Electronic Supplementary Information for:

Electrochemical Reduction of Sulfones for Radical Fluoroalkylation of Alkenes

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1. General Information

Unless otherwise mentioned, all manipulations were conducted with a standard sealed tube under argon. All solvents and reagents were purchased from commercial sources and used as received. All the melting points were uncorrected. ^{1}H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 101 MHz. ^{19}F NMR spectra were recorded at 376 MHz. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of the solvent: $CDCl_3$ δ 77.16 ppm. ^{19}F NMR chemical shifts were determined relative to external $CFCl_3$ at δ 0.00 ppm. Data for ^{1}H, ^{13}C, and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

2. Preparation of Fluorinated Sulfones and Alkenes

2.1 Preparation of fluorinated sulfones

Fluoroalkyl sulfones **1a**[1], **1b**[2], **1c**[2] and **1d**[2] were prepared according to reported methods. Their analytical data are in agreement with those reported in the literature.

2.1.1 Preparation of fluorinated sulfone 1a

Experimental Procedures:

To a flask was charged water (600 mL) and KOH (99.0 g, 1.5 mol). KOH was added slowly to avoid serious exothermic problem. When the mixture was cooled down to room temperature, dimethoxyethane (DME) (300 mL) and Et_3N (13.9 mL, 0.1 mol) were charged and the mixture was stirred vigorously for a while, then 2-mercaptobenzothiazole (83.6 g, 0.5 mol) was added in portions within 10 minutes. HCF_2Cl gas was bubbled into the above solution for approximately 3 hours until the reaction mixture got cool. Then the mixture was stirred for additional an hour. After that, the mixture was allowed to separate into layers, and the lower organic phase was

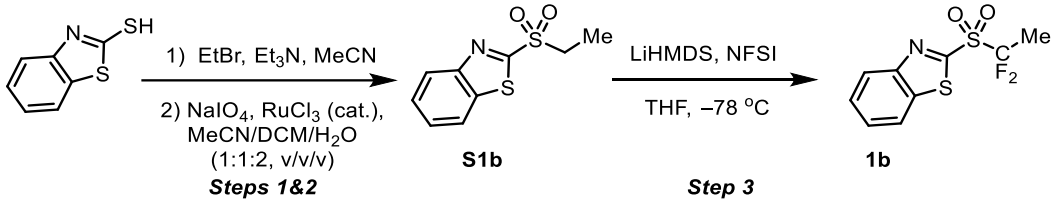
collected and the residue was extract with petroleum ether (50 mL ×3). The organic phases were combined, dried, filtered, and evaporated under reduced pressure. The residue was washed with aqueous NaOH solution (1 mol/L), and dried with anhydrous Na_2SO_4 to afford the crude product, which was directly used for next step without further purification.

To a three-necked 2-L flask containing the above-obtained crude product, was equipped with a mechanical stirrer, and charged with CCl_4 (400 mL), MeCN (400 mL), and hot water (800 mL). Then $NaIO_4$ (213.9 g, 1.0 mol) and $RuCl_3 \cdot xH_2O$ (50.0 mg) were added to the solution. The reaction mixture was stirred for 3 hours until cooling down, and filtered. The filtrate was extracted with dichloromethane (DCM) (100 mL ×3), and the white residue was washed with DCM until no more substance could be dissolved in DCM. The organic phases were combined, washed with aqueous Na_2SO_3, dried, filtered, and evaporated under reduced pressure. The crude product was recrystallized in $CHCl_3$ to afford **1a** as white solids (72.8 g, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.15 (m, 1H), 8.13 – 8.00 (m, 1H), 7.78 – 7.54 (m, 2H), 6.58 (t, J = 53.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.43 (d, J = 53.1 Hz).

2.1.2 Preparation of fluorinated sulfones 1b, 1c and 1d

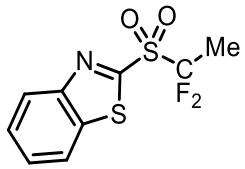
Typical Procedures:



Steps 1&2: 2-Mercaptobenzothiazole (16.7 g, 0.1 mol) was dissolved in a round-bottomed flask with MeCN (150 mL), then Et_3N (20.2 g, 0.2 mol) was charged and ethyl bromide (EtBr) was added dropwise. The reaction mixture was stirred at room temperature for 12 hours. After the completion of the reaction, the mixture was condensed under reduced pressure to about 50 mL, and filtered. The filtration was collected, and diluted with dichloromethane (50 mL) and water (100 mL). Then $NaIO_4$

(53.3 g, 0.25 mol) and $RuCl_3 \cdot xH_2O$ (10 mg) were added in one portion. The reaction was completed within 12 hours at room temperature. After the addition of water (200 mL), the mixture was extracted with dichloromethane (50 mL ×3). The organic layers were combined and dried over anhydrous Na_2SO_4. The removal of the solvent under reduced pressure afforded **S1b** as a white solid (12.7 g, 56% yield in two steps).

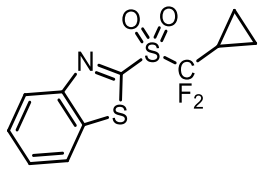
Step 3: Sulfone **S1b** (2.27 g, 10.0 mmol) and NFSI (9.45 g, 30.0 mmol) were added to a dried Schlenk flask. The flask was evacuated and backfilled with argon for 3 times. Then THF (50 mL) was charged and the mixture was cooled to –78 ºC. LiHMDS (23.0 mL, 1.0 M in THF, 23.0 mmol) was added dropwise in 15 min. Then the reaction mixture was warmed to room temperature. After the completion of the reaction, the mixture was treated with saturated aq. NH_4Cl (50 mL). The mixture was extracted with Et_2O (50 mL ×2). After the removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc (10:1, v/v) as the eluent to provide sulfone **1b** as a white solid (1.27 g, 48%).



1b

Step 3 was performed on 10 mmol scale. 1.27 g, 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.26 (m, 1H), 8.07 – 8.01 (m, 1H), 7.61 – 7.68 (m, 2H), 2.16 (t, J = 18.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.82 (q, J = 18.4 Hz).



1c

Step 3 was performed on 20 mmol scale. 2.64 g, 46% yield.

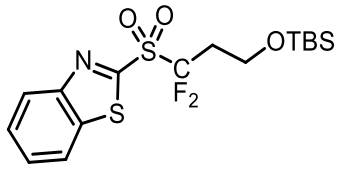
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.23 (m, 1H), 8.13 – 7.92 (m, 1H), 7.77 – 7.55 (m, 2H), 1.80 (ttt, J = 13.6, 8.2, 5.4 Hz, 1H), 0.93 (tdt, J = 8.4, 2.5, 1.2 Hz, 4H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.07 (d, J = 13.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.68, 152.97, 138.14, 128.73, 127.97, 126.18, 124.32 (t, J = 287.9), 122.25, 9.88 (t, J = 23.6 Hz), 2.46 (t, J = 3.4 Hz).

MS (EI, *m*/*z*): 289.0 (M^+), 204.4, 186.1, 134.0, 91.1, 71.1, 51.1, 39.1.

HRMS (EI, *m*/*z*): calcd. for $C_{11}H_9O_2NF_2S_2$ (M^+) 289.0037, found 289.0041.



1d

Step 3 was performed on 20 mmol scale. 5.30 g, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.22 (m, 1H), 8.11 – 7.97 (m, 1H), 7.77 – 7.57 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.82 – 2.54 (m, 2H), 0.85 (s, 9H), 0.04 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -100.46 (t, J = 18.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 153.01, 138.21, 128.80, 128.01, 126.28, 122.25 124.67 (t, J = 290.9 Hz), 55.85 (t, J = 4.1 Hz), 33.27 (t, J = 18.6 Hz), 25.72, 18.12, -5.56.

MS (FTMS, *m*/*z*): 408.1 ($M+H^+$).

HRMS (DART, *m*/*z*): Calcd. for $C_{16}H_{24}O_3NF_2S_2Si$ ($M+H^+$) 408.0929, found 408.0926.

IR (KBr): 3071, 3034, 2953, 2926, 2891, 1856, 1482, 1458, 1406, 1385, 1360, 1342, 1319, 1258, 1239, 1169, 1141, 111, 1064, 1024, 996, 955, 837, 851, 815, 797, 762, 666, 567, 518 cm^{-1}.

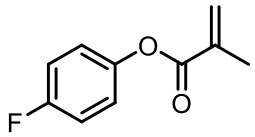
2.2 Preparation of alkenes

2.2.1 Preparation of acrylates and acrylamides

Acrylates **2a**, **2c**-**2g** and **2al** and acrylamides **2k**, **2m**-**2o**, **2q** and **2r** were prepared according to reported procedures.[9]

Typical Procedures:

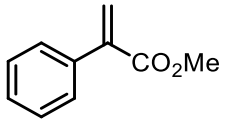
Acryloyl chloride (1.82 g, 20 mmol) was added to a stirred suspension of potassium carbonate (2.76 g, 20 mmol) in distilled water (5 mL) and acetone (20 mL) at 0 °C under an atmosphere of nitrogen, and then aniline (0.93 g, 10 mmol) was added dropwise into the mixture. The suspension was stirred at 0 °C, and the completion of the reaction was monitored by TLC. After filtration, the mixture was concentrated under reduced pressure and extracted with EtOAc (20 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with EtOAc/hexanes (1:20, v/v) to give product **2a** as a colorless liquid (2.66 g, 74% yield).



2a

Performed on 20 mmol scale. 2.66 g, 74% yield.

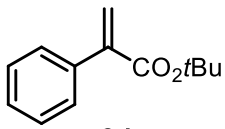
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.07 (s, 2H), 7.06 (d, J = 2.5 Hz, 2H), 6.33 (s, 1H), 5.75 (s, 1H), 2.04 (s, 3H).[10]



2c

Performed on 17 mmol scale. 0.63 g, 37% yield.

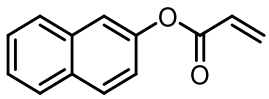
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 6.35 (d, J = 1.2 Hz, 1H), 5.88 (d, J = 1.3 Hz, 1H), 3.80 (s, 3H).[11]



2d

Performed on 10 mmol scale. 1.95 g, 96% yield.

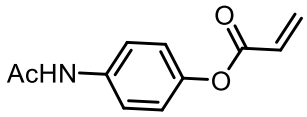
Prepared following the procedures reported by Tan, Choon-Hong *et al*.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.37 – 7.28 (m, 3H), 6.24 (t, J = 1.3 Hz, 1H), 5.81 (dd, J = 1.4, 0.7 Hz, 1H), 1.52 (s, 9H).[6]



2e

Performed on 20 mmol scale. 3.25 g, 82% yield.

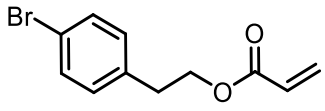
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 2.1 Hz, 1H), 8.10 – 8.01 (m, 1H), 7.89 (ddd, J = 18.7, 13.5, 7.9 Hz, 3H), 7.61 – 7.48 (m, 2H), 7.30 (ddd, J = 17.1, 10.5, 2.8 Hz, 1H), 6.50 (dd, J = 17.1, 1.7 Hz, 1H), 5.95 (ddd, J = 10.5, 3.9, 1.8 Hz, 1H).[9]



2f

Performed on 10 mmol scale. 1.61 g, 79% yield.

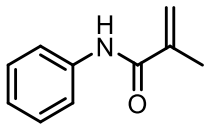
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.43 (dd, J = 8.8, 1.7 Hz, 2H), 6.99 (dd, J = 9.2, 2.7 Hz, 2H), 6.57 (dt, J = 17.3, 1.5 Hz, 1H), 6.29 (ddd, J = 17.3, 10.4, 1.6 Hz, 1H), 6.00 (dt, J = 10.4, 1.4 Hz, 1H), 2.07 (d, J = 3.7 Hz, 3H).



2g

Performed on 10 mmol scale. 2.17 g, 81% yield.

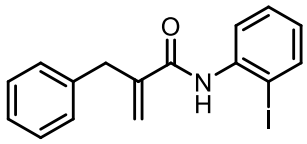
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.34 (m, 2H), 7.15 – 6.95 (m, 2H), 6.35 (dd, J = 17.3, 1.4 Hz, 1H), 6.14 – 6.00 (m, 1H), 5.79 (dd, J = 10.4, 1.4 Hz, 1H), 4.32 (t, J = 6.9 Hz, 2H), 2.90 (t, J = 6.9 Hz, 2H).



2k

Performed on 33.3 mmol scale. 2.42 g, 45% yield.

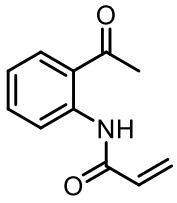
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.77 (s, 1H), 5.43 (s, 1H), 2.04 (dd, J = 1.6, 0.9 Hz, 3H).



2m

Performed on 10 mmol scale. 1.2 g, 33% yield.

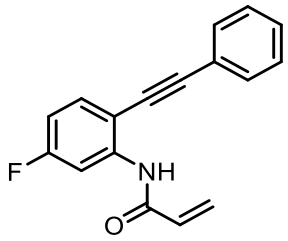
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 8.3, 1.5 Hz, 1H), 7.86 (s, 1H), 7.74 (dd, J = 8.0, 1.5 Hz, 1H), 7.38 – 7.18 (m, 6H), 6.82 (td, J = 7.7, 1.6 Hz, 1H), 6.03 (s, 1H), 5.43 (s, 1H), 3.79 (s, 2H).[12]



2n

Performed on 10 mmol scale. 1.75 g, 92% yield.

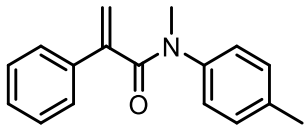
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.80 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 9.4 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.26 (dd, J = 17.1, 10.1 Hz, 1H), 5.75 (d, J = 8.9 Hz, 1H), 2.62 (s, 3H).[9]



2o

Performed on 5 mmol scale. 1.07 g, 80% yield.

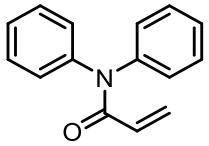
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (t, J = 7.4 Hz, 1H), 8.03 (s, 1H), 7.60 – 7.46 (m, 2H), 7.40 (dd, J = 5.1, 1.9 Hz, 3H), 7.20 (dd, J = 8.6, 3.0 Hz, 1H), 7.07 (ddd, J = 9.2, 8.1, 3.0 Hz, 1H), 6.43 (dd, J = 16.9, 1.1 Hz, 1H), 6.27 (dd, J = 16.9, 10.2 Hz, 1H), 5.80 (dd, J = 10.2, 1.1 Hz, 1H).[9]



2q

Performed on 10 mmol scale. 1.98 g. 79% yield.

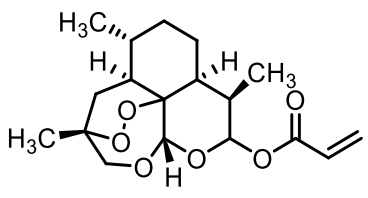
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 5H), 6.85 (dd, J = 56.2, 7.8 Hz, 4H), 5.36 (d, J = 56.3 Hz, 2H), 3.36 (s, 3H), 2.24 (s, 3H).[9]



2r

Performed on 10 mmol scale. 1.23 g, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 7.6 Hz, 4H), 7.30 – 7.14 (m, 6H), 6.46 (dd, J = 16.8, 1.9 Hz, 1H), 6.19 (dd, J = 16.8, 10.2 Hz, 1H), 5.62 (dd, J = 10.3, 2.0 Hz, 1H).[9]



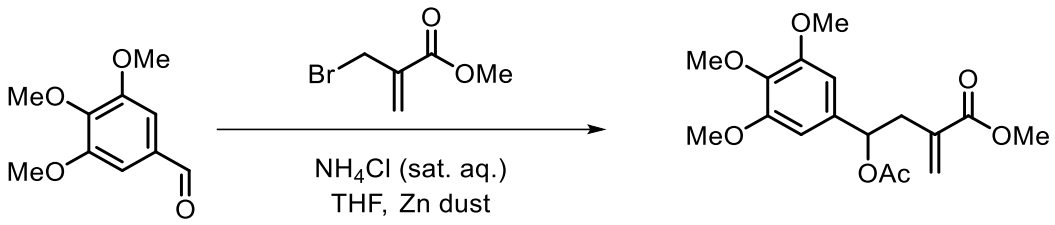
2al

Performed on 1.27 mmol scale. 0.17 g, 40% yield.

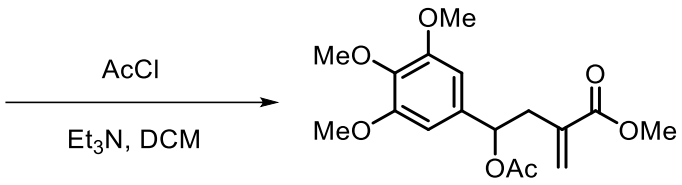
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (d, J = 17.3 Hz, 1H), 6.15 (dd, J = 17.3, 10.3 Hz, 1H), 5.85 (t, J = 10.5 Hz, 2H), 5.44 (s, 1H)., 2.59 (s, 1H), 2.44 – 2.29 (m, 1H), 2.00 (dd, *J* = 14.3, 4.0 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.81 – 1.66 (m, 2H), 1.61 (dd, *J* = 13.6, 3.3 Hz, 1H), 1.41 (d, *J* = 2.8 Hz, 5H), 1.35 – 1.21 (m, 2H), 1.02 (d, *J* = 12.6 Hz, 1H), 0.94 (dd, *J* = 6.0, 2.8 Hz, 3H), 0.83 (dd, *J* = 7.1, 2.8 Hz, 3H).

2.2.2 Preparation of alkene 2j and 2i

Typical Procedures:



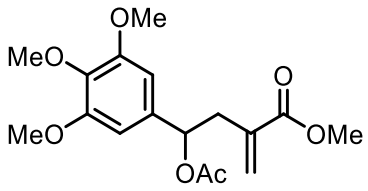
2ts



2j

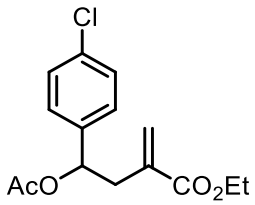
Into a flask containing 3,4,5-trimethoxybenzaldehyde (1.96 g, 10 mmol), saturated NH_4Cl aqueous solution (50 mL) and THF (10 mL) was added methyl-3-(bromomethyl)-2-oxobut-3-enoate (1.79 g, 10 mmol). Then Zinc dust (780 mg, 12 mmol) was added in portions. After the completion of the reaction, water (50 mL) was poured into the flask and the aqueous layer was extracted with Et_2O (20 mL ×3), the organic layers were combined, dried, and evaporated under reduced pressure to afford **2ts**. Then, compound **2ts** was dissolved in dry dichloromethane (DCM) (20 mL). After the addition of Et_3N (1.01 g, 10 mmol), acetyl chloride (550 mg, 7.0 mmol) was added dropwise with a syringe in 10 minutes. The reaction mixture was maintained at room temperature for another 10 hours, and quenched with water (20 mL). The organic phase

was collected and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel with EtOAc/hexanes (1:1, v/v) as eluent to give the corresponding product **2j** as a colorless liquid (1.32 g, 39% for two steps).[3, 14]



2j

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (d, J = 1.6 Hz, 2H), 6.18 (t, J = 1.6 Hz, 1H), 5.86 (ddd, J = 8.8, 4.9, 1.5 Hz, 1H), 5.56 (q, J = 1.2 Hz, 1H), 3.84 (d, J = 1.8 Hz, 6H), 3.76 (dd, J = 25.8, 1.8 Hz, 6H), 2.86 – 2.69 (m, 2H), 2.02 (d, J = 1.8 Hz, 3H).[14]

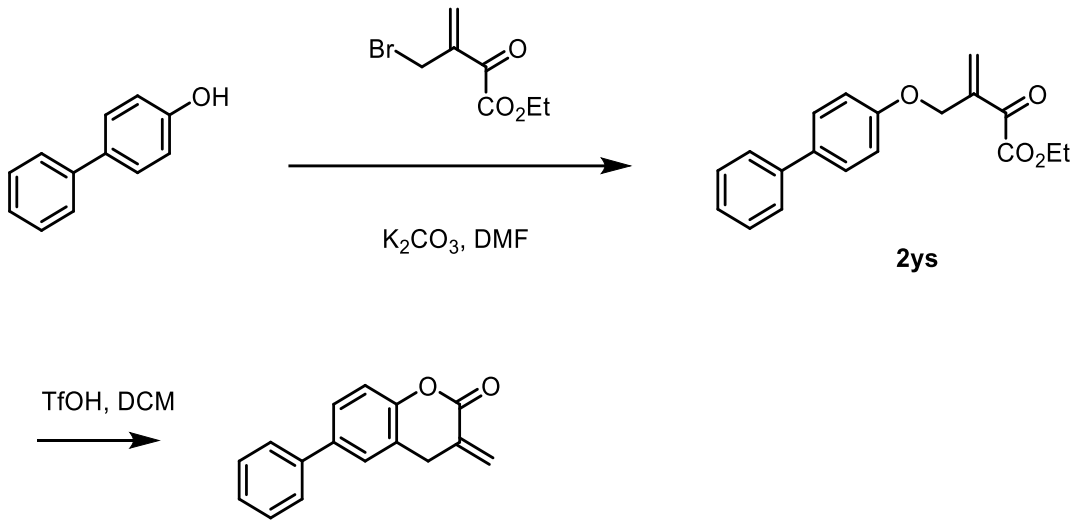


2i

Performed on 5 mmol scale. 0.42 g, 27% yield for two steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 5H), 6.19 (d, J = 1.4 Hz, 1H), 5.91 (dd, J = 8.0, 5.7 Hz, 1H), 5.51 (d, J = 1.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.87 – 2.57 (m, 2H), 2.02 (d, J = 0.6 Hz, 3H), 1.29 (td, J = 7.1, 0.6 Hz, 3H).[14]

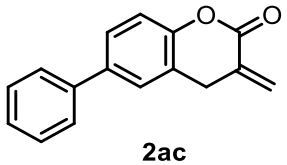
2.2.3 Preparation of alkene 2ac



Experimental Procedures:

4-Phenylphenol (1.70 g, 10 mmol) and K_2CO_3 (2.76 g, 20 mmol) were added into a flask and dissolved by DMF (20 mL). Then ethyl 3-(bromomethyl)-2-oxobut-3-enoate (1.93 g, 10 mmol) was added dropwise via syringe and stirred at room temperature for 12 hours. After the reaction was completed, water (50 mL) was added and the mixture was extracted with Et_2O (50 mL ×3), the organic layers were collected and washed with saturated brine, dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue (crude **2ys**, white solid, 2.52 g, 81%) was directly used for next step without further purification.

Into the dry DCM (20 mL) solution of crude **2ys** (2.52 g, 8 mmol) was added TfOH (2.67 g, 16 mmol) dropwise at room temperature. Then the reaction was stirred for 24 hours and monitored by TLC. When the reaction was completed, water (100 mL) was added into the reaction mixture, and the mixture was extracted with Et_2O (50 mL ×3). The organic layers were combined and sequentially washed with saturated aq. $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with EtOAc/hexanes (1:20, v/v) as eluent to give the corresponding product **2ac** as a white solid (638 mg, 32%).[4]

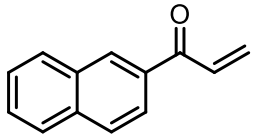


2ac

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 2H), 7.49 – 7.39 (m, 3H), 7.39 – 7.29 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.43 (td, J = 2.0, 0.9 Hz, 1H), 5.79 (td, J = 2.1, 1.0 Hz, 1H), 3.84 (dq, J = 2.2, 1.1 Hz, 2H).[4]

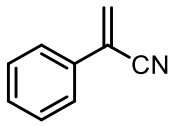
2.2.4 Preparation of other alkenes (2u, 2v, 2y and 2aq)

Alkenes **2u**,[15] **2v**,[16] **2y**[17] and **2aq**[5] were prepared according to reported procedures.



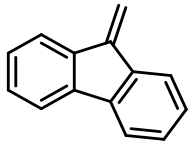
2u

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 2.1 Hz, 1H), 8.10 – 8.01 (m, 1H), 7.89 (ddd, J = 18.7, 13.5, 7.9 Hz, 3H), 7.61 – 7.48 (m, 2H), 7.30 (ddd, J = 17.1, 10.5, 2.8 Hz, 1H), 6.50 (dd, J = 17.1, 1.7 Hz, 1H), 5.95 (ddd, J = 10.5, 3.9, 1.8 Hz, 1H).



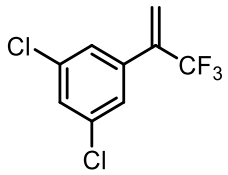
2v

Prepared follow the procedure by Merck & Co., Inc. US4366170, 1982.[16]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.41 (dd, J = 5.4, 2.0 Hz, 3H), 6.32 (s, 1H), 6.09 (s, 1H).



2y

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (ddt, J = 16.3, 7.5, 0.9 Hz, 4H), 7.37 (td, J = 7.5, 1.1 Hz, 2H), 7.30 (td, J = 7.5, 1.1 Hz, 2H), 6.07 (s, 2H).[17]



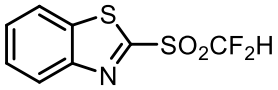
2aq

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 1.9 Hz, 1H), 7.32 (d, J = 1.9 Hz, 2H), 6.03 (q, J = 1.4 Hz, 1H), 5.80 (q, J = 1.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.99 (s, 1F).[5]

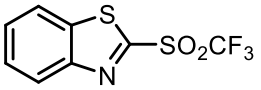
3. Development of Reaction Conditions

At the beginning, we investigated the reaction between five kinds of sulfones and six kinds of alkenes (**Scheme S1**), and the results are given in Table S1.

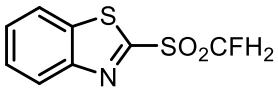
Structure of initially investigated sulfones



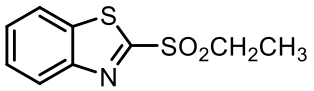
1a



1e

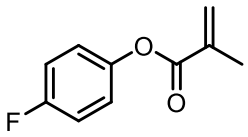


S1a

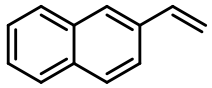


S1b

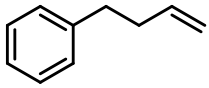
Structure of initially investigated alkenes



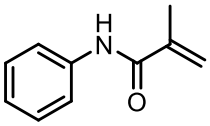
2a



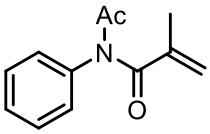
2x



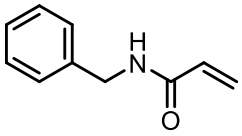
2z



2k

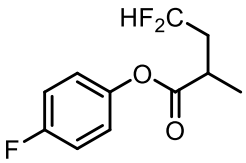


2k-Ac

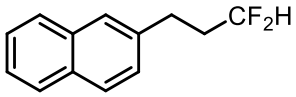


S2a

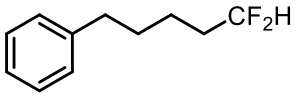
Structure of detected fluoroalkylation products



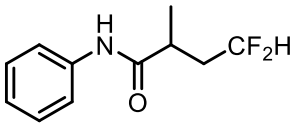
3a



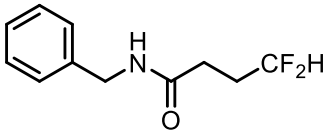
3x



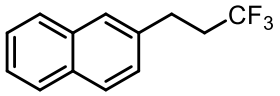
3z



3k



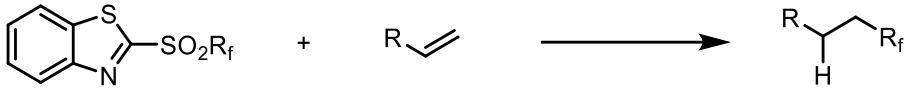
S3a



S3b

Scheme S1 Structure of initially investigated sulfones, alkenes, and detected fluoroalkylation products

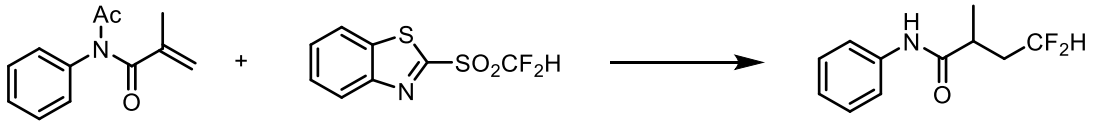
Table S1 Screening of the combination of different sulfone and alkene



Entry	Sulfone	Alkene	Solvent	Additives	Current (mA)	Product (%)
1	**1a**	**2x**	MeCN	Et_3N, H_2O, TBAOAc	5	**3x**, 25
2	**1e**	**2x**	MeCN	TBAOAc	10	**S3b**, trace
3	**1a**	**2z**	MeCN	$NaHCO_3$ TBAOAc	5	**3z**, trace
4	**1a**	**2k**	MeCN	K_2CO_3, TBAOAc	5	**3k**, 4
5	**1a**	**2k**	MeCN	TBAOAc	5	**3k**, 42
6	**1a**	**2k**-Ac	MeCN	TBAOAc	5	**3k**, 39
7	**1a**	**2k**	THF	TBAOAc	5	**3k**, 0
8	**1a**	**2k**	DMF	TBAOAc	5	**3k**, trace
9	**1a**	**2k**	DMSO	TBAOAc	5	**3k**, trace
10	**1a**	**2k** -Ac	MeCN	TBAOAc	5	**3k**, 27

Conditions: the anode and cathode are both graphite, constant current.

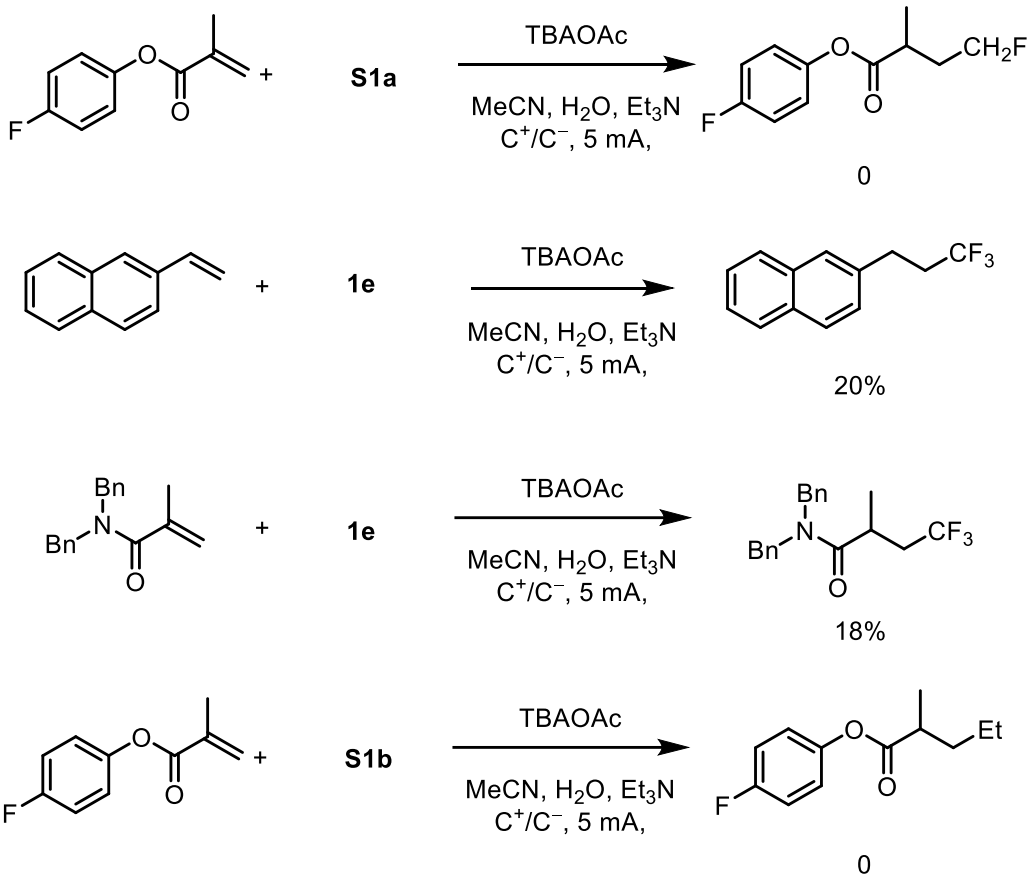
Table S2 Optimization of difluoromethylation reaction with sulfone **1a**



2k-Ac **1a** **3k**

Entry	Additive/Conditions	Current (mA)	**3k** (%)
1	HMDS	5	45
2		5	41
3	*t*BuOH	5	43
4	$PhCH_2OH$	5	52
5	Et_3N	5	61
6	–15 °C	5	23
7	$(TMS)_3SiH$	5	21
8	H_2O (0.1 mL), Et_3N (0.2 mL)	5	59
9	H_2O (0.1 mL), Et_3N (0.032 mL)	5	20
10	H_2O (0.1 mL), Et_3N (0.064 mL)	5	39
11	H_2O (0.5 mL), Et_3N (0.1 mL)	5	63
12	H_2O (0.5 mL), Et_3N (0.2 mL)	5	79
13	H_2O (0.5 mL), Et_3N (0.3 mL)	5	14
14	H_2O (0.5 mL), Et_3N (0.4 mL)	5	63
15	H_2O (0.5 mL), Et_3N (0.5 mL)	5	30
16	H_2O (0.5 mL), Et_3N (0.15 mL)	5	52
17	H_2O (0.5 mL), Et_3N (0.25 mL)	5	36
18	DIPEA (6 equiv)	5	33
19	DBU (4 equiv)	5	48
20	H_2O (0.5 mL), DMAP(6 equiv)	5	8
21	H_2O (0.5 mL), DABCO (6 equiv)	5	29
23	H_2O (0.5 mL), Et_3N (0.2 mL), 100 °C	5	11
24	H_2O (0.5 mL), piperidine (6 equiv)	5	22
25	H_2O (0.5 mL), TMEDA (6 equiv)	5	53
26	H_2O (0.5 mL), AcOK (6 equiv)	5	24
27	H_2O (0.5 mL), AcOH (6 equiv)	5	0
28	H_2O (0.5 mL), *n*-Bu_3N (6 equiv)	5	67

Conditions: the anode and cathode are both graphite, constant current, and MeCN as the solvent.

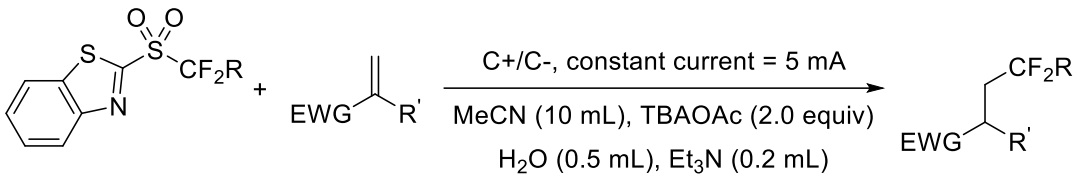


Scheme S2 Attempted trifluoromethylation, monofluoromethylation and ethylation

Summary of results:

The combination of difluoromethyl sulfone and electron-deficient alkene could smoothly undergo the desired fluoroalkylation reaction (**Table S1**). Interestingly, the reaction of *N*-acetyl-*N*-phenylamide **2k**-Ac afforded the deacetylation product **3k**. Thus, **2k**-Ac and **2k** worked equally in this electroreductive fluoroalkylation reaction (**Table S2**). However, the reaction of sulfone **S1a**/**S1b** with the alkenes in Scheme S1 failed to give the desired fluoroalkylation/alkylation products (**Scheme S2**).

4. Radical Fluoroalkylation of alkenes with Fluorinated Sulfones



1a, R = H
1b, R = Me
1c, R = Cyclopropyl
1d, R = CH_2CH_2OTBS

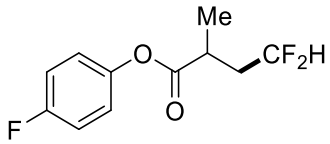
2

3

Typical Procedures:

Alkene **1a** (0.5 mmol, 1.0 equiv), sulfone **2a** (1.0 mmol, 2.0 equiv)**,** TBAOAc (1.0 mmol, 301.5 mg, 2.0 equiv), CH_3CN (10 mL) and water (0.5 mL) were added to a three-necked flask equipped with two graphite electrodes. Argon was allowed to pass through the solution for 10 min, then Et_3N (0.2 mL, 2.8 equiv.) was added. Then the electrolysis was conducted with 5 mA constant current for 10 hours. After the completion of the reaction as monitored by ^{19}F NMR, the solvent was removed carefully under reduced pressure and the residue was purified by column chromatography on silica gel with petroleum ether/EtOAc (10:1, v/v) as eluent to provide **3a** as a colorless liquid (86 mg, 74%).

4,4-Difluoro-2-methyl-*N*-phenylbutanamide (**3a**):



Colorless liquid (86 mg, 74%).

^{1}H NMR (400 MHz, **$CDCl_3$**): δ 7.49 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 6.07 – 5.71 (tt, 1H), 2.61 (h, J = 6.9 Hz, 1H), 2.36 (dddd, J = 33.8, 14.9, 8.9, 3.6 Hz, 1H), 1.91 (qt, J = 15.6, 5.3 Hz, 1H), 1.29 (d, J = 7.0 Hz, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**): δ -113.83 – -119.37 (m, 2F).

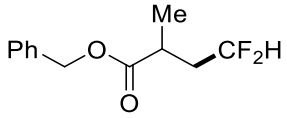
^{13}C NMR (101 MHz, **$CDCl_3$**): δ 173.1, 137.6, 129.0, 124.6, 120.1, 116.1 (t, J = 239.4), 37.8 (t, J = 21.3 Hz), 37.23 - 35.27 (t,J = 6.1Hz), 18.6.

MS (EI, *m*/*z*): 213.0 (M^+).

HRMS (EI, *m*/*z*): calcd. for $C_{11}H_{13}F_2NO$ (M^+) 213.0965, found 213.0969.

IR (KBr): 3122, 3083, 2984, 2942, 2887, 1758, 1599, 1504, 1463, 1435, 1406, 1382, 1286, 1236, 1188, 1116, 1027, 881, 821, 769, 532, 515 cm^{-1}

Benzyl 4,4-difluoro-2-methylbutanoate (3b):



Colorless liquid (81.7 mg, 72%).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.42 – 7.29 (m, 5H), 5.87 (tdd, J = 56.6, 5.2, 4.1 Hz, 1H), 5.13 (d, J = 1.3 Hz, 2H), 2.82 – 2.68 (m, 1H), 2.30 (dtdd, J = 26.5, 14.3, 8.4, 4.1 Hz, 1H), 1.91 (dddd, J = 23.1, 14.7, 10.9, 5.4 Hz, 1H), 1.26 (d, J = 7.2 Hz, 3H).

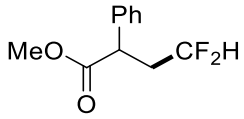
^{19}F NMR (376 MHz, **$CDCl_3$**) δ -115.05 (dddd, J = 284.9, 56.2, 17.6, 13.9 Hz), -117.13 (dddd, J = 285.1, 56.9, 21.5, 14.8 Hz).

^{13}C NMR (101 MHz, **$CDCl_3$**) δ 174.9, 135.7, 128.6, 128.3, 128.1, 116.0 (t, J = 239.0 Hz), 66.7, 37.5 (t, J = 21.6 Hz), 34.0 (t, J = 5.5 Hz), 17.5 .

MS (EI, *m*/*z*): 228.1 (M^+), 121.1, 108.1, 91.1.

HRMS (FI, *m*/*z*): calcd. for $C_{12}H_{14}O_2F_2$ (M^+) 228.0956, found 228.0960.

Methyl 4,4-difluoro-2-phenylbutanoate (3c):



Colorless liquid (53 mg, 50%).

^{1}H NMR (400 MHz, **$CDCl_3$**): δ 7.43 – 7.22 (m, 5H), 5.72 (tt, J = 56.5, 4.7 Hz, 1H), 3.90 – 3.72 (m, 1H), 3.67 (s, 3H), 2.80 – 2.54 (m, 1H), 2.39 – 2.15 (m, 1H).

^{19}F NMR (376 MHz, **$CDCl_3$**): δ -116.19 – -118.37 (m, 2F).

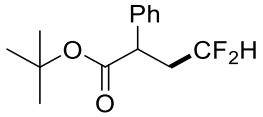
^{13}C NMR (101 MHz, **$CDCl_3$**): δ 173.0, 137.3, 129.1, 127.9, 127.7, 115.8 (t, J = 239.4Hz), 52.5, 45.3 (t, J = 6.1Hz), 37.5 (t, J = 22.1 Hz).

MS (EI, *m*/*z*): 275.1 (M^+), 155.1, 109.1.

HRMS (EI, *m*/*z*):Calcd. for $C_{11}H_{12}F_2O_2$ (M^+) 214.0805, found 214.0801.

IR (film): 2954, 2916, 2849, 1735, 1654, 1491, 1469, 1376, 1363, 1186, 1081, 1025, 968, 823, 718 cm^{-1}

***tert*-Butyl 4,4-difluoro-2-phenylbutanoate (3d):**



Colorless liquid (70.6 mg, 55%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.38 – 7.20 (m, 5H), 5.71 (tdd, J = 56.6, 5.1, 4.3 Hz, 1H), 3.68 (t, J = 7.7 Hz, 1H), 2.53-2.68 (m, 1H), 2.33 – 2.09 (m, 1H), 1.36 (s, 9H).

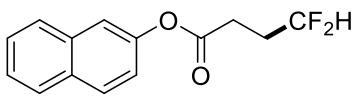
^{19}F NMR (376 MHz, **CDCl$_3$**) δ -116.40 (dddd, J = 284.8, 56.6, 20.7, 13.7 Hz, 1F), -117.58 (dddd, J = 284.8, 56.6, 18.0, 13.2 Hz, 1F).

^{13}C NMR (101 MHz, **CDCl$_3$**) δ 171.6, 138.0, 128.9, 127.6, 127.6, 116.0 (t, J = 238.9 Hz), 81.4, 46.5 (t, J = 5.8 Hz), 37.5 (t, J = 21.8 Hz), 27.8 .

MS (EI, *m*/*z*): 256.1 (M^+), 155.1, 109.1, 57.1, 41.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{14}H_{18}O_2F_2$ (M^+) 256.1269, found 256.1273.

Naphthalen-2-yl 4,4-difluorobutanoate (**3e**):



White solid (91 mg, 73%). M.p.: 52.9–53.6 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 7.91 – 7.74 (m, 3H), 7.55 (d, J = 2.3 Hz, 1H), 7.53 – 7.38 (m, 2H), 7.28 – 7.15 (m, 1H), 6.03 (tt, J = 56.5, 4.1 Hz, 1H), 2.83 (t, J = 7.4 Hz, 2H), 2.32 (ttd, J = 17.5, 7.4, 4.1 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -117.52 (dt, J = 56.5, 17.4 Hz, 2F).

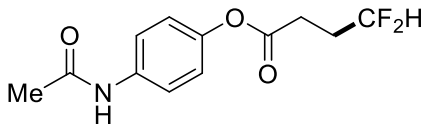
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 170.8, 148.1, 133.7, 131.5, 129.5, 127.8, 127.7, 126.7, 125.9, 120.9, 118.5, 116.0 (t, J = 239.2 Hz), 29.3 (t, J = 22.1 Hz), 27.0 (t, J = 6.1 Hz).

MS (EI, *m*/*z*): 250 (9.6, M^+), 144 (100), 115 (23.19).

HRMS (EI, *m*/*z*): calcd. for $C_{14}H_{12}F_2O_2$ (M^+) 250.0805, found 250.0798.

IR (KBr): 3062, 2974, 2941, 1754, 1628, 1509, 1463, 1441, 1423, 1386, 1355, 1276, 1243, 1211, 1170, 1149, 1122, 1081, 1070, 1037, 964, 914, 895, 817, 763, 483 cm^{-1}

4-Acetamidophenyl 4,4-difluorobutanoate (3f):



White solid (82 mg, 64%). M.p.: 97.4–97.7 °C.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.52 – 7.44 (m, 2H), 7.29 (s, 1H), 7.09 – 6.97 (m, 2H), 5.98 (tt, J = 56.5, 4.1 Hz, 1H), 2.75 (t, J = 7.4 Hz, 2H), 2.26 (ttd, J = 17.4, 7.3, 4.1 Hz, 2H), 2.15 (s, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -117.71 (dt, J = 56.4, 17.5 Hz, 2F).

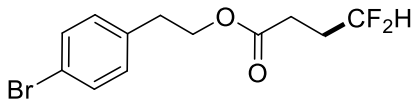
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 170.8, 168.3, 146.6, 135.8, 121.8, 120.9, 115.9 (t, J = 239.3 Hz), 29.3 (t, J = 22.3 Hz), 26.9 (t, J = 6.0 Hz), 24.5.

MS (EI, *m*/*z*): 257.1 (M^+), 151.1, 109.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_{13}NF_2O_3$ (M^+) 257.0858, found 257.0853.

IR (KBr): 3362, 3134, 3051, 2981, 1748, 1665, 1552, 1507, 1405, 1310, 1278, 1238, 1203, 1170, 1120, 1075, 1053, 952, 848, 719, 539, 522 cm^{-1}

4-Bromophenethyl 4,4-difluorobutanoate (3g):



Colorless liquid (95 mg, 63%).

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 7.40 (d, J = 8.3 Hz, 2H), 7.09 – 7.02 (m, 2H), 5.86 (tt, J = 56.6, 4.2 Hz, 1H), 4.26 (t, J = 6.9 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H), 2.45 (t, J = 7.4 Hz, 2H), 2.10 (ttd, J = 17.3, 7.4, 4.2 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -117.60 (dt, J = 56.6, 17.4 Hz, 2F).

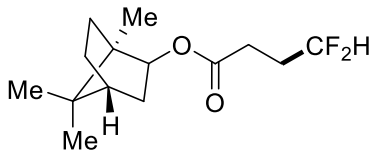
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 171.8, 153.9, 136.6, 131.6, 130.6, 116.0 (t, J = 239.1 Hz), 64.9, 34.4, 29.2 (t, J = 22.2 Hz), 26.7 (t, J = 6.0 Hz).

MS (EI, *m*/*z*): 182.0, 184.0, 169, 171, 107.

HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_{13}BrF_2O_2$ (M^+) 306.0062, found 306.0069.

IR (KBr): 2959, 1735, 1489, 1441, 1422, 1405, 1356, 1275, 1175, 1119, 1072, 1012, 948, 814, 528 cm^{-1}

(1*S*,3*R*,4*S*)-3,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4,4-difluorobutanoate (3h):



Colorless liquid (101 mg, 95%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 5.89 (tt, J = 56.7, 4.3 Hz, 1H), 4.67 (dd, J = 7.8, 3.4 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.13 (ttd, J = 17.5, 7.5, 4.3 Hz, 2H), 1.83 – 1.63 (m, 5H), 1.60 – 1.42 (m, 2H), 1.26 – 1.01 (m, 3H), 0.95 (s, 3H), 0.81 (s, 3H).

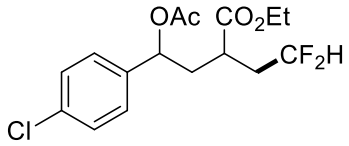
^{19}F NMR (376 MHz, **CDCl$_3$**) δ -117.54 (dt, J = 56.6, 17.4 Hz, 2F).

^{13}C NMR (101 MHz, **CDCl$_3$**) δ 171.4, 116.2(t, J=240.4 Hz), 81.6, 48.7, 46.9, 45.0, 38.7, 33.7, 29.4 (t, J = 22.1 Hz), 27.2 (t, J = 6.0 Hz), 27.0, 20.1, 19.9, 11.4. **MS** (TOF-EI, *m*/*z*): 260.2 (M^+), 136.1, 121.1, 107.0, 95.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{22}F_2O_2$ (M^+) 260.1582, found 260.1584.

IR (KBr): 2956, 2880, 1732, 1505, 1455, 1391, 1312, 1260, 1180, 1118, 1074, 972, 955, 861, 841, 804 *cm-1*

Ethyl 4-acetoxy-4-(4-chlorophenyl)-2-(2,2-difluoroethyl)butanoate (3i):



Colorless liquid (164 mg, 94%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.33 – 7.27 (m, 2H), 7.27 – 7.20 (m, 3H), 6.04 – 5.59 (m, 2H), 4.44 – 3.86 (m, 2H), 2.89 – 2.46 (m, 1H), 2.41 – 1.83 (m, 7H), 1.26 (td, J = 7.1, 2.2 Hz, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -114.99 (dddt, J = 285.7, 56.6, 25.9, 15.7 Hz, 1F), -115.96 – -117.57 (m, 1F).

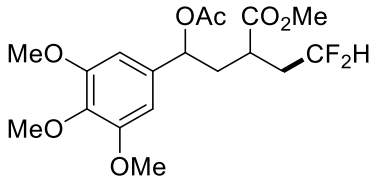
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 173.8, 169.9, 138.5, 134.0, 128.8, 127.7, 115.7, 72.8, 61.2, 38.8, 36.5, 36.2, 21.0, 14.1.

MS (EI, *m*/*z*): 348.1 (M^+), 305.1, 259.1, 215.1, 139.0.

HRMS (EI, *m*/*z*): Calcd. for $C_{16}H_{19}F_2O_4Cl$ (M^+) 348.0934, found 348.0932.

IR (KBr): 2982, 2938, 1736, 1598, 1492, 1438, 1372, 1235, 1180, 1122, 1091, 1059, 1014, 946, 921, 827, 763, 734 cm^{-1}

Methyl 4-acetoxy-2-(2,2-difluoroethyl)-4-(3,4,5-trimethoxyphenyl)butanoate (3j):



Pale yellow liquid (149 mg, 76%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 6.50 (s, 2H), 6.07 – 5.57 (m, 2H), 3.87 – 3.77 (m, 9H), 3.70 (d, J = 1.9 Hz, 3H), 2.81 – 2.53 (m, 1H), 2.41 – 1.81 (m, 7H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -114.52 – -116.43 (m, 1F), -116.47 – -117.66 (m, 1F).

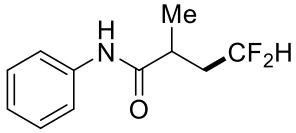
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 174.4 (d, J = 5.5 Hz), 170.0 (d, J = 7.5 Hz), 153.4, 137.8 (d, J = 7.0 Hz), 135.3 (d, J = 20.1 Hz), 115.7 (td, J = 239.7, 2.0 Hz), 103.4 (d, J = 18.4 Hz), 73.7 (d, J = 29.5 Hz), 60.8, 56.2, 52.2, 38.7 (d, J = 33.3 Hz), 36.6 (t, J = 5.3 Hz), 36.0 (t, J = 5.1 Hz), 21.1 (d, J = 2.7 Hz).

MS (EI, *m*/*z*): 390.2 (M^+), 315.2, 197.1, 169.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{18}H_{24}F_2O_7$ (M^+) 390.1485, found 390.1484.

IR (KBr): 2950, 2842, 1739, 1593, 1508, 1463, 1425, 1373, 1330, 1236, 1153, 1127, 1049, 1049, 1009, 834 cm^{-1}

4-Fluorophenyl 4,4-difluoro-2-methylbutanoate (3k):



Colorless solid (451 mg, 71%). M.p.: 72.0–72.4 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 7.12 – 6.96 (m, 4H), 5.98 (ttd, J = 56.4, 4.5, 1.2 Hz, 1H), 3.05 – 2.86 (m, 1H), 2.50 – 2.29 (m, 1H), 2.12 – 1.92 (m, 1H), 1.39 (dd, J = 7.2, 1.1 Hz, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -115.05 – -115.81 (m, 1F), -116.51 – -117.27 (m, 1F).

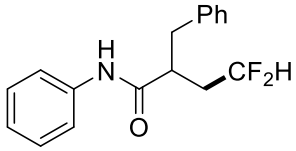
^{13}C NMR (101 MHz, **CDCl**3) δ 173.1, 137.6, 129.0, 124.6, 120.1, 116.1 (t, J = 238.9 Hz), 37.8 (t, J = 21.3 Hz), 36.52 - 36.02 (m), 18.6.

MS (EI, *m*/*z*): 232.1 (M^+), 121.1, 112.1, 93.1, 73.2.

HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{11}F_3O_2$ (M^+) 232.0711, found 232.0718.

IR (film): 3304, 3139, 3062, 2975, 2935, 1665, 1599, 1543, 1500, 1442, 1309, 1250, 1188, 1120, 1090, 1025, 754, 693 cm^{-1}

2-Benzyl-4,4-difluoro-*N*-phenylbutanamide (3l):



White solid (1.12g, 78%). M.p.: 99.4–101.1 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.35 – 7.13 (m, 9H), 7.08 (m, 2H), 5.89 (tdd, J = 56.6, 5.6, 3.1 Hz, 1H), 3.00 (dd, J = 13.4, 9.4 Hz, 1H), 2.85 (dd, J = 13.4, 5.9 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.47 (dtdd, J = 22.9, 14.7, 9.9, 3.1 Hz, 1H), 2.11 – 1.90 (m, 1H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -115.18 (ddt, J = 284.1, 56.0, 14.7 Hz, 1F), -116.64 – -117.86 (m, 1F).

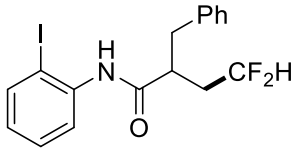
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 171.5, 138.4, 137.1, 128.9, 128.9, 128.8, 127.0, 124.7, 120.4, 116.0, 44.4, 39.6, 36.5 (t, J = 22.3 Hz).

MS (ESI, *m*/*z*): 290.1 ($M + H^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{17}H_{18}ONF_2$ ($M + H^+$) 290.1351, found 290.1349.

IR (film): 3295, 3063, 3029, 2931, 1659, 1599, 1543, 1543, 1497, 1444, 1383, 1364, 1313, 1254, 1190, 1120, 1080, 1044, 754, 697 cm^{-1}

2-Benzyl-4,4-difluoro-*N*-(2-iodophenyl)butanamide (3m):



White solid (181 mg, 87%). M.p.: 101.9–103.1 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 8.02 (dd, J = 8.3, 1.6 Hz, 1H), 7.70 (dd, J = 8.0, 1.5 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.24 – 7.14 (m, 4H), 6.82 (td, J = 7.7, 1.6 Hz, 1H), 5.92 (dddd, J = 56.8, 55.9, 5.7, 3.2 Hz, 1H), 3.07 (dd, J = 13.4, 8.9 Hz, 1H), 2.88 (dd, J = 13.4, 6.1 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.46 (dtdd, J = 22.6, 14.5, 9.8, 3.2 Hz, 1H), 2.05 (dtdd, J = 16.5, 14.6, 5.7, 4.0 Hz, 1H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -115.21 (ddt, J = 284.6, 56.1, 14.7 Hz, 1F), -116.96 (dddd, J = 284.7, 57.0, 22.6, 16.5 Hz, 1F).

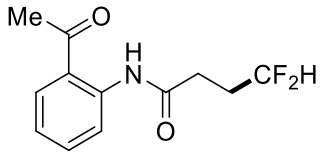
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 171.6, 138.8, 138.0, 137.6, 129.1, 128.9, 128.9, 127.1, 126.4, 122.6, 115.9 (t, J = 239.6), 90.5, 44.7 (m), 39.6, 36.4 (t, J = 21.5 Hz).

MS (EI, *m*/*z*): 415.1 (M^+), 350.1, 288.1, 219.1, 91.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{17}H_{16}ONF_2I$ (M^+) 415.0239, found 415.0238.

IR (KBr): 3282, 3023, 2853, 1663, 1576, 1528, 1495, 1464, 1434, 1401, 1377, 1287, 1241, 1219, 1190, 1123, 1097, 1083, 1027, 1017, 766, 754, 736, 699 cm^{-1}

***N*-(2-Acetylphenyl)-4,4-difluorobutanamide (3n):**



Pale yellow solid (63 mg, 53%). M.p.: 35.2–36.3 °C.

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 11.80 (s, 1H), 8.69 (dd, J = 8.4, 1.2 Hz, 1H), 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.54 (ddd, J = 8.7, 7.2, 1.6 Hz, 1H), 7.17 – 7.06 (m, 1H), 5.97 (tt, J = 56.8, 4.3 Hz, 1H), 2.65 (s, 3H), 2.62 (t, J = 7.4 Hz, 2H), 2.34 – 2.16 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -117.32 (dt, J = 56.9, 17.5 Hz, 2F).

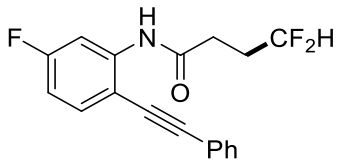
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 202.9, 170.2, 140.7, 135.2, 131.7, 122.6, 121.8, 120.7, 116.3 (t, J = 239.0 Hz), 30.5 (t, J = 5.7 Hz), 29.5 (t, J = 22.1 Hz), 28.6.

MS (ESI, *m*/*z*): 242.0 (M + H^+), 263.9 (M + Na^+).

HRMS (ESI, *m*/*z*): Calcd. for $C_{12}H_{13}O_2NF_2$ (M + H^+) 242.0987, found 242.0987.

IR (film): 3220, 2974, 1697, 1654, 1606, 1586, 1526, 1451, 1360, 1298, 1249, 1165, 1117, 1062, 951, 758, 606 cm^{-1}

4,4-Difluoro-*N*-(4-fluoro-2-(phenylethynyl)phenyl)butanamide (3o):



White solid (42 mg, 53%). M.p.: 141.8–142.9 °C.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 8.33 (dd, J = 9.1, 5.2 Hz, 1H), 7.87 (s, 1H), 7.56 – 7.48 (m, 2H), 7.40 (dd, J = 5.1, 2.0 Hz, 3H), 7.19 (dd, J = 8.6, 3.0 Hz, 1H), 7.10 – 7.00 (m, 1H), 6.00 (tt, J = 56.7, 4.1 Hz, 1H), 2.61 (t, J = 7.3 Hz, 2H), 2.28 (ddtd, J = 18.0, 14.5, 7.3, 4.2 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -117.58 (dt, J = 56.6, 17.4 Hz, 2F), -118.21 (td, J = 8.2, 5.2 Hz, 1F).

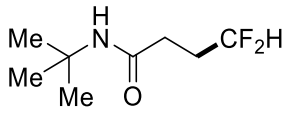
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 168.9, 158.3 (d, J = 244.0 Hz), 134.9 (d, J = 2.7 Hz), 131.6, 129.4, 128.7, 121.7, 121.2 (d, J = 8.2 Hz), 118.0 (d, J = 24.3 Hz), 116.7 (d, J = 22.0 Hz), 116.2 (t, J = 239.0), 113.7, 97.4, 83.1 (d, J = 3.1 Hz), 29.88 - 29.63 (m), 29.5 (t, J = 22.0 Hz).

MS (EI, *m*/*z*): 317.1 (M^+), 211.1, 183.1, 107.0.

HRMS (EI, *m*/*z*): Calcd. for $C_{18}H_{14}F_3NO$ (M^+) 317.1022, found 317.1024.

IR (KBr): 3300, 3049, 2987, 1659, 1612, 1532, 1443, 1421, 1378, 1294, 1260, 1198, 1124, 1089, 1064, 1044, 950, 913, 871, 753, 687, 656, 474 cm^{-1}

_N_-(_tert_-Butyl)-4,4-difluorobutanamide (3p):



White solid (1.21 g, 68%, 10 mmol scales). M.p.: 61.7–63.6 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 6.14 – 5.65 (m, 1H), 5.56 (s, 1H), 2.22 (t, J = 7.5 Hz, 2H), 2.18 – 1.99 (m, 2H), 1.28 (s, 9H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -117.34 (dt, J = 57.1, 17.6, 2F).

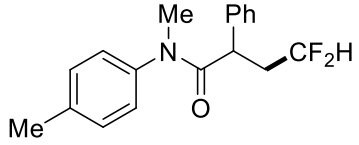
^{13}C NMR (101 MHz, **CDCl$_3$**) δ170.2, 116.6 (t, J = 238.7 Hz), 51.3, 29.7 (t, J = 21.8 Hz), 29.3 (t, J = 4.9 Hz), 28.7 .

MS (ESI, *m*/*z*): 180.1 (M+H^+).

HRMS (ESI, *m*/*z*): Calcd. for $C_8H_{16}F_2ON$ (M+H^+) 180.1194, found 180.1194.

IR (film): 3308, 2967, 1641, 1549, 1478, 1453, 1425, 1392, 1363, 1273, 1224, 1121,

4,4-Difluoro-_N_-methyl-2-phenyl-_N_-(p-tolyl)butanamide (3q):



Colorless liquid (75 mg, 50%). M.p.: 51.1–52.1 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.19 (p, J = 3.9, 3.5 Hz, 3H), 7.12 (d, J = 7.9 Hz, 2H), 7.00 – 6.92 (m, 2H), 6.79 (s, 2H), 5.68 (tt, J = 56.9, 4.7 Hz, 1H), 3.72 (dd, J = 9.1, 6.1 Hz, 1H), 3.19 (s, 3H), 2.76 – 2.56 (m, 1H), 2.37 (s, 3H), 2.17 – 1.98 (m, 1H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -116.07 (dddd, J = 284.2, 56.6, 20.0, 12.7 Hz, 1F), -118.00 (dddd, J = 284.2, 57.2, 21.6, 12.8 Hz, 1F).

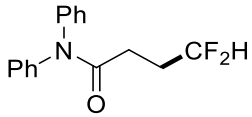
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 171.6, 140.4, 138.5, 138.1, 130.2, 128.6, 127.9, 127.6, 127.3, 115.1 (t, J = 239.0 Hz), 43.0, 38.8 (t, J = 21.3 Hz), 37.9, 21.1.

MS (EI, *m*/*z*): 303.1 (M^+), 148.1, 121.1, 109.1, 91.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{18}H_{19}FNO_2$ (M^+) 303.1429, found 303.1424.

IR (film): 3030, 2936, 1656, 1514, 1494, 1455, 1431, 1118, 1064, 1031, 826, 741, 723, 700 cm^{-1}

4,4-Difluoro-N,*N*-diphenylbutanamide (3r):



White solid (99 mg, 72%). M.p.: 73.7–75.2 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**): δ 7.57 – 7.07 (m, J = 15.2, 12.8 Hz, 10H), 5.95 (tt, J = 57.0, 4.0 Hz, 1H), 2.42 (t, J = 7.0 Hz, 2H), 2.20 (dddt, J = 24.3, 17.7, 11.1, 5.4 Hz, 2H).

^{19}F NMR (376 MHz, **$CDCl_3$**): δ -117.20 (dt, J = 57.0, 17.6 Hz, 2F).

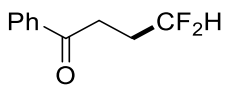
^{13}C NMR (101 MHz, **$CDCl_3$**): δ 171.1, 142.5, 129.7, 128.4, 116.7 (t, J = 238.7 Hz), 29.8 (t, J = 21.9 Hz), 28.1 (t, J = 5.8 Hz).

MS (EI, *m*/*z*): 275.1 (M^+), 169.2.

HRMS (EI, *m*/*z*): Calcd. for $C_{16}H_{15}F_2NO$ (M^+) 275.1122, found 275.1120.

IR (film): 3062, 2921, 2850, 1673, 1593, 1492, 1451, 1381, 1323, 1287, 1118, 1059, 946, 757, 702 cm^{-1}

4,4-Difluoro-1-phenylbutan-1-one (3s):



Pale yellow liquid (69 mg, 75%).

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 8.00 – 7.91 (m, 2H), 7.63 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H), 6.00 (tt, *J* = 56.9, 4.2 Hz, 1H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.29 (ttd, *J* = 18.1, 7.2, 4.2 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -117.11 (dt, *J* = 56.9, 17.9 Hz, 2F).

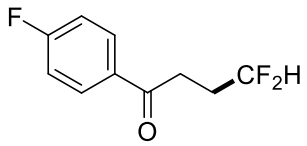
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 197.8, 136.4, 133.4, 128.7, 128.0, 116.5 (t, *J* = 238.7 Hz), 30.8 (t, *J* = 5.2 Hz), 28.4 (t, *J* = 21.8 Hz).

MS (EI, *m*/*z*): 184.1 (M^+), 105.1, 77.1, 51.1, 18.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_{10}F_2O$ (M^+) 184.0700, found 184.0694.

IR (film): 3056, 2991, 2948, 1689, 1597, 1581, 1449, 1405, 1371, 1322, 1282, 1256, 1212, 1181, 1121, 1075, 1002, 972, 917, 746, 690 cm^{-1}

4,4-Difluoro-1-(4-fluorophenyl)butan-1-one (3t):



Colorless liquid (38 mg, 37%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.98 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.00 (tt, *J* = 56.9, 4.1 Hz, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.28 (ttd, *J* = 18.1, 7.2, 4.2 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -104.66 (ddd, *J* = 13.8, 8.5, 5.4 Hz, 1F), -117.23 (dt, *J* = 57.0, 18.0 Hz, 1F).

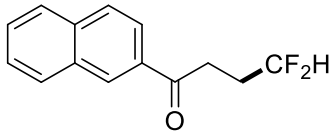
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 196.2, 165.9 (d, *J* = 255.2 Hz), 132.8 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 9.5 Hz), 116.4 (t, *J* = 238.7 Hz), 115.8 (d, *J* = 21.9 Hz), 30.7 (t, *J* = 5.3 Hz), 28.3 (t, *J* = 22.0 Hz).

MS (EI, *m*/*z*): 202.1 (M^+), 123.1, 95.1, 75.1, 51.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{10}H_9ONF_3$ (M^+) 202.0600, found 202.0598.

IR (KBr): 3392, 3182, 2953, 1919, 1847, 1694, 1644, 1598, 1506, 1467, 1417, 1235, 1157, 1116, 1061, 843, 816, 646 cm^{-1}

4,4-Difluoro-1-(naphthalen-2-yl)butan-1-one (3u):



Yellow solid (55 mg, 47%). M.p.: 54.8–56.3 °C.

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 8.46 (d, J = 1.7 Hz, 1H), 8.01 (dd, J = 8.6, 1.8 Hz, 1H), 7.95 (dd, J = 8.1, 1.4 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.57 (dddd, J = 20.1, 8.1, 6.9, 1.4 Hz, 2H), 6.12 (dt, J = 56.9, 4.2 Hz, 1H), 3.30 (t, J = 7.2 Hz, 2H), 2.35 (ttd, J = 18.1, 7.2, 4.2 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -116.99 (dt, J = 56.9, 17.8 Hz, 2F).

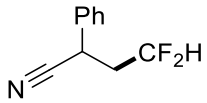
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 197.7, 135.7, 133.7, 132.5, 129.8, 129.6, 128.7, 128.6, 127.8, 126.9, 123.6, 116.6 (t, J = 238.7 Hz), 30.9 (t, J = 5.2 Hz), 28.5 (t, J = 22.0 Hz).

MS (EI, *m*/*z*): 234.1 (M^+), 155.1, 127.1, 51.1, 18.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{14}H_{12}F_2O$ (M^+) 234.0856, found 234.0858.

IR (film): 3060, 2920, 1683, 1627, 1469, 1437, 1404, 1373, 1279, 1211, 1186, 1123, 1077, 1053, 944, 896, 862, 819, 748, 476 cm^{-1}

4,4-Difluoro-2-phenylbutanenitrile (4v):



Colorless liquid (42 mg, 47%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.45 – 7.31 (m, 5H), 5.87 (tdd, J = 55.6, 5.2, 4.1 Hz, 1H), 4.00 (dd, J = 9.0, 6.5 Hz, 1H), 2.60 – 2.26 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -117.84 – -118.14 (m, 2F).

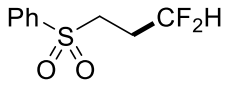
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 133.8, 129.6, 128.9, 127.2, 119.3, 114.4 (t, J = 240.6 Hz), 39.6 (t, J = 22.9 Hz), 31.4 (t, J = 6.4 Hz).

MS (EI, *m*/*z*): 181.1 (M^+), 116.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{10}H_9F_2N$ (M^+) 181.0698, found 181.0694.

IR (film): 3066, 3034, 2987, 2245, 1600, 1495, 1435, 1408, 1382, 1368, 1243, 1209, 1185, 1122, 1058, 952, 919, 756, 699, 555 cm^{-1}

((3,3-Difluoropropyl)sulfonyl)benzene (3w):



Slight yellow solid (72 mg, 65%). M.p.: 51.9–53.6 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**): δ 7.93 – 7.87 (m, 2H), 7.71 – 7.64 (m, 1H), 7.60 – 7.53 (m, 2H), 5.96 (tt, *J* = 56.5Hz, 3.9 Hz, 1H), 3.27 – 3.15 (m, 2H), 2.40 – 2.13 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -117.44 (dt, *J* = 55.8, 17.0 Hz, 2F).

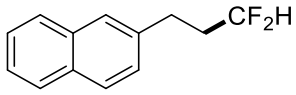
^{13}C NMR (101 MHz, **CDCl$_3$**): δ 138.4, 134.2, 129.6, 128.0, 114.7 (t, *J* = 240.5 Hz), 49.2 (t, *J* = 5.4 Hz), 27.8 (t, *J* = 23.1 Hz).

MS (EI, *m*/*z*): 220.1, 141.0, 77.1, 51.1. (M^+).

HRMS (EI, *m*/*z*): Calcd. for $C_9H_{10}F_2O_2S$ (M^+) 220.0370, found 220.0369.

IR (film): 3065, 2987, 2942, 1683, 1447, 1407, 1309, 1171, 1148, 1127, 1086, 1069, 1046, 938, 745, 689, 585, 534 cm^{-1}

2-(3,3-Difluoropropyl)naphthalene (4x):



Colorless solid (26 mg, 25%). M.p.: 31.0–32.8 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.86 – 7.75 (m, 3H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.46 (tt, *J* = 7.0, 5.2 Hz, 2H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.84 (tt, *J* = 56.7, 4.5 Hz, 1H), 3.01 – 2.89 (m, 2H), 2.33 – 2.14 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**): δ -114.35 (dt, *J* = 56.6, 17.7 Hz, 2F).

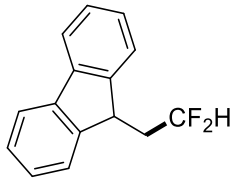
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 137.4, 133.6, 132.2, 128.4, 127.7, 127.5, 126.8, 126.6, 126.2, 125.5, 116.7 (t, *J* = 239.1 Hz), 35.6 (t, *J* = 21.1 Hz), 28.6 (t, *J* = 6.0 Hz).

MS (EI, *m*/*z*): 206 (50.57, M^+), 141 (100), 115 (19.02).

HRMS (EI, *m*/*z*): Calcd. for $C_{13}H_{12}F_2$ (M^+) 206.0907, found 206.0904.

IR (film): 3054, 2970, 2933, 2857, 1600, 1508, 1450, 1437, 1403, 1381, 1271, 1179, 1120, 1056, 959, 925, 896, 818, 797, 746, 476 cm^{-1}

9-(2,2-Difluoroethyl)-9H-fluorene (3y):



White solid (63 mg, 55%). M.p. >200 ºC (decomposed).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.78 (dd, J = 7.5, 1.2 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.45 – 7.30 (m, 4H), 5.97 (tt, J = 56.5, 4.8 Hz, 1H), 4.15 (t, J = 6.6 Hz, 1H), 2.45 (tdd, J = 16.9, 6.5, 4.7 Hz, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -114.07 (dt, J = 56.5, 17.0 Hz, 2F).

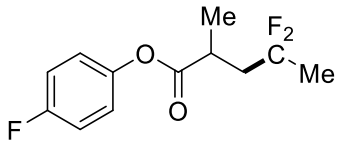
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 140.9, 130.3, 128.1, 127.6, 127.3, 124.6, 120.5, 120.1, 116.3 (t, J = 243.4 Hz), 42.1 (t, J = 5.8 Hz), 37.8 (t, J = 21.3 Hz).

MS (EI, *m*/*z*): 230.1 (M^+), 178.1, 165.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{15}H_{12}F_2$ (M^+) 230.0902, found 230.0901.

IR (KBr): 3066, 3040, 2929, 1735, 1608,, 1487, 1478, 1449, 1263, 1155, 1120, 1101, 1058, 1027, 1007, 896, 756, 739 cm^{-1}

4-Fluorophenyl 4,4-difluoro-2-methylpentanoate (3ab):



Colorless liquid, (83 mg, 68%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.10 – 6.97 (m, 4H), 3.01 (dqd, J = 9.1, 7.2, 4.3 Hz, 1H), 2.61 – 2.40 (m, 1H), 2.09 – 1.87 (m, 1H), 1.65 (t, J = 18.5 Hz, 4H), 1.37 (d, J = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -90.45 – -91.15 (m, 1F), -116.91 – -117.22 (m,1F).

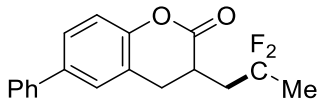
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 174.5, 161.5, 159.1, 146.5, 123.3 (t, J = 239.4 Hz), 122.8 (d, J = 8.5 Hz), 116.2, 116.0, 41.5 (t, J = 25.2 Hz), 34.4 (t, J = 3.6 Hz), 24.0 (t, J = 27.6 Hz), 18.4.

MS (EI, *m*/*z*): 246.1 (M^+), 135.1, 112.1, 87.1, 65.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_{13}F_3O_2$ (M^+) 246.0862, found 246.0864.

IR (KBr): 3082, 2981, 2942, 2884, 1760, 1599, 1504, 1459, 1394, 1281, 1238, 1187, 1139, 1083, 1059, 1013, 933, 883, 821, 800, 767, 518 cm^{-1}

3-(2,2-Difluoropropyl)-6-phenylchroman-2-one (3ac):



White solid (65 mg, 43%). M.p.: 101.1−102.6 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.57 – 7.51 (m, 2H), 7.49 – 7.39 (m, 4H), 7.37 – 7.30 (m, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.30 (dd, J = 15.1, 5.5 Hz, 1H), 3.15 – 2.71 (m, 3H), 2.08 (ddt, J = 23.7, 15.6, 7.8 Hz, 1H), 1.69 (t, J = 18.5 Hz, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -87.83 – -88.99 (m, 1F), -92.83 – -94.00 (m, 1F).

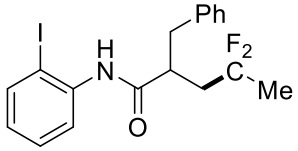
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 170.1, 150.9, 140.0, 128.9, 127.5, 127.2, 127.0, 126.8, 124.9 (t, J = 283.6 Hz), 122.9, 117.0, 37.6 (t, J = 25.1 Hz), 34.7, 30.3, 24.2 (t, J = 27.4 Hz).

MS (EI, *m*/*z*): 302.1 (M^+), 274.1, 239.1, 207.1, 182.1, 165.1, 153.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{18}H_{16}F_2O_2$ (M^+) 302.1113, found 302.1107.

IR (KBr): 3036, 3002, 2935, 1768, 1507, 1482, 1454, 1416, 1393, 1335, 1303, 1236, 1164, 1126, 873, 839, 811, 772, 743, 713 cm^{-1}

2-Benzyl-4,4-difluoro-*N*-(2-iodophenyl)pentanamide (3ad):



White solid (181.1 mg, 87%). M.p.: 88.2–89.3 ºC.

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 8.18 – 7.96 (m, 1H), 7.77 – 7.64 (m, 1H), 7.33 – 7.15 (m, 7H), 6.80 (td, J = 7.9, 1.3 Hz, 1H), 3.05 (td, J = 11.2, 3.8 Hz, 1H), 2.92 – 2.79 (m, 2H), 2.70 – 2.47 (m, 1H), 2.04 (dddd, J = 24.4, 15.0, 9.6, 2.7 Hz, 1H), 1.61 (t, J = 18.5 Hz, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -89.48 – -90.59 (m, 1F), -90.90 – -91.88 (m, 1F).

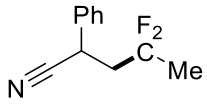
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 172.5, 138.7, 138.3, 137.9, 129.1, 129.0, 128.8, 127.0, 126.2, 123.4 (t, J = 238.9 Hz), 122.4, 90.2, 45.0, 40.2 (t, J = 25.0 Hz), 39.9, 24.2 (t, J = 27.5 Hz).

MS (EI, *m*/*z*): 429.1 (M^+), 350.1, 302.1, 219.0, 91.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{18}H_{18}ONF_2I$ (M^+) 429.0396, found 429.0403.

IR (KBr): 3285, 3176, 3022, 2928, 1659, 1604, 1573, 1521, 1470, 1455, 1393, 1358, 1303, 1381, 1238, 1190, 1176, 1159, 1135, 1114, 1042, 1030m 1016, 962, 918, 758, 737, 718, 700 cm^{-1}

4,4-Difluoro-2-phenylpentanenitrile (3ae):



Colorless liquid, (55 mg, 56%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.43 – 7.29 (m, 5H), 4.07 (dd, J = 9.9, 4.4 Hz, 1H), 2.59 (ddt, J = 20.5, 14.9, 10.6 Hz, 1H), 2.31 (dddd, J = 19.8, 14.6, 10.0, 4.4 Hz, 1H), 1.68 (t, J = 18.6 Hz, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -90.20 (dtd, J = 243.3, 18.8, 10.0 Hz, 1F), -91.14 – -92.28 (m, 1F).

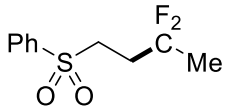
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 129.4, 128.6, 127.3, 121.9 (t, J = 240.2 Hz), 120.1, 43.9 (t, J = 26.3 Hz), 31.2 (t, J = 4.0 Hz), 23.8 (t, J = 27.0 Hz).

MS (EI, *m*/*z*): 195.1 (M^+), 174.1, 160.1, 116.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{11}H_{11}NF_2$ (M^+) 195.0854, found 195.0853.

IR (KBr): 2922, 2851, 1096, 792, 616, 474 cm^{-1}

((3,3-Difluorobutyl)sulfonyl)benzene (3f):



White solid (85 mg, 73%). M.p.: 53.5–54.8 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.93 – 7.87 (m, 2H), 7.71 – 7.63 (m, 1H), 7.58 (dd, J = 8.5, 7.0 Hz, 2H), 3.33 – 3.22 (m, 2H), 2.35 – 2.19 (m, 2H), 1.61 (t, J = 18.3 Hz, 3H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -92.53 (dtd, J = 34.4, 18.4, 15.7 Hz, 2F).

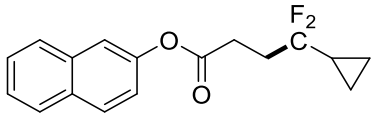
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 138.6, 134.1, 129.5, 128.0, 122.2 (t, J = 239.5 Hz), 49.9 (t, J = 4.2 Hz), 31.3 (t, J = 26.5 Hz), 23.8 (t, J = 27.2 Hz).

MS (EI, *m*/*z*): 234.0 (M^+), 141.0, 77.1, 65.1, 51.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{18}H_{24}F_2O_7$ (M^+) 234.0521, found 234.0517.

IR (KBr): 3065, 3019, 2954, 1468, 1447, 1404, 1322, 1308, 1251, 1220, 1185, 1150, 1087, 1023, 949, 927, 766, 740, 689, 543 cm^{-1}

Naphthalen-2-yl 4-cyclopropyl-4,4-difluorobutanoate (3ag):



White solid (61.3 mg, 42%). M.p.: 40.1–41.9 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.88 – 7.76 (m, 3H), 7.56 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.21 (dd, J = 8.8, 2.3 Hz, 1H), 2.87 (dd, J = 8.4, 7.0 Hz, 2H), 2.44 (dddd, J = 16.4, 15.7, 8.4, 7.0 Hz, 2H), 1.36 – 1.18 (m, 1H), 0.74 – 0.67 (m, 2H), 0.67 – 0.55 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -104.40 (td, J = 16.2, 12.4 Hz, 2F).

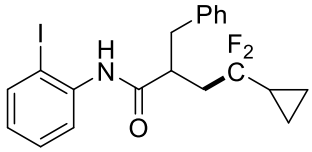
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 171.2, 148.2, 133.7, 131.5, 129.5, 127.8, 127.7, 126.6, 125.8, 123.0 (t, J = 240.0 Hz), 121.0, 118.5, 32.9 (t, J = 27.8 Hz), 27.8 (t, J = 4.3 Hz), 15.8 (t, J = 29.3 Hz), 1.3 (t, J = 4.3 Hz).

MS (EI, *m*/*z*): 290.1 (M^+), 144.1, 115.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{17}H_{16}O_2F_2$ (M^+) 290.1113, found 290.1109.

IR (KBr): 3059, 3020, 2953, 2931, 1750, 1627, 1511, 1464, 1441, 1425, 1405, 1386, 1355, 1317, 1266, 1242, 1211, 1165, 1141, 1082, 1059, 1041, 1026, 962, 942, 925, 816, 799, 782, 633, 622, 523, 503 cm^{-1}

2-Benzyl-4-cyclopropyl-4,4-difluoro-*N*-(2-iodophenyl)butanamide (3ah):



White solid, (174,2 mg, 81%). M.p. 62.2-63.7 ºC

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 8.13 – 7.97 (m, 1H), 7.68 (dd, J = 7.9, 1.3 Hz, 1H), 7.36 – 7.05 (m, 7H), 6.79 (td, J = 7.9, 1.5 Hz, 1H), 3.05 (td, J = 11.4, 3.8 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.67 (ddt, J = 24.4, 14.9, 9.5 Hz, 1H), 2.12 (dddd, J = 25.8, 15.0, 8.6, 2.7 Hz, 1H), 1.29 – 1.12 (m, 1H), 0.64 (ddt, J = 5.0, 3.9, 2.0 Hz, 2H), 0.60 – 0.48 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -101.23 (dddd, J = 240.9, 24.9, 11.3, 8.6 Hz, 1F), -103.49 (dddd, J = 240.6, 23.8, 13.2, 10.0 Hz, 1F).

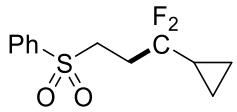
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 172.5, 138.7, 138.4, 137.9, 129.1, 129.0, 128.8, 126.9, 126.1, 123.2 (t, J = 240.2 Hz), 122.3, 90.1, 45.0, 40.0, 39.8 (t, J = 26.6 Hz), 16.3 (t, J = 29.3 Hz), 1.5 (ddd, J = 17.9, 5.8, 2.9 Hz).

MS (EI, *m*/*z*): 455.1 (M^+), 344.1, 308.2, 222.1, 91.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{20}H_{20}ONF_2I$ (M^+) 455.0552, found 455.0559.

IR (KBr): 3383, 3265, 3086, 3061, 3025, 2933, 1662, 1603, 1583, 1518, 1466, 1455, 1433, 1403, 1287, 1237, 1168, 1087, 1057, 1016, 966, 920, 892, 752, 700 cm^{-1}

((3-Cyclopropyl-3,3-difluoropropyl)sulfonyl)enzene (3ai):



White solid (81 mg, 62%). M.p.: 50.0–51.2 ºC.

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.94 – 7.82 (m, 2H), 7.72 – 7.61 (m, 1H), 7.58 (dd, J = 8.5, 7.0 Hz, 2H), 3.33 – 3.24 (m, 2H), 2.43 – 2.27 (m, 2H), 1.27 – 1.07 (m, 1H), 0.64 – 0.51 (m, 4H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -103.92 (td, J = 15.6, 12.2 Hz, 2F).

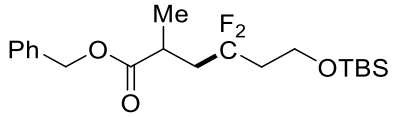
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 138.7, 129.5, 128.0, 122.0 (t, J = 242.4 Hz), 49.9 (t, J = 3.6 Hz), 31.0 (t, J = 28.3 Hz), 15.8 (t, J = 28.9 Hz), 1.4 (t, J = 4.3 Hz).

MS (EI, *m*/*z*): 260.1 (M^+), 169.0, 141.0, 125.0, 99.1, 77.1, 51.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{12}H_{14}F_2O_2S$ (M^+) 260.0677, found 260.0684.

IR (KBr): 3061, 2991, 2977, 2940, 1481, 1448, 1440, 1420, 1394, 1381, 1311, 1264, 1239, 1194, 1170, 1150, 1088, 1045, 1025, 942, 932, 891, 822, 746, 687, 598, 546, 532

Benzyl 6-((*tert*-butyldimethylsilyl)oxy)-4,4-difluoro-2-methylhexanoate (3aj):



Colorless liquid (119.1 mg, 57%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.42 – 7.26 (m, 5H), 5.11 (d, J = 1.7 Hz, 2H), 3.76 (t, J = 6.5 Hz, 2H), 2.94 – 2.75 (m, 1H), 2.54 – 2.39 (m, 1H), 2.13 - 2.01 (m, 2H), 2.01 – 1.84 (m, 1H), 1.24 (d, J = 7.1 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 6H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -95.34 – -96.22 (m, 1F), -96.22 – -97.10 (m, 1F).

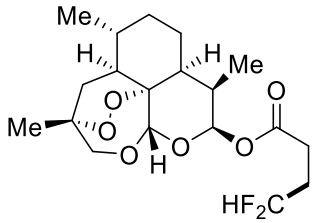
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 175.7, 136.0, 128.5, 128.2, 128.1, 123.8 (t, J = 241.2 Hz), 66.5, 57.2 (t, J = 6.7 Hz), 40.4 (t, J = 24.4 Hz), 40.0 (t, J = 24.5 Hz), 34.1 (t, J = 3.6 Hz), 25.8, 18.4, 18.2, -5.5 .

MS (EI, *m*/*z*): 415.1 (M^+), 386.2, 309.2, 279.1, 191.2, 91.1.

HRMS (EI, *m*/*z*): Calcd. for $C_{20}H_{32}O_3F_2Si$ (M^+) 386.2083, found 386.2088.

IR (KBr): 3067, 2955, 2931, 2885, 2857, 1739, 1498, 1463, 1430, 1388, 1257, 1167, 1103, 1005, 981, 911, 881, 837, 812, 777, 697 cm^{-1}

(3*S*,5a*S*,8*R*,8a*S*,11*R*,12*S*)-3,8,11-Trimethyloctahydro-5aH,7H-3,12-methano[1,2,5]trioxepino[3,4-J]isochromen-7-yl 4,4-difluorobutanoate (3am):



Colorless solid (146 mg, 75%). M.p.: 87.5–88.4 °C.

^{1}H NMR (400 MHz, **$CDCl_3$**): δ 6.07 – 5.72 (m, 2H), 5.41 (s, 1H), 2.55 (p, J = 10.0, 9.4 Hz, 3H), 2.34 (td, J = 14.0, 3.8 Hz, 1H), 2.16 (ddt, J = 23.5, 17.8, 7.8 Hz, 2H), 2.00 (dt, J = 14.8, 3.6 Hz, 1H), 1.86 (ddt, J = 13.7, 6.5, 3.6 Hz, 1H), 1.72 (ddd, J = 22.0, 13.4, 3.4 Hz, 2H), 1.60 (dd, J = 13.6, 4.5 Hz, 1H), 1.53 – 1.19 (m, 7H), 1.06 – 0.87 (m, 4H), 0.82 (d, J = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**): δ -117.62 (dtd, J = 56.6, 17.3, 7.6 Hz, 2F).

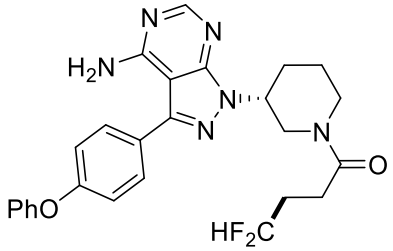
^{13}C NMR (101 MHz, **$CDCl_3$**): δ 170.9, 116.0 (t, J = 239.1 Hz), 104.5, 92.3, 91.5, 80.1, 51.5, 45.2, 37.3, 36.2, 34.1, 31.7, 29.1 (t, J = 22.3 Hz), 26.9 (t, J = 6.0 Hz), 25.9, 24.6, 22.0, 20.2, 12.1 .

MS (FTMS, *m*/*z*): 408.2 ($M+NH_4^+$), 267.2.

HRMS (DART, *m*/*z*): Calcd. for $C_{19}H_{32}O_6NF_2$ ($M+NH_4^+$) 408.2192, found 408.2190.

IR (film): 3376, 2934, 2873, 1747, 1715, 1444, 1405, 1378, 1280, 1251, 1227, 1175, 1123, 1017, 945, 876, 847, 825 cm^{-1}

1-(3-(4-Amino-3-(4-phenoxyphenyl)-1H-pyrazolo[3,4-d]pyrimidin-1-yl)piperidin-1-yl)-4,4-difluorobutan-1-one (3am):



Pale yellow liquid (0.25 mmol scales, 62 mg, 50%).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 8.31 (d, J = 12.1 Hz, 1H), 7.75 – 7.56 (m, 2H), 7.40 – 7.31 (m, 2H), 7.19 – 6.99 (m, 5H), 5.94 (tdt, J = 57.0, 13.6, 4.3 Hz, 2H), 4.86 – 4.35 (m, 2H), 4.13 – 3.78 (m, 1H), 3.49 (ddd, J = 159.5, 13.0, 10.6 Hz, 1H), 3.20 – 3.06 (m, 1H), 2.82 (td, J = 13.5, 12.7, 3.1 Hz, 1H), 2.62 – 1.86 (m, 8H), 1.75 – 1.58 (m, 1H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -117.06 – -117.61 (m, 2F).

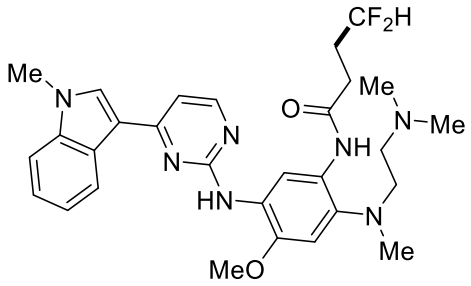
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 169.6.48, 158.7.56, 158.0.90, 156.3.28, 155.5.23, 154.1, 144.2.04, 130.0 (d, J = 1.9 Hz), 129.9, 124.1.06, 119.6.55, 119.1, 116.7 (t, J = 238.7 Hz), 98.6.49, 53.3, 52.4, 49.6, 45.9, 45.4, 42.0, 30.1, 29.9, 29.5 (t, J = 21.7 Hz), 25.6 (d, J = 6.3 Hz), 25.0, 23.9.

MS (ESI, *m*/*z*): 493.2 ($M+H^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{26}H_{27}F_2N_6O_2$ ($M+H^+$) 493.2158, found 493.2156.

IR (film): 3478, 3306, 3055, 2945, 2861, 1644, 1586, 1520, 1488, 1440, 1371, 1236, 1167, 1116, 1053, 185, 940, 869, 755, 734, 694 cm^{-1}

***N*-(2-((2-(Dimethylamino)ethyl)(methyl)amino)-4-methoxy-5-((4-(1-methyl-1H-indol-3-yl)pyrimidin-2-yl)amino)phenyl)-4,4-difluorobutanamide (3an):**



Slight yellow solid, (2.0 mmol scales, 496.5 mg, 45%). M.p. 175.1-176.6 ^oC

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 10.12 (s, 1H), 9.64 (s, 1H), 8.90 (s, 1H), 8.37 (dd, J = 5.3, 1.2 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.70 (s, 1H), 7.42 – 7.36 (m, 1H), 7.32 – 7.21 (m, 2H), 7.21 – 7.14 (m, 1H), 6.76 (s, 1H), 6.23 – 5.81 (m, 1H), 4.02 – 3.93 (m, 3H), 3.86 (d, J = 1.2 Hz, 3H), 2.90 (s, 2H), 2.74 – 2.65 (m, 3H), 2.65 – 2.53 (m, 2H), 2.39 – 2.20 (m, 10H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -117.08 (dt, J = 57.0, 17.3 Hz, 2F).

^{13}C NMR (101 MHz, **$CDCl_3$**) δ 168.4, 162.1, 159.6, 157.9, 144.0 (d, J = 33.6 Hz), 138.2 (d, J = 4.8 Hz), 134.71 - 133.68 (m), 129.5, 127.7, 126.0 (d, J = 2.7 Hz), 121.9, 120.9 (d, J = 8.1 Hz), 120.3 (d, J = 15.0 Hz), 116.8 (t, J = 238.8 Hz), 113.7, 110.0, 109.6

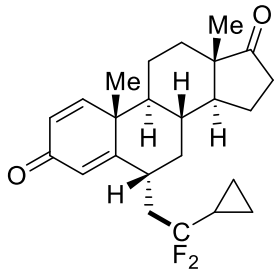
(d, *J* = 15.6 Hz), 107.9 (d, *J* = 11.6 Hz), 104.6 (d, *J* = 12.6 Hz), 57.3 (d, *J* = 3.9 Hz), 56.3, 56.1 (d, *J* = 3.5 Hz), 45.6 (d, *J* = 18.1 Hz), 45.3, 44.0 (d, *J* = 10.7 Hz), 33.1, 30.7, 30.0 (t, *J* = 21.8 Hz), 29.4 (d, *J* = 5.5 Hz).

MS (ES-API, *m*/*z*): 552.2 ($M+H^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{29}H_{36}O_2N_7F_2$ ($M+H^+$) 552.2893, found 552.2893.

IR (film): 3419, 2938, 2823, 1673, 1580, 1514, 1404, 1261, 1201, 1103, 1060, 1032, 808, 742 cm^{-1}

(6*R*,8*R*,9*S*,10*R*,13*S*,14*S*)-6-(2-Cyclopropyl-2,2-difluoroethyl)-10,13-dimethyl-7,8,9,10,11,12,13,14,15,16-decahydro-3H-cyclopenta[a]phenanthrene-3,17(6*H*)-dione (3ao):



Yellow oil, (82.2 mg, 42%).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 6.99 (d, *J* = 10.1 Hz, 1H), 5.89 (dd, *J* = 10.1, 1.0 Hz, 1H), 3.51 – 3.33 (m, 1H), 3.15 (dt, *J* = 17.8, 3.2 Hz, 1H), 2.82 – 2.51 (m, 2H), 2.51 – 2.39 (m, 1H), 2.36 – 2.18 (m, 1H), 2.08 (dt, *J* = 18.9, 9.0 Hz, 1H), 2.01 – 1.73 (m, 5H), 1.68 – 1.48 (m, 2H), 1.38 – 1.19 (m, 6H), 1.19 – 1.02 (m, 1H), 0.90 (m, 4H), 0.59 (dq, *J* = 5.0, 2.9, 1.7 Hz, 2H), 0.57 – 0.44 (m, 2H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -97.40 – -102.14 (m, 2F).

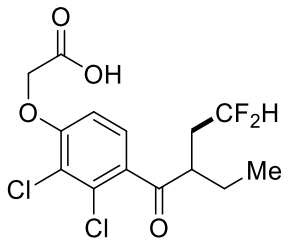
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 220.1, 197.5, 155.9, 134.4, 126.4, 124.5 (t, *J* = 3.0 Hz), 123.3 (t, *J* = 242.2 Hz), 51.5, 47.4, 45.7, 41.11 - 40.73 (m), 40.7, 36.8, 35.7, 31.3, 31.0, 21.7, 20.4, 19.6, 15.8 (t, *J* = 29.2 Hz), 13.6, 1.5 (t, *J* = 4.5 Hz), 1.3 (t, *J* = 4.3 Hz).

MS (ES-API, *m*/*z*): 411.1 ($M+Na^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{24}H_{30}O_2F_2Na$ ($M+Na^+$) 411.2106, found 411.2103.

IR (film): 3463, 2944, 1737, 1659, 1614, 1454, 1454, 1403, 1375, 1264, 1149, 1057, 1013, 927, 897, 735 cm^{-1}

2-(2,3-Dichloro-4-(2-ethyl-4,4-difluorobutanoyl)phenoxy)acetic acid (3ap):



Yellow solid, (99.4 mg, 51%) M.p. 101.3-102.6 ºC

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.34 (d, J = 8.6 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 6.10 – 5.70 (m, 1H), 4.79 (s, 2H), 3.47 (tq, J = 10.4, 6.1, 5.3 Hz, 1H), 2.57 – 2.30 (m, 1H), 2.03 – 1.85 (m, 1H), 1.75 (tq, J = 14.1, 7.1 Hz, 1H), 1.54 (tp, J = 14.2, 7.0 Hz, 1H), 0.88 (t, J = 7.5 Hz, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -114.27 (ddt, J = 283.2, 56.4, 15.5 Hz, 1F), -115.94 – -117.26 (m, 1F).

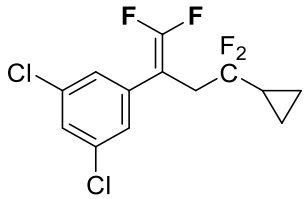
^{13}C NMR (101 MHz, **$CDCl_3$**) δ 202.9, 172.2, 155.9, 133.9, 132.0, 127.5, 124.2, 116.1 (t, J = 239.1 Hz), 110.7, 65.6, 45.5 (dd, J = 5.8, 3.7 Hz), 33.9 (t, J = 21.5 Hz), 24.9, 10.9.

MS (ES-API, *m*/*z*): 355.0 ($M+H^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{14}H_{15}O_4F_2Cl_2$ ($M+H^+$) 355.0310, found 355.0307.

IR (film): 3120, 2970, 2933, 1740, 1695, 1611, 1583, 1468, 1434, 1385, 1299, 1228, 1121, 1077, 1019, 813, 691, 626 cm^{-1}

1,3-Dichloro-5-(4-cyclopropyl-1,1,4,4-tetrafluorobut-1-en-2-yl)benzene (4a):



1,3-Dichloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**2aq**) was used as the alkene substrate. Colorless liquid (119.6 mg, 76%).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ, 7.27 (t, J = 1.9 Hz, 1H), 7.24 – 7.22 (m, 2H), 2.99 (tt, J = 14.6, 2.2 Hz, 2H), 1.21 – 1.00 (m, 1H), 0.66 – 0.57 (m, 2H), 0.56 – 0.47 (m, 2H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ, -84.82 – -84.97 (m, 1F), -85.49 (d, J = 27.5 Hz, 1F), -101.04 (qd, J = 14.3, 5.1 Hz, 2F).

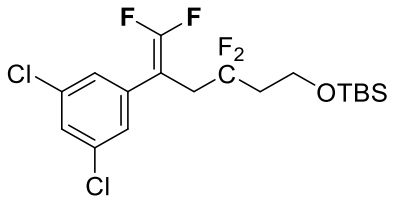
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 155.5 (dd, J = 293.9, 292.4 Hz), 136.5 (t, J = 4.0 Hz), 135.0, 127.7, 126.8 (t, J = 3.5 Hz), 124.75 - 119.56 (m), 85.92 - 84.30 (m), 36.3 (td, J = 29.6, 2.0 Hz), 15.7 (t, J = 28.7 Hz), 1.4 (t, J = 4.3 Hz).

MS (EI, *m*/*z*): 312.1 (M^+), 270.0, 91.1.

HRMS (FI, *m*/*z*): Calcd. for $C_{13}H_{10}Cl_2F_4$ (M^+) 312.0090, found 312.0093.

IR (KBr): 3080, 2955, 2930, 2885, 2858, 1736, 1589, 1561, 1472, 1463, 1437, 1413, 1388, 1362, 1347, 1315, 1257, 1136, 1108, 1033, 1007, 858, 837, 806, 779 cm^{-1}

***tert*-Butyl-((5-(3,5-dichlorophenyl)-3,3,6,6-tetrafluorohex-5-en-1-yl)oxy)dimethylsilane (4b):**



1,3-Dichloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (**2aq**) was used as the alkene substrate. Colorless liquid (123.3 mg, 57%).

^{1}H NMR (400 MHz, **CDCl$_3$**) δ 7.27 (t, J = 1.9 Hz, 1H), 7.20 (dd, J = 1.9, 1.0 Hz, 2H), 3.77 (t, J = 6.3 Hz, 2H), 2.98 (tt, J = 16.7, 2.1 Hz, 2H), 2.06 (tt, J = 15.6, 6.3 Hz, 2H), 0.88 (s, 9H), 0.05 (s, 6H).

^{19}F NMR (376 MHz, **CDCl$_3$**) δ -85.09 (dtd, J = 27.7, 6.0, 2.8 Hz, 1F), -85.40 (d, J = 27.9 Hz, 1F), -95.27 (pd, J = 16.1, 6.2 Hz, 2F).

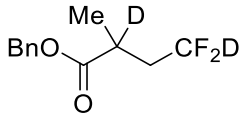
^{13}C NMR (101 MHz, **CDCl$_3$**) δ 155.4 (t, J = 293.0 Hz), 136.7 (t, J = 3.8 Hz), 135.0, 127.7, 126.9 (t, J = 3.4 Hz), 122.9 (t, J = 243.6 Hz), 85.46 - 84.80 (m), 57.1 (t, J = 6.6 Hz), 39.7 (t, J = 24.2 Hz), 35.8 (td, J = 26.0, 1.7 Hz), 25.8, 18.2, -5.6 .

MS (FTMS, *m*/*z*): 431.1 ($M+H^+$).

HRMS (DART, *m*/*z*): Calcd. for $C_{18}H_{25}OCl_2F_3Si$ ($M+H^+$) 431.0971, found 431.0979.

IR (KBr) 3096, 3022, 1733, 1589, 1561, 1436, 1413, 1343, 1315, 1254, 1202, 1169, 1155, 1136, 1119, 1085, 1060, 911, 860, 828, 803, 715 cm^{-1}

Benzyl 4,4-difluoro-2-methylbutanoate-2,4-d2 (3b-*d$_2$*):



D_2O was used instead of H_2O. Colorless liquid (95.6 mg, 83%).

^{1}H NMR (400 MHz, **$CDCl_3$**) δ 7.44 – 7.28 (m, 5H), 5.14 (s, 2H), 2.29 (dt, J = 21.4, 14.3 Hz, 1H), 1.90 (dt, J = 17.6, 14.7 Hz, 1H), 1.26 (s, 3H).

^{19}F NMR (376 MHz, **$CDCl_3$**) δ -115.80 (dddt, J = 285.5, 17.6, 14.6, 8.5 Hz, 1F), -117.35 – -118.43 (m, 1F).

^{13}C NMR (101 MHz, **$CDCl_3$**) δ 174.9, 135.8, 128.6, 128.3, 128.1, 118.47 - 112.73 (m), 66.6, 37.3 (t, J = 21.7 Hz), 34.09 - 33.02 (m), 17.4.

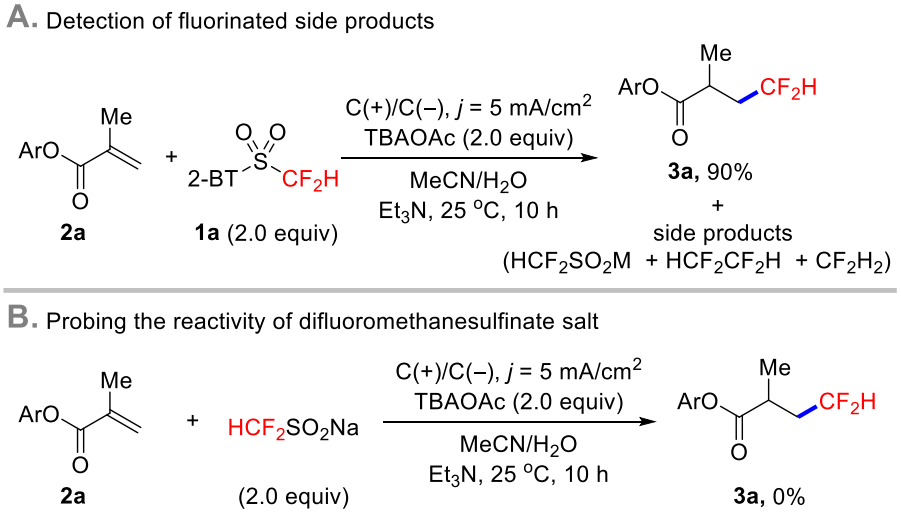
MS (ES-API, *m*/*z*): 253.0 ($M+Na^+$).

HRMS (ESI, *m*/*z*): Calcd. for $C_{12}H_{12}{}^2H_2O_2F_2Na$ ($M+Na^+$) 253.0980, found 253.0978.

IR (film): 3067, 3035, 2938, 1735, 1456, 1432, 1384, 1351, 1295, 1249, 1164, 1137, 1079, 1029, 980, 954, 749, 697 cm^{-1}

5. Mechanistic Investigation

5.1 Probing the pathway for the formation of fluoroalkyl radicals



Scheme S3 Probing the pathway for the formation of fluoroalkyl radicals**.** The reaction of sulfone **1** with alkenes. reaction conditions: **1** (1.0 mmol), **2** (0.5 mmol), Tetrabutylammonium hexafluorophosphate (1.0 mmol), Et_3N (0.2 mL) water (0.5 mL) in CH_3CN (10 mL) were conducted with the 7 mA constant current for 10 hours.

Results and discussion:

^{19}F NMR spectroscopy analysis of the reaction mixture after the completion of the reaction showed that in addition to the desired product, difluoromethanesulfinate was also formed (**Scheme S3A**). The use of HCF_2SO_2Na instead of sulfone **1a** under our optimized conditions did not afford the desired product **3a** (**Scheme S3B**). These results suggest that $\bullet R_f$ radical is generated via SET reduction of the fluoroalkyl sulfone.

5.2 H-D Exchange Experiment

Experimental procedures:

2-$BTSO_2CF_2H$ (**1a**) (10 mg) is dissolved in MeCN (5 mL) (**Figure S1**), then D_2O (0.5 mL) (**Figure S2**) and Et_3N (0.5 mL) (**Figure S3**) were added in sequence. The mixture was detected by ^{19}F NMR spectroscopy.

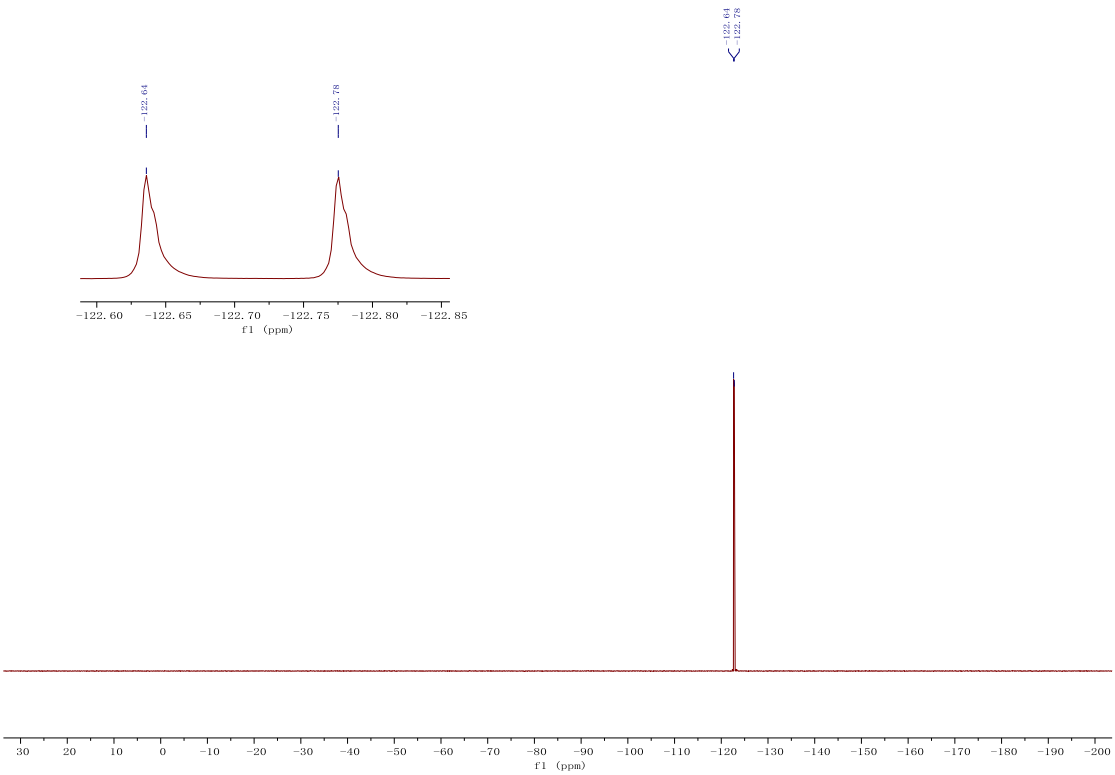


Figure S1. 2-$BTSO_2CF_2H$ in MeCN (5 mL)

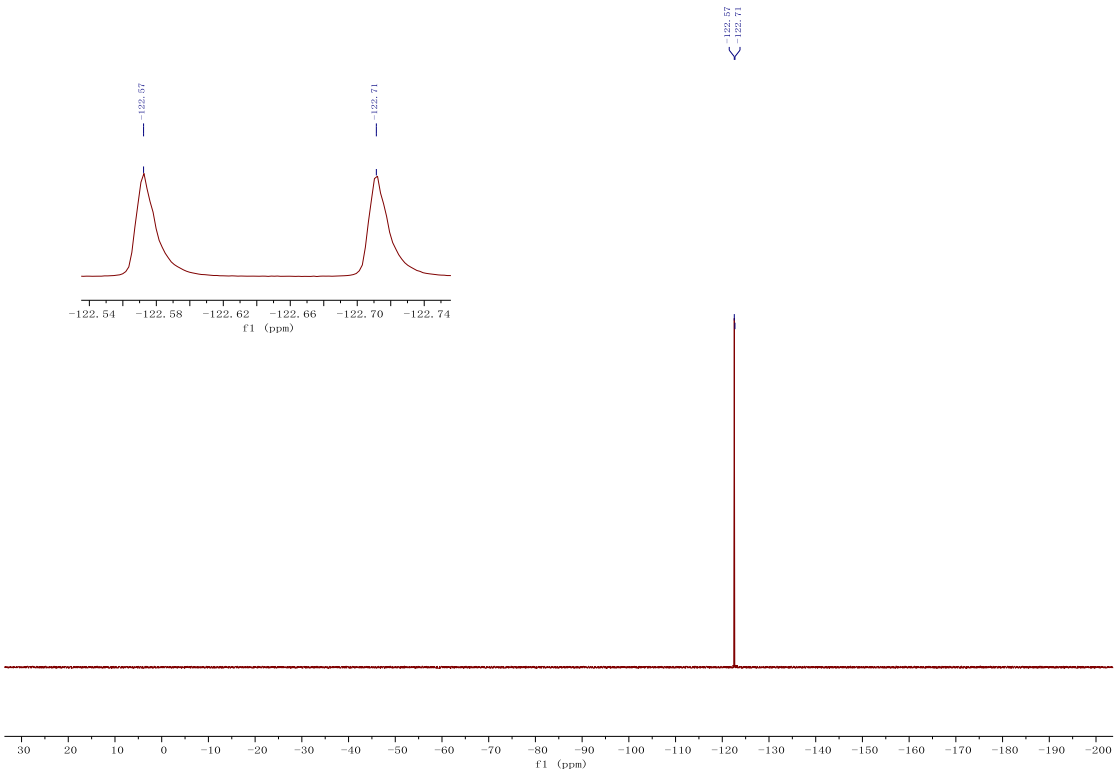


Figure S2. 2-BTSO$_2$CF$_2$H in MeCN (5 mL)/D$_2$O (0.5 mL)

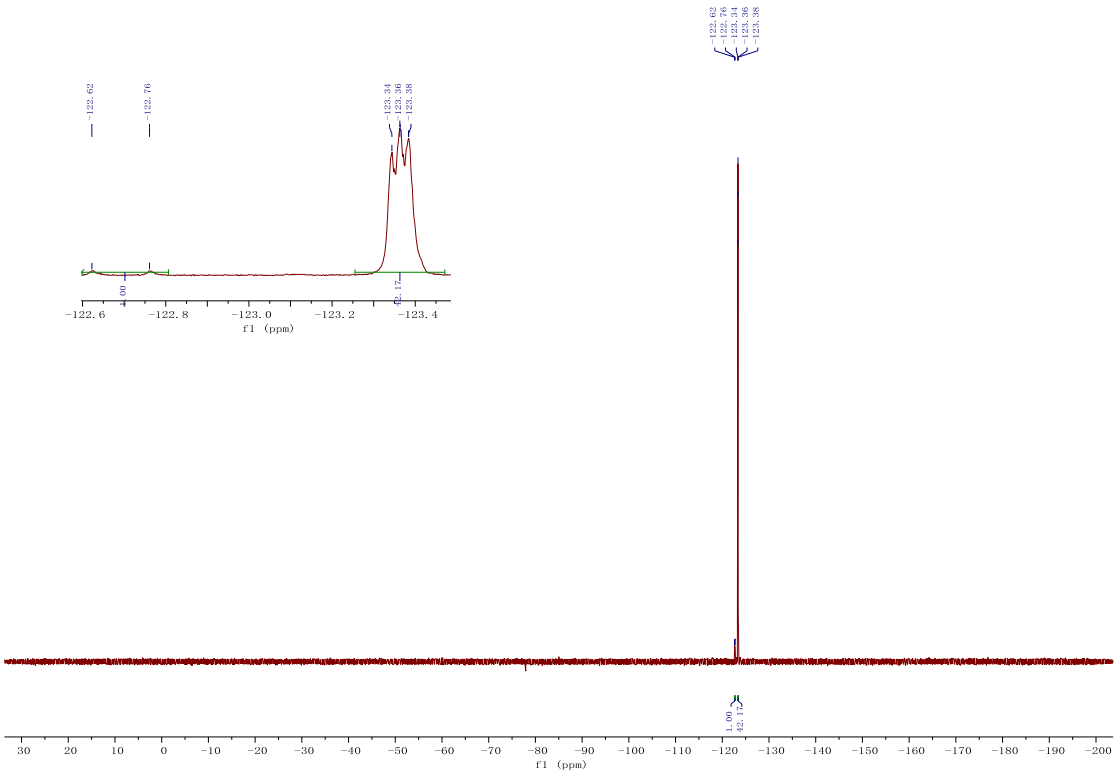
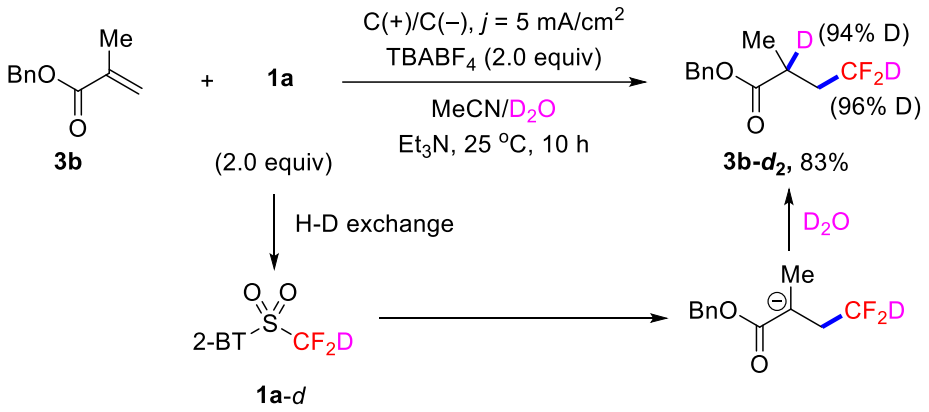


Figure S3. 2-BTSO$_2$CF$_2$H in MeCN (5 mL)/D$_2$O (0.5 mL)/Et$_3$N (0.5 mL)

Results and discussion:

Et_3N can promote the H-D exchange of sulfone **1a** and D_2O. The deuterodifluoromethylation product **3b**-d_2 is proposed to be formed as follows (Scheme S4):

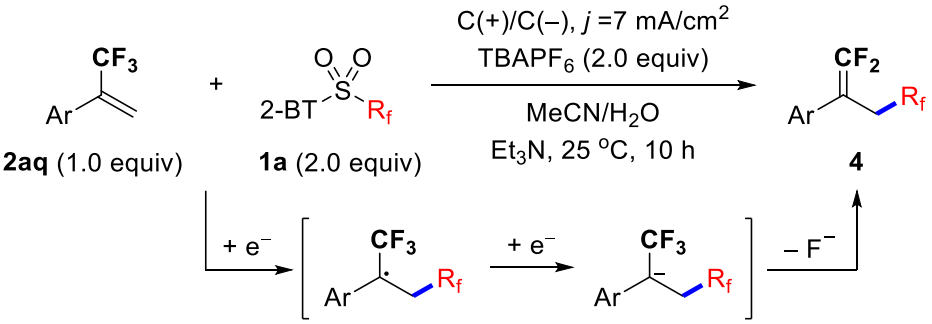


Scheme S4 Proposed pathway for the formation of deuterodifluoromethylation product **3b**-d_2

5.3 Probing the involvement of carbanion

For experimental details, see section 4 in this ESI (for compound **4a** and **4b**).

Proposed reaction pathway (Scheme S5):

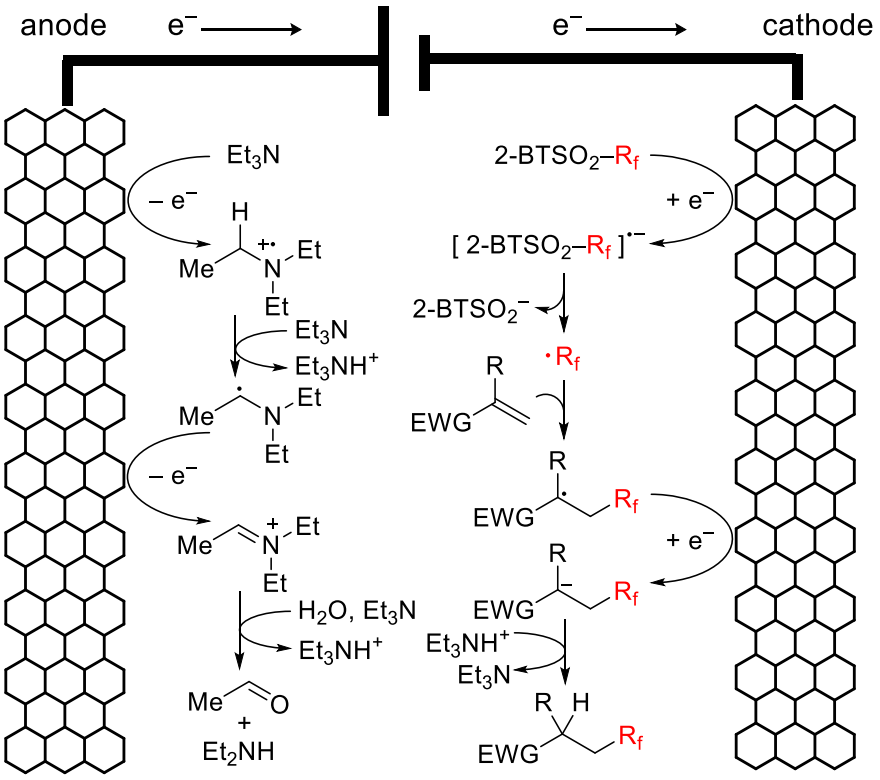


Scheme S5 Proposed pathway for the formation of defluorination product **4**

5.4 Proposed mechanism

Based on the above experimental results and previous investigations,[8] a plausible mechanism is proposed in Scheme S6. First, on the graphite cathode, SET reduction of the fluoroalkyl sulfone gives radical anion $[2\text{-BTSO}_2\text{-R}_f]^{\bullet-}$, which undergoes $R_f\text{-}SO_2$

bond cleavage to form •R_f radical and benzo[*d*]thiazole-2-sulfinate anion. The latter had been captured with benzyl bromide as a sulfone. Then •R_f radical readily reacts with the alkene to form a new carbon-centered radical, which was further converted to a carbanion by accepting an electron from either the graphite cathode or the radical anion $[2\text{-BTSO}_2\text{-R}_f]^{\bullet-}$. Finally, the carbanion was protonated by the tertiary ammonium cation Et_3NH^+ to give the hydrofluoroalkylation product. On the graphite anode, oxidation of Et_3N through two SET process followed by hydrolysis of the iminium salt by water is the most possible reaction pathway, as is supported by the detection of Et_2NH via GC-MS analysis of the crude reaction mixture. Et_3N mainly serves as the sacrificial reductant at the anode. It is clear that in the absence of water, Et_3N is the major source of proton. However, when large excess amount of water is present, water will be the major source of proton, which can promote the protonation of the carbanion.



Scheme S5 Proposed mechanism for electroreductive radical fluoroalkylation of alkenes with sulfones

6 Full List of Reference 16

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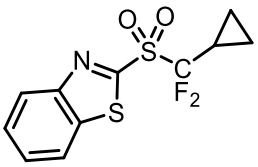
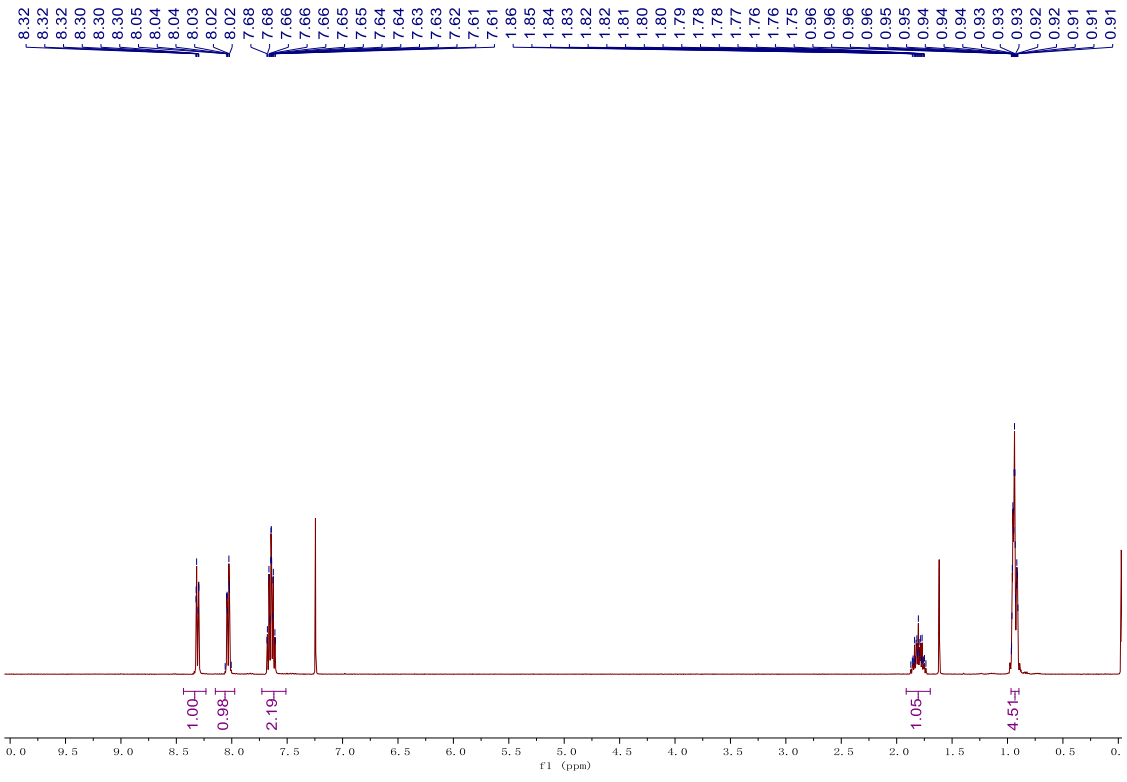
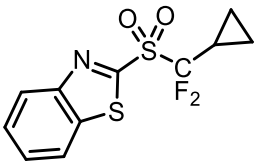
8. NMR Spetra of Compounds



1c ^{1}H NMR
(400 MHz, $CDCl_3$)





1c ^{19}F NMR
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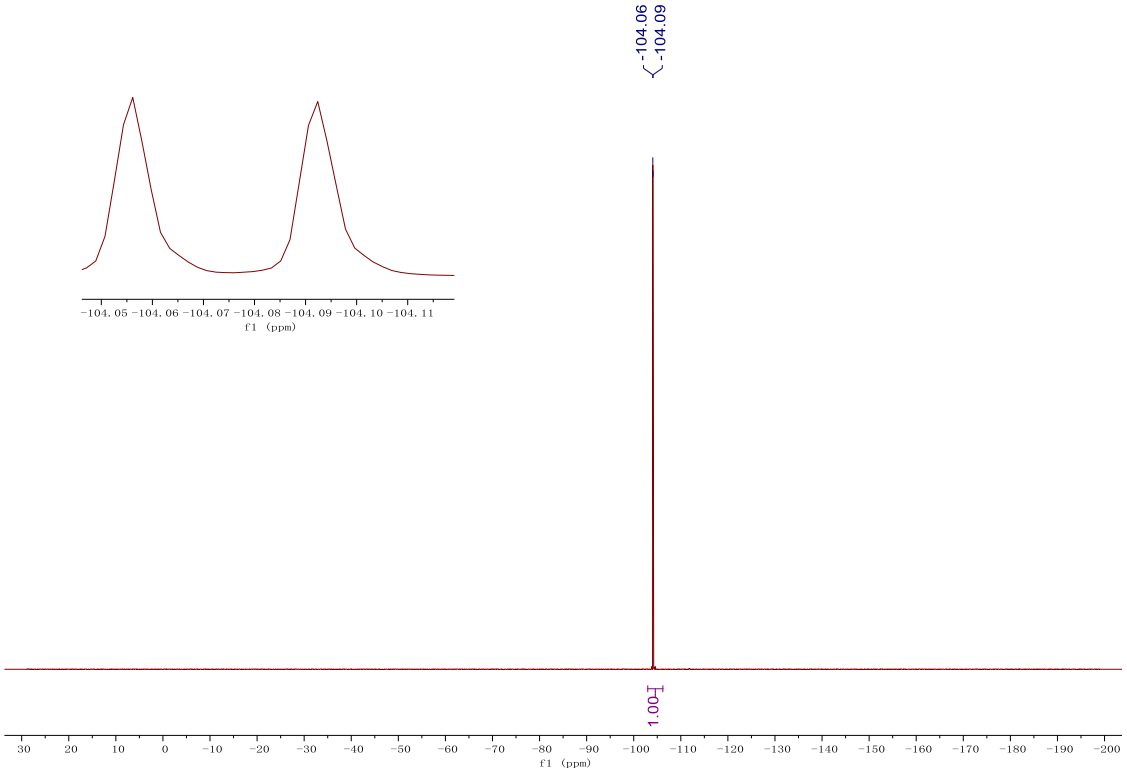

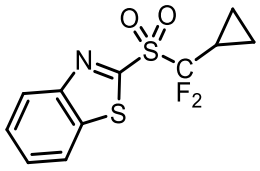

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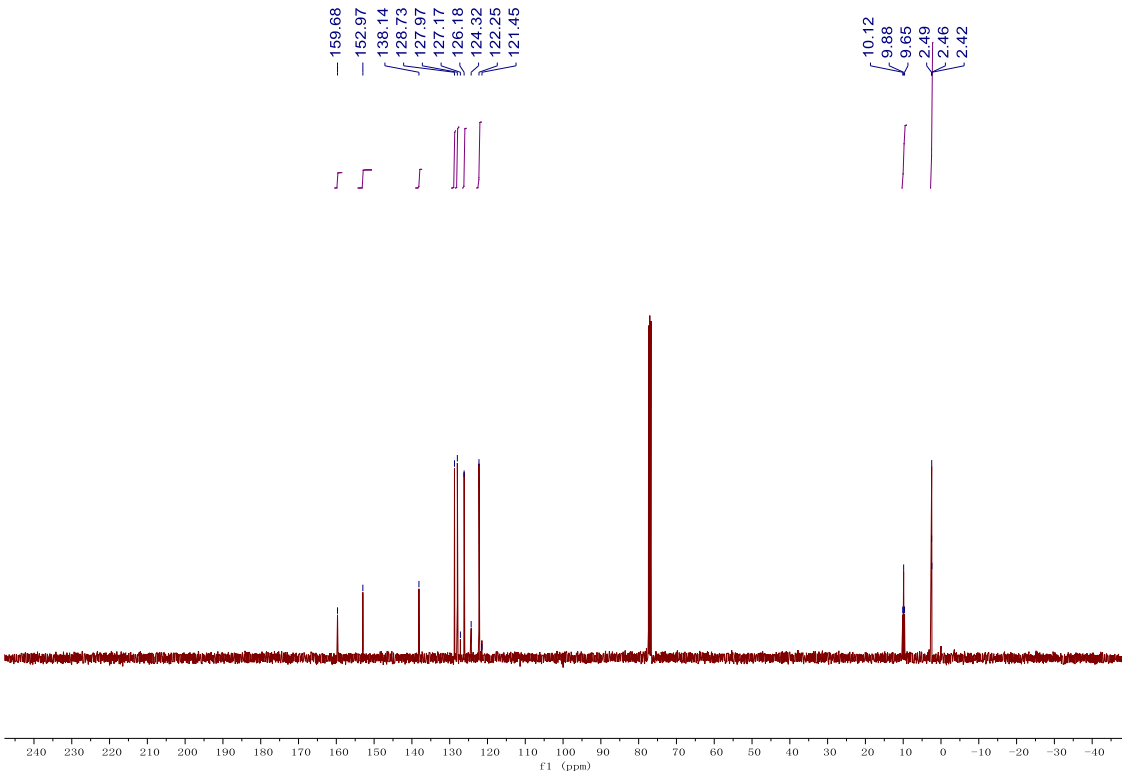

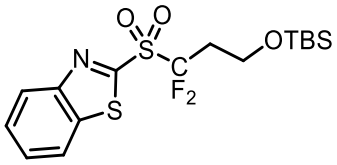

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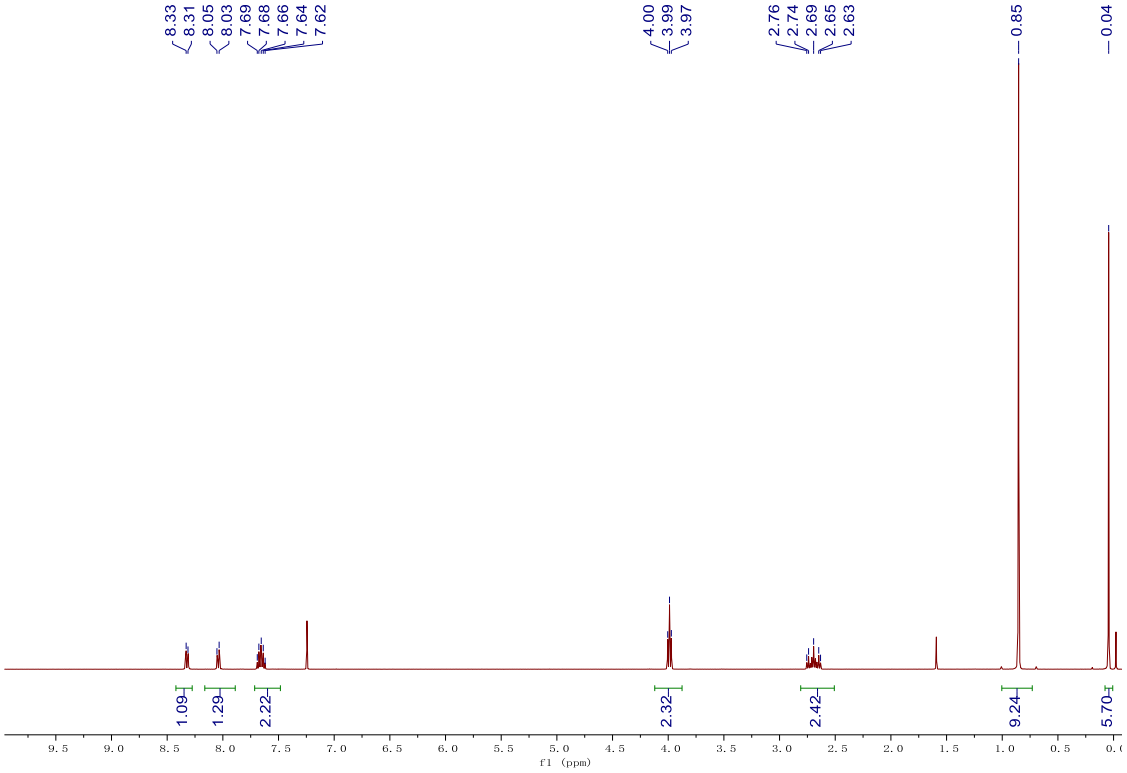

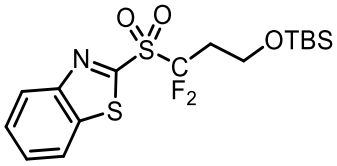

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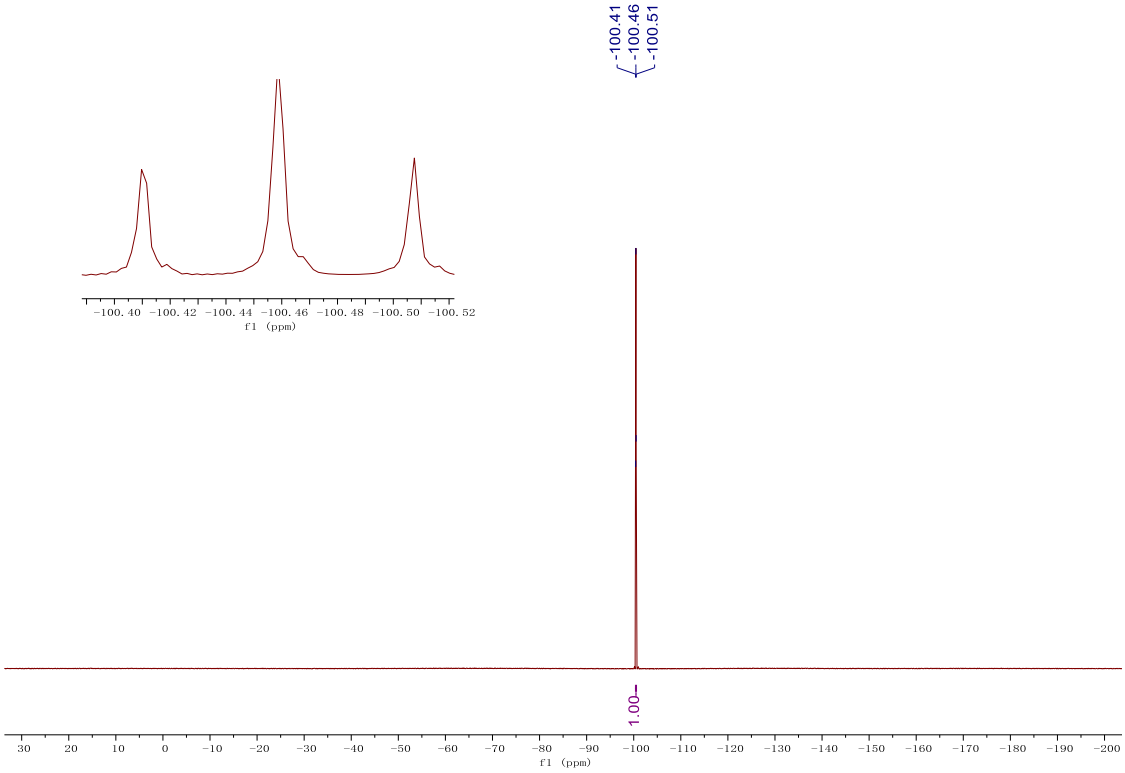

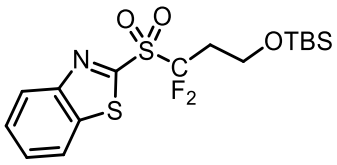

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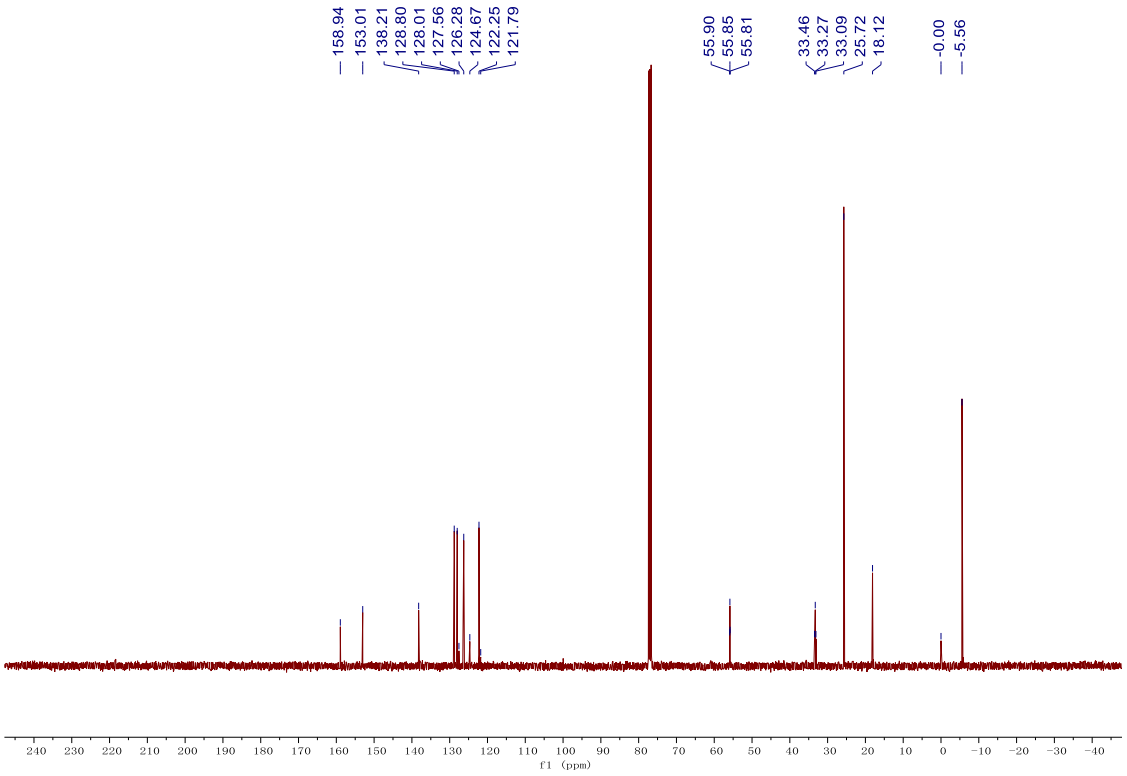
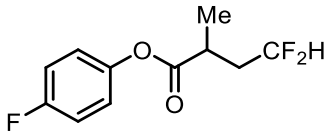
(101 MHz, $CDCl_3$)





3a ^{1}H NMR
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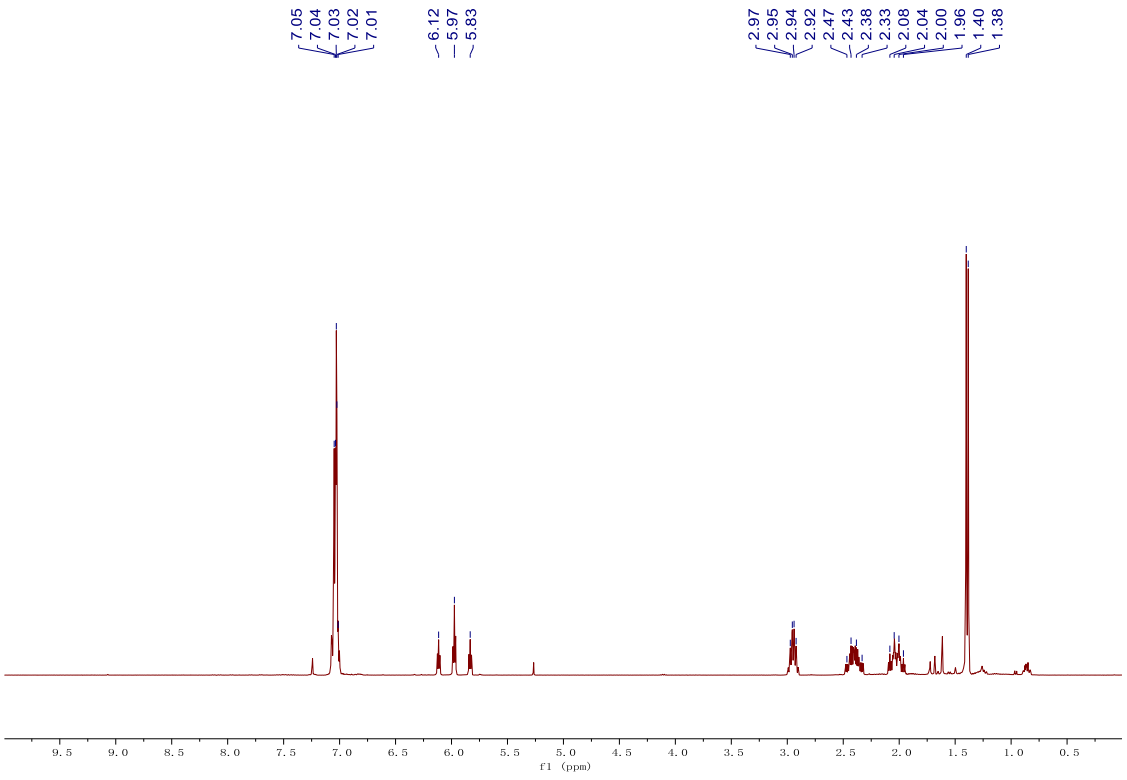

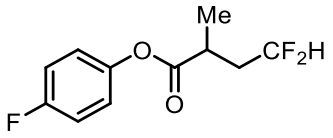

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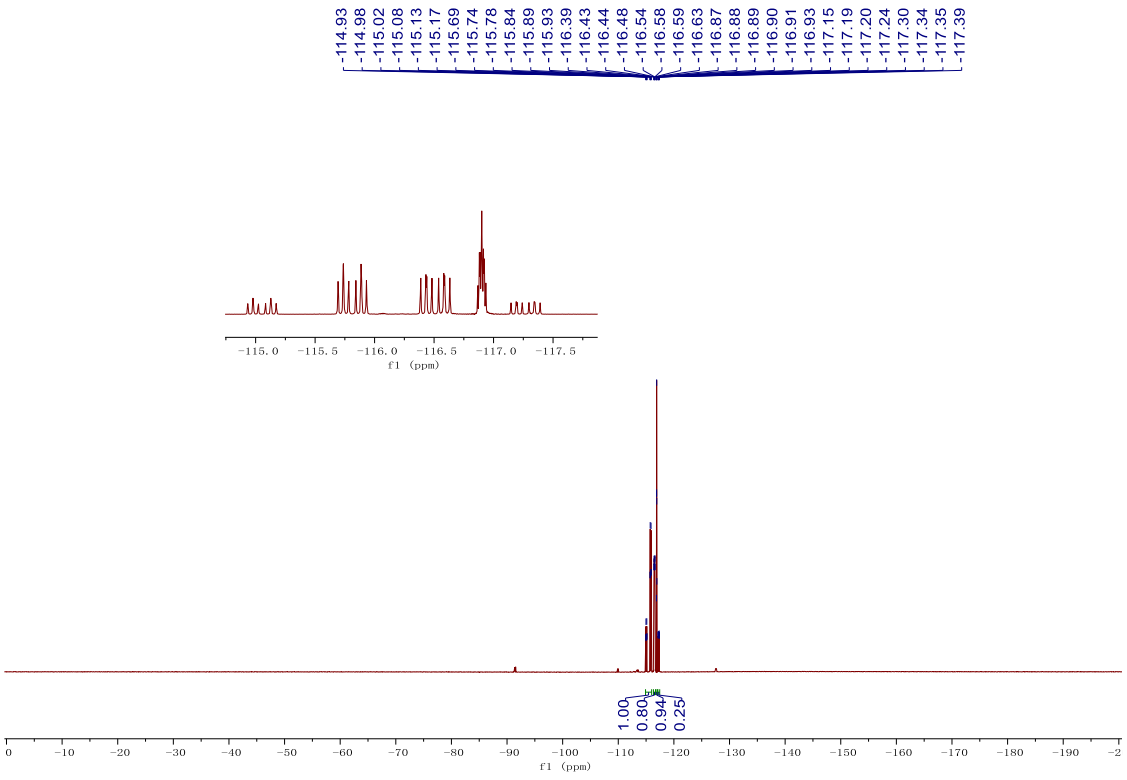

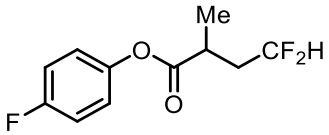

3a ^{13}C NMR
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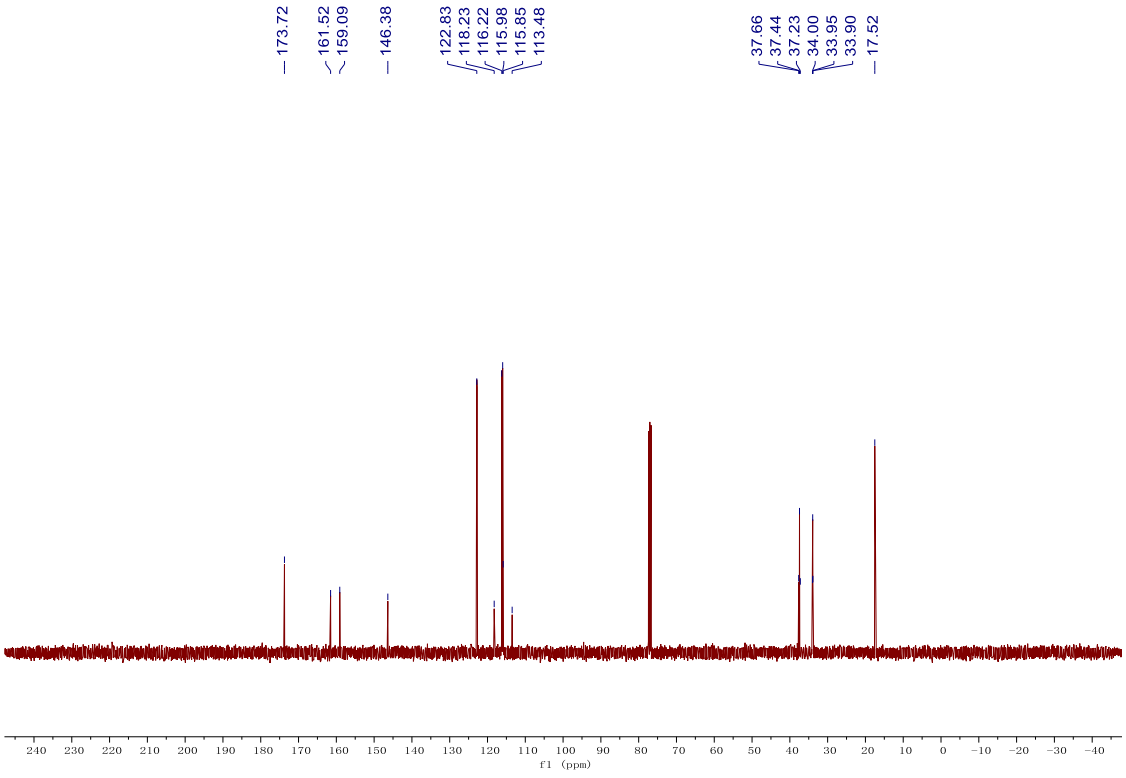

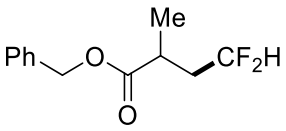

3b ^{1}H NMR
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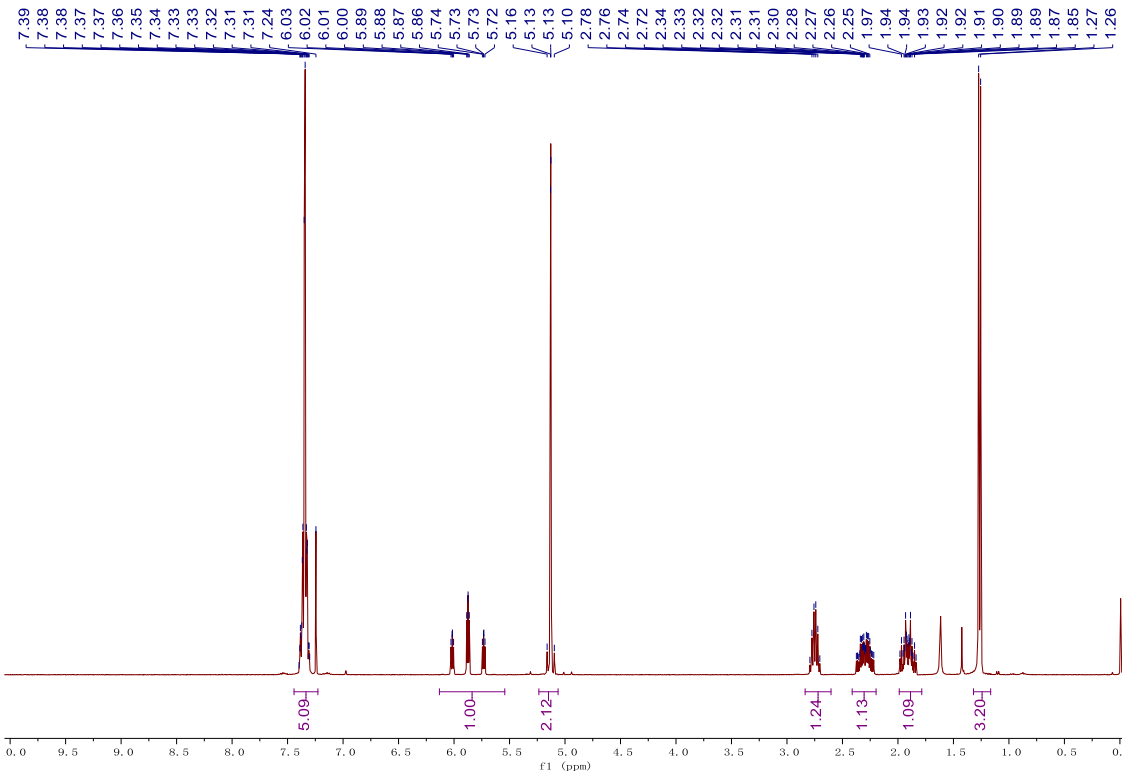

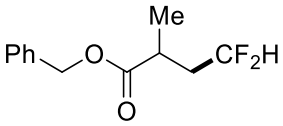

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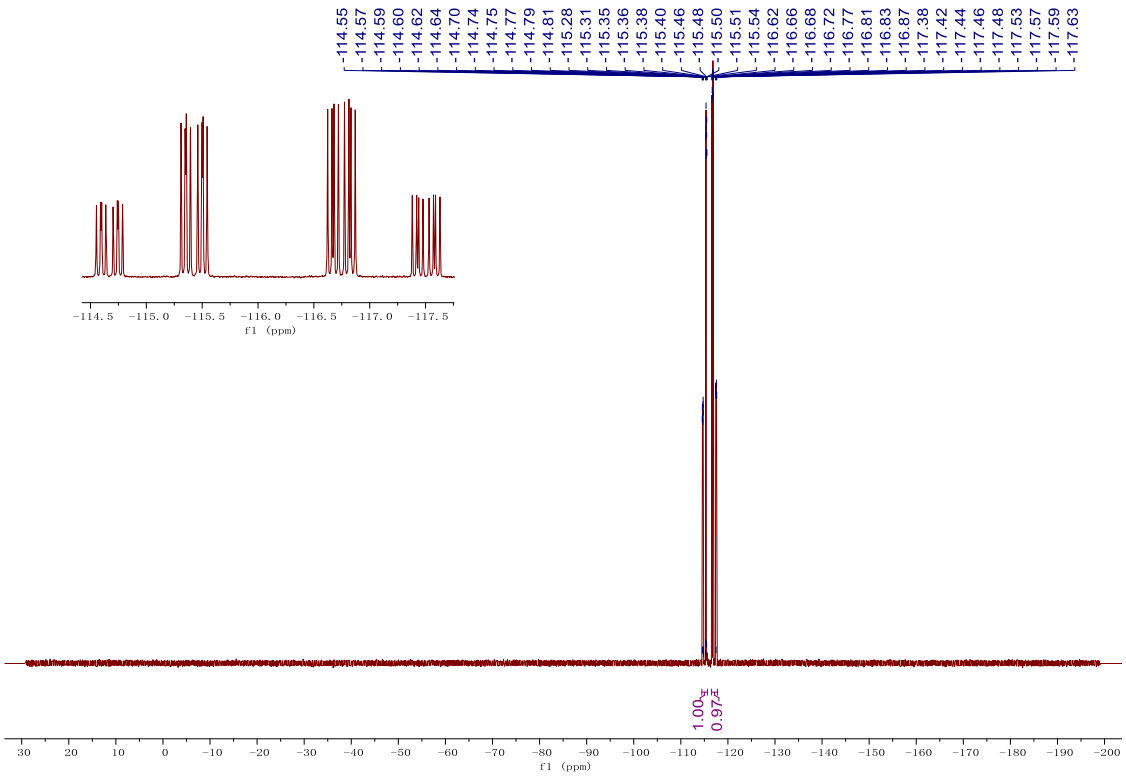

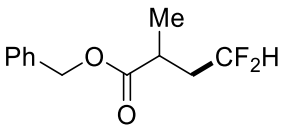

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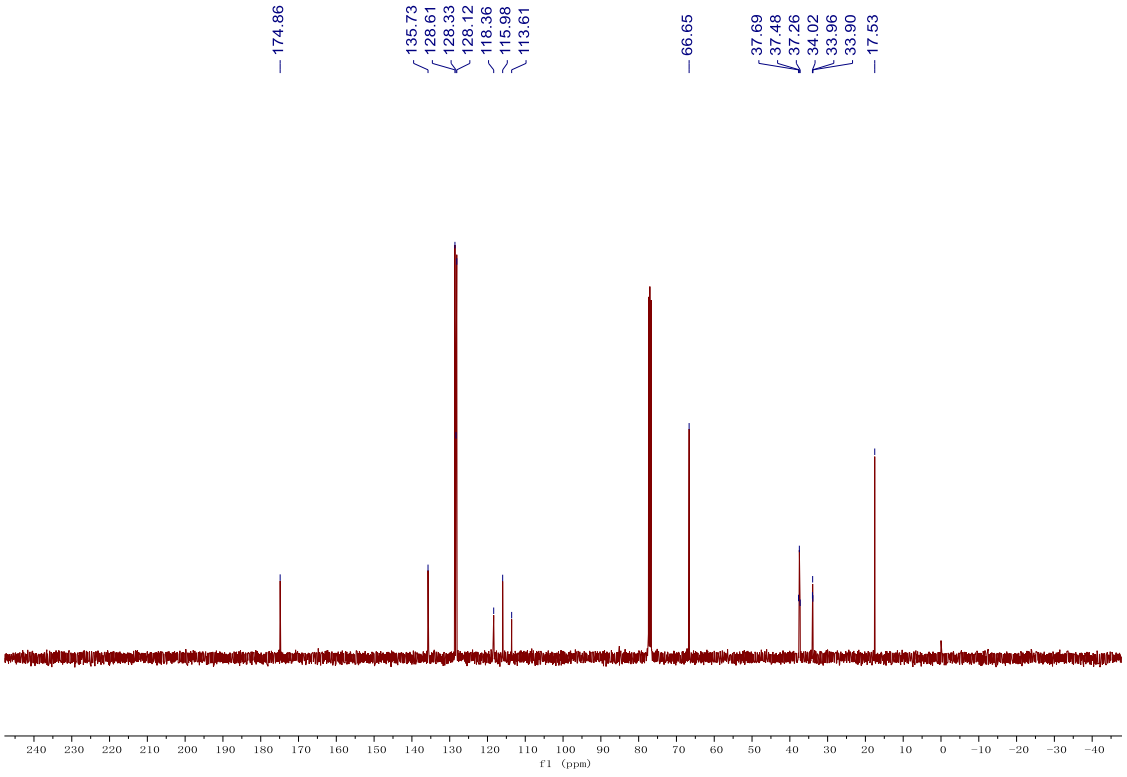
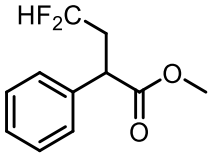
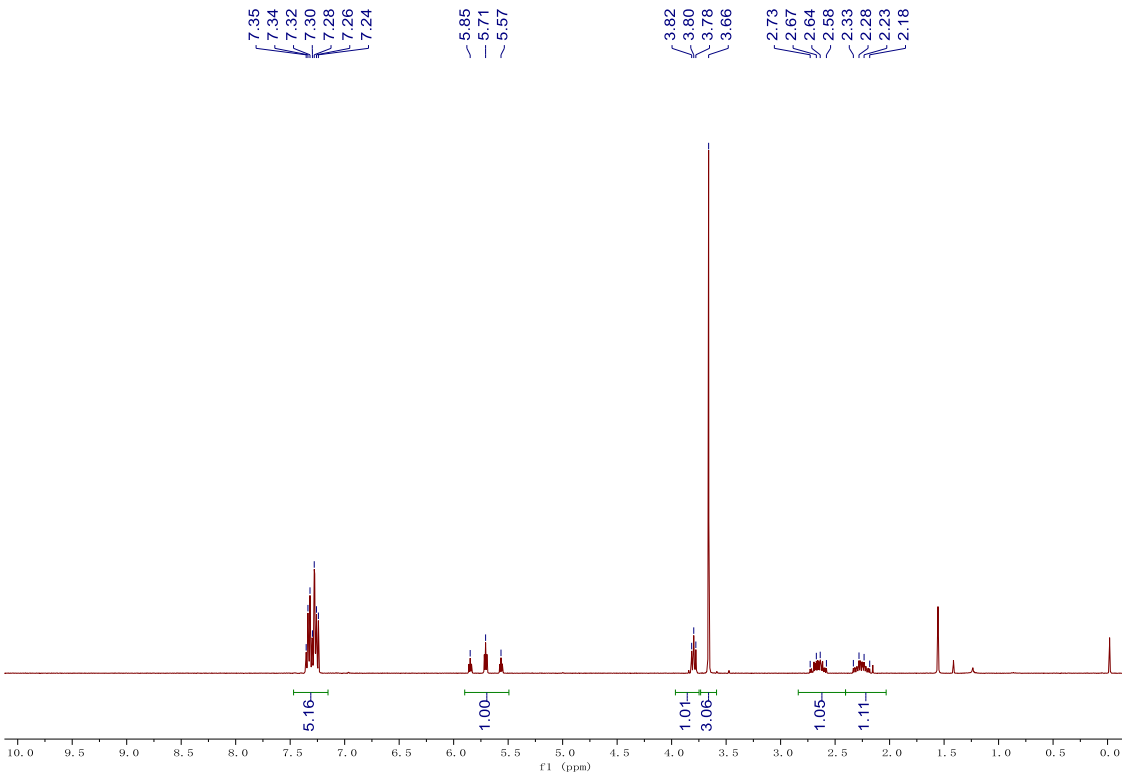
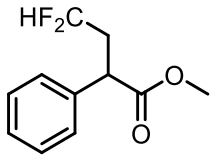


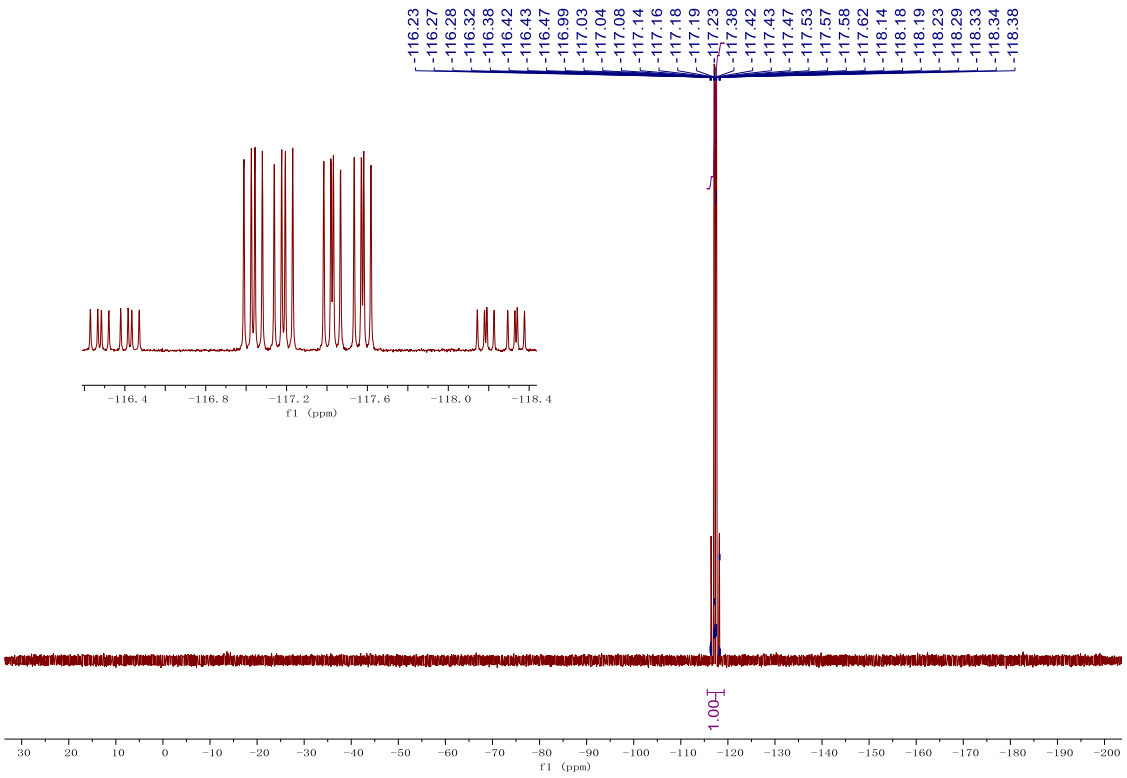


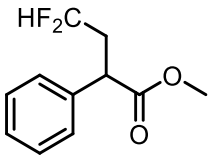
3c ^{1}H NMR
(400 MHz, $CDCl_3$)



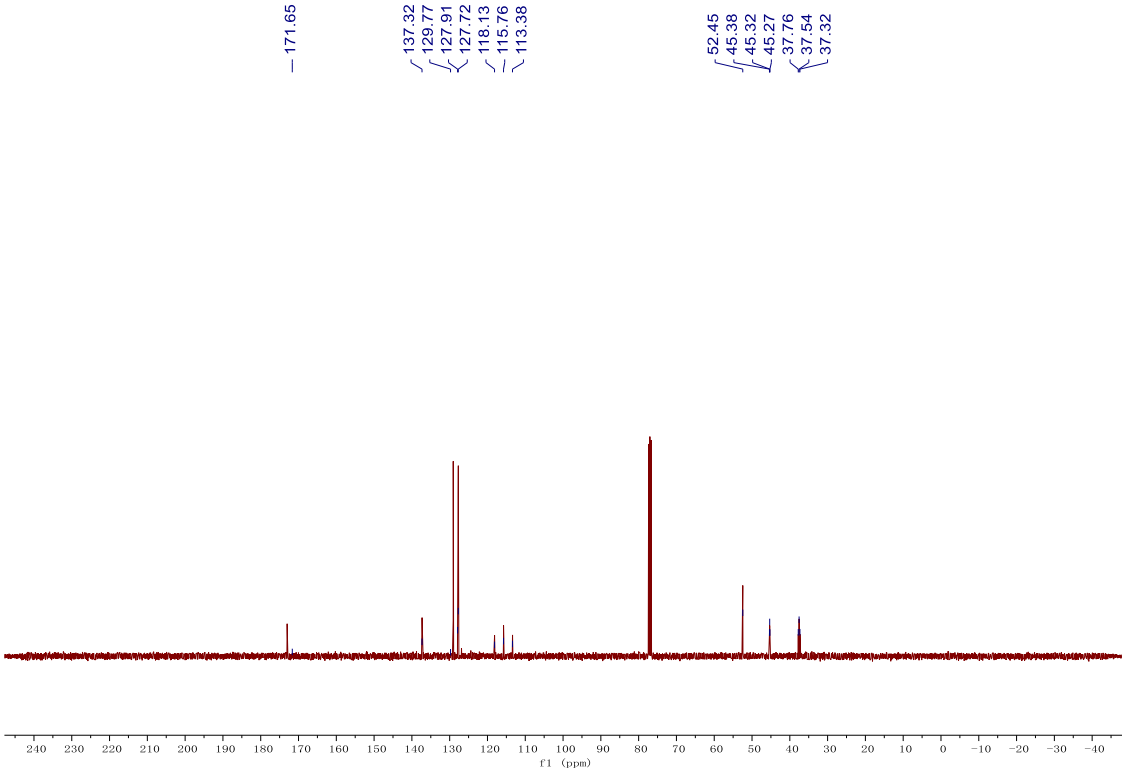


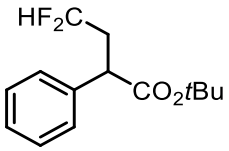
3c ^{19}F NMR
(376 MHz, $CDCl_3$)



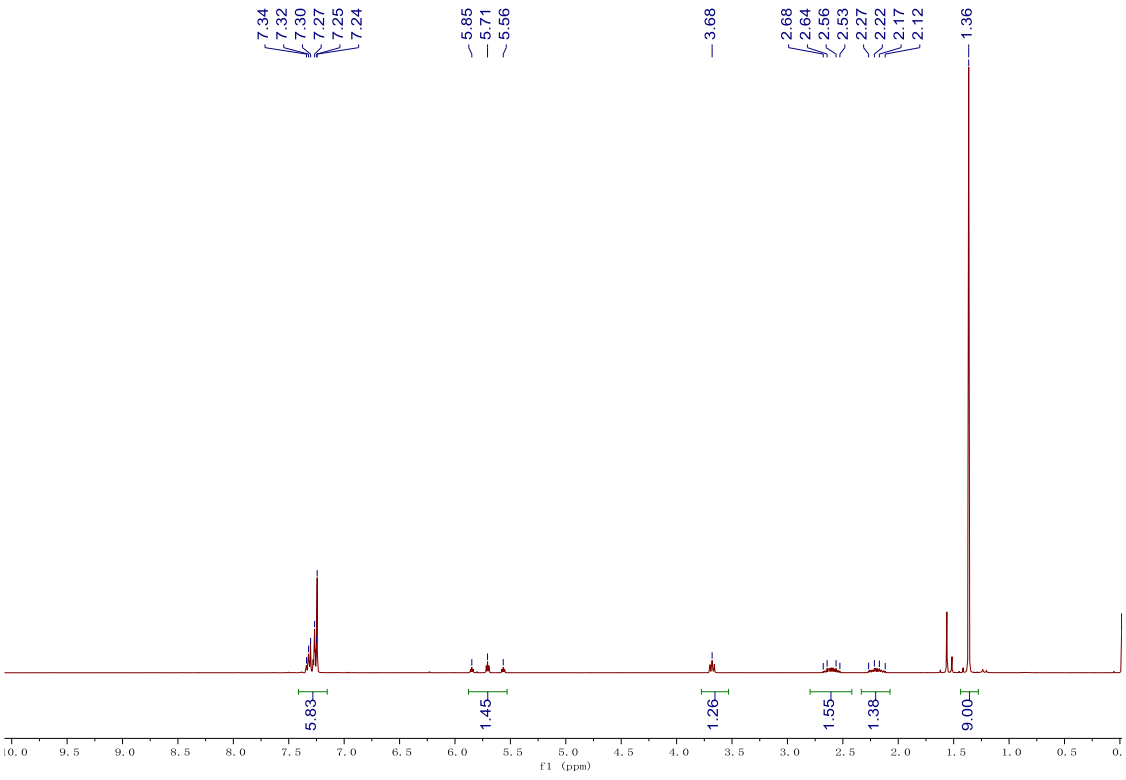


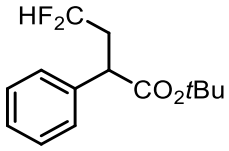
3c ^{13}C NMR
(101 MHz, $CDCl_3$)



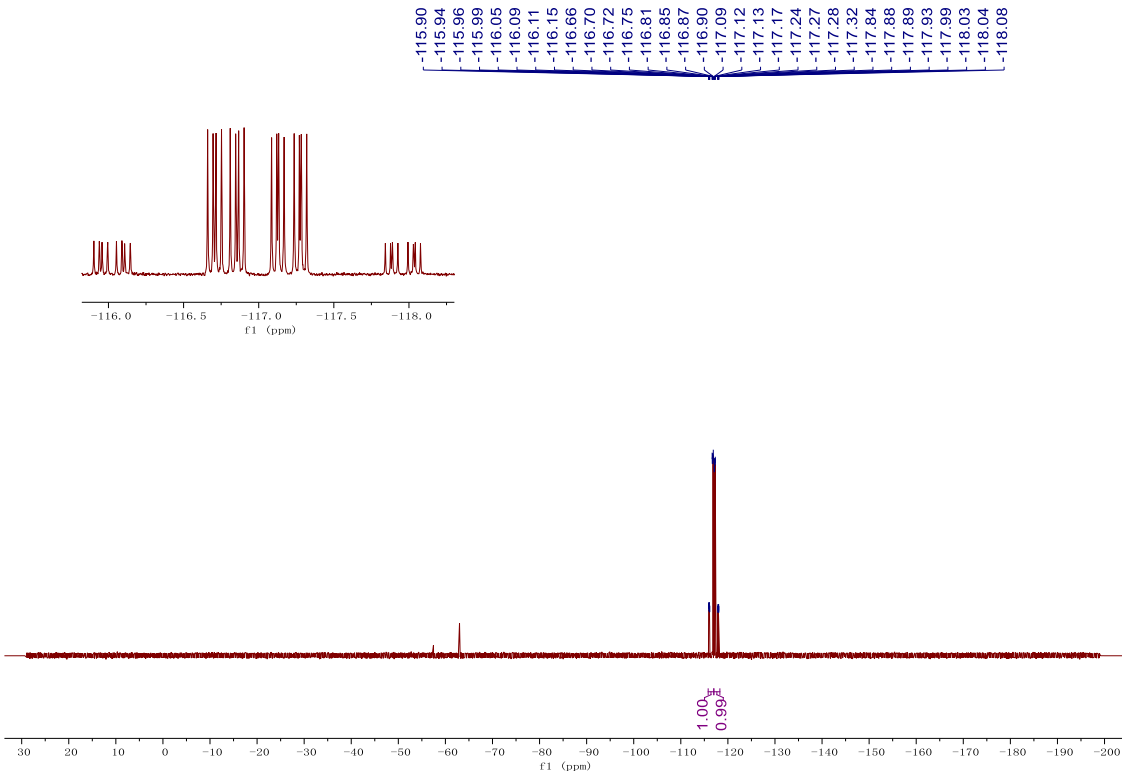


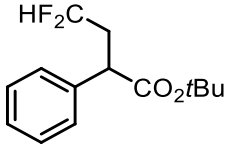
3d ^{1}H NMR
(400 MHz, $CDCl_3$)



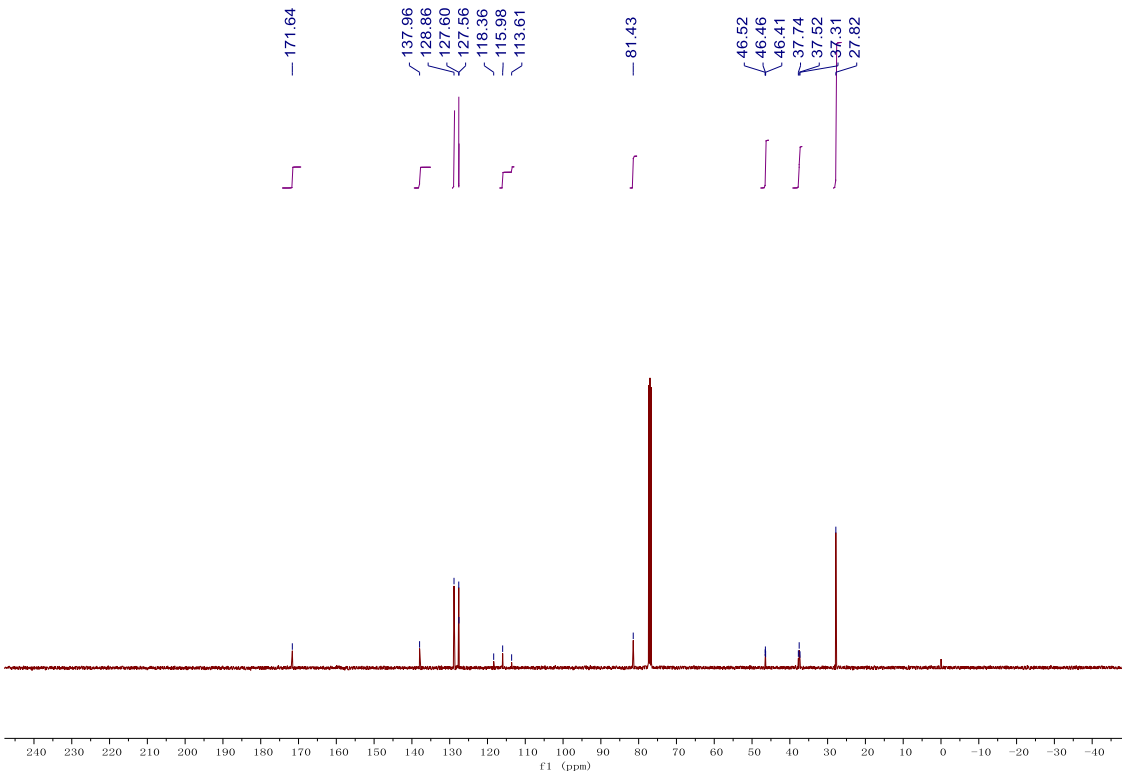


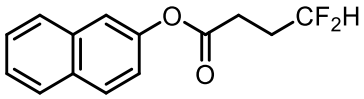
3d ^{19}F NMR
(376 MHz, $CDCl_3$)



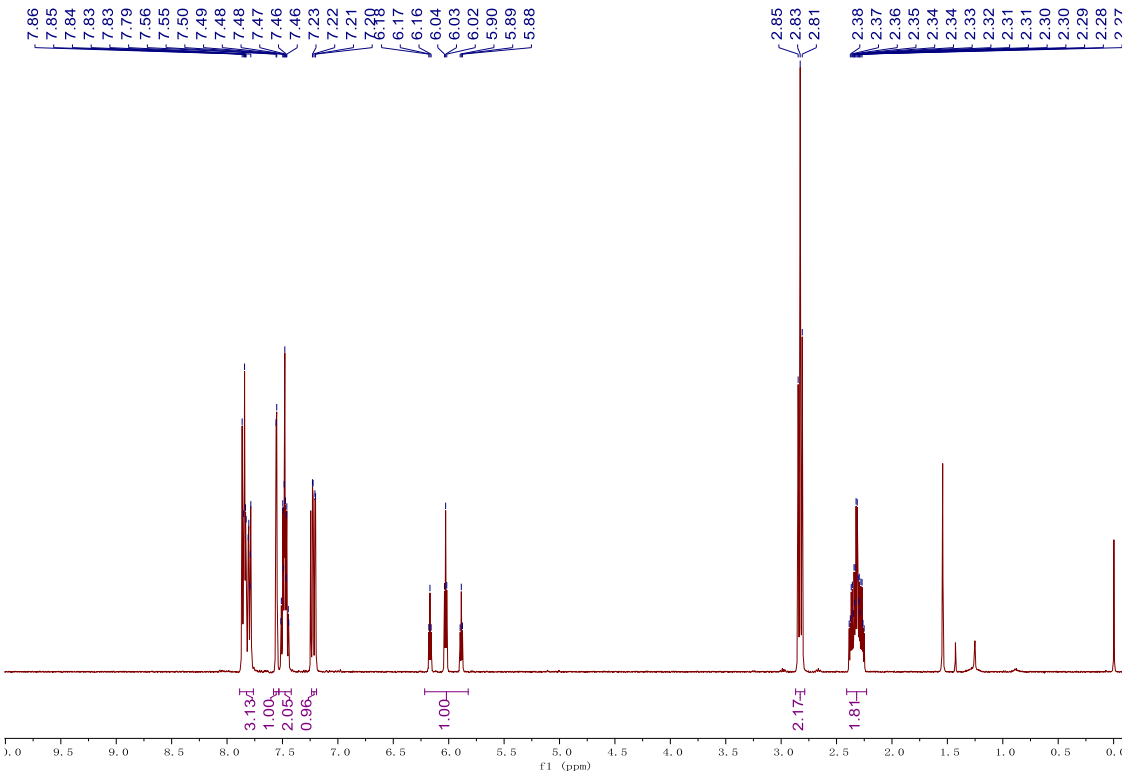


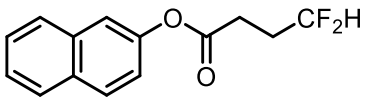
3d ^{13}C NMR
(101 MHz, $CDCl_3$)



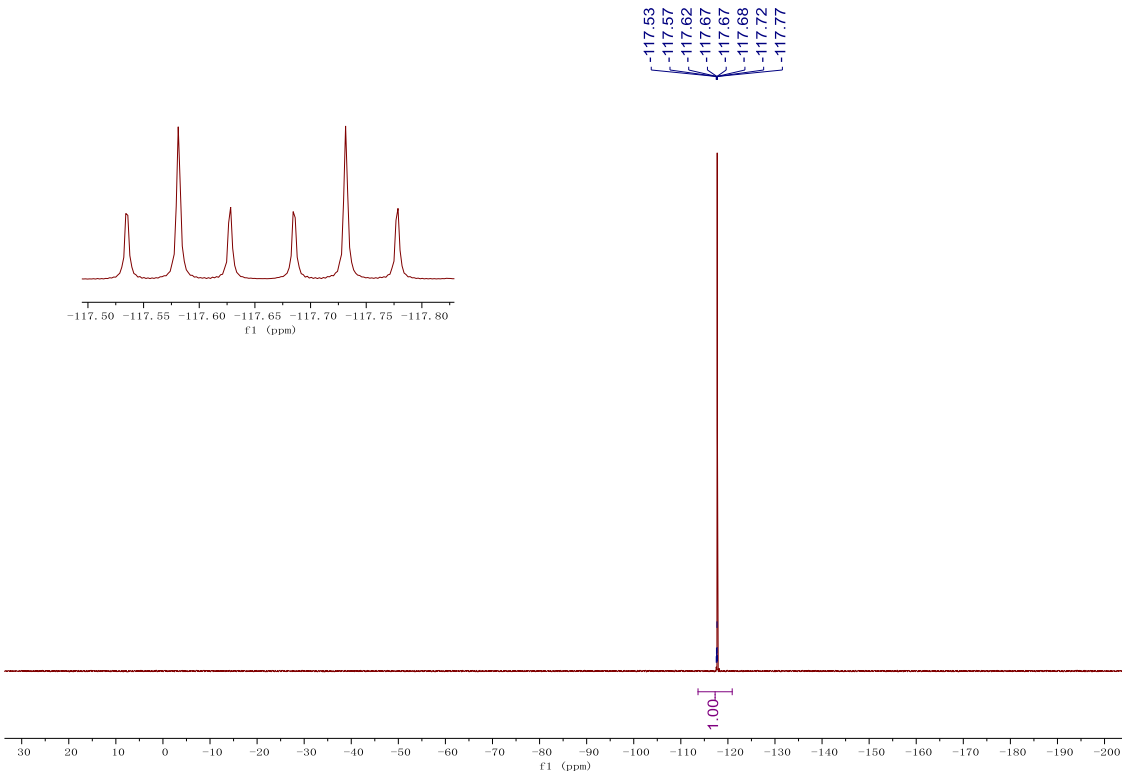


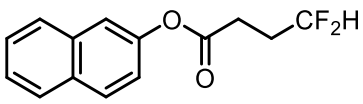
3e ^{1}H NMR
(400 MHz, $CDCl_3$)



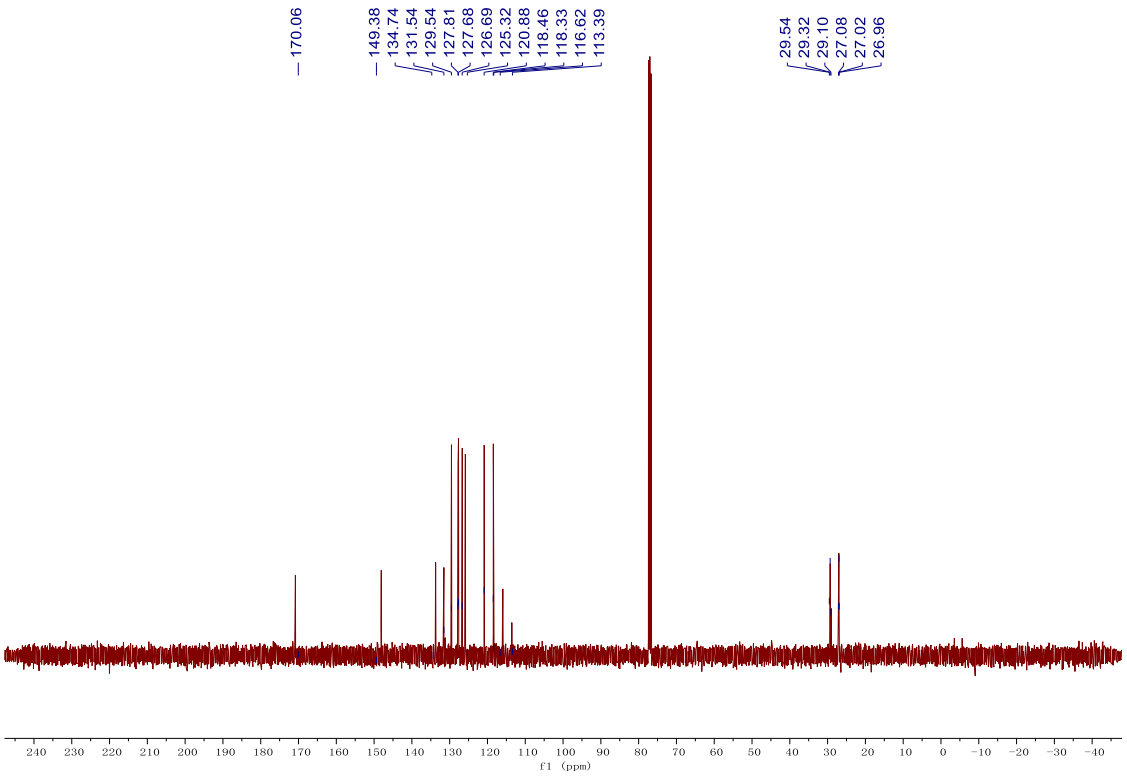


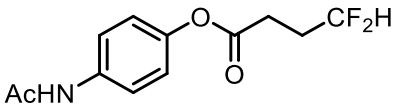
3e ^{19}F NMR
(376 MHz, $CDCl_3$)



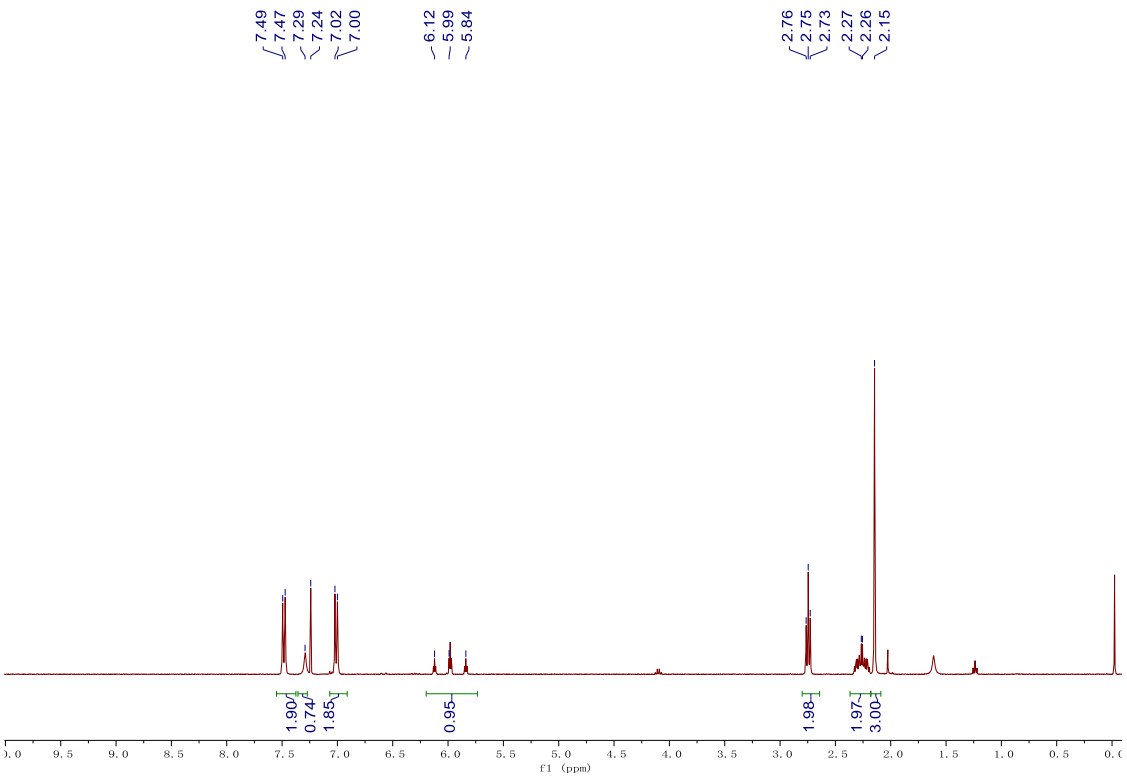


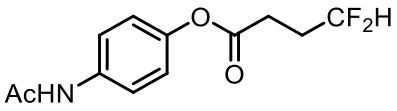
3e ^{13}C NMR
(101 MHz, $CDCl_3$)



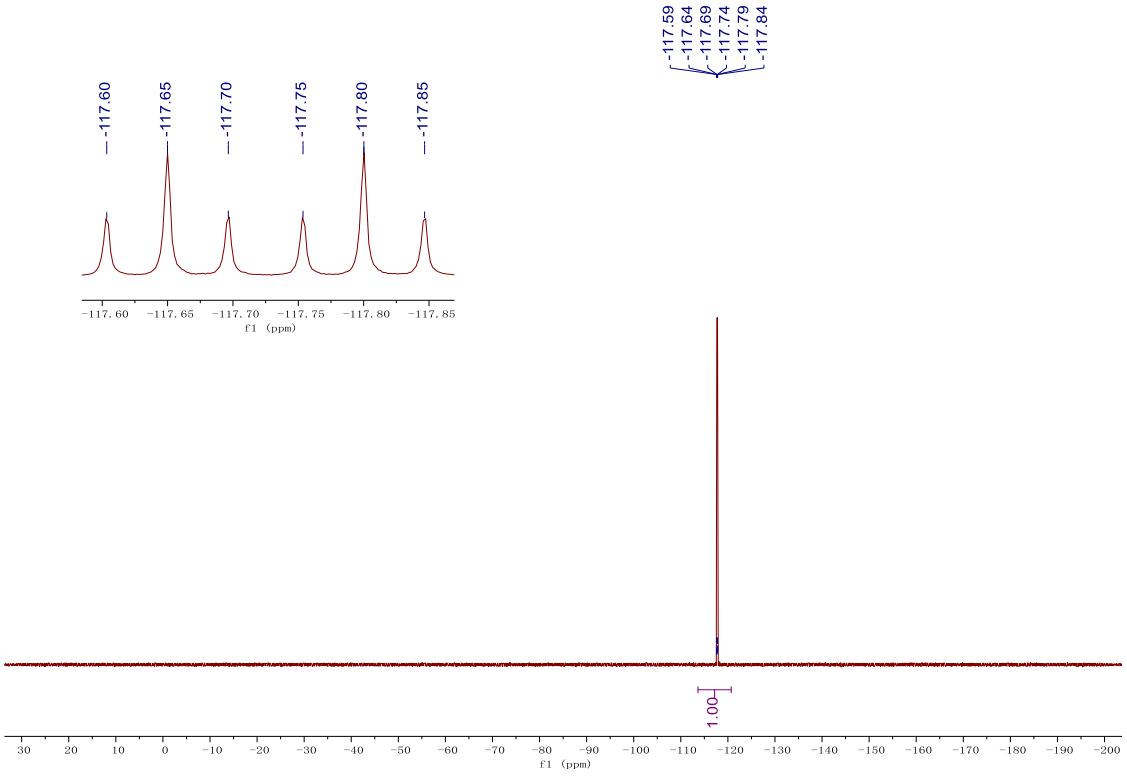


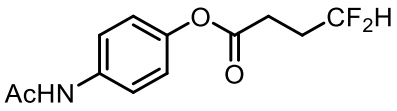
3f ^{1}H NMR
(400 MHz, $CDCl_3$)



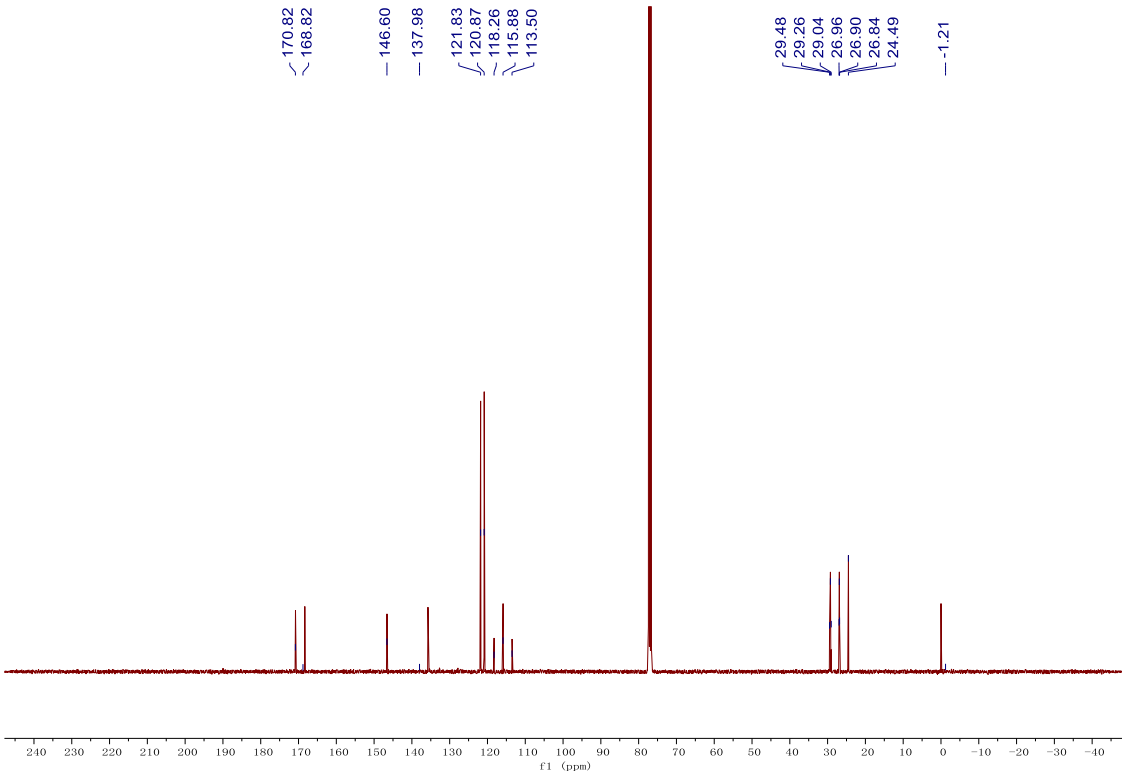


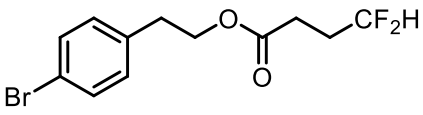
3f ^{19}F NMR
(376 MHz, $CDCl_3$)



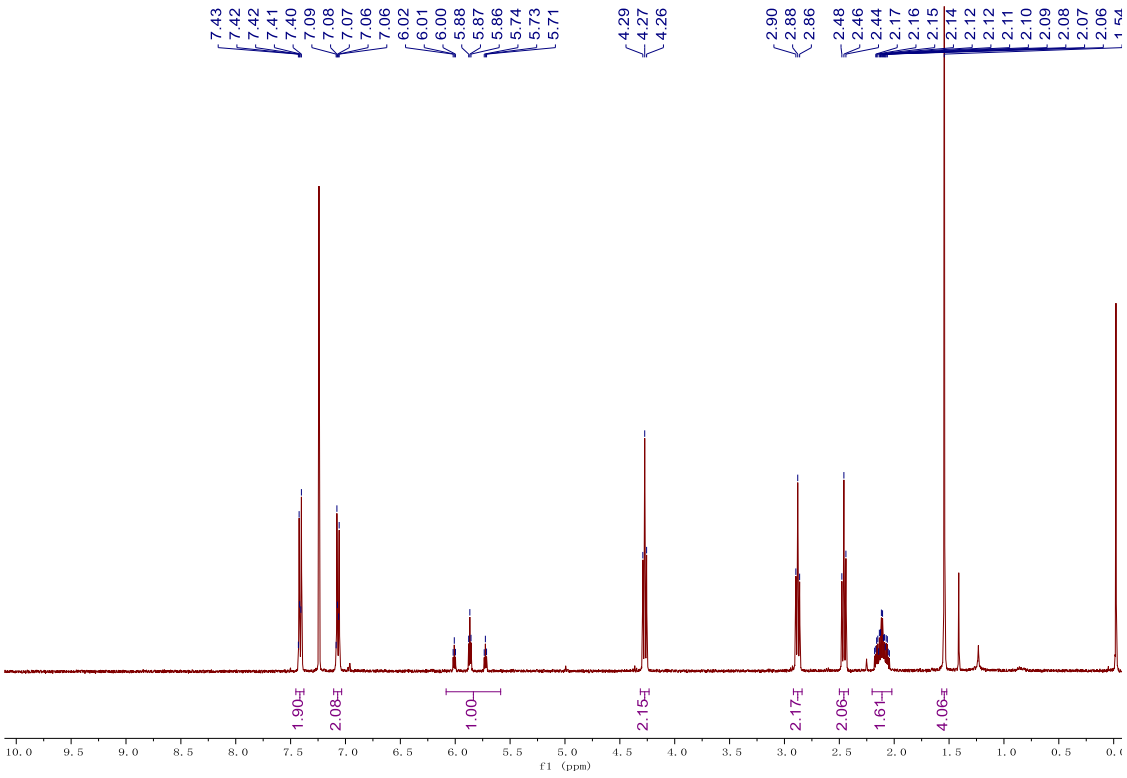


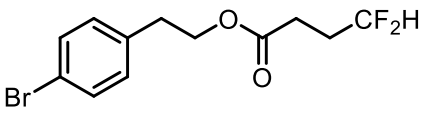
3f ^{13}C NMR
(101 MHz, $CDCl_3$)



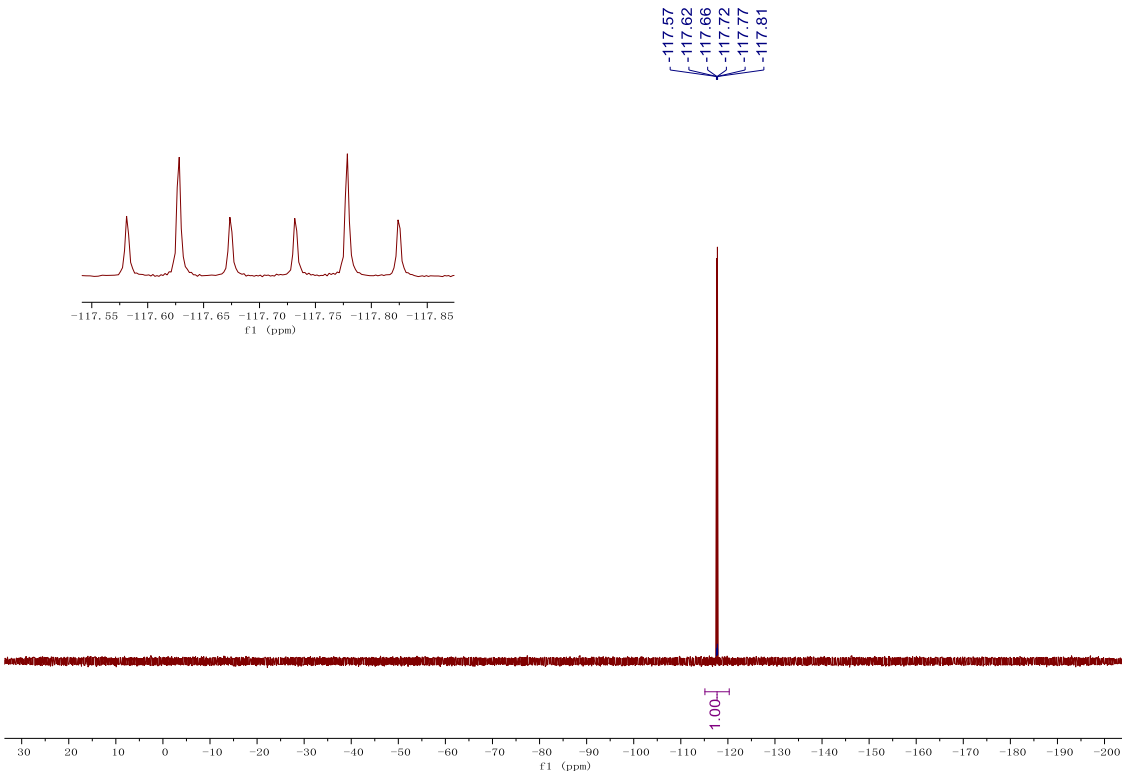


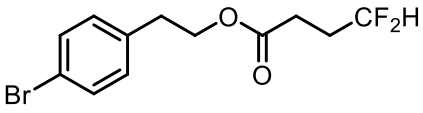
3g ^{1}H NMR
(400 MHz, $CDCl_3$)



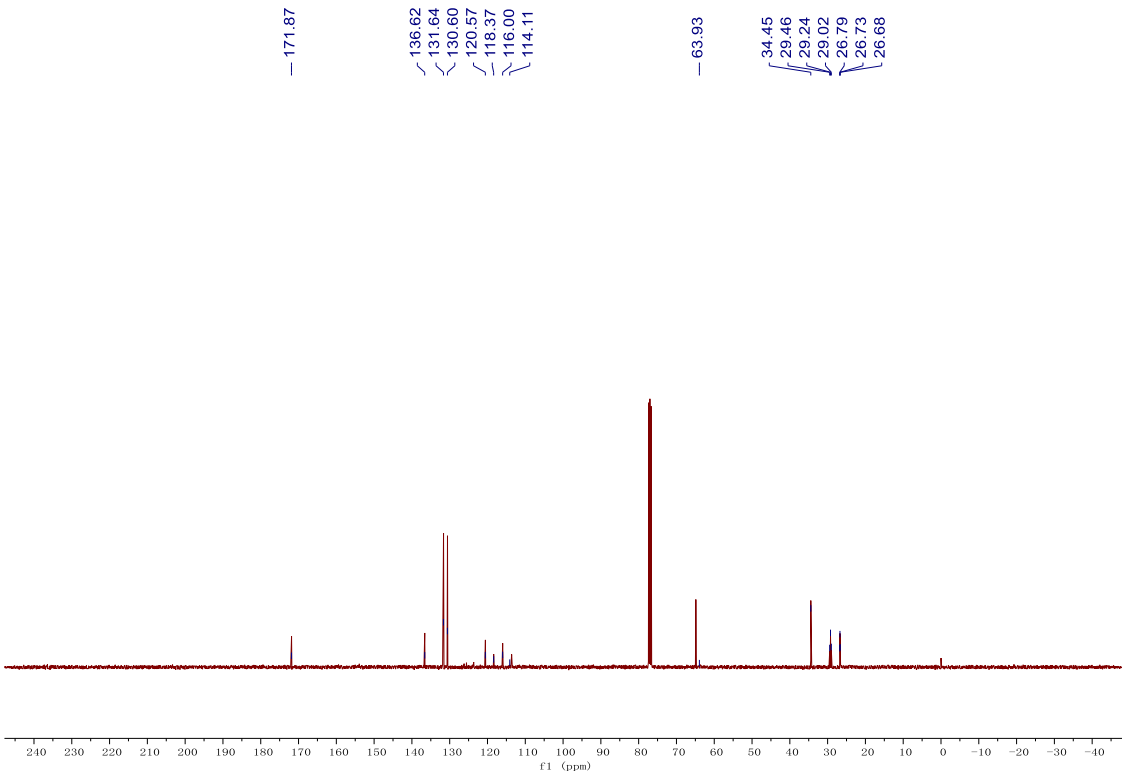


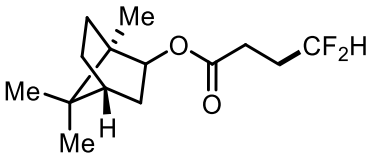
3g ^{19}F NMR
(376 MHz, $CDCl_3$)



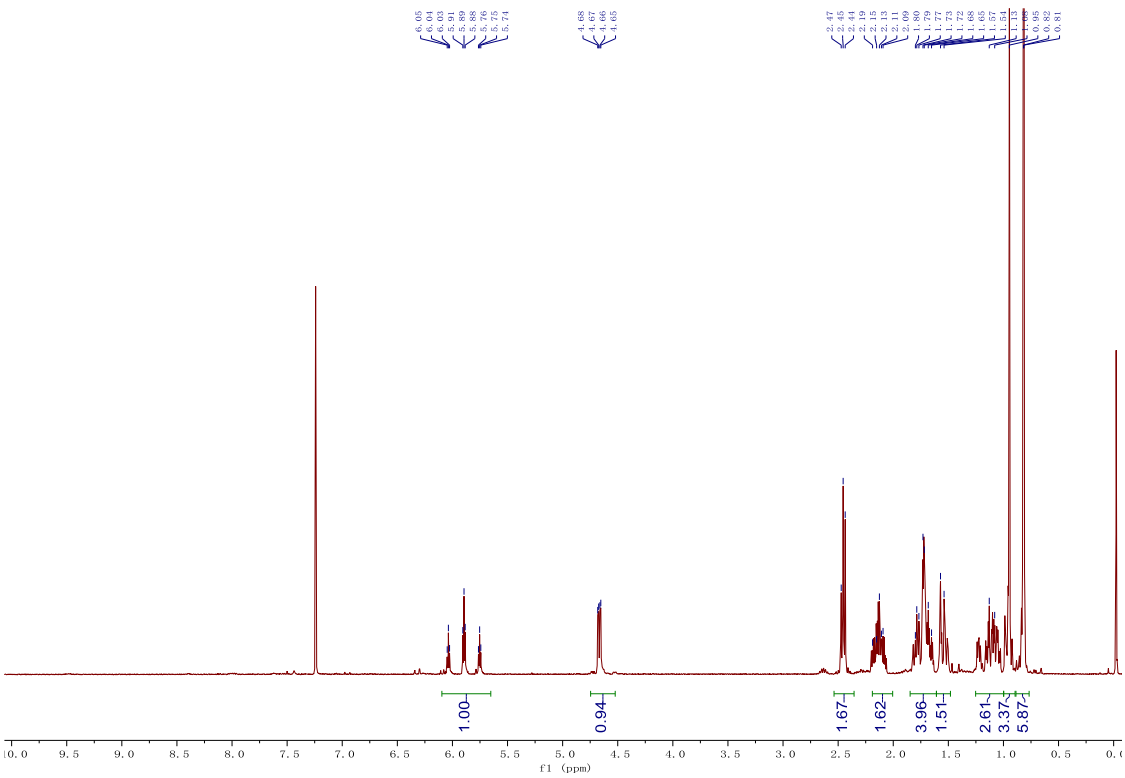


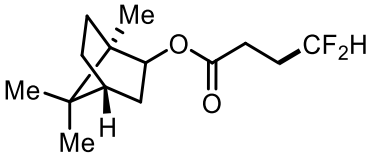
3g ^{13}C NMR
(101 MHz, $CDCl_3$)





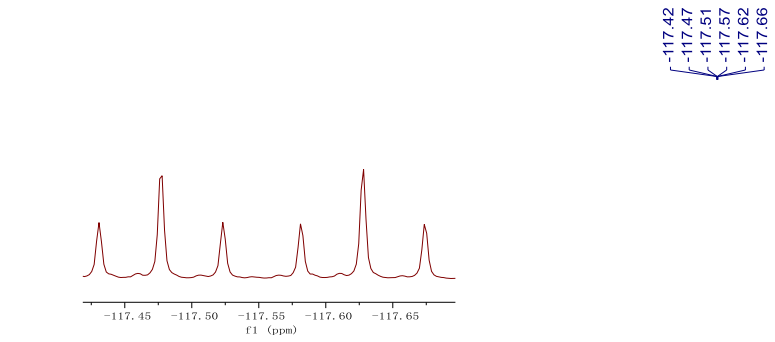
3h ^{1}H NMR
(400 MHz, $CDCl_3$)

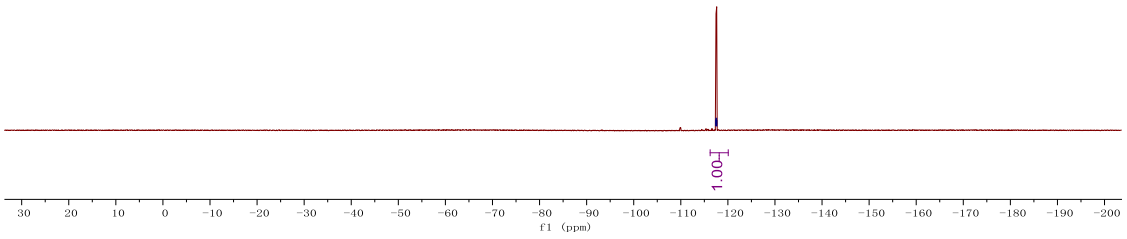


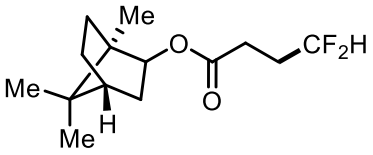


3h ^{19}F NMR

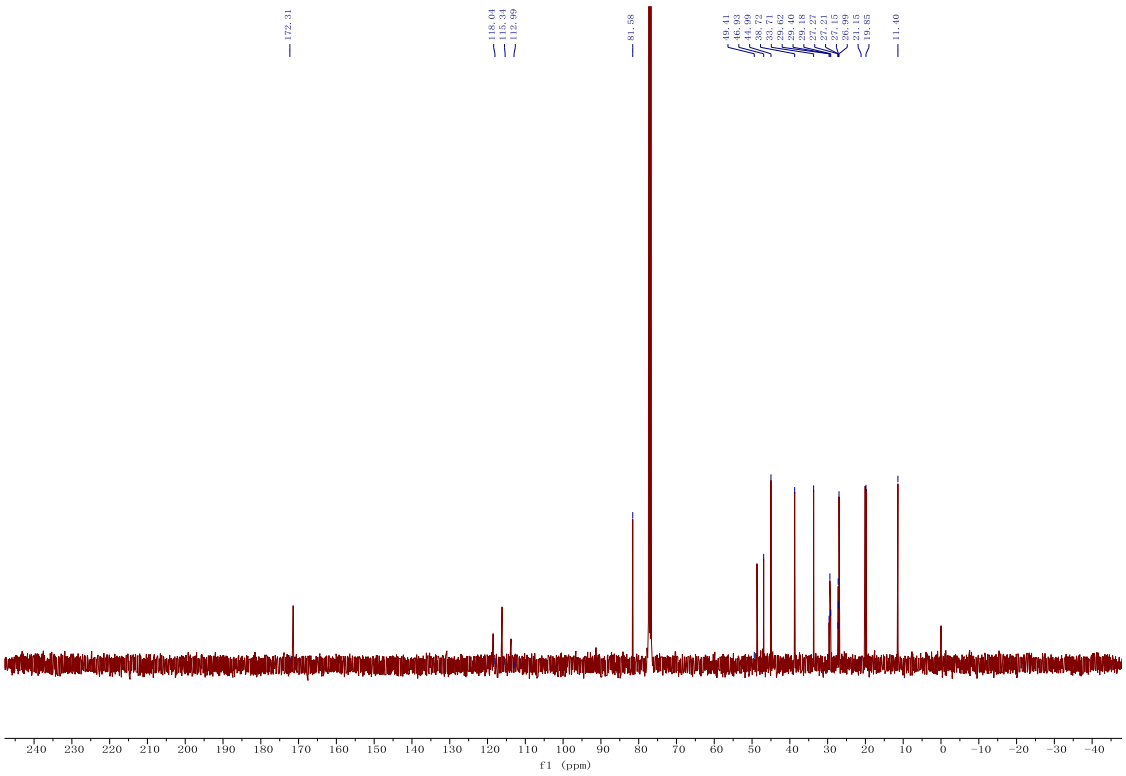
(376 MHz, $CDCl_3$)

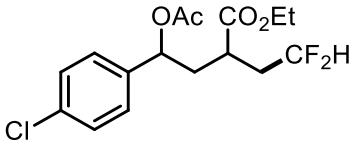




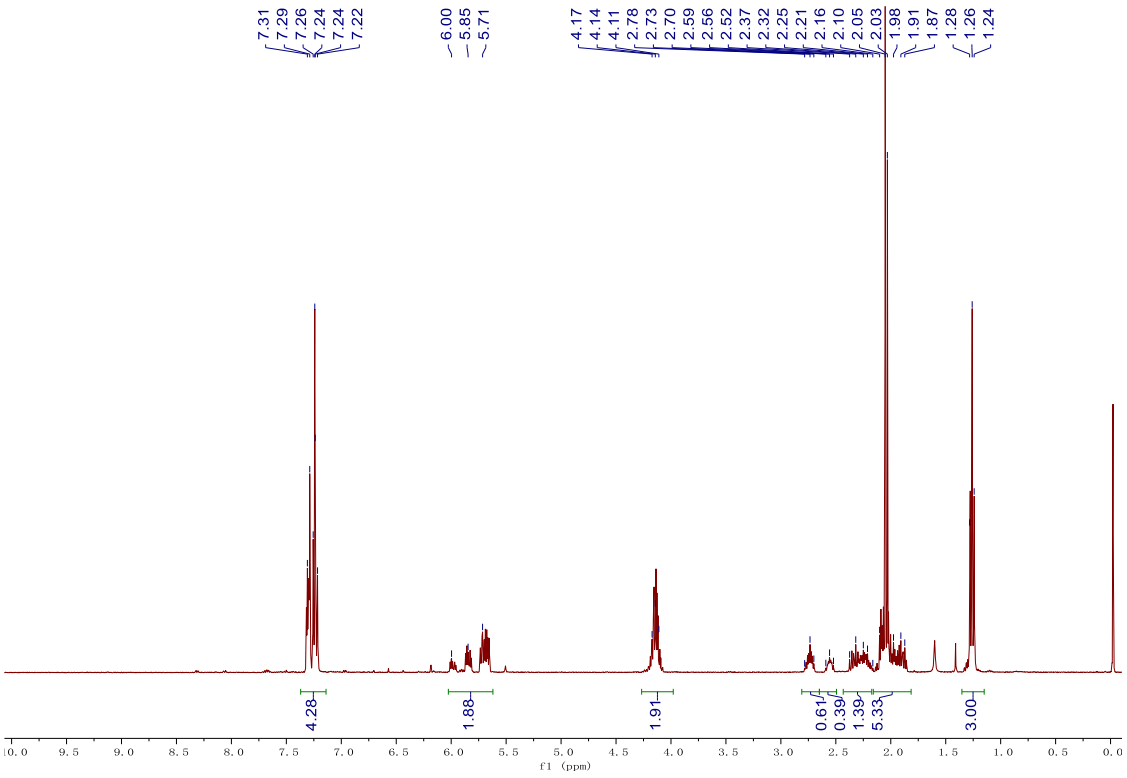


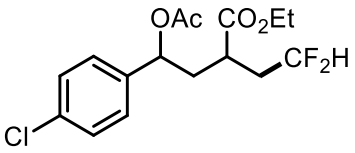
3h ^{13}C NMR
(101 MHz, $CDCl_3$)



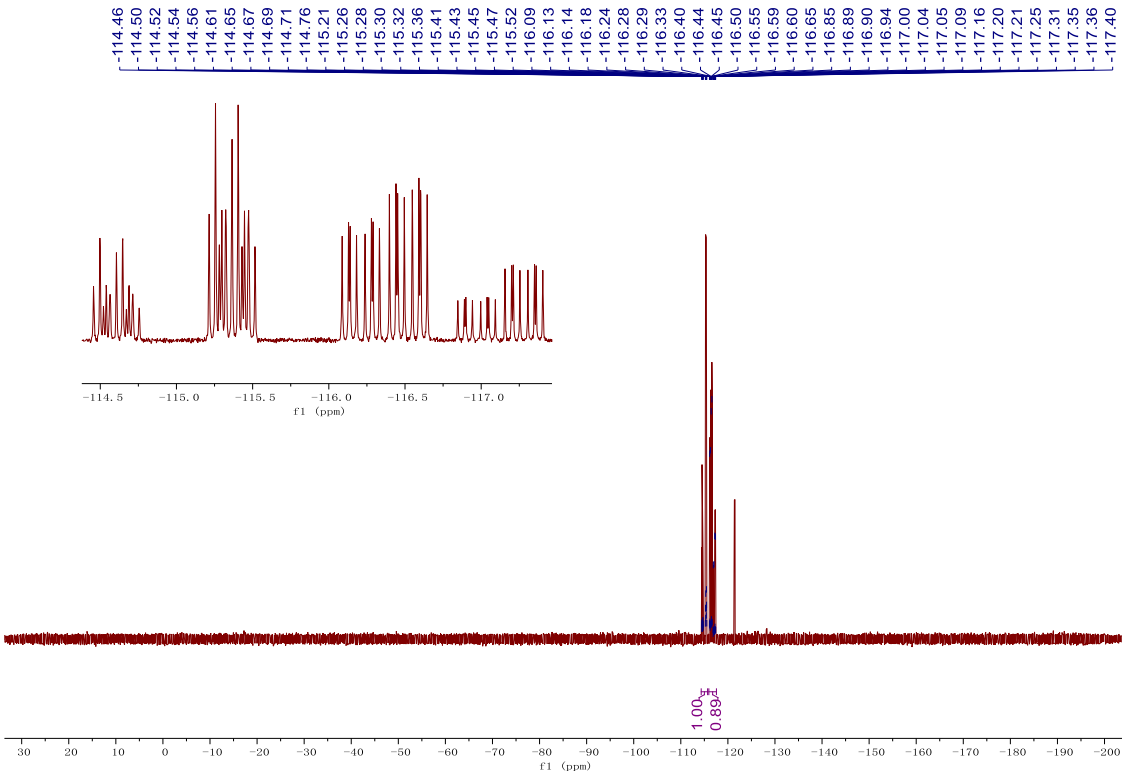


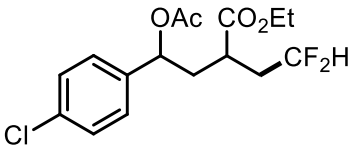
3i ^{1}H NMR
(400MHz, $CDCl_3$)



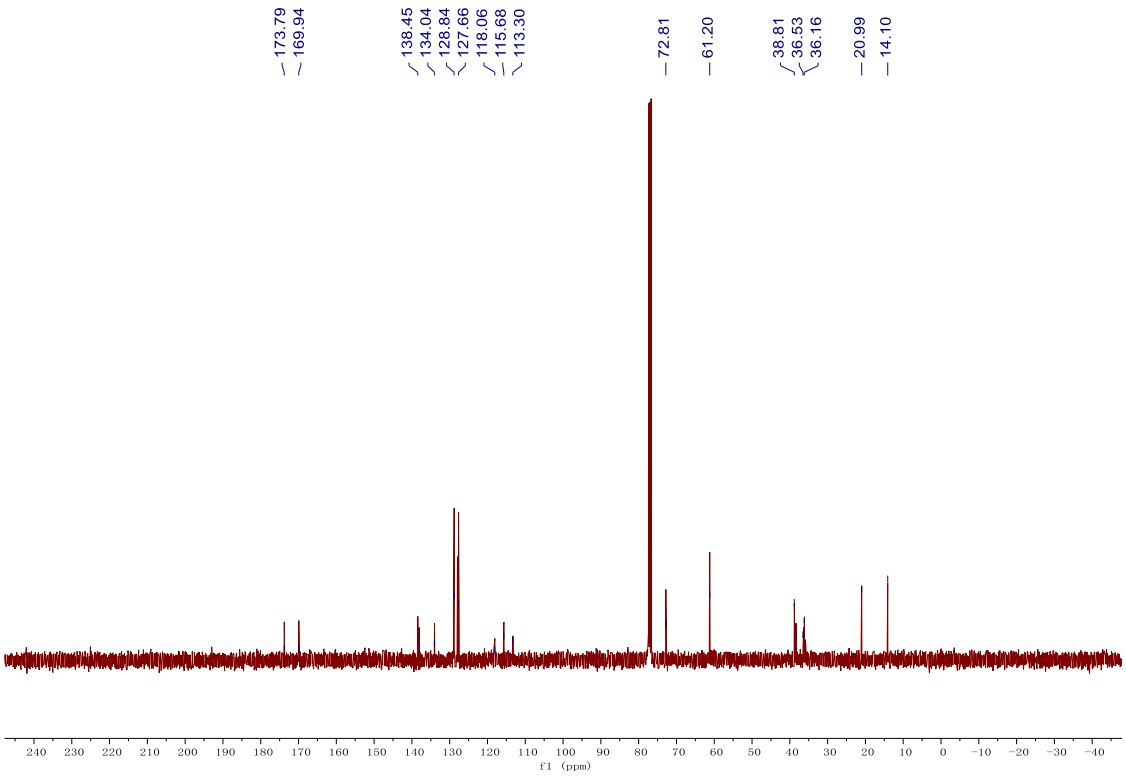


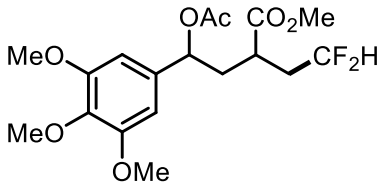
3i ^{19}F NMR
(376 MHz, $CDCl_3$)



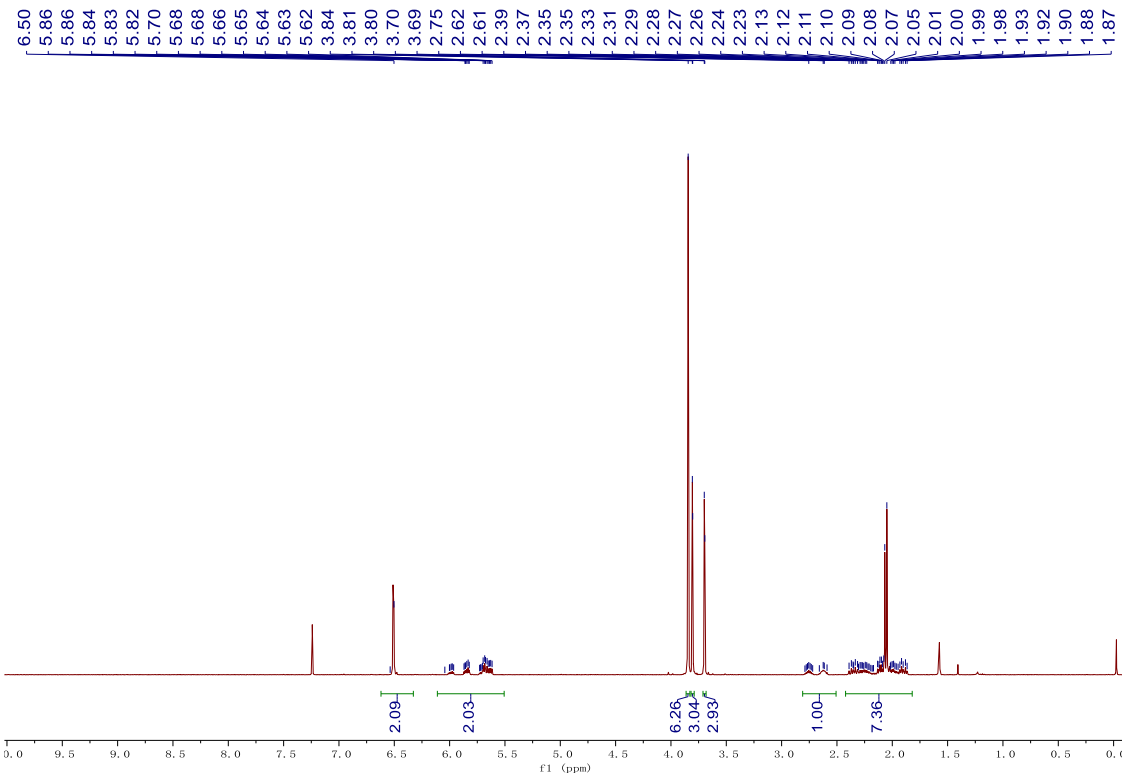


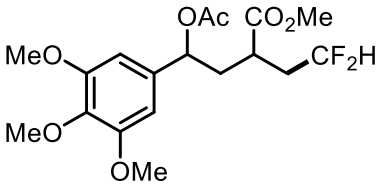
3i ^{13}C NMR
(101 MHz, $CDCl_3$)



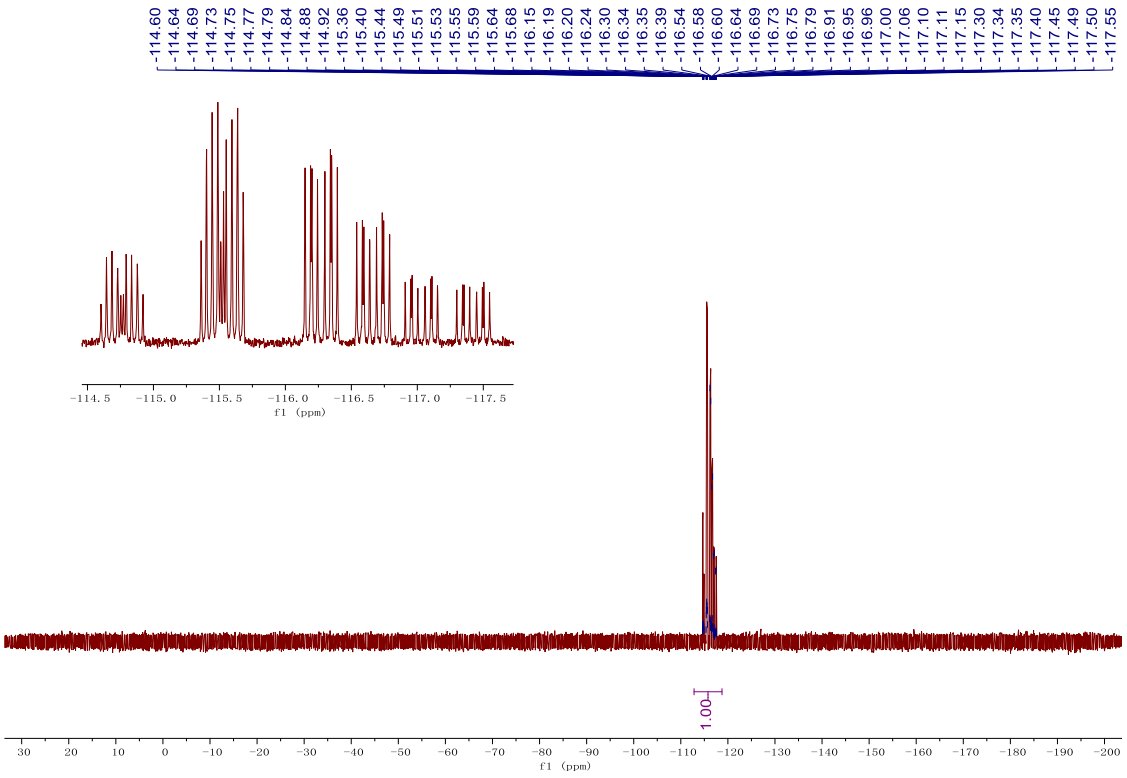


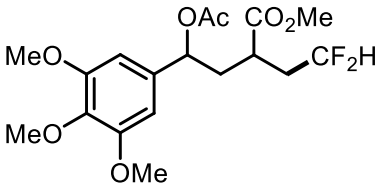
3j ^{1}H NMR
(400 MHz, $CDCl_3$)



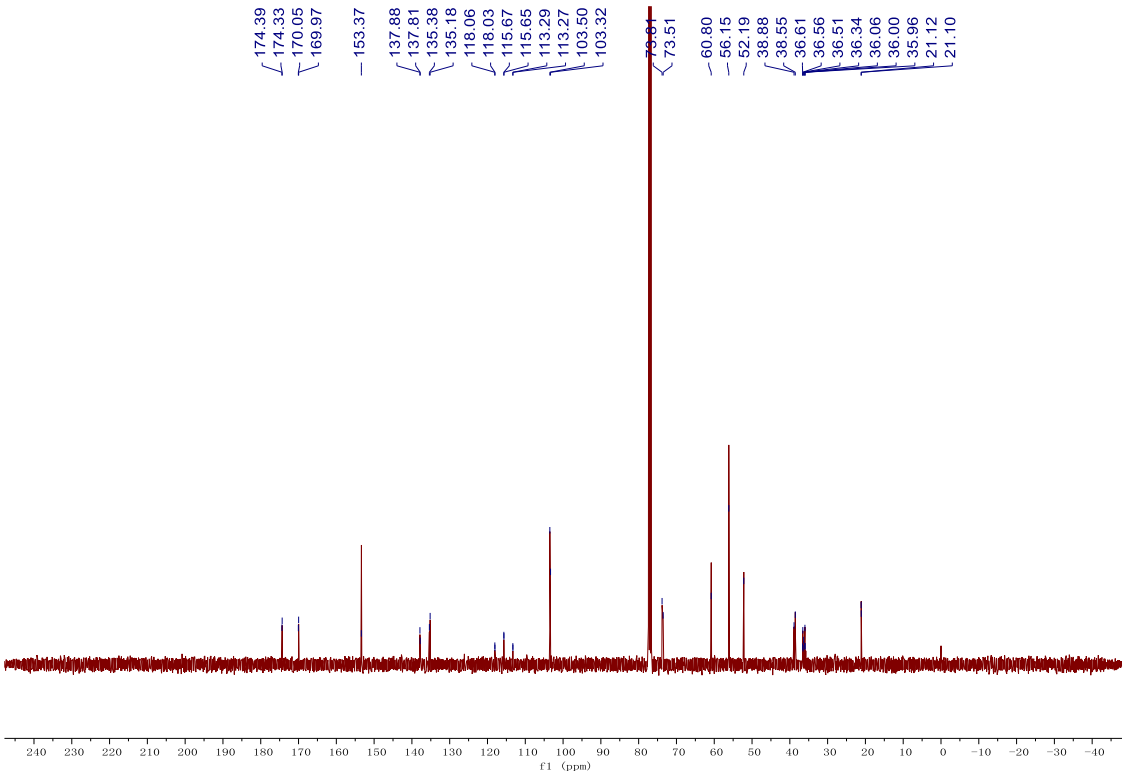


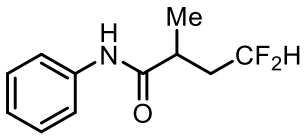
3j ^{19}F NMR
(376 MHz, $CDCl_3$)



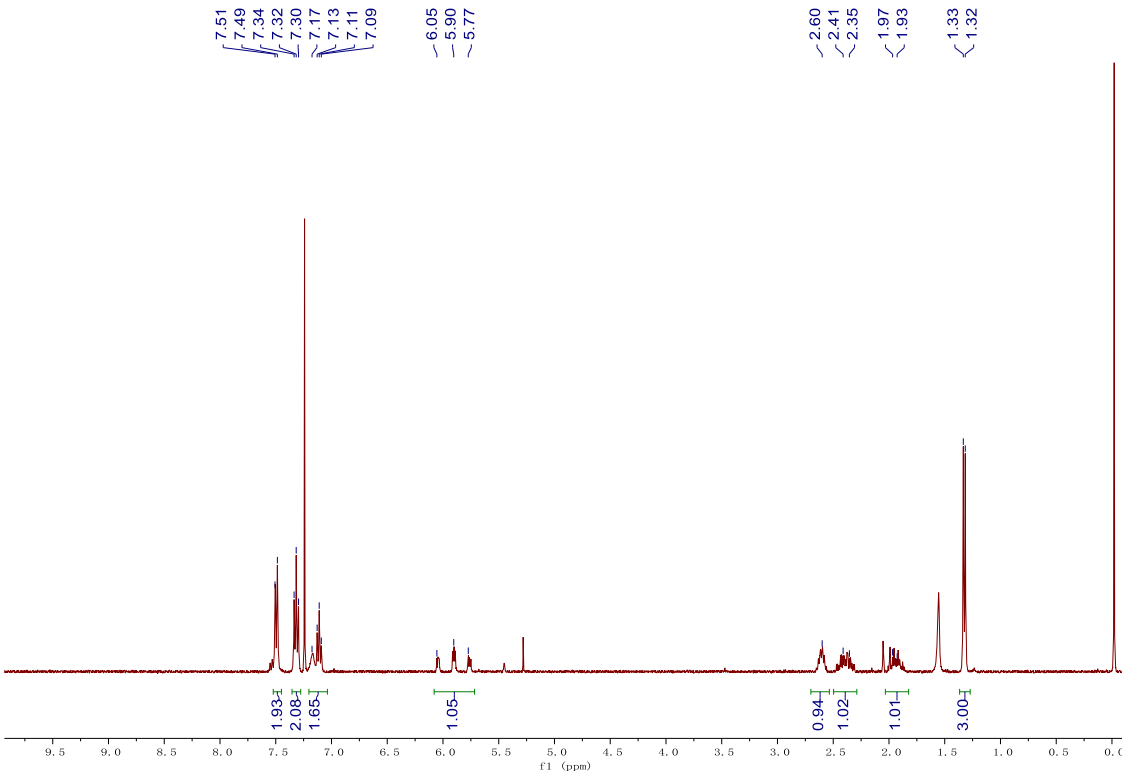


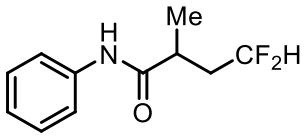
3j ^{13}C NMR
(101 MHz, $CDCl_3$)



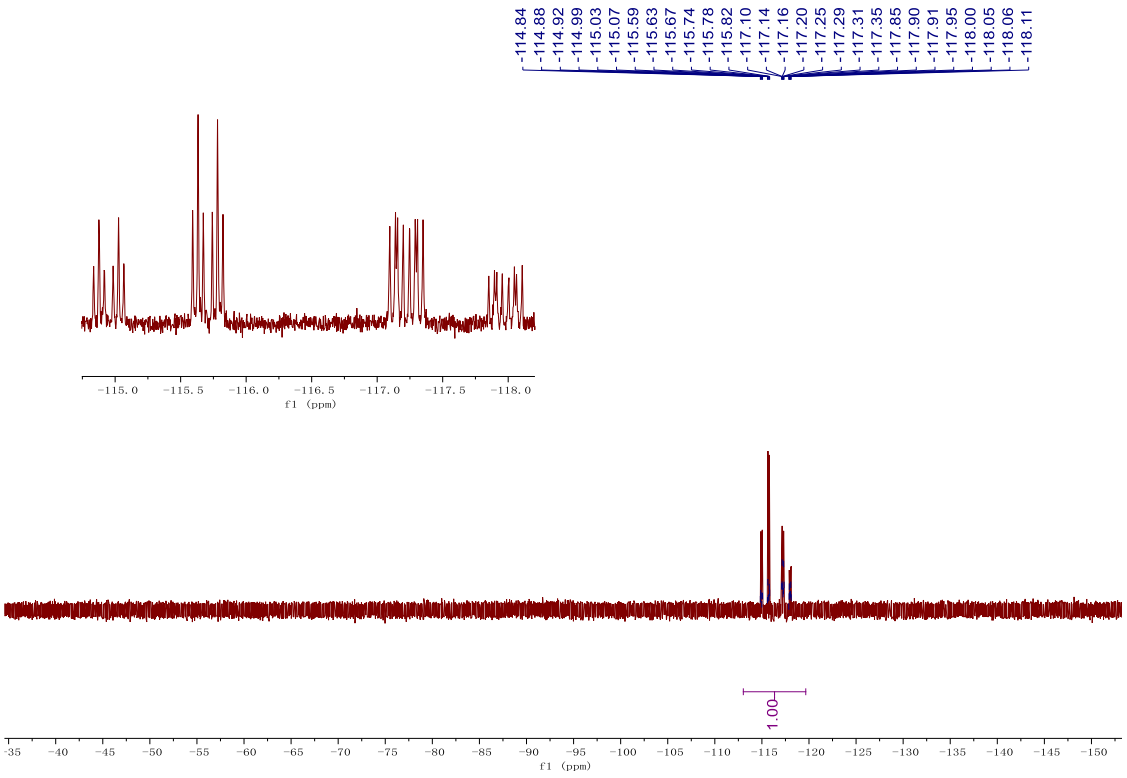


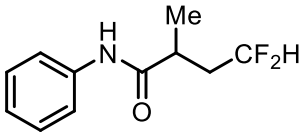
3k ^{1}H NMR
(400 MHz, $CDCl_3$)



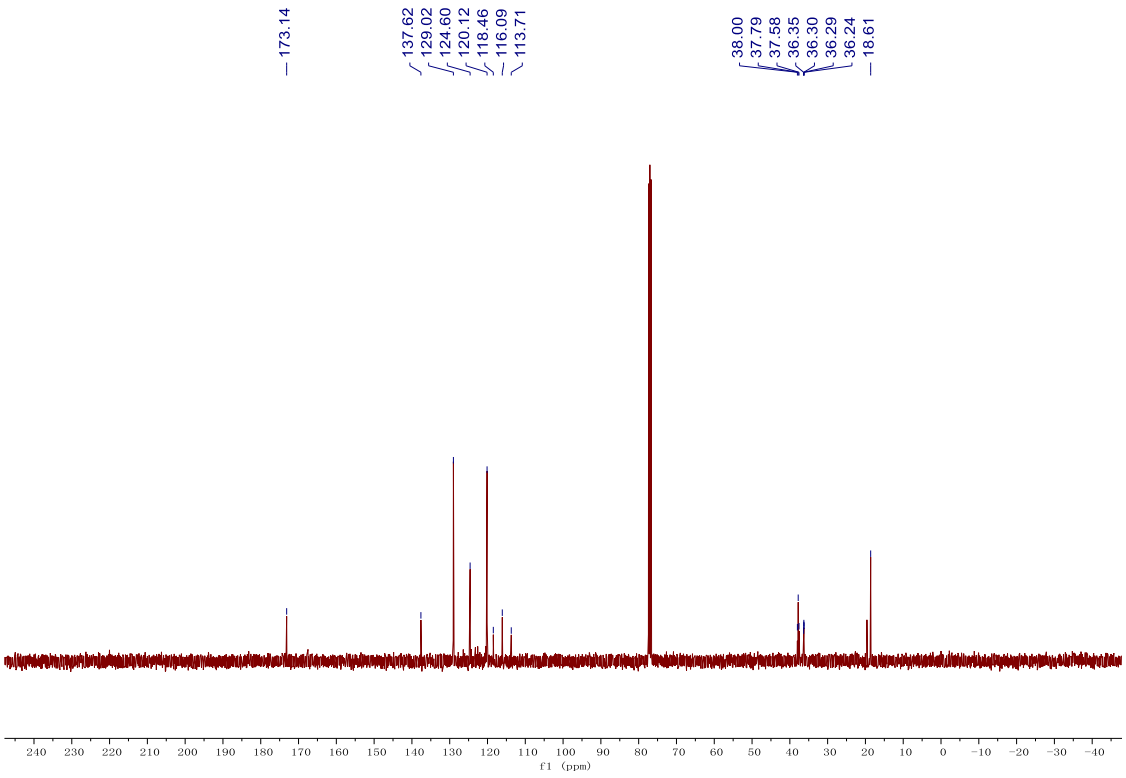


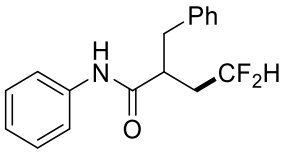
3k ^{19}F NMR
(376 MHz, $CDCl_3$)



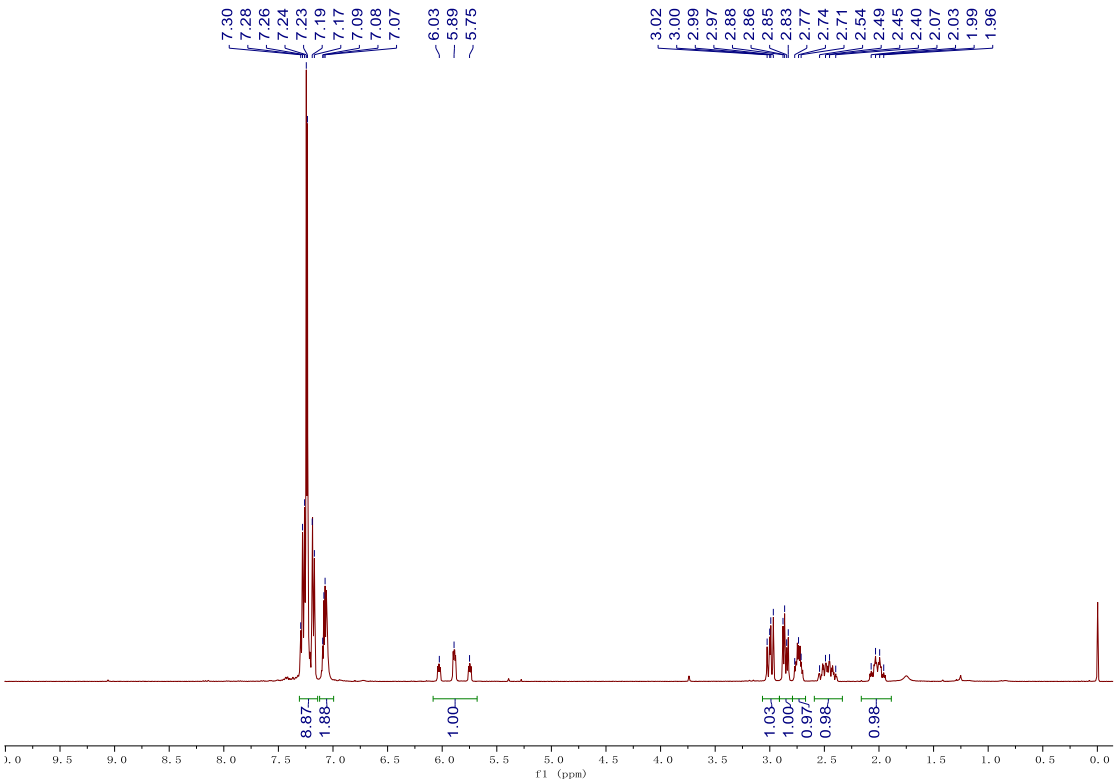


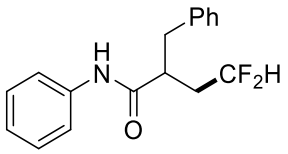
3k ^{13}C NMR
(101 MHz, $CDCl_3$)



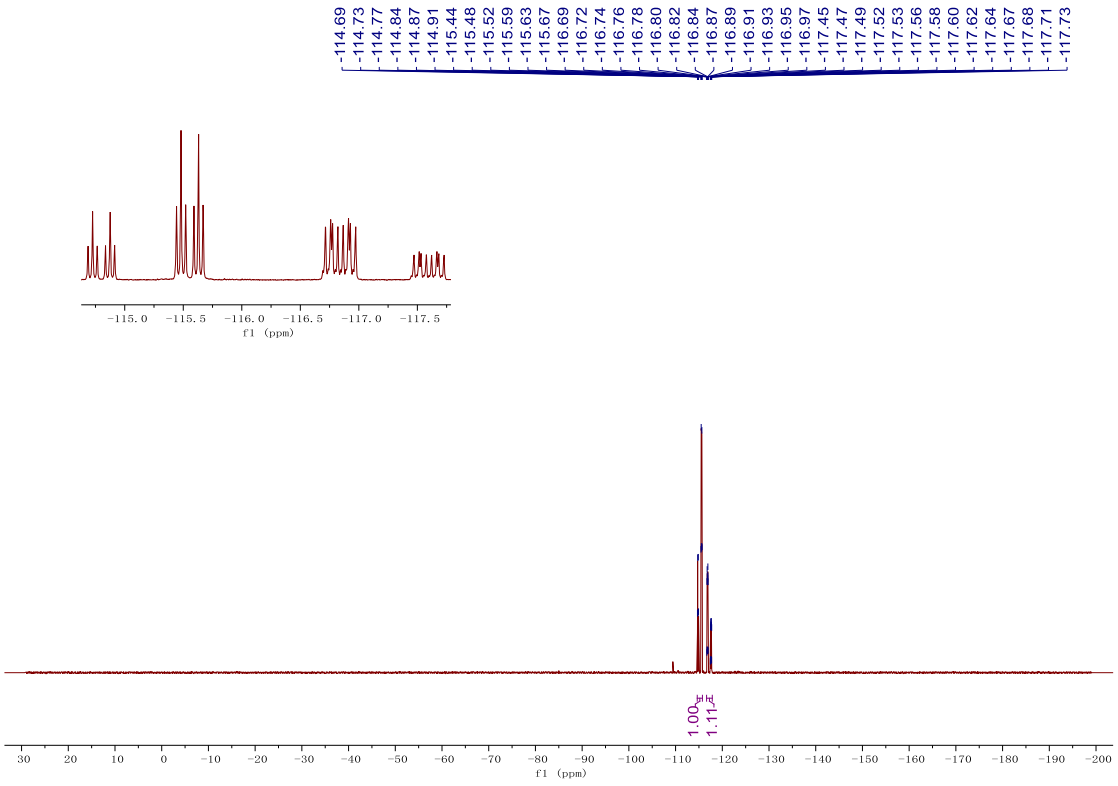


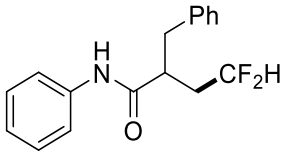
3l ^{1}H NMR
(400 MHz, $CDCl_3$)



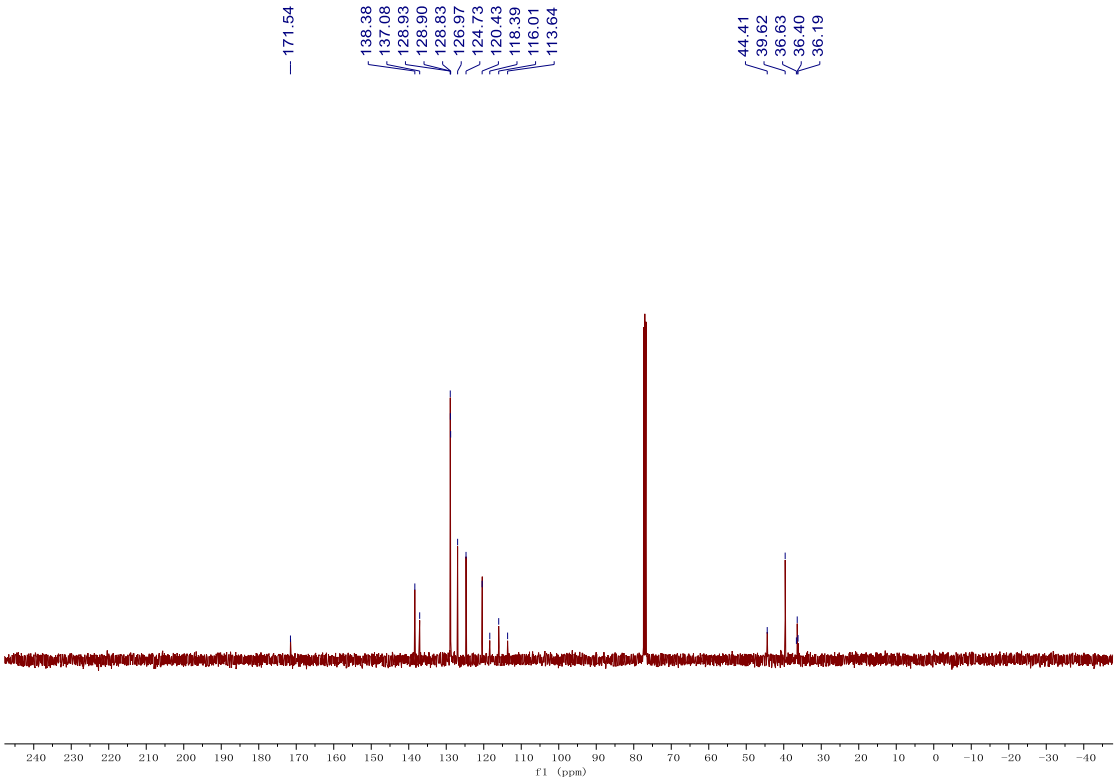


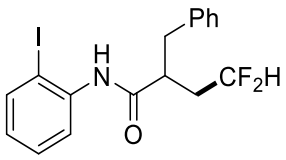
3l ^{19}F NMR
(376 MHz, $CDCl_3$)



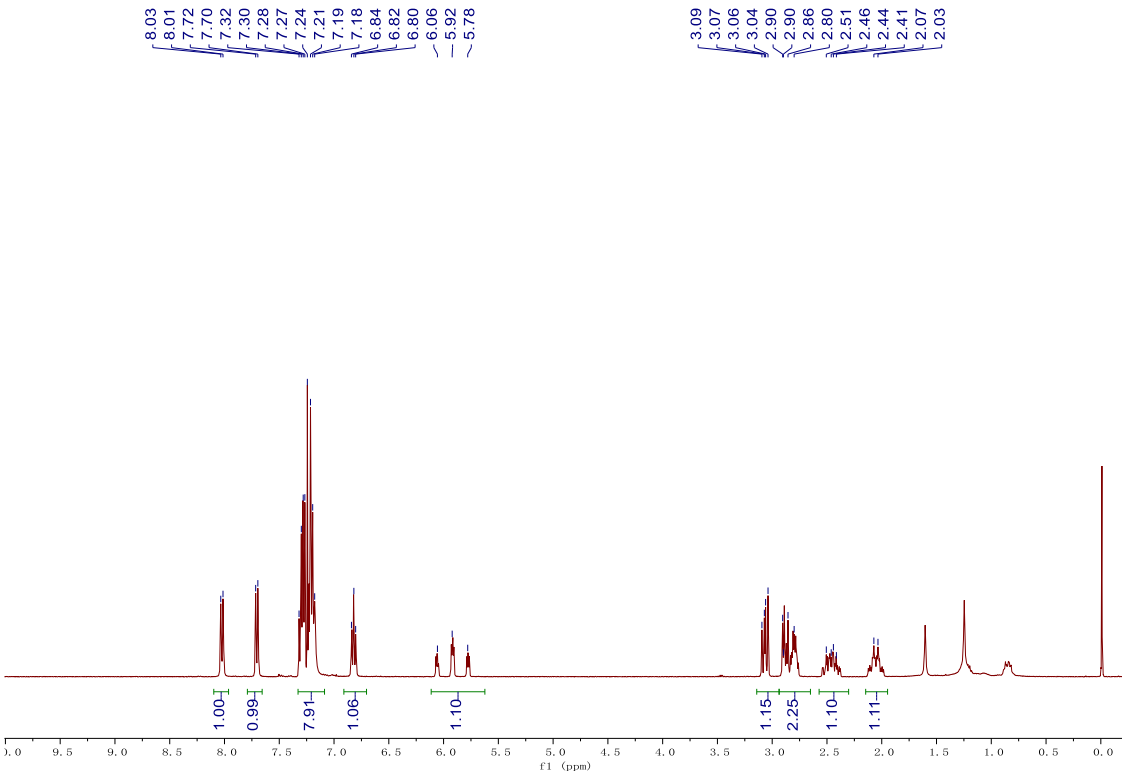


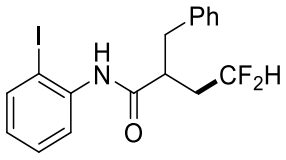
3l ^{13}C NMR
(100 MHz, $CDCl_3$)



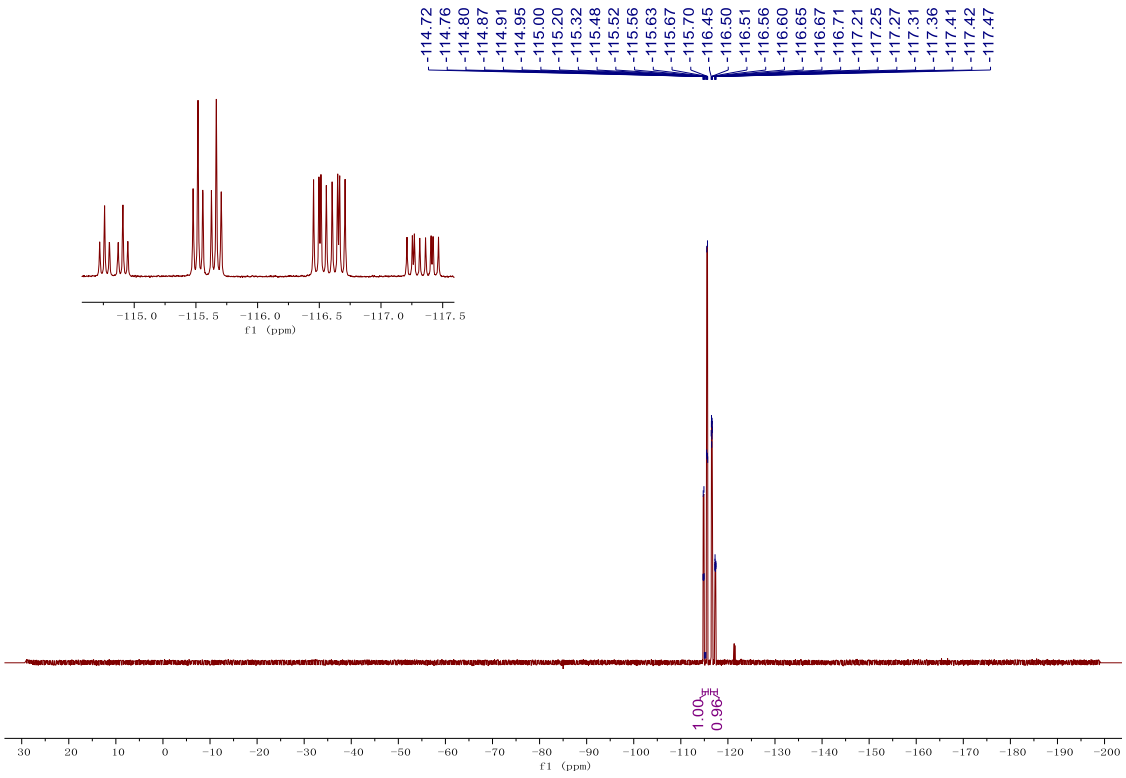


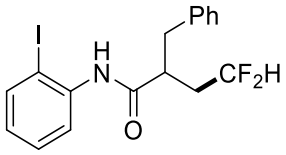
3m ^{1}H NMR
(400 MHz, $CDCl_3$)



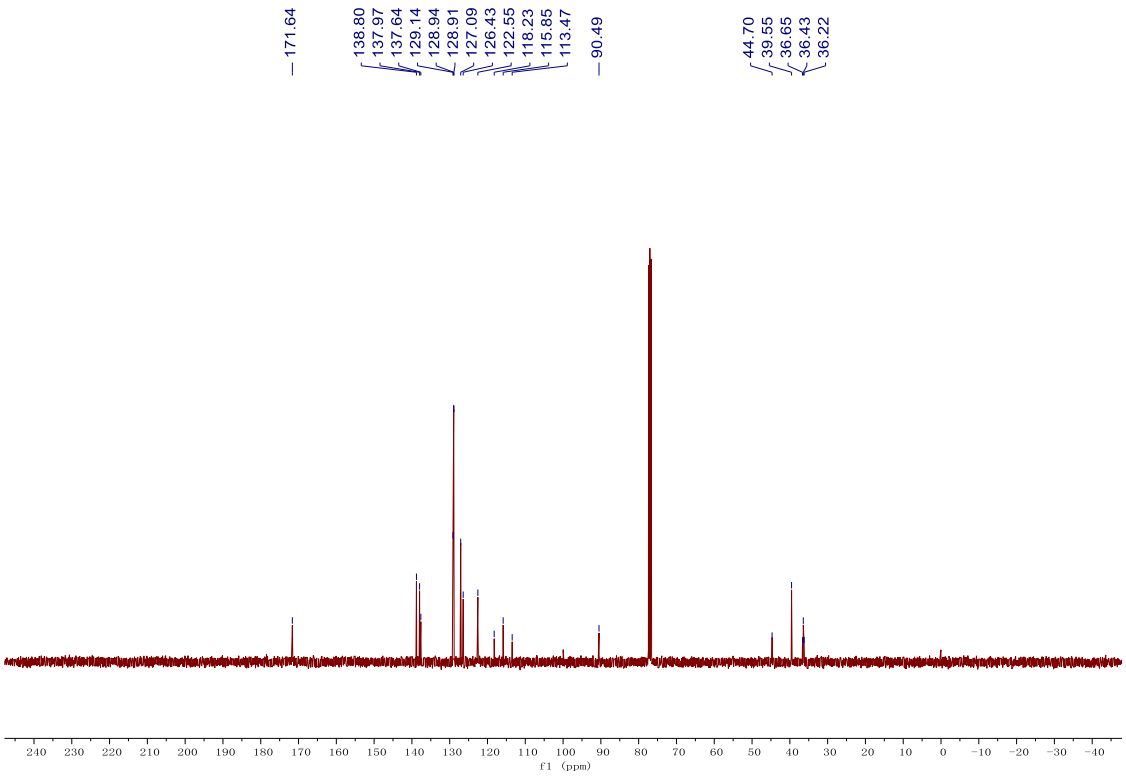


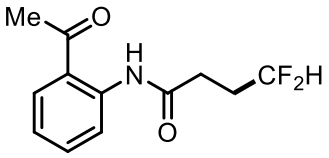
3m ^{19}F NMR
(376 MHz, $CDCl_3$)



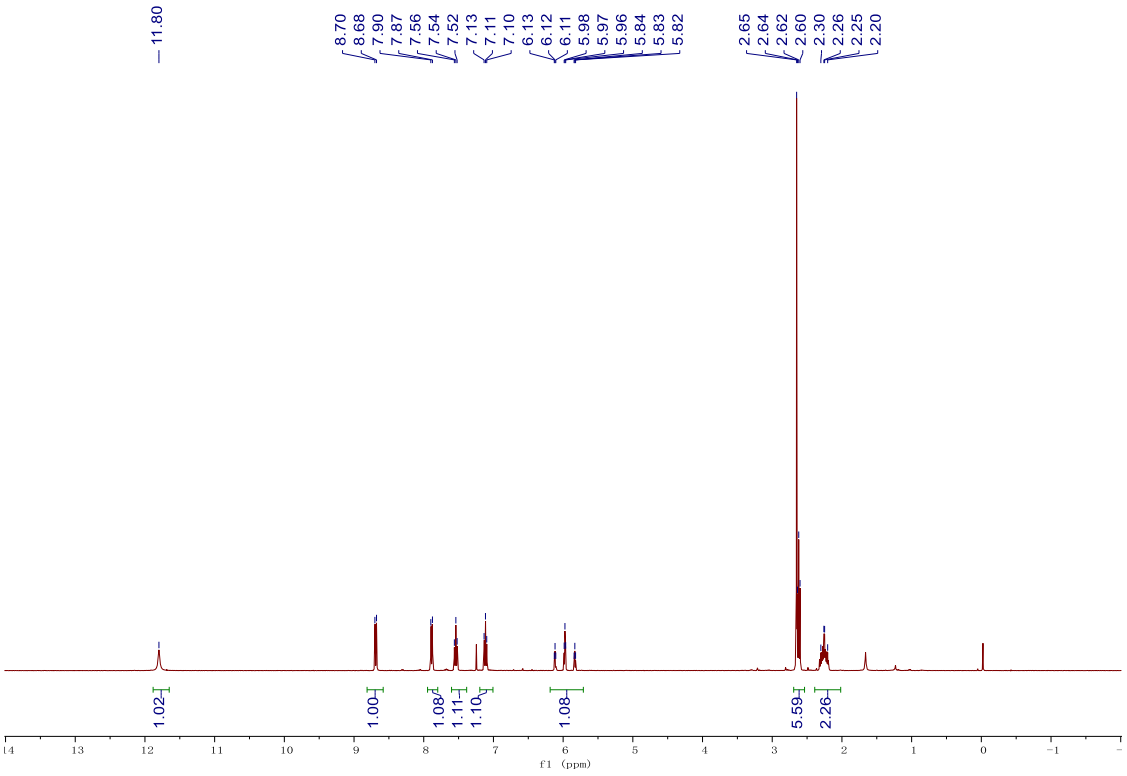


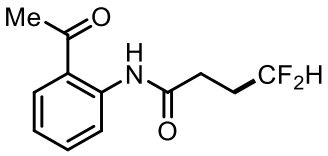
3m ^{13}C NMR
(101 MHz, $CDCl_3$)



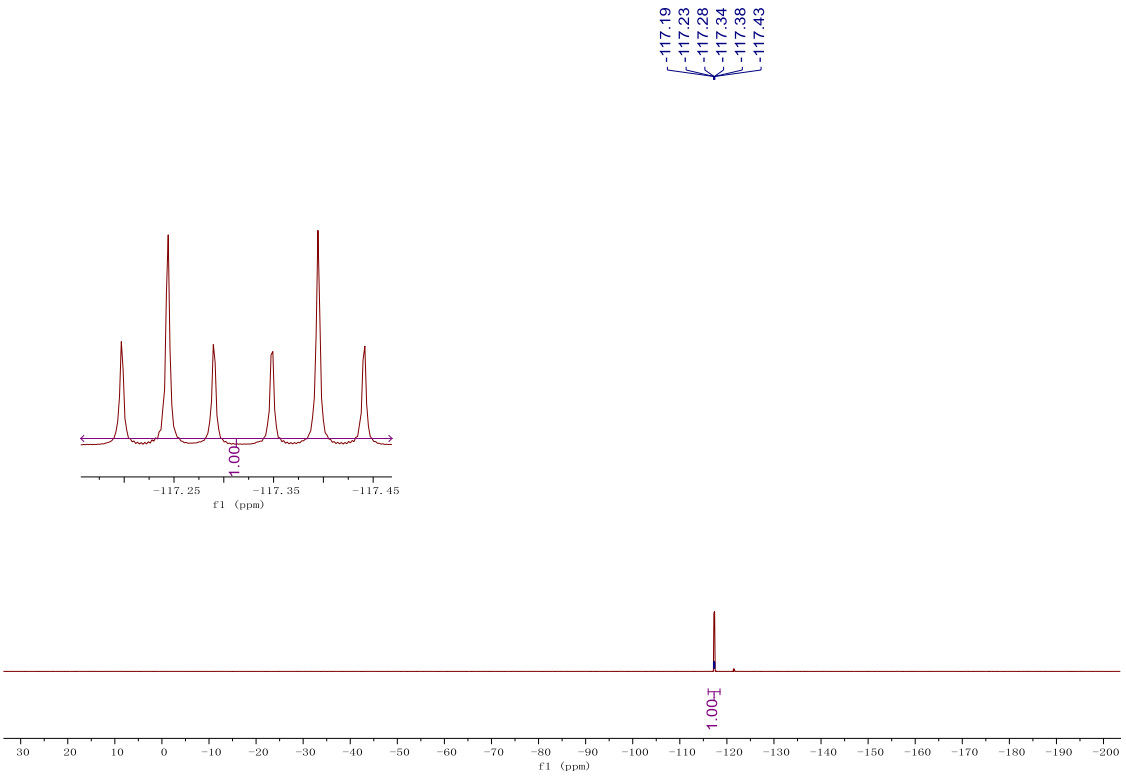


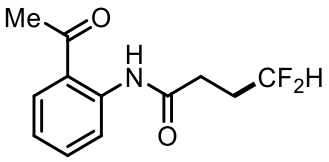
3n ^{1}H NMR
(400 MHz, $CDCl_3$)



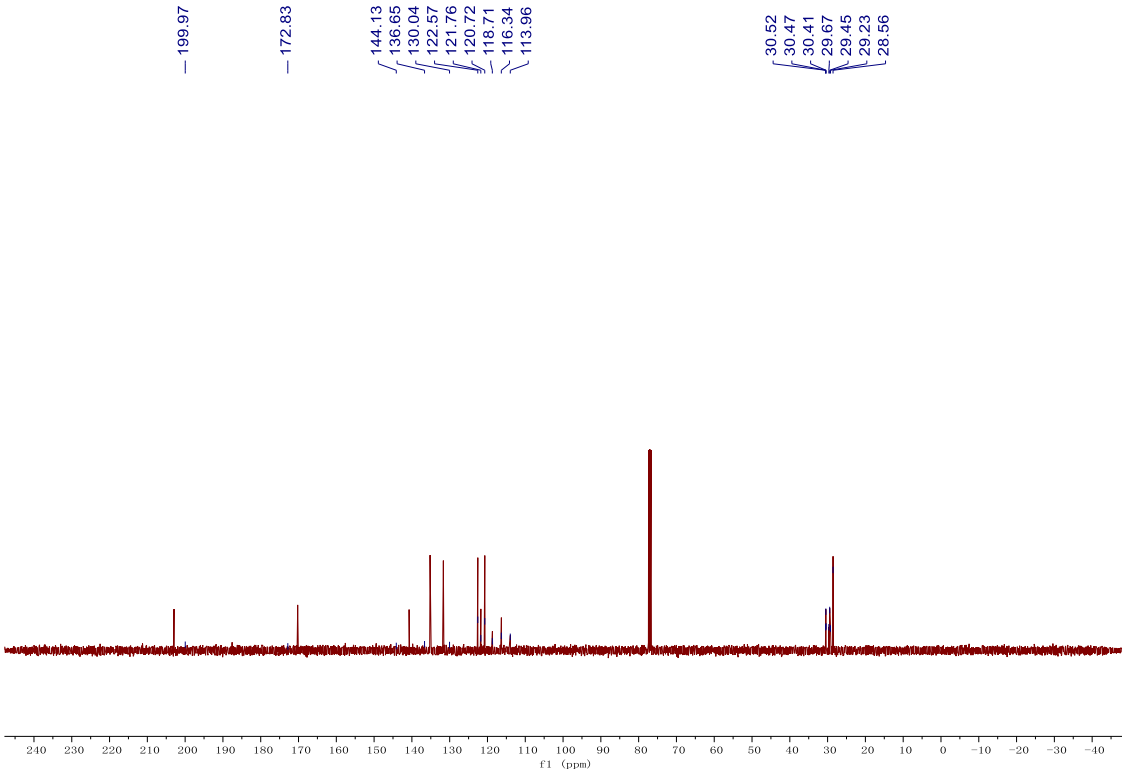


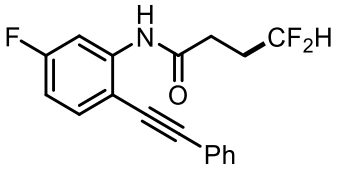
3n ^{19}F NMR
(376 MHz, $CDCl_3$)



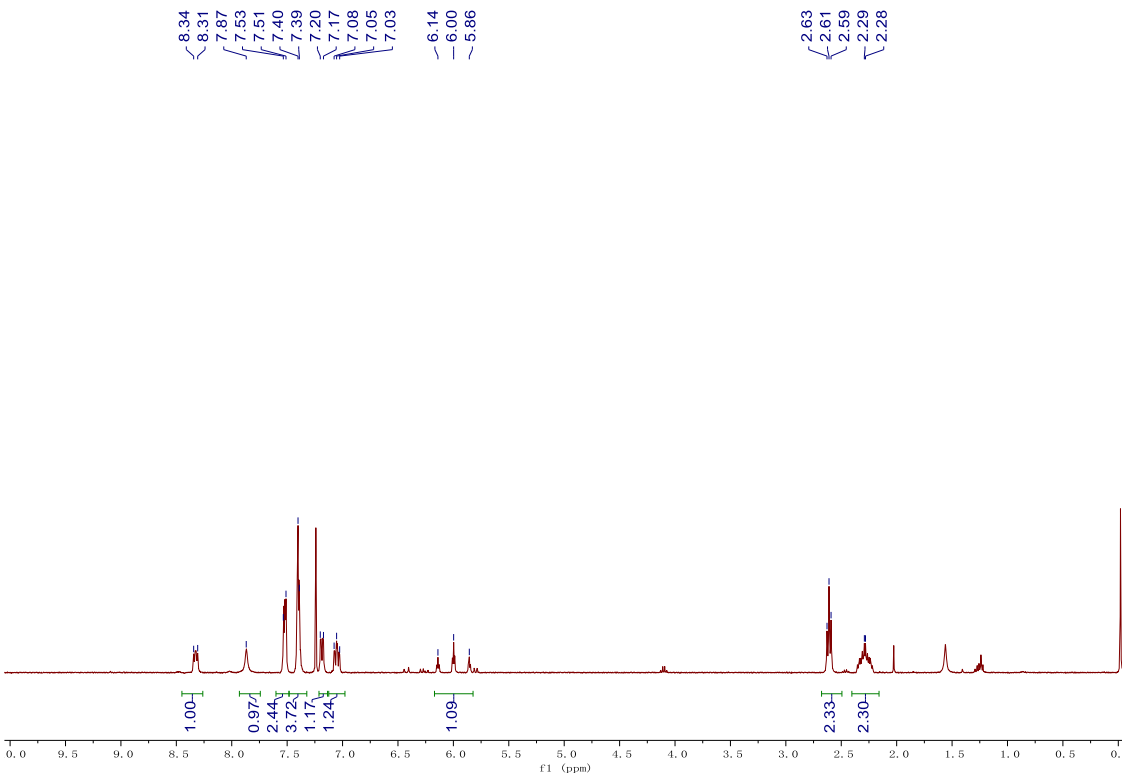


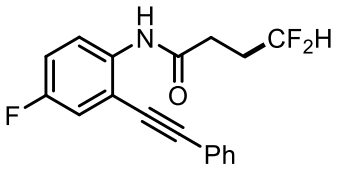
3n ^{13}C NMR
(101 MHz, $CDCl_3$)



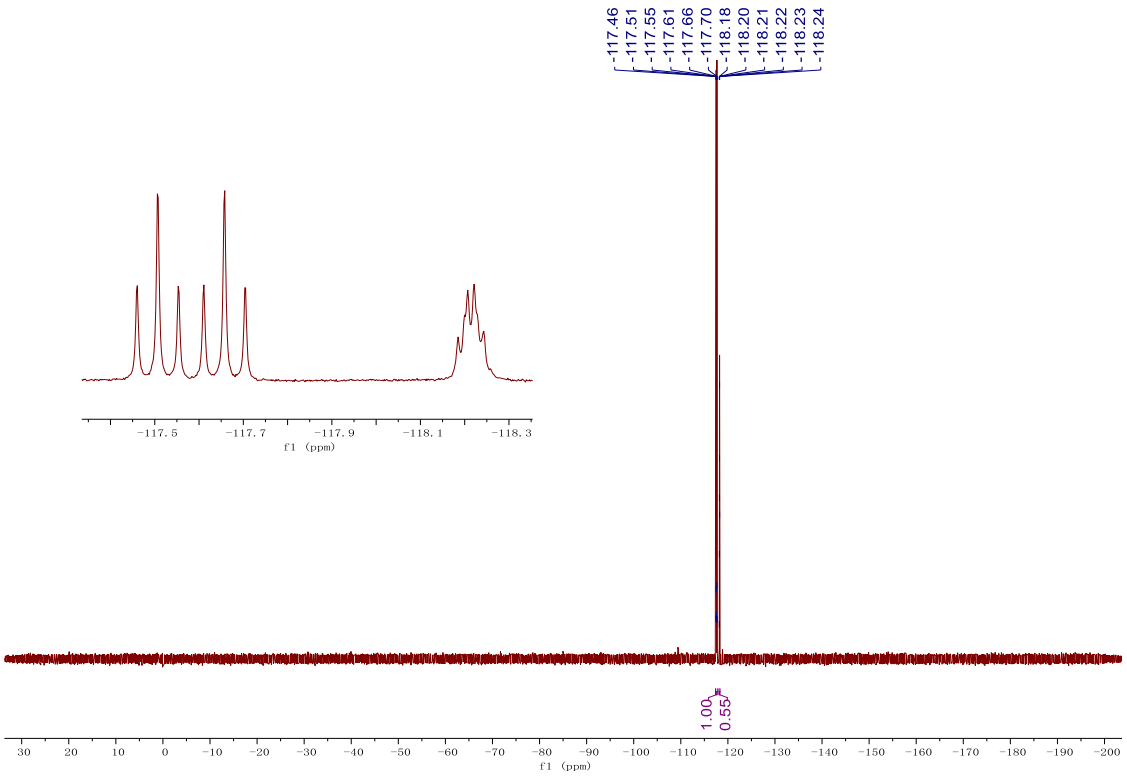


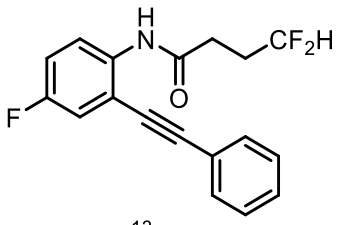
3o ^{1}H NMR
(400 MHz, $CDCl_3$)



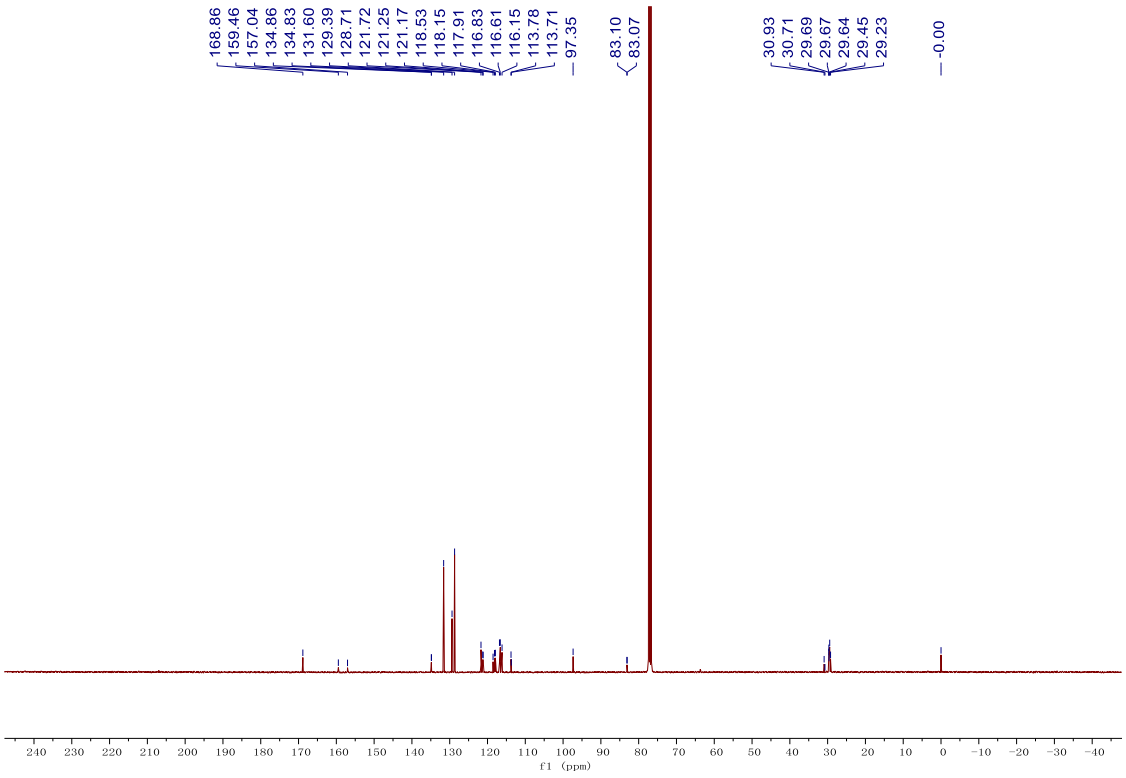


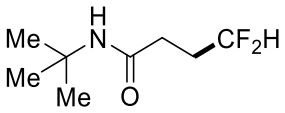
3o ^{19}F NMR
(376 MHz, $CDCl_3$)



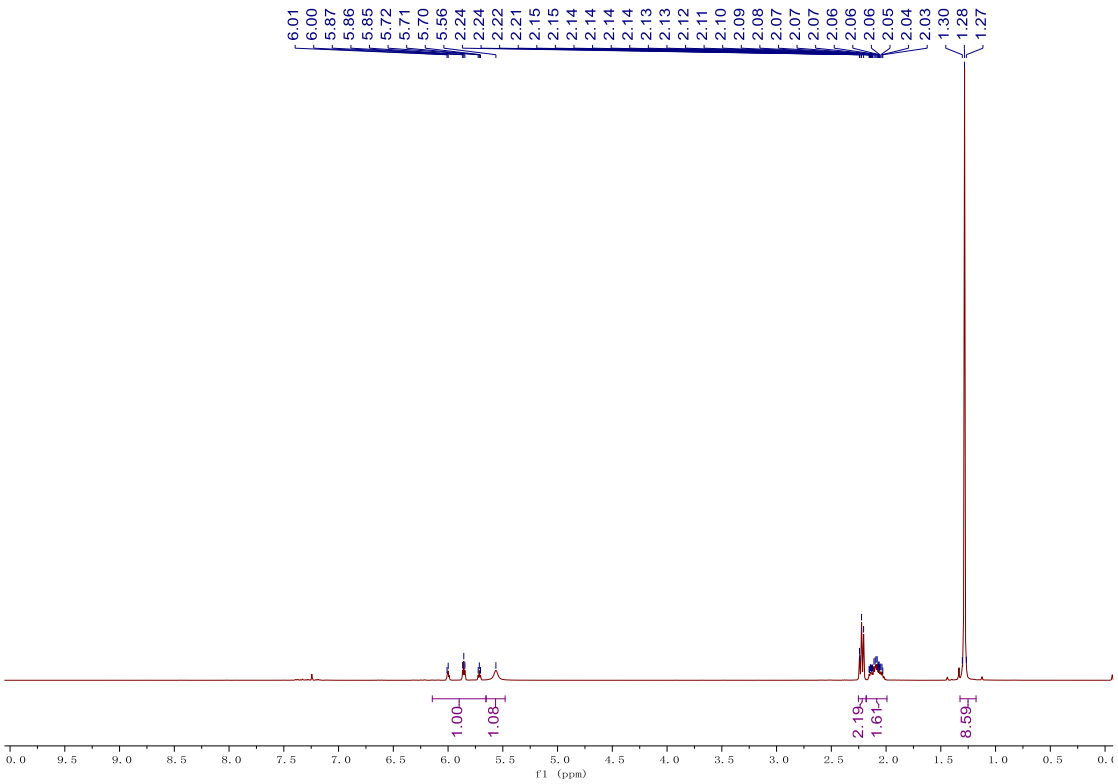


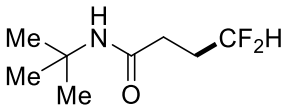
3o ^{13}C NMR
(101 MHz, $CDCl_3$)



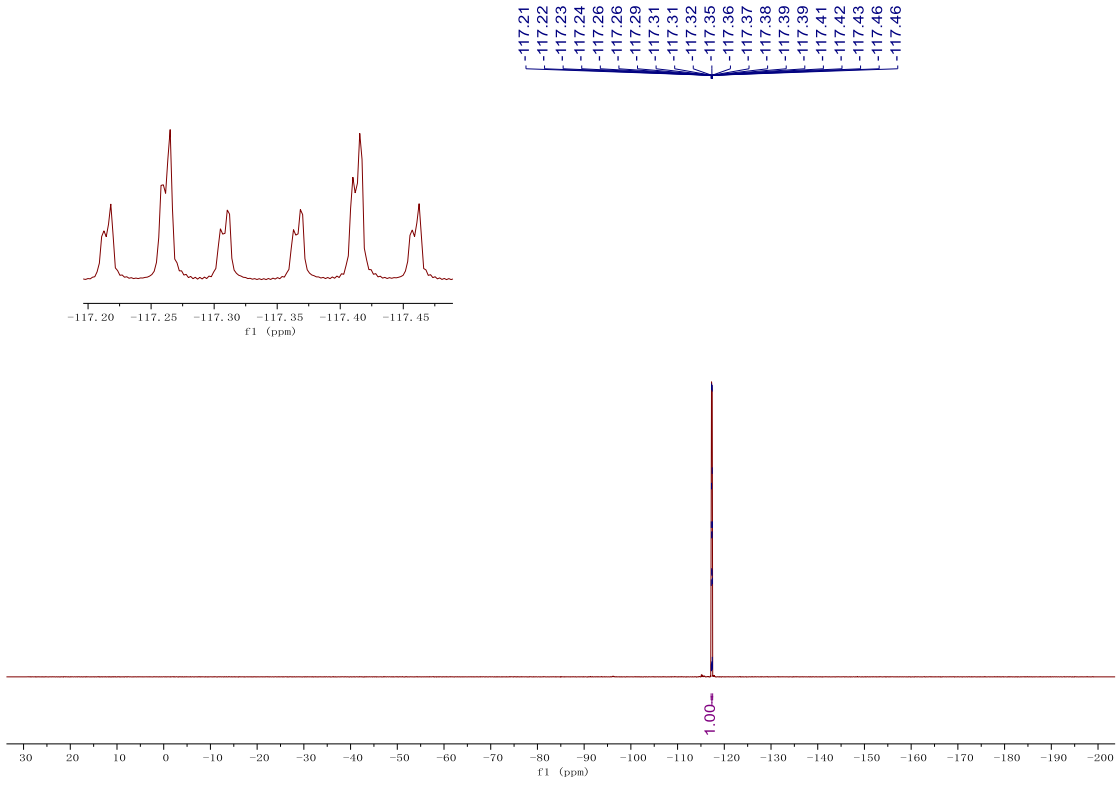


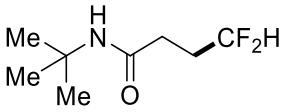
3p ^{1}H NMR
(400 MHz, $CDCl_3$)



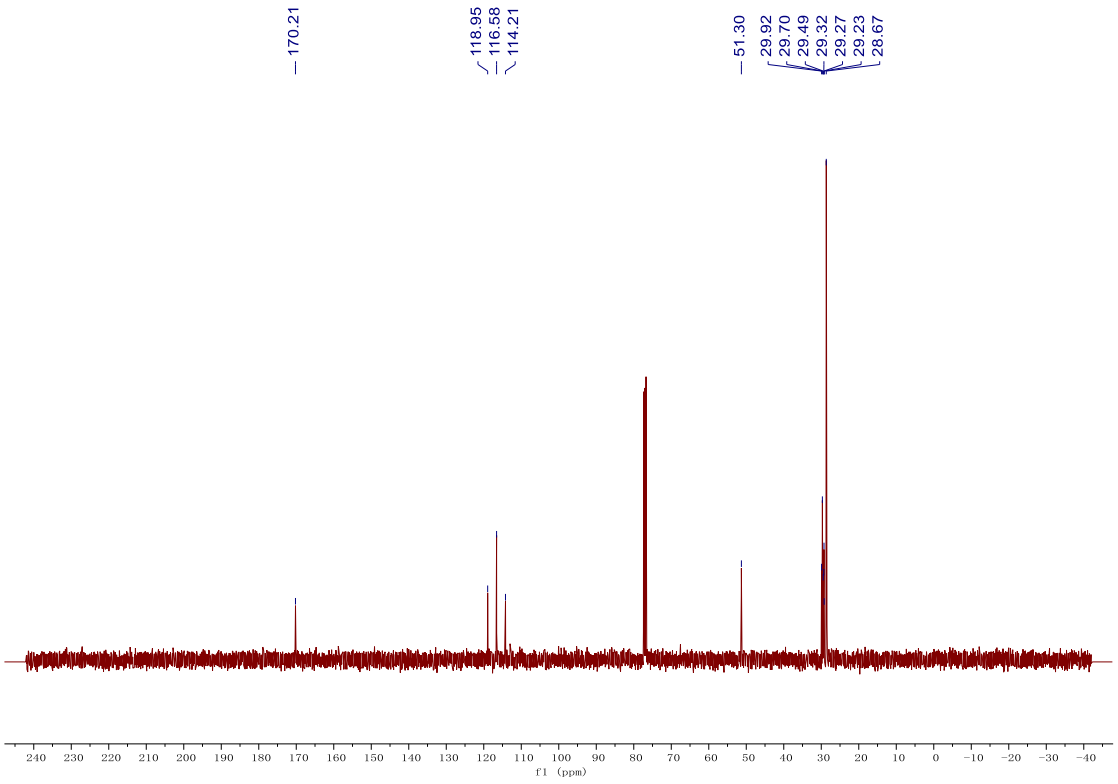


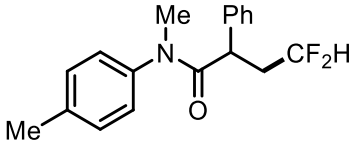
3p ^{19}F NMR
(376 MHz, $CDCl_3$)



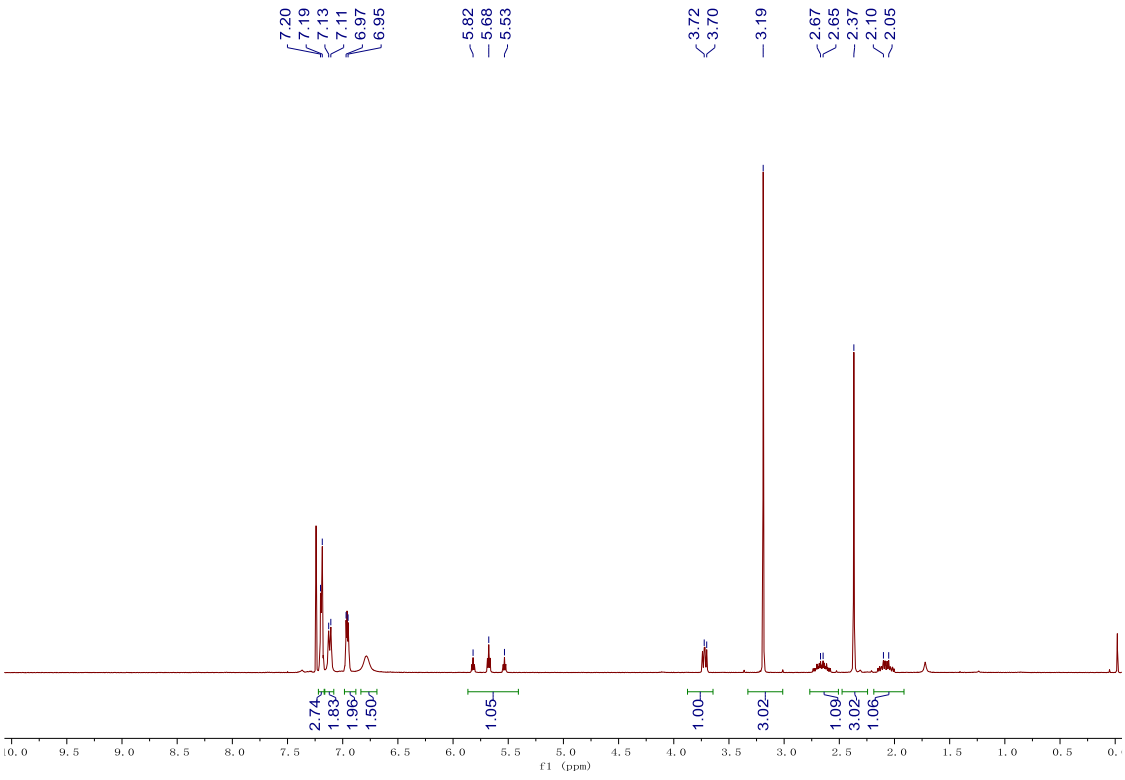


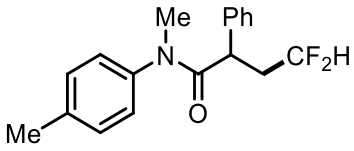
3p ^{13}C NMR
(101 MHz, $CDCl_3$)



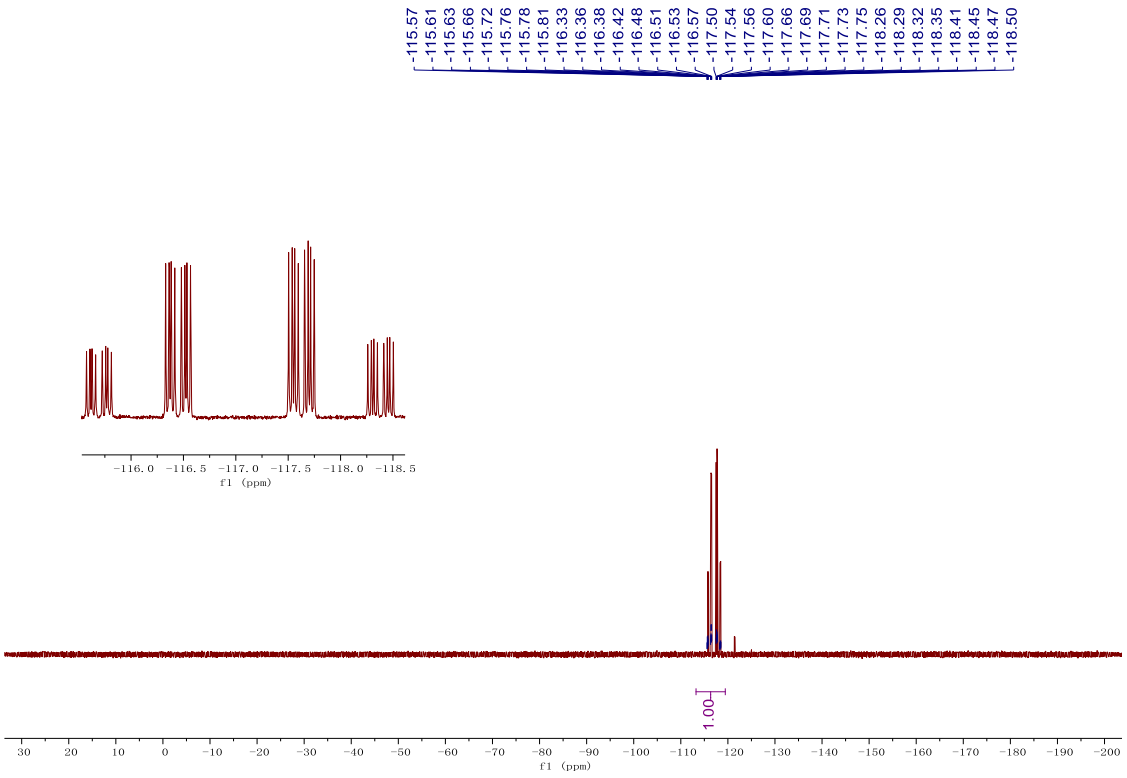


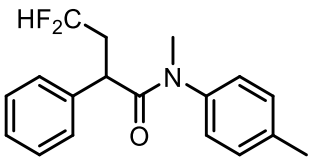
3q ^{1}H NMR
(400 MHz, $CDCl_3$)



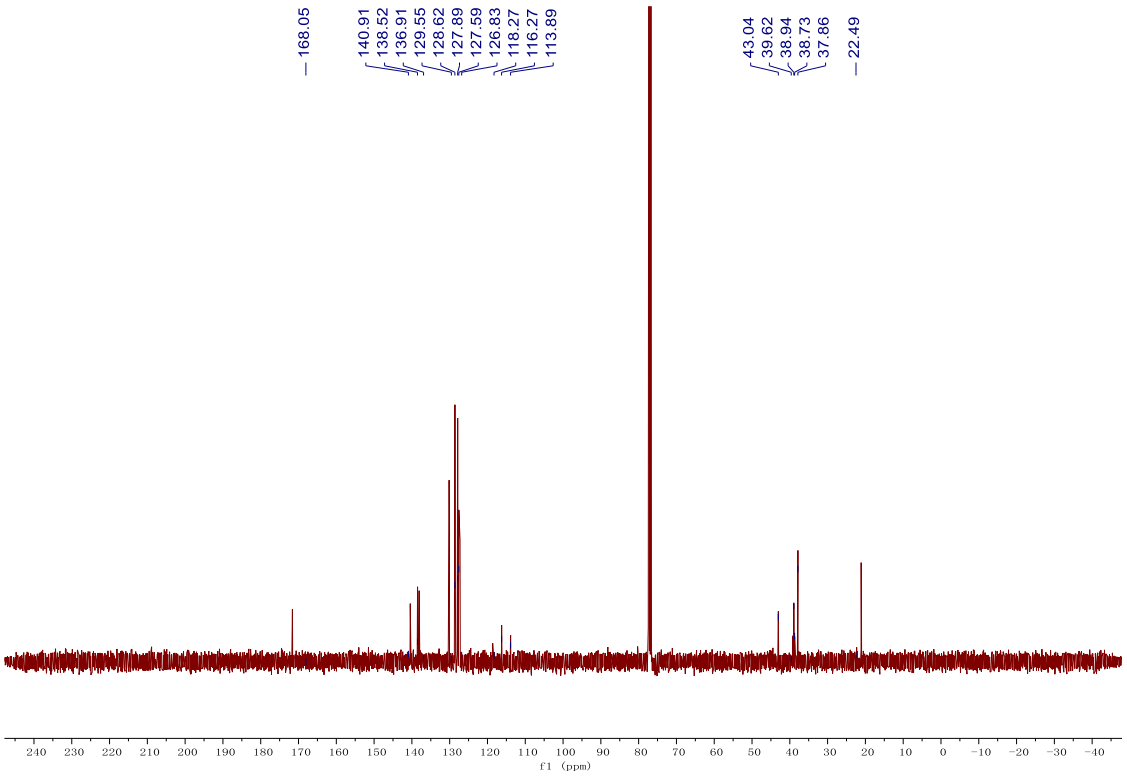


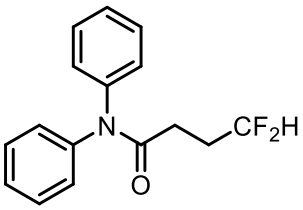
3q ^{19}F NMR
(376 MHz, $CDCl_3$)



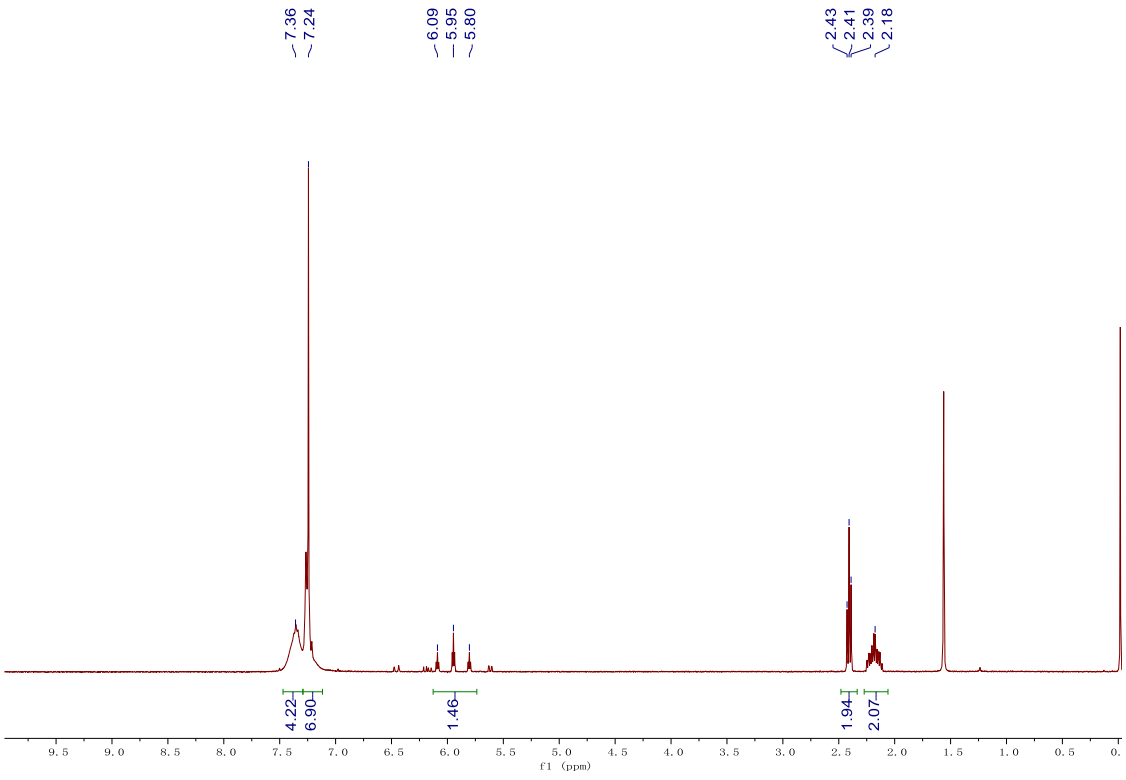


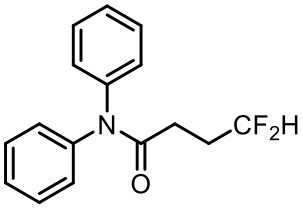
3l ^{13}C NMR
(101 MHz, $CDCl_3$)



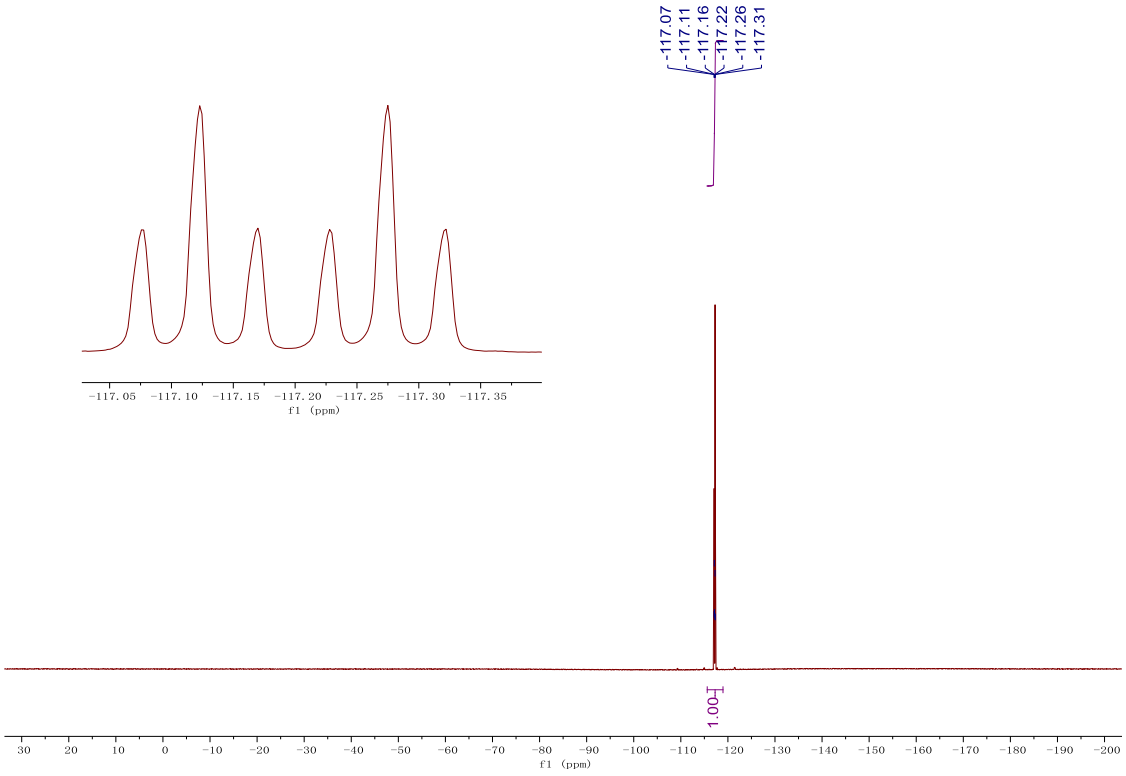


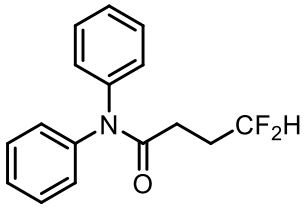
3r ^{1}H NMR
(400 MHz, $CDCl_3$)



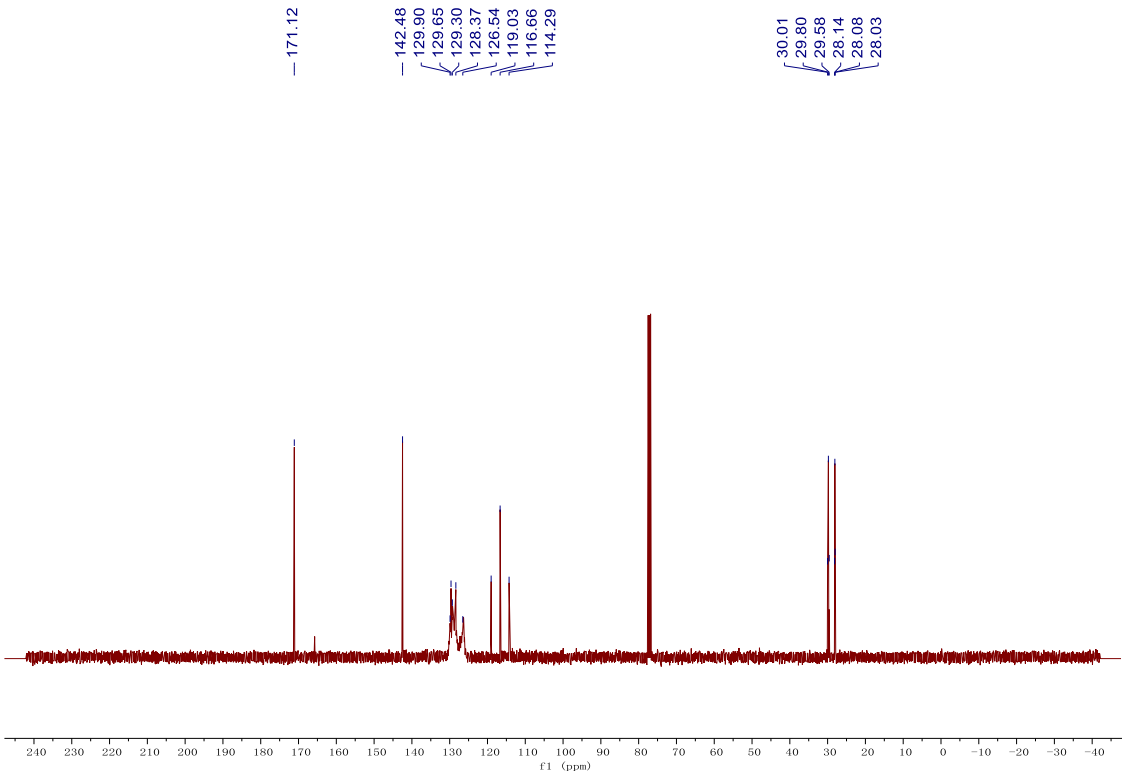


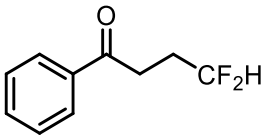
3r ^{19}F NMR
(376 MHz, $CDCl_3$)



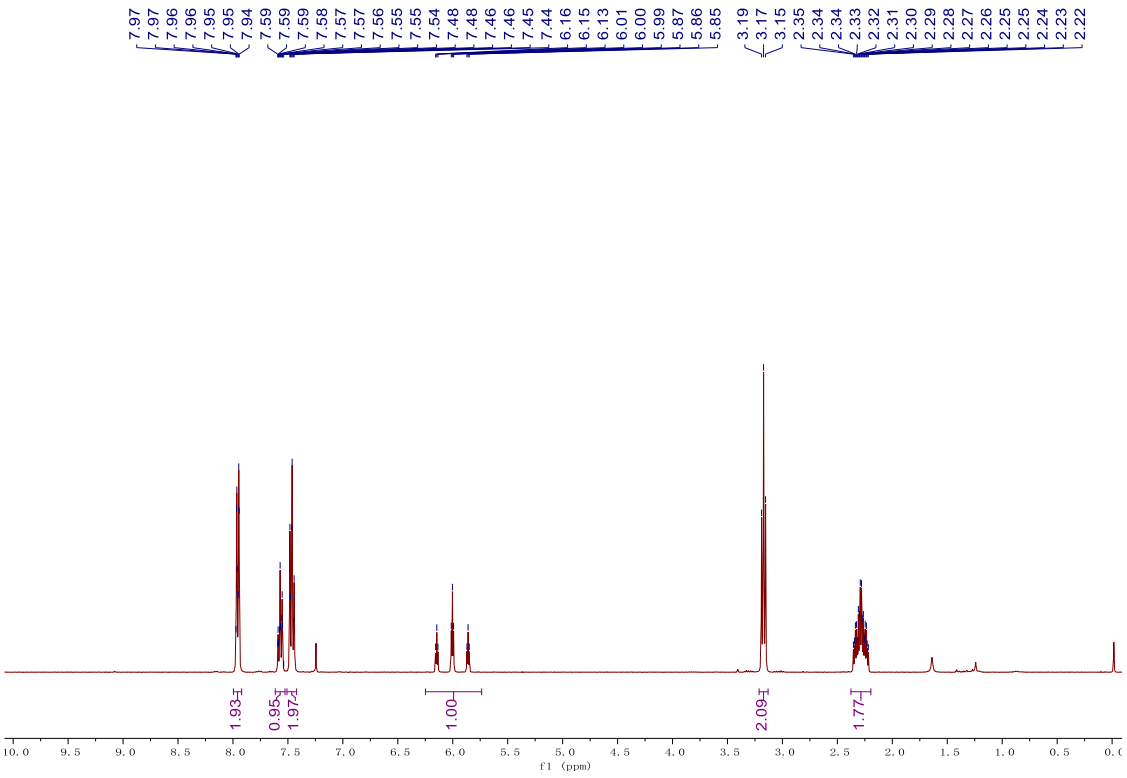


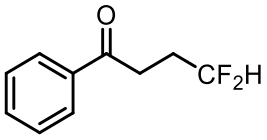
3r ^{13}C NMR
(101 MHz, $CDCl_3$)



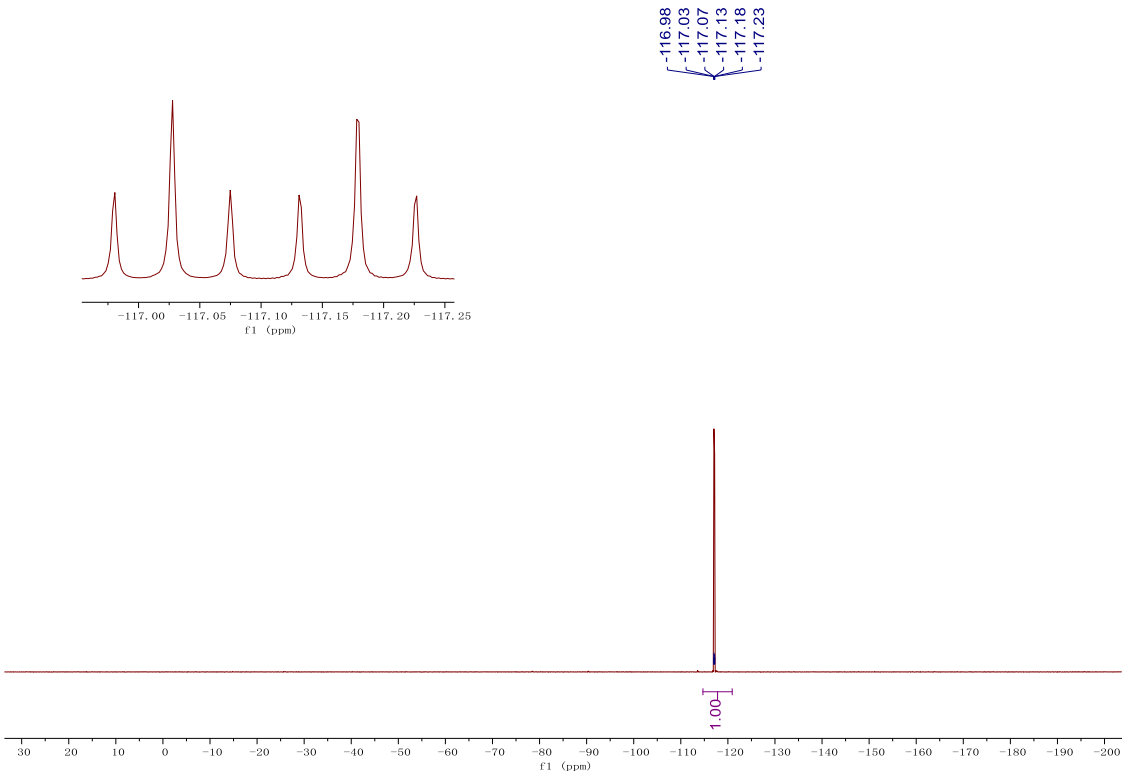


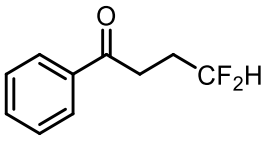
3s ^{1}H NMR
(400 MHz, $CDCl_3$)



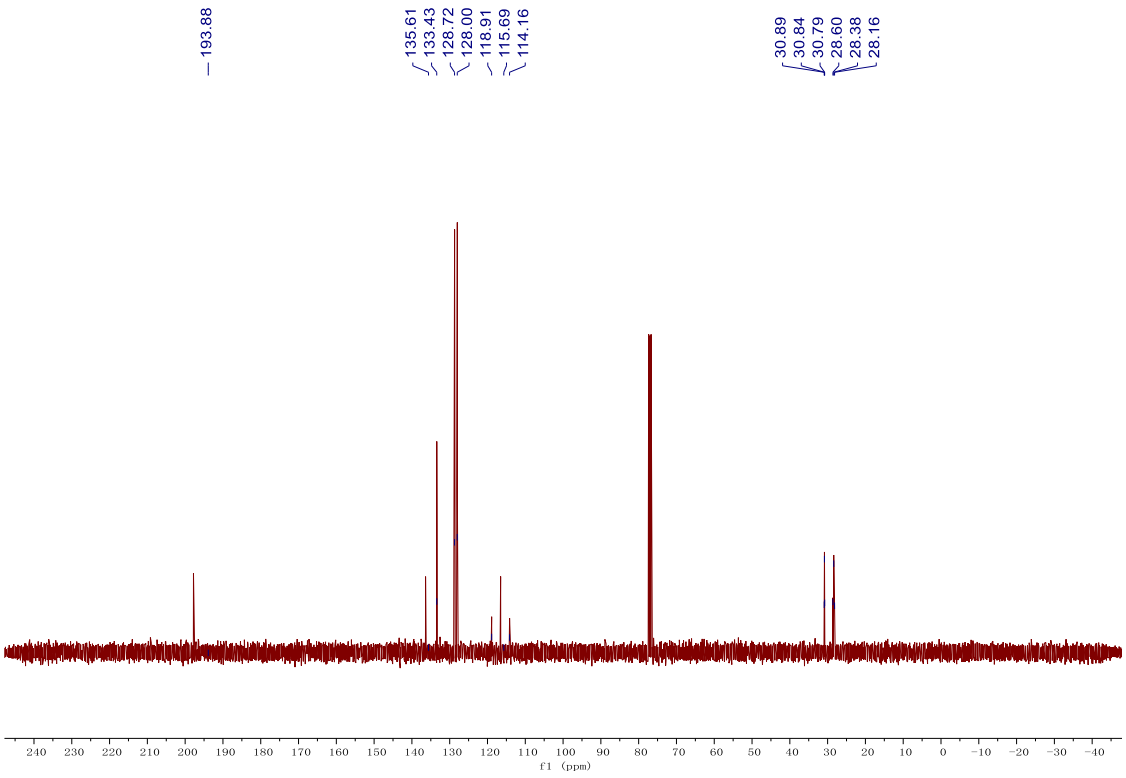


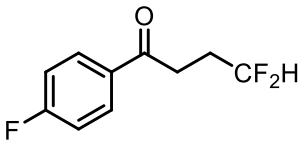
3s ^{19}F NMR
(376 MHz, $CDCl_3$)



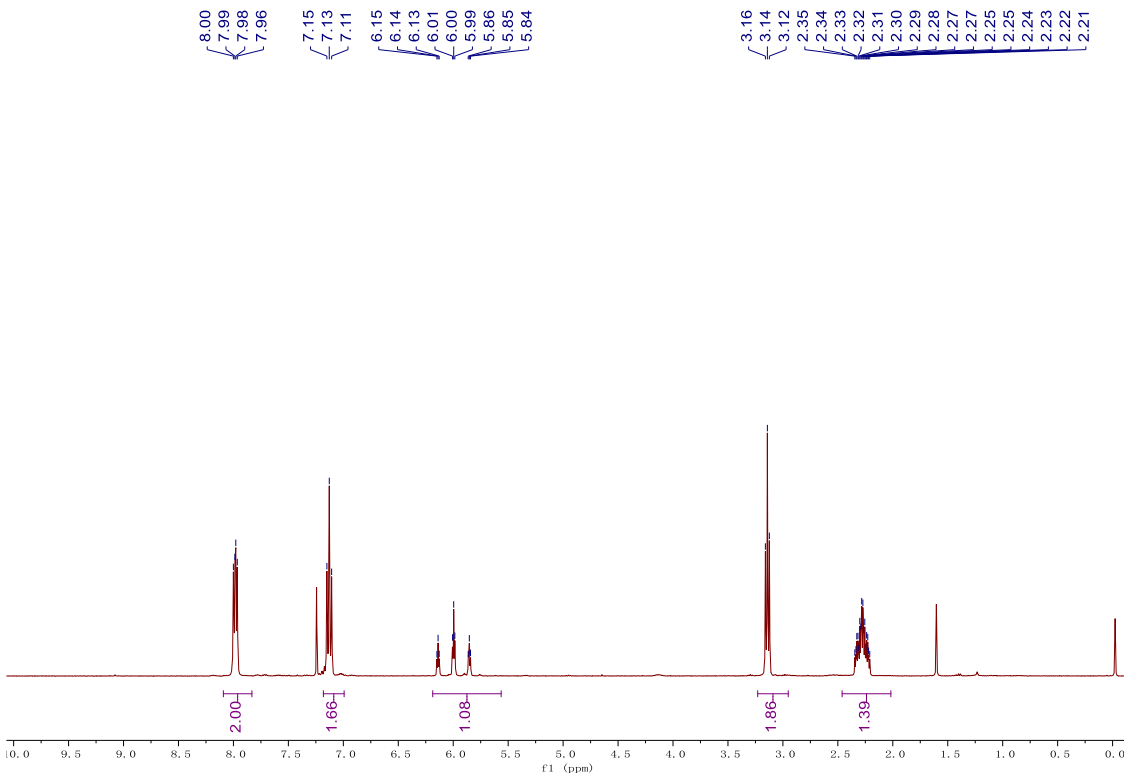


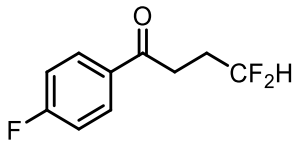
3s ^{13}C NMR
(101 MHz, $CDCl_3$)



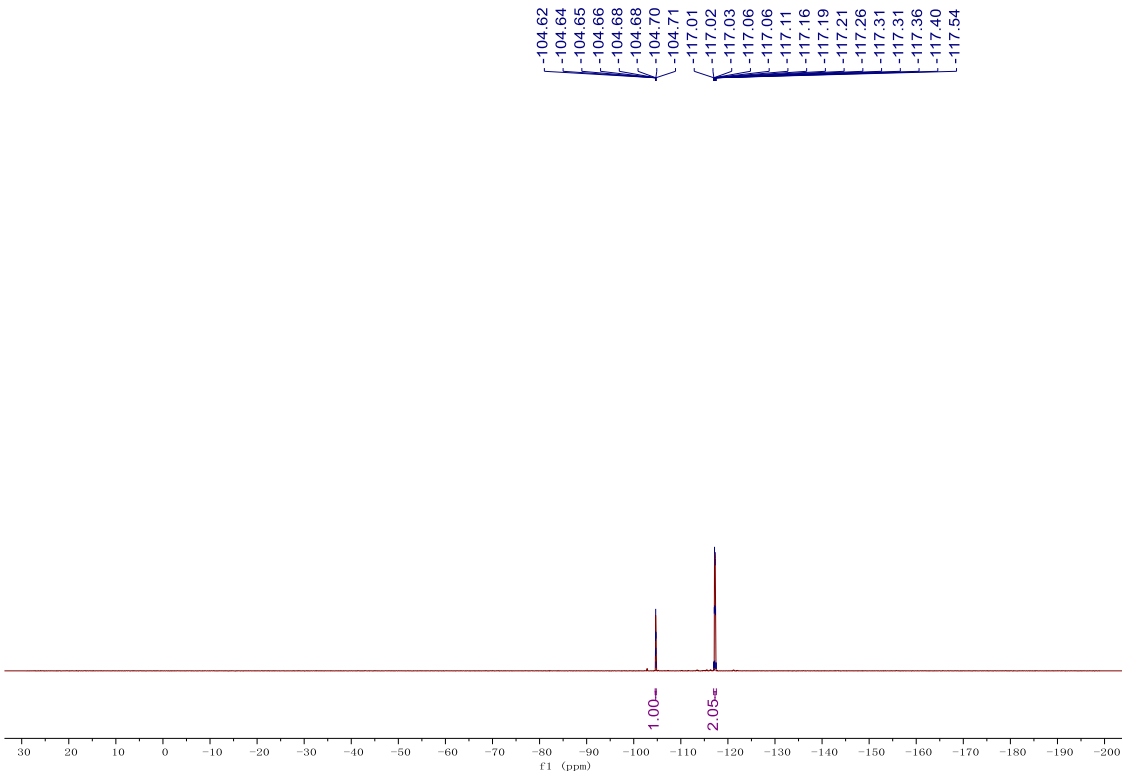


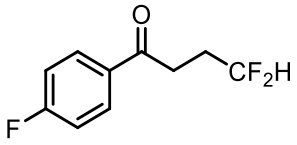
3t ^{1}H NMR
(400 MHz, $CDCl_3$)



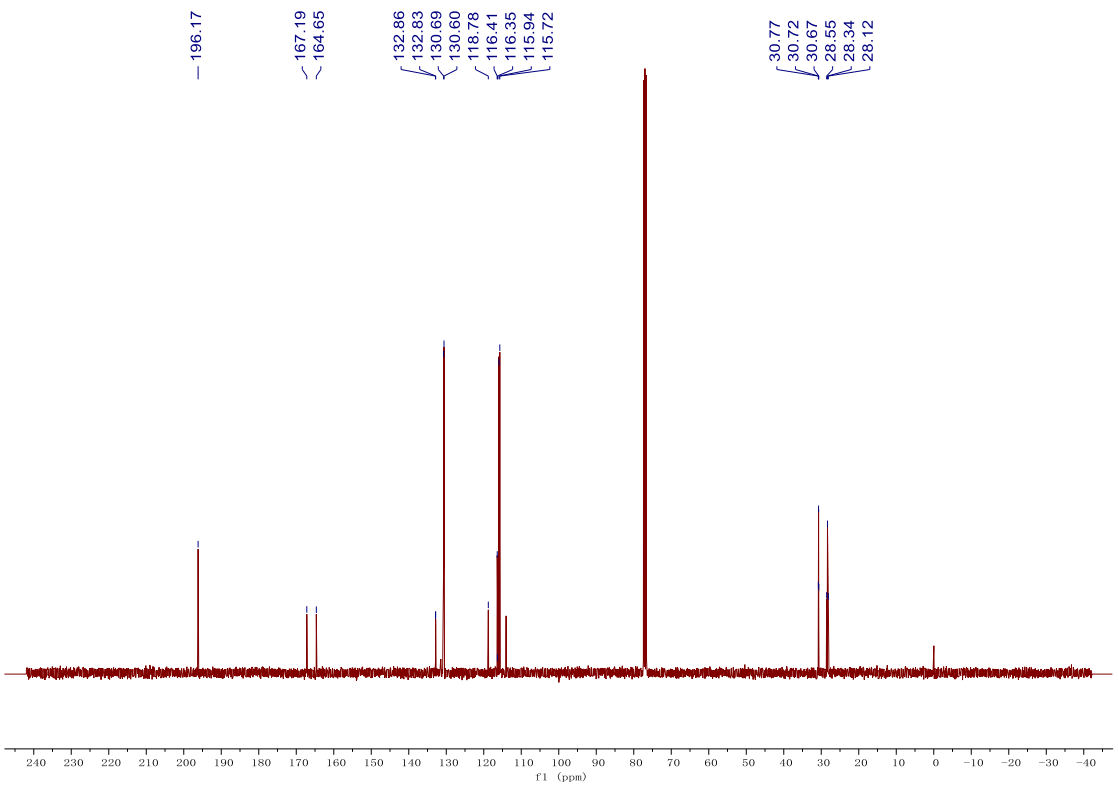


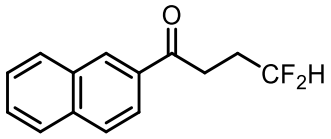
3t ^{19}F NMR
(376 MHz, $CDCl_3$)



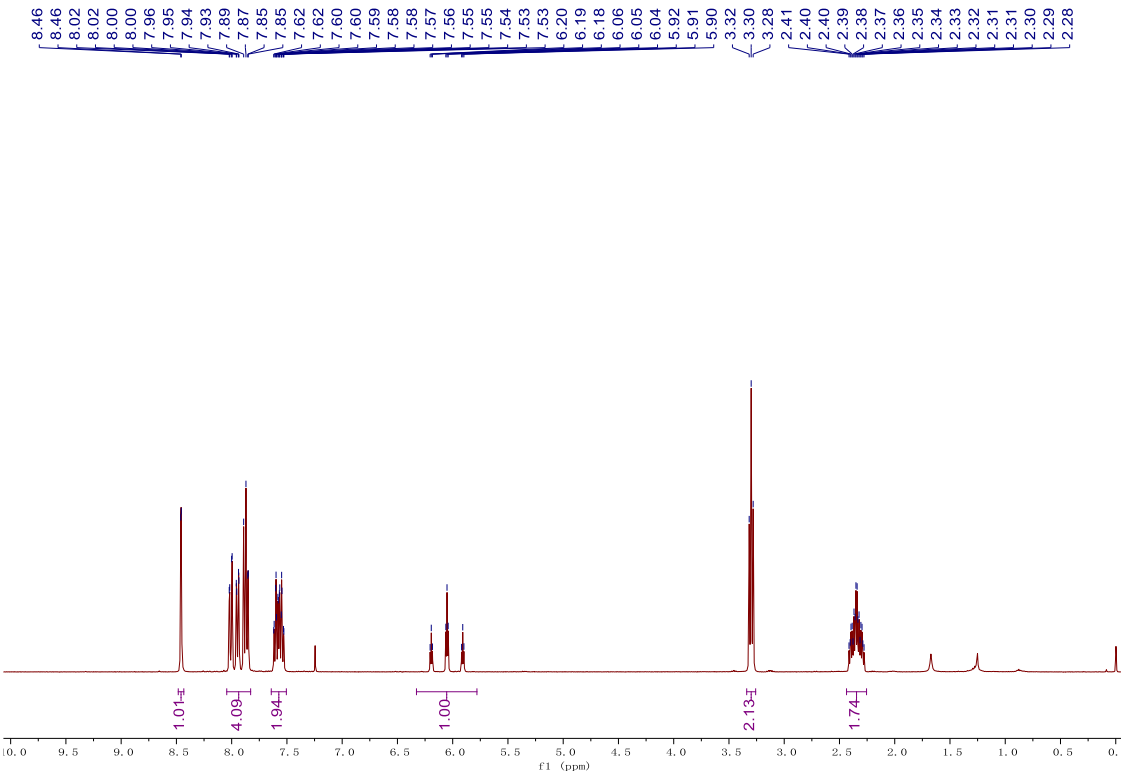


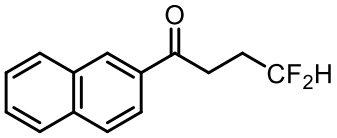
3t ^{19}F NMR
(376 MHz, $CDCl_3$)



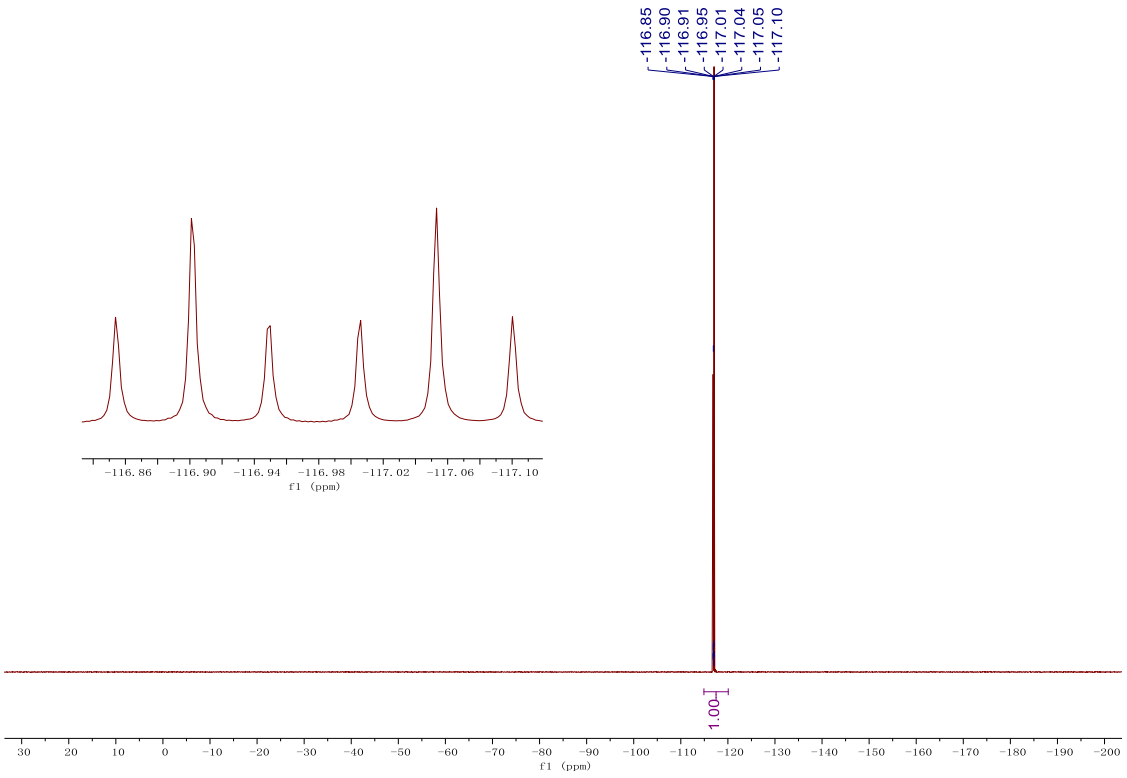


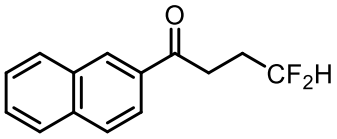
3u ^{1}H NMR
(400 MHz, $CDCl_3$)



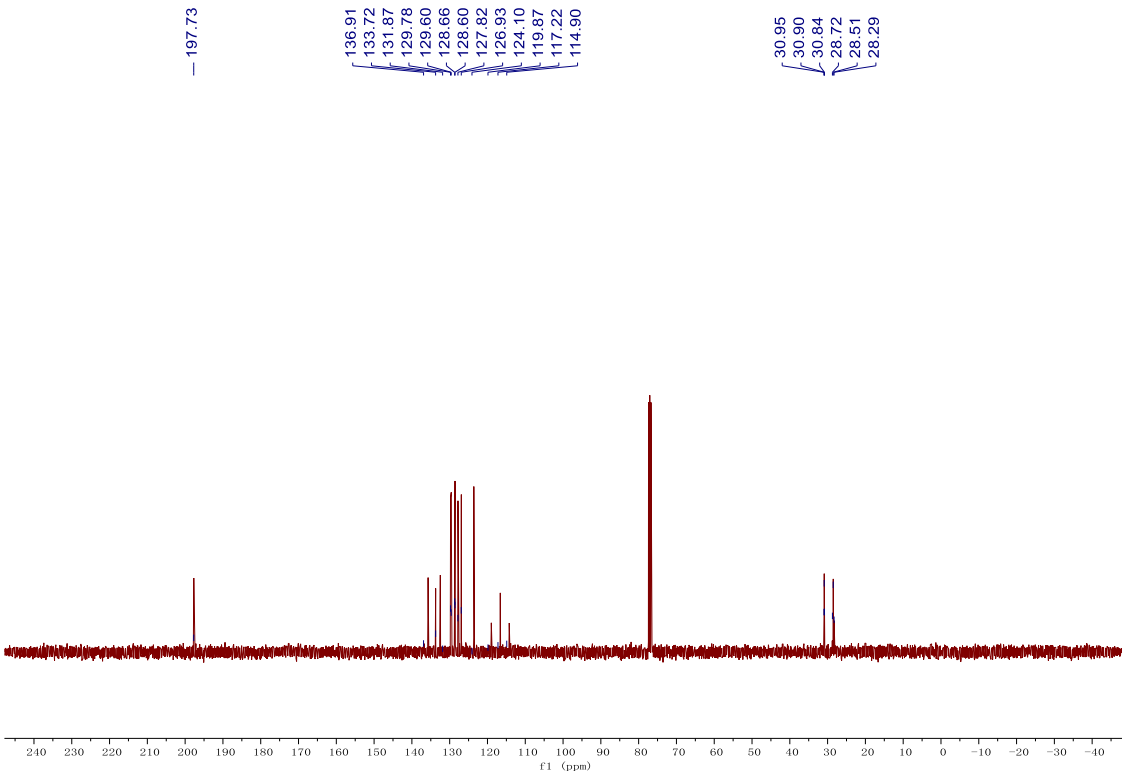


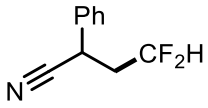
3u ^{19}F NMR
(376 MHz, $CDCl_3$)



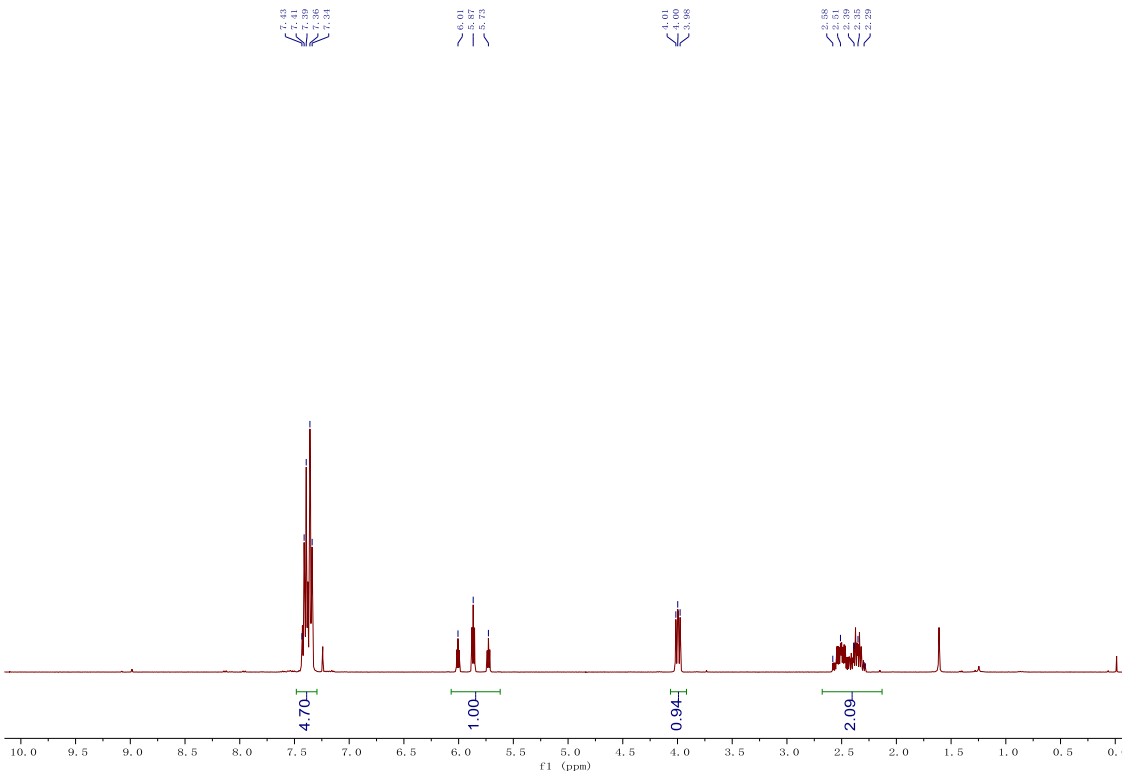


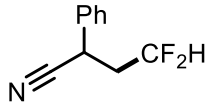
3u ^{13}C NMR
(101 MHz, $CDCl_3$)



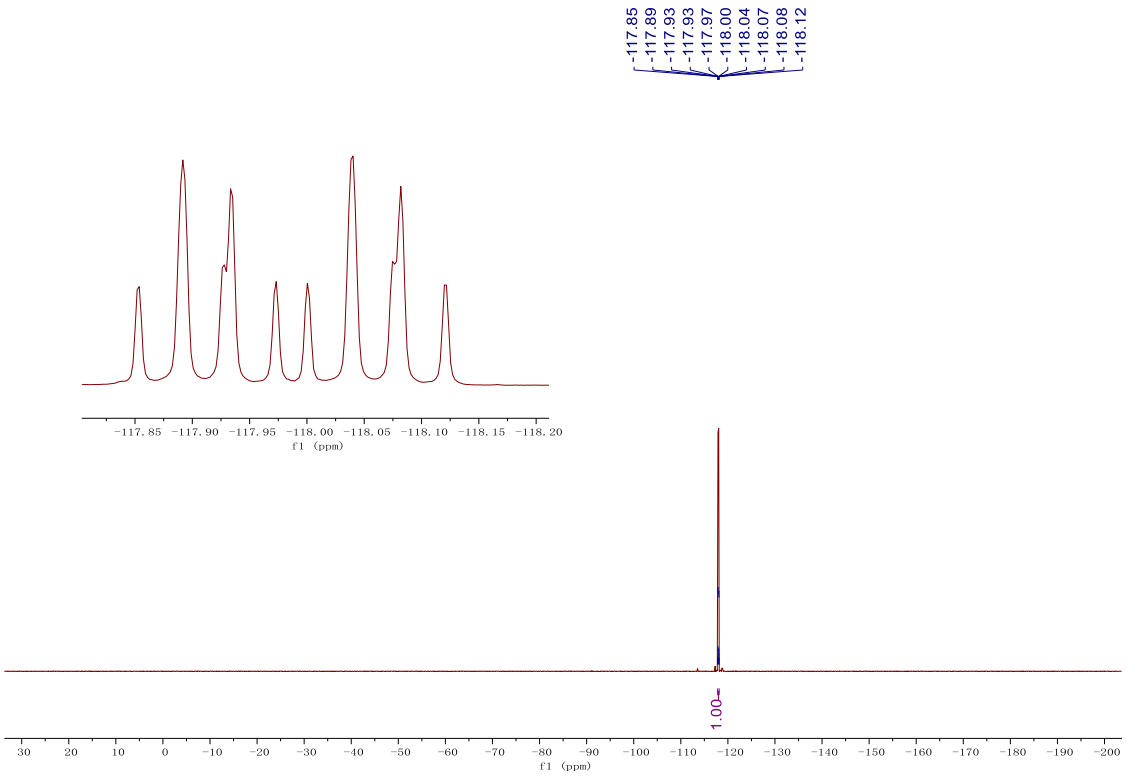


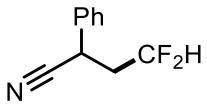
3v ^{1}H NMR
(400 MHz, $CDCl_3$)



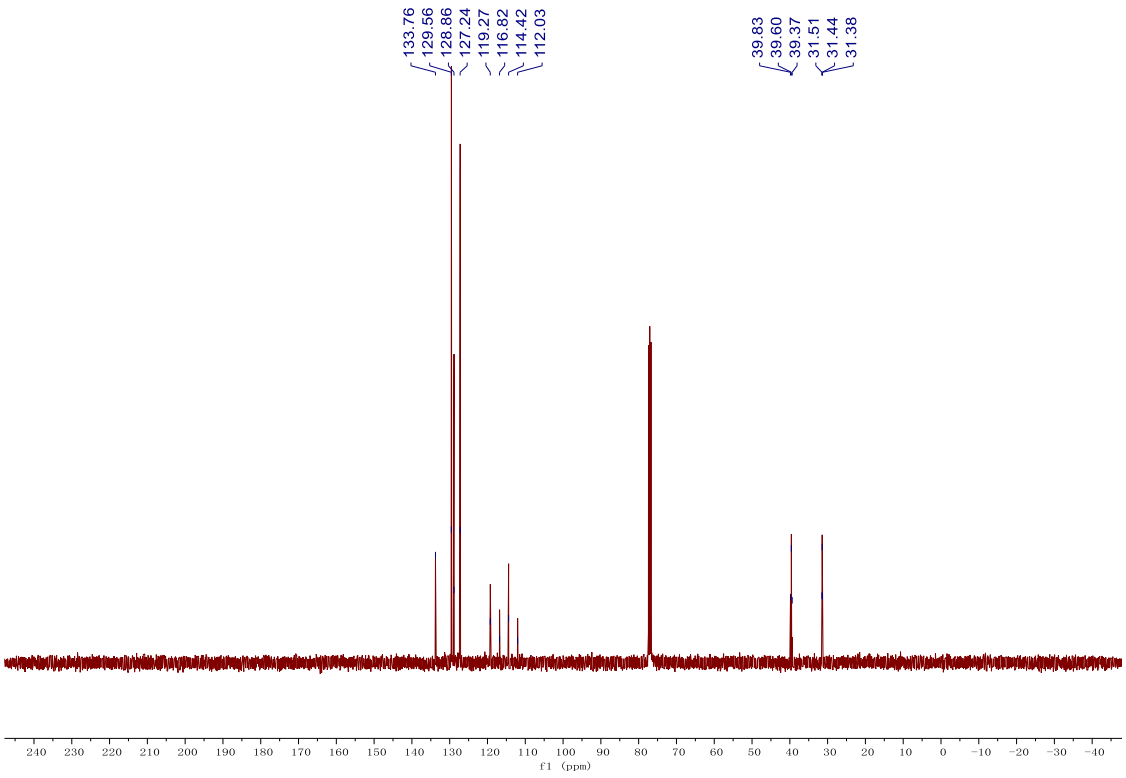


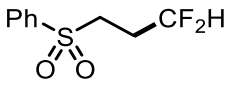
3v ^{19}F NMR
(376 MHz, $CDCl_3$)



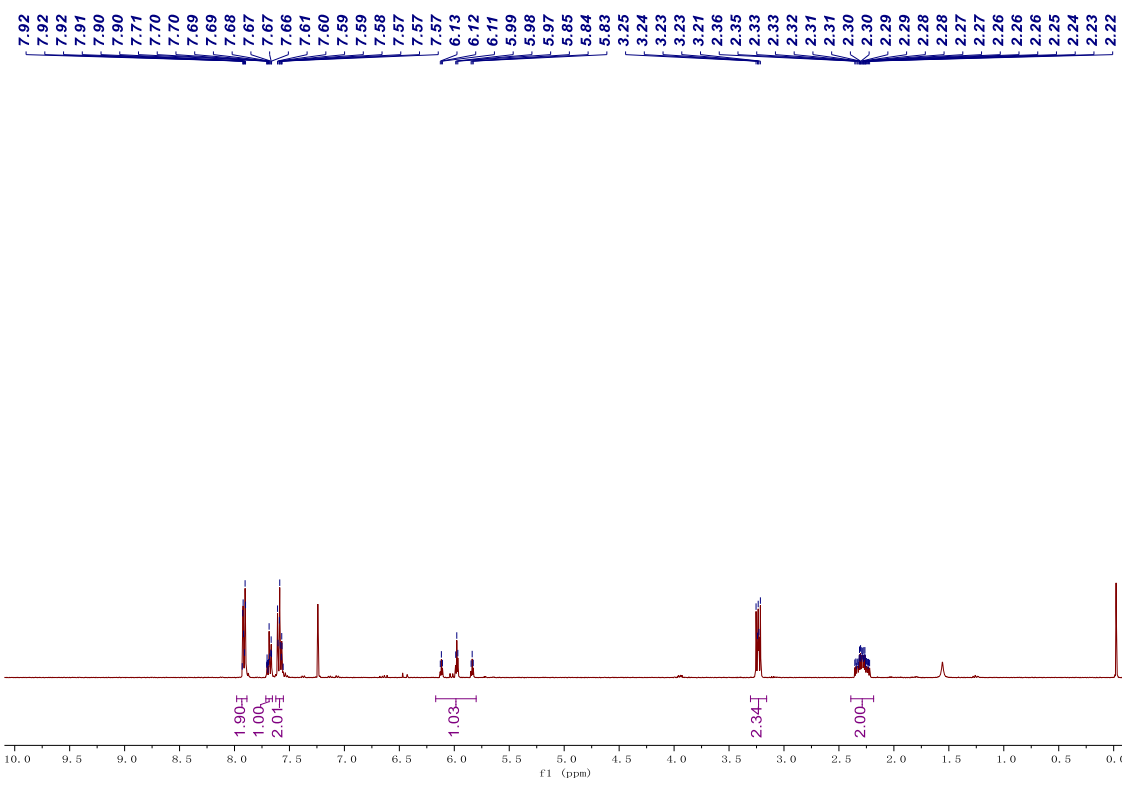


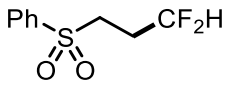
3v ^{13}C NMR
(101 MHz, $CDCl_3$)



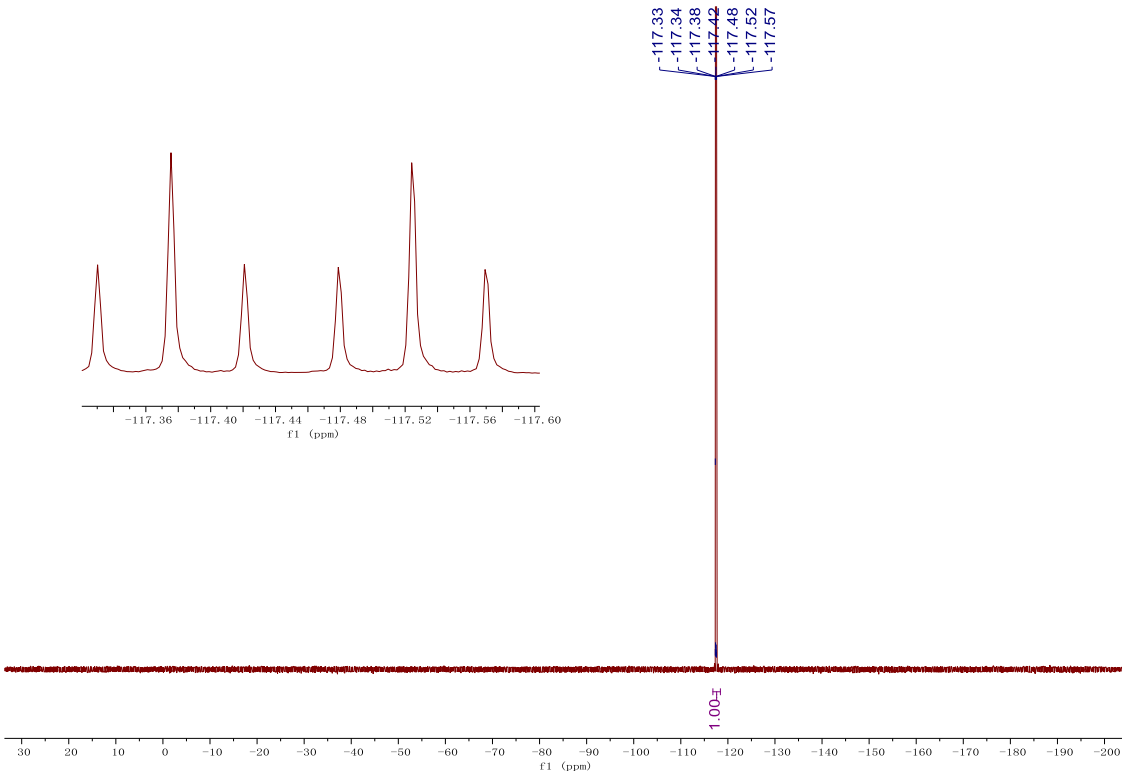


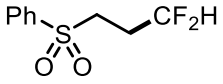
3w ^{1}H NMR
(400 MHz, $CDCl_3$)



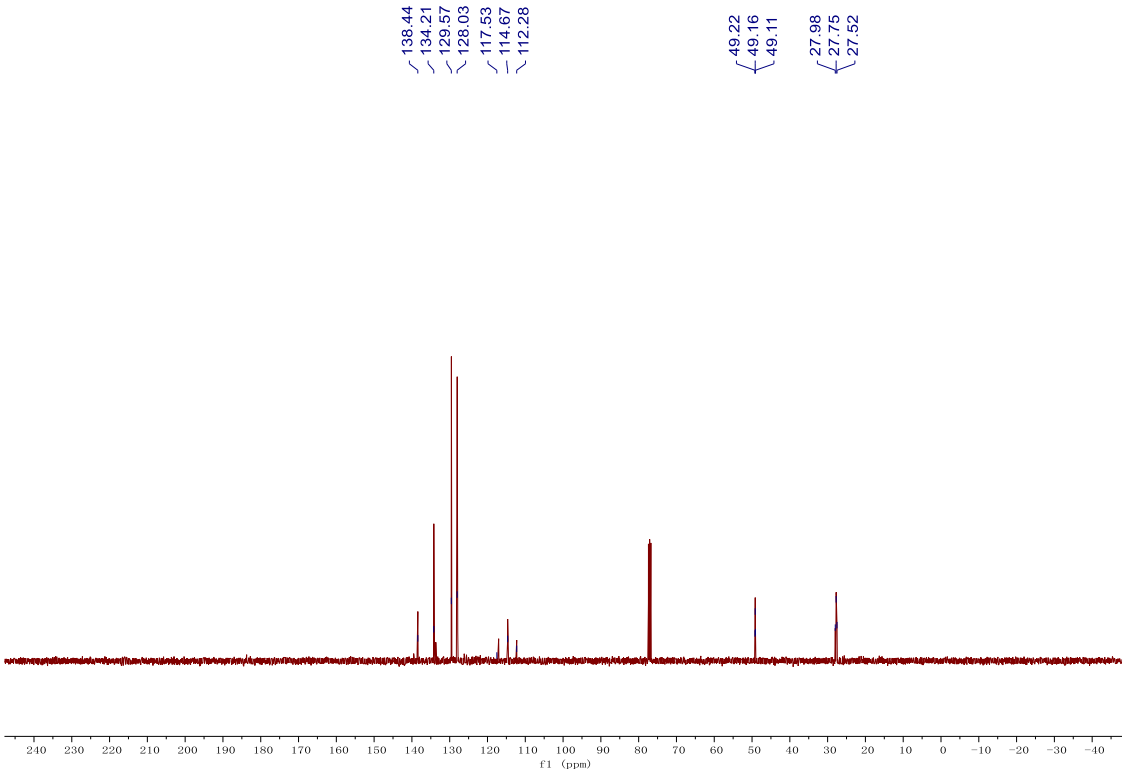


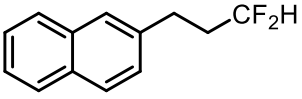
3w ^{19}F NMR
(376 MHz, $CDCl_3$)



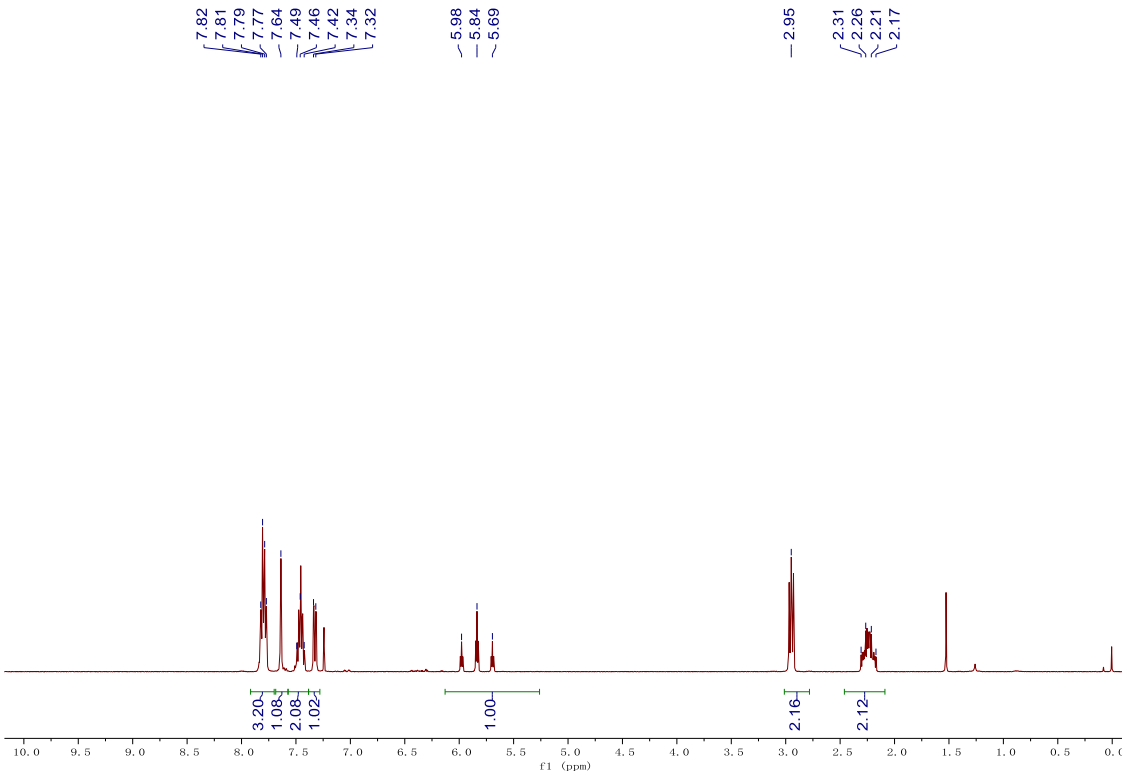


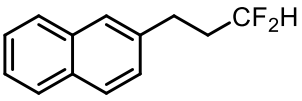
3w ^{13}C NMR
(101 MHz, $CDCl_3$)



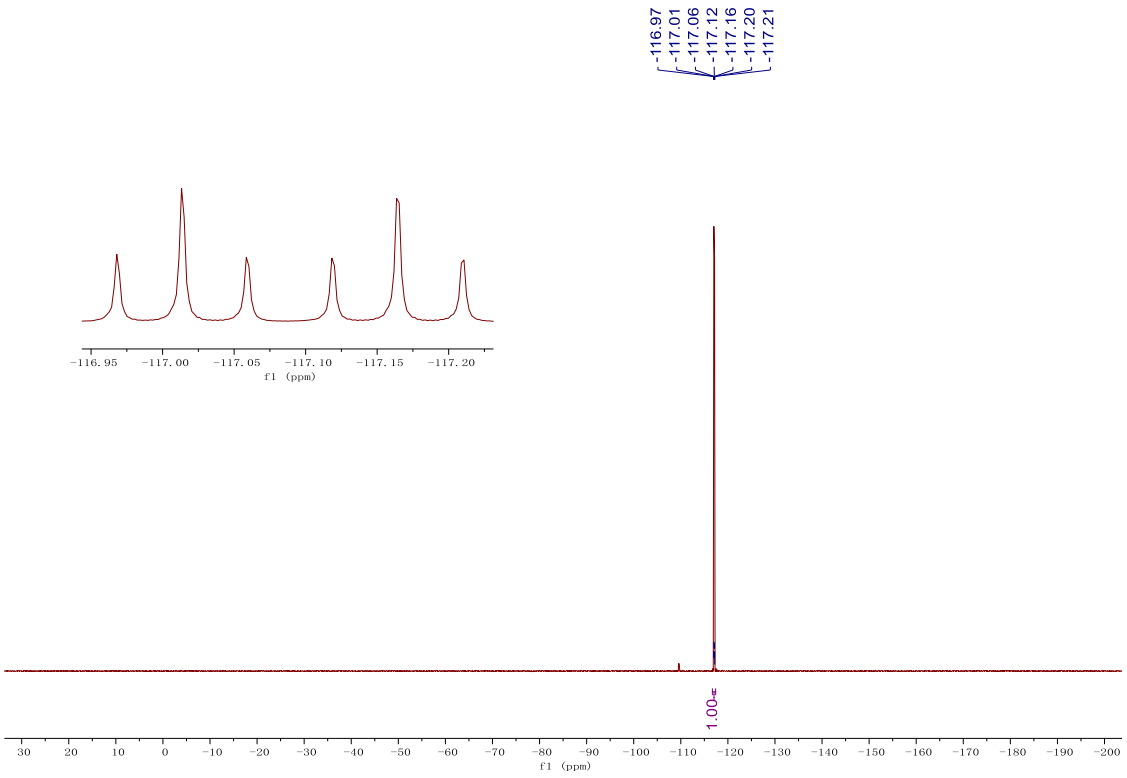


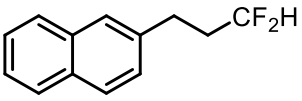
3x ^{1}H NMR
(400 MHz, $CDCl_3$)



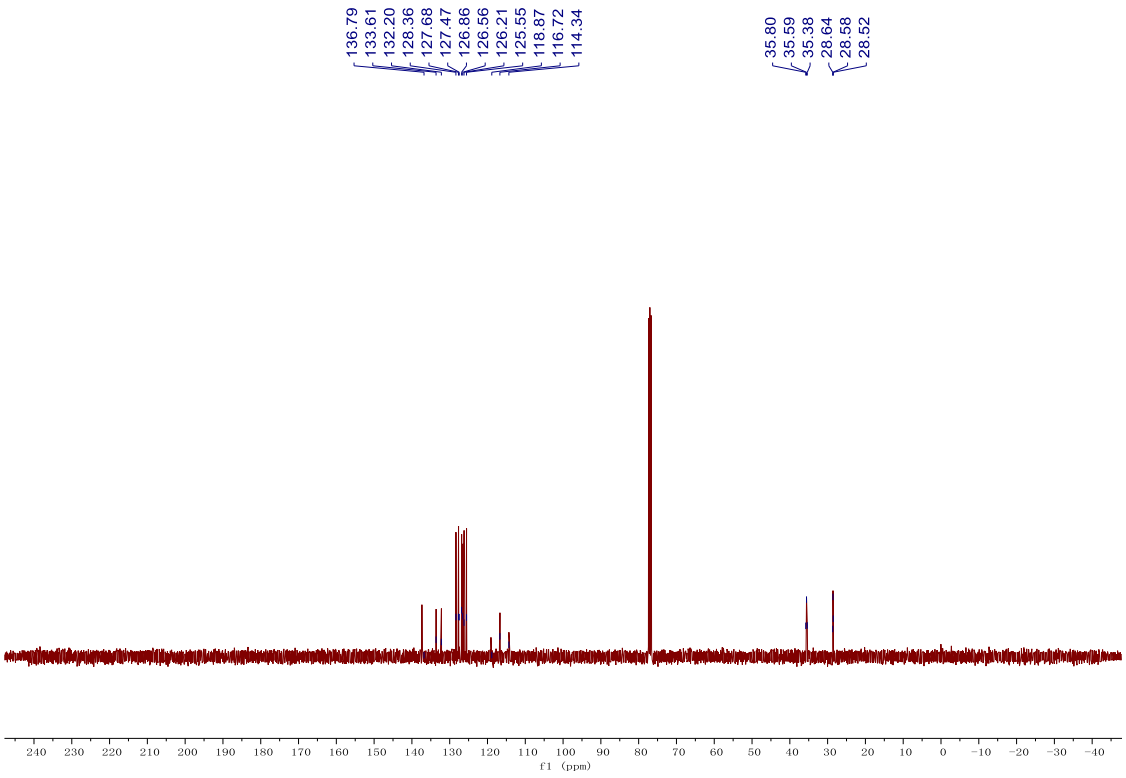


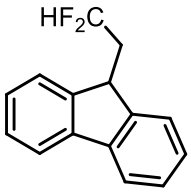
3x ^{19}F NMR
(376 MHz, $CDCl_3$)



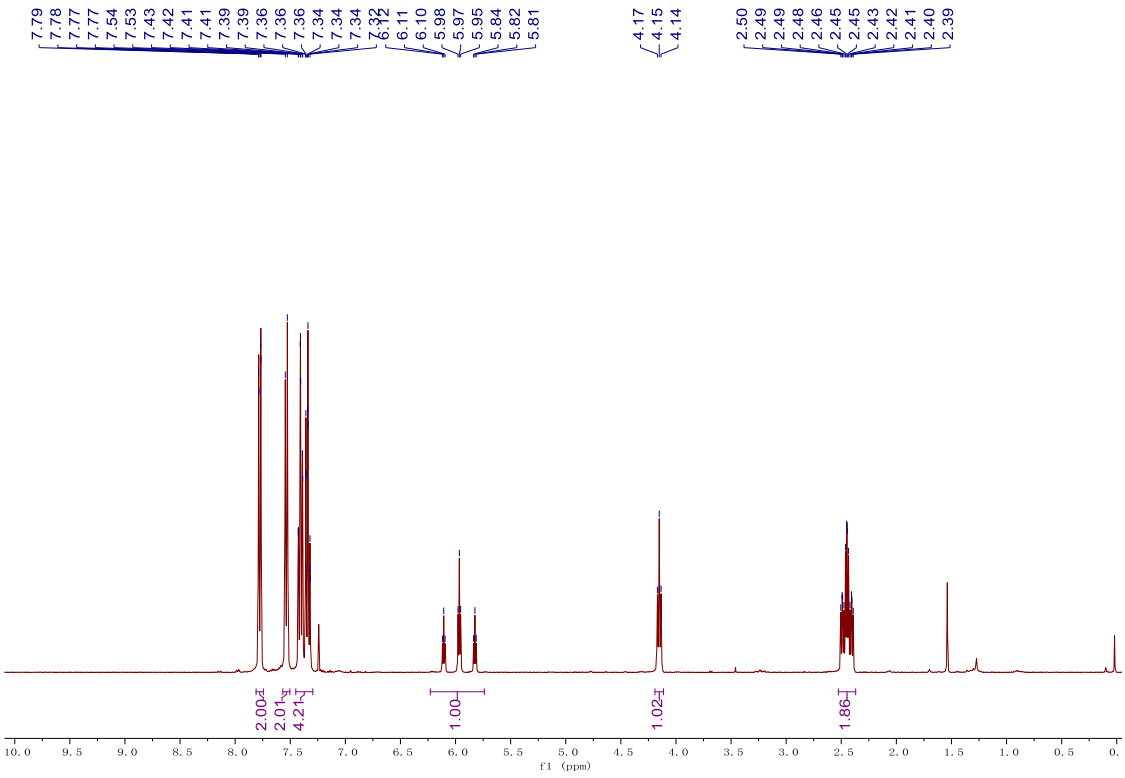


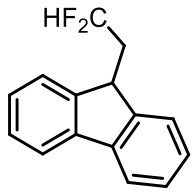
3x ^{13}C NMR
(101 MHz, $CDCl_3$)



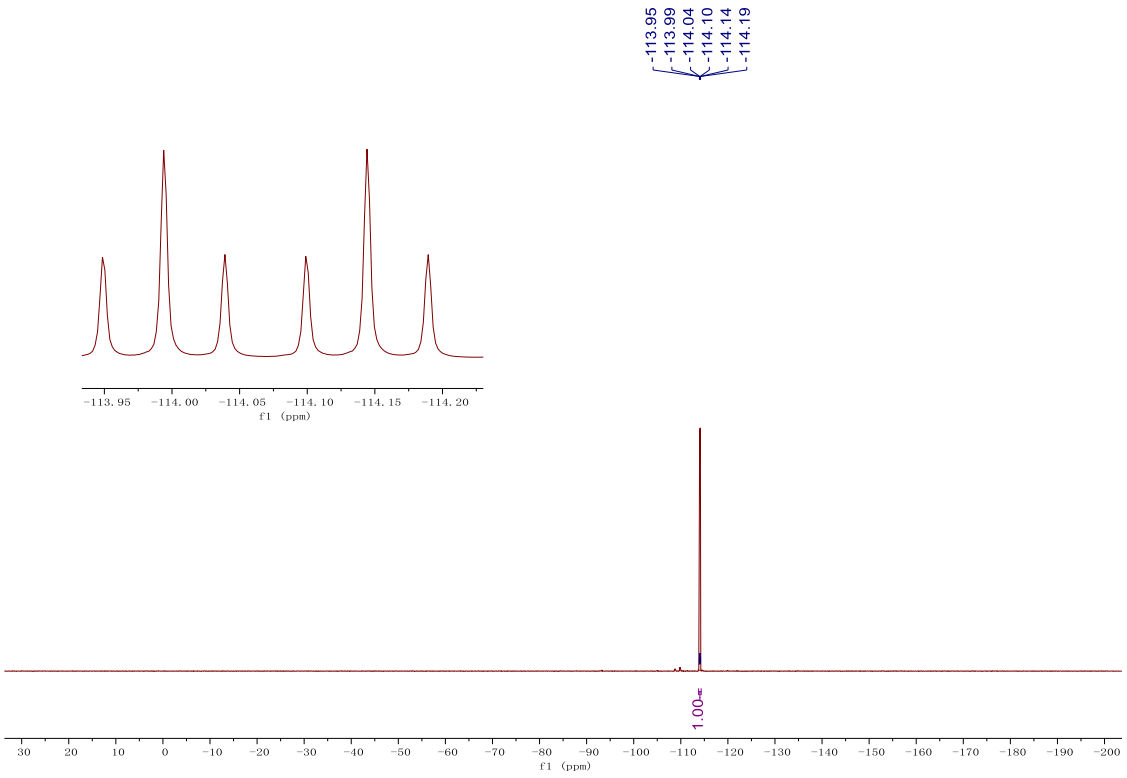


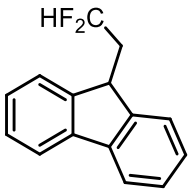
3y ^{1}H NMR
(400 MHz, $CDCl_3$)



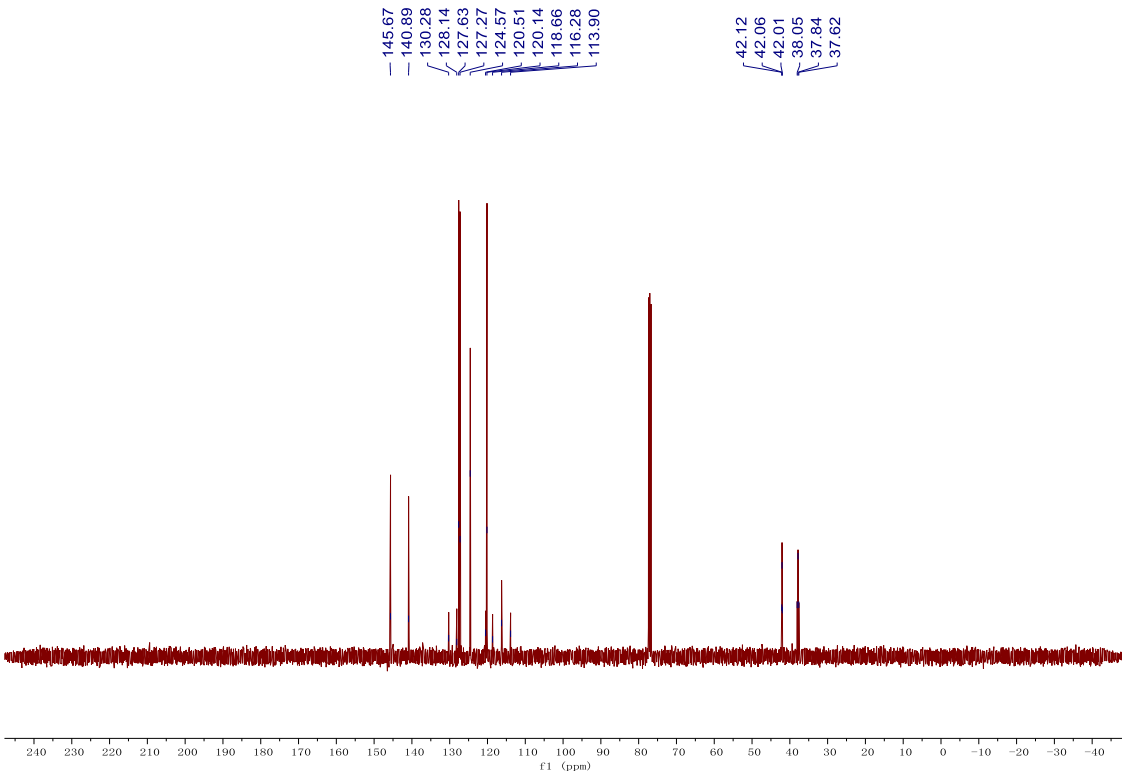


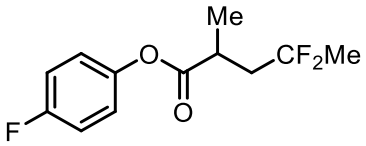
3y ^{19}F NMR
(376 MHz, $CDCl_3$)



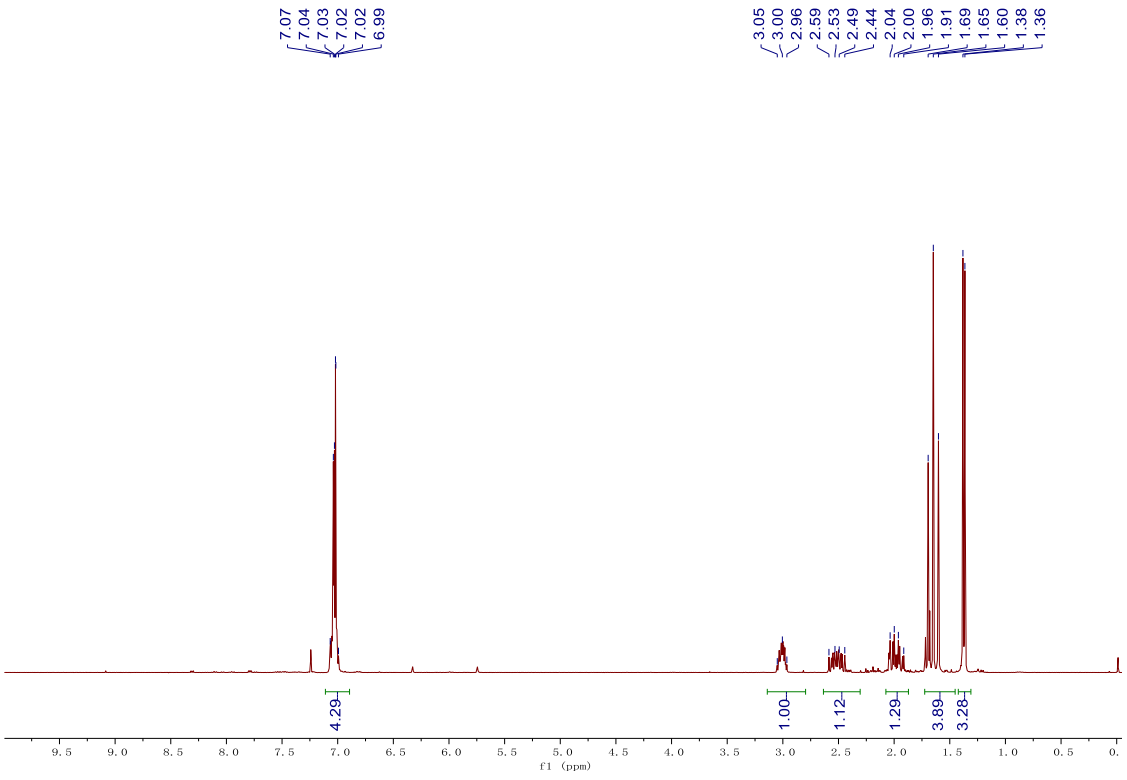


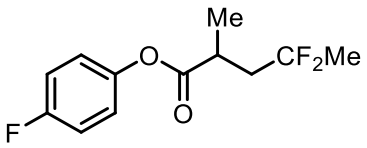
3y ^{13}C NMR
(101 MHz, $CDCl_3$)



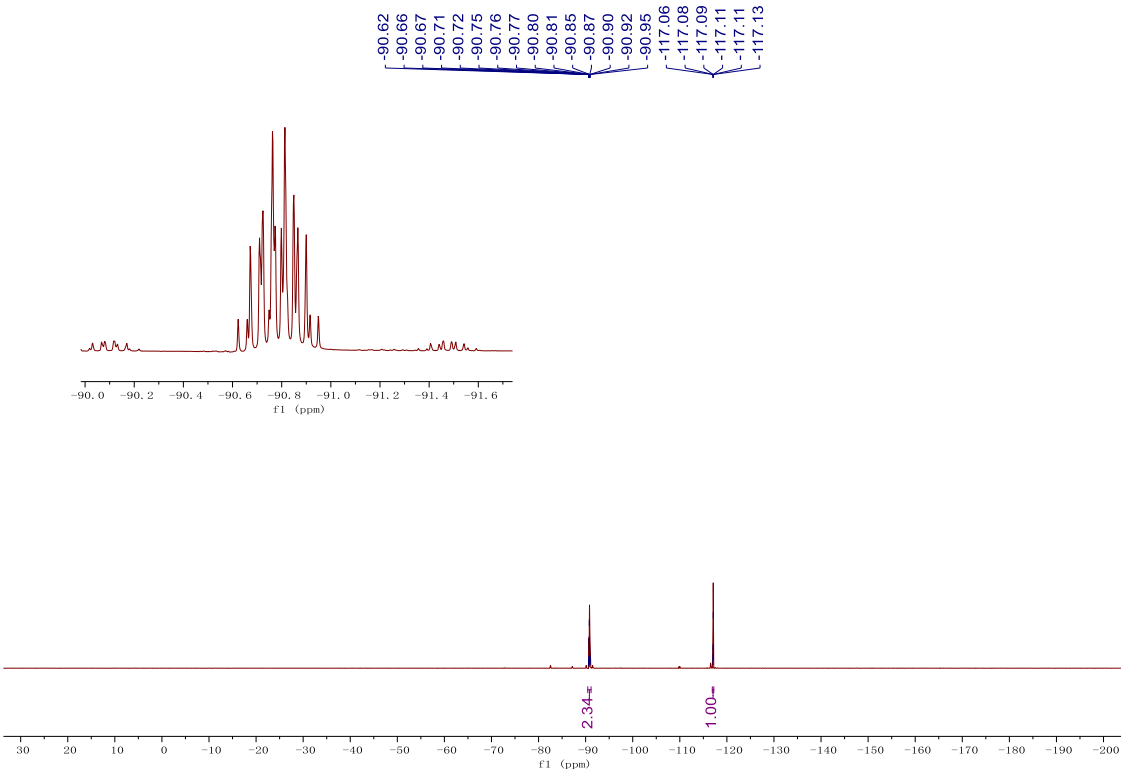


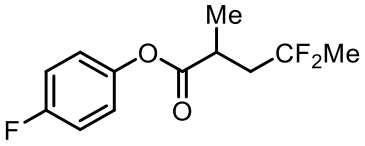
3ab ^{1}H NMR
(400 MHz, $CDCl_3$)



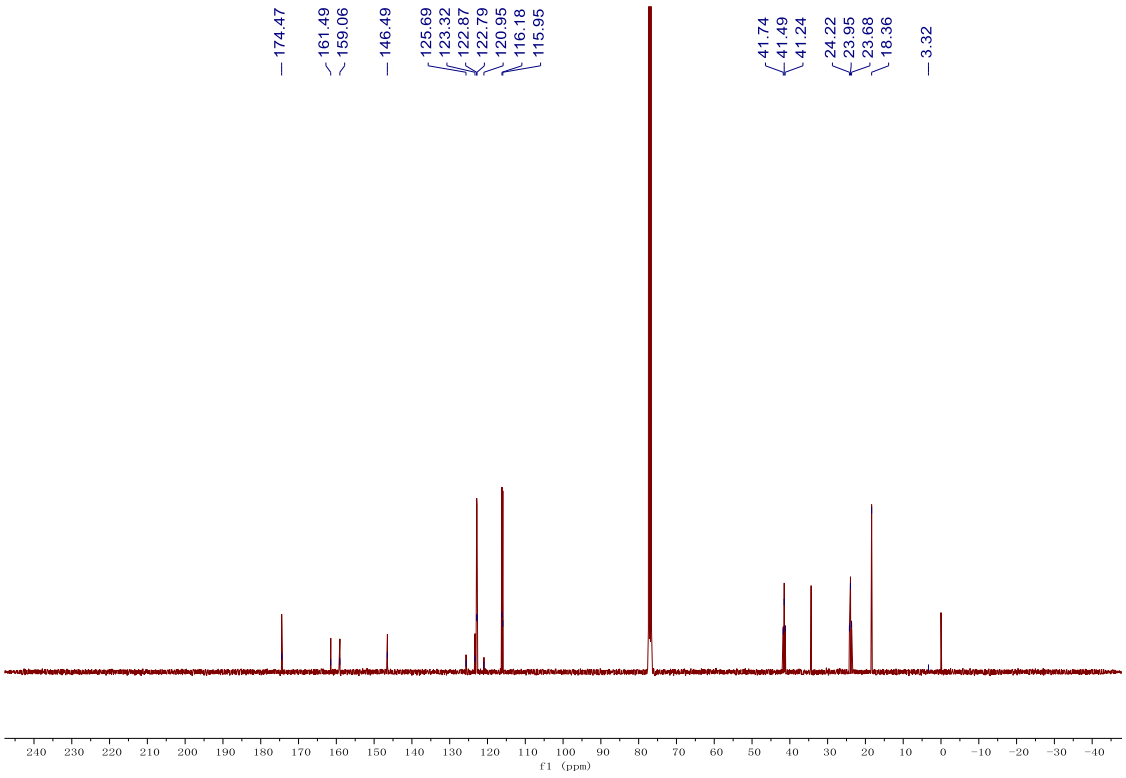


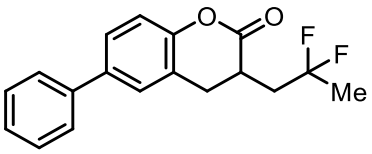
3ab ^{19}F NMR
(376 MHz, $CDCl_3$)



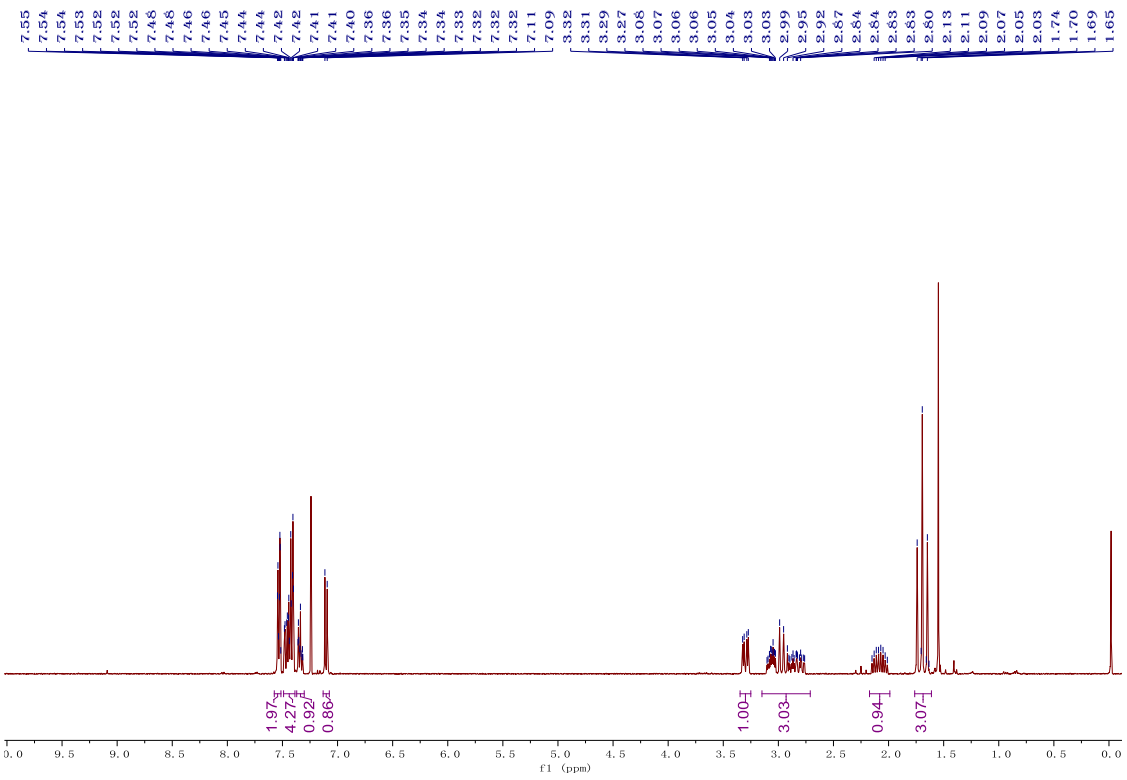


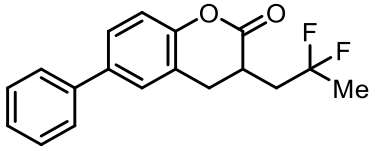
3ab ^{13}C NMR
(101 MHz, $CDCl_3$)



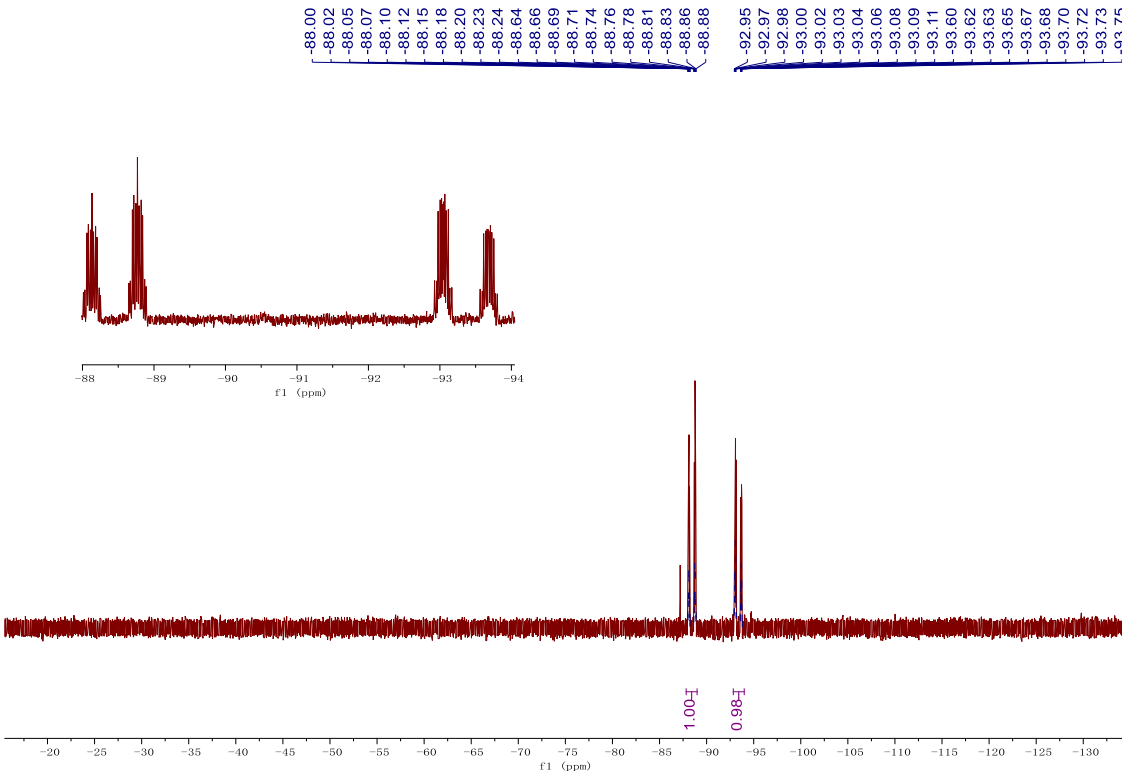


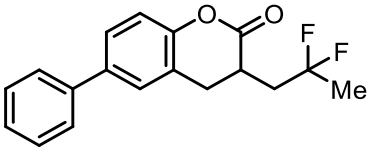
3ac ^{1}H NMR
(400MHz, $CDCl_3$)



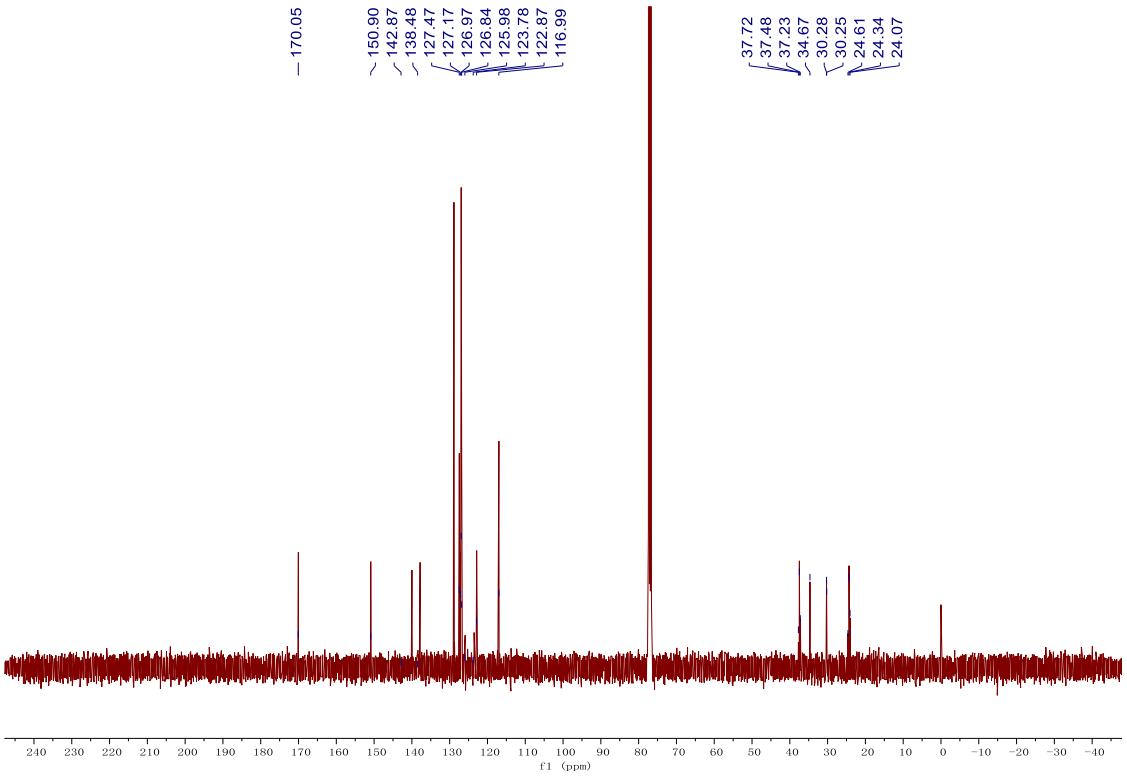


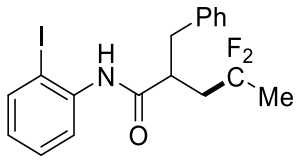
3ac ^{19}F NMR
(376 MHz, $CDCl_3$)



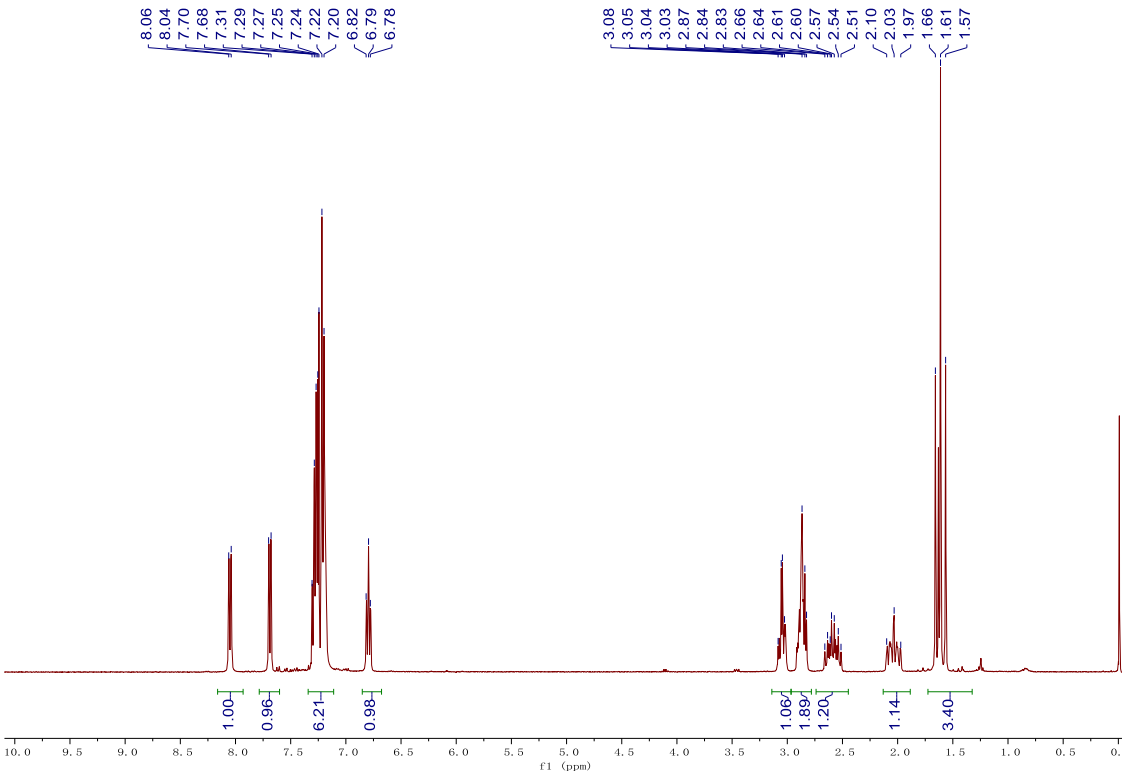


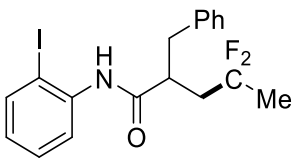
3ac ^{13}C NMR
(101 MHz, $CDCl_3$)



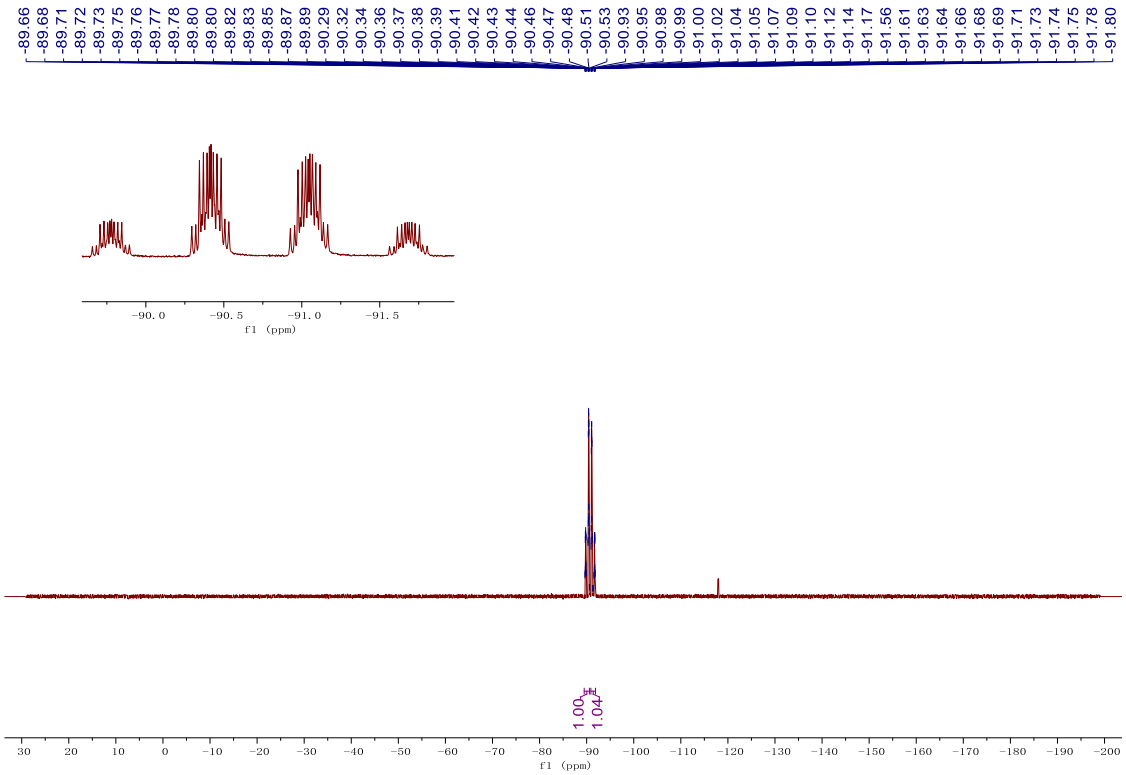


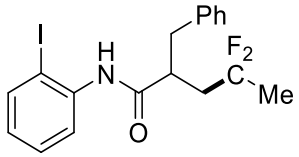
3ad ^{1}H NMR
(400 MHz, $CDCl_3$)



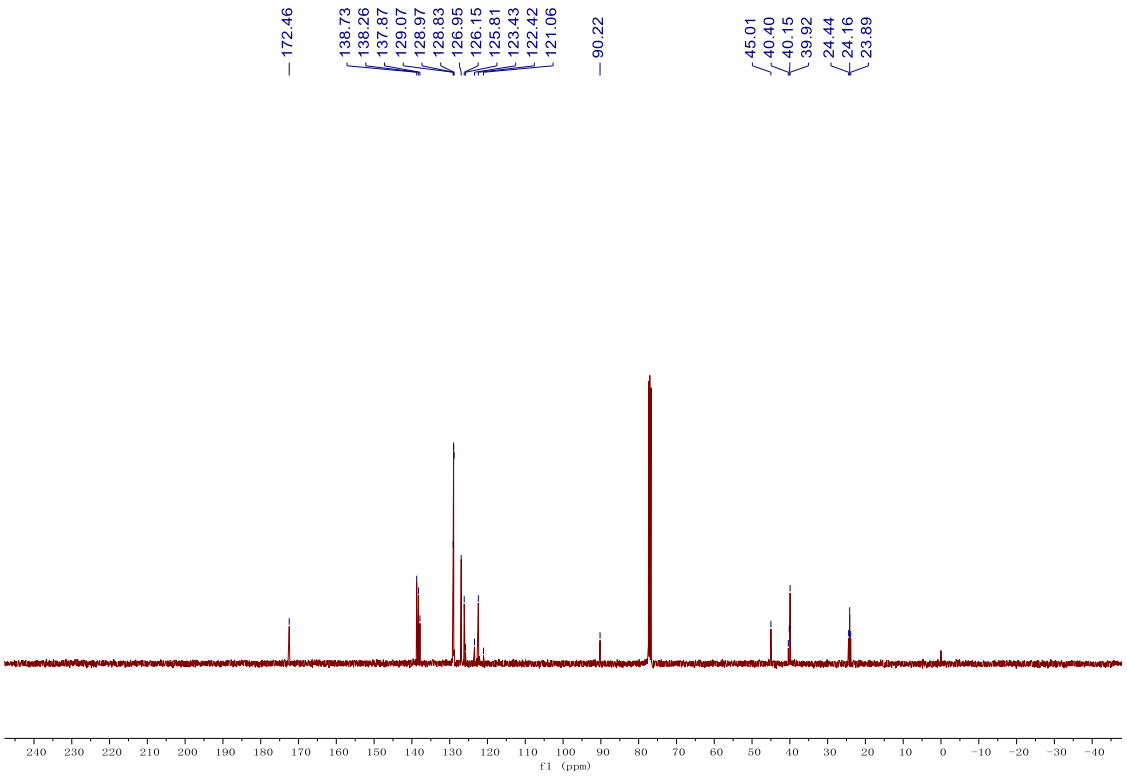


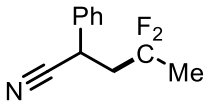
3ad ^{19}F NMR
(376 MHz, $CDCl_3$)



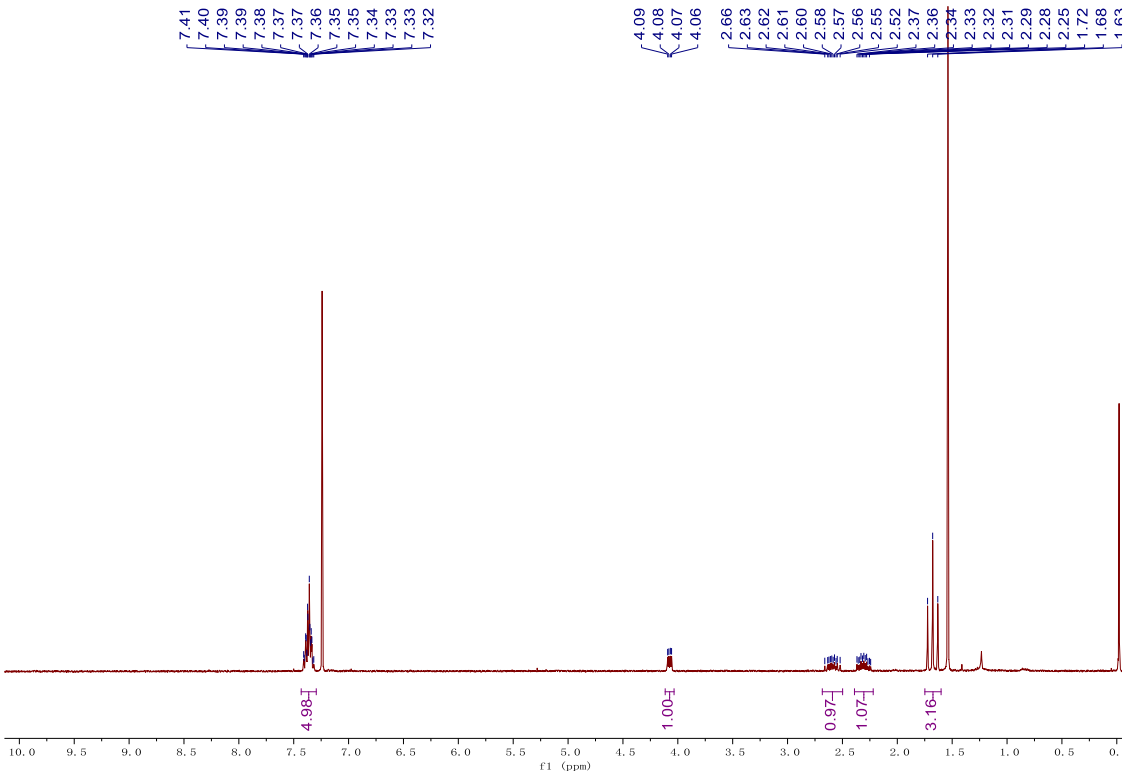


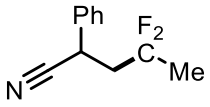
3ad ^{13}C NMR
(101 MHz, $CDCl_3$)



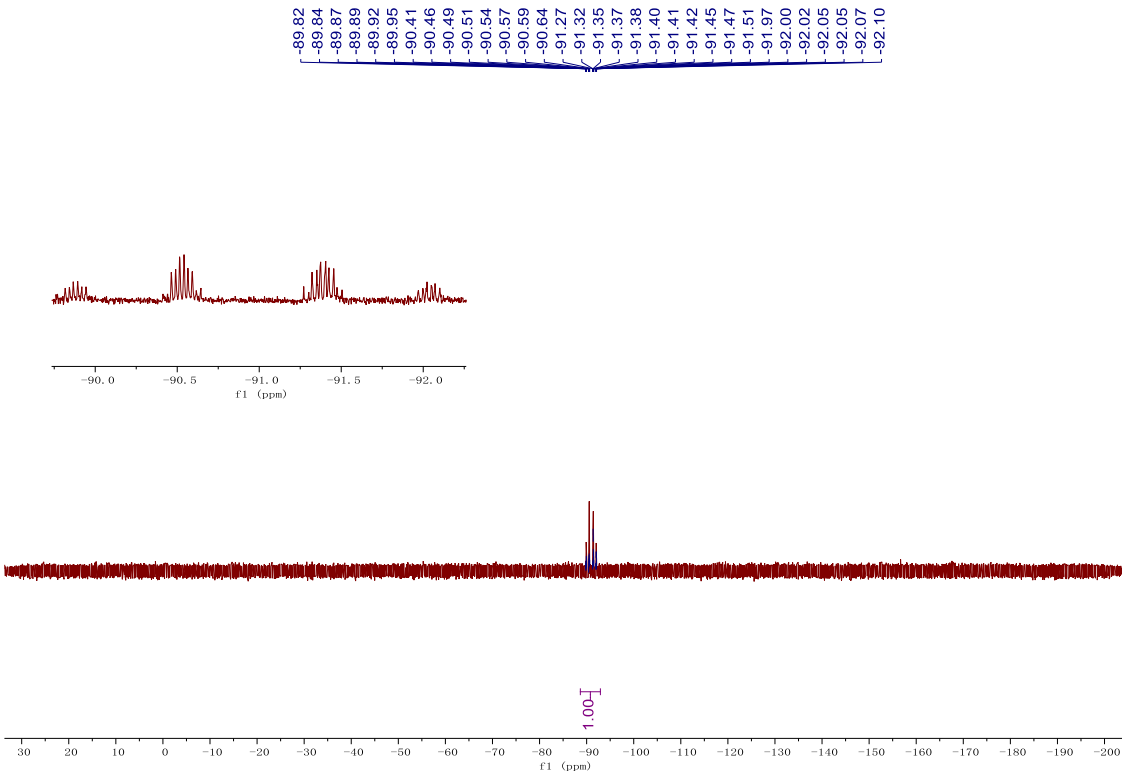


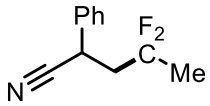
3ae ^{1}H NMR
(400 MHz, $CDCl_3$)



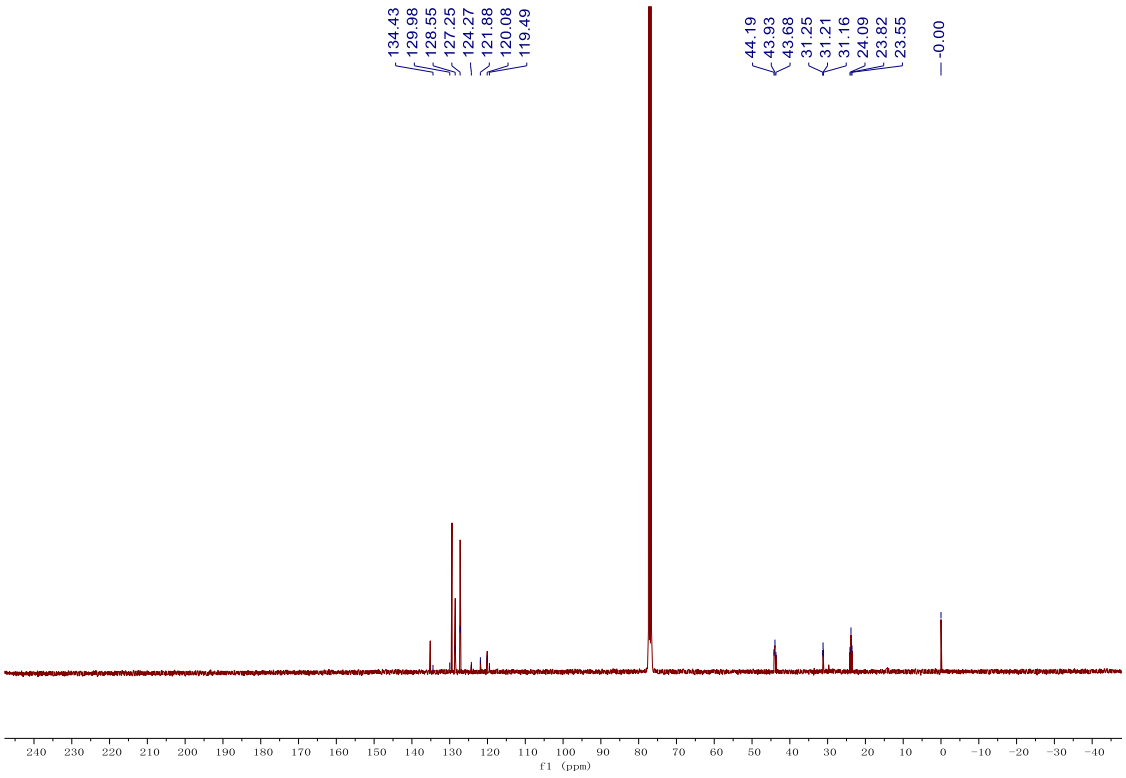


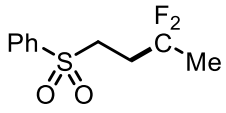
3ae ^{19}F NMR
(376 MHz, $CDCl_3$)



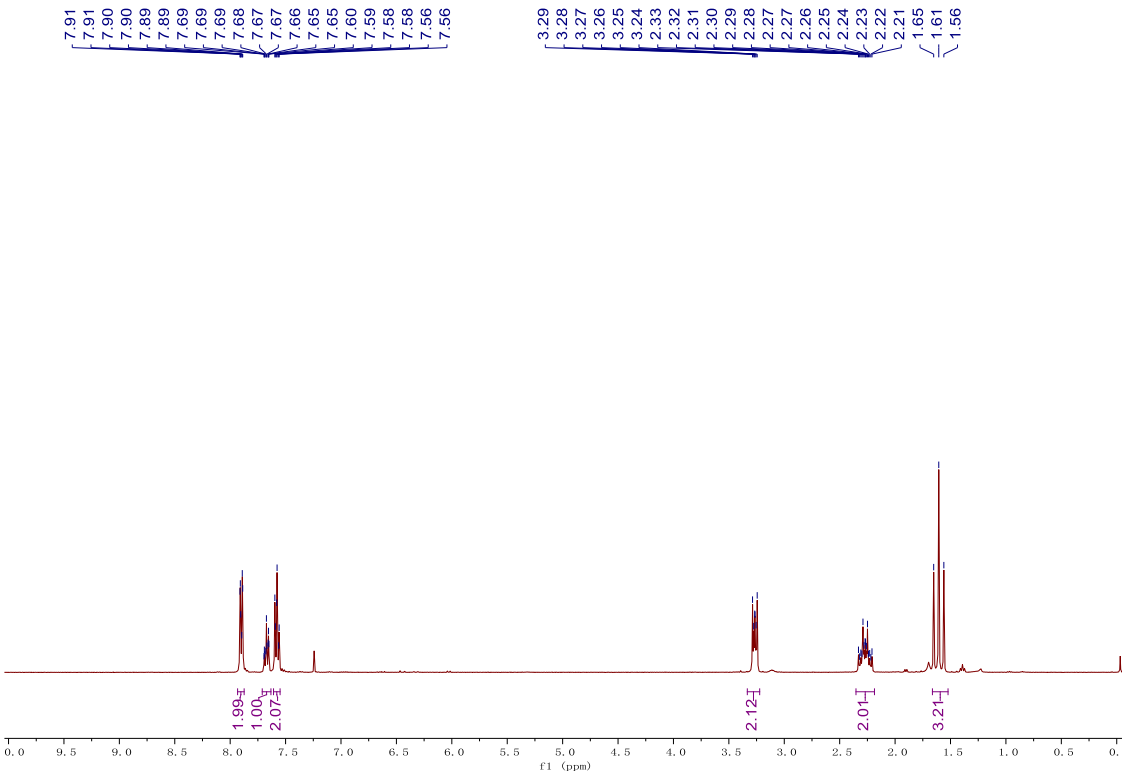


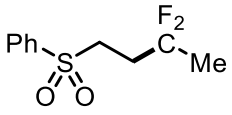
3ae ^{13}C NMR
(101 MHz, $CDCl_3$)



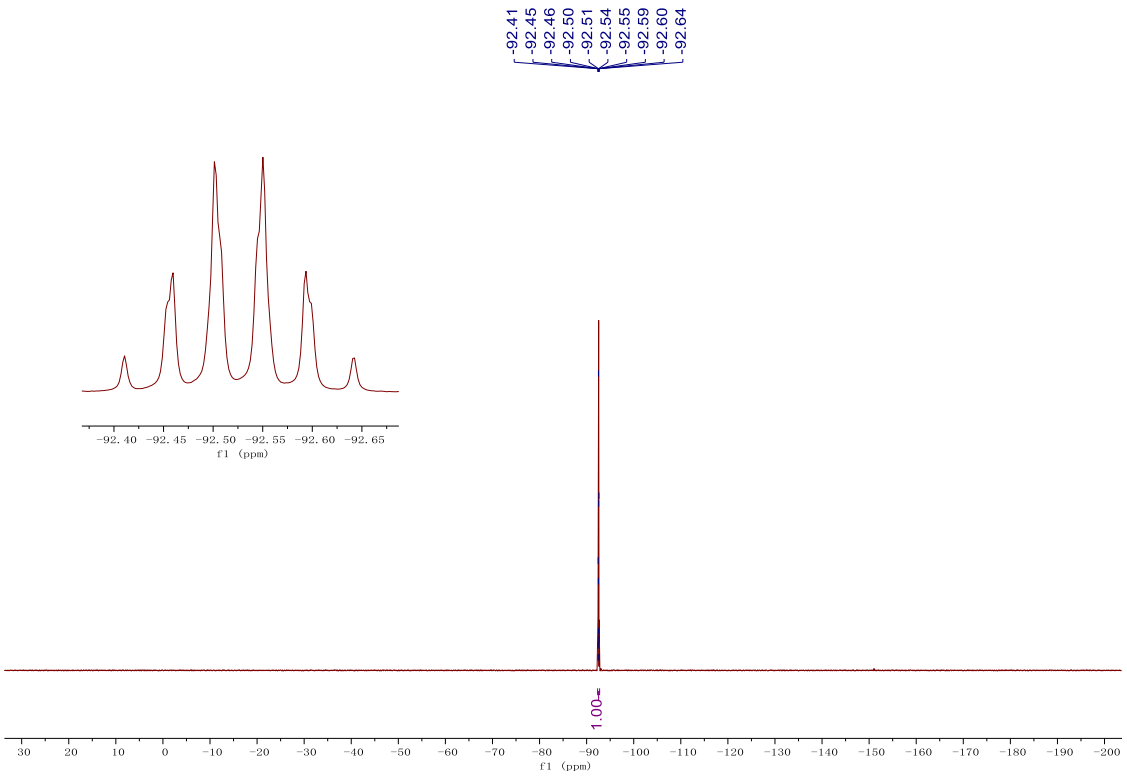


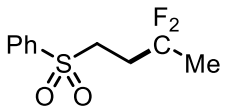
3af ^{1}H NMR
(400 MHz, $CDCl_3$)



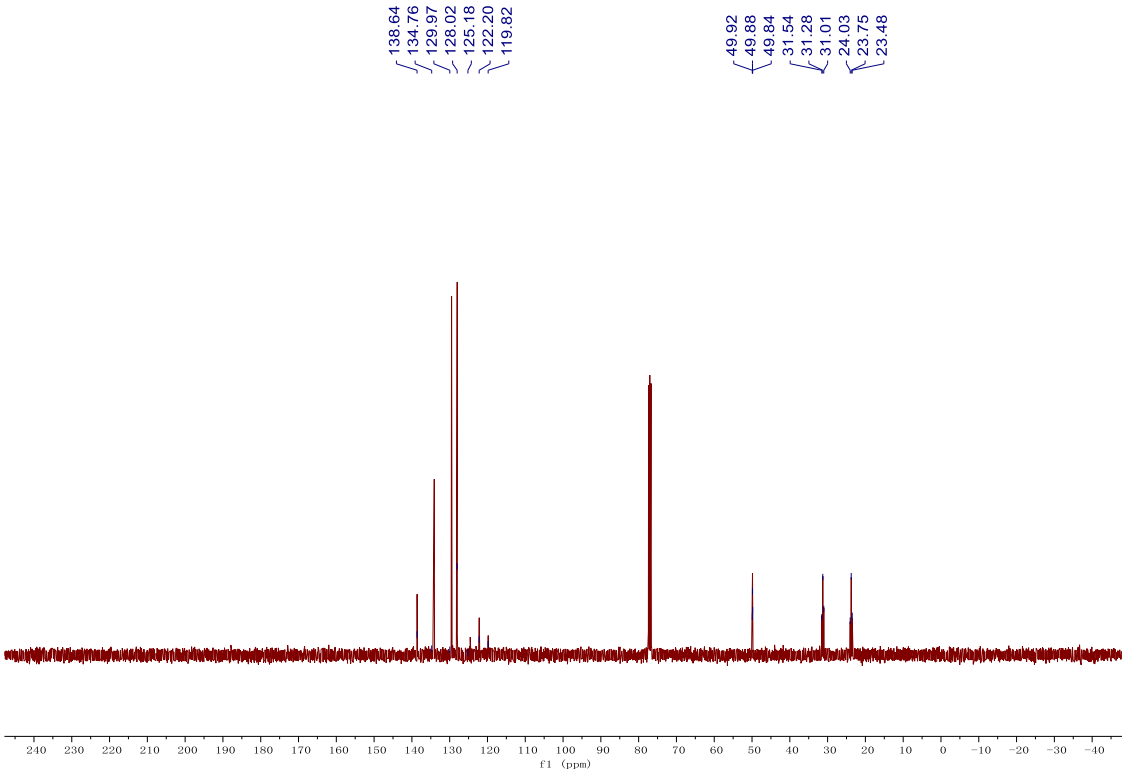


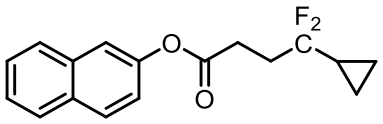
3af ^{19}F NMR
(376 MHz, $CDCl_3$)



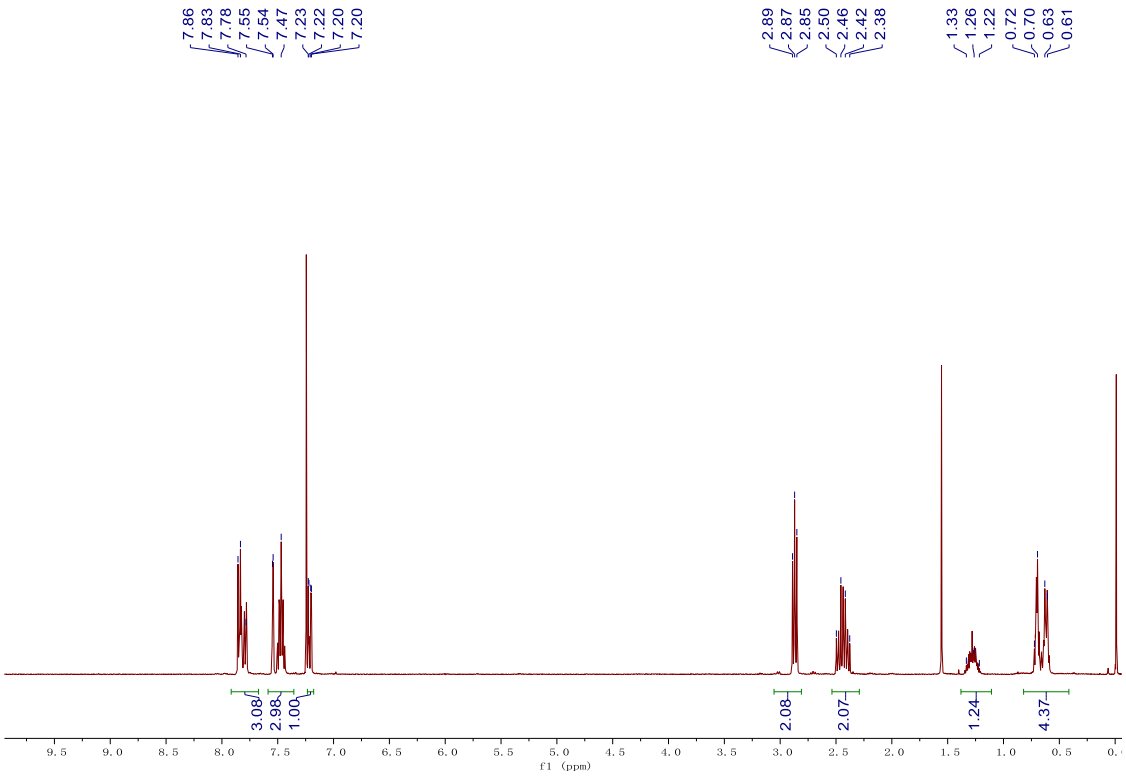


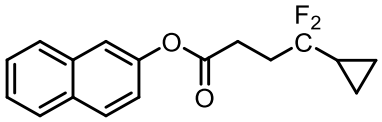
3af ^{13}C NMR
(101 MHz, $CDCl_3$)



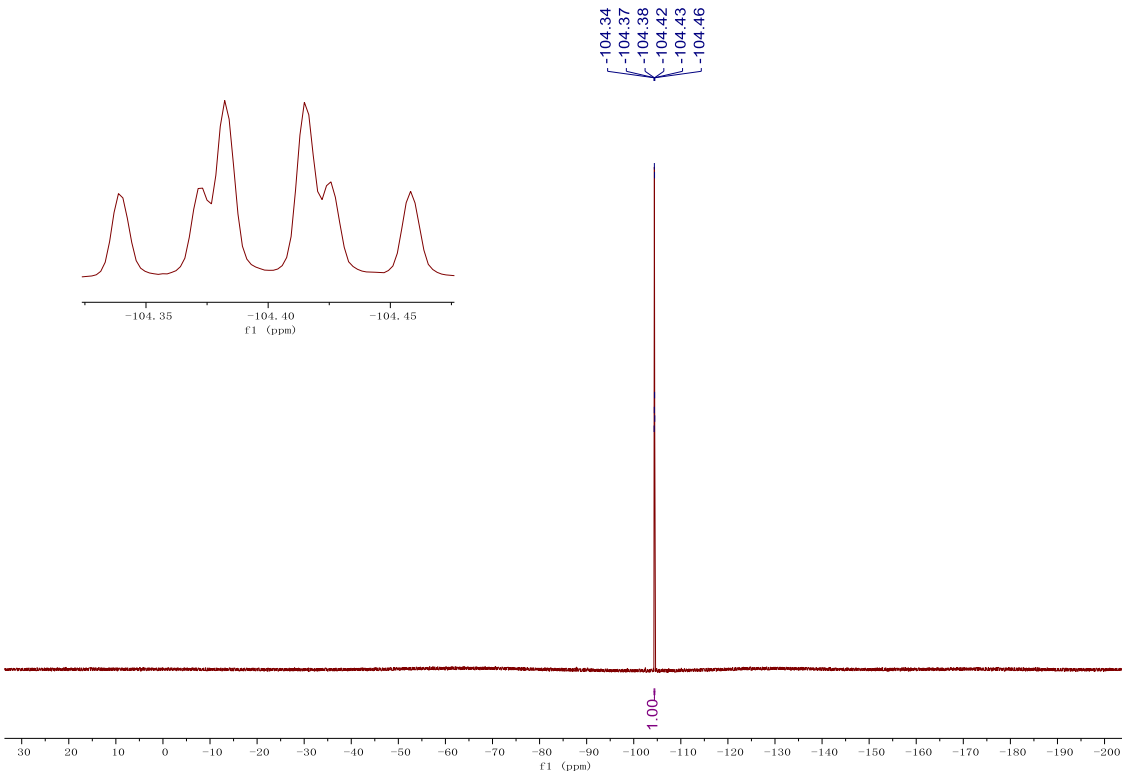


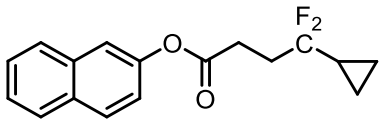
3ag ^{1}H NMR
(400 MHz, $CDCl_3$)



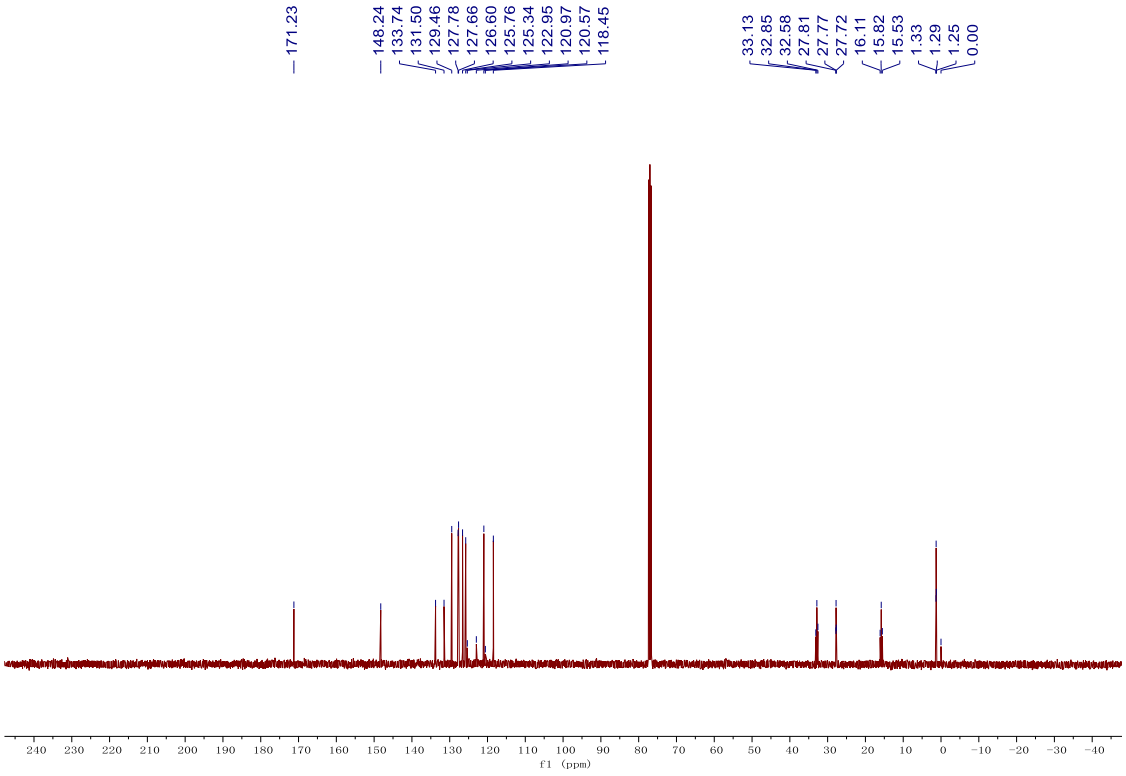


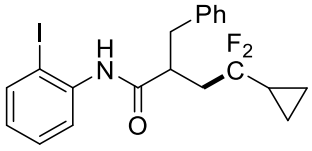
3ag ^{19}F NMR
(376 MHz, $CDCl_3$)



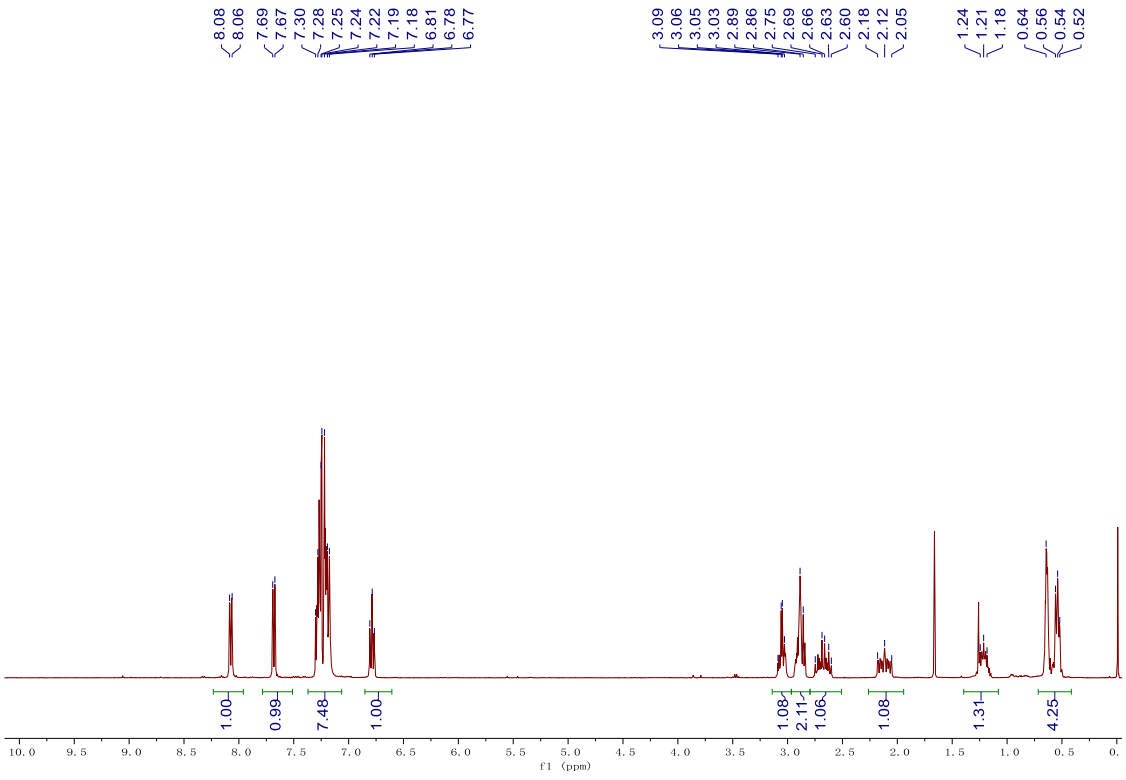


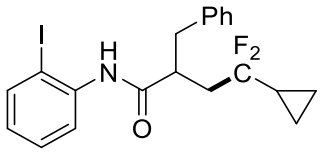
3ag ^{13}C NMR
(101 MHz, $CDCl_3$)



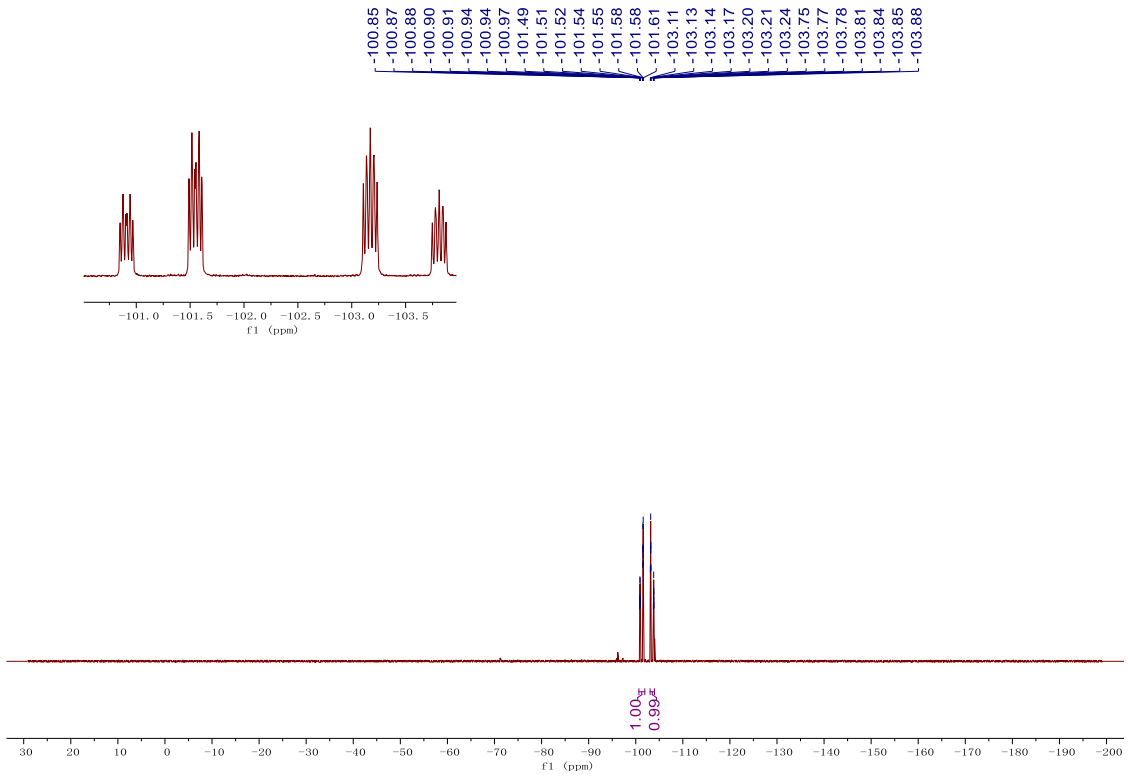


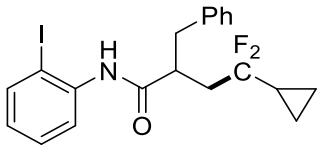
3ah ^{1}H NMR
(400 MHz, $CDCl_3$)



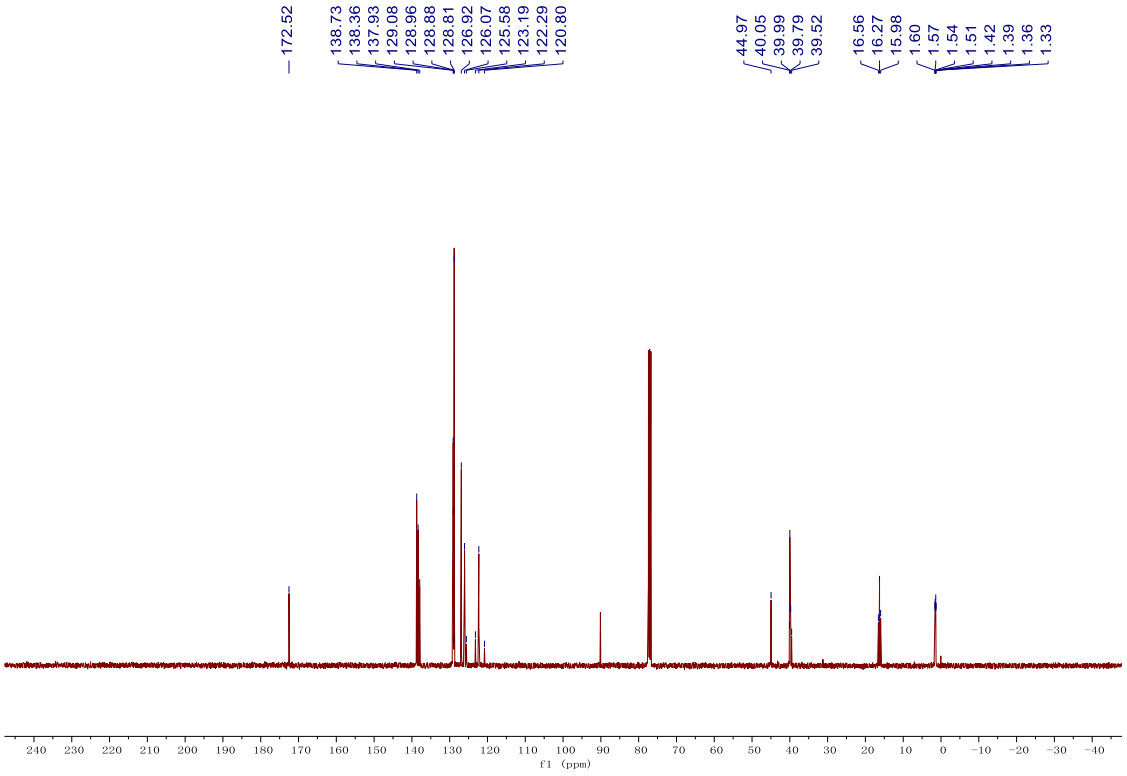


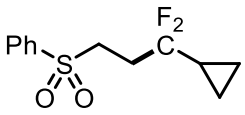
3ah ^{19}F NMR
(376 MHz, $CDCl_3$)



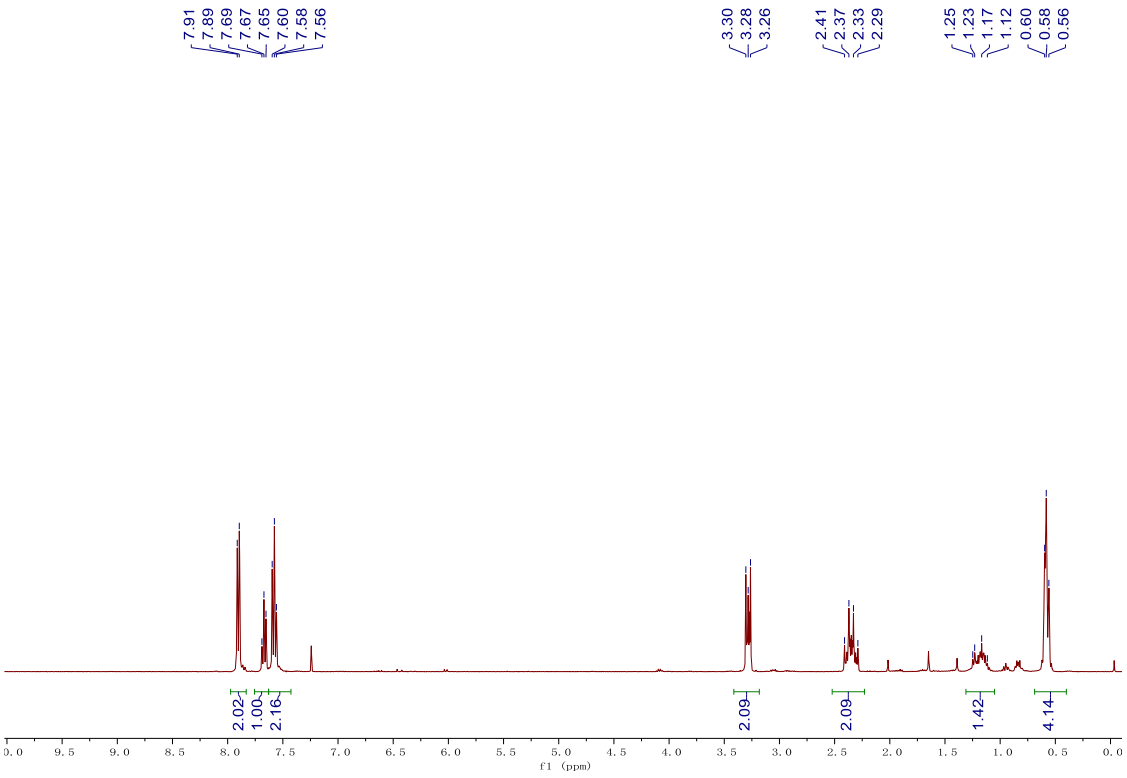


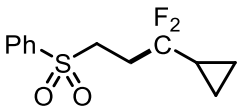
3ah ^{13}C NMR
(101 MHz, $CDCl_3$)



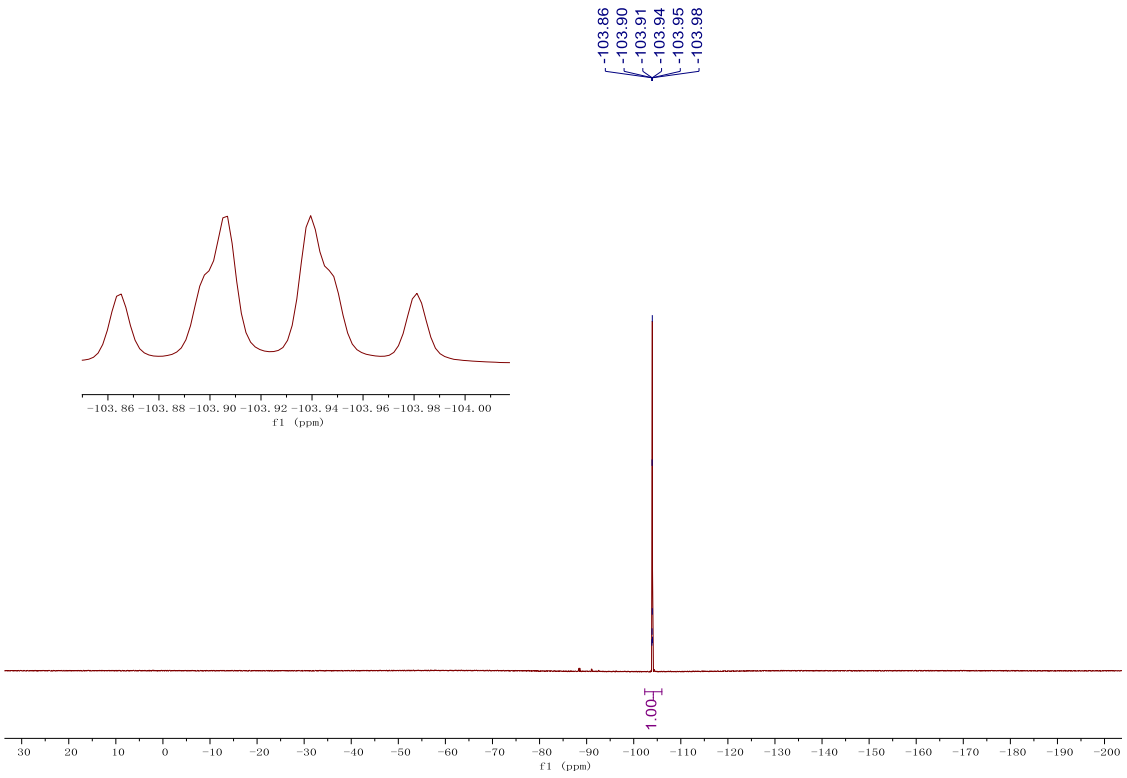


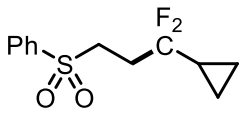
3ai ^{1}H NMR
(400 MHz, $CDCl_3$)



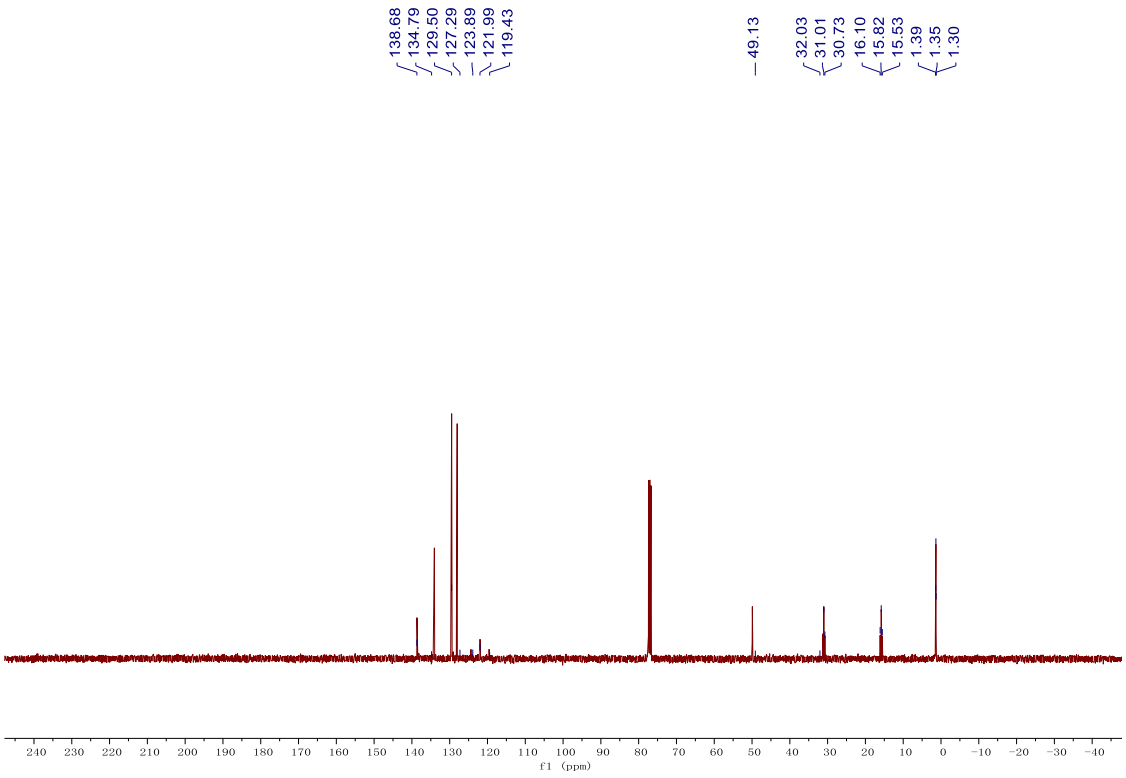


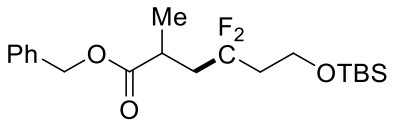
3ai ^{19}F NMR
(376 MHz, $CDCl_3$)



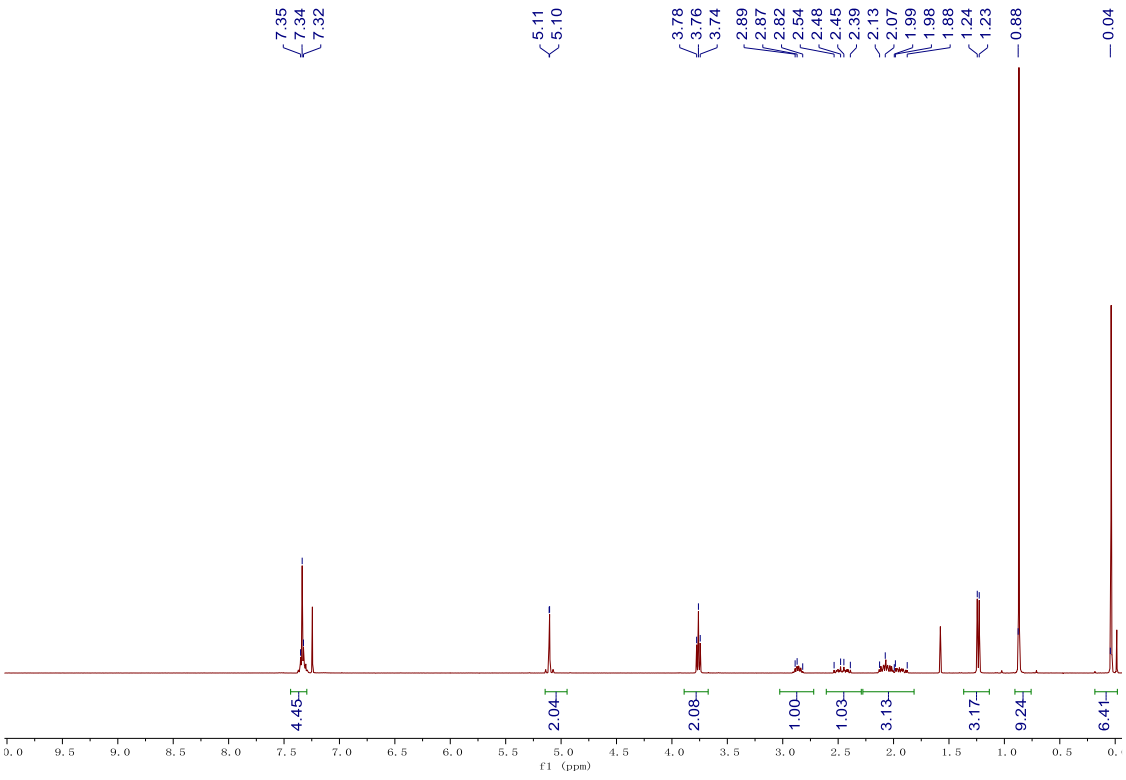


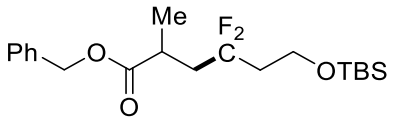
3ai ^{13}C NMR
(101 MHz, $CDCl_3$)



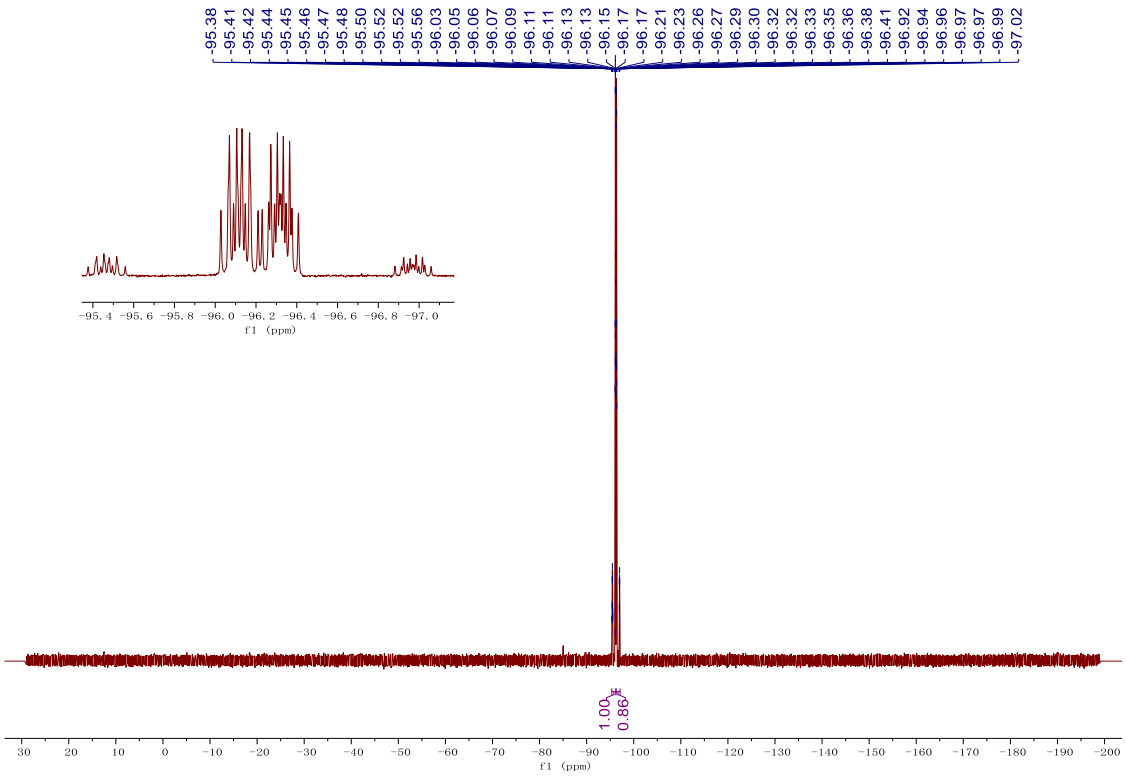


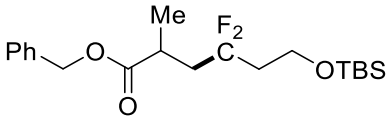
3aj ^{1}H NMR
(400 MHz, $CDCl_3$)



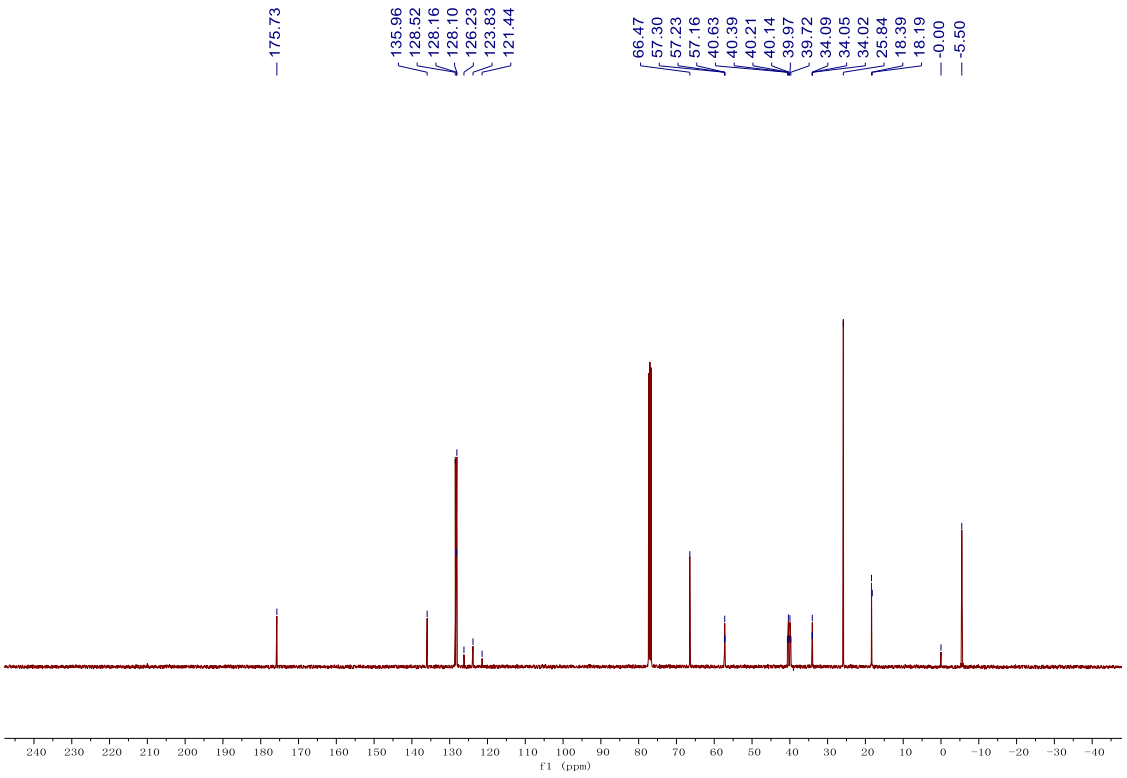


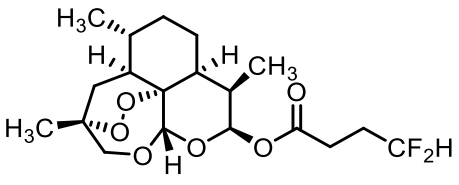
3aj ^{19}F NMR
(376 MHz, $CDCl_3$)



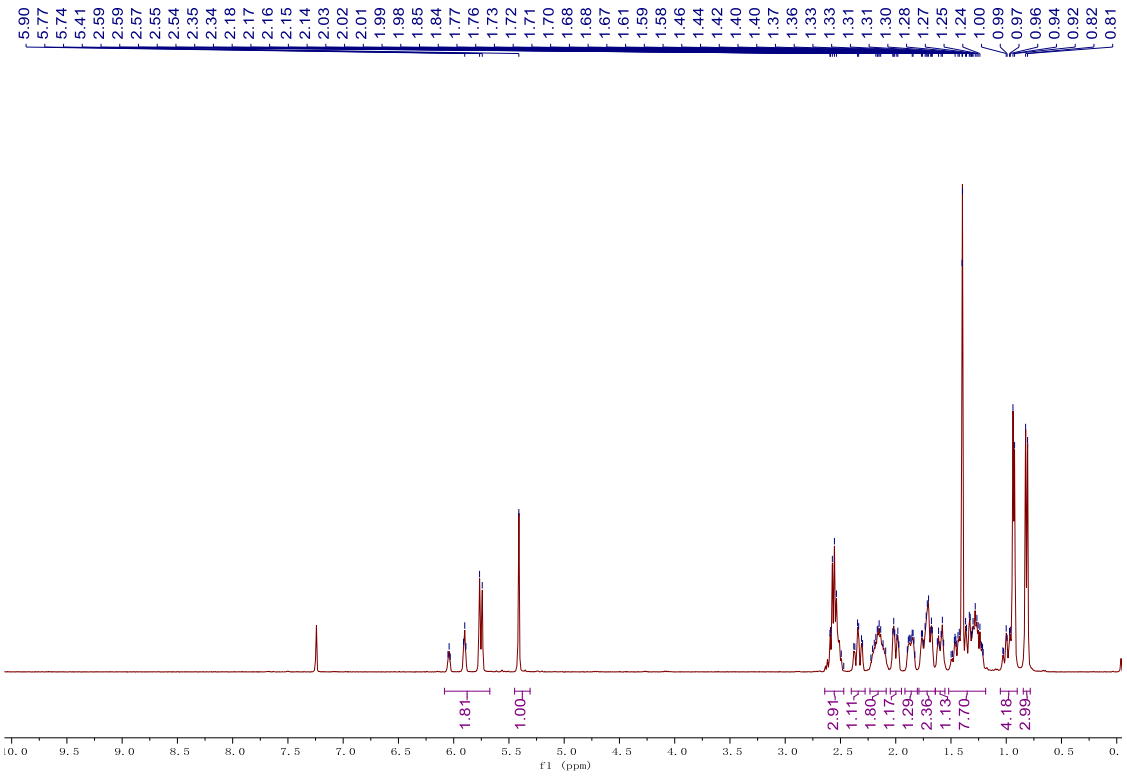


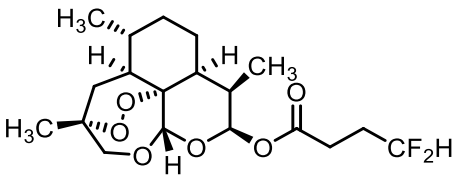
3aj ^{13}C NMR
(101 MHz, $CDCl_3$)



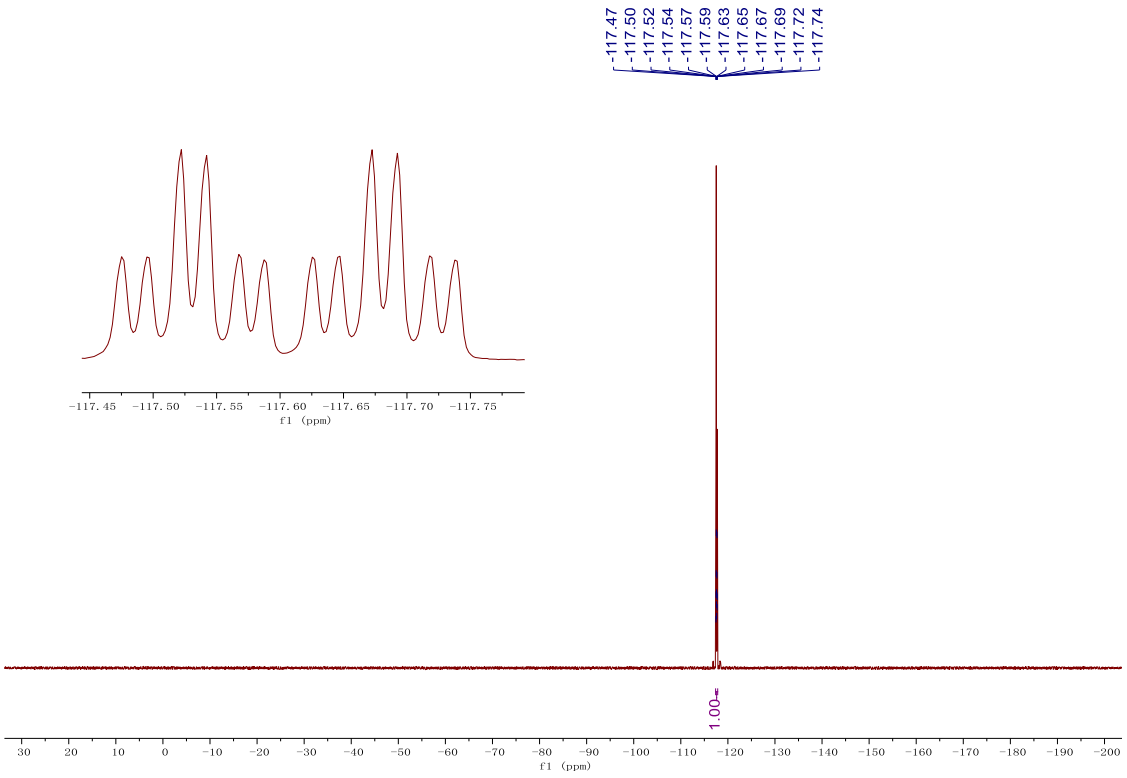


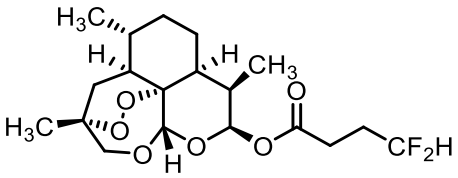
3al ^{1}H NMR
(400 MHz, $CDCl_3$)



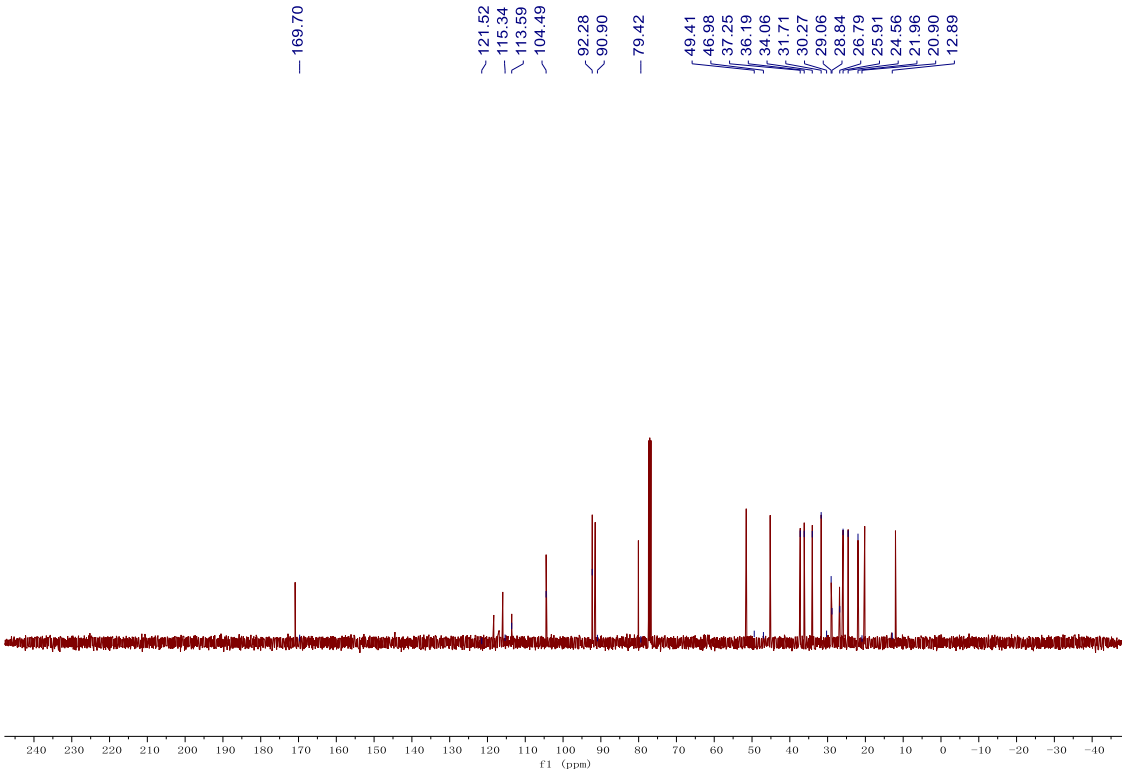


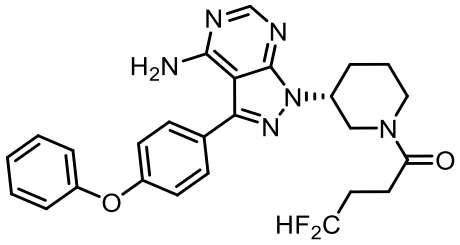
3al ^{19}F NMR
(376 MHz, $CDCl_3$)



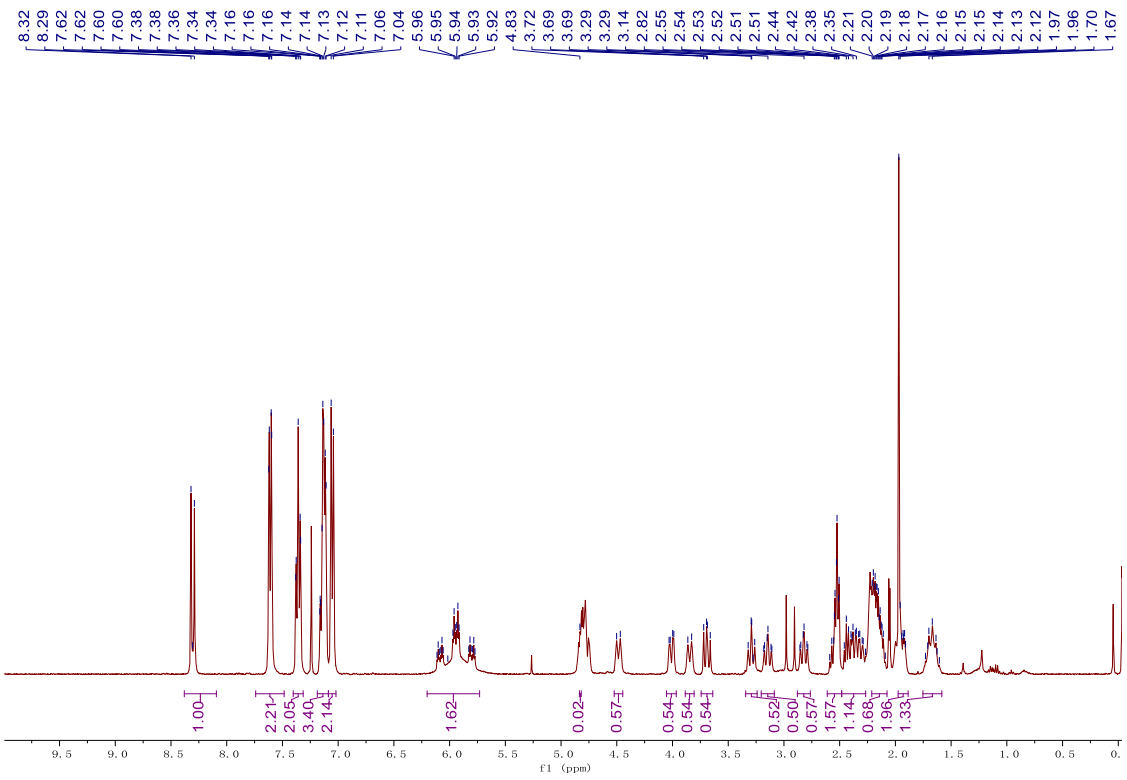


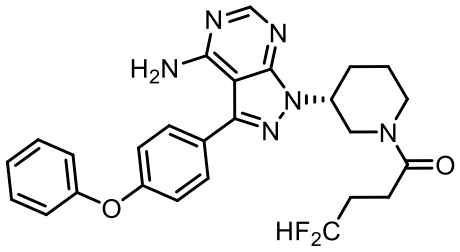
3al ^{13}C NMR
(101 MHz, $CDCl_3$)



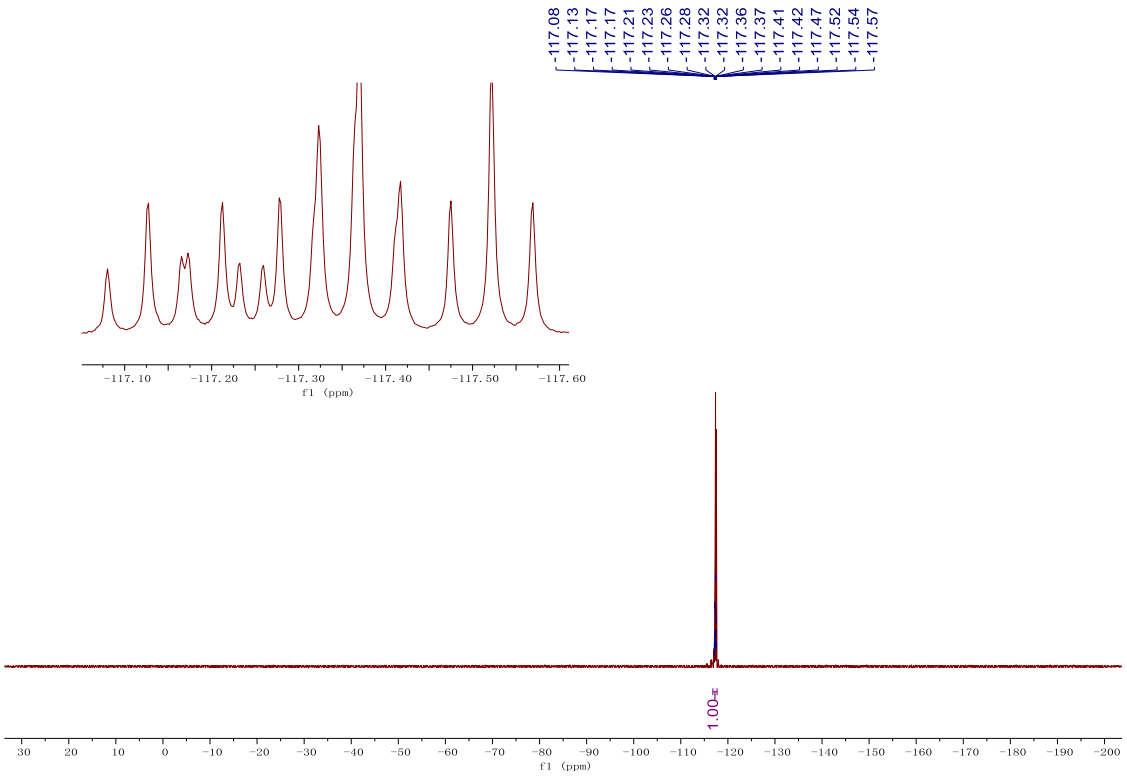


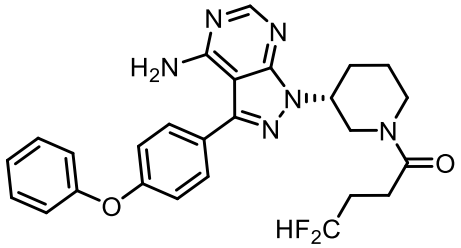
3am ^{1}H NMR
(400 MHz, $CDCl_3$)



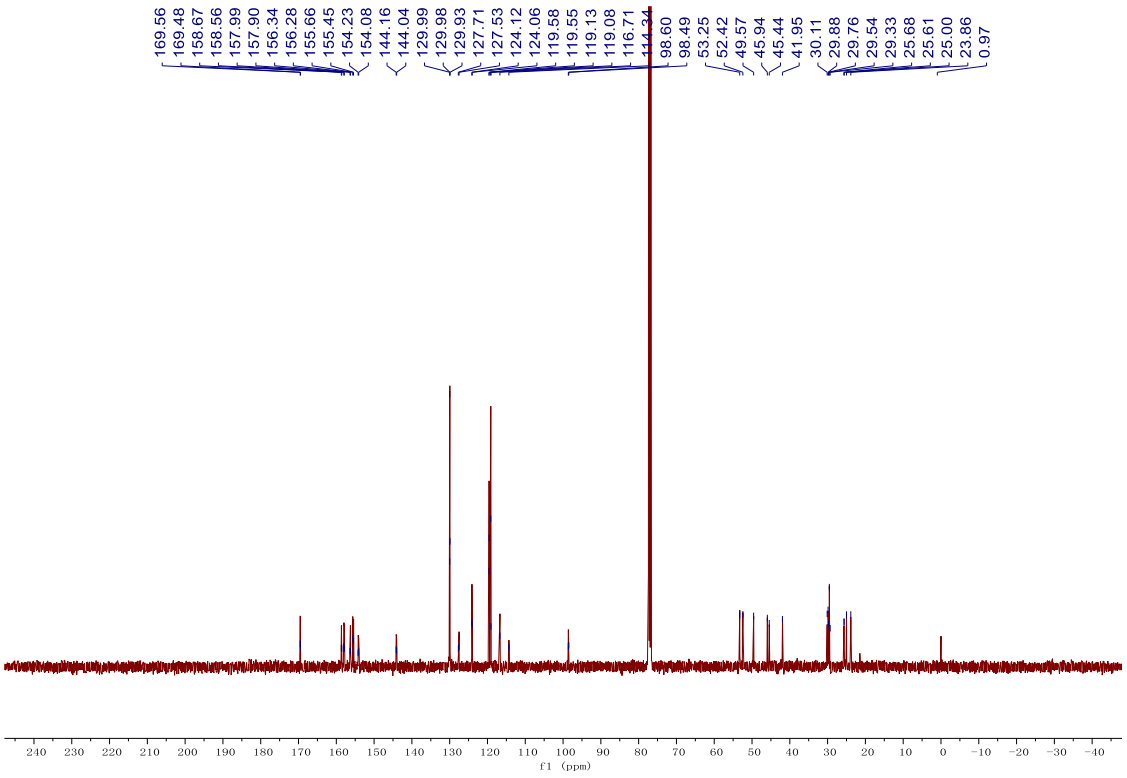


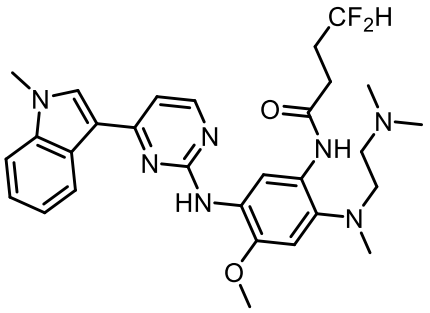
3am ^{19}F NMR
(376 MHz, $CDCl_3$)



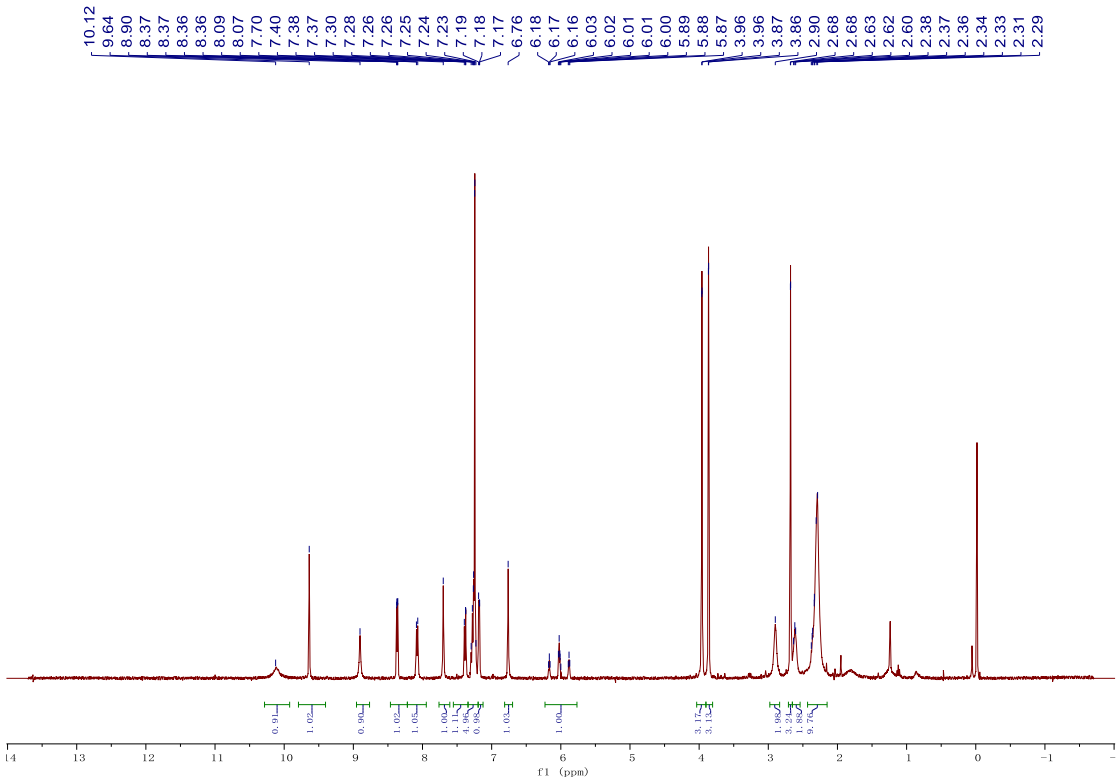


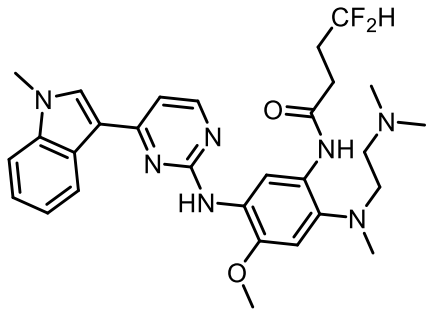
3am ^{13}C NMR
(101 MHz, $CDCl_3$)



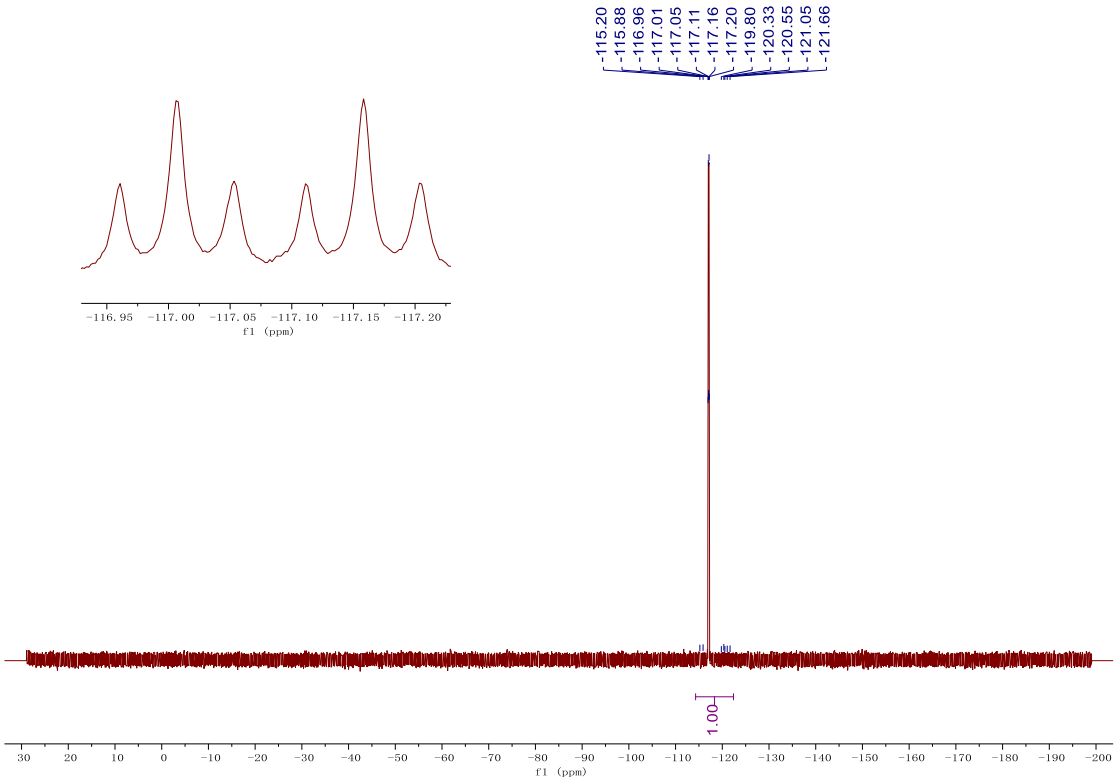


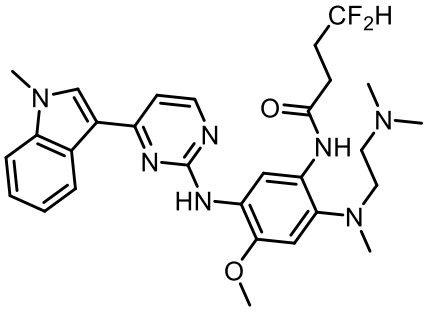
3an, ^{1}H NMR
($CDCl_3$, 400 MHz)



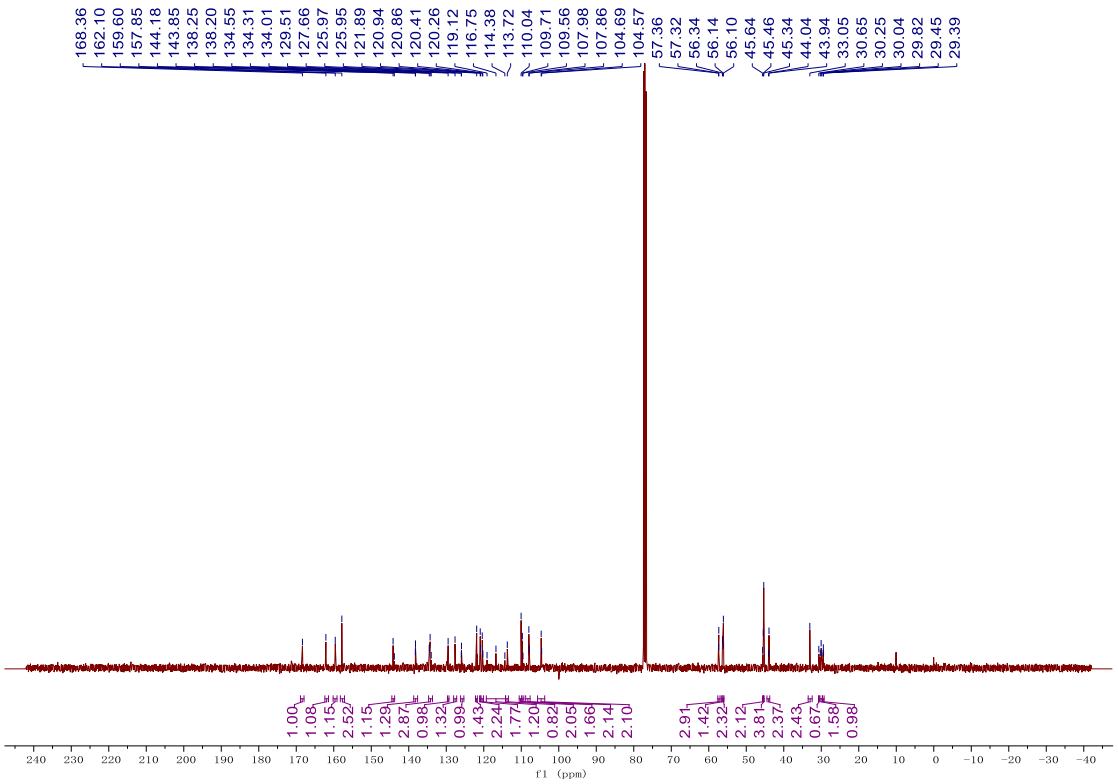


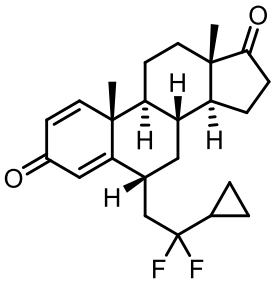
3an, ^{19}F NMR
($CDCl_3$, 376 MHz)



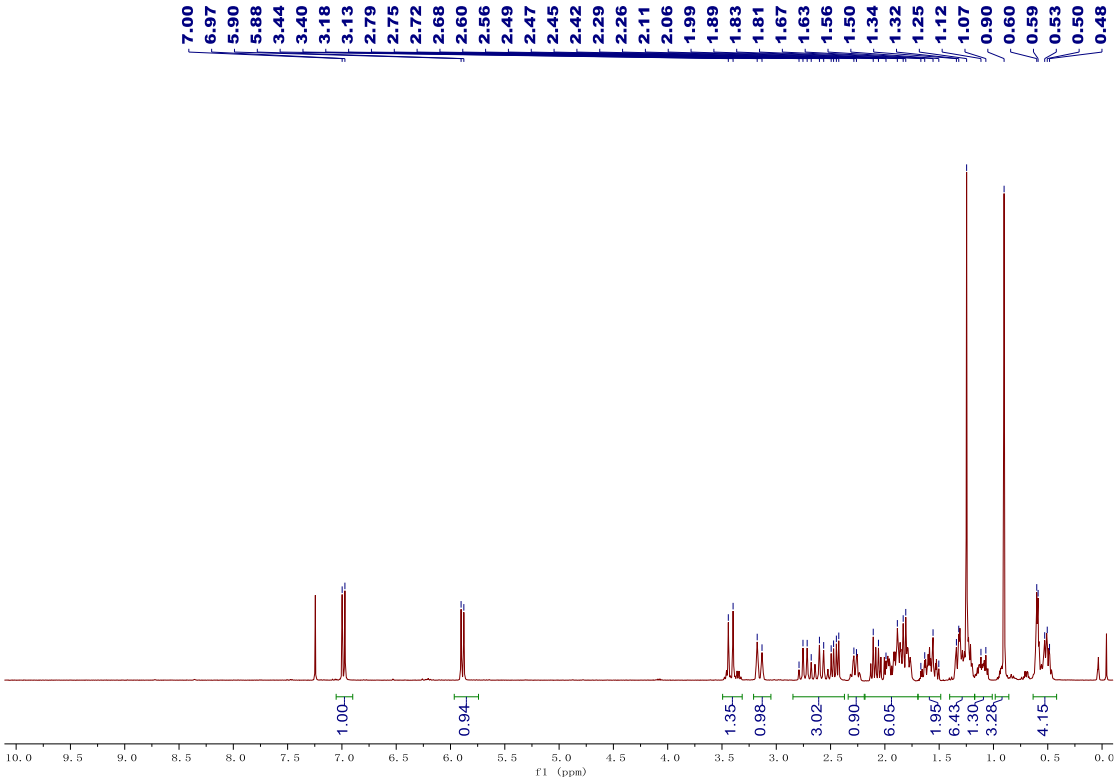


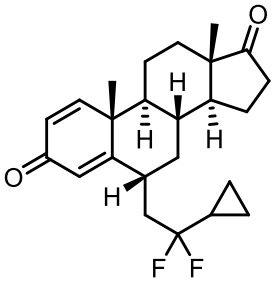
3an, ^{13}C NMR
($CDCl_3$, 101 MHz)



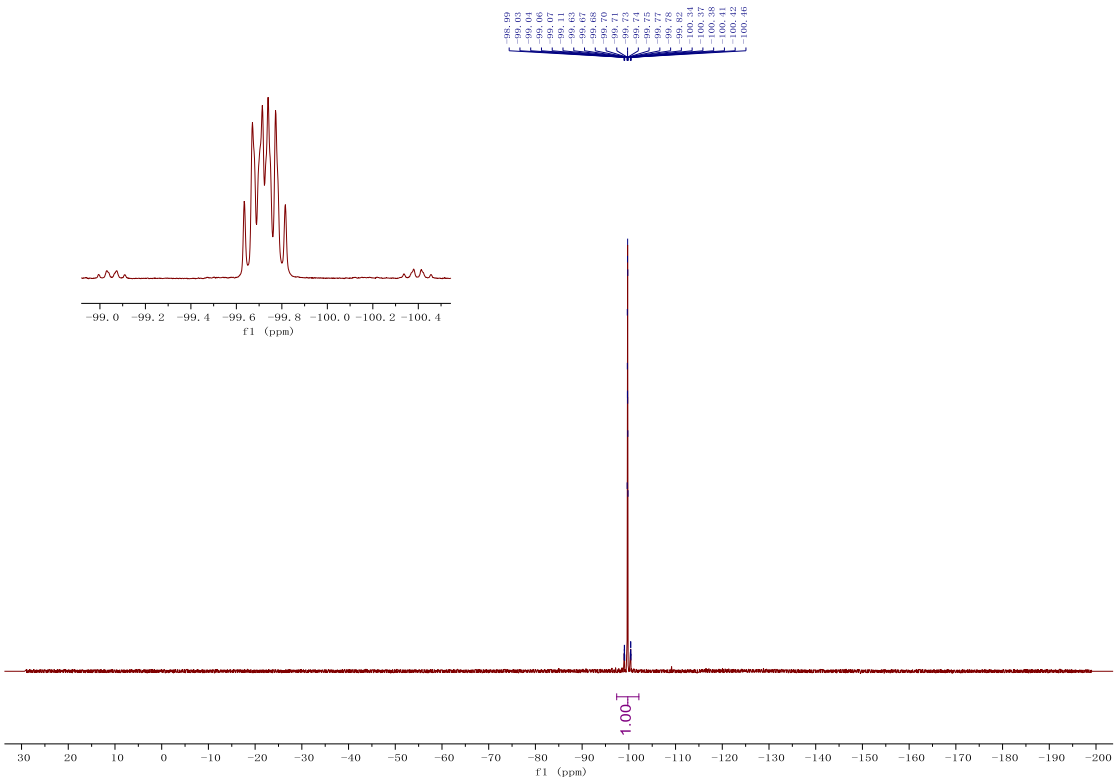


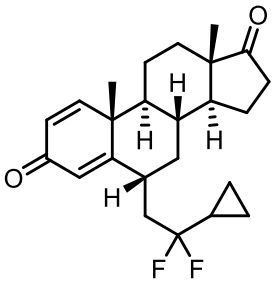
3ao, ^{1}H NMR
($CDCl_3$, 400 MHz)



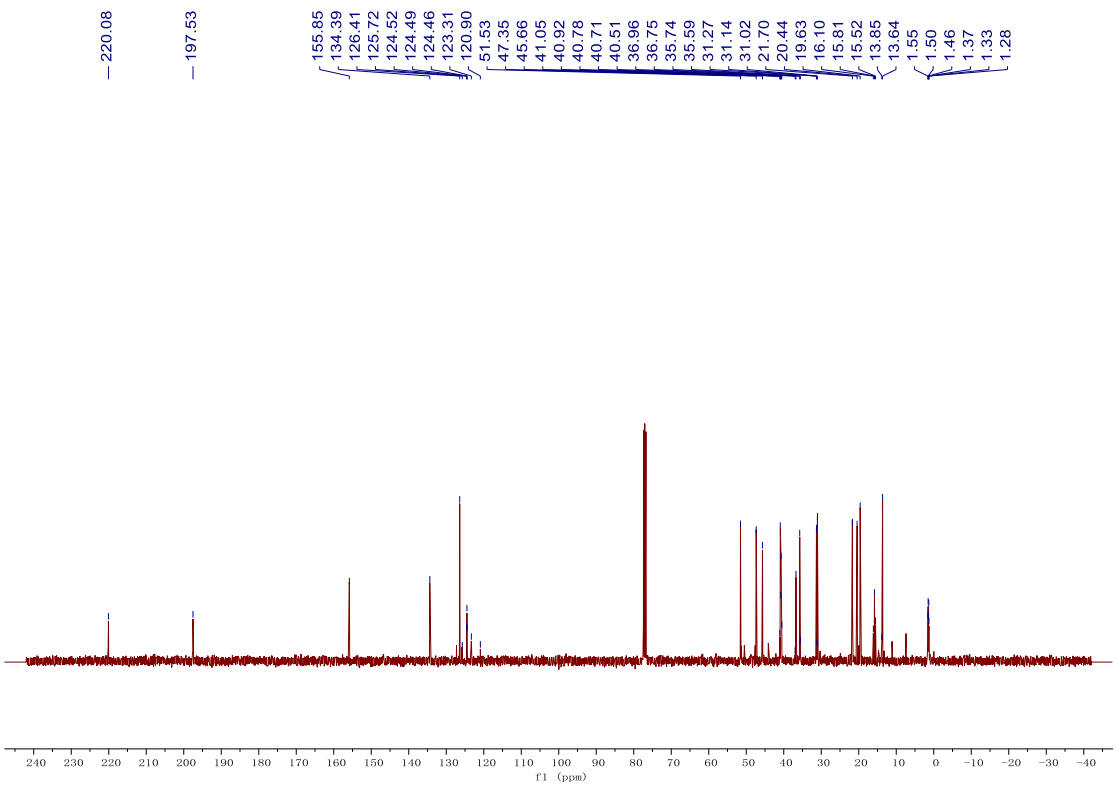


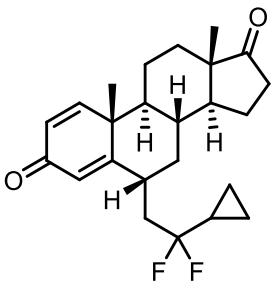
3ao, ^{19}F NMR
($CDCl_3$, 376 MHz)



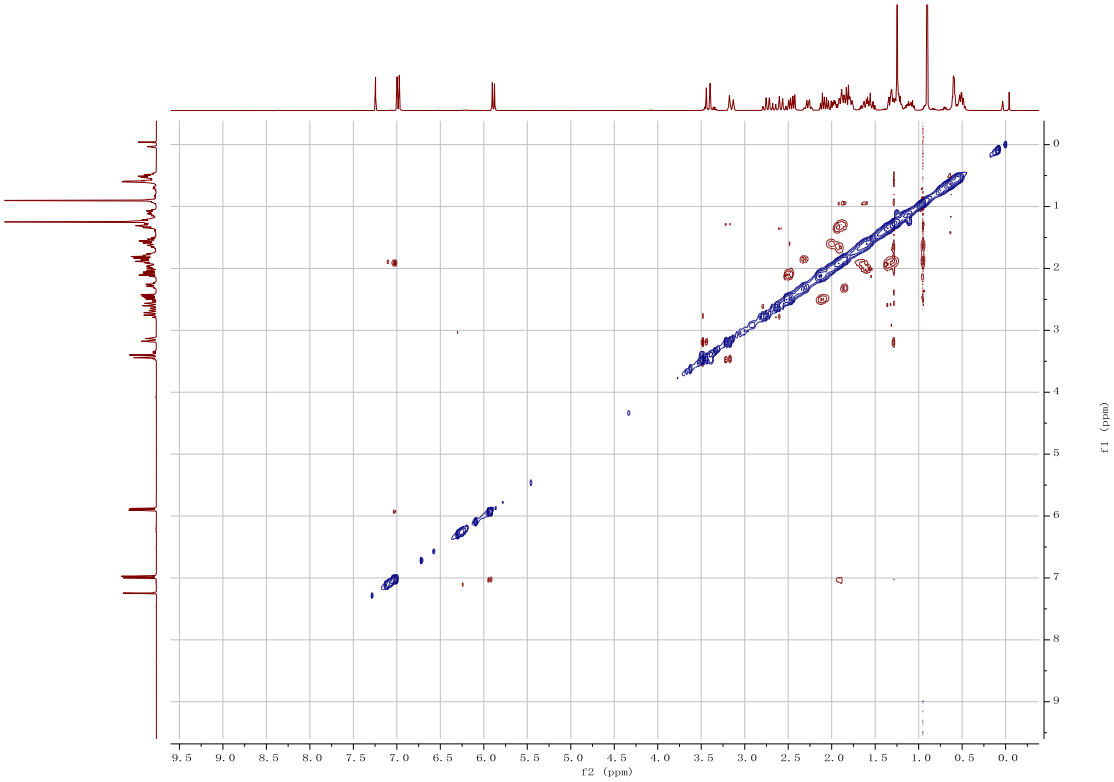


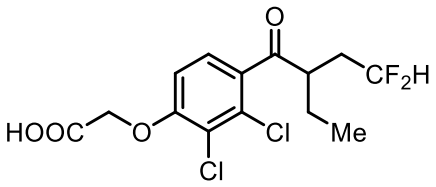
3ao, ^{13}C NMR
($CDCl_3$, 101 MHz)



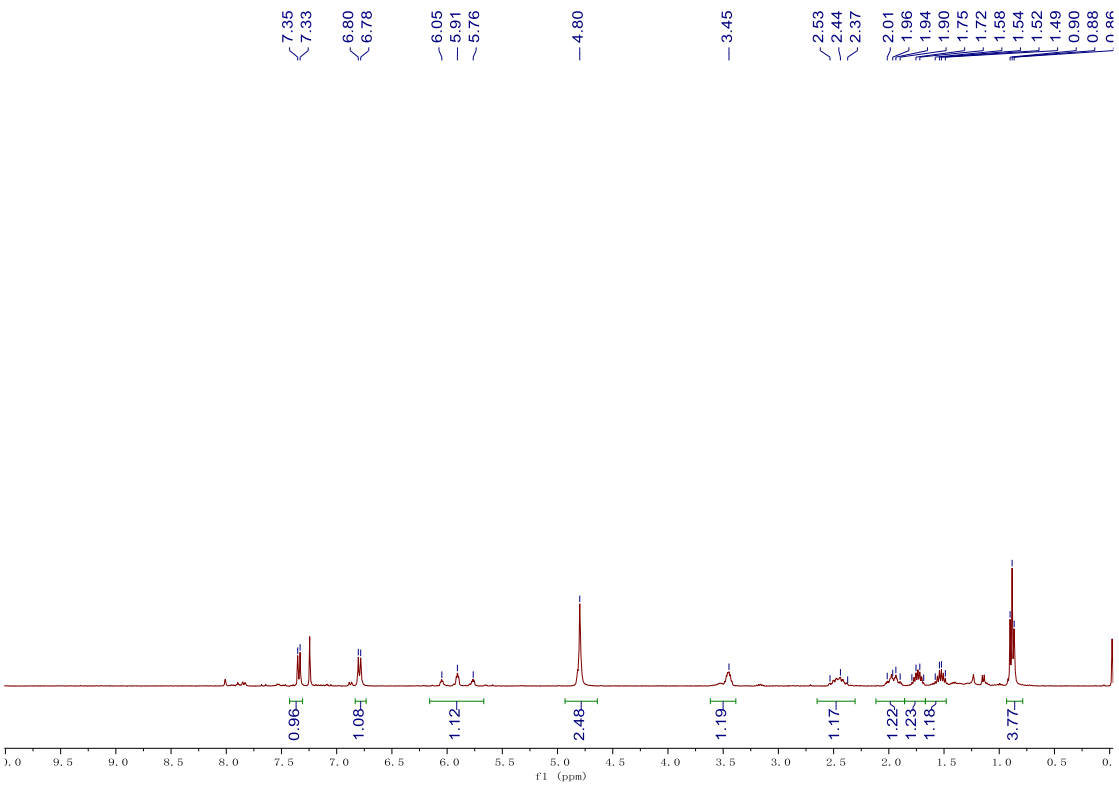


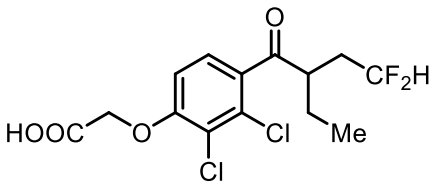
3ao, NOESY
($CDCl_3$, 400 MHz)



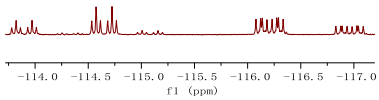


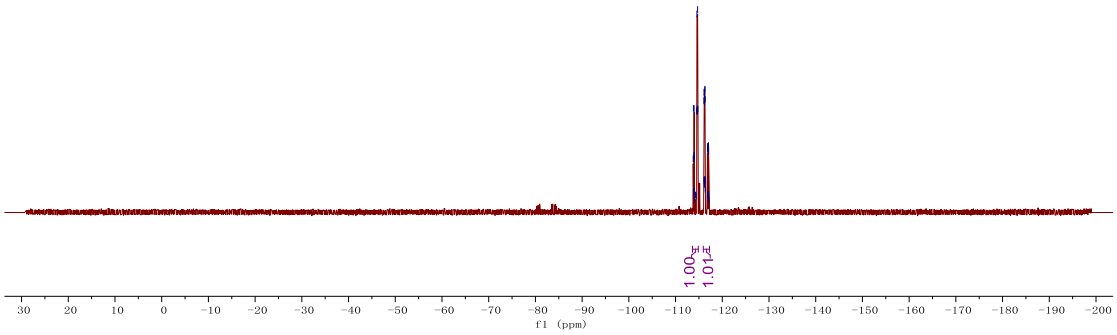
3ap, ^{1}H NMR
($CDCl_3$, 400 MHz)

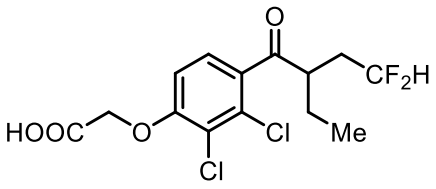




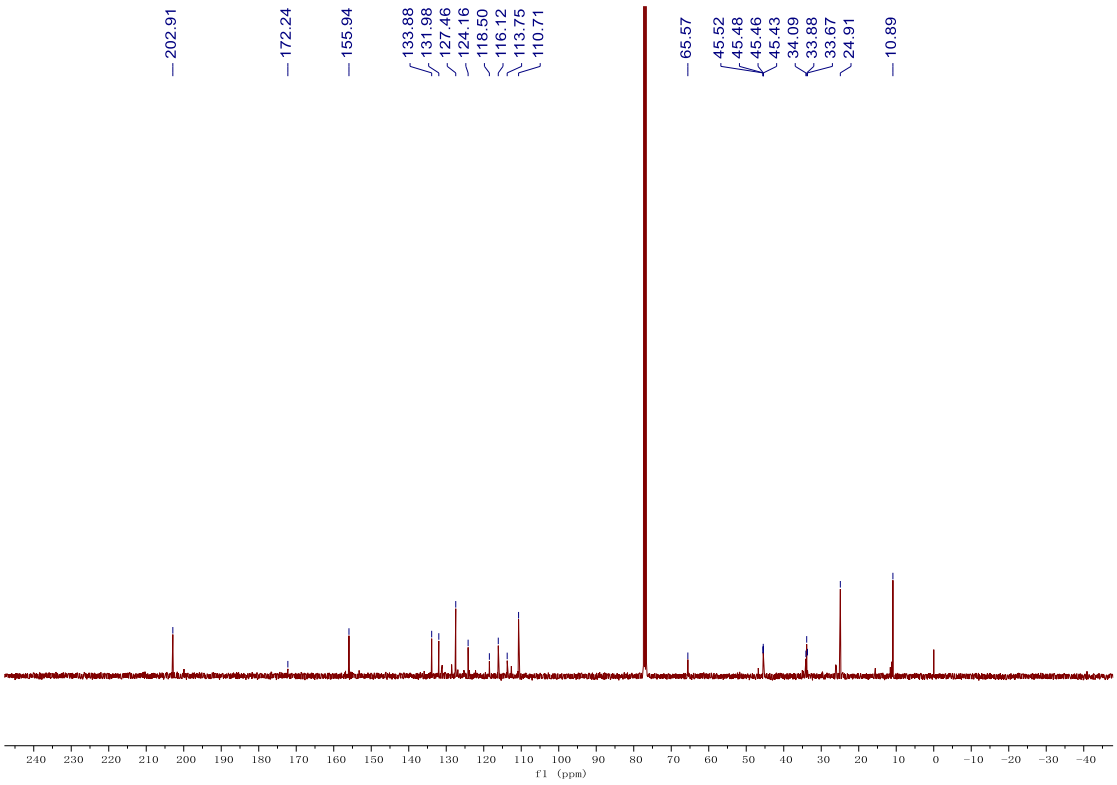
3ap, ^{19}F NMR
($CDCl_3$, 376 MHz)

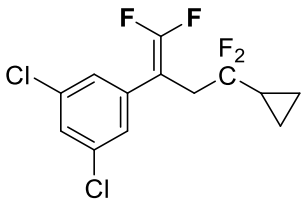




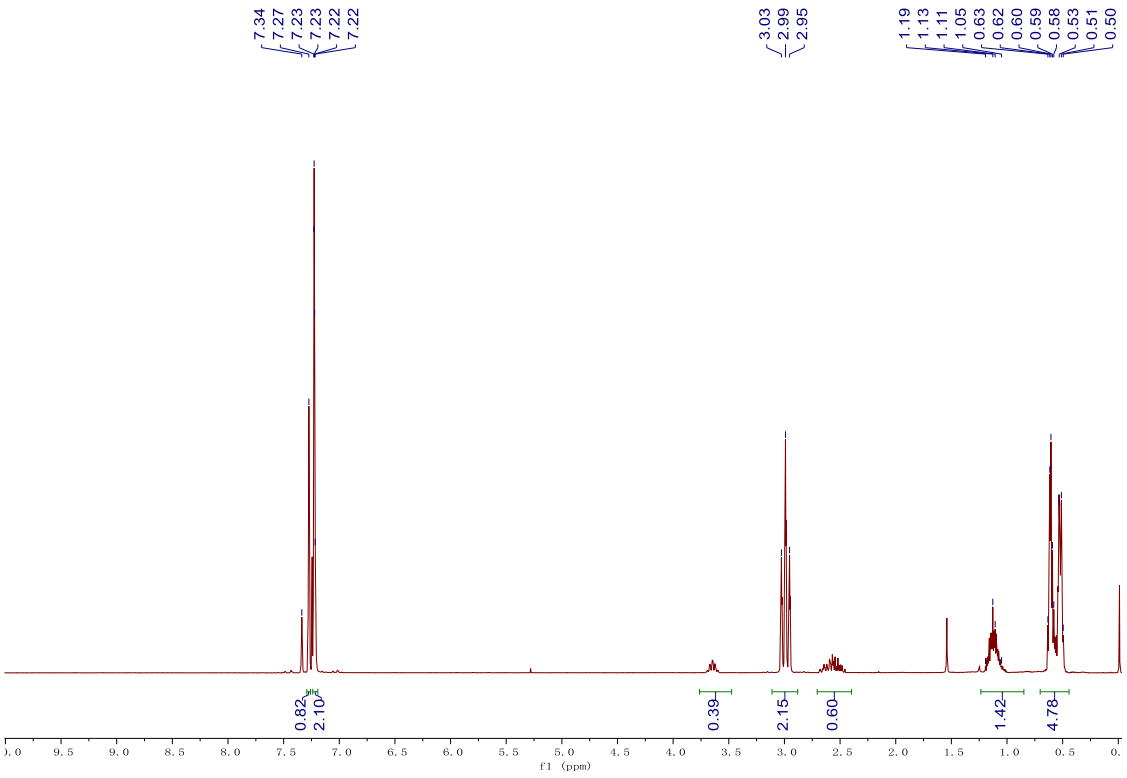


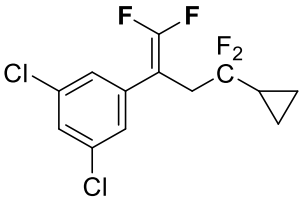
3ap, ^{13}C NMR
($CDCl_3$, 101 MHz)



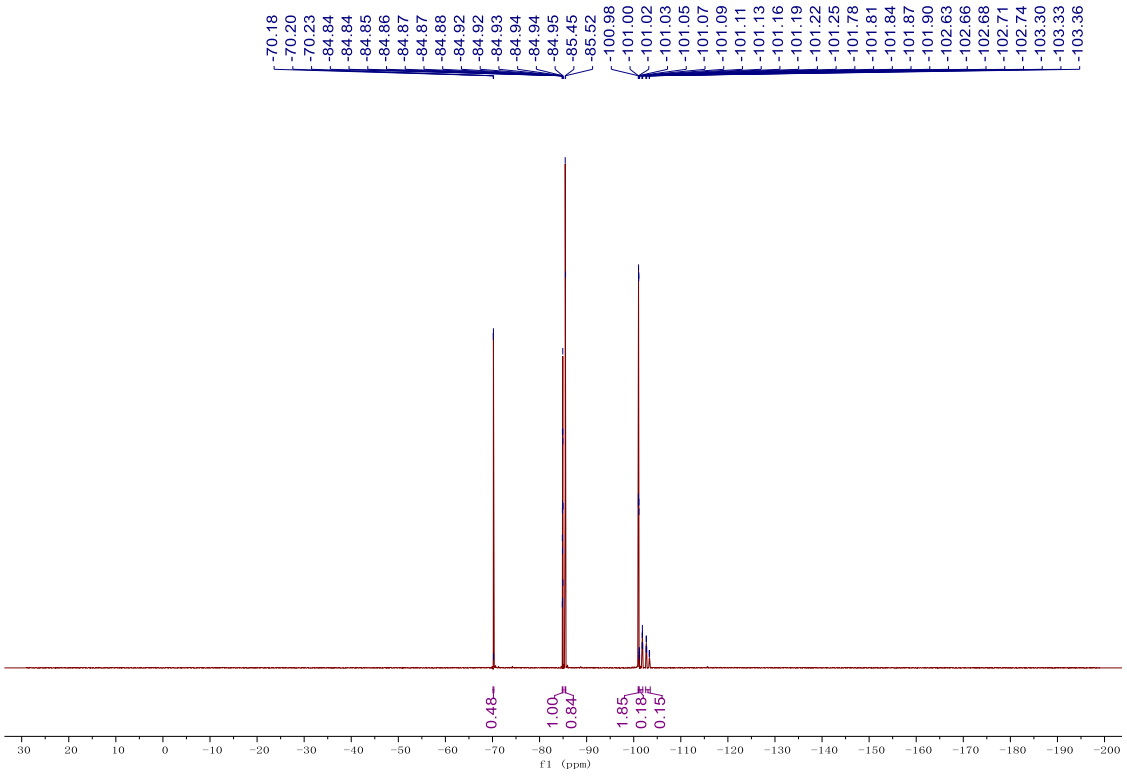


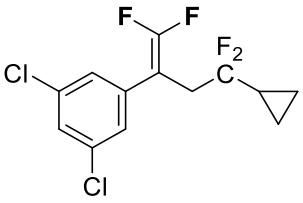
4a ^{1}H NMR
(400 MHz, $CDCl_3$)



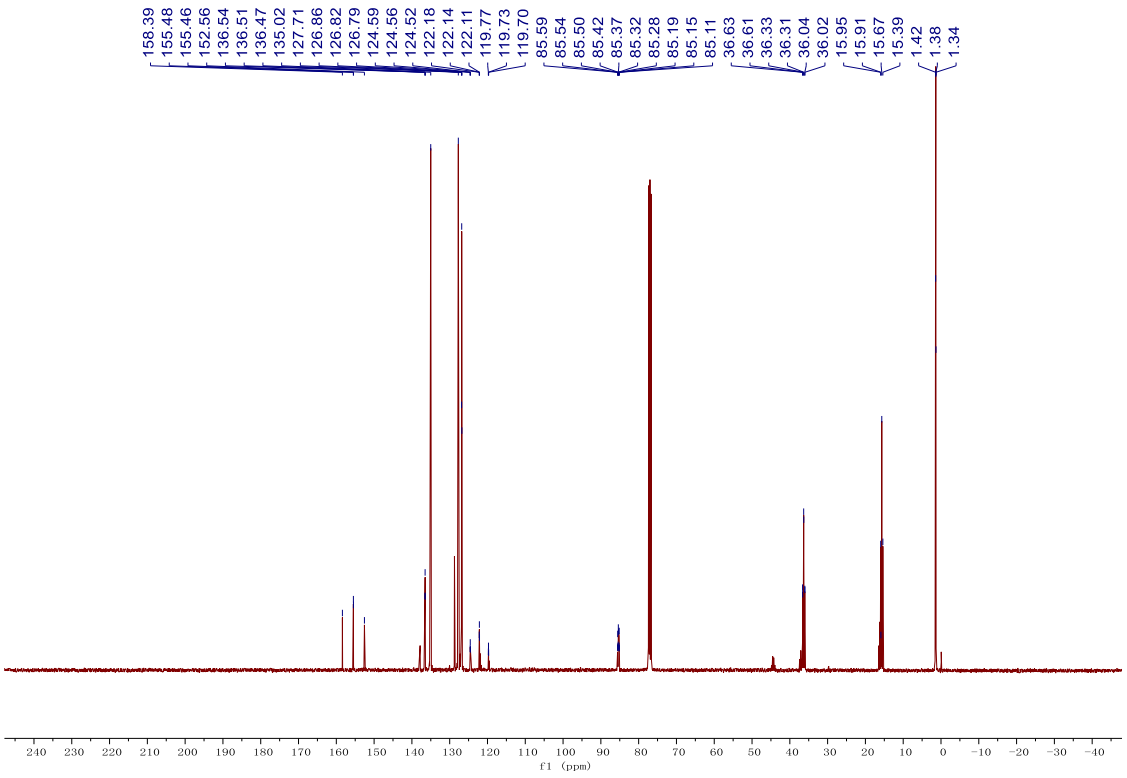


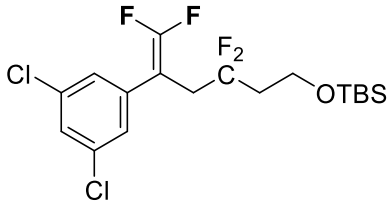
4a ^{19}F NMR
(376 MHz, $CDCl_3$)



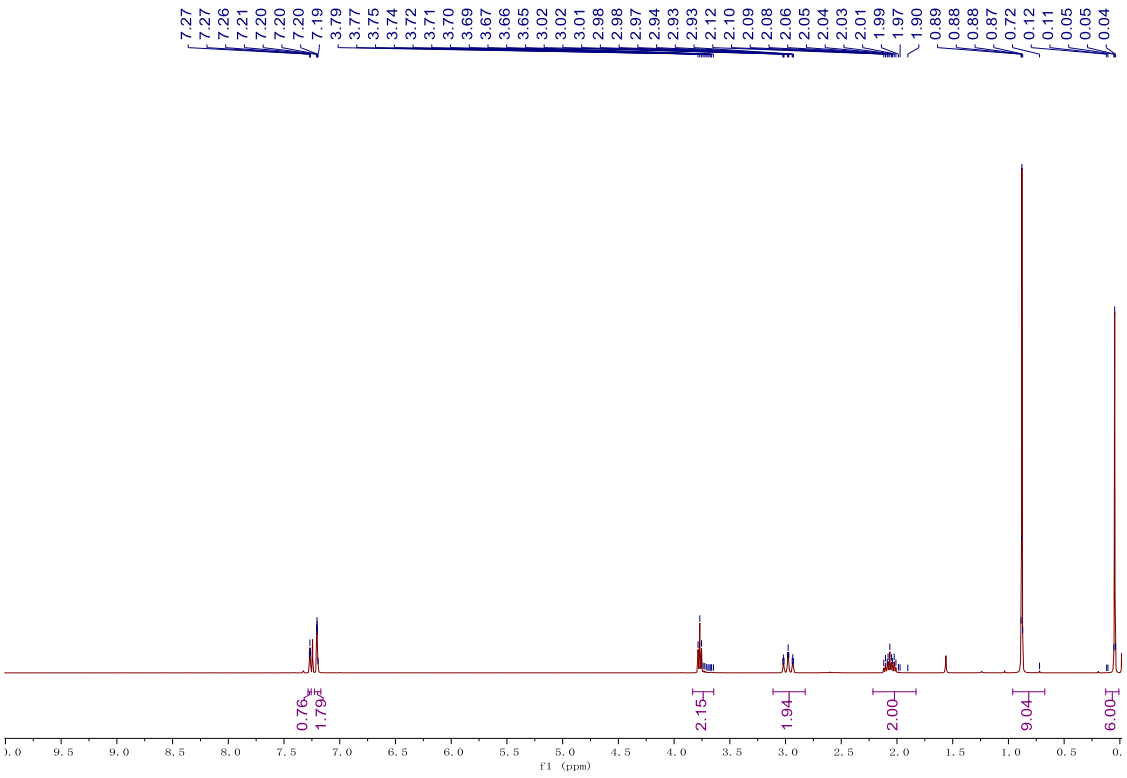


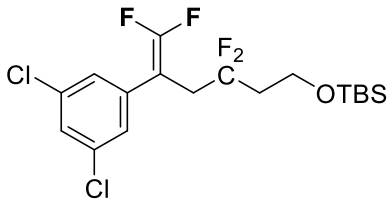
4a ^{13}C NMR
(101 MHz, $CDCl_3$)



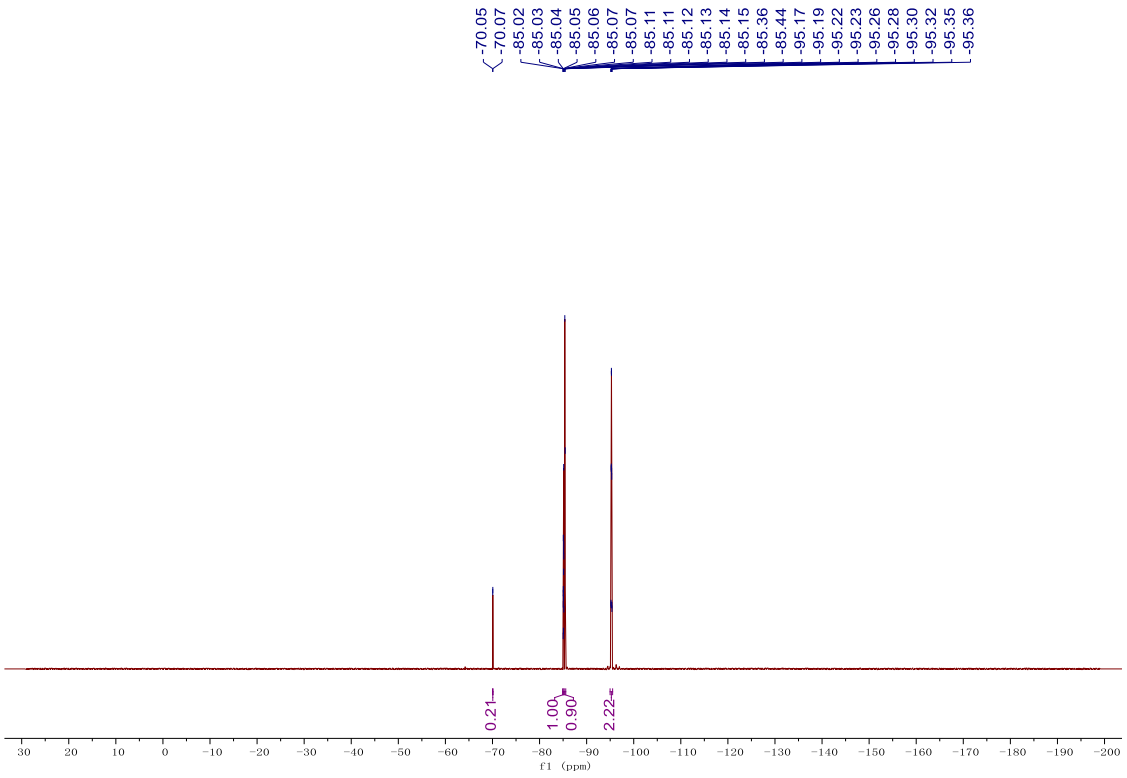


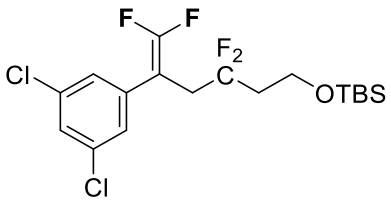
4b ^{1}H NMR
(400 MHz, $CDCl_3$)



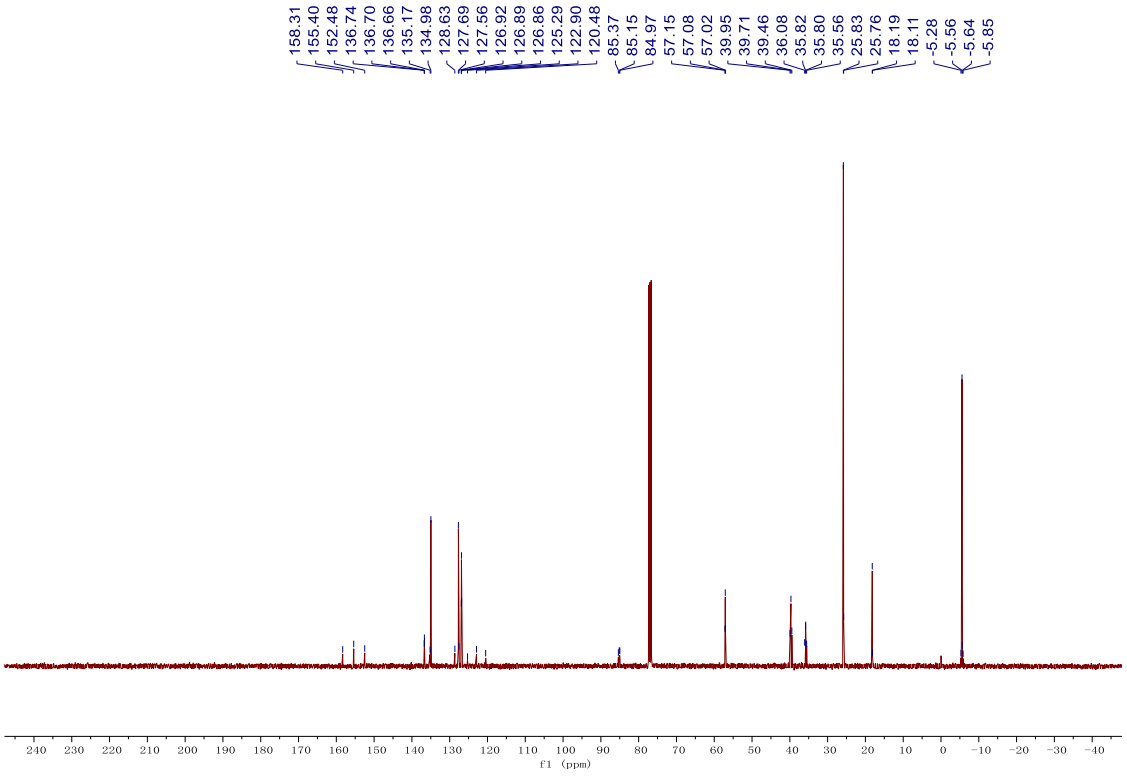


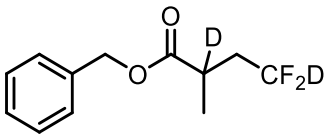
4b ^{19}F NMR
(376 MHz, $CDCl_3$)



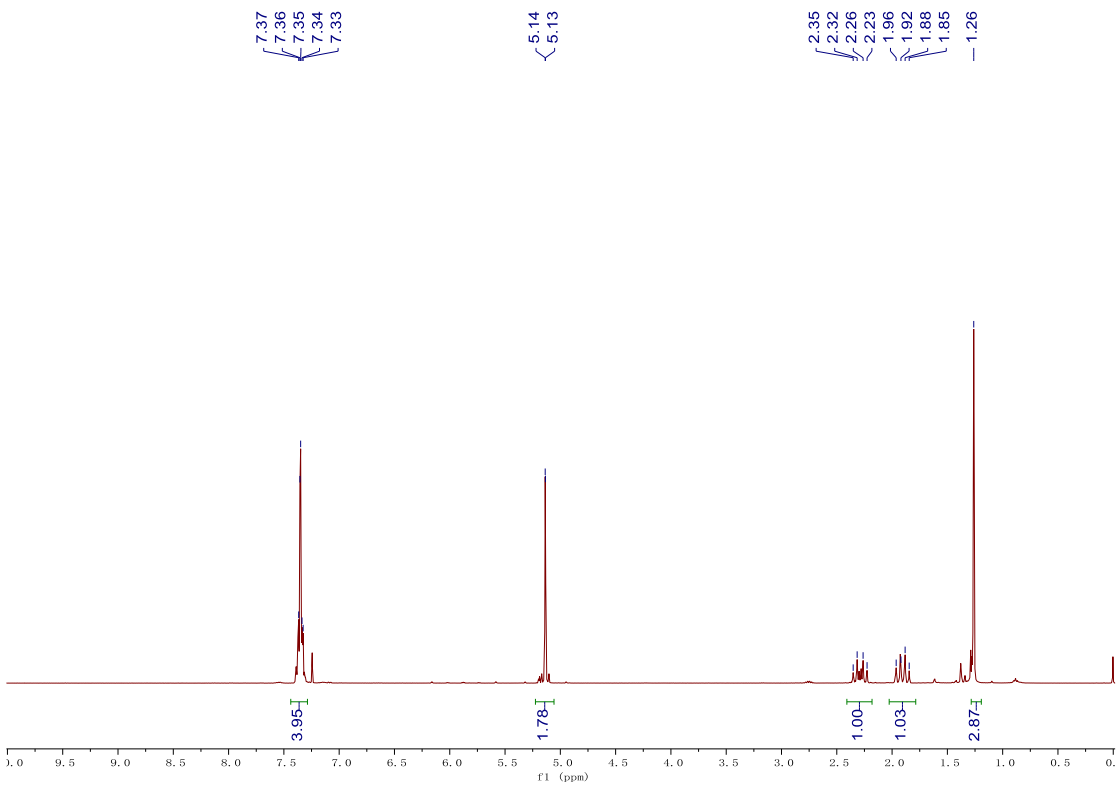


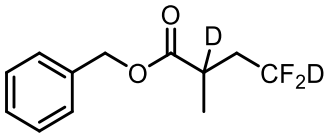
4b ^{13}C NMR
(101 MHz, $CDCl_3$)



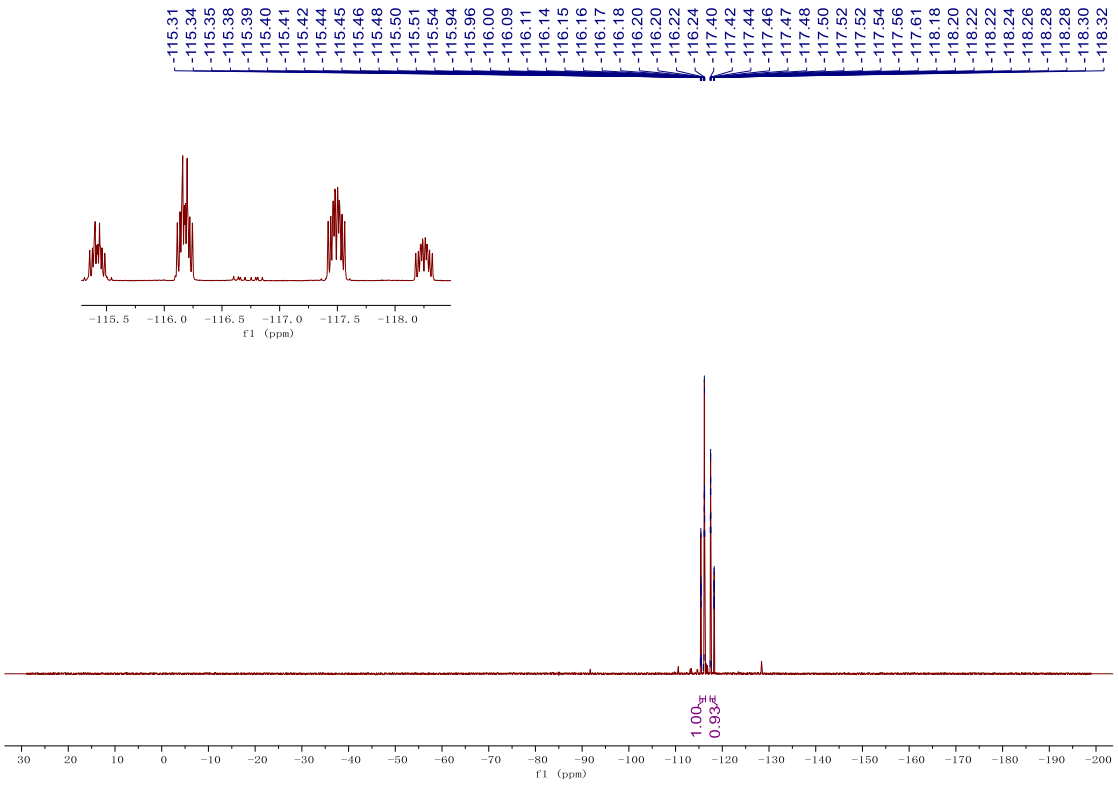


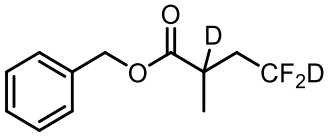
3b-d_2, ^{1}H NMR
($CDCl_3$, 400 MHz)



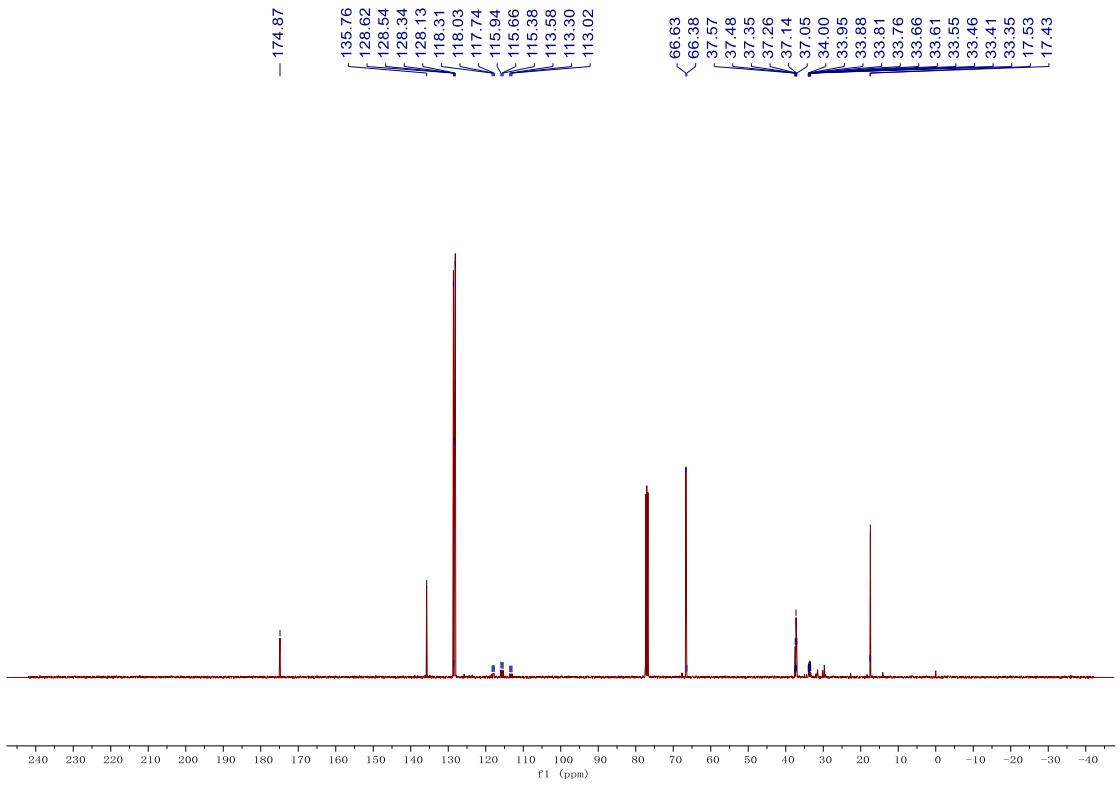


3b-*d*$_2$, ^{19}F NMR
($CDCl_3$, 376 MHz)





3b-*d*$_2$, ^{13}C NMR
($CDCl_3$, 101 MHz)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113.30
113.02
66.63
66.38
37.57
37.48
37.35
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33.61
33.55
33.46
33.41
33.35
17.53
17.43
f1 (ppm)