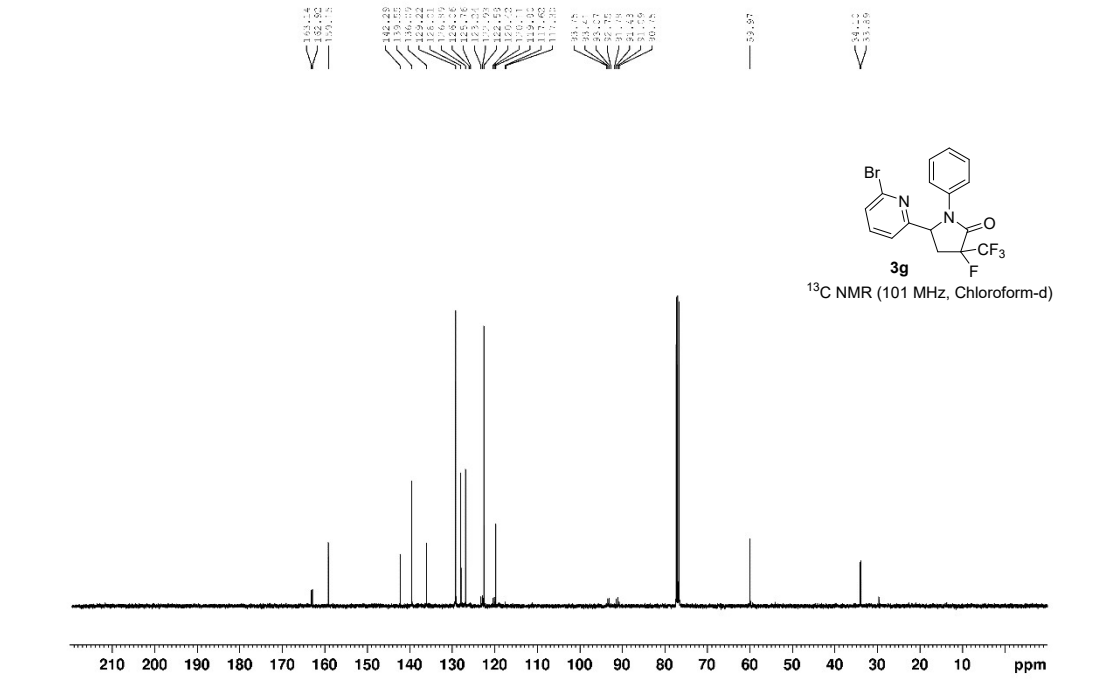

Cl
N
O
CF3
F
3f
13C NMR (101 MHz, Chloroform-d)
ppm



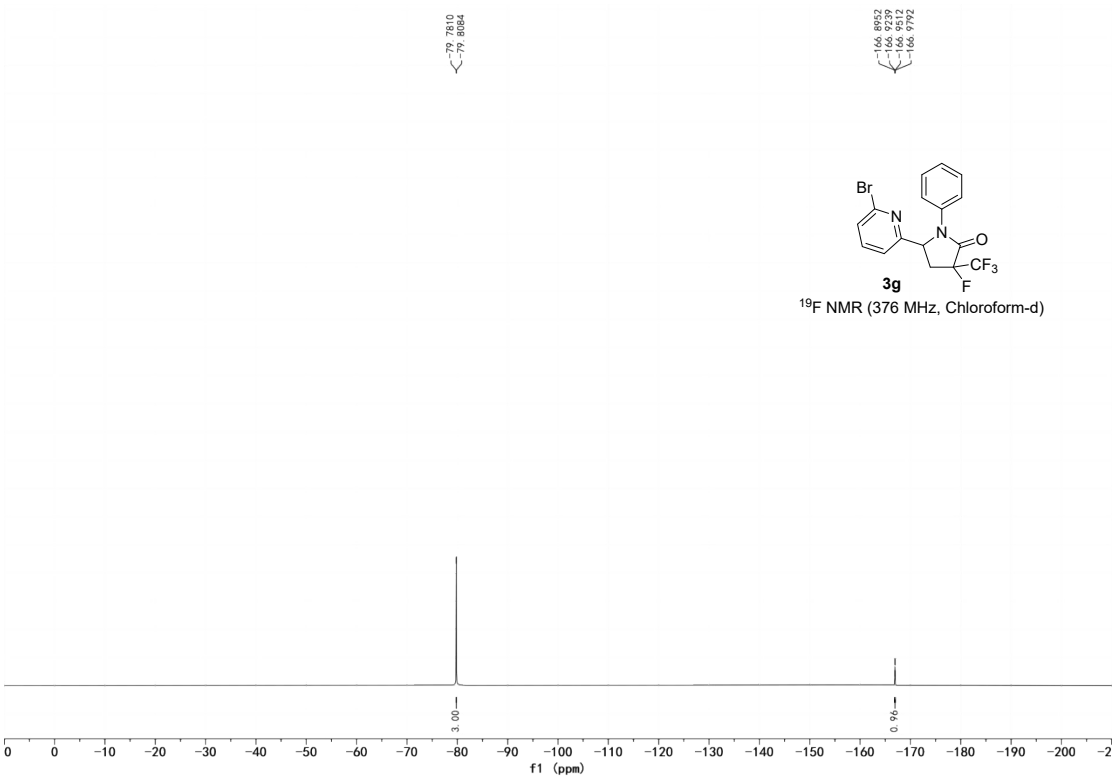
^{19}F NMR (376 MHz, Chloroform-d)



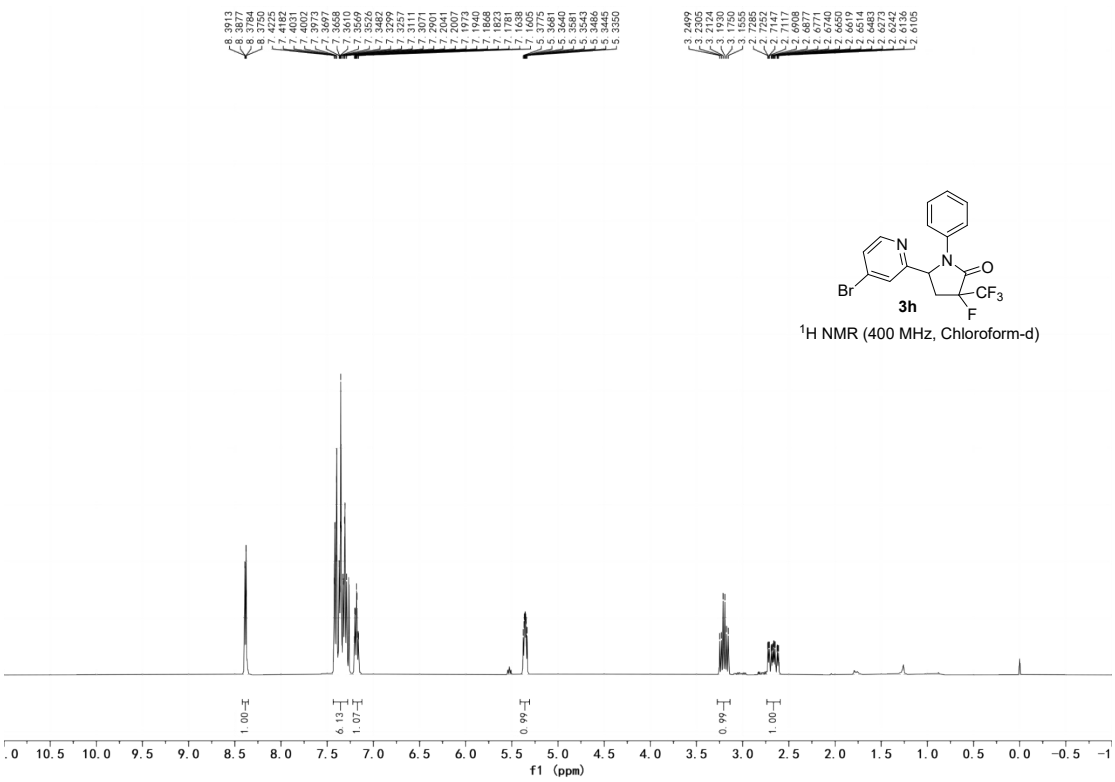
^{1}H NMR (400 MHz, Chloroform-d)



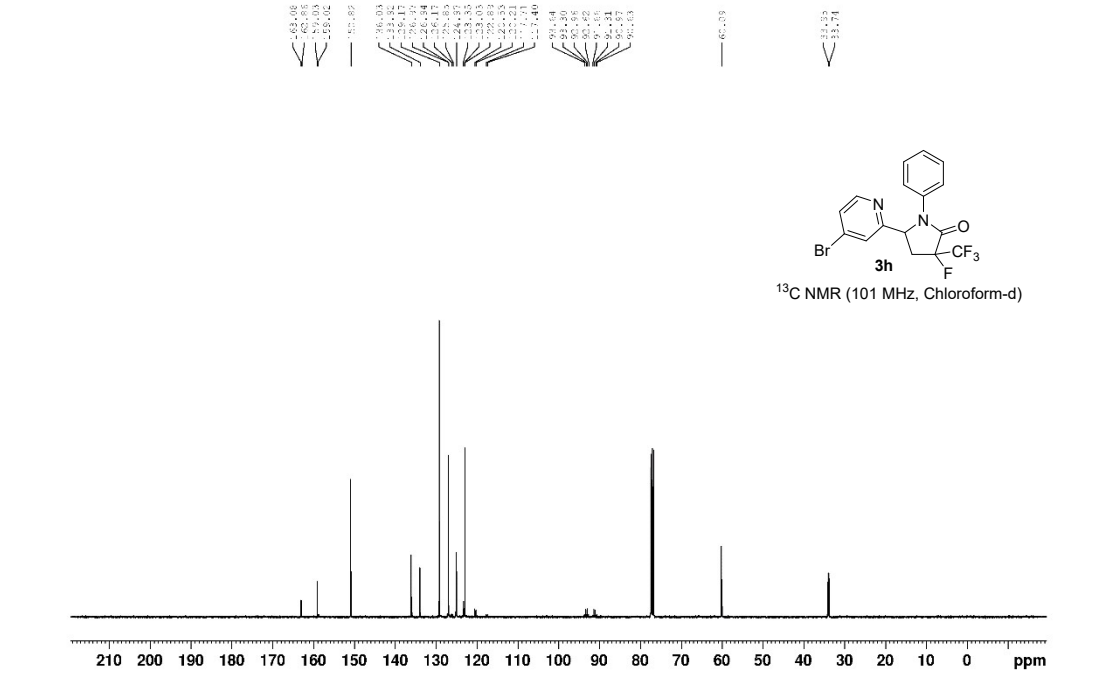
^{13}C NMR (101 MHz, Chloroform-d)



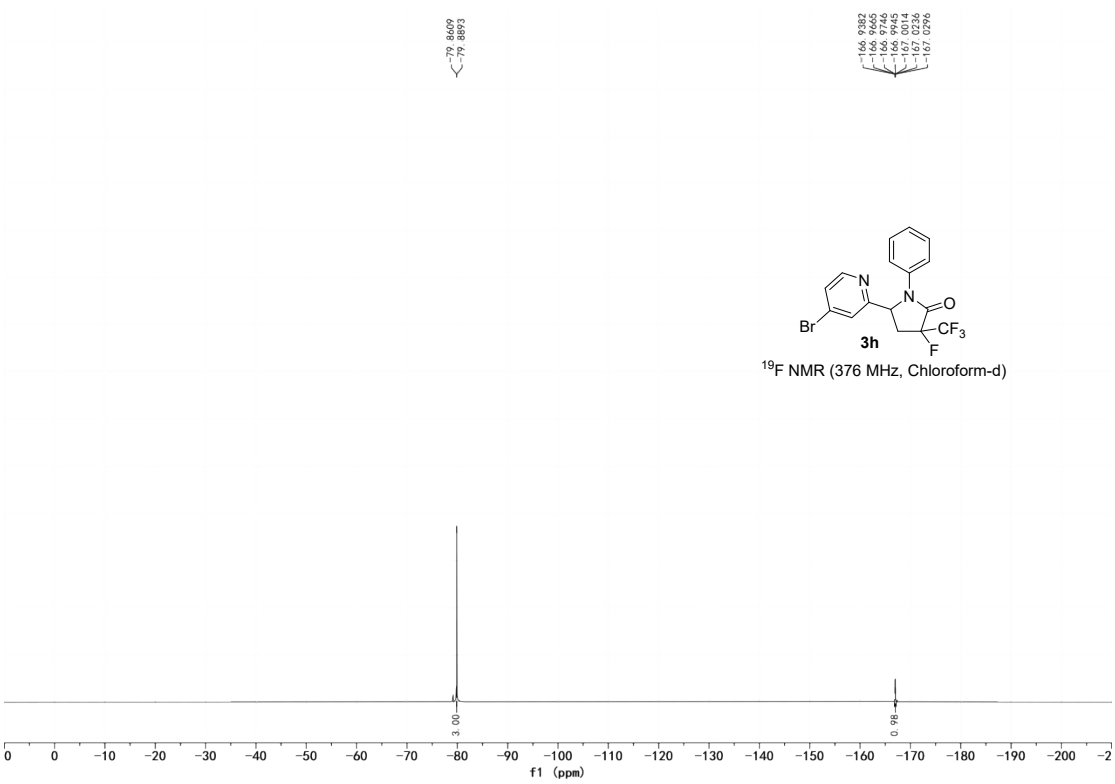
^{19}F NMR (376 MHz, Chloroform-d)



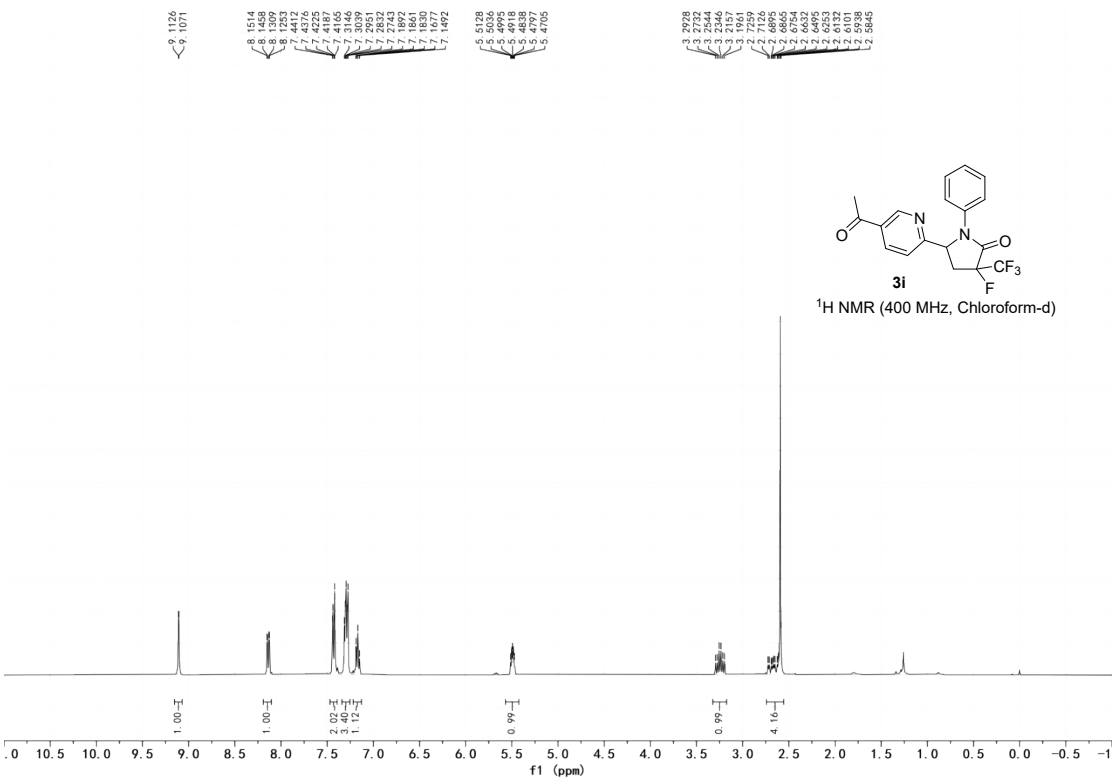
^{1}H NMR (400 MHz, Chloroform-d)

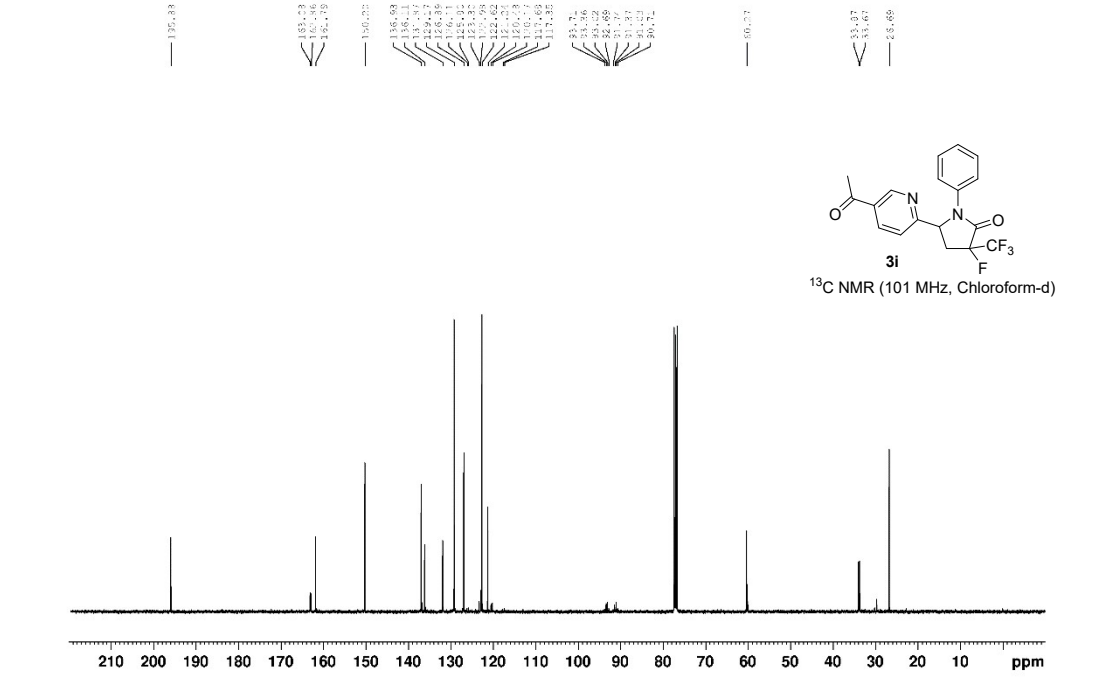


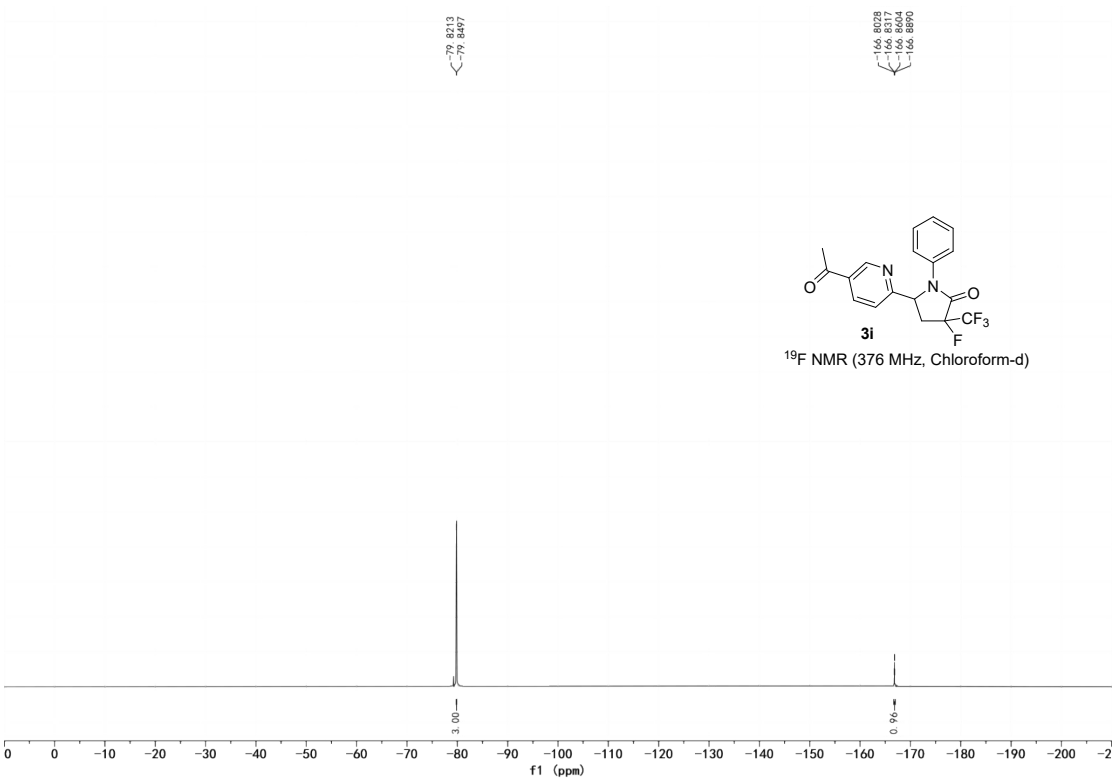
^{13}C NMR (101 MHz, Chloroform-d)



^{19}F NMR (376 MHz, Chloroform-d)

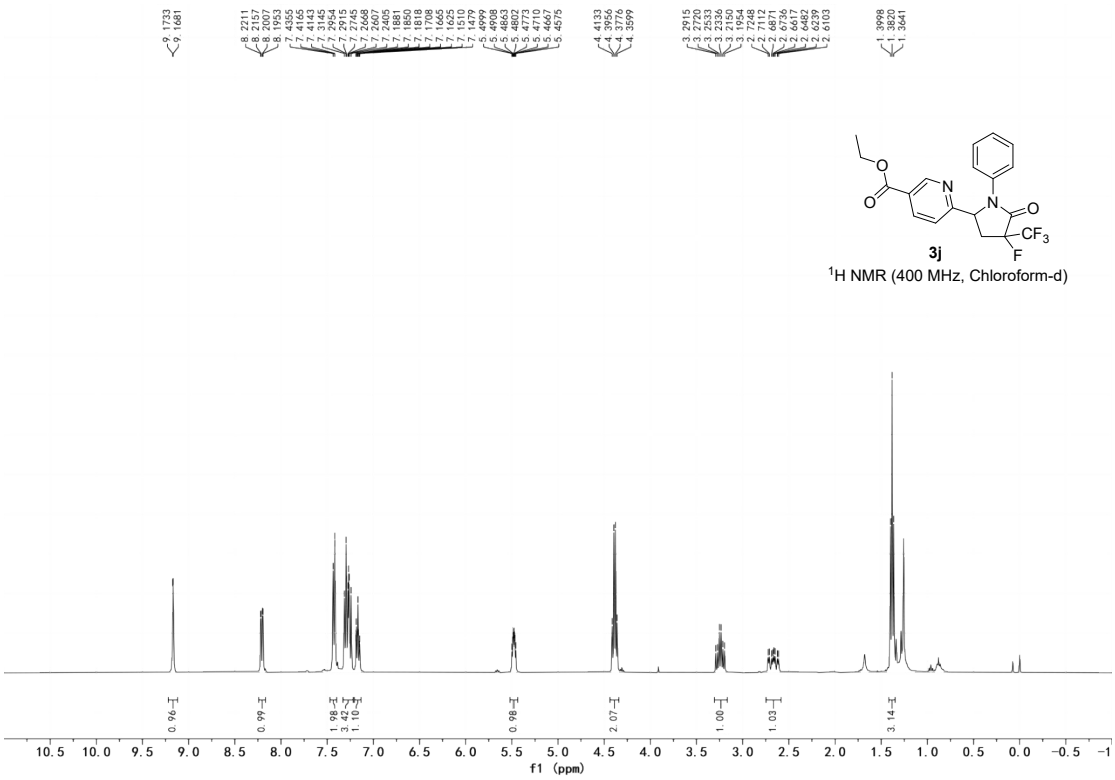

3i
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

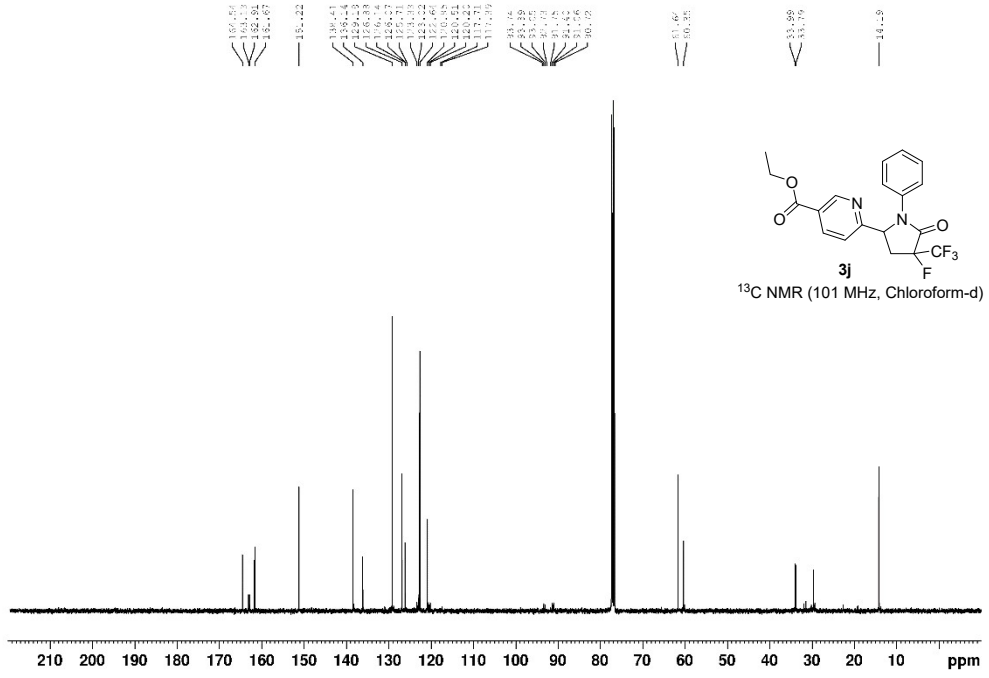

3i
13C NMR (101 MHz, Chloroform-d)
ppm

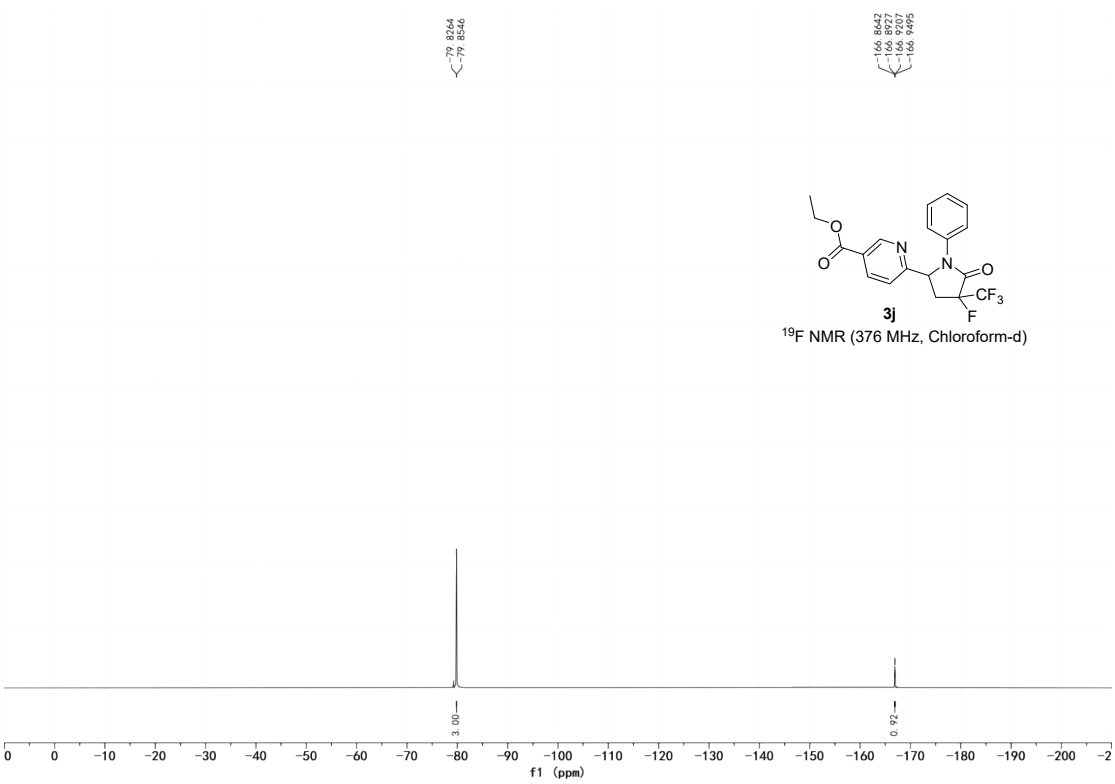


3i

^{19}F NMR (376 MHz, Chloroform-d)

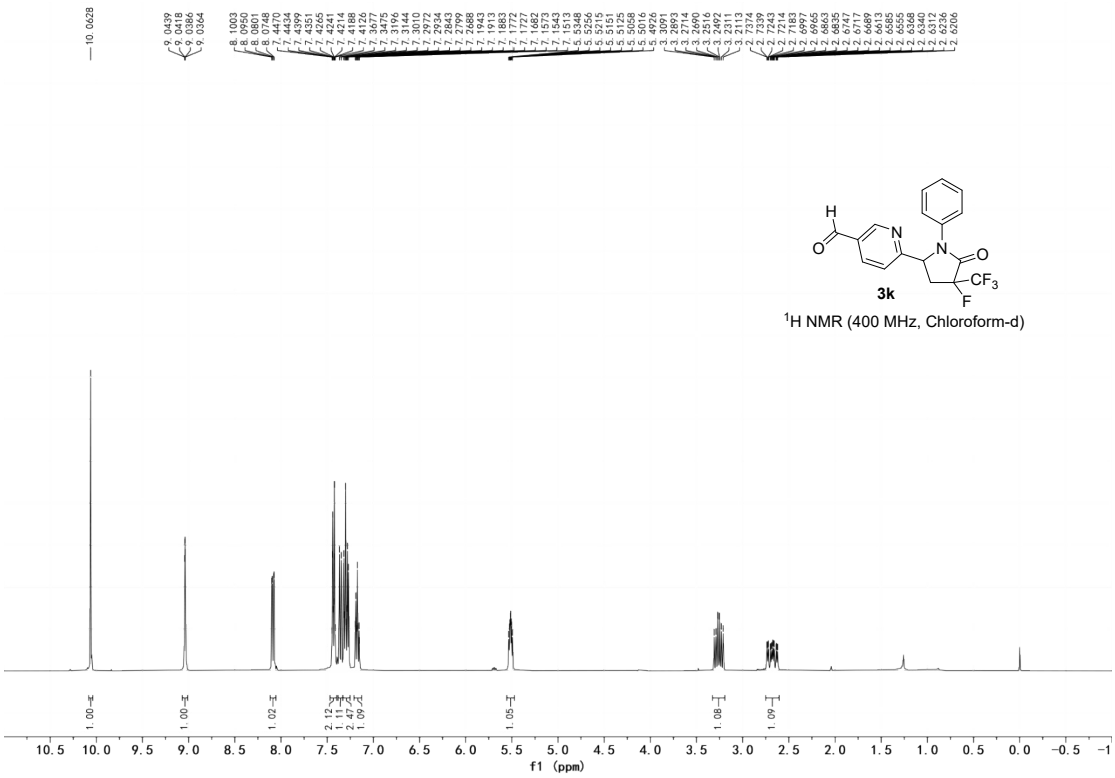

3j
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

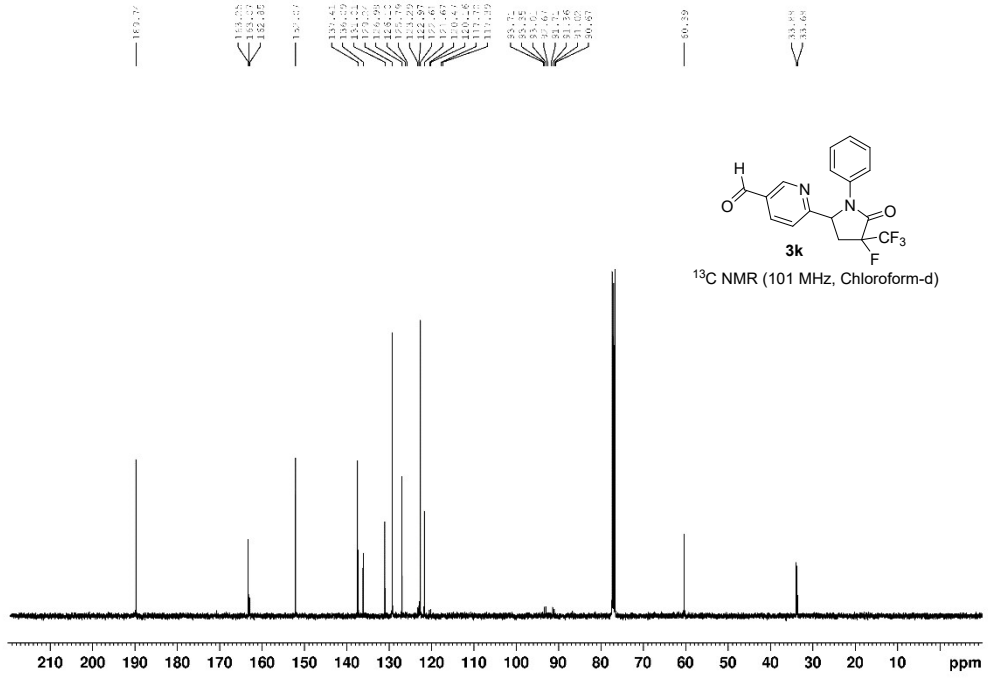

3j
13C NMR (101 MHz, Chloroform-d)
ppm

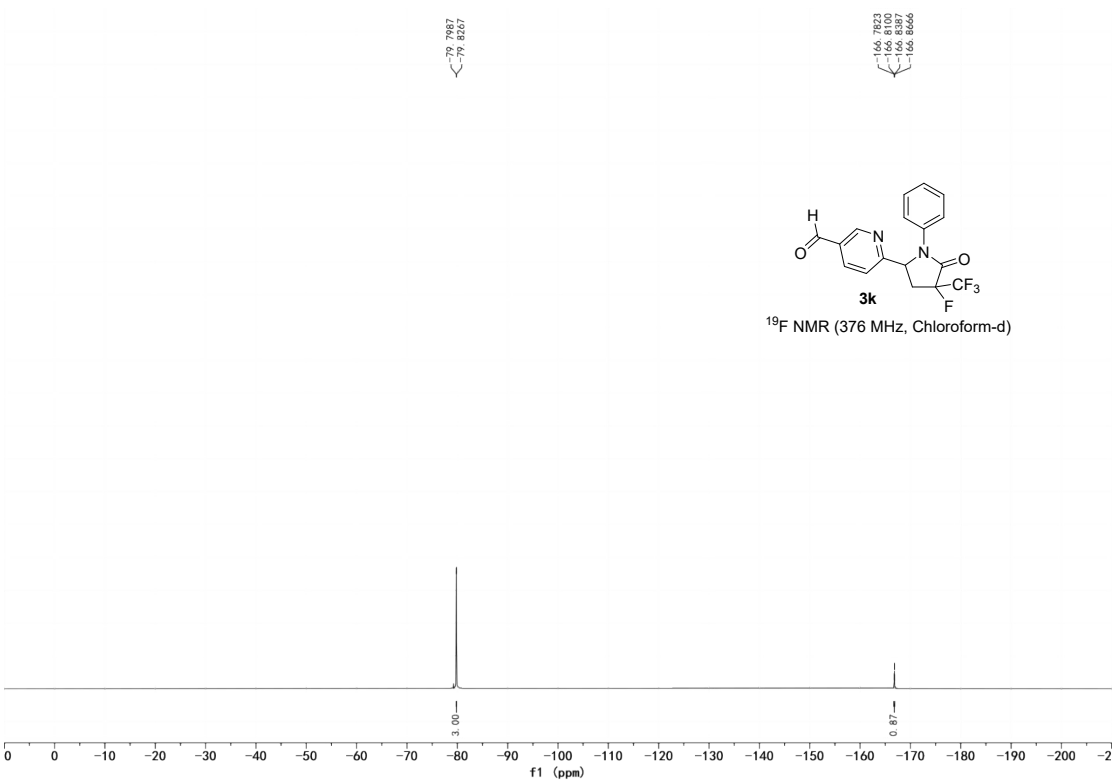


3j

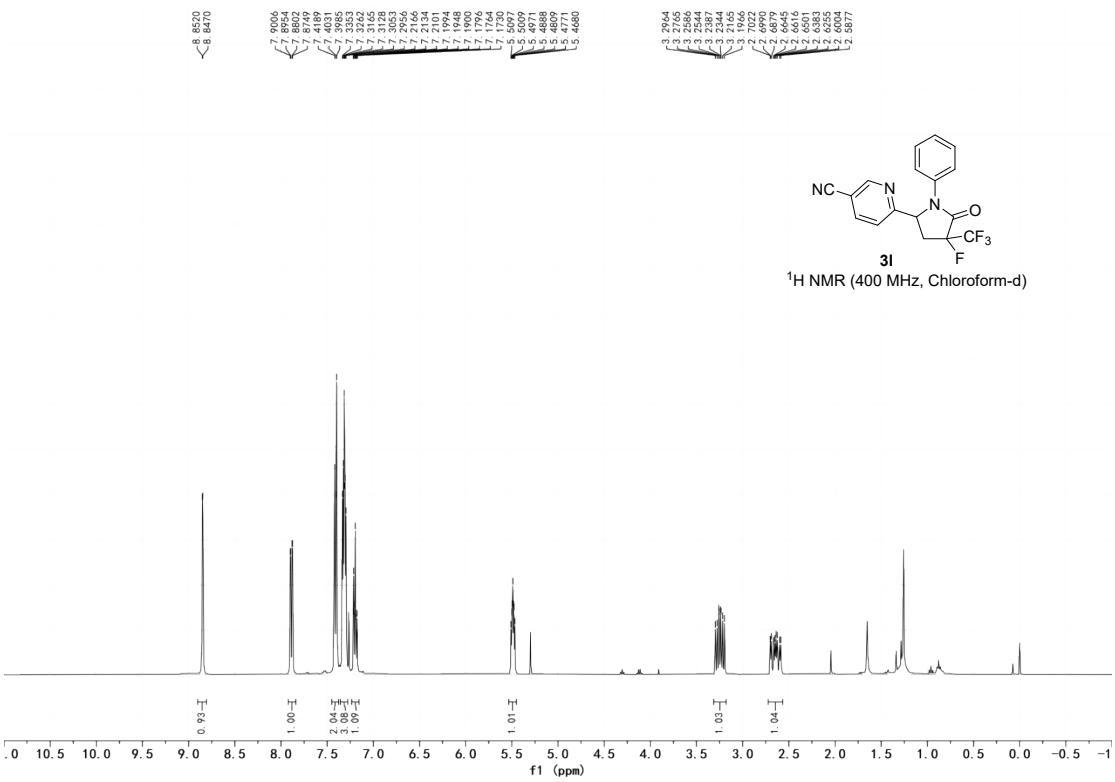
^{19}F NMR (376 MHz, Chloroform-d)

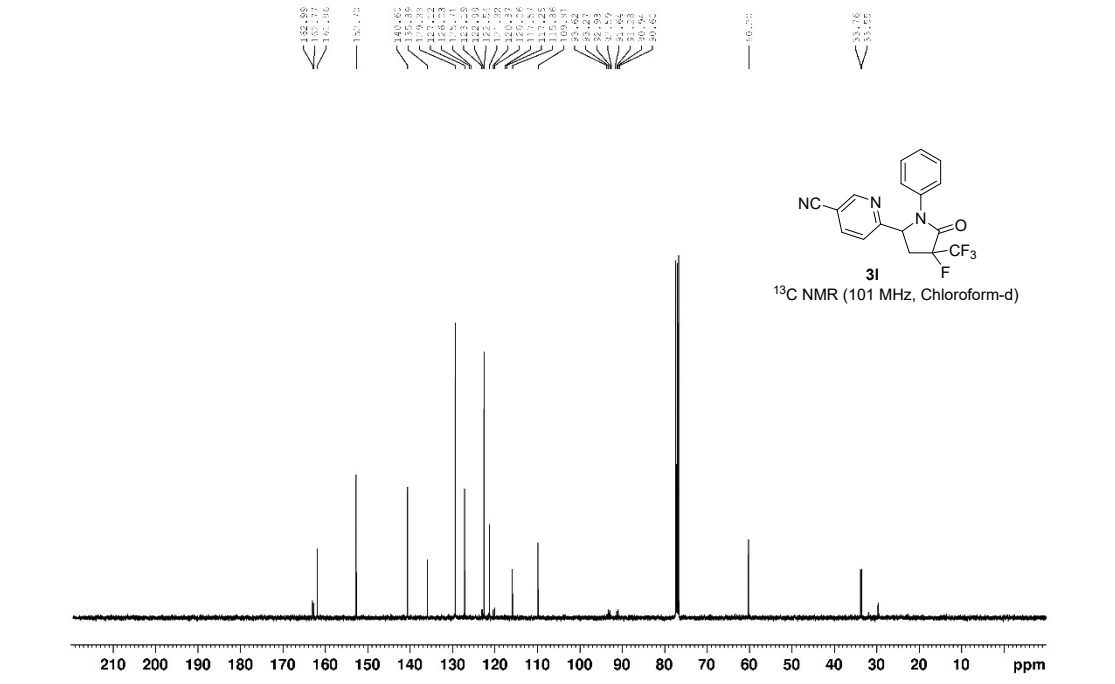

3k
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

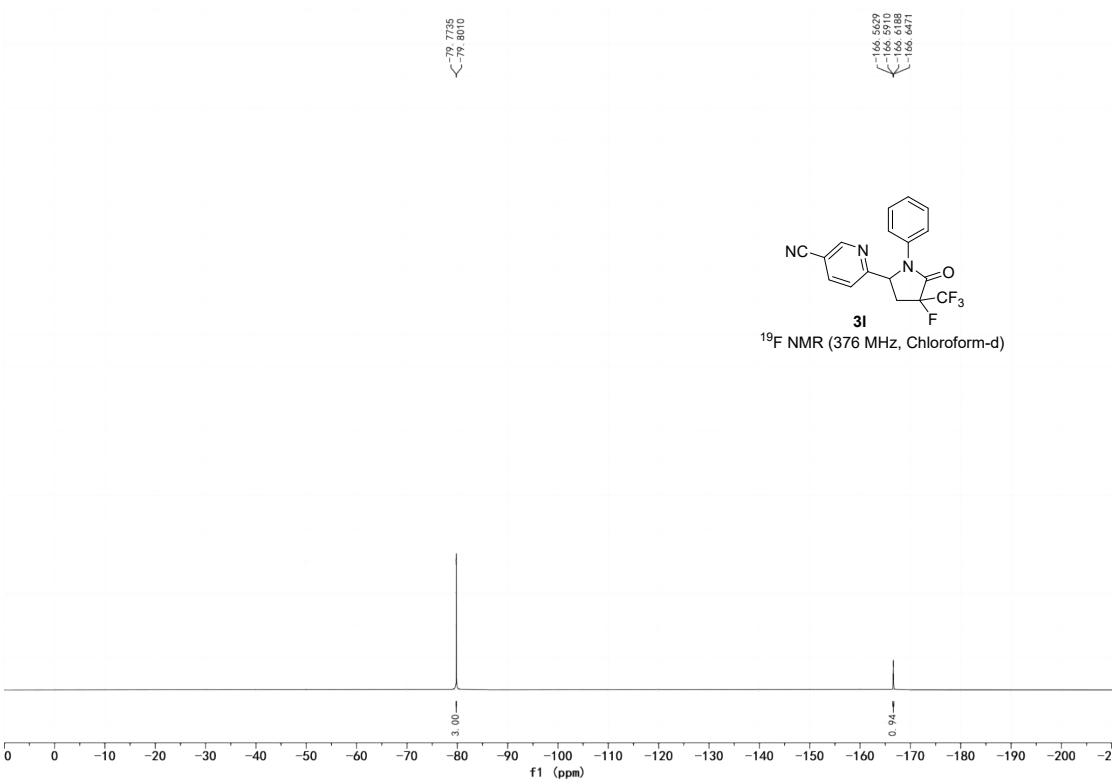

3k
13C NMR (101 MHz, Chloroform-d)
ppm



^{19}F NMR (376 MHz, Chloroform-d)

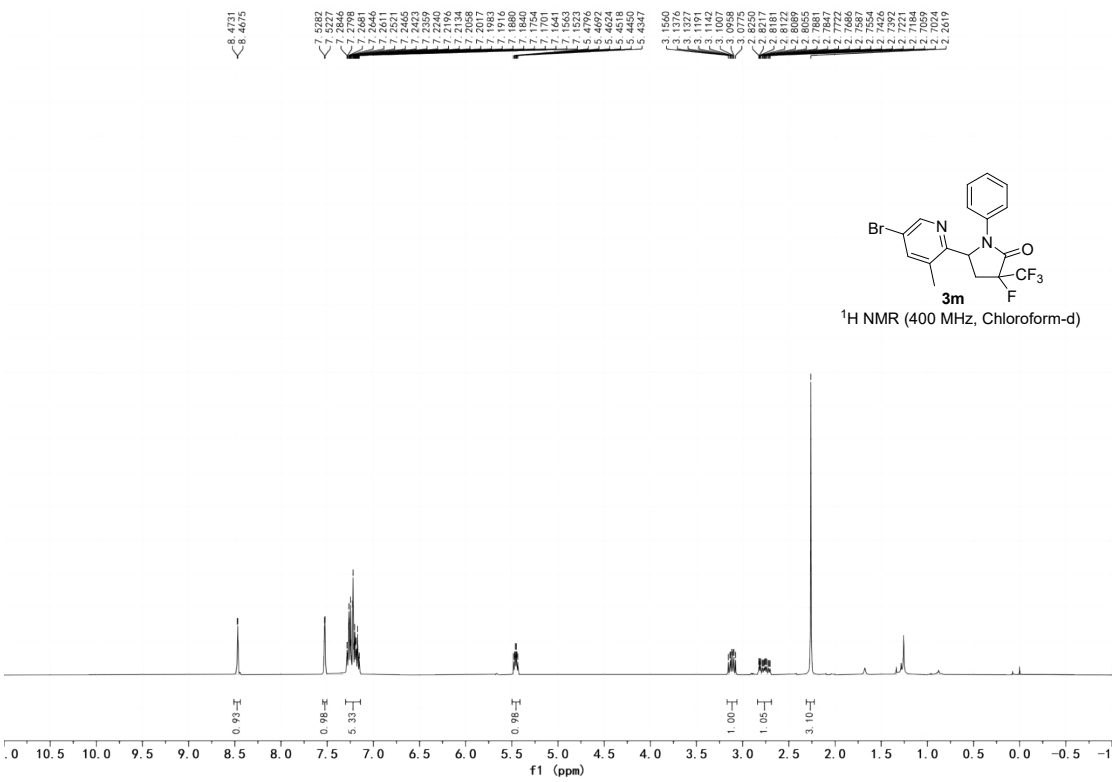

NC
N
N
O
CF3
F
3l
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)


NC
N
N
O
CF3
F
3l
13C NMR (101 MHz, Chloroform-d)
ppm

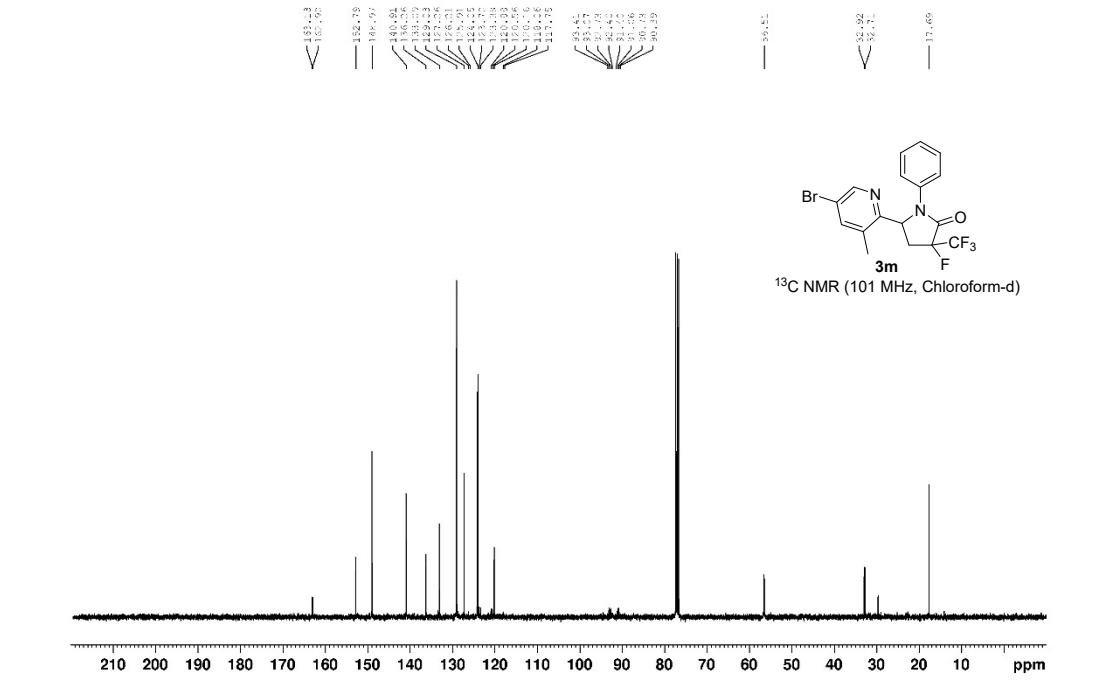


3l

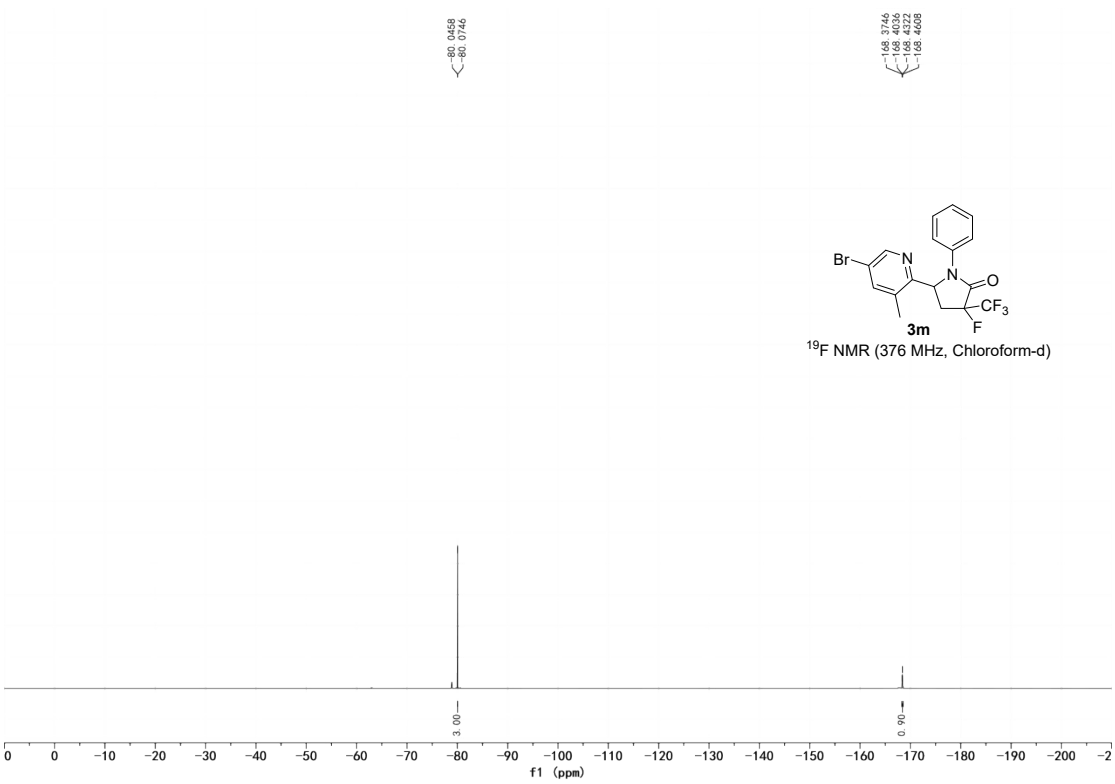
^{19}F NMR (376 MHz, Chloroform-d)



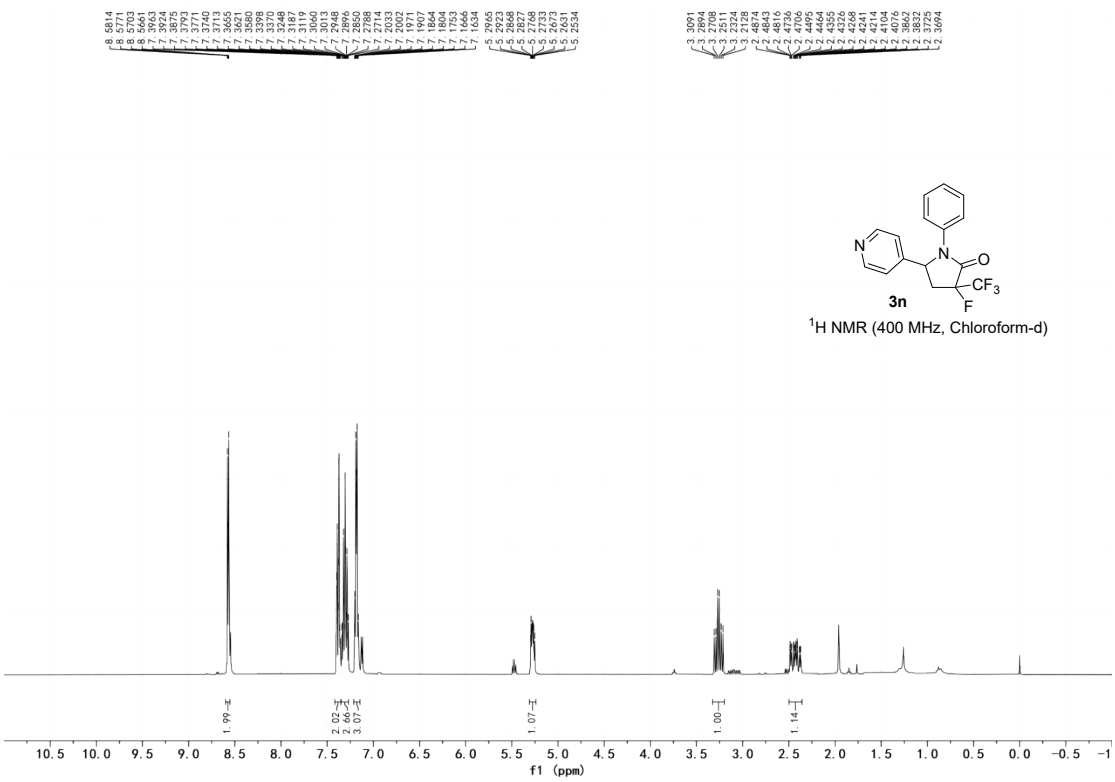
^{1}H NMR (400 MHz, Chloroform-d)

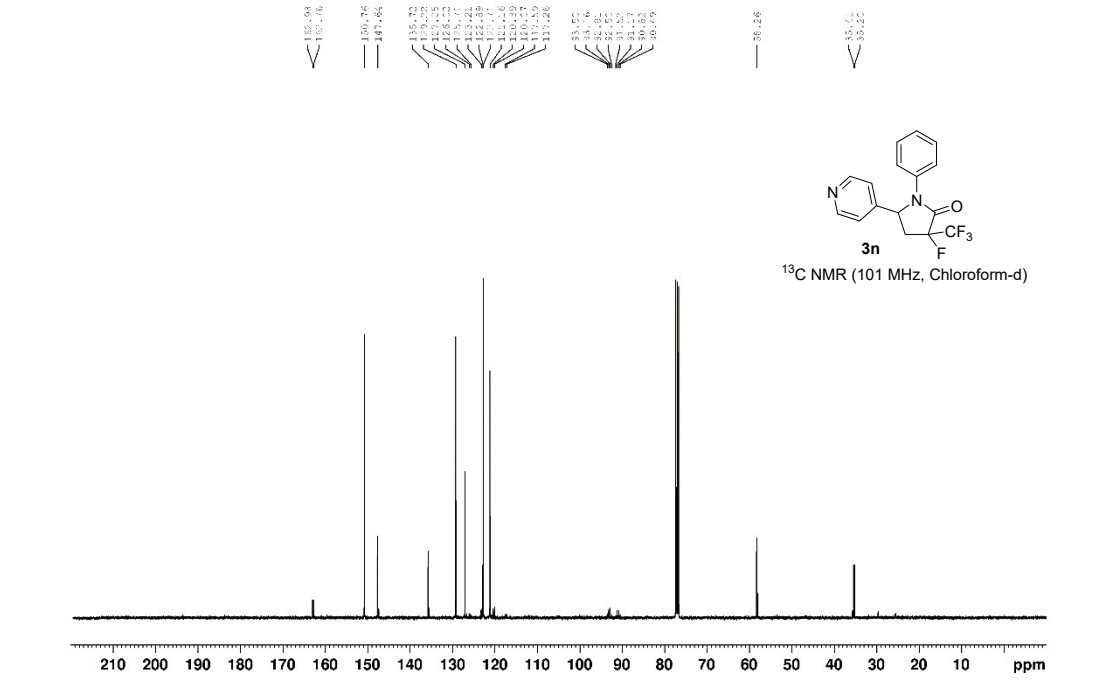


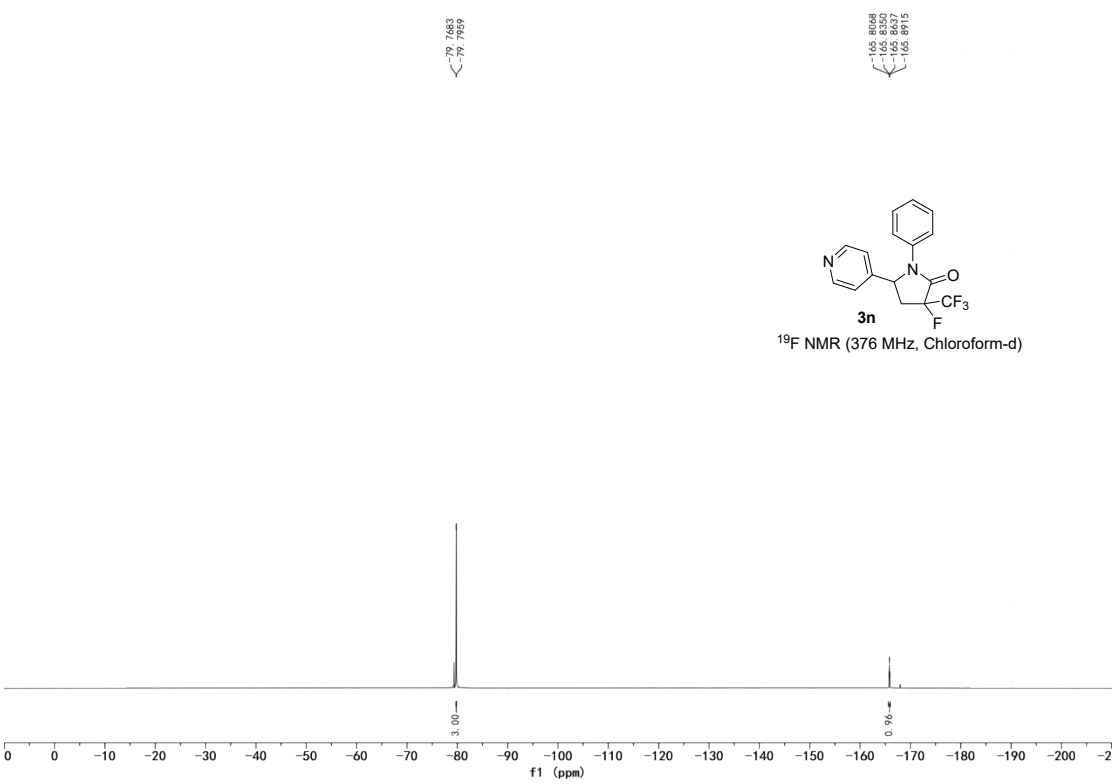
^{13}C NMR (101 MHz, Chloroform-d)



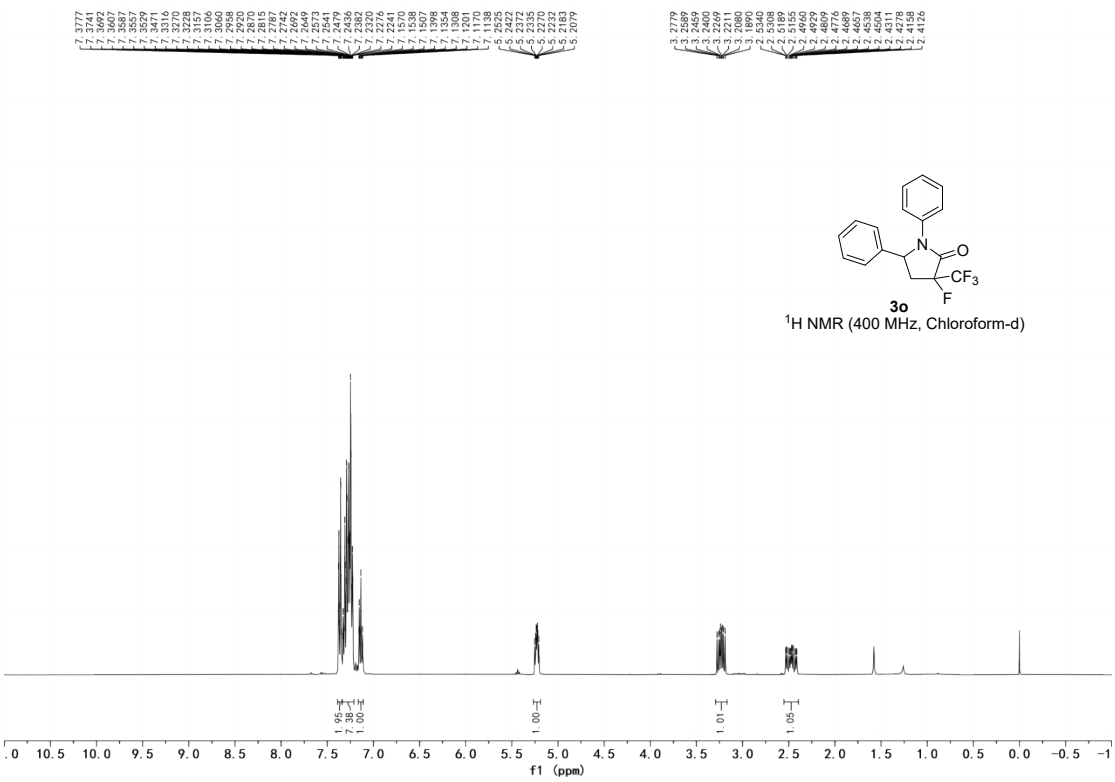
^{19}F NMR (376 MHz, Chloroform-d)

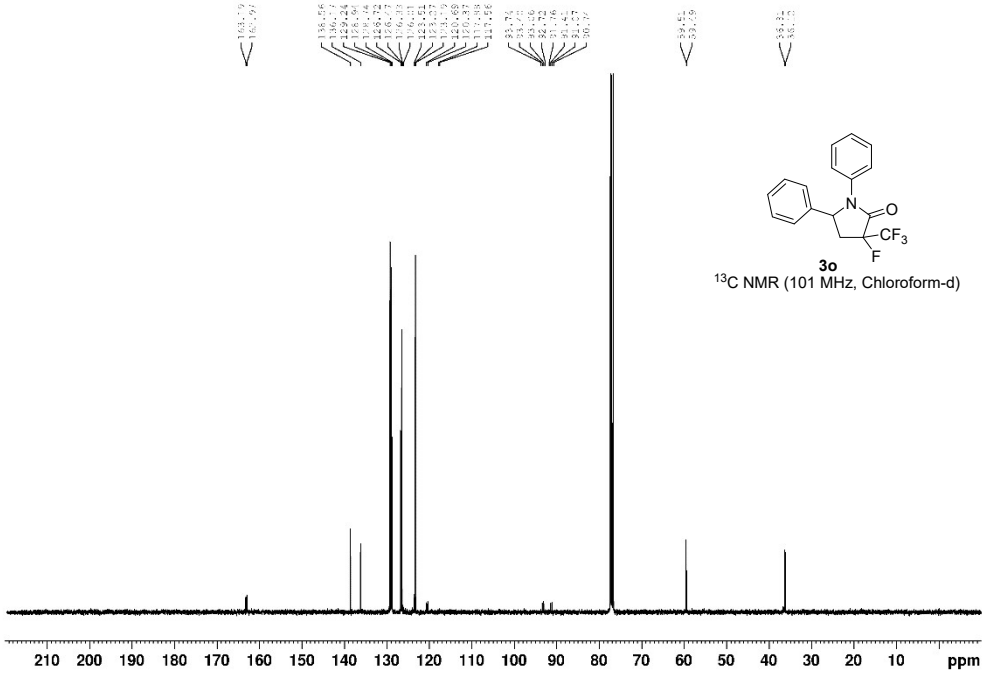

3n
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

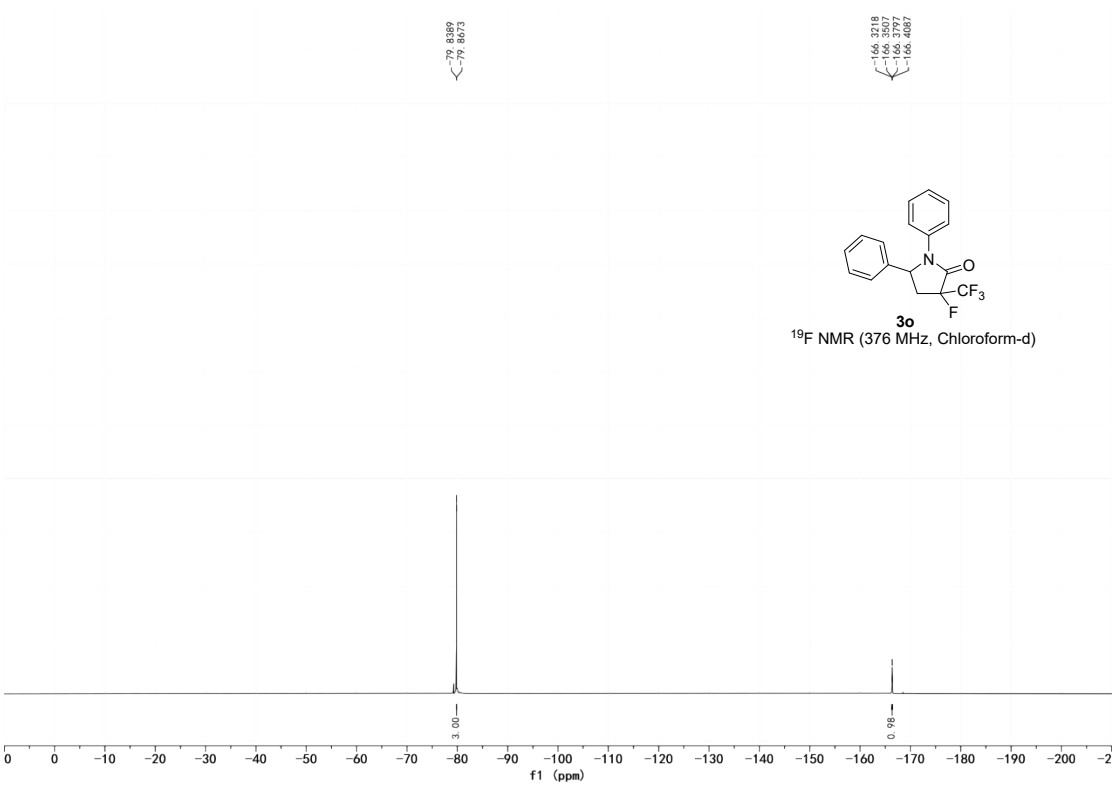

3n
13C NMR (101 MHz, Chloroform-d)
ppm

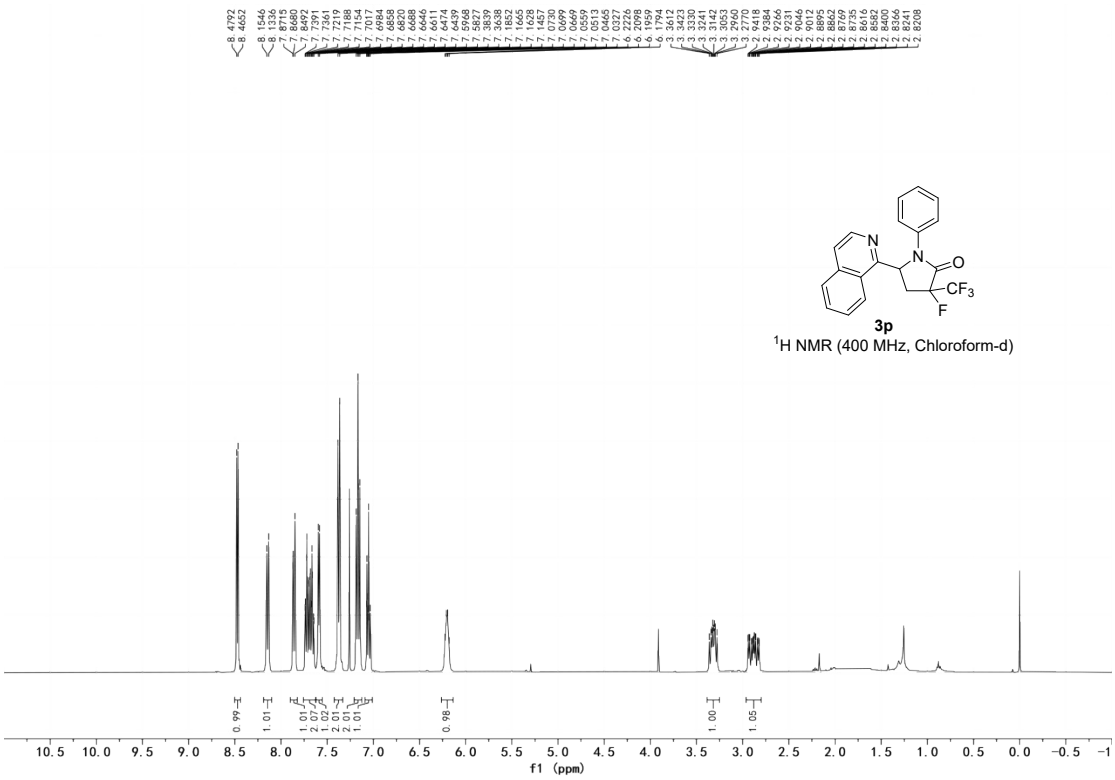


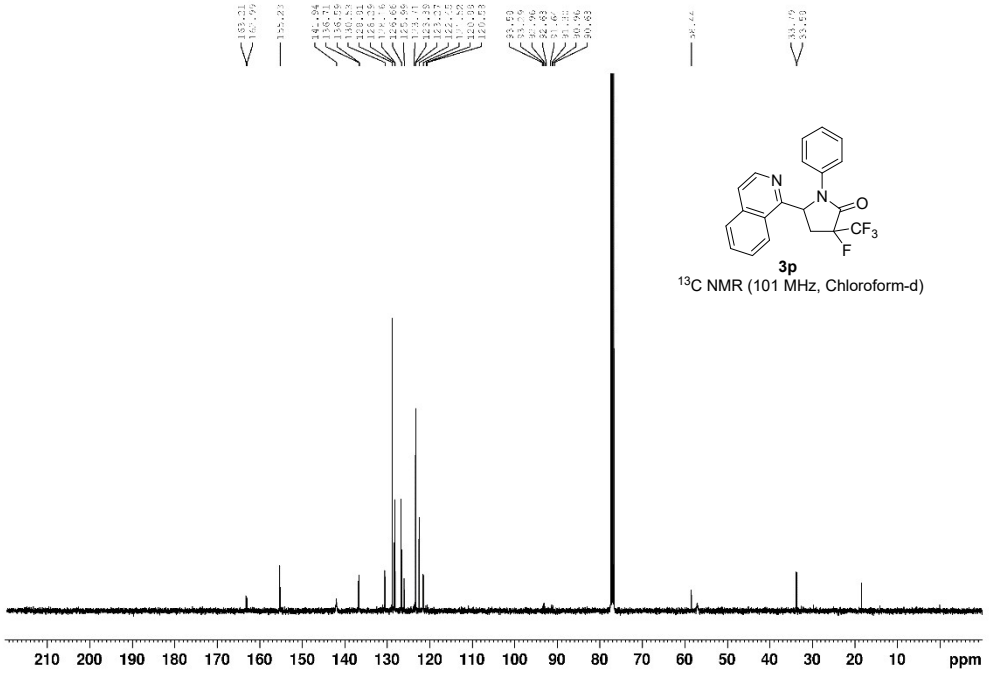
^{19}F NMR (376 MHz, Chloroform-d)

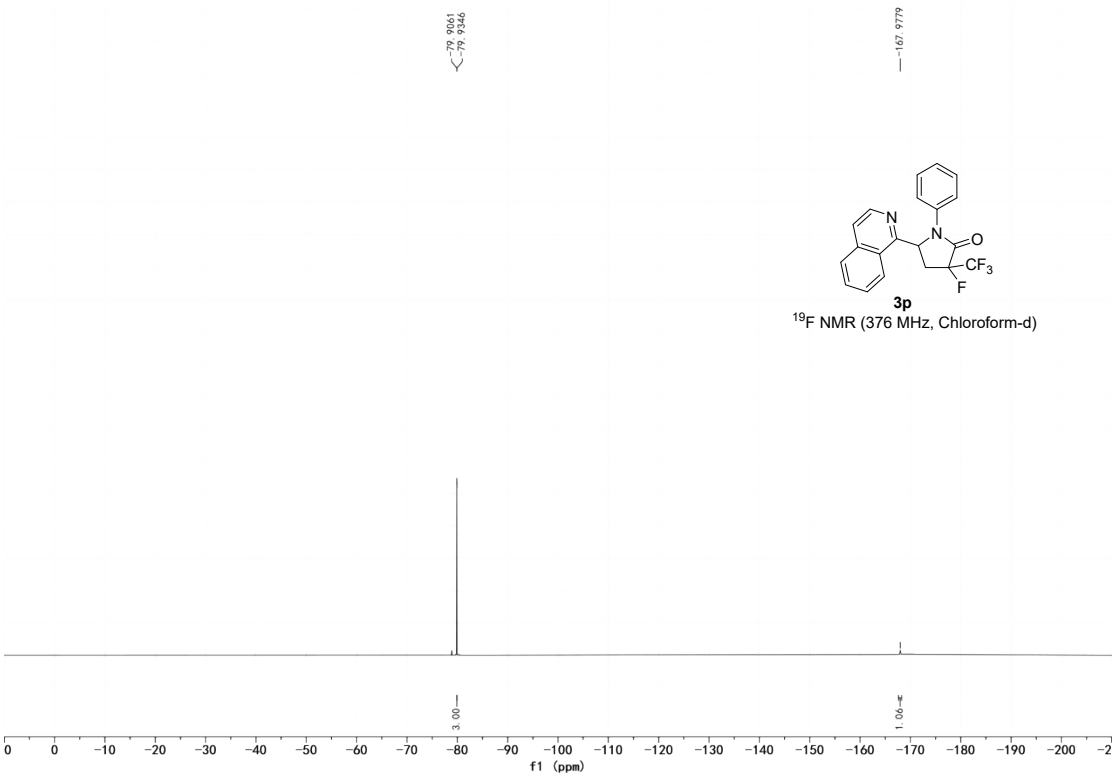

3o
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)


3o
13C NMR (101 MHz, Chloroform-d)
ppm


-79.8389
-79.8673
-166.3218
-166.3507
-166.3797
-166.4087
N
O
CF3
F
3o
19F NMR (376 MHz, Chloroform-d)
3.00
0.98
0 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −2
f1 (ppm)

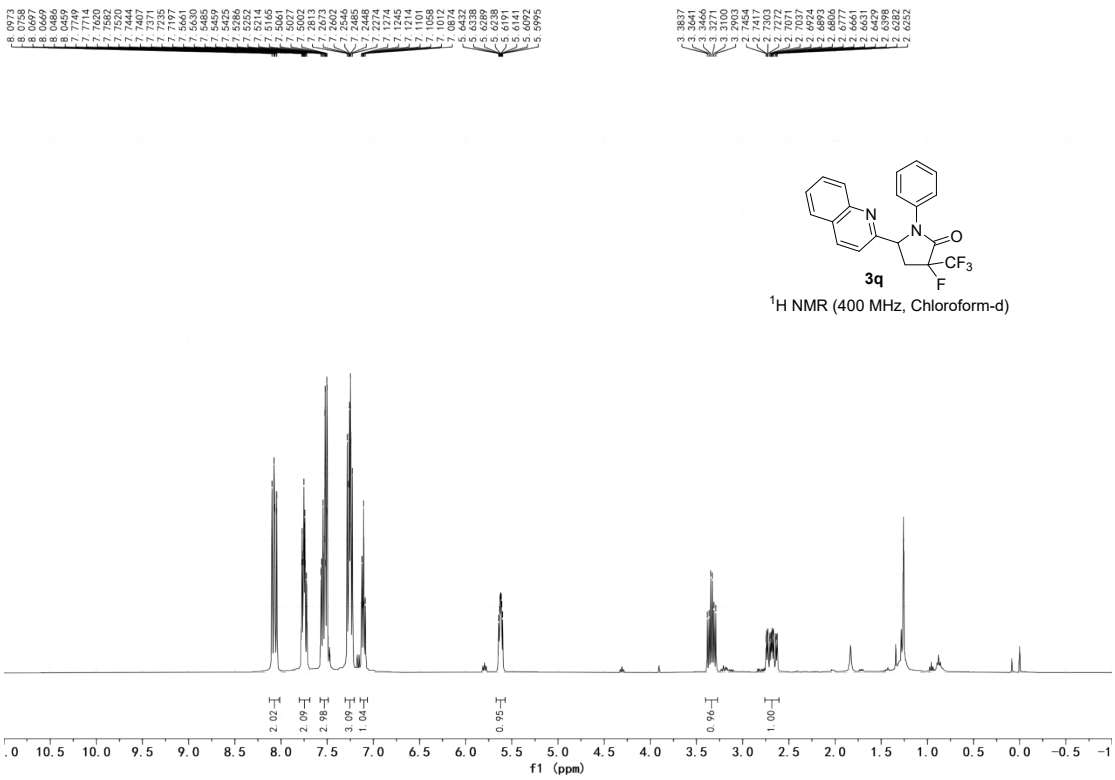

3p
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

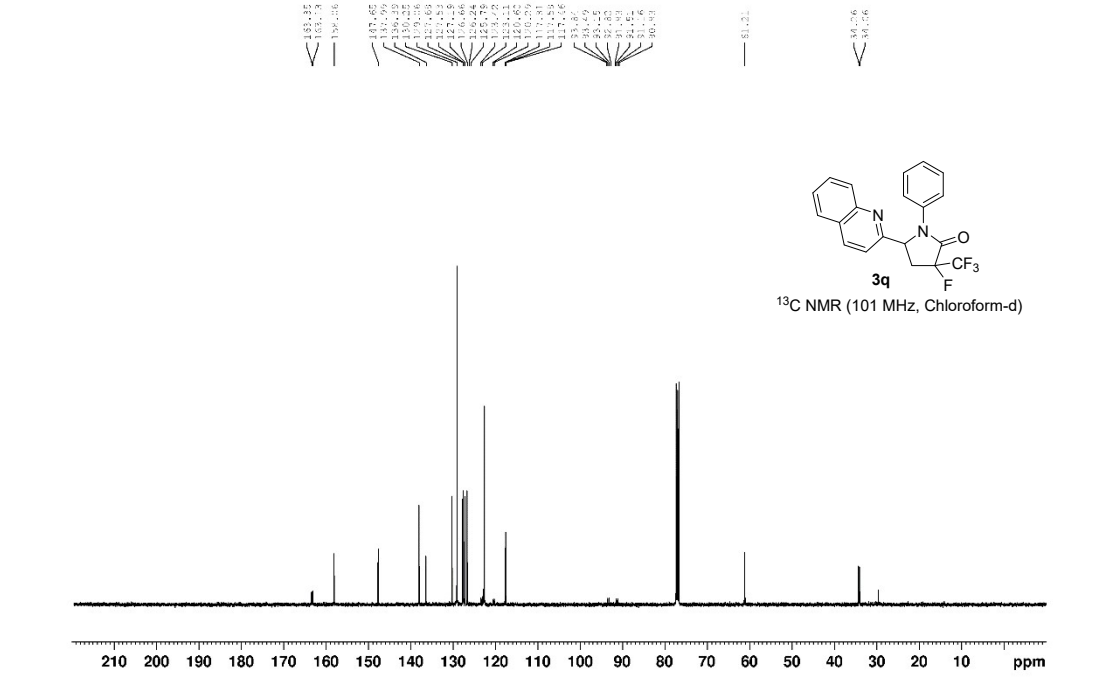

3p
13C NMR (101 MHz, Chloroform-d)
ppm

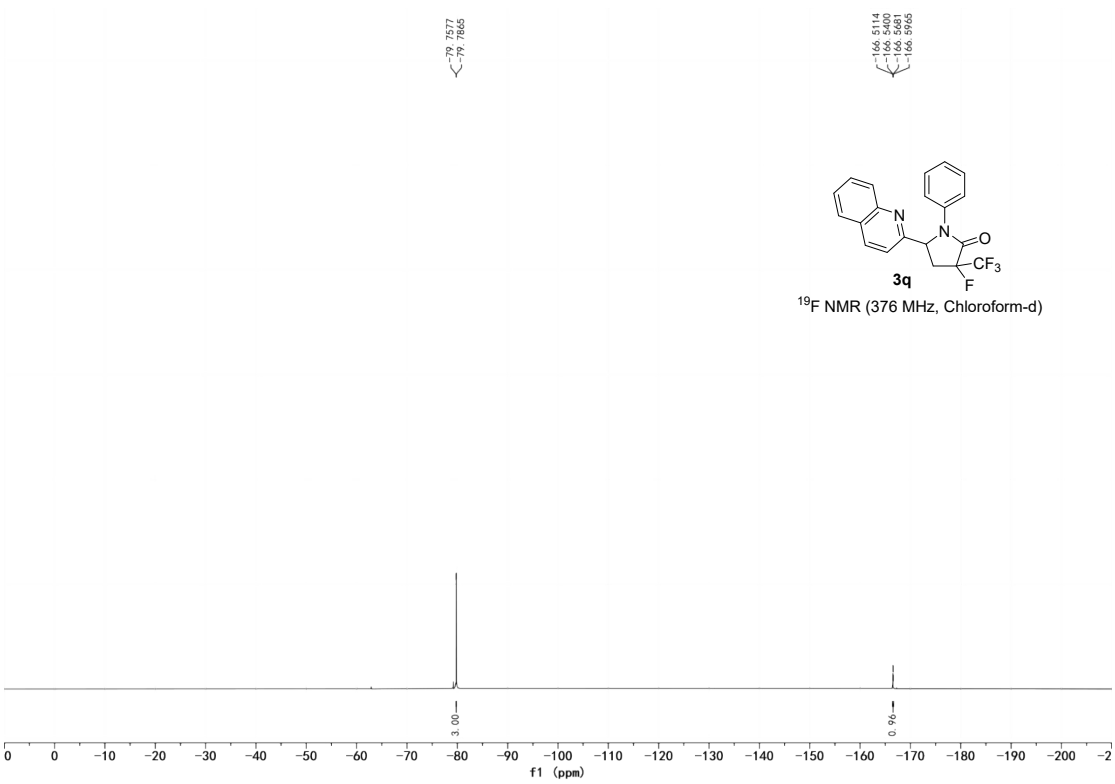


3p

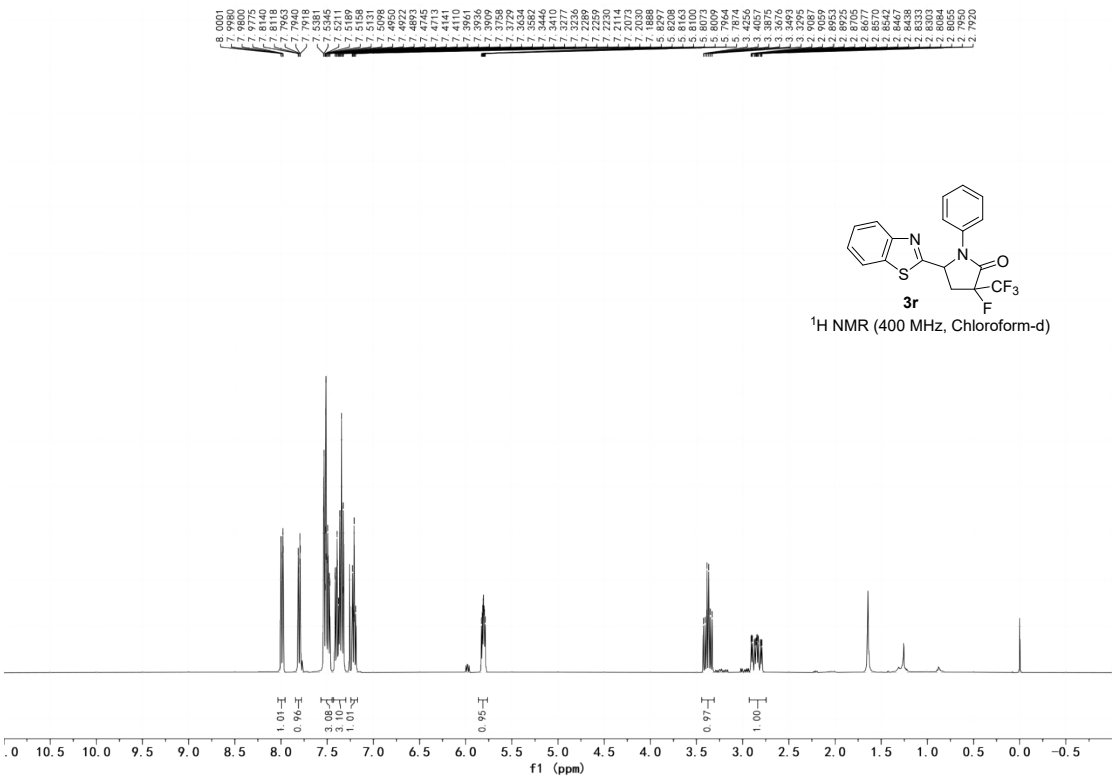
^{19}F NMR (376 MHz, Chloroform-d)

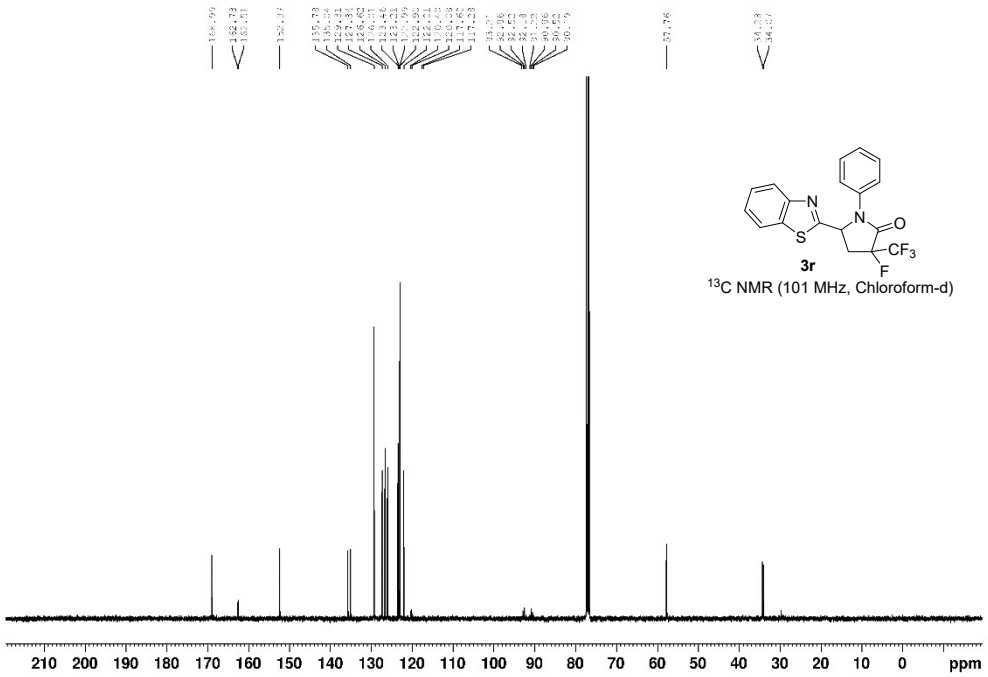

3q
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

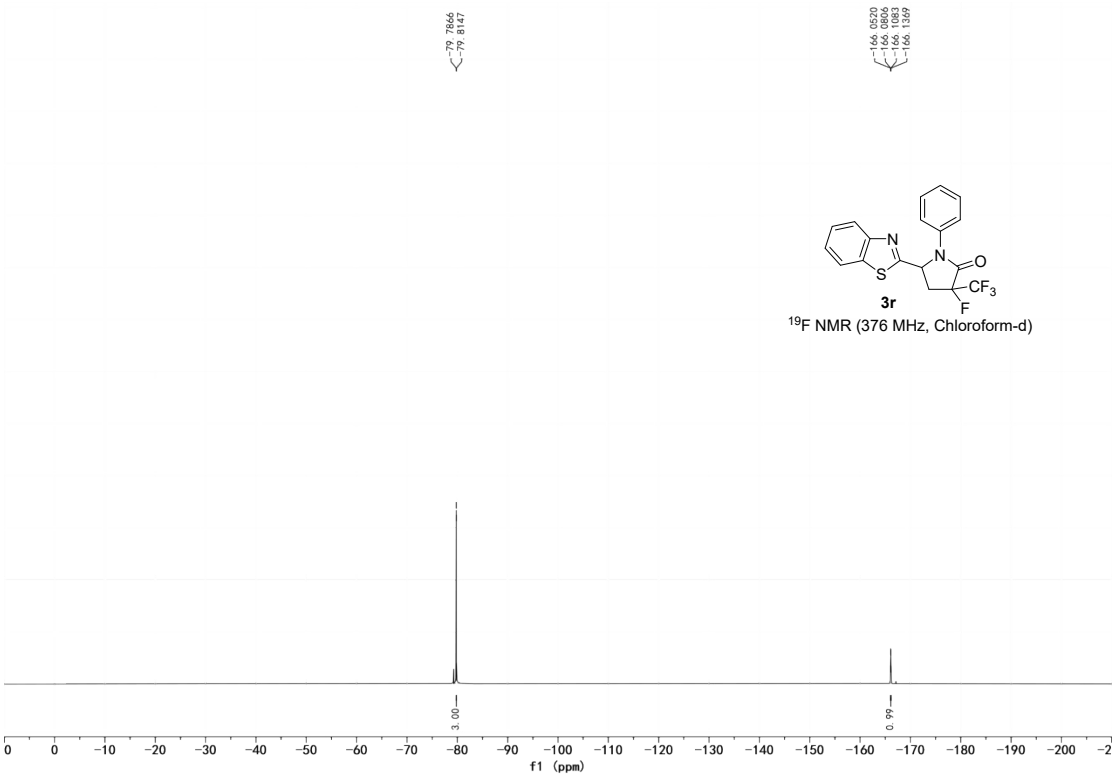

3q
13C NMR (101 MHz, Chloroform-d)
ppm



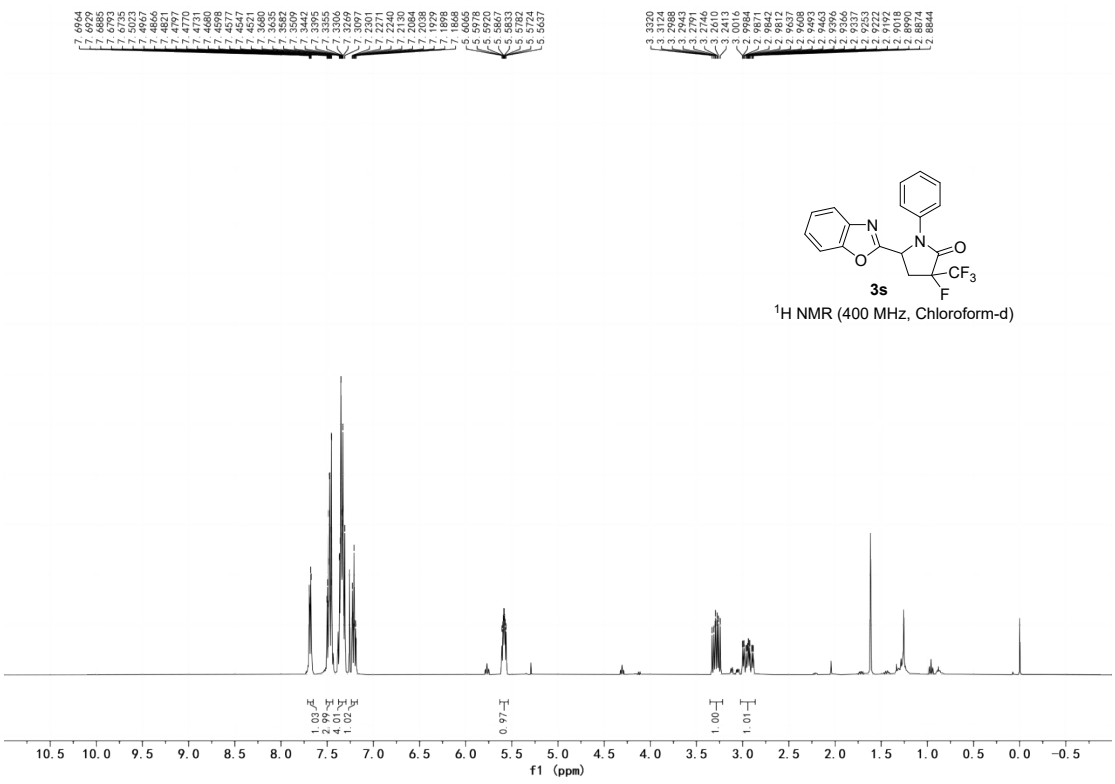
^{19}F NMR (376 MHz, Chloroform-d)

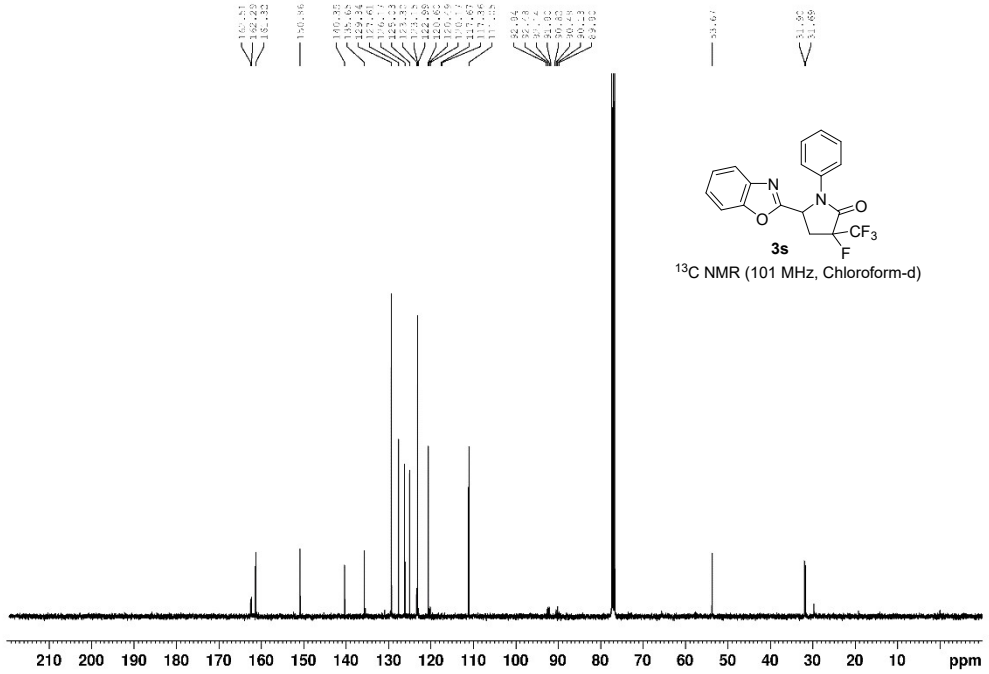

3r
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

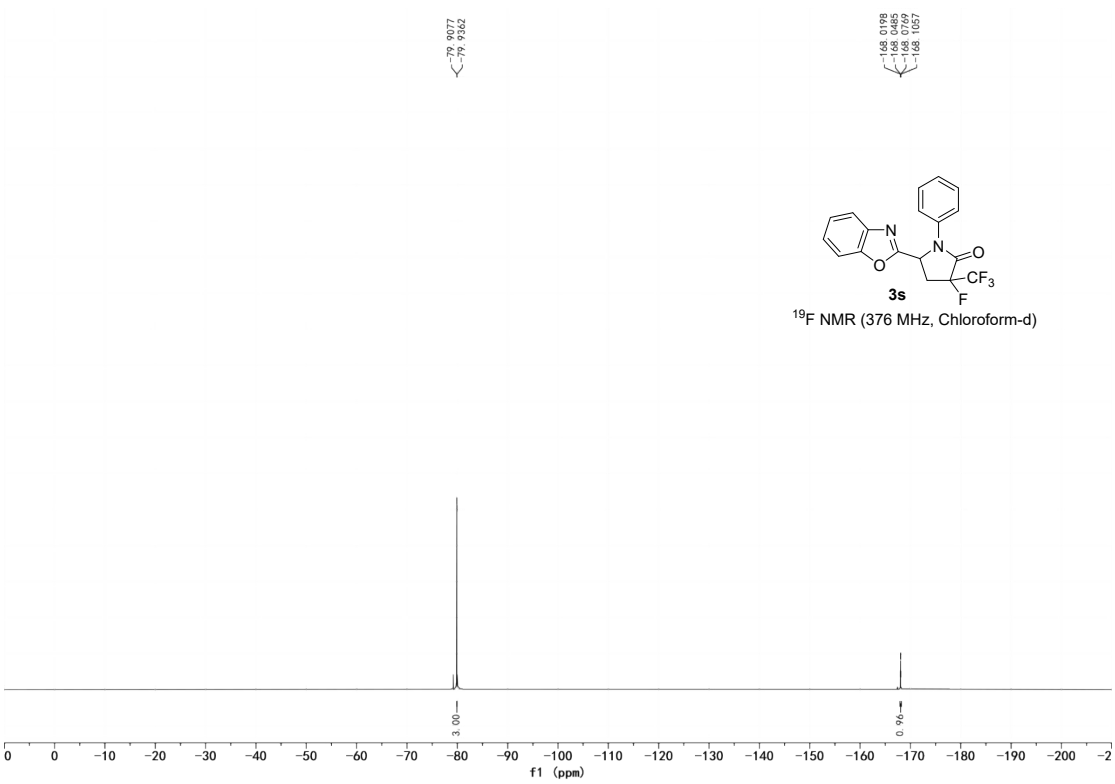

3r
13C NMR (101 MHz, Chloroform-d)
ppm



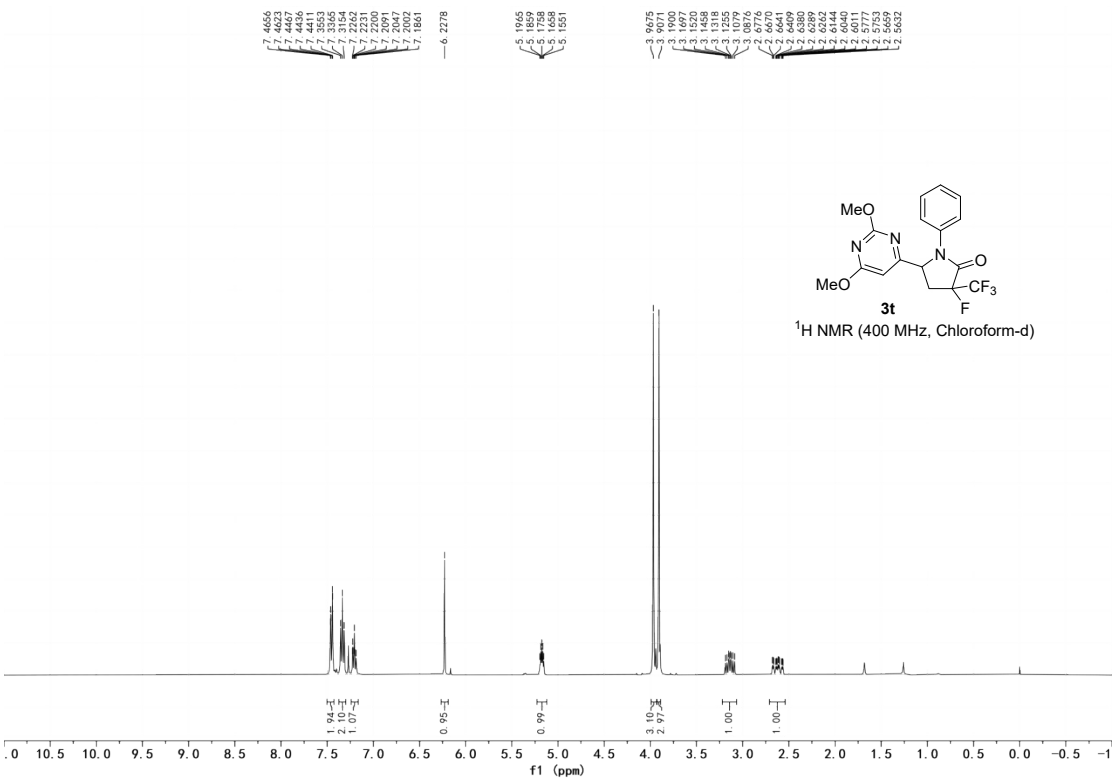
^{19}F NMR (376 MHz, Chloroform-d)

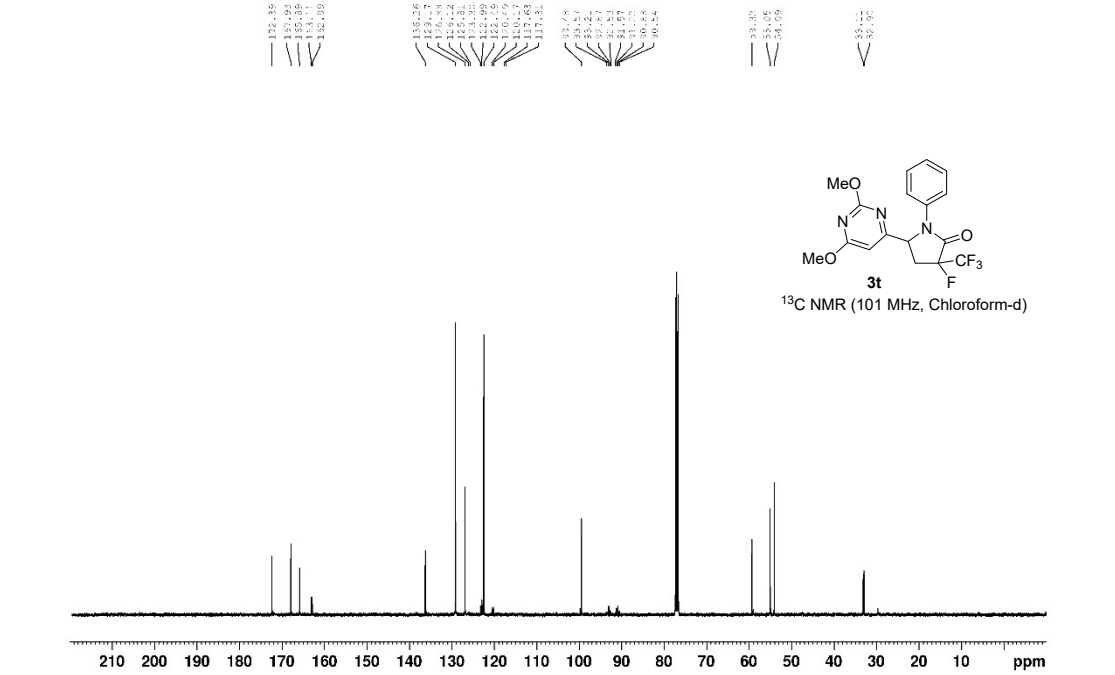

3s
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

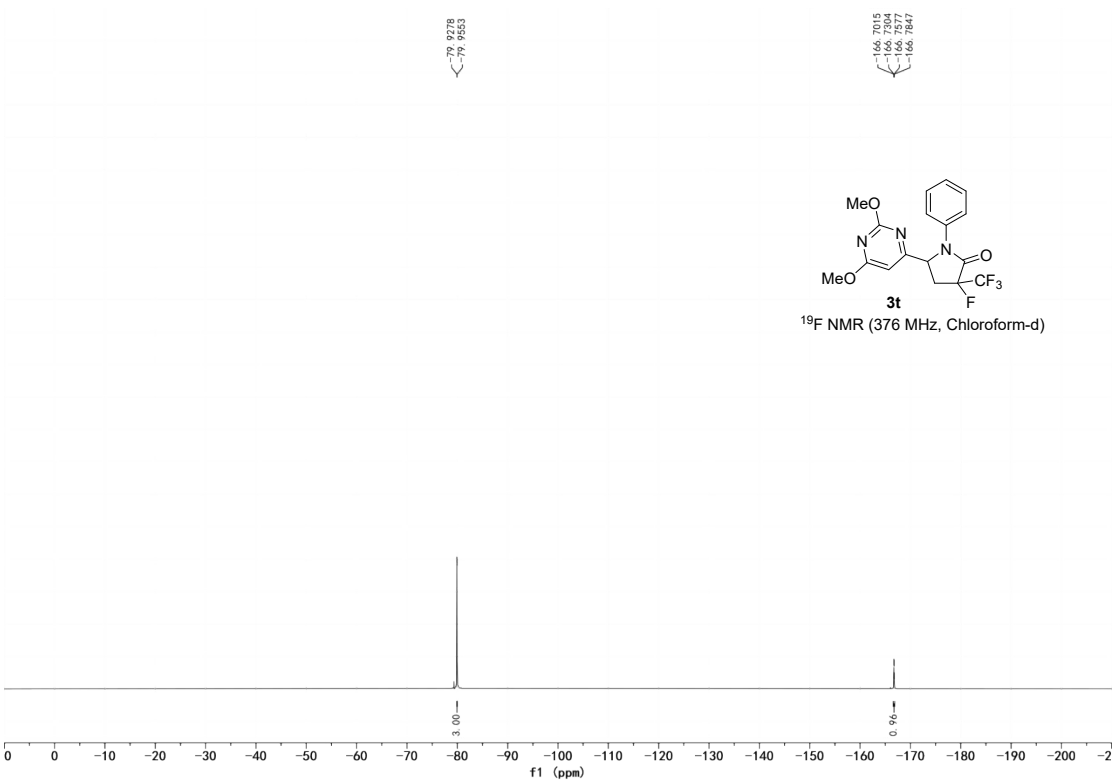

3s
13C NMR (101 MHz, Chloroform-d)
ppm



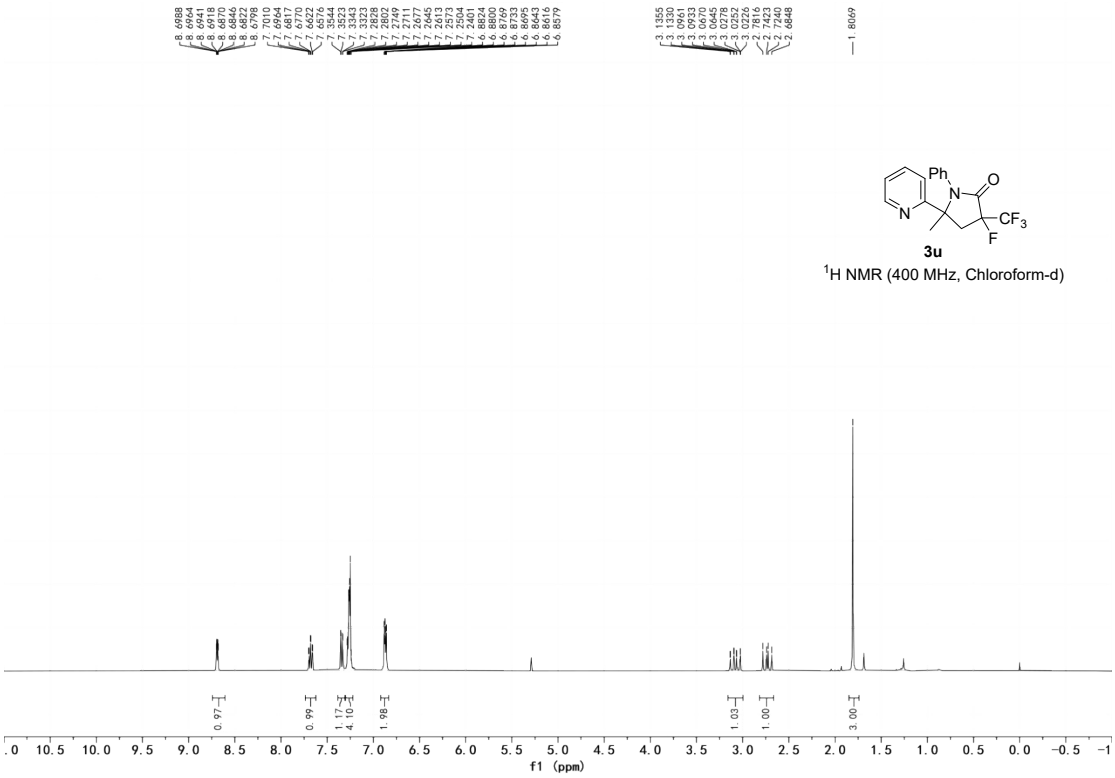
^{19}F NMR (376 MHz, Chloroform-d)


MeO
N
N
MeO
N
O
CF3
F
3t
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)


MeO
N
N
MeO
N
O
CF3
F
3t
13C NMR (101 MHz, Chloroform-d)
ppm

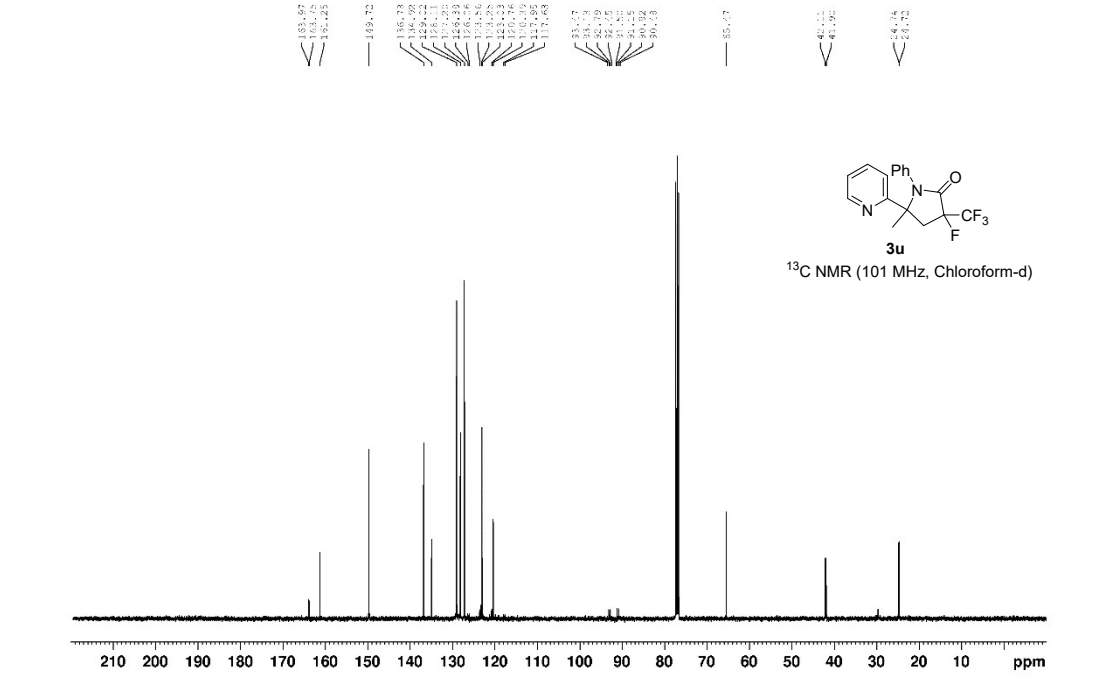


^{19}F NMR (376 MHz, Chloroform-d)



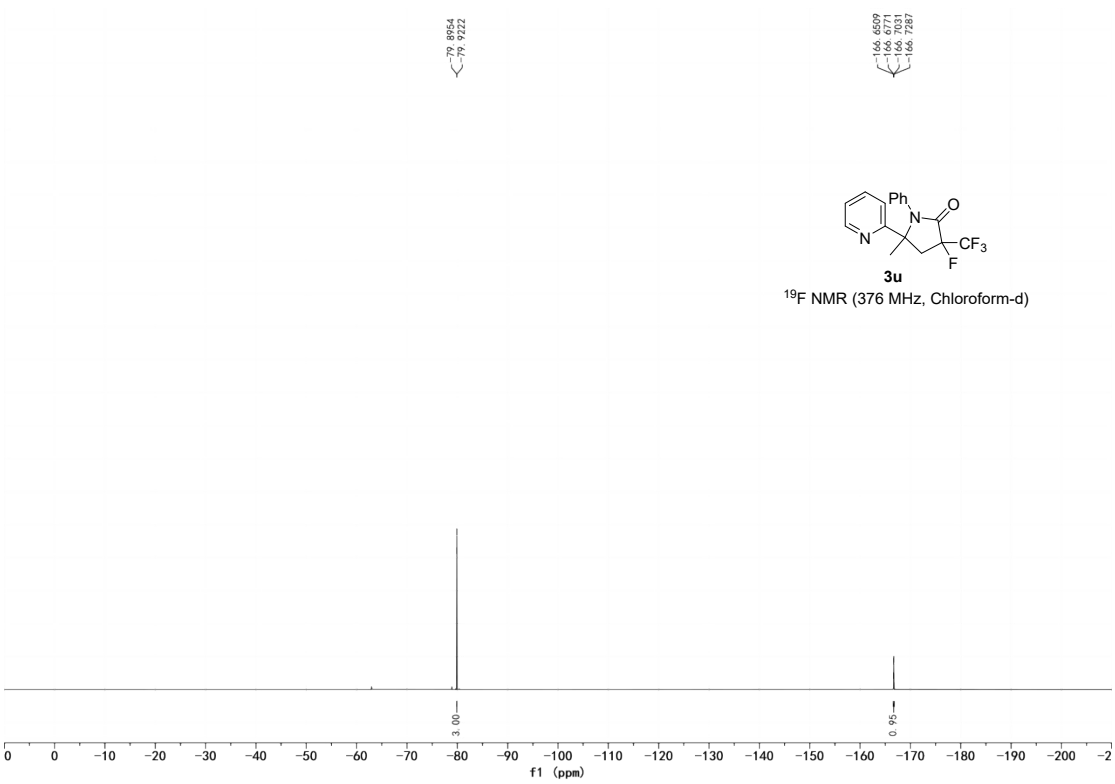
3u

^{1}H NMR (400 MHz, Chloroform-d)



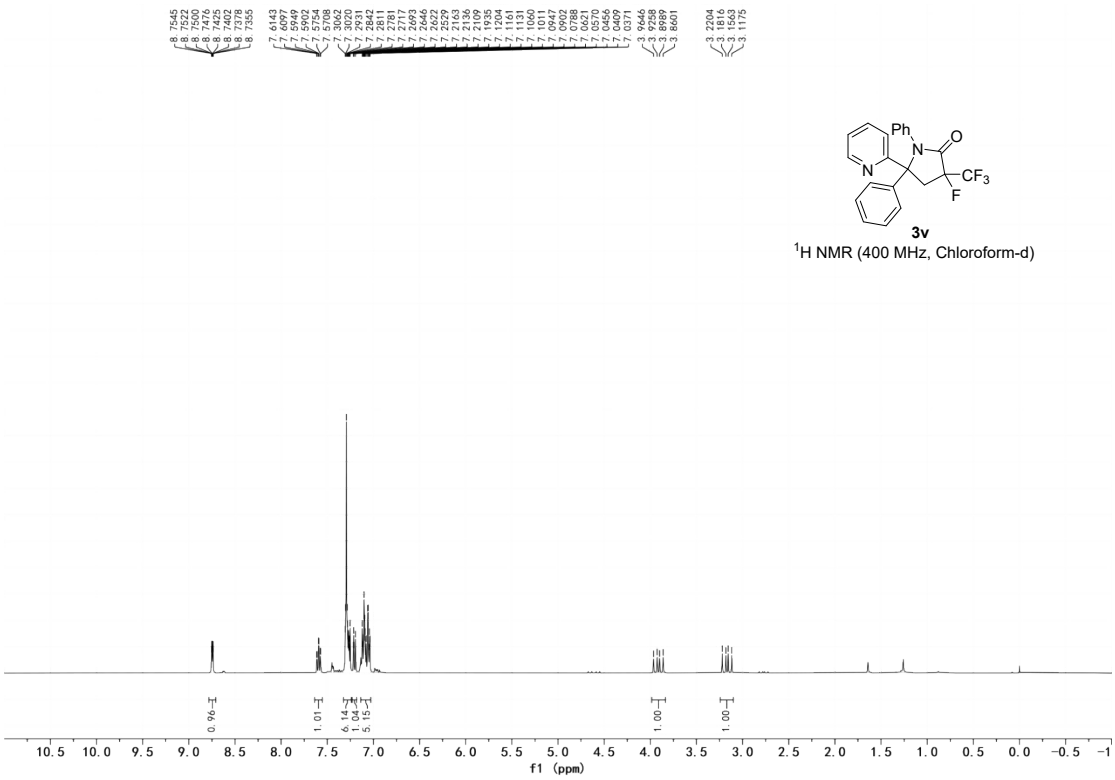
3u

^{13}C NMR (101 MHz, Chloroform-d)



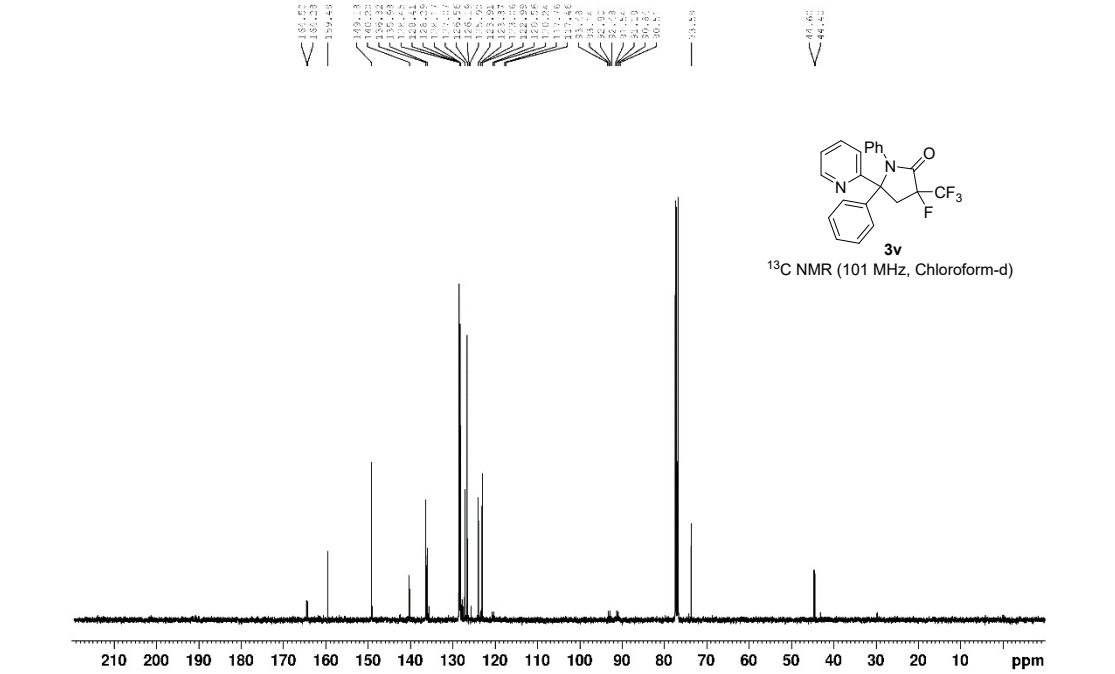
3u

^{19}F NMR (376 MHz, Chloroform-d)



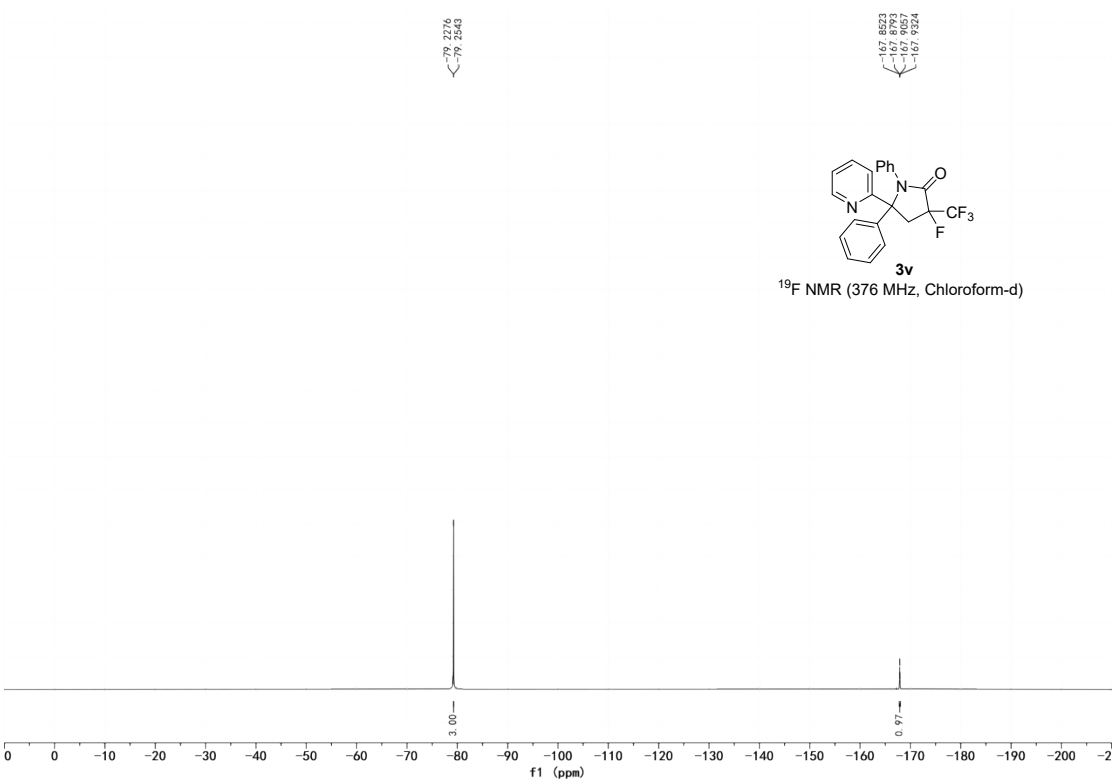
3v

^{1}H NMR (400 MHz, Chloroform-d)



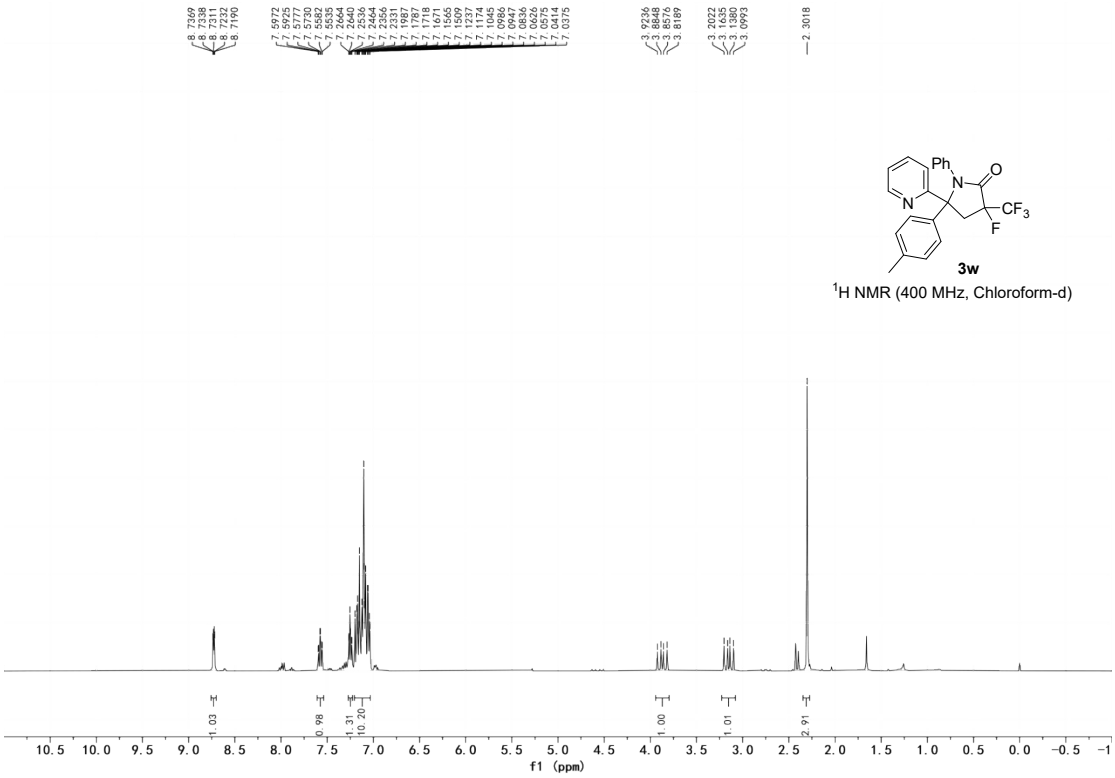
3v

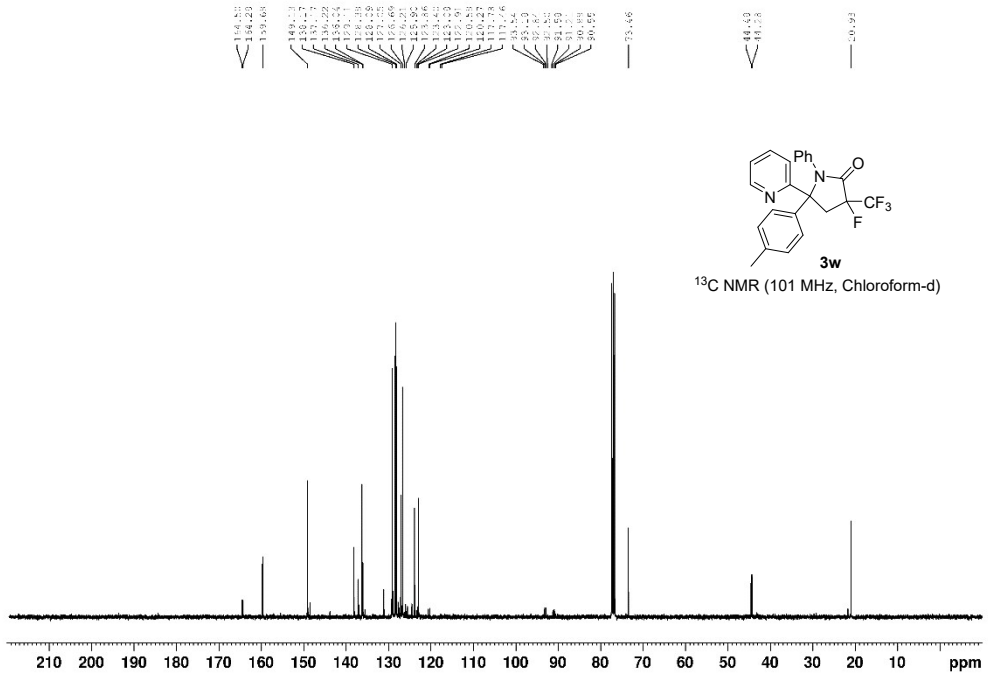
^{13}C NMR (101 MHz, Chloroform-d)

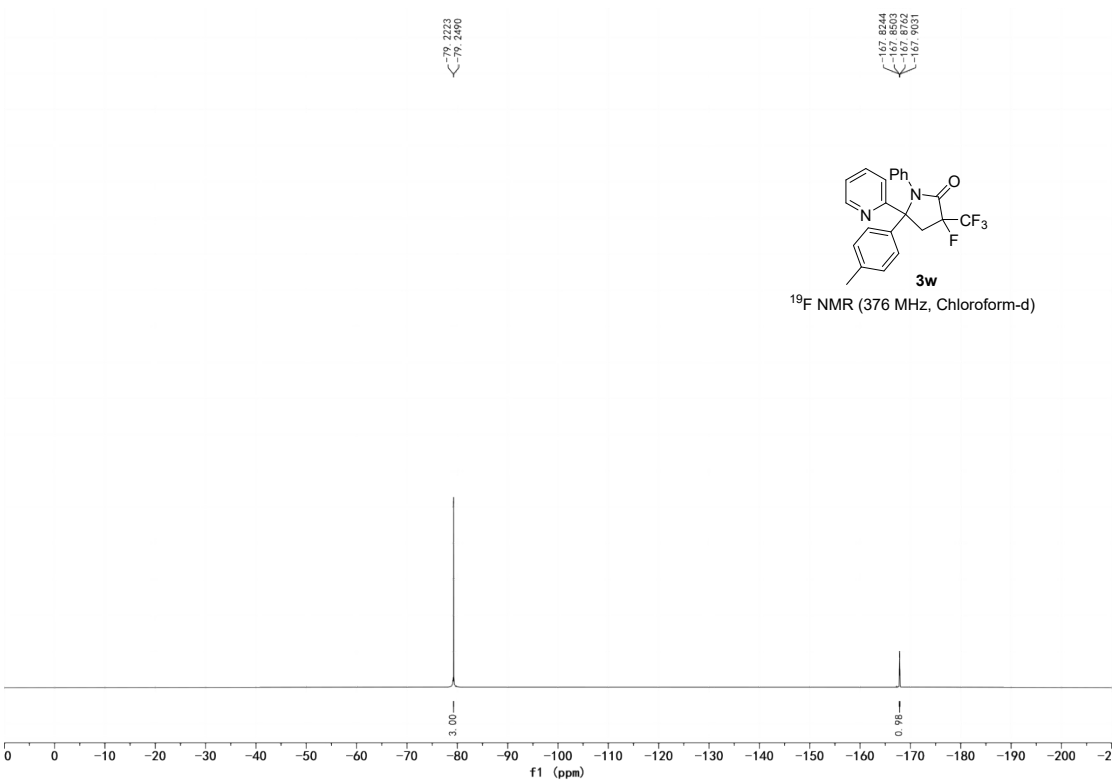


3v

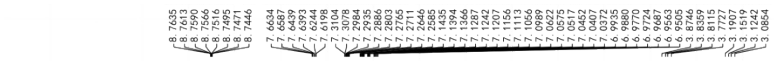
^{19}F NMR (376 MHz, Chloroform-d)

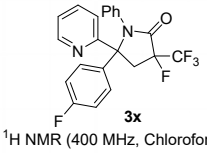

Ph
N
O
N
CF3
F
3w
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)


Ph
N
O
N
CF3
F
3w
13C NMR (101 MHz, Chloroform-d)
ppm



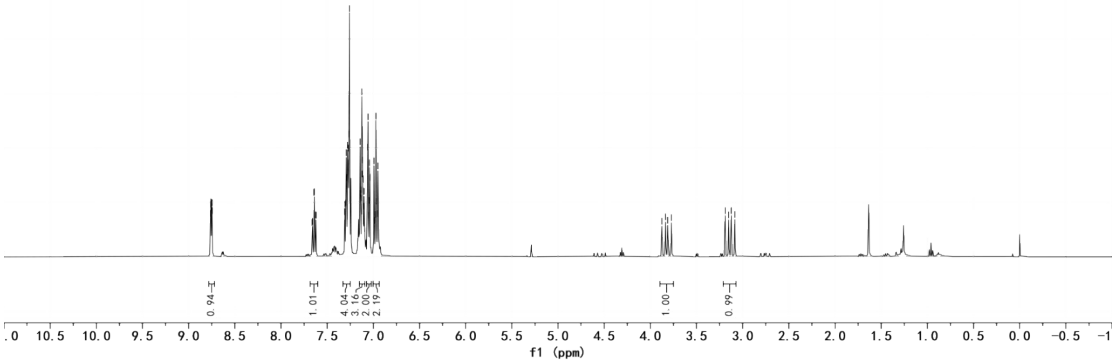
^{19}F NMR (376 MHz, Chloroform-d)

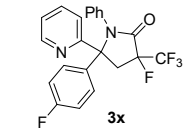




3x

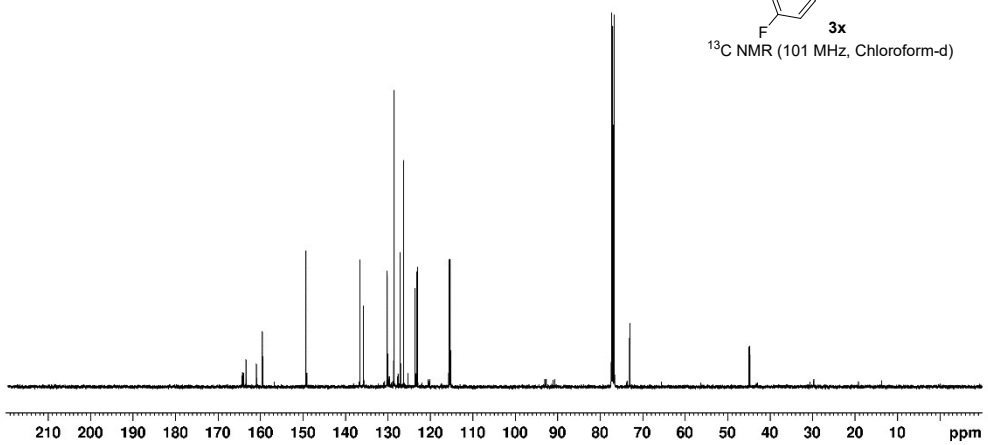
^{1}H NMR (400 MHz, Chloroform-d)

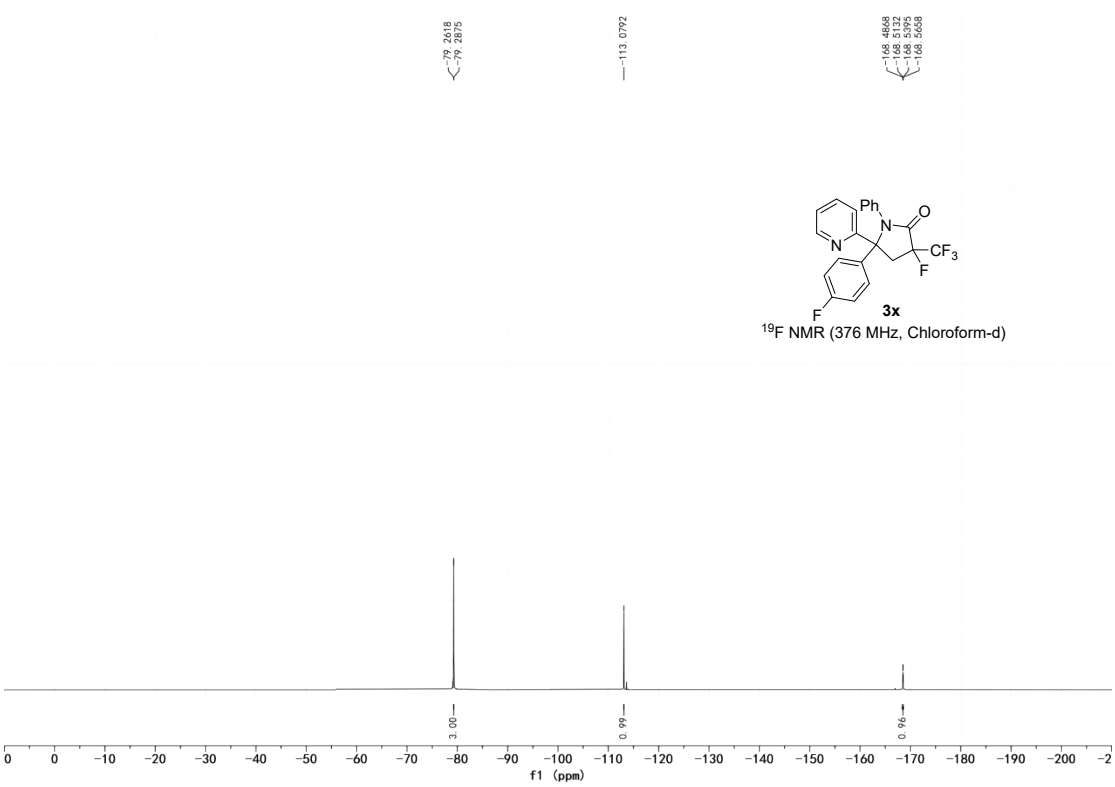




3x

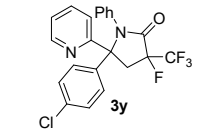
^{13}C NMR (101 MHz, Chloroform-d)





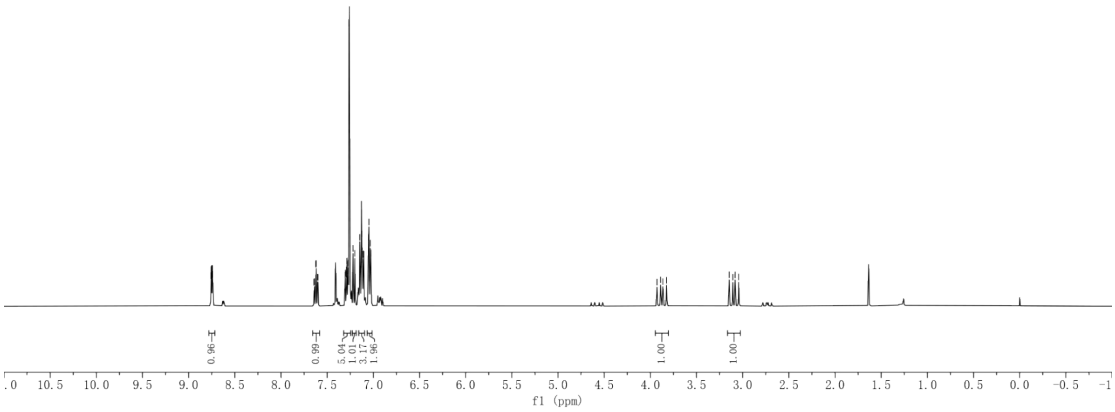
3x

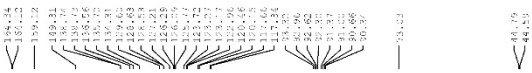
^{19}F NMR (376 MHz, Chloroform-d)

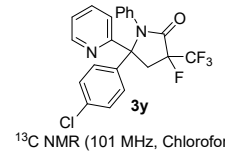


3y

^{1}H NMR (400 MHz, Chloroform-d)

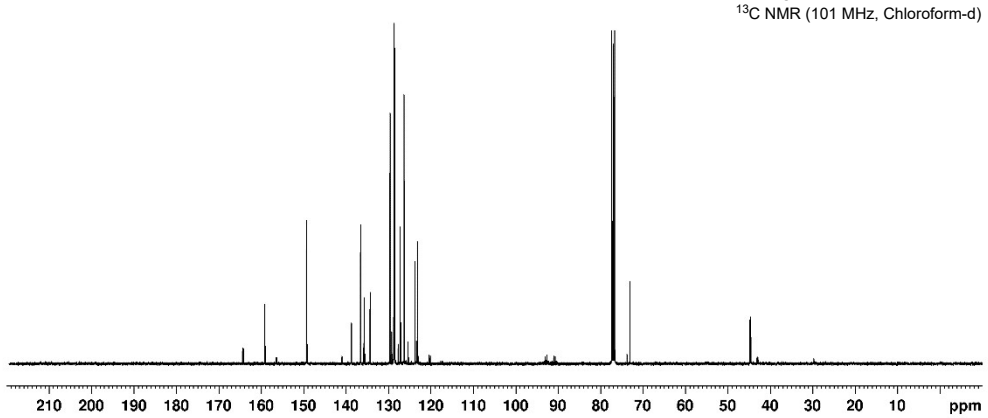


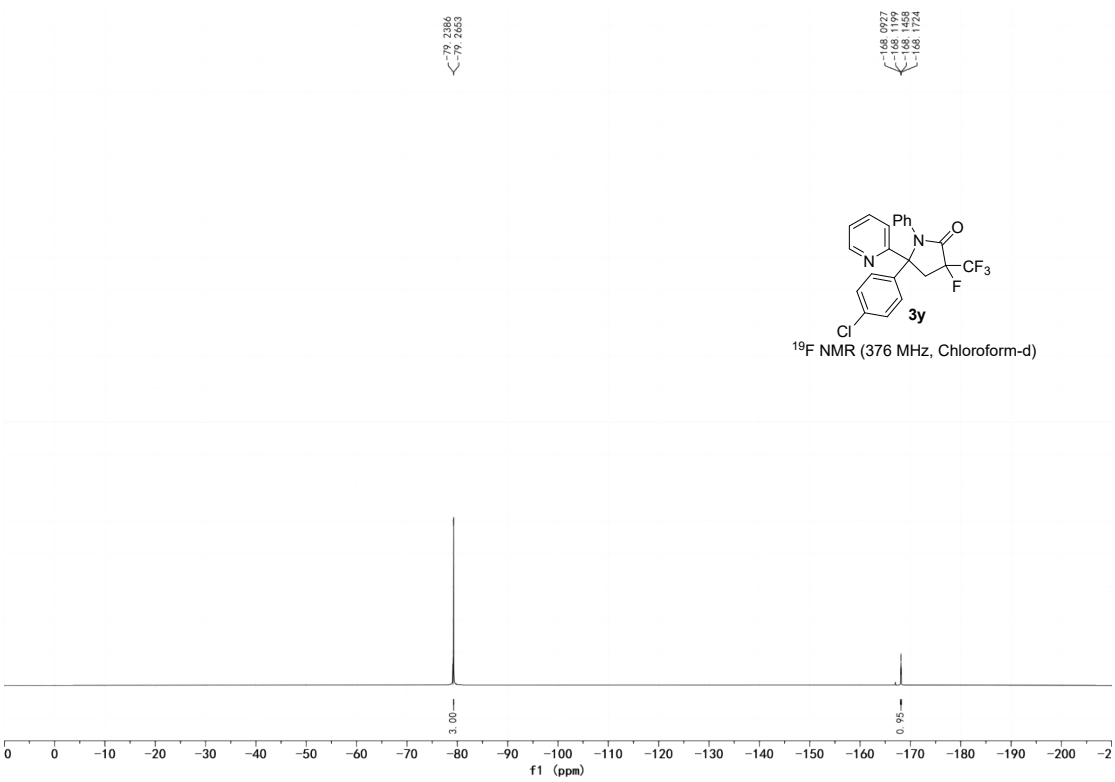




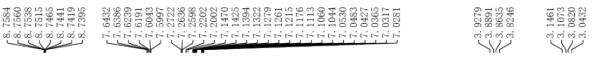
3y

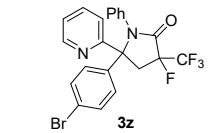
^{13}C NMR (101 MHz, Chloroform-d)





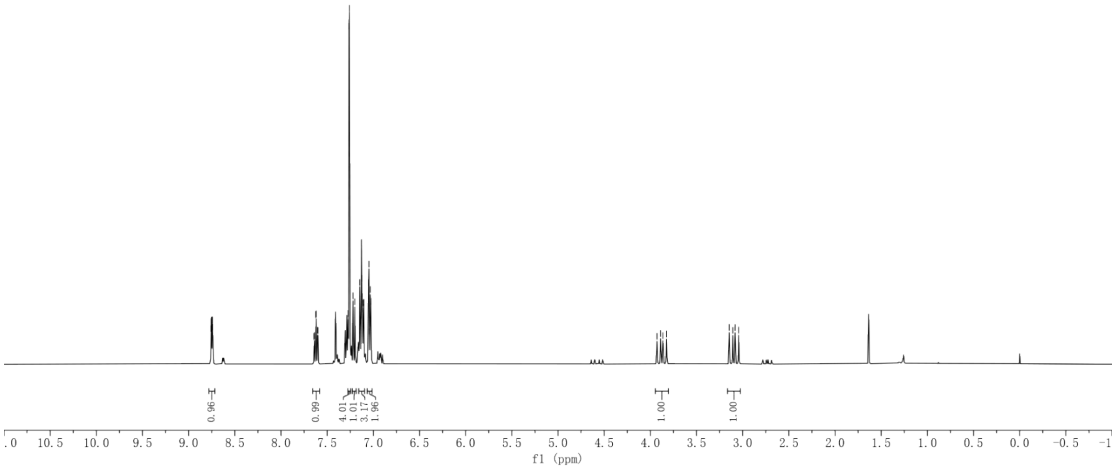
^{19}F NMR (376 MHz, Chloroform-d)

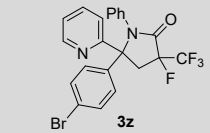




3z

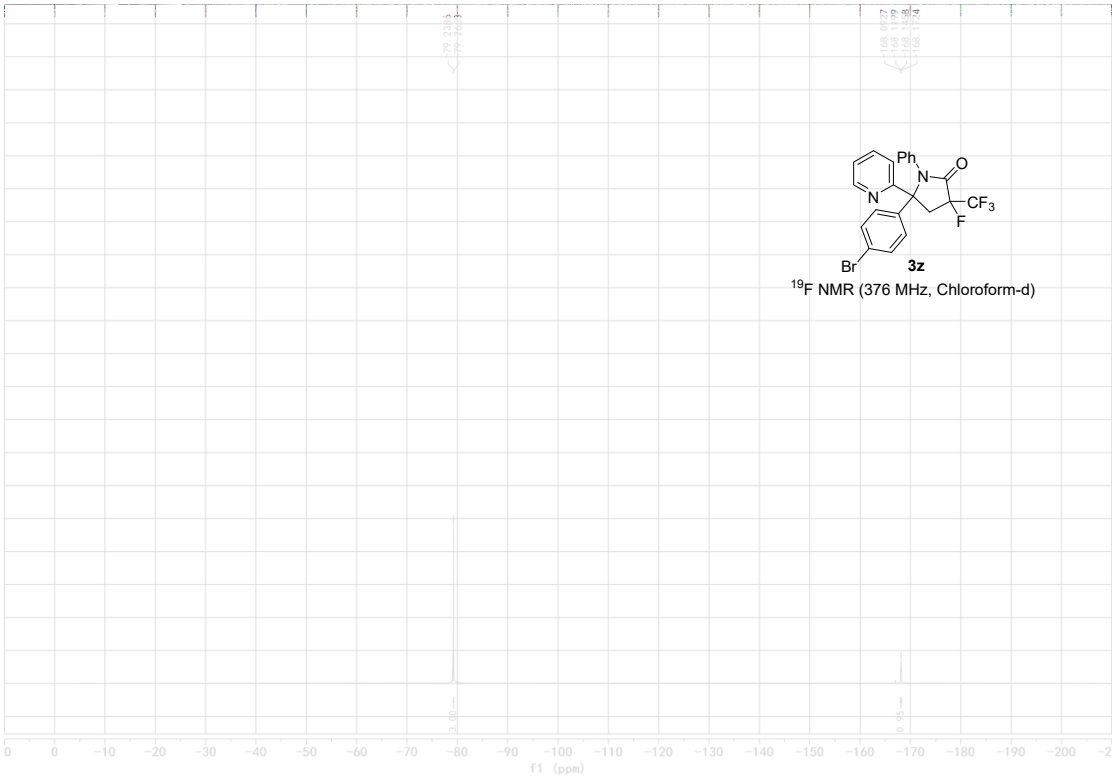
^{1}H NMR (400 MHz, Chloroform-d)

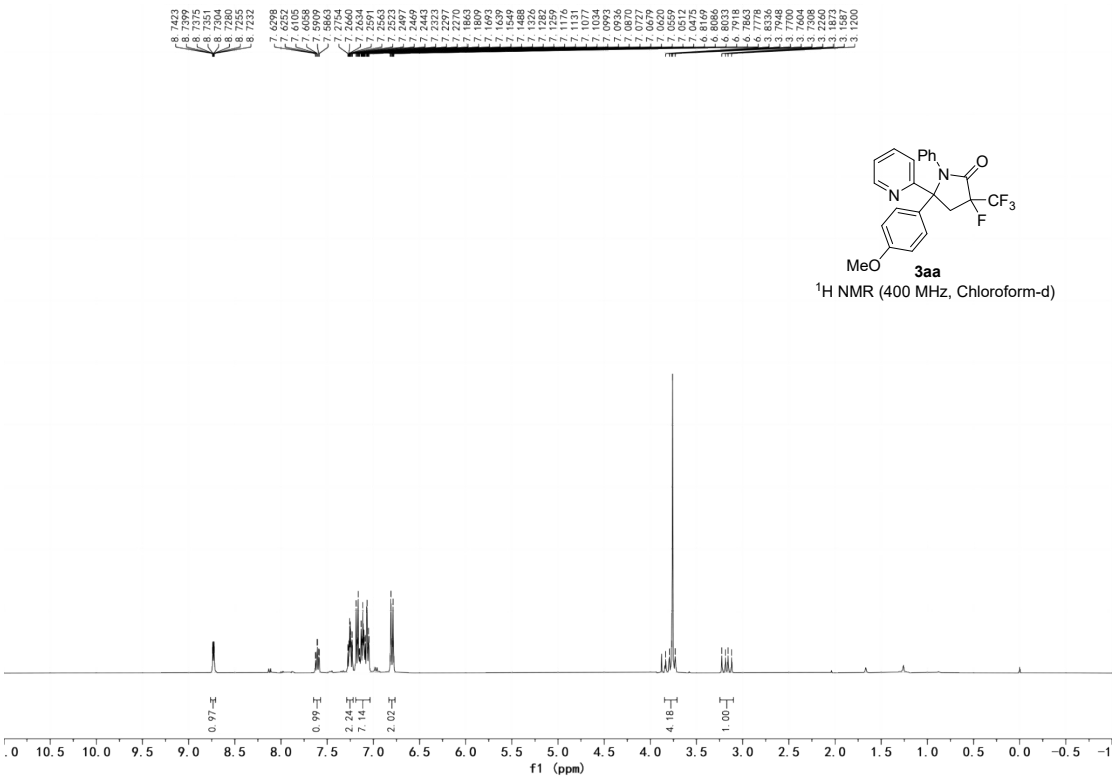




3z

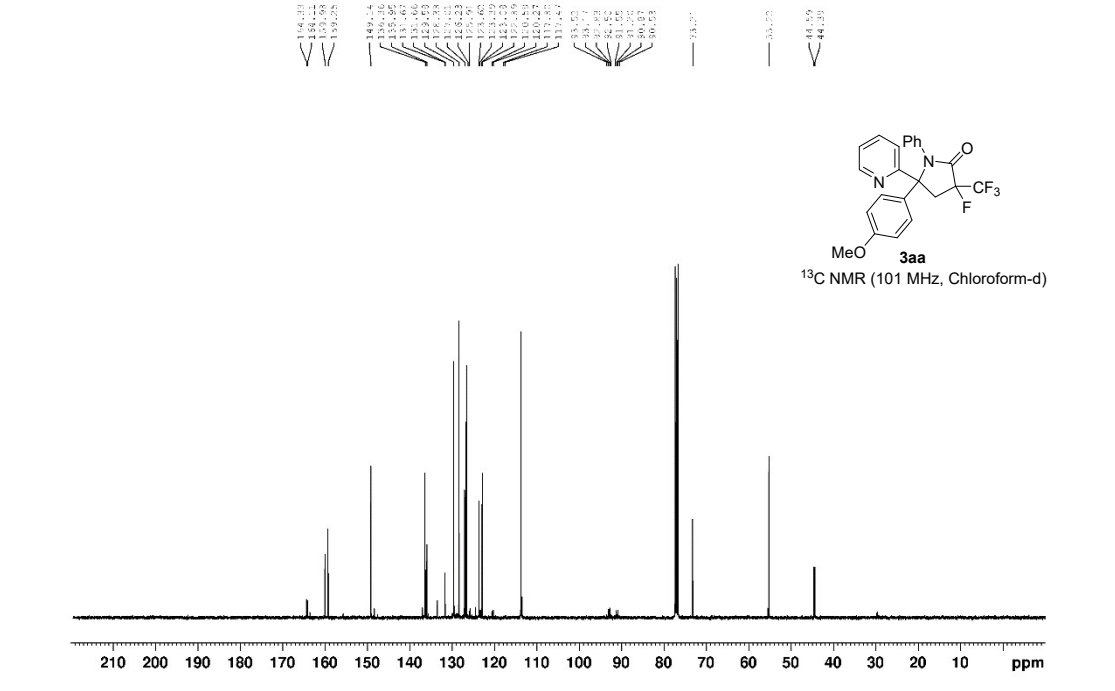
^{13}C NMR (101 MHz, Chloroform-d)


Ph
N
O
N
CF3
F
Br
3z
19F NMR (376 MHz, Chloroform-d)
f1 (ppm)



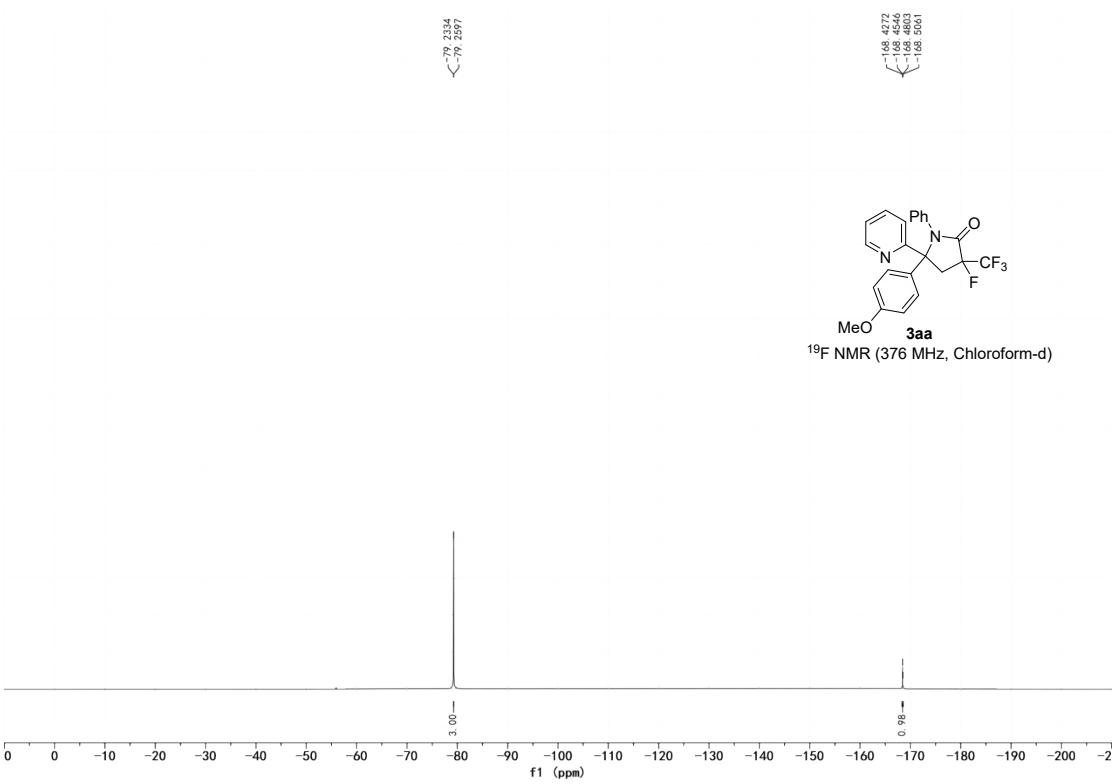
3aa

^{1}H NMR (400 MHz, Chloroform-d)



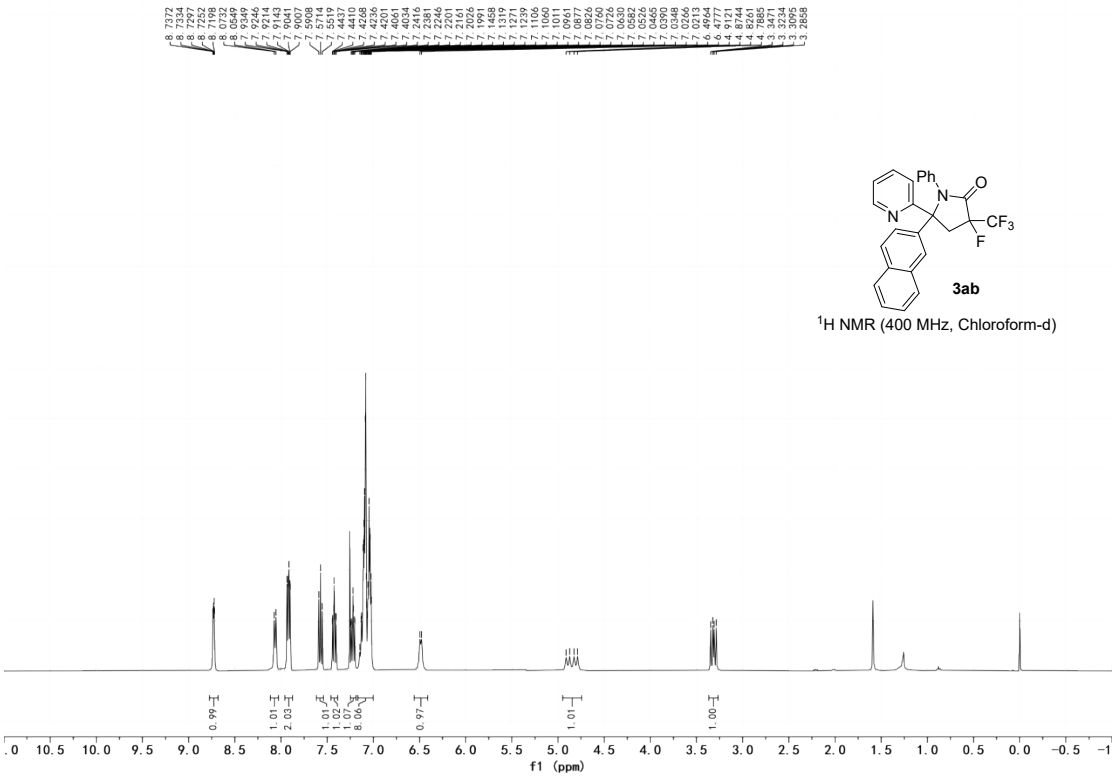
3aa

^{13}C NMR (101 MHz, Chloroform-d)

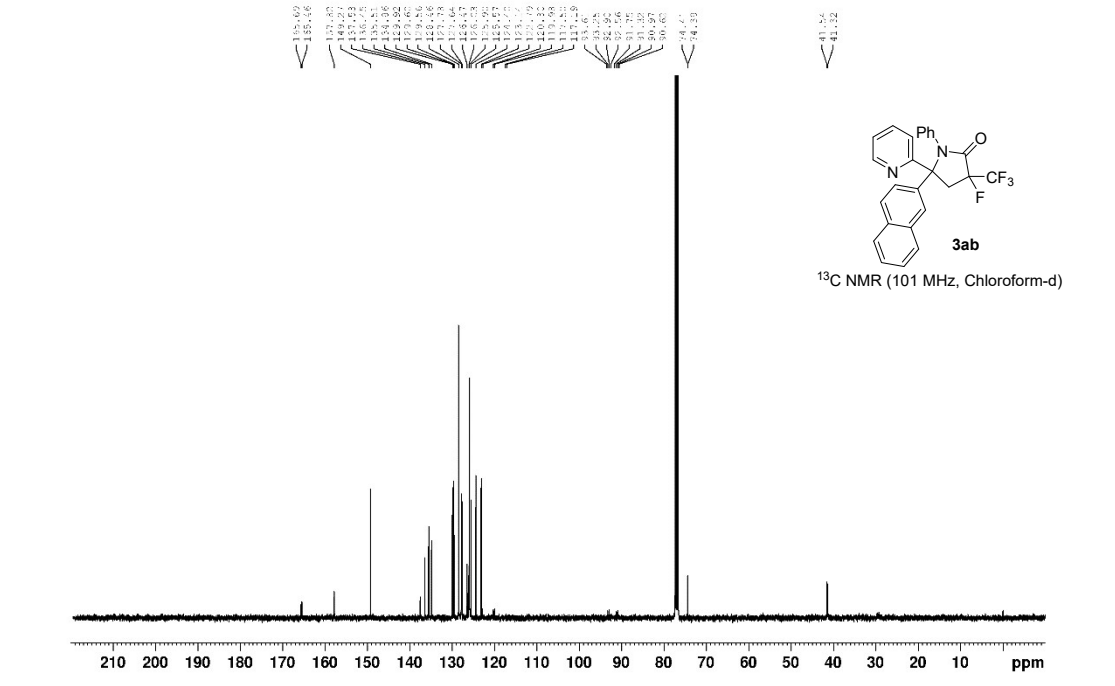


3aa

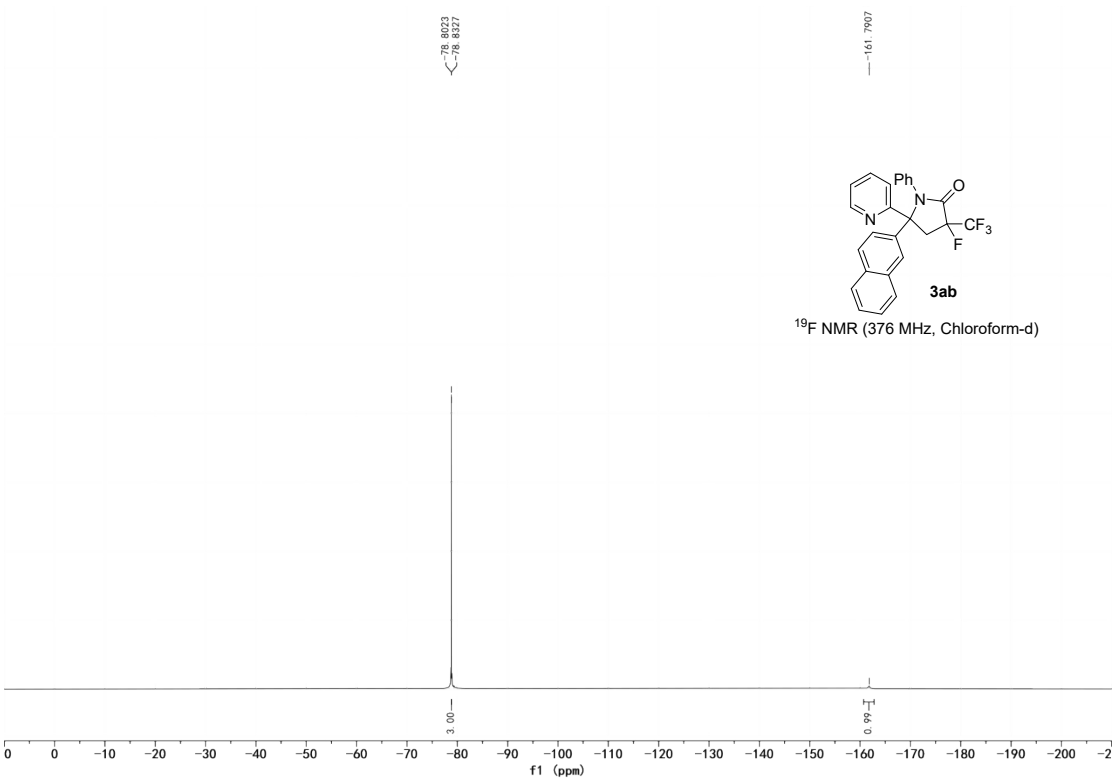
^{19}F NMR (376 MHz, Chloroform-d)



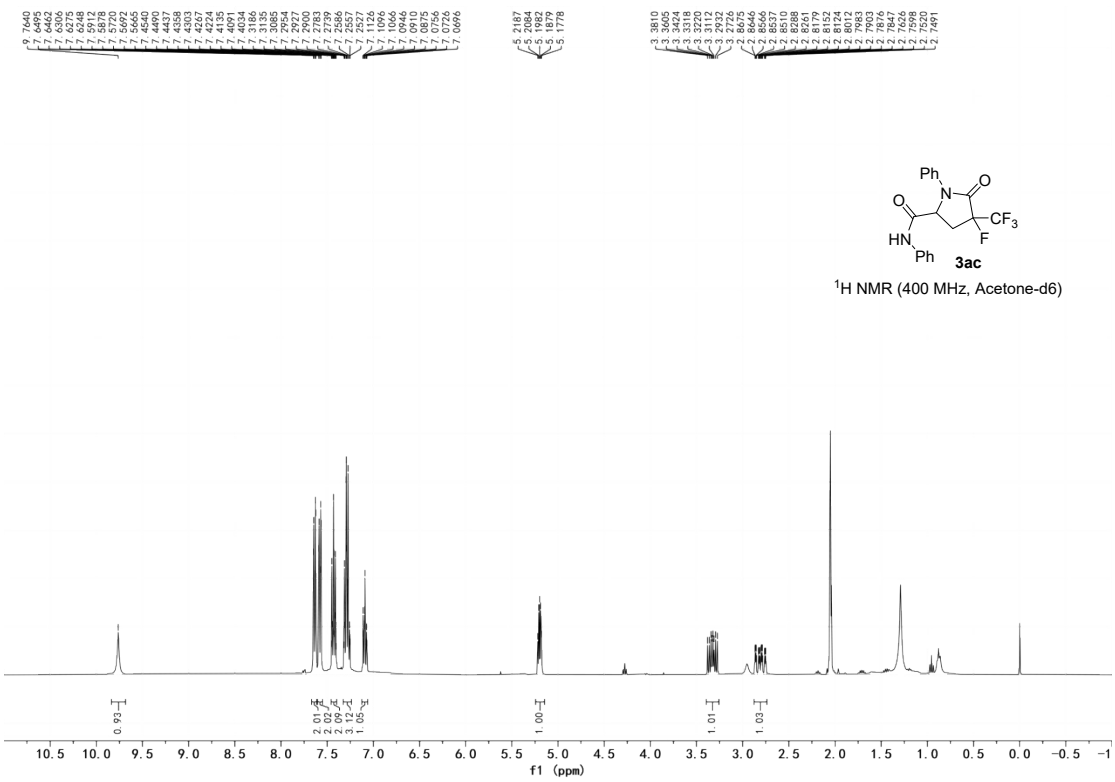
^{1}H NMR (400 MHz, Chloroform-d)



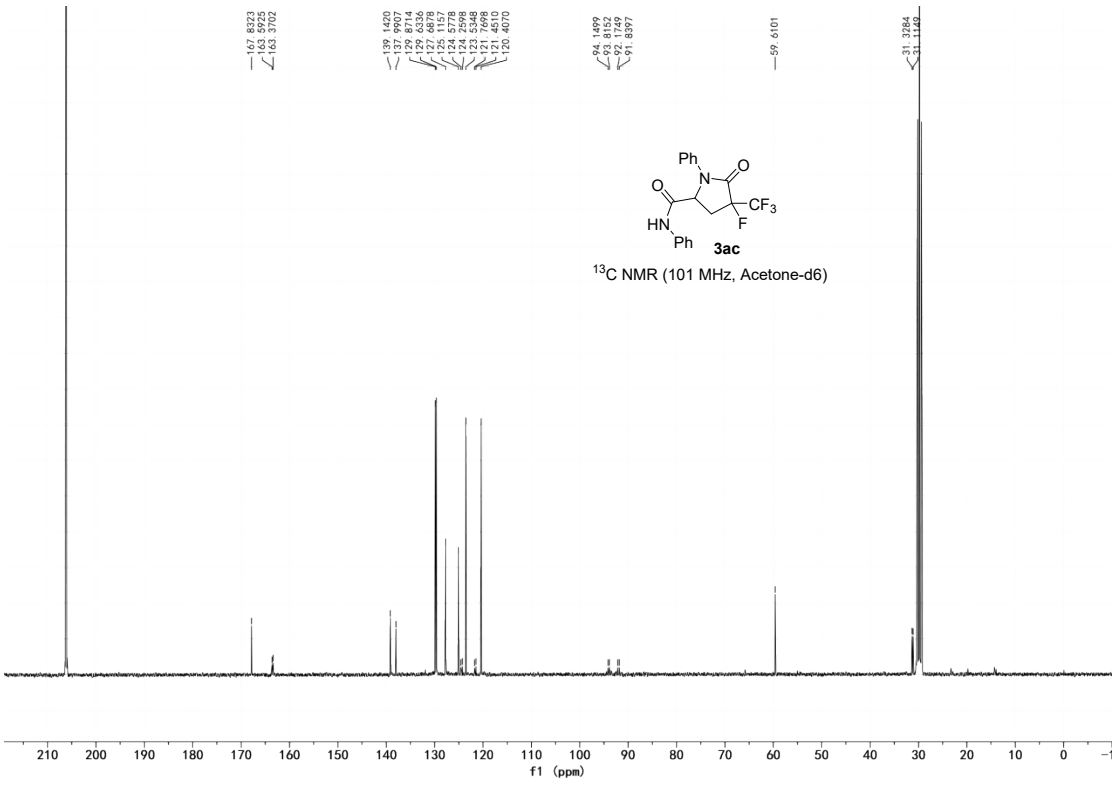
^{13}C NMR (101 MHz, Chloroform-d)



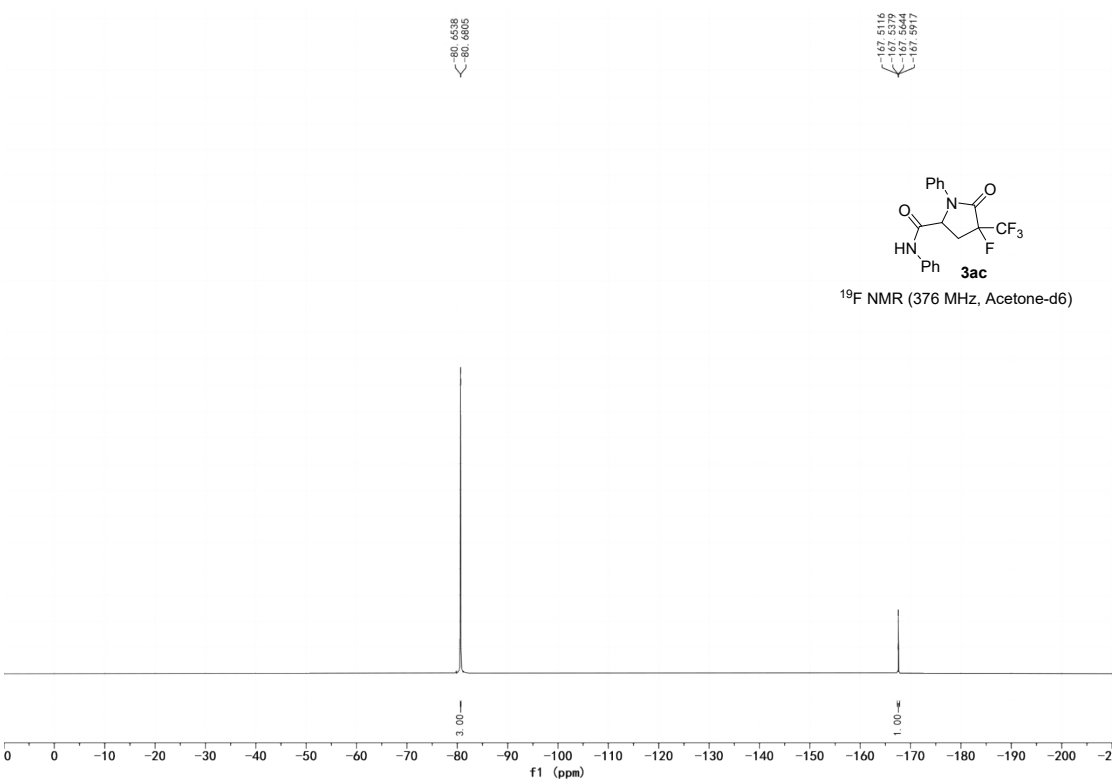
^{19}F NMR (376 MHz, Chloroform-d)



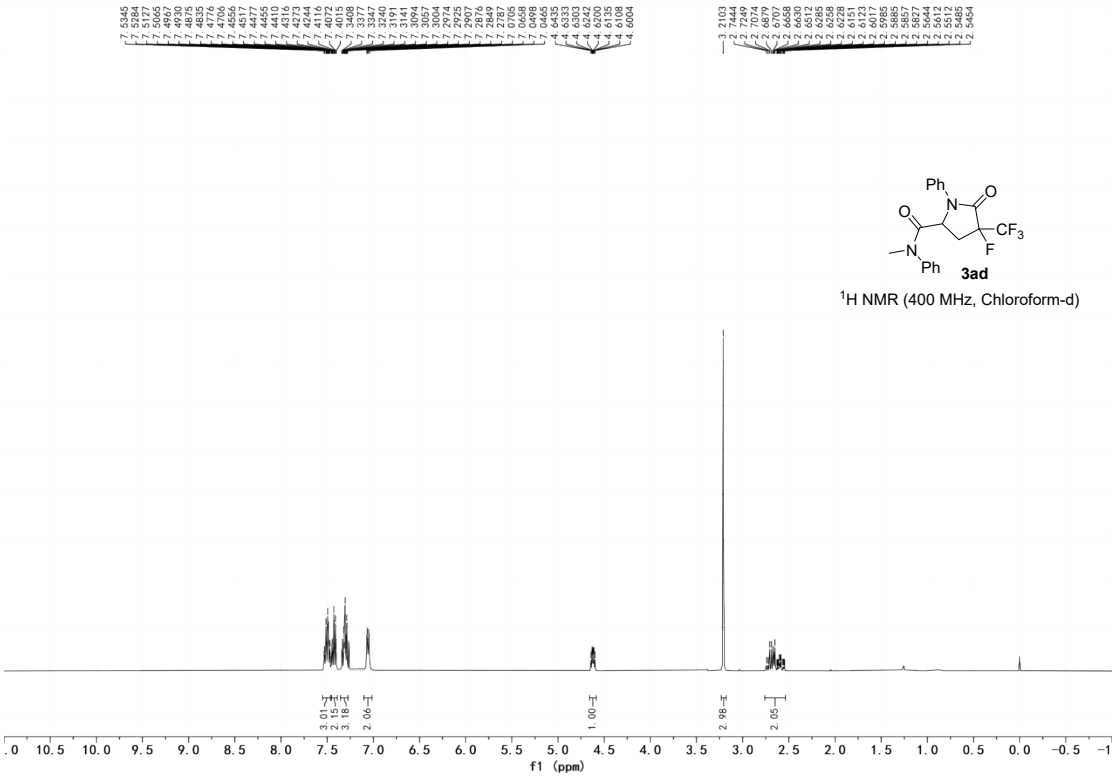
^{1}H NMR (400 MHz, Acetone-d6)



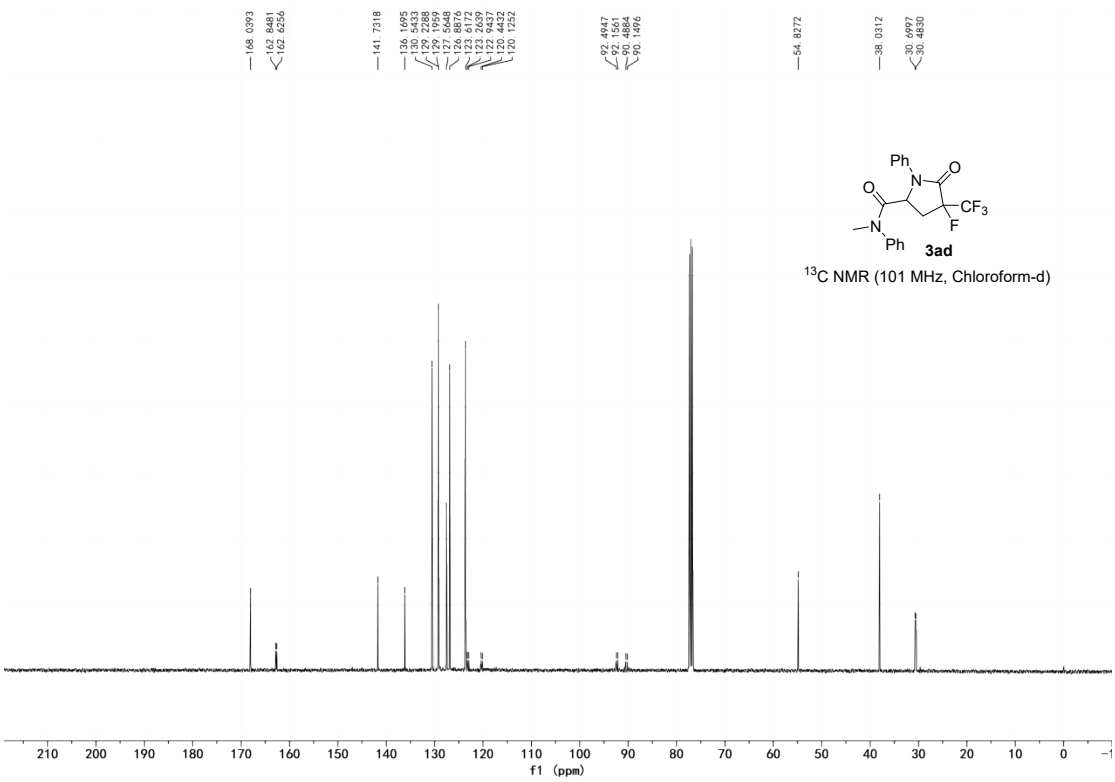
^{13}C NMR (101 MHz, Acetone-d6)

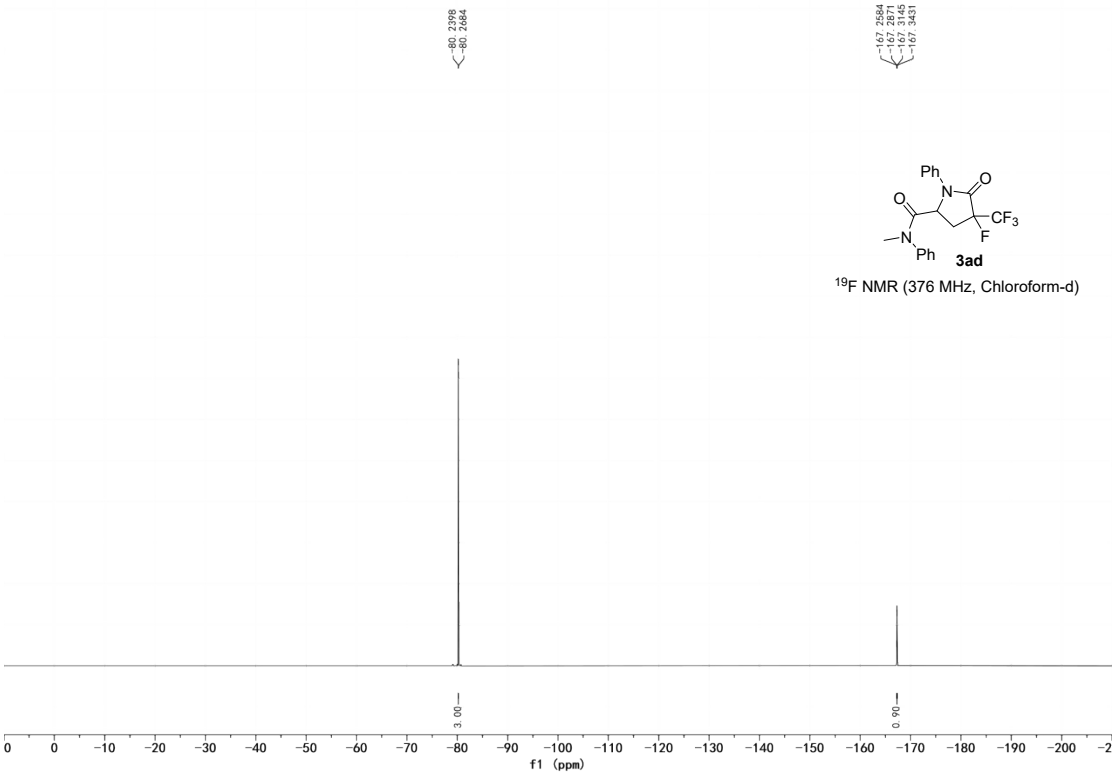


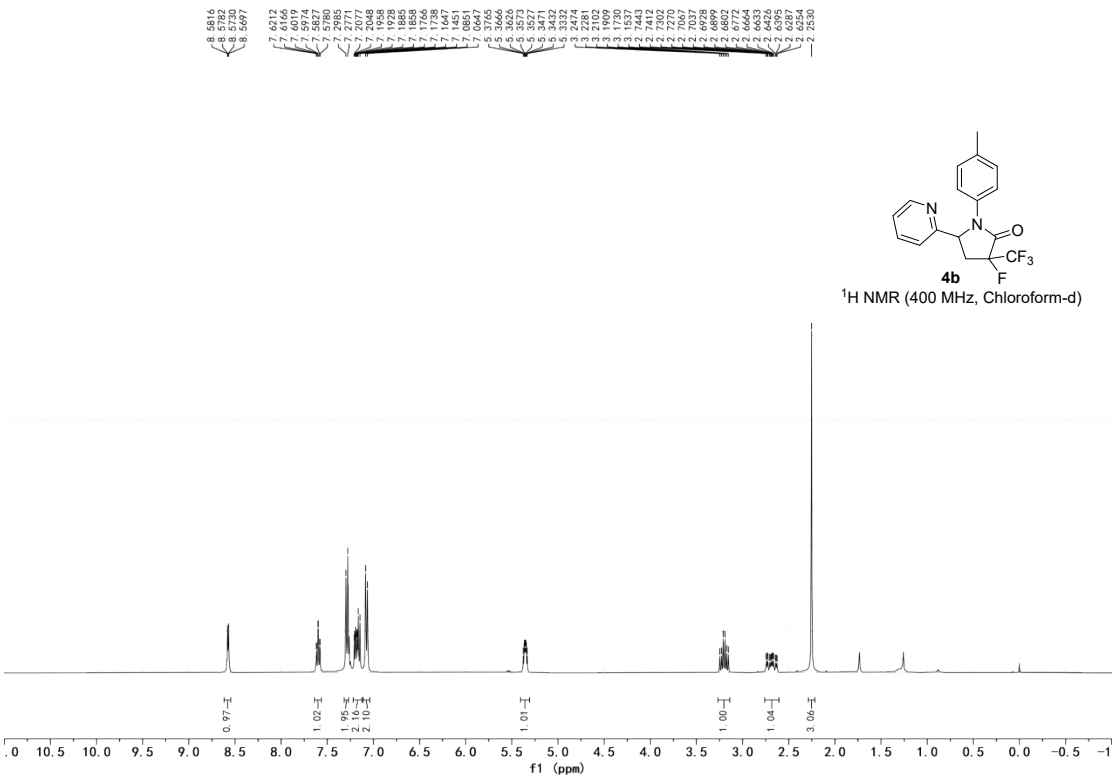
^{19}F NMR (376 MHz, Acetone-d6)

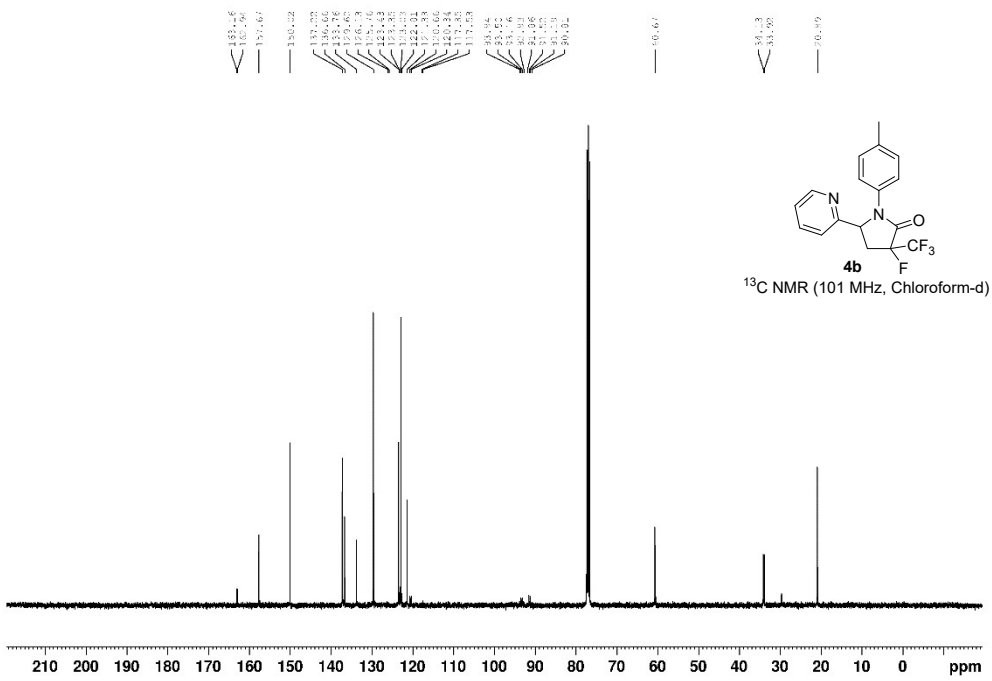


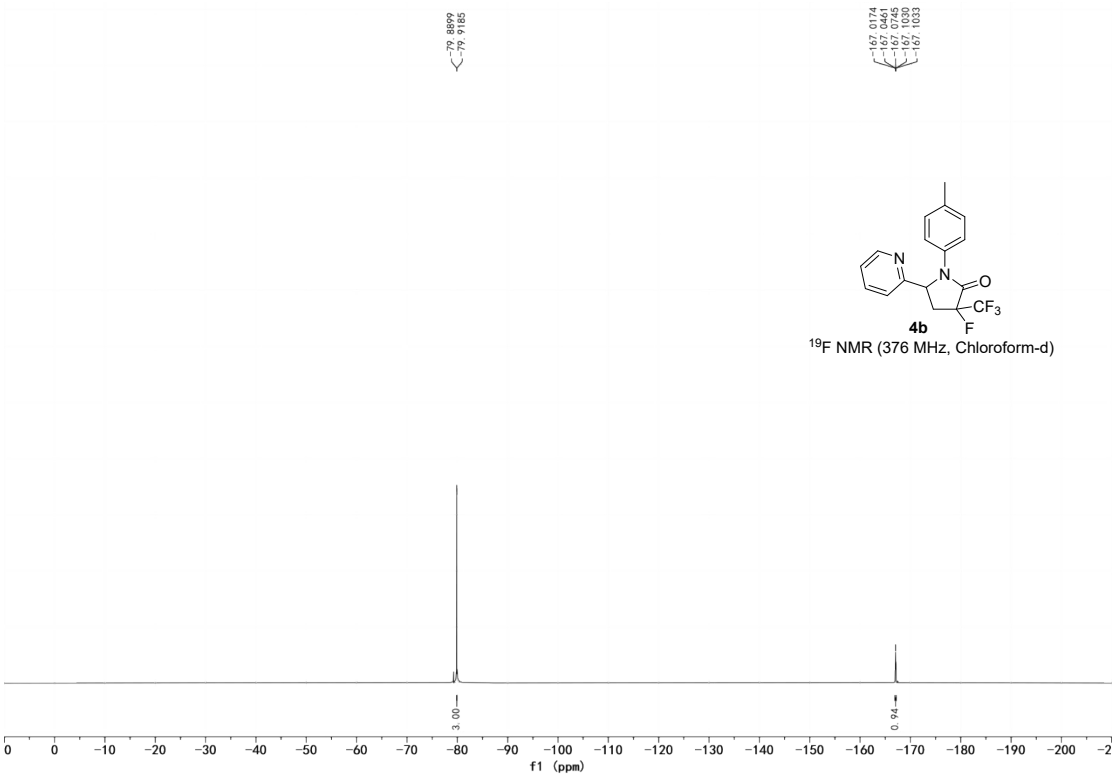
^{1}H NMR (400 MHz, Chloroform-d)


168.0393
162.8481
162.6256
141.7318
136.1695
130.5433
129.2288
128.9560
127.5648
126.8876
123.6172
123.2637
122.9101
120.4432
120.1252
92.4947
92.1561
90.4884
90.1496
54.8272
38.0312
30.6997
30.4830
Ph
N
O
O
CF3
F
N
Ph
3ad
13C NMR (101 MHz, Chloroform-d)
f1 (ppm)

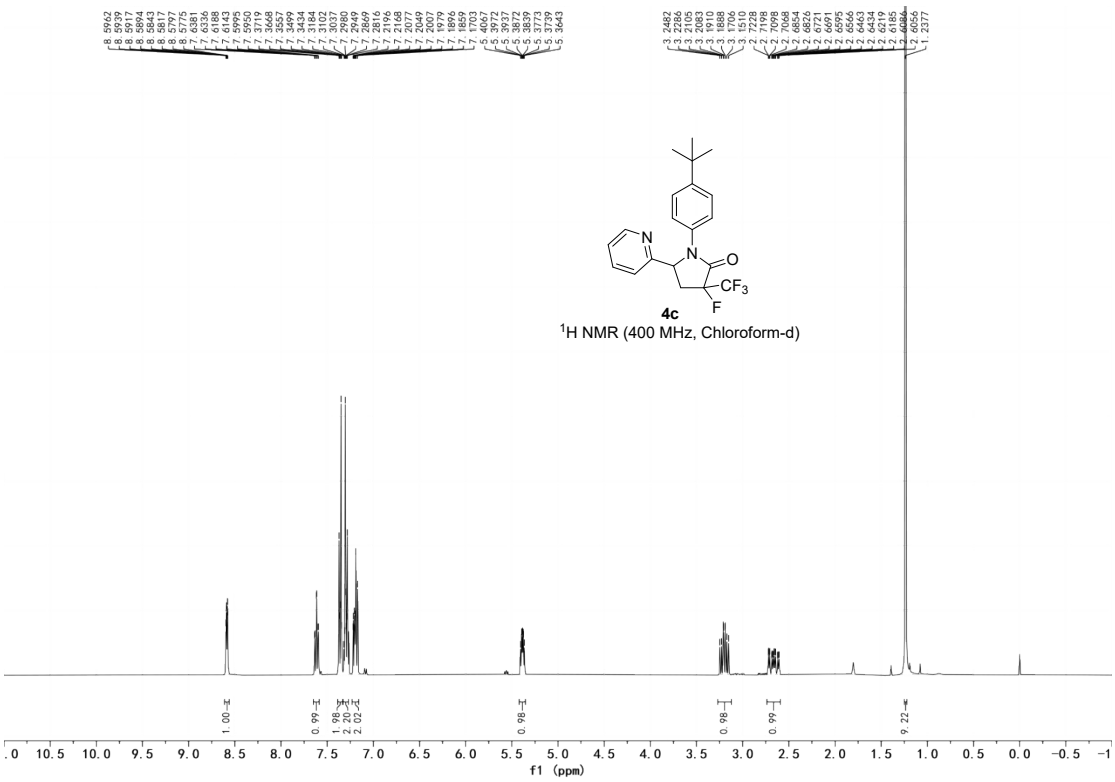

-80.2398
-80.2684
-167.2584
-167.2871
-167.3145
-167.3431
Ph
N
O
O
CF3
F
N
Ph
3ad
19F NMR (376 MHz, Chloroform-d)
3.00
0.90
f1 (ppm)


4b
^{1}H NMR (400 MHz, Chloroform-d)
f1 (ppm)


4b
^{13}C NMR (101 MHz, Chloroform-d)
ppm

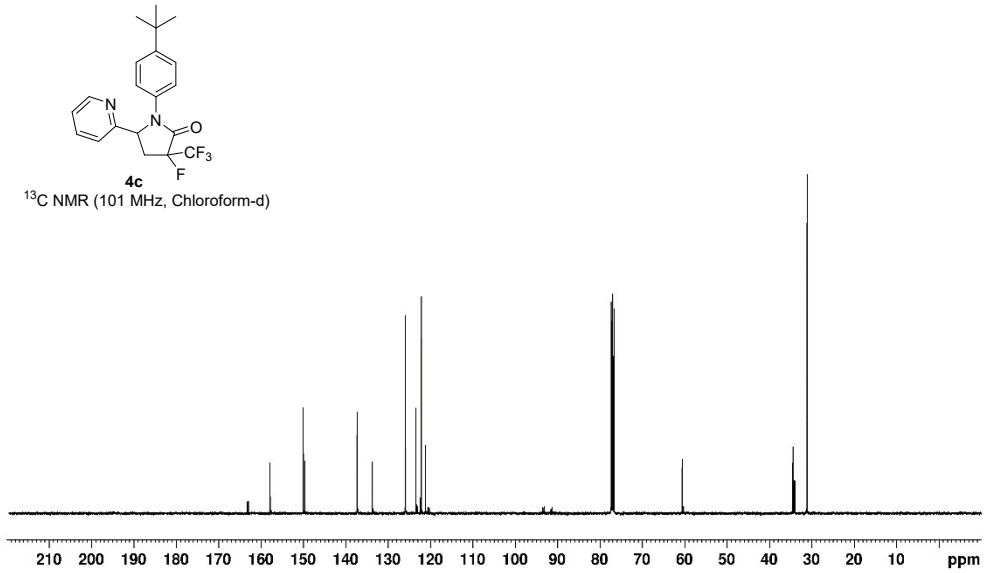


^{19}F NMR (376 MHz, Chloroform-d)



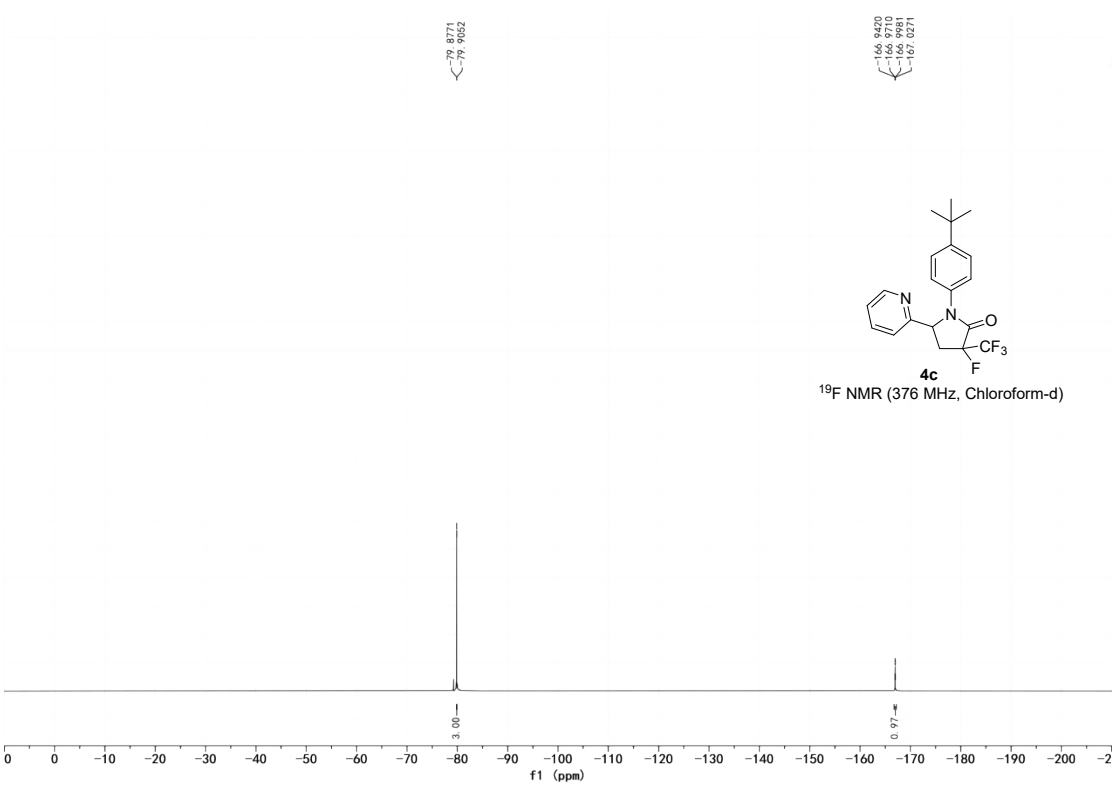
4c

^{1}H NMR (400 MHz, Chloroform-d)



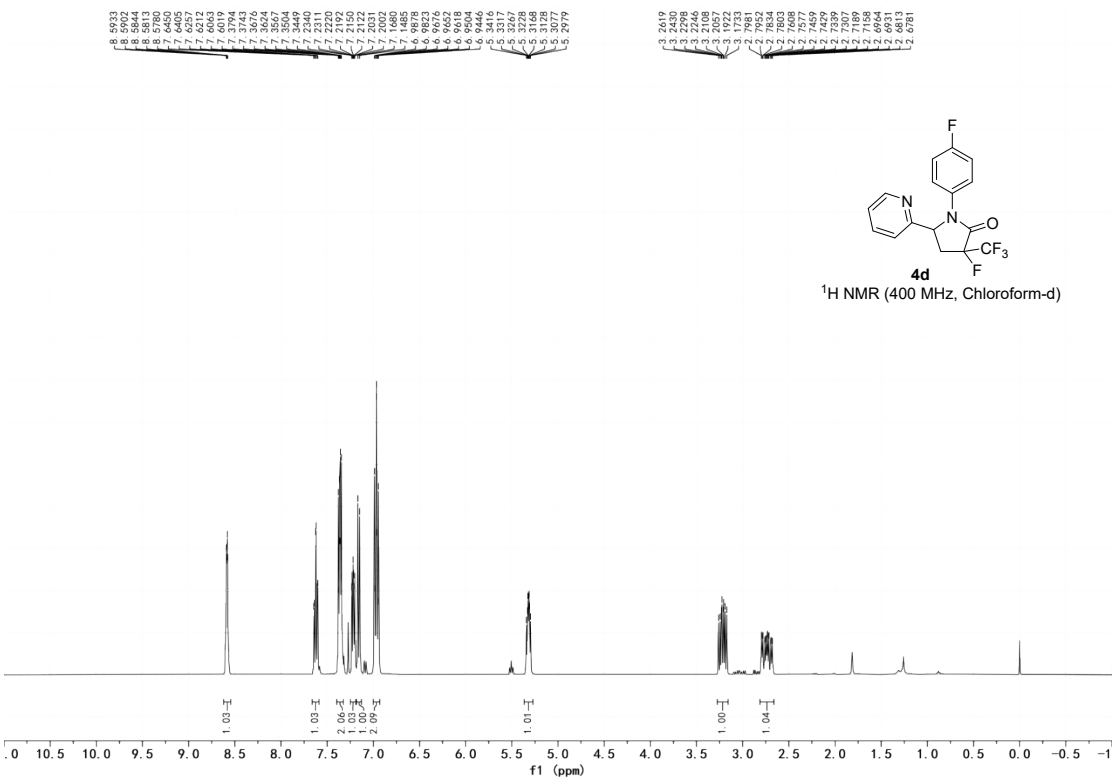
4c

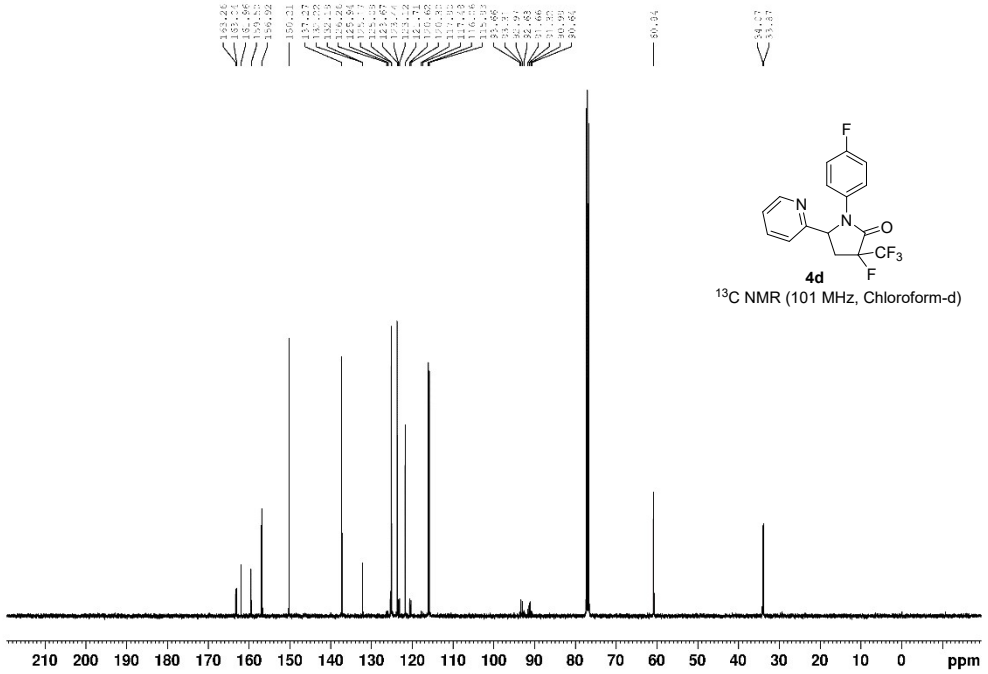
^{13}C NMR (101 MHz, Chloroform-d)

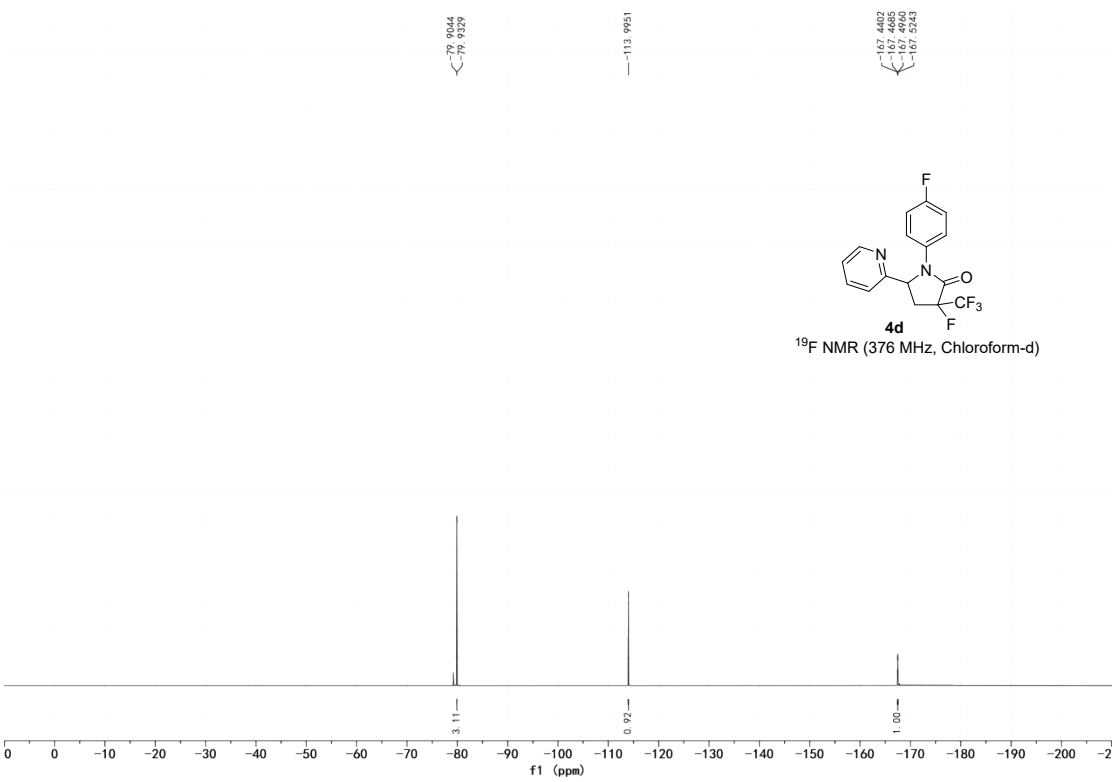


4c

^{19}F NMR (376 MHz, Chloroform-d)

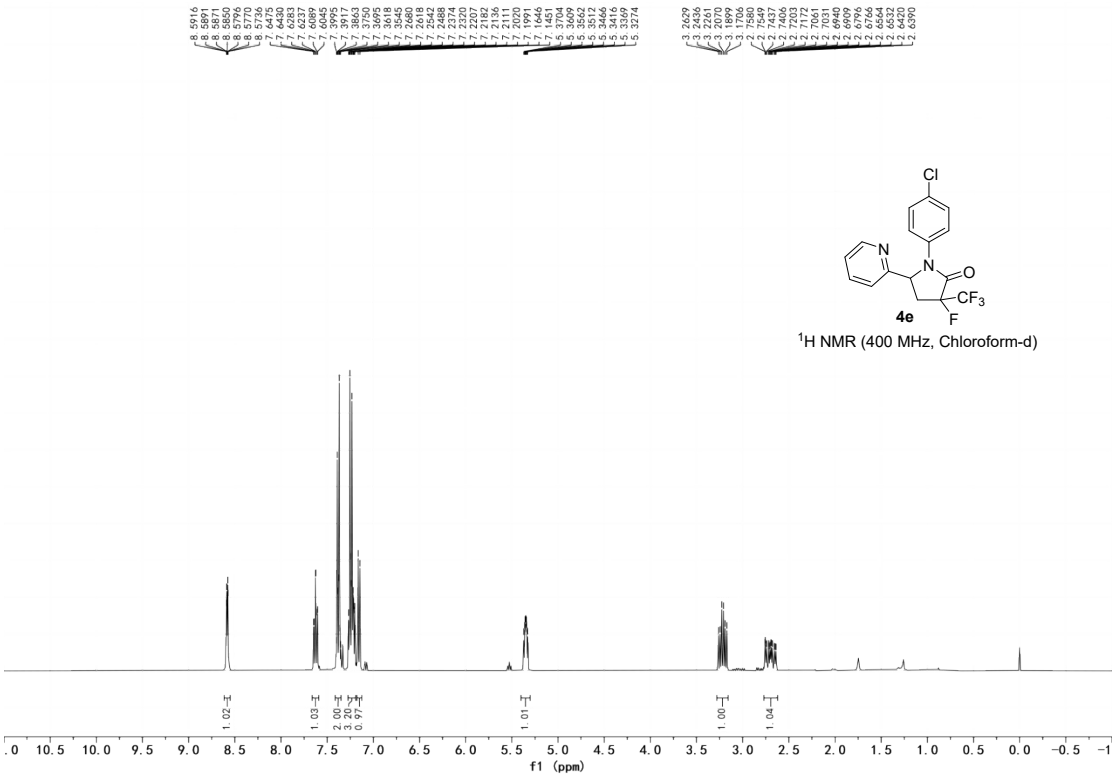

F
N
N
O
CF3
F
4d
1H NMR (400 MHz, Chloroform-d)
1.03
1.03
2.06
1.00
1.00
2.09
1.01
1.00
1.04
f1 (ppm)

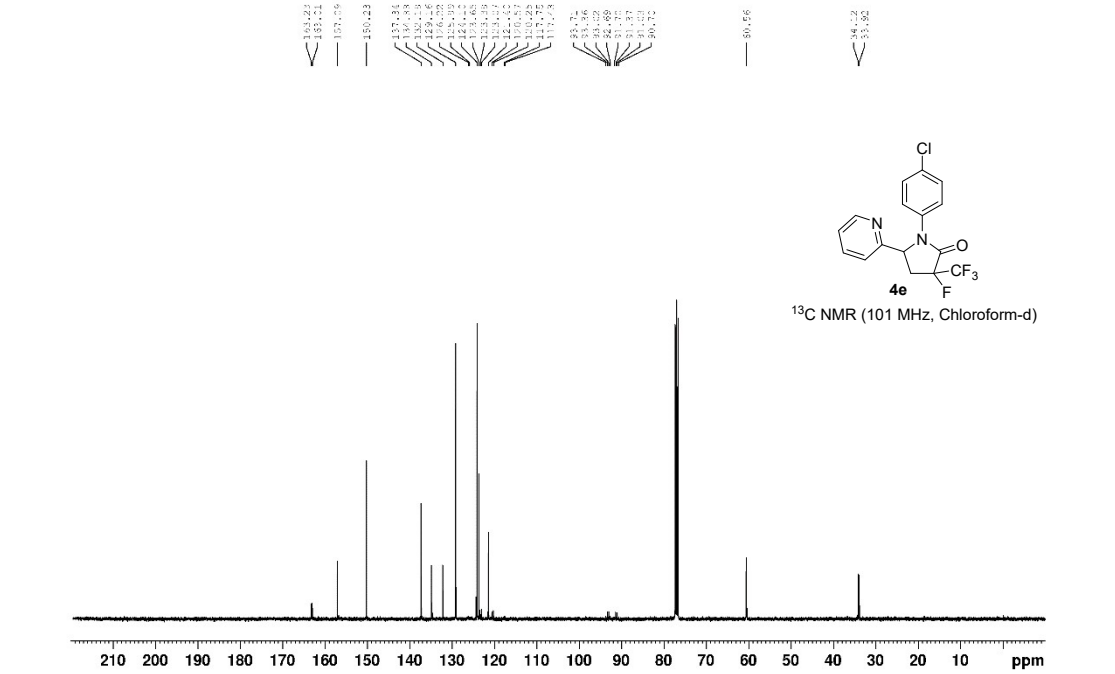

F
N
N
O
CF3
F
4d
13C NMR (101 MHz, Chloroform-d)
ppm

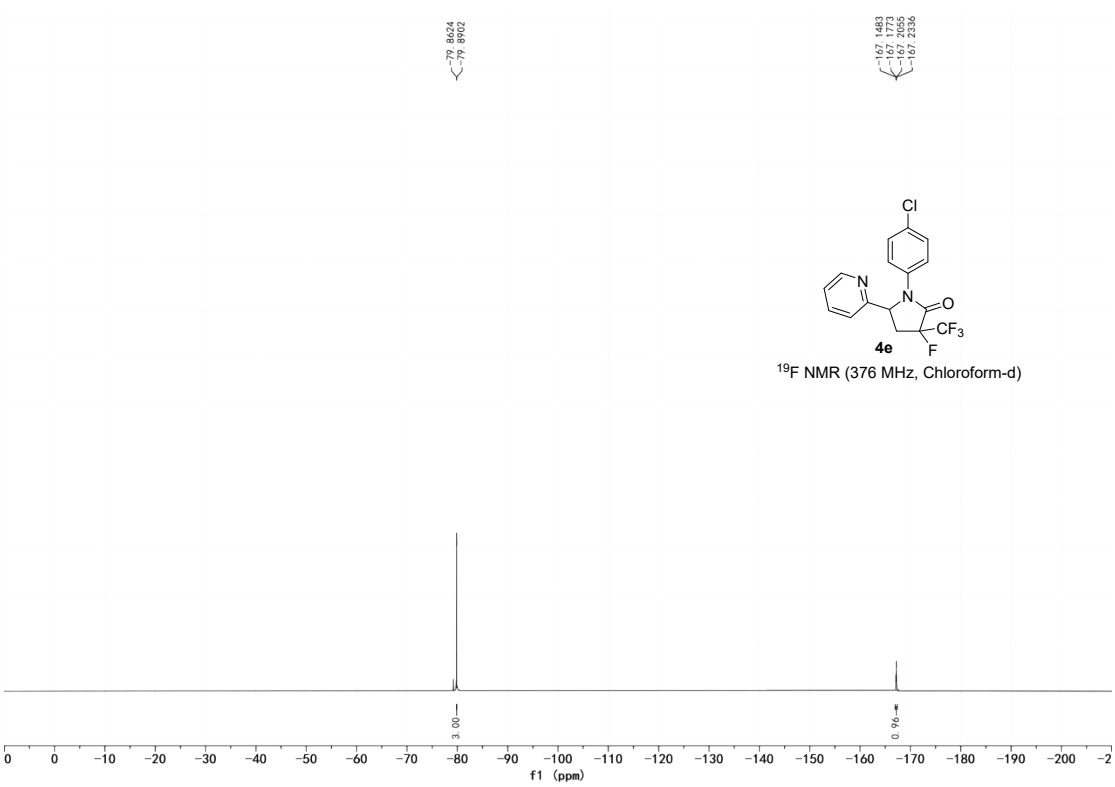


4d

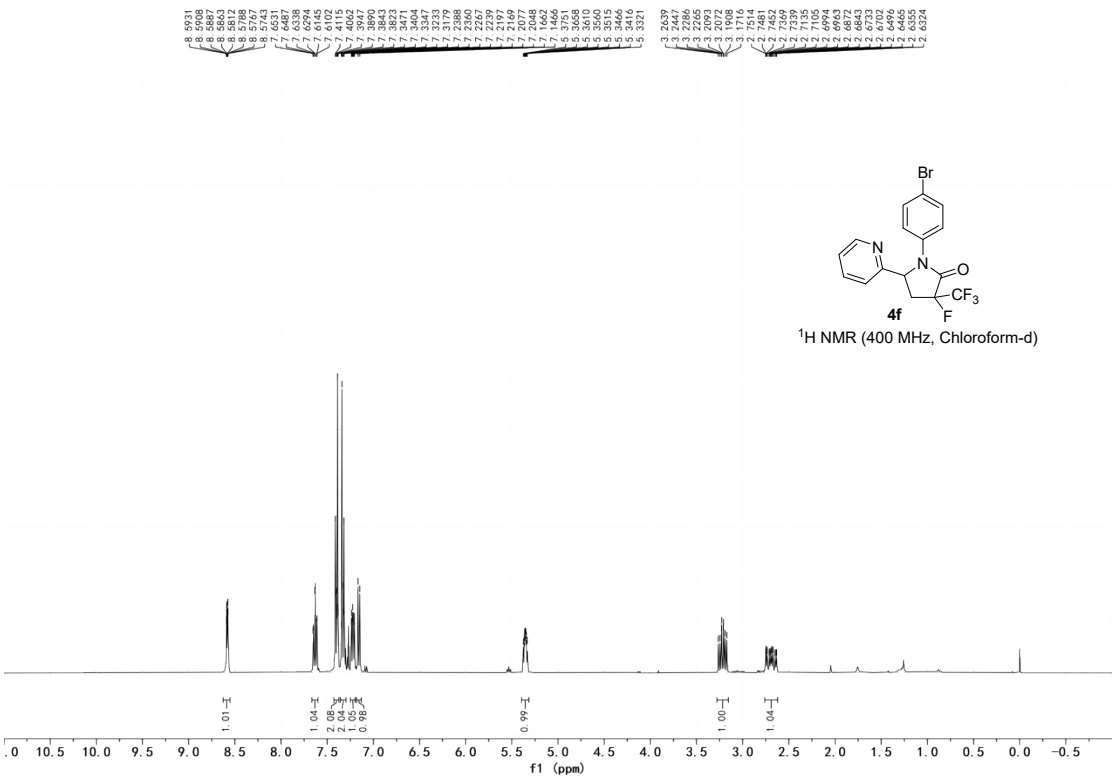
^{19}F NMR (376 MHz, Chloroform-d)

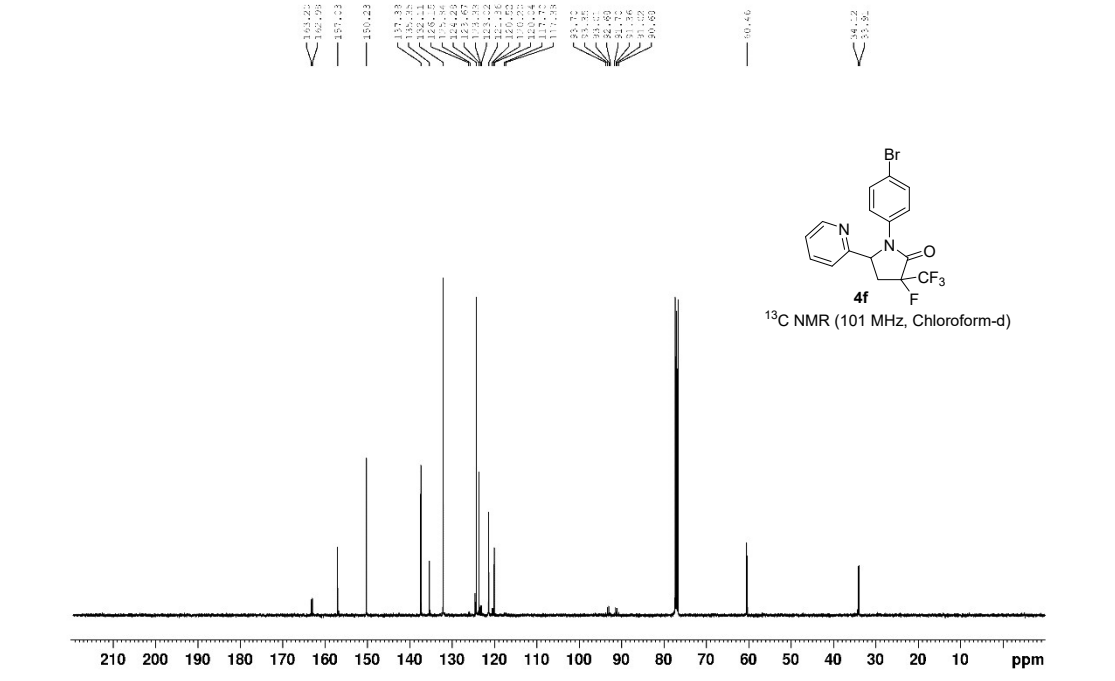

Cl
N
N
O
CF3
F
4e
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

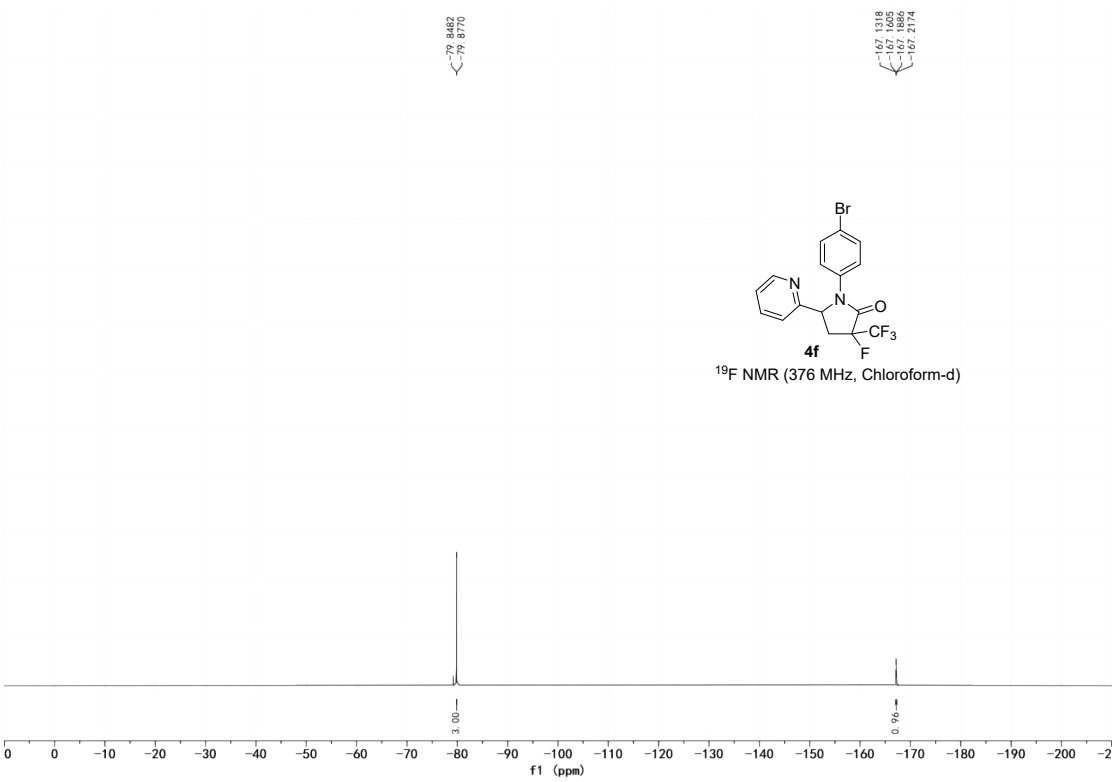

Cl
N
N
O
CF3
F
4e
13C NMR (101 MHz, Chloroform-d)
ppm



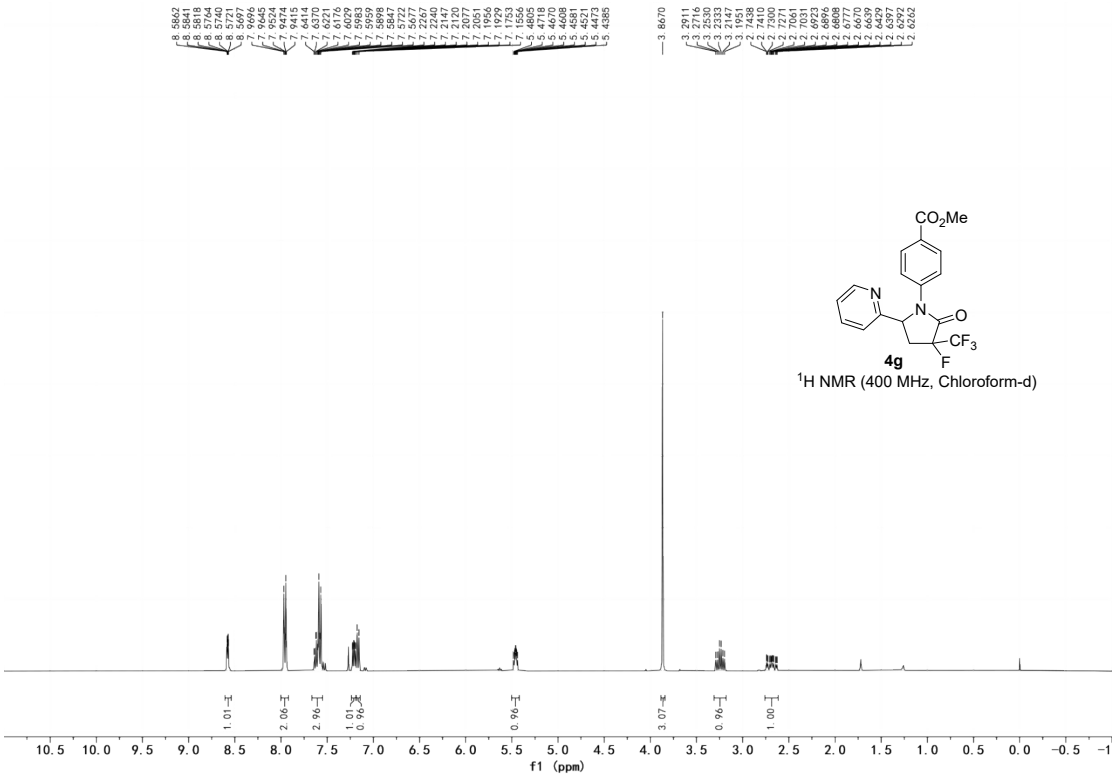
^{19}F NMR (376 MHz, Chloroform-d)

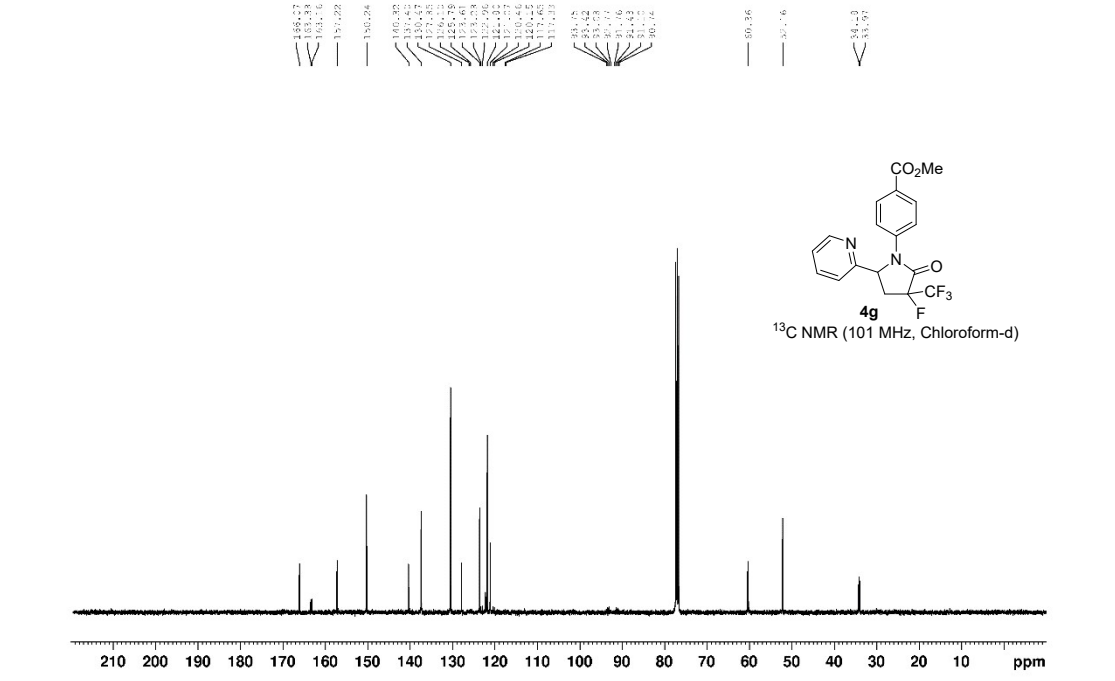

Br
N
N
O
CF3
F
4f
1H NMR (400 MHz, Chloroform-d)
1.01
1.04
2.08
2.04
1.05
0.98
0.99
1.00
1.04
f1 (ppm)

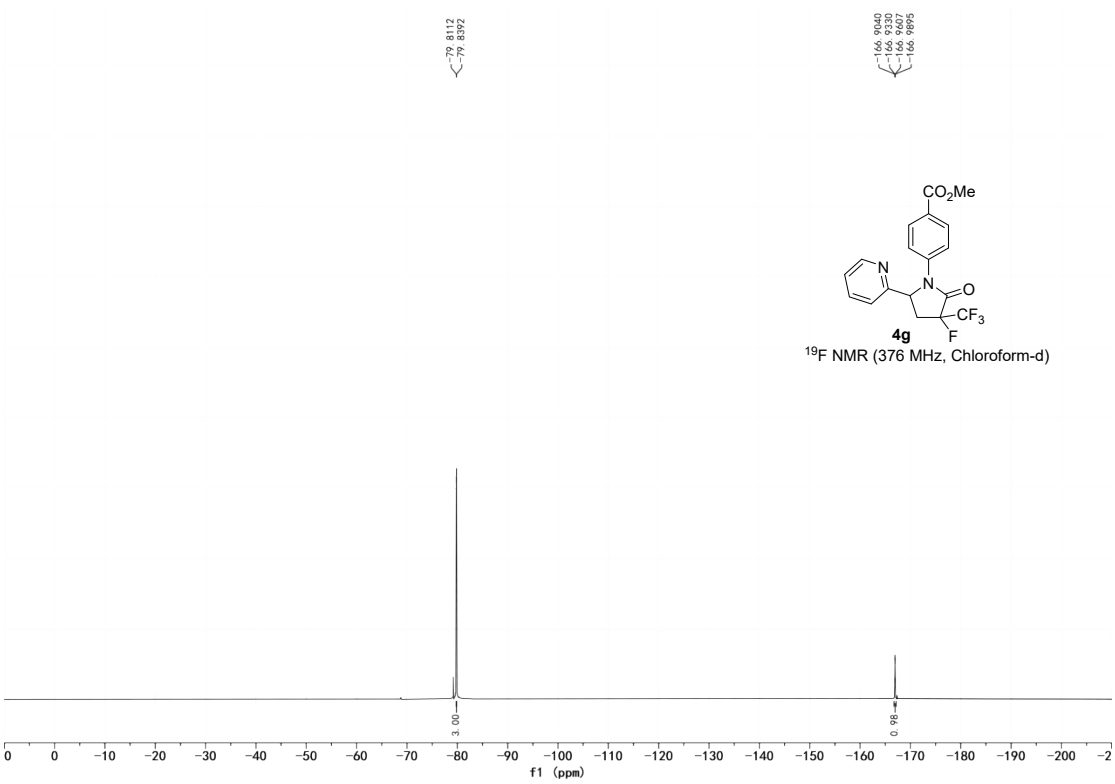

Br
N
N
O
CF3
F
4f
13C NMR (101 MHz, Chloroform-d)
ppm



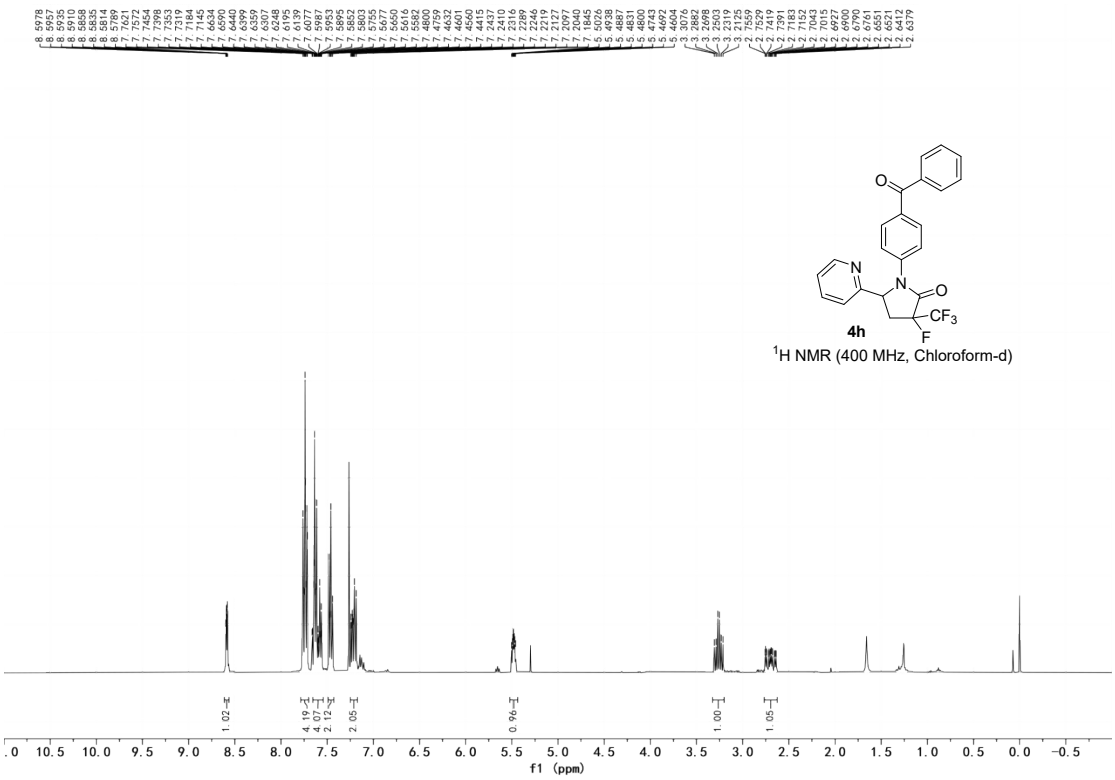
^{19}F NMR (376 MHz, Chloroform-d)

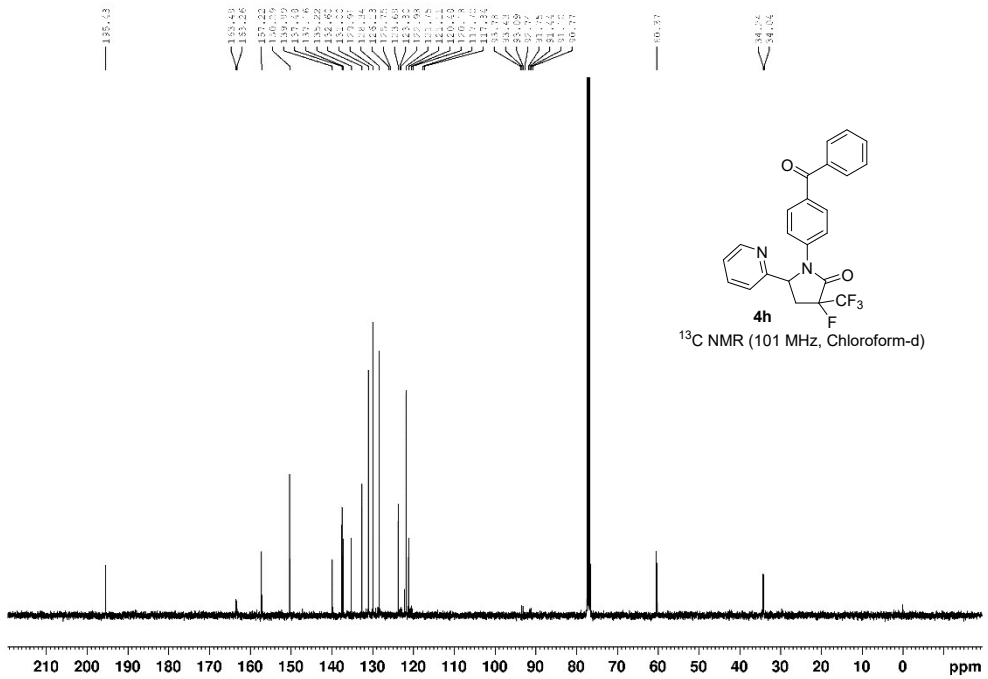

CO2Me
N
N
O
CF3
F
4g
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

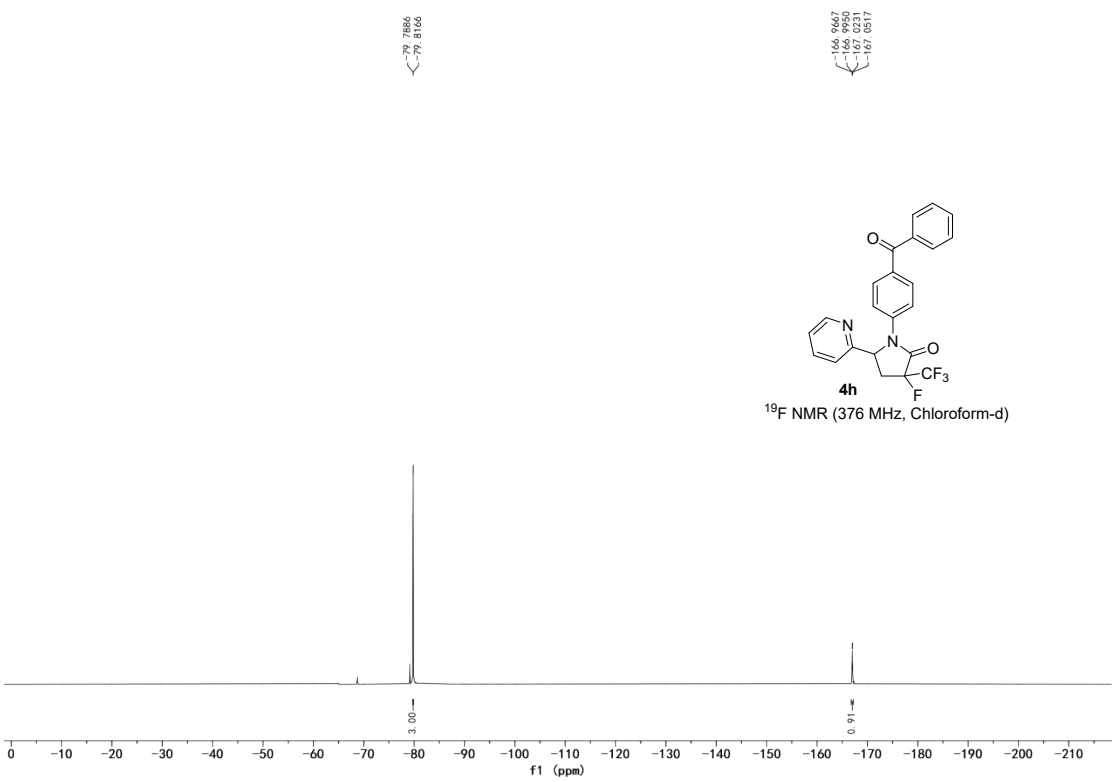

CO2Me
N
N
O
CF3
F
4g
13C NMR (101 MHz, Chloroform-d)
ppm



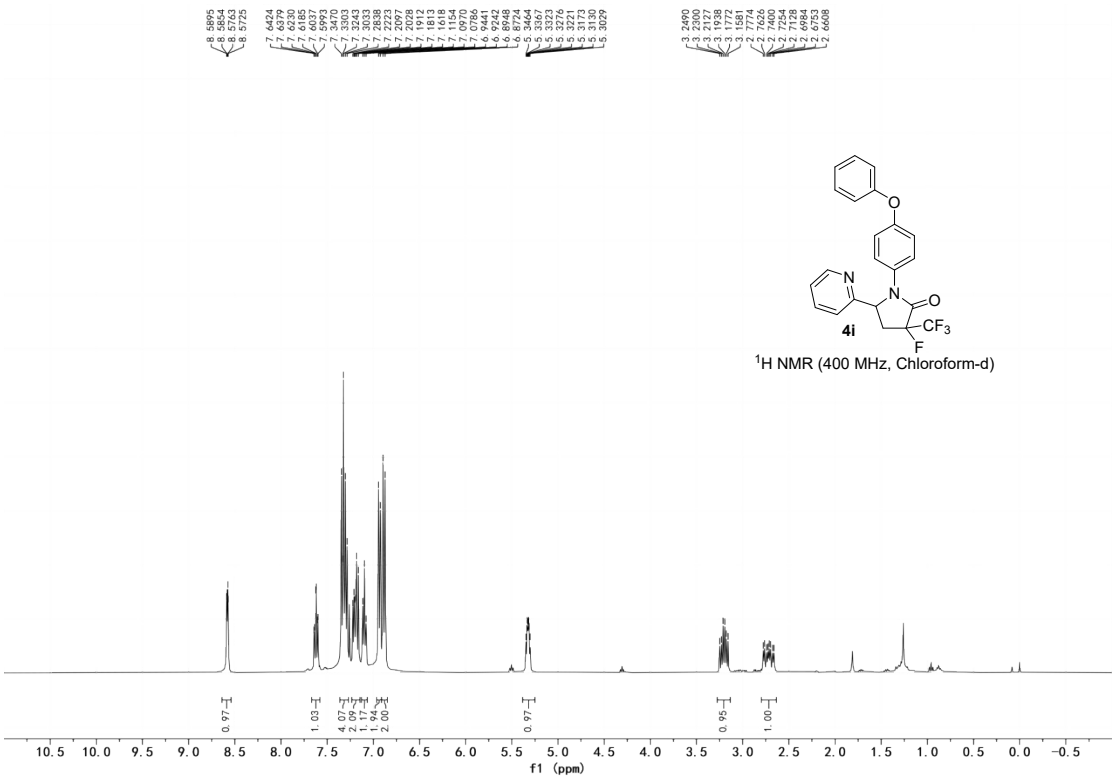
^{19}F NMR (376 MHz, Chloroform-d)

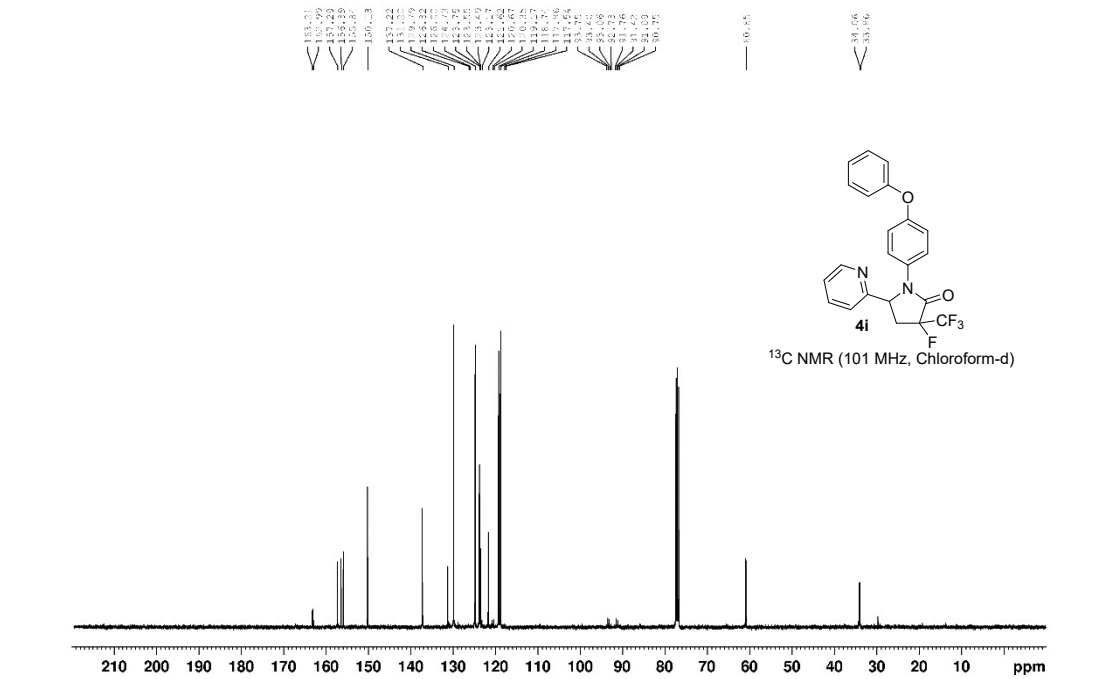

4h
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

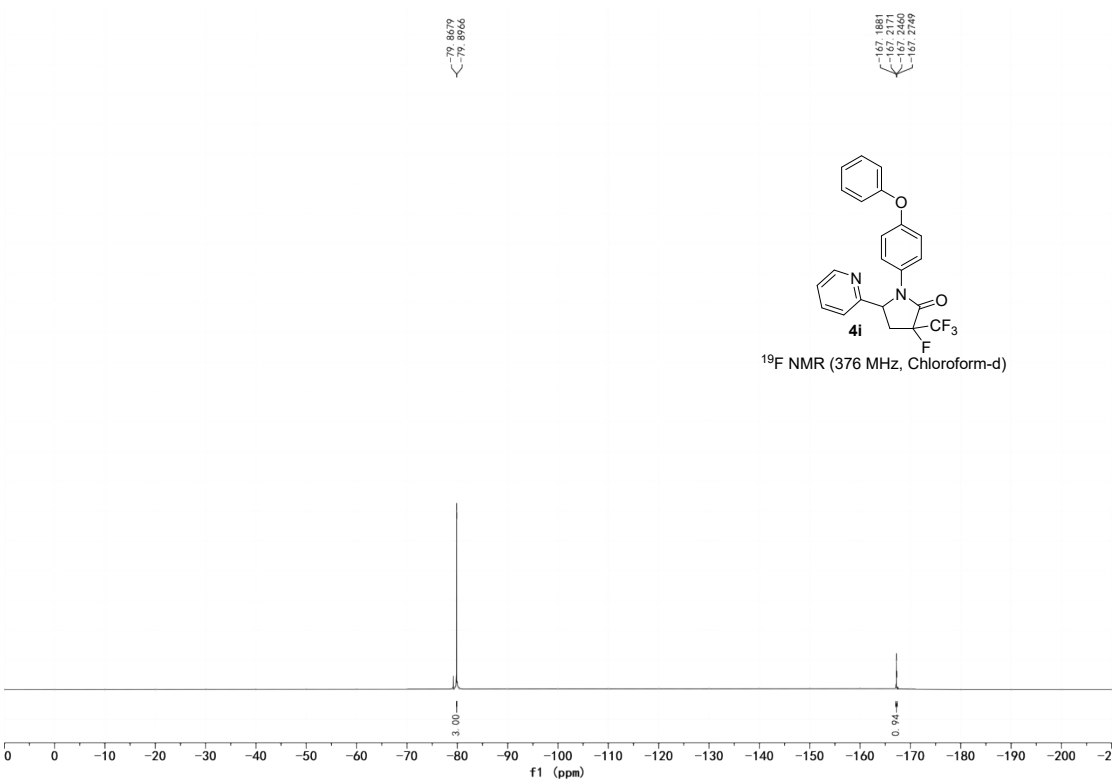

4h
13C NMR (101 MHz, Chloroform-d)
ppm



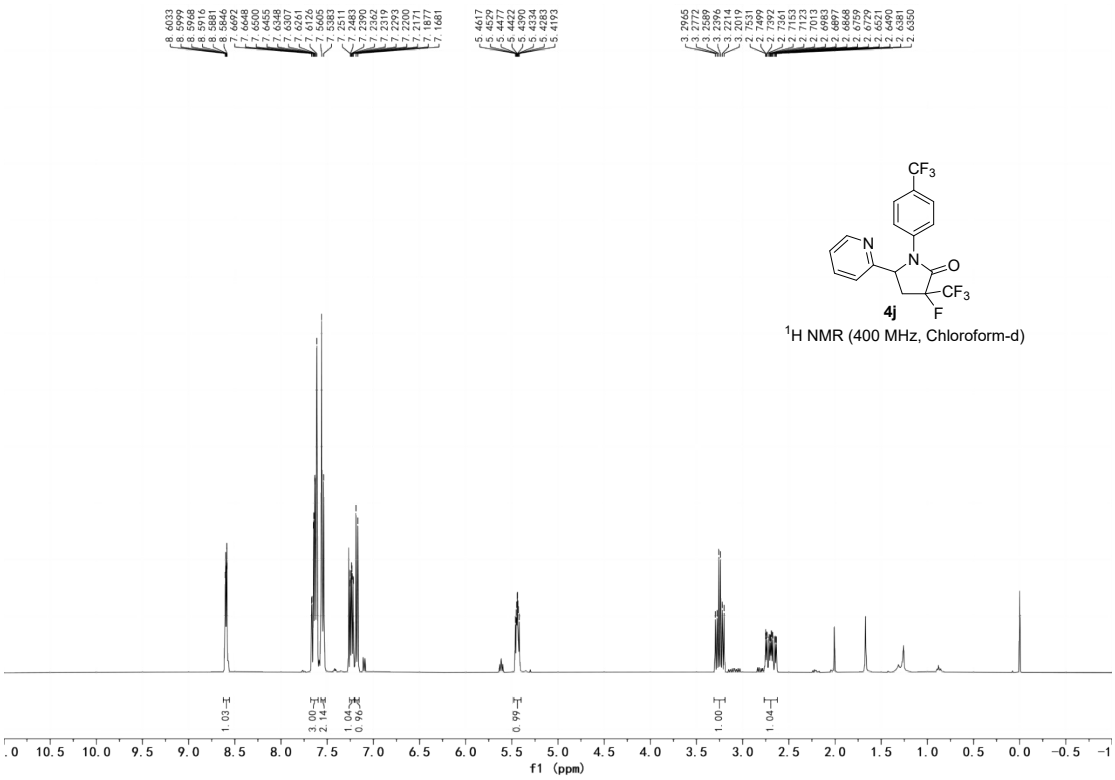
^{19}F NMR (376 MHz, Chloroform-d)


4i
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

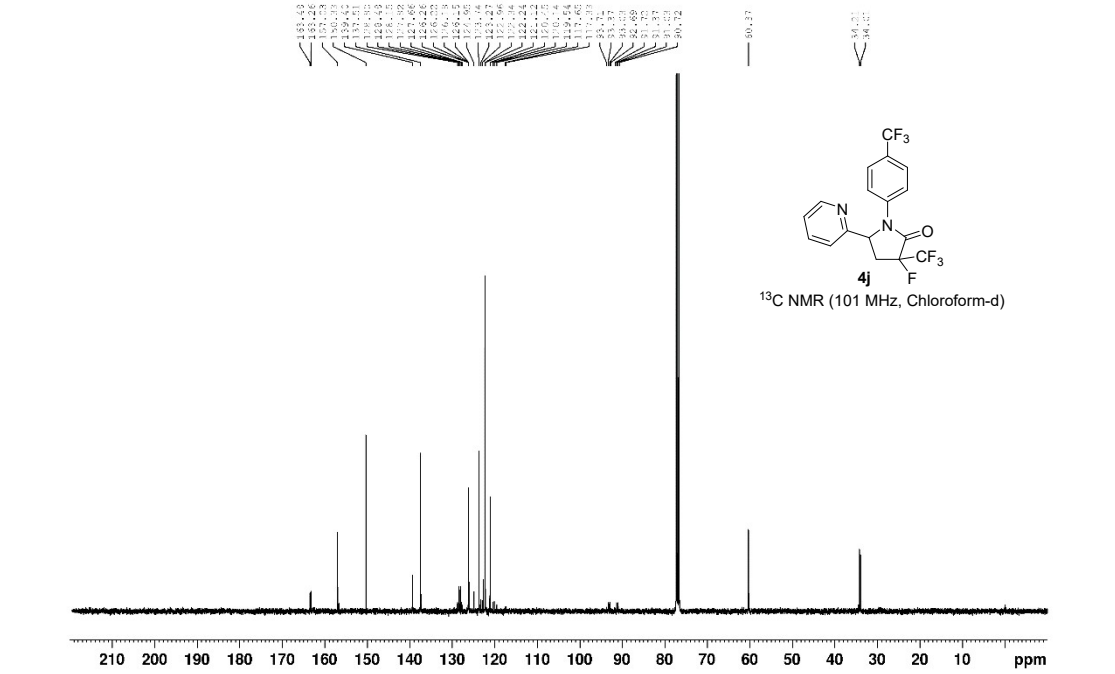

4i
13C NMR (101 MHz, Chloroform-d)
ppm



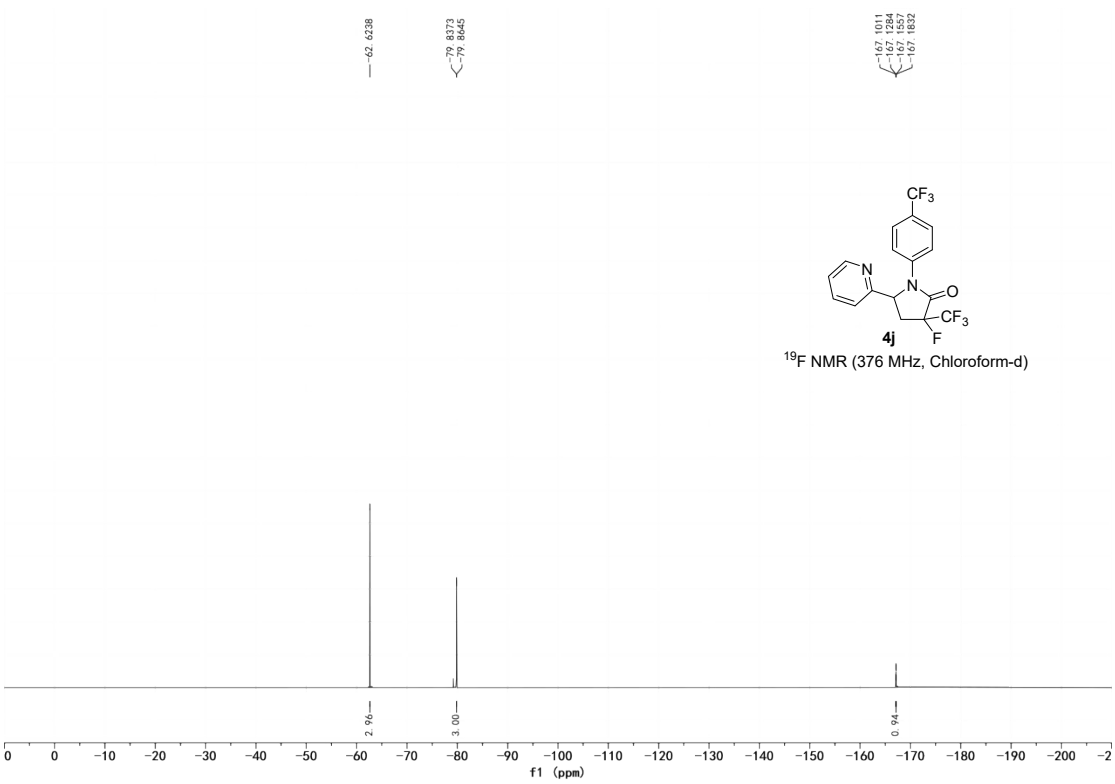
^{19}F NMR (376 MHz, Chloroform-d)



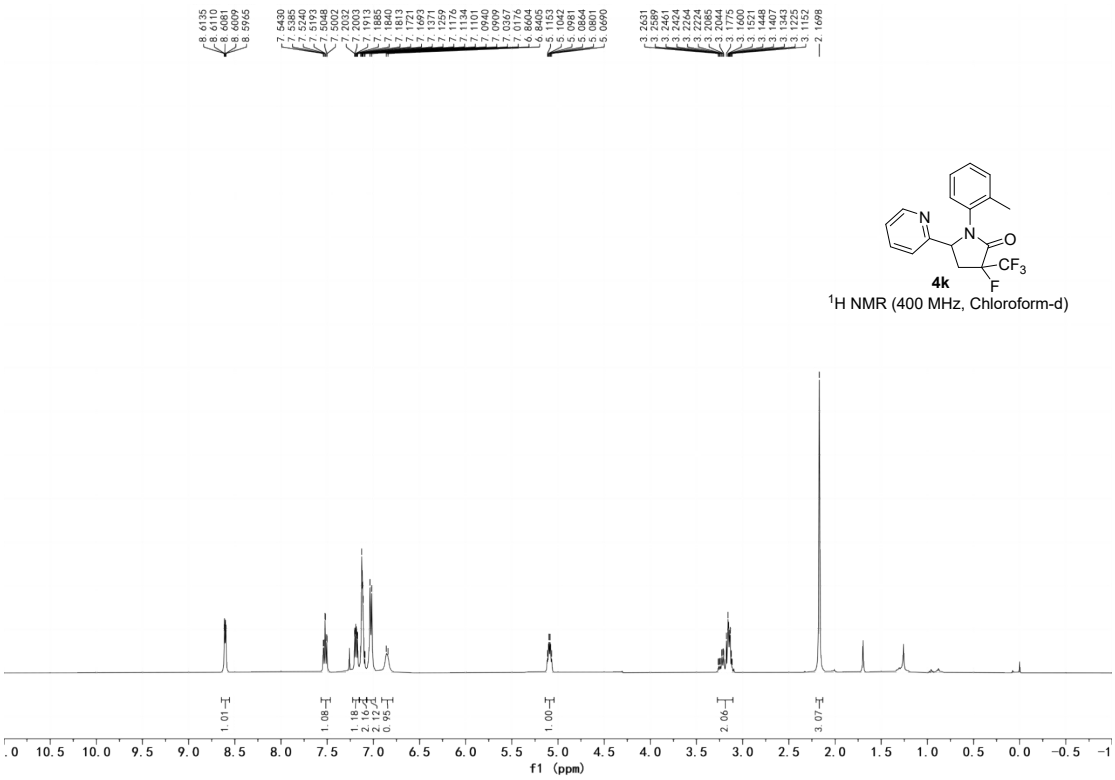
^{1}H NMR (400 MHz, Chloroform-d)

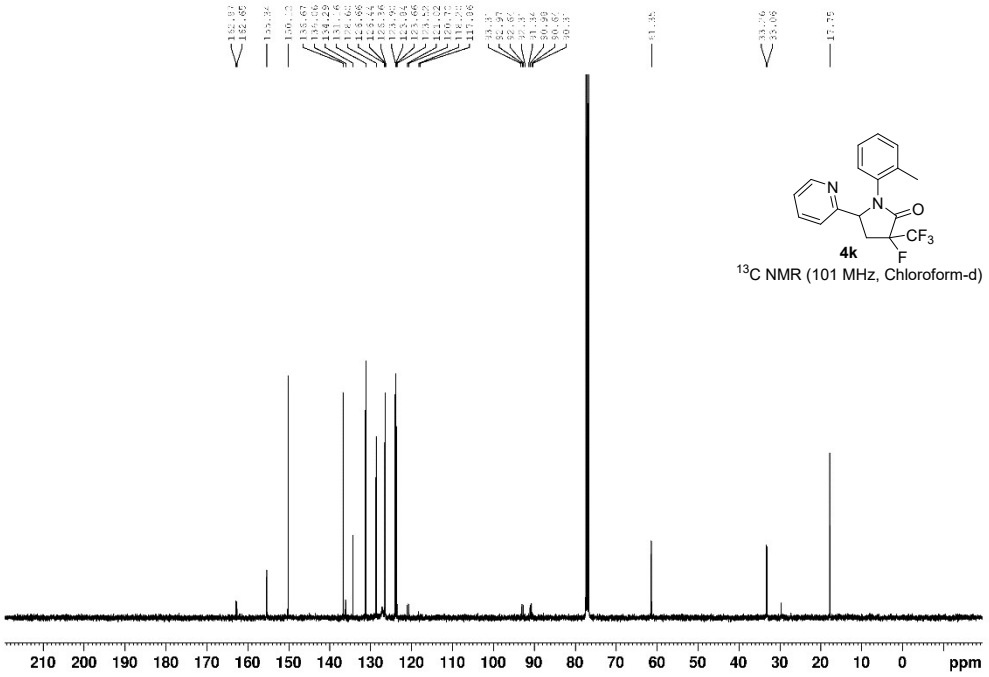


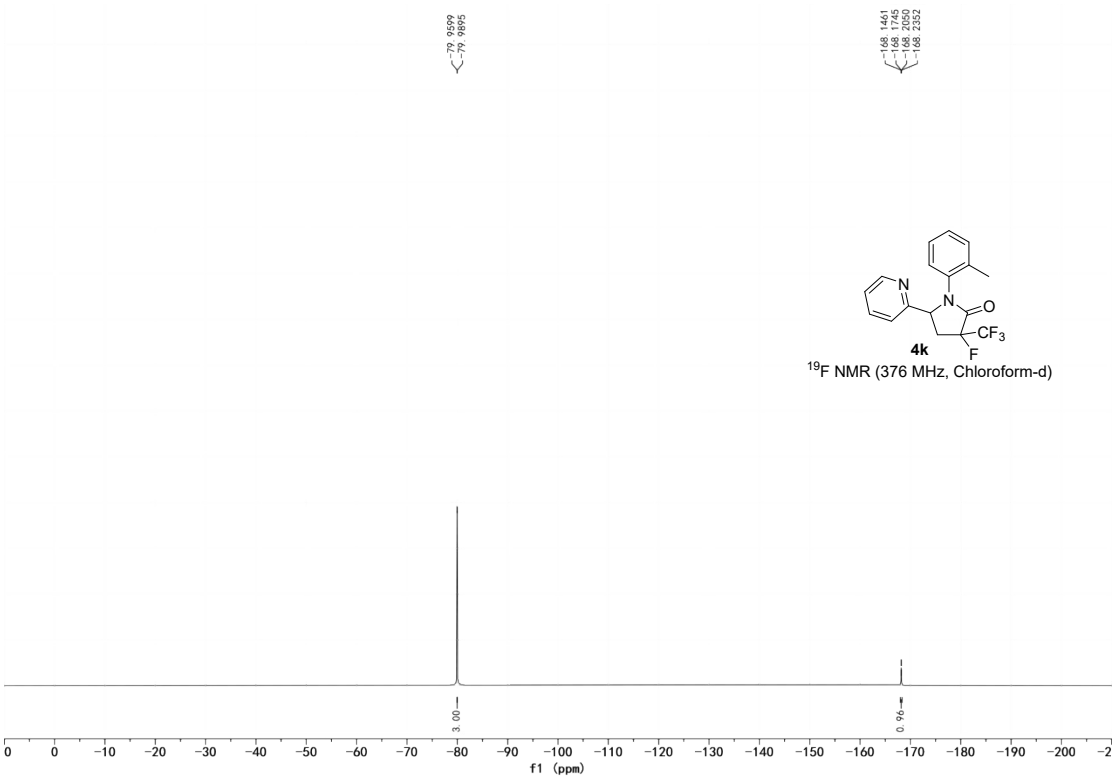
^{13}C NMR (101 MHz, Chloroform-d)



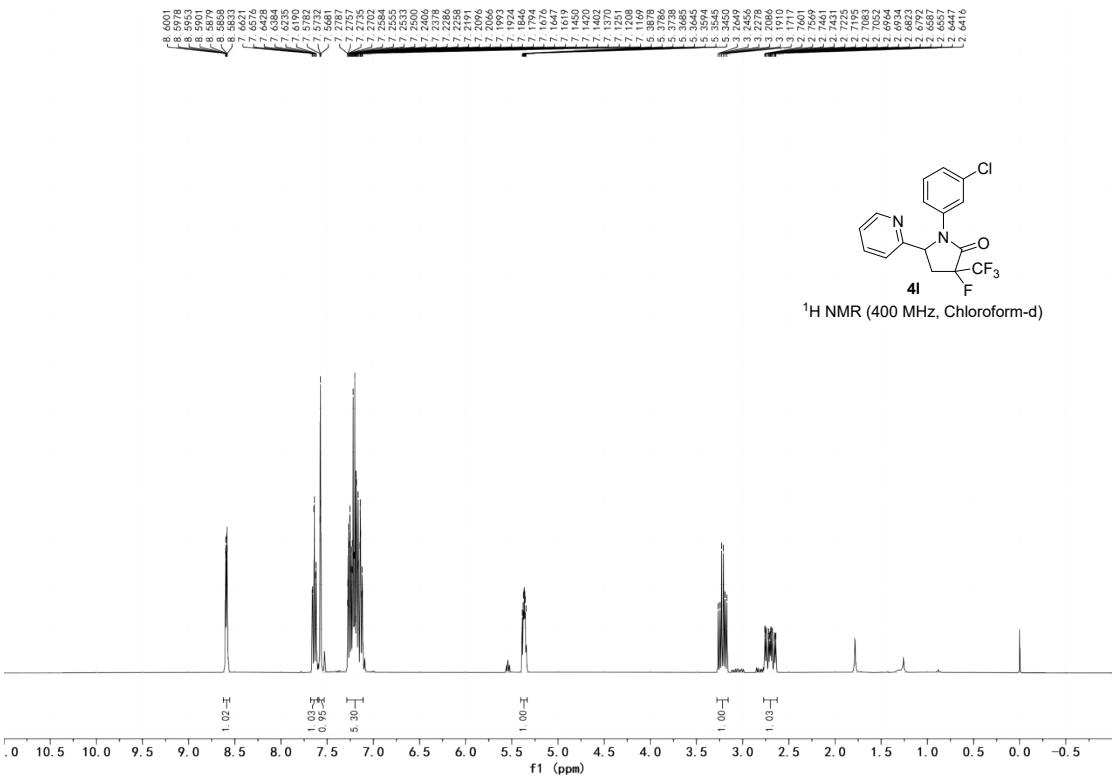
^{19}F NMR (376 MHz, Chloroform-d)


4k
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

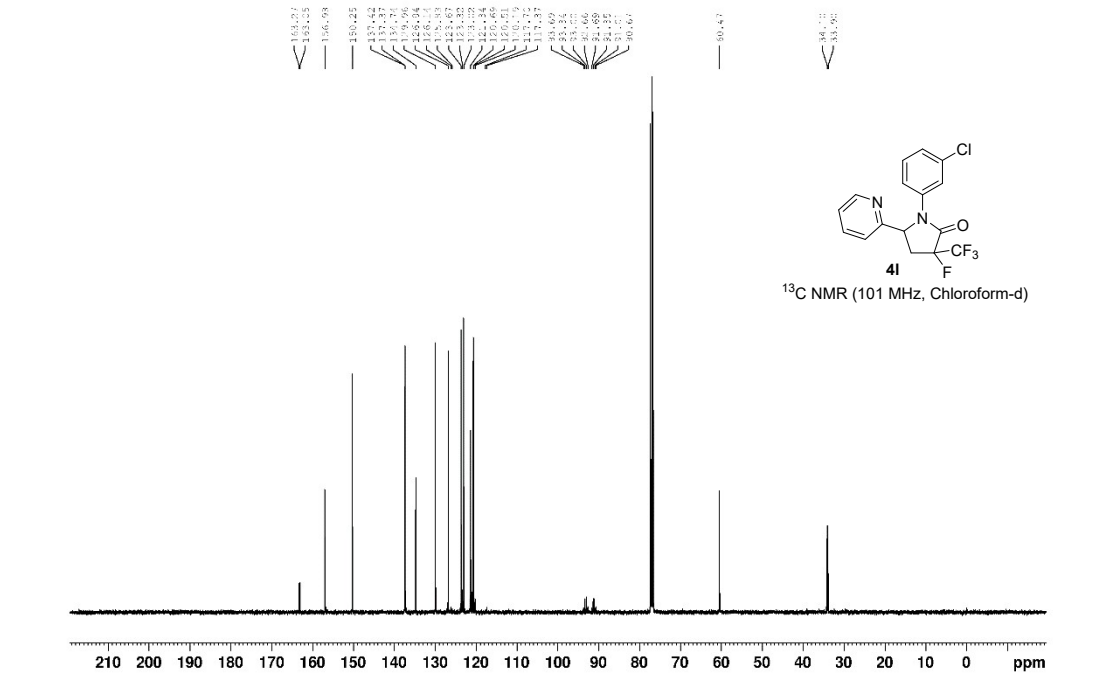

4k
13C NMR (101 MHz, Chloroform-d)
ppm



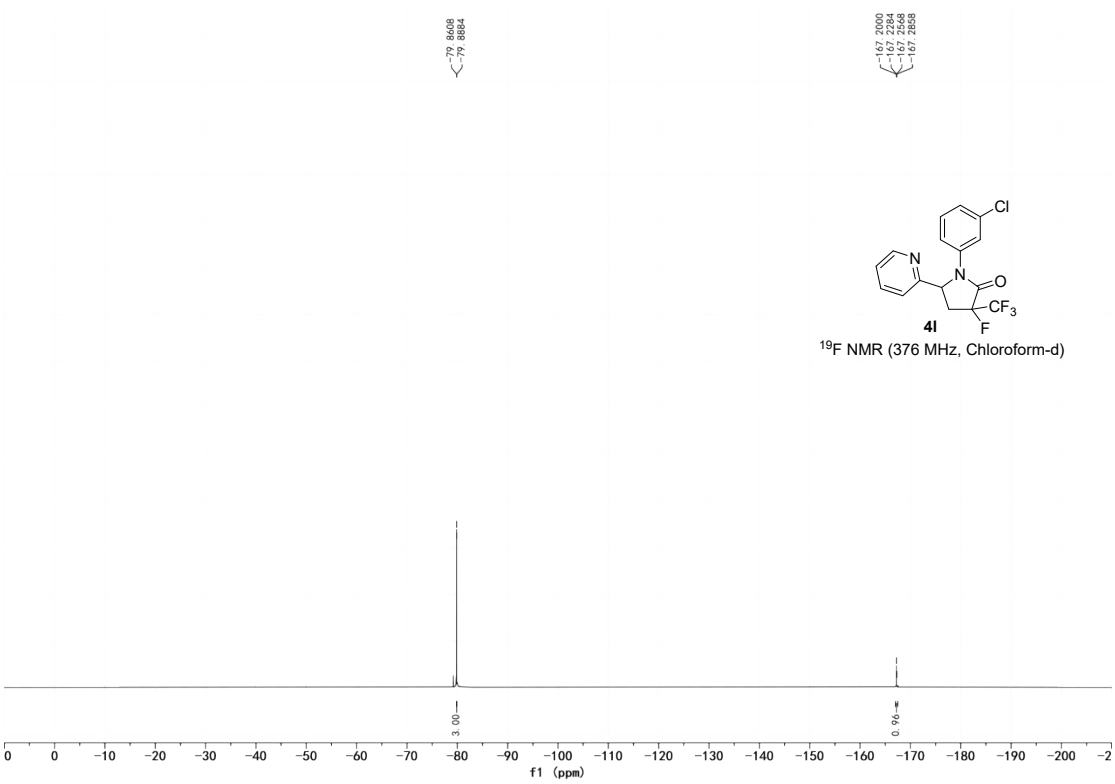
^{19}F NMR (376 MHz, Chloroform-d)



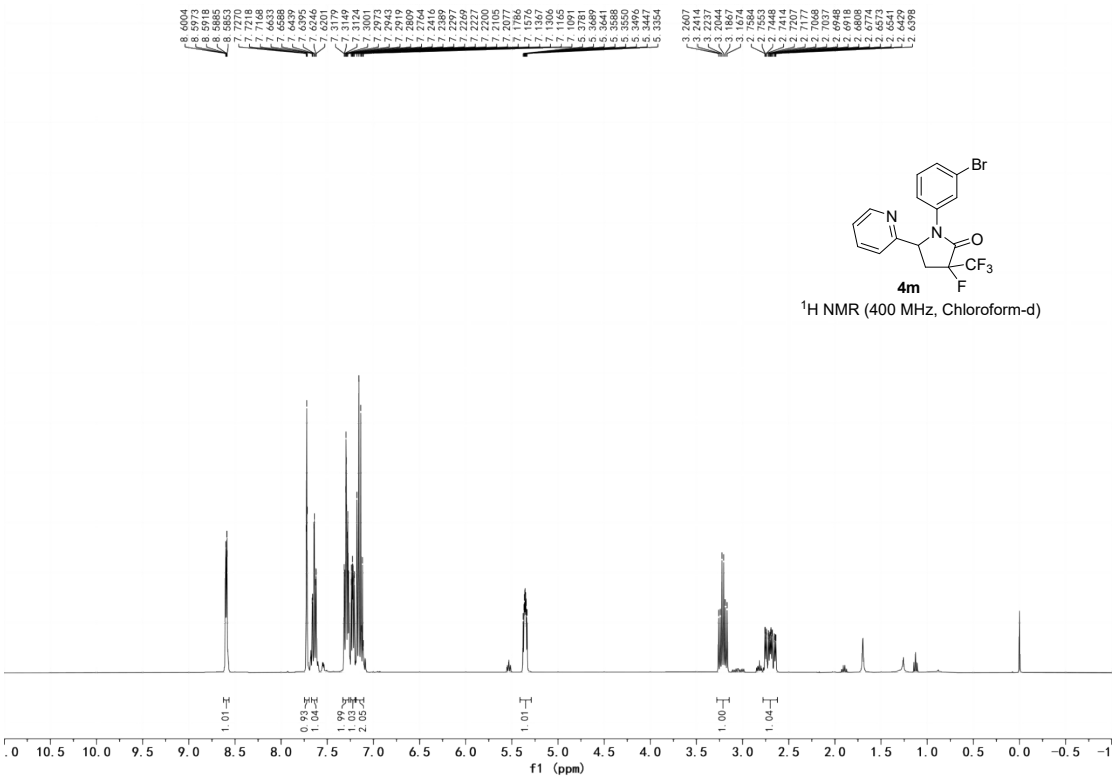
^{1}H NMR (400 MHz, Chloroform-d)

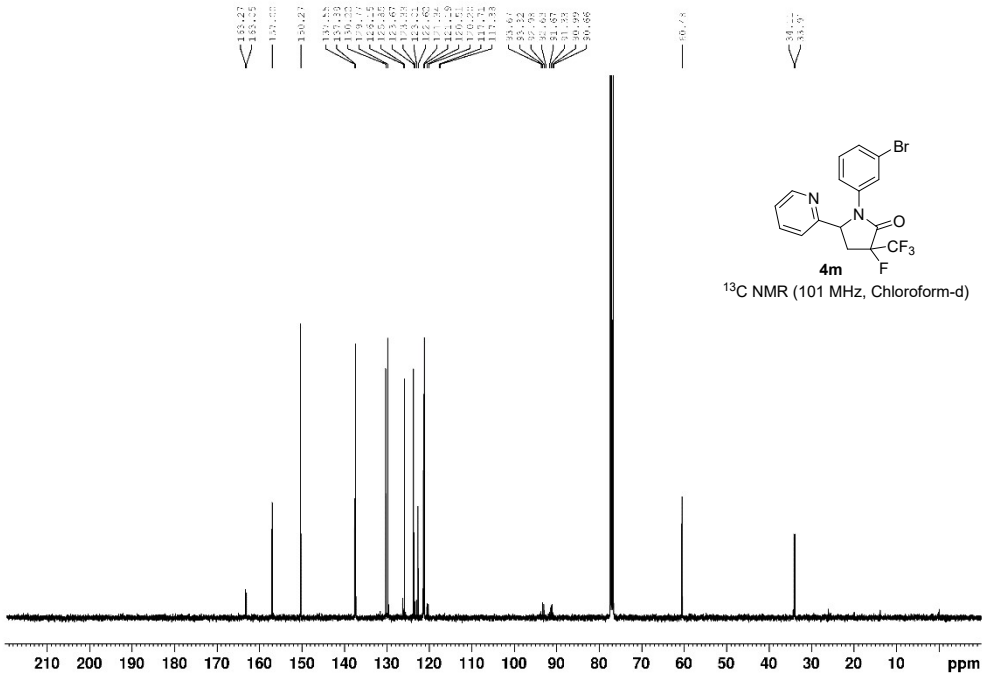


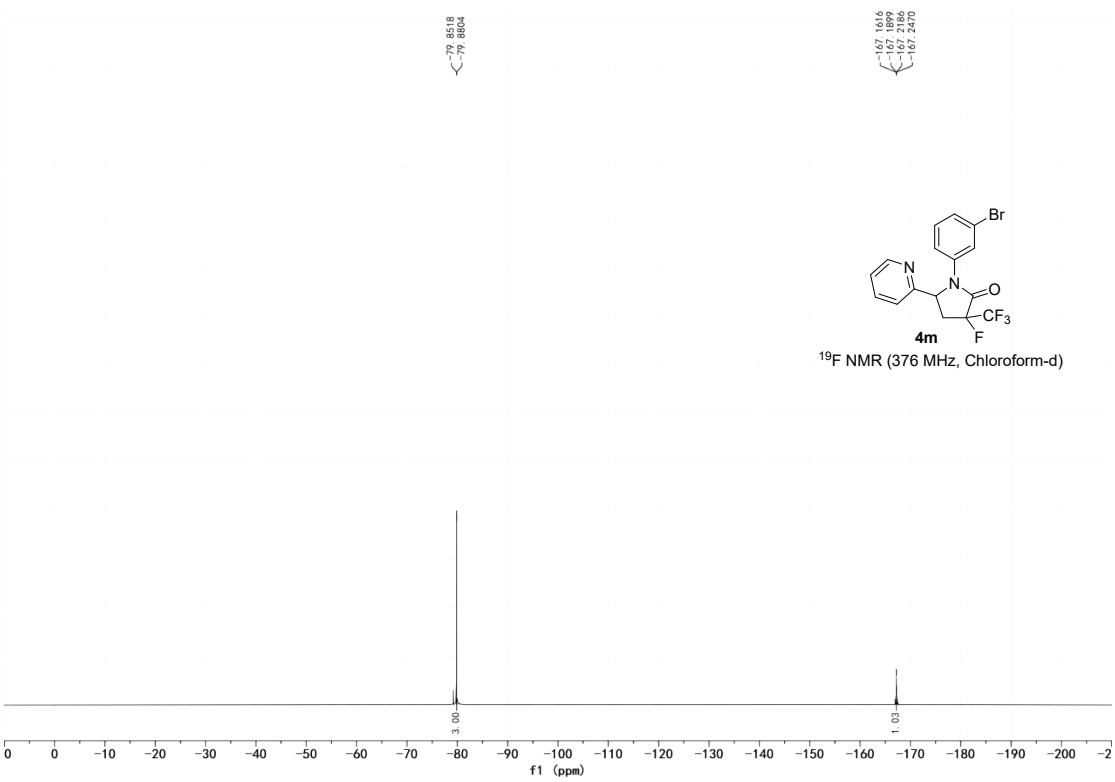
^{13}C NMR (101 MHz, Chloroform-d)



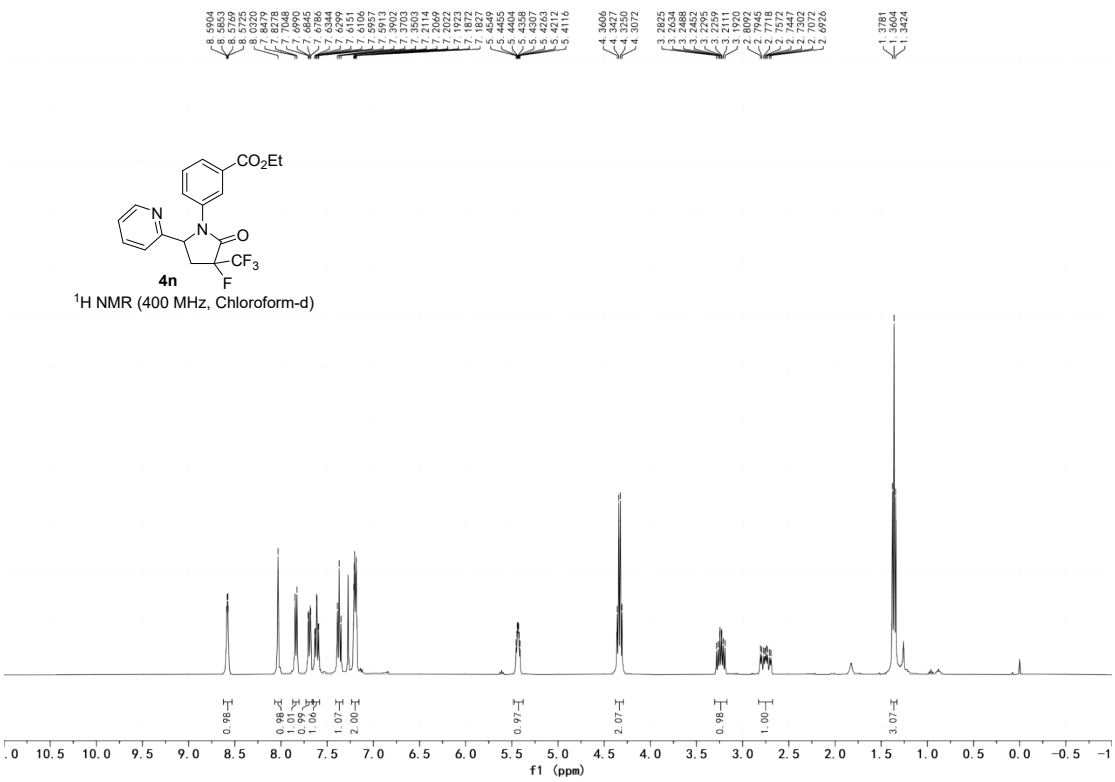
^{19}F NMR (376 MHz, Chloroform-d)

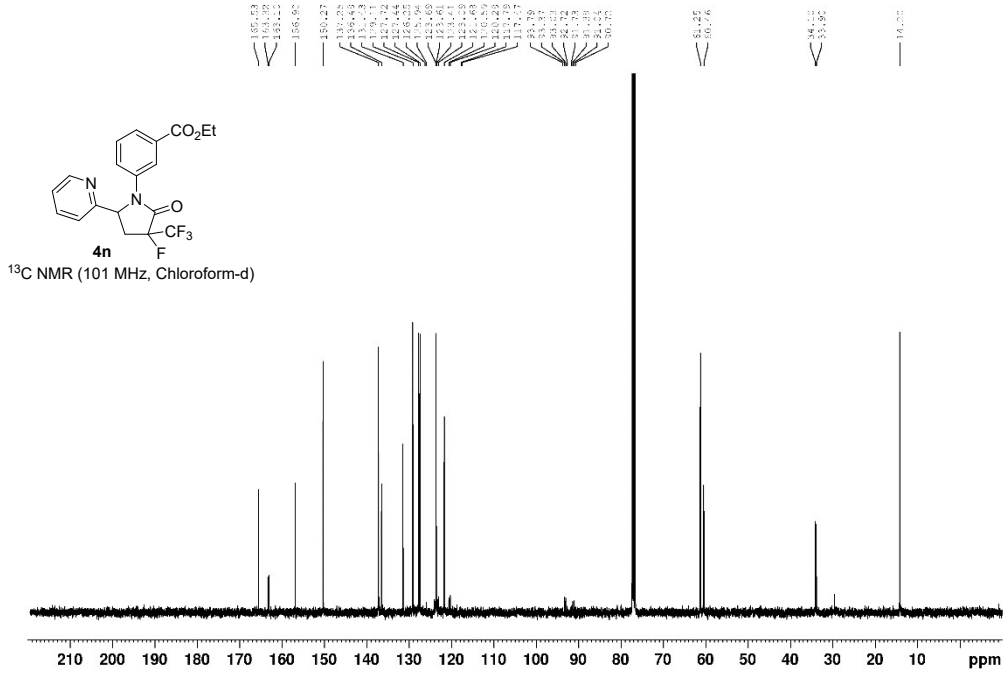

Br
N
N
O
CF3
F
4m
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

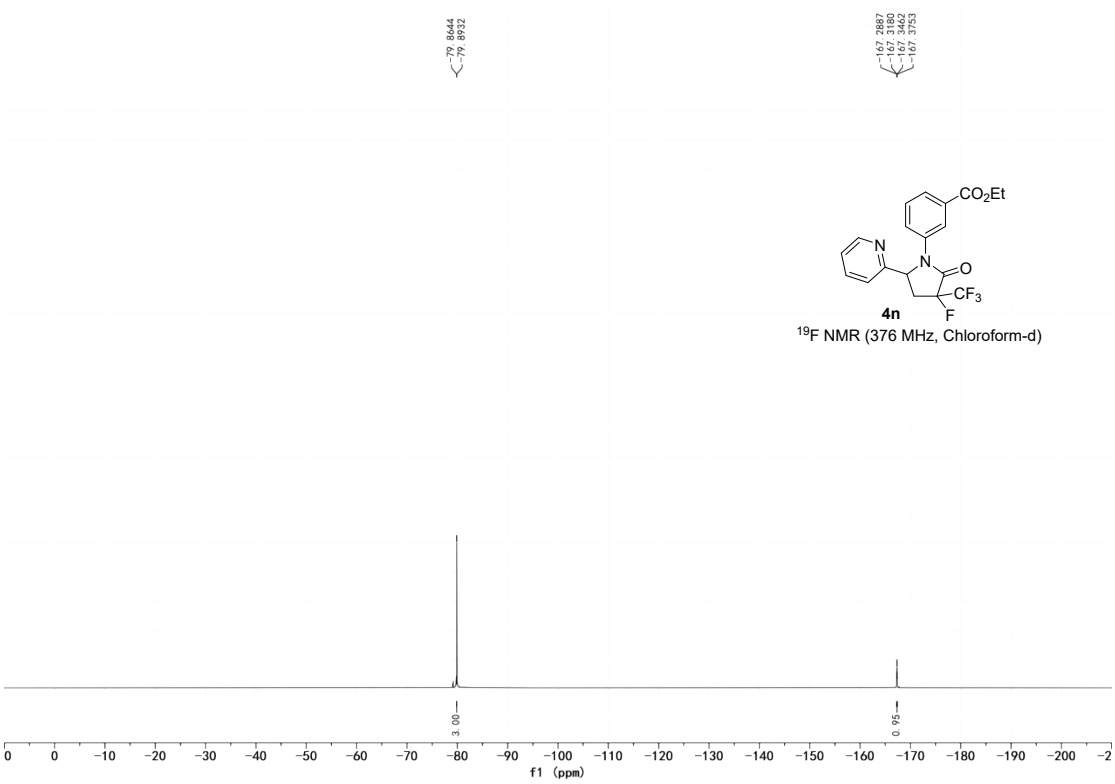

Br
N
N
O
CF3
F
4m
13C NMR (101 MHz, Chloroform-d)
ppm



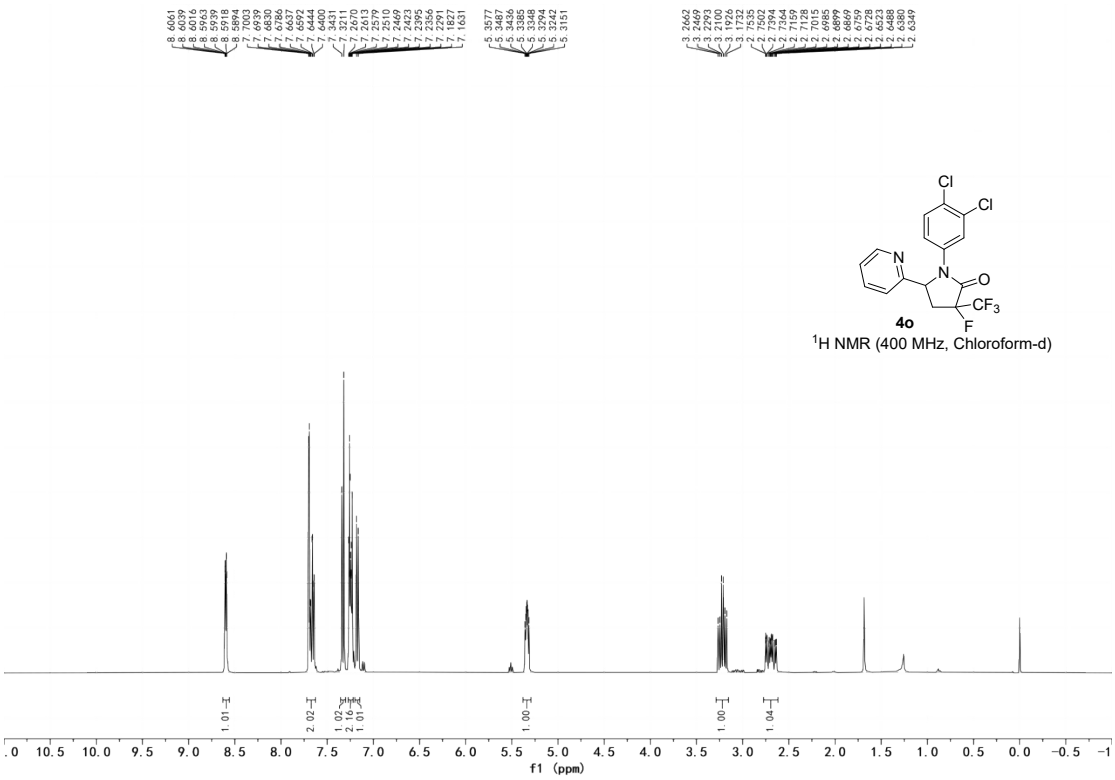
^{19}F NMR (376 MHz, Chloroform-d)

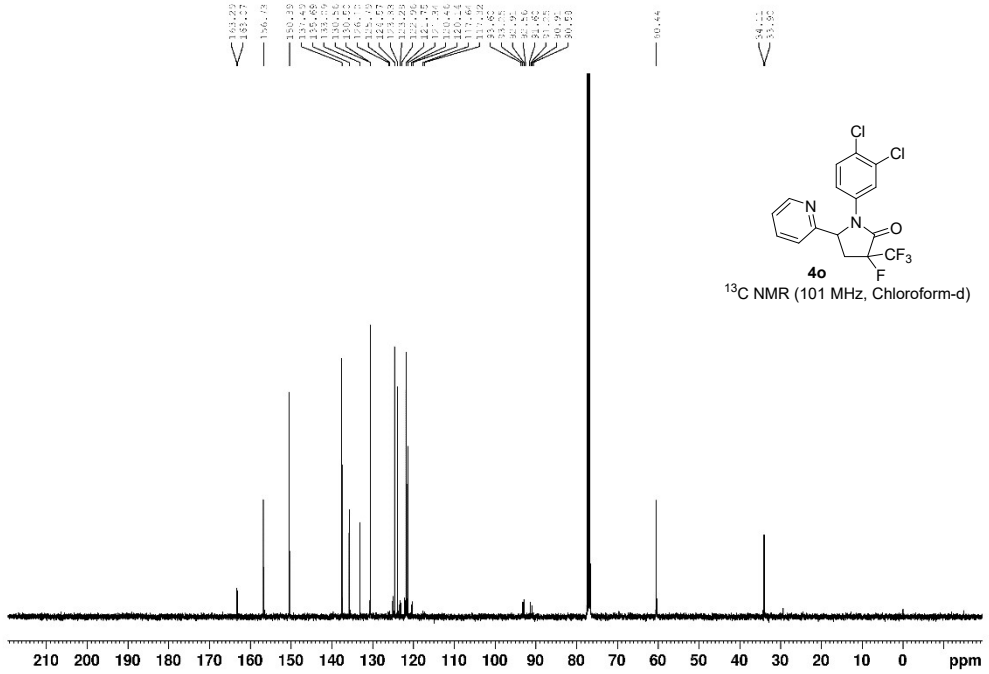

CO2Et
N
N
O
CF3
F
4n
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

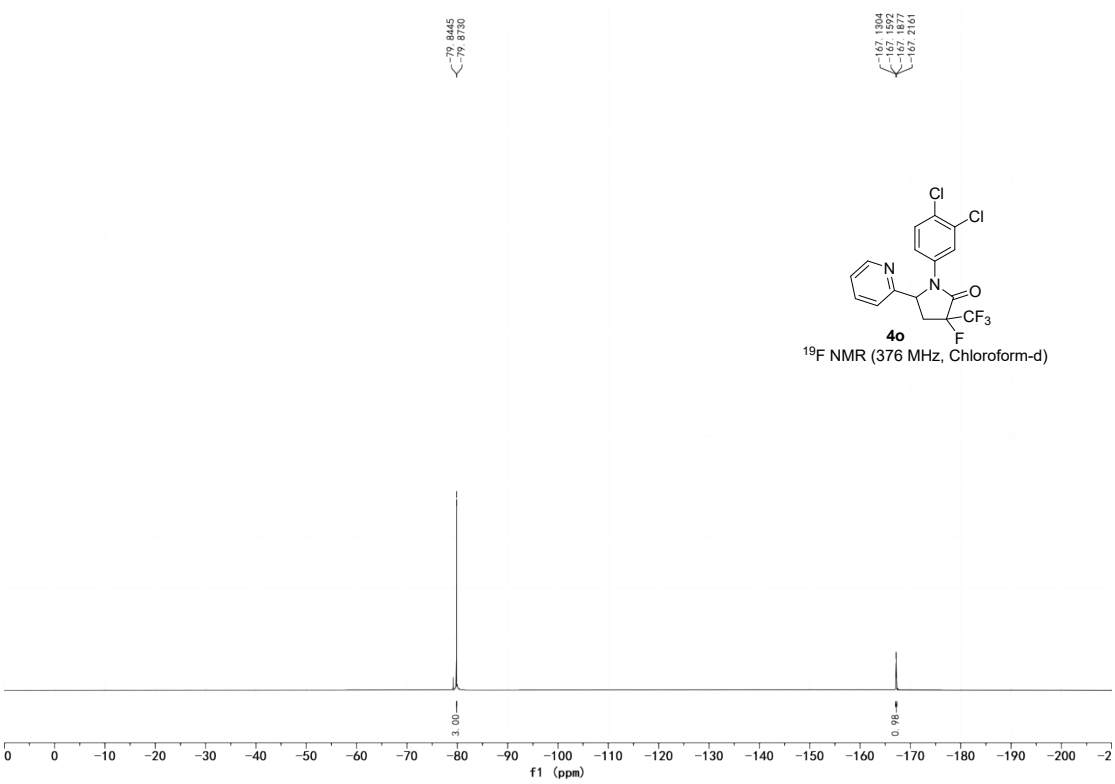

CO2Et
N
N
O
CF3
F
4n
13C NMR (101 MHz, Chloroform-d)
ppm



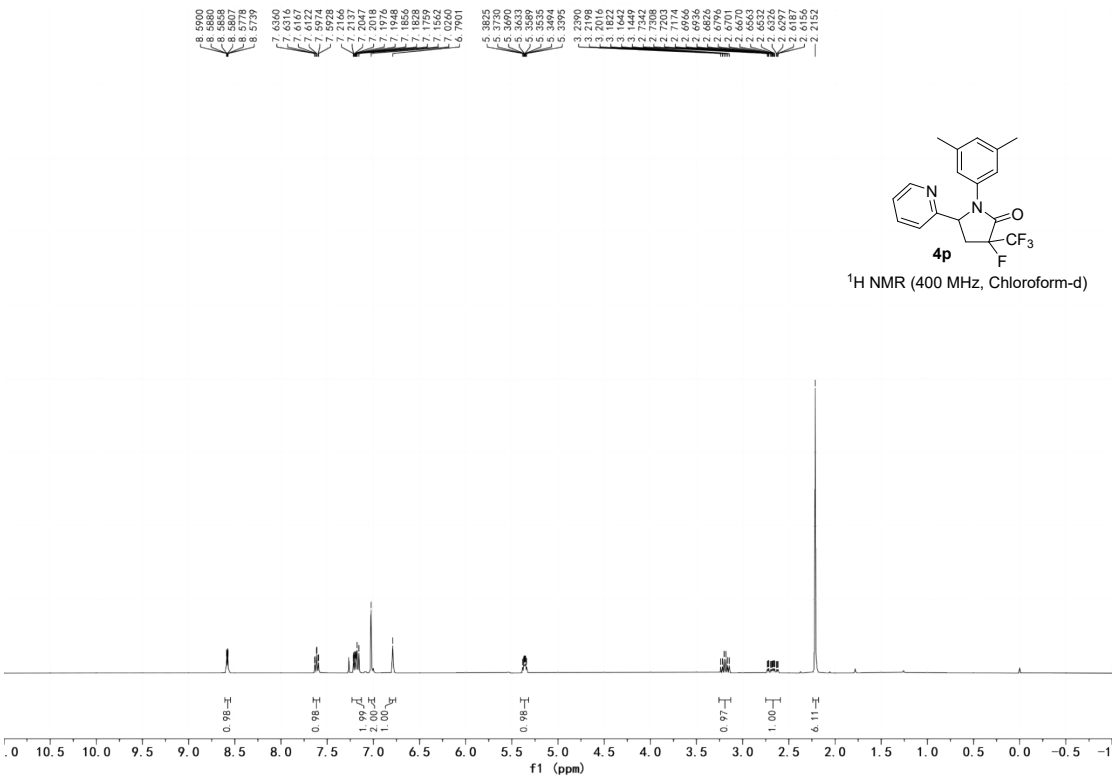
^{19}F NMR (376 MHz, Chloroform-d)


Cl
Cl
N
N
O
CF3
F
4o
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

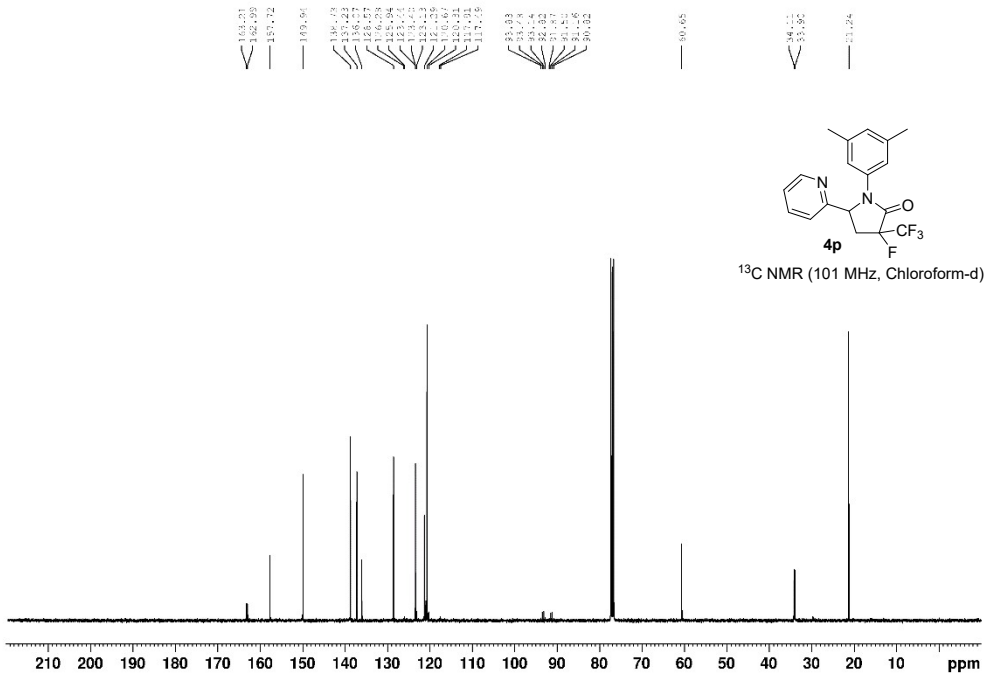

Cl
Cl
N
N
O
CF3
F
4o
13C NMR (101 MHz, Chloroform-d)
ppm



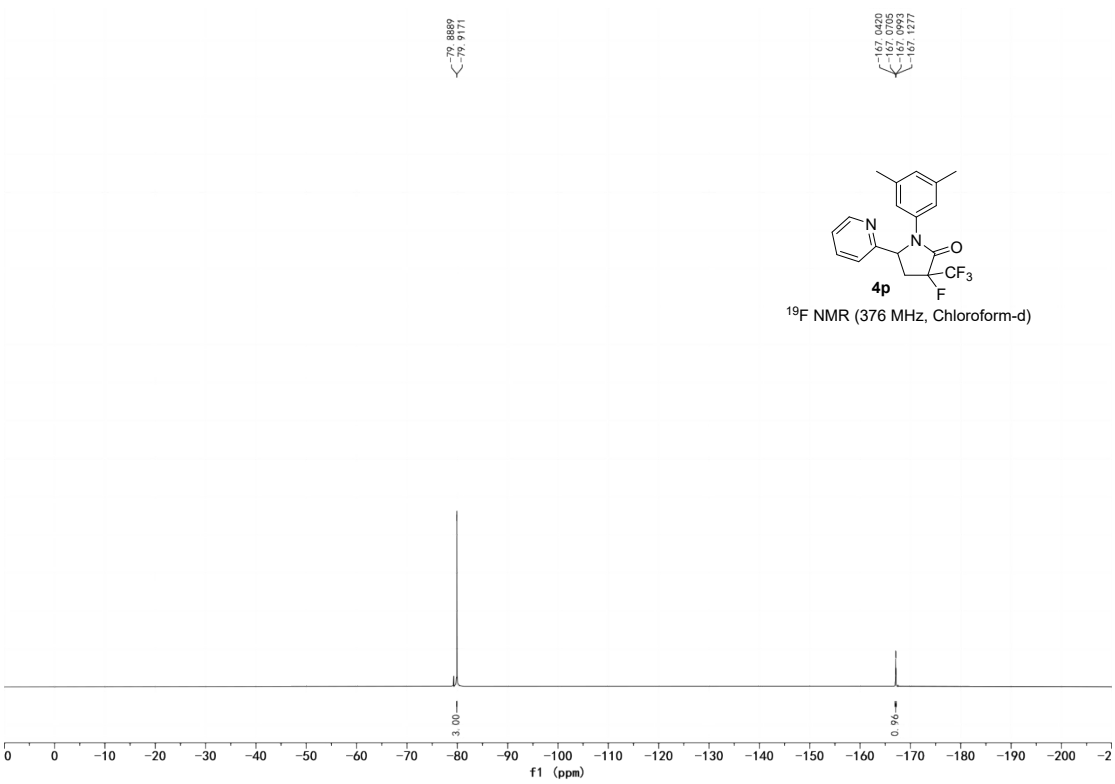
^{19}F NMR (376 MHz, Chloroform-d)



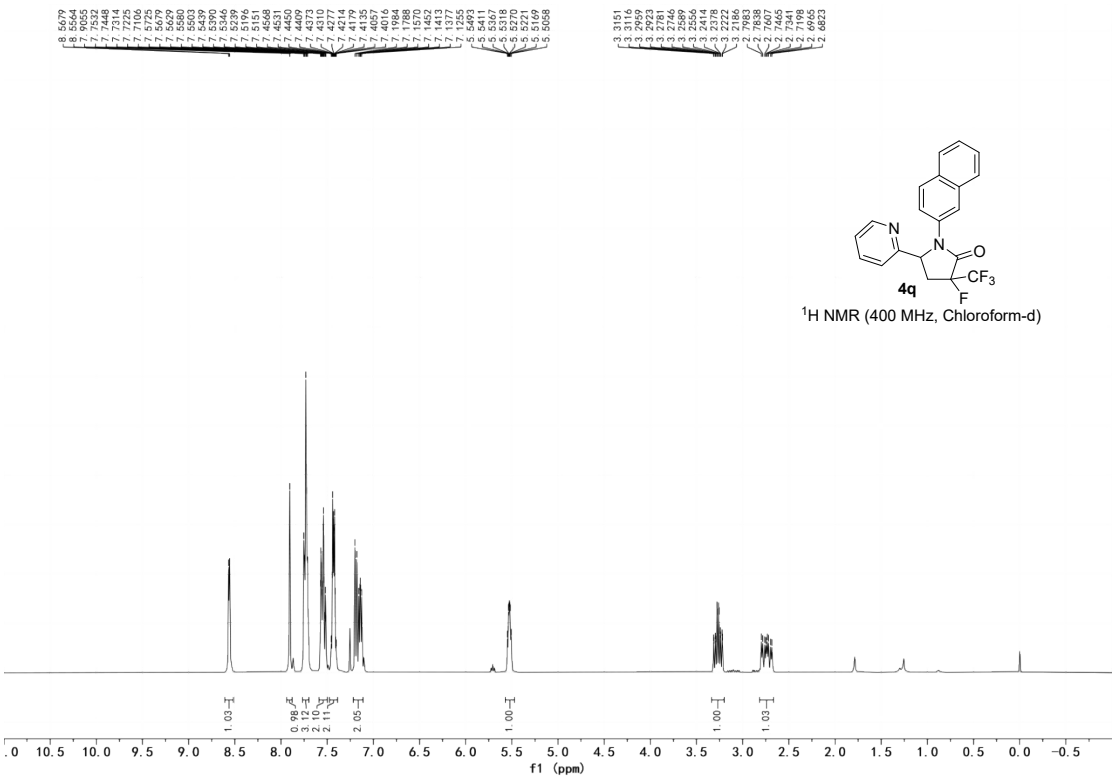
^{1}H NMR (400 MHz, Chloroform-d)

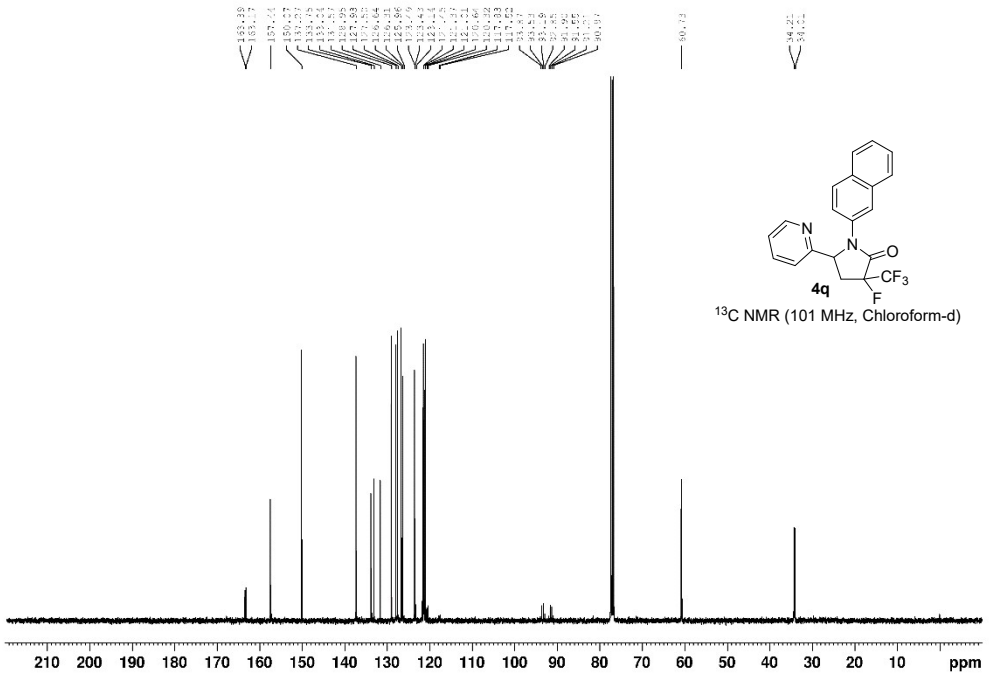


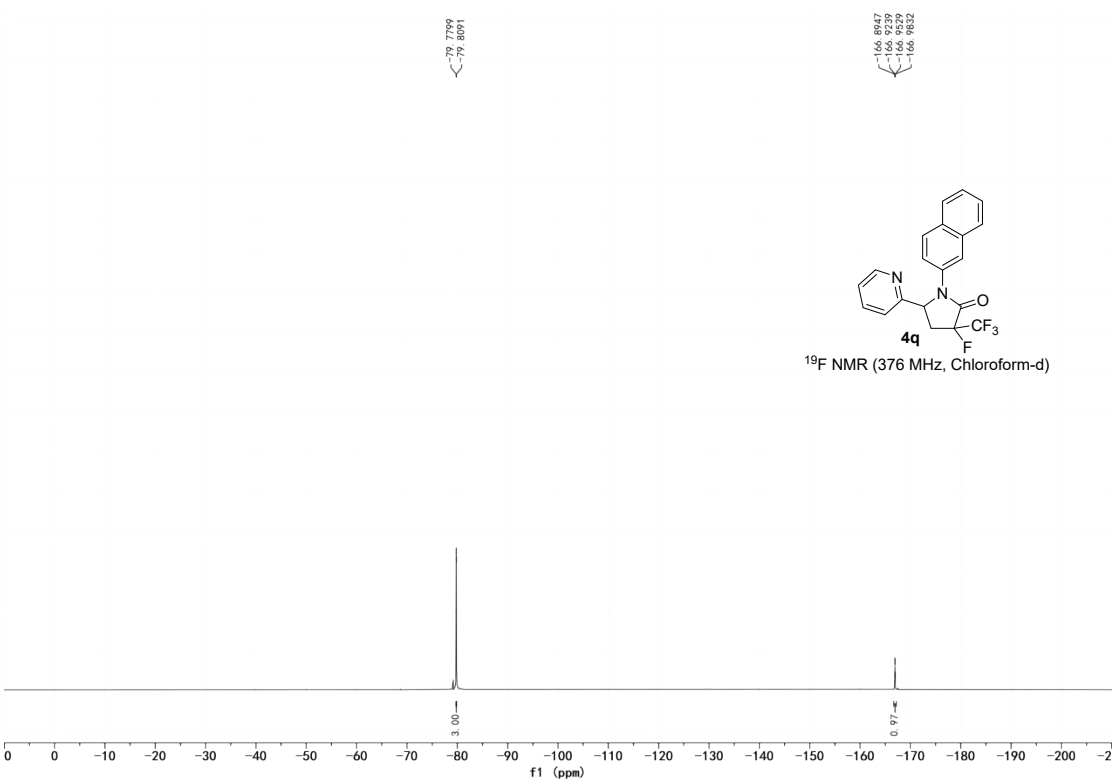
^{13}C NMR (101 MHz, Chloroform-d)



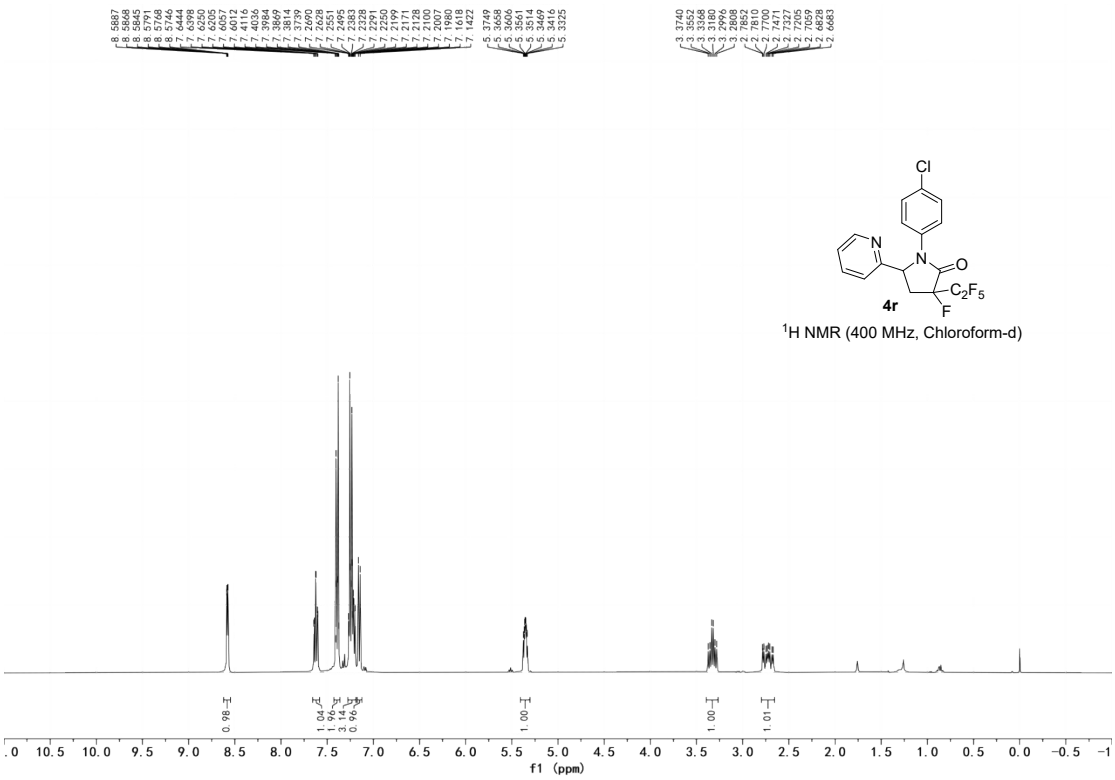
^{19}F NMR (376 MHz, Chloroform-d)


4q
1H NMR (400 MHz, Chloroform-d)
f1 (ppm)

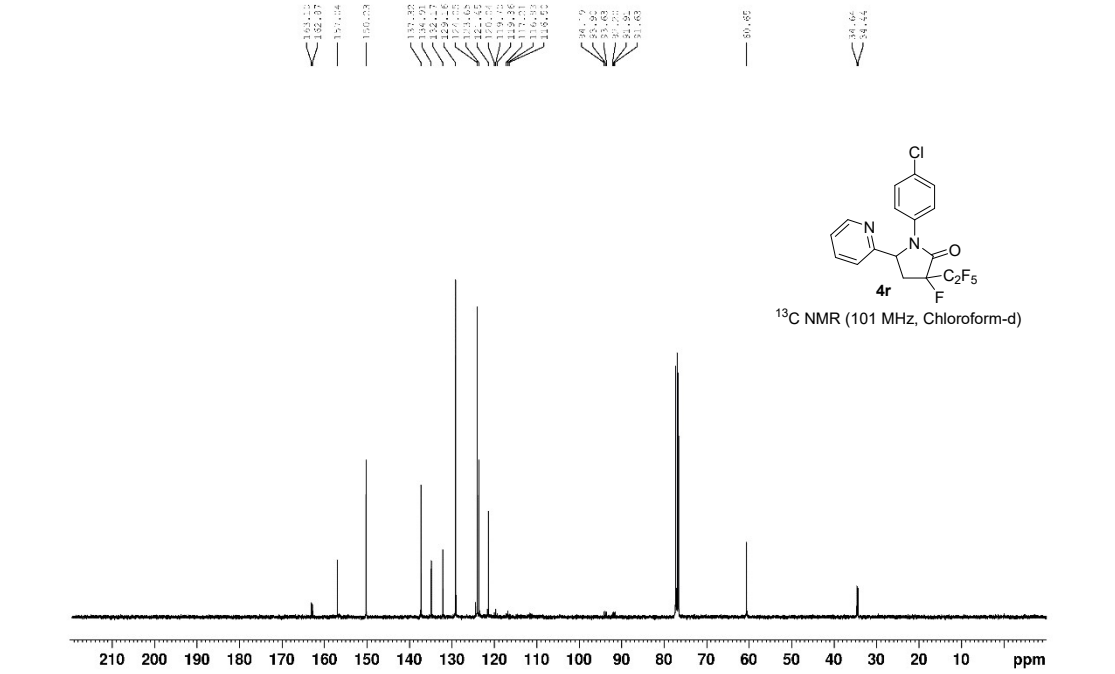

4q
13C NMR (101 MHz, Chloroform-d)
ppm



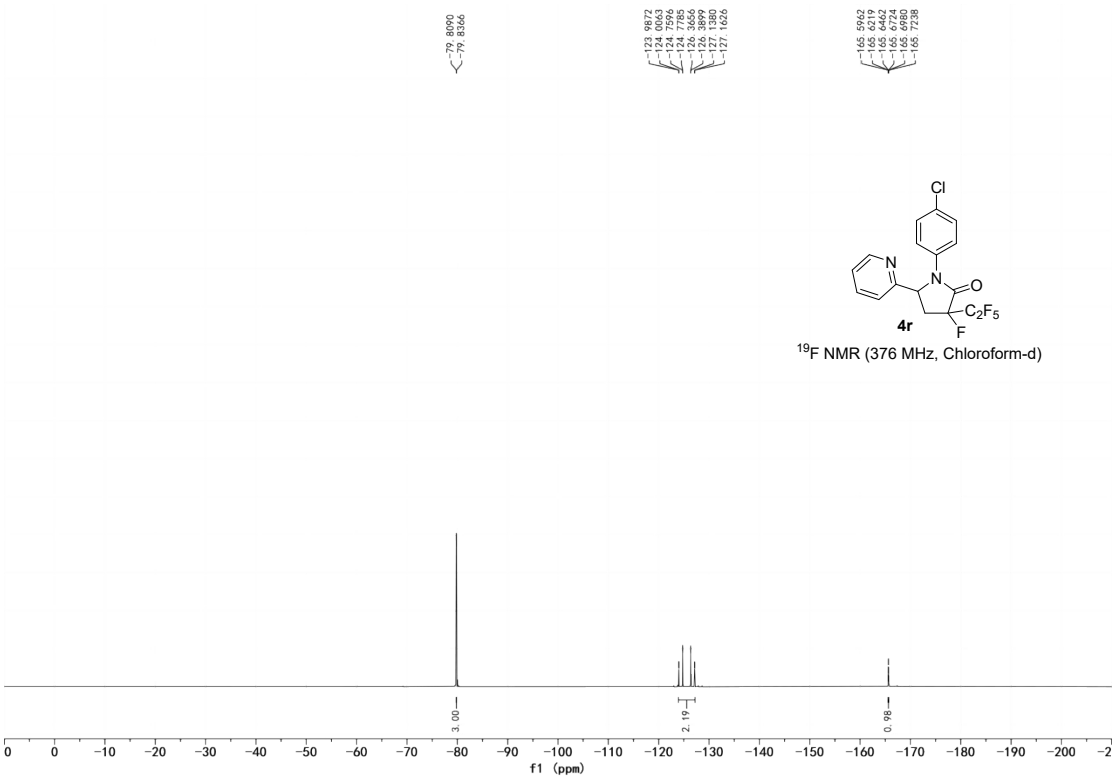
^{19}F NMR (376 MHz, Chloroform-d)



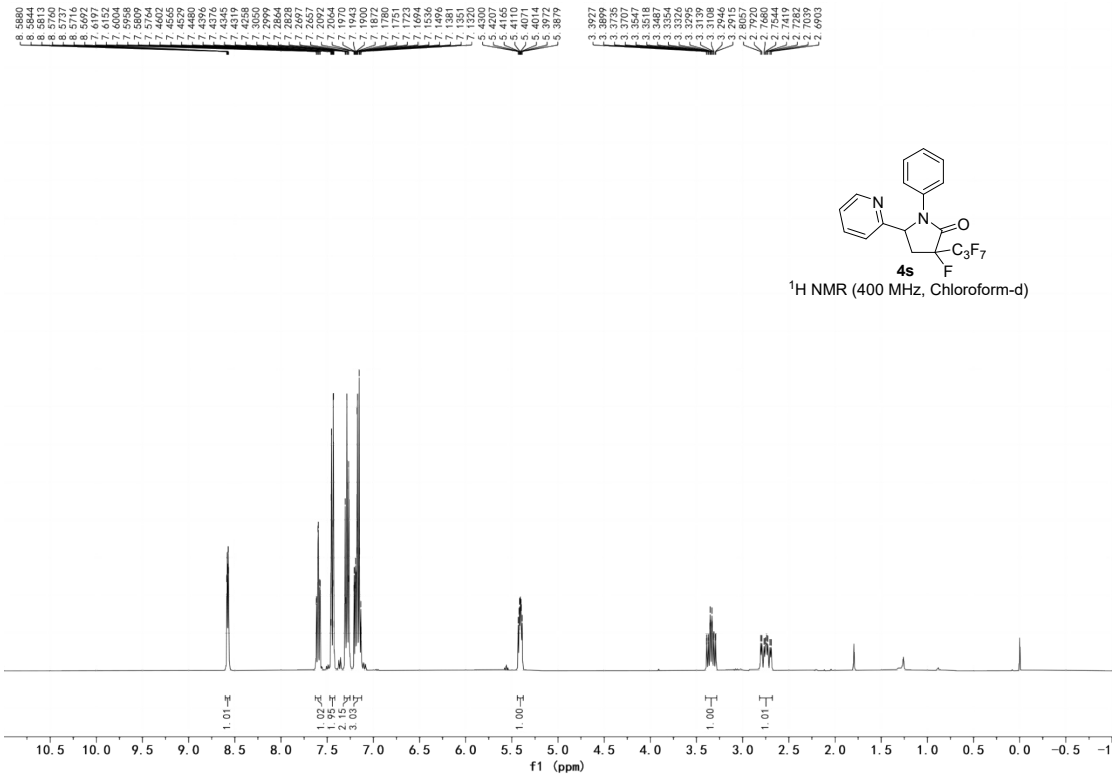
^{1}H NMR (400 MHz, Chloroform-d)

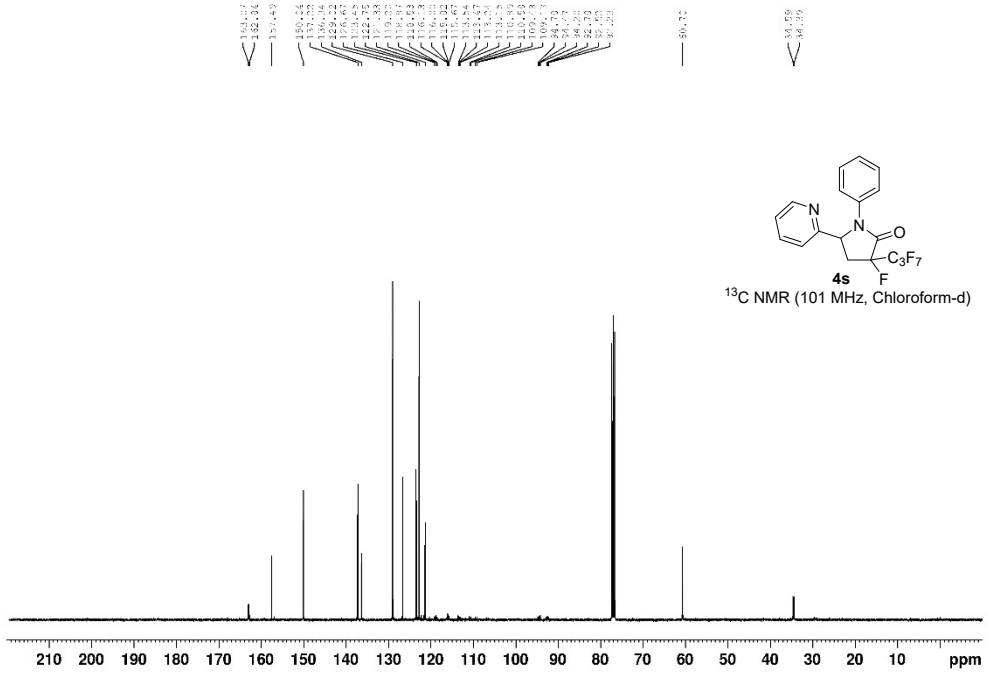


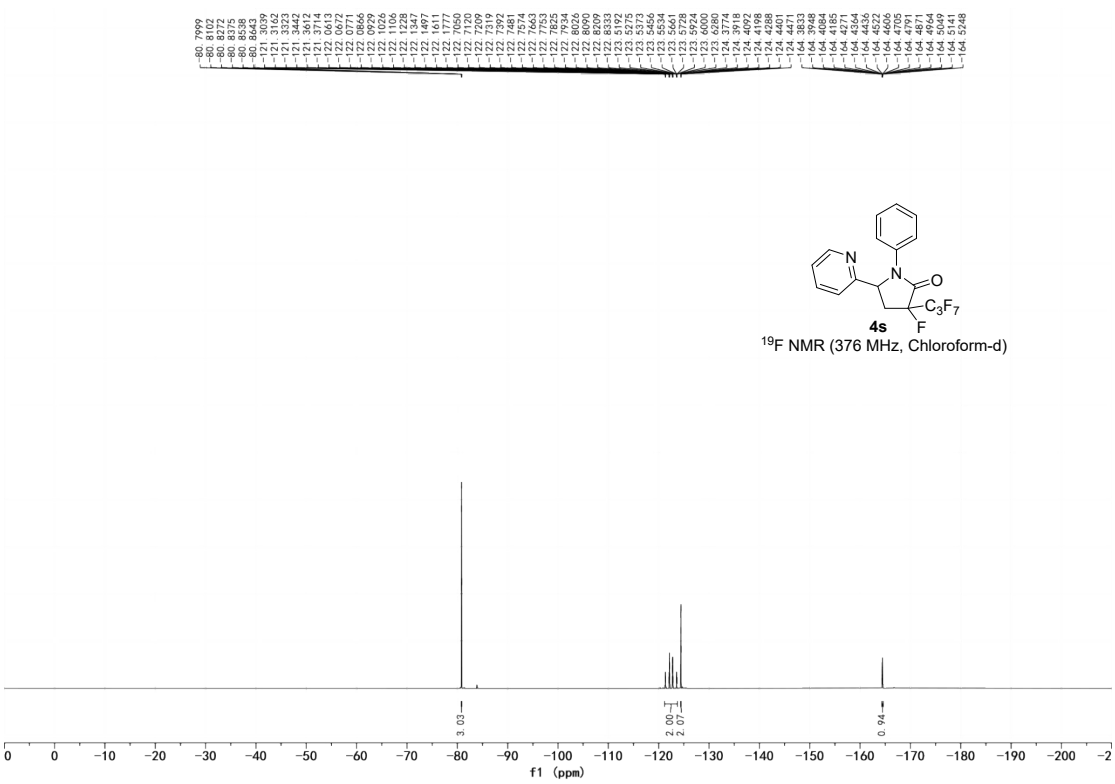
^{13}C NMR (101 MHz, Chloroform-d)



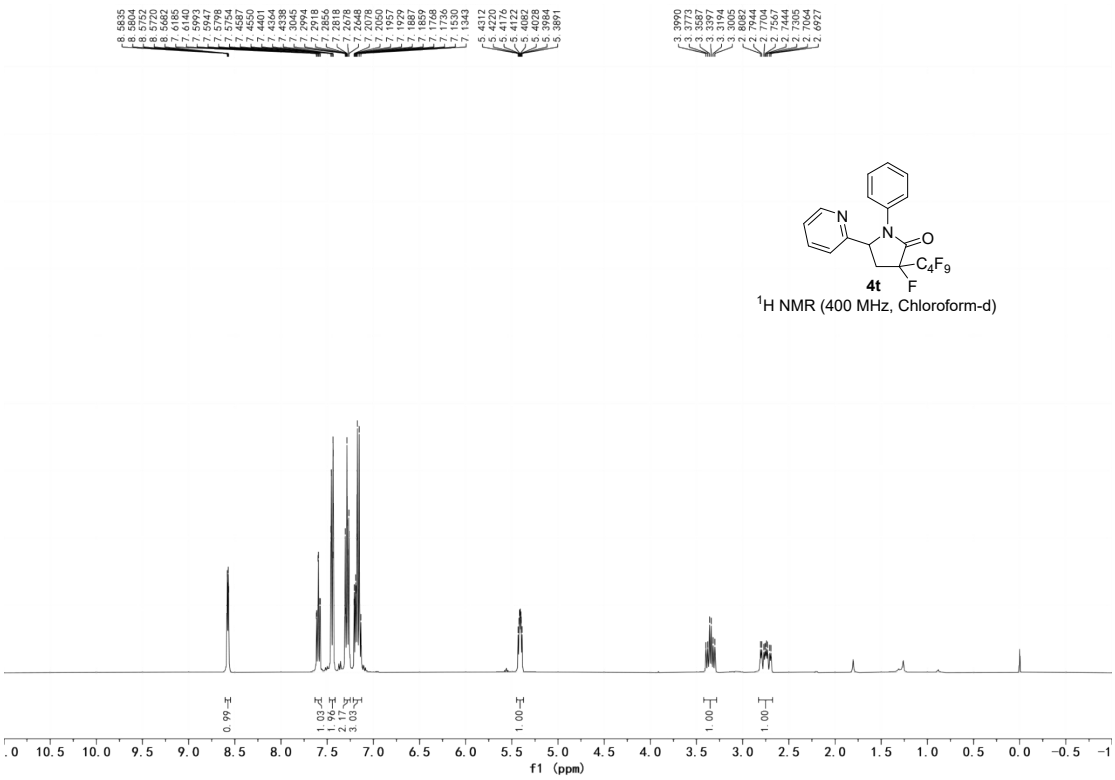
^{19}F NMR (376 MHz, Chloroform-d)

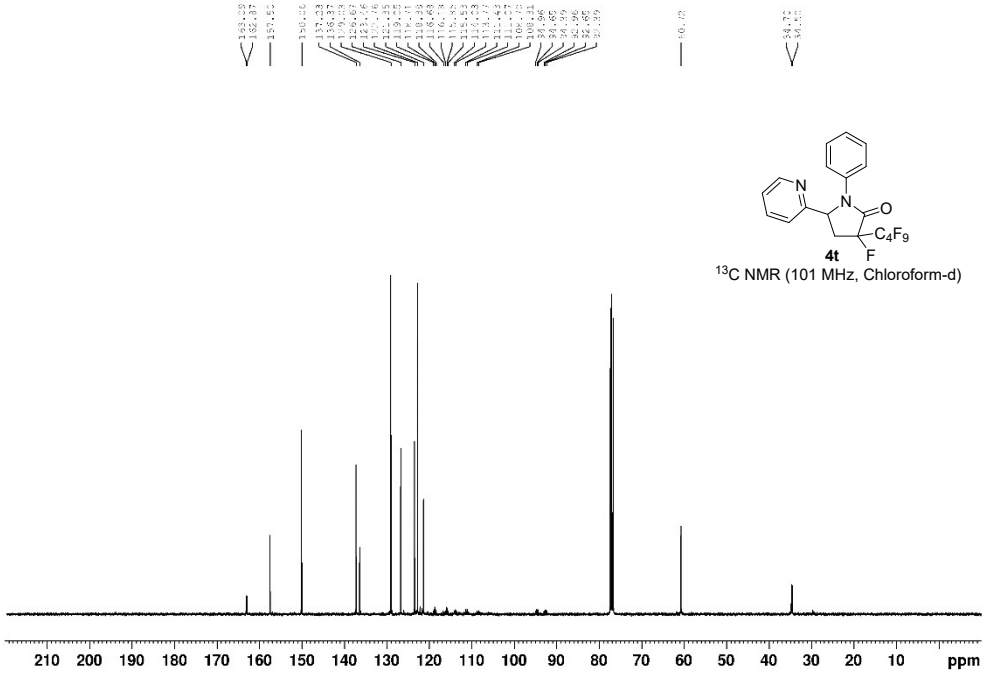

4s
^{1}H NMR (400 MHz, Chloroform-d)
f1 (ppm)

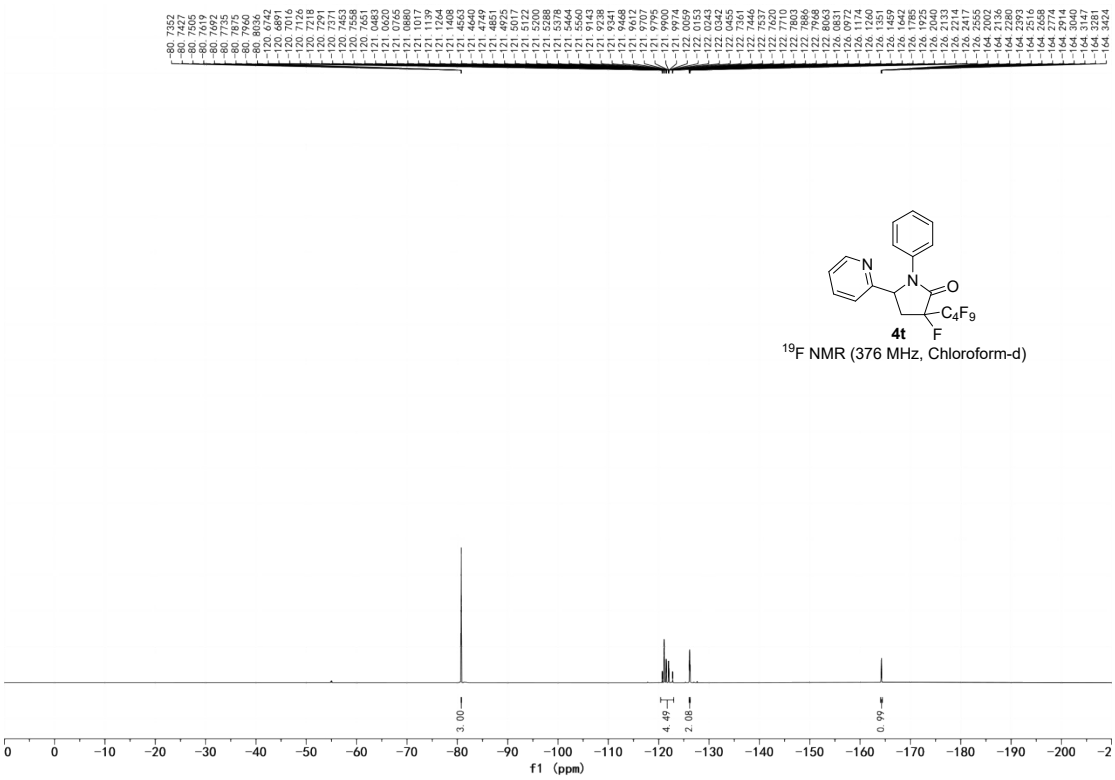

4s
^{13}C NMR (101 MHz, Chloroform-d)
ppm



^{19}F NMR (376 MHz, Chloroform-d)

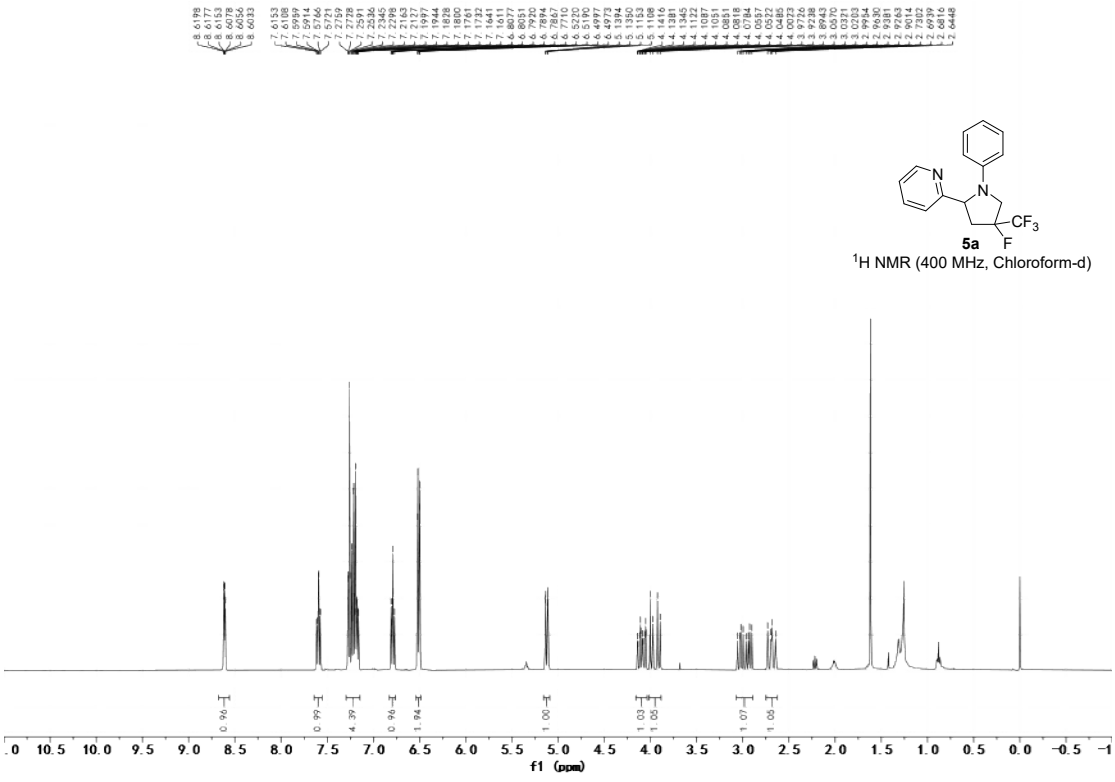

4t
^{1}H NMR (400 MHz, Chloroform-d)
f1 (ppm)


4t
^{13}C NMR (101 MHz, Chloroform-d)
ppm



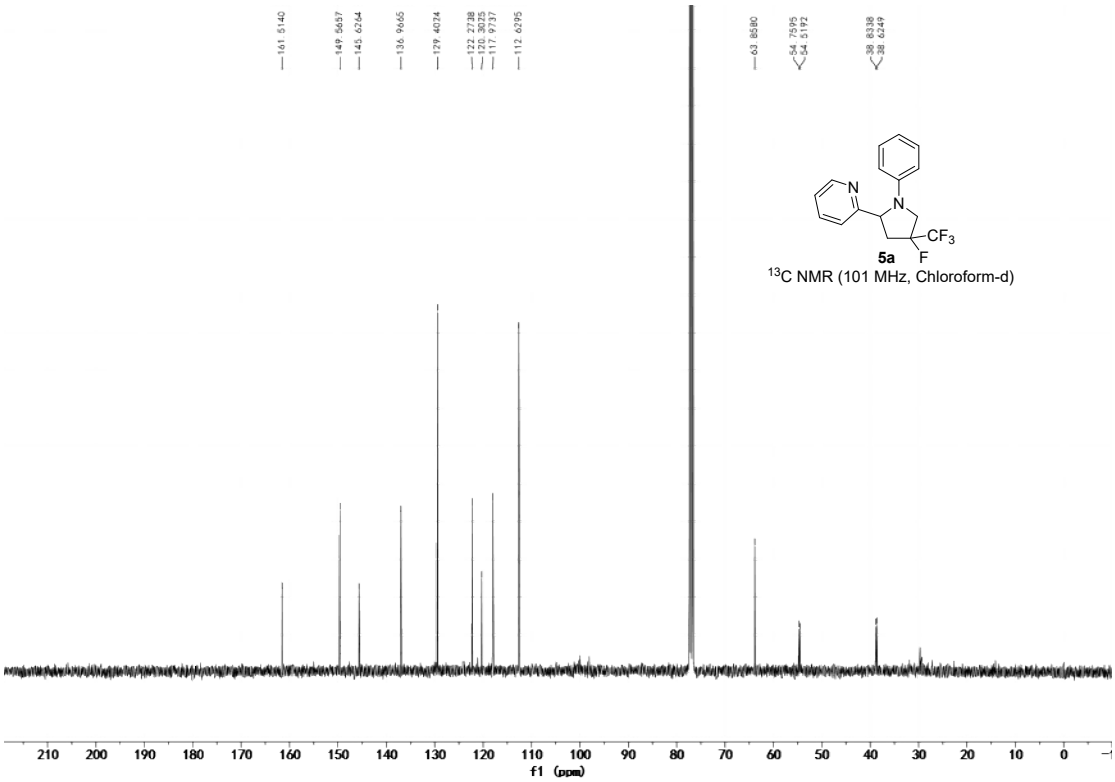
4t

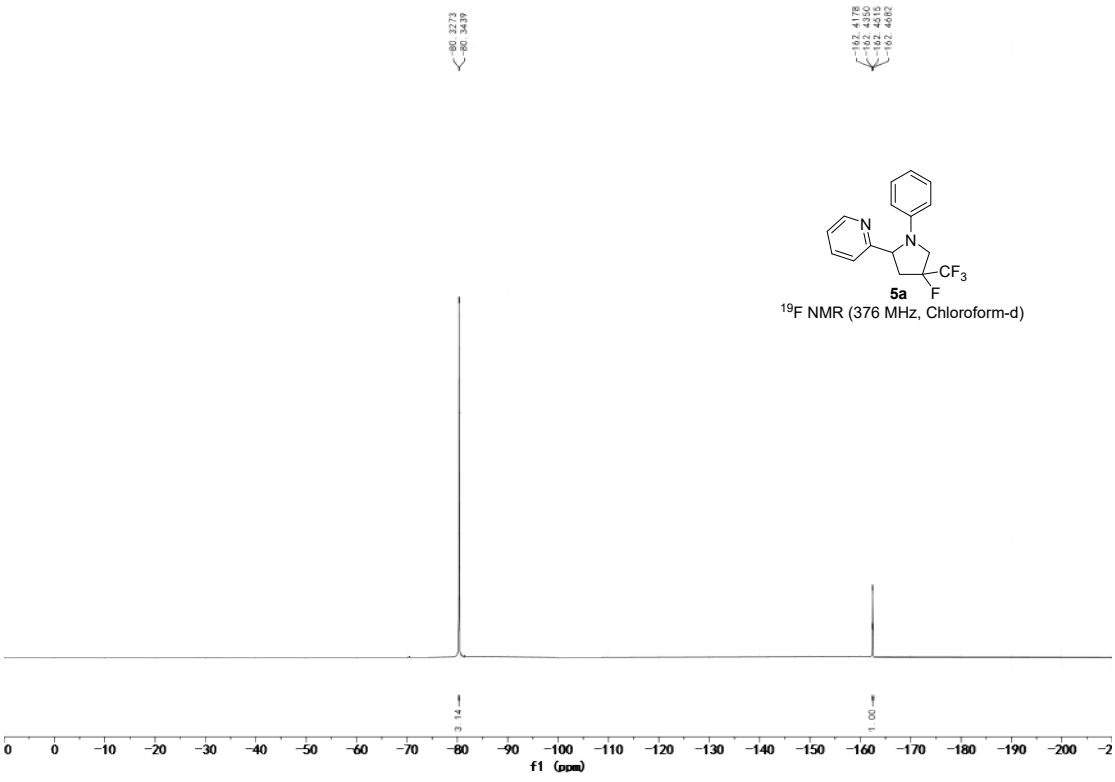
^{19}F NMR (376 MHz, Chloroform-d)

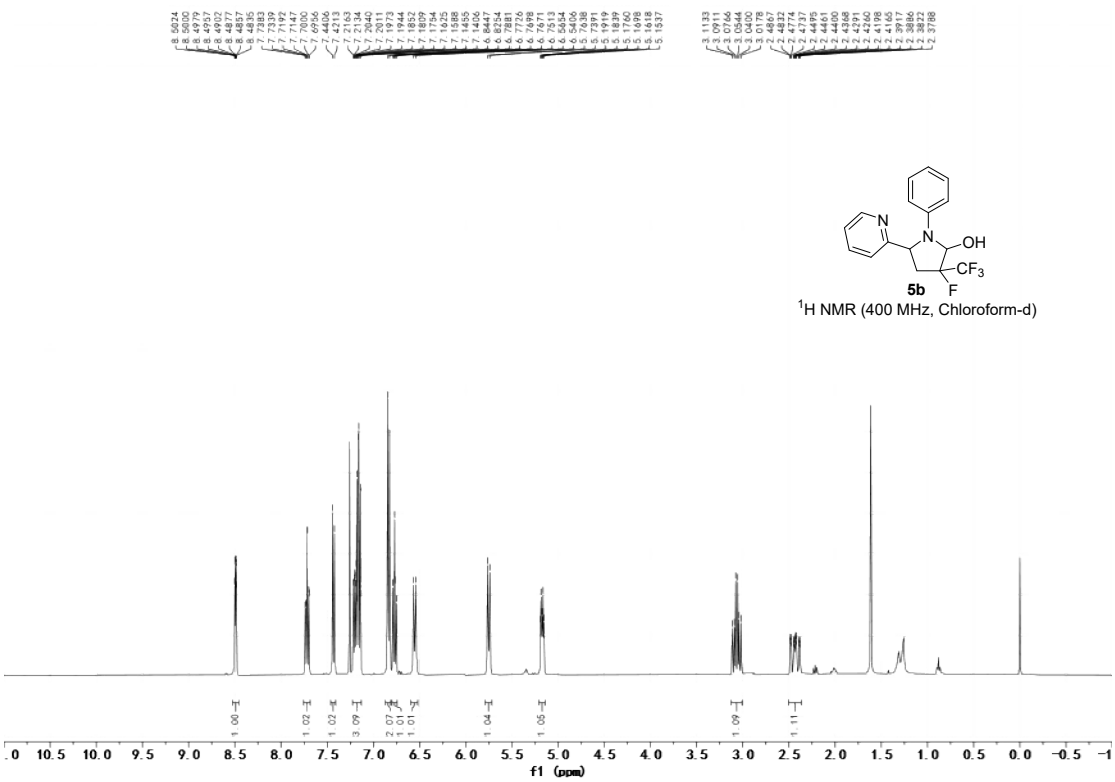


5a

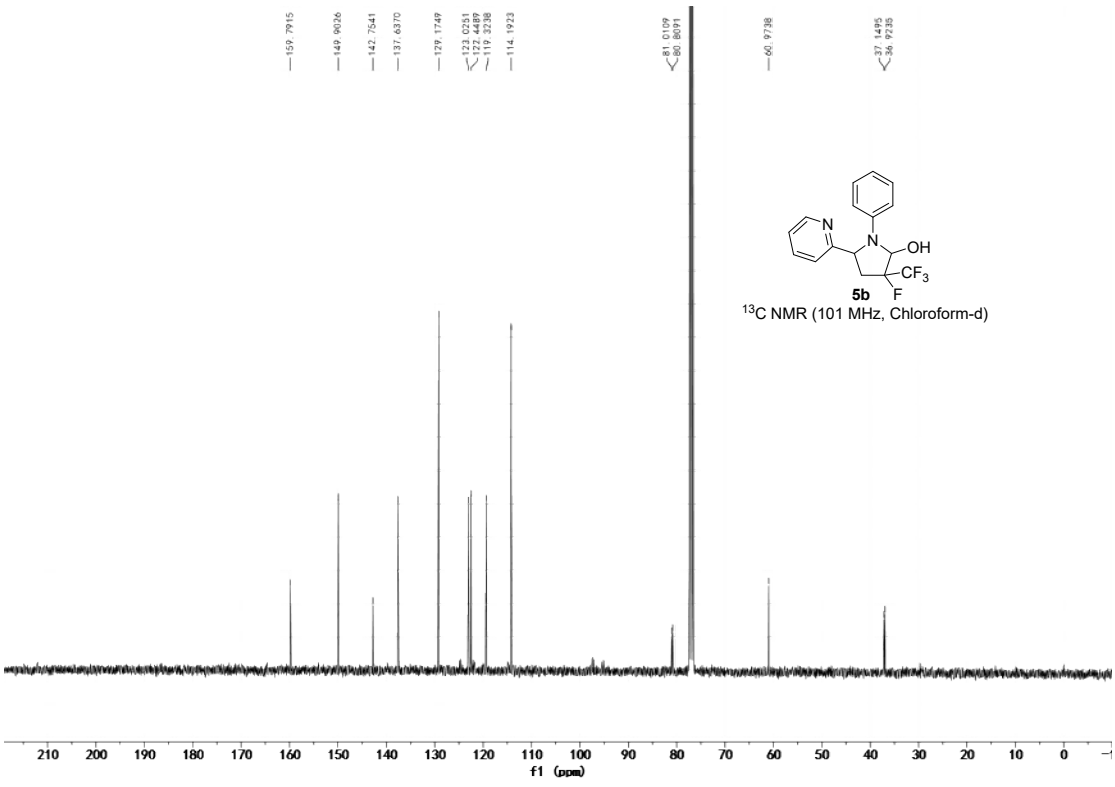
^{1}H NMR (400 MHz, Chloroform-d)


161.5140
149.5657
145.6264
136.9665
129.4024
122.2738
120.3025
117.9737
112.6295
63.8580
54.7595
54.5192
38.8338
38.6249
N
N
CF3
F
5a
13C NMR (101 MHz, Chloroform-d)
f1 (ppm)

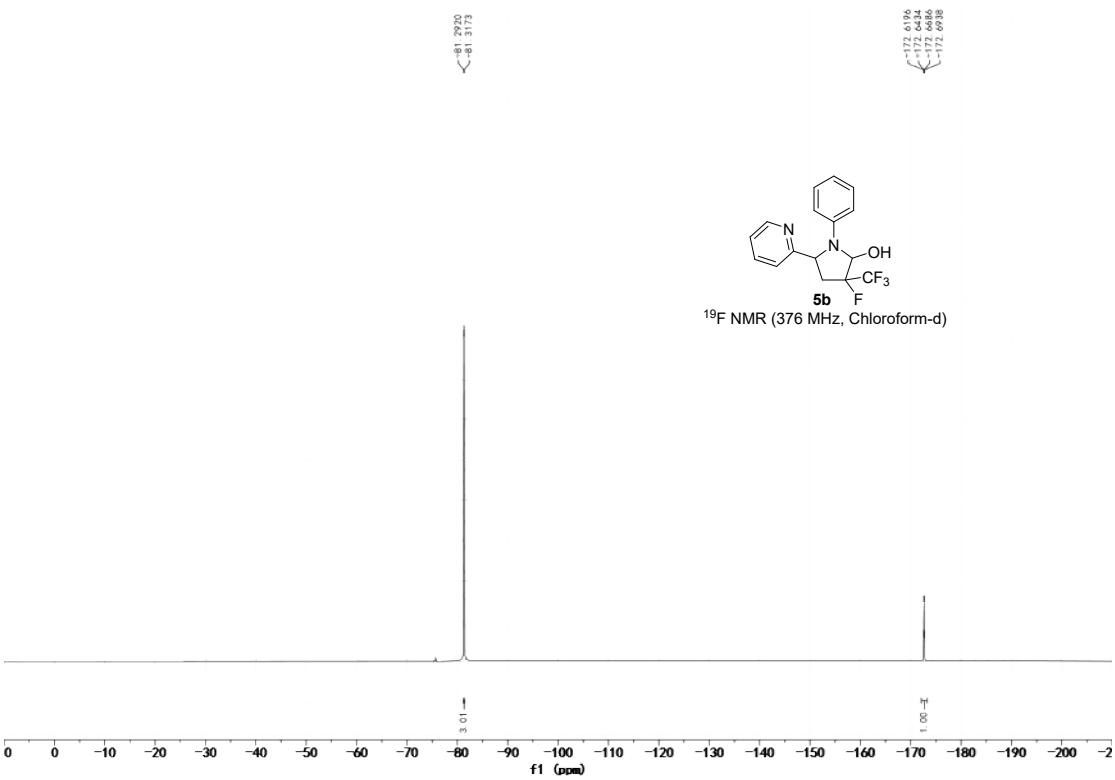

-80.3273
-80.3439
-162.4178
-162.4350
-162.4515
-162.4682
N
N
CF3
F
5a
19F NMR (376 MHz, Chloroform-d)
3.14
1.00
f1 (ppm)



^{1}H NMR (400 MHz, Chloroform-d)



^{13}C NMR (101 MHz, Chloroform-d)



5b

^{19}F NMR (376 MHz, Chloroform-d)