Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light-induced dehydrogenative *β*-trifluoromethylthiolation of tertiary amines and direct *β*-trifluoromethylthiolation of enamides

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I. General Remarks: Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$, ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. UV-Vis spectra were recorded on a TU-1950 UV spectrometer and are reported in 200-700 nm. Melting points were determined on a microscopic apparatus and were uncorrected. X-ray diffraction data collection of the compounds were recorded by Bruker D8 VENTURE system with PHOTON 100 CMOS detector. All new products were further characterized by HRMS (high resolution mass spectra), high resolution mass spectrometry (HRMS) spectra was obtained on a micrOTOF-Q instrument equipped with an ESI source; copies of their ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra are provided. All solvents were distilled from appropriate drying agents prior to use or directly taken from commercial sealed bottles. All reagents were used as received unless otherwise stated.

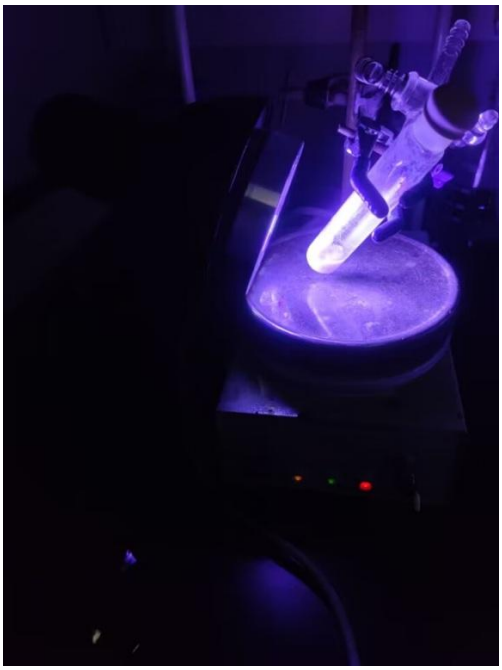
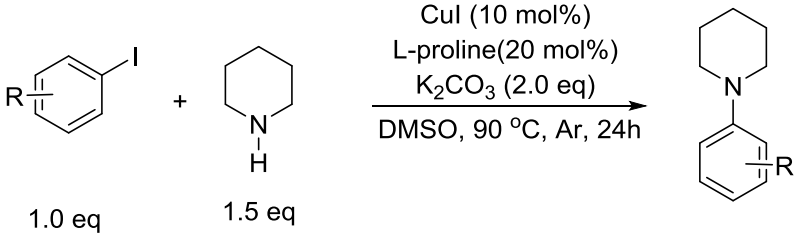


Figure S1. Typical experimental setup for photoredox catalytic reactions

II. Preparation of Starting Materials 1, 2a, 7

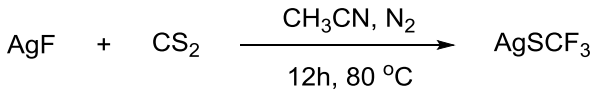
II.I General procedure for the coupling reaction of aryl iodides with amines catalyzed by CuI and L-proline:



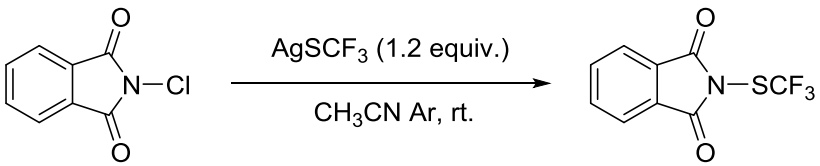
An oven-dried Schlenk tube (50 mL) was equipped with a magnetic stir bar, K_2CO_3 (4 mmol), CuI (0.2 mmol) and L-proline (0.4 mmol). The flask was evacuated and

backfilled with Ar for 3 times. Then DMSO (1 M), aryl iodide (2 mmol 1.0 equiv.) and amine (3 mmol) were added with syringe. The reaction mixture was then stirred at 90 °C in an oil bath for 24 h. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with 1/160 to 1/120 ethyl acetate/petroleum ether to afford the corresponding product[1].

II.II Procedure for synthesis of N-(trifluoromethylthio)phthalimide (2a)



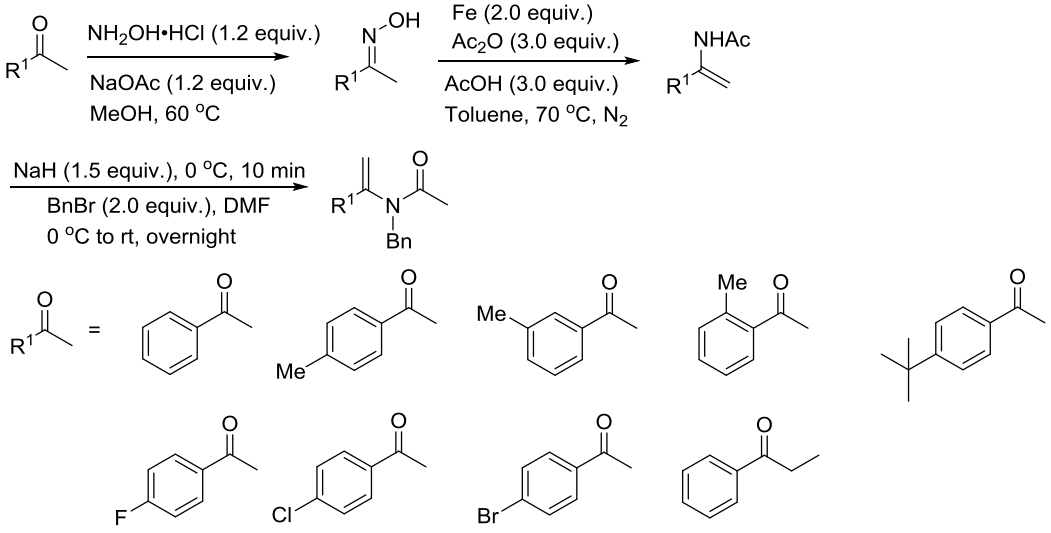
Synthetic procedure: a) To an oven dried 500 mL Schlenk flask equipped with a stir bar was added dry AgF (50 g, 0.39 mol). The flask was fitted with a glass stopper and evacuated and refilled with Ar for three times. Under Ar pressure, the stopper was removed and replaced with a reflux condenser. The system was once again evacuated and refilled with argon for three times. Dry MeCN was injected into the flask in five 50 mL portions via the side arm followed by 50 mL of CS_2. The flask was then placed into a preheated 80 °C oil bath with efficient stirring. After several minutes the reaction mixture became brown in color. After 12 h the reaction mixture was black, at which time the flask was removed from the oil bath and the contents were allowed to cool to room temperature. The reflux condenser was replaced with a distillation head and excess CS_2 was removed by distillation. The remaining solvent was removed under reduced pressure with the aid of a rotary evaporator to produce a black residue, which was then re-dissolved in EtOAc and filtered through a pad of celite. The flask was then wrapped in aluminum foil and the solvent was once again removed under reduced pressure with the aid of a rotary evaporator. The resulting yellow solid was dissolved in a minimum amount of MeCN (approximately 20 mL) to produce a clear yellow solution, which was transferred to a 500 mL round bottom flask wrapped in aluminum foil. Approximately 450 mL of Et_2O was carefully layered on top of the yellow solution. The flask was stopped and left at room temperature overnight after which it was placed in a freezer set to -20 °C for 24 h to produce an off-white solid. The flask was removed from the freezer and the solution was filtered while cold to collect the white material (26.2 g, 96%). The white solid was kept in a refrigerator (4 °C) with the exclusion of light[2].



b) To a mixture of N-Chlorophthalimide (1.81 g, 10 mmol), $AgSCF_3$ (2.5 g, 12 mmol) in a 100 mL of round bottom flask was added dried CH_3CN (20 mL) under argon atmosphere. The mixture was stirred at room temperature for 3 h. Then the solvent

was evacuated under rotary evaporator. The residue was added CH_2Cl_2 (20 mL), then filtered through a short plug of Celite. The filter was evacuated again under reduced pressure to give the title compound as a white solid (2.3 g, 93%)[3].

II.III Procedures for the Synthesis of Starting Material Enamides (7a-7n)

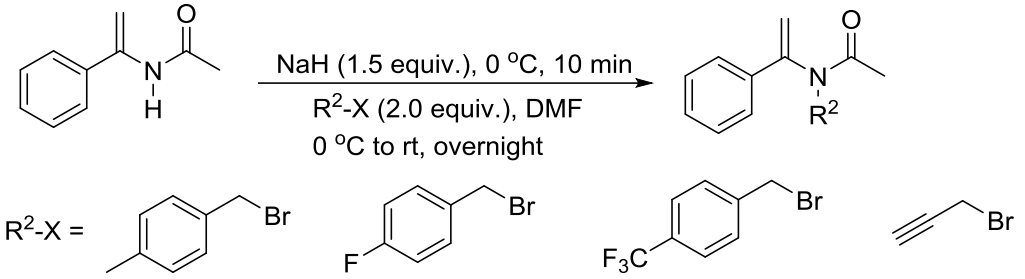


Synthetic procedure: a) A mixture of ketone (1.0 equiv.), NaOAc (1.2 equiv.) and hydroxylamine hydrochloride (1.2 equiv.) in methanol (0.5 M) was stirred for 2 h at 60 °C. Add water after cooling down to room temperature, then the mixture was extracted with ethyl acetate twice. The organic layer was collected, dried over $MgSO_4$ and vacuo to afford the ketoxime which was used without further purification for the next step.

b) To an oven-dried 50 mL two-neck round-bottom flask assembled with condenser was added the above ketoxime. The flask was vacuumed and back filled with N_2 for three times. Anhydrous toluene (0.5 M) was added followed by acetic anhydride (3.0 equiv.), acetic acid (3.0 equiv.) and iron powder (2.0 equiv.). The reaction flask was put into a 70 °C preheated oil bath and allowed to stir under nitrogen atomsphere. After the reaction completed and cooled to room temperature, ethyl acetate was added and the mixture was filtered through a short pad of celite. The solution thus was evaporated to get the crude enamide, which was directly purified by column chromatography.

c) 10 mmol (1.0 equiv.) of the N-acyl enamides was dissolved in 30 mL dry DMF in a dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 15 mmol (1.5 equiv.) sodium hydride was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then 20 mmol (2.0 equiv.) BnBr was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding 10 mL water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure

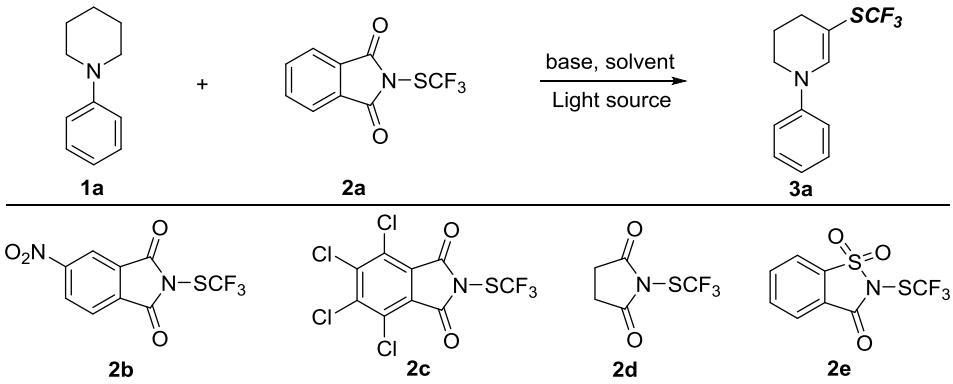
product[4].



Synthetic procedure: 10 mmol (1.0 equiv.) of the N-acyl enamides was dissolved in 30 mL dry DMF in a dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 15 mmol (1.5 equiv.) sodium hydride was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then 20 mmol (2.0 equiv.) R^2-X was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding 10 mL water at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product[5].

III. Optimization conditions for the synthesis of products 3, 8

Table S1. Screening of reaction conditions [a]

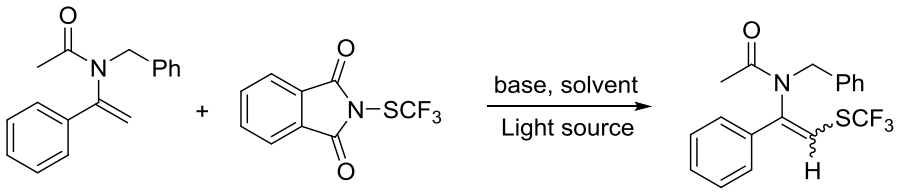


Entry	R-SCF_3 (eq.)	Solvent (mL)	Base (eq.)	Light source	Time (h)	Yield (%)
1	**2a** (2)	**CH_3CN (2)**	Na_2CO_3 (2)	Blue LED 30W	30	23
2	**2a** (2)	**Acetone (2)**	Na_2CO_3 (2)	Blue LED 30W	24	25
3	**2a** (2)	**DCM (2)**	Na_2CO_3 (2)	Blue LED 30W	24	Trace
4	**2a** (2)	**DMSO (2)**	Na_2CO_3 (2)	Blue LED 30W	5	Trace
5	**2a** (2)	**DMF (2)**	Na_2CO_3 (2)	Blue LED 30W	5	Trace
6	**2a** (2)	**DCE (2)**	Na_2CO_3 (2)	Blue LED 30W	20	Trace
7	**2a** (2)	**THF (2)**	Na_2CO_3 (2)	Blue LED 30W	20	Trace
8	**2a** (2)	Acetone (2)	**Cs_2CO_3 (2)**	Blue LED 30W	24	Trace
9	**2a** (2)	Acetone (2)	**K_2CO_3 (2)**	Blue LED 30W	24	13
10	**2a** (2)	Acetone (2)	**$NaHCO_3$ (2)**	Blue LED 30W	30	17
11	**2a** (2)	**Acetone (1)**	Na_2CO_3 (2)	Blue LED 30W	30	12

12	**2a** (2)	**Acetone (4)**	Na_2CO_3 (2)	Blue LED 30W	30	14
13	**2a** (2)	Acetone (2)	Na_2CO_3 (2)	**Blue LED 40W**	36	46
14	**2a (3)**	Acetone (2)	**Na_2CO_3 (2)**	Blue LED 40W	24	48
15	**2a** (4)	Acetone (2)	**Na_2CO_3 (2)**	Blue LED 40W	14	62
16[b]	**2a** (4)	Acetone (2)	**Na_2CO_3 (1.2)**	Blue LED 40W	34	65
17[b]	**2a (4)**	**Acetone (2)**	**Na_2CO_3 (3)**	**Blue LED 40W**	**15**	**78**
18[b]	**2a (3)**	**Acetone (2)**	**Na_2CO_3 (3)**	**Blue LED 40W**	**16**	**72**
19	**2a (4)**	**Acetone (2)**	**Na_2CO_3 (3)**	**–**	**15**	**NR**
20[c]	**2a** (4)	Acetone (2)	Na_2CO_3 (3)	Blue LED 40W	26	71
21[d]	**2a** (4)	Acetone (2)	Na_2CO_3 (3)	Blue LED 40W	26	63
22[e]	**2a** (4)	Acetone (2)	Na_2CO_3 (3)	Blue LED 40W	24	56
23	**2b (2)**	Acetone (2)	Na_2CO_3 (3)	Blue-White LED 40W	24	NR
24	**2c (2)**	Acetone (2)	Na_2CO_3 (3)	Blue-White LED 40W	7	38
25	**2d (2)**	Acetone (2)	Na_2CO_3 (3)	Blue-White LED 40W	30	15
26	**2e (2)**	Acetone (2)	Na_2CO_3 (3)	Blue-White LED 40W	7	Trace

[a] General conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (2-4 equiv.). [b] 1.0 equiv. Na_2SO_4 was used. [c] 3.0 equiv. Na_2SO_4 was used. [d] 1.0 equiv. $MgSO_4$ was used. [e] 20 mg 4Å molecular sieves was used.

Table S2. Screening of reaction conditions [a]

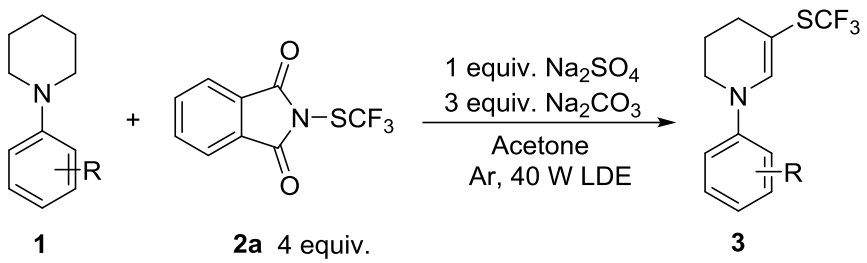


7 **2a** **8**

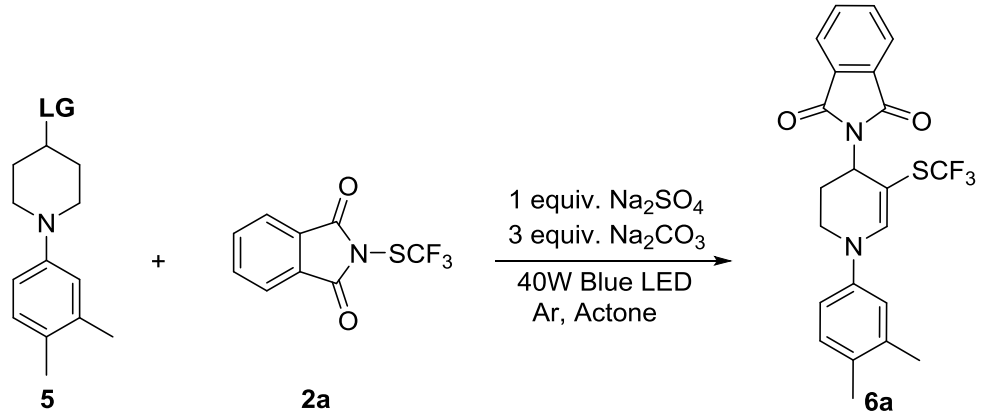
Entry	Solvent (mL)	Base (eq.)	Light source	Time (h)	Yield (%)
1	**CH_3CN (2)**	Na_2CO_3 (3)	Kessil Blue LED 40W	24	NR
2	**Acetone (2)**	**Na_2CO_3 (3)**	**Kessil Blue LED 40W**	**24**	**51**
3	**Toluene (2)**	Na_2CO_3 (3)	Kessil Blue LED 40W	24	NR
4	**DMSO (2)**	Na_2CO_3 (3)	Kessil Blue LED 40W	24	NR
5	**DMF (2)**	Na_2CO_3 (3)	Kessil Blue LED 40W	24	NR
6	Acetone (2)	**K_2CO_3 (3)**	Kessil Blue LED 40W	24	28
7	Acetone (2)	**K_3PO_4 (3)**	Kessil Blue LED 40W	24	21
8	Acetone (2)	**$NaHCO_3$ (3)**	Kessil Blue LED 40W	24	18
9	**Acetone (1)**	Na_2CO_3 (3)	Kessil Blue LED 40W	24	33
10	**Acetone (2)**	**Na_2CO_3 (3)**	**Kessil Blue LED 40W**	**36**	**62**
11	**Acetone (2)**	**Na_2CO_3 (3)**	**–**	**24**	NR

[a] General conditions: **7a** (0.1 mmol, 1.0 equiv.), **2a** (4.0 equiv.), Na_2SO_4 (1.0 equiv.) was used.

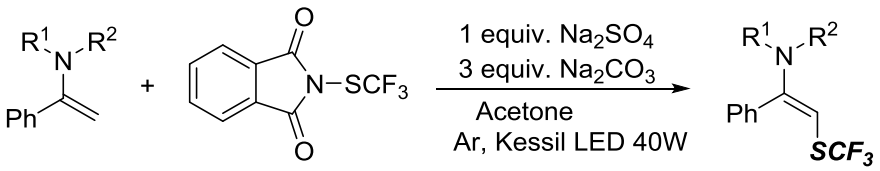
IV. General Procedure for the synthesis of products 3, 4, 6a, 8



General Procedure A: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 2-((trifluoromethyl)thio)isoindoline-1,3-dione 2a (0.4 mmol, 4 equiv., 98mg). The flask was evacuated and backfilled with Ar for 3 times. Then 1-phenylpiperidine 1a (0.1 mmol, 1 equiv., 16 mg), acetone (2 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of 40 W blue LEDs. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (200:1)).



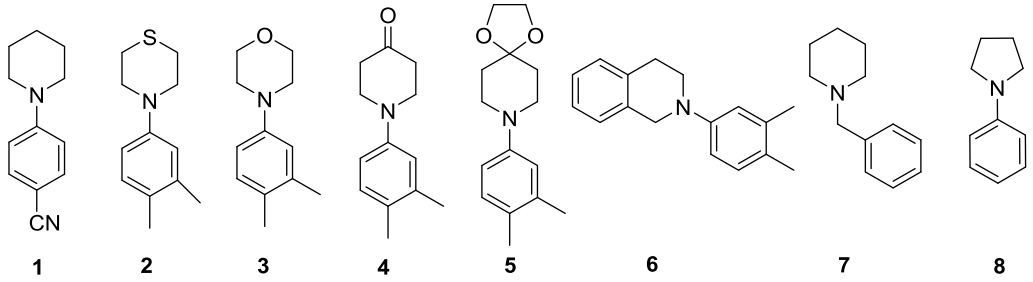
General Procedure B: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 2-((trifluoromethyl)thio)isoindoline-1,3-dione 2a (0.4 mmol, 4 equiv., 98mg). The flask was evacuated and backfilled with Ar for 3 times. Then 1-(3,4-dimethylphenyl)-4-fluoropiperidine 5a (0.1 mmol, 1 equiv., 20.7 mg), acetone (2 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (6:1)).



7 (1.0 equiv.) **2a** (4.0 equiv.) **8**

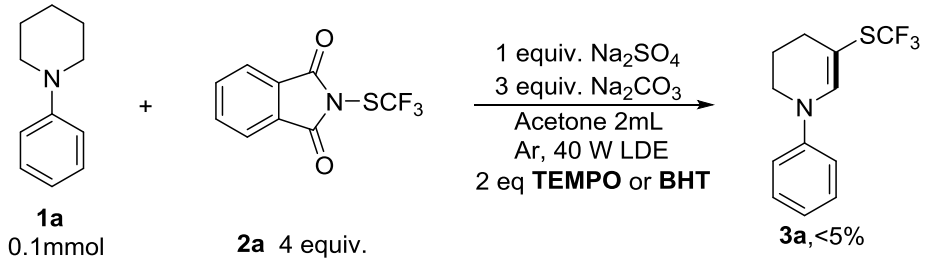
General Procedure C: An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg), 2-((trifluoromethyl)thio)isoindoline-1,3-dione 2a (0.4 mmol, 4 equiv., 98mg). The flask was evacuated and backfilled with Ar for 3 times. Then acetone (2 mL) and N-benzyl-N-(1-phenylvinyl)acetamide 7a (0.1 mmol, 1 equiv., 25.1 mg) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W, λ = 427 nm). The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. After being stirred at r.t. for the indicated time, 4 mL water was added to quench the reaction, and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography afforded the product (petroleum ether/ethyl acetate as eluent (10:1)).

Failed Substrates: The substrates (1-8) did not yield products under standard reaction conditions.



V. Mechanistic Studies

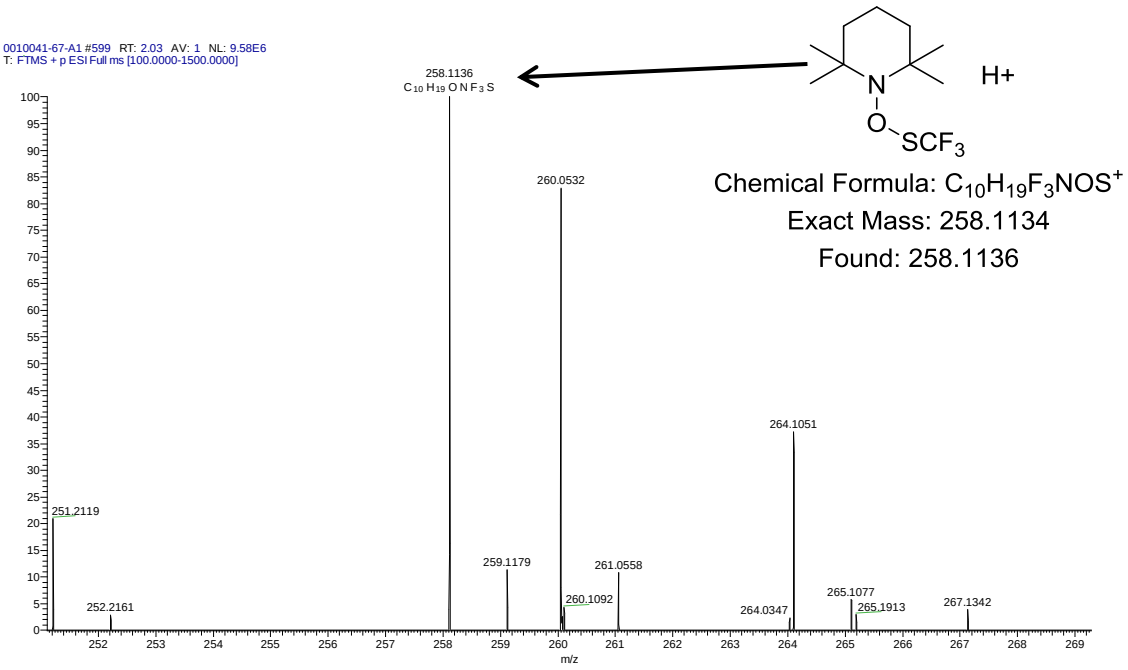
V. I Radical quenching experiment

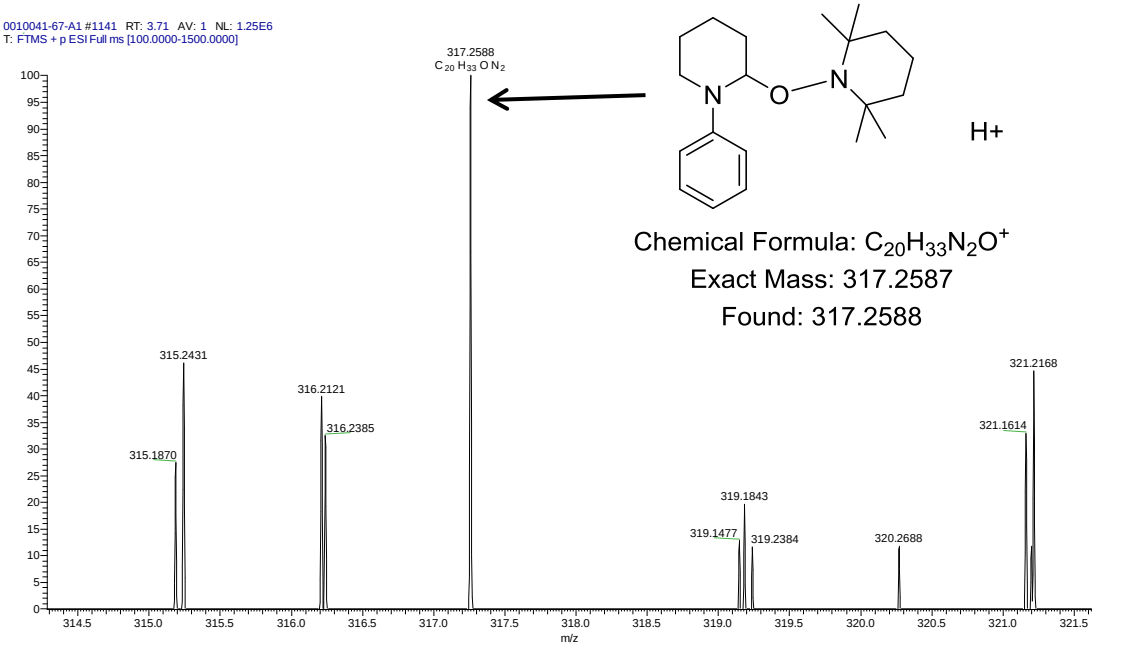


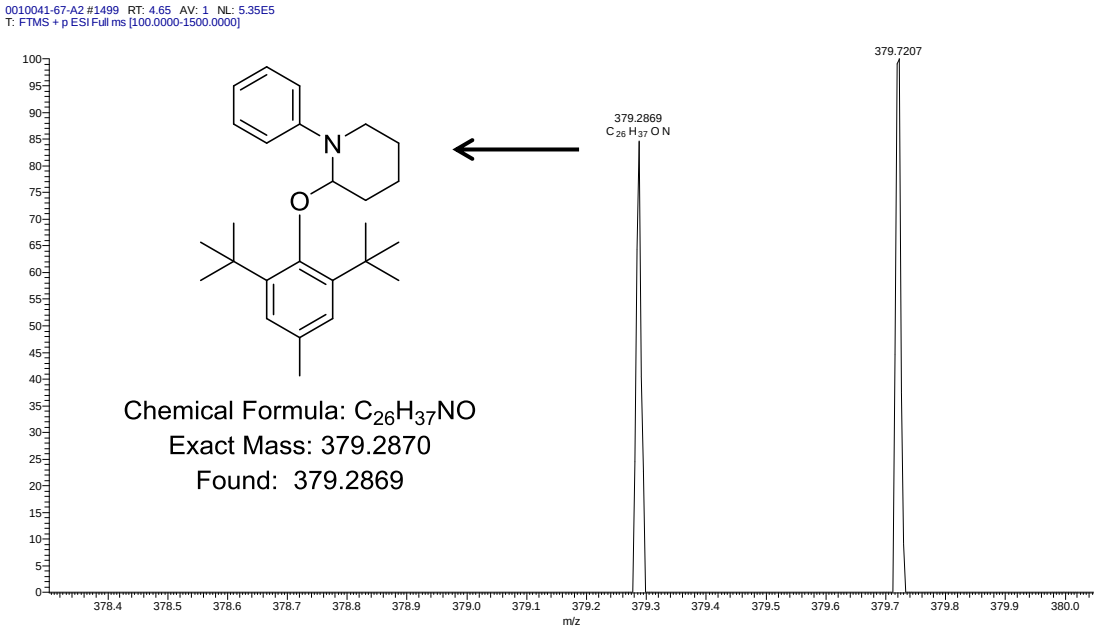
Scheme S1. Mechanistic Studies

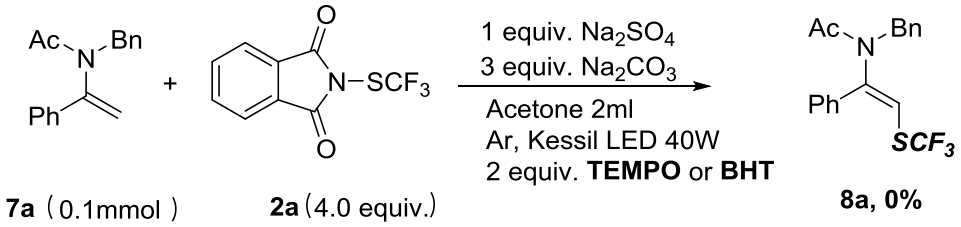
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 2-((trifluoromethyl)thio)isoindoline-1,3-dione **2a** (0.4 mmol, 4 equiv., 98 mg), Na_2SO_4 (0.1 mmol, 1 equiv., 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv., 31 mg) and a radical quencher (TEMPO or BHT, 0.2 mmol, 2 equiv., 31 mg or 44 mg). The flask was

evacuated and backfilled with Ar for 3 times. Then 1-phenylpiperidine 1a (0.1 mmol, 1 equiv., 16.1 mg), acetone (2 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of 40 W blue LEDs. The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. Stirring the reaction mixture at room temperature revealed that only trace product formation (monitored by TLC). The product 3a was significantly suppressed by radical quenchers, which indicated that a radical process was involved in this transformation.



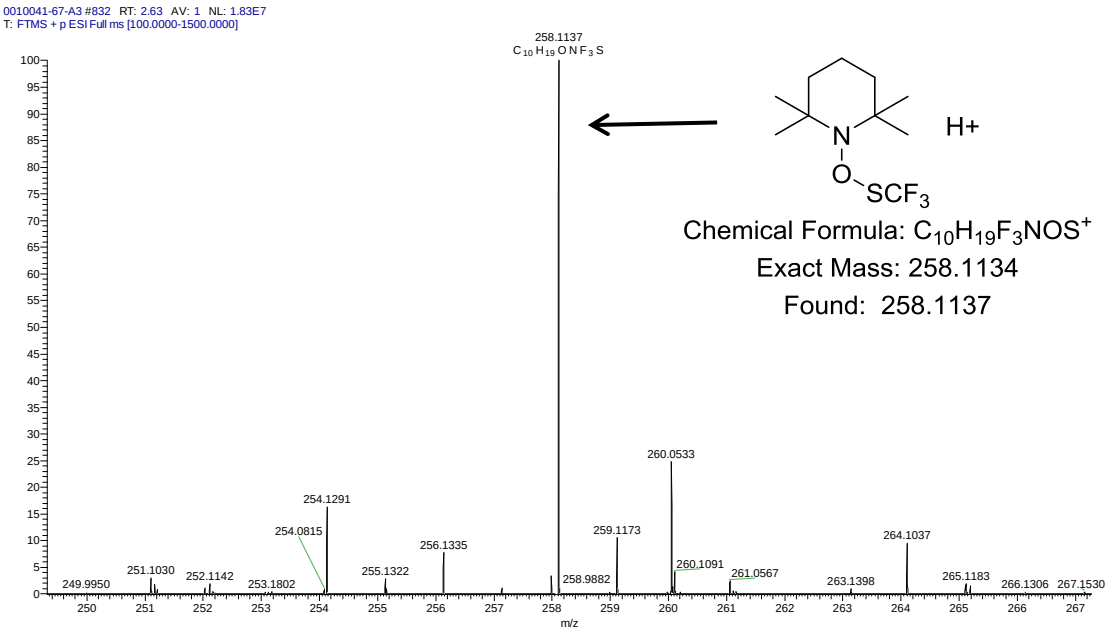






Scheme S2. Mechanistic Studies

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 2-((trifluoromethyl)thio)isoindoline-1,3-dione 2a (0.4 mmol, 4 equiv., 98 mg), Na_2SO_4 (0.1 mmol, 1 equiv, 14 mg), Na_2CO_3 (0.3 mmol, 3 equiv, 31 mg) and a radical quencher (TEMPO or BHT, 0.2 mmol, 2 equiv., 31 mg or 44 mg). The flask was evacuated and backfilled with Ar for 3 times. Then N-benzyl-N-(1-phenylvinyl)acetamide 7a (0.1 mmol, 1 equiv., 25.1 mg), acetone (2 mL) were added with syringe. The reaction mixture was then stirred at room temperature under the irradiation of blue LEDs (Kessil A 160WE TUNA BLUE 40W, λ = 427 nm). The Schlenk tube was positioned approximately 2 cm away from a 40 W blue LEDs lamp. Stirring the reaction mixture for a specified time at room temperature revealed that no product formation (monitored by TLC). The product 8a was significantly suppressed by radical quenchers, which indicated that a radical process was involved in this transformation.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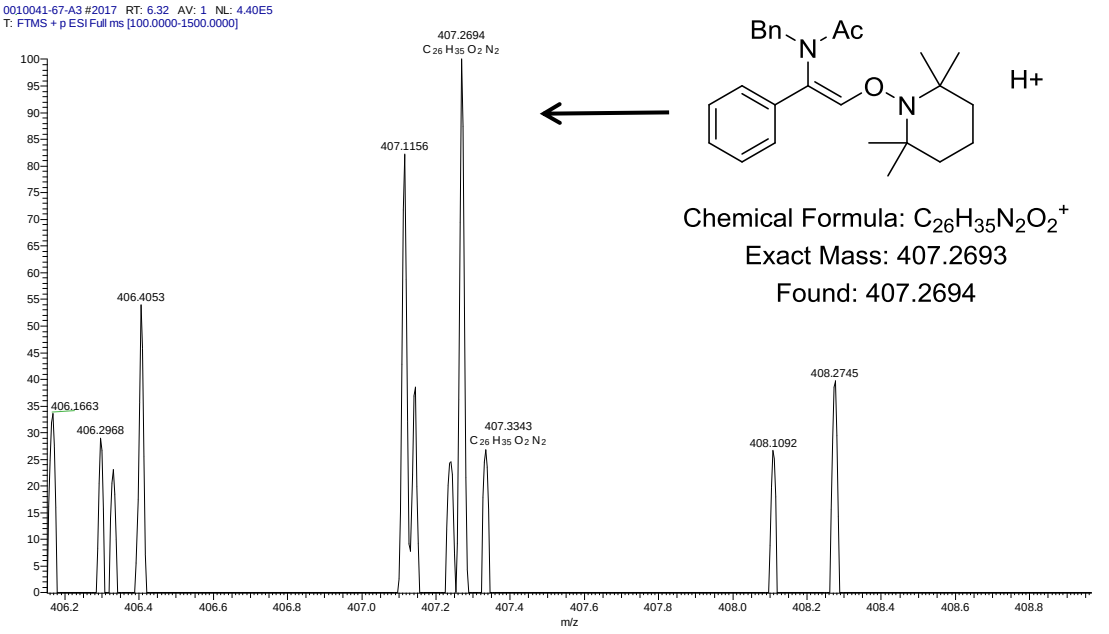
258.1137
C10 H19 O N F3 S
H+
Chemical Formula: C10H19F3NOS+
Exact Mass: 258.1134
Found: 258.1137
m/z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H+
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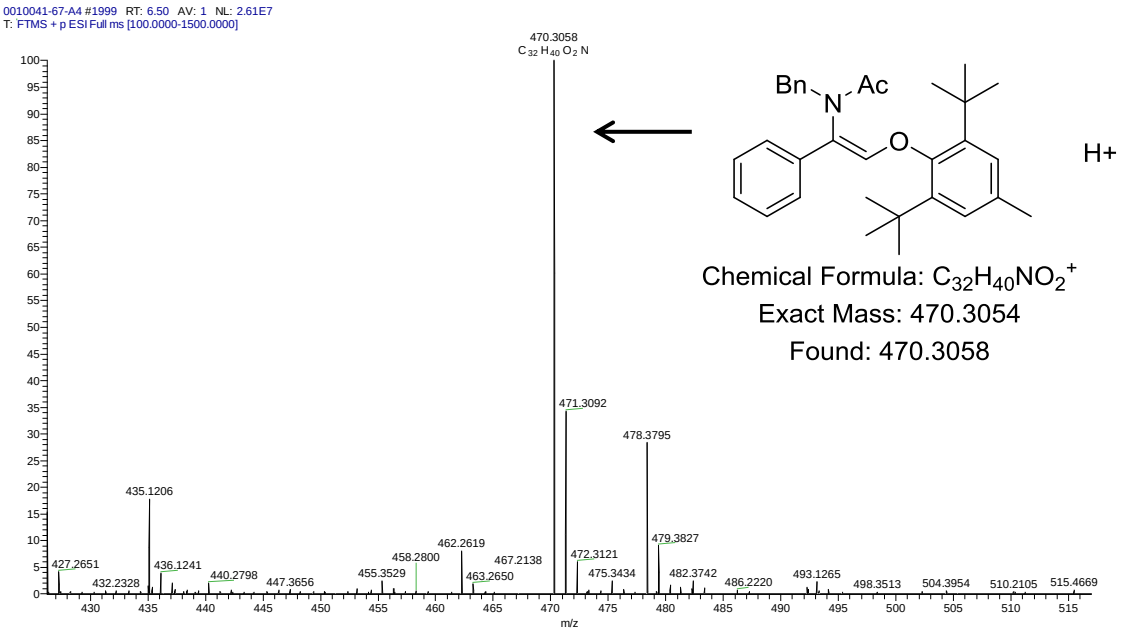
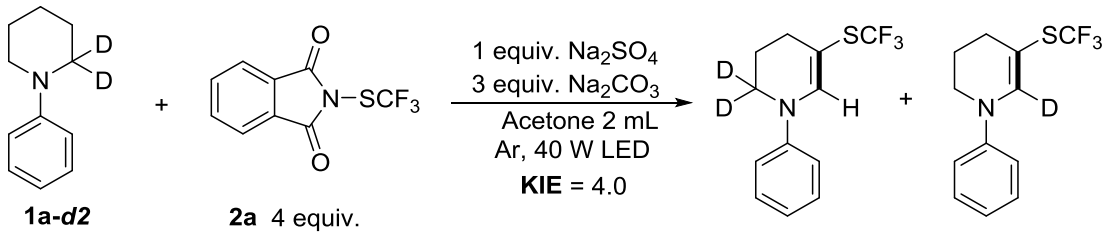


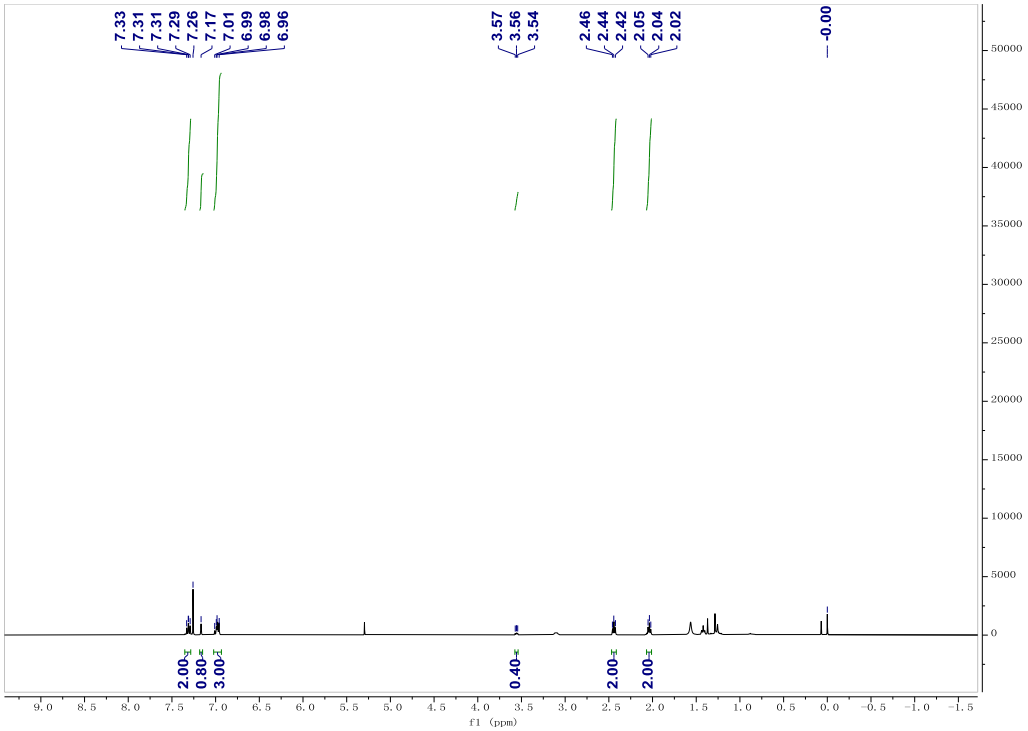
V. II Deuterium labeling experiments



1a-*d2* 0.1mmol

2a 4 equiv.

Following **Conditions A** using **1a-*d2*** yielded the desired deuterated products as a colorless oil. For the calculation of the KIE value, the ratio was determined by ^{1}H NMR spectroscopy.



V. III UV-vis absorbance experiment

Further to substantiate the formation of EDA complex, we have carried out UV-Vis spectroscopic measurements with various combinations of **1a**, **2a**, Na_2CO_3 and **1a**, **2a** with Na_2CO_3 (1:1:1) ratio in Acetone medium, and **1a**, **2a** with Na_2CO_3 (1:4:3) ratio in Acetone medium (Figure S1). As presented in Figure S1, when **1a** and **2a** were mixed in acetone in a 1:4 ratio a new peak was detected in the visible region (bathochromic shift). This result suggests the formation of EDA complex.

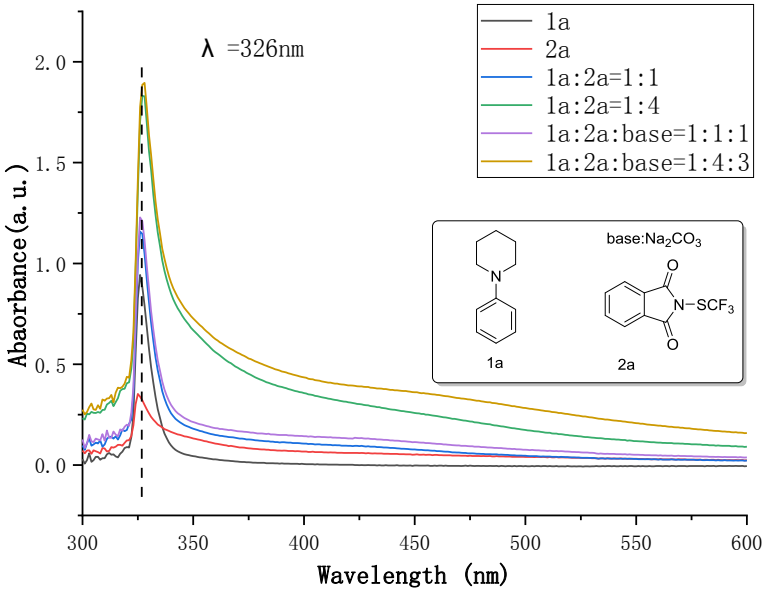


Figure S1. Comparison of the UV-vis spectra of **1a**, **2a** and the mixture of **1a**+**2a** (1:1), **1a**+**2a**+Na_2CO_3 (1:1:1), and **1a**+**2a**+Na_2CO_3 (1:4:3) in 0.01M solution of Acetone

A UV-vis absorbance experiment has been carried out for confirming the formation of EDA complex as illustrated below in Figure S2. As presented in Figure S2, when **7a** and **2a** were mixed in acetone in a 1:4 ratio, an obvious bathochromic shift of the UV-vis absorbance was observed, strongly suggesting that **7a**-**2a** EDA complex might indeed be formed in the mixed solution.

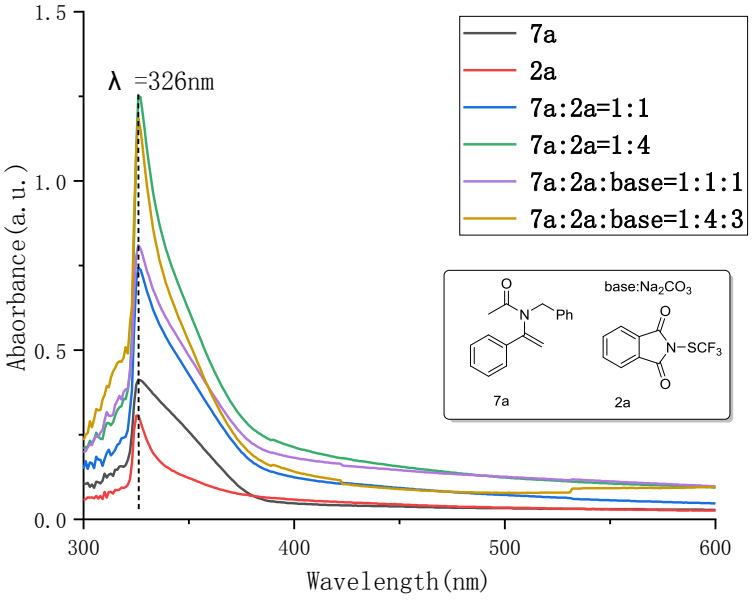


Figure S2. Comparison of the UV-vis spectra of 7a, 2a and the mixture of 7a+2a (1:1), 7a+2a+Na_2CO_3 (1:1:1), and 7a+2a+Na_2CO_3 (1:4:3) in 0.01M solution of Aceton

We observed a high degree of background reaction and that the reaction mixture changed color upon mixing two colorless reagents **1a** and **2a**.

Figure S3. Photos of 1a, 2a and the mixture of 1a+2a (1:4), and 1a+2a+Na_2CO_3 (1:4:3) in 0.03M solution of Acetone

Similarly, Figure S4 shows the light irradiation study for the mixture of **2a** (0.03 M) and Na_2CO_3 (0.04 mM) in Acetone. Thereafter, the quartz cuvette was kept under irradiation of 40 W blue LEDs for 5 minutes and the absorption spectra was recorded immediately. This process was repeated for obtaining the absorption spectra after consecutive 5 min cycles of irradiation with the light source. As presented in Figure S4, while neither Na_2CO_3 nor **2a** individually showed significant UV-vis absorption

in the visible region, the mixture of both showed a red shift, especially after irradiation. This indicates that there is a possibility of interaction between carbonate and **2a**, leading to photoinduced cross-species SET.

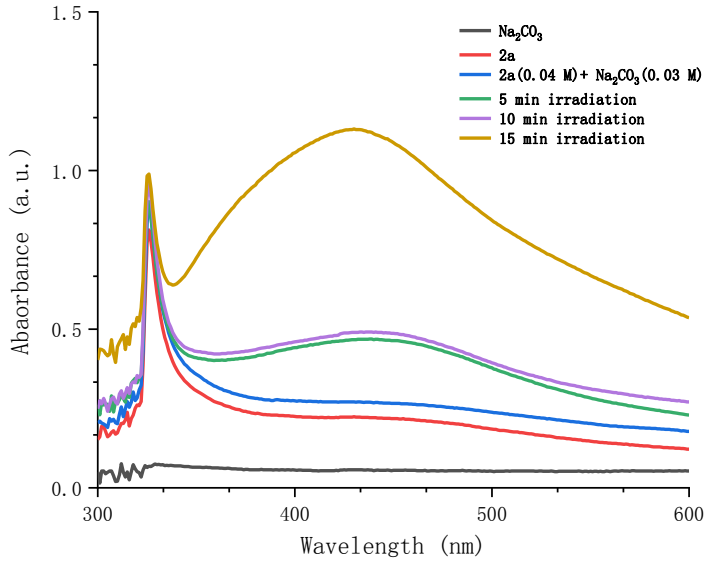


Figure S4. Comparison of the UV-vis spectra of **2a**, Na_2CO_3, and mixture of **2a** and Na_2CO_3.

Two oven-dried Schlenk tubes (10 mL) were equally equipped with a magnetic stir bar, Na_2SO_4 (0.1 mmol), Na_2CO_3 (0.3 mmol,), 2-((trifluoromethyl)thio)isoindoline-1,3-dione 2a (0.4 mmol,). The flask was evacuated and backfilled with Ar for 3 times. Then 1-phenylpiperidine **1a** (0.1 mmol,), acetone (2 mL) were added with syringe. Two oven-dried Schlenk tubes were then stirred at room temperature under the irradiation of 40 W blue LEDs at the same time. One tube stopped irradiation after 4 h of light irradiation, this resultant solution was further analysed in GC to obtain the yield of the **3a**. The other tube stopped irradiation and continued stirred for two hours, and this resultant solution was analysed similarly. The light was switched ON and OFF alternatively for a period and monitored the conversion of the product. This cycle was repeated and the yield of **3a** with respect to time was plotted (Figure S5).

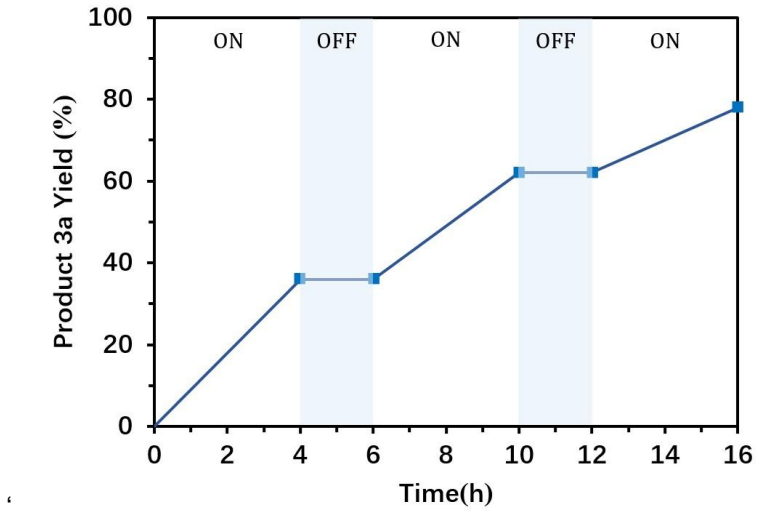
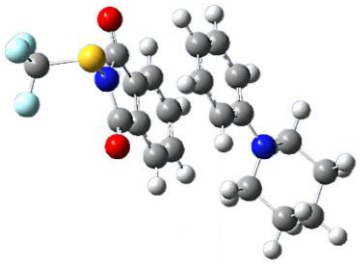


Figure S5. Graph for Switch on-off experiment

V. IV Density Functional Theory Calculations

All calculations were carried out with the Gaussian 09 package. Optimization and frequency analysis were performed at M062X/def2tzvp level with SMD solvation model (solvent = Dichloroethane). All the optimized structures were characterized to be energy minima by frequency analysis under the same level (NIMG = 0). The energies of each molecule was calculated at M062X/def2tzvp level with SMD solvation model (solvent = Dichloroethane) with the optimized geometries.

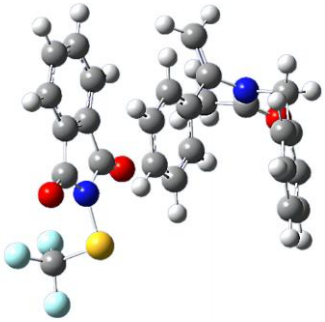
Cartesian Coordinates for the Stationary Points Computational Details



C	-2.514200	0.278954	-0.601457
C	-1.185874	0.196491	-0.183538
C	-0.316697	1.297302	-0.307859
C	-0.853774	2.489694	-0.841599
C	-2.180634	2.562102	-1.247443
C	-3.027675	1.455853	-1.139239
H	-3.163335	-0.591073	-0.481540
H	-0.836358	-0.732218	0.264772
H	-0.218731	3.365335	-0.971102

H	-2.553953	3.503101	-1.658547
H	-4.070993	1.513075	-1.454813
C	1.697780	2.332693	0.689689
C	1.618948	-0.071217	0.359372
C	3.176992	2.391275	0.327682
H	1.615844	2.218953	1.792081
H	1.193693	3.269837	0.429778
C	3.114379	-0.088612	0.042348
H	1.455033	-0.325404	1.430503
H	1.124678	-0.846477	-0.238689
C	3.850972	1.073710	0.701250
H	3.649052	3.237662	0.848321
H	3.273637	2.568629	-0.755456
H	3.537933	-1.053640	0.358125
H	3.233304	-0.019906	-1.050952
H	4.911557	1.075316	0.410413
H	3.820497	0.952692	1.798517
N	1.033572	1.215069	0.035782
C	-1.473198	0.037554	3.530977
C	-0.567996	1.107392	3.525251
C	-0.914722	2.343280	2.973750
C	-2.180539	2.458318	2.419888
C	-3.077823	1.396794	2.424796
C	-2.751356	0.169574	2.982708
H	-1.171446	-0.913045	3.973262
H	0.422147	0.970406	3.963887
H	-0.226038	3.188882	2.963878
H	-3.466204	-0.654222	2.975271

C	-2.802650	3.621212	1.721540
C	-4.326268	1.815141	1.721682
O	-2.348547	4.699447	1.487250
O	-5.310596	1.185609	1.480432
N	-4.101013	3.171389	1.356078
S	-5.112724	4.024718	0.312474
C	-6.096472	4.853459	1.602088
F	-5.347932	5.619626	2.380377
F	-6.997764	5.609133	0.990279
F	-6.719881	3.985375	2.383575



C	0.493689	-1.039815	-2.664965
C	1.280735	-1.639051	-1.683505
C	1.595659	-0.951046	-0.504053
C	1.103979	0.350971	-0.329479
C	0.328019	0.953229	-1.316370
C	0.017927	0.260200	-2.488195
H	0.263083	-1.585089	-3.581700
H	1.684812	-2.639959	-1.847608
H	1.350275	0.905757	0.577315
H	-0.022302	1.978231	-1.174014
H	-0.592588	0.731525	-3.259969
C	-1.601262	-4.134163	-1.038924
C	-0.968494	-4.069285	0.209352
C	-0.955221	-2.886946	0.954965
C	-1.592418	-1.785531	0.402982
C	-2.225511	-1.851477	-0.833925
C	-2.246025	-3.019288	-1.581350
H	-1.592649	-5.074369	-1.592141

H	-0.480080	-4.961094	0.605821
H	-0.458326	-2.820143	1.924125
H	-2.743218	-3.052287	-2.551534
C	-1.727803	-0.401275	0.942606
C	-2.795808	-0.510867	-1.158969
O	-1.294646	0.067080	1.953021
O	-3.373189	-0.145459	-2.136676
N	-2.488998	0.298075	-0.029121
S	-2.741768	1.965125	0.015258
C	-4.365211	1.905986	0.840818
F	-4.293003	1.327219	2.029223
F	-4.779918	3.155175	0.991297
F	-5.257699	1.236320	0.128226
C	2.464787	-1.566921	0.536689
C	2.512685	-2.884249	0.772213
H	1.854860	-3.573221	0.241364
H	3.206340	-3.285688	1.512650
N	3.311275	-0.678799	1.265319
C	3.048224	-0.240490	2.547905
O	3.768200	0.570799	3.092585
C	1.819180	-0.806293	3.227317
H	1.724966	-0.308036	4.197071
H	0.911072	-0.622440	2.633970
H	1.915248	-1.889892	3.375646
C	4.478017	-0.131368	0.562257
H	4.916631	-0.940978	-0.038397
C	4.150136	1.053975	-0.318229
C	4.083424	0.920504	-1.706802
C	3.831857	2.286075	0.266244
C	3.681400	1.991309	-2.504584
H	4.324915	-0.041145	-2.166801
C	3.427837	3.356074	-0.529451
H	3.888120	2.384578	1.353159
C	3.346026	3.209450	-1.915697
H	3.621655	1.870725	-3.587421
H	3.176953	4.311787	-0.066110
H	3.026285	4.047817	-2.536729
H	5.193976	0.160977	1.340523

VI. Crystal Data

Method for single crystals cultivation: The single crystal for compound **6a** (CCDC2219764) was prepared from a mixed solvent of ethyl acetate (EA) and petroleum ether (PE) (v/v = 1:4). A pure solid sample (20-30 mg) was dissolved in EA (2 mL) in a vial at room temperature, and then PE (8-9 mL) was added into the above

solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

X-ray Crystal Diffraction Data for 6a (Thermal ellipsoids are shown with 30% probability)

Datablock: 6a (CCDC2219764**)**

Bond precision: C-C = 0.0021 A Wavelength=1.54178

Cell: a=9.9803(6) b=10.0449(6) c=10.9814(7)
alpha=70.977(2) beta=87.846(3) gamma=74.416(3)

Temperature: 100 K

	Calculated	Reported
Volume	1001.00(11)	1001.00(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C22 H19 F3 N2 O2 S	C22 H19 F3 N2 O2 S
Sum formula	C22 H19 F3 N2 O2 S	C22 H19 F3 N2 O2 S
Mr	432.45	432.45
Dx,g cm^{-3}	1.435	1.435
Z	2	2
Mu (mm-1)	1.880	1.880
F000	448.0	448.0
F000’	450.16	
h,k,lmax	12,12,13	12,12,13
Nref	3663	3648
Tmin,Tmax	0.749,0.928	0.640,0.753
Tmin’	0.654	

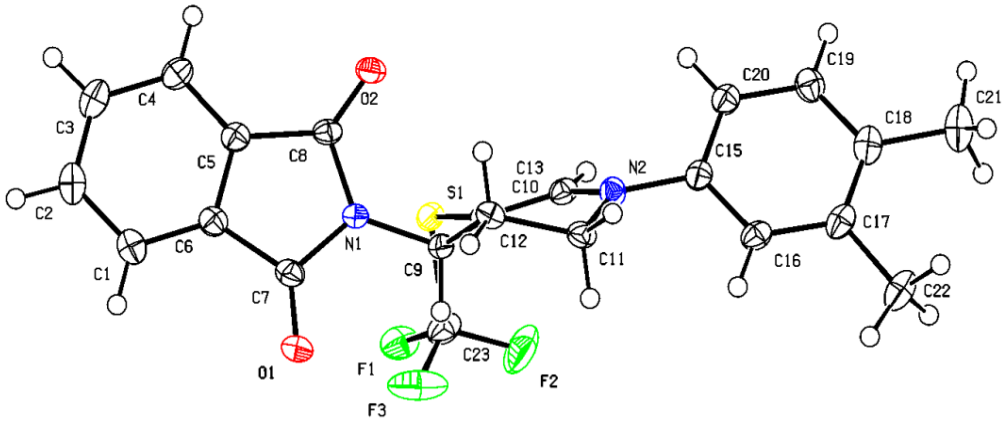
Correction method= # Reported T Limits: Tmin=0.640 Tmax=0.753

AbsCorr = MULTI-SCAN

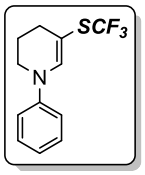
Data completeness= 0.996 Theta(max)= 68.270

R(reflections)= 0.0346(3339) wR2(reflections)= 0.0910(3648)

S = 1.057 Npar= 273

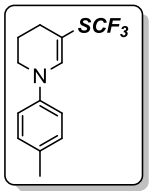


VII. Date of products 3, 4, 6a, 8



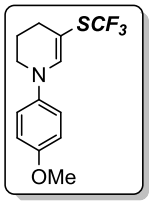
3a

1-phenyl-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 78%, 20.2 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.37 – 7.26 (m, 2H), 7.16 (s, 1H), 7.03 – 6.91 (m, 3H), 3.58 – 3.50 (m, 2H), 2.43 (t, J = 6.8 Hz, 2H), 2.04 (p, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.6, 142.4, 135.0 (q, J = 310 Hz), 129.4, 122.0, 116.6, 91.8, 45.0, 28.9, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -44.92. IR(cm^{-1}): 2929, 2852, 1617, 1595, 1494, 1316, 1111, 750, 693. HRMS (ESI) m/z calcd for $C_{12}H_{13}F_3NS^+(M+H)^+$ 260.0721, found 260.0715.



3b

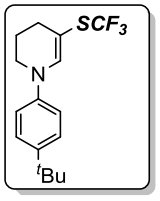
1-(p-tolyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 65%, 17.7 mg, oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.03 (d, J = 8.3 Hz, 3H), 6.79 (d, J = 8.5 Hz, 2H), 3.57 – 3.36 (m, 2H), 2.35 (t, J = 5.6 Hz, 2H), 2.22 (s, 3H), 1.95 (p, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 142.8, 135.0 (q, J = 310 Hz), 131.6, 129.9, 116.8, 90.7, 45.2, 28.9, 22.6, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$): -45.07. IR(cm^{-1}): 2924, 2853, 1606, 1514, 1324, 1145, 1111, 810. HRMS (ESI) m/z calcd for $C_{13}H_{15}F_3NS^+$ $(M+H)^+$ 274.0877, found 274.0871.



3c

1-(4-methoxyphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 51%, 14.7 mg, oil.

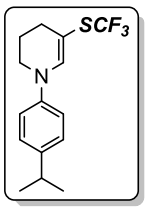
^{1}H NMR (400 MHz, $CDCl_3$): 6.97 (s, 1H), 6.89 – 6.71 (m, 4H), 3.71 (s, 3H), 3.51 – 3.31 (m, 2H), 2.35 (t, J = 6.3 Hz, 2H), 1.95 (p, J = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 155.2, 143.3, 139.9, 135.0 (q, J = 310 Hz), 118.7, 114.6, 89.8, 55.6, 45.7, 28.8, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -45.21. IR(cm^{-1}): 2927, 2852, 1613, 1511, 1244, 1110, 1032, 822. HRMS (ESI) m/z calcd for $C_{13}H_{15}F_3NOS^+$ $(M+H)^+$ 290.0826, found 290.0822.



3d

1-(4-(tert-butyl)phenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 63%, 19.8 mg, oil.

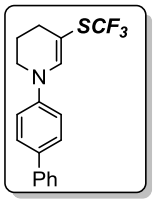
^{1}H NMR (400 MHz, $CDCl_3$): 7.26 (d, J = 8.8 Hz, 2H), 7.07 (s, 1H), 6.84 (d, J = 8.7 Hz, 2H), 3.53 – 3.40 (m, 2H), 2.36 (t, J = 6.3 Hz, 2H), 1.95 (p, J = 6.1 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.9, 143.3, 142.7, 135.0 (q, J = 310 Hz), 126.2, 116.3, 90.9, 45.0, 34.1, 31.4, 28.9, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -45.06. IR(cm^{-1}): 2959, 2863, 1605, 1517, 1262, 1146, 1111, 825. HRMS (ESI) m/z calcd for $C_{16}H_{21}F_3NS^+$ $(M+H)^+$ 316.1347, found 316.1341.



3e

1-(4-isopropylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 68%, 20.4 mg, oil.

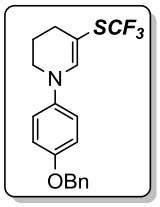
^{1}H NMR (400 MHz, $CDCl_3$): 7.13 – 7.00 (m, 3H), 6.83 (d, J = 8.6 Hz, 2H), 3.51 – 3.41 (m, 2H), 2.79 (p, J = 6.9 Hz, 1H), 2.35 (t, J = 6.6 Hz, 2H), 1.94 (p, J = 6.1 Hz, 2H), 1.15 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 142.7, 135.0 (q, J = 310 Hz), 127.3, 116.8, 90.8, 45.2, 33.4, 28.9, 24.1, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -45.06. IR(cm^{-1}): 2925, 2854, 1606, 1514, 1318, 1146, 1112, 824. HRMS (ESI) m/z calcd for $C_{15}H_{19}F_3NS^+$ $(M+H)^+$ 302.1190, found 302.1185.



3f

1-([1,1'-biphenyl]-4-yl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, M.P.= 123-125 °C, 53%, white solid, 17.7 mg.

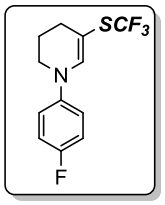
^{1}H NMR (400 MHz, $CDCl_3$): 7.59 – 7.50 (m, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 10.5 Hz, 1H), 7.03 (d, J = 8.6 Hz, 2H), 3.58 (t, J = 5.6 Hz, 2H), 2.45 (t, J = 6.3 Hz, 2H), 2.14 – 1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.8, 142.0, 140.4, 134.9 (q, J = 306 Hz), 134.7, 128.8, 127.9, 126.9, 126.6, 116.7, 92.3, 45.0, 28.9, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -44.79. IR(cm^{-1}): 2923, 2853, 1454, 1260, 1107, 1019, 820, 799. HRMS (ESI) m/z calcd for $C_{18}H_{17}F_3NS^+$ $(M+H)^+$ 336.1034, found 336.1028.



3g

1-(4-(benzyloxy)phenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, M.P.= 72-74 °C, 45%, white solid, 16.4 mg.

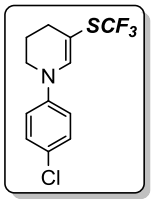
^{1}H NMR (400 MHz, $CDCl_3$): 7.36 – 7.22 (m, 5H), 6.97 (s, 1H), 6.89 – 6.77 (m, 4H), 4.95 (s, 2H), 3.48 – 3.33 (m, 2H), 2.34 (t, J = 6.3 Hz, 2H), 1.94 (p, J = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 143.2, 140.0, 137.0, 135.0 (q, J = 310 Hz), 128.5, 127.9, 127.4, 118.5, 115.7, 89.9, 70.4, 45.6, 28.8, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -45.15. IR(cm^{-1}): 2960, 2851, 1614, 1514, 1259, 1102, 1016, 799, 697. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NOS^+$ $(M+H)^+$ 366.1139, found 366.1133.



3h

1-(4-fluorophenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 58%, 16.1 mg, oil.

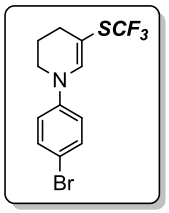
^{1}H NMR (400 MHz, $CDCl_3$): 7.06 (s, 1H), 7.04 – 6.96 (m, 2H), 6.91 (dd, J = 9.1, 4.5 Hz, 2H), 3.55 – 3.30 (m, 2H), 2.43 (t, J = 6.3 Hz, 2H), 2.04 (dt, J = 12.0, 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.5, 157.1, 142.6 (t, J = 40 Hz), 134.9 (q, J = 310 Hz), 118.4 (t, J = 10 Hz), 116.1 (t, J = 30 Hz), 91.6, 45.5, 28.7, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -44.96, -121.62. IR(cm^{-1}): 2928, 2853, 1617, 1509, 1494, 1317, 1231, 1110, 823. HRMS (ESI) m/z calcd for $C_{12}H_{12}F_4NS^+$ $(M+H)^+$ 278.0627, found 278.0622.



3i

1-(4-chlorophenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 54%, 15.8 mg, oil.

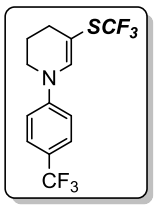
^{1}H NMR (400 MHz, $CDCl_3$): 7.28 – 7.22 (m, 2H), 7.09 (s, 1H), 6.91 – 6.80 (m, 2H), 3.61 – 3.46 (m, 2H), 2.44 (t, J = 6.3 Hz, 2H), 2.05 (dt, J = 12.2, 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.2, 141.8, 134.9 (q, J = 310 Hz), 129.3, 127.0, 117.7, 93.0, 45.1, 28.8, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -44.74. IR(cm^{-1}): 2927, 2853, 1617, 1593, 1495, 1330, 1111, 818, 525. HRMS (ESI) m/z calcd for $C_{12}H_{12}ClF_3NS^+$ $(M+H)^+$ 294.0331, found 294.0326.



3j

1-(4-bromophenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, M.P.= 36-38 °C, 38%, white solid, 12.8 mg.

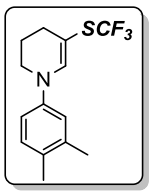
^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (dd, J = 71.6, 8.9 Hz, 2H), 7.01 (s, 1H), 6.79 – 6.61 (m, 2H), 3.52 – 3.33 (m, 2H), 2.35 (t, J = 6.3 Hz, 2H), 1.96 (p, J = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.2 (t, J = 60 Hz), 141.6 (t, J = 20 Hz), 138.2, 134.9 (q, J = 310 Hz), 132.2, 118.4 (t, J = 40 Hz), 93.2, 45.0 (t, J = 10 Hz), 28.8, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -44.68. IR(cm^{-1}): 2924, 2850, 1617, 1587, 1492, 1317, 1111, 967, 816. HRMS (ESI) m/z calcd for $C_{12}H_{12}BrF_3NS^+$ $(M+H)^+$ 337.9826, found 337.9820.



3k

1-(4-(trifluoromethyl)phenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 40%, 13.1 mg, oil.

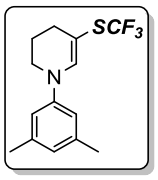
^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (d, J = 8.5 Hz, 2H), 7.12 (s, 1H), 6.94 (d, J = 8.5 Hz, 2H), 3.50 (t, J = 5.7 Hz, 2H), 2.39 (t, J = 6.1 Hz, 2H), 2.08 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.8, 140.8, 134.8 (q, J = 303 Hz), 126.7 (q, J = 3.3 Hz), 123.9 (q, J = 30 Hz), 115.6, 95.3, 44.7, 28.8, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -44.43, -61.74. IR(cm^{-1}): 2931, 2854, 1607, 1522, 1324, 1111, 1071, 968, 829. HRMS (ESI) m/z calcd for $C_{13}H_{12}F_6NS^+$ $(M+H)^+$ 328.0595, found 328.0589.



3l

1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 75%, 21.5 mg, oil.

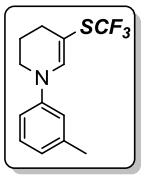
^{1}H NMR (400 MHz, $CDCl_3$): 7.12 (s, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.76 (s, 1H), 6.71 (d, J = 8.1 Hz, 1H), 3.58 – 3.44 (m, 2H), 2.46 – 2.35 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3 H), 2.02 (p, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.8, 142.9, 137.6, 135.0 (q, J = 310 Hz), 130.3, 118.3, 114.2, 90.4, 45.2, 28.9, 22.6, 20.1, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.10. IR(cm^{-1}): 2925, 2854, 1606, 1504, 1314, 1111, 1005, 807. HR MS (ESI) m/z calcd for $C_{14}H_{17}F_3NS^+$ $(M+H)^+$ 288.1034, found 288.1028.



3m

1-(3,5-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 60%, 17.2 mg, oil.

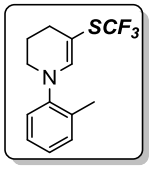
^{1}H NMR (400 MHz, $CDCl_3$): 7.14 (s, 1H), 6.62 (d, J = 22.9 Hz, 3H), 3.53 (t, J = 5.6 Hz, 2H), 2.43 (t, J = 6.3 Hz, 2H), 2.30 (s, 6H), 2.05 – 1.99 (m, 2H). ^{13}C NMR (100 M Hz, $CDCl_3$): 145.7, 142.7, 139.1, 135.0 (q, J = 310 Hz), 123.8, 114.6, 90.1, 45.1, 29.7, 28.9, 22.6, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): -44.99. IR(cm^{-1}): 2923, 2852, 1616, 1594, 1316, 1146, 1113, 831, 694. HRMS (ESI) m/z calcd for $C_{14}H_{17}F_3NS^+$ $(M+H)^+$ 288.1034, found 288.1028.



3n

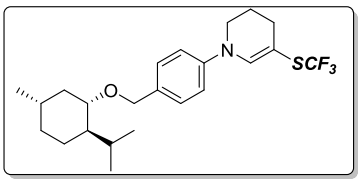
1-(m-tolyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 71%, 19.3 mg, oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.24 – 7.09 (m, 2H), 6.79 (q, J = 7.5 Hz, 3H), 3.69 – 3.39 (m, 2H), 2.43 (t, J = 6.6 Hz, 2H), 2.34 (s, 3H), 2.03 (p, J = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.7, 142.5, 139.3, 135.0 (q, J = 310 Hz), 129.2, 122.8, 117.4, 113.7, 91.4, 45.0, 28.9, 22.6, 21.6.^{19}F NMR (376 MHz, $CDCl_3$): -44.96. IR(cm^{-1}): 2924, 2853, 1616, 1599, 1493, 1315, 1111, 775, 694. HRMS (ESI) m/z calcd for $C_{13}H_{15}F_3NS^+$ $(M+H)^+$ 274.0877, found 274.0872.



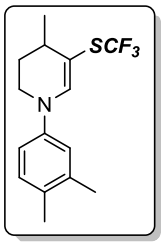
3o

1-(o-tolyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 26%, 7.1 mg, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 7.23 – 7.14 (m, 2H), 7.13 – 7.08 (m, 1H), 7.01 (d, *J* = 9.1 Hz, 1H), 6.74 (s, 1H), 3.41 – 3.35 (m, 2H), 2.45 (t, *J* = 6.3 Hz, 2H), 2.27 (s, 3H), 2.07 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.5, 146.2, 135.1 (q, *J* = 310 Hz), 133.2, 131.5, 128.9, 126.9, 125.8, 125.0, 88.0, 47.9, 28.9, 22.8, 18.2. ^{19}F NMR (376 MHz, $CDCl_3$): -45.48. IR(cm^{-1}): 2925, 2852, 1614, 1599, 1493, 1310, 1110, 759, 721. HRMS (ESI) m/z calcd for $C_{13}H_{15}F_3NS^+$ $(M+H)^+$ 274.0877, found 274.0871.



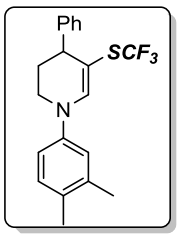
3p

1-(4-((((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-5-((trifluoro methyl)thio)-1,2,3,4-tetrahydropyridine, 53%, 22.6 mg, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 7.21 (d, *J* = 8.6 Hz, 2H), 7.07 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.27 (s, 1H), 3.49 – 3.44 (m, 2H), 3.08 (td, *J* = 10.5, 4.1 Hz, 1H), 2.36 (t, *J* = 6.3 Hz, 2H), 2.25 – 2.15 (m, 1H), 2.10 (d, *J* = 12.3 Hz, 1H), 1.96 (p, *J* = 6.1 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.38 – 1.17 (m, 4H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 7.1 Hz, 3H), 0.64 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.0, 142.4, 135.0 (q, *J* = 310 Hz), 132.8, 129.1, 116.5, 91.7, 78.7, 69.9, 48.3, 45.1, 40.4, 34.6, 31.6, 28.9, 25.6, 23.3, 22.6, 22.4, 21.0, 16.1. ^{19}F NMR (376 MHz, $CDCl_3$): -44.94. IR(cm^{-1}): 2953, 2924, 1606, 1515, 1323, 1262, 1111, 968, 811. HRMS (ESI) m/z calcd for $C_{23}H_{33}F_3NOS^+$ $(M+H)^+$ 428.2235, found 428.2230.



4a

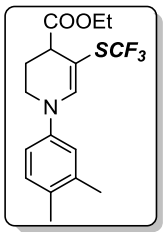
1-(3,4-dimethylphenyl)-4-methyl-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 60%, 18.1 mg, oil.
^{1}H NMR (400 MHz, $CDCl_3$): 7.12 (s, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.77 (s, 1H), 6.72 (dd, *J* = 8.2, 2.7 Hz, 1H), 3.60 – 3.46 (m, 2H), 2.53 (d, *J* = 6.3 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 2.08 (dd, *J* = 9.2, 3.7 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 143.0, 137.6, 134.9 (q, *J* = 310 Hz), 130.4, 130.4, 118.3, 114.2, 96.3, 42.9, 31.6, 30.4, 20.6, 20.1, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.23. IR(cm^{-1}): 2923, 2859, 1601, 1504, 1325, 1110, 1018, 806, 749. HRMS (ESI) m/z calcd for $C_{15}H_{19}F_3NS^+$ $(M+H)^+$ 302.1190, found 302.1186.



4b

1-(3,4-dimethylphenyl)-4-phenyl-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 58%, 20.1 mg, oil.

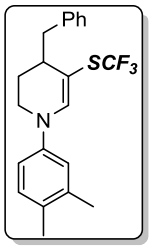
^{1}H NMR (400 MHz, $CDCl_3$): 7.34 (s, 1H), 7.24 (t, J = 7.5 Hz, 2H), 7.13 (dd, J = 27.6, 7.3 Hz, 3H), 7.00 (d, J = 8.2 Hz, 1H), 6.74 (s, 1H), 6.69 (d, J = 8.2 Hz, 1H), 3.72 (s, 1H), 3.44 (d, J = 12.2 Hz, 1H), 3.34 – 3.25 (m, 1H), 2.29 – 2.20 (m, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 1.95 (dt, J = 13.9, 4.5 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): 144.6, 144.2, 143.5, 137.7, 134.9 (q, J = 310 Hz), 130.8, 130.4, 128.7, 128.4, 128.2, 126.6, 118.4, 114.4, 91.7, 43.8, 41.9, 31.4, 20.1, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.13. IR(cm^{-1}): 3025, 2923, 2859, 1599, 1504, 1321, 1111, 1105, 806,700. HRMS (ESI) m/z calcd for $C_{20}H_{21}F_3NS^+$ $(M+H)^+$ 364.1347, found 364.1341.



4c

ethyl 1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine-4-carboxylate, 42%, 15.1 mg, oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.28 (s, 1H), 7.08 (d, J = 8.1 Hz, 1H), 6.82 (s, 1H), 6.77 (d, J = 8.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.72 – 3.55 (m, 2H), 3.47 – 3.38 (m, 1H), 2.35 – 2.28 (m, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 2.15 – 2.05 (m, 1H), 1.31 (d, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.6, 145.3, 143.4, 137.7, 134.8 (q, J = 306 Hz), 131.3, 130.4, 118.9, 114.9, 86.1, 61.0, 43.5, 42.7, 25.4, 20.0, 18.9, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): -45.77. IR(cm^{-1}): 2936, 1731, 1602, 1504, 1318, 1111, 1050, 808, 749. HRMS (ESI) m/z calcd for $C_{17}H_{21}F_3NO_2S^+$ $(M+H)^+$ 360.1245, found 360.1239.

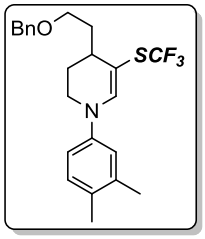


4d

4-benzyl-1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 65%, 24.5 mg, oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.23 (t, J = 7.3 Hz, 2H), 7.13 (dd, J = 11.6, 6.1 Hz, 4H), 6.98 (d, J = 8.1 Hz, 1H), 6.71 (s, 1H), 6.65 (d, J = 8.2 Hz, 1H), 3.40 (t, J = 4.2 Hz,

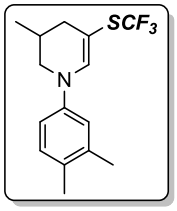
2H), 3.28 (dd, *J* = 13.6, 3.7 Hz, 1H), 2.57 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 1.82 – 1.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.7, 143.6, 140.2, 137.7, 134.9 (q, *J* = 310 Hz), 130.7, 130.4, 129.3, 126.2, 118.4, 114.4, 94.7, 42.5, 40.4, 38.8, 26.1, 20.1, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.10. IR(cm^{-1}): 3024, 2922, 2857, 1599, 1503, 1320, 1112, 806, 699. HRMS (ESI) m/z calcd for $C_{21}H_{23}F_3NS^+$ $(M+H)^+$ 378.1503, found 378.1498.



4e

4-(2-(benzyloxy)ethyl)-1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetra hydropyridine, 54%, 22.7 mg, oil.

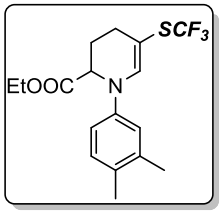
^{1}H NMR (400 MHz, $CDCl_3$): 7.27 (d, *J* = 4.4 Hz, 4H), 7.24 – 7.17 (m, 1H), 7.08 (s, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.69 (s, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 4.45 (q, *J* = 11.9 Hz, 2H), 3.57 – 3.34 (m, 4H), 2.51 (t, *J* = 9.4 Hz, 1H), 2.15 (d, *J* = 17.4 Hz, 7H), 2.02 – 1.91 (m, 1H), 1.83 (dd, *J* = 13.5, 4.9 Hz, 1H), 1.52 – 1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 138.5, 137.6, 134.8 (q, *J* = 316 Hz), 130.5, 130.3, 128.3, 127.6, 127.5, 118.2, 114.2, 94.7, 45.8, 42.6, 34.2, 27.3, 20.0, 18.8. ^{19}F NMR (376 MHz, $CDCl_3$): -45.27. IR(cm^{-1}): 3027, 2923, 2857, 1600, 1504, 1320, 1109, 807, 697. HRMS (ESI) m/z calcd for $C_{23}H_{27}F_3NOS^+$ $(M+H)^+$ 422.1765, found 422.1760.



4f

1-(3,4-dimethylphenyl)-3-methyl-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine, 56%, 16.8 mg, oil.

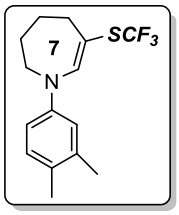
^{1}H NMR (400 MHz, $CDCl_3$): 7.03 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.68 (s, 1H), 6.63 (d, *J* = 5.5 Hz, 1H), 3.44 (d, *J* = 14.8 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.37 (d, *J* = 11.7 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.03 (d, *J* = 13.6 Hz, 2H), 0.98 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 142.4, 137.6, 135.0 (q, *J* = 310 Hz), 130.3, 118.3, 114.3, 89.8, 51.7, 37.0, 27.8, 20.0, 18.8, 18.5. ^{19}F NMR (376 MHz, $CDCl_3$): -45.05. IR(cm^{-1}): 2923, 2854, 1606, 1504, 1245, 1111, 1037, 806, 749. HRMS (ESI) m/z calcd for $C_{15}H_{19}F_3NS^+$ $(M+H)^+$ 302.1190, found 302.1185.



4g

ethyl 1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridine-2-carboxylate, 40%, 14.3 mg, oil.

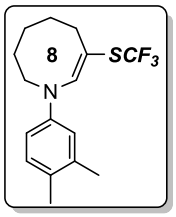
^{1}H NMR (400 MHz, $CDCl_3$): 7.09 (s, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.67 (s, 1H), 6.62 (dd, J = 8.1, 2.7 Hz, 1H), 4.40 – 4.36 (m, 1H), 4.19 – 4.09 (m, 2H), 2.42 – 2.34 (m, 1H), 2.30 (dd, J = 10.8, 4.8 Hz, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 2.06 – 1.96 (m, 1H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 171.4, 143.2, 142.1, 137.7, 134.9 (q, J = 310 Hz), 131.3, 130.4, 119.1, 115.1, 91.1, 61.5, 57.5, 26.1, 25.1, 20.0, 18.9, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): -44.97. IR(cm^{-1}): 2926, 2854, 1746, 1731, 1609, 1504, 1111, 1045, 806. HRMS (ESI) m/z calcd for $C_{17}H_{21}F_3NO_2S^+$ $(M+H)^+$ 360.1245, found 360.1239.



4h

1-(3,4-dimethylphenyl)-6-((trifluoromethyl)thio)-2,3,4,5-tetrahydro-1*H*-azepine, 27%, 8.1 mg, oil.

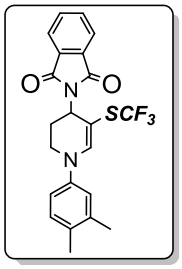
^{1}H NMR (400 MHz, $CDCl_3$): 6.97 (d, J = 8.1 Hz, 1H), 6.84 (s, 1H), 6.68 (s, 1H), 6.64 (d, J = 8.1 Hz, 1H), 3.75 (s, 2H), 2.59 (s, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 1.77 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.7, 144.2, 137.6, 135.3 (q, J = 310 Hz), 130.0, 130.0, 119.0, 114.9, 100.5, 49.9, 35.4, 27.5, 25.7, 20.1, 18.8. ^{19}F NMR (376 MHz, $CDCl_3$): -44.90. IR(cm^{-1}): 2925, 2855, 1602, 1504, 1254, 1111, 997, 812, 750. HRMS (ESI) m/z calcd for $C_{15}H_{19}F_3NS^+$ $(M+H)^+$ 302.1190, found 302.1185.



4i

1-(3,4-dimethylphenyl)-7-((trifluoromethyl)thio)-1,2,3,4,5,6-hexahydroazocine, 21%, 6.6 mg, oil.

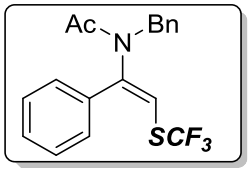
^{1}H NMR (400 MHz, $CDCl_3$): 7.08 (s, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.77 – 6.66 (m, 2H), 3.90 (t, J = 6.4 Hz, 2H), 2.87 (t, J = 6.8 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.81 – 1.68 (m, 4H), 1.61 – 1.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 148.1, 145.0, 137.6, 135.5 (q, J = 310 Hz), 131.4, 130.4, 120.9, 116.9, 92.5, 47.4, 34.4, 29.3, 28.1, 21.7, 20.1, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.98. IR(cm^{-1}): 2927, 2858, 1728, 1594, 1503, 1114, 1024, 814, 749. HRMS (ESI) m/z calcd for $C_{16}H_{21}F_3NS^+$ $(M+H)^+$ 316.1347, found 316.1342.



6a

2-(1-(3,4-dimethylphenyl)-5-((trifluoromethyl)thio)-1,2,3,4-tetrahydropyridin-4-yl)iso indoline-1,3-dione, M.P.= 116-118 °C, yellow solid.

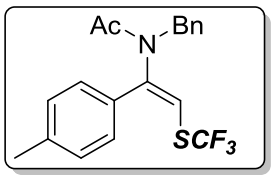
^{1}H NMR (400 MHz, $CDCl_3$): 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.29 (s, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.83 – 6.72 (m, 2H), 5.08 (s, 1H), 3.71 (d, J = 37.0 Hz, 2H), 2.42 (d, J = 17.6 Hz, 1H), 2.17 (d, J = 17.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.2, 147.3, 143.4, 137.7, 134.5 (q, J = 310 Hz), 134.0, 131.8, 131.6, 130.4, 123.2, 119.2, 115.2, 86.1, 47.4, 44.4, 28.1, 20.0, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$): -45.34. IR(cm^{-1}): 2922, 1712, 1600, 1504, 1322, 1120, 1007, 718, 643. HRMS (ESI) m/z calcd for $C_{22}H_{20}F_3N_2O_2S^+$ $(M+H)^+$ 433.1198, found 433.1193.



8a

N-benzyl-N-(1-phenyl-2-((trifluoromethyl)thio)vinyl)acetamide, 62%, 21.7 mg, oil, E /Z = 5.5.

^{1}H NMR (400 MHz, $CDCl_3$): 7.48 – 7.40 (m, 4H), 7.31 (dd, J = 16.2, 7.1 Hz, 7H), 7.16 (d, J = 7.8 Hz, 2H), 5.46 (q, J = 8.2 Hz, 1H), 4.52 (s, 2H), 2.25 (s, 3H), 2.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.9 (q, J = 6.6 Hz), 136.6, 132.9, 130.8, 128.9, 128.9, 128.7, 128.6, 127.7, 123.5, 120.8, 117.4 (q, J = 33.3 Hz), 49.6, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -42.76, -55.92. IR(cm^{-1}): 3063, 2927, 1759, 1668, 1380, 1273, 1114, 713, 699. HRMS (ESI) m/z calcd for $C_{18}H_{17}F_3NOS^+$ $(M+H)^+$ 352.0983, found 352.0976.

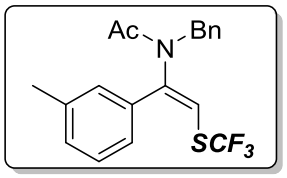


8b

N-benzyl-N-(1-(p-tolyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 55%, 20.1 mg, oil, E/Z = 4.8.

^{1}H NMR (400 MHz, $CDCl_3$): 7.32 – 7.25 (m, 5H), 7.21 – 7.13 (m, 4H), 5.40 (q, J = 8.2 Hz, 1H), 4.52 (s, 2H), 2.41 (s, 3H), 2.24 (s, 3H), 2.17 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.9 (q, J = 6.6 Hz), 141.1, 136.6, 129.7, 129.4, 128.8, 128.6, 127.6, 123.5, 120.8, 116.8 (q, J = 33.3 Hz), 49.4, 22.5, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): -42.81, -55.86. IR(cm^{-1}): 3030, 2926, 1672, 1379, 1271, 1126, 979, 730, 635. HRMS

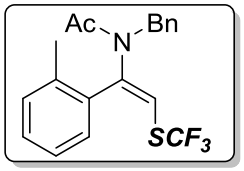
(ESI) m/z calcd for $C_{19}H_{19}F_3NOS^+$ $(M+H)^+$ 366.1139, found 366.1135.



8c

N-benzyl-N-(1-(m-tolyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 53%, 19.3 mg, oil, E/Z = 6.5.

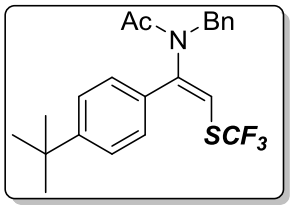
^{1}H NMR (400 MHz, $CDCl_3$): 7.33 – 7.24 (m, 6H), 7.16 (d, *J* = 7.5 Hz, 4H), 7.09 (s, 1H), 5.44 (q, *J* = 8.2 Hz, 1H), 4.52 (s, 2H), 2.37 (d, *J* = 3.6 Hz, 4H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 150.1 (q, *J* = 6.6 Hz), 138.5, 136.7, 132.8, 131.6, 128.7, 128.5, 127.7, 123.5, 120.9, 117.2 (q, *J* = 33.3 Hz), 49.6, 22.6, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): -42.82, -55.90. IR(cm^{-1}): 3030, 2927, 1671, 1454, 1378, 1272, 1126, 786, 701. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NOS^+$ $(M+H)^+$ 366.1139, found 366.1134.



8d

N-benzyl-N-(1-(o-tolyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 50%, 18.2 mg, oil, E/Z = 12.3.

^{1}H NMR (400 MHz, $CDCl_3$): 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.20 (t, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 8.3 Hz, 3H), 5.67 (q, *J* = 7.7 Hz, 1H), 4.48 (s, 2H), 2.38 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.5, 149.7, 149.6, 136.9, 135.4, 132.2, 130.7, 130.2, 128.6, 127.6, 127.4, 125.7, 123.8, 121.1, 115.6 (q, *J* = 33.3 Hz), 49.1, 23.1, 19.5. ^{19}F NMR (376 MHz, $CDCl_3$): -42.11, -56.86. IR(cm^{-1}): 3064, 2927, 1661, 1375, 1274, 1125, 982, 764, 701. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NOS^+$ $(M+H)^+$ 366.1139, found 366.1134.

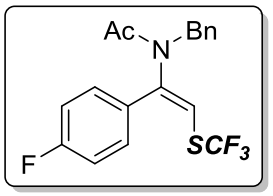


8e

N-benzyl-N-(1-(4-(tert-butyl)phenyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 51%, 20.7 mg, oil, E/Z = 1.5.

^{1}H NMR (400 MHz, $CDCl_3$): 7.39 – 7.33 (m, 2H), 7.20 (t, *J* = 6.2 Hz, 5H), 7.14 – 7.07 (m, 3H), 5.32 (q, *J* = 8.3 Hz, 1H), 4.50 (s, 1H), 4.45 (s, 1H), 2.15 (s, 2H), 2.09 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.5, 170.0, 154.3, 153.6, 149.9, 143.5, 137.0, 136.7, 129.0, 128.8, 128.5, 128.1, 127.6, 126.0, 125.6, 123.6, 120.9, 117.0 (q, *J* = 36.6 Hz), 113.5, 49.9, 49.6, 34.9, 31.2, 22.5, 22.2. ^{19}F NMR (376 MHz,

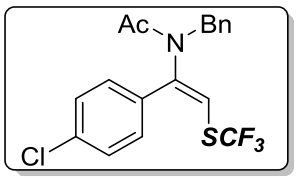
$CDCl_3$): -42.86, -55.94. IR(cm^{-1}): 3063, 2963, 1671, 1380, 1271, 1115, 978, 845, 702. HRMS (ESI) m/z calcd for $C_{22}H_{25}F_3NOS^+$ $(M+H)^+$ 408.1609, found 408.1602.



8f

N-benzyl-N-(1-(4-fluorophenyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 38%, 14.0 mg, oil, E/Z = 11.

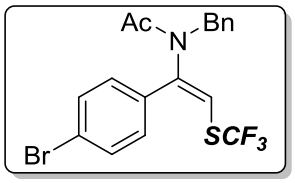
^1H NMR (400 MHz, $CDCl_3$): 7.32 – 7.26 (m, 5H), 7.16 – 7.08 (m, 5H), 5.46 (q, *J* = 8.1 Hz, 1H), 4.53 (s, 2H), 2.24 (s, 3H), 2.18 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 165.3, 162.8, 148.8, 148.8, 136.4, 131.1 (q, *J* = 3.3 Hz), 131.0 (q, *J* = 3.3 Hz), 128.6, 127.8, 123.4, 120.7, 117.4 (q, *J* = 33.3 Hz), 116.1, 115.9, 49.6, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -42.62, -55.97, -108.66. IR(cm^{-1}): 3066, 2929, 1673, 1602, 1509, 1378, 1127, 847, 703. HRMS (ESI) m/z calcd for $C_{18}H_{16}F_4NOS^+$ $(M+H)^+$ 370.0889, found 370.0884.



8g

(E)-N-benzyl-N-(1-(4-chlorophenyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 37%, 14.2 mg, oil.

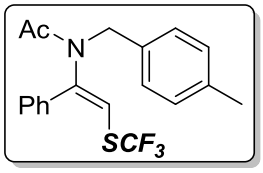
^1H NMR (400 MHz, $CDCl_3$): 7.41 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.23 (m, 6H), 7.13 (dd, *J* = 7.5, 1.9 Hz, 2H), 5.48 (q, *J* = 8.1 Hz, 1H), 4.53 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 148.7, 137.0, 136.3, 131.4, 130.2, 129.1, 128.7, 128.6, 127.8, 123.4, 120.7, 117.8 (q, *J* = 33.3 Hz), 49.7, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.92. IR(cm^{-1}): 3065, 2928, 1674, 1491, 1378, 1275, 1127, 843, 703. HRMS (ESI) m/z calcd for $C_{18}H_{16}ClF_3NOS^+$ $(M+H)^+$ 386.0593, found 386.0589.



8h

(E)-N-benzyl-N-(1-(4-bromophenyl)-2-((trifluoromethyl)thio)vinyl)acetamide, 32%, 13.7 mg, oil.

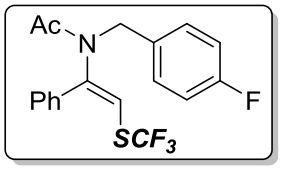
^1H NMR (400 MHz, $CDCl_3$): 7.49 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.12 – 7.04 (m, 4H), 5.41 (q, *J* = 8.1 Hz, 1H), 4.45 (s, 2H), 2.16 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): 169.9, 148.8, 136.3, 132.0, 130.4, 128.7, 128.6, 127.8, 125.3, 123.3, 120.7, 117.8 (q, *J* = 33.3 Hz), 49.7, 22.6. ^{19}F NMR (376 MHz, $CDCl_3$): -55.93. IR(cm^{-1}): 3064, 2928, 1674, 1652, 1378, 1276, 1127, 841, 702. HRMS (ESI) m/z calcd for $C_{18}H_{16}BrF_3NOS^+$ $(M+H)^+$ 430.0088, found 430.0083.



8i

N-(4-methylbenzyl)-N-(1-phenyl-2-((trifluoromethyl)thio)vinyl)acetamide, 45%, 16.4 mg, oil, E/Z = 7.2.

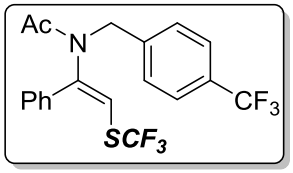
^{1}H NMR (400 MHz, $CDCl_3$): 7.49 – 7.40 (m, 4H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.12 – 7.03 (m, 5H), 5.45 (q, *J* = 8.2 Hz, 1H), 4.48 (s, 2H), 2.33 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 149.9 (q, *J* = 6.6 Hz), 137.4, 133.5, 133.0, 130.7, 129.2, 128.9, 128.7, 123.5, 120.8, 117.4 (q, *J* = 33.3 Hz), 49.3, 22.6, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$): -42.74, -55.87. IR(cm^{-1}): 3064, 2930, 1673, 1504, 1379, 1129, 1007, 778, 699. HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NOS^+$ $(M+H)^+$ 366.1139, found 366.1134.



8j

N-(4-fluorobenzyl)-N-(1-phenyl-2-((trifluoromethyl)thio)vinyl)acetamide, 34%, 12.5 mg, oil, E/Z = 7.5.

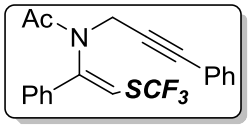
^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (dt, *J* = 14.5, 7.0 Hz, 3H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.06 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.93 – 6.87 (m, 2H), 5.36 (q, *J* = 8.1 Hz, 1H), 4.40 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 163.5, 161.1, 149.7 (q, *J* = 6.6 Hz), 132.7, 132.4, 132.4, 130.9, 130.5, 128.9, 128.8, 123.4, 120.7, 117.5 (q, *J* = 36.6 Hz), 115.5, 115.3, 48.7, 22.5. ^{19}F NMR (376 MHz, $CDCl_3$): -42.75, -55.97, -114.43. IR(cm^{-1}): 3065, 2930, 1672, 1509, 1379, 1273, 1127, 980, 699. HRMS (ESI) m/z calcd for $C_{18}H_{16}F_4NOS^+$ $(M+H)^+$ 370.0889, found 370.0883.



8k

(E)-N-(1-phenyl-2-((trifluoromethyl)thio)vinyl)-N-(4-(trifluoromethyl)benzyl)acetamide, 22%, 9.2 mg, oil.

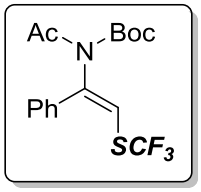
^{1}H NMR (400 MHz, $CDCl_3$): 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 16.1, 7.6 Hz, 3H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 6.5 Hz, 2H), 5.49 (q, *J* = 8.0 Hz, 1H), 4.54 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.2, 149.8, 140.6, 132.5, 131.0, 128.9, 128.8, 125.6 (q, *J* = 3.3 Hz), 123.4, 122.7, 120.7, 117.4 (q, *J* = 33.3 Hz), 49.1, 22.4. ^{19}F NMR (376 MHz, $CDCl_3$): -55.97, -62.62. IR(cm^{-1}): 3065, 2930, 1673, 1379, 1324, 1125, 1018, 778, 699. HRMS (ESI) m/z calcd for $C_{19}H_{16}F_6NOS^+$ $(M+H)^+$ 420.0857, found 420.0850.



8l

(Z)-N-(1-phenyl-2-((trifluoromethyl)thio)vinyl)-N-(3-phenylprop-2-yn-1-yl)acetamide, 35%, 13.1 mg, oil.

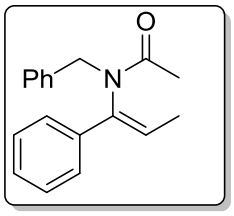
^{1}H NMR (400 MHz, $CDCl_3$): 7.50 – 7.42 (m, 5H), 7.38 (dd, J = 7.4, 2.3 Hz, 2H), 7.31 (d, J = 7.6 Hz, 3H), 5.92 (q, J = 8.1 Hz, 1H), 4.46 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.6, 149.7, 149.6, 132.9, 131.7, 130.8, 129.0, 128.7, 128.5, 128.3, 122.4, 117.2 (q, J = 33.3 Hz), 84.8, 83.3, 37.0, 22.7. ^{19}F NMR (376 MHz, $CDCl_3$): -55.83. IR(cm^{-1}): 3062, 2925, 1677, 1490, 1372, 1272, 1128, 756, 691. HRMS (ESI) m/z calcd for $C_{22}H_{17}F_3NOS^+$ $(M+H)^+$ 376.0983, found 376.0977.



8m

Tert-butyl acetyl(1-phenyl-2-((trifluoromethyl)thio)vinyl)carbamate, 20%, 7.22 mg, oil, E/Z = 2.2.

^{1}H NMR (400 MHz, $CDCl_3$): 7.36 – 7.27 (m, 6H), 5.70 (q, J = 8.0 Hz, 1H), 2.55 (s, 1H), 2.46 (s, 2H), 1.30 (s, 7H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 172.3, 151.5, 150.9, 135.2, 134.5, 130.2, 129.7, 128.8, 128.0, 126.1, 119.8 (q, J = 33.3 Hz), 114.7 (q, J = 36.6 Hz), 84.3, 84.1, 27.7, 27.6, 26.2, 25.9. ^{19}F NMR (376 MHz, $CDCl_3$): -56.90, -60.65. IR(cm^{-1}): 2980, 2931, 1746, 1714, 1370, 1253, 1132, 987, 846. HRMS (ESI) m/z calcd for $C_{16}H_{19}F_3NO_3S^+$ $(M+H)^+$ 362.1038, found 362.1032.



8n

(Z)-N-benzyl-N-(1-phenylprop-1-en-1-yl)acetamide, 53%, 14.0 mg, oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.40 – 7.32 (m, 5H), 7.28 – 7.21 (m, 5H), 6.09 (q, J = 7.0 Hz, 1H), 5.43 (d, J = 13.7 Hz, 1H), 3.67 (d, J = 13.7 Hz, 1H), 2.04 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 139.5, 137.1, 136.3, 130.0, 128.9, 128.2, 128.1, 127.5, 125.5, 125.1, 48.9, 21.2, 13.5. IR(cm^{-1}): 3028, 2926, 2852, 1658, 1493, 1392, 1233, 758, 696.

VIII. References

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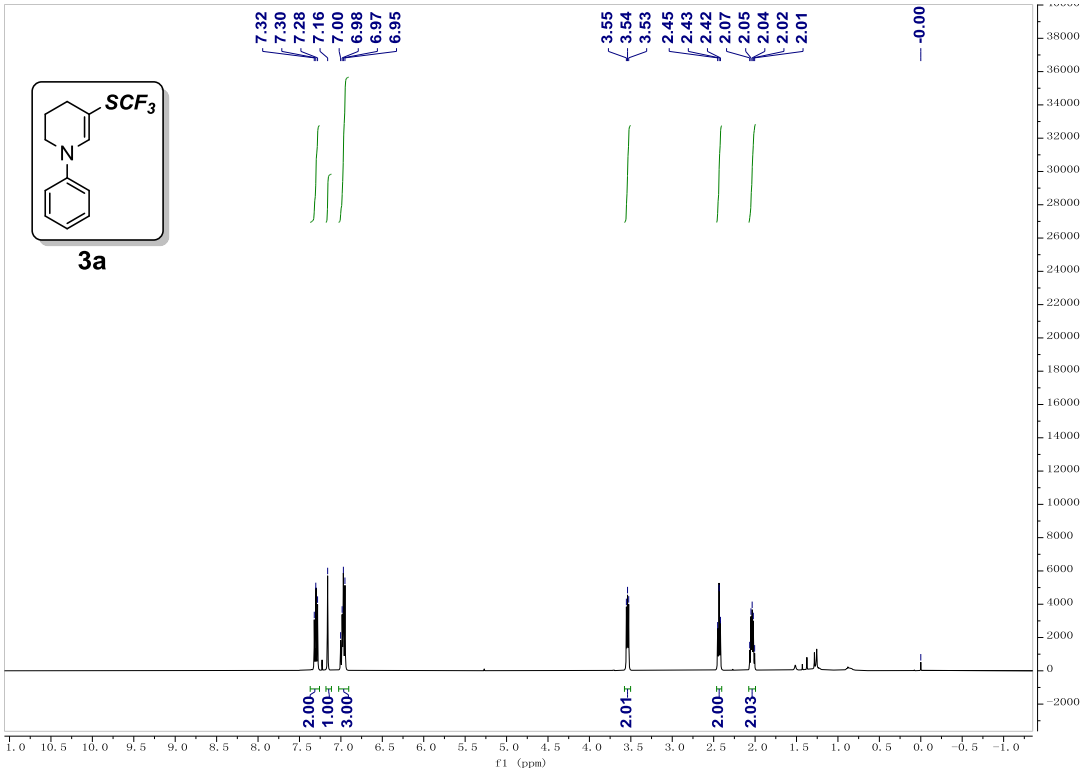
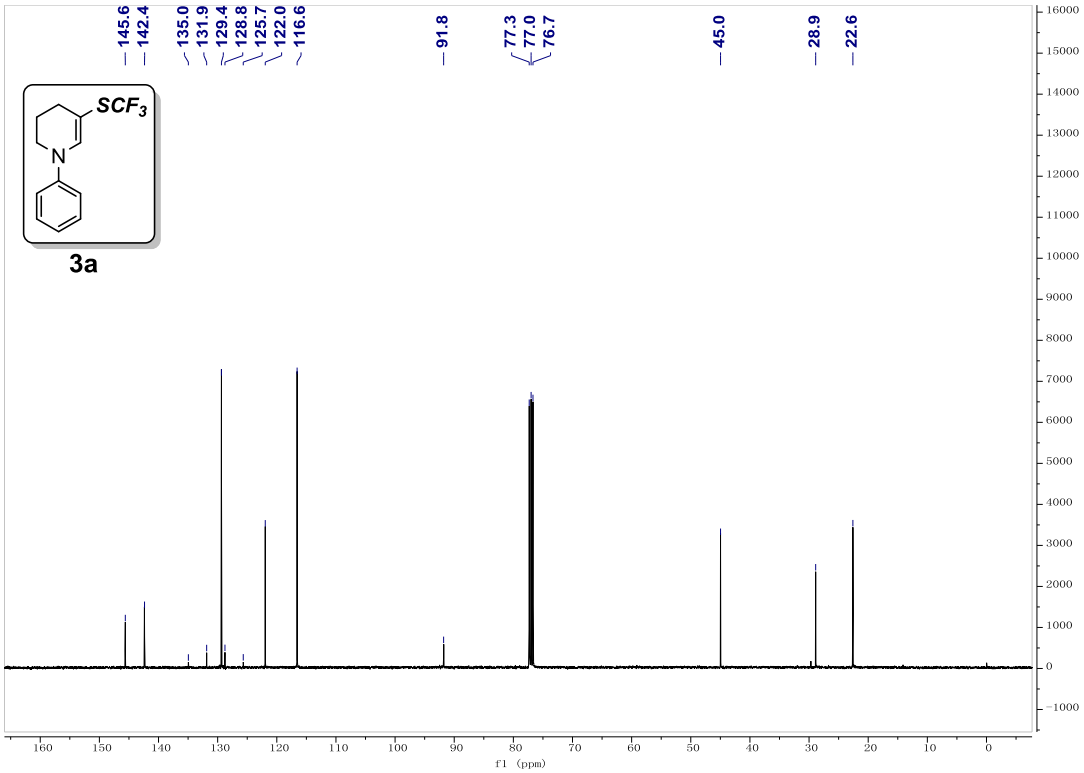
[4] X-H Chang, Z-L Wang, M Zhao, C Yang, J-J Li, W-W M, Y-H Xu. Synthesis of Functionalized Vinylsilanes via Metal-Free Dehydrogenative Silylation of Enamides. *Org. Lett.*, **2020**, 22, 1326-1330.
[5] X Li, Z Cheng, J Liu, Z Zhang, S Song, N Jiao. Synthesis of Functionalized Vinylsilanes via Metal-Free Dehydrogenative Silylation of Enamides. *Chem. Sci.*, **2022**, 13, 9056-9061.

IX. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound 3, 4, 6a, 8

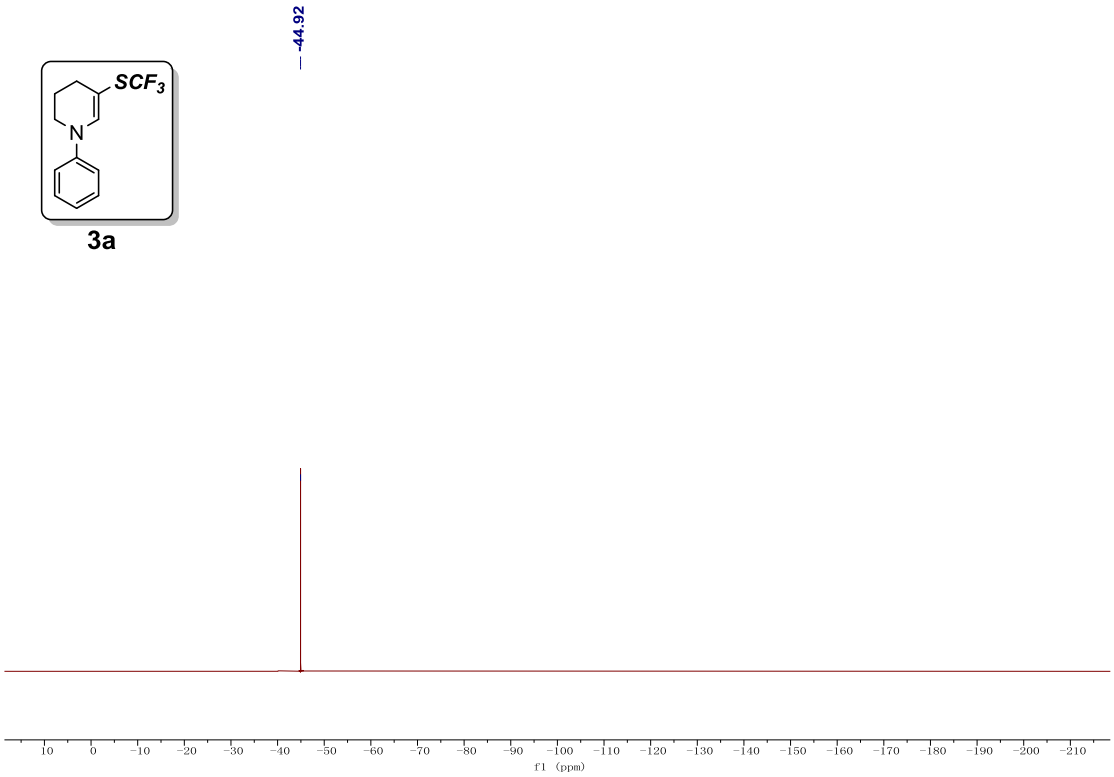
^{1}H NMR (400 MHz) Spectrum of **3a** in $CDCl_3$



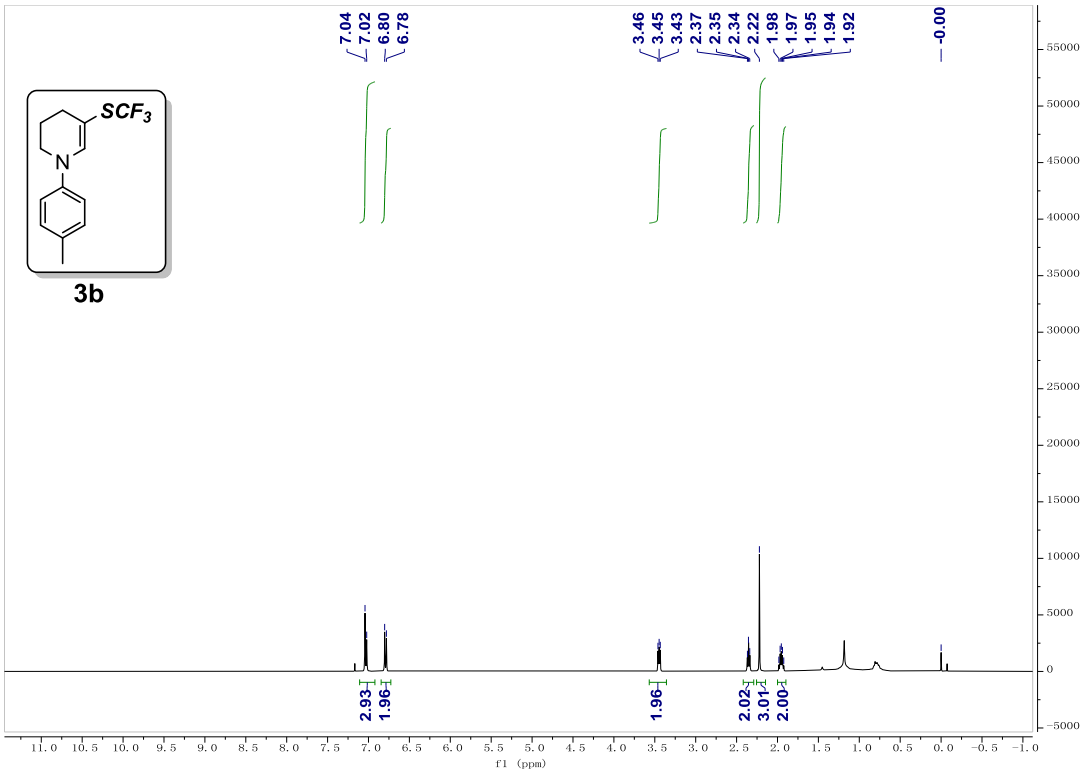
^{13}C NMR (100 MHz) Spectrum of **3a** in $CDCl_3$



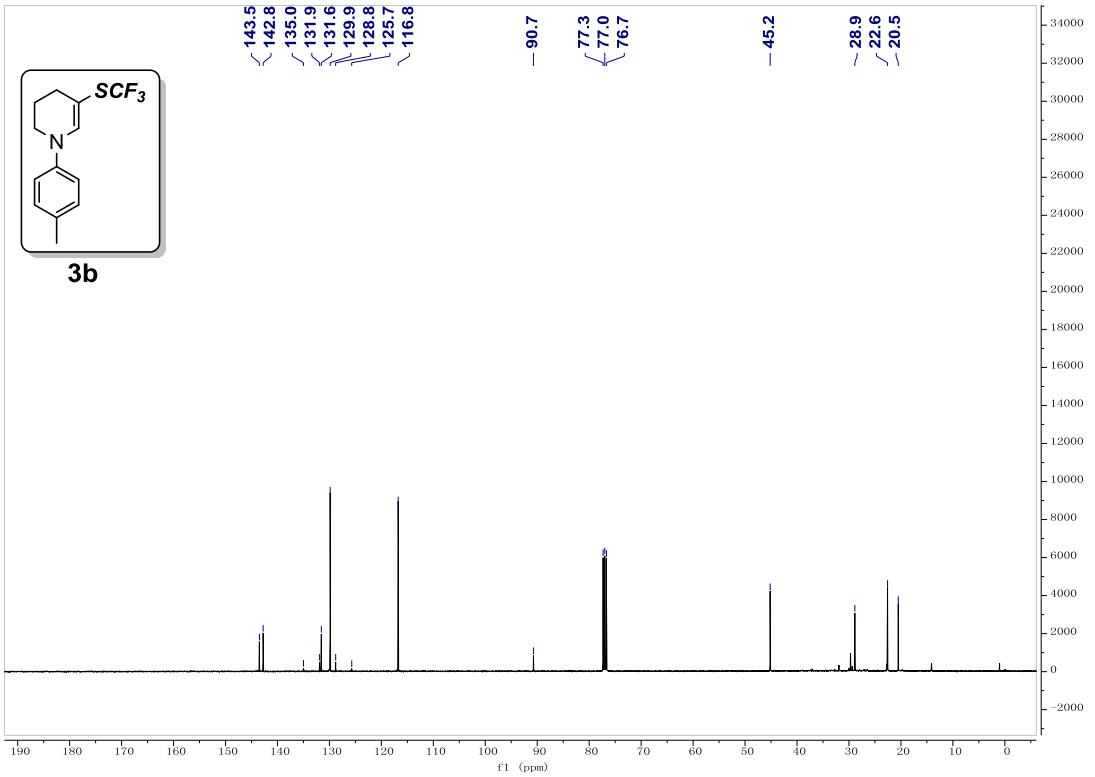
^{19}F NMR (376 MHz) Spectrum of **3a** in $CDCl_3$



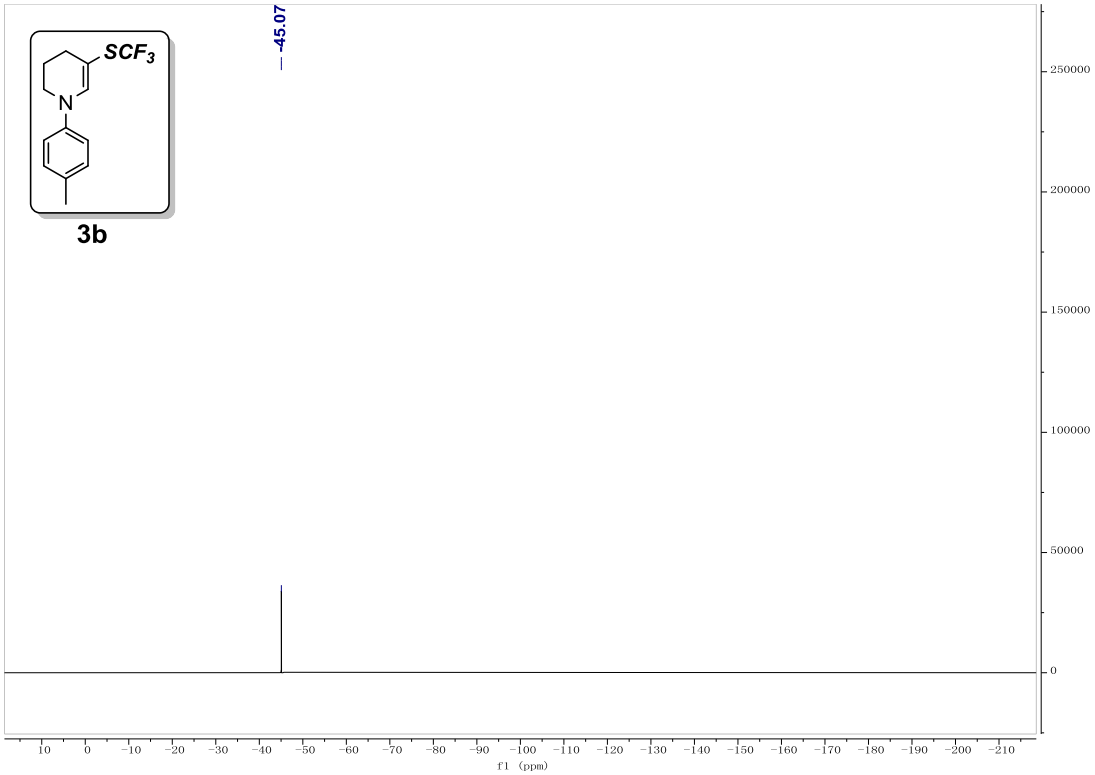
^{1}H NMR (400 MHz) Spectrum of **3b** in $CDCl_3$



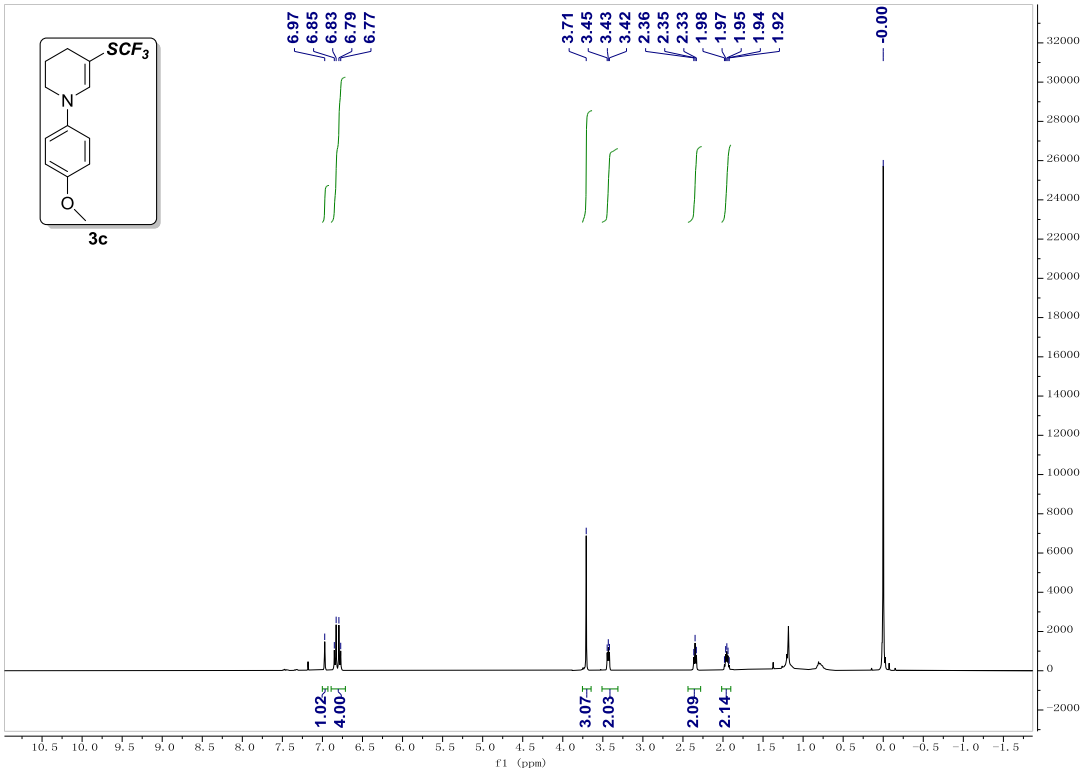
^{13}C NMR (100 MHz) Spectrum of **3b** in $CDCl_3$



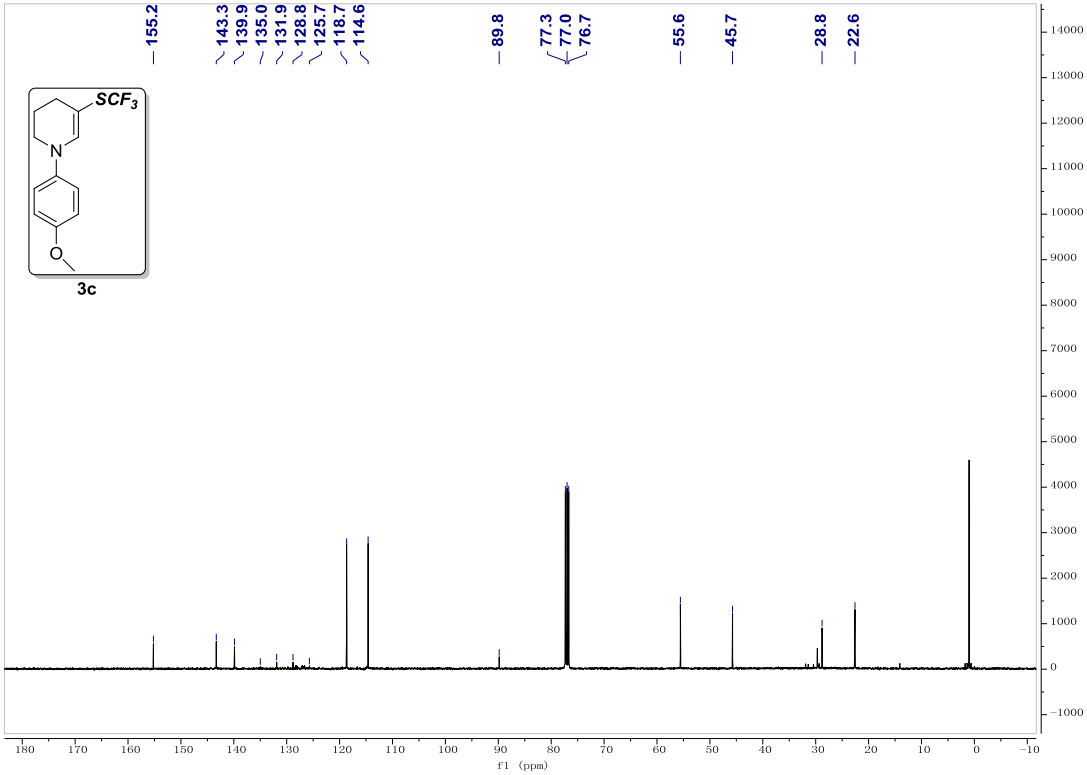
^{19}F NMR (376 MHz) Spectrum of **3b** in $CDCl_3$



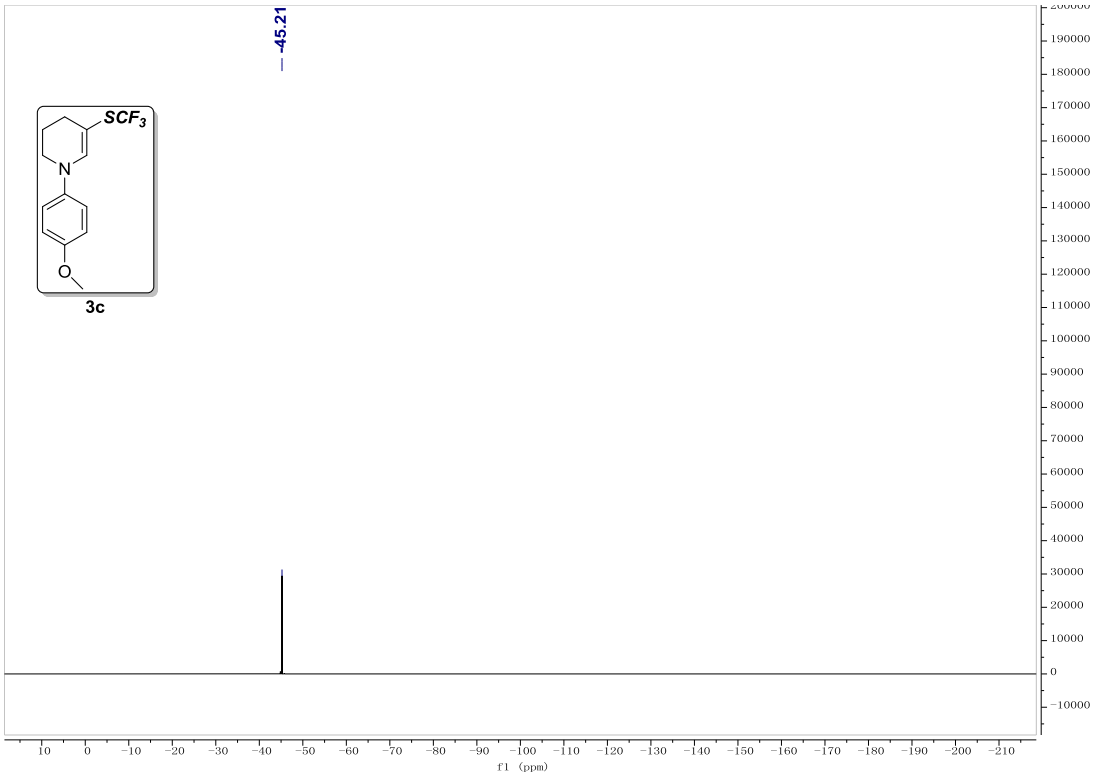
^{1}H NMR (400 MHz) Spectrum of **3c** in $CDCl_3$



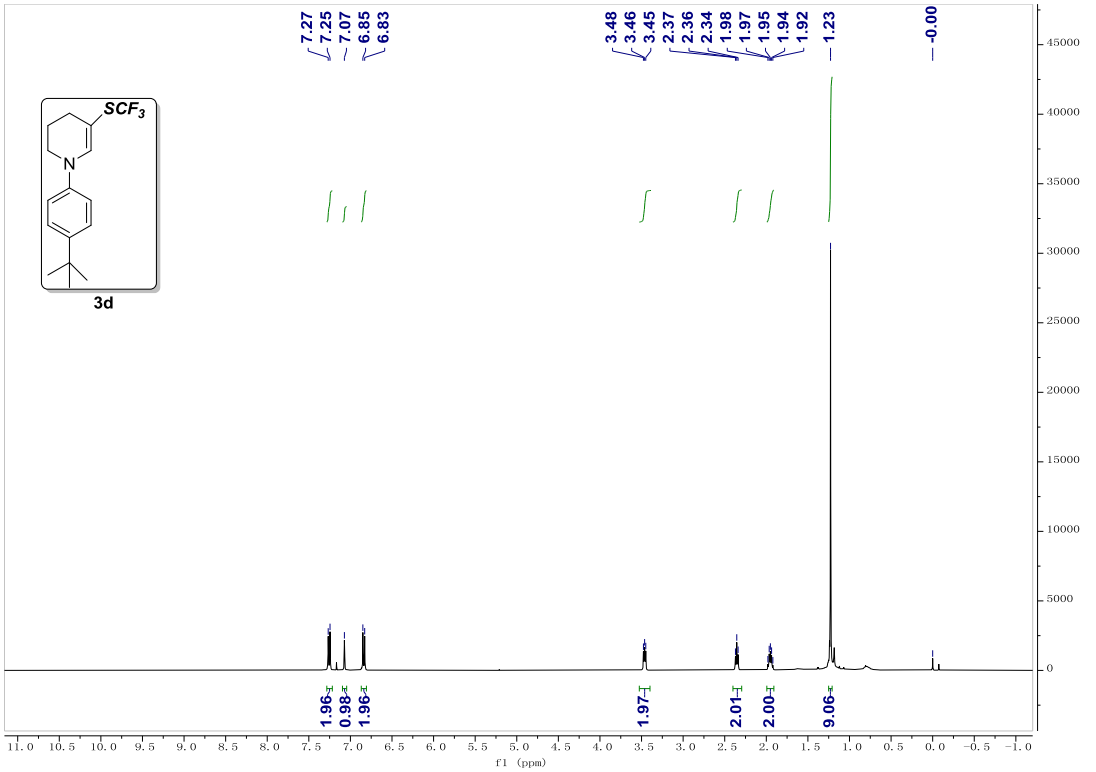
^{13}C NMR (100 MHz) Spectrum of **3c** in $CDCl_3$



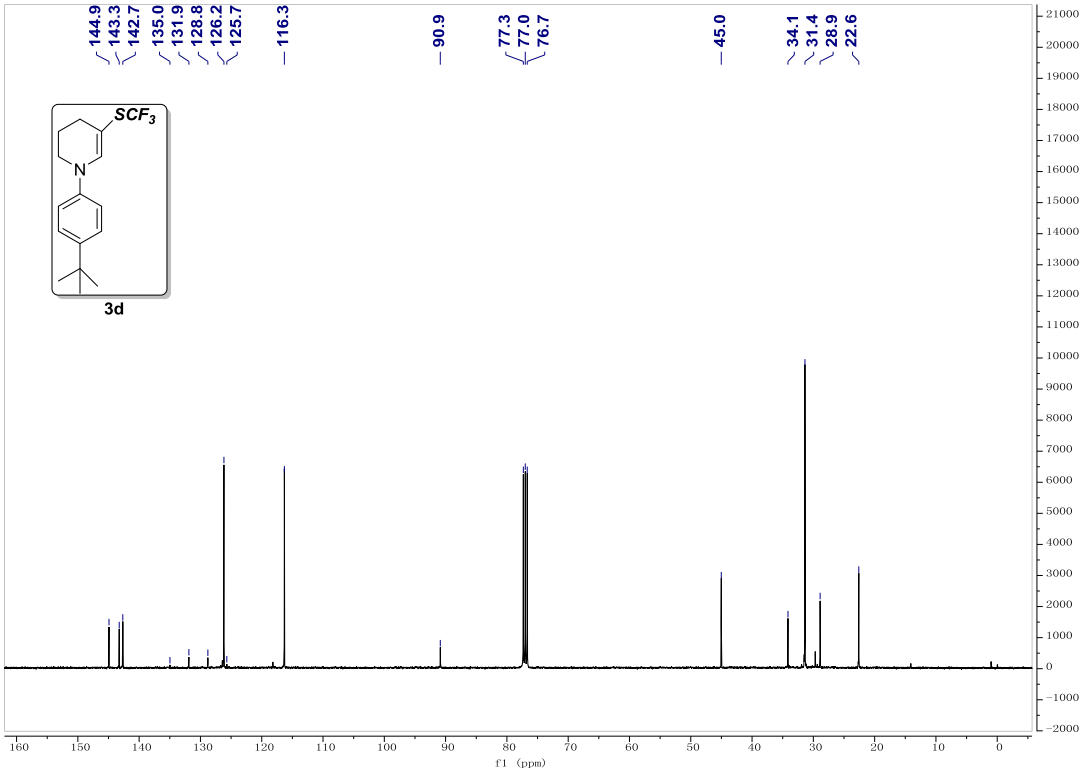
^{19}F NMR (376 MHz) Spectrum of **3c** in $CDCl_3$



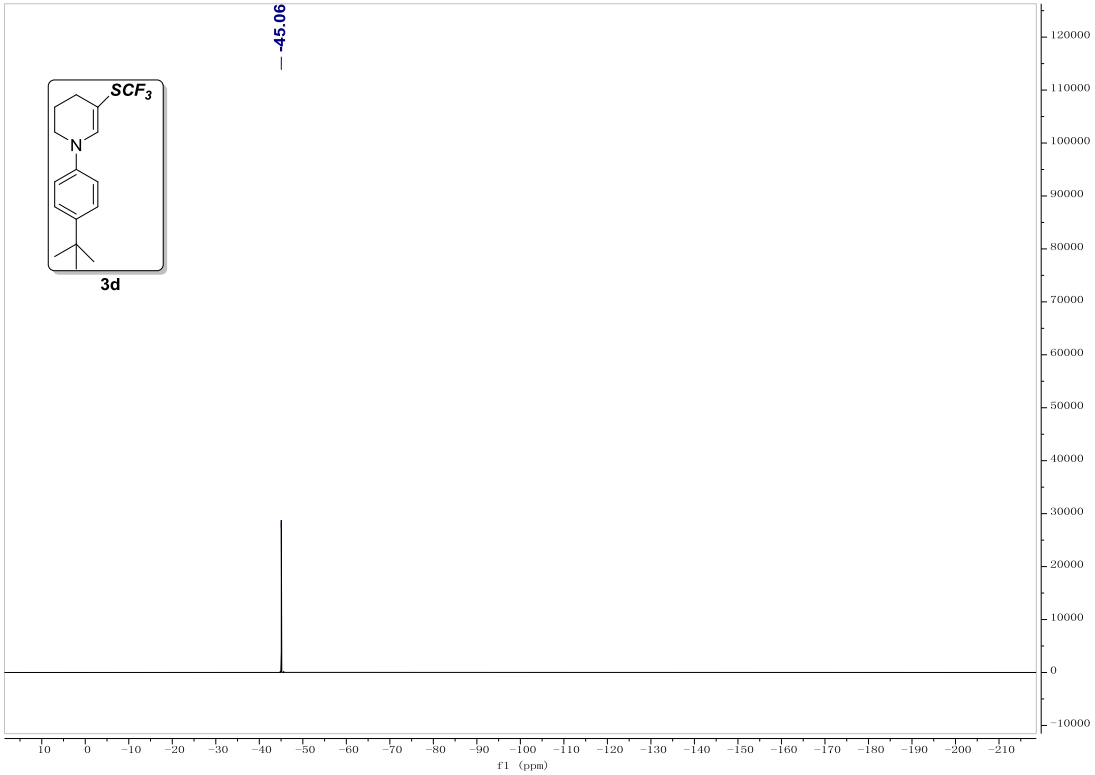
^{1}H NMR (400 MHz) Spectrum of **3d** in $CDCl_3$



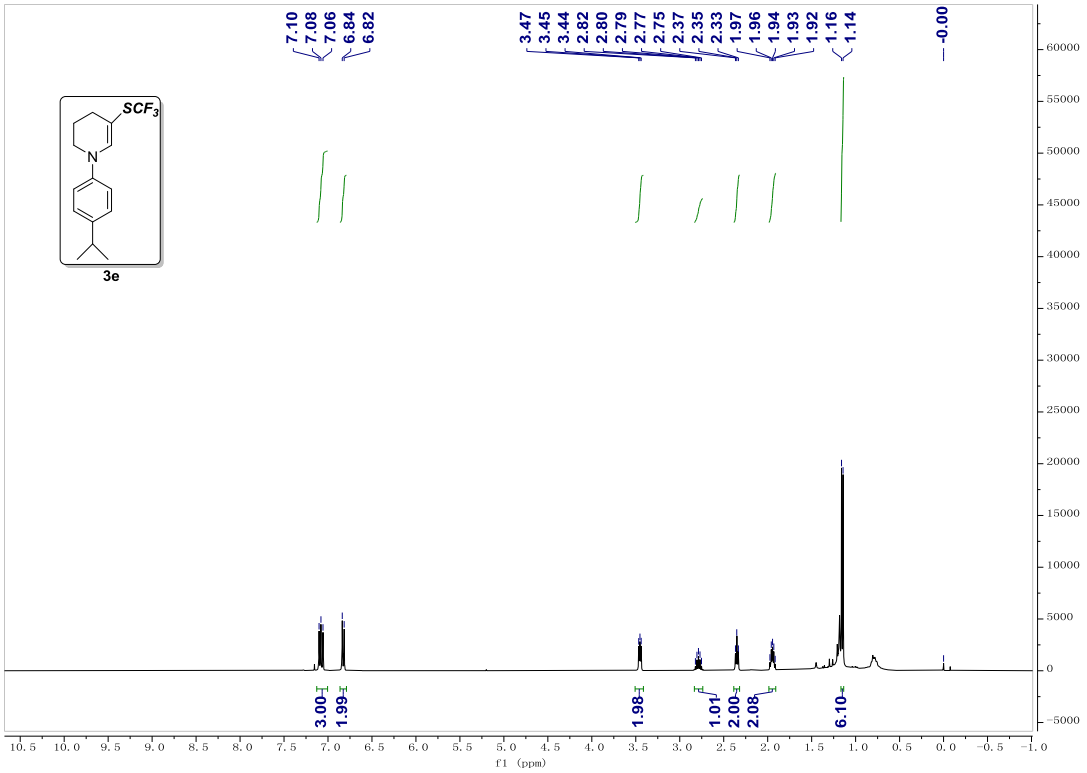
^{13}C NMR (100 MHz) Spectrum of **3d** in $CDCl_3$



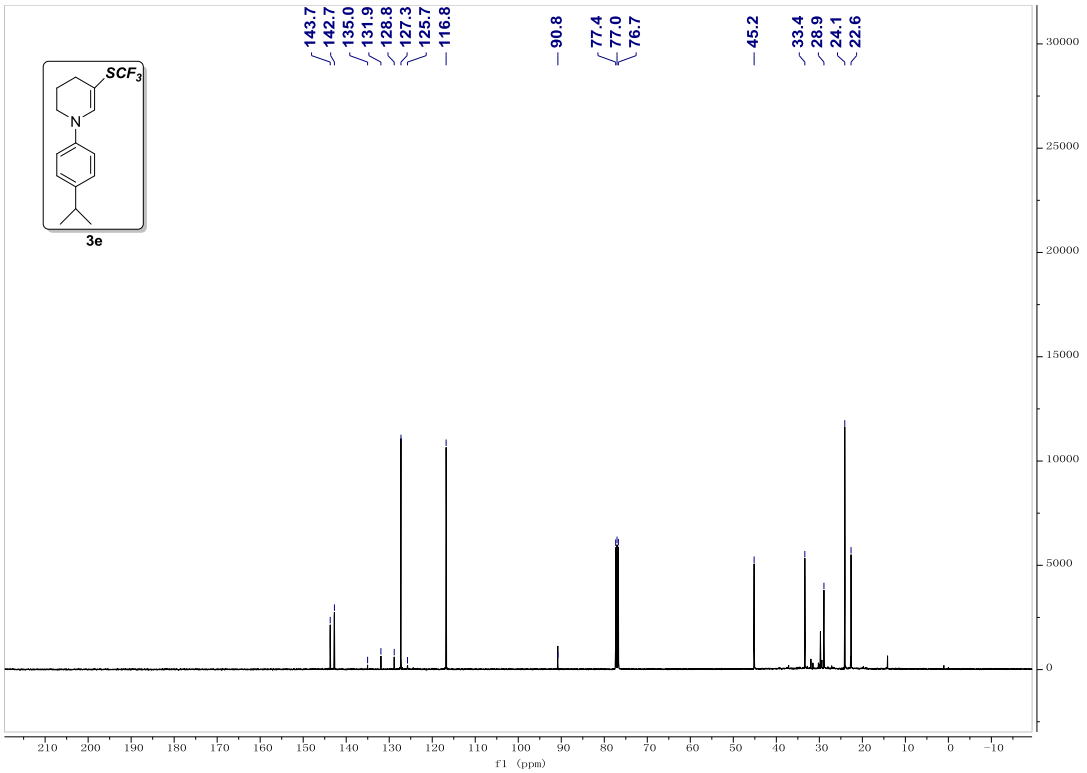
^{19}F NMR (376 MHz) Spectrum of **3d** in $CDCl_3$



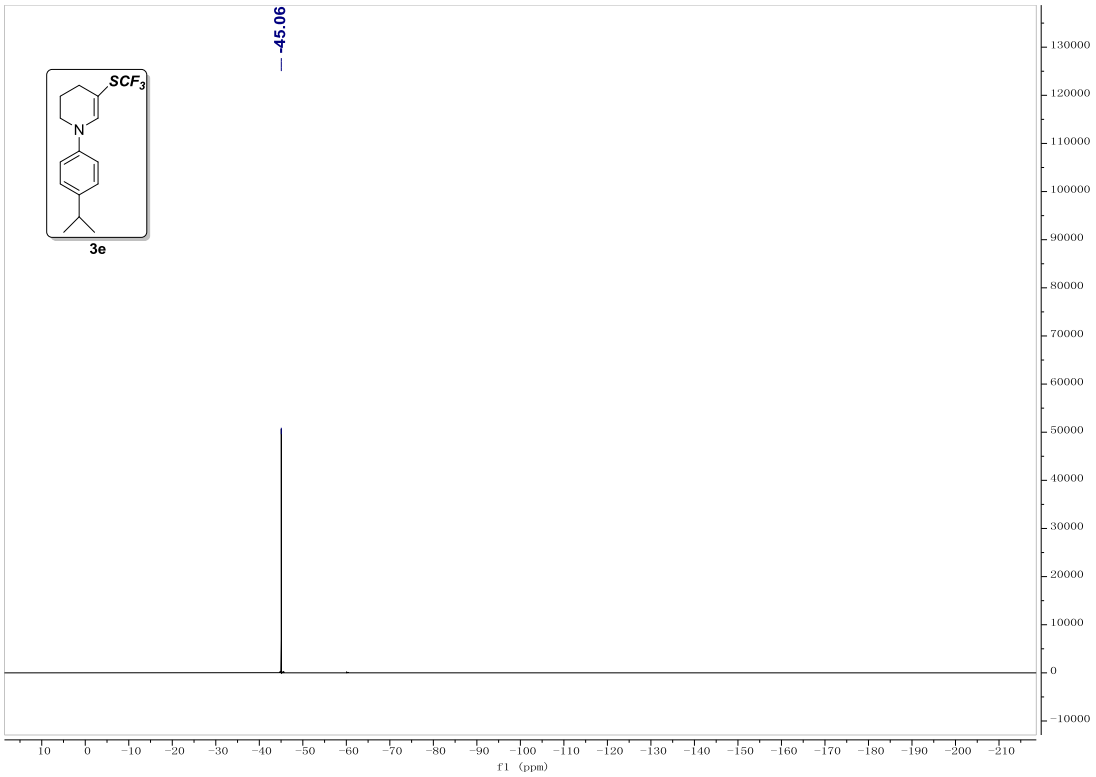
^{1}H NMR (400 MHz) Spectrum of **3e** in $CDCl_3$



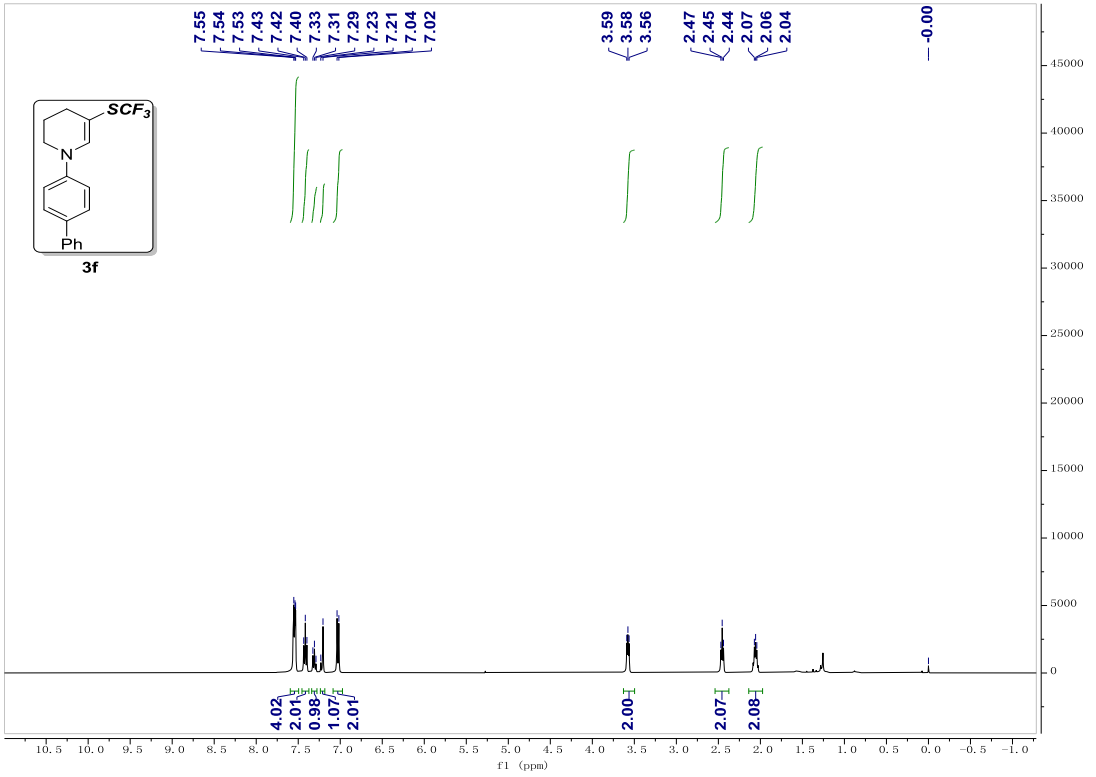
^{13}C NMR (100 MHz) Spectrum of **3e** in $CDCl_3$



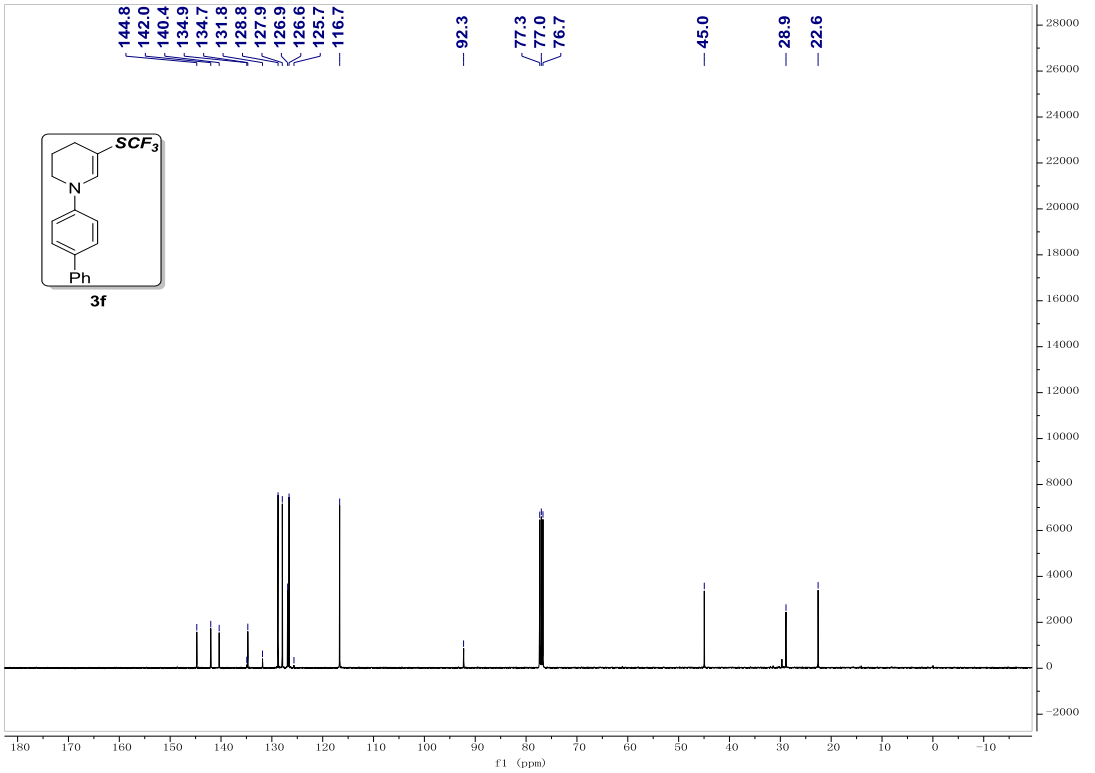
^{19}F NMR (376 MHz) Spectrum of **3e** in $CDCl_3$



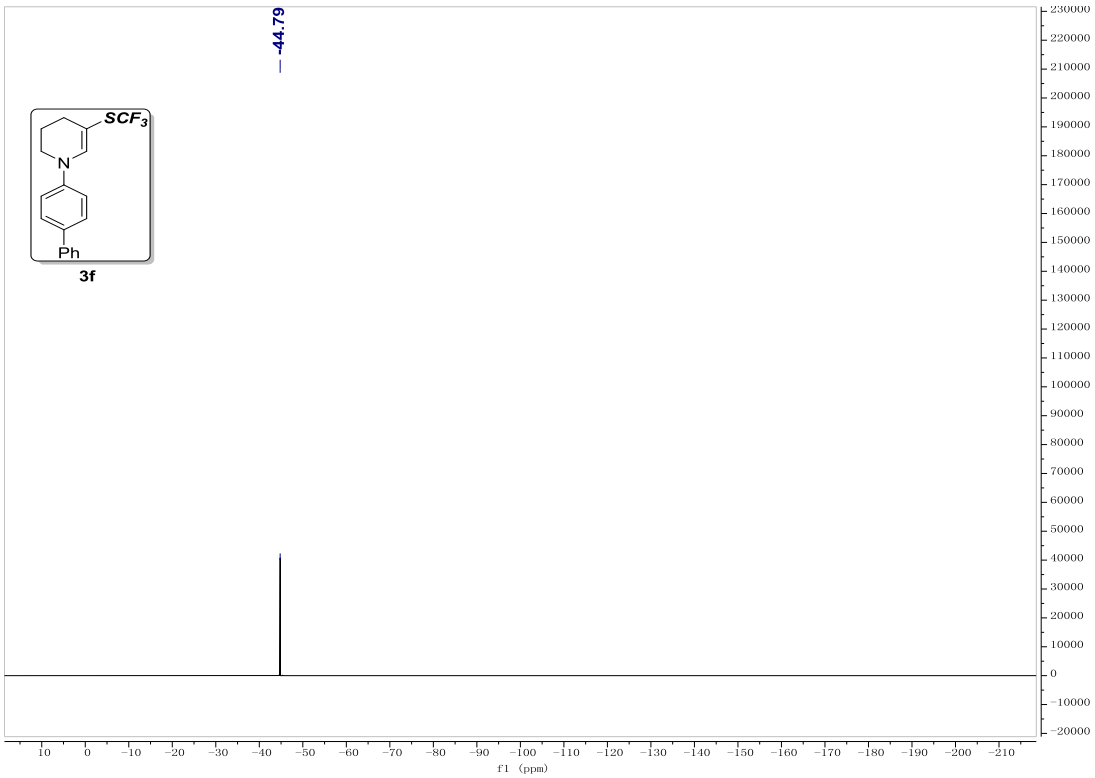
^{1}H NMR (400 MHz) Spectrum of **3f** in $CDCl_3$



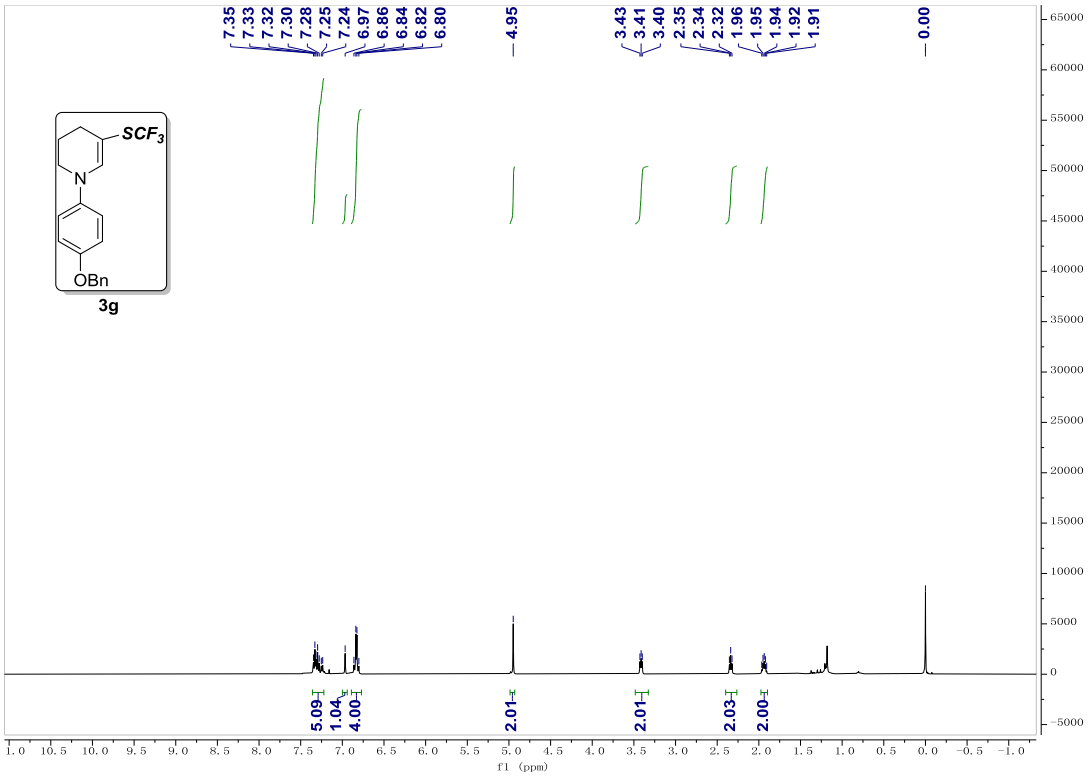
^{13}C NMR (100 MHz) Spectrum of **3f** in $CDCl_3$



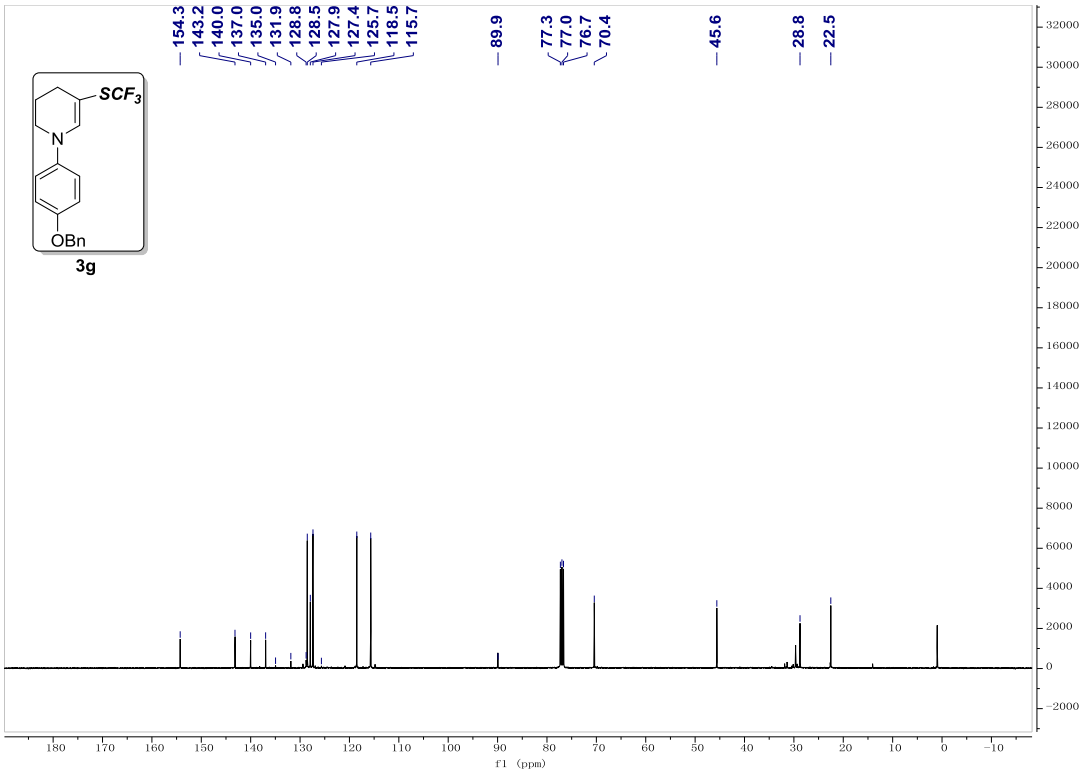
^{19}F NMR (376 MHz) Spectrum of **3f** in $CDCl_3$



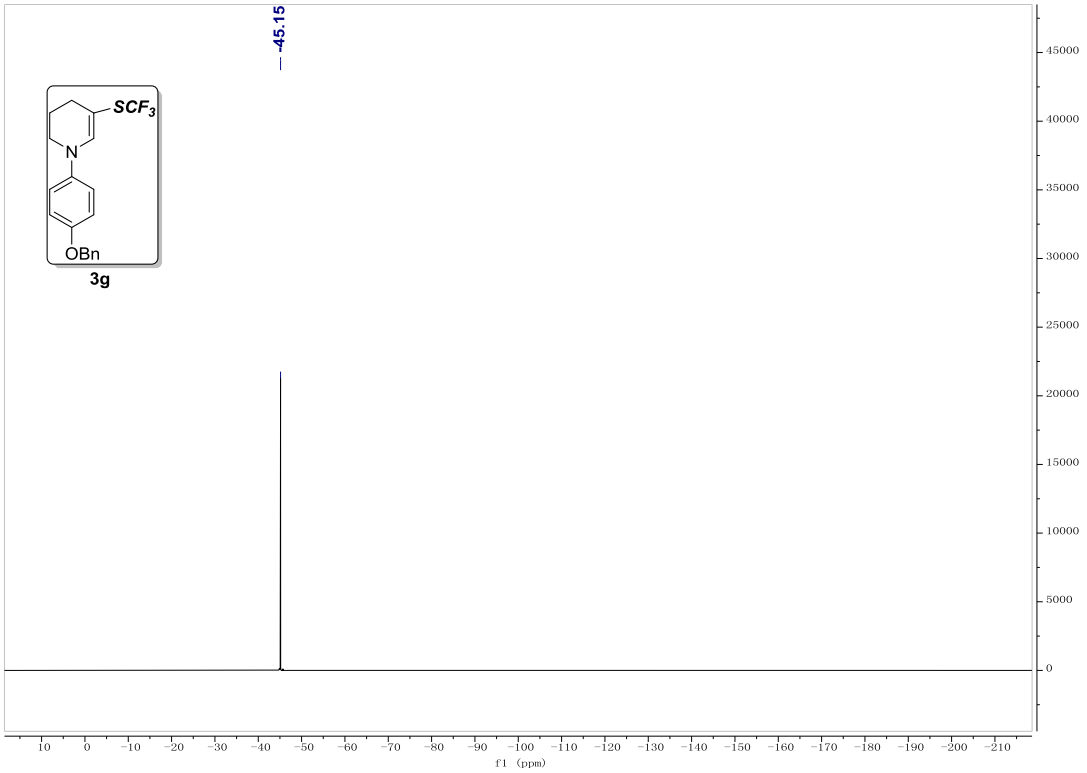
^{1}H NMR (400 MHz) Spectrum of **3g** in $CDCl_3$



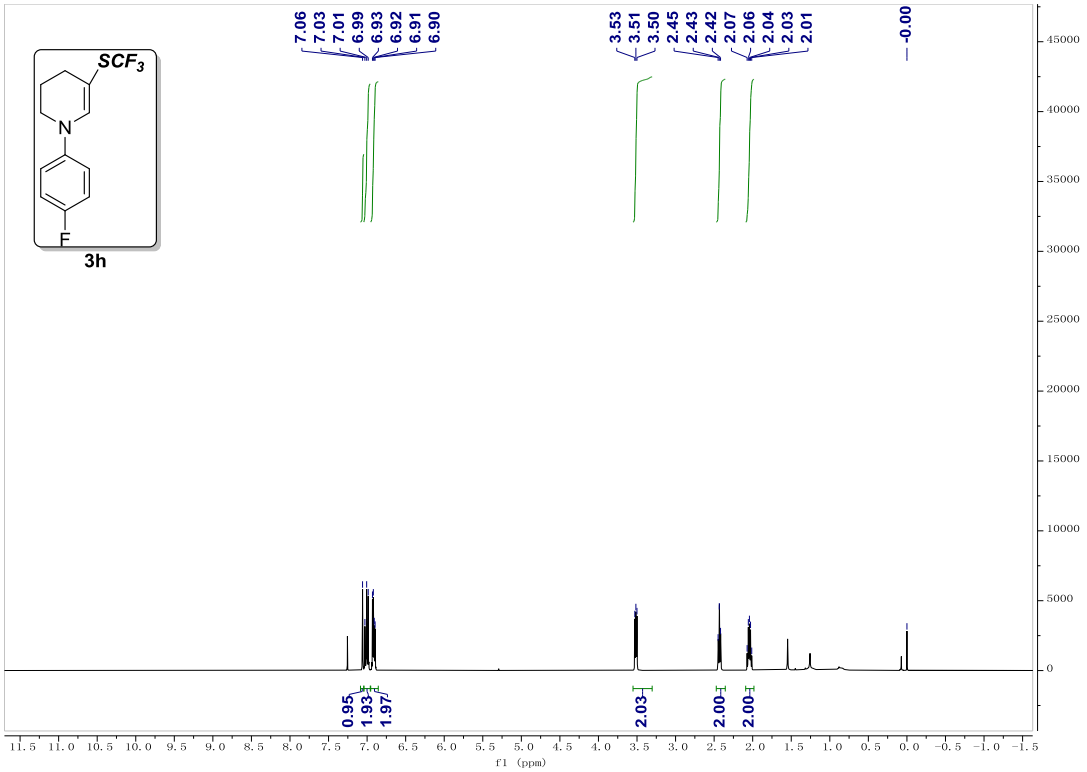
^{13}C NMR (100 MHz) Spectrum of **3g** in $CDCl_3$



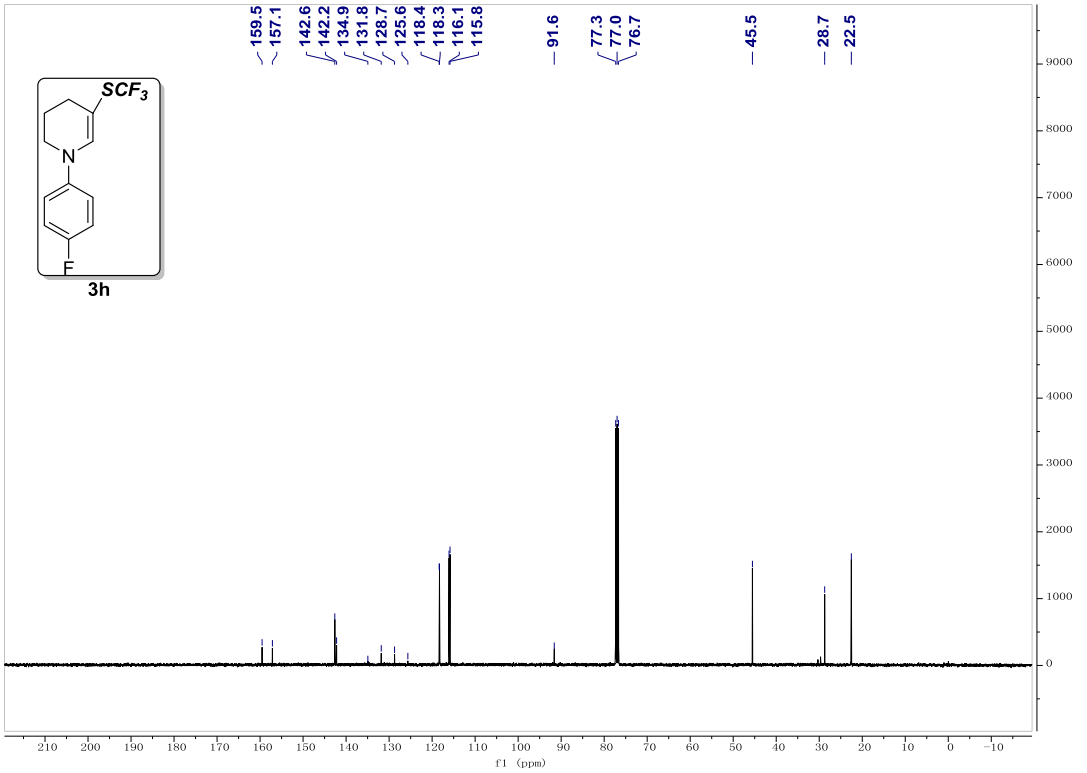
^{19}F NMR (376 MHz) Spectrum of **3g** in $CDCl_3$



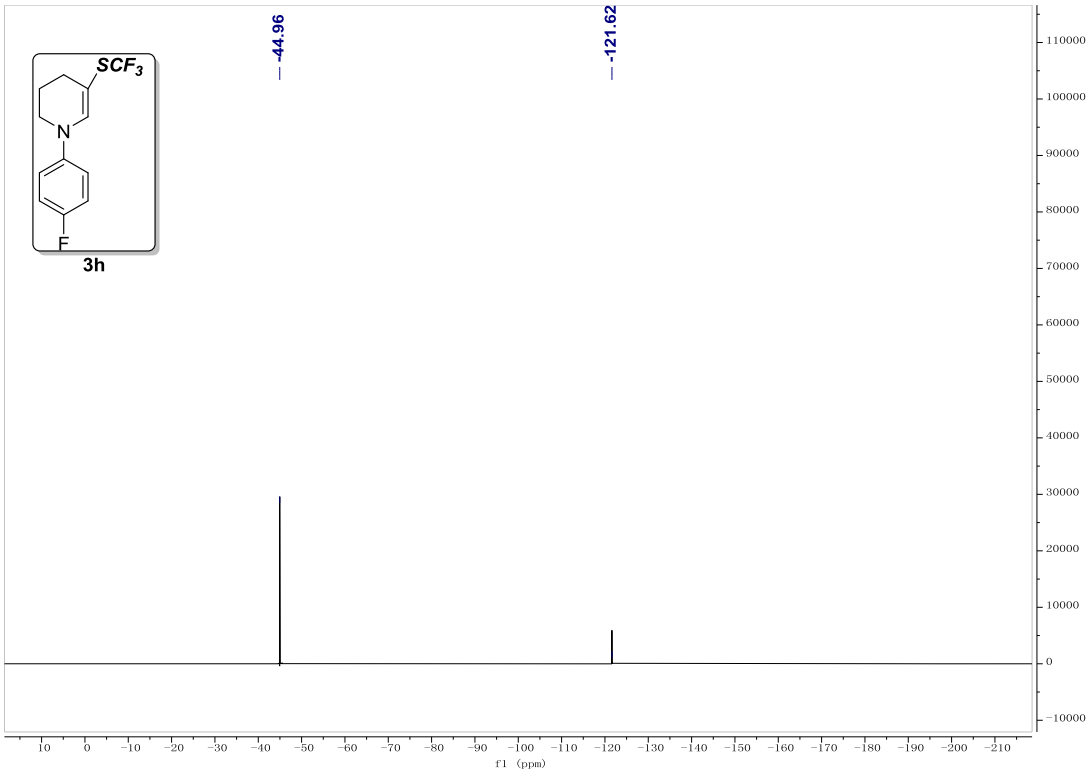
^{1}H NMR (400 MHz) Spectrum of **3h** in $CDCl_3$



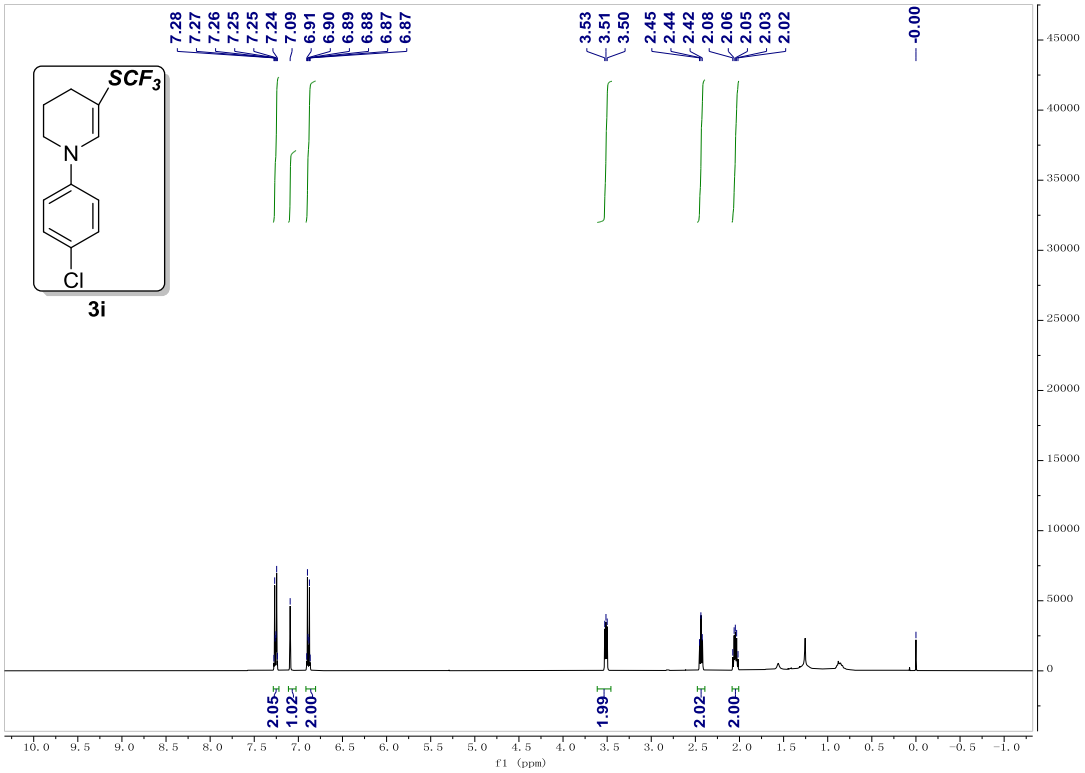
^{13}C NMR (100 MHz) Spectrum of **3h** in $CDCl_3$



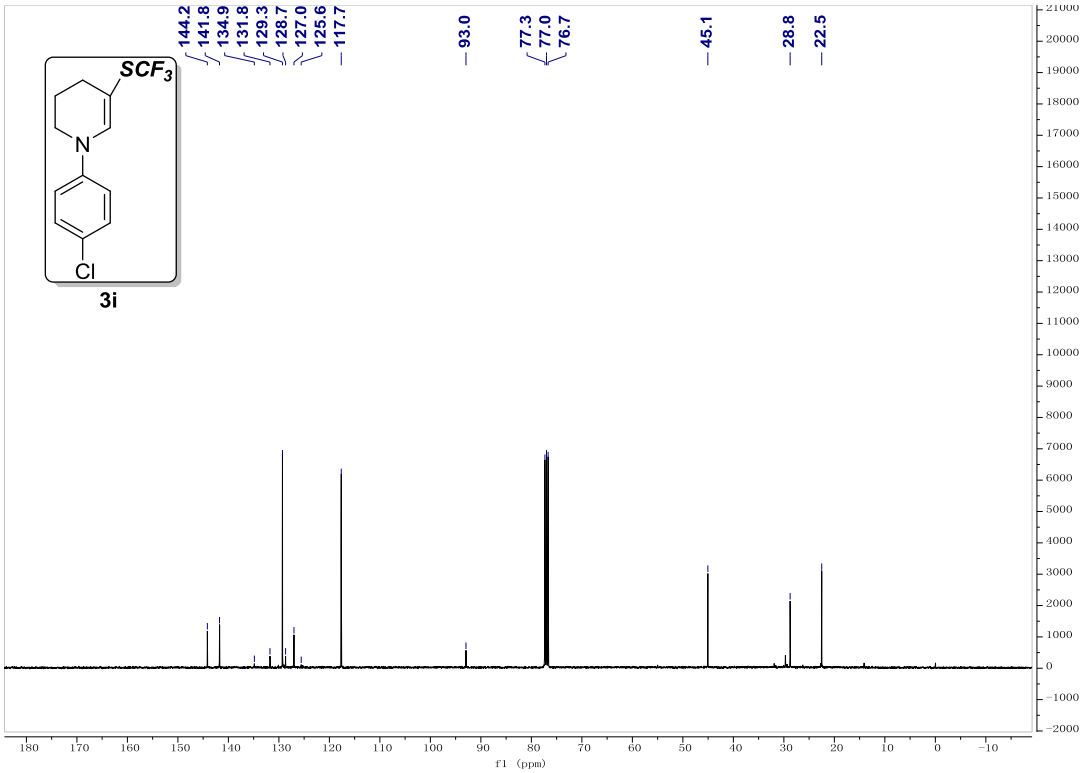
^{19}F NMR (376 MHz) Spectrum of **3h** in $CDCl_3$



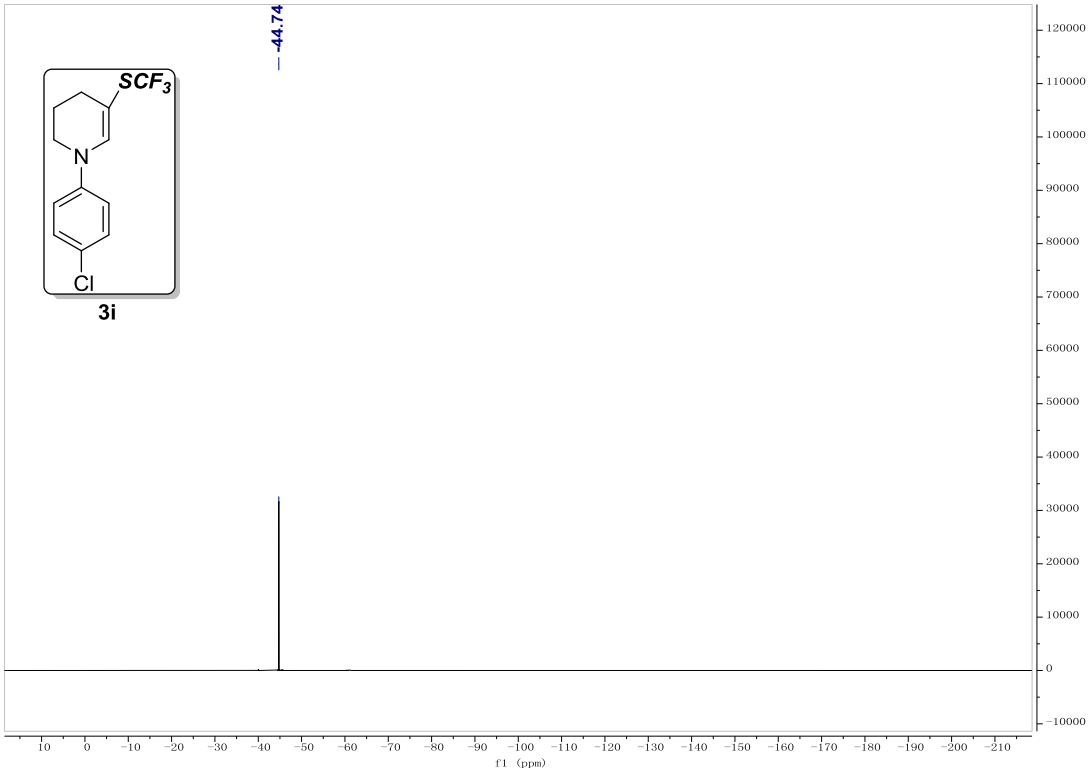
^{1}H NMR (400 MHz) Spectrum of **3i** in $CDCl_3$



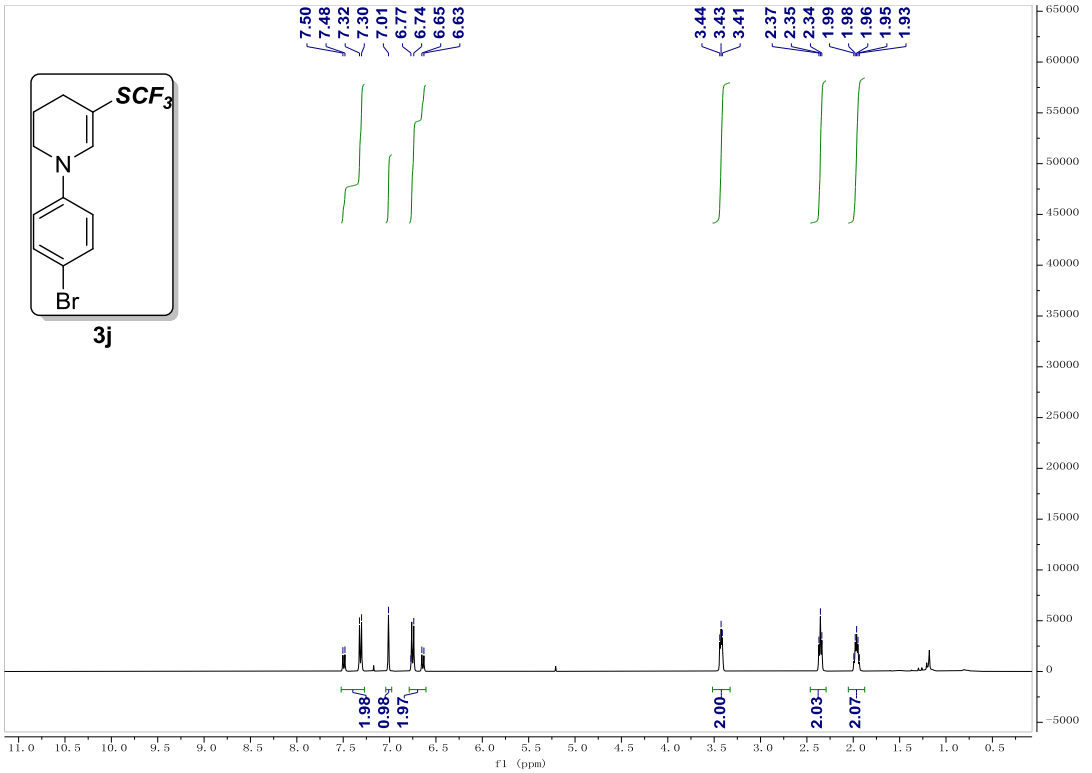
^{13}C NMR (100 MHz) Spectrum of **3i** in $CDCl_3$



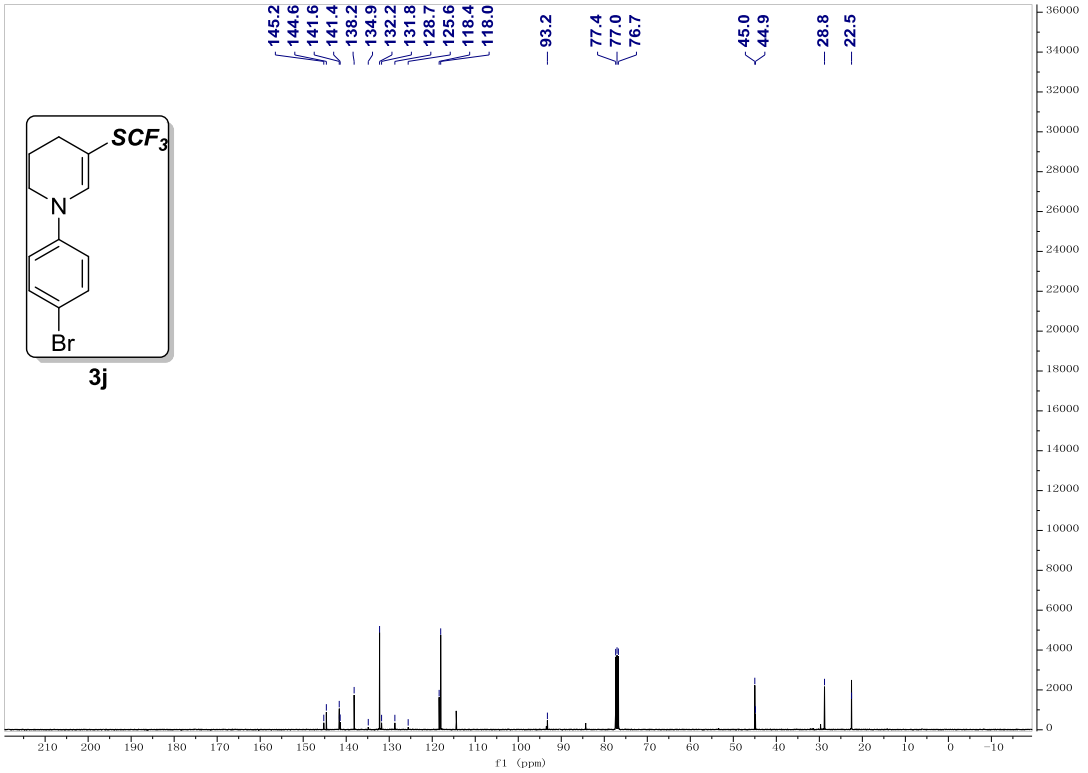
^{19}F NMR (376 MHz) Spectrum of **3i** in $CDCl_3$



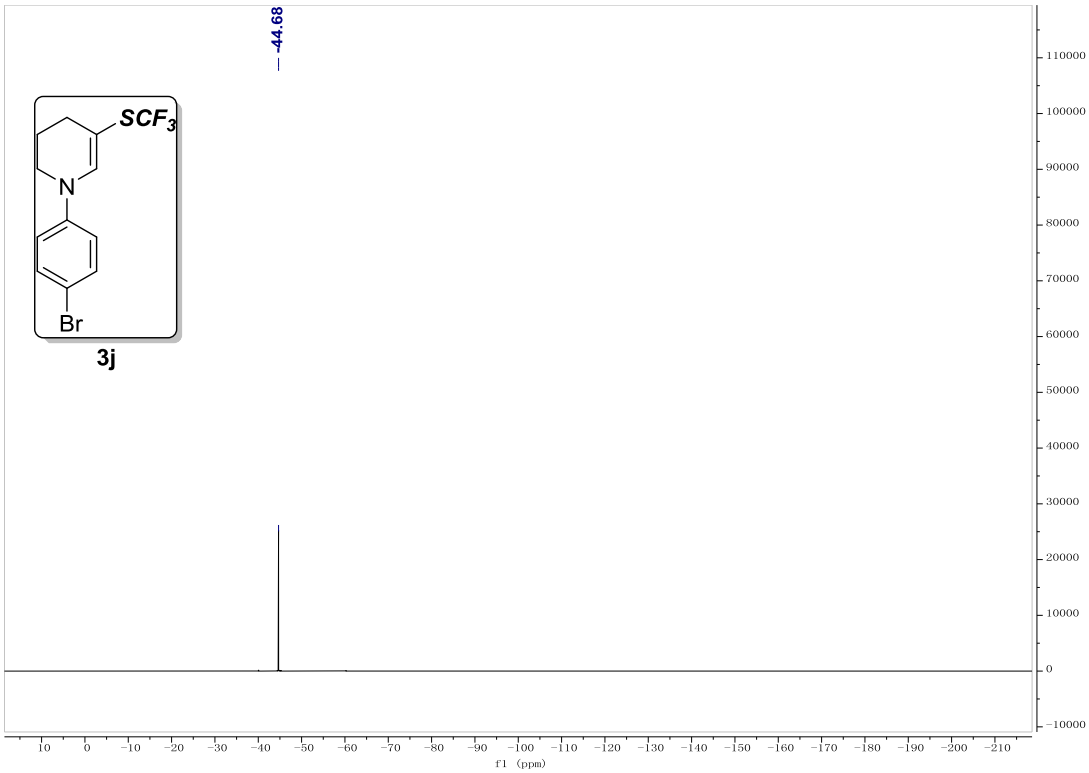
^{1}H NMR (400 MHz) Spectrum of **3j** in $CDCl_3$



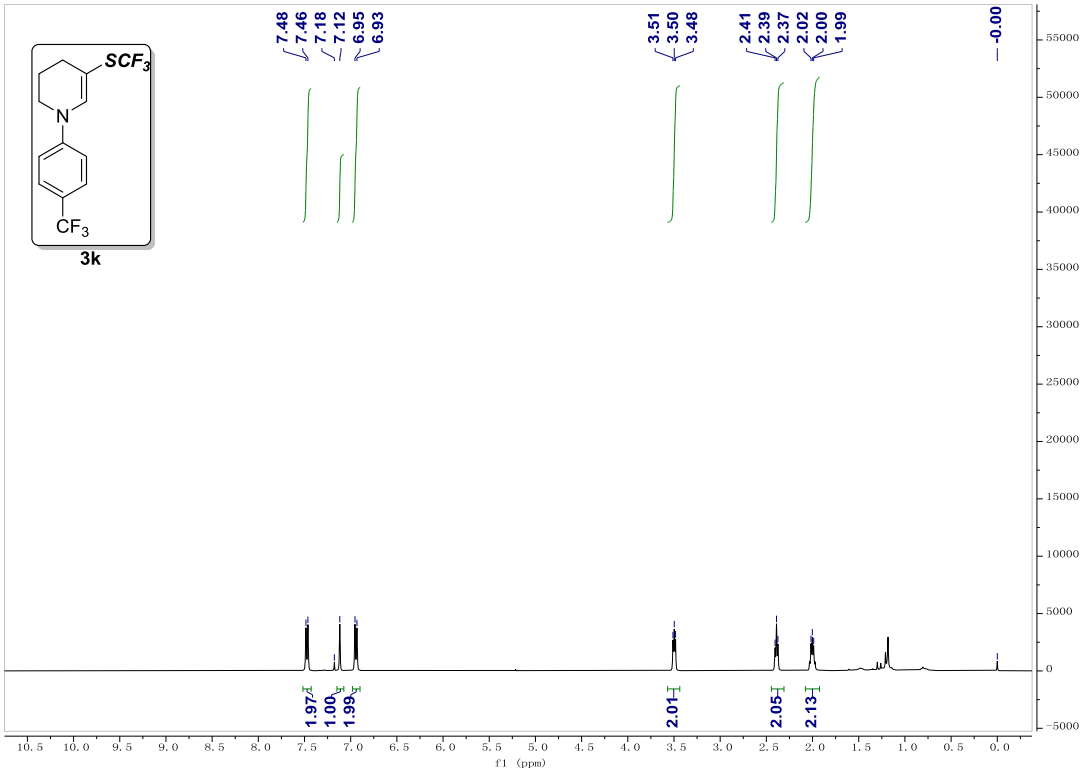
^{13}C NMR (100 MHz) Spectrum of **3j** in $CDCl_3$



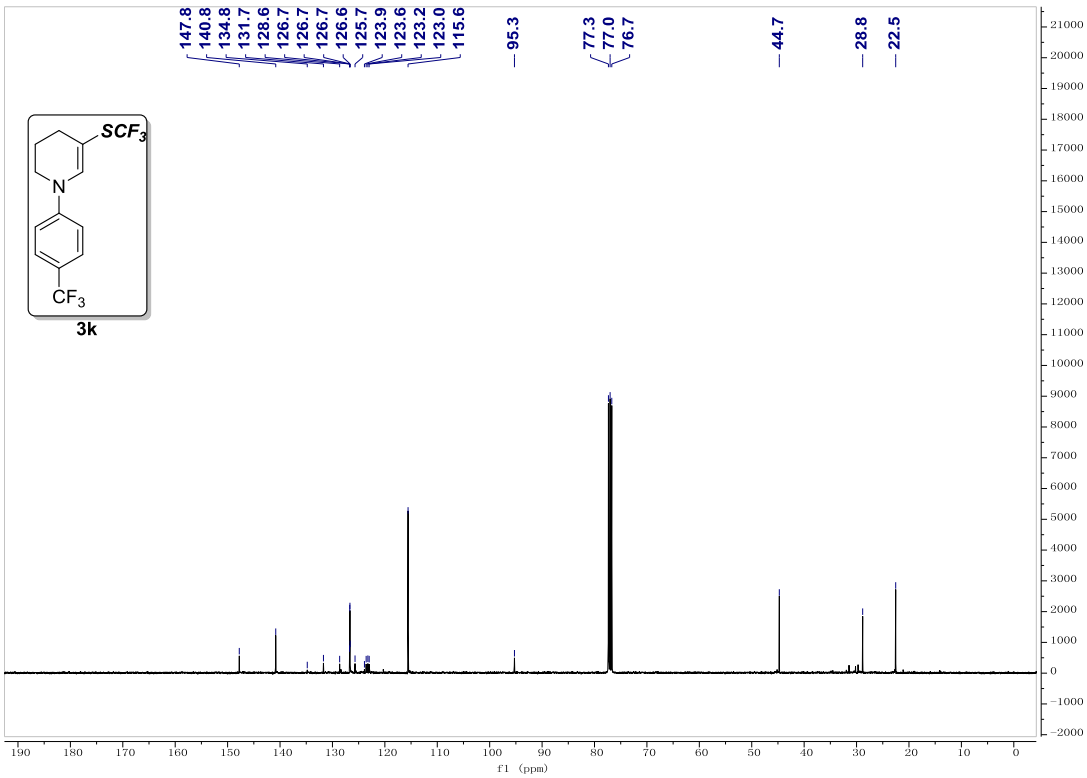
^{19}F NMR (376 MHz) Spectrum of **3j** in $CDCl_3$



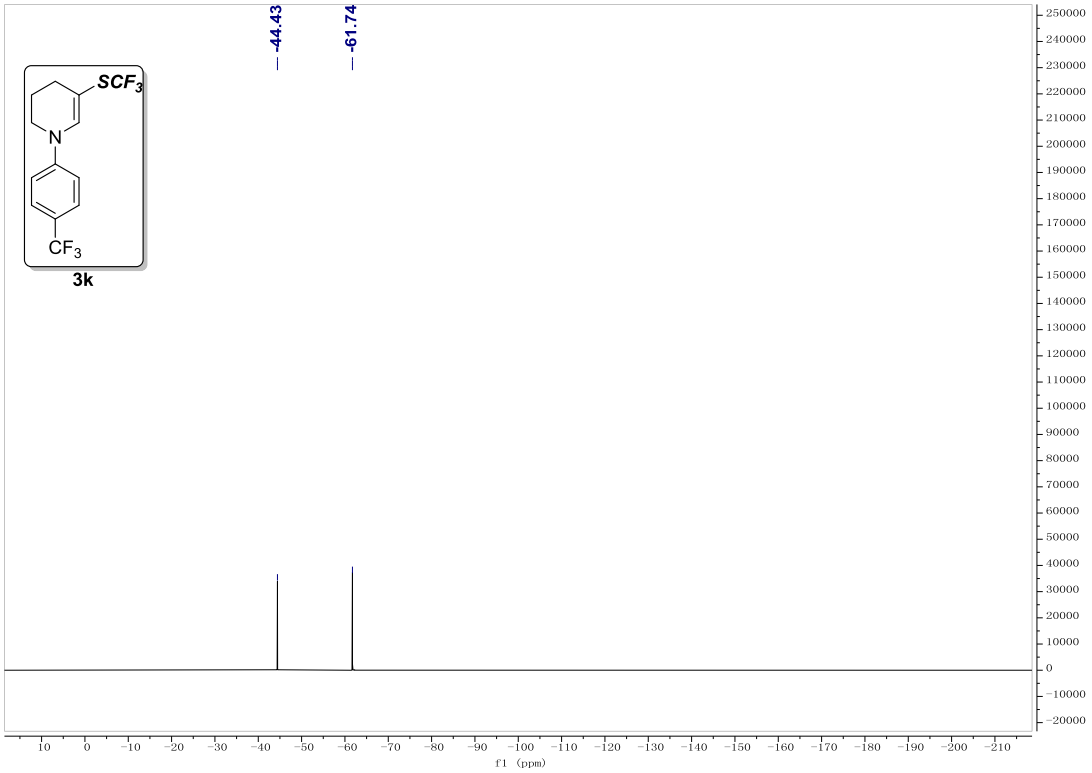
^{1}H NMR (400 MHz) Spectrum of **3k** in $CDCl_3$



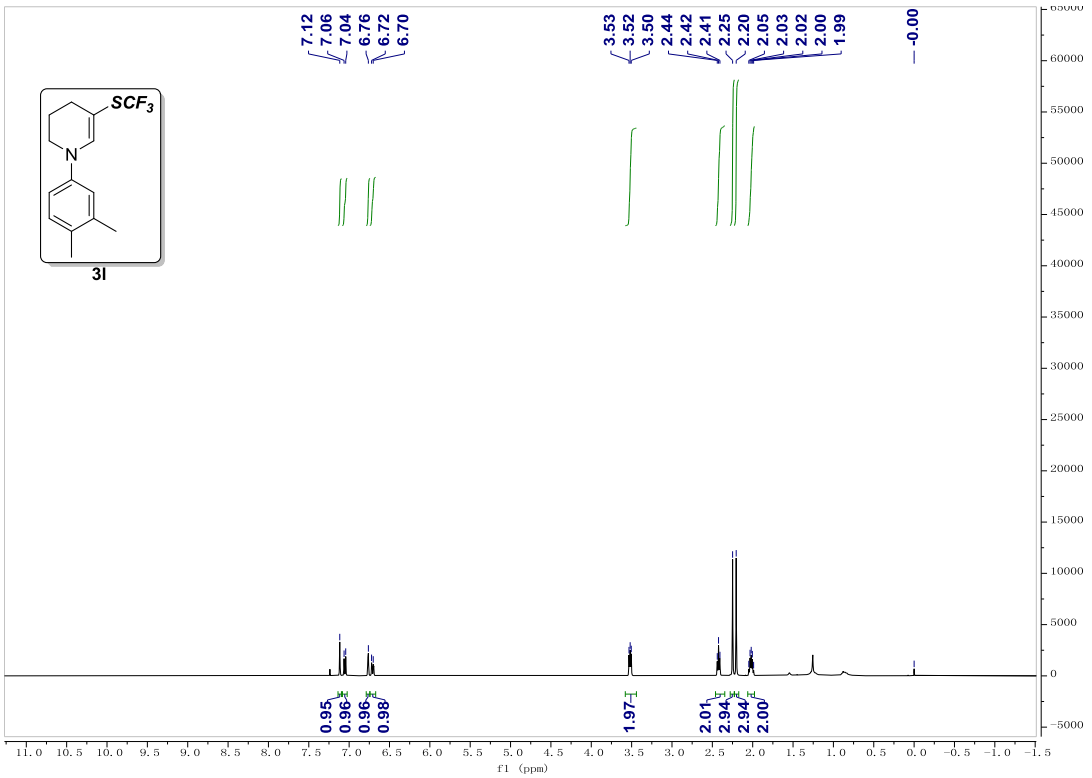
^{13}C NMR (100 MHz) Spectrum of **3k** in $CDCl_3$



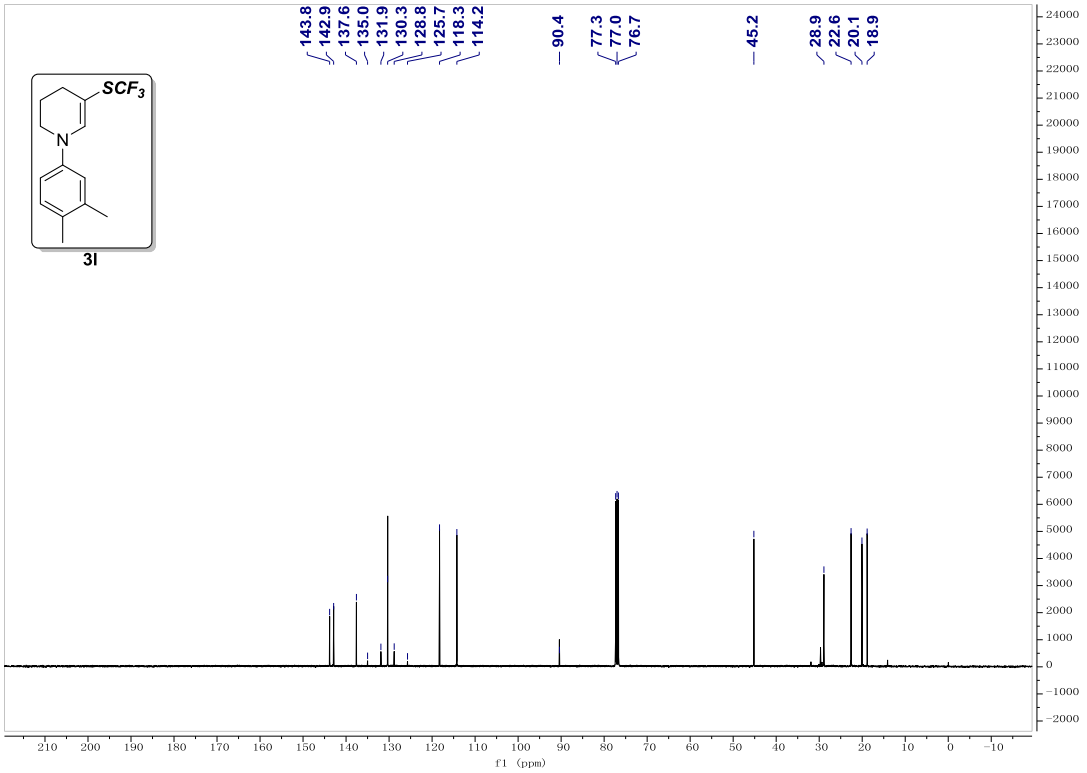
^{19}F NMR (376 MHz) Spectrum of **3k** in $CDCl_3$



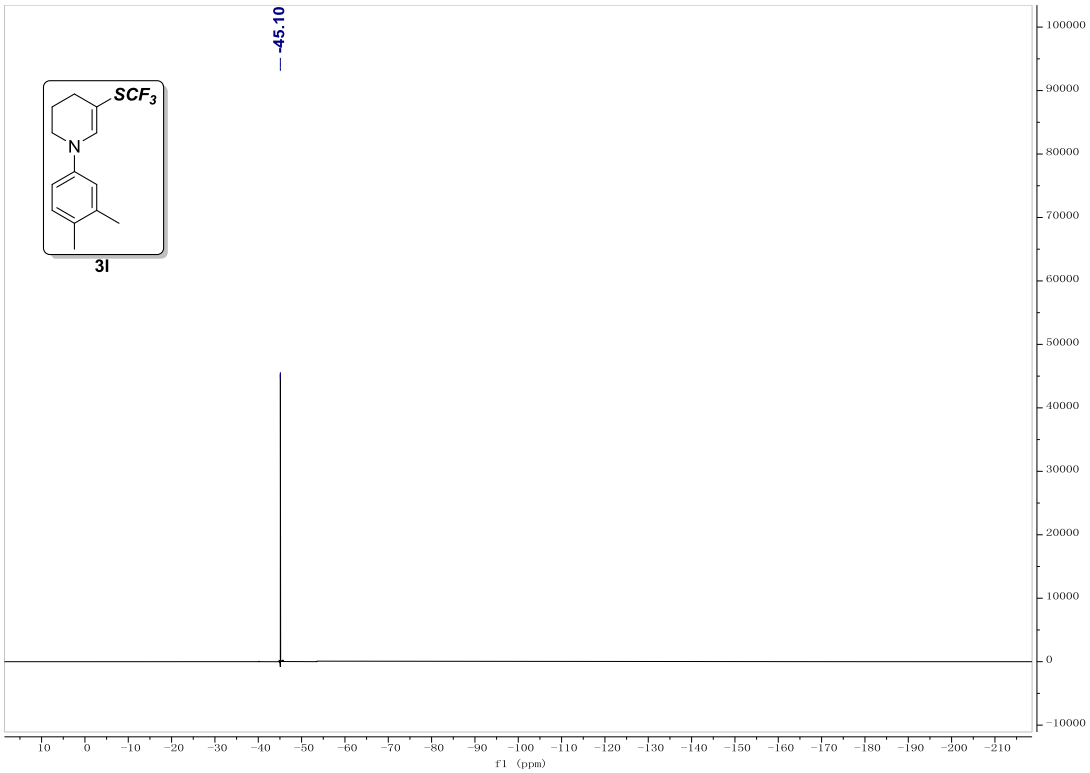
^{1}H NMR (400 MHz) Spectrum of **3l** in $CDCl_3$



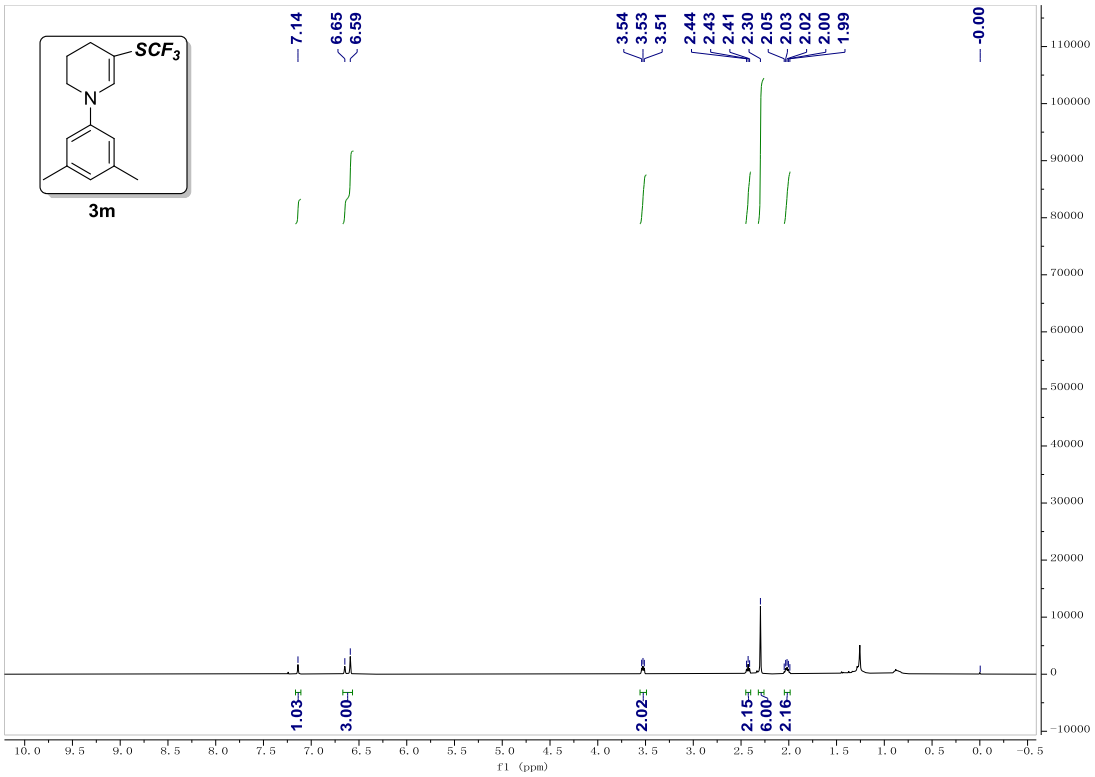
^{13}C NMR (100 MHz) Spectrum of **3l** in $CDCl_3$



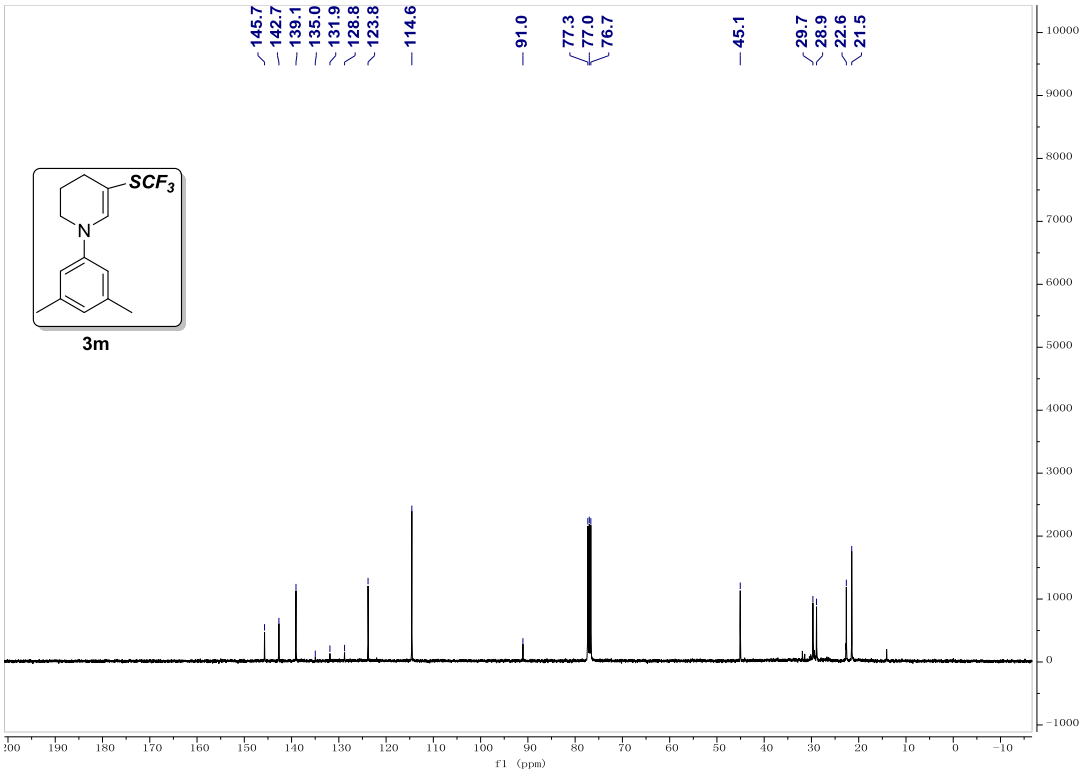
^{19}F NMR (376 MHz) Spectrum of **3l** in $CDCl_3$



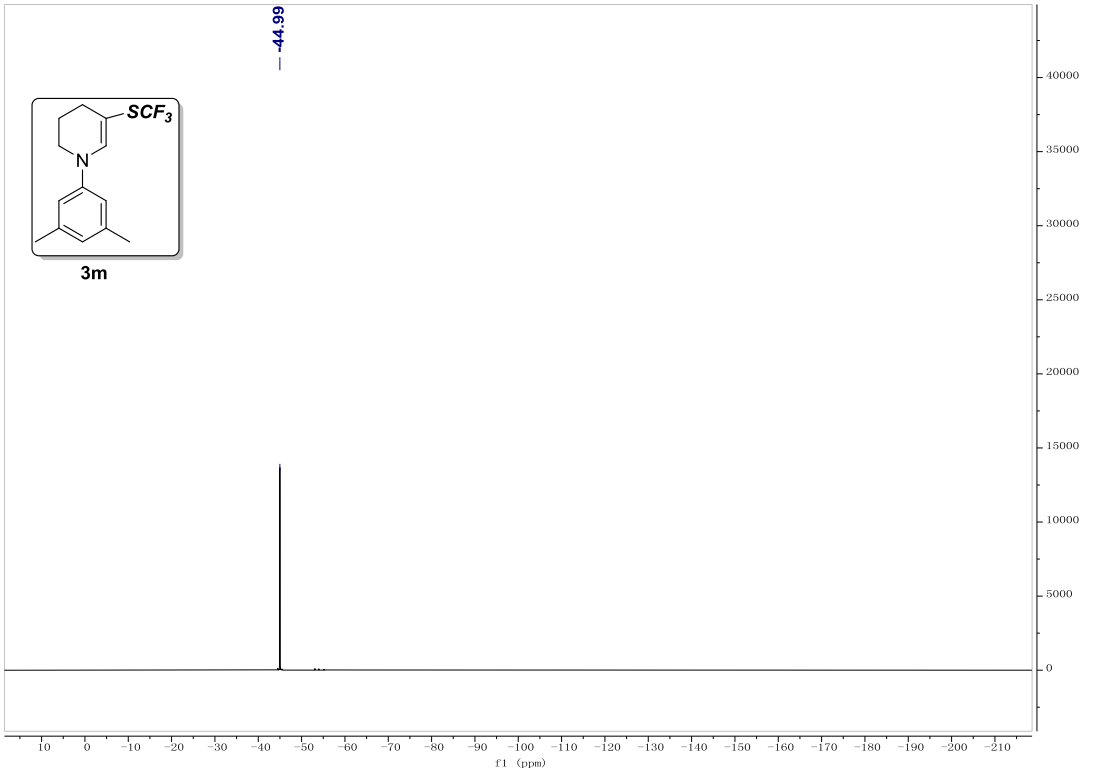
^{1}H NMR (400 MHz) Spectrum of **3m** in $CDCl_3$



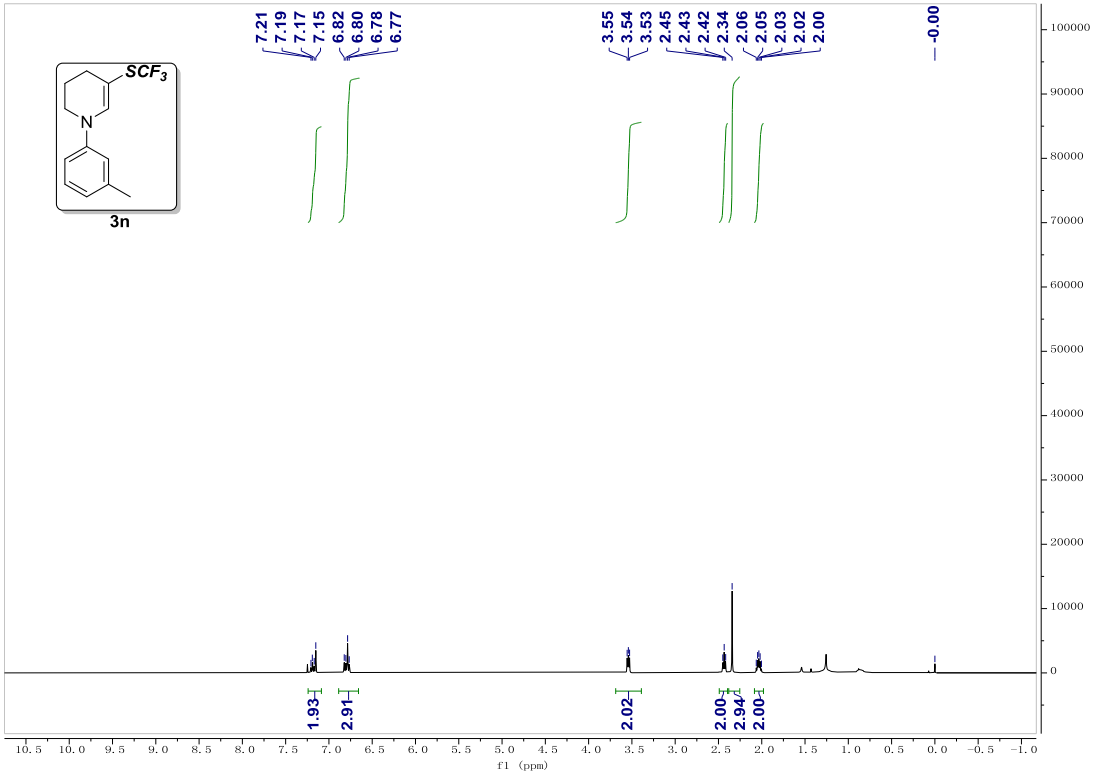
^{13}C NMR (100 MHz) Spectrum of **3m** in $CDCl_3$



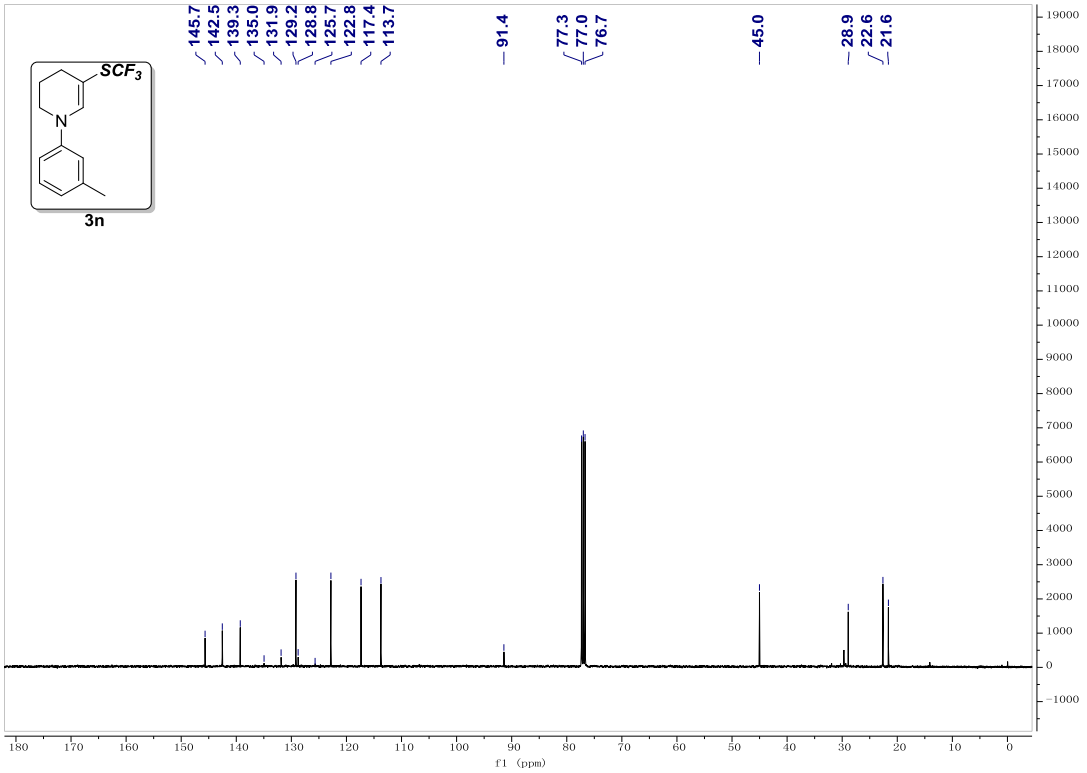
^{19}F NMR (376 MHz) Spectrum of **3m** in $CDCl_3$



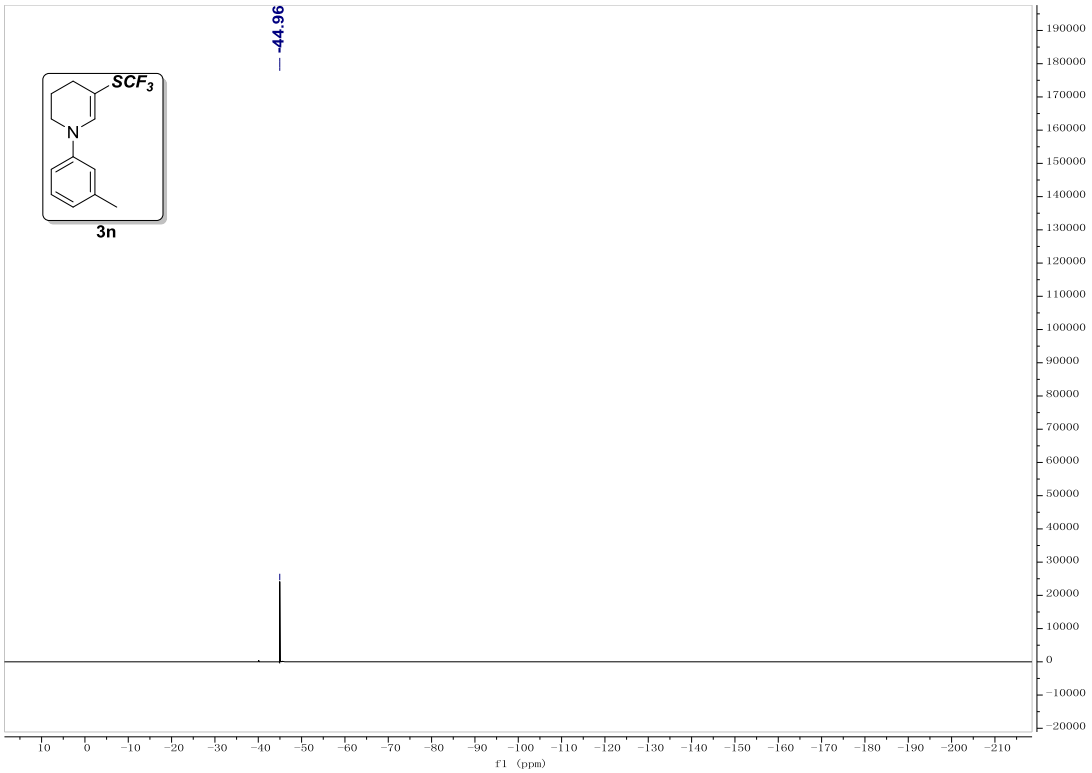
^{1}H NMR (400 MHz) Spectrum of **3n** in $CDCl_3$



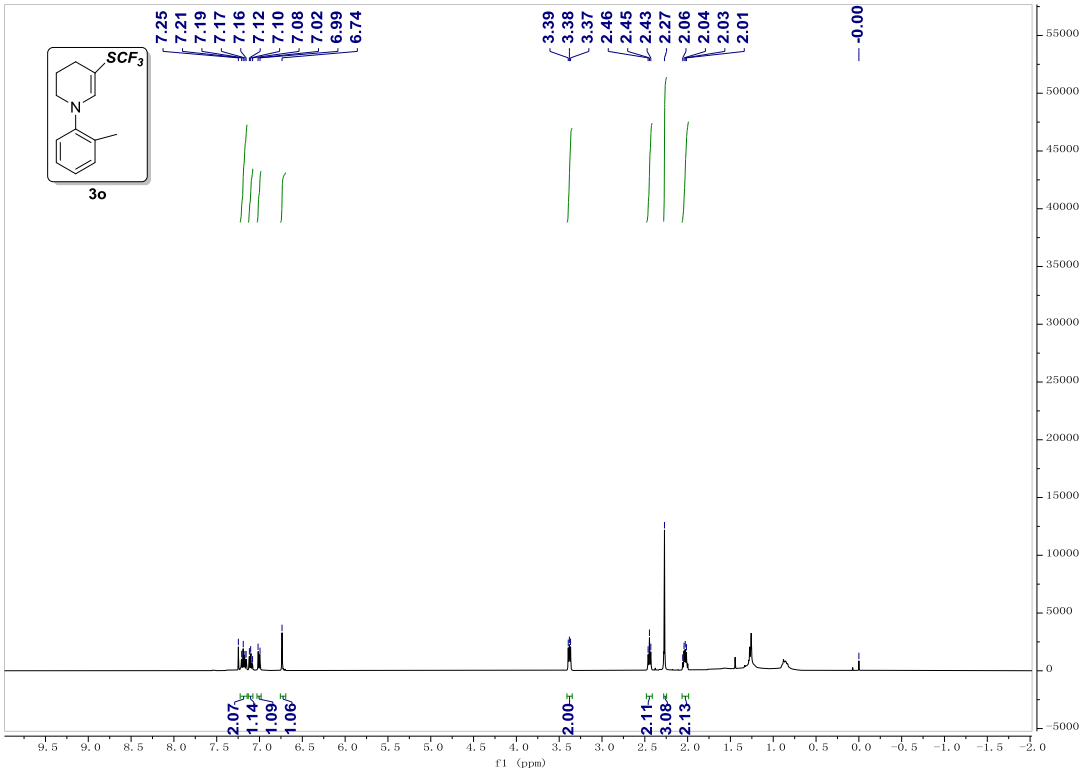
^{13}C NMR (100 MHz) Spectrum of **3n** in $CDCl_3$



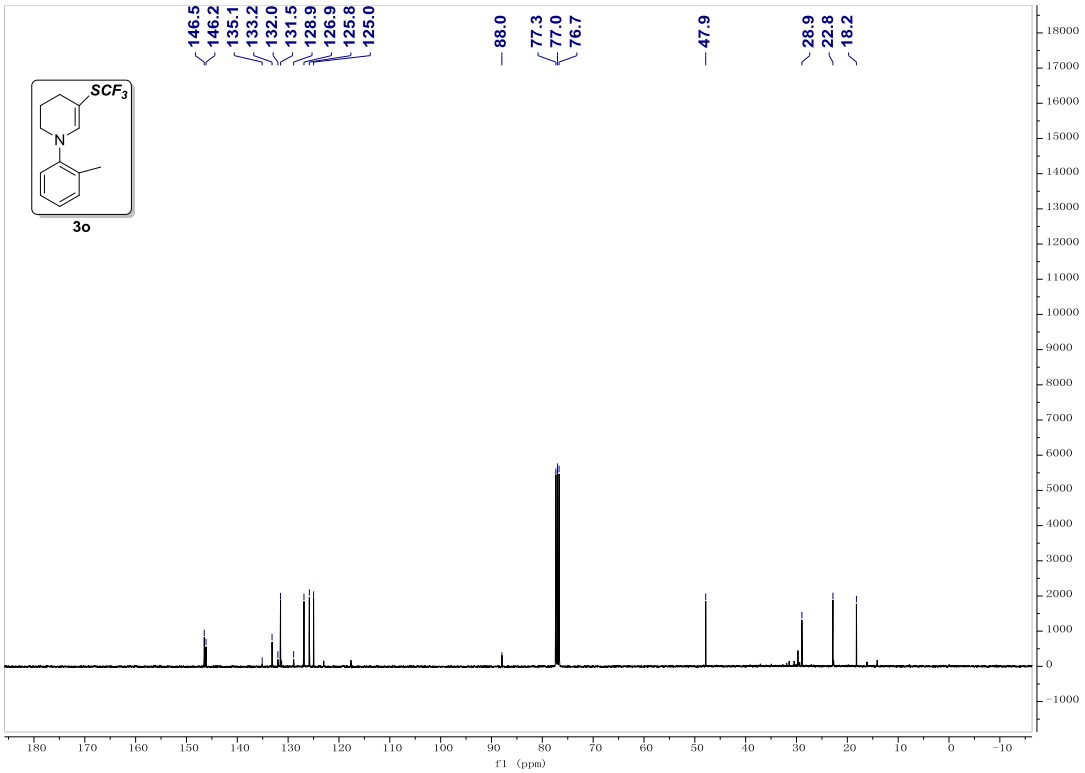
^{19}F NMR (376 MHz) Spectrum of **3n** in $CDCl_3$



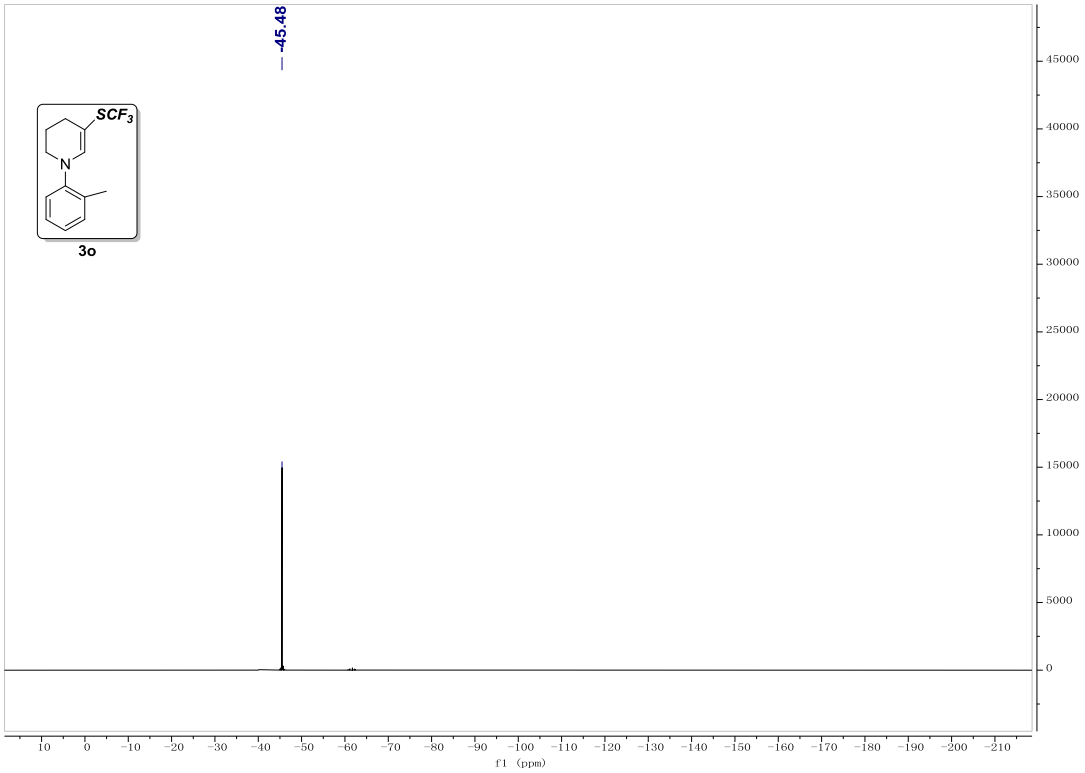
^{1}H NMR (400 MHz) Spectrum of **3o** in $CDCl_3$



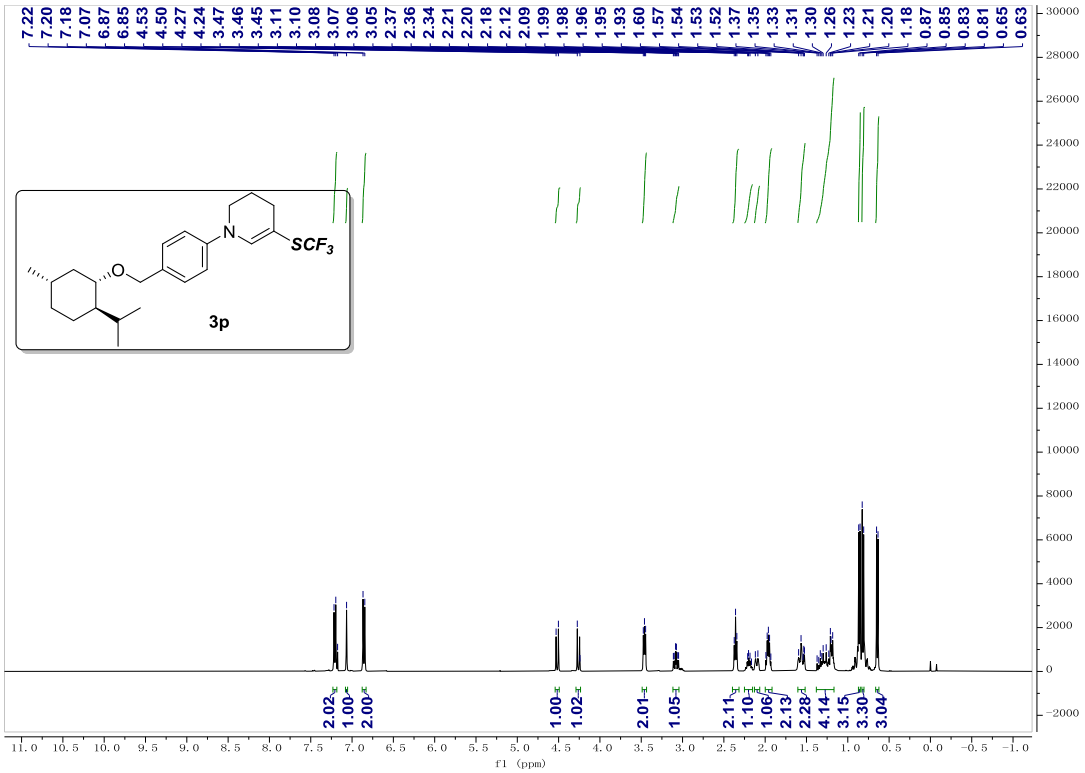
^{13}C NMR (100 MHz) Spectrum of **3o** in $CDCl_3$



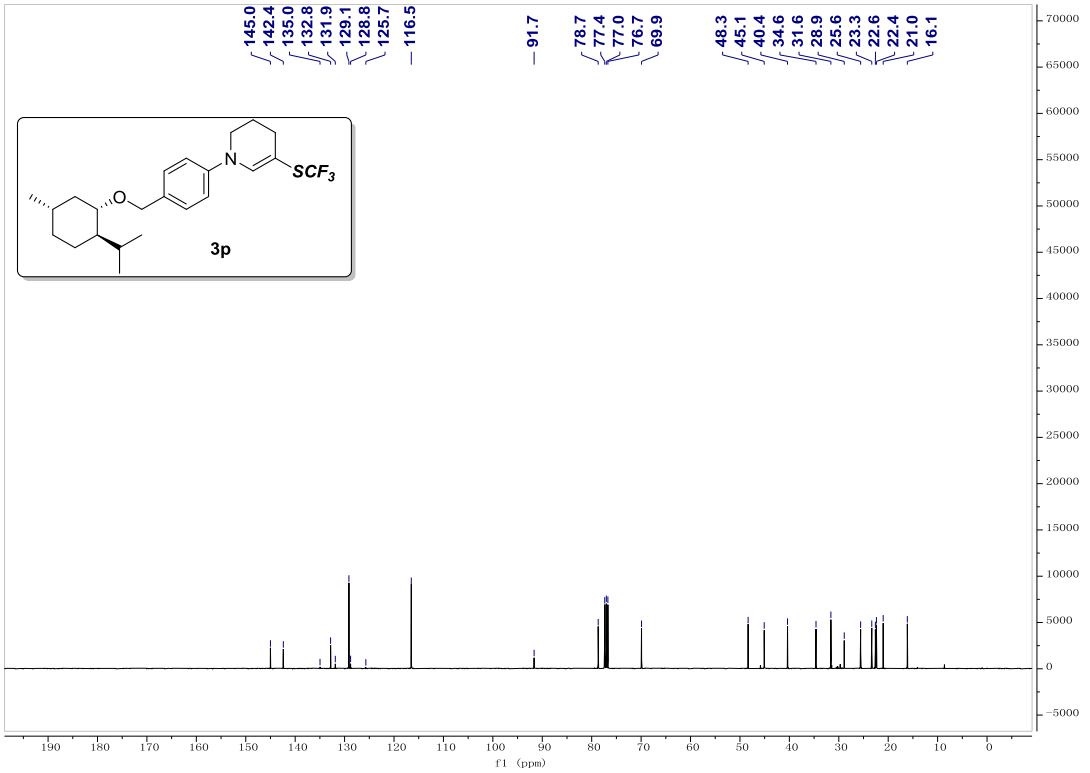
^{19}F NMR (376 MHz) Spectrum of **3o** in $CDCl_3$



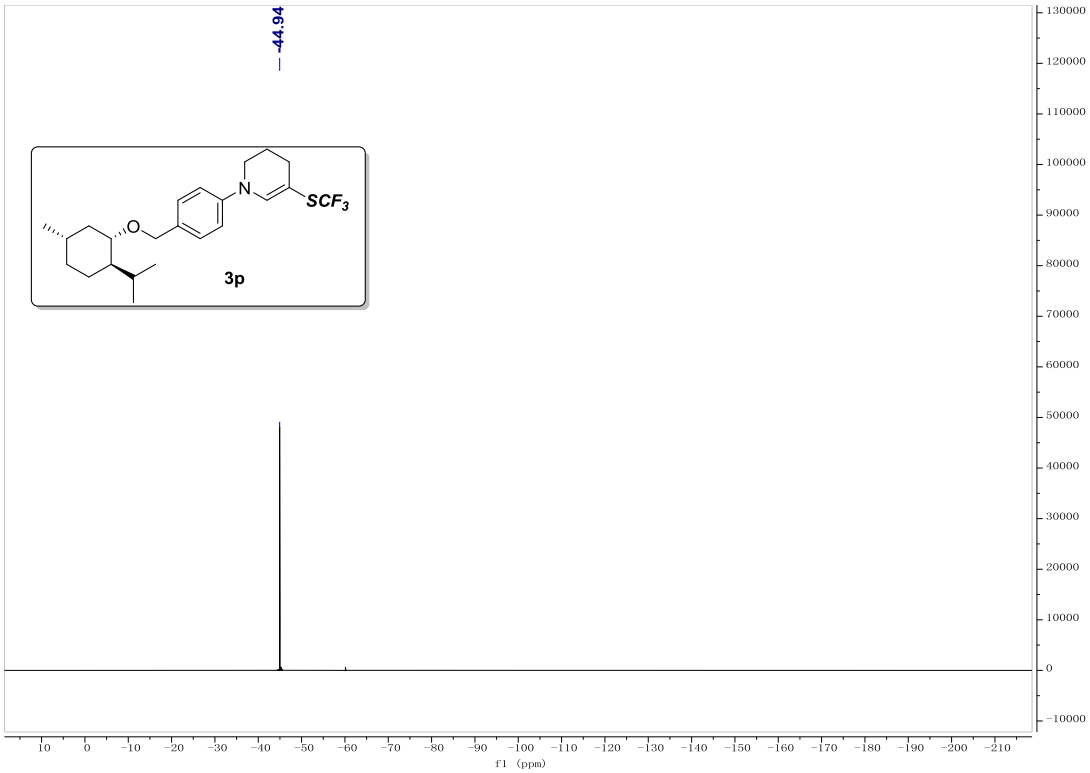
^{1}H NMR (400 MHz) Spectrum of **3p** in $CDCl_3$



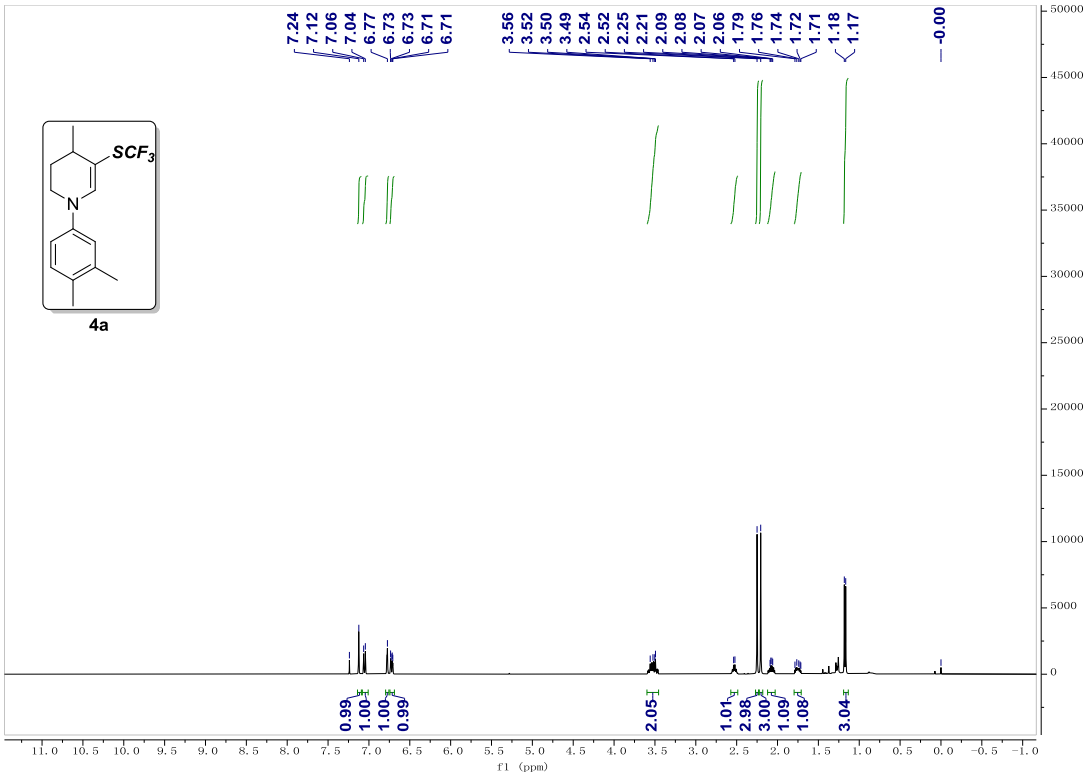
^{13}C NMR (100 MHz) Spectrum of **3p** in $CDCl_3$



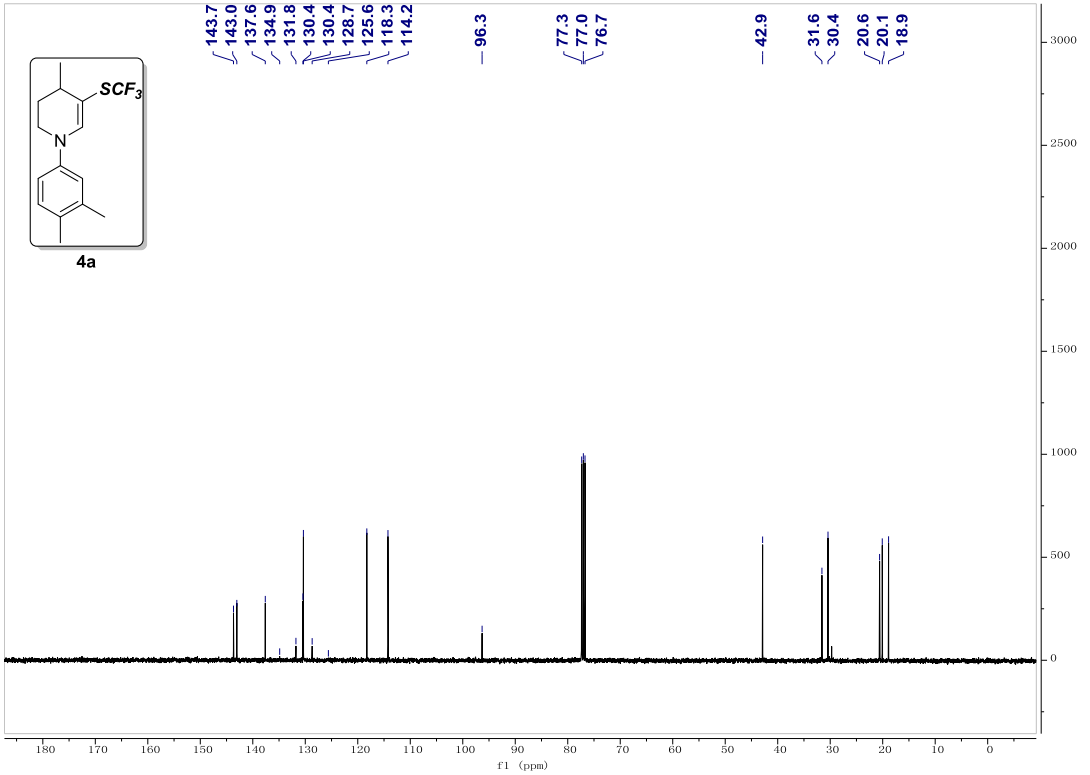
^{19}F NMR (376 MHz) Spectrum of **3p** in $CDCl_3$



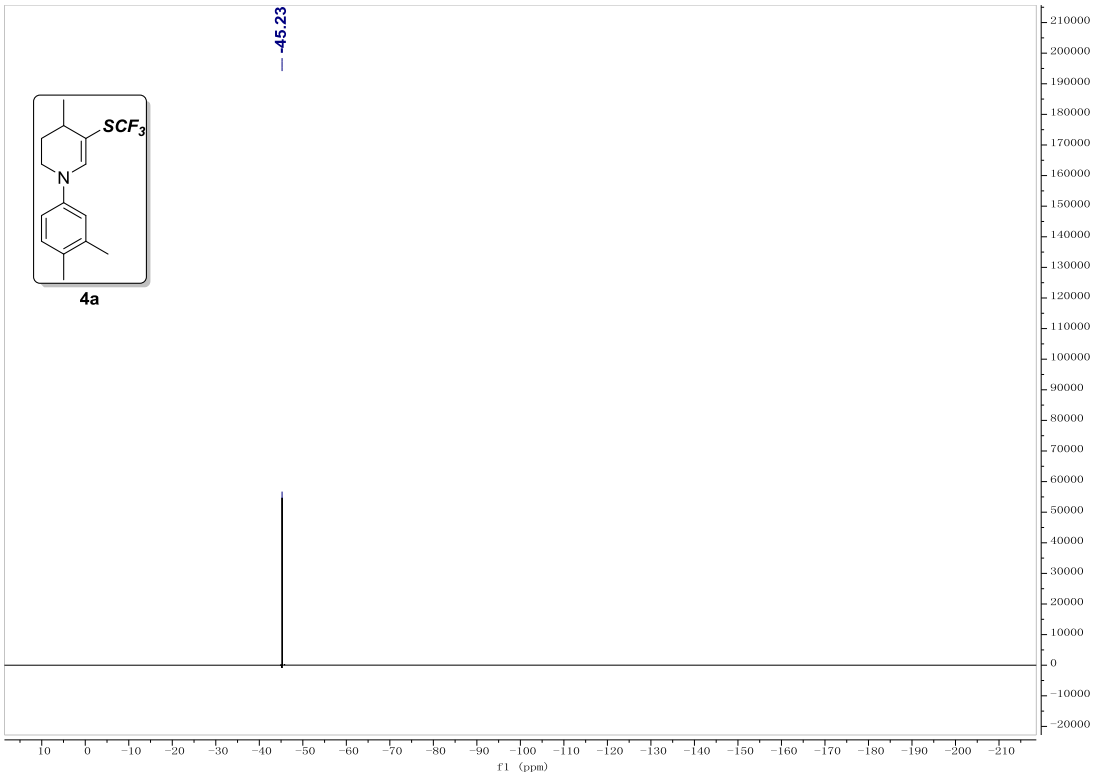
^{1}H NMR (400 MHz) Spectrum of **4a** in $CDCl_3$



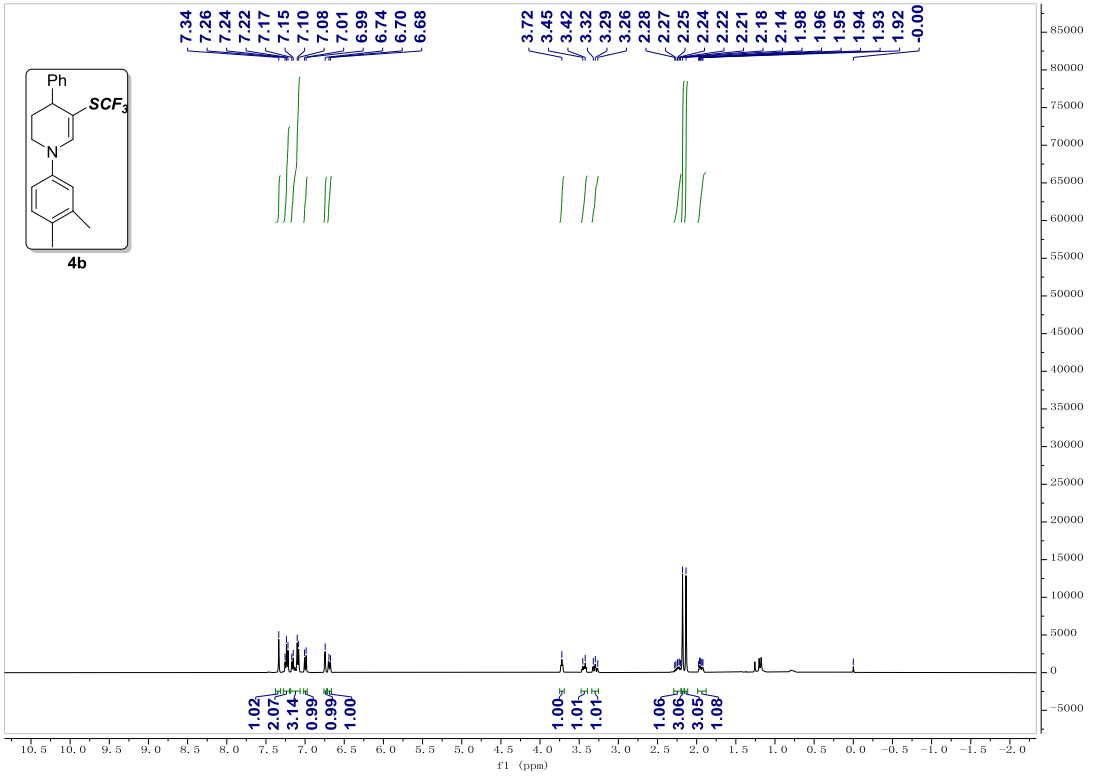
^{13}C NMR (100 MHz) Spectrum of **4a** in $CDCl_3$



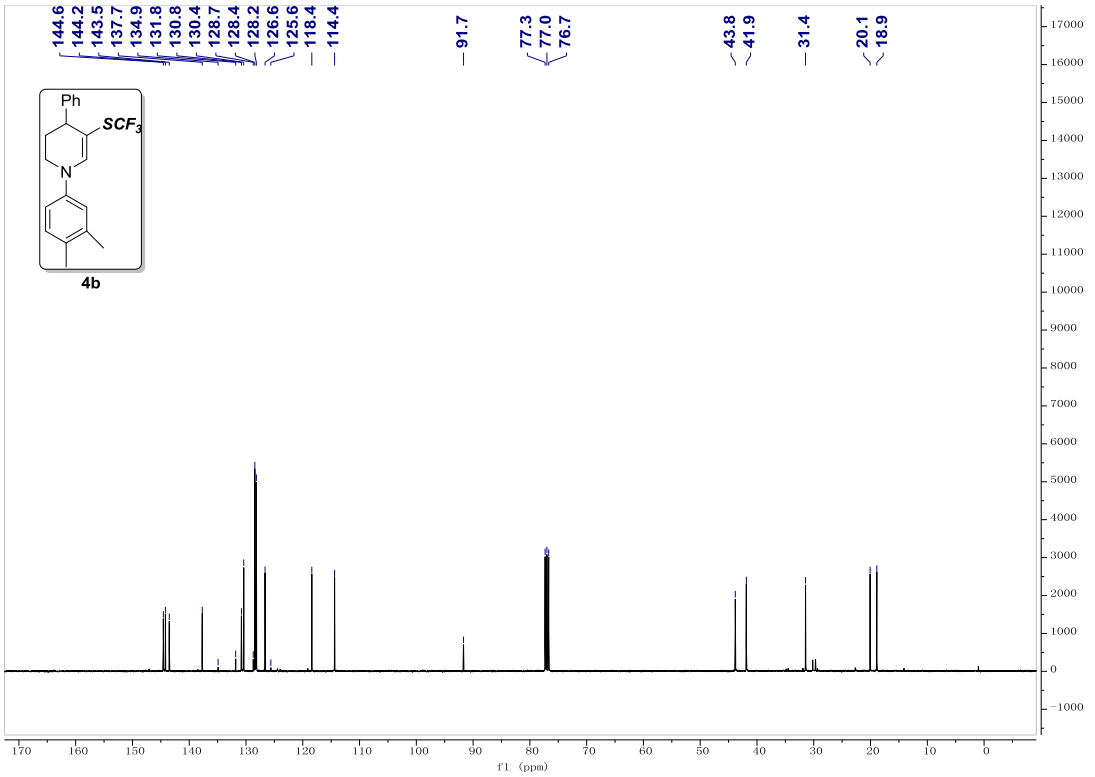
^{19}F NMR (376 MHz) Spectrum of **4a** in $CDCl_3$



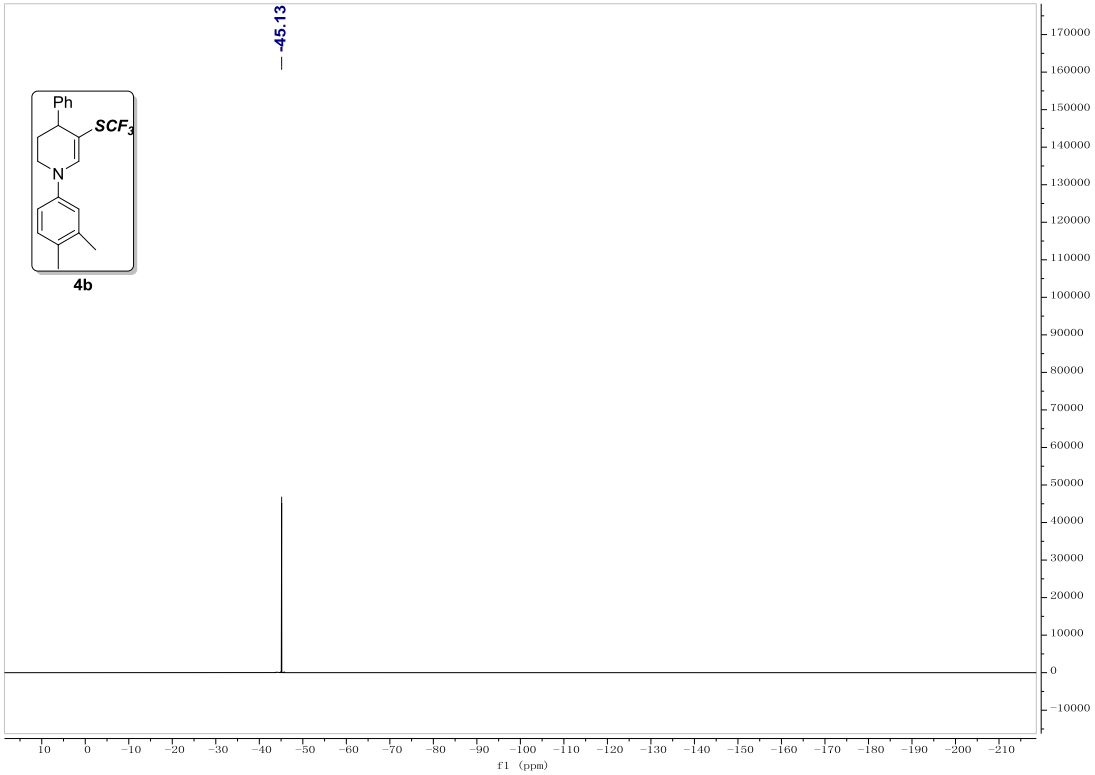
^{1}H NMR (400 MHz) Spectrum of **4b** in $CDCl_3$



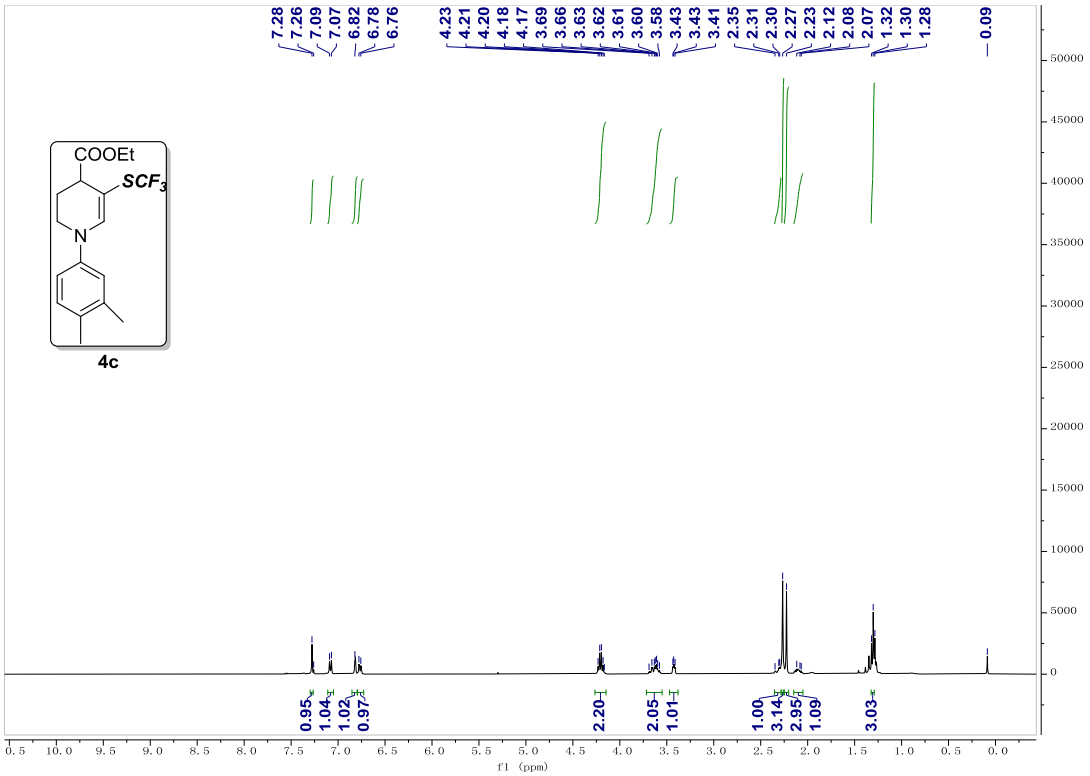
^{13}C NMR (100 MHz) Spectrum of **4b** in $CDCl_3$



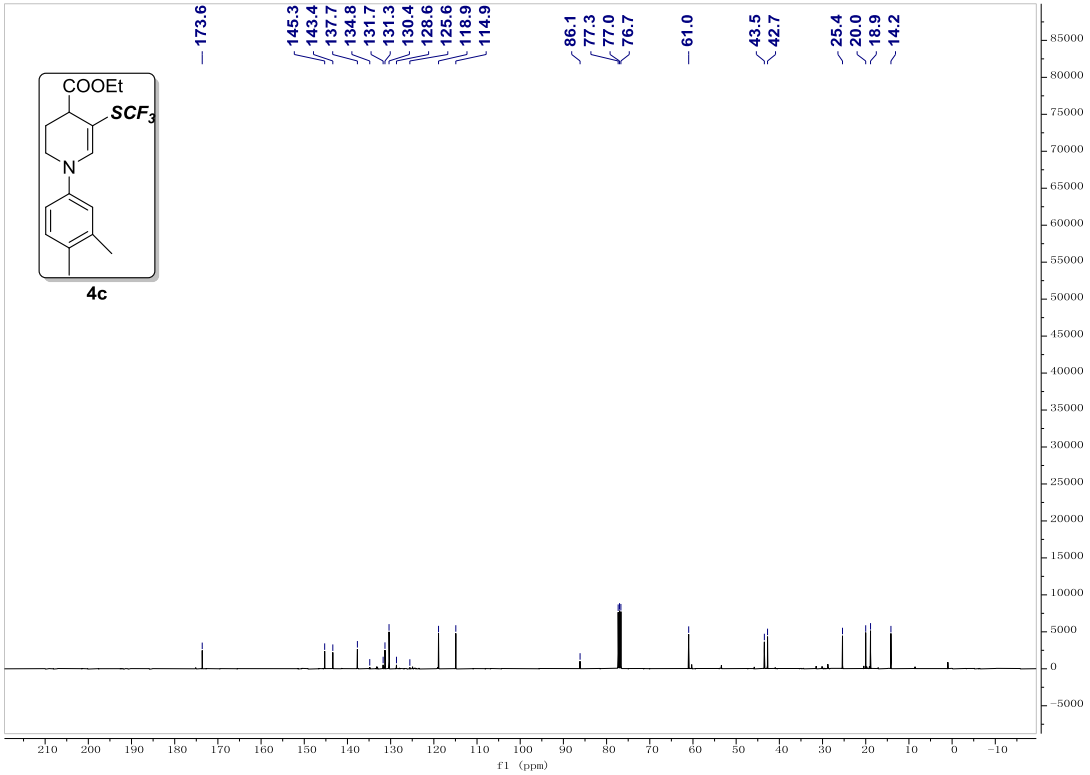
^{19}F NMR (376 MHz) Spectrum of **4b** in $CDCl_3$



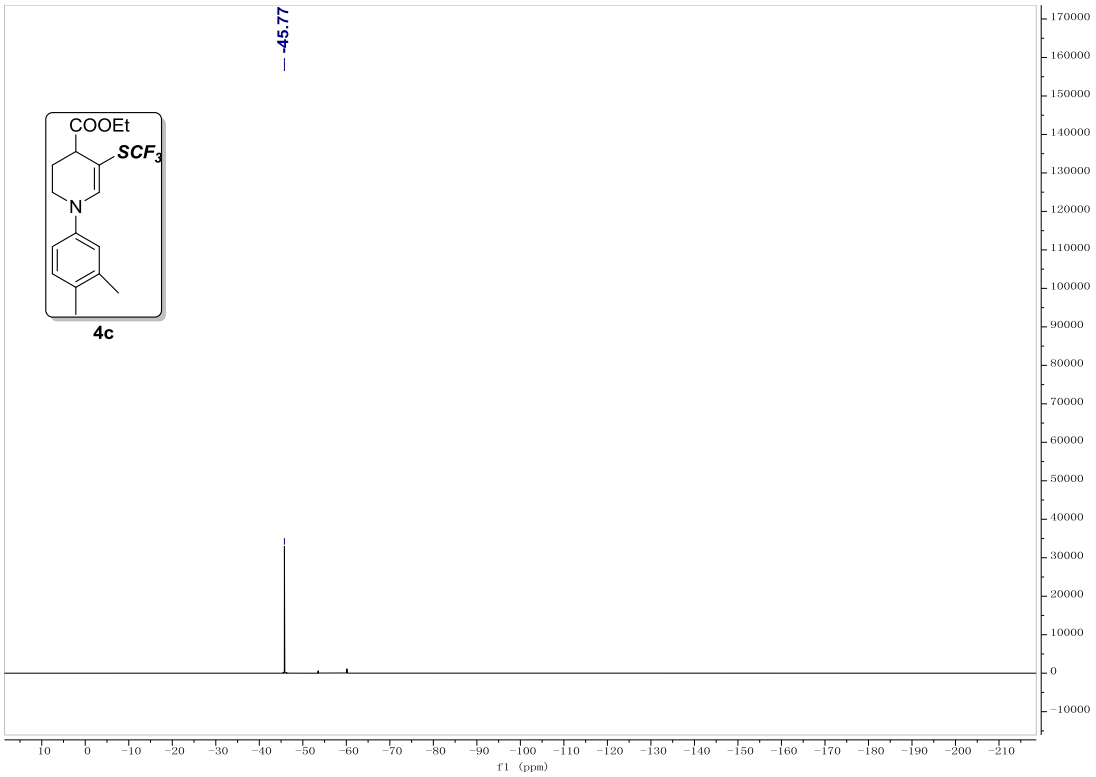
^{1}H NMR (400 MHz) Spectrum of **4c** in $CDCl_3$



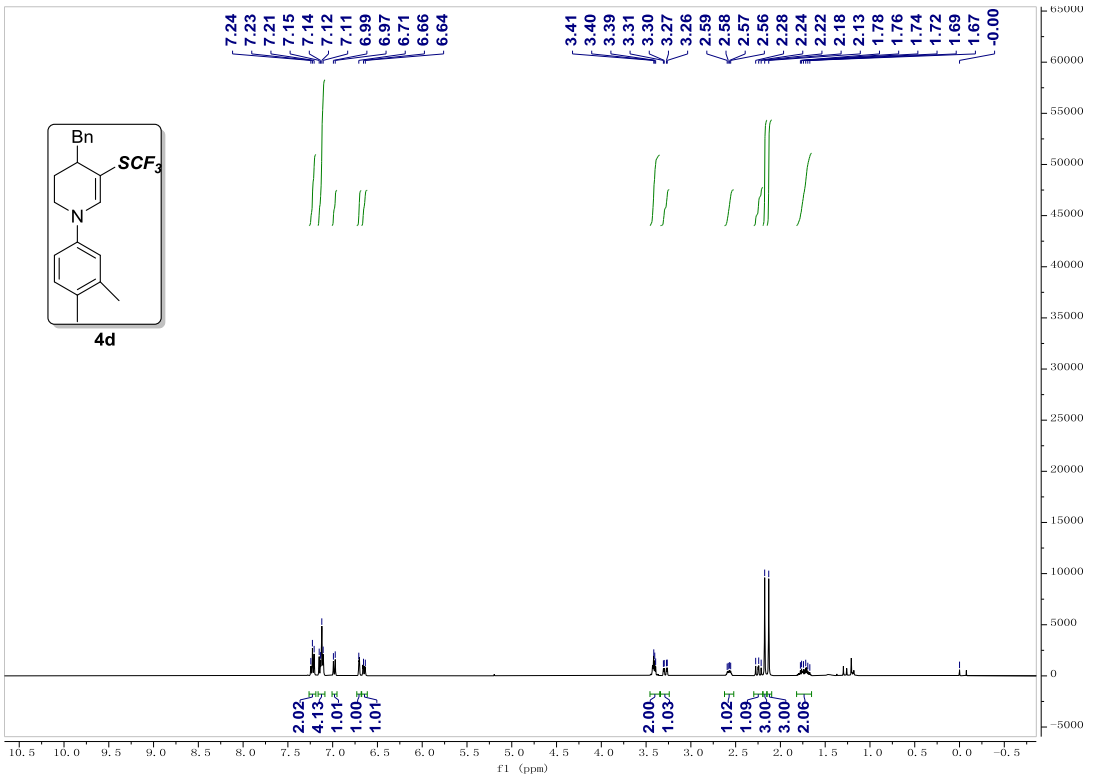
^{13}C NMR (100 MHz) Spectrum of **4c** in $CDCl_3$



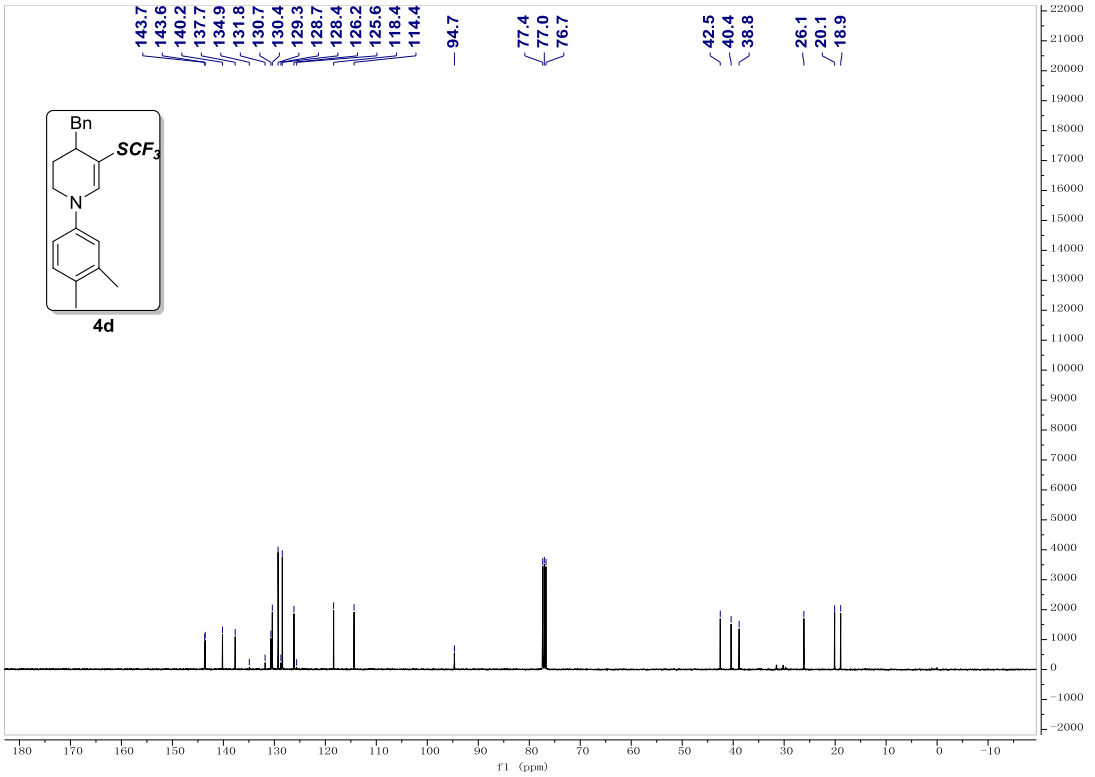
^{19}F NMR (376 MHz) Spectrum of **4c** in $CDCl_3$



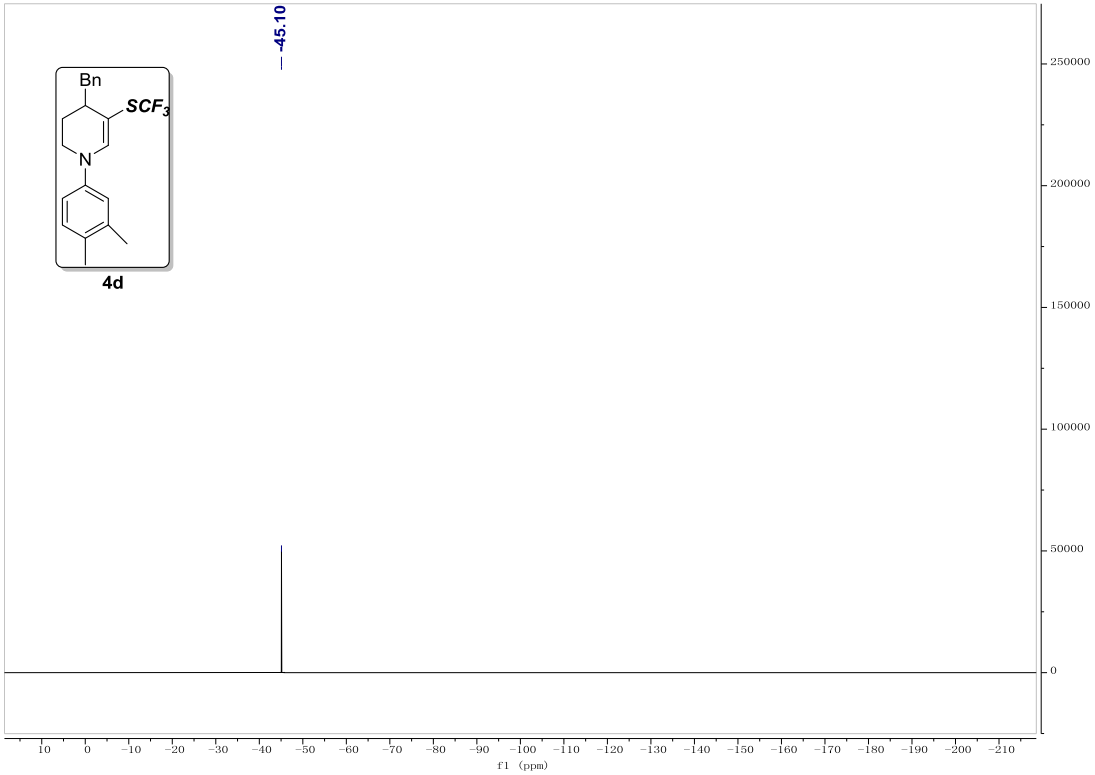
^{1}H NMR (400 MHz) Spectrum of **4d** in $CDCl_3$



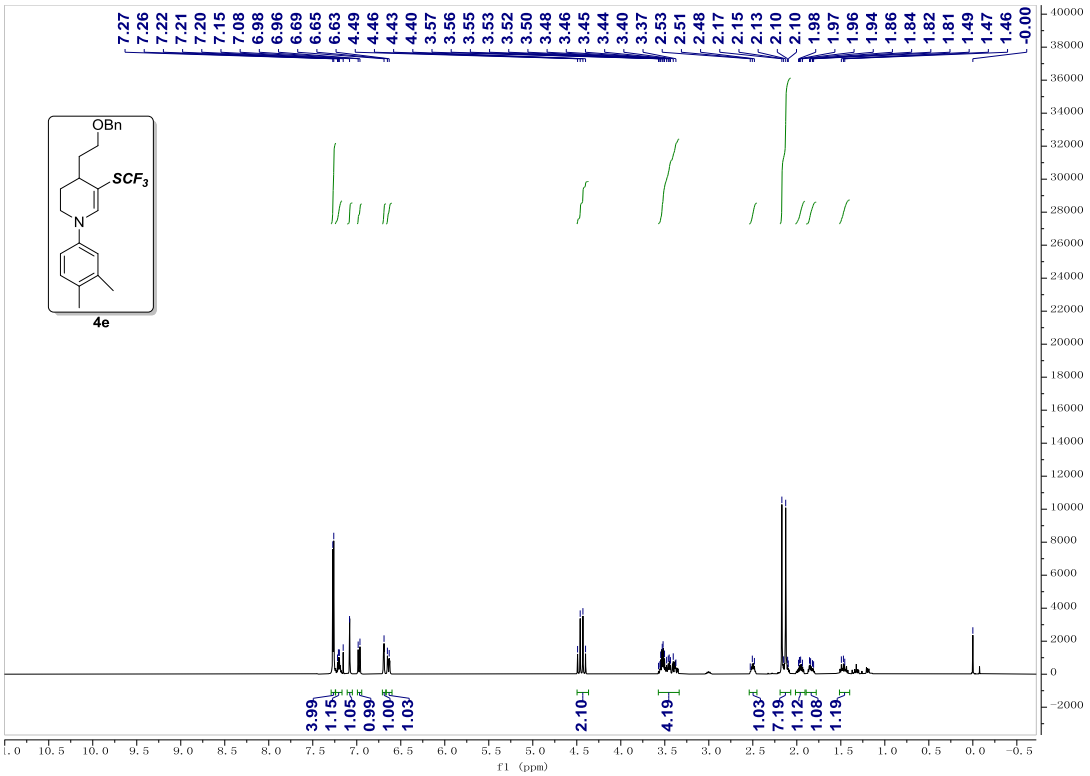
^{13}C NMR (100 MHz) Spectrum of **4d** in $CDCl_3$



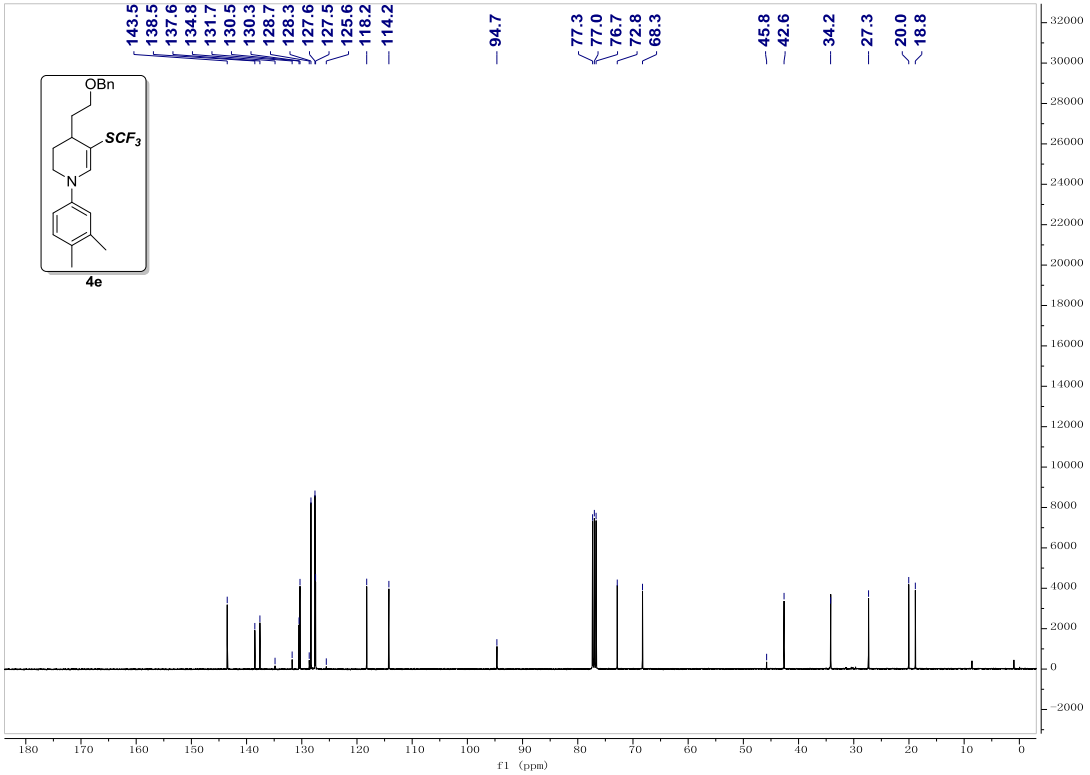
^{19}F NMR (376 MHz) Spectrum of **4d** in $CDCl_3$



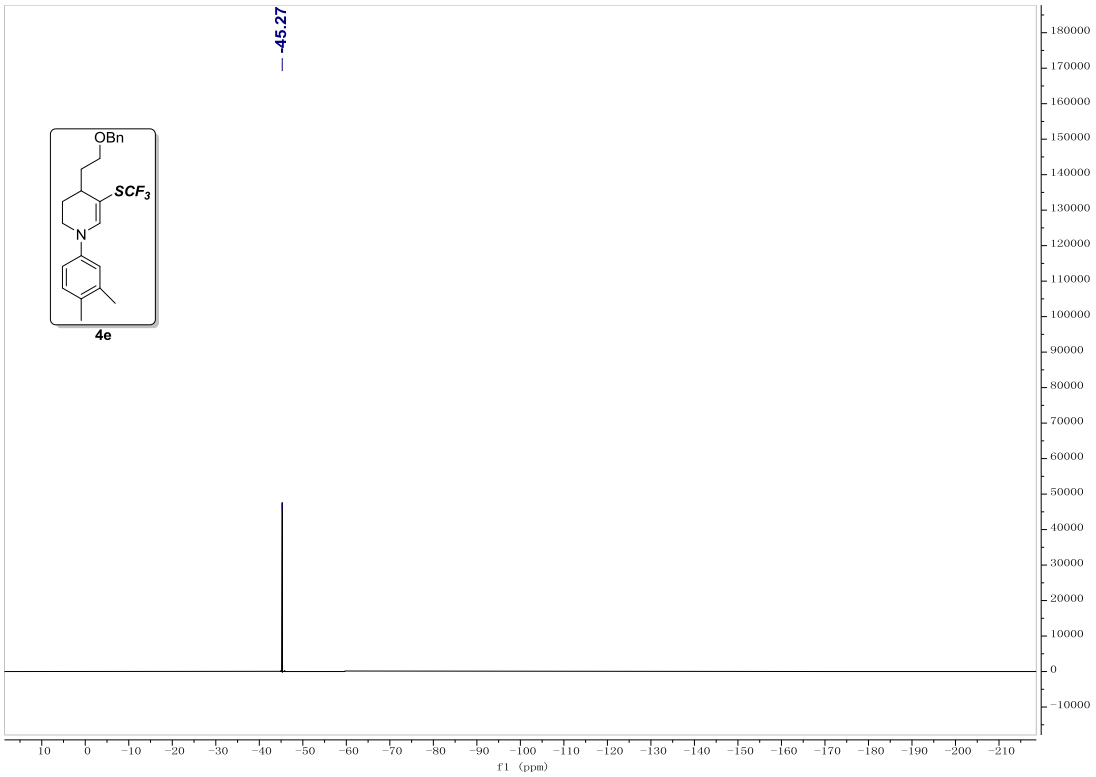
^{1}H NMR (400 MHz) Spectrum of **4e** in $CDCl_3$



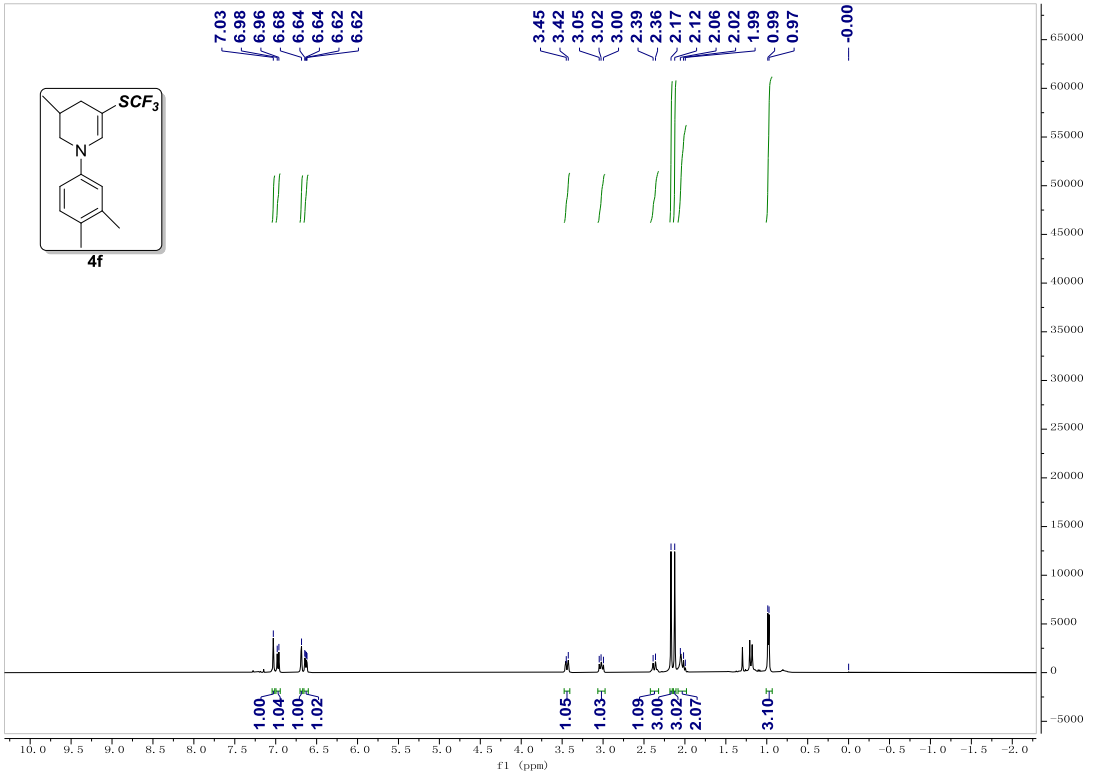
^{13}C NMR (100 MHz) Spectrum of **4e** in $CDCl_3$



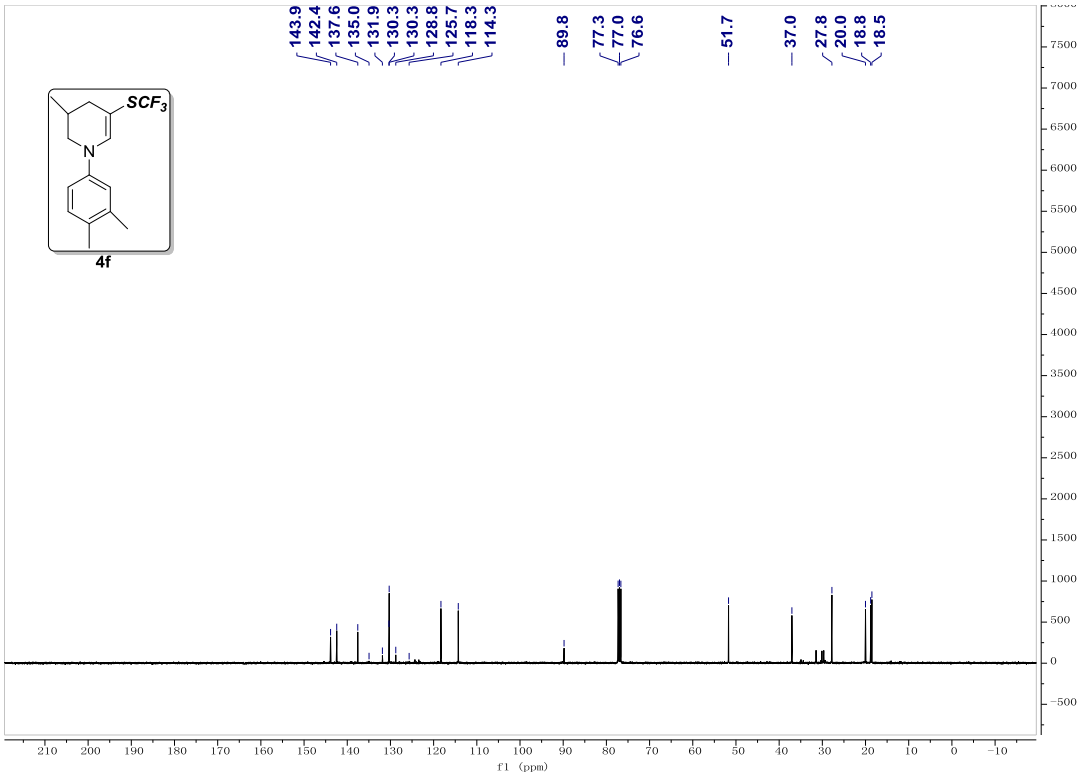
^{19}F NMR (376 MHz) Spectrum of **4e** in $CDCl_3$



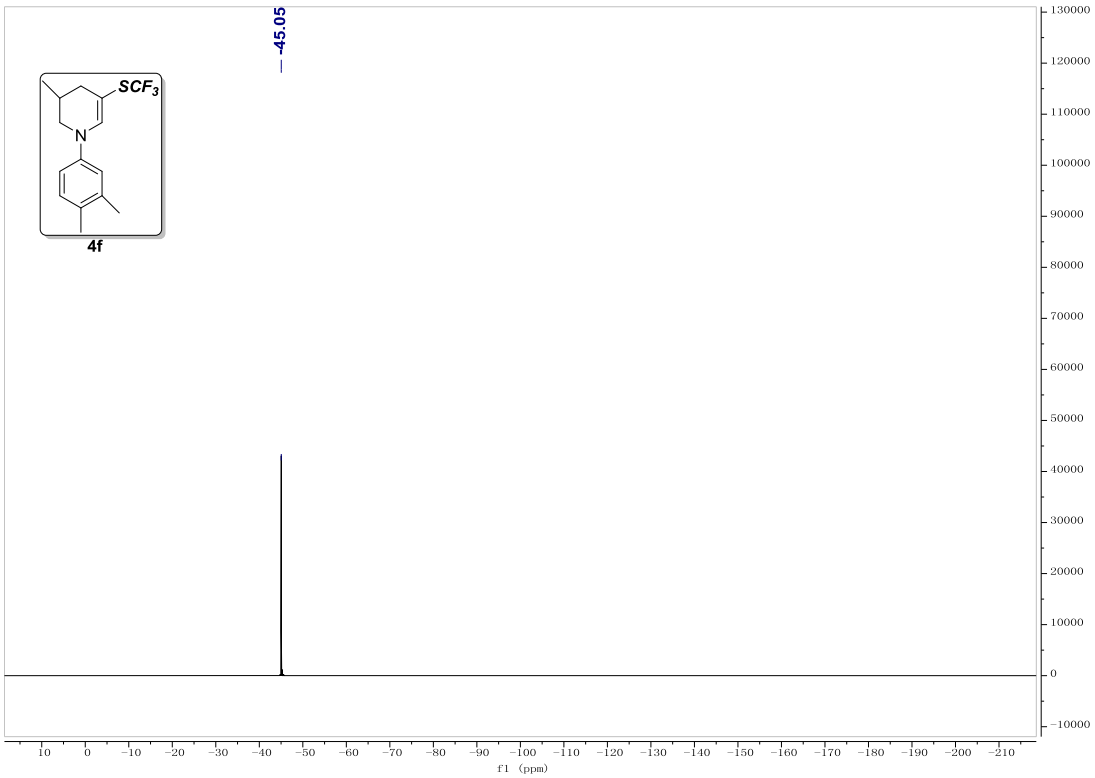
^{1}H NMR (400 MHz) Spectrum of **4f** in $CDCl_3$



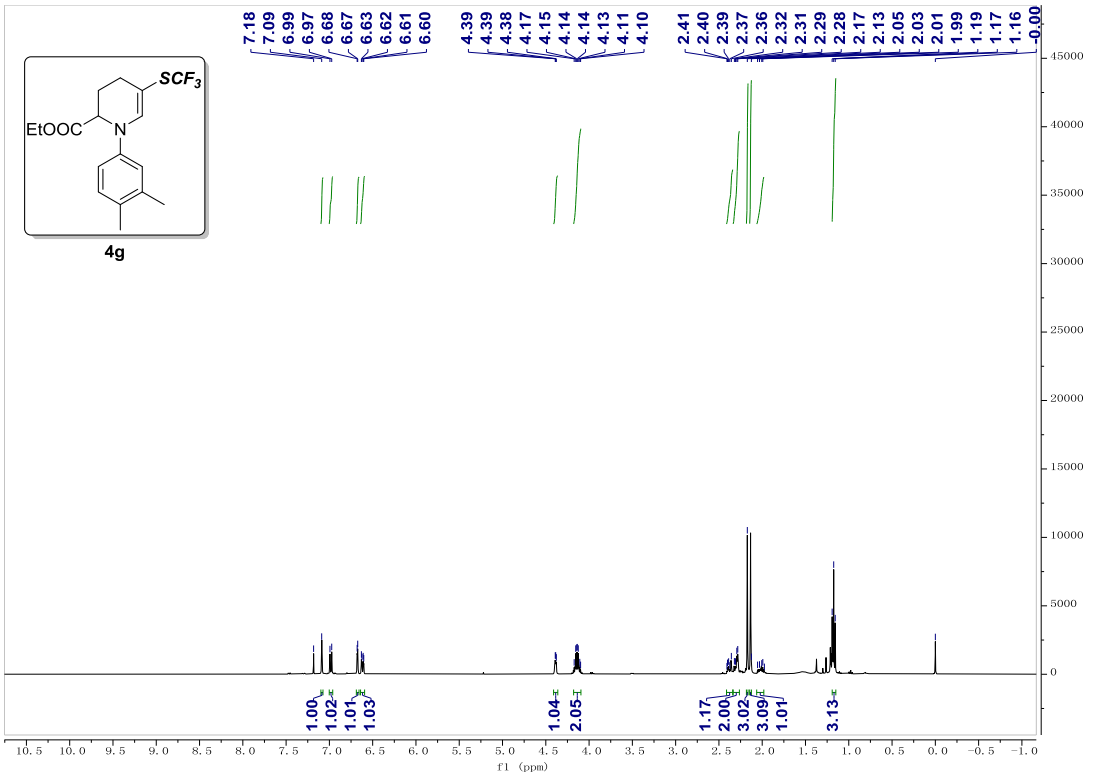
^{13}C NMR (100 MHz) Spectrum of **4f** in $CDCl_3$



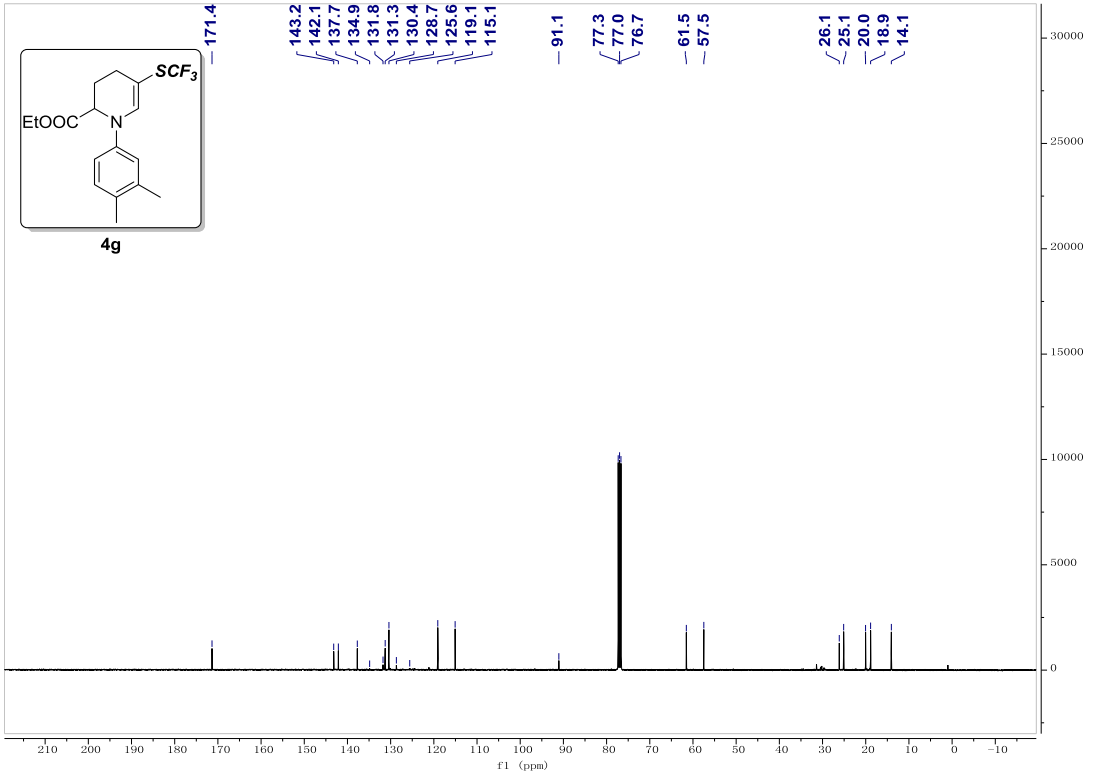
^{19}F NMR (376 MHz) Spectrum of **4f** in $CDCl_3$



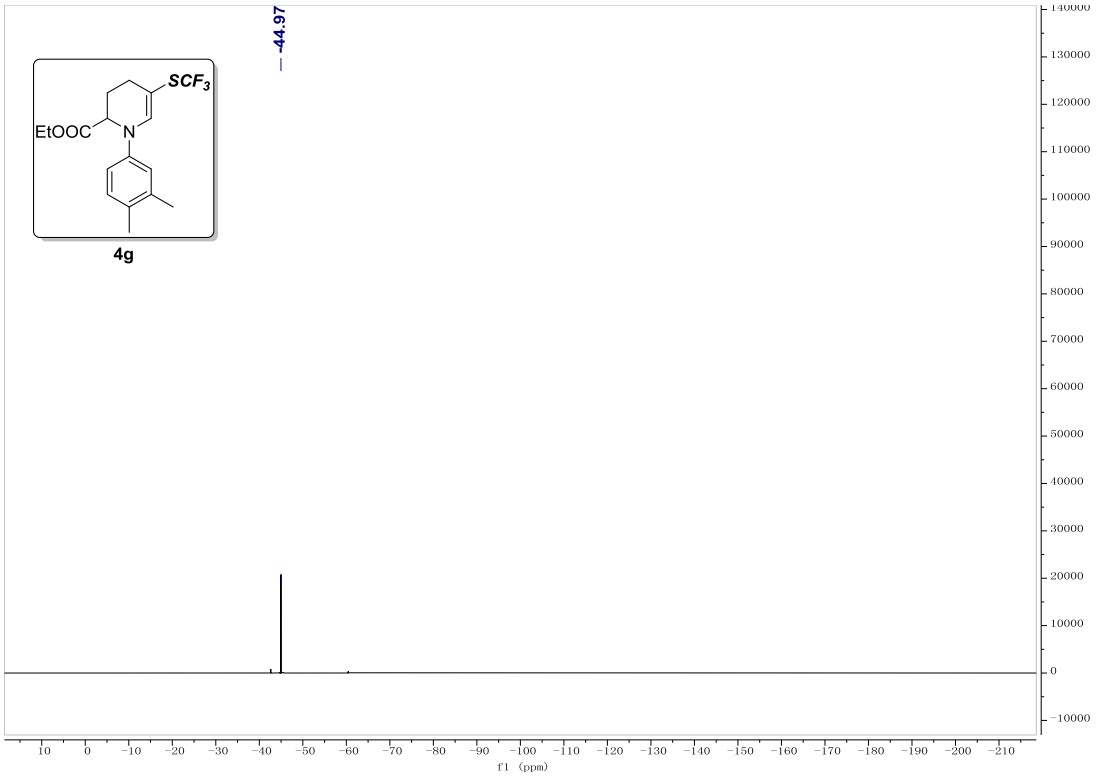
^{1}H NMR (400 MHz) Spectrum of **4g** in $CDCl_3$



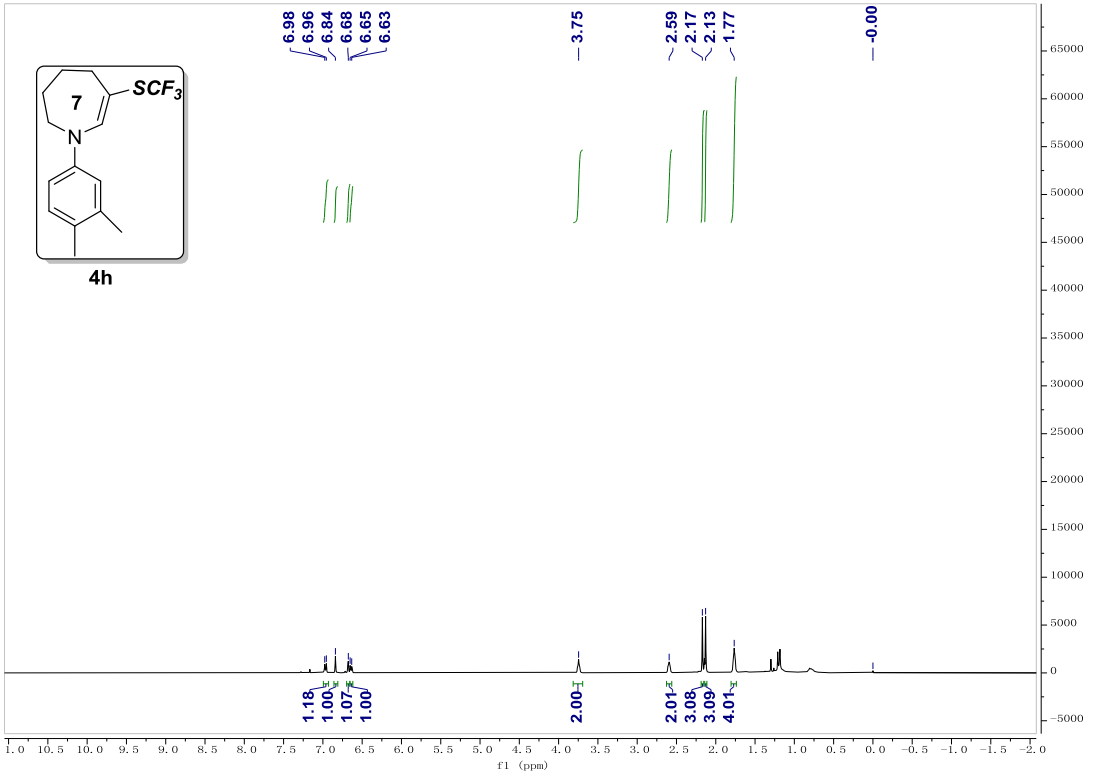
^{13}C NMR (100 MHz) Spectrum of **4g** in $CDCl_3$



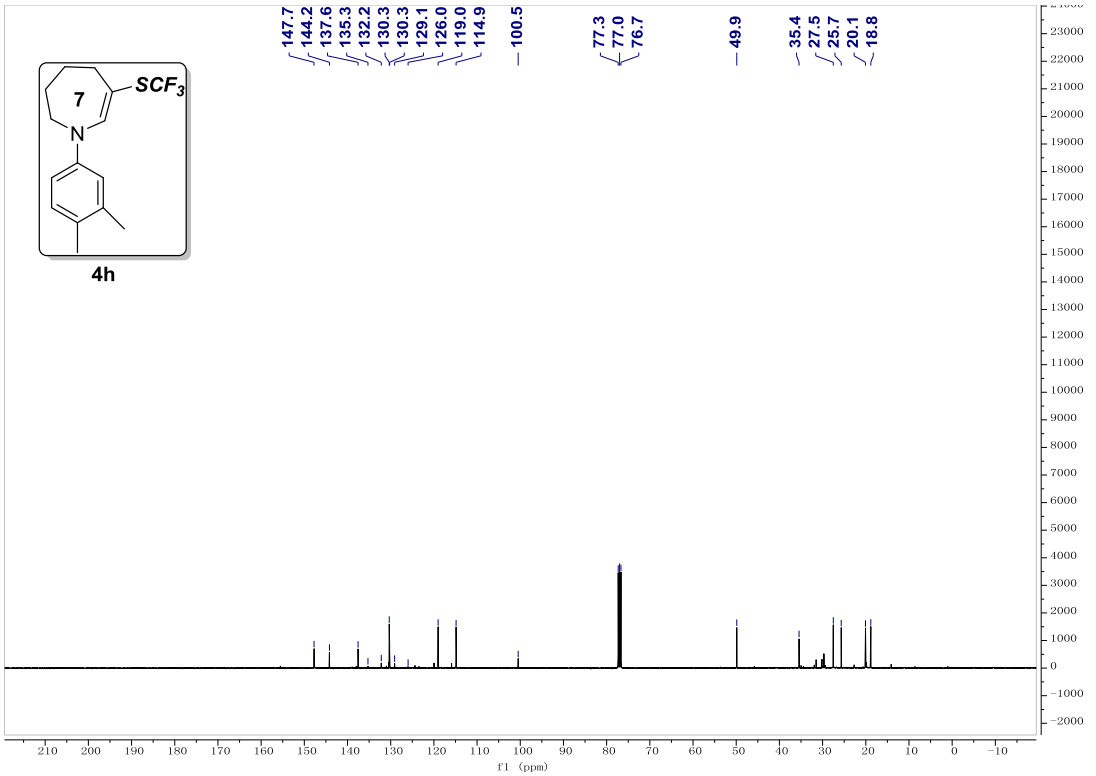
^{19}F NMR (376 MHz) Spectrum of **4g** in $CDCl_3$



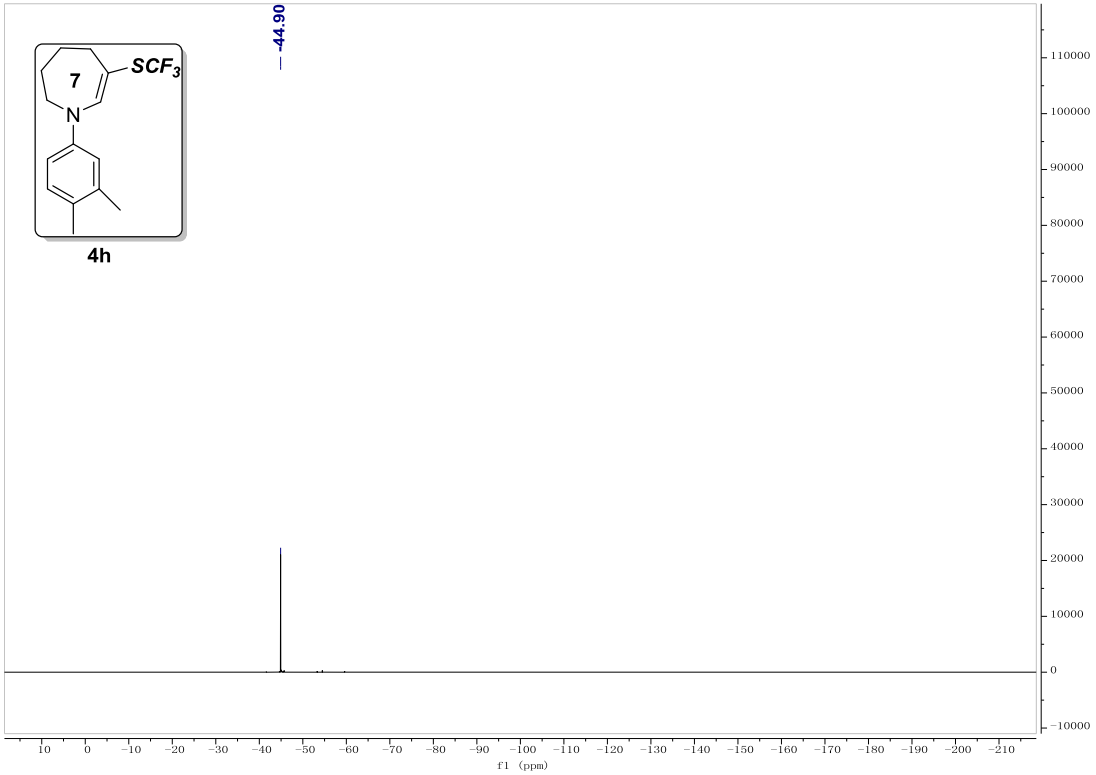
^{1}H NMR (400 MHz) Spectrum of **4h** in $CDCl_3$



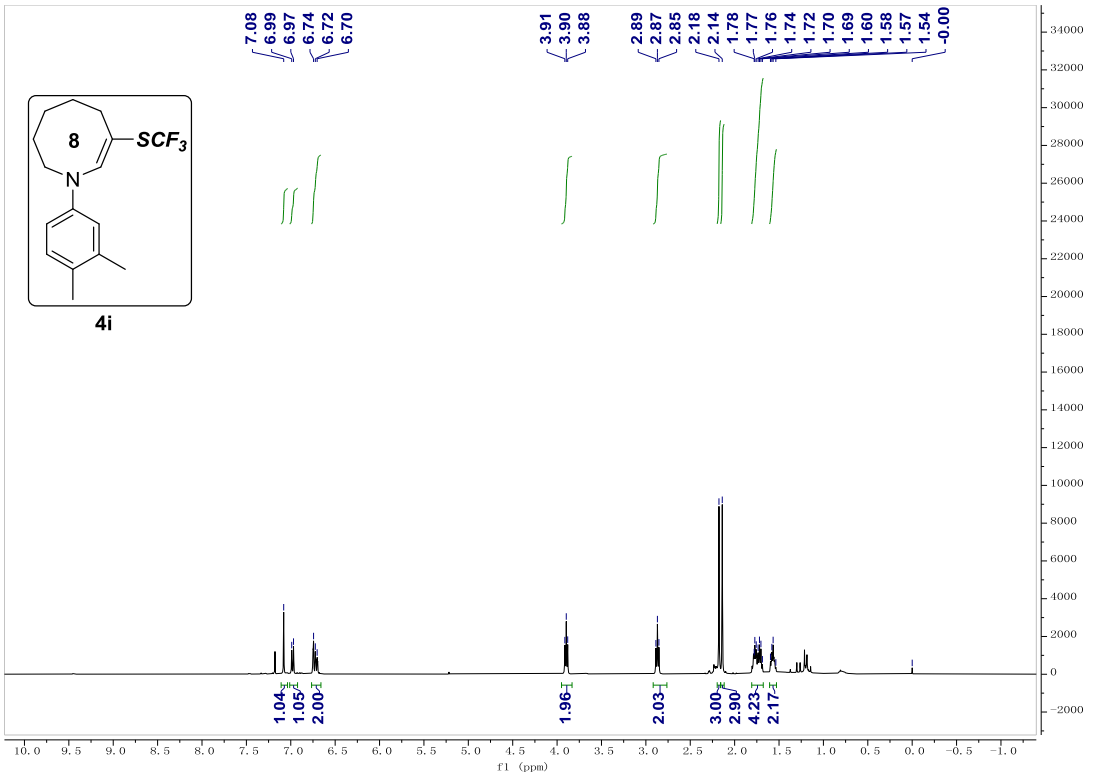
^{13}C NMR (100 MHz) Spectrum of **4h** in $CDCl_3$



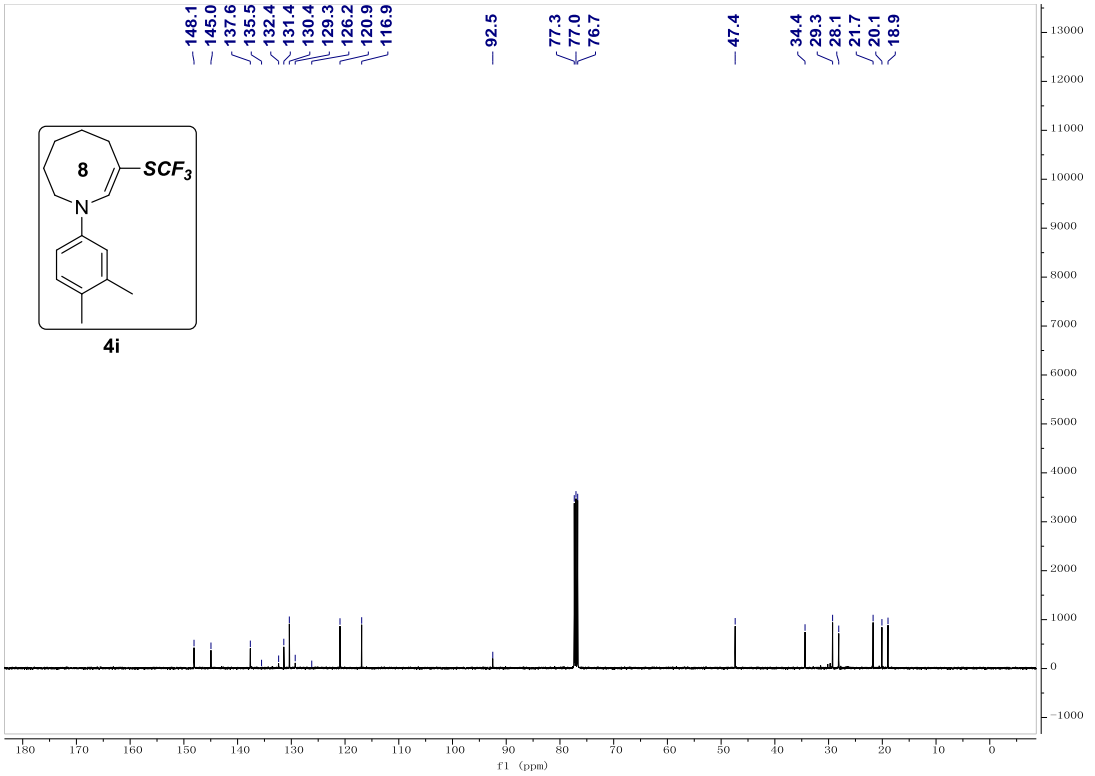
^{19}F NMR (376 MHz) Spectrum of **4h** in $CDCl_3$



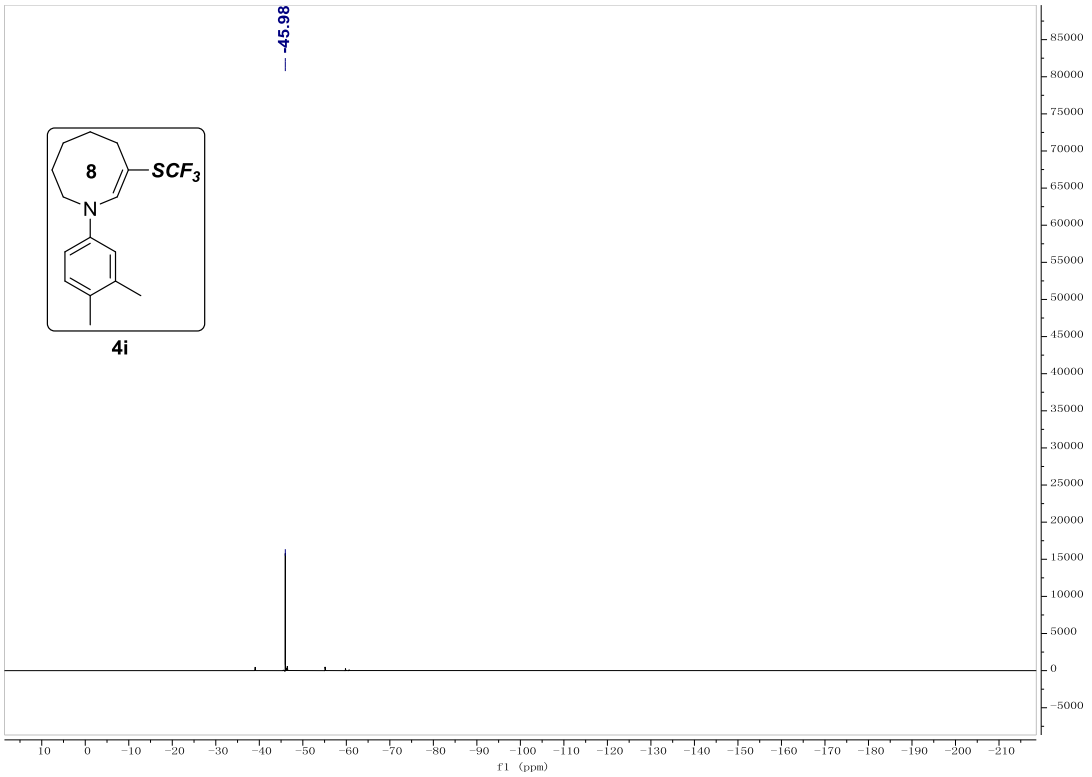
^{1}H NMR (400 MHz) Spectrum of **4i** in $CDCl_3$



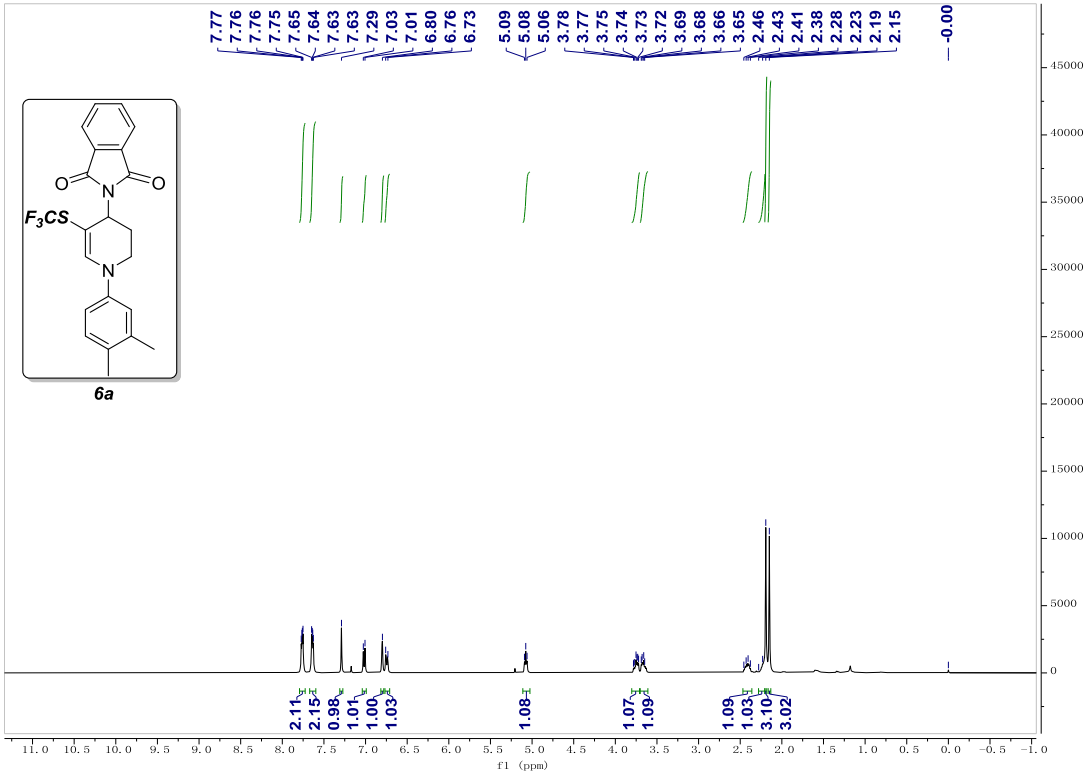
^{13}C NMR (100 MHz) Spectrum of **4i** in $CDCl_3$



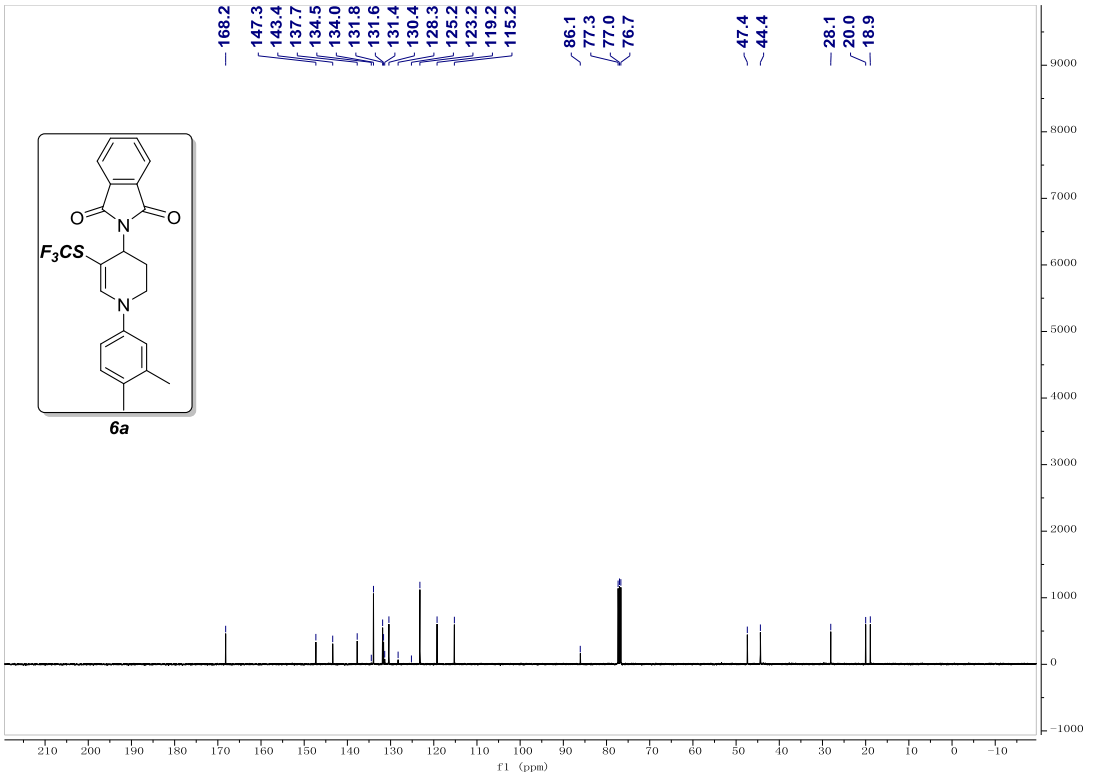
^{19}F NMR (376 MHz) Spectrum of **4i** in $CDCl_3$



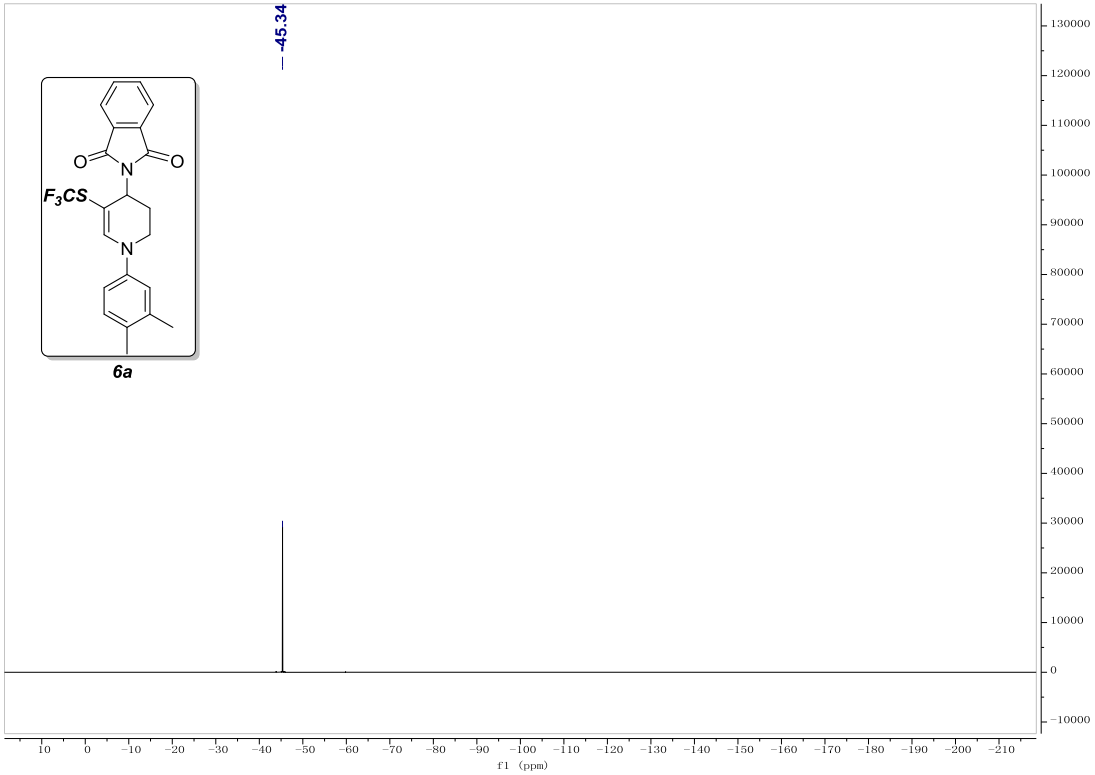
^{1}H NMR (400 MHz) Spectrum of **6a** in $CDCl_3$



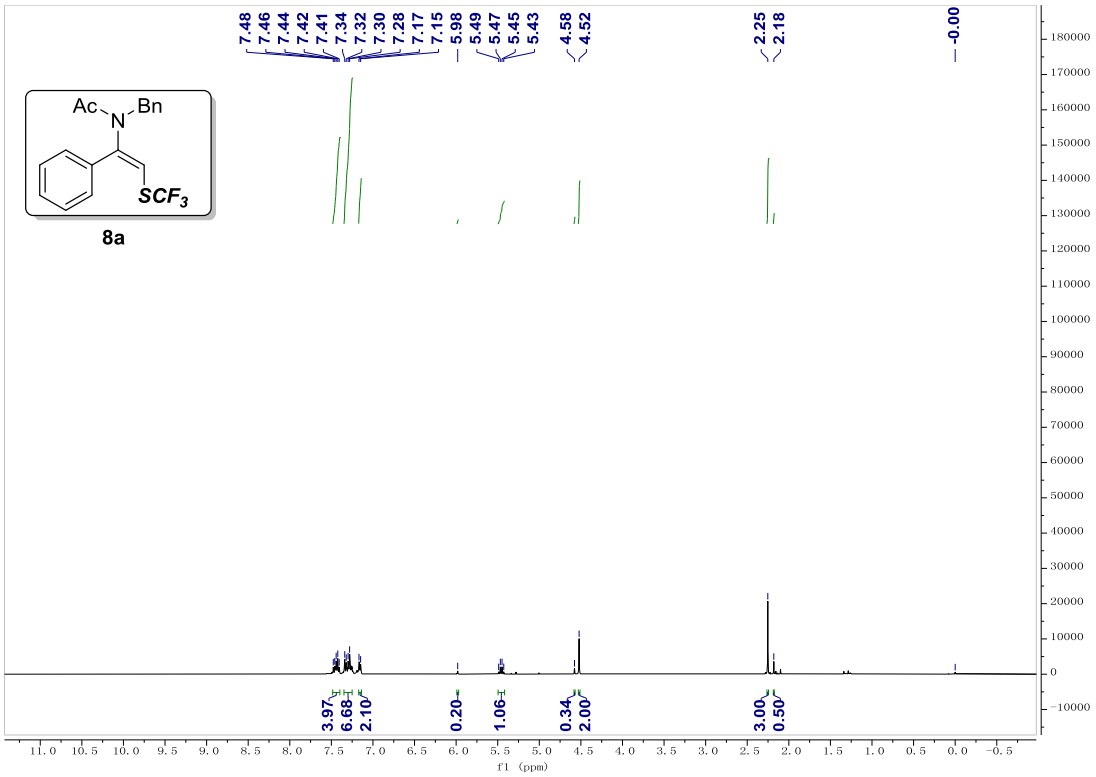
^{13}C NMR (100 MHz) Spectrum of **6a** in $CDCl_3$



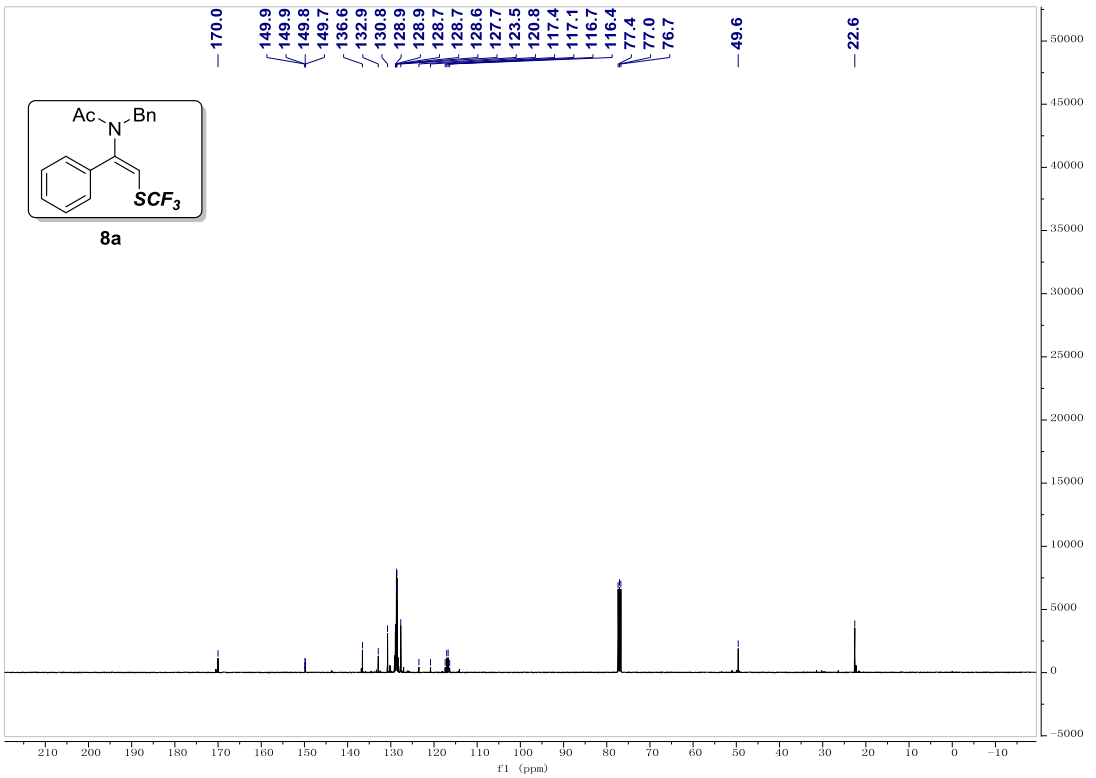
^{19}F NMR (376 MHz) Spectrum of **6a** in $CDCl_3$



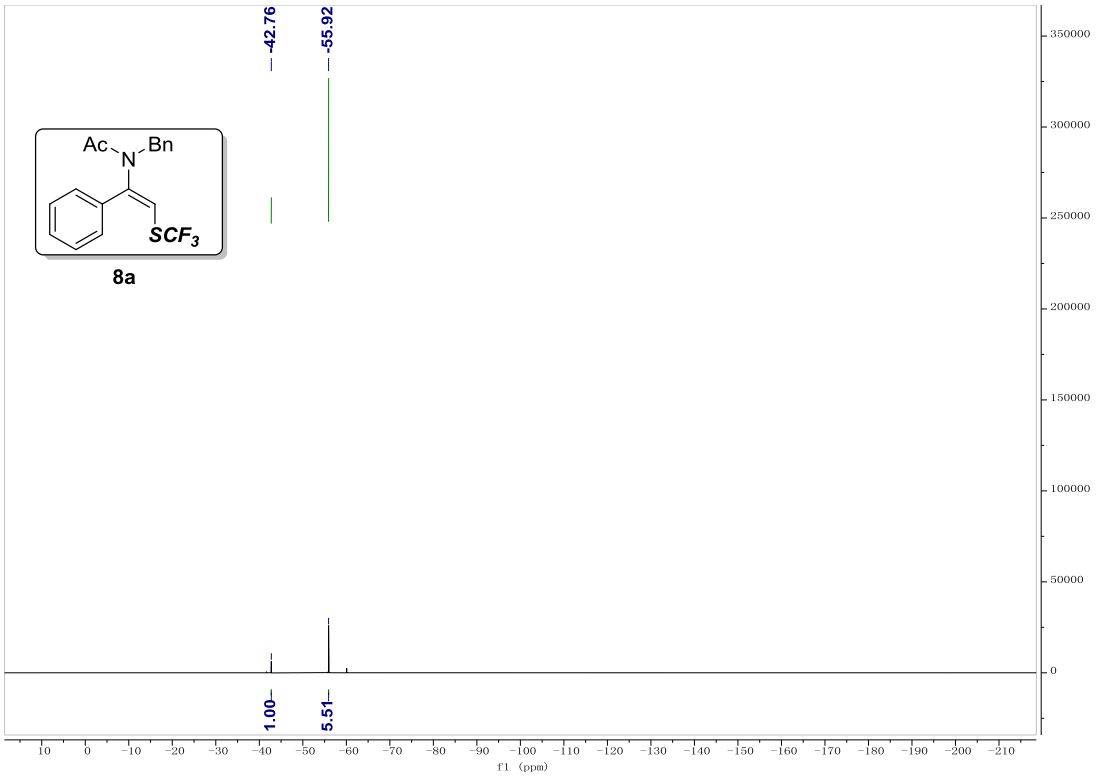
^{1}H NMR (400 MHz) Spectrum of **8a** in $CDCl_3$



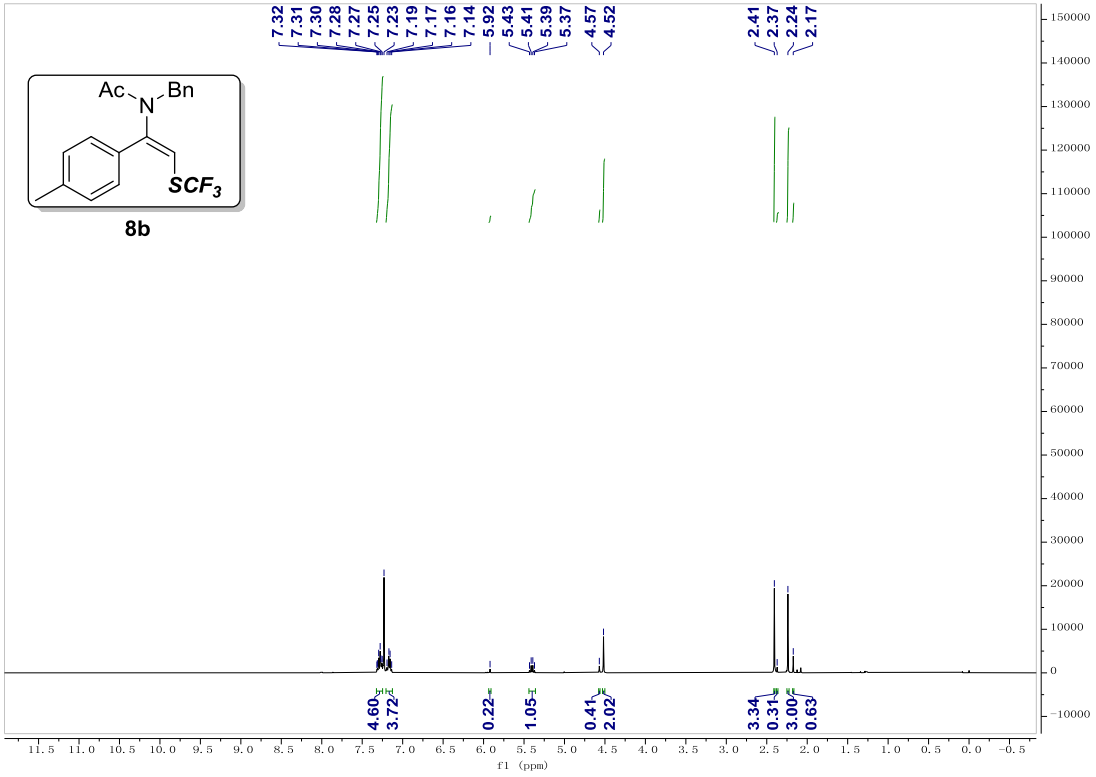
^{13}C NMR (100 MHz) Spectrum of **8a** in $CDCl_3$



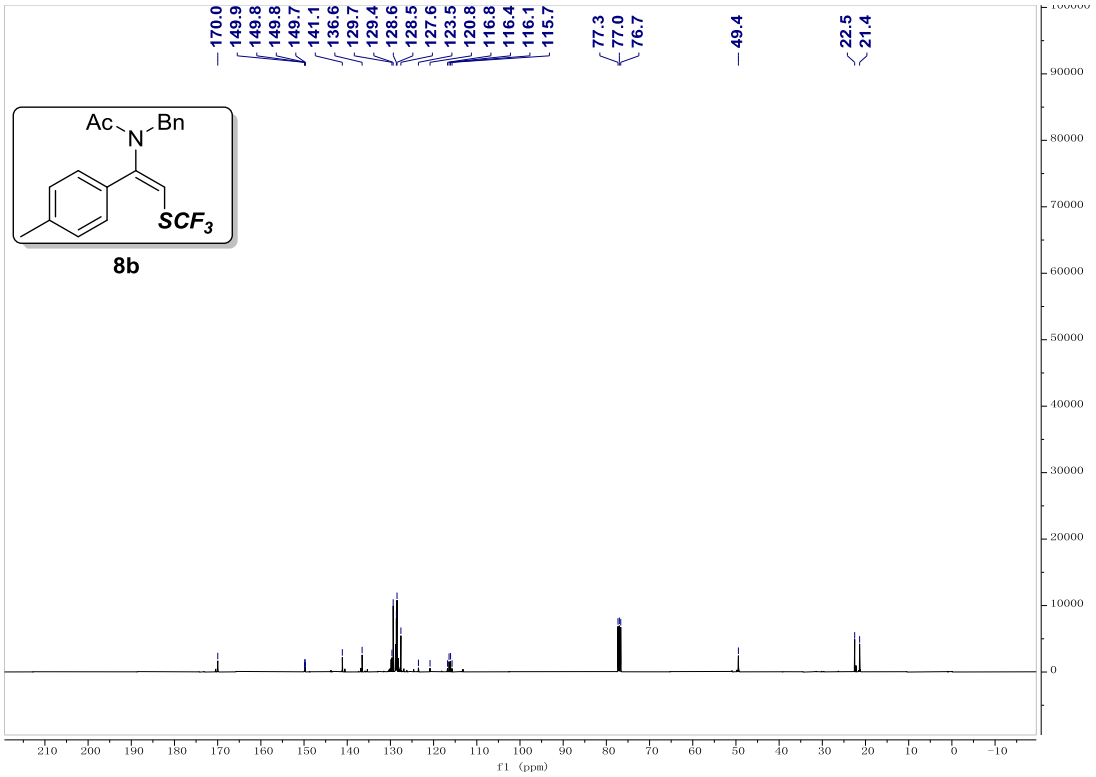
^{19}F NMR (376 MHz) Spectrum of **8a** in $CDCl_3$



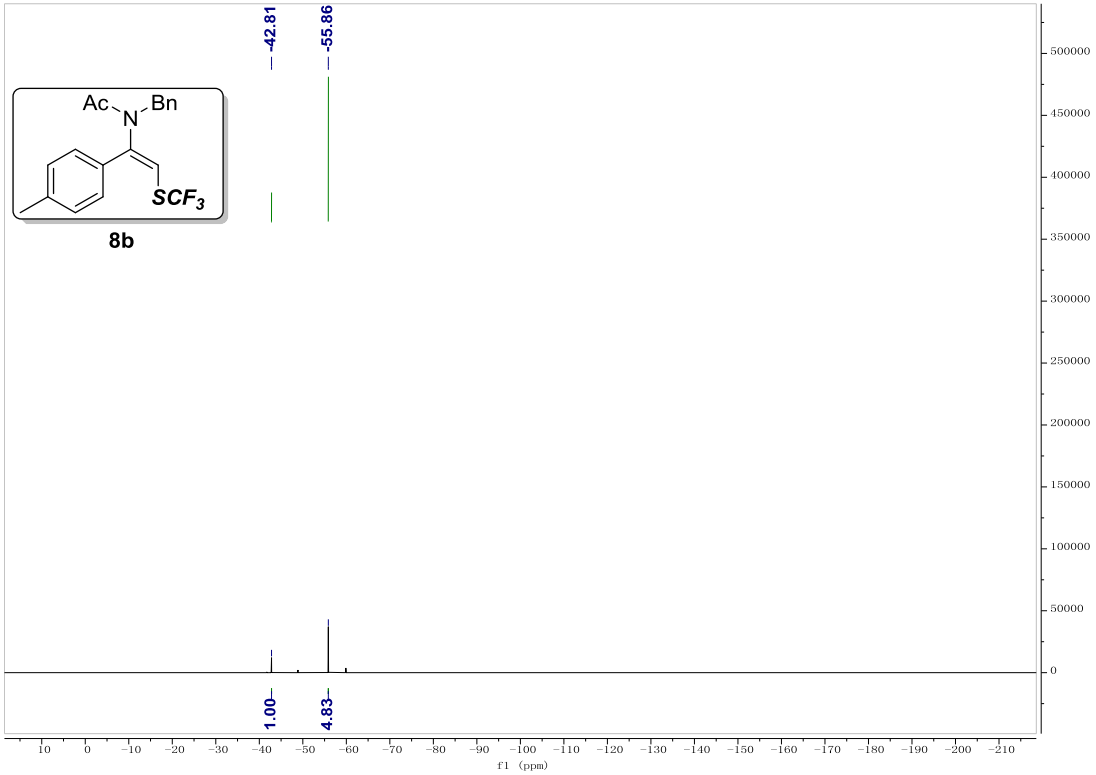
^{1}H NMR (400 MHz) Spectrum of **8b** in $CDCl_3$



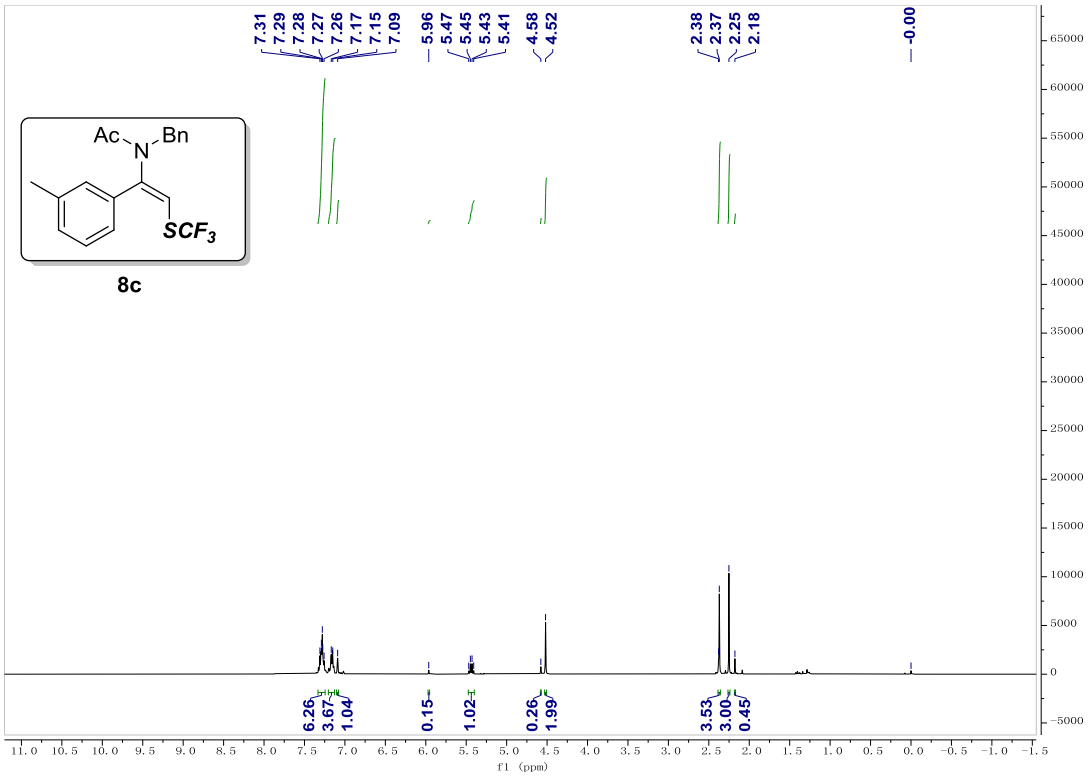
^{13}C NMR (100 MHz) Spectrum of **8b** in $CDCl_3$



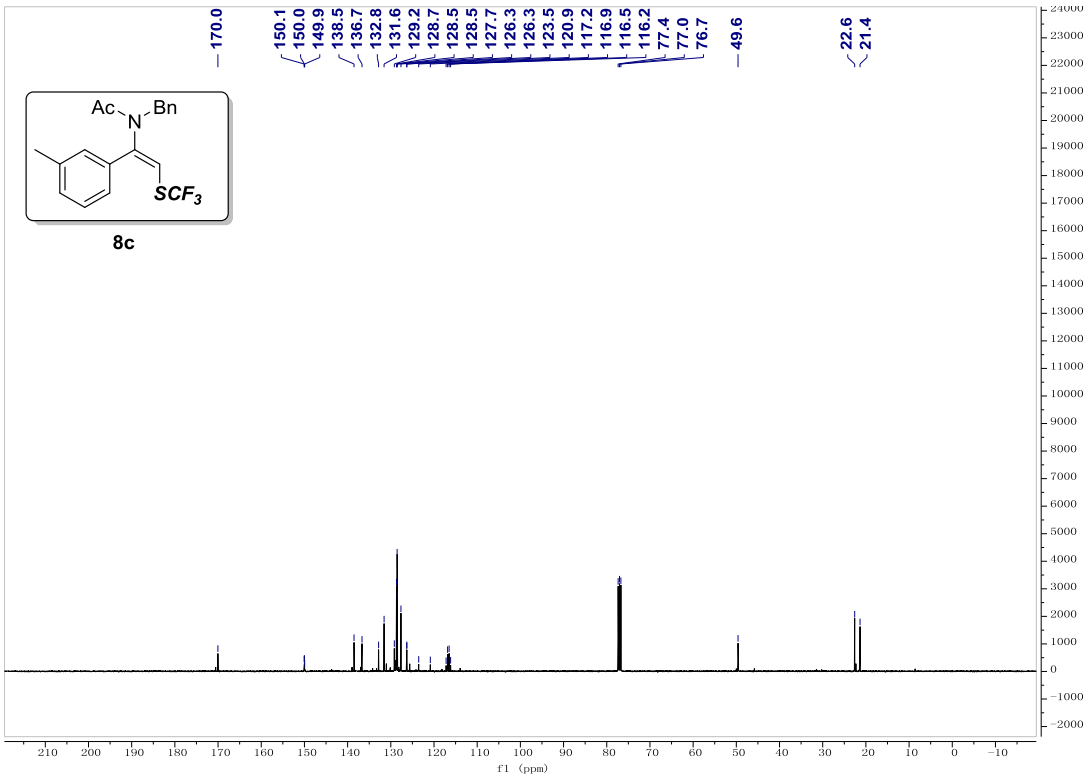
^{19}F NMR (376 MHz) Spectrum of **8b** in $CDCl_3$



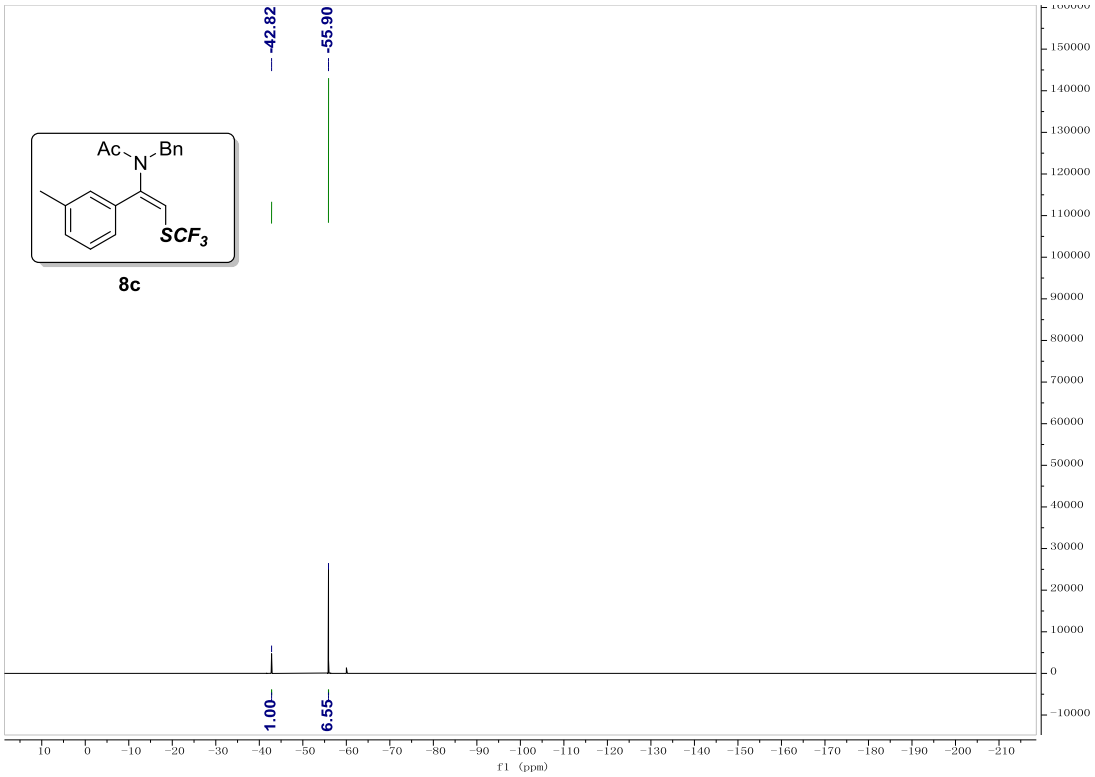
^{1}H NMR (400 MHz) Spectrum of **8c** in $CDCl_3$



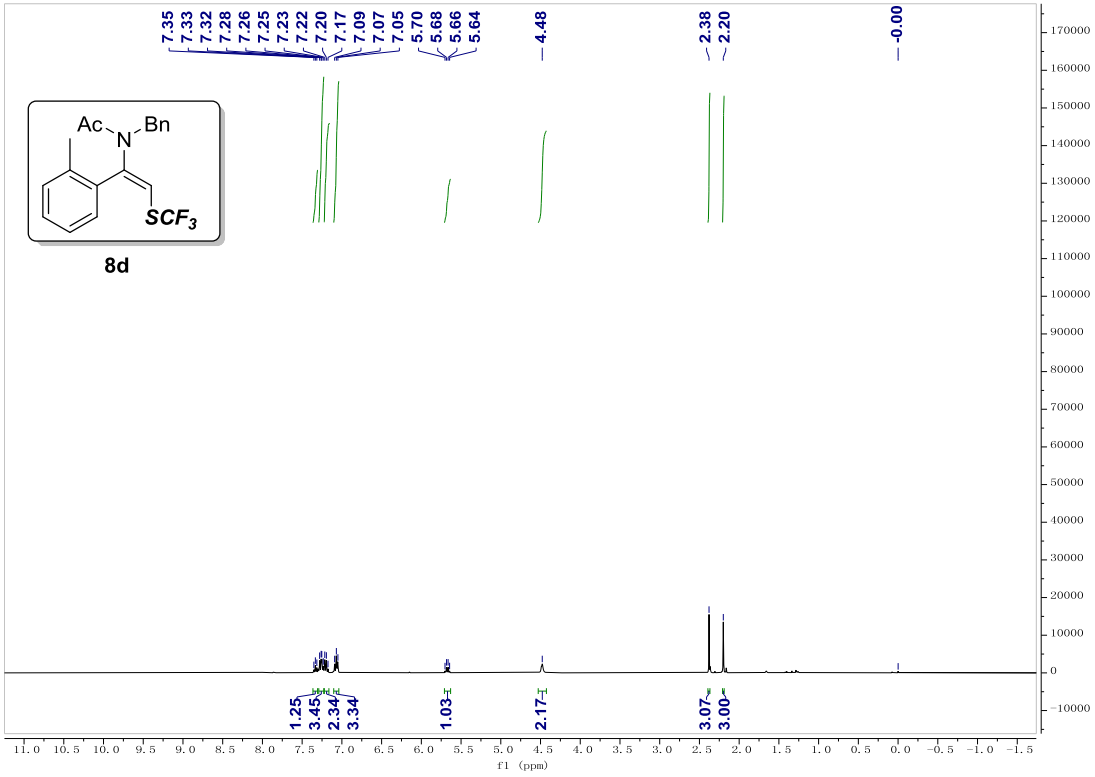
^{13}C NMR (100 MHz) Spectrum of **8c** in $CDCl_3$



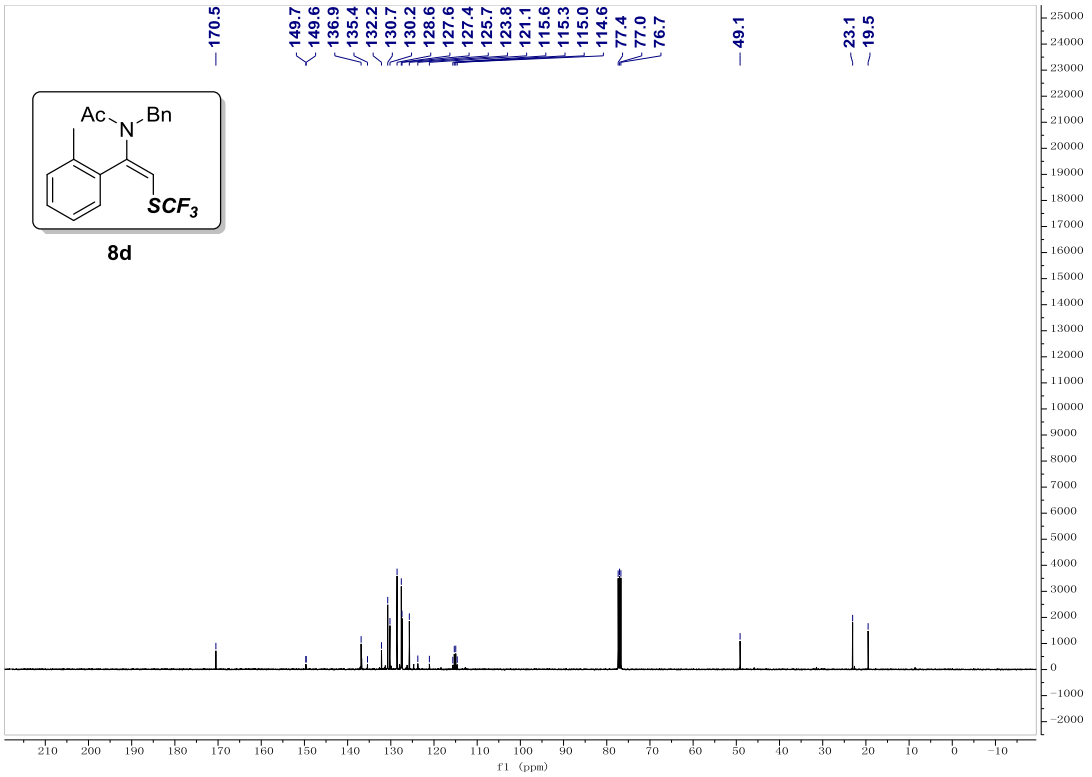
^{19}F NMR (376 MHz) Spectrum of **8c** in $CDCl_3$



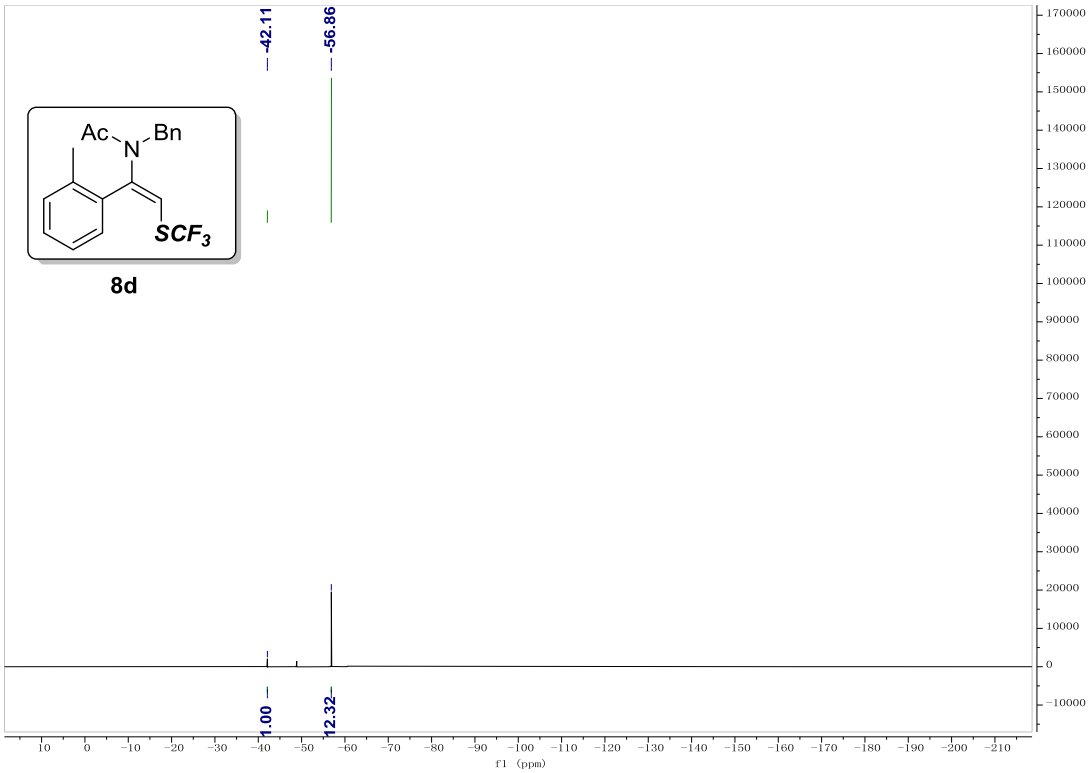
^{1}H NMR (400 MHz) Spectrum of **8d** in $CDCl_3$



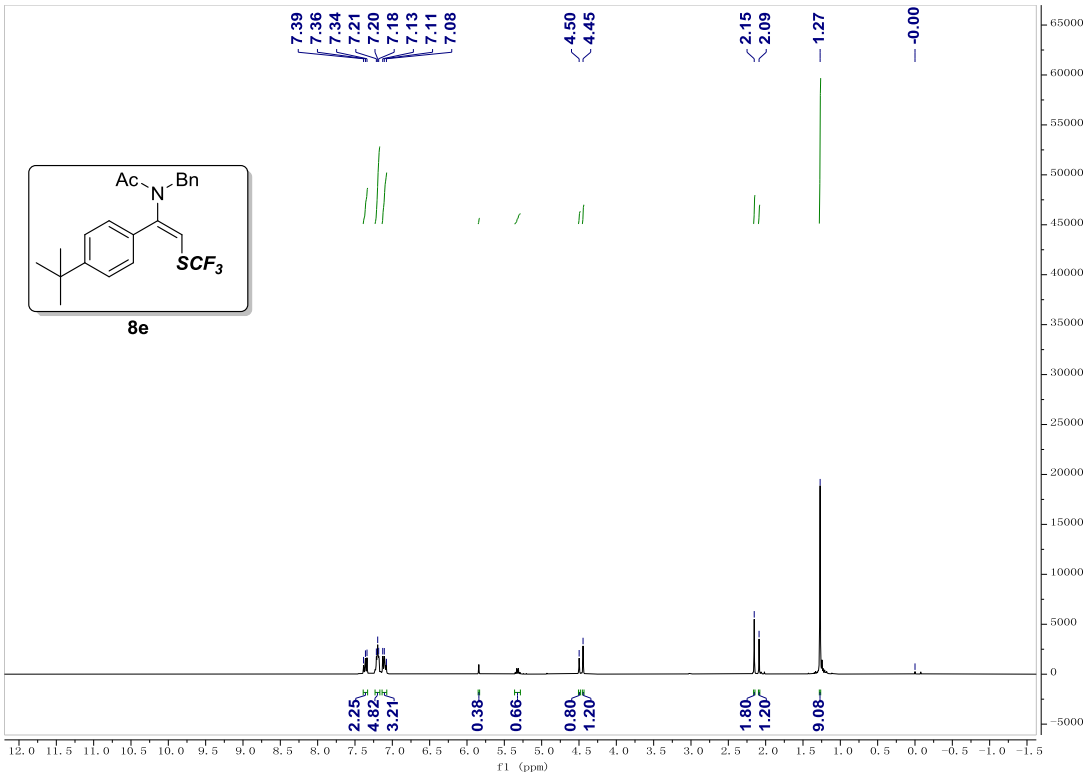
^{13}C NMR (100 MHz) Spectrum of **8d** in $CDCl_3$



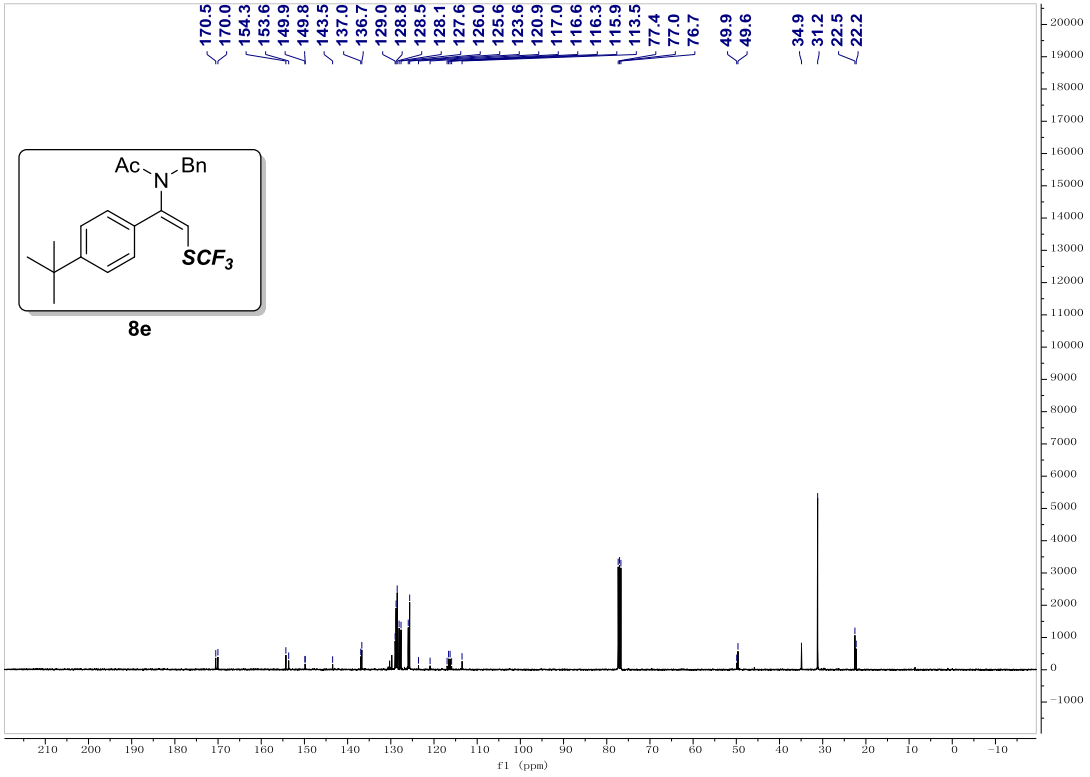
^{19}F NMR (376 MHz) Spectrum of **8d** in $CDCl_3$



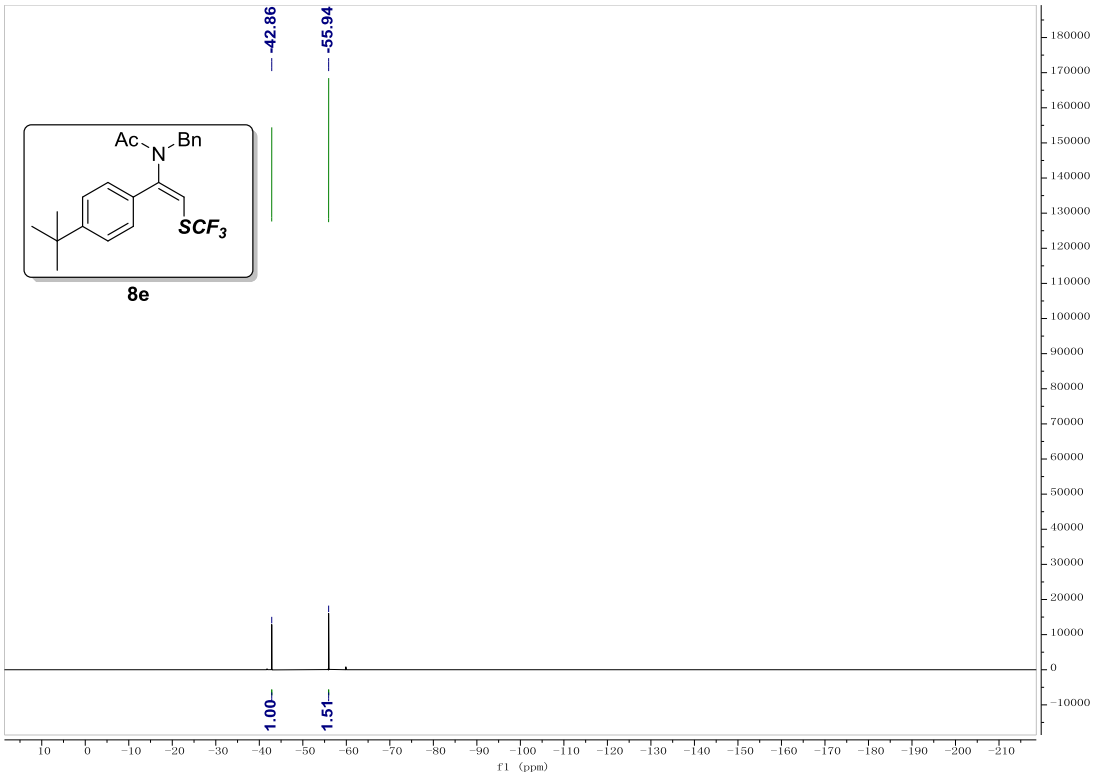
^{1}H NMR (400 MHz) Spectrum of **8e** in $CDCl_3$



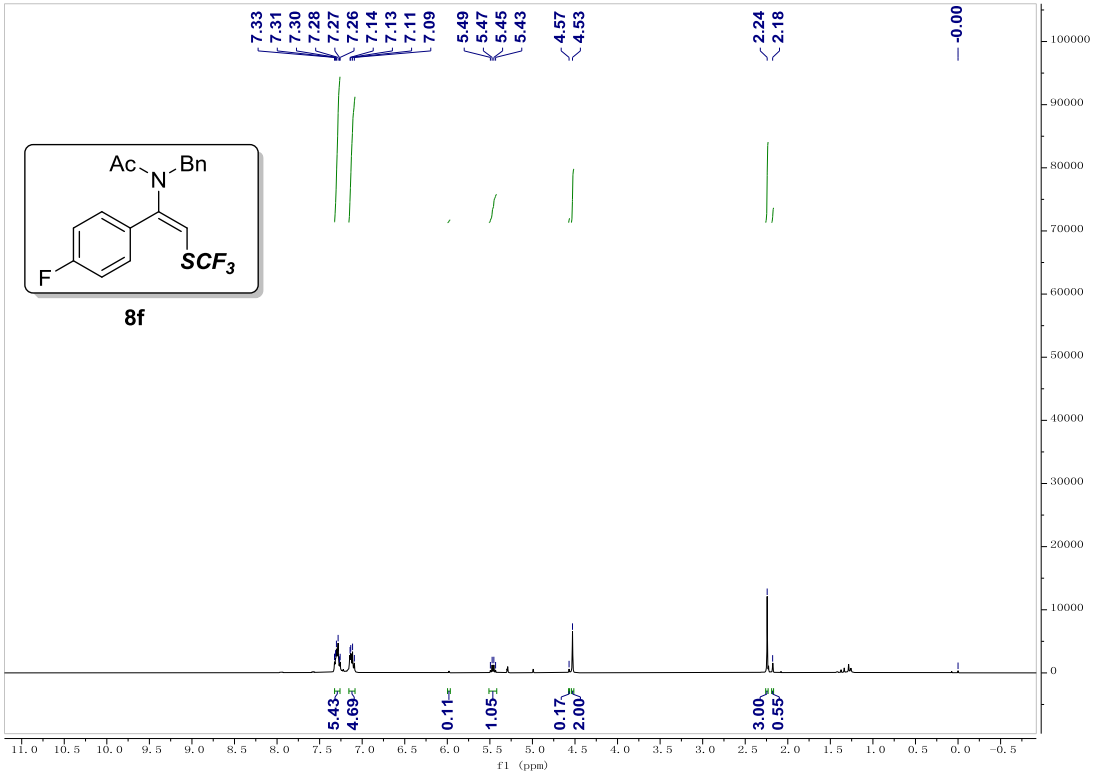
^{13}C NMR (100 MHz) Spectrum of **8e** in $CDCl_3$



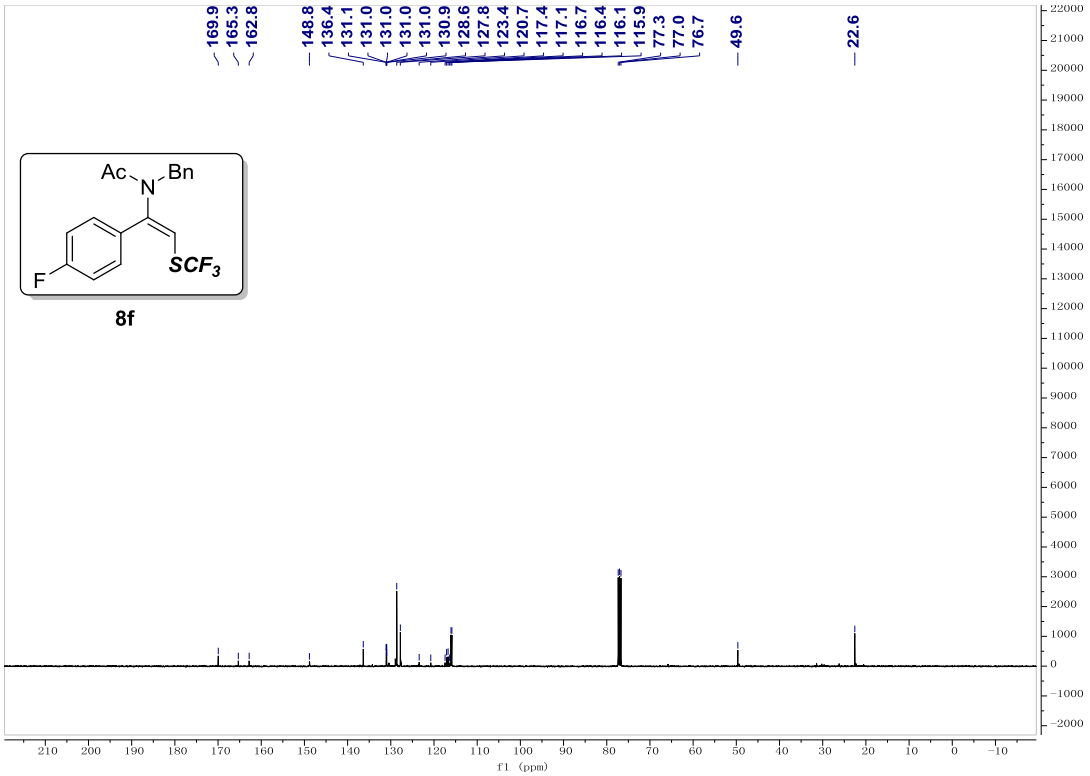
^{19}F NMR (376 MHz) Spectrum of **8e** in $CDCl_3$



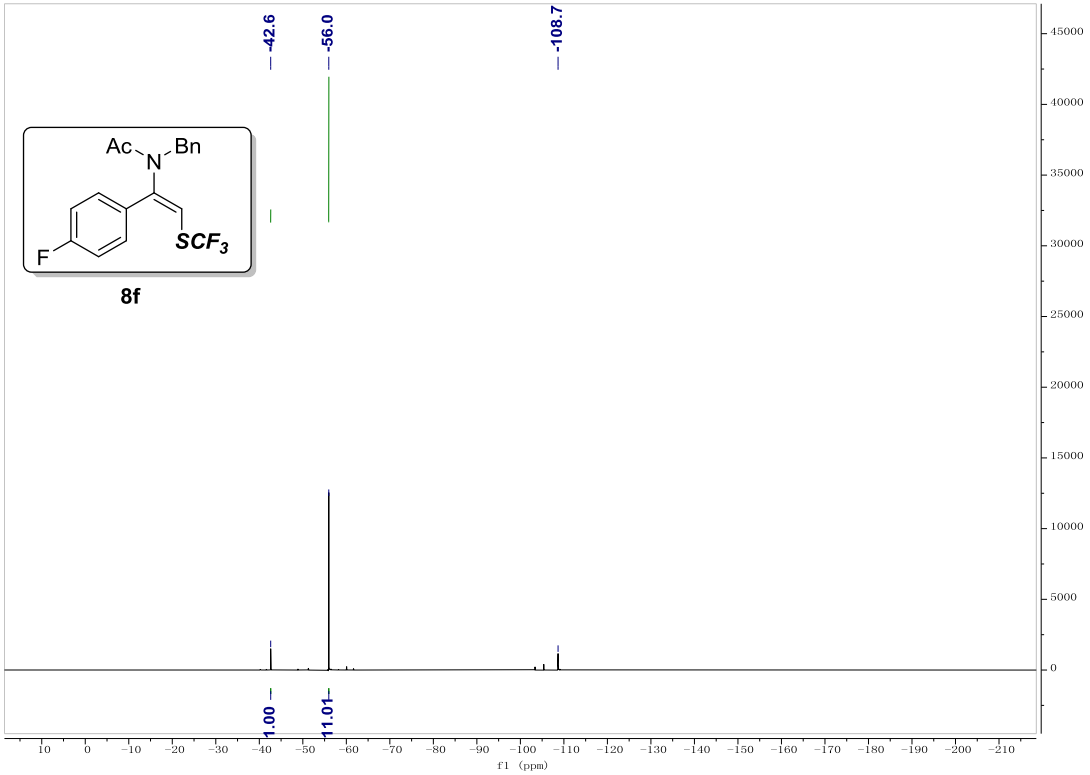
^{1}H NMR (400 MHz) Spectrum of **8f** in $CDCl_3$



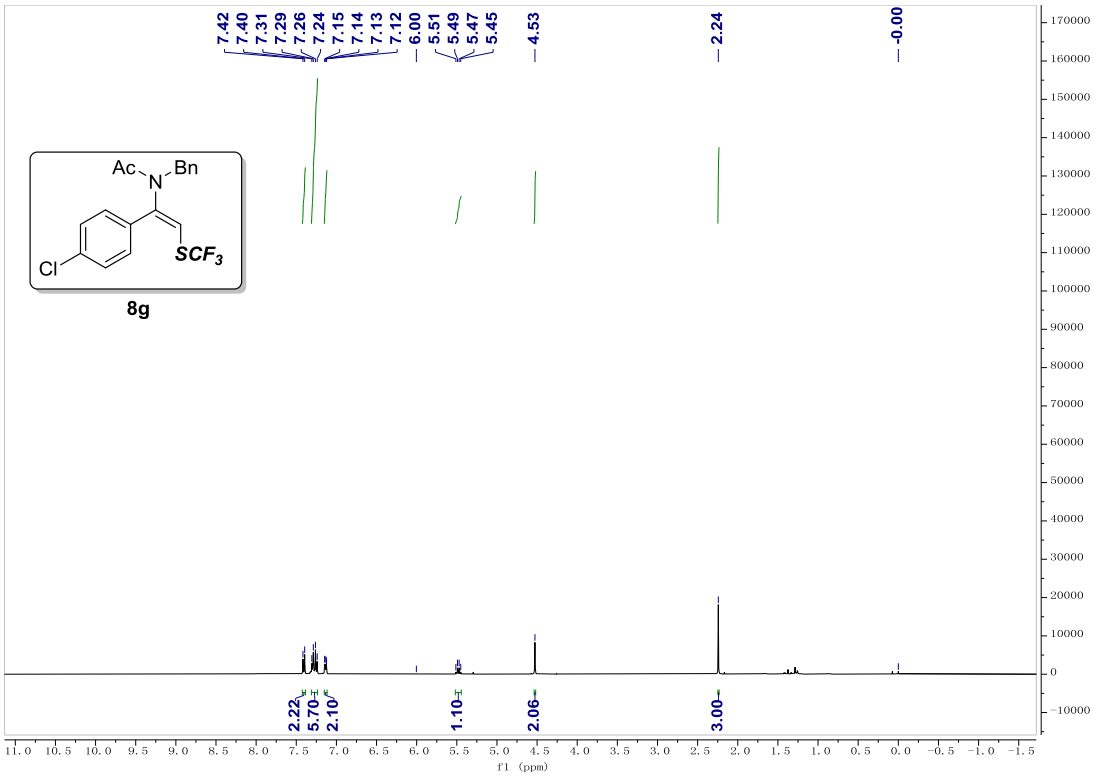
^{13}C NMR (100 MHz) Spectrum of **8f** in $CDCl_3$



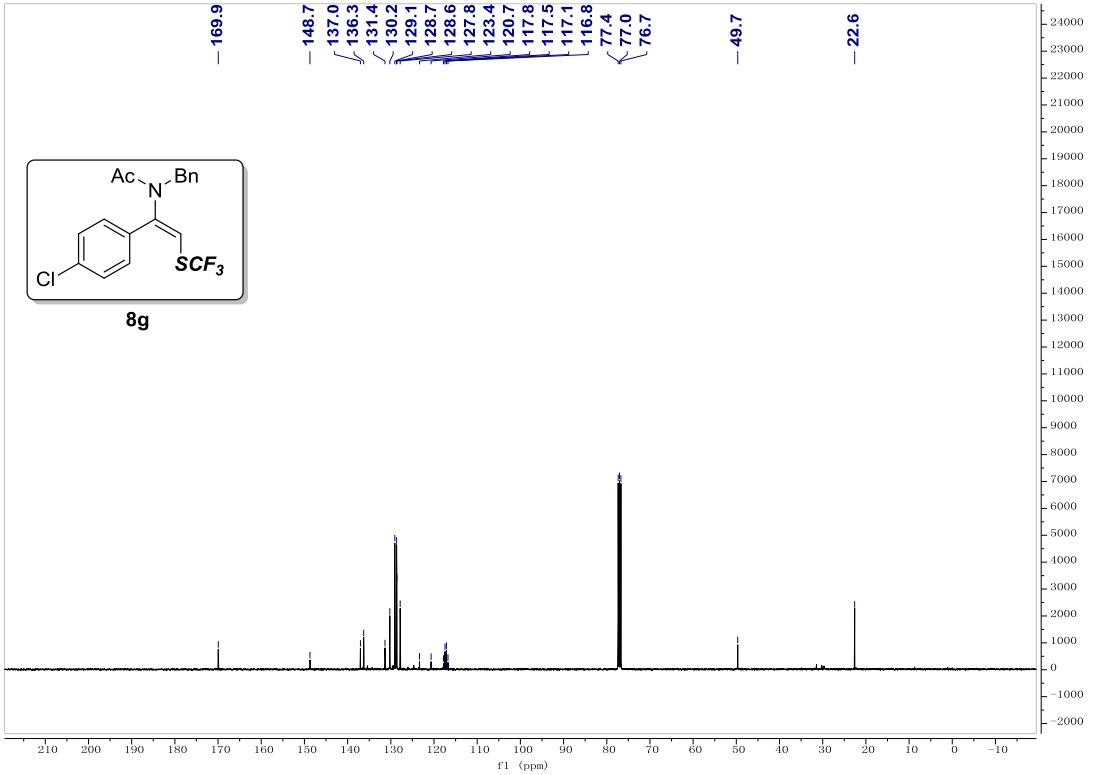
^{19}F NMR (376 MHz) Spectrum of **8f** in $CDCl_3$



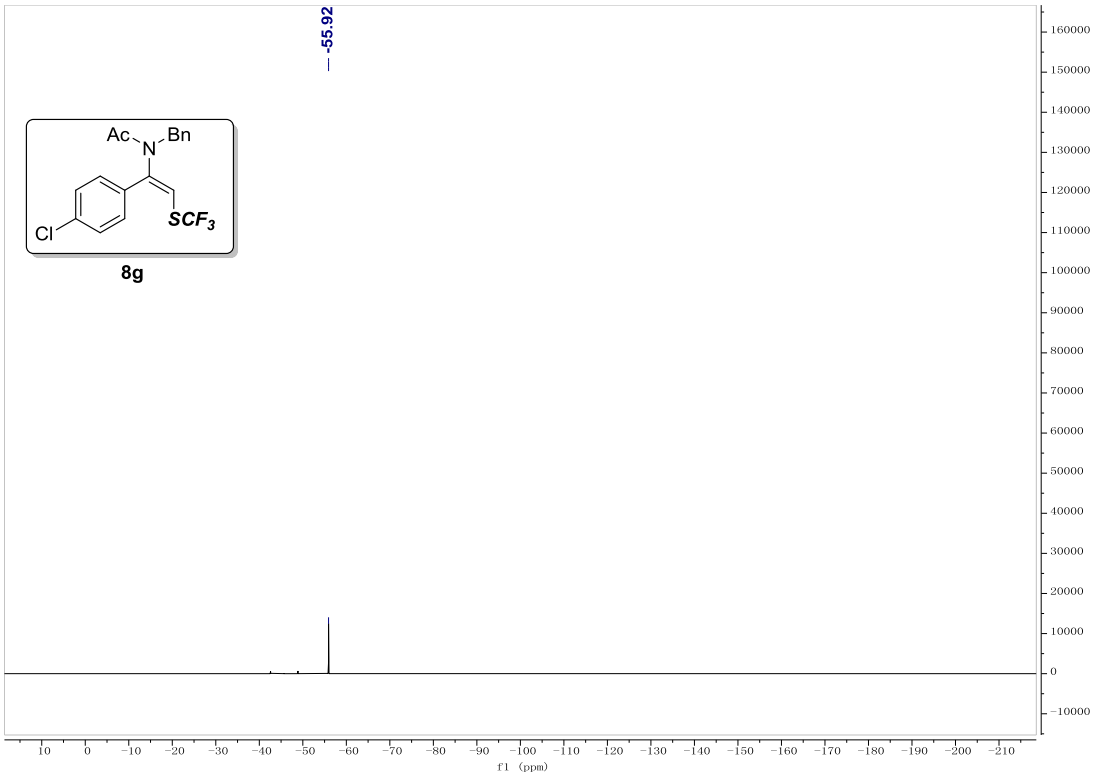
^{1}H NMR (400 MHz) Spectrum of **8g** in $CDCl_3$



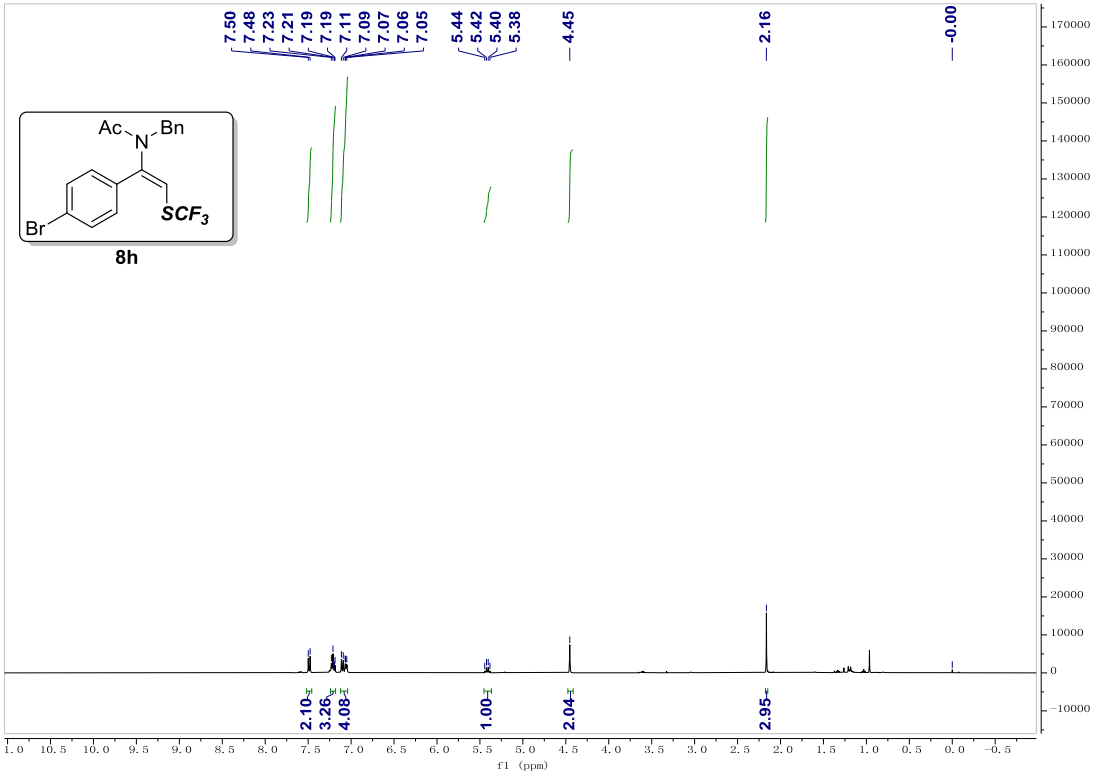
^{13}C NMR (100 MHz) Spectrum of **8g** in $CDCl_3$



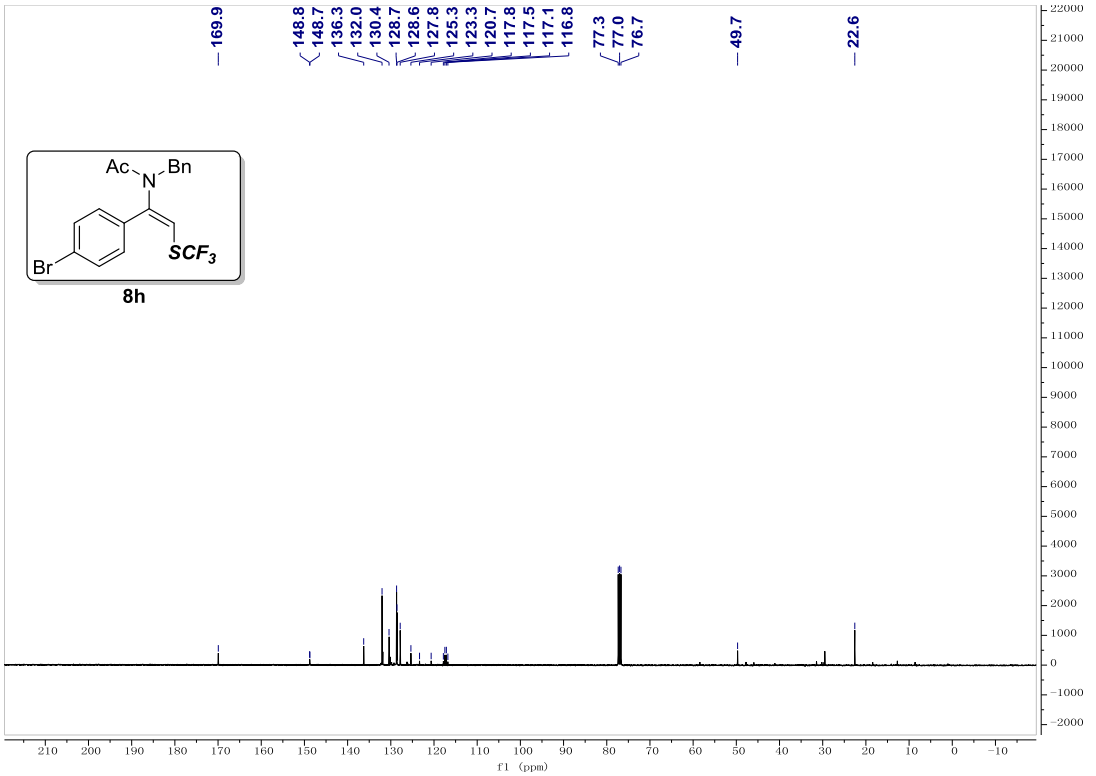
^{19}F NMR (376 MHz) Spectrum of **8g** in $CDCl_3$



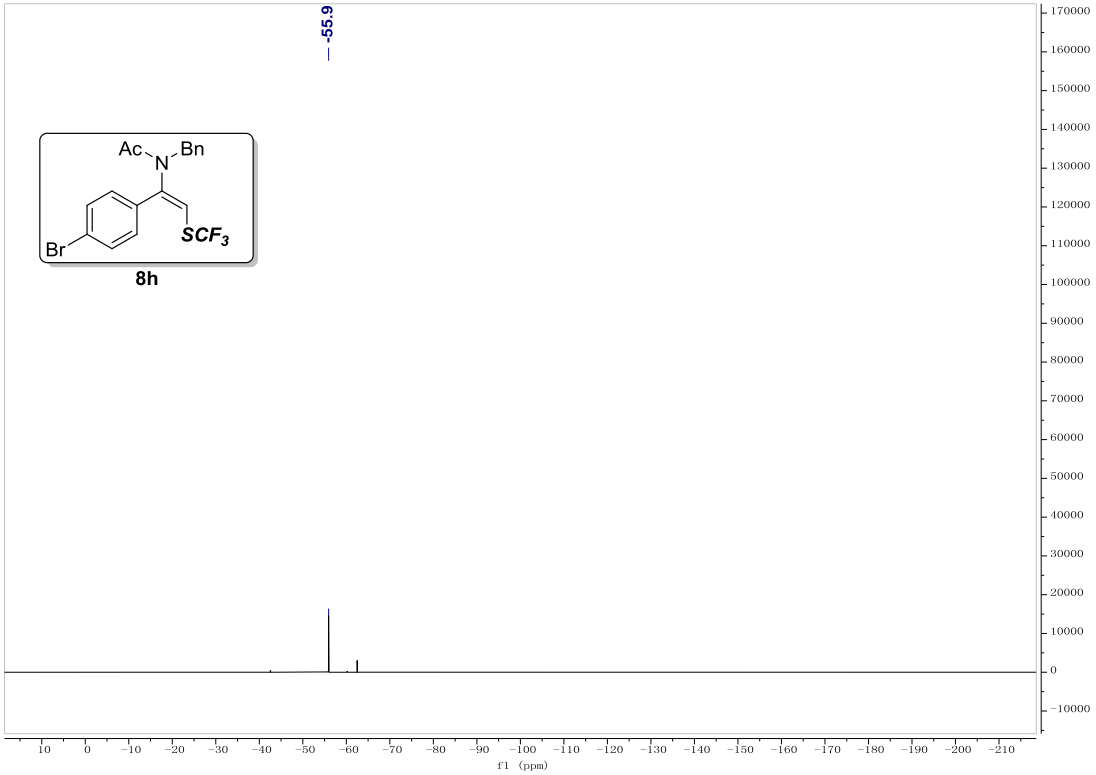
^{1}H NMR (400 MHz) Spectrum of **8h** in $CDCl_3$



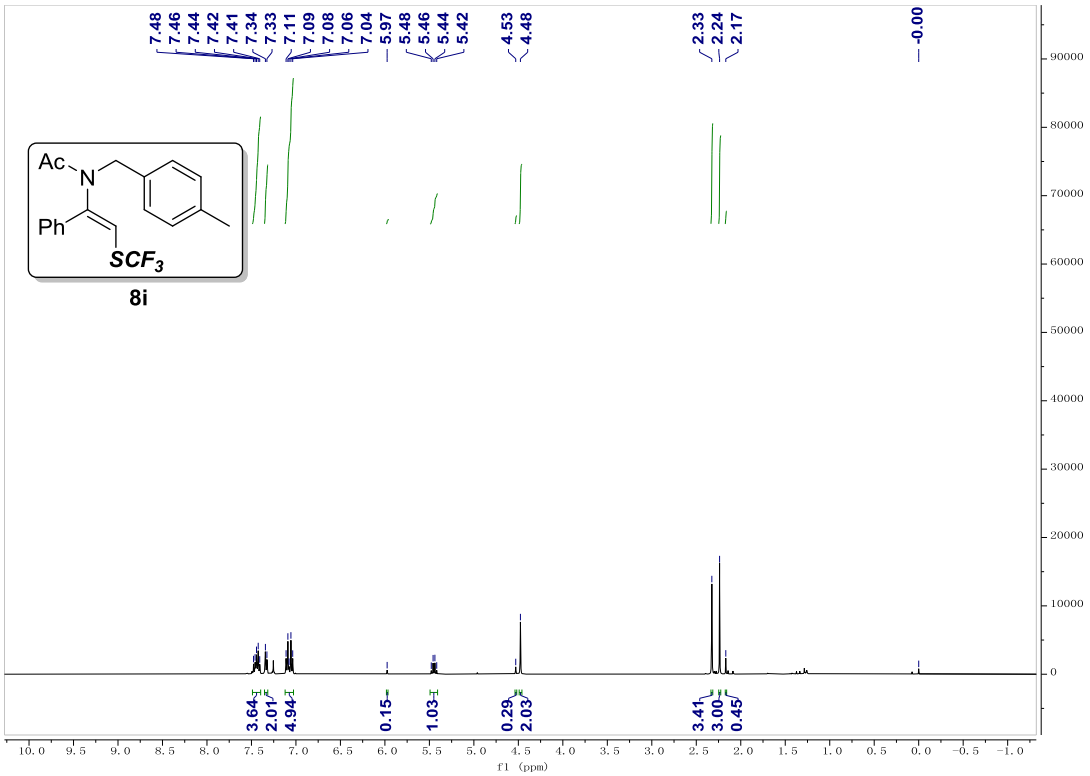
^{13}C NMR (100 MHz) Spectrum of **8h** in $CDCl_3$



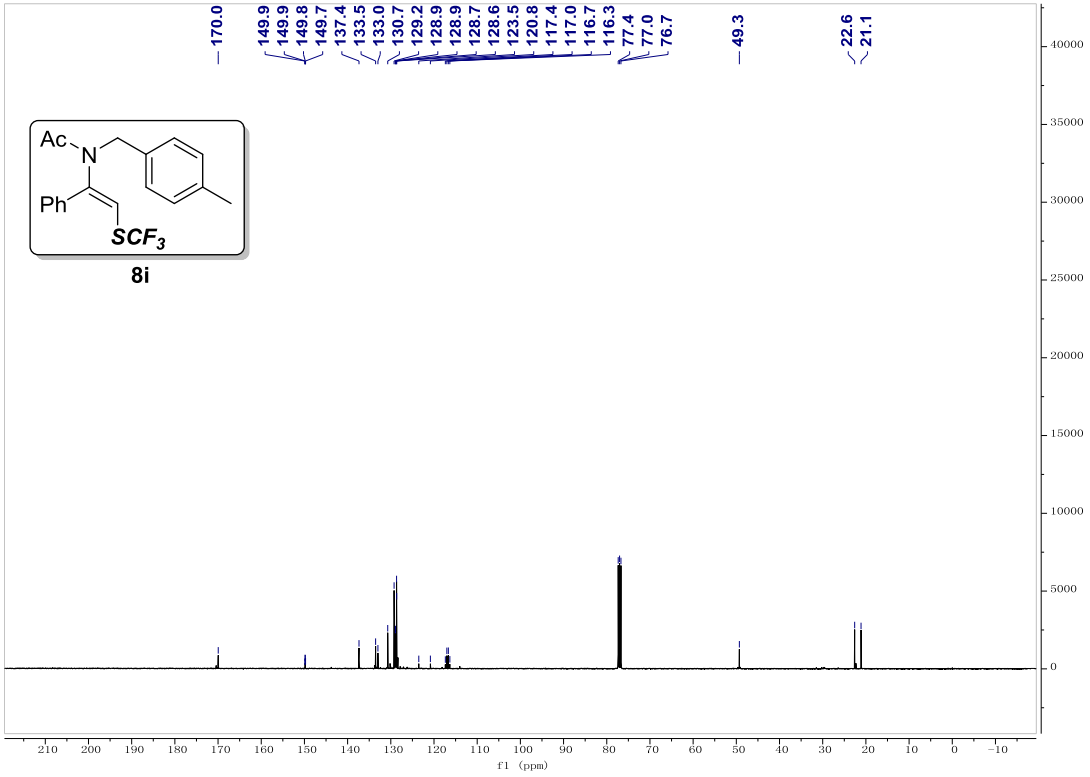
^{19}F NMR (376 MHz) Spectrum of **8h** in $CDCl_3$



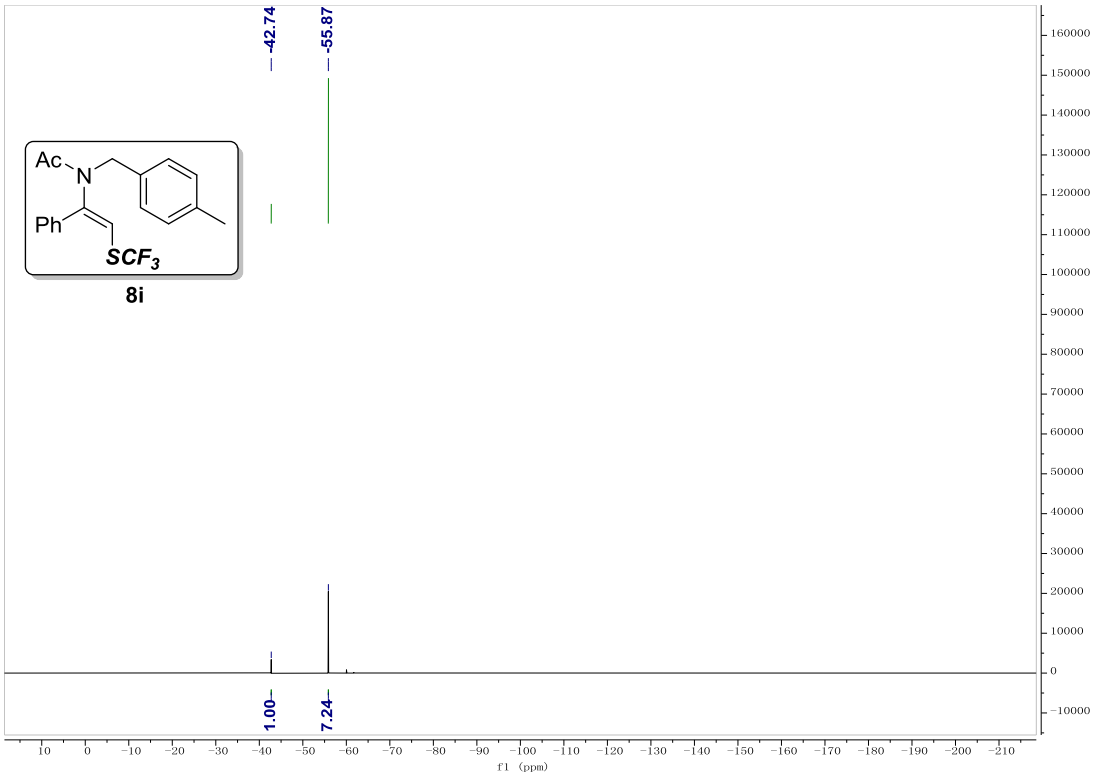
^{1}H NMR (400 MHz) Spectrum of **8i** in $CDCl_3$



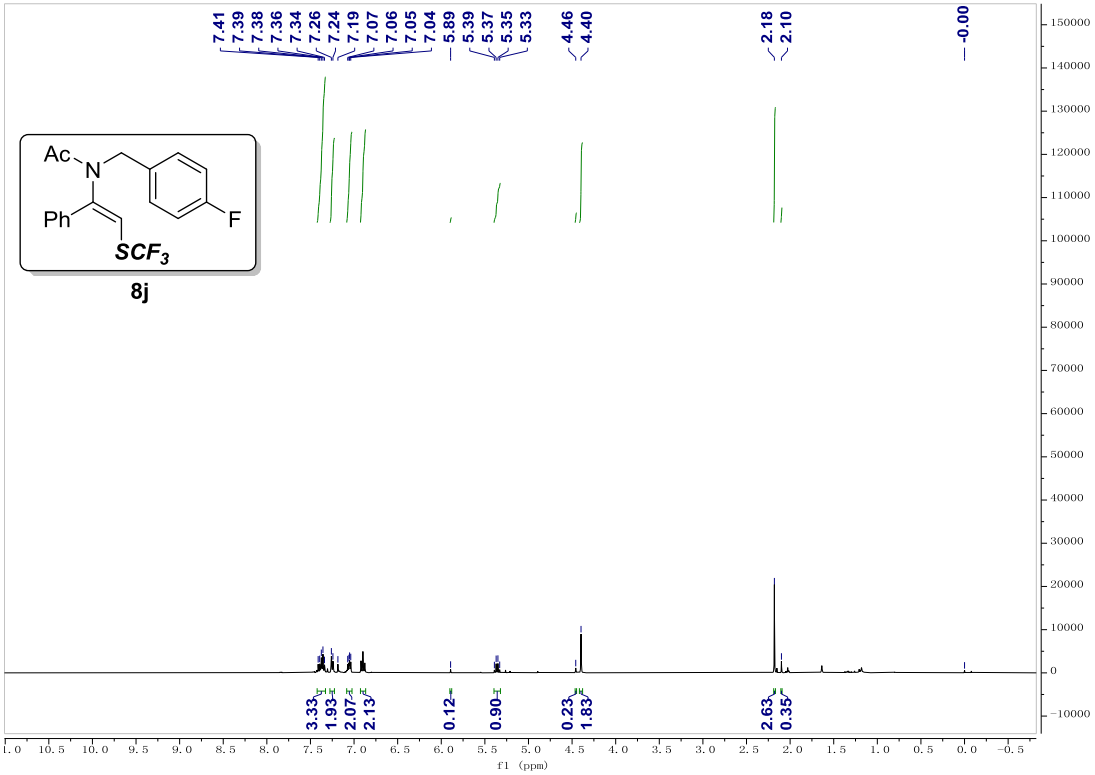
^{13}C NMR (100 MHz) Spectrum of **8i** in $CDCl_3$



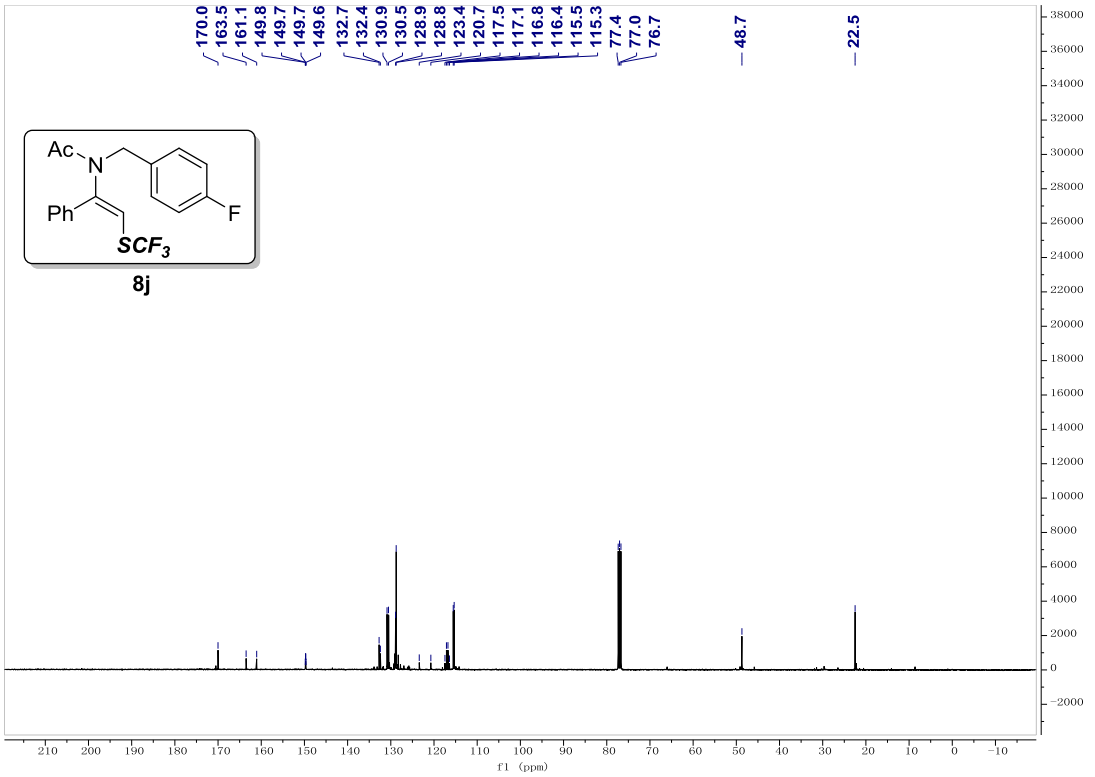
^{19}F NMR (376 MHz) Spectrum of **8i** in $CDCl_3$



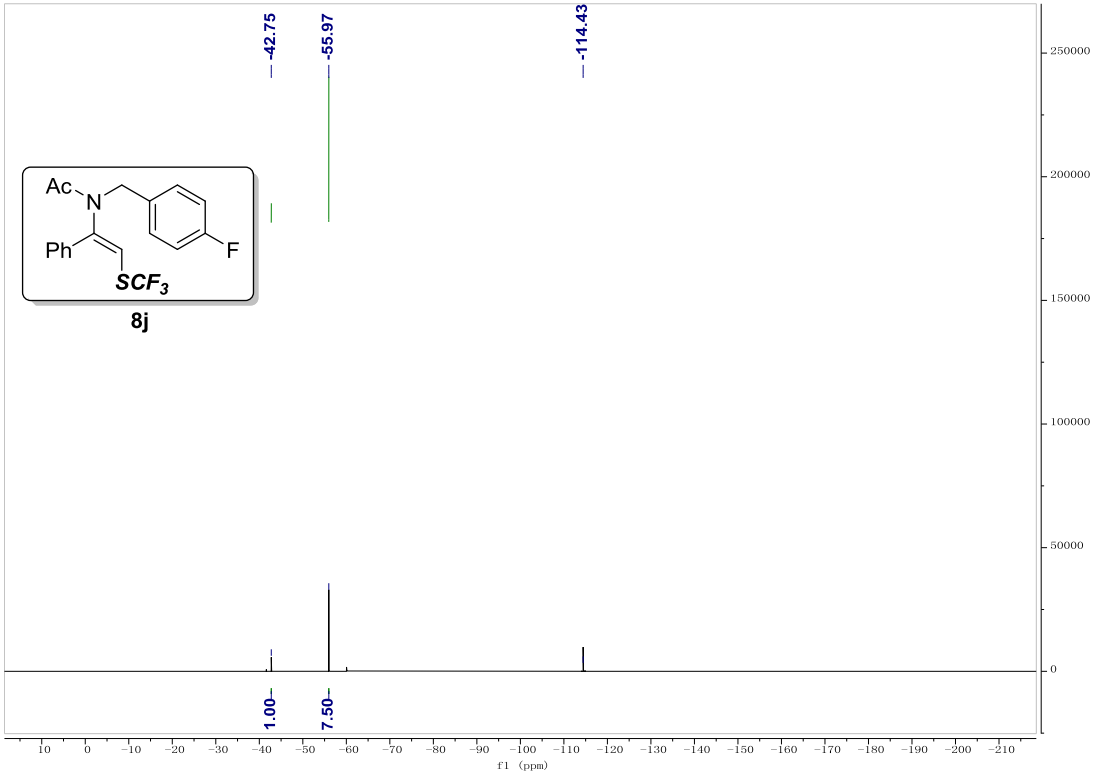
^{1}H NMR (400 MHz) Spectrum of **8j** in $CDCl_3$



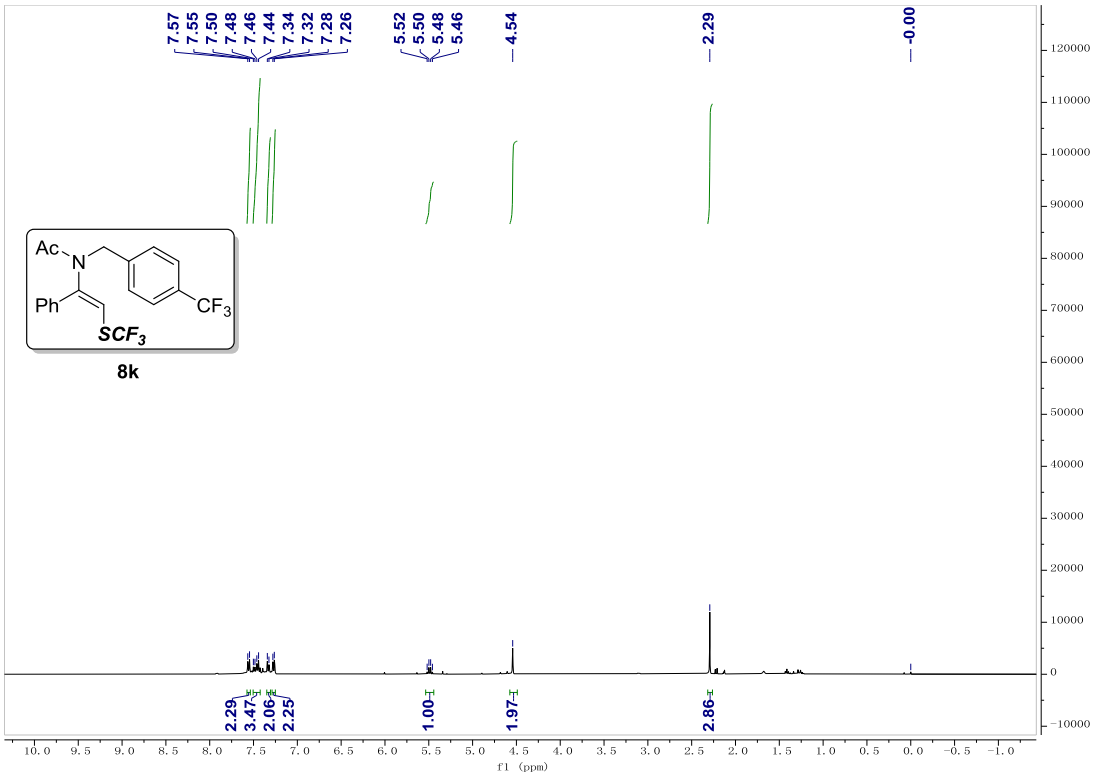
^{13}C NMR (100 MHz) Spectrum of **8j** in $CDCl_3$



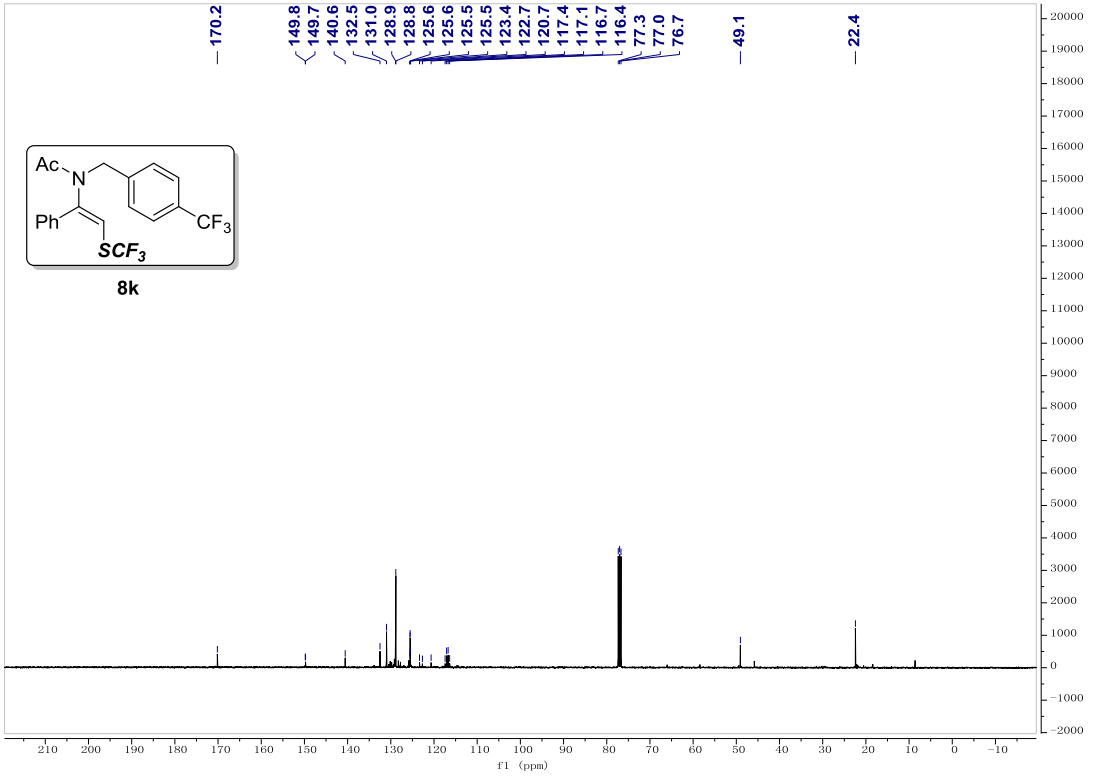
^{19}F NMR (376 MHz) Spectrum of **8j** in $CDCl_3$



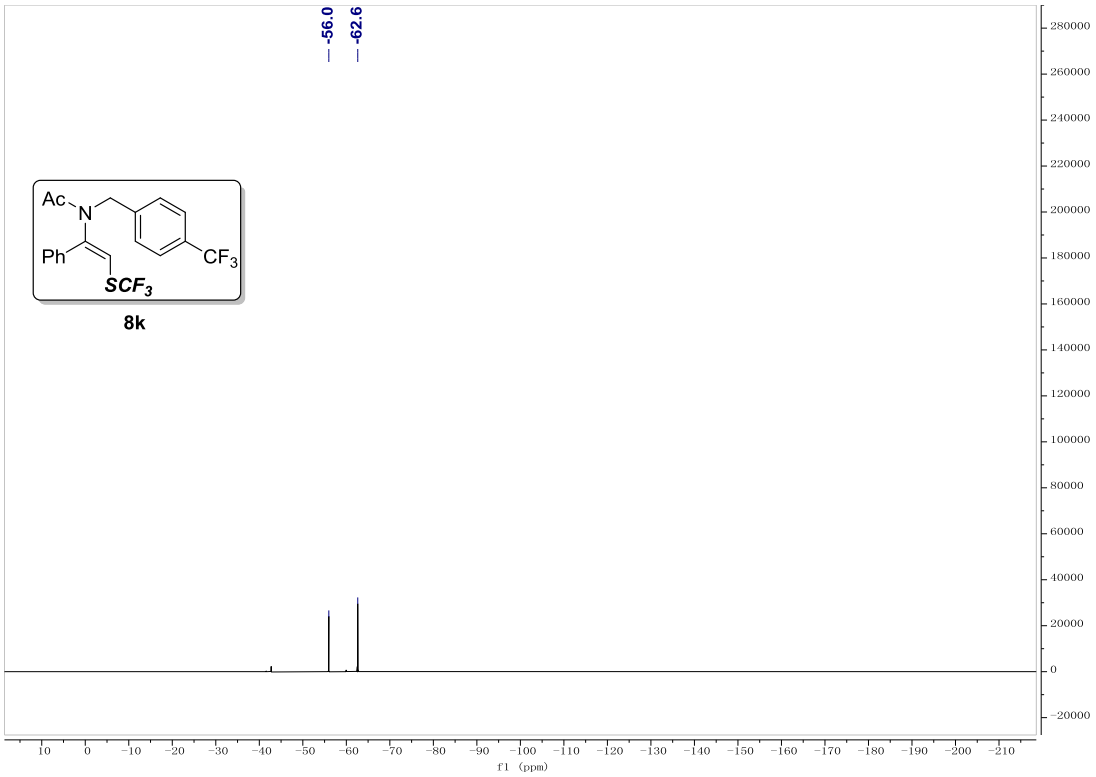
^{1}H NMR (400 MHz) Spectrum of **8k** in $CDCl_3$



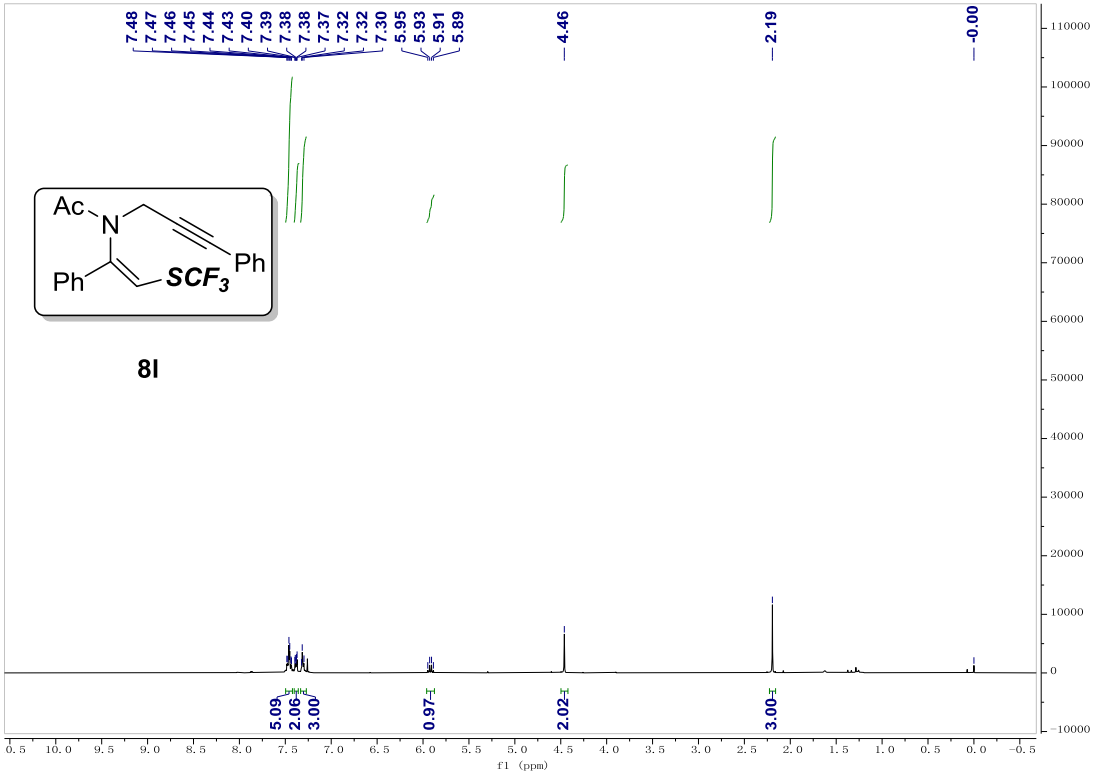
^{13}C NMR (100 MHz) Spectrum of **8k** in $CDCl_3$



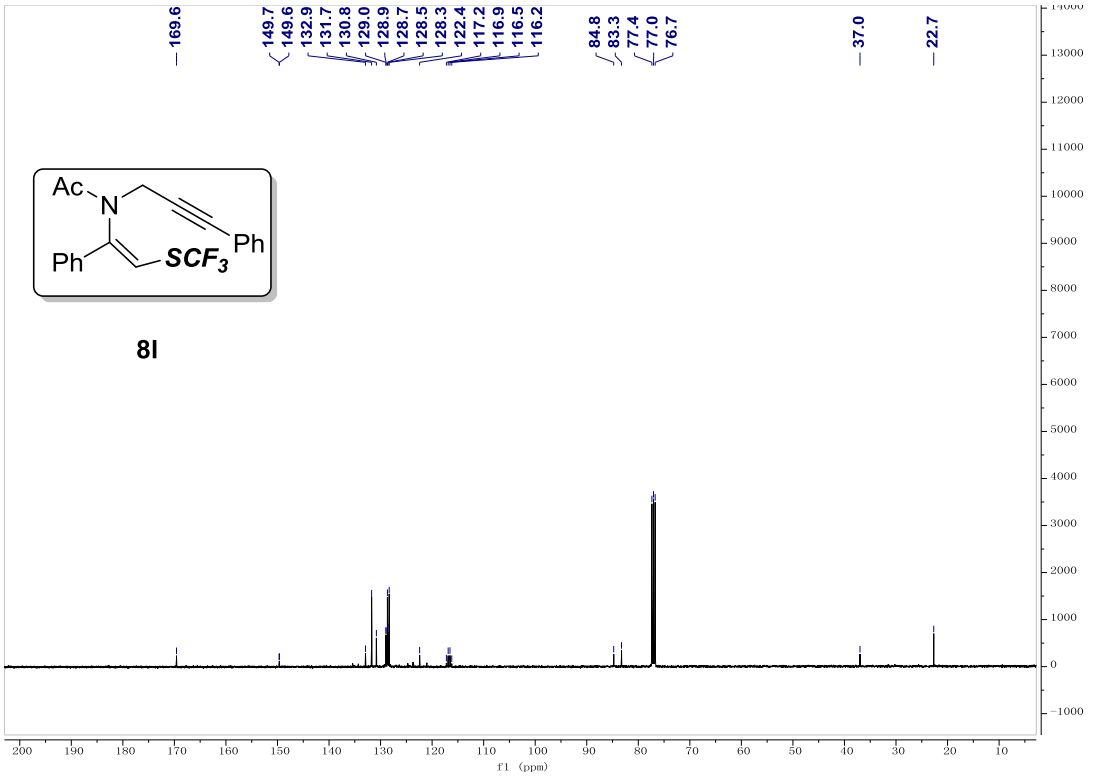
^{19}F NMR (376 MHz) Spectrum of **8k** in $CDCl_3$



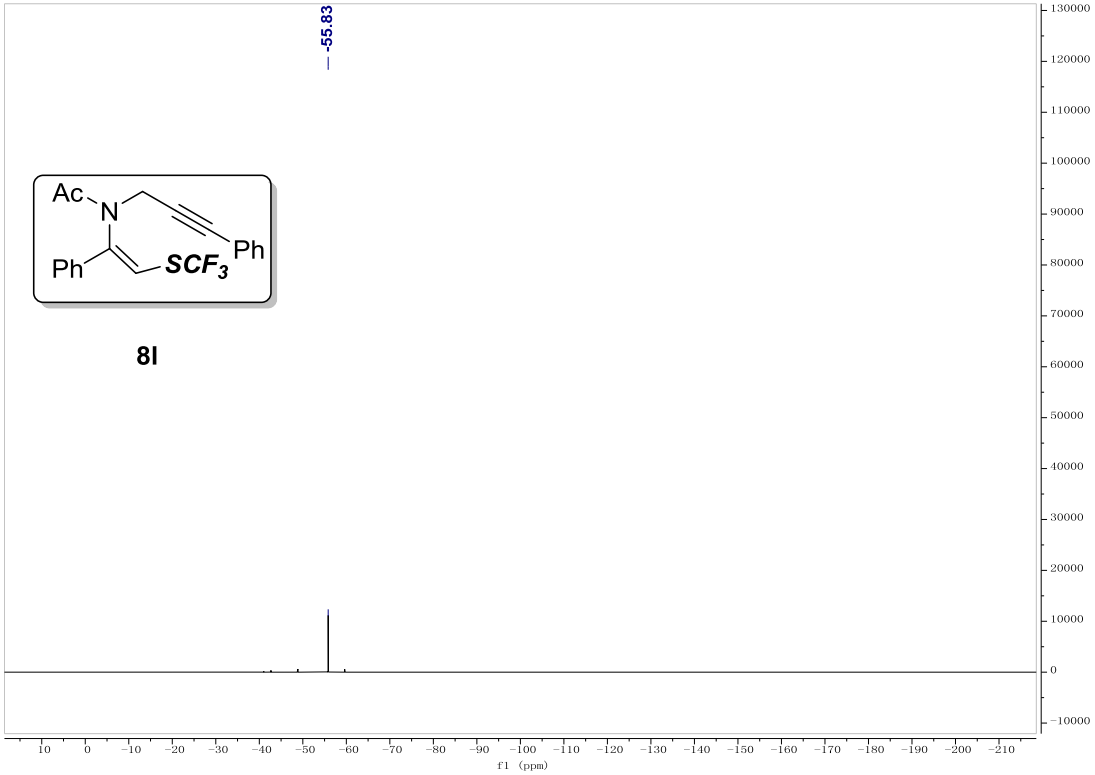
^{1}H NMR (400 MHz) Spectrum of **8l** in $CDCl_3$



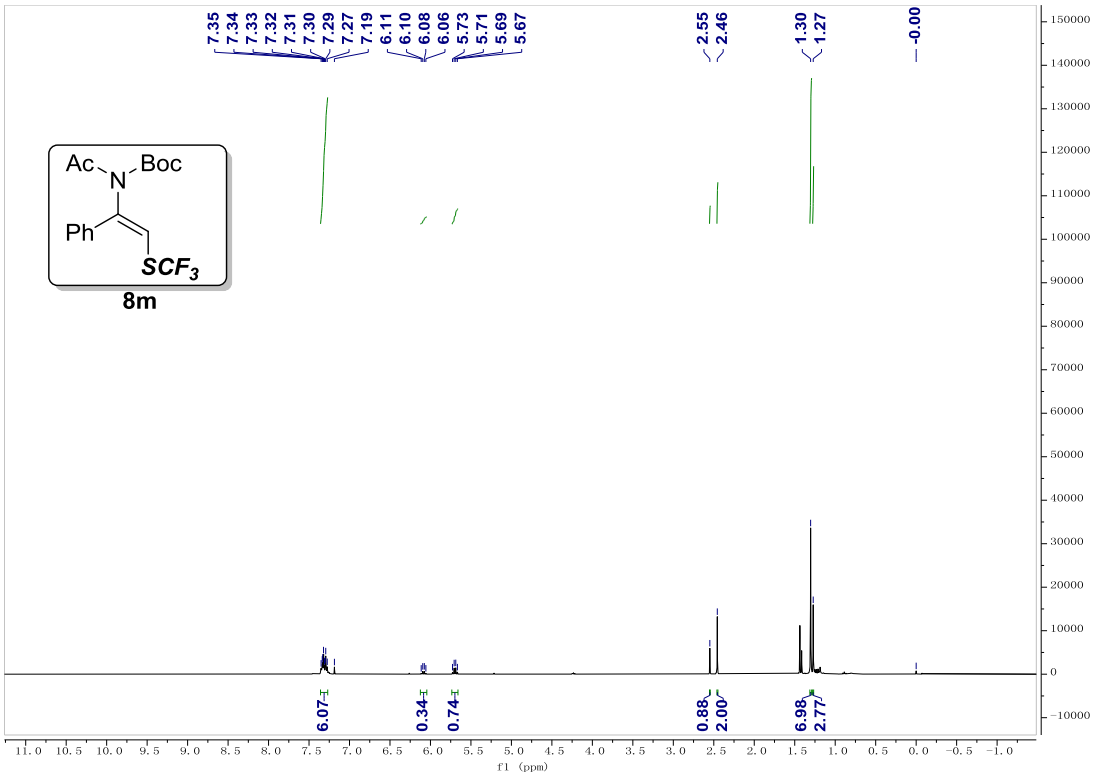
^{13}C NMR (100 MHz) Spectrum of **8l** in $CDCl_3$



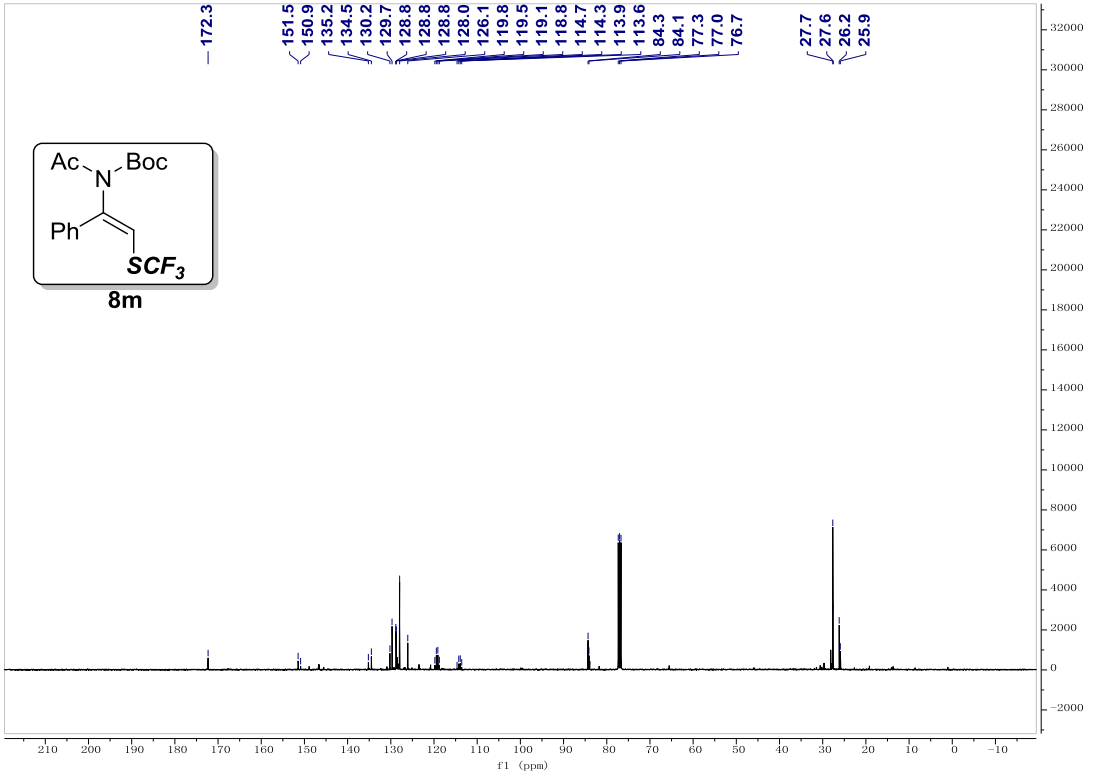
^{19}F NMR (376 MHz) Spectrum of **8l** in $CDCl_3$



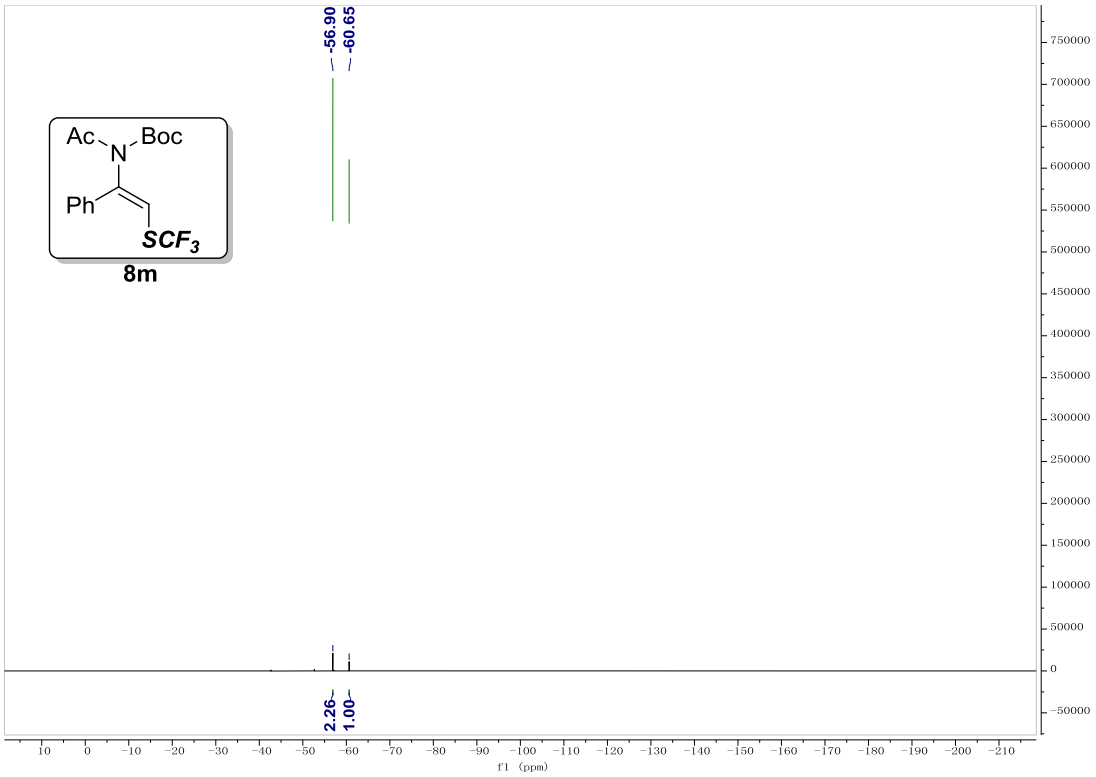
^{1}H NMR (400 MHz) Spectrum of **8m** in $CDCl_3$



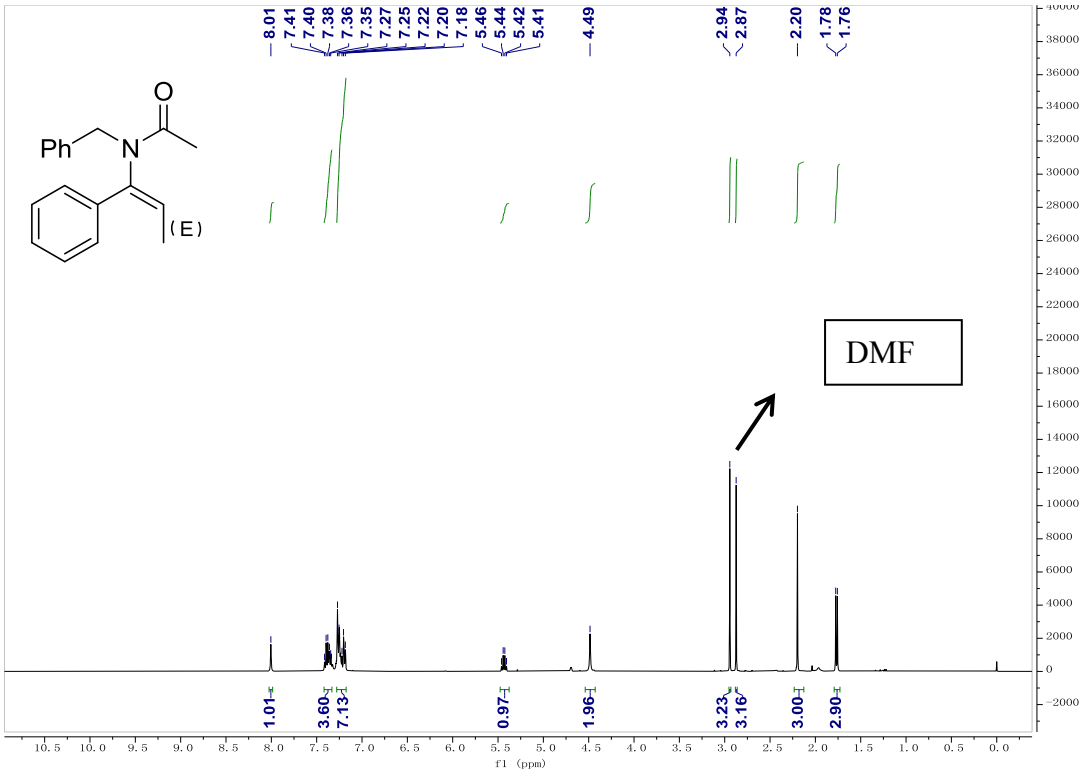
^{13}C NMR (100 MHz) Spectrum of **8m** in $CDCl_3$



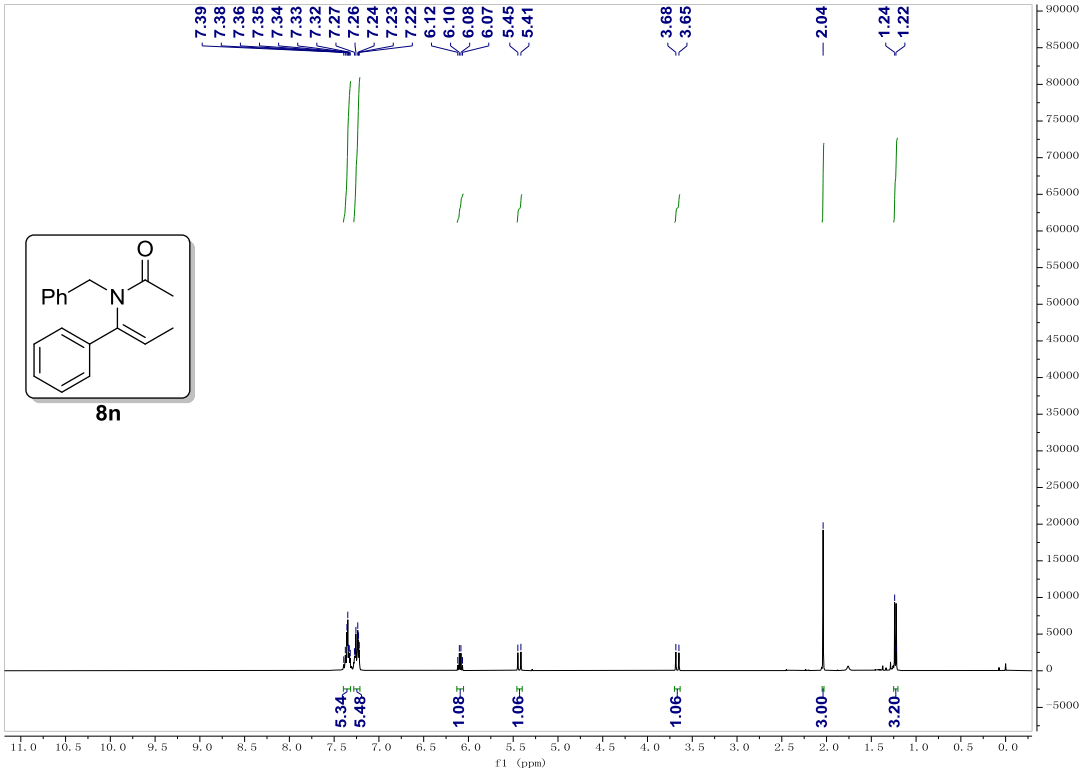
^{19}F NMR (376 MHz) Spectrum of **8m** in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of **7n** in $CDCl_3$



^{1}H NMR (400 MHz) Spectrum of **8n** in $CDCl_3$



^{13}C NMR (100 MHz) Spectrum of **8n** in $CDCl_3$