Advanced Synthesis & Catalysis

Supporting Information

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I. General.

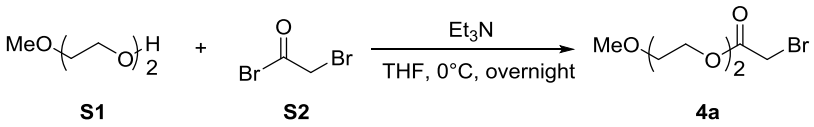
Unless otherwise noted, proton (^{1}H), proton-decoupled carbon [^{13}C{^{1}H}] and proton-decoupled fluorine [^{19}F{^{1}H}] NMR spectra were recorded on Bruker Avance 400 MHz or 500 MHz spectrometers. ^{1}H NMR spectra were referenced to tetramethylsilane (s, 0.00 ppm) using $CDCl_3$ as solvent, ^{13}C NMR spectra were referenced to solvent carbons (77.16 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.90 ppm) in $CDCl_3$. All reactions were performed under an argon atmosphere. Unless otherwise indicated, all reagents were obtained from commercial supplier and used without prior purification. Glassware was dried at 120 ^{o}C for at least 3 hours and cooled under an argon atmosphere before used. THF, dioxane, MeOH and toluene were distilled over sodium before use and stored under MS 4Å. EtOAc, CH_3Cl, DMF, NMP, MeCN and DMSO were dried over CaH_2 and freshly distilled prior to use. Flash chromatography was performed on silica gel (200 - 300 mesh) with either EtOAc/petroleum ether (PE, 60 - 90^{o}C). High-resolution mass spectrometry (HRMS) was recorded on a LTQ Orbitrap Elite or Agilent 1100-MSD spectrometers. Crystal was measured on a XtaLAB PRO MM007HF diffractometer.

Munavalli's SCF_3 reagent **2a**[1] was prepared according to reported procedure.

The known compounds **1a-1p**[2-3] and **1a'**[4] were prepared according to reported procedures, and all the spectra data are in agreement with the reports.

II. Synthesis of substrates

Preparation of compounds 4a-n (**4a** as an example).

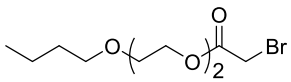


S1 **S2** **4a**

Glycol monomethyl ether **S1** (2.40 g, 20 mmol, 1.0 equiv) was charged into a dry 100 mL round bottom flask along with magnetic stir bar, anhydrous tetrahydrofuran (20 mL) and triethylamine (2.18 g, 20 mmol, 1.0 equiv) at 0 ^{o}C (ice bath). Then, a solution of bromoacetyl bromide **S2** (4.04 g, 20 mmol, 1.0 equiv) in THF (5 mL) was added with a syringe over 10 min and the reaction mixture was stirred overnight. After removal of the solvent under reduced pressure, the residue was dissolved with DCM, washed with water, saturated ammonium chloride solution, saturated sodium bicarbonate solution, and saturated NaCl, respectively. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford the desired product **4a** (3.11 g, 65% yield) as a light yellow liquid.

2-(2-Methoxyethoxy)ethyl 2-bromoacetate (4a)[5]

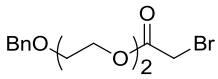
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 – 4.31 (m, 2H), 3.89 (s, 2H), 3.78 – 3.70 (m, 2H), 3.70 – 3.63 (m, 2H), 3.60 – 3.53 (m, 2H), 3.39 (s, 3H).



2-(2-butoxyethoxy)ethyl 2-bromoacetate (4b)[5]

The product (0.80 g, 48% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a light yellow liquid.

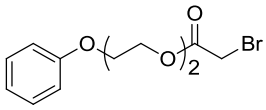
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 – 4.29 (m, 2H), 3.86 (s, 2H), 3.76 – 3.69 (m, 2H), 3.65 – 3.61 (m, 2H), 3.58 – 3.54 (m, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 1.61 – 1.49 (m, 2H), 1.34 (dq, *J* = 14.5, 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).



2-(2-(benzyloxy)ethoxy)ethyl 2-bromoacetate(4c)

The product (1.3 g, 54% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a light yellow liquid.

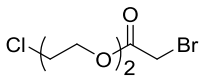
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 5H), 4.56 (s, 2H), 4.37 – 4.26 (m, 2H), 3.84 (s, 2H), 3.76 – 3.57 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 138.0, 128.2, 127.6, 127.5, 73.0, 70.5, 69.2, 68.6, 65.1, 25.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{17}BrO_4Na^+$ 339.0202, found 339.0211.



2-(2-phenoxyethoxy)ethyl 2-bromoacetate(4d)

The product (0.81 g, 51% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a light yellow liquid.

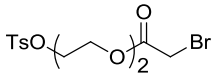
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 2H), 6.99 – 6.87 (m, 3H), 4.38 – 4.30 (m, 2H), 4.17 – 4.10 (m, 2H), 3.90 – 3.84 (m, 4H), 3.84 – 3.74 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.7, 129.5, 121.0, 114.6, 69.8, 69.0, 67.3, 65.34, 25.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{12}H_{15}BrO_4Na^+$ 325.0046, found 325.0055.



2-(2-Chloroethoxy)ethyl 2-bromoacetate (4e)[6]

The product (1.39 g, 71% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a yellow liquid.

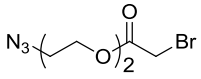
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 – 4.32 (m, 2H), 3.89 (s, 2H), 3.80 – 3.74 (m, 4H), 3.64 (t, *J* = 5.7 Hz, 2H).



2-(2-(Tosyloxy)ethoxy)ethyl 2-bromoacetate (4f)

The product (1.65 g, 75% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 7/1) as a colorless oil.

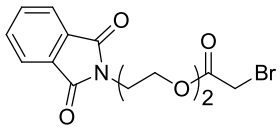
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.33 – 4.14 (m, 4H), 3.86 (s, 2H), 3.78 – 3.62 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 145.0, 132.7, 129.9, 127.9, 69.2, 68.8, 68.6, 65.0, 25.9, 21.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{17}BrO_6SNa^+$ 402.9821, found 402.9830.



2-(2-Azidoethoxy)ethyl 2-bromoacetate (4g)

The product (1.06 g, 66% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a light yellow liquid.

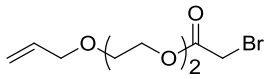
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 – 4.32 (m, 2H), 3.88 (s, 2H), 3.76 – 3.73 (m, 2H), 3.71 – 3.68 (m, 2H), 3.39 (t, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 70.1, 68.6, 65.1, 50.5, 25.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_6H_{10}BrN_3O_3Na^+$ 273.9798, found 273.9803.



2-(2-(1,3-Dioxoisoindolin-2-yl)ethoxy)ethyl 2-bromoacetate (4h)

The product (2.91 g, 71% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 7/1) as a colorless oil.

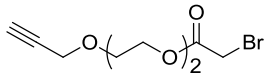
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.31 – 4.25 (m, 2H), 3.93 – 3.89 (m, 2H), 3.81 (s, 2H), 3.76 (t, *J* = 5.6 Hz, 2H), 3.74 – 3.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 167.9, 166.9, 133.8, 131.5, 122.9, 67.7, 67.5, 64.8, 36.7, 25.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{14}BrNO_5Na^+$ 377.9948, found 377.9955.



2-(2-(Allyloxy)ethoxy)ethyl 2-bromoacetate (4i)

The product (3.23 g, 69% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 8/1) as a light yellow liquid.

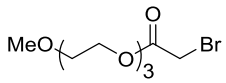
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 – 5.86 (m, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.37 – 4.32 (m, 2H), 4.04 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.88 (s, 2H), 3.77 – 3.72 (m, 2H), 3.71 – 3.65 (m, 2H), 3.65 – 3.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 134.5, 117.3, 72.2, 70.6, 69.3, 68.7, 65.3, 25.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_9H_{15}BrO_4Na^+$ 289.0046, found 289.0054.



2-(2-(Prop-2-yn-1-yloxy)ethoxy)ethyl 2-bromoacetate (4j)

The product (1.83 g, 68% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 7/1) as a light yellow liquid.

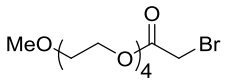
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 – 4.31 (m, 2H), 4.25 – 4.19 (m, 2H), 3.89 (s, 2H), 3.77 – 3.73 (m, 2H), 3.70 (s, 4H), 2.45 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 79.5, 74.7, 70.4, 69.0, 68.7, 65.2, 58.4, 25.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_9H_{13}BrO_4Na^+$ 286.9889, found 286.9895.



2-(2-(2-Methoxyethoxy)ethoxy)ethyl 2-bromoacetate (4k)[5]

The product (0.98 g, 57% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3/1) as a light yellow liquid.

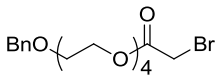
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 – 4.31 (m, 2H), 3.90 (s, 2H), 3.72 – 3.64 (m, 8H), 3.61 – 3.56 (m, 2H), 3.40 (s, 3H).



2,5,8,11-Tetraoxatridecan-13-yl 2-bromoacetate (4l)[7]

The product (0.60 g, 63% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 3/1) as a light yellow liquid.

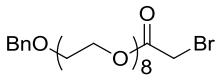
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 – 4.26 (m, 2H), 3.85 (s, 2H), 3.74 – 3.67 (m, 2H), 3.67 – 3.58 (m, 10H), 3.56 – 3.49 (m, 2H), 3.35 (s, 3H).



1-phenyl-2,5,8,11-tetraoxatridecan-13-yl 2-bromoacetate (4m)

The product (0.75 g, 42% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 5/1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 4.56 (s, 2H), 4.33 – 4.27 (m, 2H), 3.86 (s, 2H), 3.73 – 3.60 (m, 14H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 138.0, 128.1, 127.5, 127.4, 72.9, 70.4, 70.3, 69.2, 68.5, 65.1, 25.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{17}H_{25}BrO_6Na^+$ 427.0727, found 427.0737.



1-phenyl-2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl 2-bromoacetate (4n)

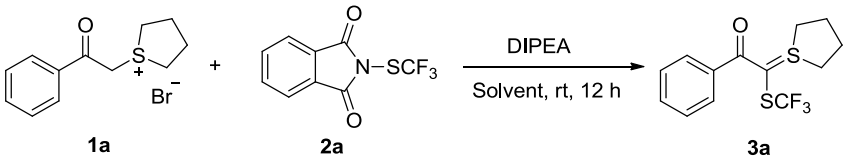
The product (2.08 g, 97% yield) was purified with silica gel chromatography (ethyl acetate) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 4.58 (s, 2H), 4.37 – 4.30 (m, 2H), 3.89 (s, 2H), 3.77 – 3.70 (m, 2H), 3.69 – 3.55 (m, 28H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 138.3, 128.4, 127.8, 127.6, 73.3, 70.7, 70.6, 69.4, 68.8, 65.4, 25.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{25}H_{41}BrO_{10}Na^+$ 603.1775, found 603.1797.

III. Condition optimization

A dry reaction tube was charged with sulfonium salt **1a** (0.1 mmol), SCF_3 reagent **2a** (0.1 mmol, 1.0 equiv) and indicated solvent (1.0 mL). DIPEA (0.1 mmol, 1.0 equiv) was added to the reaction mixture in the end. The mixture kept stirring at the room temperature for 12 hours. The reaction solution was analyzed by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

Table S1. Effect of solvent

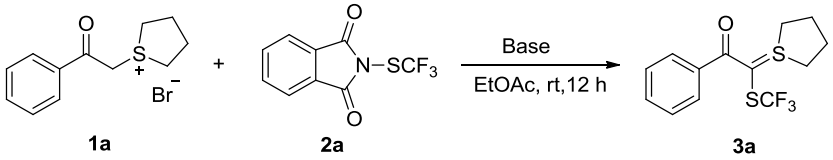


1a **2a** **3a**

Entry	Solvent	**3a** (%)
1	MeOH	＞99%
2	DMSO	＞99%
3	DMF	＞99%
4	MeCN	＞99%
5	THF	＞99%
6	PhMe	＞99%
7	NMP	＞99%
8	EtOAc	＞99%
9	$CHCl_3$	＞99%
10	dioxane	＞99%

Reaction condition: sulfonium salt **1a** (0.1 mmol, 1.0 equiv), SCF_3 reagent **2a** (0.1 mmol, 1.0 equiv), DIPEA (0.1 mmol, 1.0 equiv) in solvent (1.0 mL) at rt for 12 h. Yields were determined by crude ^{19}F NMR analysis using $PhCF_3$ as an internal standard.

Table S2. Effect of base



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

Entry	Base	**3a** (%)
1	NaOH	89%
2	NaH	68%
3	K_2CO_3	＞99%
4	KF	43%
5	Cs_2CO_3	97%
6	KOAc	54%
7	KO^{t}Bu	43%
8	Et_3N	94%
9	DIPEA	＞99%
10	DMAP	＞99%

Reaction condition: sulfonium salt **1a** (0.1 mmol, 1.0 equiv), SCF_3 reagent **2a** (0.1 mmol, 1.0 equiv), base (0.1 mmol, 1.0 equiv) in EtOAc (1.0 mL) at rt for 12 h. Yields were determined by crude ^{19}F NMR analysis using $PhCF_3$ as an internal standard.

Table S3. Effect of PEGylated sulfonium salts.

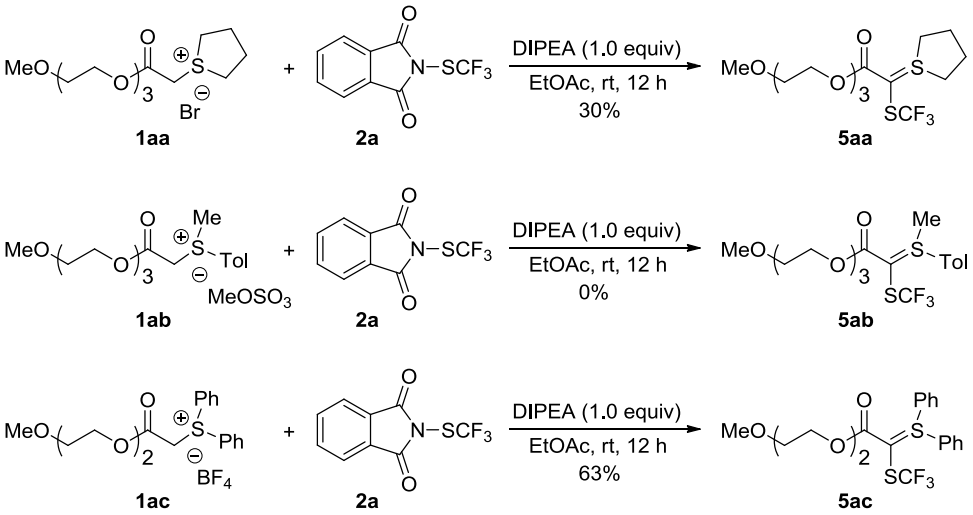
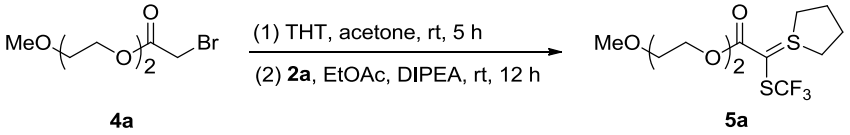


Table S4. Effect of equivalent of SCF_3 reagent on α-bromoacetic ester **4a**.



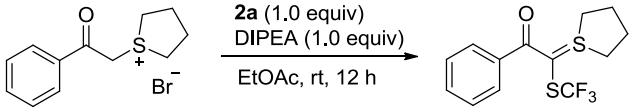
4a **5a**

Entry	Equivalent of SCF_3 reagent	**5a** (%)
1	1.0	69%
2	1.5	90%
3	2.0	76%

Standard conditions: (1) α-bromoacetic ester **4a** (0.5 mmol) and THT (0.5 mmol, 1.0 equiv) in acetone (0.1 mL) at rt for 5 h; (2) Munavalli's SCF_3 reagent **2a**, DIPEA (0.5 mmol, 1.0 equiv), EtOAc (5.0 mL) at rt for 12 h. Yields were determined by crude ^{19}F NMR analysis using $PhCF_3$ as an internal standard. THT = tetrahydrothiophene.

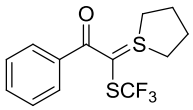
IV. Isolation of products

General procedure for trifluoromethylthiolation of sulfonium salts (**3a** as an example).



1a **3a**

A dry reaction tube was charged with sulfonium salt **1a** (0.5 mmol, 1.0 equiv), Munavalli's SCF_3 reagent **2a** (0.5 mmol, 1.0 equiv) and EtOAc (5.0 mL). DIPEA (0.5 mmol, 1.0 equiv) was added to the reaction mixture in the end. The mixture kept stirring at the room temperature for 12 hours. After the reaction completion, the residue was directly purified by flash column chromatography on deactivation silica gel to afford the desired product **3a**.



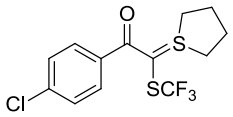
1-Phenyl-2-(tetrahydro-1λ^4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3a)

The product (150.6 mg, 95% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 2/1) as a white solid.

Melting point: 98-101 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 6.7, 2.4 Hz, 2H), 7.46 – 7.27 (m, 3H), 3.81 – 3.59

(m, 2H), 3.43 – 3.14 (m, 2H), 2.91 – 2.62 (m, 2H), 2.20 – 1.93 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 140.9, 129.5 (q, *J* = 315.7 Hz), 129.2, 128.0, 127.6, 55.2, 42.5, 28.6. HRMS-ESI m/z : $[M+H]^+$ calcd for $C_{13}H_{14}F_3OS_2^+$ 307.0433, found 307.0429.

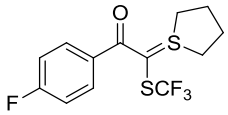


1-(4-Chlorophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3b)

The product (157.1 mg, 93% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 114-117 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.76 – 3.51 (m, 2H), 3.43 – 3.16 (m, 2H), 2.81 – 2.57 (m, 2H), 2.14 – 1.92 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 139.1, 134.5, 129.3, 129.1 (q, *J* = 317.1 Hz), 127.5, 55.5, 42.3, 28.3. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}ClF_3OS_2Na^+$ 362.9862, found 362.9858.

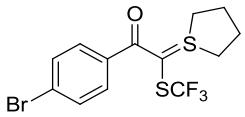


1-(4-Fluorophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3c)

The product (158.9 mg, 98% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 104-105 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 3.63 (s, 2H), 3.41 – 3.18 (m, 2H), 2.69 (s, 2H), 2.12 – 1.92 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.5, -115.0 (tt, *J* = 11.0, 6.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 163.0 (d, *J* = 248.0 Hz), 136.7, 130.0 (d, *J* = 8.3 Hz), 129.2 (q, *J* = 315.6 Hz), 114.3 (d, *J* = 21.4 Hz), 55.3, 42.3, 28.3. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}F_4OS_2Na^+$ 347.0158, found 347.0155.

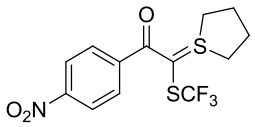


1-(4-Bromophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3d)

The product (188.4 mg, 98% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 109-110 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.72 – 3.52 (m, 2H), 3.44 – 3.20 (m, 2H), 2.78 – 2.60 (m, 2H), 2.13 – 1.94 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.5. ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 139.6, 130.6, 129.6, 129.1 (q, *J* = 315.6 Hz), 123.0, 55.7, 42.4, 28.4. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}BrF_3OS_2Na^+$ 406.9357, found 406.9359.

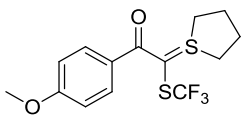


1-(4-Nitrophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3e)

The product (166.0 mg, 94% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a yellow solid.

Melting point: 134-135 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 3.74 – 3.58 (m, 2H), 3.49 – 3.29 (m, 2H), 2.83 – 2.63 (m, 2H), 2.19 – 2.01 (m, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 147.5, 147.4, 128.9 (q, *J* = 315.4 Hz), 128.6, 122.8, 56.8, 42.5, 28.5. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}F_3NO_3S_2Na^+$ 374.0103, found 374.0102.

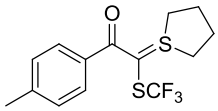


1-(4-Methoxyphenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3f)

The product (170.2 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a yellow solid.

Melting point: 134-136 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.72 – 3.57 (m, 2H), 3.35 – 3.22 (m, 2H), 2.78 – 2.63 (m, 2H), 2.10 – 1.94 (m, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -53.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 160.3, 132.8, 129.8, 129.4 (q, *J* = 315.8 Hz), 112.6, 55.0 (q, *J* = 7.6 Hz), 54.5, 42.2, 28.3. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{15}F_3O_2S_2Na^+$ 359.0358, found 359.0356.

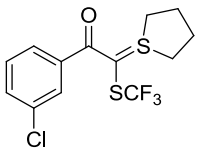


2-(Tetrahydro-1l4-thiophen-1-ylidene)-1-(p-tolyl)-2-((trifluoromethyl)thio)ethan-1-one (3g)

The product (166.2 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a white solid.

Melting point: 155-157 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 3.72 – 3.56 (m, 2H), 3.35 – 3.23 (m, 2H), 2.79 – 2.62 (m, 2H), 2.36 (s, 3H), 2.10 – 1.95 (m, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ -53.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 138.9, 137.7, 129.3 (q, *J* = 315.6 Hz), 128.1, 127.9, 54.8, 42.2, 28.3, 21.2. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{15}F_3OS_2Na^+$ 343.0409, found 343.0407.

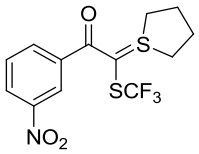


1-(3-Chlorophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3h)

The product (166.0 mg, 98% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 3.74 – 3.57 (m, 2H), 3.43 – 3.25 (m, 2H), 2.80 – 2.64 (m, 2H), 2.11

– 1.98 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 142.6, 133.3, 129.2 (q, *J* = 315.5 Hz), 128.9, 127.9, 126.0, 56.0, 42.4, 28.4. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}ClF_3OS_2Na^+$ 362.9862, found 362.9861.

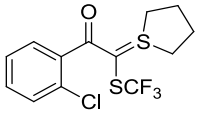


1-(3-Nitrophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3i)

The product (179.0 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a yellow solid.

Melting point: 103-105 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.22 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 3.77 – 3.59 (m, 2H), 3.46 – 3.31 (m, 2H), 2.82 – 2.61 (m, 2H), 2.16 – 1.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 147.6, 142.5, 134.0, 129.2 (q, *J* = 315.5 Hz), 128.8, 123.8, 123.2, 56.6, 42.6, 28.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}F_3NO_3S_2Na^+$ 374.0103, found 374.0100.

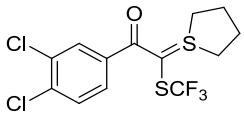


1-(2-Chlorophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3j)

The product (175.4 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a white solid.

Melting point: 103-104 ^{o}C.

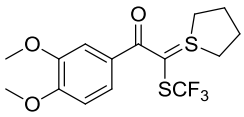
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 1H), 7.30 – 7.21 (m, 3H), 3.81 – 3.66 (m, 2H), 3.34 (s, 2H), 2.73 (s, 2H), 2.04 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.3. ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 130.3, 129.2 (q, *J* = 314.8 Hz), 129.0, 128.9, 128.4, 126.1, 28.5. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{12}ClF_3OS_2Na^+$ 362.9862, found 362.9860.



1-(3,4-Dichlorophenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3k)

The product (184.2 mg, 98% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.69 – 3.55 (m, 2H), 3.40 – 3.26 (m, 2H), 2.76 – 2.61 (m, 2H), 2.10 – 1.94 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 140.7, 133.0, 131.8, 130.1, 129.7, 129.2 (q, *J* = 315.5 Hz), 127.5, 56.1, 42.5, 28.6. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{13}H_{11}Cl_2F_3OS_2Na^+$ 396.9472, found 396.9473.



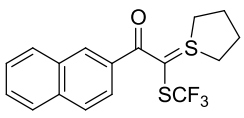
1-(3,4-Dimethoxyphenyl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3l)

The product (175. 6 mg, 96% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 110-112 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.91 (s, 6H), 3.71 – 3.58 (m, 2H), 3.36 – 3.25 (m, 2H), 2.79 – 2.64 (m, 2H), 2.09 – 1.95 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 149.8, 147.9, 132.8, 129.3 (q, *J* = 315.9 Hz), 121.5, 111.4, 109.6, 55.7, 28.3.

HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{15}H_{17}F_3O_3S_2Na^+$ 389.0463, found 389.0461.

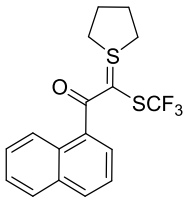


1-(Naphthalen-2-yl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)ethan-1-one (3m)

The product (135.0 mg, 98% yield) was purified with silica gel chromatography (petroleum

ether/ethyl acetate = 1/1) as a yellow oil.

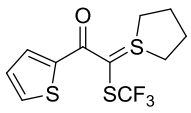
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 – 7.80 (m, 3H), 7.64 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 3.72 (dt, *J* = 12.4, 6.5 Hz, 2H), 3.33 (dt, *J* = 11.7, 6.0 Hz, 2H), 2.78 – 2.71 (m, 2H), 2.09 – 2.00 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 138.2, 133.7, 132.7, 129.4 (q, *J* = 315.6 Hz), 128.7, 127.8, 127.7, 127.2, 126.6, 126.1, 125.7, 55.6, 28.60. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{17}H_{15}F_3OS_2Na^+$ 379.0409, found 379.0404.



1-(Naphthalen-1-yl)-2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)etha n-1-one (3n)

The product (128.0 mg, 99% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 3H), 7.49 – 7.36 (m, 4H), 3.79 (dt, *J* = 11.6, 7.4 Hz, 2H), 3.37 (dt, *J* = 12.2, 6.1 Hz, 2H), 2.75 (ddd, *J* = 10.7, 5.3, 2.7 Hz, 2H), 2.10 – 1.96 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.3. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 139.3, 133.5, 130.6, 129.3 (q, *J* = 315.0 Hz), 128.4, 128.3, 126.2, 125.7, 125.2, 124.8, 57.6, 42.8, 28.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{17}H_{15}F_3OS_2Na^+$ 379.0409, found 379.0406.

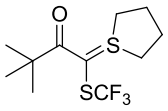


2-(Tetrahydro-1l4-thiophen-1-ylidene)-1-(thiophen-2-yl)-2-((trifluoromethyl)thio)ethan-1-one (3o)

The product (134.7 mg, 86% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow solid.

Melting point: 118-120 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 3.8 Hz, 1H), 7.42 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.78 – 3.59 (m, 2H), 3.28 (s, 2H), 2.77 – 2.59 (m, 2H), 2.09 – 1.90 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.3. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 143.8, 130.9, 129.7 (q, *J* = 316.1 Hz), 129.6, 127.0, 54.3, 42.6, 28.4. HRMS-ESI m/z : $[M+H]^+$ calcd for $C_{11}H_{12}F_3OS_3^+$ 312.9997, found 312.9998.

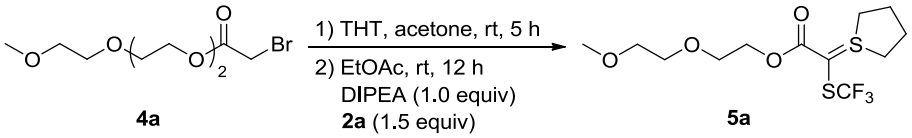


3,3-Dimethyl-1-(tetrahydro-1l4-thiophen-1-ylidene)-1-((trifluoromethyl)thio)butan-2-one (3p)

The product (103.0 mg, 73% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 20/1) as a yellow oil.

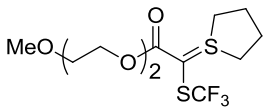
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 – 3.35 (m, 2H), 3.17 (s, 2H), 2.67 – 2.46 (m, 2H), 1.97 (s, 2H), 1.29 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.0. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 129.2 (q, *J* = 317.0 Hz), 53.4, 42.1, 28.8, 28.2. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{11}H_{17}F_3OS_2Na^+$ 309.0565, found 309.0564.

General procedure for trifluoromethylthiolation using α-bromoacetic esters (**5a** as an example).



A dry reaction tube was charged with α-bromoacetic ester **4a** (0.5 mmol, 1.0 equiv), acetone (0.1 mL) and tetrahydrothiophene (THT, 0.5 mmol, 1.0 equiv) was added to the reaction mixture in the end. The mixture kept stirring at the room temperature for 5 hours. The reaction mixture was concentrated under reduce pressure, and the residue was washed with ether (5 × 3.0 mL) and acetone (3 × 3.0 mL). After drying under reduced pressure, Munavalli's SCF_3 reagent **2a** (0.75 mmol, 1.5 equiv), EtOAc (5.0 mL) and DIPEA (0.5 mmol, 1.0 equiv) was added to the crude reactant. The mixture was allowed to stir at room

temperature for 12 hours. After solvent was removed under reduced pressure, the crude residue was directly purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to afford the compound **5a**.

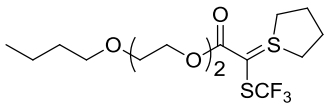


2-(2-Methoxyethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5a)

The product (129.3 mg, 75% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 2H), 3.78 – 3.63 (m, 4H), 3.59 – 3.50 (m, 2H), 3.38 (s, 5H), 3.32 – 3.20 (m, 2H), 2.57 (s, 2H), 2.01 – 1.83 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.0. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 161.4, 129.7 (q, J = 316.0 Hz), 71.8, 70.3, 69.5, 58.8, 43.7, 27.6. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{12}H_{19}F_3O_4S_2Na^+$ 371.0569, found 371.0565.

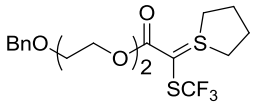


2-(2-butoxyethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5b)

The product (150.2 mg, 77% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 2/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.79 – 3.44 (m, 8H), 3.39 (s, 2H), 3.28 (s, 2H), 2.57 (s, 2H), 2.03 – 1.85 (m, 2H), 1.62 – 1.51 (m, 2H), 1.36 (dq, *J* = 14.5, 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 161.5, 129.8 (q, *J* = 315.4 Hz), 71.1, 70.6, 70.0, 69.6, 63.3, 43.6, 31.6, 27.7, 19.2, 13.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{15}H_{25}F_3O_4S_2Na^+$ 413.1039, found 413.1045.

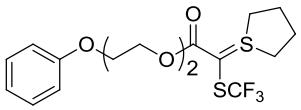


2-(2-(benzyloxy)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5c)

The product (145.0 mg, 73% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 5H), 4.55 (s, 2H), 4.24 (s, 2H), 3.76 – 3.60 (m, 6H), 3.34 (s, 2H), 3.24 – 3.10 (m, 2H), 2.52 (s, 2H), 1.87 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 161.5, 138.2, 129.7 (q, *J* = 328.5 Hz), 128.2, 127.6, 127.5, 73.1, 70.5, 69.6, 69.4, 63.2, 43.6, 27.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{18}H_{23}F_3NaO_4S_2^+$ 447.0882, found 447.0893.

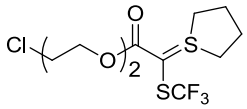


2-(2-phenoxyethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5d)

The product (180.6 mg, 89% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 2H), 6.97 – 6.84 (m, 3H), 4.26 (s, 2H), 4.15 – 3.98 (m, 2H), 3.87 (s, 2H), 3.76 (s, 2H), 3.32 (s, 2H), 3.24 – 3.09 (m, 2H), 2.50 (s, 2H), 1.85 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 161.4, 158.6, 129.7 (q, *J* = 316.2 Hz), 129.3, 120.6, 114.4, 69.7, 69.5, 67.2, 63.1, 43.5, 27.6. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{17}H_{21}F_3O_4S_2Na^+$ 433.0726, found 433.0733.



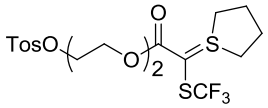
2-(2-Chloroethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5e)

The product (100.1mg, 60% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 2H), 3.88 – 3.69 (m, 4H), 3.64 (t, *J* = 5.8 Hz, 2H), 3.39 (s, 2H), 3.29 (s, 2H), 2.57 (s, 2H), 2.01 – 1.86 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 160.8, 129.8 (q, *J* = 314.9 Hz), 71.3, 69.7, 63.3, 43.8,

43.0, 27.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{11}H_{16}ClF_3O_3S_2Na^+$ 375.0074, found 375.0073.

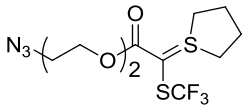


2-(2-(Tosyloxy)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5f)

The product (135.4 mg, 56% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.29 – 4.06 (m, 4H), 3.71 (s, 2H), 3.63 (t, *J* = 4.8 Hz, 2H), 3.36 (s, 2H), 3.28 (s, 2H), 2.54 (s, 2H), 2.45 (s, 3H), 2.00 – 1.85 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 164.2, 144.9, 132.6, 129.8, 129.8 (q, *J* = 316.1 Hz), 127.8, 69.6, 69.4, 68.5, 63.1, 43.6, 27.7, 21.5. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{18}H_{23}F_3O_6S_3Na^+$ 511.0501, found 511.0505.

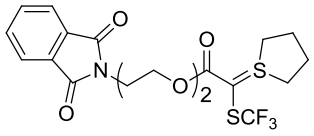


2-(2-Azidoethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5g)

The product (75.4 mg，45% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (s, 2H), 3.79 – 3.63 (m, 4H), 3.38 (t, *J* = 5.1 Hz, 4H), 3.27 (s, 2H), 2.56 (s, 2H), 1.97 – 1.87 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 129.8 (q, J = 315.4 Hz), 70.0, 69.7, 63.3, 50.9, 43.7, 27.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{11}H_{16}F_3N_3O_3S_2Na^+$ 382.0477, found 382.0471.

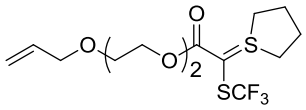


2-(2-(1,3-Dioxoisoindolin-2-yl)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5h)

The product (100.3 mg, 45% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.73 (d, *J* = 3.1 Hz, 2H), 4.19 (s, 2H), 3.89 (t, *J* = 5.8 Hz, 2H), 3.78 (s, 2H), 3.70 (t, *J* = 4.9 Hz, 2H), 3.38 (s, 2H), 3.27 (s, 2H), 2.56 (s, 2H), 2.06 – 1.80 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.0. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 161.3, 133.9, 132.0, 129.7 (q, *J* = 316.3 Hz), 123.2, 69.1, 67.8, 63.1, 43.6, 37.3, 27.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{19}H_{20}F_3NO_5S_2Na^+$ 486.0627, found 486.0629.

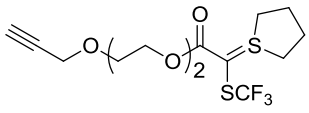


2-(2-(Allyloxy)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5i)

The product (128.6 mg, 69% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddd, *J* = 16.1, 10.8, 5.7 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.18 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.23 (s, 2H), 4.03 (d, *J* = 5.6 Hz, 2H), 3.75 – 3.57 (m, 6H), 3.39 (s, 2H), 3.27 (s, 2H), 2.57 (s, 2H), 1.95 – 1.84 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 161.5, 129.8 (q, *J* = 315.6 Hz), 134.7, 117.1, 72.2, 70.6, 69.7, 69.4, 63.4, 43.6, 27.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{21}F_3O_4S_2Na^+$ 397.0726, found 397.0727.

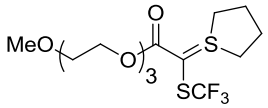


2-(2-(Prop-2-yn-1-yloxy)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5j)

The product (143.3 mg, 77% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 – 4.13 (m, 4H), 3.78 – 3.63 (m, 6H), 3.38 (s, 2H), 3.30 (s, 2H), 2.56 (s, 2H), 2.48 (s, 1H), 2.05 – 1.84 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.8. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 161.5, 129.7 (q, *J* = 316.3 Hz), 79.5, 74.5, 70.2, 69.5, 69.0, 63.2, 58.2, 43.6, 27.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{19}F_3O_4S_2Na^+$ 395.0569, found 395.0570.

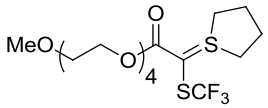


2-(2-(2-Methoxyethoxy)ethoxy)ethyl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5k)

The product (142.4 mg, 75% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 2H), 3.69 – 3.54 (m, 8H), 3.52 – 3.44 (m, 2H), 3.31 (s, 5H), 3.20 (s, 2H), 2.50 (s, 2H), 1.94 – 1.76 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 165.8, 129.8 (q, *J* = 316.8 Hz), 71.9, 70.6, 70.5, 69.6, 63.4, 59.0, 43.6, 27.8. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{23}F_3O_5S_2Na^+$ 415.0831, found 415.0831.



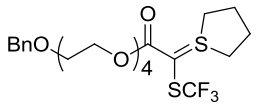
2,5,8,11-Tetraoxatridecan-13-yl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5l)

The product (148.8 mg, 68% yield) was purified with silica gel chromatography (ethyl acetate) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 2H), 3.67 – 3.53 (m, 12H), 3.51 – 3.44 (m, 2H), 3.30 (s, 5H), 3.21 (s, 2H), 2.49 (s, 2H), 1.93 – 1.80 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 161.3, 129.6 (q, *J* = 313.6 Hz), 71.6, 70.4, 70.3, 70.3, 70.2,

69.4, 63.0, 58.7, 43.5, 27.6. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{16}H_{27}F_3O_6S_2Na^+$ 459.1093, found 459.1096.

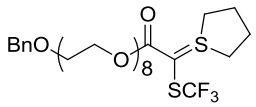


1-phenyl-2,5,8,11-tetraoxatridecan-13-yl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5m)

The product (142.3 mg, 57% yield) was purified with silica gel chromatography (petroleum ether/ethyl acetate = 1/4) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 4.56 (s, 2H), 4.21 (s, 2H), 3.72 – 3.60 (m, 14H), 3.36 (s, 2H), 3.27 – 3.13 (m, 2H), 2.53 (s, 2H), 1.88 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 161.4, 138.1, 129.6 (q, *J* = 329.7 Hz), 128.2, 127.6, 127.4, 73.0, 70.4, 70.4, 69.5, 69.3, 68.1, 66.4, 63.2, 43.5, 27.7. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{22}H_{31}F_3O_6S_2Na^+$ 535.1406, found 535.1412.

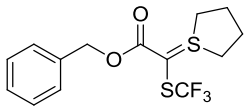


1-phenyl-2,5,8,11,14,17,20,23-octaoxapentacosan-25-yl

2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5n)

The product (173.0 mg, 50% yield) was purified with silica gel chromatography (dichloromethane/methanol = 20/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.16 (m, 5H), 4.56 (s, 2H), 4.37 – 4.13 (m, 2H), 3.76 – 3.60 (m, 30H), 3.35 (s, 2H), 3.26 (s, 2H), 2.53 (s, 2H), 2.10 – 1.79 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.9. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 166.9, 137.9, 129.5 (d, *J* = 327.9 Hz), 128.4, 127.1, 127.3, 72.8, 70.2, 70.2, 69.3, 69.1, 68.4, 65.0, 63.0, 43.4, 27.5. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{30}H_{47}F_3O_{10}S_2Na^+$ 711.2455, found 711.2465.



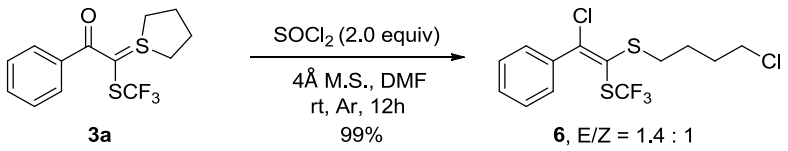
benzyl 2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio)acetate (5o)

The product (122.8 mg, 73% yield) was purified with silica gel chromatography (petroleum

ether/ethyl acetate = 5/1) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 5.15 (s, 2H), 3.41 (s, 2H), 3.30 – 3.13 (m, 2H), 2.56 (s, 2H), 1.90 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 137.7, 129.9 (q, *J* = 315.4 Hz), 128.4, 127.5, 127.2, 65.5, 43.8, 27.9. HRMS-ESI m/z : $[M+Na]^+$ calcd for $C_{14}H_{15}F_3O_2S_2Na^+$ 359.0358, found 359.0363.

V. Transformation of the product

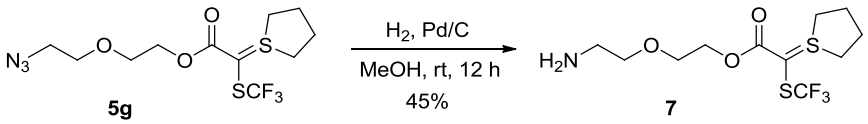


3a **6**, E/Z = 1.4 : 1

(*E*)-(2-Chloro-1-((4-chlorobutyl)thio)-2-phenylvinyl)(trifluoromethyl)sulfane (6)[3]

In an argon-filled glove box, a dry reaction tube was charged with **3a** (91.9 mg, 0.3 mmol, 1.0 equiv), 4Å MS (120 mg), anhydrous DMF (3.0 mL) and $SOCl_2$ (71.4 mg, 0.6 mmol, 2.0 equiv) was added to the reaction mixture in the end. The mixture kept stirring at the room temperature for 12 hours. The reaction mixture was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford the compound **6** (107.2 mg, 99% yield) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.81 (dt, *J* = 9.8, 7.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.9.



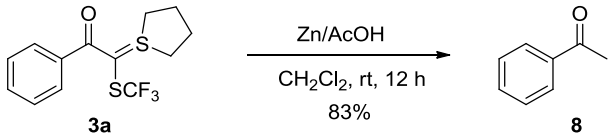
5g **7**

2-(2-Azidoethoxy)ethyl 2-(tetrahydro-1l4-thiophen-1-ylidene)-2-((trifluoromethyl)thio) acetate (7)

Under an atmosphere of H_2, a mixture of compound **5g** (58.0 mg, 0.16 mmol) and Pd/C (10% on carbon (34.4 mg, 0.032 mmol) in dry MeOH (3.2 mL) was stirred at rt overnight. The mixture was filtrated through a pad of Celite, and the filtrate was concentrated. The crude

product was purified by column chromatography on silica gel to give **7** as light yellow oil (24 mg, 45% yield) with MeOH/DCM (1/10) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (s, 2H), 3.69 (t, *J* = 4.8 Hz, 2H), 3.59 (t, *J* = 5.1 Hz, 2H), 3.34 (d, *J* = 44.5 Hz, 4H), 2.91 (t, *J* = 5.2 Hz, 2H), 2.61 (s, 2H), 1.94 (q, *J* = 5.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.8. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 131.1, 128.6, 69.92, 69.4, 63.1, 62.3, 40.6, 28.0. HRMS-ESI m/z : $[M+H]^+$ calcd for $C_{11}H_{19}F_3NO_3S_2^+$ 334.0753, found 334.0715.



Acetophenone (8)[8]

To a suspension of the ylide **3a** (61.2 mg, 0.2 mmol, 1.0 equiv), and zinc powder (40 mg, 0.6 mmol, 3.0 equiv) in CH_2C1_2 (2.0 mL), AcOH (150 μL) was added dropwise with stirring at 0 ^{o}C (ice bath). After stirring for 12h at room temperature, the mixture was filtered and the filtrate was directly purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the compound **8** (20 mg, 83% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 2H).

VI. X-ray crystallographic data

X-ray sample was crystaled from liquid-liquid diffusion in CH_2Cl_2 and n-hexane (1:5) as the anti-solvent at 4 ^oC and acquired using CuKα (λ = 1.54184 Å) radiation.

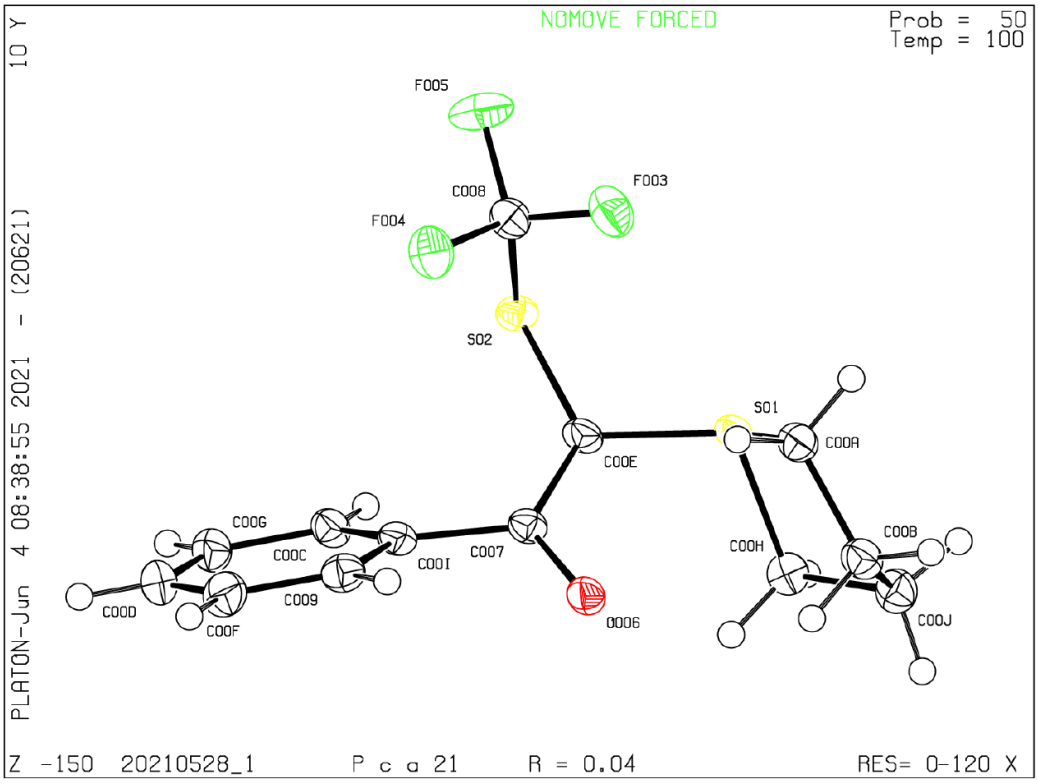


Figure S1. X-Ray structure of **3a** (50% probability level shown)

Crystal Data

Identification code	20210528_1
Empirical formula	$C_{13}H_{13}F_3OS_2$
Formula weight	306.35
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	24.3479(7)
b/Å	6.0346(2)
c/Å	9.3782(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1377.94(7)
Z	4
$\rho_{calc}g/cm^3$	1.477
μ/mm^{-1}	3.749
F(000)	632.0

Crystal size/mm^3	0.5 × 0.25 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.262 to 148.814
Index ranges	$-30 \leq h \leq 30$, $-7 \leq k \leq 5$, $-11 \leq l \leq 11$
Reflections collected	12072
Independent reflections	2760 [R_{int} = 0.0511, R_{sigma} = 0.0311]
Data/restraints/parameters	2760/1/172
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.1042
Final R indexes [all data]	R_1 = 0.0372, wR_2 = 0.1048
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.50
Flack parameter	0.009(15)

The crystal structure is deposited in the Cambridge Crystallographic Data Centre (CCDC Code: 2101452).

VII. References

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[6] Nishumura, K.; Kanada, S. Haloacetates as antifouling agents. *Japan. Kokai 76,* 41, 425; *Chem. Abs.* **1976**, *85*, 58097h.

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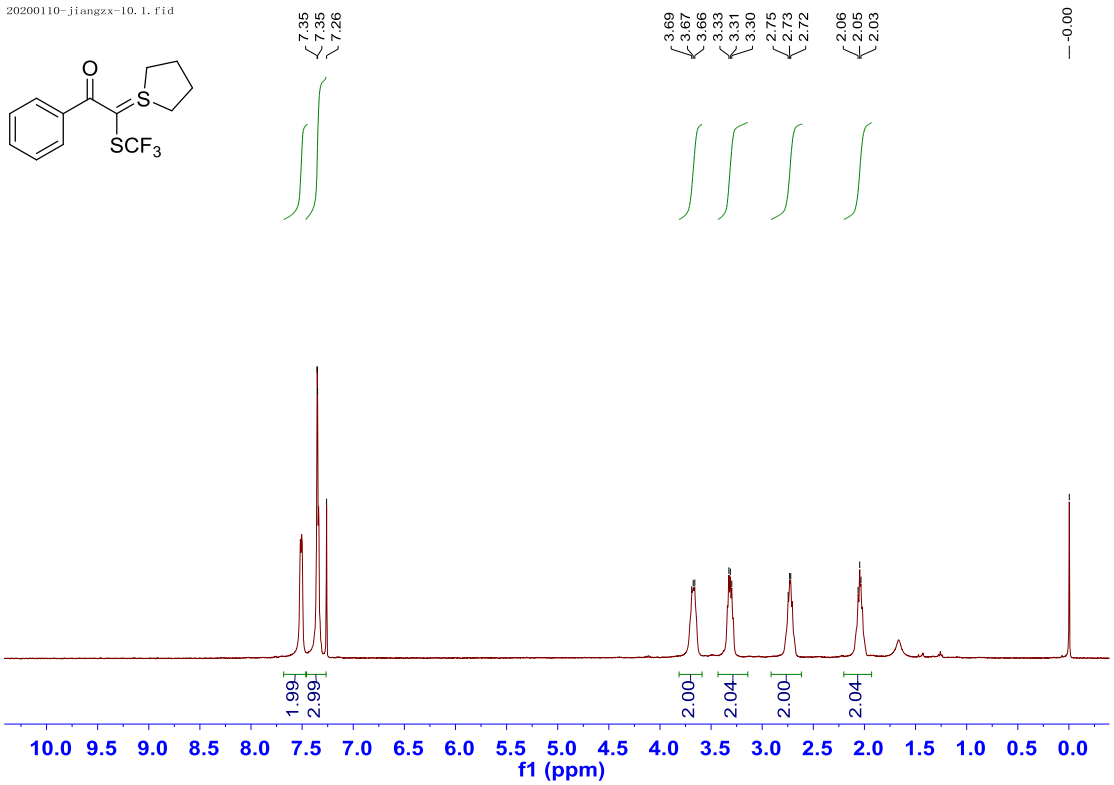
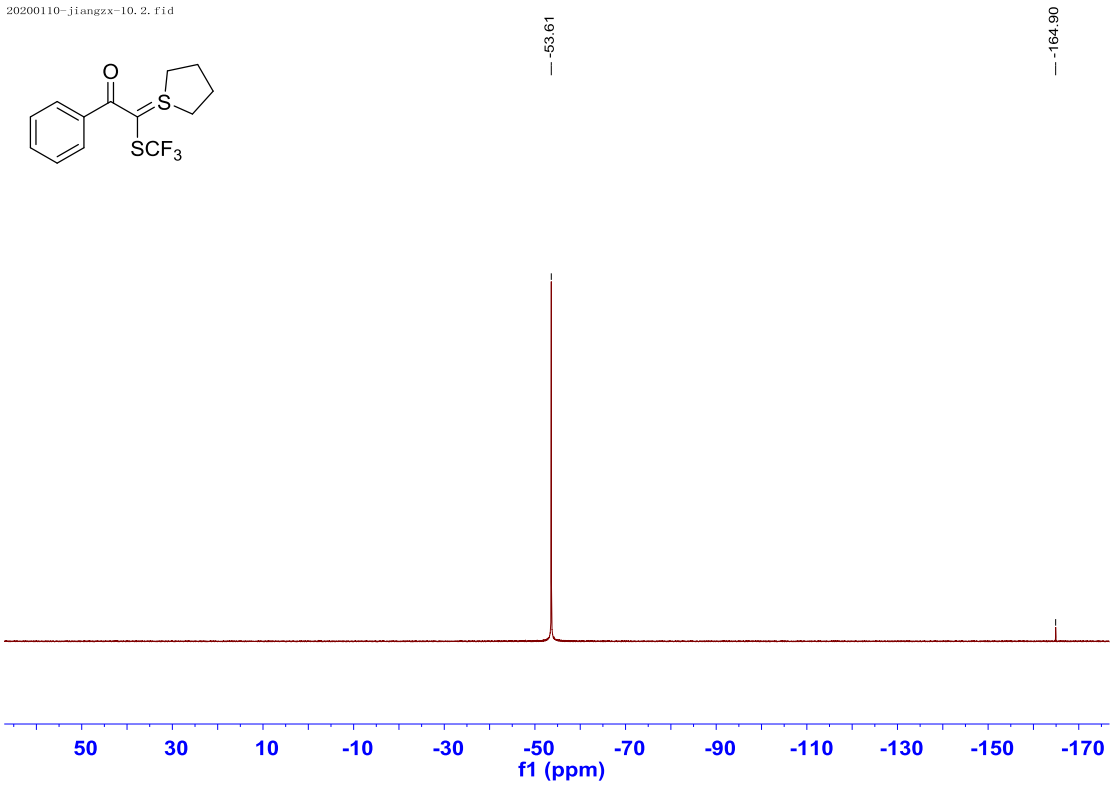
VIII. Copies of the NMR spectra

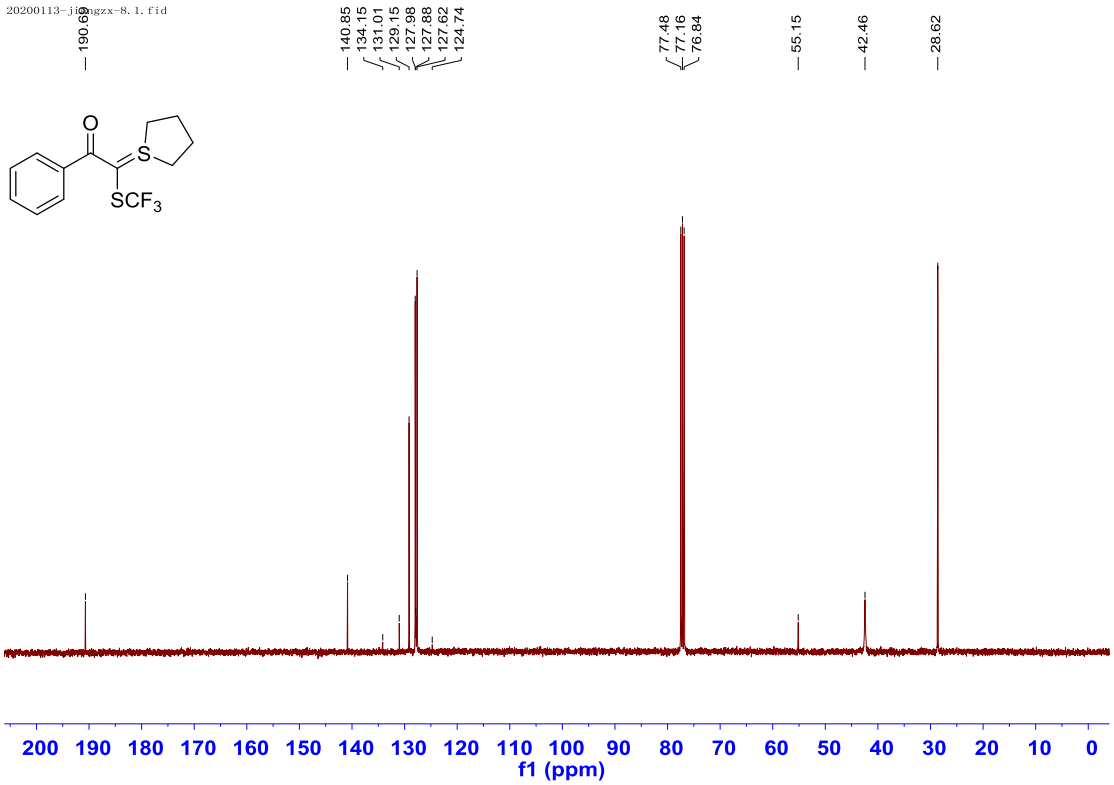
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**.



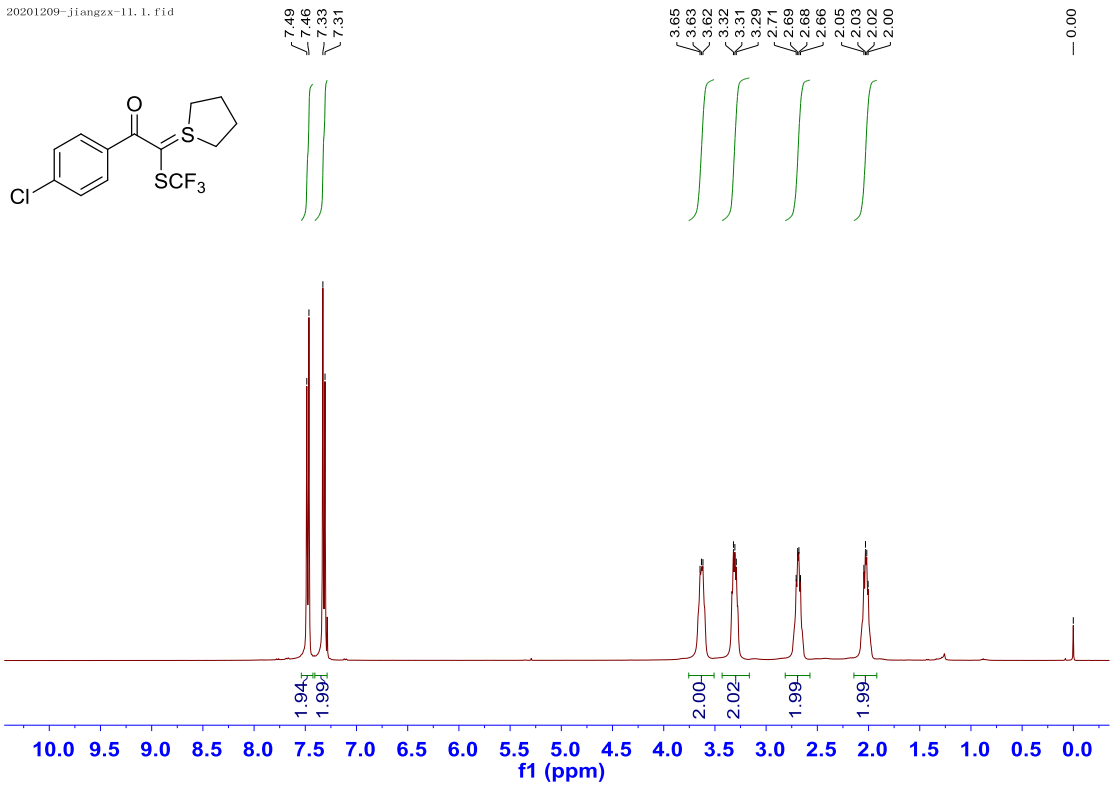
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3a**.



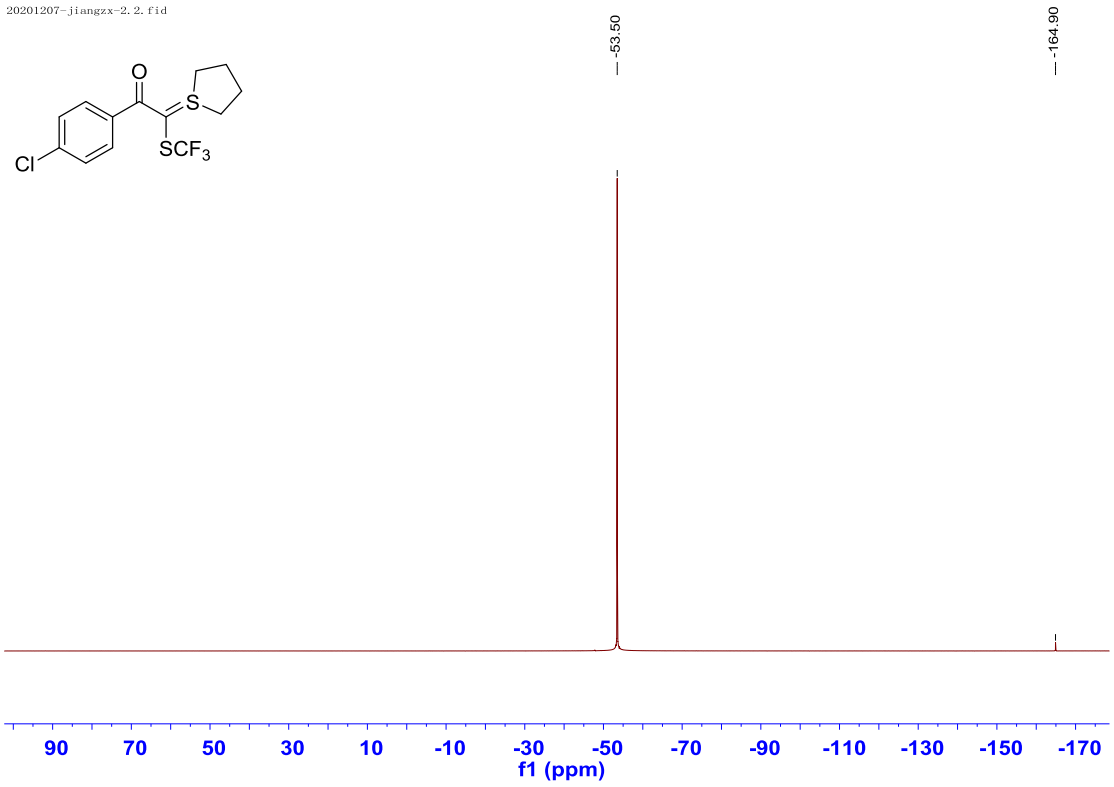
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3a**.



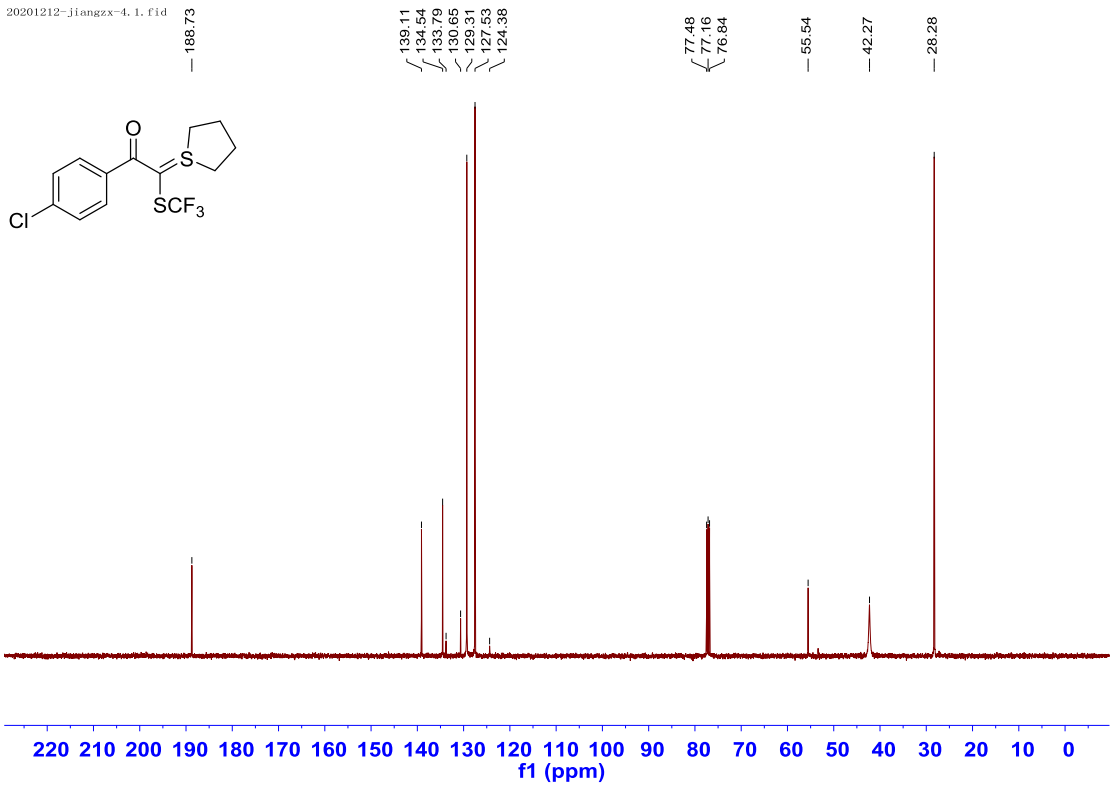
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**.



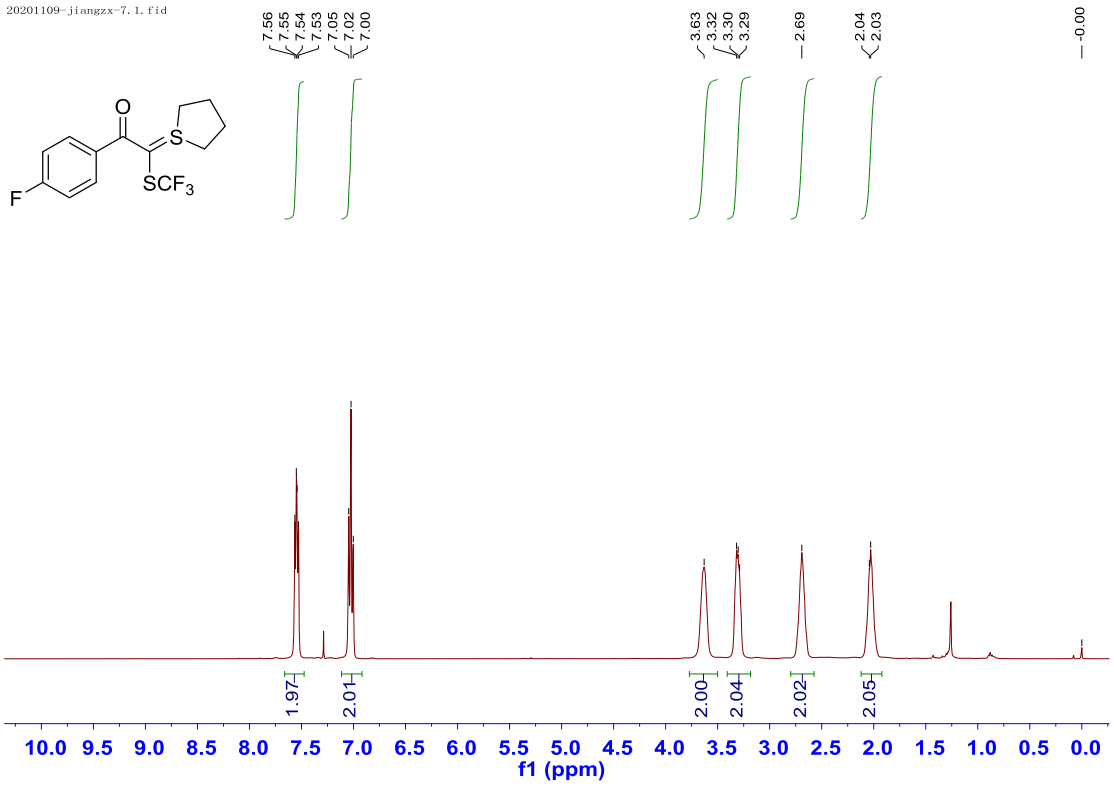
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3b**.



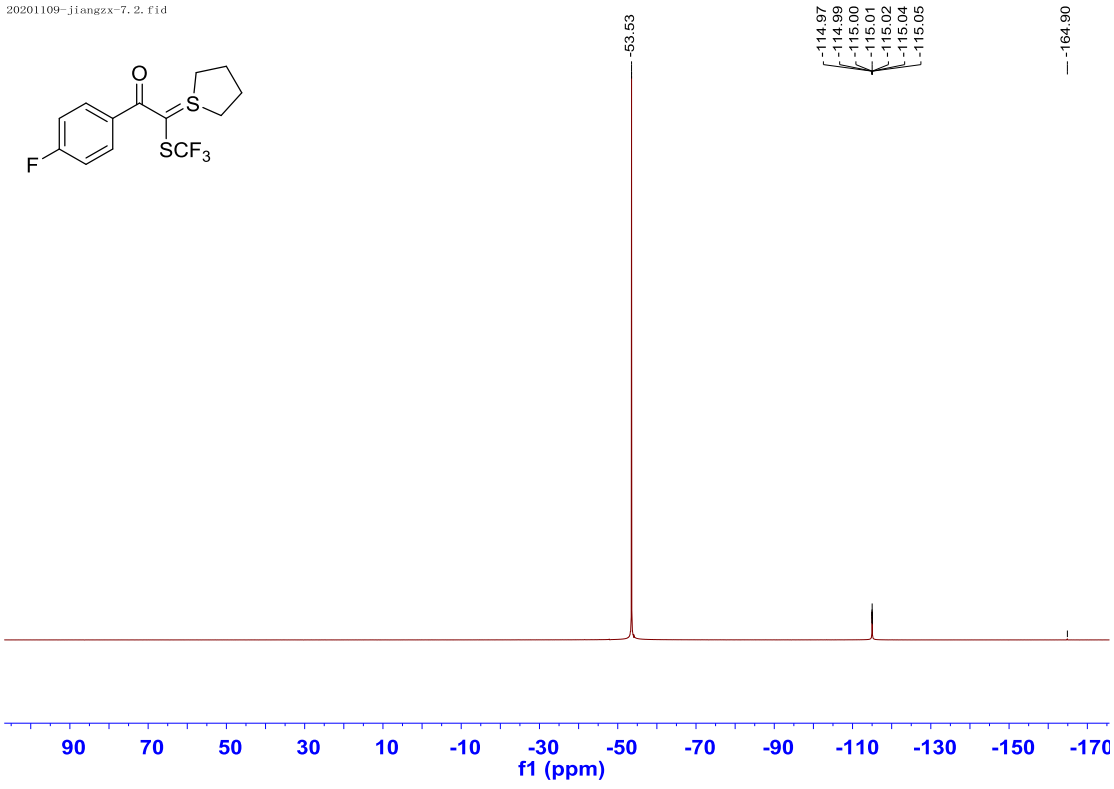
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3b**.



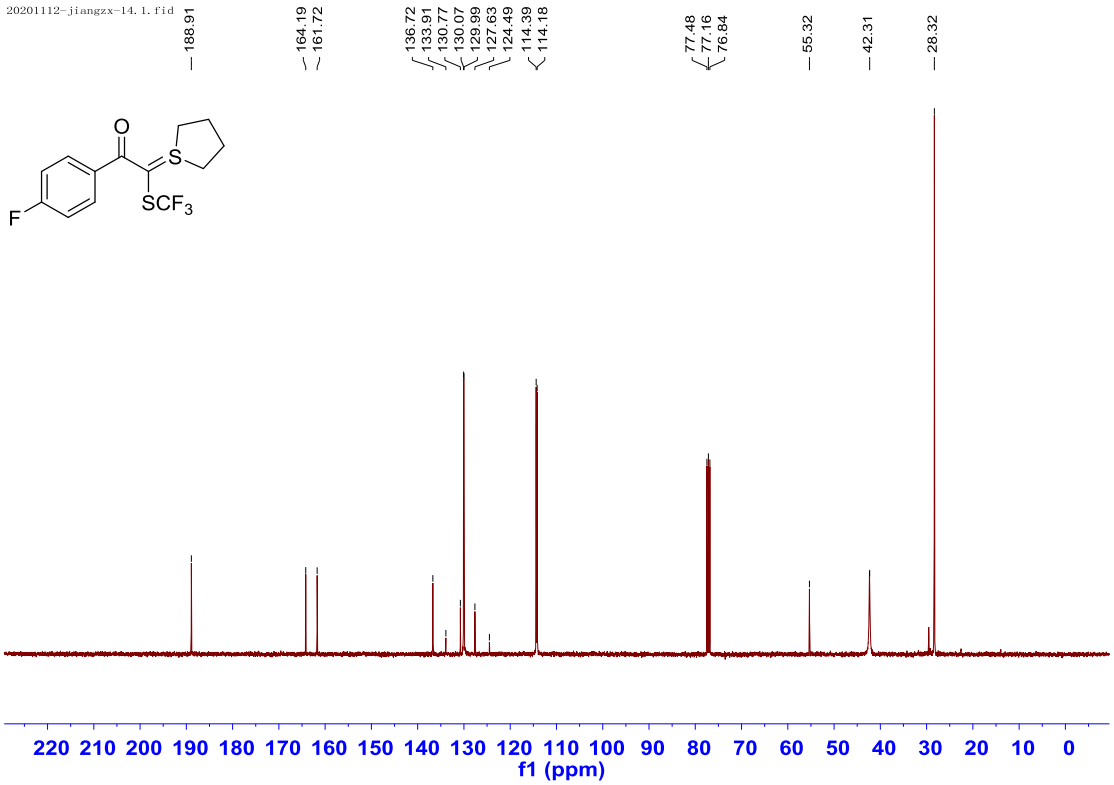
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**.



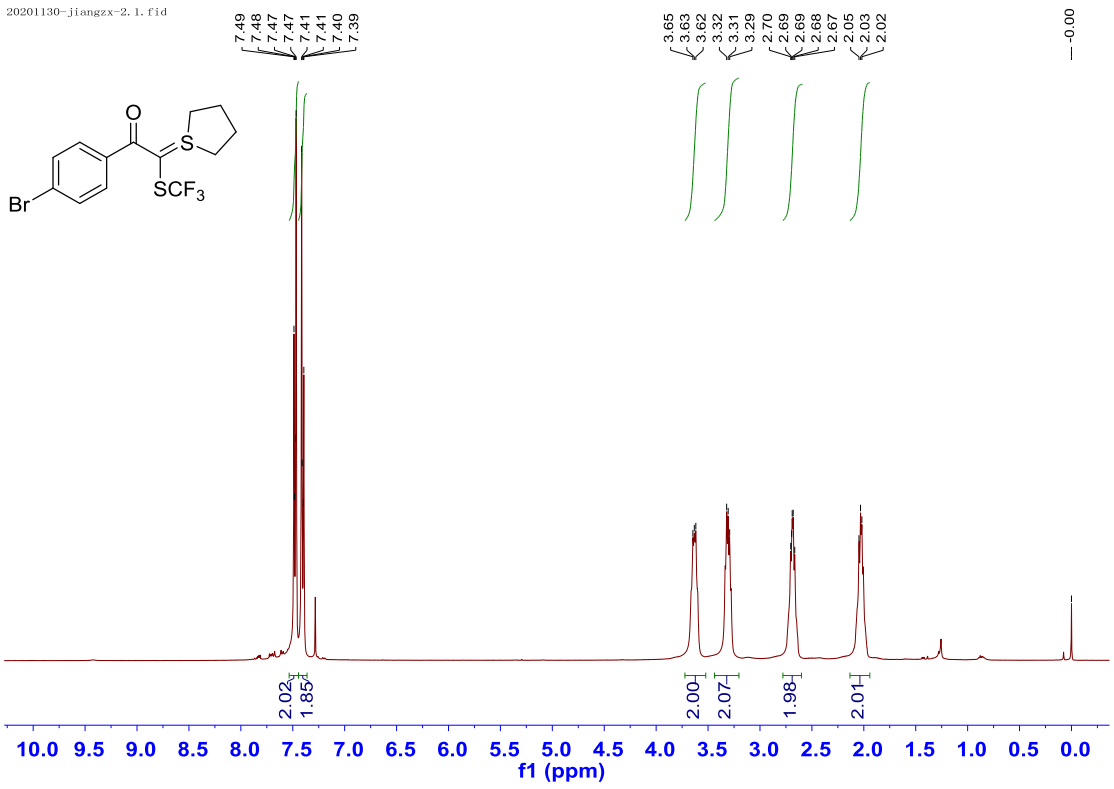
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3c**.



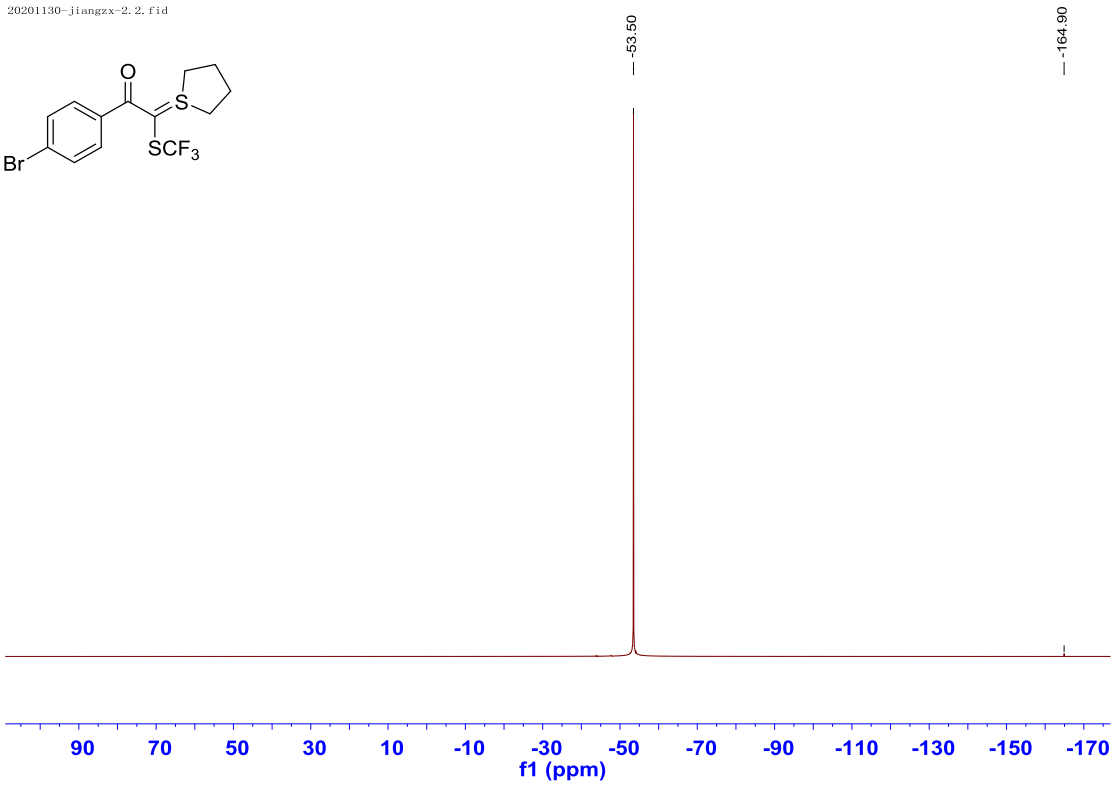
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3c**.



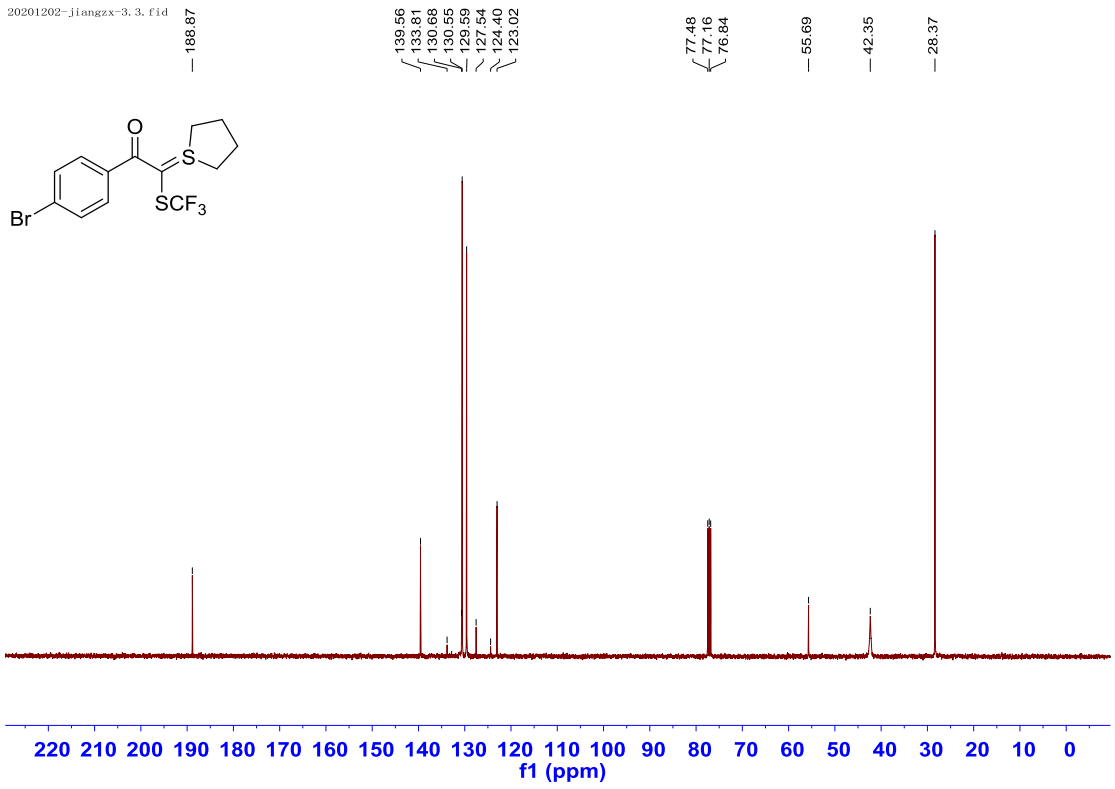
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**.



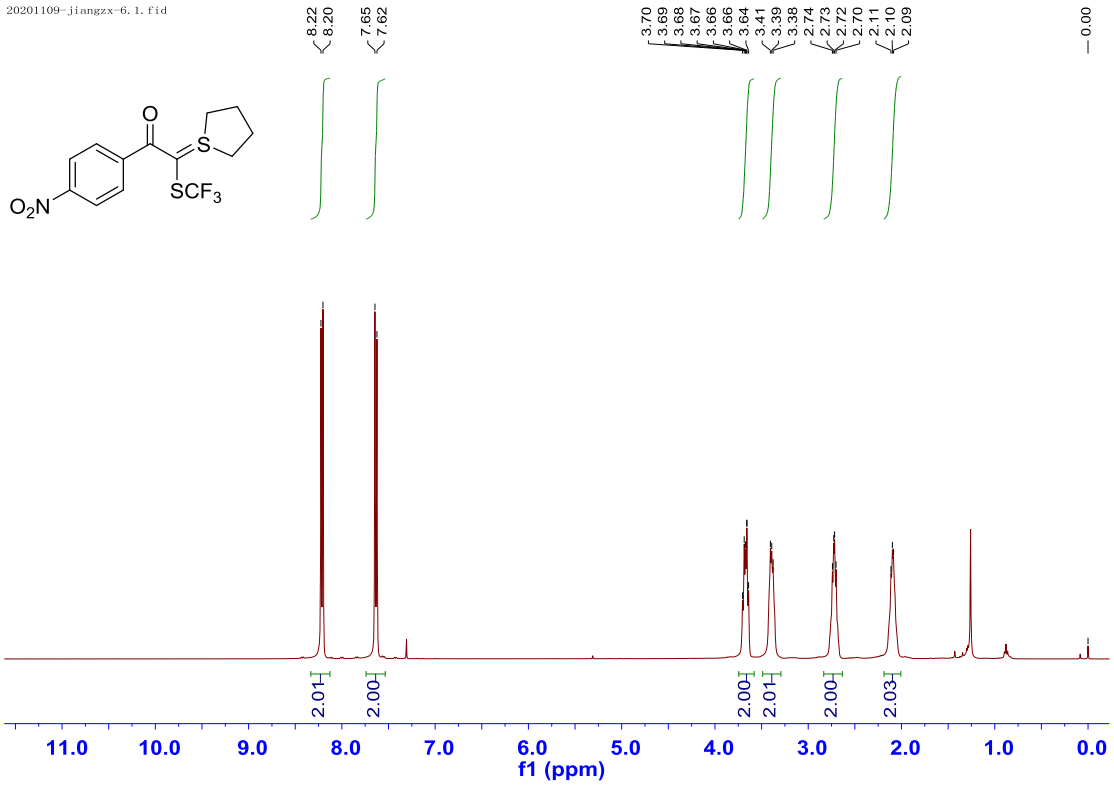
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3d**.



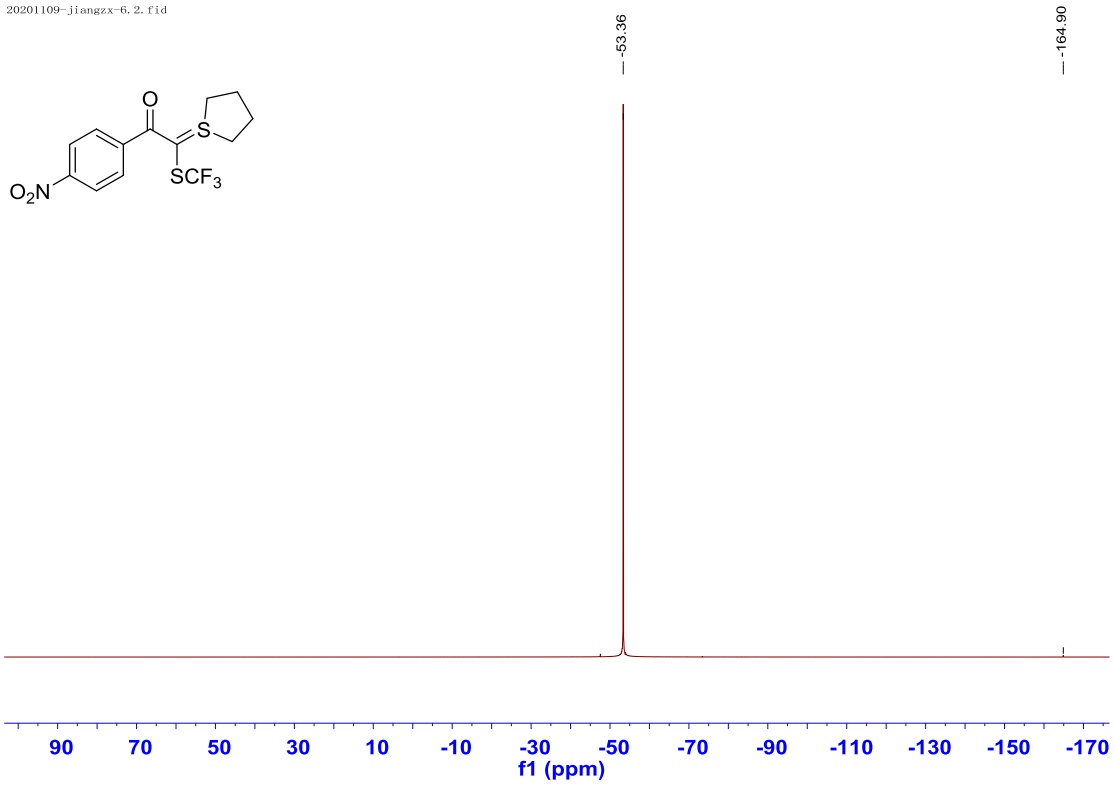
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3d**.



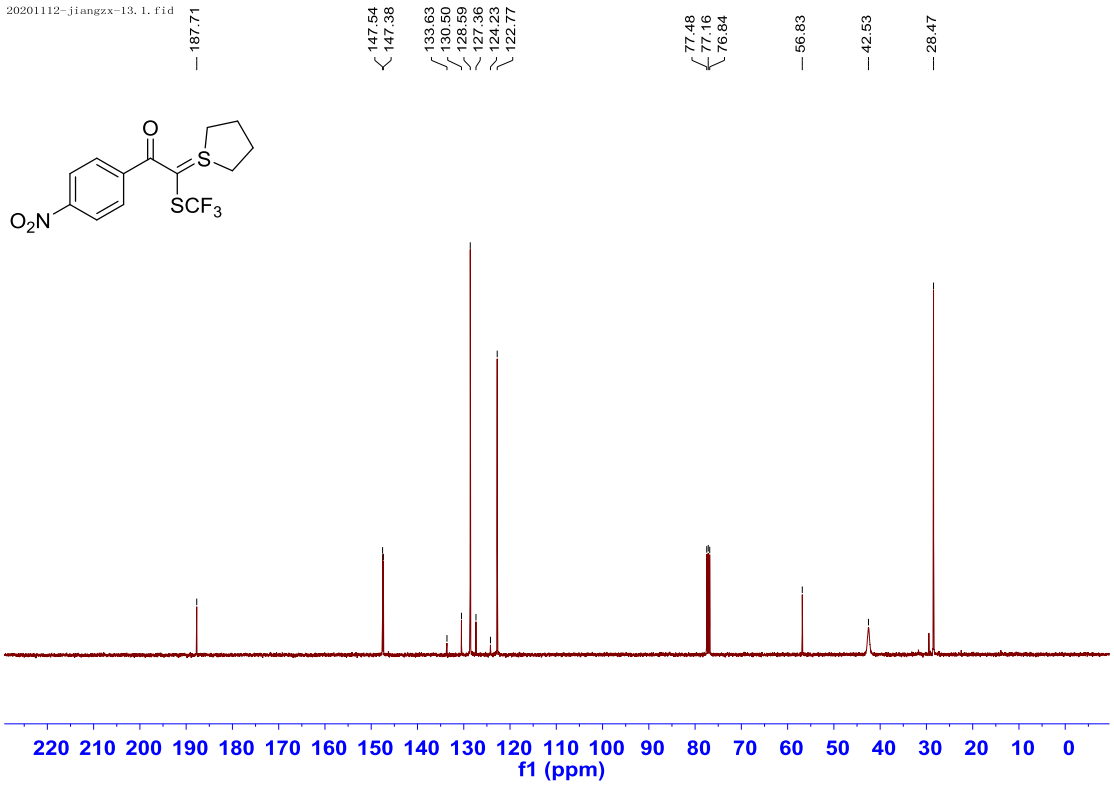
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**.



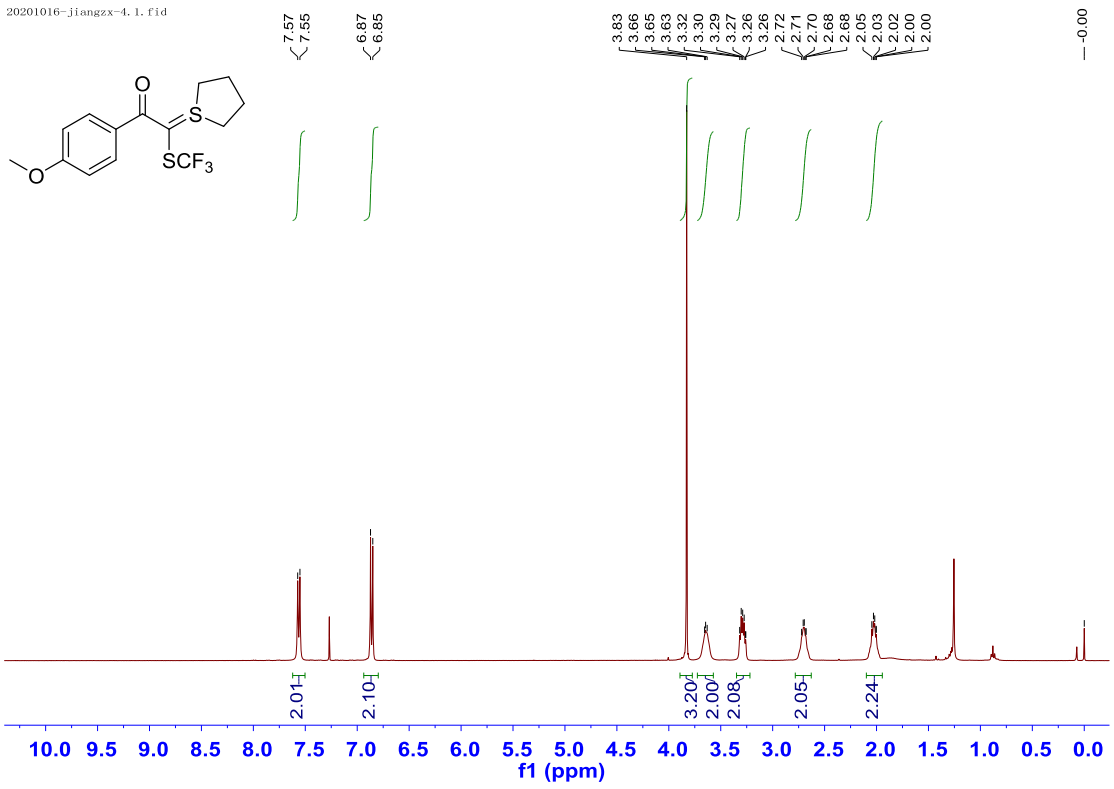
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3e**.



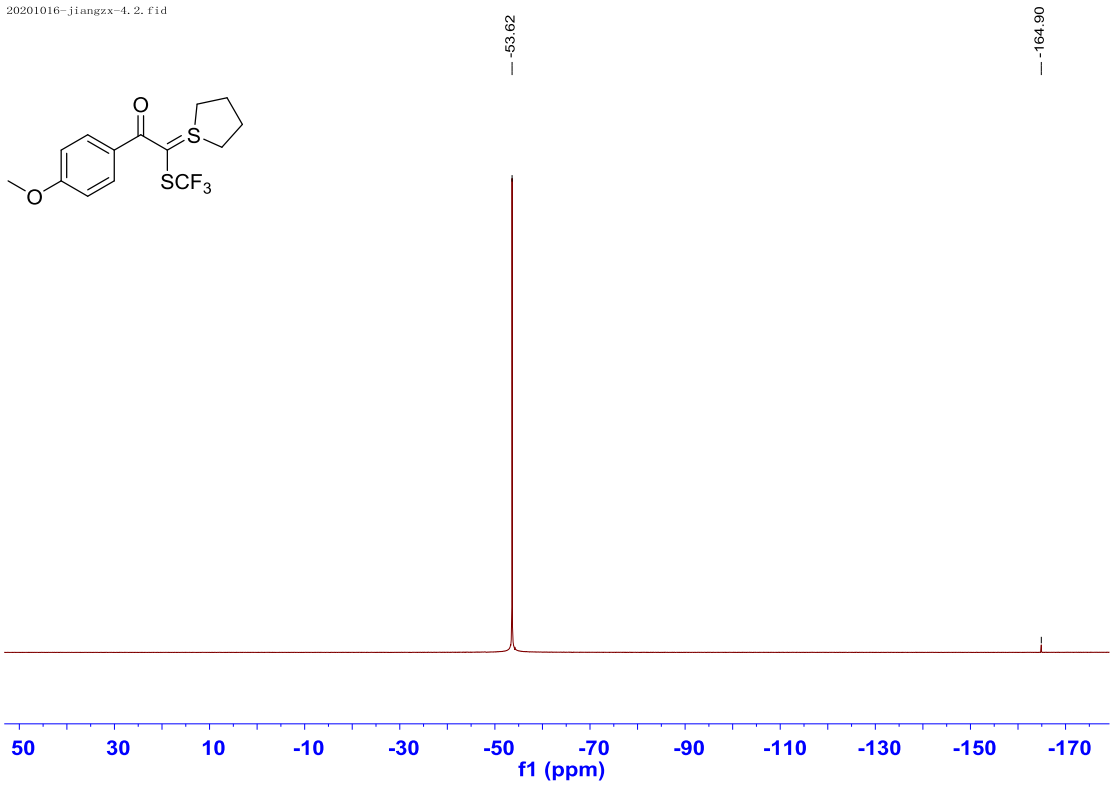
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3e**.



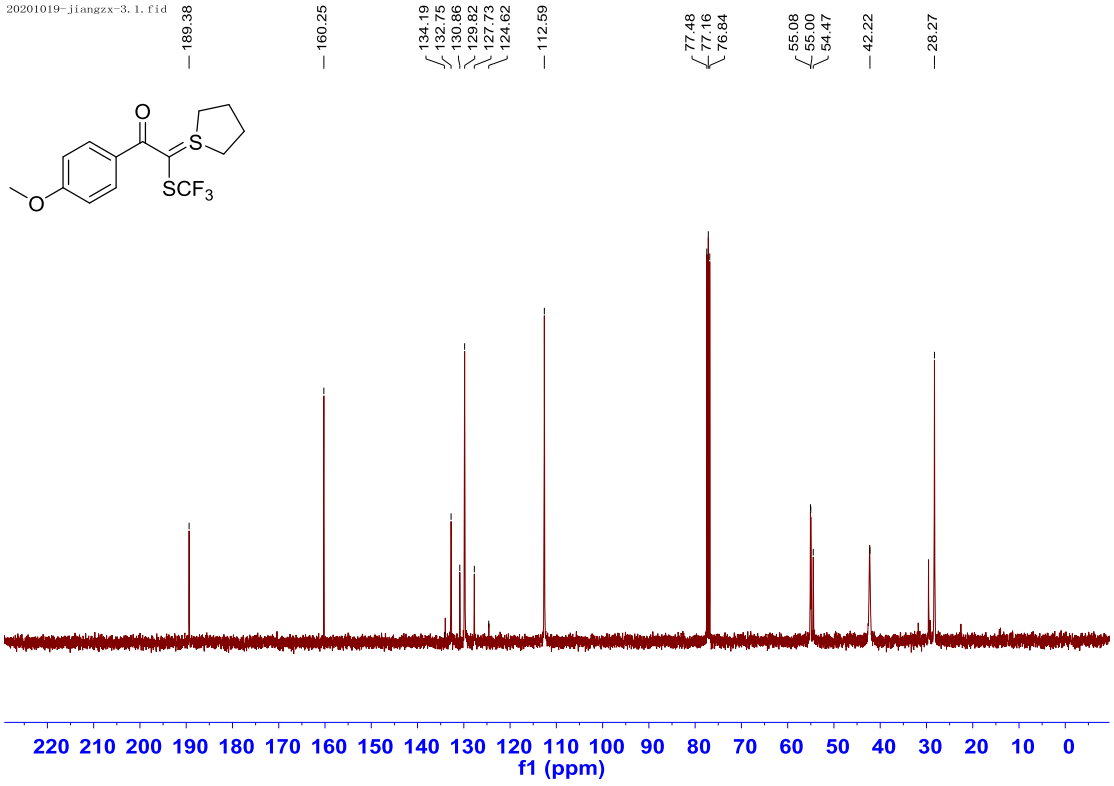
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**.



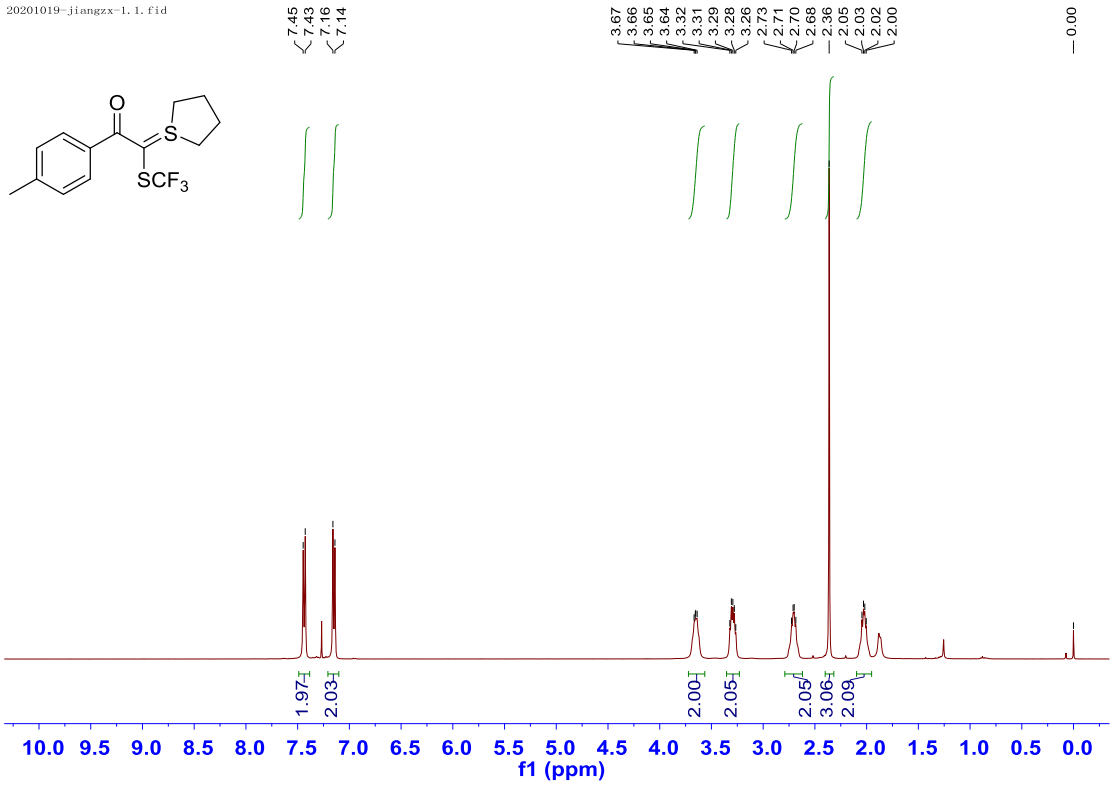
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3f**.



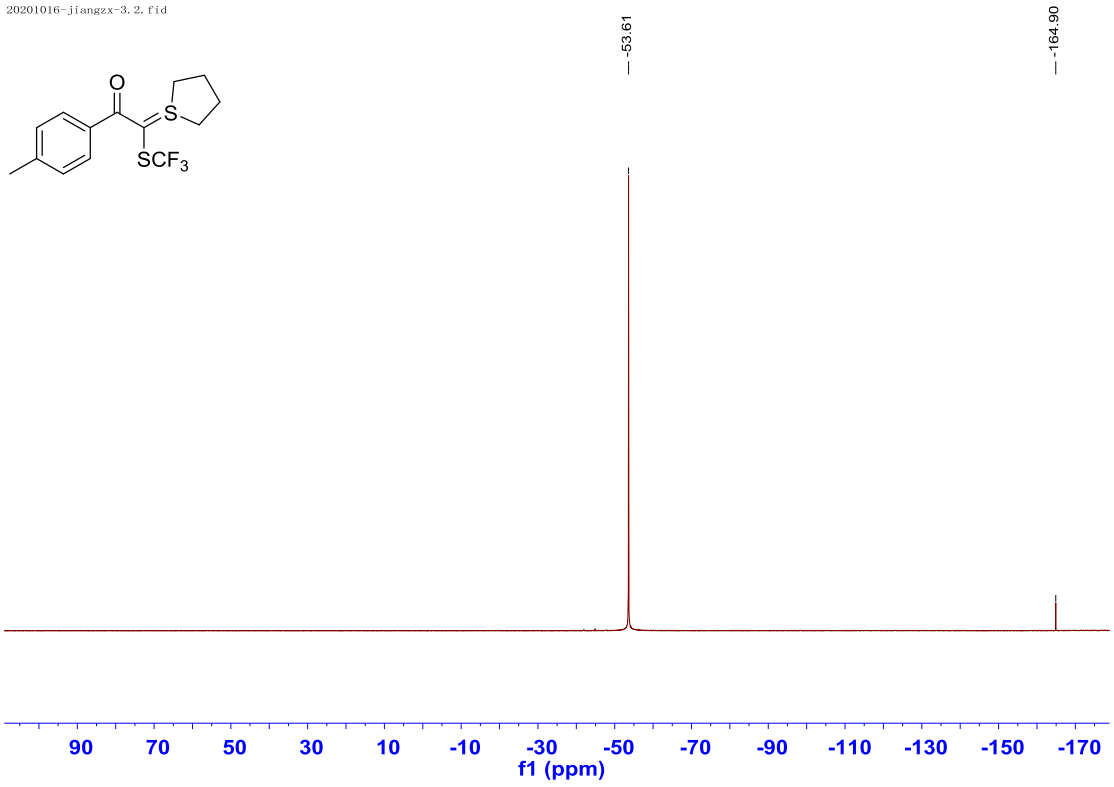
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3f**.



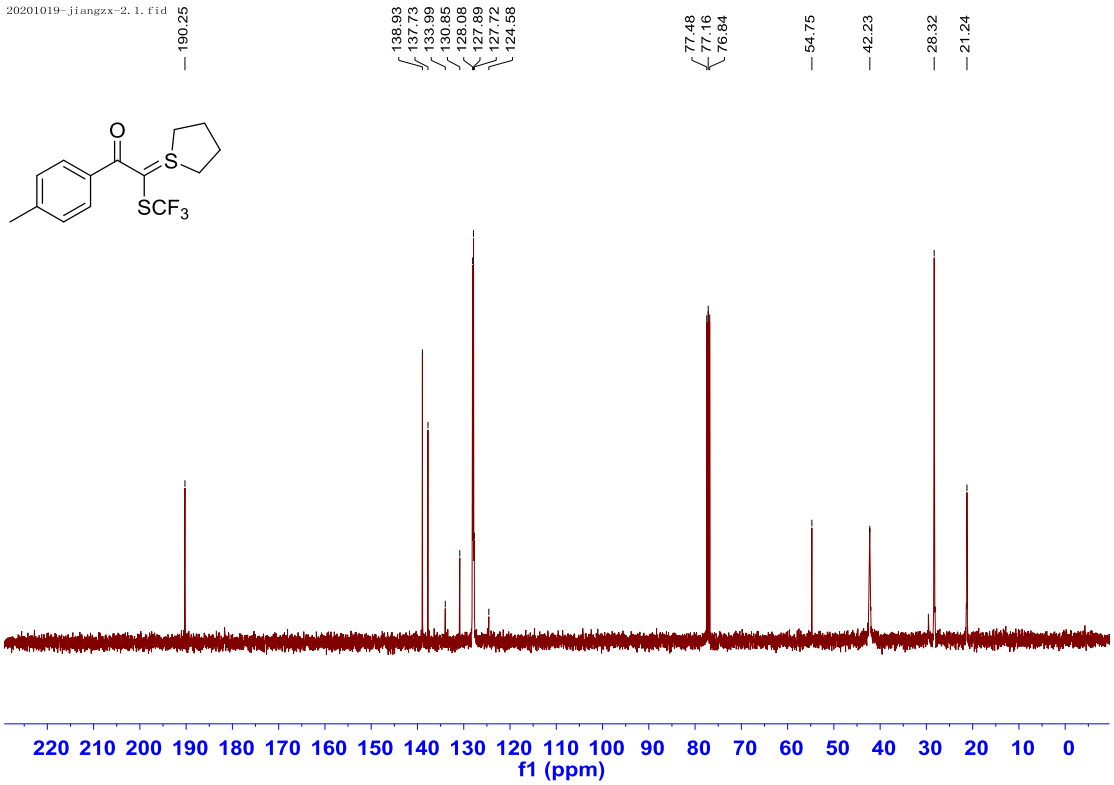
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**.



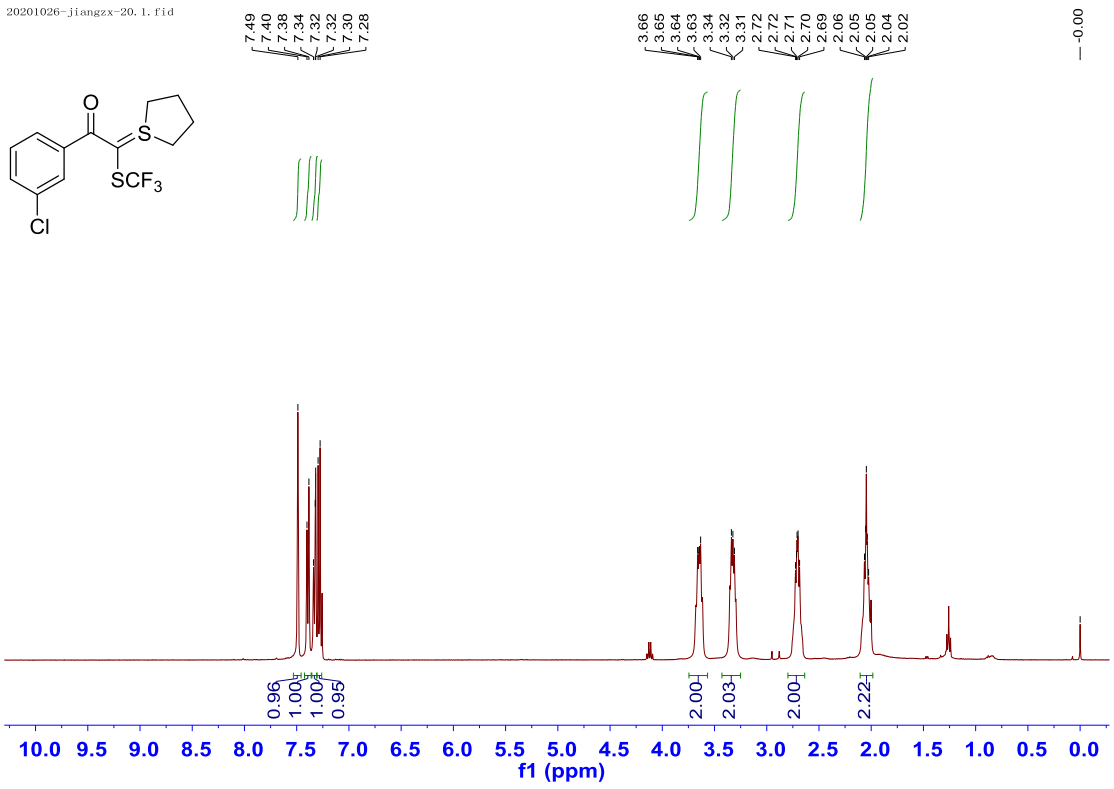
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3g**.



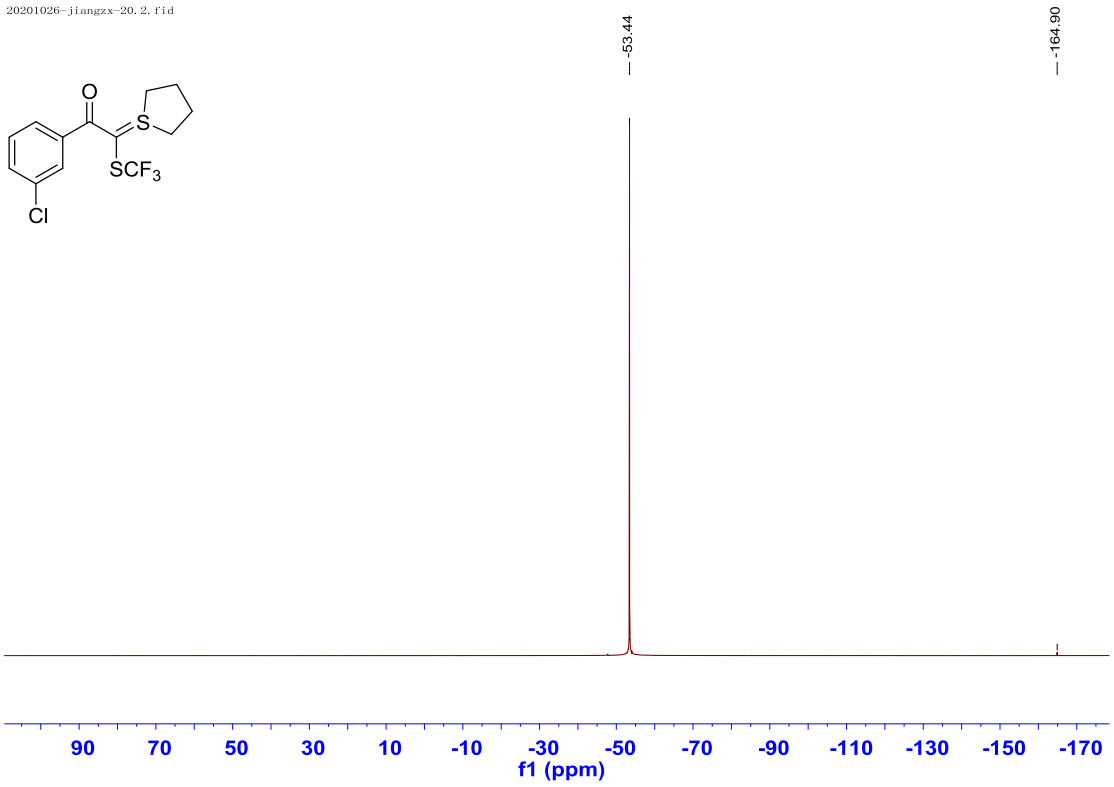
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3g**.



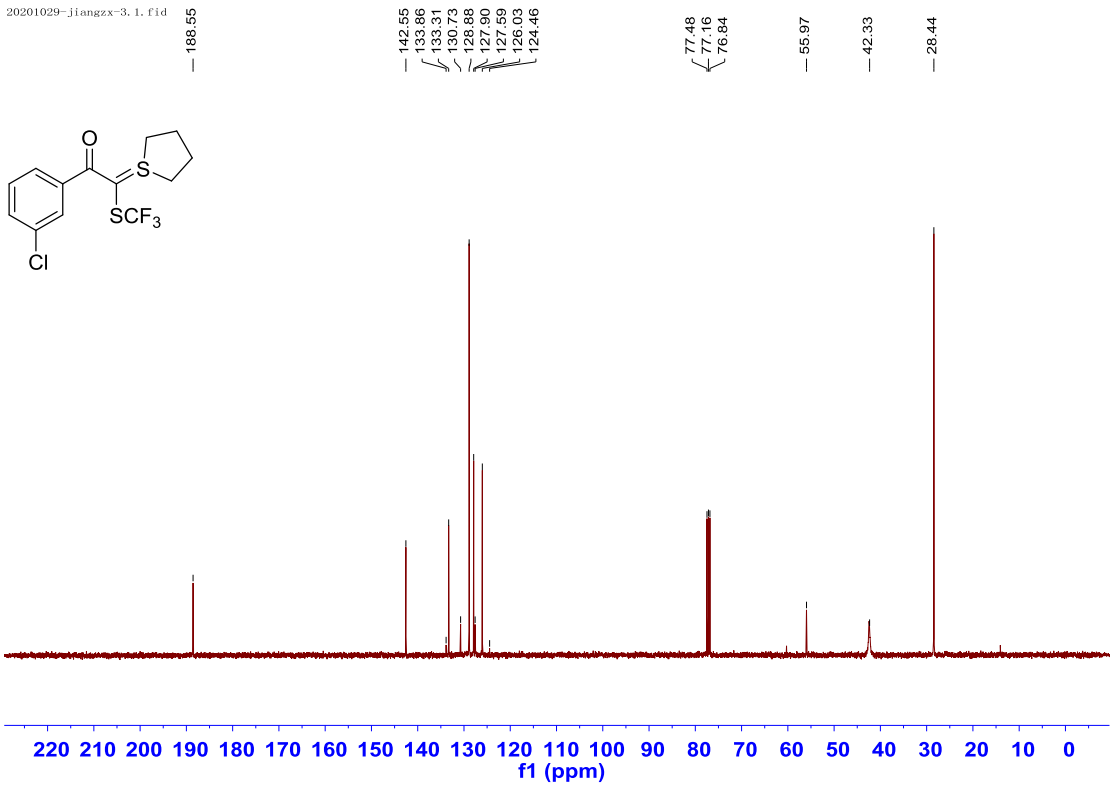
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**.



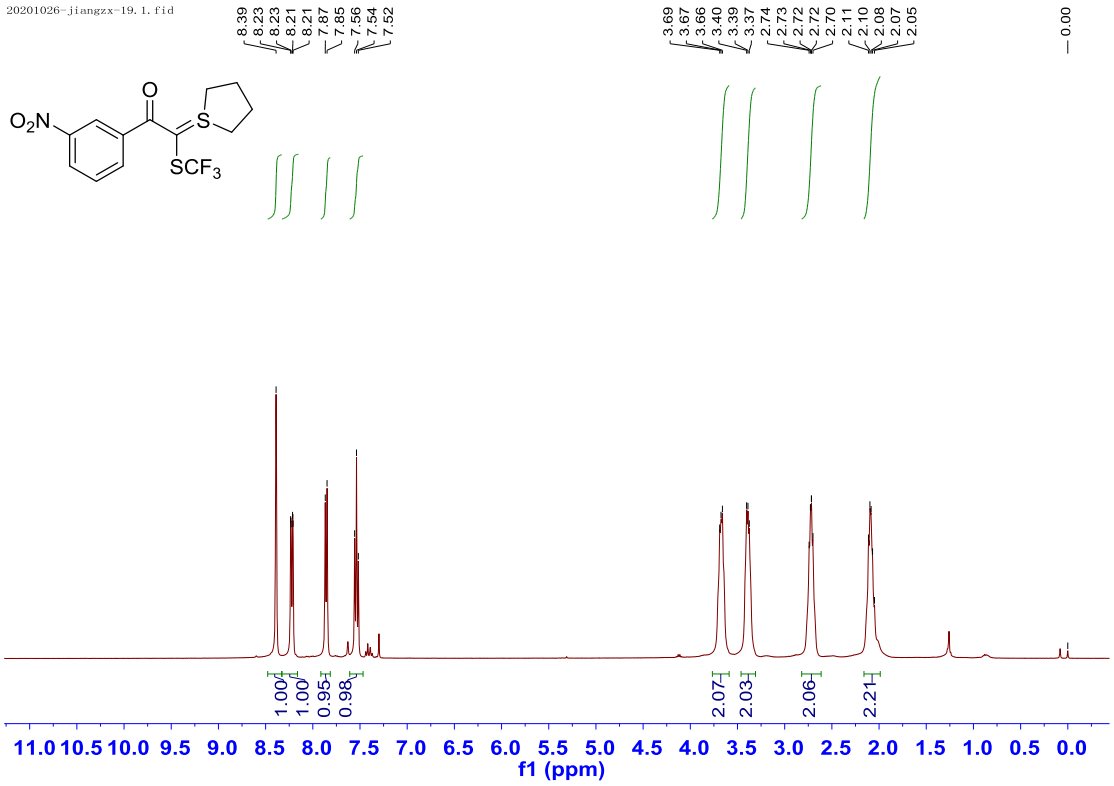
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3h**.



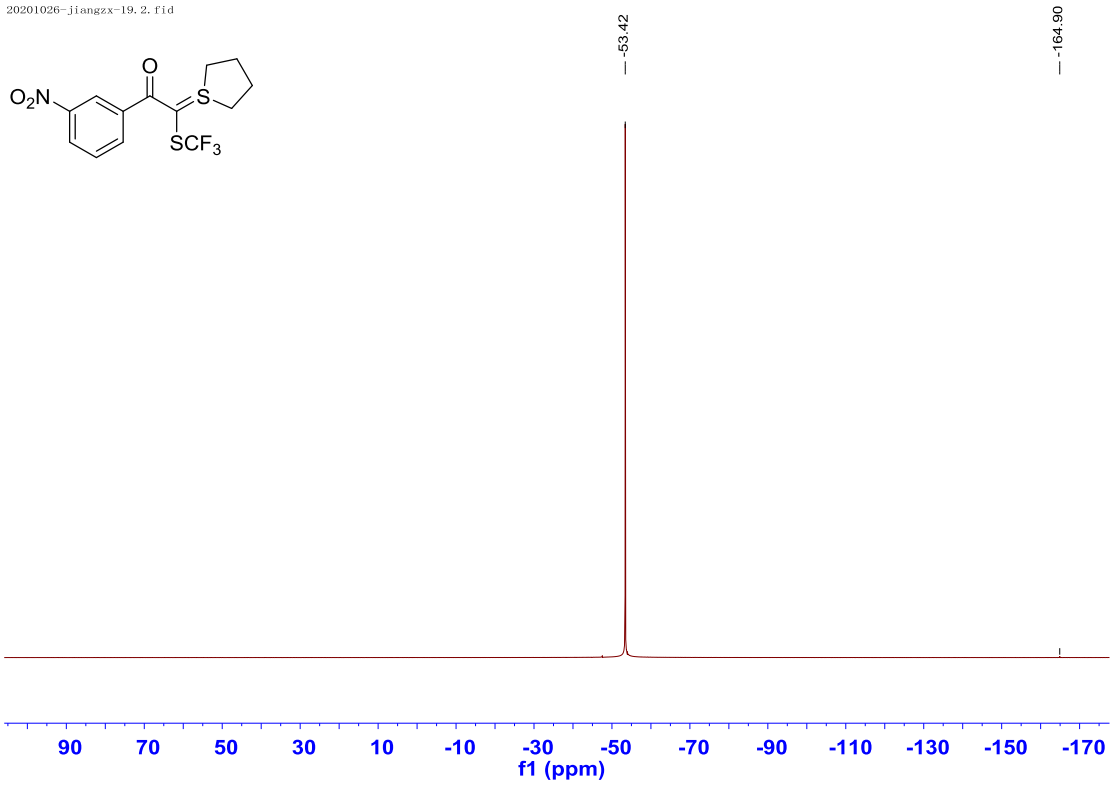
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**.



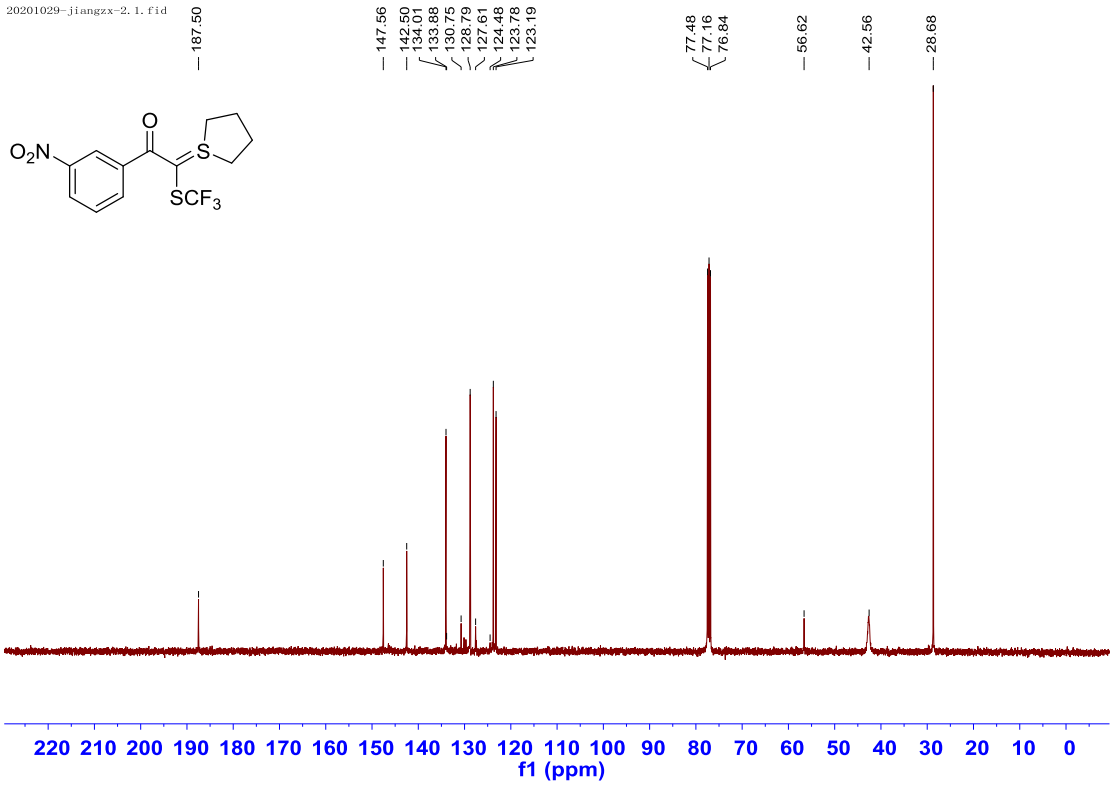
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**.



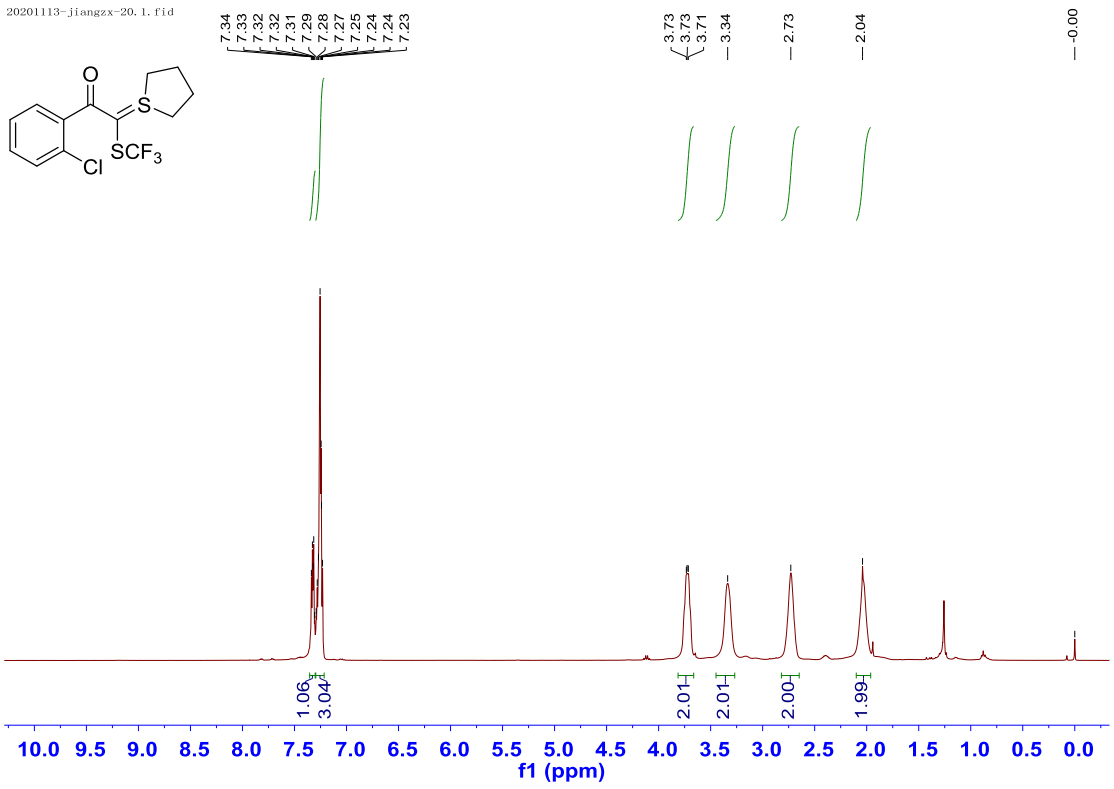
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3i**.



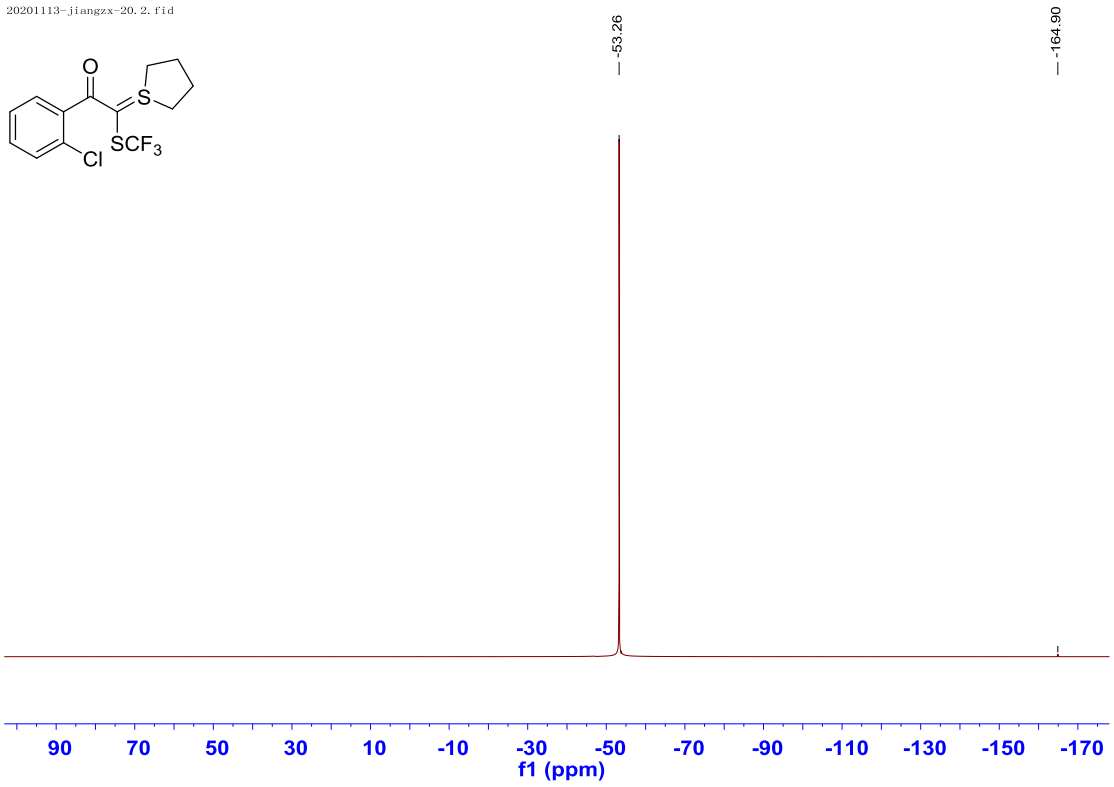
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**.



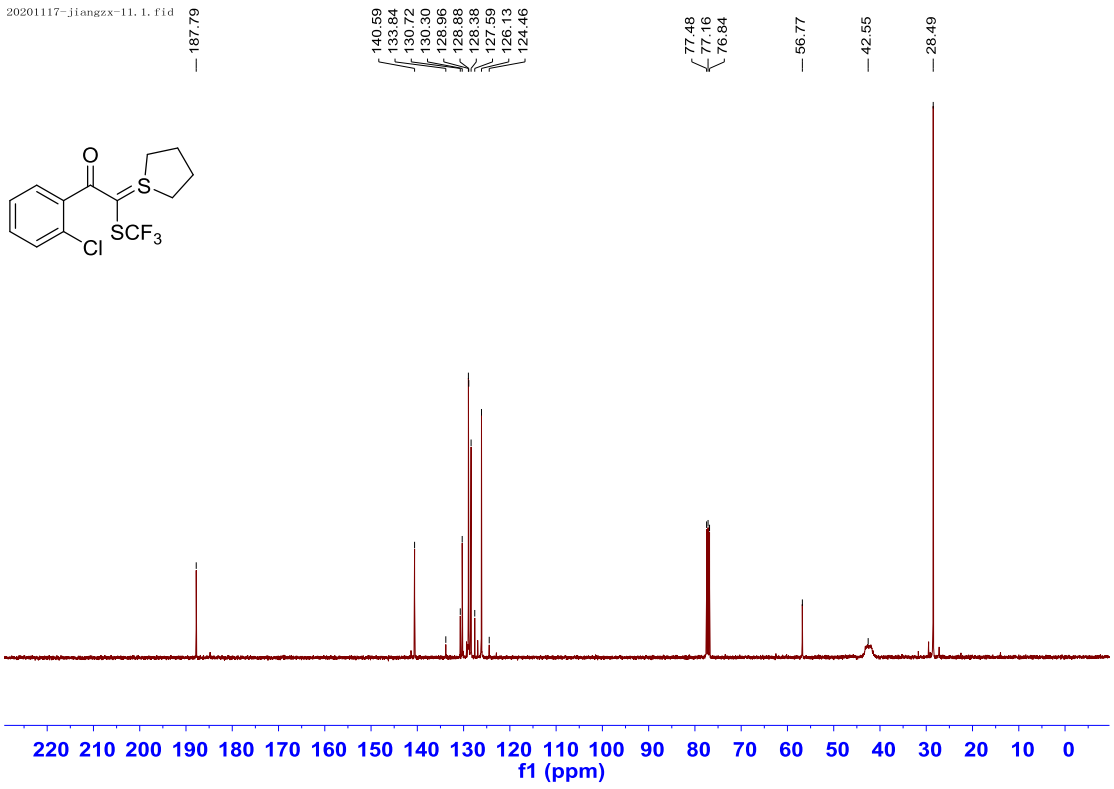
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**.



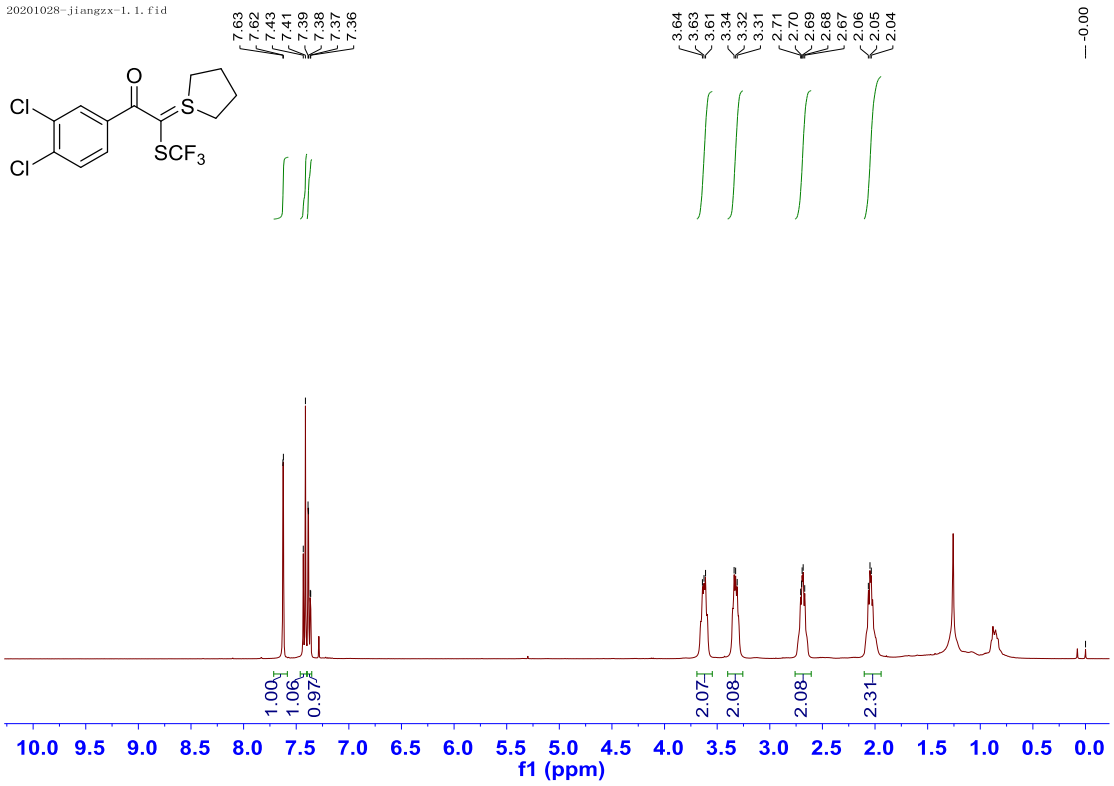
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3j**.



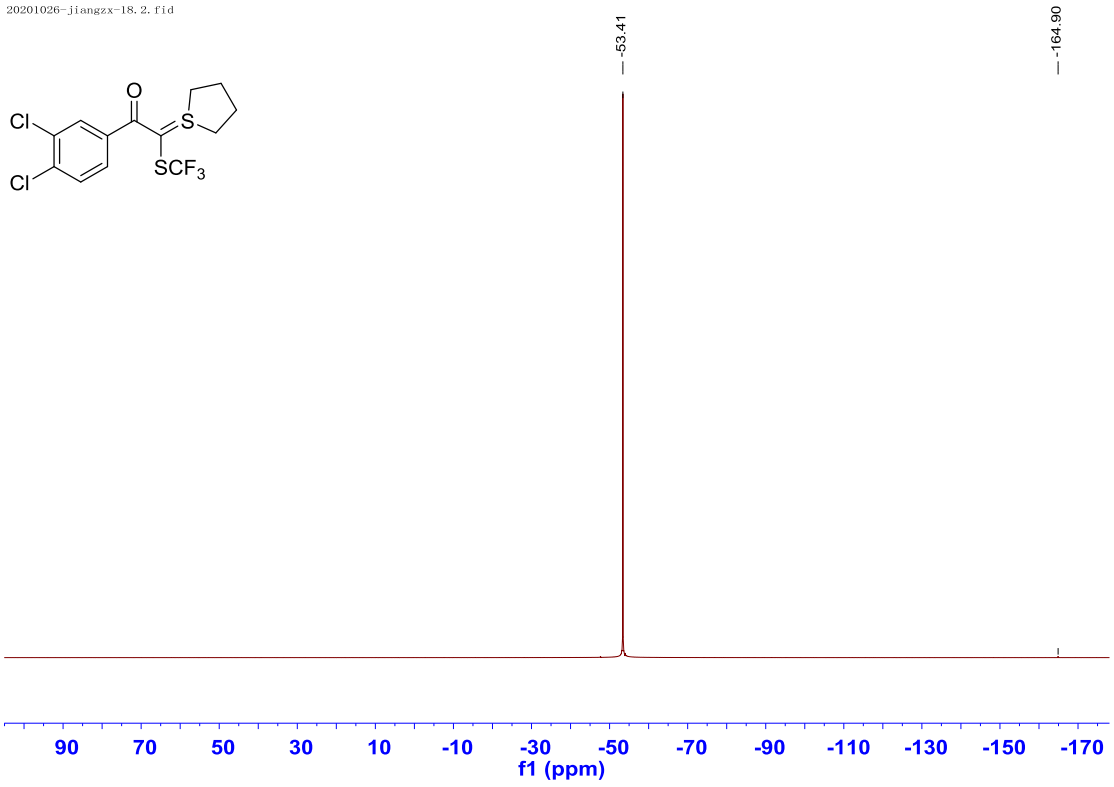
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**.



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3k**.



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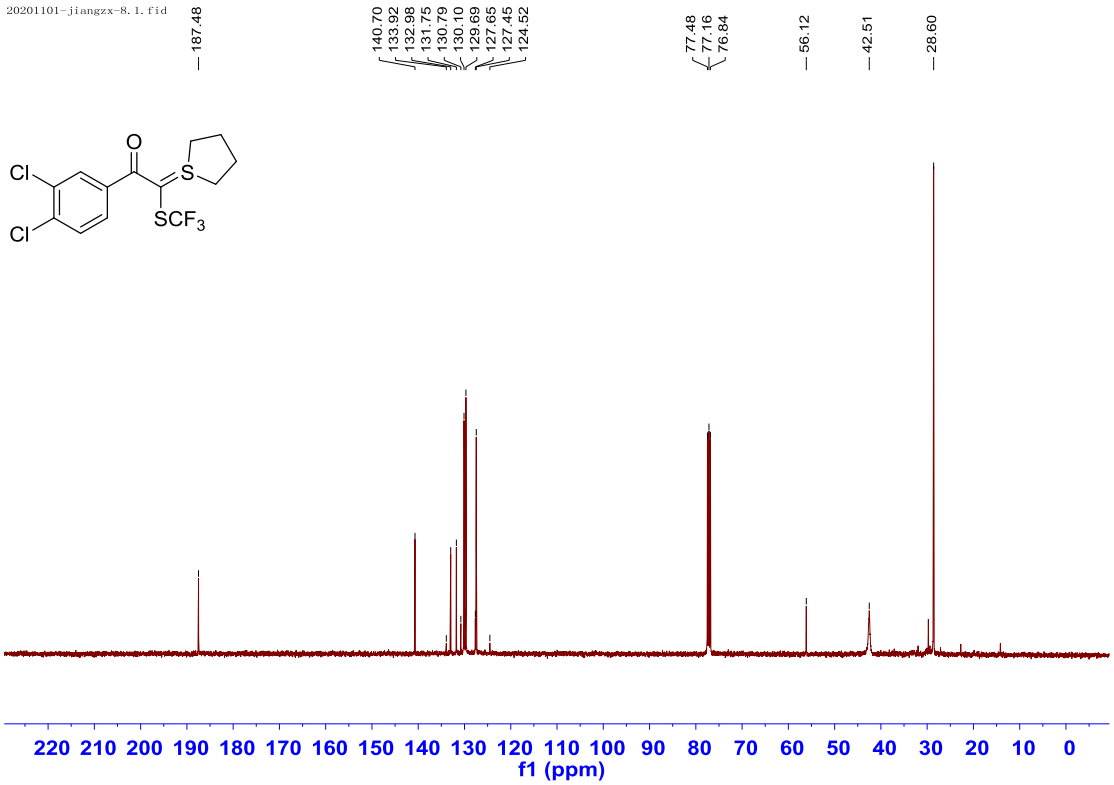

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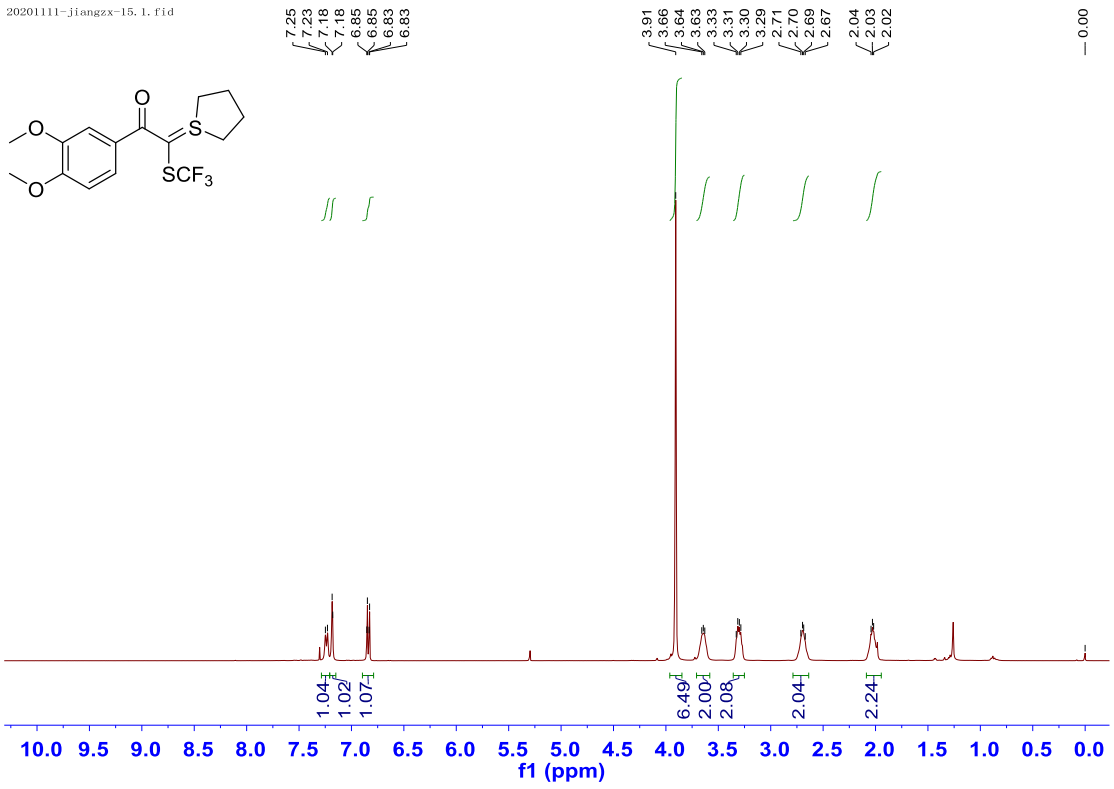
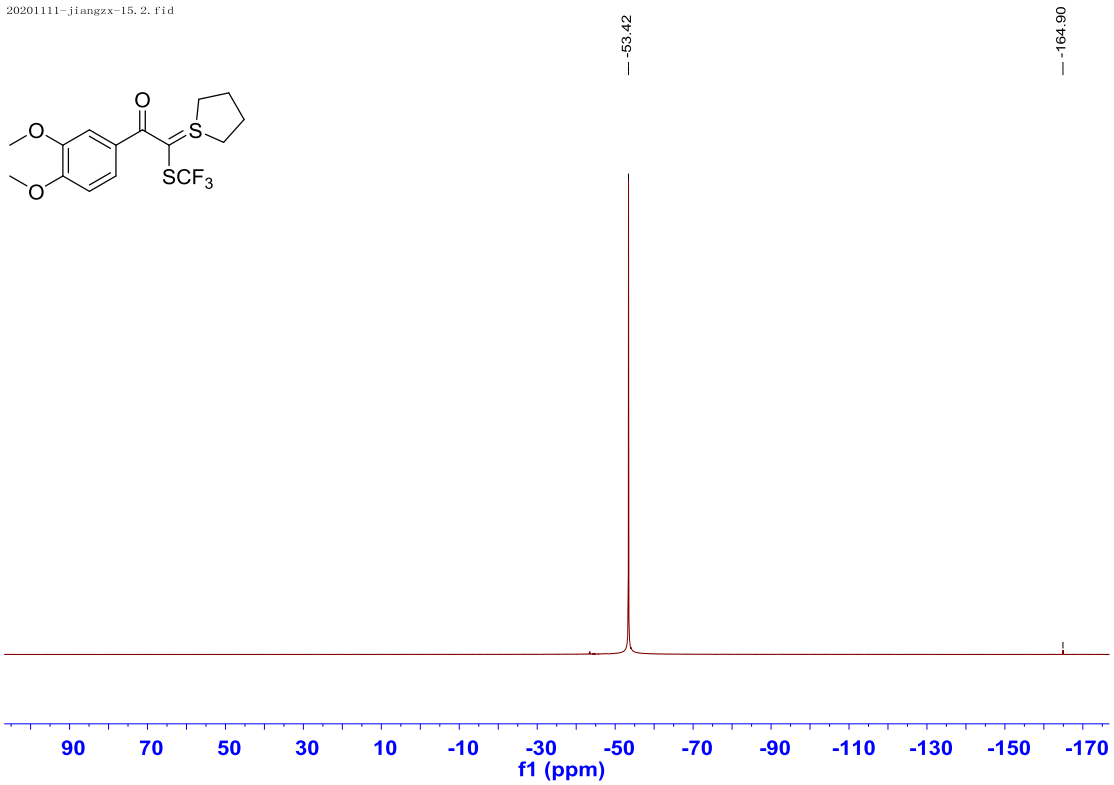
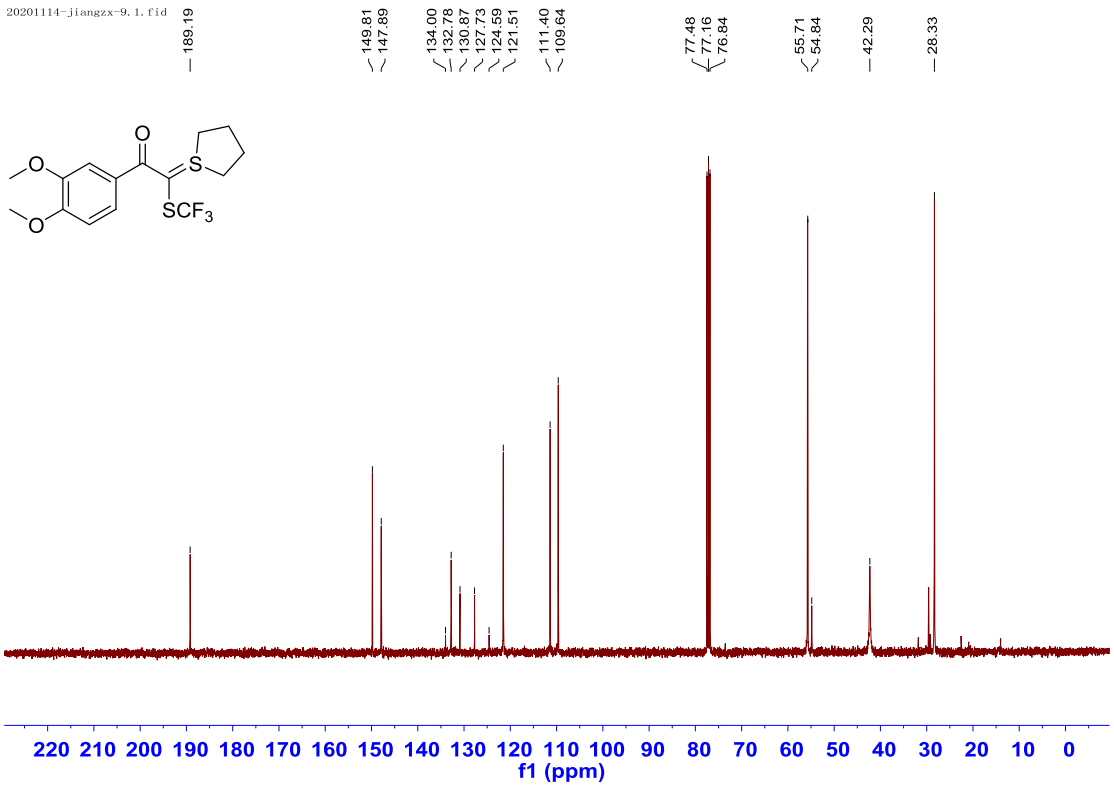


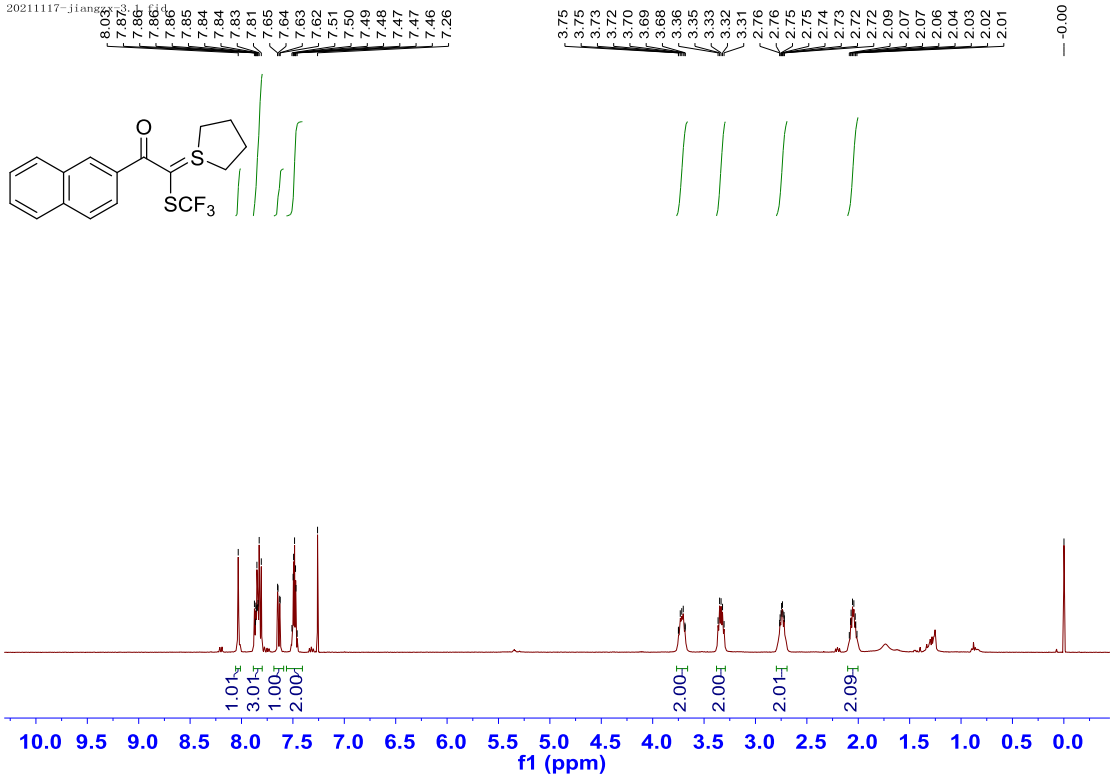
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3l**.



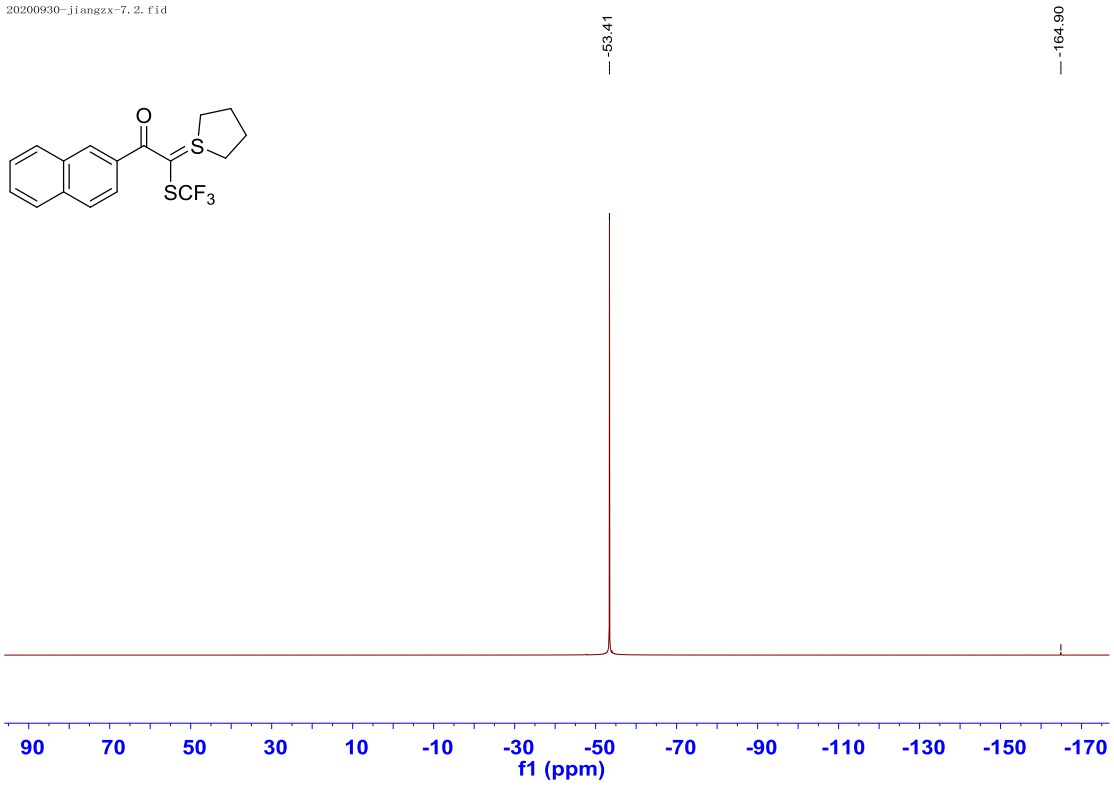
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3l**.



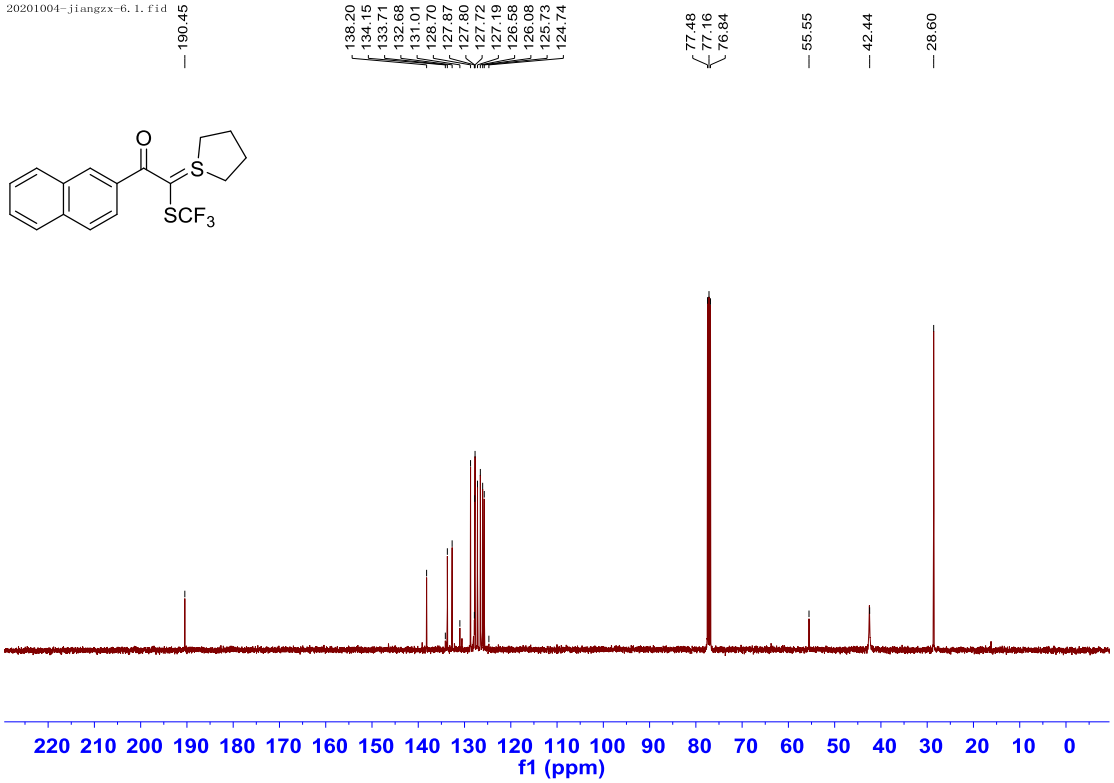
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**.



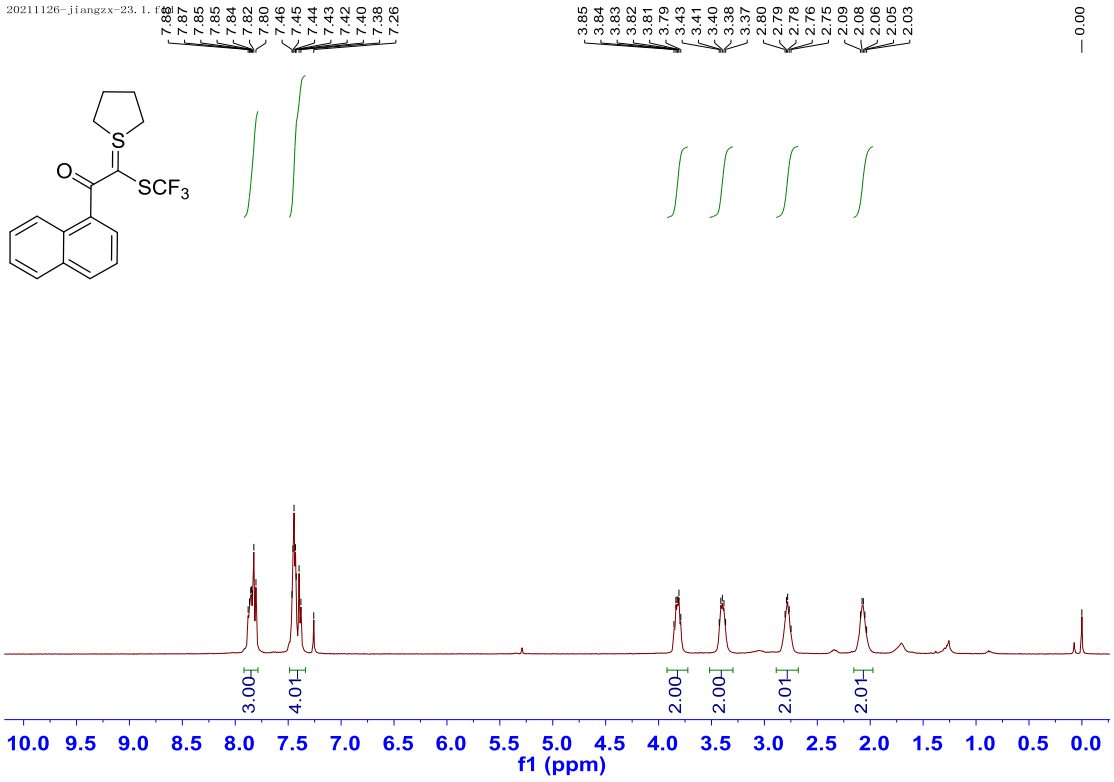
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3m**.



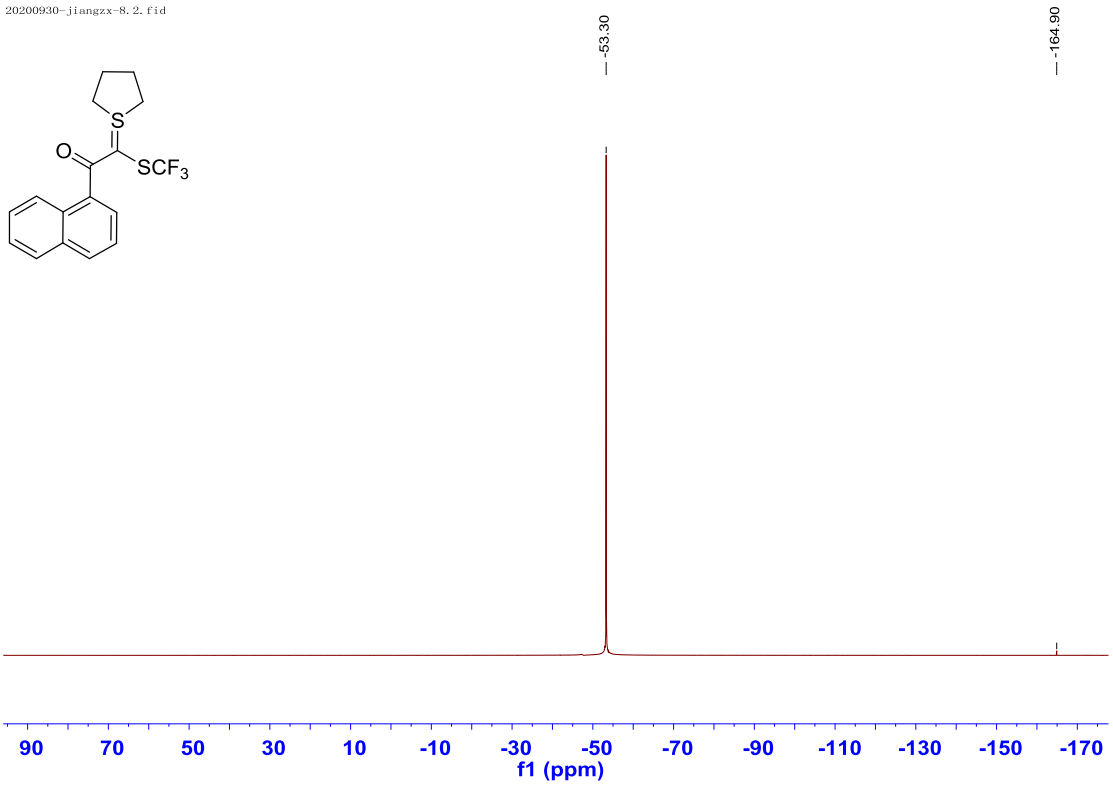
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3m**.



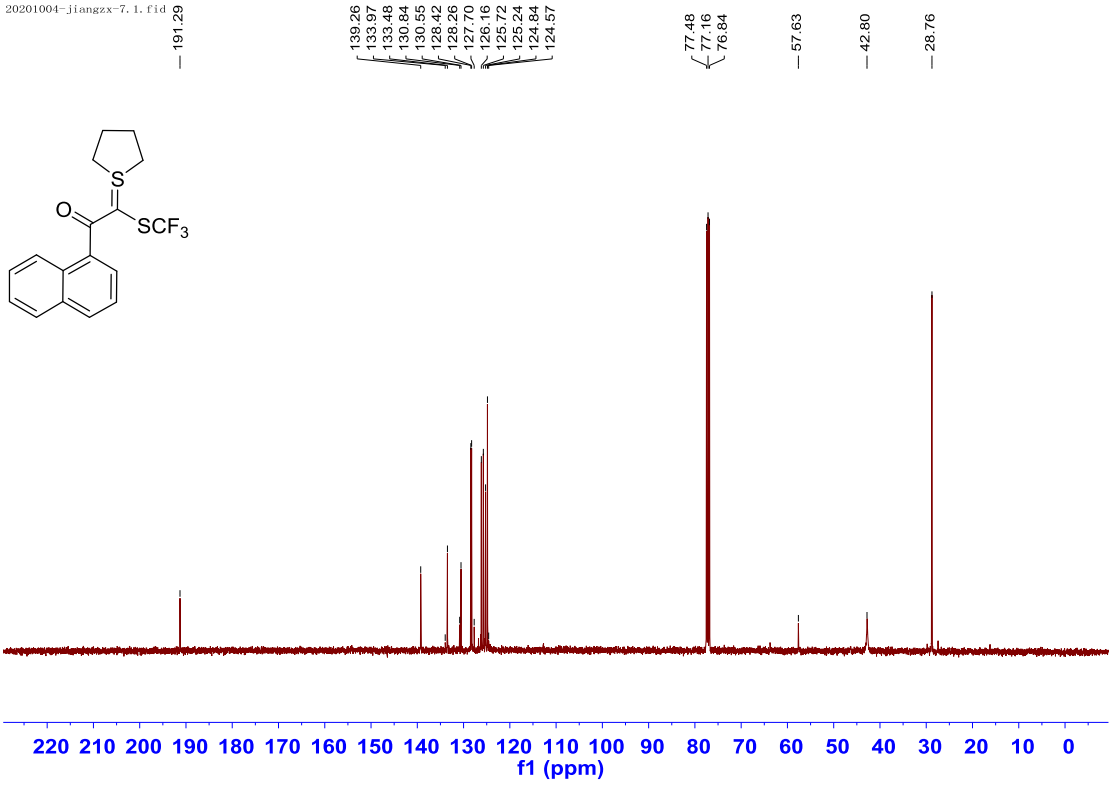
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**.



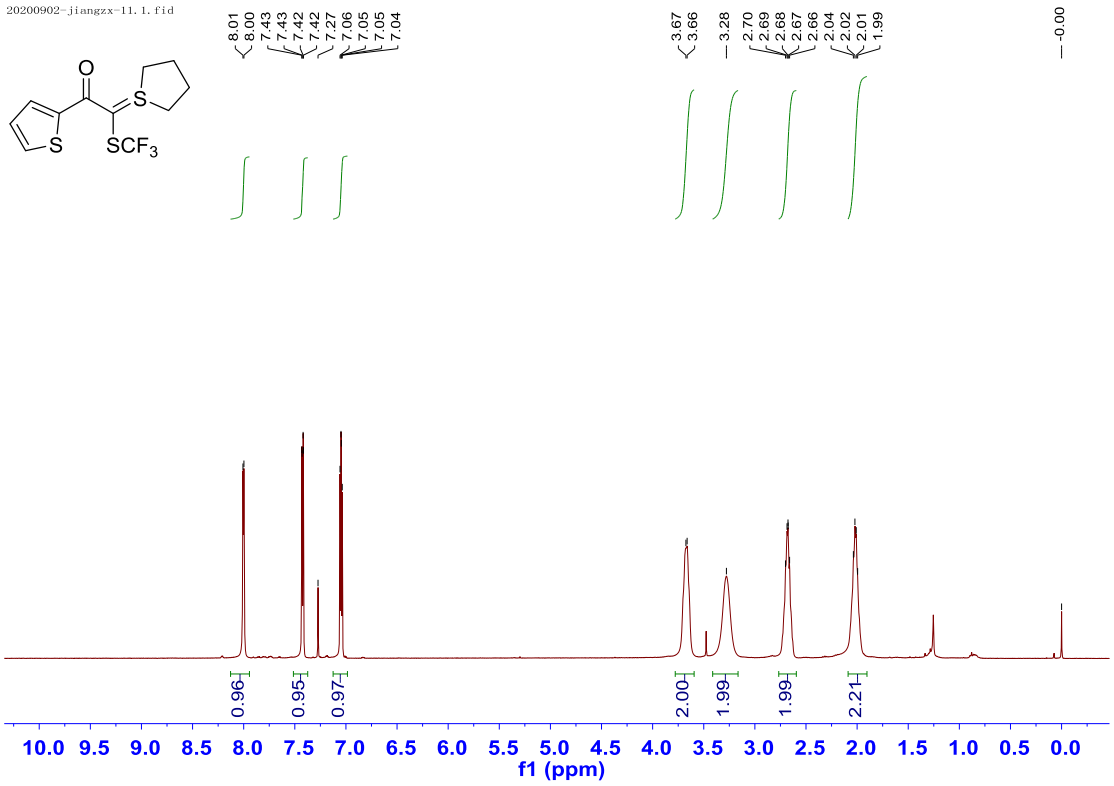
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3n**.



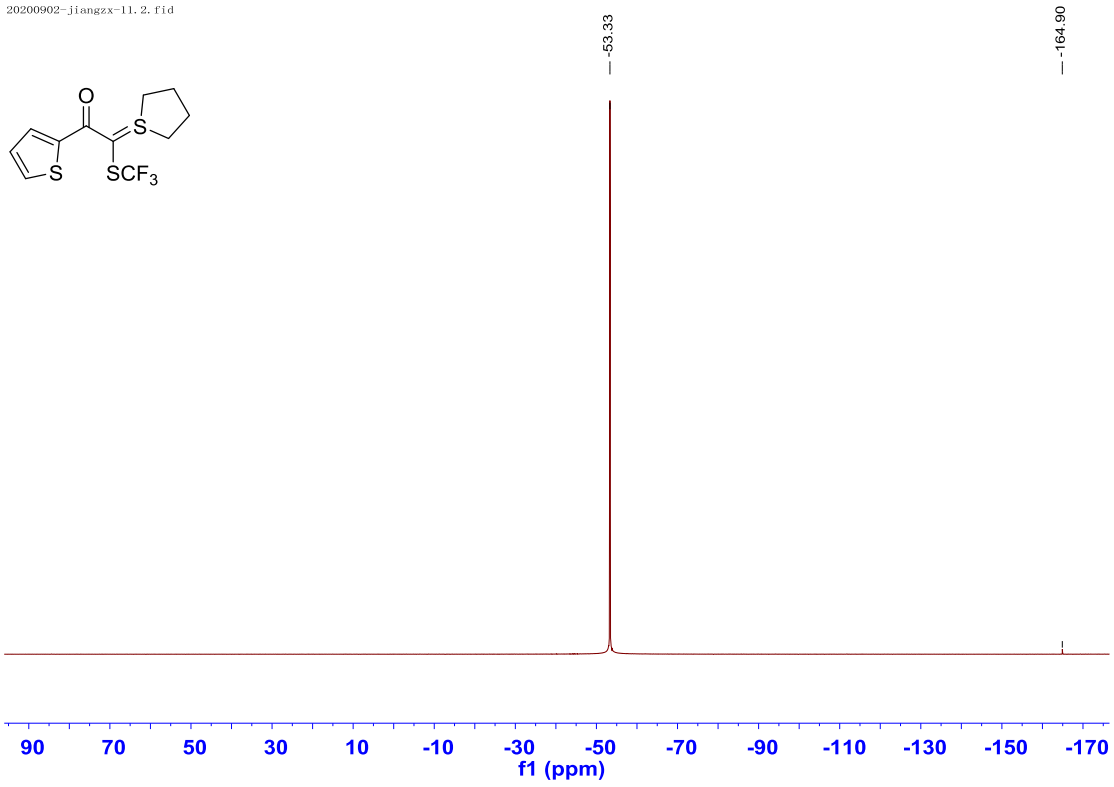
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3n**.



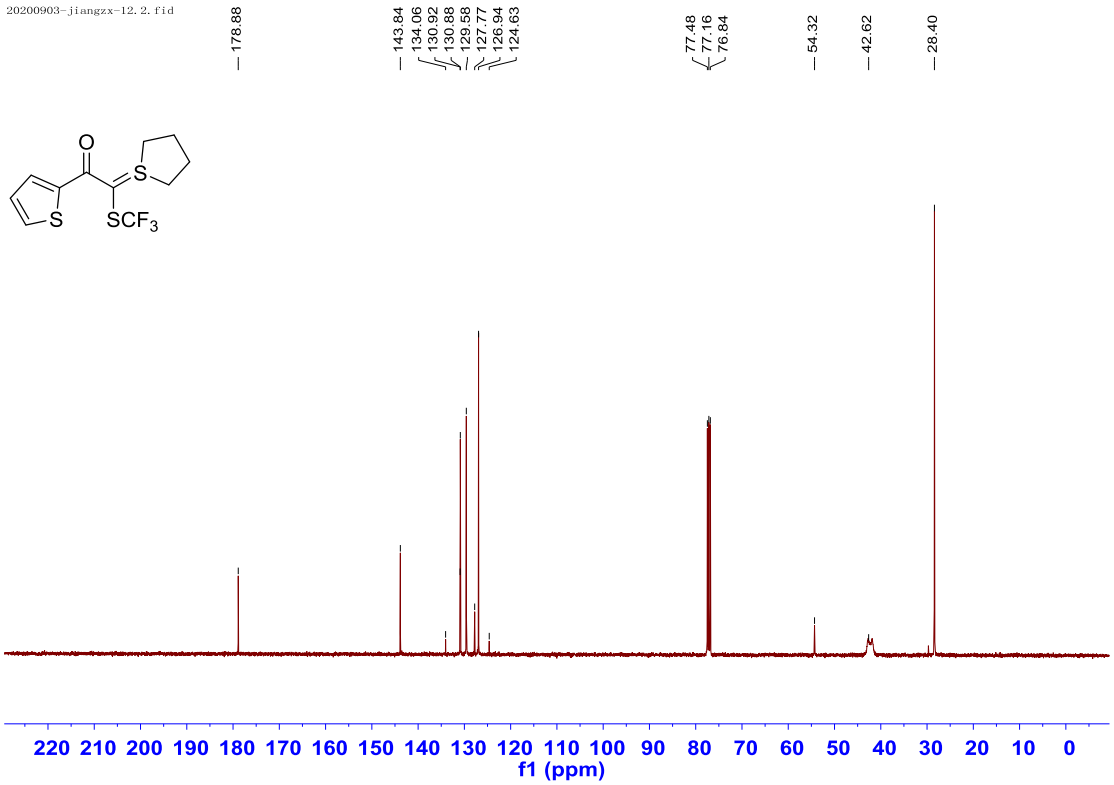
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**.



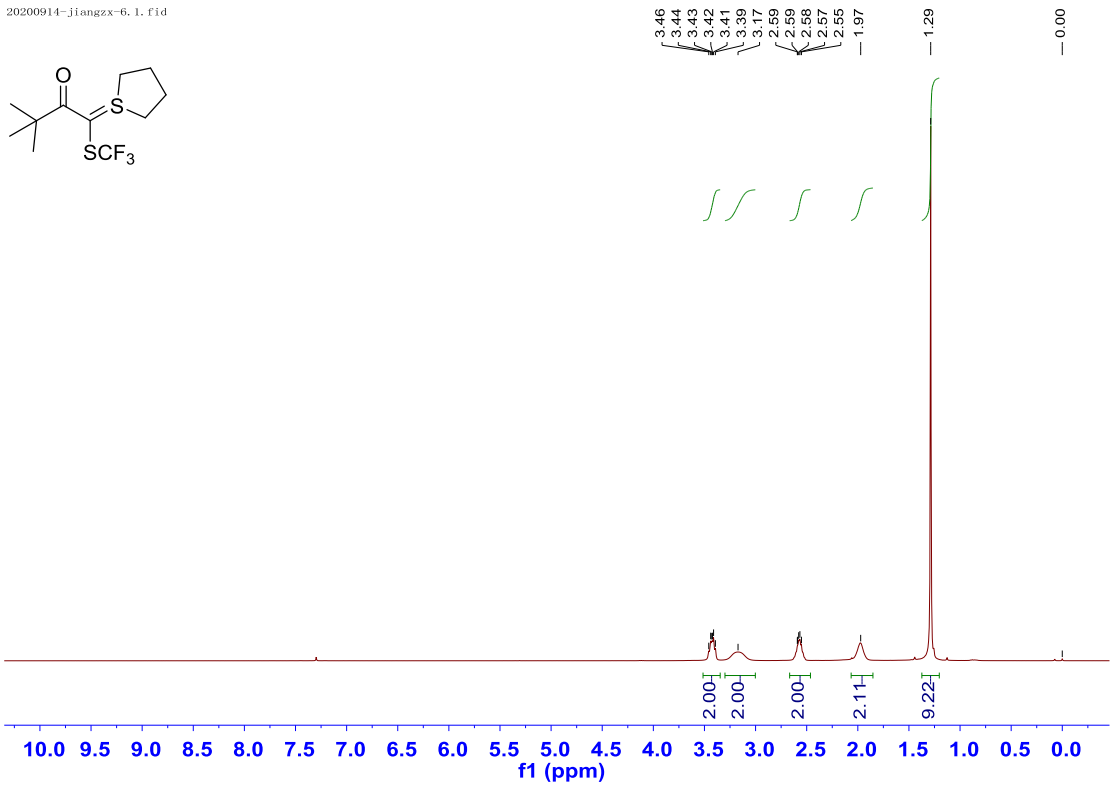
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3o**.



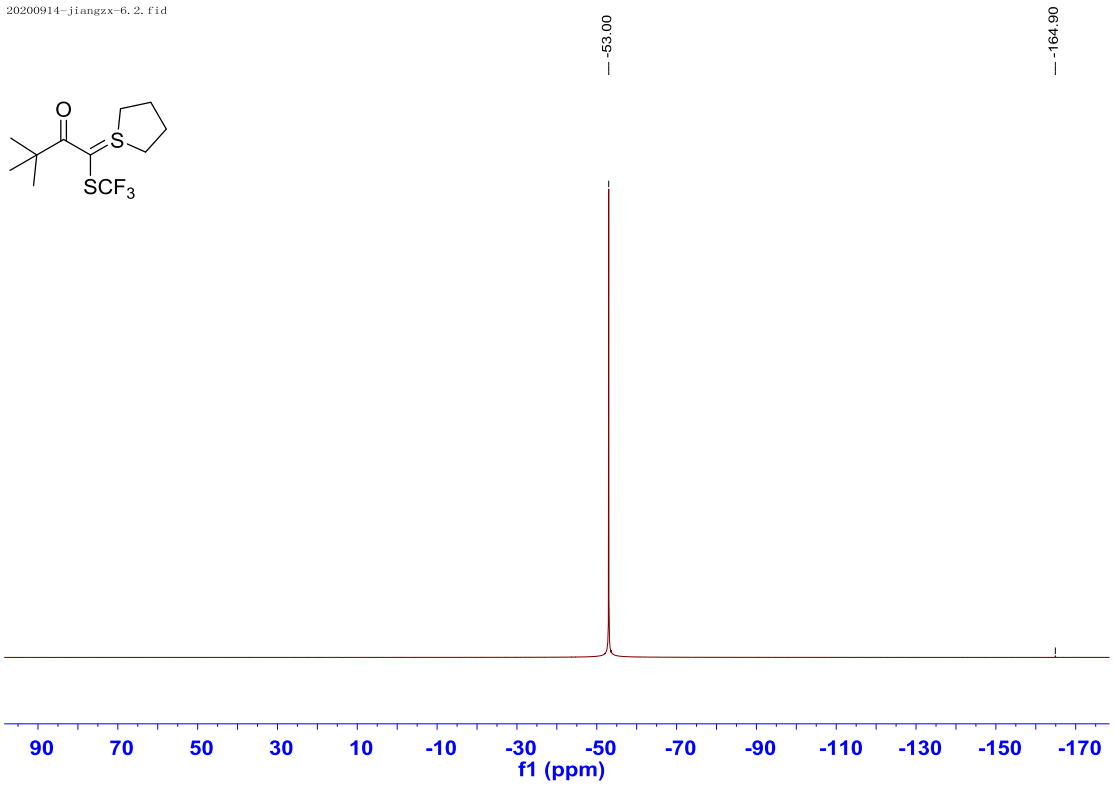
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3o**.



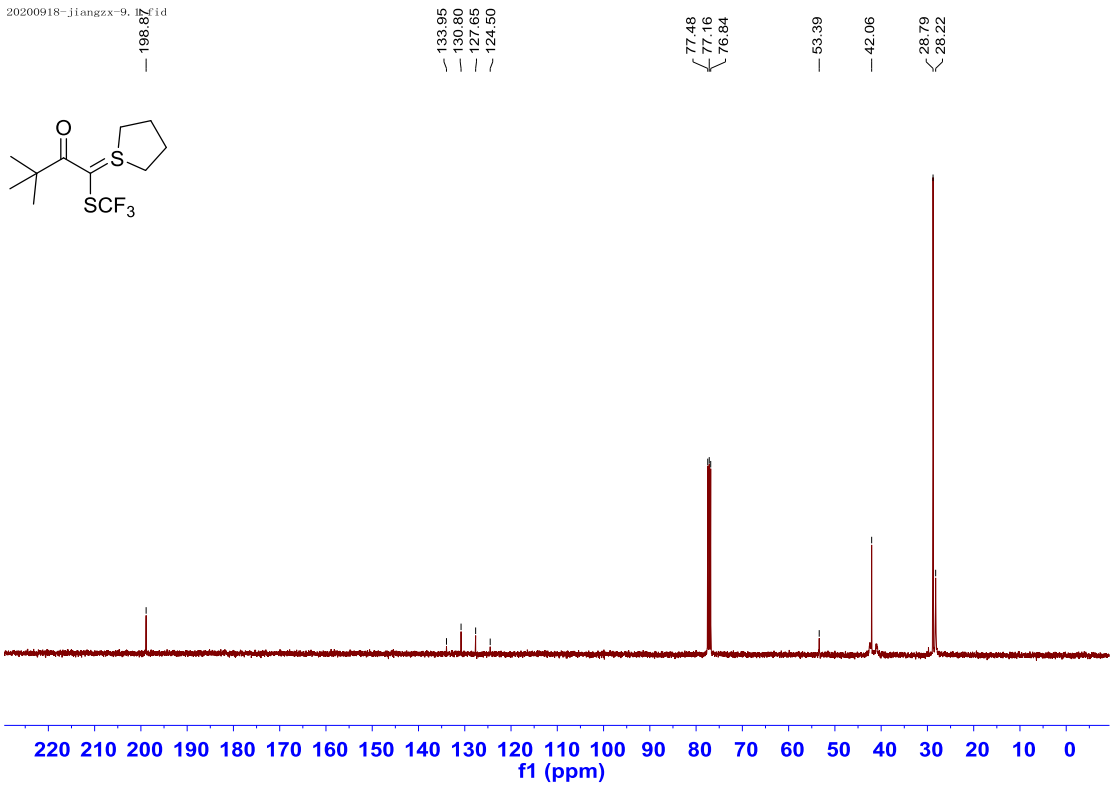
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**.



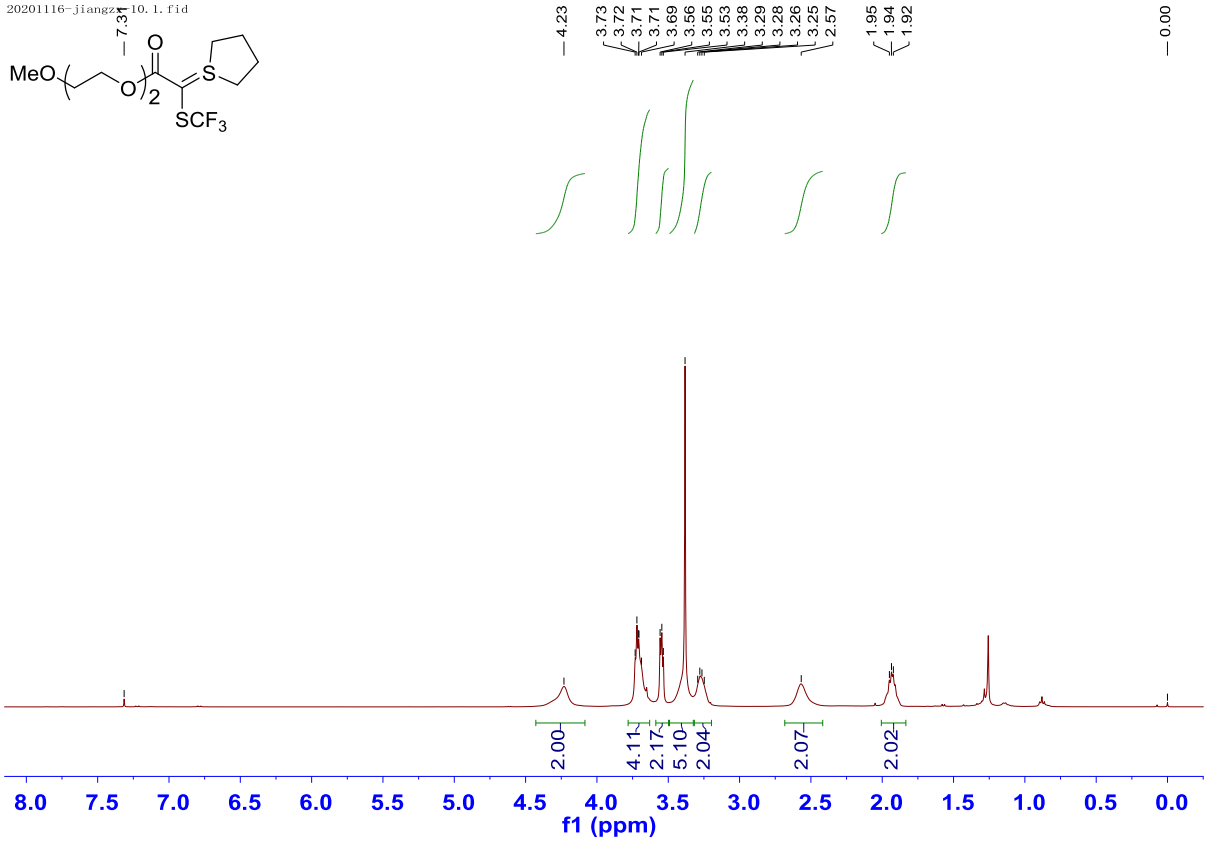
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3p**.



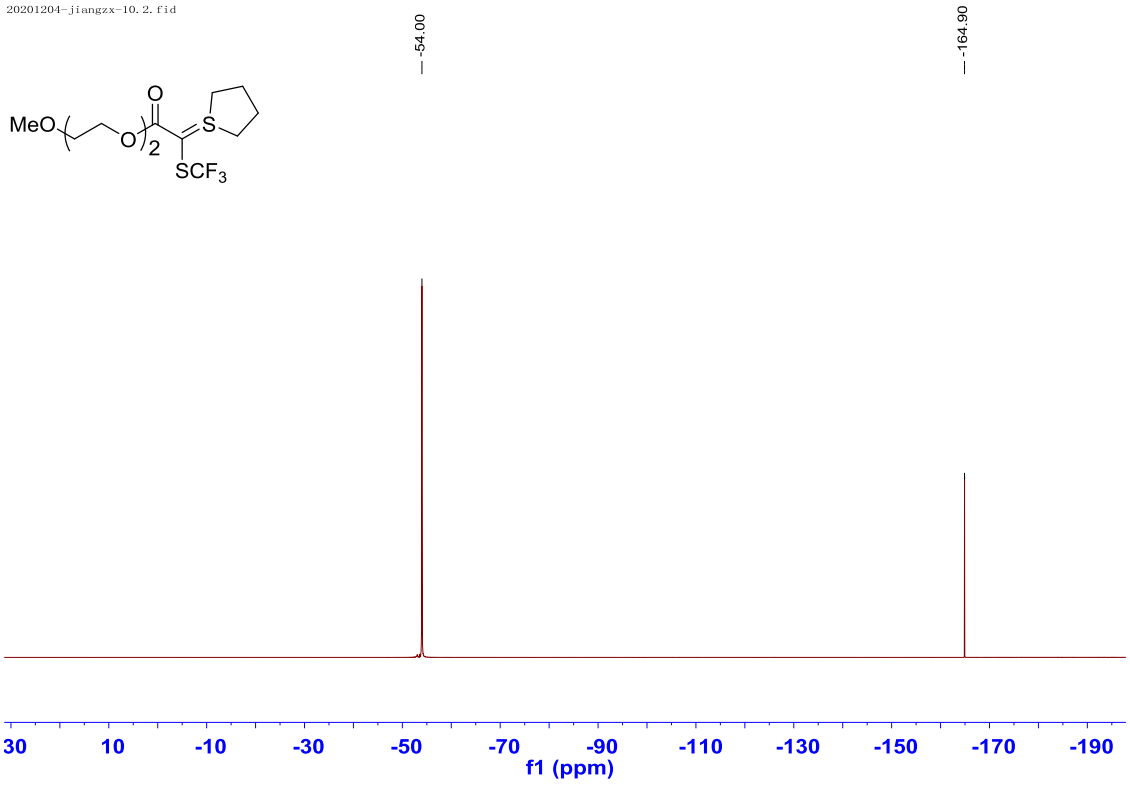
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3p**.



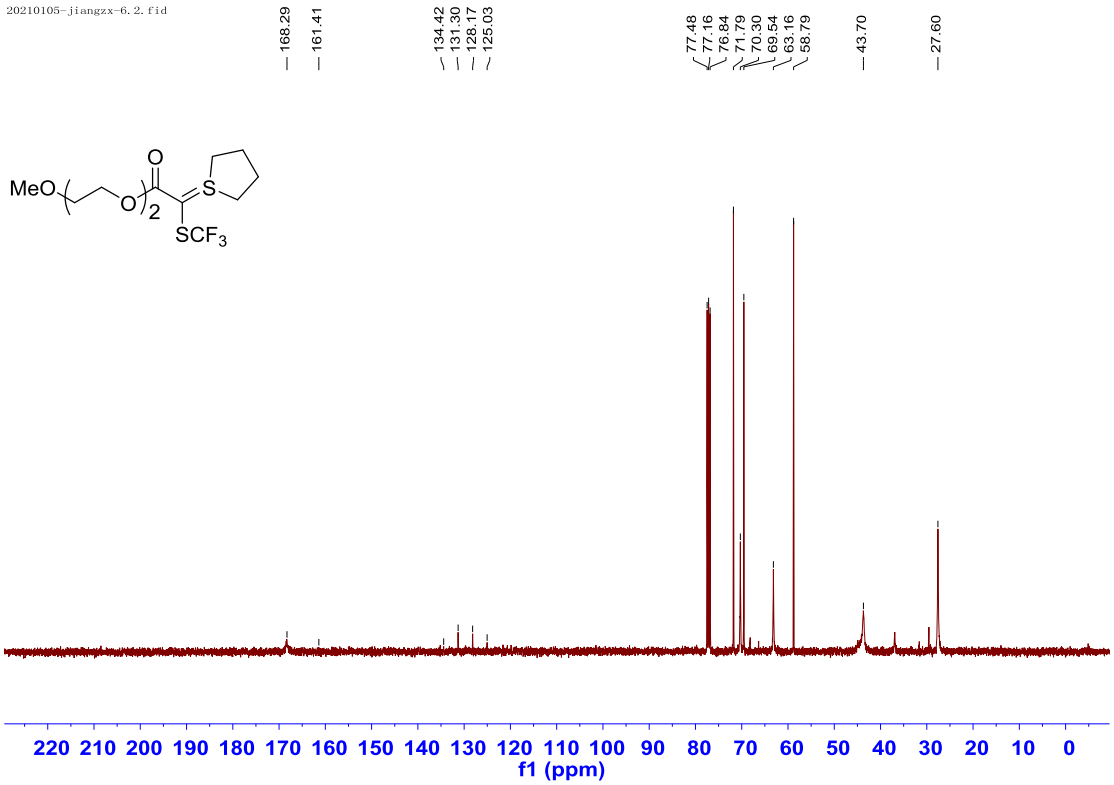
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**.



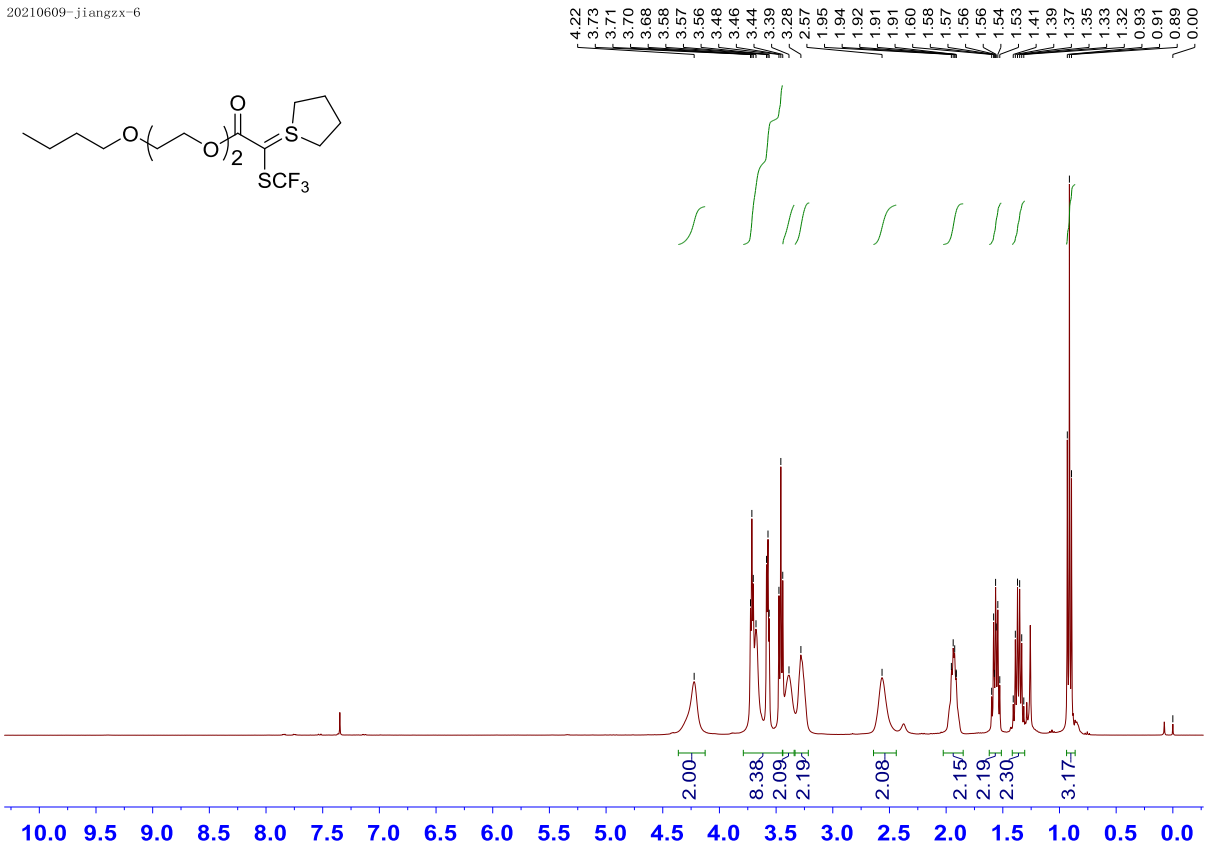
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5a**.



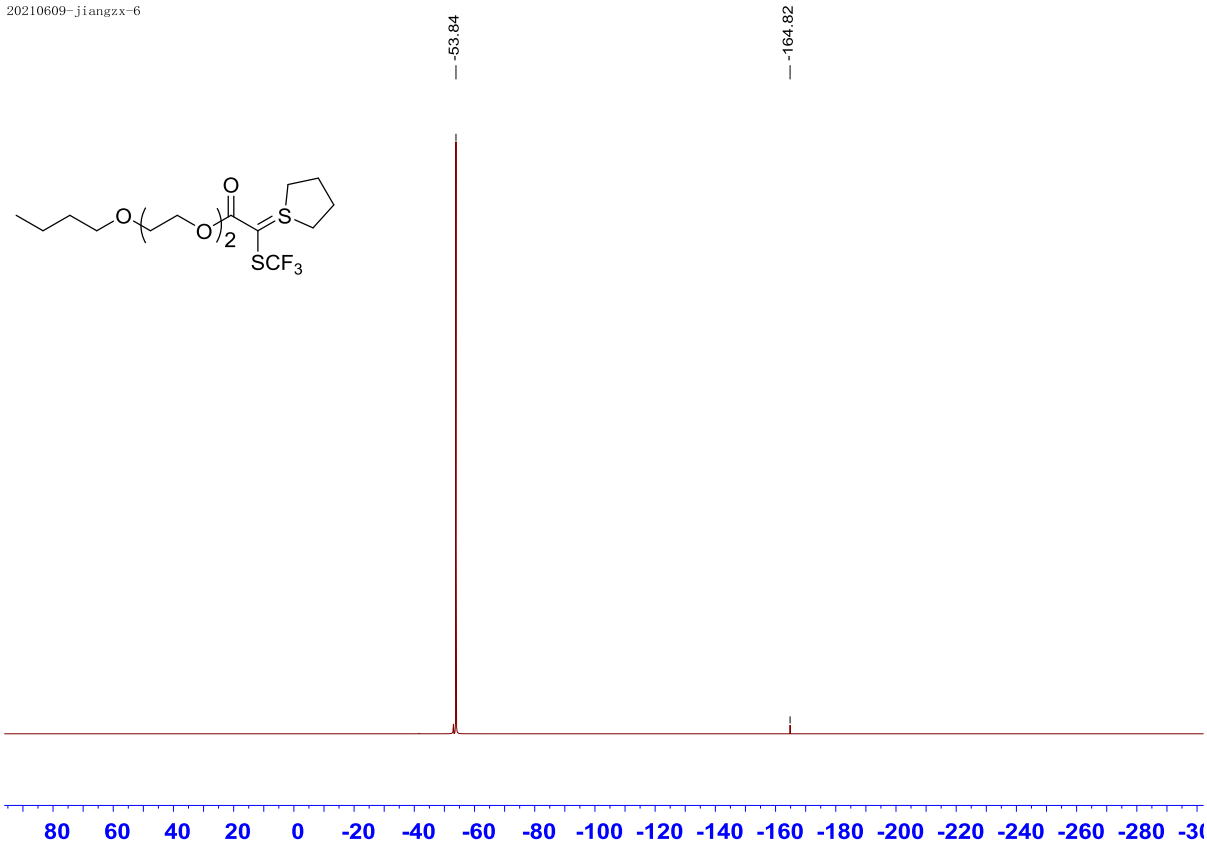
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5a**.



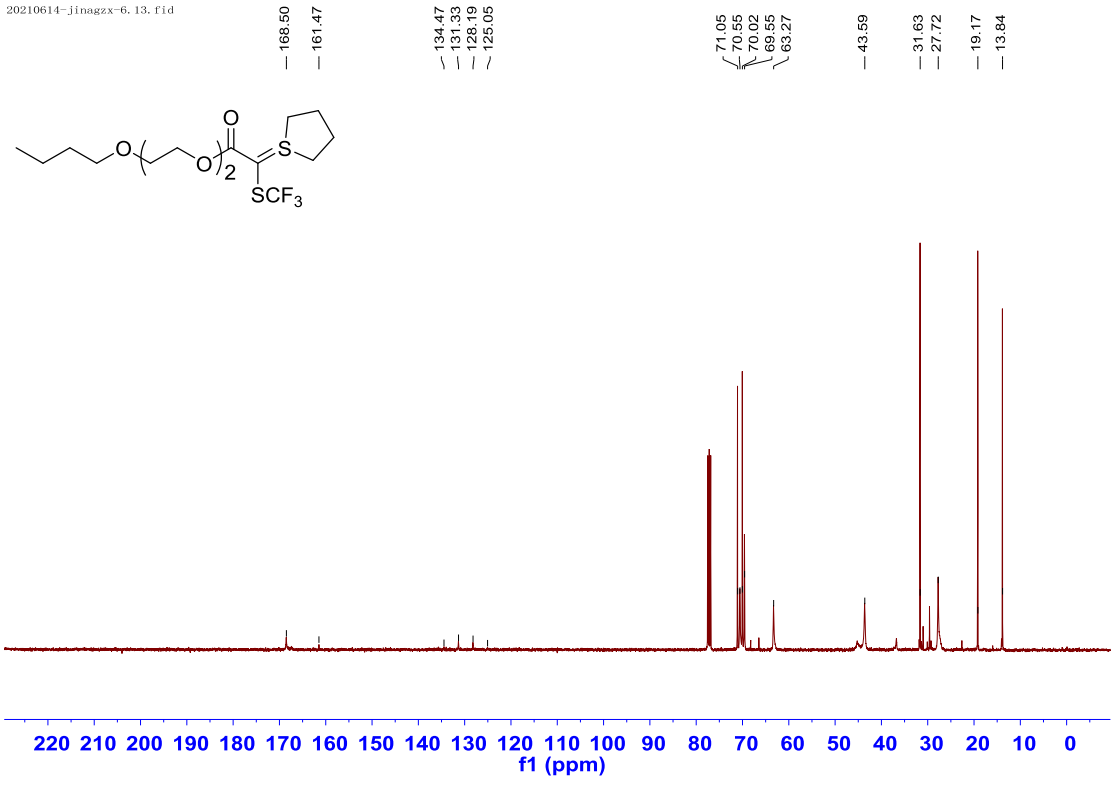
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**.



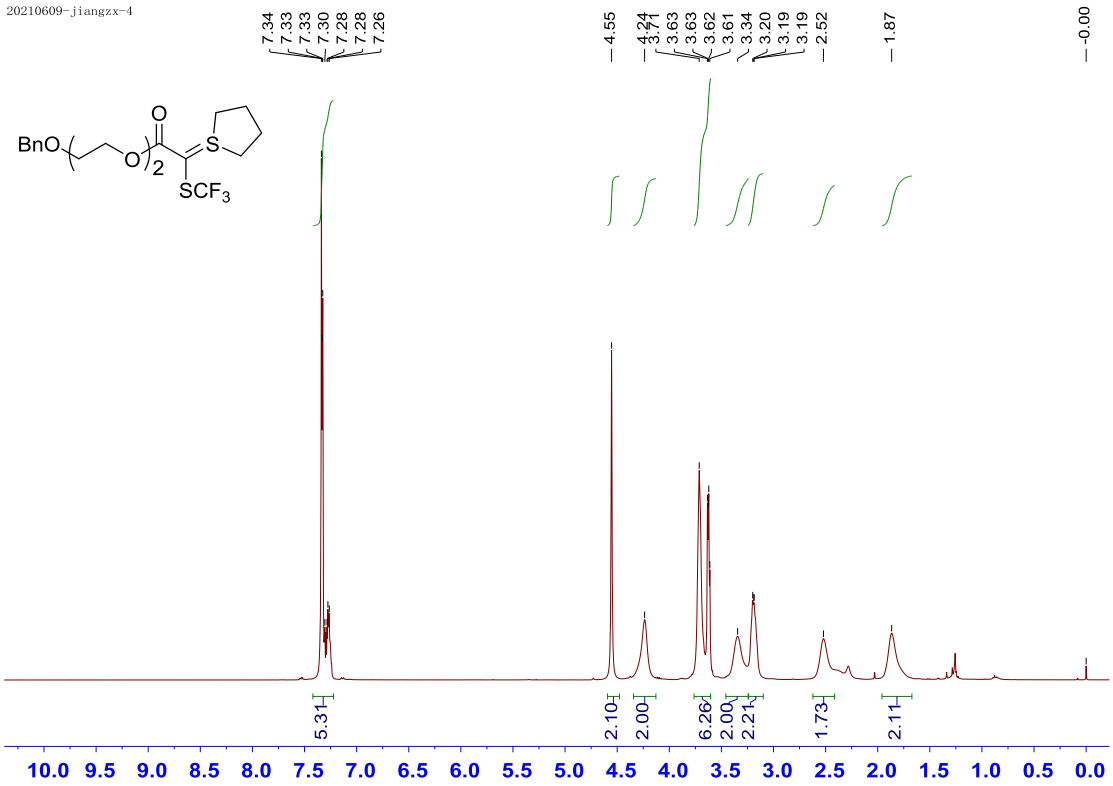
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5b**.



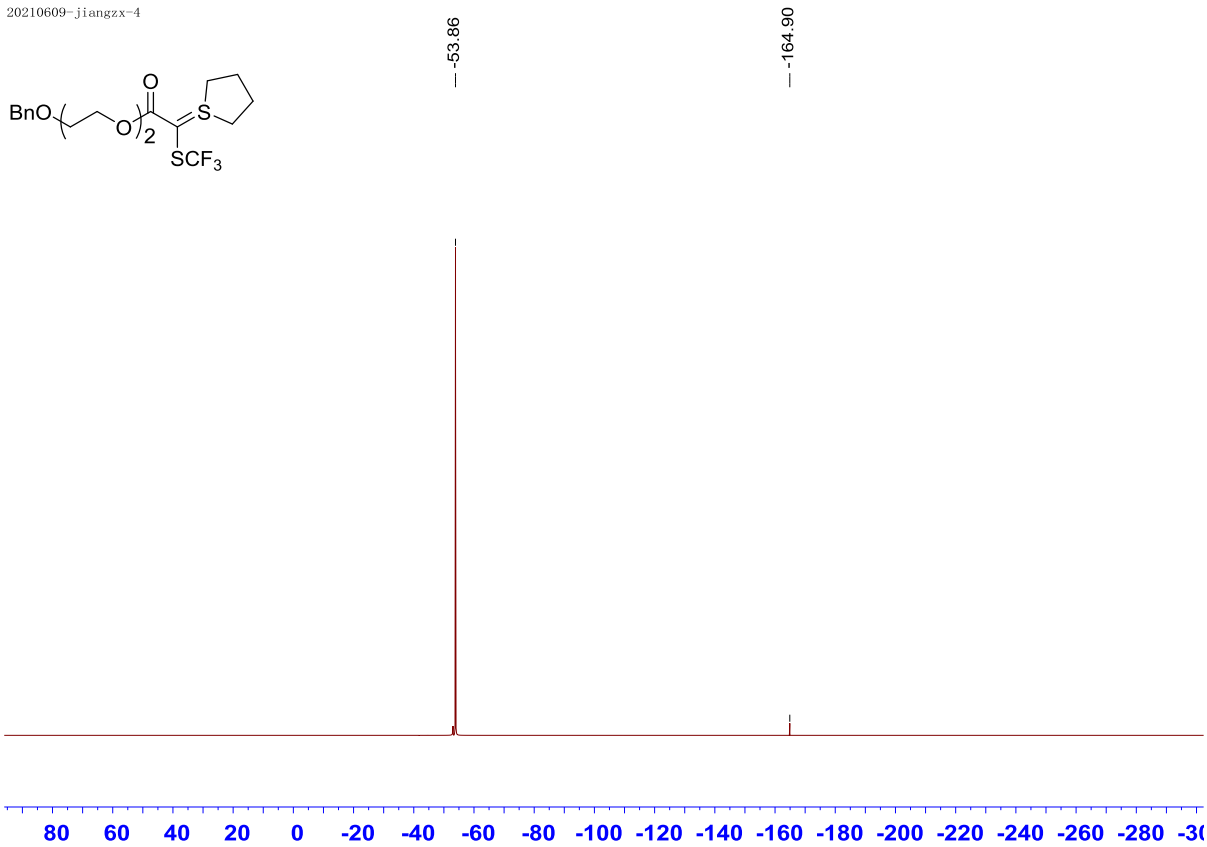
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5b**.



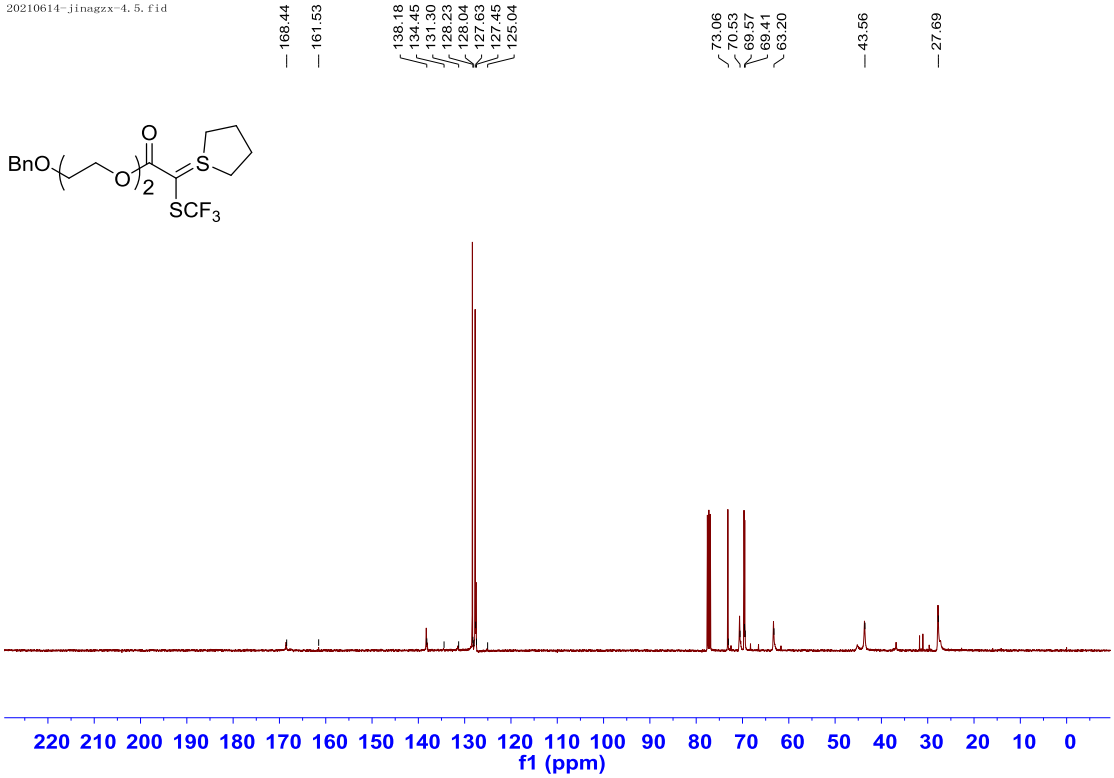
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**.



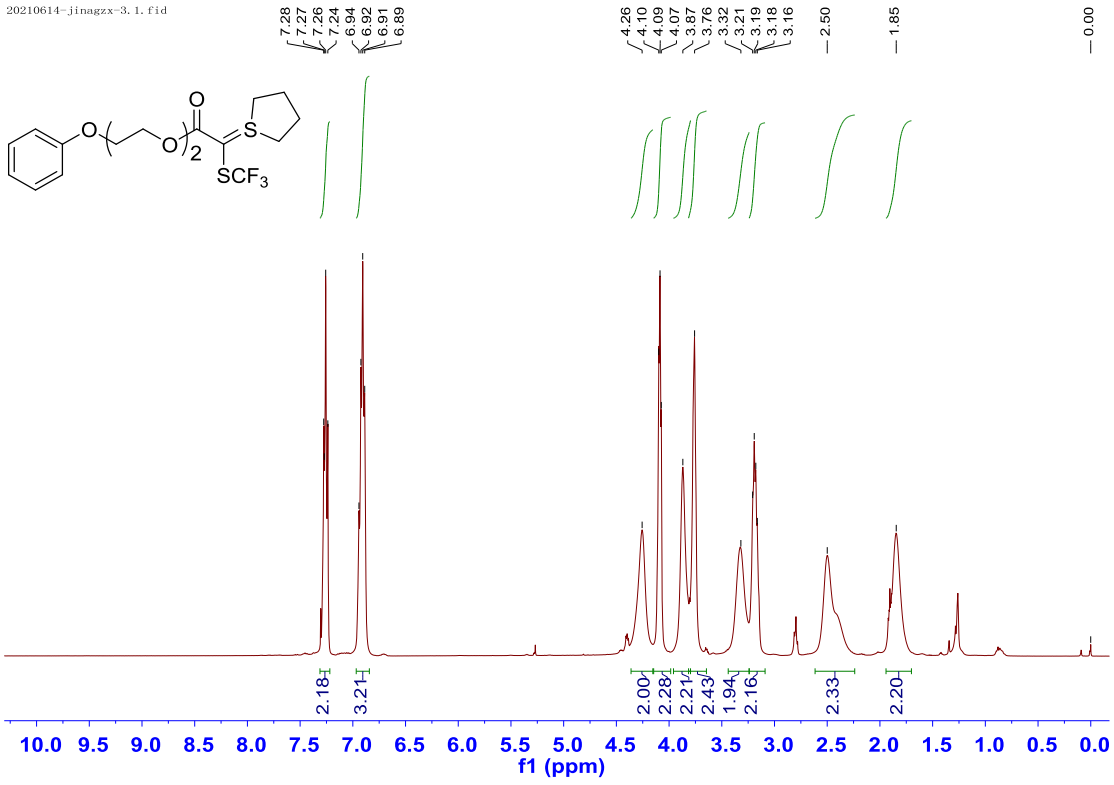
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5c**.



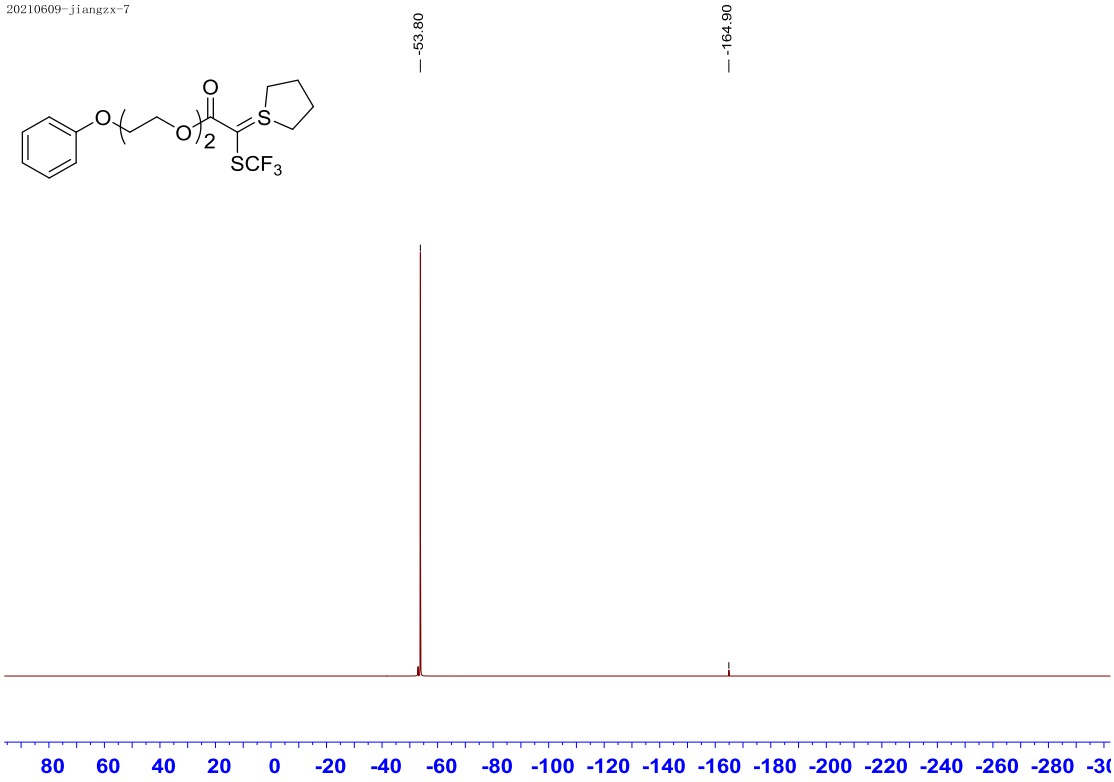
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5c**.



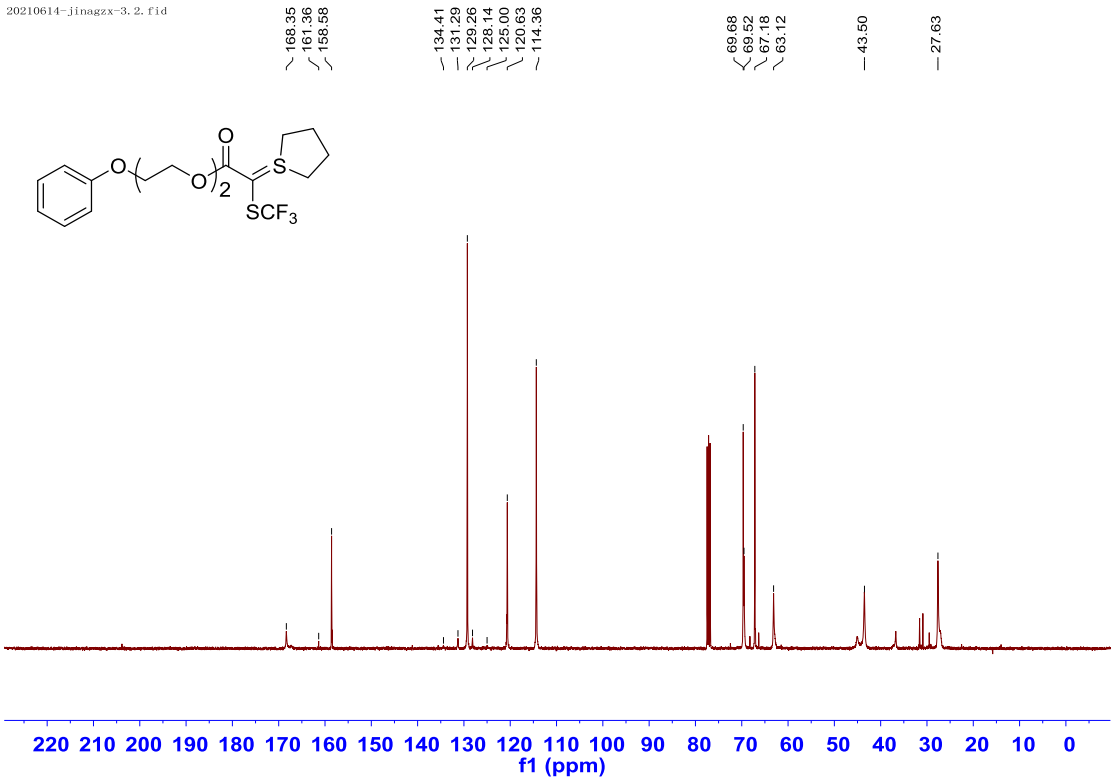
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**.



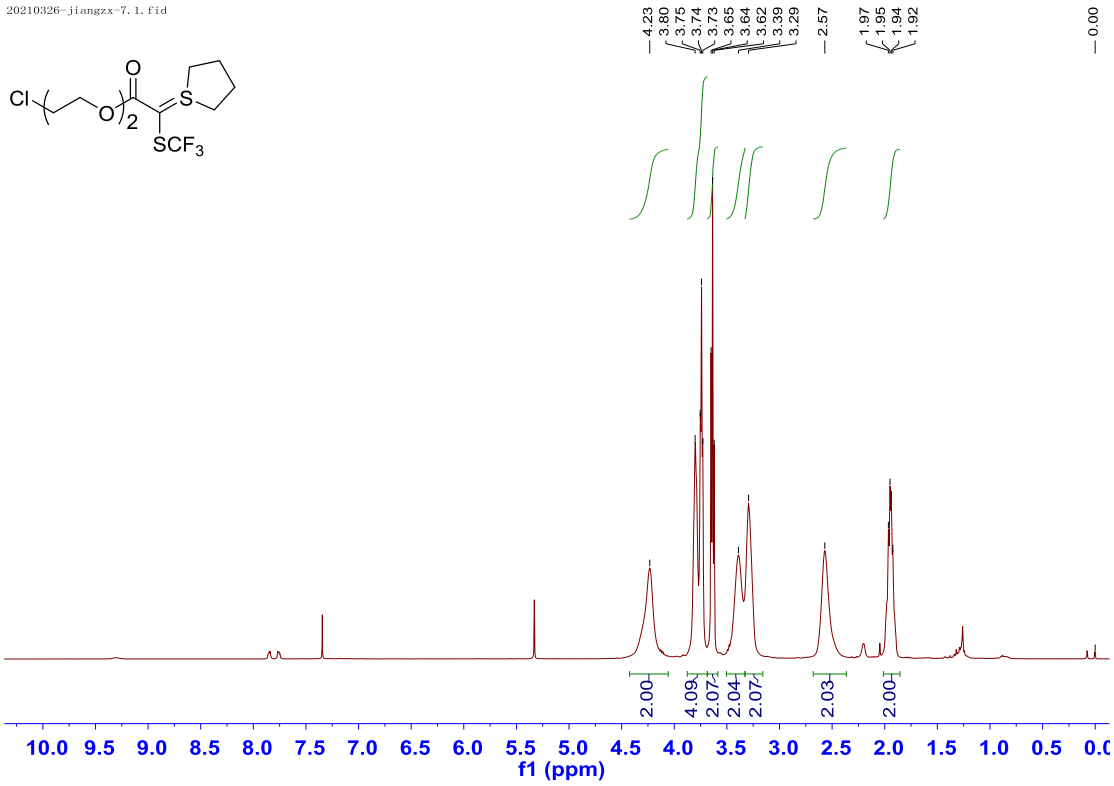
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5d**.



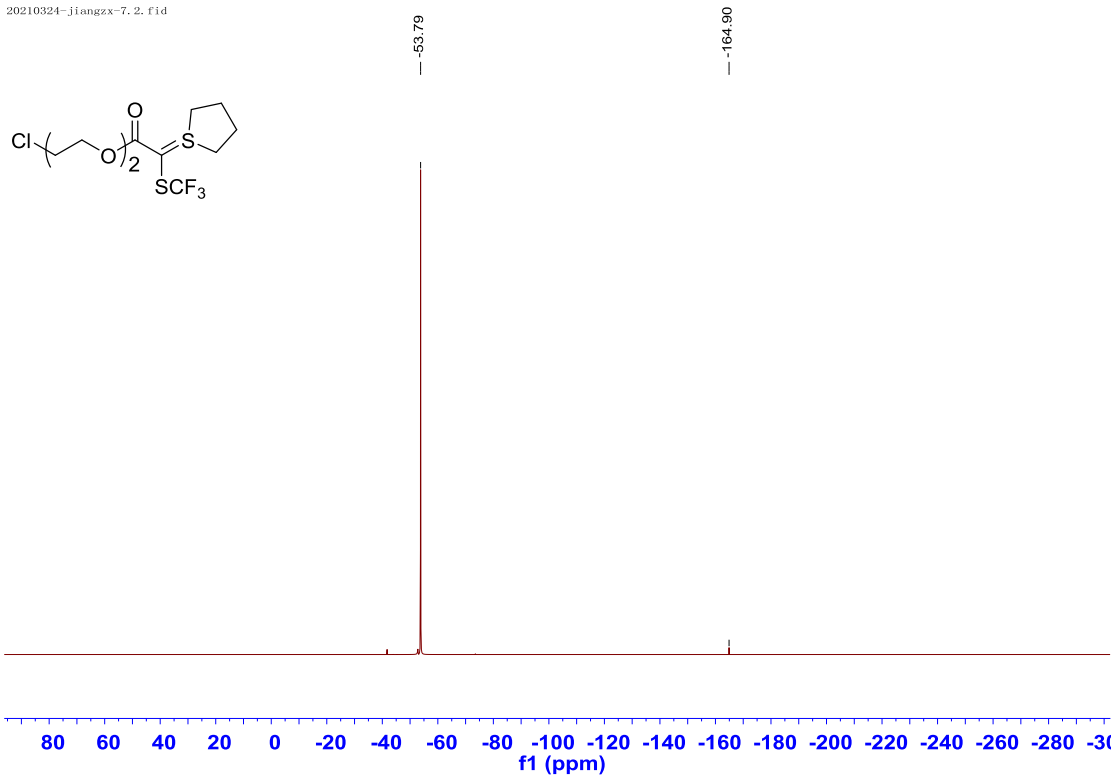
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5d**.



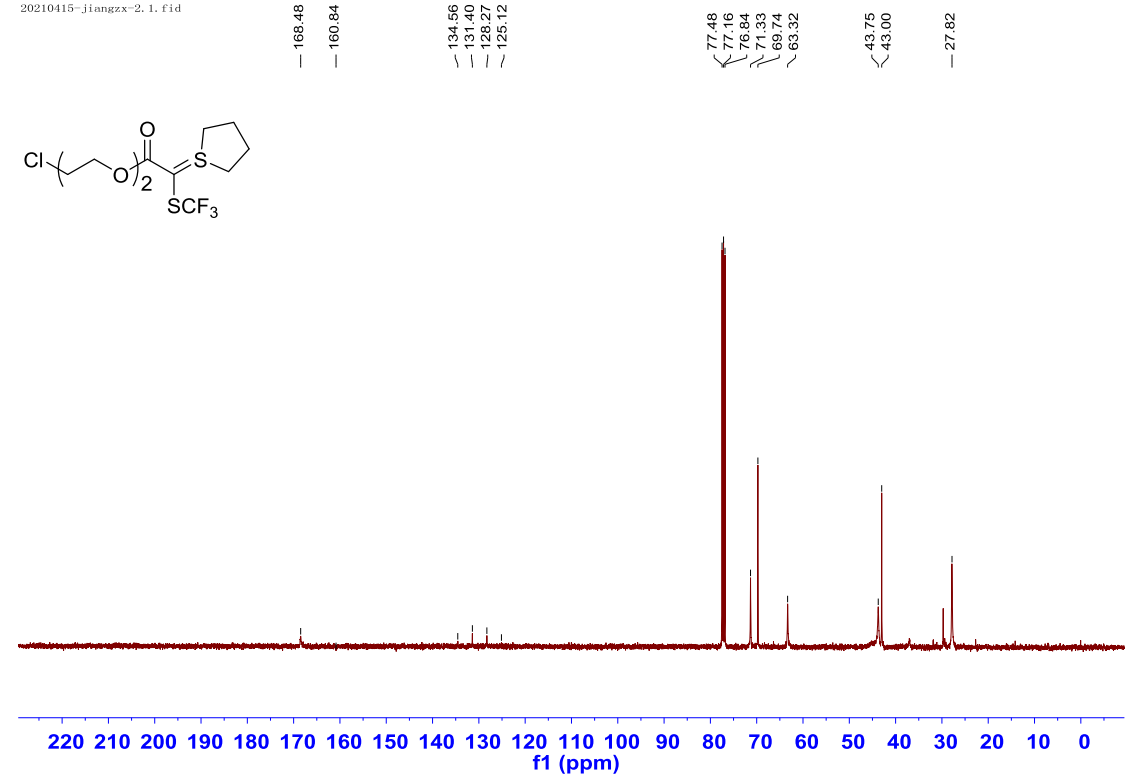
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**.



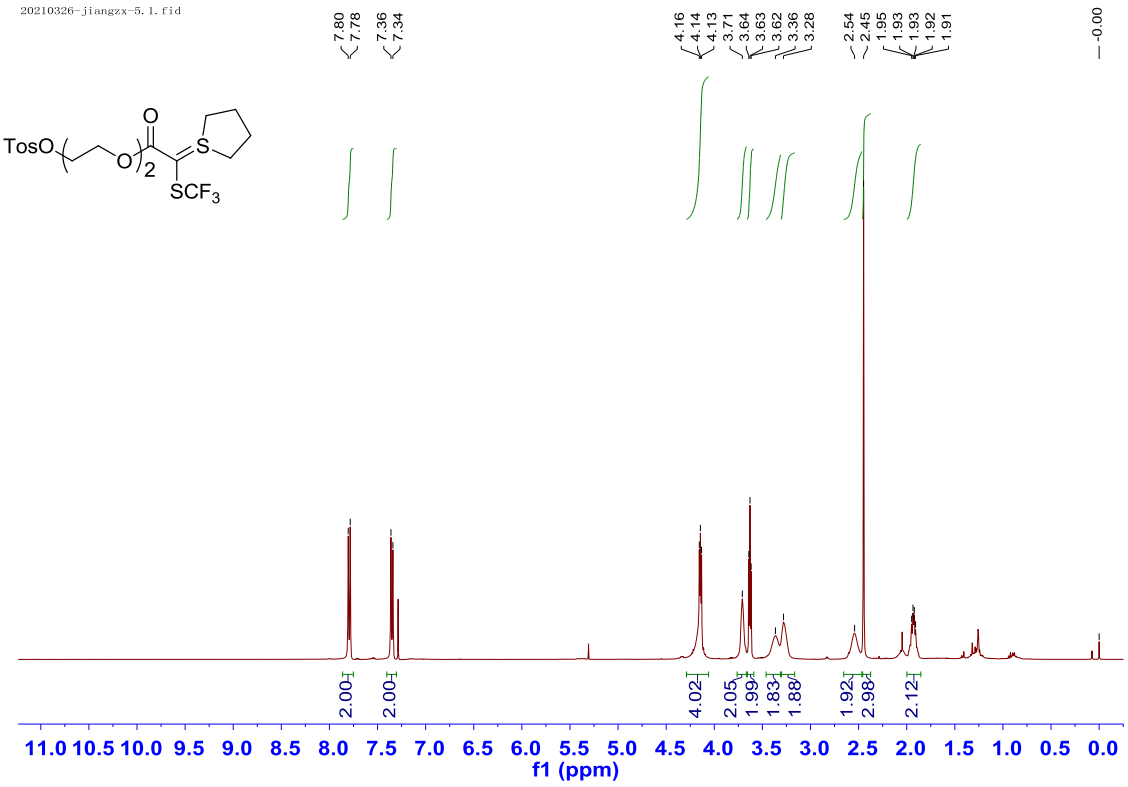
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5e**.



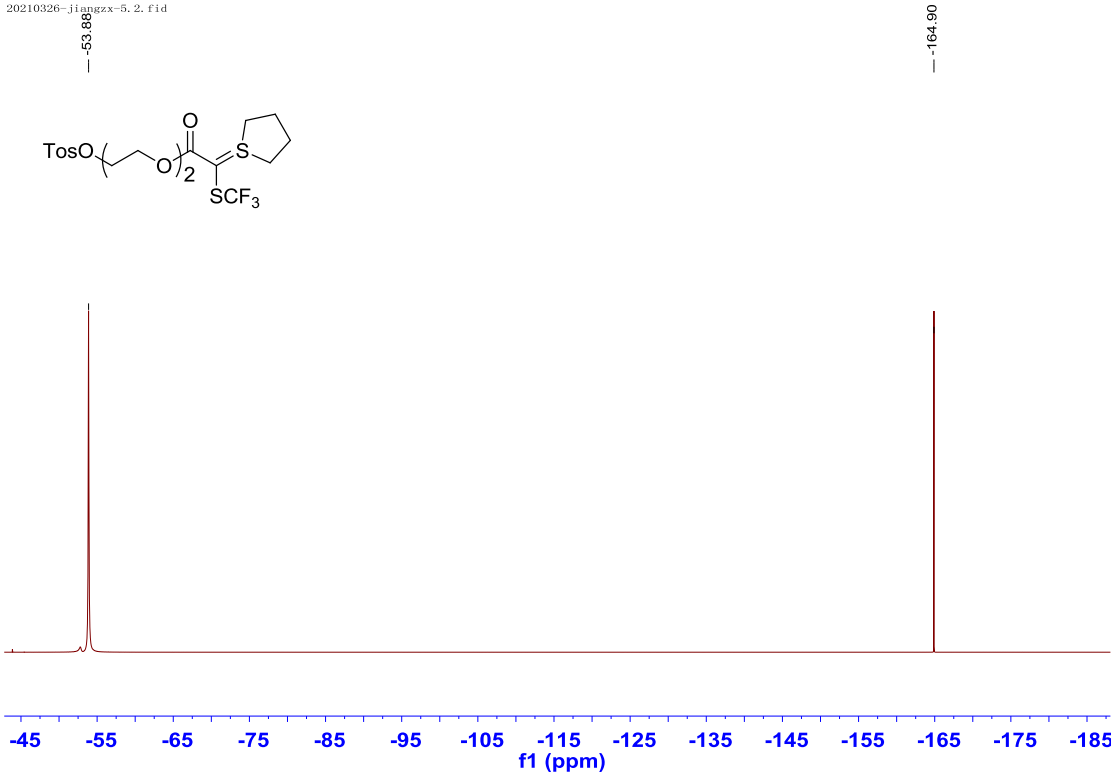
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5e**.



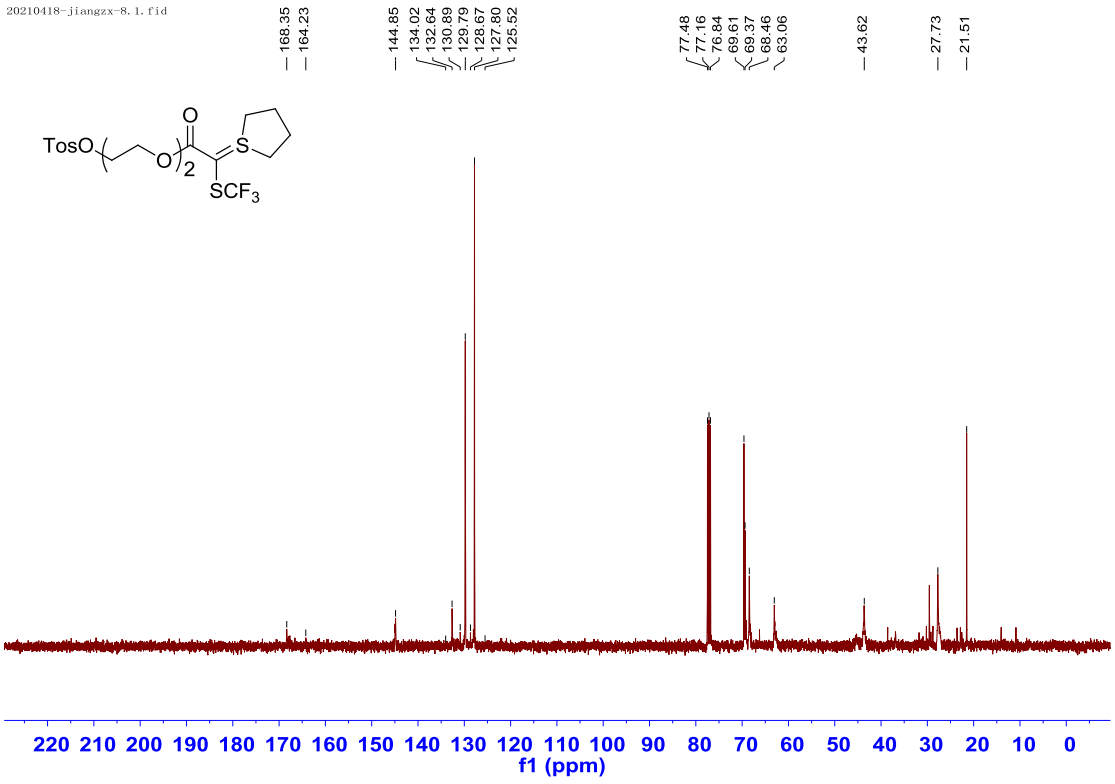
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**.



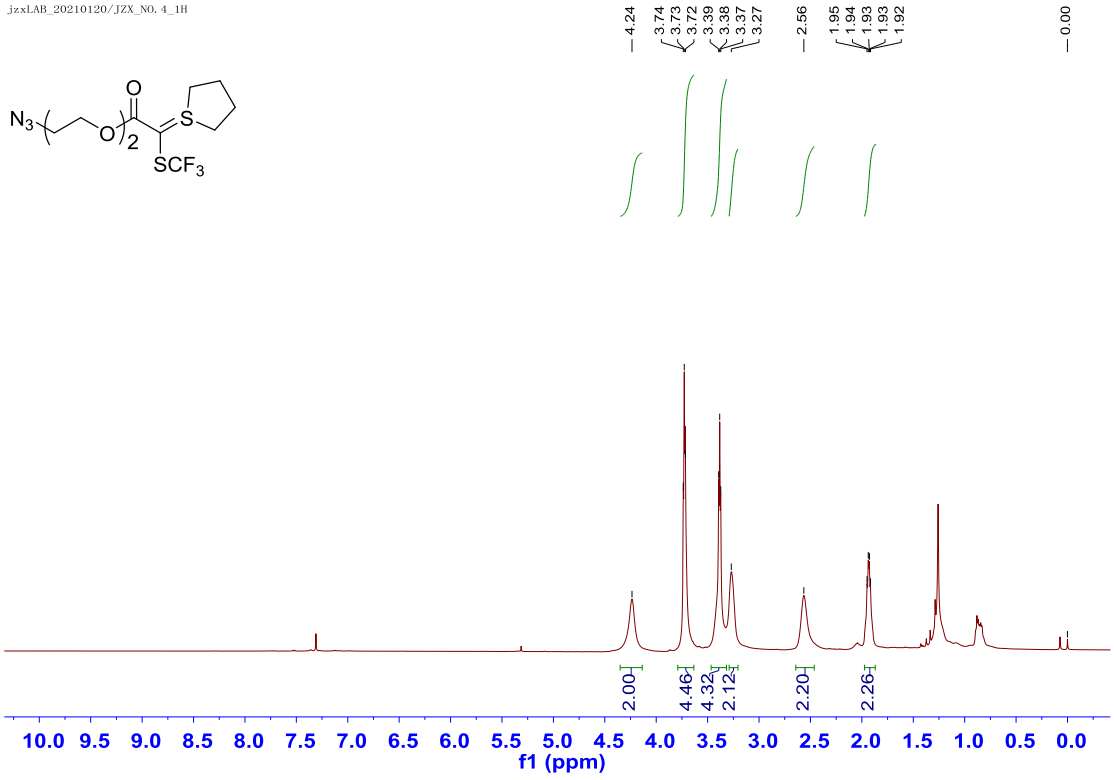
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5f**.



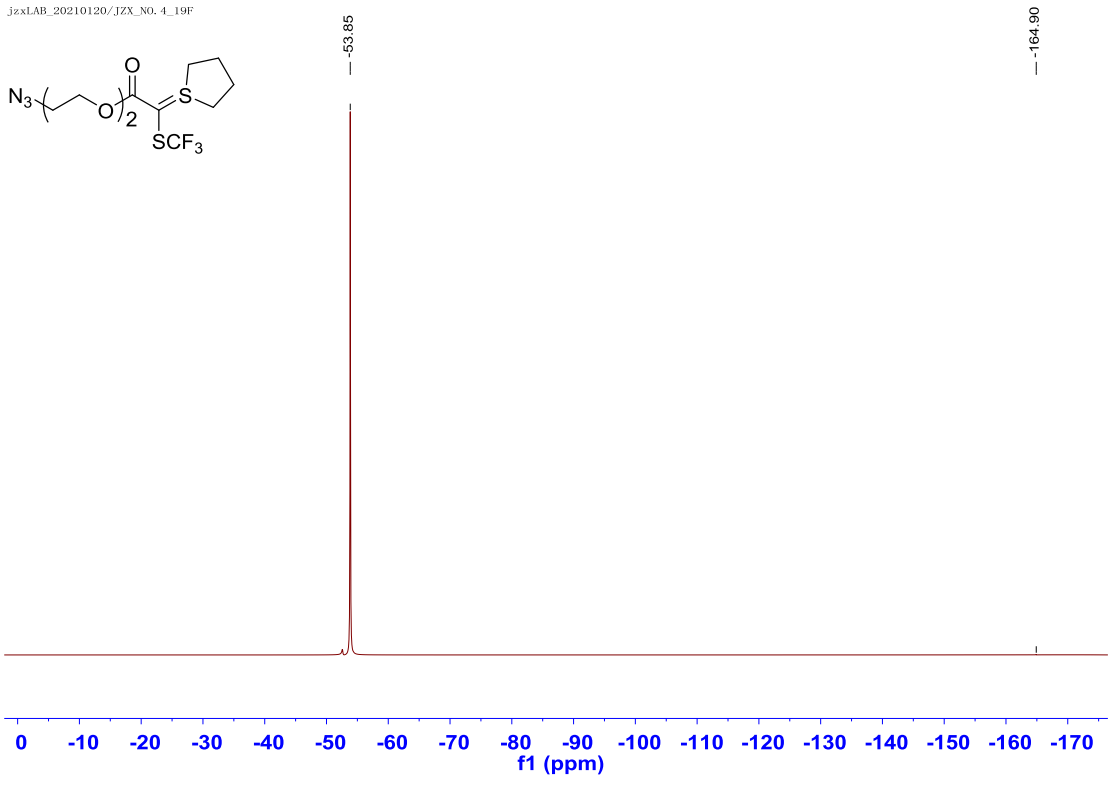
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5f**.



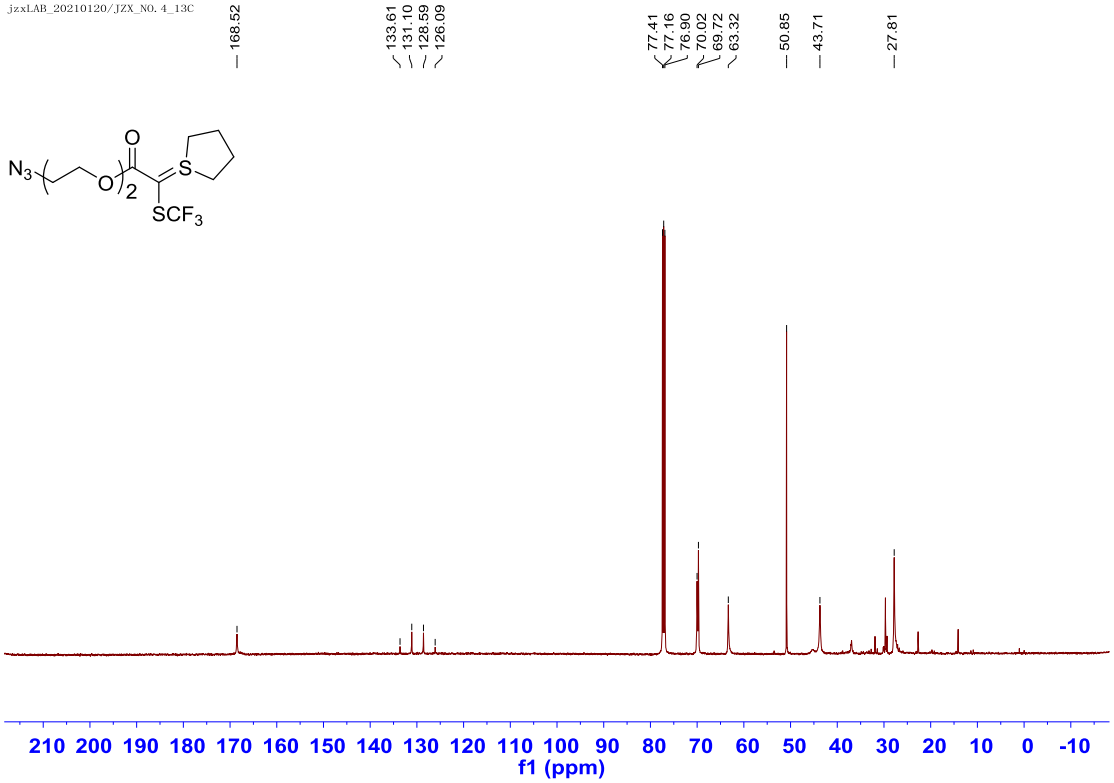
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5g**.



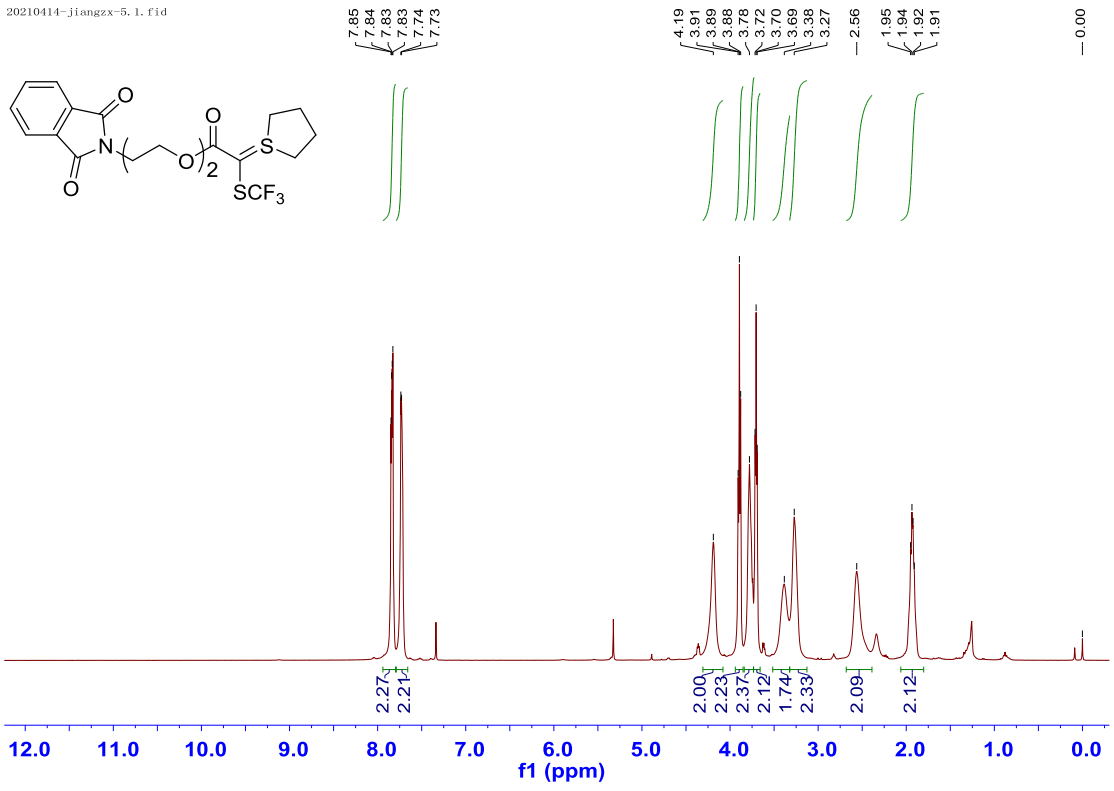
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5g**.



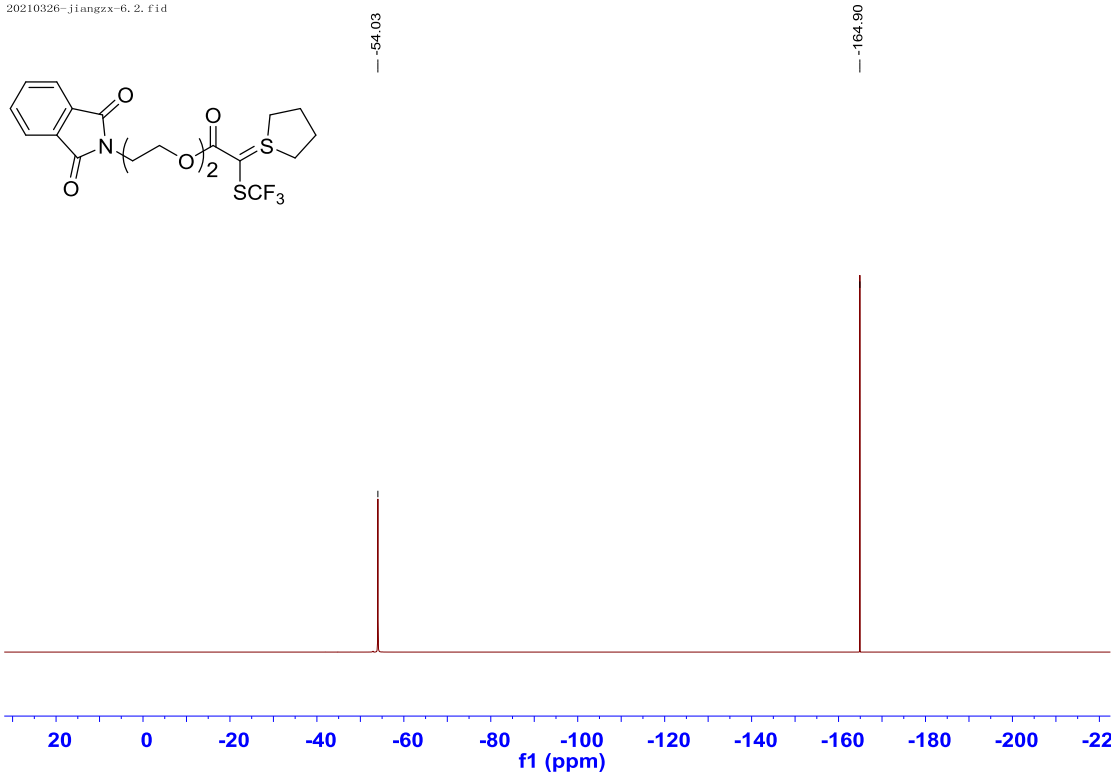
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5g**.



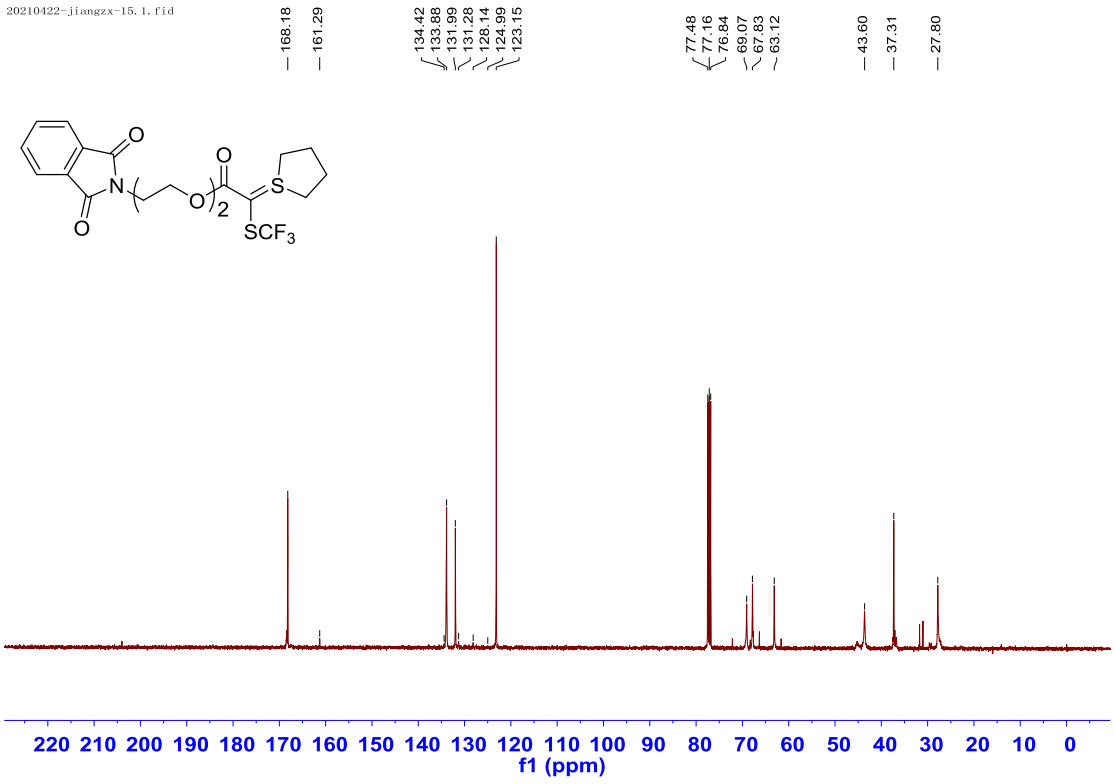
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**.



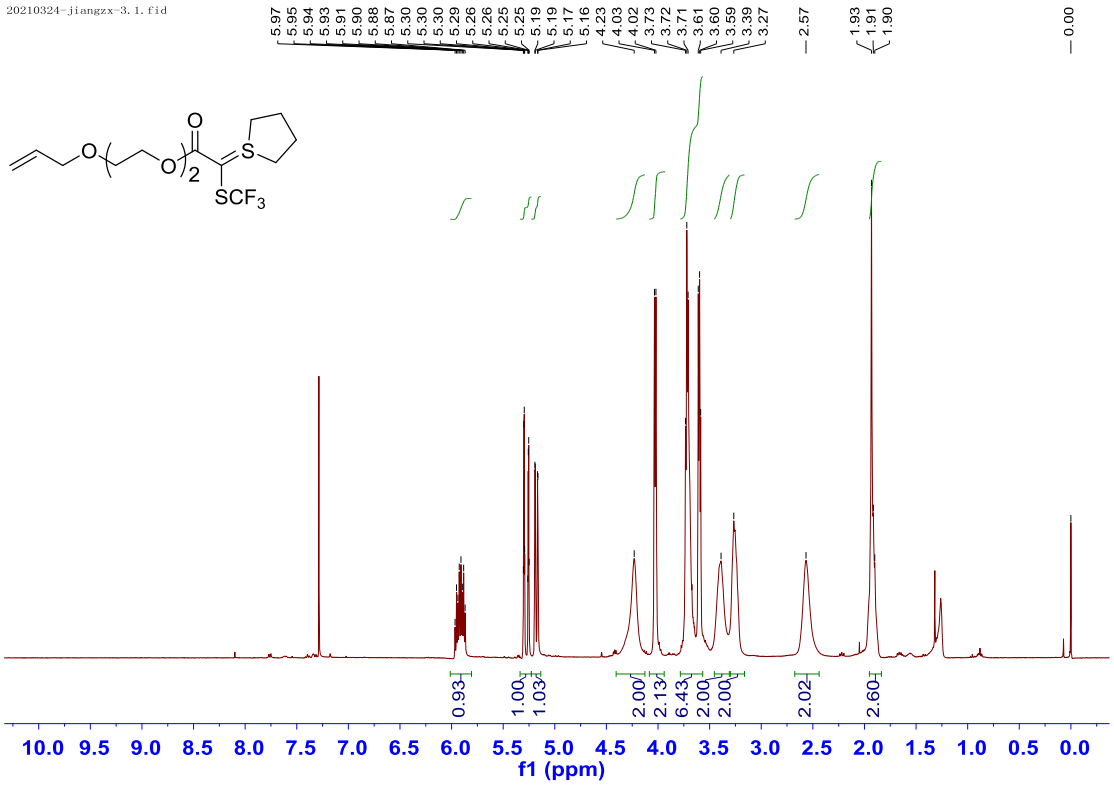
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5h**.



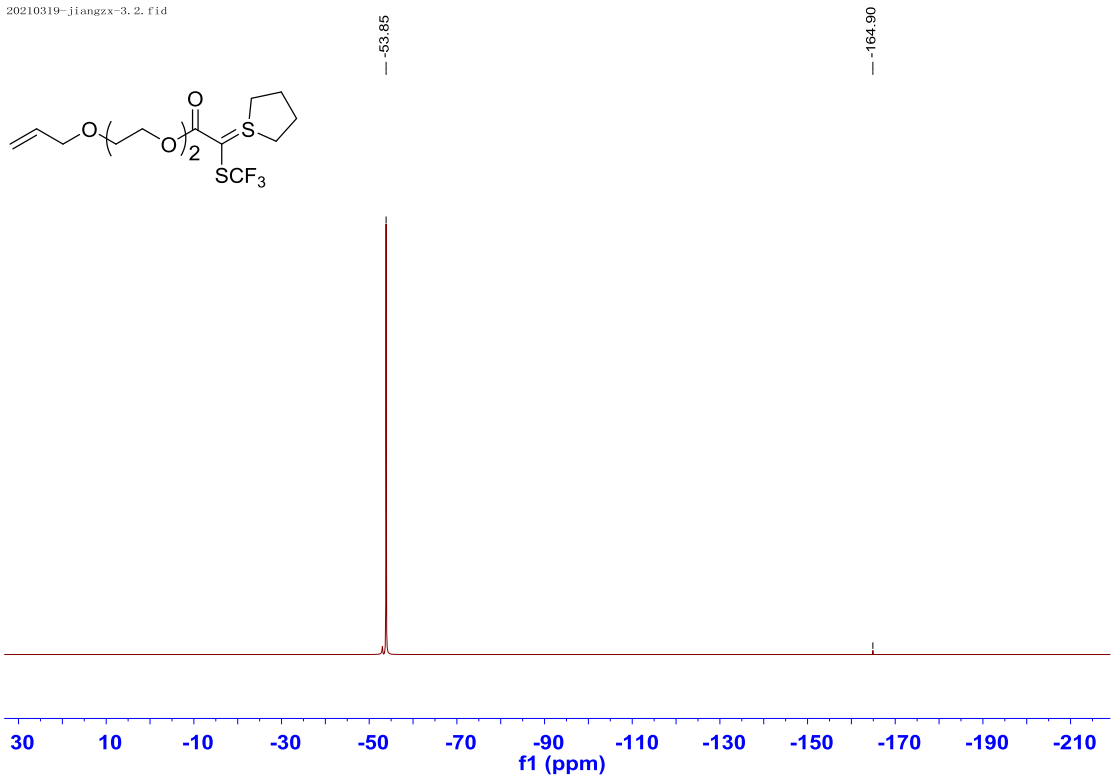
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5h**.



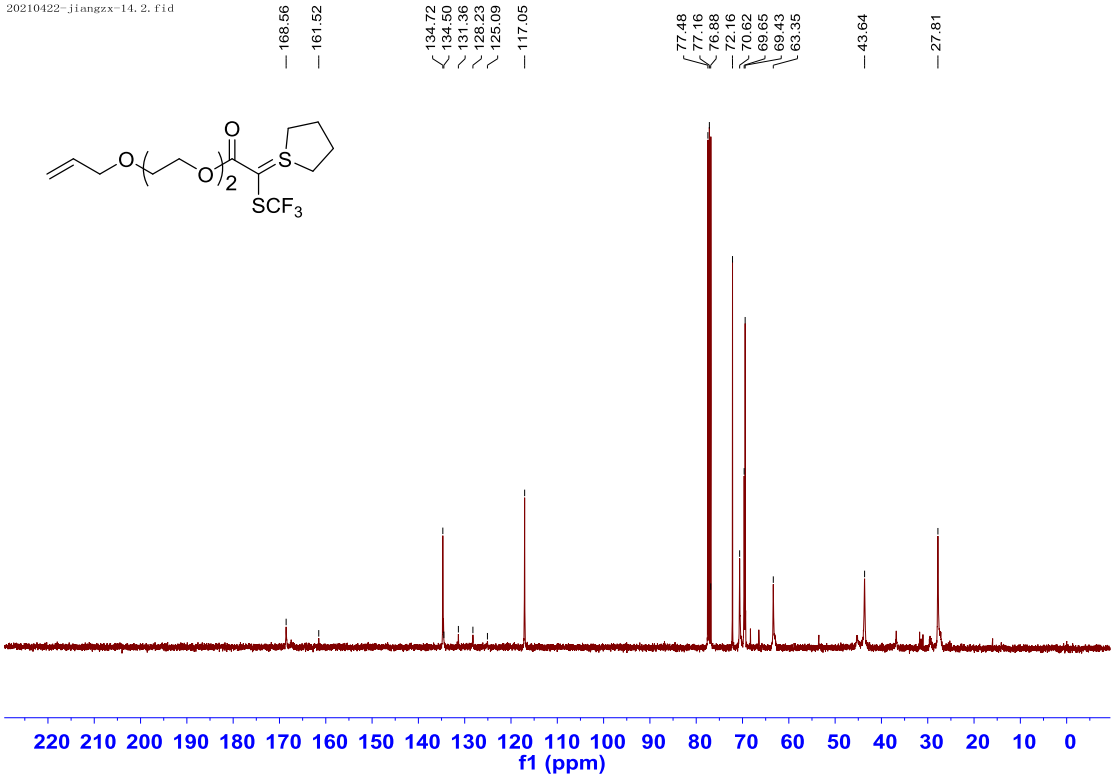
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**.



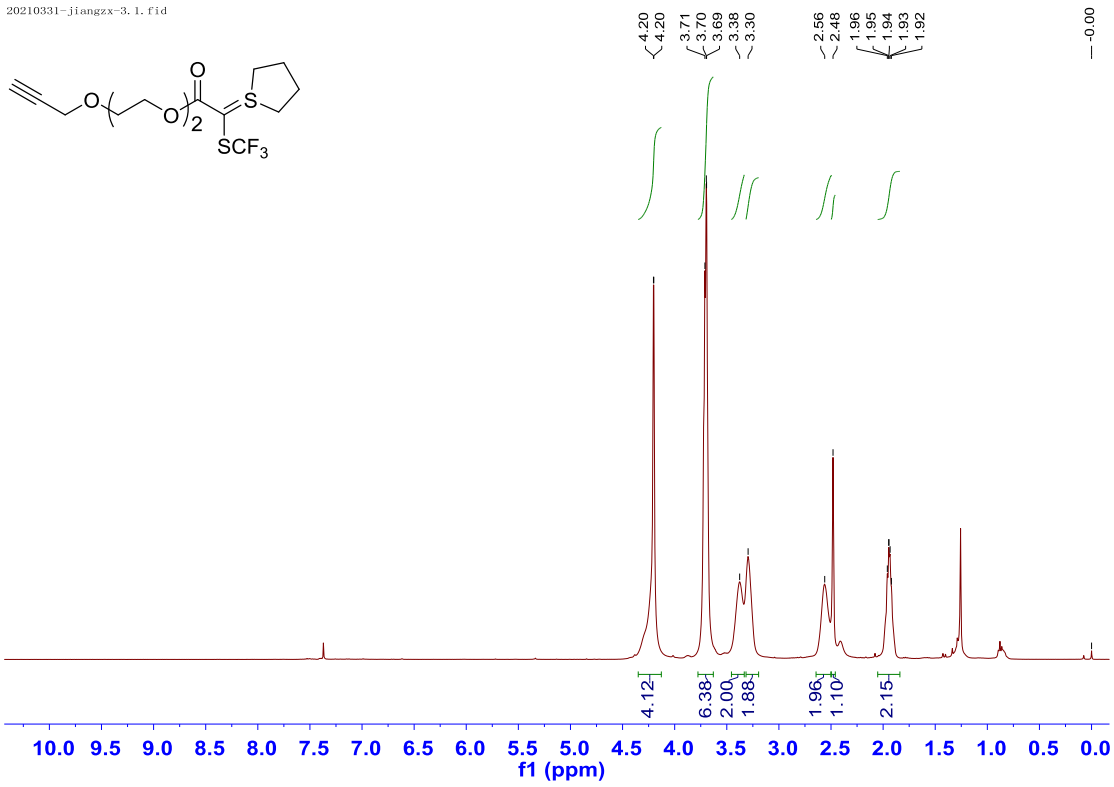
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5i**.



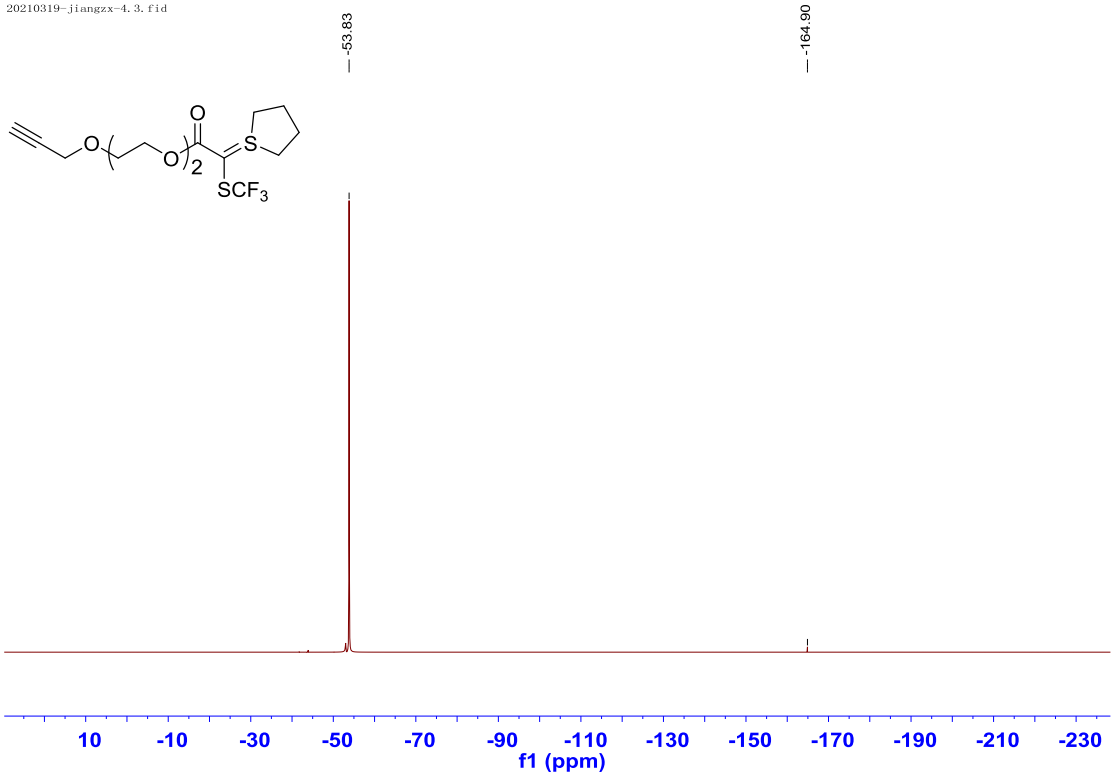
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5i**.



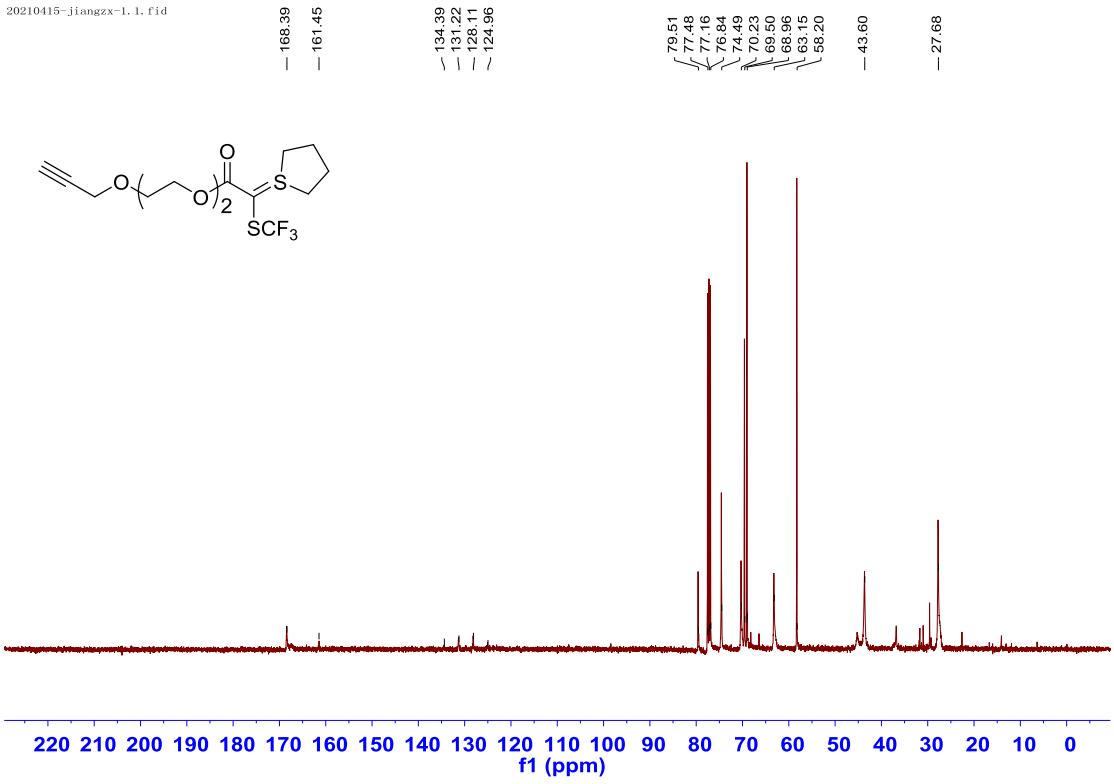
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5j**.



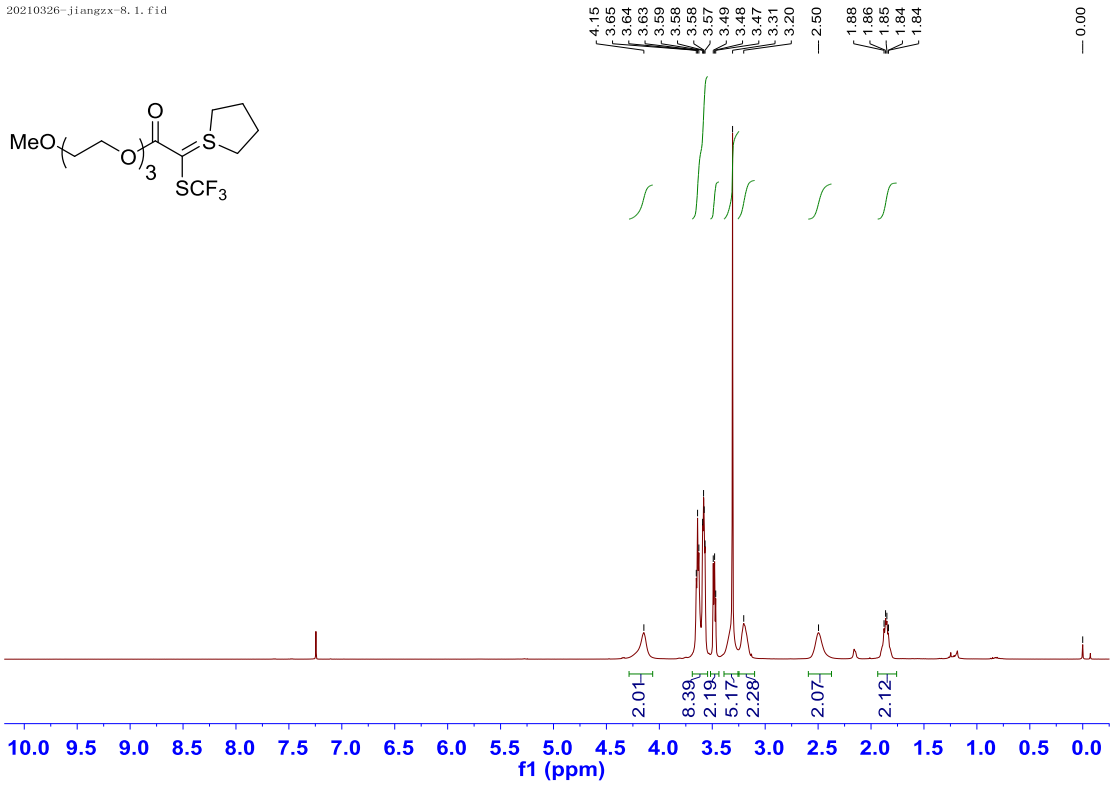
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5j**.



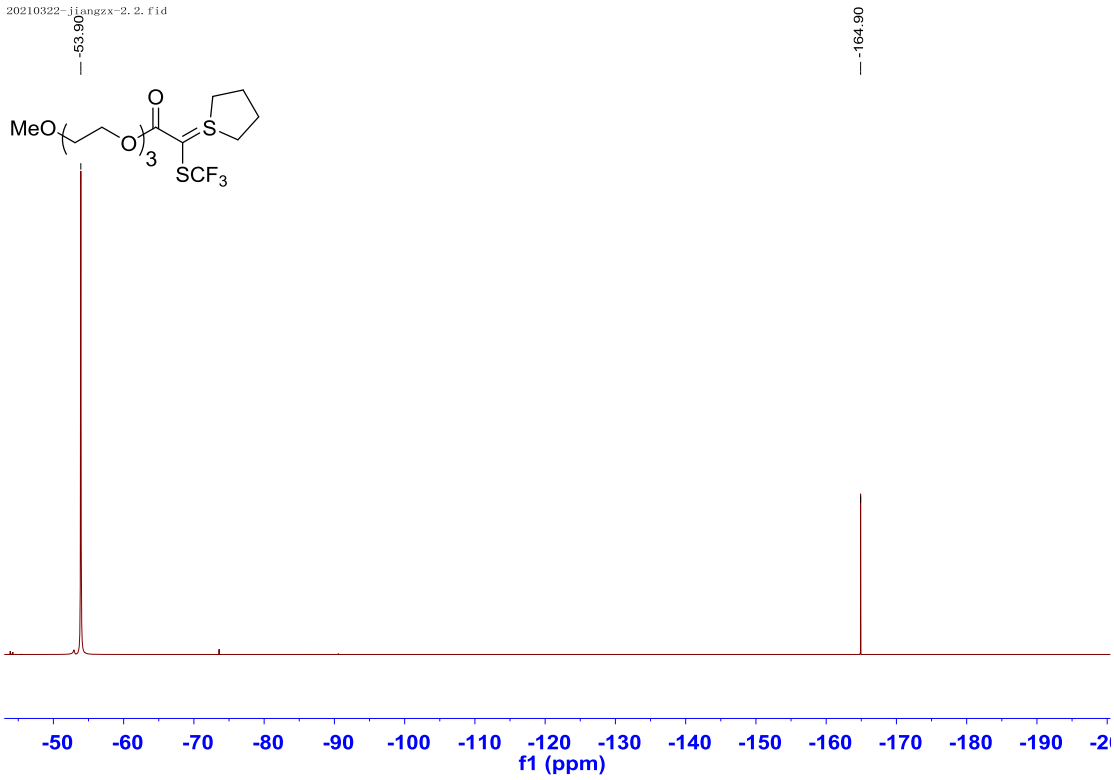
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5j**.



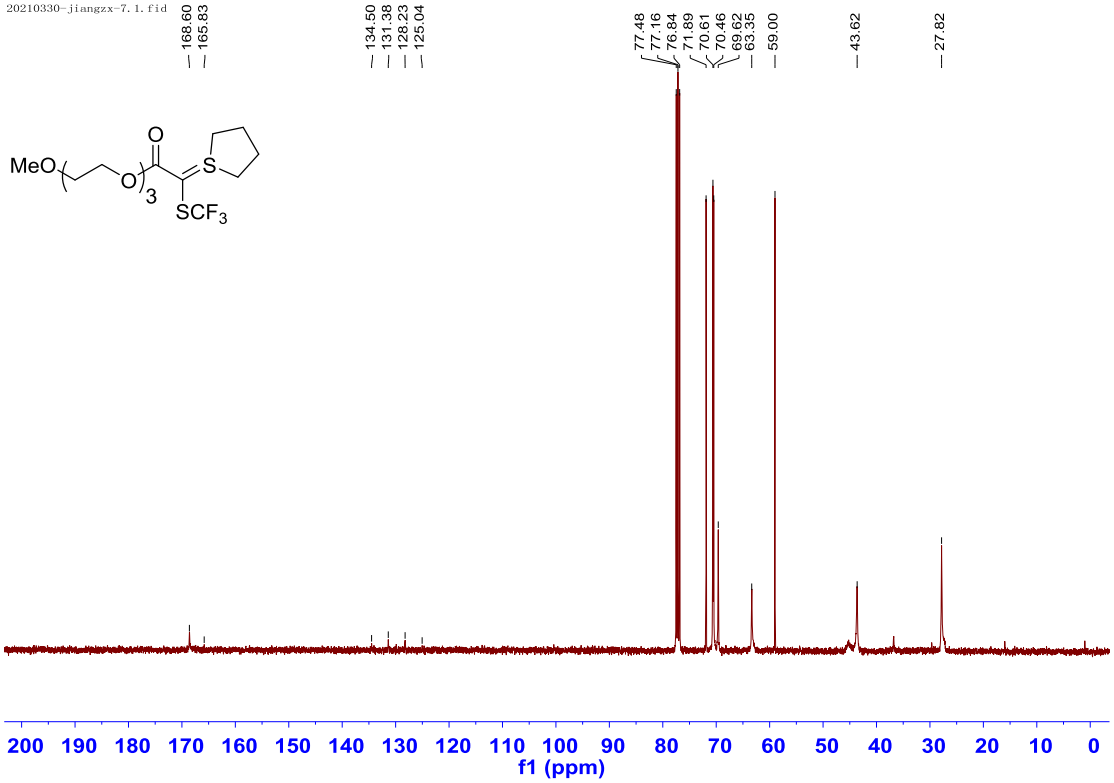
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5k**.



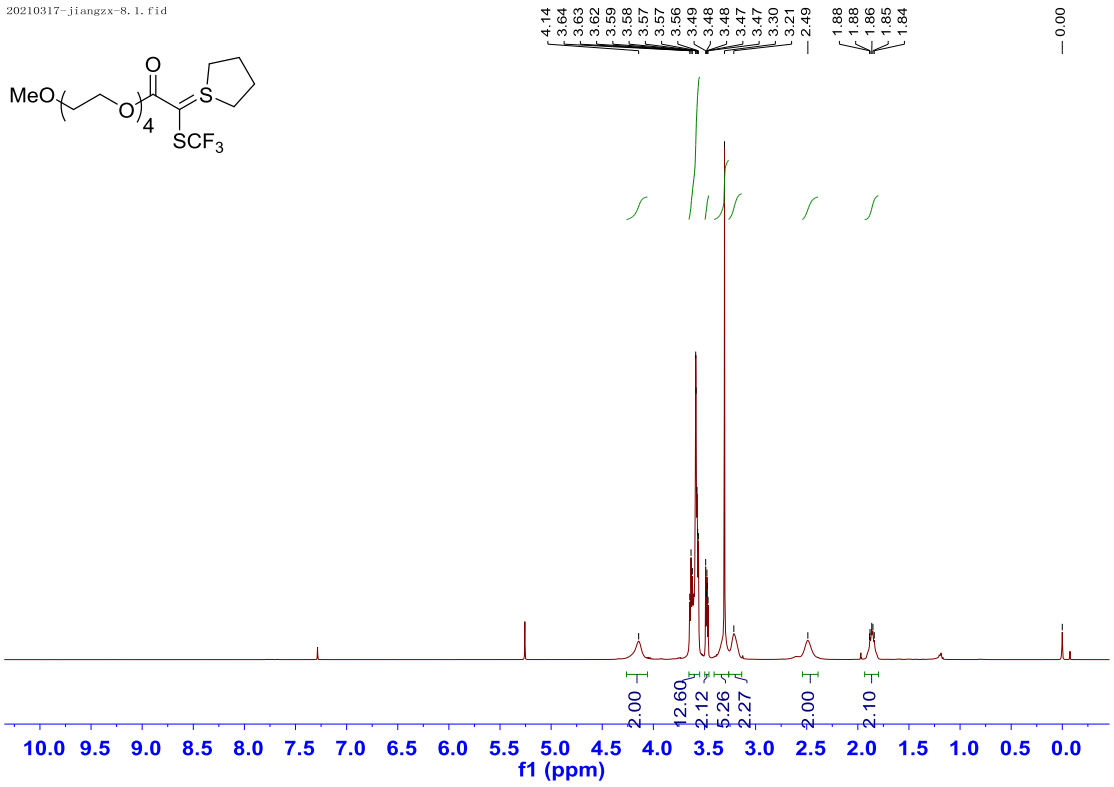
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5k**.



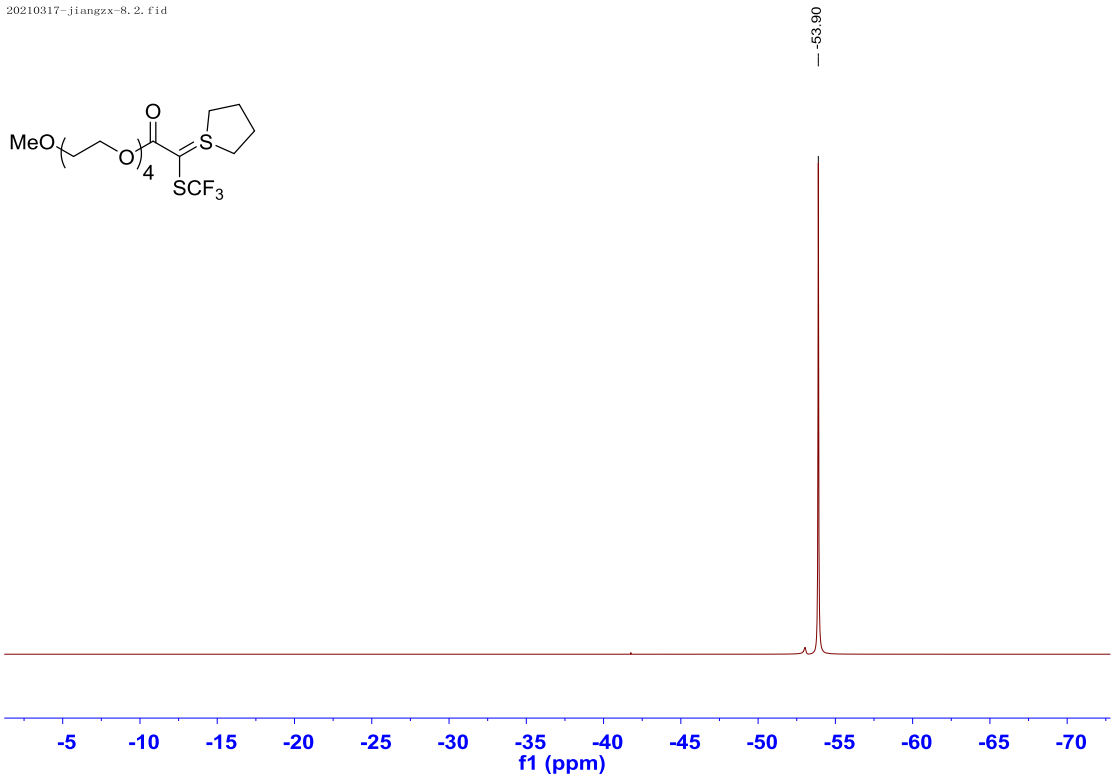
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5k**.



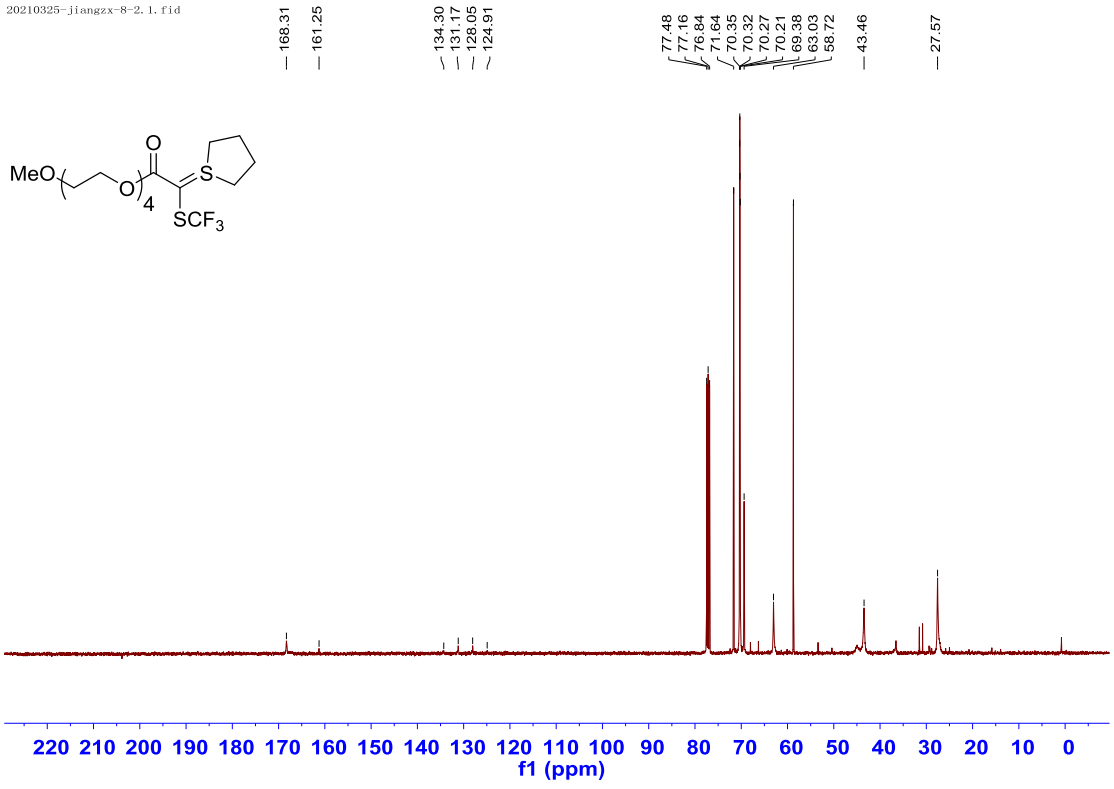
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5l**.



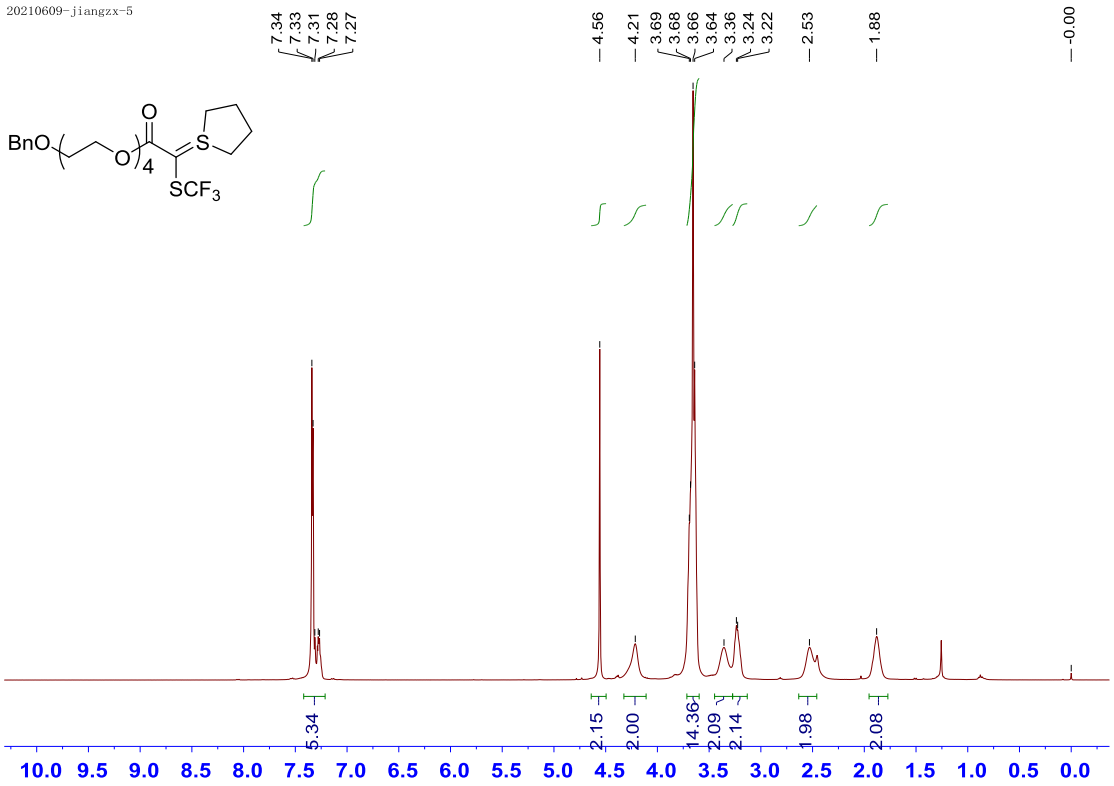
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5l**.



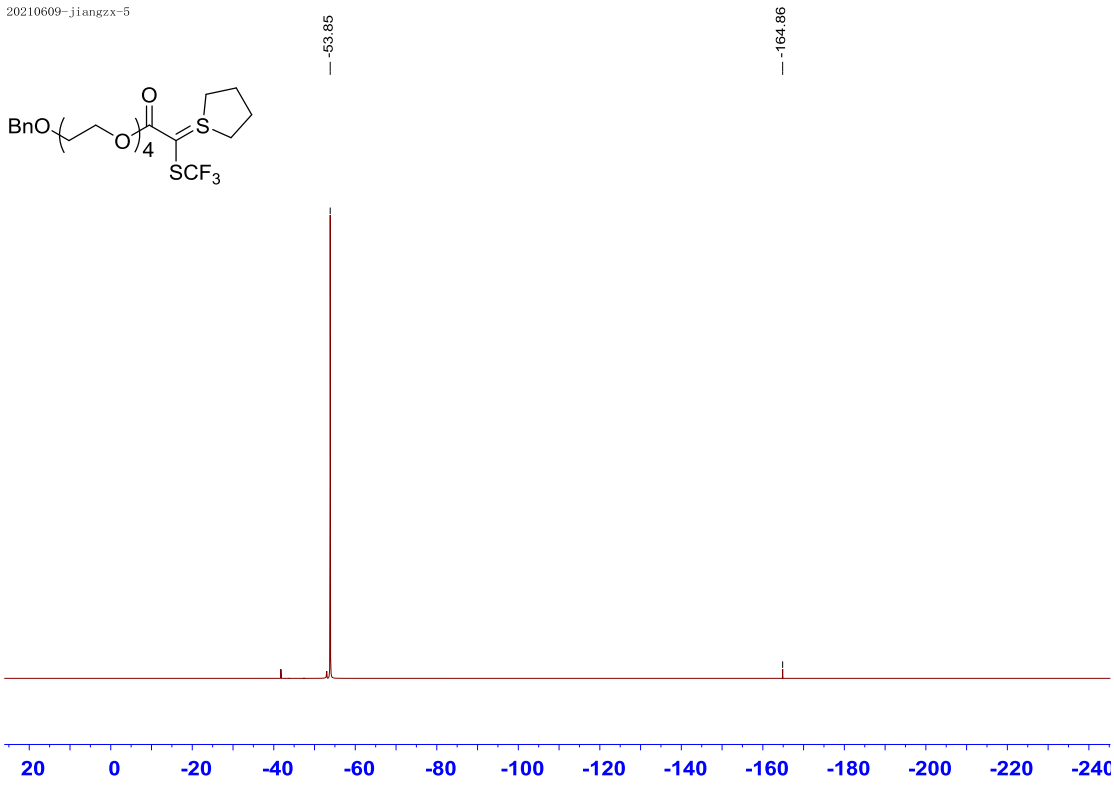
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5l**.



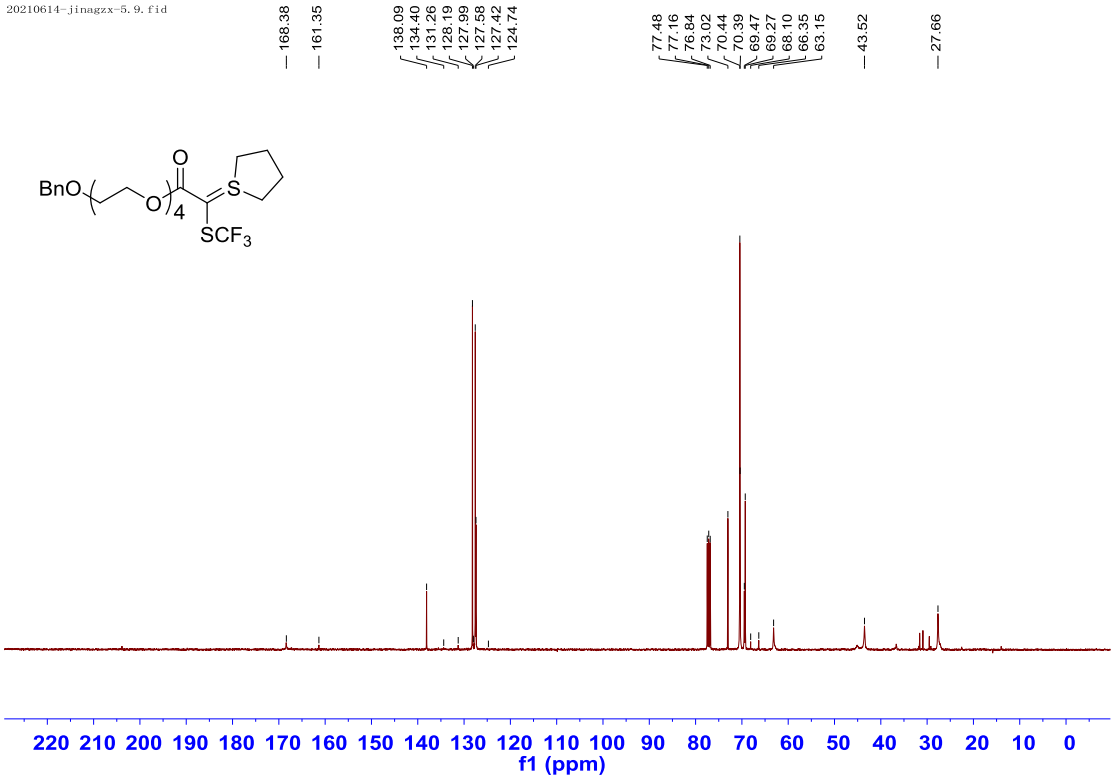
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5m**.



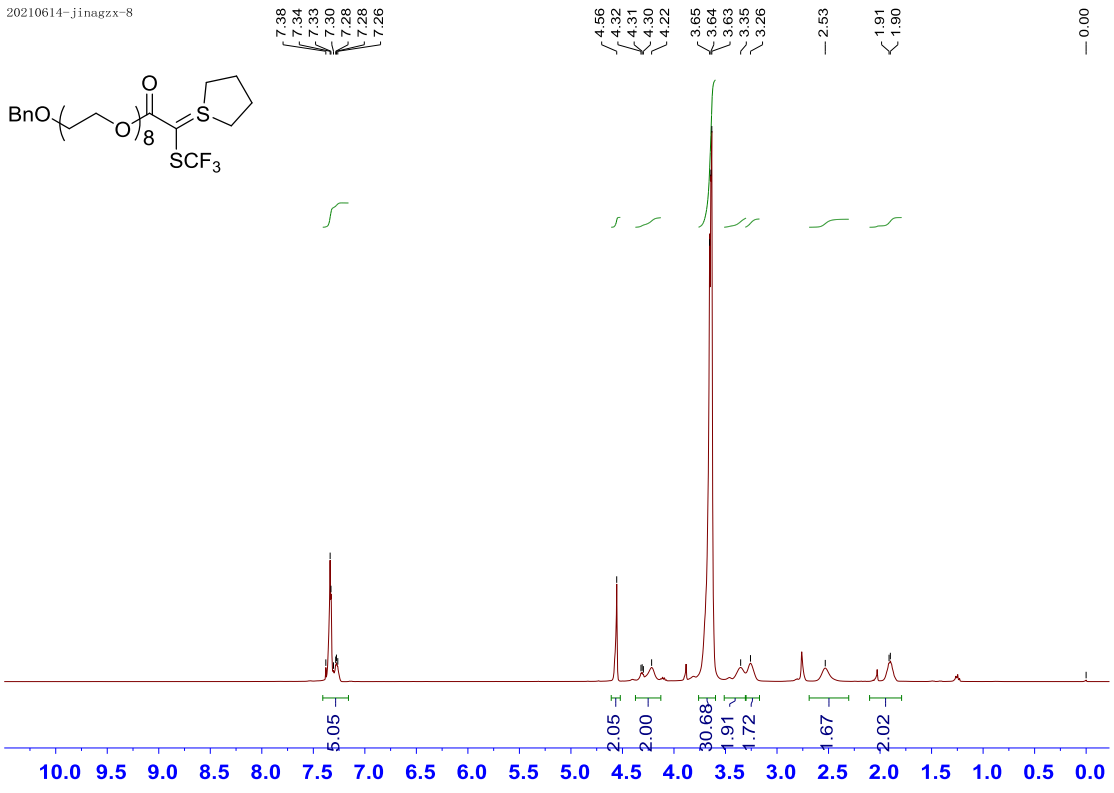
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5m**.



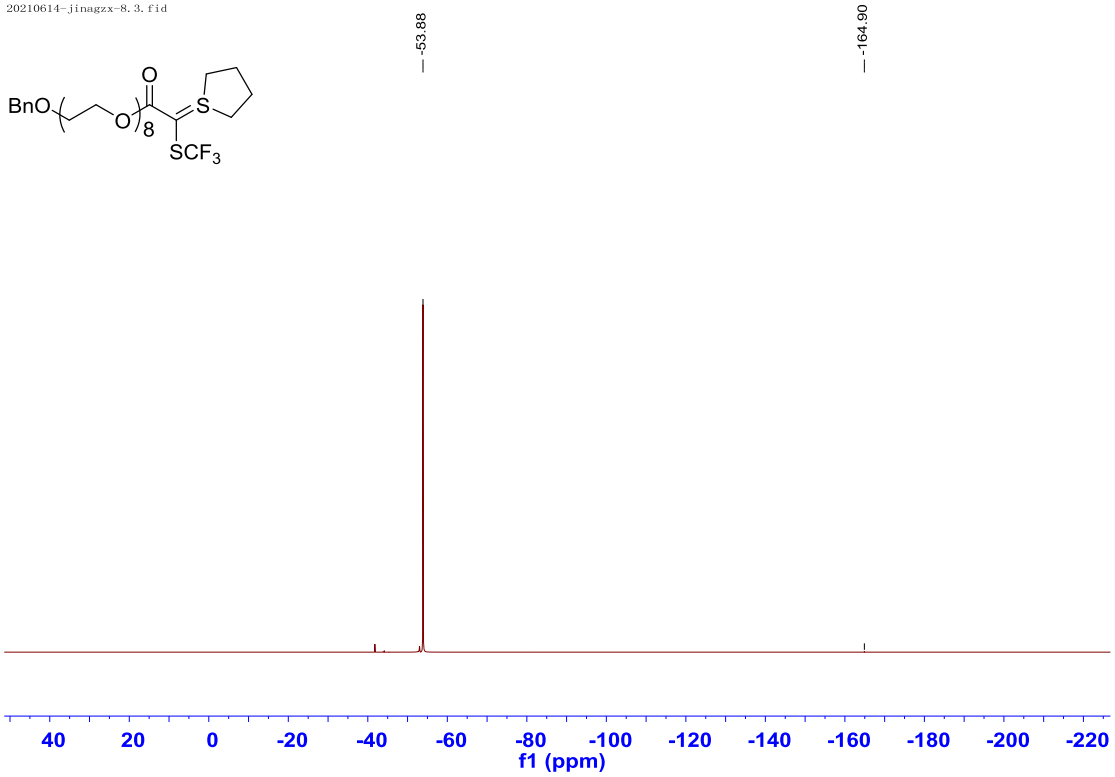
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5m**.



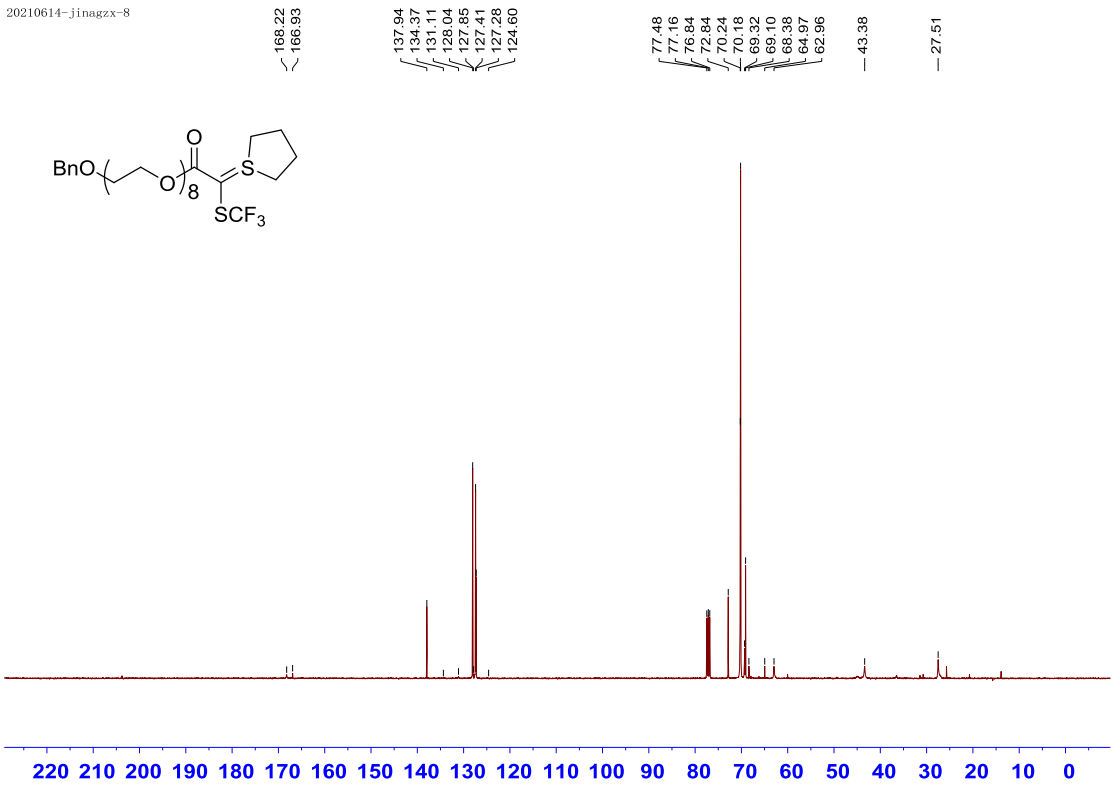
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**.



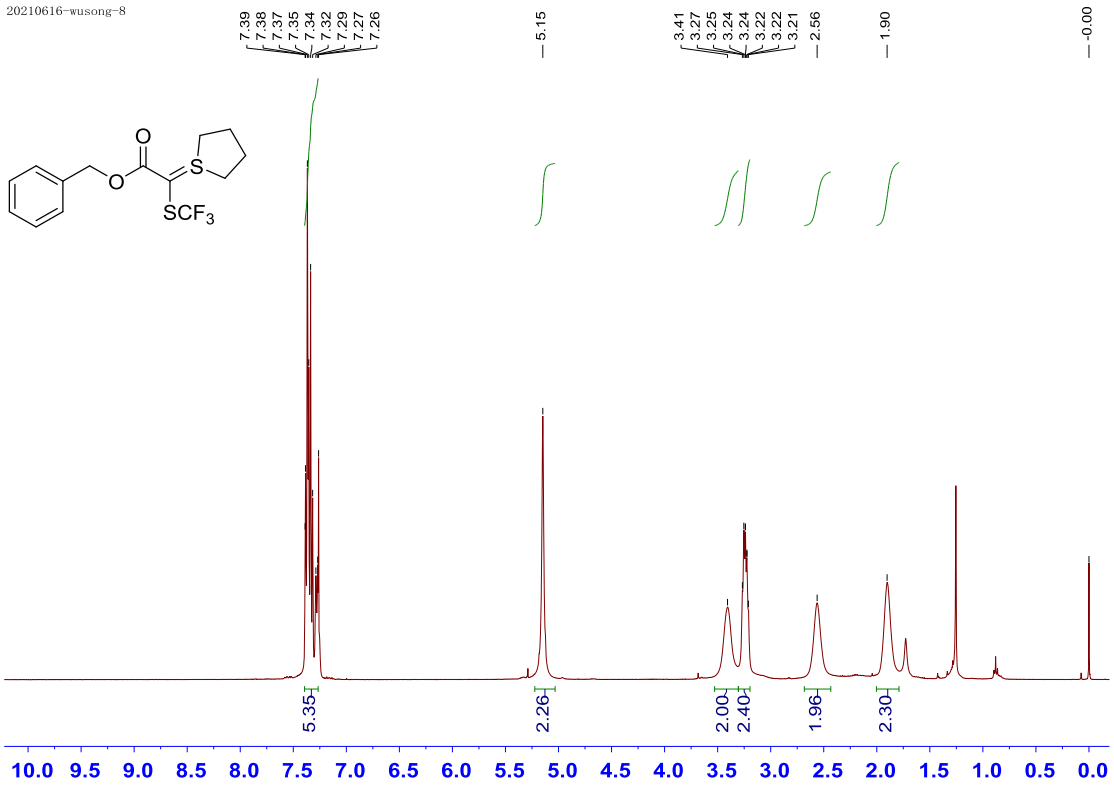
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5n**.



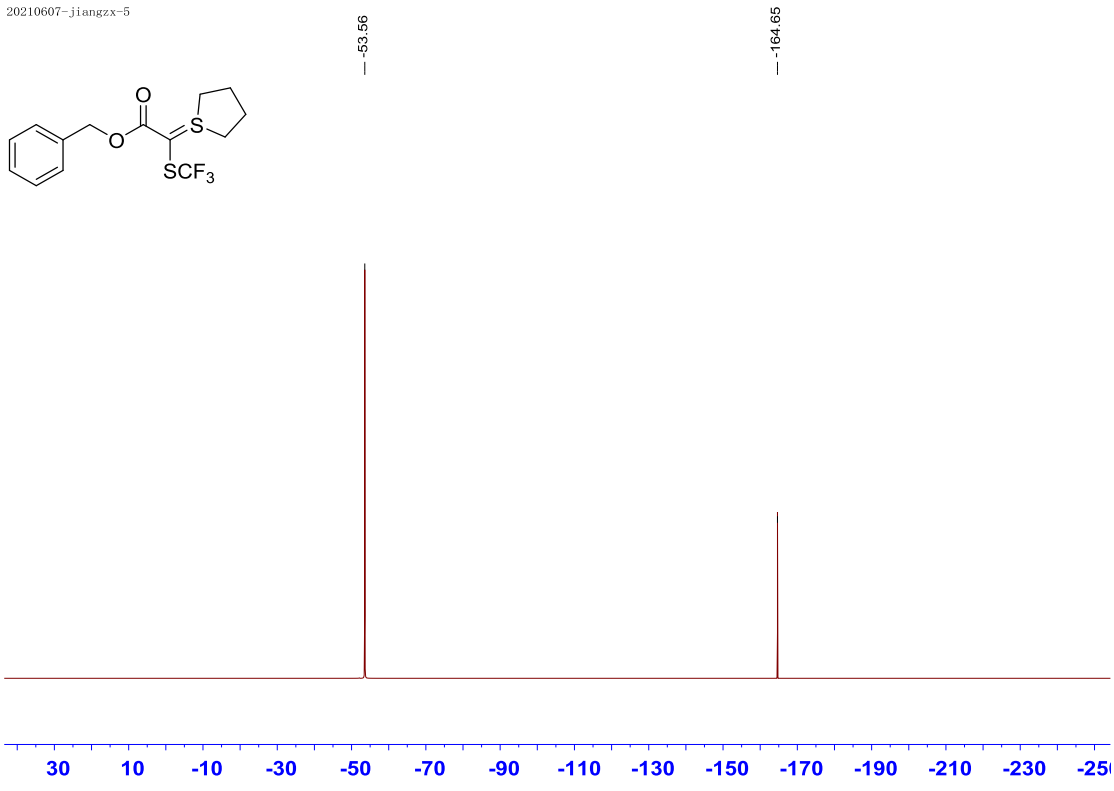
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5n**.



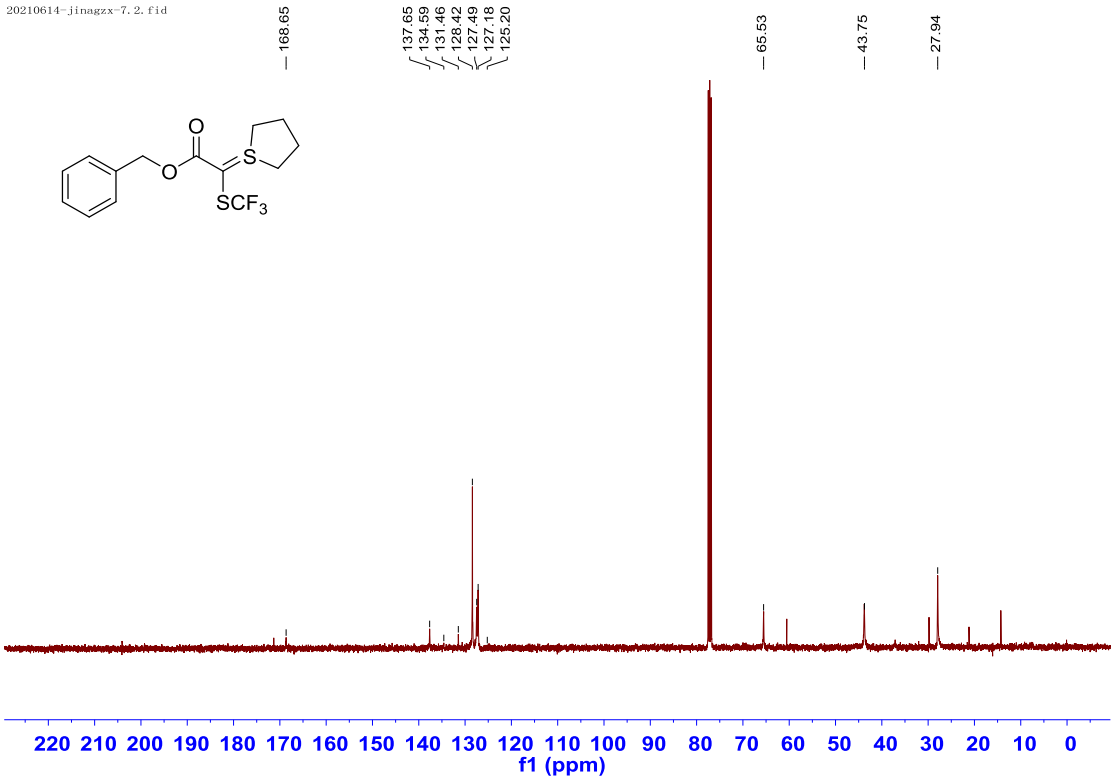
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**.



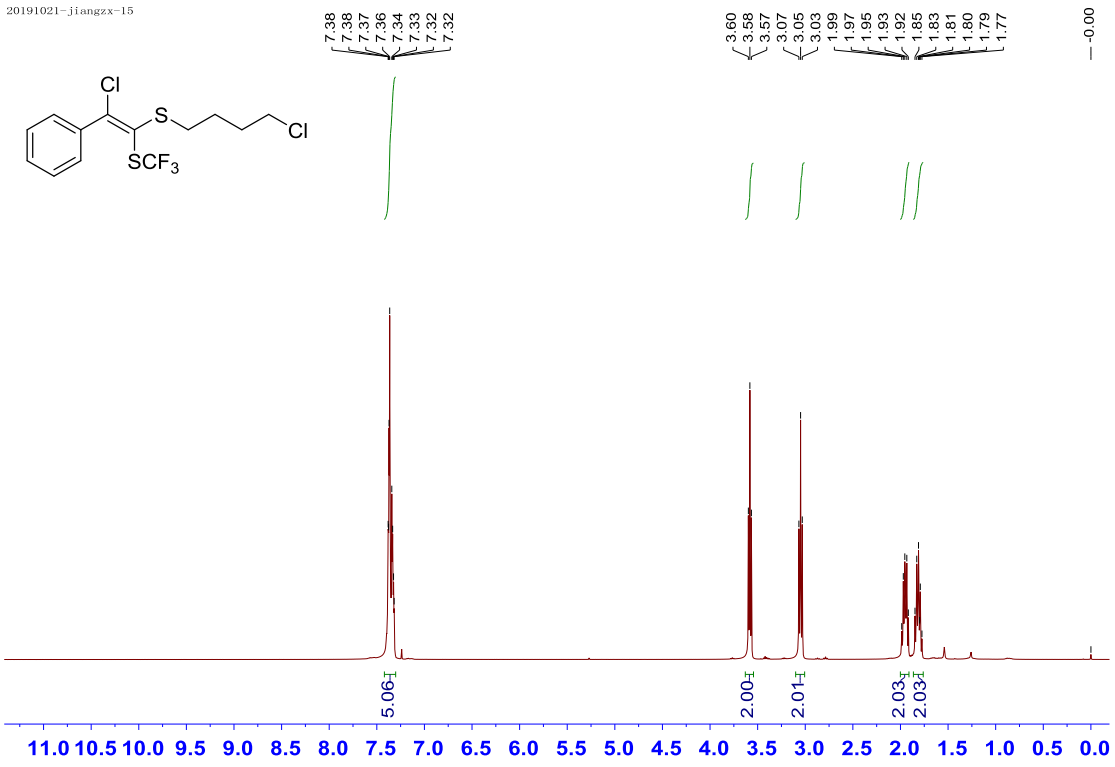
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5o**.



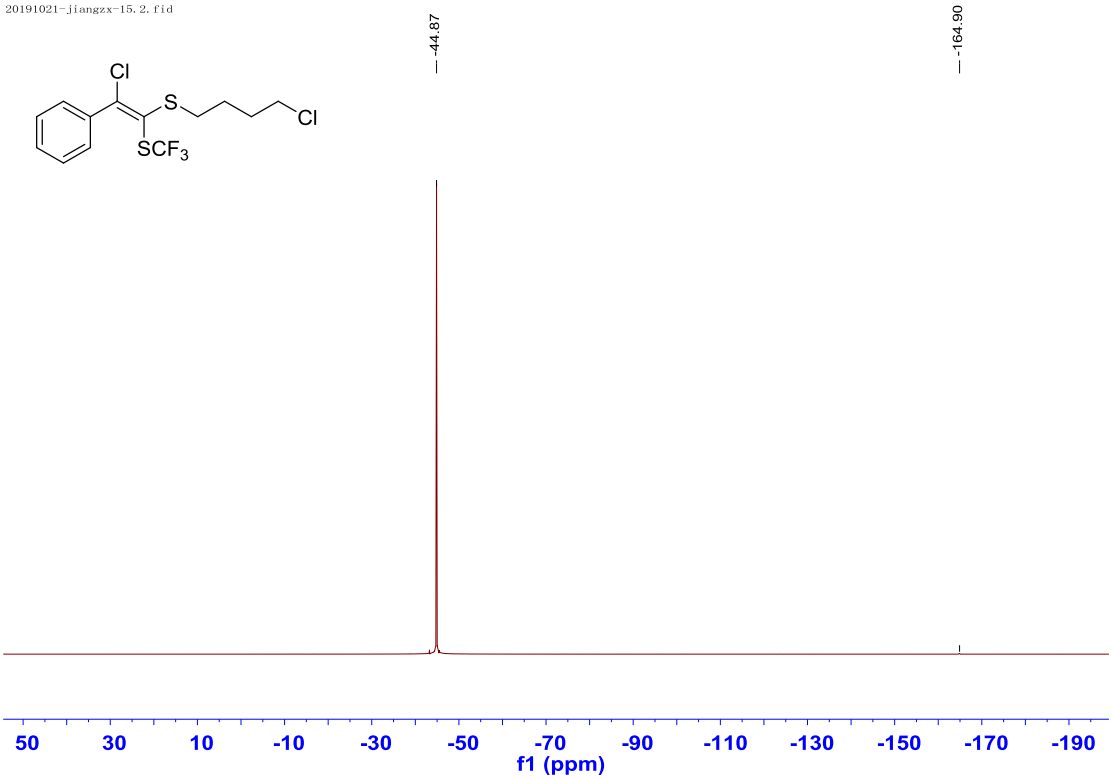
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5o**.



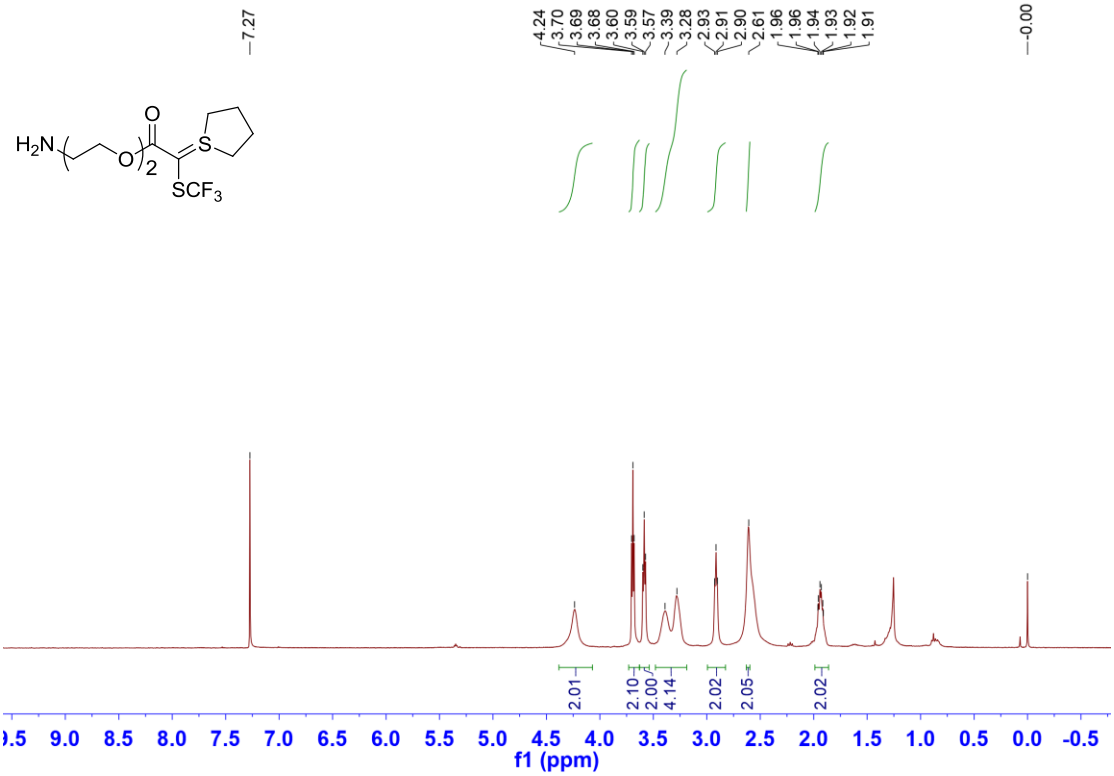
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**.



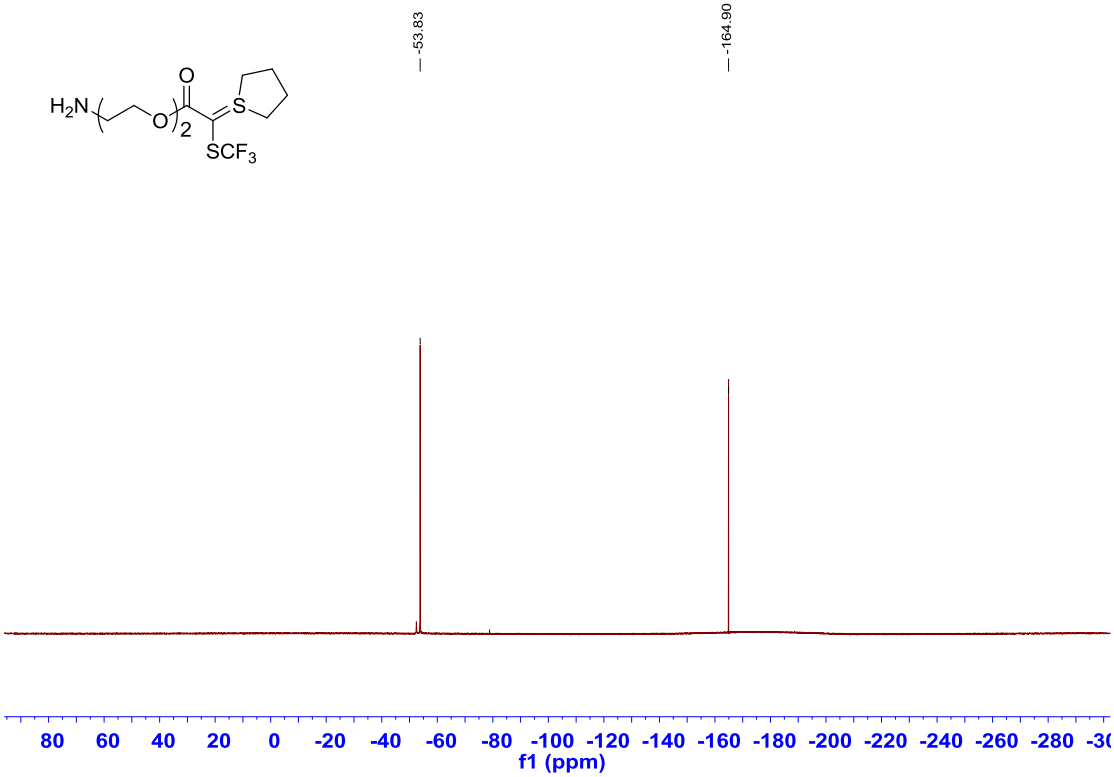
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6**.



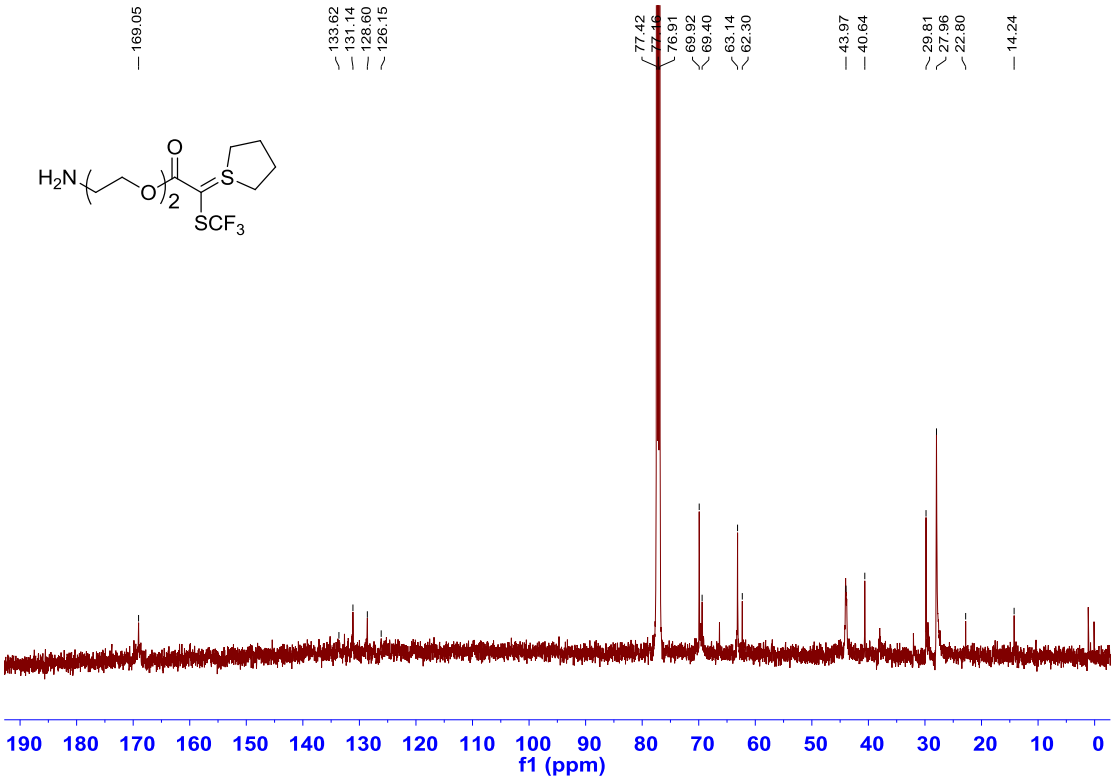
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**.



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **7**.



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **7**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**.