Supporting Information for

Photocatalytic carboxylation of alkenes via synergistic hydrogen-atom transfer and proton transfer

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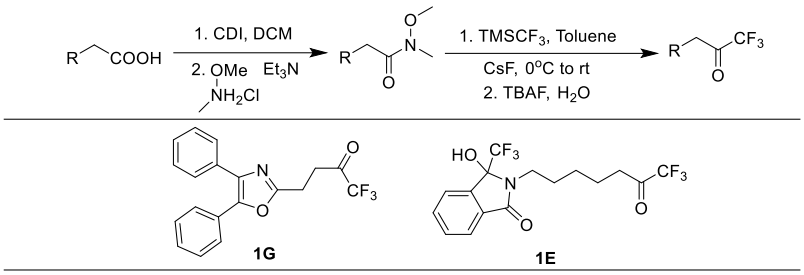
1. General information

All operations were performed under an argon atmosphere unless otherwise specified. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at ambient temperature using JNM-ECZ500R/S1 (500 MHz) spectrometer or JNM-ECZ600R/S1 (600 MHz) spectrometer. ^{1}H NMR chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm), as internal standards. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.1 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet. GCMS data were obtained on SHIMADZU GCMS-QP2020 NX with EI mode. HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm), phosphomolybdic acid or $KMnO_4$ staining solutions followed by heating, also by Gas Chromatograph Mass spectrometer analysis (GC-MS). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Synthesis of starting materials

Substrates **1A** [1]**, 1B-1D** [2]**, 1F** [2]**, 1H** [3]**, 1K** [4]**, 1L** [5]**,** 1**S** [6]**,** 1**a** [1]**, 1l** [7]**,** 1**s** [8]**, 2a-2s** [9] were prepared according to the reported procedures.

Method A: Synthesis of Trifluoromethyl ketone



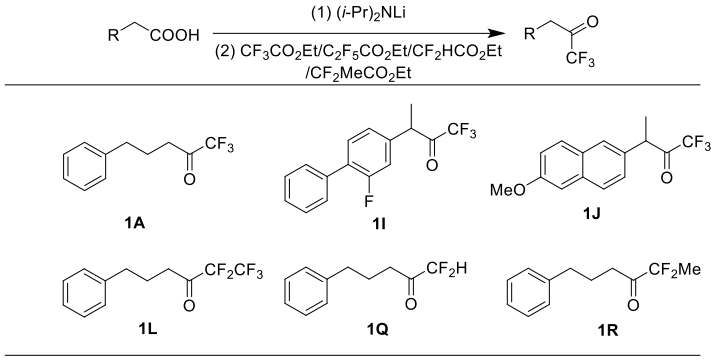
To a 250 mL round bottom flask equipped with a stir bar was added Oxaprozin (7.3 g, 25 mol) and DCM (85 mL). To this stirred solution was added 1,1′- carbonyl diimidazole (4.87 g, 30 mmol) in one portion, turning the solution a clear pale-yellow and resulting in the evolution of CO_2 gas. The reaction mixture was allowed to stir for 1 h at rt. After this time, N-O-dimethylhydroxylamine hydrochloride (2.93 g, 30 mmol,) and Et_3N (8.7 mL, 62.5 mmol) were added all at once, and the reaction mixture was stirred overnight. The reaction mixture was then quenched with 60 mL of 2 M aq HCl and stirred vigorously for 10 min. After this time, the solution was transferred to a separatory funnel, and the layers were separated. The aq layer was extracted with DCM (3 × 40 mL). The combined organic layers were washed with 2 M aq HCl (75 mL), H_2O (75 mL), saturated aq $NaHCO_3$ (2 × 50 mL), and brine (75 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo via rotary evaporation without further purification, affording the pure amide as a clear.

To a 100 mL round bottom flask equipped with a stir bar was added 3-(4,5-diphenyloxazol-2-yl)-N-methoxy-N-methylpropanamide (6.72 g, 20 mmol). CsF (0.61 g, 40 mol), followed by toluene (40 mL), was then added to the flask. The flask was cooled to 0 °C for 15 min. TMS-CF_3 (5.68 g, 40 mmol) was added to the reaction mixture. After completion of the addition, the reaction mixture was allowed to stir for

10 min at 0 ºC. And the reaction mixture was allowed to stir at room temperature overnight.

Once complete conversion to the silylated, tetrahedral intermediate was confirmed, toluene was removed in vacuo via rotary evaporation. Hexanes (20 mL), followed by deionized H_2O (20 mL) followed by 1 M solution of TBAF in THF (20 mL, 20 mmol) were added to the reaction flask. The flask was equipped with a reflux condenser and then heated to 50ºC in an oil bath for 8 h to facilitate cleavage of the silyl ether. The reaction mixture was then diluted with Et_2O (60 mL) and deionized H_2O (50 mL), and then transferred to a separatory funnel. The layers were separated, and the aq layer was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with 2 M aq HCl (60 mL), H_2O (75 mL), and brine (75 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation, affording the crude trifluoromethyl ketone. Further purification was accomplished by column chromatography on silica gel. (**1G** and **1E** were prepare in 64 and 58% yields.)

Method B: Synthesis of Trifluoromethyl ketone

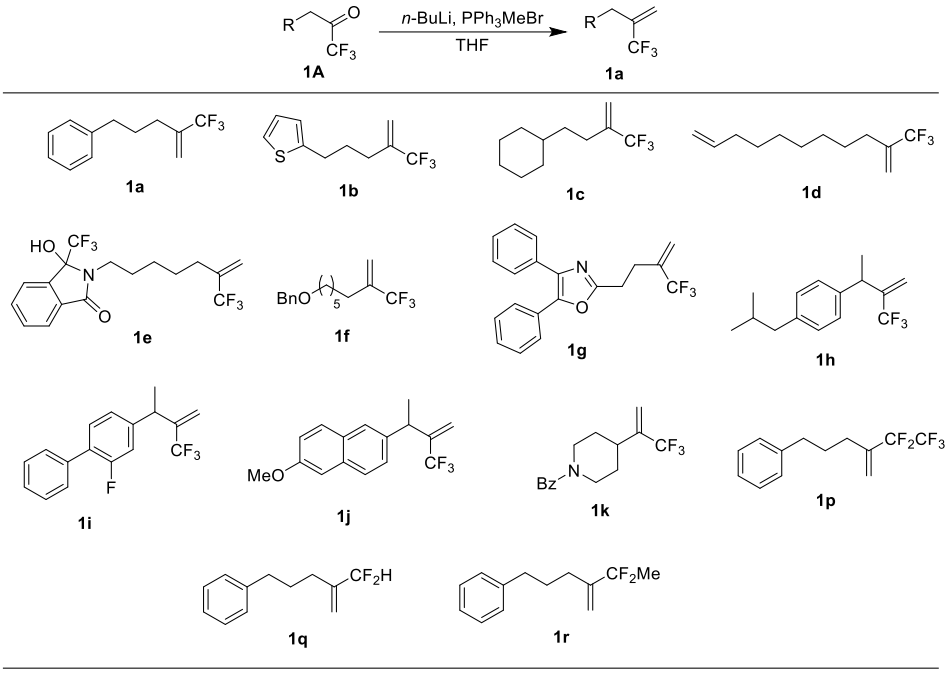


A solution of 4-Phenylbutyric acid (14 mmol, 2.3 g) in dry THF (10 mL) was added dropwise to the LDA (2 M in THF, 15 mL) solution at -65ºC under N_2 atmosphere. After the addition, the reaction mixture was allowed to warm temperature and stirred for 2h. The mixture was cooled back to -65ºC and ethyl 2,2,2-trifluoroacetate (5.26g, 37 mmol) was added dropwise over 15 min. Upon completion of the addition, the reaction mixture was stirred at -65ºC for 15min and at room temperature for 30 min. The reaction was quenched with 6 M HCl (20 mL) at -65ºC and extracted with EtOAc (40 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4,

concentrated via rotary evaporation, and purified by column chromatography on silica gel (PE: EA = 50:1) to afford trifluoromethyl ketone as a colorless oil (2.42 g, 80% yield).

1I, **1J**, **1L**, **1Q**, and **1R** were prepared, respectively, in 75%, 64%, 80%, 85%, and 78% yields from the corresponding bromides by following a similar procedure.

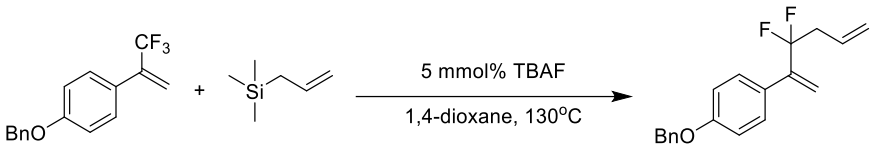
Method C: Synthesis of Trifluoromethyl Alkenes



The *n*-BuLi (2.5 M in THF, 2.4 mL) was added to a solution of PPh_3MeBr (2.23 g, 6.25 mmol) in dry THF at 0°C under N_2 atmosphere. After the addition, the reaction mixture was stirred at 0°C for 1.5h. The reaction mixture was cooled to – 78°C. A solution of 1,1,1-trifluoro-5-phenylpentan-2-one (5 mmol, 1.08g) in THF (6 mL) was added dropwise to the flask over 5 min. Then the mixture was stirred at room temperature overnight. The reaction was quenched with saturated NH_4Cl and extracted with DCM (10 mL x 3), washed with brine (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated via rotary evaporation, and purified by column chromatography on silica gel (PE) to afford the pure **1a** (909 mg, 85% yield).

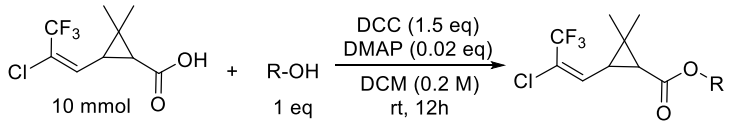
1b, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1p**, **1q**, and **1r** were prepared in 80%, 65%, 72%, 57%, 74%, 64%, 84%, 77%, 70%, 52%, 83%, 88% and 85% yields from the corresponding bromides by following a similar procedure.

Method D: Synthesis of difluoromethyl alkene



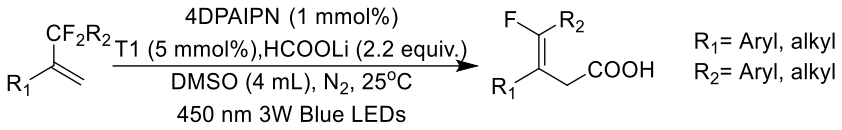
Compounds **1t** was prepared according to the literature [10]. In an oven-dried 10 mL Schlenk tube containing a stir bar was charged with trifluoromethylalkene (1 mmol, 1.0 equiv), allylsilane 2 (2 mmol, 2.0 equiv), 1,4-dioxane (5 mL) and TBAF (1.0mol/L in THF, 5 ul, 5 mol%). Then the reaction was heated at 130 °C with stirring for 12 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to afford the product **1t** in 83% yield.

Method E: Synthesis of **1n**-**1o**



To a flame-dried 100 mL round bottom flask under inert atmosphere was charged with DCC (3.09 g, 1.5 eq, 15 mmol) and DMAP (24 mg, 0.02 eq, 0.20 mmol). Then, 3-(2-Chloro-3,3,3-trifluoroprop-1-en-1-yl)-2,2-dimethylcyclopropanecarboxylic acid (2.4 g, 1 eq, 10 mmol) was added to the mixture. Then, anhydrous DCM (50 mL) was added to the flask, followed by addition of R-OH (10mmol). The solution was let stir for 12 hours at room temperature. After that, the crude mixture in dichloromethane was filtered and extracted with 50 mL brine. The organic layer was collected, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel to afford the product **1n**, **1o** in 75%, 67% yield.

3. General procedure for the synthesis of carboxylic acids



A dry tube equipped with a stirring bar was charged with the photocatalyst (1 mmol%), **1a** (85.6 mg, 0.4 mmol, 1.0 equiv.), HCOOLi (45.8 mg, 0.88 mmol, 2.2 equiv.), T1 (3.5mg, 0.02mmol ,5 mmol%), anhydrous DMSO (4 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred and irradiated with a 3W 450 nm Blue LEDs for 3 hours. The resulting mixture was diluted with 10 mL EA. The reaction mixture was extracted by EtOAc three times, and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA/AcOH = 10/1/0.1%~1/1/0.1%) to obtain the pure product (T1 is lithium 2-(methoxycarbonyl)benzenethiolate).

4. Mechanism studies

4.1 Stern-Volmer emission quenching experiment

Samples for the quenching experiments were prepared in a 4 mL quart cuvette with a cap. 4DPAIPN was irradiated at 450 nm and the emission intensity at about 529 nm was observed. In a typical, the emission spectrum of a 10^{-5} M solution of 4DPAIPN in DMSO was collected.

T1: A stock solution of T1 (10^{-3} M) in DMSO was prepared. Then different amounts of this stock solution were added to the 2 mL of 4DPAIPN in DMSO (10^{-5}).

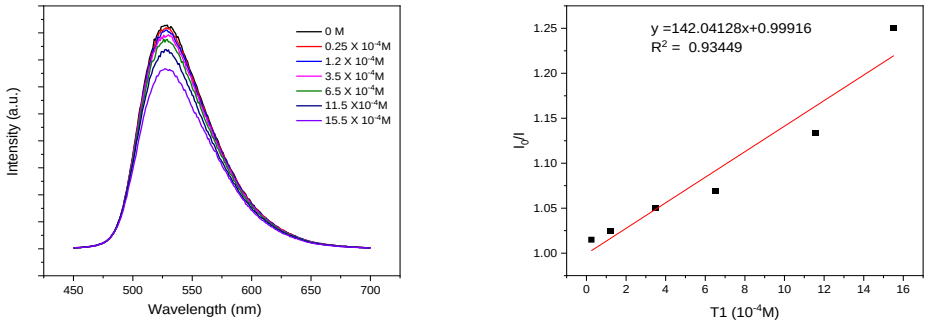


Figure S1 Stern-Volmer fluorescence quenching experiments using 4DPAIPN with T1

α-CF_3 Alkene **1a**: A stock solution of **1a** (10.7 mg, 0.05 mmol) in 10 mL DMSO was prepared. Different amounts of this stock solution were added to 2 mL of 4CzIPN in DMSO (10^{-5} M).

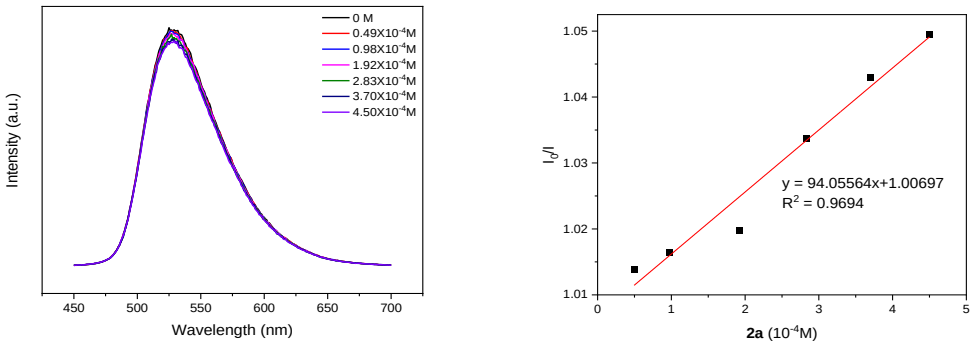


Figure S2 Stern-Volmer fluorescence quenching experiments using 4DPAIPN with α-CF_3 Alkene **2a**

HCOOLi: Different amounts of HCOOLi were added to 2 mL of 4CzIPN in DMSO (10^{-5} M).

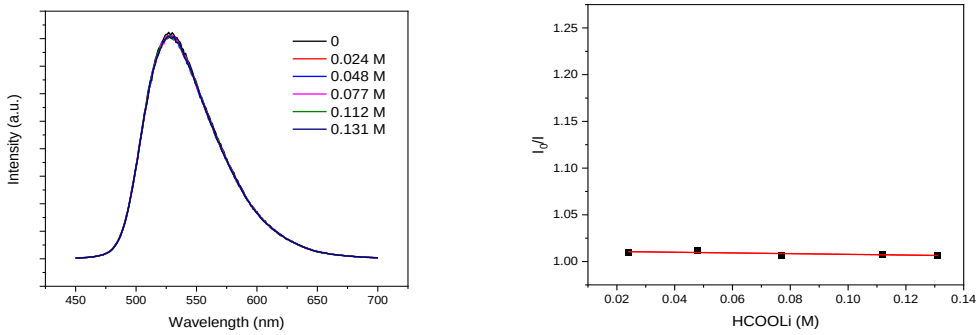
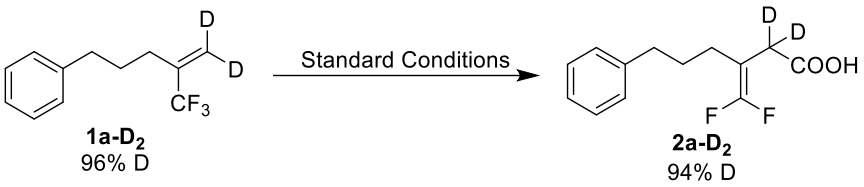


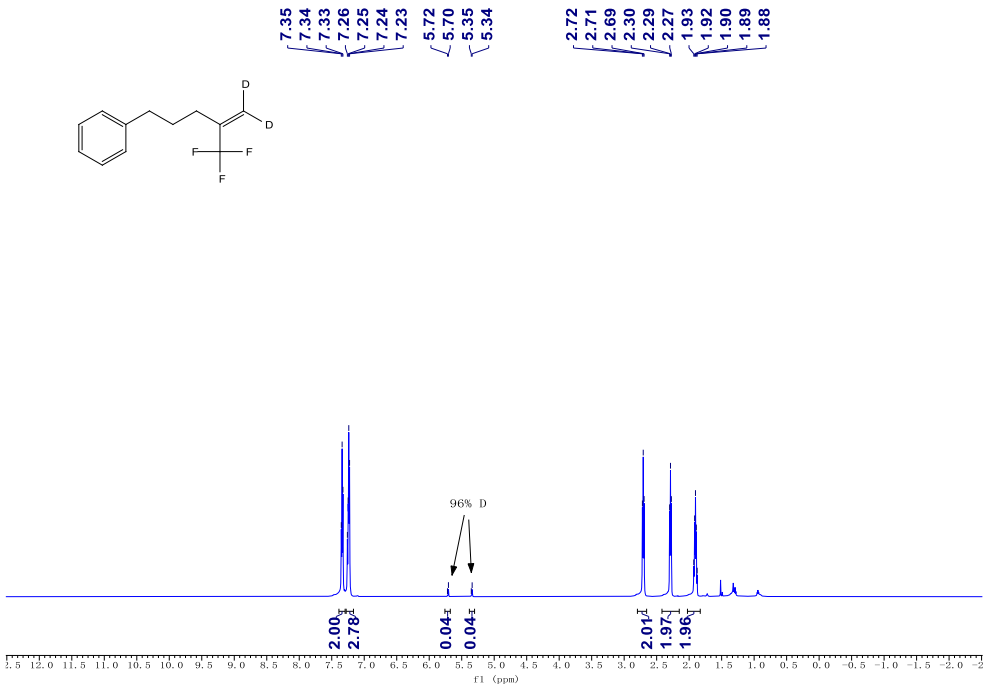
Figure S3 Stern-Volmer fluorescence quenching experiments using 4DPAIPN with HCOOLi

4.2 Deuterium-labeling Studies

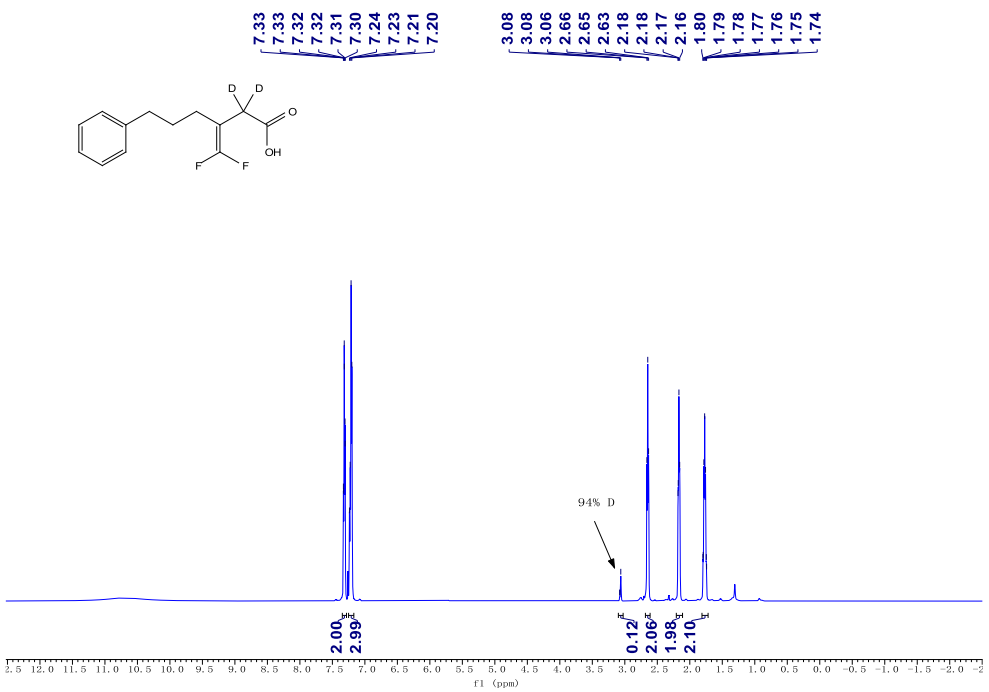


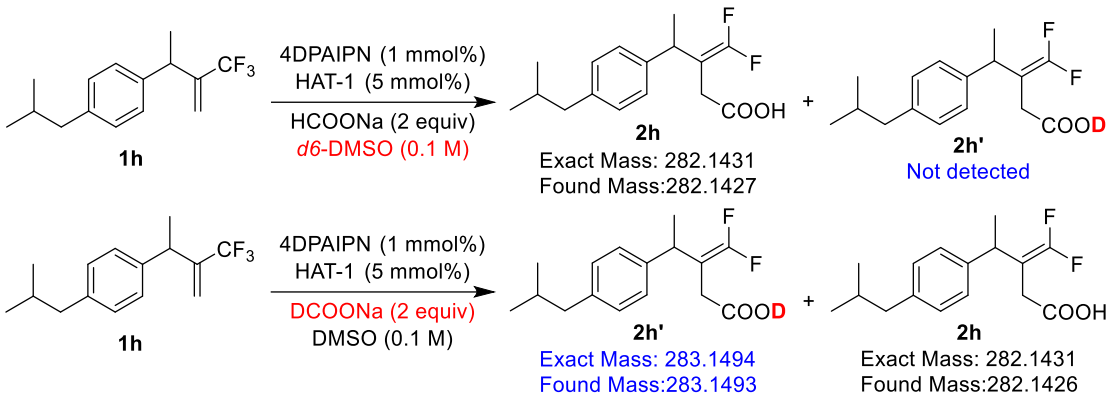
A dry tube equipped with a stirring bar was charged with the photocatalyst (1 mmol%), **1a-D2** (86.4 mg, 0.4 mmol, 1.0 equiv.), HCOOLi (45.8 mg, 0.88 mmol, 2.2 equiv.), T1 (3.5mg, 0.02mmol ,5 mmol%), anhydrous DMSO (4 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred and irradiated with a 3W 450 nm Blue LEDs for 3 hours. The resulting mixture was diluted with 10 mL EA. The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA/AcOH 10/1/0.1%~1/1/0.1%) to give the pure desired product **2a-D2**.

1a-D_2


7.35
7.34
7.33
7.26
7.25
7.24
7.23
5.72
5.70
5.35
5.34
2.72
2.71
2.69
2.30
2.29
2.27
1.93
1.92
1.90
1.89
1.88
D
D
F
F
F
96% D
2.00
2.78
0.04
0.04
2.01
1.97
1.96
f1 (ppm)

2a-D_2


7.33
7.33
7.32
7.32
7.31
7.30
7.24
7.23
7.21
7.20
3.08
3.08
3.06
2.66
2.65
2.63
2.18
2.18
2.17
2.16
1.80
1.79
1.78
1.77
1.76
1.75
1.74
D
D
O
OH
F
F
94% D
2.00
2.99
0.12
2.06
1.98
2.10
f1 (ppm)



A dry tube equipped with a stirring bar was charged with the photocatalyst (1 mmol%), **1h** (102.4 mg, 0.4 mmol, 1.0 equiv.), HCOONa (59.8 mg, 0.88 mmol, 2.2 equiv.)/DCOONa (60.7 mg, 0.88 mmol, 2.2 equiv.), T1 (3.5mg, 0.02mmol ,5 mmol%), anhydrous DMSO/d_6-DMSO (4 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred and irradiated with a 3W 450 nm Blue LEDs for 3 hours. The resulting mixture was diluted with 10 mL EA. The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA/AcOH 10/1/0.1%~1/1/0.1%) to give the pure desired product.

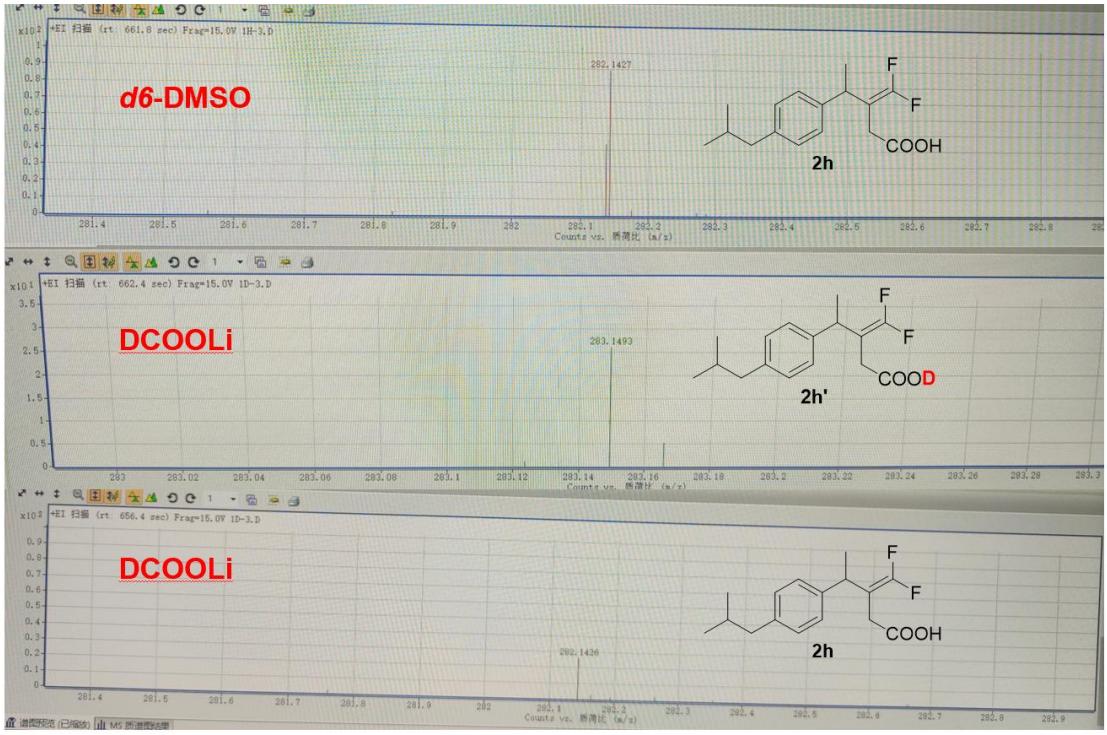
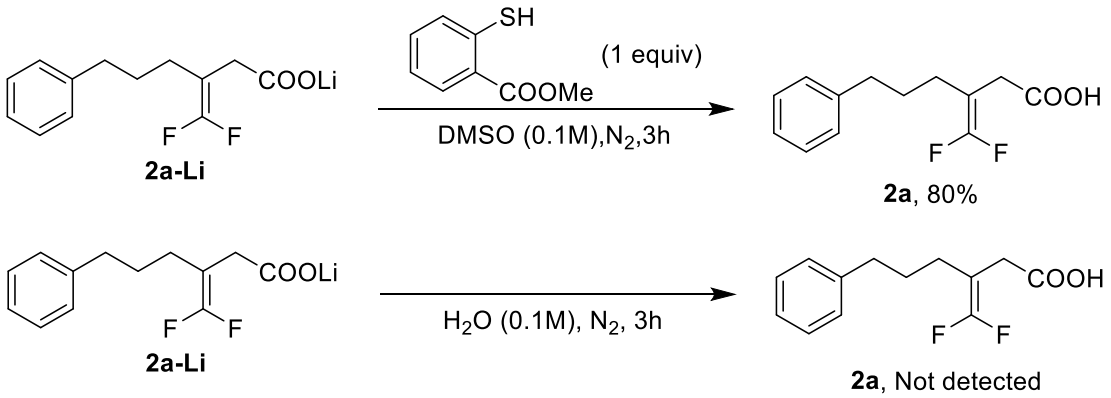


Figure S4. Deuterium product detected by MS (EI)

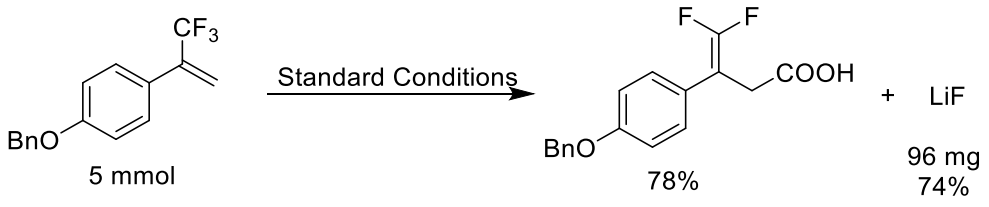
4.3 Proton transfer experiment



A dry tube equipped with a stirring bar was charged with **2a-Li** (86.4 mg, 0.1 mmol, 1.0 equiv.), HAT-1 (16.8 mg, 0.1mmol ,1.0 euqiv.), anhydrous DMSO (1 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred for 3 hours. The resulting mixture was diluted with 5 mL EA. The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The yield of **2a** by ^{19}F NMR using 1,4-dichlorobenzene as the internal standard.

A dry tube equipped with a stirring bar was charged with **2a-Li** (86.4 mg, 0.1 mmol, 1.0 equiv.), H_2O (1 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred for 3 hours. The resulting mixture was diluted with 5 mL EA. The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The yield of **2a** by ^{19}F NMR using 1,4-difluorobenzene as the internal standard.

4.4 Separation of LiF

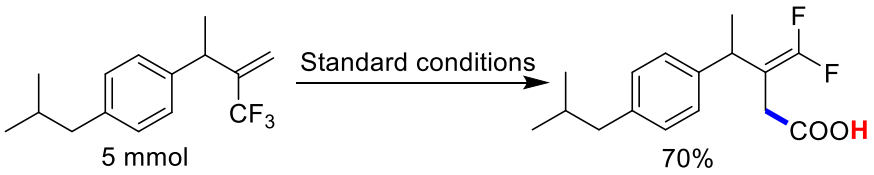


A dry tube equipped with a stirring bar was charged with the photocatalyst (1 mmol%), **3b** (1.39 g, 5 mmol, 1.0 equiv.), HCOOLi (572 mg, 11 mmol, 2.2 equiv.), T1 (43.5mg, 0.25 mmol ,5 mmol%), anhydrous DMSO (50 mL). Then evacuated under

high vacuum and backfilled with N_2 (x 3). The reaction was stirred and irradiated with 50 W 450 nm Blue LEDs for 3 hours. The resulting mixture was diluted with 100 mL EA. Filter out white solid and wash with EtOH to provide LiF (96 mg, 74%).

The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA/AcOH 10/1/0.1%~1/1/0.1%) to give the pure desired product.

4.5 Scaled-up reaction



A dry tube equipped with a stirring bar was charged with the photocatalyst (1 mmol%), **1h** (1.28 g, 5 mmol, 1.0 equiv.), HCOOLi (572 mg, 11 mmol, 2.2 equiv.), T1 (43.5 mg, 0.25 mmol ,5 mmol%), anhydrous DMSO (50 mL). Then evacuated under high vacuum and backfilled with N_2 (x 3). The reaction was stirred and irradiated with 50 W 450 nm Blue LEDs for 3 hours. The resulting mixture was diluted with 100 mL EA. The reaction mixture was extracted by EtOAc three times and the combined organic phases were concentrated in vacuo. The residue was purified by silica gel flash column chromatography (PE/EA/AcOH 10/1/0.1%~1/1/0.1%) to give the pure desired product (988.0 mg, 70%).

4.6 The apparent quantum yield (AQY) measurement

The AQY for defluorinative carboxylation of α-CF_3 alkene **1a** was measured using 450 nm Blue LED lamps. The irradiation area was controlled as 1.77 cm^2. The intensities were 38426 $uW \cdot cm^{-2}$, respectively. The AQY was calculated as $AQY=N_e/N_p*100\% = M N_A hc/SPt\lambda*100\%$, where Ne is the amount of reaction electrons, N_p is the amount of incident photons, M is the amount of defluorinative carboxylation products (0.124×10^{-3} mol), N_A is Avogadro constant (6.02×10^{23} mol^{-1}), h is the Planck

constant (6.626 x 10^{-34} J•S), c is the speed of light (3 x 10^{8} m/s), S is the irradiation area (1.77 cm^2), P is the intensity of the irradiation (3.843x 10 $^{-2}$ J•S^{-1}•cm^2), t is the photo-irradiation time, and λ is the wavelength of the light (4.5 x 10^{-7}m).

$$AQY=N_e/N_p*100\% = M\ N_A hc/SPt\lambda*100\% = 20.2\%$$

4.7 DFT calculations

Computational methods

All density functional theory (DFT) calculations were carried out using the Gaussian 16 software package [11]. The geometries were optimized in dimethylsulfoxide solvent using the M06 [12] functional with a basis set of def2-TZVP for all atoms. The SMD continuum solvation model [13] was used in geometry optimization. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency.

Relative stabilities of different lithium salt complexes in DMSO

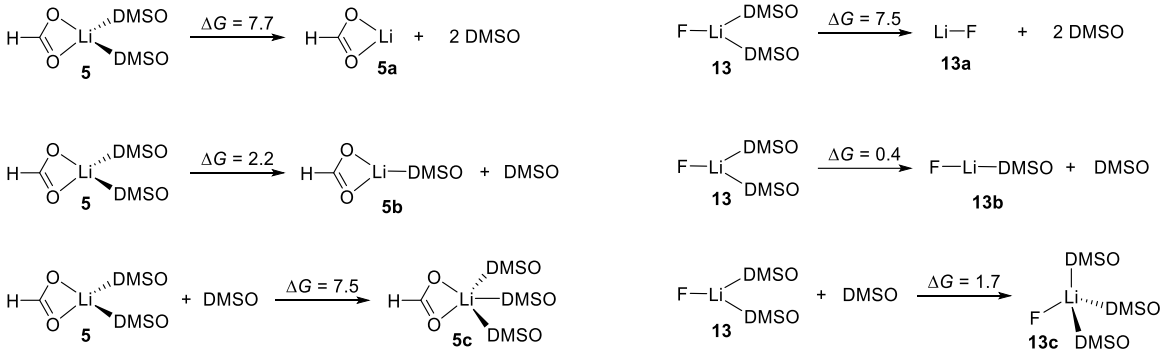


Figure S5. DFT studies of the coordination number of HCOOLi and LiF. All energies are in kcal/mol.

The Gibbs free energy changes for the formation of HCOOLi and LiF in DMSO with different coordination numbers are shown in Figure S5. These results indicate that intermediates **5** and **13** are the most stable structure of HCOOLi and LiF.

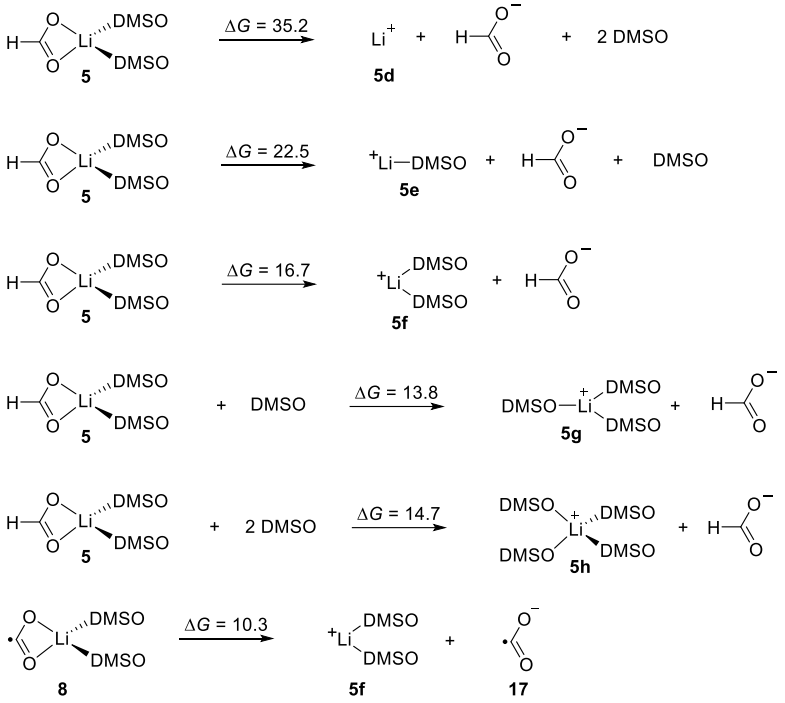


Figure S6. DFT studies of the relative stabilities of different anionic and cationic lithium salt complexes. All energies are in kcal/mol.

The Gibbs free energy changes for the formation of different anionic and cationic lithium salt complexes are shown in Figure S6. These results indicate that the formation of anionic and cationic complexes are thermodynamically unfavourable, and intermediate **5** and **8** are the most stable structure.

The other possible single electron transfer pathways

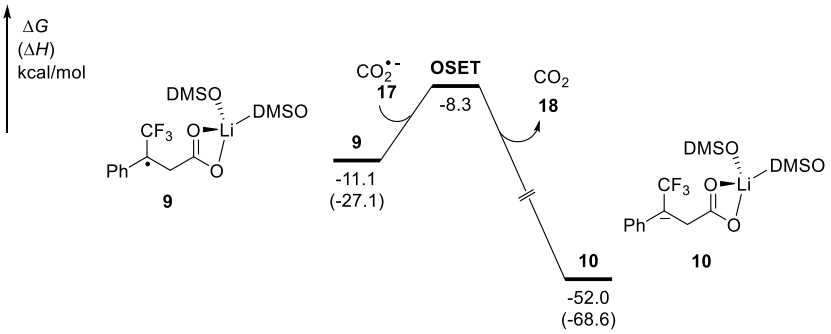


Figure S7. Free energy profile of the single-electron reduction of radical **9** by the carbon dioxide radical anion **17**.

We have calculated the single-electron reduction of radical **9** to anion **10** by the carbon dioxide radical anion. The energy barrier for this outer-sphere electron transfer

(OSET) process was estimated to be 2.8 kcal/mol using Marcus theory. However, this energy barrier is 2.7 kcal/mol higher than the OSET with the reduced photocatalyst (Figure 3), which indicates this pathway is kinetically less favored.

The other possible β-fluoride elimination pathways

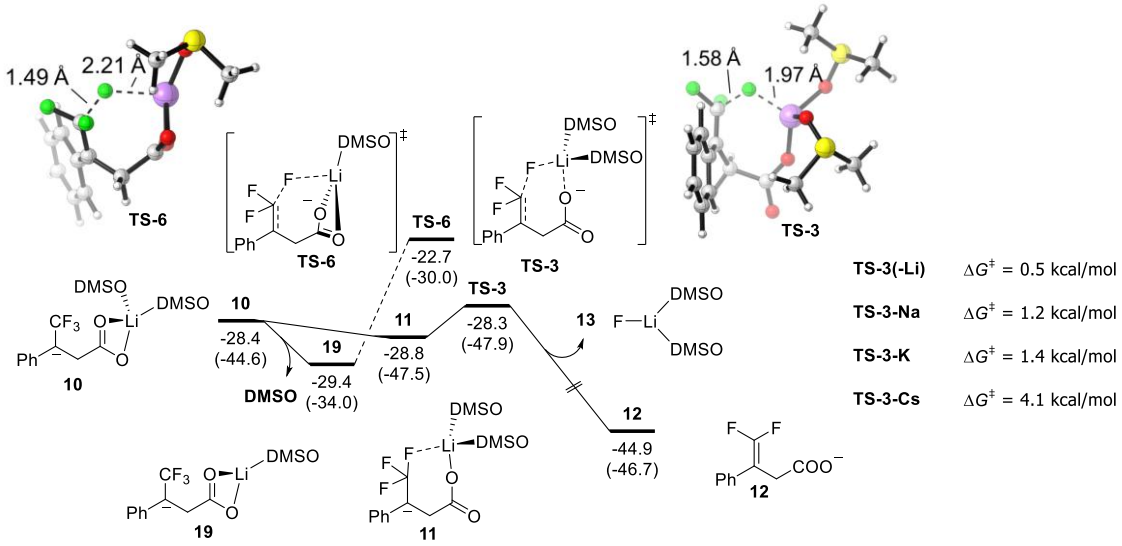


Figure S8. Free energy profile of β-fluoride elimination through **TS-6**.

As demonstrated in Figure S8, one DMSO could dissociate from the anionic lithium complex **10** to produce a more stable complex **19**. However, the β-fluoride elimination of **19** through **TS-6** was identified as a kinetically unfavourable pathway due to the higher energy barrier of **TS-6** ($\Delta\Delta G^{\ddagger}$ = 5.6 kcal/mol vs **TS-3**). In order to verify the effect of alkali cations on the β-fluoride elimination, the intermediate formed by Na, K, Cs ions and the corresponding elimination transition states were also calculated (**TS-3-Na**, **TS-3-K**, **TS-3-Cs**). Computational results demonstrate that the energy barrier of β-fluoride elimination **TS-3(-Li)** is the lowest among all four metals, thereby corroborating the experimental findings that lithium salts are the most effective. This validates the hypothesis that the lithium ions can effectively promote the reaction through the formation of Li-F bonding.

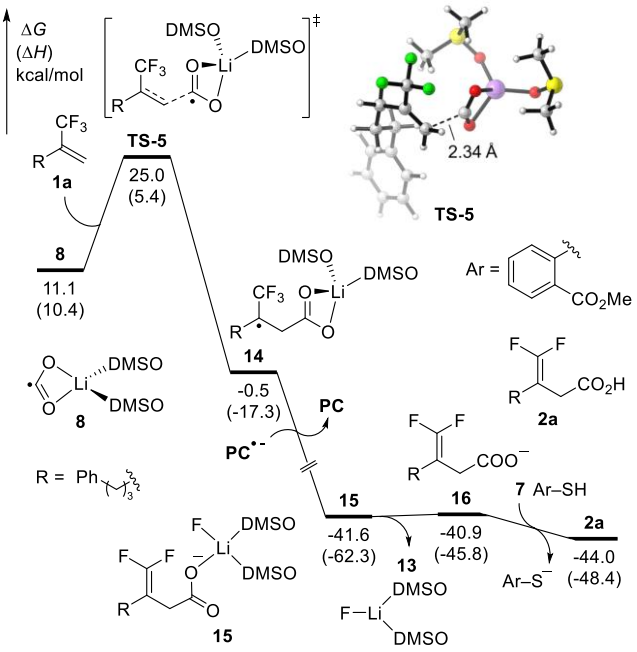


Figure S9. Free energy profile of the defluorinative carboxylation of aliphatic alkene **1a** with HAT-1. All energies were calculated at the M06/def2-TZVP/SMD(DMSO) level of theory.

Cartesian coordinates and energies of optimized structures

1a

M06 SCF energy in solution: -764.47523945 a.u.

M06 enthalpy in solution: -764.237390 a.u.

M06 free energy in solution: -764.296768 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.295690	0.362484	-0.386377
C	2.129155	1.261285	-1.342589
H	2.967057	1.733176	-1.839512
H	1.140364	1.560883	-1.667267
C	3.681297	-0.027971	0.032549
F	4.644248	0.612971	-0.624015
F	3.897623	-1.338872	-0.150685

F	3.884330	0.205038	1.337292
C	1.209726	-0.346416	0.360029
C	-0.200348	0.024311	-0.039841
H	1.341913	-0.160839	1.433716
H	1.348446	-1.428635	0.240057
C	-1.234494	-0.743068	0.771888
H	-0.362017	1.100167	0.098202
H	-0.358283	-0.178219	-1.105986
H	-1.080422	-1.817619	0.624172
H	-1.074461	-0.540388	1.836696
C	-2.632334	-0.370815	0.387391
C	-3.271456	0.706676	0.991859
C	-3.300566	-1.055686	-0.621683
C	-4.545469	1.087486	0.603665
H	-2.758777	1.250144	1.780930
C	-4.575070	-0.679277	-1.013706
H	-2.811149	-1.898700	-1.101797
C	-5.202088	0.394416	-0.401266
H	-5.029649	1.927552	1.089635
H	-5.082397	-1.228672	-1.799237
H	-6.200691	0.688375	-0.704444

2a

M06 SCF energy in solution: -646.58646107 a.u.

M06 enthalpy in solution: -646.437454 a.u.

M06 free energy in solution: -646.484537 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.334424	-0.420933	0.063411
C	2.943778	0.877039	0.350826
C	1.611614	1.236629	0.269219
C	0.640351	0.309907	-0.109664
C	1.045215	-0.996047	-0.384976
C	2.379520	-1.354353	-0.302245
H	4.378229	-0.705157	0.131472
H	3.679850	1.613432	0.652765
H	1.313725	2.248400	0.521203
H	0.321199	-1.744422	-0.683900
H	2.672799	-2.373266	-0.527918
C	-0.768208	0.739909	-0.217415
C	-1.138707	1.954514	-0.602927
H	-2.177996	2.251406	-0.651226
H	-0.404429	2.694341	-0.897483
C	-1.833905	-0.265351	0.123047
F	-3.031156	0.288101	0.297701
F	-1.550329	-0.932257	1.246037
F	-1.981611	-1.186135	-0.841579

3a

M06 SCF energy in solution: -853.77605197 a.u.

M06 enthalpy in solution: -853.512567 a.u.

M06 free energy in solution: -853.576896 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	-1.913455	0.454501	-0.041893
C	-2.387694	1.606021	0.389512
C	-2.117533	-0.794455	0.758629
H	-1.162308	-1.171434	1.134397
H	-2.756418	-0.604318	1.624424
C	-2.752955	-1.904015	-0.033215
O	-2.301140	-3.008903	-0.164645
O	-3.916783	-1.527094	-0.572120
F	-3.094894	1.783197	1.483841
F	-2.223741	2.766178	-0.206878
H	-4.277833	-2.286989	-1.057341
C	-1.112426	0.364381	-1.305011
C	0.321188	-0.096247	-1.077480
H	-1.103871	1.332181	-1.811918
C	1.103684	0.834130	-0.161840
H	0.335188	-1.110862	-0.660796
H	0.828010	-0.159854	-2.046222
H	1.094479	1.844619	-0.587319
H	0.600463	0.894438	0.809737
C	2.511357	0.365104	0.031627
C	2.809069	-0.584204	1.004269
C	3.538697	0.816904	-0.789011
C	4.098615	-1.064977	1.158554
H	2.012126	-0.946079	1.649399
C	4.831058	0.339639	-0.638505
H	3.318305	1.556572	-1.553733
C	5.115220	-0.603174	0.336579
H	4.312342	-1.801611	1.925328
H	5.620669	0.707365	-1.284766
H	6.126255	-0.975669	0.457349

H	-1.605273	-0.336421	-1.990376

4a

M06 SCF energy in solution: -735.88793341 a.u.

M06 enthalpy in solution: -735.713331 a.u.

M06 free energy in solution: -735.767066 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.452091	-0.132049	0.063199
C	-2.779339	0.696269	0.947428
C	-1.416662	0.895504	0.818533
C	-0.698797	0.277237	-0.204599
C	-1.384159	-0.567222	-1.077572
C	-2.747940	-0.765348	-0.947046
H	-4.519531	-0.289632	0.166945
H	-3.317356	1.184367	1.752304
H	-0.898156	1.524330	1.533524
H	-0.849898	-1.066199	-1.879092
H	-3.262454	-1.419347	-1.642038
C	0.759276	0.454582	-0.347223
C	1.337333	1.635453	-0.196466
C	1.596964	-0.738830	-0.696185
H	1.383075	-1.091152	-1.707441
H	2.660207	-0.486583	-0.672198
C	1.408205	-1.908425	0.230229
O	1.313101	-3.052461	-0.121745
O	1.395215	-1.539737	1.514291

F	2.625964	1.860008	-0.289302
F	0.719263	2.766859	0.035423
H	1.293797	-2.343035	2.050743

5

M06 SCF energy in solution: -1303.16682338 a.u.

M06 enthalpy in solution: -1302.962953 a.u.

M06 free energy in solution: -1303.032970 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.024379	1.087208	0.030358
O	-1.869795	0.908453	-0.150676
S	-2.572062	-0.393674	-0.420795
C	-2.399810	-1.358221	1.072343
C	-4.307987	-0.021195	-0.242203
H	-3.008794	-2.259826	0.988228
H	-1.346708	-1.625573	1.162047
H	-2.719251	-0.753143	1.923303
H	-4.878455	-0.949323	-0.303121
H	-4.468988	0.471560	0.718517
H	-4.592242	0.639204	-1.061434
O	0.704578	-0.715640	-0.025305
S	2.011881	-1.207212	-0.584148
C	3.282580	-0.194286	0.156723
C	2.365356	-2.702676	0.323054
H	4.257240	-0.620797	-0.086682
H	3.197338	0.804790	-0.271873

H	3.130223	-0.167391	1.237625
H	3.355725	-3.063496	0.041370
H	2.318782	-2.489227	1.392676
H	1.613247	-3.442082	0.048000
C	1.426102	2.873811	0.190153
O	0.876946	2.481108	1.239375
O	1.250439	2.387397	-0.947825
H	2.136859	3.732711	0.274384

5a

M06 SCF energy in solution: -196.76852523 a.u.

M06 enthalpy in solution: -196.740303 a.u.

M06 free energy in solution: -196.771258 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.000118	1.618349	-0.000002
C	-0.000027	-0.569630	-0.000001
O	1.105921	0.015308	0.000001
O	-1.105936	0.015397	0.000001
H	-0.000075	-1.682900	-0.000004

5b

M06 SCF energy in solution: -749.96976149 a.u.

M06 enthalpy in solution: -749.853561 a.u.

M06 free energy in solution: -749.904658 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-1.245202	-0.684802	0.455126
O	0.505797	-0.965917	-0.059551
S	1.739500	-0.238954	-0.518921
C	1.366603	1.499442	-0.370053
C	2.882945	-0.339986	0.846164
H	2.270748	2.071706	-0.584796
H	0.598603	1.739816	-1.105495
H	1.010903	1.705439	0.641577
H	3.762563	0.261230	0.610656
H	2.393297	0.024308	1.751158
H	3.171662	-1.384758	0.960165
C	-3.217671	0.247864	0.023906
O	-3.060678	-0.948549	-0.302346
O	-2.357295	0.951019	0.596666
H	-4.198016	0.723585	-0.214161

5c

M06 SCF energy in solution: -1856.35569011 a.u.

M06 enthalpy in solution: -1856.064000 a.u.

M06 free energy in solution: -1856.145796 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-0.075558	-0.156406	0.686431
O	-1.950123	-0.664879	1.064921

S	-2.978093	-0.598451	-0.026978
C	-2.394299	-1.677875	-1.327679
C	-4.312913	-1.646239	0.533608
H	-3.174885	-1.776799	-2.084137
H	-1.508794	-1.208455	-1.757153
H	-2.147705	-2.650283	-0.896362
H	-5.051090	-1.742522	-0.264251
H	-3.909132	-2.622563	0.808433
H	-4.769910	-1.167771	1.399868
O	1.012642	-1.614315	-0.058313
S	2.151453	-1.267686	-0.970032
C	3.357881	-0.421829	0.045288
C	3.070767	-2.787573	-1.164286
H	4.256133	-0.238717	-0.547181
H	2.914241	0.523714	0.359760
H	3.585952	-1.039441	0.916779
H	3.987456	-2.582152	-1.719307
H	3.297483	-3.194637	-0.176965
H	2.448139	-3.482471	-1.727997
O	-0.394405	0.830835	-1.089513
S	-0.292313	2.300592	-1.377624
C	-1.065536	3.125997	0.007683
C	1.392981	2.759995	-0.992424
H	-0.910283	4.202232	-0.087096
H	-2.132904	2.905532	-0.033249
H	-0.621353	2.742074	0.929502
H	1.503434	3.838335	-1.121338
H	1.605206	2.455729	0.036057
H	2.041407	2.239696	-1.699183
C	1.394478	0.706089	2.833781

O	1.187193	-0.361938	3.406398
O	0.885967	1.129273	1.760345
H	2.126168	1.413232	3.312129

5d

M06 SCF energy in solution: -7.43123706 a.u.

M06 enthalpy in solution: -7.428877 a.u.

M06 free energy in solution: -7.443985 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.000000	0.000000	0.000000

5e

M06 SCF energy in solution: -560.63870844 a.u.

M06 enthalpy in solution: -560.549681 a.u.

M06 free energy in solution: -560.588990 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-2.833457	-0.164815	0.704895
O	-1.253536	-0.405680	-0.071923
S	0.128958	-0.032419	-0.538405
C	0.504519	1.509099	0.273258
C	1.229230	-1.068481	0.404321
H	1.544773	1.767322	0.069003

H	-0.151975	2.272415	-0.144516
H	0.336496	1.398813	1.346237
H	2.256254	-0.770761	0.186988
H	1.007448	-0.954636	1.466908
H	1.069831	-2.098283	0.085089

5f

M06 SCF energy in solution: -1113.84243461 a.u.

M06 enthalpy in solution: -1113.665186 a.u.

M06 free energy in solution: -1113.722949 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.028722	-1.135515	0.494605
O	-1.305719	-0.072573	-0.112222
S	-2.737179	0.235072	-0.455975
C	-3.664029	-1.226174	-0.024573
C	-3.324095	1.275039	0.867640
H	-4.727470	-1.014566	-0.147692
H	-3.367275	-2.022220	-0.707454
H	-3.441802	-1.500197	1.008534
H	-4.393376	1.444253	0.730609
H	-3.126858	0.783785	1.822242
H	-2.791014	2.223627	0.805526
O	1.843059	-1.107330	0.336058
S	2.994552	-0.378525	-0.304009
C	2.289990	1.084630	-1.041979
C	3.840319	0.430228	1.040649

H	3.098029	1.701603	-1.438885
H	1.639305	0.765738	-1.856788
H	1.723487	1.632274	-0.285994
H	4.618308	1.073986	0.627114
H	3.118754	1.012718	1.616343
H	4.293956	-0.342316	1.661264

5g

M06 SCF energy in solution: -1667.04366356 a.u.

M06 enthalpy in solution: -1666.778612 a.u.

M06 free energy in solution: -1666.852319 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-0.159151	-0.511114	-0.270773
O	-1.769943	-0.902559	0.597578
S	-3.260382	-0.735652	0.508556
C	-3.550411	0.404931	-0.834164
C	-3.854758	-2.201012	-0.318577
H	-4.622227	0.445093	-1.035937
H	-3.203304	1.390182	-0.522433
H	-3.005254	0.064579	-1.717248
H	-4.924806	-2.092385	-0.502793
H	-3.309740	-2.328194	-1.255900
H	-3.679955	-3.048324	0.344350
O	1.243418	-1.749680	-0.237282
S	2.719998	-1.796975	-0.516093
C	3.305418	-0.120263	-0.340296

C	3.456051	-2.447223	0.972868
H	4.394820	-0.117560	-0.403081
H	2.885914	0.465238	-1.158662
H	2.971638	0.270448	0.623981
H	4.542115	-2.407127	0.875168
H	3.119643	-1.854782	1.825887
H	3.134525	-3.483485	1.076204
O	0.176122	1.250329	-0.845108
S	0.087375	2.612830	-0.213541
C	-0.063409	2.320324	1.541741
C	1.755350	3.248112	-0.188180
H	0.043756	3.267787	2.072418
H	-1.053594	1.905260	1.731285
H	0.714418	1.616378	1.849908
H	1.741563	4.229123	0.289849
H	2.406228	2.562966	0.357520
H	2.083637	3.350967	-1.222809

5h

M06 SCF energy in solution: -2220.24330968 a.u.

M06 enthalpy in solution: -2219.890173 a.u.

M06 free energy in solution: -2219.975581 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-0.218839	-0.138676	-0.617816
O	1.323032	-0.993214	-1.390469
S	2.670438	-0.572555	-1.903503

C	3.176549	0.811459	-0.893875
C	3.816867	-1.767018	-1.235052
H	4.196885	1.090634	-1.162268
H	2.491968	1.633571	-1.106549
H	3.117161	0.527071	0.159618
H	4.833494	-1.464115	-1.491369
H	3.690704	-1.820400	-0.151391
H	3.594615	-2.730740	-1.693740
O	-0.035978	1.808543	-0.698898
S	-0.309363	2.688238	0.489036
C	1.132601	2.580023	1.540253
C	-0.020940	4.350026	-0.094600
H	1.000189	3.260004	2.383545
H	1.191679	1.552392	1.901008
H	2.024763	2.845885	0.970234
H	-0.057244	5.036035	0.753202
H	0.955529	4.386957	-0.582415
H	-0.810593	4.598048	-0.803629
O	-0.437543	-0.450561	1.317436
S	0.003881	-1.591744	2.192452
C	0.233289	-2.992152	1.106630
C	1.734192	-1.298628	2.527336
H	0.678902	-3.807778	1.678692
H	-0.747864	-3.298448	0.743101
H	0.879191	-2.696384	0.275512
H	2.147246	-2.162719	3.050325
H	2.252231	-1.136100	1.579010
H	1.809081	-0.416484	3.163544
O	-1.890115	-0.832119	-1.336505
S	-3.119010	-1.020419	-0.494328

C	-3.486484	0.576935	0.218873
C	-4.474294	-1.052063	-1.656517
H	-4.461386	0.531099	0.707324
H	-2.713698	0.789793	0.957877
H	-3.486383	1.328877	-0.573380
H	-5.415781	-1.080359	-1.105944
H	-4.421368	-0.164556	-2.289897
H	-4.373805	-1.955245	-2.258271

6

M06 SCF energy in solution: -857.55070048 a.u.

M06 enthalpy in solution: -857.407018 a.u.

M06 free energy in solution: -857.456201 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.302731	-1.652420	-0.123981
C	0.925272	-1.672935	0.063428
C	0.218434	-0.492325	0.117504
C	0.885360	0.751732	0.003687
C	2.283684	0.740919	-0.183815
C	2.978163	-0.443655	-0.249471
H	2.849904	-2.586490	-0.172342
H	0.403157	-2.618491	0.161853
H	2.798253	1.691144	-0.269174
H	4.051725	-0.435016	-0.394615
C	-1.256455	-0.529663	0.341330
O	-1.760843	-0.690022	1.419600

O	-1.923793	-0.397238	-0.797025
C	-3.346586	-0.354783	-0.682491
H	-3.652696	0.498012	-0.073584
H	-3.730335	-0.244340	-1.693975
H	-3.729523	-1.274142	-0.237755
S	0.033936	2.224137	0.123865

7

M06 SCF energy in solution: -858.18634684 a.u.

M06 enthalpy in solution: -858.032792 a.u.

M06 free energy in solution: -858.080819 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.497983	-2.283748	0.000079
C	-0.235278	-1.737348	0.000137
C	-0.022289	-0.353611	0.000107
C	-1.146144	0.493282	0.000073
C	-2.420665	-0.075712	-0.000100
C	-2.599585	-1.440697	-0.000091
H	-1.625115	-3.359340	0.000144
H	0.625070	-2.392536	0.000183
H	-3.285683	0.579921	-0.000238
H	-3.604133	-1.848190	-0.000202
C	1.372323	0.148050	-0.000015
O	1.711319	1.310886	0.000151
O	2.265830	-0.838417	-0.000193
C	3.634904	-0.446302	-0.000053

H	3.872859	0.139392	0.889138
H	4.212551	-1.367986	0.000400
H	3.873205	0.138663	-0.889611
S	-1.160892	2.255771	-0.000018
H	0.176617	2.414504	-0.000012

8

M06 SCF energy in solution: -1302.51234788 a.u.

M06 enthalpy in solution: -1302.320555 a.u.

M06 free energy in solution: -1302.390666 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-0.013036	1.087467	0.024534
O	-1.892791	0.889013	-0.081951
S	-2.596566	-0.393953	-0.437228
C	-2.285654	-1.511174	0.920466
C	-4.317064	-0.085366	-0.084009
H	-2.881977	-2.414373	0.781166
H	-1.223347	-1.757299	0.898321
H	-2.547727	-1.013894	1.856609
H	-4.873888	-1.015951	-0.205240
H	-4.409099	0.292785	0.935833
H	-4.676635	0.653888	-0.799711
O	0.776832	-0.625527	-0.094414
S	2.131646	-1.066969	-0.581537
C	3.325083	-0.108628	0.338430
C	2.420850	-2.625086	0.236711

H	4.320269	-0.513904	0.147197
H	3.274753	0.921622	-0.016121
H	3.082028	-0.162770	1.401527
H	3.434457	-2.960688	0.012521
H	2.283162	-2.493291	1.311626
H	1.700810	-3.342978	-0.156129
C	1.322773	2.911397	0.160600
O	0.881393	2.528738	1.244989
O	1.134453	2.511818	-0.990393

9

M06 SCF energy in solution: -1949.16179330 a.u.

M06 enthalpy in solution: -1948.817409 a.u.

M06 free energy in solution: -1948.907485 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.483464	2.221371	-1.024630
C	-3.600857	1.771237	-1.997639
C	-2.871279	0.619112	-1.804197
C	-2.994360	-0.142810	-0.619039
C	-3.903041	0.337433	0.353868
C	-4.625066	1.492392	0.149262
H	-5.054772	3.129296	-1.178878
H	-3.477778	2.330093	-2.918582
H	-2.176271	0.305693	-2.572946
H	-4.043233	-0.195839	1.284734
H	-5.310528	1.831580	0.917790

C	-2.192823	-1.304640	-0.432475
C	-1.190835	-1.741944	-1.439802
H	-0.939348	-2.793882	-1.302245
H	-1.575572	-1.620382	-2.452182
C	-2.257445	-2.043719	0.865417
F	-1.483931	-3.125386	0.891133
F	-3.501603	-2.475343	1.148182
F	-1.885020	-1.288005	1.915444
C	0.110408	-0.933601	-1.285021
O	0.713971	-1.042450	-0.191036
O	0.481976	-0.202759	-2.225307
Li	1.955229	0.386261	-0.933988
O	3.786080	0.023204	-1.385803
O	1.834883	1.991075	0.148895
S	5.057985	0.100018	-0.592014
S	0.965137	2.311987	1.333173
C	4.567651	0.173042	1.124862
C	5.700233	-1.566010	-0.561358
C	-0.709038	1.929305	0.834569
C	1.156174	0.945947	2.472456
H	5.459205	0.117799	1.751783
H	4.064548	1.127886	1.278695
H	3.893688	-0.659818	1.339327
H	6.570339	-1.597946	0.096501
H	4.919300	-2.241816	-0.207137
H	5.997775	-1.826045	-1.577195
H	-1.374297	2.071566	1.688471
H	-0.981566	2.617021	0.032945
H	-0.734079	0.895106	0.489514
H	0.424034	1.054881	3.274809

H	1.002297	0.012960	1.924630
H	2.162787	0.994333	2.888921

10

M06 SCF energy in solution: -1949.27866025 a.u.

M06 enthalpy in solution: -1948.936201 a.u.

M06 free energy in solution: -1949.028267 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.200150	2.843773	0.495607
C	-3.200911	2.645441	-0.450242
C	-2.744576	1.381883	-0.768398
C	-3.265196	0.200141	-0.162751
C	-4.284996	0.442490	0.806903
C	-4.726871	1.711194	1.113547
H	-4.552655	3.837527	0.745581
H	-2.754460	3.500494	-0.952097
H	-1.954828	1.294006	-1.506896
H	-4.741069	-0.394153	1.323935
H	-5.507878	1.822176	1.861162
C	-2.783394	-1.077697	-0.522978
C	-1.658988	-1.205682	-1.503761
H	-1.559779	-2.242366	-1.841839
H	-1.856577	-0.632932	-2.418599
C	-3.178348	-2.237115	0.242281
F	-2.589926	-3.380695	-0.155132
F	-4.529871	-2.528677	0.227050

F	-2.932272	-2.193002	1.603310
C	-0.257141	-0.814458	-1.035642
O	0.072211	-1.015025	0.157859
O	0.541513	-0.349290	-1.894384
Li	1.886858	-0.405565	-0.392678
O	3.422208	-1.562432	-0.282370
O	2.651352	1.330472	0.093352
S	4.821085	-1.074161	-0.030399
S	2.301449	2.701233	-0.416816
C	4.864138	-0.576779	1.684758
C	5.797909	-2.557375	0.149445
C	0.523206	2.724416	-0.573703
C	2.417090	3.774787	1.004628
H	5.893105	-0.343569	1.963425
H	4.241334	0.313213	1.775816
H	4.471244	-1.389219	2.299416
H	6.809255	-2.282002	0.452576
H	5.331278	-3.203785	0.895177
H	5.828125	-3.054705	-0.820003
H	0.205922	3.727558	-0.863922
H	0.267242	2.001724	-1.350753
H	0.077953	2.435105	0.380754
H	2.058579	4.767506	0.727651
H	1.816053	3.357155	1.814646
H	3.465761	3.831267	1.296578

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M06 SCF energy in solution: -1949.28342460 a.u.

M06 enthalpy in solution: -1948.940918 a.u.

M06 free energy in solution: -1949.028896 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.032444	1.200369	-1.954276
C	-4.127707	1.239604	-0.568723
C	-3.399491	0.379920	0.229696
C	-2.524695	-0.606000	-0.304943
C	-2.444375	-0.612254	-1.725924
C	-3.172531	0.258250	-2.510543
H	-4.601898	1.879394	-2.578055
H	-4.780433	1.966785	-0.093379
H	-3.495191	0.473394	1.305595
H	-1.790731	-1.317806	-2.224688
H	-3.062892	0.200857	-3.589995
C	-1.801473	-1.479511	0.556114
C	-1.788444	-1.217560	2.035405
H	-2.805561	-1.149202	2.438831
H	-1.324559	-2.056789	2.562655
C	-0.827086	-2.372869	0.015604
F	0.322105	-1.748834	-0.619628
F	-1.229561	-3.185048	-0.998679
F	-0.235704	-3.178618	0.908836
C	-1.022482	0.033290	2.499736
O	0.101205	0.232054	1.949343
O	-1.518463	0.733889	3.390005
Li	1.078173	-0.170838	0.434586
O	1.142143	1.278553	-0.877372
O	2.917191	-0.757320	0.757991

S	0.875689	2.732394	-0.596096
S	4.112691	-0.835504	-0.143610
C	-0.832974	2.832298	-0.083236
C	1.596514	3.058554	1.007752
C	3.498012	-1.256859	-1.769474
C	4.564020	0.852608	-0.525093
H	-1.059740	3.867474	0.178476
H	-1.447403	2.523958	-0.930908
H	-0.980234	2.167785	0.771021
H	1.322720	4.068685	1.318068
H	1.215945	2.311655	1.712245
H	2.680374	2.988960	0.907411
H	4.326805	-1.208031	-2.478122
H	3.114734	-2.276361	-1.728046
H	2.709389	-0.555346	-2.049972
H	5.385651	0.843243	-1.243503
H	3.692634	1.367159	-0.934546
H	4.894571	1.322513	0.401362

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M06 SCF energy in solution: -735.40907417 a.u.

M06 enthalpy in solution: -735.247726 a.u.

M06 free energy in solution: -735.301009 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.457553	-0.288678	0.042560
C	-2.850981	0.669587	0.839024

C	-1.495390	0.920286	0.723745
C	-0.710442	0.223674	-0.196300
C	-1.331863	-0.751880	-0.976934
C	-2.688954	-1.000621	-0.863096
H	-4.519576	-0.485799	0.134776
H	-3.436189	1.221806	1.566161
H	-1.036058	1.654050	1.375529
H	-0.746972	-1.323586	-1.688715
H	-3.147426	-1.759764	-1.487273
C	0.740587	0.453295	-0.331564
C	1.260908	1.663032	-0.203608
C	1.623980	-0.714845	-0.638798
H	1.385127	-1.118743	-1.626886
H	2.668331	-0.396144	-0.684476
C	1.548512	-1.862003	0.402129
O	1.686082	-3.011054	-0.058597
O	1.401875	-1.520565	1.590733
F	2.543444	1.948903	-0.300547
F	0.600587	2.783323	0.008420

13

M06 SCF energy in solution: -1213.87209191 a.u.

M06 enthalpy in solution: -1213.691947 a.u.

M06 free energy in solution: -1213.753572 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.035769	1.541280	-0.463444

F	0.641472	3.004333	0.206373
O	-1.795220	0.996408	-0.464003
S	-2.534195	-0.310348	-0.472918
C	-1.417166	-1.519463	0.221232
C	-3.653625	-0.227808	0.915116
H	-1.956120	-2.457636	0.364023
H	-0.601259	-1.658364	-0.487899
H	-1.036659	-1.142014	1.173607
H	-4.148694	-1.193676	1.028105
H	-3.089020	0.027789	1.813843
H	-4.394465	0.541612	0.698496
O	1.201362	0.097082	-0.972215
S	2.534006	-0.300070	-0.401304
C	2.619600	0.457238	1.214165
C	2.333241	-1.984142	0.159752
H	3.512686	0.098009	1.728208
H	2.676478	1.536446	1.071592
H	1.718847	0.196931	1.776201
H	3.257261	-2.302365	0.645480
H	1.493075	-2.040927	0.854497
H	2.148894	-2.604823	-0.717477

13a

M06 SCF energy in solution: -107.474338 a.u.

M06 enthalpy in solution: -107.469281 a.u.

M06 free energy in solution: -107.492180 a.u.

Cartesian coordinates

ATOM	X	Y	Z

Li	0.000000	0.000000	-1.237498
F	0.000000	0.000000	0.412499

13b

M06 SCF energy in solution: -660.67546115 a.u.

M06 enthalpy in solution: -660.583052 a.u.

M06 free energy in solution: -660.628276 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	-2.002564	-0.853586	-0.042162
F	-3.309857	0.118517	0.358348
O	-0.200414	-0.987479	-0.462256
S	1.002167	-0.086024	-0.530674
C	0.418770	1.535426	-0.066896
C	1.931316	-0.421373	0.954704
H	1.273110	2.210176	0.008662
H	-0.254387	1.884003	-0.850662
H	-0.104464	1.468232	0.889487
H	2.764126	0.281455	1.013935
H	1.272349	-0.318397	1.818901
H	2.313798	-1.439467	0.883008

13c

M06 SCF energy in solution: -1767.06689717 a.u.

M06 enthalpy in solution: -1766.799010 a.u.

M06 free energy in solution: -1766.875541 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Li	0.046843	0.091642	1.033375
F	0.373765	1.295231	2.299895
O	-1.683532	-0.911559	1.102034
S	-2.455111	-1.174128	-0.155641
C	-1.359923	-2.064228	-1.255054
C	-3.523099	-2.553509	0.233746
H	-1.935789	-2.415844	-2.113153
H	-0.591865	-1.365121	-1.584740
H	-0.918229	-2.904086	-0.715546
H	-4.049450	-2.865797	-0.669624
H	-2.919467	-3.370729	0.633343
H	-4.242598	-2.214180	0.979030
O	1.446684	-1.263294	0.679310
S	2.467747	-1.212225	-0.416141
C	3.154327	0.438321	-0.384955
C	3.904461	-2.050081	0.238059
H	4.030480	0.474898	-1.034598
H	2.384770	1.113365	-0.758524
H	3.422392	0.689988	0.643831
H	4.723952	-1.966520	-0.477597
H	4.175641	-1.597934	1.194160
H	3.641764	-3.099152	0.374581
O	-0.156606	0.963414	-0.794635
S	-0.621486	2.388588	-0.927936
C	-1.891944	2.611074	0.310920
C	0.628930	3.381719	-0.122125
H	-2.189269	3.661079	0.322504

H	-2.744785	1.993632	0.026435
H	-1.487331	2.302429	1.278587
H	0.266582	4.407546	-0.035523
H	0.817369	2.936832	0.860359
H	1.524146	3.363559	-0.744432

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M06 SCF energy in solution: -2067.03521445 a.u.

M06 enthalpy in solution: -2066.602097 a.u.

M06 free energy in solution: -2066.705890 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.306690	1.282366	0.142536
C	0.521790	0.955777	-1.065354
H	0.620288	1.719690	-1.843251
H	0.876191	0.017709	-1.508166
C	1.713660	2.684571	0.350818
F	2.802332	3.020981	-0.386100
F	2.033043	2.959494	1.619559
F	0.763363	3.560596	-0.007972
C	-0.978113	0.773900	-0.791239
O	-1.419436	1.033736	0.350382
O	-1.679771	0.355442	-1.740309
Li	-3.149493	0.262330	-0.359178
O	-4.836088	1.149816	-0.328837
O	-3.542646	-1.592582	0.045371
S	-6.167386	0.450479	-0.345467

S	-2.801313	-2.812008	-0.428972
C	-6.374099	-0.241806	1.287436
C	-7.372343	1.756556	-0.184706
C	-1.098643	-2.592523	0.072189
C	-3.209751	-4.084817	0.753548
H	-7.380807	-0.653662	1.375825
H	-5.634561	-1.035406	1.394107
H	-6.209354	0.541940	2.029526
H	-8.362333	1.313169	-0.066368
H	-7.116530	2.371941	0.679943
H	-7.342950	2.350932	-1.097798
H	-0.569218	-3.537295	-0.062832
H	-0.658660	-1.831094	-0.572337
H	-1.078219	-2.281846	1.118819
H	-2.634275	-4.982490	0.522505
H	-2.982402	-3.724939	1.758777
H	-4.274675	-4.296085	0.655915
C	1.719971	0.239396	1.114772
C	3.220780	-0.048908	1.097918
H	1.173459	-0.680304	0.877459
C	3.713628	-0.519990	-0.263339
H	3.776085	0.850998	1.389153
H	3.449291	-0.810592	1.851555
H	3.166337	-1.425401	-0.550423
H	3.480796	0.245145	-1.013862
C	5.185611	-0.788405	-0.258996
C	6.092420	0.250346	-0.446097
C	5.681380	-2.063878	-0.013268
C	7.457169	0.020981	-0.395926
H	5.715466	1.252152	-0.636968

C	7.046191	-2.299014	0.037566
H	4.982982	-2.882750	0.135583
C	7.938816	-1.256644	-0.154362
H	8.149048	0.842053	-0.549006
H	7.414433	-3.301779	0.225176
H	9.006934	-1.439258	-0.118399
H	1.424296	0.526276	2.130417

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M06 SCF energy in solution: -2067.19771215 a.u.

M06 enthalpy in solution: -2066.764774 a.u.

M06 free energy in solution: -2066.864547 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.783892	0.645450	0.542411
C	0.679339	-0.229773	1.747122
H	1.667324	-0.620921	2.011402
H	0.310914	0.336541	2.605991
C	0.418219	1.909977	0.582032
F	-2.076314	0.588437	-1.594958
F	0.485951	2.764921	-0.423404
F	-0.065064	2.540153	1.637768
C	-0.283138	-1.410562	1.518016
O	-1.441333	-1.096203	1.139878
O	0.138174	-2.552997	1.735146
Li	-2.642396	-0.138930	-0.020448
O	-4.053681	-1.611719	-0.498377
O	-3.694079	1.279925	1.007397

S	-3.707717	-3.039996	-0.783148
S	-4.283431	2.480793	0.331072
C	-2.057668	-3.040276	-1.482952
C	-3.257290	-3.777136	0.785324
C	-2.903173	3.376865	-0.374711
C	-4.954257	1.897439	-1.222779
H	-1.735229	-4.073771	-1.623104
H	-2.107976	-2.538808	-2.449783
H	-1.390025	-2.509139	-0.799917
H	-2.893835	-4.791078	0.606527
H	-2.488374	-3.147841	1.244730
H	-4.157989	-3.815642	1.398905
H	-3.284940	4.184044	-1.002618
H	-2.325696	3.798292	0.448276
H	-2.316849	2.656978	-0.954426
H	-5.283286	2.754648	-1.812890
H	-4.164591	1.335969	-1.731501
H	-5.808018	1.258654	-0.996043
C	1.304140	0.032021	-0.722349
C	2.763132	-0.394447	-0.634770
H	1.180547	0.723795	-1.559865
C	3.700872	0.766239	-0.333982
H	2.887659	-1.169689	0.131196
H	3.054691	-0.855222	-1.585063
H	3.558640	1.544785	-1.093154
H	3.428360	1.209576	0.630333
C	5.132413	0.332778	-0.300958
C	5.685479	-0.186605	0.865290
C	5.923830	0.383089	-1.443327
C	6.994970	-0.636674	0.893146

H	5.074460	-0.232778	1.763336
C	7.234754	-0.065456	-1.420984
H	5.502397	0.784733	-2.360765
C	7.774983	-0.576660	-0.251583
H	7.410310	-1.033894	1.812954
H	7.838279	-0.013646	-2.320682
H	8.801480	-0.925110	-0.231362
H	0.690508	-0.847700	-0.954603

16

M06 SCF energy in solution: -853.29660238 a.u.

M06 enthalpy in solution: -853.046447 a.u.

M06 free energy in solution: -853.109780 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.953943	0.420403	-0.030867
C	-2.452272	1.558316	0.405833
C	-2.149262	-0.856876	0.716770
H	-1.182420	-1.223894	1.079466
H	-2.778838	-0.693939	1.595730
C	-2.820640	-1.965854	-0.136641
O	-2.284029	-3.089467	-0.097502
O	-3.847798	-1.625303	-0.754208
F	-3.176366	1.717490	1.500440
F	-2.315400	2.738644	-0.177122
C	-1.149271	0.374739	-1.294682
C	0.287765	-0.078266	-1.077102
H	-1.145795	1.353148	-1.782660
C	1.065244	0.842938	-0.147623

H	0.305655	-1.098485	-0.675315
H	0.797339	-0.123177	-2.046023
H	1.049304	1.860004	-0.557354
H	0.560740	0.884544	0.824242
C	2.476253	0.382235	0.039149
C	2.780616	-0.582549	0.994564
C	3.501387	0.857269	-0.771197
C	4.073964	-1.055026	1.142444
H	1.985387	-0.963150	1.630999
C	4.797539	0.388194	-0.627319
H	3.276048	1.609038	-1.522617
C	5.088171	-0.569732	0.331003
H	4.292566	-1.803990	1.895807
H	5.584970	0.774234	-1.265571
H	6.102142	-0.935821	0.446801
H	-1.639893	-0.320297	-1.985677

17

M06 SCF energy in solution: -188.63601843 a.u.

M06 enthalpy in solution: -188.623380 a.u.

M06 free energy in solution: -188.651221 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.335600	0.000000
O	1.137863	-0.125825	0.000000
O	-1.137863	-0.125875	0.000000

18

M06 SCF energy in solution: -188.58638790 a.u.

M06 enthalpy in solution: -188.570861 a.u.

M06 free energy in solution: -188.595736 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	-0.000001
O	0.000000	0.000000	-1.154060
O	0.000000	0.000000	1.154061

19

M06 SCF energy in solution: -1396.08372123 a.u.

M06 enthalpy in solution: -1395.829167 a.u.

M06 free energy in solution: -1395.905075 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.932005	3.684432	-0.269309
C	-0.240122	2.774810	-1.060324
C	-0.592631	1.440490	-1.108405
C	-1.687356	0.907983	-0.365669
C	-2.368737	1.868350	0.441453
C	-2.000374	3.195593	0.479836
H	-0.649341	4.729894	-0.231738
H	0.607554	3.109790	-1.653153
H	-0.004538	0.777036	-1.733922
H	-3.213227	1.556598	1.045473
H	-2.565017	3.872902	1.115071
C	-2.033546	-0.459125	-0.452886
C	-1.208672	-1.387747	-1.290173
H	-1.719881	-2.347741	-1.413678

H	-1.076739	-1.001941	-2.308837
C	-3.015714	-1.012983	0.449435
F	-3.203003	-2.338219	0.308174
F	-4.286499	-0.478780	0.347807
F	-2.768292	-0.853519	1.801606
C	0.180241	-1.747320	-0.773851
O	0.348583	-1.958027	0.454356
O	1.118385	-1.869604	-1.609043
Li	2.207767	-2.267110	-0.032106
O	3.814444	-1.412193	0.380962
S	4.298515	-0.025414	0.050434
C	2.833049	0.918335	-0.338867
C	4.645674	0.737328	1.624881
H	3.117005	1.958550	-0.507124
H	2.405531	0.494482	-1.248934
H	2.126414	0.839662	0.490493
H	4.891579	1.787629	1.459913
H	3.769390	0.639841	2.268464
H	5.501739	0.223622	2.062151

ArS-anion

M06 SCF energy in solution: -857.71414353 a.u.

M06 enthalpy in solution: -857.570881 a.u.

M06 free energy in solution: -857.618634 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.322223	-1.666461	-0.114418
C	-0.950144	-1.666645	0.075162
C	-0.238899	-0.476575	0.120982

C	-0.871544	0.777459	0.002833
C	-2.264650	0.740511	-0.192632
C	-2.970657	-0.445270	-0.251733
H	-2.873941	-2.598258	-0.154943
H	-0.414548	-2.605805	0.186029
H	-2.790482	1.685506	-0.291759
H	-4.045362	-0.417457	-0.403215
C	1.230582	-0.543005	0.341877
O	1.758352	-0.721013	1.409926
O	1.909397	-0.448012	-0.804130
C	3.324158	-0.390823	-0.680881
H	3.720086	-1.291616	-0.208497
H	3.718980	-0.302726	-1.691287
H	3.621229	0.481126	-0.092980
S	0.006394	2.276643	0.125196

DMSO

M06 SCF energy in solution: -553.17565016 a.u.

M06 enthalpy in solution: -553.090198 a.u.

M06 free energy in solution: -553.124738 a.u.

Cartesian coordinates

ATOM	X	Y	Z
O	0.000008	1.470514	0.384241
S	0.000000	0.232101	-0.440517
C	1.332055	-0.795255	0.181387
H	1.304418	-1.768219	-0.312093
H	2.271495	-0.293193	-0.051312
H	1.221341	-0.905984	1.262251
C	-1.332062	-0.795242	0.181388

H	-1.304441	-1.768200	-0.312107
H	-1.221338	-0.905989	1.262249
H	-2.271500	-0.293169	-0.051294

PC

M06 SCF energy in solution: -2485.51436437 a.u.

M06 enthalpy in solution: -2484.657103 a.u.

M06 free energy in solution: -2484.794147 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.154054	1.208778	-0.380219
C	0.746932	0.177736	-0.040246
C	0.245301	-1.108049	0.200246
C	-1.122969	-1.384817	0.063529
C	-2.000439	-0.400924	-0.397571
C	-1.497436	0.874874	-0.654978
N	-3.354389	-0.676948	-0.604437
N	1.096178	-2.138707	0.660522
N	2.123394	0.453814	0.165822
N	0.208273	2.550890	-0.379476
C	-1.615720	-2.679069	0.389100
N	-2.013174	-3.727981	0.647702
C	-2.348039	1.826945	-1.282862
N	-3.023667	2.573122	-1.841646
C	-3.730962	-1.724409	-1.474535
C	-4.807007	-2.549354	-1.169553
C	-3.002359	-1.952610	-2.636480
C	-5.144168	-3.584717	-2.017808
H	-5.361018	-2.387099	-0.252571

C	-3.336248	-3.004679	-3.469475
H	-2.176094	-1.295289	-2.888698
C	-4.409627	-3.823325	-3.167707
H	-5.979879	-4.226884	-1.765526
H	-2.759809	-3.173587	-4.371654
H	-4.672834	-4.643588	-3.824207
C	-4.312190	0.068215	0.127100
C	-5.466116	0.536305	-0.488964
C	-4.084857	0.352655	1.468005
C	-6.379546	1.276911	0.233539
H	-5.624652	0.334441	-1.541971
C	-4.998149	1.109995	2.179643
H	-3.196088	-0.037279	1.955439
C	-6.148834	1.572434	1.567778
H	-7.272521	1.646069	-0.256909
H	-4.814116	1.324540	3.226036
H	-6.865188	2.161567	2.127337
C	1.857772	-2.845624	-0.304747
C	3.185968	-3.171091	-0.049121
C	1.297279	-3.201122	-1.525602
C	3.944099	-3.808086	-1.010540
H	3.615276	-2.920682	0.913899
C	2.065440	-3.832714	-2.488417
H	0.254463	-2.979867	-1.728714
C	3.391845	-4.131819	-2.239845
H	4.981025	-4.044058	-0.801945
H	1.615989	-4.098829	-3.438154
H	3.992755	-4.622877	-2.995559
C	0.947199	-2.609458	1.981898
C	1.214846	-3.936105	2.307030

C	0.512009	-1.747054	2.985664
C	1.076275	-4.374350	3.609714
H	1.515544	-4.629818	1.531636
C	0.366706	-2.200396	4.282546
H	0.303990	-0.707296	2.756121
C	0.654974	-3.513603	4.608297
H	1.287070	-5.412187	3.841152
H	0.037717	-1.507324	5.048624
H	0.546619	-3.864360	5.627220
C	3.032739	0.351014	-0.902453
C	4.315321	0.888678	-0.797713
C	2.666675	-0.247151	-2.106568
C	5.203502	0.795396	-1.851078
H	4.614571	1.393891	0.112280
C	3.564447	-0.338183	-3.153116
H	1.669533	-0.650331	-2.230912
C	4.843291	0.174773	-3.035300
H	6.192924	1.225325	-1.742552
H	3.252770	-0.824325	-4.070891
H	5.547308	0.098243	-3.854655
C	2.560239	0.584042	1.511072
C	3.602887	-0.190128	2.009953
C	1.909298	1.463575	2.368177
C	3.965843	-0.100343	3.339342
H	4.125443	-0.867432	1.345597
C	2.268801	1.540287	3.702825
H	1.115888	2.093978	1.984869
C	3.295417	0.756999	4.196532
H	4.772935	-0.719715	3.713111
H	1.745414	2.228970	4.355998

H	3.577644	0.817315	5.240541
C	-0.646405	3.501235	0.243216
C	-0.828743	4.756223	-0.324530
C	-1.318894	3.182065	1.419153
C	-1.672102	5.671085	0.273726
H	-0.323851	5.001317	-1.251274
C	-2.174540	4.098879	2.000429
H	-1.188998	2.203845	1.872452
C	-2.353627	5.348295	1.434577
H	-1.812747	6.642165	-0.186089
H	-2.697940	3.833711	2.911396
H	-3.022564	6.065419	1.894155
C	1.360226	3.024514	-1.065838
C	2.272497	3.845611	-0.414819
C	1.542725	2.713323	-2.403735
C	3.362326	4.341393	-1.102107
H	2.117736	4.093068	0.629603
C	2.647293	3.199660	-3.082333
H	0.809345	2.094537	-2.910916
C	3.556138	4.016125	-2.436280
H	4.072687	4.979564	-0.589745
H	2.790080	2.943211	-4.125328
H	4.417593	4.399276	-2.969907

PC-radical-anion

M06 SCF energy in solution: -2485.60168836 a.u.

M06 enthalpy in solution: -2484.747990 a.u.

M06 free energy in solution: -2484.887255 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.181289	1.171879	-0.447554
C	0.696625	0.184207	0.025275
C	0.220903	-1.046945	0.454522
C	-1.204480	-1.295069	0.463840
C	-2.049812	-0.388540	-0.178430
C	-1.564432	0.812260	-0.672695
N	-3.416589	-0.719193	-0.360947
N	1.100398	-2.084991	0.870846
N	2.102599	0.441276	0.036506
N	0.186580	2.535754	-0.542204
C	-1.734919	-2.467758	1.033097
N	-2.170053	-3.442063	1.483657
C	-2.403809	1.651440	-1.435201
N	-3.077874	2.344934	-2.070621
C	-3.737283	-1.766012	-1.236336
C	-4.854592	-2.571584	-1.025991
C	-2.907370	-2.044311	-2.321614
C	-5.139917	-3.609831	-1.890090
H	-5.485648	-2.390137	-0.164430
C	-3.192705	-3.098223	-3.168945
H	-2.036181	-1.421505	-2.498025
C	-4.313729	-3.884565	-2.967294
H	-6.011361	-4.227966	-1.703892
H	-2.532471	-3.296946	-4.006299
H	-4.537300	-4.706608	-3.636830
C	-4.382997	0.030919	0.331433
C	-5.594127	0.374631	-0.262788
C	-4.115249	0.477124	1.622680
C	-6.522439	1.123926	0.432347

H	-5.789235	0.068971	-1.283809
C	-5.043459	1.242473	2.302795
H	-3.174428	0.206941	2.091402
C	-6.256008	1.564073	1.718407
H	-7.457889	1.387970	-0.048503
H	-4.818275	1.581308	3.307936
H	-6.983803	2.160158	2.256161
C	1.632885	-2.921679	-0.139411
C	2.993188	-3.218539	-0.182599
C	0.812388	-3.404704	-1.155257
C	3.519176	-3.960612	-1.222544
H	3.639542	-2.847019	0.603860
C	1.347012	-4.137513	-2.198972
H	-0.251405	-3.195692	-1.130051
C	2.701897	-4.418643	-2.242418
H	4.583914	-4.164217	-1.245979
H	0.689798	-4.498466	-2.982635
H	3.118599	-4.989964	-3.063605
C	1.282401	-2.337967	2.232367
C	1.864724	-3.520840	2.694470
C	0.868793	-1.400012	3.182415
C	2.069634	-3.724999	4.045458
H	2.150723	-4.290738	1.989716
C	1.078680	-1.618269	4.528608
H	0.390644	-0.484460	2.855173
C	1.691679	-2.775424	4.978312
H	2.528132	-4.652806	4.371141
H	0.759916	-0.860662	5.236526
H	1.860095	-2.939316	6.035912
C	2.841972	0.222673	-1.131053

C	4.142326	0.714465	-1.265533
C	2.288256	-0.466460	-2.212529
C	4.868594	0.482325	-2.417583
H	4.580660	1.294604	-0.462677
C	3.024016	-0.690890	-3.358925
H	1.272878	-0.838961	-2.148645
C	4.323740	-0.228624	-3.473295
H	5.875218	0.879540	-2.492300
H	2.568643	-1.247464	-4.170982
H	4.900200	-0.412334	-4.372044
C	2.714845	0.686830	1.285884
C	3.819825	-0.045172	1.713866
C	2.180005	1.646460	2.139276
C	4.358344	0.165258	2.967898
H	4.245585	-0.793997	1.056737
C	2.719124	1.846902	3.397626
H	1.330552	2.234634	1.811819
C	3.808757	1.107850	3.821703
H	5.205718	-0.430065	3.289131
H	2.280690	2.595446	4.048263
H	4.227521	1.262668	4.809055
C	-0.482191	3.468447	0.260275
C	-0.568519	4.815459	-0.100566
C	-1.125404	3.061250	1.433994
C	-1.243860	5.716711	0.696788
H	-0.111808	5.149733	-1.023730
C	-1.809044	3.972751	2.215627
H	-1.095653	2.016857	1.726164
C	-1.870074	5.309115	1.863642
H	-1.294615	6.755692	0.388949

H	-2.302234	3.624339	3.116647
H	-2.407328	6.019658	2.480263
C	1.139106	2.946835	-1.499634
C	2.200819	3.770809	-1.136075
C	1.046970	2.504024	-2.813092
C	3.138559	4.155134	-2.075023
H	2.286062	4.096676	-0.104832
C	1.997016	2.880303	-3.744633
H	0.222675	1.856060	-3.091631
C	3.043198	3.712647	-3.384734
H	3.964591	4.790761	-1.775428
H	1.916988	2.518855	-4.763682
H	3.788365	4.002457	-4.116231

TS-1

M06 SCF energy in solution: -2160.70701189 a.u.

M06 enthalpy in solution: -2160.363563 a.u.

M06 free energy in solution: -2160.456284 a.u.

Imaginary frequency: -504.3507 cm-1

Cartesian coordinates

ATOM	X	Y	Z
Li	2.113238	0.742841	-0.136497
O	3.841081	1.477167	-0.289023
S	5.152762	0.795212	-0.006854
C	4.832088	-0.360303	1.318686
C	5.365483	-0.413523	-1.305110
H	5.733646	-0.948393	1.498237
H	4.590092	0.219034	2.210082
H	3.997649	-1.009011	1.039855

H	6.242390	-1.021812	-1.077018
H	4.463816	-1.027336	-1.366641
H	5.527570	0.128182	-2.237135
O	2.072045	-1.073177	-0.710660
S	1.108066	-2.223411	-0.826307
C	0.381502	-2.441091	0.792233
C	-0.340216	-1.571629	-1.643050
H	-0.310628	-3.284274	0.744168
H	1.194074	-2.675757	1.481344
H	-0.139864	-1.535048	1.112206
H	-1.128038	-2.327283	-1.608540
H	-0.650502	-0.653001	-1.138400
H	-0.072939	-1.366746	-2.679875
C	0.287165	1.162171	1.168667
O	0.197360	1.495893	-0.009974
O	1.219072	0.867661	1.898957
H	-1.138788	0.806723	1.880713
S	-2.261129	0.036270	2.458693
C	-2.946283	-0.506566	0.924322
C	-3.123161	0.287165	-0.221343
C	-3.333458	-1.847046	0.870109
C	-3.667914	-0.290009	-1.368758
C	-2.802556	1.740793	-0.255418
C	-3.902968	-2.391214	-0.263880
H	-3.172537	-2.468610	1.744634
C	-4.069886	-1.609906	-1.396288
H	-3.793289	0.325125	-2.250898
O	-2.894545	2.498359	0.674096
O	-2.453270	2.131433	-1.483831
H	-4.203289	-3.433024	-0.265783

H	-4.506066	-2.026809	-2.296187
C	-2.128972	3.507220	-1.621855
H	-1.291338	3.771671	-0.974600
H	-1.851167	3.653736	-2.663806
H	-2.984577	4.139909	-1.377772

TS-2

M06 SCF energy in solution: -1949.11390700 a.u.

M06 enthalpy in solution: -1948.771986 a.u.

M06 free energy in solution: -1948.863361 a.u.

Imaginary frequency: -40.2885 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	4.516601	-2.047127	-1.163038
C	3.476242	-1.696435	-2.009332
C	2.739316	-0.551748	-1.773388
C	3.028079	0.287669	-0.692342
C	4.078309	-0.082097	0.152326
C	4.809945	-1.233677	-0.081491
H	5.090326	-2.949012	-1.342794
H	3.224154	-2.329074	-2.853170
H	1.902818	-0.321038	-2.423574
H	4.342979	0.534302	1.002409
H	5.620829	-1.492944	0.590007
C	2.211403	1.491903	-0.472472
C	1.468222	2.065099	-1.428320
H	0.862227	2.938718	-1.235341
H	1.532285	1.744906	-2.459646
C	2.144533	2.057648	0.912518

F	1.225105	3.010807	1.044606
F	3.310130	2.609901	1.297455
F	1.856980	1.125081	1.834975
C	-0.825043	0.661094	-1.382427
O	-1.298890	0.808553	-0.258511
O	-1.019882	-0.161491	-2.271253
Li	-2.293207	-1.050930	-0.877908
O	-4.159042	-0.778548	-1.078664
O	-1.713869	-2.408712	0.309329
S	-5.054356	0.240147	-0.430448
S	-0.721761	-2.510451	1.433931
C	-4.433603	0.450497	1.232738
C	-4.533362	1.827075	-1.065069
C	0.831750	-1.932521	0.765059
C	-1.030972	-1.109845	2.500818
H	-4.992924	1.251302	1.719495
H	-4.599005	-0.486892	1.764707
H	-3.368620	0.692038	1.190275
H	-5.081961	2.612761	-0.542710
H	-3.456786	1.936685	-0.915535
H	-4.778706	1.852649	-2.126908
H	1.578328	-1.914661	1.561485
H	1.134555	-2.637095	-0.010195
H	0.684148	-0.935267	0.345892
H	-0.252326	-1.075696	3.265415
H	-1.029103	-0.198757	1.898475
H	-2.000714	-1.261008	2.975702

TS-3

M06 SCF energy in solution: -1949.28295204 a.u.

M06 enthalpy in solution: -1948.941534 a.u.

M06 free energy in solution: -1949.028122 a.u.

Imaginary frequency: -284.5831 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-3.968236	1.358784	-1.927981
C	-4.091361	1.341945	-0.545784
C	-3.400673	0.426525	0.225370
C	-2.545398	-0.552292	-0.338539
C	-2.432655	-0.500749	-1.751107
C	-3.122303	0.422838	-2.511467
H	-4.506868	2.080249	-2.531327
H	-4.734202	2.064622	-0.051379
H	-3.514609	0.473302	1.302211
H	-1.778299	-1.193091	-2.265725
H	-2.990066	0.413607	-3.589495
C	-1.854556	-1.482747	0.508475
C	-1.837950	-1.248947	1.993705
H	-2.854163	-1.171016	2.396667
H	-1.388893	-2.107699	2.501305
C	-0.955178	-2.417802	-0.023521
F	0.402926	-1.821731	-0.555330
F	-1.292392	-3.077849	-1.145200
F	-0.457787	-3.323494	0.819401
C	-1.046695	-0.023102	2.479491
O	0.087911	0.149836	1.946182
O	-1.537849	0.681014	3.370198
Li	1.071082	-0.250045	0.420964
O	1.152187	1.247190	-0.859425

O	2.968158	-0.698827	0.792271
S	0.921107	2.695740	-0.529219
S	4.142585	-0.813231	-0.130474
C	-0.789648	2.826581	-0.027935
C	1.636511	2.947845	1.090446
C	3.495680	-1.278324	-1.732460
C	4.598323	0.859118	-0.574317
H	-0.986752	3.856637	0.275015
H	-1.406679	2.572767	-0.892004
H	-0.966304	2.132619	0.796668
H	1.399451	3.958722	1.427081
H	1.222799	2.194706	1.769237
H	2.717656	2.838179	0.995518
H	4.318694	-1.288635	-2.449413
H	3.076036	-2.280383	-1.643873
H	2.729018	-0.562420	-2.035594
H	5.393215	0.820979	-1.321304
H	3.717623	1.371122	-0.966907
H	4.966868	1.351662	0.325616

TS-4

M06 SCF energy in solution: -1593.60584523 a.u.

M06 enthalpy in solution: -1593.292828 a.u.

M06 free energy in solution: -1593.368522 a.u.

Imaginary frequency: -1470.7462 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.201039	0.029469	3.123036
C	-2.595229	-0.972342	2.249588

C	-1.674840	-1.591798	1.424195
C	-0.323419	-1.224407	1.440398
C	0.054930	-0.219220	2.334891
C	-0.868145	0.398688	3.160466
H	-2.925234	0.511224	3.770086
H	-3.633356	-1.284378	2.212549
H	-2.019499	-2.384411	0.774694
H	1.088946	0.100188	2.386930
H	-0.536541	1.179831	3.836248
C	0.709140	-1.858319	0.601597
C	0.439121	-2.606598	-0.460915
C	2.151931	-1.646773	0.952092
H	2.296444	-1.793257	2.024528
H	2.770503	-2.397895	0.454987
C	2.778126	-0.294925	0.582771
O	3.591837	0.181347	1.370661
O	2.480687	0.224842	-0.541628
F	1.350949	-3.195043	-1.202144
F	-0.742960	-2.904721	-0.942358
C	-3.212720	1.287277	-0.600356
C	-2.005699	1.889229	-0.298965
C	-0.831184	1.518478	-0.948947
C	-0.846791	0.472837	-1.883761
C	-2.077689	-0.120281	-2.176121
C	-3.244862	0.286126	-1.559146
H	-4.118824	1.598124	-0.093422
H	-1.966504	2.680560	0.442484
H	-2.102393	-0.933593	-2.894059
H	-4.182020	-0.196393	-1.814844
C	0.386058	2.334996	-0.674964

O	1.008262	2.936352	-1.509418
O	0.643055	2.394371	0.631420
C	1.814949	3.104267	1.008621
H	2.694815	2.634290	0.565858
H	1.756203	4.152106	0.706603
H	1.872641	3.039007	2.094535
S	0.592221	-0.160658	-2.682484
H	1.550835	-0.052515	-1.502086

TS-5

M06 SCF energy in solution: -2066.99661737 a.u.

M06 enthalpy in solution: -2066.566010 a.u.

M06 free energy in solution: -2066.665205 a.u.

Imaginary frequency: -252.3551 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.931795	2.254810	-0.983428
C	0.720130	1.241074	-1.855159
H	-0.049482	1.314166	-2.612065
H	1.489618	0.499496	-2.033221
C	-0.075183	3.339444	-0.860999
F	-1.056161	3.281455	-1.761211
F	0.475857	4.564622	-0.987493
F	-0.674094	3.353387	0.350991
C	-0.651369	-0.411286	-0.929892
O	-1.735129	0.066318	-0.605486
O	-0.154695	-1.521333	-0.787092
Li	-1.892370	-1.812878	0.417795

O	-3.344160	-2.819629	-0.266192
O	-1.831523	-1.378316	2.260923
S	-4.588524	-2.349277	-0.966657
S	-1.649487	-0.116973	3.057765
C	-5.021384	-0.788339	-0.209887
C	-4.048767	-1.691762	-2.537995
C	-0.155652	0.653612	2.445658
C	-2.799432	1.074893	2.383885
H	-5.880371	-0.368813	-0.736640
H	-5.292460	-0.992388	0.826471
H	-4.165032	-0.112058	-0.263985
H	-4.901170	-1.227141	-3.036627
H	-3.252927	-0.963712	-2.365376
H	-3.683697	-2.526332	-3.136826
H	-0.006547	1.592942	2.982079
H	0.670362	-0.025841	2.658637
H	-0.250274	0.831925	1.372876
H	-2.603343	2.044110	2.846897
H	-2.665830	1.123901	1.301320
H	-3.807378	0.746664	2.638848
C	2.081906	2.382081	-0.025390
C	3.197911	1.366132	-0.186317
H	1.708884	2.343196	1.009670
C	2.904521	0.009748	0.446117
H	3.434500	1.232924	-1.248835
H	4.107834	1.765808	0.274298
H	2.792846	0.146788	1.527923
H	1.953446	-0.384690	0.074466
C	3.997525	-0.973366	0.165676
C	3.953647	-1.770902	-0.973578

C	5.107228	-1.070066	0.998368
C	4.985516	-2.646090	-1.270475
H	3.091556	-1.703430	-1.632360
C	6.142394	-1.943620	0.706134
H	5.153590	-0.451305	1.890529
C	6.084356	-2.735368	-0.430078
H	4.931259	-3.263305	-2.160673
H	6.997616	-2.008543	1.370035
H	6.892060	-3.421582	-0.658740
H	2.503001	3.388392	-0.133466

TS-6

M06 SCF energy in solution: -1396.07638952 a.u.

M06 enthalpy in solution: -1395.822816 a.u.

M06 free energy in solution: -1395.894342 a.u.

Imaginary frequency: -194.9776 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-5.115058	-0.393177	-1.221214
C	-4.758672	-1.227556	-0.168140
C	-3.585213	-1.039680	0.532269
C	-2.673691	0.007516	0.240157
C	-3.059078	0.826909	-0.853271
C	-4.238532	0.632286	-1.547499
H	-6.036576	-0.542988	-1.771451
H	-5.413151	-2.045714	0.118677
H	-3.371459	-1.716169	1.352524
H	-2.412055	1.631972	-1.178117
H	-4.469060	1.295806	-2.376290

C	-1.480310	0.193962	1.015466
C	-0.790265	-0.996410	1.662992
H	-0.345815	-0.751822	2.631745
H	-1.508287	-1.799089	1.828501
C	-0.591649	1.269985	0.715220
F	-1.142437	2.471235	0.468305
F	0.238777	1.107806	-0.506317
F	0.364169	1.482274	1.632105
C	0.299797	-1.488197	0.726033
O	1.500929	-1.227791	1.005152
O	-0.036449	-1.982383	-0.381270
Li	1.384411	-0.723096	-0.956216
O	3.028486	-0.171217	-1.719882
S	4.271039	0.174511	-0.941999
C	3.728282	1.125931	0.471826
C	4.712446	-1.306574	-0.044750
H	4.597377	1.339908	1.096622
H	3.310081	2.061156	0.097972
H	2.977949	0.552284	1.022879
H	5.535677	-1.074393	0.633104
H	3.833126	-1.653715	0.503794
H	5.035698	-2.050800	-0.772703

11-Cs

M06 SCF energy in solution: -1961.85870080 a.u.

M06 enthalpy in solution: -1961.517502 a.u.

M06 free energy in solution: -1961.611996 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	-0.577704	-1.100618	-3.336985
C	-0.777291	0.238876	-3.017875
C	-1.639343	0.625352	-2.012454
C	-2.374980	-0.314486	-1.228627
C	-2.171750	-1.677831	-1.605945
C	-1.304319	-2.044099	-2.612710
H	0.103107	-1.397922	-4.125852
H	-0.235357	1.008175	-3.562128
H	-1.732185	1.683976	-1.792577
H	-2.701432	-2.463796	-1.079626
H	-1.189328	-3.100601	-2.840141
C	-3.180099	0.112706	-0.152523
C	-3.243684	1.566614	0.205021
H	-3.529519	2.176252	-0.662323
H	-4.032427	1.743795	0.942806
C	-3.723184	-0.863211	0.763554
F	-2.801791	-1.702792	1.381357
F	-4.590834	-1.784058	0.214836
F	-4.406690	-0.331752	1.791964
C	-1.977286	2.223023	0.803455
O	-1.234612	1.500937	1.513652
O	-1.812145	3.434775	0.561330
O	2.157090	1.147957	-0.792565
O	3.193637	-1.564999	1.555538
S	2.346942	2.602311	-0.485435
S	4.313989	-1.825544	0.602123
C	0.974636	3.467855	-1.239409
C	1.825256	2.818789	1.212265
C	3.592280	-1.884124	-1.038785
C	5.159227	-0.261260	0.386293

H	1.084103	4.534574	-1.030823
H	1.036600	3.300910	-2.315447
H	0.029474	3.105734	-0.824157
H	1.878297	3.880102	1.465295
H	0.799212	2.444735	1.335255
H	2.528174	2.262216	1.836221
H	4.392281	-2.007317	-1.771355
H	2.930948	-2.750992	-1.077992
H	3.040570	-0.958667	-1.224407
H	5.913820	-0.361098	-0.395859
H	4.416372	0.494098	0.118377
H	5.640767	-0.011996	1.332023
Cs	0.314966	-0.822507	0.688309

11-K

M06 SCF energy in solution: -2541.64048289 a.u.

M06 enthalpy in solution: -2541.299163 a.u.

M06 free energy in solution: -2541.391923 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.824682	2.006868	-0.854734
C	-4.377441	1.941227	0.460067
C	-3.585935	0.901291	0.905677
C	-3.185224	-0.172785	0.058738
C	-3.664711	-0.075757	-1.280678
C	-4.448120	0.974216	-1.710067
H	-5.441523	2.827886	-1.200925

H	-4.643951	2.729733	1.158994
H	-3.236397	0.919454	1.932231
H	-3.410981	-0.846571	-1.999327
H	-4.777432	0.987222	-2.745627
C	-2.365419	-1.219191	0.546940
C	-1.896985	-1.213824	1.975710
H	-2.735537	-1.016705	2.655386
H	-1.518374	-2.203380	2.249282
C	-1.858819	-2.211704	-0.359103
F	-1.077987	-1.727843	-1.435321
F	-2.788653	-2.952168	-1.049199
F	-1.050850	-3.126174	0.207598
C	-0.768902	-0.223179	2.324174
O	0.263389	-0.293522	1.600181
O	-0.931349	0.542377	3.287457
O	1.947679	1.379141	-1.121363
O	4.040249	-1.545928	-0.420753
S	1.021022	2.529771	-0.843717
S	5.086857	-0.587599	0.057643
C	-0.633811	1.848567	-0.896615
C	1.072391	2.795399	0.924735
C	5.276060	0.630303	-1.240281
C	4.271802	0.495592	1.227981
H	-1.345758	2.631797	-0.626823
H	-0.823332	1.524214	-1.920997
H	-0.694971	1.009925	-0.195382
H	0.296965	3.517733	1.189384
H	0.899781	1.833369	1.424127
H	2.051094	3.208226	1.172547
H	5.954066	1.413541	-0.895944

H	5.709436	0.125987	-2.104241
H	4.292782	1.042821	-1.482380
H	4.971143	1.272902	1.541393
H	3.396466	0.938455	0.744984
H	3.983871	-0.103927	2.092140
K	1.420159	-1.165814	-0.483093

11-Na

M06 SCF energy in solution: -2104.02248097 a.u.

M06 enthalpy in solution: -2103.681024 a.u.

M06 free energy in solution: -2103.773329 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.761798	1.607041	-1.951662
C	-3.924385	1.510393	-0.575370
C	-3.273994	0.540377	0.161761
C	-2.412864	-0.421869	-0.434018
C	-2.268008	-0.294067	-1.843999
C	-2.920084	0.684309	-2.565913
H	-4.270995	2.371841	-2.526401
H	-4.572445	2.212784	-0.058248
H	-3.429006	0.518891	1.235018
H	-1.623547	-0.979452	-2.382847
H	-2.765146	0.729079	-3.640343
C	-1.762586	-1.404438	0.363158
C	-1.936258	-1.384532	1.853617
H	-2.992463	-1.465117	2.151396

H	-1.446127	-2.253896	2.302092
C	-1.044829	-2.475069	-0.267932
F	0.095840	-2.079782	-1.024722
F	-1.716057	-3.206503	-1.215359
F	-0.539063	-3.386278	0.576384
C	-1.365406	-0.169497	2.624231
O	-0.292550	0.337557	2.190587
O	-1.980097	0.187110	3.639018
O	1.327161	1.578452	-0.963372
O	2.923785	-1.078962	0.769028
S	1.035428	2.960169	-0.444309
S	4.155488	-0.997925	-0.080631
C	-0.719296	2.986127	-0.106374
C	1.578487	2.965894	1.261365
C	3.603166	-1.131704	-1.777959
C	4.598639	0.733993	-0.150456
H	-0.976684	3.932597	0.372892
H	-1.240533	2.903247	-1.061670
H	-0.964049	2.141799	0.545933
H	1.326607	3.930515	1.706462
H	1.080308	2.154263	1.803724
H	2.661720	2.837865	1.263096
H	4.452463	-0.958535	-2.441411
H	3.225333	-2.143235	-1.927561
H	2.819310	-0.392222	-1.961608
H	5.444700	0.856714	-0.828987
H	3.732796	1.302600	-0.498817
H	4.888067	1.040702	0.855014
Na	0.805224	-0.250753	0.349073

TS-3-Cs

M06 SCF energy in solution: -1961.85229714 a.u.

M06 enthalpy in solution: -1961.511801 a.u.

M06 free energy in solution: -1961.605534 a.u.

Imaginary frequency: -416.3070 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.846994	0.291573	3.608597
C	1.191257	1.421469	2.881357
C	1.950629	1.327935	1.729859
C	2.420890	0.090748	1.234576
C	2.054761	-1.043296	1.997751
C	1.291707	-0.940045	3.144784
H	0.247173	0.366026	4.508231
H	0.855096	2.400420	3.210443
H	2.175812	2.238634	1.185811
H	2.350338	-2.032024	1.670552
H	1.033404	-1.845913	3.685039
C	3.158749	0.044227	-0.001204
C	3.275274	1.290802	-0.833742
H	3.807386	2.076841	-0.282474
H	3.889984	1.088490	-1.715380
C	3.635121	-1.151541	-0.507088
F	2.440578	-2.175352	-1.167415
F	4.125068	-2.086078	0.315060
F	4.415608	-1.120197	-1.579603
C	1.976356	1.922205	-1.379353

O	1.105859	1.135418	-1.824809
O	1.912738	3.166384	-1.374054
O	-1.960615	1.252105	0.715240
O	-3.290883	-1.750560	-1.207378
S	-2.252123	2.591629	0.111024
S	-4.375636	-1.801574	-0.182249
C	-0.847402	3.637920	0.471771
C	-1.936253	2.425341	-1.642559
C	-3.577633	-1.665981	1.418070
C	-5.119373	-0.172127	-0.160926
H	-1.022097	4.615072	0.015585
H	-0.792798	3.749670	1.555243
H	0.065725	3.193665	0.063220
H	-2.061333	3.401237	-2.117038
H	-0.914944	2.048129	-1.791557
H	-2.679599	1.732264	-2.042163
H	-4.345704	-1.621448	2.192587
H	-2.969941	-2.560322	1.562063
H	-2.961559	-0.762757	1.435908
H	-5.854534	-0.118295	0.643861
H	-4.326001	0.564102	-0.012110
H	-5.612713	-0.020046	-1.121095
Cs	-0.322438	-1.054948	-0.579325

TS-3-K

M06 SCF energy in solution: -2541.63705782 a.u.

M06 enthalpy in solution: -2541.296654 a.u.

M06 free energy in solution: -2541.389686 a.u.

Imaginary frequency: -390.6845 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	4.850288	-1.989215	-0.818883
C	4.418284	-1.910865	0.496975
C	3.627674	-0.862573	0.931420
C	3.227671	0.187454	0.072574
C	3.674604	0.073624	-1.265640
C	4.459188	-0.980131	-1.690383
H	5.466520	-2.813638	-1.158521
H	4.694025	-2.688186	1.203591
H	3.283113	-0.865496	1.959242
H	3.388107	0.820351	-1.995024
H	4.769193	-1.015149	-2.730600
C	2.391147	1.250609	0.564249
C	1.876285	1.199635	1.979701
H	2.709238	1.025090	2.671009
H	1.457486	2.172312	2.250991
C	1.940643	2.253846	-0.283449
F	0.846842	1.763977	-1.439808
F	2.779129	2.818393	-1.166953
F	1.209896	3.231071	0.242371
C	0.779485	0.163232	2.281364
O	-0.276464	0.276200	1.600613
O	0.989556	-0.677274	3.170235
O	-1.944669	-1.367842	-1.170983
O	-4.113321	1.555160	-0.383014
S	-1.004286	-2.507860	-0.900215
S	-5.110785	0.555918	0.114817

C	0.641355	-1.801463	-0.917987
C	-1.076162	-2.806200	0.862411
C	-5.295028	-0.654480	-1.191078
C	-4.220351	-0.509914	1.246156
H	1.358398	-2.569717	-0.619656
H	0.852064	-1.482911	-1.939719
H	0.665475	-0.954454	-0.225622
H	-0.308657	-3.538672	1.121978
H	-0.903206	-1.856168	1.383631
H	-2.060522	-3.217721	1.089818
H	-5.936964	-1.463921	-0.838318
H	-5.768040	-0.155437	-2.037133
H	-4.305645	-1.031291	-1.464526
H	-4.872708	-1.328010	1.557086
H	-3.335728	-0.897632	0.733712
H	-3.942086	0.084771	2.116840
K	-1.468582	1.195508	-0.451173

TS-3-Na

M06 SCF energy in solution: -2104.02283517 a.u.

M06 enthalpy in solution: -2103.682087 a.u.

M06 free energy in solution: -2103.771342 a.u.

Imaginary frequency: -373.4708 cm-1

Cartesian coordinates

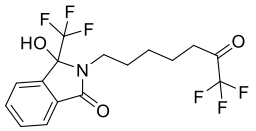
ATOM	X	Y	Z
C	-1.649076	1.367532	-3.338001
C	-2.236046	1.994492	-2.248210

C	-2.482269	1.309025	-1.073532
C	-2.172545	-0.062499	-0.921502
C	-1.551522	-0.668222	-2.041360
C	-1.306501	0.027792	-3.209638
H	-1.456422	1.907833	-4.257485
H	-2.505293	3.044900	-2.309261
H	-2.930635	1.847441	-0.245726
H	-1.253099	-1.708515	-1.995844
H	-0.830168	-0.490086	-4.036747
C	-2.450102	-0.733052	0.321170
C	-2.850682	0.075095	1.522820
H	-3.782888	0.624684	1.340250
H	-3.072493	-0.591080	2.361554
C	-2.202809	-2.095139	0.471048
F	-0.613847	-2.490171	0.580468
F	-2.477854	-2.935657	-0.536316
F	-2.608986	-2.680113	1.591747
C	-1.831220	1.092657	2.074853
O	-0.612916	0.771189	2.010960
O	-2.286575	2.130741	2.576999
O	1.607774	1.206694	-0.688423
O	2.531816	-1.473402	1.110526
S	1.946332	2.556904	-0.125350
S	3.528364	-1.957782	0.105055
C	0.391224	3.401576	0.132418
C	2.320685	2.294968	1.605086
C	2.660187	-2.044169	-1.460287
C	4.553909	-0.550851	-0.311401
H	0.593194	4.356455	0.622033
H	-0.052368	3.581454	-0.847299

H	-0.252765	2.771584	0.754111
H	2.498241	3.264660	2.074579
H	1.471318	1.786683	2.073772
H	3.227700	1.692106	1.659947
H	3.367179	-2.317187	-2.245777
H	1.899536	-2.821269	-1.373563
H	2.207446	-1.073288	-1.680393
H	5.231869	-0.833738	-1.118710
H	3.907656	0.275614	-0.614811
H	5.131227	-0.288615	0.575582
Na	0.475602	-0.472648	0.513102

5. Synthesis and characterization of final products

3-hydroxy-2-(7,7,7-trifluoro-6-oxoheptyl)-3-(trifluoromethyl)isoindolin-1-one (1E)



White solid (72% yield over two steps). R_f = 0.10 (silica gel, petroleum ether/ethyl acetate = 5:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, v/v).

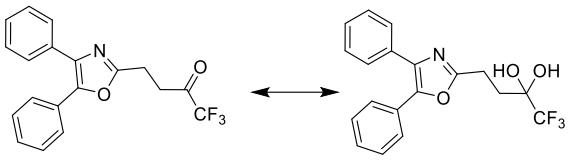
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.65 (m, 1H), 7.64 – 7.39 (m, 3H), 5.97 (s, 1H), 3.41 – 3.27 (m, 1H), 3.12 – 2.92 (m, 1H), 2.79 – 2.54 (m, 2H), 1.77 – 1.56 (m, 3H), 1.54 – 1.45 (m, 1H), 1.35 – 1.19 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.7 (q, *J* = 35.0 Hz), 168.9, 140.8, 133.0, 131.2, 123.9, 123.4, 122.1, 116.6, 114.6, 87.9 (t, *J* = 32.5 Hz), 39.5, 36.1, 27.5, 26.1, 21.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -78.61 (d, *J* = 9.9 Hz), -79.23.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{16}F_6NO_3^+$:384.1029, found: 384.1033.

4-(4,5-diphenyloxazol-2-yl)-1,1,1-trifluorobutan-2-one (1G)



Yellow solid. (1.86:1) (65% yield over two steps). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, v/v).

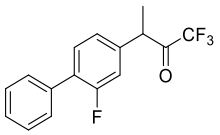
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 1.32H), 7.62 – 7.57 (m, 2.68H), 7.44 – 7.31 (m, 6H), 3.37 (t, *J* = 7.0 Hz, 1.3H), 3.32 – 3.20 (m, 2H), 2.44 – 2.31 (m, 0.7H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.8 (q, *J* = 35.9 Hz), 164.3, 160.7, 145.9, 145.8, 135.1, 133.6, 132.1, 131.0, 129.1, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.6, 126.7, 126.6, 123.7 (q, *J* = 287.5 Hz), 115.5 (q, *J* = 291.4 Hz), 93.1 (q, 31.2 Hz), 33.3, 28.7, 21.3, 21.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -78.87, -86.60.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{19}H_{15}F_3NO_2^+$:346.1049, found: 346.1053.

1,1,1-trifluoro-3-(2-fluoro-[1,1'-biphenyl]-4-yl)butan-2-one (1I)



Yellow oil. (75% yield). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

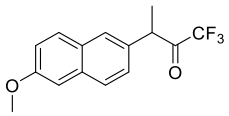
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (q, *J* = 8.1 Hz, 3H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.12 – 7.06 (m, 2H), 4.25 (q, *J* = 7.0 Hz, 1H), 1.58 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.6 (q, *J* = 33.7 Hz), 160.0 (d, *J* = 249.6 Hz), 138.1 (d, *J* = 7.6 Hz), 135.2, 131.5 (d, *J* = 3.9 Hz), 129.0 (d, *J* = 2.1 Hz), 128.6, 128.0, 124.1 (d, *J* = 3.6 Hz), 115.8 (q, *J* = 23.9 Hz), 46.6, 18.0.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -76.47, -116.39 (t, *J* = 9.6 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{13}F_4O^+$:297.0897, found: 297.0905.

1,1,1-trifluoro-3-(6-methoxynaphthalen-2-yl)butan-2-one (1J)



White Solid. (80% Yield). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

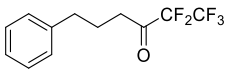
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 14.3, 8.7 Hz, 2H), 7.61 (s, 1H), 7.29 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 1.59 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.1 (q, *J* = 33.3 Hz), 158.2, 134.2, 131.9, 129.4, 129.1, 127.9, 127.1, 126.1, 119.5, 117.0 (t, *J* = 292.9 Hz), 105.7, 55.4, 47.2, 18.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -76.21.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{14}F_3O_2^+$ 283.0940, Found 283.0943.

1,1,1,2,2-pentafluoro-6-phenylhexan-3-one (1L)



Colorless oil (68% yield). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

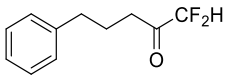
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.23 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.75 – 2.66 (m, 2H), 2.09 – 1.98 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 194.3 (t, *J* = 26.5 Hz), 140.7, 128.7, 128.5, 126.4, 118.0 (qt, *J* = 268.1, 26.9 Hz), 107.0 (tq, *J* = 266.7, 38.9 Hz), 36.6, 34.5, 23.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -81.88 (d, *J* = 6.3 Hz), -123.21.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{12}F_5O^+$ 267.0803, Found 267.0801.

1,1-difluoro-5-phenylpentan-2-one (1Q)



Colorless oil (74% yield). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

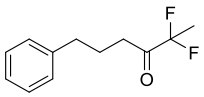
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 2H), 7.27 – 7.18 (m, 3H), 5.67 (t, *J* = 54.0 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 4H), 2.01 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.6 (t, *J* = 26.0 Hz), 141.0, 128.5, 128.5, 126.2, 109.8 (t, *J* = 252.6 Hz), 35.3, 34.7, 23.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -126.92 (d, *J* = 6.3 Hz), -127.01 (d, *J* = 6.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{13}F_2O^+$ 199.0929, Found 199.0931.

2,2-difluoro-6-phenylhexan-3-one (1R)



Colorless oil (68% yield). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.32 – 7.24 (m, 3H), 2.75 (dt, *J* = 27.5, 7.7 Hz, 4H), 2.05 (p, *J* = 7.4 Hz, 2H), 1.81 – 1.67 (m, 3H).

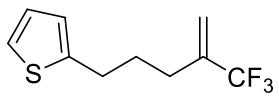
^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.5 (t, *J* = 31.9 Hz), 141.2, 128.4, 126.1, 117.5 (t, *J* =

248.9 Hz), 34.7, 34.7, 24.2, 19.1 (t, *J* = 25.1 Hz).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -99.94 (q, *J* = 19.1 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{15}F_2O^+$ 213.1085, Found 213.1091.

2-(4-(trifluoromethyl)pent-4-en-1-yl)thiophene (1b)



Colorless oil. (80% yield). R_f = 0.60 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

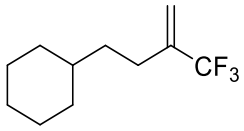
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 5.3 Hz, 1H), 7.01 – 6.94 (m, 1H), 6.86 (s, 1H), 5.75 (s, 1H), 5.38 (s, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.42 – 2.26 (m, 4H), 2.15 – 1.88 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 144.4, 138.1 (q, *J* = 29.2 Hz), 126.9 (q, *J* = 273.8 Hz), 124.5, 123.9, 123.2, 118.0 (q, *J* = 5.9 Hz), 29.5, 29.2, 28.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -68.36.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{12}F_3S^+$:221.0606, found:221.0609

(3-(trifluoromethyl)but-3-en-1-yl)cyclohexane (1c)



Colorless oil. (65% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

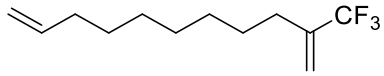
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 6.91 (d, *J* = 1.5 Hz, 1H), 3.85 – 3.80 (m, 2H), 3.41 – 3.30 (m, 4H), 3.30 – 3.26 (m, 1H), 3.10 – 2.99 (m, 2H), 2.93 – 2.84 (m, 3H), 2.83 – 2.75 (m, 1H), 2.61 – 2.50 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 139.3 (q, *J* = 29.0 Hz), 124.1 (q, *J* = 273.7 Hz), 117.0 (q, *J* = 5.9 Hz), 37.4, 35.2, 33.3, 26.8, 26.7, 26.4.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -68.62.

HRMS (EI-QTOF) *m/z:* $[M]^+$ Calcd. for $C_{11}H_{17}F_3$ 206.1282; Found 206.1285.

2-(trifluoromethyl)undeca-1,10-diene (1d)



Colorless oil. (72% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

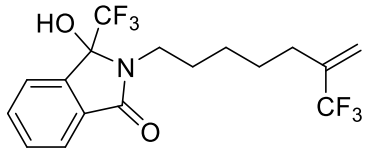
^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.86 – 5.76 (m, 1H), 5.64 (s, 1H), 5.28 (d, *J* = 3.0 Hz, 1H), 5.06 – 4.96 (m, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 2.18 (t, *J* = 8.5 Hz, 2H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.51 (p, *J* = 7.6 Hz, 2H), 1.44 – 1.35 (m, 2H), 1.36 – 1.27 (m, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 139.2, 138.9 (d, *J* = 29.4 Hz), 124.1, 117.3 (q, *J* = 6.0 Hz), 114.3, 33.9, 29.5, 29.3, 29.1, 29.1, 29.0, 26.9.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -68.64.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{20}F_3^+$:221.1512, found:221.1515.

3-hydroxy-3-(trifluoromethyl)-2-(6-(trifluoromethyl)hept-6-en-1-yl)isoindolin-1-one (1e)



White Solid. (57% yield). R_f = 0.10 (silica gel, petroleum ether/ethyl acetate = 5:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, v/v).

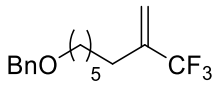
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.48 (m, 2H), 5.66 (d, *J* = 1.4 Hz, 1H), 5.30 (d, *J* = 1.4 Hz, 1H), 5.26 – 4.95 (m, 1H), 3.44 – 3.28 (m, 1H), 3.08 – 2.91 (m, 1H), 2.18 (t, *J* = 7.8 Hz, 2H), 1.79 – 1.63 (m, 1H), 1.62 – 1.44 (m, 3H), 1.37 – 1.25 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.7, 140.7, 138.4 (q, *J* = 28.8 Hz), 133.0, 131.3, 123.9, 123.9 (qd, *J* = 268.0, 136.5 Hz)., 123.6, 117.7 (q, *J* = 5.7 Hz), 87.8 (q, *J* = 32.0 Hz), 39.8, 29.4, 27.7, 27.0, 26.6.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -68.45, -78.68.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{18}F_6NO_2^+$:382.1236, found:382.1240.

(((7-(trifluoromethyl)oct-7-en-1-yl)oxy)methyl)benzene (1f)



Colorless oil. (74% yield). R_f = 0.50 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

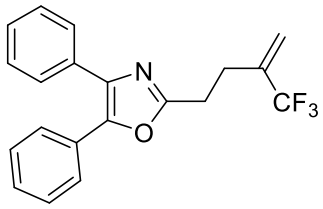
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 5.66 (s, 1H), 5.30 (s, 1H), 4.52 (s, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.20 (t, *J* = 7.9 Hz, 2H), 1.76 – 1.61 (m, 2H), 1.58 – 1.50 (m, 2H), 1.47 – 1.34 (m, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 138.7 (t, *J* = 11.2 Hz), 133.8, 128.4, 127.7, 127.6, 123.9 (q, *J* = 273.9 Hz), 117.4 (q, *J* = 5.8 Hz), 73.0, 70.4, 29.7, 29.4, 28.9, 27.4, 26.0.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -68.50.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{22}F_3O^+$:287.1617, found:287.1620.

4,5-diphenyl-2-(3-(trifluoromethyl)but-3-en-1-yl)oxazole (1g)



Colorless oil. (64% yield). R_f = 0.30 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

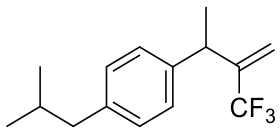
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.68 (m, 2H), 7.65 – 7.59 (m, 2H), 7.46 – 7.31 (m, 6H), 5.80 (s, 1H), 5.49 (q, *J* = 1.4 Hz, 1H), 3.38 – 3.01 (m, 2H), 3.01 – 2.71 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 161.7, 145.5, 136.9 (q, *J* = 29.6 Hz), 135.2, 132.4, 128.9, 128.6, 128.6, 128.5, 128.1, 127.9, 126.5, 123.6 (q, *J* = 273.7 Hz), 118.9 (q, *J* = 5.7 Hz), 26.7, 26.45.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -68.31.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{20}H_{17}F_3NO^+$:344.1257, found:344.1263.

1-isobutyl-4-(3-(trifluoromethyl)but-3-en-2-yl)benzene (1h)



Colorless oil. (84% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

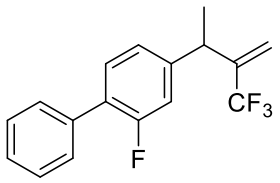
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.05 (m, 4H), 5.86 (s, 1H), 5.45 (s, 1H), 3.77 (q, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.96 – 1.86 (m, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 143.5 (q, *J* = 28.1 Hz), 140.4, 140.2, 129.3, 127.1, 124.1 (q, *J* = 274.6 Hz), 118.3 (d, *J* = 5.8 Hz), 45.2, 39.0, 30.3, 22.5, 21.3.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -66.51**.**

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{20}F_3^+$:257.1512, found:257.1517.

2-fluoro-4-(3-(trifluoromethyl)but-3-en-2-yl)-1,1'-biphenyl (1i)



Colorless oil. (77% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

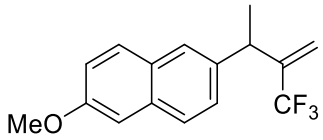
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.03 (d, *J* = 11.7 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 159.8 (d, *J* = 248.0 Hz), 144.8 (d, *J* = 7.3 Hz), 142.6 (q, *J* = 28.4 Hz), 135.7, 130.8 (d, *J* = 4.1 Hz), 129.0 (d, *J* = 2.9 Hz), 128.5, 127.7, 127.5 (d, *J* = 13.6 Hz), 123.9 (q, *J* = 275.1 Hz), 123.4 (d, *J* = 3.2 Hz), 119.0 (q, *J* = 5.7 Hz), 115.0 (d, *J* = 23.3 Hz), 38.9, 20.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -66.58, -117.76 (t, *J* = 9.9 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{17}H_{15}F_4^+$:295.1104, found:295.1107.

2-methoxy-6-(3-(trifluoromethyl)but-3-en-2-yl)naphthalene (1j)



Colorless oil. (70% yield). R_f = 0.60 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

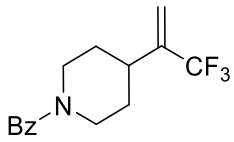
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.7, 7.0 Hz, 2H), 7.67 (s, 1H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.23 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.18 (d, *J* = 2.6 Hz, 1H), 5.93 (q, *J* = 1.5 Hz, 1H), 5.51 (p, *J* = 1.4 Hz, 1H), 3.95 (s, 4H), 1.61 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 157.7, 143.2 (q, *J* = 27.8 Hz), 138.3, 133.6, 129.3, 129.1, 127.1, 126.5, 125.6, 124.1 (q, *J* = 274.7 Hz), 119.0, 118.6 (q, *J* = 5.7 Hz), 105.7, 55.3, 39.3, 21.2.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -66.31.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{16}H_{16}F_3O^+$:281.1148, found:281.1153.

phenyl(4-(3,3,3-trifluoroprop-1-en-2-yl)piperidin-1-yl)methanone (1k)



Colorless oil. (52% yield). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 50:1, v/v), column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1, v/v).

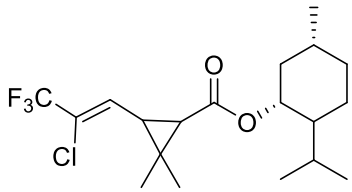
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (s, 5H), 5.73 (d, *J* = 1.6 Hz, 1H), 5.36 (s, 1H), 4.85 – 4.73 (m, 1H), 3.93 – 3.66 (m, 1H), 3.12 – 2.64 (m, 2H), 2.47 – 2.33 (m, 1H), 1.96 – 1.70 (m, 2H), 1.63 – 1.29 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.8, 141.9 (q, *J* = 28.2 Hz), 135.9, 129.6, 128.4, 126.8, 124.0 (q, *J* = 274.2 Hz), 117.7 (q, *J* = 6.2 Hz), 47.9, 42.4, 36.4, 32.3, 31.3.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -67.07.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{15}H_{17}F_3NO^+$:284.1257, found:284.1259.

(1R,5R)-2-isopropyl-5-methylcyclohexyl-3-((Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2,2-dimethylcyclopropane-1-carboxylate (1n)



White solid. (75% yield, dr =1:1). R_f= 0.60 (silica gel, petroleum ether/ethyl acetate = 10:1, v/v). The diastereomeric ratio was determined by ^{19}F NMR.

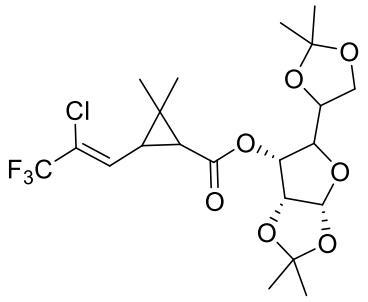
^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.94 (dd, *J* = 49.0, 9.4 Hz, 1H), 4.75 – 4.63 (m, 1H), 2.12 (t, *J* = 8.9 Hz, 1H), 1.95 (dd, *J* = 8.4, 3.7 Hz, 2H), 1.89 – 1.78 (m, 1H), 1.70 – 1.64 (m, 2H), 1.53 – 1.42 (m, 1H), 1.40 – 1.33 (m, 1H), 1.30 (d, *J* = 3.4 Hz, 3H), 1.27 (d, *J* = 16.9 Hz, 3H), 1.09 – 0.94 (m, 2H), 0.93 – 0.86 (m, 7H), 0.74 (dd, *J* = 15.0, 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.9, 130.5 (dd, *J* = 15.1, 4.5 Hz), 121.4, 119.6, 74.7, 74.6, 47.2, 47.2, 41.2, 41.2, 34.3, 34.3, 33.6, 33.4, 31.5, 30.7, 30.6, 28.5, 28.4, 28.4, 28.2, 26.5, 26.4, 23.6, 23.5, 22.1, 22.0, 20.8, 20.7, 16.4, 16.3, 15.2, 15.0.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -68.54, -68.60.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{19}H_{29}ClF_3O_2^+$:381.1803, found:381.1811.

(3aR,6R,6aR)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 3-((Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2,2-dimethylcyclopropane-1-carboxylate (1o)



White solid. (65% yield, dr = 1:1). R_f= 0.40 (silica gel, petroleum ether/ethyl acetate = 10:1, v/v). The diastereomeric ratio was determined by ^{1}H NMR.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.99 (d, *J* = 9.3 Hz, 1H), 6.92 – 6.81 (m, 1H), 5.77 (dd, *J* = 5.7, 3.8 Hz, 1H), 4.99 – 4.66 (m, 1H), 4.30 – 4.00 (m, 1H), 3.97 – 3.79 (m, 1H), 3.66 – 3.58 (m,

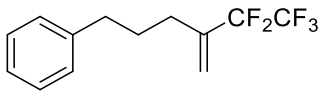
1H), 2.24 – 2.03 (m, 1H), 2.03 – 1.89 (m, 2H), 1.87 – 1.66 (m, 4H), δ 1.63 – 1.56 (m, 1H), 1.54 – 1.46 (m, 1H), 1.43 – 1.34 (m, 1H), 1.33 – 1.28 (m, 2H), 1.28 – 1.18 (m, 6H), 1.17 (s, 2H), 1.15 – 1.08 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 169.2, 153.8, 131.5, 131.5, 130.0, 120.9 (q, *J* = 37.4 Hz), 120.6 (q, *J* = 271.1 Hz), 113.3, 113.2, 110.0, 104.2, 104.1, 77.9, 77.9, 75.3, 75.1, 72.9, 72.4, 65.9, 65.7, 56.4, 50.0, 35.6, 32.9, 32.7, 31.2, 31.1, 30.5, 28.3, 27.9, 26.5, 26.4, 25.5, 24.8, 24.78, 15.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -68.38.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{21}H_{29}ClF_3O_7^+$:485.1548, found:485.1556.

(5,5,6,6,6-pentafluoro-4-methylenehexyl)benzene (1p)



Colorless oil. (83% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

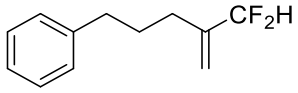
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 2H), 7.27 – 7.20 (m, 3H), 5.74 (s, 1H), 5.52 (s, 1H), 2.73 – 2.67 (m, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.94 – 1.81 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 141.7, 137.9 (t, *J* = 21.2 Hz), 128.5, 128.5, 126.1, 120.6 (t, *J* = 8.8 Hz), 120.3 (qt, *J* = 268.0, 27.1 Hz), 113.5 (tq, *J* = 268.1, 26.9 Hz), 35.4, 29.6, 29.3.

^{19}F NMR (565 MHz, CHLOROFORM-*D*) δ -83.64, -116.00.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{14}F_5^+$:265.1010, found: 265.1018.

(4-(difluoromethyl)pent-4-en-1-yl)benzene (1q)



Colorless oil. (88% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

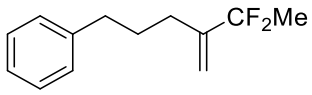
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 2H), 7.36 – 7.29 (m, 3H), 6.44 – 5.91 (m, 1H), 5.47 (s, 1H), 5.33 (s, 1H), 2.97 – 2.72 (m, 2H), 2.41 – 2.25 (m, 2H), 2.16 – 1.91 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 142.6 (t, J = 20.6 Hz), 142.0, 128.5, 128.4, 125.9, 117.1 (t, J = 10.0 Hz), 116.5 (t, J = 237.6 Hz), 35.5, 29.3, 28.1.

^{19}F NMR (565 MHz, Chloroform-d) δ -115.22, -115.32.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{15}F_2^+$:197.1136, found:197.1141.

(5,5-difluoro-4-methylenehexyl)benzene (1r)



Colorless oil. (85% yield). R_f = 0.70 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

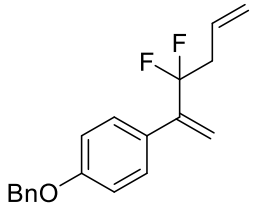
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 6.7 Hz, 3H), 5.45 (s, 1H), 5.15 (s, 1H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.26 (t, *J* = 7.9 Hz, 2H), 1.91 (p, *J* = 7.8, 7.3 Hz, 2H), 1.77 – 1.74 (m, 3H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 145.3 (t, *J* = 24.2 Hz), 142.1, 128.5, 128.4, 125.9, 122.2 (t, *J* = 237.6 Hz), 113.5 (t, *J* = 8.5 Hz), 35.6, 29.7, 29.6, 23.4 (t, *J* = 29.3 Hz).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.07 (q, *J* = 18.0 Hz).

HRMS (EI-QTOF) *m/z:* $[M]^+$ Calcd. for $C_{13}H_{16}F_2$ 210.1220; Found 210.1215.

1-(benzyloxy)-4-(3,3-difluorohexa-1,5-dien-2-yl)benzene (1t)



White Solid (80% yields). R_f = 0.30 (silica gel, petroleum ether), column chromatography (silica gel, petroleum ether).

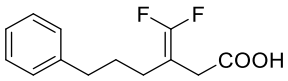
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.44 – 7.40 (m, 2H), 7.41 – 7.35 (m, 3H), 7.01 – 6.92 (m, 2H), 5.80 – 5.70 (m, 1H), 5.69 (s, 1H), 5.45 (s, 1H), 5.18 (d, *J* = 10.8 Hz,1H), 5.10 - 5.07 (m, 3H), 2.76 – 2.66 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.9, 143.8 (t, *J* = 23.5 Hz), 136.2, 129.6, 129.5, 129.2, 128.7, 128.1, 127.6, 121.6 (t, *J* = 243.6 Hz), 120.2, 117.5 (t, *J* = 8.5 Hz), 114.7, 70.1, 41.1 (t, *J* = 27.0 Hz).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -95.43.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd. for $C_{19}H_{19}F_2O^+$:301.1398, found:301.1406.

3-(difluoromethylene)-6-phenylhexanoic acid (2a)



Colorless oil. Yield: 80.0 mg (84%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

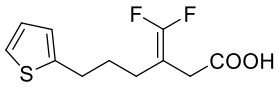
^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 7.33 – 7.29 (m, 2H), 7.24 – 7.17 (m, 3H), 3.07 (d, *J* = 2.2 Hz, 2H), 2.71 – 2.55 (m, 2H), 2.22 – 2.11 (m, 2H), 1.83 – 1.69 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.1, 154.9 (t, *J* = 285.8 Hz), 141.8, 128.5, 128.4, 126.0, 83.4 (dd, *J* = 23.4, 16.0 Hz), 34.7, 31.9, 28.8, 26.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.81 (d, *J* = 47.5 Hz), -92.80 (d, *J* = 47.0 Hz).

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{13}H_{13}F_2O_2^-$:239.0889, found: 239.0884.

3-(difluoromethylene)-6-(thiophen-2-yl)hexanoic acid (2b)



Colorless oil. Yield: 78.7 mg (80%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

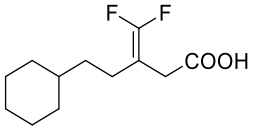
^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.17 – 7.11 (m, 1H), 7.00 – 6.91 (m, 1H), 6.82 (s, 1H), 3.09 (s, 2H), 2.94 – 2.76 (m, 2H), 2.20 (s, 2H), 1.89 – 1.76 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.1, 154.8 (t, *J* = 286.1 Hz), 144.5, 126.8, 124.3, 123.2, 83.2 (dd, *J* = 22.6, 16.6 Hz), 31.8, 29.2, 29.1, 26.2.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.56 (d, *J* = 45.2 Hz), -92.58 (d, *J* = 46.0 Hz).

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{11}H_{11}F_2O_2S^-$: 245.0453, found: 245.0450.

5-cyclohexyl-3-(difluoromethylene)pentanoic acid (2c)



Colorless oil. Yield: 53.9 mg (58%). R_f = 0.40 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

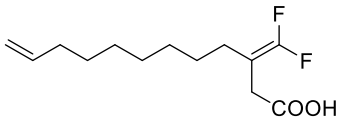
^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.03 (s, 2H), 2.16 – 1.98 (m, 2H), 1.72 – 1.67 (m, 4H), 1.66 – 1.61 (m, 1H), 1.30 – 1.24 (m, 2H), 1.24 – 1.08 (m, 4H), 0.96 – 0.83 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.3, 154.4 (t, *J* = 285.5 Hz), 84.0 (dd, *J* = 23.5, 15.7 Hz), 37.2, 34.7, 33.2, 31.8, 26.7, 26.3, 24.0.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -92.65 (d, *J* = 47.6 Hz), -93.68 (d, *J* = 47.8 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{12}H_{17}F_2O_2^-$: 231.1202, found:231.1201.

3-(difluoromethylene)dodec-11-enoic acid (2d)



Colorless oil. Yield: 61.0 mg (62%). R_f = 0.4 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

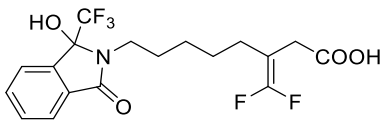
^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.85 – 5.76 (m, 1H), 5.02 – 4.97 (m, 1H), 4.95 – 4.91 (m, 1H), 3.03 (t, *J* = 2.0 Hz, 2H), 2.09 – 2.01 (m, 4H), 1.44 – 1.34 (m, 4H), 1.32 – 1.25 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.3, 154.7 (t, *J* = 285.6 Hz), 139.2, 114.3, 83.7 (dd, *J* = 23.3, 15.7 Hz), 33.8, 31.8, 29.2, 29.1, 29.0, 28.9, 27.0, 26.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -92.54 (d, *J* = 48.3 Hz), -93.51 (d, *J* = 48.0 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{13}H_{19}F_2O_2^-$: 245.1359, found: 245.1355.

3-(difluoromethylene)-8-(1-hydroxy-3-oxo-1-(trifluoromethyl)isoindolin-2-yl)octanoic acid (2e)



White Solid. Yield: 123.8 mg (76%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 1:1, v/v),

column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 3:1, v/v).

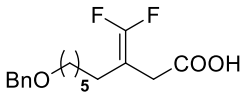
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.52 – 7.47 (m, 1H), 6.66 (s, 1H), 3.48 – 3.37 (m, 1H), 3.25 – 3.13 (m, 1H), 2.96 (s, 2H), 2.00 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.60 (m, 1H), 1.58 – 1.46 (m, 1H), 1.42 – 1.30 (m, 2H), 1.32 – 1.17 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 175.5, 169.0, 154.6 (t, *J* = 285.7 Hz), 140.8, 132.9, 131.3, 131.2, 123.1 (q, *J* = 285.9 Hz), 88.0 (q, *J* = 33.4 Hz), 83.5 (dd, *J* = 23.1, 16.0 Hz), 40.0, 32.0, 27.6, 26.6, 26.5, 26.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -78.76, -92.26 (d, *J* = 47.6 Hz), -93.32 (d, *J* = 47.8 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{18}H_{17}F_5NO_4^-$: 406.1083, found: 406.1084.

9-(benzyloxy)-3-(difluoromethylene)nonanoic acid (2f)



Colorless oil. Yield: 83.7 mg (67%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

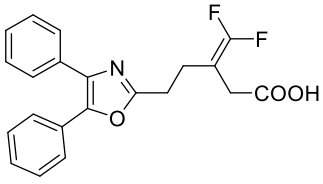
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 4.52 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.03 (s, 2H), 2.07 (t, *J* = 7.7 Hz, 2H), 1.82 – 1.54 (m, 2H), 1.51 – 1.35 (m, 4H), 1.34 – 1.26 (m, 2H).

^{13}C NMR (600 MHz, Chloroform-*d*) δ 176.5, 154.7 (t, *J* = 285.4 Hz), 138.5, 128.4, 127.8, 127.6, 83.7 (dd, *J* = 23.2, 15.8 Hz), 72.9, 70.3, 31.7, 29.6, 28.8, 27.0, 26.5, 25.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -92.50 (d, *J* = 49.3 Hz), -93.47 (d, *J* = 49.2 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{17}H_{21}F_2O_3^-$:311.1464, found: 311.1463.

3-(difluoromethylene)-5-(4,5-diphenyloxazol-2-yl)pentanoic acid (2g)



Brown oil. Yield: 125.5 mg (85%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

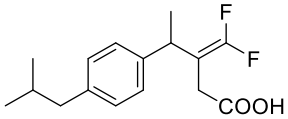
^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 7.65 – 7.61 (m, 2H), 7.58 (d, *J* = 6.7 Hz, 2H), 7.43 – 7.30 (m, 6H), 3.14 (s, 2H), 3.08 (t, *J* = 7.9 Hz, 2H), 2.69 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 162.7, 154.9 (t, *J* = 286.9 Hz), 145.7, 134.7, 131.7, 128.7, 128.7, 128.6, 128.6, 128.4, 128.1, 126.5, 82.9 (dd, J = 21.9, 17.8 Hz), 31.9, 26.0, 24.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.96 (d, *J* = 43.6 Hz), -91.60 (d, *J* = 44.4 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{21}H_{16}F_2NO_3^-$:368.1104, found: 368.1101.

3-(difluoromethylene)-4-(4-isobutylphenyl)pentanoic acid (2h)



Colorless oil. Yield: 84.6 mg (75%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

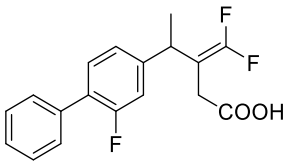
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 3.94 – 3.86 (m, 1H), 2.95 – 2.79 (m,2H), 2.48 (t, *J* = 5.6 Hz, 2H), 1.95 – 1.82 (m, 1H), 1.47 (t, *J* = 5.7 Hz, 3H), 0.93 (t, *J* = 5.5 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.4, 155.0 (t, *J* = 287.1 Hz), 140.3, 139.4, 129.3, 127.2, 88.3 (dd, *J* = 20.4, 14.7 Hz), 45.1, 36.4, 30.3, 22.4, 17.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.70 (d, *J* = 46.4 Hz), -92.39 (d, *J* = 46.9 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{16}H_{19}F_2O_2^-$:281.1359, found: 281.1355.

3-(difluoromethylene)-4-(2-fluoro-[1,1'-biphenyl]-4-yl)pentanoic acid (2i)



Colorless oil. Yield: 99.9 mg (78%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 (q, *J* = 6.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 13.6 Hz, 1H), 3.91 (q, *J* = 7.3 Hz, 1H), 2.95 – 2.83 (m, 2H), 1.47 (d, *J* = 7.3 Hz, 3H).

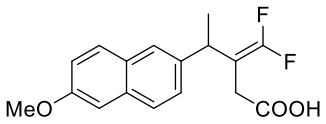
^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.0, 159.8 (d, *J* = 248.5 Hz), 155.0 (t, *J* = 287.9 Hz),

143.9 (d, *J* = 6.5 Hz), 135.6, 130.7 (d, *J* = 3.8 Hz), 129.0 (d, *J* = 2.6 Hz), 128.5, 127.7, 127.6 (d, *J* = 13.4 Hz), 123.5, 123.5, 115.2 (d, *J* = 23.5 Hz), 87.8 (dd, *J* = 20.1, 15.5 Hz), 36.4, 30.2, 30.2, 17.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.80 (d, *J* = 44.5 Hz), -91.34 (d, *J* = 44.5 Hz), -117.55 (t, *J* = 10.1 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{18}H_{14}F_3O_2^-$:319.0951, found: 319.0949.

3-(difluoromethylene)-4-(6-methoxynaphthalen-2-yl)pentanoic acid (2j)



White Solid. Yield: 89.4 mg (73%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

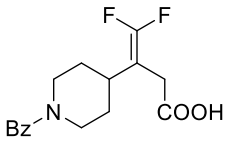
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 16.0, 8.7 Hz, 2H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.92 (s, 3H), 2.94 – 2.76 (m, 2H), 1.56 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.1, 157.7, 155.0 (t, *J* = 287.3 Hz), 137.3, 133.6, 129.3, 128.9, 127.2, 126.8, 125.3, 118.9, 105.7 (dd, *J* = 9.3, 5.7 Hz) , 88.2 (dd, *J* = 20.3, 15.0 Hz), 55.3, 36.7, 30.1, 17.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.31 (d, *J* = 47.4 Hz), -92.00 (d, *J* = 44.8 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{17}H_{15}F_2O_3^-$:305.0995, found: 305.0993.

3-(1-benzoylpiperidin-4-yl)-4,4-difluorobut-3-enoic acid (2k)



White Solid. Yield: 84.1 mg (68%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

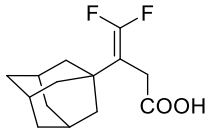
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 4.52 (s, 1H), 3.54 (s, 1H), 3.11 – 2.88 (m, 3H), 2.81 – 2.61 (m, 1H), 2.57 – 2.38 (m, 1H), 1.68 – 1.33 (m, 4H).

^{13}C NMR (151 MHz, DMSO-D_6) δ 171.8, 169.0, 153.8 (t, *J* = 285.3 Hz), 136.4, 129.3, 128.4, 126.7, 88.45 (dd, *J* = 18.4, 14.8 Hz), 47.2, 41.6, 34.8, 29.7, 29.5, 29.0.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.80 (d, *J* = 47.7 Hz), -91.64 (d, *J* = 47.8 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{16}H_{16}F_2NO_3^-$:308.1104, found: 308.1102.

3-((3r,5r,7r)-adamantan-1-yl)-4,4-difluorobut-3-enoic acid (2l)



White Solid. Yield: 68.6 mg (65%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

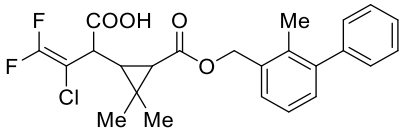
^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.04 (s, 2H), 1.99 (s, 3H), 1.78 (s, 6H), 1.73 – 1.63 (m, 6H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 178.2, 154.7 (dd, *J* = 294.4, 285.0 Hz), 91.8 (t, *J* = 13.2 Hz), 40.4, 40.3, 36.6, 34.2 (d, *J* = 4.0 Hz), 30.2 (t, *J* = 3.6 Hz), 28.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -84.84 (d, *J* = 49.1 Hz), -85.33 (d, *J* = 49.1 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{14}H_{17}F_2O_2^-$:255.1202, found: 255.1198.

3-chloro-2-(2,2-dimethyl-3-(((2-methyl-[1,1'-biphenyl]-3-yl)methoxy)carbonyl)cyclopropyl)-4,4-difluorobut-3-enoic acid (2m)



Colorless oil. Yield: 95 mg (53%) (dr = 1.14:1). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

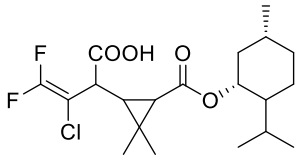
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.31 (t, *J* = 8.3 Hz, 2H), 7.28 – 7.24 (m, 2H), 5.34 – 5.07 (m, 2H), 4.55 – 4.26 (m, 1H), 2.24 – 2.21 (m, 3H), 1.99 – 1.64 (m, 2H), 1.36 – 1.31 (m, 2H), 1.28 – 1.23 (m, 4H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 176.6, 176.4, 171.8, 171.1, 156.8, 156.6, 154.8, 154.7, 153.2, 152.9, 143.0, 143.0, 141.9, 141.9, 134.4, 134.4, 130.4, 130.3, 129.4, 128.4, 128.2, 128.2, 128.1, 126.9, 125.6, 91.2, 91.0, 90.9, 90.7, 90.6, 90.5, 90.4, 90.2, 65.4, 65.3, 40.2, 39.8, 31.3, 30.8, 28.9, 28.5, 28.3, 27.6, 27.0, 25.7, 16.1, 16.1, 14.4, 14.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.12 (d, *J* = 33.2 Hz), -86.68 (d, *J* = 36.4 Hz), -88.67 (d, *J* = 33.3 Hz), -90.52 (d, *J* = 36.4 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{24}H_{22}ClF_2O_4^-$:447.1180, found: 447.1178.

3-chloro-4,4-difluoro-2-(3-((((1R,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-2,2-dimethylcyclopropyl)but-3-enoic acid (2n)



Colorless oil. Yield: 76.4 mg (47%) (dr =1.66:1). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

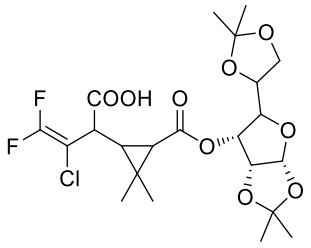
^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.73 – 4.59 (m, 1H), 4.37 (dd, *J* = 131.9, 10.5 Hz, 1H), 1.99 – 1.78 (m, 2H), 1.78 – 1.53 (m, 4H), 1.50 – 1.42 (m, 1H), 1.41 – 1.32 (m, 1H), 1.32 – 1.15 (m, 6H), 1.10 – 0.94 (m, 2H), 0.94 – 0.83 (m, 7H), 0.78 – 0.69 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*)δ 176.7, 176.4, 172.2, 170.8, 170.8, 156.6, 154.9, 154.8, 154.7, 152.8, 91.5, 91.3, 91.2, 91.1, 90.9, 90.8, 90.7, 90.5, 90.4, 90.2, 74.5, 74.3, 74.2, 47.1, 47.1, 34.3, 31.5, 31.4, 31.1, 31.1, 30.4, 29.3, 28.6, 28.4, 28.0, 27.8, 26.66, 26.6, 26.5, 26.5, 25.1, 23.7, 23.7, 23.6, 22.1, 22.0, 22.0, 20.7, 20.6, 16.5, 16.5, 16.2, 14.5, 14.3, 14.2.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.40 (d, *J* = 33.8 Hz), -86.61 (d, *J* = 33.6 Hz), -86.97 (d, *J* = 36.7 Hz), -88.75 (dd, *J* = 33.8, 23.7 Hz), -90.77 (d, *J* = 36.7 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{20}H_{28}ClF_2O_4^-$:405.1650, found: 405.1646.

3-chloro-2-(3-((((3aR,6R,6aR)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)carbonyl)-2,2-dimethylcyclopropyl)-4,4-difluorobut-3-enoic acid (2o)



Colorless oil. Yield: 89.8 mg (44%) (dr = 1:1). R_f = 0.10 (silica gel, petroleum ether/ethyl acetate = 1:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 3:1, v/v).

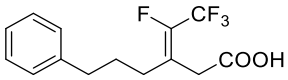
^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.82 – 5.78 (m, 1H), 4.81 – 4.74 (m, 2H), 4.36 – 4.14 (m, 3H), 4.06 (q, *J* = 8.5 Hz, 1H), 3.91 (dd, *J* = 8.6, 5.7 Hz, 1H), 1.79 – 1.61 (m, 2H), 1.53 (d, *J* = 13.9 Hz, 3H), 1.41 (d, *J* = 7.4 Hz, 3H), 1.37 – 1.24 (m, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.3, 170.3, 170.2, 156.8, 156.7, 154.9, 154.8, 153.2, 152.9, 113.1, 110.1, 104.3, 90.7, 90.6, 90.4, 90.4, 90.3, 90.3, 77.8, 77.7, 77.6, 77.6, 75.9, 75.2, 65.6, 40.1, 39.9, 32.0, 31.5, 28.53, 28.5, 27.7, 27.3, 27.0, 26.9, 26.7, 26.5, 26.3, 26.2, 25.2, 25.1, 14.4, 14.3.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -85.86 (dd, *J* = 33.6, 14.5 Hz), -89.04 (dd, *J* = 103.0, 33.7 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{22}H_{28}ClF_2O_9^-$:509.1395, found: 509.1390.

3-(perfluoroethylidene)-6-phenylhexanoic acid (2p)



Colorless oil. Yield: 81.2 mg (70%) (Z: E = 1.1:1). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

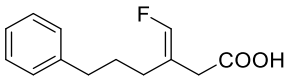
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.17 (m, 3H), 3.42 – 3.25 (m, 2H), 2.76 – 2.62 (m, 2H), 2.44 – 2.25 (m, 2H), 1.91 – 1.75 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.8, 175.8, 145.7, 145., 145.4, 145.2, 145.1, 144.9, 144.9, 144.6, 144.0, 143.8, 143.7, 143.5, 143.5, 143.3, 143.2, 143.0, 141.3, 141.2, 128.5, 128.5, 128.4, 128.4, 126.2, 126.2, 35.5, 35.5, 34.1, 34.0, 33.1, 29.6, 29.6, 29.4, 28.6, 28.5, 28.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -65.56 (dd, *J* = 300.3, 8.2 Hz), -126.98 (d, *J* = 974.1 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{14}H_{13}F_4O_2^-$:289.0857, found: 289.0869.

3-(fluoromethylene)-6-phenylhexanoic acid (2q)



Black oil. Yield: 47.1 mg (53%) (Z: E = 1:1.15). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

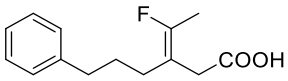
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 2H), 7.26 – 7.16 (m, 3H), 6.57 (dd, *J* = 84.5, 14.9 Hz, 1H), 3.22 (s, 1H), 2.96 (d, *J* = 3.2 Hz, 1H), 2.65 (dd, *J* = 14.1, 7.8 Hz, 2H), 2.31 (t, *J* = 8.0 Hz, 1H), 2.08 (t, *J* = 9.5 Hz, 1H), 1.83 – 1.71 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.7, 177.3, 147.7, 147.1, 146.0, 145.4, 142.0, 141.8, 128.5, 128.4, 128.4, 126.0, 125.9, 115.9, 115.8, 115.0, 115.0, 35.6, 35.2, 34.6, 34.6, 31.7, 31.7, 29.3, 29.3, 28.8, 26.2, 26.2.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -129.02 (d, *J* = 84.2 Hz), -131.17 (d, *J* = 84.7 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{13}H_{14}FO_2^-$:221.0983, found: 221.0976.

3-(1-fluoroethylidene)-6-phenylhexanoic acid (2r)



Orange oil. Yield: 54.8 mg (42%) (Z: E = 1.2:1). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

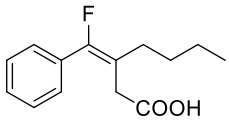
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 2H), 7.25 – 7.15 (m, 3H), 3.19 (s, 0.67H), 3.00 (s, 0.78H), 2.64 (s, 2.28H), 2.51 (s, 0.27H), 2.41 – 2.34 (m, 0.26H), 2.27 (s, 0.81H), 2.10 (s, 0.68H), 2.07 – 1.84 (m, 2.18H), 1.81 – 1.65 (m, 2.32H), 1.65 – 1.52 (m, 0.76H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 179.0, 179.0, 178.3, 178.2, 142.3, 141.9, 141.8, 128.4, 128.3, 126.8, 125.9, 125.8, 125.2, 123.6, 109.2, 109.1, 108.4, 108.4, 42.4, 42.3, 42.1, 35.8, 35.7, 35.4, 33.7, 32.9, 32.8, 29.9, 29.8, 29.4, 29.4, 29.3, 29.0, 28.7, 28.1, 28.1, 21.5, 21.3, 21.1, 15.0, 14.8, 14.6, 14.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.39 (qt, *J* = 19.0, 7.6 Hz), -91.83 (qt, *J* = 19.2, 7.7 Hz), -95.32 – -95.61 (m), -95.79 – -96.04 (m), -96.84 – -97.02 (m), -97.58 – -97.74 (m).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{14}H_{16}FO_2^-$:235.1140, found: 235.1134.

3-(fluoro(phenyl)methylene)heptanoic acid (2s)



Colorless oil. Yield: 39.7 mg (47%) (Z: E = 1.13:1). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

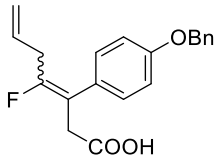
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 6.7 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.42 – 7.35 (m, 3H), 3.36 (d, *J* = 2.9 Hz,1H), 3.15 (s, 1H), 2.43 – 2.33 (m, 1H), 2.23 – 2.18 (m, 1H), 1.56 – 1.43 (m, 2H), 1.43 – 1.35 (m, 1H), 1.34 – 1.26 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 1.5H), 0.87 (t, *J* = 7.4 Hz, 1.5H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.2, 177.7, 156.7, 156.1, 155.1, 154.5, 132.3, 132.1, 129.3, 129.1, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 112.6, 112.5, 112.2, 112.2, 36.0, 35.9, 33.4, 33.4, 30.2, 29.7, 28.3, 28.2, 22.6, 22.6, 14.0, 13.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -98.92, -99.70.

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{14}H_{16}FO_2^-$:235.1140, found: 235.1135.

3-(4-(benzyloxy)phenyl)-4-fluorohepta-3,6-dienoic acid (2t)



Brown Solid. Yield: 108.3 mg (83%) (Z: E = 4.25:1). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

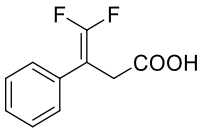
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.7 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.31 (m, 1.45H), 7.19 (d, *J* = 8.6 Hz, 1.57H), 7.00 – 6.94 (m, 2H), 6.01 – 5.79 (m, 1H), 5.28 – 5.15 (m, 2H), 5.07 (s, 2H), 3.49 (d, *J* = 2.4 Hz, 1.54H), 3.38 (s, 0.37H), 3.18 (dd, *J* = 23.1, 6.3 Hz, 0.36H), 3.00 (dd, *J* = 23.5, 5.9 Hz, 1.58H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.3, 158.3, 157.9, 156.5, 155.5, 137.0, 136.9, 132.6, 131.8, 129.9, 128.7, 128.1, 128.0, 127.6, 117.6, 117.4, 114.8, 114.6, 112.6, 112.5, 111.1, 110.9, 70.1, 70.0, 36.9, 36.9, 35.9, 35.9, 34.5, 34.3, 34.0, 33.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -101.83 (t, *J* = 23.6 Hz), -103.20 (t, *J* = 23.7 Hz).

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{20}H_{18}FO_3^-$:325.1245, found: 325.1246.

4,4-difluoro-3-phenylbut-3-enoic acid (4a)



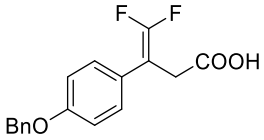
Colorless oil. Yield: 67.3 mg (85%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [14].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 3.46 (s, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-*D*) δ 176.9, 155.2 (t, *J* = 290.4 Hz), 132.8, 128.7, 127.9, 127.8, 86.7 (t, *J* = 19.5 Hz), 33.7.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.99 (d, *J* = 33.1 Hz), -88.43 (d, *J* = 34.8 Hz).

3-(4-(benzyloxy)phenyl)-4,4-difluorobut-3-enoic acid (4b)



Colorless oil. Yield: 111.9 mg (92%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

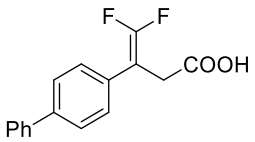
^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.95 (s, 1H), 7.52 – 7.48 (m, 2H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.07 – 7.01 (m, 2H), 5.11 (s, 2H), 3.47 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.0, 158.2, 154.8 (t, *J* = 290.7 Hz), 129.0, 128.6, 128.1, 127.5, 125.1, 115.0, 86.1 (t, *J* = 19.6 Hz), 70.0, 33.7, 33.7.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -87.99 (d, *J* = 35.0 Hz), -89.24 (d, *J* = 36.7 Hz).

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{17}H_{13}F_2O_3^-$:303.0838, found: 303.0845.

3-([1,1'-biphenyl]-4-yl)-4,4-difluorobut-3-enoic acid (4c)



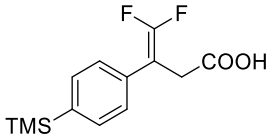
Colorless oil. Yield: 96.5 mg (88%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [14].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 4H), 7.49 – 7.41 (m, 4H), 7.40 – 7.34 (m, 1H), 3.50 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.7, 155.3 (t, *J* = 292.9 Hz), 140.6, 140.4, 131.7, 128.9, 128.2, 127.6, 127.4, 127.1, 86.4 (dd, *J* = 21.6, 18.0 Hz), 33.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.56 (d, *J* = 31.8 Hz), -87.96 (d, *J* = 34.6 Hz).

4,4-difluoro-3-(4-(trimethylsilyl)phenyl)but-3-enoic acid (4d)



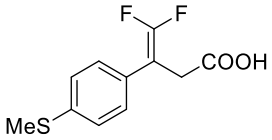
Colorless oil. Yield: 79.9 mg (74%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [14].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 3.47 (s, 2H), 0.29 (d, *J* = 1.9 Hz, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.9, 155.1 (dd, *J* = 293.8, 289.7 Hz), 140.2, 133.7, 133.1, 127.0, 86.7 (dd, *J* = 21.2, 17.7 Hz), 29.8, -1.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.43 (d, *J* = 33.4 Hz), -87.89 (d, *J* = 33.4 Hz).

4,4-difluoro-3-(4-(methylthio)phenyl)but-3-enoic acid (4e)



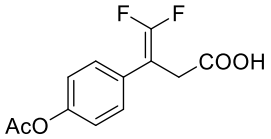
Colorless oil. Yield: 68.3 mg (70%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 (q, *J* = 8.8 Hz, 4H), 3.41 (s, 2H), 2.47 (s, 3H)**.**

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.7, 155.0 (dd, *J* = 292.9, 289.5 Hz), 138.3, 129.2, 128.2, 126.4, 86.2 (dd, *J* = 21.6, 18.0 Hz), 33.5, 15.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.85 (d, *J* = 33.5 Hz), -88.09 (d, *J* = 33.6 Hz).

3-(4-acetoxyphenyl)-4,4-difluorobut-3-enoic acid (4f)



Colorless oil. Yield: 71.7 mg (70%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

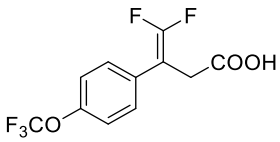
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 3.42 (t, *J* = 2.2 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.3, 169.6, 155.1 (dd, *J* = 293.2, 289.7 Hz), 150.0, 130.4, 129.0, 121.8, 86.1 (dd, *J* = 22.1, 18.2 Hz), 33.6, 15.3.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.68 (d, *J* = 33.8 Hz), -88.11 (d, *J* = 33.5 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{12}H_9F_2O_4^-$:255.0474, found: 255.0472.

4,4-difluoro-3-(4-(trifluoromethoxy)phenyl)but-3-enoic acid (4g)



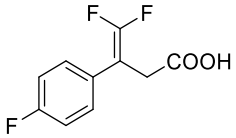
Colorless oil. Yield: 73.3 mg (65%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.43 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.3, 155.1 (dd, *J* = 293.3, 290.7 Hz), 148.6, 131.5 (t, *J* = 3.8 Hz), 129.4 (t, *J* = 3.3 Hz), 121.2, 120.5 (q, *J* = 257.7 Hz), 85.9 (dd, *J* = 22.4, 18.1 Hz), 33.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ-57.78, -86.16 (d, *J* = 31.9 Hz), -87.63 (d, *J* = 31.8 Hz).

4,4-difluoro-3-(4-fluorophenyl)but-3-enoic acid (4h)



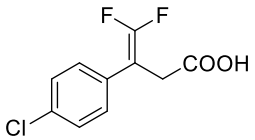
Colorless oil. Yield: 58.8 mg (68%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [15].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 3.42 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.6, 162.2 (d, *J* = 247.8 Hz), 155.0 (t, *J* = 291.3 Hz), 129.7 (dt, *J* = 7.8, 3.5 Hz), 128.7 (d, *J* = 3.9 Hz), 114.6, 85.9 (dd, *J* = 22.0, 18.6 Hz), 33.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -87.27 (d, *J* = 33.9 Hz), -88.59 (d, *J* = 34.3 Hz), -113.69.

3-(4-chlorophenyl)-4,4-difluorobut-3-enoic acid (4i)



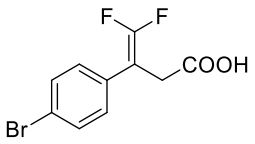
White Solid. Yield: 63.1 mg (58%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [15].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 3.41 (t, *J* = 2.2 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.5, 155.1 (dd, *J* = 293.6, 290.2 Hz), 134.4, 131.2 (t, *J* = 4.0 Hz), 129.2 (t, *J* = 3.7 Hz), 128.9, 86.0 (dd, *J* = 22.2, 18.2 Hz), 33.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.21 (d, *J* = 32.3 Hz), -87.54 (d, *J* = 33.1 Hz)**.**

3-(4-bromophenyl)-4,4-difluorobut-3-enoic acid (4j)



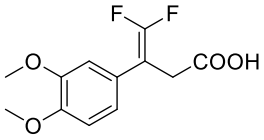
White Solid. Yield: 55.2 mg (50%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.42 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.6, 155.1 (dd, *J* = 293.7, 290.3 Hz), 131.9, 131.7 (t, *J* = 4.0 Hz), 129.5 (t, *J* = 3.6 Hz), 121.9, 86.0 (dd, *J* = 22.2, 18.0 Hz), 33.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.03 (d, *J* = 31.7 Hz), -87.38 (d, *J* = 31.8 Hz)**.**

3-(3,4-dimethoxyphenyl)-4,4-difluorobut-3-enoic acid (4k)



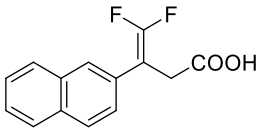
Colorless oil. Yield: 89.8 mg (87%). R_f = 0.40 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.90 – 6.82 (m, 3H), 3.86 (d, *J* = 3.9 Hz, 6H), 3.41 (t, *J* = 2.2 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.5, 154.9 (dd, *J* = 291.8, 289.0 Hz), 148.9, 148.6, 125.2, 120.3, 111.3, 111.2, 86.4 (dd, *J* = 21.5, 18.2 Hz), 55.9, 55.9, 33.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -87.99 (d, *J* = 36.4 Hz), -88.92 (d, *J* = 36.1 Hz).

4,4-difluoro-3-(naphthalen-2-yl)but-3-enoic acid (4l)



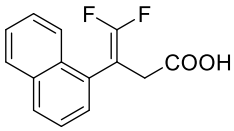
White Solid. Yield: 81.4 mg (82%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.77 (m, 4H), 7.54 – 7.46 (m, 3H), 3.57 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.9, 155.2 (t, *J* = 292.1 Hz), 133.2, 132.6, 130.1, 128.4, 128.1, 127.7, 127.0, 126.5, 126.5, 125.5, 86.8 (t, *J* = 19.7 Hz), 33.7.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.51 (d, *J* = 32.4 Hz), -88.11 (d, *J* = 33.0 Hz).

4,4-difluoro-3-(naphthalen-1-yl)but-3-enoic acid (4m)



White Solid. Yield: 72.4 mg (73%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

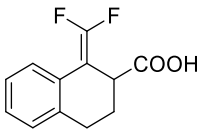
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 – 7.80 (m, 3H), 7.68 – 7.43 (m, 4H), 3.51 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 182.1, 154.8 (dd, *J* = 291.9, 289.0 Hz), 133.9, 131.3, 130.2, 129.0, 128.7, 127.9, 126.7, 126.1, 125.4, 124.7, 84.5 (t, *J* = 22.5 Hz), 35.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.02 (d, *J* = 33.5 Hz), -88.57 (d, *J* = 33.8 Hz)**.**

HRMS (ESI) *m/z*: $[M-H]^-$ Calcd. for $C_{14}H_9F_2O_2^-$:247.0576, found: 247.0571.

1-(difluoromethylene)-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (4n)



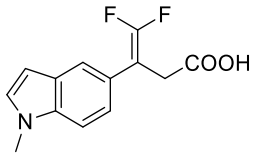
Colorless oil. Yield: 64.5 mg (72%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [15].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.80 (s, 1H), 2.95 – 2.85 (m, 1H), 2.75 (dt, *J* = 10.0, 7.5 Hz, 1H), 2.34 – 2.22 (m, 1H), 2.16 – 2.02 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 179.3, 154.4 (dd, *J* = 298.9, 286.9 Hz), 136.6, 128.9, 127.5, 127.4, 127.1, 126.7, 87.5 (dd, *J* = 22.6, 11.6 Hz), 39.5, 27.2, 25.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -84.19 (d, *J* = 34.9 Hz), -85.95 (d, *J* = 31.9 Hz).

4,4-difluoro-3-(1-methyl-1H-indol-5-yl)but-3-enoic acid (4o)



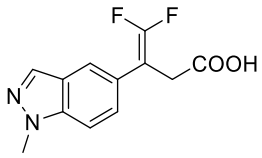
White Solid. Yield: 86.4 mg (86%). R_f = 0.30 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-d) δ 7.59 (d, J = 0.9 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.06 (d, J = 3.1 Hz, 1H), 6.48 (dd, J = 3.1, 0.9 Hz, 1H), 3.78 (s, 3H), 3.50 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.8, 155.1 (t, *J* = 289.4 Hz), 136.1, 129.6, 128.6, 123.7 (t, *J* = 3.6 Hz), 121.7 (t, *J* = 3.5 Hz), 120.6 (t, *J* = 3.5 Hz), 109.4, 101.3, 87.3 (t, *J* = 20.0 Hz), 34.5, 34.5, 32.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.17 (d, *J* = 38.1 Hz), -90.56 (d, *J* = 38.6 Hz).

4,4-difluoro-3-(1-methyl-1H-indazol-5-yl)but-3-enoic acid (4p)



White Solid. Yield: 83.7 mg (83%). R_f = 0.10 (silica gel, petroleum ether/ethyl acetate = 1:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

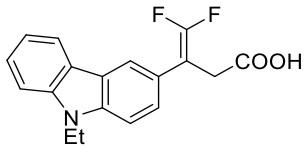
^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.06 (s, 1H), 7.74 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 4.04 (s, 3H), 3.44 (s, 2H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 171.8, 154.5 (t, *J* = 287.5 Hz), 139.3, 133.1, 126.7, 125.4, 124.0, 120.7, 110.4, 88.9 (dd, *J* = 21.4, 16.8 Hz), 35.9, 34.4.

^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ -90.11 (d, *J* = 41.2 Hz), -92.16 (d, *J* = 41.3 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{12}H_9F_2N_2O_2^-$:251.0638, found: 251.0634.

3-(9-ethyl-9H-carbazol-3-yl)-4,4-difluorobut-3-enoic acid (4q)



Colorless oil. Yield: 103.3 mg (82%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v).

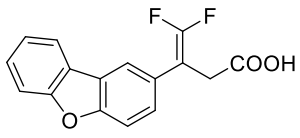
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 – 8.09 (m, 1H), 8.07 (s, 1H), 7.50 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.27 – 7.20 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.56 (d, *J* = 2.3 Hz, 2H), 1.41 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 177.0, 155.1 (t, *J* = 289.9 Hz), 140.4, 139.4, 126.1, 125.6, 123.1, 122.8, 120.7, 120.1, 119.2, 108.7, 108.7, 87.2 (t, *J* = 20.3 Hz), 37.7, 34.5, 13.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.72 (d, *J* = 37.9 Hz), -90.29 (d, *J* = 38.0 Hz).

HRMS (ESI) *m/z*: [M-H]$^-$ Calcd. for $C_{18}H_{14}F_2NO_2^-$:314.0998, found: 314.0999.

3-(dibenzo[b,d]furan-2-yl)-4,4-difluorobut-3-enoic acid (4r)



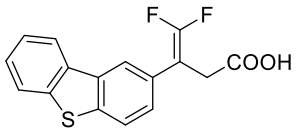
White Solid. Yield: 86.4 mg (75%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [14].

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.24 – 8.12 (m, 2H), 7.76 – 7.65 (m, 2H), 7.58 – 7.50 (m, 2H), 7.44 – 7.38 (m, 1H), 3.51 (s, 2H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 171.8, 156.4, 155.2, 154.6 (t, *J* = 288.1 Hz), 128.4, 128.0, 124.3, 123.8, 123.8, 121.8, 121.3, 112.3, 88.8 (dd, *J* = 21.7, 16.8 Hz), 34.4.

^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ -89.73 (d, *J* = 39.9 Hz), -91.68 (d, *J* = 39.9 Hz).

3-(dibenzo[b,d]thiophen-2-yl)-4,4-difluorobut-3-enoic acid (4s)



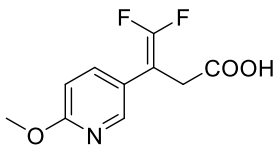
White Solid. Yield: 93.6 mg (77%). R_f = 0.20 (silica gel, petroleum ether/ethyl acetate = 3:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 5:1, v/v). The spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.39 (s, 2H), 8.15 – 7.92 (m, 2H), 7.65 – 7.34 (m, 3H), 3.57 (s, 2H).

^{13}C NMR (151 MHz, DMSO-*D*$_6$) δ 171.8, 154.7 (t, *J* = 288.2 Hz), 139.5, 138.4, 135.8, 135.2, 130.1, 127.9, 127.3, 125.4, 123.6, 122.7, 121.9, 88.8 (dd, *J* = 21.7, 16.4 Hz), 34.1.

^{19}F NMR (565 MHz, DMSO-*d*$_6$) δ -89.05 (d, *J* = 38.5 Hz), -90.96 (d, *J* = 38.3 Hz)**.**

4,4-difluoro-3-(6-methoxypyridin-3-yl)but-3-enoic acid (4t)



Colorless oil. Yield: 34.8 mg (38%). R_f = 0.10 (silica gel, petroleum ether/ethyl acetate = 2:1, v/v), column chromatography (silica gel, 0.1% AcOH in petroleum ether/ethyl acetate = 1:1, v/v). The

spectroscopic properties of this compound were consistent with the data reported in the literature [16].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.78 (br, 1H), 8.15 (d, *J* = 2.6 Hz, 1H), 7.59 (dd, *J* = 9.3, 2.0 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 3.39 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.8, 163.4, 155.9 (m), 145.7, 138.8, 122.2, 110.9, 84.0 (dd, J = 23.0, 18.7 Hz), 53.9, 33.5.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -86.96 (d, *J* = 33.3 Hz), -88.21 (d, *J* = 35.5 Hz).

6. Reference

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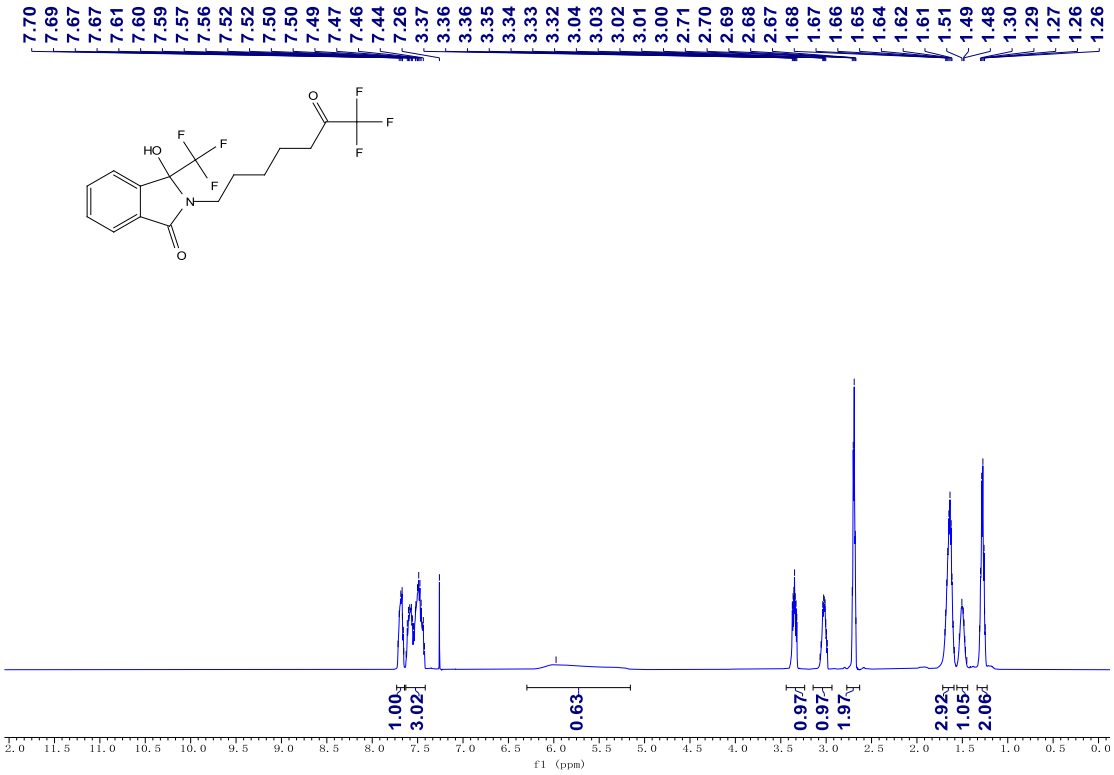
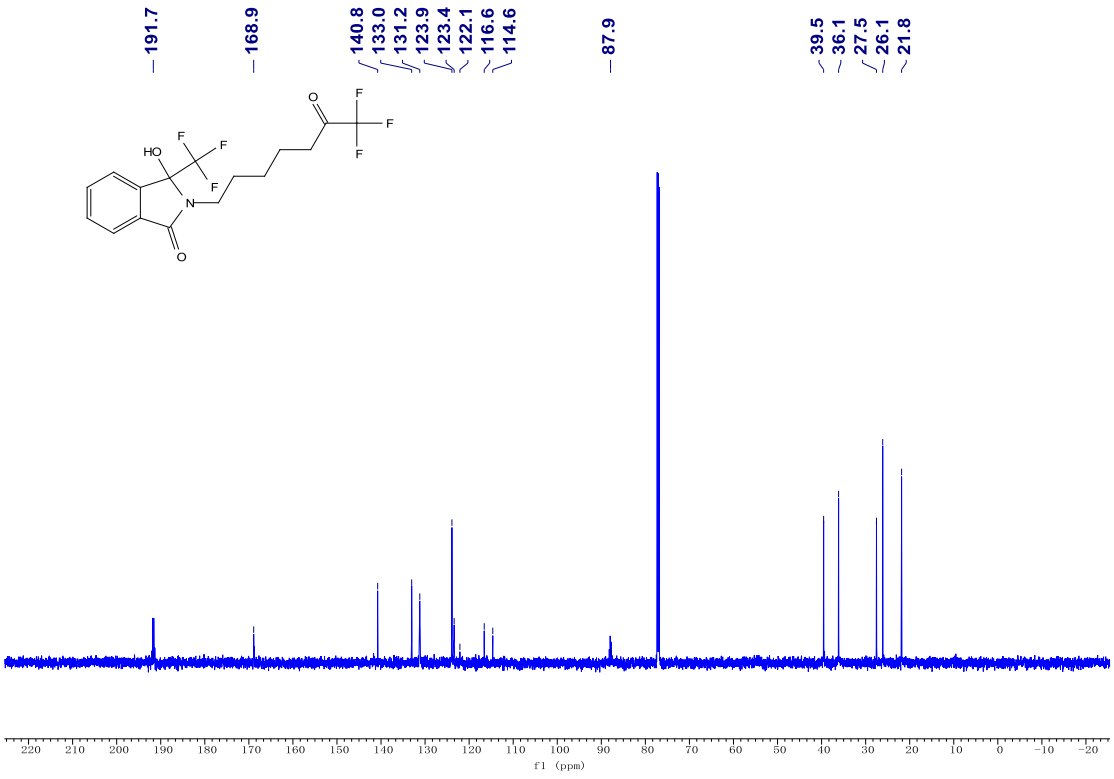
7. NMR Spectra

^{1}H NMR Spectra of 1E (600 MHz, Chloroform-*d*)

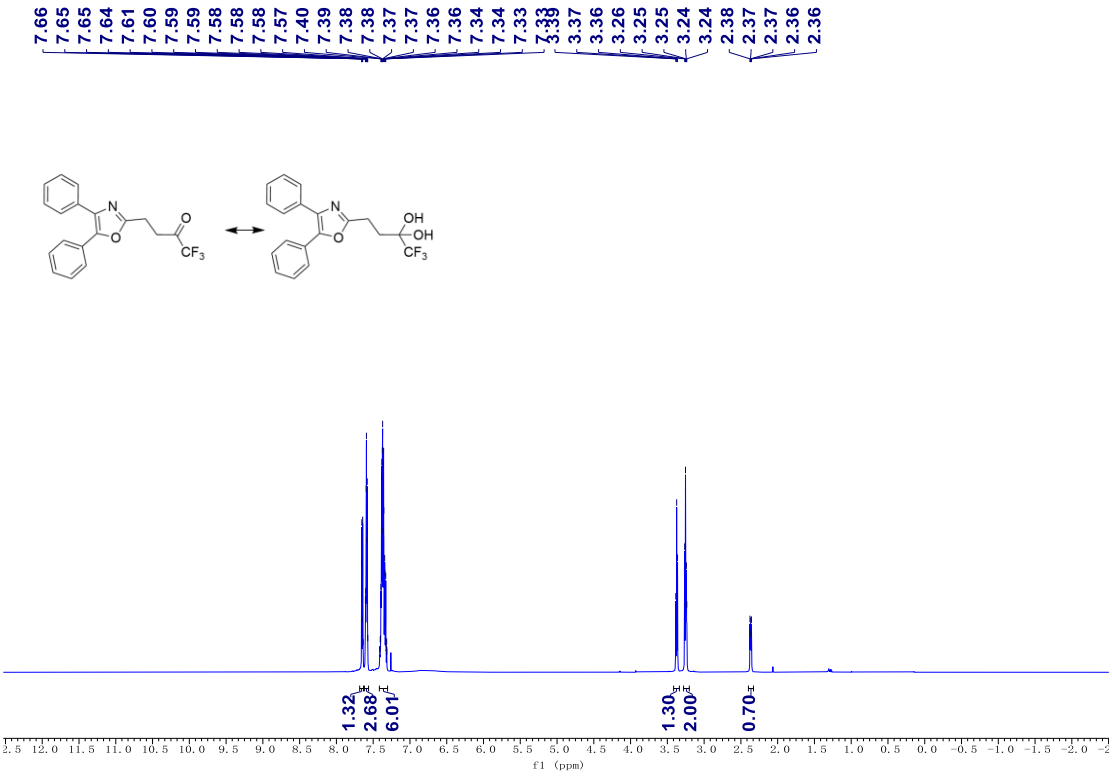


^{13}C NMR Spectra of 1E (151 MHz, Chloroform-*d*)

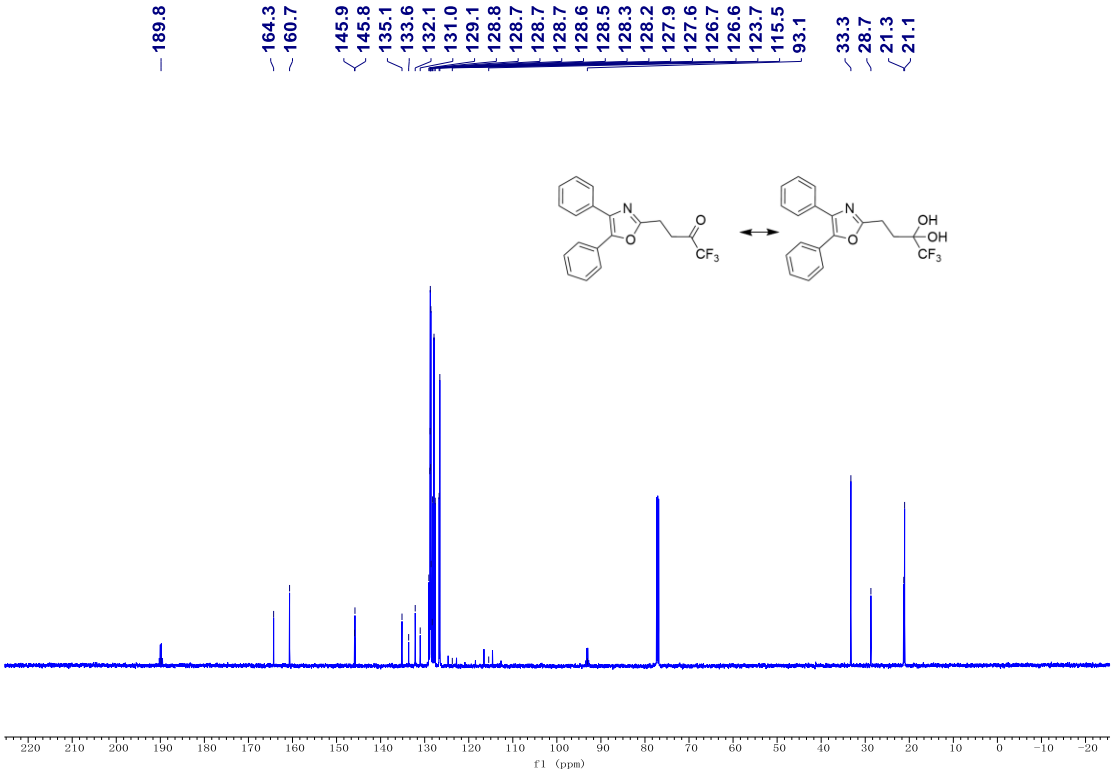


^{19}F NMR Spectra of 1E (565 MHz, Chloroform-*d*)

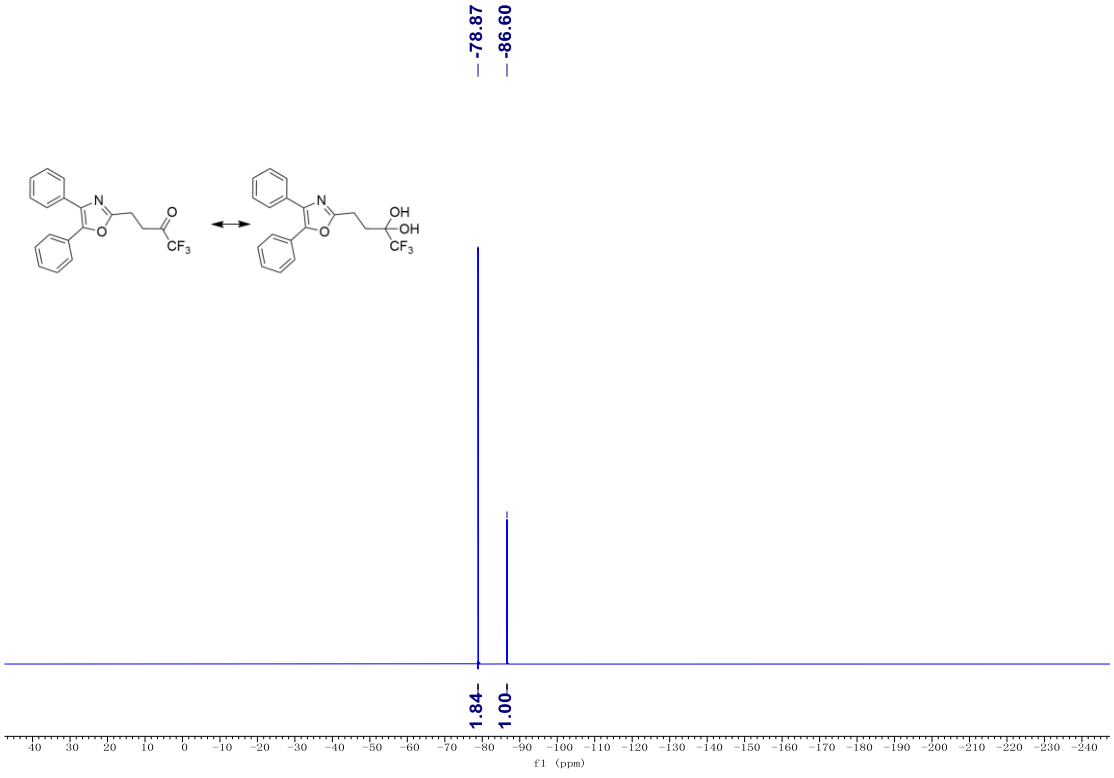
^{1}H NMR Spectra of 1G (600 MHz, Chloroform-*d*)



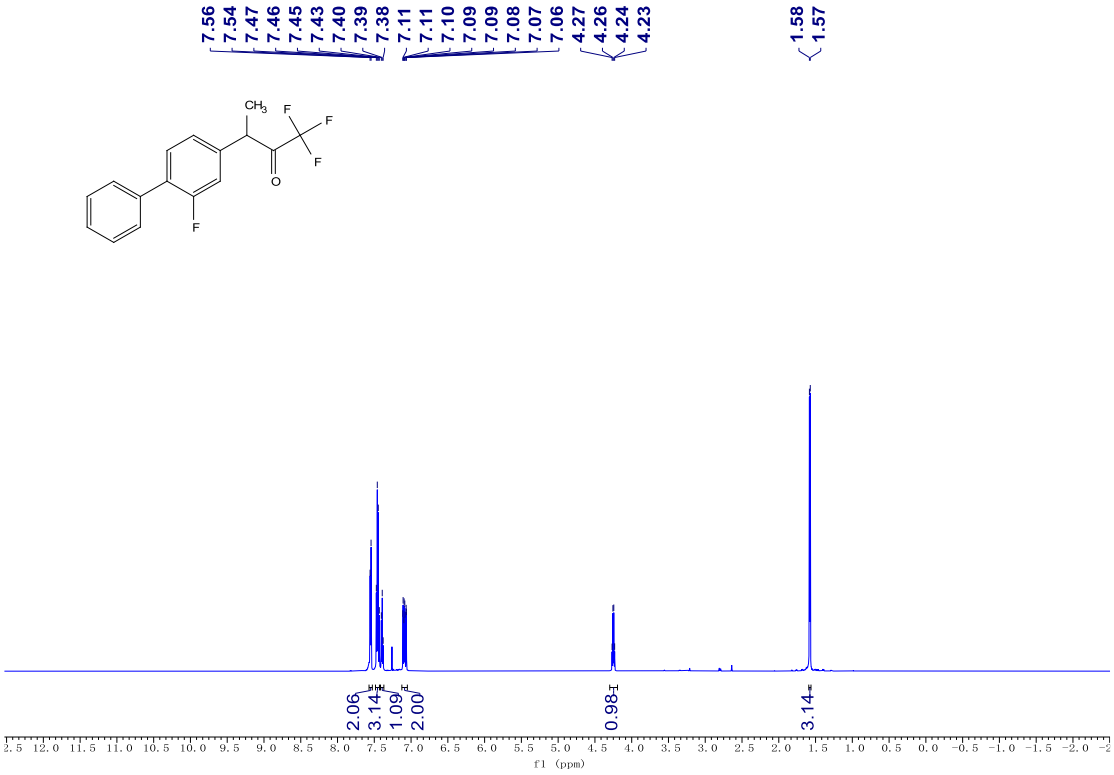
^{13}C NMR Spectra of 1G (151 MHz, Chloroform-*d*)



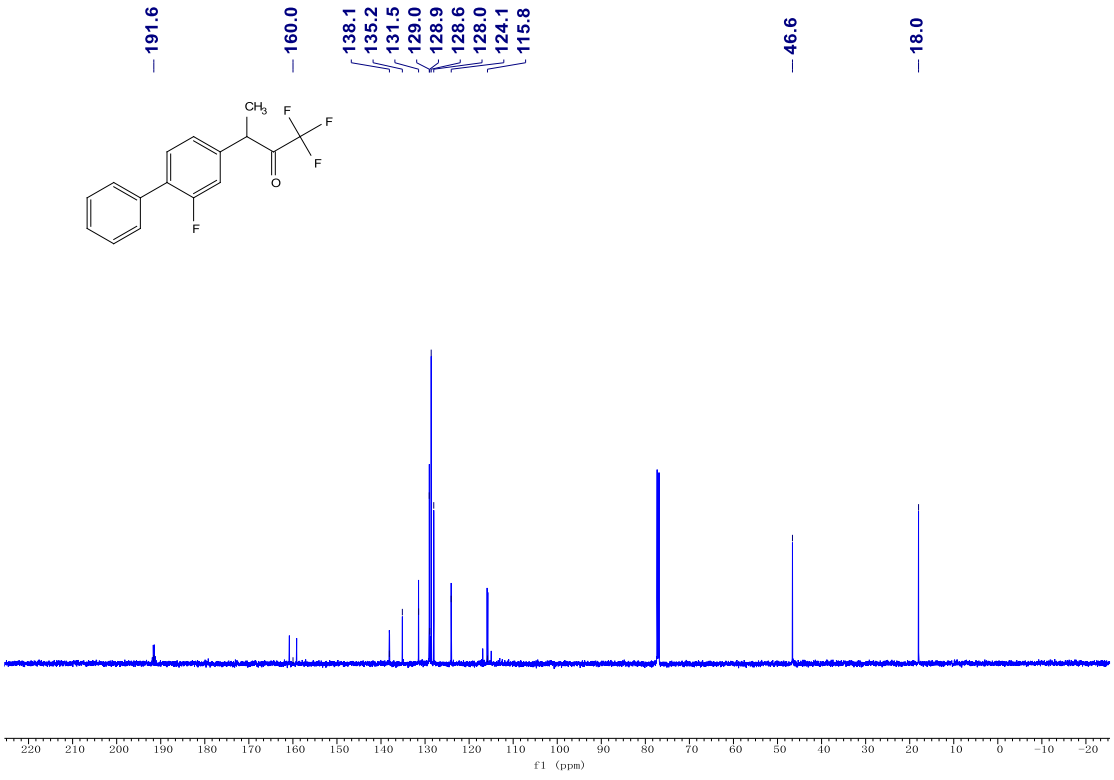
^{19}F NMR Spectra of 1G (565 MHz, Chloroform-*d*)



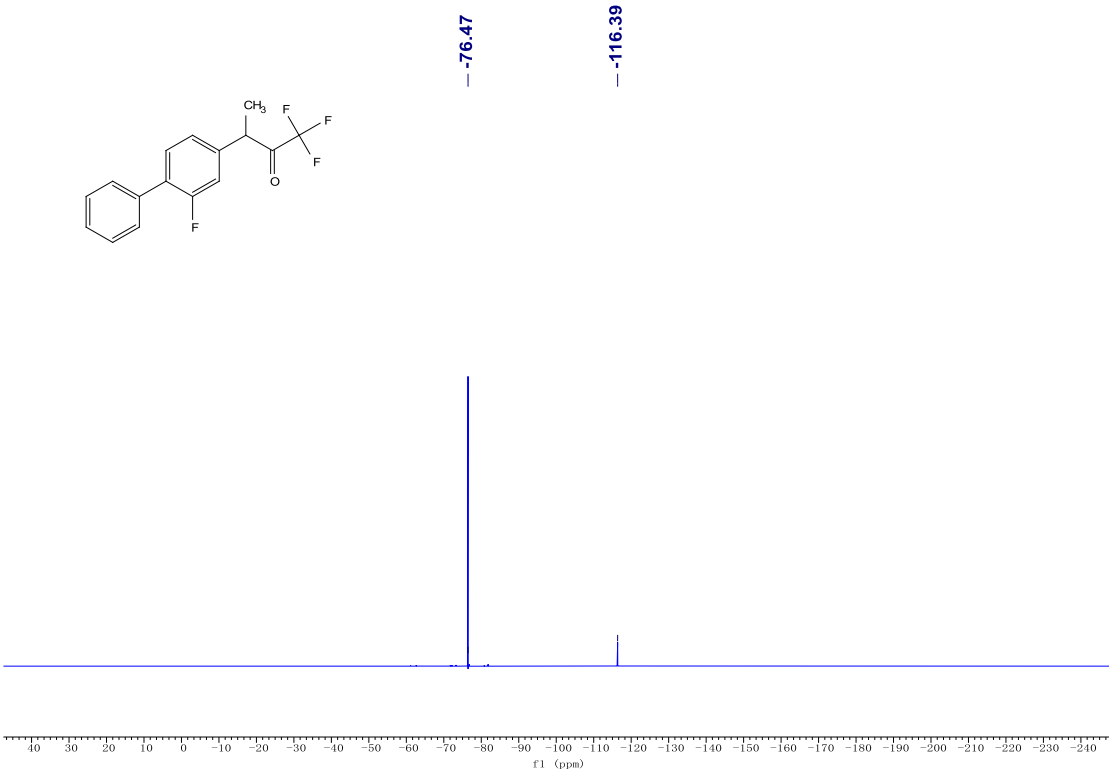
^{1}H NMR Spectra of 1I (600 MHz, Chloroform-*d*)



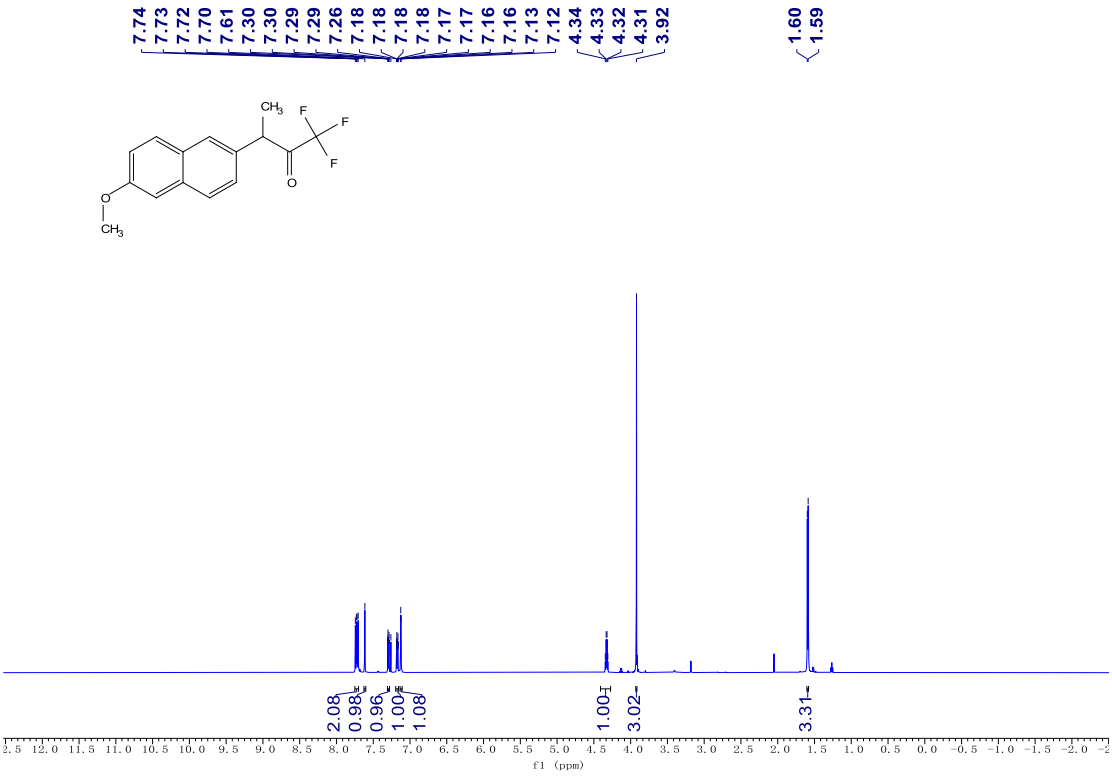
^{13}C NMR Spectra of 1I (151 MHz, Chloroform-*d*)



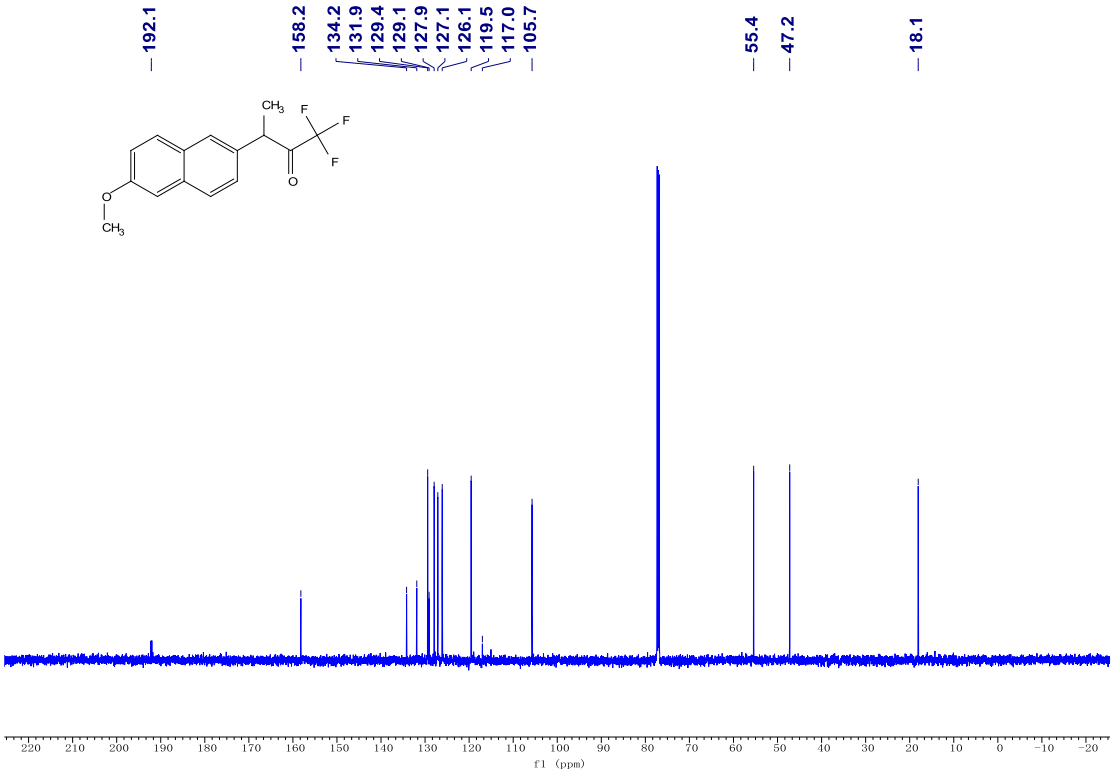
^{19}F NMR Spectra of 1I (565 MHz, Chloroform-*d*)



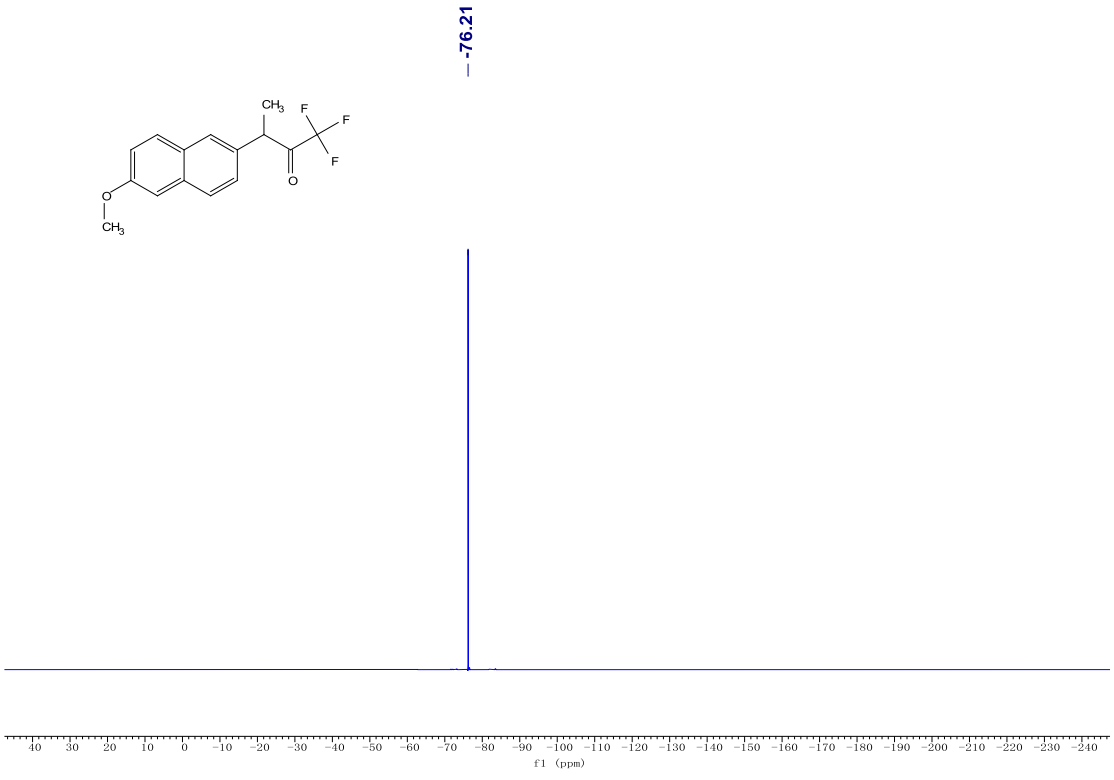
^{1}H NMR Spectra of 1J (600 MHz, Chloroform-*d*)



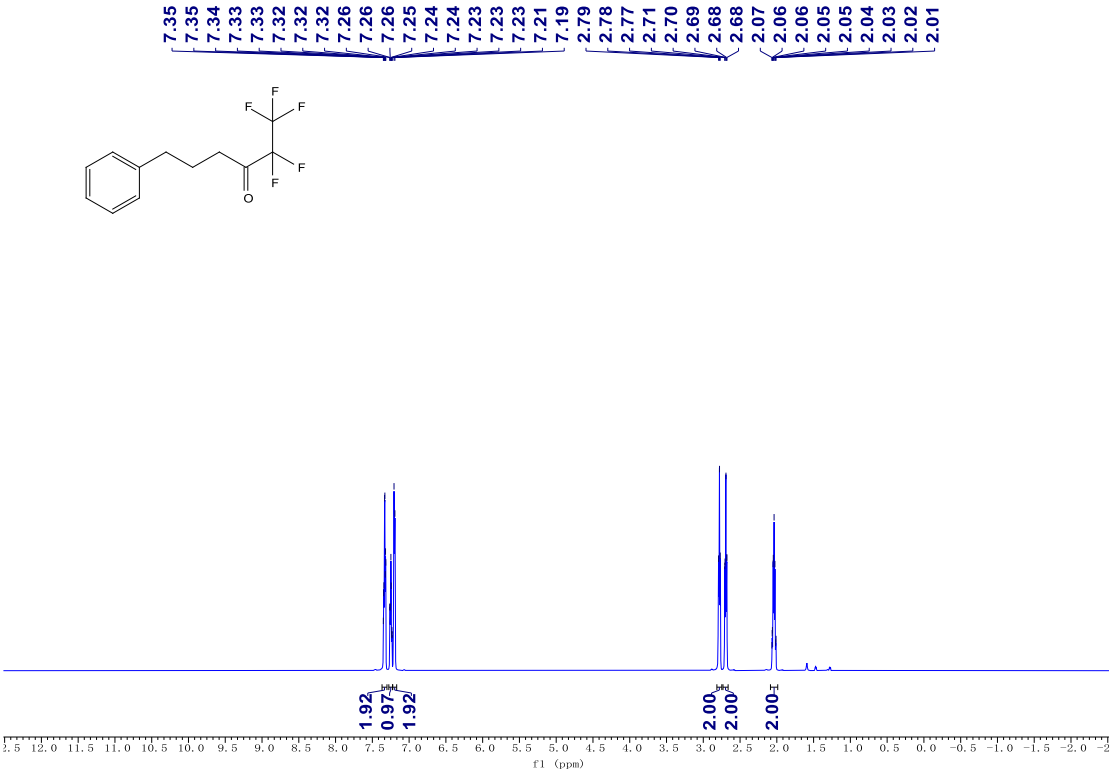
^{13}C NMR Spectra of 1J (151 MHz, Chloroform-*d*)



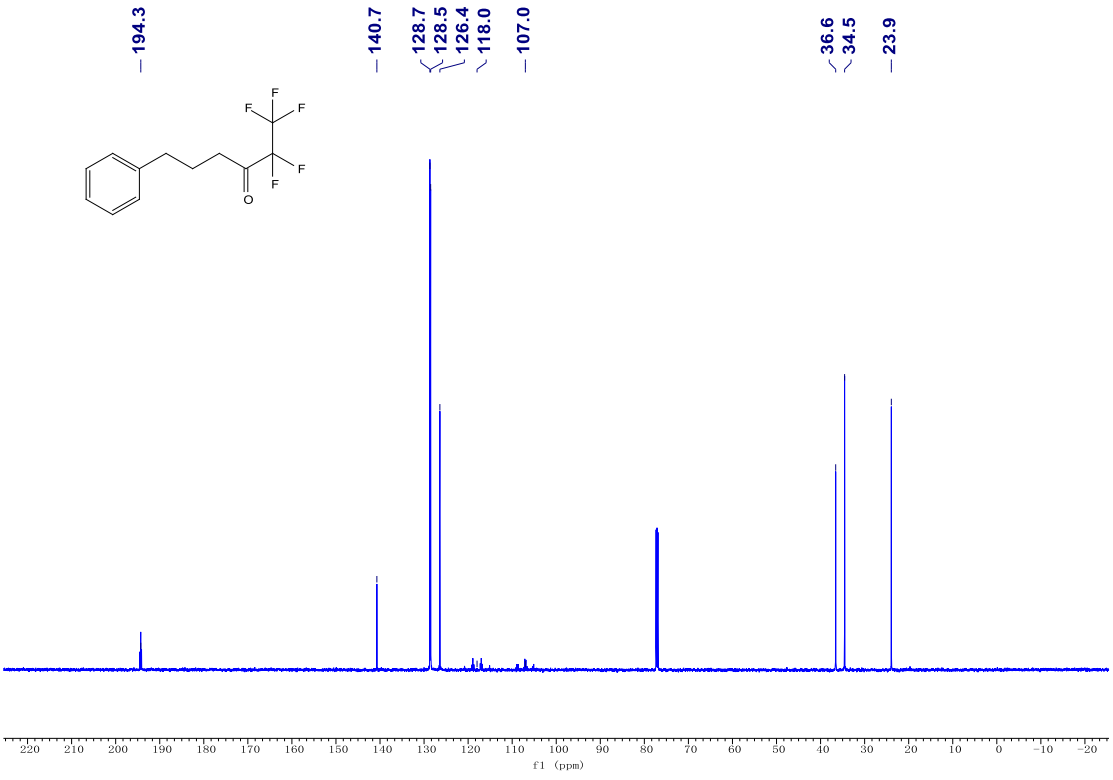
^{19}F NMR Spectra of 1J (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 1L (600 MHz, Chloroform-*d*)

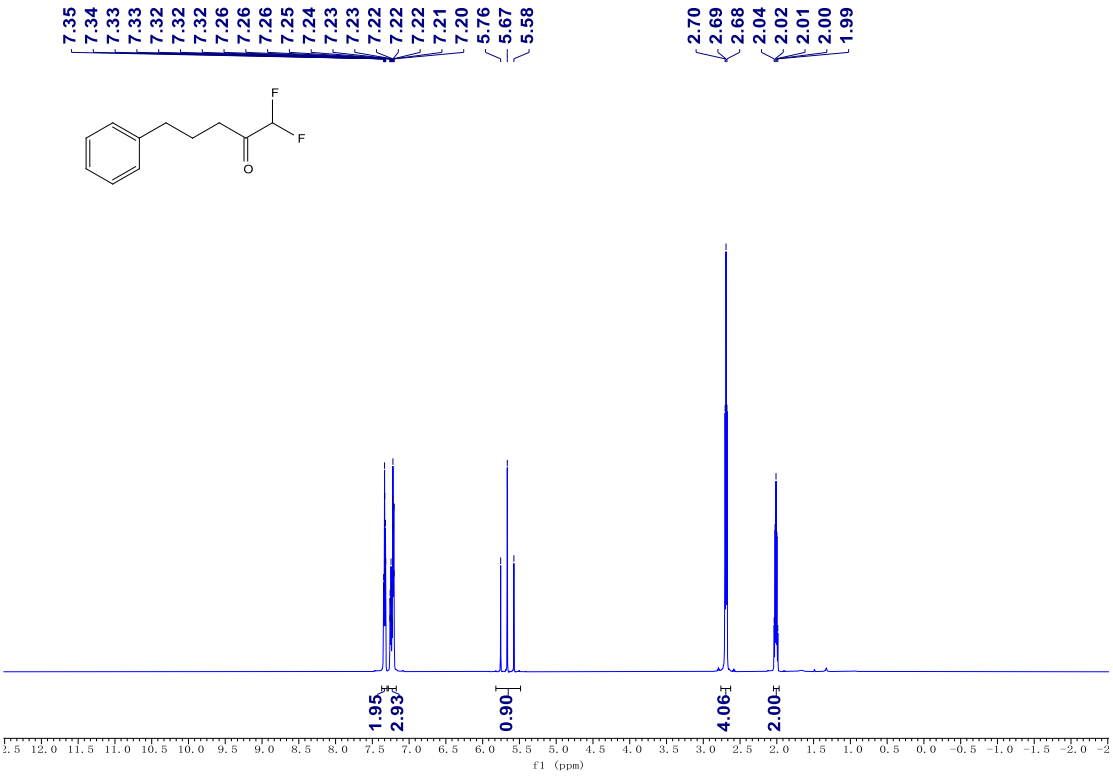


^{13}C NMR Spectra of 1L (151 MHz, Chloroform-*d*)

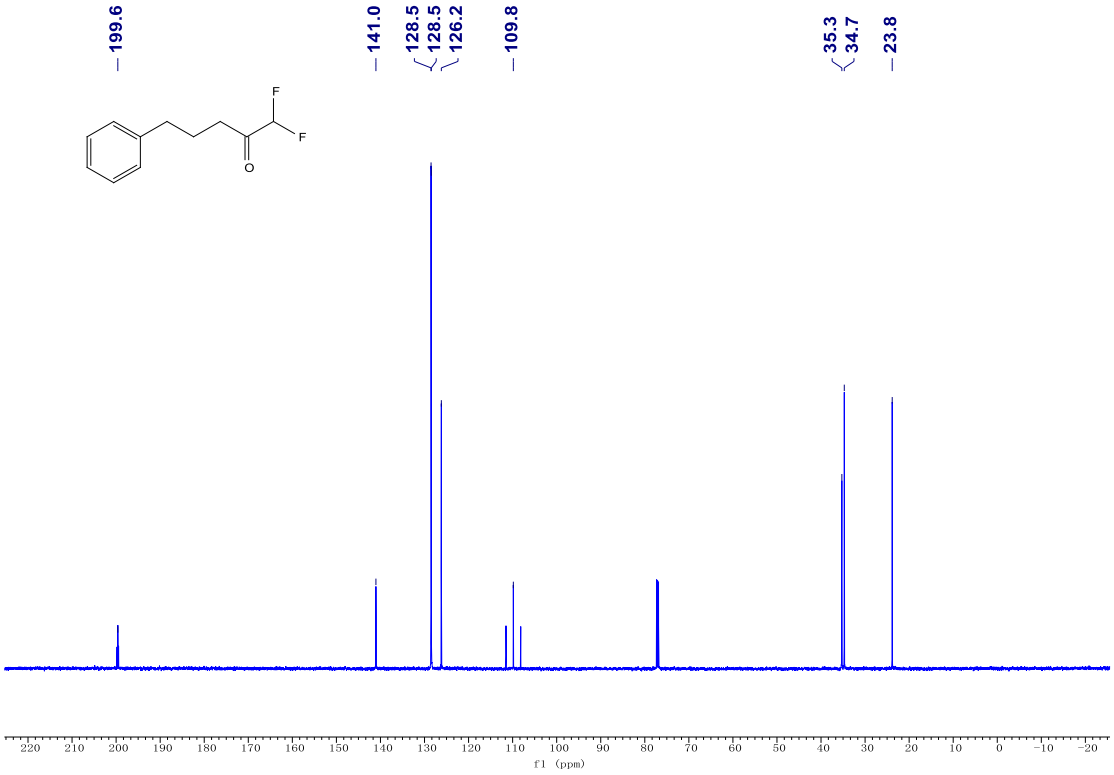


^{19}F NMR Spectra of 1L (565 MHz, Chloroform-*d*)

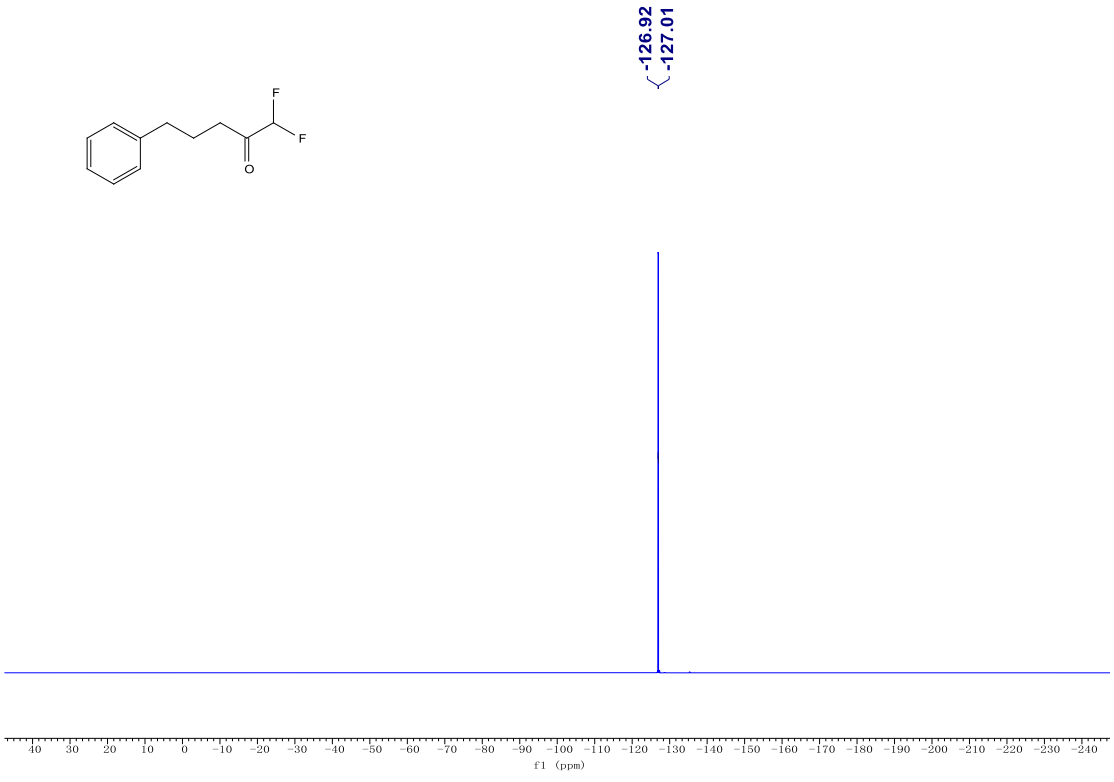
^{1}H NMR Spectra of 1Q (600 MHz, Chloroform-*d*)



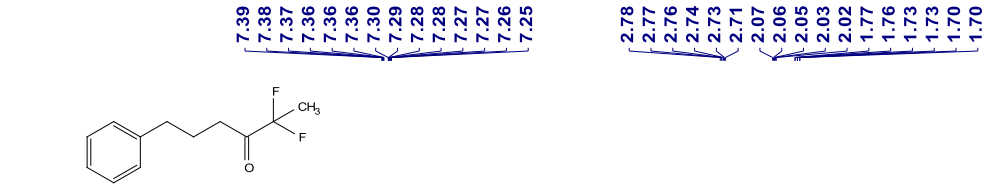
^{13}C NMR Spectra of 1Q (151 MHz, Chloroform-*d*)

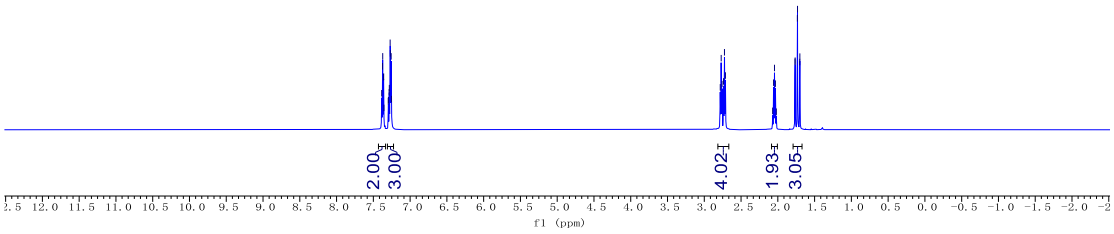


^{19}F NMR Spectra of 1Q (565 MHz, Chloroform-*d*)

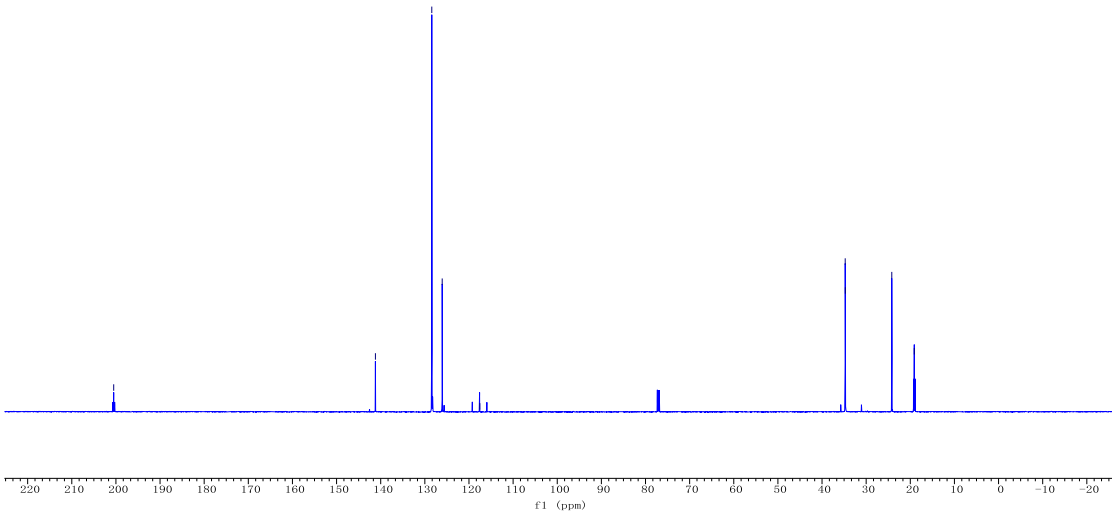


^{1}H NMR Spectra of 1R (600 MHz, Chloroform-*d*)



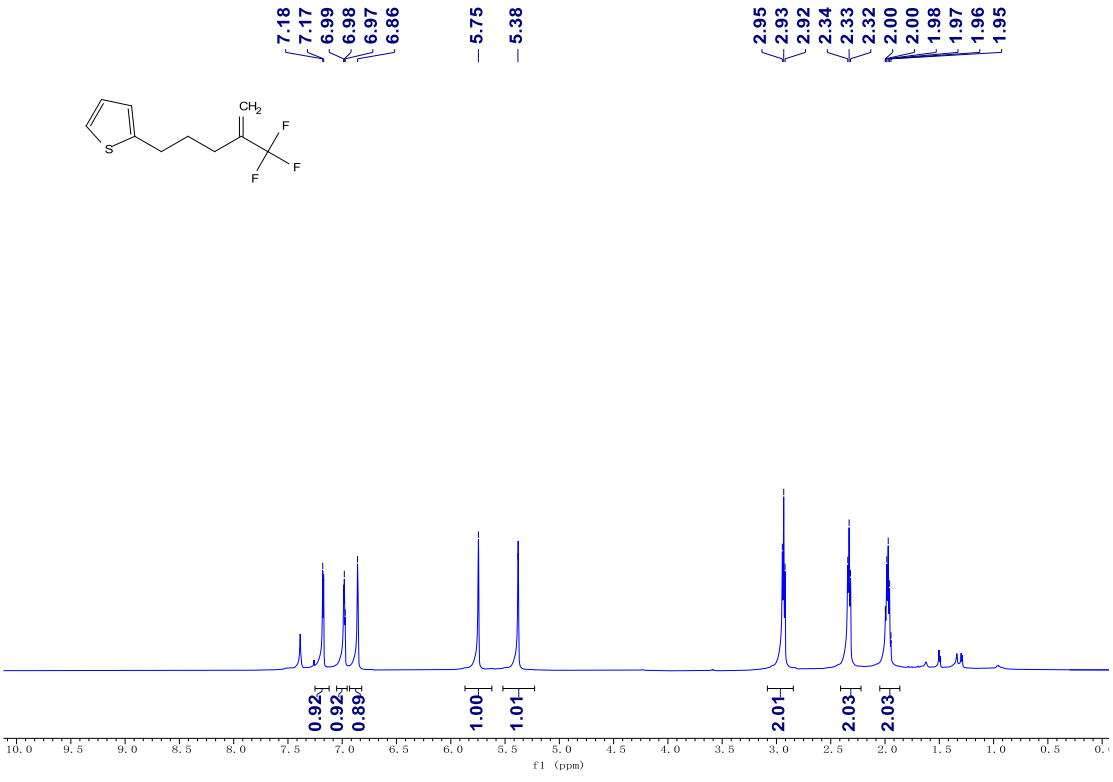


^{13}C NMR Spectra of 1R (151 MHz, Chloroform-*d*)

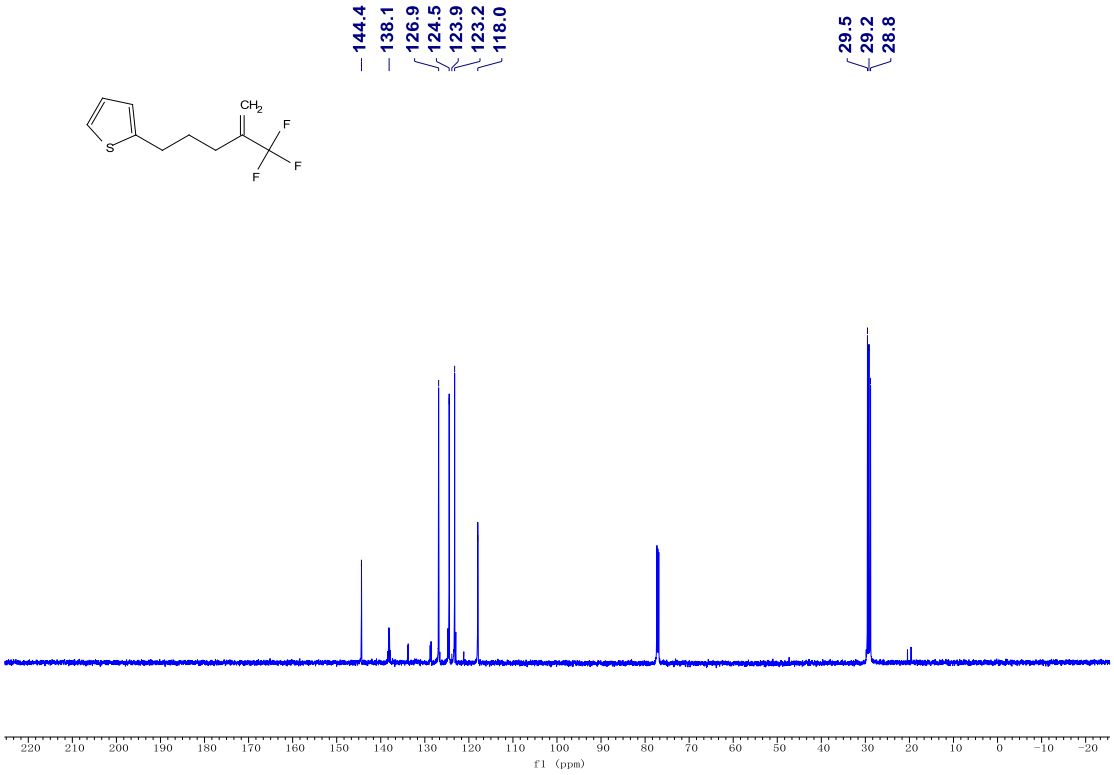


^{19}F NMR Spectra of 1R (565 MHz, Chloroform-*d*)

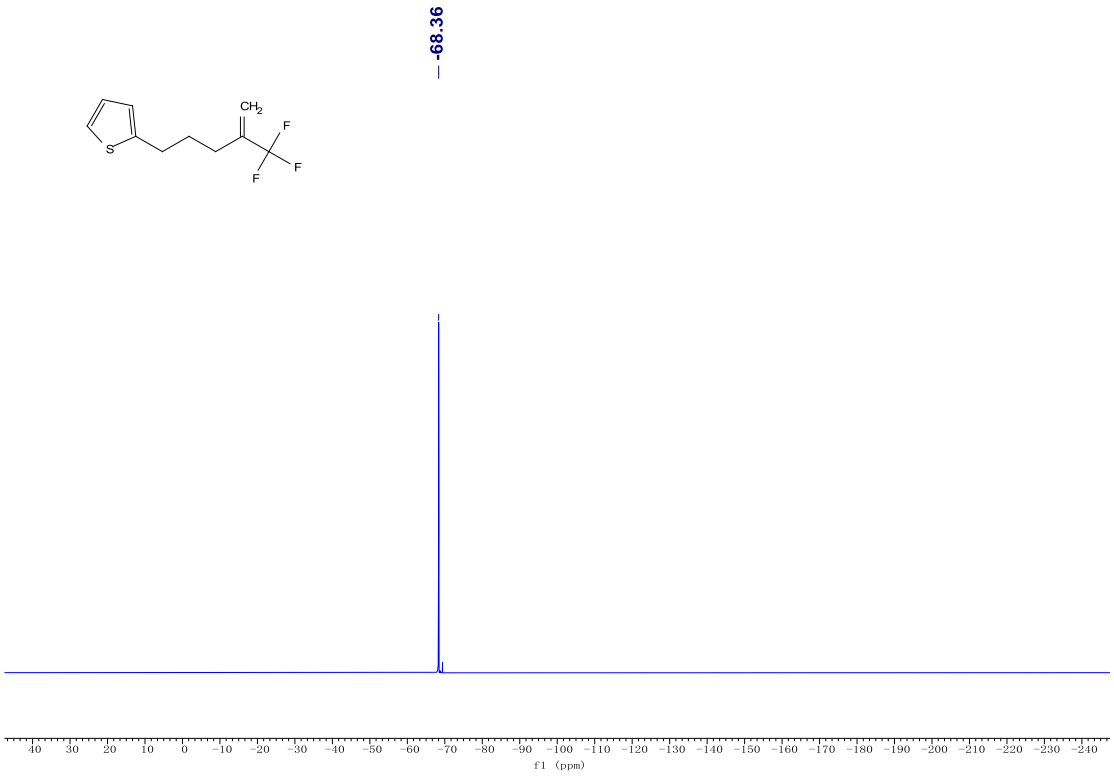
^{1}H NMR Spectra of 1b (600 MHz, Chloroform-*d*)



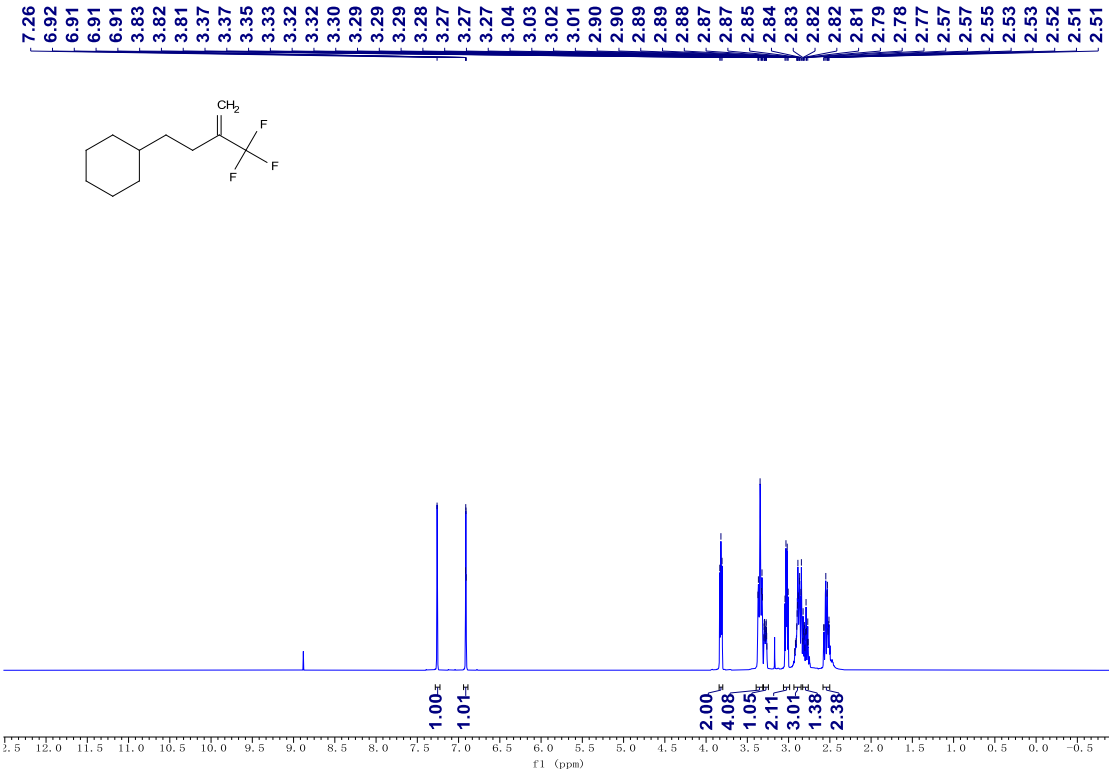
^{13}C NMR Spectra of 1b (151 MHz, Chloroform-*d*)



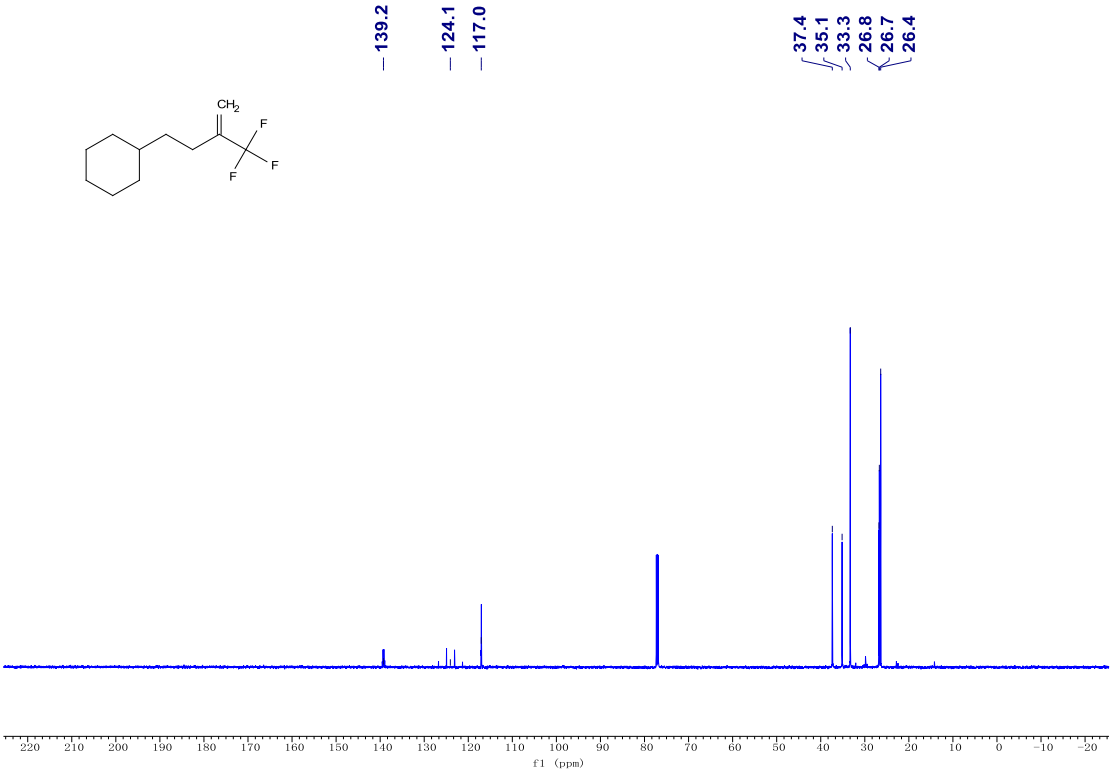
^{19}F NMR Spectra of 1b (565 MHz, Chloroform-*d*)



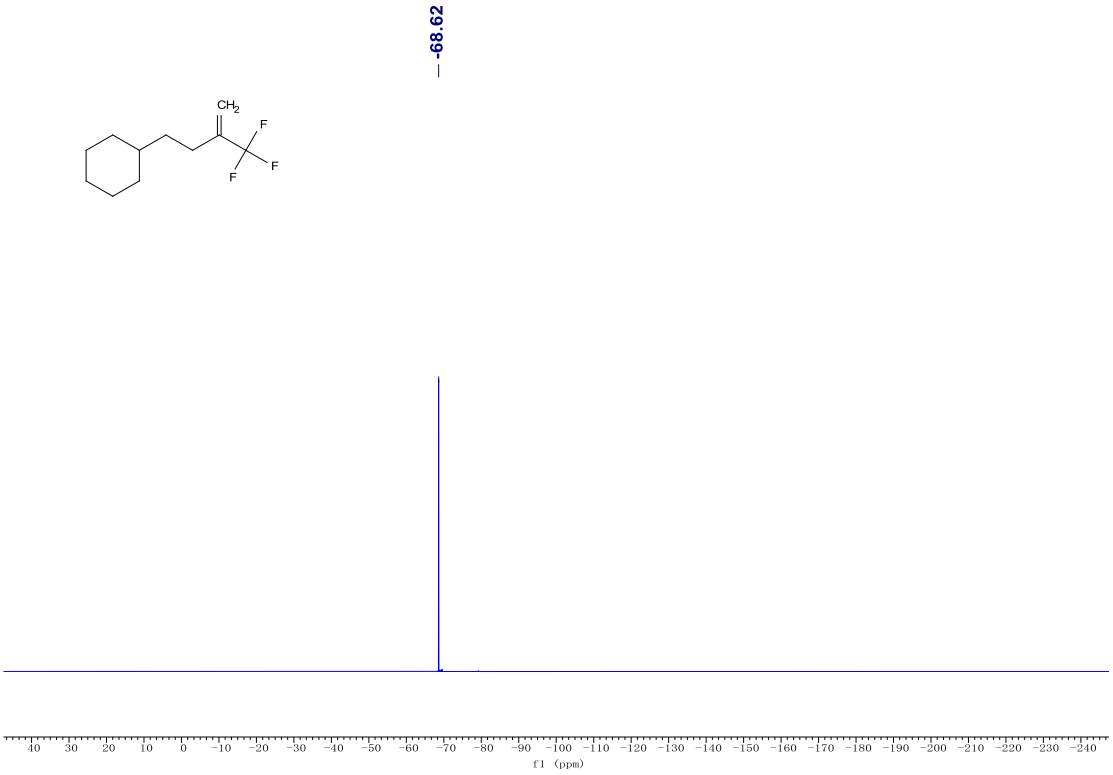
^{1}H NMR Spectra of 1c (600 MHz, Chloroform-*d*)



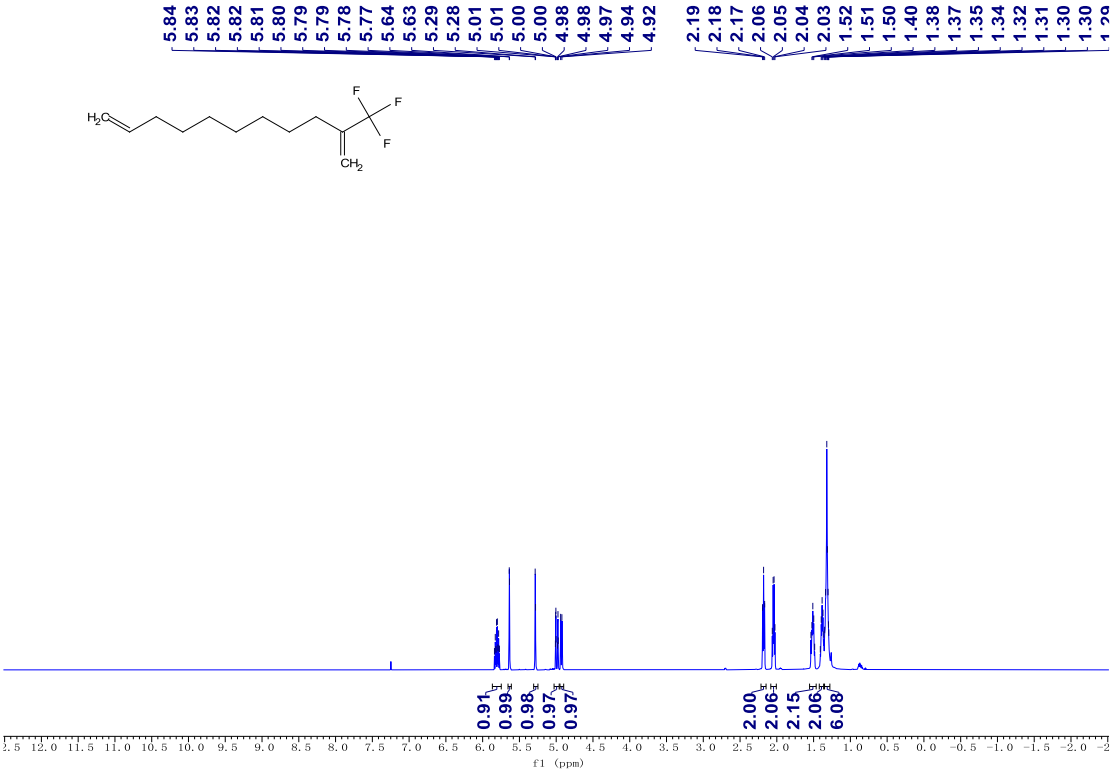
^{13}C NMR Spectra of 1c (151 MHz, Chloroform-*d*)



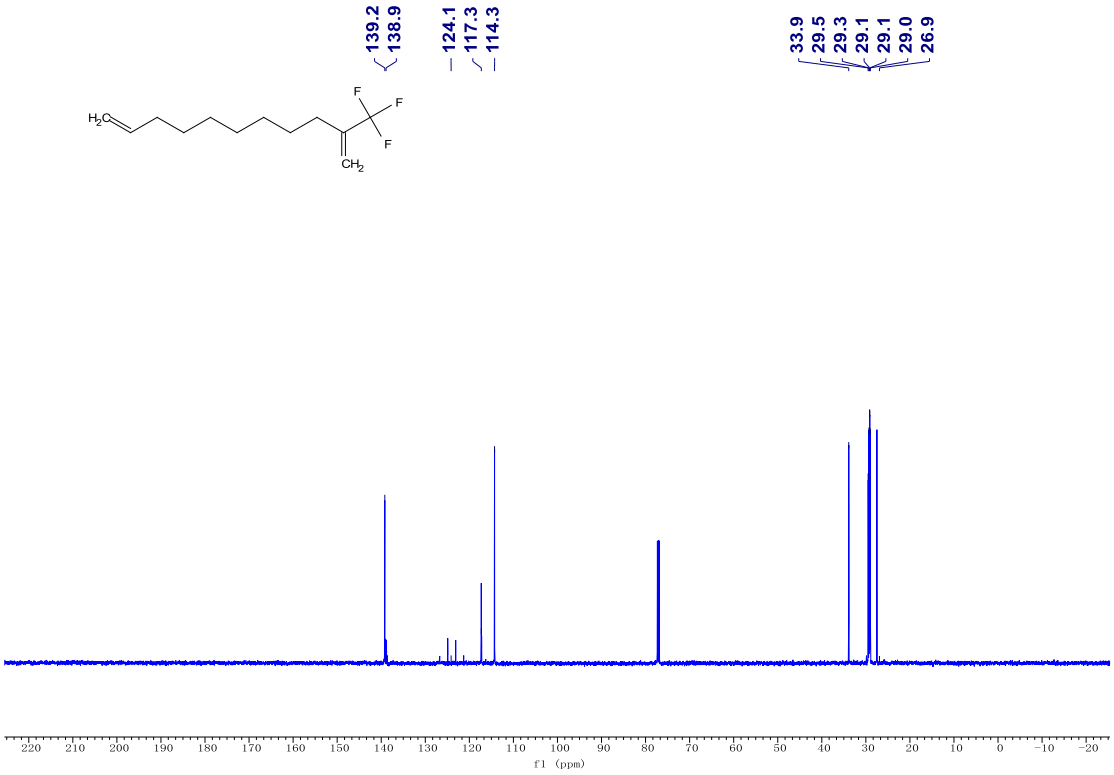
^{19}F NMR Spectra of 1c (565 MHz, Chloroform-*d*)



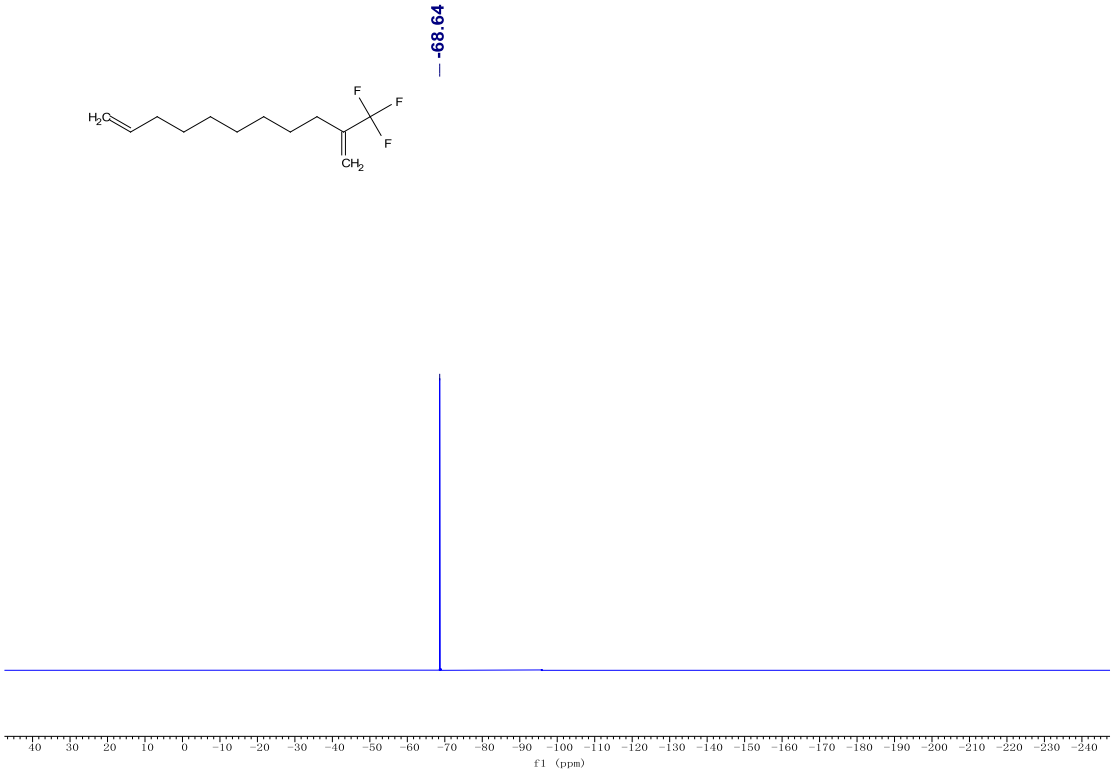
^{1}H NMR Spectra of 1d (600 MHz, Chloroform-*d*)



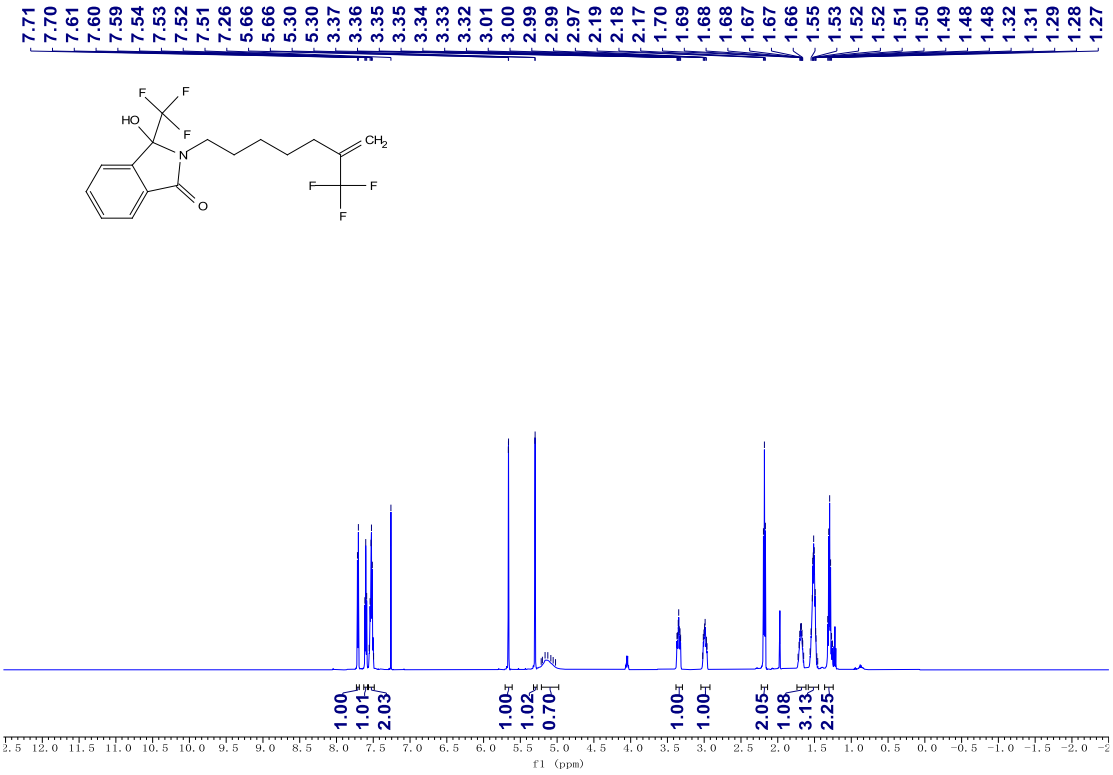
^{13}C NMR Spectra of 1d (151 MHz, Chloroform-*d*)



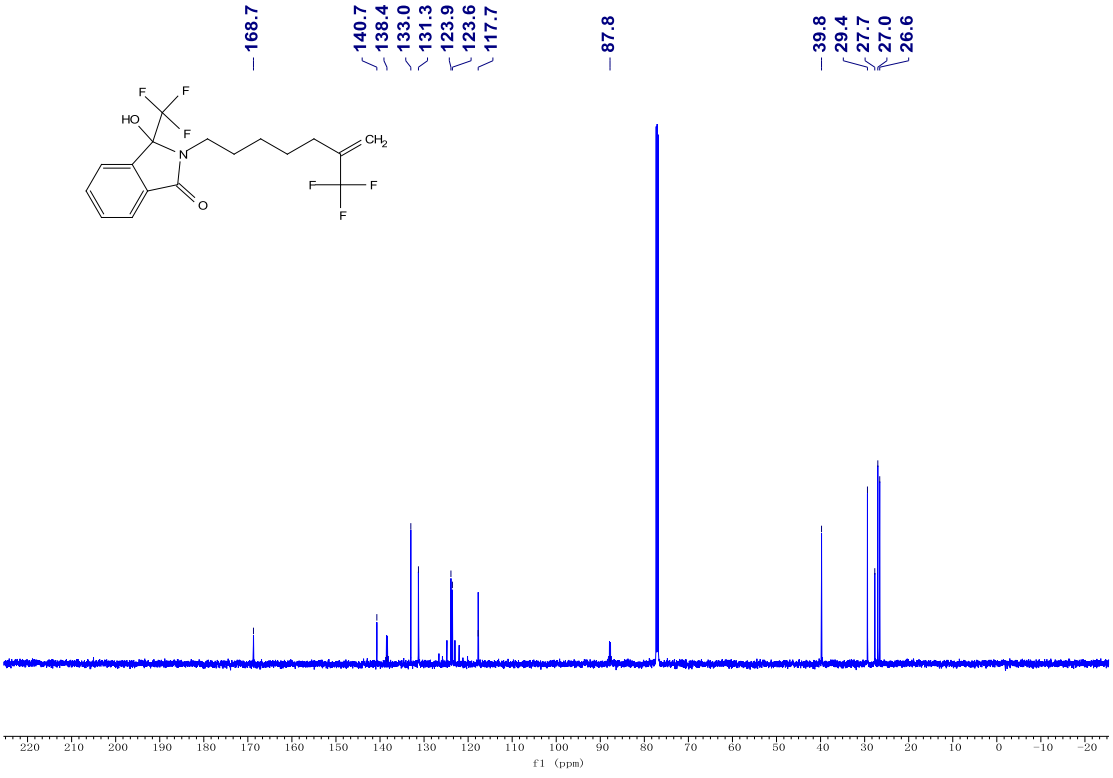
^{19}F NMR Spectra of 1d (565 MHz, Chloroform-*d*)



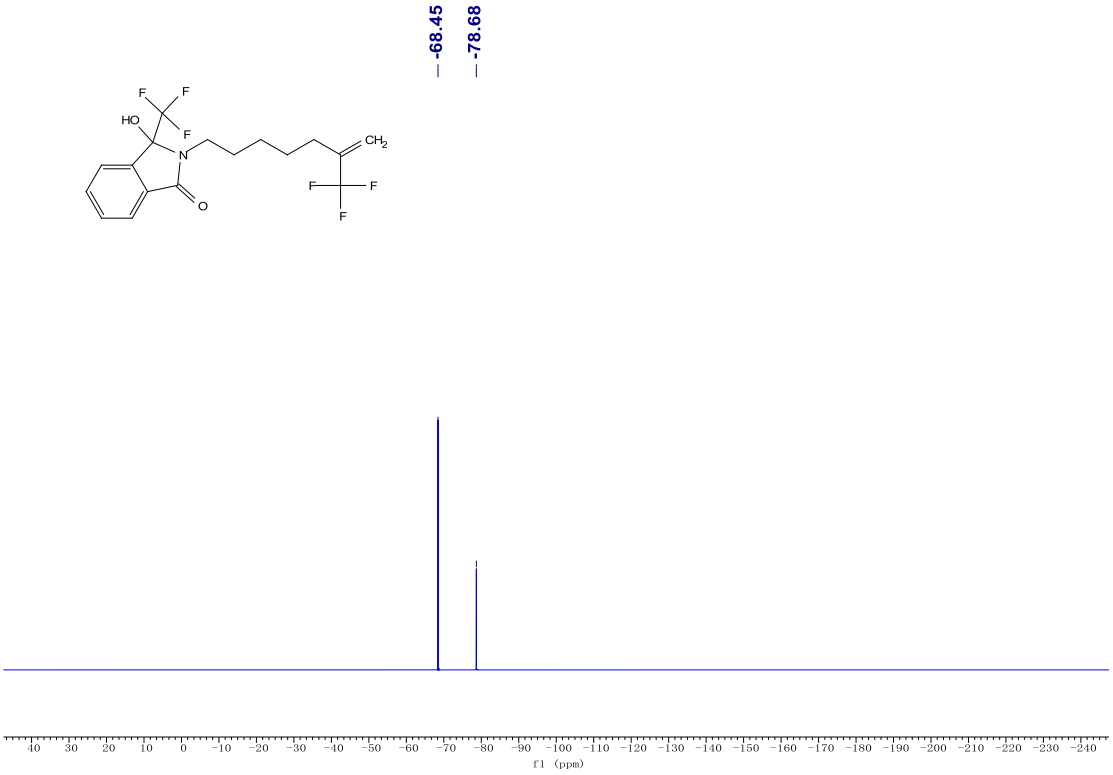
^{1}H NMR Spectra of 1e (600 MHz, Chloroform-*d*)



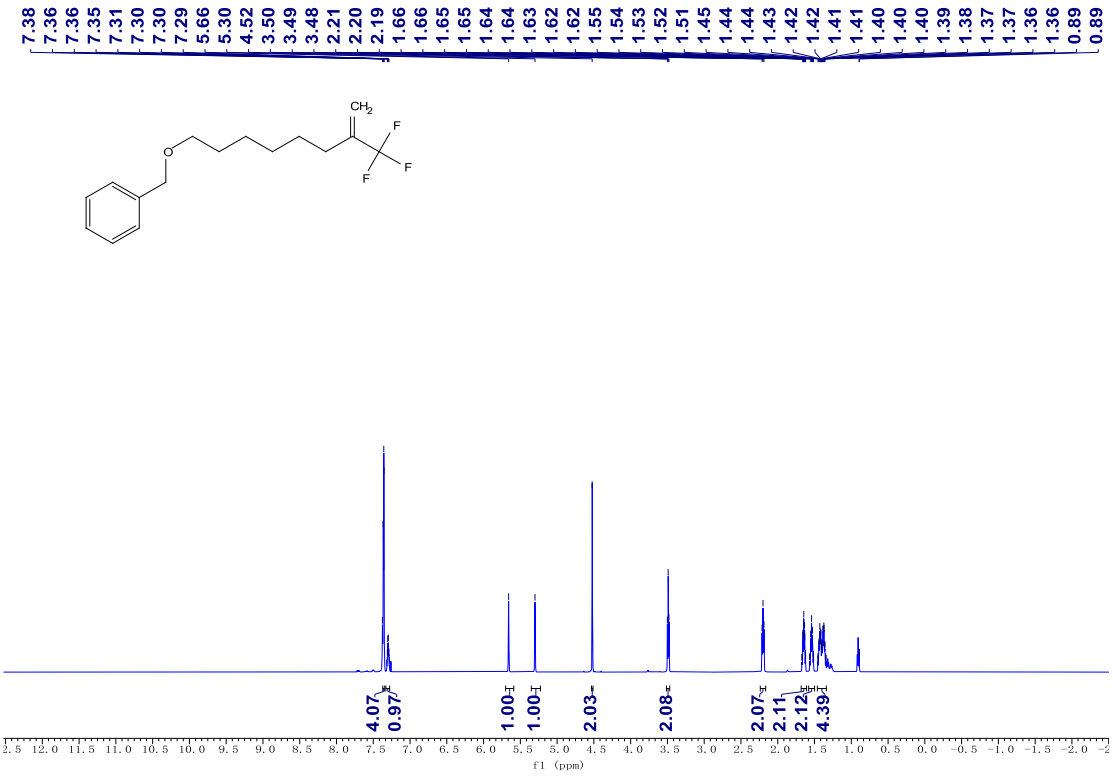
^{13}C NMR Spectra of 1e (151 MHz, Chloroform-*d*)



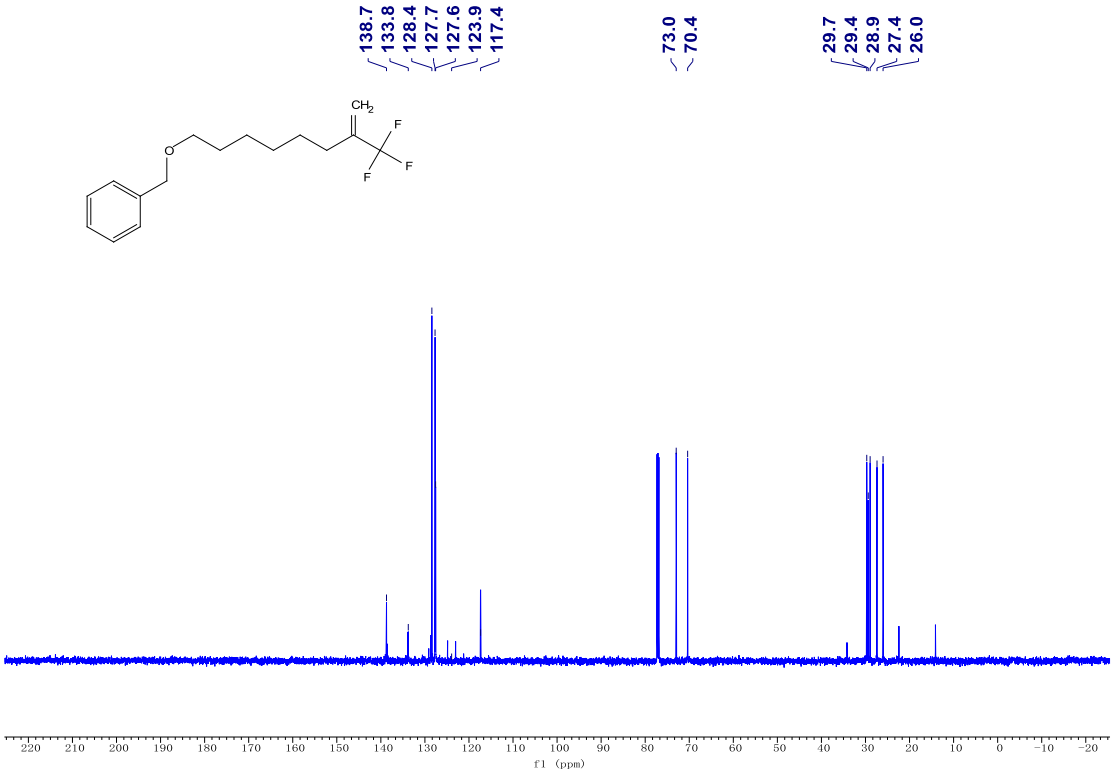
^{19}F NMR Spectra of 1e (565 MHz, Chloroform-*d*)



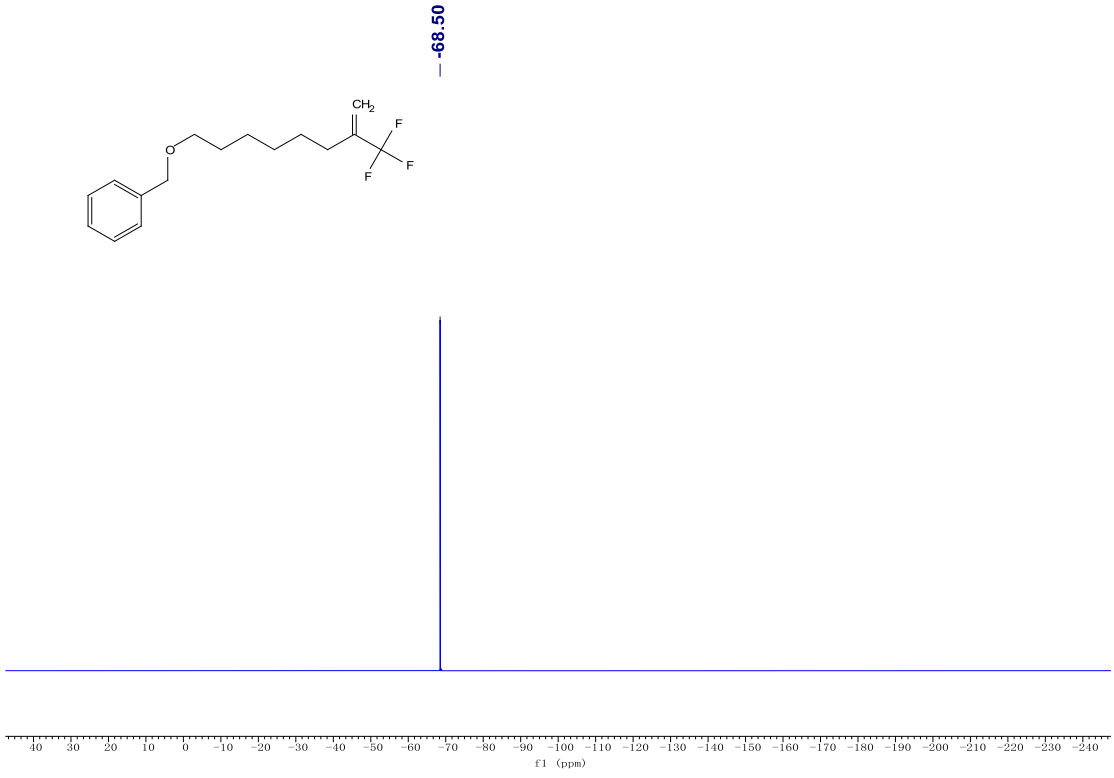
^{1}H NMR Spectra of 1f (600 MHz, Chloroform-*d*)



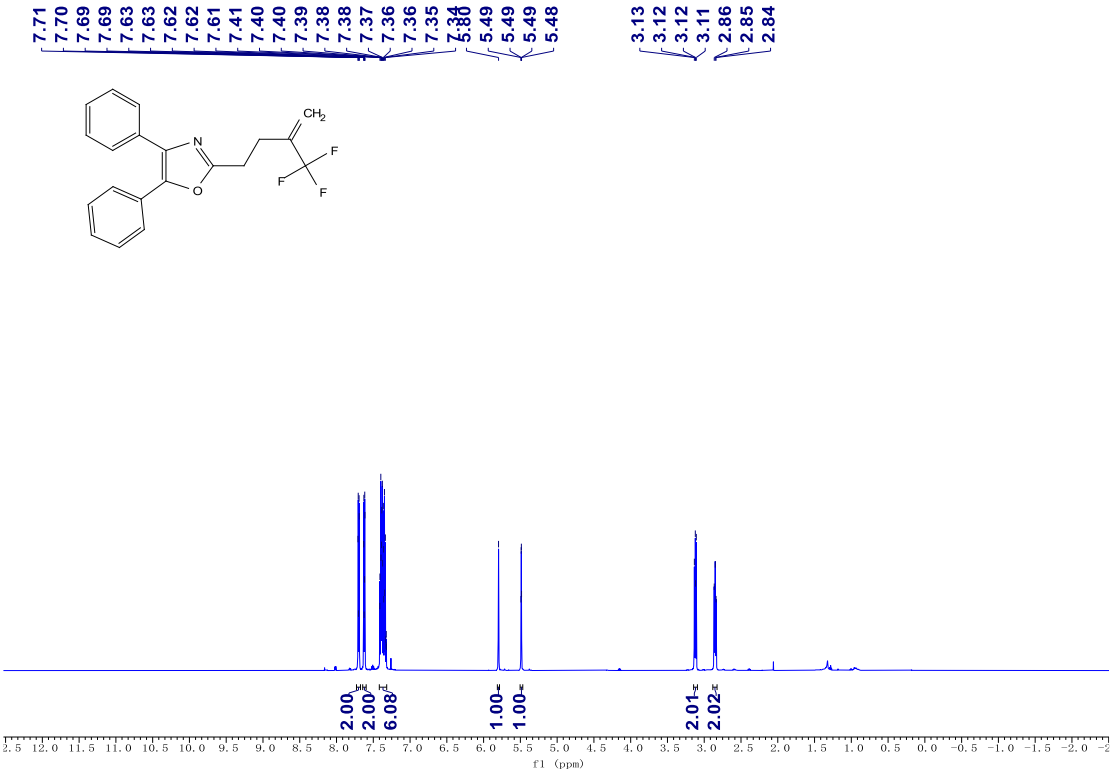
^{13}C NMR Spectra of 1f (151 MHz, Chloroform-*d*)



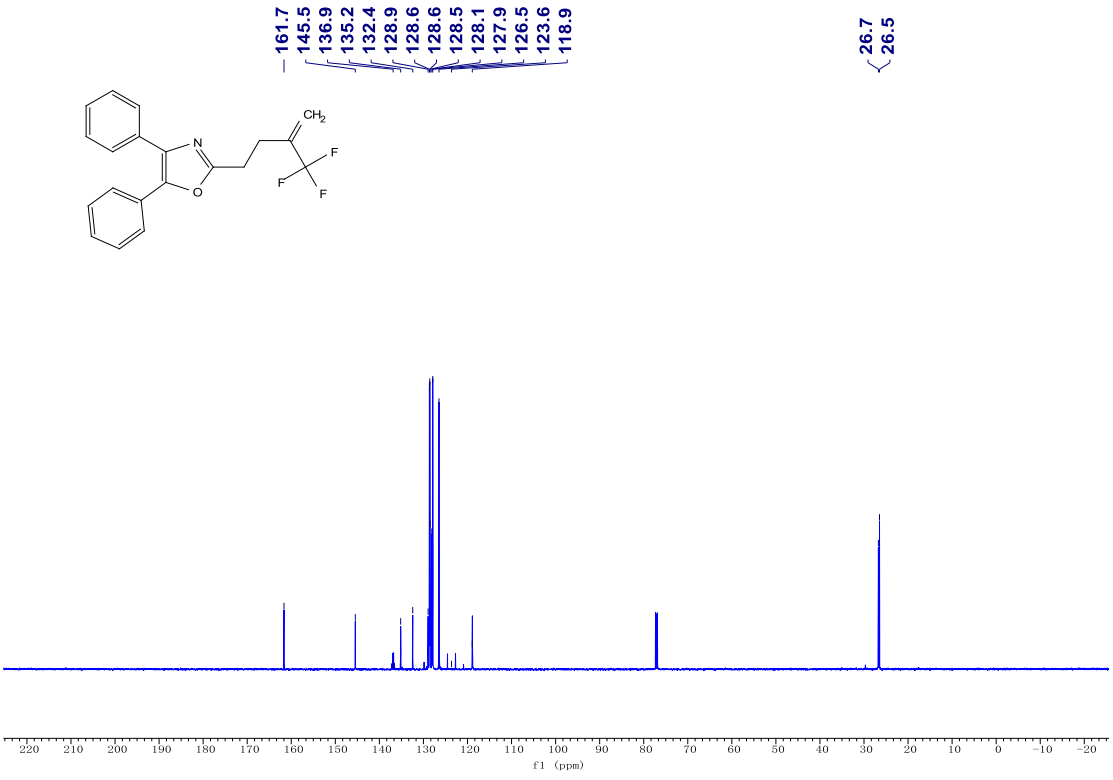
^{19}F NMR Spectra of 1f (565 MHz, Chloroform-*d*)



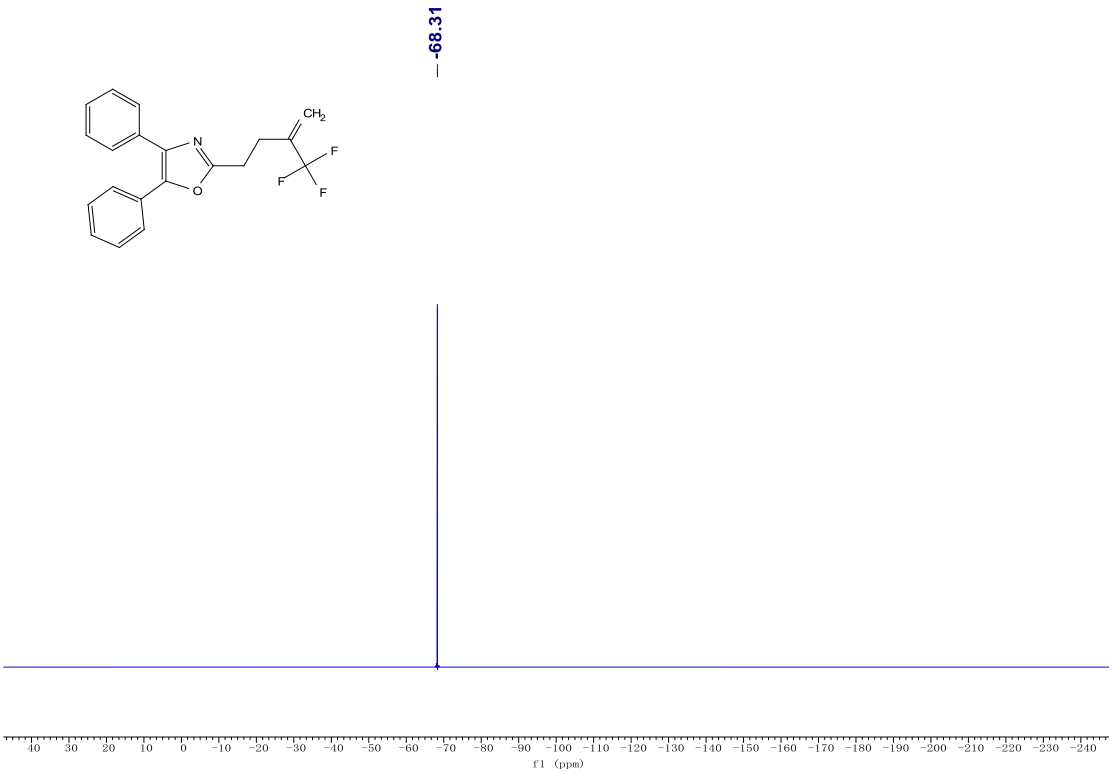
^{1}H NMR Spectra of 1g (600 MHz, Chloroform-*d*)



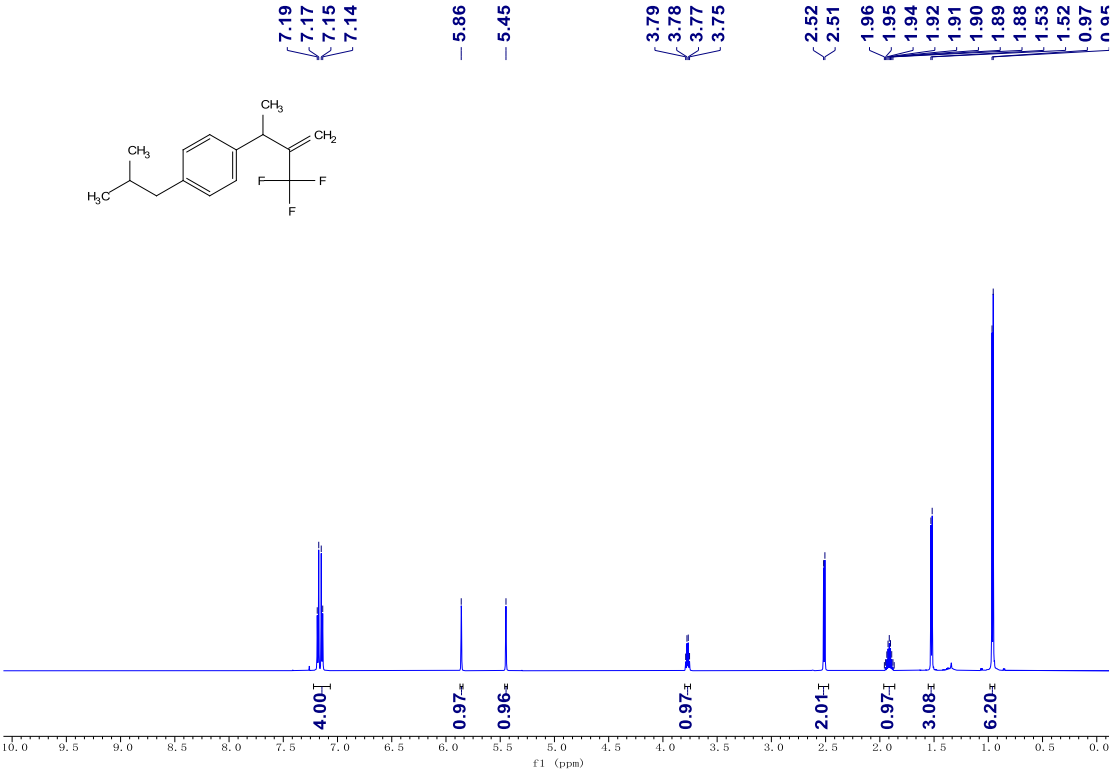
^{13}C NMR Spectra of 1g (151 MHz, Chloroform-*d*)



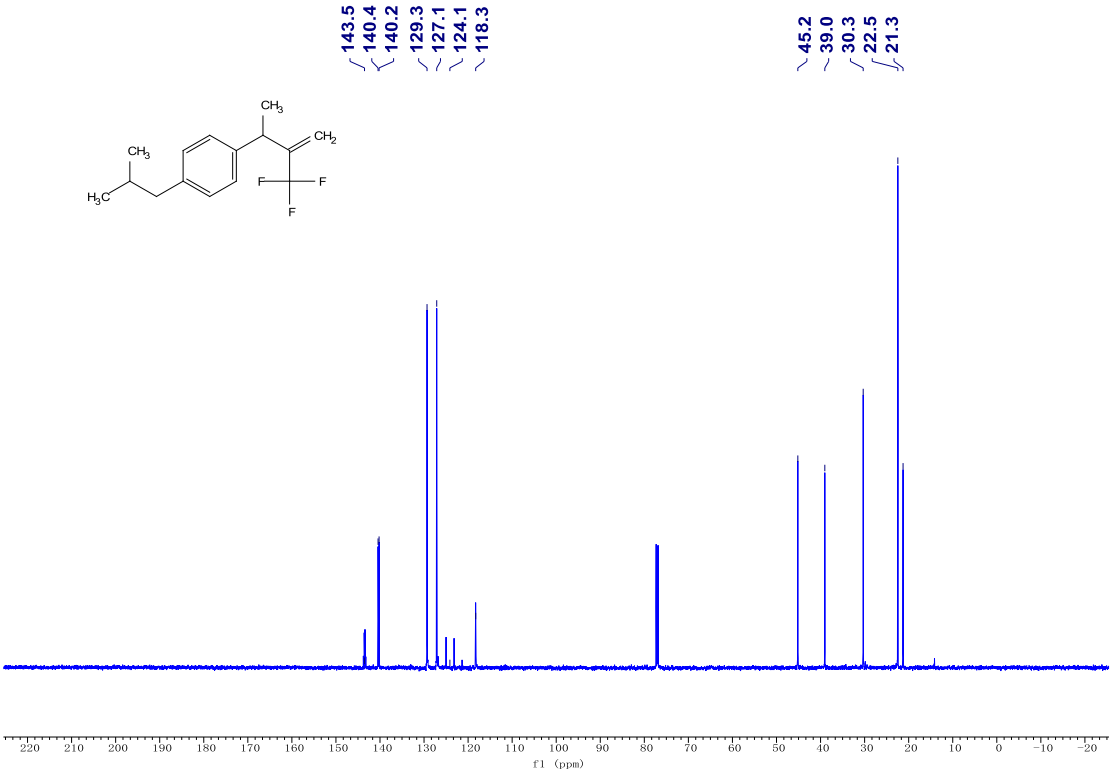
^{19}F NMR Spectra of 1g (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 1h (600 MHz, Chloroform-*d*)

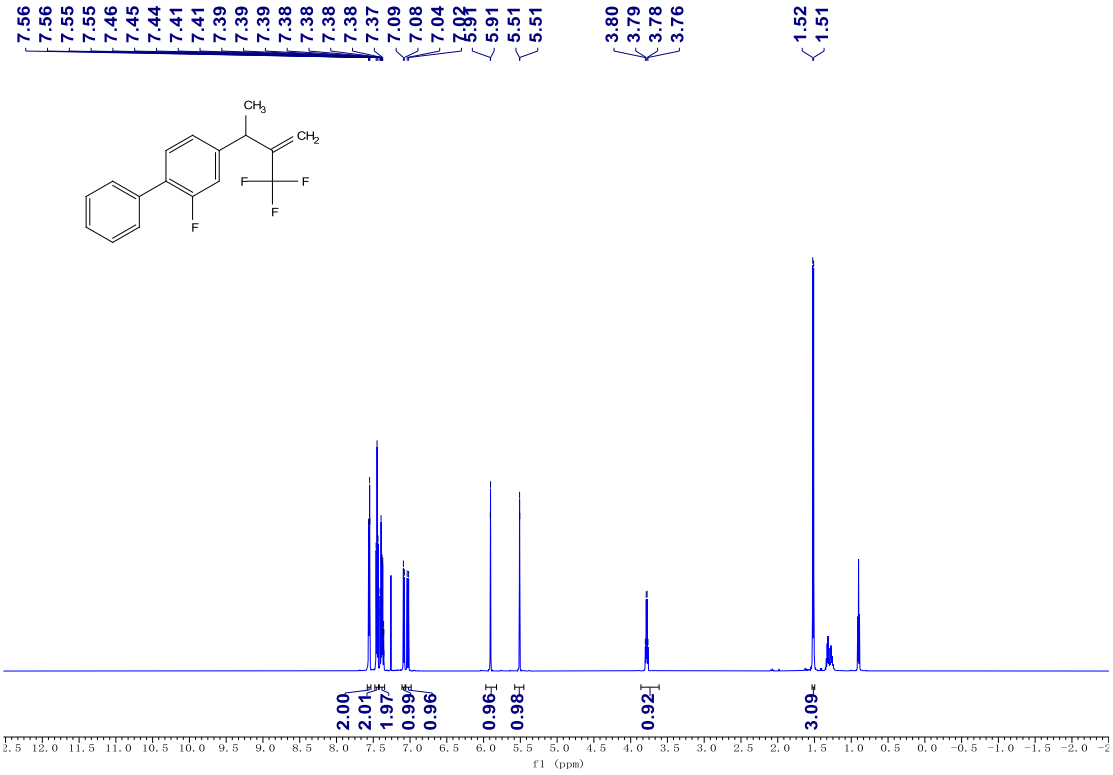


^{13}C NMR Spectra of 1h (151 MHz, Chloroform-*d*)

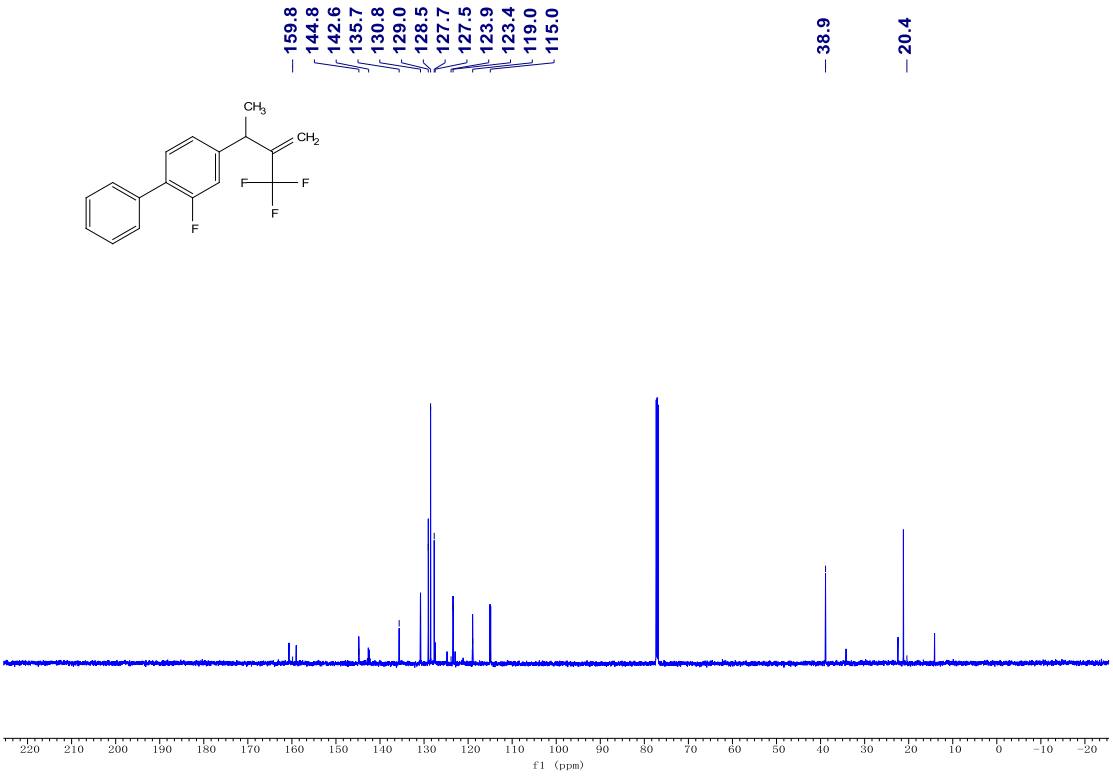


^{19}F NMR Spectra of 1h (565 MHz, Chloroform-*d*)

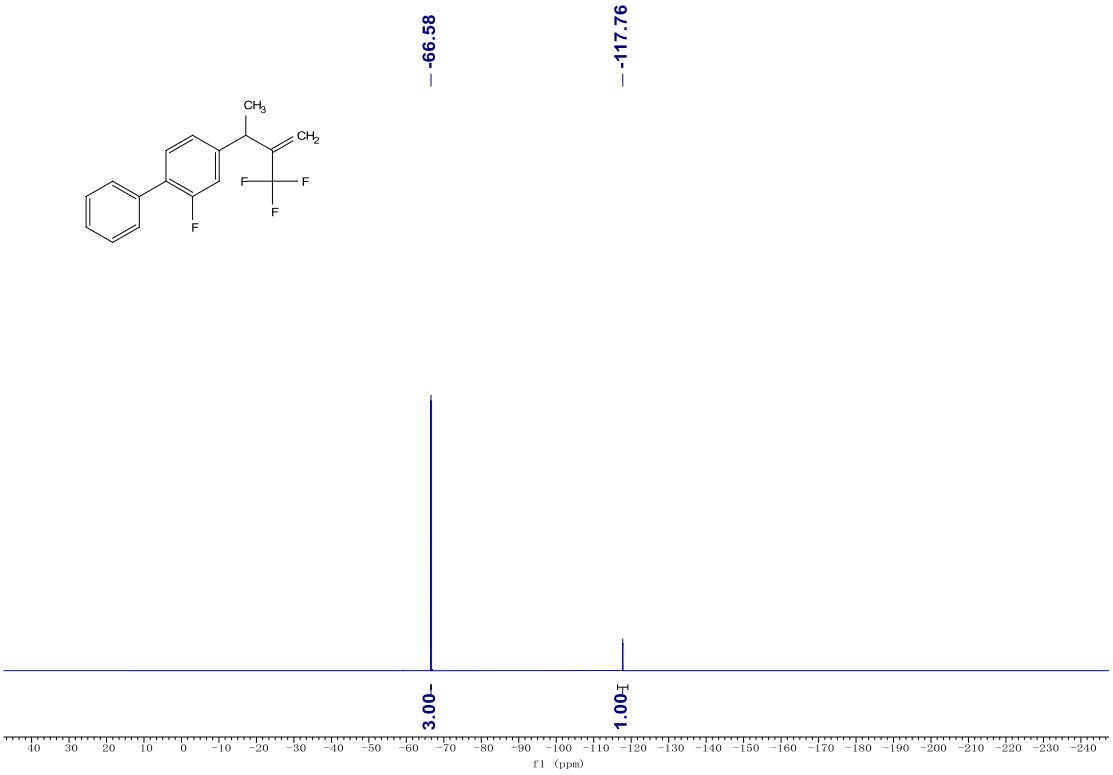
^{1}H NMR Spectra of 1i (600 MHz, Chloroform-*d*)



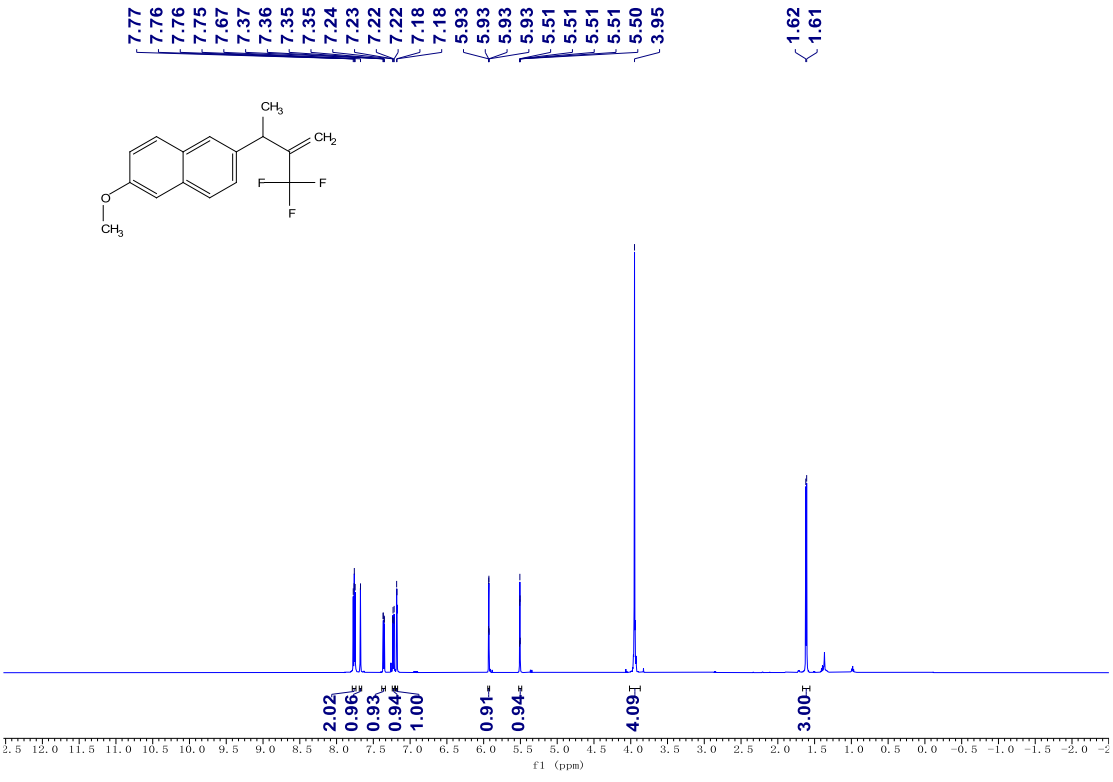
^{13}C NMR Spectra of 1i (151 MHz, Chloroform-*d*)



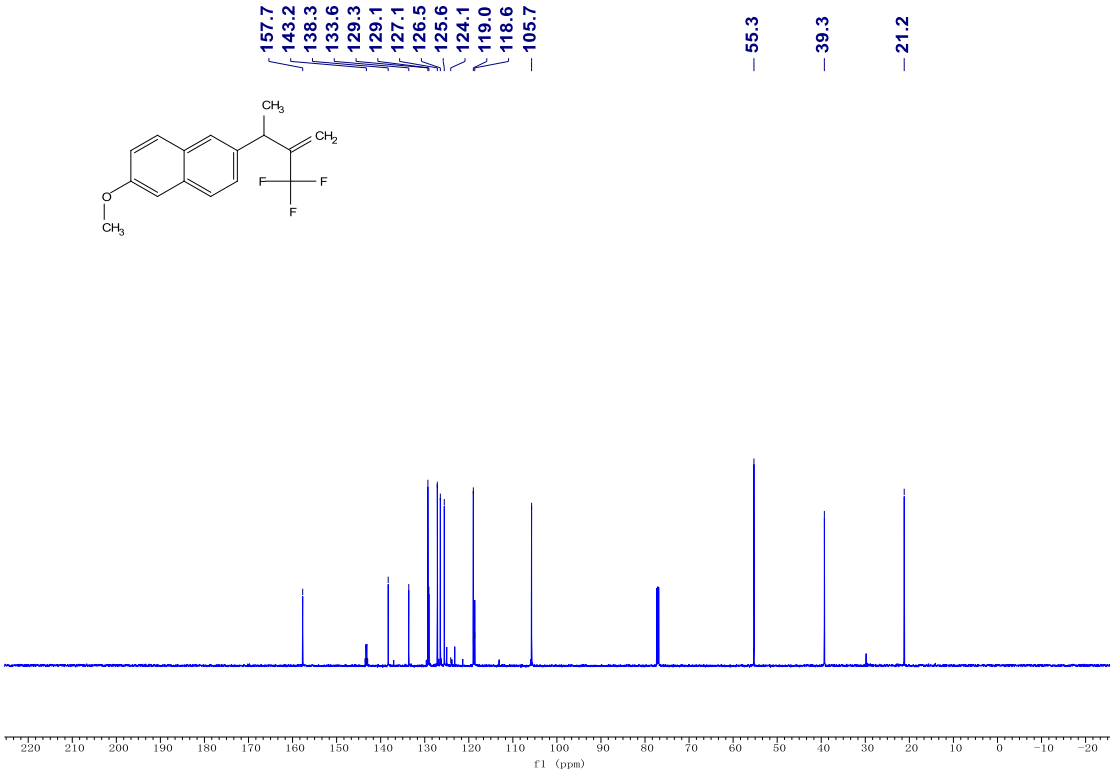
^{19}F NMR Spectra of 1i (565 MHz, Chloroform-*d*)



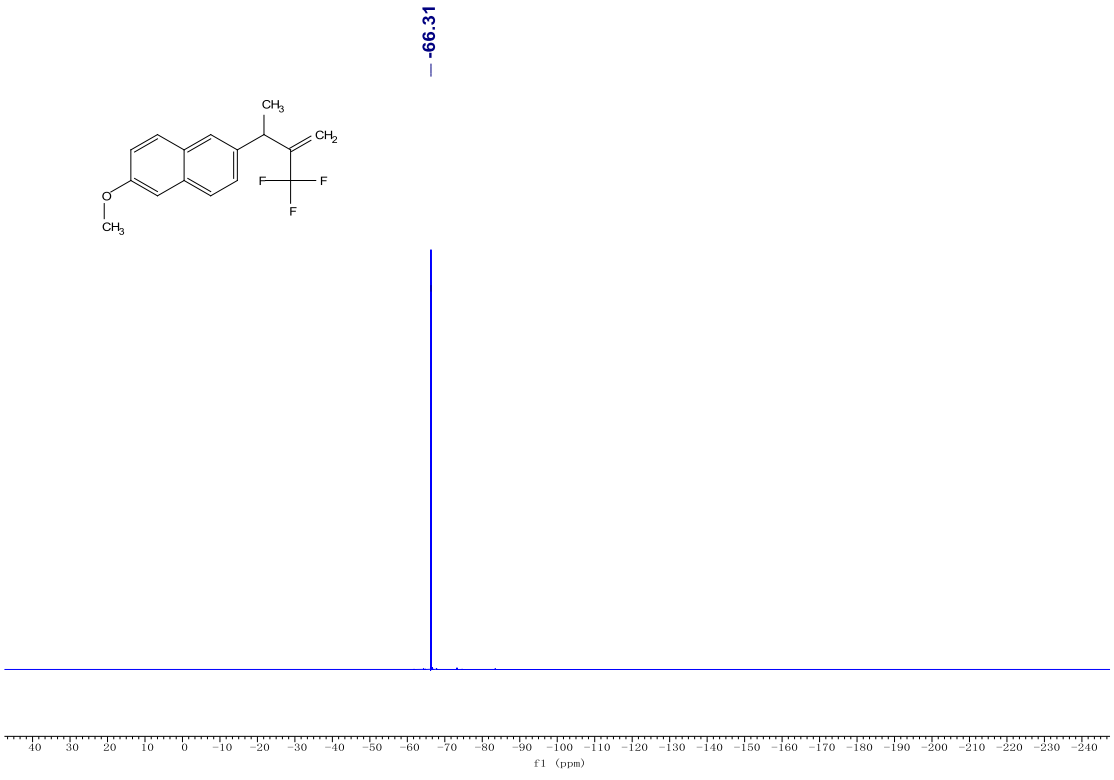
^{1}H NMR Spectra of 1j (600 MHz, Chloroform-*d*)



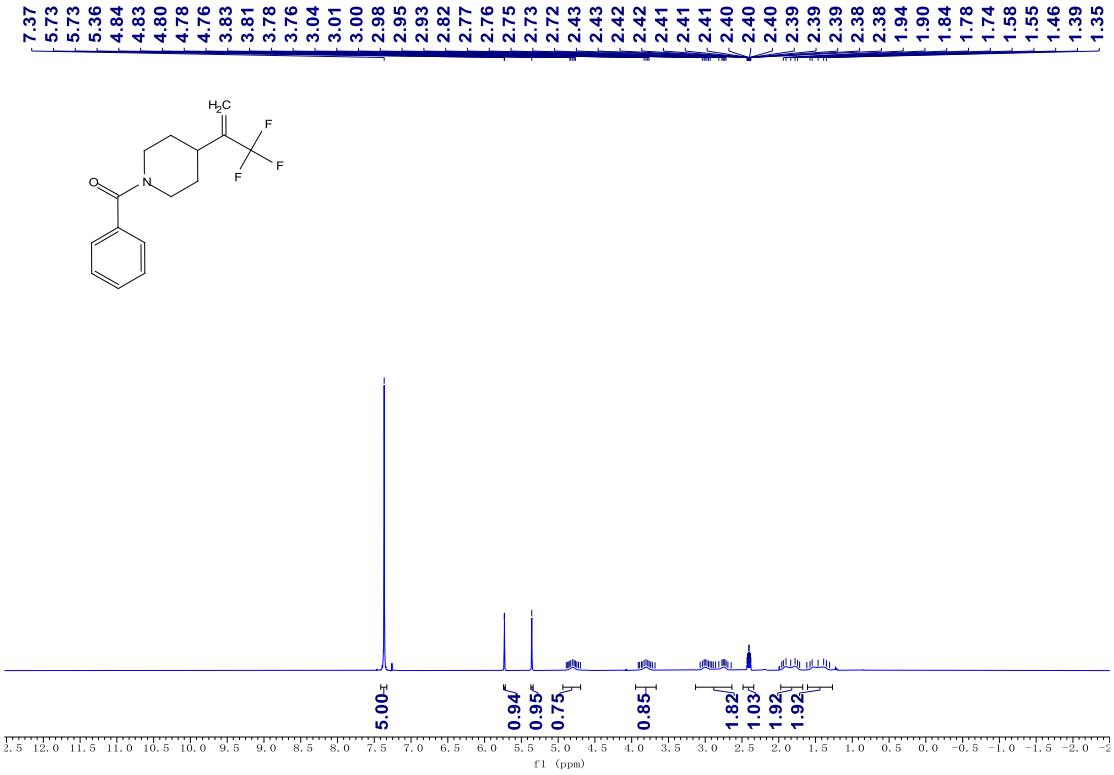
^{13}C NMR Spectra of 1j (151 MHz, Chloroform-*d*)



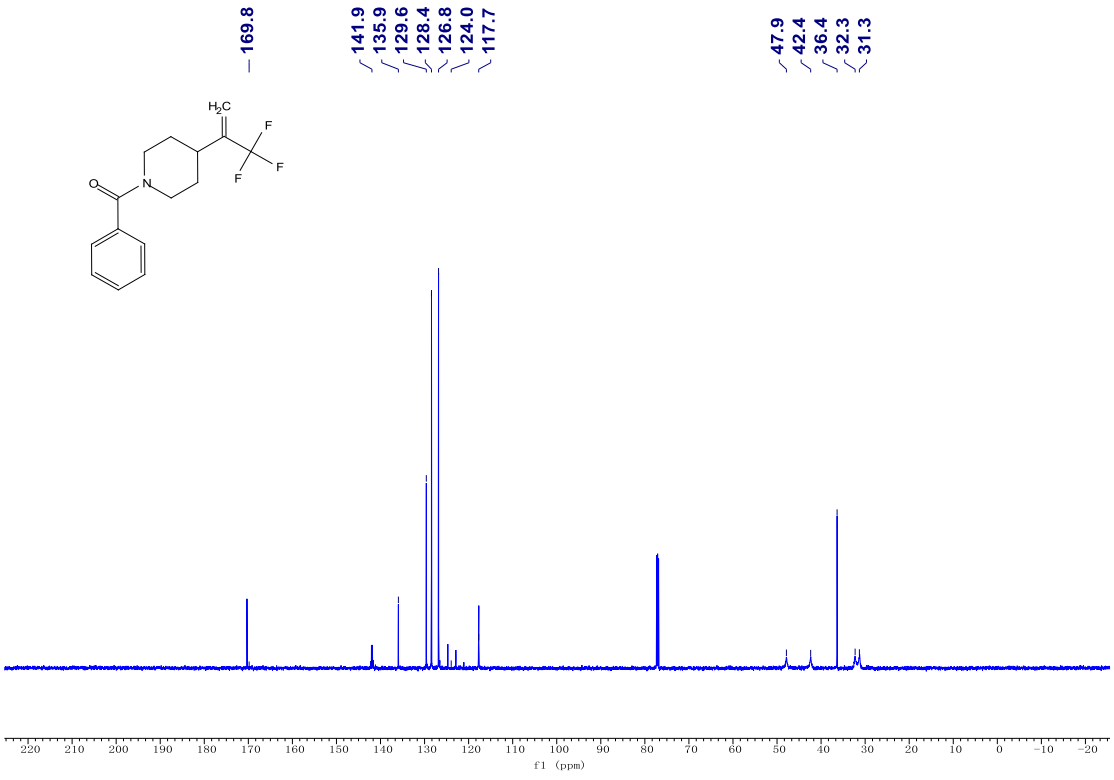
^{19}F NMR Spectra of 1j (565 MHz, Chloroform-*d*)



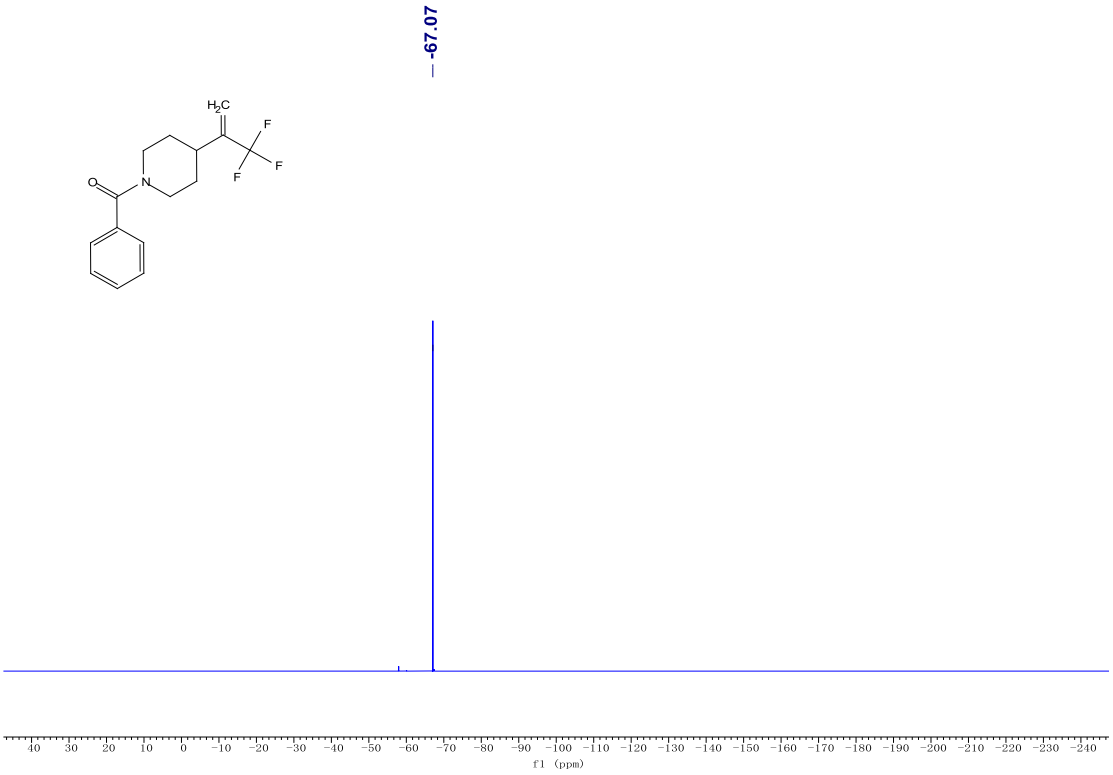
^{1}H NMR Spectra of 1k (600 MHz, Chloroform-*d*)



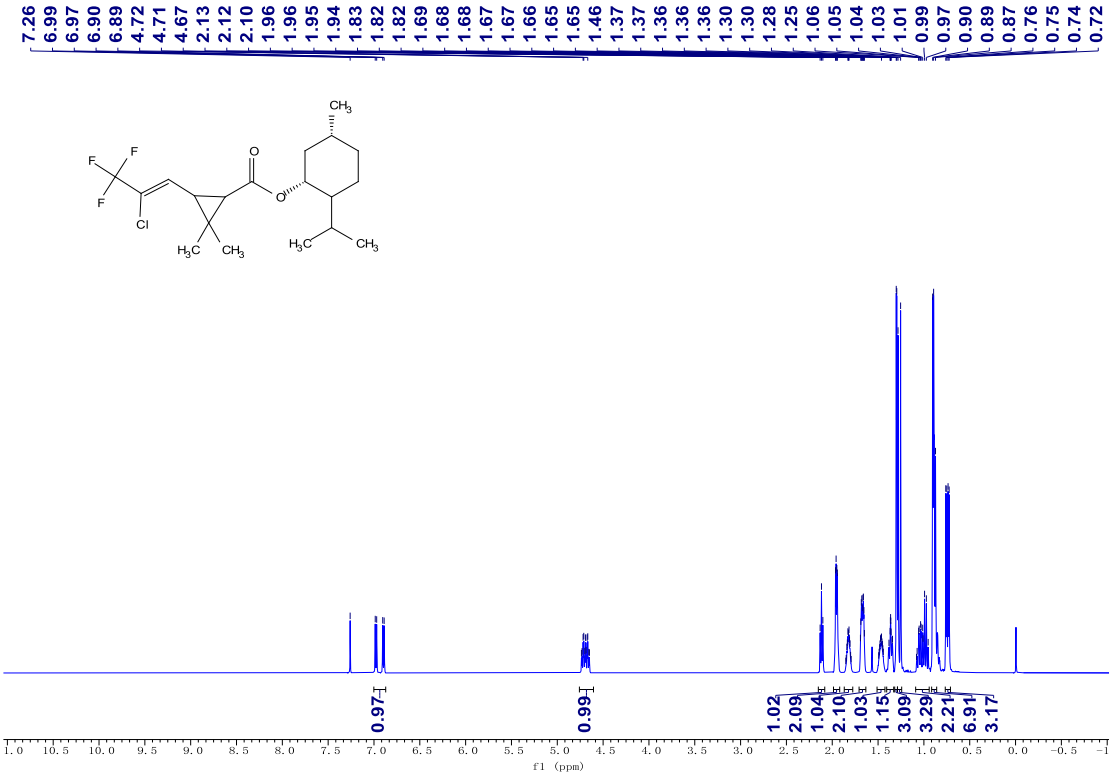
^{13}C NMR Spectra of 1k (151 MHz, Chloroform-*d*)



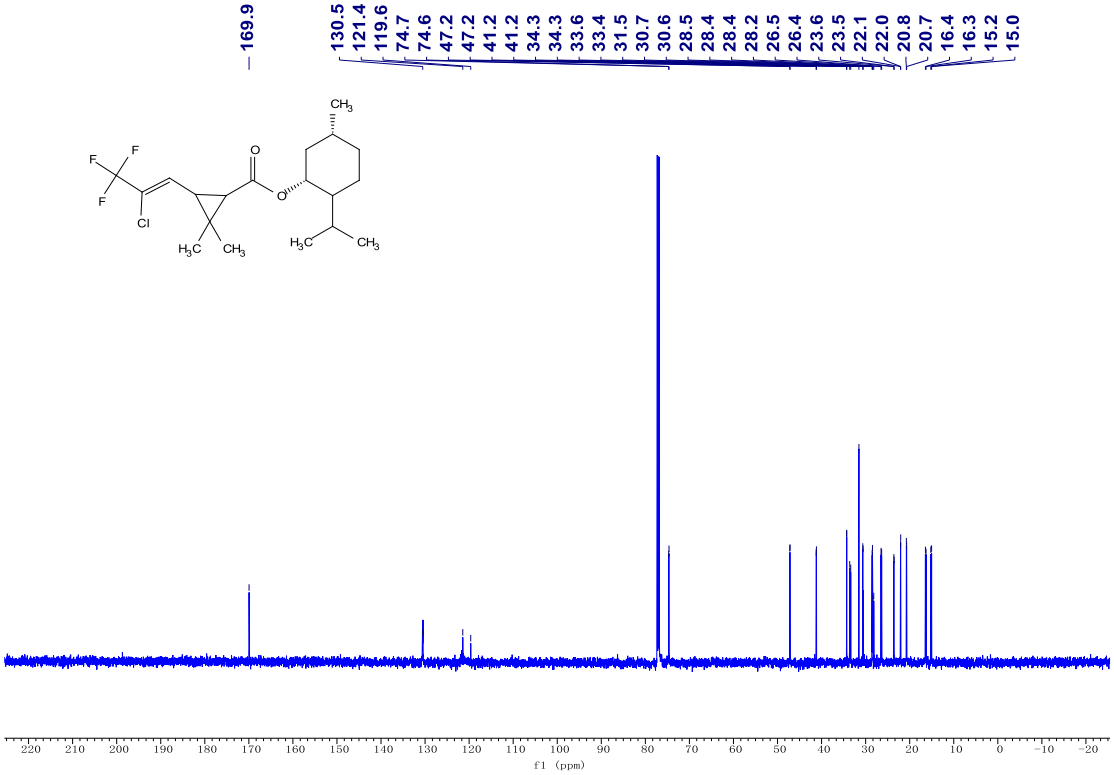
^{19}F NMR Spectra of 1k (565 MHz, Chloroform-*d*)



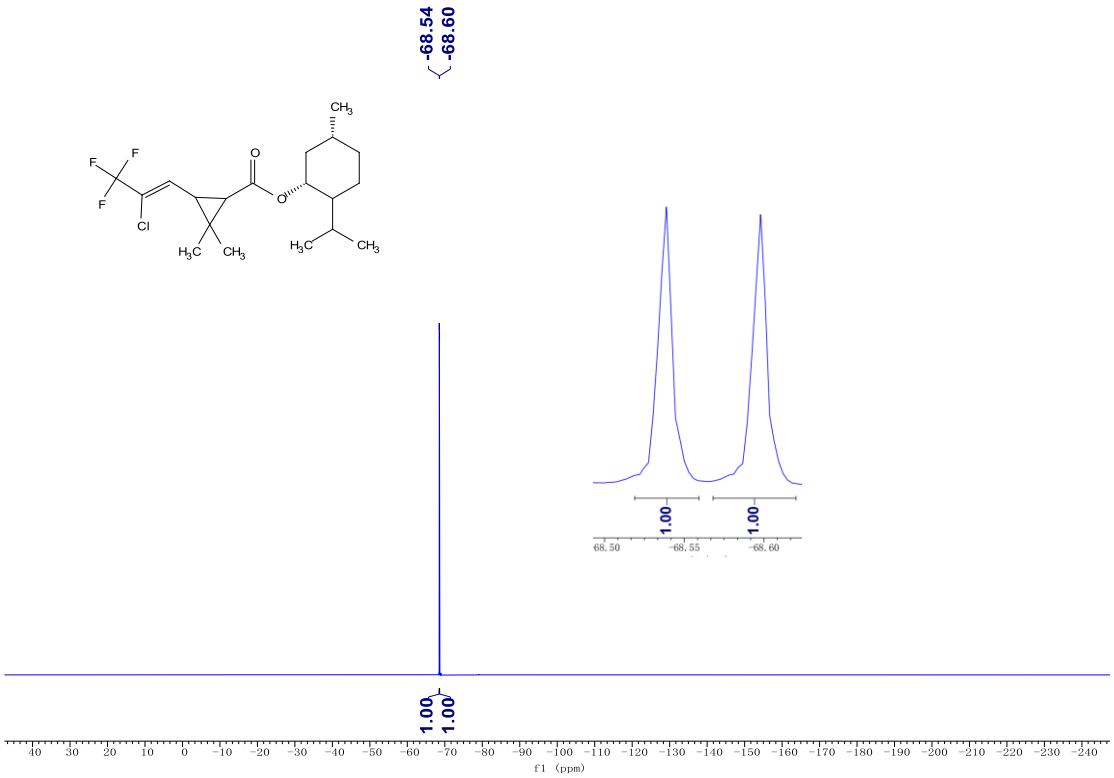
^{1}H NMR Spectra of 1n (600 MHz, Chloroform-*d*)



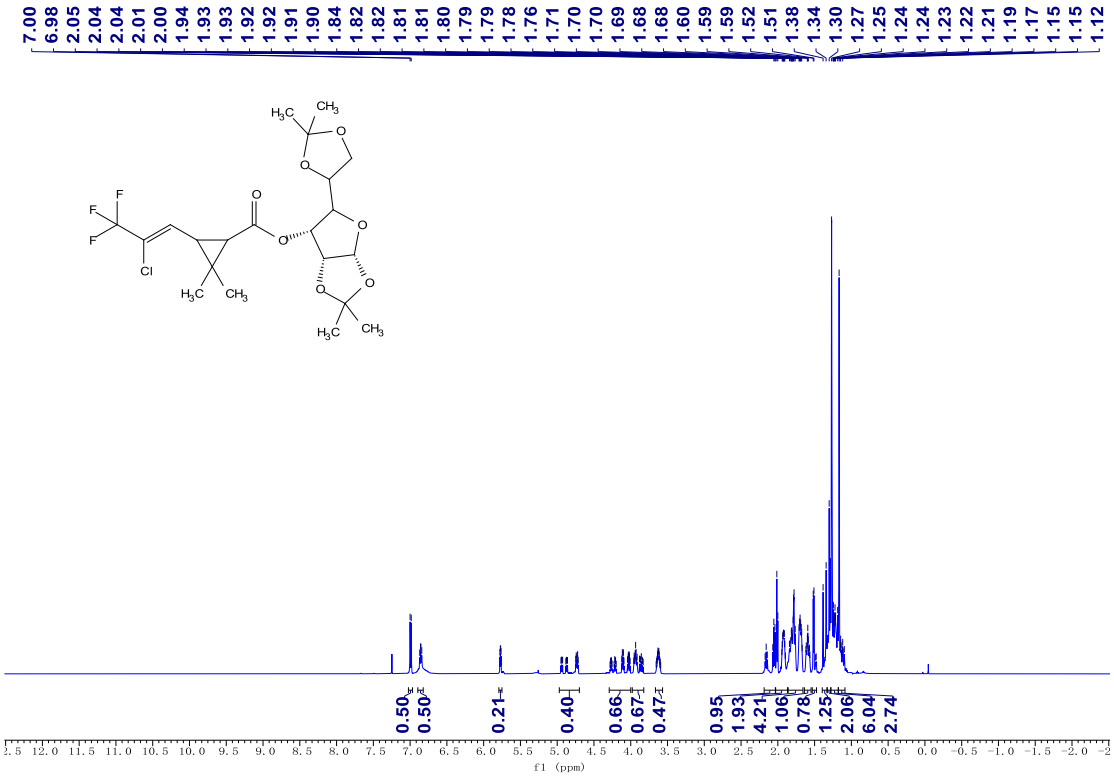
^{13}C NMR Spectra of 1n (151 MHz, Chloroform-*d*)



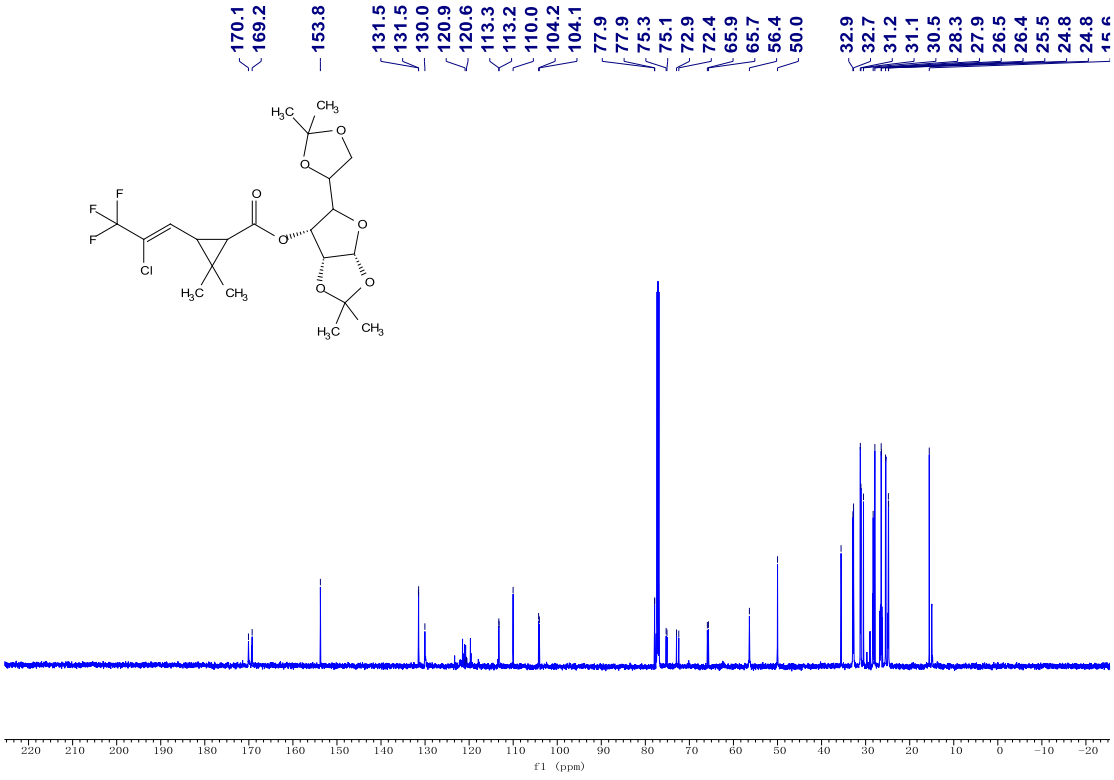
^{19}F NMR Spectra of 1n (565 MHz, Chloroform-*d*)



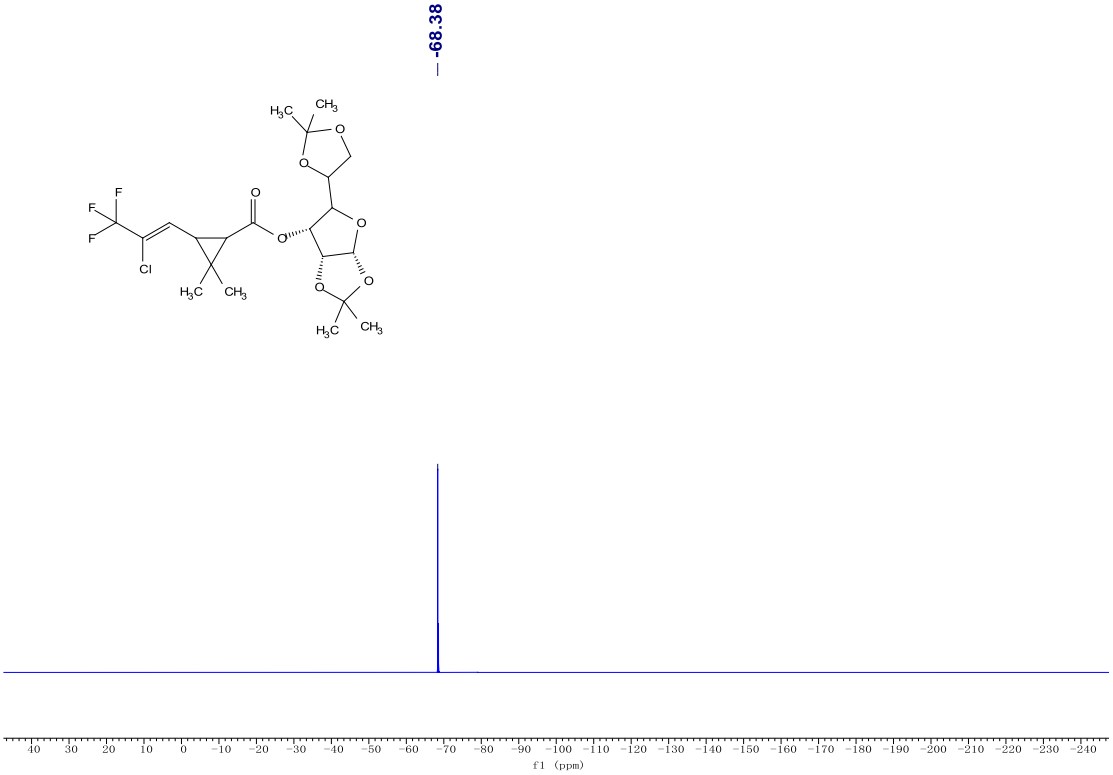
^{1}H NMR Spectra of 1o (600 MHz, Chloroform-*d*)



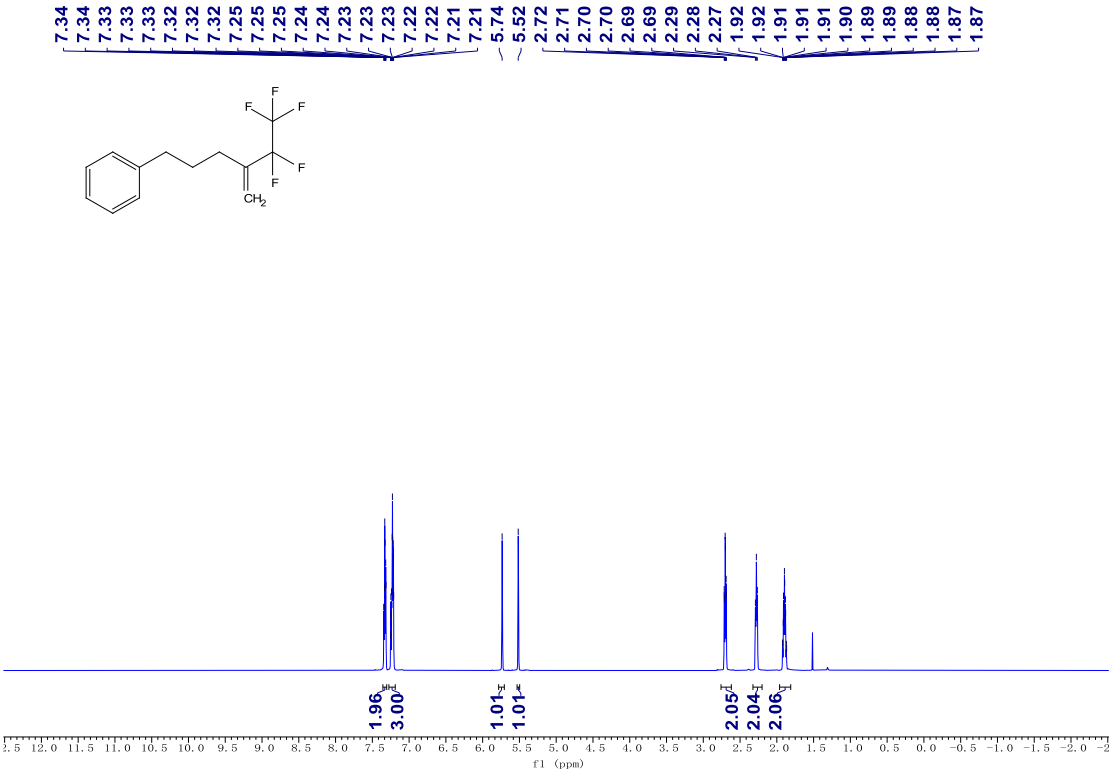
^{13}C NMR Spectra of 1o (151 MHz, Chloroform-*d*)



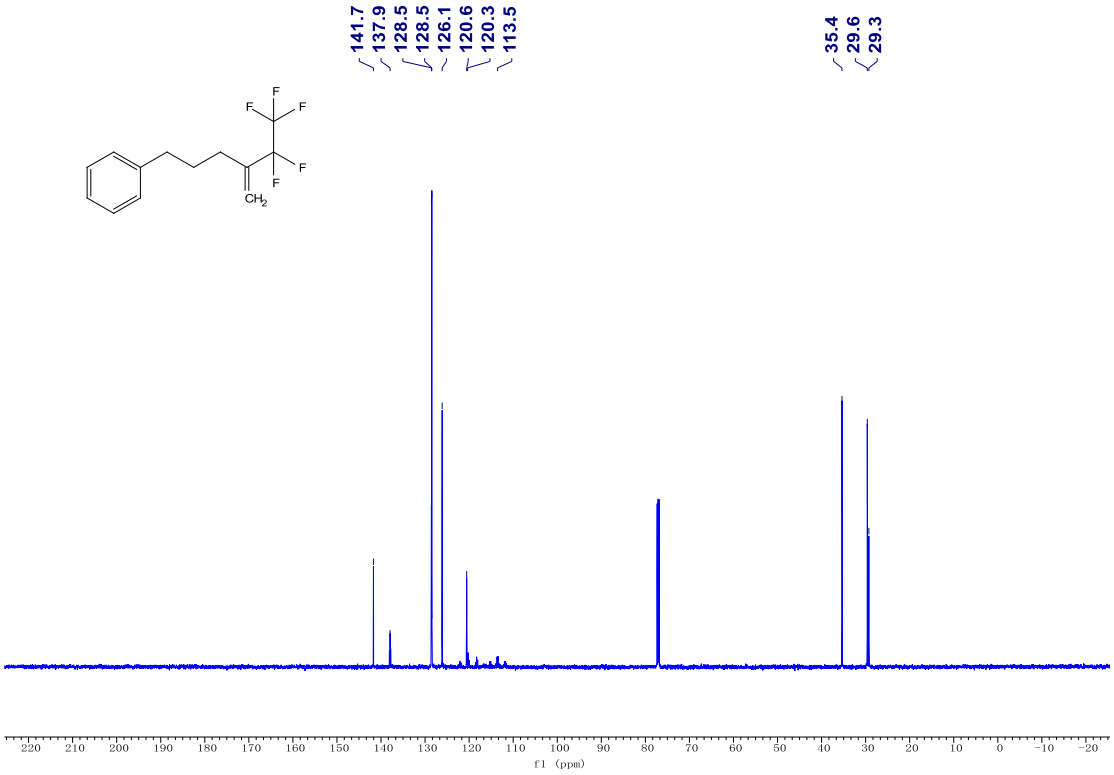
^{19}F NMR Spectra of 1o (565 MHz, Chloroform-*d*)



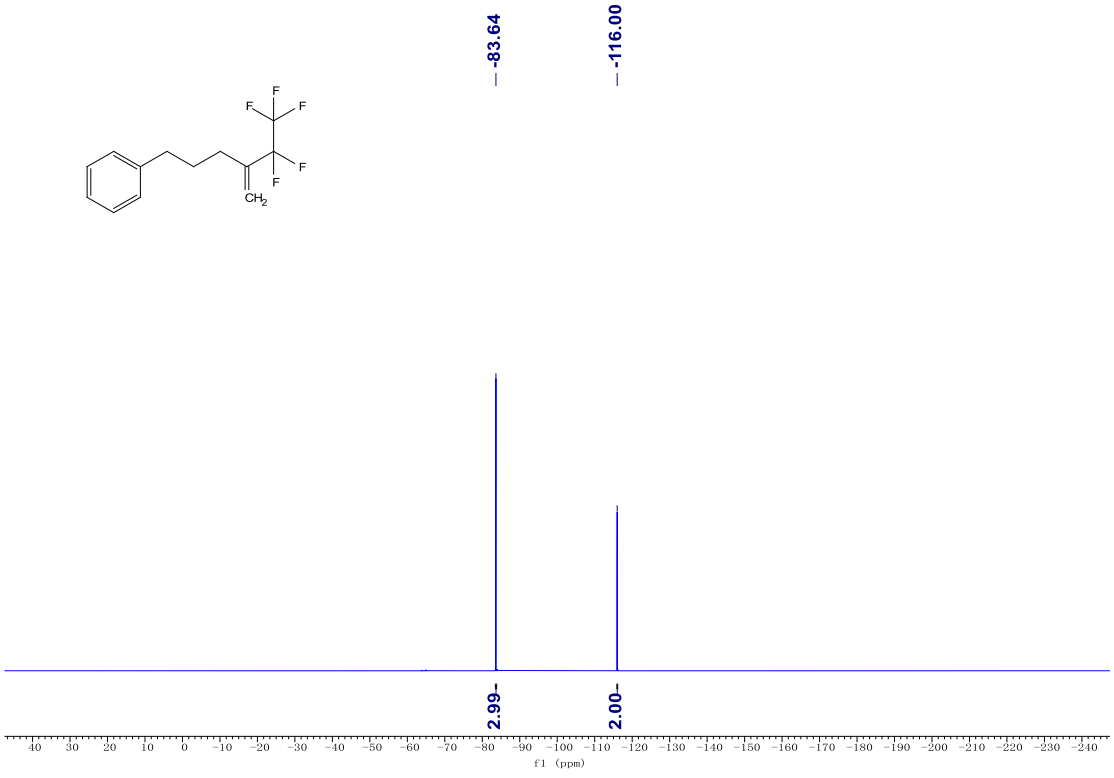
^{1}H NMR Spectra of 1p (600 MHz, Chloroform-*d*)



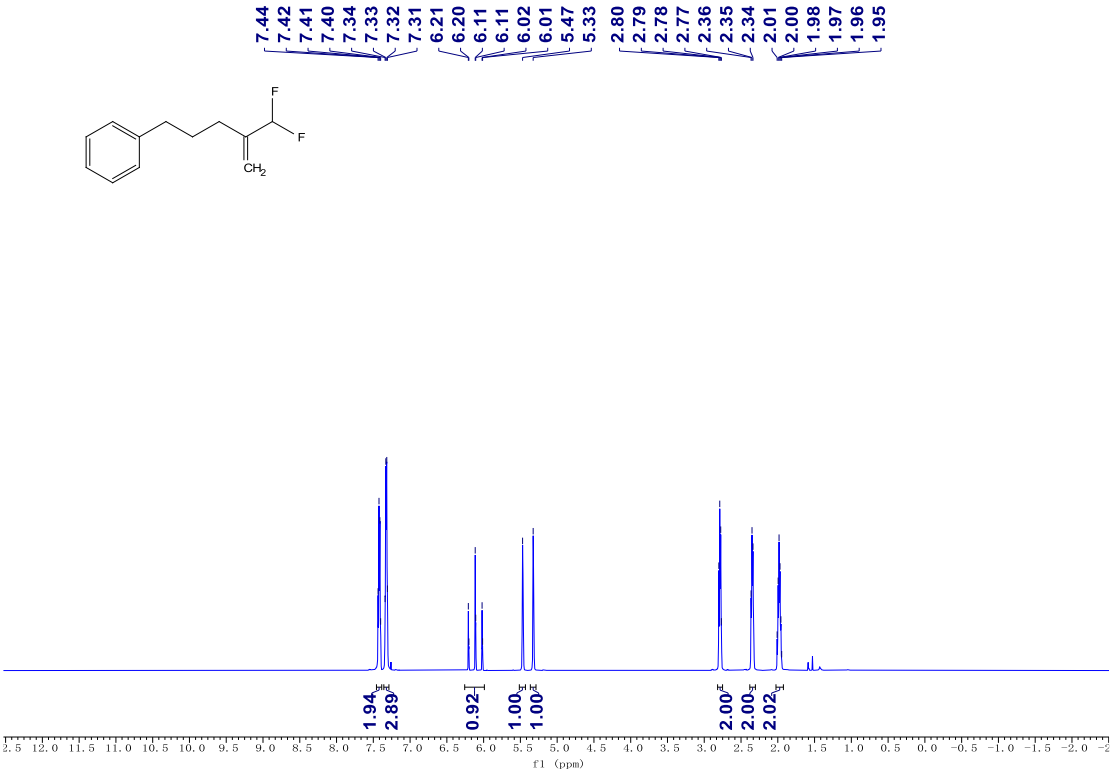
^{13}C NMR Spectra of 1p (151 MHz, Chloroform-*d*)



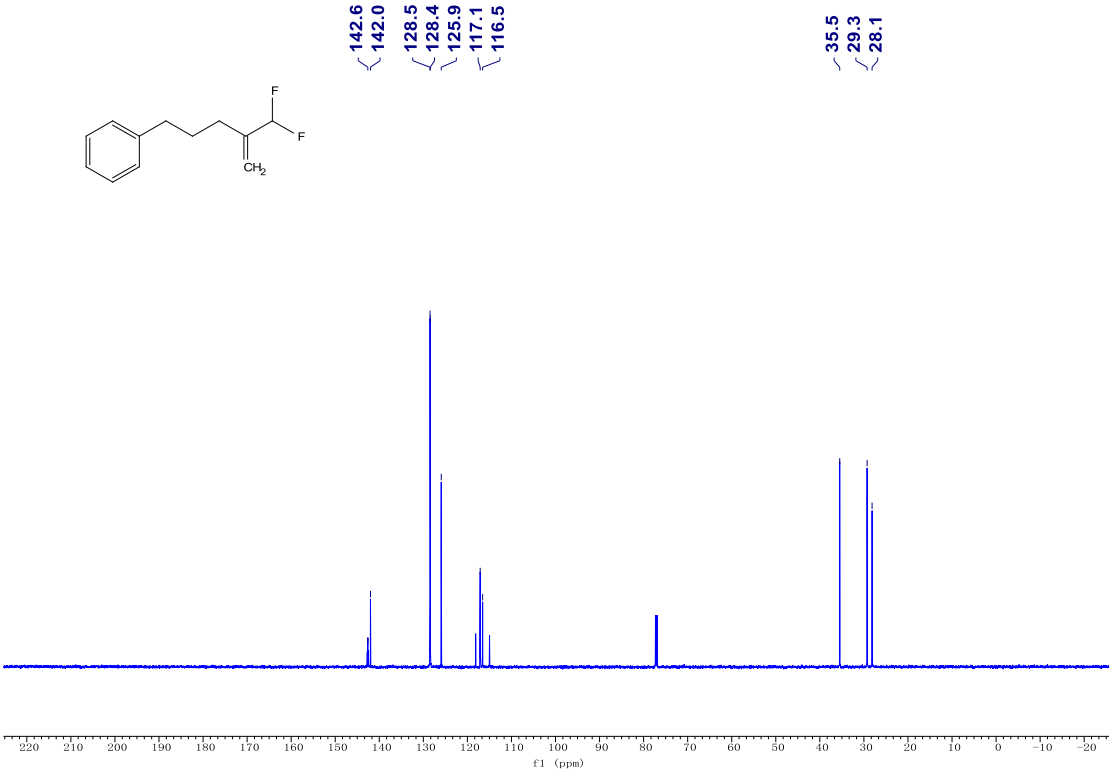
^{19}F NMR Spectra of 1p (565 MHz, Chloroform-*d*)



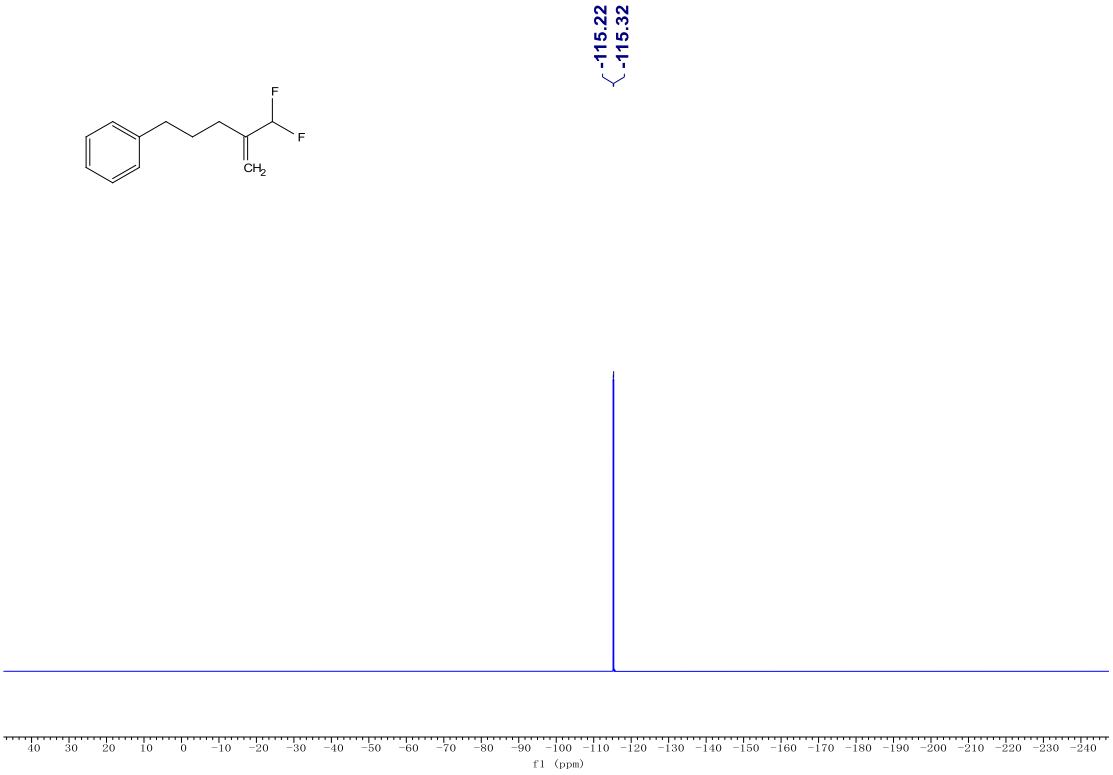
^{1}H NMR Spectra of 1q (600 MHz, Chloroform-*d*)



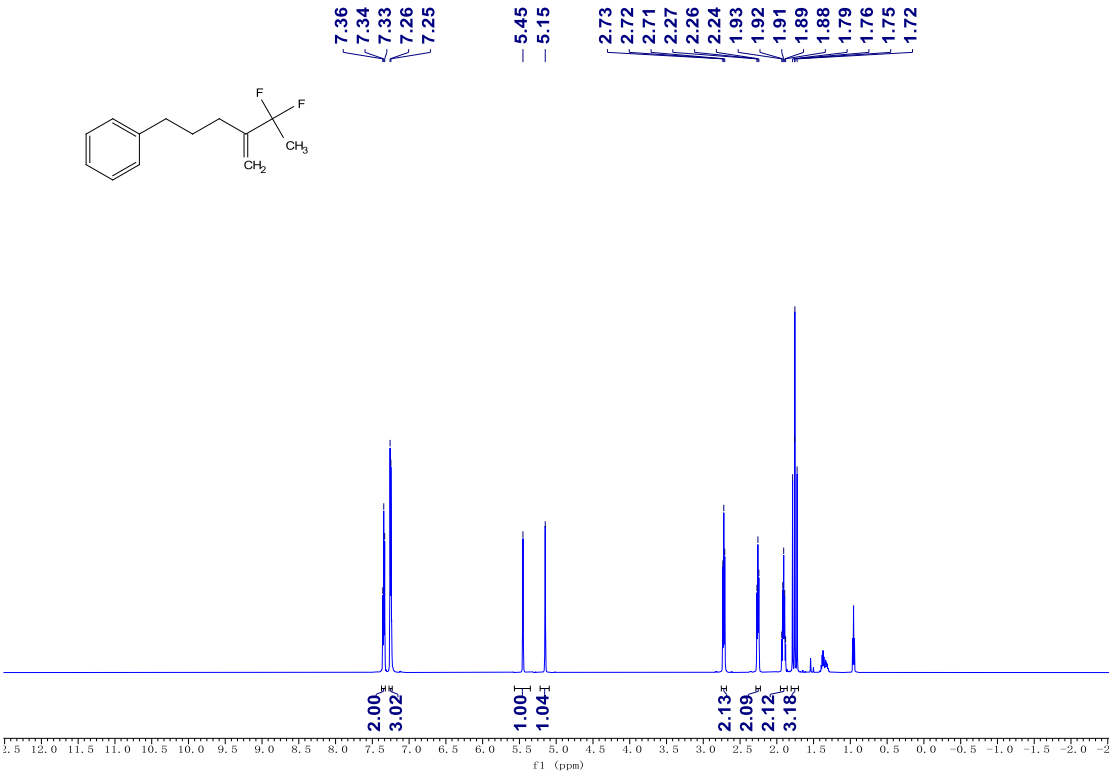
^{13}C NMR Spectra of 1q (151 MHz, Chloroform-*d*)



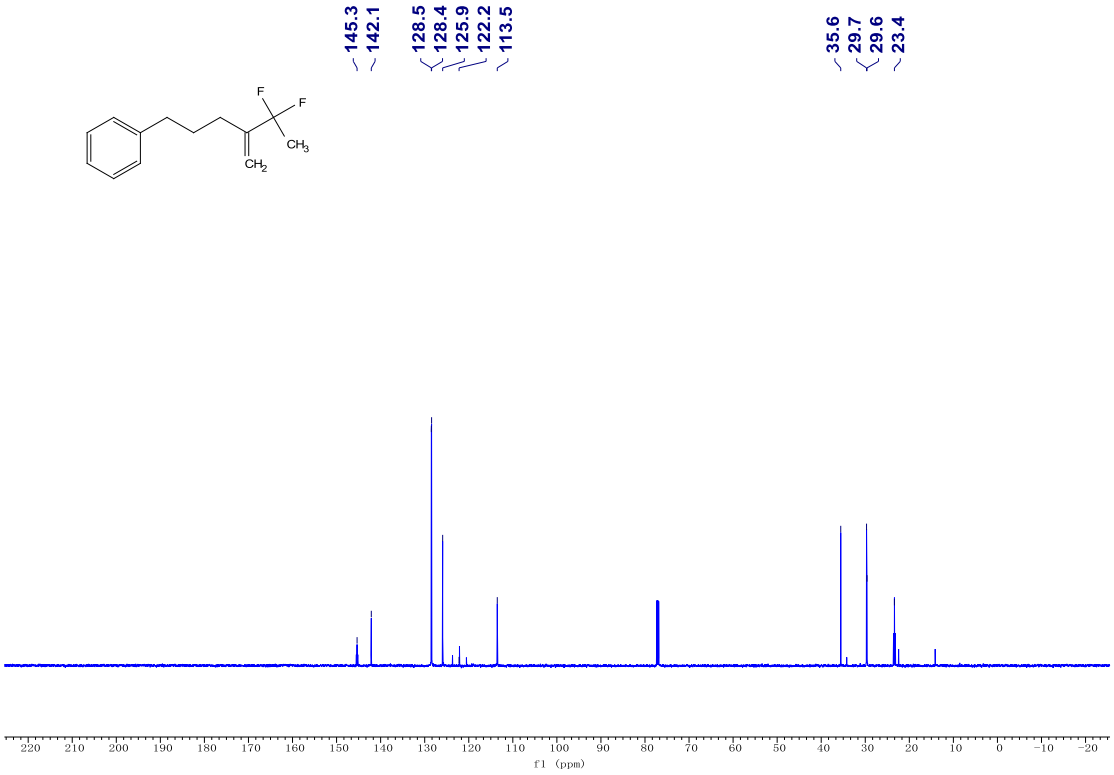
^{19}F NMR Spectra of 1q (565 MHz, Chloroform-*d*)



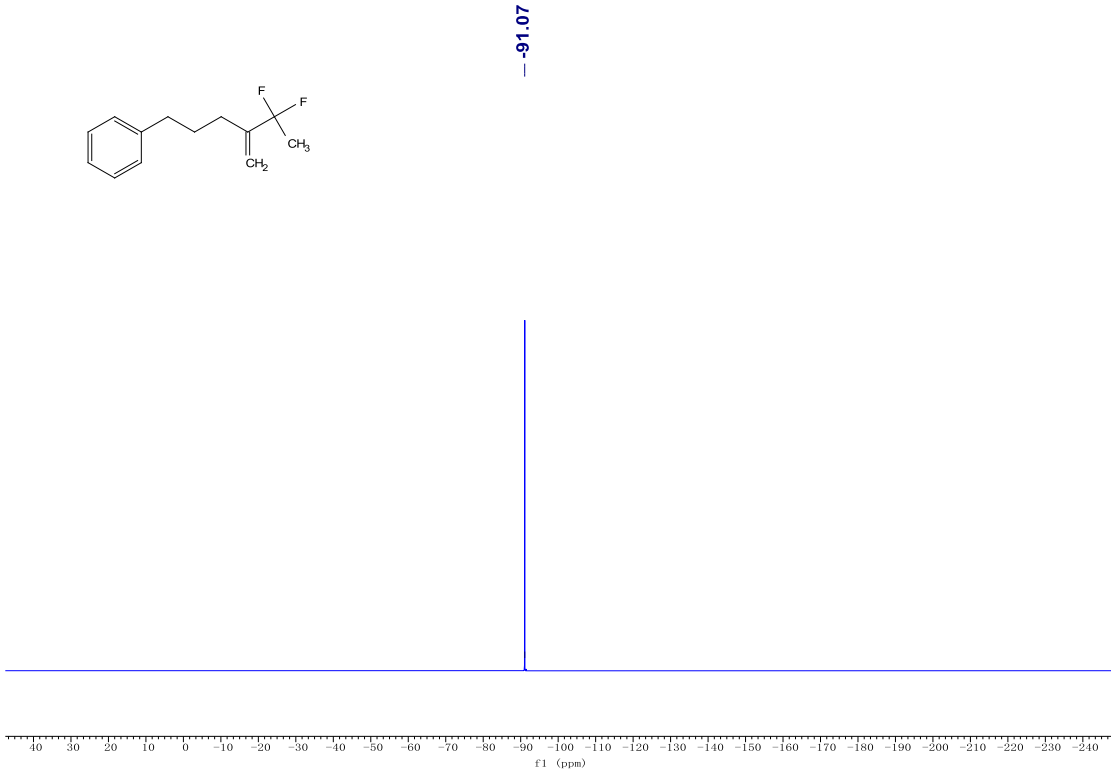
^{1}H NMR Spectra of 1r (600 MHz, Chloroform-*d*)



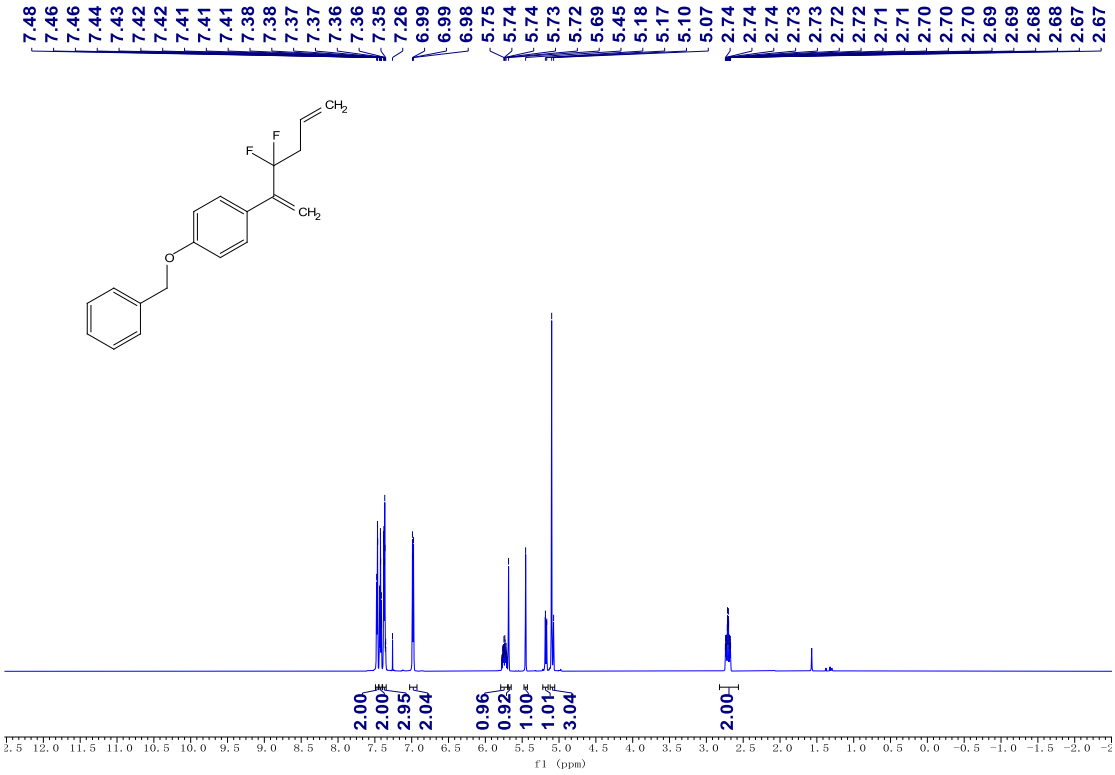
^{13}C NMR Spectra of 1r (151 MHz, Chloroform-*d*)



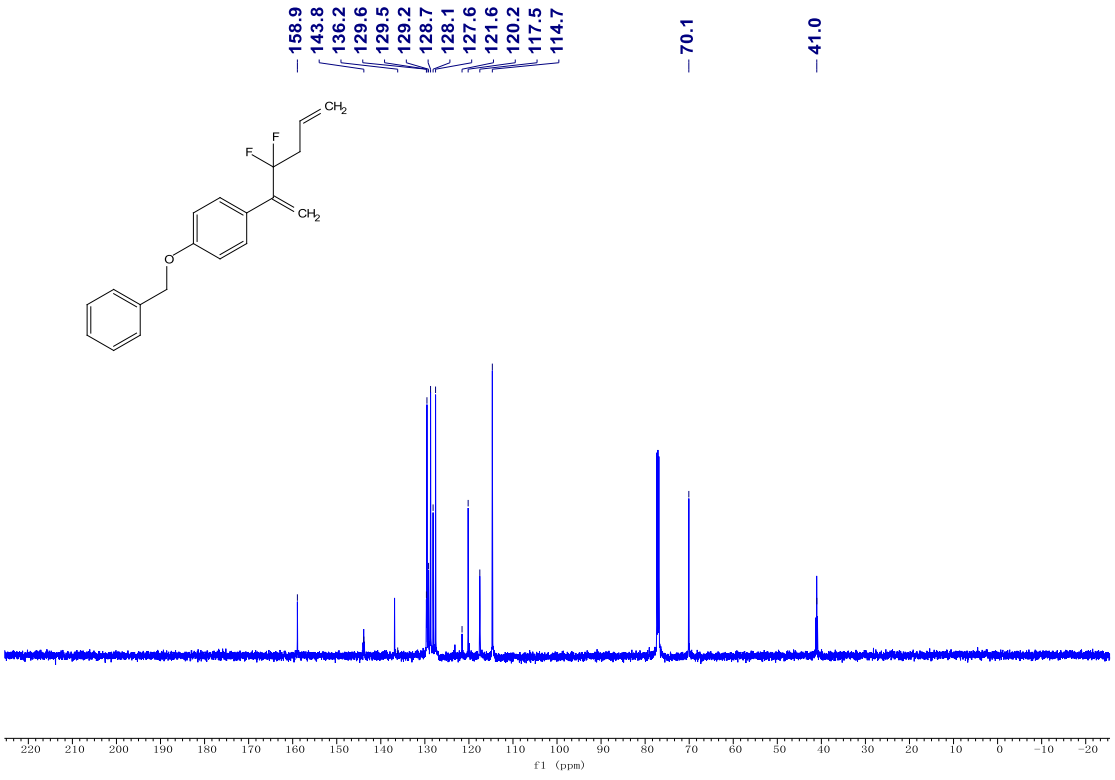
^{19}F NMR Spectra of 1r (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 1t (600 MHz, Chloroform-*d*)

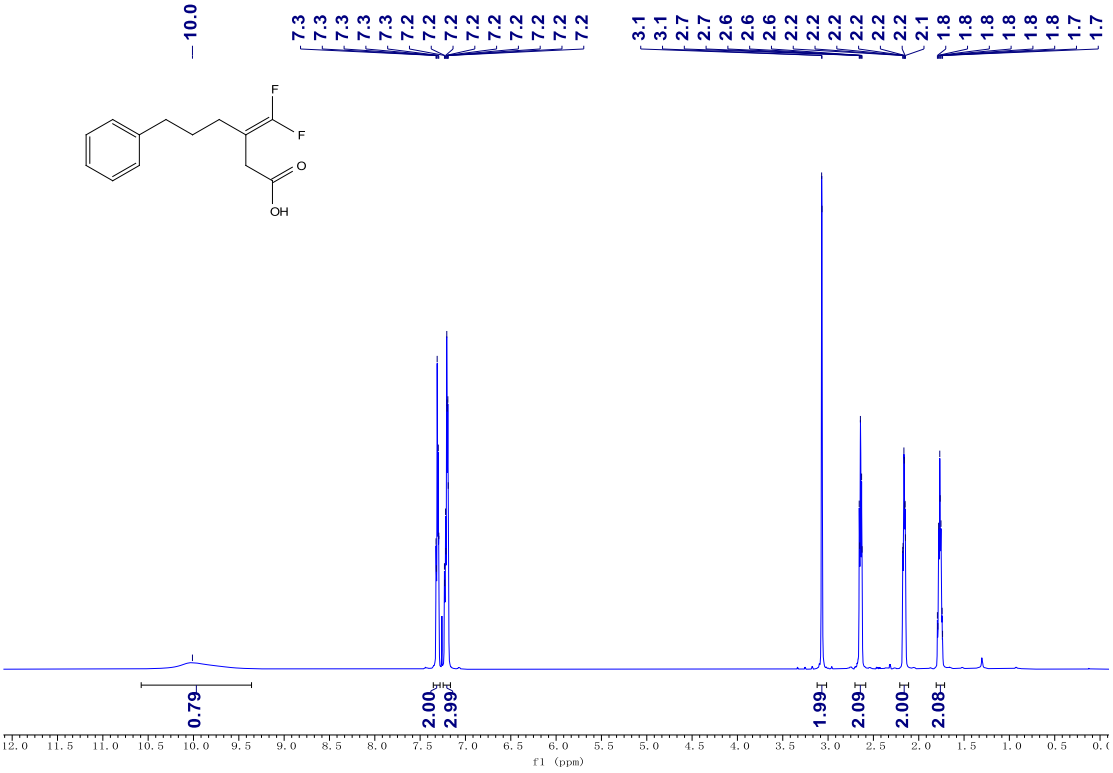


^{13}C NMR Spectra of 1t (151 MHz, Chloroform-*d*)

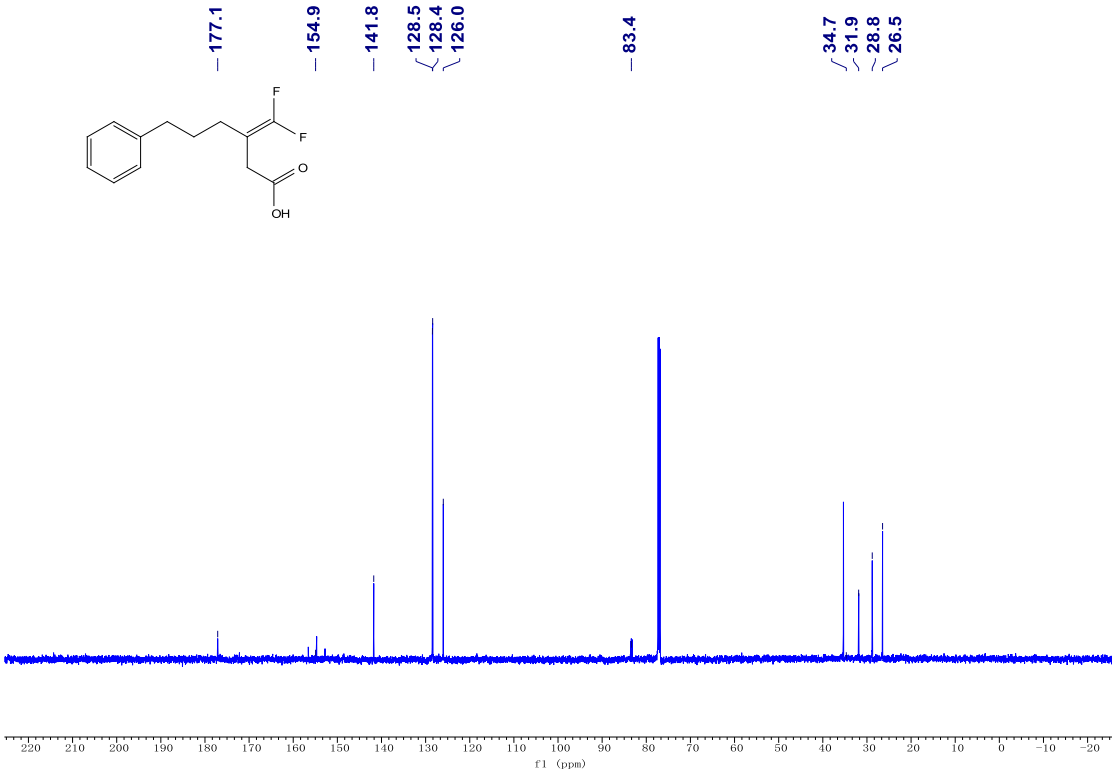


^{19}F NMR Spectra of 1t (565 MHz, Chloroform-*d*)

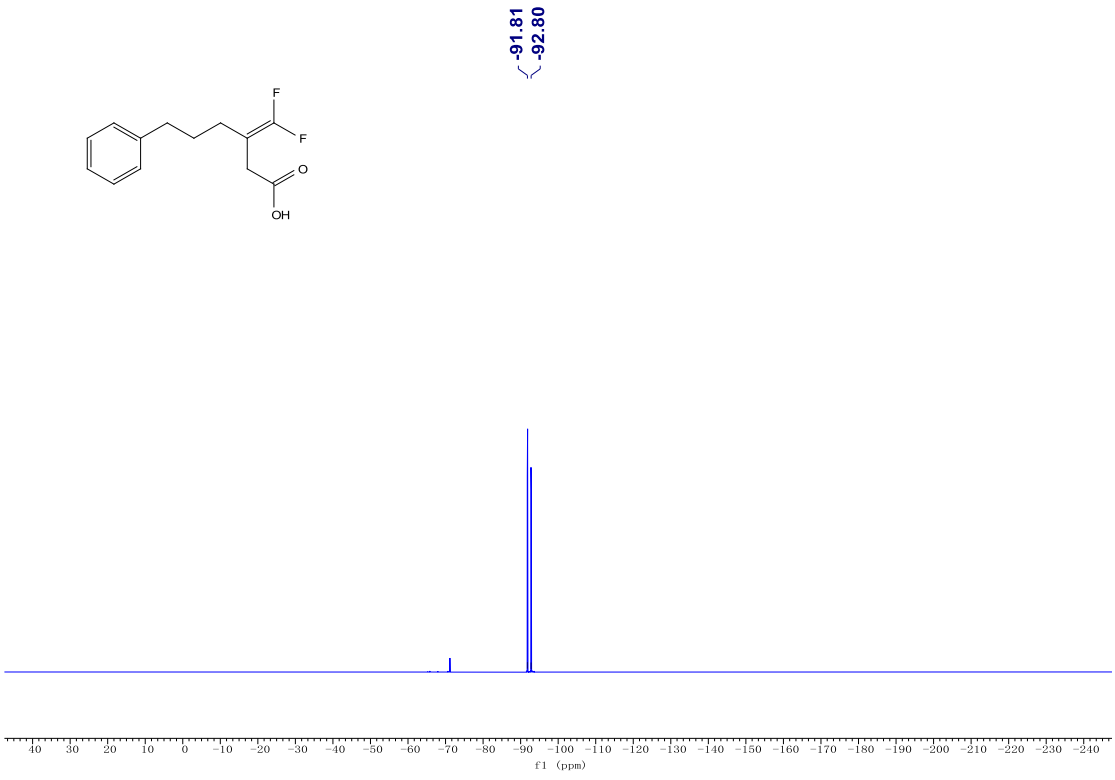
^{1}H NMR Spectra of 2a (600 MHz, Chloroform-*d*)



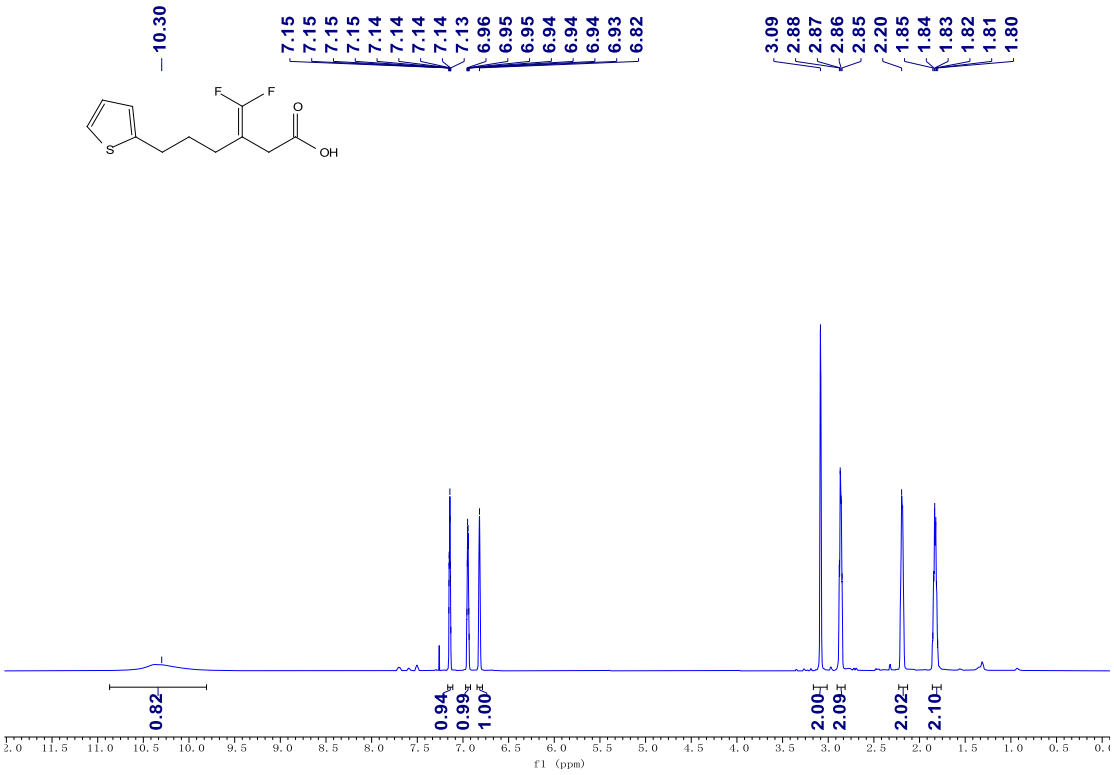
^{13}C NMR Spectra of 2a (151 MHz, Chloroform-*d*)



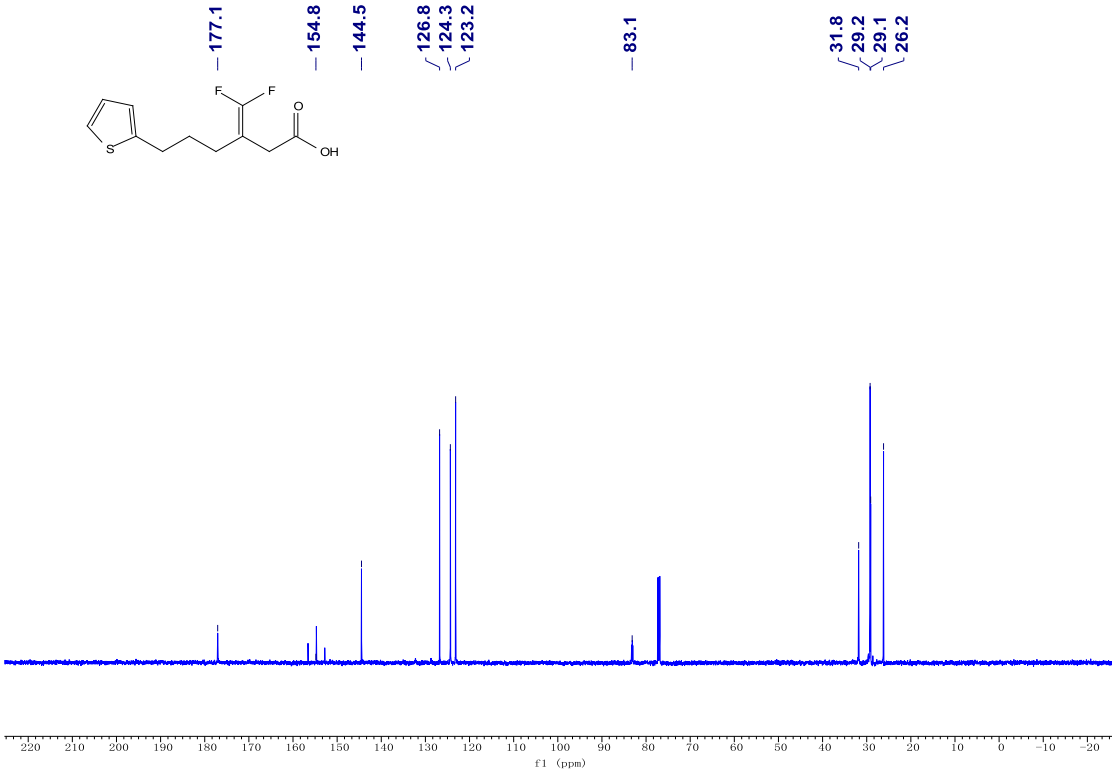
^{19}F NMR Spectra of 2a (565 MHz, Chloroform-*d*)



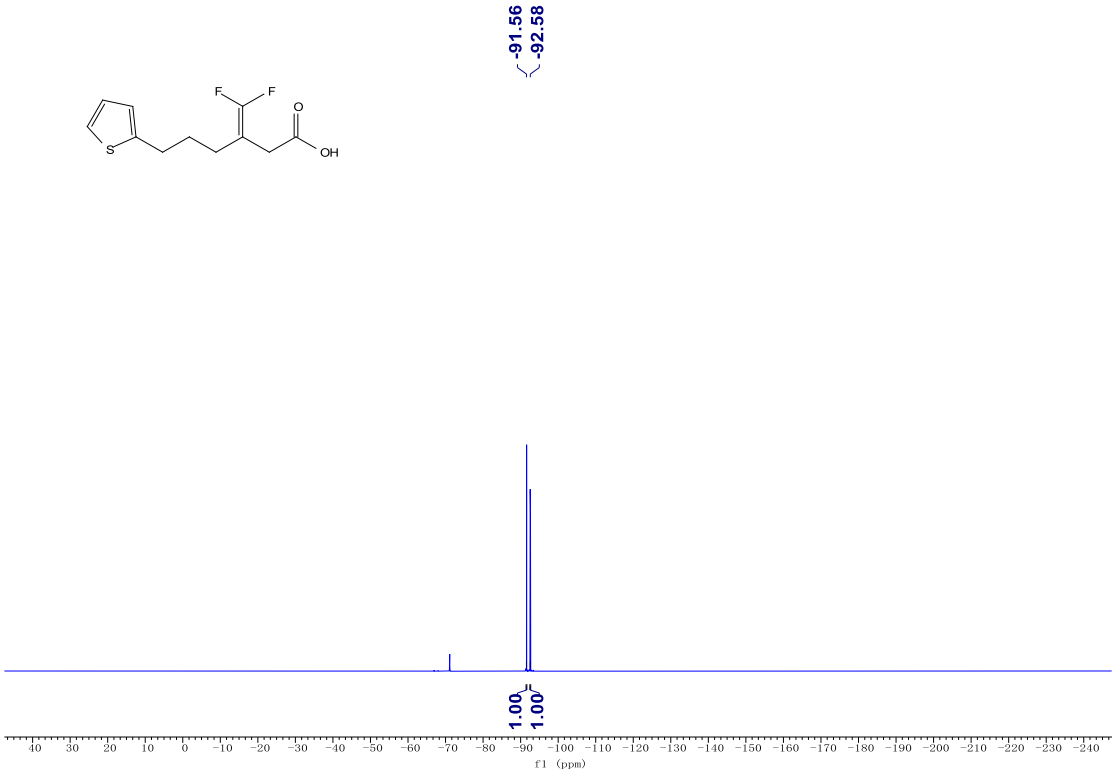
^{1}H NMR Spectra of 2b (600 MHz, Chloroform-*d*)



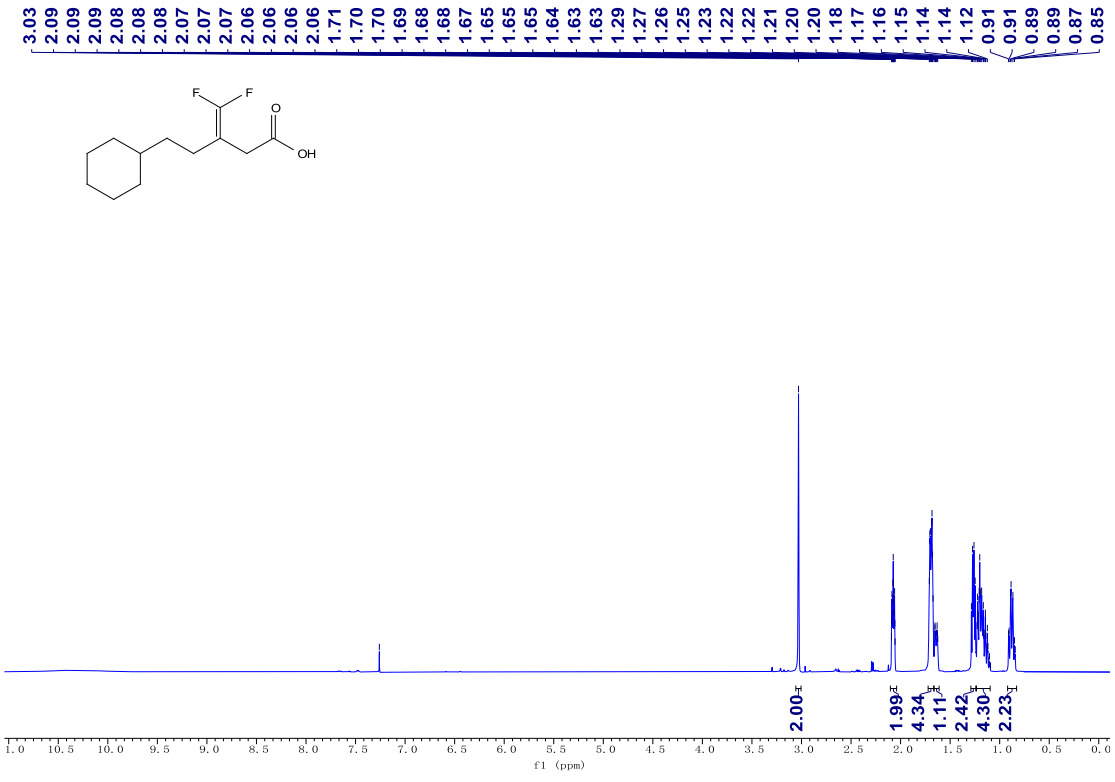
^{13}C NMR Spectra of 2b (151 MHz, Chloroform-*d*)



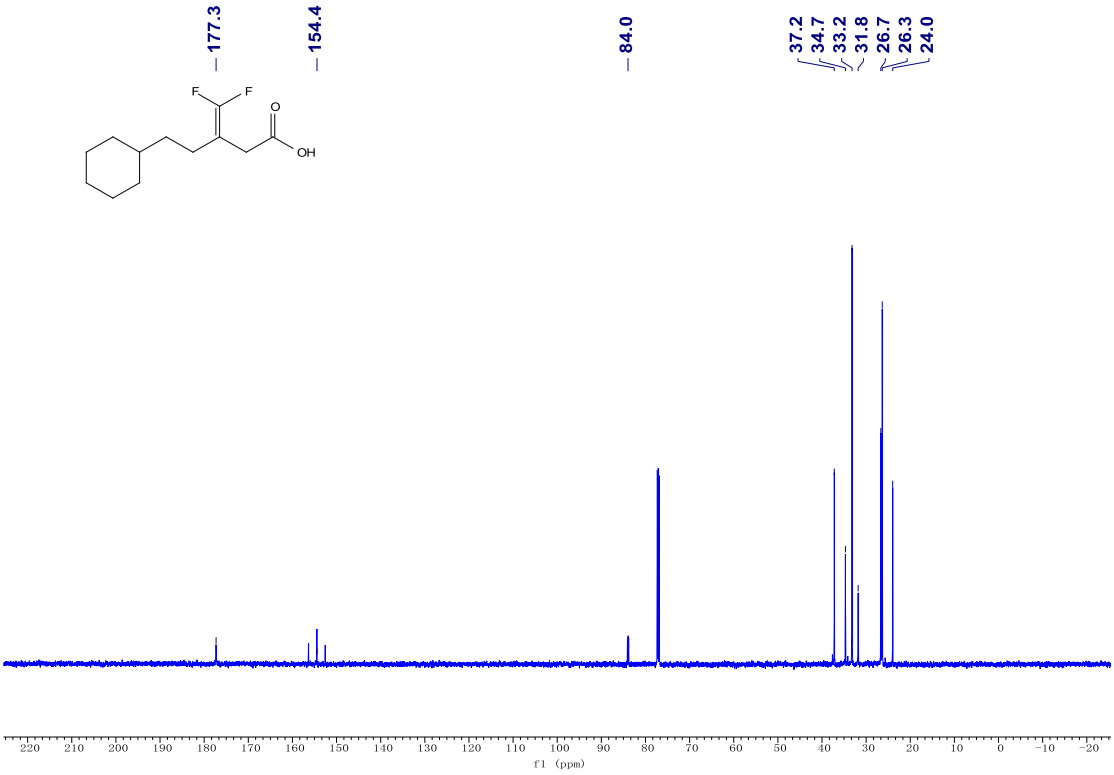
^{19}F NMR Spectra of 2b (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 2c (600 MHz, Chloroform-*d*)

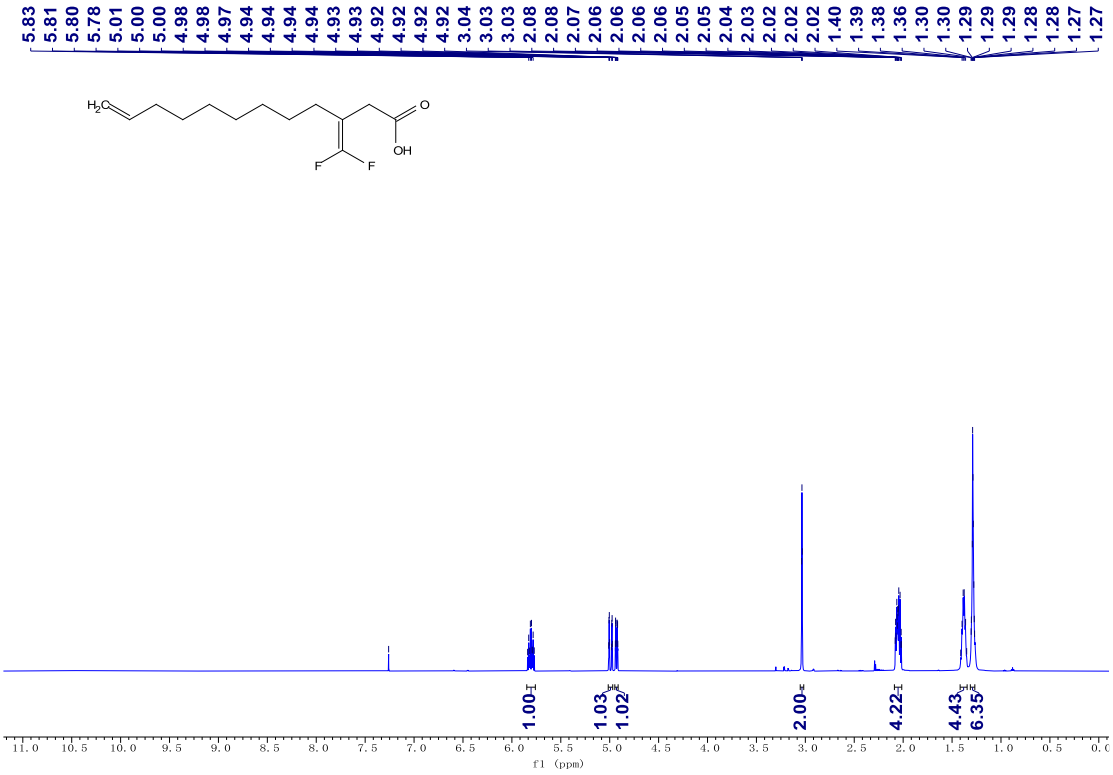


^{13}C NMR Spectra of 2c (151 MHz, Chloroform-*d*)

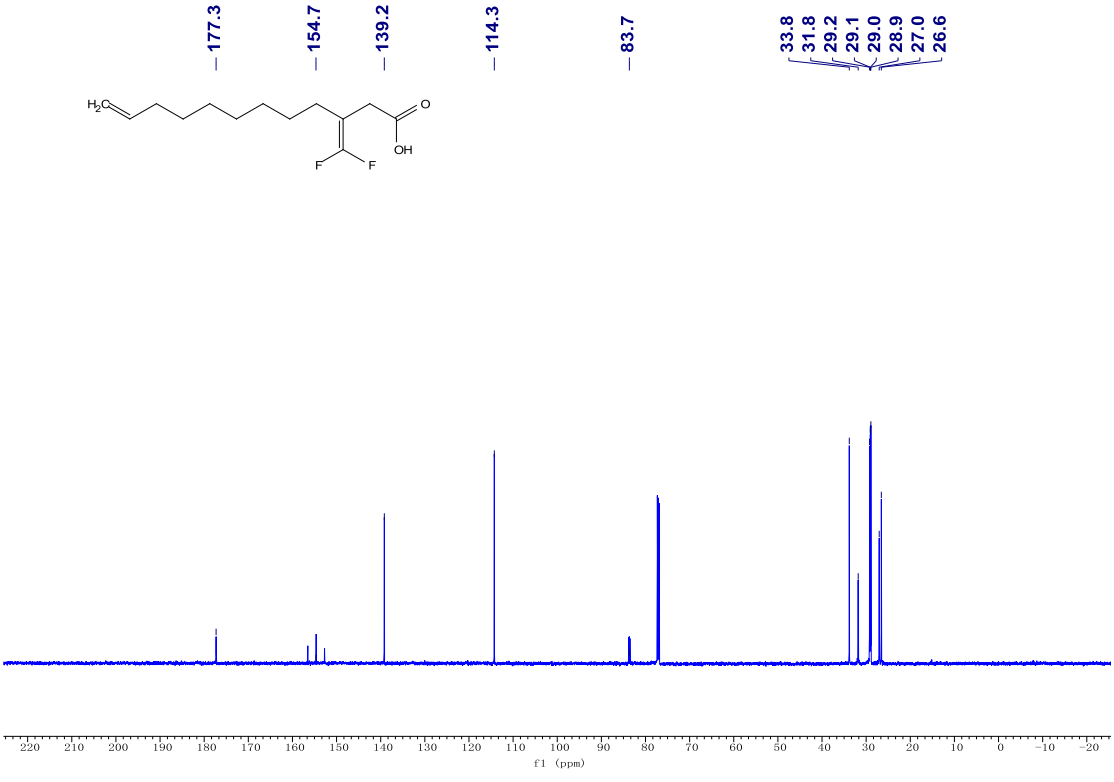


^{19}F NMR Spectra of 2c (565 MHz, Chloroform-*d*)

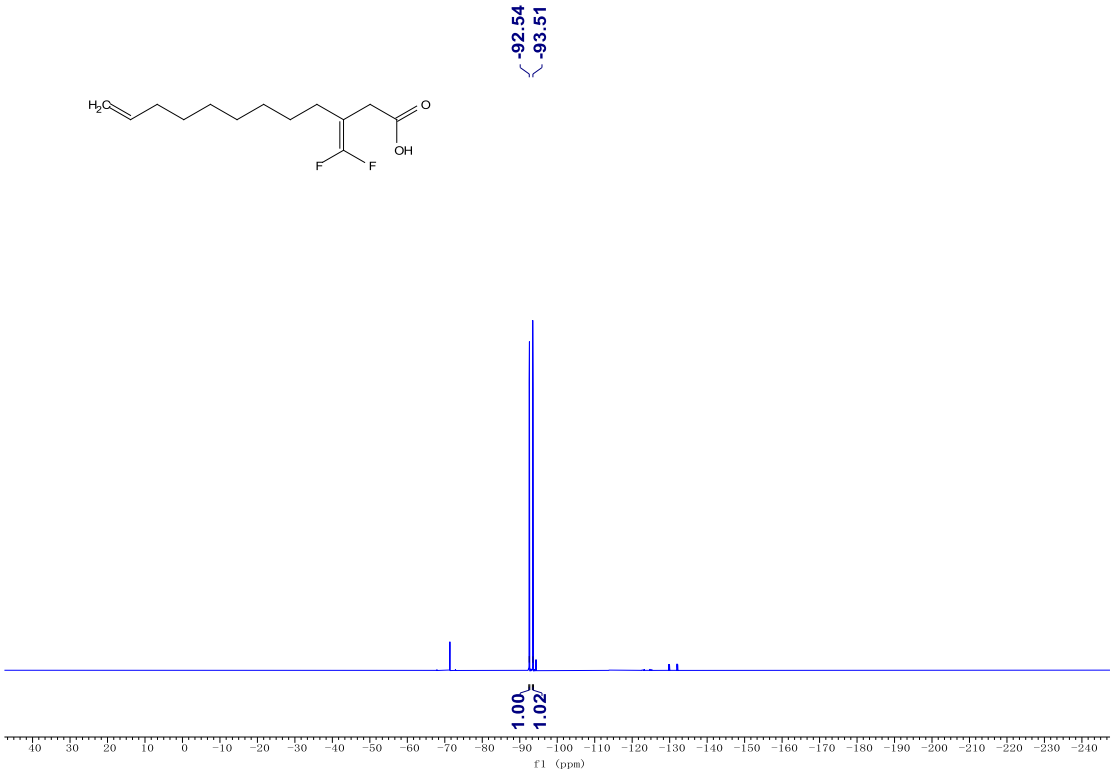
^{1}H NMR Spectra of 2d (600 MHz, Chloroform-*d*)



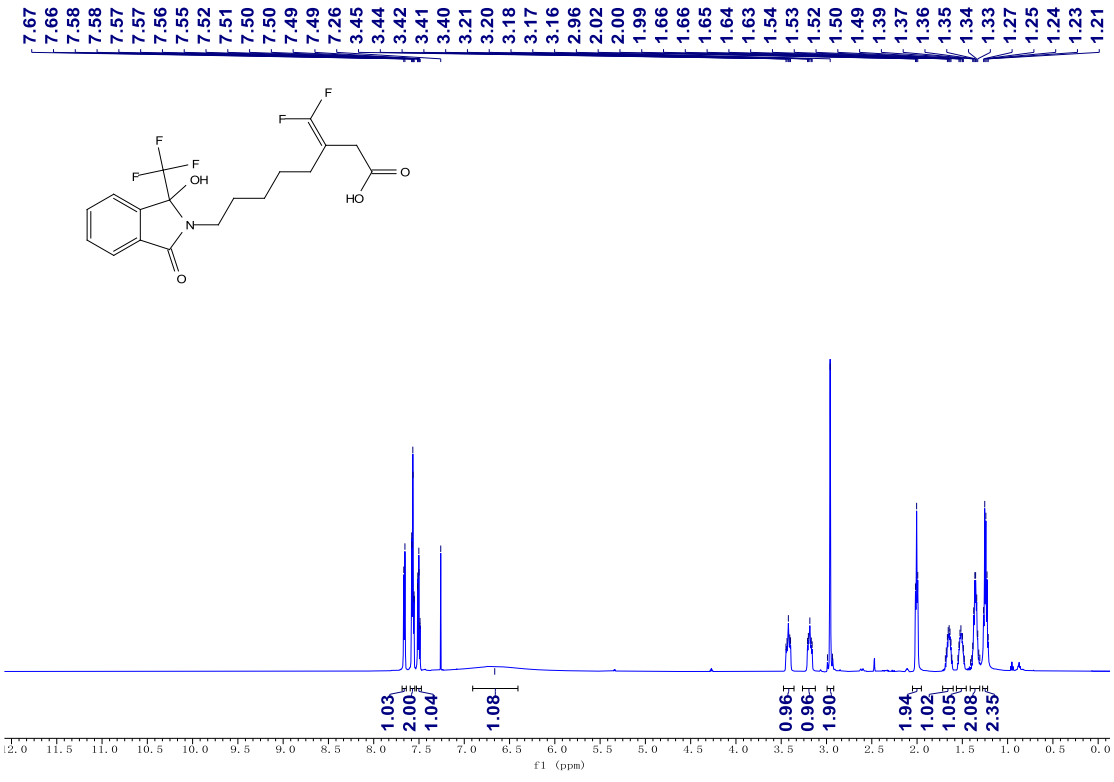
^{13}C NMR Spectra of 2d (151 MHz, Chloroform-*d*)



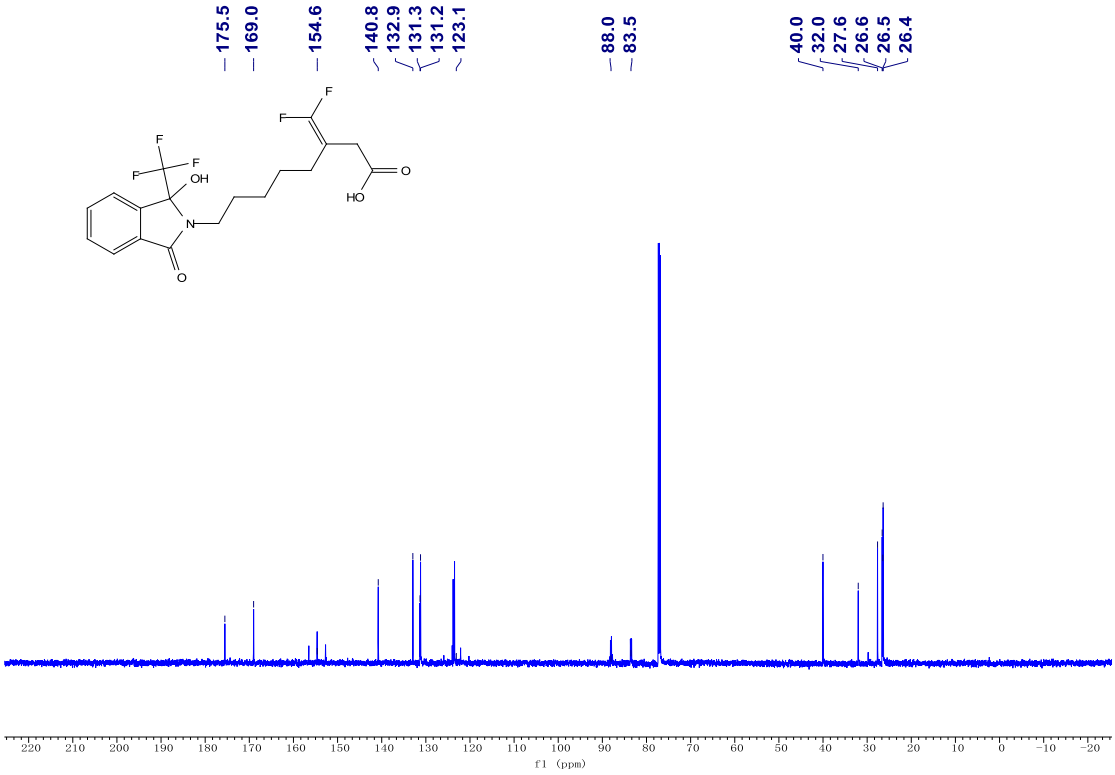
^{19}F NMR Spectra of 2d (565 MHz, Chloroform-*d*)



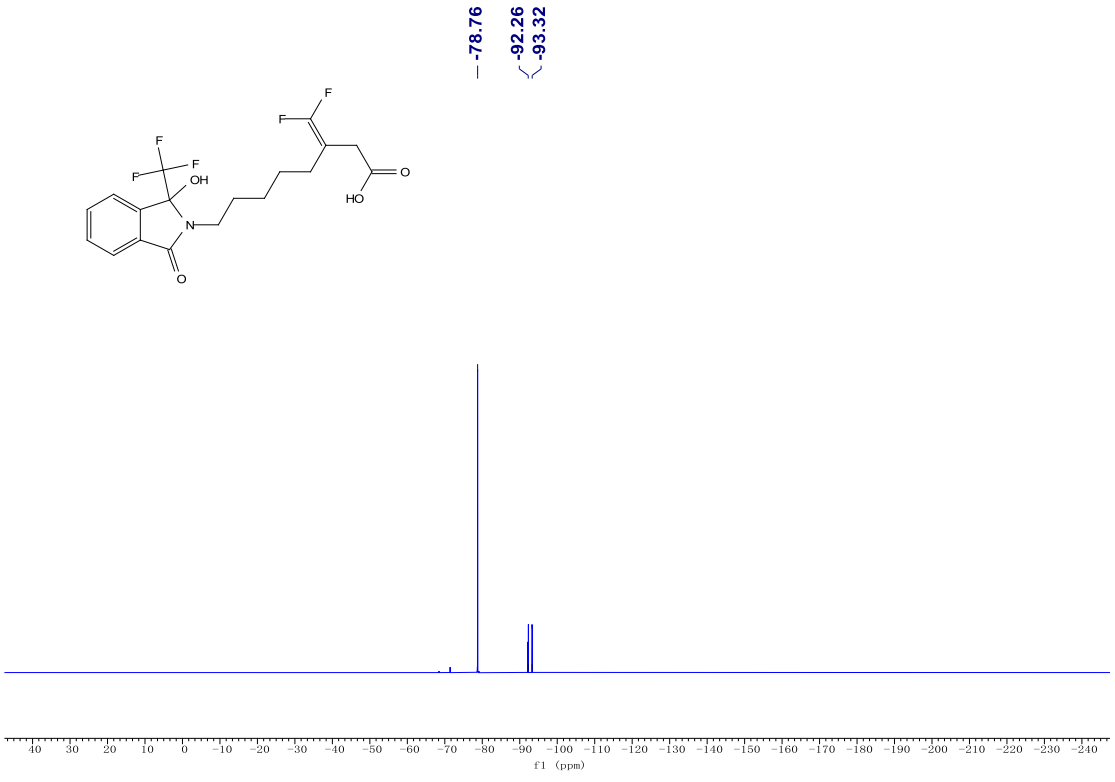
^{1}H NMR Spectra of 2e (600 MHz, Chloroform-*d*)



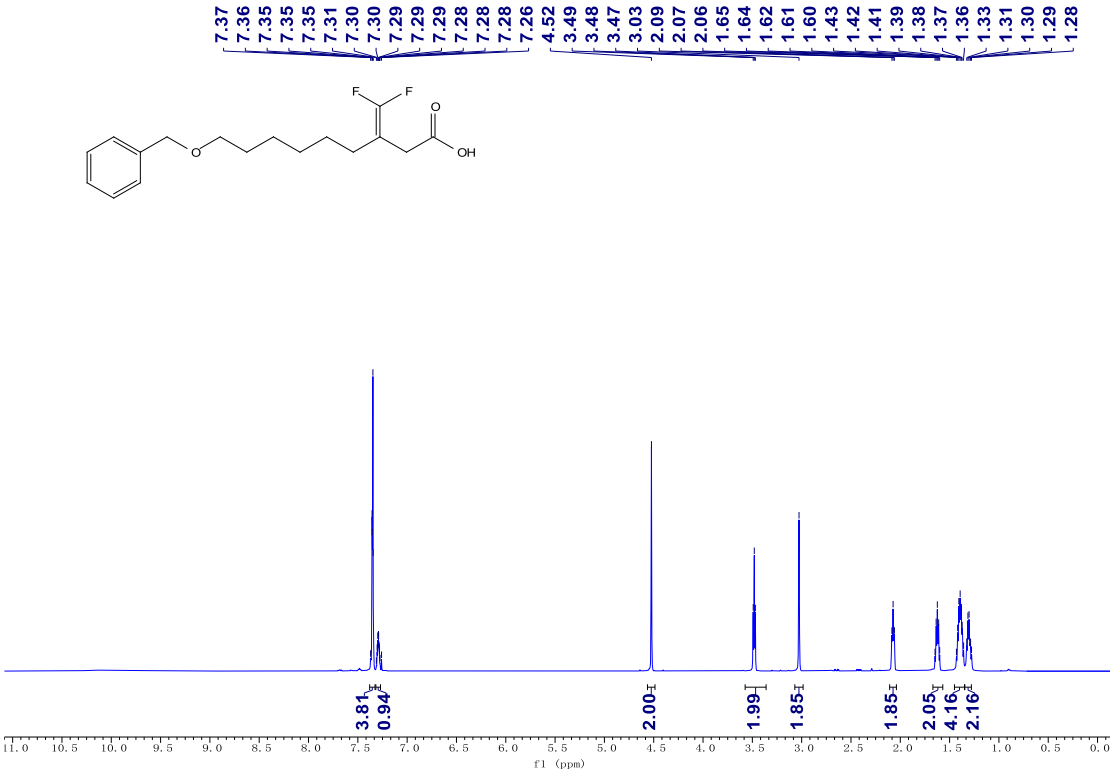
^{13}C NMR Spectra of 2e (151 MHz, Chloroform-*d*)



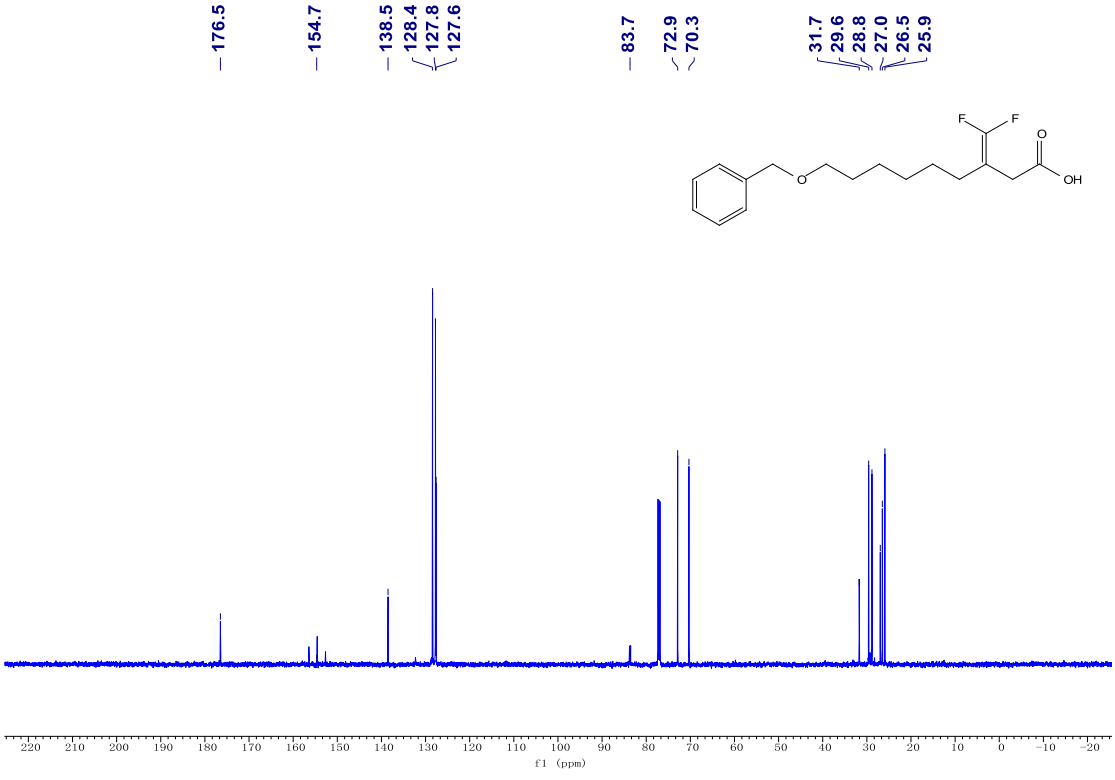
^{19}F NMR Spectra of 2e (565 MHz, Chloroform-*d*)



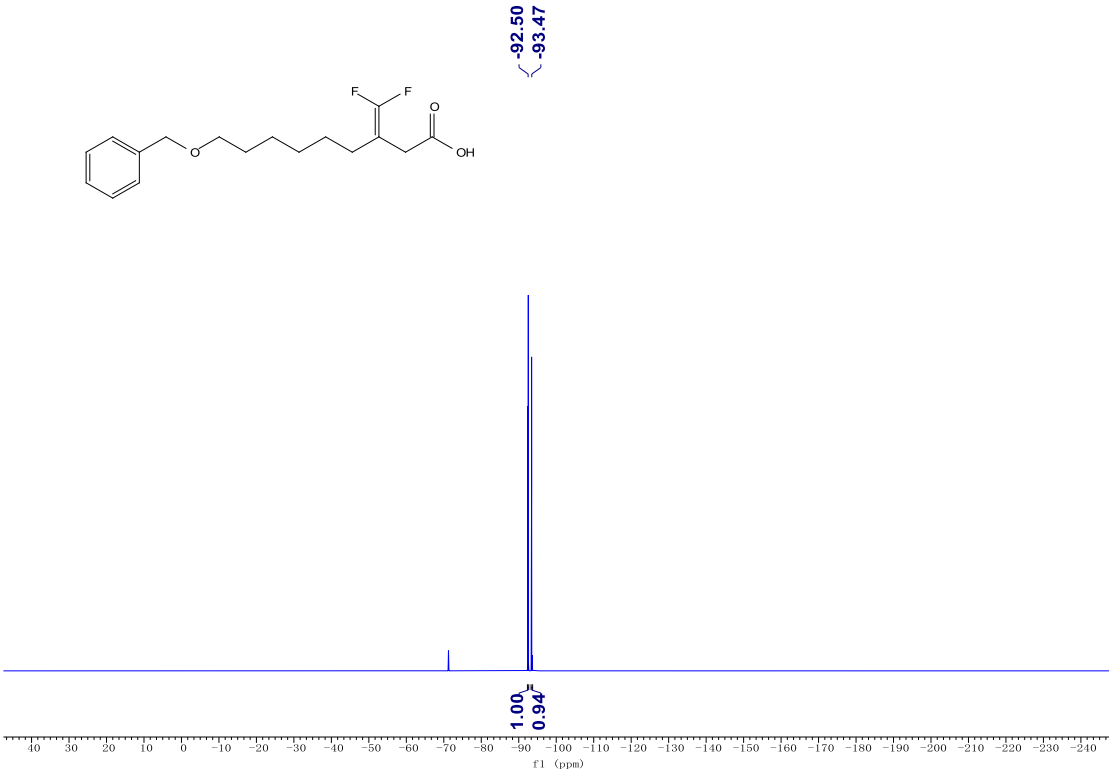
^{1}H NMR Spectra of 2f (600 MHz, Chloroform-*d*)



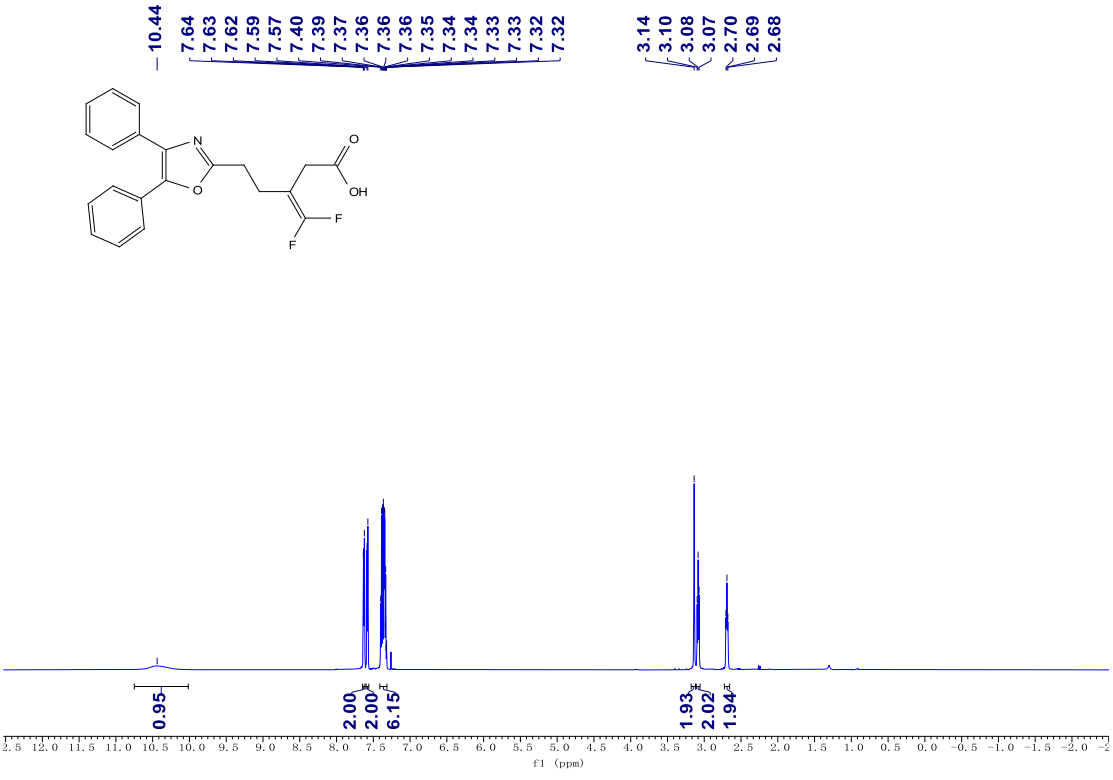
^{13}C NMR Spectra of 2f (151 MHz, Chloroform-*d*)



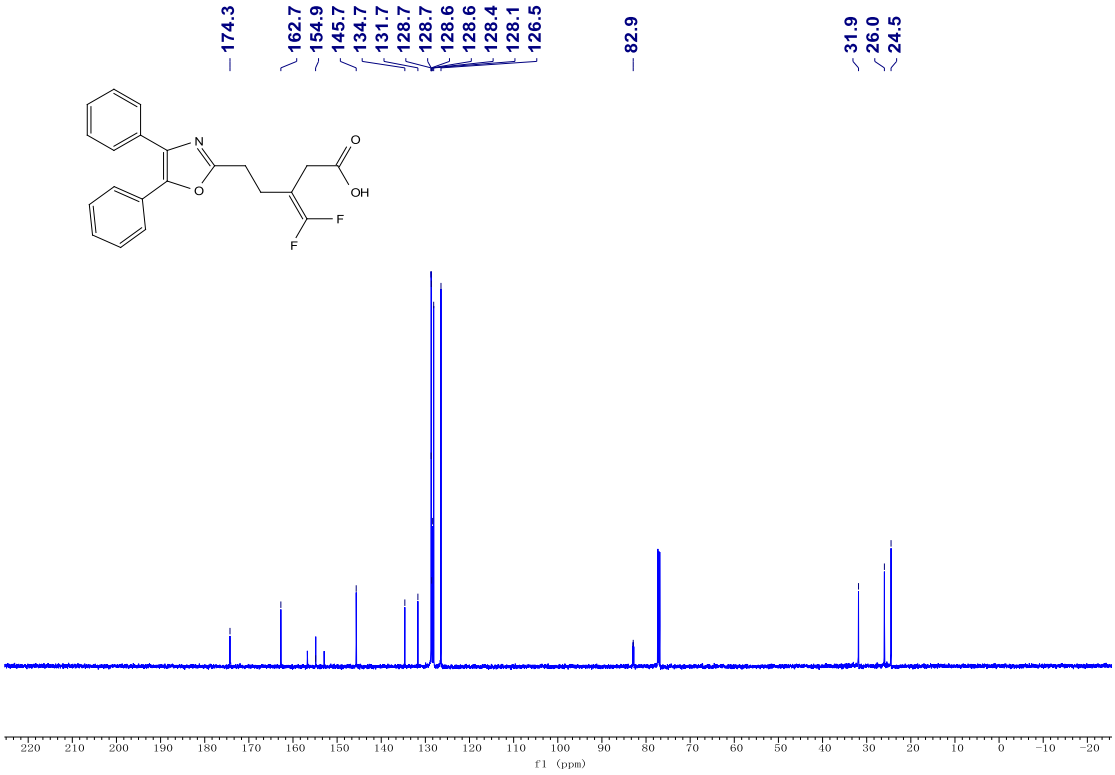
^{19}F NMR Spectra of 2f (565 MHz, Chloroform-*d*)



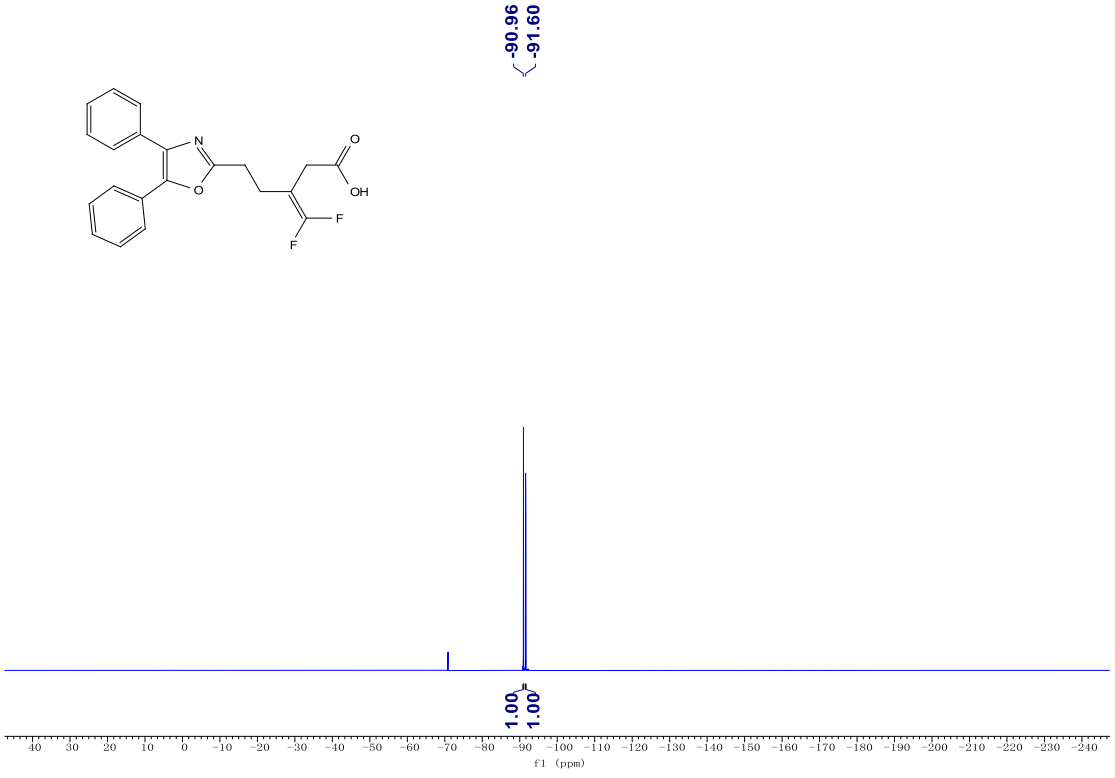
^{1}H NMR Spectra of 2g (600 MHz, Chloroform-*d*)



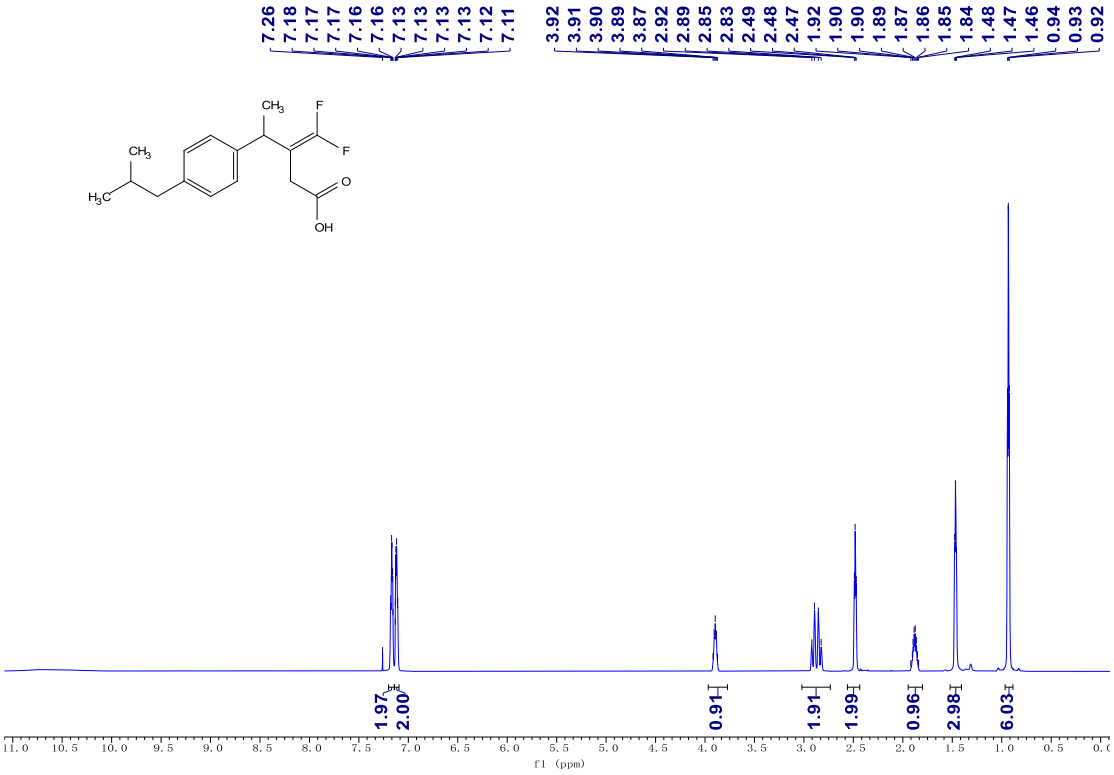
^{13}C NMR Spectra of 2g (151 MHz, Chloroform-*d*)



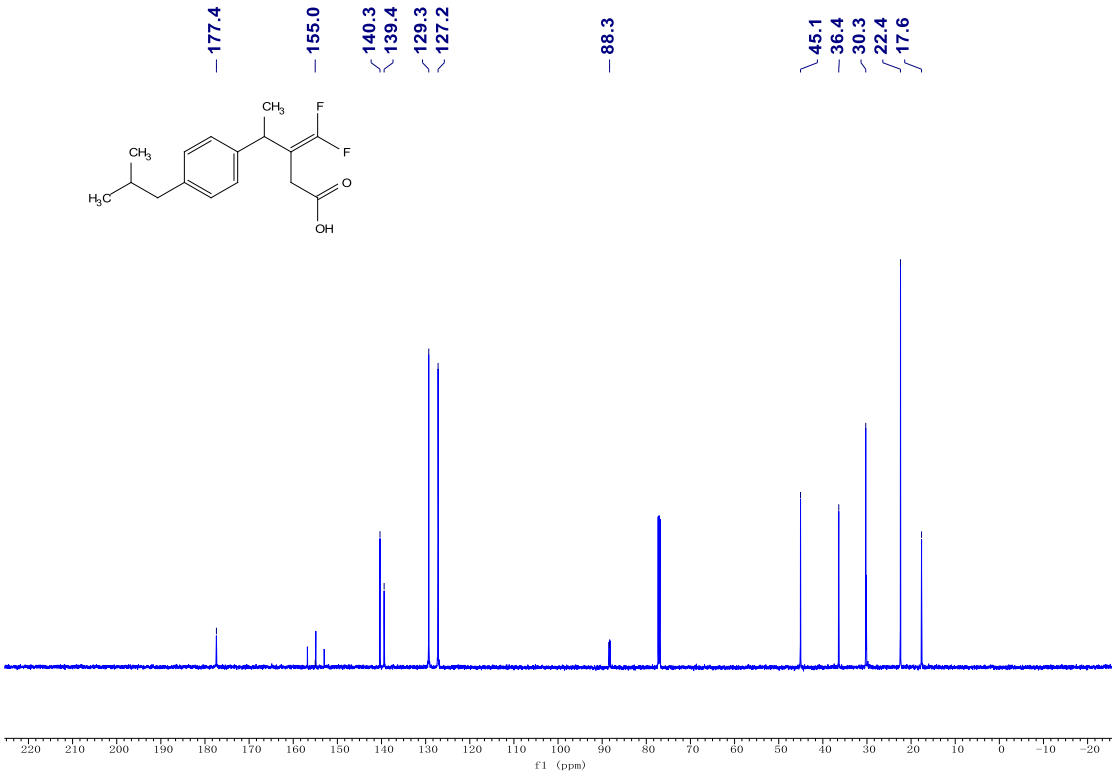
^{19}F NMR Spectra of 2g (565 MHz, Chloroform-*d*)



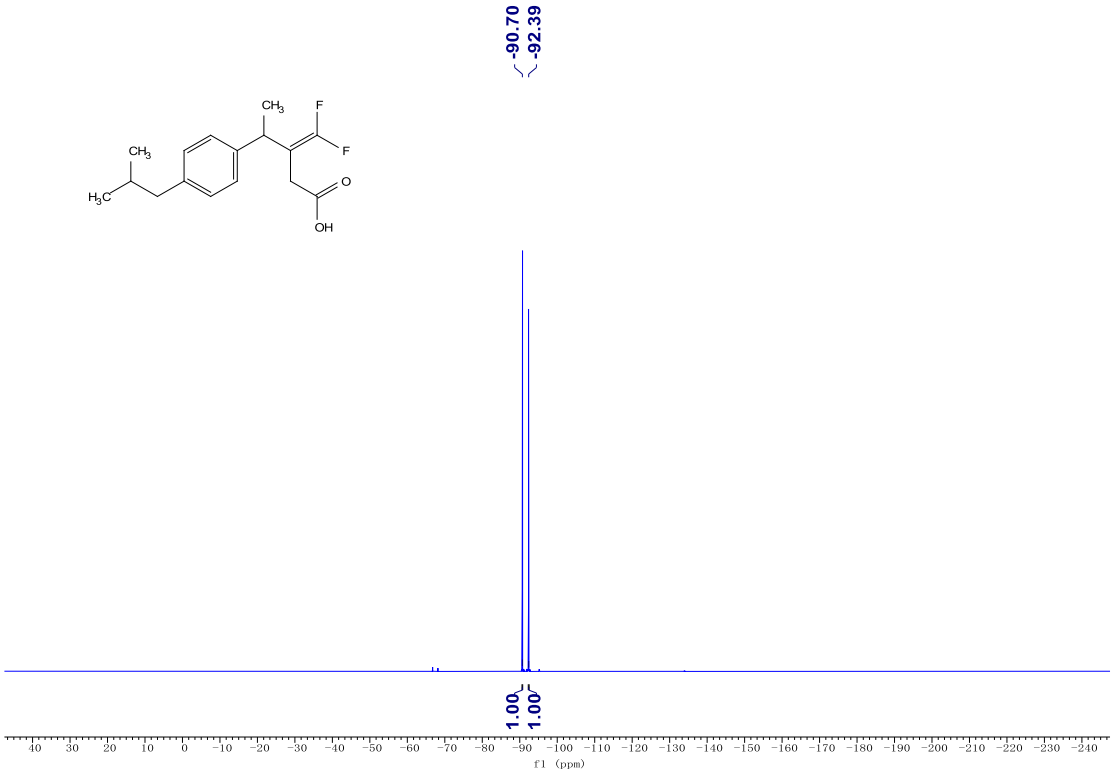
^{1}H NMR Spectra of 2h (600 MHz, Chloroform-*d*)



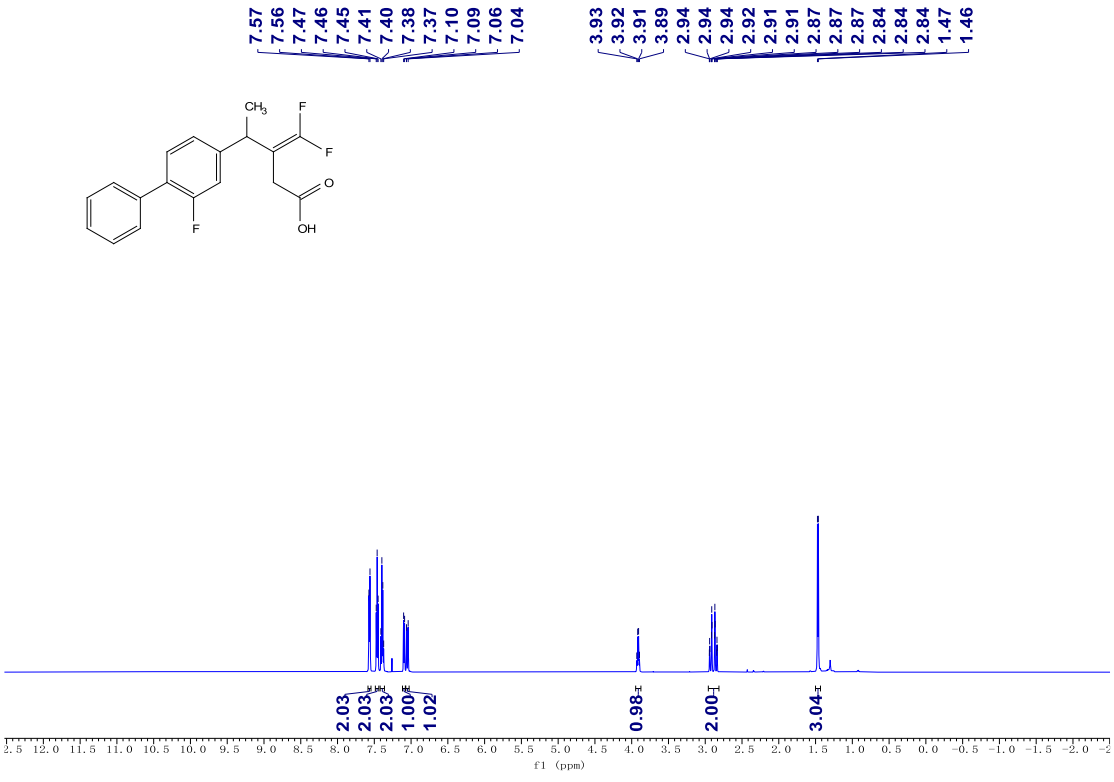
^{13}C NMR Spectra of 2h (151 MHz, Chloroform-*d*)



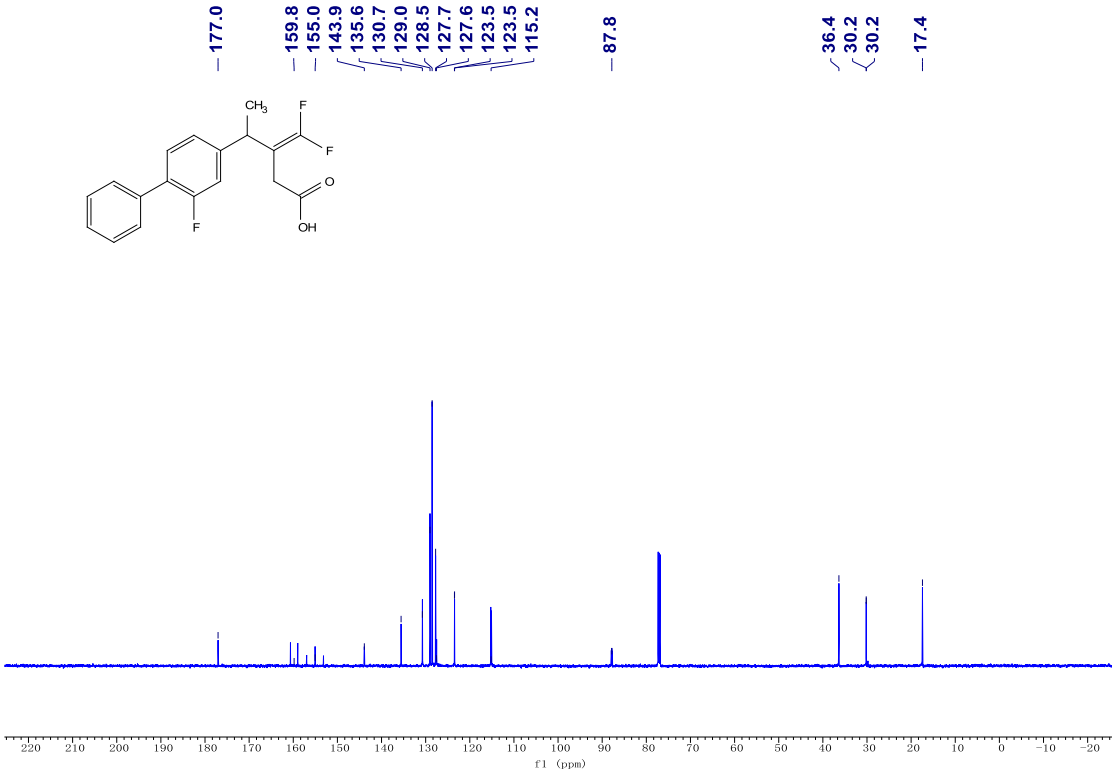
^{19}F NMR Spectra of 2h (565 MHz, Chloroform-*d*)



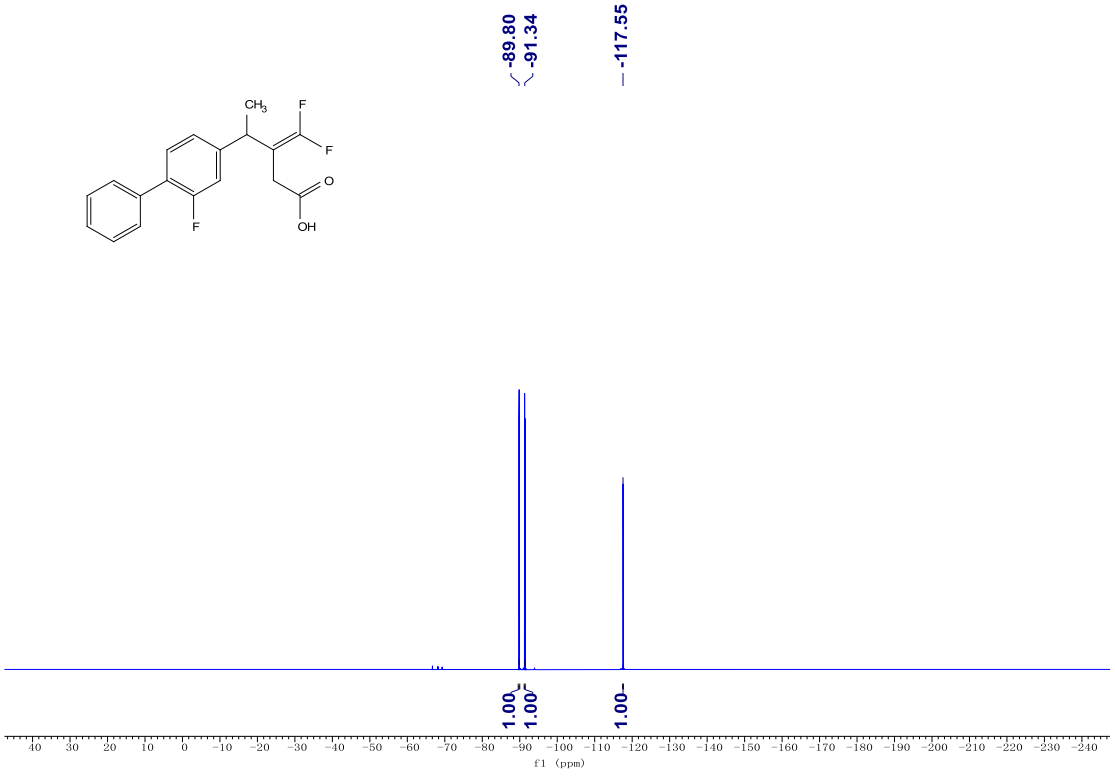
^{1}H NMR Spectra of 2i (600 MHz, Chloroform-*d*)



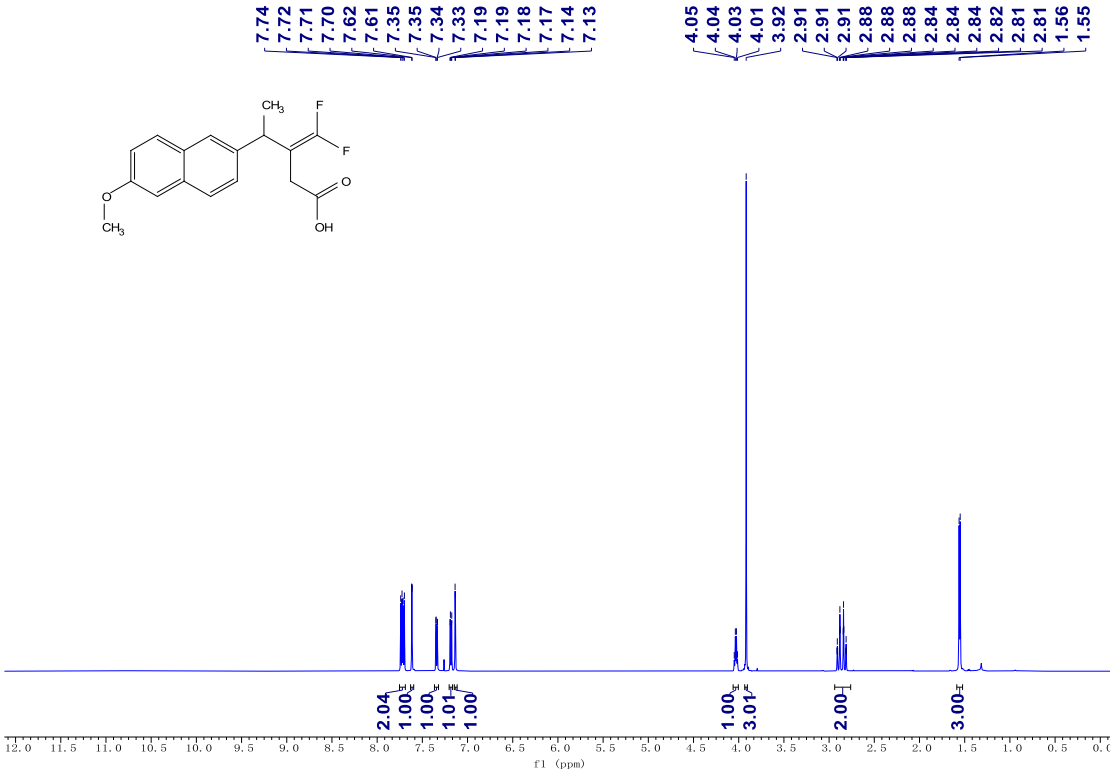
^{13}C NMR Spectra of 2i (151 MHz, Chloroform-*d*)



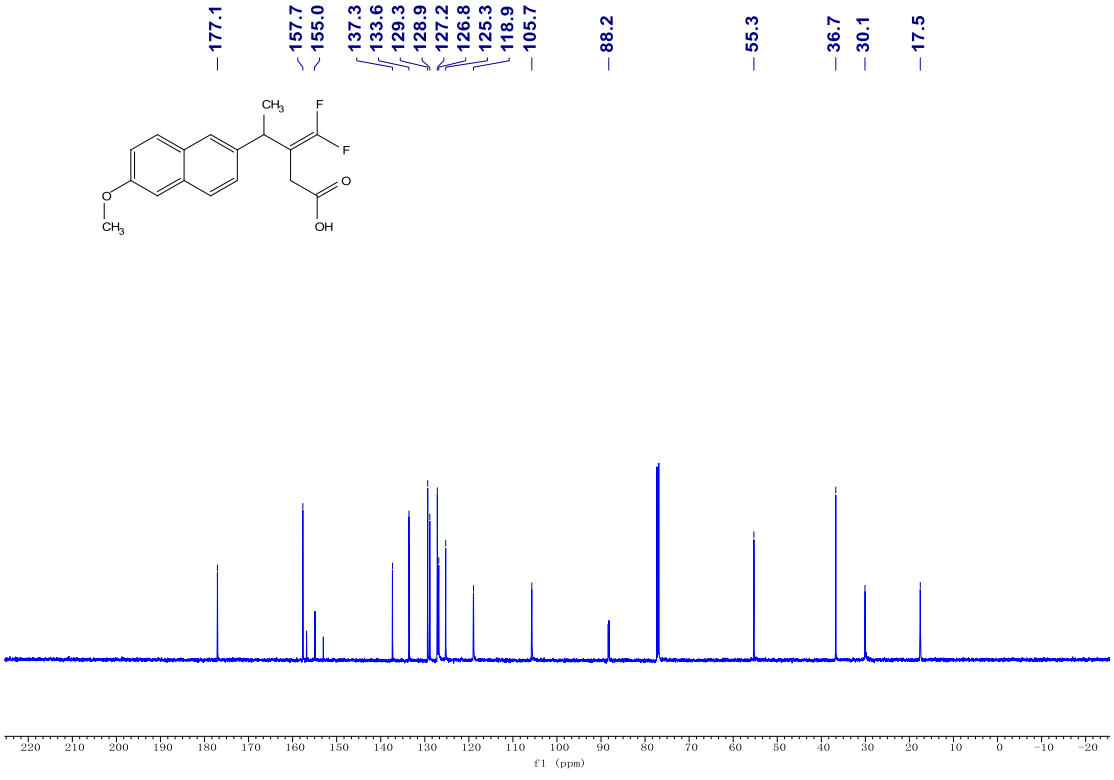
^{19}F NMR Spectra of 2i (565 MHz, Chloroform-*d*)



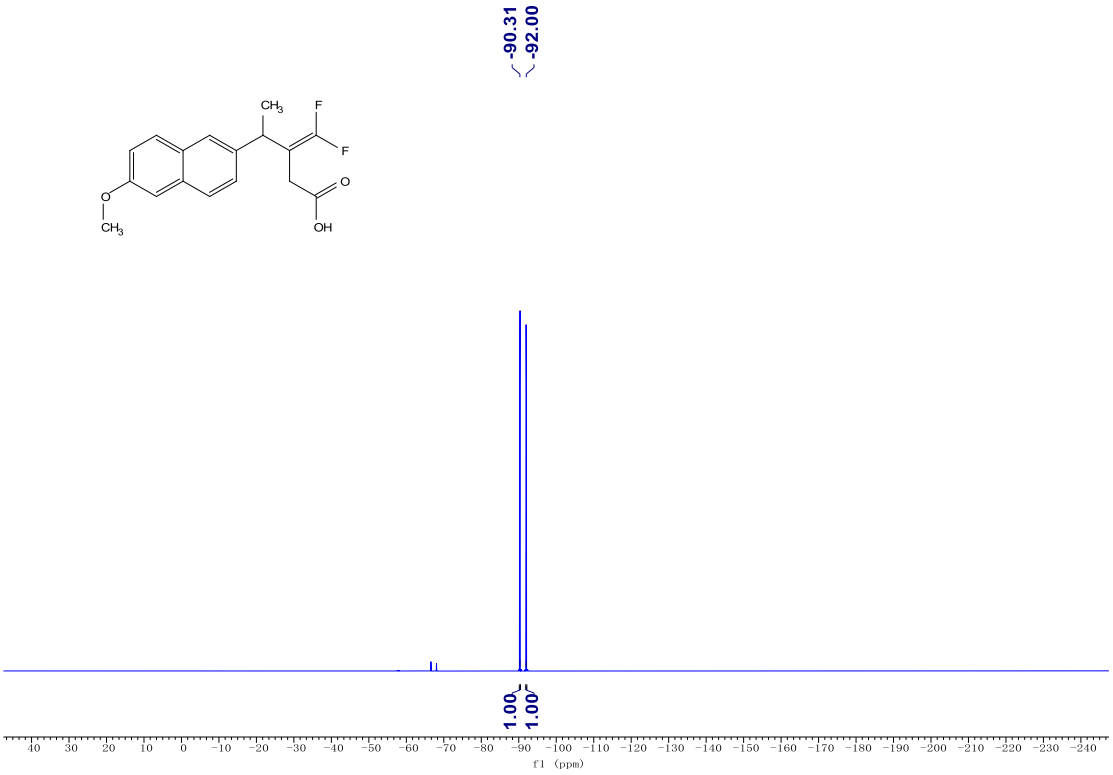
^{1}H NMR Spectra of 2j (600 MHz, Chloroform-*d*)



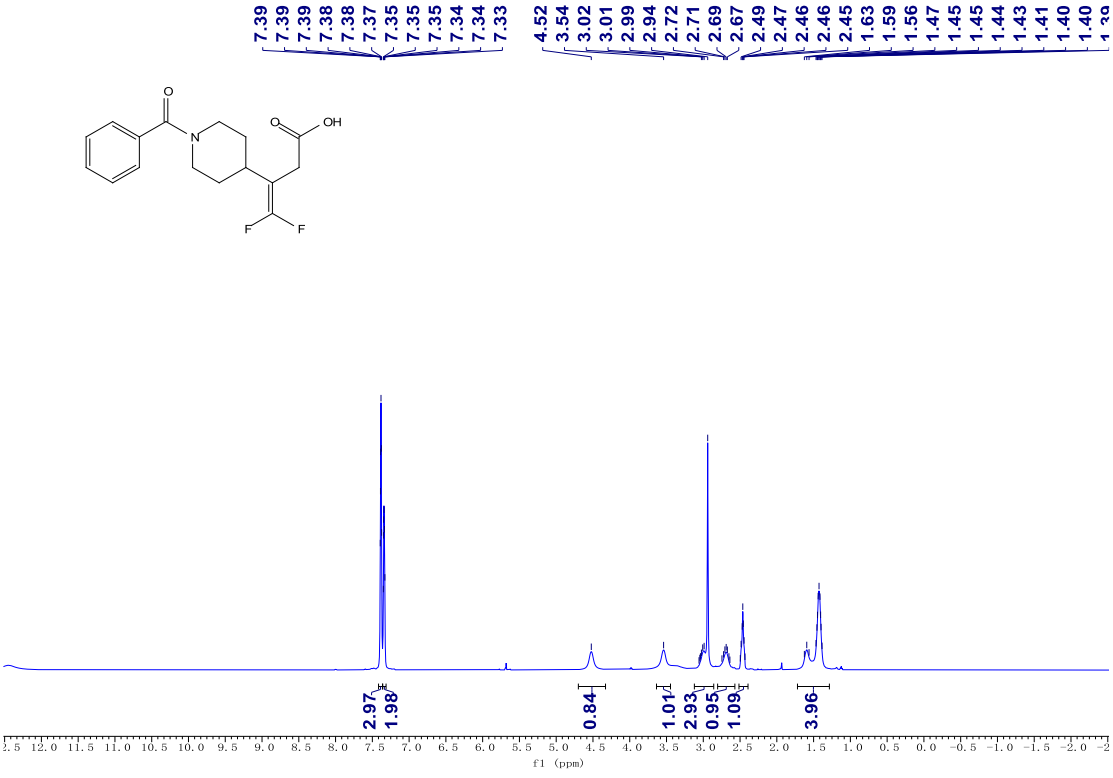
^{13}C NMR Spectra of 2j (151 MHz, Chloroform-*d*)



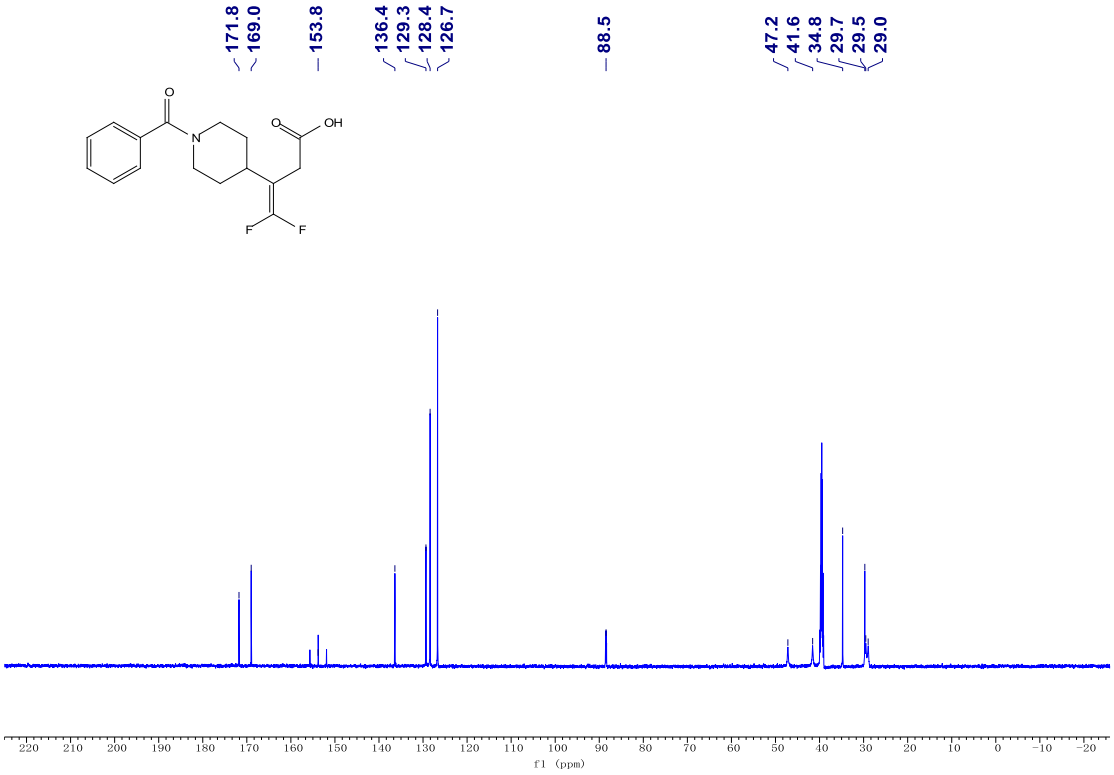
^{19}F NMR Spectra of 2j (565 MHz, Chloroform-*d*)



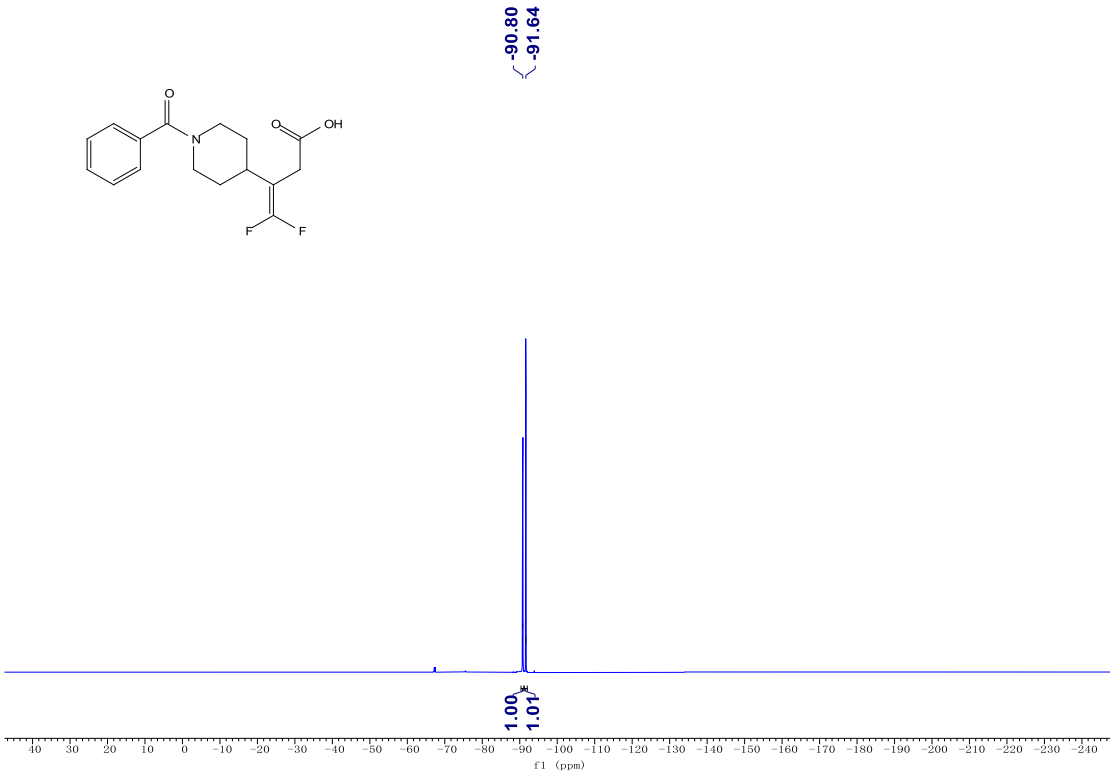
^{1}H NMR Spectra of 2k (600 MHz, DMSO-d_6)



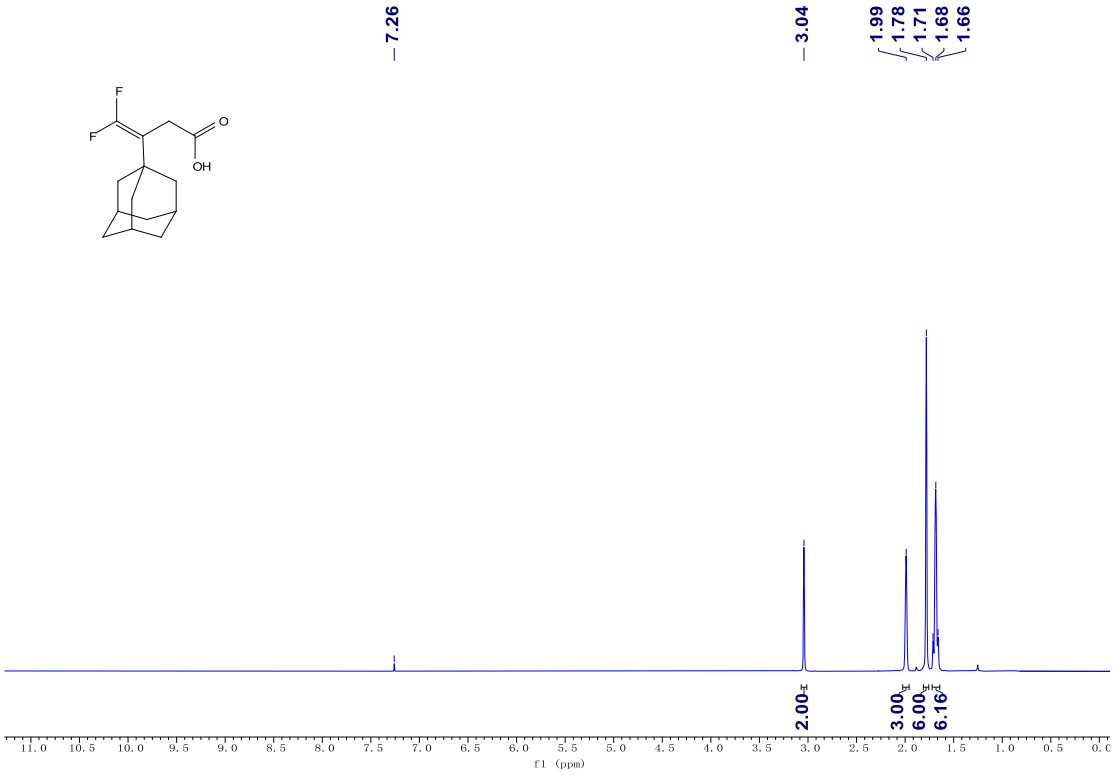
^{13}C NMR Spectra of 2k (151 MHz, DMSO-D_6)



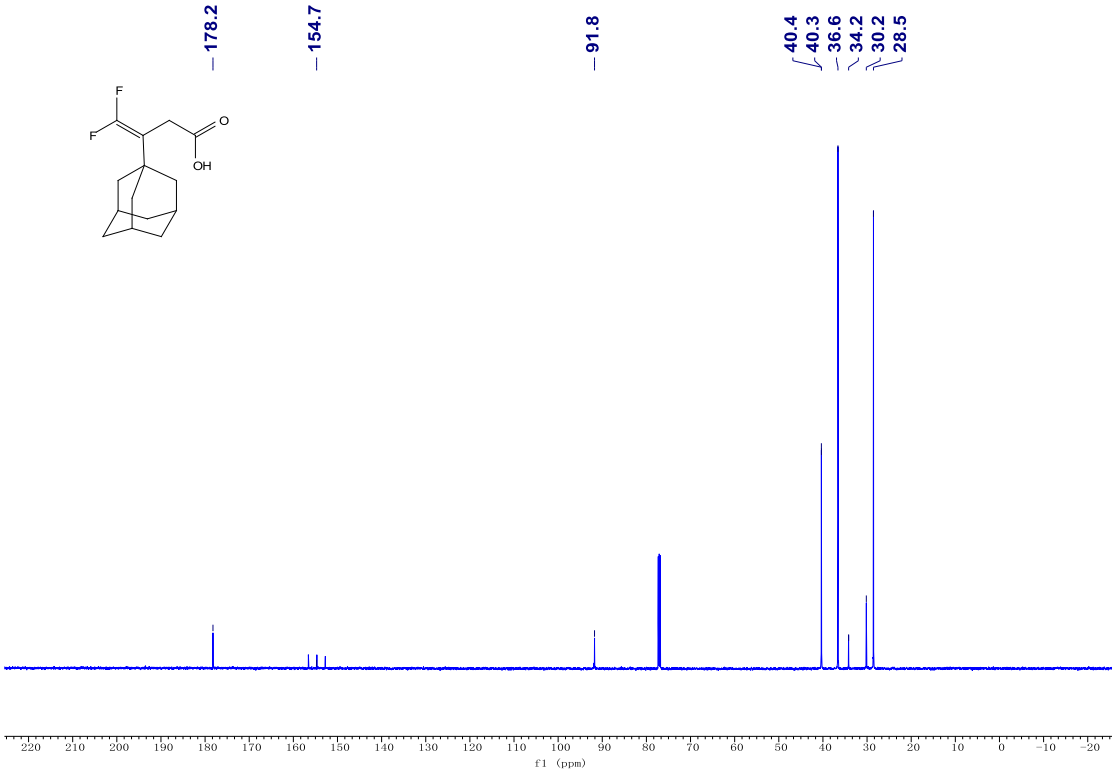
^{19}F NMR Spectra of 2k (565 MHz, Chloroform-*d*)



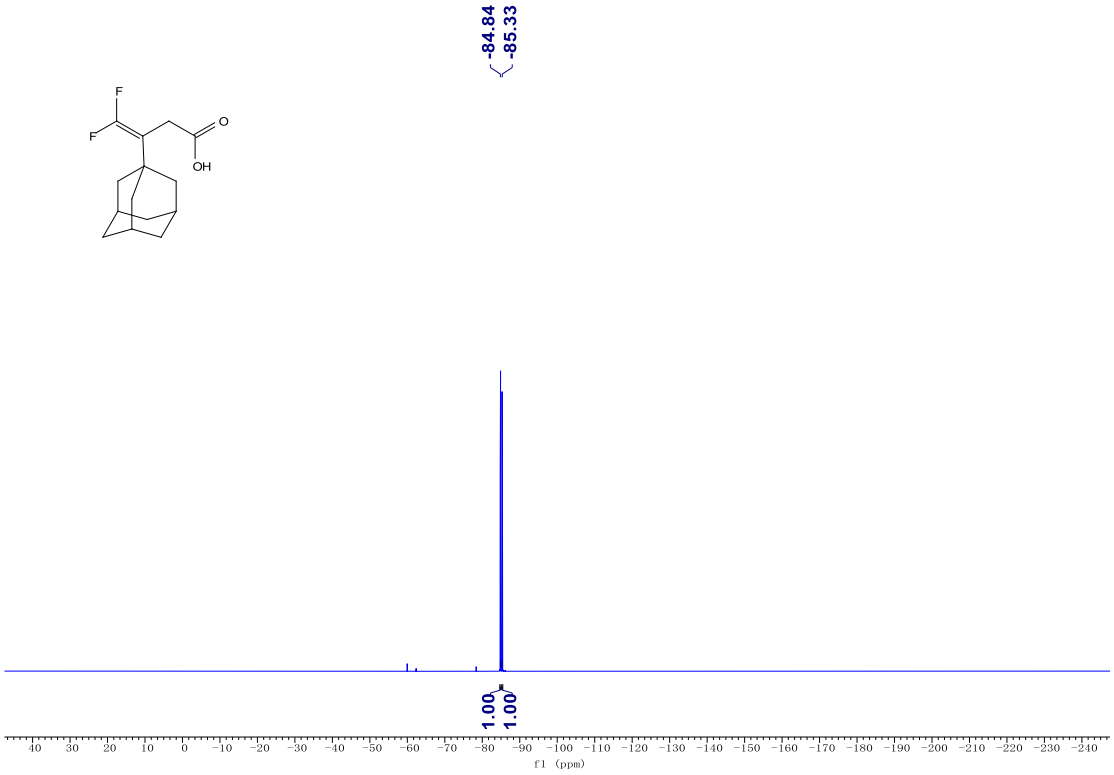
^{1}H NMR Spectra of 2l (600 MHz, Chloroform-*d*)



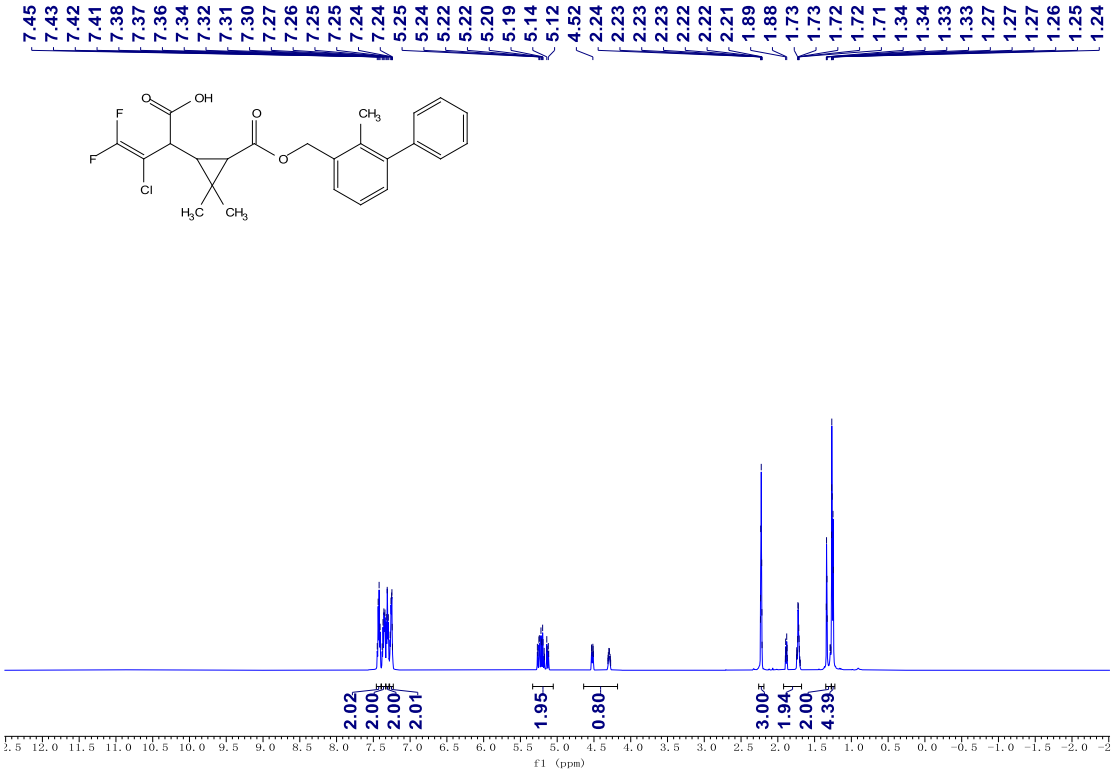
^{13}C NMR Spectra of 2l (151 MHz, Chloroform-*d*)



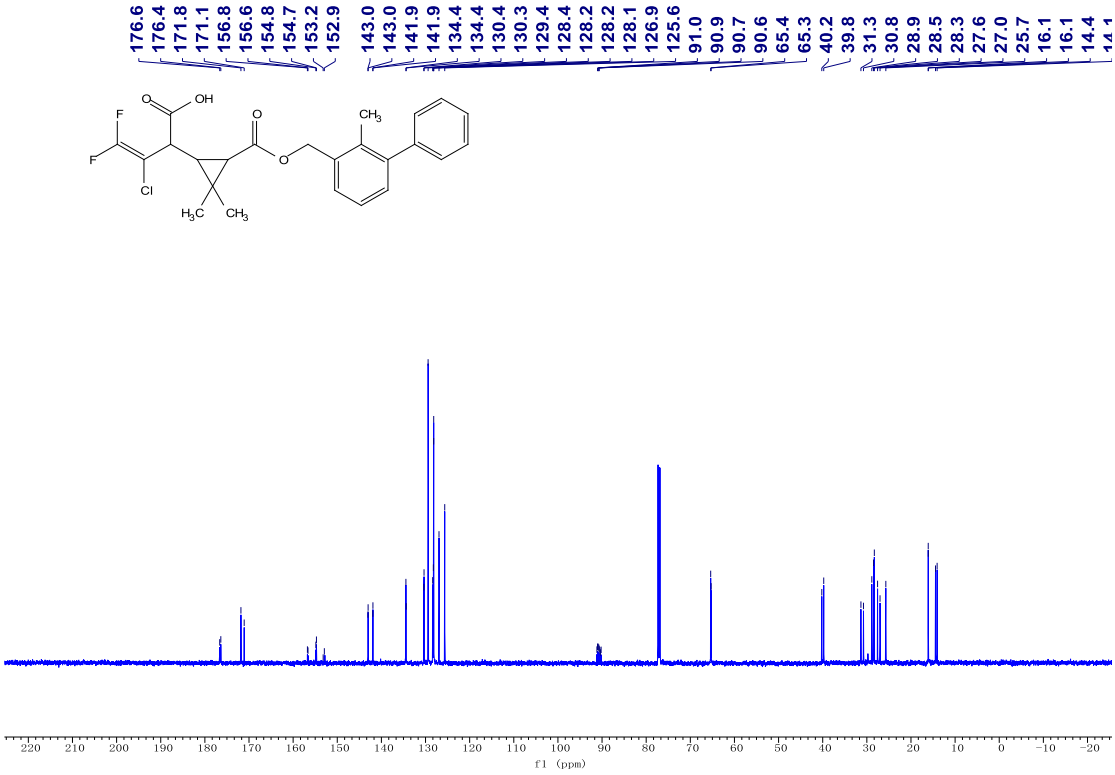
^{19}F NMR Spectra of 2l (565 MHz, Chloroform-*d*)



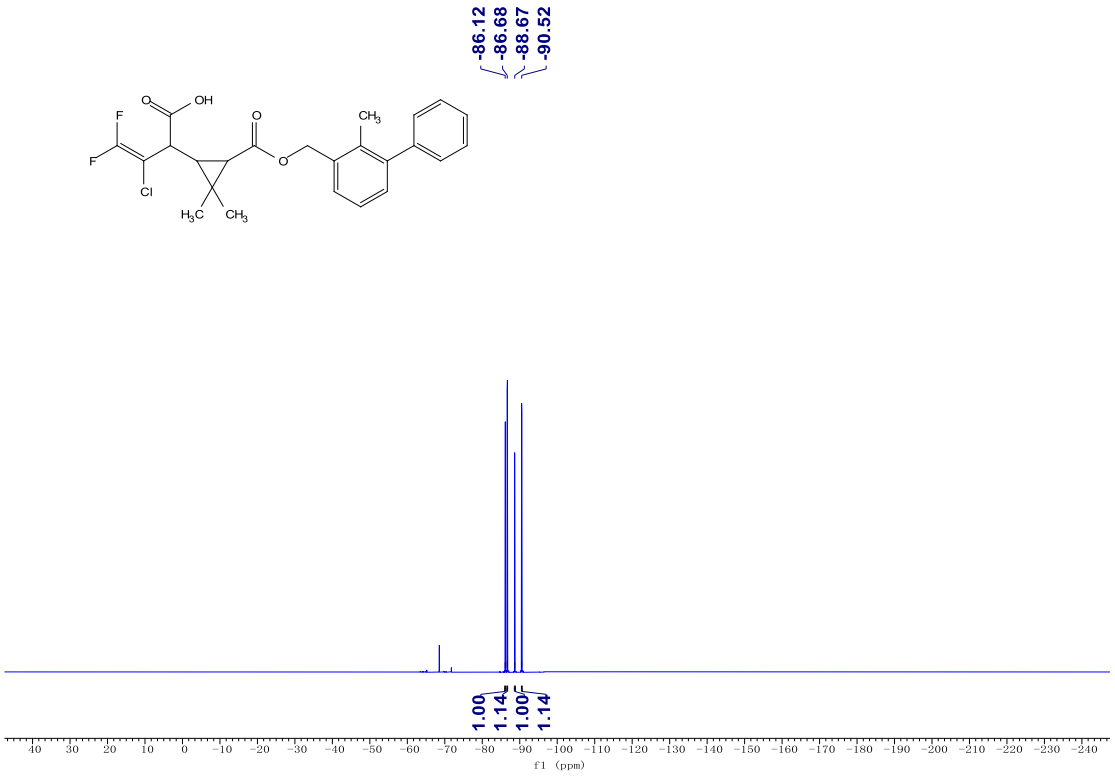
^{1}H NMR Spectra of 2m (600 MHz, Chloroform-*d*)



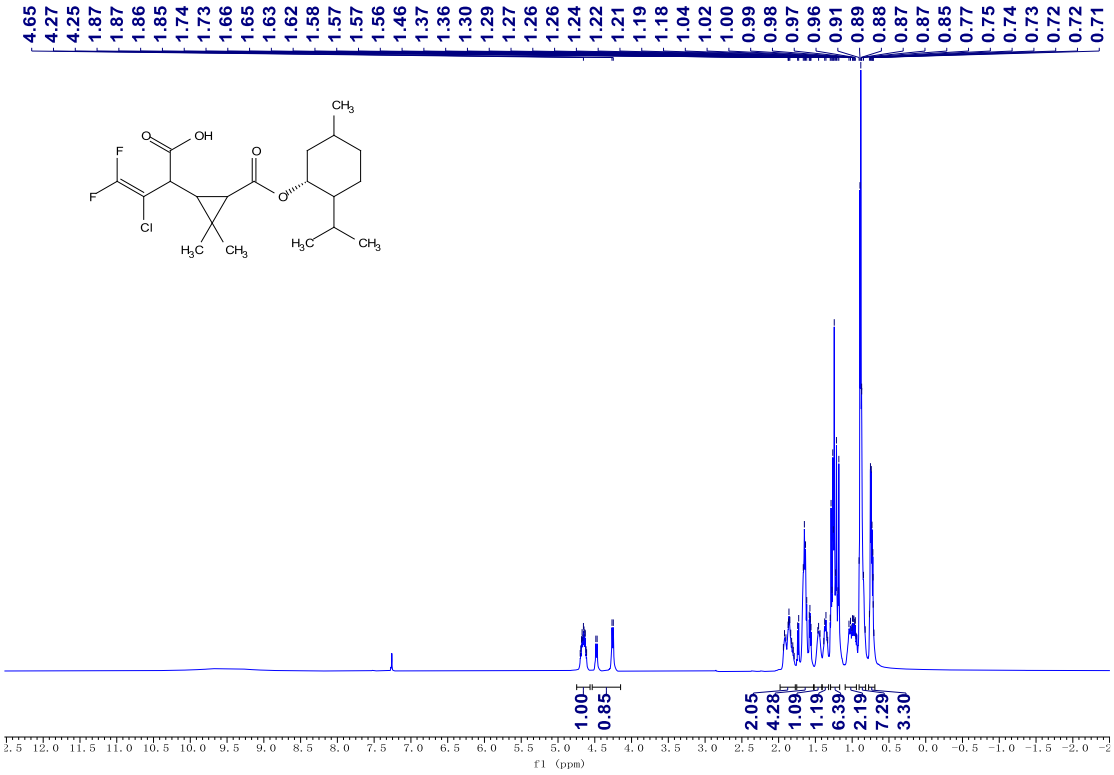
^{13}C NMR Spectra of 2m (151 MHz, Chloroform-*d*)



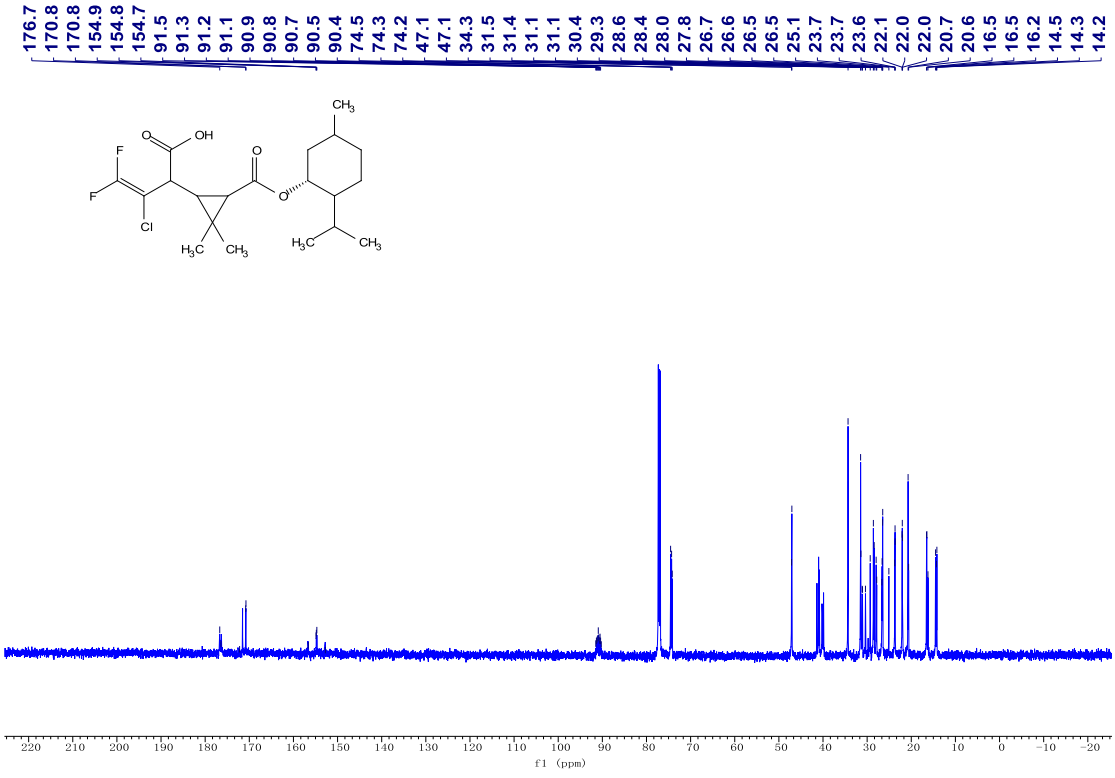
^{19}F NMR Spectra of 2m (565 MHz, Chloroform-*d*)



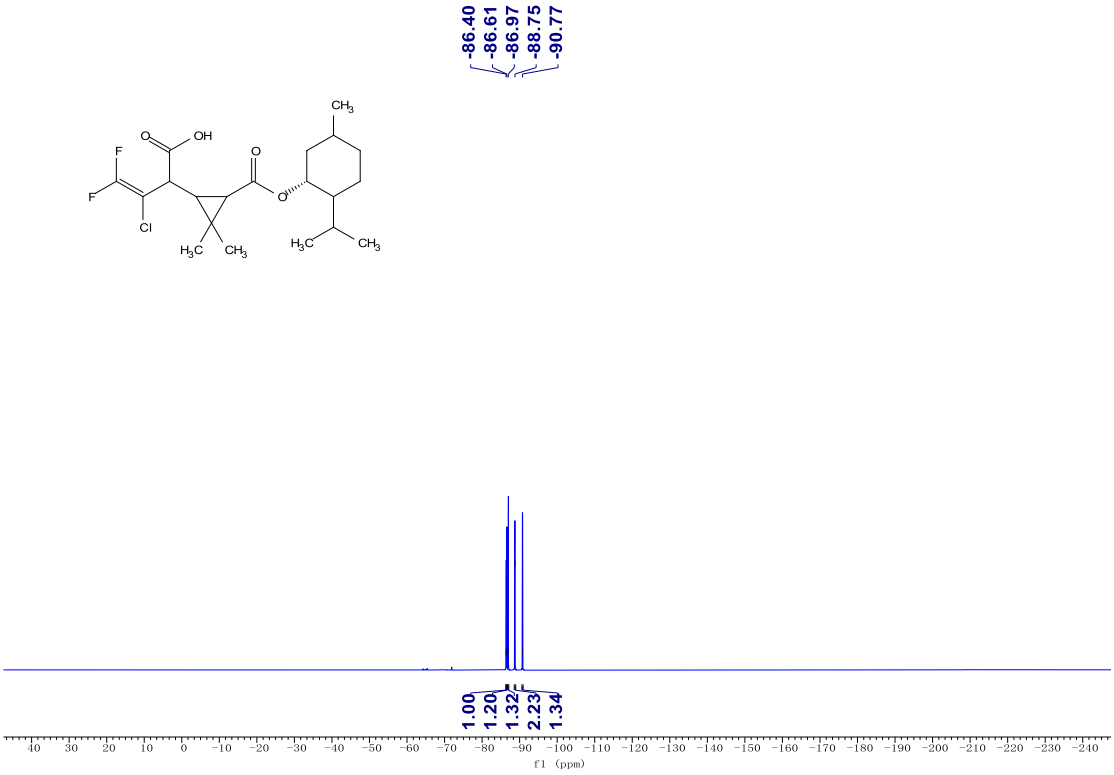
^{1}H NMR Spectra of 2n (600 MHz, Chloroform-*d*)



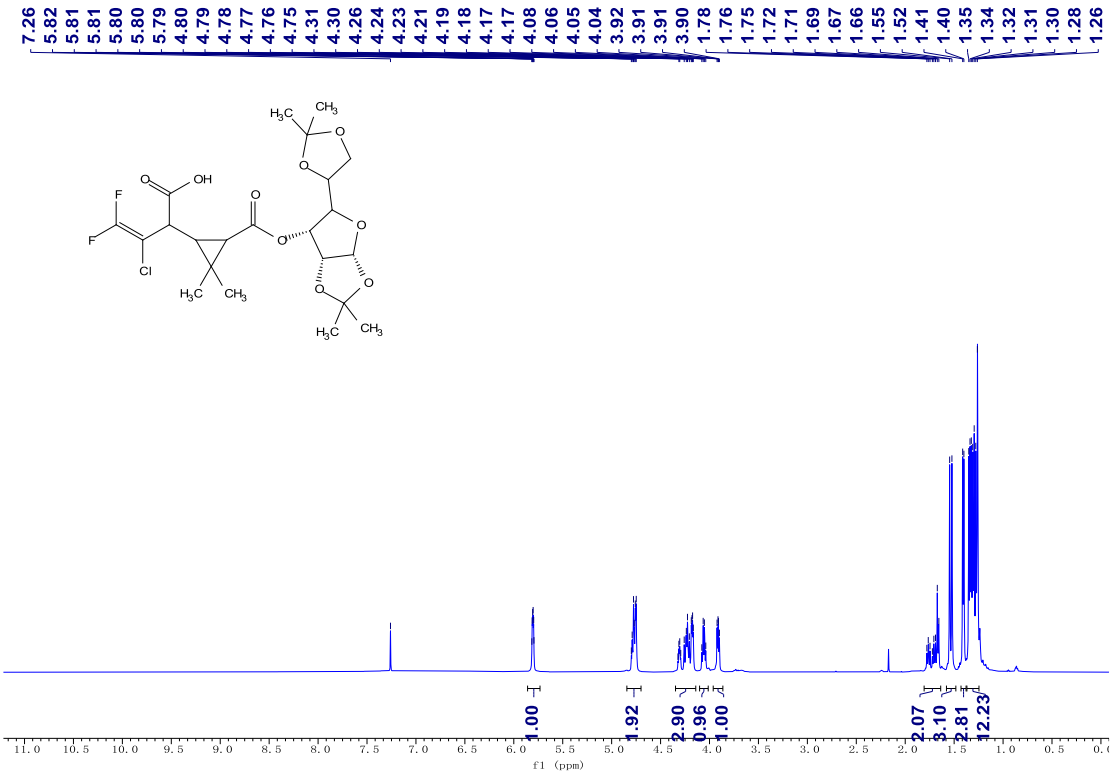
^{13}C NMR Spectra of 2n (151 MHz, Chloroform-*d*)



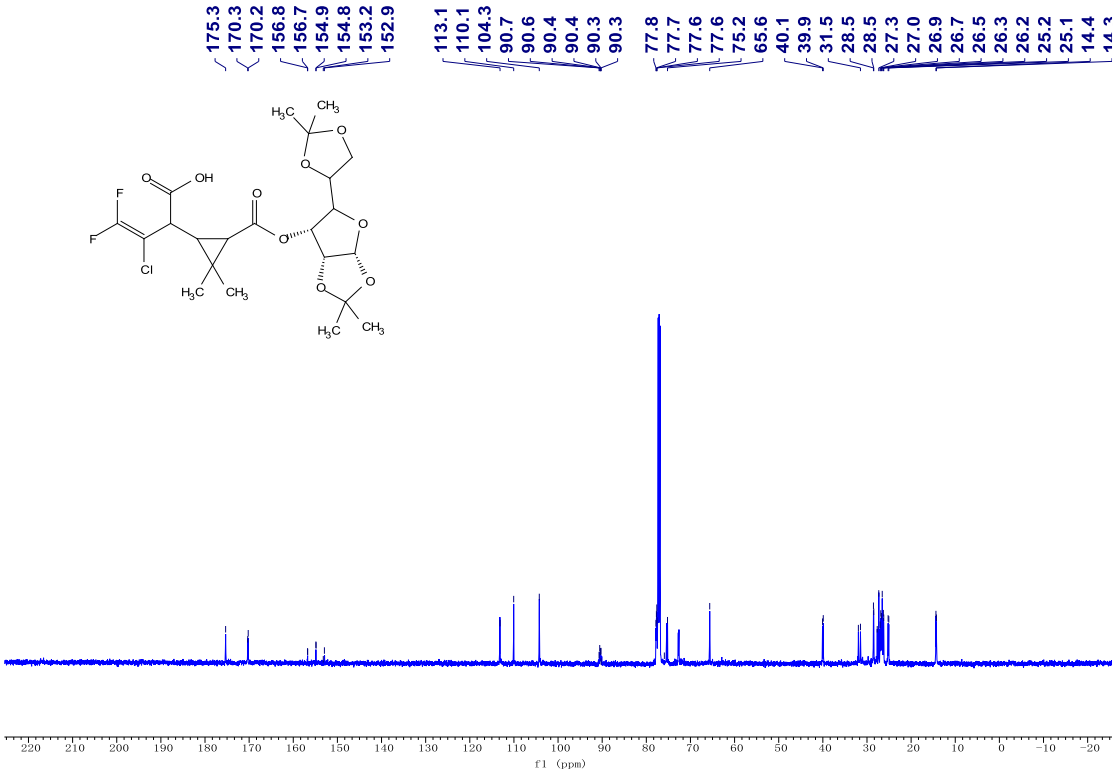
^{19}F NMR Spectra of 2n (565 MHz, Chloroform-*d*)



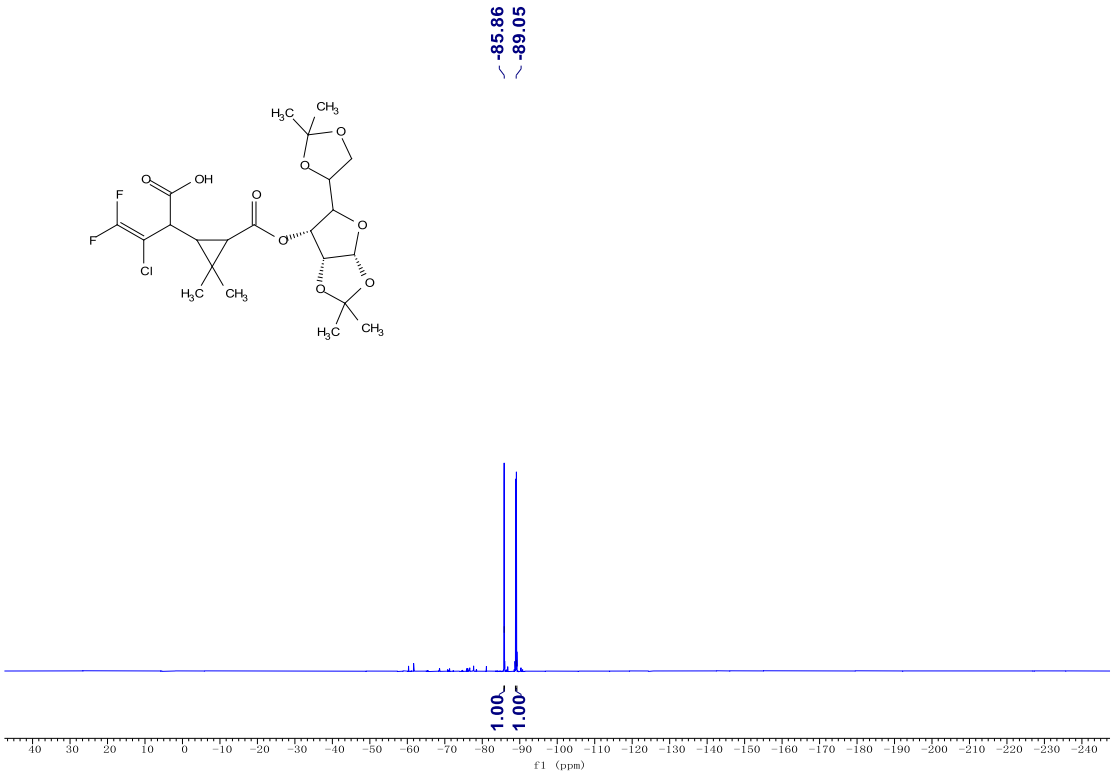
^{1}H NMR Spectra of 2o (600 MHz, Chloroform-*d*)



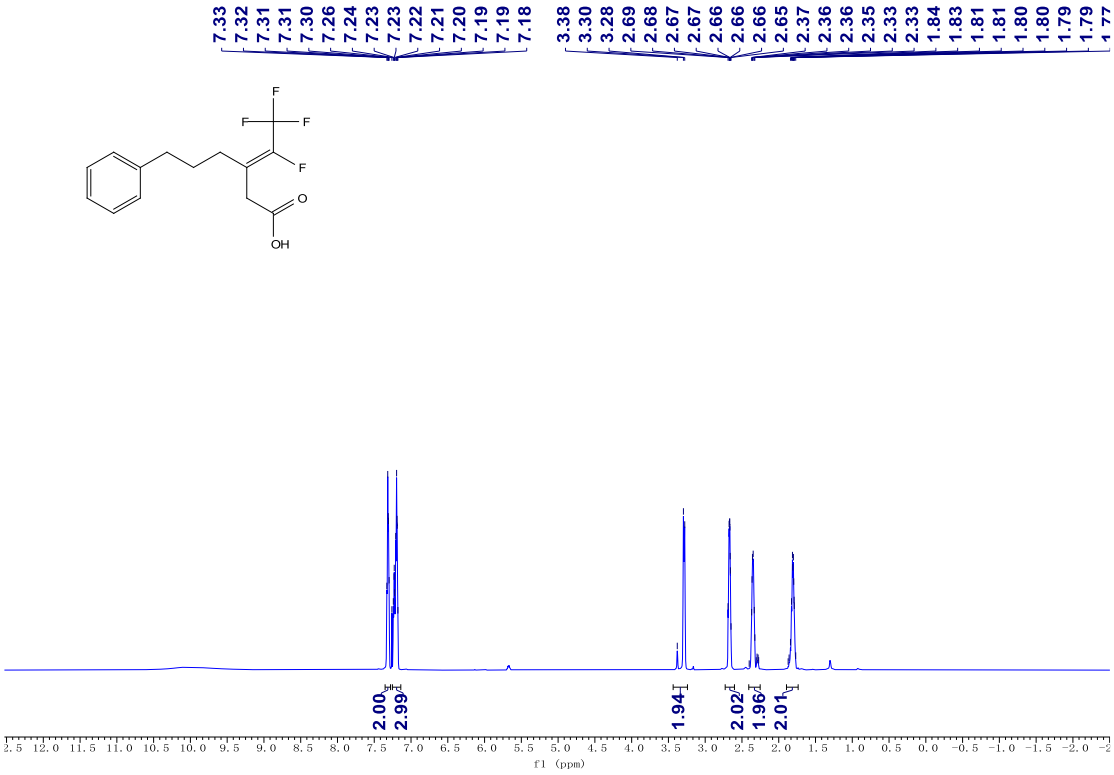
^{13}C NMR Spectra of 2o (151 MHz, Chloroform-*d*)



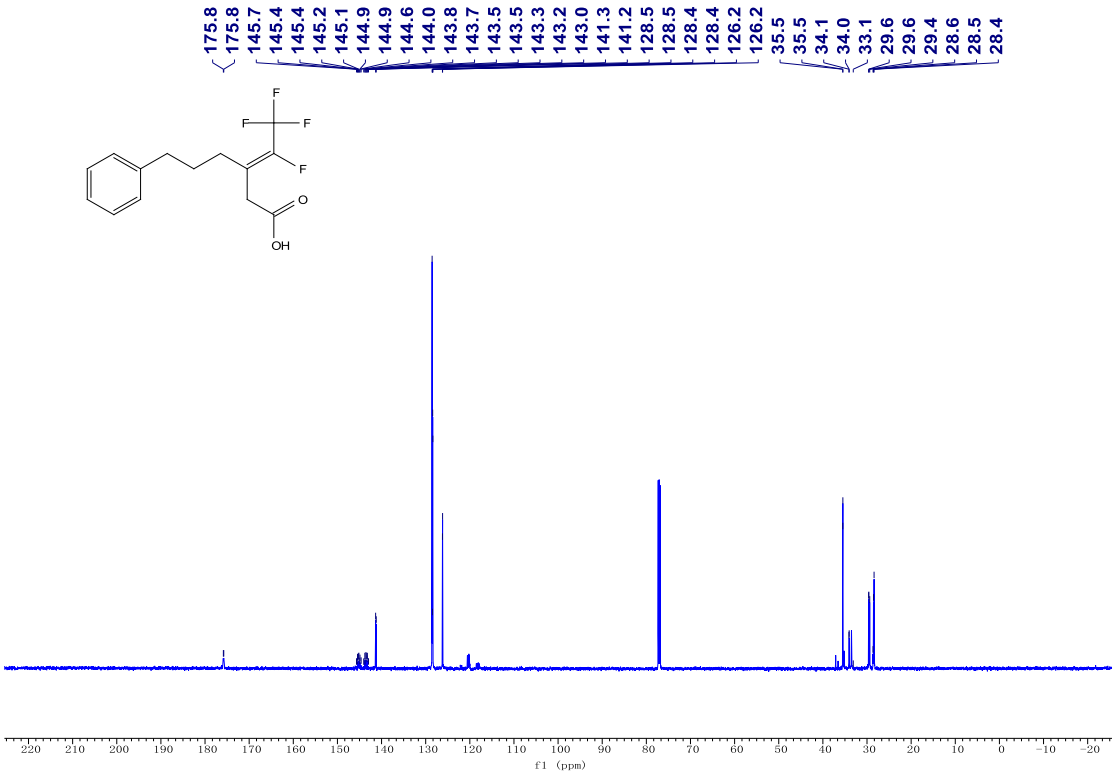
^{19}F NMR Spectra of 2o (565 MHz, Chloroform-*d*)



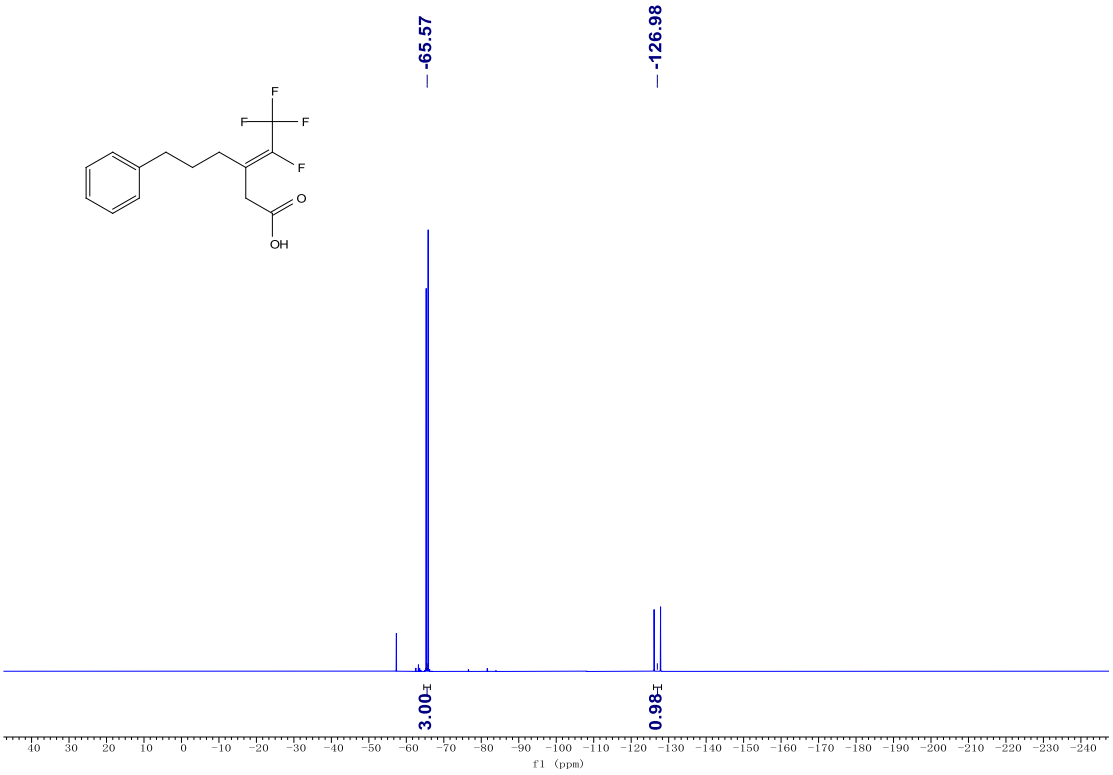
^{1}H NMR Spectra of 2p (600 MHz, Chloroform-*d*)



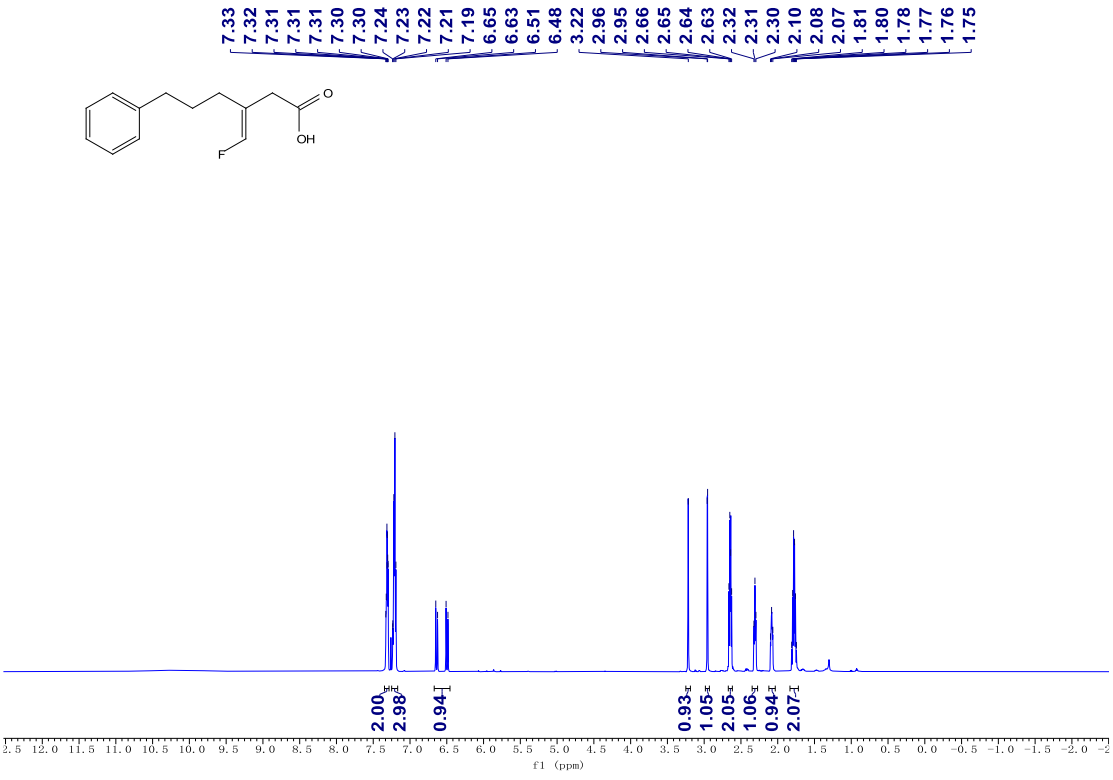
^{13}C NMR Spectra of 2p (151 MHz, Chloroform-*d*)



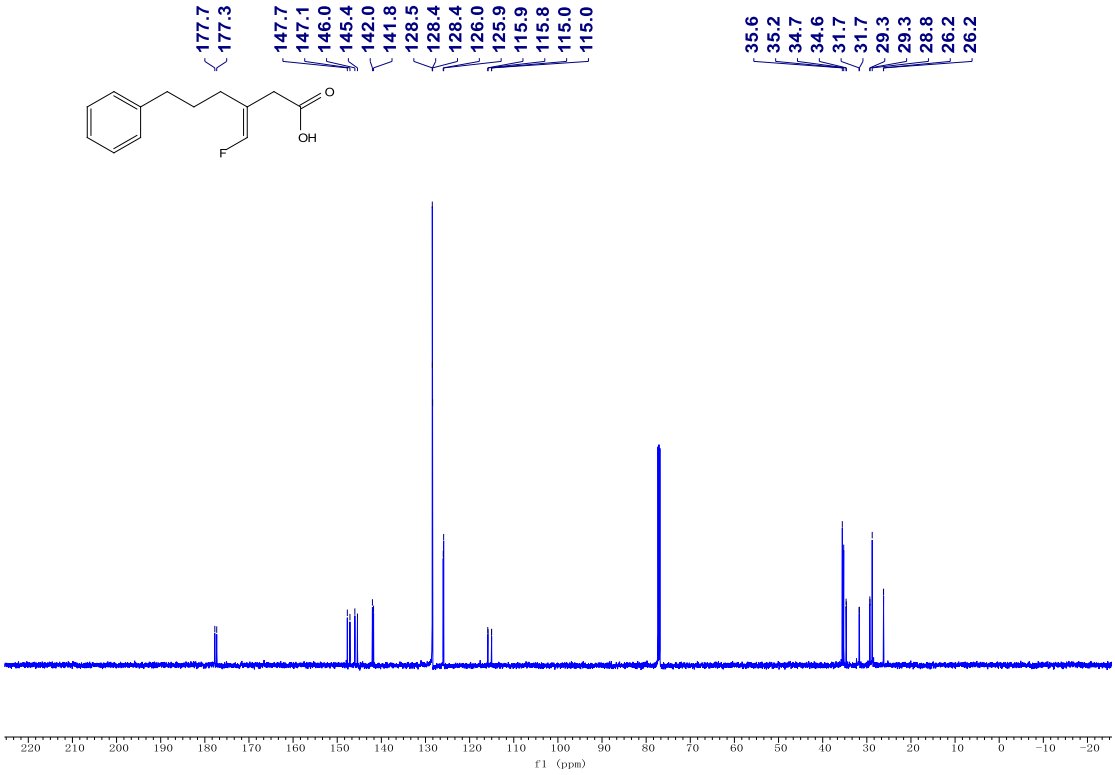
^{19}F NMR Spectra of 2p (565 MHz, Chloroform-*d*)



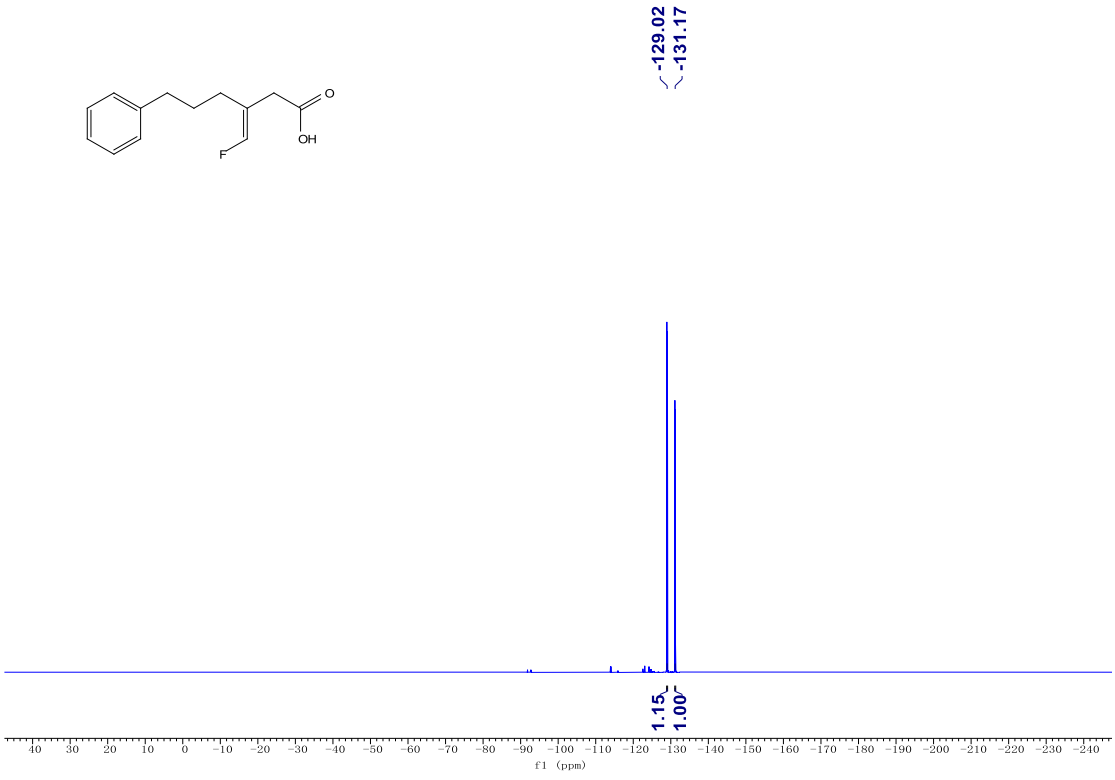
^{1}H NMR Spectra of 2q (600 MHz, Chloroform-*d*)



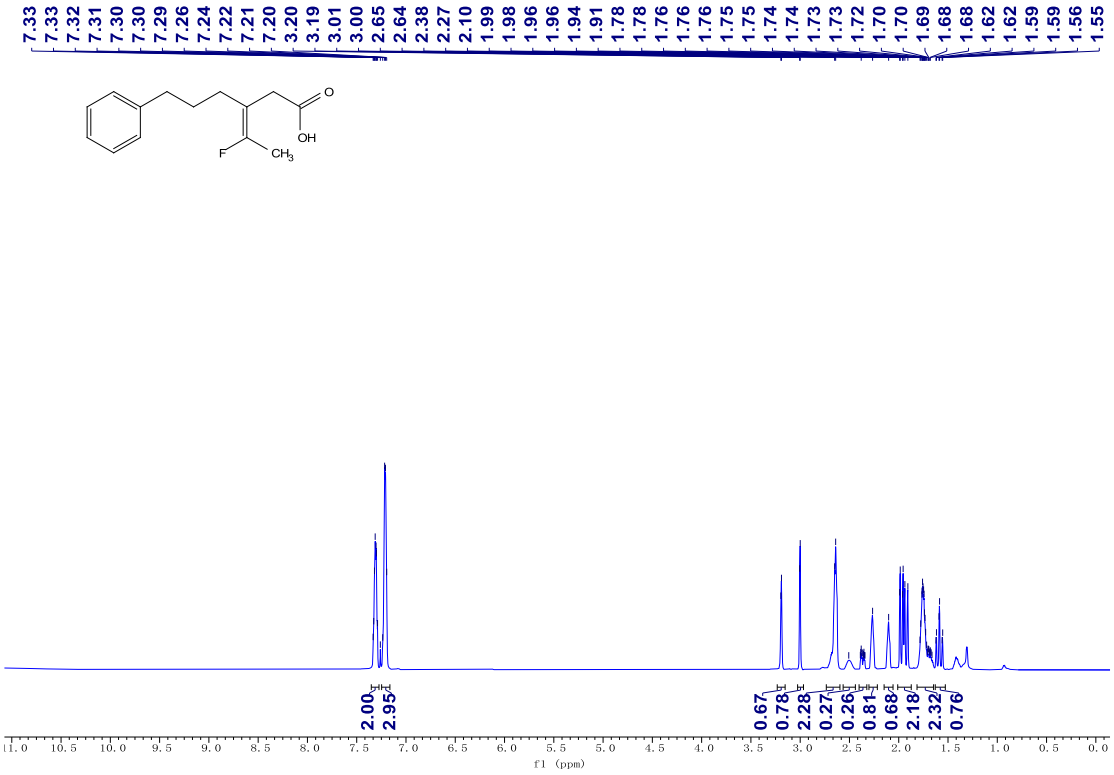
^{13}C NMR Spectra of 2q (151 MHz, Chloroform-*d*)



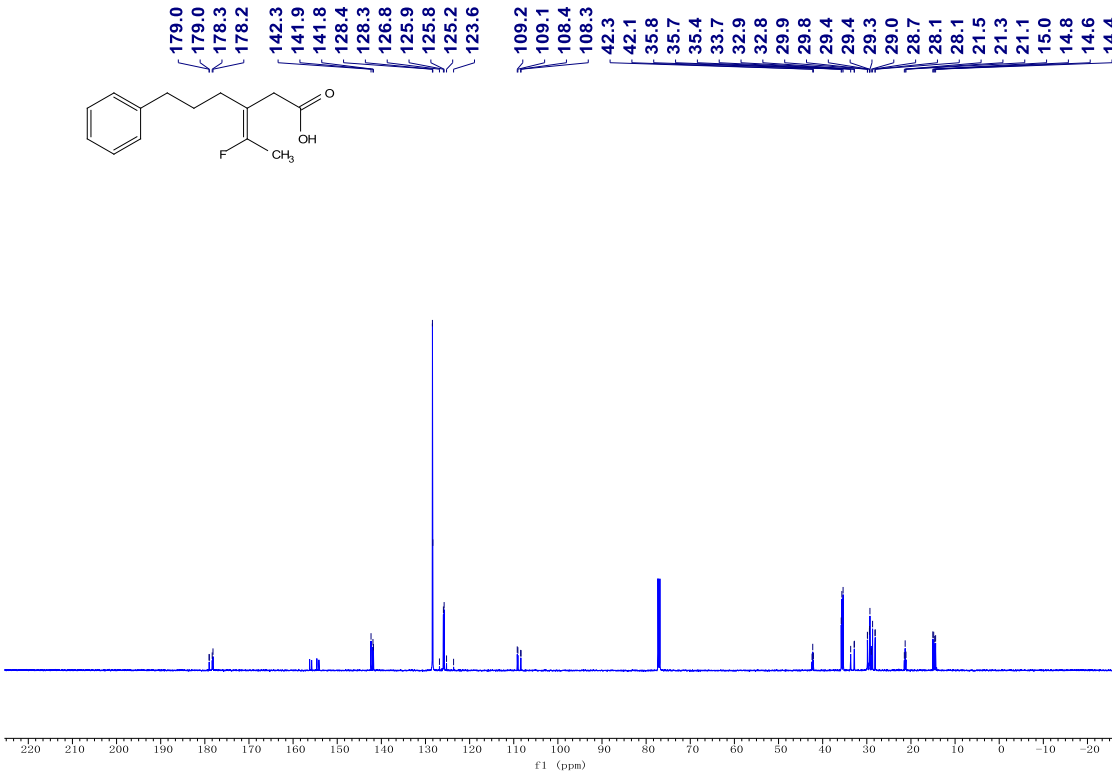
^{19}F NMR Spectra of 2q (565 MHz, Chloroform-*d*)



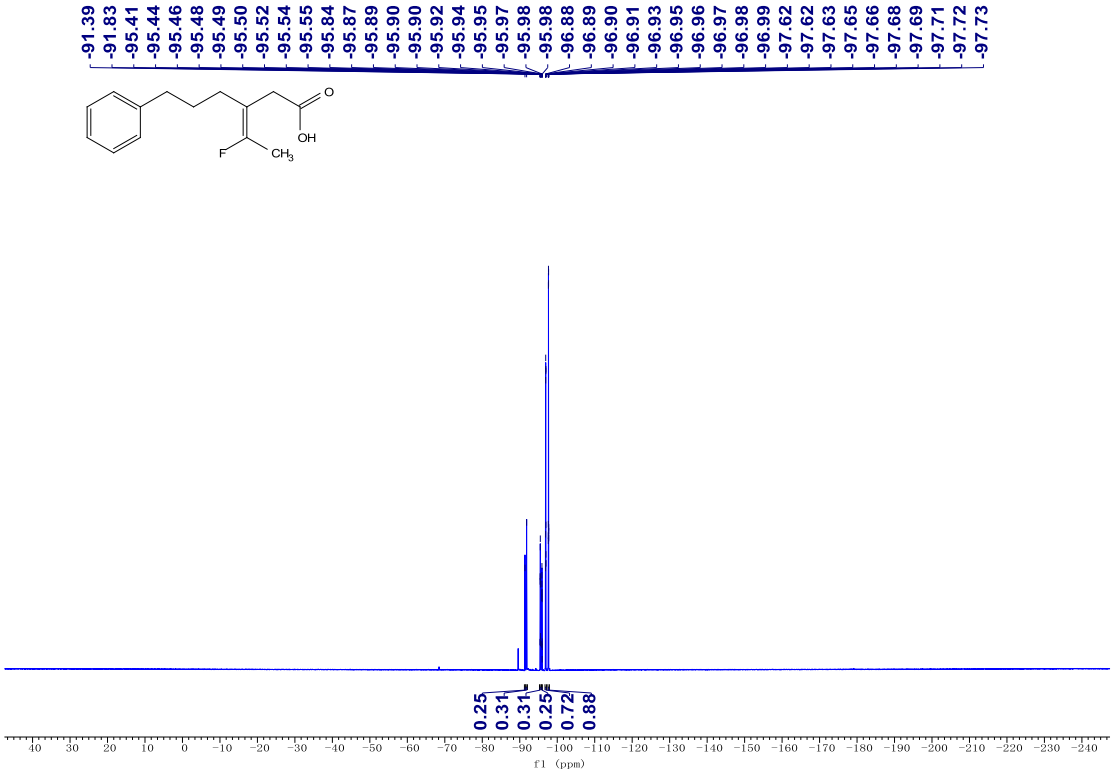
^{1}H NMR Spectra of 2r (600 MHz, Chloroform-*d*)



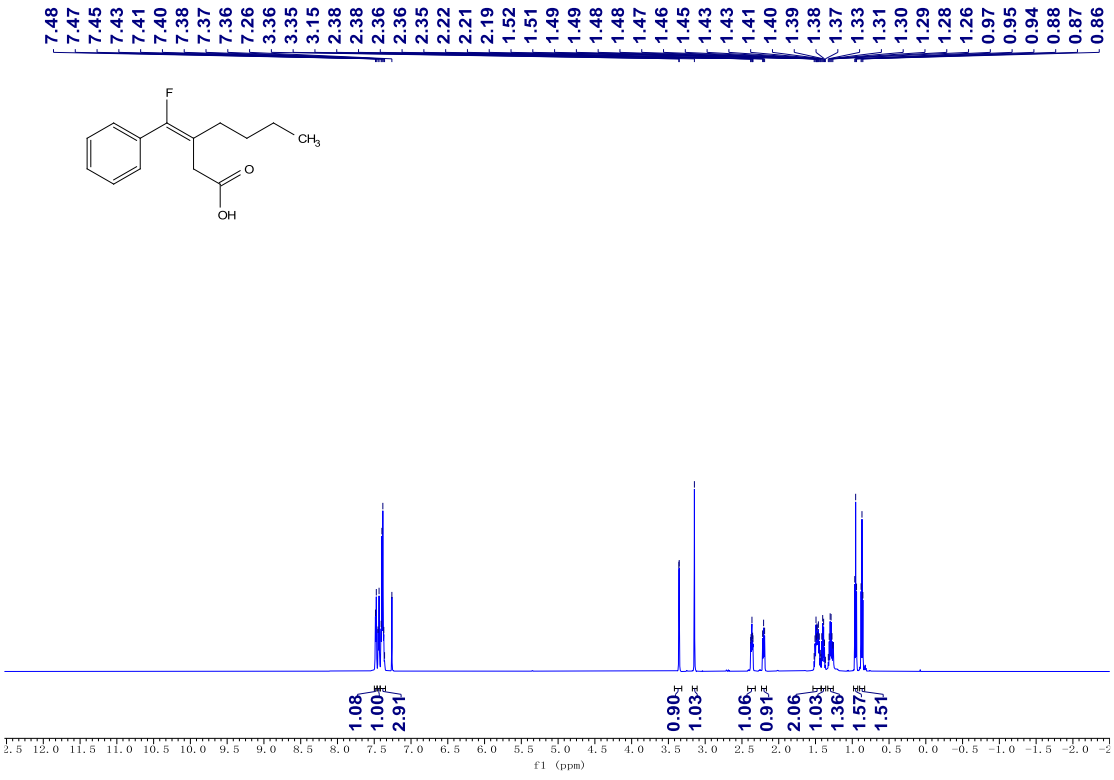
^{13}C NMR Spectra of 2r (151 MHz, Chloroform-*d*)



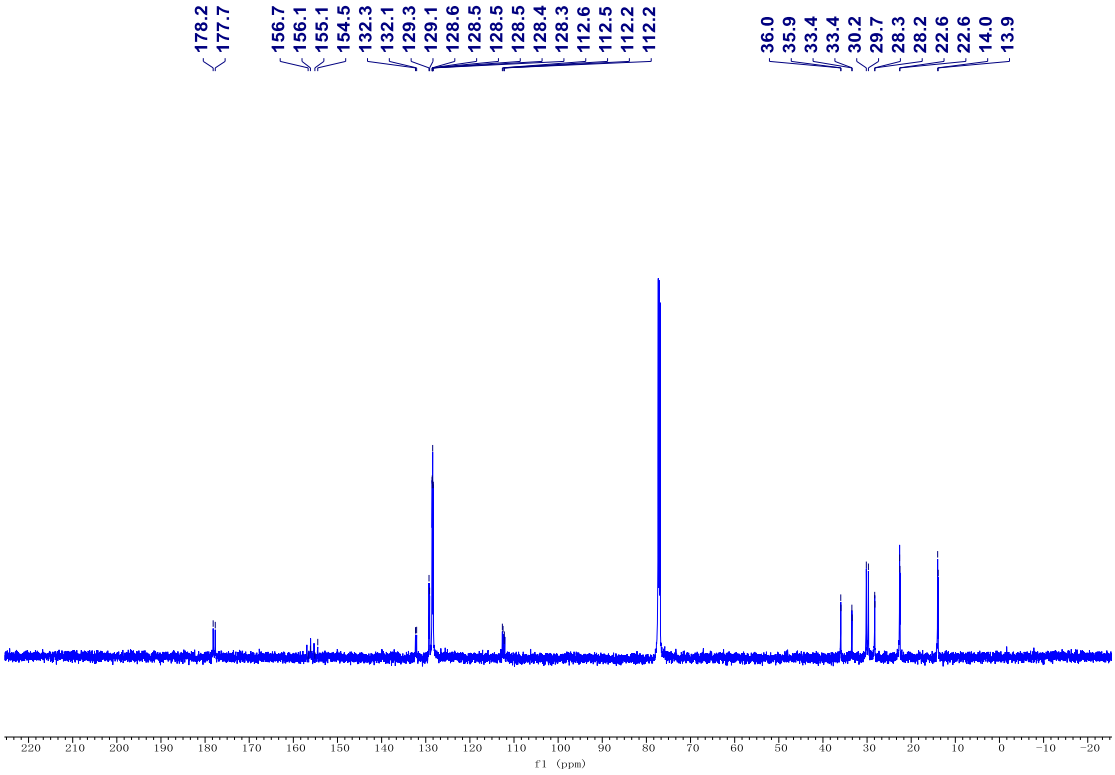
^{19}F NMR Spectra of 2r (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 2s (600 MHz, Chloroform-*d*)

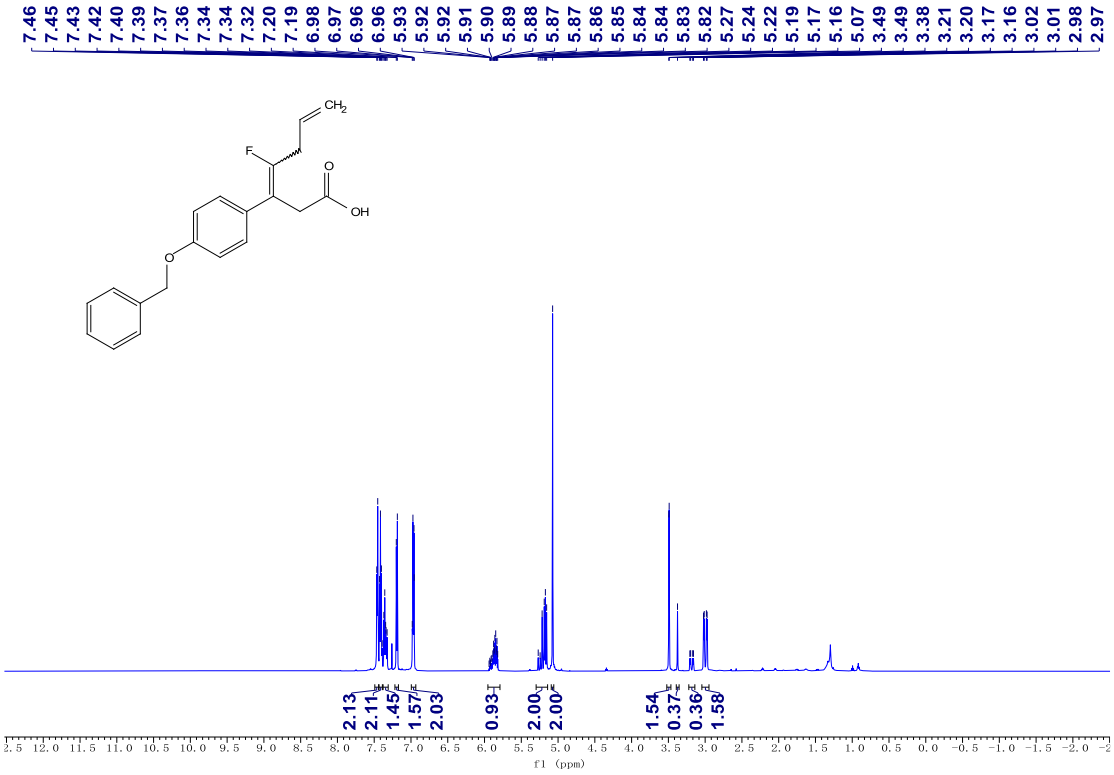


^{13}C NMR Spectra of 2s (151 MHz, Chloroform-*d*)

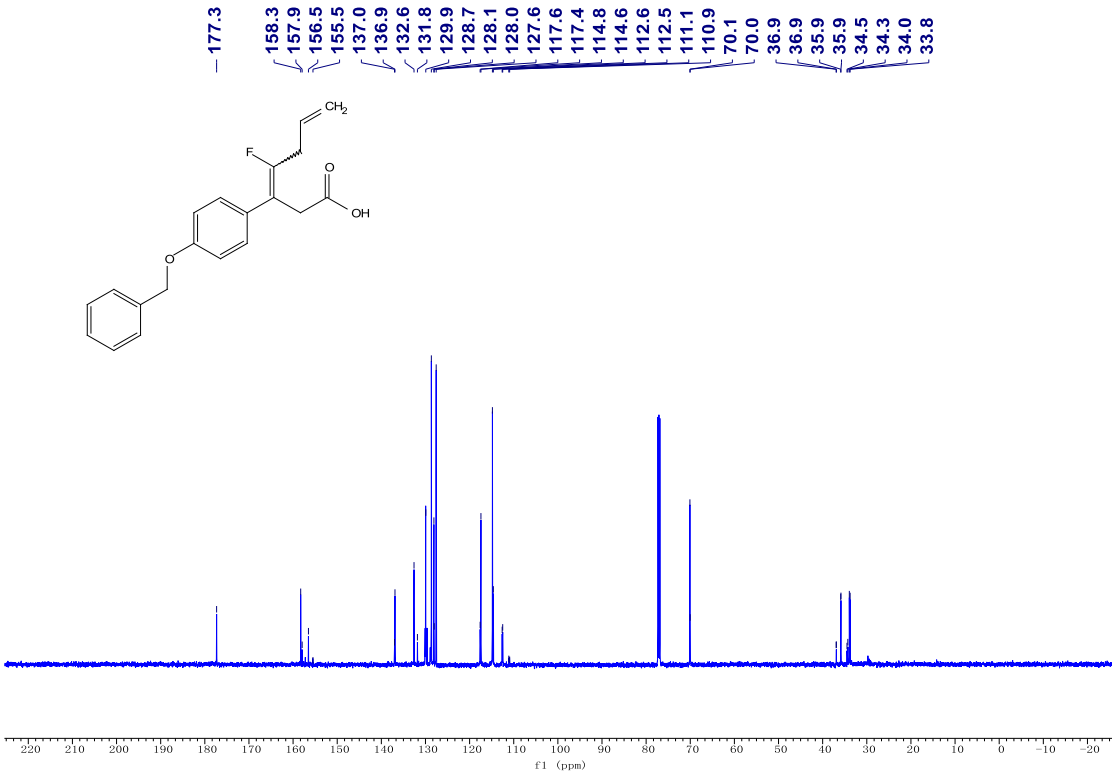


^{19}F NMR Spectra of 2s (565 MHz, Chloroform-*d*)

^{1}H NMR Spectra of 2t (600 MHz, Chloroform-*d*)

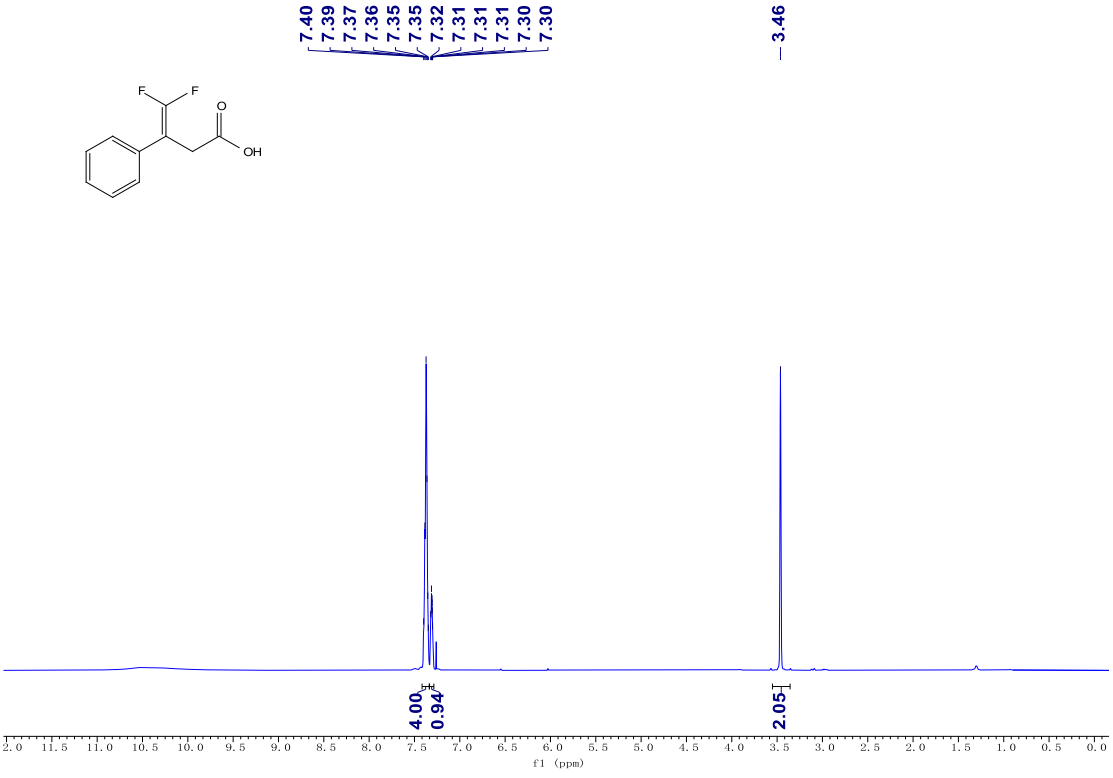


^{13}C NMR Spectra of 2t (151 MHz, Chloroform-*d*)

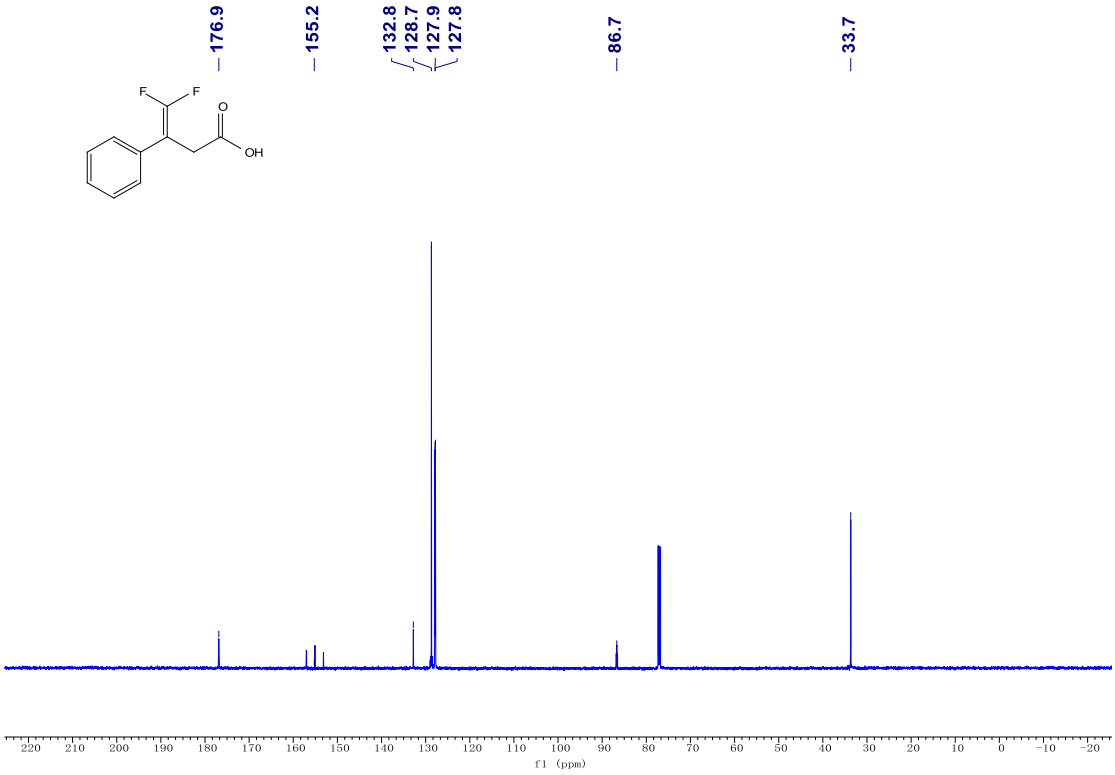


^{19}F NMR Spectra of 2t (565 MHz, Chloroform-*d*)

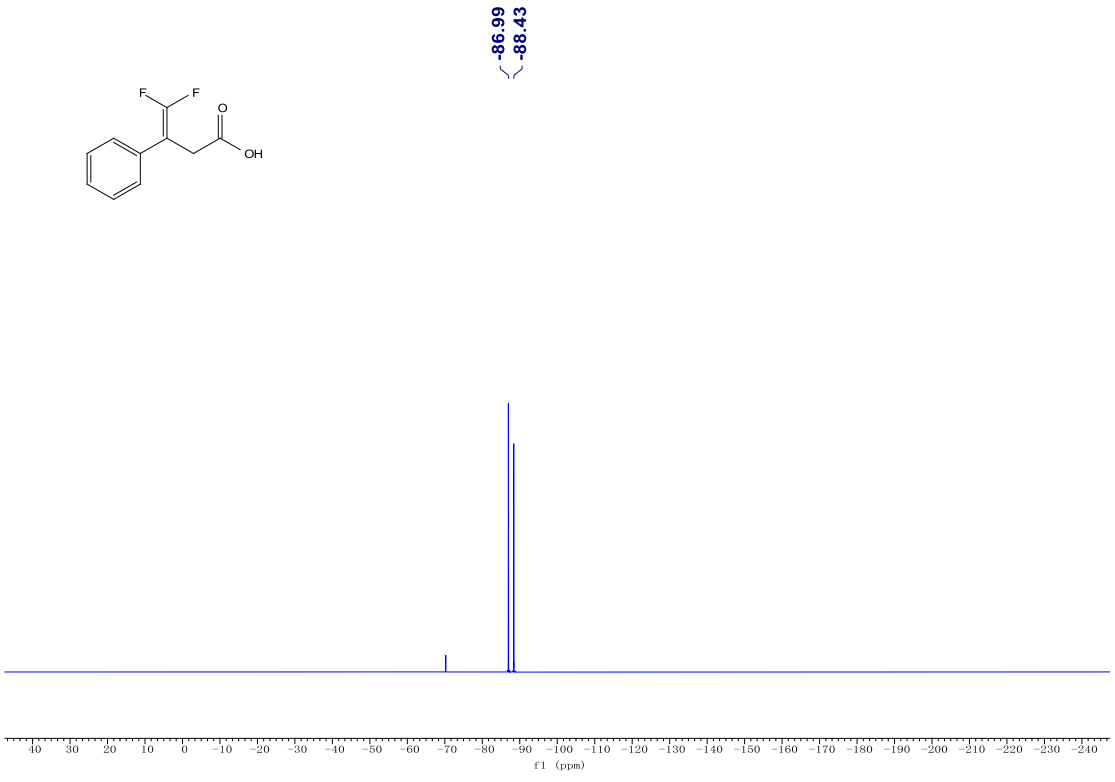
^{1}H NMR Spectra of 4a (600 MHz, Chloroform-*d*)



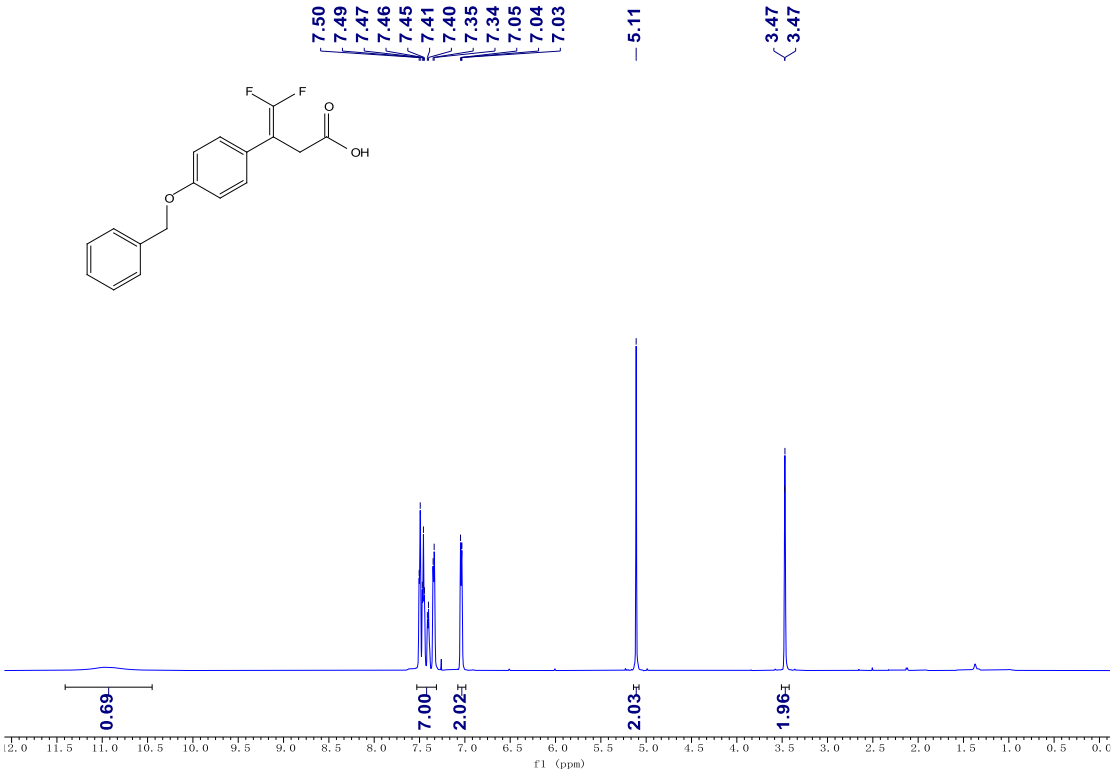
^{13}C NMR Spectra of 4a (151 MHz, Chloroform-*d*)



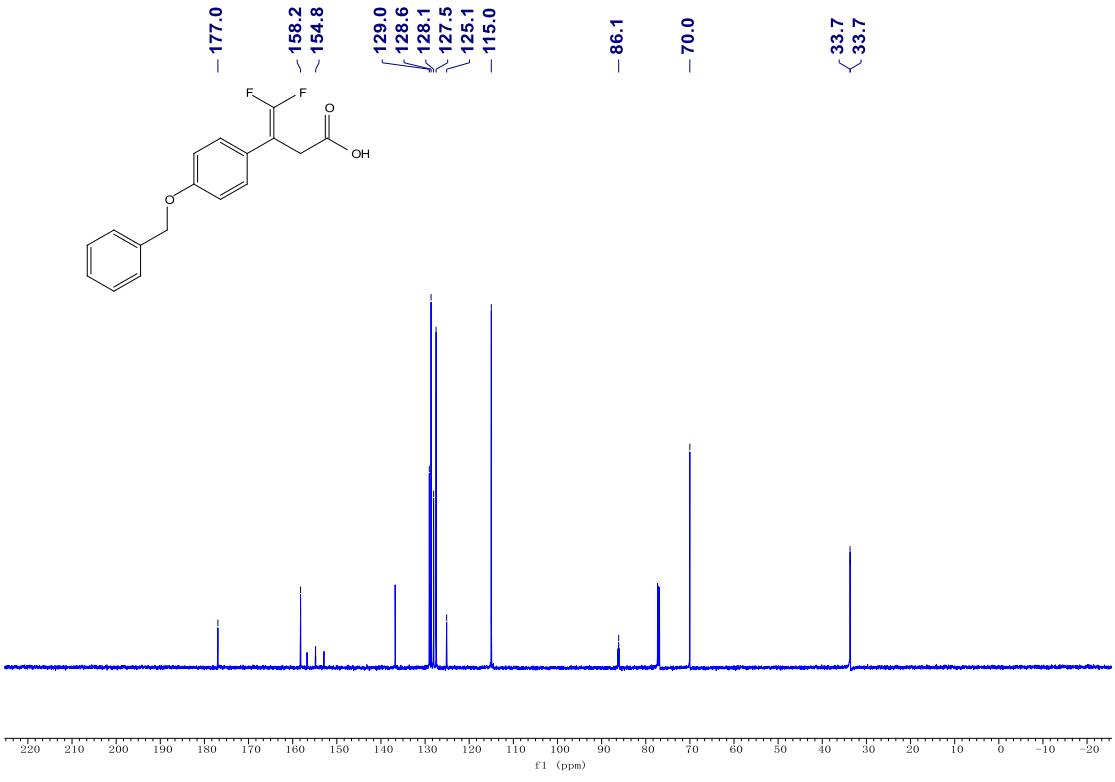
^{19}F NMR Spectra of 4a (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 4b (600 MHz, Chloroform-*d*)

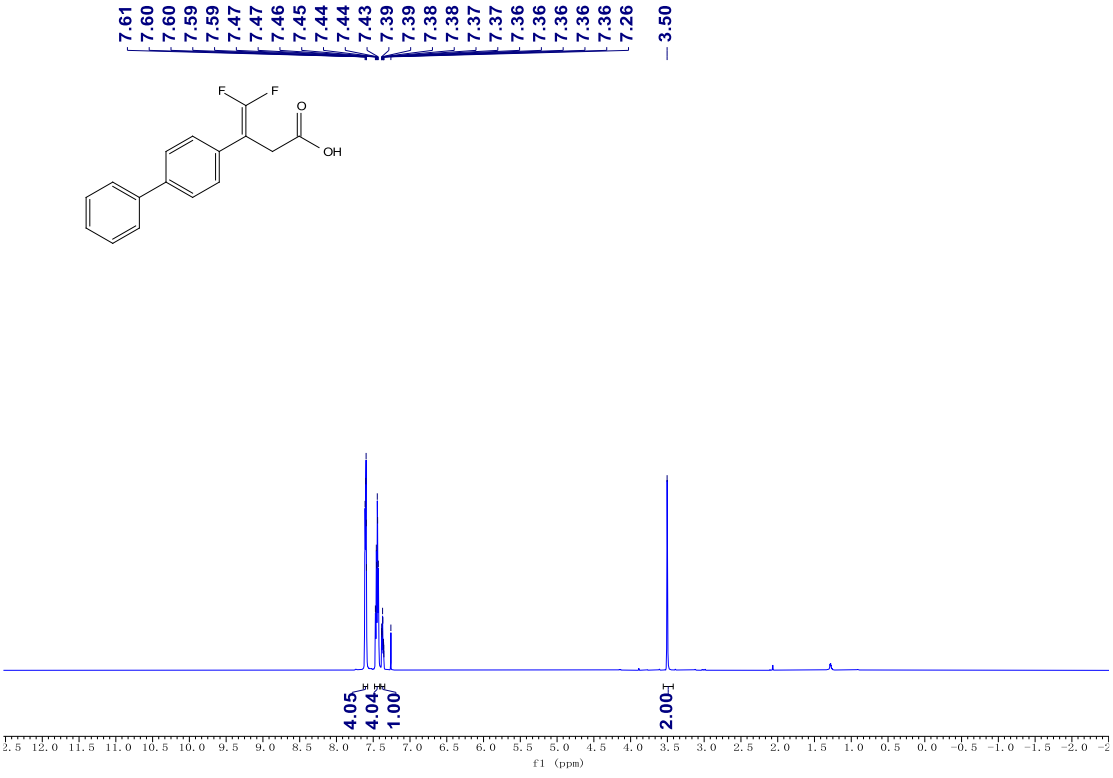


^{13}C NMR Spectra of 4b (151 MHz, Chloroform-*d*)

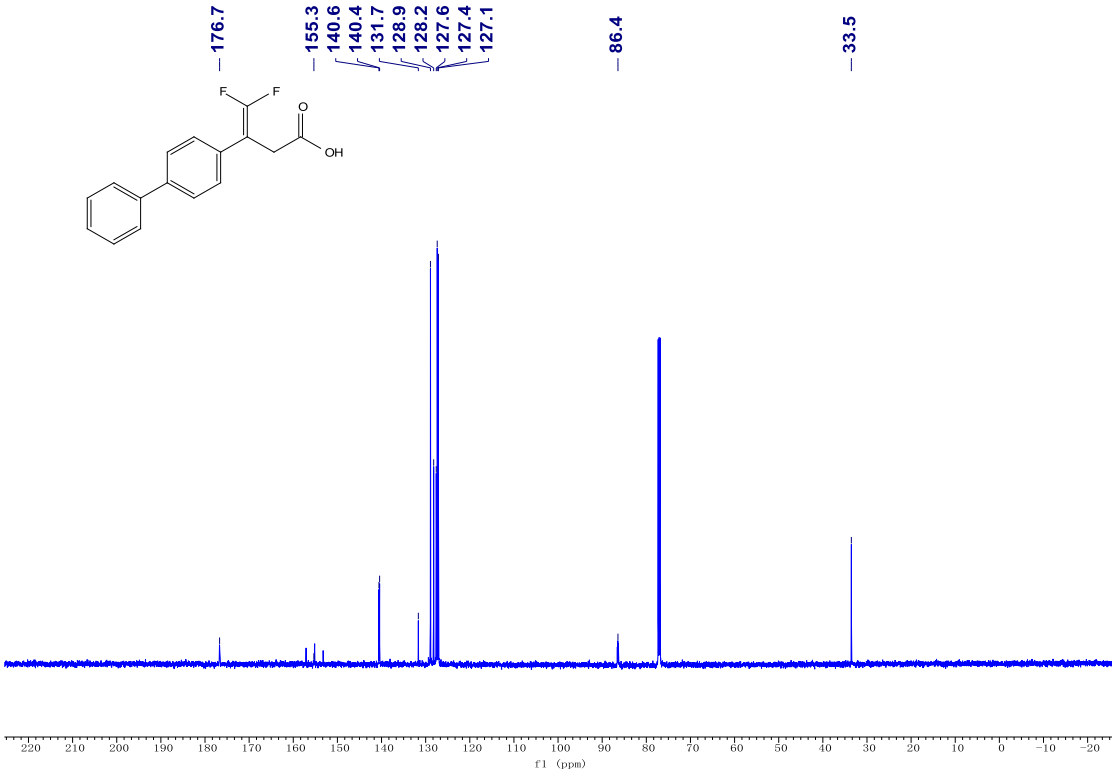


^{19}F NMR Spectra of 4b (565 MHz, Chloroform-*d*)

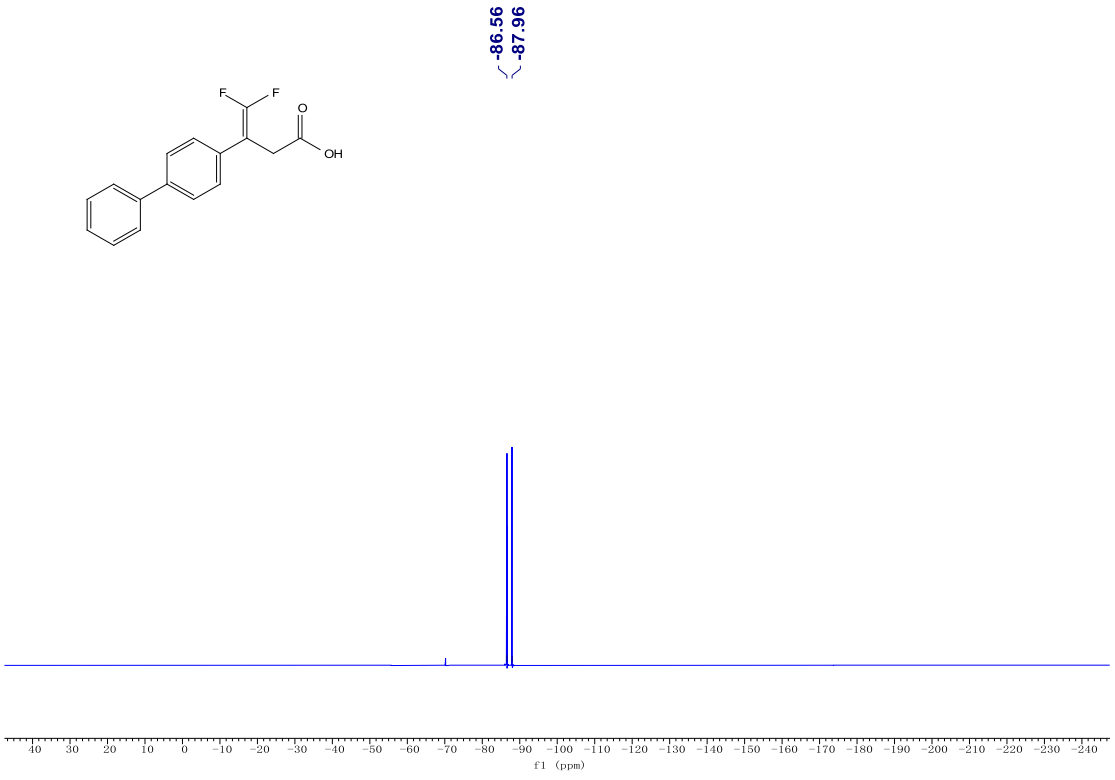
^{1}H NMR Spectra of 4c (600 MHz, Chloroform-*d*)



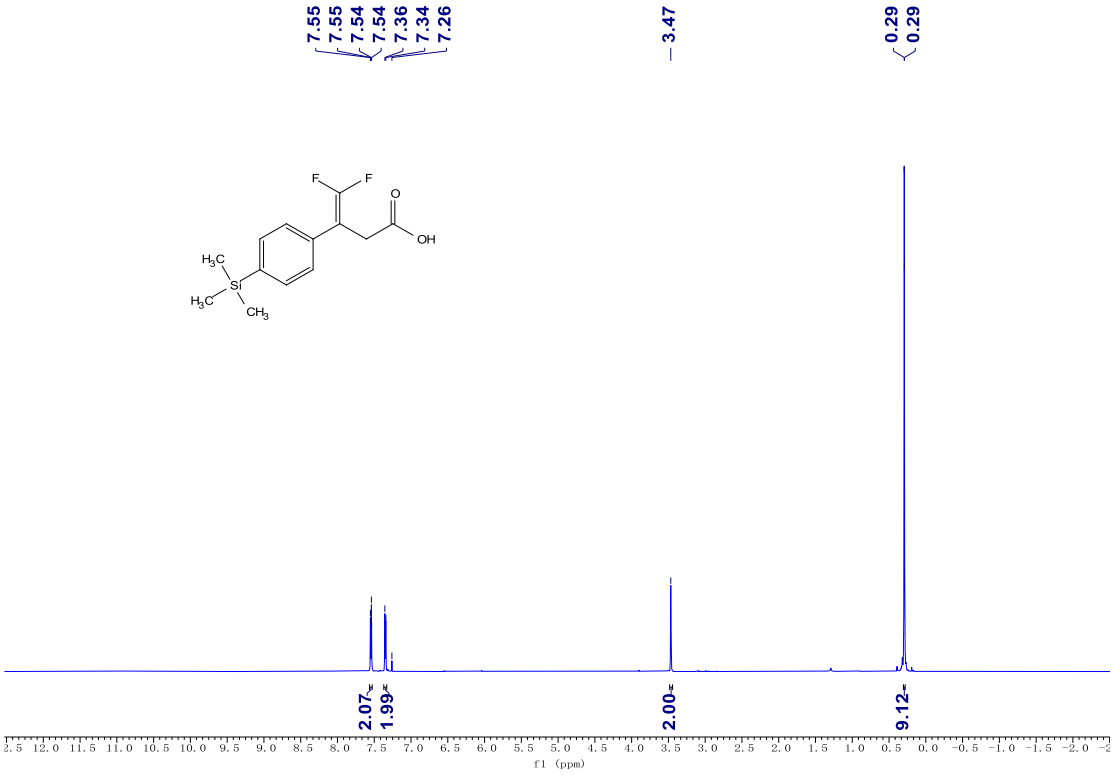
^{13}C NMR Spectra of 4c (151 MHz, Chloroform-*d*)



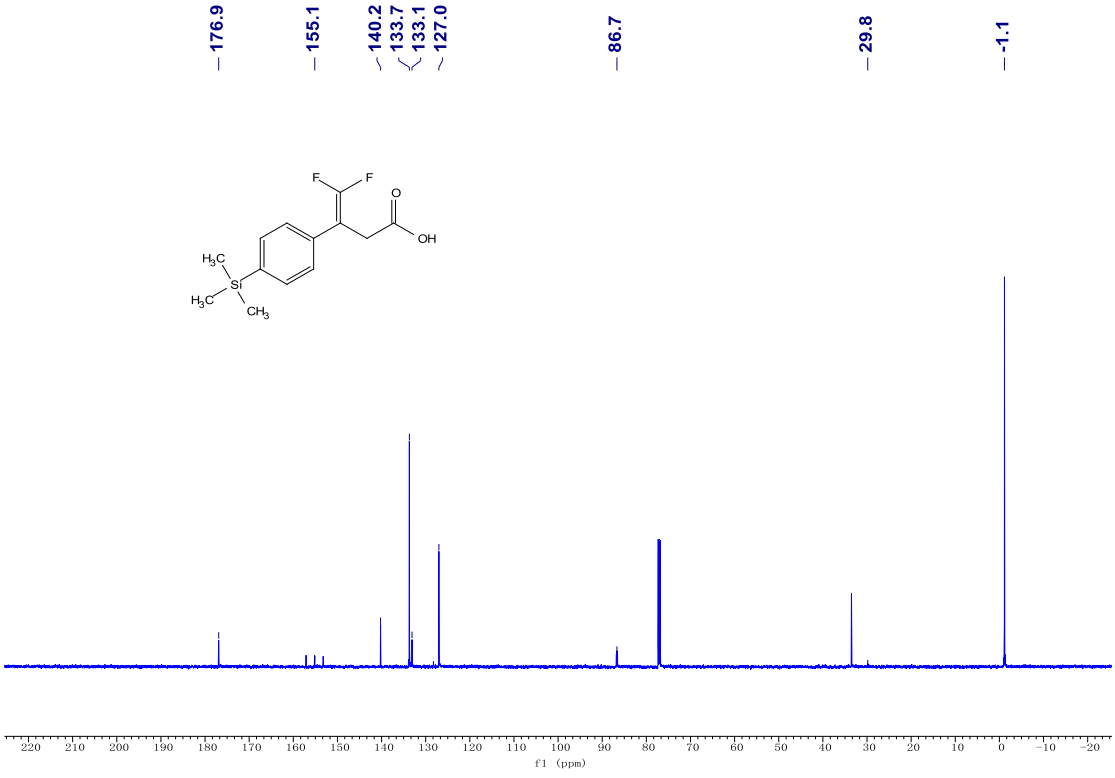
^{19}F NMR Spectra of 4c (565 MHz, Chloroform-*d*)



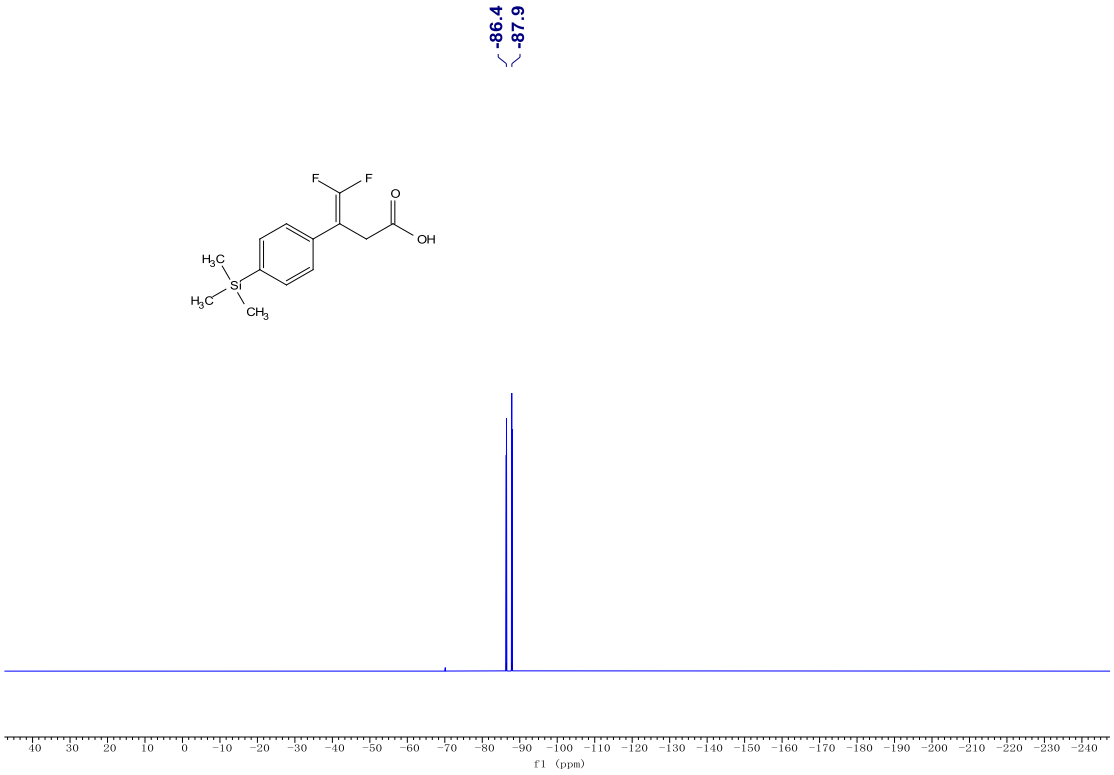
^{1}H NMR Spectra of 4d (600 MHz, Chloroform-*d*)



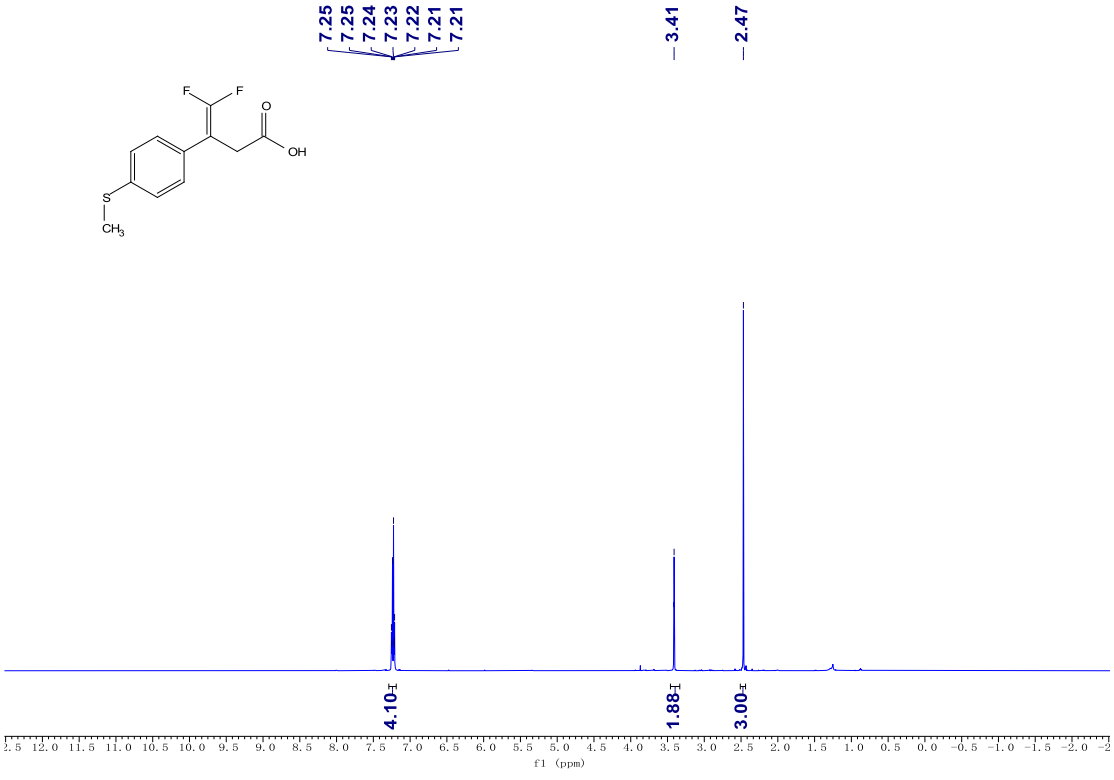
^{13}C NMR Spectra of 4d (151 MHz, Chloroform-*d*)



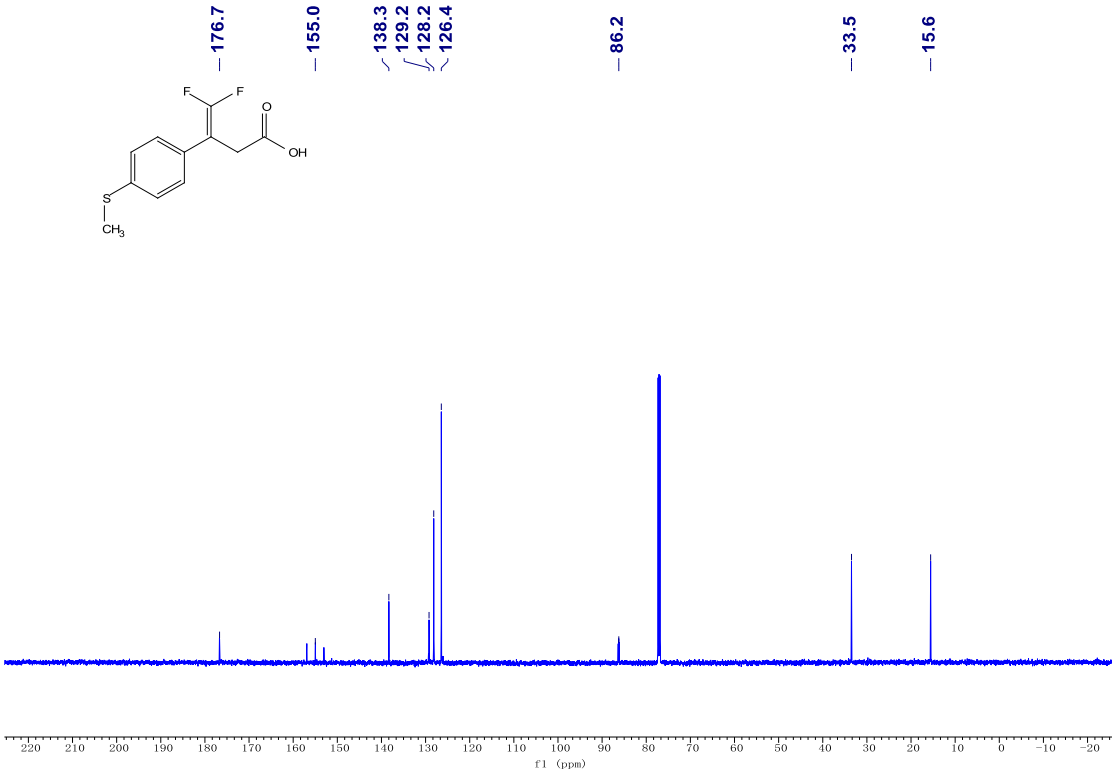
^{19}F NMR Spectra of 4d (565 MHz, Chloroform-*d*)



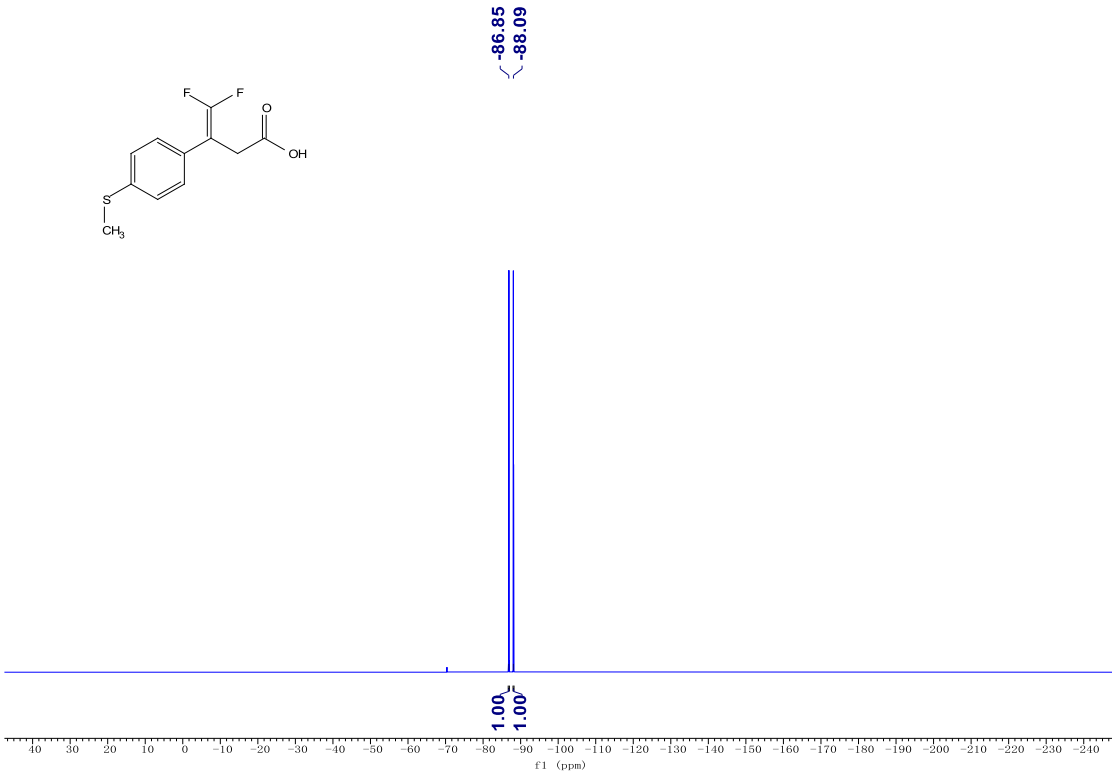
^{1}H NMR Spectra of 4e (600 MHz, Chloroform-*d*)



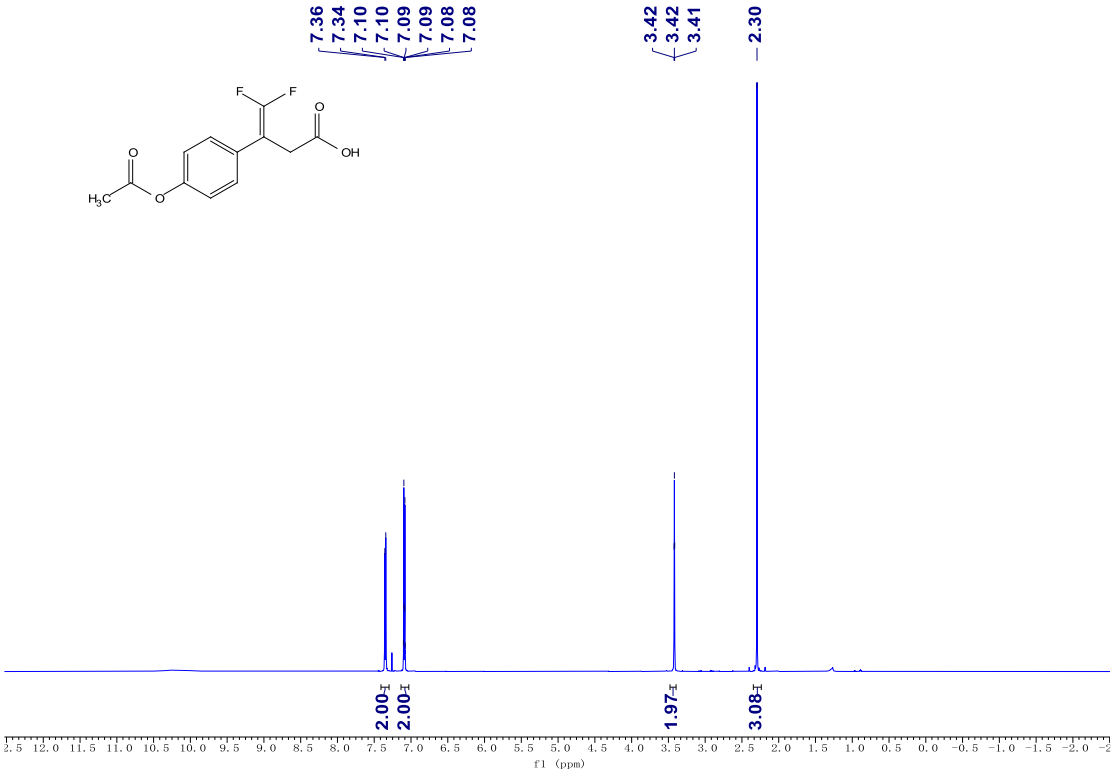
^{13}C NMR Spectra of 4e (151 MHz, Chloroform-*d*)



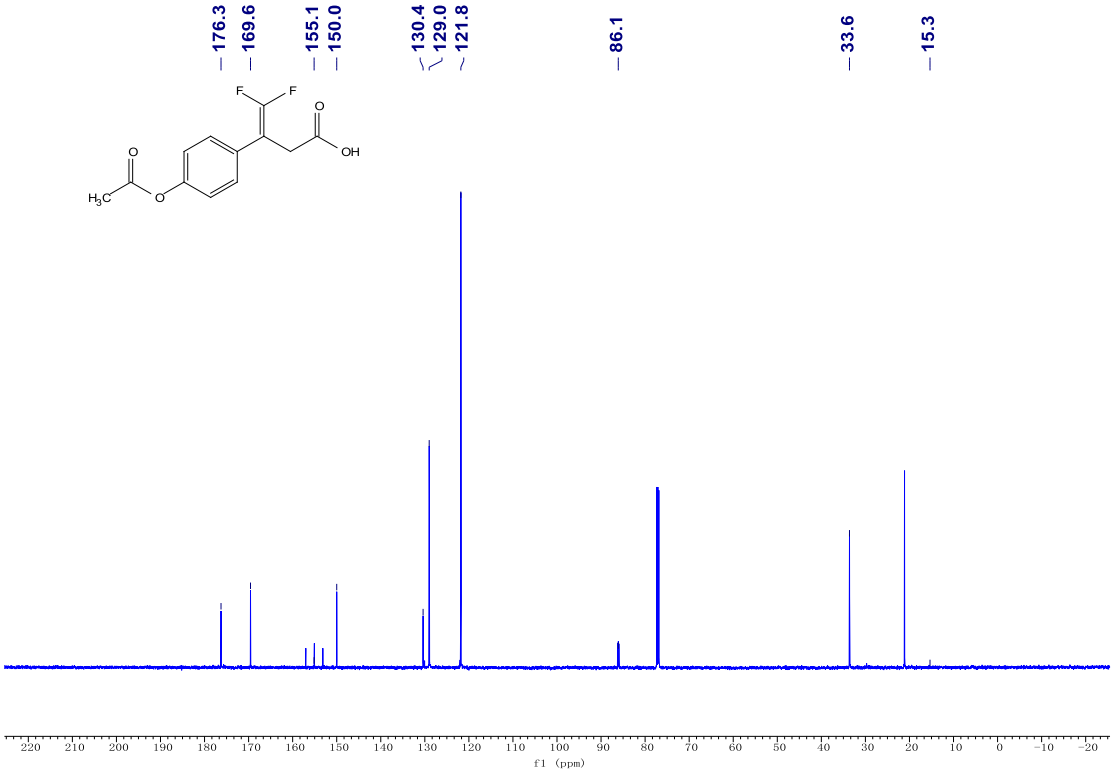
^{19}F NMR Spectra of 4e (565 MHz, Chloroform-*d*)



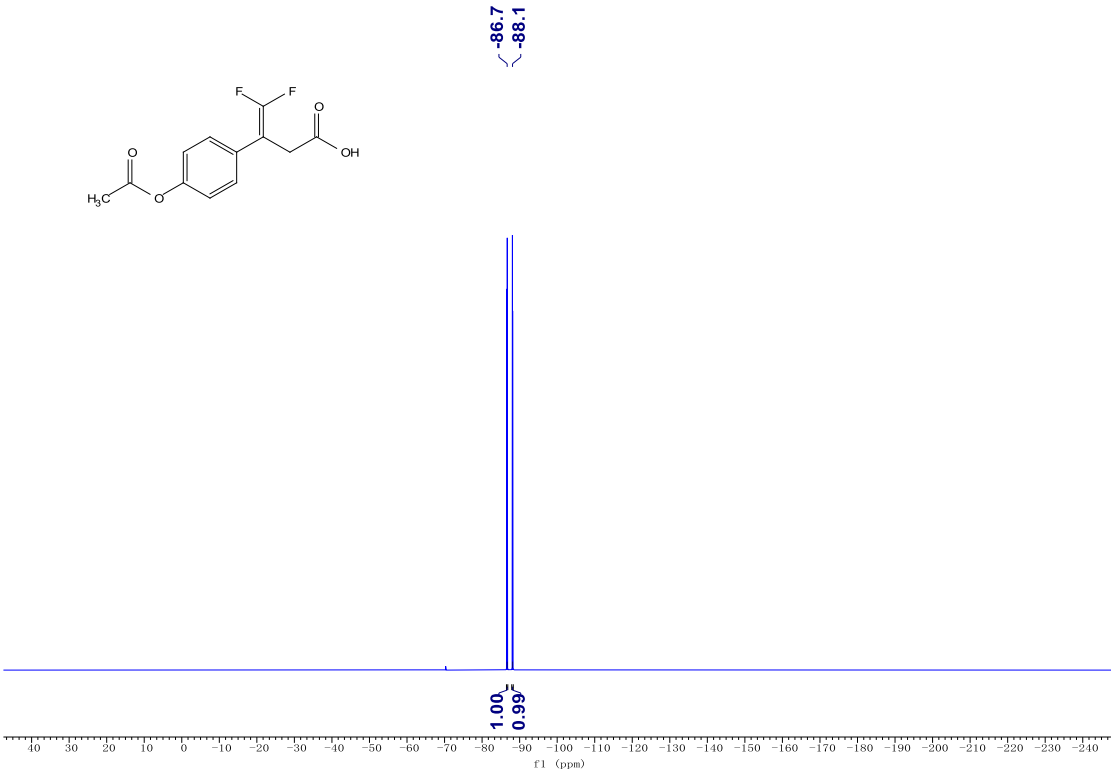
^{1}H NMR Spectra of 4f (600 MHz, Chloroform-*d*)



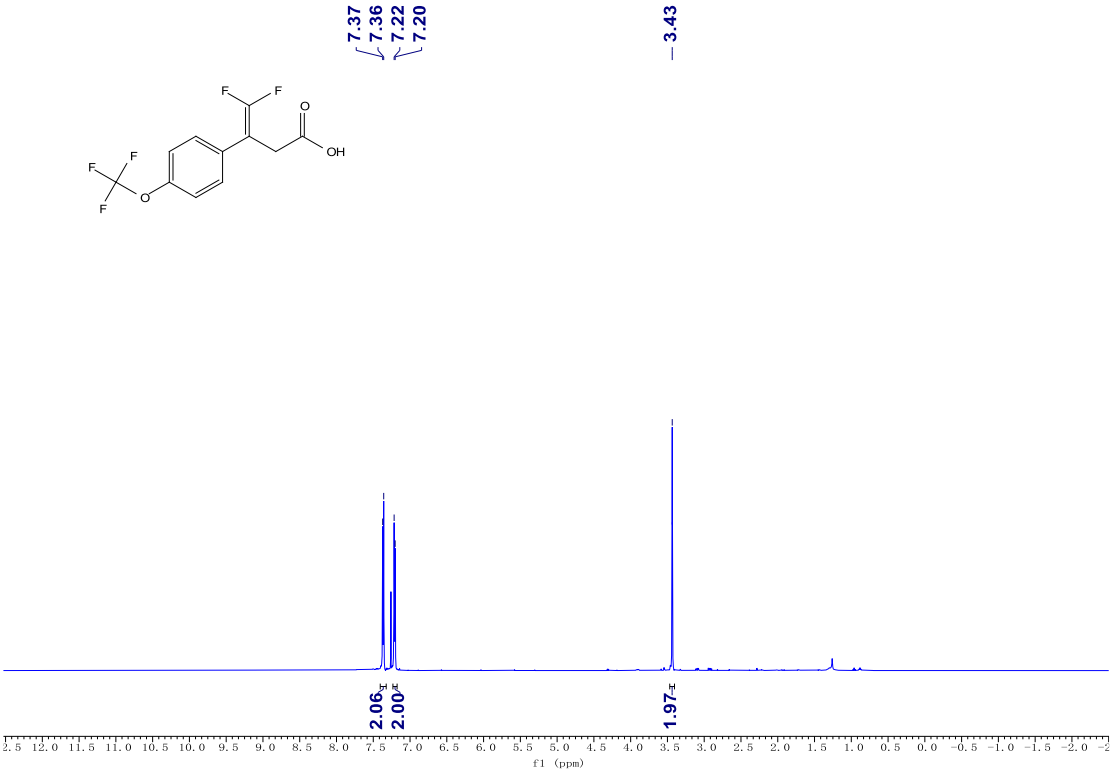
^{13}C NMR Spectra of 4f (151 MHz, Chloroform-*d*)



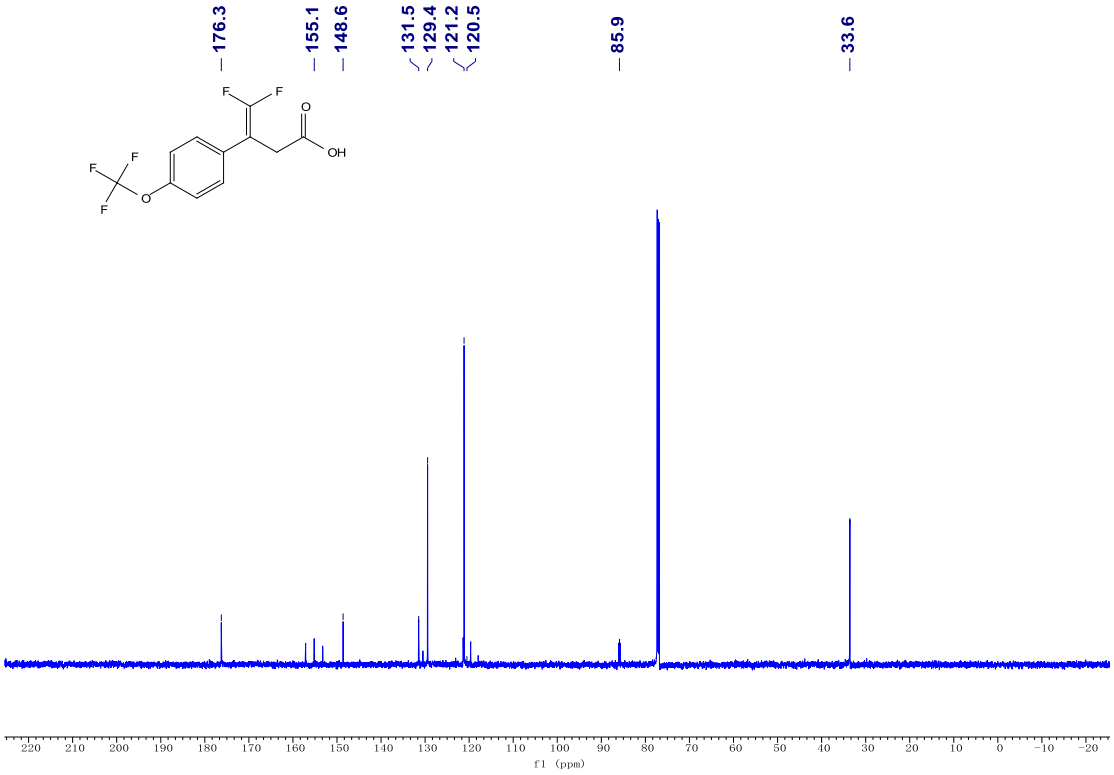
^{19}F NMR Spectra of 4f (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 4g (600 MHz, Chloroform-*d*)

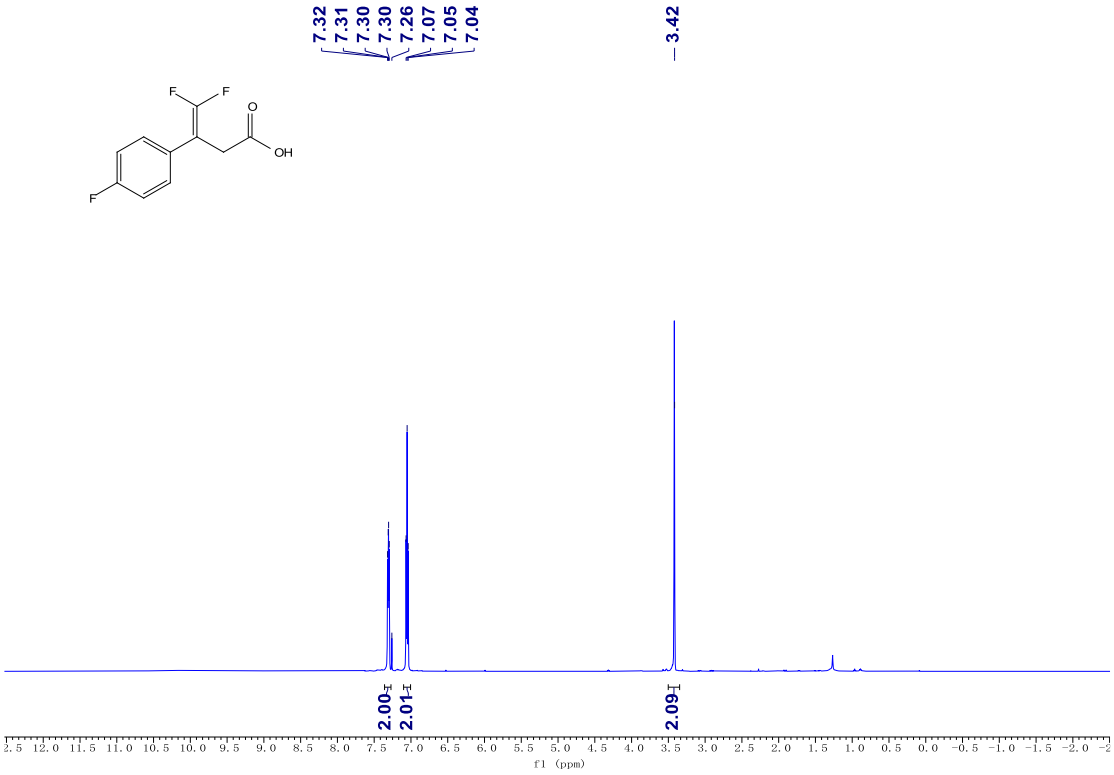


^{13}C NMR Spectra of 4g (151 MHz, Chloroform-*d*)

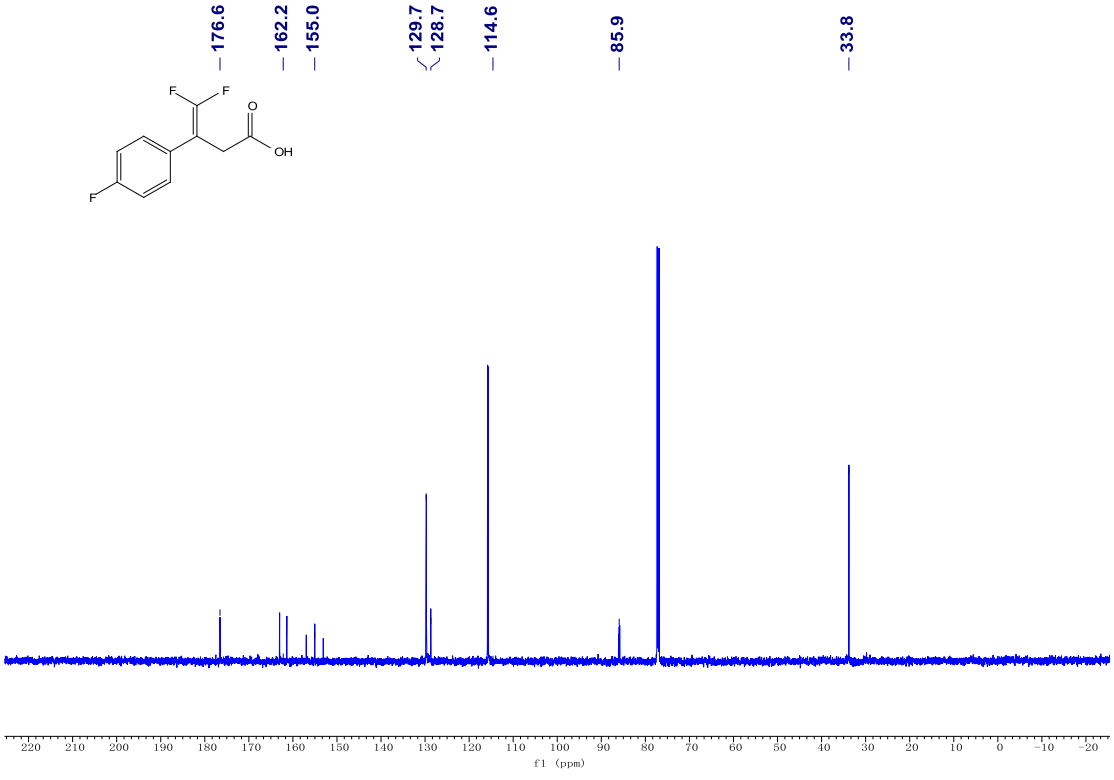


^{19}F NMR Spectra of 4g (565 MHz, Chloroform-*d*)

^{1}H NMR Spectra of 4h (600 MHz, Chloroform-*d*)



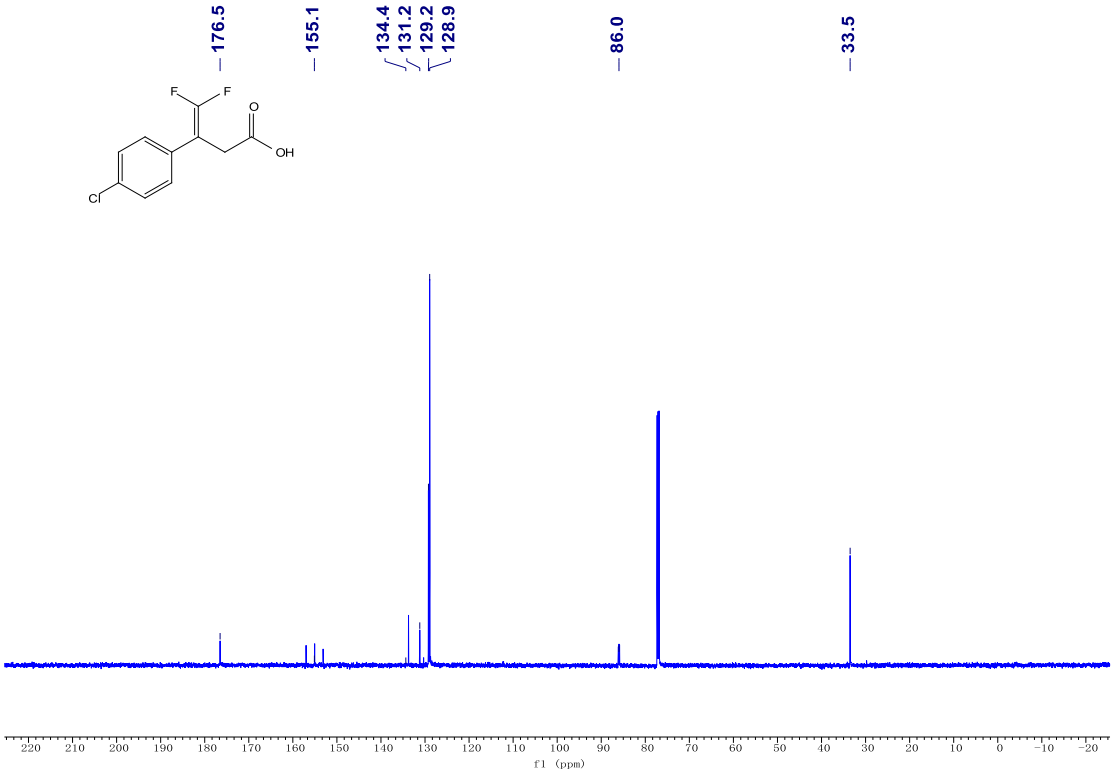
^{13}C NMR Spectra of 4h (151 MHz, Chloroform-*d*)



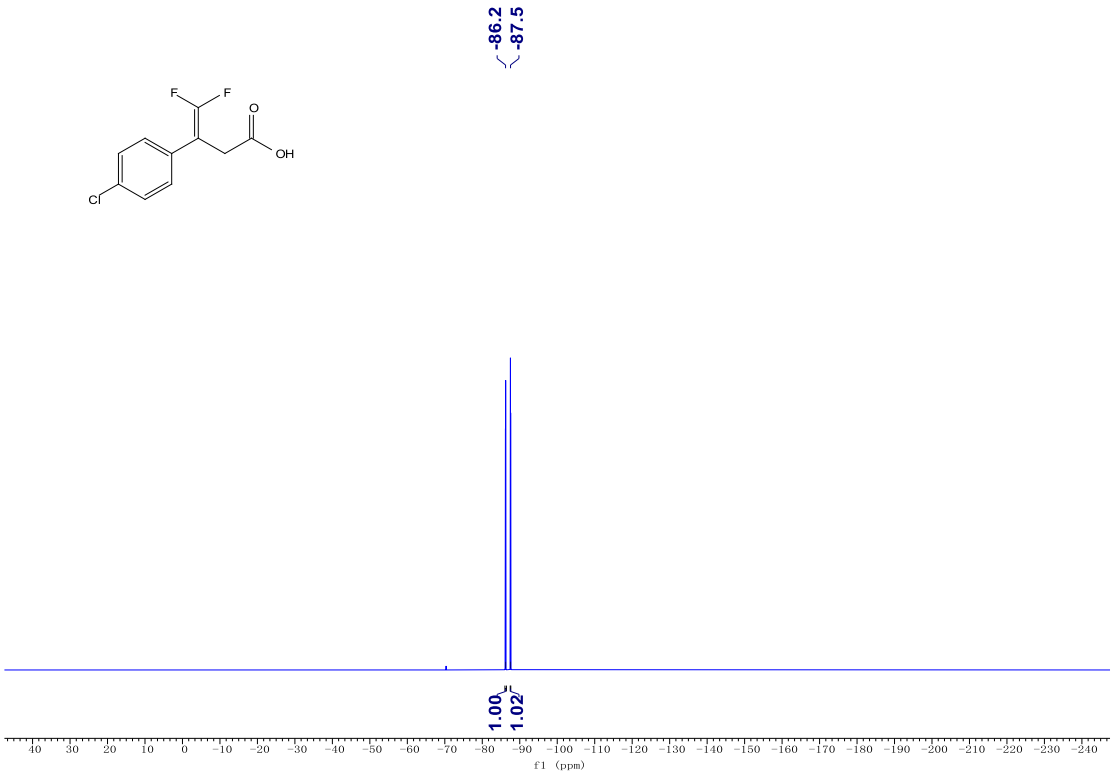
^{19}F NMR Spectra of 4h (565 MHz, Chloroform-*d*)

^{1}H NMR Spectra of 4i (600 MHz, Chloroform-*d*)

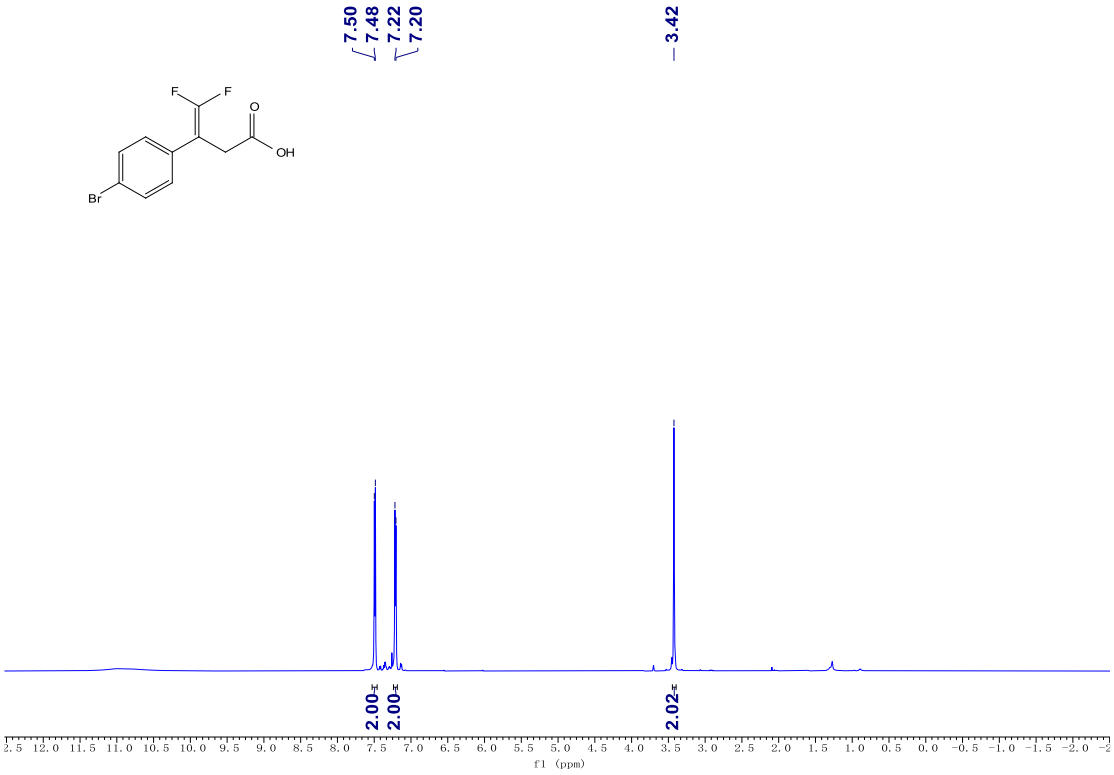
^{13}C NMR Spectra of 4i (151 MHz, Chloroform-*d*)



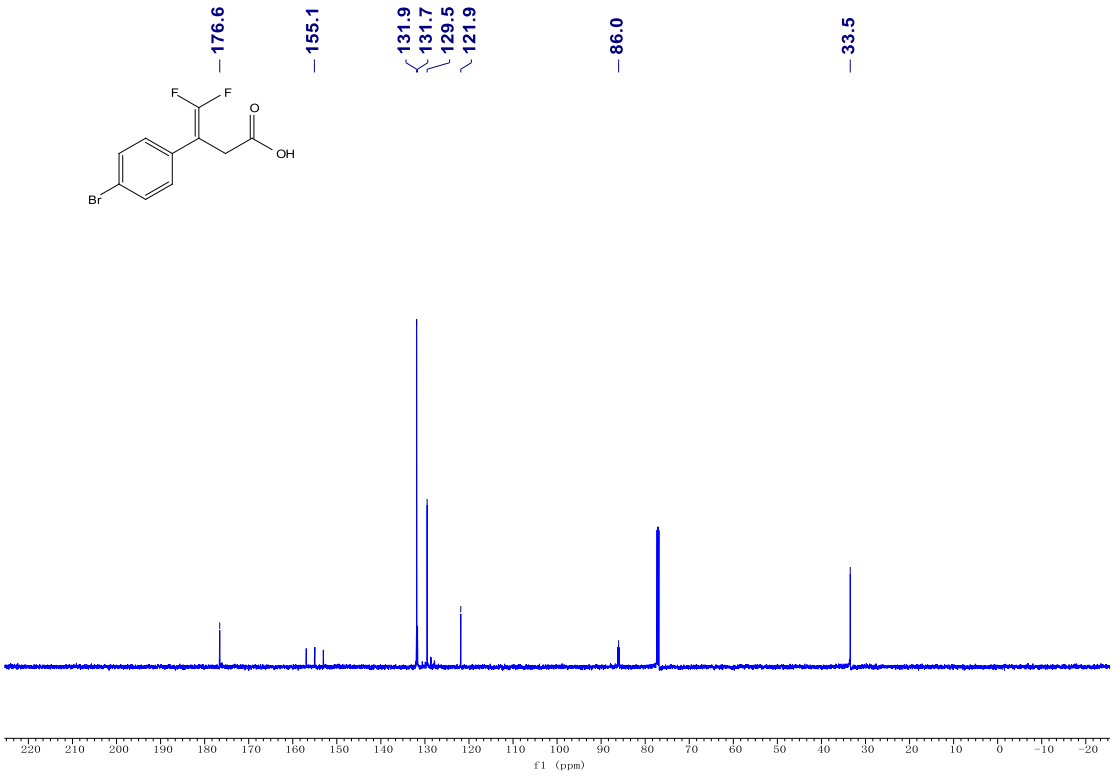
^{19}F NMR Spectra of 4i (565 MHz, Chloroform-*d*)



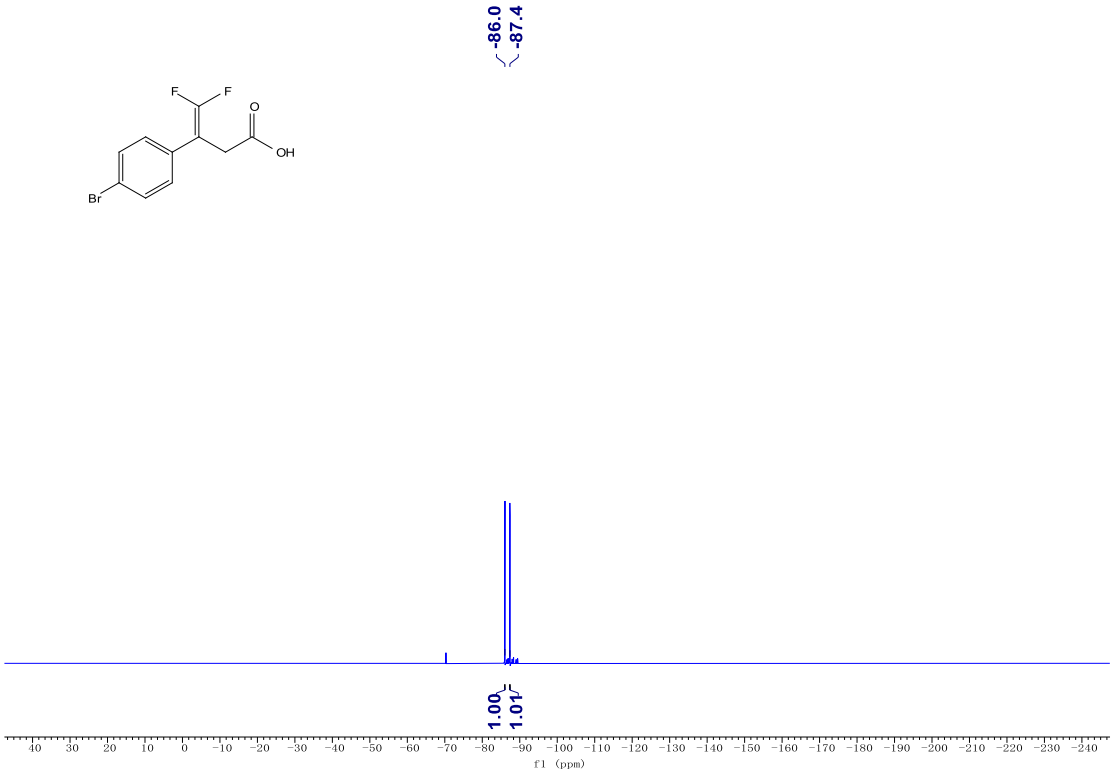
^{1}H NMR Spectra of 4j (600 MHz, Chloroform-*d*)



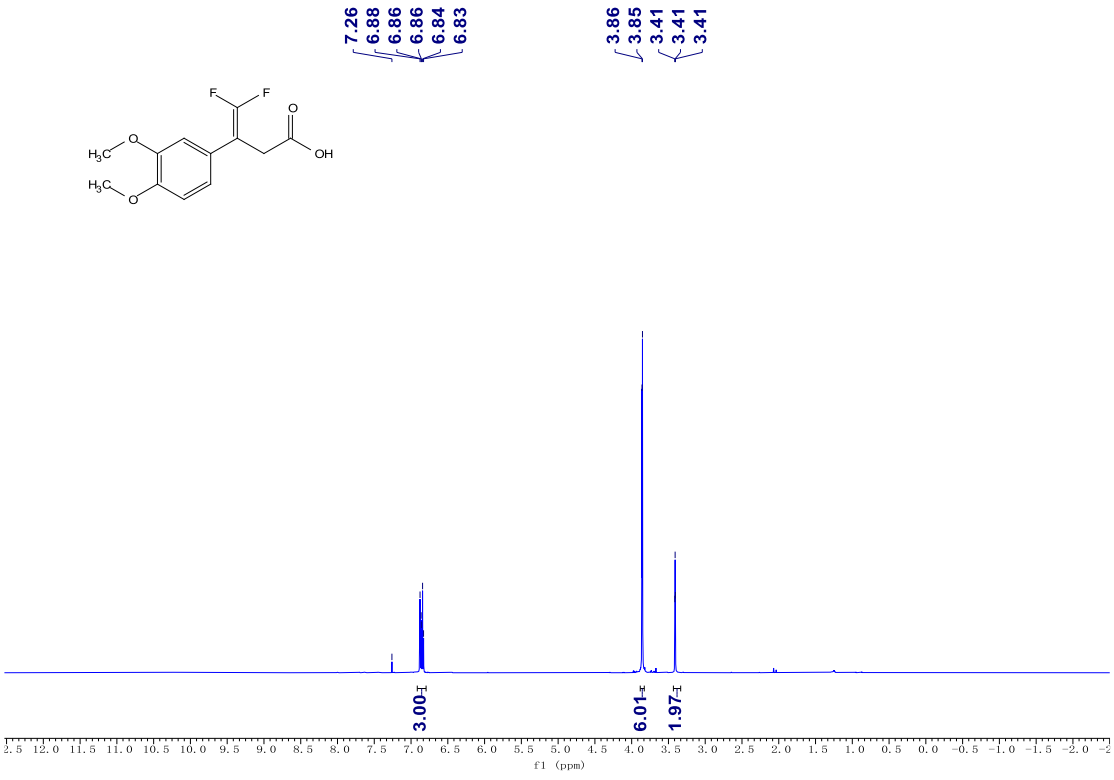
^{13}C NMR Spectra of 4j (151 MHz, Chloroform-*d*)



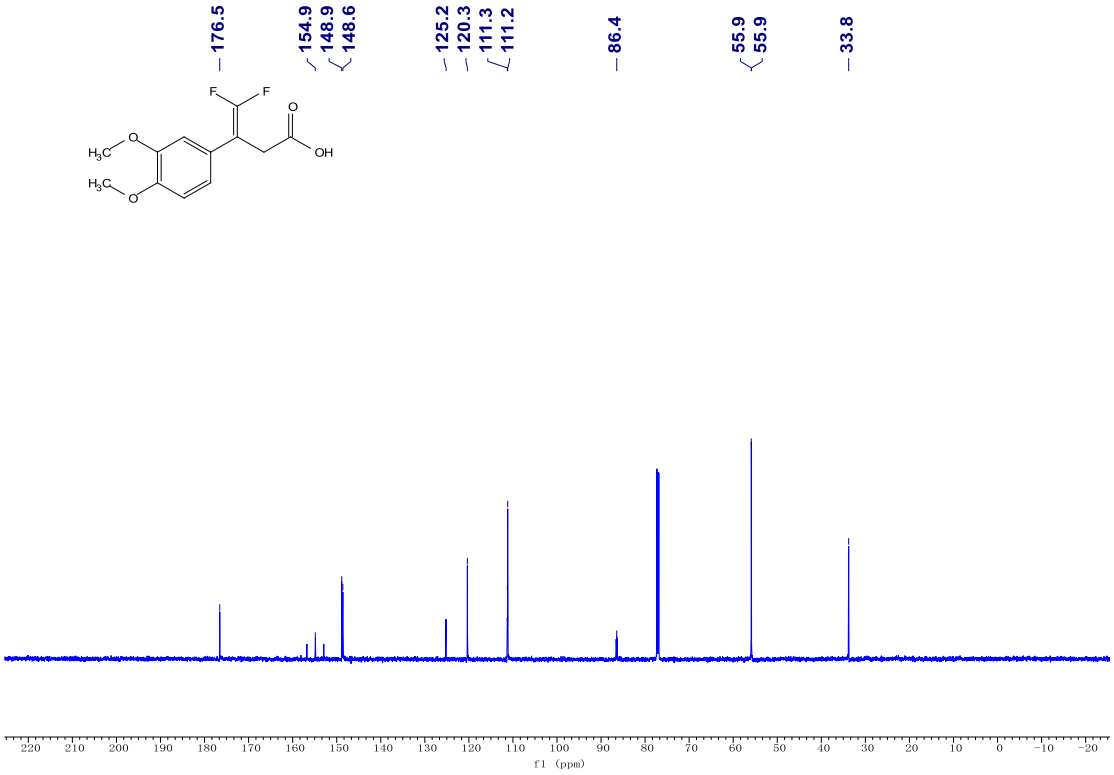
^{19}F NMR Spectra of 4j (565 MHz, Chloroform-*d*)



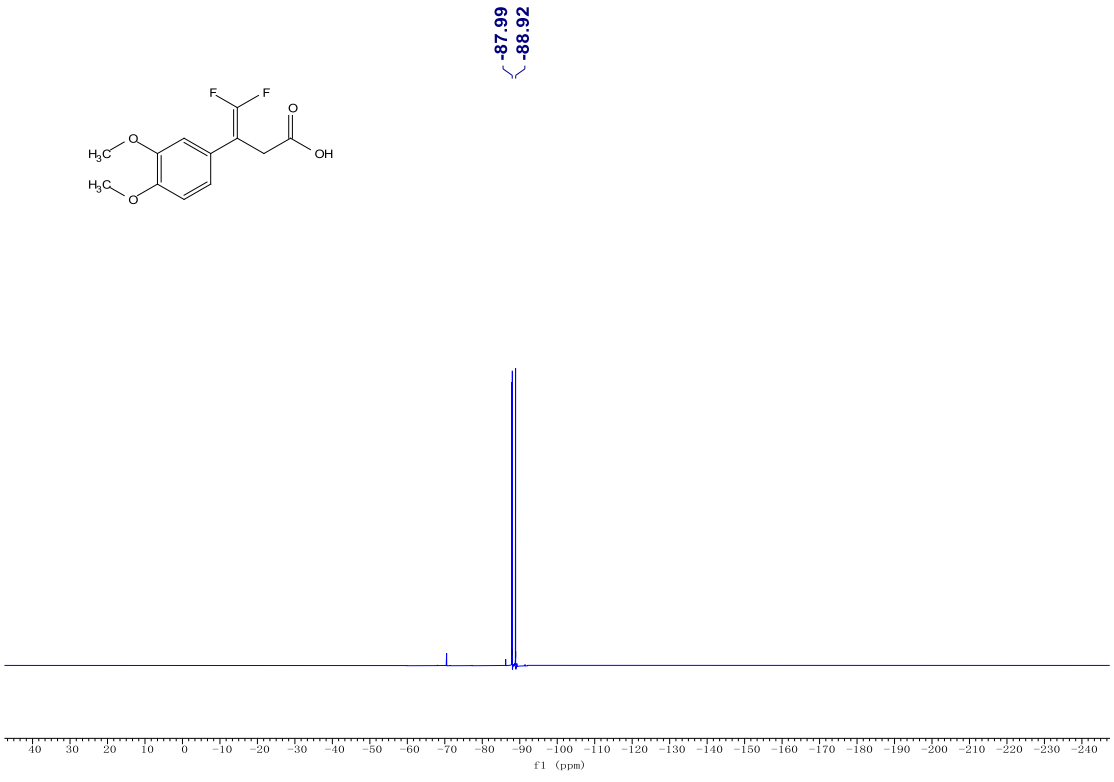
^{1}H NMR Spectra of 4k (600 MHz, Chloroform-*d*)



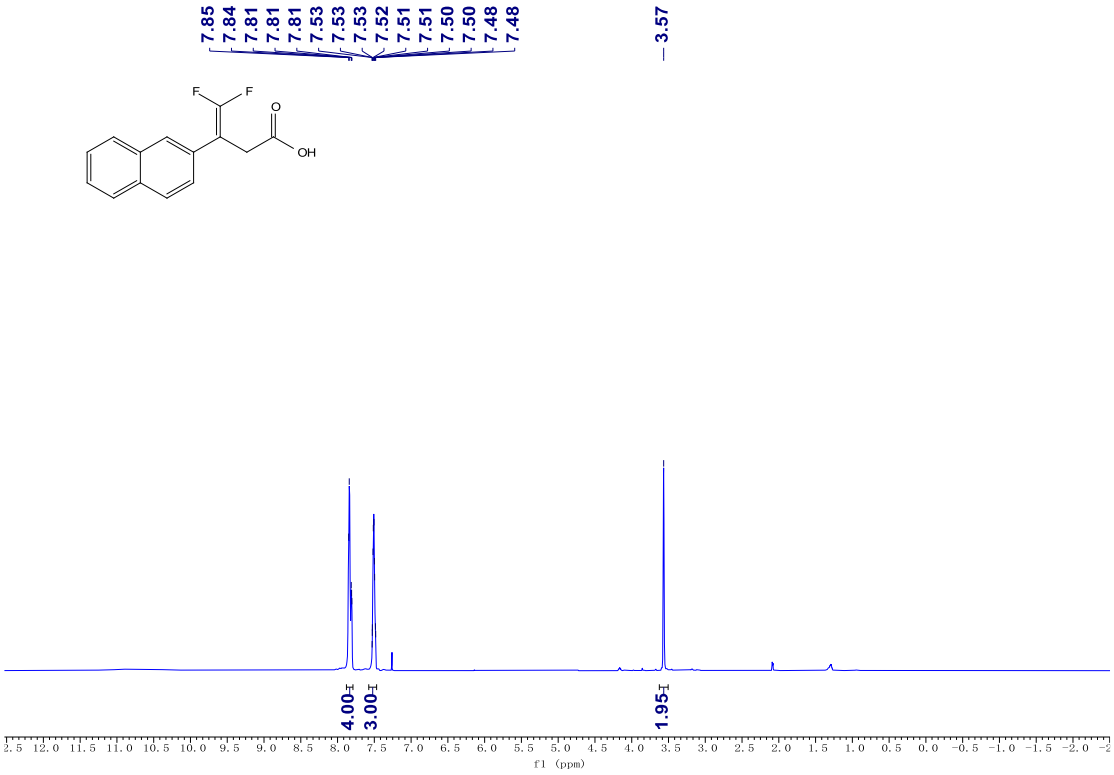
^{13}C NMR Spectra of 4k (151 MHz, Chloroform-*d*)



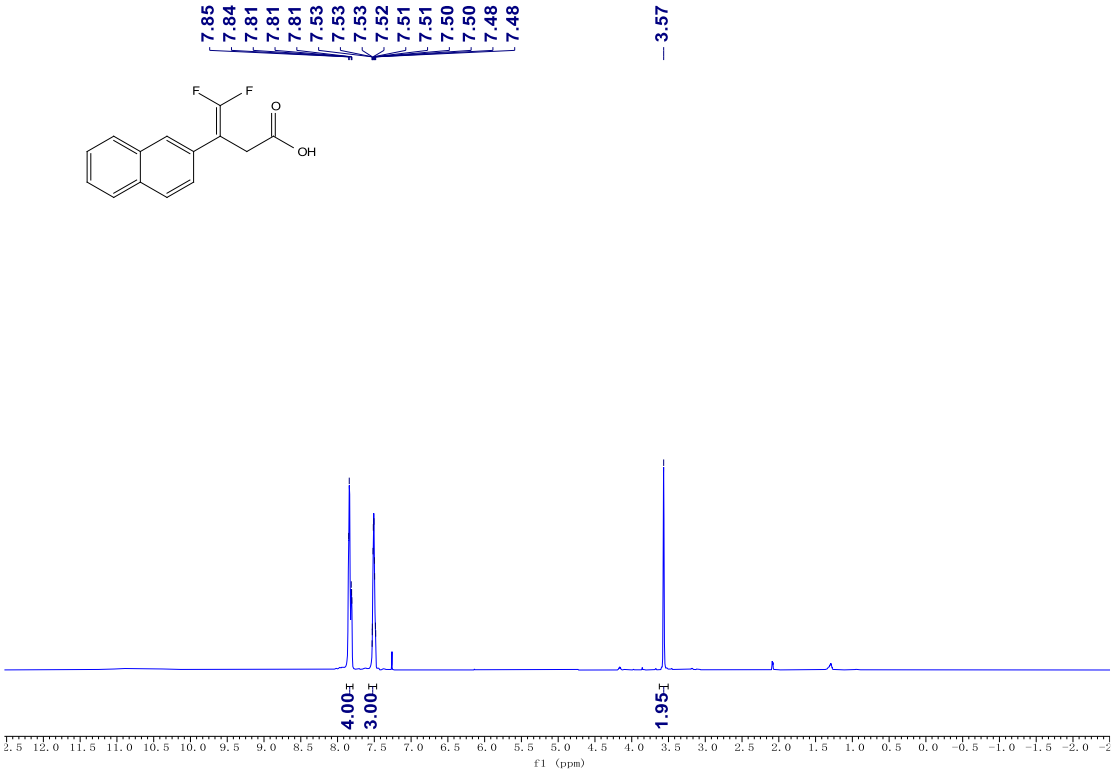
^{19}F NMR Spectra of 4k (565 MHz, Chloroform-*d*)



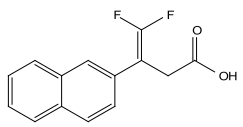
^{1}H NMR Spectra of 4l (600 MHz, Chloroform-*d*)



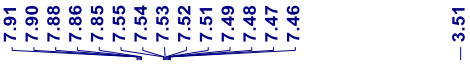
^{13}C NMR Spectra of 4l (151 MHz, Chloroform-*d*)

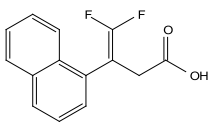


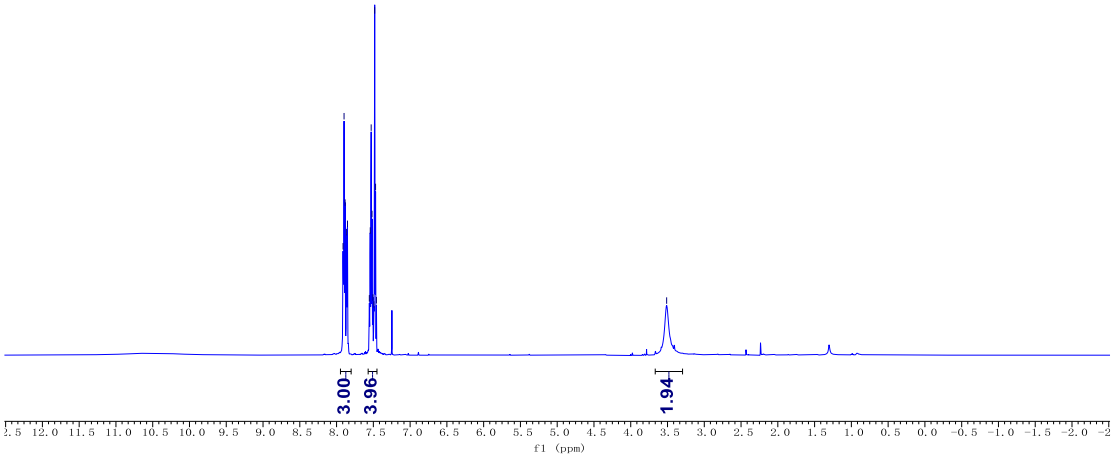
^{19}F NMR Spectra of 4l (565 MHz, Chloroform-*d*)



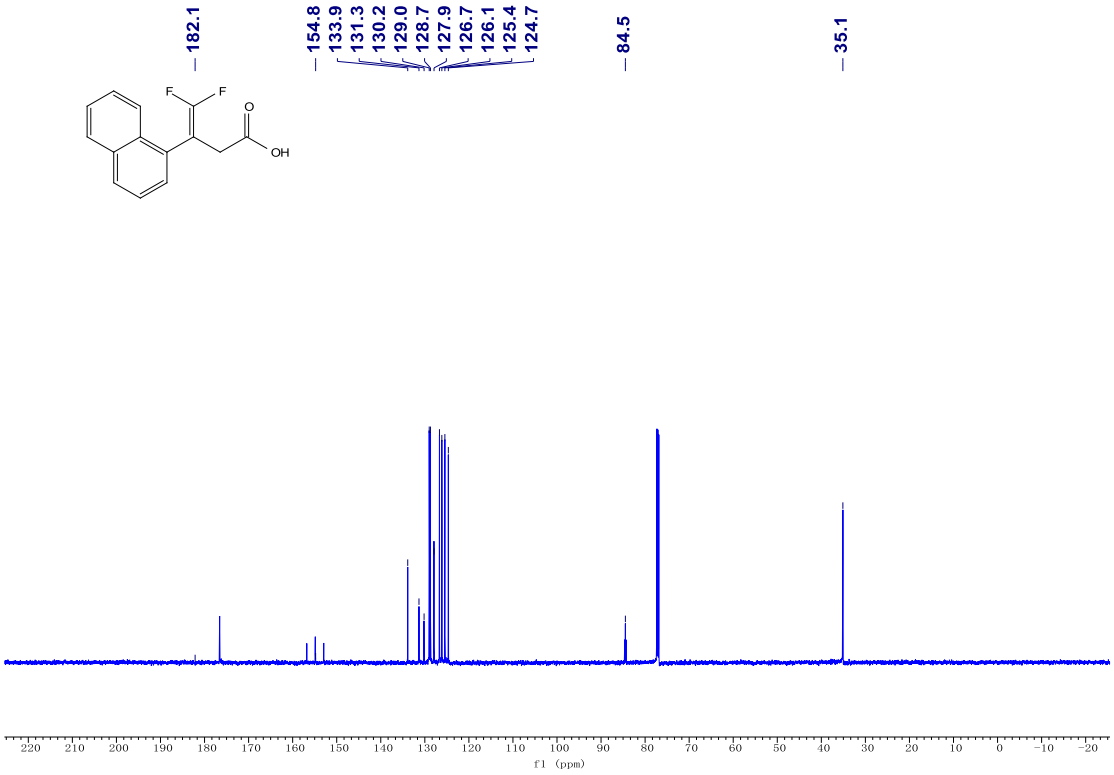
^{1}H NMR Spectra of 4m (600 MHz, Chloroform-*d*)





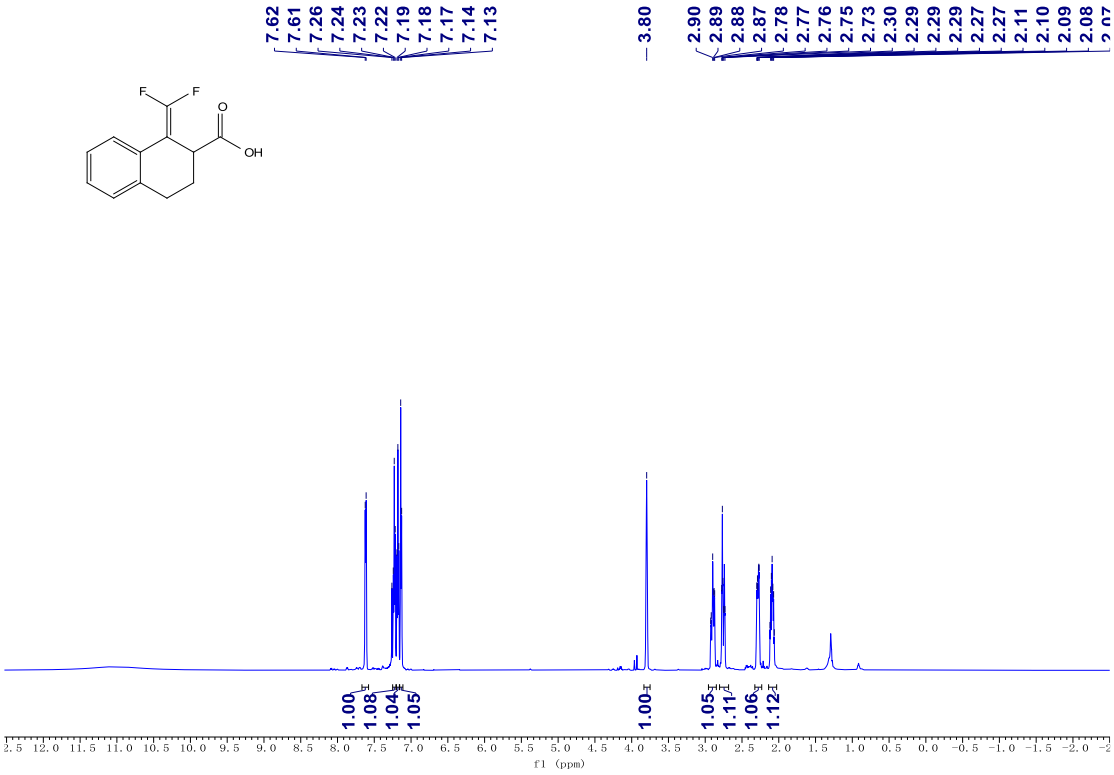


^{13}C NMR Spectra of 4m (151 MHz, Chloroform-*d*)

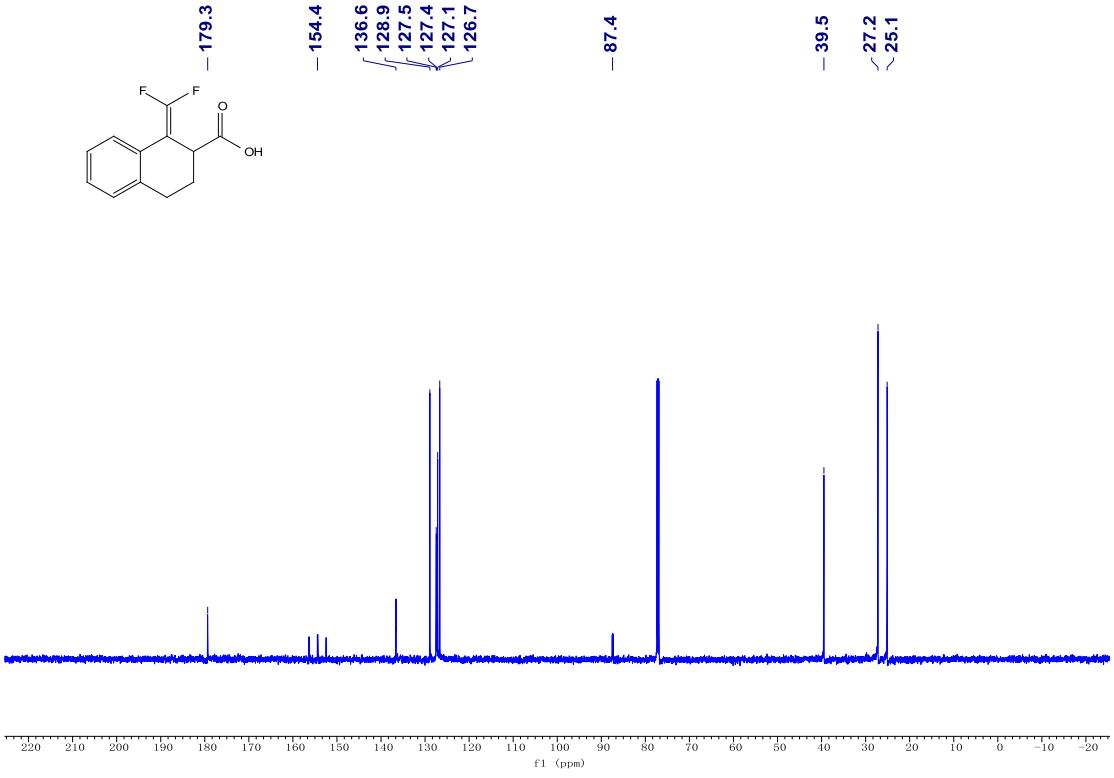


^{19}F NMR Spectra of 4m (565 MHz, Chloroform-*d*)

^{1}H NMR Spectra of 4n (600 MHz, Chloroform-*d*)

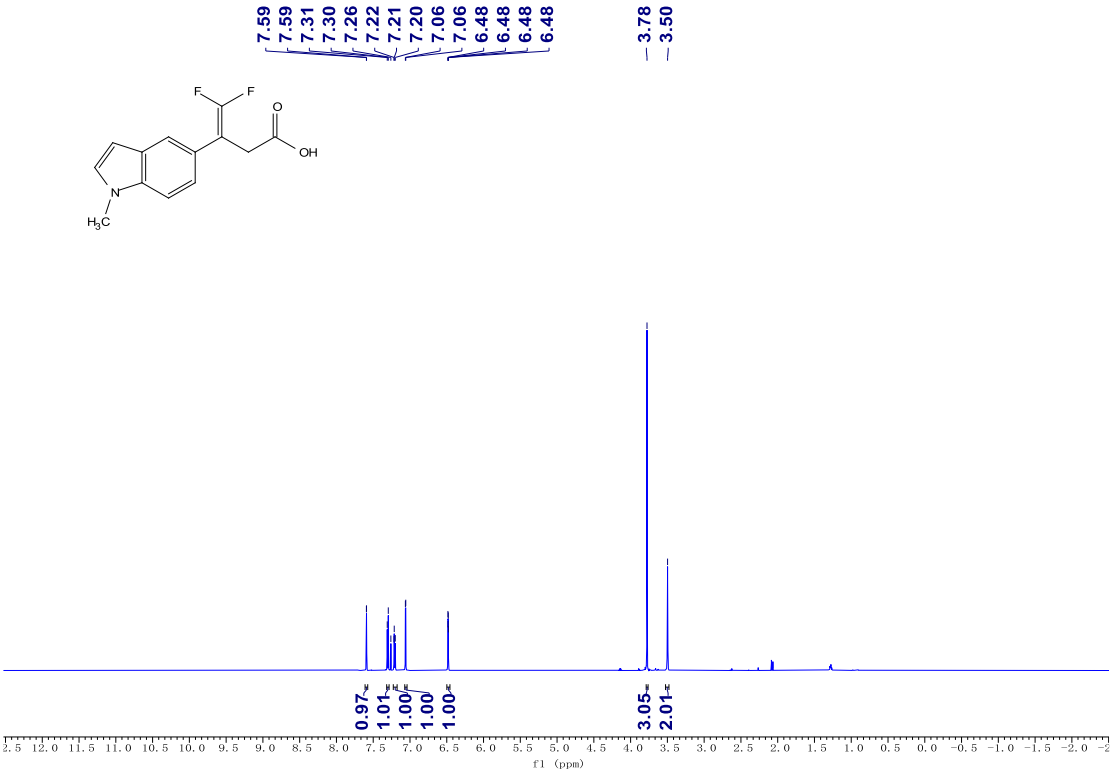


^{13}C NMR Spectra of 4n (151 MHz, Chloroform-*d*)

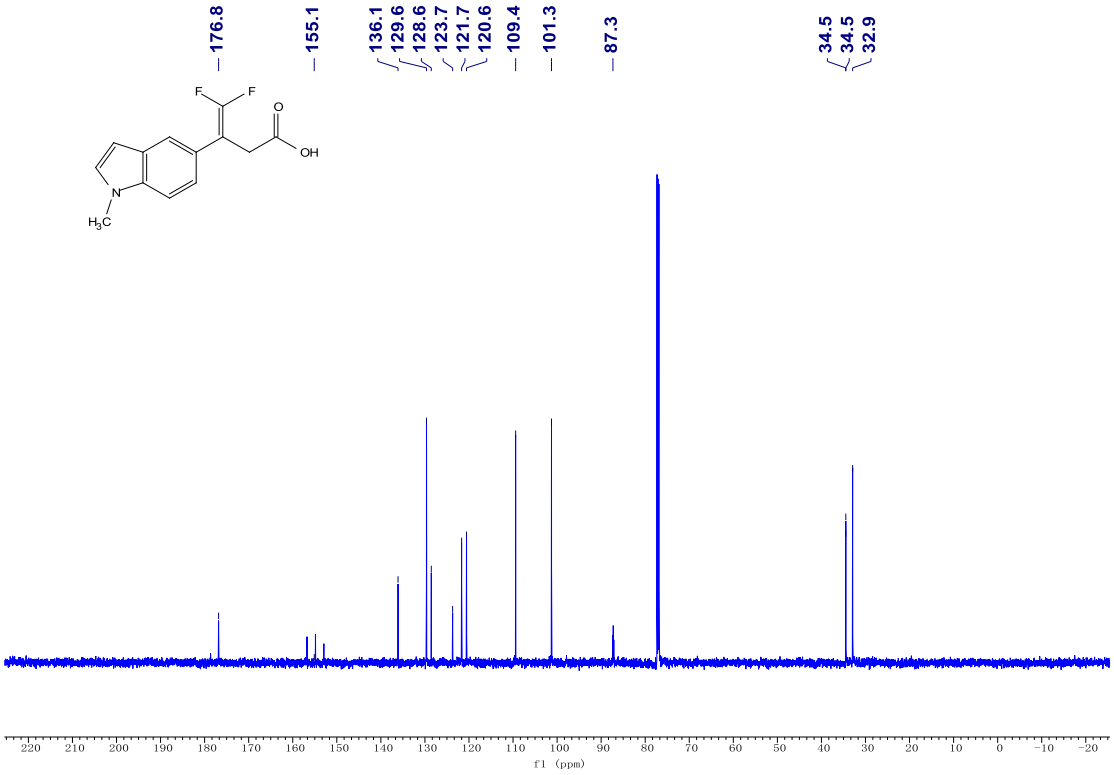


^{19}F NMR Spectra of 4n (565 MHz, Chloroform-*d*)

^{1}H NMR Spectra of 4o (600 MHz, Chloroform-*d*)

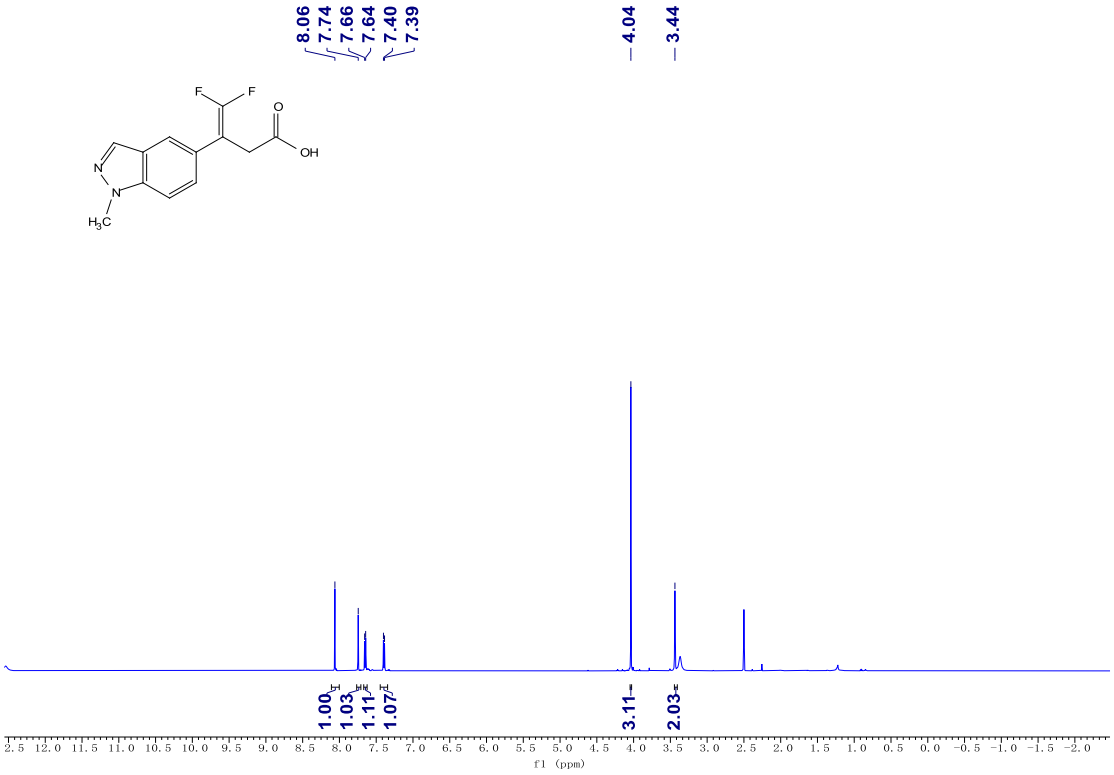


^{13}C NMR Spectra of 4o (151 MHz, Chloroform-*d*)

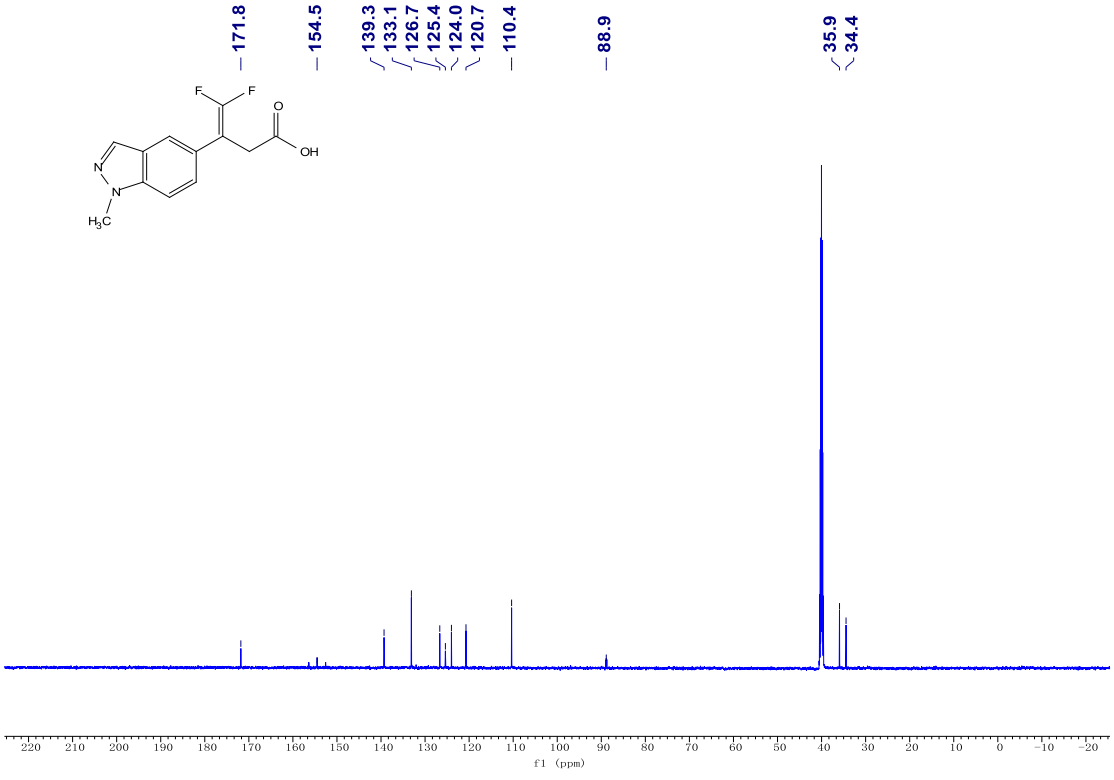


^{19}F NMR Spectra of 4o (565 MHz, Chloroform-*d*)

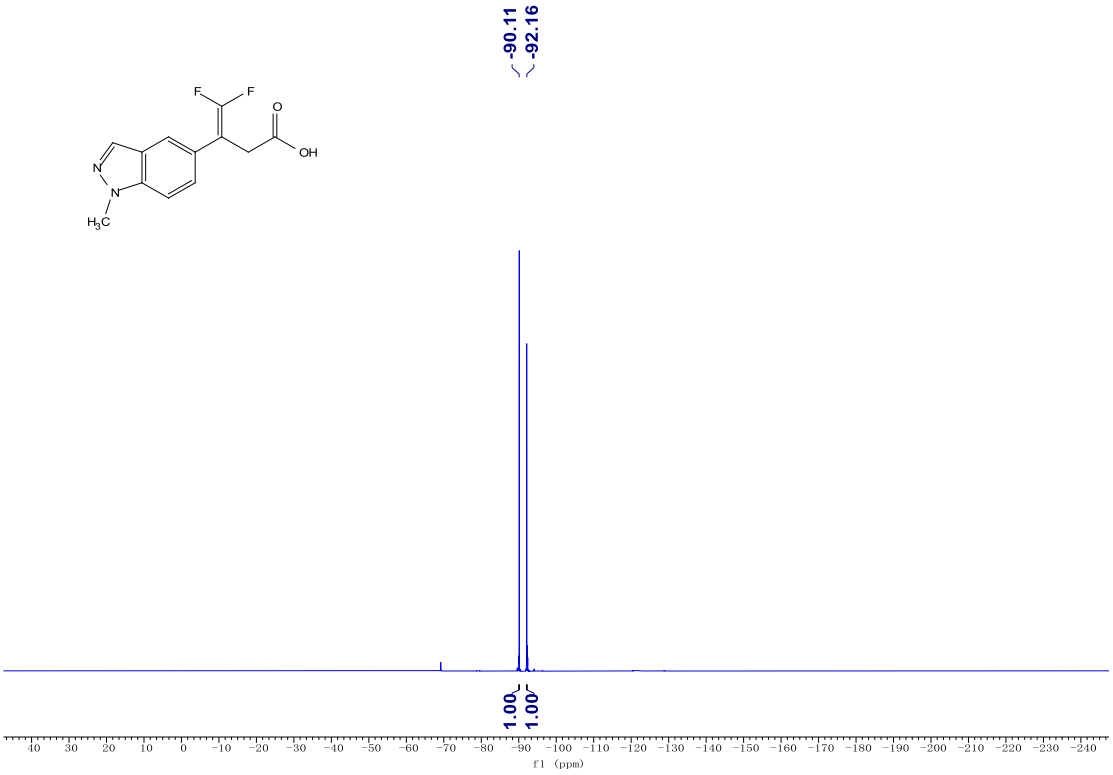
^{1}H NMR Spectra of 4p (600 MHz, DMSO-d_6)



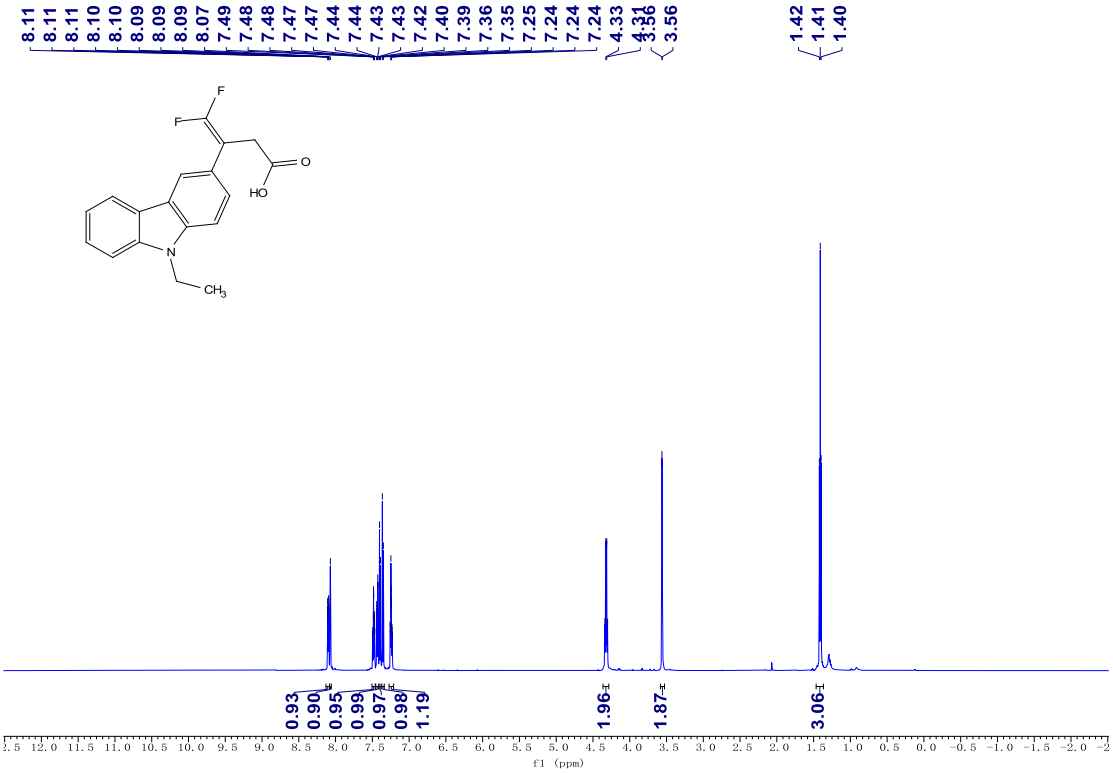
^{13}C NMR Spectra of 4p (151 MHz, DMSO-D_6)



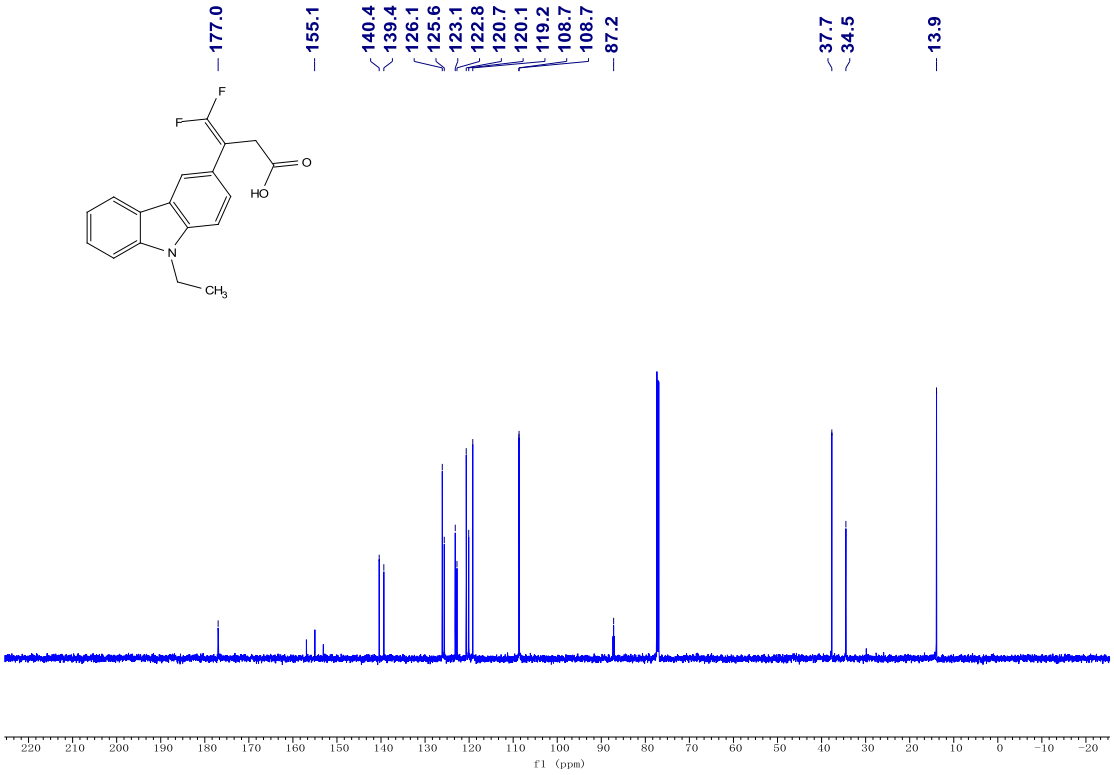
^{19}F NMR Spectra of 4p (565 MHz, Chloroform-*d*)



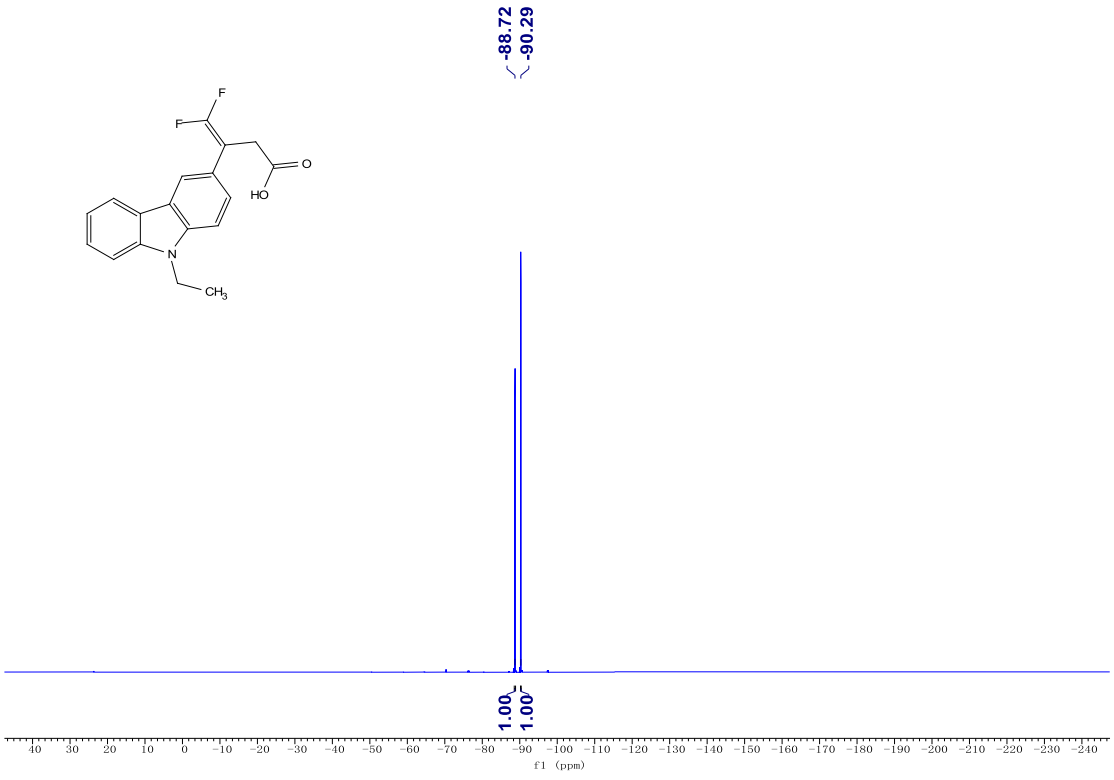
^{1}H NMR Spectra of 4q (600 MHz, DMSO-d_6)



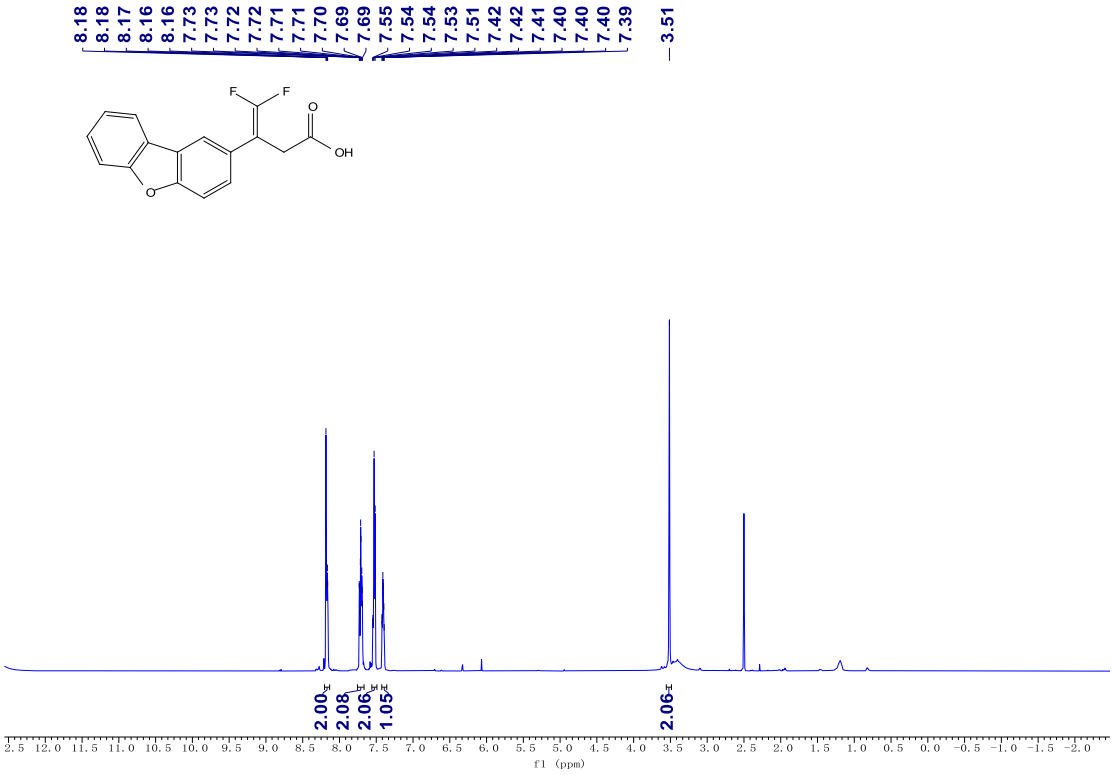
^{13}C NMR Spectra of 4q (151 MHz, DMSO-D_6)



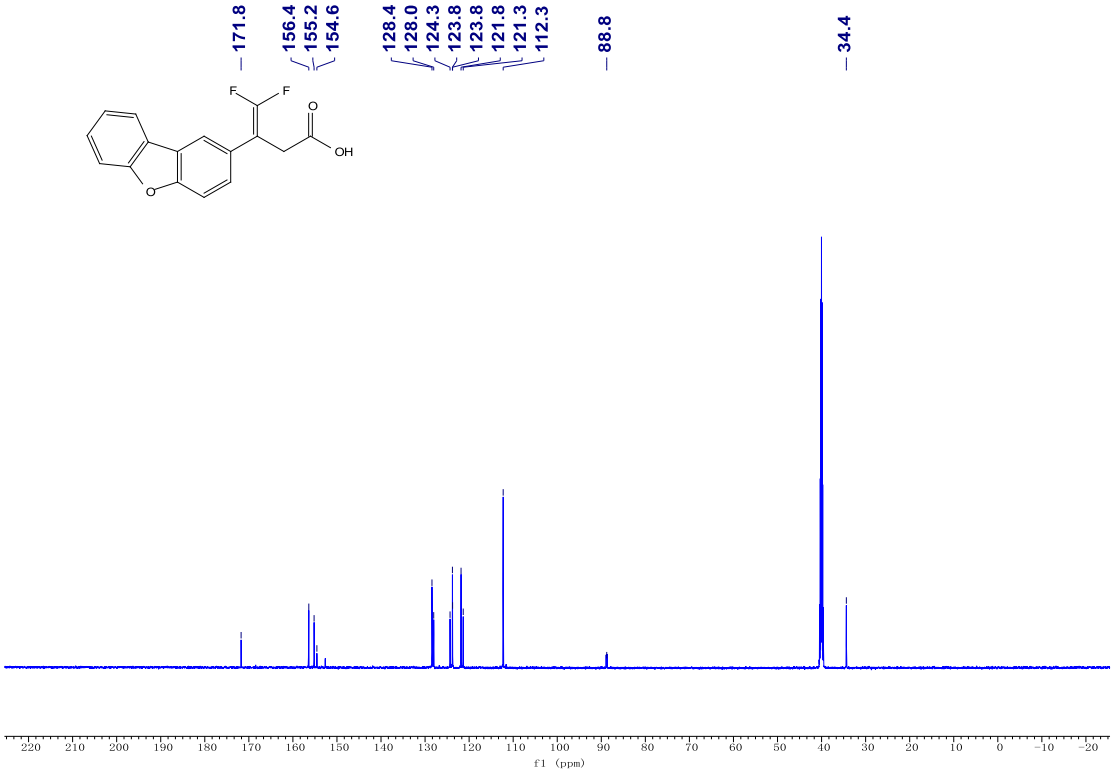
^{19}F NMR Spectra of 4q (565 MHz, Chloroform-*d*)



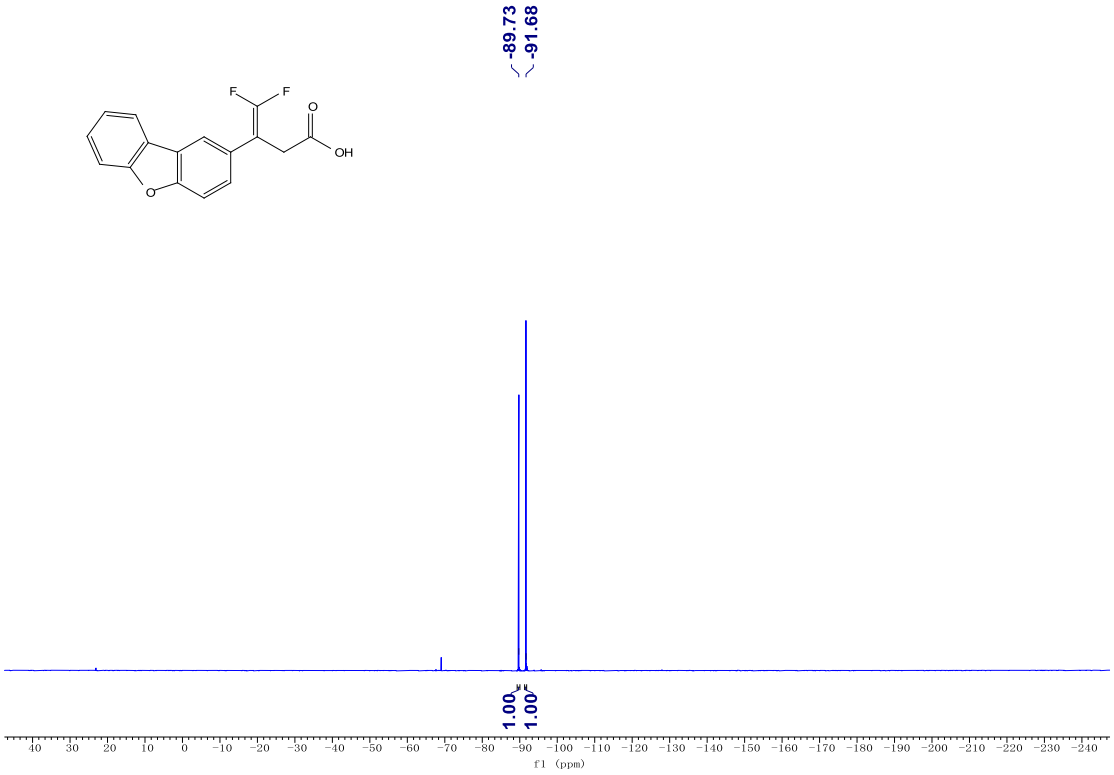
^{1}H NMR Spectra of 4r (600 MHz, DMSO-d_6)



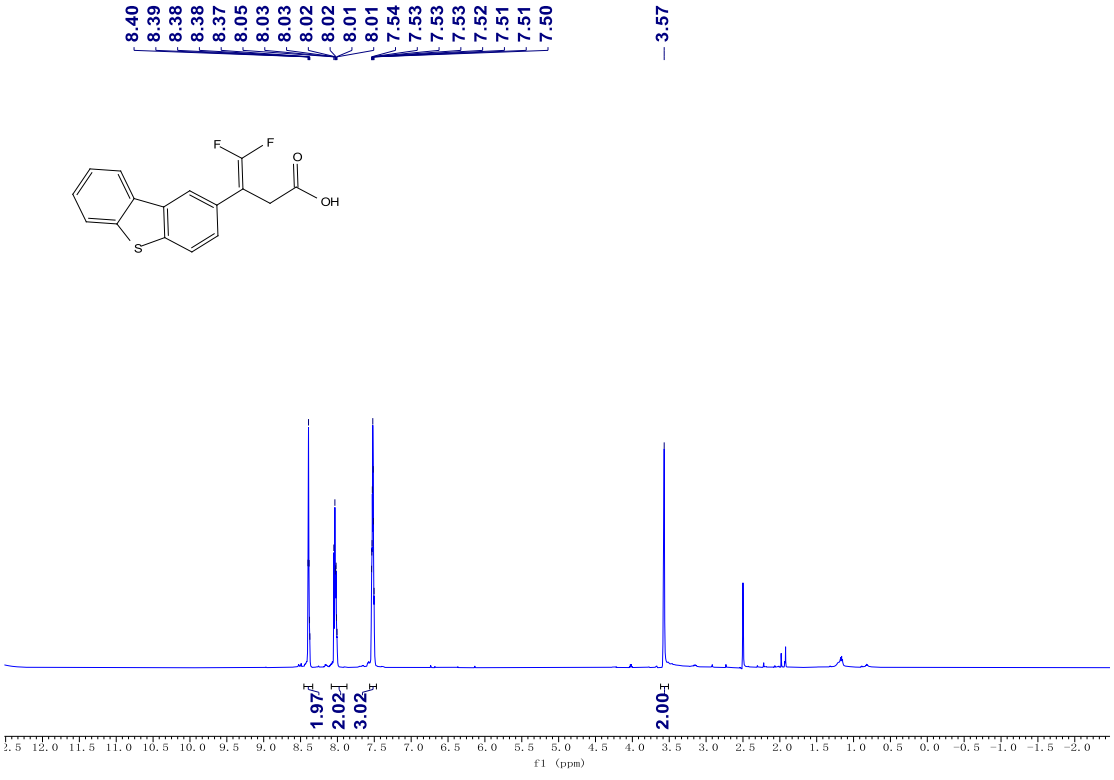
^{13}C NMR Spectra of 4r (151 MHz, DMSO-D_6)



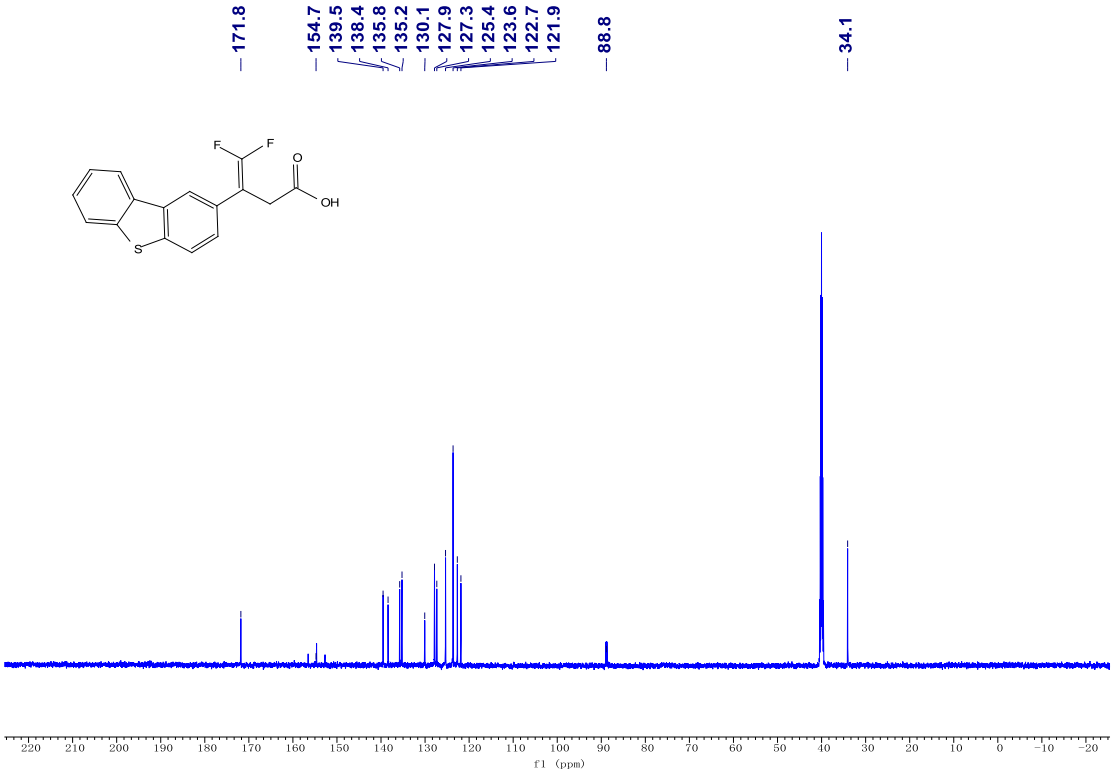
^{19}F NMR Spectra of 4r (565 MHz, Chloroform-*d*)



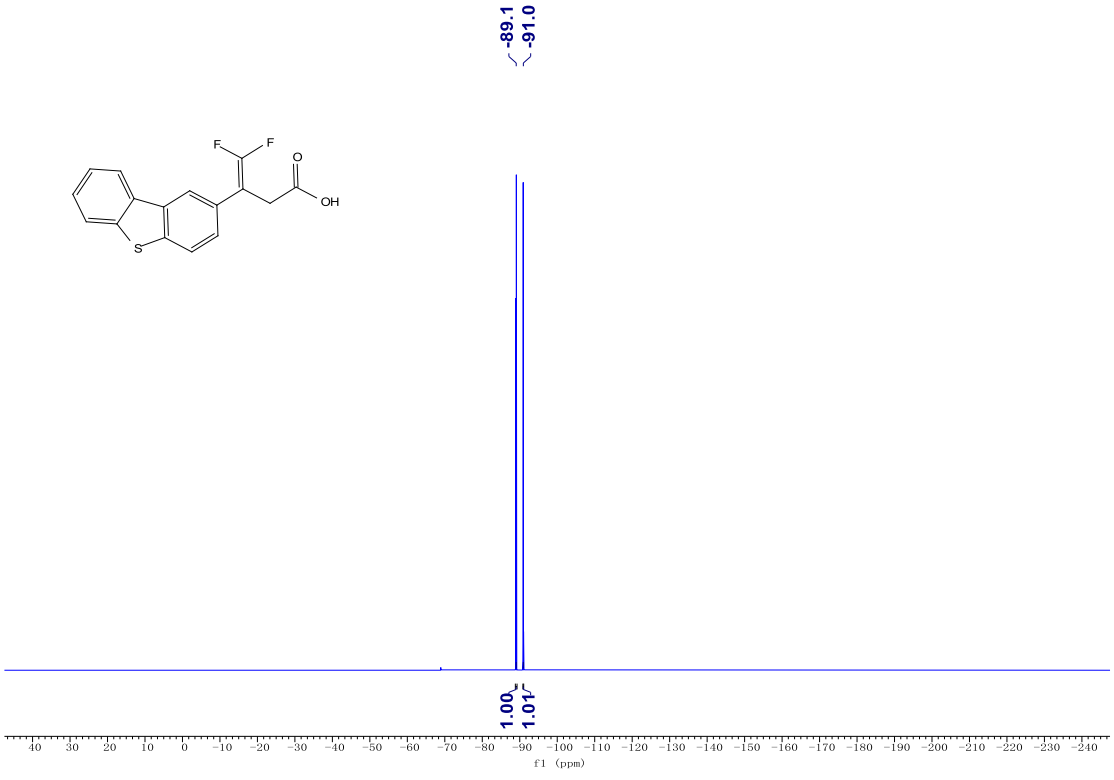
^{1}H NMR Spectra of 4s (600 MHz, DMSO-d_6)



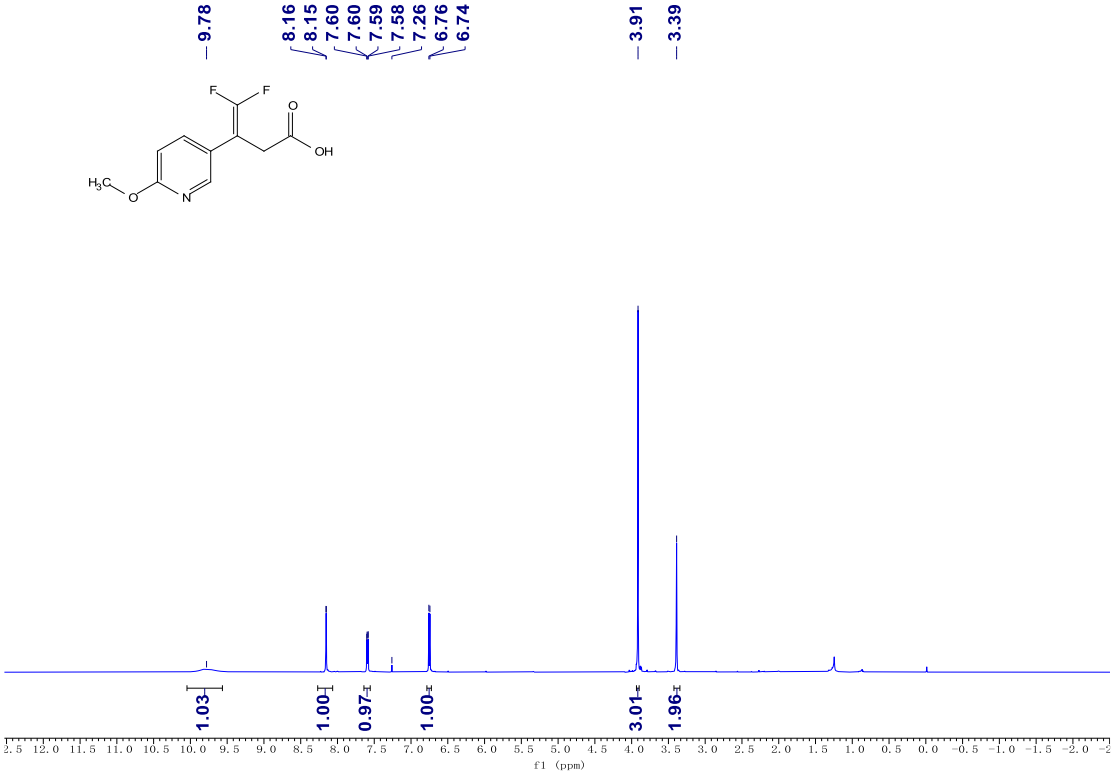
^{13}C NMR Spectra of 4s (151 MHz, DMSO-D_6)



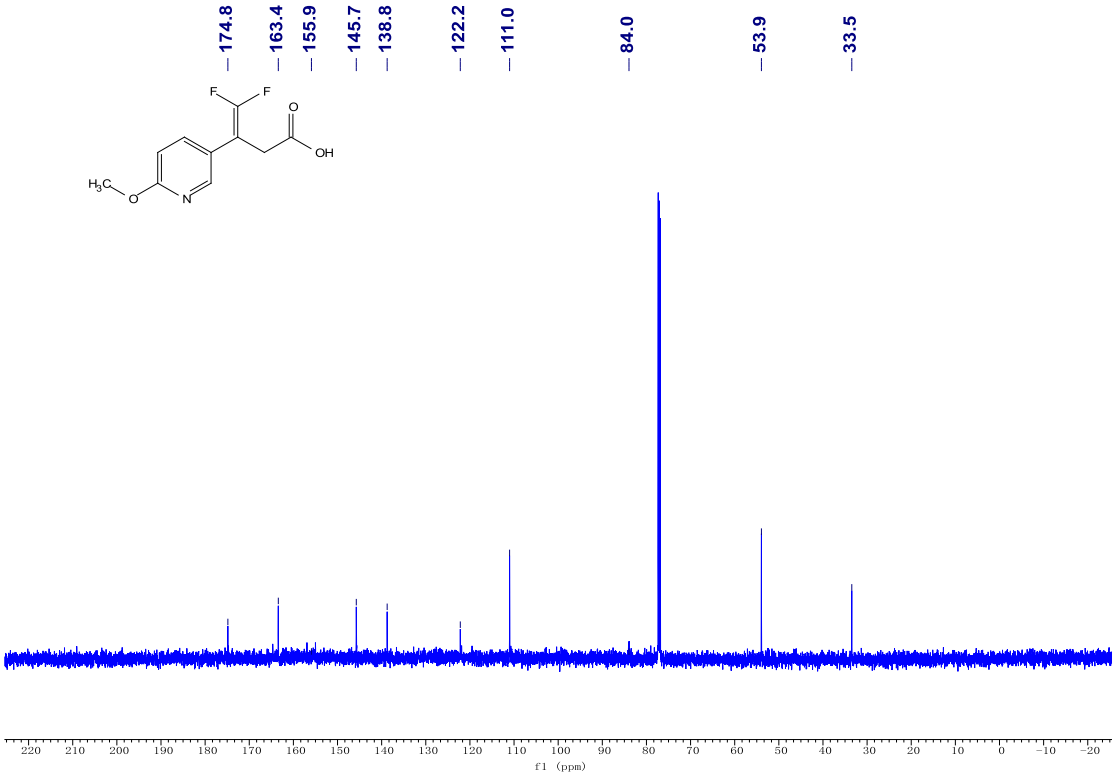
^{19}F NMR Spectra of 4s (565 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 4t (600 MHz, Chloroform-*d*)



^{13}C NMR Spectra of 4t (151 MHz, Chloroform-*d*)



^{19}F NMR Spectra of 4t (565 MHz, Chloroform-*d*)