Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Synthesis of Trifluoromethylated Thioethers via Ni-Catalyzed Reductive C–S Coupling

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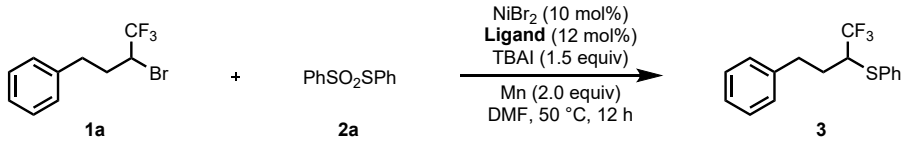
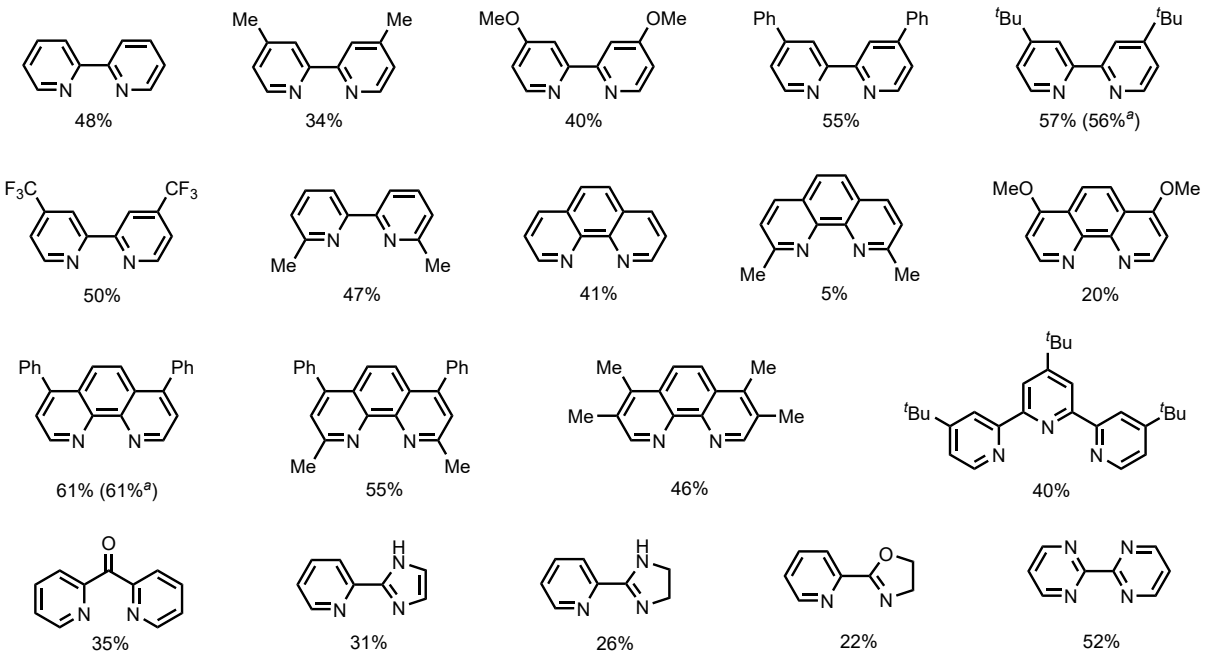
General Information

NMR spectra were recorded on Bruker-600 (600 MHz for ^{1}H; 151 MHz for ^{13}C and 565 MHz for ^{19}F). All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature. ^{1}H NMR spectra were referenced relative to $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were referenced relative to $CDCl_3$ at δ 77.16 ppm. The ^{13}C NMR spectra were obtained with ^{1}H decoupling. Data for ^{1}H, ^{13}C, ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet et al.), integration, and coupling constant (Hz). {note: some of the NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H; 101 MHz for ^{13}C and 376 MHz for ^{19}F) and Bruker-500 (500 MHz for ^{1}H; 126 MHz for ^{13}C and 471 MHz for ^{19}F)}). High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight). $Ni(ClO_4)_2 \cdot 6H_2O$ was obtained from Sigma-Aldrich. 4,7-diphenyl-1,10-phenanthroline was purchased from Strem Chemicals. Mn powder was purchased from Alfa. Anhydrous DMF was purchased from *J&K* Chemicals. TBAI was purchased from Sigma-Aldrich. Secondary alkyl bromides were synthesized *via* following method described in this supplementary information.

Optimization of conditions

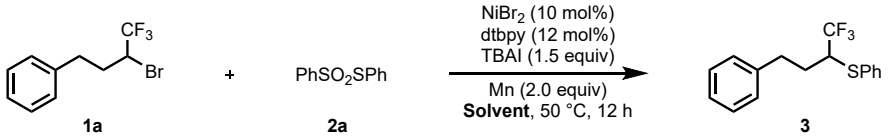
Table S1. Optimization of Ligands





Unless otherwise noted, the reaction conditions were as follows: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), $NiBr_2$ (10 mol%), **Ligand** (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [a]Isolated yield.

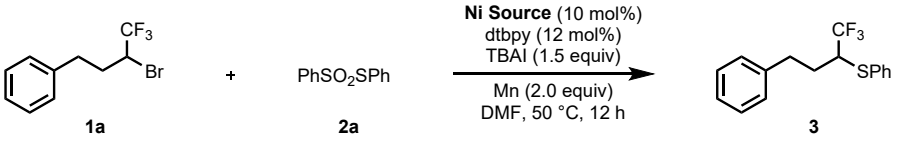
Table S2. Optimization of Solvents



Entry	**Solvent**	Yield (%)
1	DMA	ND
2	DMF	56
3	NMP	31
4	DME	ND
5	THF	ND
6	1,4-Dioxane	ND
7	DCM	ND
8	CH_3CN	ND
9	Toluene	ND
10	CH_3OH	6

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), $NiBr_2$ (10 mol%), dtbpy (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), **Solvent** (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

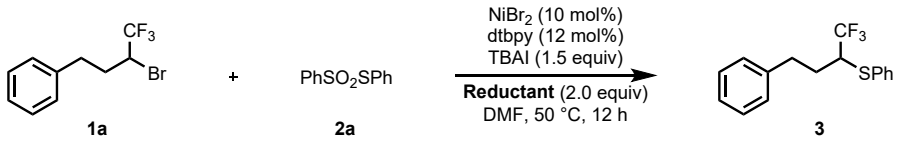
Table S3. Optimization of Ni-Catalysts



Entry	**Ni Source**	Yield (%)
1	$NiCl_2$	27
2	$NiBr_2$	56
3	NiI_2	51
4	$NiCl_2$•DME	51
5	$NiBr_2$•DME	47
6	$Ni(BF_4)_2$•$6H_2O$	51
7	$Ni(NO_3)_2$•$6H_2O$	ND
8	$Ni(ClO_4)_2$•$6H_2O$	59
9	$Ni(OTf)_2$	45
10	$Ni(OAc)_2$	36
11	$Ni(acac)_2$	39
12	$Ni(PPh_3)_2Br_2$	46

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), **Ni Source** (10 mol%), dtbpy (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

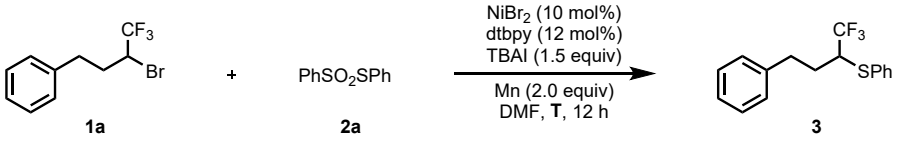
Table S4. Optimization of Reductants



Entry	**Reductant**	Yield (%)
1	Mn	56
2	Zn	ND
3	B_2Pin_2, K_2CO_3	23
4	B_2Neo_2, K_2CO_3	10

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), $NiBr_2$ (10 mol%), dtbpy (12 mol%), **Reductant** (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

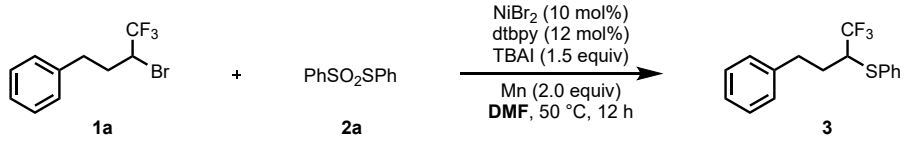
Table S5. Optimization of Temperature



Entry	**T** (°C)	Yield (%)
1	30	ND
2	40	50
3	50	56
4	60	53
5	70	45

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), $NiBr_2$ (10 mol%), dtbpy (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), **T**, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

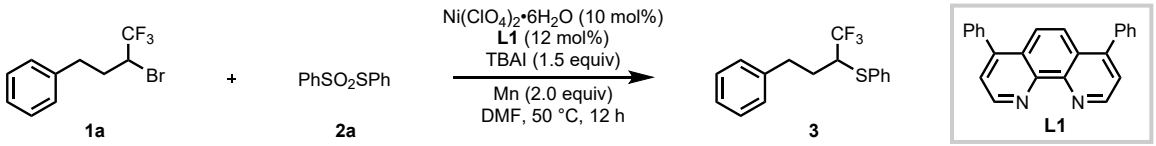
Table S6. Adjustment of Solvent



Entry	**DMF (x mL)**	Yield (%)
1	0.5	47
2	0.8	44
3	1.0	53
4	1.2	56
5	1.5	51
6	2.0	49

Unless otherwise noted, the reaction conditions were as follows: 1a (0.10 mmol, 1.0 equiv), 2a (0.15 mmol, 1.5 equiv), $NiBr_2$ (10 mol%), dtbpy (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), **DMF (x mL)**, 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

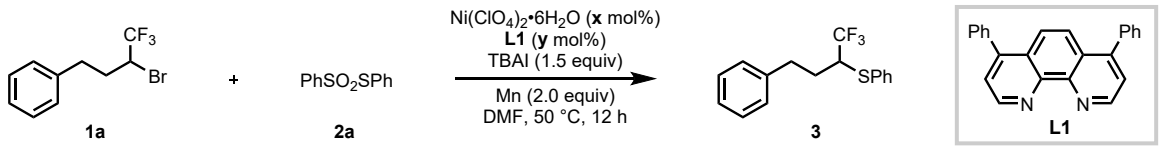
Table S7. Quant of 1a and 2a



Entry	**x : y**	Yield (%)
1	1.0 : 2.0	42
2	1.0 : 1.5	56
3	1.0 : 1.0	60
4	1.5 : 1.0	78 (78[a])
5	2.0 : 1.0	60

Unless otherwise noted, the reaction conditions were as follows: **1a** (0.**x** mmol, **x** equiv), **2a** (0.**y** mmol, **y** equiv), $Ni(ClO_4)_2$•$6H_2O$ (10 mol%), $\mathbf{L_1}$ (12 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [a]Isolated yield.

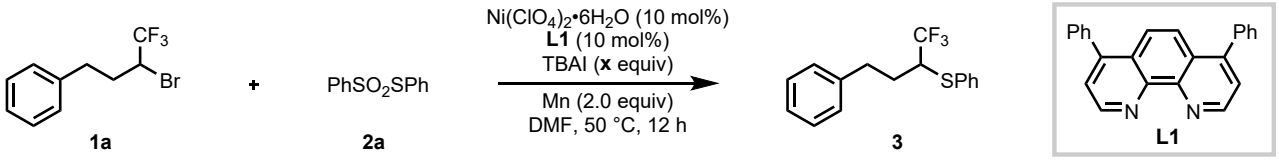
Table S8. Quant of Ni Source and Ligand



Entry	**x : y**	Yield (%)
1	5 : 6	24
2	7.5 : 9	78
3	10 : 10	92 (91[a])
4	10 :12	81
5	10 : 15	73
6	15 : 18	76

Unless otherwise noted, the reaction conditions were as follows: **1a** (0.15 mmol, 1.5 equiv), **2a** (0.10 mmol, 1.0 equiv), $Ni(ClO_4)_2•6H_2O$ (**x** mol%), **L1** (**y** mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.15 mmol, 1.5 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [a]Isolated yield.

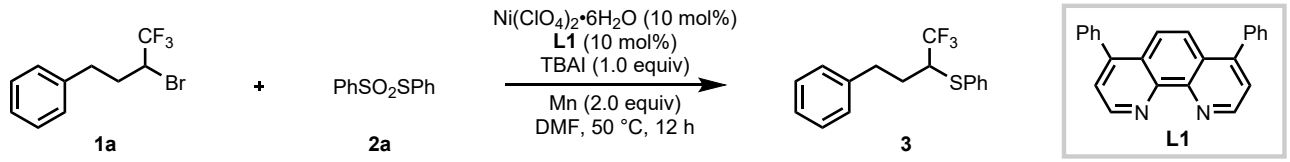
Table S9. Quant of Additive



Entry	**x**	Yield (%)
1	1.5	90
2	1.0	94 (94[a])
3	0.8	81
4	0.5	73
5	0.2	76

Unless otherwise noted, the reaction conditions were as follows: **1a** (0.15 mmol, 1.5 equiv), **2a** (0.10 mmol, 1.0 equiv), $Ni(ClO_4)_2•6H_2O$ (10 mol%), **L1** (10 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.**x** mmol, **x** equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [a]Isolated yield.

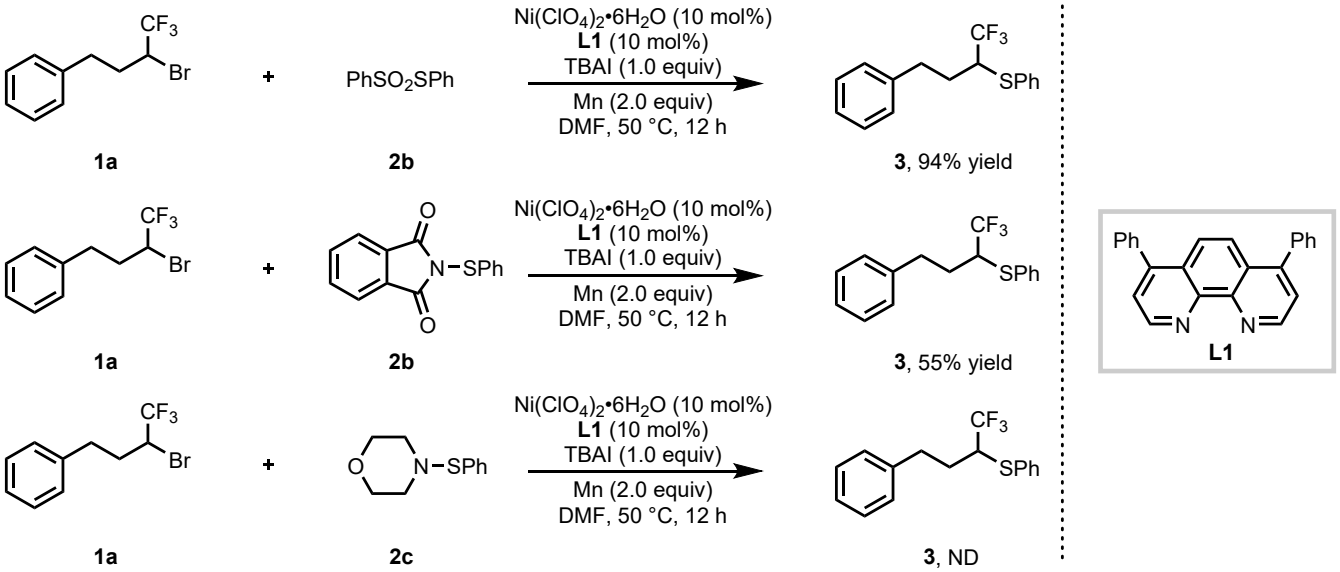
Table S10. Control Experiments



Entry	conditions	Yield (%)
1	without $Ni(ClO_4)_2•6H_2O$	0
2	without Mn	0
3	without Ligand	49
4	without TBAI	62

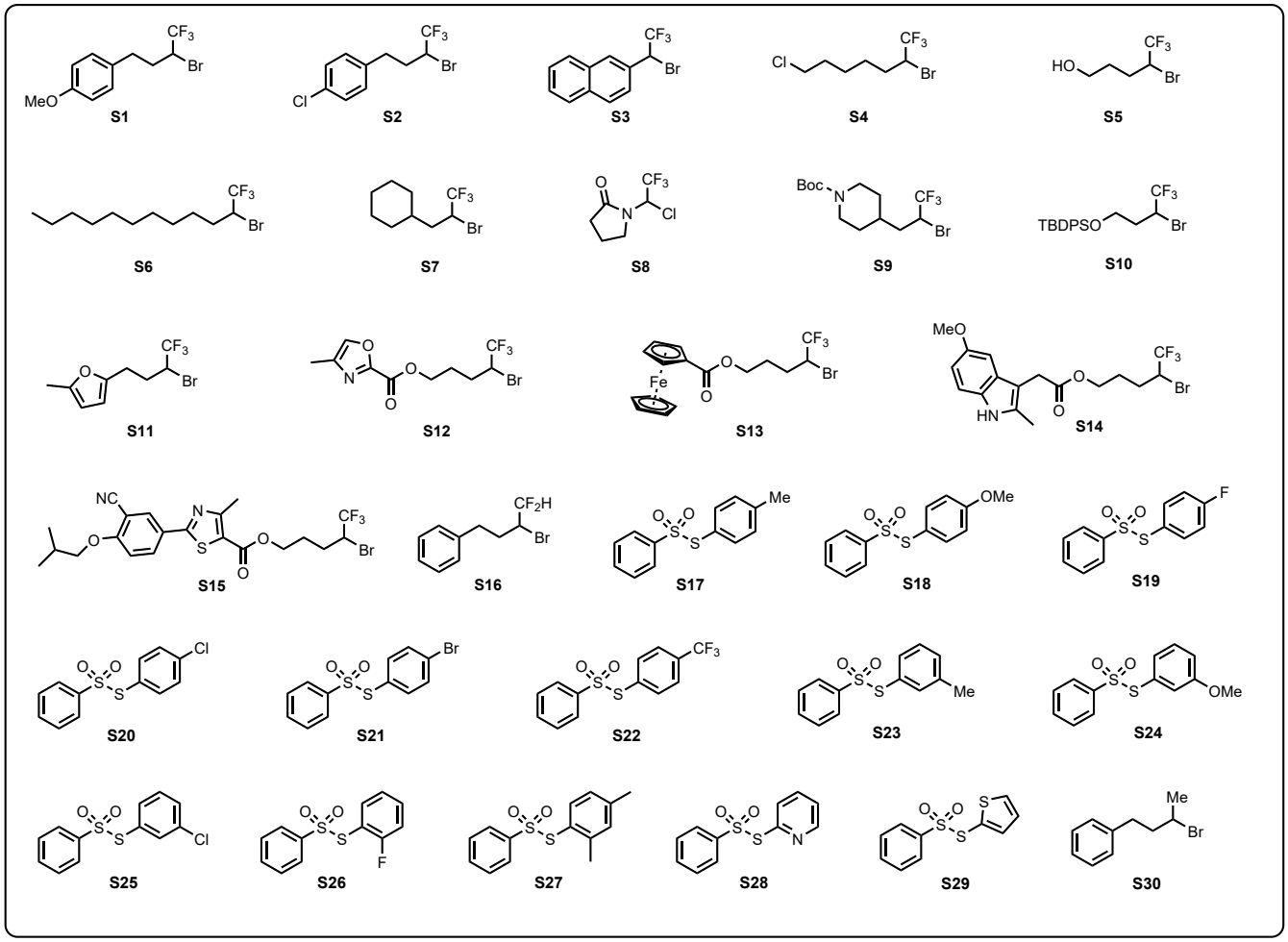
Unless otherwise noted, the reaction conditions were as follows: **1a** (0.15 mmol, 1.5 equiv), **2a** (0.10 mmol, 1.0 equiv), $Ni(ClO_4)_2•6H_2O$ (10 mol%), **L1** (10 mol%), Mn (0.20 mmol, 2.0 equiv), TBAI (0.1 mmol, 1.0 equiv), DMF (1.0 mL), 50 °C, 12 h. Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Table S11. Optimization of The Sulfuration Reagents



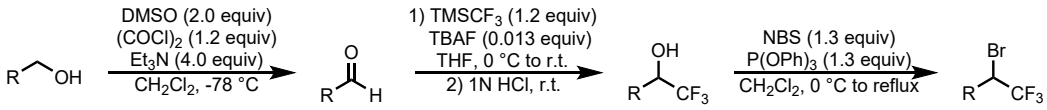
General Procedures

Synthesis of the substrates



General procedure A for preparation of trifluoromethylated alkyl bromides

All of trifluoromethylated alkyl bromides **S1-S7, S9-S15** were prepared through the reported procedures.[1-2]



Swern oxidation of the alcohol. DMSO (2.84 mL, 40 mmol, 2.0 equiv) was added slowly to a solution of oxalyl chloride (2.03 mL, 24 mmol, 1.2 equiv) in CH_2Cl_2 (150 mL) at -78 °C. The resulting mixture was allowed to stir for 30 min. Next, a solution of the alcohol (20 mmol) in CH_2Cl_2 (30 mL) was added over 5 min to the mixture. The resulting mixture was stirred at -78 °C for 45 min, and then Et_3N (11.1 mL, 80 mmol, 4.0 equiv) was added in one portion. The mixture was allowed to warm to r.t., and then it was stirred for 2 h. Next, an aqueous saturated solution of NH_4Cl (30 mL) was added to quench the reaction. The resulting mixture was extracted with CH_2Cl_2 (3 × 70 mL), and the combined

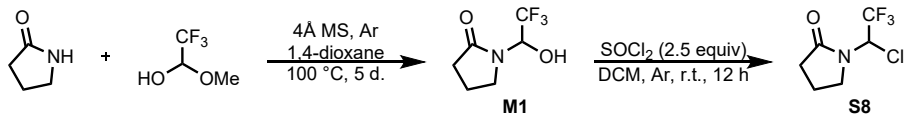
organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel.

Trifluoromethylation of the aldehyde. A solution of TBAF (1.0 M in THF, 0.20 mL, 0.20 mmol, 0.013 equiv) was added over 3 min to a solution of the aldehyde (15 mmol) and trifluoromethyltrimethylsilane (2.66 mL, 18 mmol, 1.2 equiv) in THF (20 mL) at 0 °C (CAUTION: very exothermic). The reaction mixture was allowed to warm to r.t., and it was stirred for 1 h. Next, an aqueous solution of 1 N HCl (30 mL) was added, and the mixture was allowed to stir at r.t. for another 2 h. Then, the mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel.

Bromination of the alcohol. Triphenylphosphite (4.03 g, 3.41 mL, 1.3 equiv) was added over 5 min to a solution of N-bromosuccinimide (2.31 g, 13 mmol, 1.3 equiv) in CH_2Cl_2 (10 mL) at 0 °C (CAUTION: exothermic). Next, a solution of the alcohol (10 mmol) in CH_2Cl_2 (12 mL) was added to the mixture at 0 °C. The reaction mixture was heated to 40 °C and then stirred for 12 h. Next, the solvent was evaporated, and the product was purified by flash chromatography on silica gel.

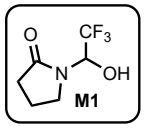
General procedure B for preparation of S8

The trifluoromethyl alkyl chloride **S8** was synthesized by the following methods.[3]



Synthesis of the trifluoromethyl alcohol. Following a slightly modified procedure, a 10 mL pressure tube was charged with pyrrolidin-2-one (703 mg, 6 mmol), 2,2,2-trifluoro-1-methoxyethanol (0.77 mL, 6.6 mmol, 1.1 equiv), 4Å MS (1 g) and dioxane (8 mL). The tube was sealed under Argon atmosphere. The resulting mixture was heated at 100 °C for 5 d and then cooled down to r.t., The mixture was filtered over Celite and the cake was washed with ether (3 × 20 mL). The volatiles were removed under reduced pressure and the resulting solid was recrystallized in chloroform to afford white crystals.

Chlorination of the alcohol. $SOCl_2$ (357 mg, 7.5 mmol, 2.5 equiv) was added over 10 min to a solution of alcohol (540 mg, 3 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture stirred at r.t. for 12 h. Next, the solvent was evaporated, and the product was purified by flash chromatography on silica gel.



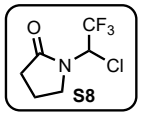
1-(2,2,2-trifluoro-1-hydroxyethyl)pyrrolidin-2-one

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.78 (q, *J* = 5.8 Hz, 1H), 3.76 – 3.65 (m, 1H), 3.53 – 3.40 (m, 1H), 2.54 – 2.30 (m, 2H), 2.19 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.98, 122.76 (q, *J* = 283.3 Hz), 72.36 (q, *J* = 36.0 Hz), 42.84, 31.13, 18.33.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -78.55 (d, *J* = 6.3 Hz).

HRMS (ESI): m/z calcd. for $C_6H_9F_3NO_2^+$ [M + H$^+$]: 184.0580, found: 184.0585.



1-(1-chloro-2,2,2-trifluoroethyl)pyrrolidin-2-one

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.49 (q, *J* = 6.1 Hz, 1H), 3.70 – 3.59 (m, 1H), 3.55 – 3.45 (m, 1H), 2.55 – 2.35 (m, 2H), 2.20 – 2.10 (m, 2H).

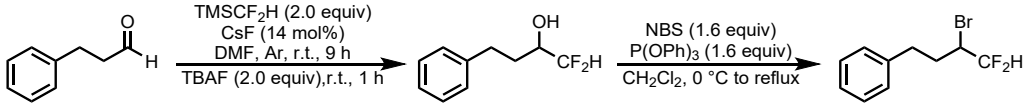
^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.64, 121.42 (q, *J* = 280.7 Hz), 63.00 (q, *J* = 39.2 Hz), 42.25, 29.40, 17.41.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -74.96 (d, *J* = 6.1 Hz).

HRMS (ESI): m/z calcd. for $C_6H_7ClF_3NNaO^+$ [M + Na$^+$]: 224.0060, found: 224.0057.

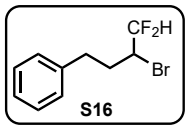
General procedure C for preparation of difluoromethyl alkyl bromide

The difluoromethyl alkyl bromide **S16** was synthesized by the following methods.



Difluoromethylation of the aldehyde. An oven-dried 100 mL flask, equipped with a stirring bar, was charged with CsF (213 mg, 1.4 mmol, 14 mol%), and it was evacuated and backfilled with Argon for three times. A solution of the aldehyde (1.34 g, 10 mmol, 1.0 equiv) and difluoromethyltrimethylsilane (2.48 g, 20 mmol, 2.0 equiv) in DMF (50 mL) was added to the flask and the reaction mixture was stirred at r.t. for 9 h. Next, an aqueous solution of TBAF (1.0 M in THF, 20 mL, 20 mmol, 2.0 equiv) was added, and the mixture was allowed to stir at r.t. for another 1 h. Then, the mixture was extracted with Et_2O (3 × 30 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel.

Bromination of the alcohol. Triphenylphosphite (1.5 g, 4.8 mmol, 1.6 equiv) was added over 5 min to a solution of N-bromosuccinimide (854 mg, 4.8 mmol, 1.6 equiv) in CH_2Cl_2 (10 mL) at 0 °C (CAUTION: exothermic). Next, a solution of the alcohol (559 mg, 3 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added to the mixture at 0 °C. The reaction mixture was heated to 55 °C and then stirred for 12 h. Next, the solvent was evaporated, and the product was purified by flash chromatography on silica gel.



(3-bromo-4,4-difluorobutyl)benzene

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 5.80 (td, *J* = 55.9, 3.6 Hz, 1H), 3.93 – 3.79 (m, 1H), 3.00 – 2.91 (m, 1H), 2.79 – 2.70 (m, 1H), 2.32 – 2.20 (m, 1H), 2.18 – 2.05 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.87, 128.80, 128.67, 126.63, 114.87 (t, *J* = 245.6 Hz), 49.94 (t, *J* = 24.1 Hz),

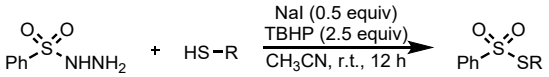
32.74, 32.45 (t, J = 2.7 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -117.38 (ddd, J = 276.9, 55.8, 10.9 Hz), -122.24 (ddd, J = 277.1, 56.0, 13.0 Hz).

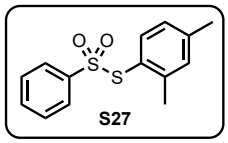
HRMS (ESI): m/z calcd. for $C_{10}H_{11}BrF_2Na^+$ [M + Na^+]: 272.0880, found: 272.0868.

General procedure D for preparation of thiosulfonates

All of thiosulfonates **S17-S26**, **S28**, **S29** were prepared through the reported procedures.[4] The substrate **S27** was synthesized according to the reported literature with modifications.



An oven-dried 100 mL flask, equipped with a stirring bar, was charged with benzenesulfonyl hydrazide (1.03 g, 6 mmol, 1.5 equiv), thiol (4 mmol, 1.0 equiv), NaI (300 mg, 2 mmol, 0.5 equiv) and CH_3CN (25 mL). Then TBHP (901 mg, 10 mmol, 2.5 equiv) was added to the reaction mixture and it was stirred at r.t. for 12 h. After removal of the solvent, the crude product was purified by flash chromatography on silica gel.



S-(2,4-dimethylphenyl) benzenesulfonothioate

The product was isolated by column chromatography as white solid (98% yield).

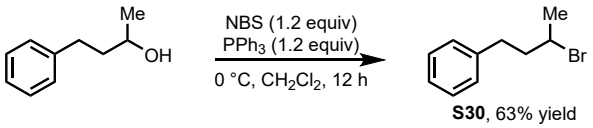
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 3H), 7.47 – 7.41 (m, 2H), 7.19 (d, J = 7.8 Hz, 1H), 7.05 (s, 1H), 6.96 (d, J = 7.9 Hz, 1H), 2.34 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.06, 143.59, 142.73, 138.32, 133.68, 131.96, 129.02, 127.93, 127.59, 123.79, 21.54, 20.60.

HRMS (ESI): m/z calcd. for $C_{14}H_{14}NaO_2S_2^+$ [M + Na^+]: 301.0327, found: 301.0335.

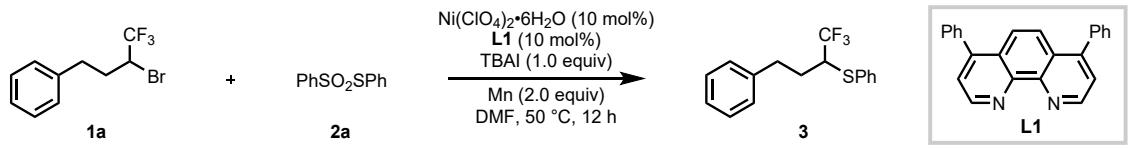
General procedure E for preparation of (3-bromobutyl)benzene S30

The secondary alkyl bromide S30 was synthesized by the following methods.

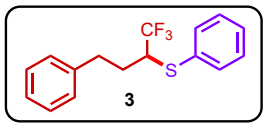


Bromination of the alcohol. Triphenylphosphine (1.12 g, 3.6 mmol, 1.6 equiv) was added to a solution of N-bromosuccinimide (854 mg, 3.6 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) at 0 °C (CAUTION: exothermic). Next, a solution of the alcohol (450 mg, 3 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added to the mixture at 0 °C. The reaction mixture then stirred for 12 h. Next, the solvent was evaporated, and the product was purified by flash chromatography on silica gel.

General Procedure for Synthesis of Trifluoromethylated Thioethers via Ni-Catalyzed Reductive C–S Coupling.



An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with *S*-phenyl benzenesulfonothioate **2a** (25 mg, 0.10 mmol, 1.0 equiv), Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2 \cdot 6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then alkyl bromide **1a** (40 mg, 0.15 mmol, 1.5 equiv) and dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired products.



phenyl(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

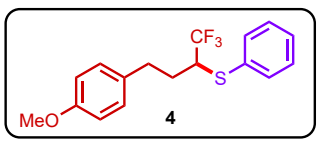
The product was isolated by column chromatography as colorless oil (94% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.33 – 7.26 (m, 5H), 7.23 – 7.19 (m, 1H), 7.19 – 7.15 (m, 2H), 3.34 – 3.25 (m, 1H), 3.13 – 3.05 (m, 1H), 2.90 – 2.82 (m, 1H), 2.28 – 2.19 (m, 1H), 1.95 – 1.87 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.20, 133.42, 133.16, 129.28, 128.77, 128.67, 128.44, 126.85 (q, J = 279.0 Hz), 126.56, 51.63 (q, J = 28.6 Hz), 32.43, 29.90.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.08 (d, J = 11.1 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{15}F_3NaS^+$ [M + Na^+]: 319.0739, found: 319.0721.



phenyl(1,1,1-trifluoro-4-(4-methoxyphenyl)butan-2-yl)sulfane.

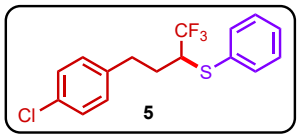
The product was isolated by column chromatography as colorless oil (74% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.37 – 7.29 (m, 3H), 7.09 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.36 – 3.21 (m, 1H), 3.09 – 2.98 (m, 1H), 2.90 – 2.75 (m, 1H), 2.26 – 2.13 (m, 1H), 1.95 – 1.81 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.30, 133.36, 133.23, 132.16, 129.62, 129.27, 128.39, 126.88 (q, J = 278.9 Hz), 114.15, 55.40, 51.46 (q, J = 28.5 Hz), 31.49, 30.11.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.11 (d, *J* = 9.9 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{18}F_3OS^+$ [M + H$^+$]: 327.1025, found: 327.1003.



(4-(4-chlorophenyl)-1,1,1-trifluorobutan-2-yl)(phenyl)sulfane.

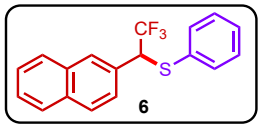
The product was isolated by column chromatography as colorless oil (48% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.44 (m, 2H), 7.37 – 7.28 (m, 3H), 7.26 – 7.23 (m, 2H), 7.12 – 7.04 (m, 2H), 3.30 – 3.22 (m, 1H), 3.09 – 3.03 (m, 1H), 2.88 – 2.80 (m, 1H), 2.24 – 2.16 (m, 1H), 1.92 – 1.87 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.62, 133.39, 132.99, 132.33, 130.00, 129.35, 128.87, 128.54, 126.73 (q, *J* = 279.0 Hz), 51.55 (q, *J* = 28.7 Hz), 31.77, 29.89.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.09 (d, *J* = 12.1 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{15}ClF_3S^+$ [M + H$^+$]: 331.0530, found: 331.0518.



phenyl(2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl)sulfane.

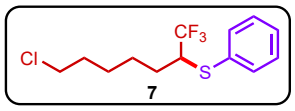
The product was isolated by column chromatography as white solid (94% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.92 – 7.85 (m, 3H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.53 – 7.50 (m, 2H), 7.36 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 5.36 – 5.28 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ137.15, 133.87, 132.86, 130.13, 129.23, 129.21, 129.16, 128.41, 127.90, 127.62, 127.58, 127.29, 127.05, 125.75, 123.64 (q, *J* = 278.3 Hz), 47.64 (q, *J* = 34.2 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -70.02 (d, *J* = 9.0 Hz).

HRMS (ESI): m/z calcd. for $C_{18}H_{14}F_3S^+$ [M + H$^+$]: 319.0763, found: 319.0779.



(7-chloro-1,1,1-trifluoroheptan-2-yl)(phenyl)sulfane.

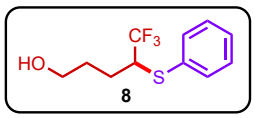
The product was isolated by column chromatography as colorless oil (71% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.31 (m, 3H), 3.55 (t, *J* = 6.6 Hz, 2H), 3.33 – 3.27 (m, 1H), 1.95 – 1.88 (m, 1H), 1.87 – 1.76 (m, 3H), 1.68 – 1.41 (m, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 133.62, 133.36, 129.31, 128.53, 126.82 (q, *J* = 279.0 Hz), 52.83 (q, *J* = 28.4 Hz), 44.98, 32.33, 28.39, 26.42, 25.99.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -70.25 (d, *J* = 11.9 Hz).

HRMS (ESI): m/z calcd. for $C_{13}H_{17}ClF_3S^+$ [M + H$^+$]: 297.0686, found: 297.0696.



5,5,5-trifluoro-4-(phenylthio)pentan-1-ol.

The product was isolated by column chromatography as colorless oil (70% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.38 – 7.29 (m, 3H), 3.77 – 3.66 (m, 2H), 3.44 – 3.33 (m, 1H), 2.12 – 2.00 (m, 2H), 1.87 – 1.74 (m, 1H), 1.74 – 1.65 (m, 1H), 1.46 (s, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 133.56, 133.37, 129.32, 128.53, 126.84 (q, J = 279.0 Hz), 62.33, 53.17, 52.83 (q, J = 28.6 Hz), 29.72, 25.36.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -70.38 (d, J = 8.6 Hz).

HRMS (ESI): m/z calcd. for $C_{11}H_{13}F_3NaOS^+$ [M + Na^+]: 273.0531, found: 273.0549.

phenyl(1,1,1-trifluorododecan-2-yl)sulfane.

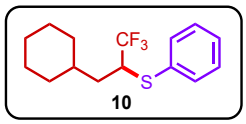
The product was isolated by column chromatography as colorless oil (72% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.36 – 7.28 (m, 3H), 3.36 – 3.25 (m, 1H), 1.95 – 1.85 (m, 1H), 1.81 – 1.76 (m, 1H), 1.67 – 1.49 (m, 2H), 1.39 – 1.23 (m, 14H), 0.90 (t, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 133.67, 133.58, 129.24, 128.40, 126.96 (q, J = 279.1 Hz), 52.97 (q, J = 28.2 Hz), 32.07, 29.76, 29.68, 29.50, 29.47, 29.20, 28.55, 26.73, 22.85, 14.26.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -70.36 (d, J = 9.1 Hz).

HRMS (ESI): m/z calcd. for $C_{18}H_{28}F_3S^+$ [M + H^+]: 333.1858, found: 333.1874.



(3-cyclohexyl-1,1,1-trifluoropropan-2-yl)(phenyl)sulfane.

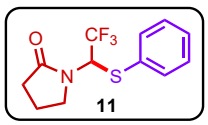
The product was isolated by column chromatography as colorless oil (40% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, J = 6.2 Hz, 2H), 7.34 – 7.31 (m, 3H), 3.47 – 3.39 (m, 1H), 1.84 – 1.77 (m, 1H), 1.75 – 1.68 (m, 5H), 1.67 – 1.62 (m, 1H), 1.58 – 1.48 (m, 1H), 1.37 – 1.30 (m, 1H), 1.28 – 1.23 (m, 1H), 1.20 – 1.13 (m, 1H), 1.07 – 0.98 (m, 1H), 0.92 – 0.83 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 133.64, 133.48, 129.24, 128.44, 127.12 (q, J = 278.9 Hz), 50.12 (q, J = 28.3 Hz), 35.64, 34.14, 34.04, 31.87, 26.53, 26.33, 26.01.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.46 (d, J = 11.4 Hz).

HRMS (ESI): m/z calcd. for $C_{15}H_{20}F_3S^+$ [M + H^+]: 289.1232, found: 289.1239.



1-(2,2,2-trifluoro-1-(phenylthio)ethyl)pyrrolidin-2-one.

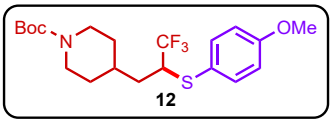
The product was isolated by column chromatography as colorless oil (88% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.45 (m, 2H), 7.34 – 7.31 (m, 3H), 6.07 – 6.01 (m, 1H), 3.75 – 3.68 (m, 1H), 3.47 – 3.42 (m, 1H), 2.43 – 2.35 (m, 1H), 2.27 – 2.19 (m, 1H), 2.07 – 2.03 (m, 1H), 1.96 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.65, 133.33, 130.32, 129.56, 129.06, 123.54 (q, J = 282.5 Hz), 61.09 (q, J = 33.4 Hz), 43.48, 30.32, 18.24.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.40 (d, J = 11.7 Hz).

HRMS (ESI): m/z calcd. for $C_{12}H_{13}F_3NOS^+$ [M + H$^+$]: 276.0664, found: 276.0678.



12

tert-butyl 4-(3,3,3-trifluoro-2-((4-methoxyphenyl)thio)propyl)piperidine-1-carboxylate

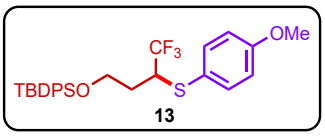
The product was isolated by column chromatography as colorless oil (68% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, J = 6.9 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 4.23 – 3.99 (m, 2H), 3.80 (s, 3H), 3.26 – 3.16 (m, 1H), 2.81 – 2.65 (m, 2H), 2.03 – 1.93 (m, 1H), 1.69 – 1.59 (m, 3H), 1.59 – 1.51 (m, 1H), 1.45 (s, 9H), 1.27 – 1.16 (m, 1H), 1.12 – 1.01 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.48, 154.89, 136.78, 126.95 (q, J = 279.1 Hz), 122.84, 114.78, 79.55, 55.46, 50.52 (q, J = 28.1 Hz), 44.12, 34.68, 32.69, 30.86, 28.55.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.15 (d, J = 10.4 Hz).

HRMS (ESI): m/z calcd. for $C_{20}H_{29}F_3NO_3S^+$ [M + H$^+$]: 420.1815, found: 420.1808.



13

tert-butyldiphenyl(4,4,4-trifluoro-3-((4-methoxyphenyl)thio)butoxy)silane.

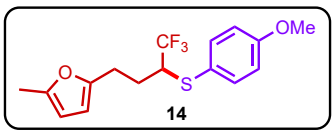
The product was isolated by column chromatography as colorless oil (68% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H), 7.50 – 7.39 (m, 8H), 6.87 – 6.81 (m, 2H), 4.21 – 4.15 (m, 1H), 3.92 – 3.87 (m, 1H), 3.82 (s, 3H), 3.75 – 3.67 (m, 1H), 2.21 – 2.14 (m, 1H), 1.68 – 1.60 (m, 1H), 1.08 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.25, 136.40, 135.67, 133.57, 133.42, 129.96, 129.92, 127.91, 127.28 (q, J = 278.7 Hz), 123.55, 114.72, 59.66, 55.43, 49.80 (q, J = 28.4 Hz), 31.17, 26.92, 19.32.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.16 (d, J = 9.4 Hz).

HRMS (ESI): m/z calcd. for $C_{27}H_{32}F_3O_2SSi^+$ [M + H$^+$]: 505.1839, found: 505.1863.



14

2-methyl-5-(4,4,4-trifluoro-3-((4-methoxyphenyl)thio)butyl)furan.

The product was isolated by column chromatography as yellow oil (75% yield).

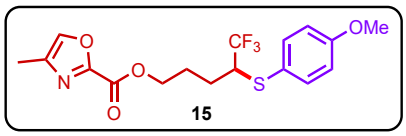
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 5.96 – 5.81 (m, 2H), 3.81 (s, 3H), 3.23 – 3.15 (m, 1H), 3.06 – 2.99 (m, 1H), 2.98 – 2.90 (m, 1H), 2.25 (s, 3H), 2.24 – 2.17 (m, 1H), 1.86 – 1.77 (m,

1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.41, 152.13, 151.07, 136.77, 126.94 (q, *J* = 279.0 Hz), 123.05, 114.71, 106.72, 106.05, 55.45, 52.51 (q, *J* = 28.1 Hz), 26.86, 25.01, 13.63.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.02 (d, *J* = 12.4 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{18}F_3O_2S^+$ [M + H$^+$]: 331.0974, found: 331.0978.



15

5,5,5-trifluoro-4-((4-methoxyphenyl)thio)pentyl 4-methyloxazole-2-carboxylate.

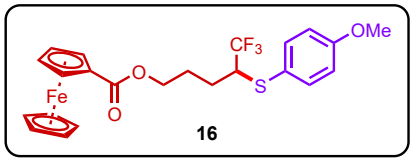
The product was isolated by column chromatography as colorless oil (76% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.2 Hz, 2H), 3.78 (s, 3H), 3.23 – 3.14 (m, 1H), 2.76 (s, 3H), 2.29 – 2.20 (m, 1H), 2.03 – 1.93 (m, 2H), 1.70 – 1.63 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.06, 160.92, 160.49, 155.56, 136.80, 126.70 (q, *J* = 279.1 Hz), 122.55, 122.04, 114.77, 64.47, 55.41, 53.00 (q, *J* = 28.1 Hz), 25.95, 25.04, 17.44.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.91 (d, *J* = 12.2 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{19}F_3NO_4S^+$ [M + H$^+$]: 390.0987, found: 390.0969.



16

4-(phenylthio)-5,5,5-trifluoropentyl ferrocene-1-carboxylate

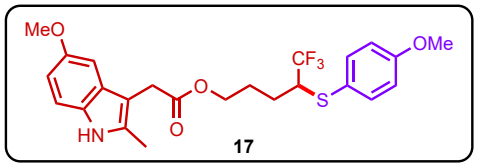
The product was isolated by column chromatography as brown oil (78% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.82 – 4.76 (m, 2H), 4.44 – 4.39 (m, 2H), 4.30 – 4.25 (m, 2H), 4.23 – 4.17 (m, 5H), 3.80 (s, 3H), 3.27 – 3.18 (m, 1H), 2.29 – 2.22 (m, 1H), 2.07 – 1.93 (m, 2H), 1.74 – 1.66 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.60, 160.28, 136.64, 126.61 (q, *J* = 279.1 Hz), 122.50, 114.61, 71.33, 70.89, 70.06, 70.02, 69.68, 63.13, 55.23, 52.95 (q, *J* = 28.1 Hz), 26.00, 24.95.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.87 (d, *J* = 9.5 Hz).

HRMS (ESI): m/z calcd. for $C_{23}H_{23}F_3FeNaO_3S^+$ [M + Na$^+$]: 5150562, found: 5150565.



17

5,5,5-trifluoro-4-((4-methoxyphenyl)thio)pentyl 2-(5-methoxy-2-methyl-1H-indol-3-yl)acetate

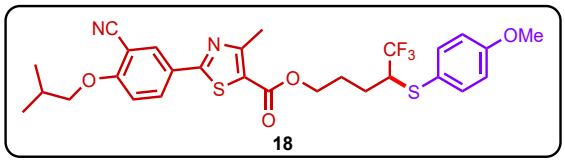
The product was isolated by column chromatography as colorless oil (73% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.99 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 1H), 4.17 – 4.06 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 3.66 (s, 2H), 3.12 – 3.04 (m, 1H), 2.36 (s, 3H), 2.16 – 2.08 (m, 1H), 1.90 – 1.79 (m, 2H), 1.58 – 1.47 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.15, 160.44, 154.23, 136.76, 133.61, 130.23, 128.94, 126.74 (q, *J* = 279.3 Hz), 122.82, 114.78, 111.12, 111.06, 104.35, 100.35, 63.85, 55.95, 55.45, δ53.11 (q, *J* = 28.4 Hz), 30.57, 25.97, 24.93, 11.86.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.03 (d, *J* = 12.8 Hz).

HRMS (ESI): m/z calcd. for $C_{24}H_{27}F_3NO_4S^+$ [M + H$^+$]: 482.1607, found: 482.1606.



18

5,5,5-trifluoro-4-((4-methoxyphenyl)thio)pentyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate

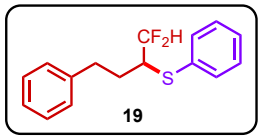
The product was isolated by column chromatography as white solid (73% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.3 Hz, 1H), 8.07 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 6.1 Hz, 2H), 3.89 (d, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.26 – 3.15 (m, 1H), 2.75 (s, 3H), 2.31 – 2.23 (m, 1H), 2.22 – 2.16 (m, 1H), 2.05 – 1.96 (m, 2H), 1.72 – 1.63 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.45, 162.63, 161.94, 161.47, 160.49, 136.81, 132.70, 132.15, 126.72 (q, *J* = 279.1 Hz), 125.90, 122.56, 121.50, 115.47, 114.77, 112.70, 103.02, 75.76, 64.50, 55.41, 53.03 (q, *J* = 28.1 Hz), 28.23, 25.99, 25.10, 19.13, 17.58.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -69.98 (d, *J* = 9.1 Hz).

HRMS (ESI): m/z calcd. for $C_{28}H_{30}F_3N_2O_4S_2^+$ [M + H$^+$]: 579.1594, found: 579.1596.



19

(1,1-difluoro-4-phenylbutan-2-yl)(phenyl)sulfane.

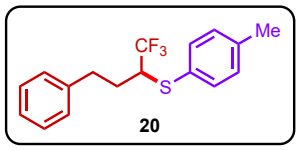
The product was isolated by column chromatography as colorless oil (61% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H), 7.33 – 7.28 (m, 5H), 7.24 – 7.19 (m, 3H), 5.80 (t, *J* = 56.3 Hz, 1H), 3.20 – 3.11 (m, 1H), 3.09 – 3.02 (m, 1H), 2.89 – 2.81 (m, 1H), 2.23 – 2.14 (m, 1H), 1.90 – 1.80 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.75, 133.17, 133.14, 129.32, 128.69, 128.13, 126.41, 116.69 (t, *J* = 245.8 Hz), 50.77 (t, *J* = 21.3 Hz), 32.60, 28.80.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.21 (ddd, *J* = 276.7, 56.1, 11.9 Hz), -123.70 (ddd, *J* = 275.8, 57.3, 18.7 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{16}F_2NaS^+$ [M + Na$^+$]: 301.0833, found: 301.0814.



20

p-tolyl(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

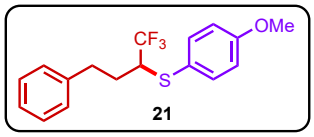
The product was isolated by column chromatography as colorless oil (77% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.16 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.24 – 3.18 (m, 1H), 3.11 – 3.05 (m, 1H), 2.89 – 2.81 (m, 1H), 2.33 (s, 3H), 2.24 – 2.16 (m, 1H), 1.92 – 1.85 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.30, 138.84, 134.07, 130.04, 129.28, 128.74, 128.66, 126.90 (q, *J* = 279.0 Hz), 126.52, 51.93 (q, *J* = 28.3 Hz), 32.45, 29.78, 21.27.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.99 (d, *J* = 10.6 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{18}F_3S^+$ [M + H$^+$]: 311.1076, found: 311.1082.



21

(4-methoxyphenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

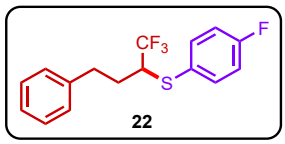
The product was isolated by column chromatography as colorless oil (55% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.20 – 3.11 (m, 2H), 2.93 – 2.85 (m, 1H), 2.25 – 2.17 (m, 1H), 1.93 – 1.84 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.40, 140.34, 136.68, 128.74, 128.64, 126.92 (q, *J* = 278.9 Hz), 126.51, 122.87, 114.74, 55.45, 52.29 (q, *J* = 28.0 Hz), 32.47, 29.58.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.83 (d, *J* = 11.6 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{17}F_3NaOS^+$ [M + Na$^+$]: 349.0844, found: 349.0822.



22

(4-fluorophenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

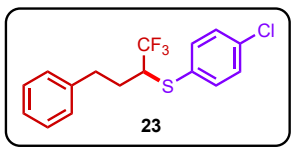
The product was isolated by column chromatography as colorless oil (84% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.05 – 6.97 (m, 2H), 3.24 – 3.15 (m, 1H), 3.14 – 3.06 (m, 1H), 2.91 – 2.83 (m, 1H), 2.27 – 2.19 (m, 1H), 1.93 – 1.84 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.19 (d, *J* = 249.3 Hz), 140.06, 136.44 (d, *J* = 8.2 Hz), 128.82, 128.64, 127.89 (d, *J* = 3.5 Hz), 126.79 (q, *J* = 279.0 Hz), 126.64, 116.43 (d, *J* = 21.9 Hz), 52.14 (q, *J* = 28.2 Hz), 32.40, 29.59.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.99 (d, *J* = 12.4 Hz), -111.94 – -112.14 (m).

HRMS (ESI): m/z calcd. for $C_{16}H_{14}F_4NaS^+$ [M + Na$^+$]: 337.0645, found: 337.0651.



23

(4-chlorophenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

The product was isolated by column chromatography as colorless oil (75% yield).

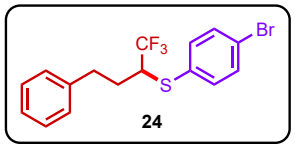
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 3.25 – 3.19 (m, 1H), 3.09 – 3.04 (m, 1H), 2.88 – 2.80 (m, 1H), 2.27 – 2.19 (m, 1H), 1.93 – 1.86 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.93, 134.83, 131.49, 129.64, 129.45, 128.82, 128.63, 126.73 (q, *J* = 278.9

Hz), 126.66, 51.70 (q, J = 28.7 Hz), 32.34, 29.59.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.01 (d, J = 8.9 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{15}ClF_3S^+$ [M + H$^+$]: 331.0530, found: 331.0508.



24

(4-bromophenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

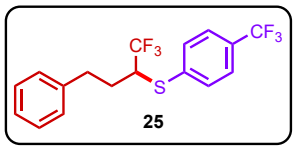
The product was isolated by column chromatography as colorless oil (44% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 4H), 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 3.37 – 3.29 (m, 1H), 3.15 – 3.09 (m, 1H), 2.94 – 2.87 (m, 1H), 2.31 – 2.23 (m, 1H), 1.99 – 1.90 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.14, 140.11, 133.72, 132.70, 128.81, 128.69, 127.79, 126.82 (q, J = 279.1 Hz), 126.62, 51.55 (q, J = 28.5 Hz), 32.42, 29.80.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.08 (d, J = 11.4 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{15}BrF_3S^+$ [M + H$^+$]: 375.0024, found: 375.0022.



25

(1,1,1-trifluoro-4-phenylbutan-2-yl)(4-(trifluoromethyl)phenyl)sulfane.

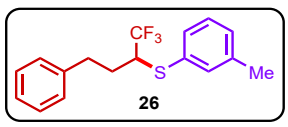
The product was isolated by column chromatography as colorless oil (87% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, J = 8.9 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.20 – 7.16 (m, 2H), 3.43 – 3.35 (m, 1H), 3.12 – 3.05 (m, 1H), 2.92 – 2.84 (m, 1H), 2.35 – 2.27 (m, 1H), 2.00 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.71, 138.62, 131.82, 129.97 (q, J = 33.1 Hz), 128.88, 128.66, 126.78, 126.62 (q, J = 279.0 Hz), 126.10 (q, J = 3.8 Hz), 123.98 (q, J = 272.0 Hz), 50.69 (q, J = 29.1 Hz), 32.27, 29.64.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.61 (s), -70.31 (d, J = 12.0 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{14}F_6NaS^+$ [M + Na$^+$]: 387.0613, found: 387.0606.



26

m-tolyl(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

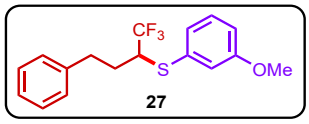
The product was isolated by column chromatography as colorless oil (68% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 4H), 7.25 – 7.22 (m, 1H), 7.22 – 7.18 (m, 3H), 7.12 (d, J = 7.6 Hz, 1H), 3.34 – 3.26 (m, 1H), 3.15 – 3.07 (m, 1H), 2.92 – 2.84 (m, 1H), 2.33 (s, 3H), 2.29 – 2.21 (m, 1H), 1.96 – 1.88 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.25, 139.14, 133.87, 132.94, 130.29, 129.23, 129.08, 128.75, 128.71, 126.88 (q, J = 279.1 Hz), 126.56, 51.60 (q, J = 28.4 Hz), 32.41, 29.87, 21.37.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.17 (d, J = 10.1 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{17}F_3NaS^+$ [M + Na^+]: 333.0895, found: 333.0882.



27

(3-methoxyphenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

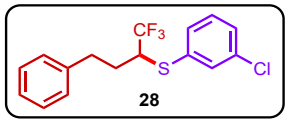
The product was isolated by column chromatography as colorless oil (71% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.00 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 3.37 – 3.28 (m, 1H), 3.13 – 3.06 (m, 1H), 2.91 – 2.83 (m, 1H), 2.30 – 2.21 (m, 1H), 1.97 – 1.88 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.88, 140.14, 134.36, 130.03, 128.75, 128.64, 126.78 (q, *J* = 279.0 Hz), 126.54, 125.22, 118.20, 114.27, 55.44, 51.46 (q, *J* = 28.6 Hz), 32.36, 29.82.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.18 (d, *J* = 11.7 Hz).

HRMS (ESI): m/z calcd. for $C_{17}H_{18}F_3OS^+$ [M + H^+]: 327.1025, found: 327.1010.



28

(3-chlorophenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

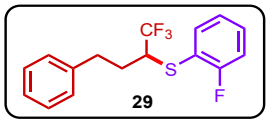
The product was isolated by column chromatography as colorless oil (70% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 7.35 – 7.30 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 3.35 – 3.27 (m, 1H), 3.13 – 3.06 (m, 1H), 2.91 – 2.83 (m, 1H), 2.32 – 2.24 (m, 1H), 1.97 – 1.88 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.87, 135.23, 134.84, 132.61, 131.00, 130.30, 128.86, 128.66, 128.56, 126.72, 126.68 (q, *J* = 279.1 Hz), 51.47 (q, *J* = 28.7 Hz), 32.34, 29.68.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.21 (d, *J* = 10.0 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{14}ClF_3NaS^+$ [M + Na^+]: 353.0349, found: 353.0329.



29

(2-fluorophenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

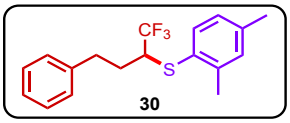
The product was isolated by column chromatography as colorless oil (85% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.26 – 7.20 (m, 3H), 7.14 – 7.08 (m, 2H), 3.49 – 3.37 (m, 1H), 3.19 – 3.11 (m, 1H), 2.94 – 2.85 (m, 1H), 2.29 – 2.21 (m, 1H), 1.96 – 1.87 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.74 (d, *J* = 247.3 Hz), 140.36, 136.35, 131.14 (d, *J* = 8.1 Hz), 128.73, 128.64, 126.71 (q, *J* = 279.3 Hz), 126.52, 124.81 (d, *J* = 3.8 Hz), 119.89 (d, *J* = 17.7 Hz), 116.22 (d, *J* = 23.0 Hz), 50.51 (q, *J* = 29.5, 28.8 Hz), 32.53, 30.11.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.38 (d, *J* = 9.1 Hz), -106.53 (s).

HRMS (ESI): m/z calcd. for $C_{16}H_{15}F_4S^+$ [M + Na^+]: 315.0825, found: 315.0804.



(2,4-dimethylphenyl)(1,1,1-trifluoro-4-phenylbutan-2-yl)sulfane.

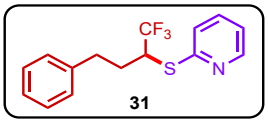
The product was isolated by column chromatography as colorless oil (60% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.04 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.31 – 3.23 (m, 1H), 3.13 – 3.06 (m, 1H), 2.91 – 2.83 (m, 1H), 2.44 (s, 3H), 2.30 (s, 3H), 2.29 – 2.21 (m, 1H), 2.01 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.94, 140.35, 138.67, 134.31, 131.51, 129.11, 128.71, 128.60, 127.59, 126.92 (q, *J* = 279.3 Hz), 126.49, 51.37 (q, *J* = 28.2 Hz), 32.64, 30.26, 21.13, 20.86.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -70.12 (d, *J* = 11.7 Hz).

HRMS (ESI): m/z calcd. for $C_{18}H_{19}F_3NaS^+$ [M + Na^+]: 347.1052, found: 347.1060.



2-((1,1,1-trifluoro-4-phenylbutan-2-yl)thio)pyridine.

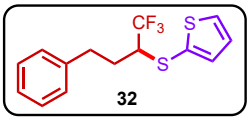
The product was isolated by column chromatography as colorless oil (60% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 4.9 Hz, 1H), 7.53 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.19 – 7.16 (m, 2H), 7.05 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 4.96 – 4.84 (m, 1H), 3.04 – 2.94 (m, 1H), 2.85 – 2.75 (m, 1H), 2.41 – 2.28 (m, 1H), 2.09 – 1.97 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.73, 149.45, 140.78, 136.57, 128.68, 128.60, 126.83 (q, *J* = 278.5 Hz), 126.36, 122.65, 120.55, 44.87 (q, *J* = 29.2 Hz), 32.55, 30.40.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -70.45 (d, *J* = 8.8 Hz).

HRMS (ESI): m/z calcd. for $C_{15}H_{15}F_3NS^+$ [M + H^+]: 298.0880, found: 298.0880.



2-((1,1,1-trifluoro-4-phenylbutan-2-yl)thio)thiophene.

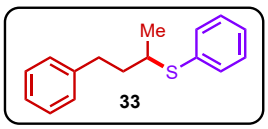
The product was isolated by column chromatography as colorless oil (66% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 5.4 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.22 (m, 3H), 7.00 – 6.97 (m, 1H), 3.12 – 3.06 (m, 2H), 2.90 – 2.82 (m, 1H), 2.20 – 2.11 (m, 1H), 1.91 – 1.82 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.12, 137.40, 131.61, 129.58, 128.78, 128.68, 127.90, 126.58, 126.53 (q, *J* = 279.2 Hz), 53.16 (q, *J* = 28.1 Hz), 32.37, 29.08.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -69.74 (d, *J* = 9.9 Hz).

HRMS (ESI): m/z calcd. for $C_{14}H_{14}F_3S_2^+$ [M + H^+]: 303.0484, found: 303.0486.



phenyl(4-phenylbutan-2-yl)sulfane.

The product was isolated by column chromatography as colorless oil (66% yield).

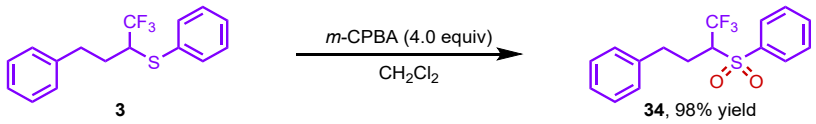
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.17 (m, 4H), 3.27 – 3.17 (m, 1H), 2.88 – 2.75 (m, 2H), 2.00 – 1.89 (m, 1H), 1.89 – 1.78 (m, 1H), 1.33 (d, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.79, 135.17, 132.13, 128.93, 128.59, 128.52, 126.86, 126.03, 42.63, 38.30, 33.28, 21.32.

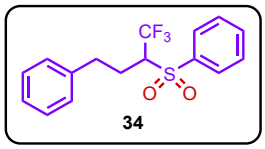
HRMS (EI): m/z calcd. for $C_{16}H_{18}S$ [M]: 242.1129, found: 242.1124.

General procedure for further transformations

Synthesis of (4,4,4-trifluoro-3-(phenylsulfonyl)butyl)benzene (34):



In a round-bottomed flask (5.0 mL) equipped with a stir bar, a solution of **3** (59.3 mg, 0.20 mmol, 1.0 equiv) in CH_2Cl_2 (2.0 mL) was prepared. The solution was cooled to 0 °C. And then a solution of *m*-CPBA (purity: 85%, 191.0 mg, 2.0 mmol, 4.0 equiv) in CH_2Cl_2 (3.0 mL) was added dropwise and the mixture was stirred at 25 °C. After disappearance of the sulfide, the reaction mixture was quenched by adding H_2O (10.0 mL), extracted with EtOAc (3 × 5.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel (10→20% ethyl acetate/Petroleum ether).



(4,4,4-trifluoro-3-(phenylsulfonyl)butyl)benzene.

The product was isolated by column chromatography as white solid (98% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.85 (m, 2H), 7.75 – 7.67 (m, 1H), 7.63 – 7.51 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.13 (m, 2H), 3.68 – 3.57 (m, 1H), 3.04 – 2.95 (m, 1H), 2.93 – 2.84 (m, 1H), 2.61 – 2.52 (m, 1H), 2.32 – 2.22 (m, 1H).

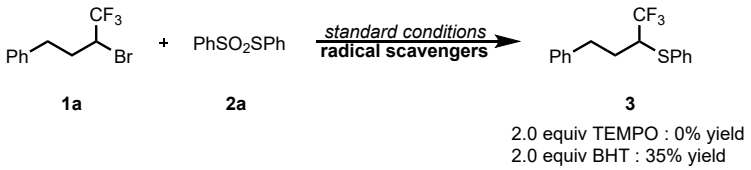
^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.19, 138.13, 134.67, 129.44, 129.17, 128.92, 128.69, 126.86, 123.40 (q, J = 281.3 Hz), 65.87 (q, J = 27.2 Hz), 33.13, 25.87.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.99 (d, J = 7.9 Hz).

HRMS (ESI): m/z calcd. for $C_{16}H_{16}F_3O_2S^+$ [M + H$^+$]: 329.0818, found: 329.0811.

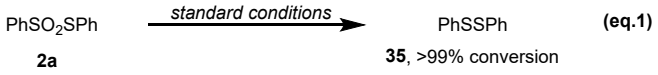
General procedure for mechanium studies

Radical trapping experiments:

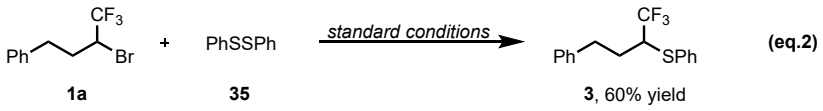


An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with *S*-phenyl benzenesulfonothioate **2a** (25 mg, 0.10 mmol, 1.0 equiv), Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2·6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv) and TEMPO (32 mg, 0.20 mmol, 2.0 equiv) or BHT (44 mg, 0.20 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then alkyl bromide **1a** (40 mg, 0.15 mmol, 1.5 equiv) and dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL). And the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired product **3**.

Control experiments:



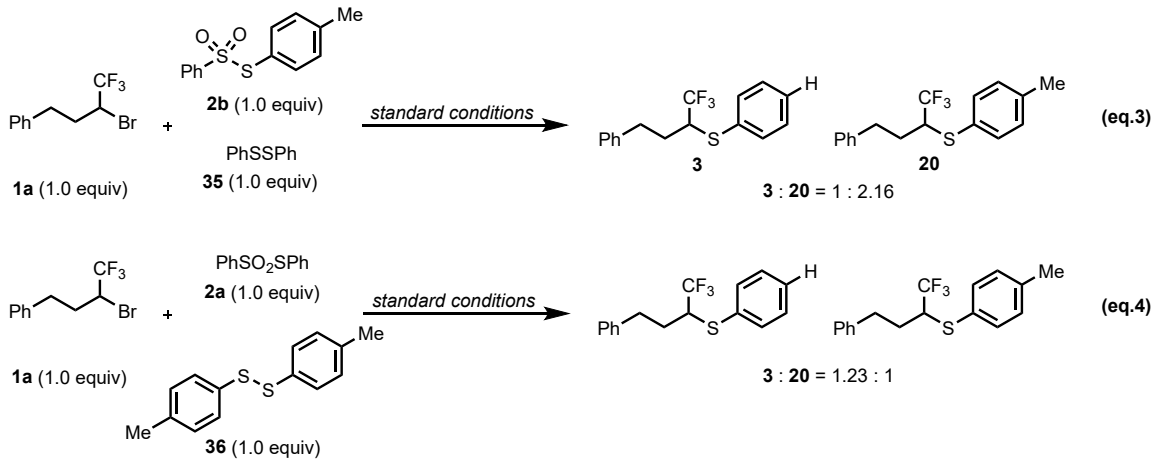
Eq.1: An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with *S*-phenyl benzenesulfonothioate **2a** (25 mg, 0.10 mmol, 1.0 equiv), Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2·6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired product **35**.



Eq.2: An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with diphenyl disulfide **35** (21.8 mg, 0.10 mmol, 1.0 equiv), Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2·6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then alkyl bromide **1a** (40 mg, 0.15 mmol, 1.5 equiv) and dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired

product **3**.

Competitive experiments:



Eq.3: An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with *S*-(p-tolyl) benzenesulfonothioate **2b** (26.4 mg, 0.10 mmol, 1.0 equiv), diphenyl disulfide **35** (21.8 mg, 0.10 mmol, 1.0 equiv), Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2 \cdot 6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then alkyl bromide **1a** (26.7 mg, 0.10 mmol, 1.0 equiv) and dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired products **3** and **20**.

Eq.4: An oven-dried 10 mL glass schlenck, equipped with a stirring bar, was charged with *S*-phenyl benzenesulfonothioate **2a** (25 mg, 0.10 mmol, 1.0 equiv), 1,2-di-p-tolyldisulfane **36** (24.6 mg, 0.10 mmol, 1.0 equiv) Mn (11 mg, 0.20 mmol, 2.0 equiv), $Ni(ClO_4)_2 \cdot 6H_2O$ (3.7 mg, 0.01 mmol, 10 mol%), 4,7-diphenyl-1,10-phenanthroline (3.3 mg, 0.01 mmol, 10 mol%), TBAI (36.9 mg, 0.10 mmol, 1.0 equiv). The mixture was evacuated and backfilled with Argon for three times. Then alkyl bromide **1a** (26.7 mg, 0.10 mmol, 1.0 equiv) and dry DMF (1.0 mL) was added under Argon and the mixture was allowed to stir for 12 h at 50 °C. After cooling to room temperature, the reaction mixture was then diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (3×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired products **3** and **20**.

References

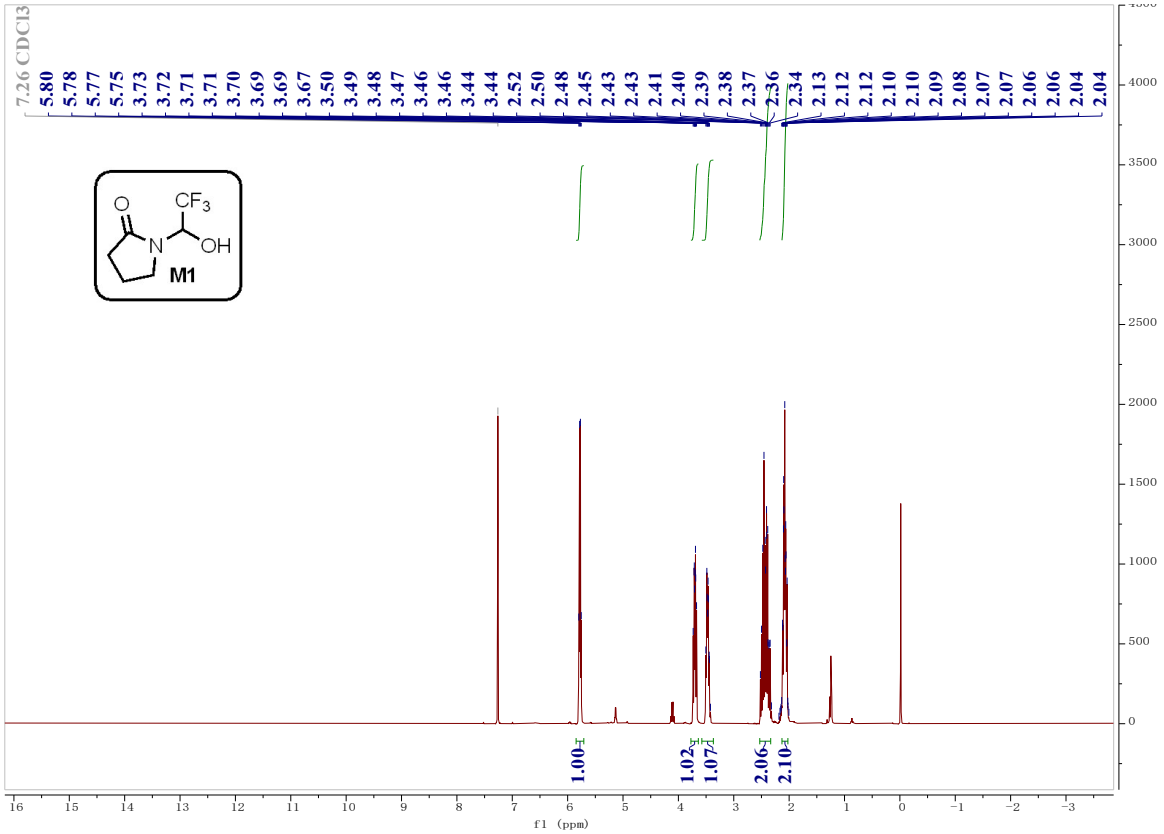
[1] Wu, B.-B.; Xu, J.; Bian, K.-J.; Gao, Q.; Wang, X.-S. Enantioselective Synthesis of Secondary β-Trifluoromethyl Alcohols via Catalytic Asymmetric Reductive Trifluoroalkylation and Diastereoselective Reduction. *J. Am. Chem. Soc*. **2022**, *144*, 6543.

[2] Jin, R.-X.; Wu, B.-B.; Bian, K.-J.; Yu, J.-L.; Dai, J.-C.; Zuo, Y.-W.; Zhang, Y.-F.; Wang, X.-S. Asymmetric construction of allylicstereogenic carbon center featuring atrifluoromethyl group via enantioselective reductive fluoroalkylation. *Nat. Commun.* **2022**, *13*, 7035.

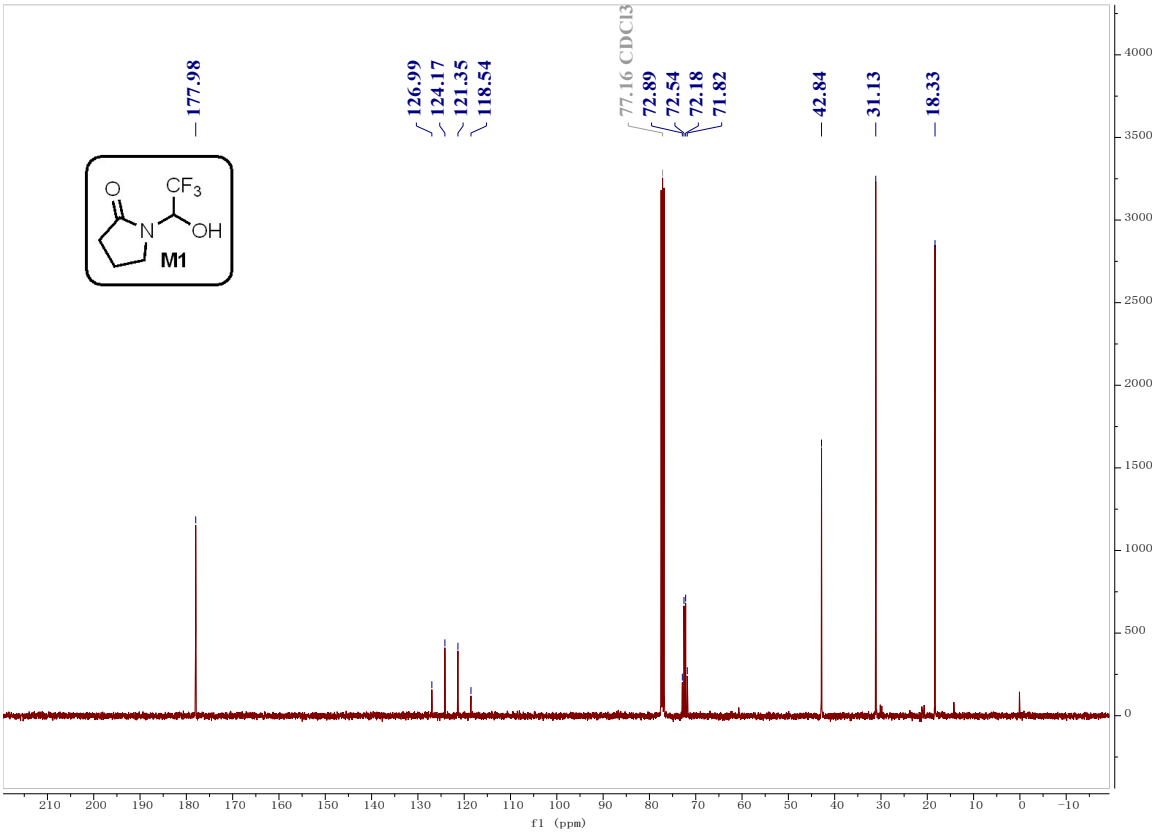
[3] Orcel, U.; Waser, J. One-Pot Three-Component Synthesis of Vicinal Diamines via In Situ Aminal Formation and Carboamination. *Angew. Chem. In. Ed.* **2016**, *55*, 12881.

[4] Chen, Q; Huang, Y.; Wang, X.; Wu, J.; Yu, G. Metal-free NaI/TBHP-mediated sulfonylation of thiols with sulfonyl hydrazides. *Org. Biomol. Chem*. **2018,** *16*, 1713.

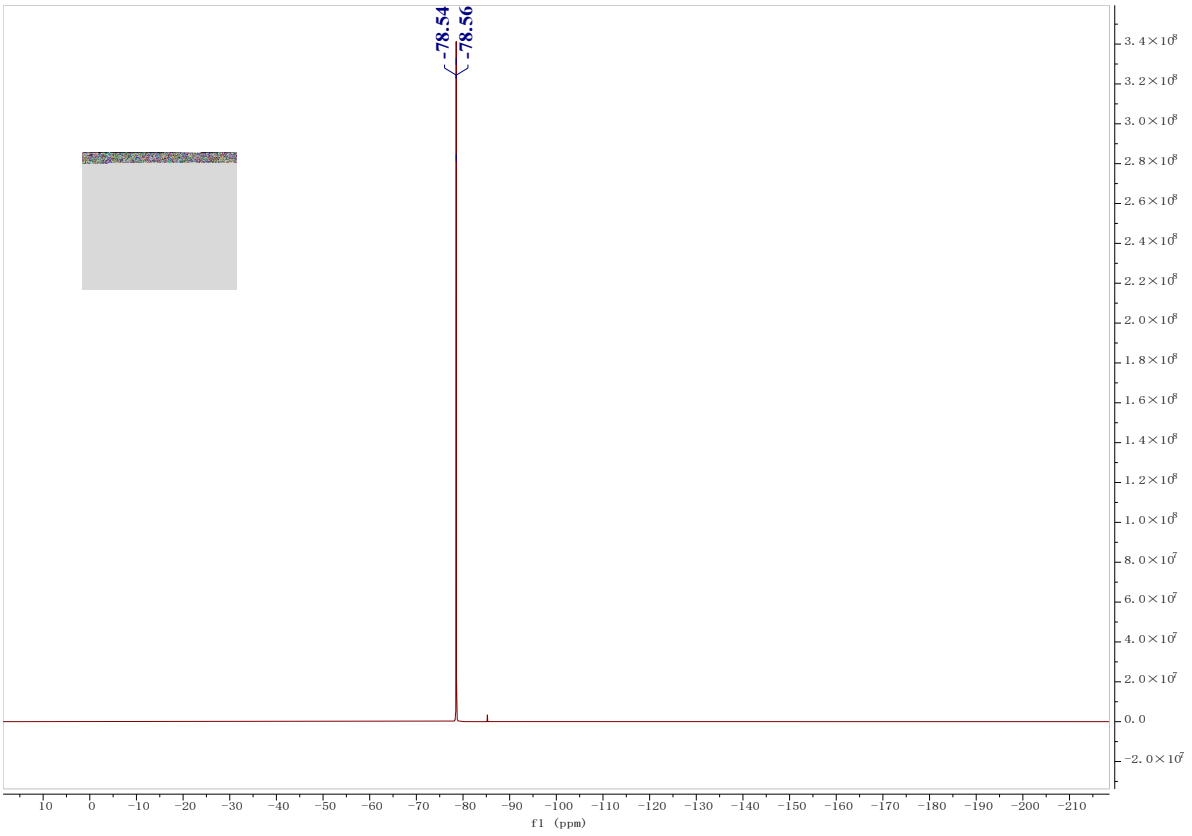
NMR Spectra of New Compounds



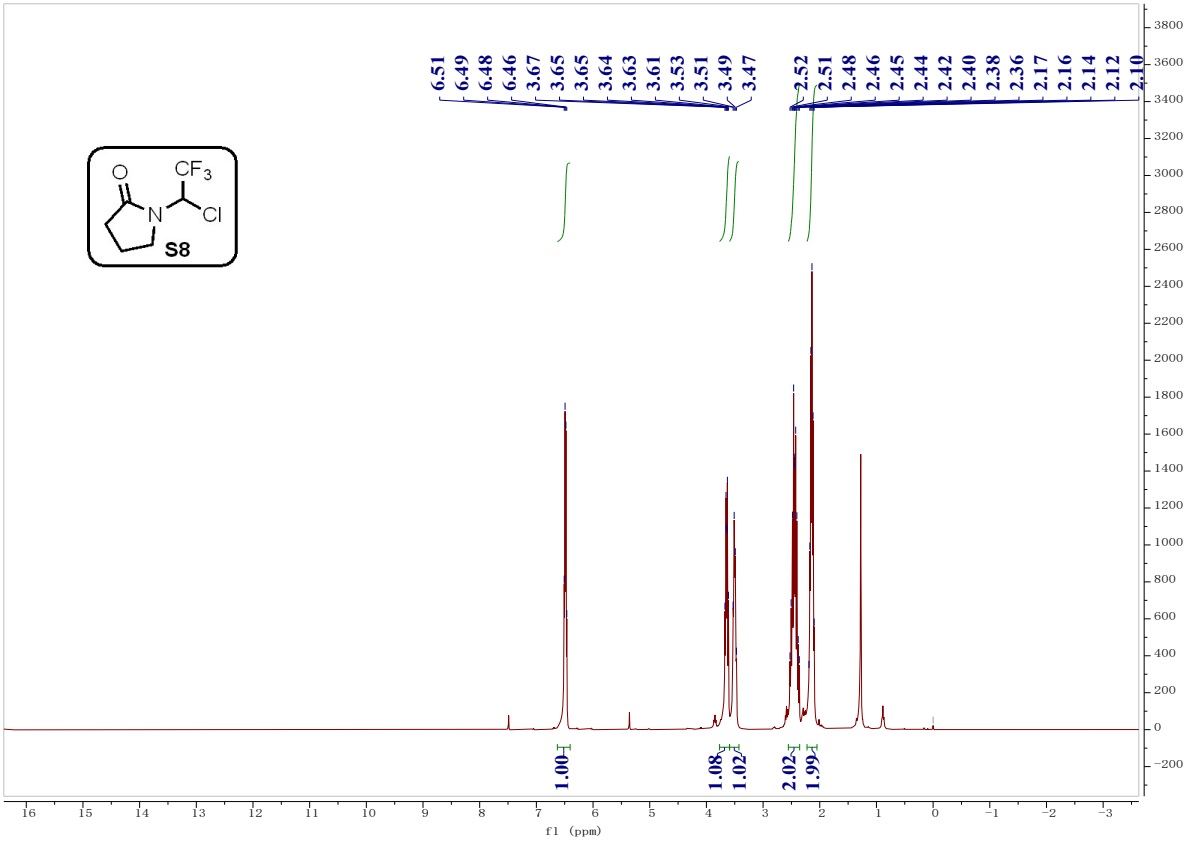
^{1}H NMR Spectrum of Compound **M1**



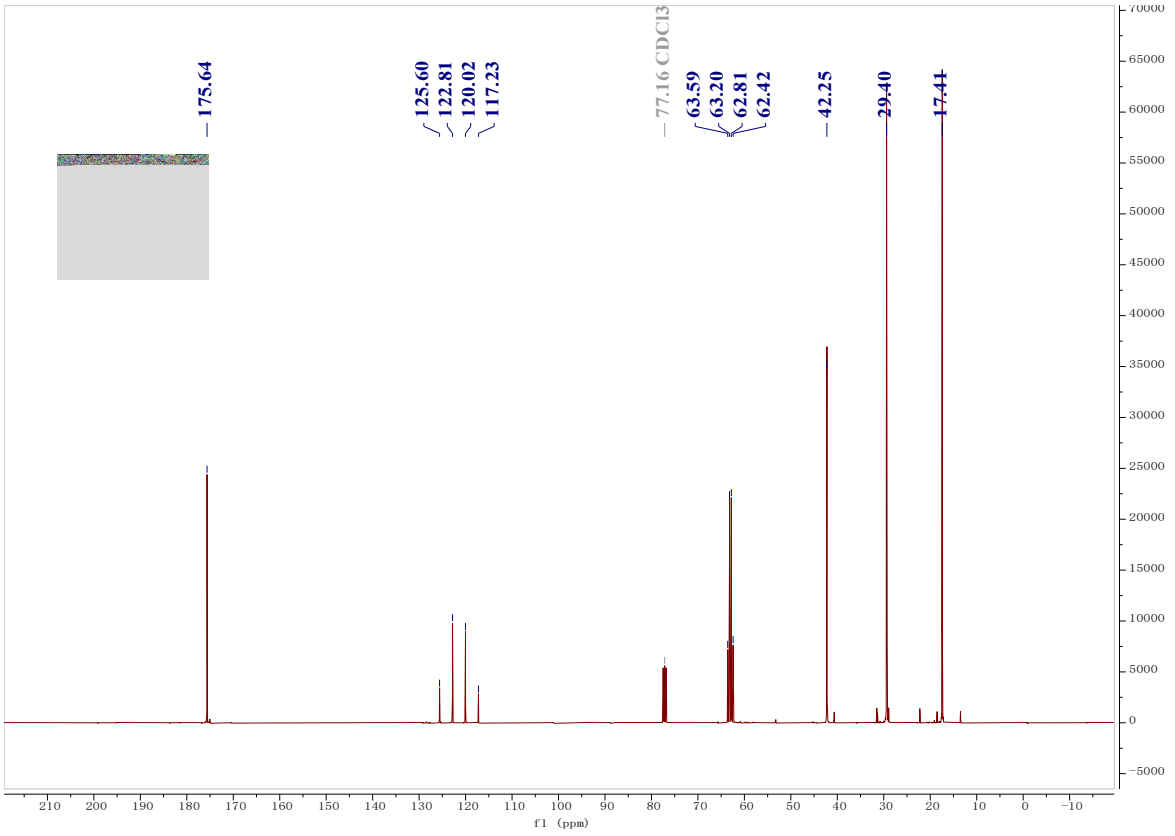
^{13}C NMR Spectrum of Compound **M1**



^{19}F NMR Spectrum of Compound **M1**



^{1}H NMR Spectrum of Compound **S8**



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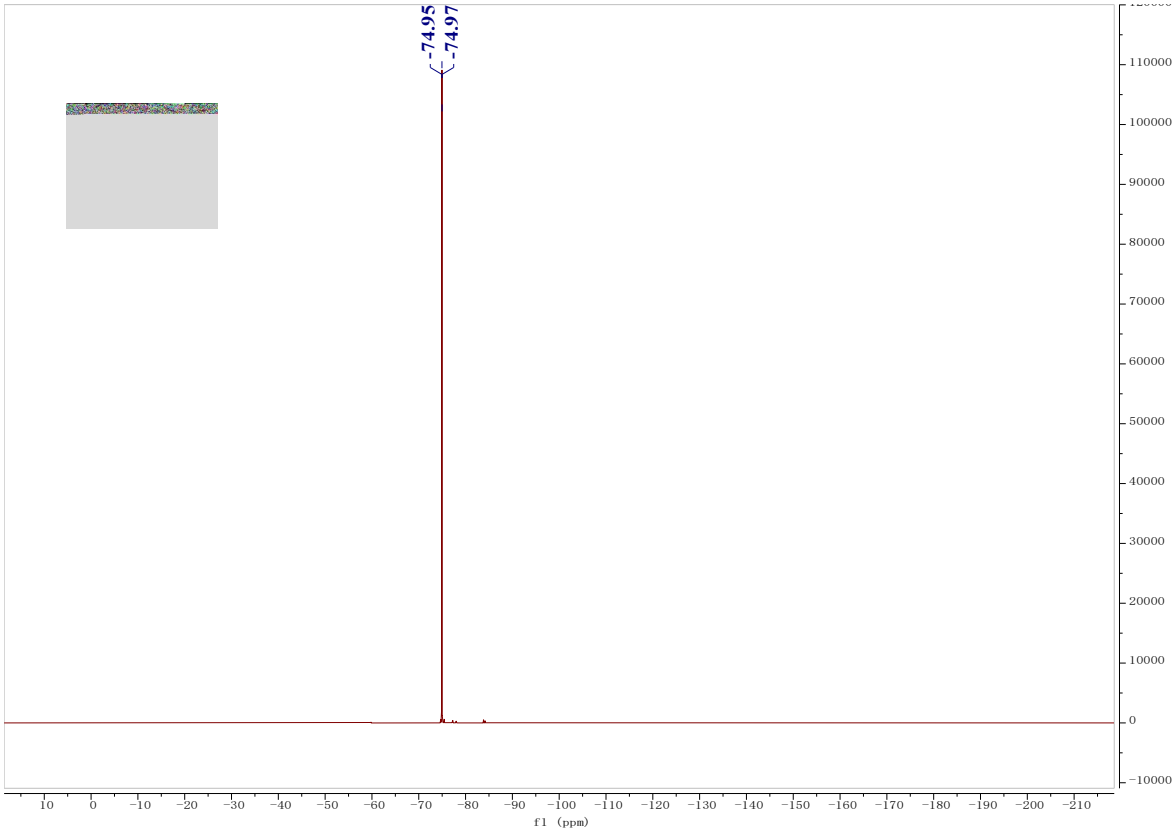

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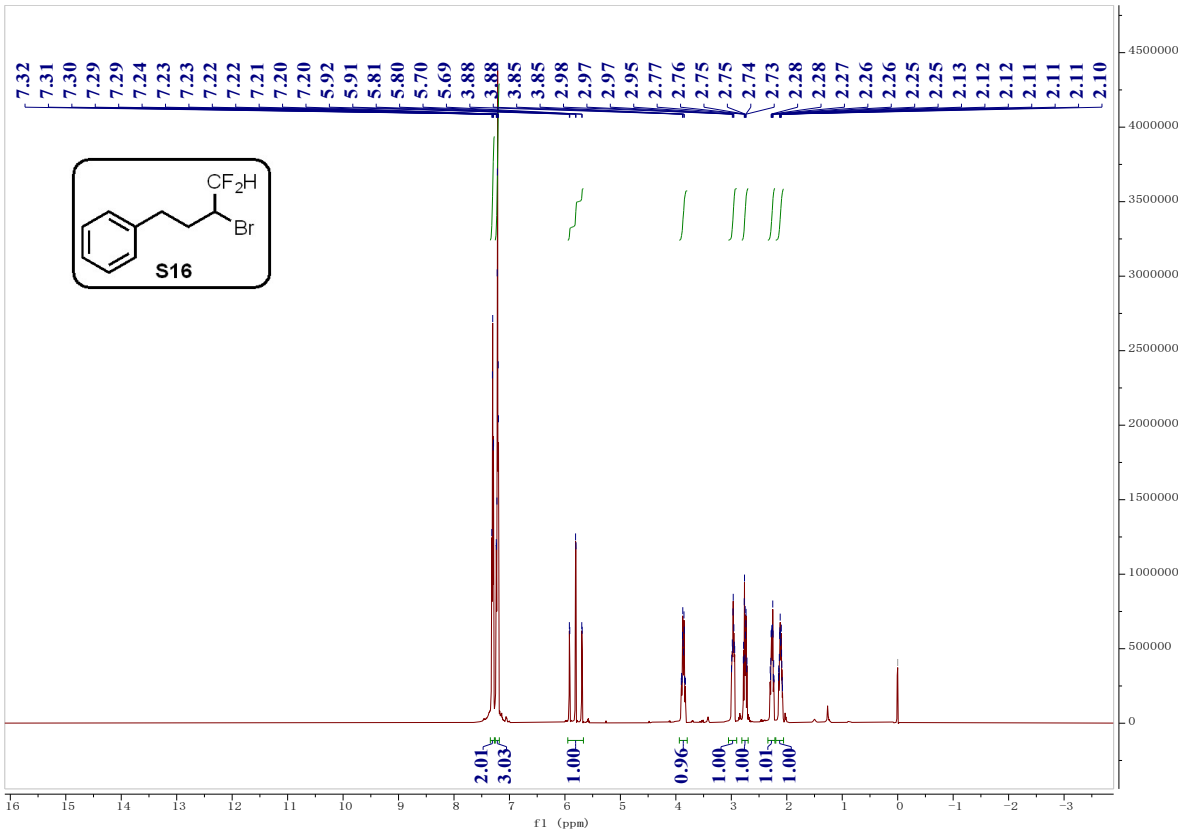
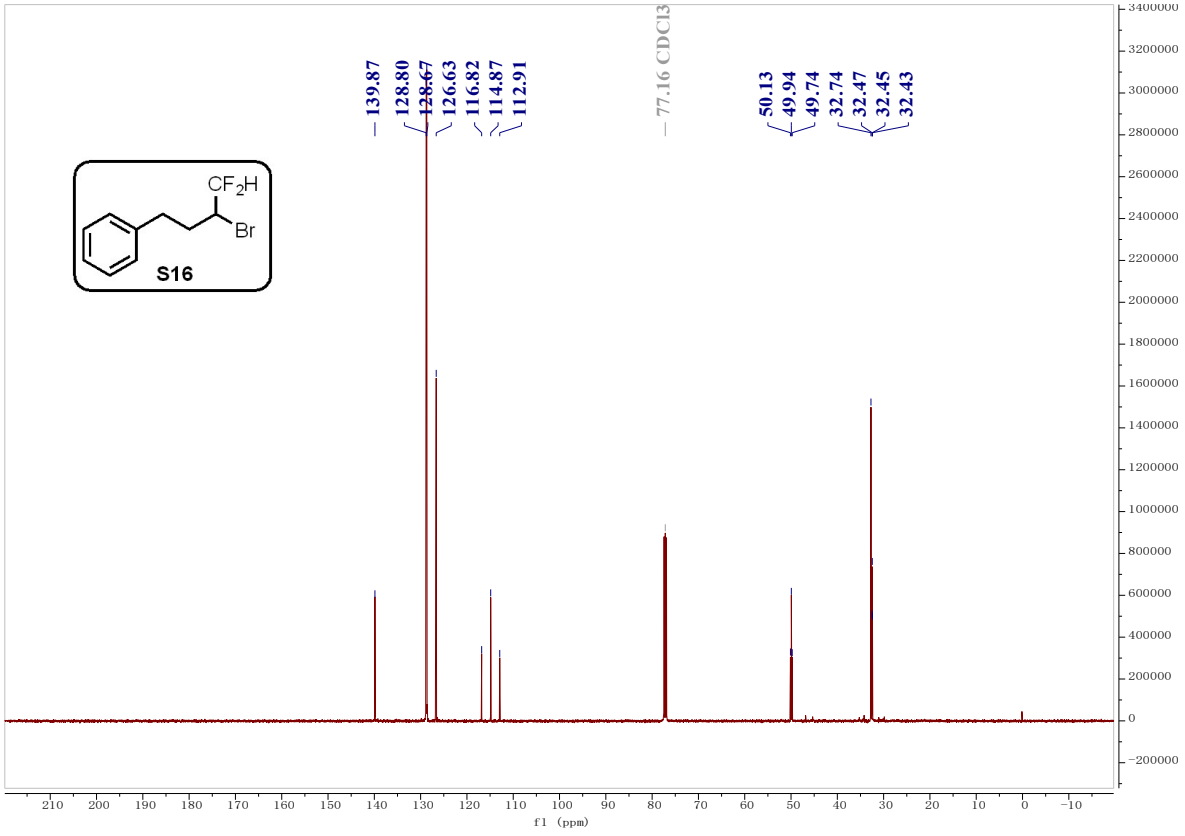
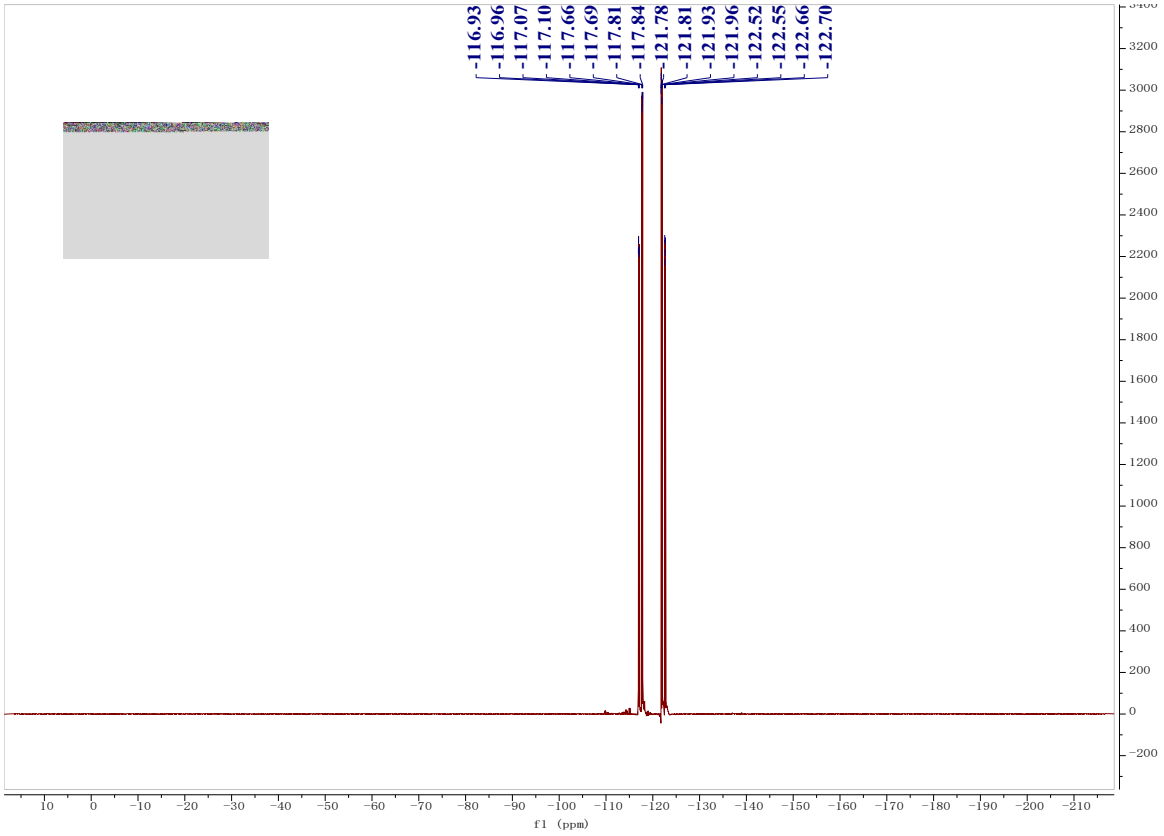


^{1}H NMR Spectrum of Compound **S16**



^{13}C NMR Spectrum of Compound **S16**



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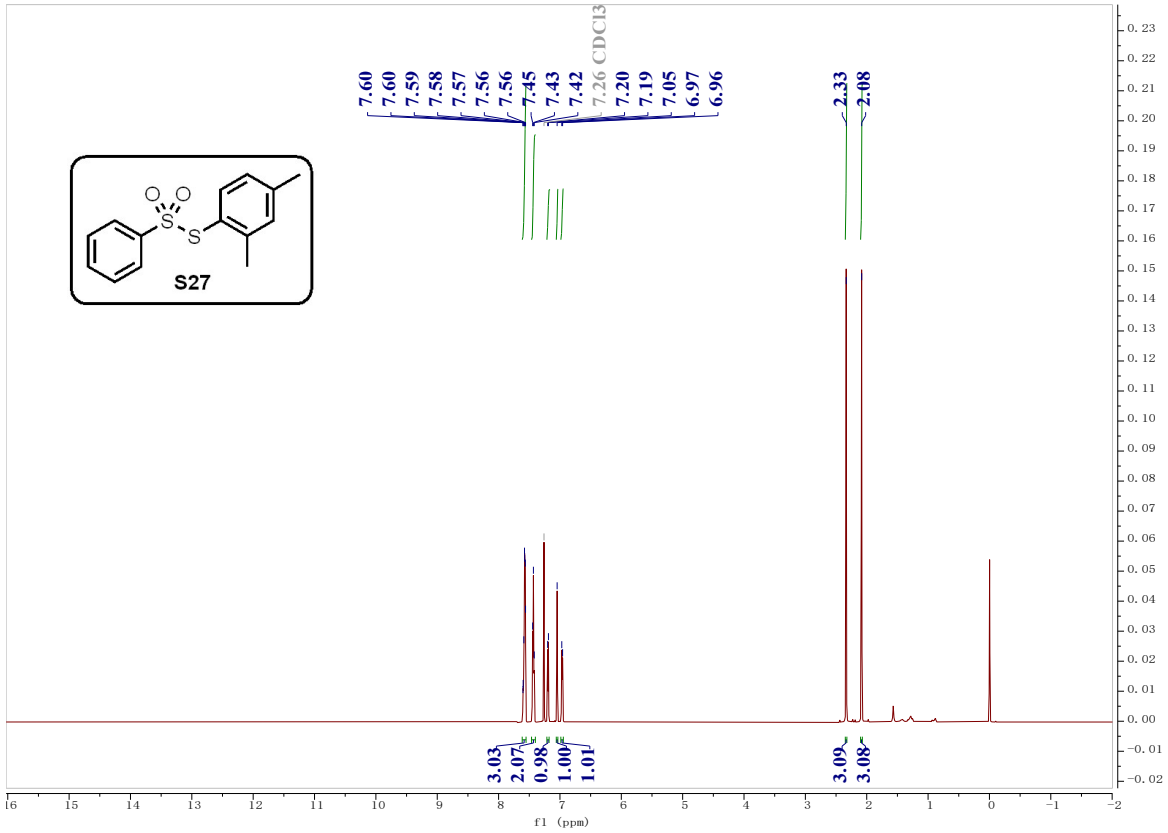

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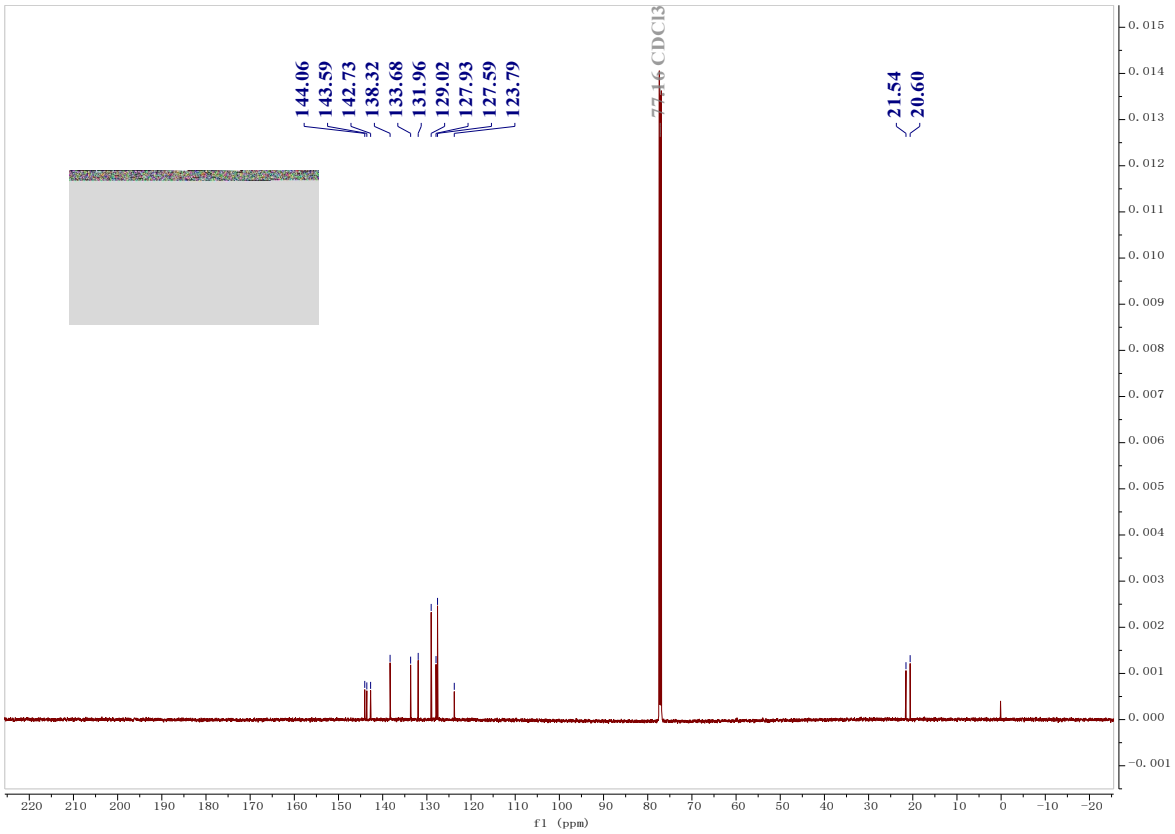
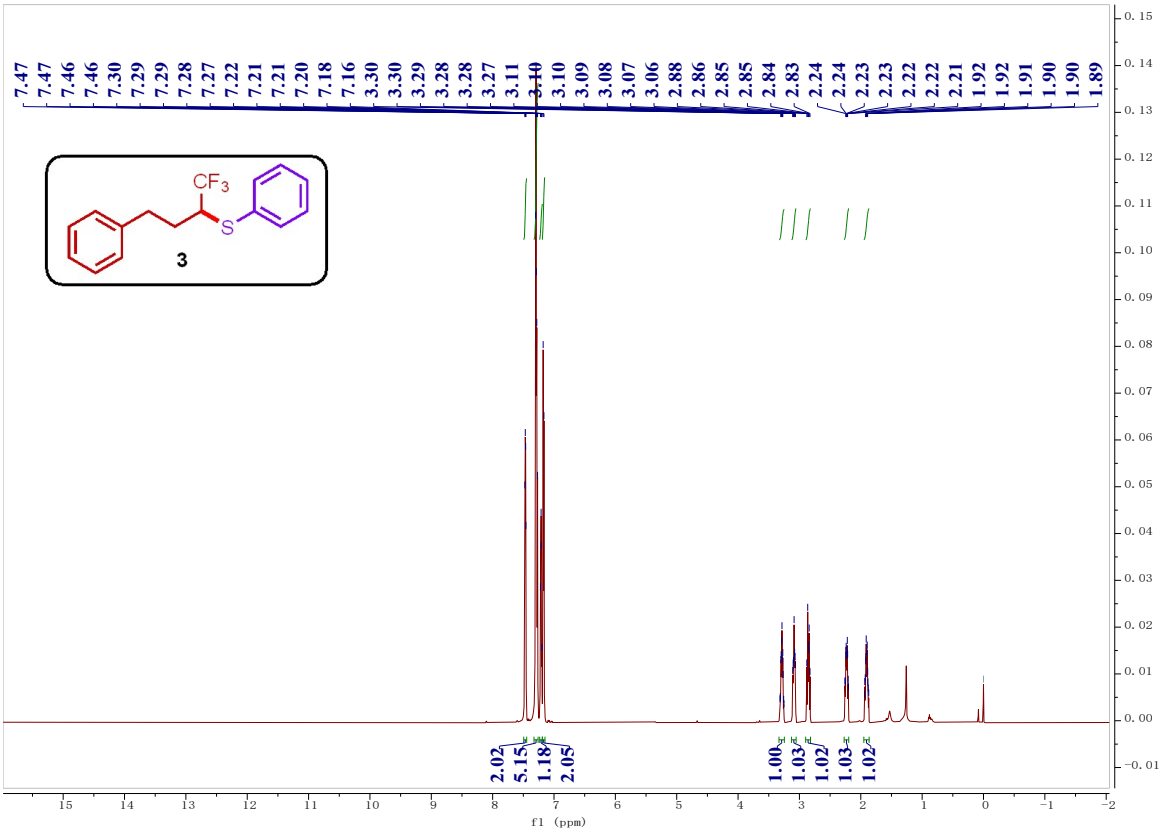
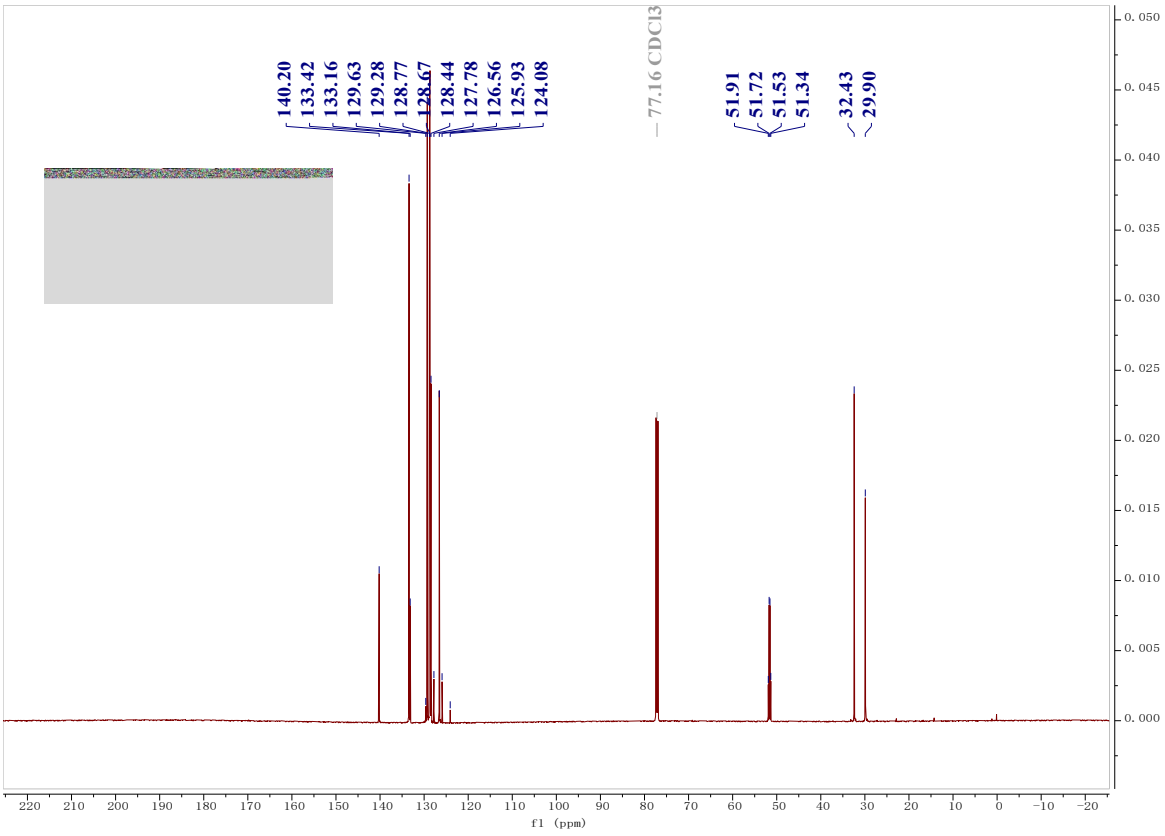


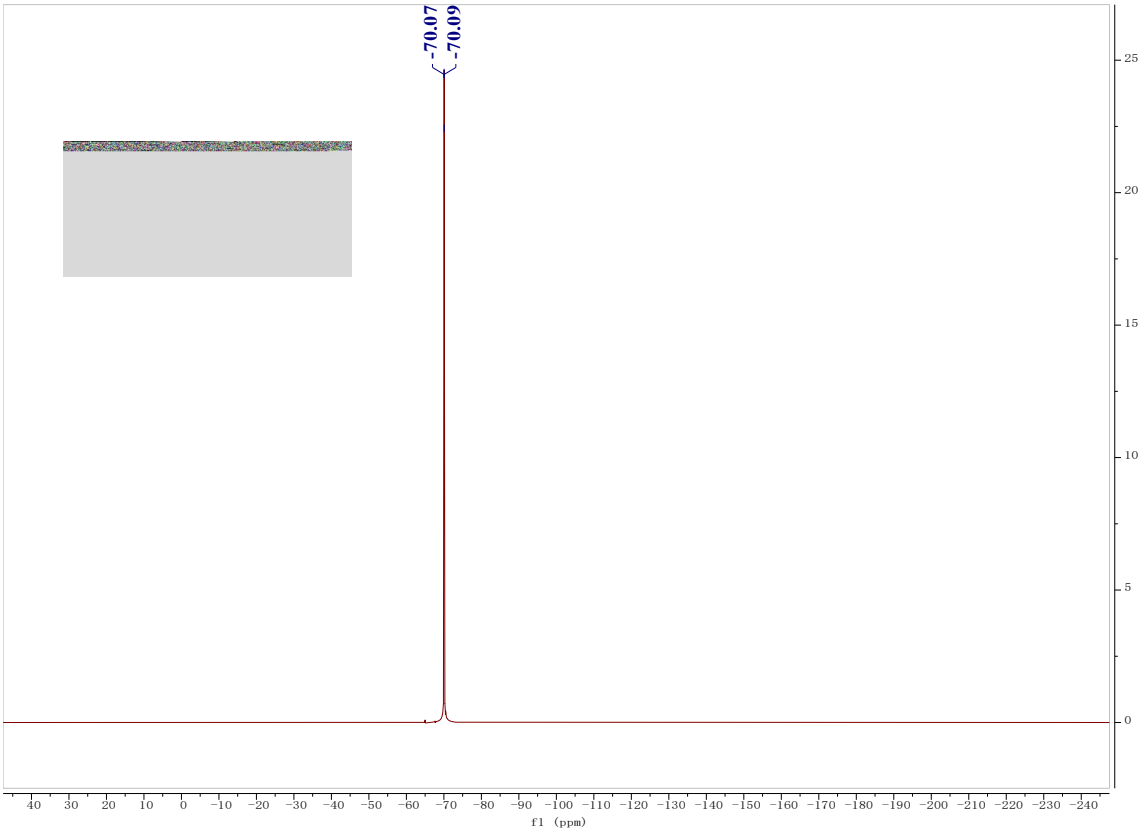
^{13}C NMR Spectrum of Compound **S27**



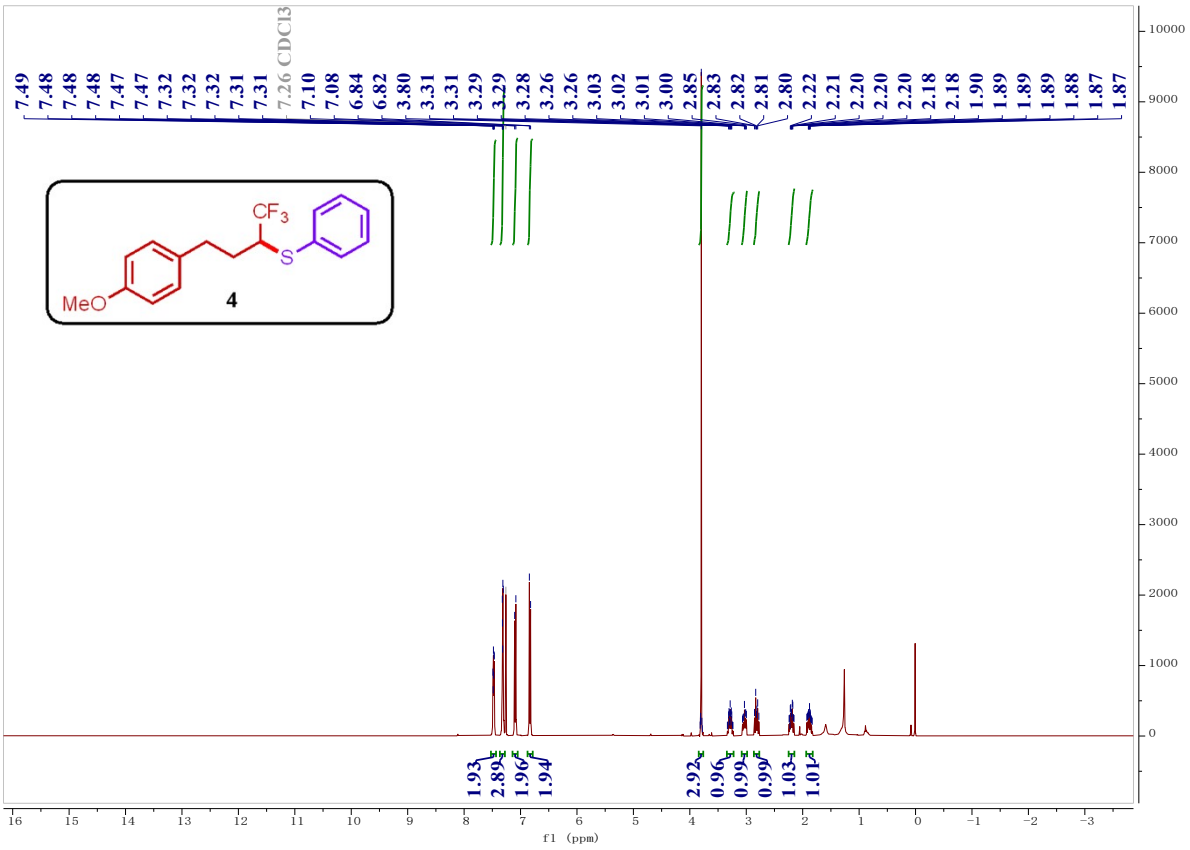
^{1}H NMR Spectrum of Compound **3**



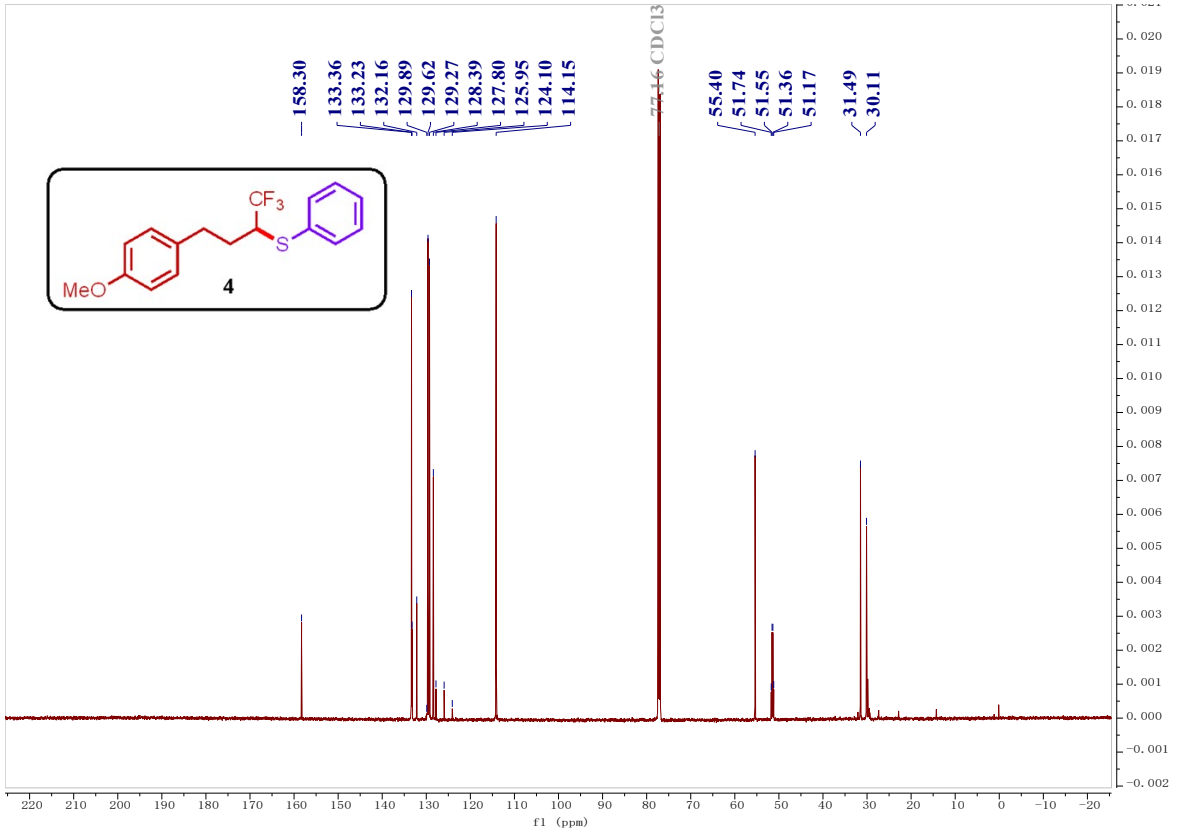
^{13}C NMR Spectrum of Compound **3**



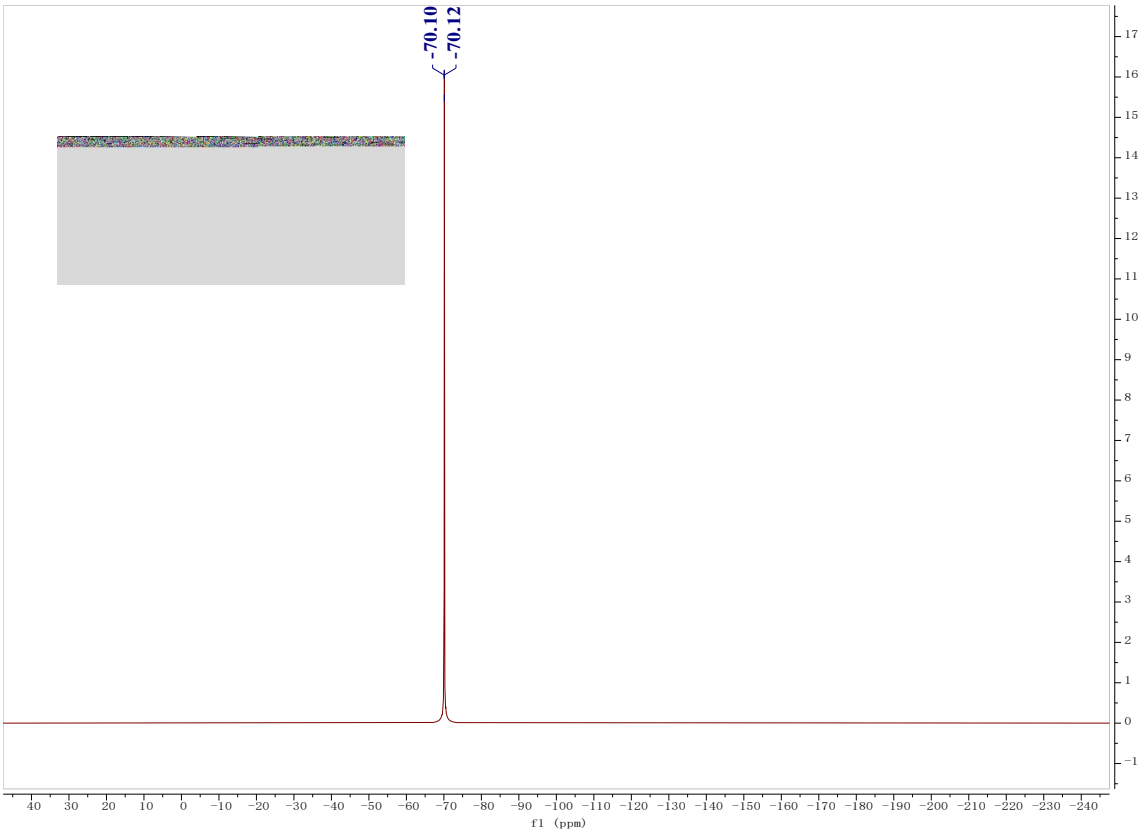
^{19}F NMR Spectrum of Compound **3**



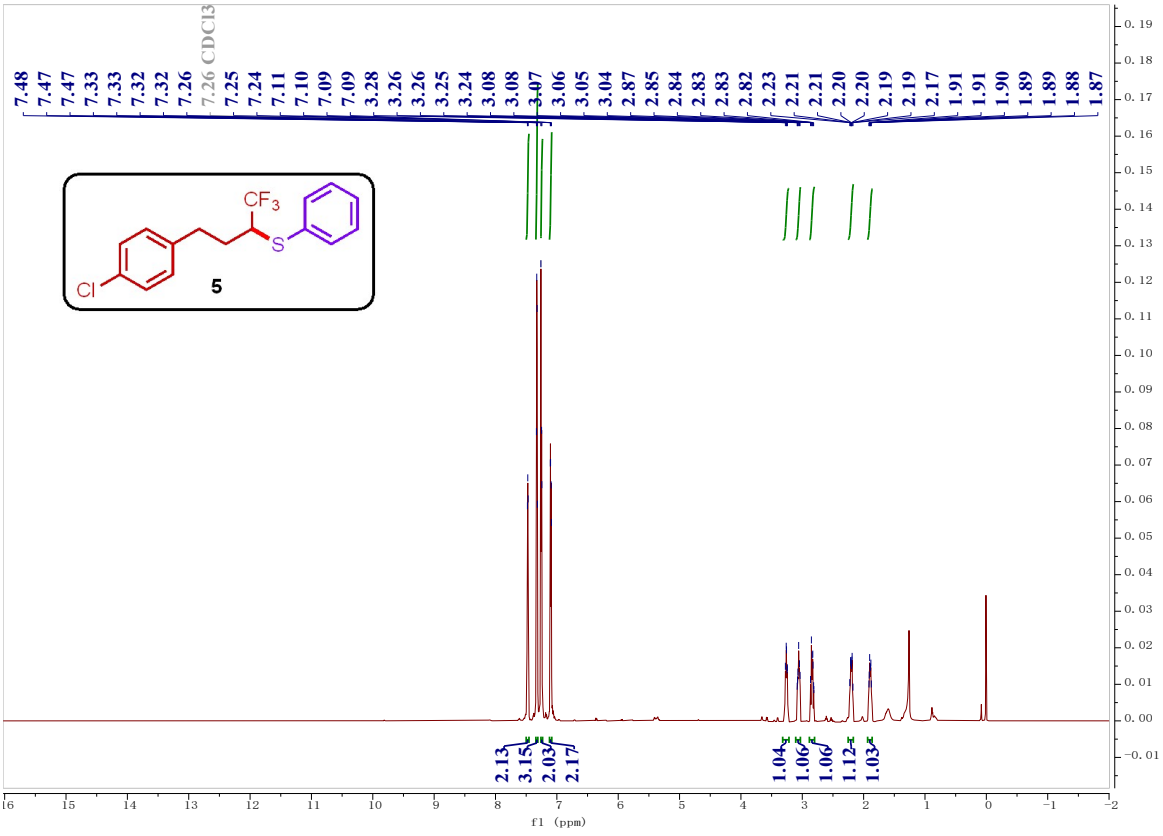
^{1}H NMR Spectrum of Compound **4**



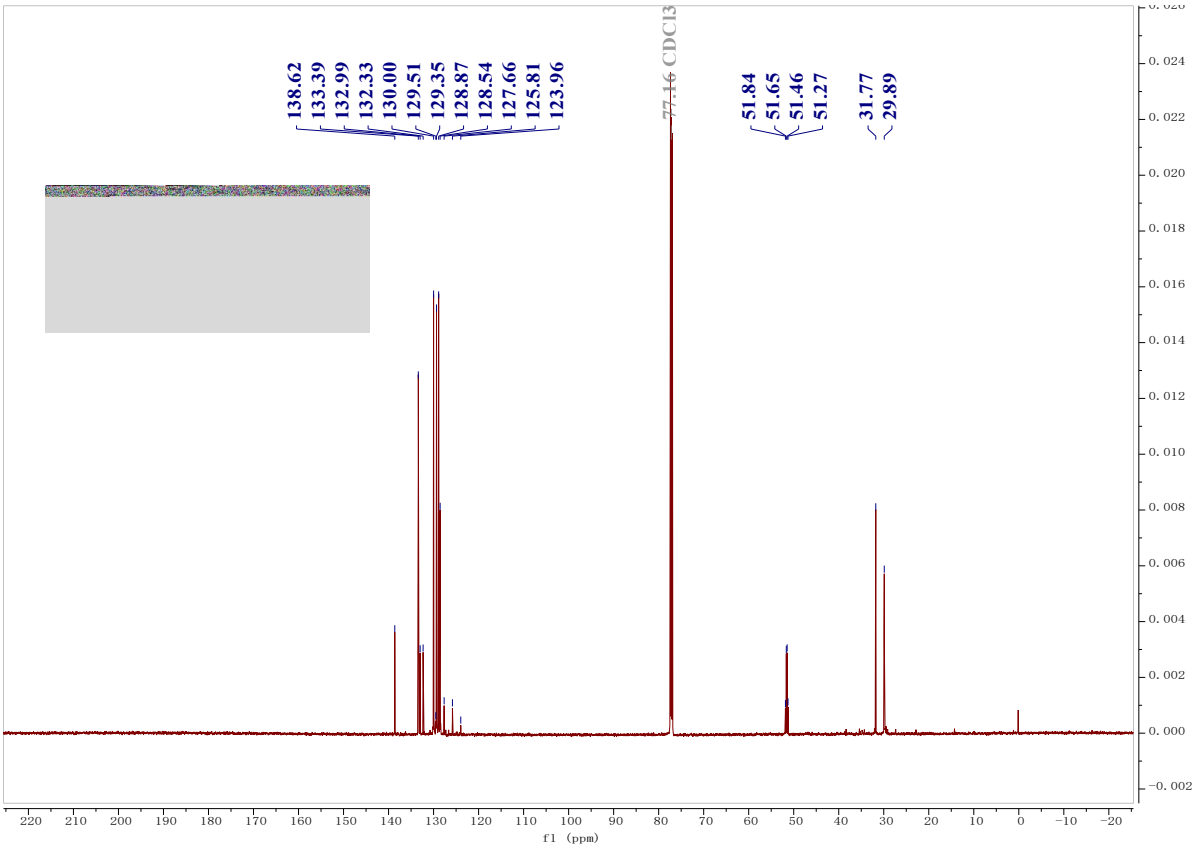
^{13}C NMR Spectrum of Compound **4**



^{19}F NMR Spectrum of Compound **4**



^{1}H NMR Spectrum of Compound **5**



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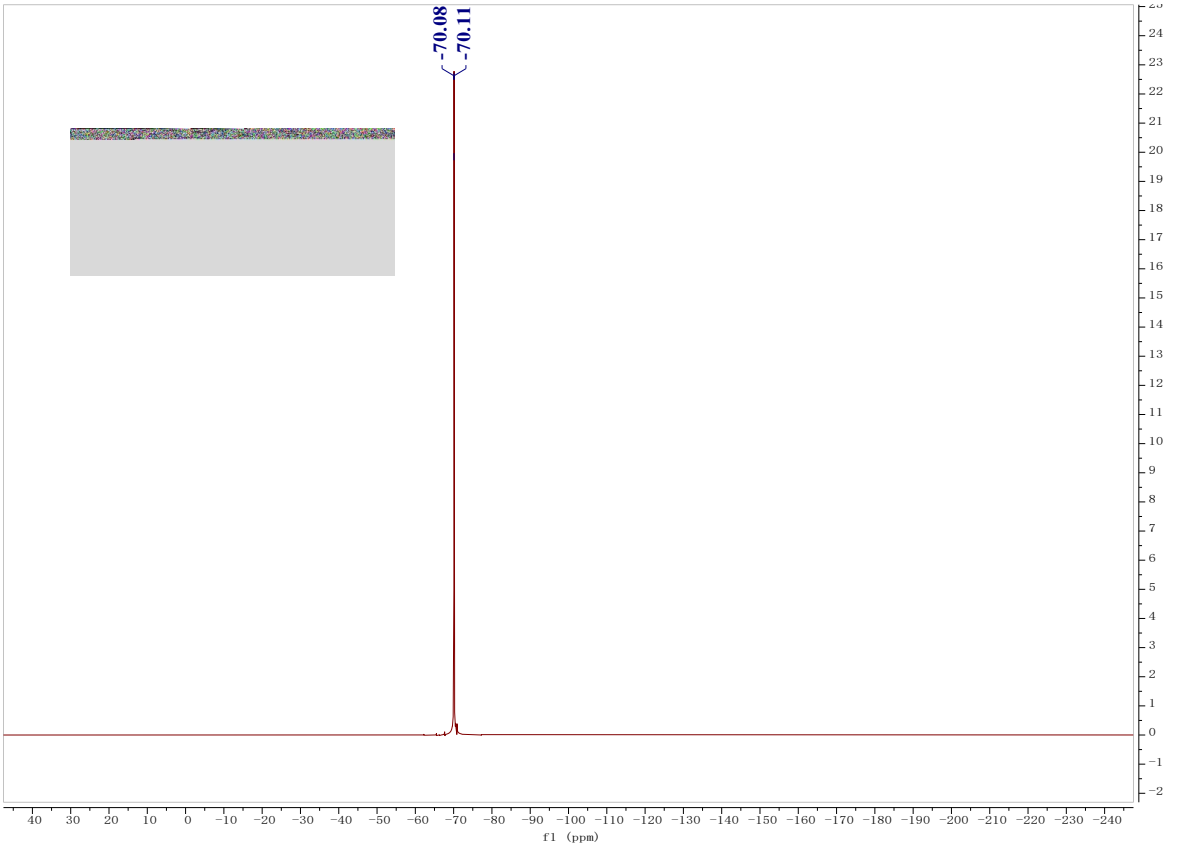

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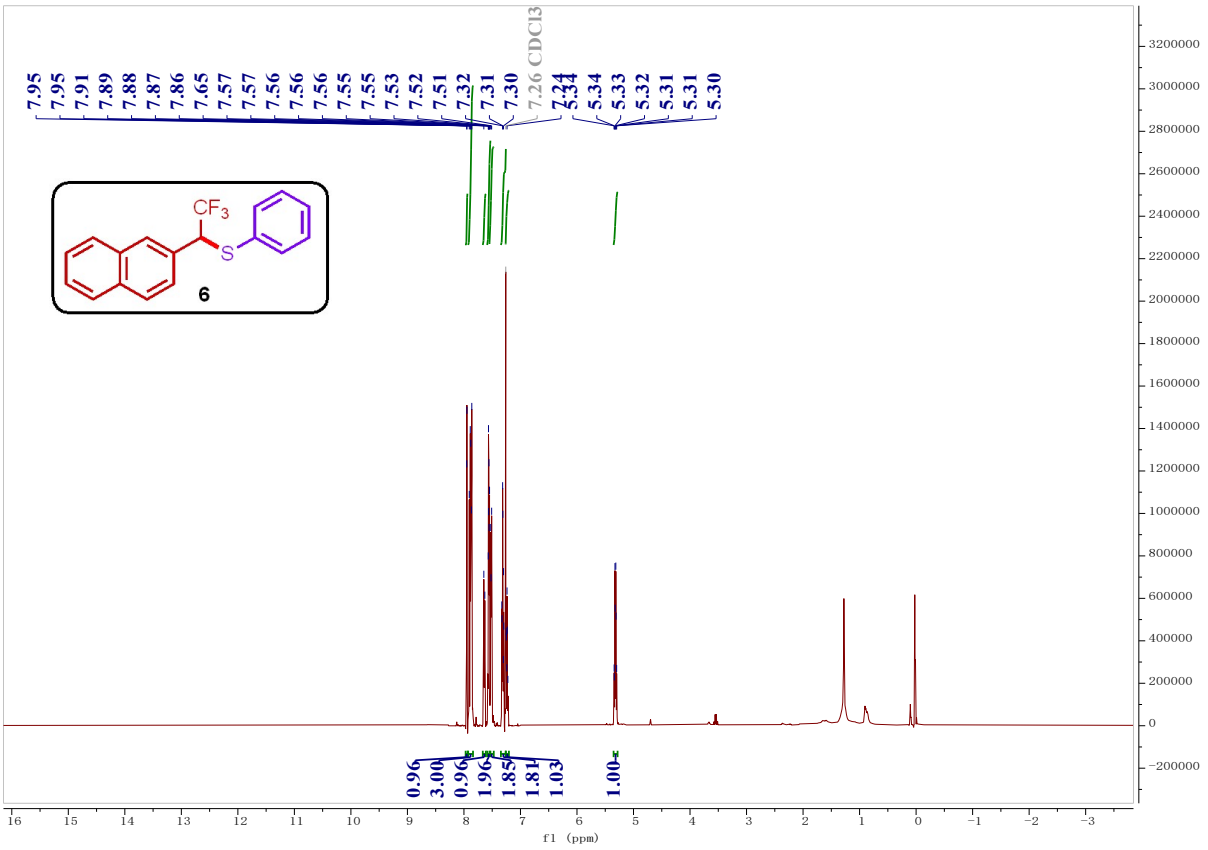
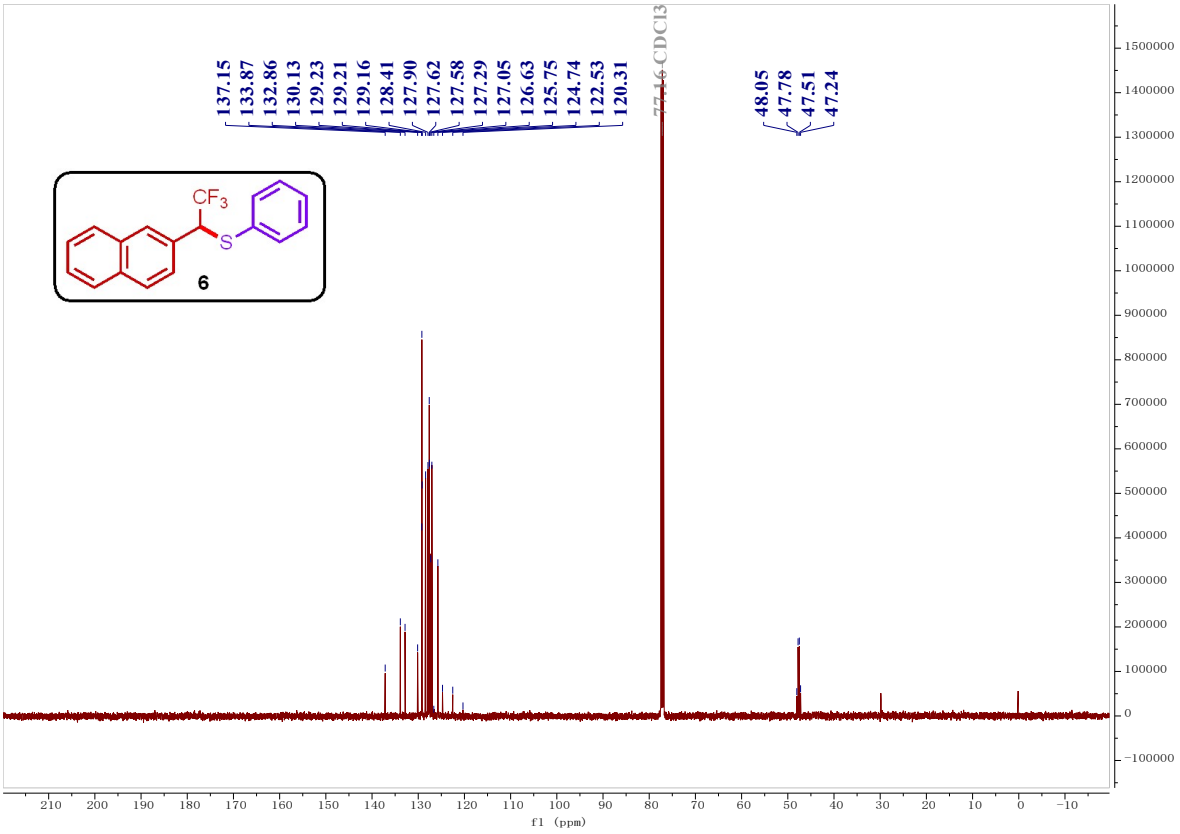
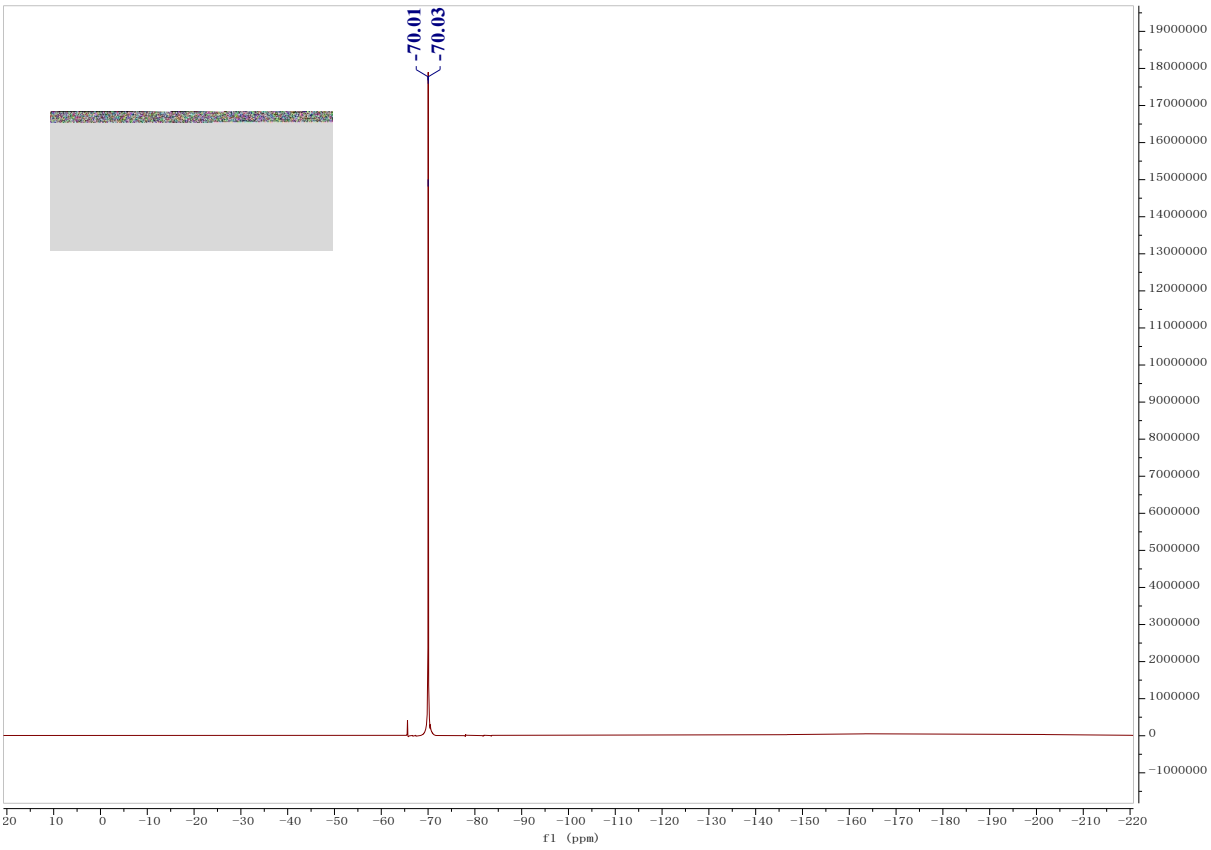


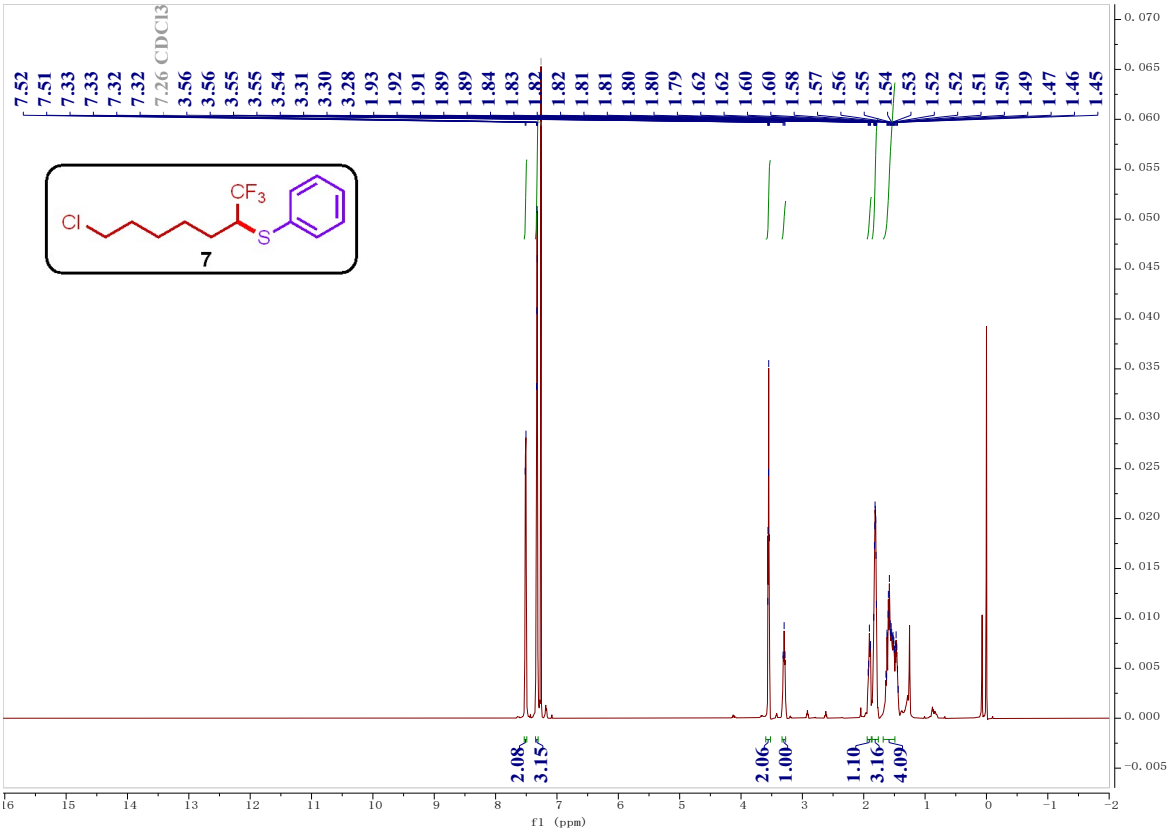
^{1}H NMR Spectrum of Compound **6**



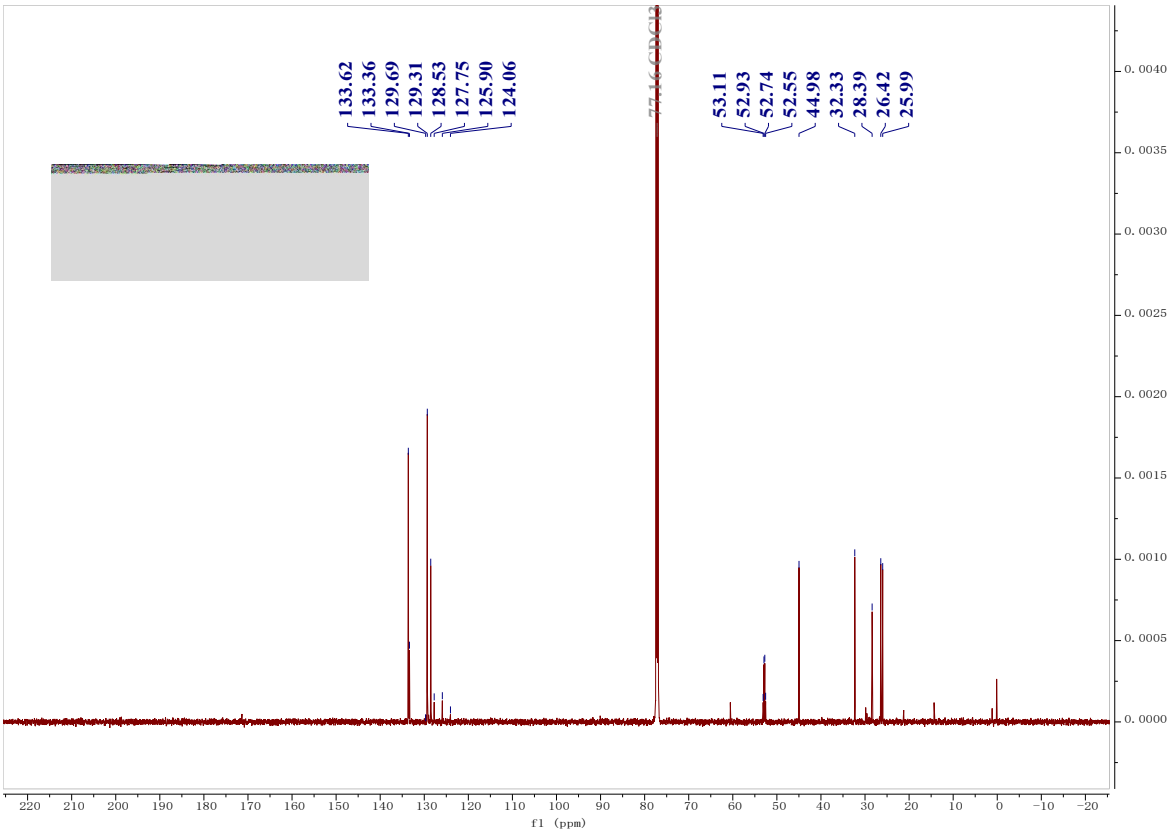
^{13}C NMR Spectrum of Compound **6**



^{19}F NMR Spectrum of Compound **6**



^{1}H NMR Spectrum of Compound **7**



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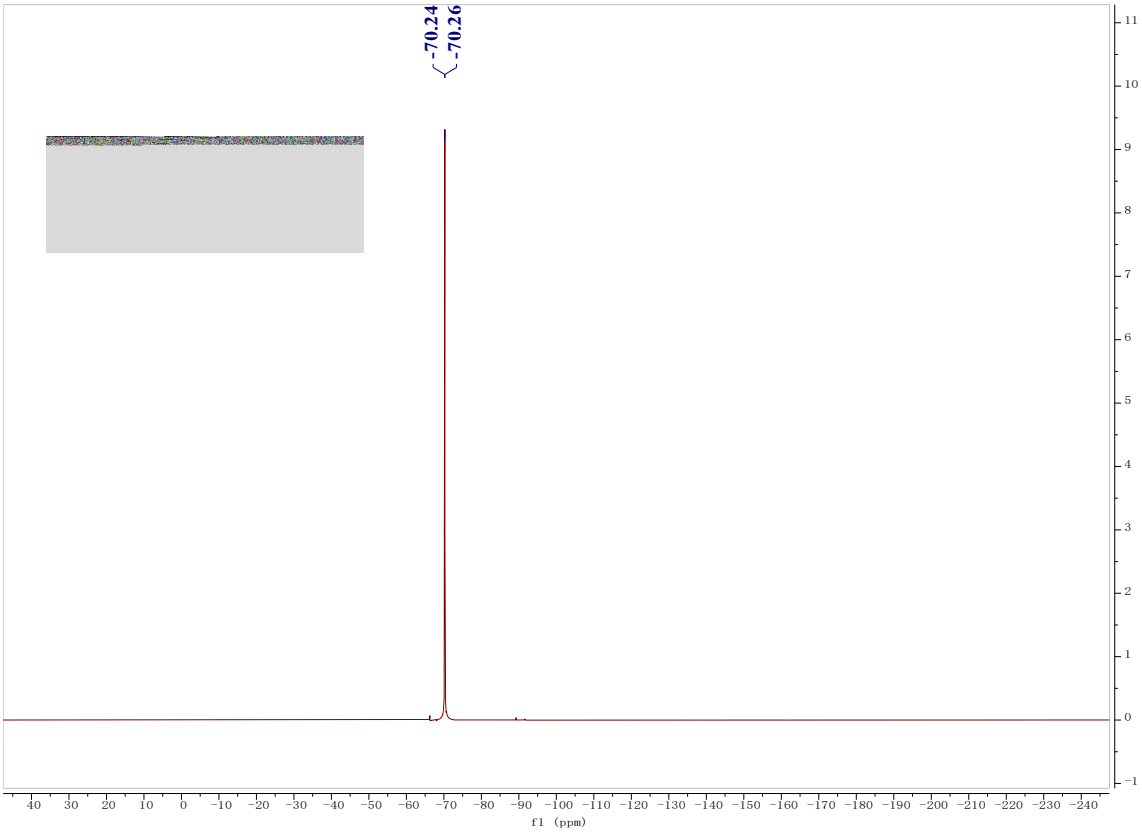

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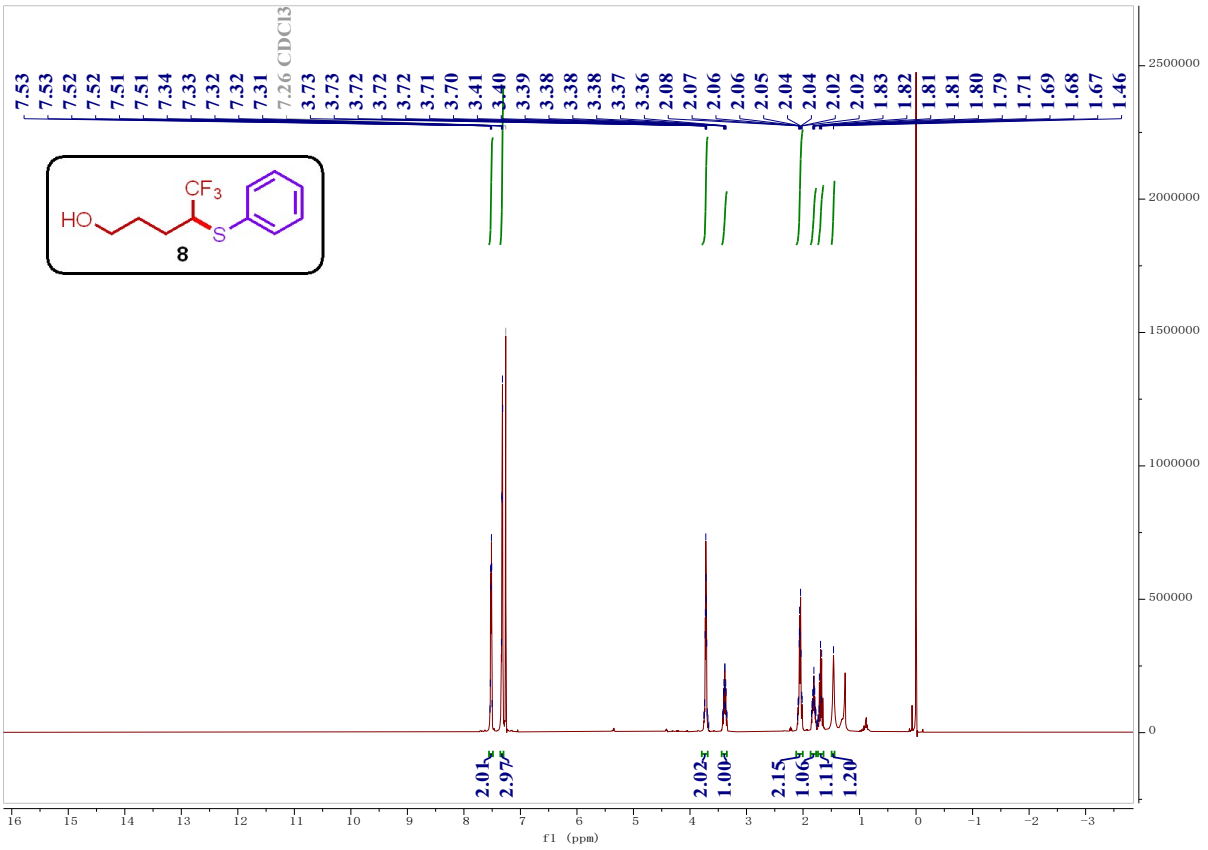
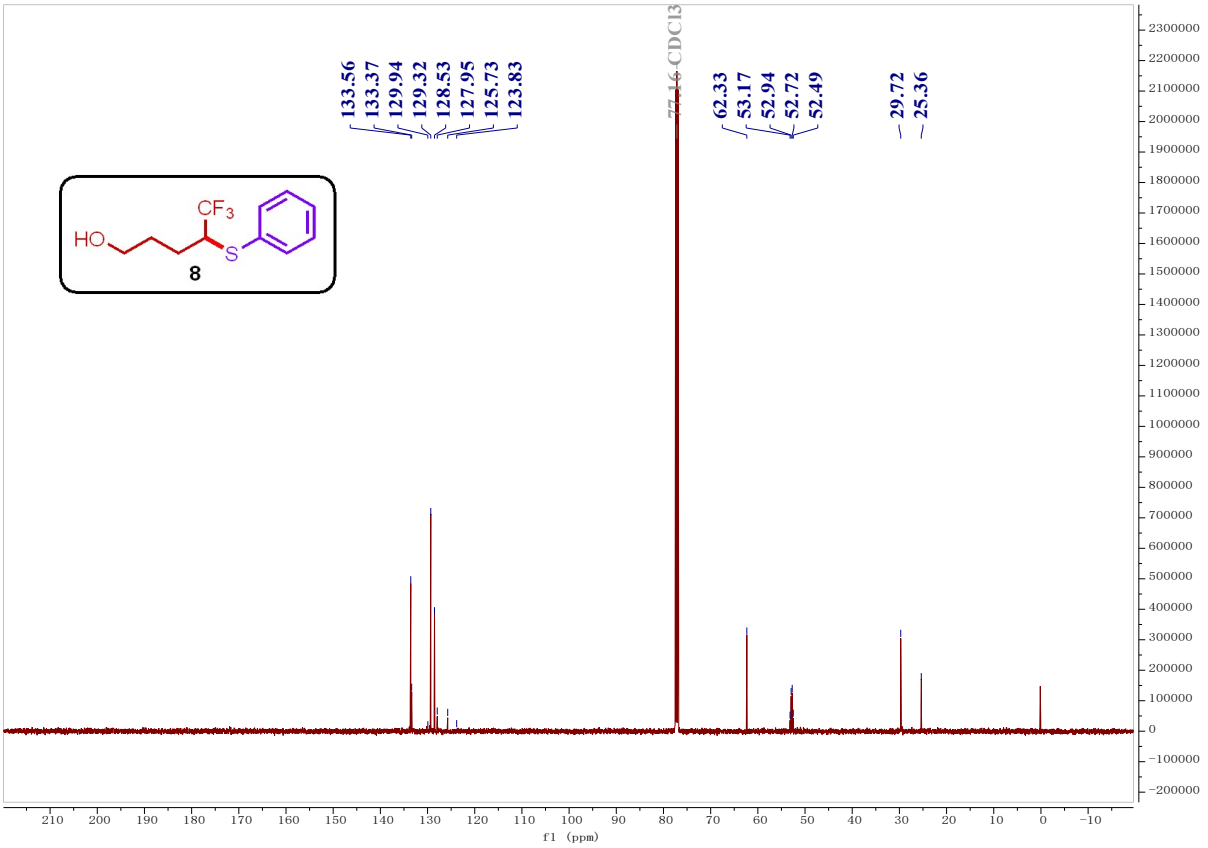
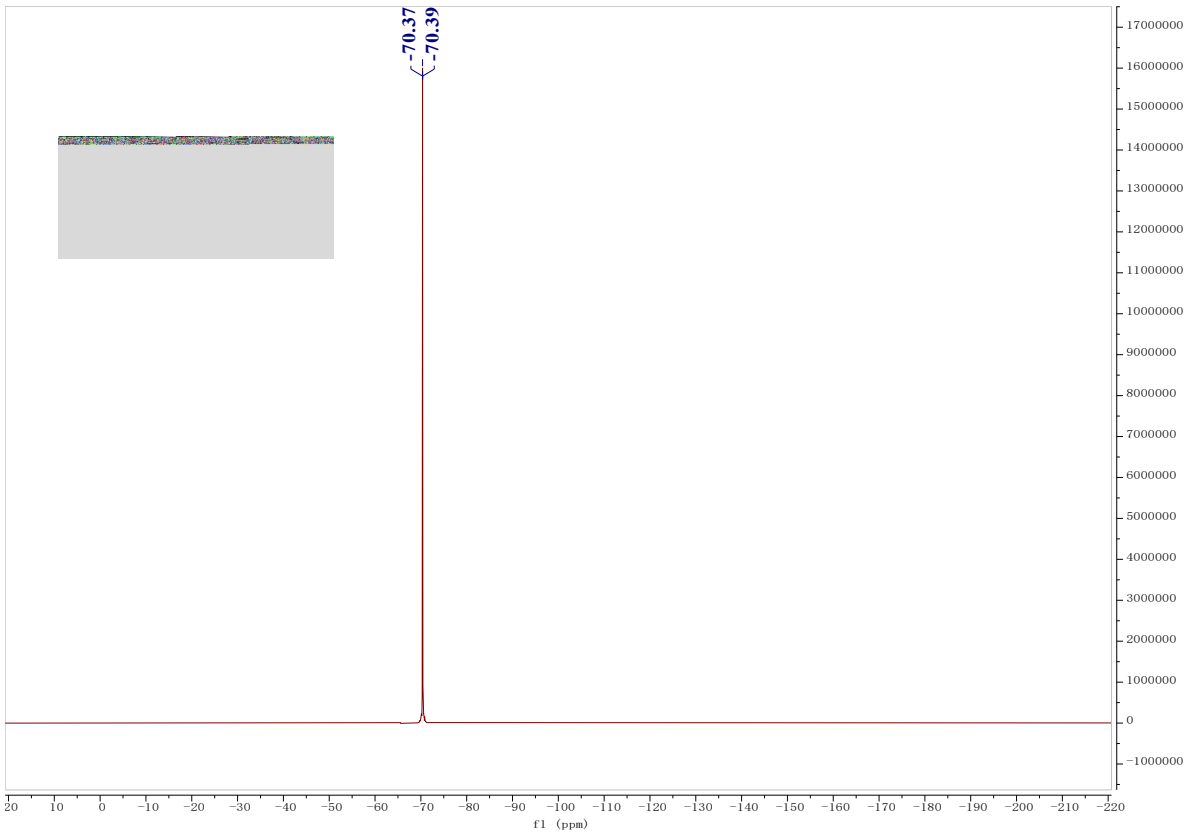


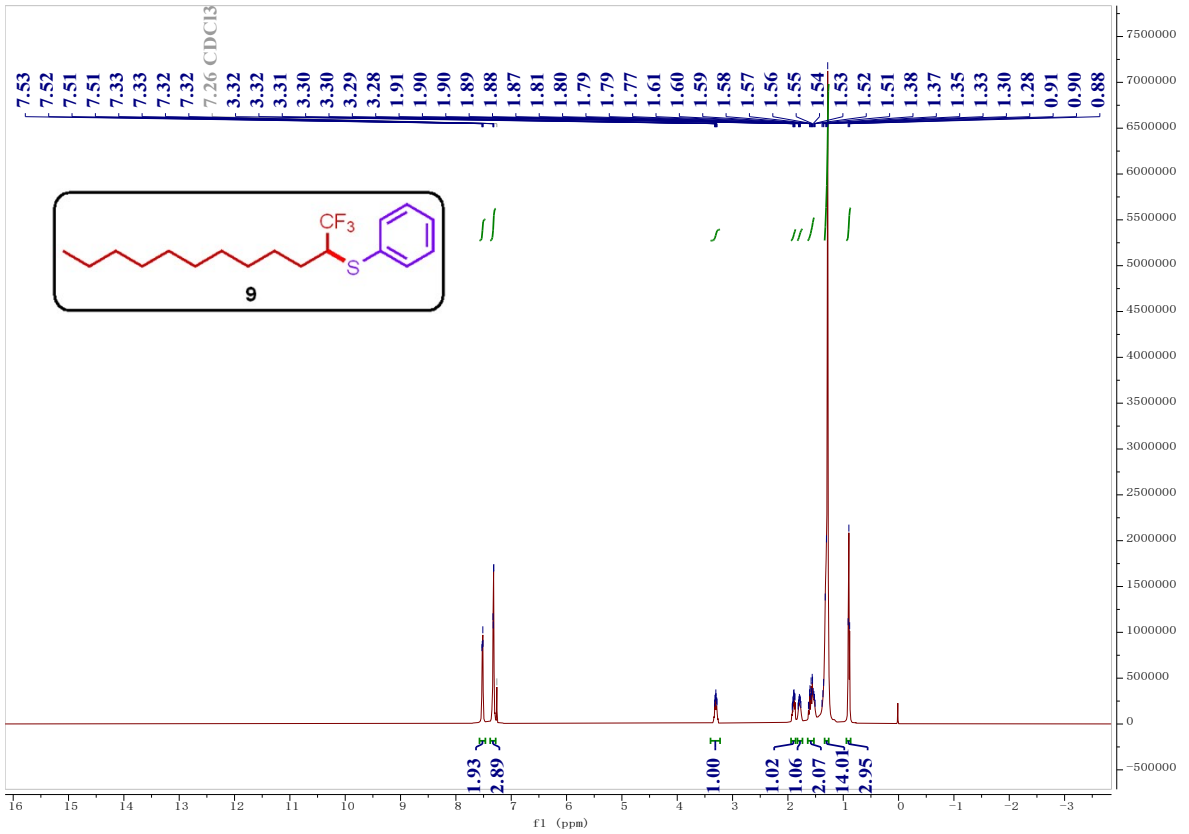
^{1}H NMR Spectrum of Compound **8**



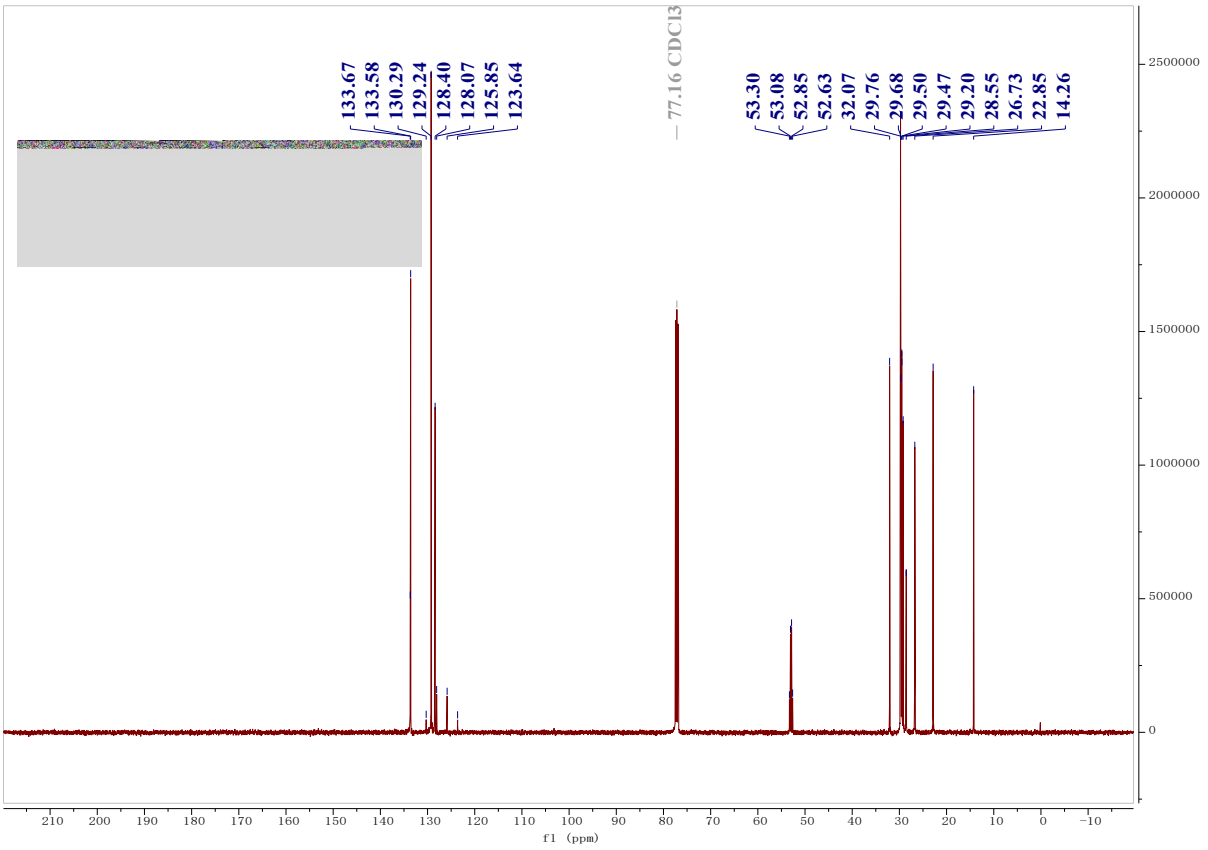
^{13}C NMR Spectrum of Compound **8**



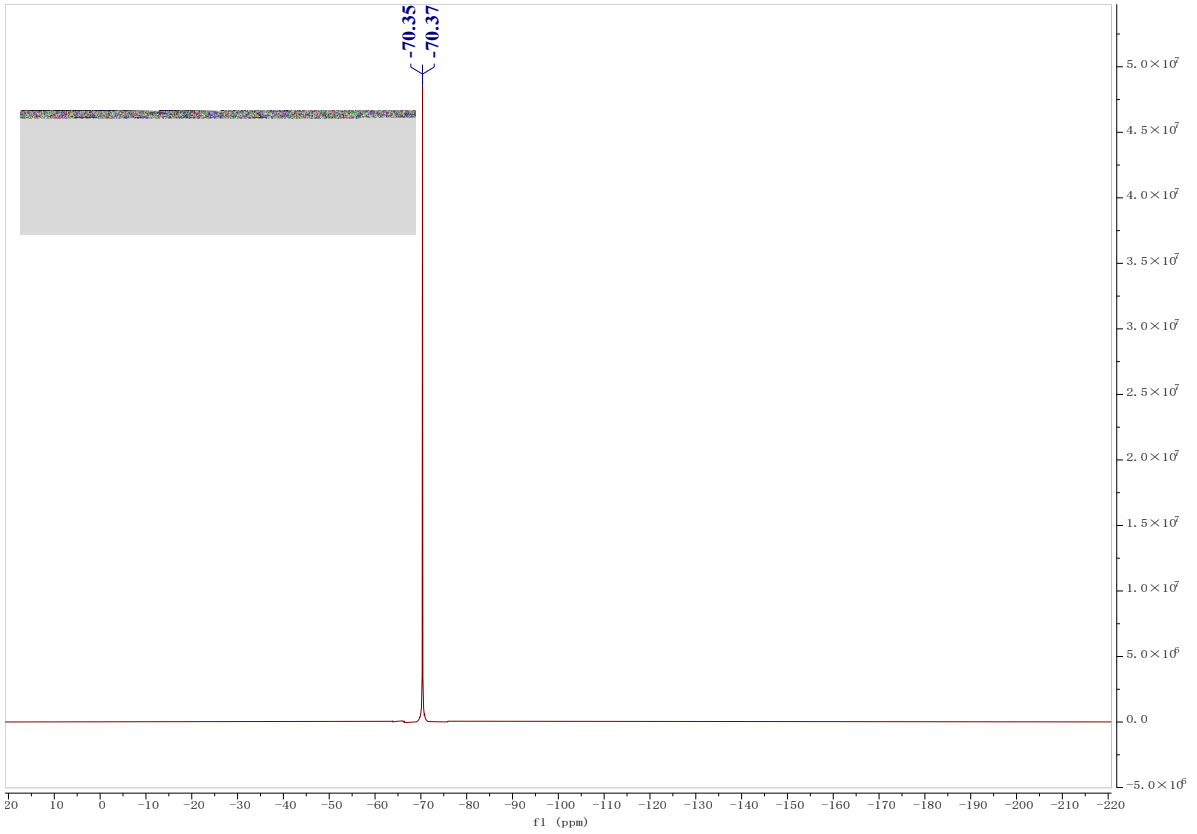
^{19}F NMR Spectrum of Compound **8**



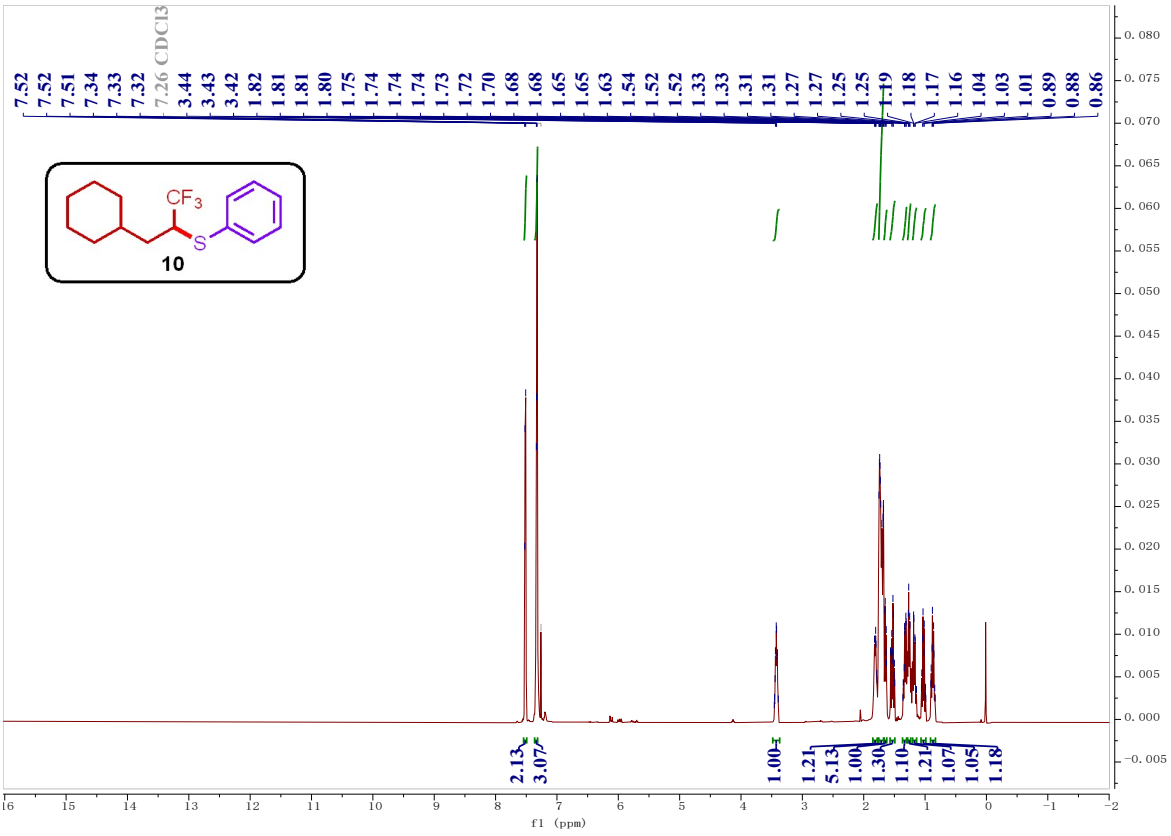
^{1}H NMR Spectrum of Compound **9**



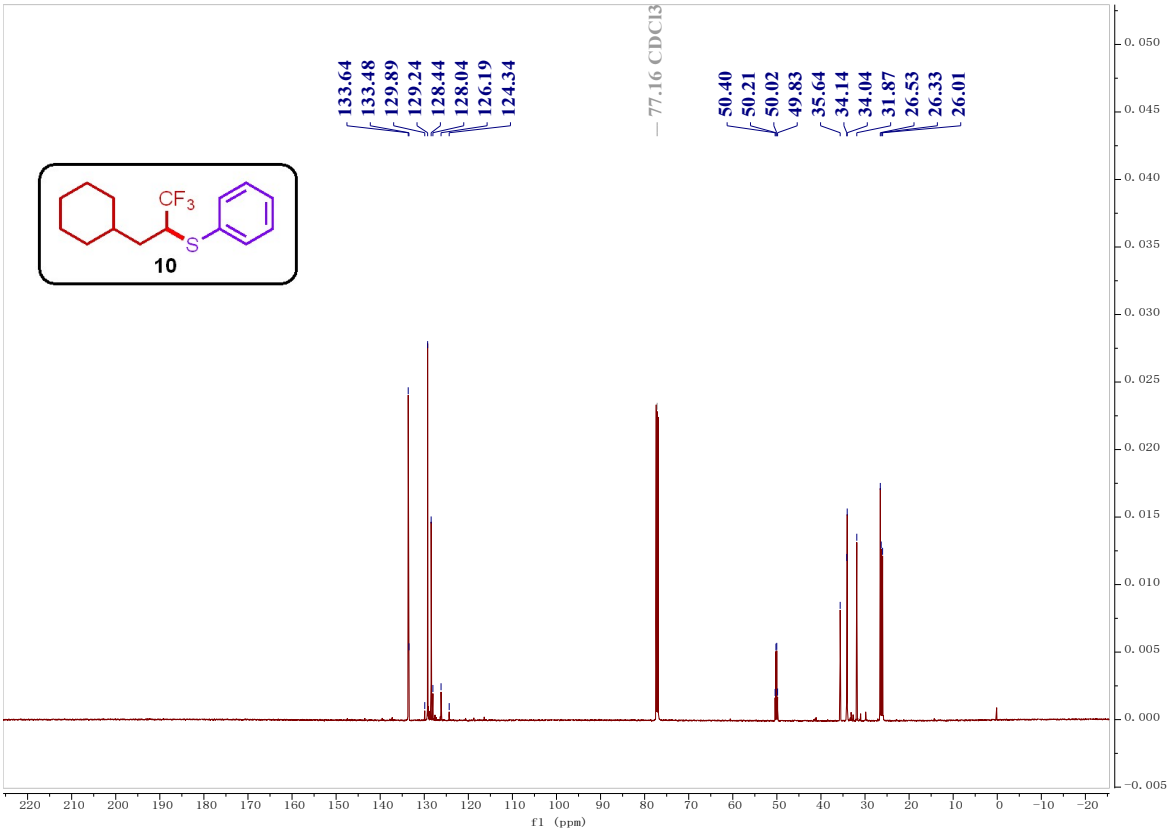
^{13}C NMR Spectrum of Compound **9**



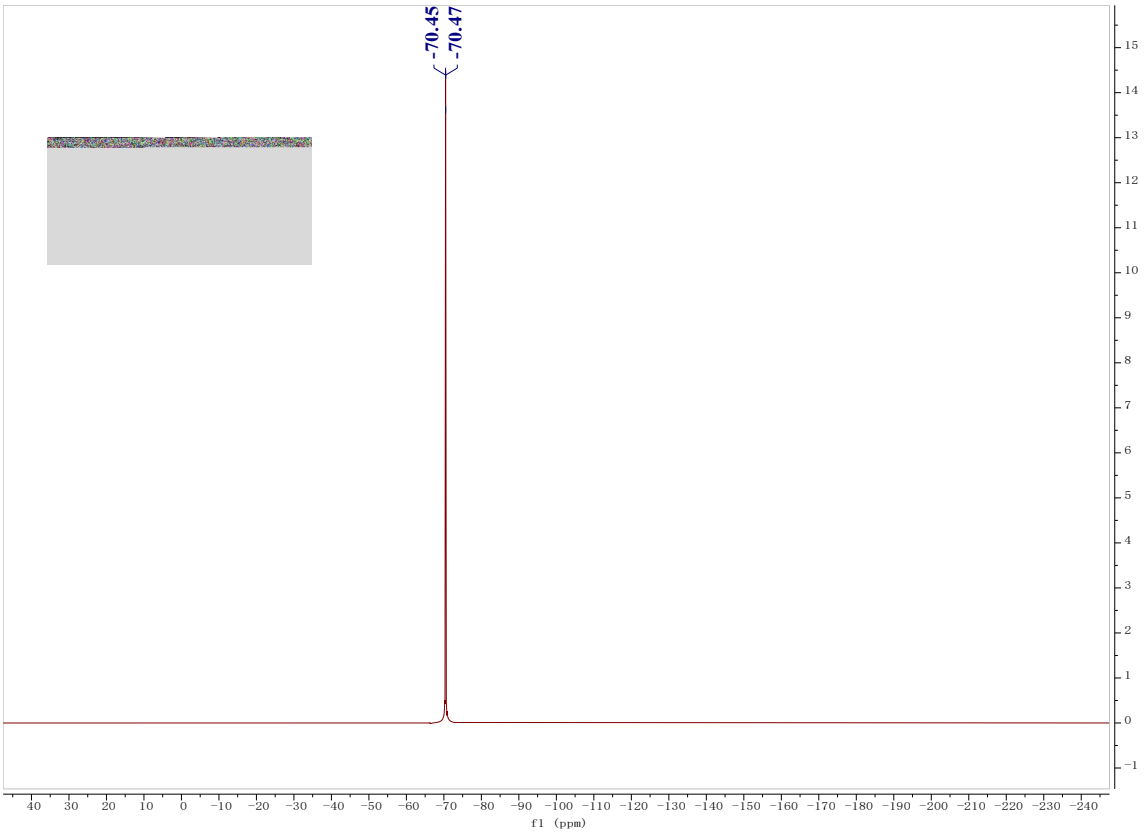
^{19}F NMR Spectrum of Compound **9**



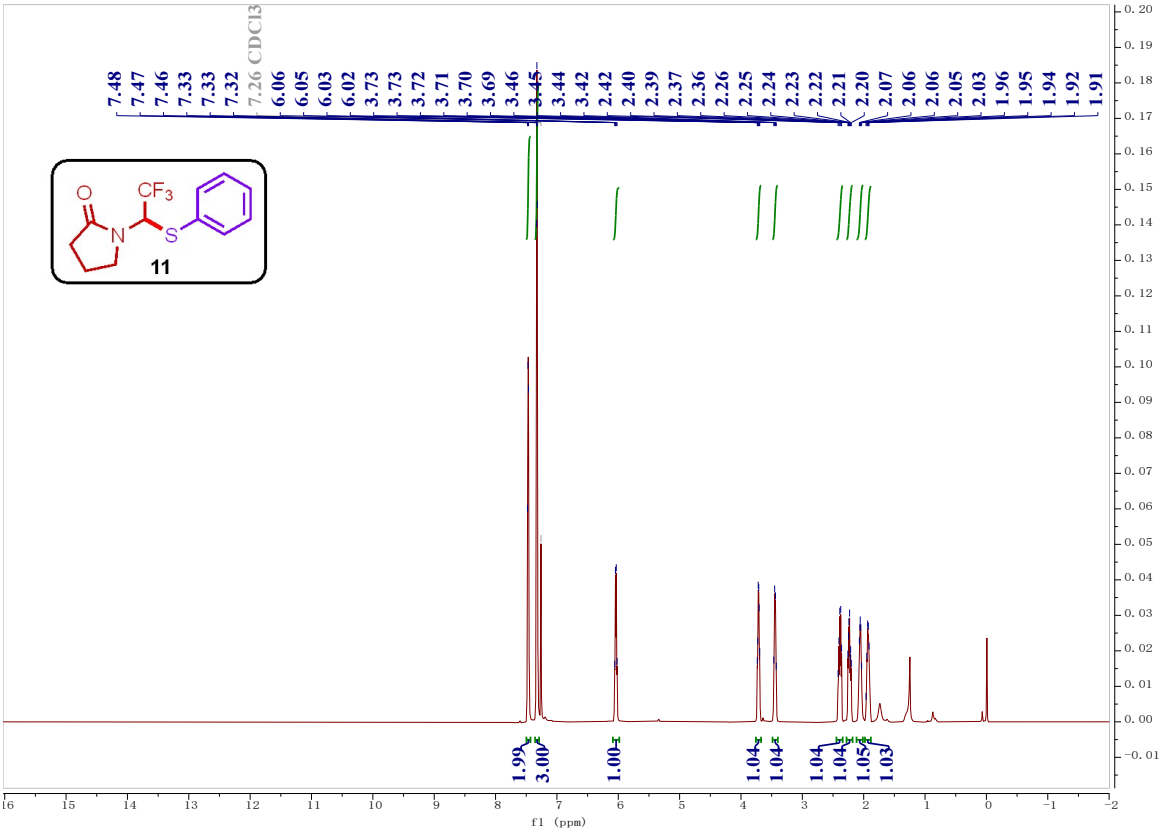
^{1}H NMR Spectrum of Compound **10**



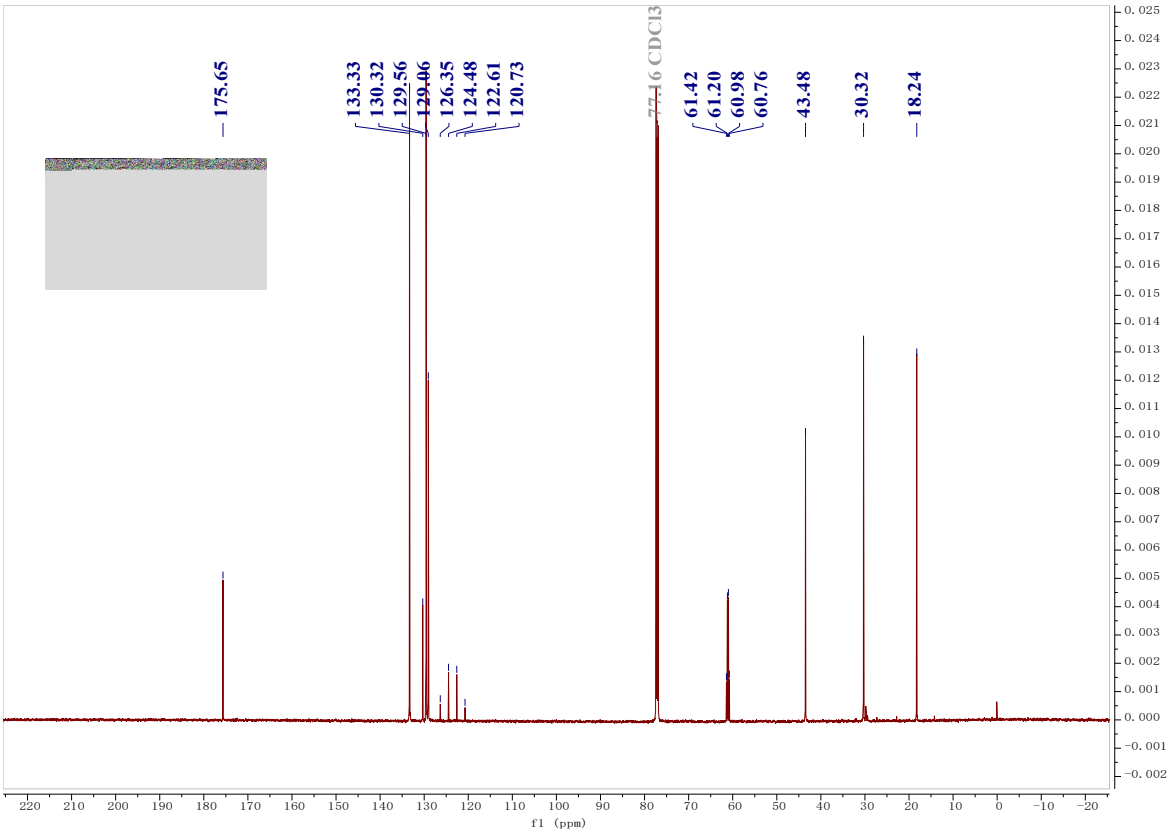
^{13}C NMR Spectrum of Compound **10**



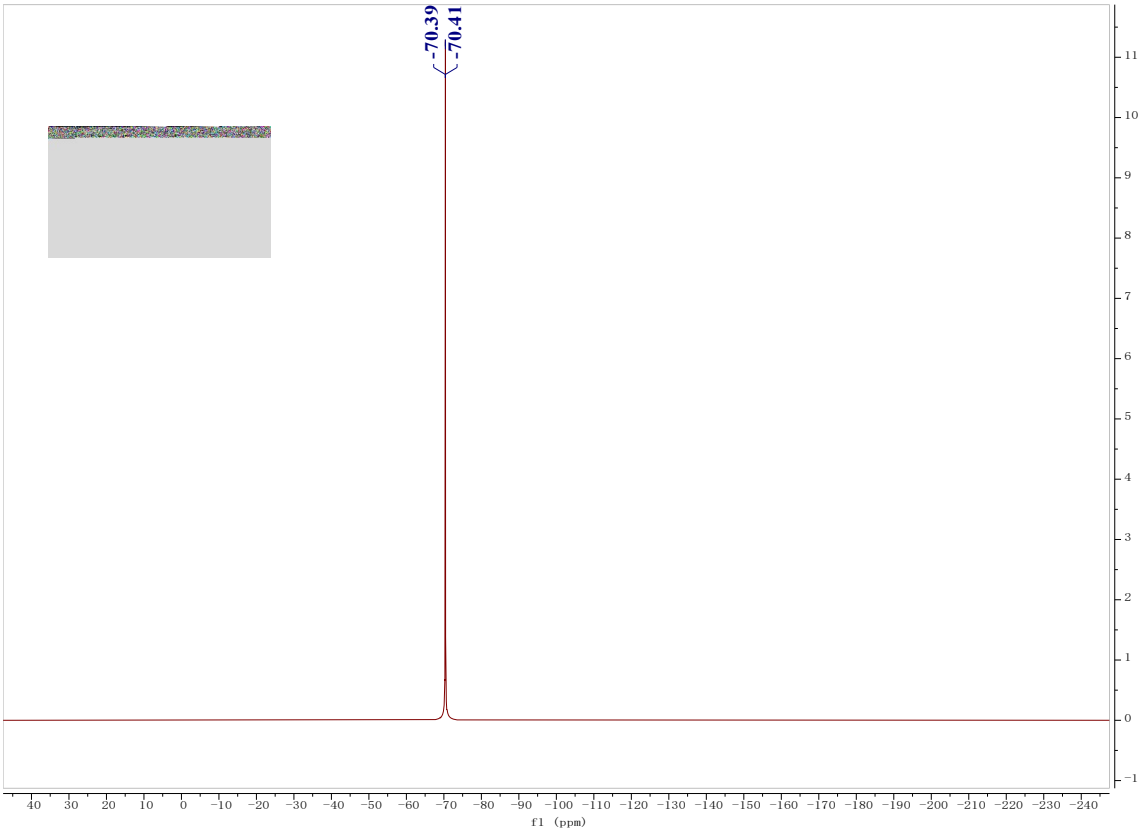
^{19}F NMR Spectrum of Compound **10**



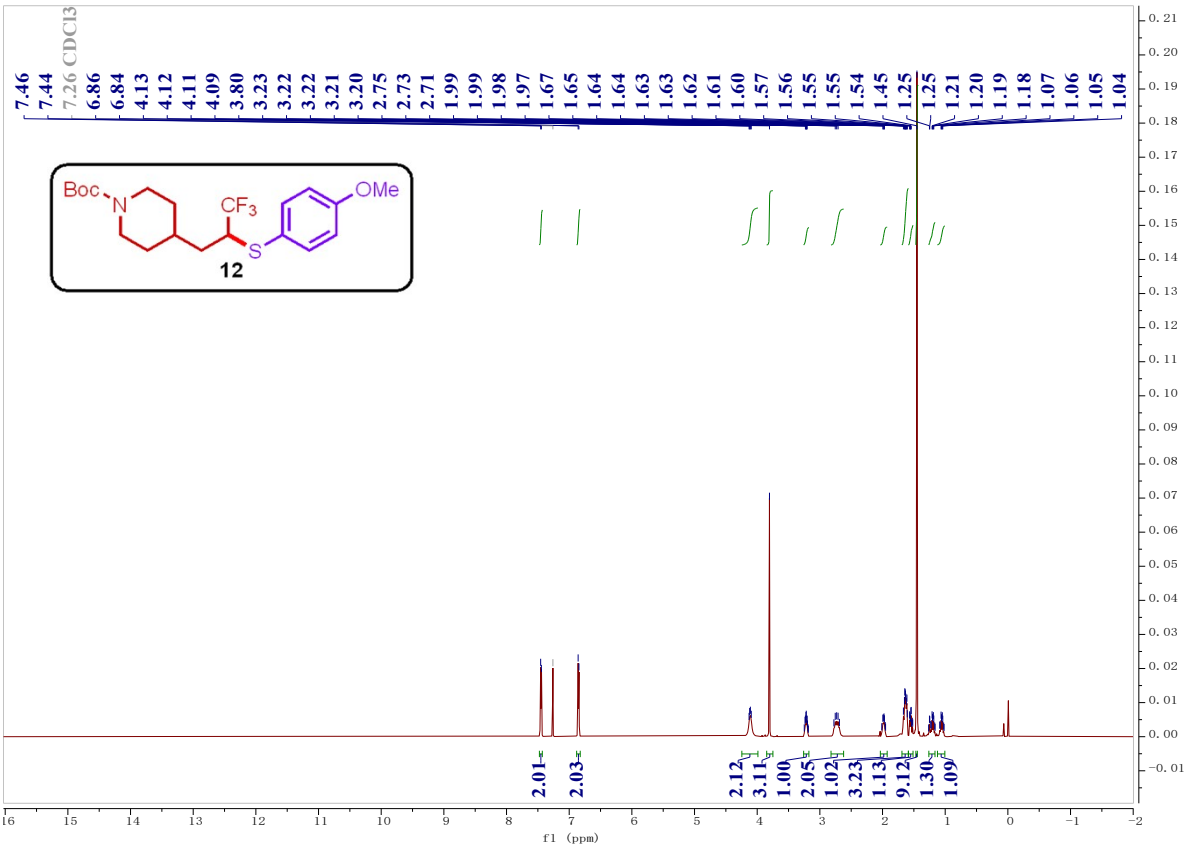
^{1}H NMR Spectrum of Compound **11**



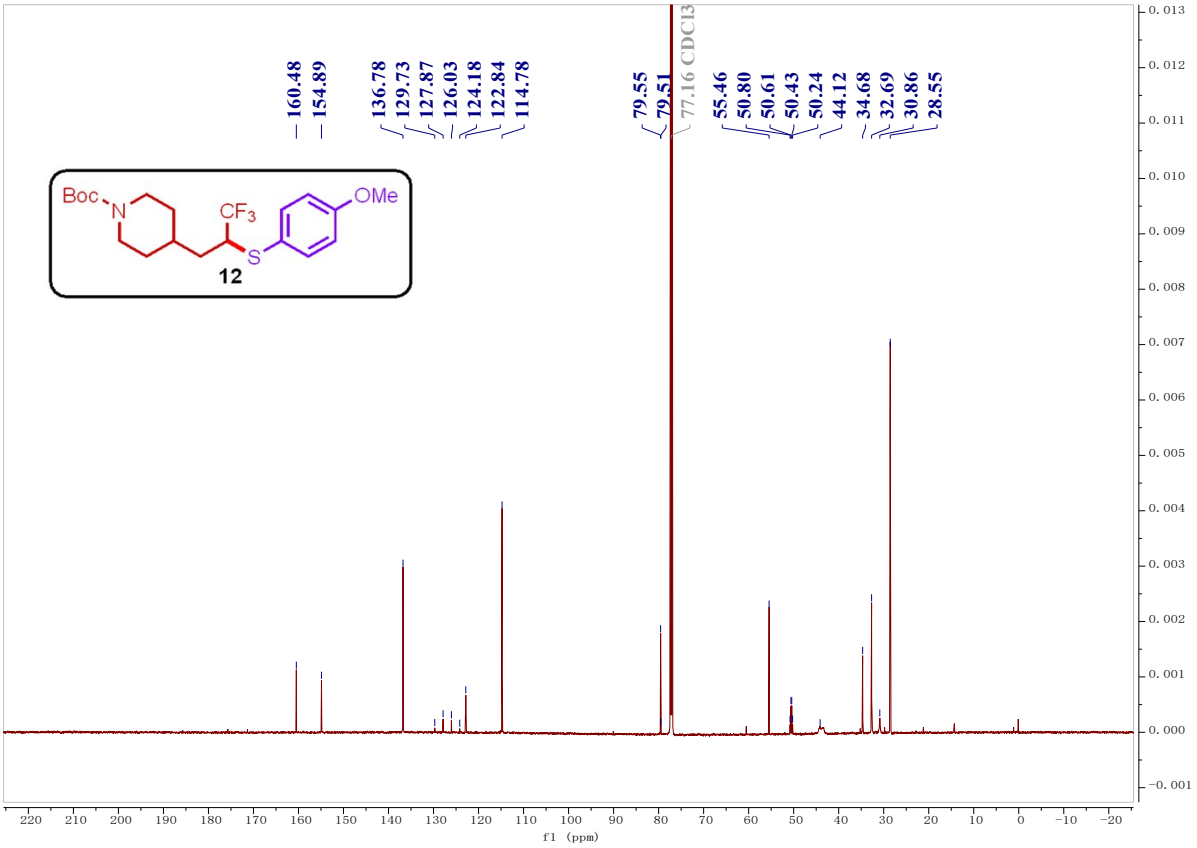
^{13}C NMR Spectrum of Compound **11**



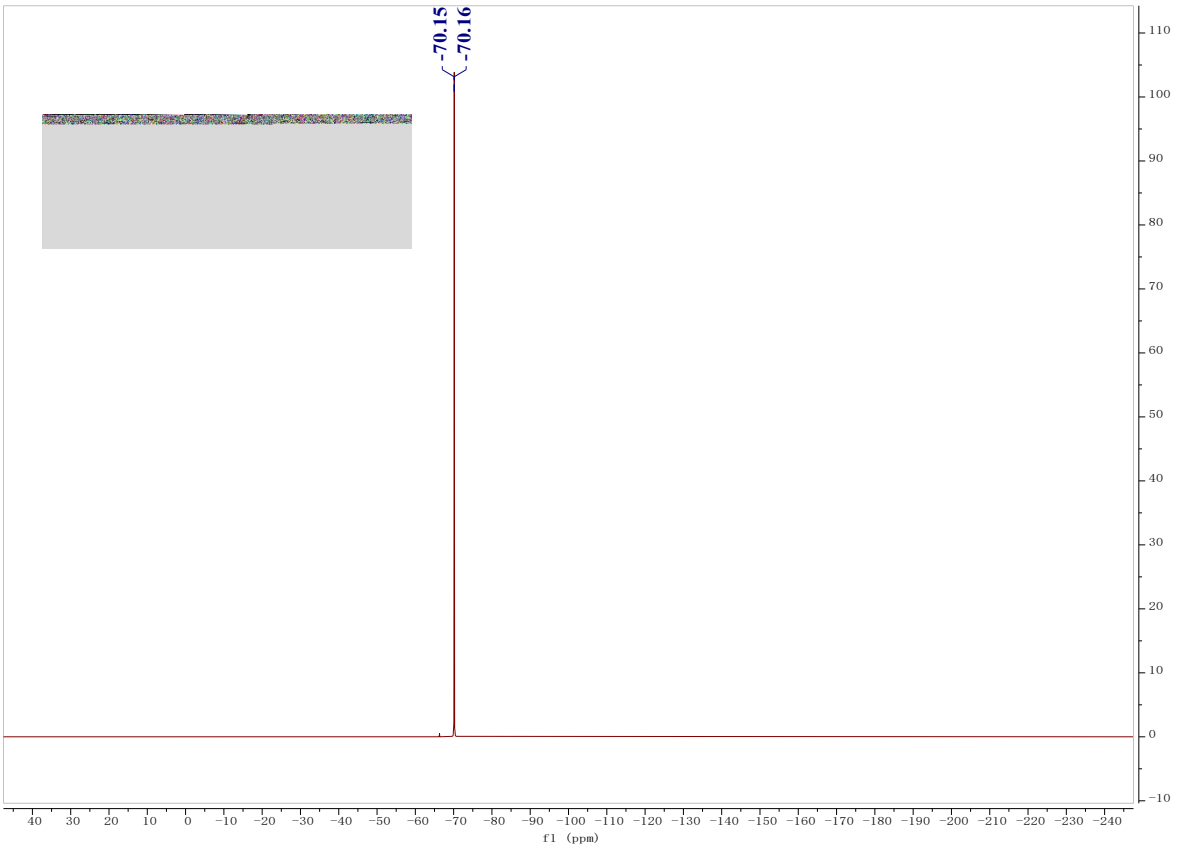
^{19}F NMR Spectrum of Compound **11**



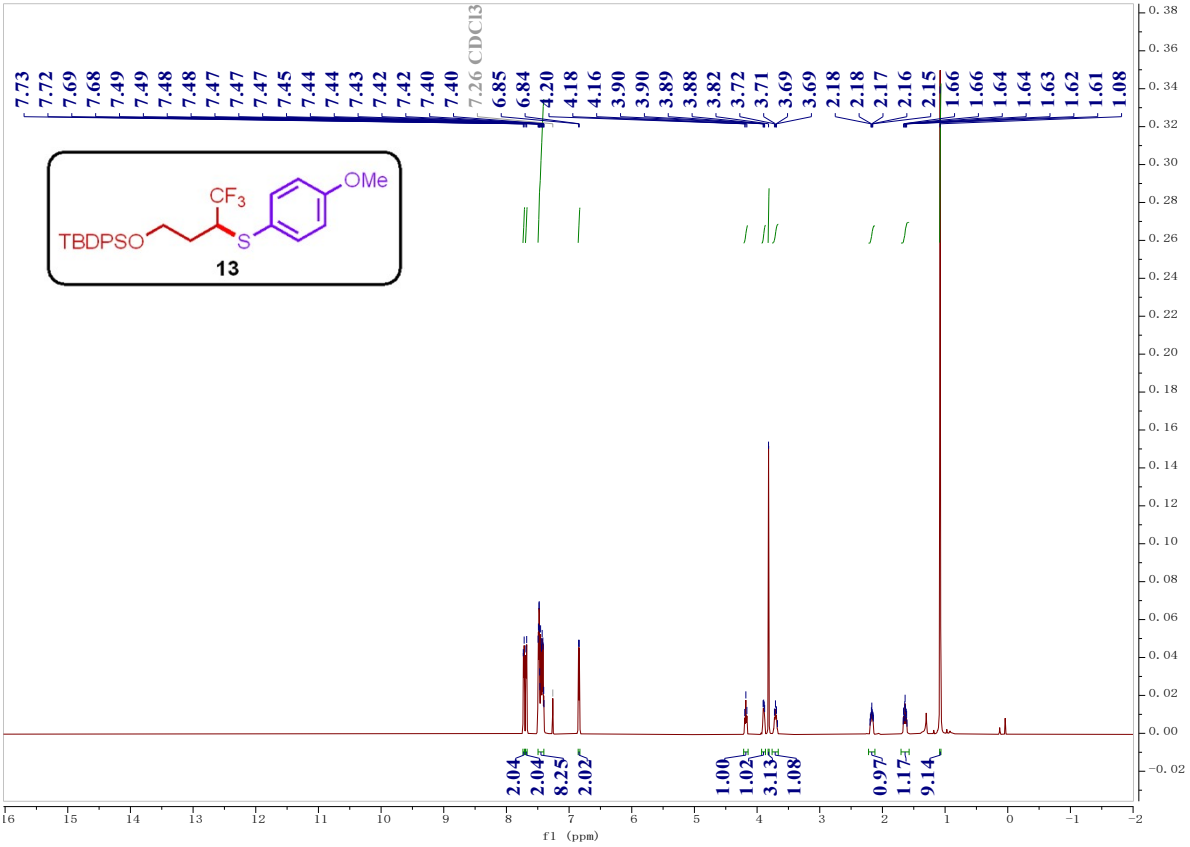
^{1}H NMR Spectrum of Compound **12**



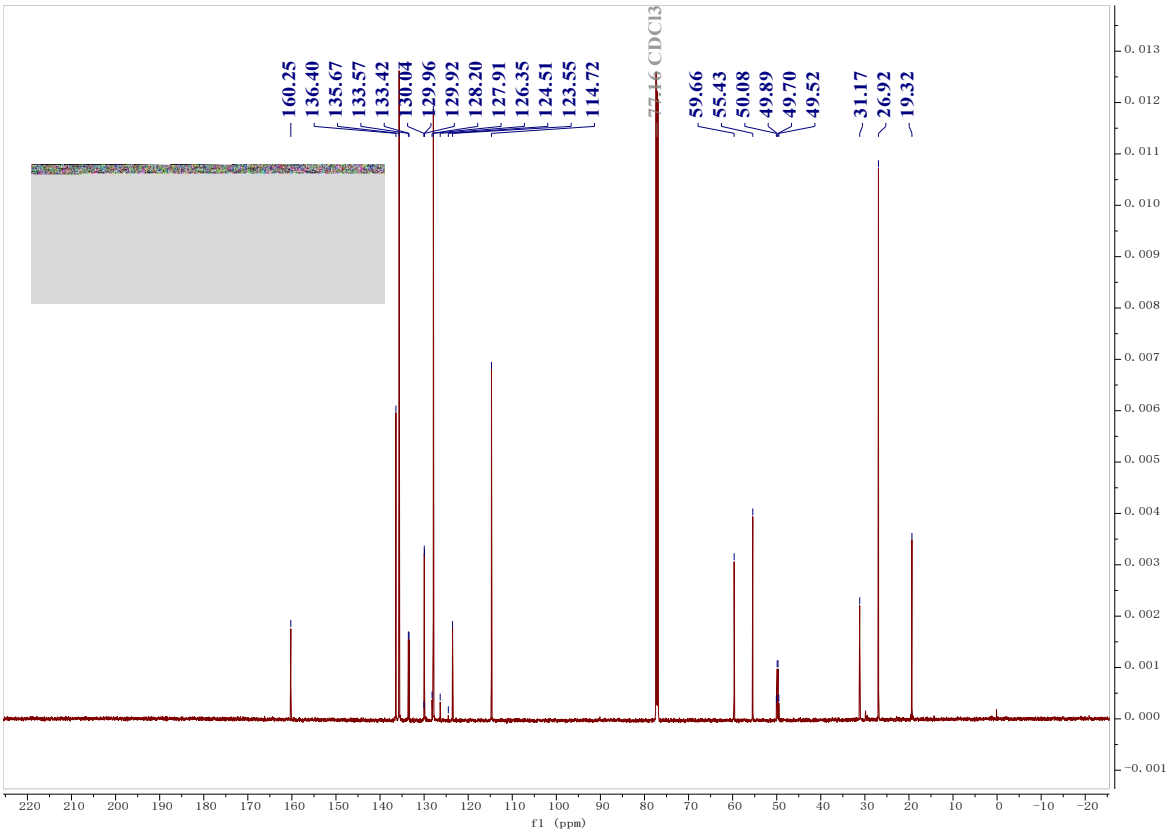
^{13}C NMR Spectrum of Compound **12**



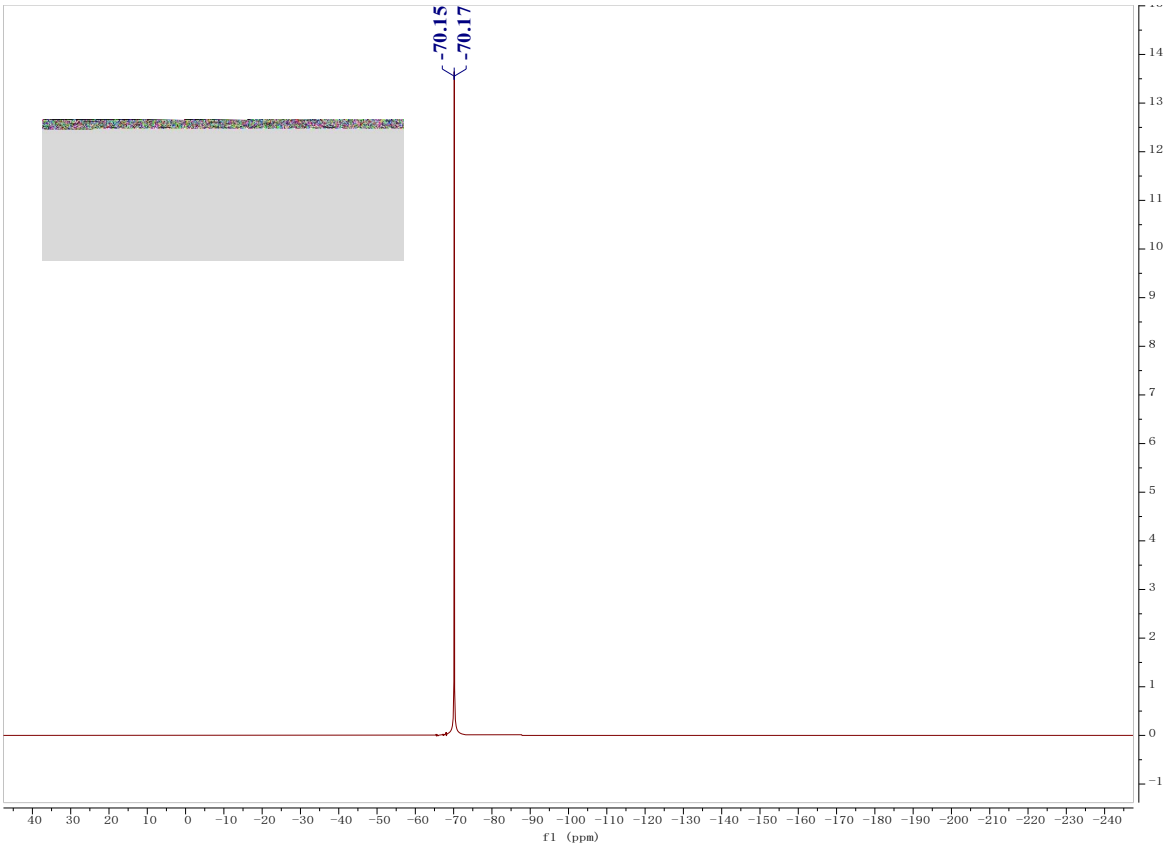
^{19}F NMR Spectrum of Compound **12**



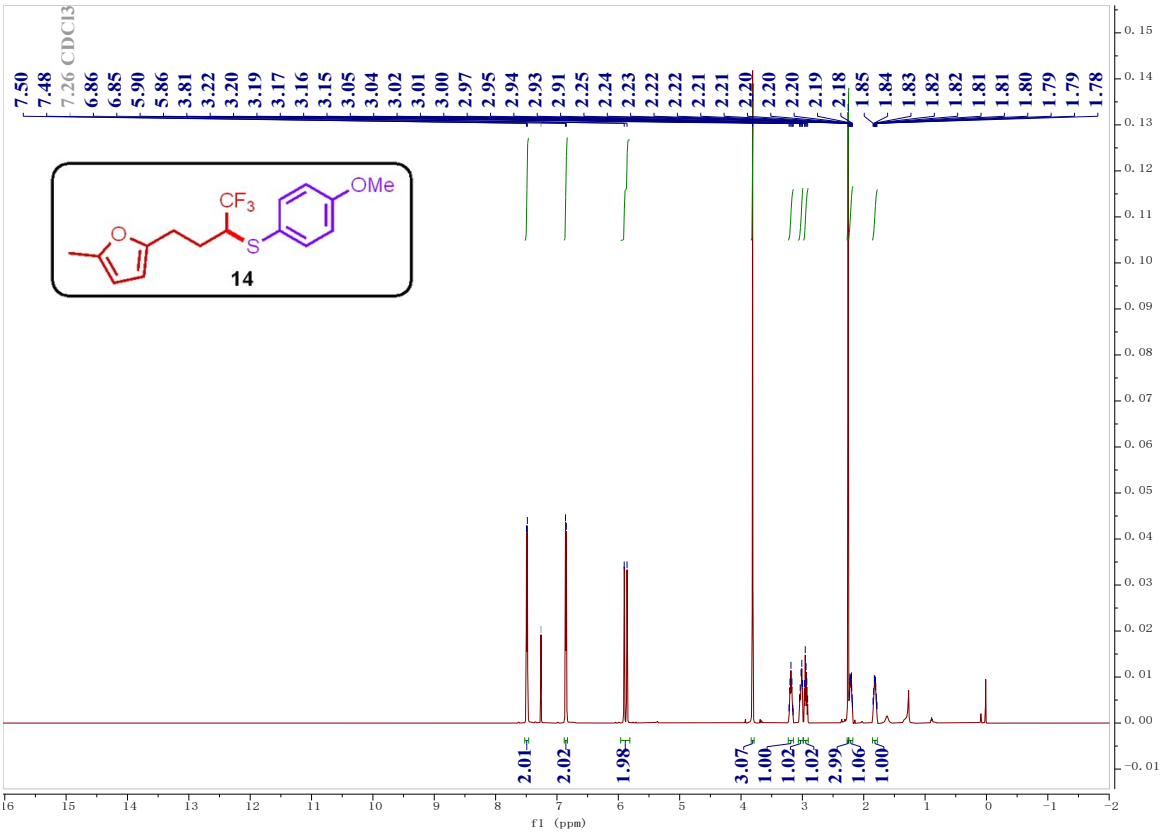
^{1}H NMR Spectrum of Compound **13**



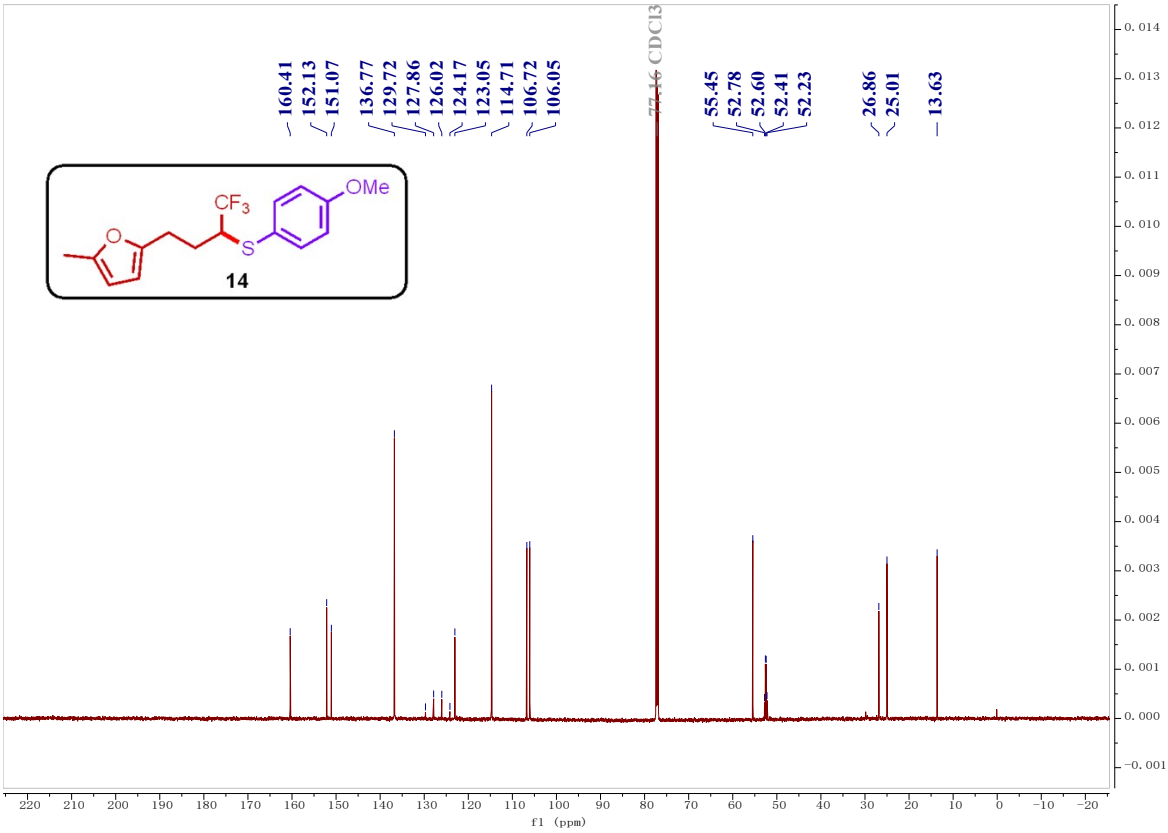
^{13}C NMR Spectrum of Compound **13**



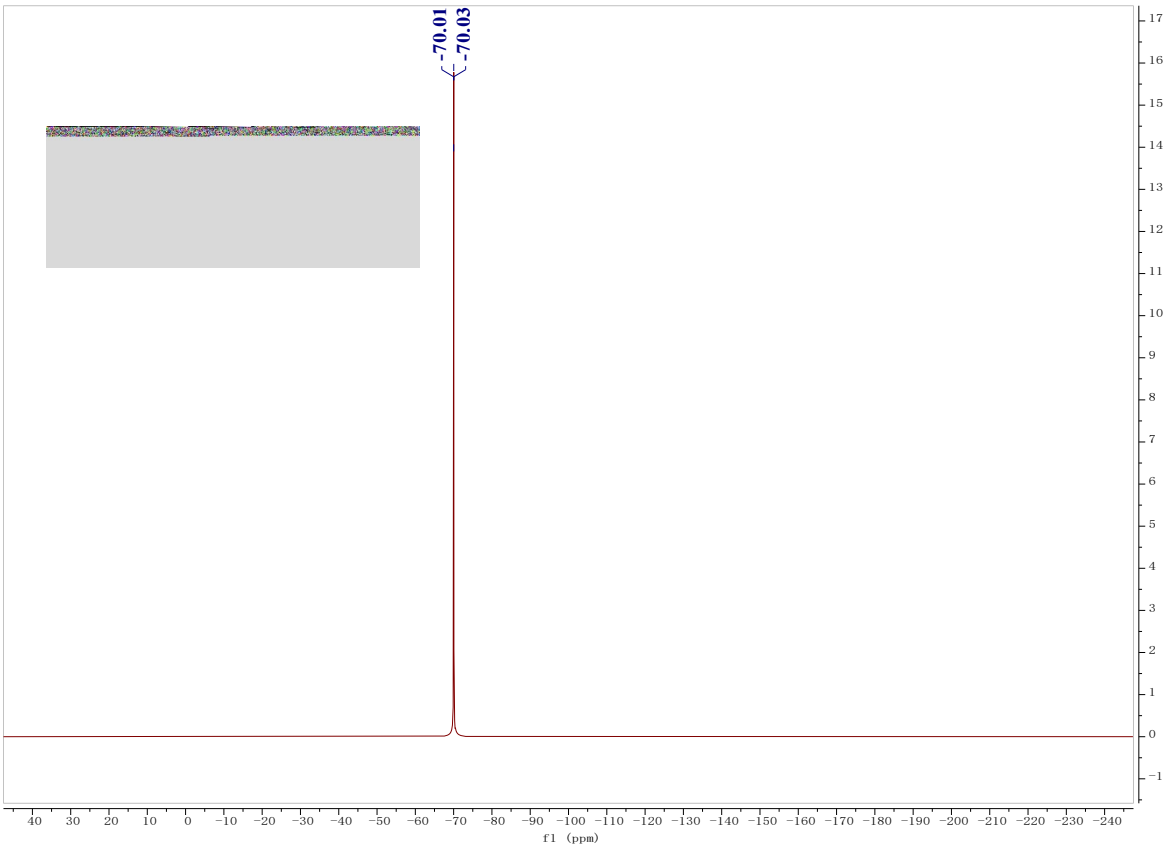
^{19}F NMR Spectrum of Compound **13**



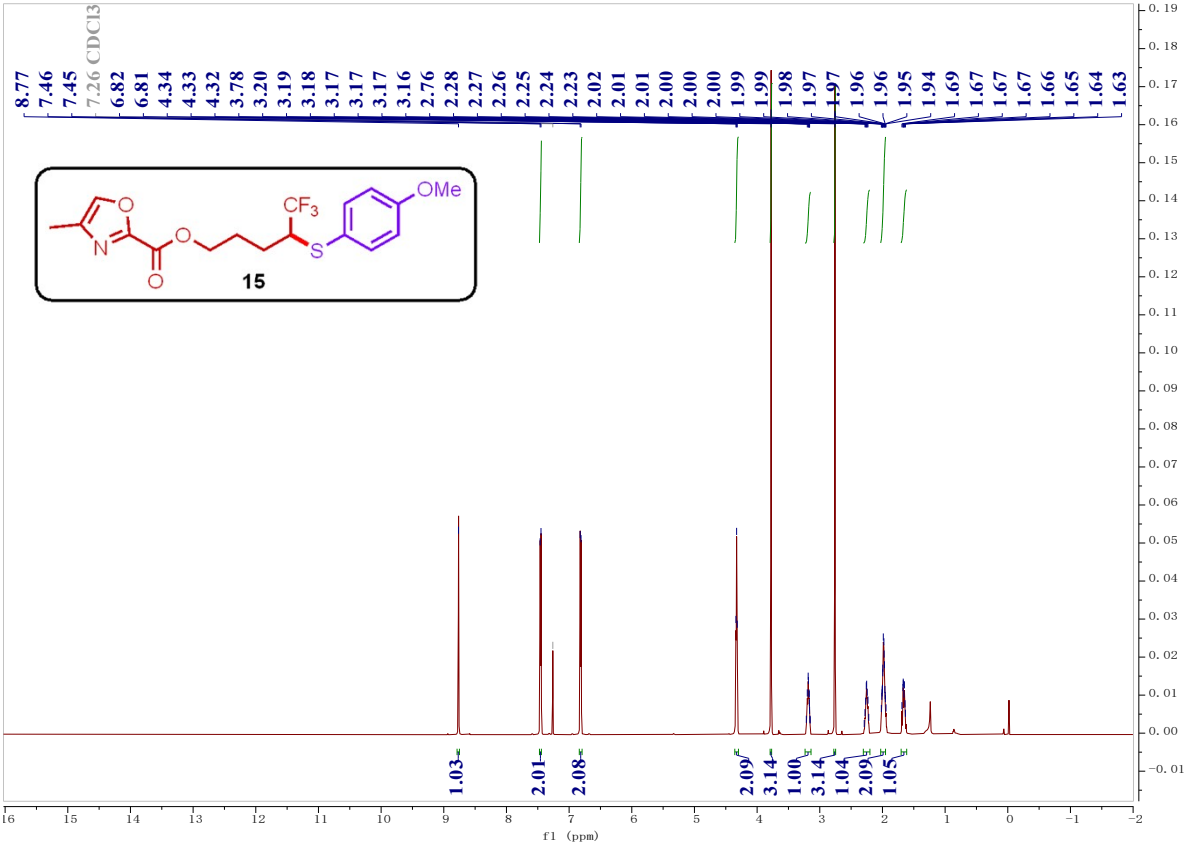
^{1}H NMR Spectrum of Compound **14**



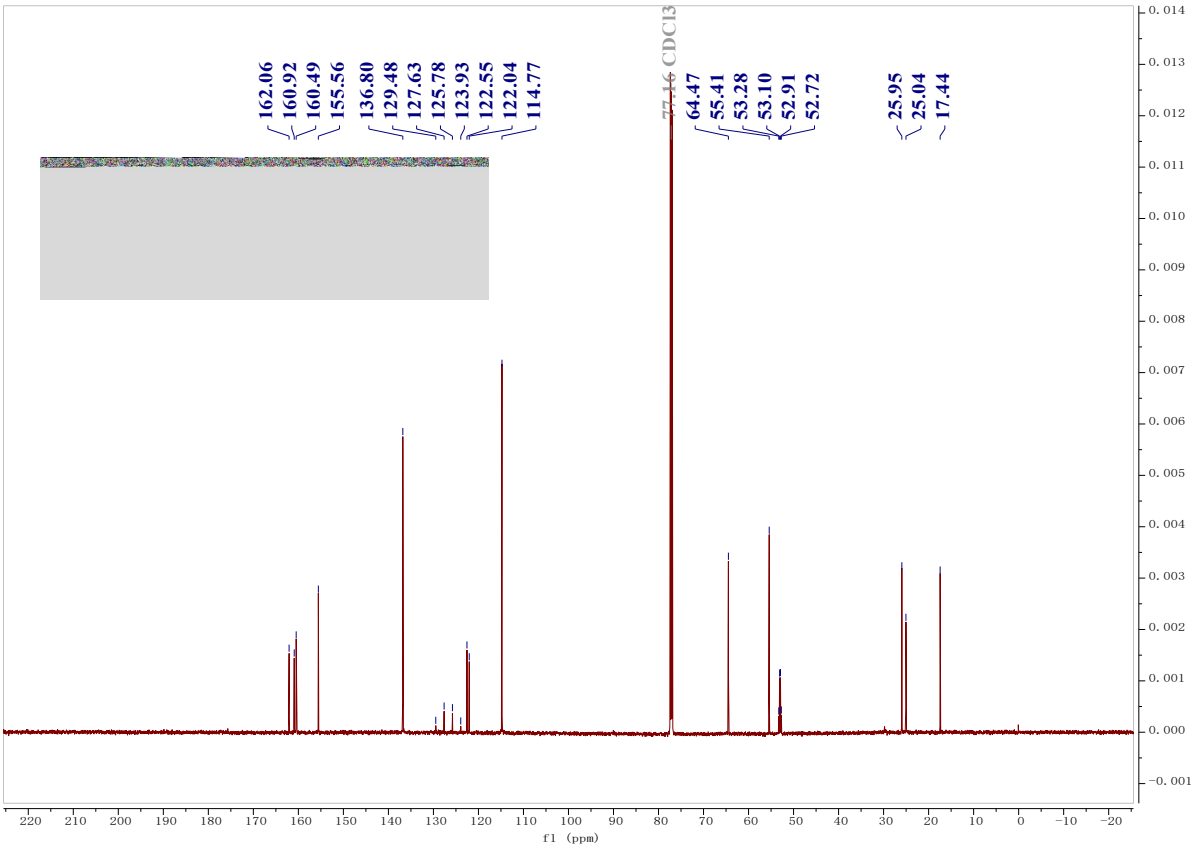
^{13}C NMR Spectrum of Compound **14**



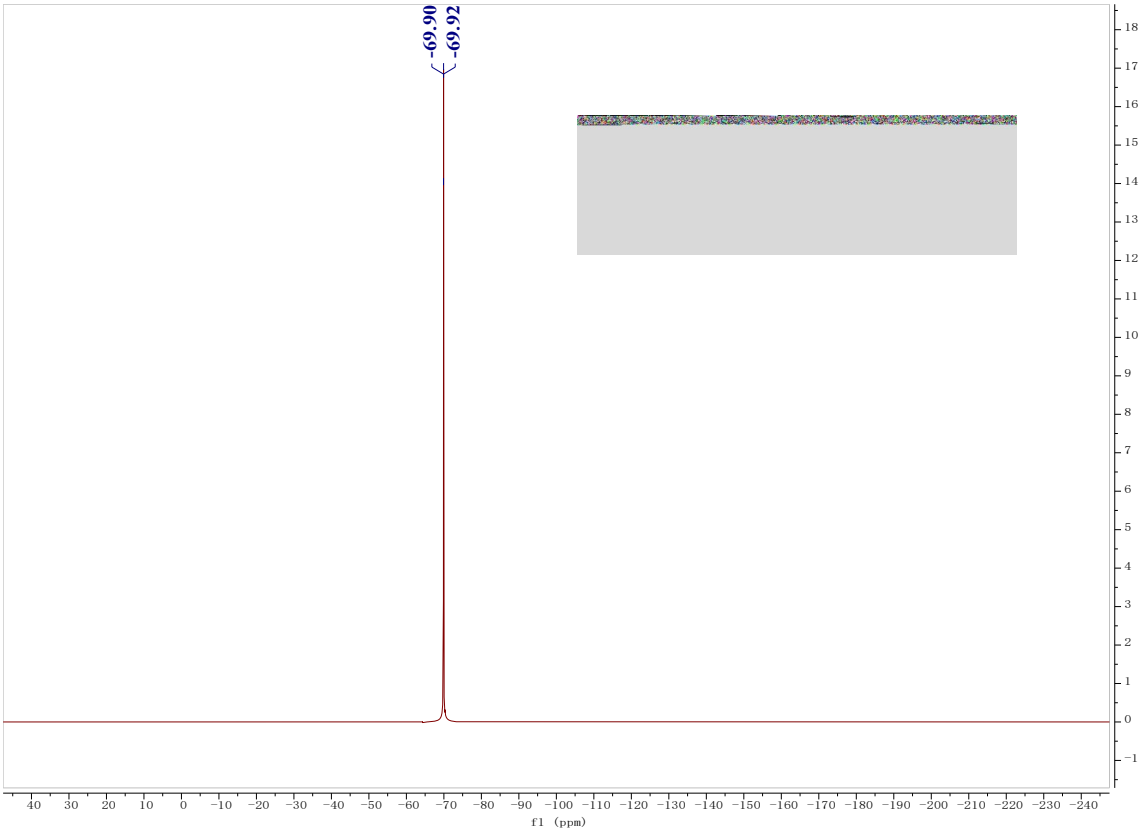
^{19}F NMR Spectrum of Compound **14**



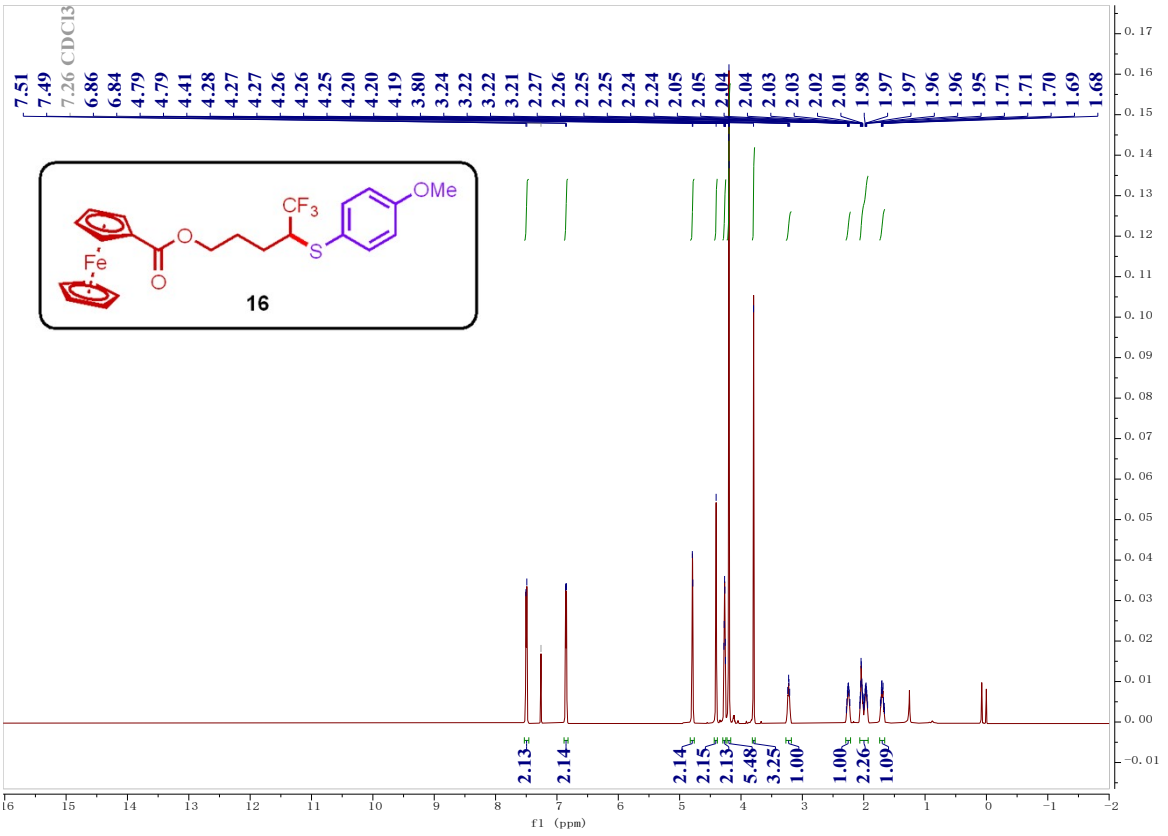
^{1}H NMR Spectrum of Compound **15**



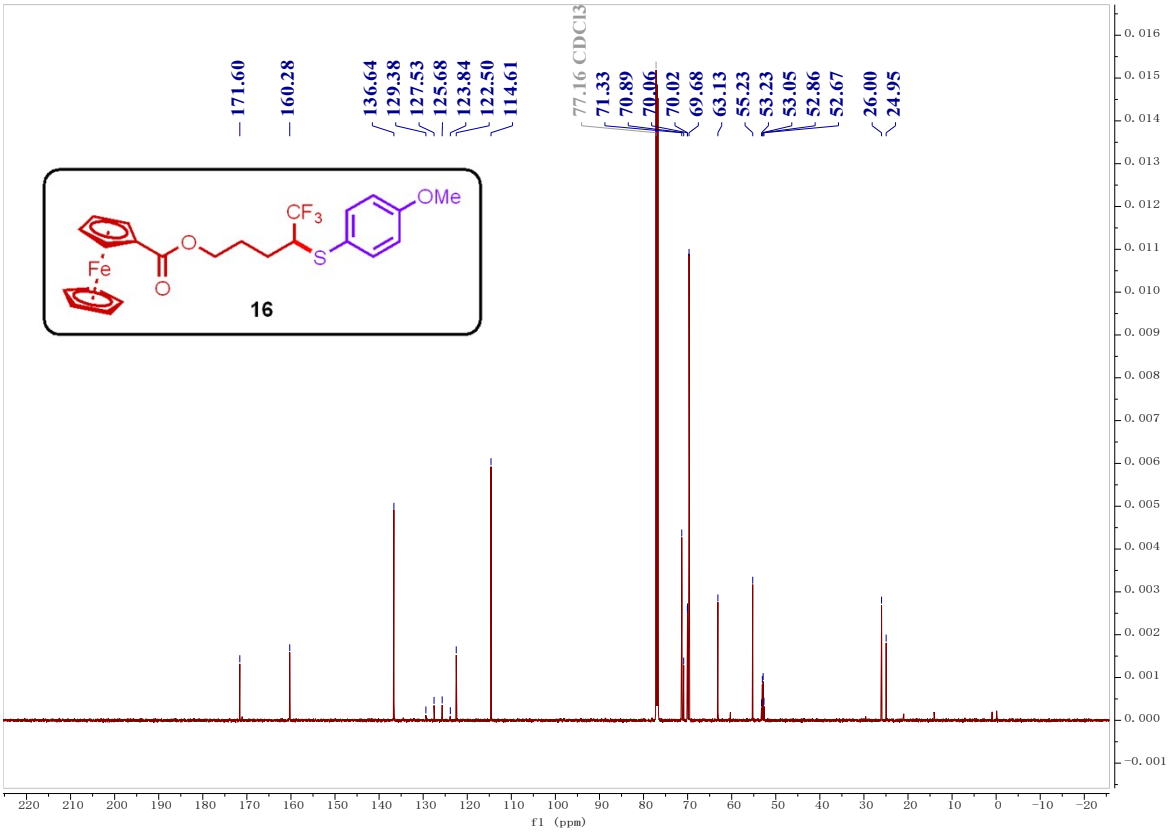
^{13}C NMR Spectrum of Compound **15**



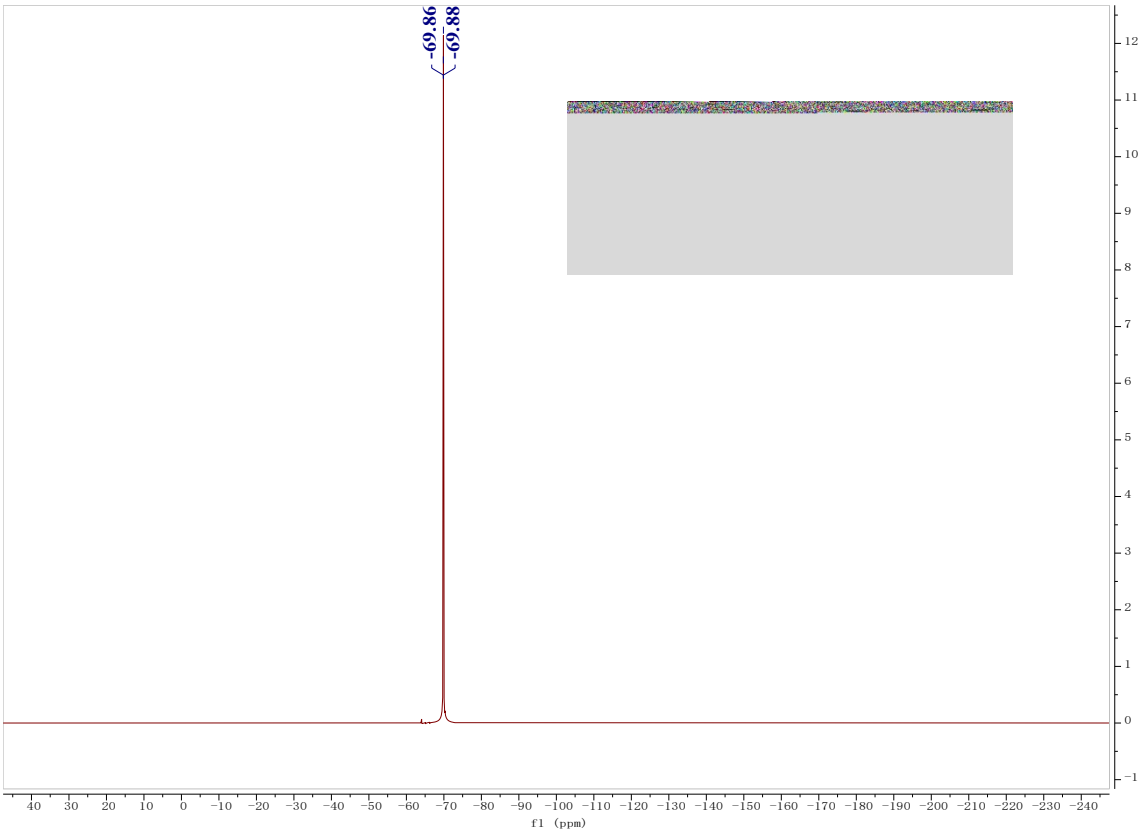
^{19}F NMR Spectrum of Compound **15**



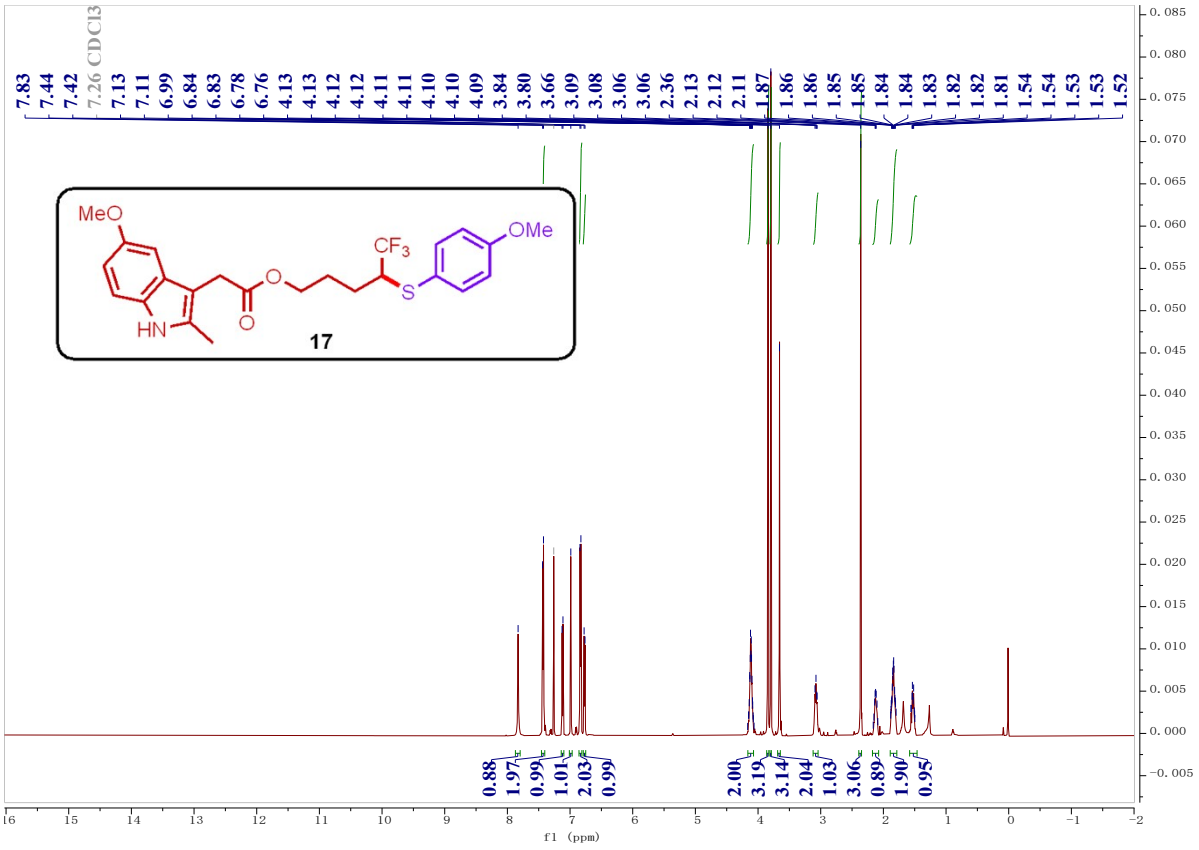
^{1}H NMR Spectrum of Compound **16**



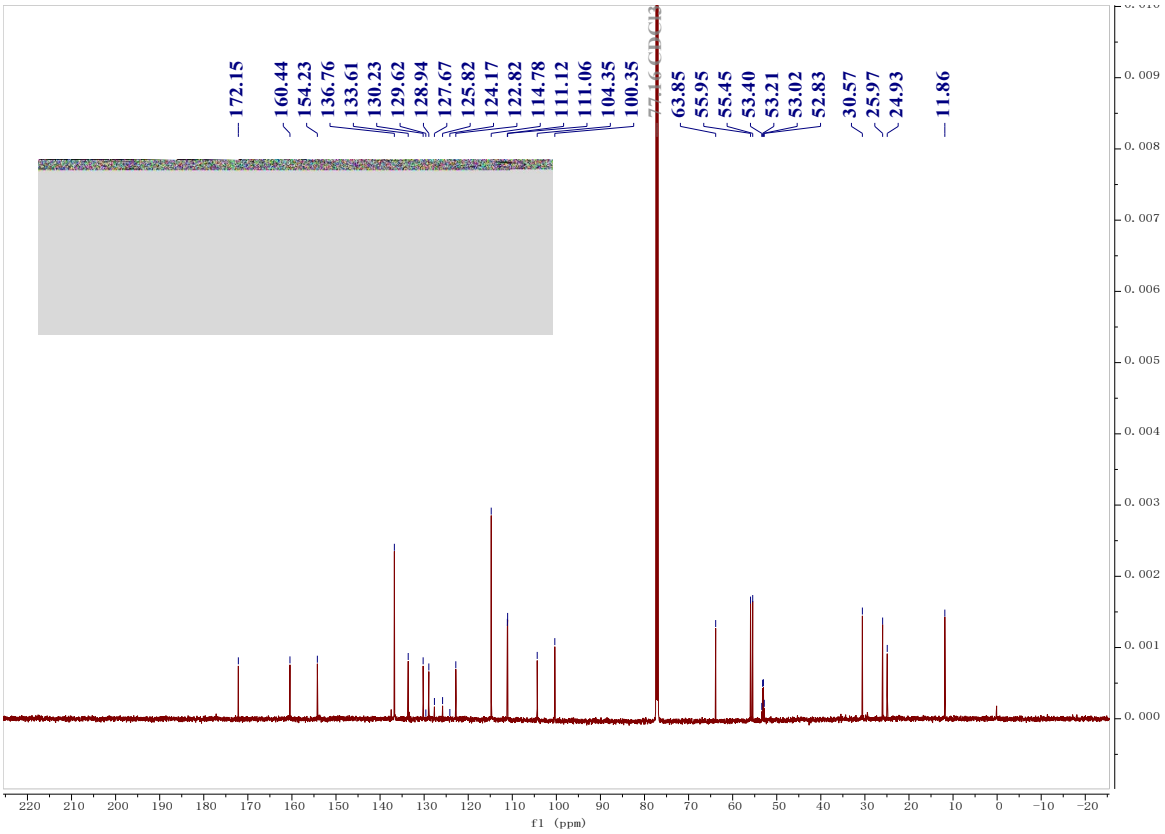
^{13}C NMR Spectrum of Compound **16**



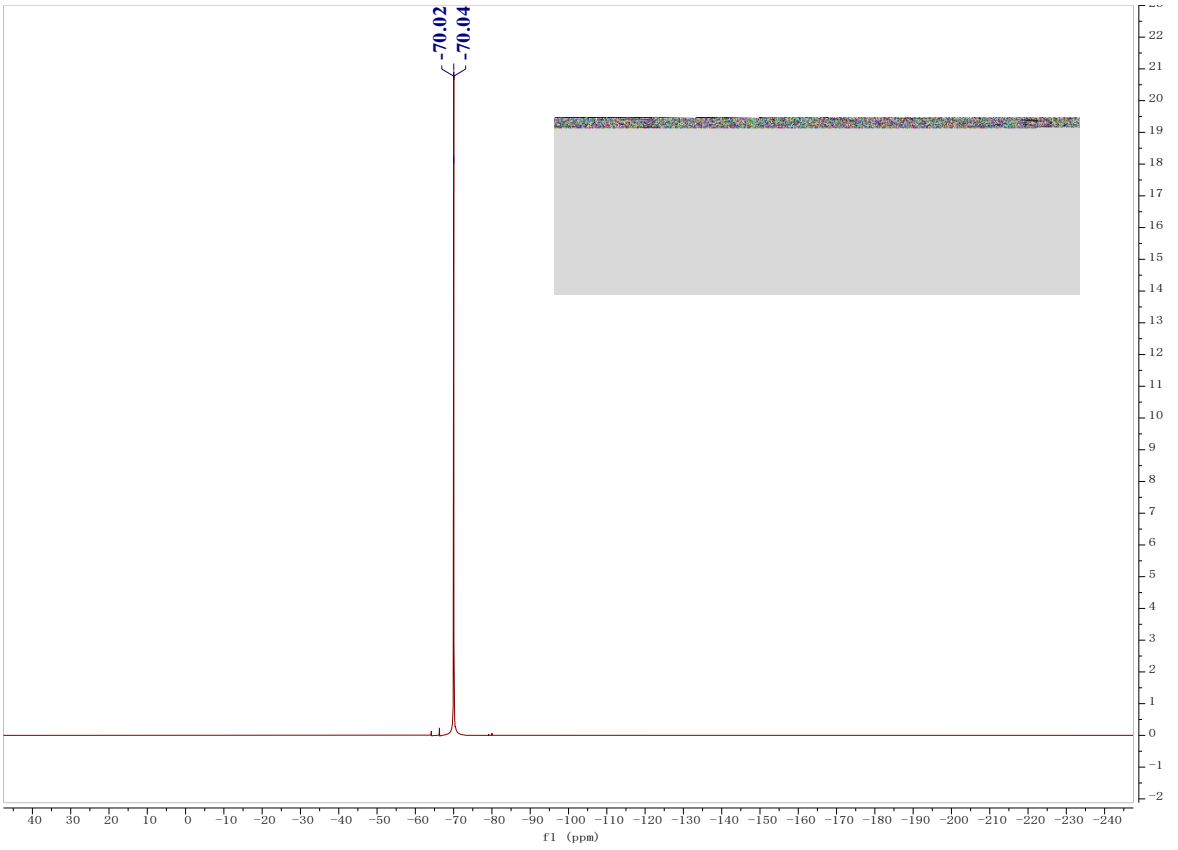
^{19}F NMR Spectrum of Compound **16**



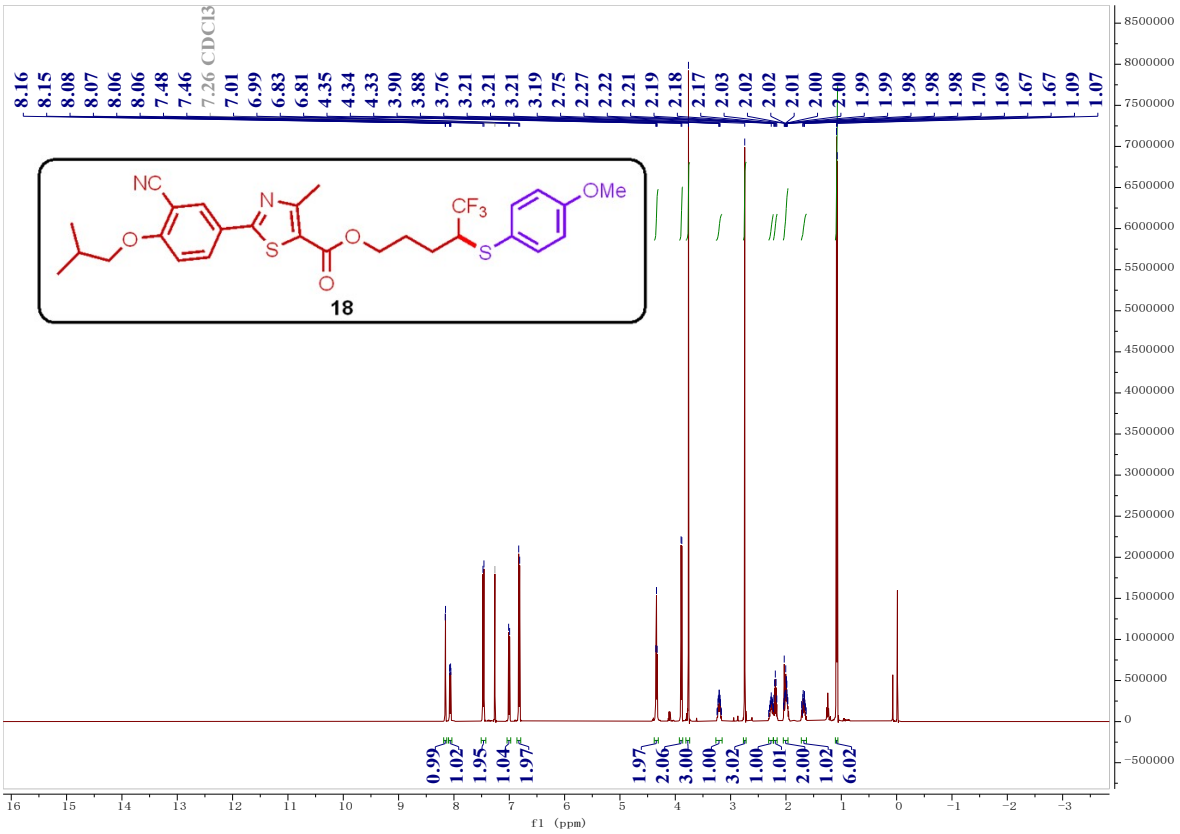
^{1}H NMR Spectrum of Compound **17**



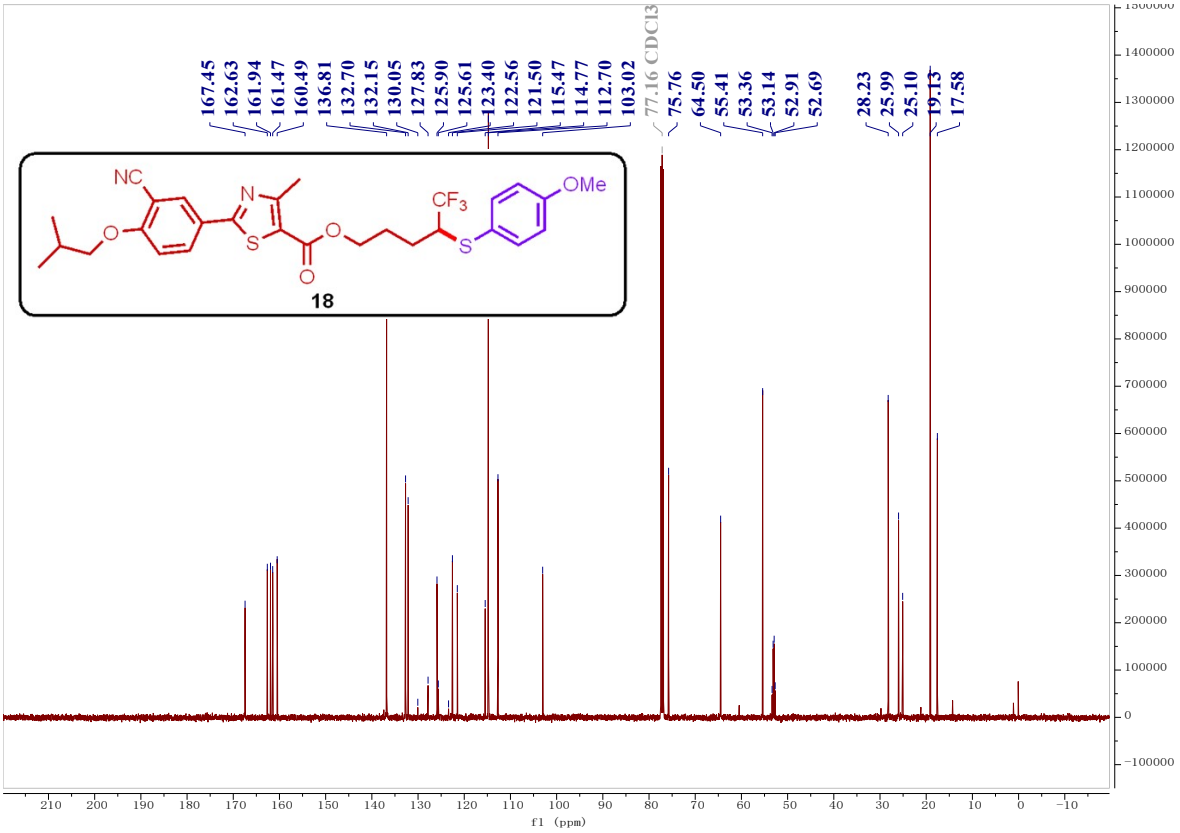
^{13}C NMR Spectrum of Compound **17**



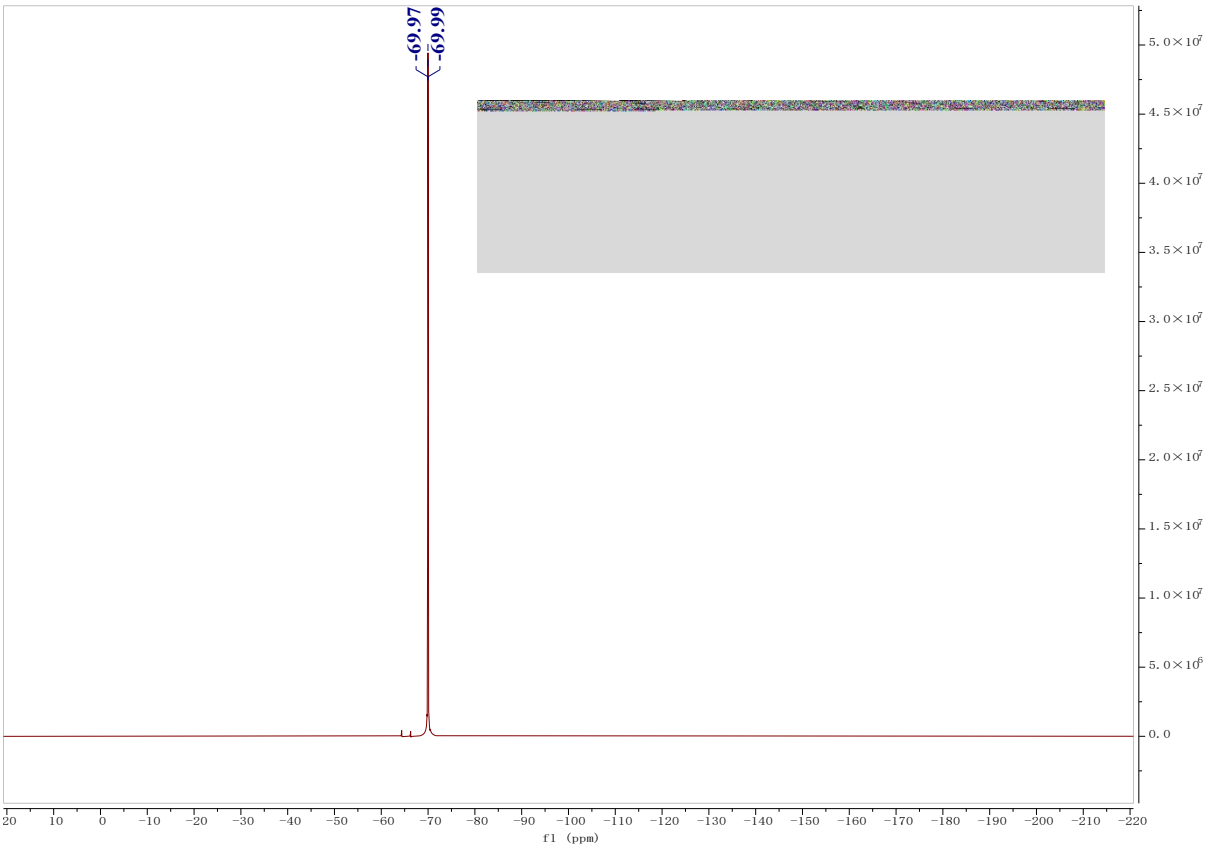
^{19}F NMR Spectrum of Compound **17**



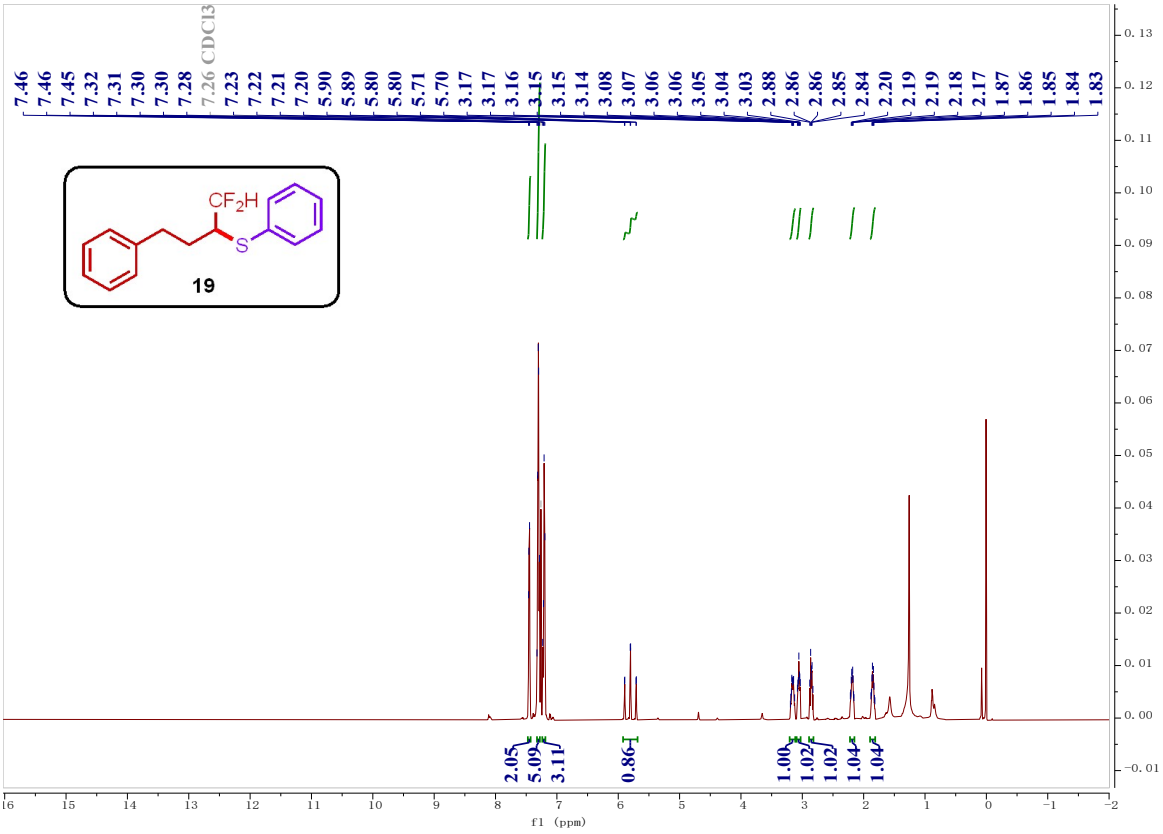
^{1}H NMR Spectrum of Compound **18**



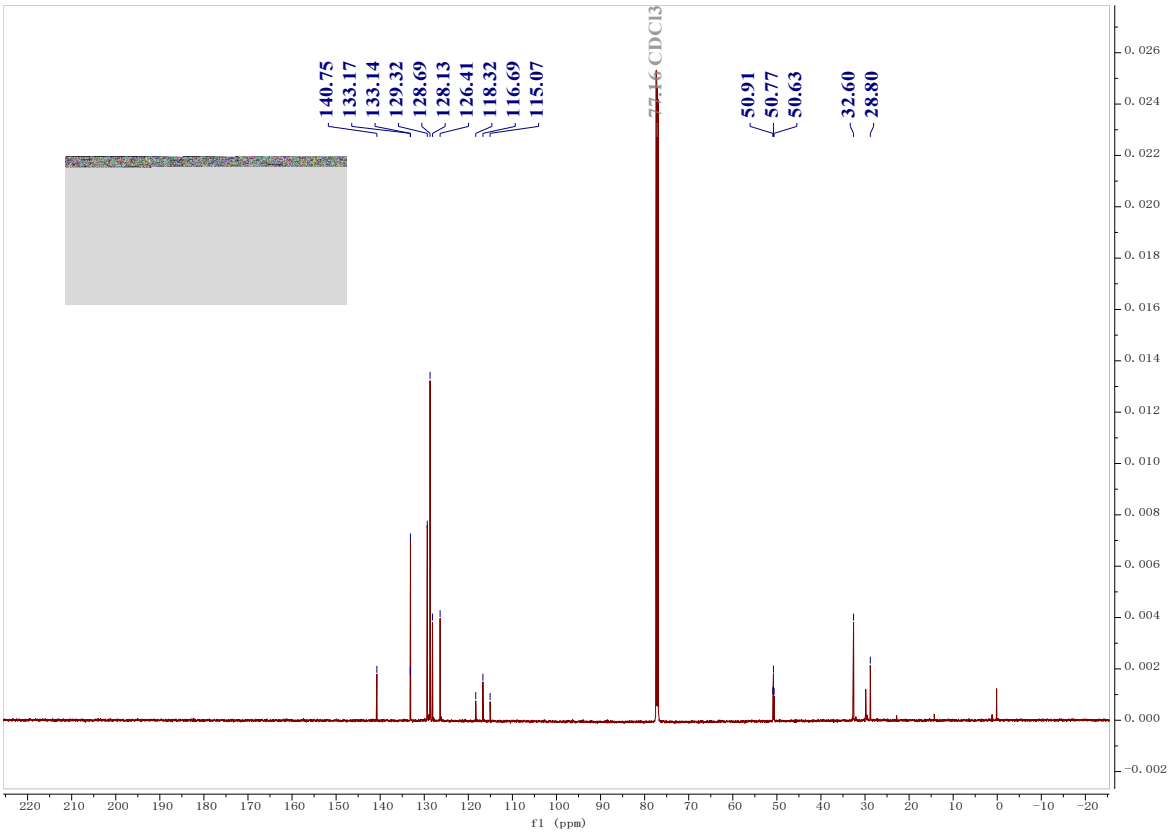
^{13}C NMR Spectrum of Compound **18**



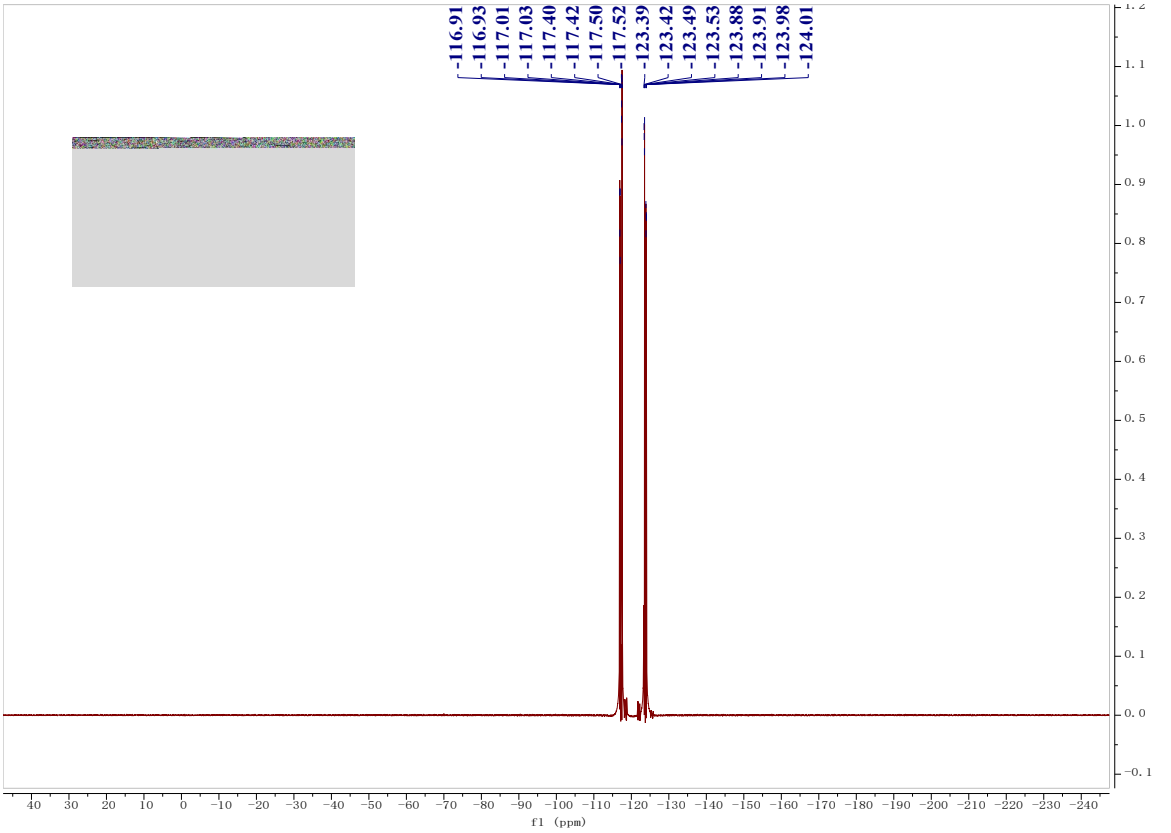
^{19}F NMR Spectrum of Compound **18**



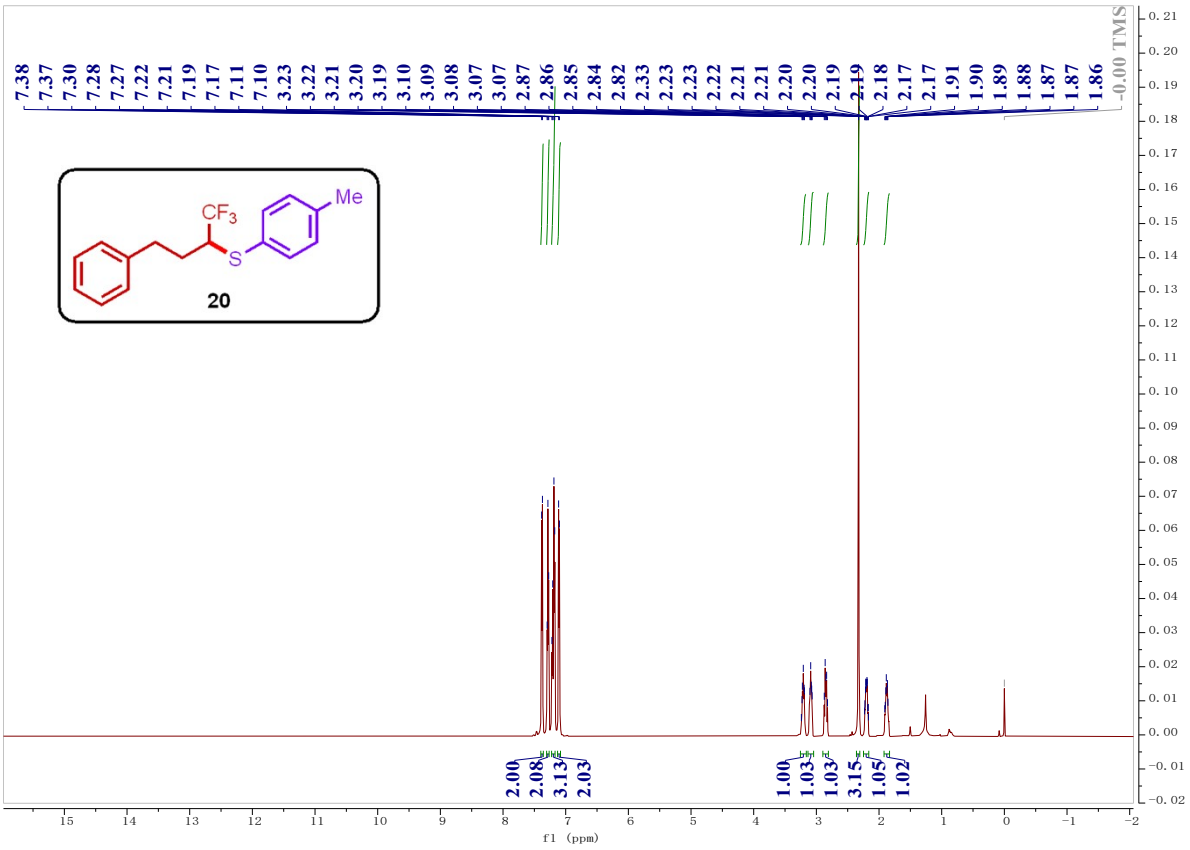
^{1}H NMR Spectrum of Compound **19**



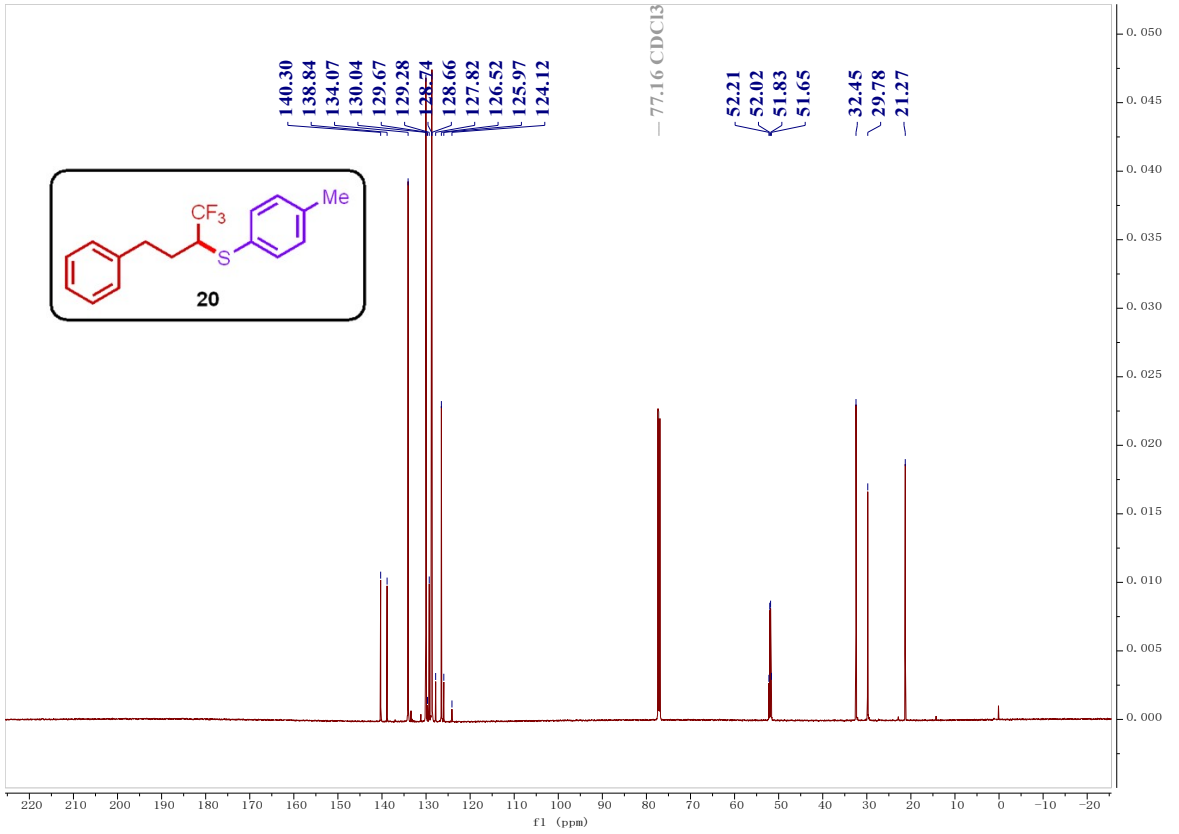
^{13}C NMR Spectrum of Compound **19**



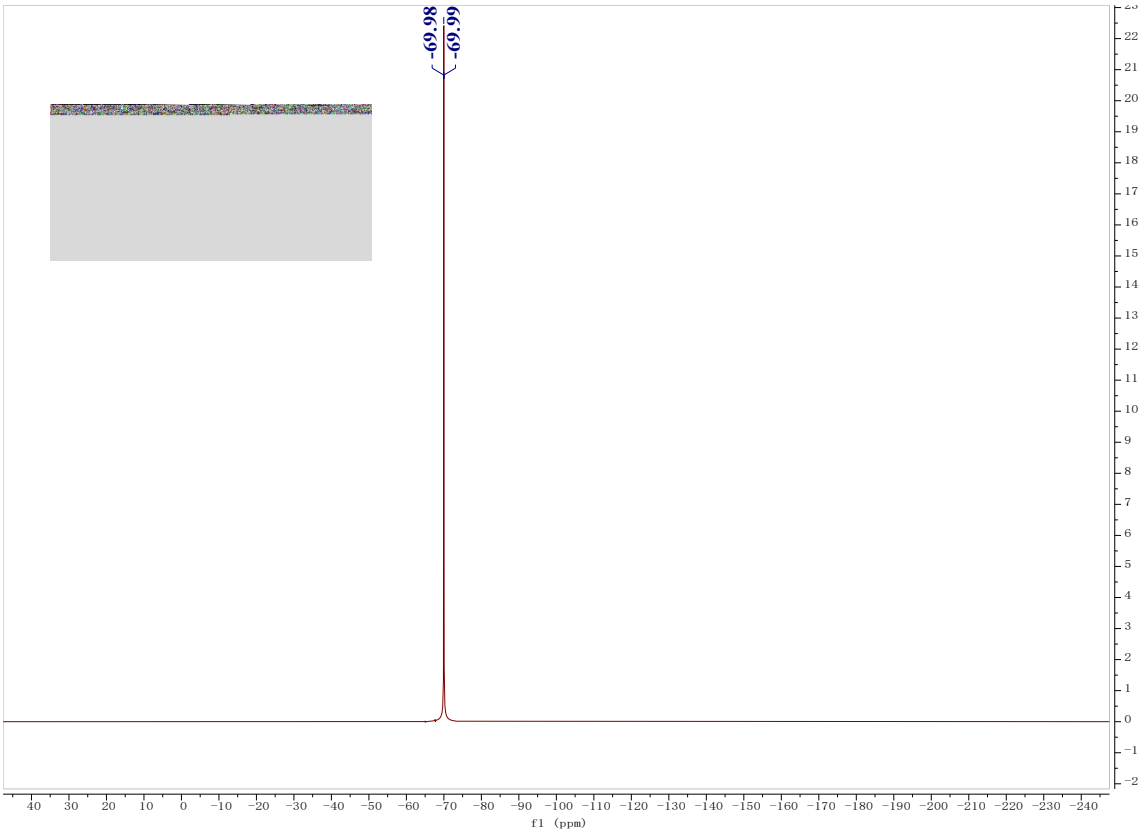
^{19}F NMR Spectrum of Compound **19**



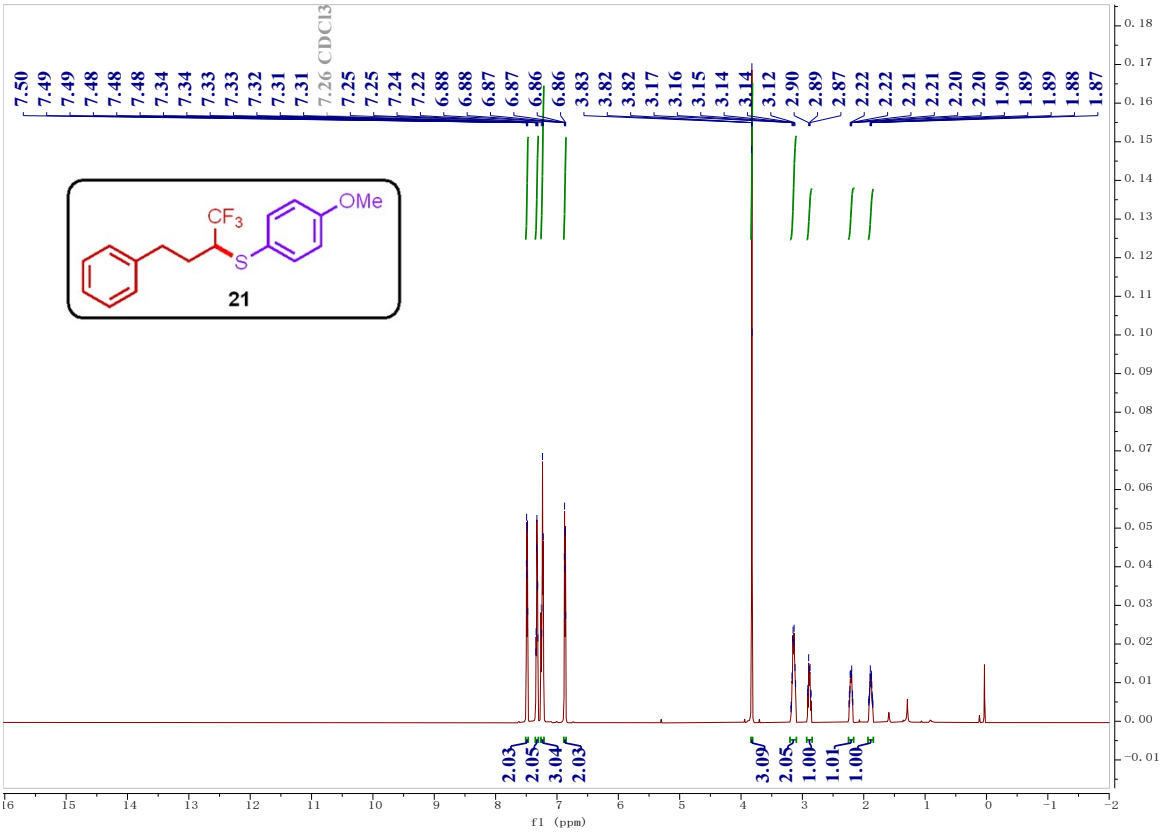
^{1}H NMR Spectrum of Compound **20**



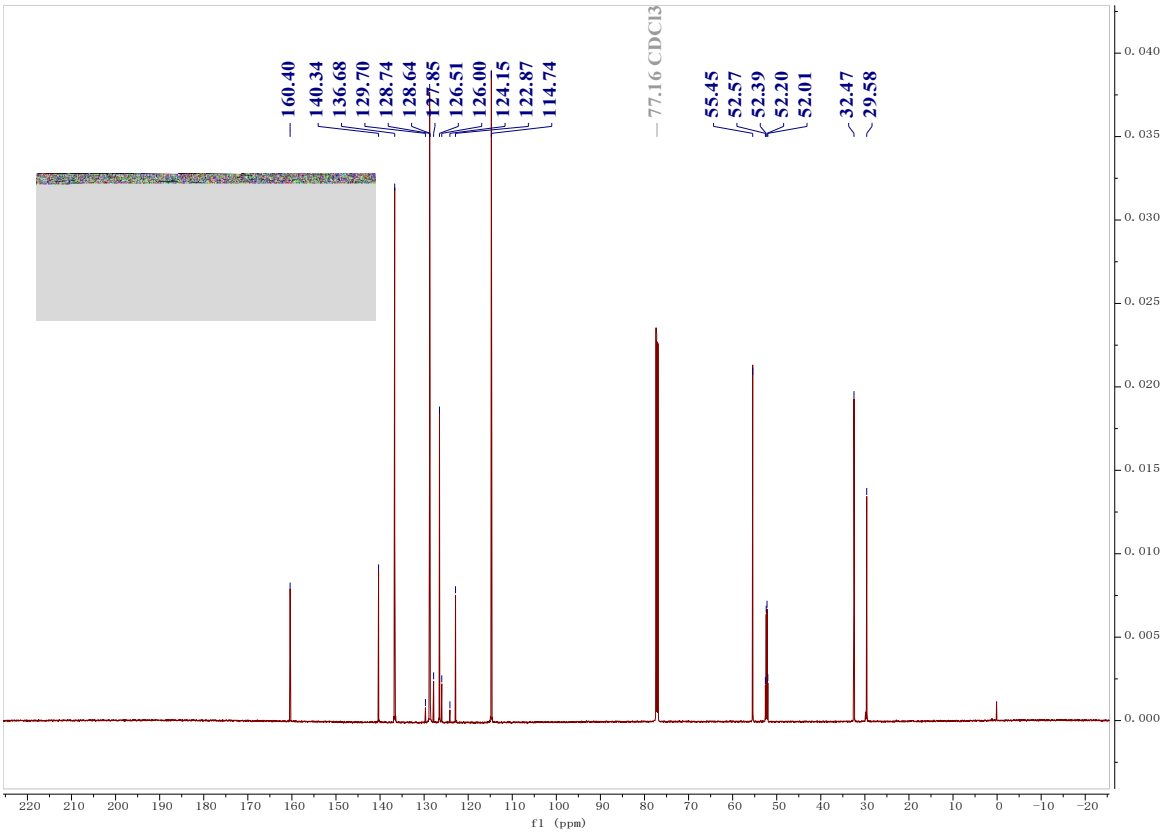
^{13}C NMR Spectrum of Compound **20**



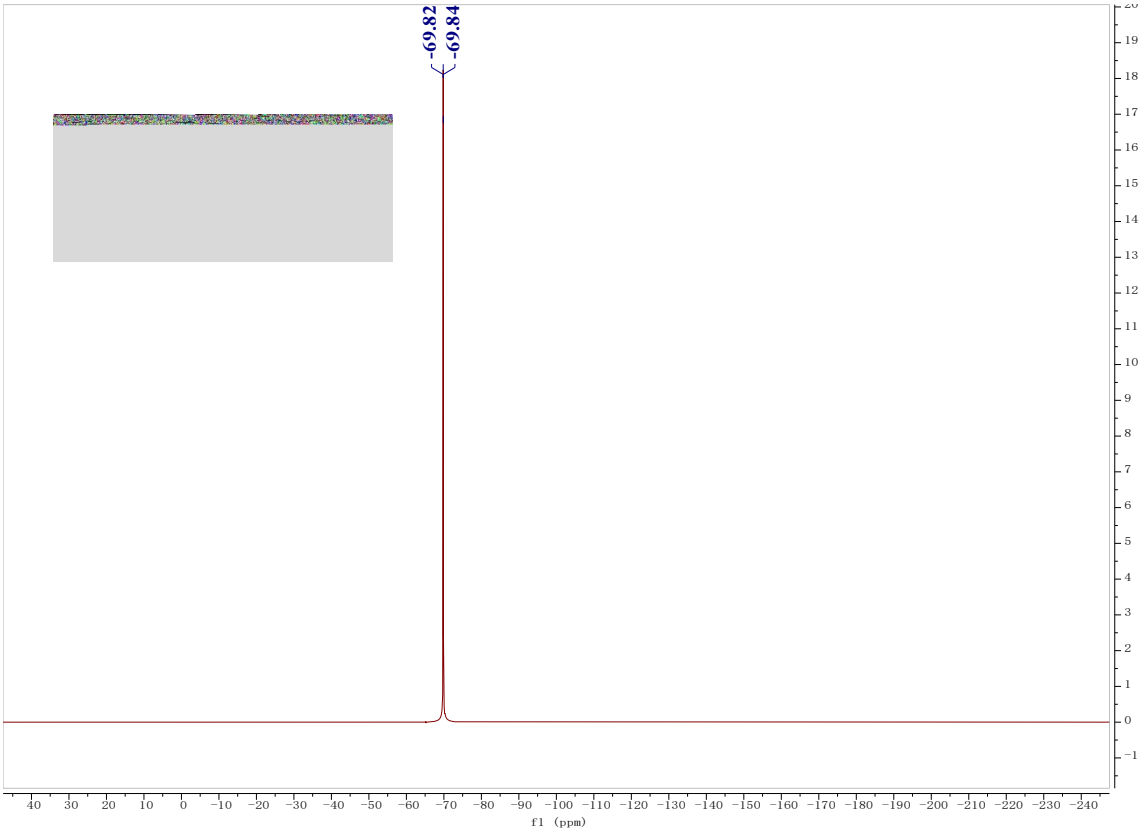
^{19}F NMR Spectrum of Compound **20**



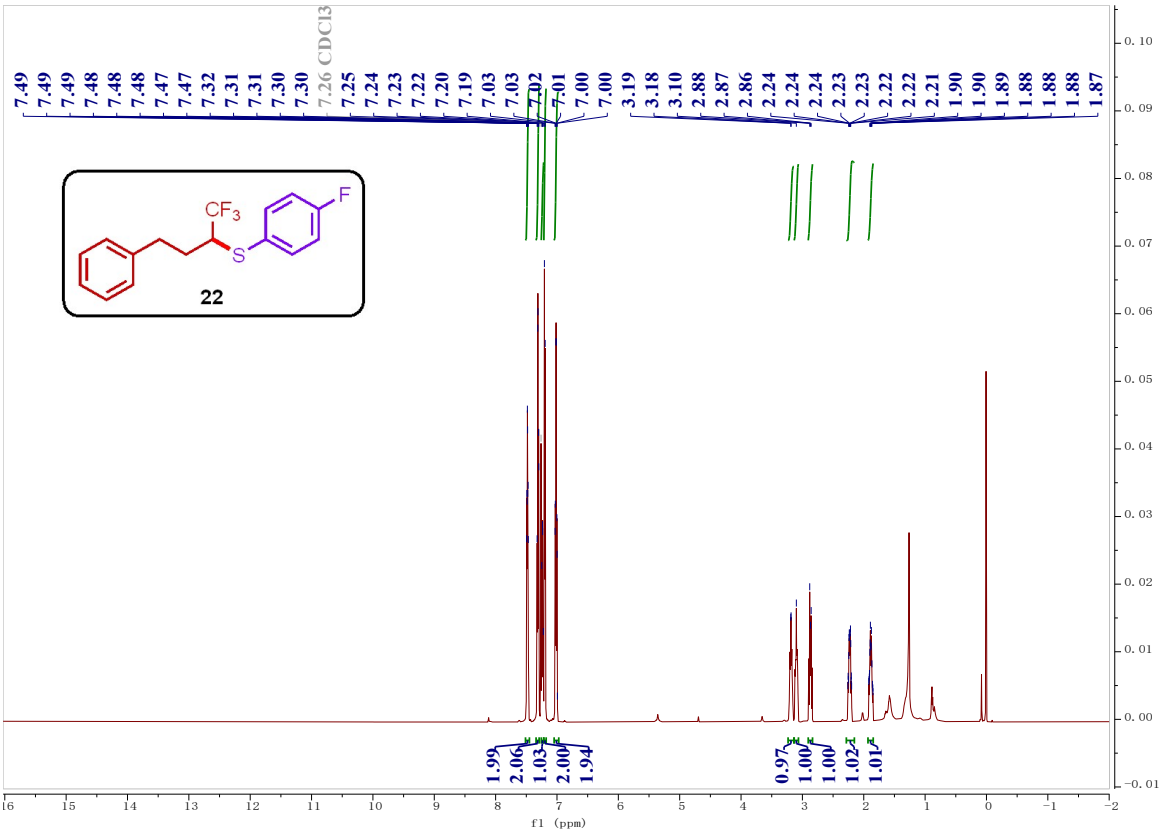
^{1}H NMR Spectrum of Compound **21**



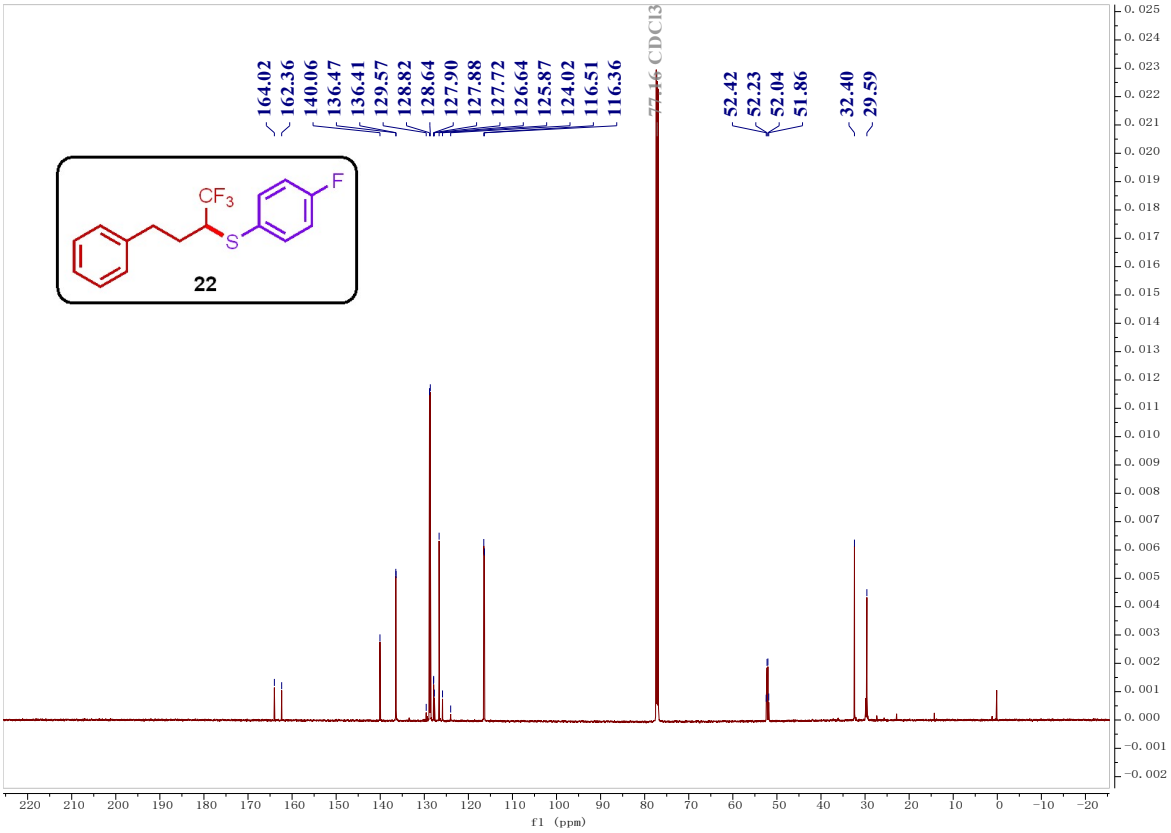
^{13}C NMR Spectrum of Compound **21**



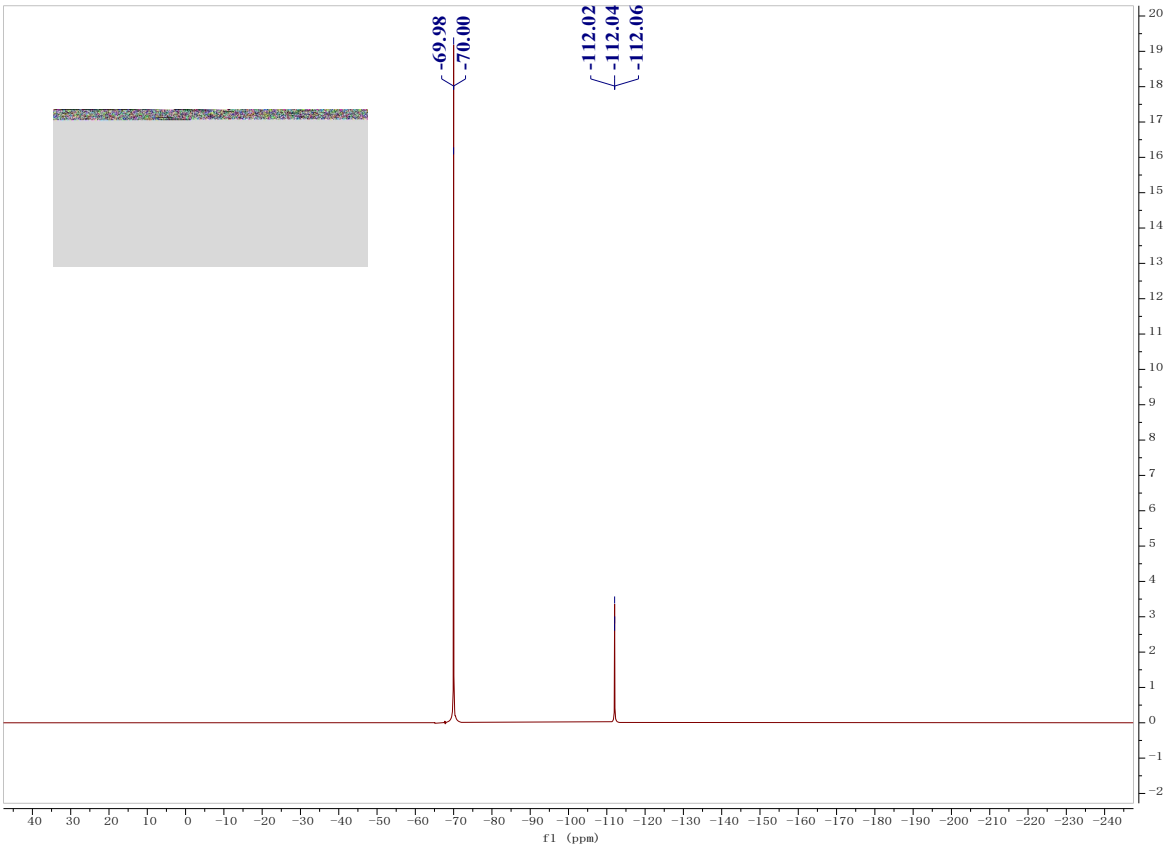
^{19}F NMR Spectrum of Compound **21**



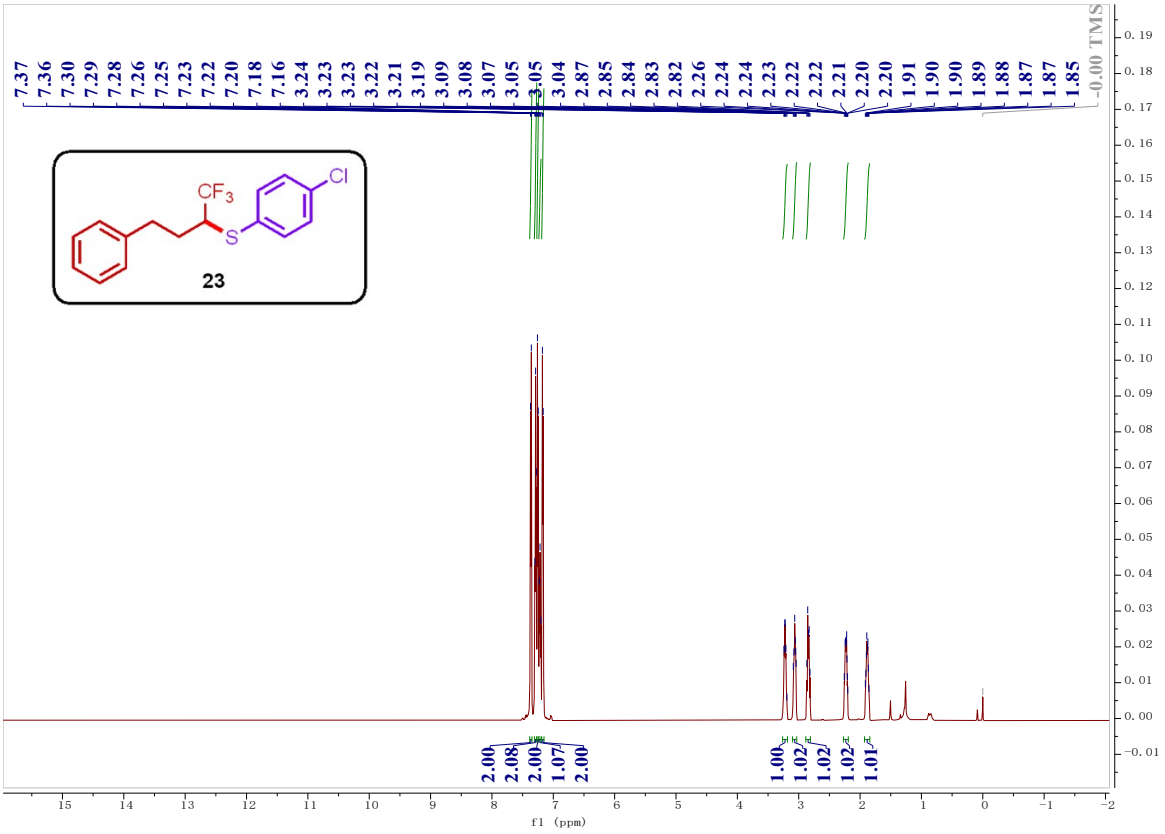
^{1}H NMR Spectrum of Compound **22**



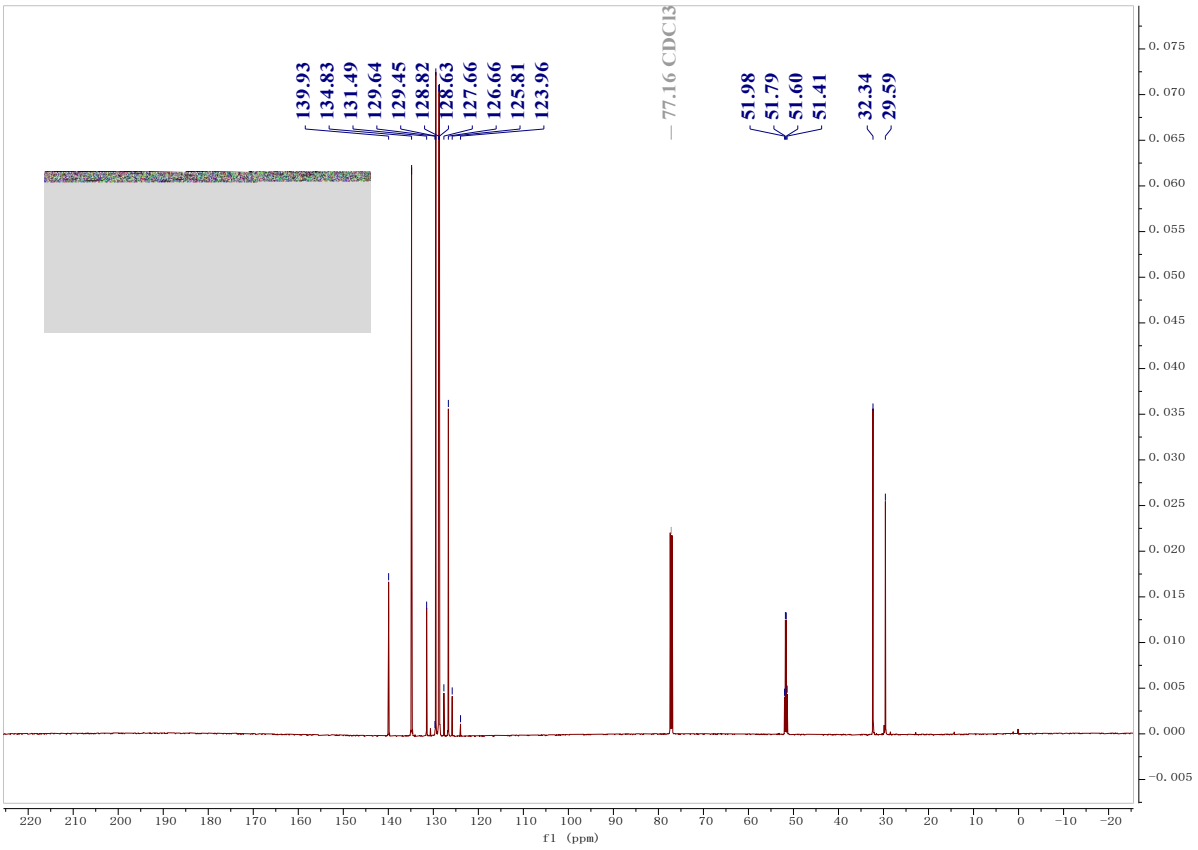
^{13}C NMR Spectrum of Compound **22**



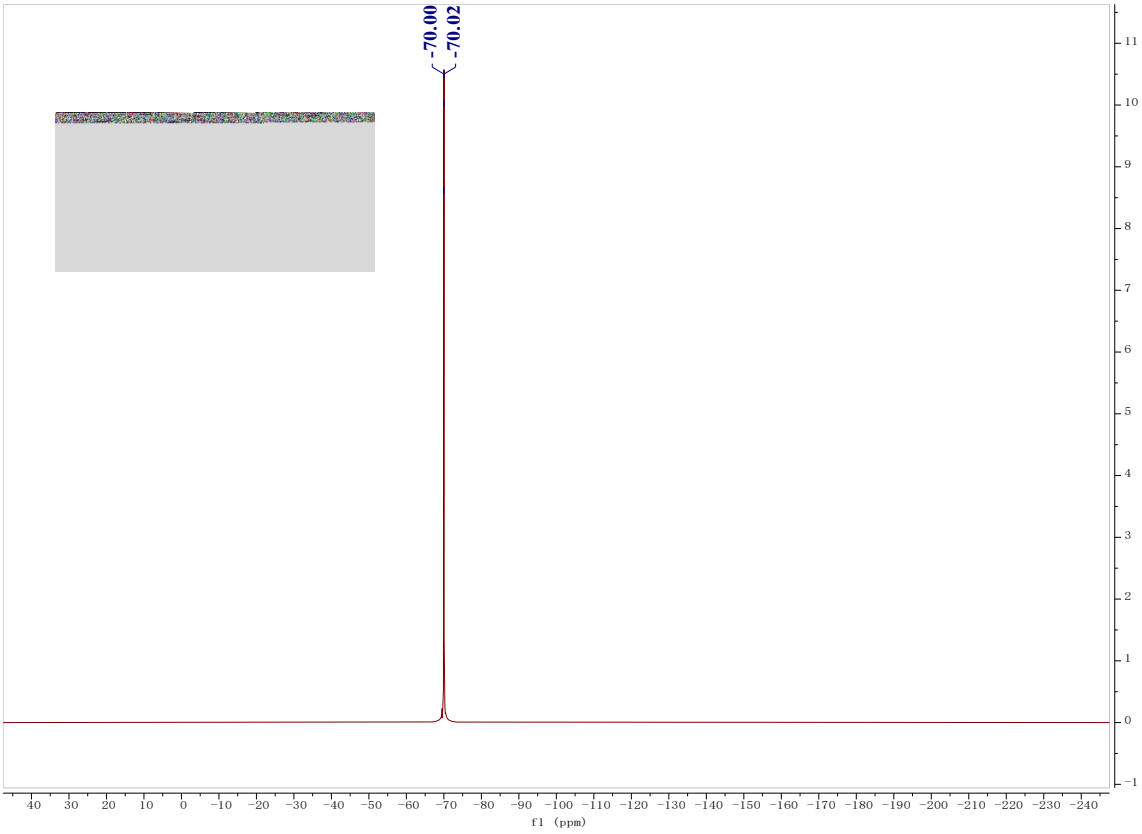
^{19}F NMR Spectrum of Compound **22**



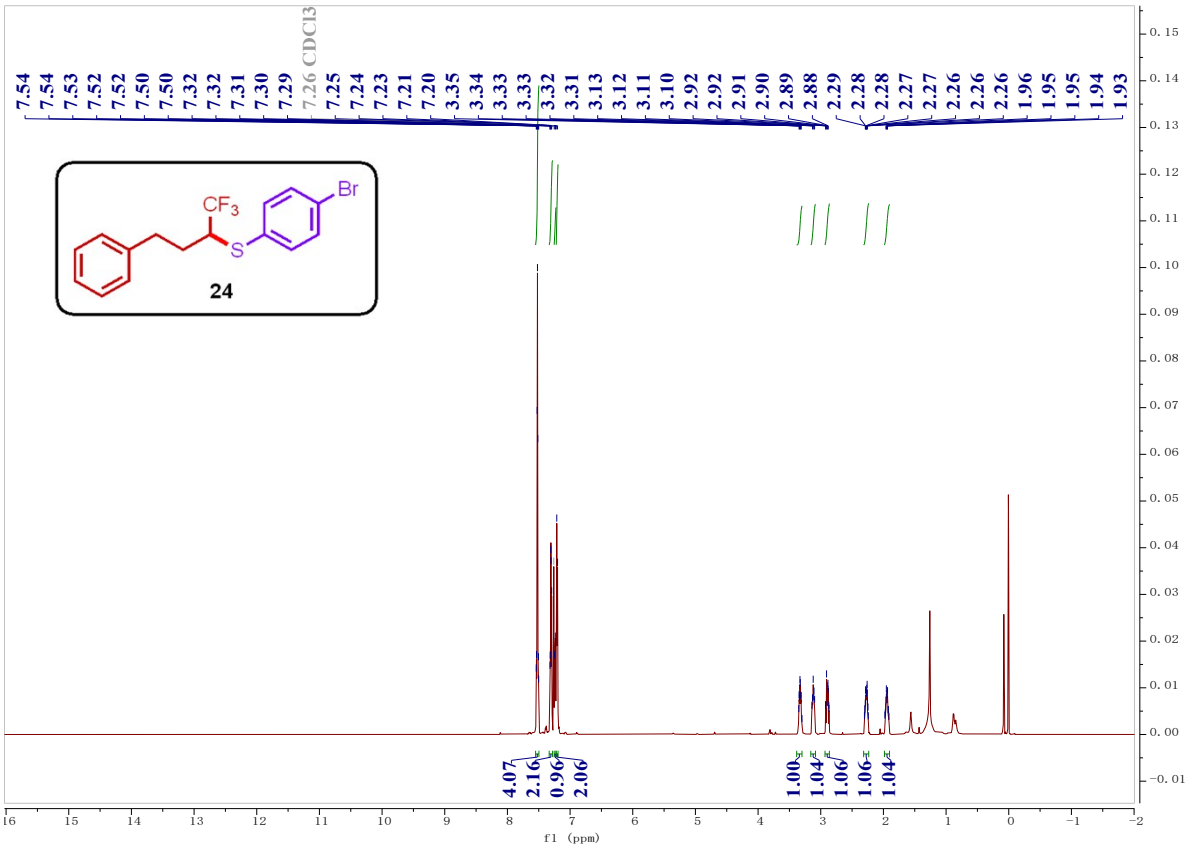
^{1}H NMR Spectrum of Compound **23**



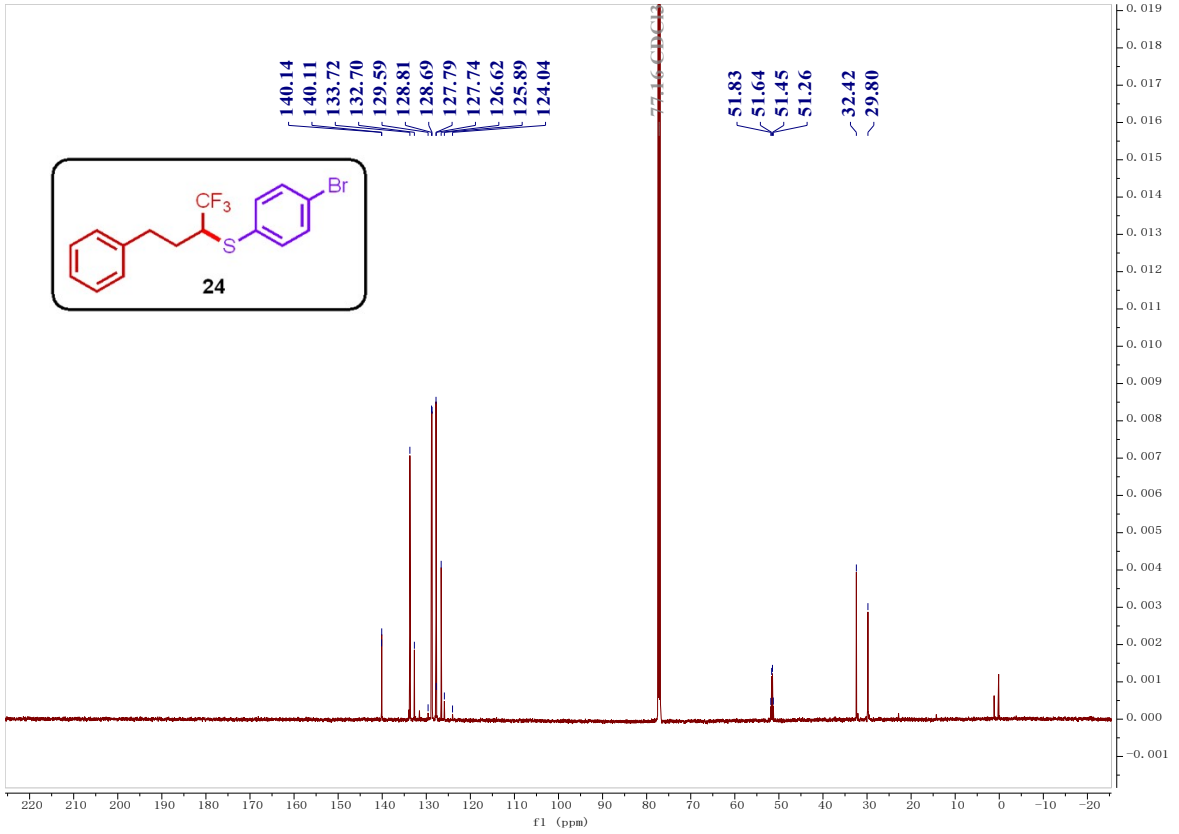
^{13}C NMR Spectrum of Compound **23**



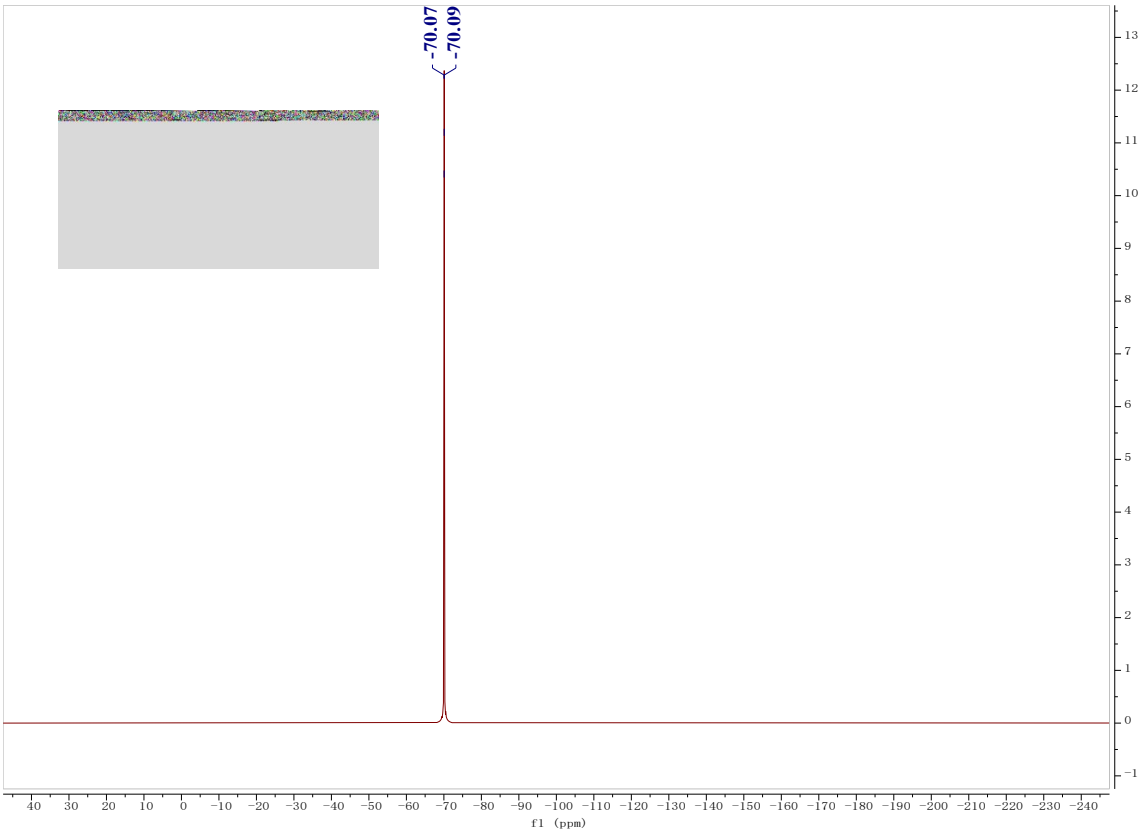
^{19}F NMR Spectrum of Compound **23**



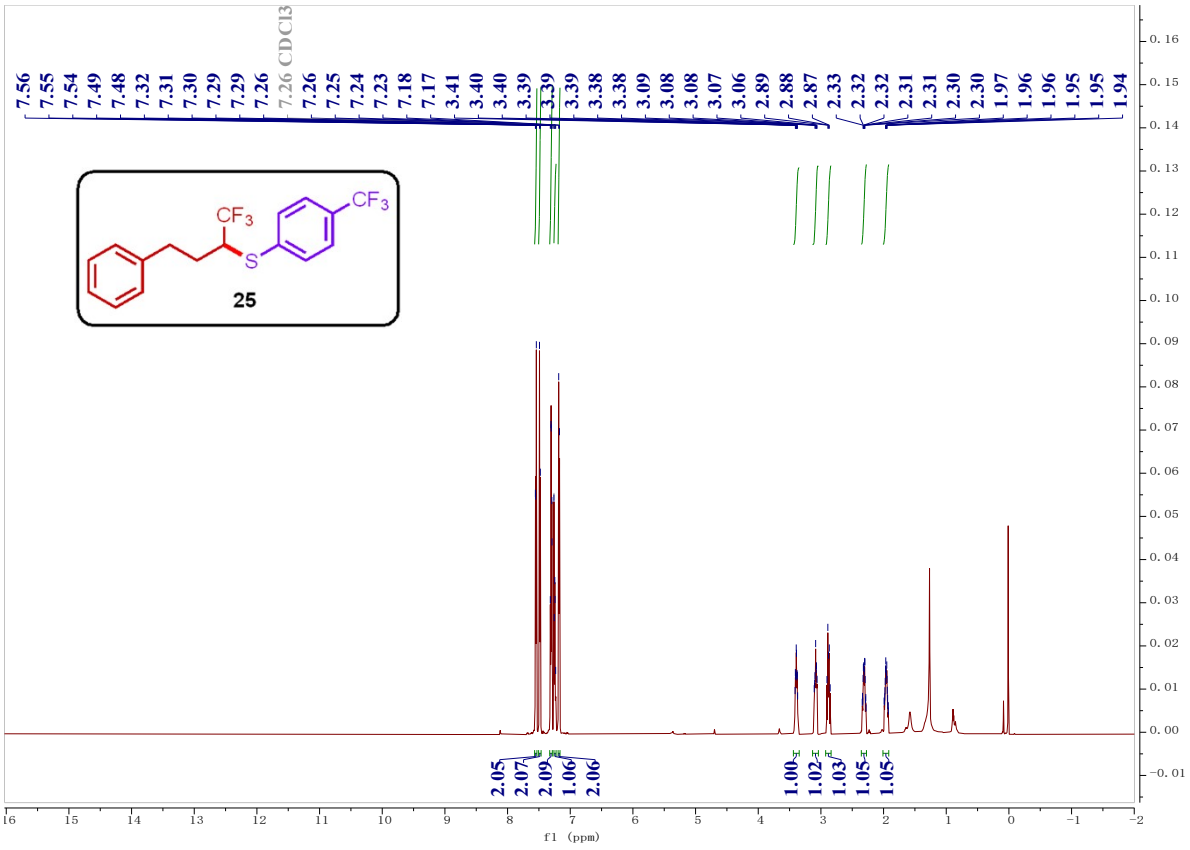
^{1}H NMR Spectrum of Compound **24**



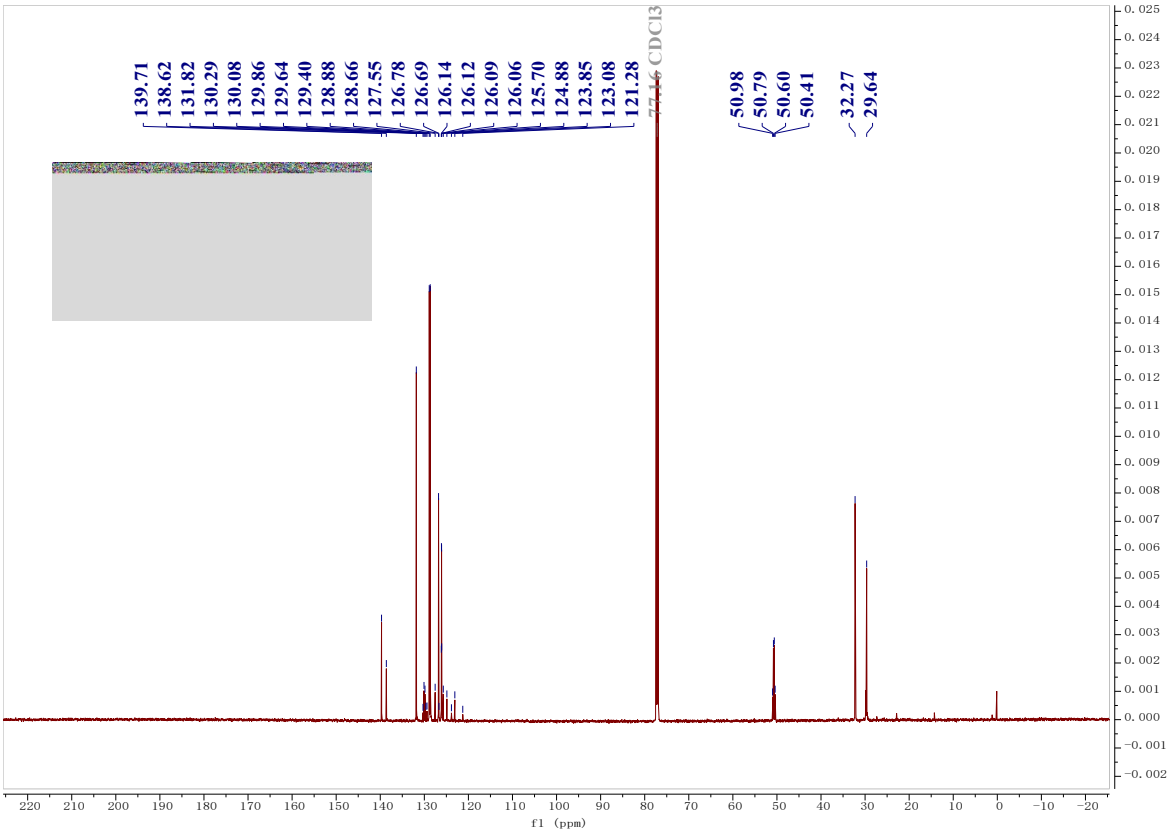
^{13}C NMR Spectrum of Compound **24**



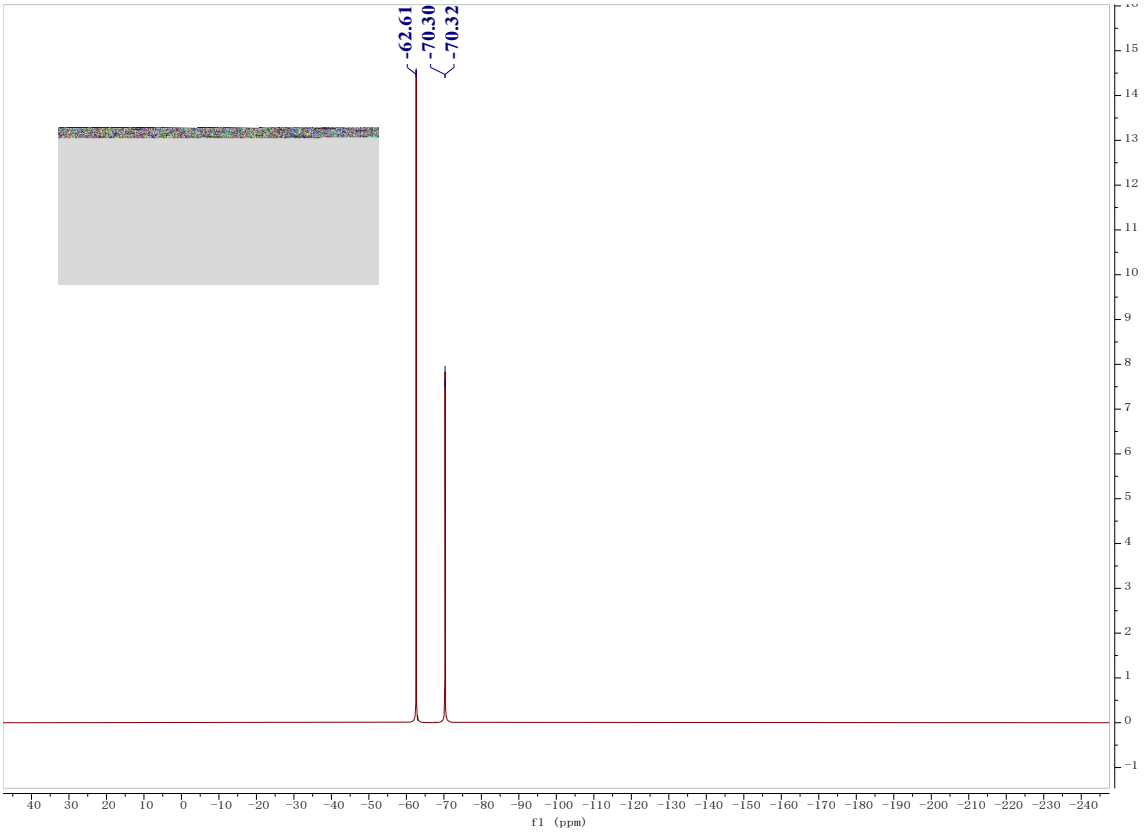
^{19}F NMR Spectrum of Compound **24**



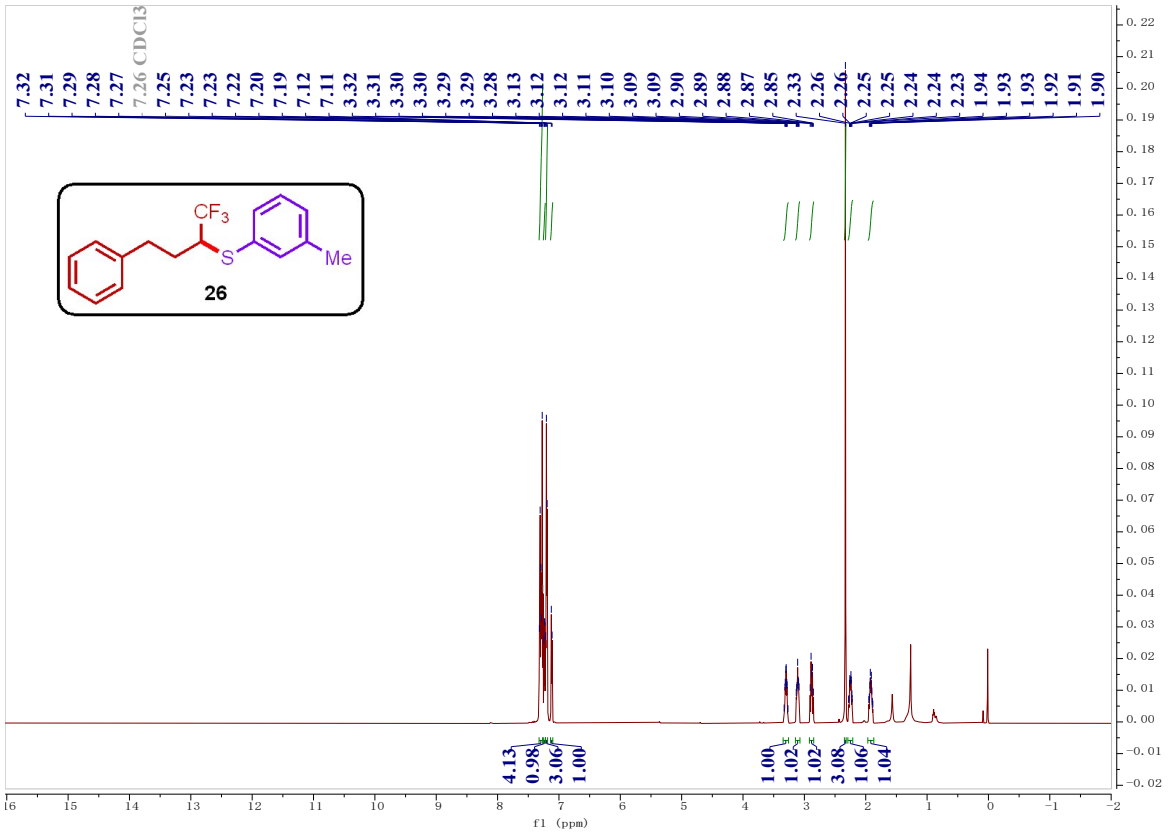
^{1}H NMR Spectrum of Compound **25**



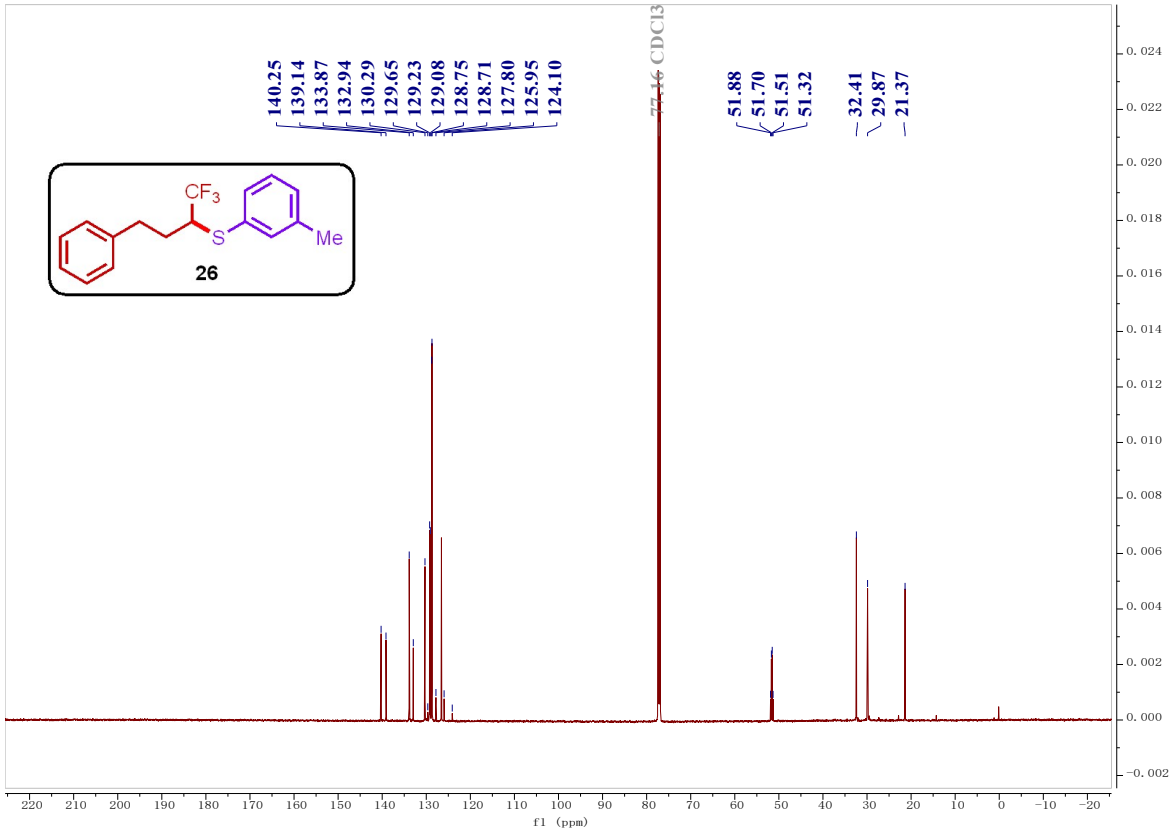
^{13}C NMR Spectrum of Compound **25**



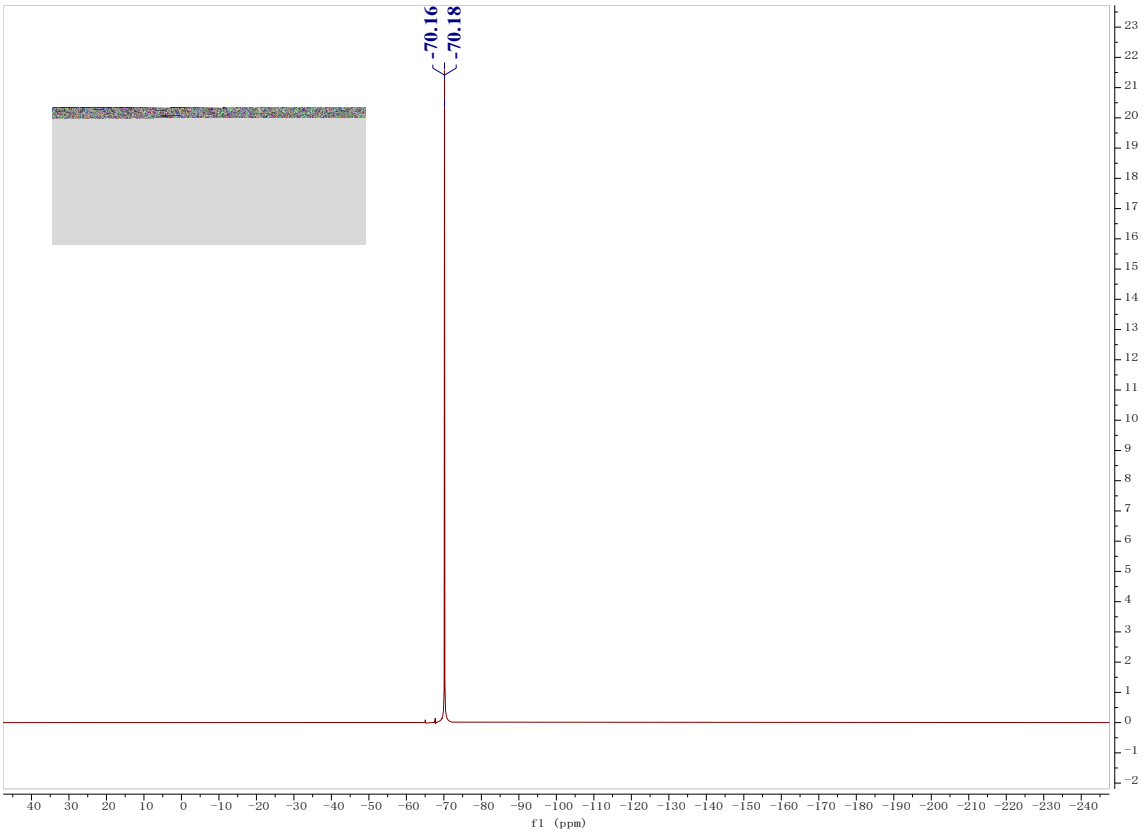
^{19}F NMR Spectrum of Compound **25**



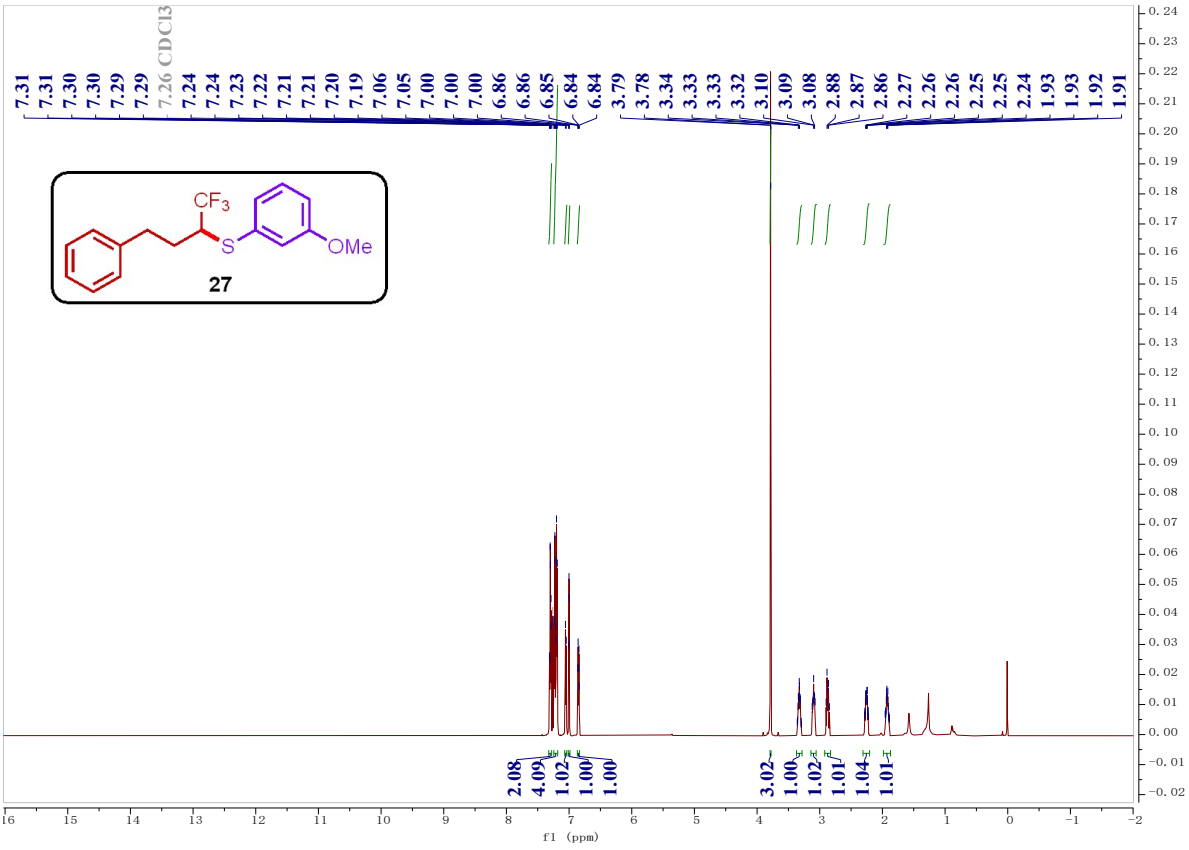
^{1}H NMR Spectrum of Compound **26**



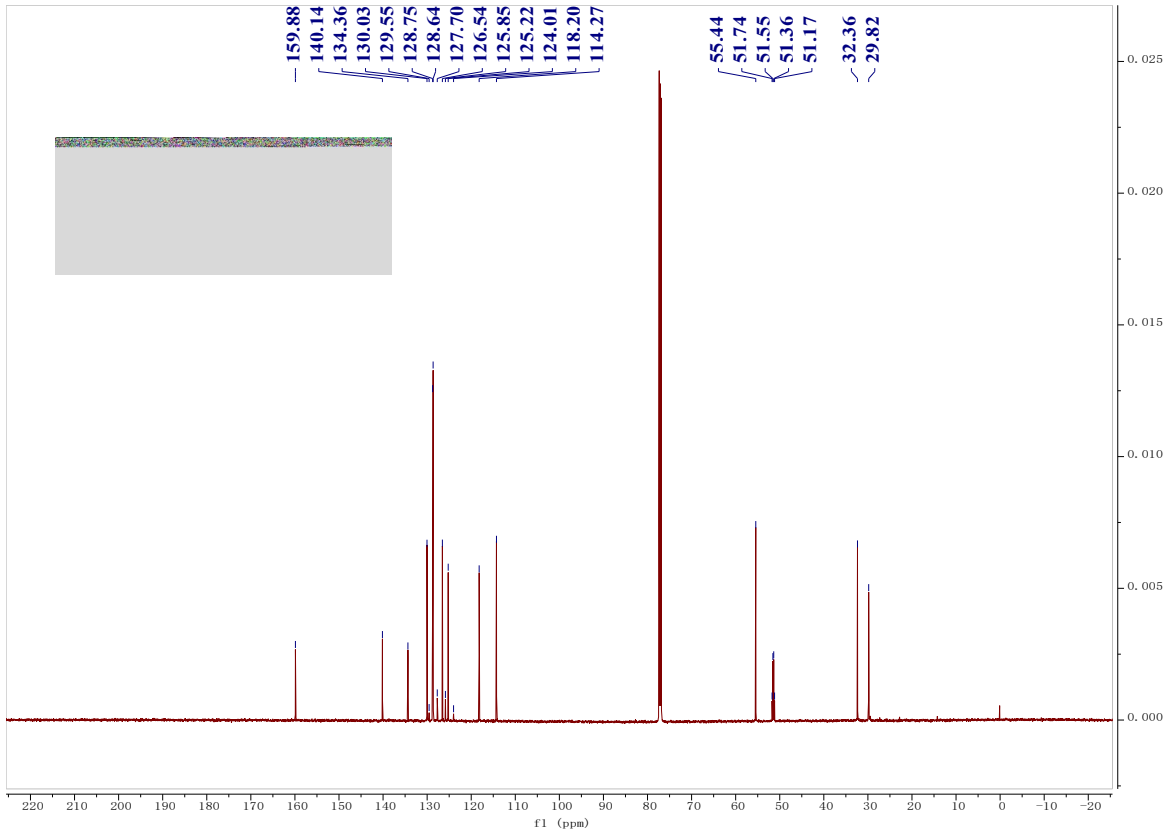
^{13}C NMR Spectrum of Compound **26**



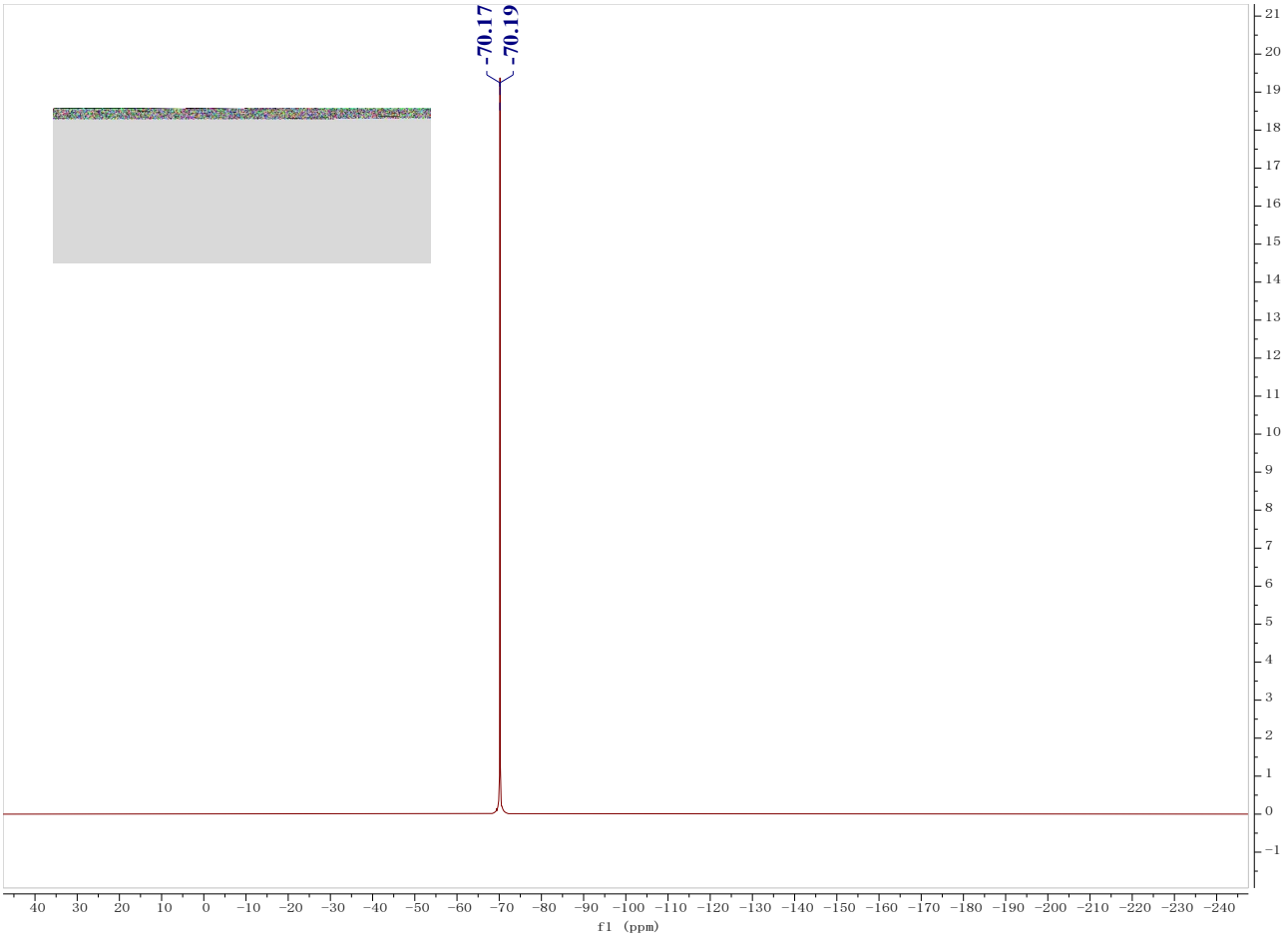
^{19}F NMR Spectrum of Compound **26**



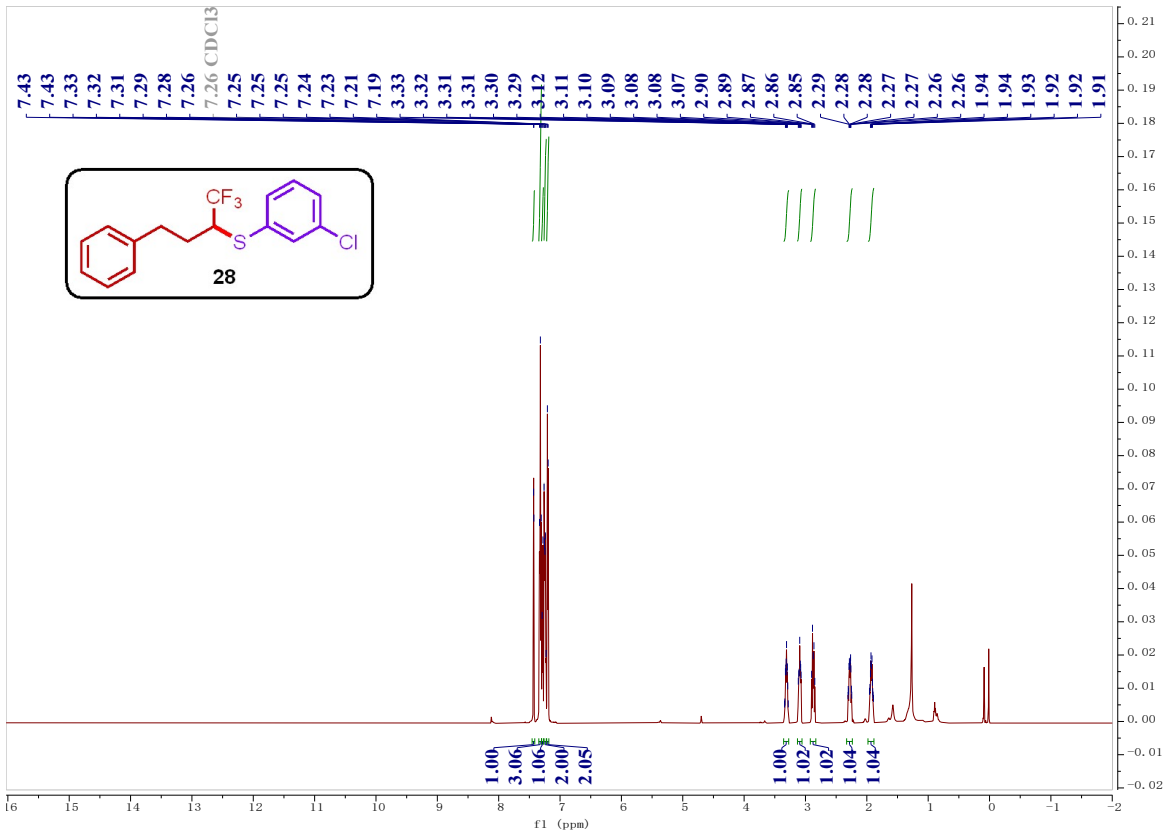
^{1}H NMR Spectrum of Compound **27**



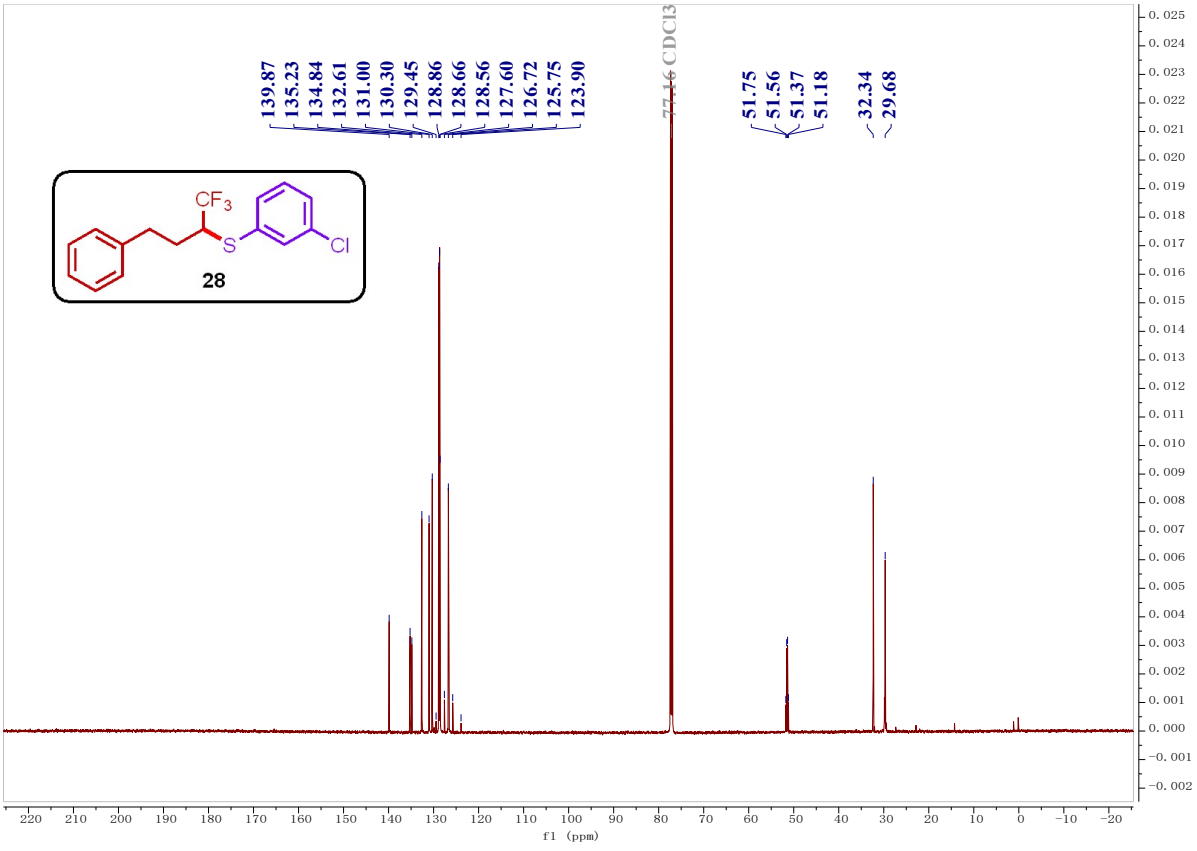
^{13}C NMR Spectrum of Compound **27**



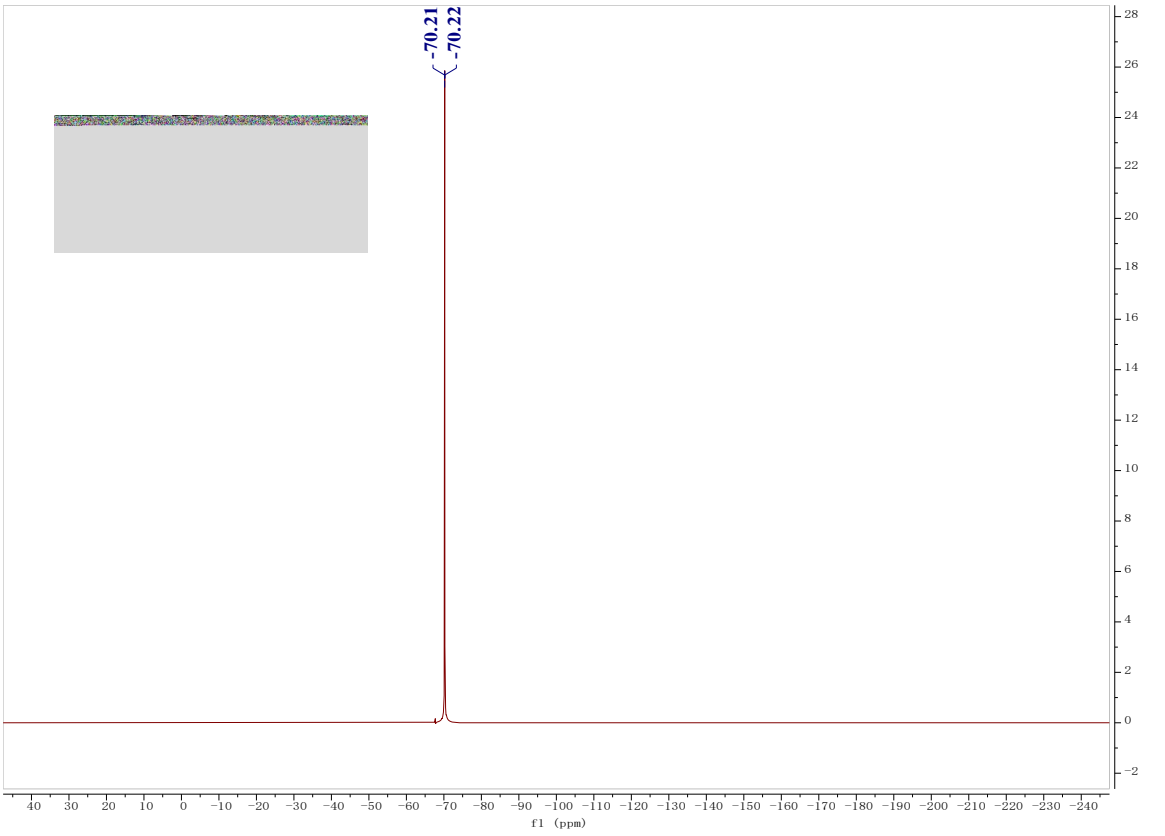
^{19}F NMR Spectrum of Compound **27**



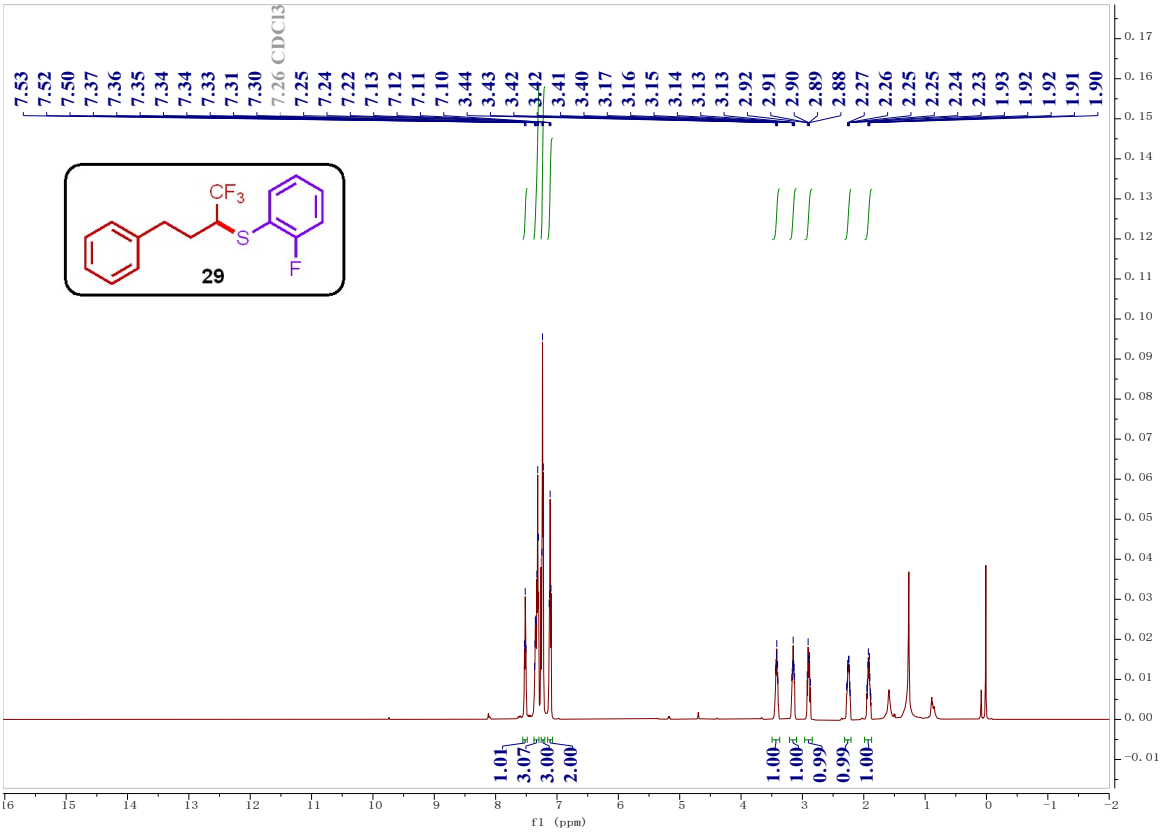
^{1}H NMR Spectrum of Compound **28**



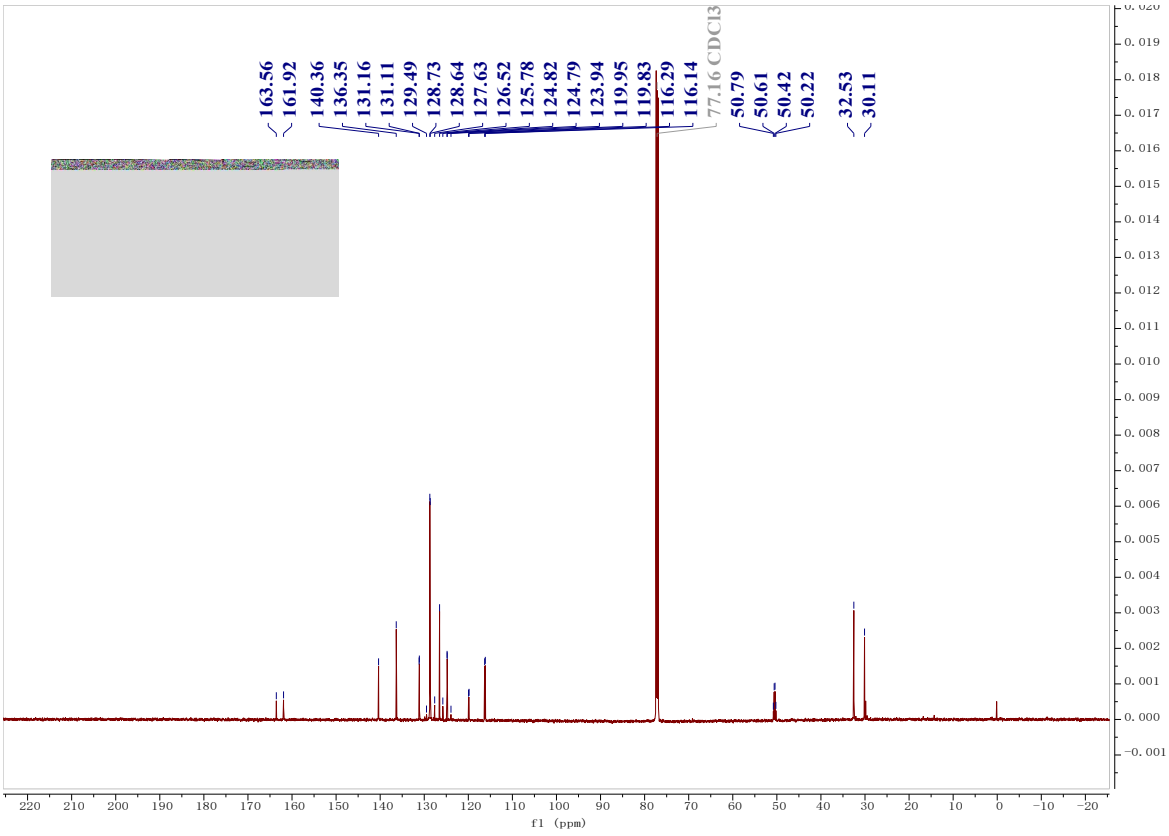
^{13}C NMR Spectrum of Compound **28**



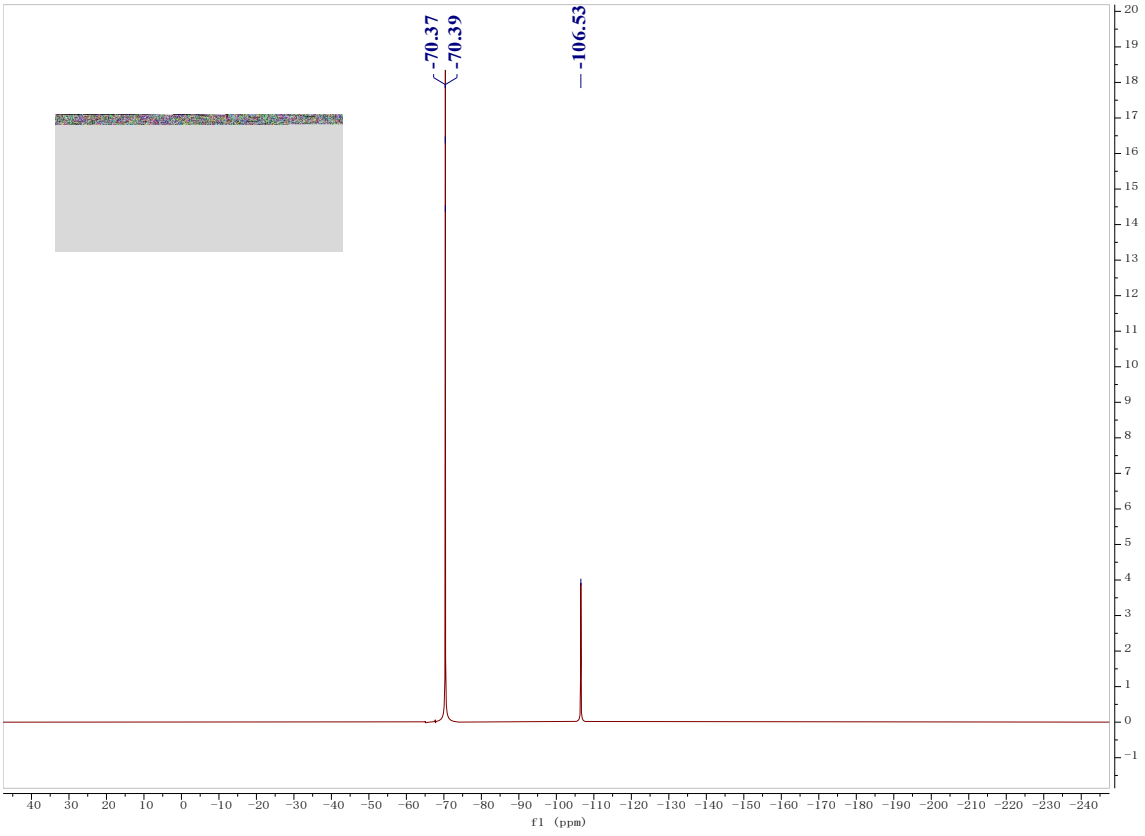
^{19}F NMR Spectrum of Compound **28**



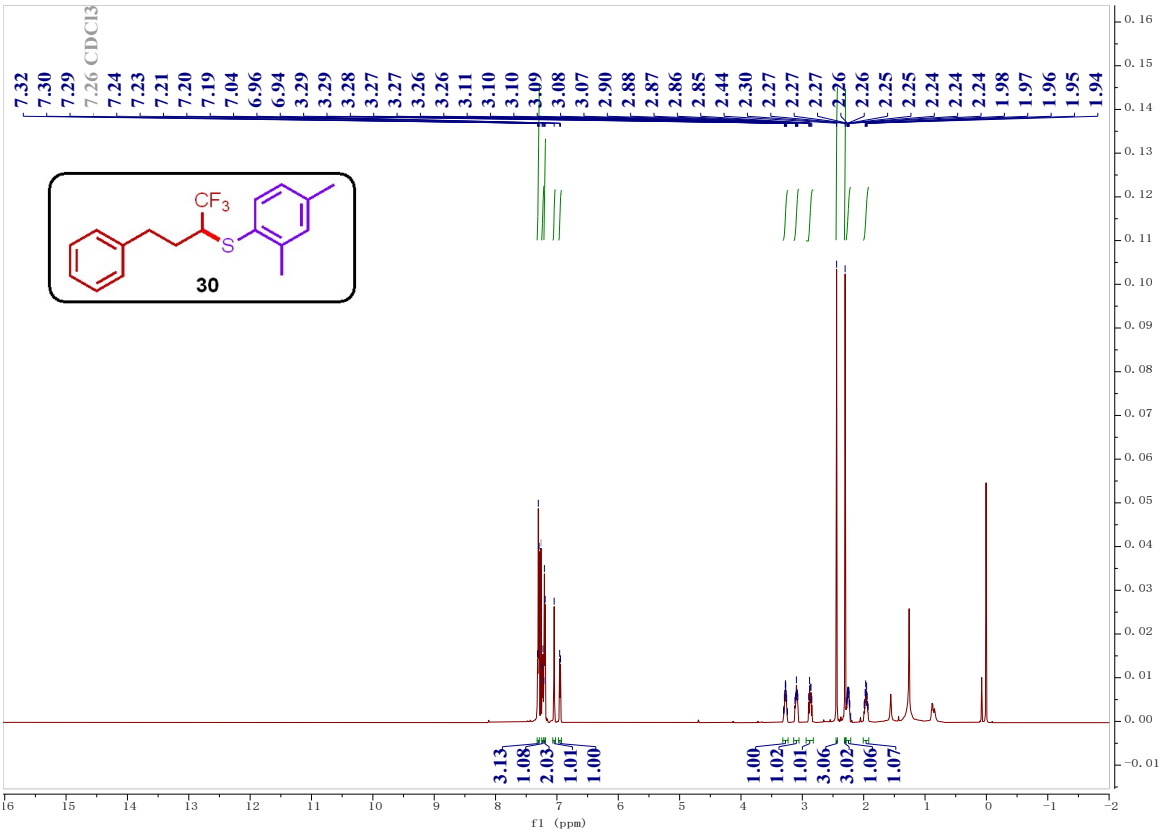
^{1}H NMR Spectrum of Compound **29**



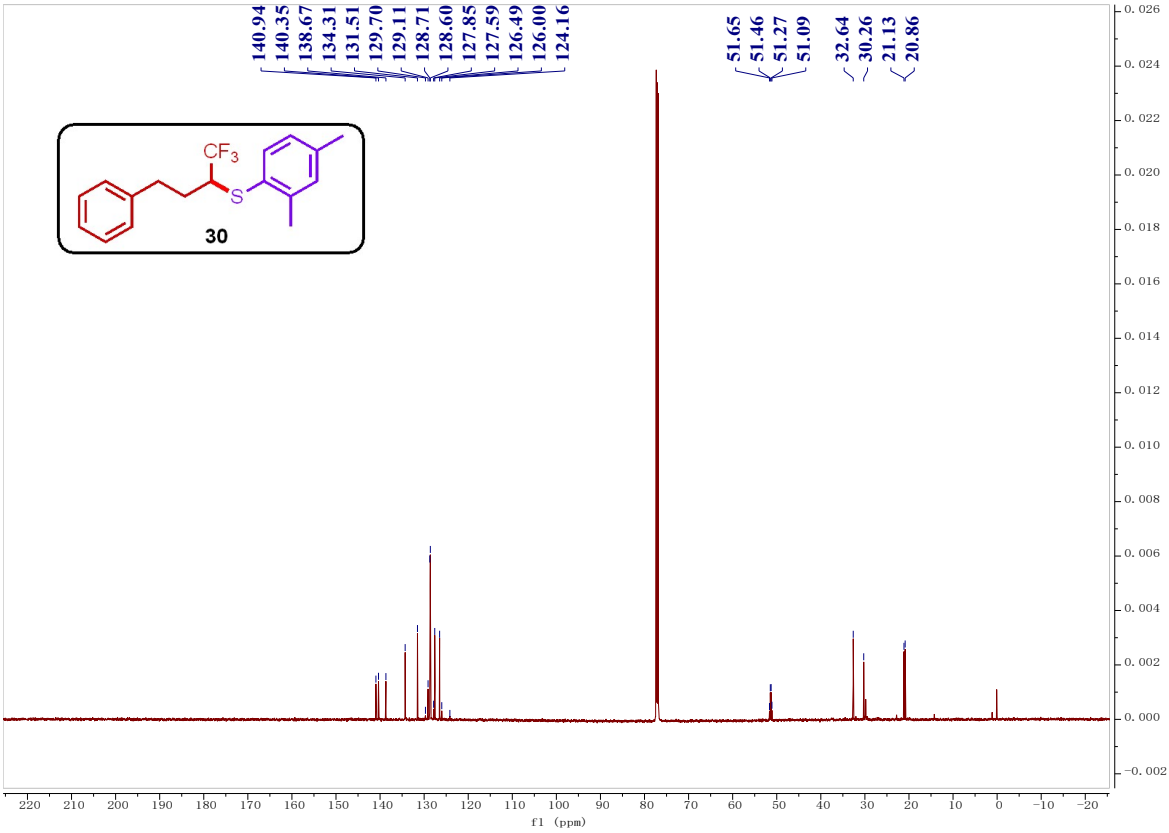
^{13}C NMR Spectrum of Compound **29**



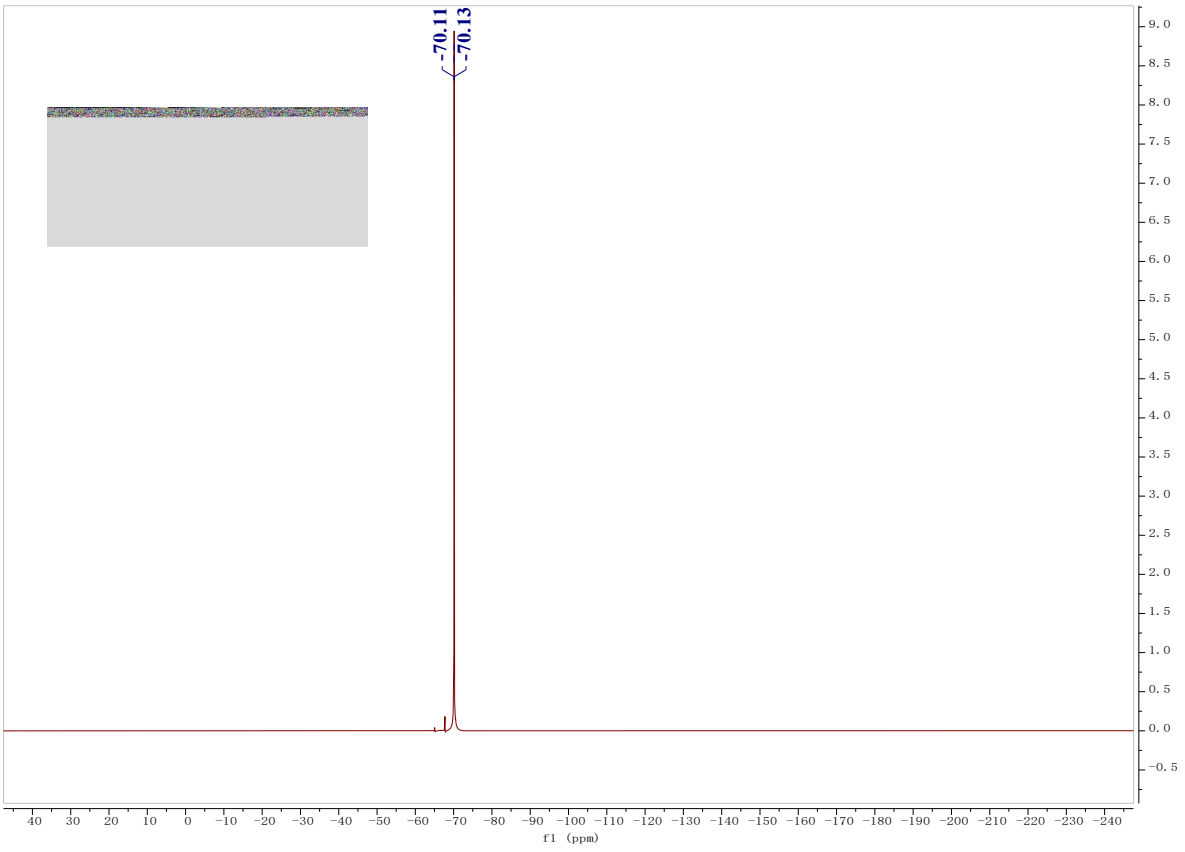
^{19}F NMR Spectrum of Compound **29**



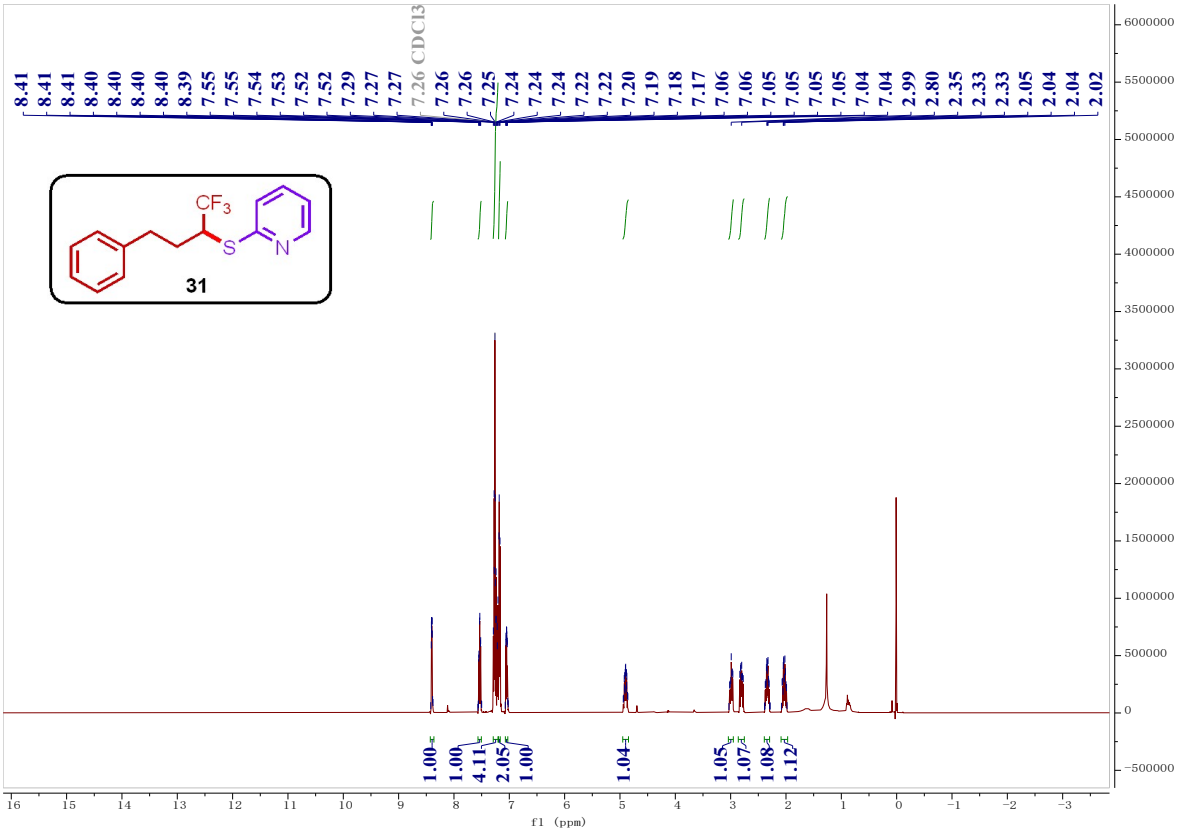
^{1}H NMR Spectrum of Compound **30**



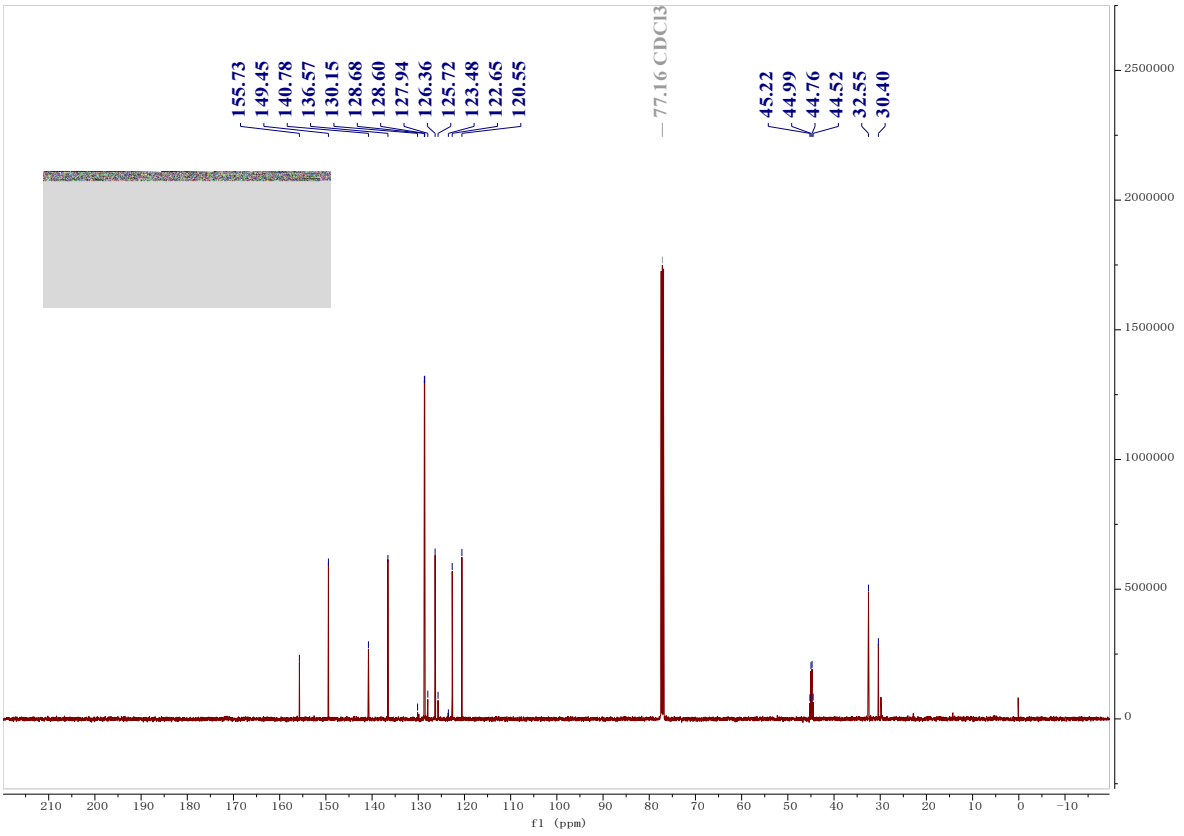
^{13}C NMR Spectrum of Compound **30**



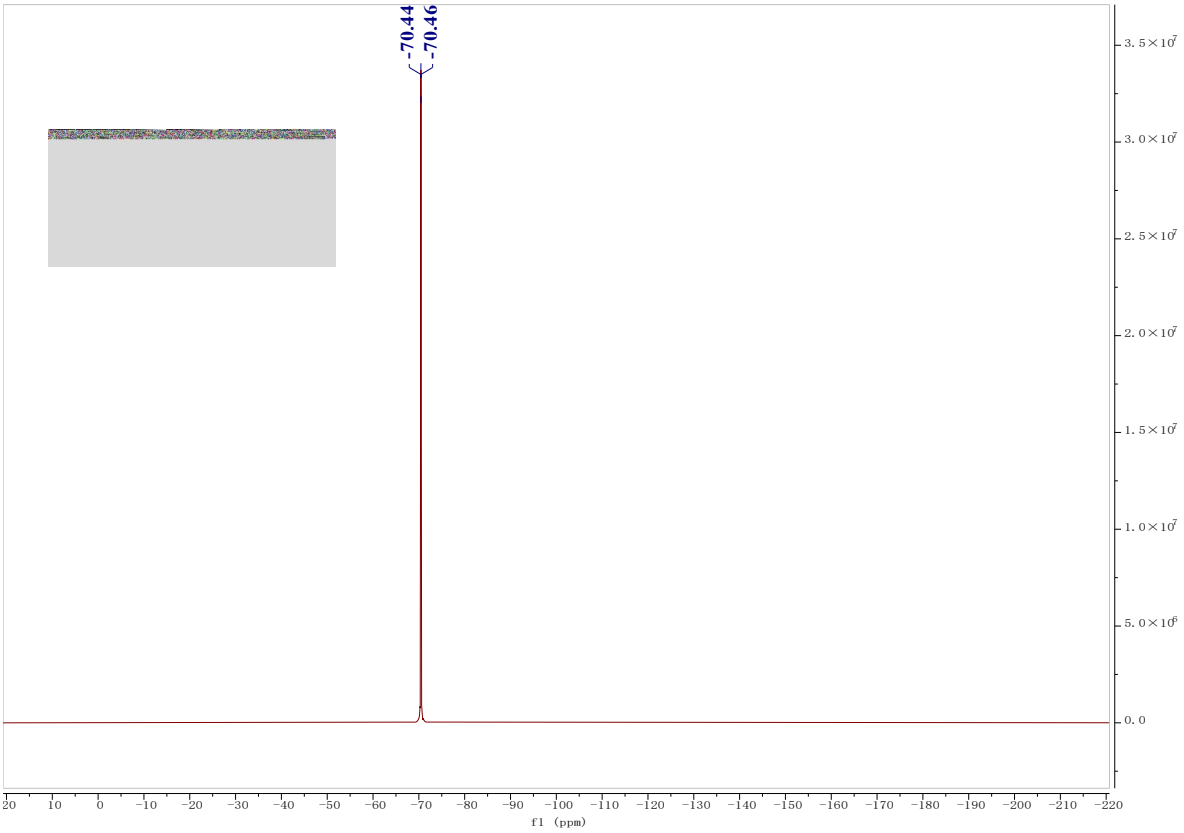
^{19}F NMR Spectrum of Compound **30**



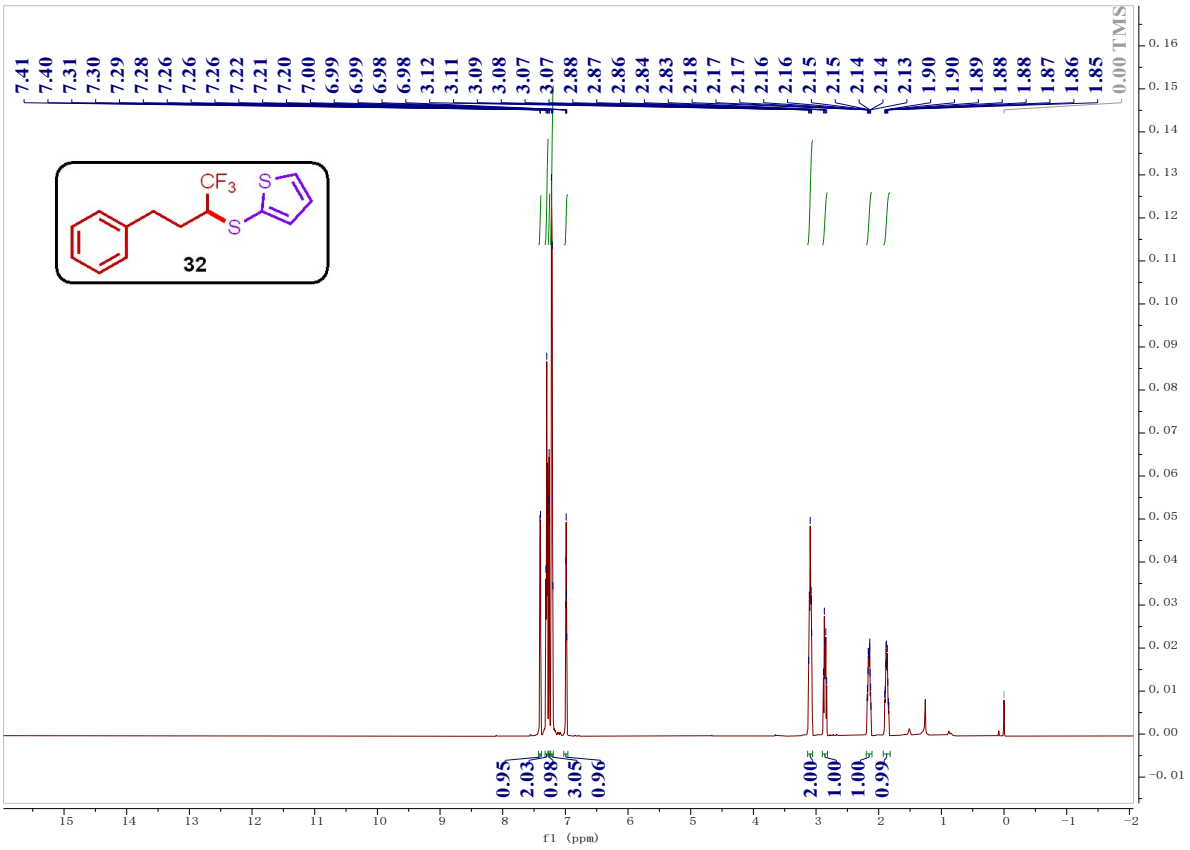
^{1}H NMR Spectrum of Compound **31**



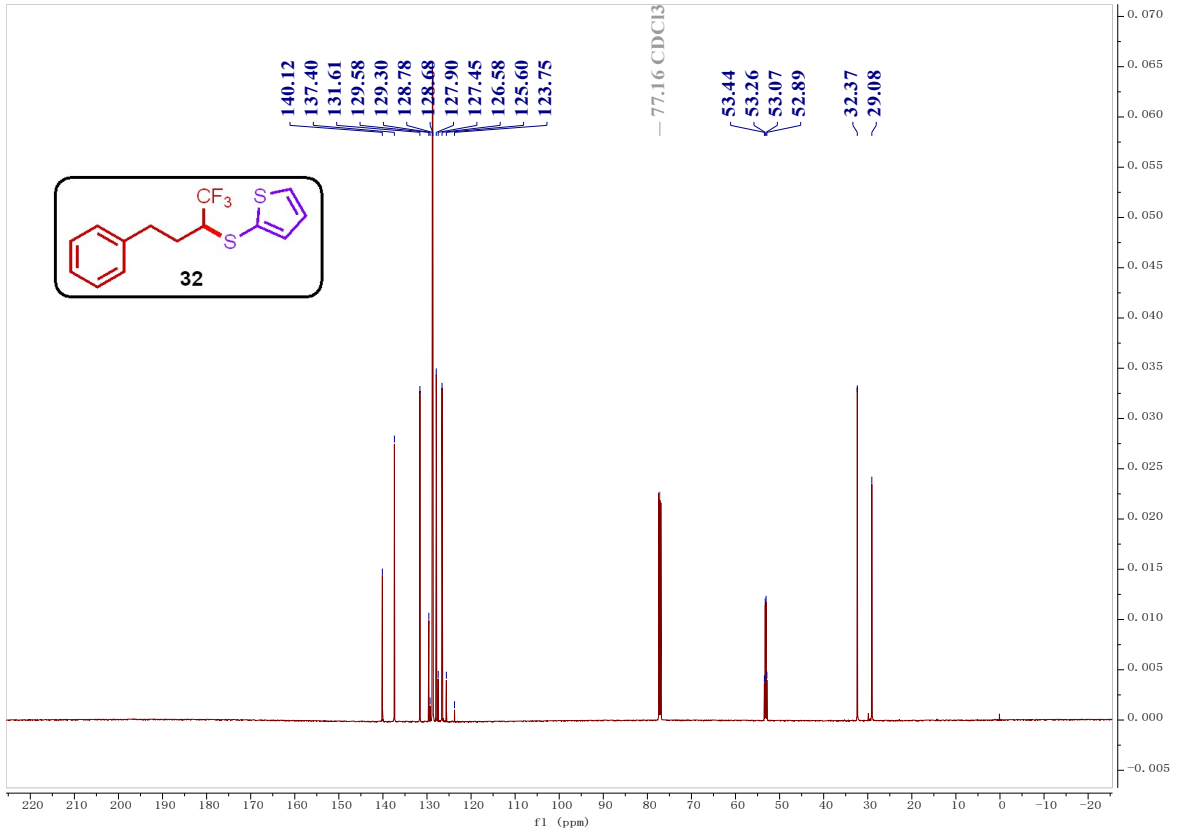
^{13}C NMR Spectrum of Compound **31**



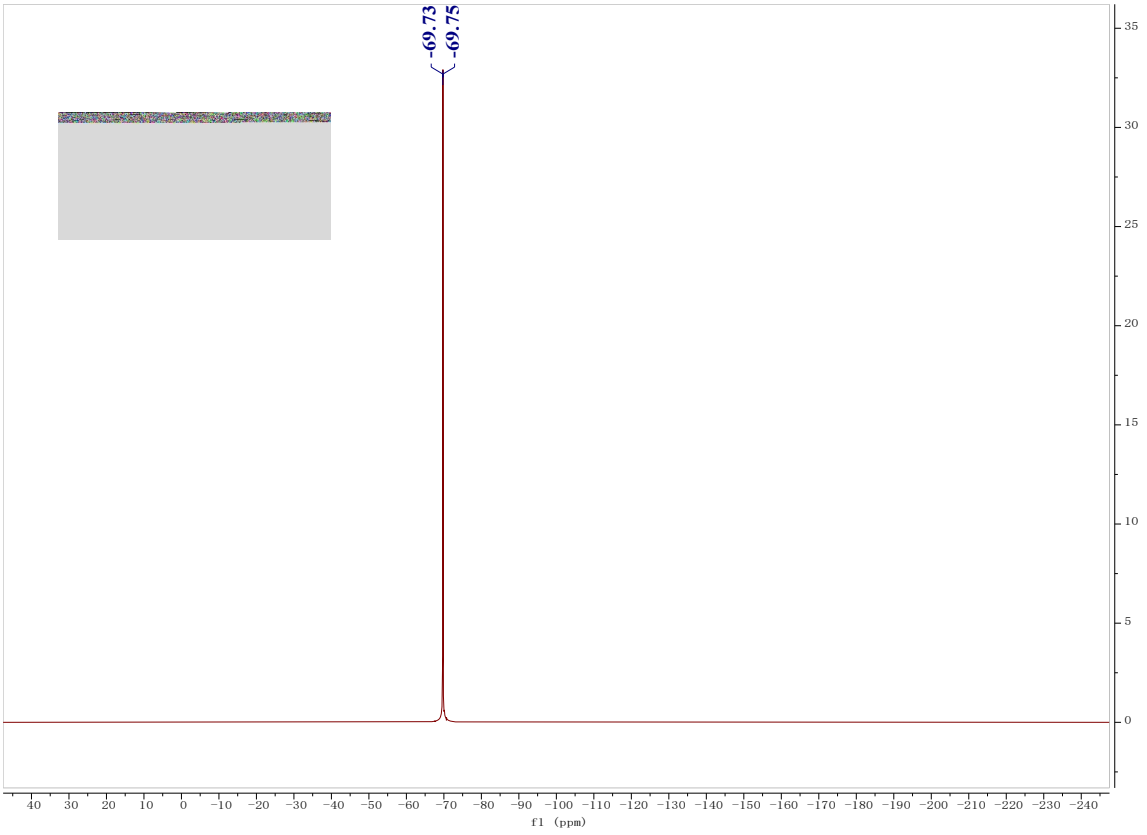
^{19}F NMR Spectrum of Compound **31**



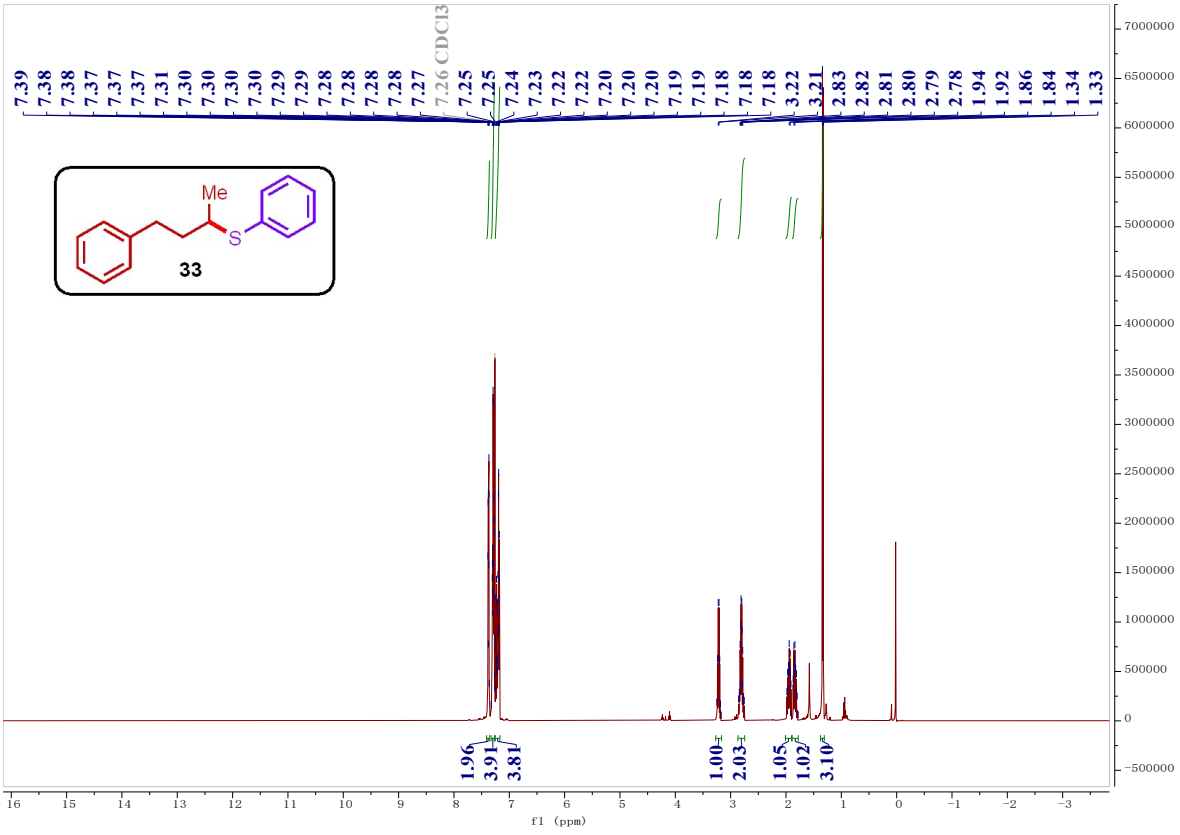
^{1}H NMR Spectrum of Compound **32**



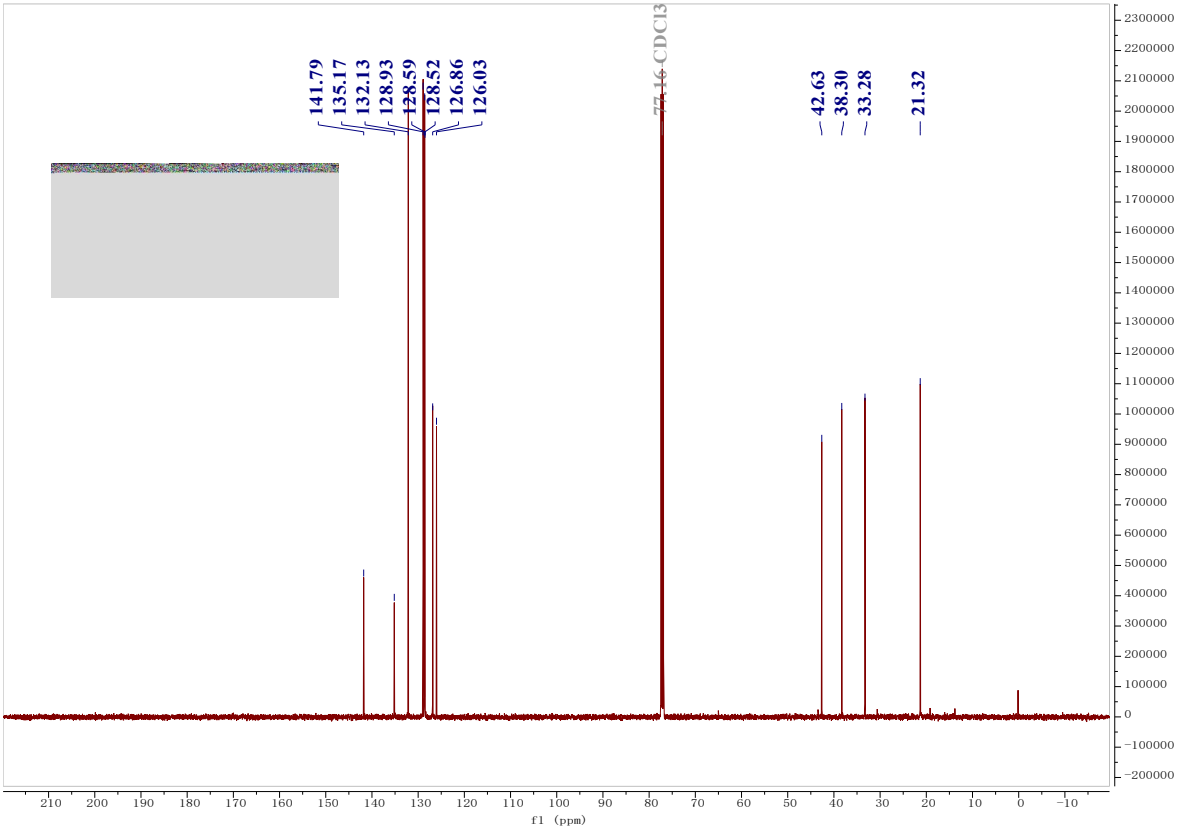
^{13}C NMR Spectrum of Compound **32**



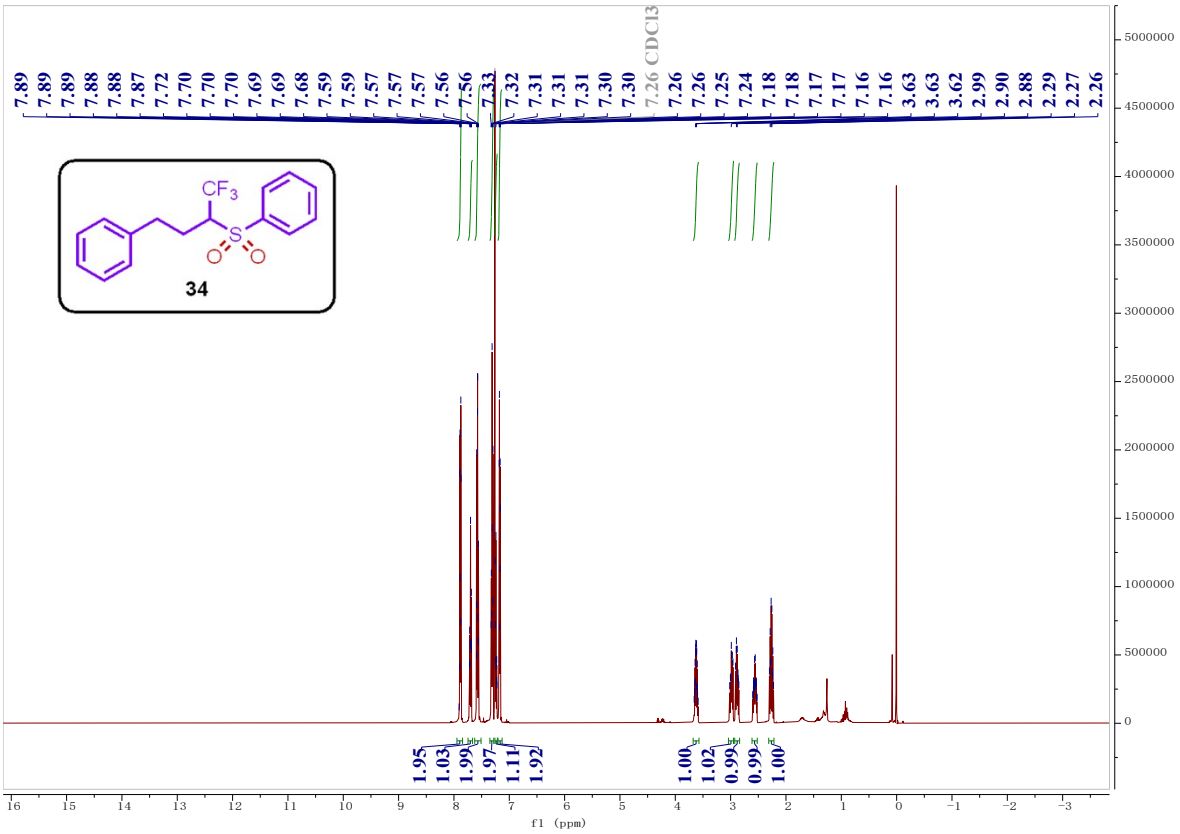
^{19}F NMR Spectrum of Compound **32**



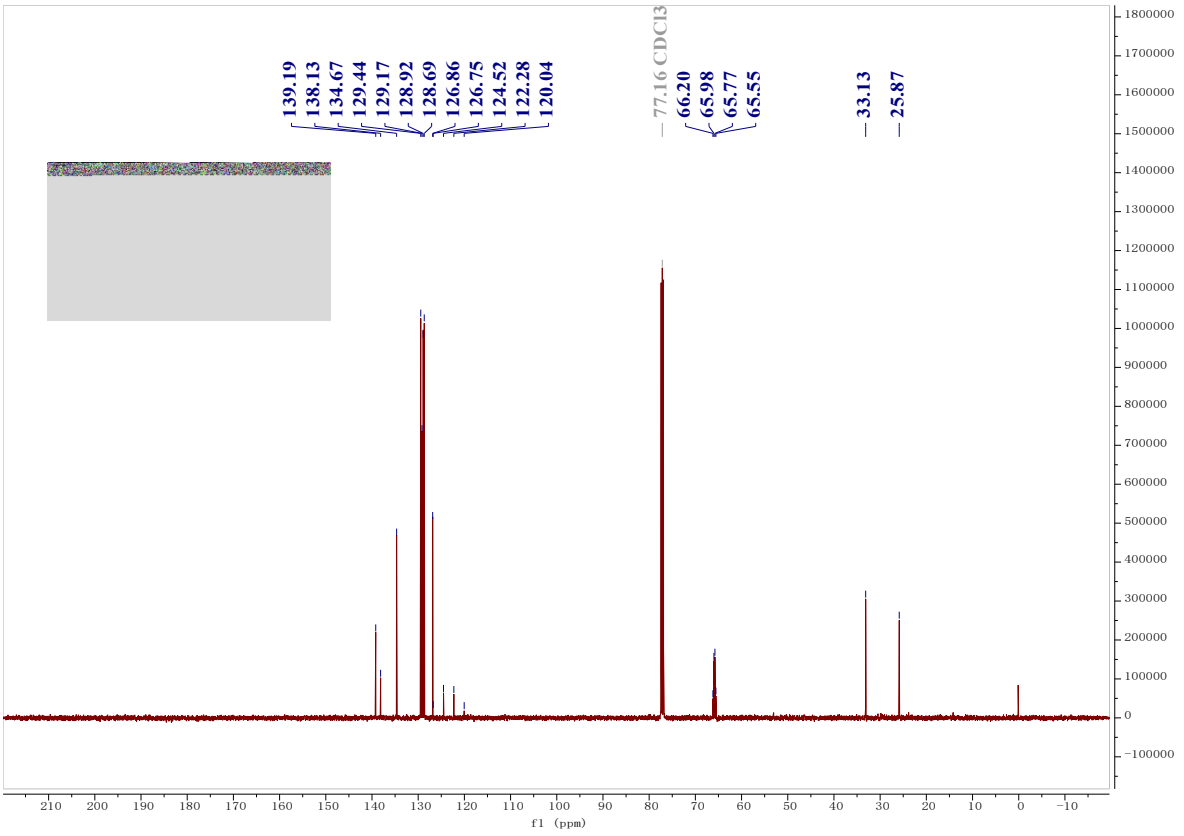
^{1}H NMR Spectrum of Compound **33**



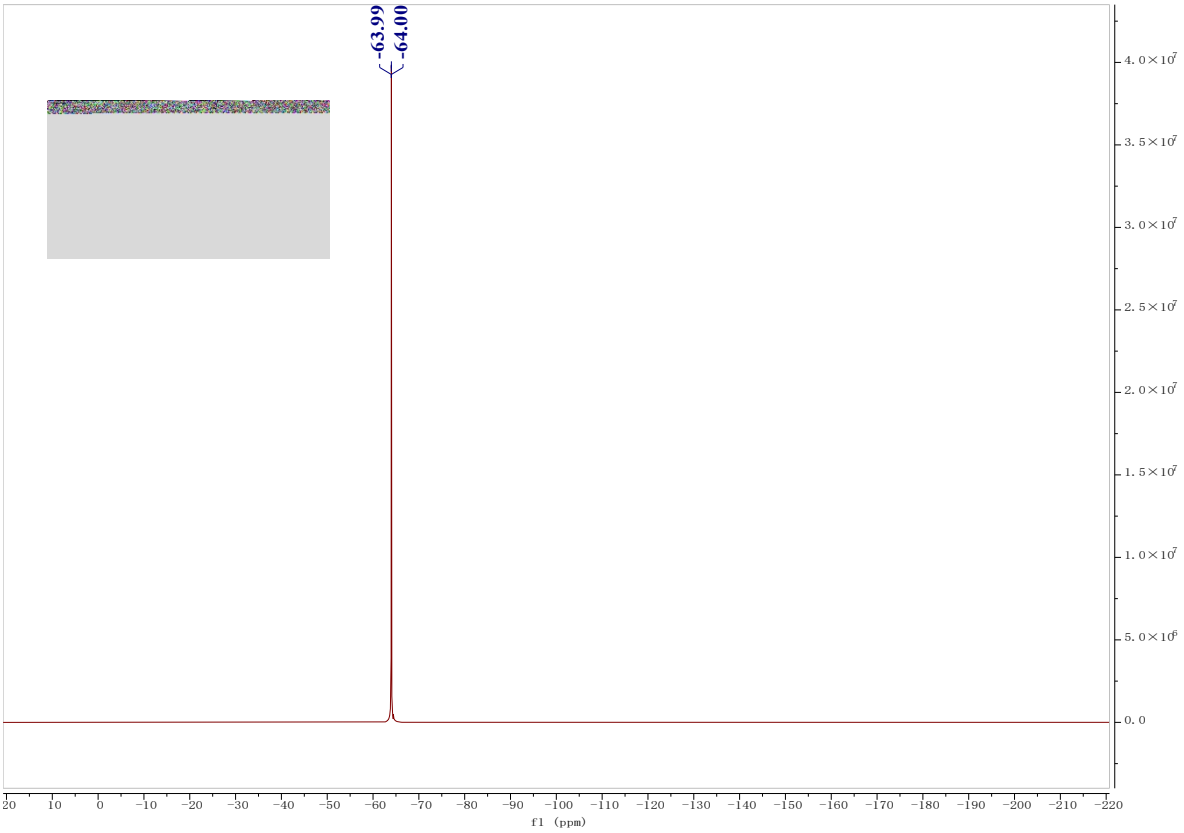
^{13}C NMR Spectrum of Compound **33**



^{1}H NMR Spectrum of Compound **34**



^{13}C NMR Spectrum of Compound **34**



^{19}F NMR Spectrum of Compound **34**