Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Nickel Catalyzed Reductive Defluorination of Iodo Allylic *gem*-Difluorides: Allenyl Monofluorides Synthesis

Yiming You,[a] Jiayue Wu, [a] Lixin Yang [a] and Tao Wu*[a]

[a] Y. You, J. Wu, L. Yang, Prof. Dr. T. Wu,
The college of chemistry
Nanchang University
999 Xuefu Road, Nanchang, Jiangxi, China, 330031
E-mail: taowu@ncu.edu.cn

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1. General Experimental Details

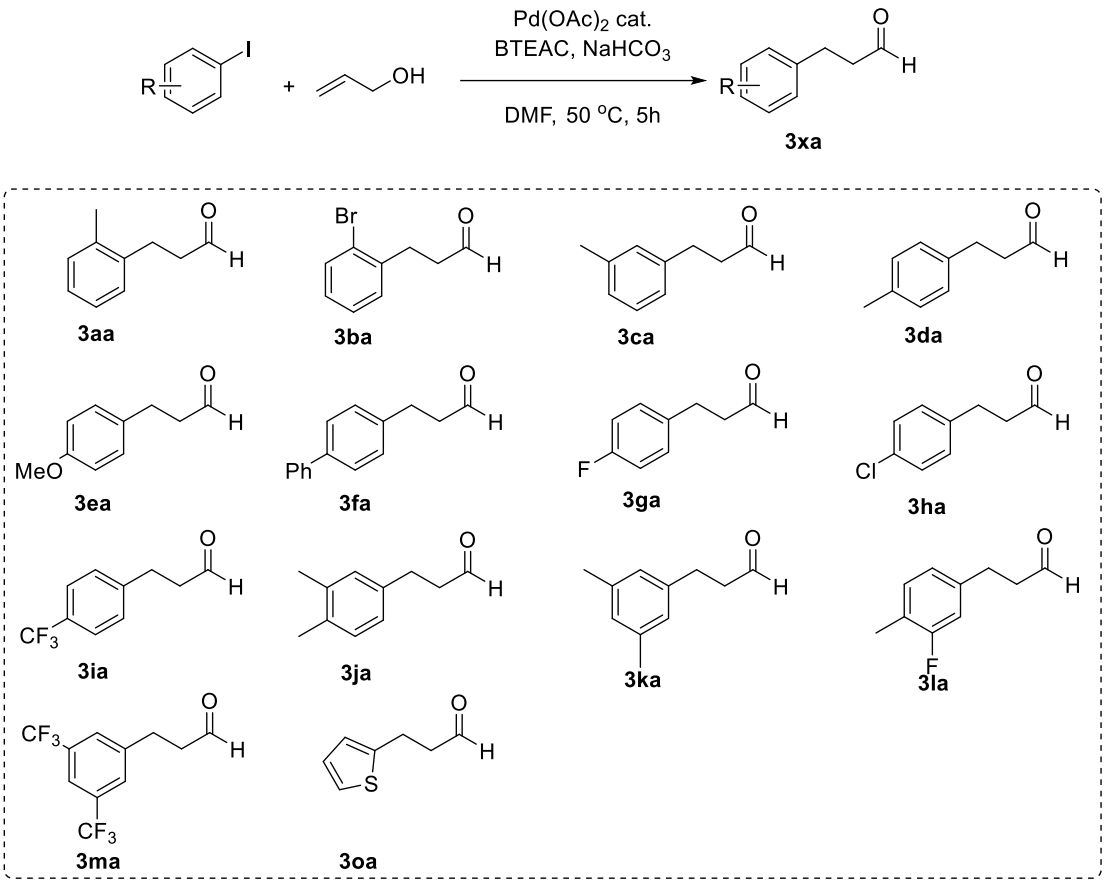
Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. $Ni(COD)_2$, corresponding ligands were obtained from Leyan, Tansoole and Innochem Chemical. All dry solvents were obtained from Energy Chemical. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas in dried glassware using standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using silica gel HSGF254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200-300 mesh). Preparative thin-layer chromatography (PTLC) was performed using YanTai jiangyou chemical Plant HuangHai GF254 silica coated plates (0.20 ± 0.03mm) prepared in our laboratory. Gas chromatography (GC) analysis was conducted on Agilent Technologies 7080A gas chromatography instrument with a FID detector with n-tetradecane as an internal standard. High performance liquid chromatography (HPLC) was performed on Agilent Technologies 1260 Infinity II High performance liquid chromatography instrument. The high-resolution mass spectra were conducted on Agilent Technologies 6545 Q-TOF LC MS spectrometer, or Agilent Technologies 7250 GCQTOF spectrometer, or Agilent Technologies 6224 TOF LC MS spectrometer, or Thermo Fisher Scientific LTQ FT Ultra spectrometer, or Bruker micrOTOF-QII spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance III (400 MHz) spectrometers or Agilent- 400 MHz spectrometer with tetramethylsilane as an internal standard. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual peak of $CDCl_3$ (δ 7.26 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, q = quartet, m = multiplet), coupling constant (Hz), and integration.

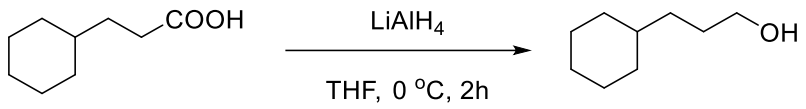
2. Starting Material Synthesis

2.1 Preparation of Substrates 1 and 3a - 3u

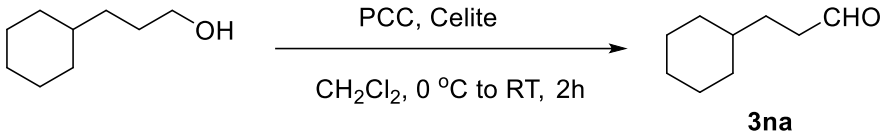
2.1.1 Synthesis Process of Aldehyde



Adapted from a literature procedure.[1] To a round-bottom flask was added palladium acetate $Pd(OAc)_2$ (1.00 mol%), benzyl(triethyl)ammonium chloride BTEAC (1.00 equiv.), sodium bicarbonate $NaHCO_3$ (2.50 equiv.) the correspondent aryl iodide (1.00 equiv.), 2-propen-1-ol (1.50 equiv.) and DMF (0.25 M). The reaction was heated at 50 °C and stirred at this temperature for 5h. After this time, the mixture was diluted with water and EtOAc, layers were separated, the aq. layer was washed with EtOAc (2x). The combined organics were sequentially washed with water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica to yield the desired aldehyde.
(**Note:** all iodobenzene were commercially available.)

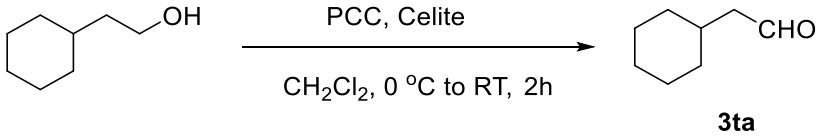


Adapted from a literature procedure.[2] To an oven-dried 500 mL flask equipped with stir bar was added $LiAlH_4$ (1.43 g, 37.5 mmol, 1.5 equiv) followed by dry THF (83 mL) under nitrogen atmosphere. The flask was cooled to 0 °C via an ice-water bath and the suspension was stirred for 10 minutes. After this time, 3-cyclohexylpropanoic acid (CAS No.: 701-97-3, commercially available) (4.28 mL, 25 mmol, 1 equiv) in dry THF (25 mL) was added very slowly dropwise to the flask. The mixture was stirred at 0 °C for 2 h and then quenched at 0 °C by very careful addition of deionized water (1.04 mL), 2 M NaOH (2.08 mL), and additional deionized water (3.12 mL). The quenched solution was allowed to stir for about 10 minutes, resulting in a white suspension. The solids were removed by filtration, washing the solids with diethyl ether (100 mL). The filtrate was transferred to a separatory funnel and washed with saturated $NaHCO_3$ (2 X 100 mL), deionized water (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo by rotary evaporation affording the pure alcohol (3.74 g, 99%).



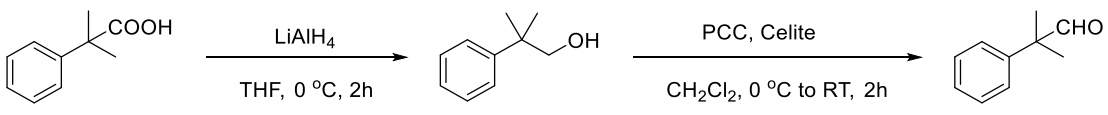
3na

To an oven-dried 250 mL flask equipped with stir bar was added PCC (8.47 g, 39.44 mmol, 1.5 equiv), celite (4.23 g) and anhydrous dichloromethane (80 mL) under nitrogen atmosphere. The flask was cooled to 0 °C via an ice-water bath. After this time, the alcohol (3.74 g, 26.29 mmol, 1equiv) in 20 mL of anhydrous dichloromethane was added dropwise to the flask. Then the solution was transferred to room temperature and stirred for one hour. After confirming the complete consumption of the alcohol by TLC analysis, the solution was filtered with silica gel. and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica (PE : EtOAc = 200 : 1) to yield the desired aldehyde **3na** (2.02 g, 55%).



3ta

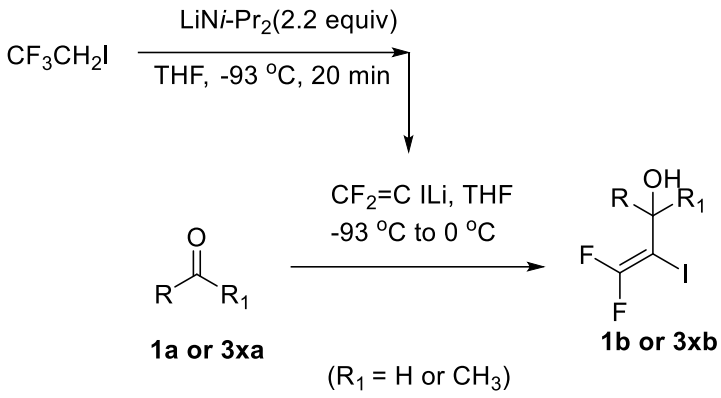
2-cyclohexylacetaldehyde (**3ta**) was prepared by 2-cyclohexylethan-1-ol (CAS No.: 4442-79-9, commercially available) according to the synthesis process of 3-cyclohexylpropanal (1.41 g, 45%).

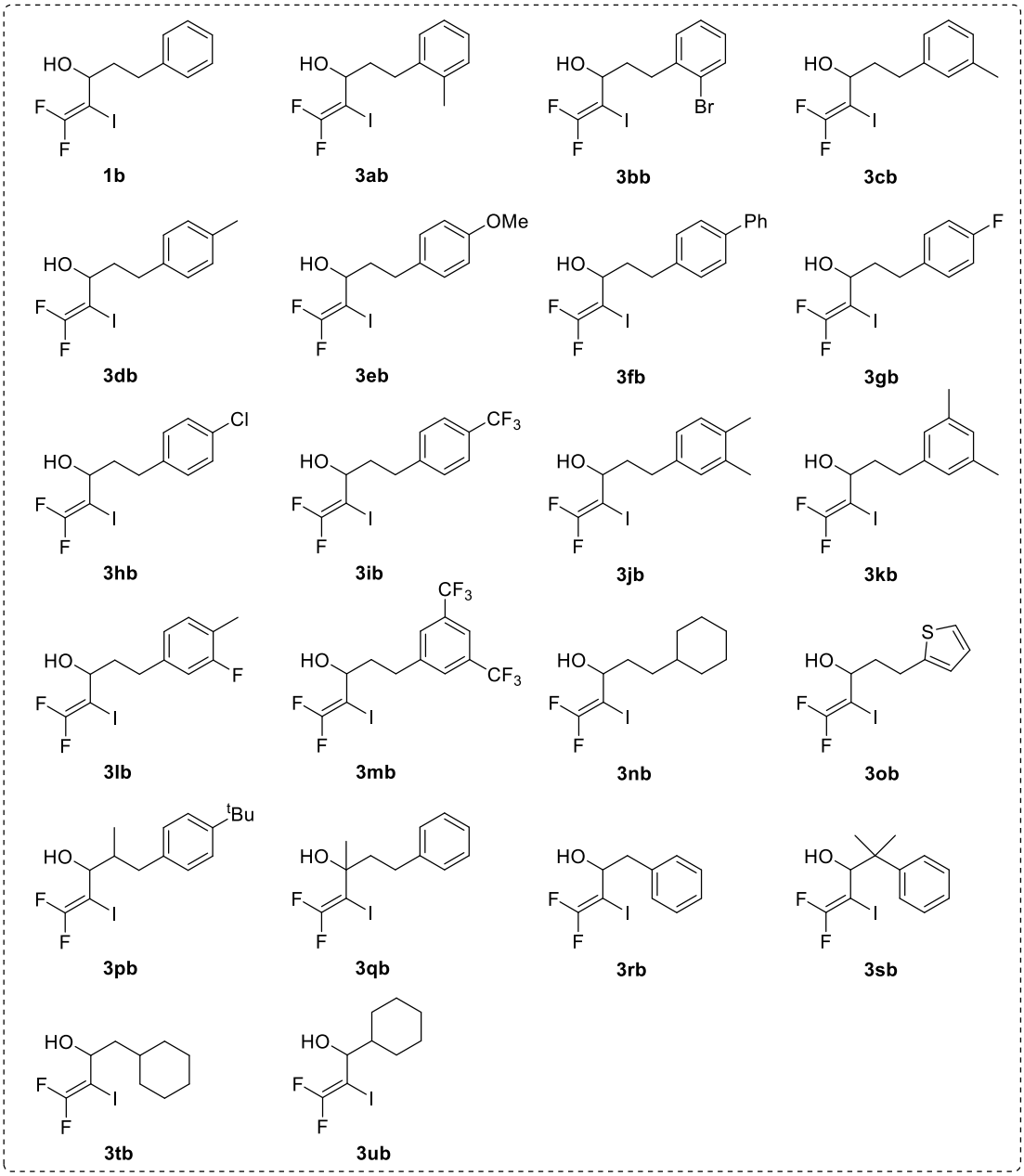


3sa

2-methyl-2-phenylpropanal (**3sa**) was prepared by 2-methyl-2-phenylpropanoic acid (CAS No.: 826-55-1, commercially available) according to the synthesis processes of 3-cyclohexylpropan-1-ol (3.63 g, 99%) and **3ta** (1.0 g, 31%).

2.1.2 Synthesis Process of Allyl Alcohol

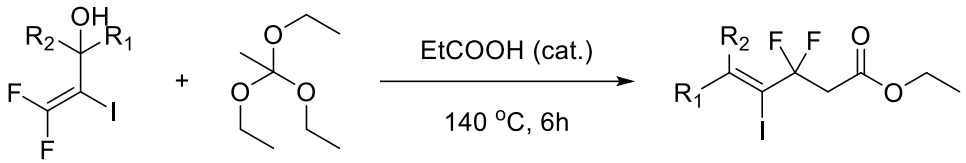




A 250ml three-necked flask is equipped with a stir bar, an internal thermometer, and a 60ml dropping funnel. Under a nitrogen atmosphere, diisopropylamine (8.2 mL, 5.9 g, 58.5 mmol, 2.24 equiv) and THF (40 mL) were added to the flask with a dropping funnel, and the mixture was placed at 0 °C. Within 40 minutes, n-butyllithium (35.7 mL, 1.64 M in n-hexane, 58.5 mmol, 2.24 equiv) was added to the THF solution of diisopropylamine through a dropping funnel at 0 °C. The inside of the dropping funnel was rinsed with THF (5 mL). The reaction mixture was stirred at 0 °C for another 10 minutes, and then frozen with ethanol and liquid nitrogen (internal temperature was -93 °C; ice bath temperature was -95 °C). Add 1,1,1-trifluoro-2-iodoethane (2.8 mL, 6.1 g, 28.7 mmol, 1.1 equiv) to the THF solution of LDA via a syringe within 15 minutes, during which the internal temperature was kept at -90 °C the following. The reaction mixture was stirred for 30 min. The aldehyde (26.1 mmol, 1 equiv) was dissolved in 10 mL of THF and added via a dropping funnel within 15 minutes. The inside of the dropping funnel was rinsed with THF (5 mL). After the aldehyde was added, the solution was slowly raised to 0 °C and then stirred for another 30 minutes. After confirming the complete consumption of the aldehyde by TLC analysis, saturated ammonium chloride was added to quench the reaction, liquid separation, the aqueous layer was extracted three times with EtOAc. The combined organics were sequentially washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica to yield the desired alcohol.

Note: 1a (CAS No.: 104-53-0), **3pa** (CAS No.: 80-54-6), **3qa** (CAS No.: 2550-26-7), **3ra** (CAS No.: 122-78-1), **3ua** (CAS No.: 2043-61-0) are commercially available.

2.1.3 Synthesis Process of Allyl gem-Difluorides 1 and 3a - 3u

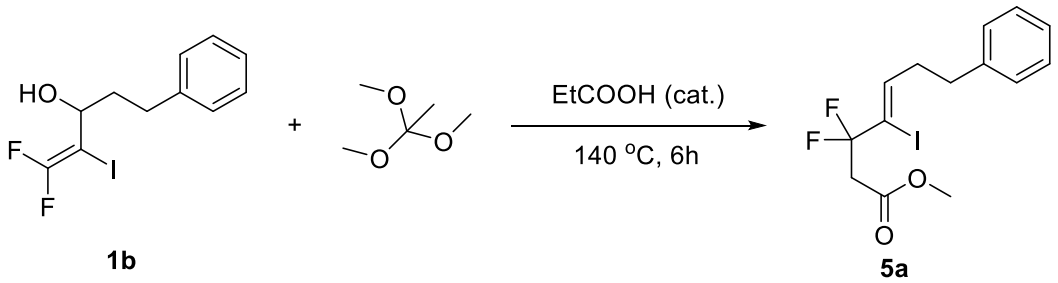


1b or 3xb (R_2 = H or CH_3) **1 or 3x**

Adapted from a literature procedure.[3] Triethyl orthoacetate (0.92 mL, 5 mmol, 5.0 equiv) and propanoic acid (7 uL, 0.01 mmol, 0.01 equiv) were added to allyl alcohol (1 mmol, 1.0 equiv) under an atmosphere of nitrogen at 0 °C, and the mixture was heated at 140 °C. After being stirred for 5 h at this temperature, the solution was cooled to room temperature and then poured into 10% HCl and ice, the aqueous layer was extracted three times with EtOAc. The combined organics were sequentially washed with saturated sodium bicarbonate solution and water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica to yield the desired product.

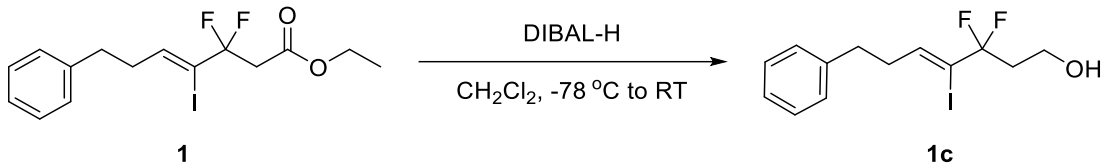
2.2 Preparation of Substrates 5a- 5k

2.2.1 Preparation of Substrate 5a

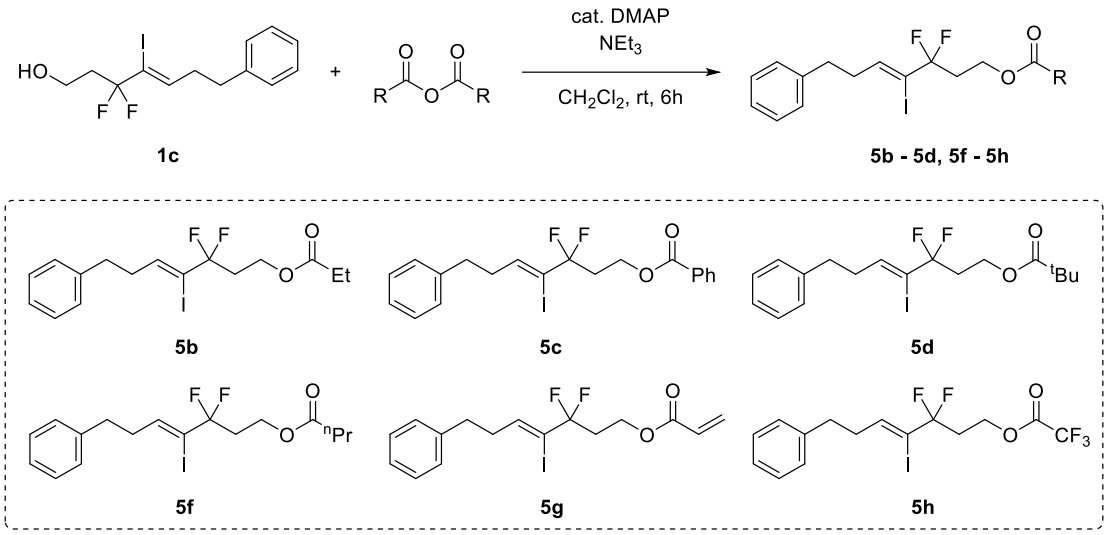


Substrate **5a** was prepared according to procedure **2.1.3**. Flash column chromatography (eluent: PE : EtOAc = 200 : 1) to afford **5a** as a yellow oil (273.6 mg, 72%). R_f = 0.4 (PE : EtOAc = 20:1), by staining with potassium permanganate.

2.2.2 Preparation of Substrates 5b -5d and 5f – 5h

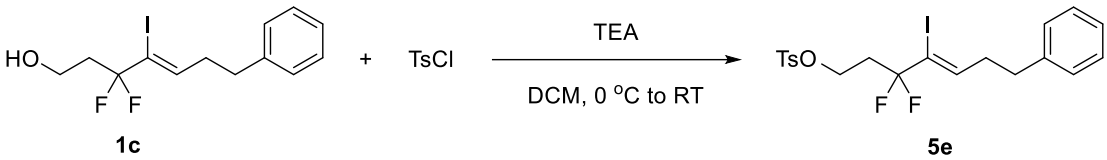


To a flame dried round-bottom flask was added **1** (394 mg, 1 mmol, 1.0 equiv) and anhydrous DCM (10 mL) under a nitrogen atmosphere. After cooling down to -78 °C, DIBAL-H (1.5 mol/L in toluene) (1.3 mL, 2 mmol, 2.0 equiv) was added dropwise. Then the solution was slowly raised to room temperature and stirred overnight. After the reaction was determined complete by TLC, the flask was cooled down to 0 °C and quenched with water. The mixture was filtered with a silicone pad. The organic phase was separated by separating funnel, and the aqueous phase was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: PE : EtOAc = 20 : 1) to give **1c** as colorless oil (140.8 mg, 40%).



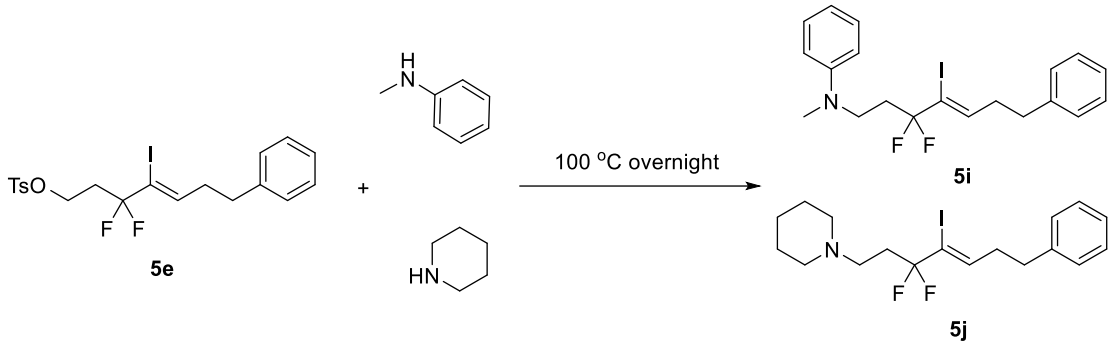
Adapted from a literature procedure.[4] Under a nitrogen atmosphere, the synthesized alcohol **1c** (704 mg, 2 mmol, 1.0 equiv) was dissolved in dichloromethane (10 mL), N, N-dimethylaminopyridine (49 mg, 0.4 mmol, 0.2 equiv), triethylamine (1.2 mL, 8 mmol, 4.0 equiv) and anhydride (12 mmol, 6.0 equiv) were sequentially added. The resulting mixture was stirred for 6 hours at room temperature. The solution was washed with saturated sodium bicarbonate solution and then with brine. The organic layer was dried over $MgSO_4$ and concentrated to orange-yellow oil. The residue was purified by column chromatography on silica gel to give the desired allyl gem-difluorides.

2.2.3 Preparation of Substrate 5e



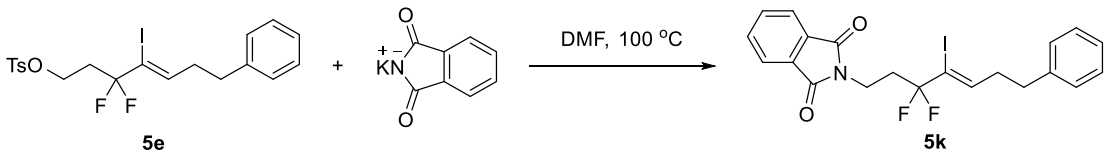
Adapted from a literature procedure.[5] Under a nitrogen atmosphere, a 25 mL round-bottom flask was charged with a stir bar and alcohol **1c** (704 mg, 2 mmol, 1.0 equiv), and then taken up in 2 mL of dichloromethane. The reaction mixture was submerged in an ice bath. Triethylamine (1 mL, 7.2 mmol, 3.6 equiv) was added via syringe, followed by p-toluenesulfonyl chloride (477 mg, 2.5 mmol, 1.3 equiv). The reaction mixture was allowed to warm to room temperature and stir for 15 h. The solution was washed twice with 2M HCl, then with saturated sodium bicarbonate solution, and then with brine. The organic layer was dried over $MgSO_4$ and concentrated to orange-yellow oil. Purification on silica (PE : EtOAc = 20 : 1) afforded **5e** as a clear oil (814 mg, 80% yield), which solidified at reduced temperature.

2.2.4 Preparation of Substrates 5i and 5j



Under a nitrogen atmosphere, a flame dried round-bottom flask was added **5e** (506 mg, 1 mmol, 1.0 equiv) and N-methylaniline or piperidine (45.0 equiv). The mixture was stirred and heated at 100 °C overnight. The mixture was cooling to room temperature. Most of the unreacted N-methylaniline or piperidine was removed by vacuum distillation. The rest oil was purified by flash column chromatography on silica to yield the desired **5i** (340 mg, 75% yield) or **5j** (324 mg, 91% yield).

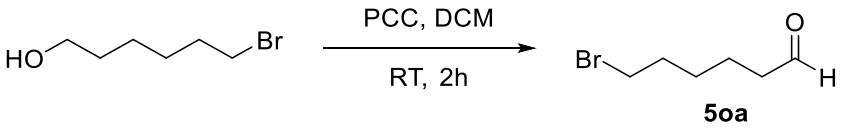
2.2.5 Preparation of Substrate 5k



A 50 mL round-bottom flask was charged with **5e** (759 mg, 1.5 mmol, 1.5 equiv), potassium phtalimide (185 mg, 1.0 mmol, 1.0 equiv) and 10 mL DMF. The solution was stirred over night at 100 °C. Cooling the mixture to room temperature, 10 mL of water were added. Then the mixture was extracted three times with EtOAc, the combined organic fractions were washed two times with water. The organic layer was dried over $MgSO_4$, filtered and concentrated to orange-yellow oil. Purification on silica (PE : EtOAc = 20 : 1) afforded **5k** as a clear oil (302 mg, 60% yield).

2.3 Preparation of Substrates 5l - 5s

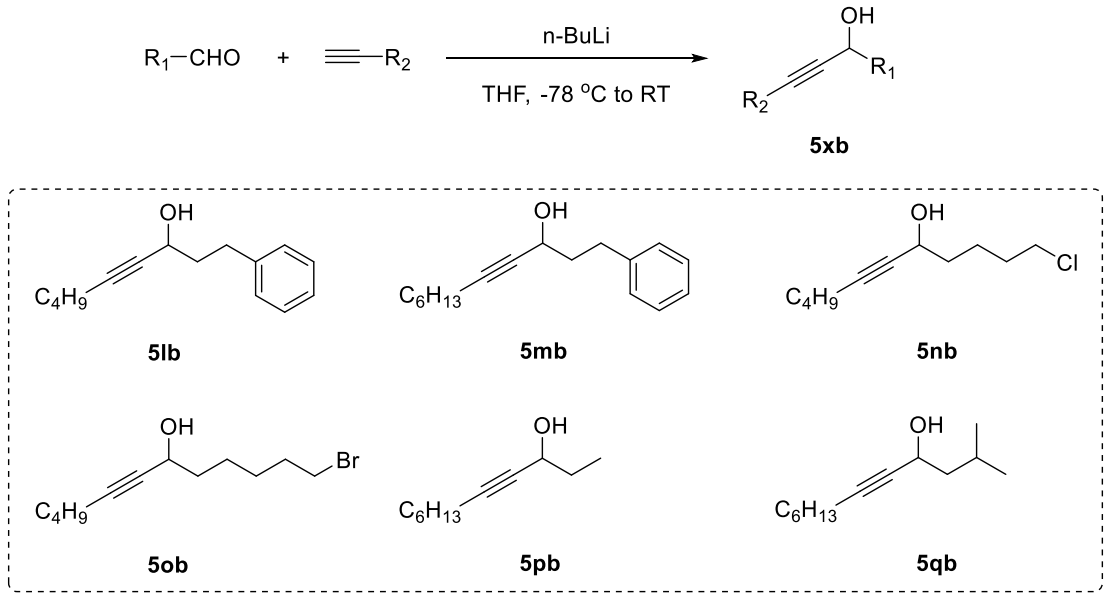
2.3.1 Synthesis Process of 6-bromohexanal



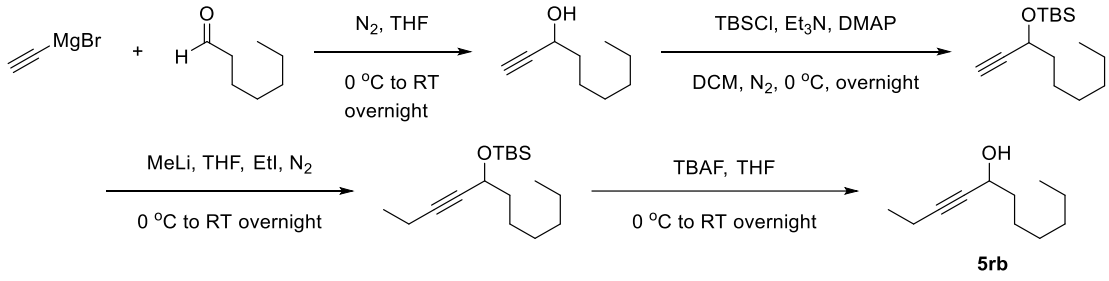
6-bromohexanal (**5oa**) was prepared by PCC oxidation of alcohol 6-bromo-1-hexanol (CAS No.:

4286-55-9 commercially available) according to the synthesis process of **3na** (997mg, 56%).

2.3.2 Synthesis Process of Propargyl Alcohols

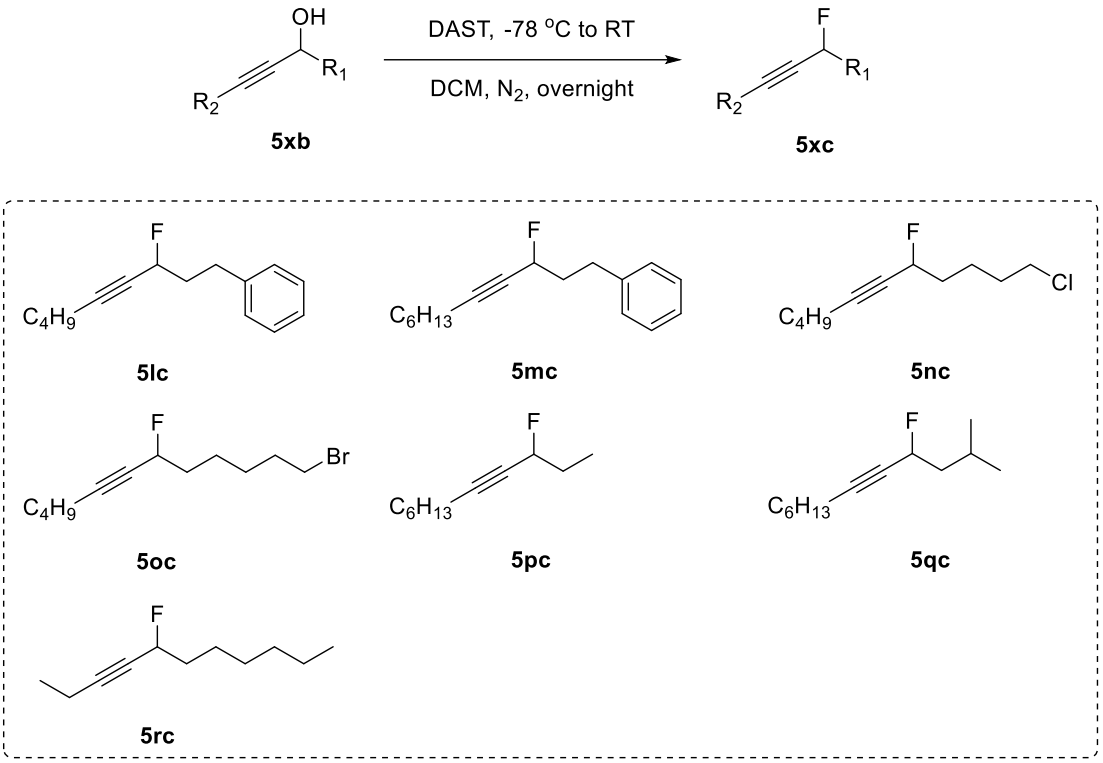


Adapted from a literature procedure.[6] To a flame dried round-bottom flask was added the alkyne (20 mmol, 1.0 equiv) and anhydrous THF (30 mL) under a nitrogen atmosphere. After cooling down to -78 °C, n-BuLi (1.6 M solution in hexanes, 21 mmol, 1.05 equiv) was added dropwise over the course of 15 minutes. After 2 hours at -78 °C, the aldehyde (24 mmol, 1.2 equiv) was added dropwise and the reaction mixture was slowly warmed up to ambient temperature over the course of 16 hours. After the reaction was determined complete by TLC, the flask was cooled down to 0 °C and quenched with saturated aqueous NH_4Cl. The reaction mixture was extracted with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. After evaporation, the residue was purified by column chromatography on silica gel to give the desired propargyl alcohols.



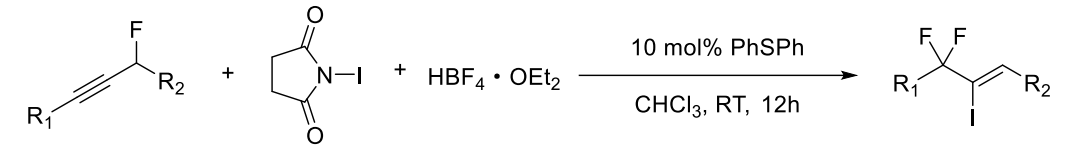
Undec-3-yn-5-ol (**5rb**) was prepared according to the literature procedure. [6]

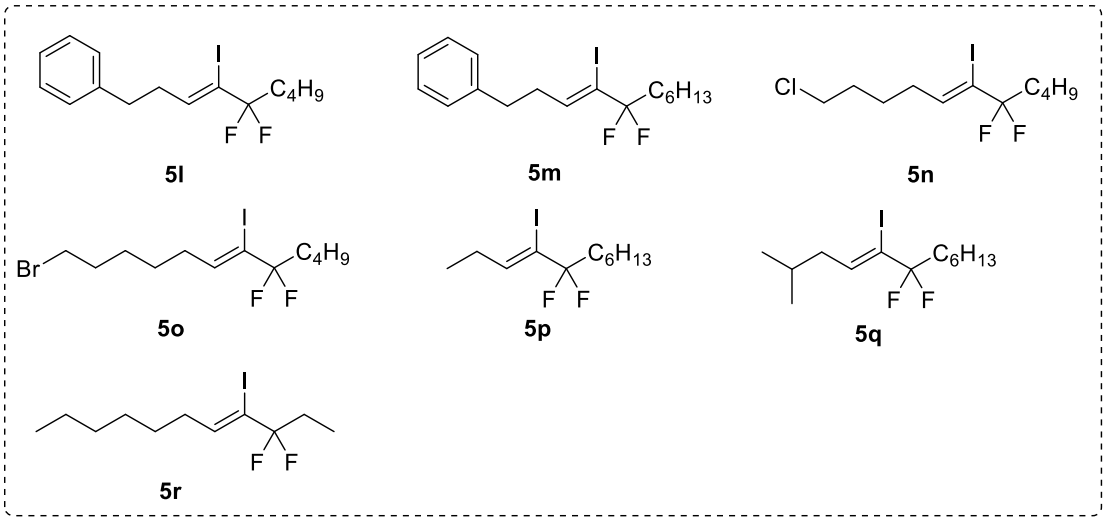
2.3.3 Synthesis Process of Propargyl Fluorides



Adapted from a literature procedure.[6] To a solution of propargyl alcohols (1.0 equiv) in dried DCM (4 mL/mmol) under N_2 at -78 °C was added DAST (1.3 equiv) dropwise. Then, the solution was warmed to room temperature and stirred overnight. The reaction was quenched carefully by addition of saturated $NaHCO_3$ aqueous solution dropwise, until no bubbles were observed. The organic phase was separated by separating funnel, and the aqueous phase was extracted with DCM (4 mL/mmol x 2). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give the desired propargyl fluorides.

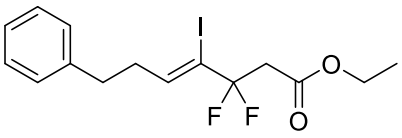
2.3.4 Synthesis Process of Allyl gem-Difluorides 5l - 5s





Adapted from a literature procedure.[6] To a solution of propargyl fluorides (0.2 mmol, 1.0 equiv) in $CHCl_3$ (8 mL) were added NIS (67.5 mg, 0.3 mmol, 1.5 equiv), PhSPh (3.4 μL, 0.02 mmol, 10 mol%), and $HBF_4{\cdot}OEt_2$ (27.2 μL, 0.2 mmol, 1.0 equiv) successively. The reaction was stirred at room temperature for 12 h and quenched by saturated $Na_2S_2O_3$ aqueous solution until the color of the mixture faded. The mixture was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give disubstituted iodinated allyl gem-difluorides .

2.4 Characterization Data of Allyl gem-Difluorides



Ethyl (Z)-3,3-difluoro-4-iodo-7-phenylhept-4-enoate (1)

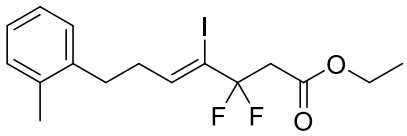
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **1** as a light-yellow oil (289.9 mg, 74%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.29 (m, 2H), 7.24 -7.20 (m, 3H), 6.42 (tt, *J* = 6.9, 1.6 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.58 -2.51 (m, 2H), 1.25 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.04 (t, *J* = 5.6 Hz), 140.89 (t, *J* = 8.1 Hz), 140.54, 128.56, 128.43, 126.33, 117.53 (t, *J* = 248.6 Hz), 98.42 (t, *J* = 27.3 Hz), 61.31, 41.99 (t, *J* =29.3 Hz), 37.71, 33.78, 14.11.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.98 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{17}F_2IO_2Na$ [$(M+Na)^+$]: 417.0139, found: 417.0134.



Ethyl (Z)-3,3-difluoro-4-iodo-7-(o-tolyl)hept-4-enoate (3a)

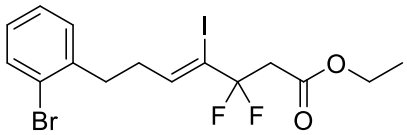
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3a** as a light-yellow oil (253.1 mg, 62%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 4H), 6.46 (tt, *J* = 6.9, 1.7 Hz, 1H), 4.17 (q, *J* = 6.7 Hz, 2H), 3.21 (t, *J* = 14.0 Hz, 2H), 2.77 – 2.73 (m, 2H), 2.54 -2.47 (m, 2H), 2.35 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.02 (t, *J* = 6.1 Hz), 140.95 (t, *J* = 8.1 Hz), 138.65, 135.96, 130.35, 128.82, 126.46, 126.14, 117.52 (t, *J* = 247.5 Hz), 98.29 (t, *J* = 27.3 Hz), 61.28, 41.97 (t, *J* =29.3 Hz), 36.53, 31.09, 19.39, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.03 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 431.0295, found: 431.0290.



Ethyl (Z)-7-(2-bromophenyl)-3,3-difluoro-4-iodohept-4-enoate (3b)

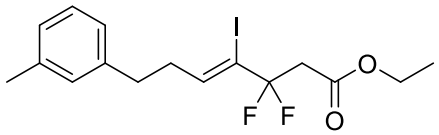
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3b** as a light-yellow oil (282.6 mg, 60%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.11 – 7.07 (m, 1H), 6.44 (tt, *J* = 6.9, 1.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.20 (t, *J* = 14.8 Hz, 2H), 2.89 (t, J = 8.0 Hz, 2H), 2.59 -2.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.99 (t, *J* = 5.6 Hz), 140.44 (t, *J* = 8.1 Hz), 139.71, 132.96 130.51, 128.12, 127.60, 124.46, 117.50 (t, *J* = 248.0 Hz), 98.71 (t, *J* = 27.3 Hz), 61.28, 41.99 (t, *J* =28.8 Hz), 36.05, 34.08, 14.10.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.15 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{16}BrF_2IO_2Na$ [$(M+Na)^+$]: 494.9244, found: 494.9239.



Ethyl (Z)-3,3-difluoro-4-iodo-7-(m-tolyl)hept-4-enoate (3c)

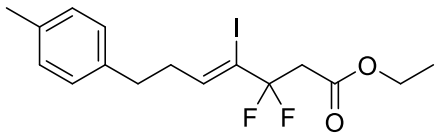
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3c** as a light-yellow oil (333.9 mg, 82%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (td, *J* = 7.2, 1.3 Hz, 1H), 7.04 – 6.99 (m, 3H), 6.42 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.56 -2.50 (m, 2H), 2.34 (s, 3H), 1.25 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.00 (t, *J* = 5.6 Hz), 140.99 (t, *J* = 8.6 Hz), 140.47, 138.13, 129.23, 128.45, 127.05, 125.40, 117.52 (t, *J* = 246.9 Hz), 98.35 (t, *J* = 27.3 Hz), 61.27, 42.03 (t, *J* =29.3 Hz), 37.71, 33.70, 21.42, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.05 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 431.0295, found: 431.0299.



Ethyl (Z)-3,3-difluoro-4-iodo-7-(p-tolyl)hept-4-enoate (3d)

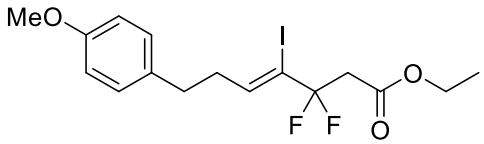
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3d** as a light-yellow oil (249.1 mg, 61%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 4H), 6.42 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.55 -2.49 (m, 2H), 2.33 (s, 3H), 1.25 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01 (t, *J* = 6.1 Hz), 141.02 (t, *J* = 8.1 Hz), 137.46, 135.79, 129.22, 128.27, 117.51 (t, *J* = 247.5 Hz), 98.29 (t, *J* = 27.8 Hz), 61.26, 42.02 (t, *J* =29.3 Hz), 37.83, 33.34, 21.03, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.94 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 431.0295, found: 431.0294.



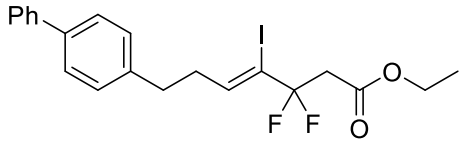
Ethyl (Z)-3,3-difluoro-4-iodo-7-(4-methoxyphenyl)hept-4-enoate (3e)

Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 100:1) to afford **3e** as a light-yellow oil (237.9 mg, 56%, 1 mmol scale). R_f = 0.2 (PE/EA = 20:1), by staining with potassium permanganate.

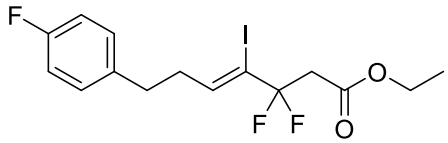
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.10 (m, 2H), 6.86 – 6.83 (m, 2H), 6.41 (tt, *J* = 6.8, 1.7 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.79 (s, 3H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.54 -2.47 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.00 (t, *J* = 6.1 Hz), 158.13, 140.99 (t, *J* = 8.1 Hz), 132.61, 129.34, 117.50 (t, *J* = 248.0 Hz), 113.95, 98.31 (t, *J* = 27.3 Hz), 61.26, 55.29, 42.01 (t, *J* =28.8 Hz), 37.95, 32.89, 14.09.

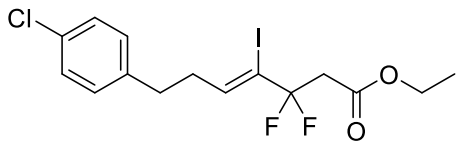
^{19}F NMR (376 MHz, $CDCl_3$) δ -89.95 (t, *J* = 13.2 Hz).
HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_3Na$ [$(M+Na)^+$]: 447.0245, found: 447.0239.



Ethyl (Z)-7-([1,1'-biphenyl]-4-yl)-3,3-difluoro-4-iodohept-4-enoate (3f)
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3f** as a light-yellow oil (264.3 mg, 56%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.46 – 7.42 (m, 2H), 7.36 – 7.32 (m, 1H), 7.30 – 7.27 (m, 2H), 6.46 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.21 (t, *J* = 14.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.62 -2.55 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.02 (t, *J* = 5.6 Hz), 140.96, 140.88 (t, *J* = 8.1 Hz), 139.65, 139.32, 128.87, 128.80, 127.30, 127.20, 127.05, 117.56 (t, *J* = 248.0 Hz), 98.57 (t, *J* = 27.3 Hz), 61.30, 42.03 (t, *J* =28.8 Hz), 37.67, 33.43, 14.12.
^{19}F NMR (376 MHz, $CDCl_3$) δ -90.01 (t, *J* = 13.2 Hz).
HRMS (ESI) *m/z* calcd for $C_{21}H_{21}F_2IO_2Na$ [$(M+Na)^+$]: 493.0452, found: 493.0447.



Ethyl (Z)-3,3-difluoro-7-(4-fluorophenyl)-4-iodohept-4-enoate (3g)
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3g** as a light-yellow oil (235.5 mg, 57%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 2H), δ 7.01 – 6.95 (m, 2H), 6.40 (tt, *J* = 6.9, 1.6 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.55 -2.48 (m, 2H), 1.25 (t, *J* = 6.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.96 (t, *J* = 5.6 Hz), 161.54 (d, *J* = 245.5Hz), 140.57 (t, *J* = 8.1 Hz), 136.11 (d, *J* = 4.0), 129.83 (d, *J* = 8.1Hz), 117.50 (t, *J* = 247.5 Hz), 115.29 (d, *J* = 21.2Hz), 98.65 (t, *J* = 27.3 Hz), 61.26, 41.94 (t, *J* =28.8 Hz), 37.73, 32.96, 14.08.
^{19}F NMR (376 MHz, $CDCl_3$) δ -90.01 (t, *J* = 13.2 Hz), -116.98 - -117.06 (m).
HRMS (ESI) *m/z* calcd for $C_{15}H_{16}F_3IO_2Na$ [$(M+Na)^+$]: 435.0045, found: 435.0039.



Ethyl (Z)-7-(4-chlorophenyl)-3,3-difluoro-4-iodohept-4-enoate (3h)
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3h** as a light-yellow oil (214.5 mg, 50%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by

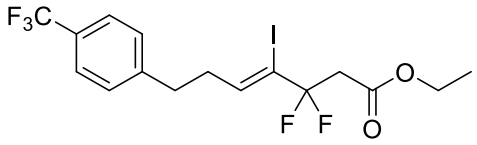
staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.25 (m, 2H), 7.15 – 7.11 (m, 2H), 6.40 (tt, *J* = 6.8, 1.7 Hz, 1H), 4.15 (q, *J* = 8.0 Hz, 2H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.55 -2.48 (m, 2H), 1.25 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.95 (t, *J* = 5.6 Hz), 140.42 (t, *J* = 8.1 Hz), 138.90, 132.06, 129.77, 128.62, 117.49 (t, *J* = 248.0 Hz), 98.73 (t, *J* = 27.3 Hz), 61.27, 41.90 (t, *J* =29.3 Hz), 37.47, 33.09, 14.07.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.05 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{16}ClF_2IO_2Na$ [$(M+Na)^+$]: 450.9749, found: 450.9744.



Ethyl (Z)-3,3-difluoro-4-iodo-7-(4-(trifluoromethyl)phenyl)hept-4-enoate (3i)

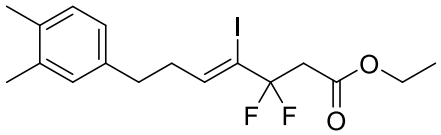
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3i** as a light-yellow oil (321.5 mg, 70%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.44 – 6.38 (m, 1H), 4.14 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.59 -2.52 (m, 2H), 1.25 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93 (t, *J* = 6.1 Hz), 144.53, 140.18 (t, *J* = 8.1 Hz), 128.77, 128.75 (d, *J* = 33.3 Hz), 125.48 (q, *J* = 10.6 Hz), 122.91, 117.50 (t, *J* = 247.5 Hz), 98.98 (t, *J* = 27.3 Hz), 61.26, 41.89 (t, *J* =28.8 Hz), 37.23, 33.56, 14.05.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.41, -90.03 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{17}F_5IO_2$ [$(M+H)^+$]: 463.0193, found: 463.0188.



Ethyl (Z)-7-(3,4-dimethylphenyl)-3,3-difluoro-4-iodohept-4-enoate (3j)

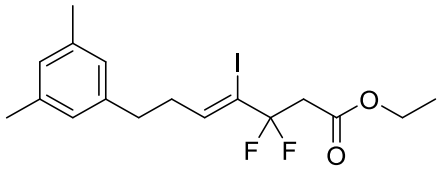
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3j** as a light-yellow oil (270.1 mg, 64%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.42 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.55 -2.48 (m, 2H), 2.25 (d, *J* = 4.0 Hz, 6H), 1.25 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.02 (t, *J* = 6.1 Hz), 141.13 (t, *J* = 8.1 Hz), 137.98, 136.65, 134.43, 129.78, 129.75, 125.71, 117.53 (t, *J* = 248.0 Hz), 98.22 (t, *J* = 27.3 Hz), 61.27, 42.04 (t, *J* =28.8 Hz), 37.88, 33.31, 19.77, 19.35, 14.10.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.97 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}F_2IO_2Na$ [$(M+Na)^+$]: 445.0447, found: 445.0441.



Ethyl (Z)-7-(3,5-dimethylphenyl)-3,3-difluoro-4-iodohept-4-enoate (3k)

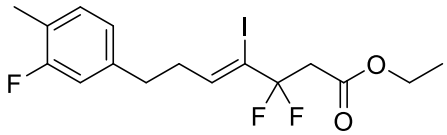
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3k** as a light-yellow oil (265.9 mg, 63%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.82 (s, 2H), 6.42 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.55 -2.48 (m, 2H), 2.30 (s, 6H), 1.26 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01 (t, *J* = 5.6 Hz), 141.10 (t, *J* = 8.1 Hz), 140.46, 138.03, 127.94, 126.24, 117.54 (t, *J* = 248.0 Hz), 98.25 (t, *J* = 27.8 Hz), 61.27, 42.04 (t, *J* =28.8 Hz), 37.74, 33.61, 21.30, 14.10.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.02 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}F_2IO_2Na$ [$(M+Na)^+$]: 445.0447, found: 445.0443.



Ethyl (Z)-3,3-difluoro-7-(3-fluoro-4-methylphenyl)-4-iodohept-4-enoate (3l)

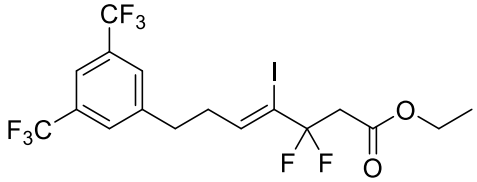
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3l** as a light-yellow oil (183.4 mg, 43%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (t, *J* = 8.0 Hz, 1H), 6.88 – 6.84 (m, 2H), 6.40 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 16.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.54 -2.48 (m, 2H), 2.24 (d, *J* = 2.0 Hz, 3H), 1.25 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97 (t, *J* = 6.1 Hz), 161.31 (d, *J* = 246.4 Hz), 140.58 (t, *J* = 8.1 Hz), 140.14 (d, *J* = 7.1 Hz), 131.42 (d, *J* = 6.1 Hz), 123.75 (d, *J* = 3.0 Hz), 122.56 (d, *J* = 17.2 Hz), 117.51 (t, *J* = 247.5 Hz), 114.88 (d, *J* = 22.2 Hz), 98.63 (t, *J* = 27.3 Hz), 61.27, 41.95 (t, *J* =29.3 Hz), 37.48, 33.14, 14.18 (d, *J* = 4.0 Hz), 14.08.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.05 (t, *J* = 15.0 Hz), -117.76 (t, *J* = 9.4 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{18}F_3IO_2Na$ [$(M+Na)^+$]: 449.0196, found: 449.0202.



Ethyl (Z)-7-(3,5-bis(trifluoromethyl)phenyl)-3,3-difluoro-4-iodohept-4-enoate (3m)

Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 100:1) to afford **3m** as a light-yellow oil (233.2 mg, 44%, 1 mmol scale). R_f = 0.3 (PE/EA = 10:1), by

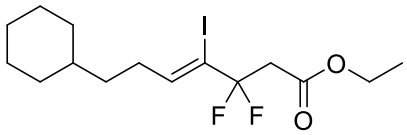
staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.66 (s, 2H), 6.42 (tt, *J* = 7.0, 1.7 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.63 -2.57 (m, 2H), 1.26 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89 (t, *J* = 6.6 Hz), 142.74, 139.38 (t, *J* = 8.1 Hz), 131.78 (q, *J* = 16.7 Hz), 128.75 (d, *J* = 3.0 Hz), 134.69 (t, *J* = 273.7 Hz), 120.49 (m), 117.50 (t, *J* = 247.5 Hz), 99.75 (t, *J* = 27.3 Hz), 61.26, 41.74 (t, *J* =29.3 Hz), 36.90, 33.39, 14.05.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88, -90.27 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{17}H_{15}F_8IO_2Na$ [$(M+Na)^+$]: 552.9881, found: 552.9884.



Ethyl (Z)-7-cyclohexyl-3,3-difluoro-4-iodohept-4-enoate (3n)

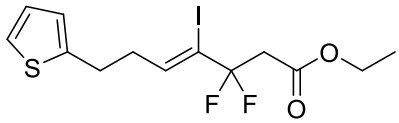
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3n** as a light-yellow oil (277.7 mg, 69%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (tt, *J* = 6.9, 1.6 Hz, 1H), 4.17 (q, *J* = 8.0 Hz, 2H), 3.21 (t, *J* = 14.0 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.75 – 1.64 (m, 6H), 1.37 – 1.29 (m, 2H), 1.27 (t, *J* = 6.0 Hz, 3H), 1.22 – 1.12 (m, 3H), 0.90 (qd, *J* = 13.6, 12.5, 3.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.07 (t, *J* = 5.6 Hz), 142.36 (t, *J* = 8.1 Hz), 117.53 (t, *J* = 247.5 Hz), 97.24 (t, *J* = 27.3 Hz), 61.24, 42.04 (t, *J* =28.8 Hz), 37.22, 35.19, 33.52, 33.17, 26.58, 26.26, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.79 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{23}F_2IO_2Na$ [$(M+Na)^+$]: 423.0603, found: 423.0605.



Ethyl (Z)-3,3-difluoro-4-iodo-7-(thiophen-2-yl)hept-4-enoate (3o)

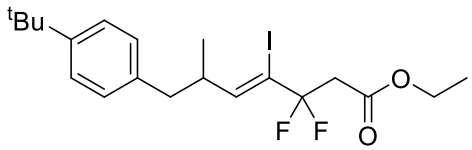
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 100:1) to afford **3o** as a light-yellow oil (296.1 mg, 74%, 1 mmol scale). R_f = 0.2 (PE/EA = 10:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.84 - 6.82 (m, 1H), 6.44 (tt, *J* = 6.8, 1.6 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.20 (t, *J* = 14.0 Hz, 2H), 3.00 (t, *J* = 8.0 Hz, 2H), 2.63 -2.56 (m, 2H), 1.26 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.96 (t, *J* = 5.6 Hz), 143.08, 140.36 (t, *J* = 8.6 Hz), 126.89, 124.74, 123.58, 117.48 (t, *J* = 248.0 Hz), 98.87 (t, *J* = 27.3 Hz), 61.28, 41.94 (t, *J* =28.8 Hz), 37.85, 27.88, 14.07.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.11 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}F_2IO_2S$ Na [$(M+Na)^+$]: 422.9698, found: 422.9700.



Ethyl (Z)-7-(4-(tert-butyl)phenyl)-3,3-difluoro-4-iodo-6-methylhept-4-enoate (3p)

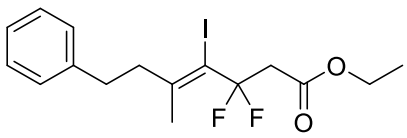
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3p** as a light-yellow oil (282.4 mg, 61%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.21 (dt, *J* = 8.8, 1.4 Hz, 1H), 4.15 (q, *J* = 8.0 Hz, 2H), 3.25 – 3.06 (m, 2H), 2.81 – 2.71 (m, 2H), 2.58 – 2.52 (m, 1H), 1.31 (s, 9H), 1.26 (t, *J* = 8 Hz, 3H), 1.02 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.96 (t, *J* = 5.6 Hz), 149.07, 146.35 (t, *J* = 8.1 Hz), 135.86, 128.90, 125.16, 117.42 (t, *J* = 248.5 Hz), 96.23 (t, *J* = 27.3 Hz), 61.23, 42.41, 42.02 (t, *J* =28.8 Hz), 41.03, 34.36, 31.37, 18.13, 14.07.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.19 (td, *J* = 14.9, 9.3 Hz).

HRMS (ESI) *m/z* calcd for $C_{20}H_{27}F_2IO_2Na$ [$(M+Na)^+$]: 487.0916, found: 487.0909.



Ethyl -3,3-difluoro-4-iodo-5-methyl-7-phenylhept-4-enoate (Z/E = 1:0.8) (3q)

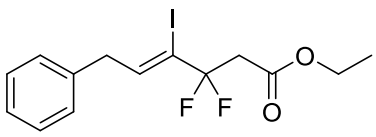
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3q** as a light-yellow oil (242.9 mg, 12%, 5 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m, 5H), 4.19 (dq, *J* = 10.3, 7.1 Hz, 2H), 3.17 (dt, *J* = 28.2, 15.0 Hz, 2H), 2.80 – 2.64 (m, 4H), 2.12 (dt, *J* = 25.8, 2.9 Hz, 3H), 1.31 – 1.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.05 (t, *J* = 4.0 Hz), 150.31 (t, *J* = 3.0 Hz), 149.46 (t, *J* = 4.0 Hz), 141.06, 140.75, 128.52 (d, *J* = 4.0 Hz), 128.38 (d, *J* = 4.0 Hz), 126.26, 126.22, 124.46, 123.99, 118.67 (t, *J* = 249.0 Hz), 118.47 (t, *J* = 249.5 Hz), 94.07 (t, *J* = 28.3 Hz), 61.36, 61.30, 49.20, 43.17 (t, *J* =28.3 Hz), 42.90 (t, *J* =28.8 Hz), 38.20 (t, *J* = 4.5 Hz), 35.12, 32.90 (t, *J* = 2.0 Hz), 32.68, 31.44, 30.19, 20.24 (t, *J* = 5.1 Hz), 14.12, 14.08.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.54 (td, *J* = 15.0, 3.7 Hz), -81.03 (tq, *J* = 15.1, 2.3 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 431.0290, found: 431.0296.



Ethyl (Z)-3,3-difluoro-4-iodo-6-phenylhex-4-enoate (3r)

Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3r** as a light-yellow oil (271.5 mg, 71%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

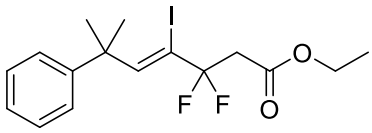
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.24 – 7.20 (m, 3H), 6.55 (tt, *J* = 6.9, 1.6 Hz,

1H), 4.12 (q, *J* = 8.0 Hz, 2H), 3.59 (dt, *J* = 7.0, 2.7 Hz, 2H), 3.24 (t, *J* = 16.0 Hz, 2H), 1.21 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.98 (t, *J* = 6.1 Hz), 140.80 (t, *J* = 8.6 Hz), 137.44, 128.78, 128.53, 126.83, 117.64 (t, *J* = 248.0 Hz), 98.63 (t, *J* = 27.3 Hz), 61.33, 42.03 (t, *J* =28.8 Hz), 42.21, 14.03.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.74 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}F_2IO_2$ [$(M)^+$]: 380.0073, found: 380.0073.



Ethyl (Z)-3,3-difluoro-4-iodo-6-methyl-6-phenylhept-4-enoate (3s)

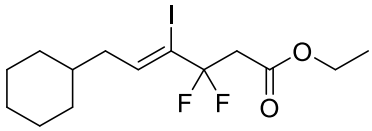
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3s** as a light-yellow oil (253.7 mg, 31%, 2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 7.12 (t, *J* = 1.7 Hz, 1H), 4.20 (q, *J* = 8.0 Hz, 2H), 3.21 (t, *J* = 14.0 Hz, 2H), 1.54 (s, 6H), 1.30 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.10 (t, *J* = 6.1 Hz), 149.75 (t, *J* = 8.6 Hz), 146.87, 128.32, 127.12, 126.01, 118.11 (t, *J* = 248.5 Hz), 95.25 (t, *J* = 26.3 Hz), 61.27, 41.99 (t, *J* =29.3 Hz), 41.98, 29.90, 14.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.03 (t, *J* = 13.2 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 431.0293, found: 431.0290.



Ethyl (Z)-6-cyclohexyl-3,3-difluoro-4-iodohex-4-enoate (3t)

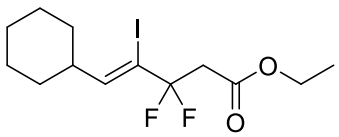
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3t** as a light-yellow oil (185.1 mg, 48%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (tt, *J* = 7.0, 1.7 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.21 (t, *J* = 14.0 Hz, 2H), 2.15 – 2.10 (m, 2H), 1.73 – 1.61 (m, 6H), 1.54 – 1.44 (m, 1H), 1.26 (t, *J* = 6.0 Hz, 3H), 1.21 – 1.12 (m, 2H), 1.04 – 0.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.06 (t, *J* = 6.1 Hz), 141.07 (t, *J* = 8.1 Hz), 117.55 (t, *J* = 247.5 Hz), 98.11 (t, *J* = 26.8 Hz), 61.24, 43.45, 42.06 (t, *J* =29.3 Hz), 37.29, 33.04, 26.27, 26.18, 14.07.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.51 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{14}H_{21}F_2IO_2Na$ [$(M+Na)^+$]: 409.0447, found: 409.0449.



Ethyl (Z)-5-cyclohexyl-3,3-difluoro-4-iodopent-4-enoate (3u)

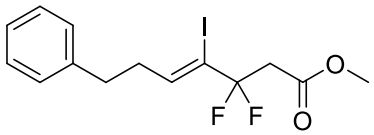
Prepared according to the procedure **2.1.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **3u** as a light-yellow oil (246.4 mg, 66%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (dt, *J* = 8.0, 1.5 Hz, 1H), 4.15 (q, *J* = 6.7 Hz, 2H), 3.19 (t, *J* = 14.0 Hz, 2H), 2.33 – 2.25 (m, 1H), 1.75 – 1.64 (m, 5H), 1.37 – 1.30 (m, 2H), 1.26 (t, *J* = 8.0 Hz, 3H), 1.21 – 1.11 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.06 (t, *J* = 5.6 Hz), 146.32 (t, *J* = 7.6 Hz), 117.51 (t, *J* = 248.0 Hz), 94.87 (t, *J* = 27.3 Hz), 61.25, 44.97, 42.06 (t, *J* =29.3 Hz), 30.86, 25.70, 25.32, 14.09.

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.78 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{13}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 395.0290, found: 395.0292.



Methyl (Z)-3,3-difluoro-4-iodo-7-phenylhept-4-enoate (5a)

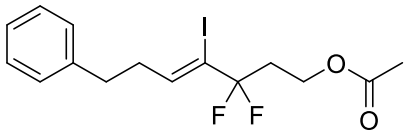
Prepared according to the procedure **2.2.1**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5a** as a light-yellow oil (274.3 mg, 72%, 1 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 6.43 (tt, *J* = 6.8, 1.6 Hz, 1H), 3.70 (s, 3H), 3.21 (t, *J* = 16.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.51 (m Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.46 (t, *J* = 5.6 Hz), 141.00 (t, *J* = 8.1 Hz), 140.50, 128.55, 128.43, 126.32, 117.43 (t, *J* = 247.5 Hz), 98.30 (t, *J* = 27.3 Hz), 52.26, 41.77 (t, *J* =29.3 Hz), 37.65, 33.76.

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.18 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}F_2IO_2Na$ [$(M+Na)^+$]: 402.9977, found: 402.9980.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl acetate (5b)

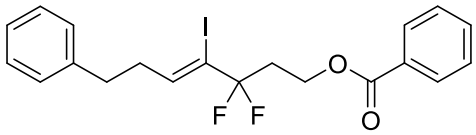
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5b** as a light-yellow oil (527.8 mg, 67%, 2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 6.37 (tt, *J* = 6.8, 1.5 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.59 – 2.44 (m, 4H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 140.44, 140.18 (t, *J* = 8.1 Hz), 128.55, 128.40, 126.32, 119.33 (t, *J* = 246.9 Hz), 99.46 (t, *J* = 27.8 Hz), 58.18 (t, *J* = 5.1 Hz), 37.62, 35.31 (t, *J* = 26.8 Hz), 33.82, 20.87.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.26 (t, *J* = 16.9 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{17}F_2IO_2$ [$(M)^+$]: 394.0230, found: 394.0230.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl benzoate (5c)

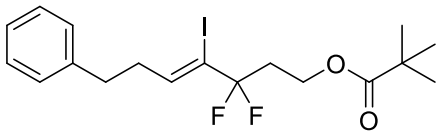
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5c** as a colorless oil (610.6 mg, 67%, 2 mmol scale). R_f = 0.5 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.14 (m, 5H), 6.38 (t, *J* = 6.0 Hz, 1H), 4.41 (t, *J* = 6.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.68 – 2.57 (m, 2H), 2.54 – 2.47 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25, 140.42, 140.23 (t, *J* = 8.1 Hz), 133.14, 129.82, 129.68, 128.51, 128.40, 128.35, 126.28, 119.43 (t, *J* = 246.9 Hz), 99.46 (t, *J* = 27.8 Hz), 58.71 (t, *J* = 5.1 Hz), 37.58, 35.41 (t, *J* = 26.8 Hz), 33.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.86 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{20}H_{19}F_2IO_2Na$ [$(M+Na)^+$]: 479.0289, found: 479.0290.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl pivalate (5d)

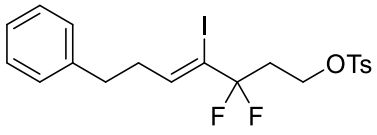
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5d** as a colorless oil (573.2 mg, 66%, 2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 3H), 6.36 (t, *J* = 6.0 Hz, 1H), 4.15 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.57 – 2.51 (m, 2H), 2.49 – 2.42 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.26, 140.44, 140.13 (t, *J* = 8.1 Hz), 128.53, 128.40, 126.30, 119.40 (t, *J* = 246.4 Hz), 99.55 (t, *J* = 27.8 Hz), 58.16 (t, *J* = 5.1 Hz), 38.65, 37.61, 35.32 (t, *J* = 26.8 Hz), 33.84, 27.11.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.82 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}F_2IO_2Na$ [$(M+Na)^+$]: 459.0606, found: 459.0603.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl 4-methylbenzenesulfonate (5e)

Prepared according to the procedure **2.2.3**. Flash column chromatography (eluent: PE/EA = 50:1) to afford **5e** as a colorless oil (863.0 mg, 85%, 2 mmol scale). R_f = 0.5 (PE/EA = 5:1), by staining with potassium permanganate.

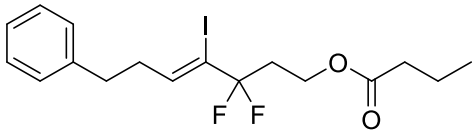
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.24 – 7.18 (m, 3H), 6.31 (t, *J* = 6.0 Hz, 1H), 4.13 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.56 – 4.47 (m, 4H),

2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.12, 140.71 (t, *J* = 8.1 Hz), 140.40, 132.71, 129.97, 128.57, 128.41, 127.99, 126.37, 118.76 (t, *J* = 246.9 Hz), 98.78 (t, *J* = 27.8 Hz), 63.70 (t, *J* = 5.1 Hz), 37.58, 35.76 (t, *J* = 26.8 Hz), 33.73, 21.70.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.34 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{20}H_{21}F_2IO_3SNa$ [$(M+Na)^+$]: 529.0116, found: 529.0114.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl butyrate (5f)

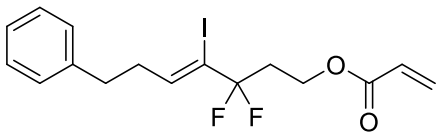
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5f** as a colorless oil (565.6mg, 67%, 2 mmol scale). R_f = 0.5 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 6.36 (tt, *J* = 6.9, 1.6 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.42 (m, 4H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.66 (p, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.35, 140.45, 140.15 (t, *J* = 8.1 Hz), 128.54, 128.40, 126.31, 119.35 (t, *J* = 246.4 Hz), 99.49 (t, *J* = 28.3 Hz), 57.95 (t, *J* = 5.6 Hz), 37.61, 36.05, 35.38 (t, *J* = 27.3 Hz), 33.83, 18.34, 13.67.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.10 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}F_2IO_2$ [$(M)^+$]: 422.0549, found: 422.0546.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl acrylate (5g)

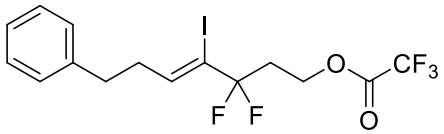
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5g** as a colorless oil (544.1 mg, 67%, 2 mmol scale). R_f = 0.5 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 6.42 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.36 (tt, *J* = 6.9, 1.6 Hz, 1H), 6.10 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.85 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.25 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.47 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 140.44, 140.19 (t, *J* = 8.1 Hz), 131.27, 128.54, 128.38, 128.06, 126.31, 119.32 (t, *J* = 246.4 Hz), 99.41 (t, *J* = 27.8 Hz), 58.28 (t, *J* = 5.6 Hz), 37.61, 35.32 (t, *J* = 27.3 Hz), 33.81.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.12 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{16}H_{17}F_2IO_2$ [$(M)^+$]: 406.0230, found: 406.0231.



(Z)-3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl 2,2,2-trifluoroacetate (5h)

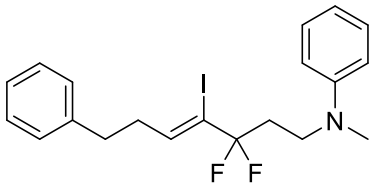
Prepared according to the procedure **2.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **5h** as a light-yellow oil (354.1 mg, 40%, 2 mmol scale). R_f = 0.6 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 3H), 6.38 (t, *J* = 6.8 Hz, 1H), 4.43 (t, *J* = 6.5 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.65 – 2.54 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.18 (q, *J* = 42.8), 140.84 (t, *J* = 8.6 Hz), 140.33, 128.58, 128.42, 126.39, 118.84 (t, *J* = 246.9 Hz), 115.80, (t, *J* = 286.8 Hz), 98.59 (t, *J* = 27.3 Hz), 61.63 (t, *J* = 5.1 Hz), 37.53, 35.00 (t, *J* = 27.3 Hz), 33.75.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.00 (s), -92.70 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{15}H_{14}F_5IO_2$ [$(M)^+$]: 447.9955, found: 447.9957.



(Z)-N-(3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl)-N-methylaniline (5i)

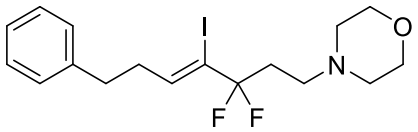
Prepared according to the procedure **2.2.4**. Flash column chromatography (eluent: PE/EA = 400:1) to afford **5i** as a yellow oil (338.9 mg, 77%, 1 mmol scale). R_f = 0.5 (PE/EA = 40:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8 7.33 – 7.26 (m, 3H), 7.26 – 7.18 (m, 4H), 6.78 – 6.62 (m, 3H), 6.33 (tt, *J* = 6.9, 1.6 Hz, 1H), 3.47 – 3.38 (m, 2H), 2.91 (s, 3H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.51 (m, 2H), 2.42 – 2.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.46, 140.48, 139.93 (t, *J* = 8.1 Hz), 129.36, 128.56, 128.43, 126.36, 120.07 (t, *J* = 245.4 Hz), 116.71, 112.34, 100.02 (t, *J* = 28.3 Hz), 46.15 (t, *J* = 4.5 Hz), 38.20, 37.56, 33.86, 32.42 (t, *J* = 25.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.78 (t, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{20}H_{23}F_2IN$ [$(M+H)^+$]: 442.0838, found: 442.0843.



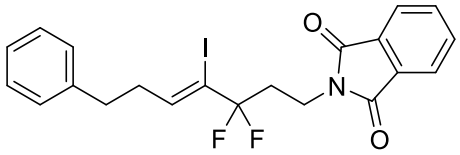
(Z)-4-(3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl)morpholine (5j)

Prepared according to the procedure **2.2.4**. Flash column chromatography (eluent: PE/EA = 40:1) to afford **5j** as a colorless oil (382.8 mg, 91%, 1 mmol scale). R_f = 0.3 (PE/EA = 5:1), by staining with potassium permanganate.

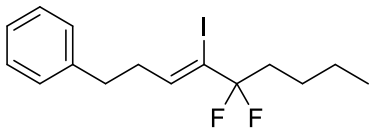
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 3H), 6.31 (t, *J* = 6.9 Hz, 1H), 3.70 (t, *J* = 4.0 Hz, 4H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.58 – 2.52 (m, 2H), 2.44 – 2.36 (m, 6H), 2.34 – 2.25 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.48, 139.74 (t, *J* = 8.1 Hz), 128.55, 128.42, 126.34, 120.08 (t, *J* = 245.9 Hz), 100.15 (t, *J* = 28.3 Hz), 66.90, 53.61, 51.88 (t, *J* = 4.5 Hz), 37.48, 33.86, 33.41 (t, *J* = 26.3 Hz).

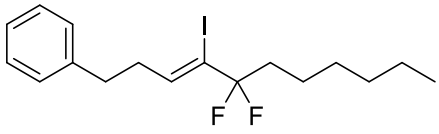
^{19}F NMR (376 MHz, $CDCl_3$) δ -92.32 (t, *J* = 15.0 Hz).
HRMS (ESI) *m/z* calcd for $C_{17}H_{23}F_2INO$ [$(M+H)^+$]: 422.0787, found: 422.0787.



(Z)-2-(3,3-difluoro-4-iodo-7-phenylhept-4-en-1-yl)isoindoline-1,3-dione (5k)
Prepared according to the procedure **2.2.5**. Flash column chromatography (eluent: PE/EA = 50:1) to afford **5k** as a colorless oil (432.9 mg, 60%, 1.5 mmol scale). R_f = 0.5 (PE/EA = 5:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.75 – 7.70 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.18 (m, 3H), 6.40 (t, *J* = 6.7 Hz, 1H), 3.81 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.9 Hz, 2H), 2.62 – 2.48 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 140.81 (t, *J* = 8.6 Hz), 140.56, 134.11, 132.01, 128.53, 128.44, 126.27, 123.35, 119.44 (t, *J* = 246.4 Hz), 99.02 (t, *J* = 27.8 Hz), 37.70, 34.38 (t, *J* =26.8 Hz), 33.80, 31.90 (t, *J* = 5.6 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -92.94 (t, *J* = 16.9 Hz).
HRMS (ESI) *m/z* calcd for $C_{21}H_{18}F_2INO_2Na$ [$(M+Na)^+$]: 504.0243, found: 504.0242.



(Z)-(5,5-difluoro-4-iodonon-3-en-1-yl)benzene (5l)
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5l** as a colorless oil (412.7 mg, 63%, 1.8 mmol scale). R_f = 0.6 (PE), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 6.29 (tt, *J* = 6.9, 1.6 Hz, 1H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.59 – 2.52 (m, 2H), 2.14 – 2.02 (m, 2H), 1.37 – 1.28 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 139.39 (t, *J* = 8.1 Hz), 128.48, 128.42, 126.25, 120.77 (t, *J* = 245.9 Hz), 100.65 (t, *J* = 28.8 Hz), 37.53, 35.72 (t, *J* =26.3 Hz), 33.91, 24.31 (t, *J* = 4.0 Hz), 22.22, 13.81.
^{19}F NMR (376 MHz, $CDCl_3$) δ -92.67 (t, *J* = 15.0 Hz).
HRMS (ESI) *m/z* calcd for $C_{15}H_{20}F_2I$ [$(M+H)^+$]: 365.0578, found: 365.0572.



(Z)-(5,5-difluoro-4-iodoundec-3-en-1-yl)benzene (5m)
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5m** as a colorless oil (451.8 mg, 64%, 1.8 mmol scale). R_f = 0.6 (PE), by staining with potassium

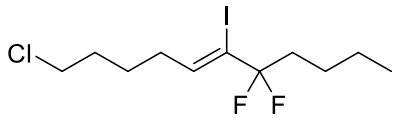
permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 6.29 (tt, *J* = 6.9, 1.6 Hz, 1H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.59 – 2.52 (m, 2H), 2.13 – 2.01 (m, 2H), 1.35 – 1.26 (m, 8H), 0.90 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.58, 139.38 (t, *J* = 8.1 Hz), 128.48, 128.41, 126.24, 120.76 (t, *J* = 245.9 Hz), 100.66 (t, *J* = 28.3 Hz), 37.53, 36.01 (t, *J* =26.8 Hz), 33.91, 31.48, 29.76, 22.48, 22.17 (t, *J* = 4.0 Hz), 14.03.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.70 (t, *J* = 16.9 Hz).

The spectra are in accordance with those of the compound reported in the literature[6].



(Z)-1-chloro-7,7-difluoro-6-iodoundec-5-ene (5n)

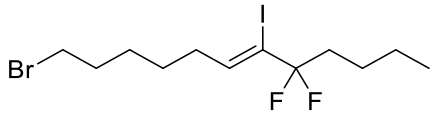
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5n** as a light-yellow oil (435.7 mg, 69%, 1.8 mmol scale). R_f = 0.7 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (tt, *J* = 6.9, 1.6 Hz, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.30 – 2.23 (m, 2H), 2.16 – 2.04 (m, 2H), 1.85 – 1.79 (m, 2H), 1.67 – 1.60 (m, 2H), 1.40 – 1.33 (m, 4H), 0.92 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.59 (t, *J* = 8.1 Hz), 120.74 (t, *J* = 245.4 Hz), 100.59 (t, *J* = 28.8 Hz), 44.62, 35.74 (t, *J* =26.3 Hz), 35.06, 31.86, 25.09, 24.35 (t, *J* = 4.0 Hz), 22.22, 13.82.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.92 (t, *J* = 16.9 Hz).

HRMS (ESI) *m/z* calcd for $C_{11}H_{18}ClF_2I$ [$(M)^+$]: 350.0104, found: 350.0106.



(Z)-1-bromo-8,8-difluoro-7-iodododec-6-ene (5o)

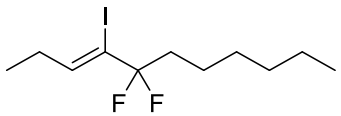
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5o** as a colorless oil (506.7 mg, 69%, 1.8 mmol scale). R_f = 0.7 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, *J* = 7.0 Hz, 1H), 3.42 (t, *J* = 6.8 Hz, 2H), 2.27 – 2.21 (m, 2H), 2.16 – 2.04 (m, 2H), 1.92 – 1.85 (m, 2H), 1.51 – 1.48 (m, 4H), 1.40 – 1.33 (m, 4H), 0.92 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.95 (t, *J* = 8.1 Hz), 120.79 (t, *J* = 246.4 Hz), 100.22 (t, *J* = 28.8 Hz), 35.74 (t, *J* =26.8 Hz), 35.63, 33.62, 32.45, 27.62, 26.97, 24.36 (t, *J* = 4.0 Hz), 22.23, 13.85.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.81 (t, *J* = 16.9 Hz).

HRMS (ESI) *m/z* calcd for $C_{12}H_{20}BrF_2I$ [$(M)^+$]: 407.9756, found: 407.9764.



(Z)-5,5-difluoro-4-iodoundec-3-ene (5p)

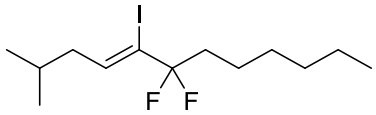
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5p** as a colorless oil (313.7 mg, 55%, 1.8 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (tt, *J* = 6.8, 1.6 Hz, 1H), 2.28 – 2.18 (m, 2H), 2.15 – 2.02 (m, 2H), 1.38 – 1.25 (m, 8H), 1.05 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.77 (t, *J* = 8.1 Hz), 120.75 (t, *J* = 246.4 Hz), 99.15 (t, *J* = 28.3 Hz), 36.02 (t, *J* =25.3 Hz), 31.60, 29.46, 28.77, 22.48, 22.19 (t, *J* = 3.5 Hz), 14.04, 12.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.85 (t, *J* = 16.9 Hz).

The spectra are in accordance with those of the compound reported in the literature[6]



(Z)-6,6-difluoro-5-iodo-2-methyldodec-4-ene (5q)

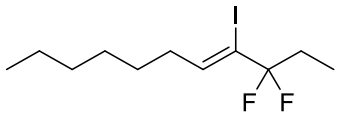
Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5q** as a colorless oil (254.4 mg, 41%, 1.8 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (tt, *J* = 7.0, 1.6 Hz, 1H), 2.19 – 2.03 (m, 4H), 1.87 – 1.77 (m, 1H), 1.40 – 1.28 (m, 8H), 0.95 (d, *J* = 6.7 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.52 (t, *J* = 8.1 Hz), 120.88 (t, *J* = 245.4 Hz), 100.41 (t, *J* = 28.3 Hz), 44.62, 36.05 (t, *J* =26.3 Hz), 31.51, 28.75, 27.89, 22.47, 22.36, 22.26 (t, *J* = 4.0 Hz), 14.04.

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.61 (t, *J* = 16.9 Hz).

The spectra are in accordance with those of the compound reported in the literature[6]



(Z)-3,3-difluoro-4-iodoundec-4-ene (5r)

Prepared according to the procedure **2.3.4**. Flash column chromatography (eluent: PE) to afford **5r** as a colorless oil (243.9 mg, 43%, 1.8 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (tt, *J* = 6.9, 1.6 Hz, 1H), 2.25 – 2.18 (m, 2H), 2.16 – 2.07 (m, 2H), 1.49 – 1.42 (m, 2H), 1.37 – 1.27 (m, 6H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.87 (t, *J* = 8.1 Hz), 121.04 (t, *J* = 245.4 Hz), 99.27 (t, *J* = 28.3 Hz), 35.92, 31.60, 29.43 (t, *J* =27.8 Hz), 28.83, 27.82, 22.55, 14.06, 6.65 (t, *J* = 4.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -94.70 (t, *J* = 15.0 Hz).

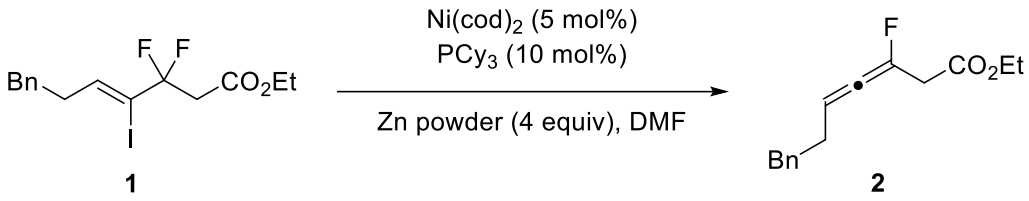
The spectra are in accordance with those of the compound reported in the literature[6]

3. Optimization of the Reaction

3.1 The Influence of Temperature

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), PCy_3 (0.01 mmol, 2.8 mg, 10 mol%), and zinc powder (0.4 mmol, 26.2 mg, 4.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run for one day. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard).

***Table S1*:** The influence of temperature



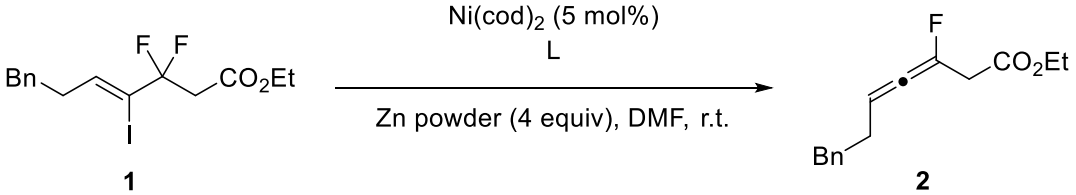
1 **2**

Entry	Temp.	Yield of 2 (%)	Recovery of 1 (%)
1	-20 °C	0	92
2	0 °C	4	75
3	RT	96	0

3.2 The Influence of Ligands

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), ligand, and zinc powder (0.4 mmol, 26.2 mg, 4.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run at room temperature for one day. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard).

***Table S2*:** The influence of ligands



1 **2**

Entry	Ligand	Yield of 2 (%)	Recovery of 1 (%)
1	PCy_3[a]	96	0
2	RuPhos[a]	73[c]	19
3	XantPhos[b]	92	0

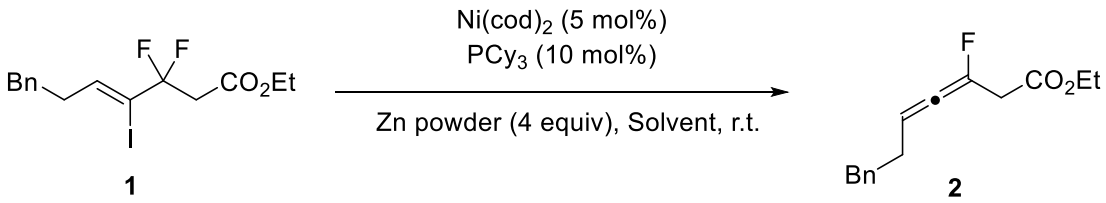
4	DPPB[b]	14	0
5	Rac-BINAP[b]	15[c]	0
6	2,2'-Dipyridyl[b]	0	90
7	4,4'-Dimethyl-2,2'-bipyridyl[b]	0	92
8	1,10-Phenanthroline[b]	0	88
9	4,7-diphenyl-1,10-phenanthroline[b]	0	87

[a] 0.01 mmol, 10 mol%. [b] 0.005 mmol, 5 mol%. [c] Reaction for 16 hours.

3.3 The Influence of Solvents

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), PCy_3 (0.01 mmol, 2.8 mg, 10 mol%), and zinc powder (0.4 mmol, 26.2 mg, 4.0 equiv) in 1 mL solvent under a nitrogen atmosphere, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard).

***Table S3*:** The influence of solvents



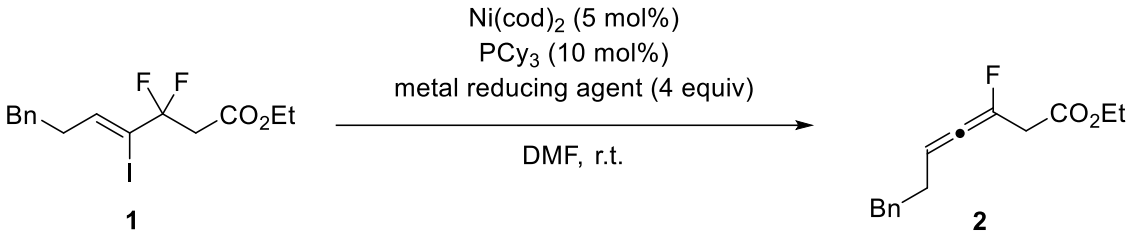
Entry	Solvent	Yield of 2 (%)	Recovery of 1 (%)
1	THF	0	95
2	MeCN	0	99
3	DMA	93	0
4	MTBE	0	95
5	n-Hexane	0	93
6	Benzonitrile	5	91
7	tert-Butanol	0	92
8	Benzotrifluoride	4	91
9	Chlorobenzene	0	91
10	DMSO	62	0

3.4 Screen Metal Reducing Agent

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), PCy_3 (0.01 mmol, 2.8 mg, 10 mol%), and metal

reducing agent (0.4 mmol, 4.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard).

***Table S4*:** The influence of metal reducing agent



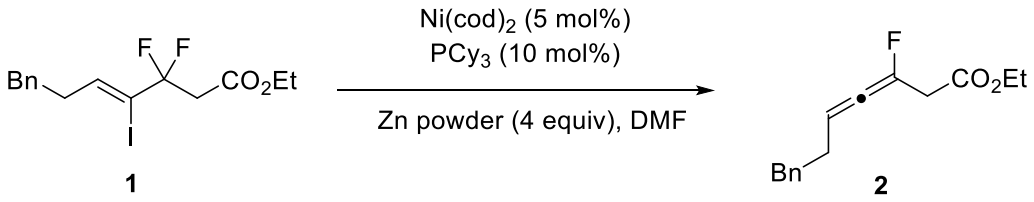
Entry	Metal reducing agent	Yield of 2 (%)	Recovery of 1 (%)
1	Fe	4	90
2	Mg	2	95
3	Mn[a]	23	59
4	Mn[b]	6	72

[a] With 1 equiv TFA. [b] With 1 equiv TMSCl..

3.5 Screen for Other Conditions

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1 equiv), $Ni(cod)_2$ or others catalysts (0.005 mmol, 1.4 mg, 5 mol%), PCy_3 (0.01 mmol, 2.8 mg, 10 mol%), and zinc powder (0.4 mmol, 26.2 mg, 4 equiv) in 1 mL DMF, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product 2 was determined by GC (n-tetradecane as internal standard).

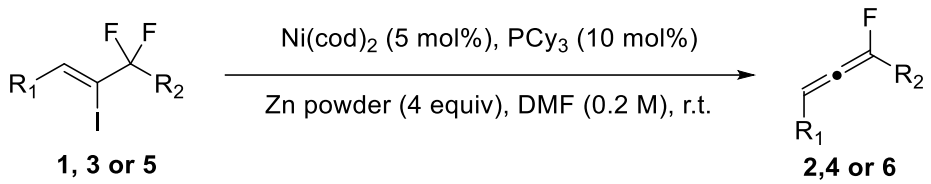
***Table S5*:** Screen for other conditions



Entry	Condition	Yield of 2 (%)	Recovery of 1 (%)
1	Without $Ni(cod)_2$	0	97
2	Without PCy_3	67	0
3	Without zinc powder	3	93
4	$Pd(PPh_3)_4$ as cat	0	94
5	CuCl as cat	0	99
6	$CuCl_2$ as cat	0	94

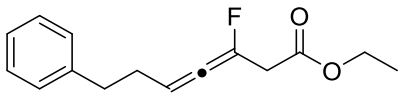
7	$Cu(OAc)_2$ as cat	0	95
8	CuTc as cat	0	99

4 Catalytic Access to Functionalized Allenyl Monofluoride

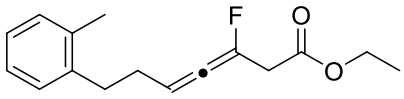


1, 3 or 5 **2,4 or 6**

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1, 3 or 5** (0.2 mmol, 1.0 equiv), $Ni(cod)_2$ (0.01 mmol, 2.8 mg, 5 mol%), PCy_3 (0.02 mmol, 5.6 mg, 10 mol%), and zinc powder (0.8 mmol, 52.4 mg, 4.0 equiv) in 2 mL DMF under a nitrogen atmosphere, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. The mixture was washed 7 times with water to remove the DMF. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give allenyl monofluoride **2, 4 or 6**.
For **5m** the reaction was run for 48 h; **5p** the reaction was run at 40 °C for 48 h; **5q** the reaction was run at 50 °C for 48 h.



Ethyl 3-fluoro-7-phenylhepta-3,4-dienoate (2)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **2** as a light-yellow oil (45.1 mg, 91%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 6.02 - 5.97 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.24 (dt, *J* = 16.4, 2.2 Hz, 2H), 2.80 (td, *J* = 8.0, 7.5, 2.4 Hz, 2H), 2.53 - 2.46 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.83 (d, *J* = 23.2 Hz), 168.68, 141.04, 134.60 (d, *J* = 237.4 Hz), 128.48, 128.40, 126.07, 109.10 (d, *J* = 11.1 Hz), 61.29, 37.63 (d, *J* =36.4 Hz), 34.16 (d, *J* = 3.0 Hz), 32.08, 14.17.
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.11 - -133.20 (m).
HRMS (ESI) *m/z* calcd for $C_{15}H_{17}FO_2$ [$(M)^+$]: 248.1216, found: 248.1212.



Ethyl 3-fluoro-7-(o-tolyl)hepta-3,4-dienoate (4a)

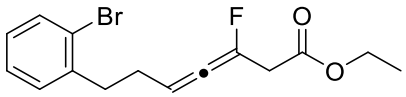
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4a** as a light-yellow oil (45.7 mg, 87%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

1H NMR (400 MHz, CDCl3) δ 7.15 – 7.10 (m, 4H), 6.04 – 6.00 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.26 (dd, *J* = 16.3, 2.1 Hz, 2H), 2.78 (td, *J* = 7.4, 2.9 Hz, 2H), 2.47 – 2.40 (m, 2H), 2.31 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.71 (d, *J* = 24.2 Hz), 168.68, 139.19, 135.98, 134.62 (d, *J* = 237.4 Hz), 130.26, 128.81, 126.24, 126.00, 109.24 (d, *J* = 11.1 Hz), 61.28, 37.64 (d, *J* =35.4 Hz), 31.58 (d, *J* = 3.0 Hz), 30.89 (t, *J* = 62.1 Hz), 19.29, 14.18.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.99 - -133.12 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_2$ [$(M+H)^+$]: 263.1442, found: 263.1444.



Ethyl 7-(2-bromophenyl)-3-fluorohepta-3,4-dienoate (4b)

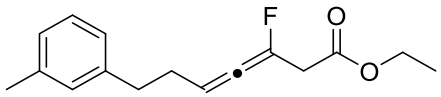
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4b** as a light-yellow oil (59.5 mg, 92%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.09 – 7.04 (m, 1H), 6.03 – 5.98 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.27 (dt, *J* = 16.2, 1.9 Hz, 2H), 2.95 – 2.87 (m, 2H), 2.52 – 2.45 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.88 (d, *J* = 23.2 Hz), 168.61, 140.30, 134.72 (d, *J* = 238.4 Hz), 132.88, 130.53, 127.89, 127.46, 124.45, 108.74 (d, *J* = 10.1 Hz), 61.32, 37.67 (d, *J* =35.4 Hz), 34.51 (d, *J* = 3.0 Hz), 30.50, 14.18.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.84 - -132.97 (m).

HRMS (ESI) *m/z* calcd for $C_{15}H_{17}BrFO_2$ [$(M+H)^+$]: 327.0379, found: 327.0379.



Ethyl 3-fluoro-7-(m-tolyl)hepta-3,4-dienoate (4c)

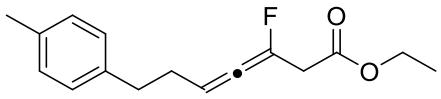
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4c** as a light-yellow oil (41.9 mg, 80%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

1H NMR (400 MHz, CDCl3) δ 7.20 – 7.16 m, 1H), 7.04 – 6.97 (m, 3H), 6.01 – 5.97 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.25 (dt, *J* = 16.5, 2.5 Hz, 2H), 2.76 (td, *J* = 8.0, 7.5, 2.0 Hz, 2H), 2.51 – 2.43 m, 2H), 2.33 (s, 3H), 1.28 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.73 (d, *J* = 24.2 Hz), 168.67, 140.98, 137.93, 134.54 (d, *J* = 237.4 Hz), 129.30, 128.28, 126.78, 125.45, 109.15 (d, *J* = 10.1 Hz), 61.28, 37.63 (d, *J* =35.4 Hz), 34.14 (d, *J* = 3.0 Hz), 32.13, 21.37, 14.16.

^{19}F NMR (376 MHz, CDCl3) δ -133.12 - -133.25 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_2$ [$(M+H)^+$]: 263.1442, found: 263.1446.



Ethyl 3-fluoro-7-(p-tolyl)hepta-3,4-dienoate (4d)

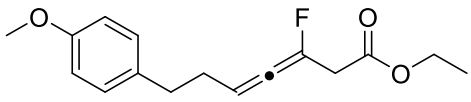
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4d** as a light-yellow oil (43.7 mg, 83%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.07 (m, 4H), 6.00 – 5.96 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.25 (dt, *J* = 16.2, 1.8 Hz, 2H), 2.80 – 2.72 (m, 2H), 2.50 – 2.42 (m, 2H), 2.32 (s, 3H), 1.29 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.77 (d, *J* = 24.2 Hz), 168.67, 137.98, 135.52, 134.56 (d, *J* = 237.4 Hz), 129.09, 128.36, 109.18 (d, *J* = 10.1 Hz), 61.27, 37.65 (d, *J* =35.4 Hz), 33.76 (d, *J* = 4.0 Hz), 32.25, 21.00, 14.17.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.13 - -133.26 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_2$ [$(M+H)^+$]: 263.1442, found: 263.1447.



Ethyl 3-fluoro-7-(4-methoxyphenyl)hepta-3,4-dienoate (4e)

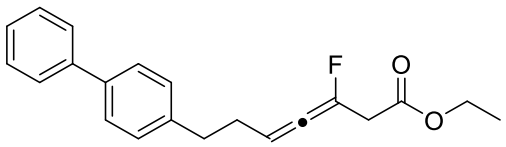
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 100:1) to afford **4e** as a light-yellow oil (47.5 mg, 85%, 0.2 mmol scale). R_f = 0.2 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.00 – 5.95 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.25 (dt, *J* = 16.3, 1.7 Hz, 2H), 2.73 (td, *J* = 7.9, 7.4, 1.8 Hz, 2H), 2.48 – 2.40 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.76 (d, *J* = 23.2 Hz), 168.68, 157.96, 134.53 (d, *J* = 237.4 Hz), 133.11, 129.37, 113.81, 109.16 (d, *J* = 11.1 Hz), 61.28, 55.26, 37.65 (d, *J* =35.4 Hz), 33.29 (d, *J* = 4.0 Hz), 32.36, 14.16.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.14 - -133.27 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_3$ [$(M+H)^+$]: 279.1391, found: 279.1387.

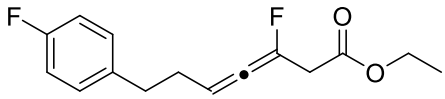


Ethyl 7-([1,1'-biphenyl]-4-yl)-3-fluorohepta-3,4-dienoate (4f)

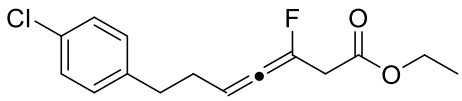
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4f** as a light-yellow oil (54.5 mg, 84%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.27 (d, *J* = 4 Hz, 2H), 6.04 – 5.99 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.25 (dt, *J* = 16.3, 1.9 Hz, 2H), 2.84 (td, *J* = 7.5, 2.5 Hz, 2H), 2.58 – 2.44 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

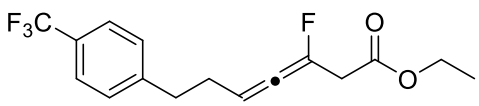
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.89 (d, *J* = 24.2 Hz), 168.68, 141.00, 140.17, 139.03, 134.65 (d, *J* = 237.4 Hz), 128.92, 128.76, 127.14, 127.11, 127.02, 109.05 (d, *J* = 10.1 Hz), 61.32, 37.64 (d, *J* =35.4 Hz), 33.79 (d, *J* = 3.0 Hz), 32.06, 14.17.
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.03 - -133.16 (m).
HRMS (ESI) *m/z* calcd for $C_{21}H_{22}FO_2$ [$(M+H)^+$]: 325.1598, found: 325.1594.



Ethyl 3-fluoro-7-(4-fluorophenyl)hepta-3,4-dienoate (4g)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4g** as a light-yellow oil (67.9 mg, 85%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 5.99 – 5.95 m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.25 (dd, *J* = 16.3, 2.0 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.51 – 2.42 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.95 (d, *J* = 23.2 Hz), 168.61, 161.38 (d, *J* = 244.4 Hz), 136.64 (d, *J* = 3.0 Hz), 134.69 (d, *J* = 237.4 Hz), 129.82 (d, *J* = 7.1 Hz), 115.12 (d, *J* = 21.2 Hz), 108.80 (d, *J* = 10.1 Hz), 61.30, 37.98 (d, *J* =35.4 Hz), 33.28 (d, *J* = 3.0 Hz), 32.14, 14.14.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.35 - -117.42 (m), -133.04 - -133.17 (m).
HRMS (ESI) *m/z* calcd for $C_{15}H_{16}F_2O_2$ [$(M)^+$]: 266.1113, found: 266.1111.



Ethyl 7-(4-chlorophenyl)-3-fluorohepta-3,4-dienoate (4h)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4h** as a light-yellow oil (75.4 mg, 89%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.99 – 5.94 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.25 (dd, *J* = 16.3, 2.1 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.49 – 2.42 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.99 (d, *J* = 23.2 Hz), 168.60, 139.48, 134.77 (d, *J* = 237.4 Hz), 131.80, 129.83, 128.48, 108.71 (d, *J* = 10.1 Hz), 61.33, 37.60 (d, *J* =35.4 Hz), 33.40 (d, *J* = 3.0 Hz), 31.90, 14.16.
^{19}F NMR (376 MHz, $CDCl_3$) δ -132.95 - -133.09 (m).
HRMS (ESI) *m/z* calcd for $C_{15}H_{17}ClFO$ [$(M+H)^+$]: 283.0896, found: 283.0892.



Ethyl 3-fluoro-7-(4-(trifluoromethyl)phenyl)hepta-3,4-dienoate (4i)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4i** as a light-yellow oil (73.2 mg, 77%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by

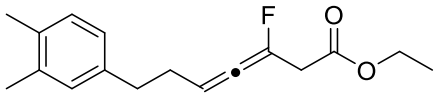
staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.00 – 5.96 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.24 (dd, *J* = 16.2, 2.2 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.54 – 2.46 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.13 (d, *J* = 24.2 Hz), 168.52, 145.15, 134.94 (d, *J* = 237.4 Hz), 128.79, 128.66, 125.65 (t, *J* = 272.2 Hz), 125.31 (q, *J* = 4.0 Hz), 108.76 (d, *J* = 10.1 Hz), 61.30, 37.56 (d, *J* =35.4 Hz), 33.82 (d, *J* = 3.0 Hz), 14.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39, -132.82 - -132.96 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{16}F_4O_2$ [$(M)^+$]: 316.1074, found: 316.1077.



Ethyl 7-(3,4-dimethylphenyl)-3-fluorohepta-3,4-dienoate (4j)

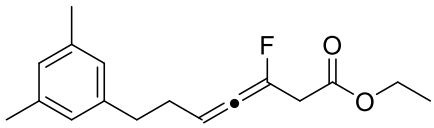
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4j** as a light-yellow oil (72.3 mg, 87%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.01 – 5.97 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.26 (dt, *J* = 16.4, 2.3 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.50 – 2.41 (m, 2H), 2.23 (d, *J* = 4.0 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.64 (d, *J* = 23.2 Hz), 168.67, 138.45, 136.44, 134.46 (d, *J* = 237.4 Hz), 134.13, 129.82, 129.61, 125.76, 109.26 (d, *J* = 11.1 Hz), 61.25, 37.63 (d, *J* =36.4 Hz), 33.71 (d, *J* = 3.0 Hz), 32.28, 19.70, 19.27, 14.16.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.12 - -133.25 (m).

HRMS (ESI) *m/z* calcd for $C_{17}H_{22}FO_2$ [$(M+H)^+$]: 277.1598, found: 277.1594.



Ethyl 7-(3,5-dimethylphenyl)-3-fluorohepta-3,4-dienoate (4k)

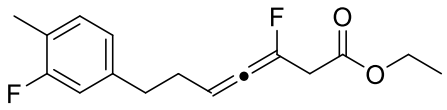
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4k** as a light-yellow oil (77.2 mg, 93%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.82 (s, 2H), 6.02 – 5.97 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.26 (dt, *J* = 16.5, 2.5 Hz, 2H), 2.72 (td, *J* = 7.4, 1.7 Hz, 2H), 2.50 – 2.42 (m, 2H), 2.29 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.72 (d, *J* = 24.2 Hz), 168.71, 140.98, 137.87, 134.51 (d, *J* = 237.4 Hz), 127.69, 126.33, 109.27 (d, *J* = 11.1 Hz), 61.30, 37.66 (d, *J* =36.4 Hz), 34.40 (d, *J* = 4.0 Hz), 32.21, 21.26, 14.18.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.13 - -133.26 (m).

HRMS (ESI) *m/z* calcd for $C_{17}H_{22}FO_2$ [$(M+H)^+$]: 277.1598, found: 277.1598.



Ethyl 3-fluoro-7-(3-fluoro-4-methylphenyl)hepta-3,4-dienoate (4l)

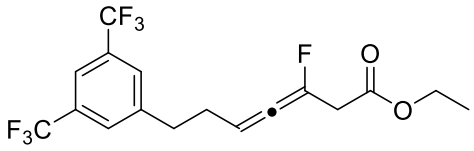
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4l** as a light-yellow oil (77.3 mg, 92%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.99 – 5.95 (tq, *J* = 6.1, 2.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.25 (dd, *J* = 16.4, 2.2 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.50 – 2.41 (m, 2H), 2.23 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.90 (d, *J* = 24.2 Hz), 168.62, 161.26 (d, *J* = 244.2 Hz), 140.69 (d, *J* = 8.1 Hz), 134.72 (d, *J* = 237.4 Hz), 131.25 (d, *J* = 5.1 Hz), 123.81 (d, *J* = 4.0 Hz), 122.26 (d, *J* = 17.2 Hz), 114.90 (d, *J* = 22.2 Hz), 108.82 (d, *J* = 11.1 Hz), 61.32, 37.79, 37.44, 37.62 (d, *J* =35.4 Hz), 33.46 (d, *J* = 1.3 Hz), 14.16 (t, *J* = 1.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.07 (t, *J* = 9.4 Hz), -133.03 - -133.16 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}F_2O_2$ [$(M+H)^+$]: 281.1348, found: 281.1348.



Ethyl 7-(3,5-bis(trifluoromethyl)phenyl)-3-fluorohepta-3,4-dienoate (4m)

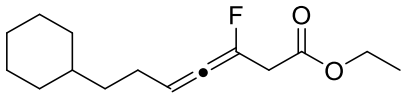
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4m** as a light-yellow oil (92.4 mg, 80%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.66 (s, 2H), 6.02 – 5.98 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 16.4, 2.1 Hz, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.60 – 2.50 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.45 (d, *J* = 24.2 Hz), 168.46, 143.48, 135.37 (d, *J* = 239.4 Hz), 131.63 (q, *J* = 33.3 Hz), 128.71 (d, *J* = 3.0 Hz), 123.38 (d, *J* = 273.7 Hz), 120.22 (m), 107.88 (d, *J* = 10.1 Hz), 61.39, 37.52 (d, *J* =35.4 Hz), 33.38 (d, *J* = 3.0 Hz), 31.32, 14.11.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88 (s), -132.37 - -132.50 (m).

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}F_7O_2$ [$(M+H)^+$]: 385.1033, found: 385.1033.



Ethyl 7-cyclohexyl-3-fluorohepta-3,4-dienoate (4n)

Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4n** as a light-yellow oil (61.6 mg, 81%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

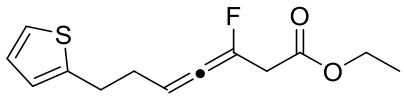
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.93 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.31 (dd, *J* = 16.1, 2.2 Hz, 2H), 2.20 – 2.11 (m, 2H), 1.71 – 1.63 (m, 5H), 1.35 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz,

3H), 1.24 – 1.07 (m, 4H), 0.92 – 0.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.03 (d, *J* = 23.2 Hz), 168.71, 134.06 (d, *J* = 236.3 Hz), 110.38 (d, *J* = 11.1 Hz), 61.21, 37.72 (d, *J* = 35.4 Hz), 37.05, 35.53 (d, *J* = 3.0 Hz), 33.14 (d, *J* = 6.1 HZ), 28.03, 26.59, 26.31 (d, *J* = 1.0 Hz), 14.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.27 - -133.40 (m).

HRMS (ESI) *m/z* calcd for $C_{15}H_{24}FO_2$ [$(M+H)^+$]: 255.1755, found: 255.1759.



Ethyl 3-fluoro-7-(thiophen-2-yl)hepta-3,4-dienoate (4o)

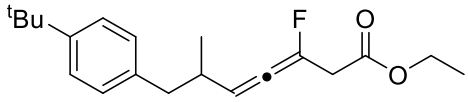
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4o** as a light-yellow oil (59.4 mg, 78%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 4.0 Hz, 1H), 6.92 (t , *J* = 4.0 Hz, 1H), 6.81 (d, *J* = 4.0 Hz, 1H), 6.03 – 5.99 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.28 (dt, *J* = 16.4, 1.8 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.58 – 2.50 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.01 (d, *J* = 24.2 Hz), 168.65, 143.77, 134.90 (d, *J* = 238.4 Hz), 126.78, 124.61, 123.31, 109.54 (d, *J* = 11.1 Hz), 61.34, 37.64 (d, *J* =35.4 Hz), 32.32, 28.23 (d, *J* = 3.0 Hz), 14.18.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.94 - -133.08 (m).

HRMS (ESI) *m/z* calcd for $C_{13}H_{16}FO_2S$ [$(M+H)^+$]: 255.0850, found: 255.0846.



Ethyl 3-fluoro-7-(4-(trifluoromethyl)phenyl)hepta-3,4-dienoate (4p) (dr = 1:1)

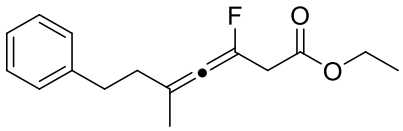
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4p** as a light-yellow oil (89.4 mg, 94%, 0.3 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate. The two configurations have the same polarity and cannot be separated.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.01 – 5.86 (m, 1H), 4.22 – 4.15 (m, 2H), 3.28 – 3.04 (m, 2H), 2.78 – 2.52 (m, 3H), 1.31 (s, 9H), 1.30 – 1.25 (m, 3H), 1.08 (dd, *J* = 19.2, 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.52 (d, *J* = 24.2 Hz), 189.41 (d, *J* = 24.2 Hz), 168.71, 148.88, 148.86, 136.99, 136.69, 135.29 (d, *J* = 237.4 Hz), 134.61 (d, *J* = 237.4 Hz), 128.86, 128.82, 125.13, 125.12, 115.00 (d, *J* = 10.1 Hz), 114.55 (d, *J* = 10.1 Hz), 61.26, 61.22, 42.05 (d, *J* =57.6 Hz), 42.06 (d, *J* =57.6 Hz), 37.70 (d, *J* = 36.4 Hz), 37.56 (d, *J* = 35.4 Hz), 37.58, 36.42, 34.36, 31.38, 19.34 (d, *J* = 3.0 Hz), 18.80 (d, *J* = 3.0 Hz), 14.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.93 - -133.04 (m), -133.12 - -133.23 (m).

HRMS (ESI) *m/z* calcd for $C_{20}H_{28}FO_2$ [$(M+H)^+$]: 319.2068, found: 319.2064.



Ethyl 3-fluoro-5-methyl-7-phenylhepta-3,4-dienoate (4q)

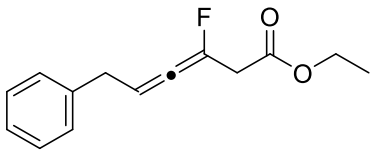
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4q** as a light-yellow oil (46.7 mg, 89%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.20 (d, *J* = 15.9 Hz, 2H), 2.80 (t, *J* = 7.8 Hz, 2H), 2.48 – 2.35 (m, 2H), 1.87 (d, *J* = 8.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.86 (d, *J* = 22.2 Hz), 168.92, 141.42, 132.75 (d, *J* = 237.4 Hz), 128.40, 128.34, 125.93, 119.27 (d, *J* = 12.1 Hz), 61.15, 37.83 (d, *J* =38.4 Hz), 37.21, 33.35 (d, *J* = 2.0 Hz), 21.20, 14.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -129.01 - -129.16 (m).

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_2$ [$(M+H)^+$]: 263.1442, found: 263.1447.



Ethyl 3-fluoro-6-phenylhexa-3,4-dienoate (4r)

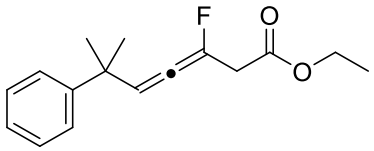
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4r** as a light-yellow oil (36.6 mg, 78%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.20 (m, 3H), 6.10 – 6.05 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.49 (t, *J* = 7.3 Hz, 2H), 3.31 (dd, *J* = 16.0, 2.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.36 (d, *J* = 25.4 Hz), 168.55, 138.29, 134.30 (d, *J* = 238.4 Hz), 128.57, 128.56, 126.59, 108.69 (d, *J* = 11.1 Hz), 61.32, 37.60 (d, *J* =34.3 Hz), 37.30, 14.13.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.20 - -133.33 (m).

HRMS (ESI) *m/z* calcd for $C_{14}H_{16}FO_2$ [$(M+H)^+$]: 235.1129, found: 235.1125.

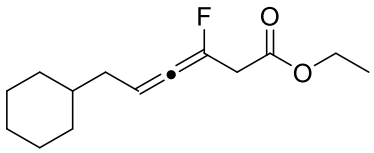


Ethyl 3-fluoro-6-methyl-6-phenylhepta-3,4-dienoate (4s)

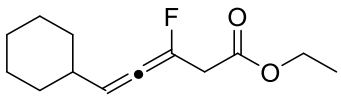
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4s** as a light-yellow oil (48.3 mg, 92%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.25 – 7.19 (m, 1H), 6.14 – 6.11 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.38 (dd, *J* = 15.8, 2.2 Hz, 2H), 1.47 (d, *J* = 4.4 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

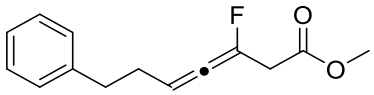
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.14 (d, *J* = 24.2 Hz), 168.56, 147.26 (d, *J* = 4.0 Hz), 135.76 (d, *J* = 238.4 Hz), 128.32, 126.30, 125.90, 119.62 (d, *J* = 11.1 Hz), 61.33, 37.89 (d, *J* =35.3 Hz), 28.71 (d, *J* = 3.0 Hz), 28.32 (d, *J* = 2.0 Hz), 14.12.
^{19}F NMR (376 MHz, $CDCl_3$) δ -131.48 (t, *J* = 15.0 Hz).
HRMS (ESI) *m/z* calcd for $C_{16}H_{20}FO_2$ [$(M+H)^+$]: 263.1442, found: 263.1440.



Ethyl 6-cyclohexyl-3-fluorohexa-3,4-dienoate (4t)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4t** as a light-yellow oil (42.4 mg, 88%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.86 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.25 (m, 2H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.76 – 1.61 (m, 5H), 1.47 – 1.37 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.24 – 1.10 (m, 3H), 0.97 – 0.87 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.74 (d, *J* = 25.3 Hz), 168.72, 133.55 (d, *J* = 237.4 Hz), 108.58 (d, *J* = 11.1 Hz), 61.22, 38.47, 37.70 (d, *J* = 35.4 Hz), 37.20 (d, *J* = 4.0 Hz), 32.91 (d, *J* = 6.1 Hz), 26.38, 26.15, 14.12.
^{19}F NMR (376 MHz, $CDCl_3$) δ -134.06 - -134.19 (m).
HRMS (ESI) *m/z* calcd for $C_{14}H_{22}FO_2$ [$(M+H)^+$]: 241.1598, found: 241.1595.



Ethyl 5-cyclohexyl-3-fluoropenta-3,4-dienoate (4u)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **4u** as a light-yellow oil (41.3 mg, 91%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.90 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.31 (dd, *J* = 15.9, 2.2 Hz, 2H), 2.18 – 2.05 (m, 1H), 1.84 – 1.59 (m, 6H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.24 – 1.07 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.91 (d, *J* = 23.2 Hz), 168.75, 134.81 (d, *J* = 236.3 Hz), 115.55 (d, *J* = 11.1 Hz), 61.23, 39.01, 37.82 (d, *J* = 36.4 Hz), 31.96 (dd, *J* = 4.0, 3.0 Hz), 25.96, 25.74 (d, J = 2.0 Hz), 14.10.
^{19}F NMR (376 MHz, $CDCl_3$) δ -132.95 - -133.06 (m).
HRMS (ESI) *m/z* calcd for $C_{13}H_{19}FO_2$ [$(M)^+$]: 226.1364, found: 226.1366.



Methyl 3-fluoro-7-phenylhepta-3,4-dienoate (6a)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to

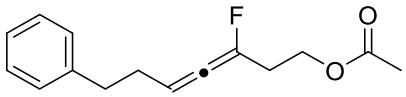
afford **6a** as a light-yellow oil (40.2 mg, 86%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.21 - 7.18 (m, 3H), 6.01 – 5.97 (m, 1H), 3.74 (s, 3H), 3.24 (ddd, *J* = 16.8, 4.3, 2.1 Hz, 2H), 2.80 (td, *J* = 8.0, 7.6, 2.7 Hz, 2H), 2.53 – 2.45 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.80 (d, *J* = 24.2 Hz), 169.14, 141.00, 134.37 (d, *J* = 237.4 Hz), 128.48, 128.41, 126.09, 109.13 (d, *J* = 11.1 Hz), 52.33, 37.37 (d, *J* = 35.4 Hz), 34.16 (d, *J* = 3.0 Hz), 32.04.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.16 - -133.29 (m).

HRMS (ESI) *m/z* calcd for $C_{14}H_{15}FO_2Na$ [$(M+Na)^+$]: 257.0954, found: 257.0951.



3-fluoro-7-phenylhepta-3,4-dien-1-yl acetate (6b)

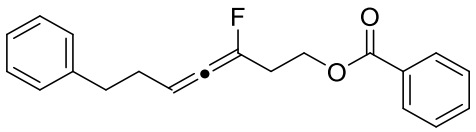
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6b** as a light-yellow oil (45.2 mg, 91%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 4.0 Hz, 2H), 7.19 (t, *J* = 6.0 Hz, 3H), 5.98 – 5.94 (m, 1H), 4.13 (td, *J* = 6.7, 2.7 Hz, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.63 – 2.56 (m, 2H), 2.51 – 2.42 (m, 2H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.02 (d, *J* = 24.2 Hz), 170.87, 141.07, 137.80 (d, *J* = 237.4 Hz), 128.45, 128.43, 126.10, 109.17 (d, *J* = 11.1 Hz), 60.55 (d, *J* = 2.0 Hz), 34.29 (d, *J* = 4.0 Hz), 32.31, 30.46 (d, *J* = 34.3 Hz), 20.90.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.83 - -134.95 (m).

HRMS (ESI) *m/z* calcd for $C_{15}H_{17}FO_2Na$ [$(M+Na)^+$]: 271.1105, found: 271.1109.



3-fluoro-7-phenylhepta-3,4-dien-1-yl benzoate (6c)

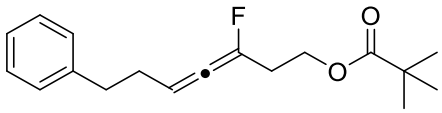
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6c** as a light-yellow oil (59.0 mg, 95%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 14.7 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 2H), 5.99 – 5.94 (m, 1H), 4.40 (t, *J* = 6.4 Hz, 2H), 2.79 – 2.70 (m, 4H), 2.46 – 2.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.07 (d, *J* = 24.2 Hz), 166.40, 141.01, 137.83 (d, *J* = 238.4 Hz), 133.04, 130.07, 129.62, 128.40, 128.37, 126.03, 109.25 (d, *J* = 11.1 Hz), 61.02 (d, *J* = 1.0 Hz), 34.36 (d, *J* = 3.0 Hz), 32.34, 30.64 (d, *J* = 33.3 Hz), 20.90.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.74 - -134.86 (m).

HRMS (ESI) *m/z* calcd for $C_{20}H_{20}FO_2$ [$(M+H)^+$]: 311.1442, found: 311.1443.



3-fluoro-7-phenylhepta-3,4-dien-1-yl pivalate (6d)

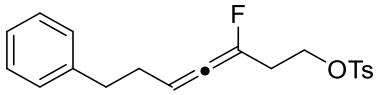
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6d** as a light-yellow oil (51.6 mg, 89%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.1 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 3H), 5.97 – 5.90 (m, 1H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.63 – 2.53 (m, 2H), 2.50 – 2.42 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.13 (d, *J* = 26.3 Hz), 178.31, 140.99, 137.85 (d, *J* = 238.4 Hz), 128.41, 128.39, 126.05, 108.90 (d, *J* = 11.1 Hz), 60.45 (d, *J* = 1.0 Hz), 38.69, 34.42 (d, *J* = 3.0 Hz), 32.23, 30.56 (d, *J* = 33.3 Hz), 27.14.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.82 - -134.93 (m).

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}FO_2Na$ [$(M+Na)^+$]: 313.1580, found: 313.1579.



3-fluoro-7-phenylhepta-3,4-dien-1-yl 4-methylbenzenesulfonate (6e)

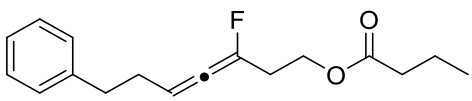
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 5:1) to afford **6e** as a light-yellow oil (61.9 mg, 86%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 5:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.17 (t, *J* = 6.1 Hz, 3H), 5.95 – 5.91 (m, 1H), 4.09 – 4.01 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.63 – 2.56 (m, 2H), 2.45 - 2.39 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.85 (d, *J* = 23.2 Hz), 144.96, 141.02, 136.44 (d, *J* = 237.4 Hz), 132.94, 129.91, 128.46, 128.42, 127.93, 126.10, 109.79 (d, *J* = 11.1 Hz), 66.04 (d, *J* = 1.0 Hz), 34.14 (d, *J* = 3.0 Hz), 32.12, 30.86 (d, *J* = 34.3 Hz), 21.66.

^{19}F NMR (376 MHz, $CDCl_3$) δ -135.52 - -135.64 (m).

HRMS (ESI) *m/z* calcd for $C_{20}H_{22}FO_3S$ [$(M+H)^+$]: 361.1268, found: 361.1272.

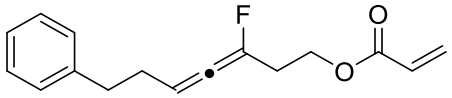


3-fluoro-7-phenylhepta-3,4-dien-1-yl butyrate (6f)

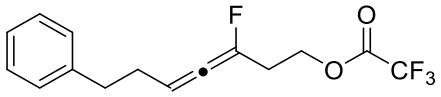
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6f** as a light-yellow oil (42.5 mg, 77%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 3H), 5.98 – 5.94 (m, 1H), 4.14 (td, *J* = 6.6, 2.9 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.63 – 2.56 (m, 2H), 2.51 – 2.42 (m, 2H),

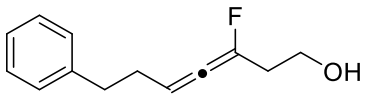
2.28 (t, *J* = 7.4 Hz, 2H), 1.65 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.03 (d, *J* = 24.2 Hz), 173.48, 141.05, 137.84 (d, *J* = 238.4 Hz), 128.45, 128.41, 126.07, 109.17 (d, *J* = 12.1 Hz), 60.30 (d, *J* = 2.0 Hz), 36.11, 34.31 (d, *J* = 3.0 Hz), 32.29, 30.53 (d, *J* = 33.3 Hz), 18.41, 13.64.
^{19}F NMR (376 MHz, $CDCl_3$) δ -134.79 - -134.91 (m).
HRMS (ESI) *m/z* calcd for $C_{17}H_{21}FO_2Na$ [$(M+Na)^+$]: 299.1423, found: 299.1418.



3-fluoro-7-phenylhepta-3,4-dien-1-yl acrylate (6g)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6g** as a light-yellow oil (28.6 mg, 55%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 3H), 6.41 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.96 (tt, *J* = 6.3, 2.7 Hz, 1H), 5.98 – 5.94 (m, 1H), 4.23 (t, *J* = 6.5 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.68 – 2.61 (m, 2H), 2.50 – 2.40 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.00 (d, *J* = 24.2 Hz), 165.97, 141.06, 137.73 (d, *J* = 237.4 Hz), 131.05, 128.43, 128.42, 128.24, 126.07, 109.22 (d, *J* = 11.1 Hz), 60.59 (d, *J* = 2.0 Hz), 34.31 (d, *J* = 3.0 Hz), 32.30, 30.48 (d, *J* = 33.3 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -134.81 - -134.92 (m).
HRMS (ESI) *m/z* calcd for $C_{16}H_{18}FO_2$ [$(M+H)^+$]: 261.1285, found: 261.1283.



3-fluoro-7-phenylhepta-3,4-dien-1-yl 2,2,2-trifluoroacetate (6ha)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **6ha** as a light-yellow oil (28.4 mg, 47%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 3H), 6.01 – 5.96 (m, 1H), 4.35 (td, *J* = 6.5, 2.1 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.72 – 2.65 (m, 2H), 2.53 – 2.44 (dq, *J* = 15.4, 7.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.85 (d, *J* = 24.2 Hz), 157.29 (q, *J* = 42.4 Hz), , 140.89, 136.26 (d, *J* = 237.4 Hz), 128.45, 128.44, 126.12, 114.48 (d, *J* = 205.0 Hz), 109.85 (d, *J* = 11.1 Hz), 60.86 (d, *J* = 1.0 Hz), 34.22 (d, *J* = 3.0 Hz), 32.15, 30.03 (d, *J* = 34.3 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -75.03 (s), -135.44 - -135.55 (m).
HRMS (ESI) *m/z* calcd for $C_{15}H_{15}F_4O_2$ [$(M+H)^+$]: 303.1008, found: 303.1012.



3-fluoro-7-phenylhepta-3,4-dien-1-ol (6hb)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 20:1) to

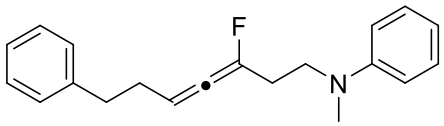
afford **6hb** as a light-yellow oil (19.5 mg, 47%, 0.2 mmol scale). R_f = 0.2 (PE/EA = 5:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 3H), 5.99 – 5.94 (m, 1H), 3.68 (td, *J* = 6.3, 2.0 Hz, 2H), 2.82 – 2.75 (m, 2H), 2.55 – 2.44 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.31 (d, *J* = 24.2 Hz), 141.07, 138.44 (d, *J* = 238.4 Hz), 128.48, 128.43, 126.09, 108.85 (d, *J* = 11.1 Hz), 59.16 (d, *J* = 2.0 Hz), 34.37 (d, *J* = 3.0 Hz), 34.34 (d, *J* = 32.3 Hz), 32.39.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.64 - -134.76 (m).

HRMS (ESI) *m/z* calcd for $C_{13}H_{15}FONa$ [$(M+Na)^+$]: 229.0999, found: 229.0994.



N-(3-fluoro-7-phenylhepta-3,4-dien-1-yl)-N-methylaniline (6i)

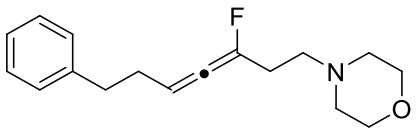
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 40:1) to afford **6i** as a light-yellow oil (50.8 mg, 86%, 0.2 mmol scale). R_f = 0.2 (PE/EA = 400:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.15 (m, 5H), 6.70 (d, *J* = 8.1 Hz, 3H), 5.93 – 5.89 (m, 1H), 3.45 (dt, *J* = 6.7, 4.6 Hz, 2H), 2.94 (s, 3H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.55 – 2.40 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.32 (d, *J* = 24.2 Hz), 148.78, 141.19, 139.18 (d, *J* = 238.4 Hz), 129.34, 128.53, 128.48, 126.15, 116.49, 112.29, 108.55 (d, *J* = 11.1 Hz), 49.41, 38.38, 34.47 (d, *J* = 4.0 Hz), 32.40, 28.38 (d, *J* = 31.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.14 - -134.26 (m).

HRMS (ESI) *m/z* calcd for $C_{20}H_{23}FN$ [$(M+H)^+$]: 296.1809, found: 296.1807.



4-(3-fluoro-7-phenylhepta-3,4-dien-1-yl)morpholine (6j)

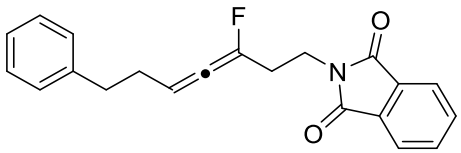
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 20:1) to afford **6j** as a light-yellow oil (32.1 mg, 58%, 0.2 mmol scale). R_f = 0.2 (PE/EA = 5:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 3H), 5.94 – 5.91 (m, 1H), 3.71 (t, *J* = 4.6 Hz, 4H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.47 – 2.43 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.04 (d, *J* = 25.3 Hz), 141.14, 139.70 (d, *J* = 237.4 Hz), 128.44, 128.42, 126.08, 108.57 (d, *J* = 11.1 Hz), 66.94, 55.06 (d, *J* = 2.0 Hz), 53.54, 34.38 (d, *J* = 4.0 Hz), 32.34, 28.38 (d, *J* = 32.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.61 - -133.71 (m).

HRMS (ESI) *m/z* calcd for $C_{17}H_{23}FNO$ [$(M+H)^+$]: 276.1758, found: 276.1758.



2-(3-fluoro-7-phenylhepta-3,4-dien-1-yl)isoindoline-1,3-dione (6k)

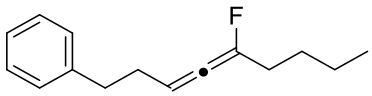
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE/EA = 50:1) to afford **6k** as a light-yellow oil (45.7 mg, 68%, 0.2 mmol scale). R_f = 0.5 (PE/EA = 5:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.70 – 7.63 (m, 2H), 7.26 – 7.21 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.90 – 5.85 (m, 1H), 3.88 – 3.74 (m, 2H), 2.72 – 2.60 (m, 4H), 2.37 – 2.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.05 (d, *J* = 24.2 Hz), 168.05, 140.99, 137.68 (d, *J* = 238.4 Hz), 134.00, 131.99, 128.39, 128.35, 126.00, 123.28, 109.02 (d, *J* = 12.1 Hz), 34.79, 34.30 (d, *J* = 3.0 Hz), 32.30, 29.94 (d, *J* = 34.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.47 - -134.59 (m).

HRMS (ESI) *m/z* calcd for $C_{21}H_{18}FNO_2Na$ [$(M+Na)^+$]: 358.1214, found: 358.1217.



(5-fluorononа-3,4-dien-1-yl)benzene (6l)

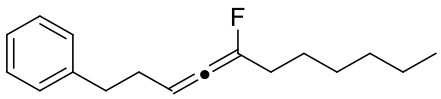
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6l** as a light-yellow oil (41.1 mg, 94%, 0.2 mmol scale). R_f = 0.7 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.94 – 5.87 (m, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.51 – 2.42 (m, 2H), 2.30 – 2.21 (m, 2H), 1.42 – 1.33 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.11 (d, *J* = 26.3 Hz), 141.78 (d, *J* = 237.4 Hz), 141.33, 128.48, 128.40, 126.03, 108.03 (d, *J* = 11.1 Hz), 34.53 (d, *J* = 4.0 Hz), 32.57, 30.60 (d, *J* = 31.3 Hz), 27.98 (d, *J* = 1.0 Hz), 22.07, 13.85.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.25 - -133.37 (m).

HRMS (ESI) *m/z* calcd for $C_{15}H_{19}F$ [$(M)^+$]: 218.1464, found: 218.1464.

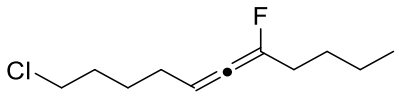


(5-fluoroundeca-3,4-dien-1-yl)benzene (6m)

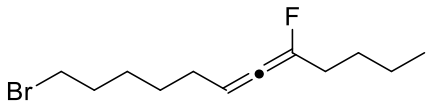
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6m** as a light-yellow oil (42.2 mg, 86%, 0.2 mmol scale). R_f = 0.7 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.92 – 5.88 (m, 1H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.49 – 2.41 (m, 2H), 2.29 – 2.21 (m, 2H), 1.42 – 1.26 (m, 8H), 0.89 (t, *J* = 6.5 Hz, 3H).

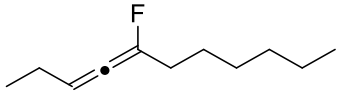
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.13 (d, *J* = 25.3 Hz), 141.81 (d, *J* = 237.4 Hz), 141.32, 128.46, 128.38, 126.01, 108.00 (d, *J* = 12.1 Hz), 34.51 (d, *J* = 3.0 Hz), 32.55, 31.59, 30.66 (d, *J* = 31.3 Hz), 28.64, 25.83 (d, *J* = 2.0 Hz), 22.61, 14.10.
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.24 - -133.35 (m).
HRMS (ESI) *m/z* calcd for $C_{17}H_{24}F$ [$(M+H)^+$]: 247.1857, found: 247.1859.



1-chloro-7-fluoroundeca-5,6-diene (6n)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6n** as a light-yellow oil (33.2 mg, 81%, 0.2 mmol scale). R_f = 0.6 (PE), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.81 (m, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.35 – 2.25 (m, 2H), 2.16 (dt, *J* = 14.9, 7.2 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.65 – 1.58 (m, 2H), 1.48 – 1.33 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.00 (d, *J* = 25.3 Hz), 141.63 (d, *J* = 237.4 Hz), 108.09 (d, *J* = 12.1 Hz), 44.77, 31.82, 30.32 (d, *J* = 31.3 Hz), 30.08, 27.99 (d, *J* = 1.0 Hz), 25.38 (d, *J* = 3.0 Hz), 22.03, 13.83.
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.41 - -133.52 (m).
HRMS (ESI) *m/z* calcd for $C_{11}H_{19}ClF$ [$(M+H)^+$]: 205.1161, found: 205.1156.

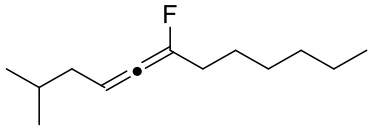


12-bromo-5-fluorododeca-5,6-diene (6o)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6o** as a light-yellow oil (27.9 mg, 53%, 0.2 mmol scale). R_f = 0.6 (PE), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.81 (m, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.37 – 2.21 (m, 2H), 2.18 – 2.04 (m, 2H), 1.94 – 1.81 (m, 2H), 1.53 – 1.31 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.82 (d, *J* = 25.3 Hz), 141.31 (d, *J* = 238.4 Hz), 108.44 (d, *J* = 12.1 Hz), 33.70, 32.59, 30.69, 30.35 (d, *J* = 32.3 Hz), 28.05, 27.58, 27.36 (d, *J* = 4.0 Hz), 22.04, 13.82.
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.44 - -133.56 (m).
HRMS (ESI) *m/z* calcd for $C_{12}H_{21}BrF$ [$(M+H)^+$]: 263.0805, found: 263.0805.

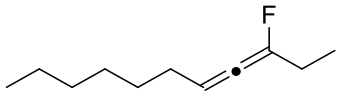


5-fluoroundeca-3,4-diene (6p)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6p** as a light-yellow oil (23.2 mg, 68%, 0.2 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.89 (m, 1H), 2.33 - 2.30 (m, 2H), 2.17 – 2.08 (m, 2H), 1.49 – 1.42 (m, 2H), 1.37 – 1.26 (m, 6H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.04 (d, *J* = 25.3 Hz), 141.91 (d, *J* = 237.4 Hz), 110.49 (d, *J* = 12.1 Hz), 31.56, 30.62 (d, *J* = 31.6 Hz), 28.58, 25.90 (d, *J* = 1.0 Hz), 24.11, 22.55, 14.02, 12.46 (d, *J* = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.04 - -133.16 (m).
HRMS (ESI) *m/z* calcd for $C_{11}H_{19}F$ [$(M)^+$]: 170.1465, found: 170.1467.



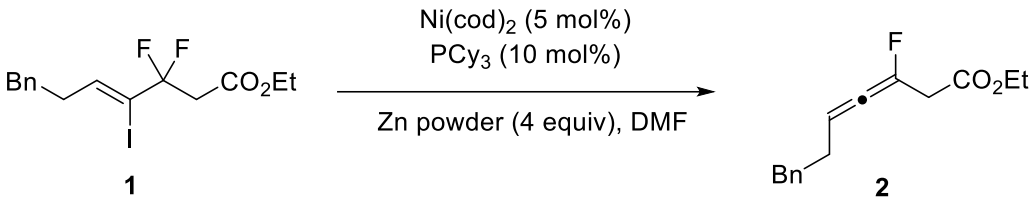
6-fluoro-2-methyldodeca-4,5-diene (6q)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6q** as a light-yellow oil (30.4 mg, 77%, 0.2 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.78 (m, 1H), 2.33 – 2.26 (m, 2H), 2.07 – 1.96 (m, 2H), 1.79 – 1.71 (m, 1H), 1.49 – 1.43 (m, 2H), 1.38 – 1.27 (m, 6H), 0.94 (d, *J* = 6.7 Hz, 6H), 0.89 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.41 (d, *J* = 25.3 Hz), 140.83 (d, *J* = 236.4 Hz), 107.63 (d, *J* = 11.1 Hz), 40.34, 31.59, 30.69 (d, *J* = 31.3 Hz), 28.62, 27.95 (d, *J* = 4.0 Hz), 25.90 (d, *J* = 1 Hz), 22.60, 22.25 (d, *J* = 10.1 Hz), 14.07.
^{19}F NMR (376 MHz, $CDCl_3$) δ -134.41 - -134.51 (m).
HRMS (ESI) *m/z* calcd for $C_{13}H_{24}F$ [$(M+H)^+$]: 199.1852, found: 199.1857.



3-fluoroundeca-3,4-diene (6r)
Prepared according to the procedure **4**. Flash column chromatography (eluent: PE) to afford **6r** as a light-yellow oil (22.2 mg, 65%, 0.2 mmol scale). R_f = 0.8 (PE), by staining with potassium permanganate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.86 (m, 1H), 2.36 – 2.28 (m, 2H), 2.16 – 2.08 (m, 2H), 1.48 – 1.39 (m, 2H), 1.35 – 1.26 (m, 6H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.01 (d, *J* = 25.3 Hz), 142.72 (d, *J* = 236.3 Hz), 109.64 (d, *J* = 12.1 Hz), 31.65, 30.99, 28.72, 28.26 (d, *J* = 3.0 Hz), 23.81 (d, *J* = 33.3 Hz), 22.60, 14.07, 10.47 (d, *J* = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -133.04 - -133.14 (m).
HRMS (ESI) *m/z* calcd for $C_{11}H_{19}FK$ [$(M+K)^+$]: 209.1108, found: 209.1107.

5. Scale-Up Reactions and Derivatizations of Allenyl Monofluorides.

5.1 Scale-Up Reaction

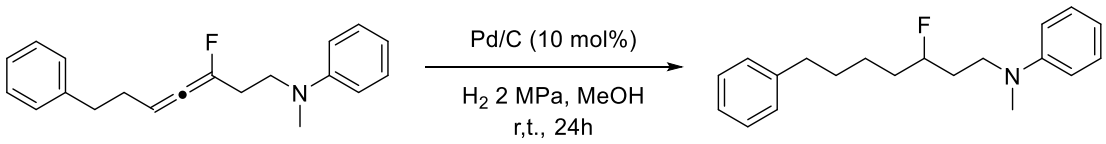


1 2

To an oven-dried 50 mL flask equipped with a magnetic stirring bar, dissolve **1** (2 mmol, 788 mg, 1.0 equiv), $Ni(cod)_2$ (0.1 mmol, 28 mg, 5 mol%), PCy_3 (0.2 mmol, 56 mg, 10 mol%), and zinc powder (8 mmol, 520 mg, 4.0 equiv) in 20 mL DMF under a nitrogen atmosphere, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. The mixture was washed 7 times with water to remove the DMF. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give **2** (0.39 g, 80%).

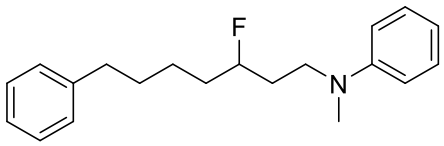
5.2 Derivatizations of Allenyl Monofluorides

5.2.1 Synthesis of 7



6i 7

To an oven-dried autoclave equipped with a magnetic stirring bar was added **6i** (0.6 mmol, 177.1 mg, 1 equiv), Pd/C (5%, with 55% water) (10 mol%, 127.7 mg) and 6 mL methanol, then the autoclave was filled with hydrogen to 2 MPa. The resulting mixture was stirred for 24 hours at room temperature, then the pressure of autoclave was reduced to normal pressure. The mixture was passed through a short pad of silica gel with EtOAc. The solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (PE : EtOAc = 400 : 1) to give **7** as yellow oil (0.1109 g, 62%).



N-(3-fluoro-7-phenylheptyl)-N-methylaniline (7)

Prepared according to the procedure **5.2.1**. Flash column chromatography (eluent: PE/EA = 400:1) to afford **7** as a yellow oil (110.9 mg, 62%, 0.6 mmol scale). R_f = 0.5 (PE/EA = 40:1).

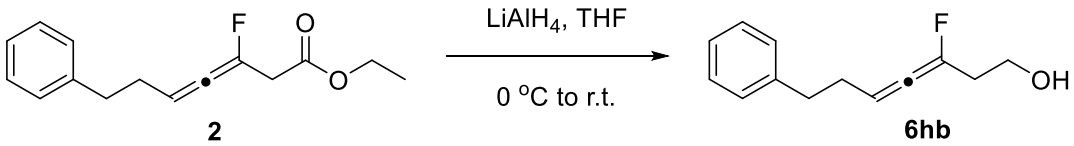
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 7H), 6.72 – 6.08 (m, 3H), 4.63-4.46 (m, 1H), 3.55 – 3.40 (m, 2H), 2.93 (s, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.92 – 1.58 (m, 6H), 1.53 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.09, 142.41, 129.27, 128.40, 128.33, 125.75, 116.26, 112.21, 92.46 (d, *J* = 167.7 Hz), 48.78 (d, *J* = 4.0 Hz), 38.43, 35.83, 35.29 (d, *J* = 20.2 Hz), 32.40 (d, *J* = 21.2 Hz), 31.29, 24.85 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -182.41 - -182.81 (m).

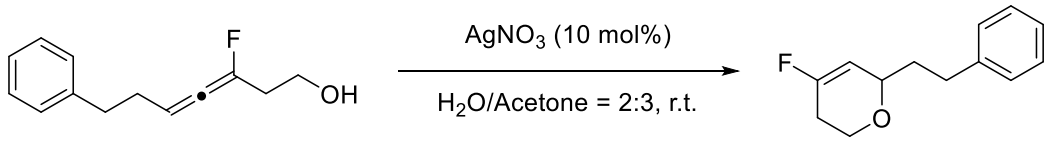
HRMS (ESI) *m/z* calcd for $C_{20}H_{27}FN$ [$(M+H)^+$]: 300.2122, found: 300.2120.

5.2.2 Synthesis of 8



2 **6hb**

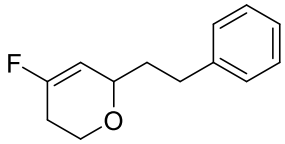
To an oven-dried 25 mL flask equipped with stir bar was added $LiAlH_4$ (56.9 mg, 1.5 mmol, 1.5 equiv) followed by dry THF (5 mL) under nitrogen atmosphere. The flask was cooled to 0 °C via an ice-water bath and the suspension was stirred for 10 minutes. After this time, **2** (248.1 mg, 1 mmol, 1.0 equiv) in dry THF (5 mL) was added dropwise to the flask. The mixture was stirred at 0 °C for 2 h and then quenched at 0 °C by very careful addition of deionized water (1.0 mL), 2 M NaOH (2 mL), and additional deionized water (3 mL). The quenched solution was allowed to stir for about 10 minutes, resulting in a white suspension. The solids were removed by filtration, washing the solids with diethyl ether (10 mL). The filtrate was transferred to a separatory funnel and washed with saturated $NaHCO_3$ (2 X 10 mL), deionized water (10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo by rotary evaporation. The residue was purified by flash column chromatography (PE : EtOAc = 20:1) to give **6hb** as colorless liquid (146.5 mg, 71%).



6hb **8**

To an oven-dried tube equipped with stir bar was added **6hb** (72.1 mg, 0.35 mmol, 1.0 equiv), $CaCO_3$ (35.0 mg, 0.35 mmol, 1.0 equiv), $AgNO_3$ (5.9 mg, 0.035 mmol, 0.1 equiv) and water/acetone = 1.0 mL : 1.5 mL under a nitrogen atmosphere. The solution was placed in the dark and stirred for 48 hours at room temperature. Then 10 mL ether was added and the solution was

washed three times with water. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed in vacuo by rotary evaporation. The residue was purified by flash column chromatography (PE : EtOAc = 200:1) to give **8** as colorless liquid (39.1 mg, 54%).



4-fluoro-6-phenethyl-3,6-dihydro-2H-pyran (8)

Prepared according to the procedure **5.2.2**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **8** as a colorless oil (39.1 mg, 54%, 0.35 mmol scale). R_f = 0.5 (PE/EA = 20:1).

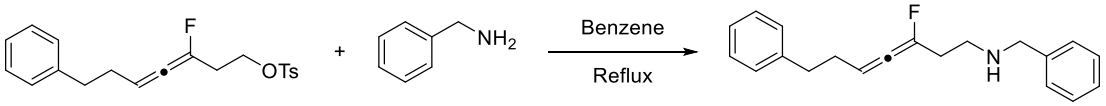
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 3H), 5.16 (d, *J* = 16.0 Hz, 1H), 4.18 – 4.06 (m, 2H), 3.73 – 3.65 (m, 1H), 2.80 – 2.74 (m, 2H), 2.55 – 2.45 (m, 1H), 2.16 – 2.06 (m, 1H), 1.91 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.67 (d, *J* = 262.6 Hz), 141.89, 128.50, 128.41, 125.88, 105.00 (d, *J* = 10.1 Hz), 72.29 (d, *J* = 7.1 Hz), 63.24 (d, *J* = 9.1 Hz), 37.26 (d, *J* = 2.0 Hz), 31.36, 26.70 (d, *J* = 20.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.46 - -101.56 (m).

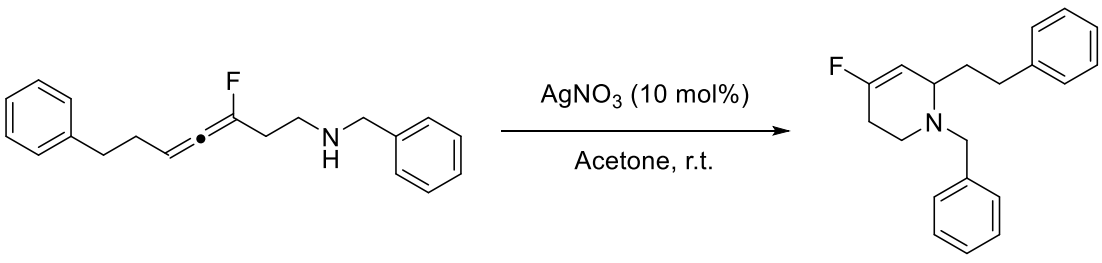
HRMS (ESI) *m/z* calcd for $C_{13}H_{15}FONa$ [$(M+Na)^+$]: 229.1005, found: 229.0999.

5.2.3 Synthesis of 10



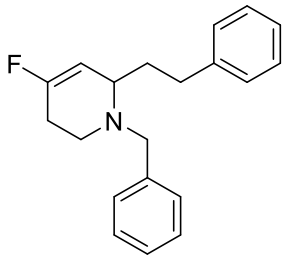
6e **9**

To an oven-dried 25 mL flask equipped with stir bar was added benzylamine (0.23 mL, 2.1 mmol, 3.0 equiv) and benzene (5 mL) under a nitrogen atmosphere. Then **6e** (0.24 g, 0.67 mmol, 1.0 equiv) in benzene (5 mL) was added dropwise to the flask. The mixture was placed at 110 °C under stirring and refluxing overnight. The mixture was cooled to room temperature and washed with 5 M NaOH, the aqueous layer was extracted three times with benzene. The organic phases were combined, dried with Na_2SO_4, filtered, and the solvent was removed in vacuo by rotary evaporation. The residue was purified by flash column chromatography (PE : EtOAc = 20 : 1) to give **9** as yellow oil(134.4 mg, 68%).



9 **10**

To an oven-dried tube equipped with stir bar was added **9** (73.7 mg, 0.25 mmol, 1.0 equiv), $AgNO_3$ (4.2 mg, 0.025 mmol, 0.1 equiv) and acetone (2.5 mL) under a nitrogen atmosphere. The solution was placed in the dark and stirred for 48 hours at room temperature. Then 10 mL ether was added and the solution was washed three times with water. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed in vacuo by rotary evaporation. The residue was purified by flash column chromatography (PE : EtOAc = 200 : 1) to give **10** as yellow oil(38.4 mg, 52%).



1-benzyl-4-fluoro-6-phenethyl-1,2,3,6-tetrahydropyridine (10)

Prepared according to the procedure **5.2.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **8** as a yellow oil (38.4 mg, 52%, 0.25 mmol scale). R_f = 0.5 (PE/EA = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 4H), 7.28 (dd, *J* = 13.2, 5.9 Hz, 3H), 7.17 (dd, *J* = 18.0, 7.5 Hz, 3H), 5.21 (dd, *J* = 17.3, 3.4 Hz, 1H), 3.85 (d, *J* = 13.5 Hz, 1H), 3.52 (d, *J* = 13.5 Hz, 1H), 3.16 – 3.09 (m, 1H), 3.06 – 3.00 (m, 1H), 2.72 – 2.64 (m, 3H), 2.35 – 2.28 (m, 1H), 2.13 (d, *J* = 17.2 Hz, 1H), 1.86 (q, *J* = 6.8 Hz, 2H).

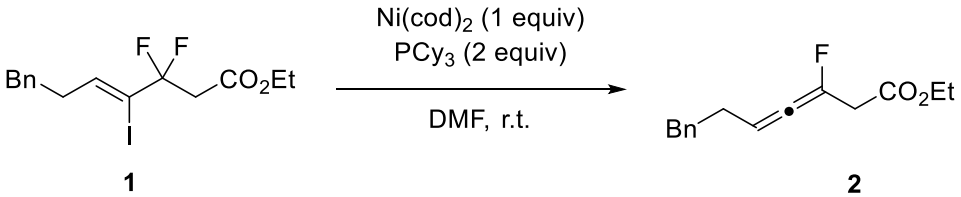
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.05 (d, *J* = 260.6 Hz), 142.54, 139.36, 128.83, 128.41, 128.35, 128.33, 127.06, 125.70, 104.35 (d, *J* = 11.1 Hz), 57.28 (d, *J* = 1.0 Hz), 66.86 (d, *J* = 8.1 Hz), 44.82 (d, *J* = 8.1 Hz), 35.81 (d, *J* = 3.0 Hz), 31.84, 23.64 (d, *J* = 21.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.25 (d, *J* = 15.0 Hz).

HRMS (ESI) *m/z* calcd for $C_{20}H_{23}FN$ $[(M+H)^+]$: 296.1815, found: 296.1809.

6. Mechanistic Studies

6.1 Stoichiometric Reaction



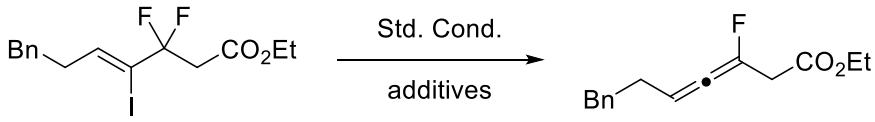
To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.1 mmol, 27.5 mg, 1.0 equiv) and PCy_3 (0.2 mmol, 56.1 mg, 2.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run for one day at room temperature.

Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (56%) (n-tetradecane as internal standard).

6.2 Radical Scavenger Tests

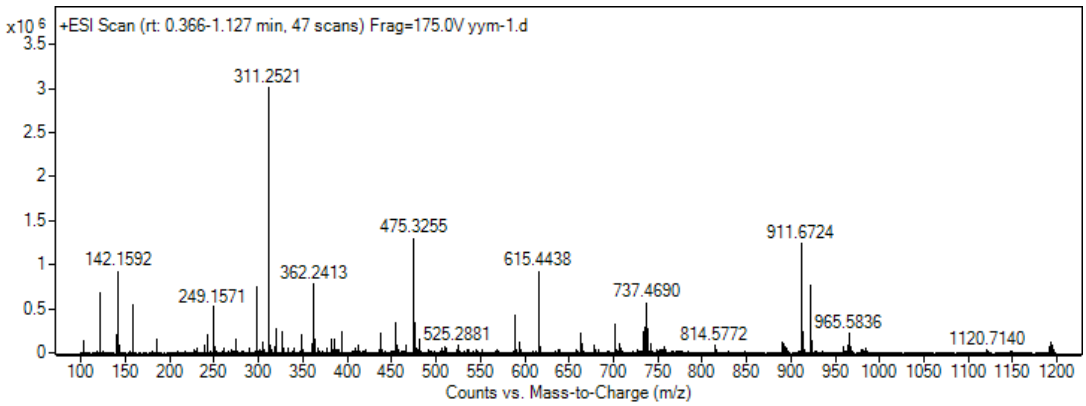
To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), PCy_3 (0.01 mmol, 2.8 mg, 10 mol%), zinc powder (0.4 mmol, 26.2 mg, 4.0 equiv), and radical scavenger (0.2 mmol, 2.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run for one day. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard).

***Table S6*:** Radical scavenger tests



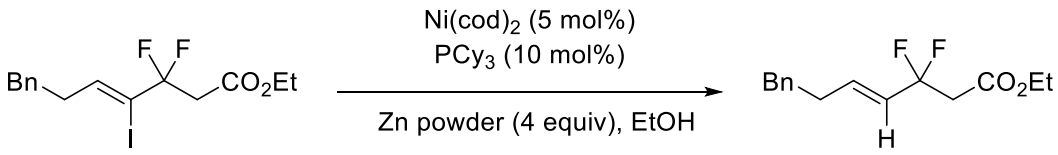
1 **2**

Entry	Radical Scavenger	Yield of 2 (%)	Recovery of 1 (%)
1	TEMPO	36	0
2	BHT	96	0



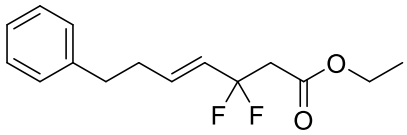
Picture 1: HRMS spectra of **entry 1**

6.3 Hydrolysis Side Product



1 **11**

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.2 mmol, 1.0 equiv), $Ni(cod)_2$ (0.01 mmol, 2.8 mg, 5 mol%), PCy_3 (0.02 mmol, 5.6 mg, 10 mol%), and zinc powder (0.8 mmol, 52.4 mg, 4.0 equiv) in 2 mL EtOH, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. The organic layers was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE : EtOAc = 200 : 1) to give **11**.



Ethyl (E)-3,3-difluoro-7-phenylhept-4-enoate (11)

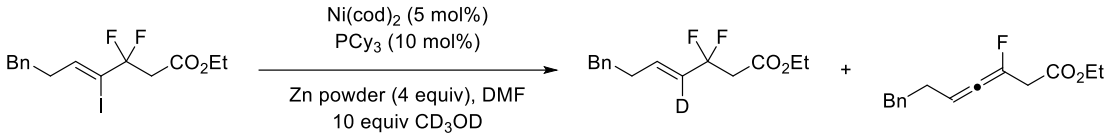
Prepared according to the procedure **6.3**. Flash column chromatography (eluent: PE/EA = 200:1) to afford **11** as a light-yellow oil (44.5 mg, 83%, 0.2 mmol scale). R_f = 0.4 (PE/EA = 20:1), by staining with potassium permanganate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.17 (m, 3H), 6.22 – 6.14 (m, 1H), 5.80 – 5.70 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.96 (t, *J* = 14.2 Hz, 2H), 2.74 (t, *J* = 8.0 Hz,2H), 2.48 – 2.40 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.75 (t, *J* = 7.1 Hz), 141.01, 135.80 (t, *J* = 9.1 Hz), 128.45, 128.40, 126.11, 124.71 (t, *J* = 25.8 Hz), 118.15 (t, *J* = 241.4 Hz), 61.16, 43.39 (t, *J* =29.8 Hz), 34.79, 33.55, 14.11.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.71 - -91.82 (m).

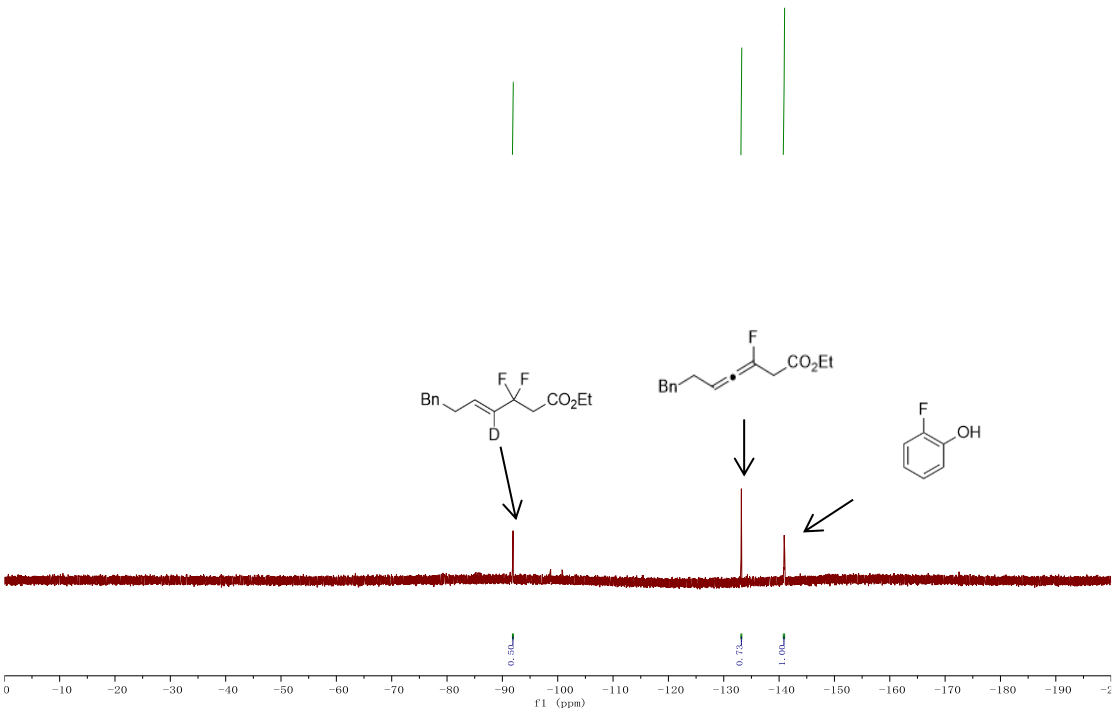
HRMS (ESI) *m/z* calcd for $C_{15}H_{18}F_2O_2Na$ [$(M+Na)^+$]: 291.1173, found: 291.1167.



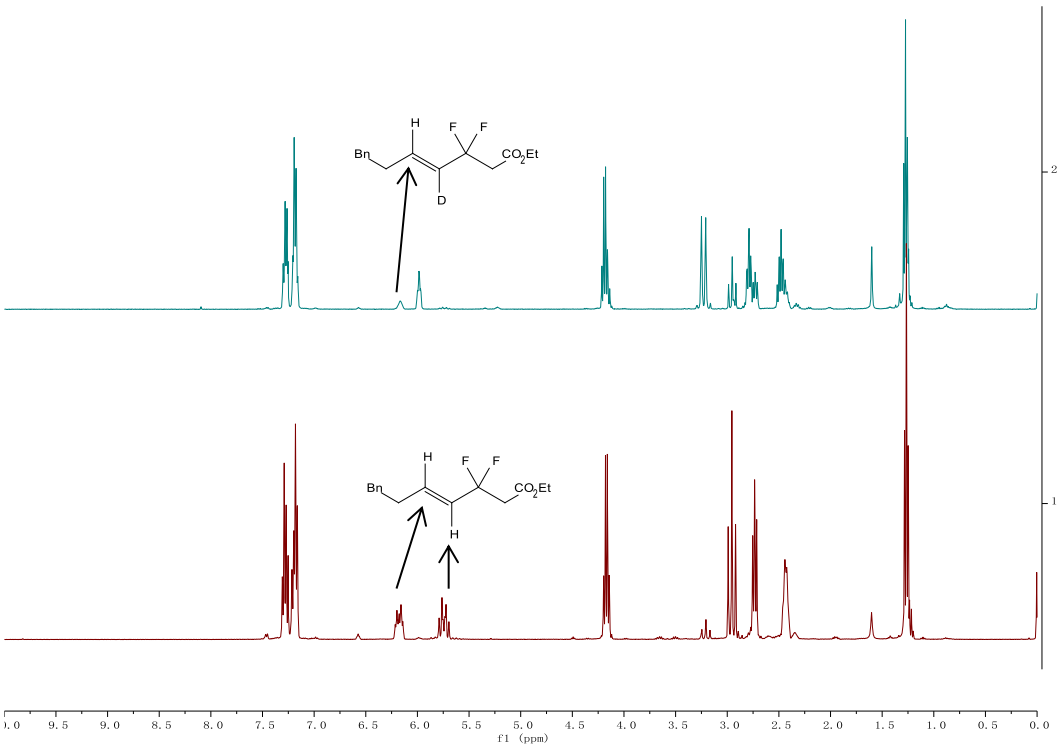
1 **11-D** **2**

To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.2 mmol, 1.0 equiv), $Ni(cod)_2$ (0.01 mmol, 2.8 mg, 5 mol%), PCy_3 (0.02 mmol, 5.6 mg, 10 mol%), CD_3OD (2 mmol, 81.2 μL, 10 equiv) and zinc powder (0.8 mmol, 52.4 mg, 4.0 equiv) in 2 mL DMF under a nitrogen atmosphere, and the mixture reacts for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. The yield of **11-D** (25%) and **2** (73%) was determined by NMR (by adding 2-hydroxyfluorobenzene (0.2 mmol, 18.2 μL) as internal standard).

Note: The polarities of **2** and **11-D** are so similar that they are difficult to separate.

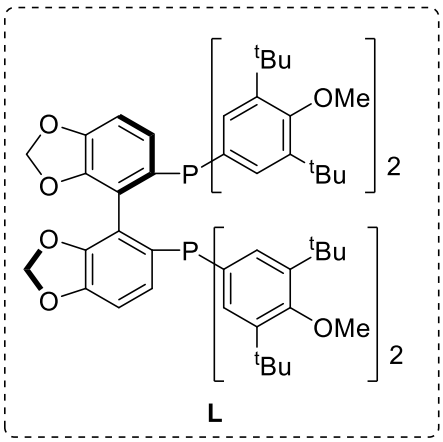


Picture 2: Fluorometric yield of **11-D** and **2**

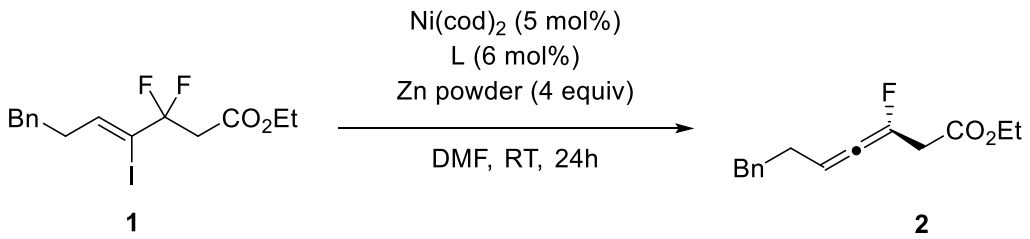


Picture 3: Comparison of hydrogen spectra between **11** and **11-D**

6.4 Asymmetric synthesis of fluorinated allenes



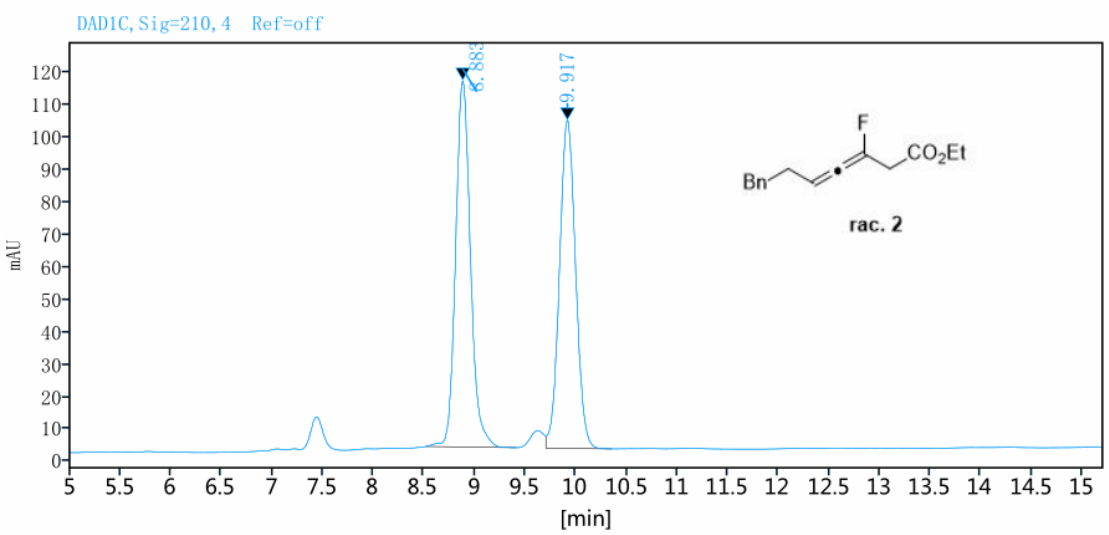
L



1 **2**

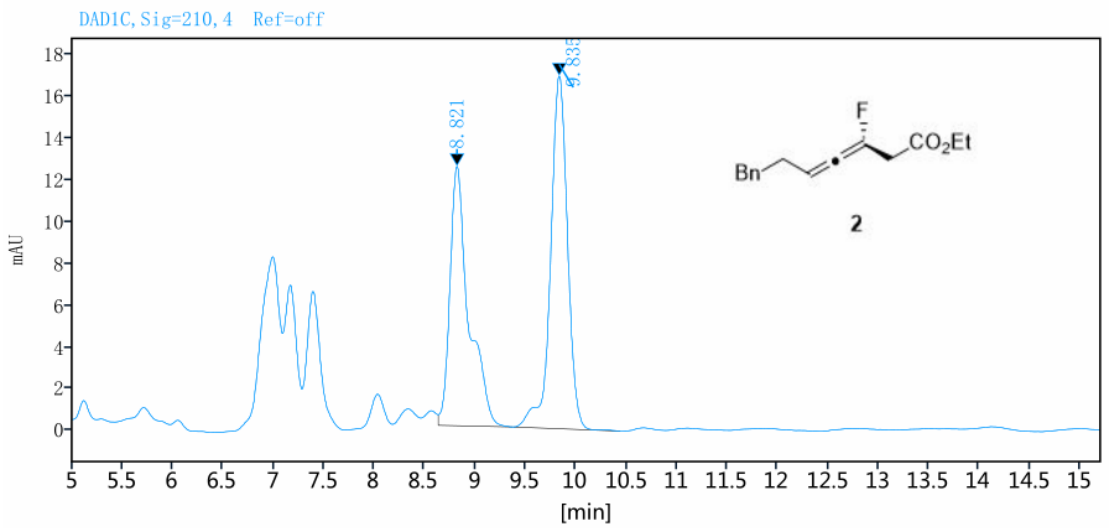
To an oven-dried tube equipped with a magnetic stirring bar, dissolve **1** (0.1 mmol, 39.4 mg, 1.0 equiv), $Ni(cod)_2$ (0.005 mmol, 1.4 mg, 5 mol%), **L** (0.006 mmol, 7.1 mg, 6 mol%), zinc powder (0.4 mmol, 26.2 mg, 4.0 equiv) in 1 mL DMF under a nitrogen atmosphere, and the mixture was run for one day at room temperature. Then the mixture was passed through a short pad of silica gel with EtOAc. Yield of the product **2** was determined by GC (n-tetradecane as internal standard). The ee (10%) was determined by HPLC analysis (IC column, λ = 210 nm, n-hexane/isopropanol = 99.0/1.0, flow rate = 0.5 mL/min): t_R(minor) = 8.8 min, t_R(major) = 9.8 min.

HPLC Data of 6.4



Signal: DAD1C,Sig=210,4 Ref=off

Time[min]	Type	Width[min]	Height	Area	Area%
8.883	MB m	0.1571	112.8479	1152.2817	50.6923
9.917	VB	0.6507	101.0219	1120.8079	49.3077



Signal: DAD1C,Sig=210,4 Ref=off

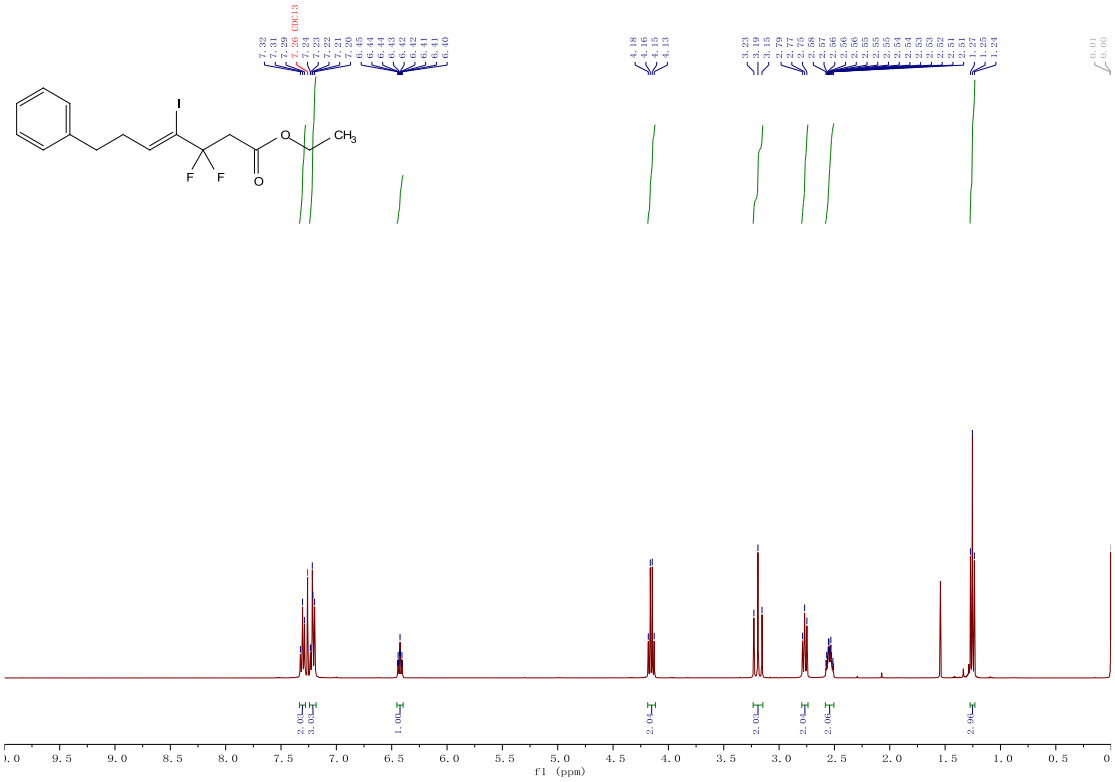
Time[min]	Type	Width[min]	Height	Area	Area%
8.821	VB	0.7367	12.4460	161.4073	44.9054
9.835	BB	1.0611	16.9245	198.0309	55.0946

7. References

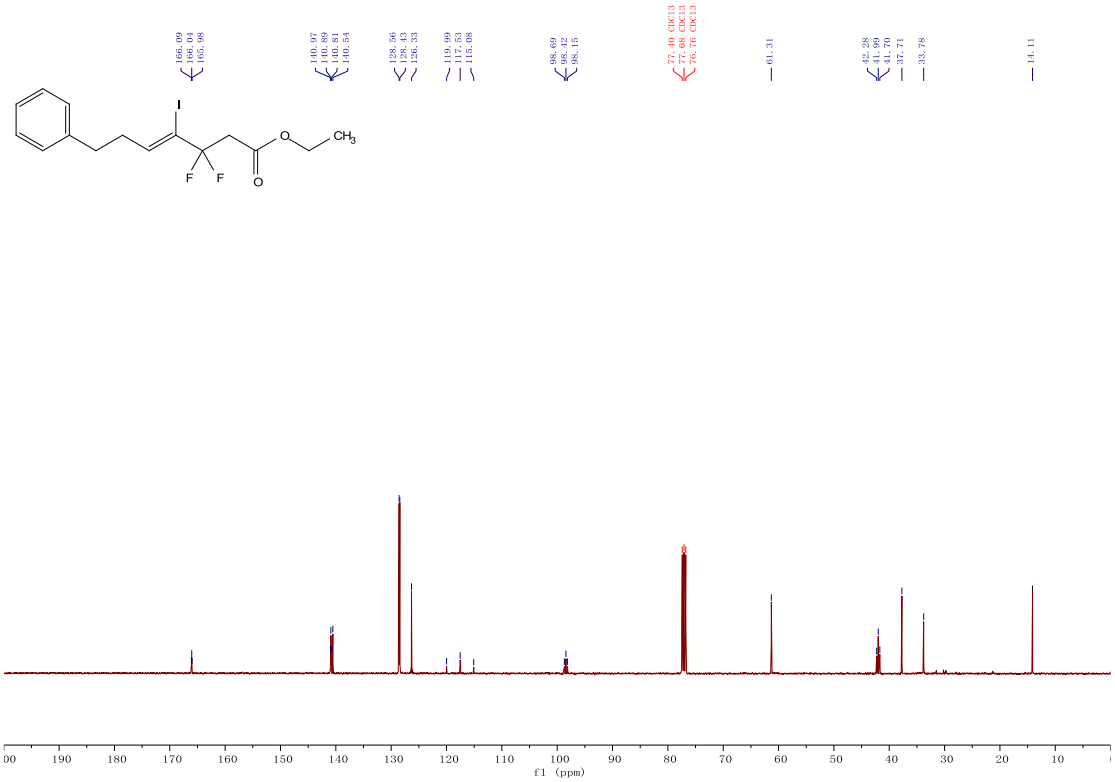
(1) Shang, Y.; Jie, X.; Jonnada, K.; Zafar, S. N.; Su, W., Dehydrogenative desaturation-relay via formation of multicenter-stabilized radical intermediates. *Nature Communications* **2017,** *8* (1).
(2) Kelly, C. B.; Mercadante, M. A.; Wiles, R. J.; Leadbeater, N. E., Oxidative esterification of aldehydes using a recyclable oxoammonium salt. *Org. Lett.* **2013,** *15 (9)*, 2222–2225.
(3) Takagi, T.; Okikawa, N.; Johnoshita, S.; Koyama, M.; Ando, A.; Kumadaki, I., *Synlett.* **1996,** *(1)*, 82-84.
(4) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y., Asymmetric dearomatizing spirolactonization of naphthols catalyzed by spirobiindane-based chiral hypervalent iodine species. *J Am Chem Soc* **2013,** *135* (11), 4558-4566.
(5) Weinstein, A. B.; Stahl, S. S., Reconciling the stereochemical course of nucleopalladation with the development of enantioselective wacker-type cyclizations. *Angew Chem Int Ed Engl* **2012,** *51* (46), 11505-11509.
(6) Liao, L.; An, R.; Li, H.; Xu, Y.; Wu, J. J.; Zhao, X., Catalytic Access to Functionalized Allylic gem-Difluorides via Fluorinative Meyer-Schuster-Like Rearrangement. *Angew Chem Int Ed Engl* **2020,** *59* (27), 11010-11019.

8. NMR Spectra

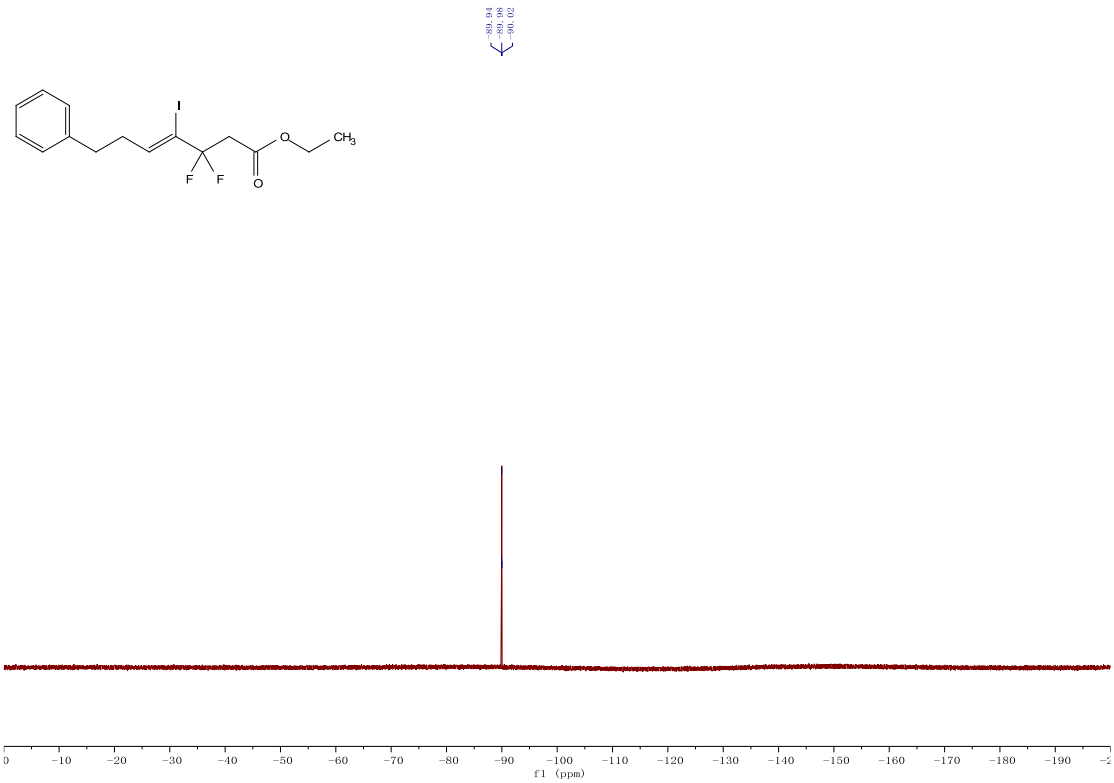
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**



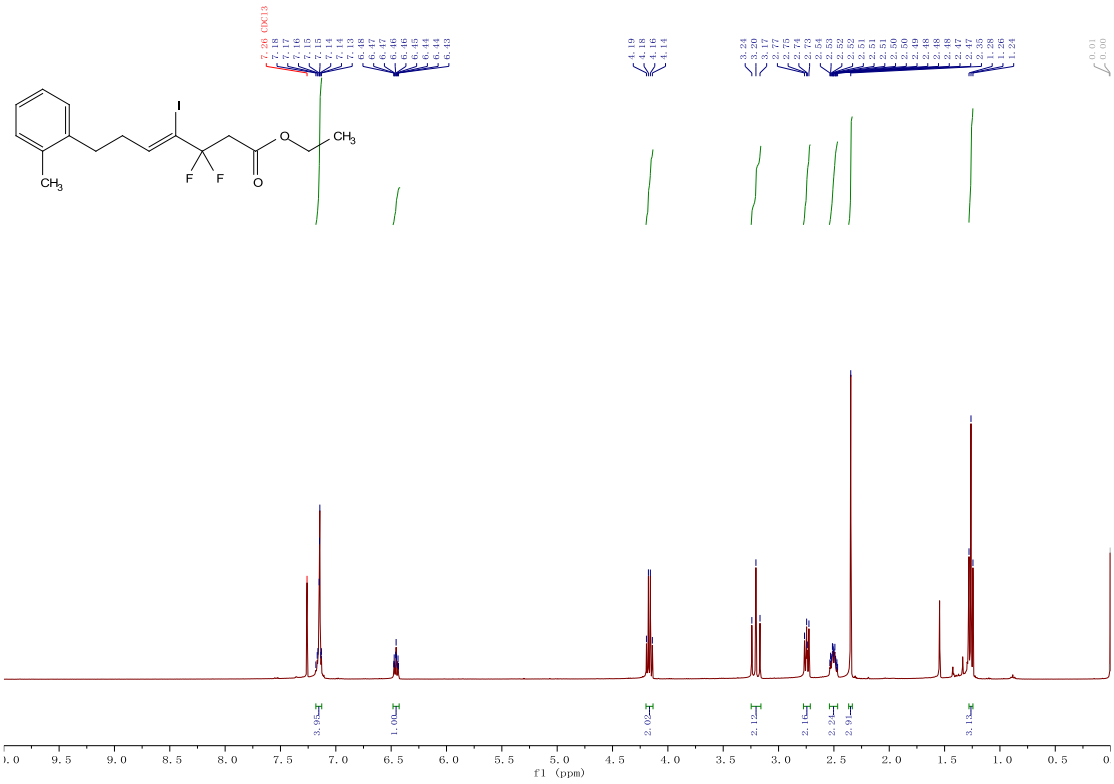
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **1**



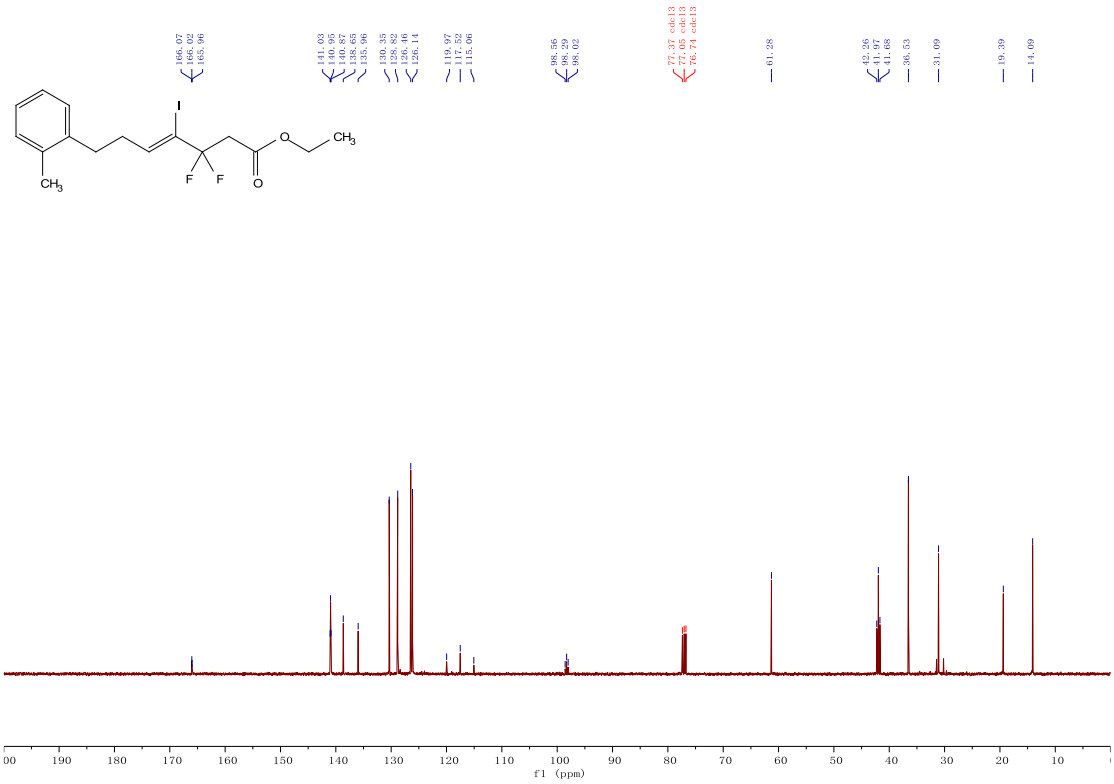
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1**



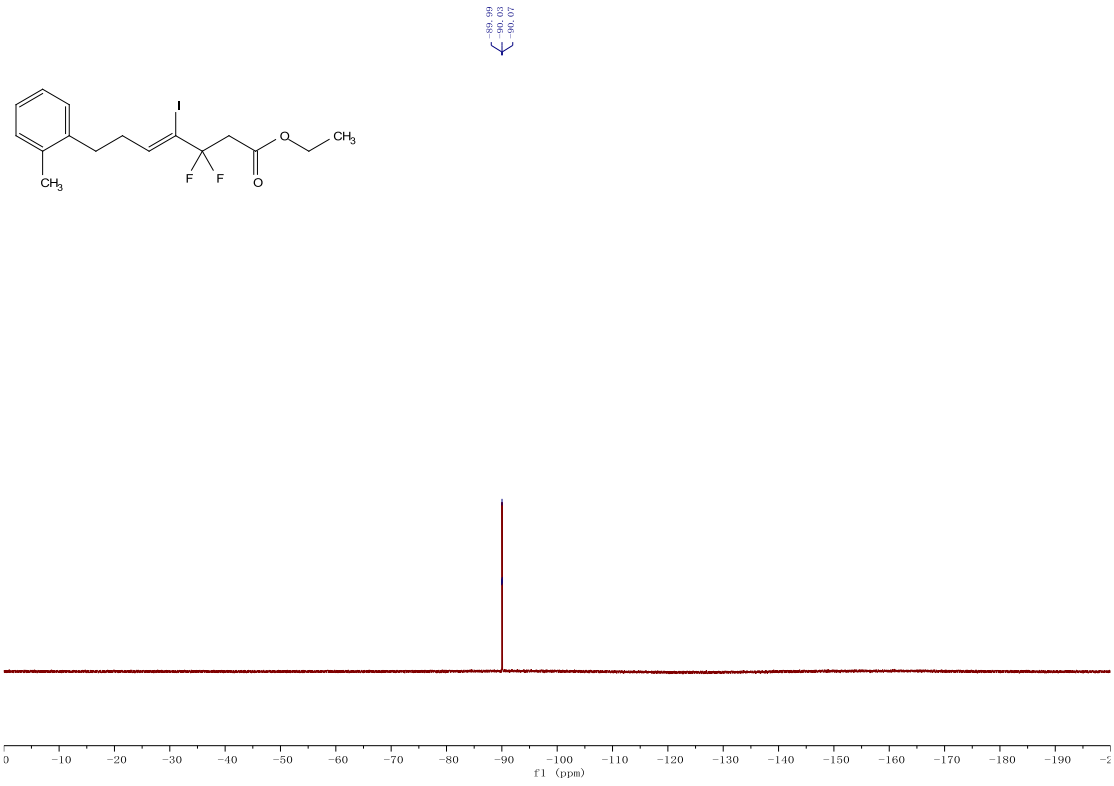
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



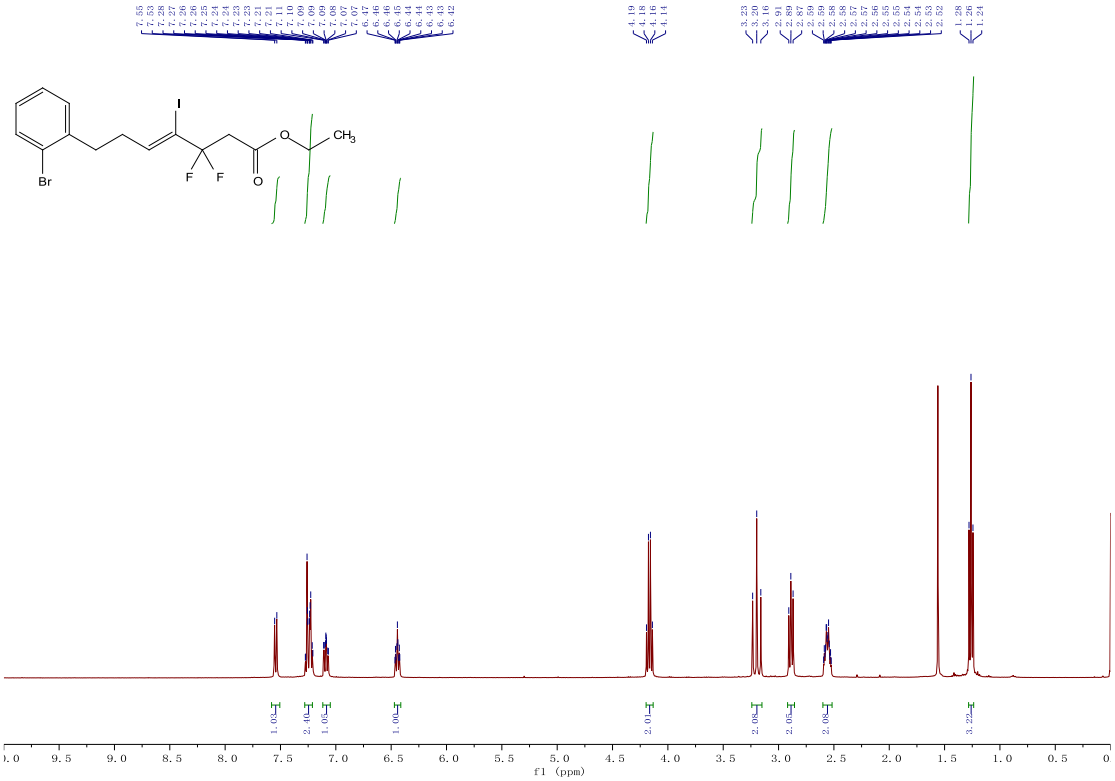
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3a**



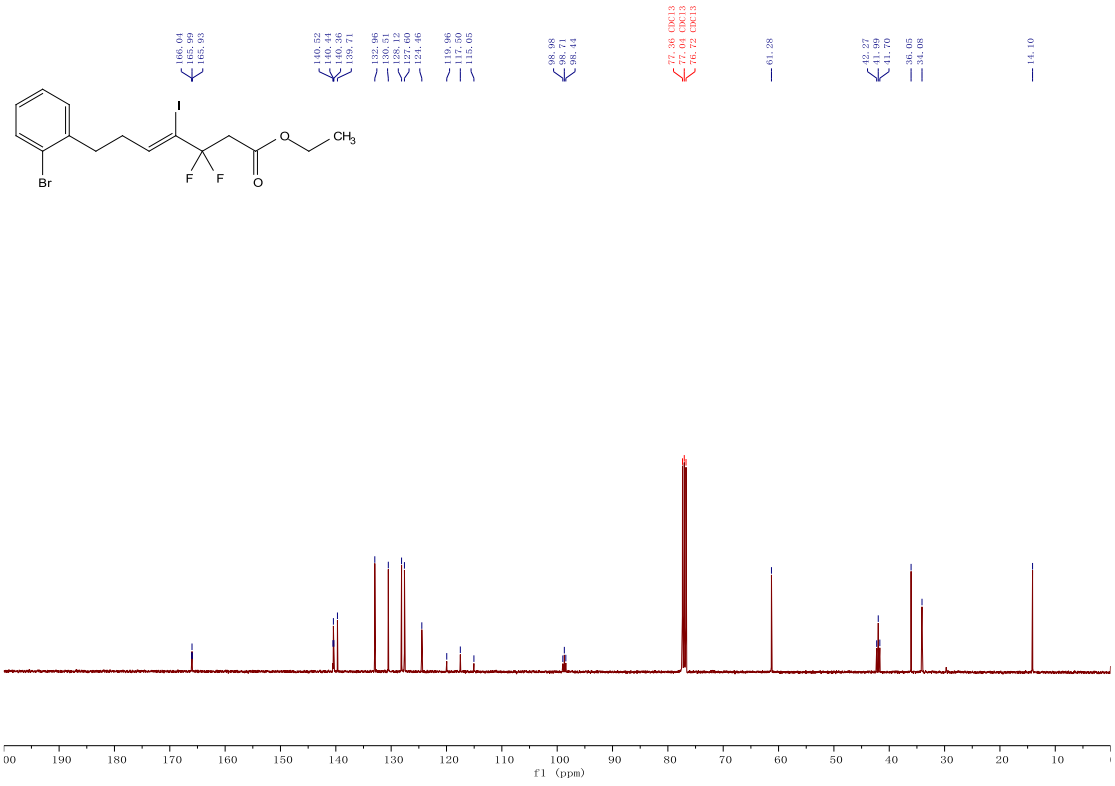
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3a**



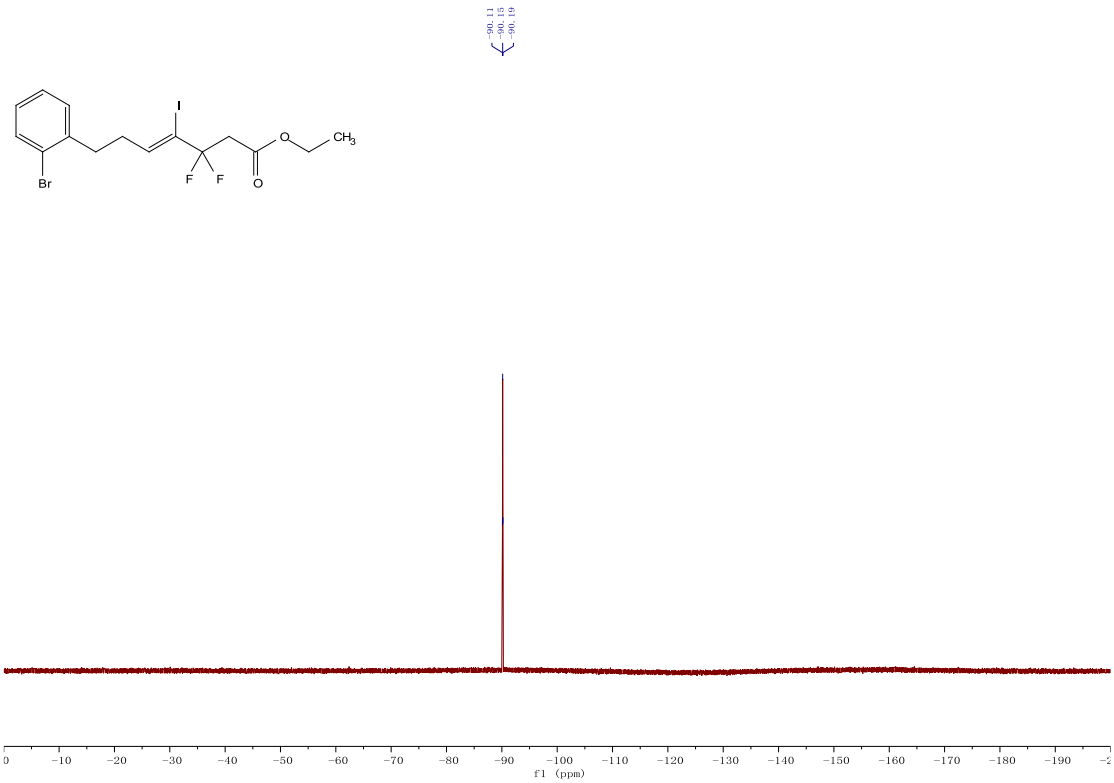
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



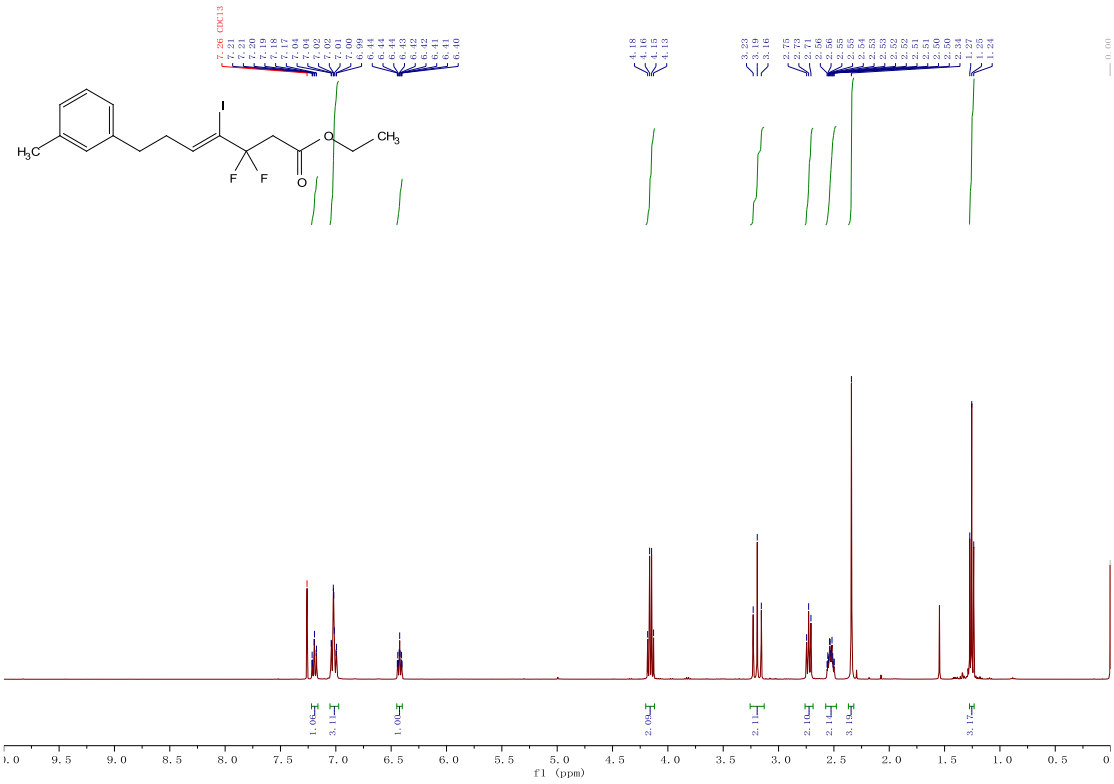
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3b**



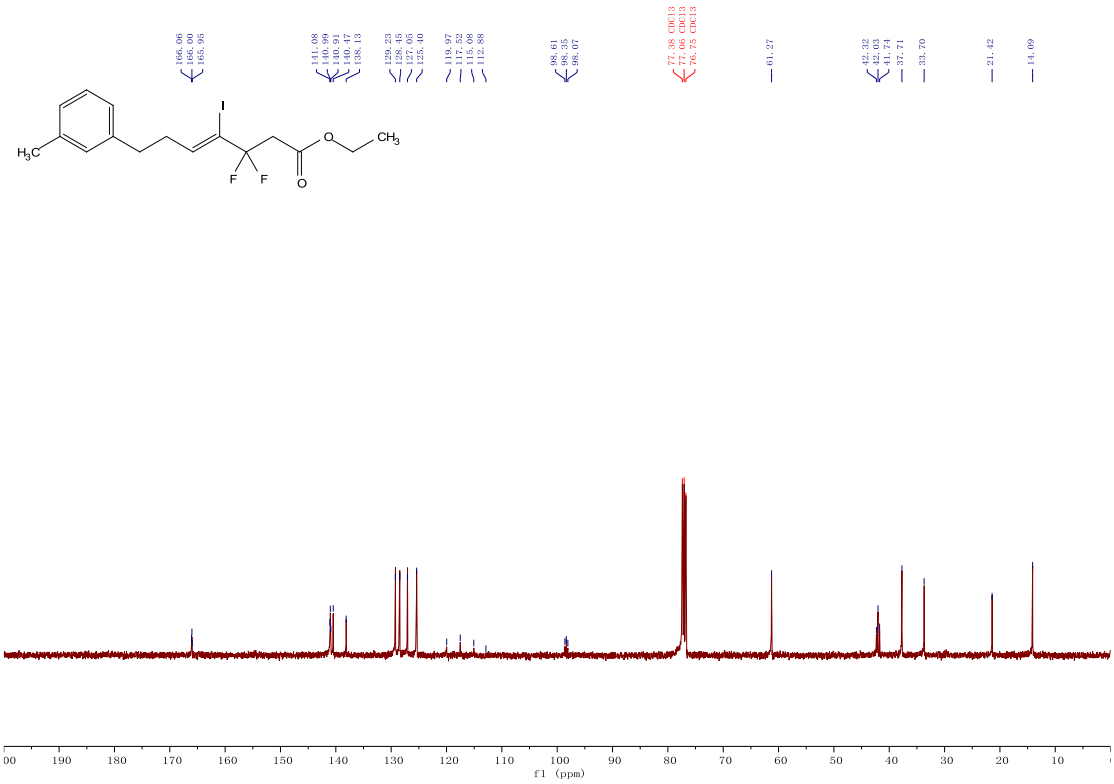
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3b**



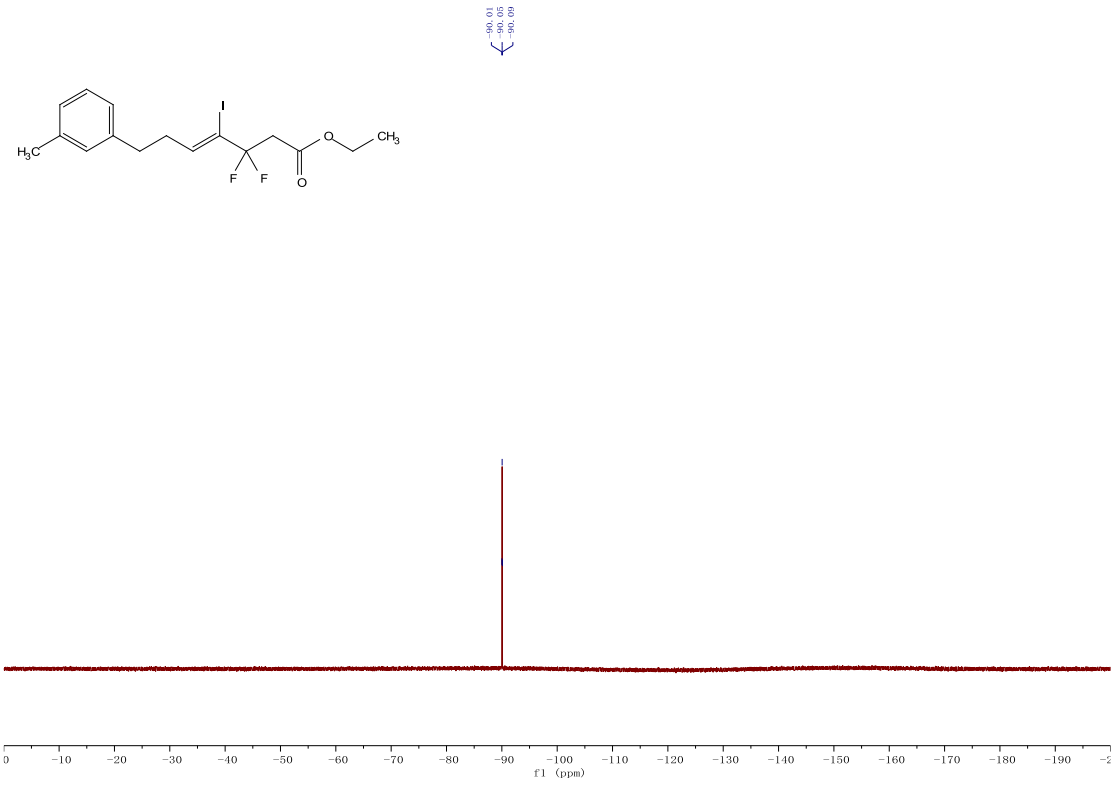
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



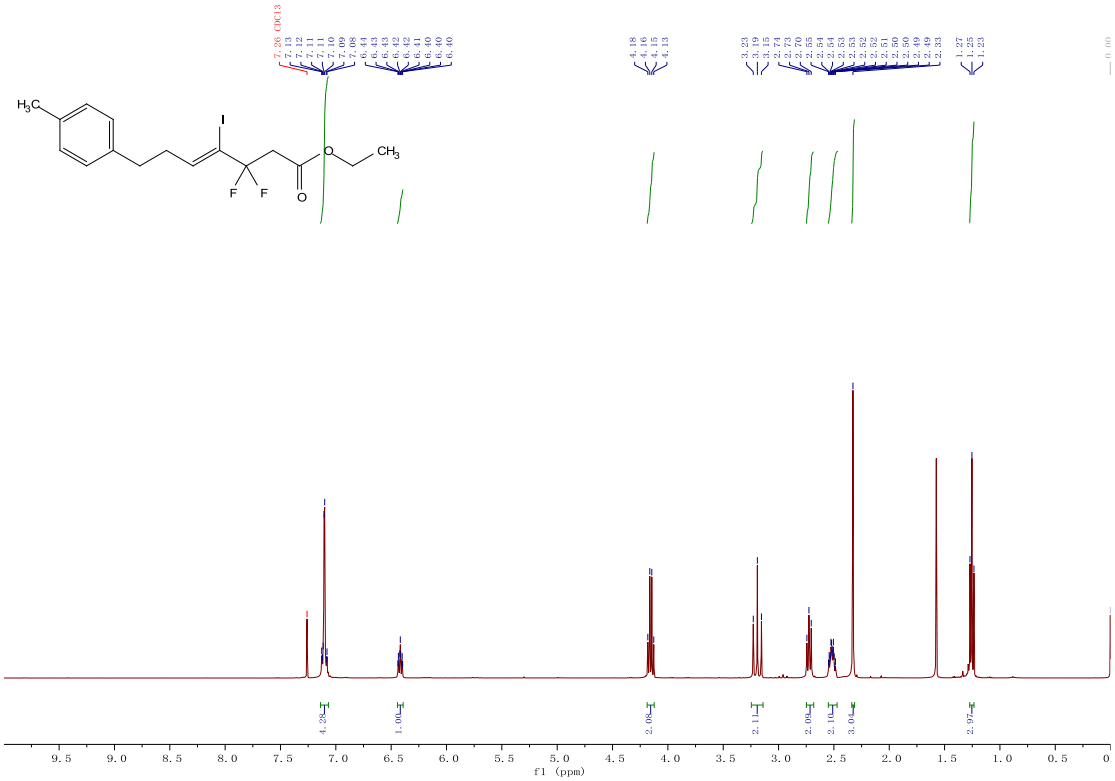
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3c**



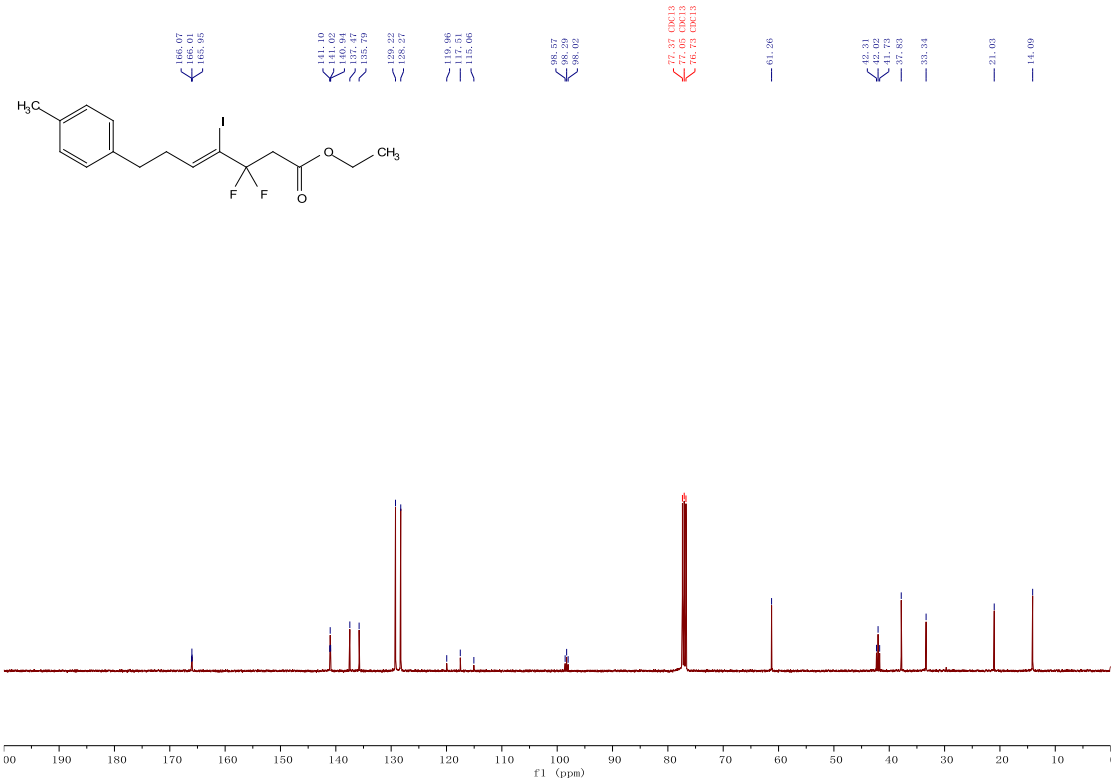
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3c**



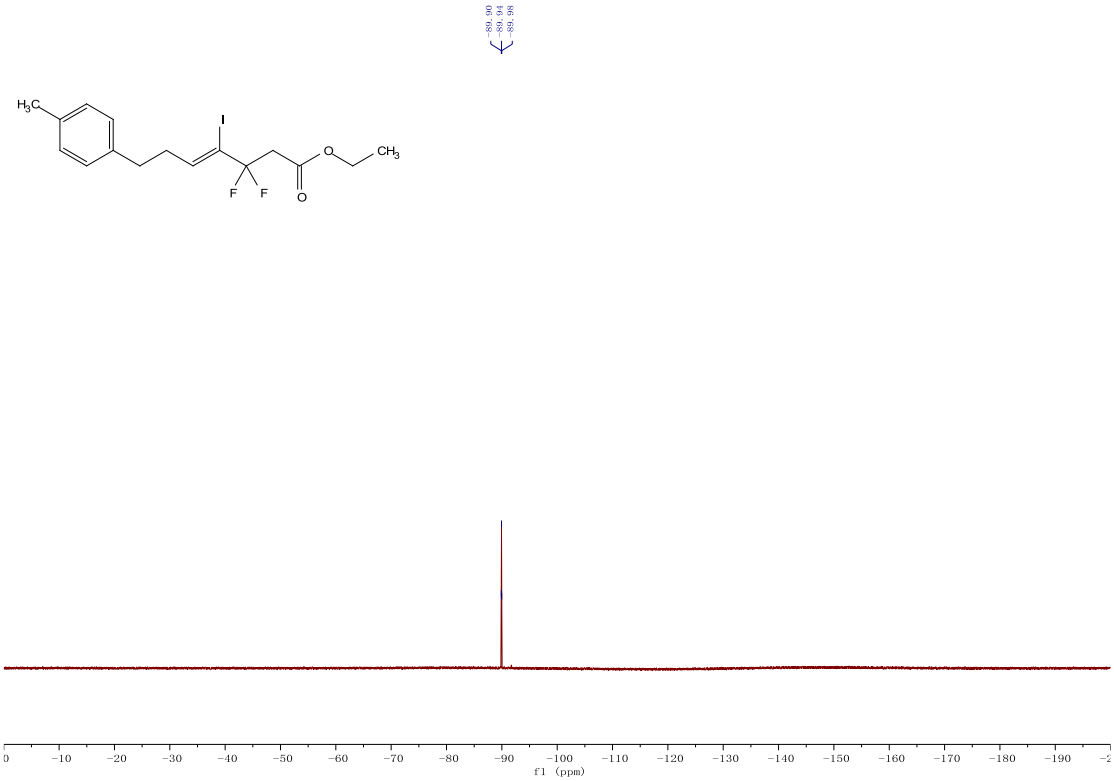
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



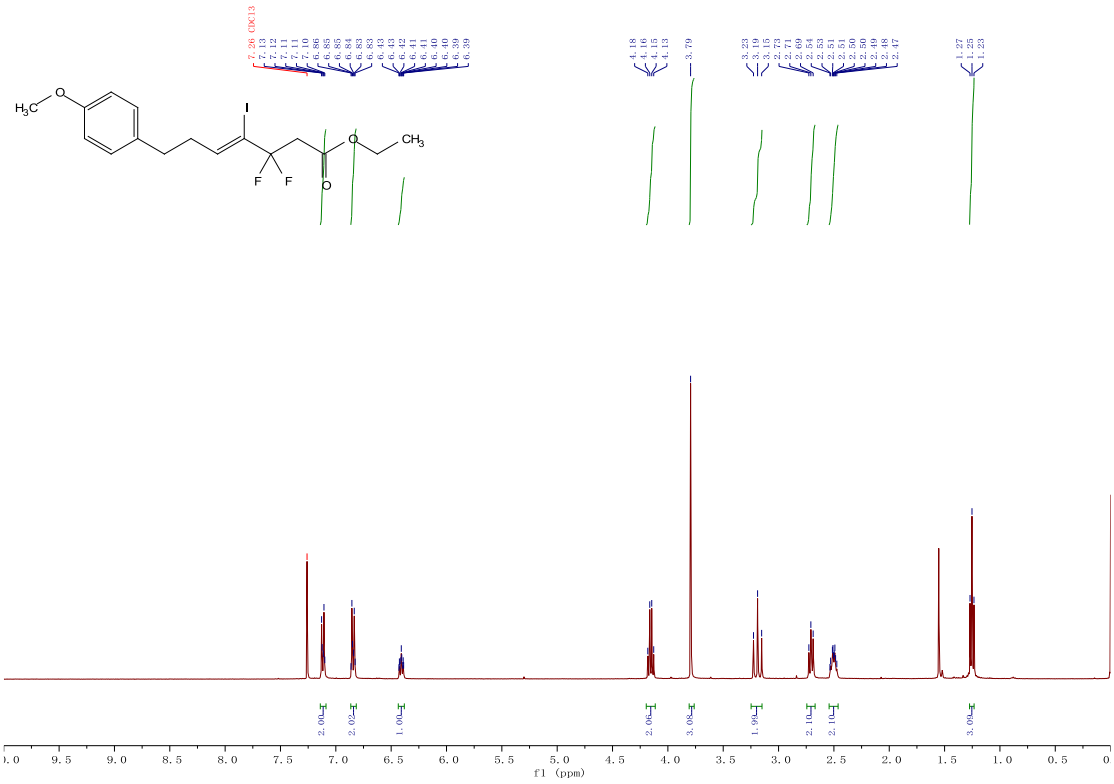
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3d**



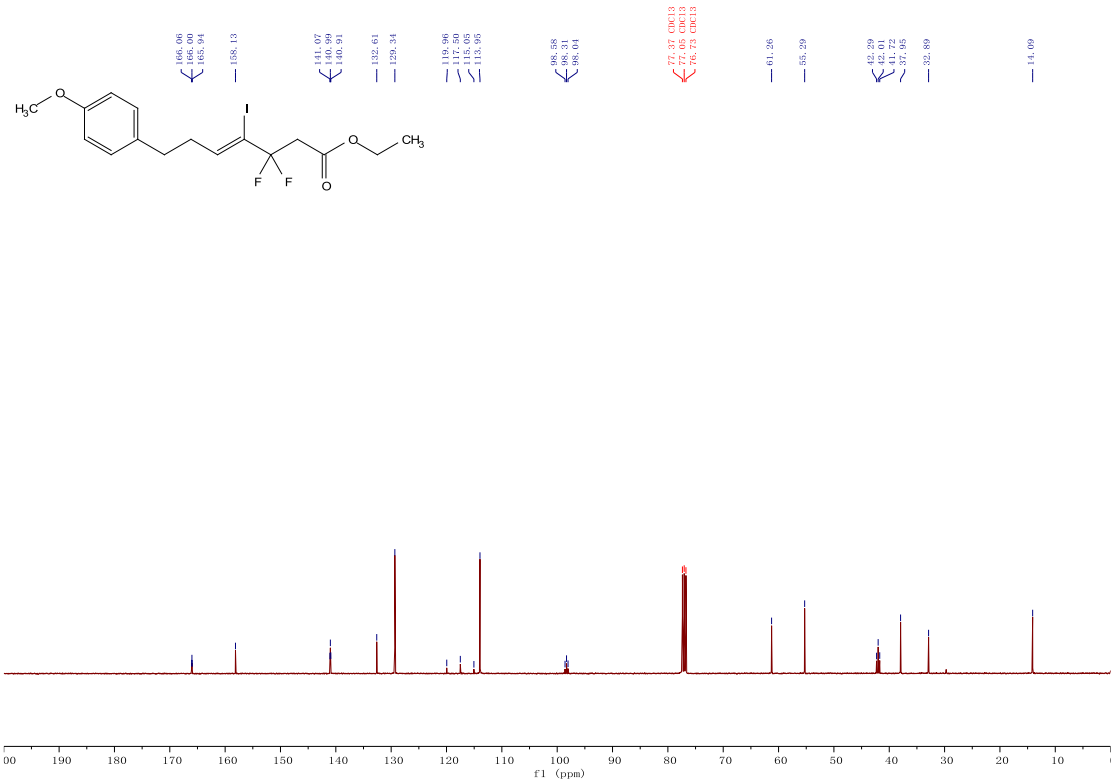
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3d**



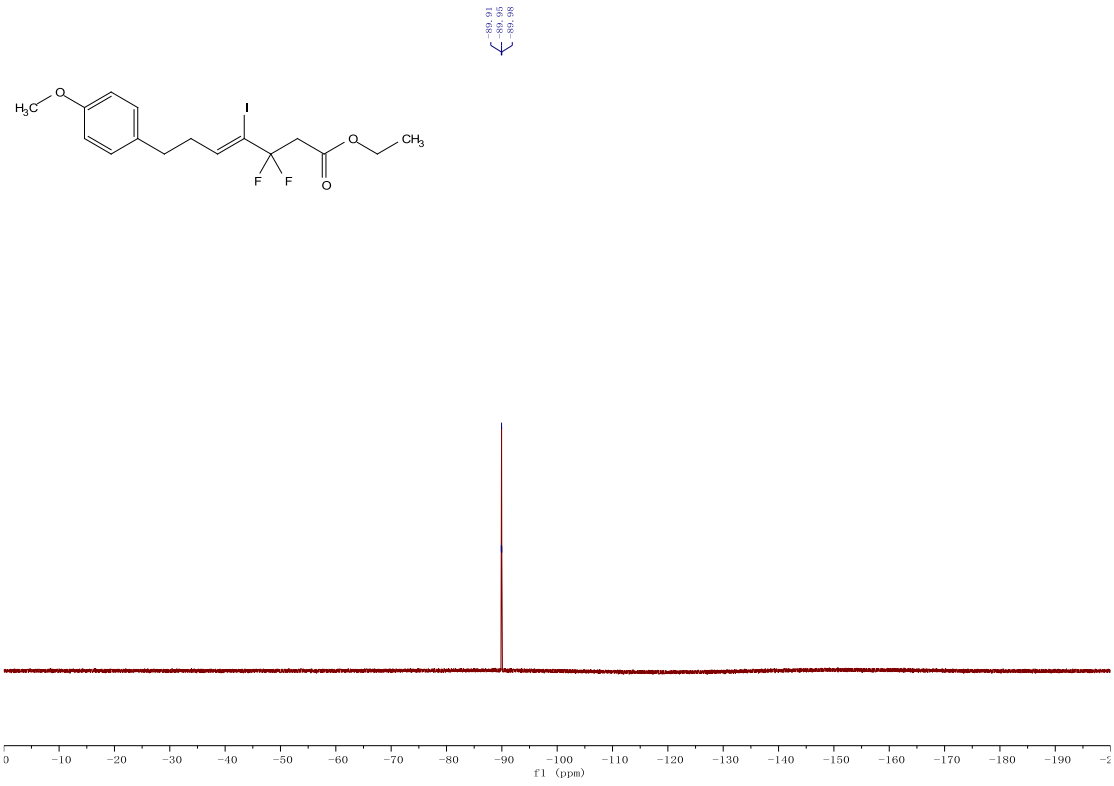
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



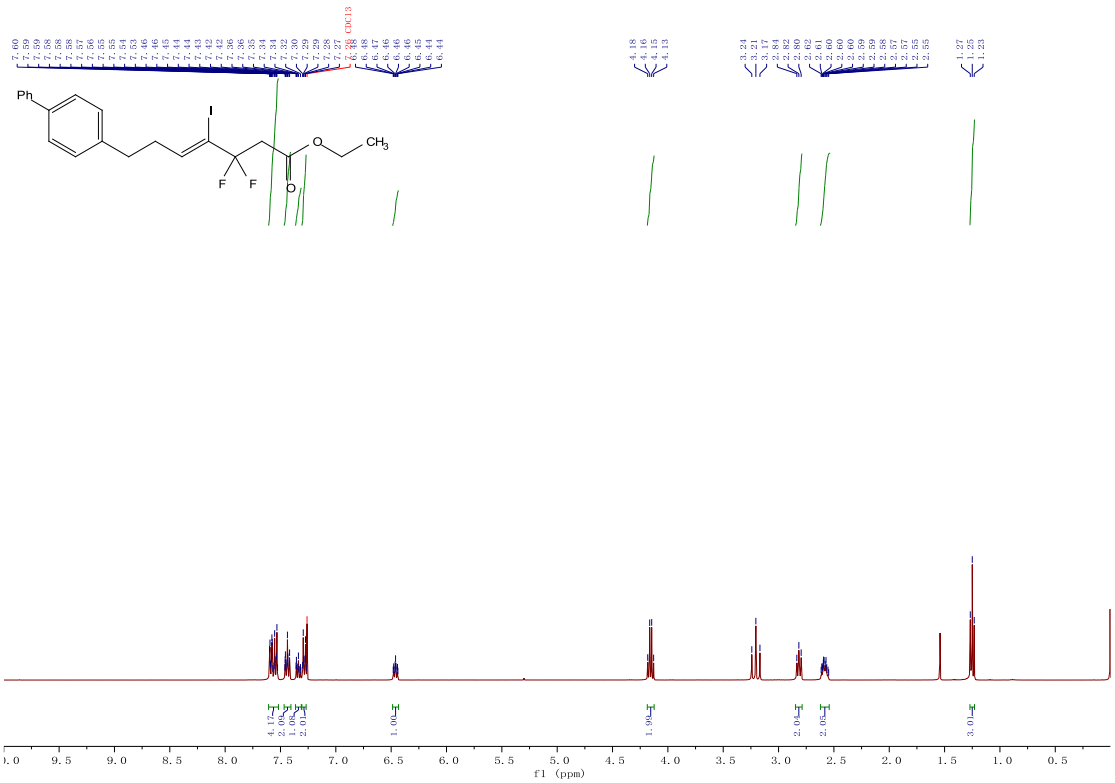
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3e**



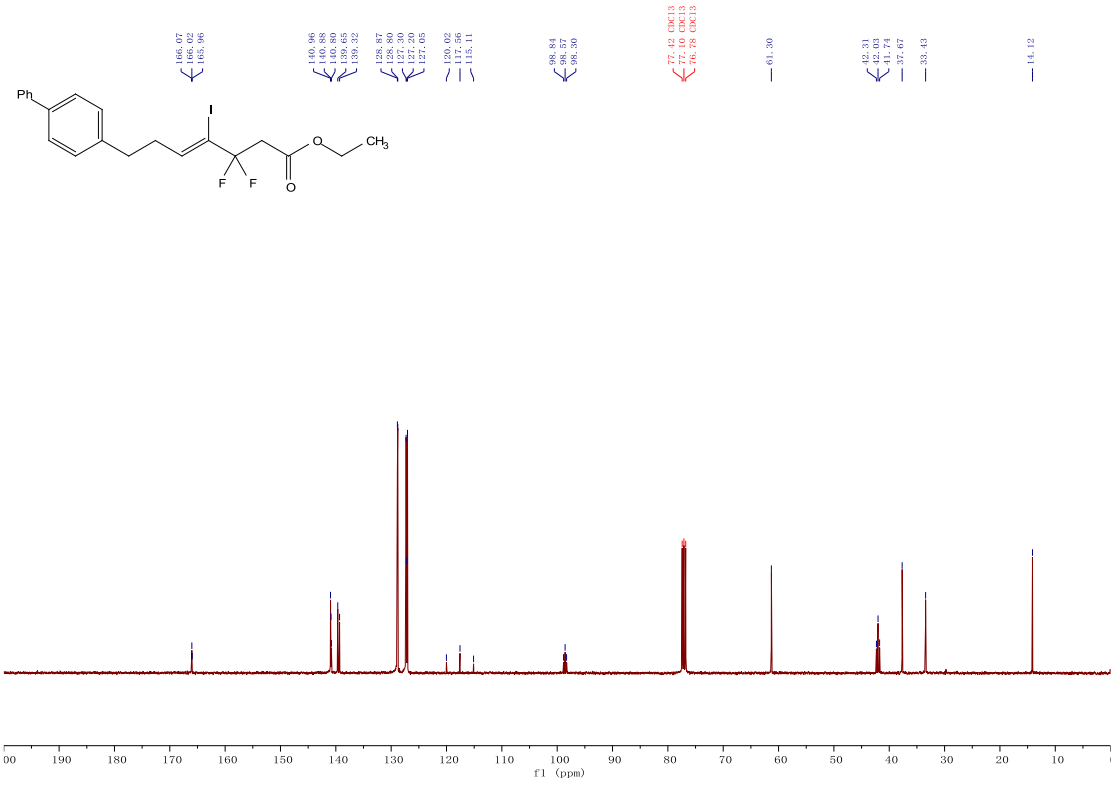
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3e**



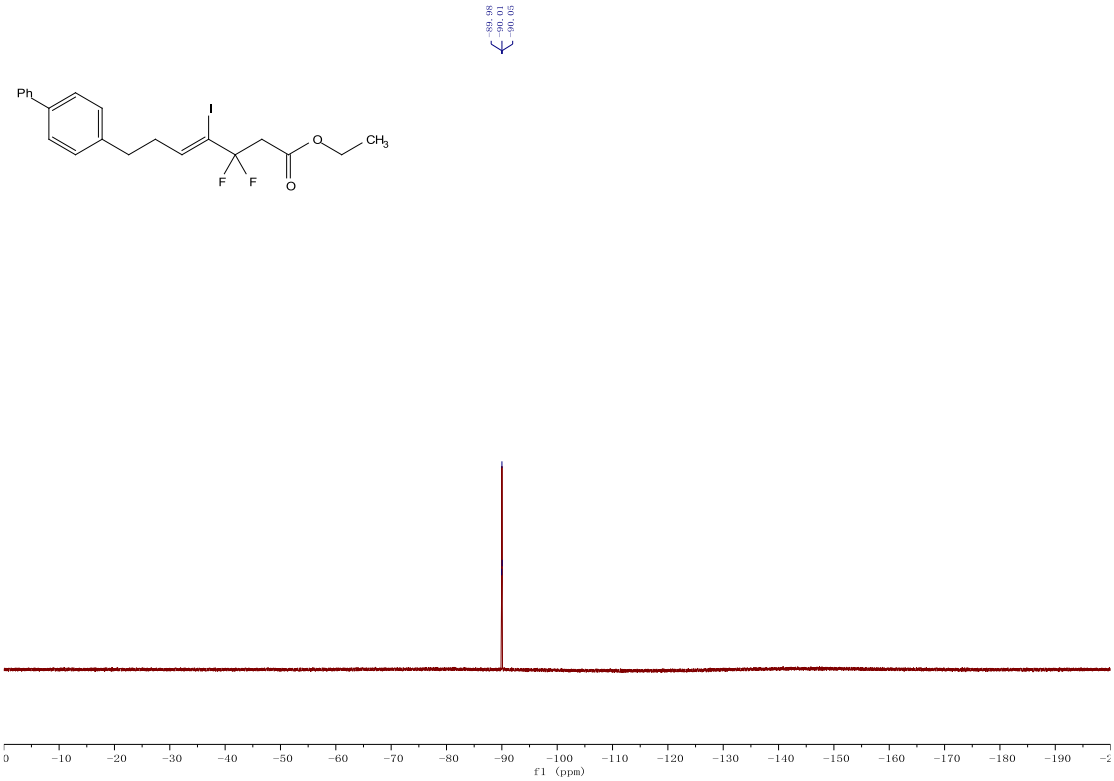
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**



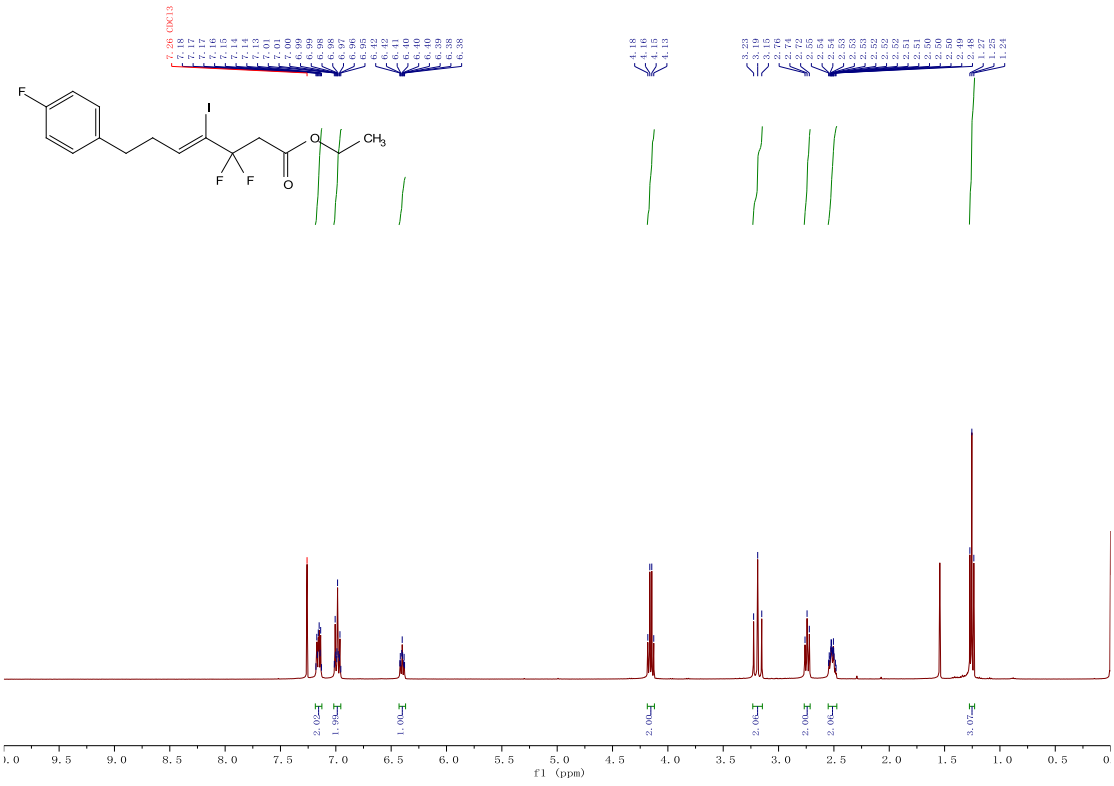
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3f**



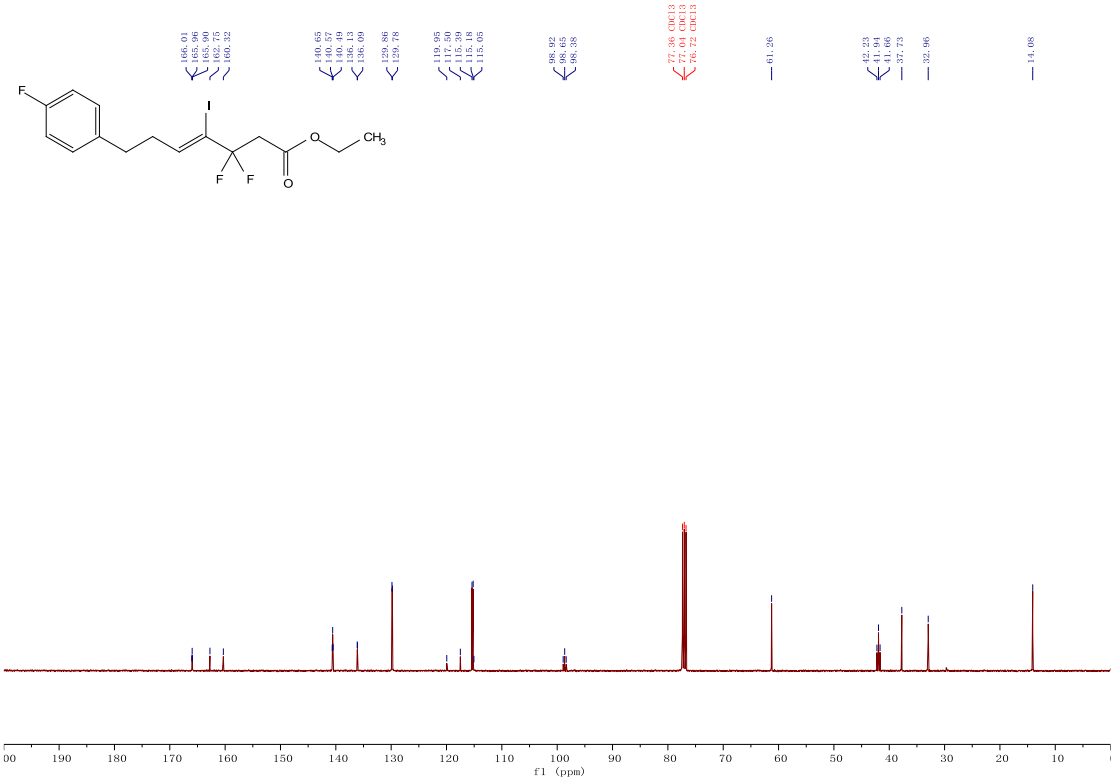
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3f**



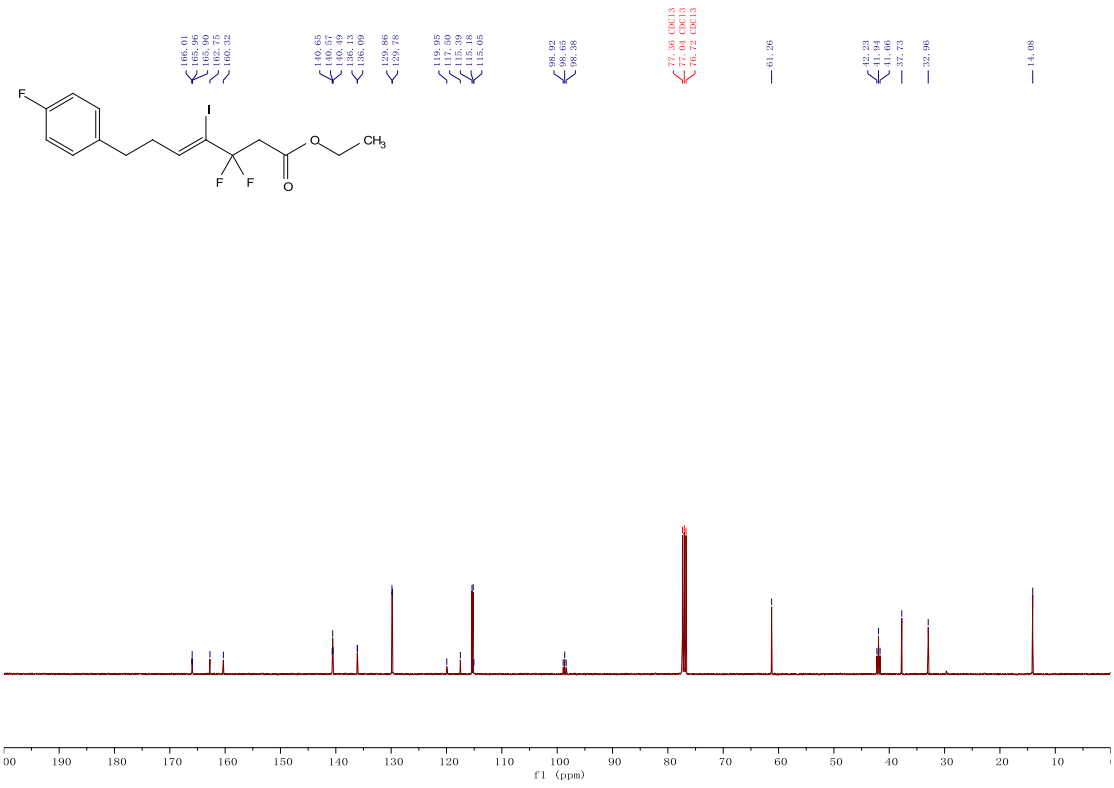
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



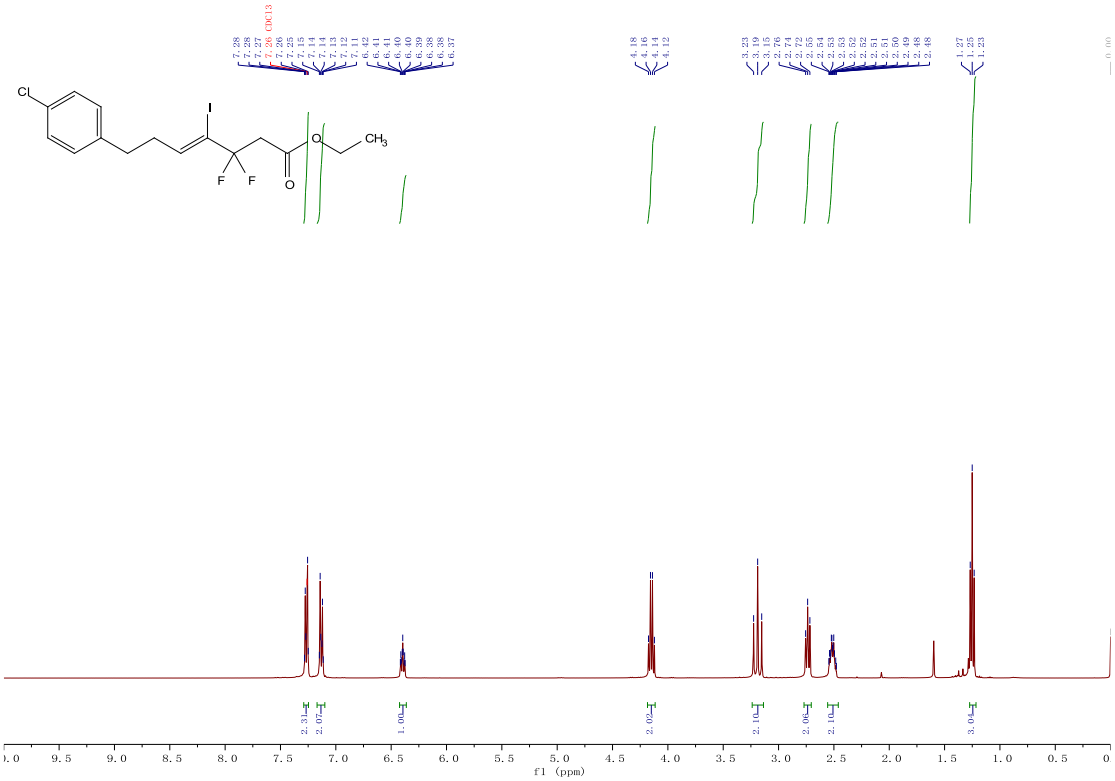
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3g**



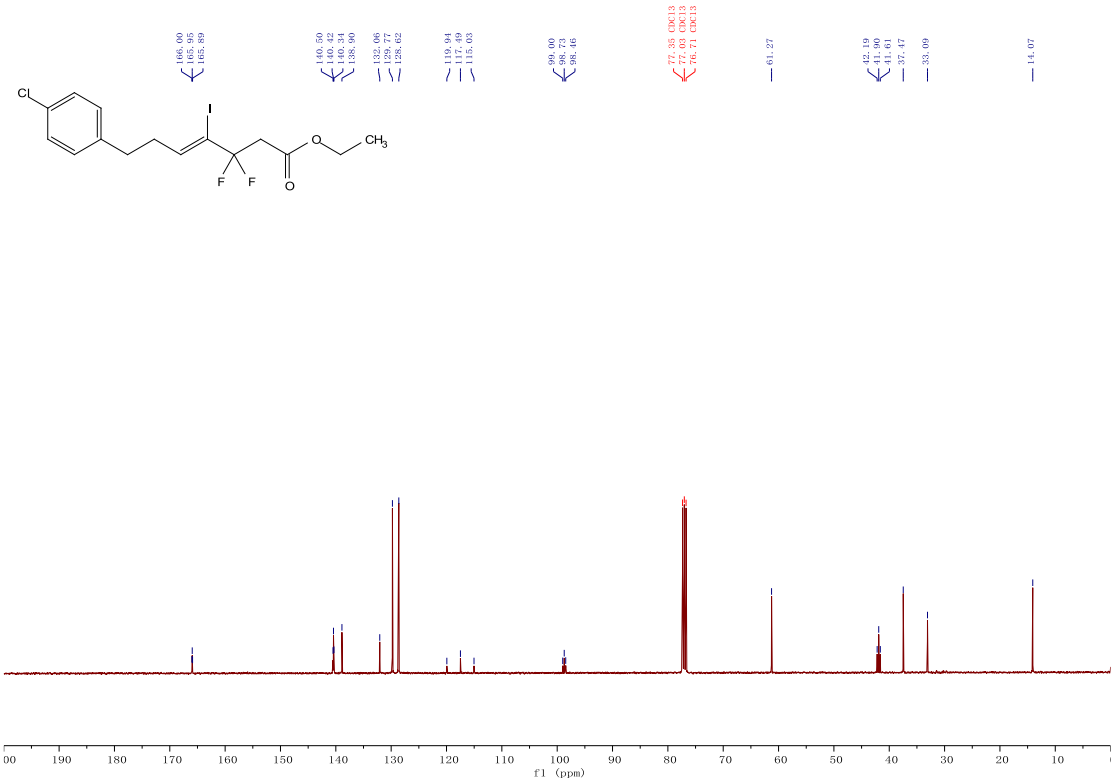
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3g**



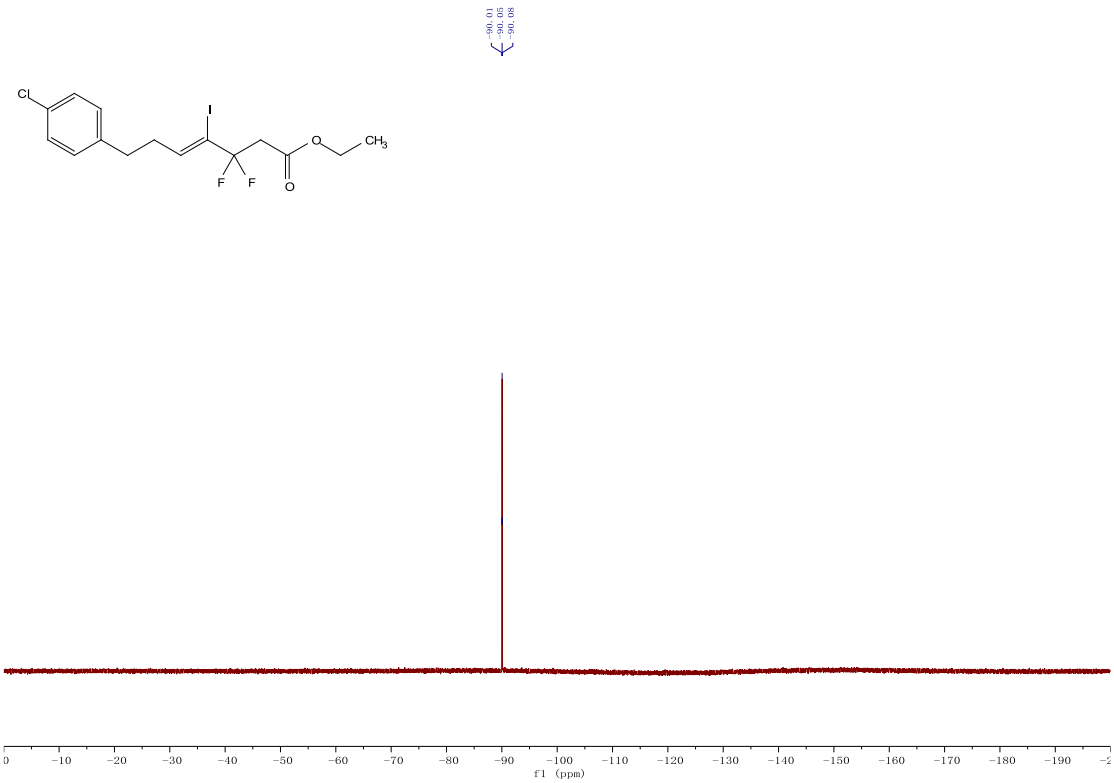
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



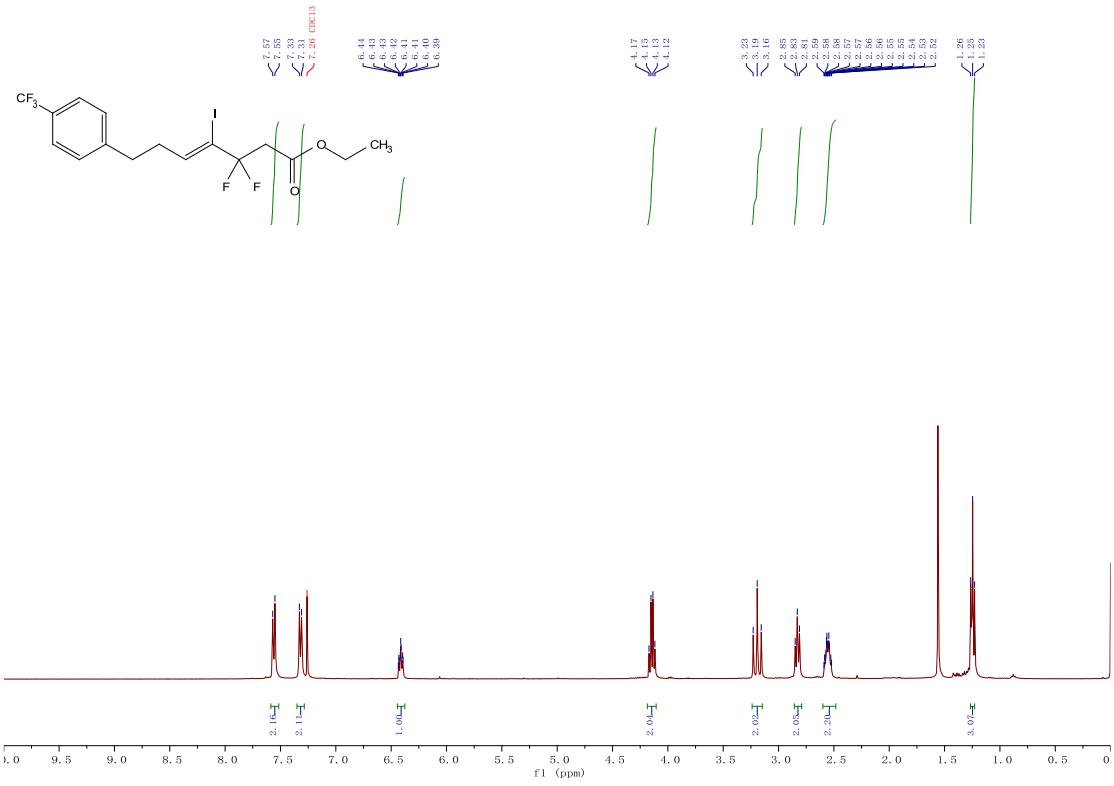
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**



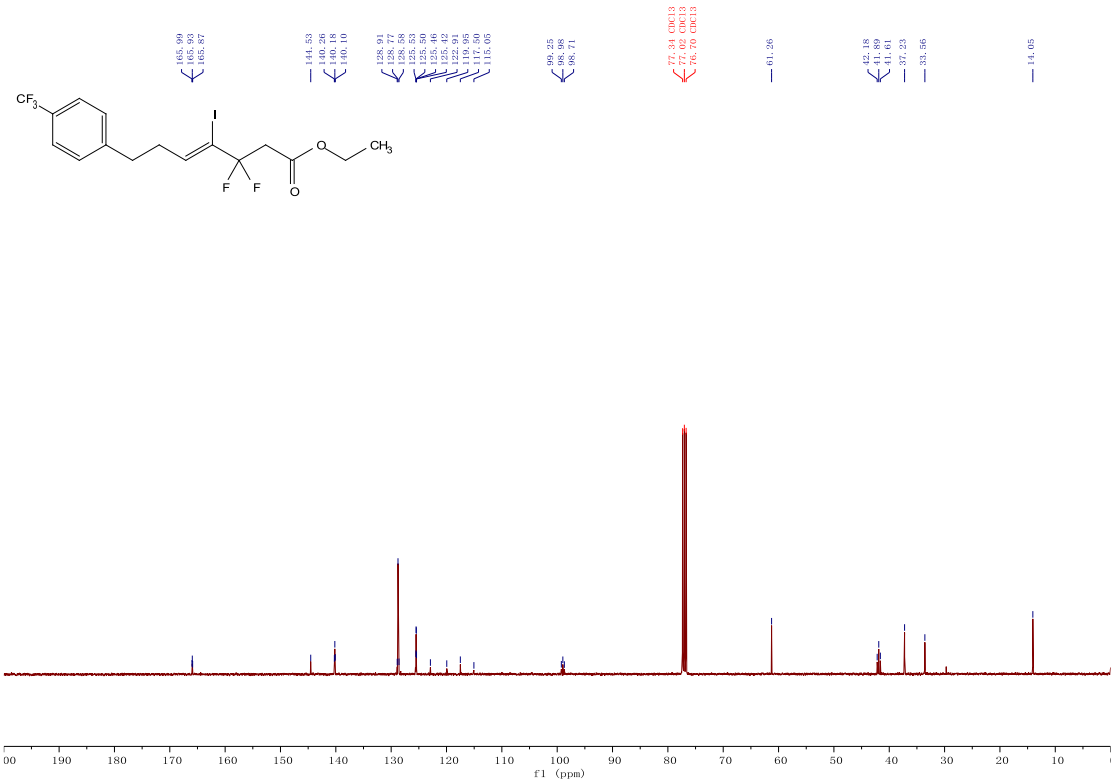
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3h**



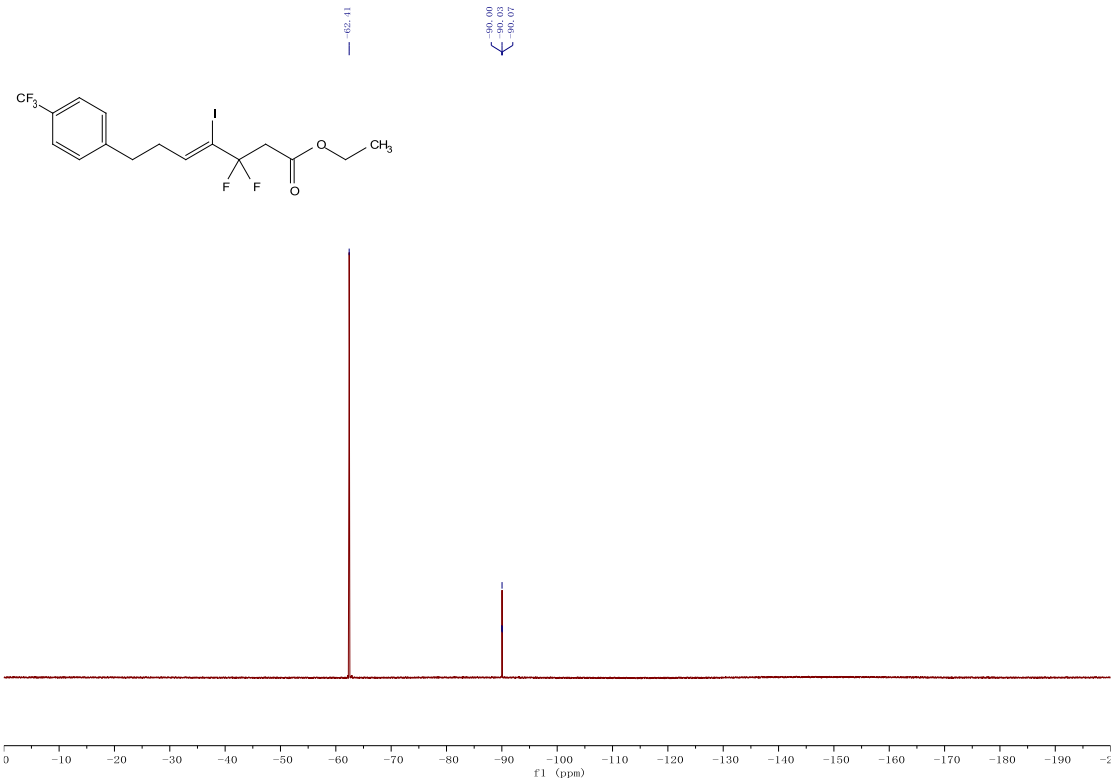
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



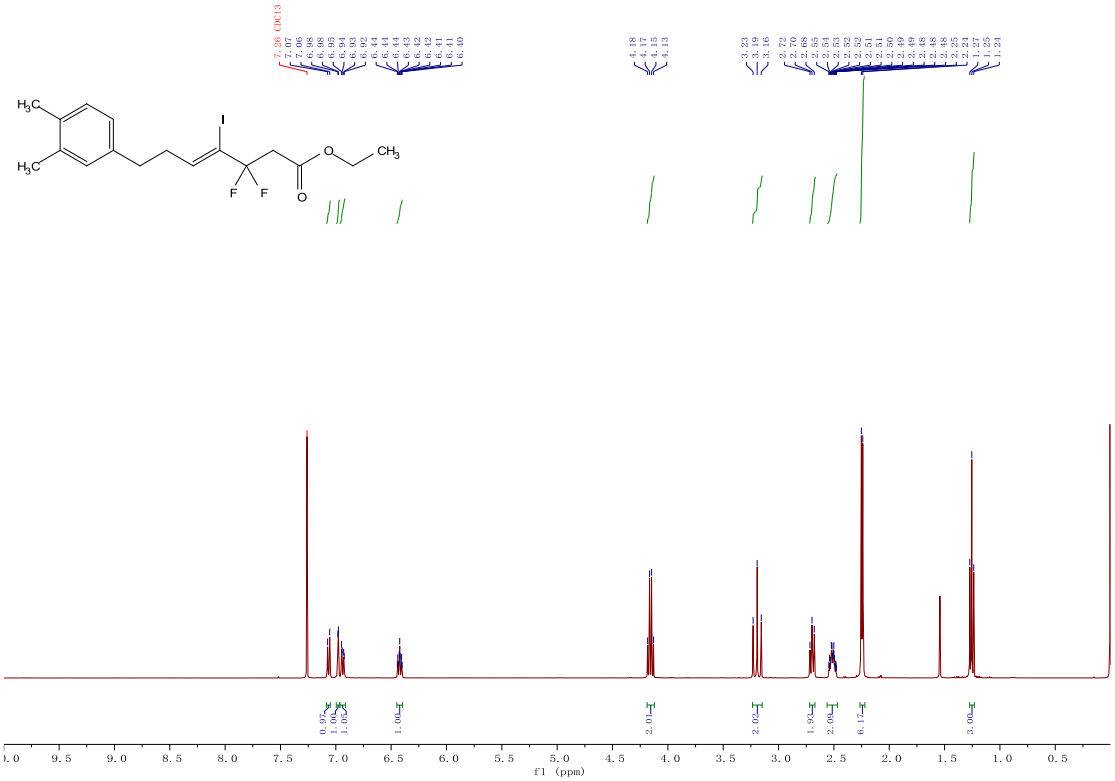
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**



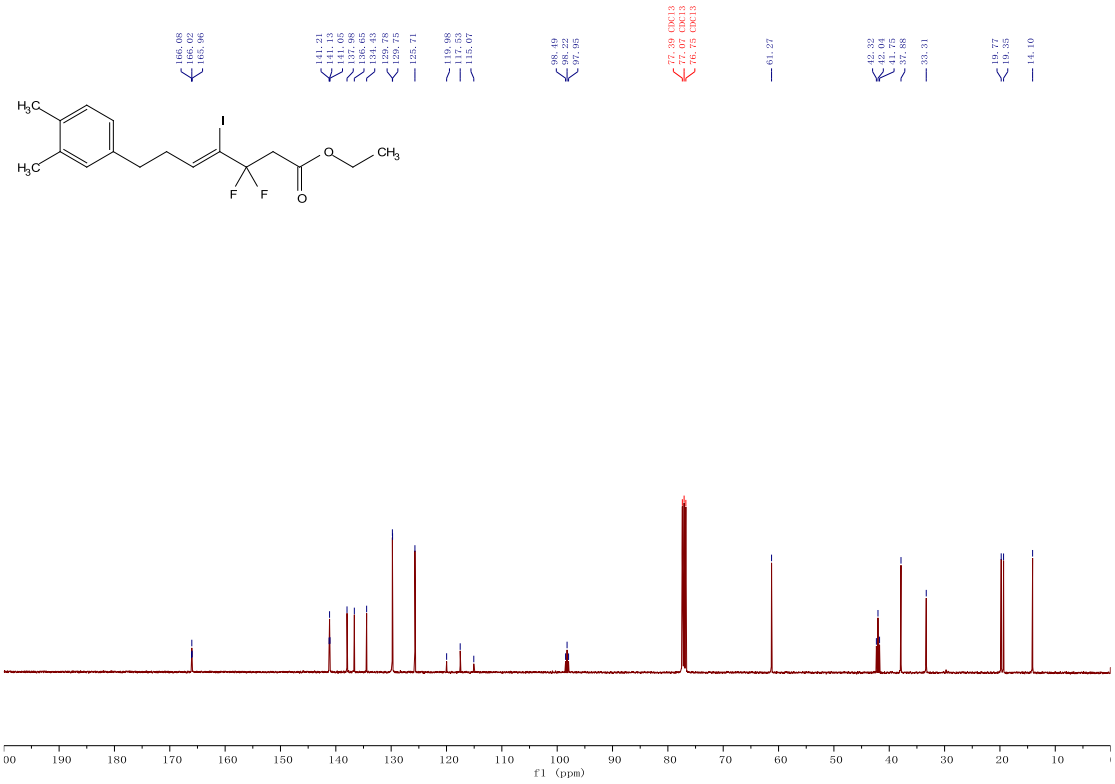
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3i**



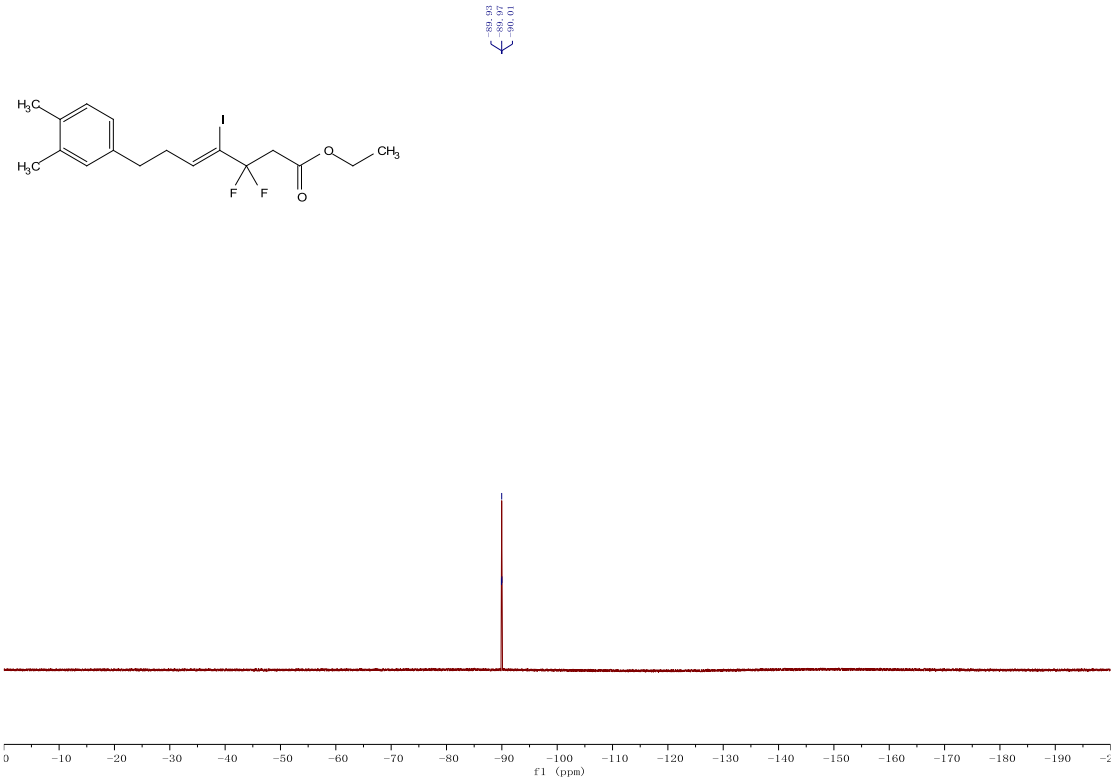
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



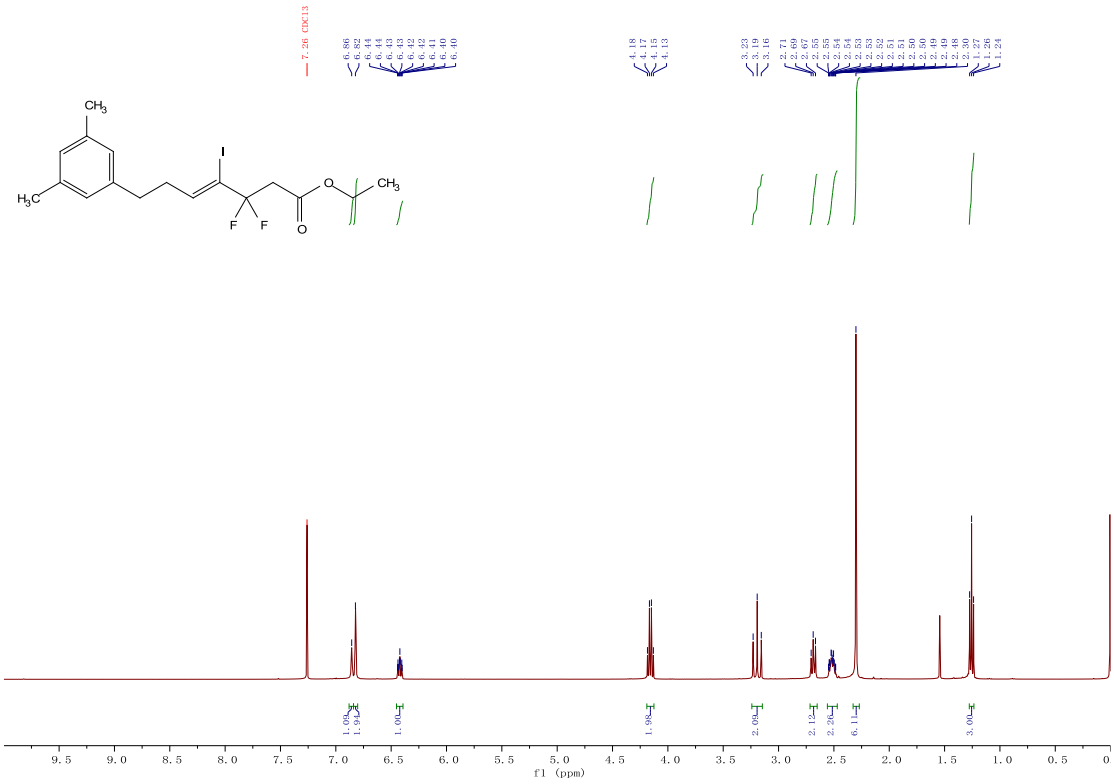
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**



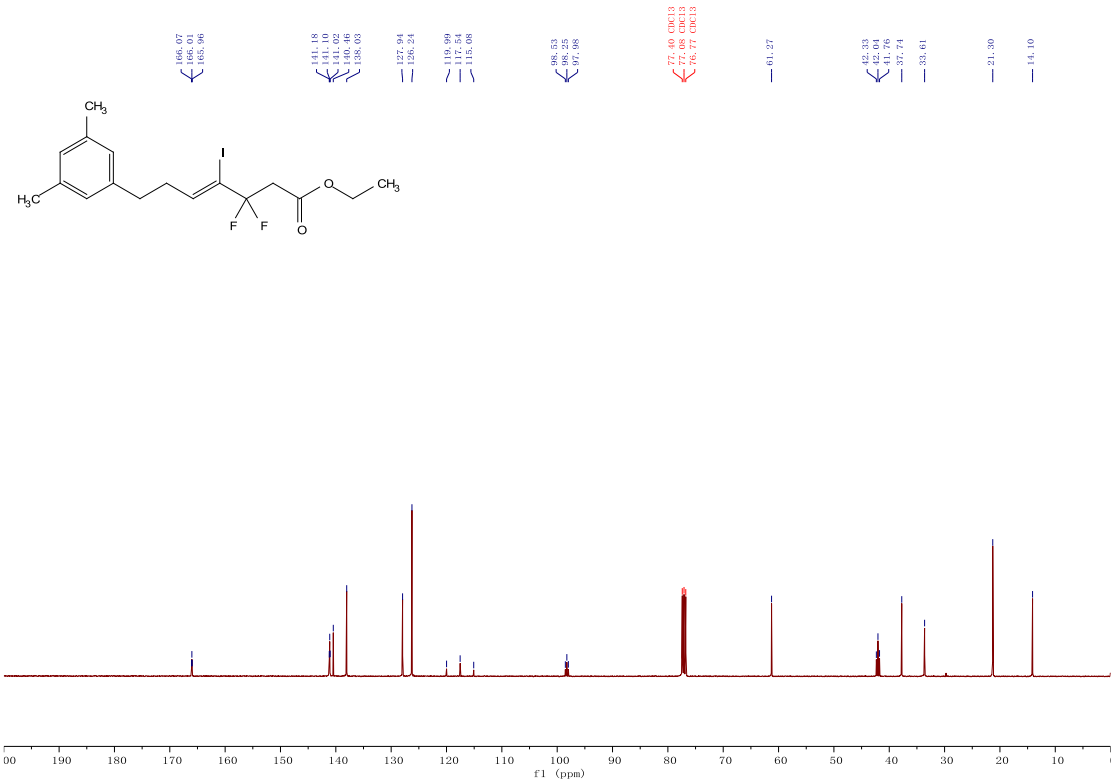
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3j**



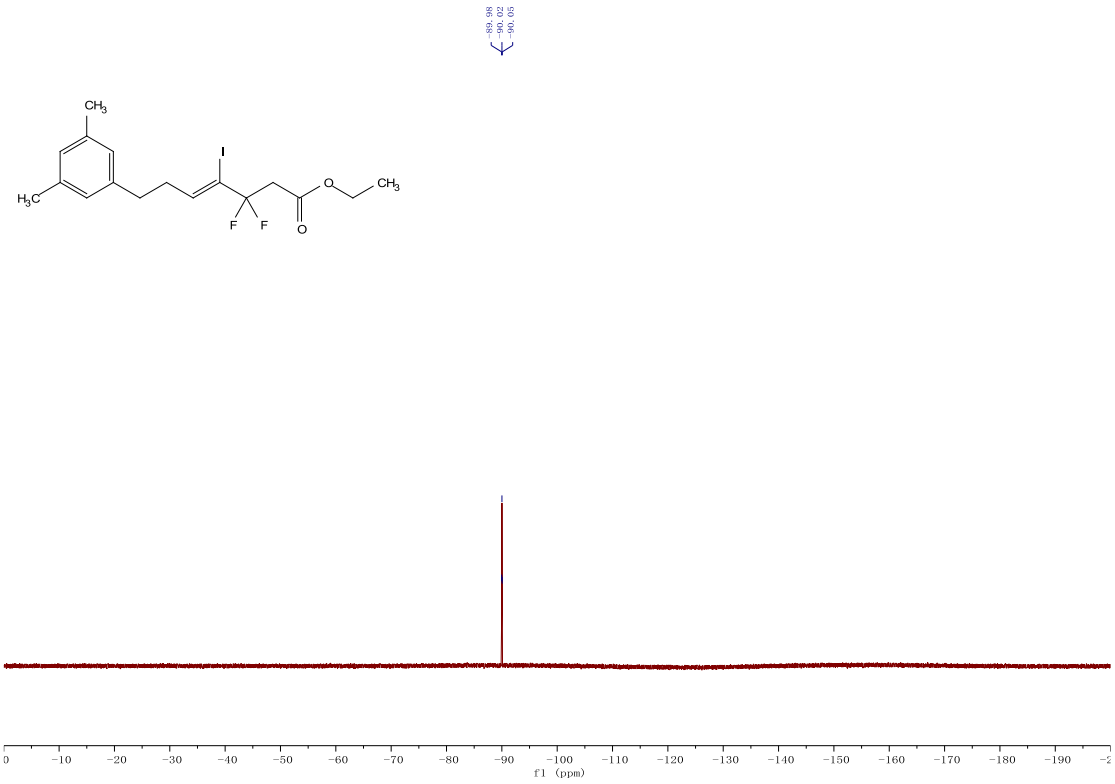
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



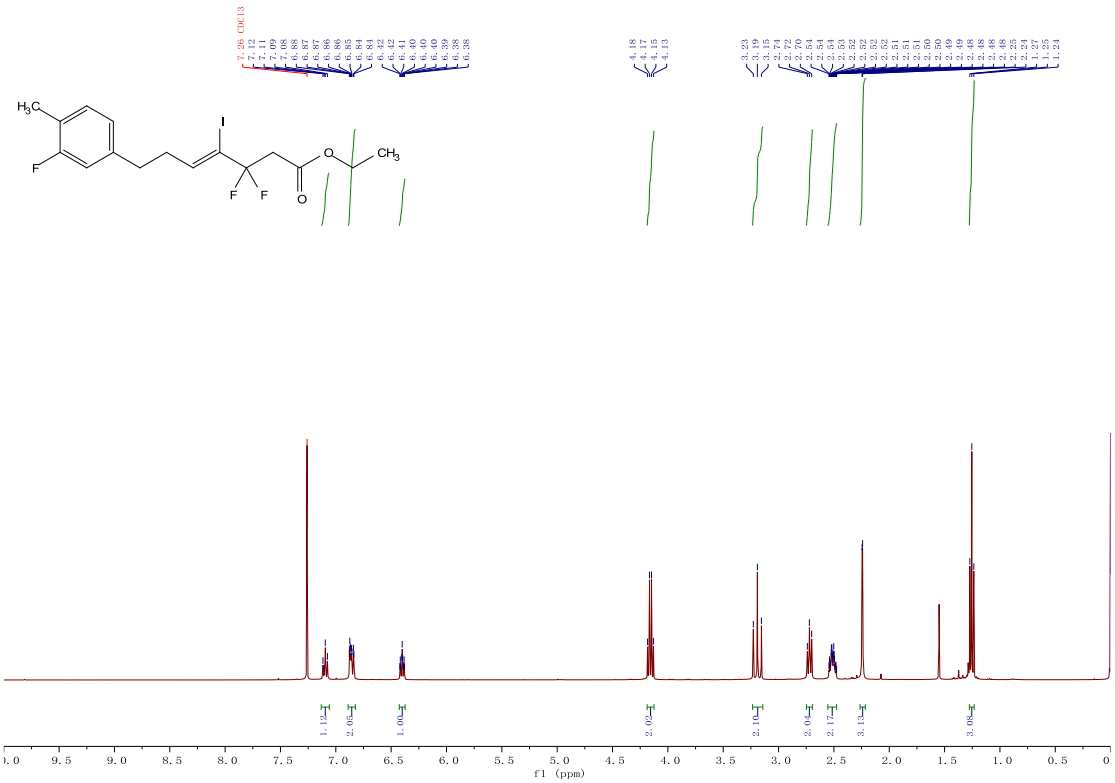
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3k**



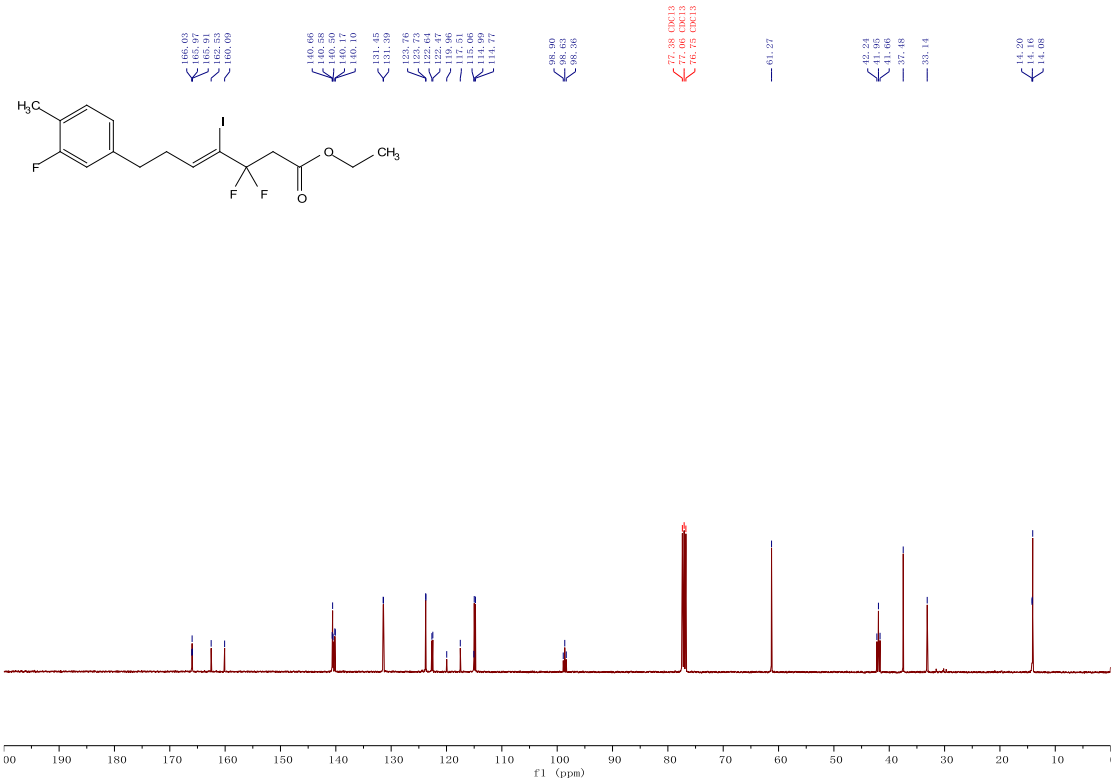
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3k**



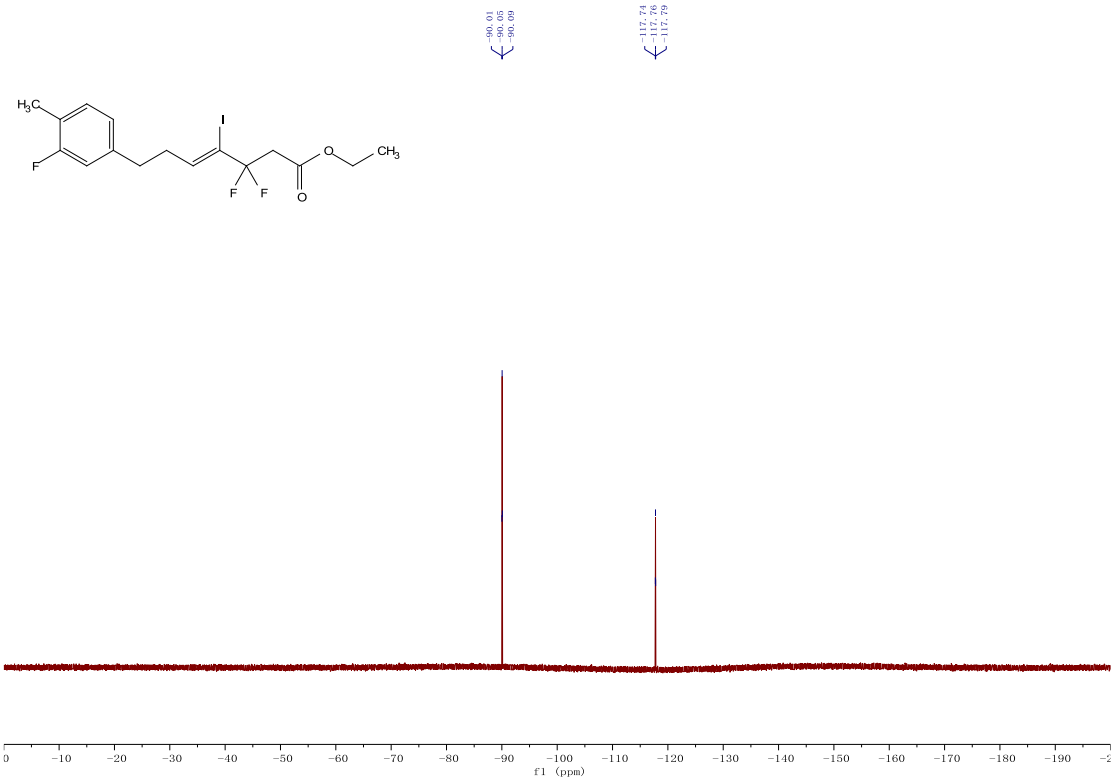
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



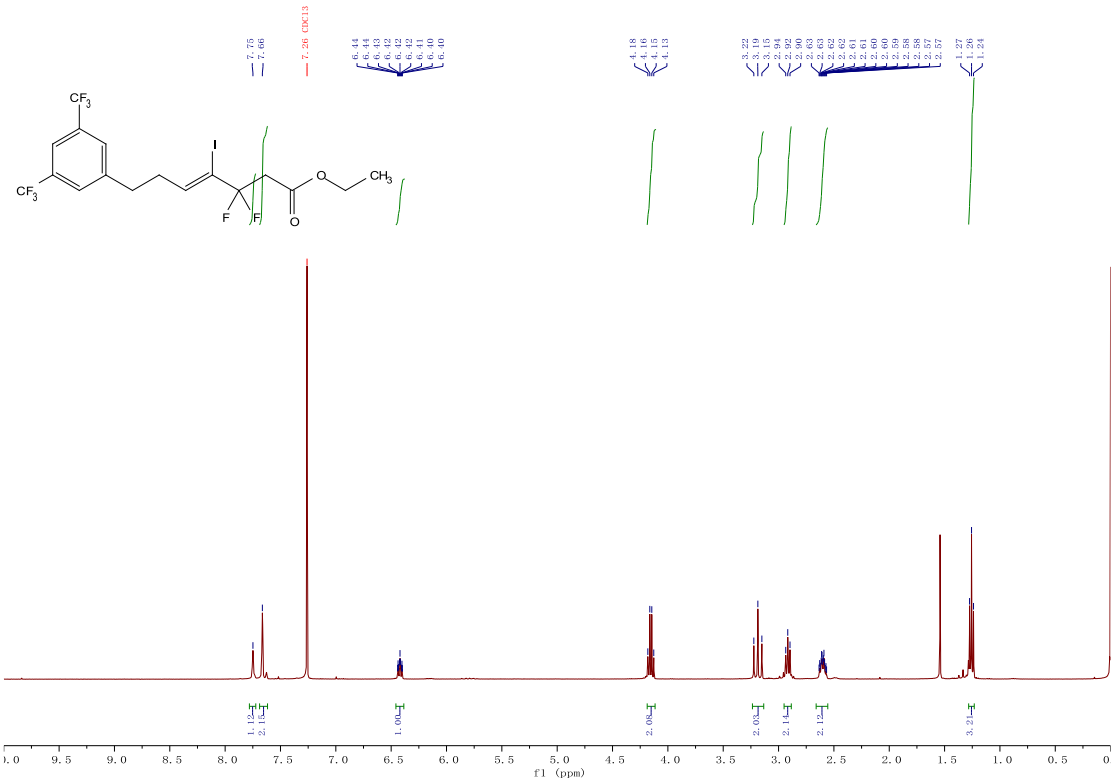
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3l**



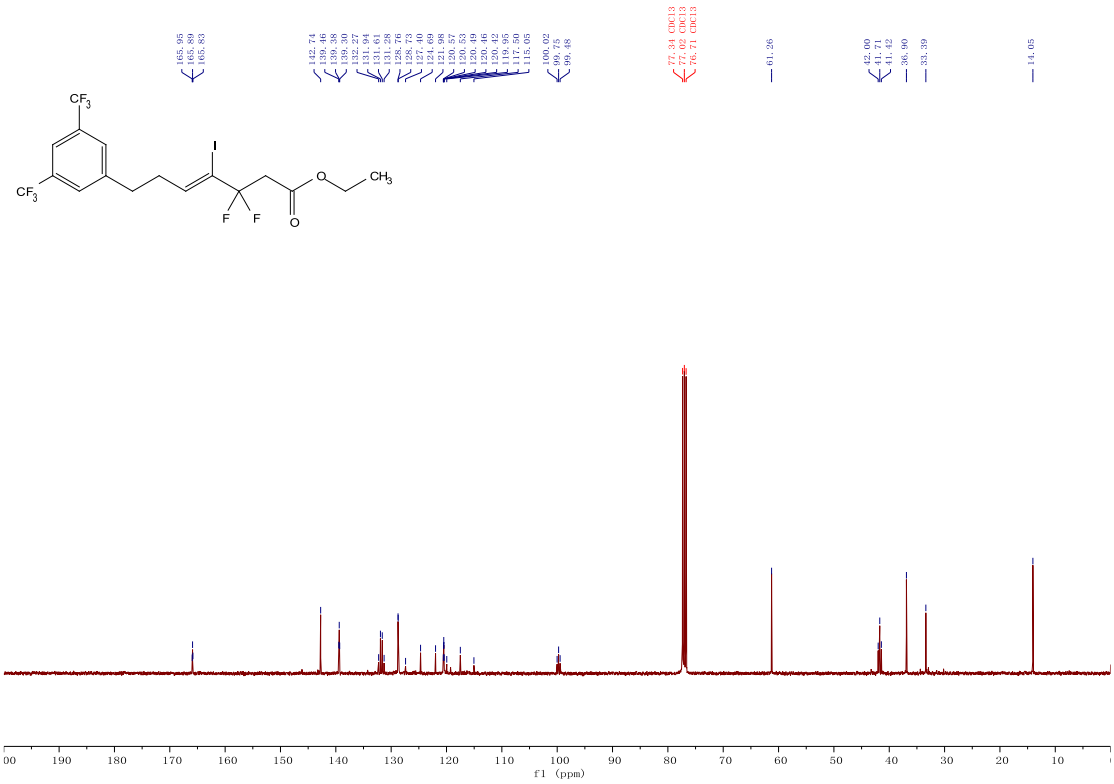
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3l**



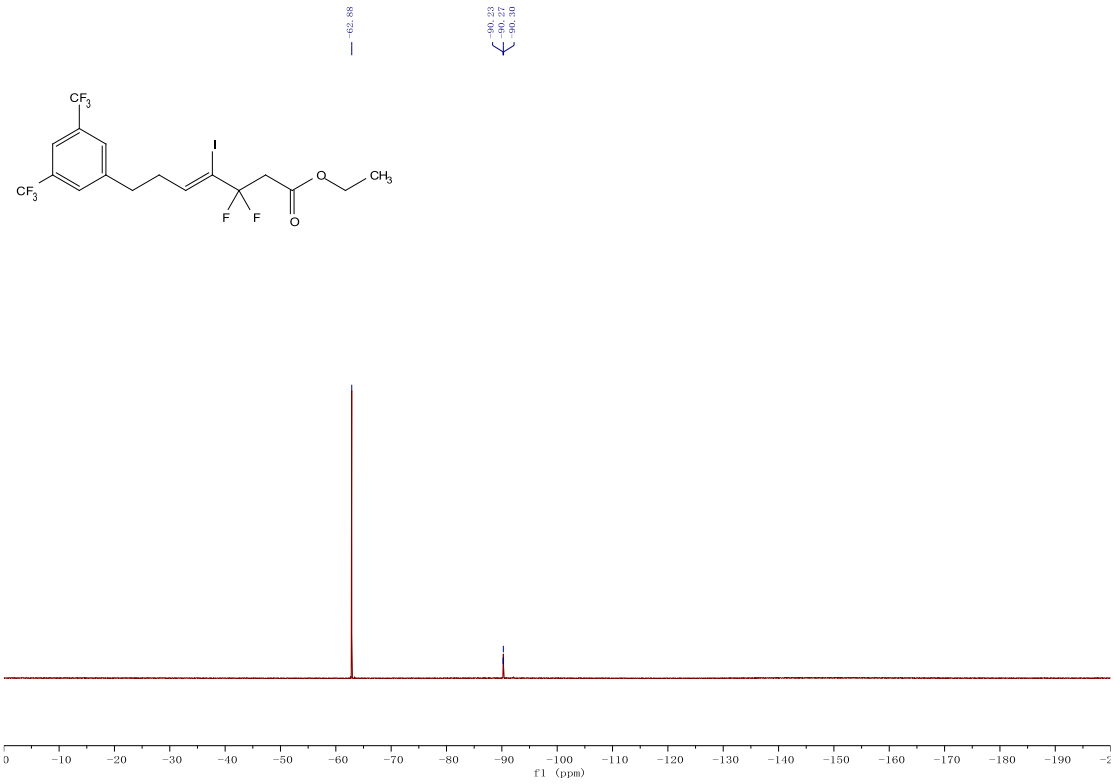
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



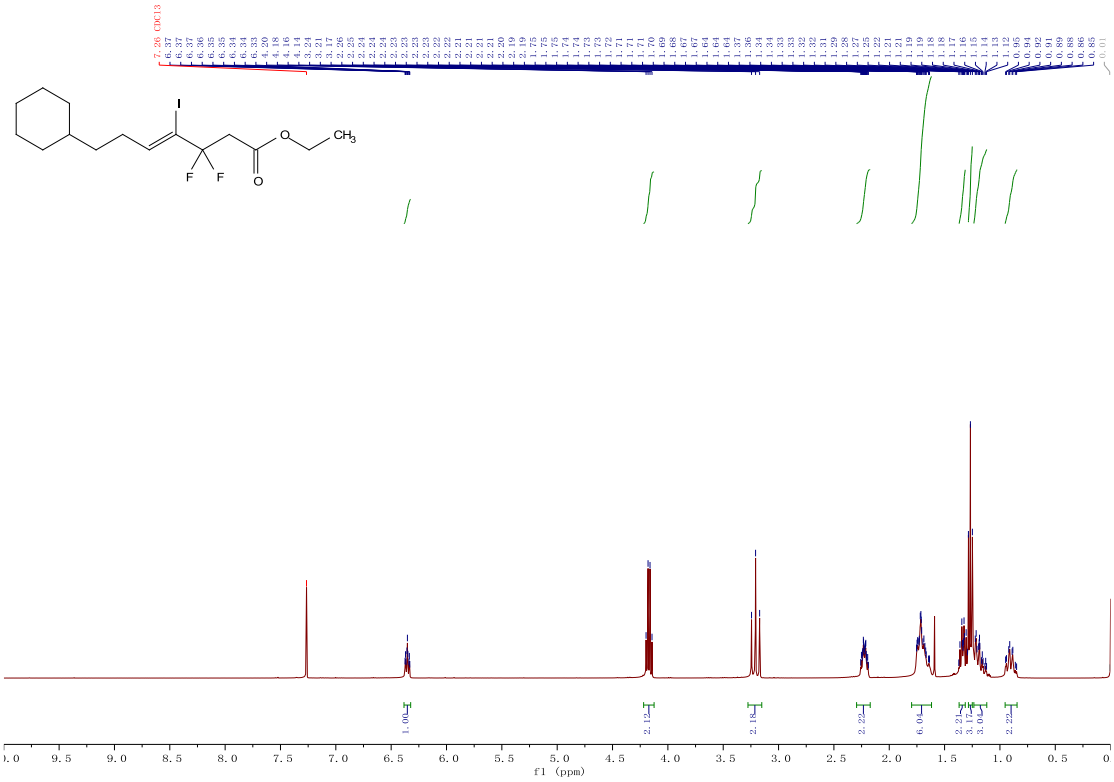
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3m**



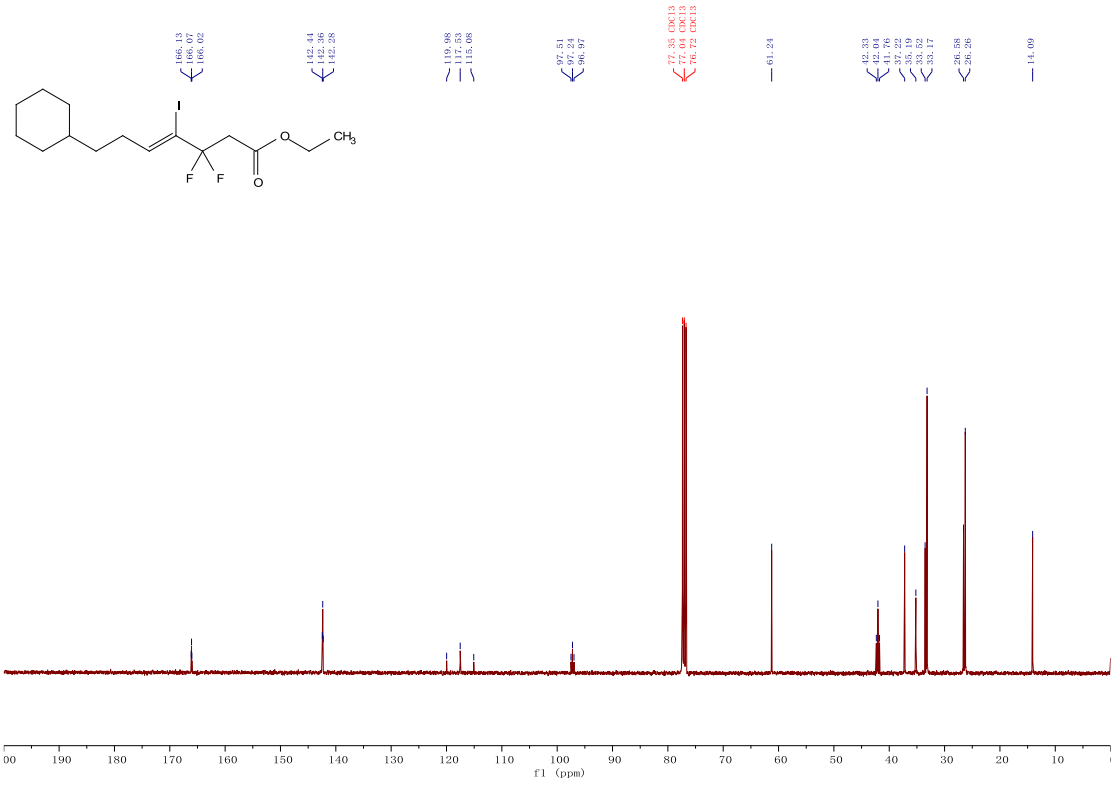
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3m**



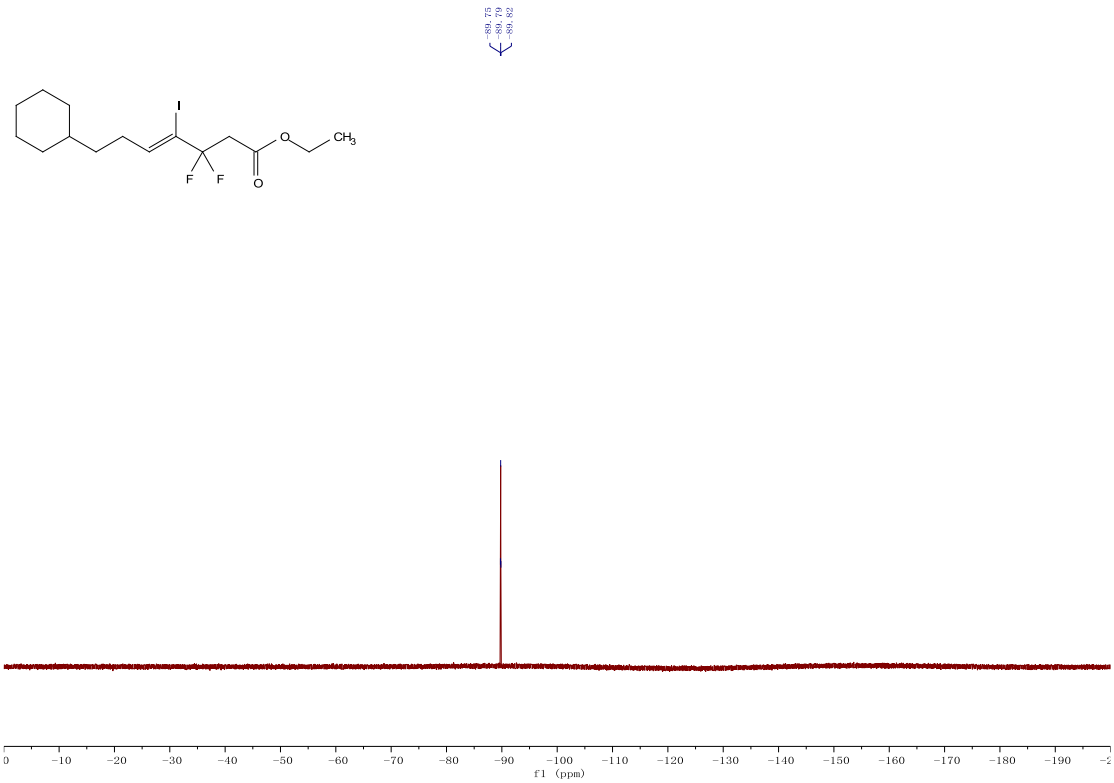
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



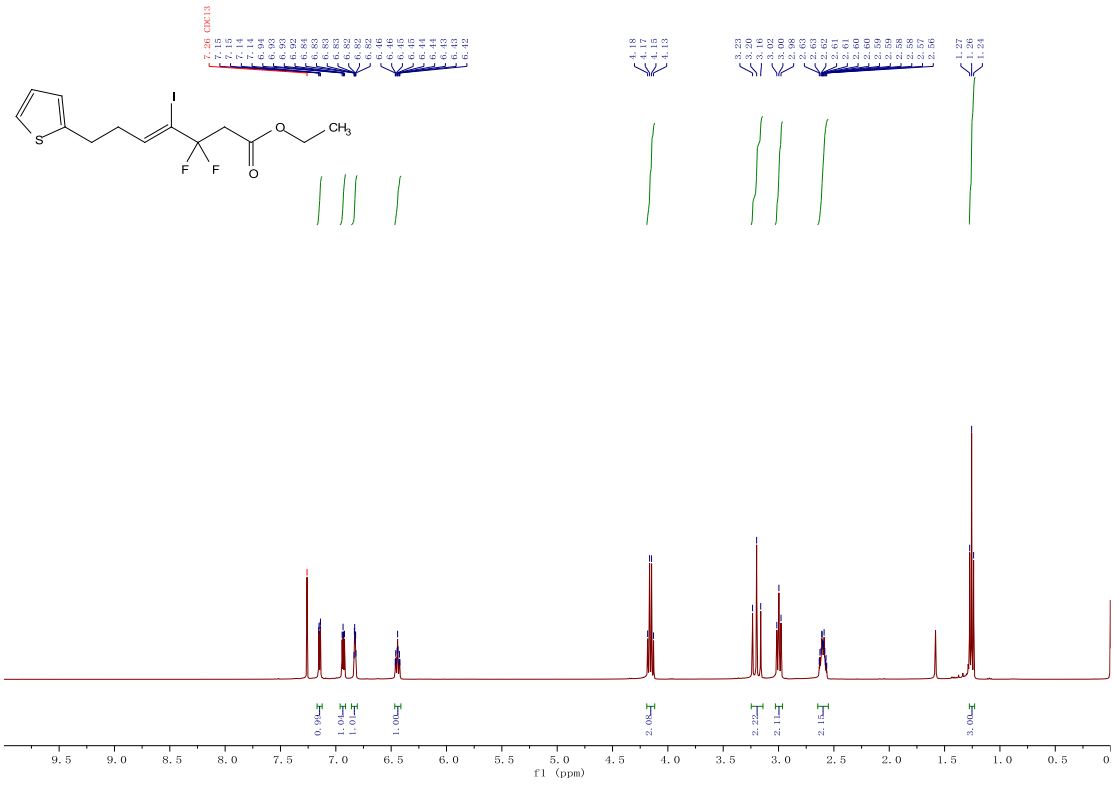
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3n**



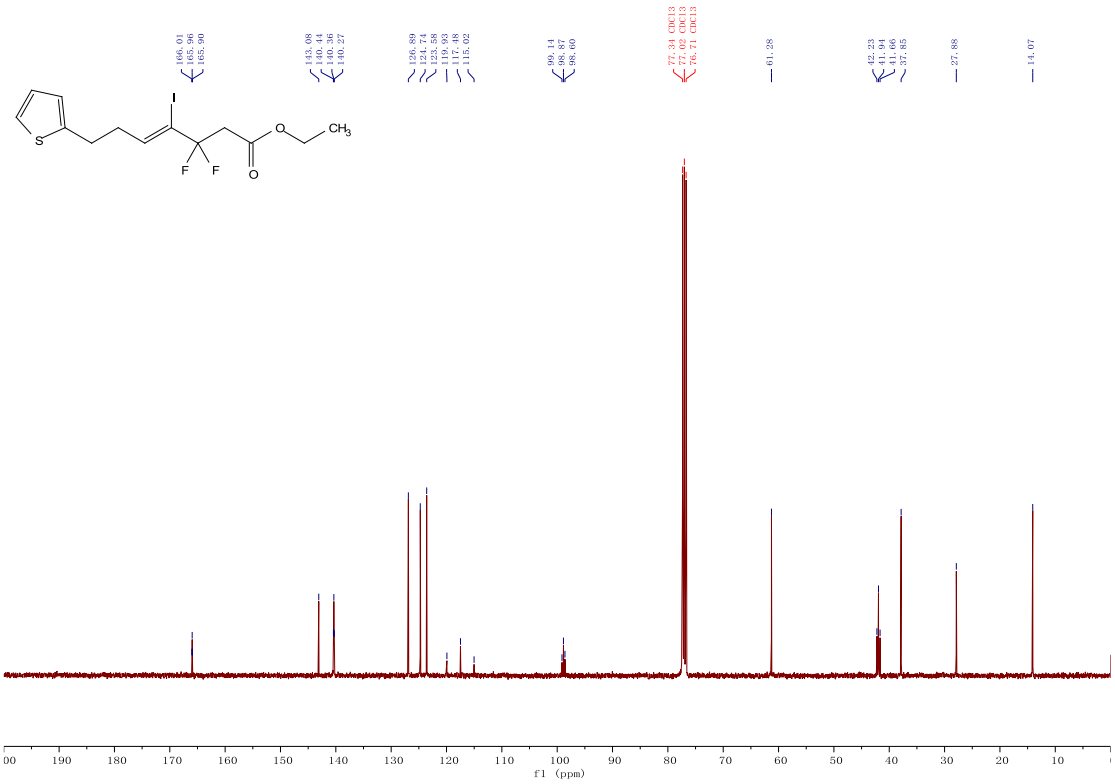
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3n**



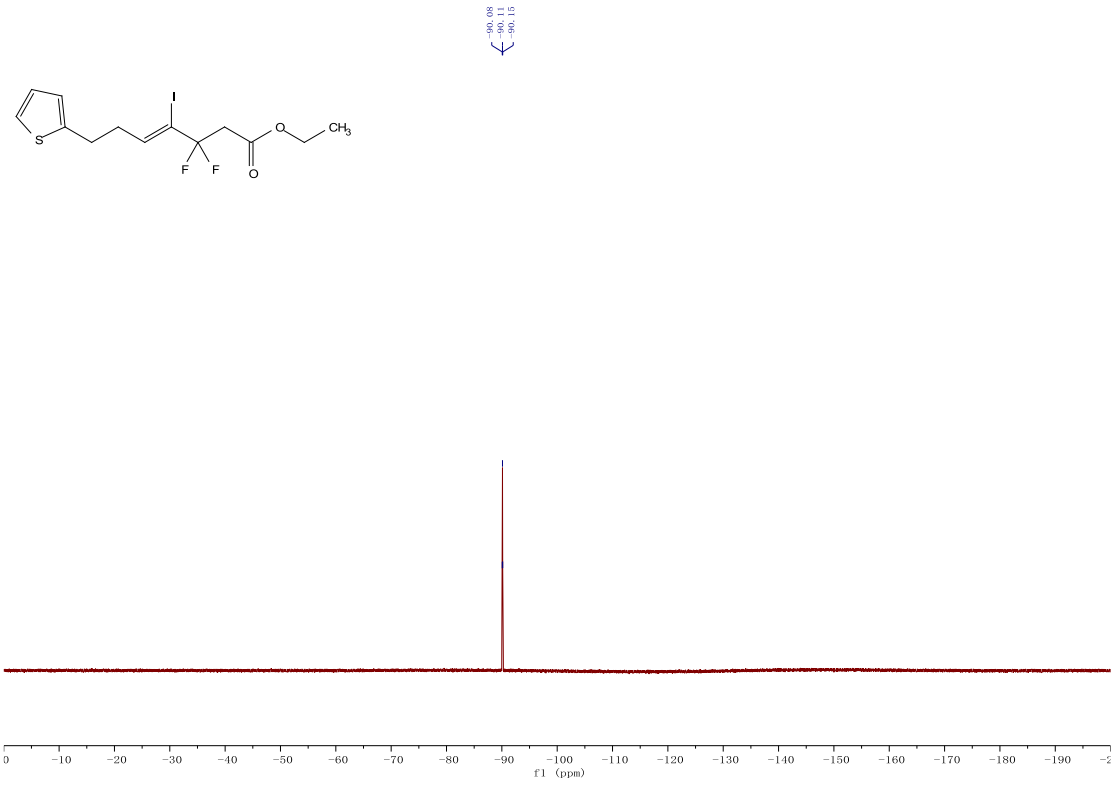
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



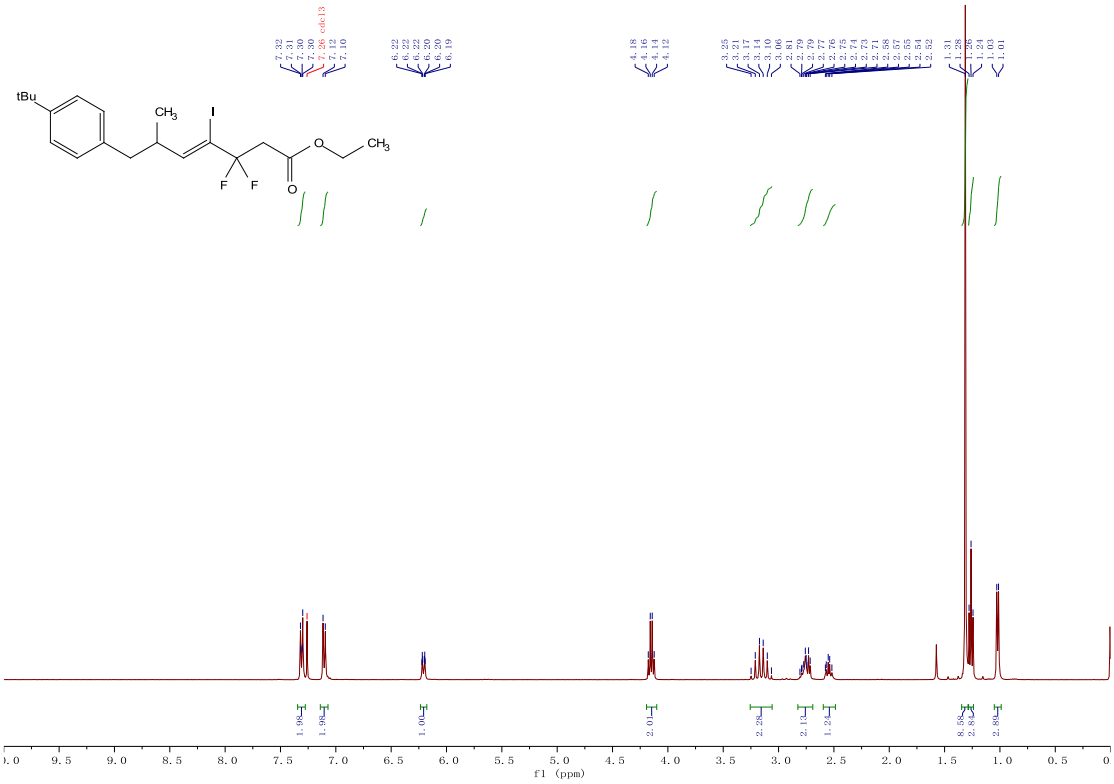
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3o**



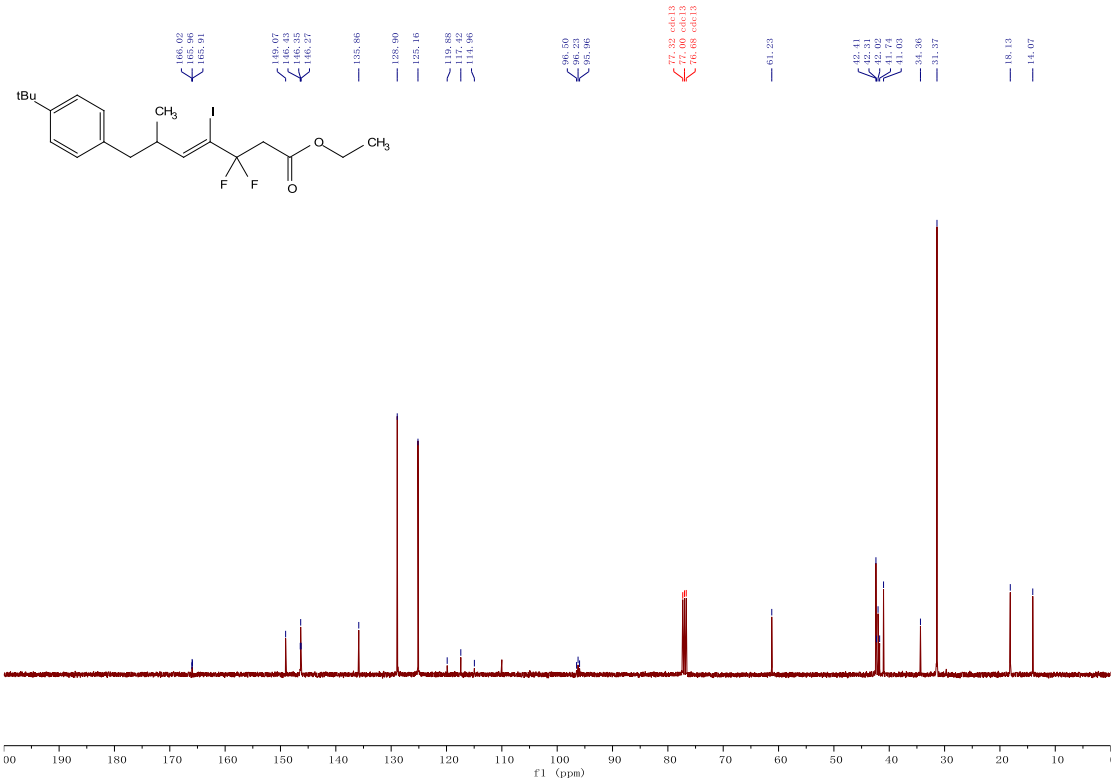
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3o**



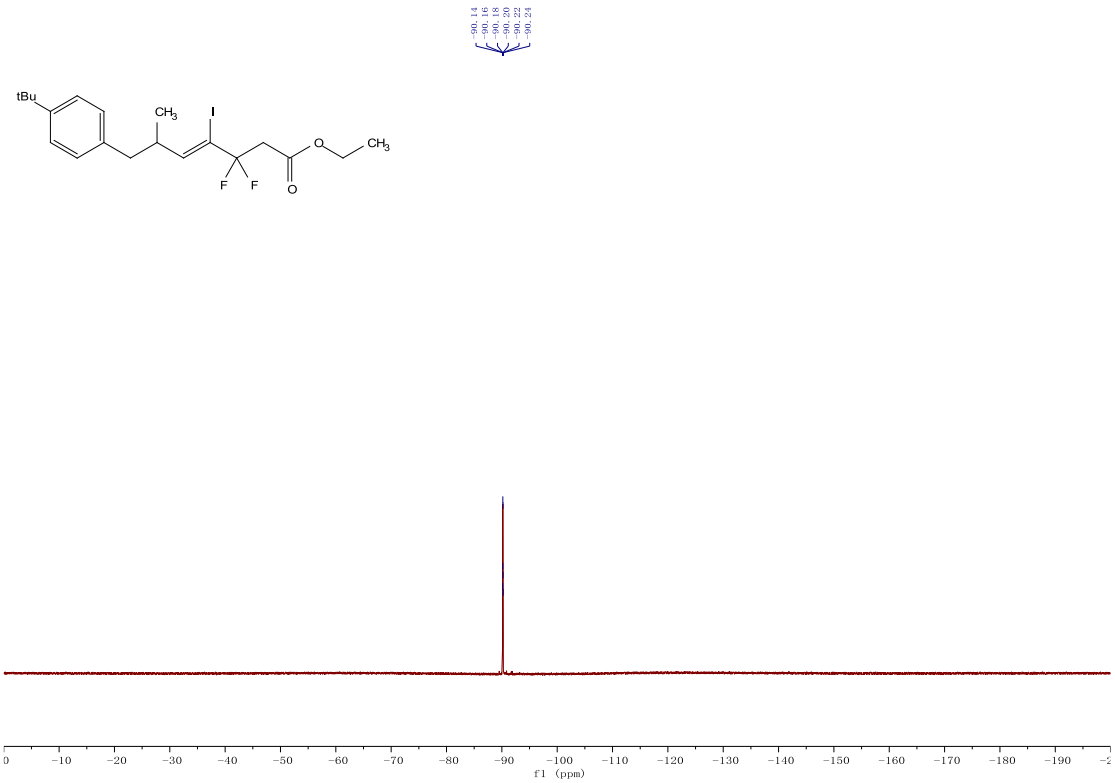
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



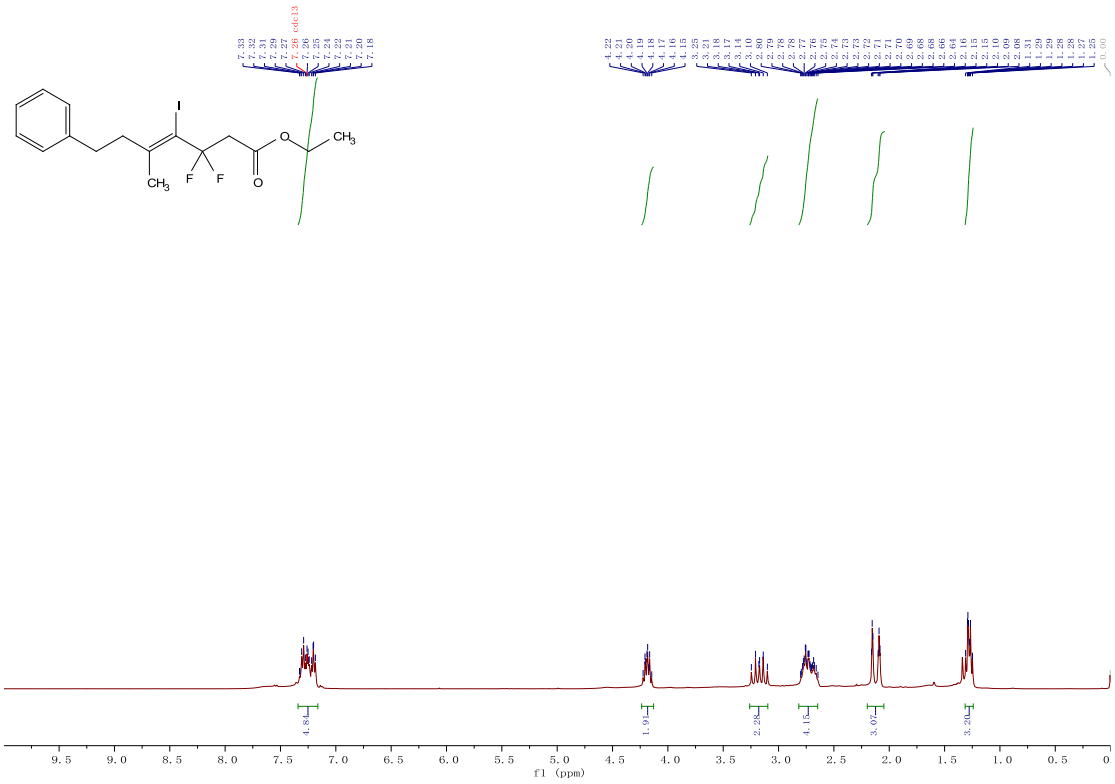
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3p**



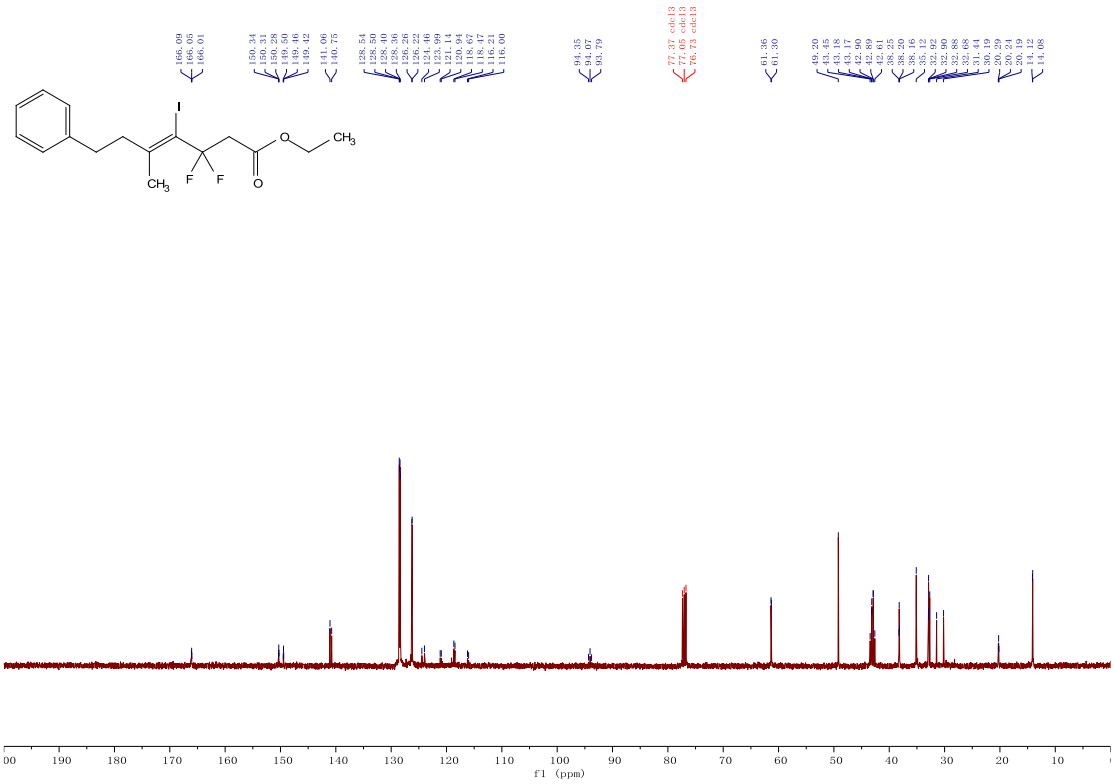
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3p**



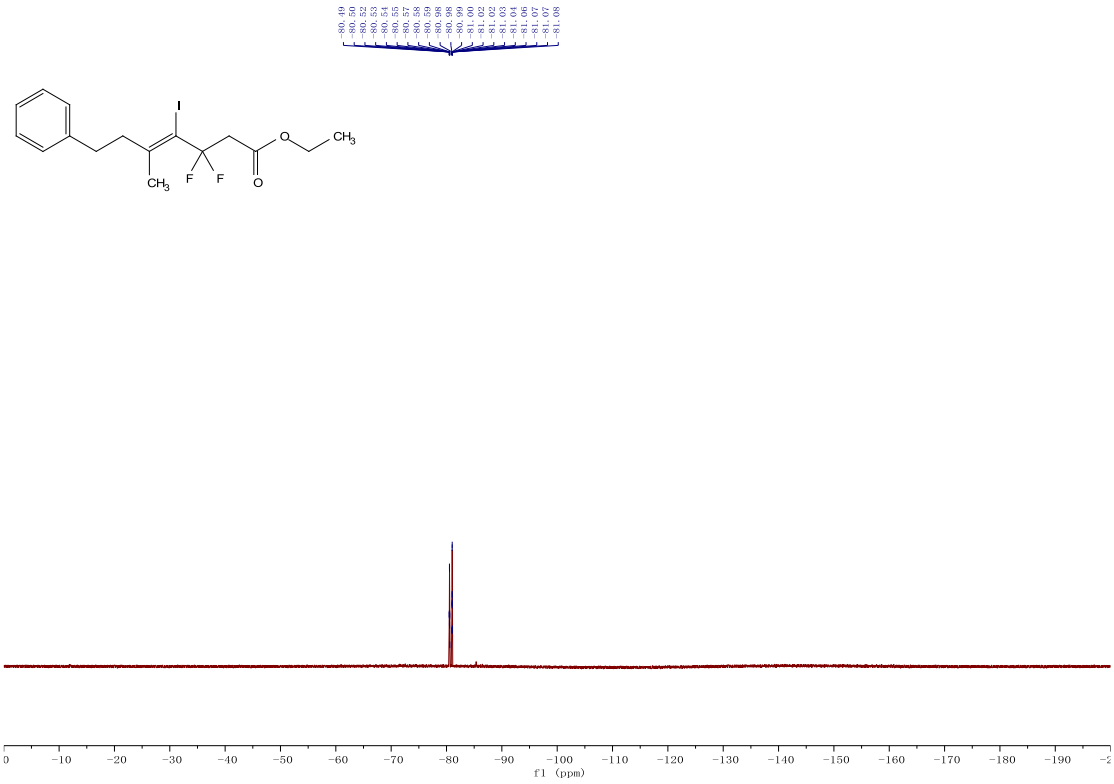
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**



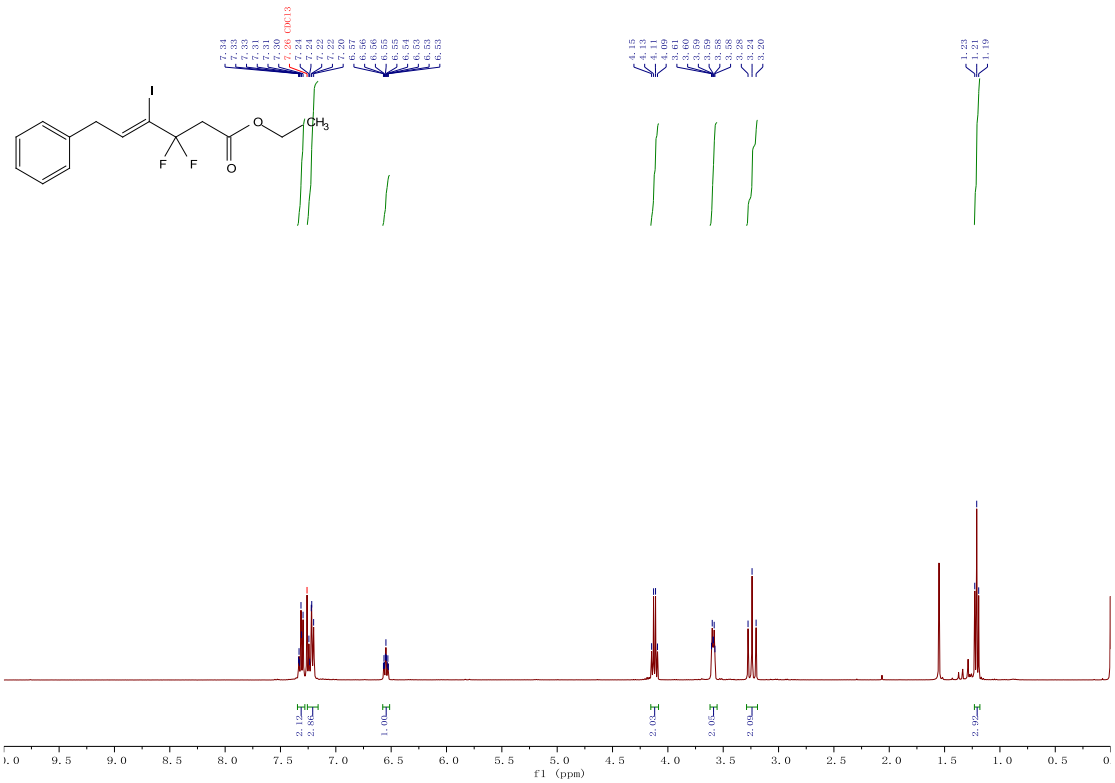
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3q**



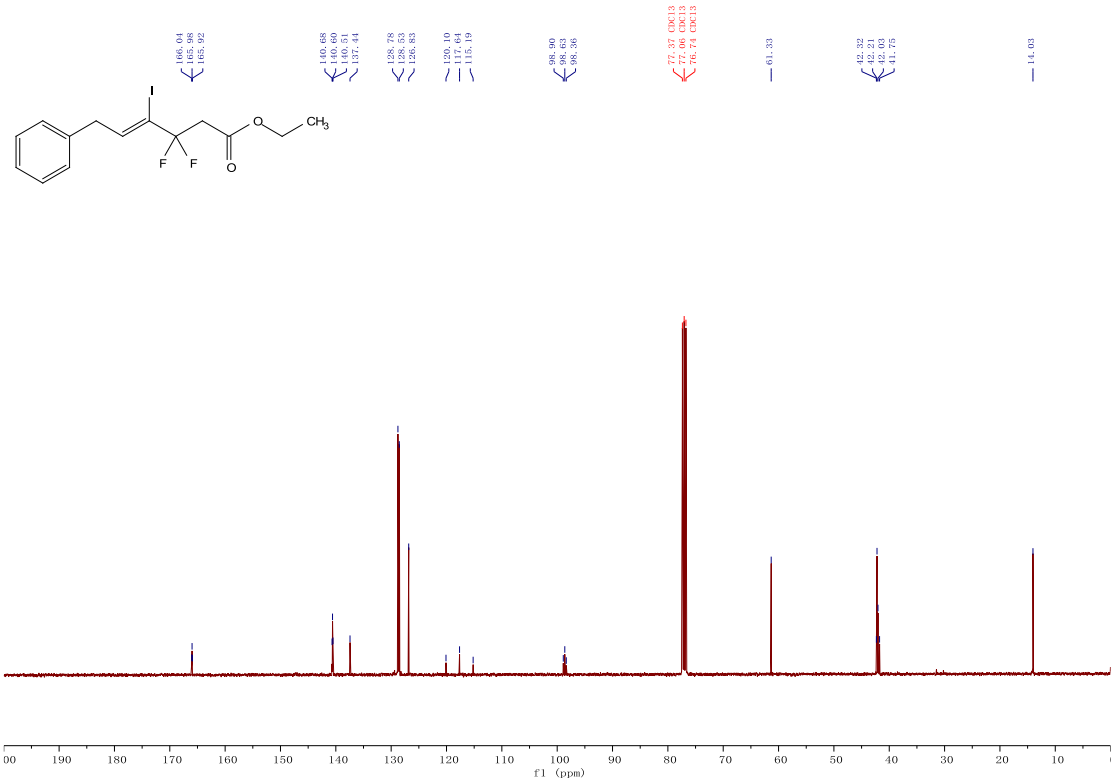
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3q**



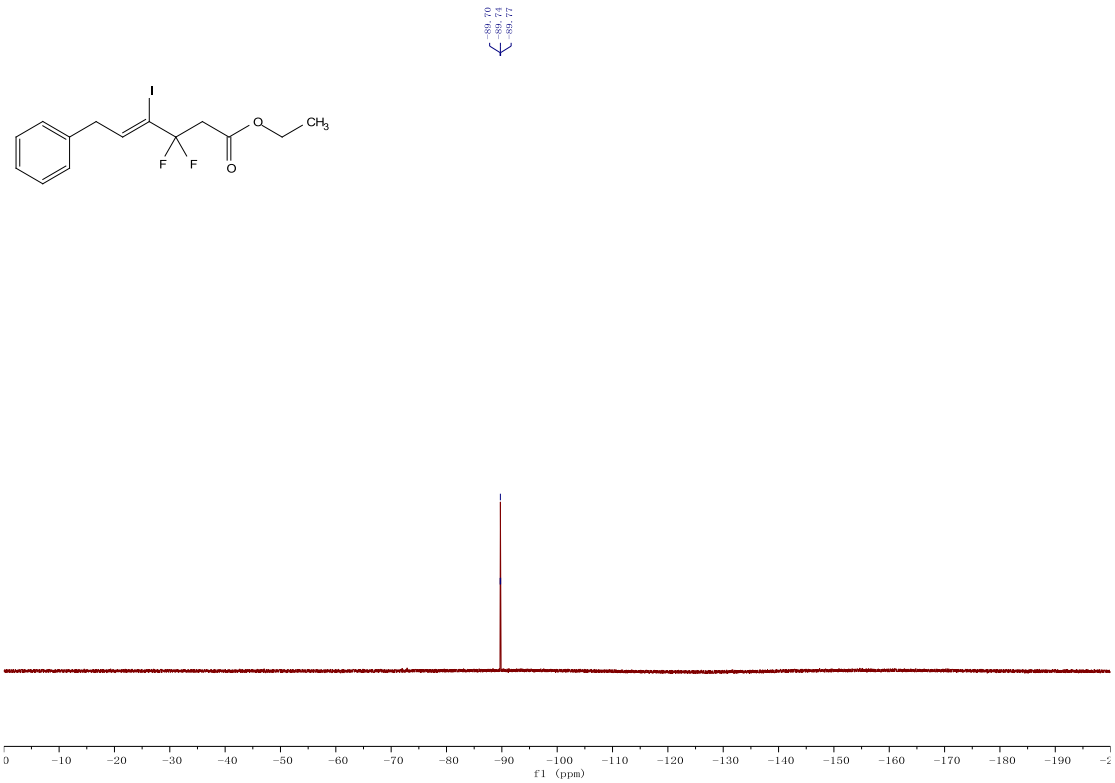
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



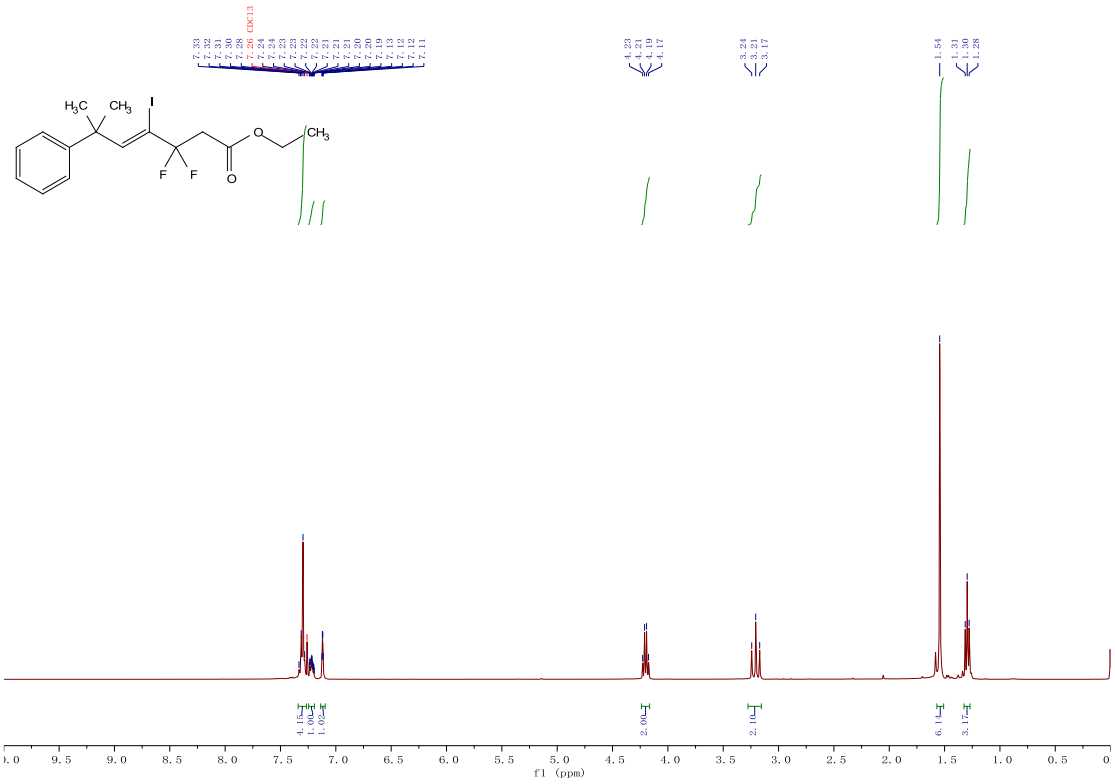
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3r**



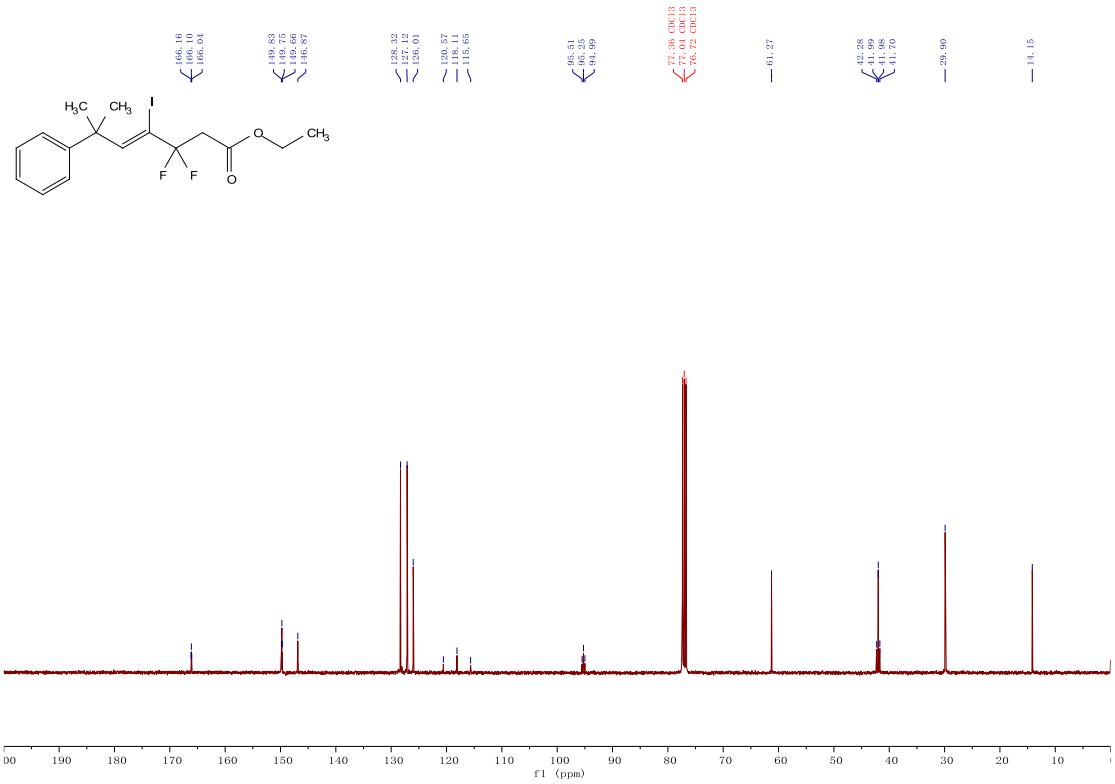
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3r**



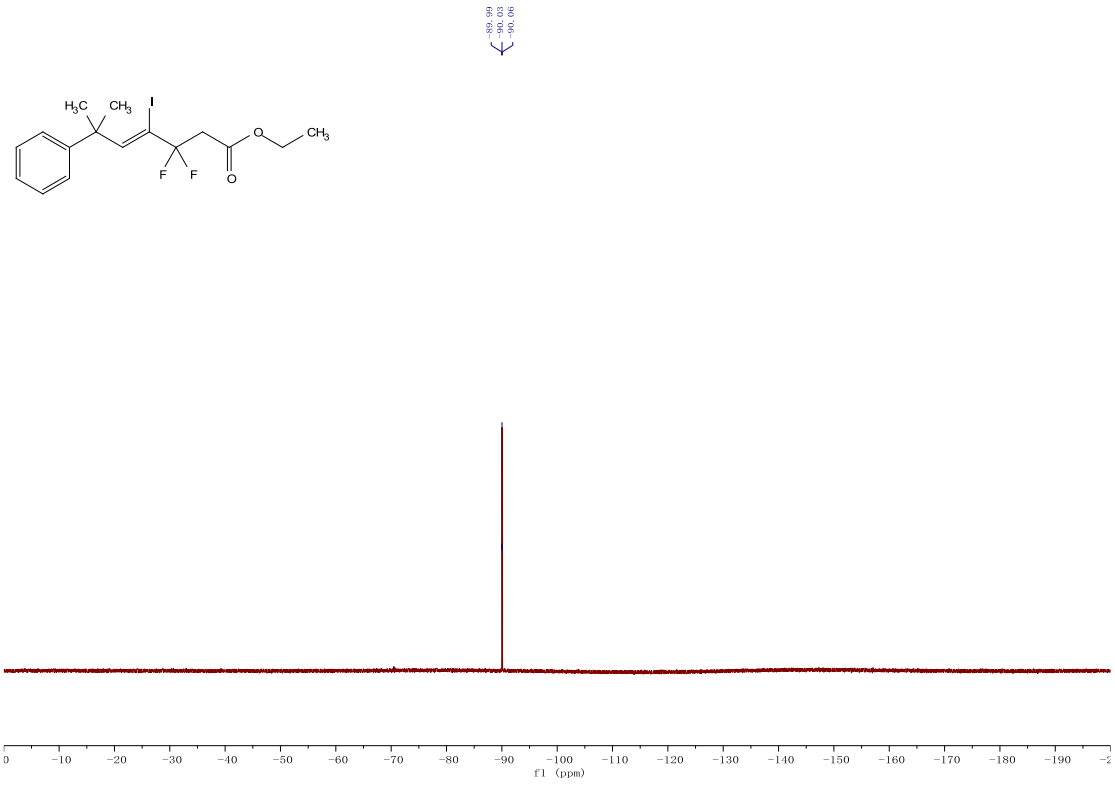
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**



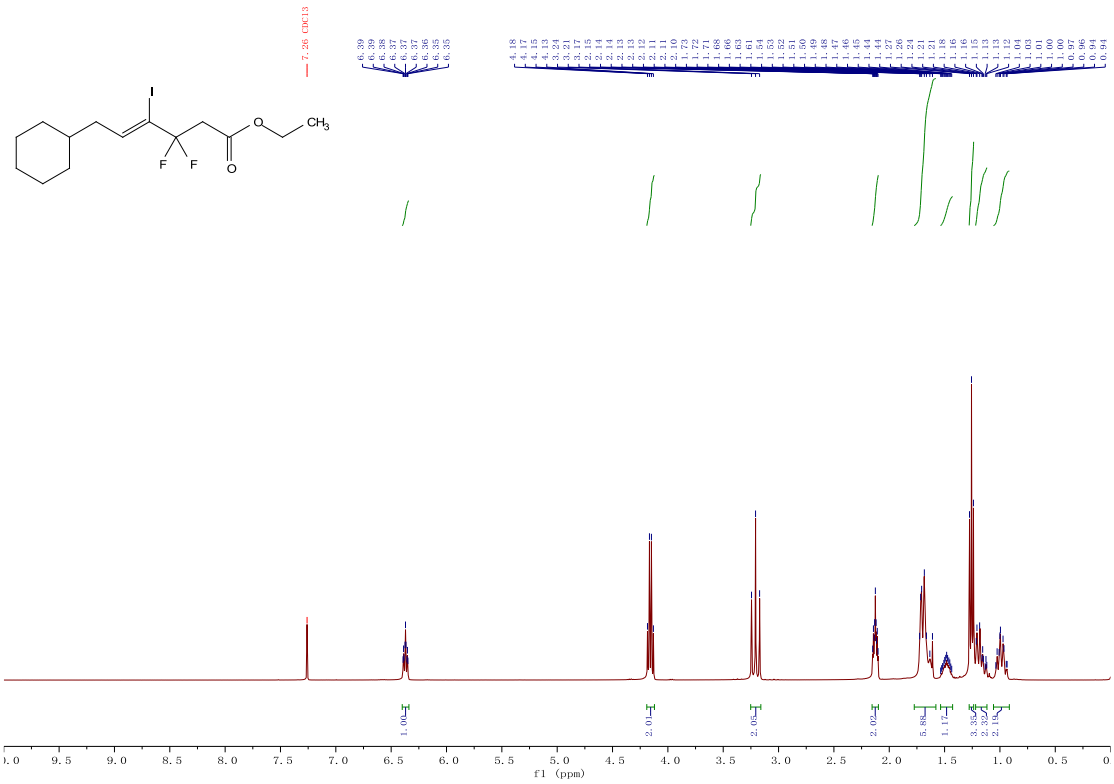
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3s**



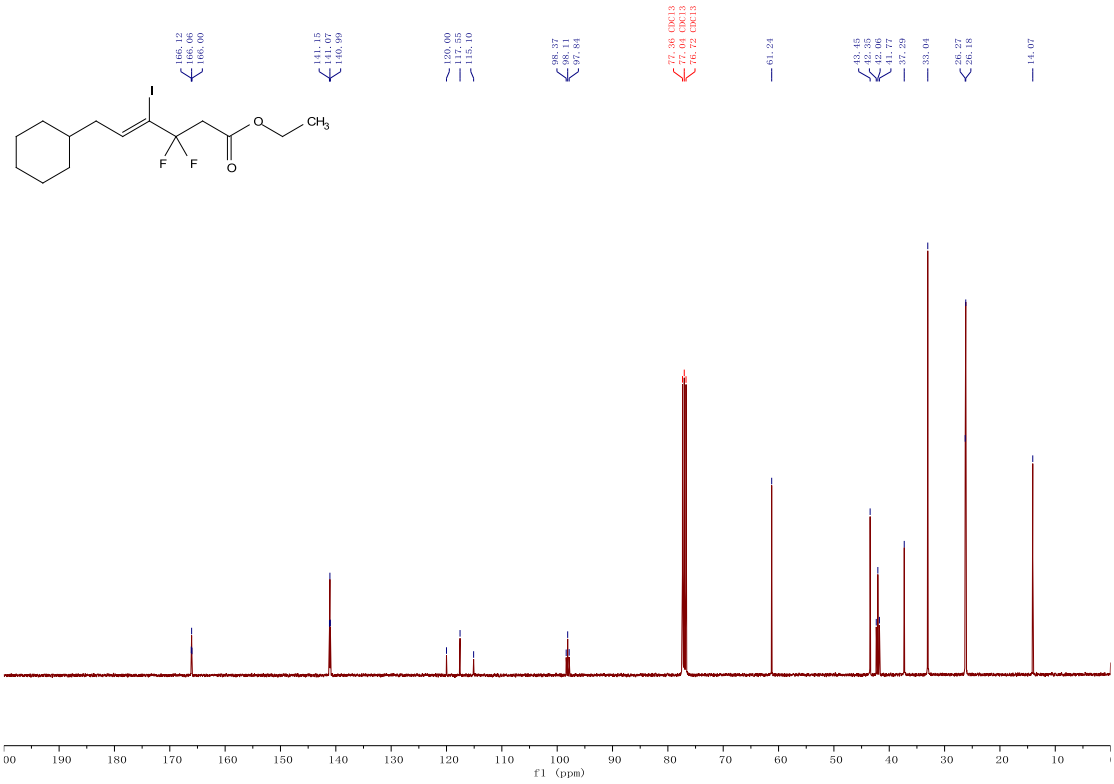
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3s**



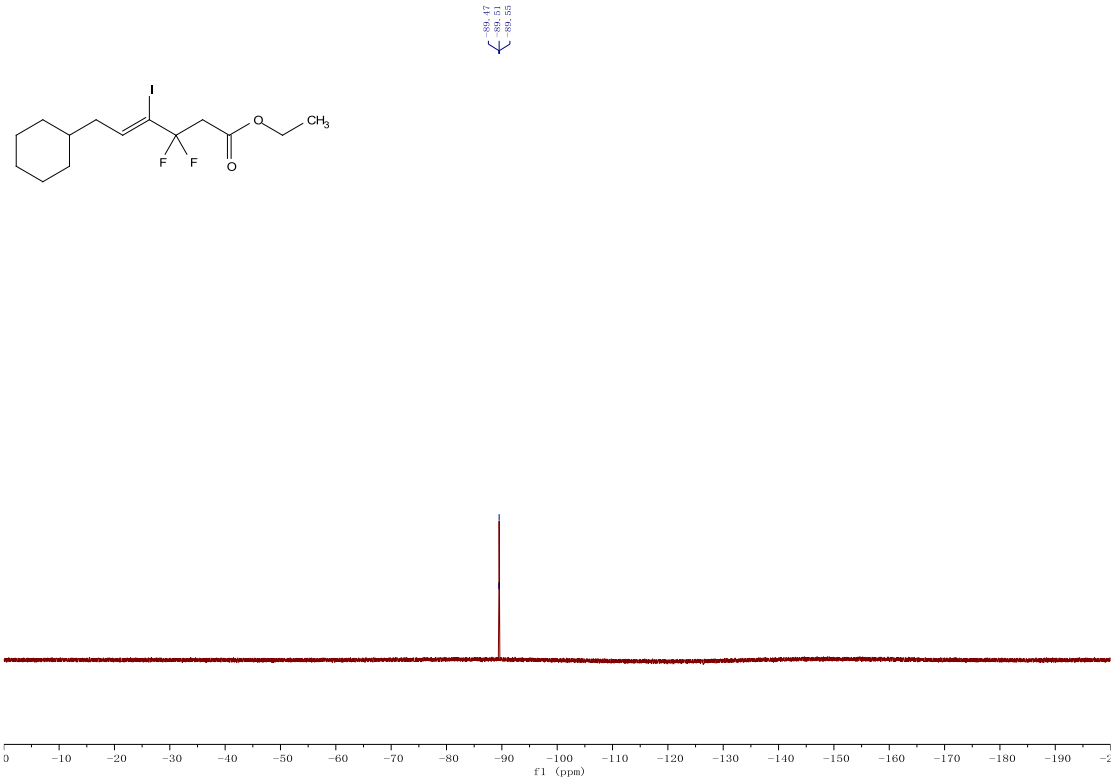
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**



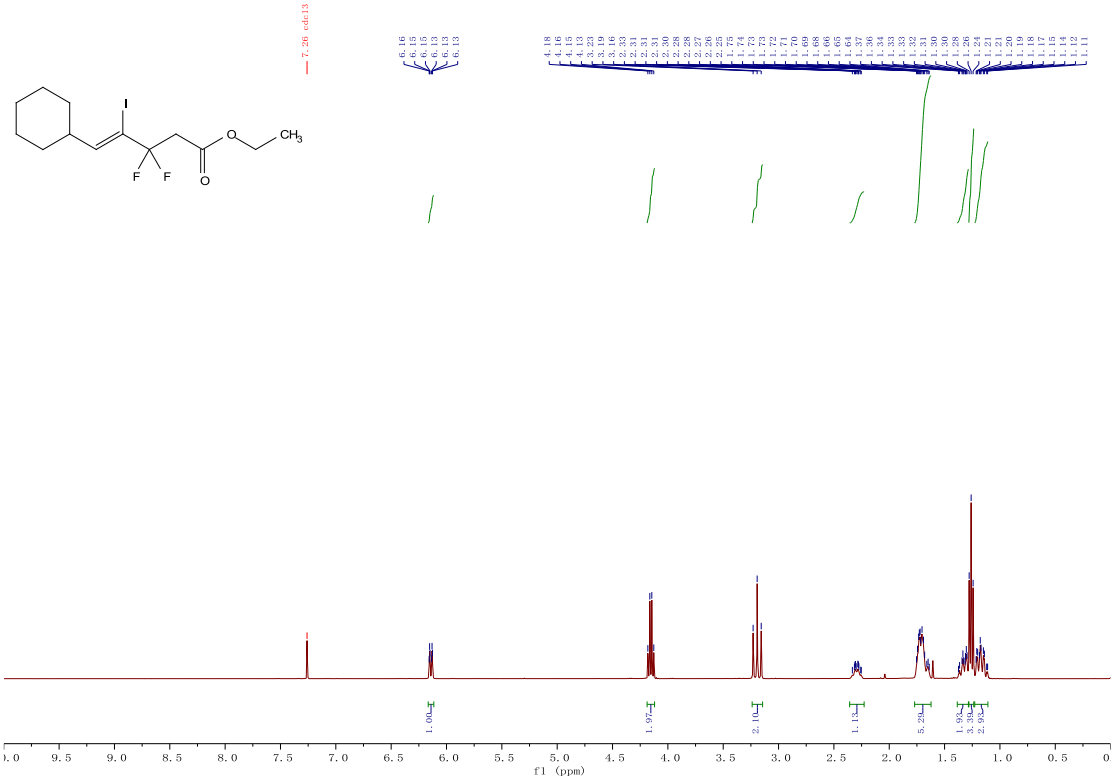
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3t**



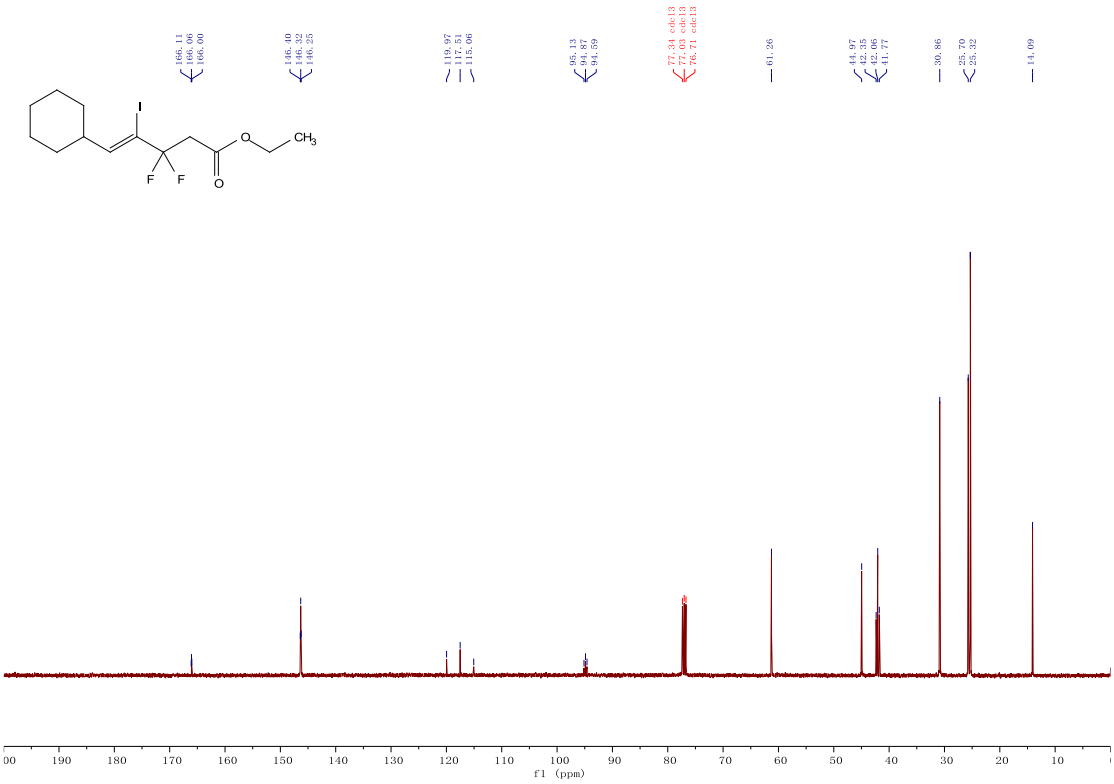
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3t**



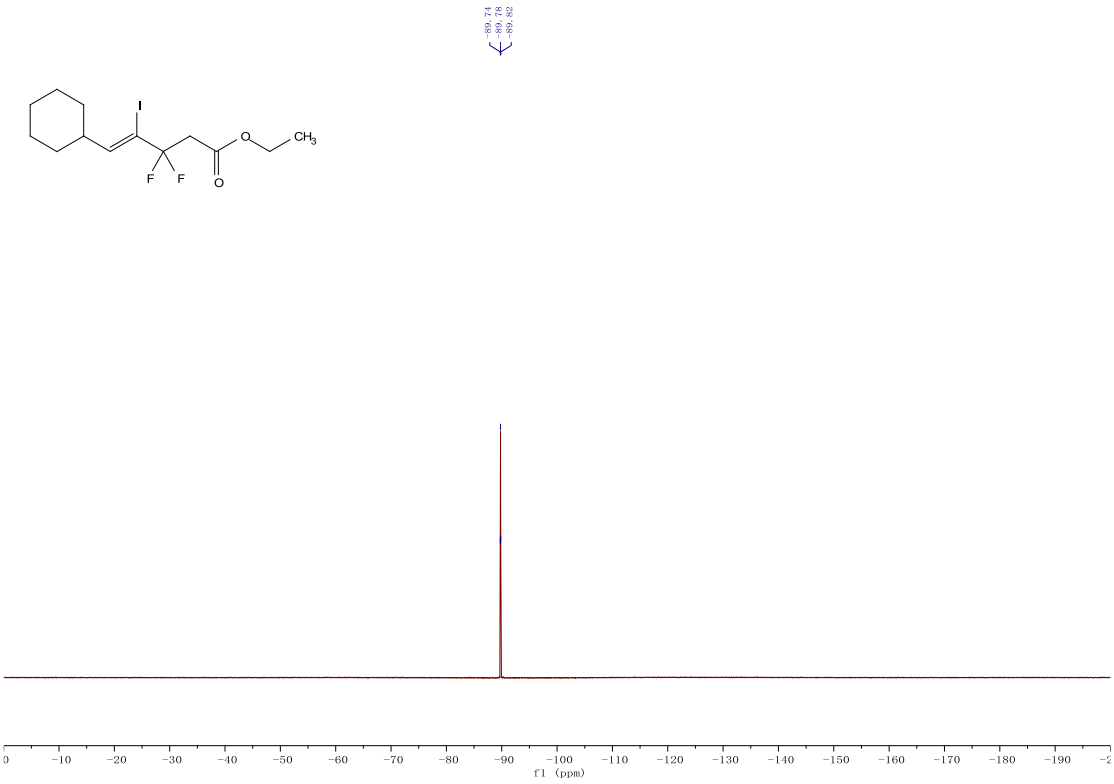
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**



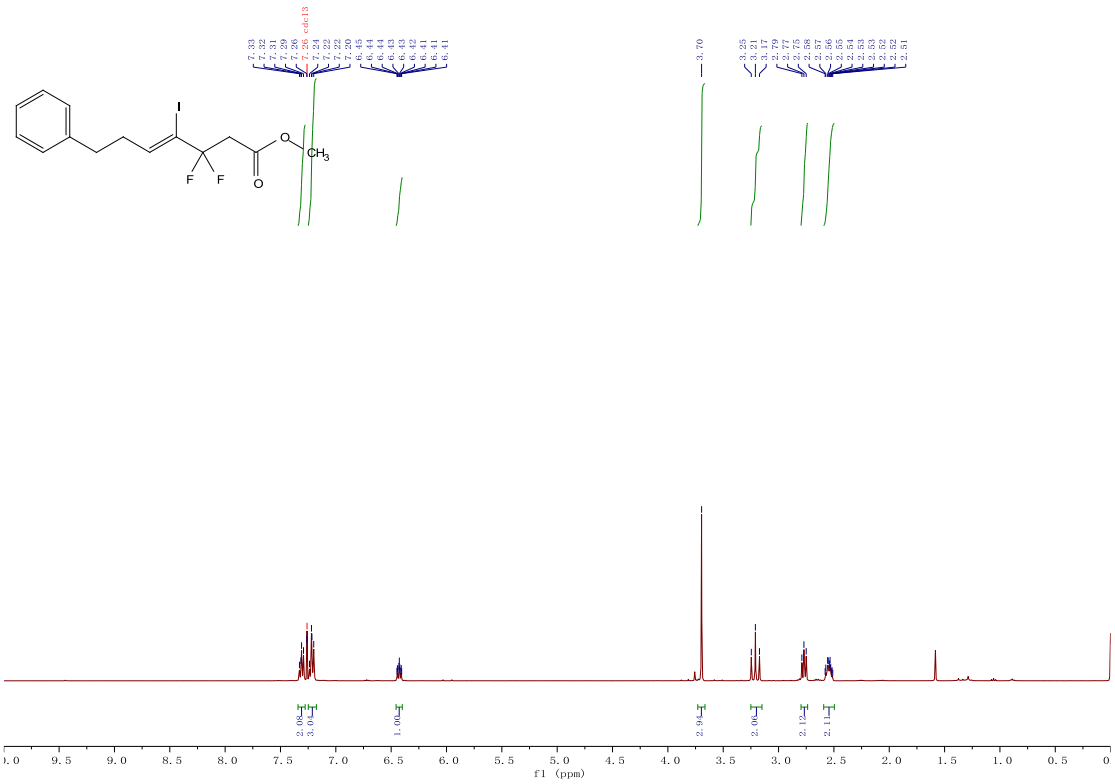
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3u**



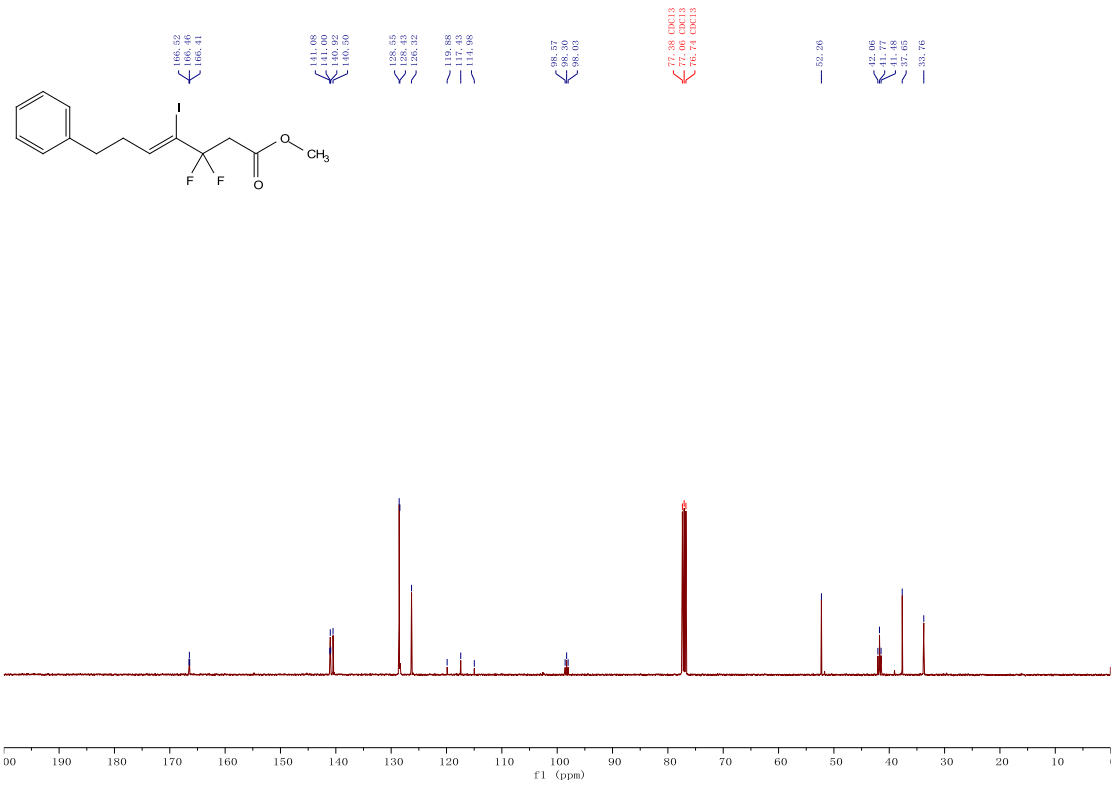
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3u**



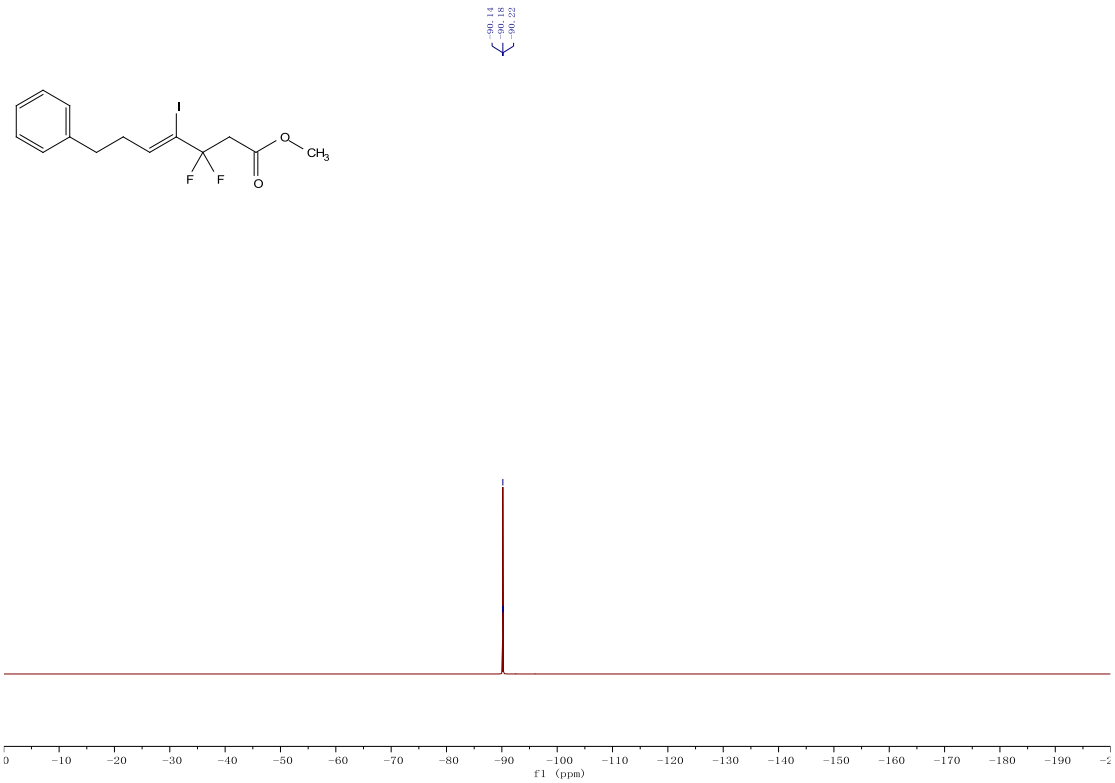
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**



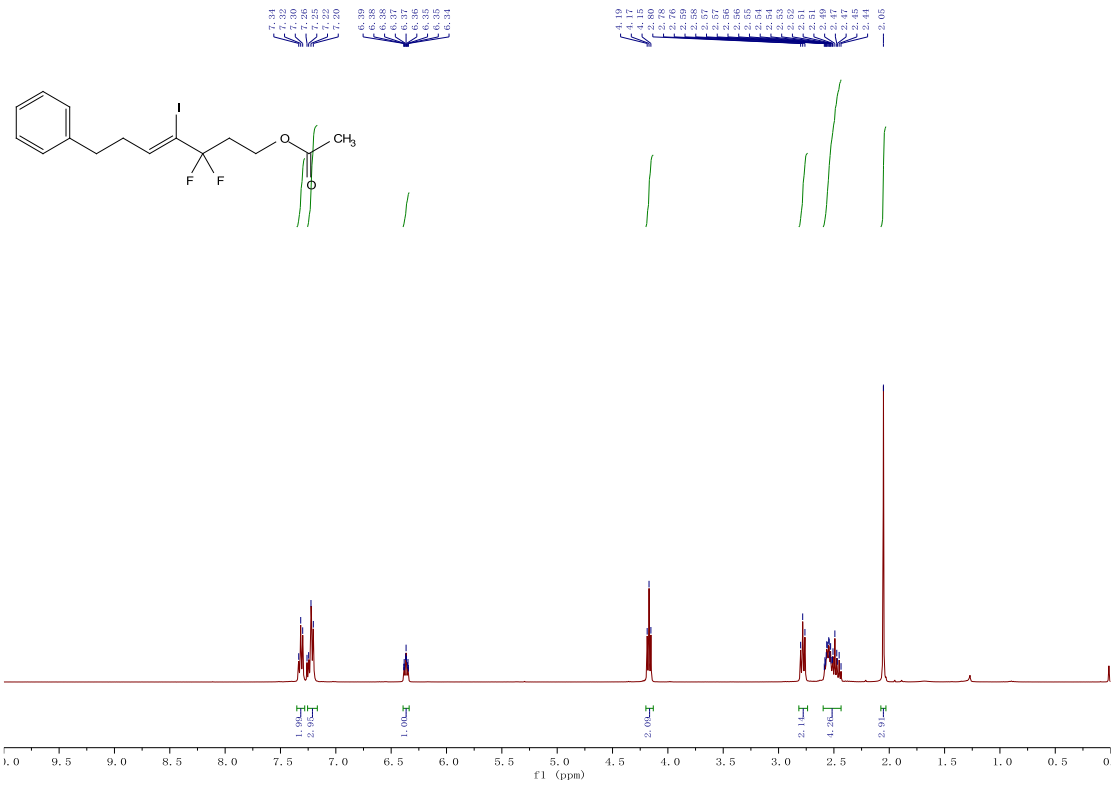
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5a**



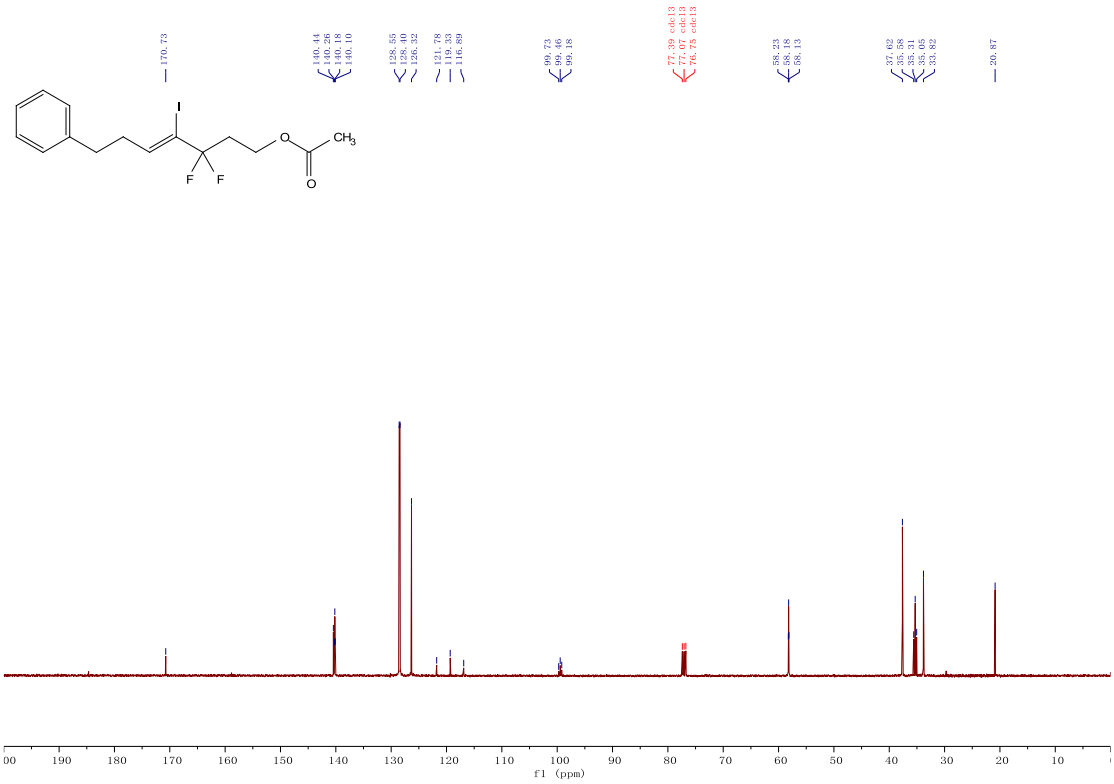
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5a**



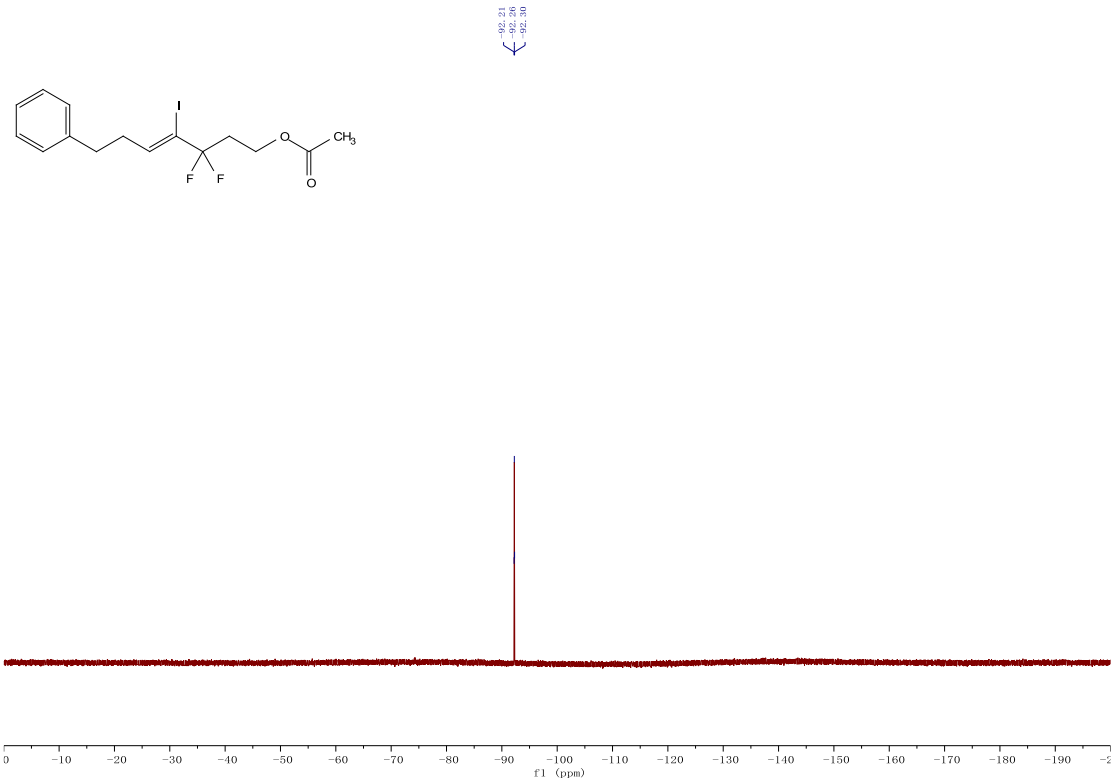
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**



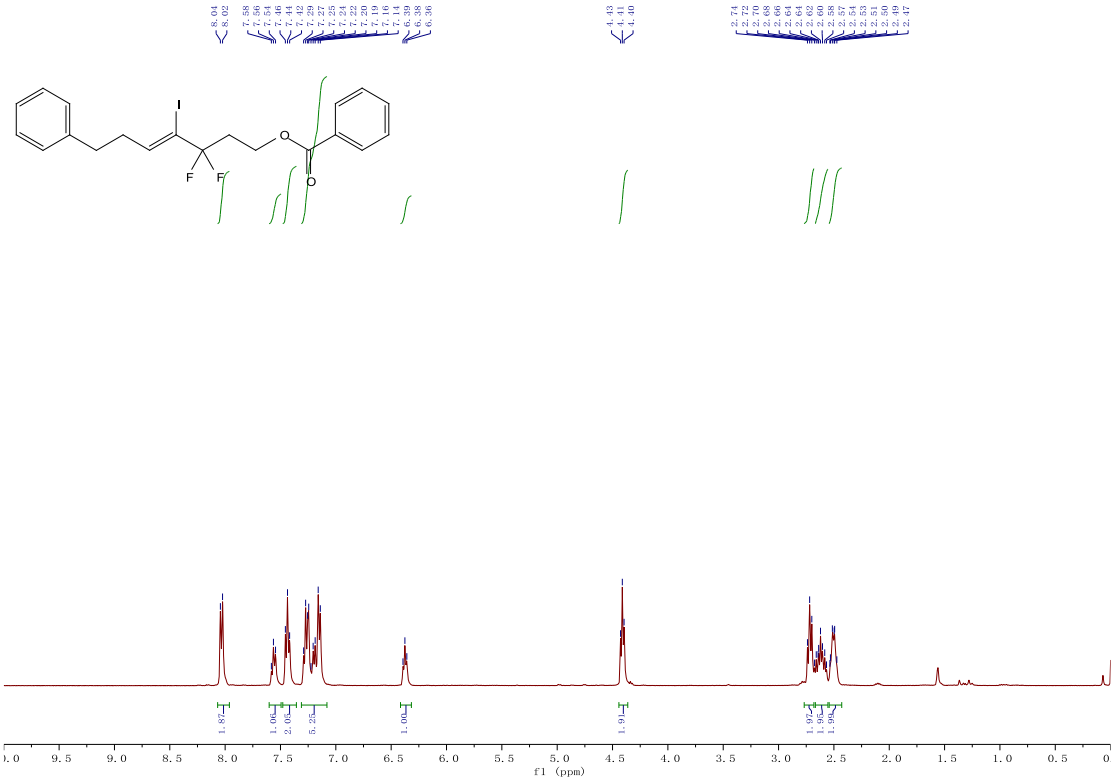
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5b**



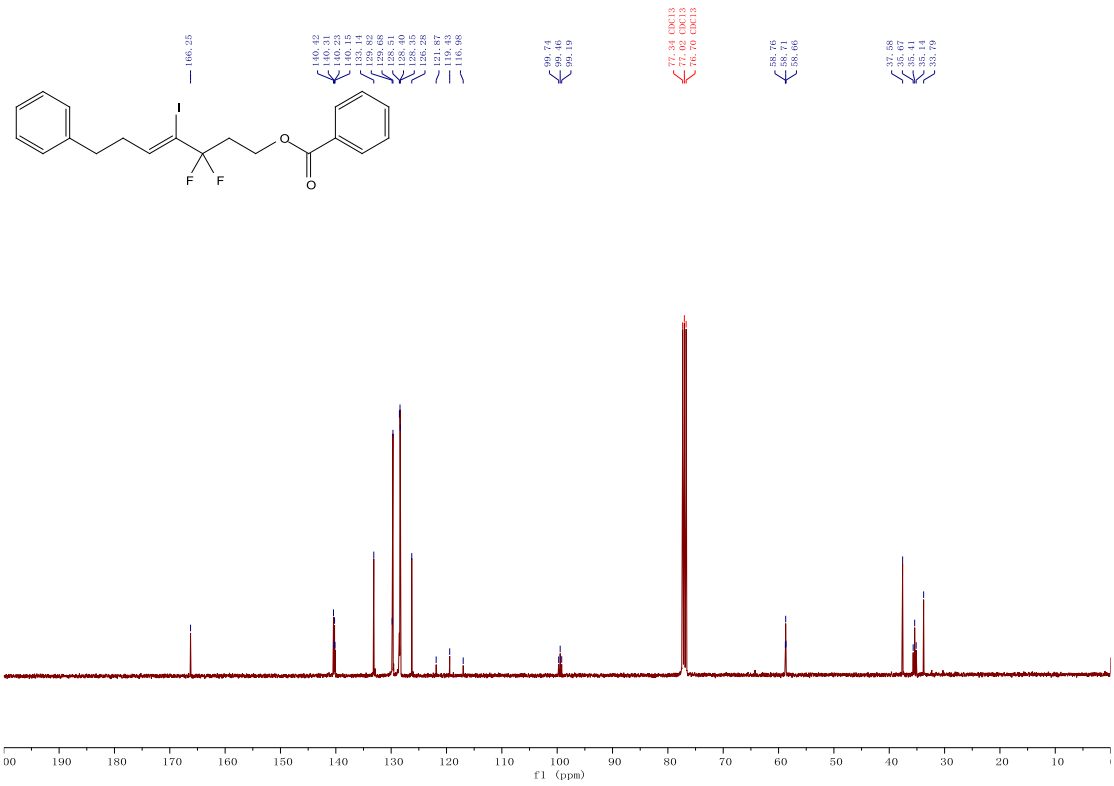
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5b**



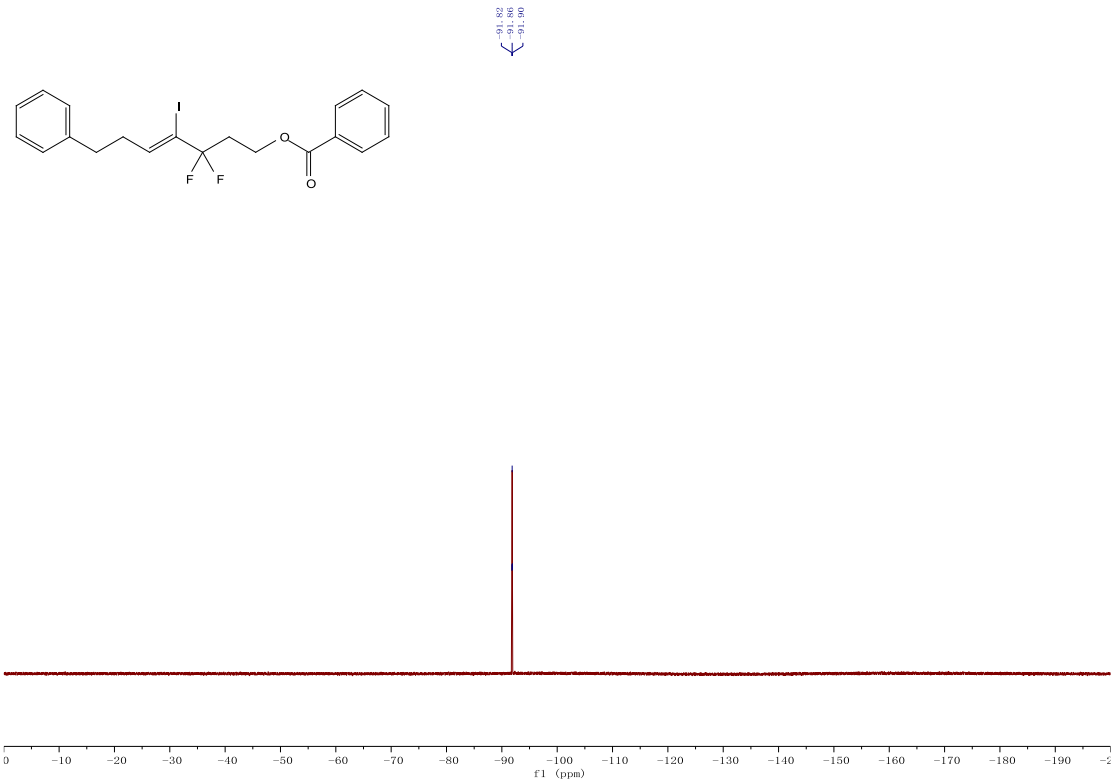
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**



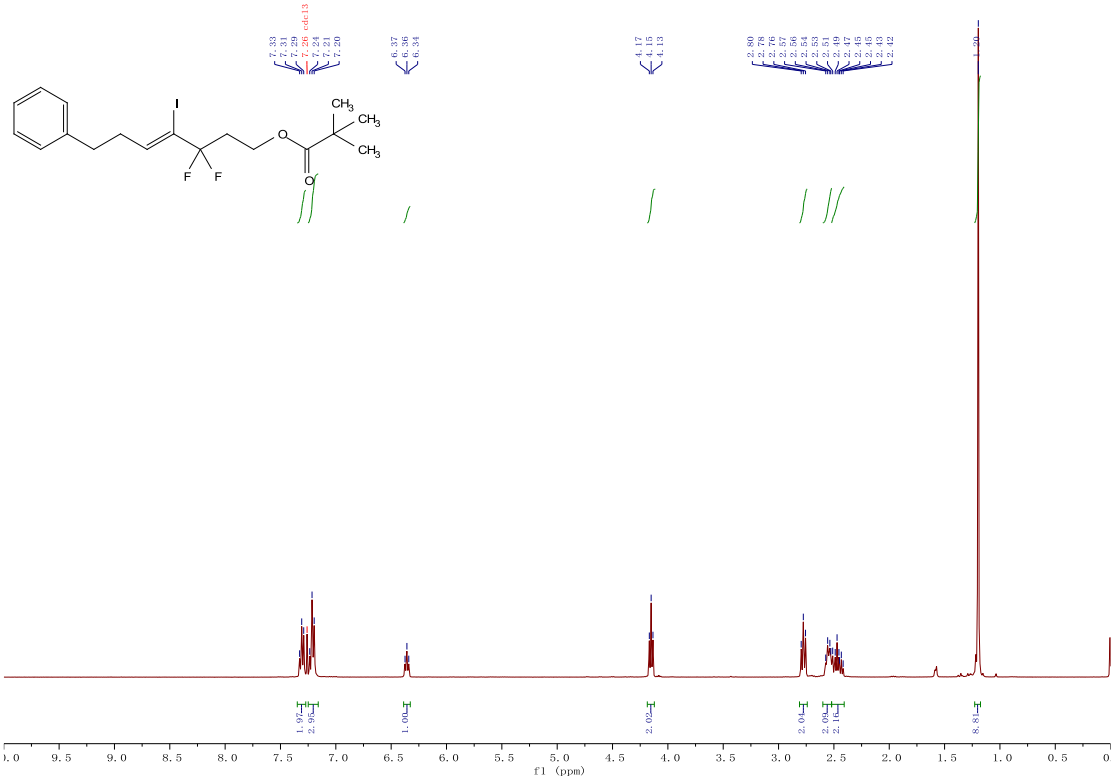
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5c**



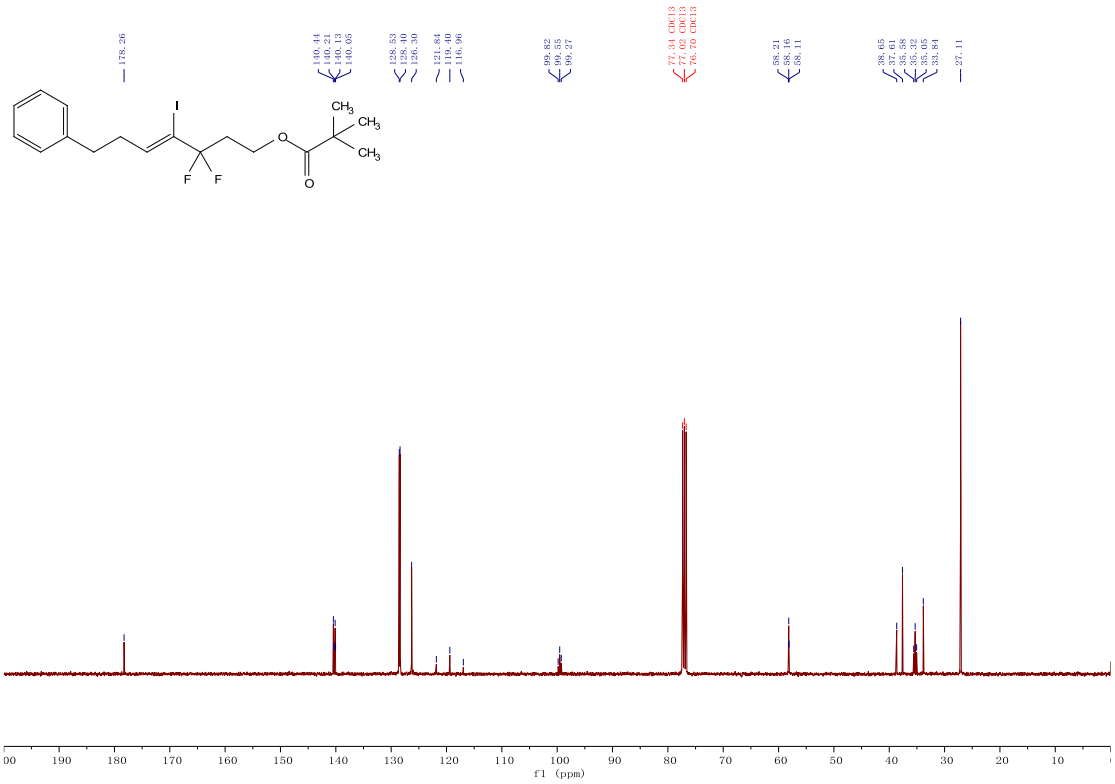
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5c**



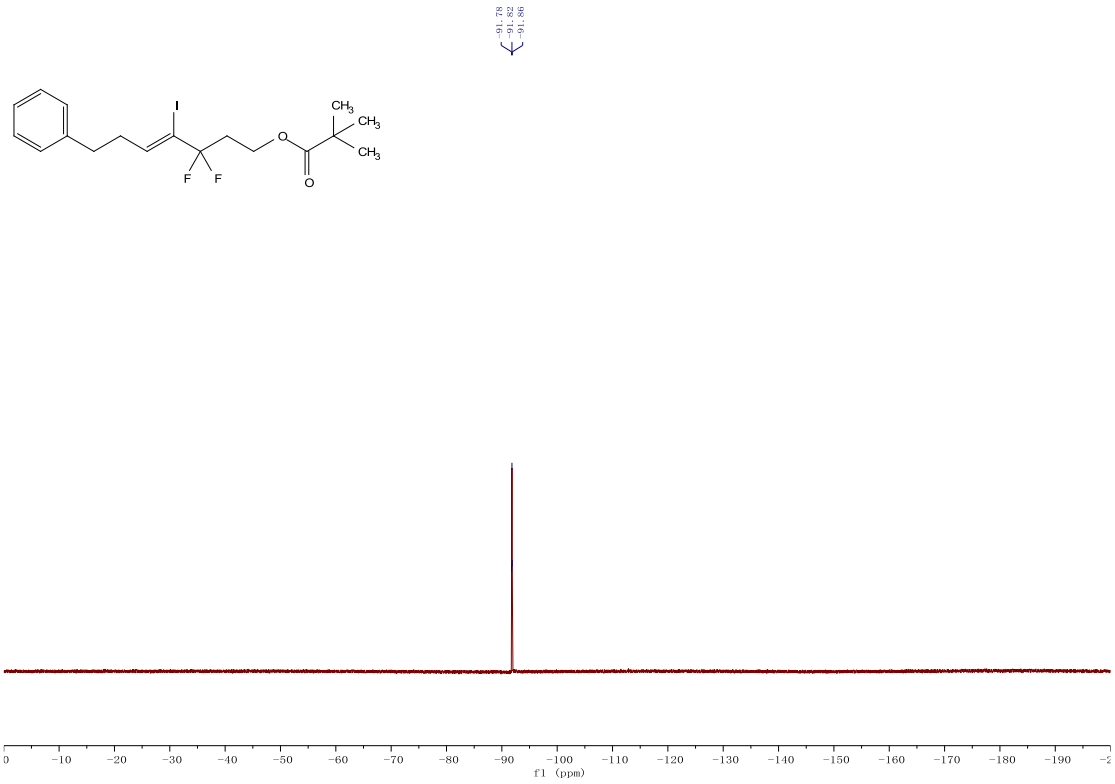
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**



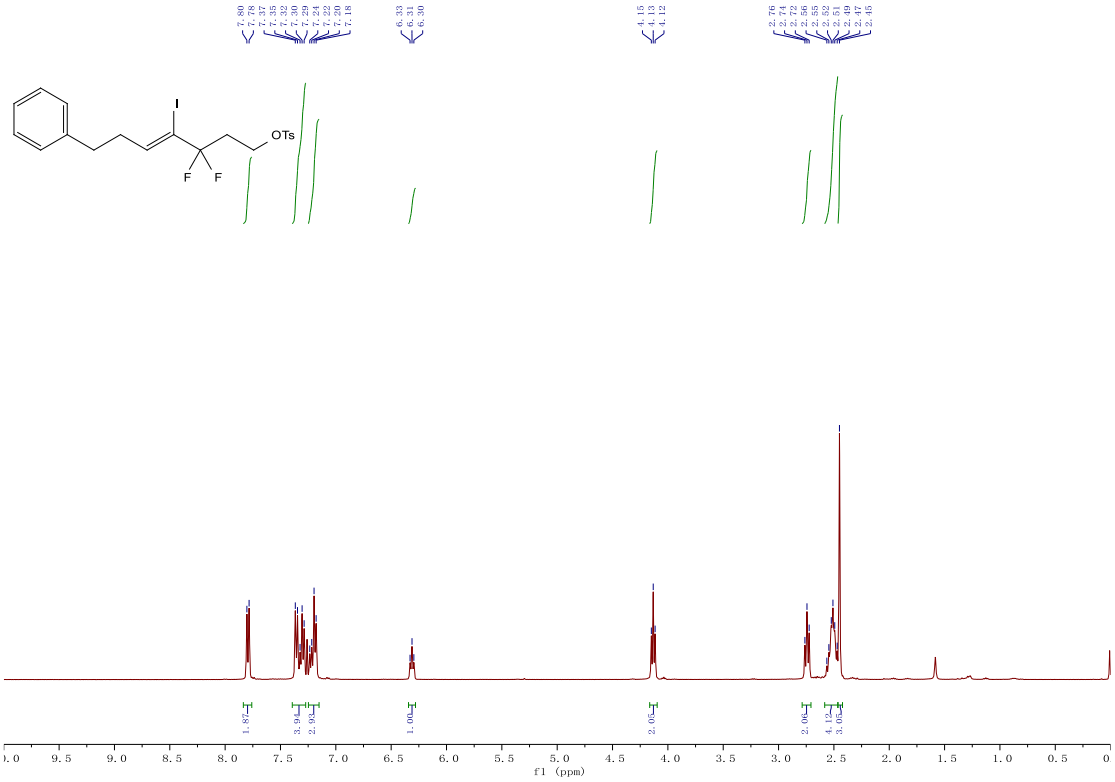
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5d**



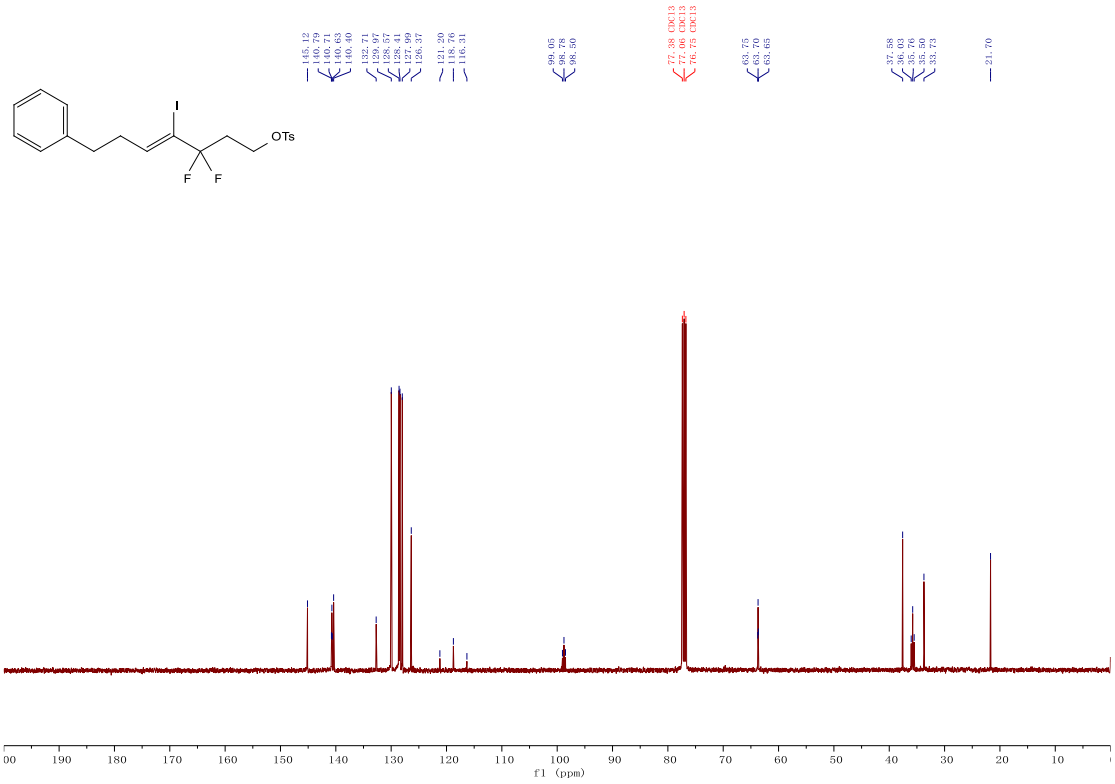
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5d**



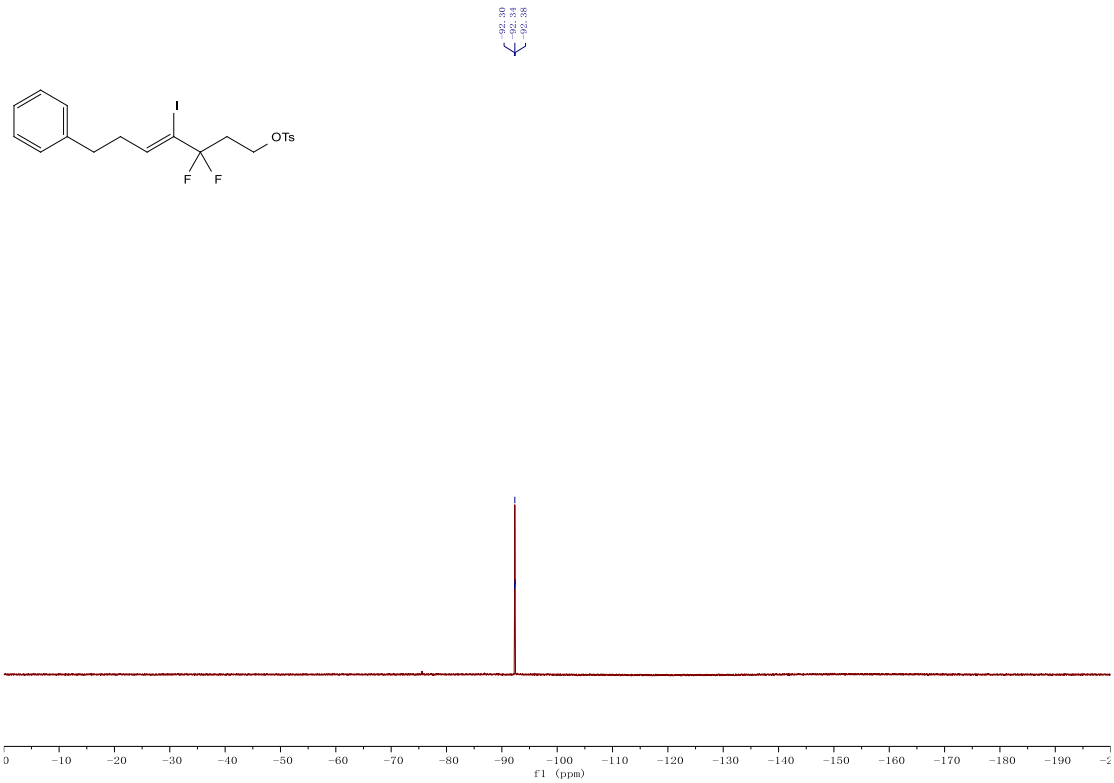
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**



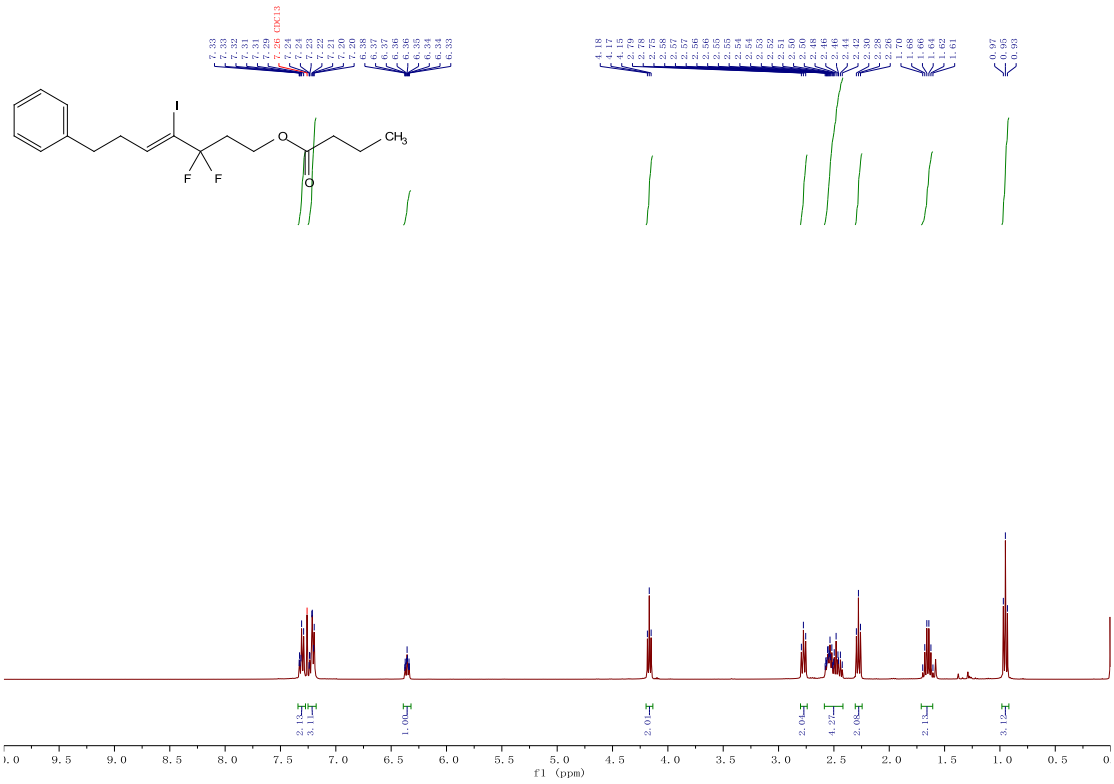
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5e**



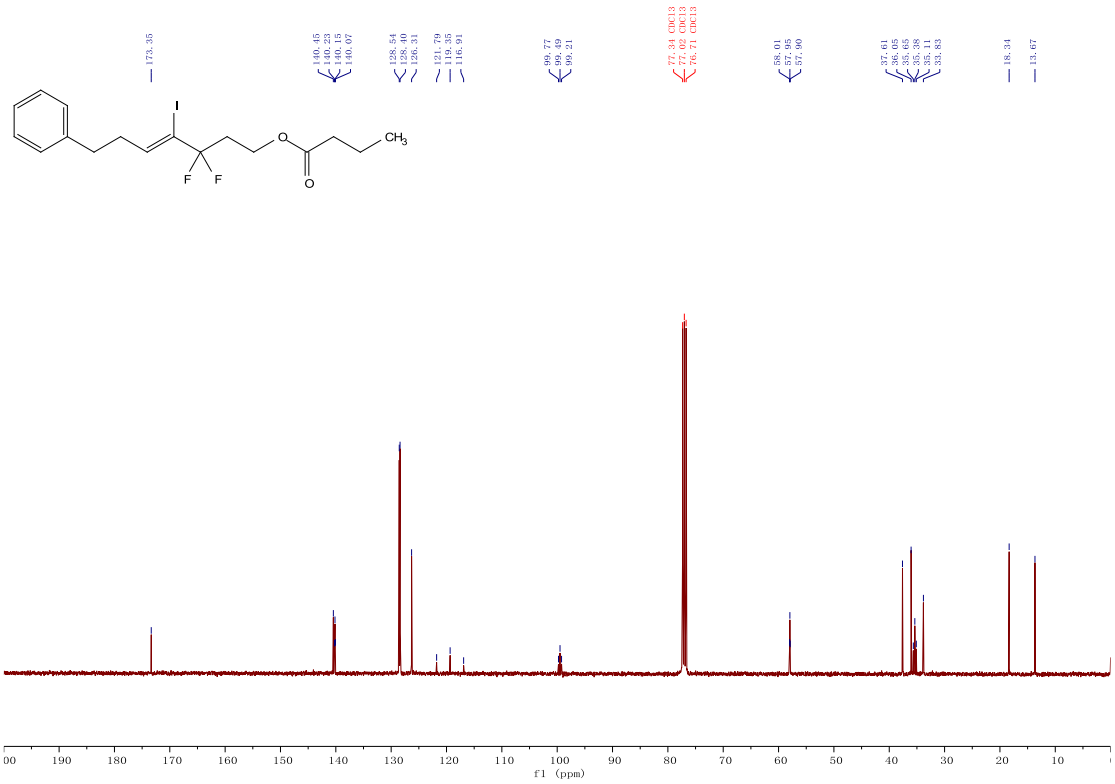
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5e**



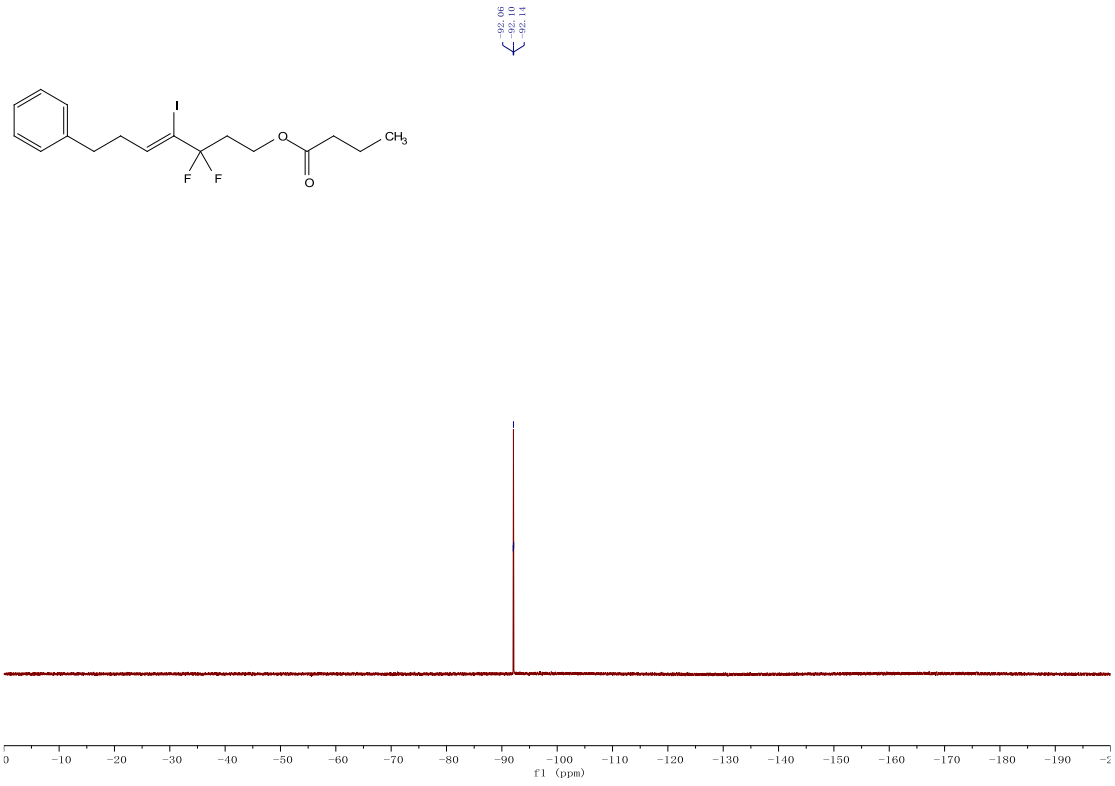
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**



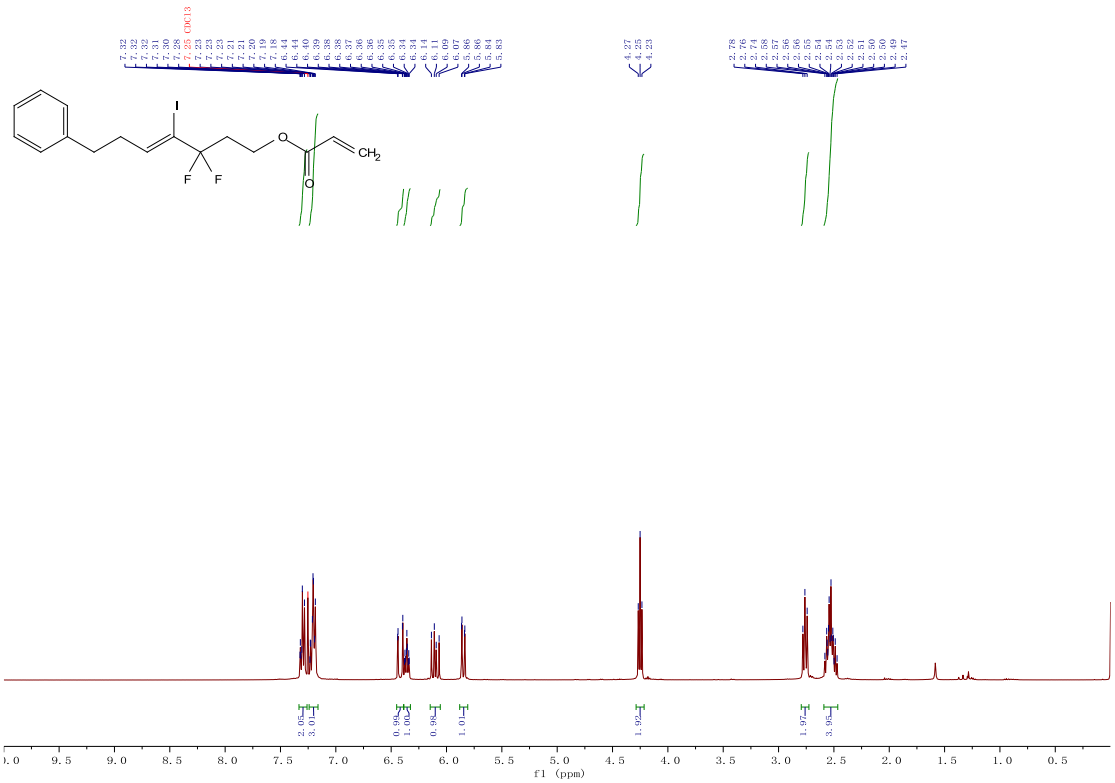
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5f**



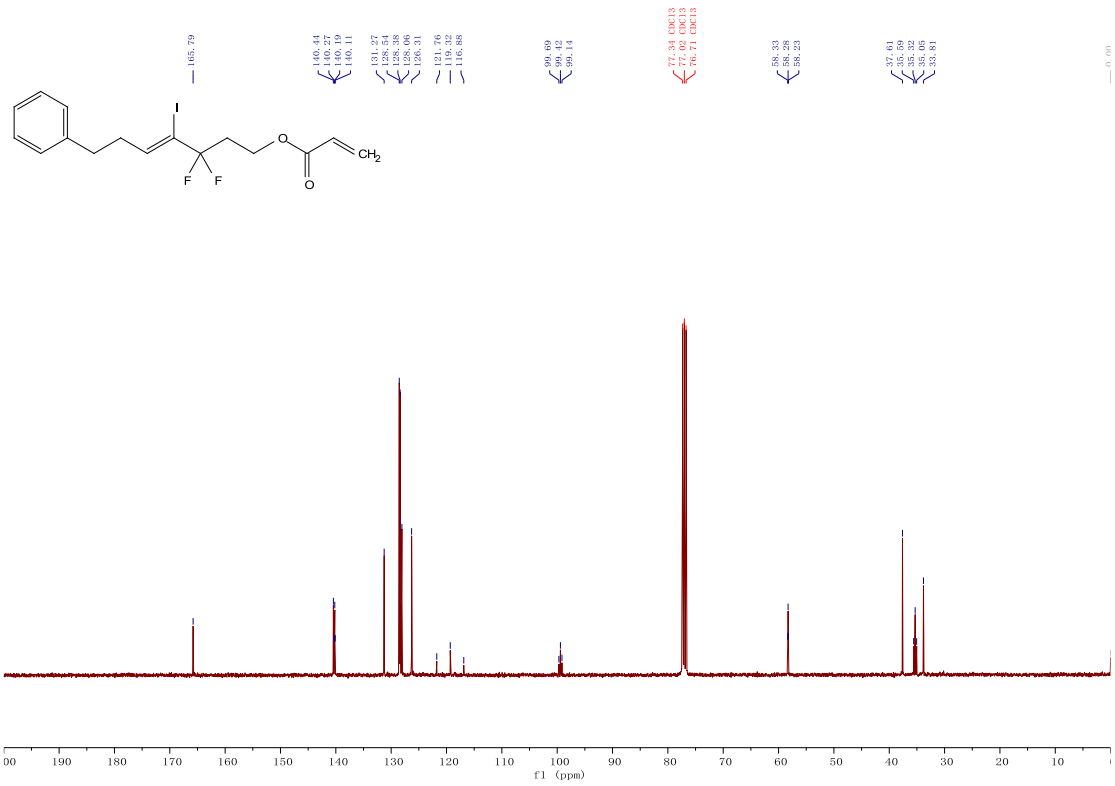
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5f**



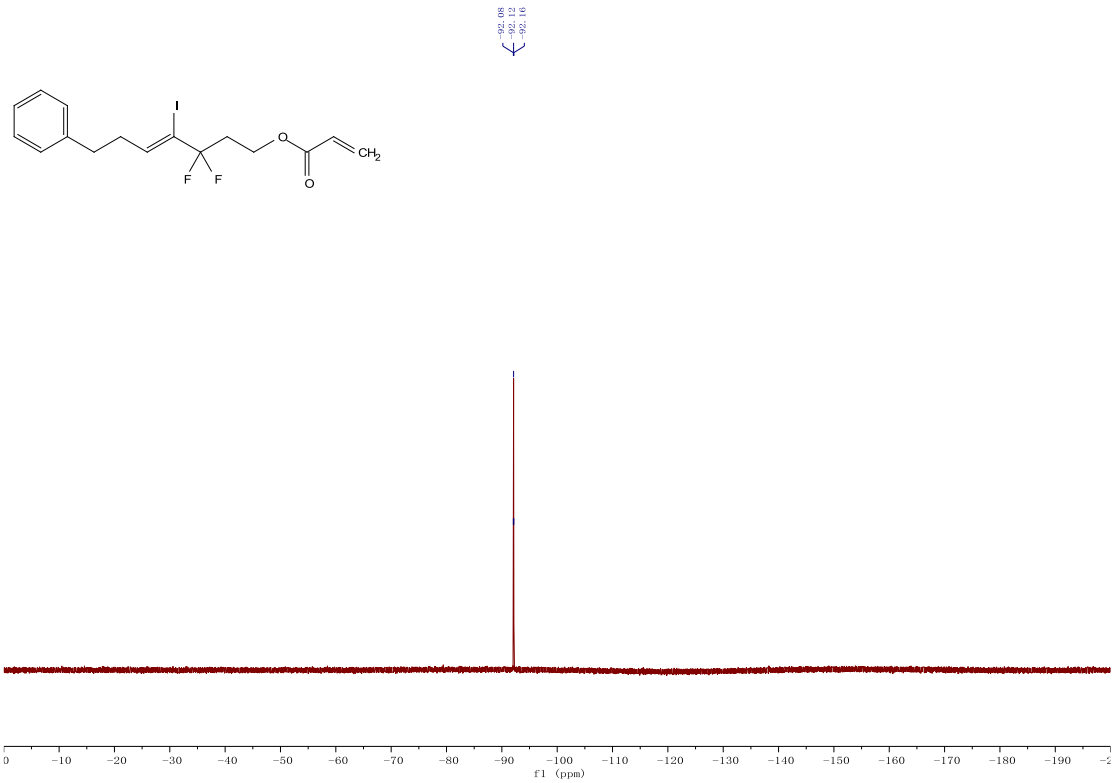
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5g**



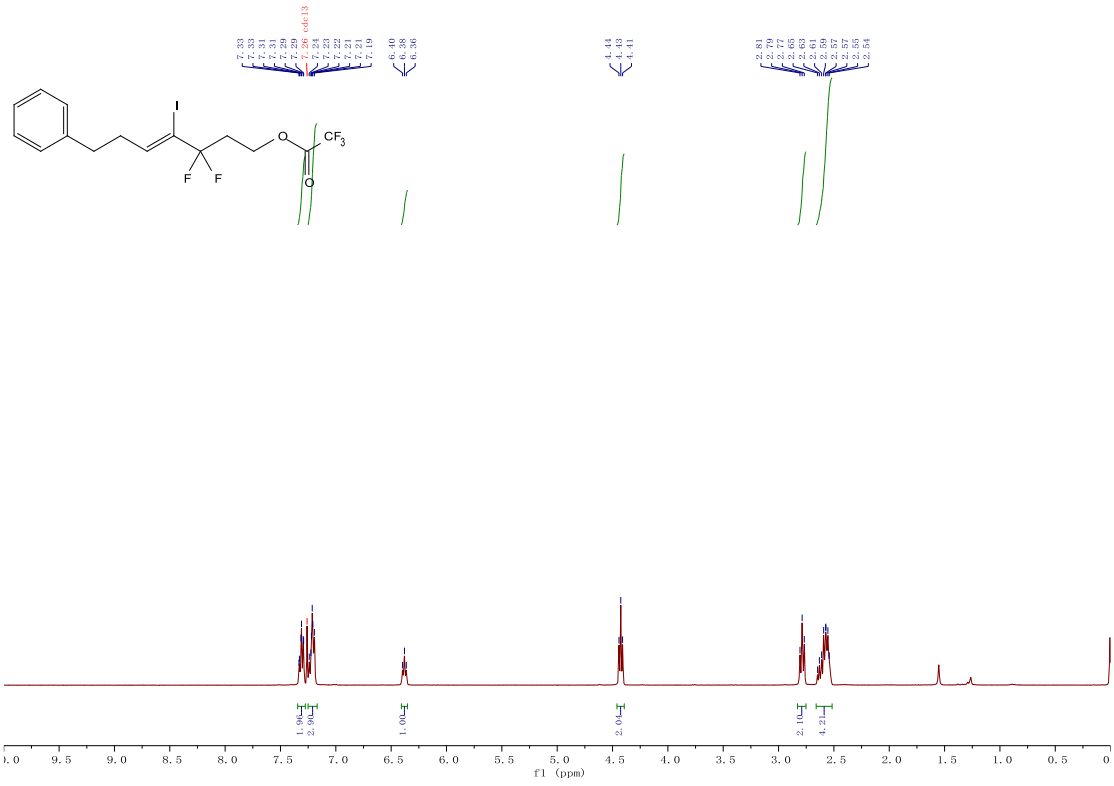
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5g**



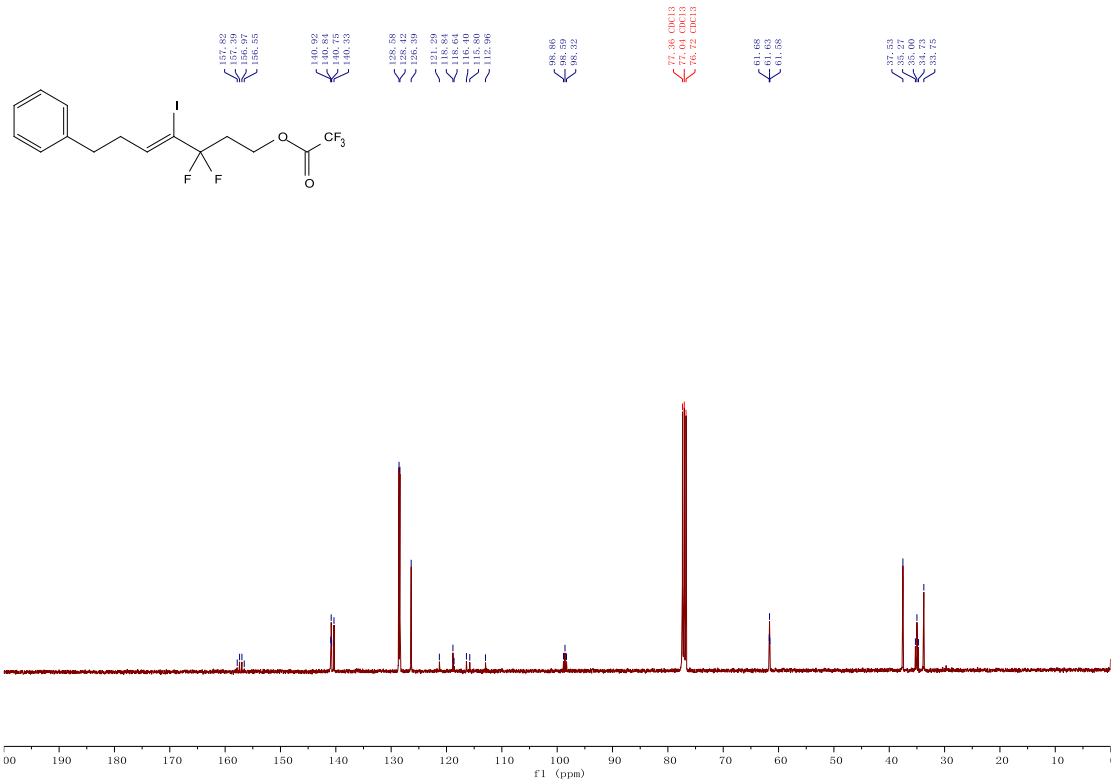
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5g**



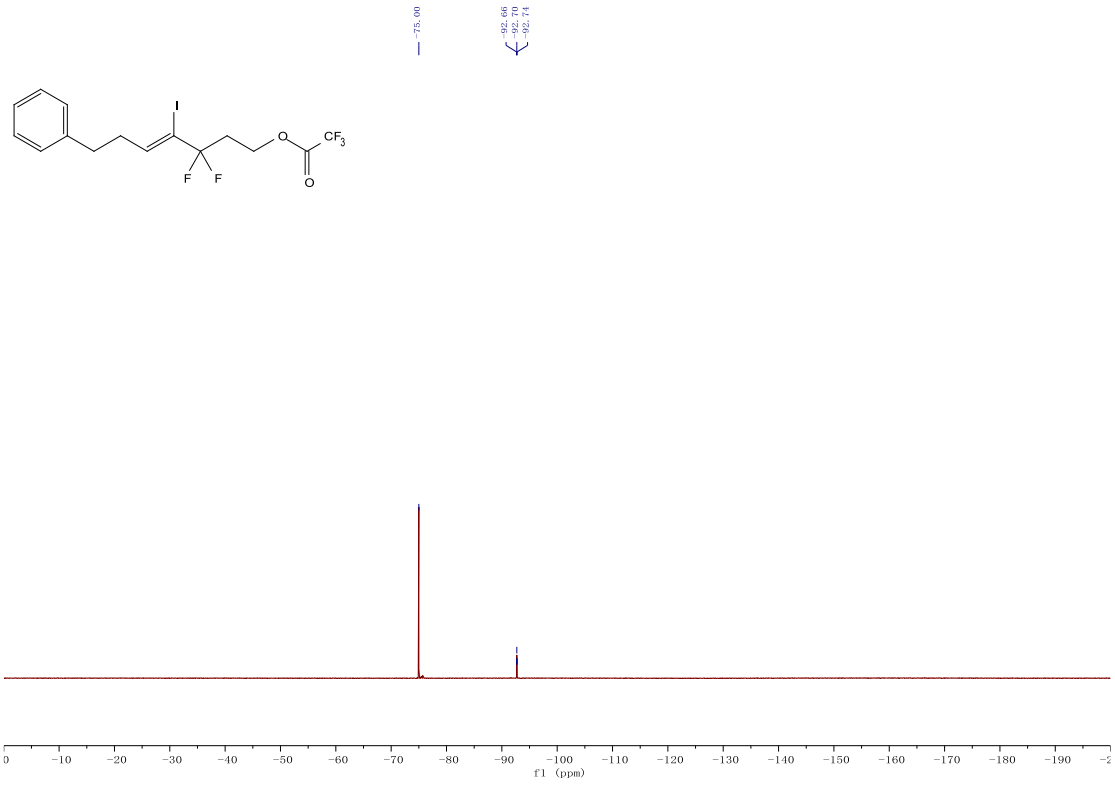
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**



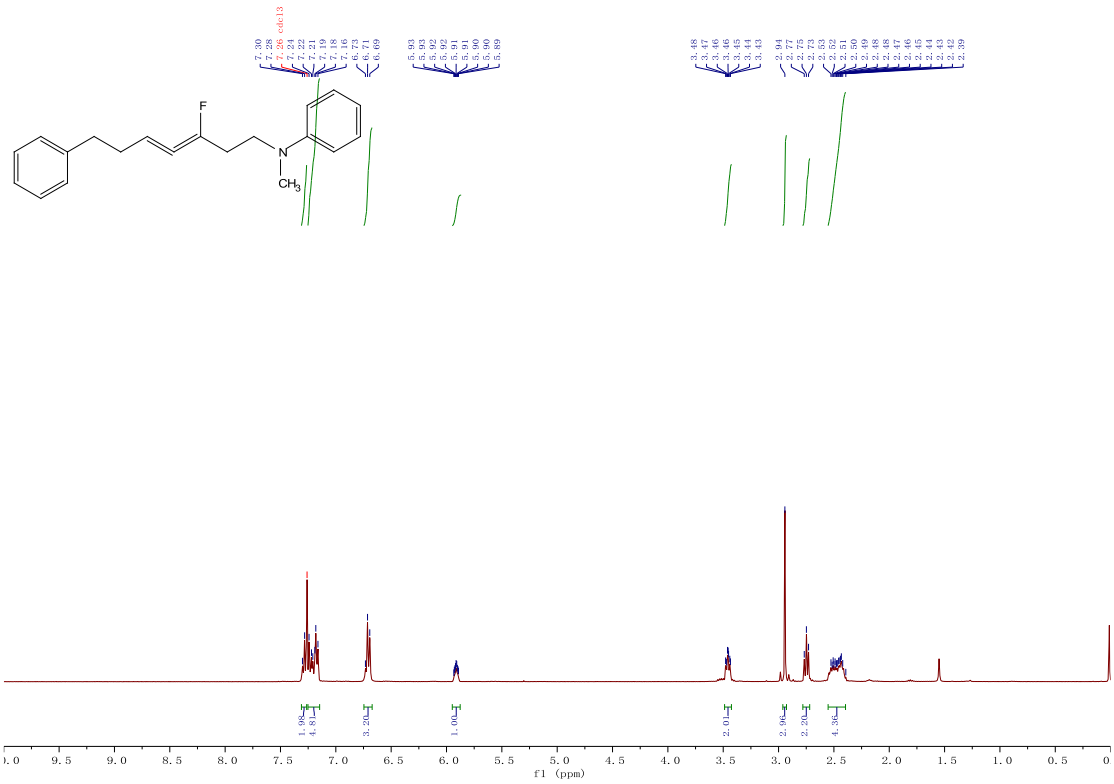
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5h**



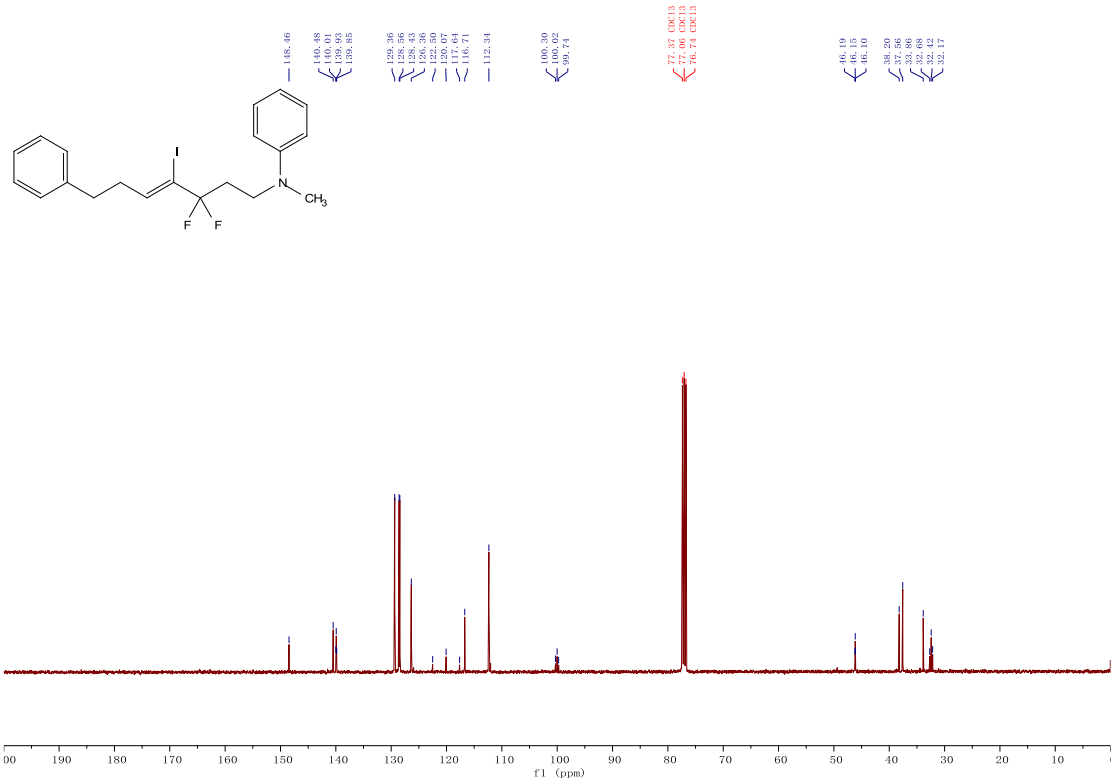
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5h**



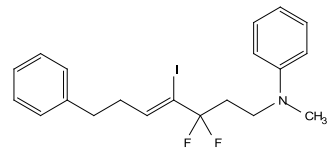
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**

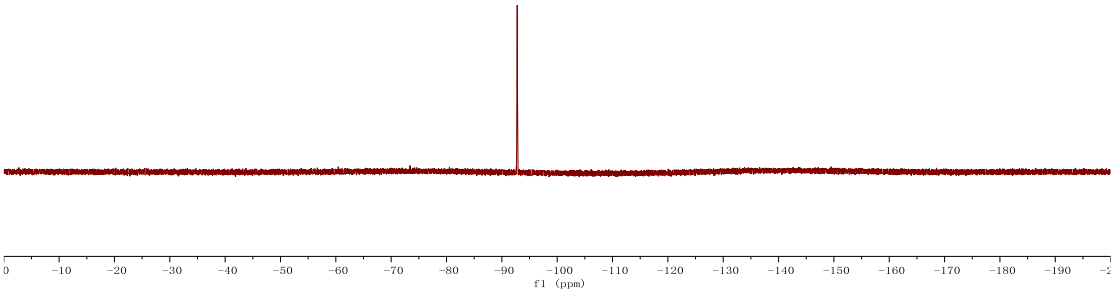


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5i**

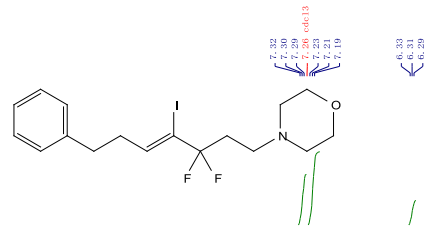


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5i**

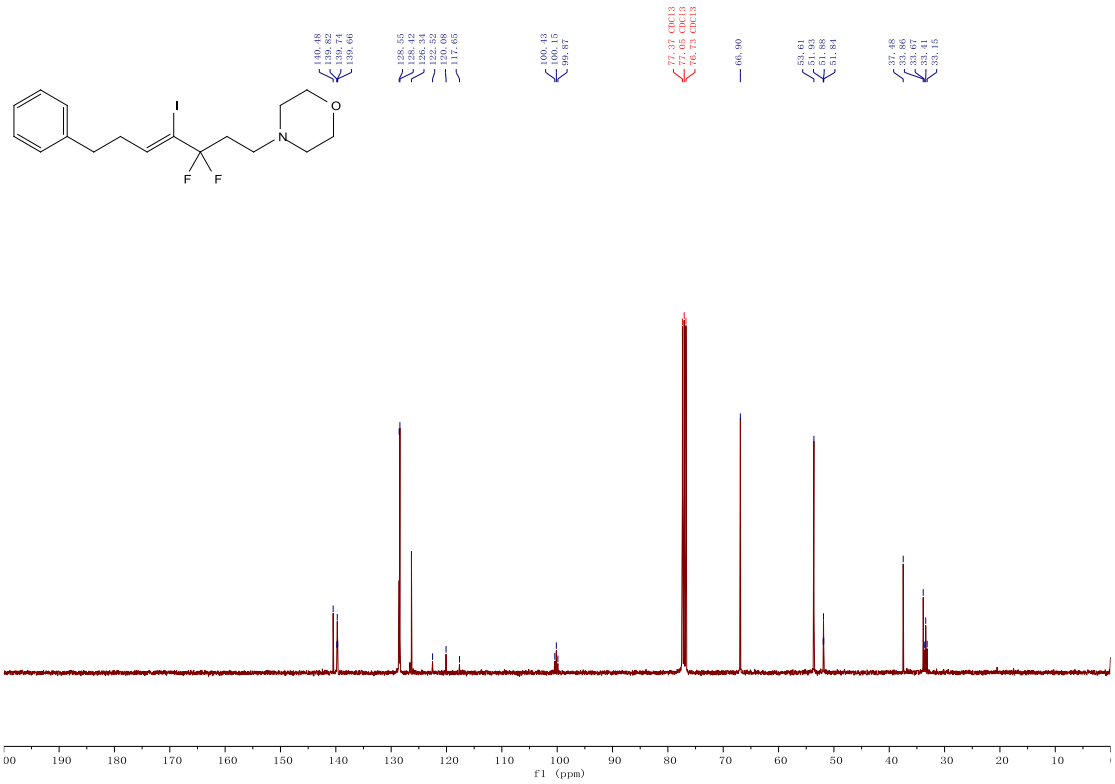




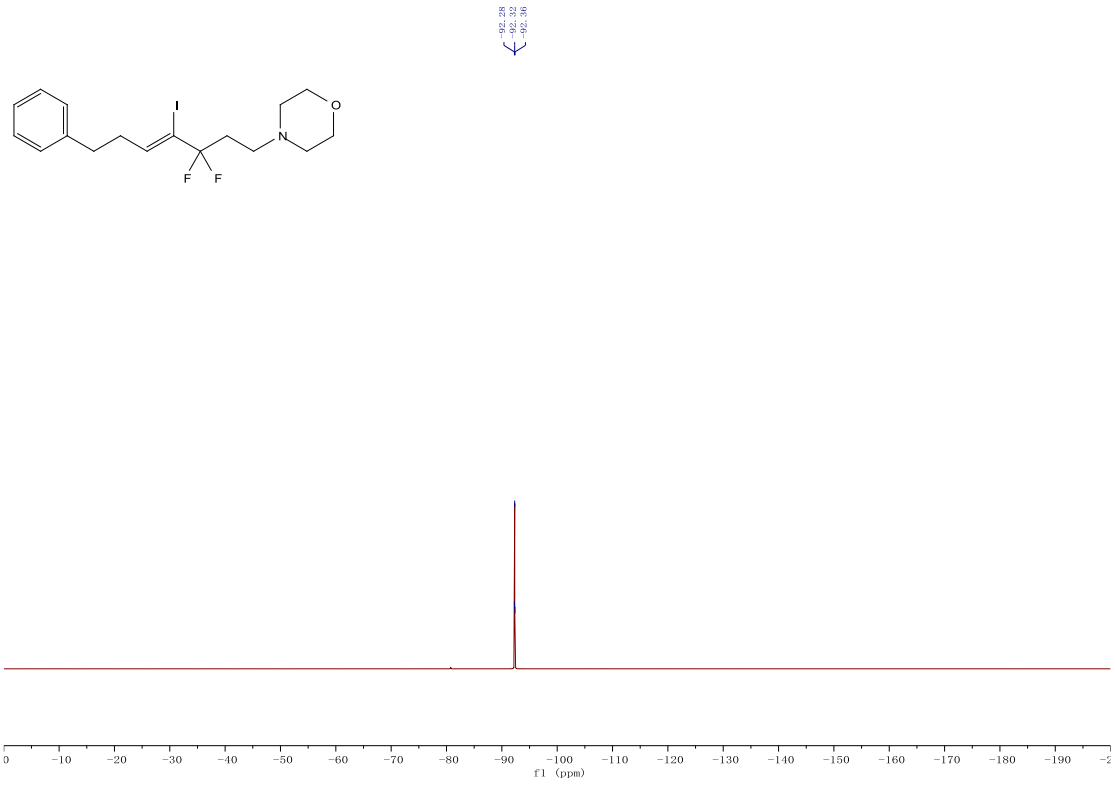
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5j**



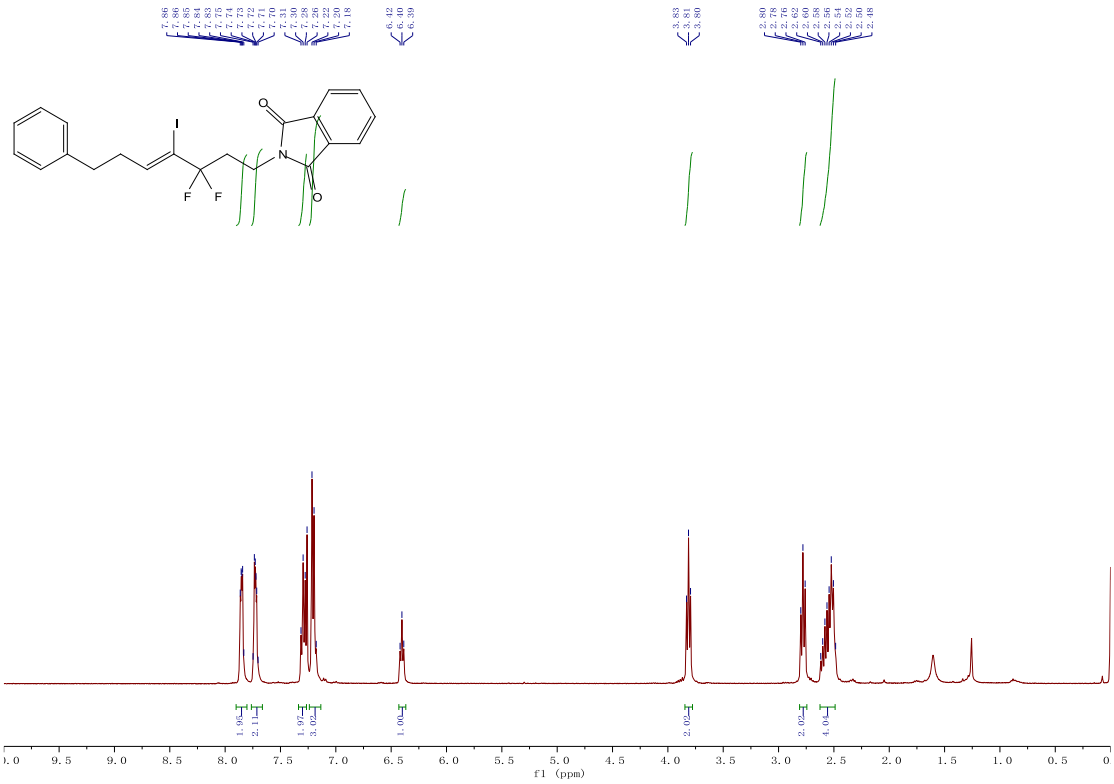
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5j**



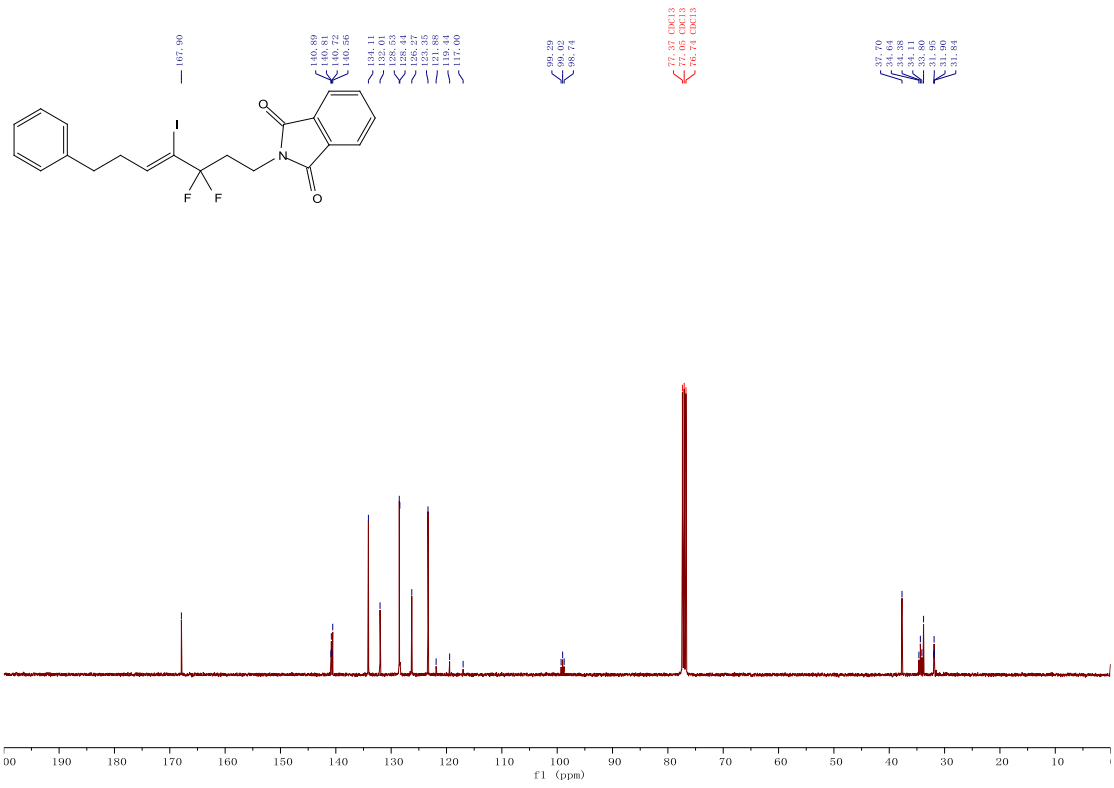
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5j**



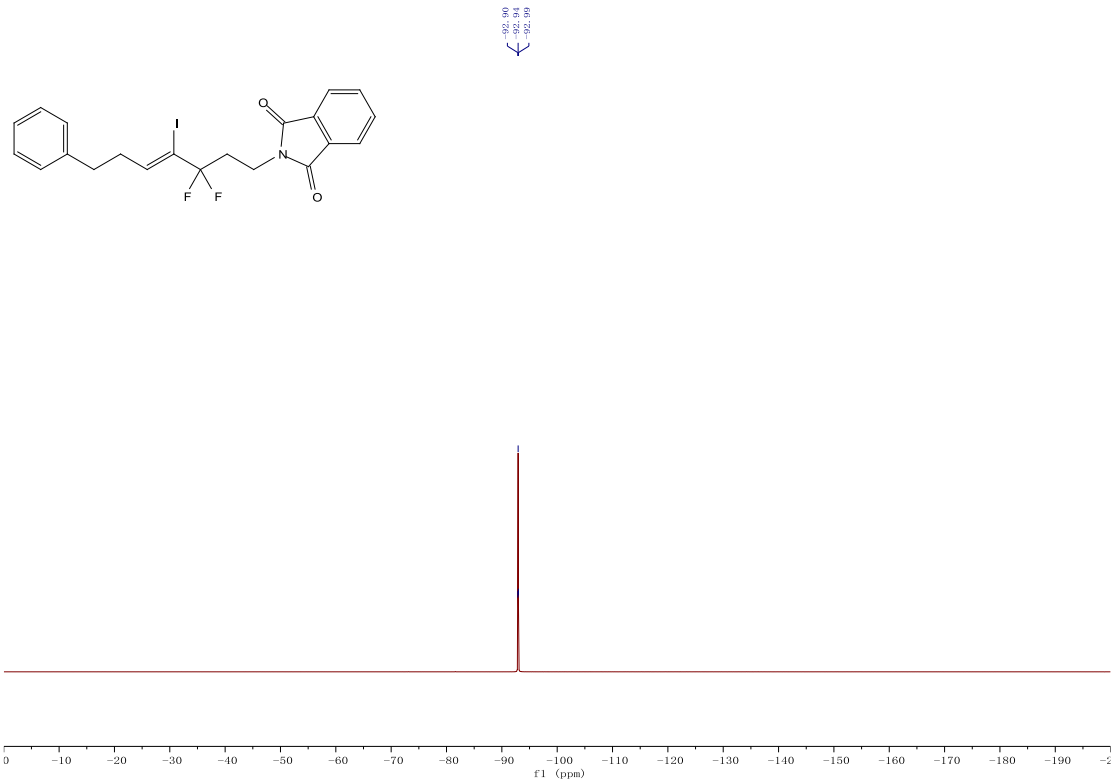
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5k**



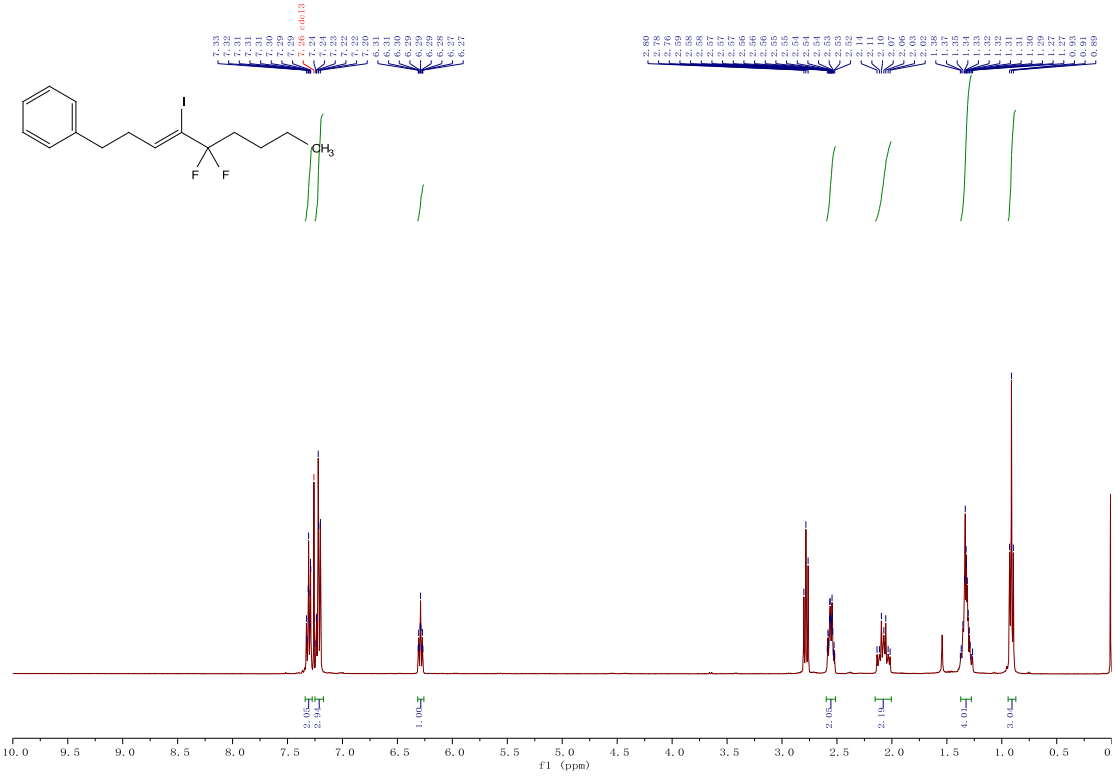
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5k**



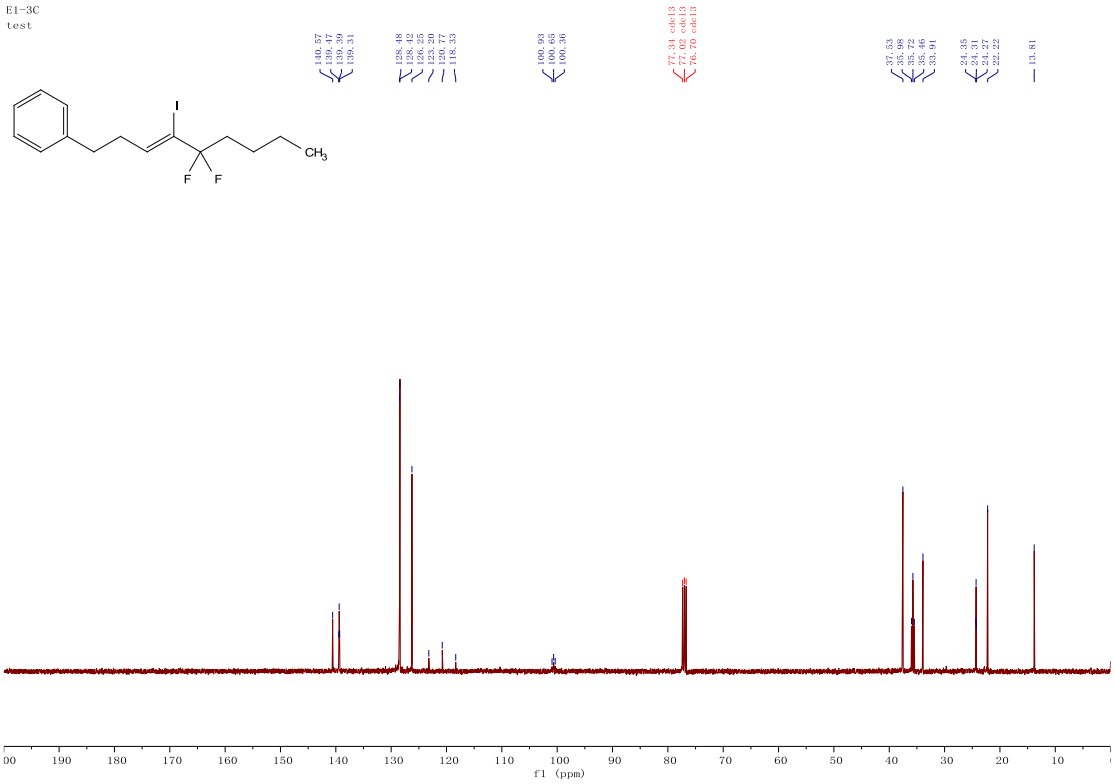
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5k**



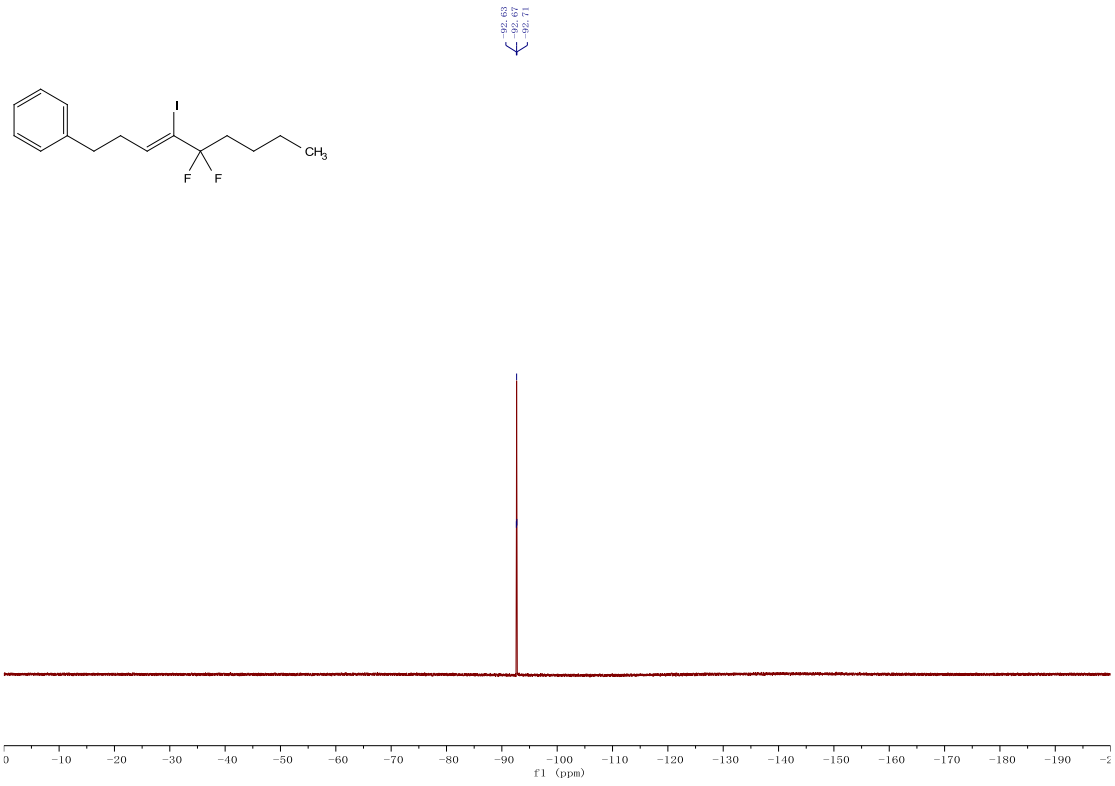
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5l**



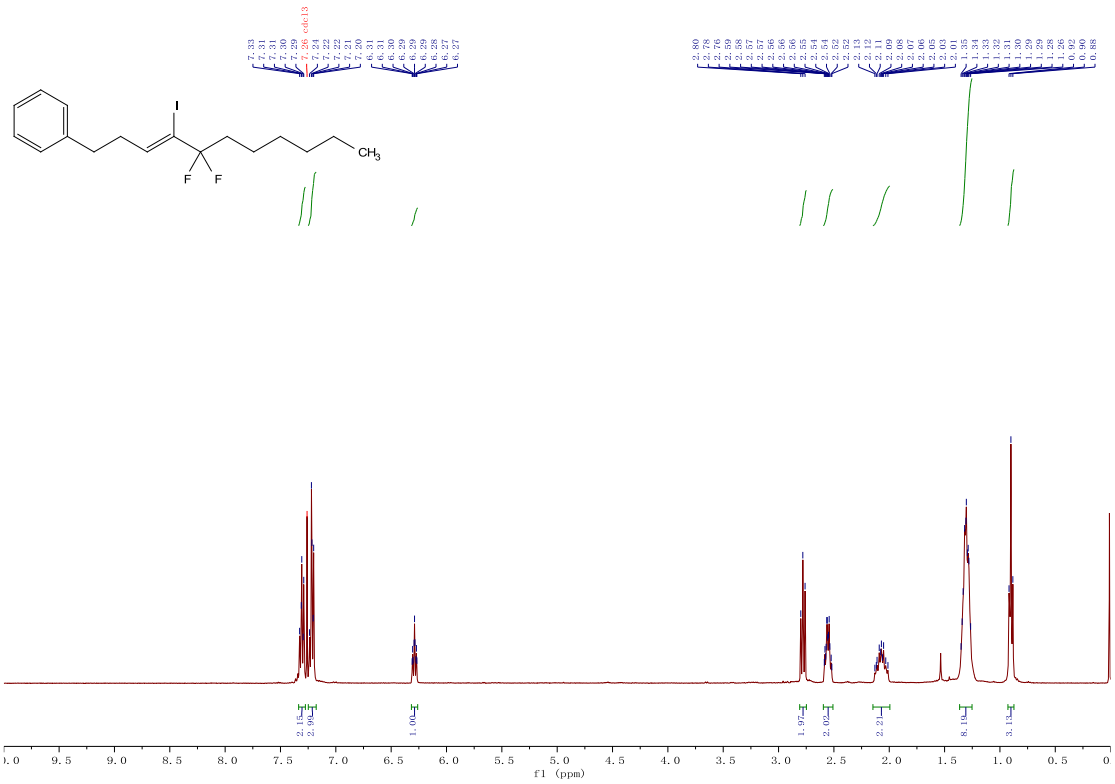
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5l**



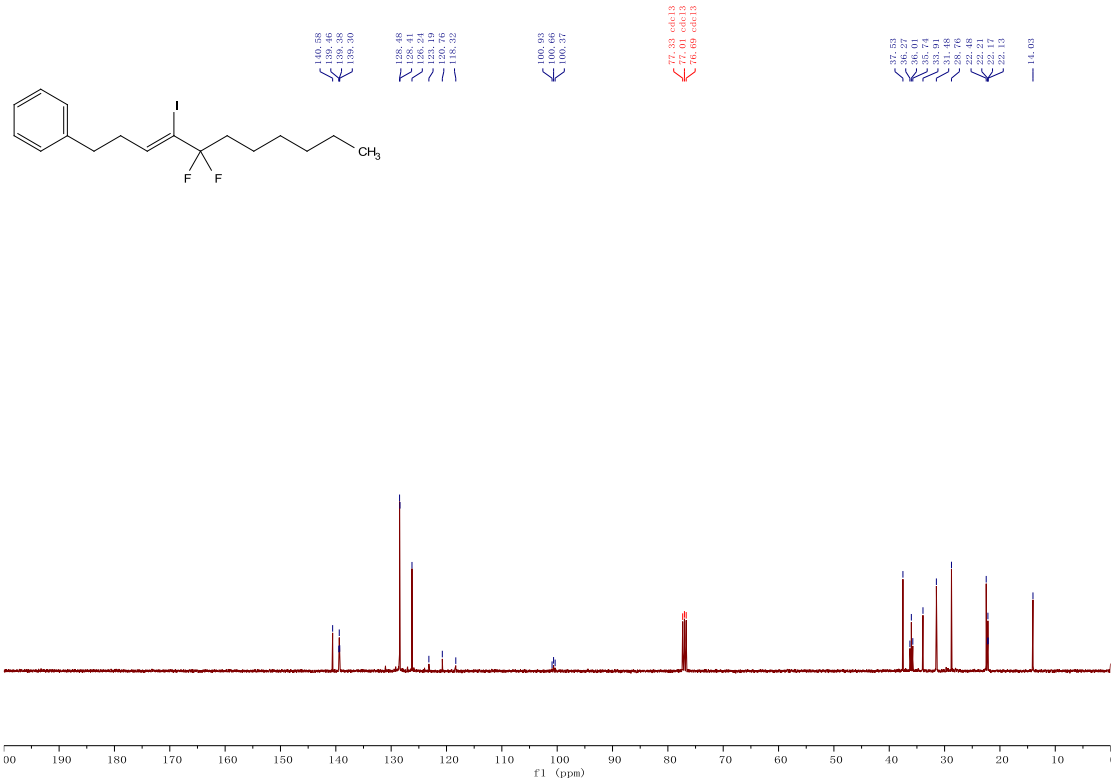
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5l**



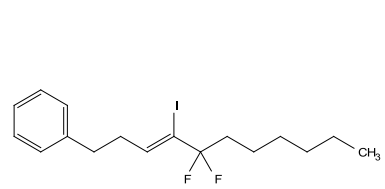
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5m**



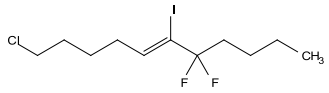
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5m**



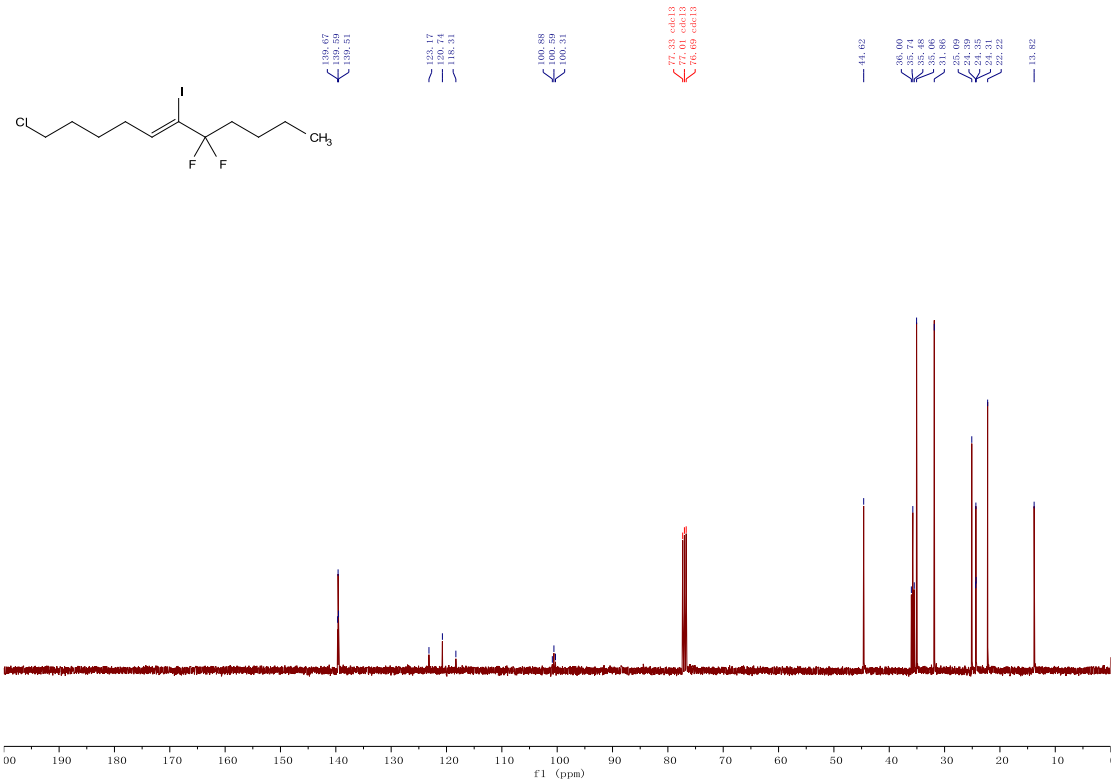
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5m**



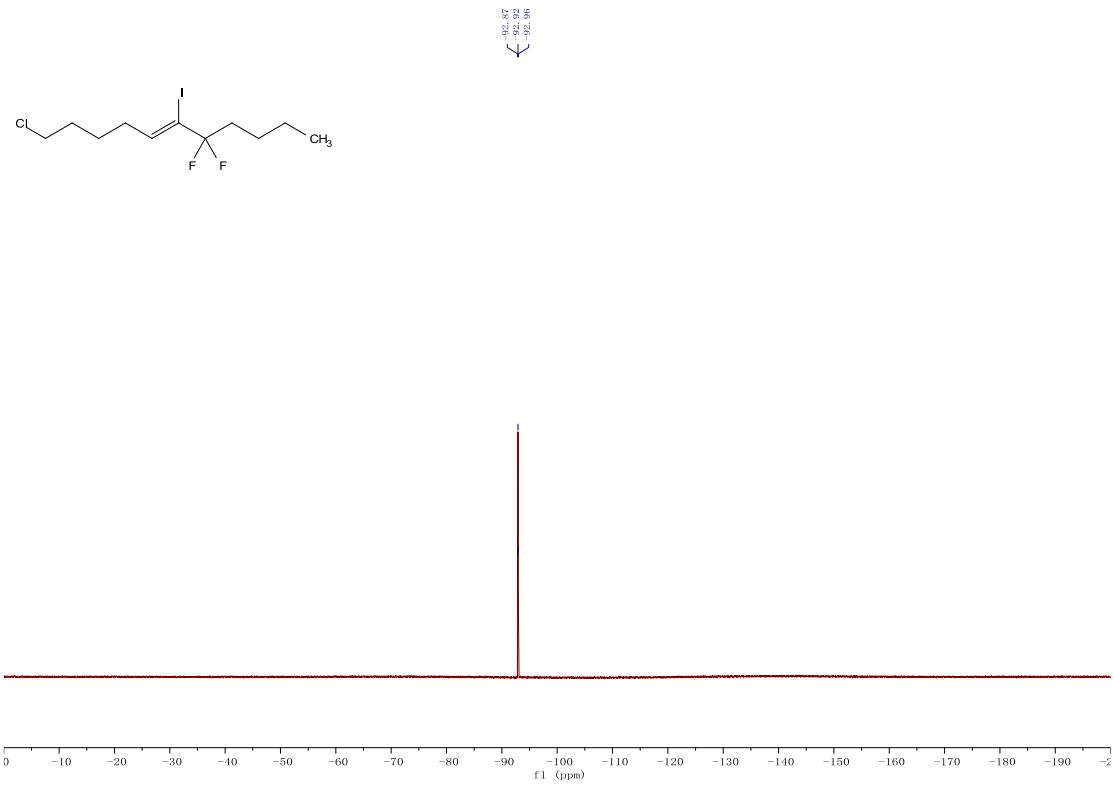
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**



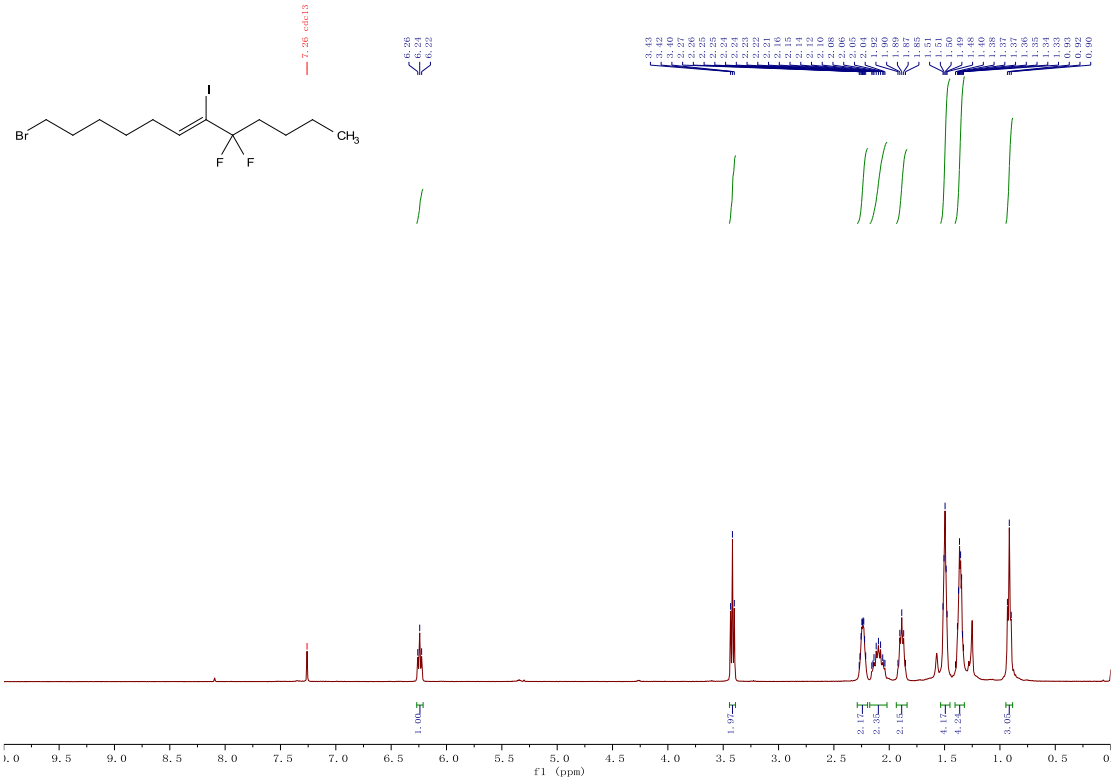
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5n**



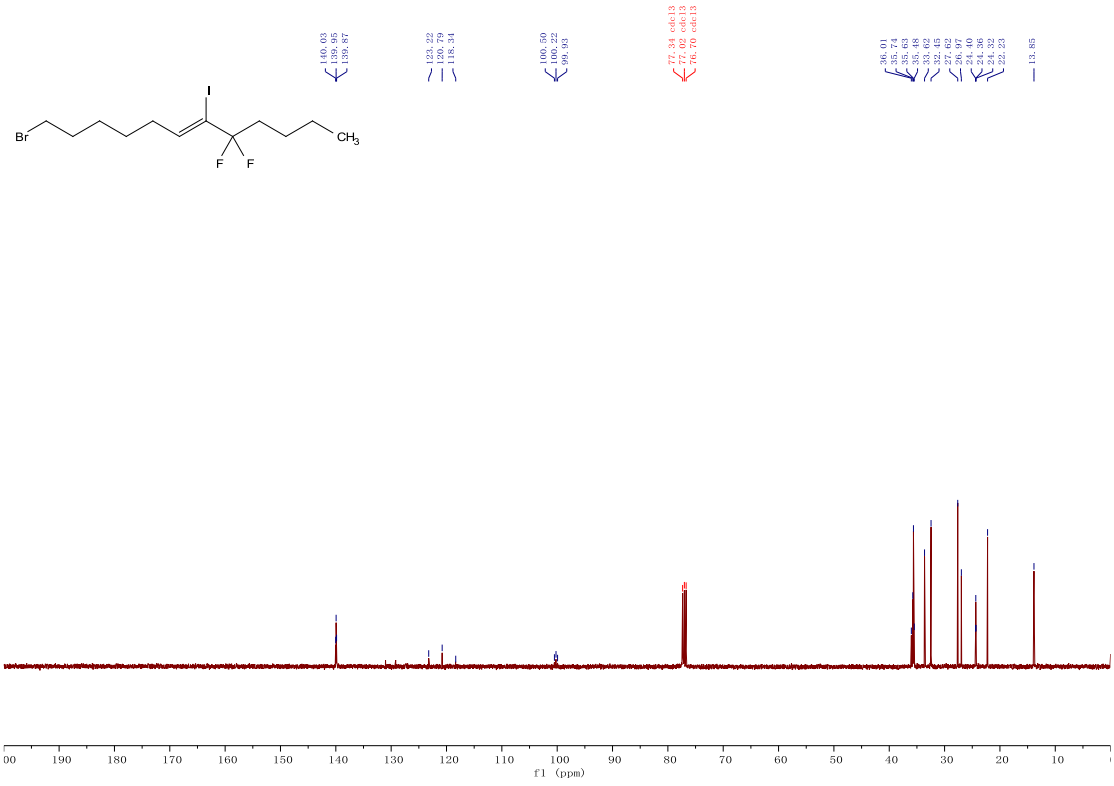
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5n**



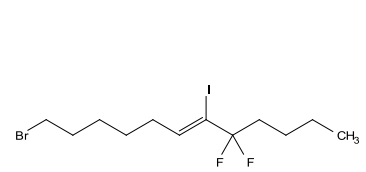
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**



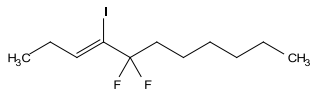
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5o**



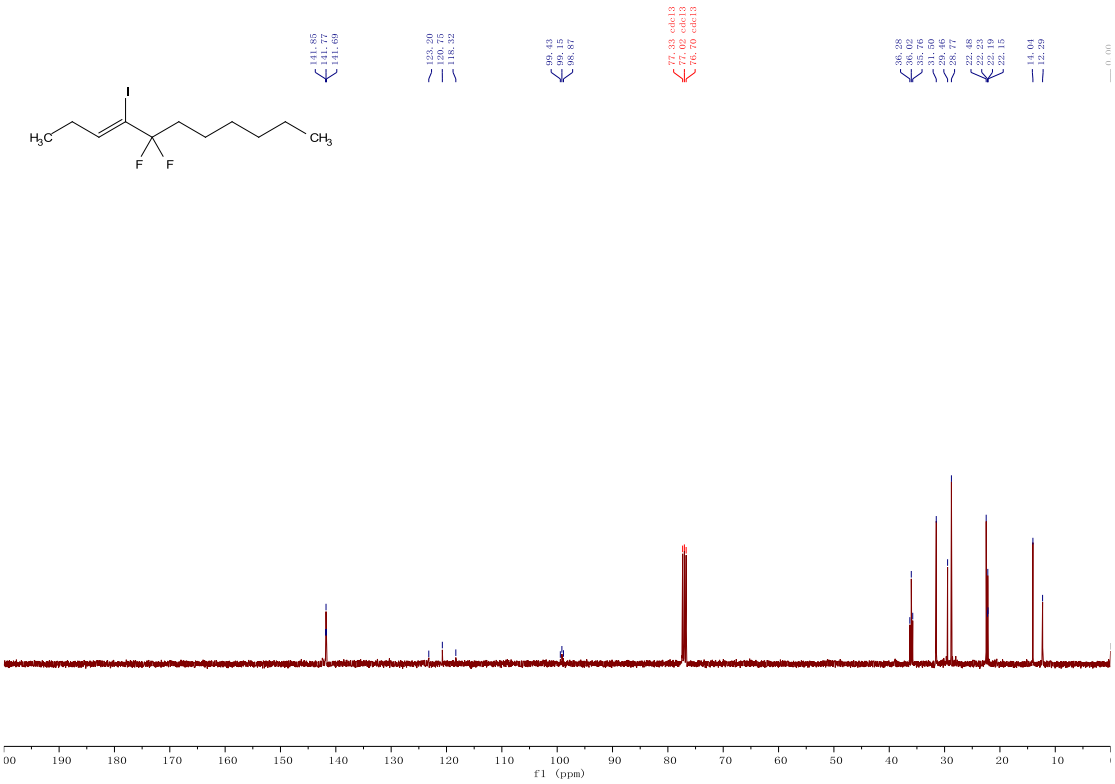
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5o**



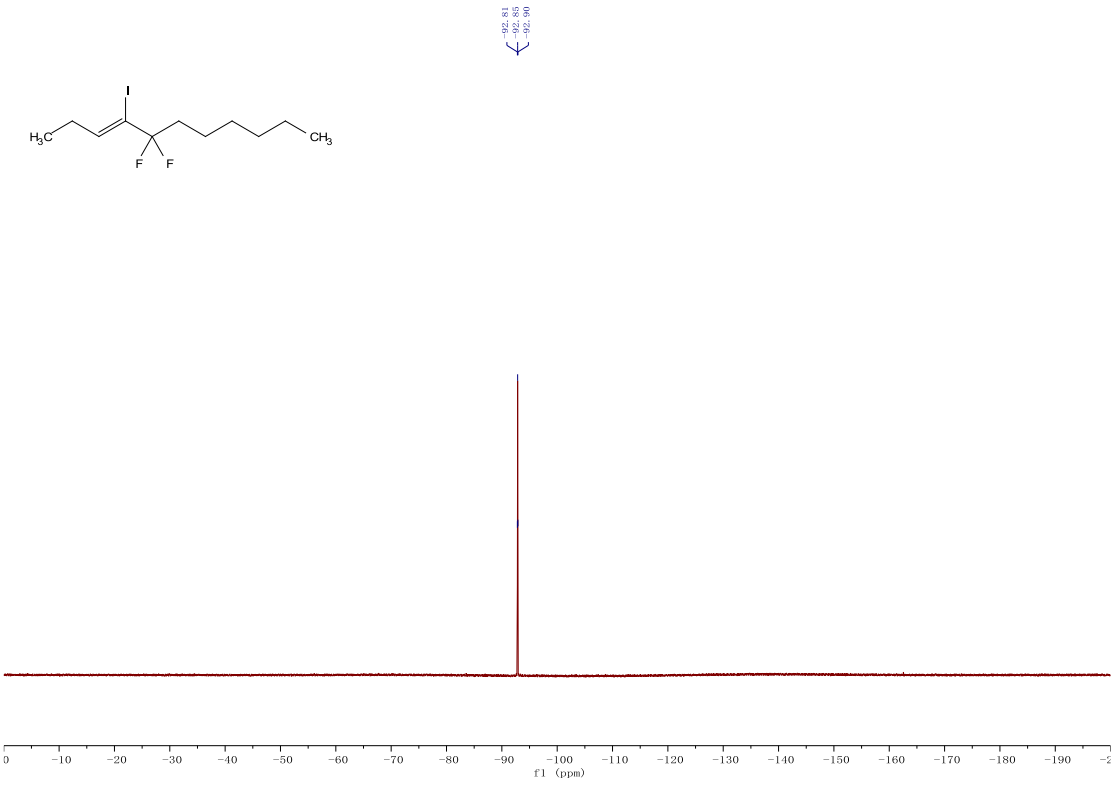
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5p**



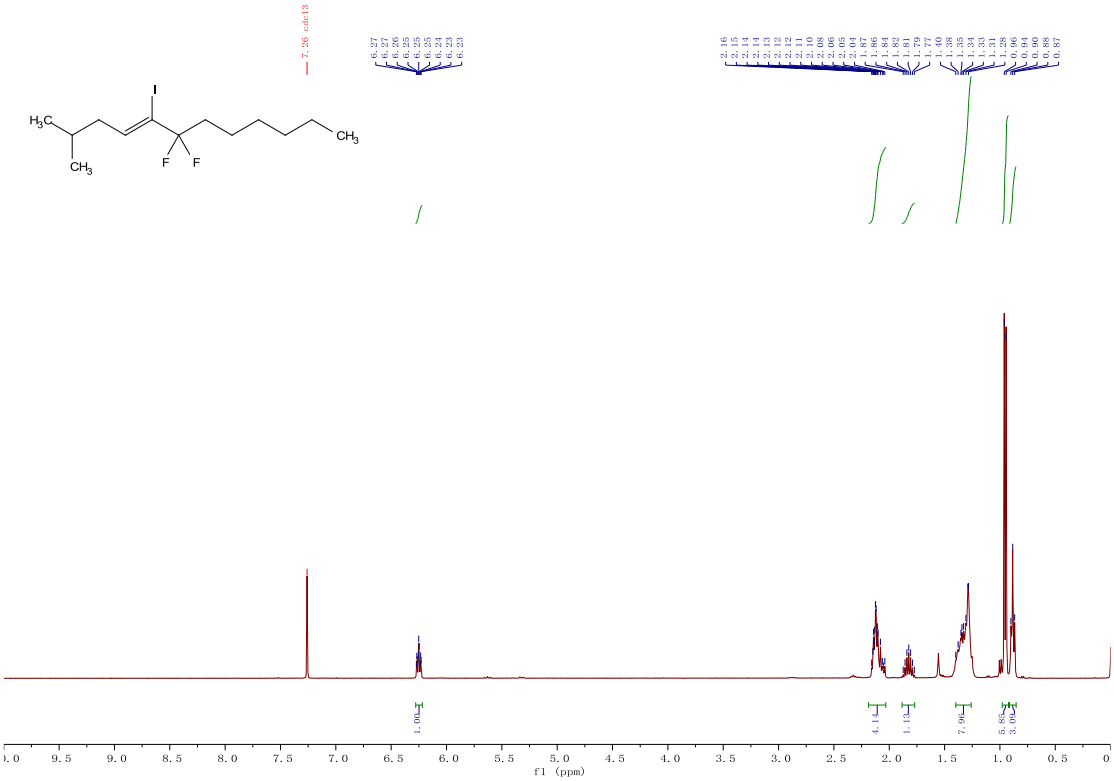
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5p**



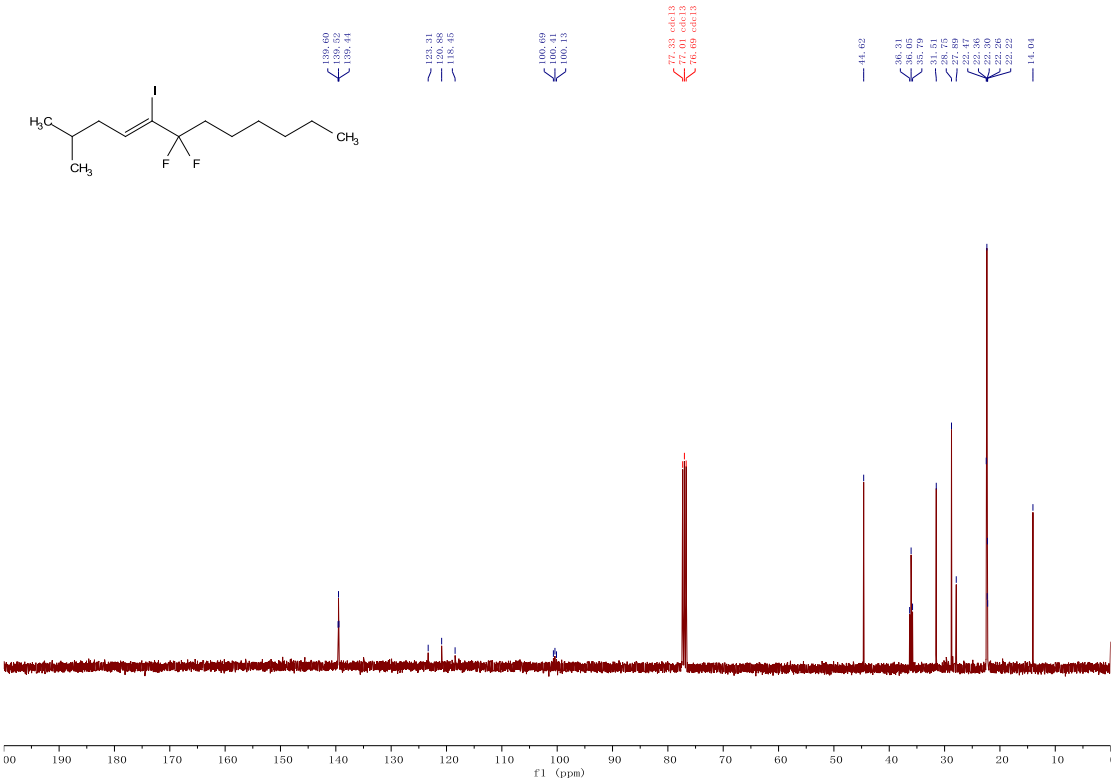
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5p**



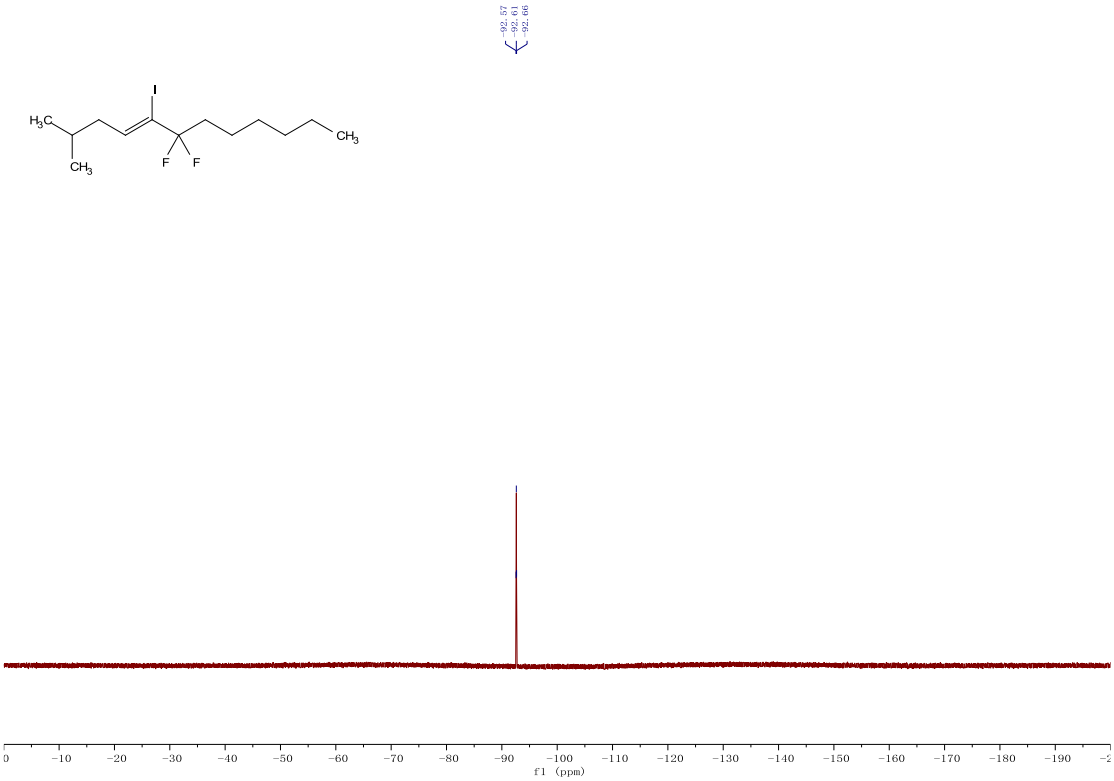
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5q**



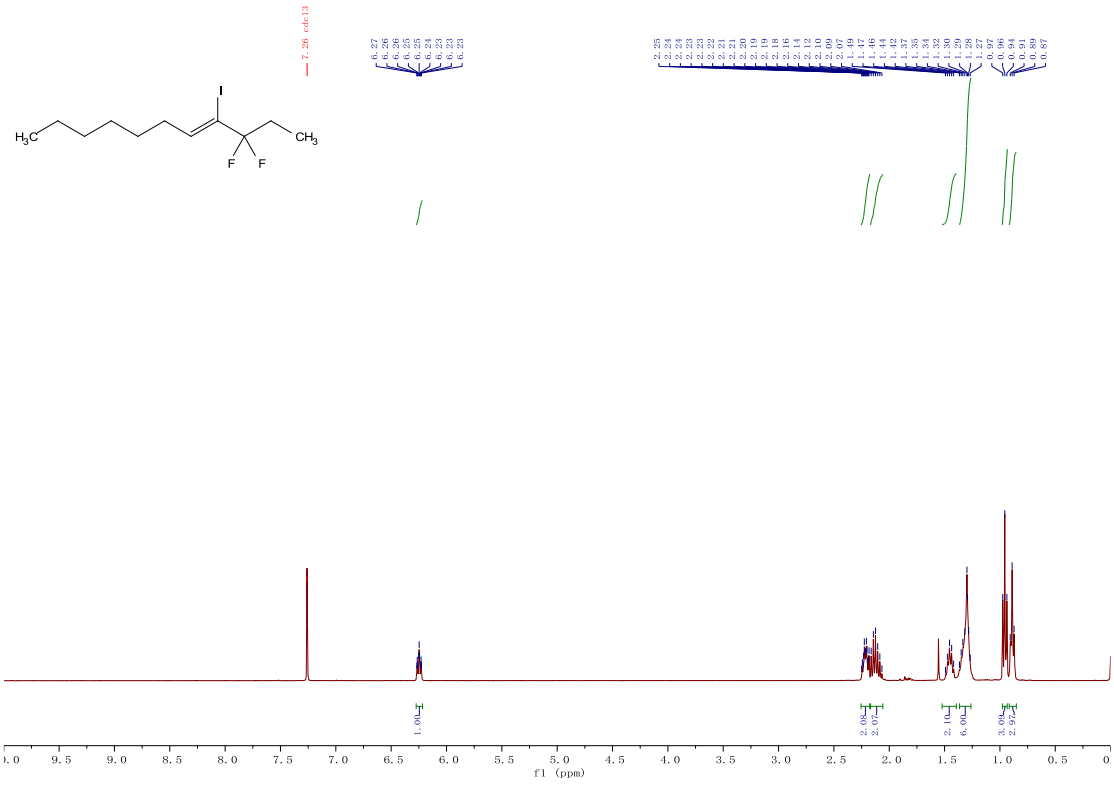
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5q**



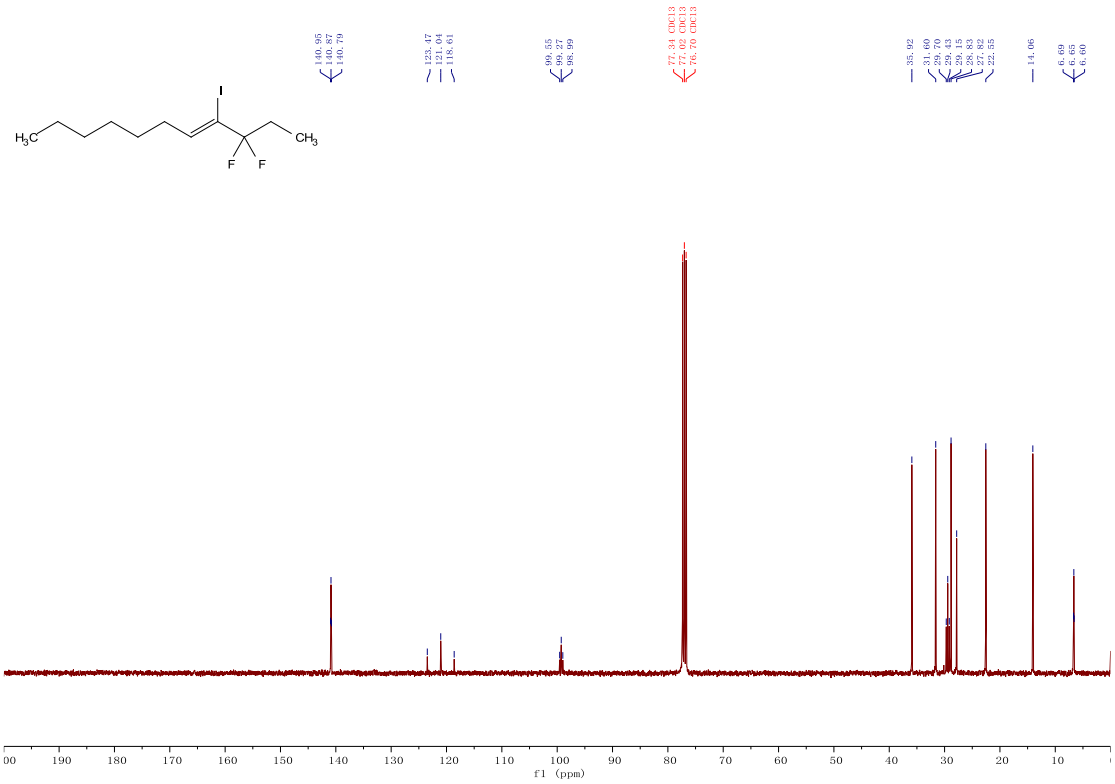
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5q**



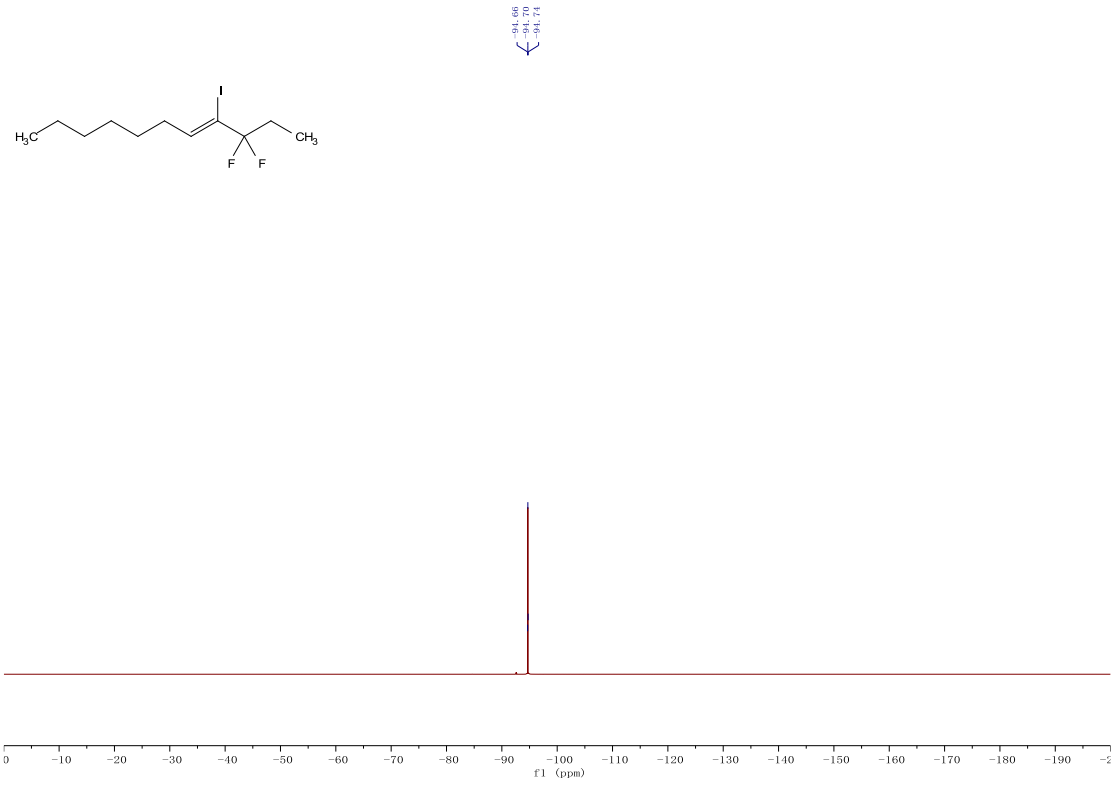
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5r**



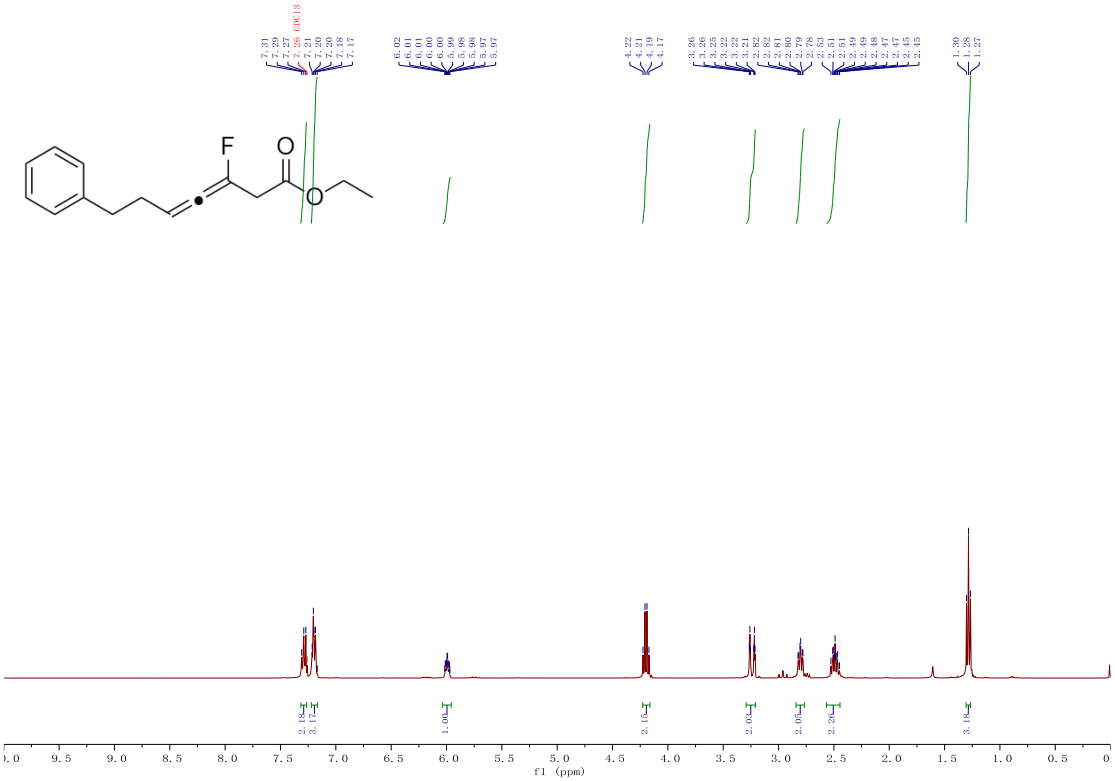
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **5r**



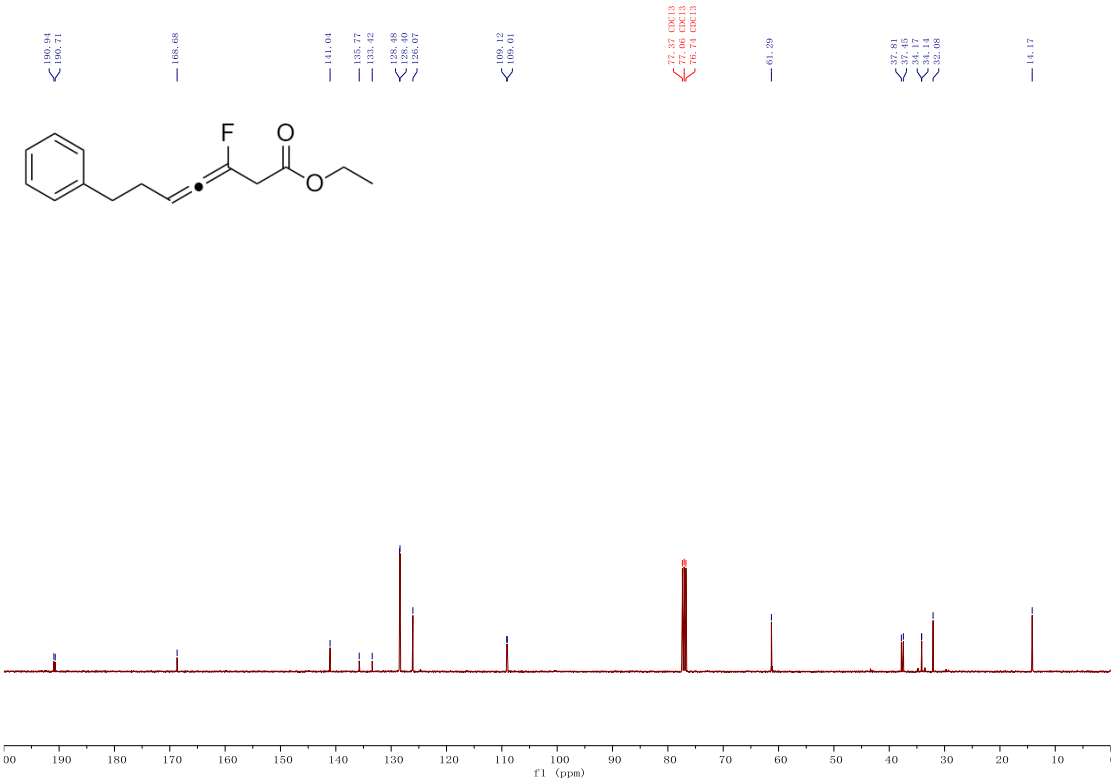
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5r**



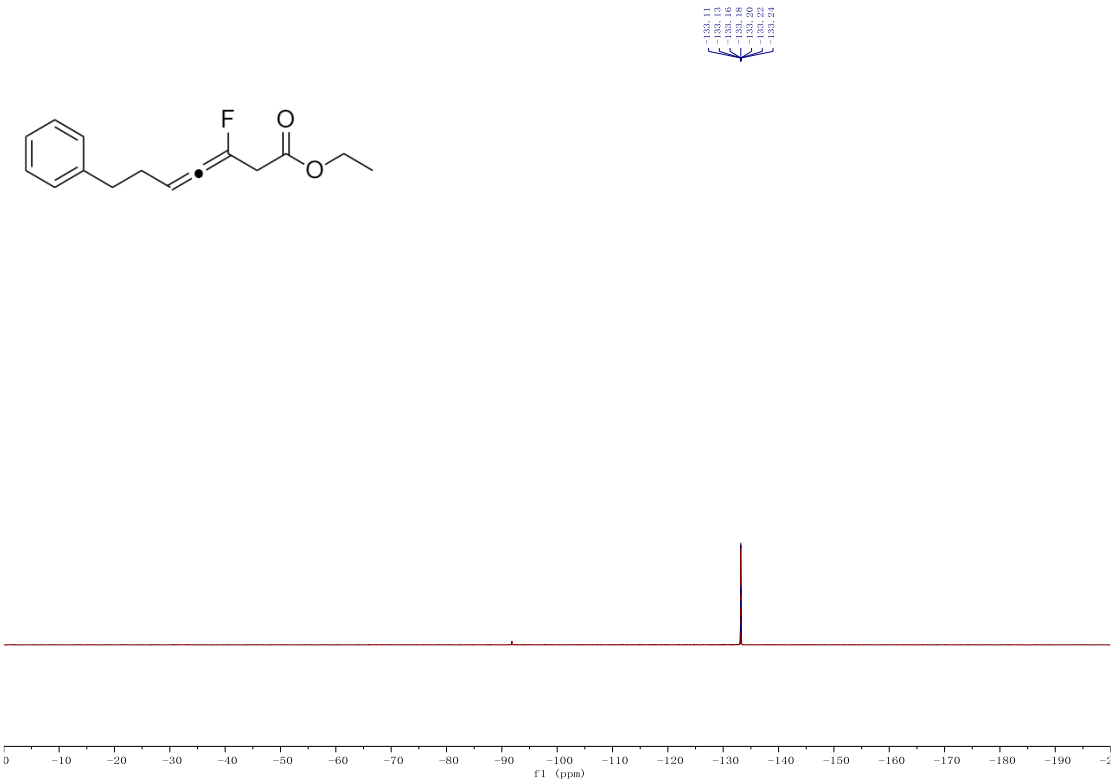
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2**



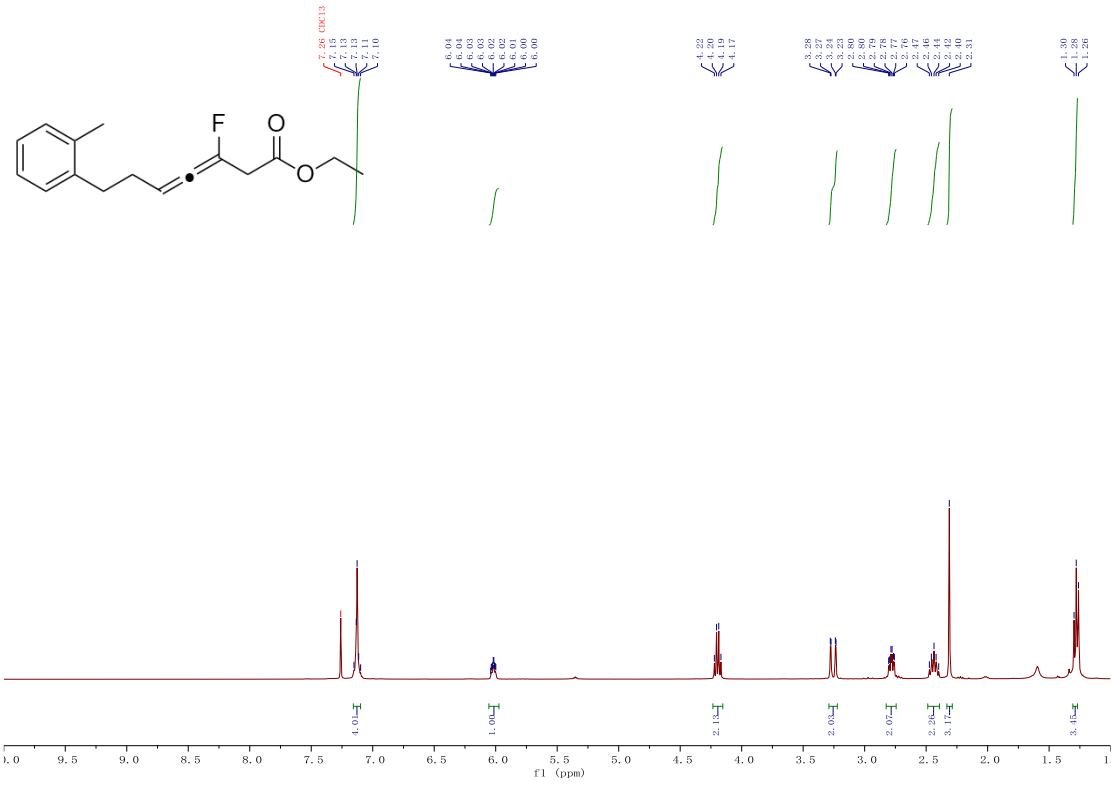
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **2**



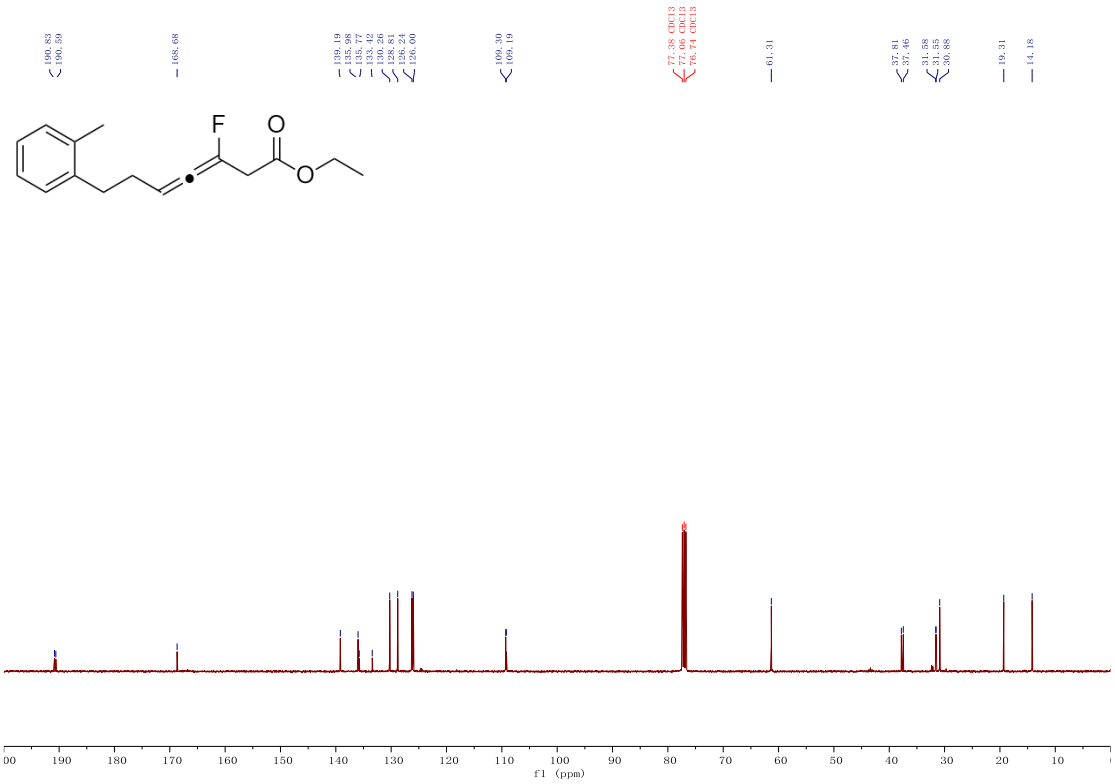
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2**



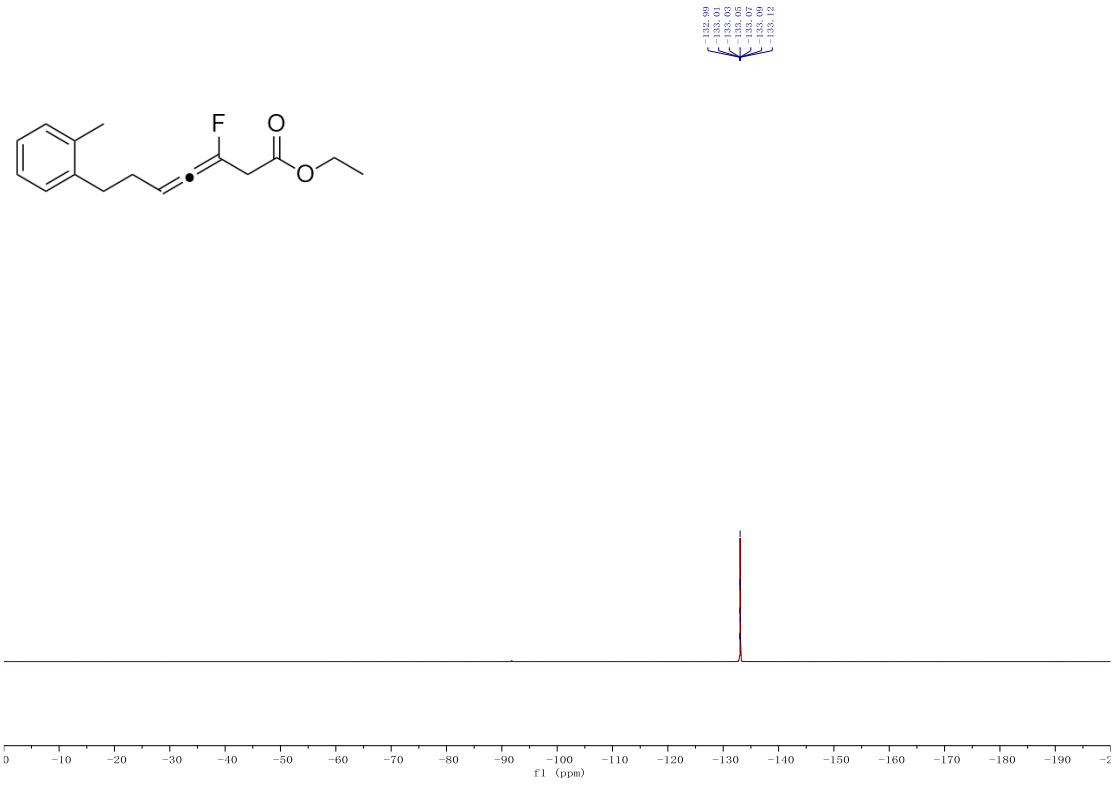
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**



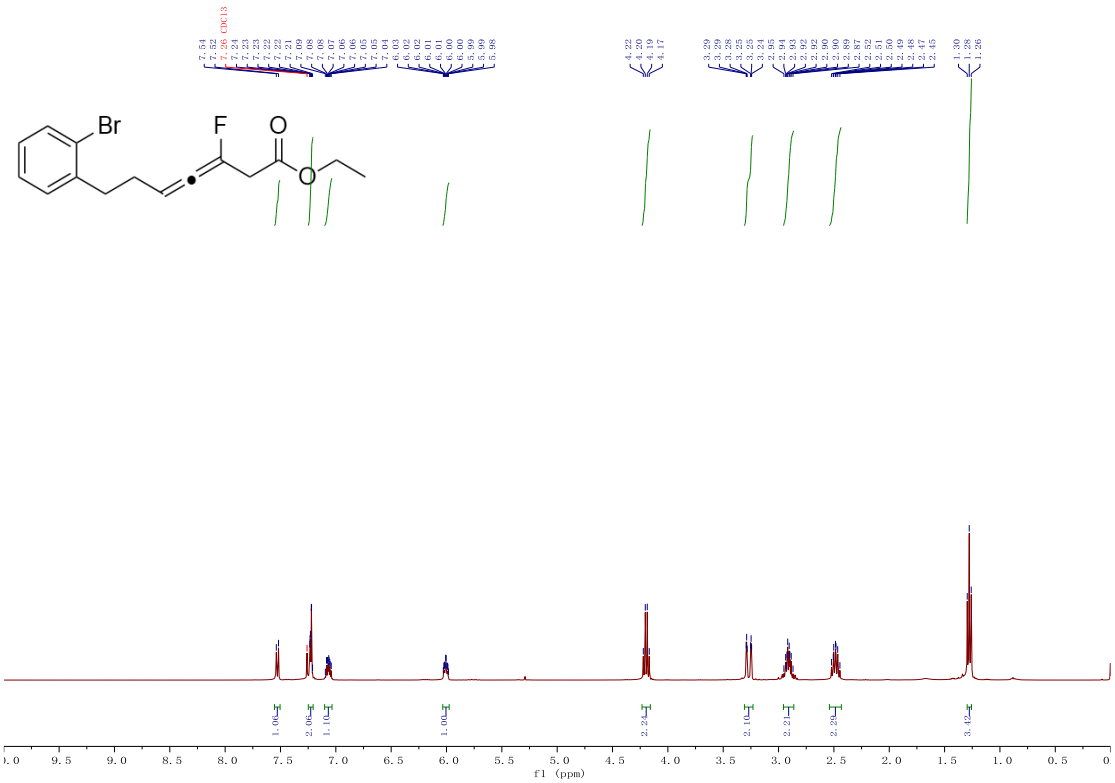
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4a**



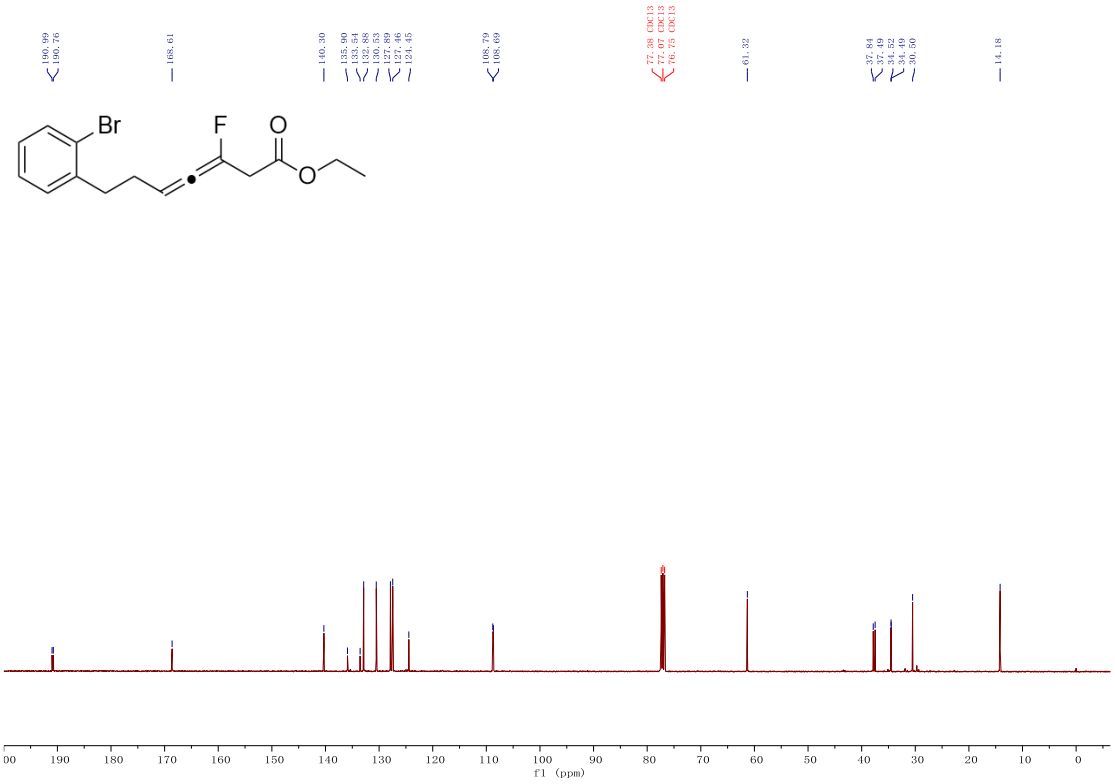
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4a**



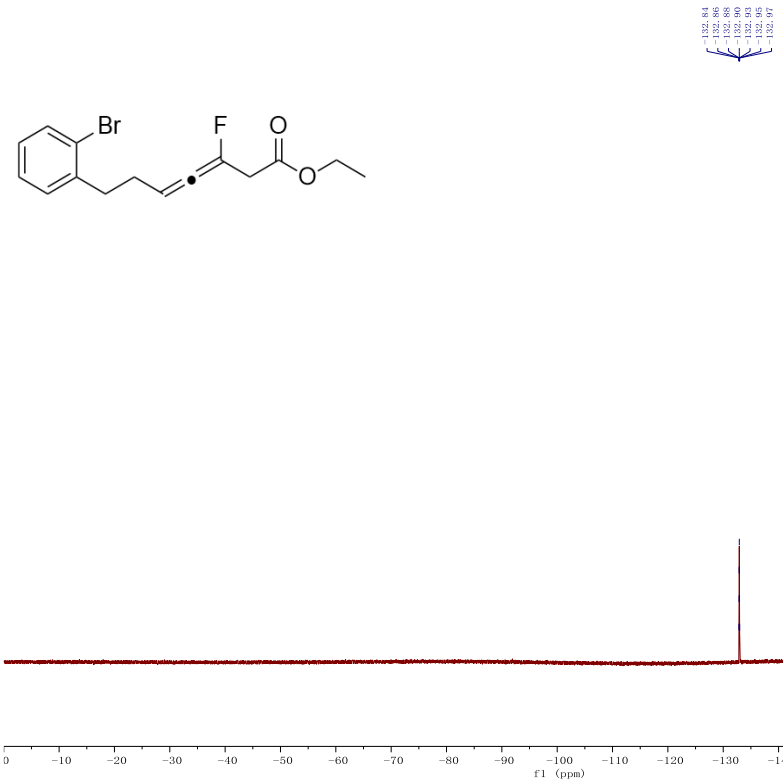
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**



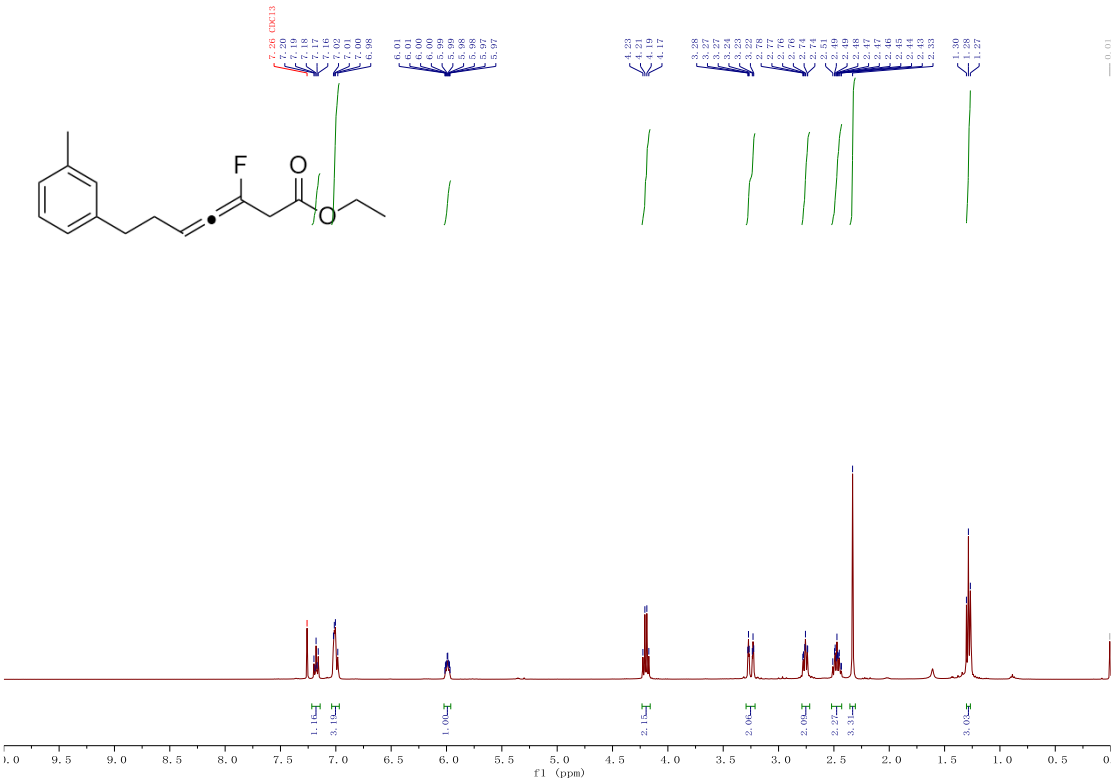
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4b**



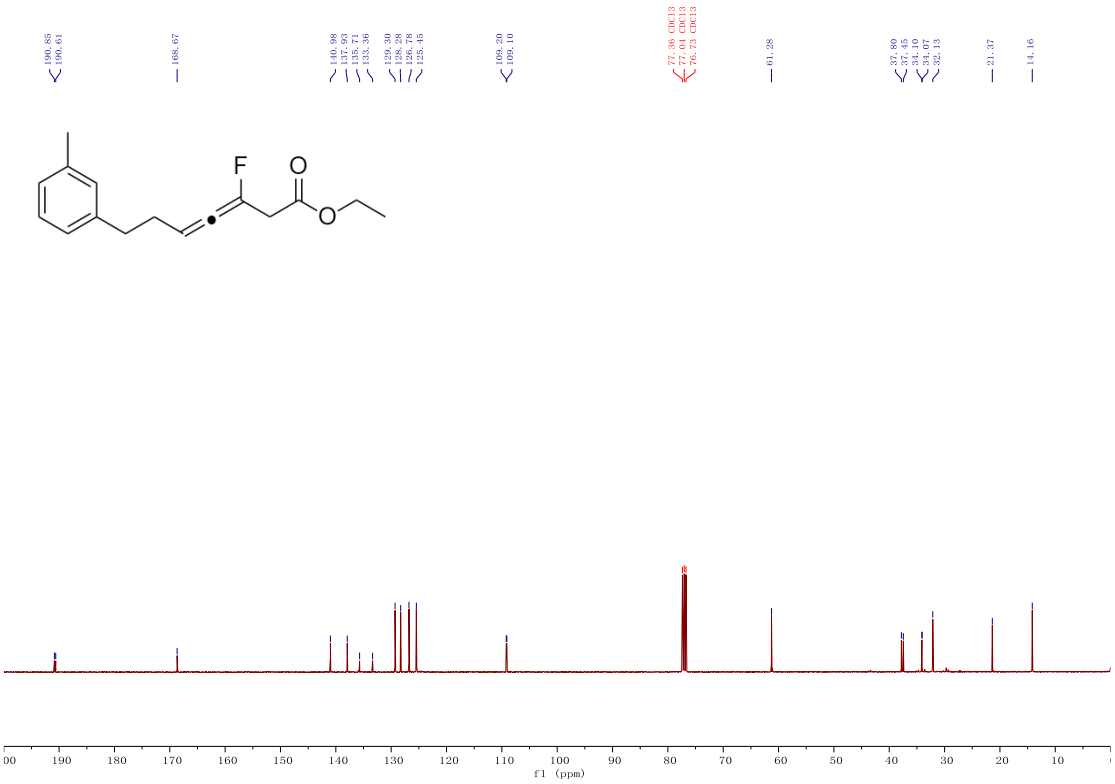
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4b**



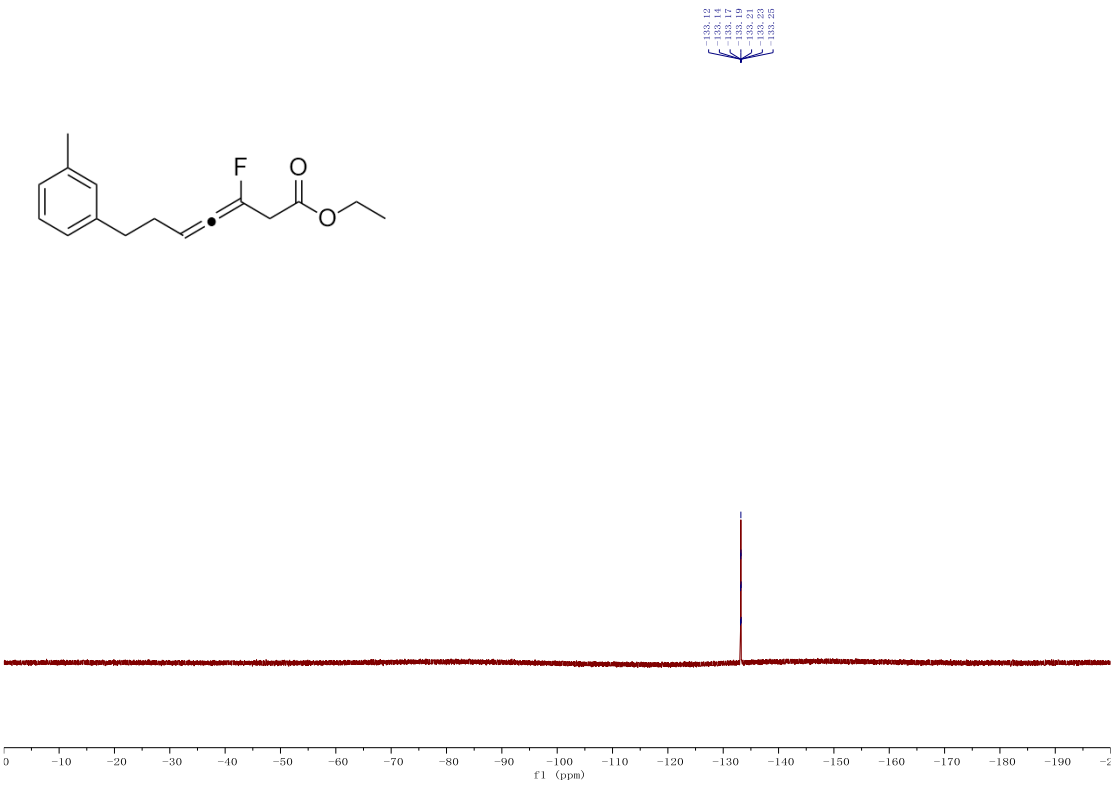
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**



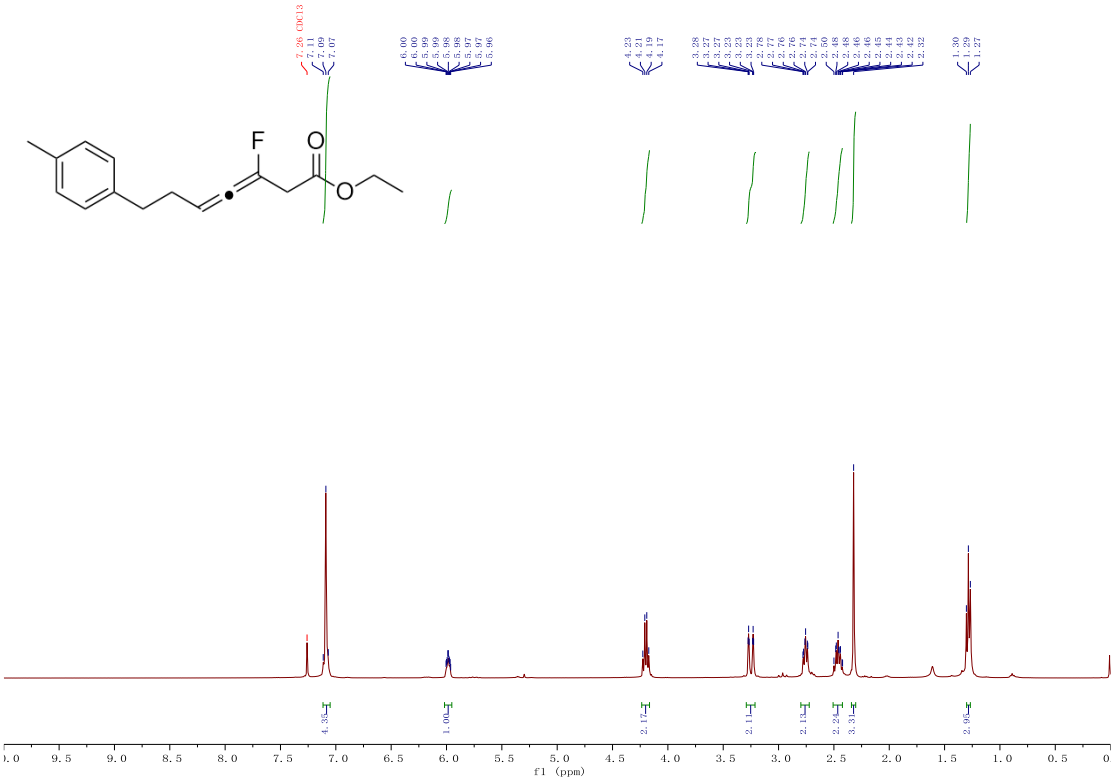
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4c**



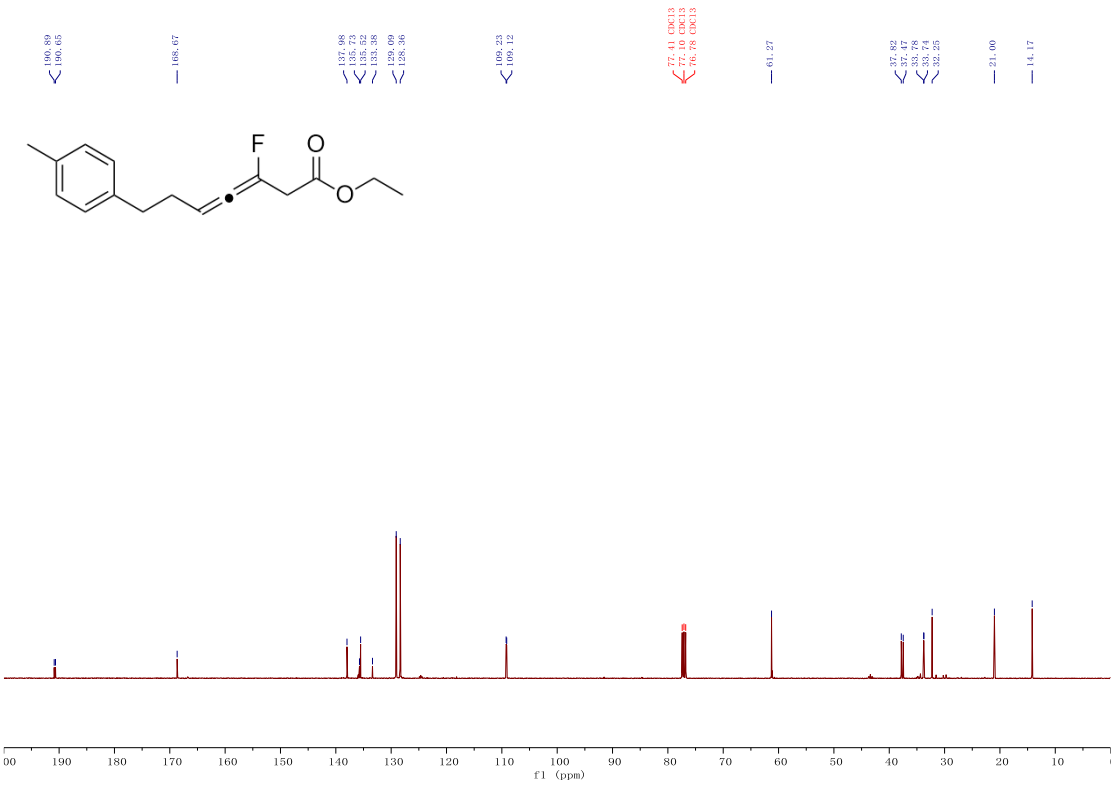
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4c**



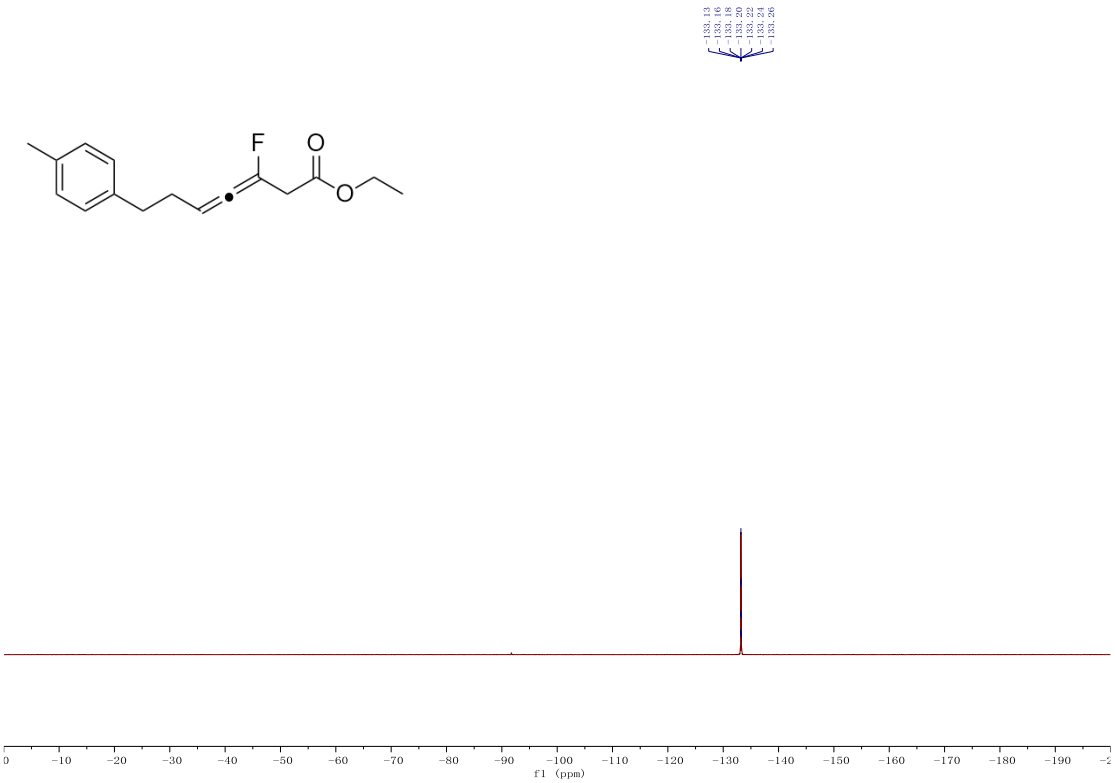
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4d**



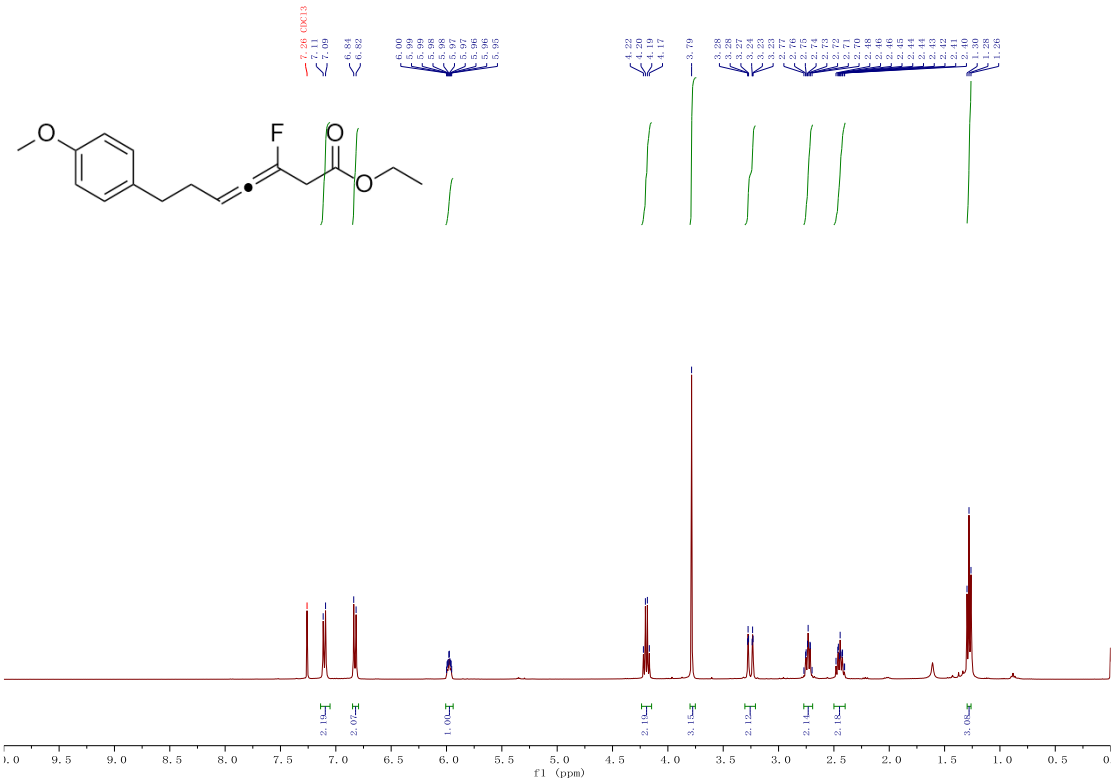
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4d**



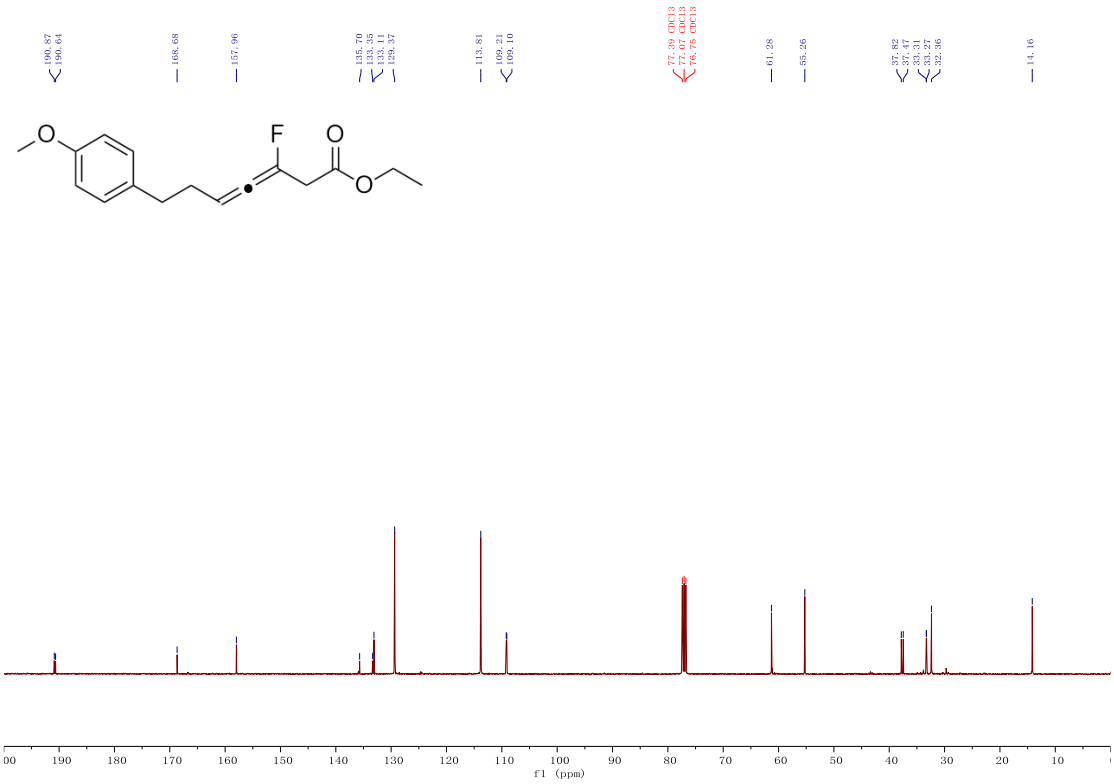
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4d**



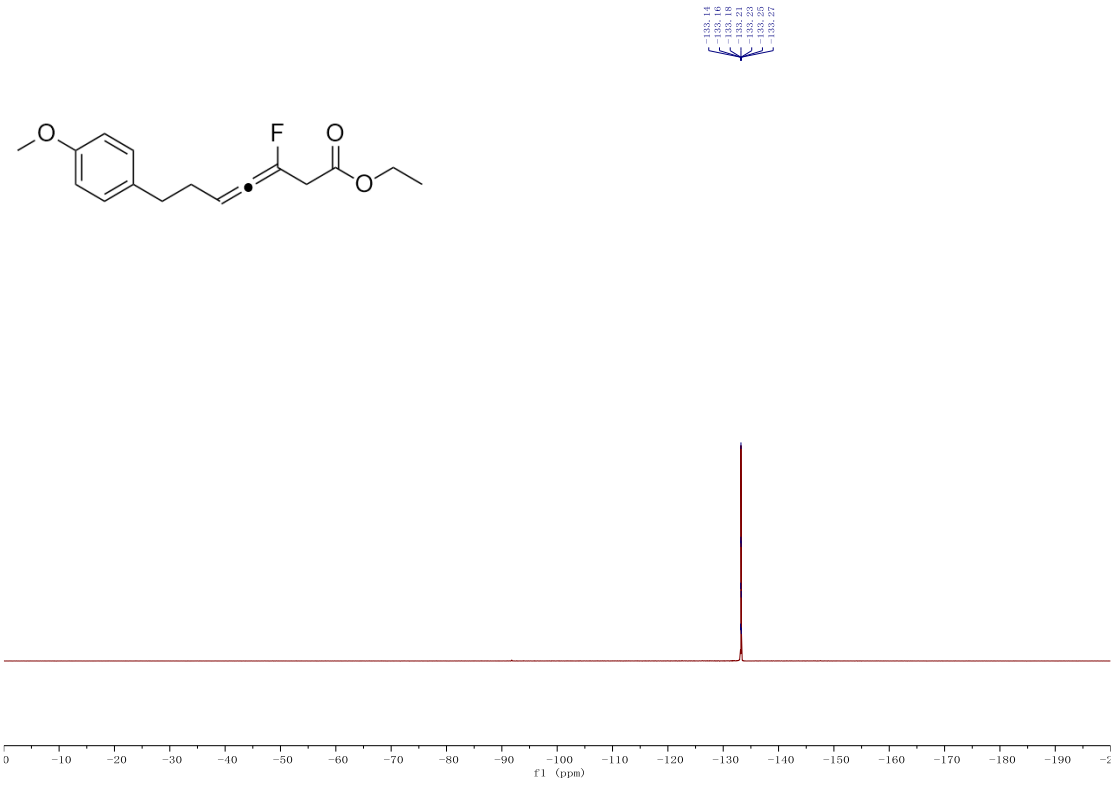
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4e**



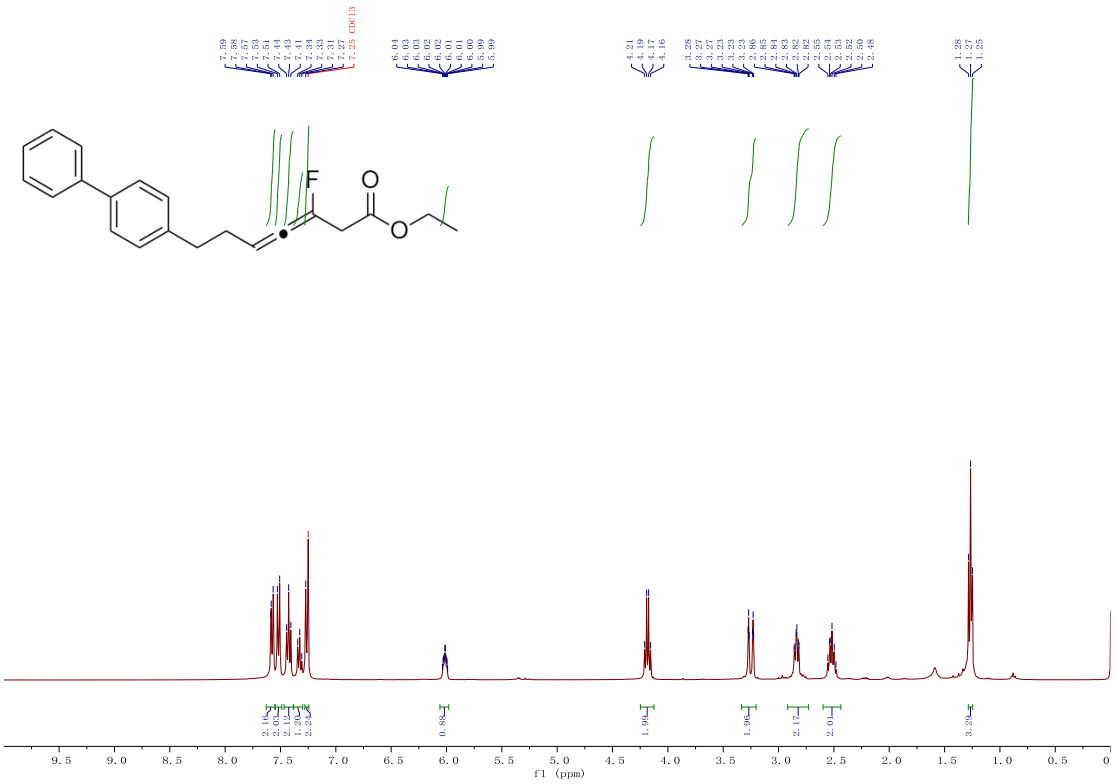
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4e**



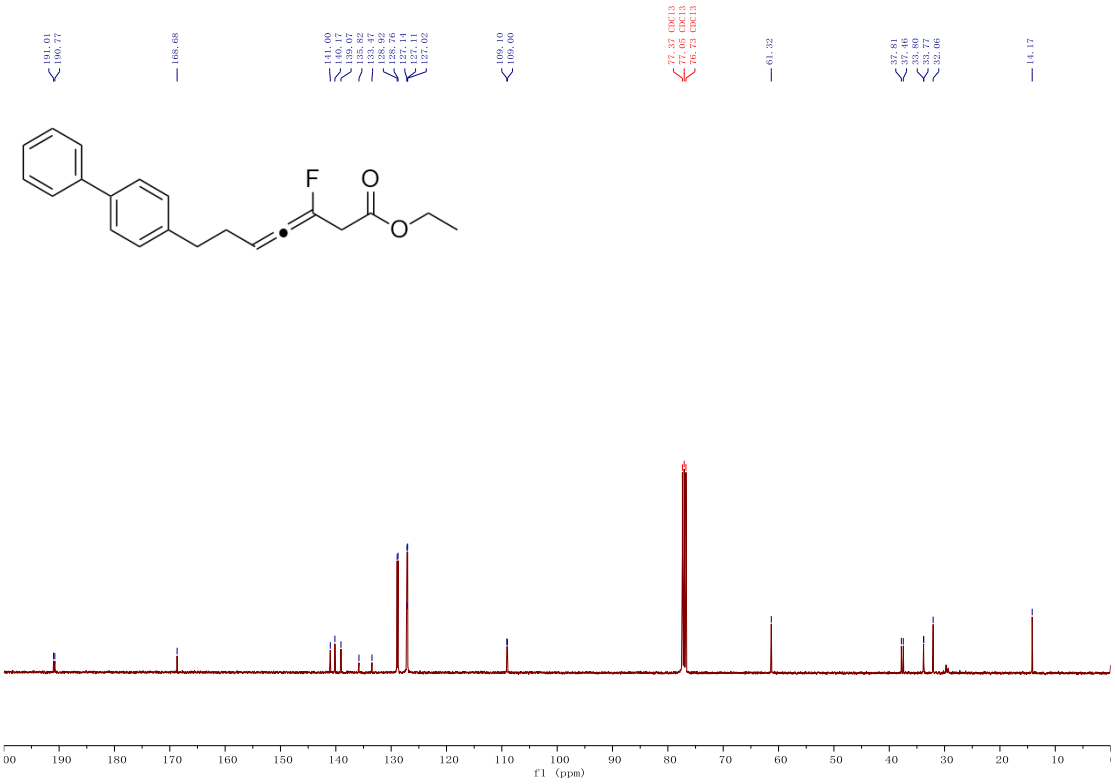
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4e**



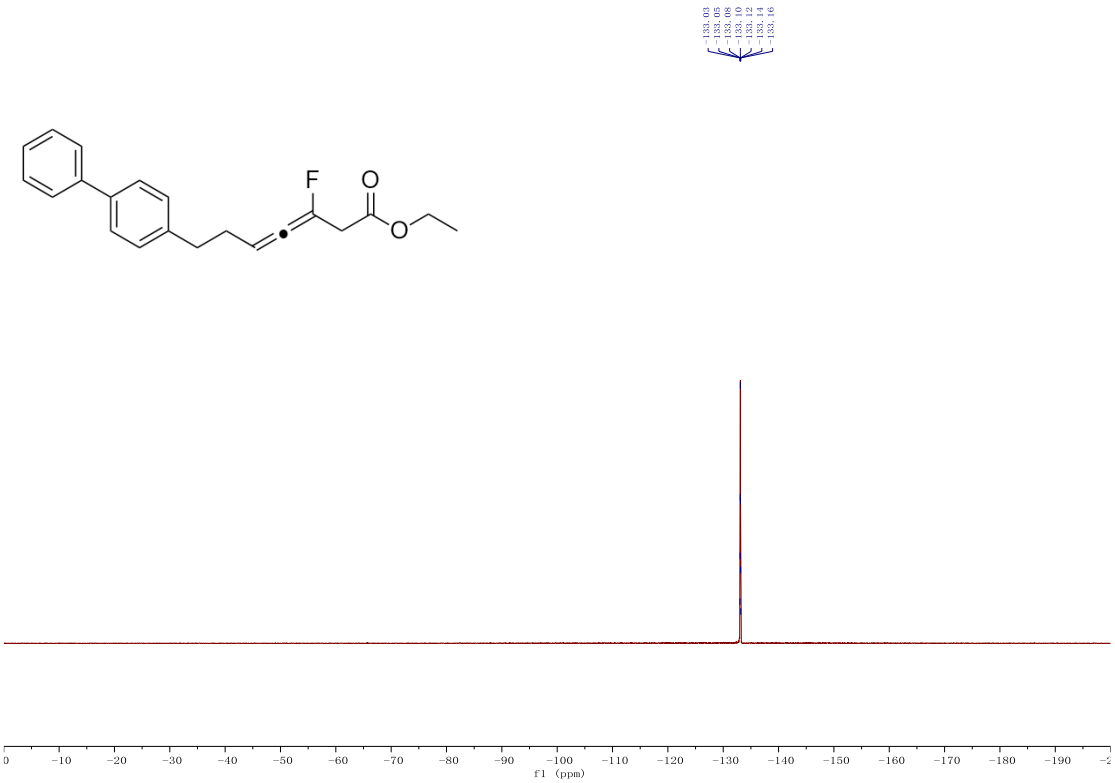
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4f**



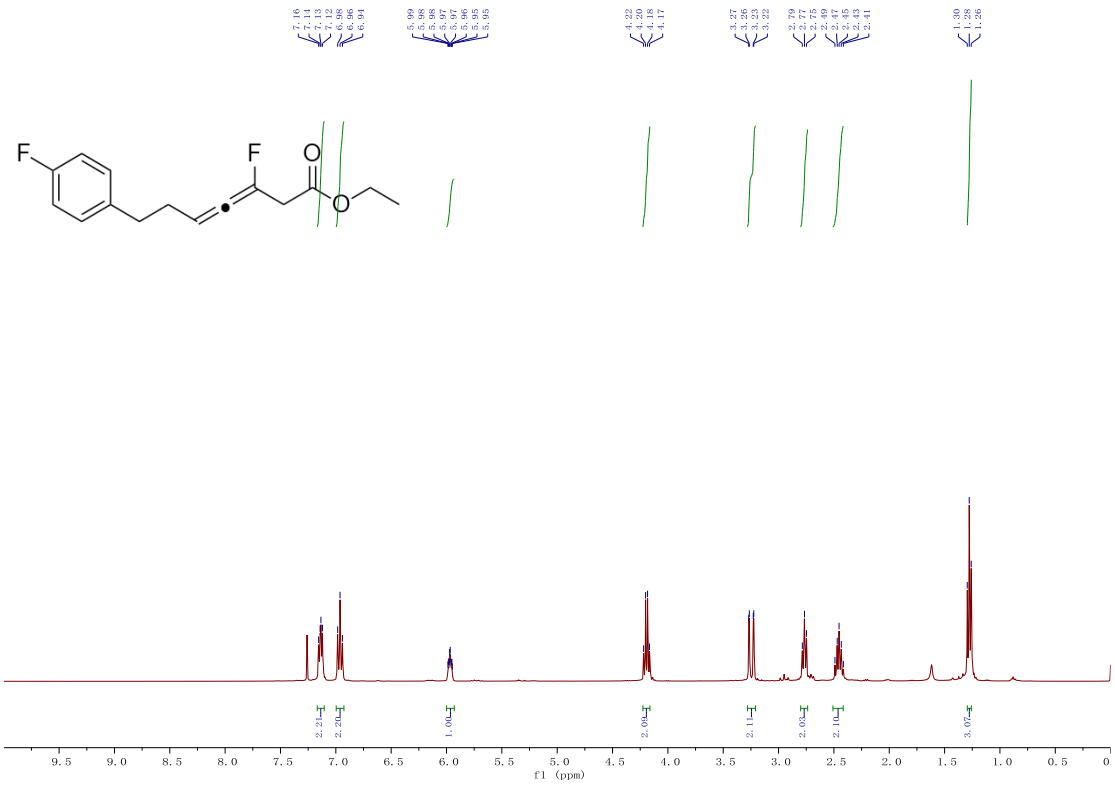
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4f**



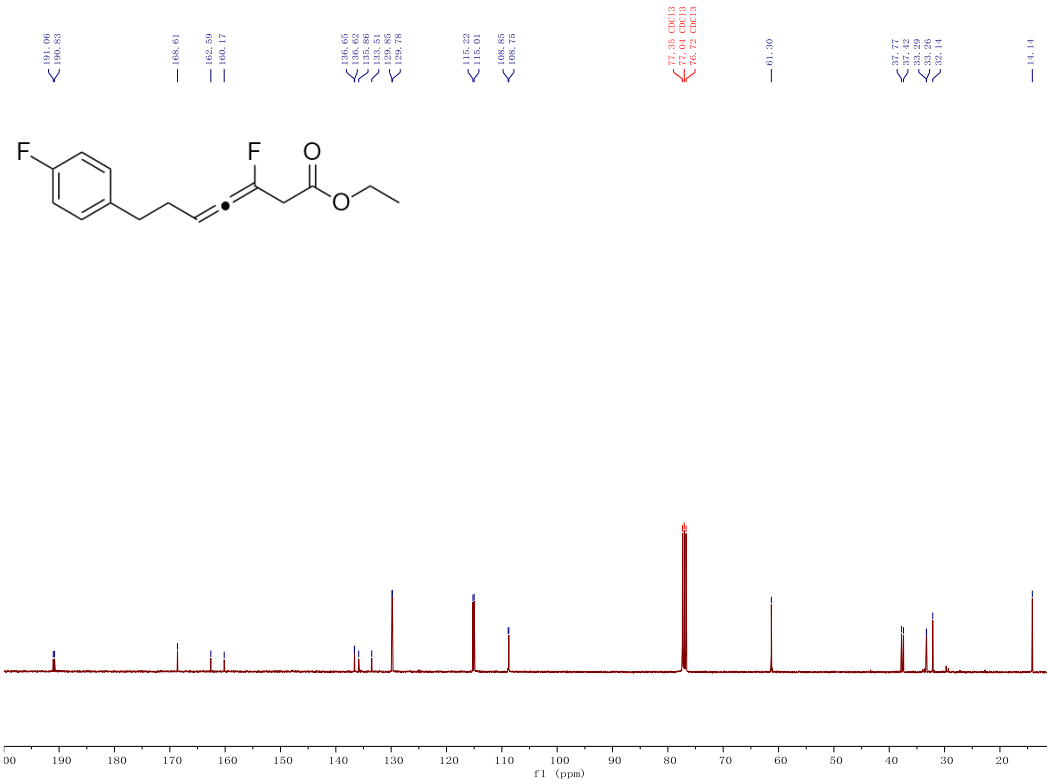
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4f**



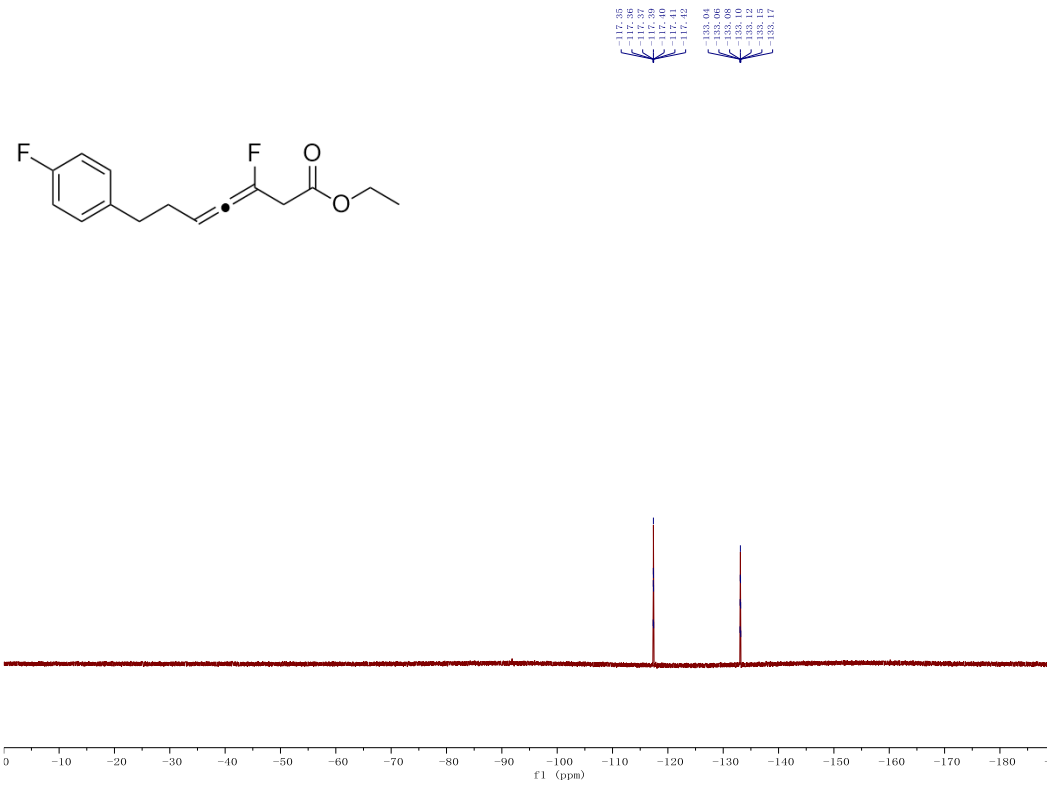
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4g**



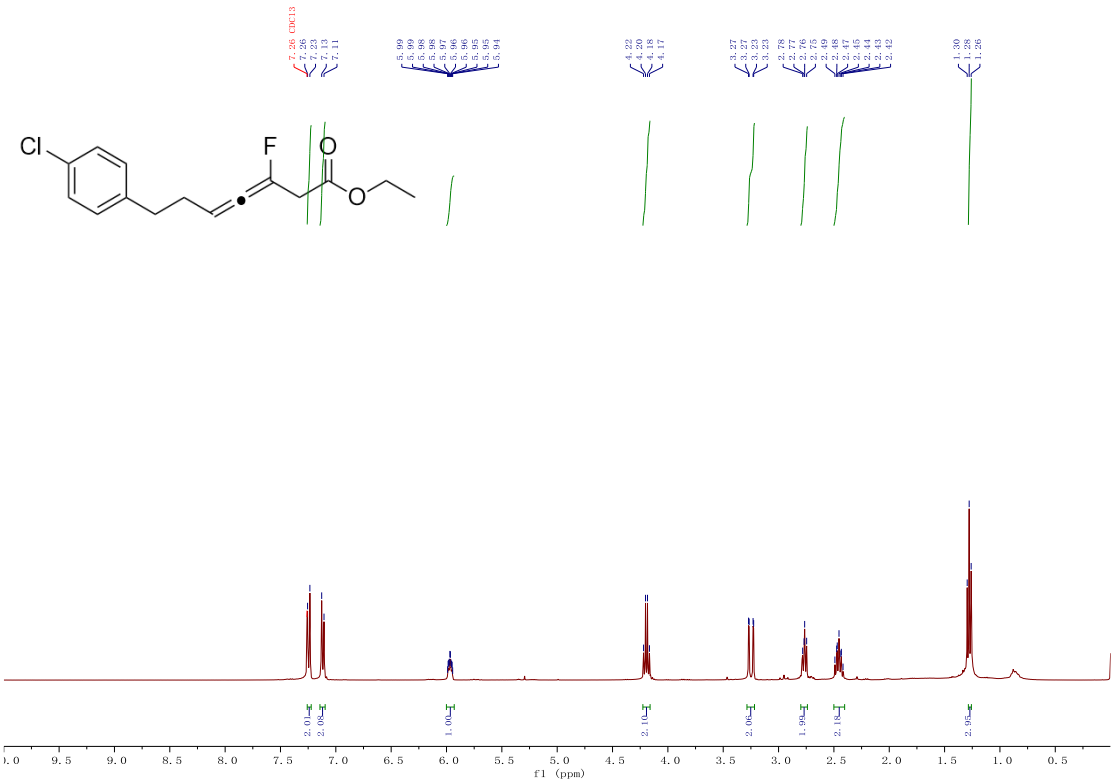
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4g**



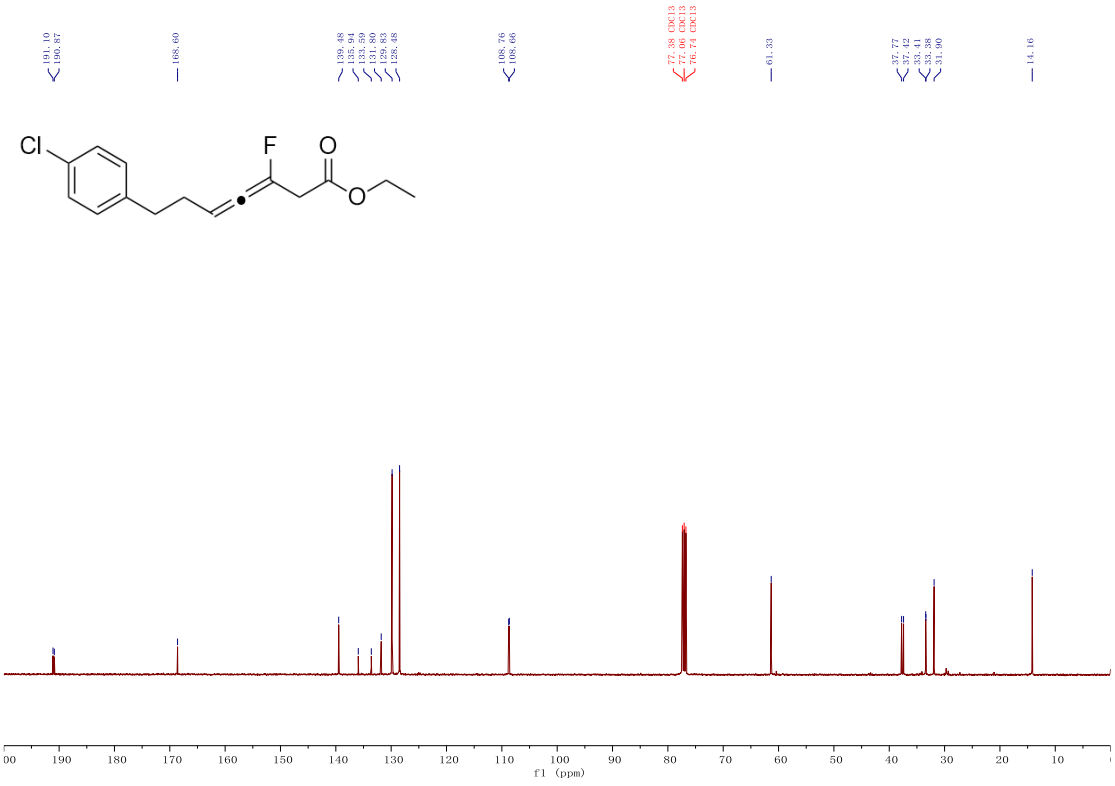
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4g**



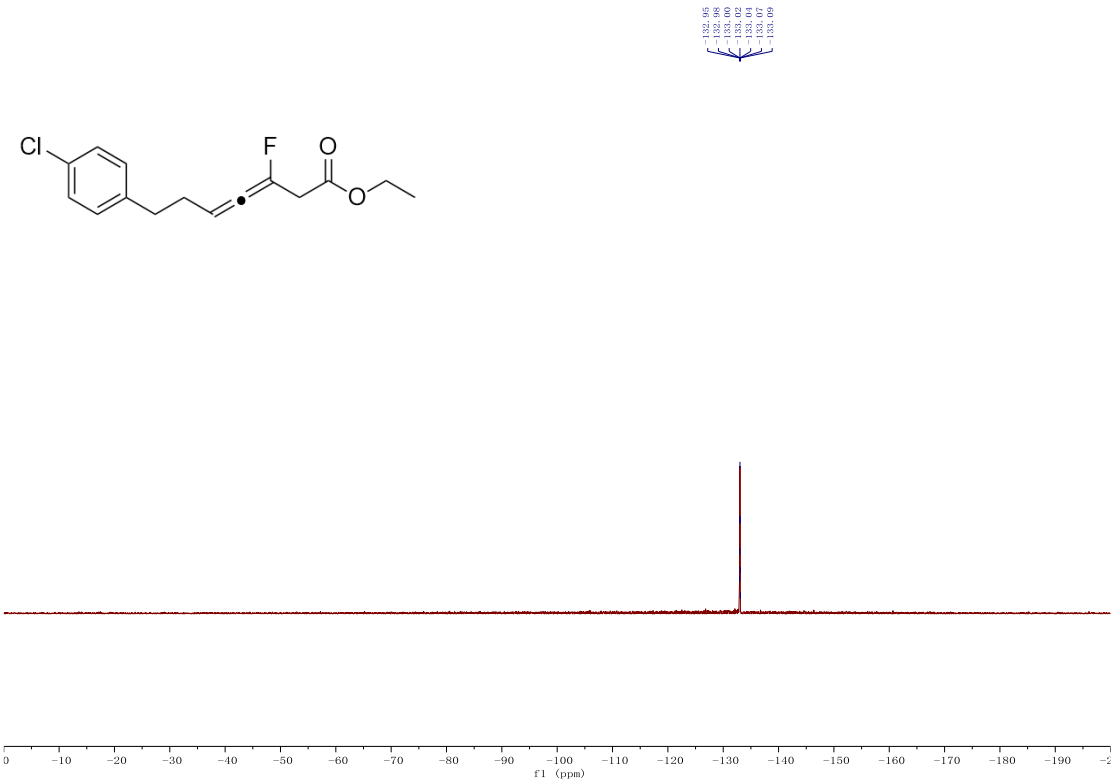
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4h**



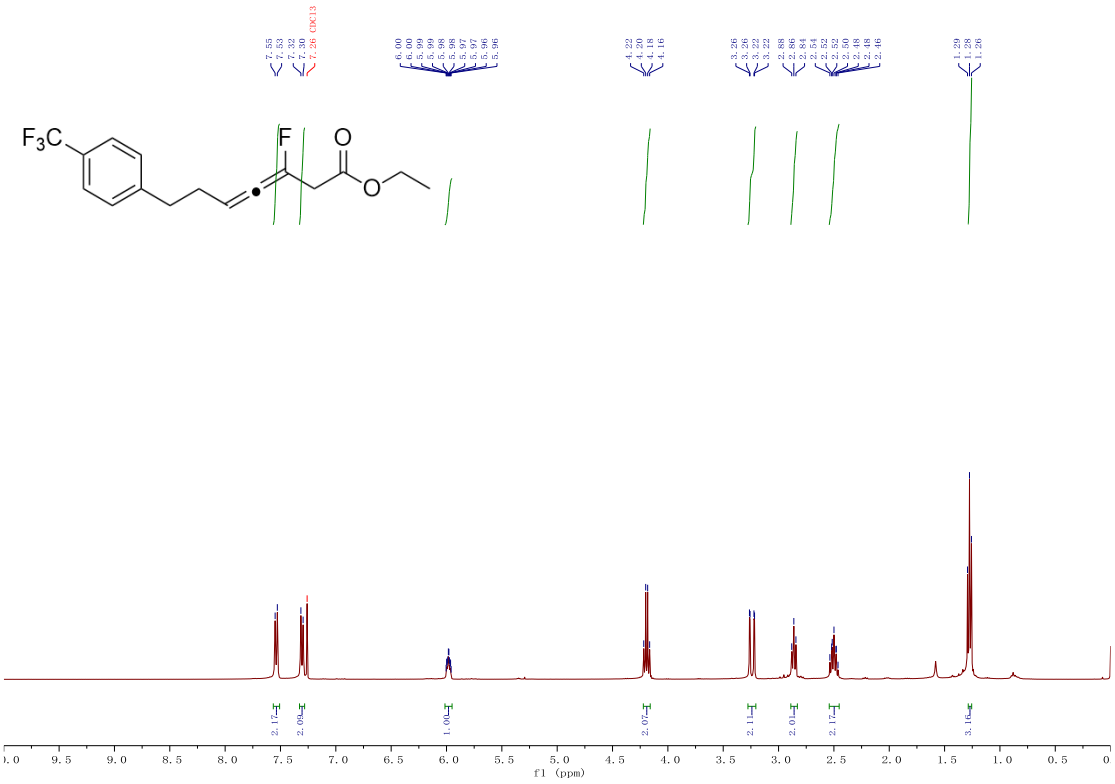
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4h**



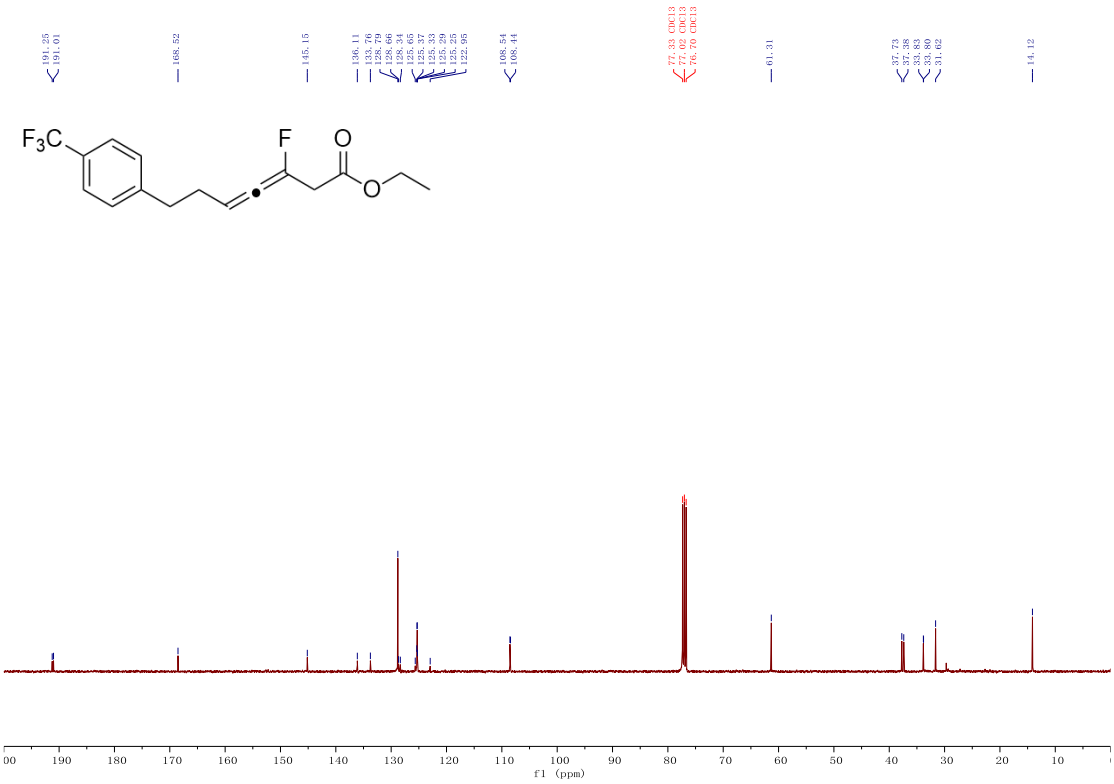
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4h**



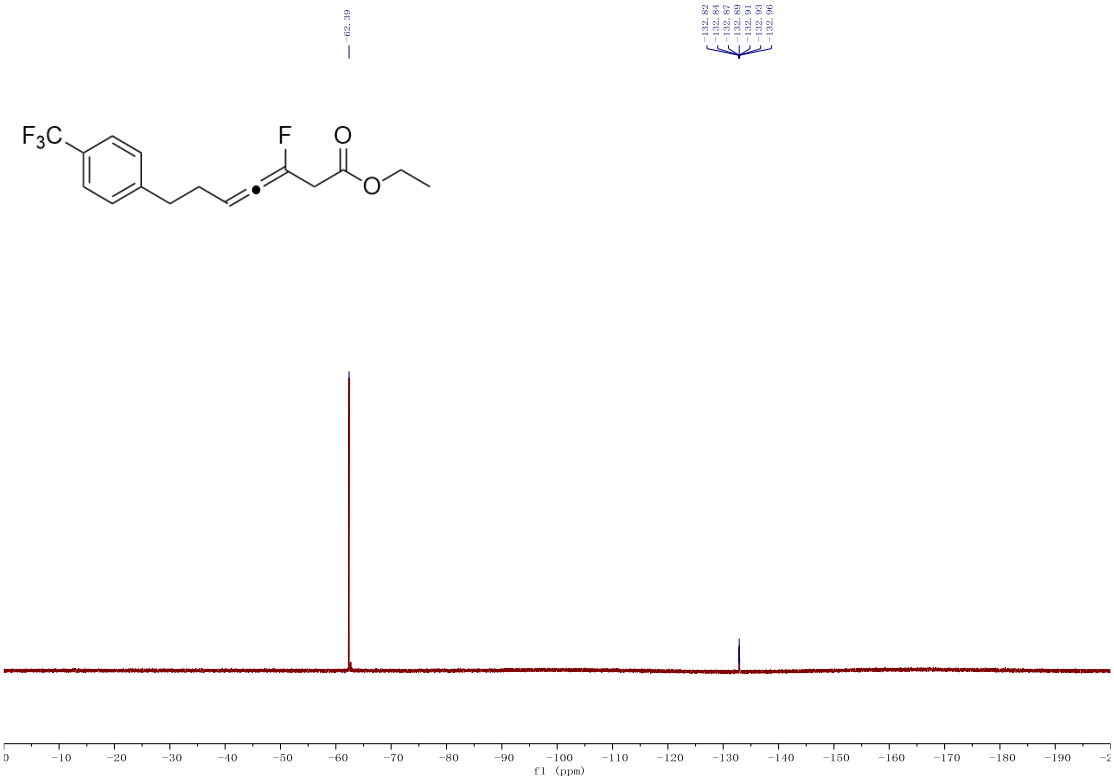
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4i**



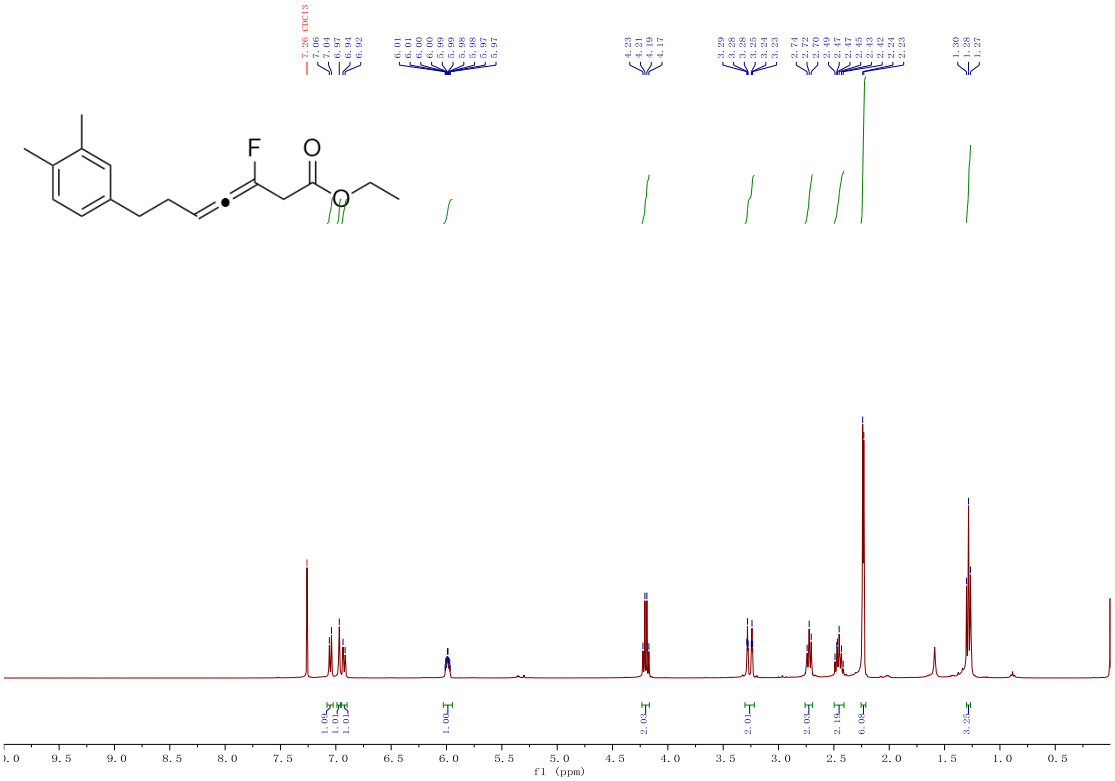
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4i**



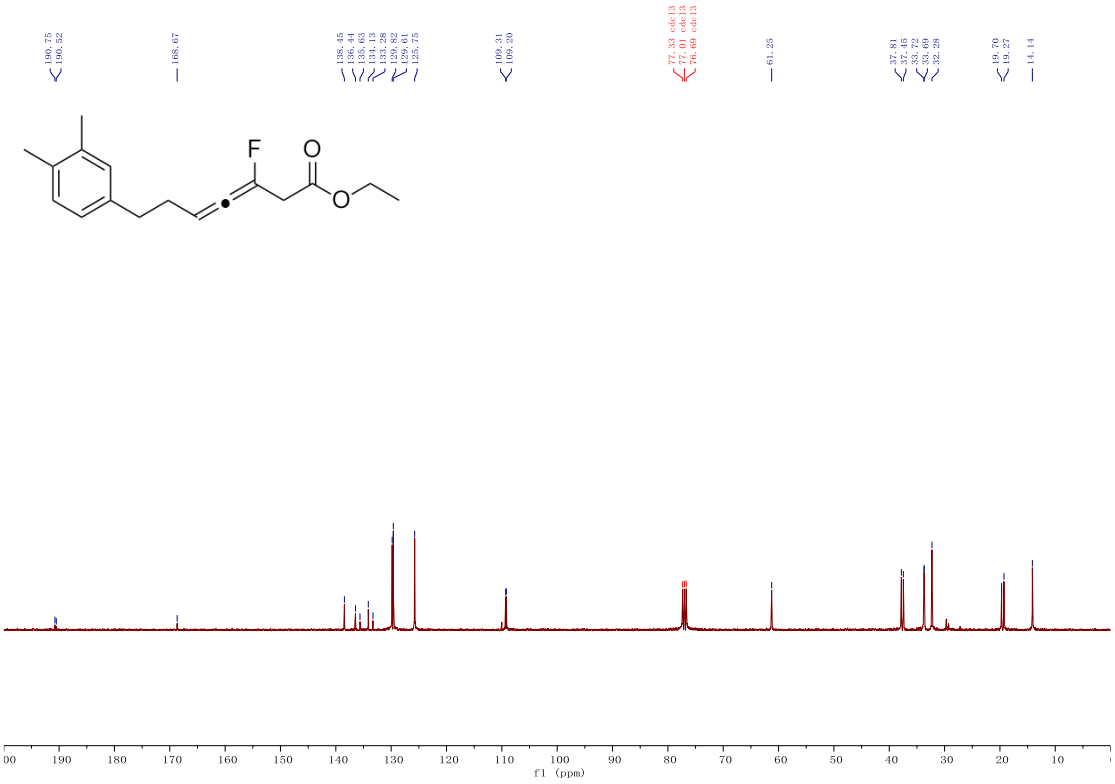
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4i**



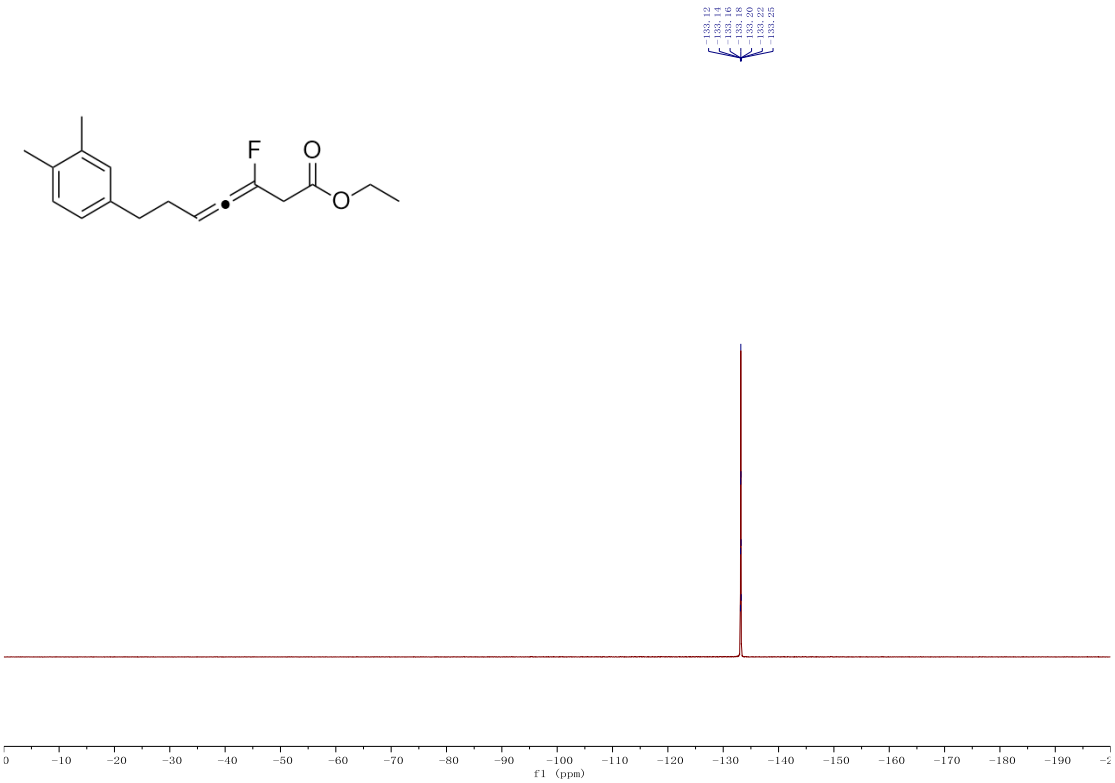
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4j**



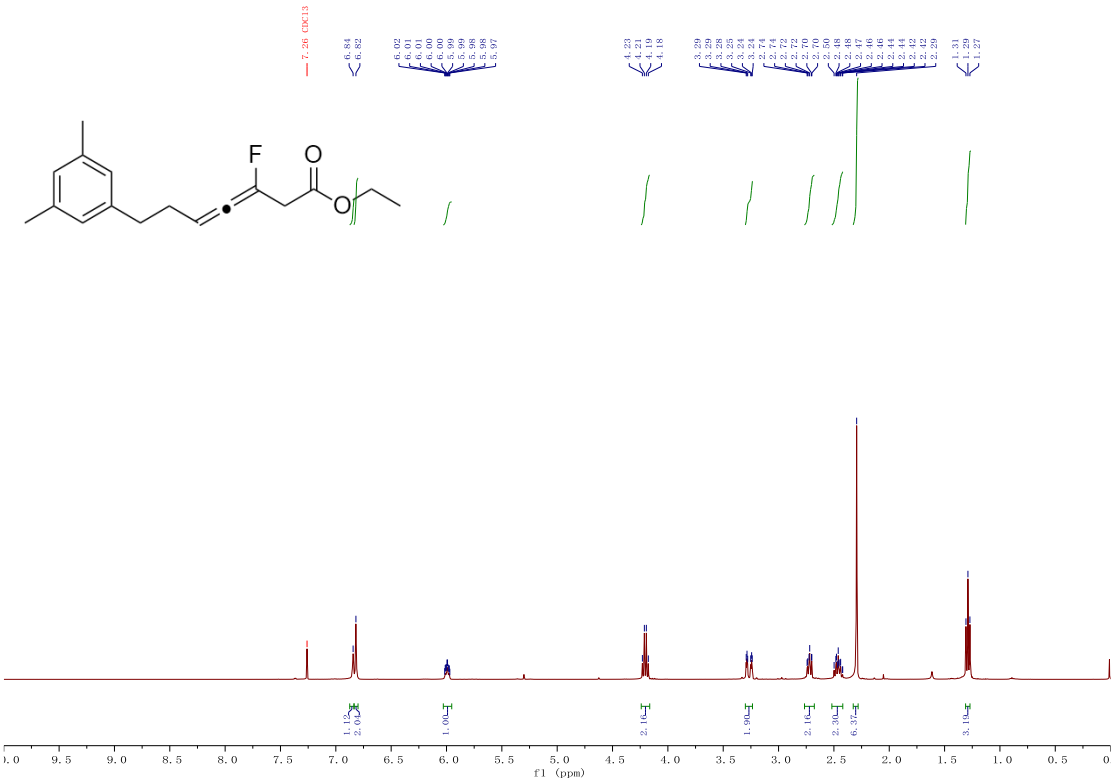
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4j**



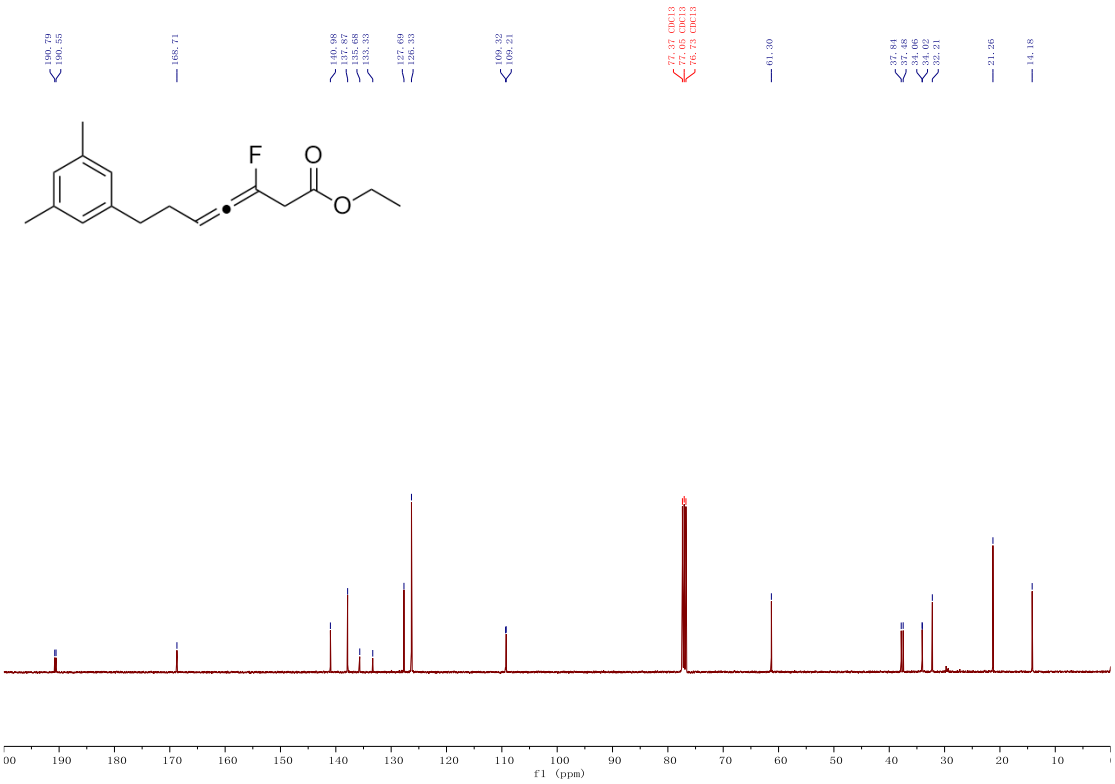
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4j**



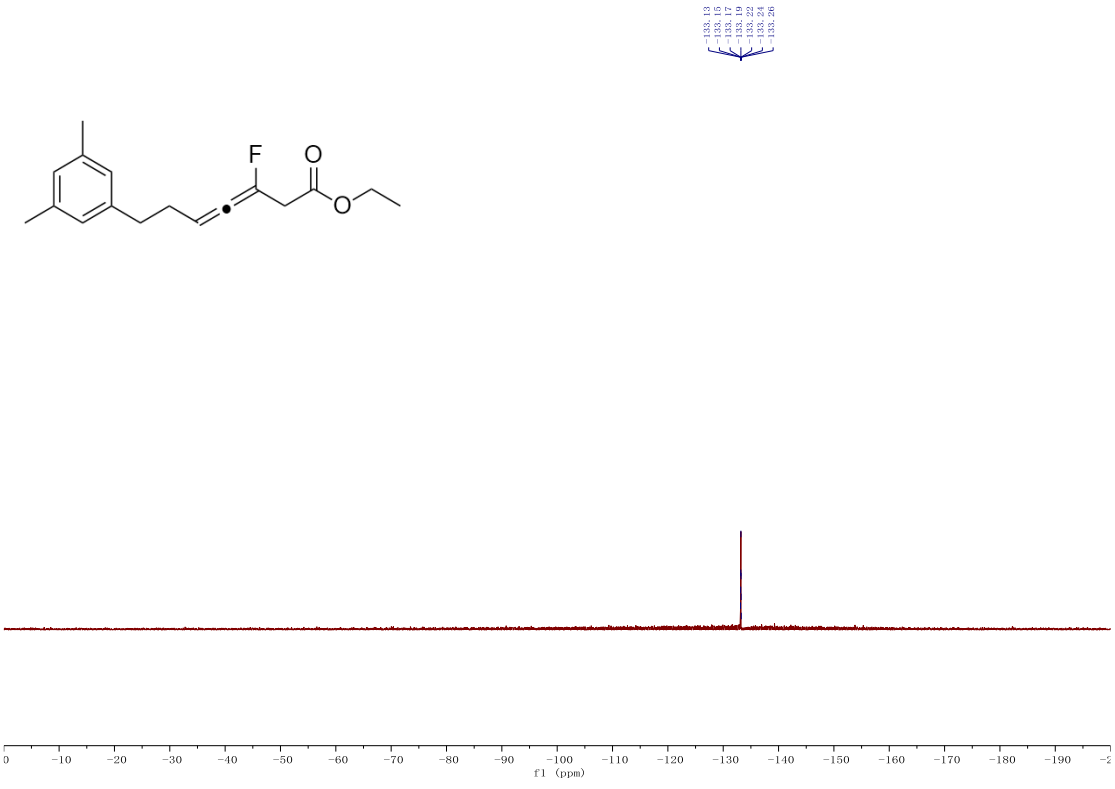
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4k**



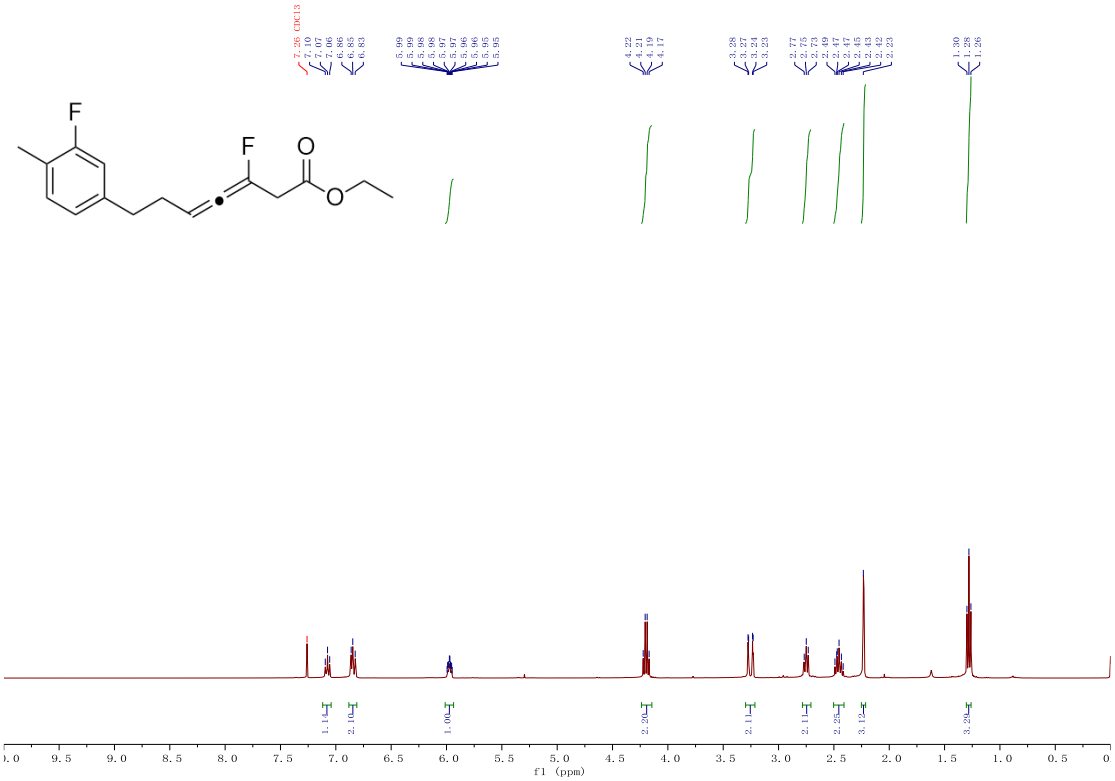
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4k**



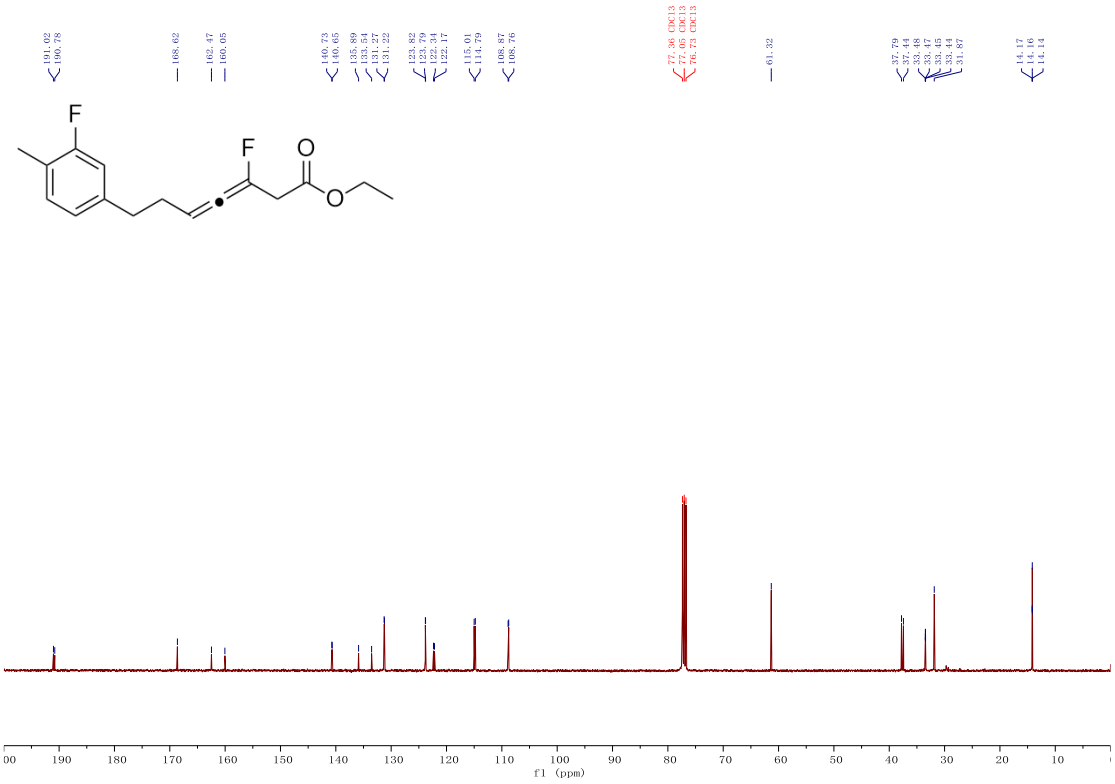
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4k**



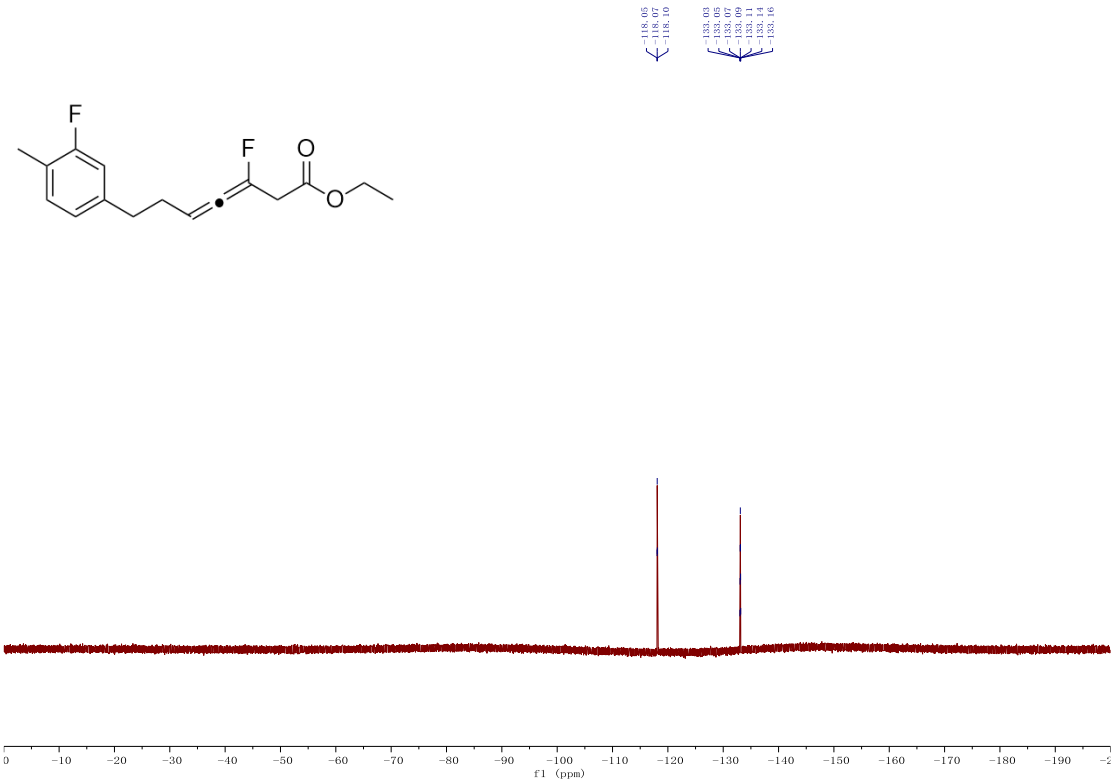
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4l**



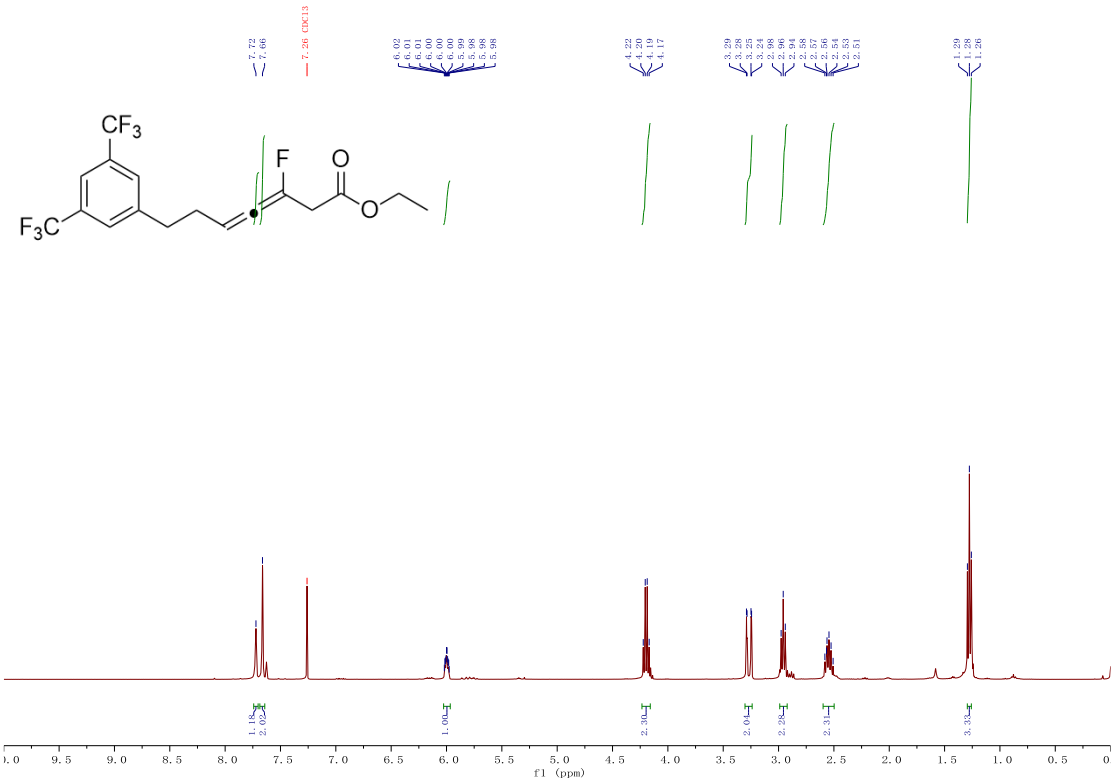
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4l**



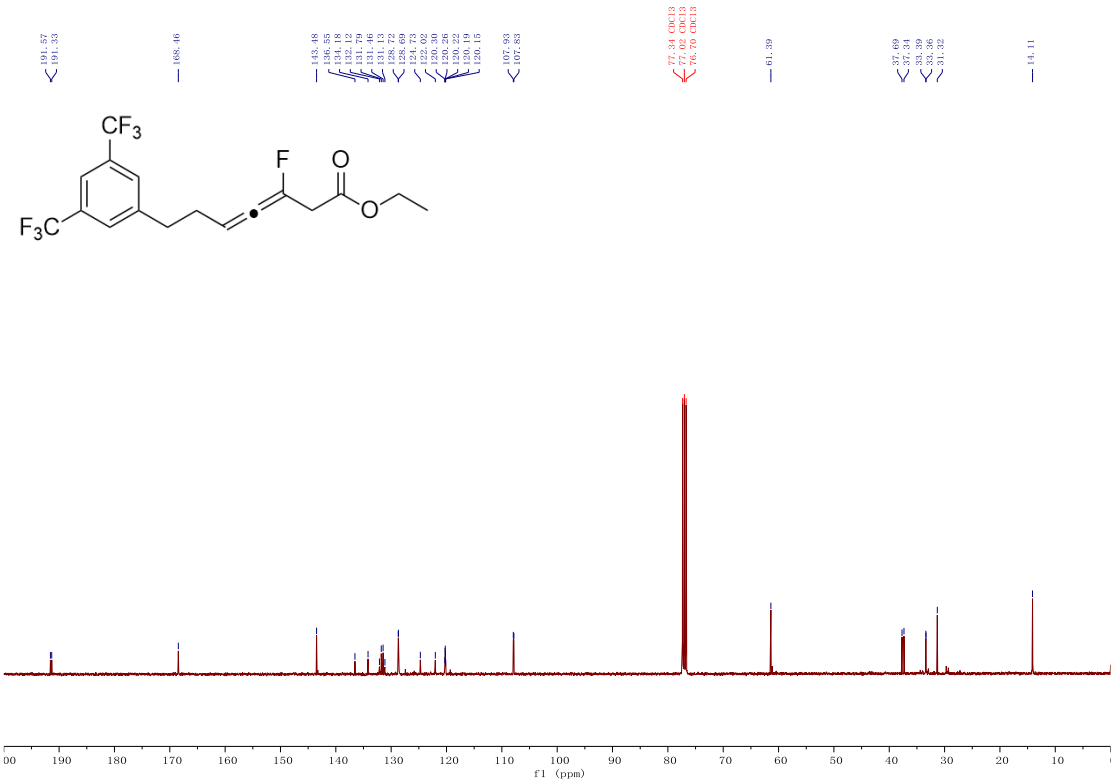
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4l**



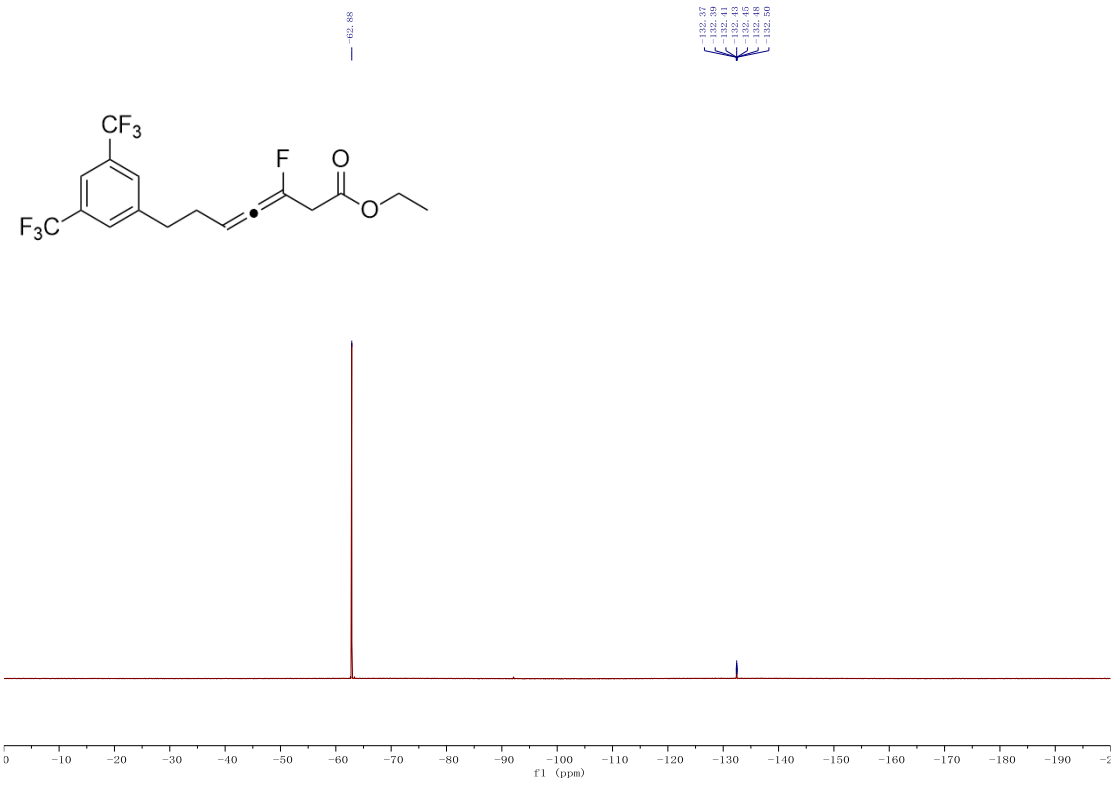
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4m**



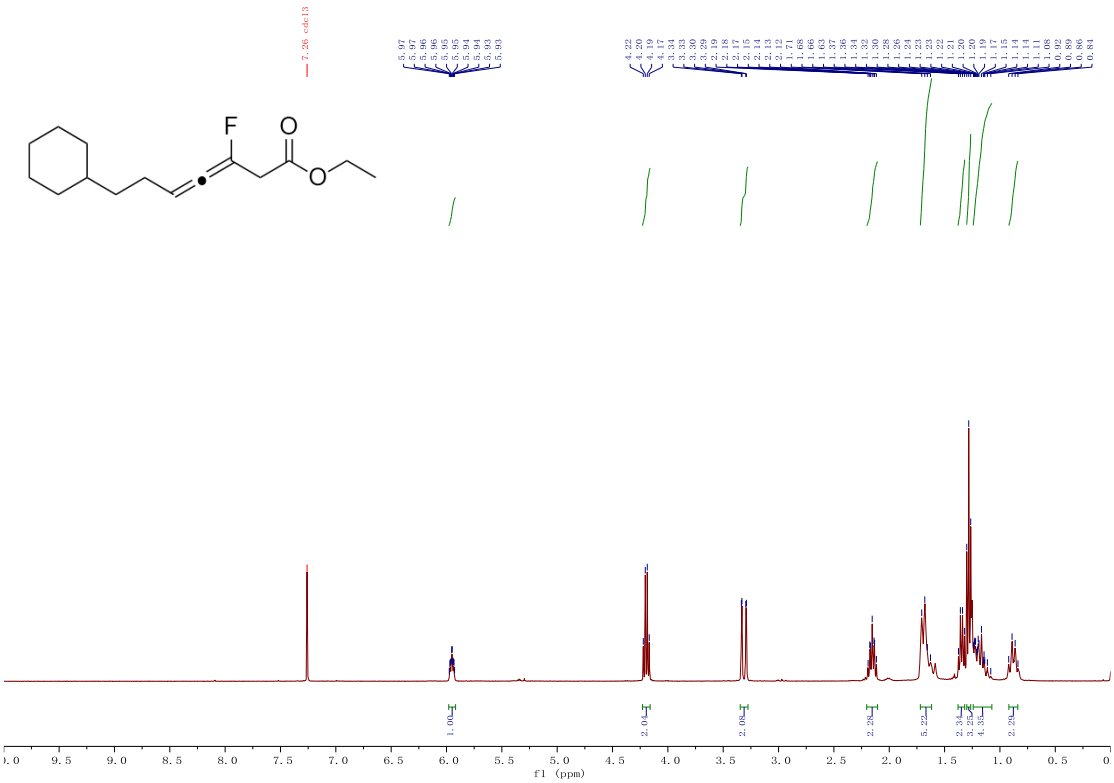
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4m**



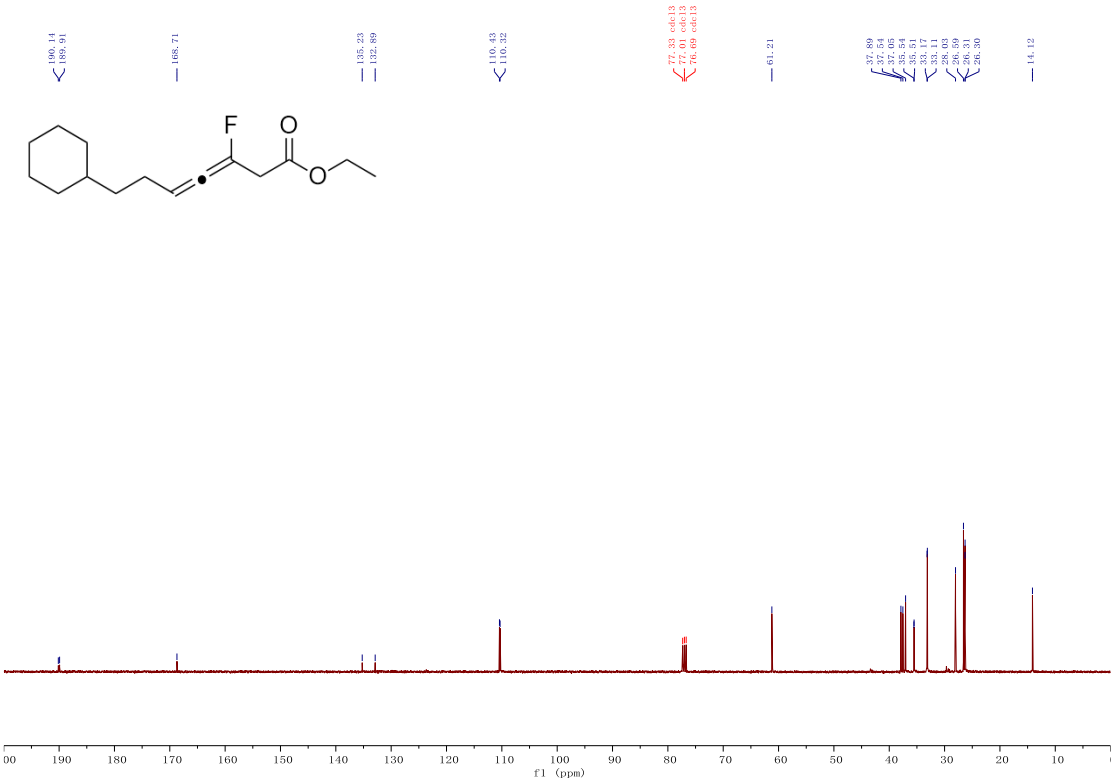
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4m**



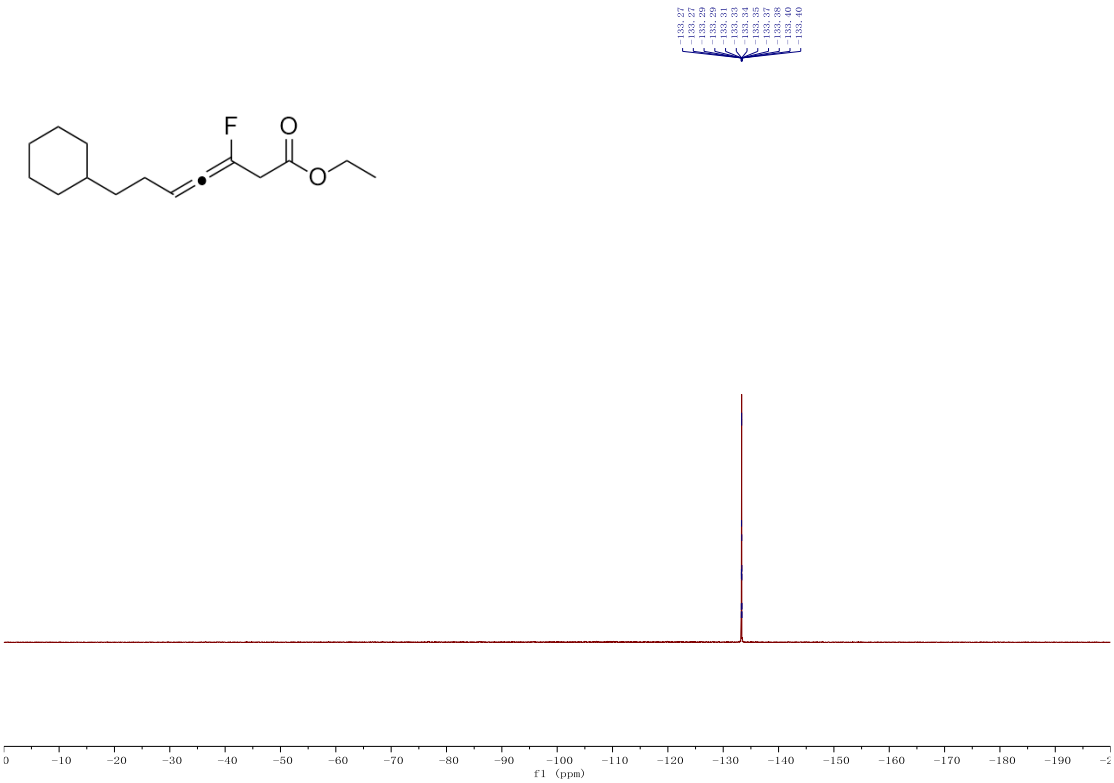
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4n**



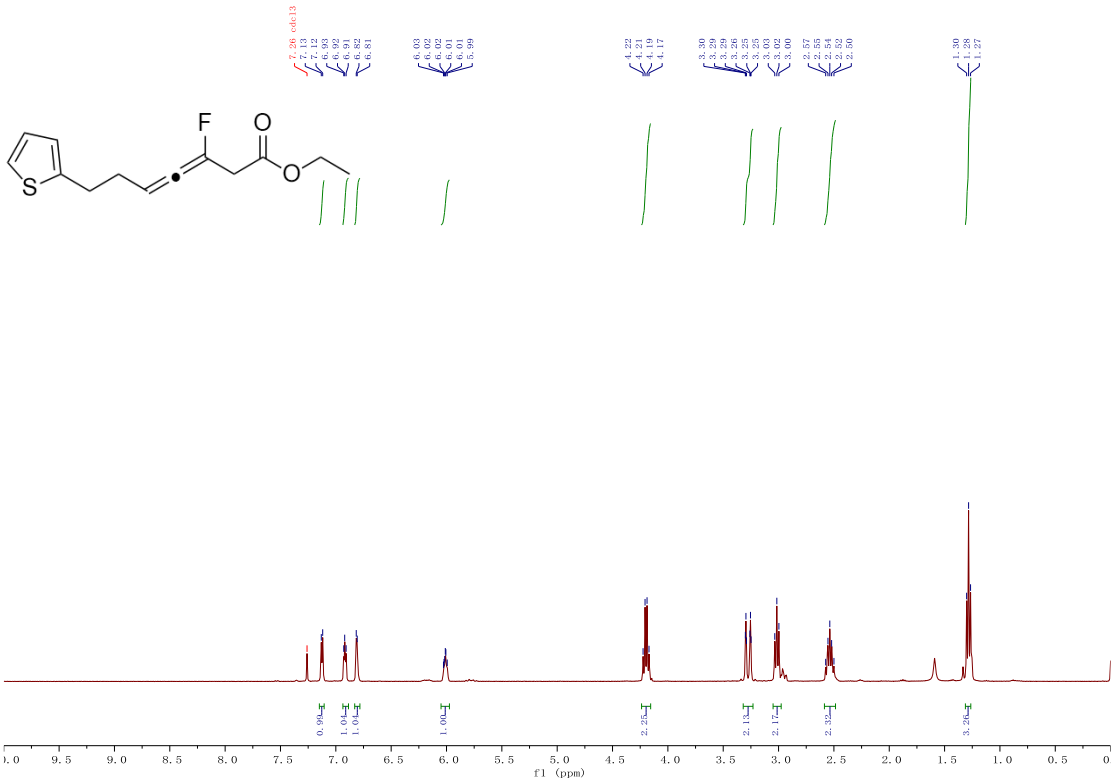
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4n**



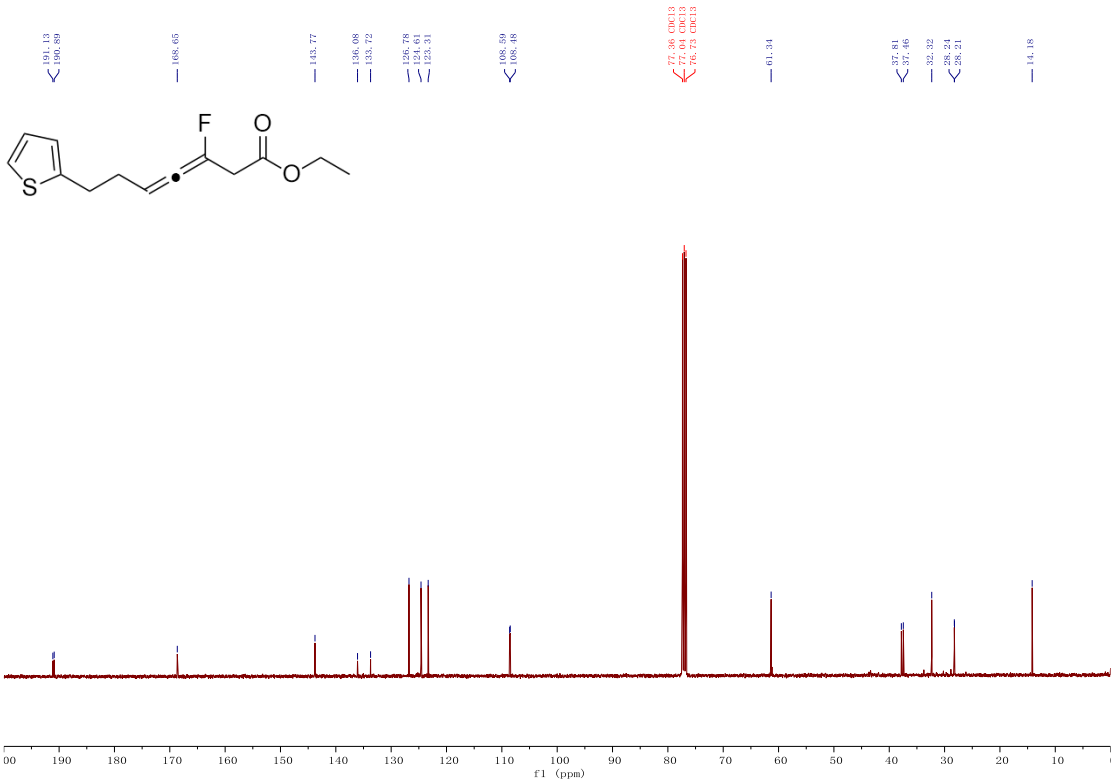
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4n**



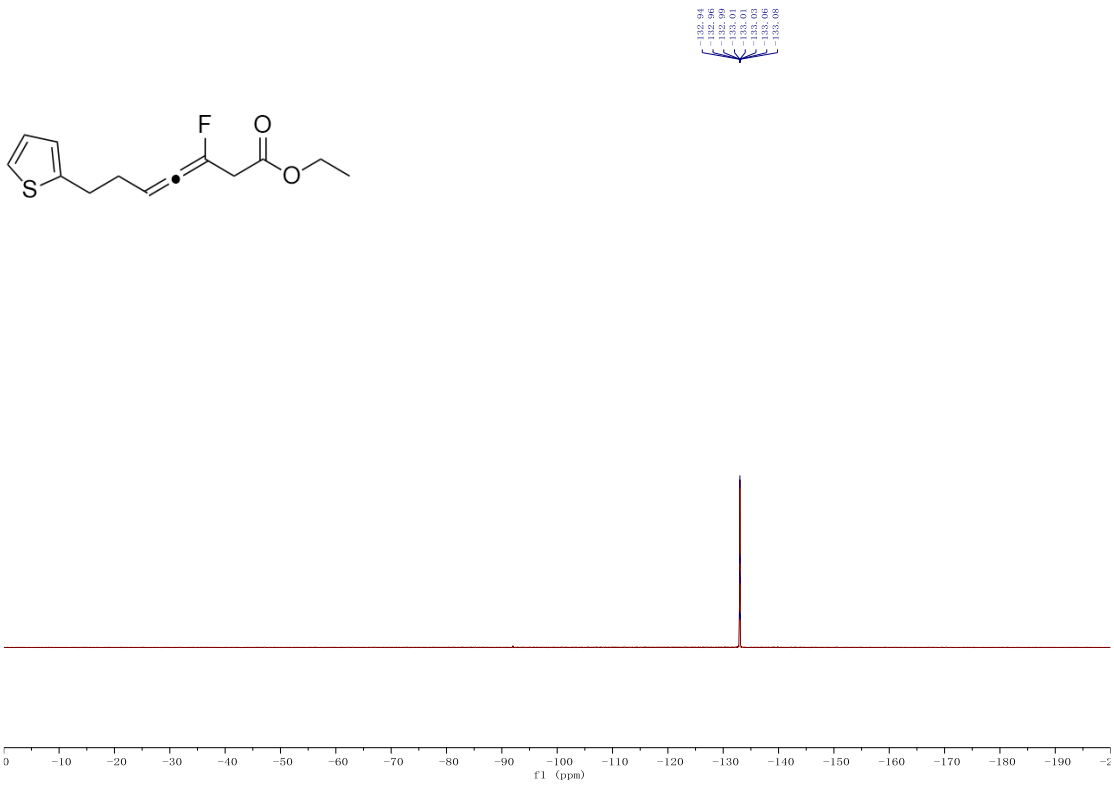
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4o**



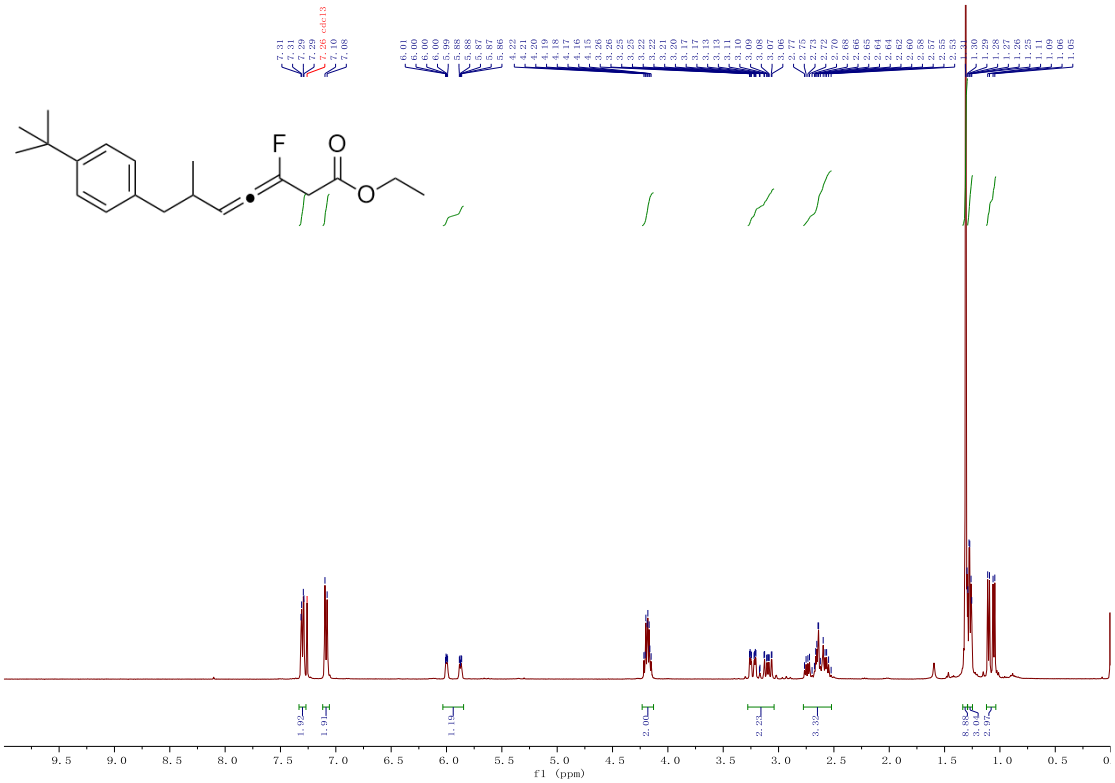
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4o**



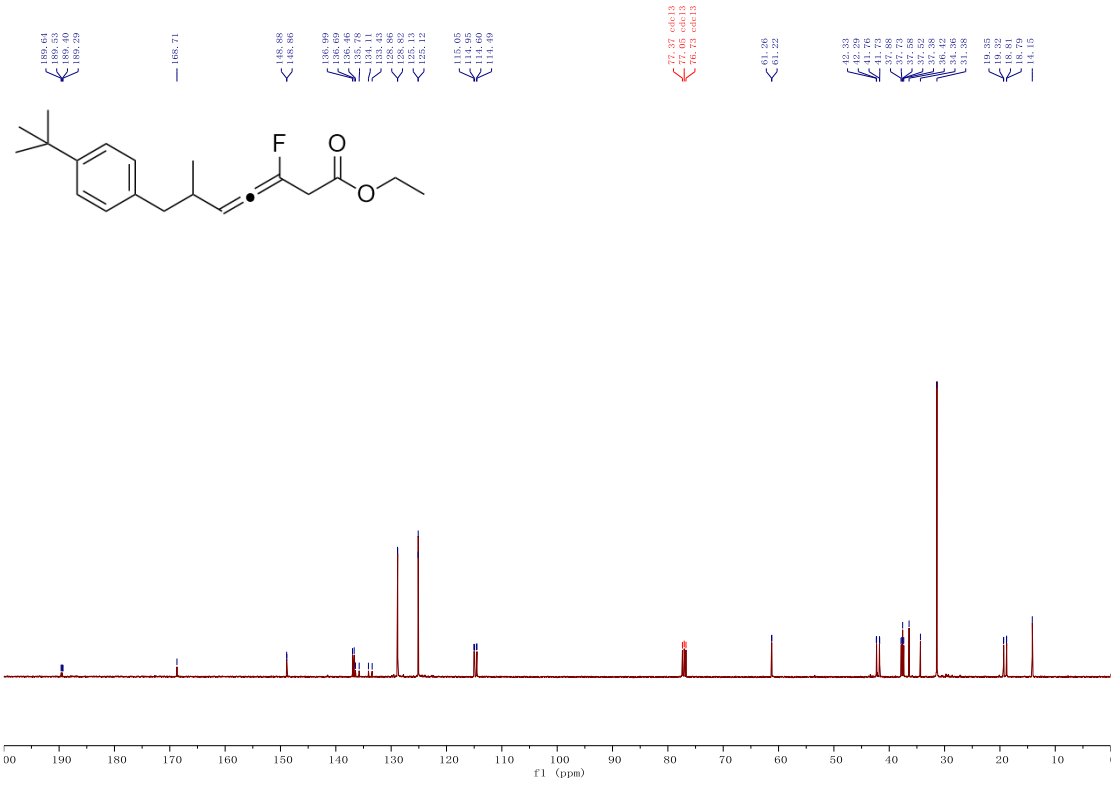
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4o**



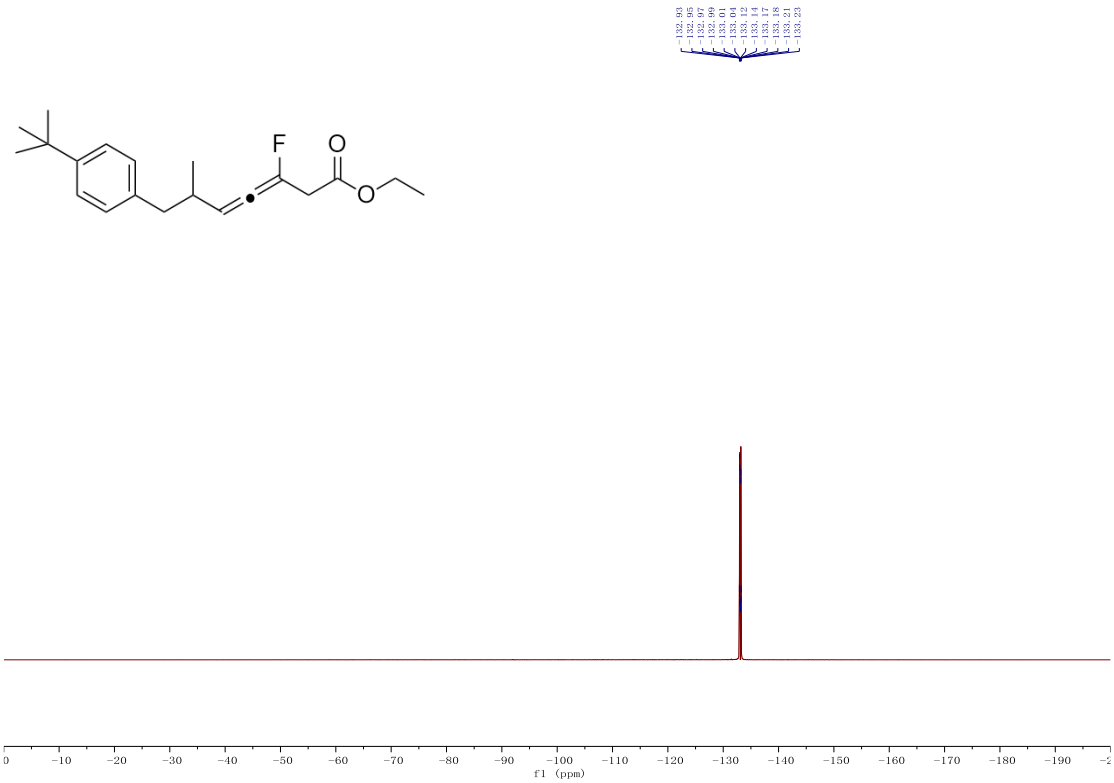
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p**



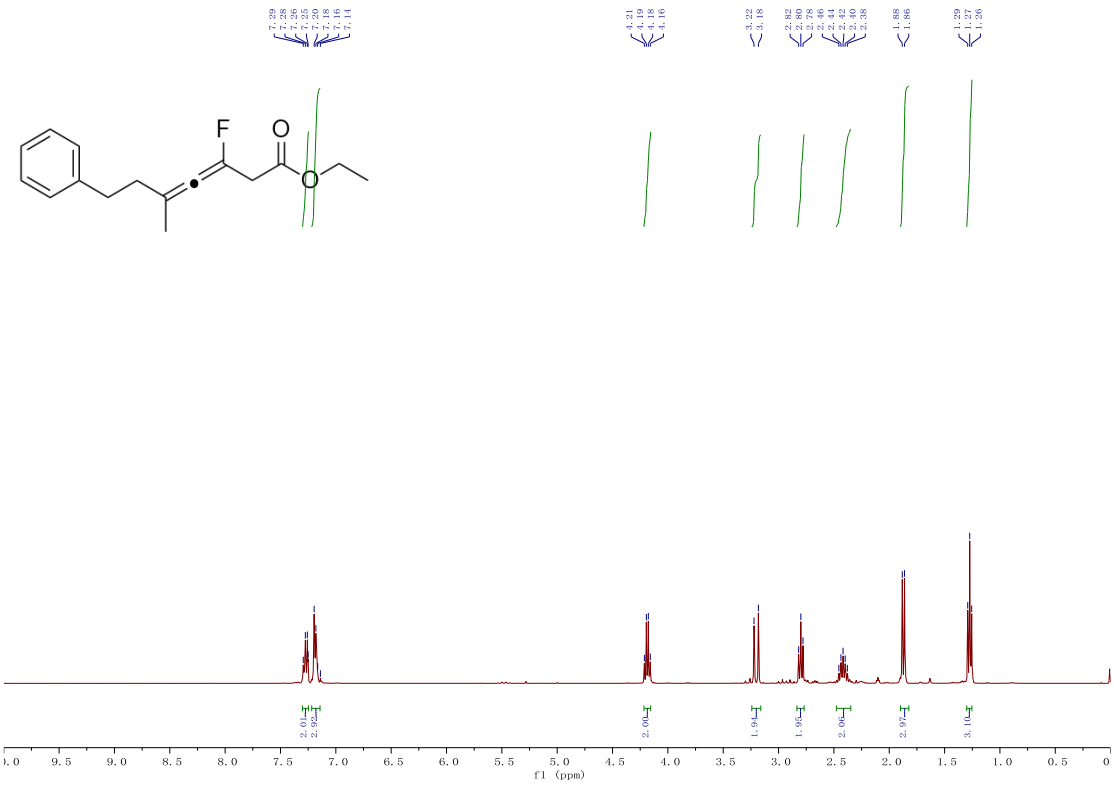
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4p**



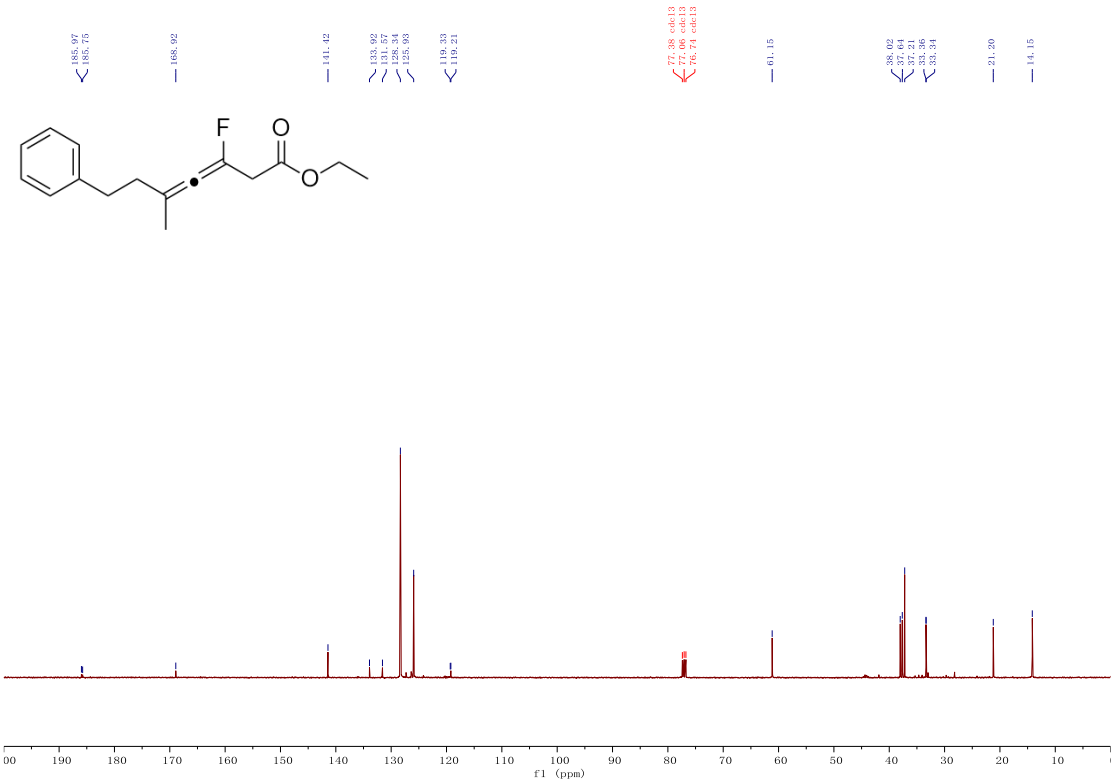
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4p**



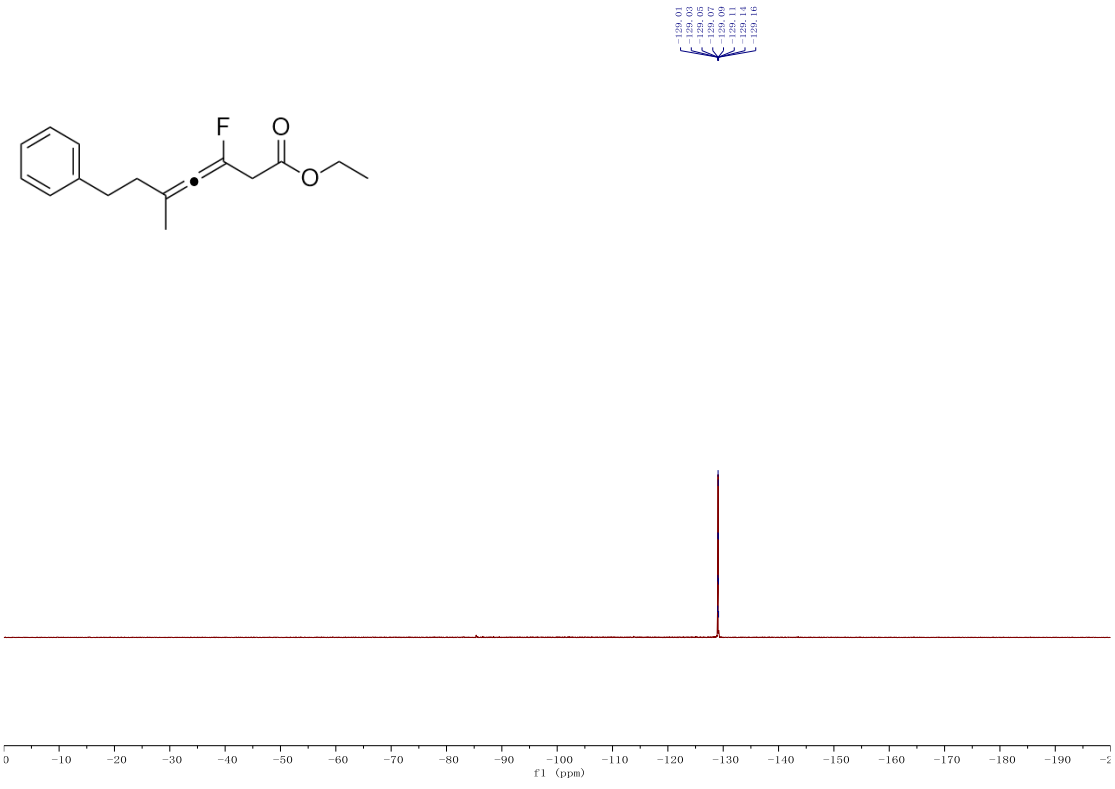
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4q**



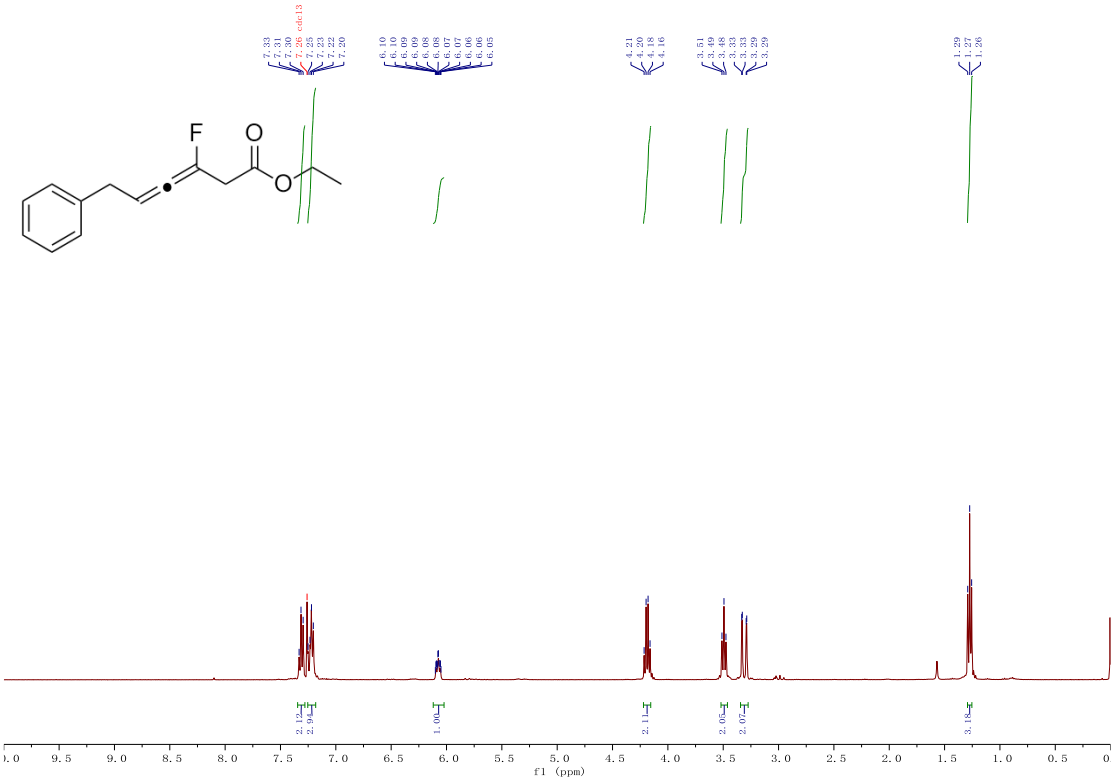
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4q**



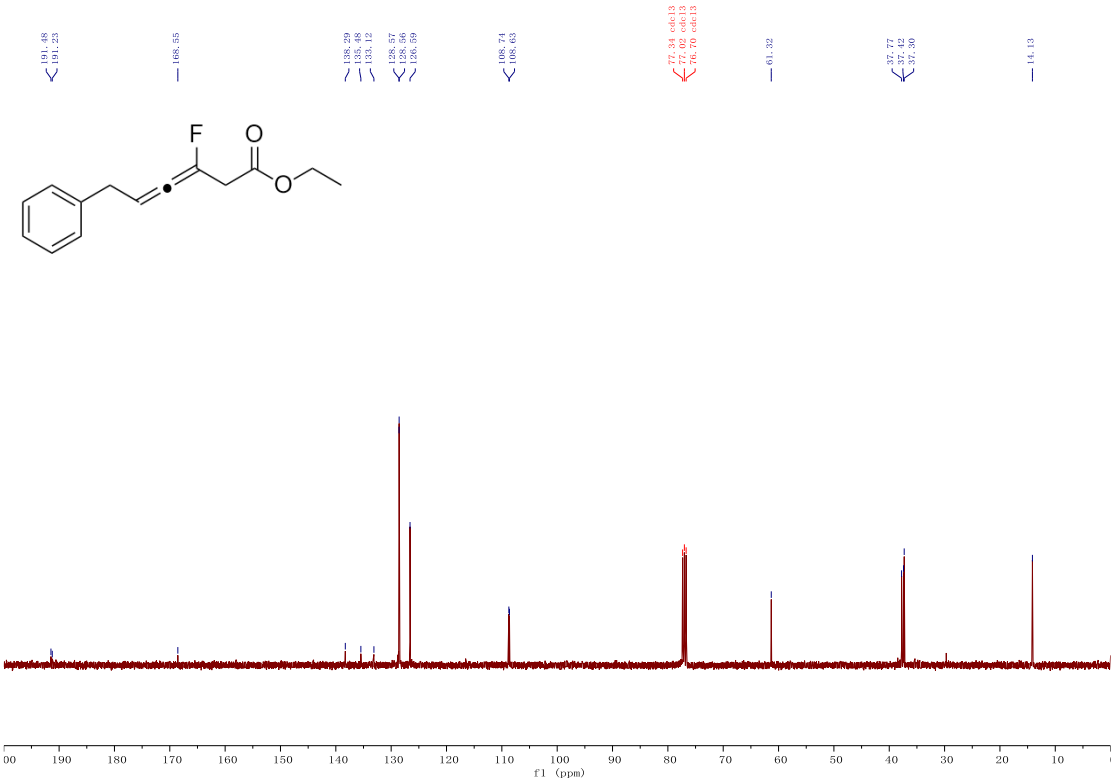
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4q**



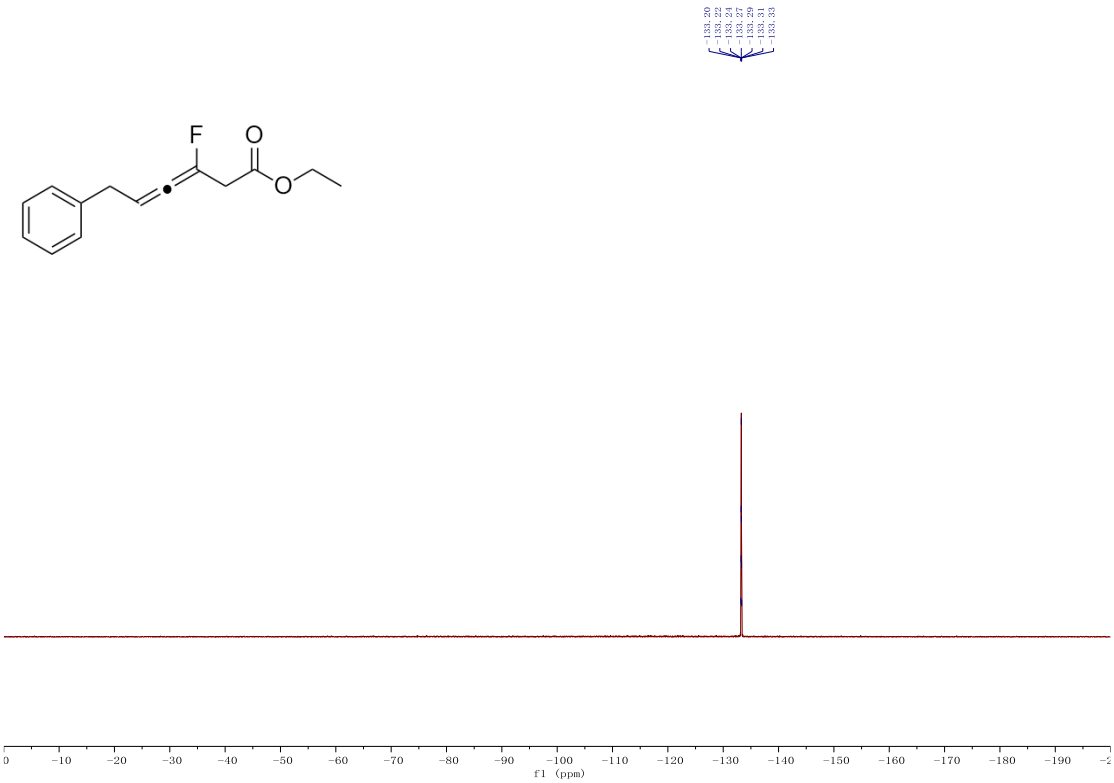
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4r**



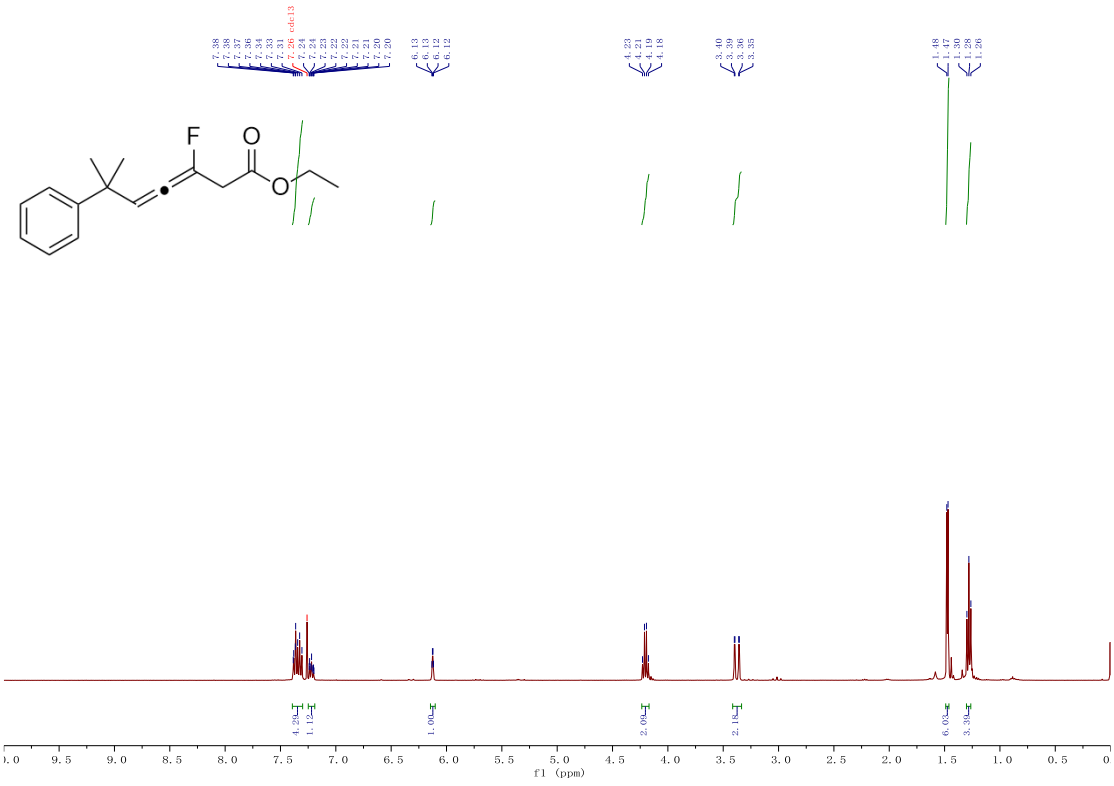
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4r**



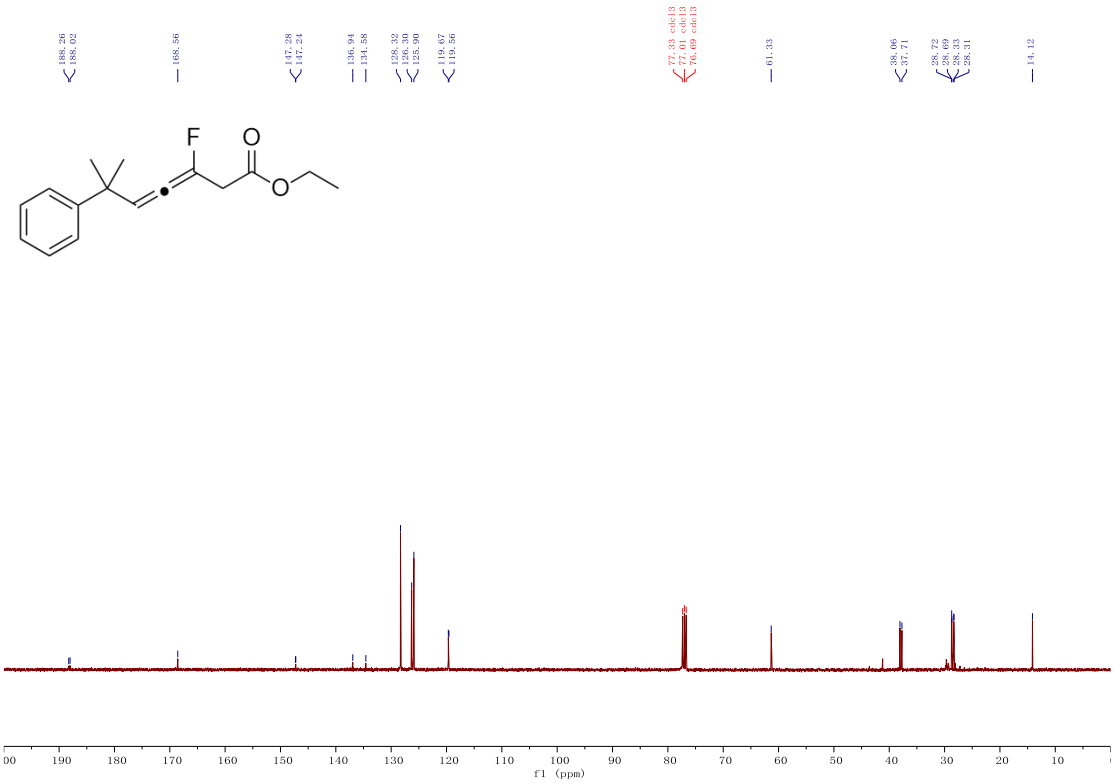
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4r**



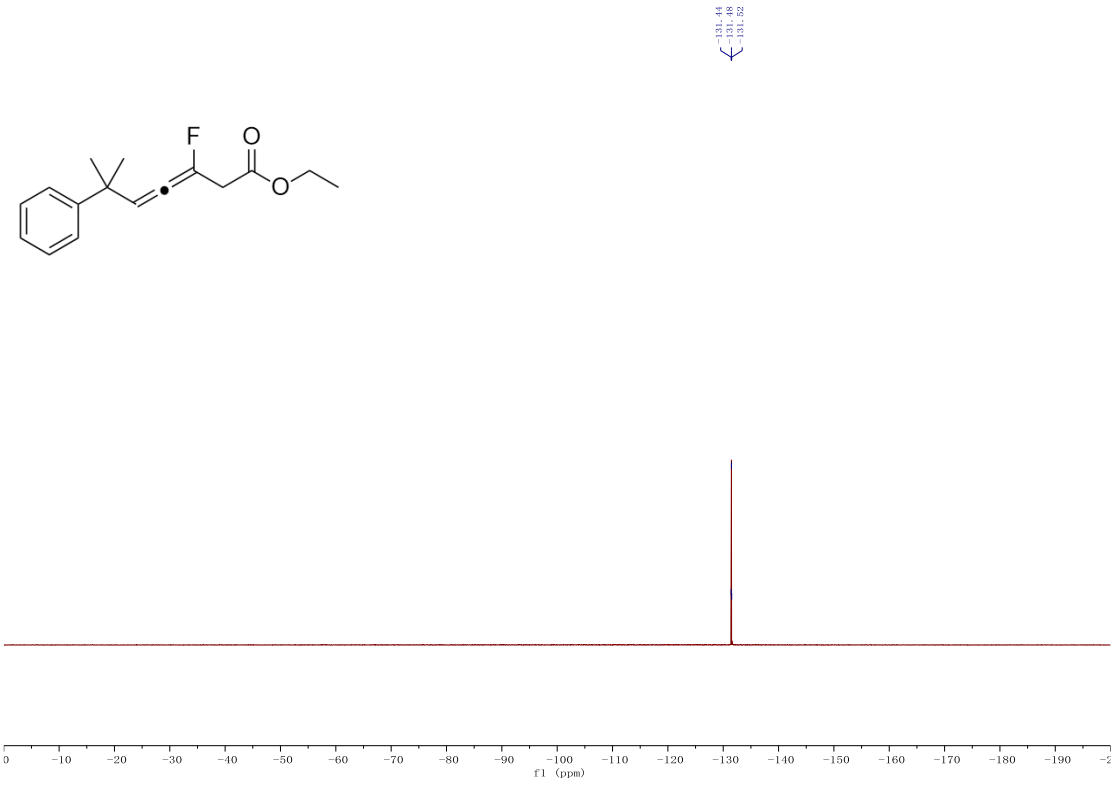
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4s**



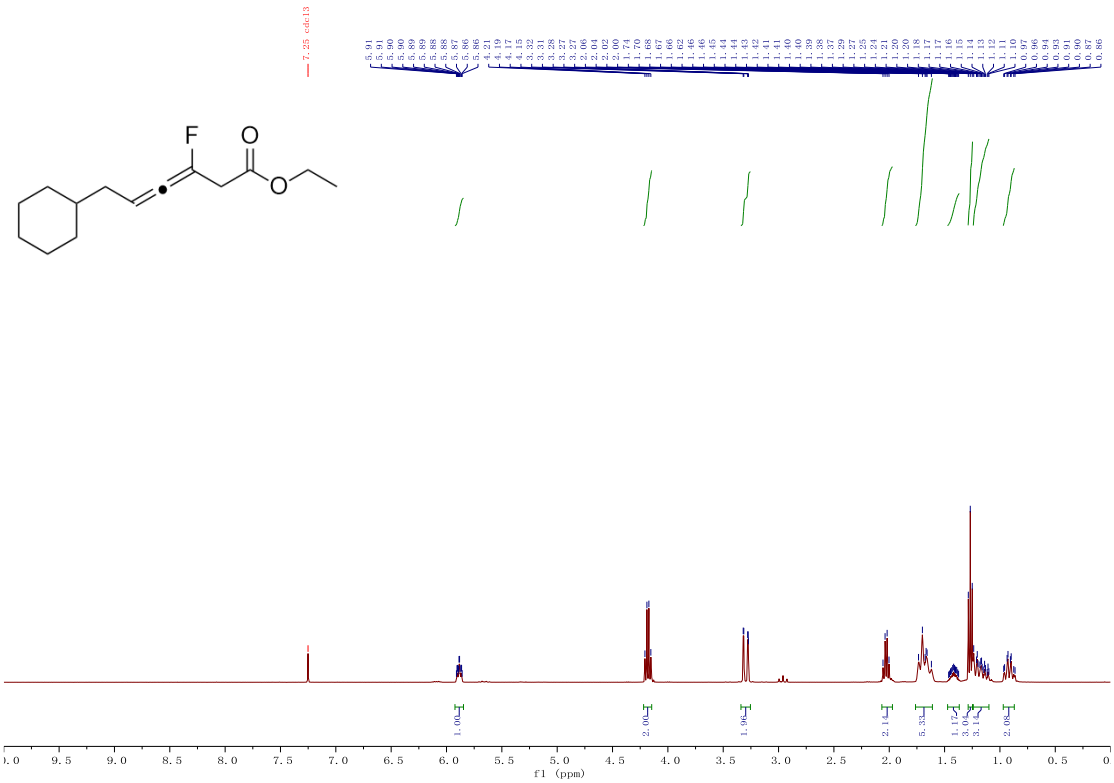
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4s**



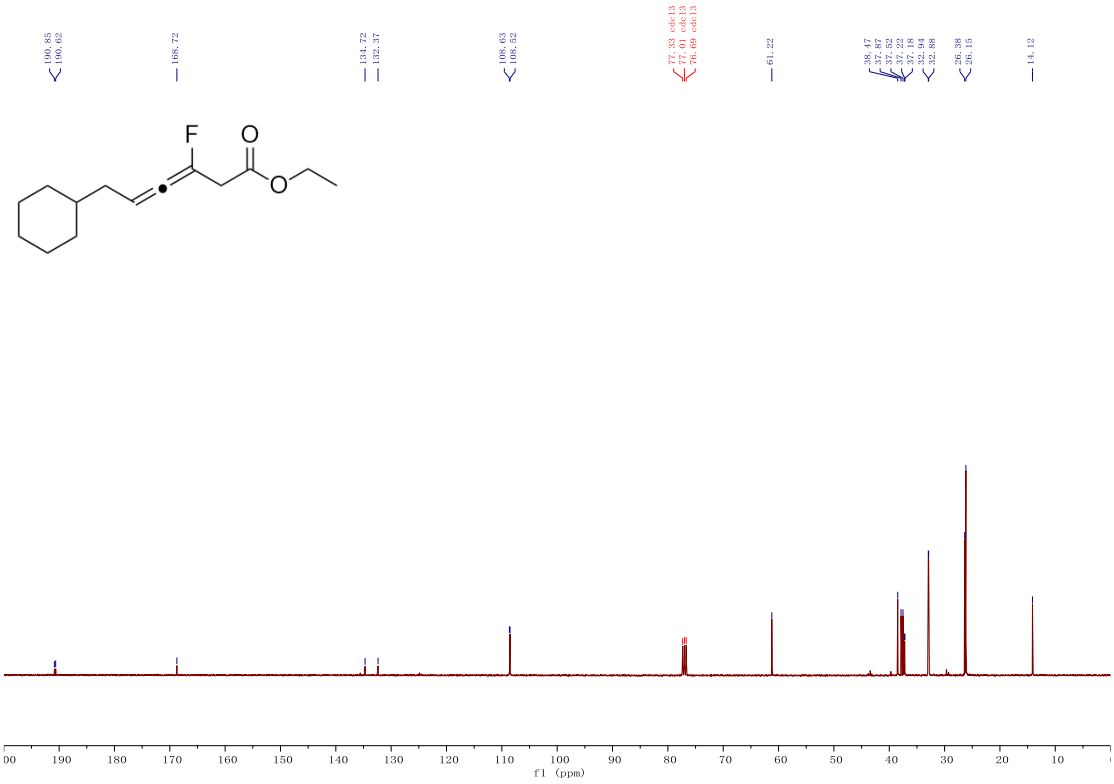
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4s**



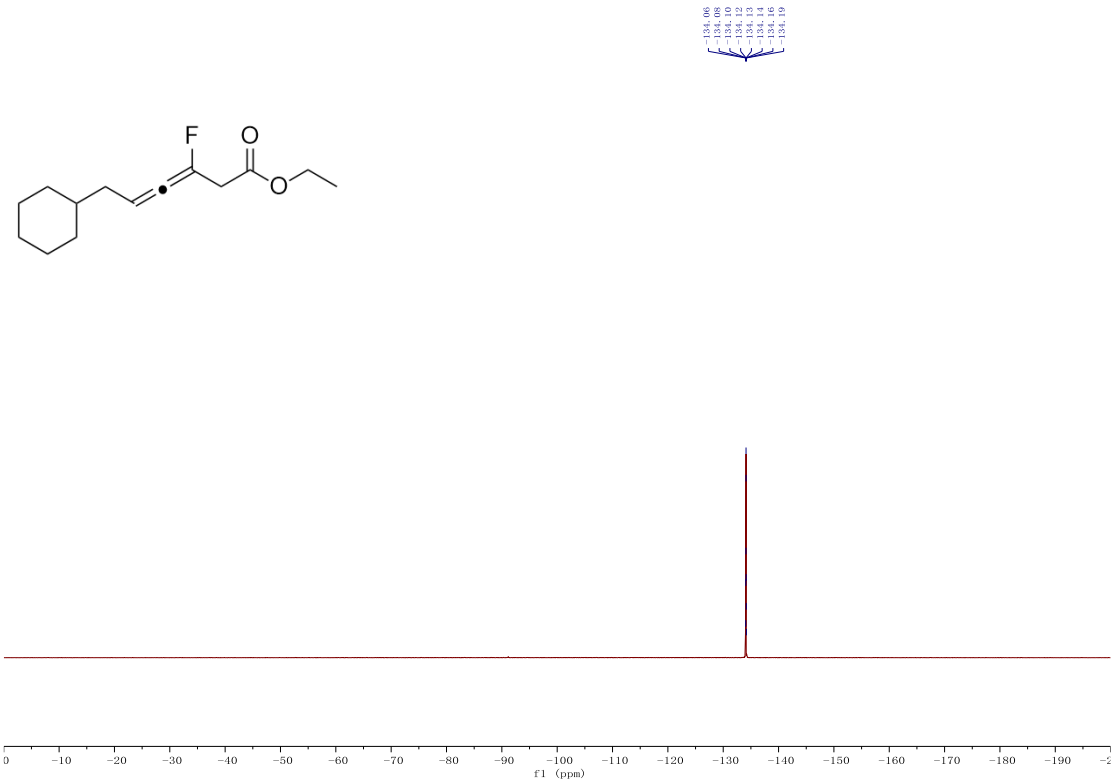
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4t**



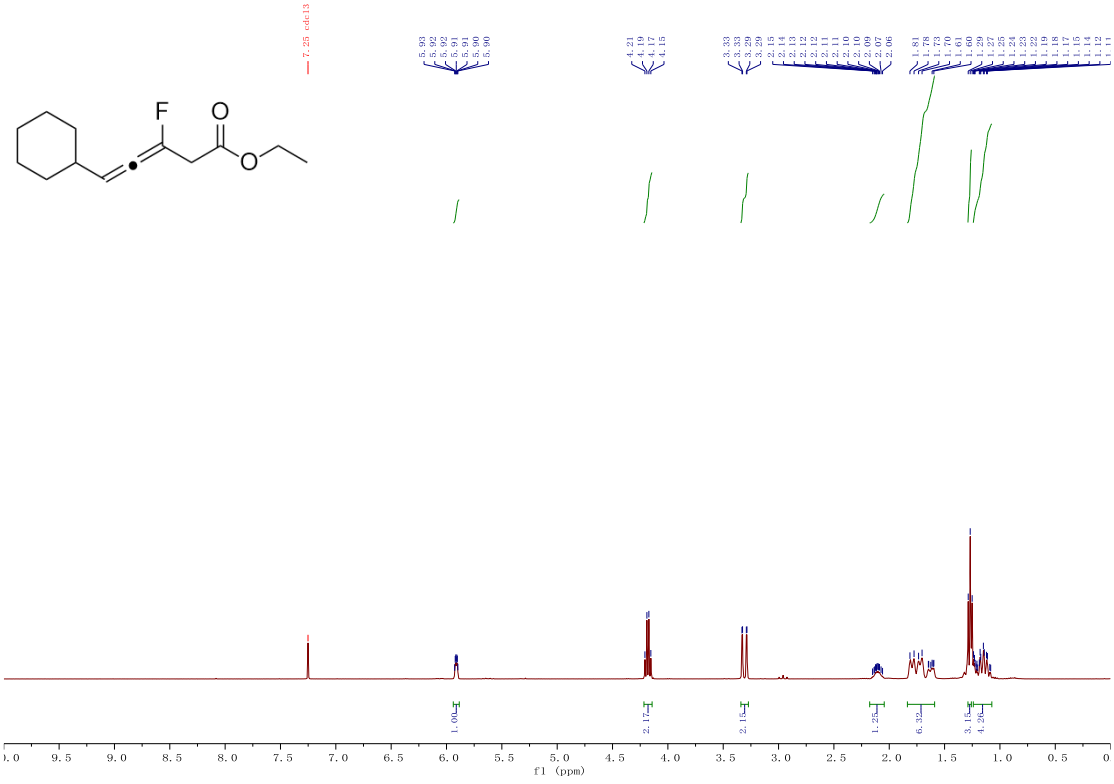
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4t**



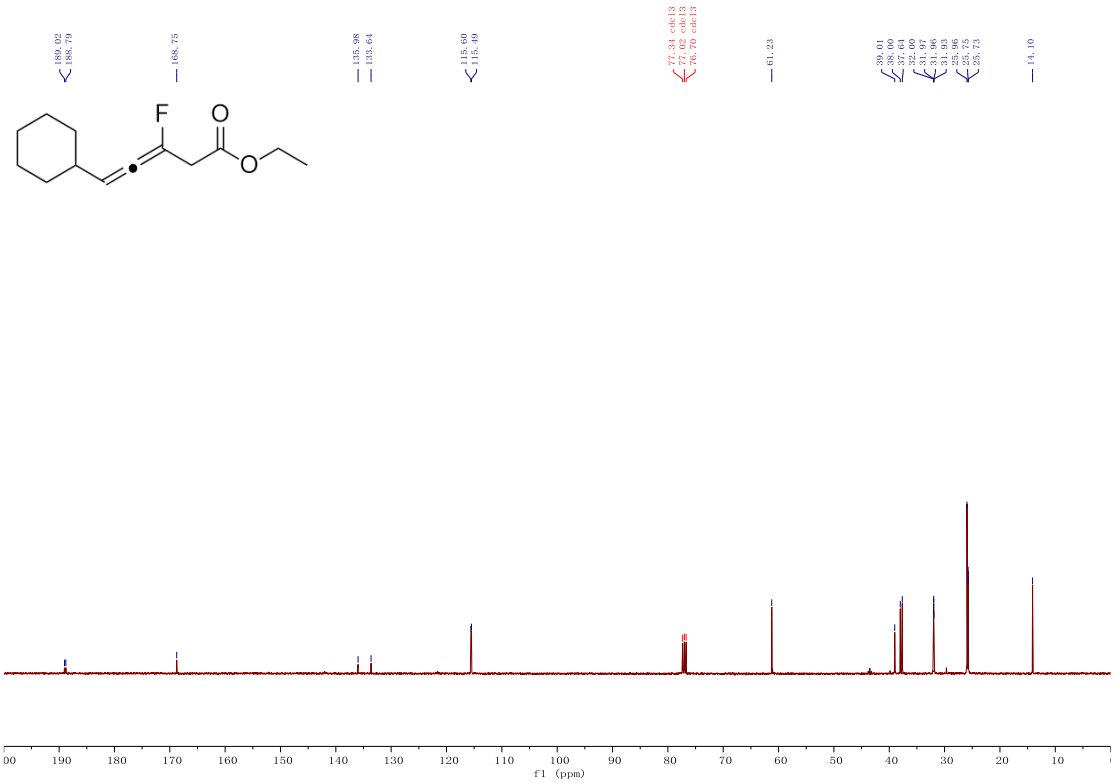
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4t**



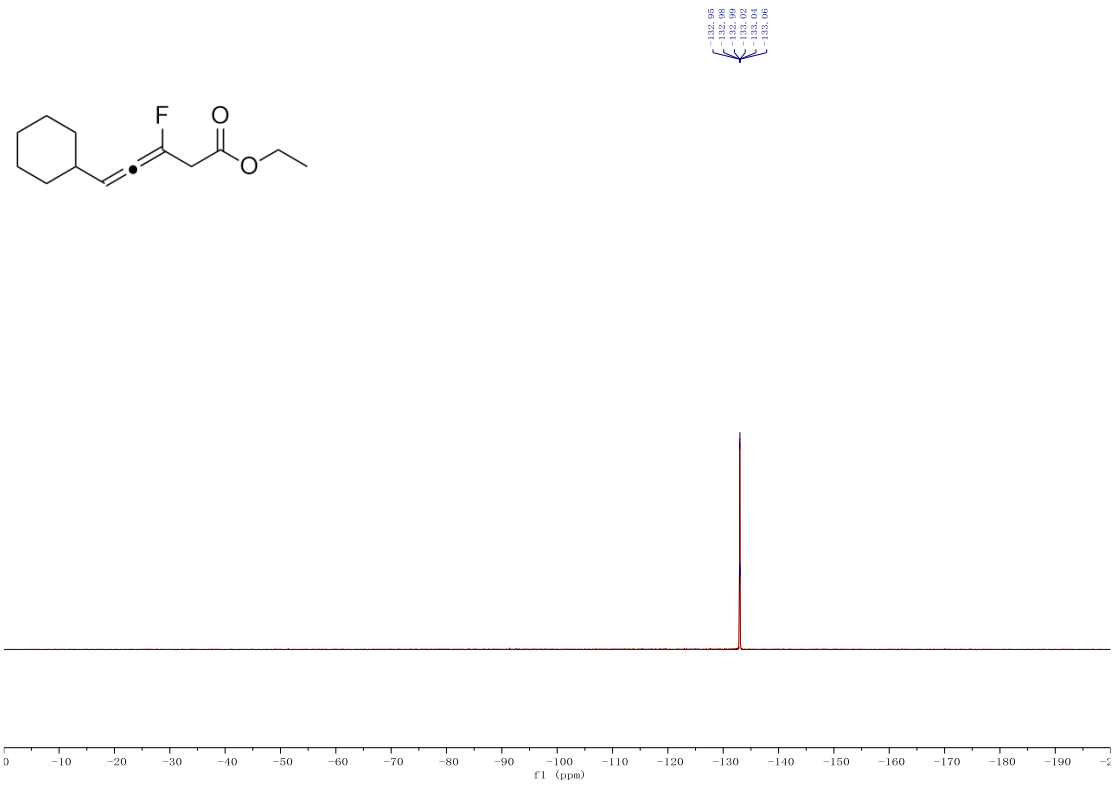
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4u**



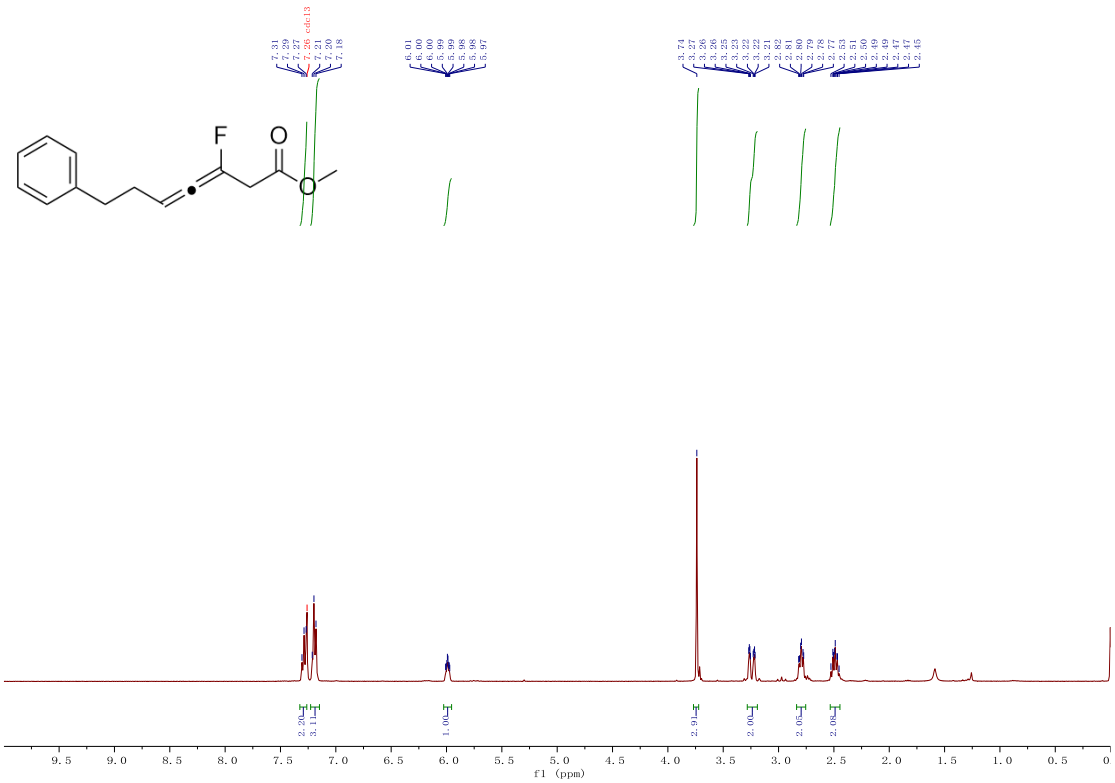
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **4u**



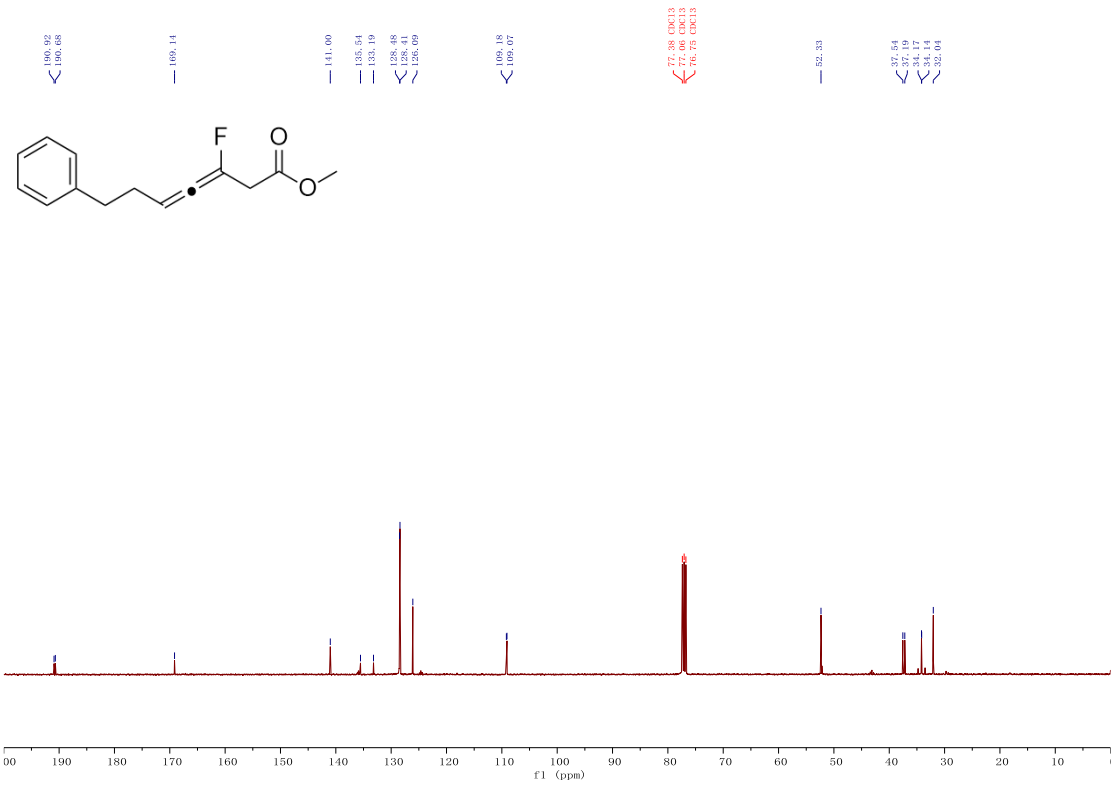
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4u**



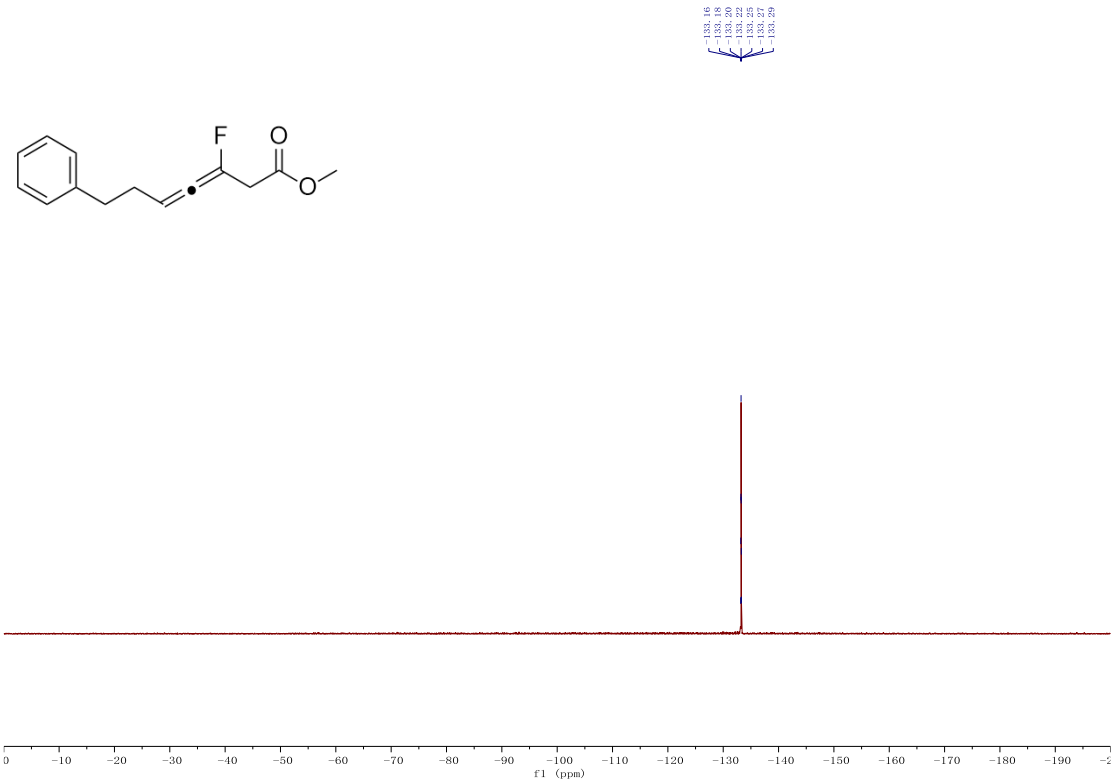
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6a**



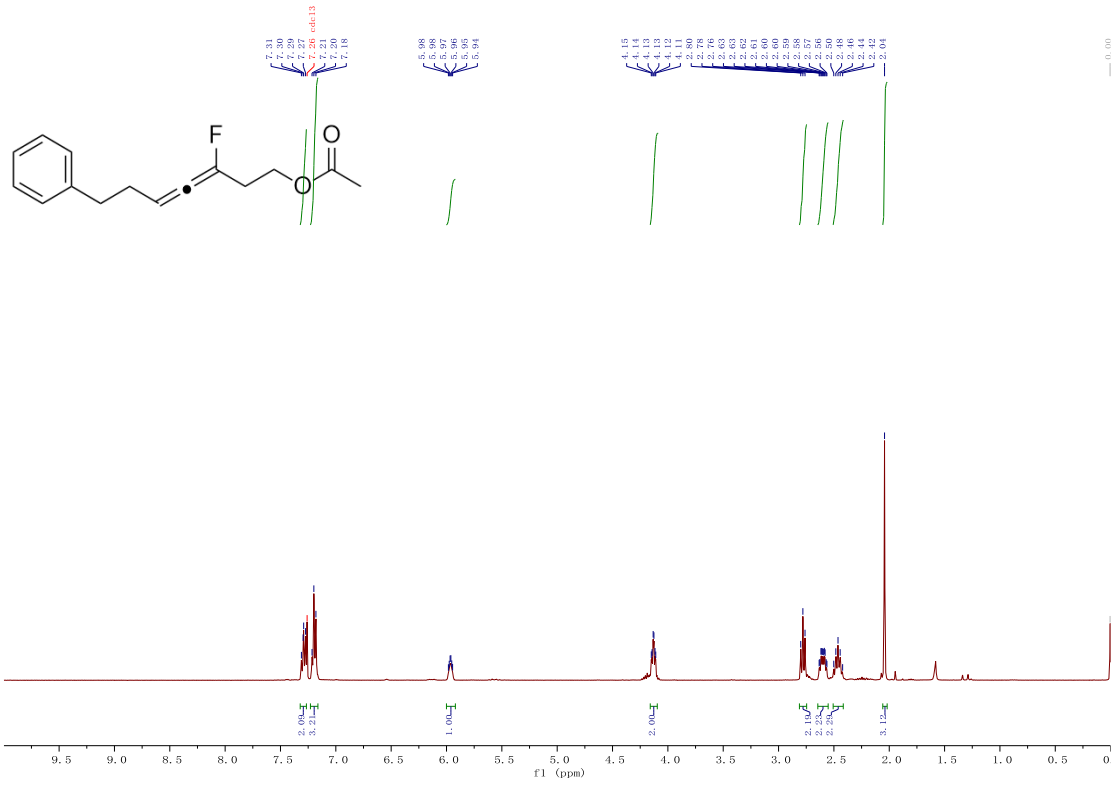
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6a**



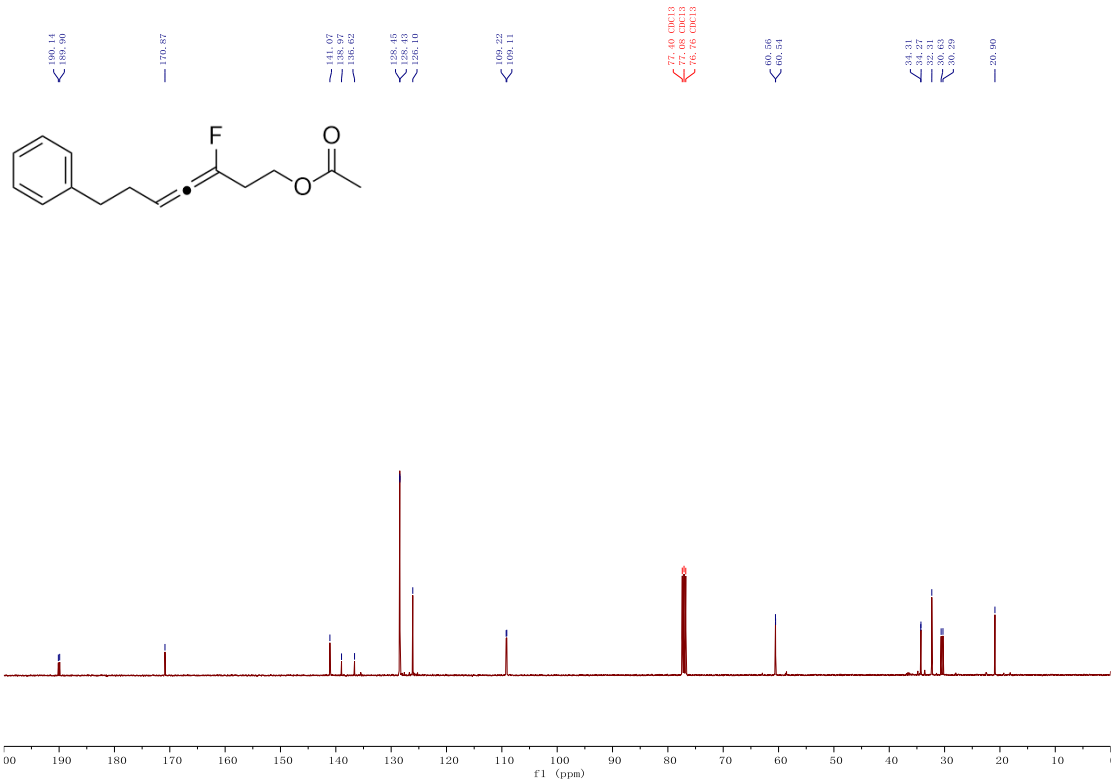
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6a**



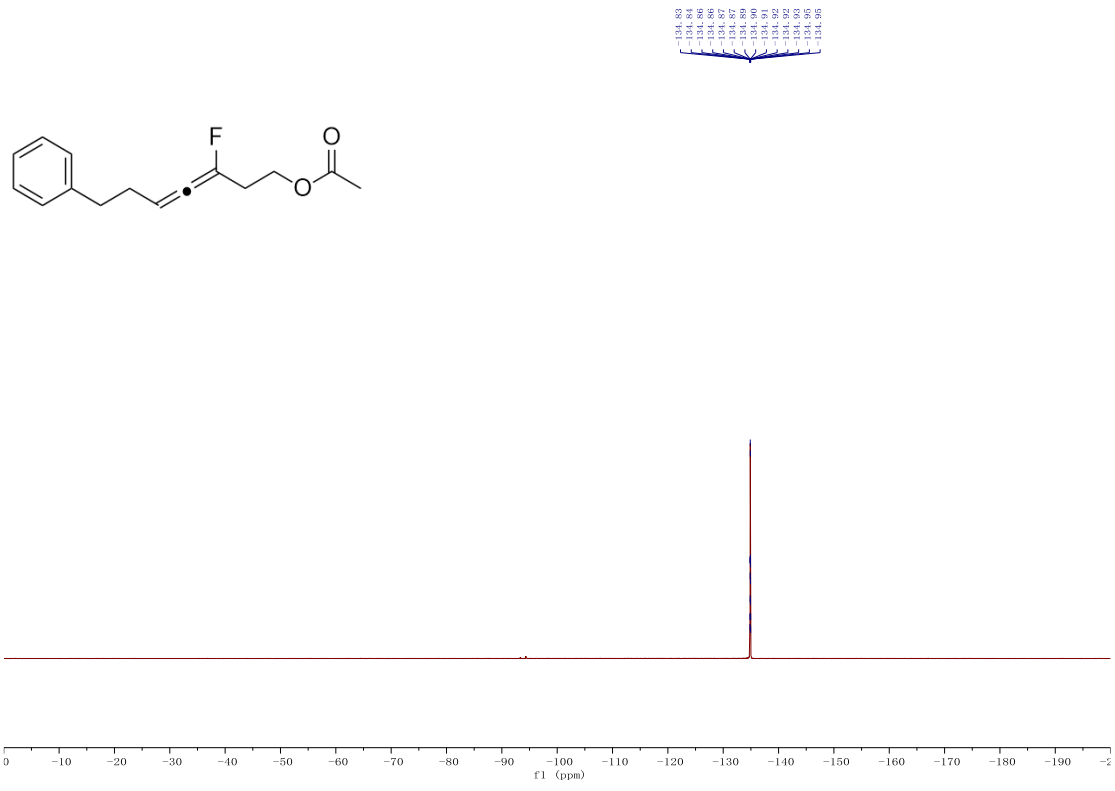
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6b**



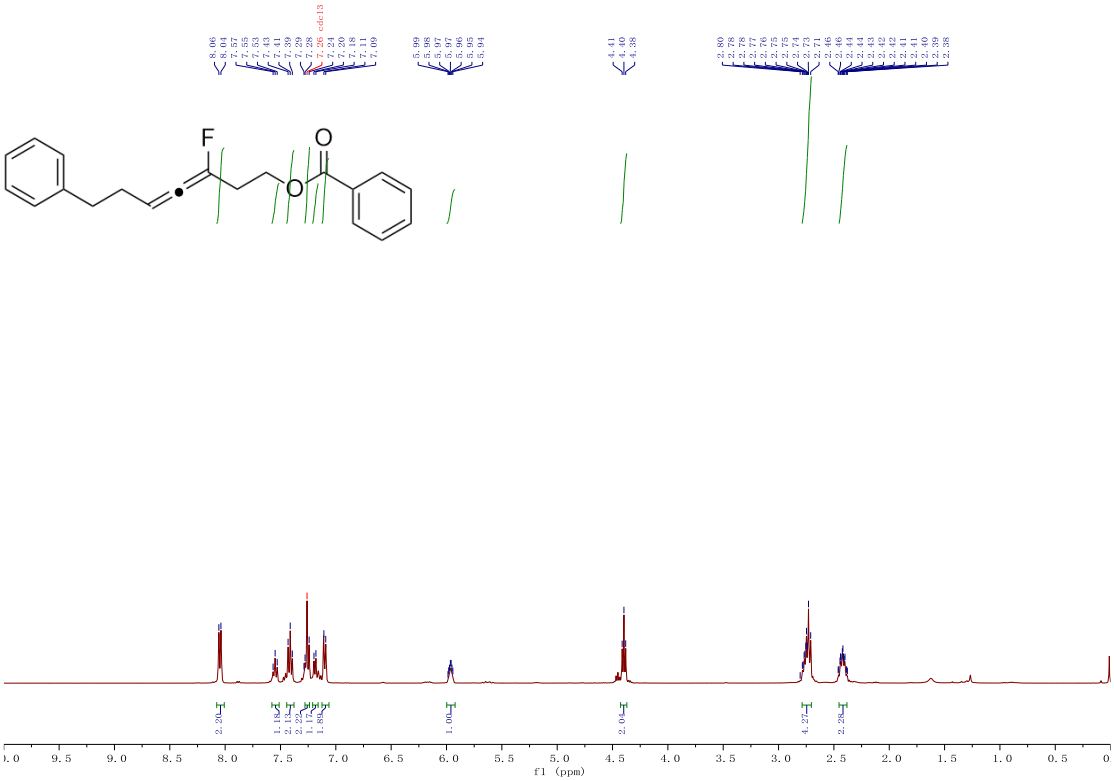
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6b**



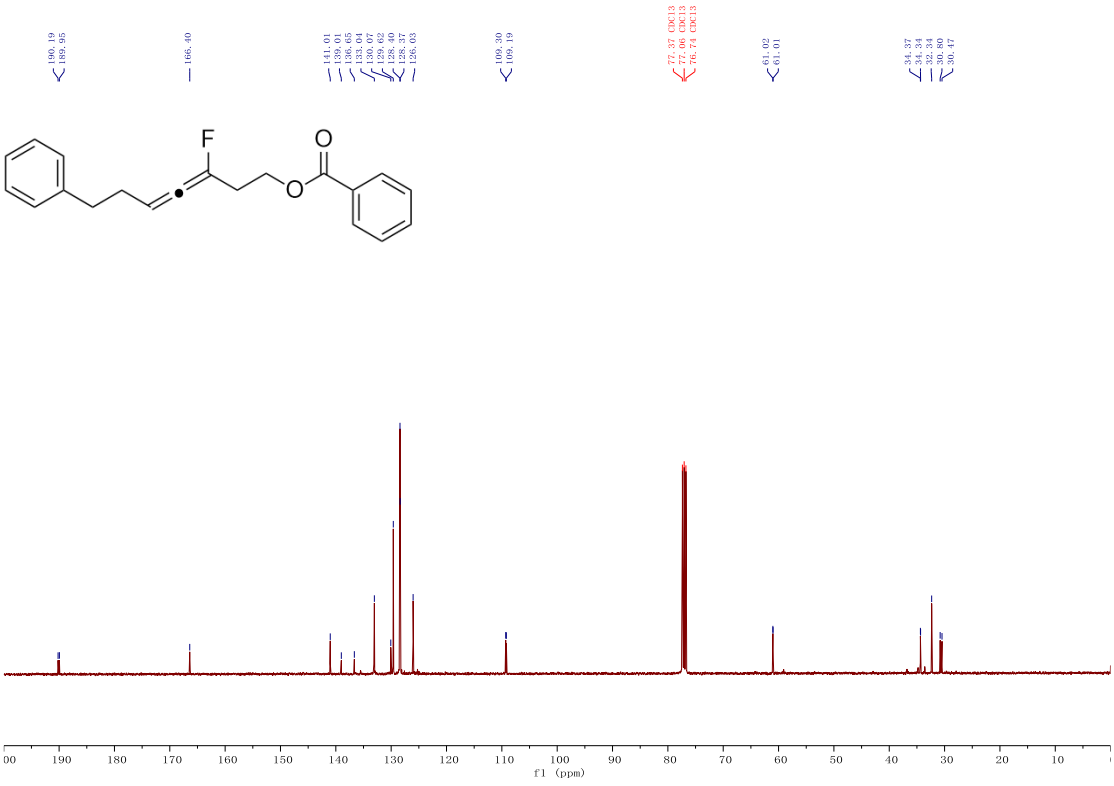
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6b**



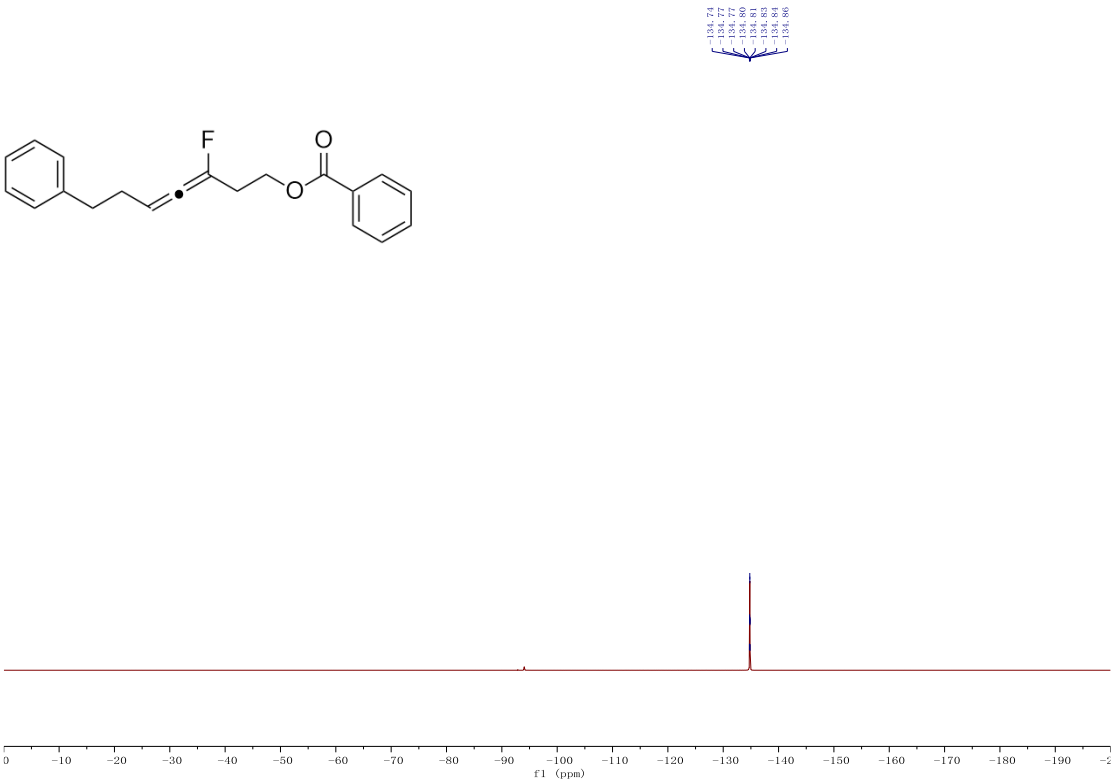
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6c**



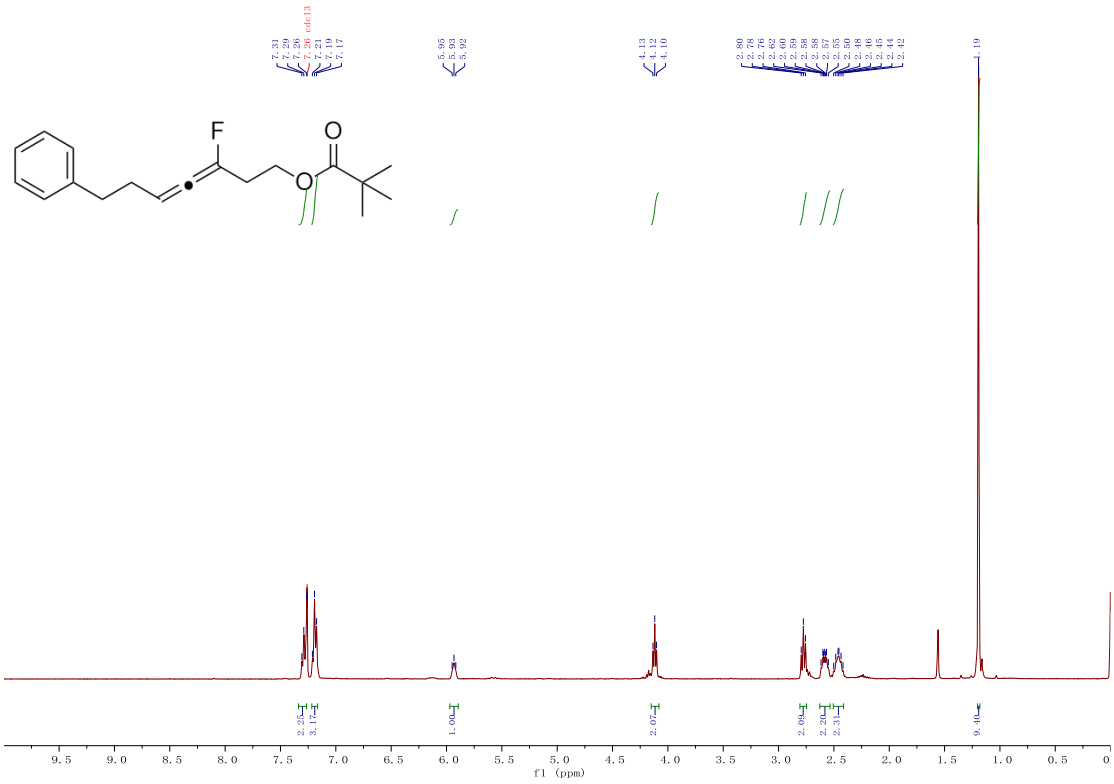
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6c**



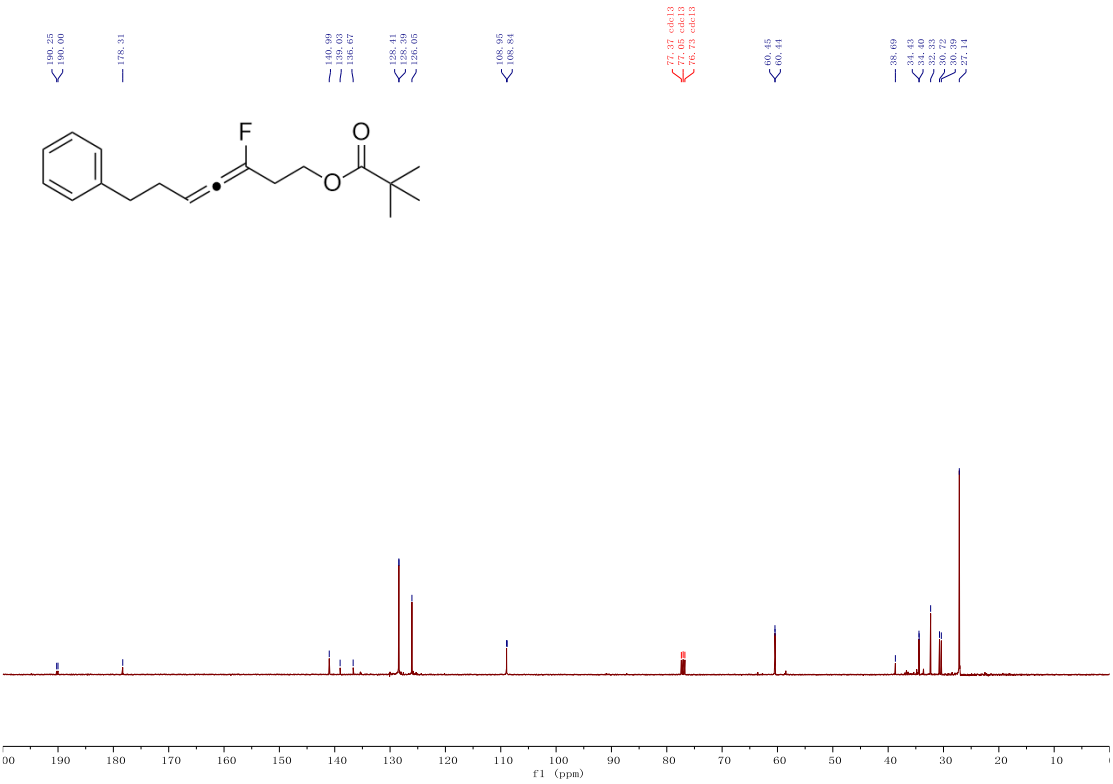
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6c**



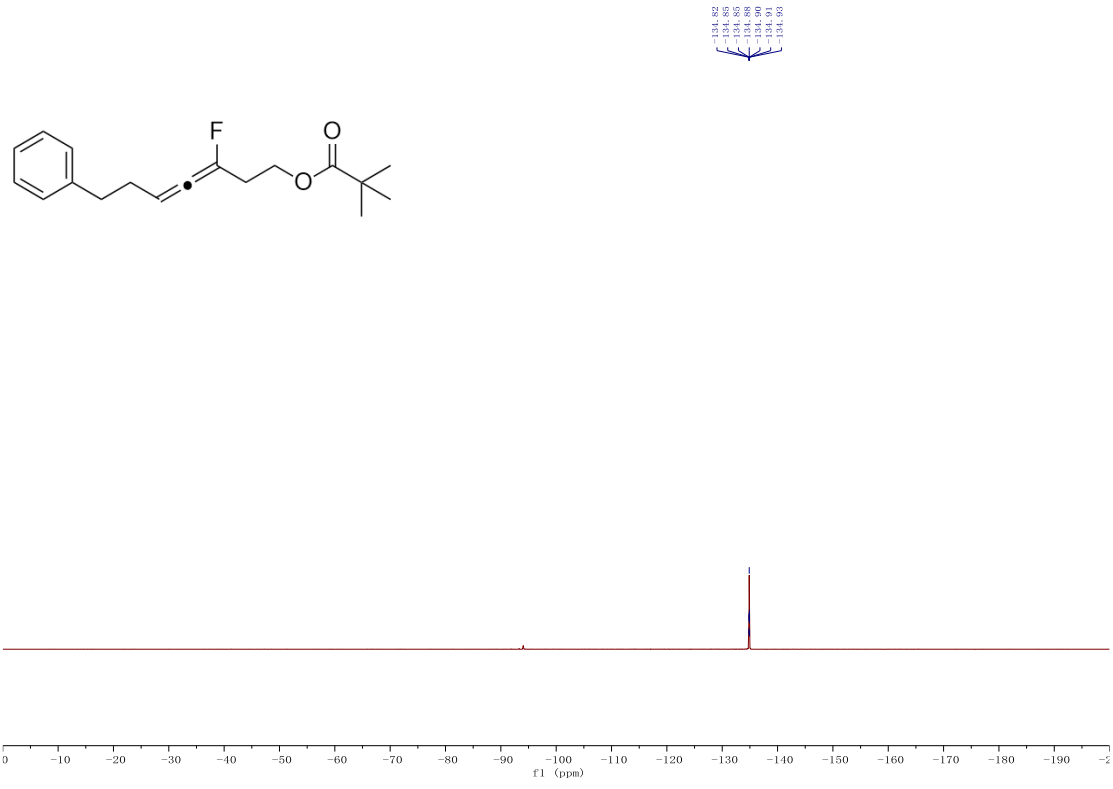
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6d**



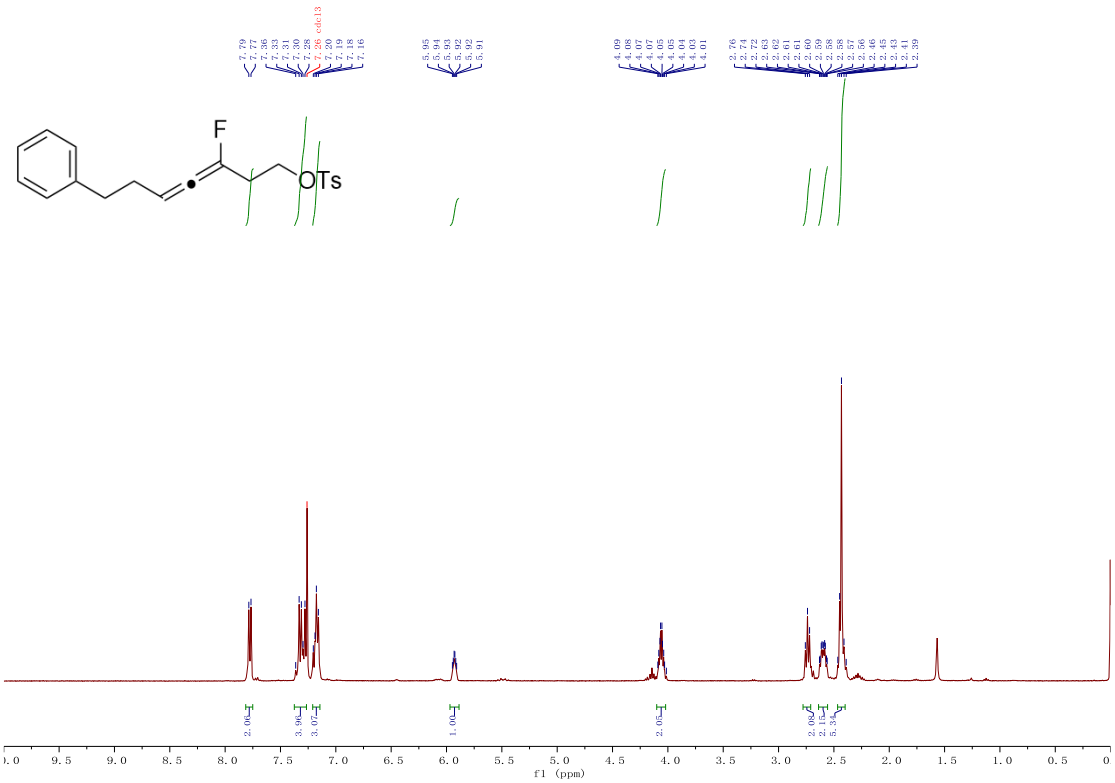
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6d**



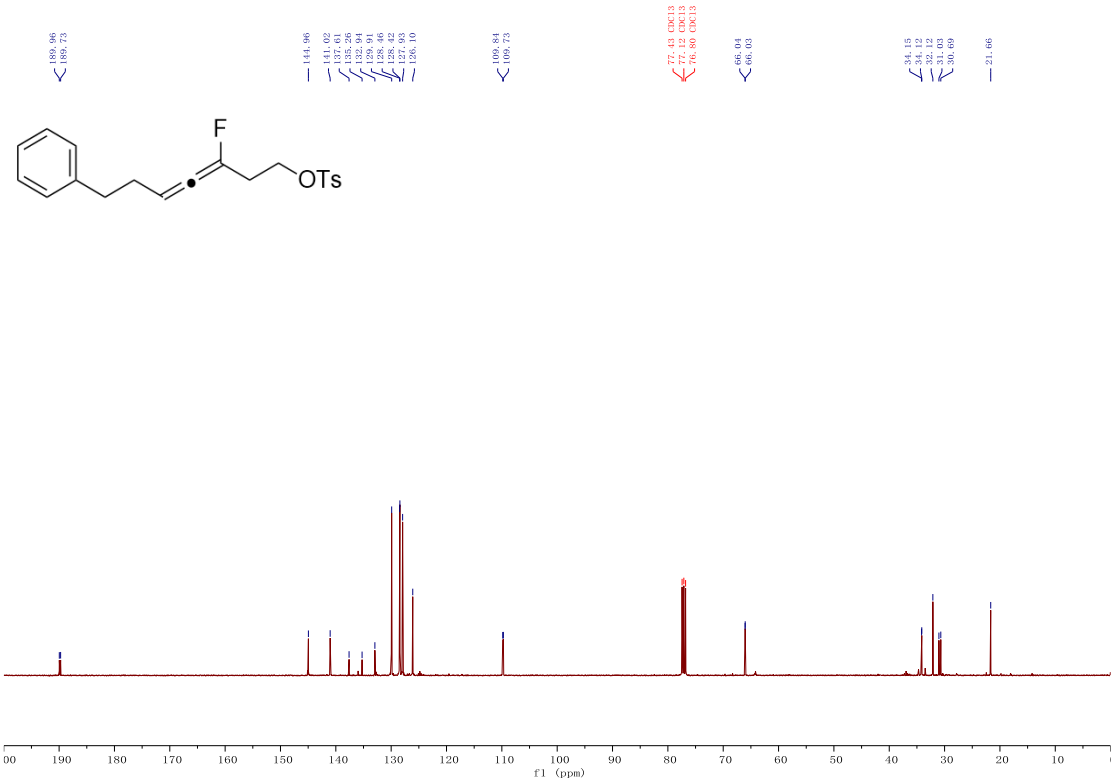
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6d**



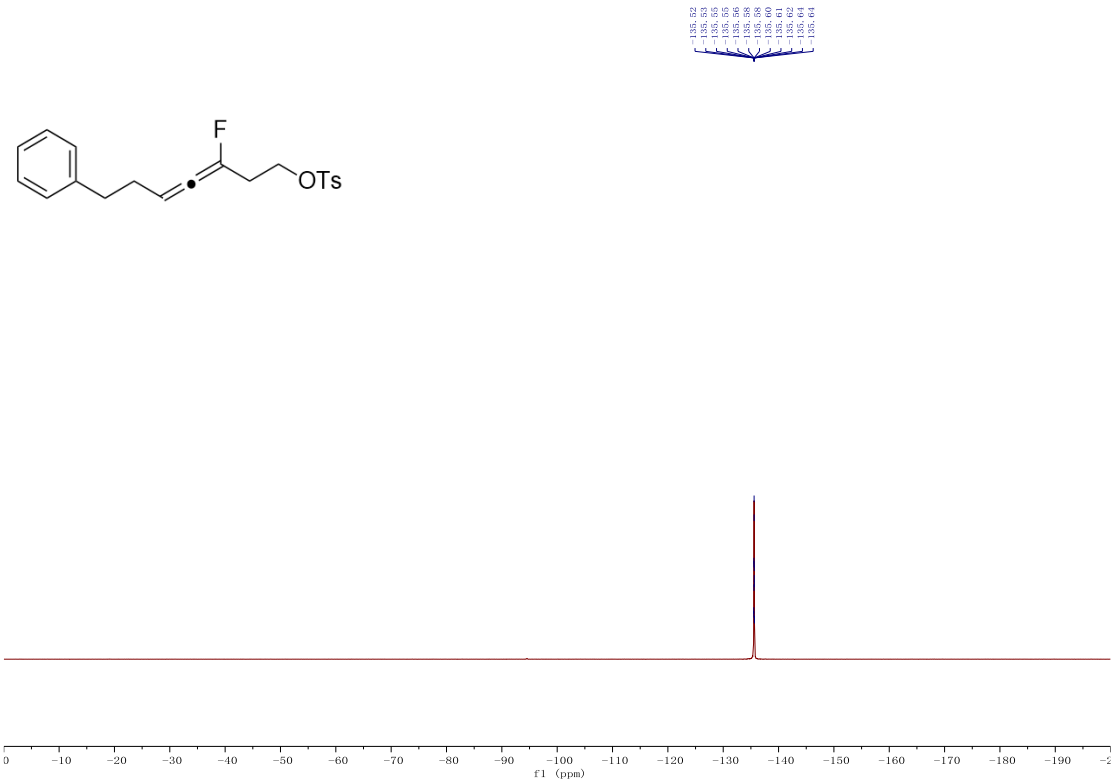
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6e**



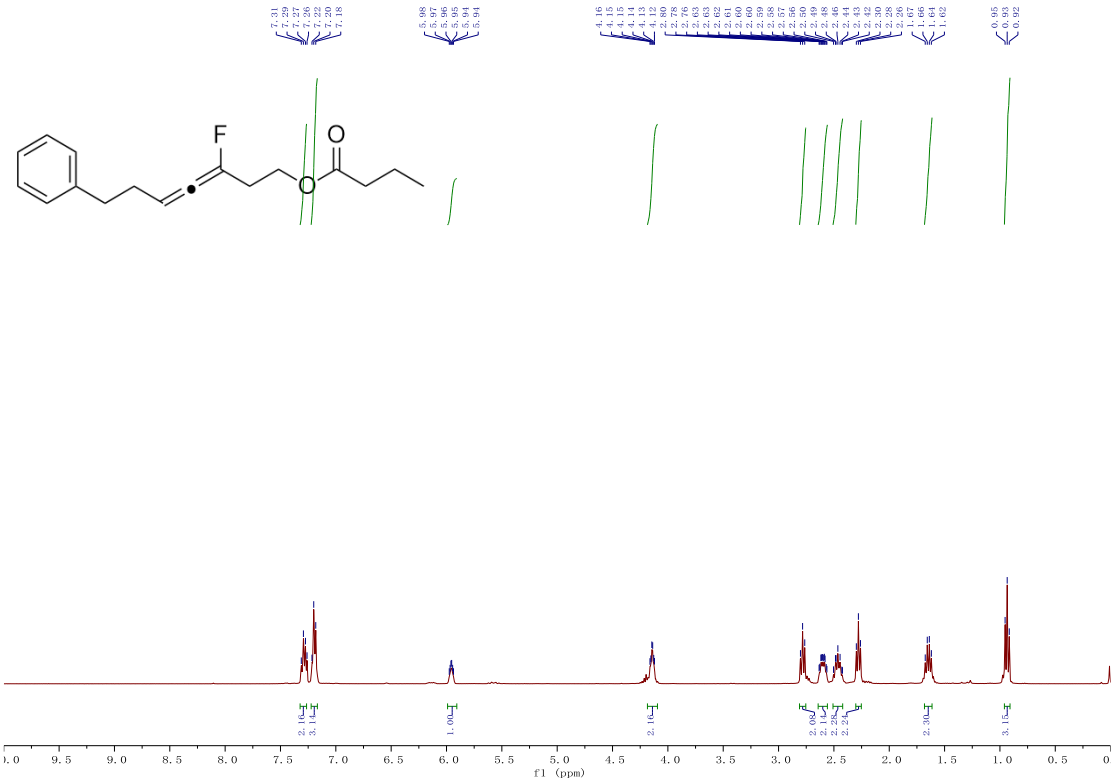
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6e**



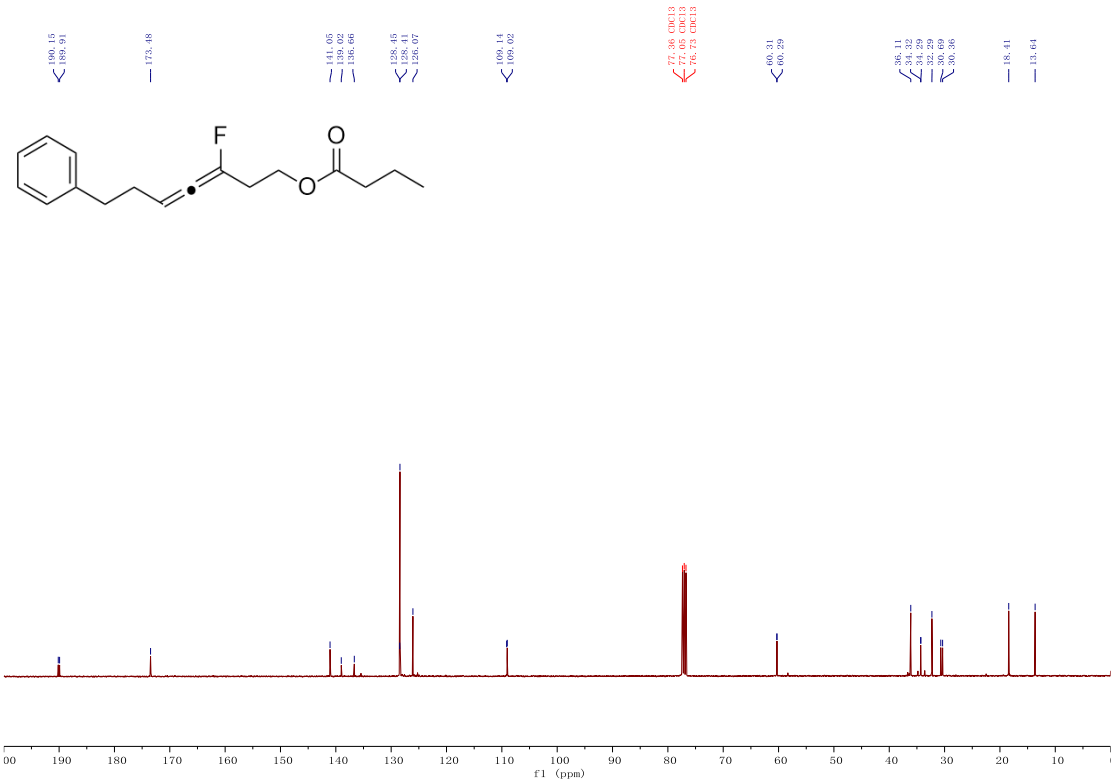
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6e**



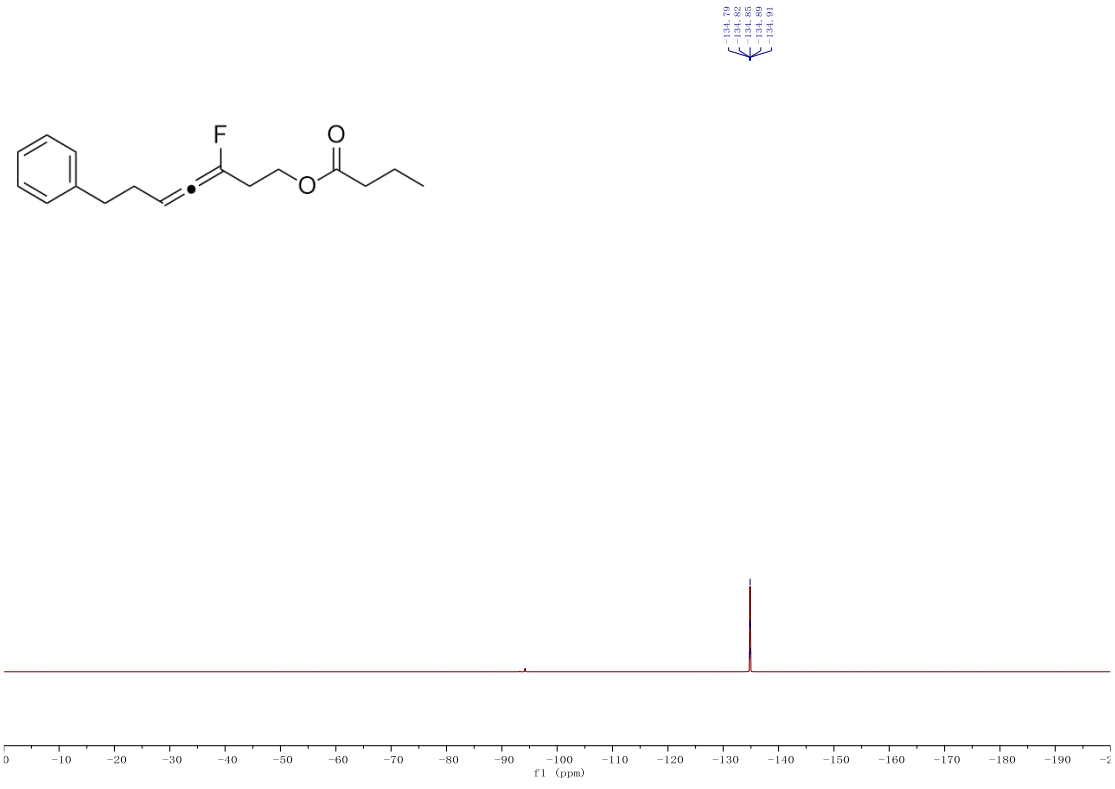
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6f**



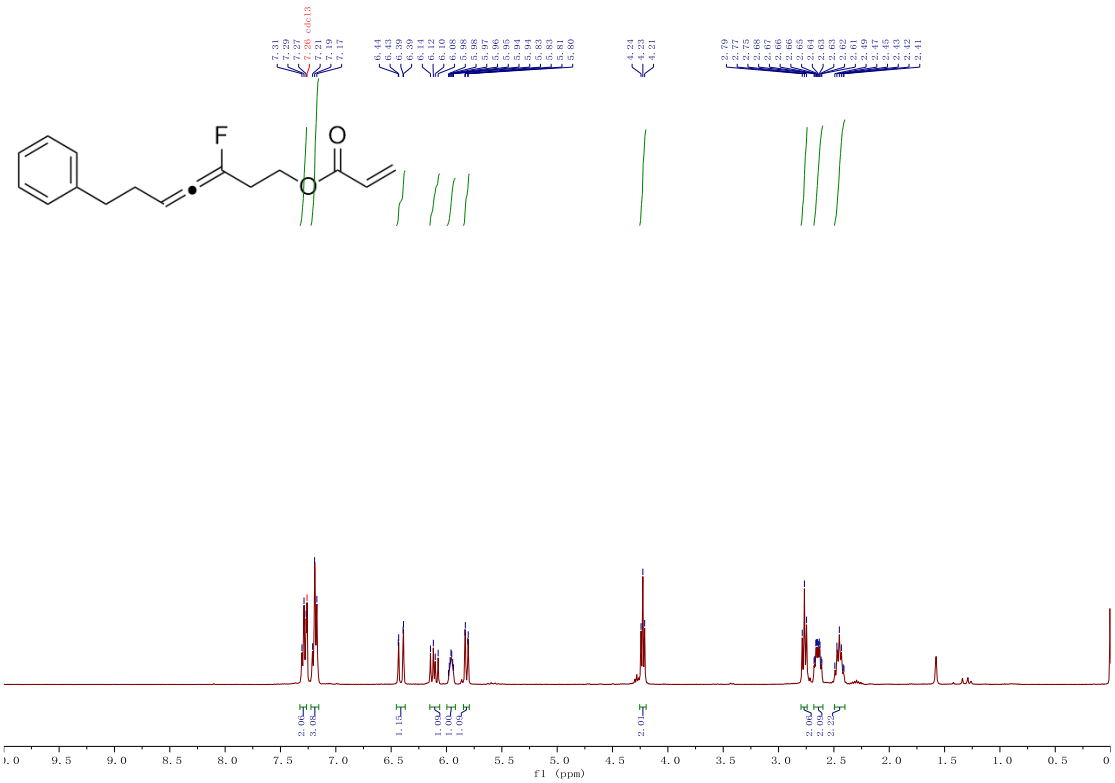
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6f**



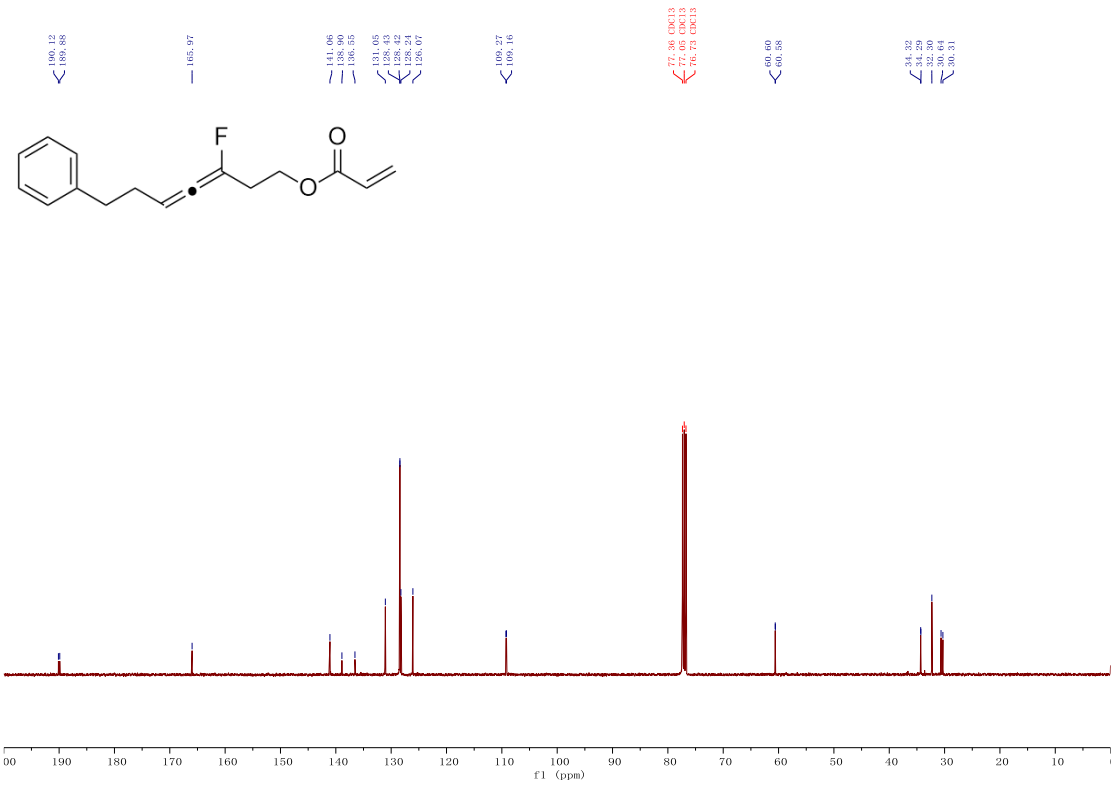
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6f**



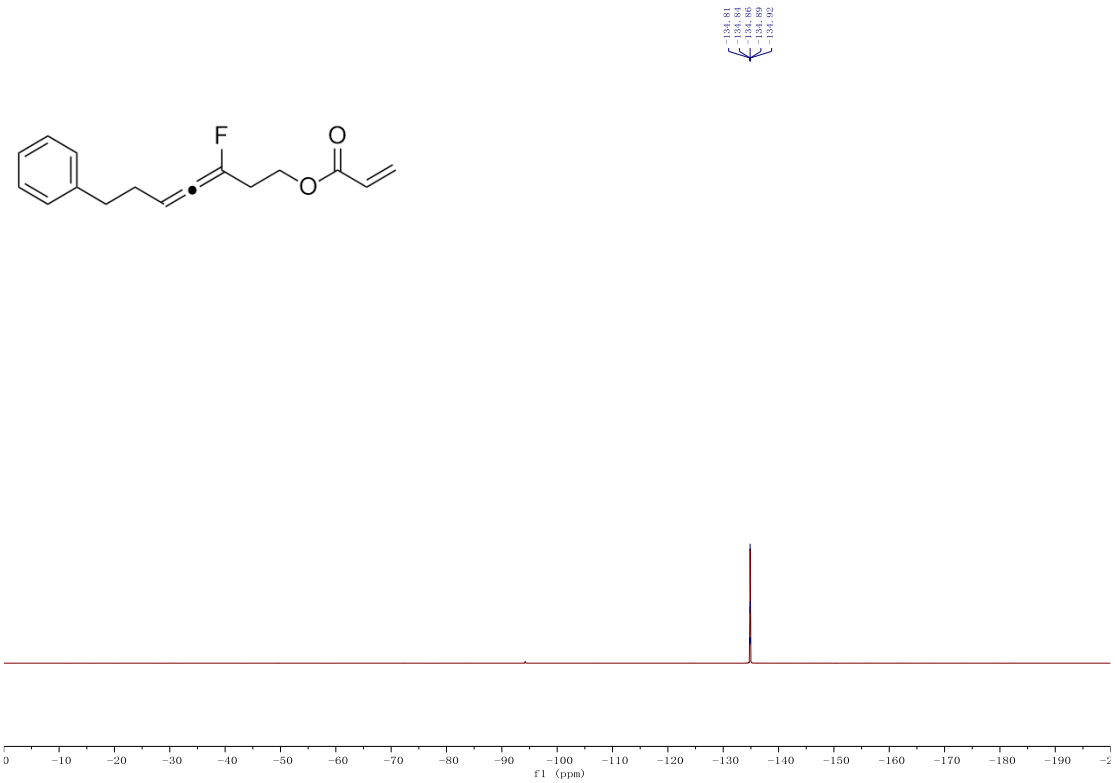
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6g**



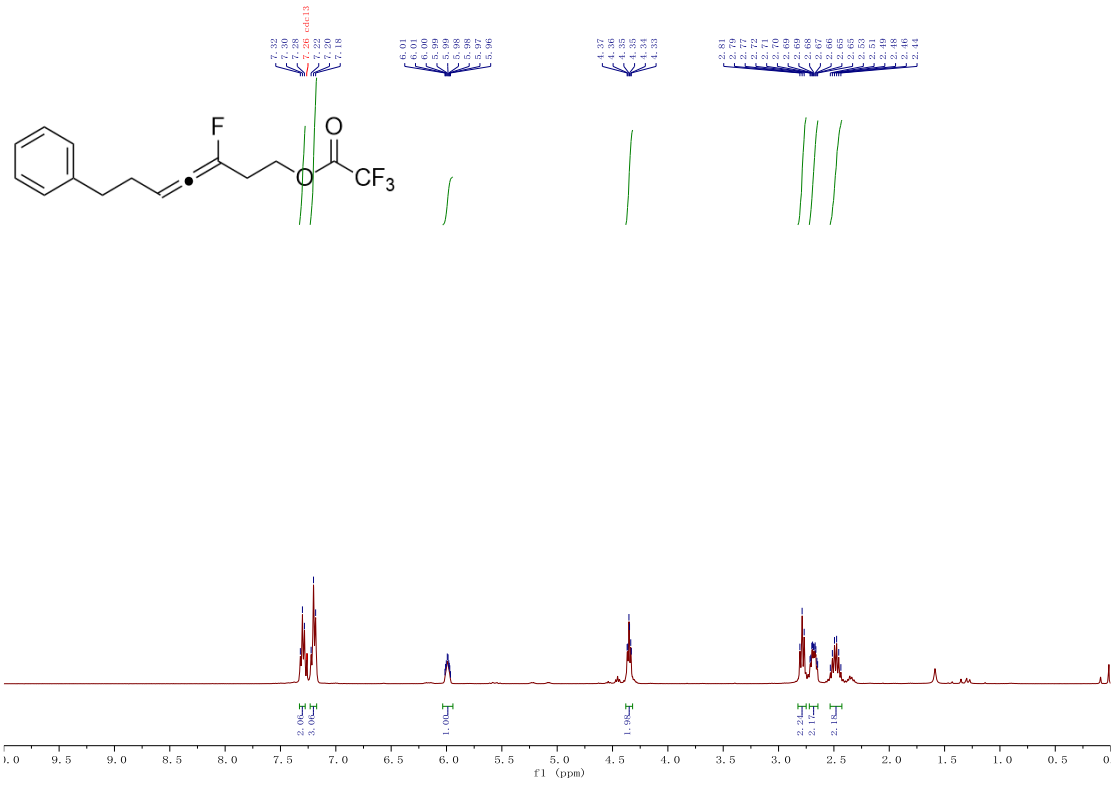
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6g**



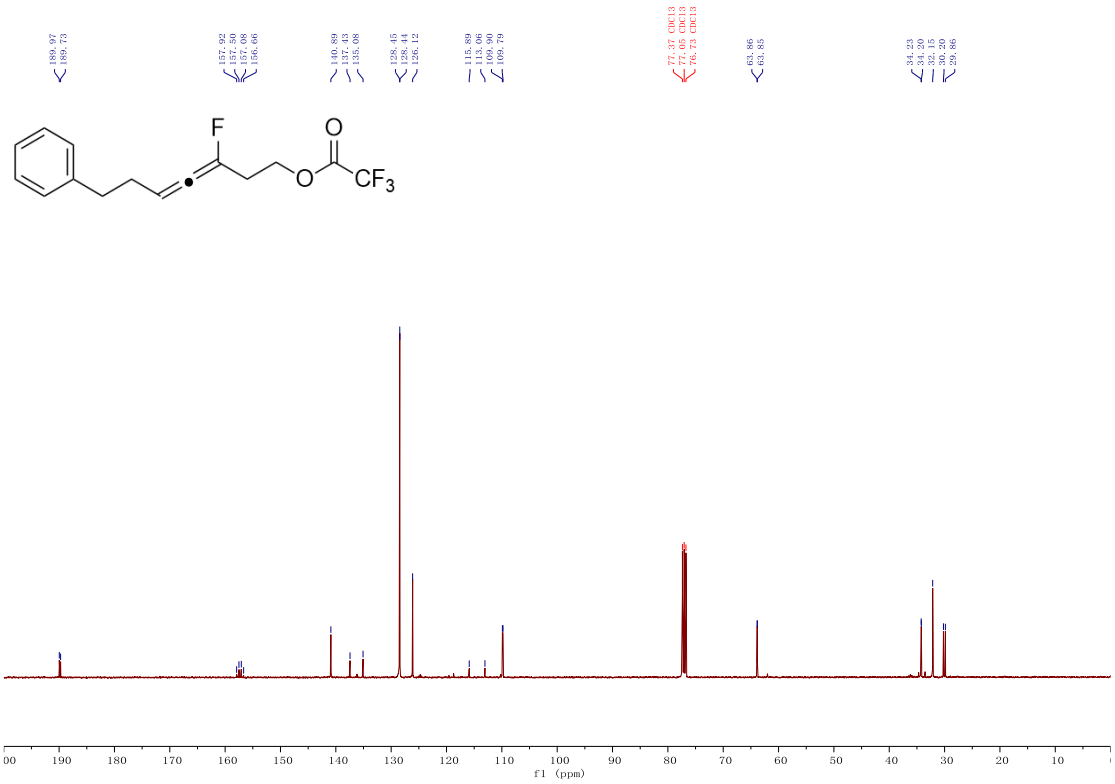
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6g**



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

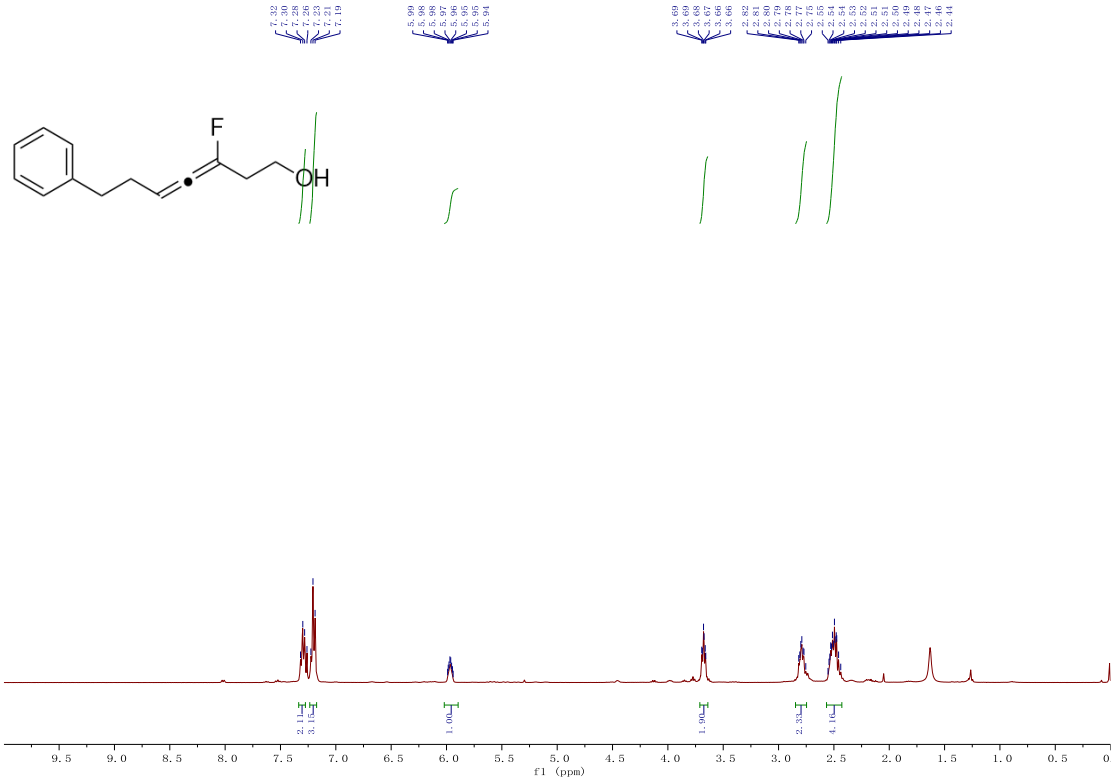


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6ha**

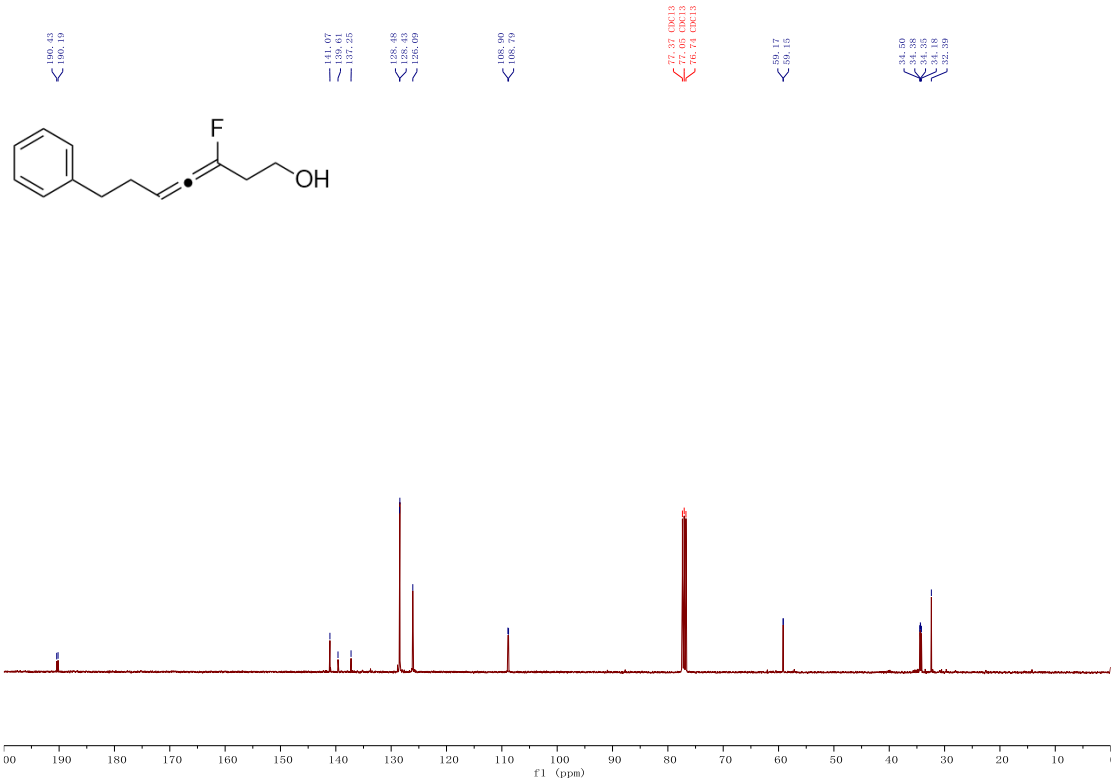


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6ha**

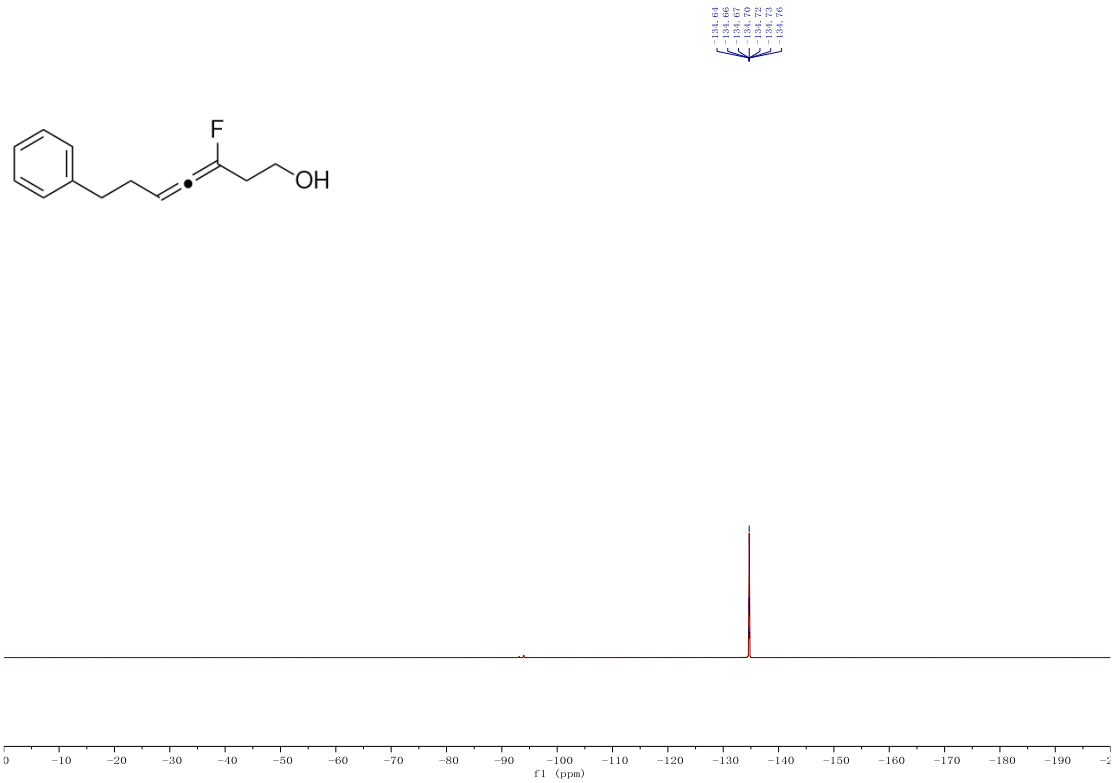
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6hb**



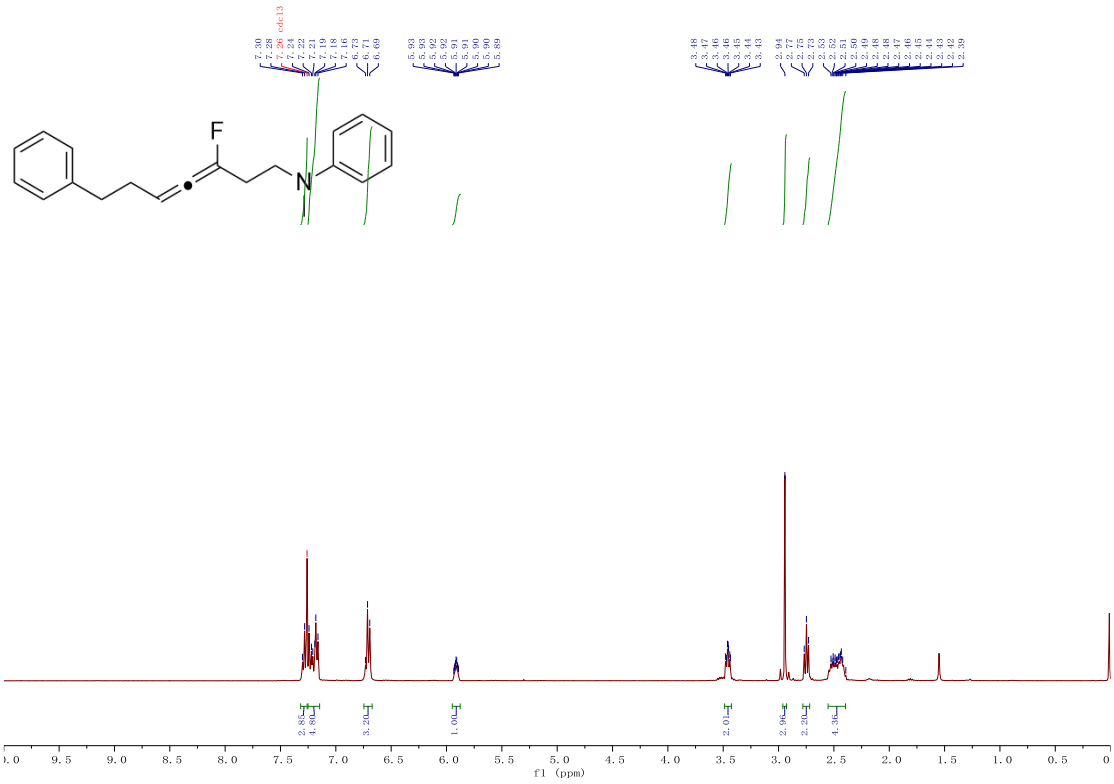
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6hb**



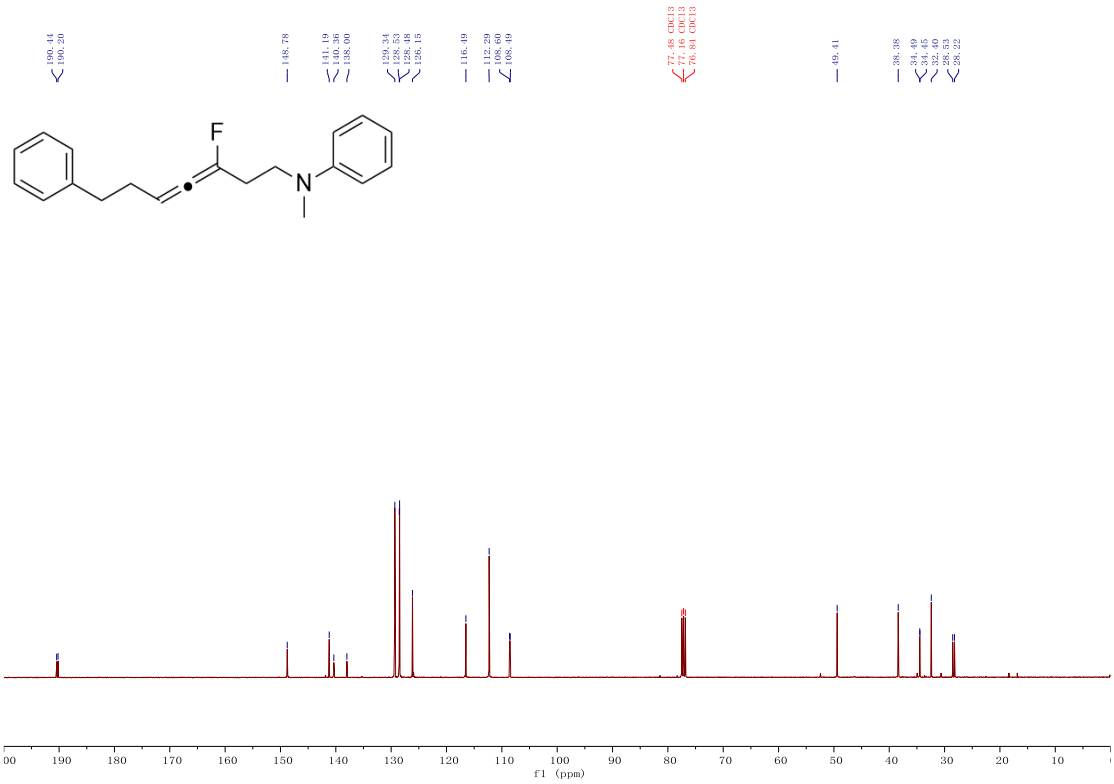
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6hb**



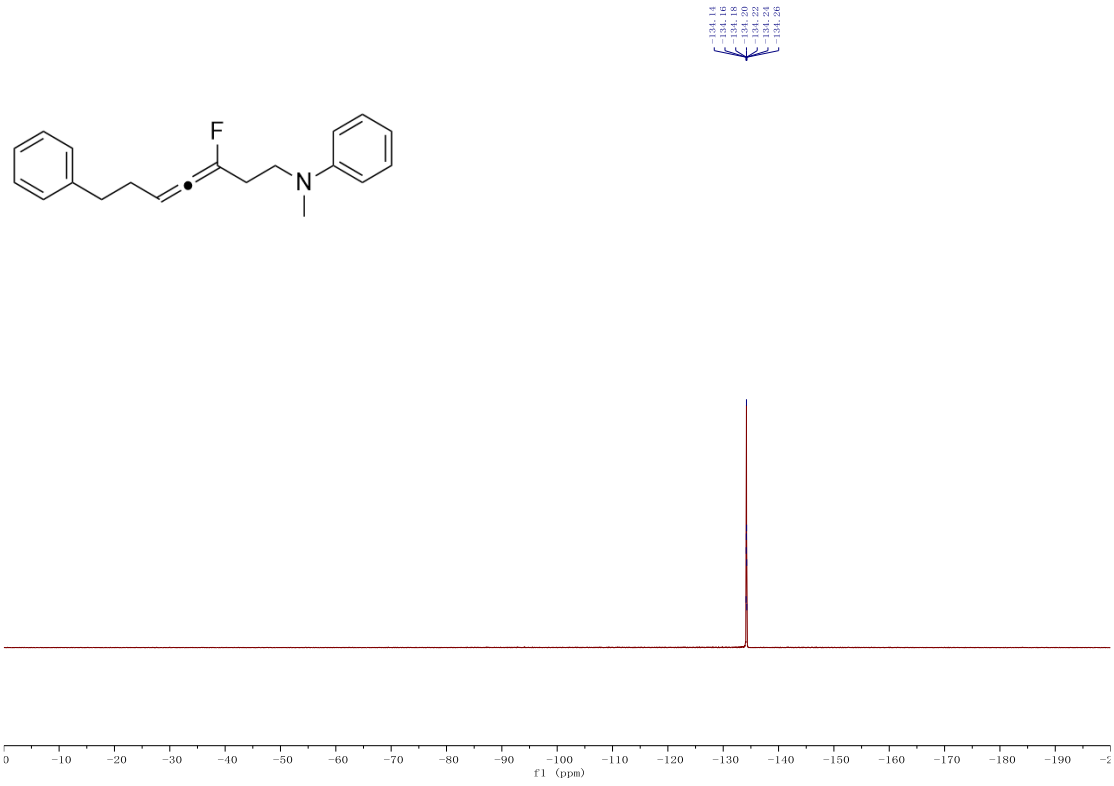
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6i**



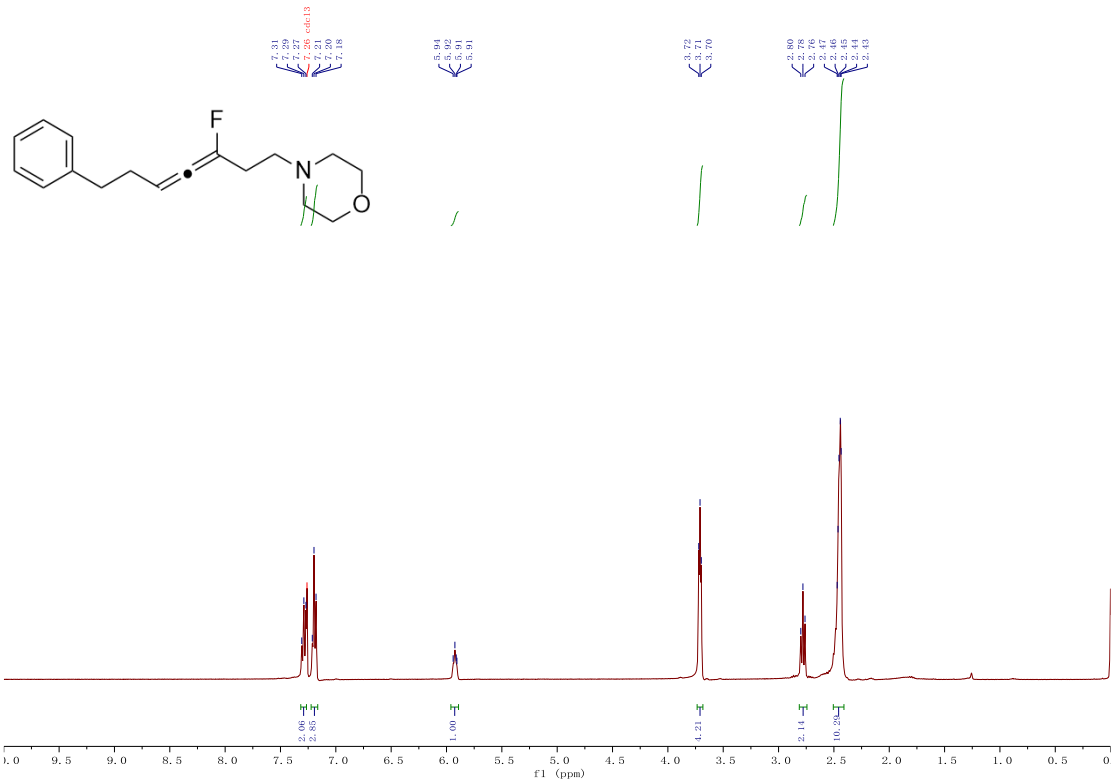
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6i**



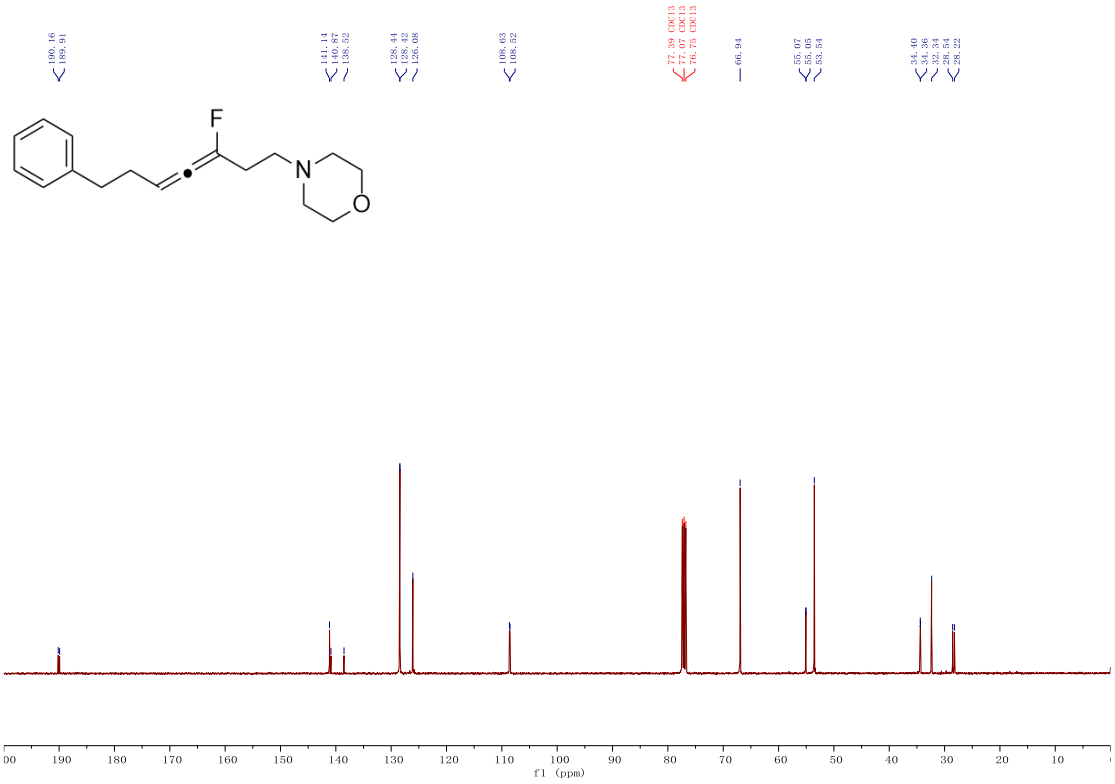
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6i**



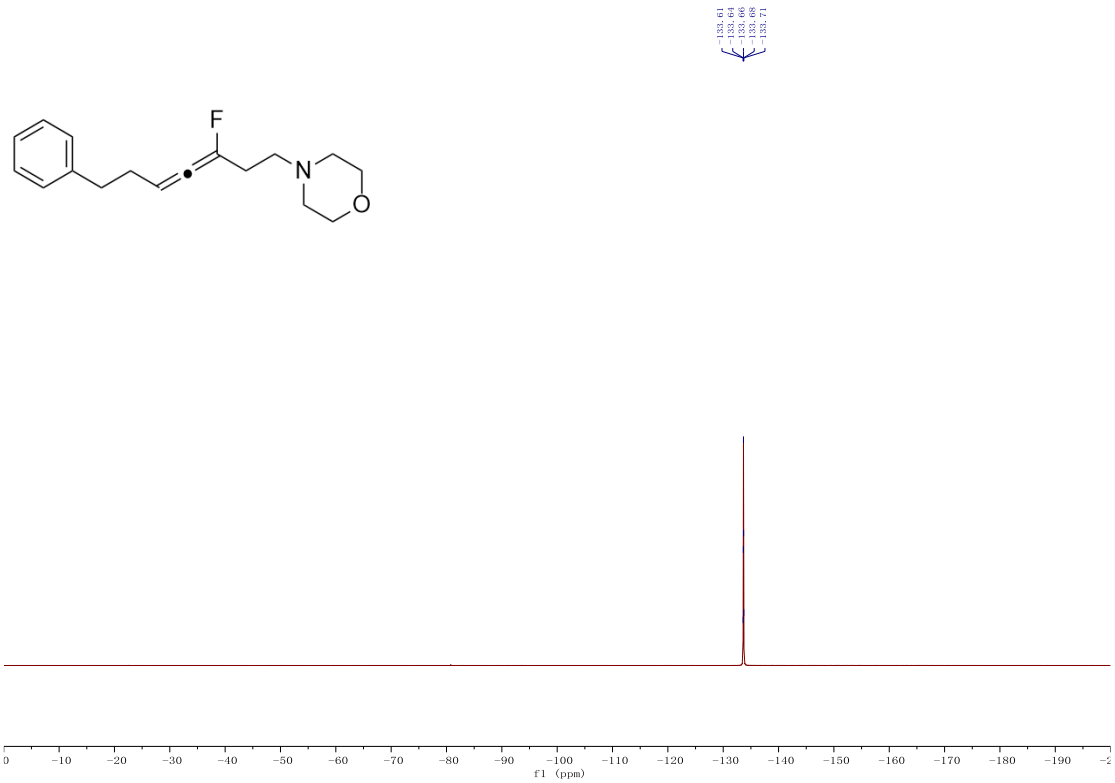
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6j**



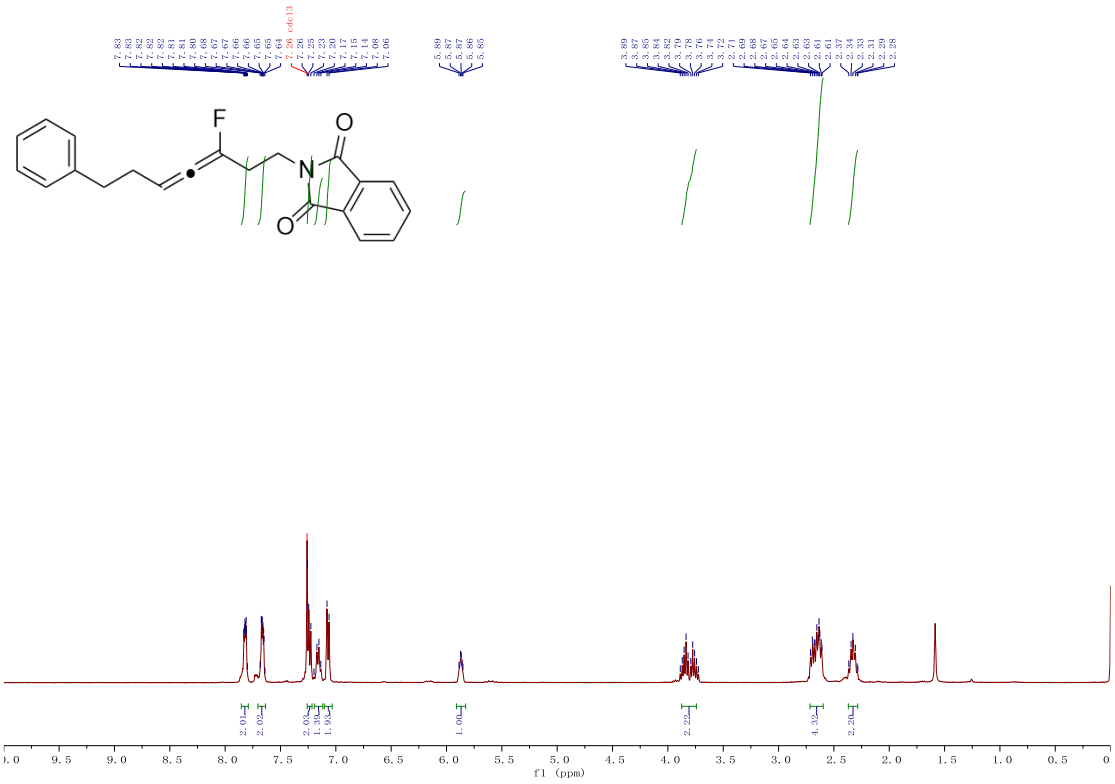
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6j**



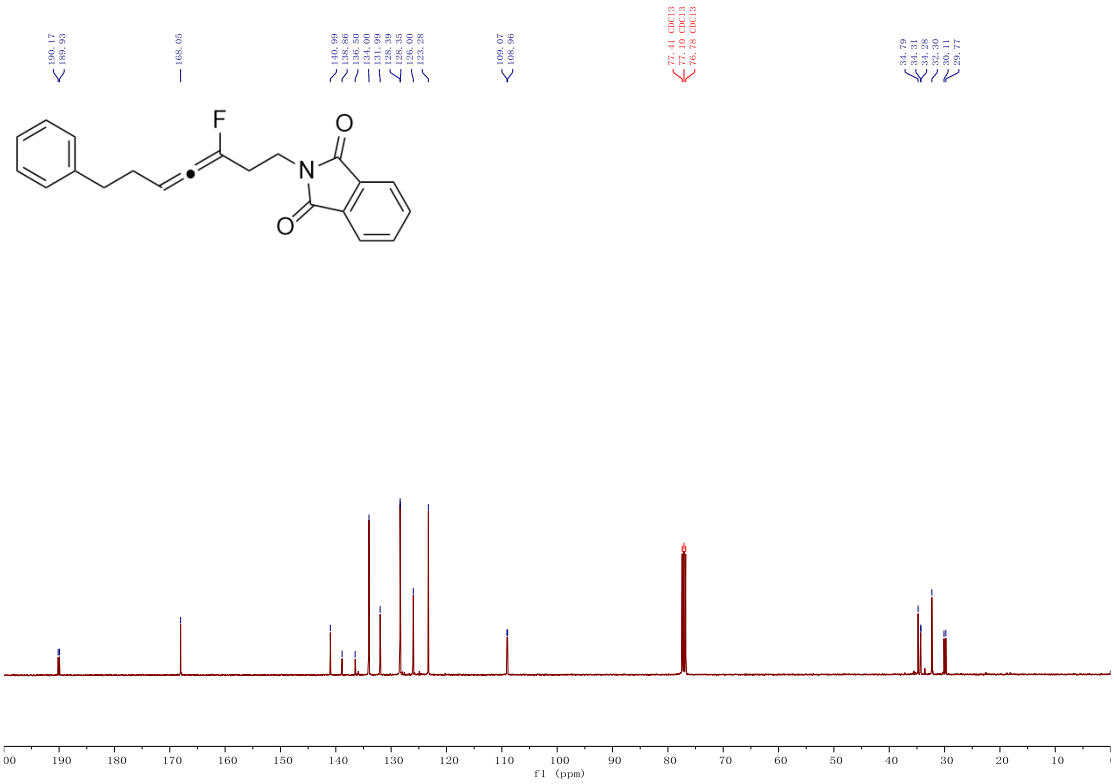
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6j**



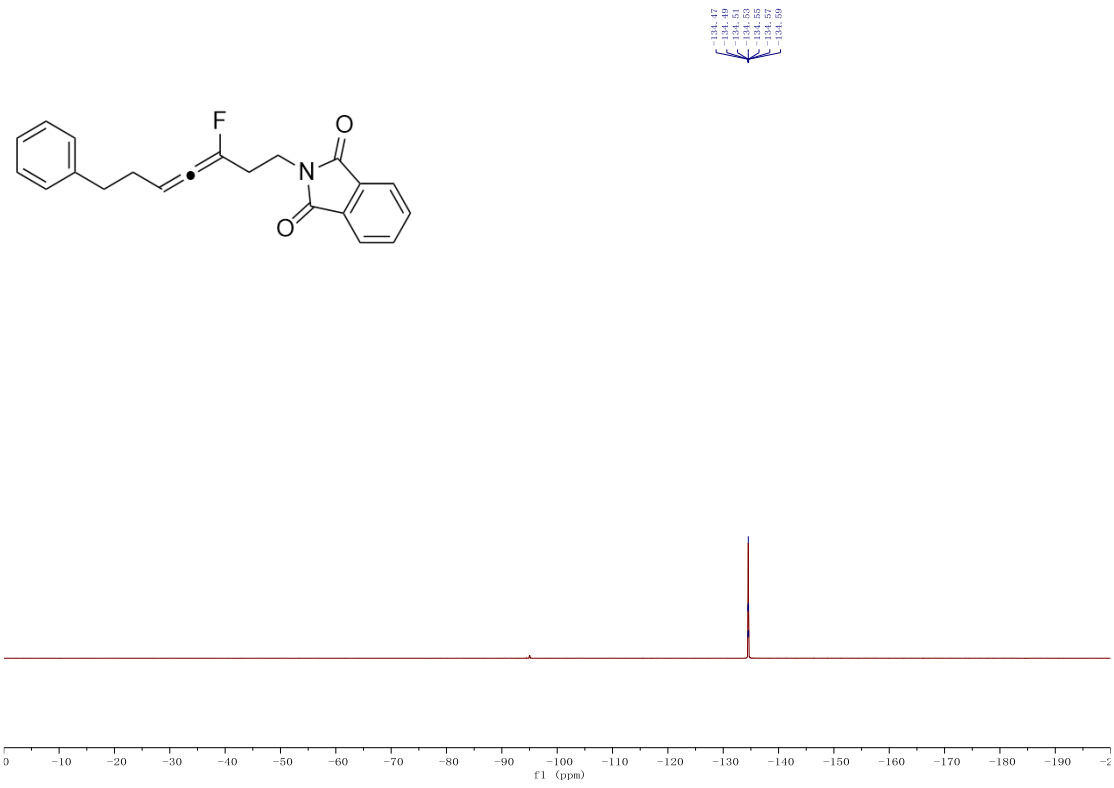
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6k**



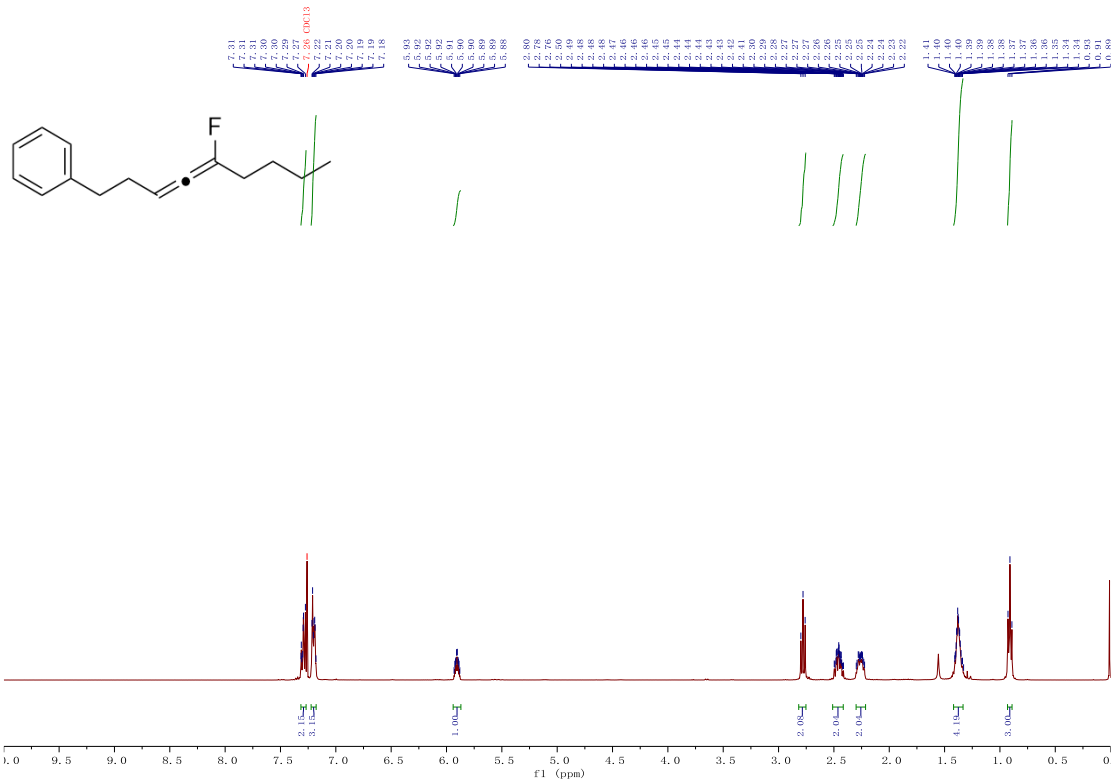
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6k**



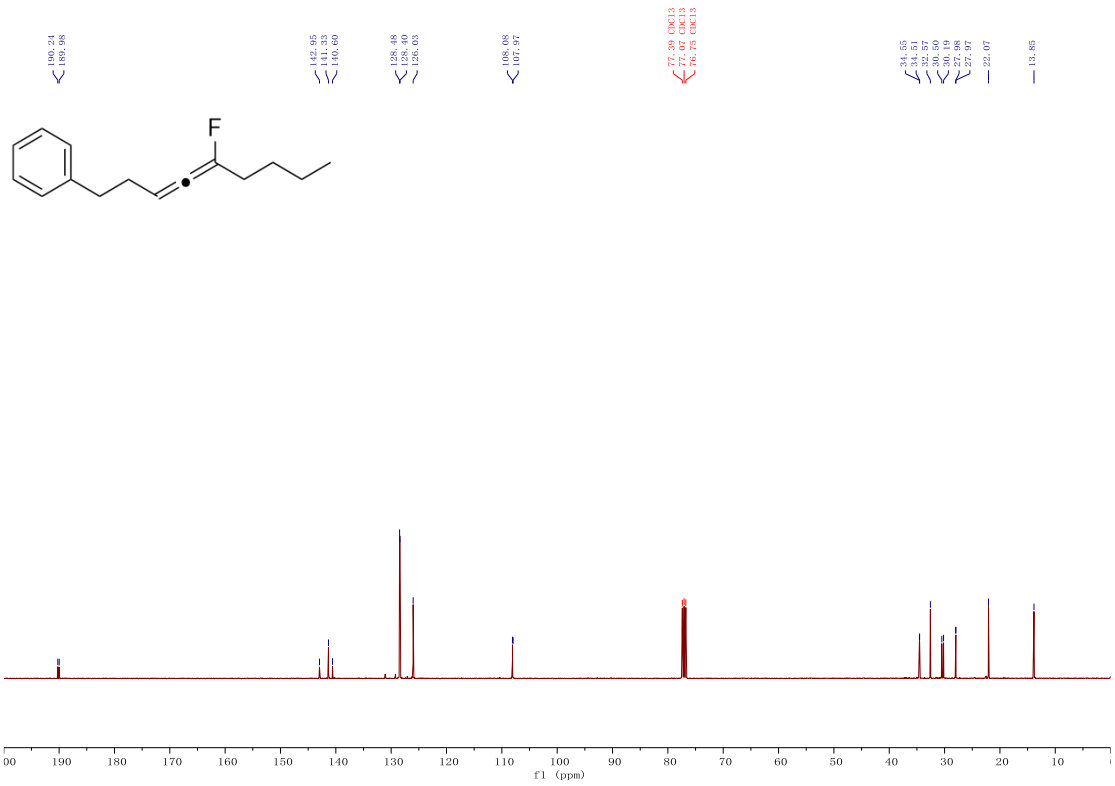
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6k**



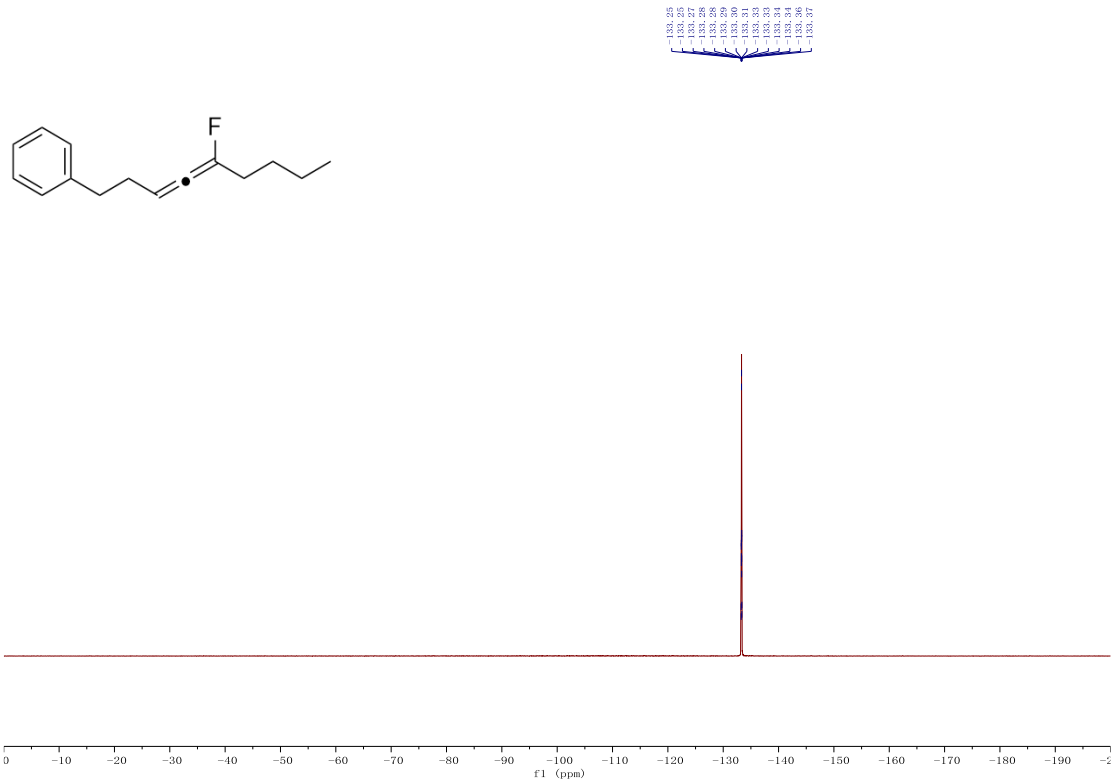
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6l**



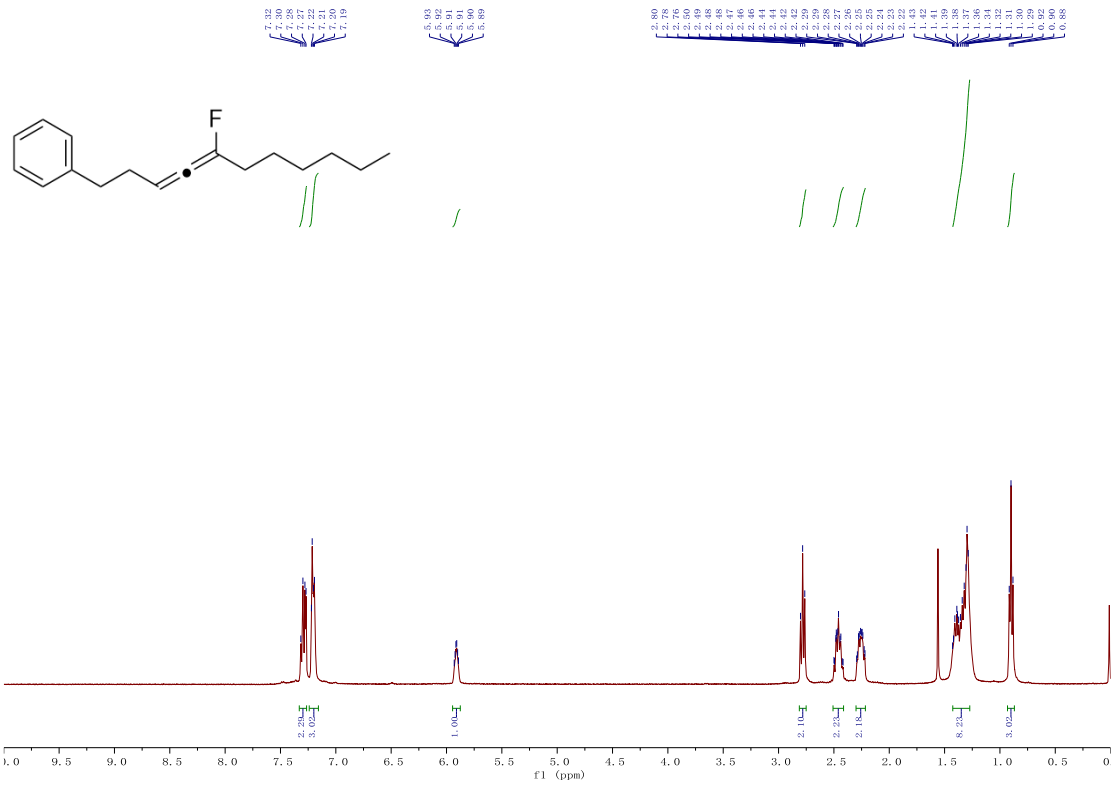
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6l**



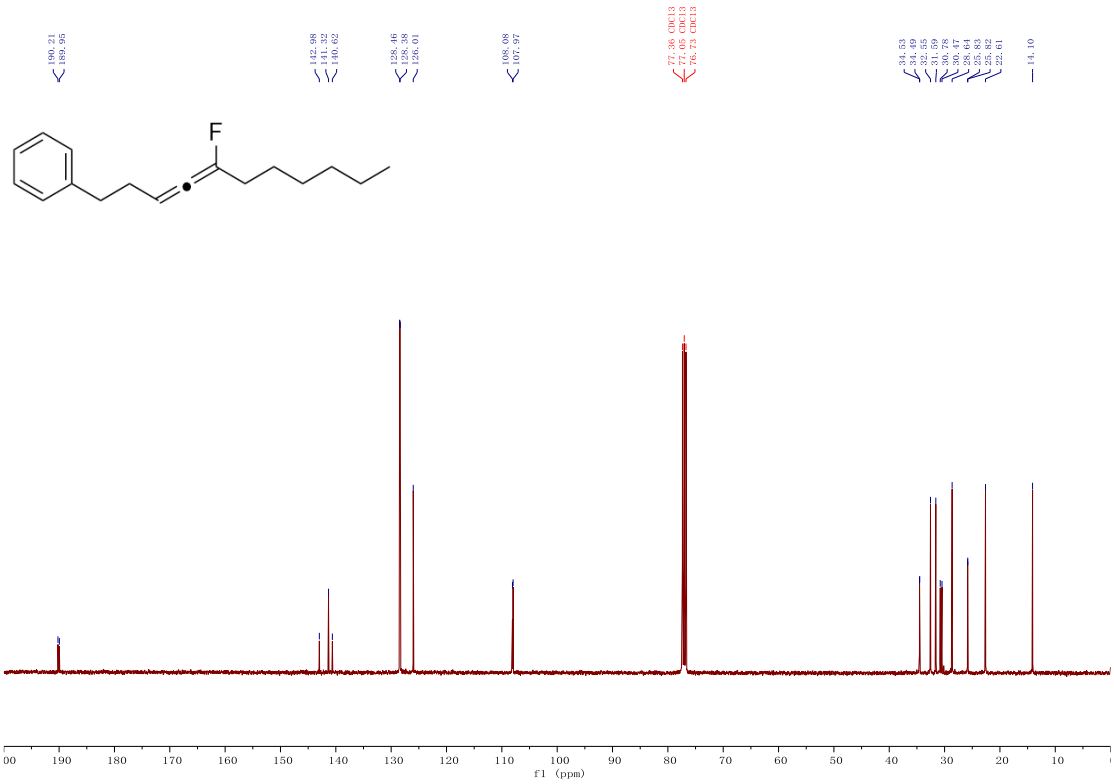
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6l**



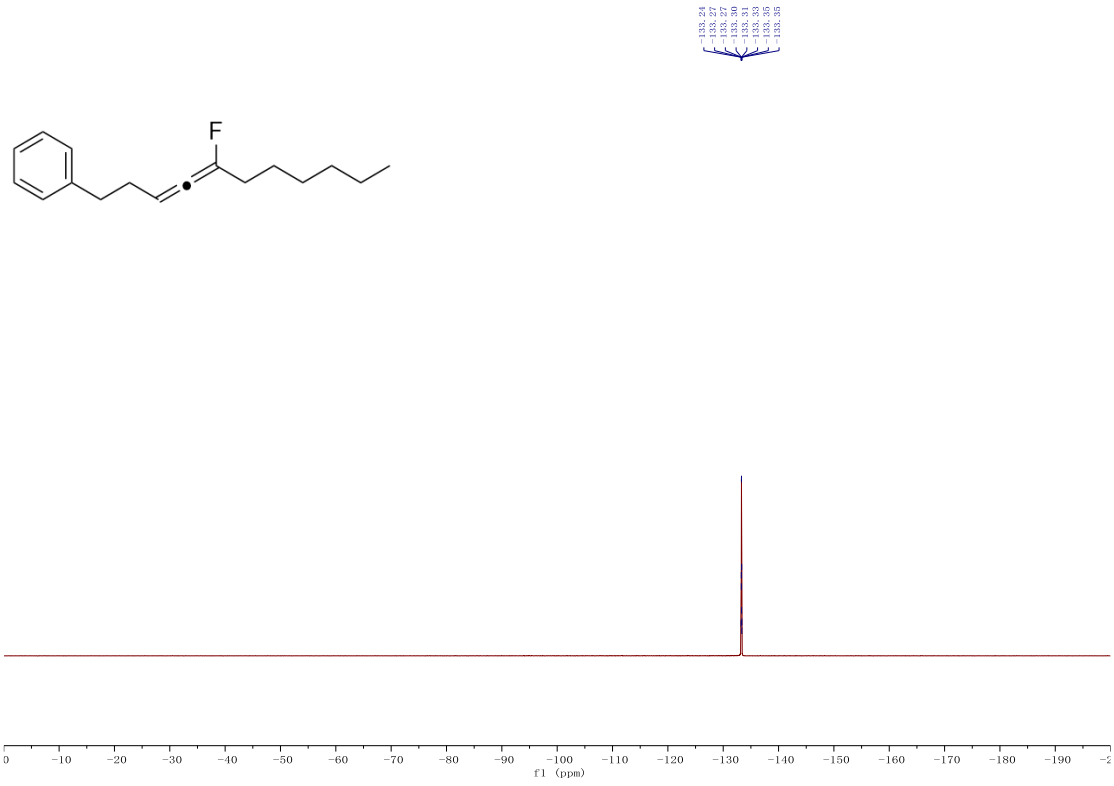
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6m**



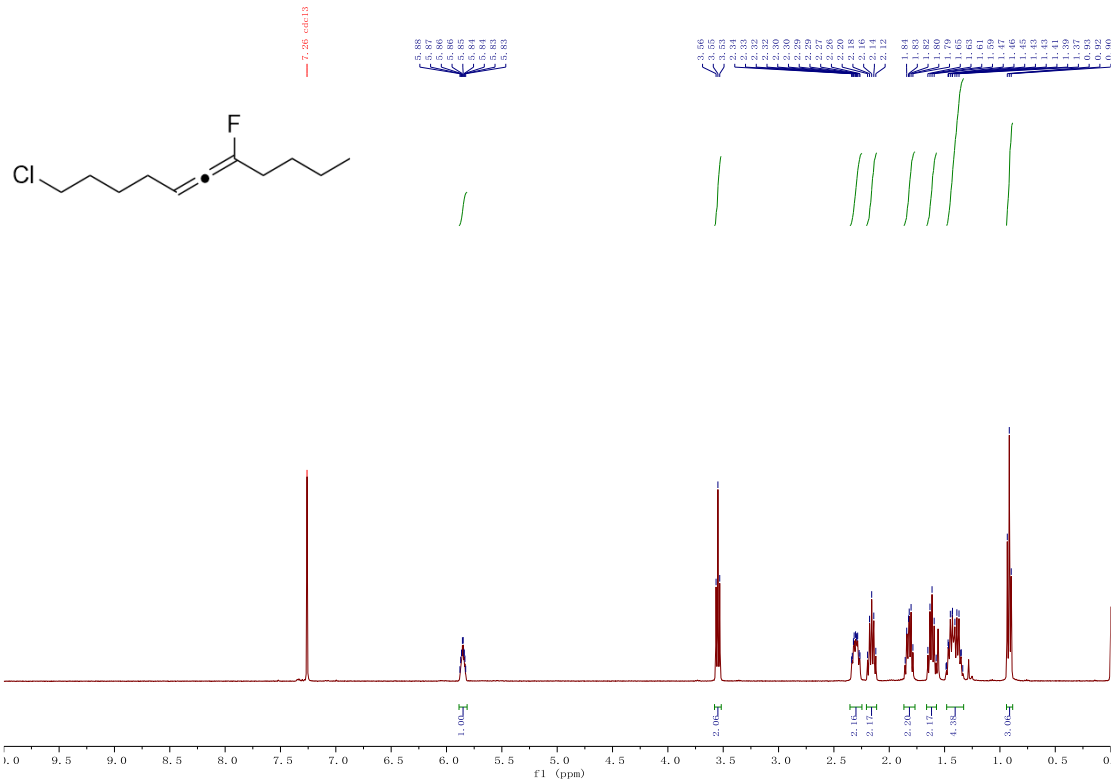
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6m**



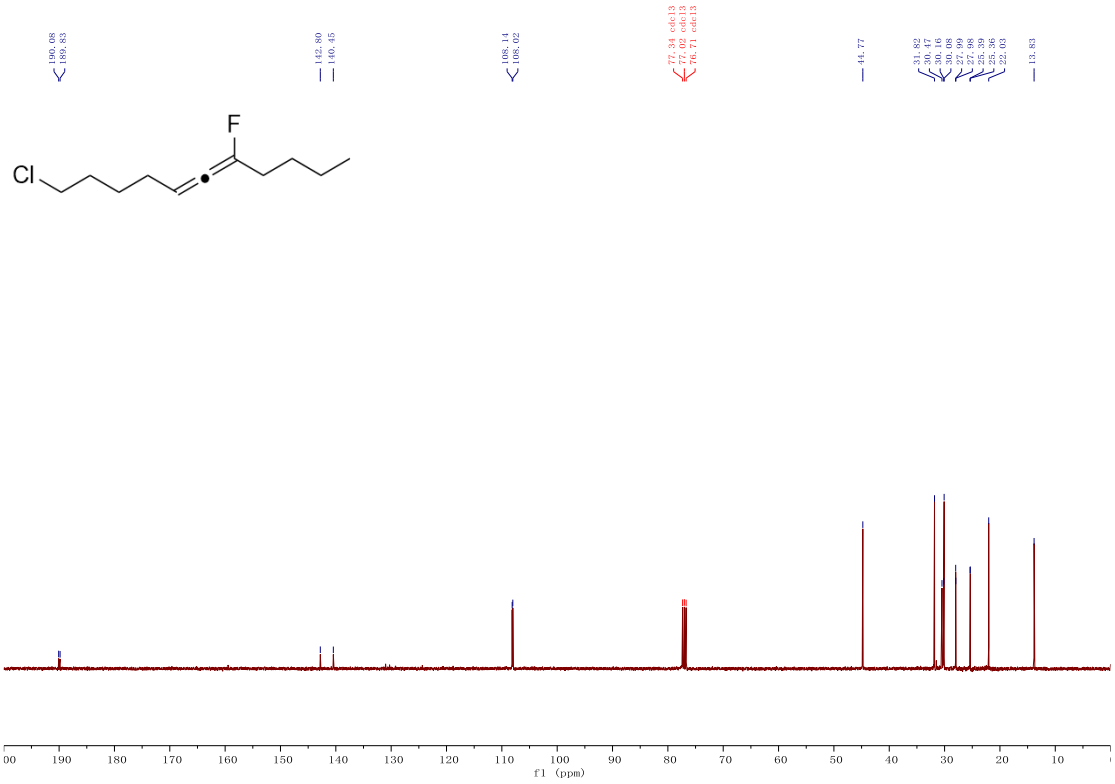
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6m**



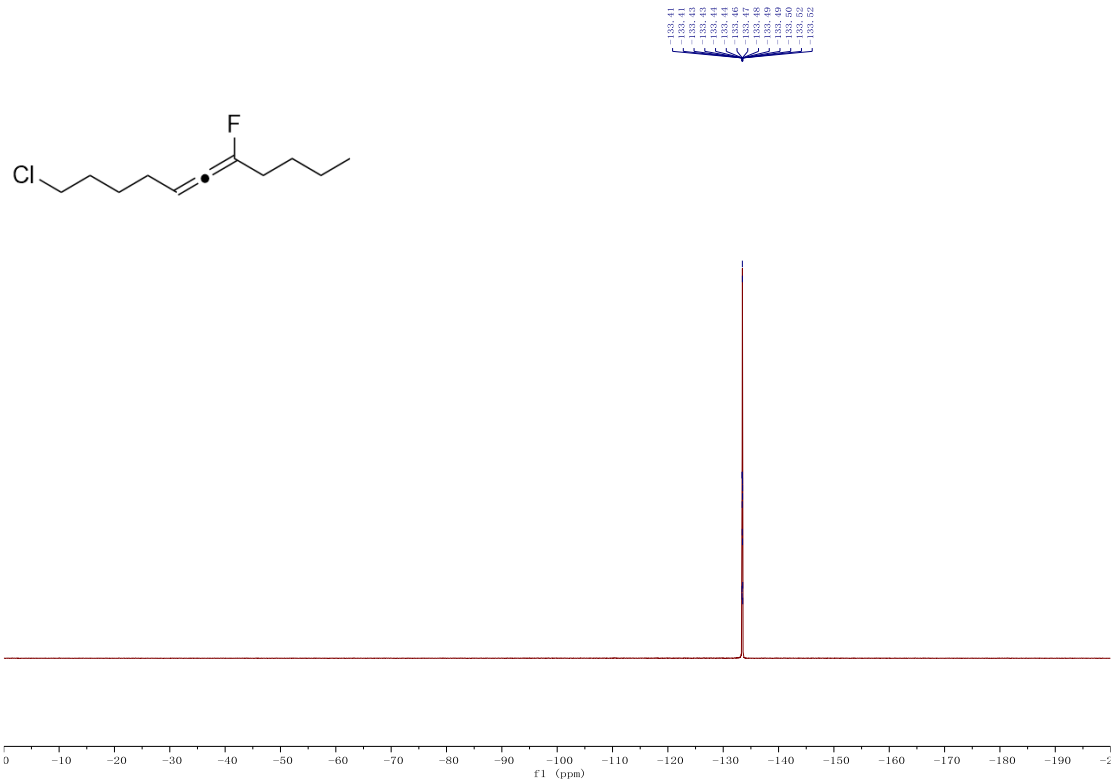
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6n**



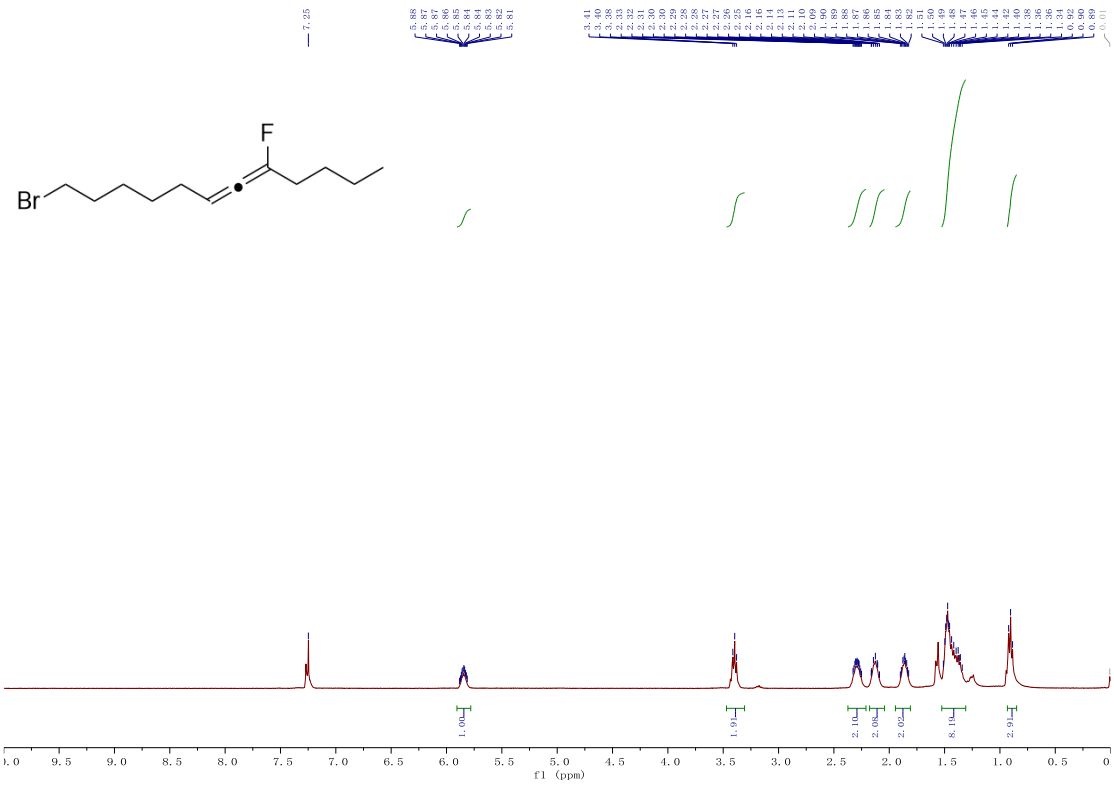
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6n**



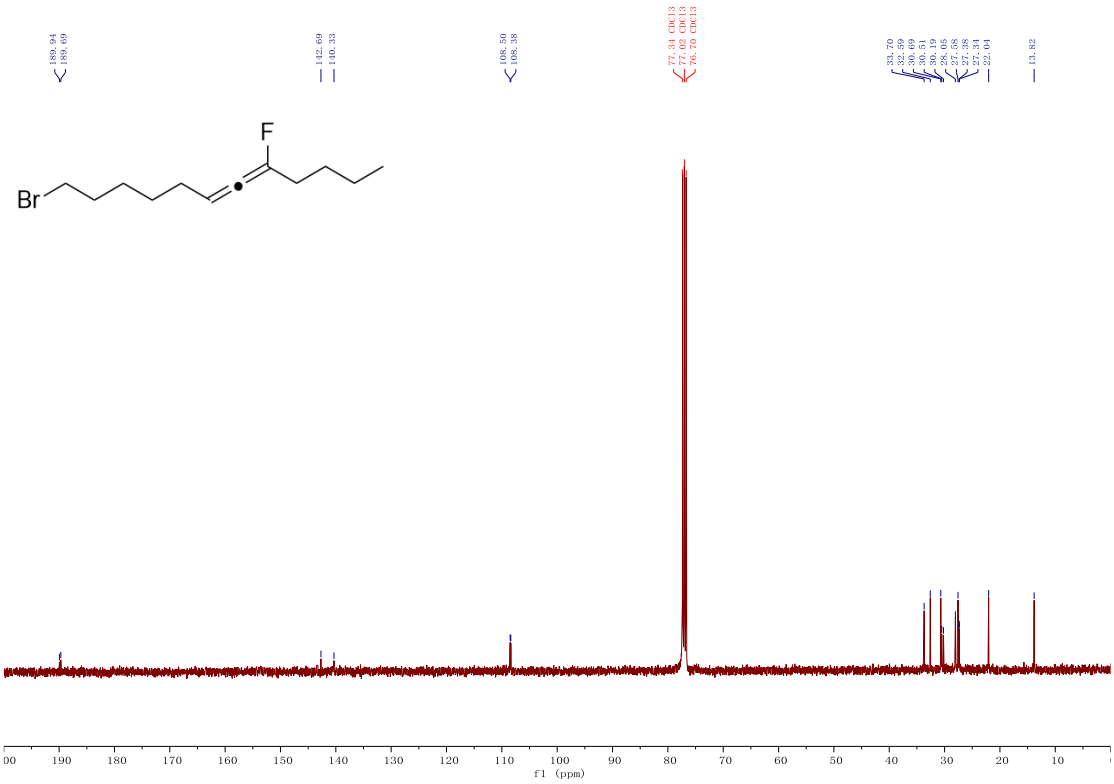
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6n**



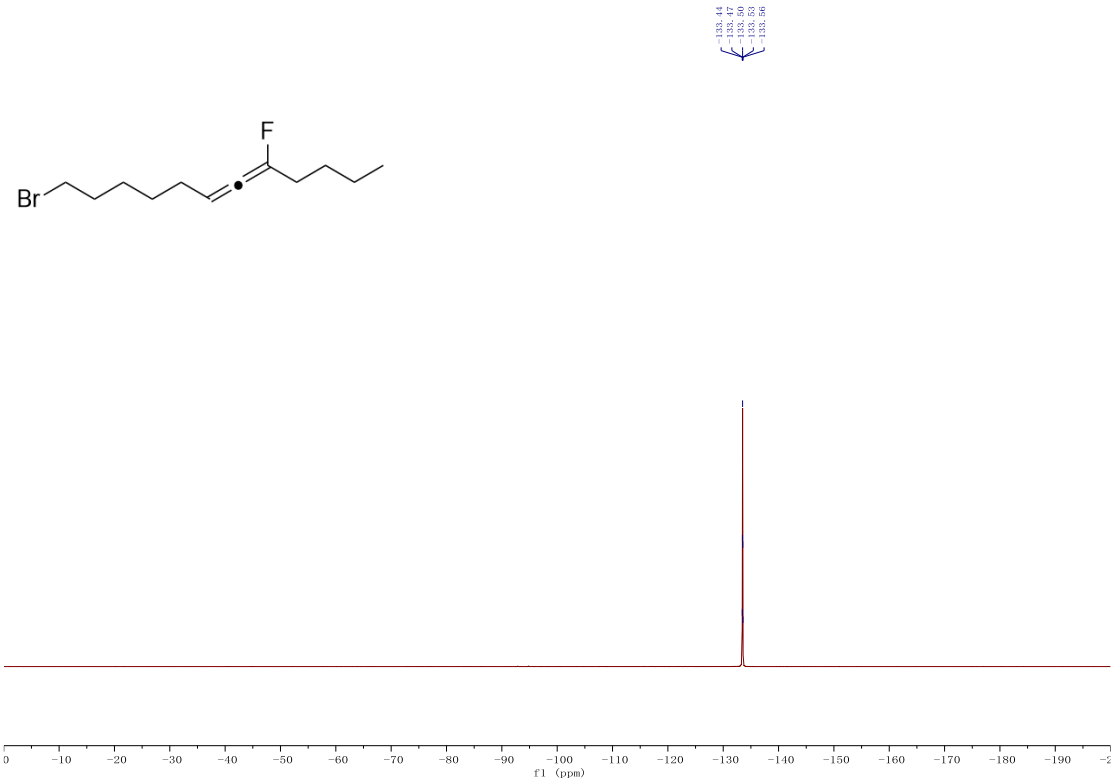
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6o**



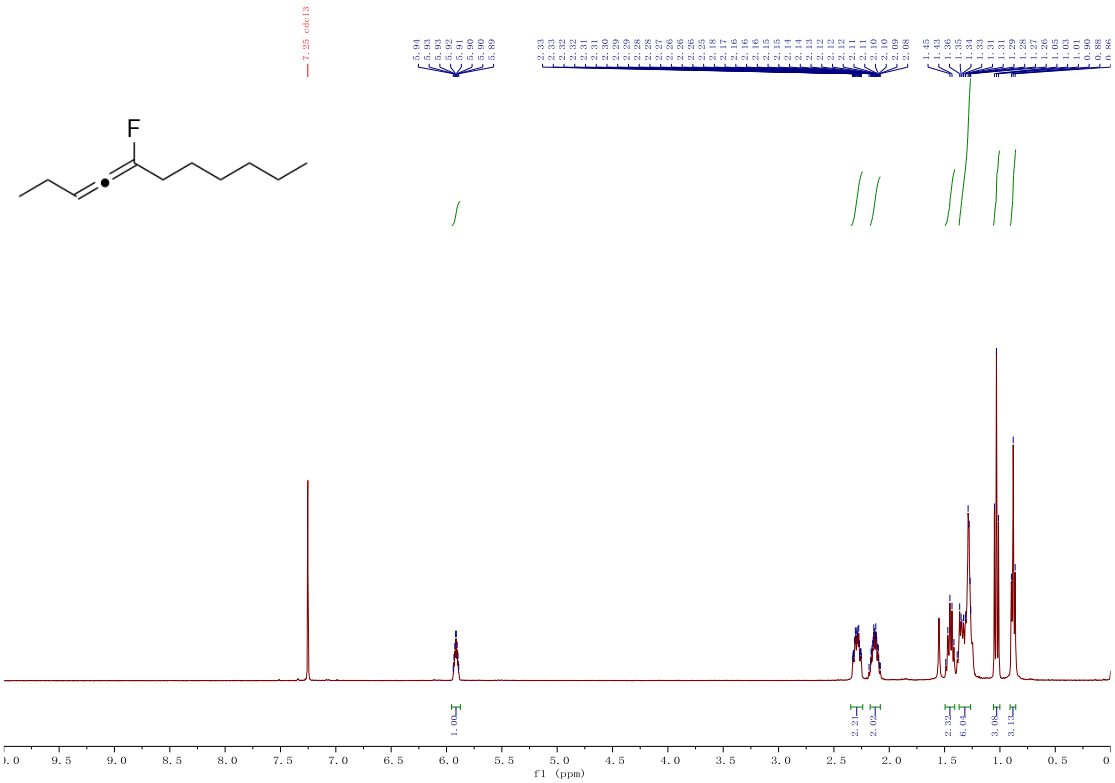
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6o**



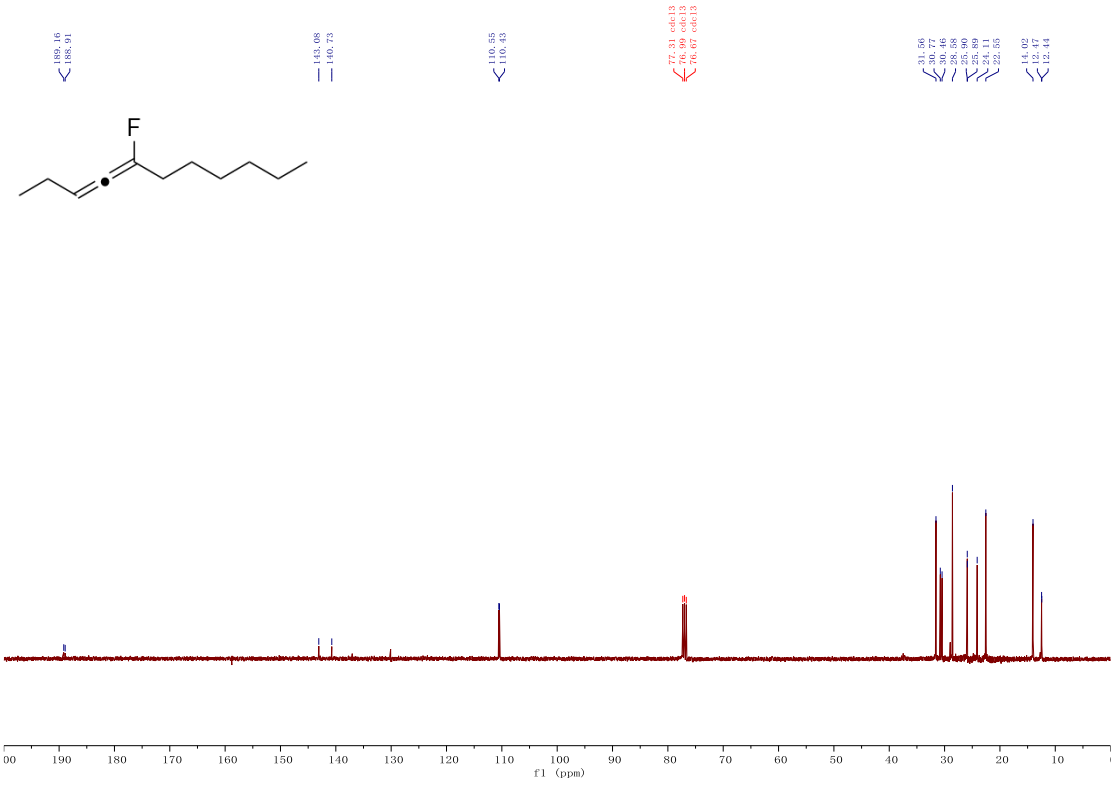
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6o**



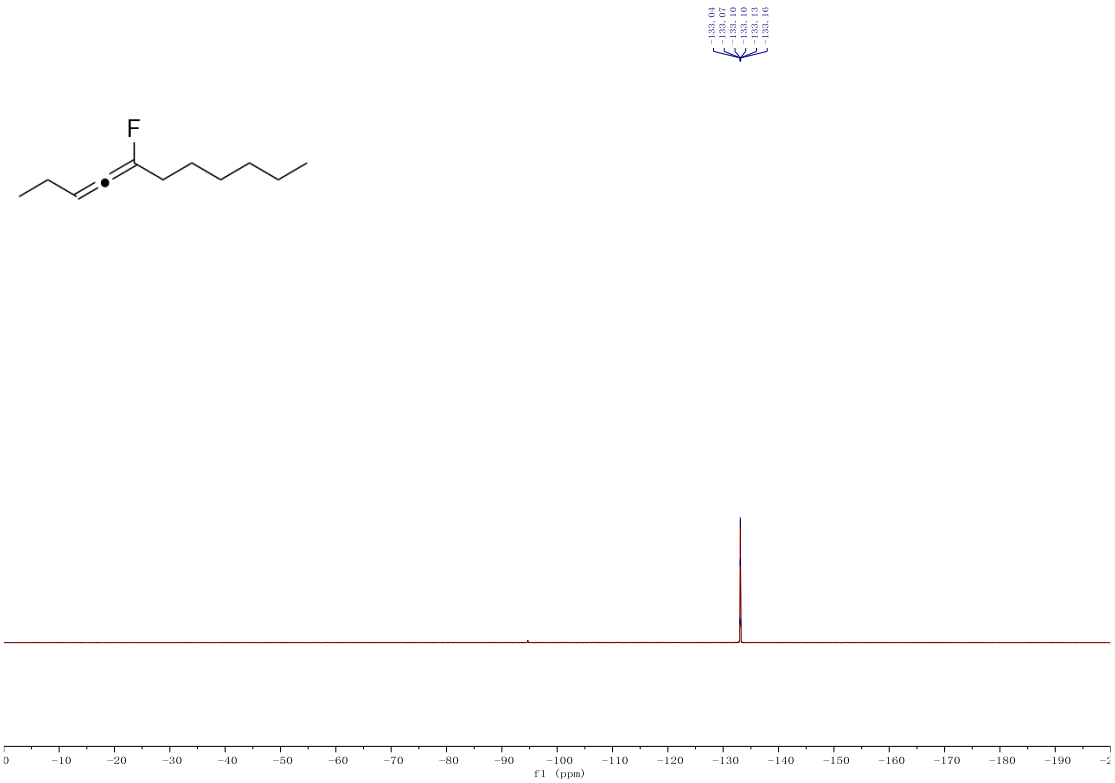
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6p**



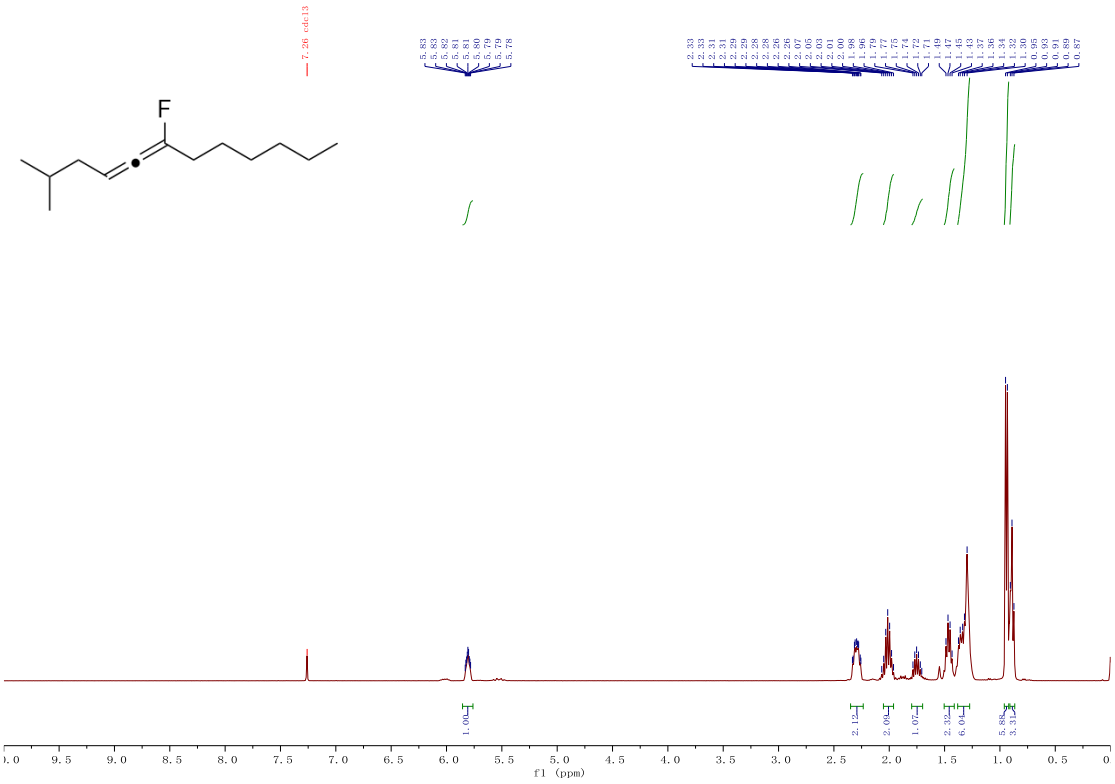
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6p**



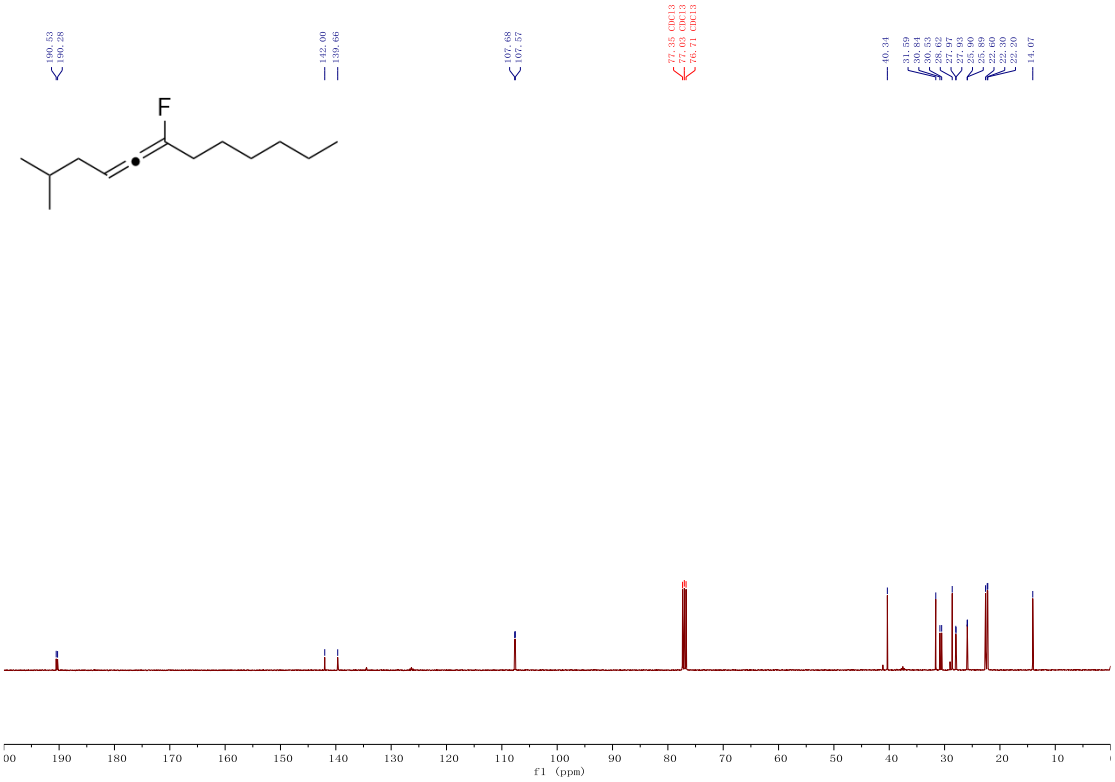
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6p**



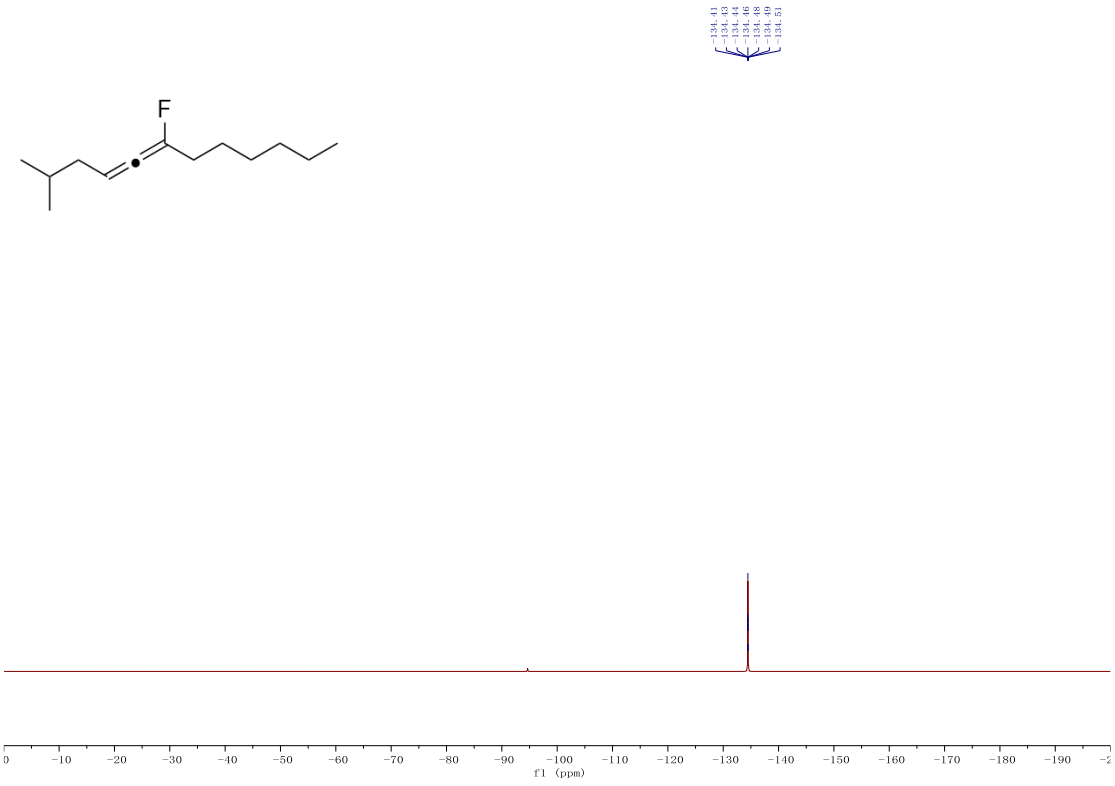
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6q**



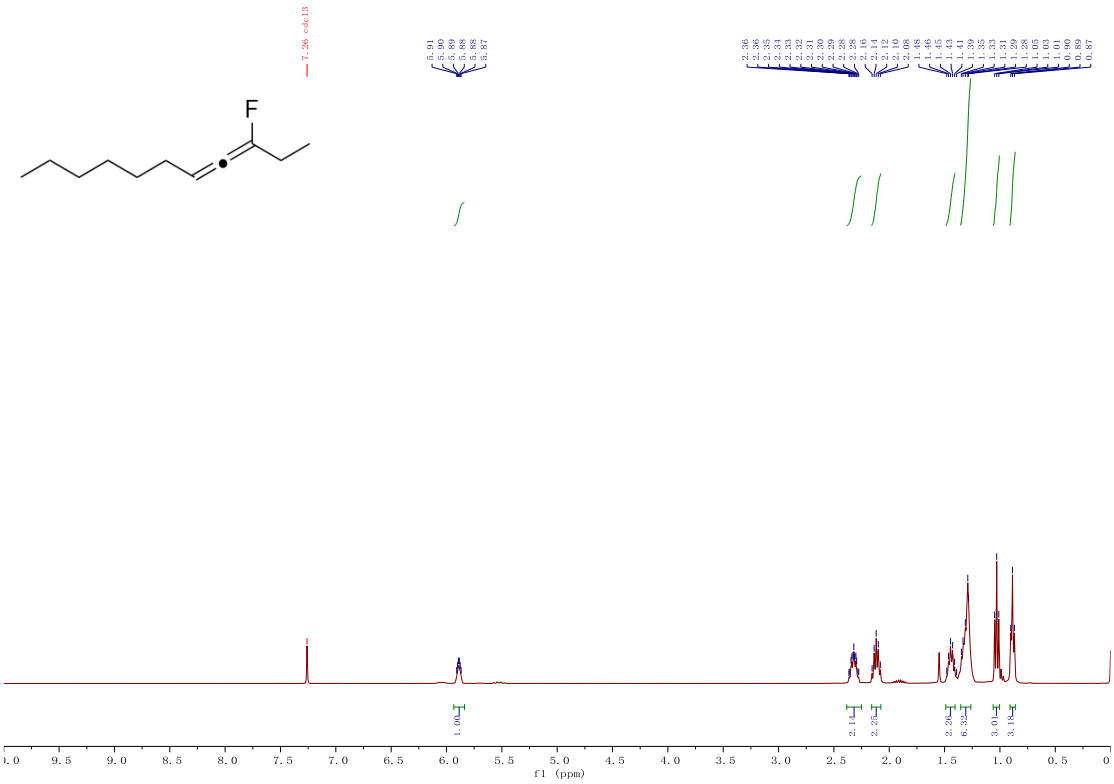
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6q**



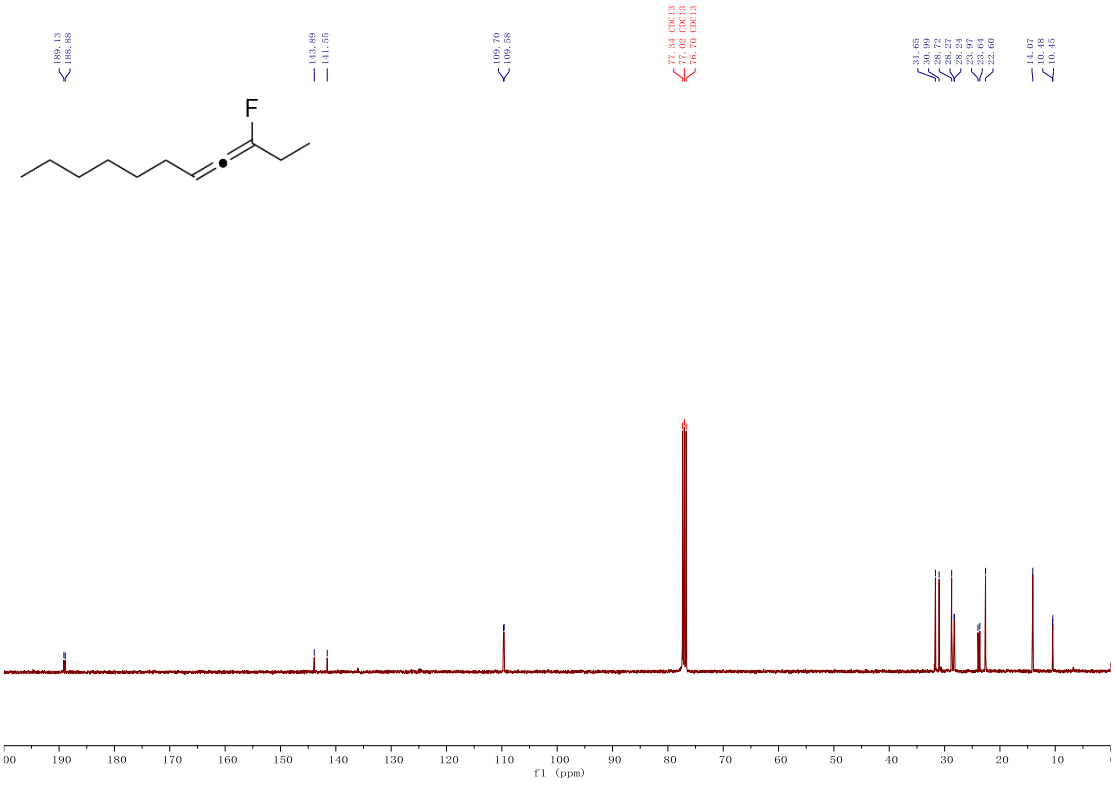
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6q**



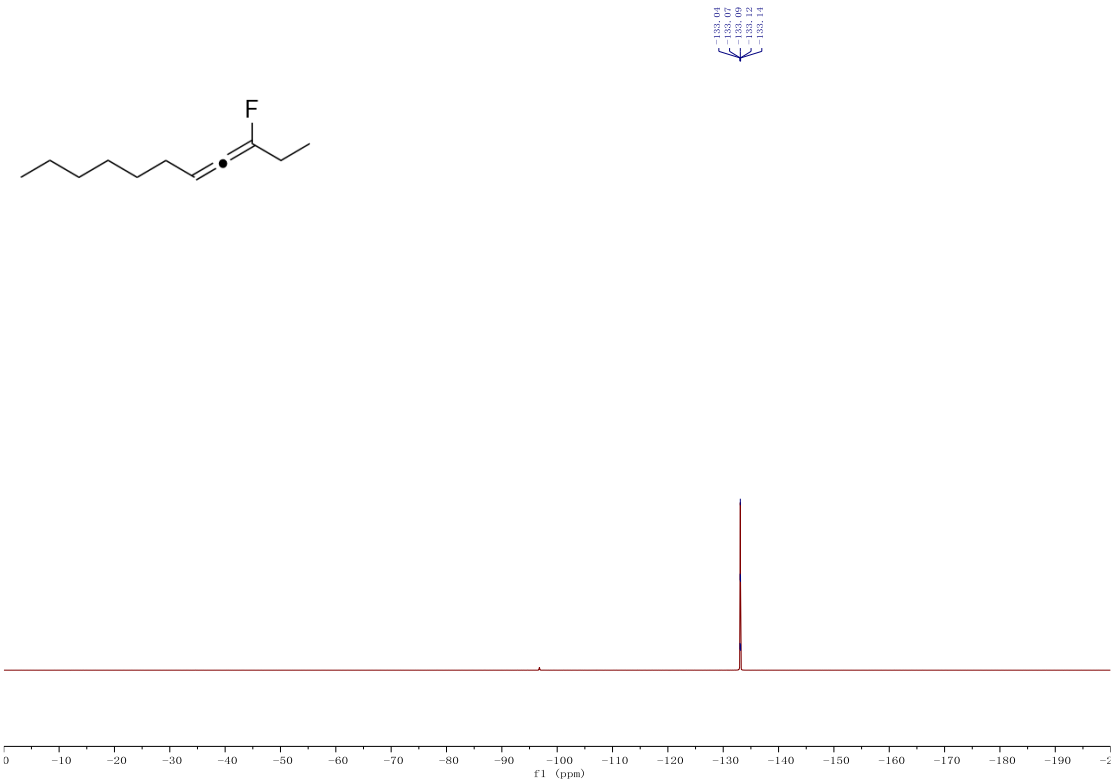
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6r**



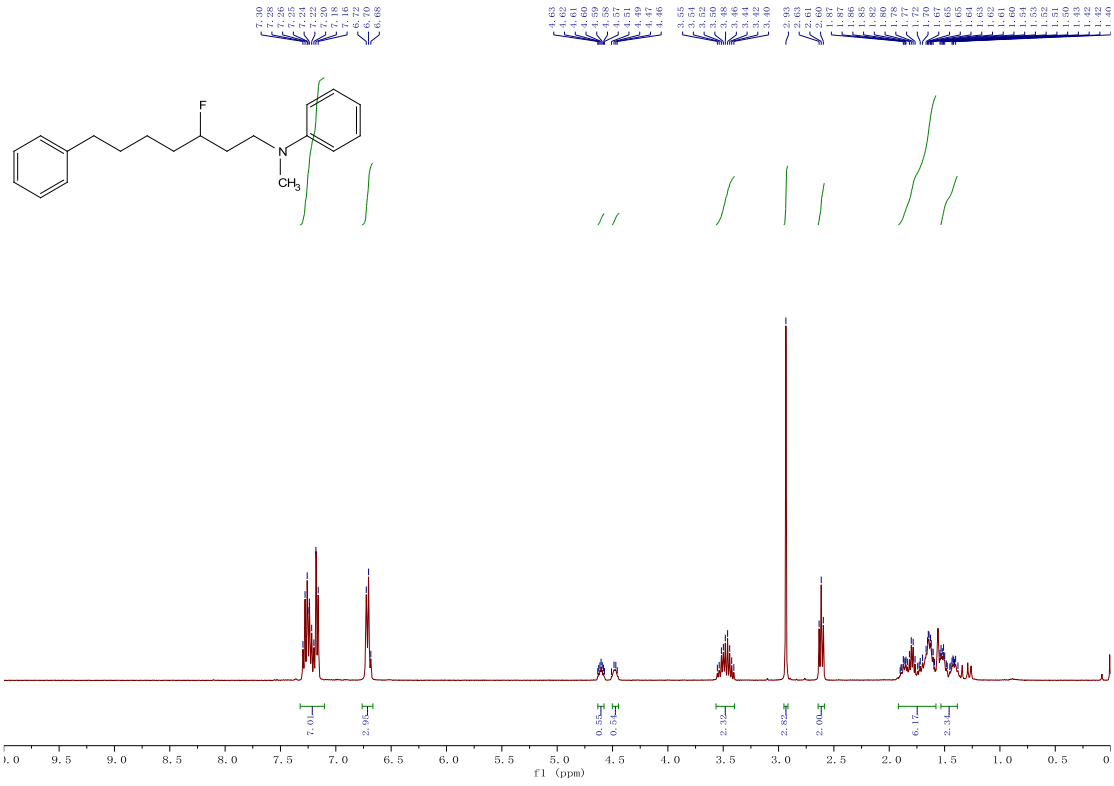
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6r**



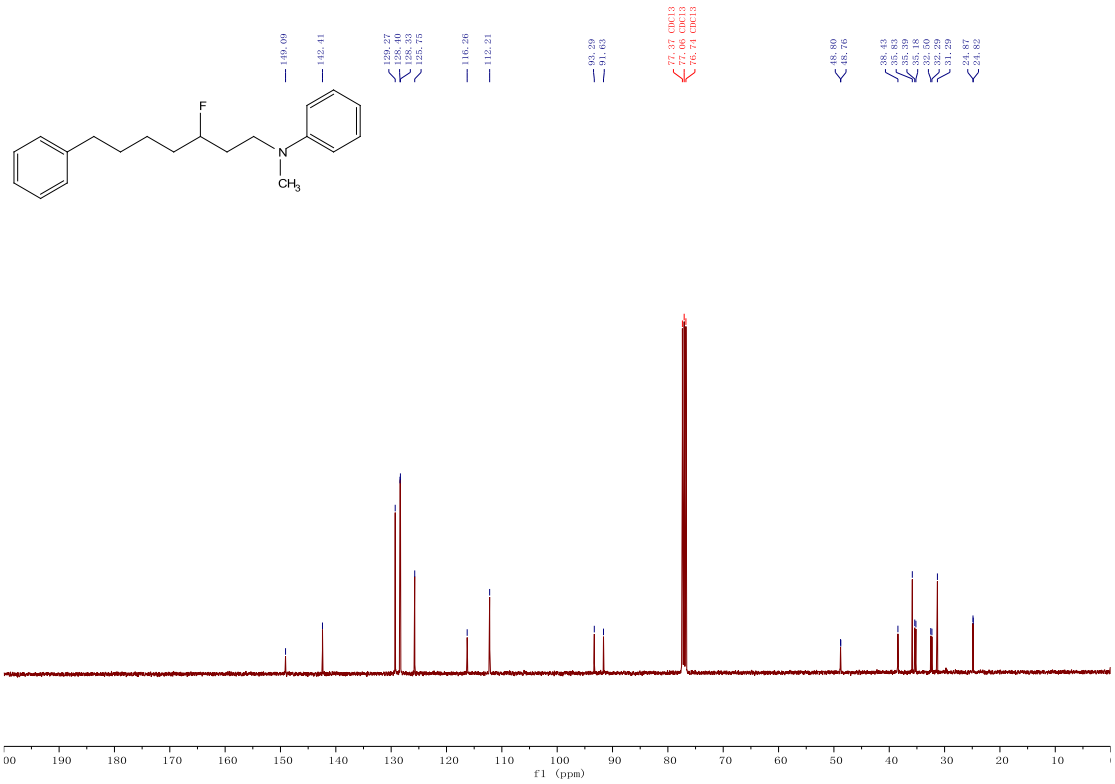
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6r**



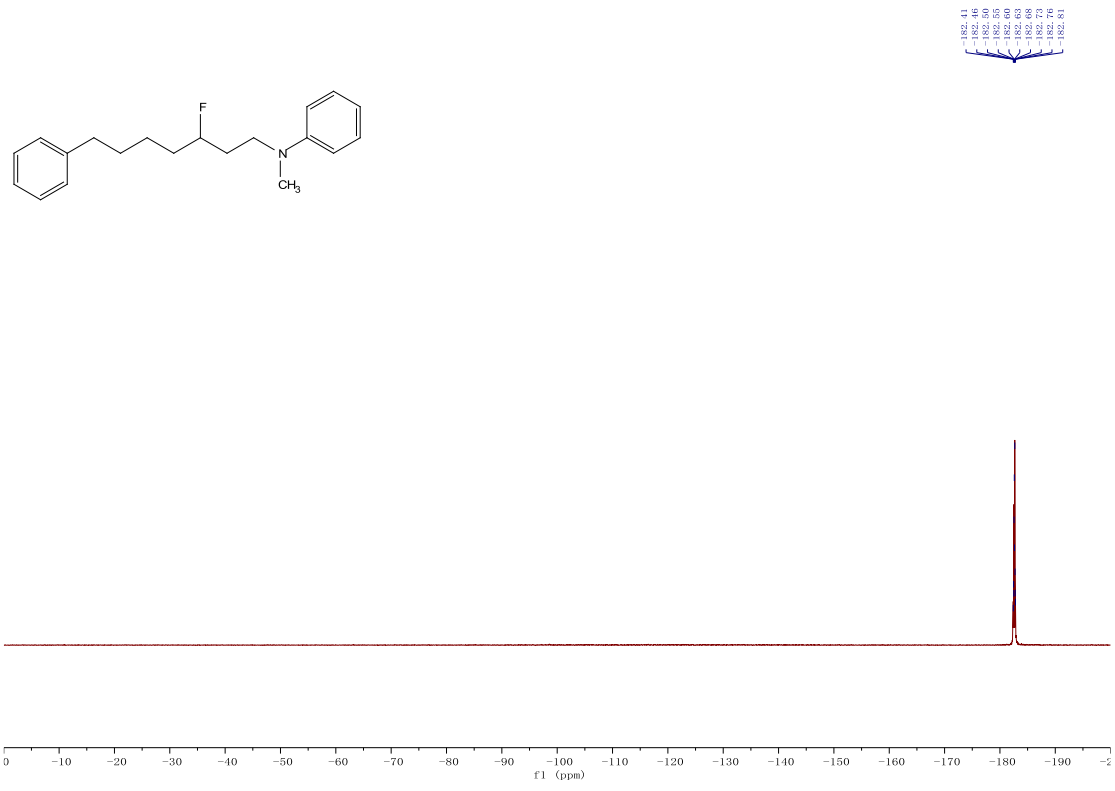
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



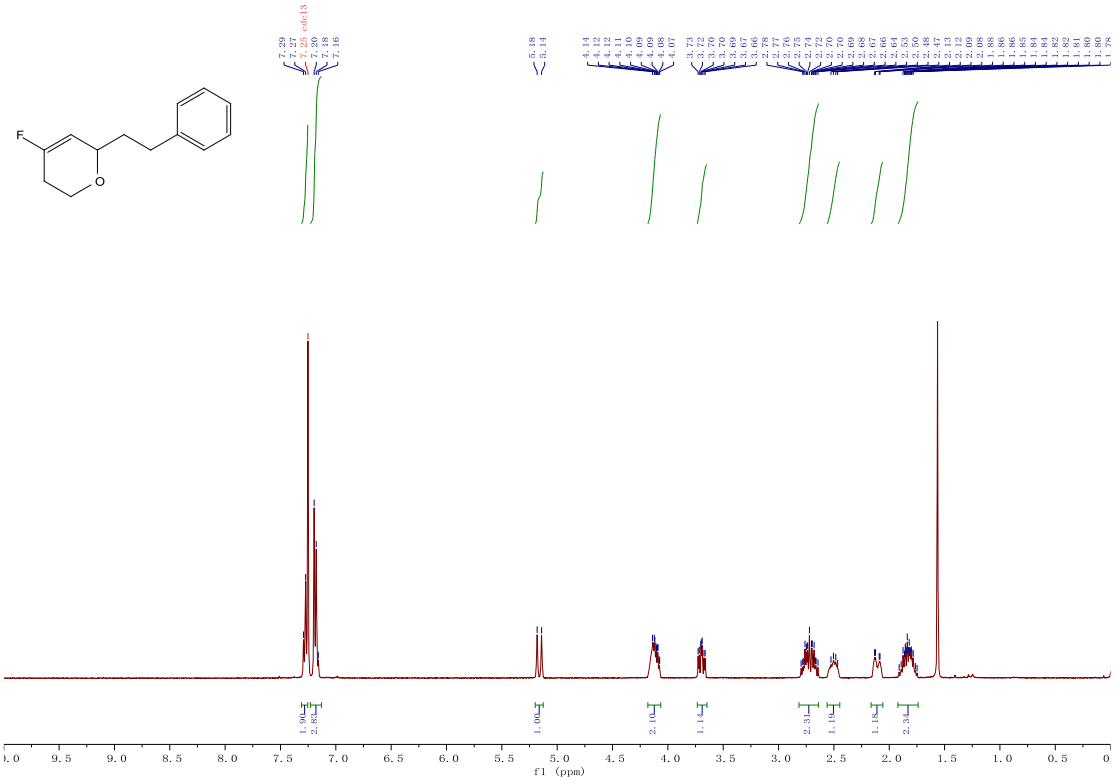
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **7**



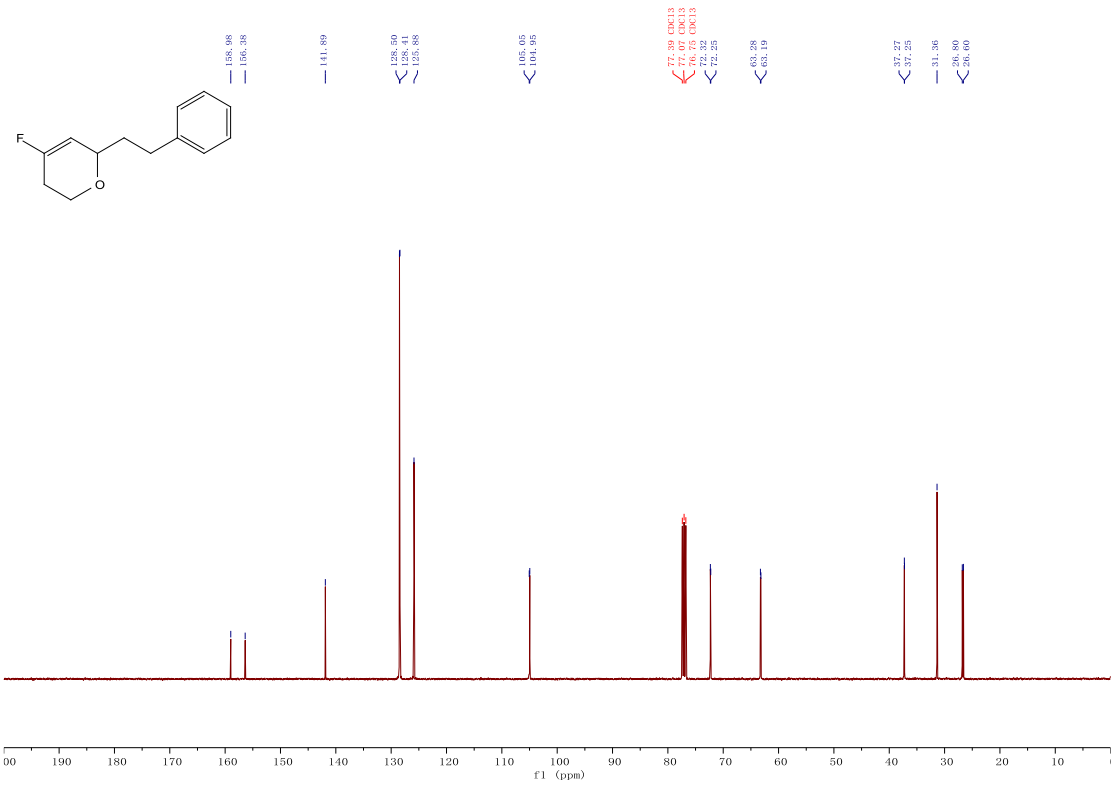
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **7**



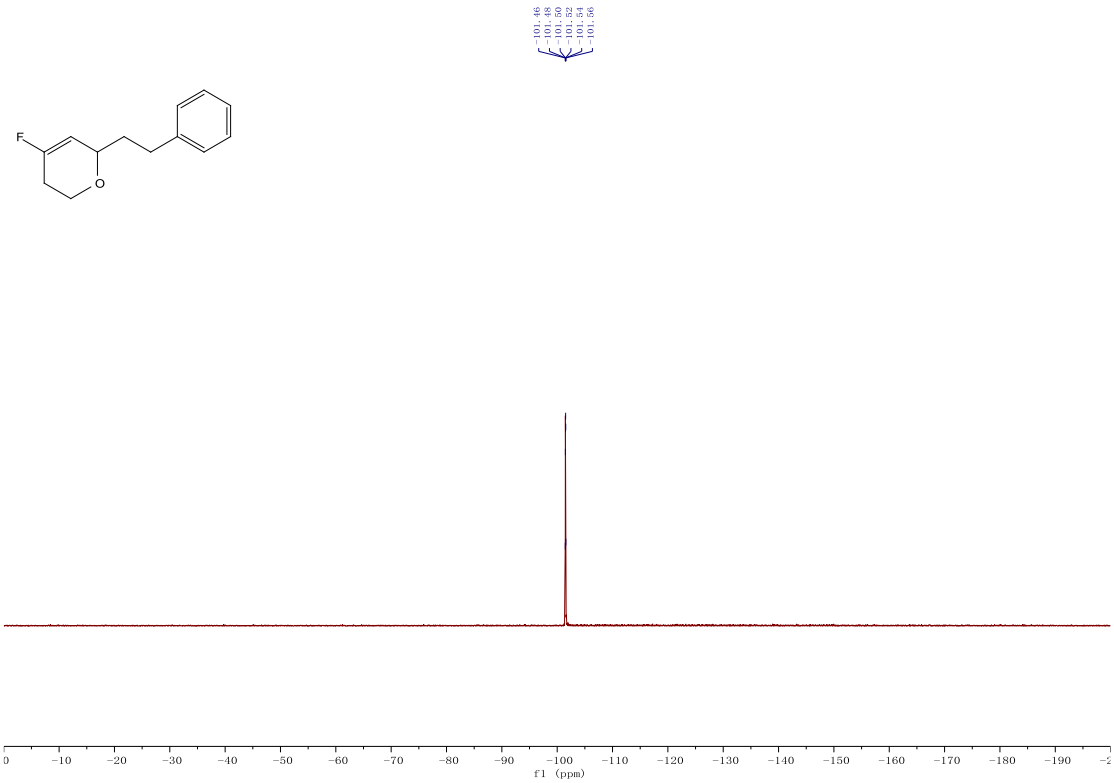
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



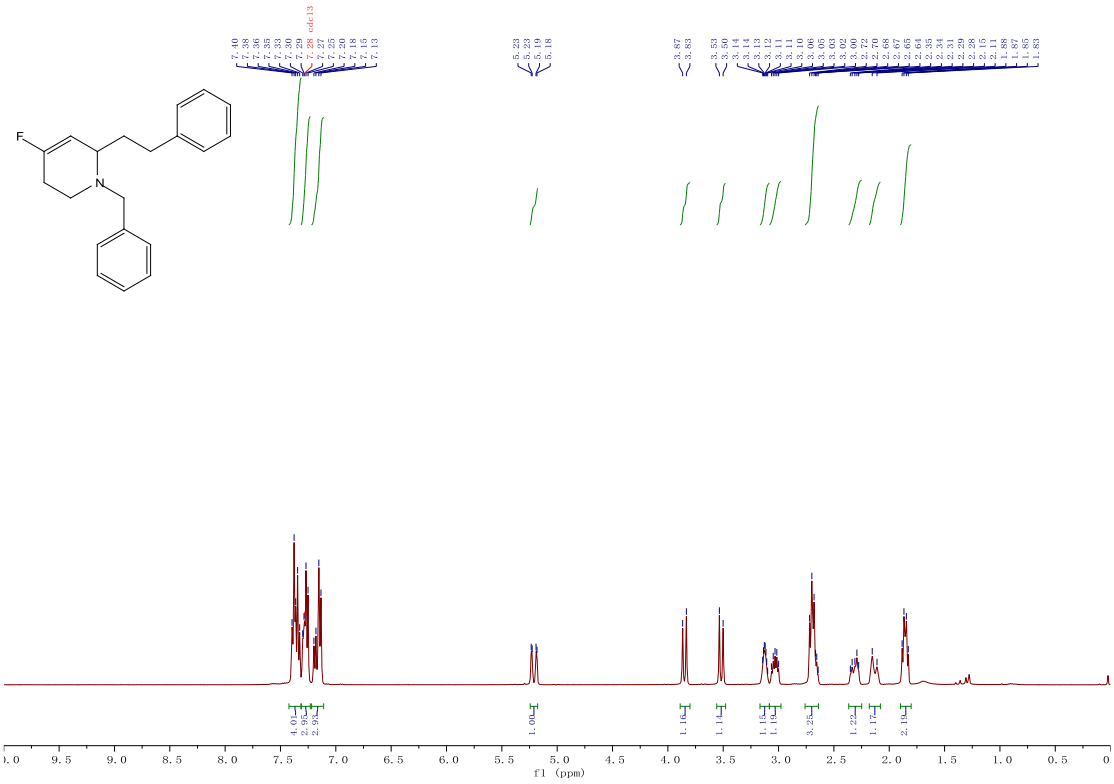
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **8**



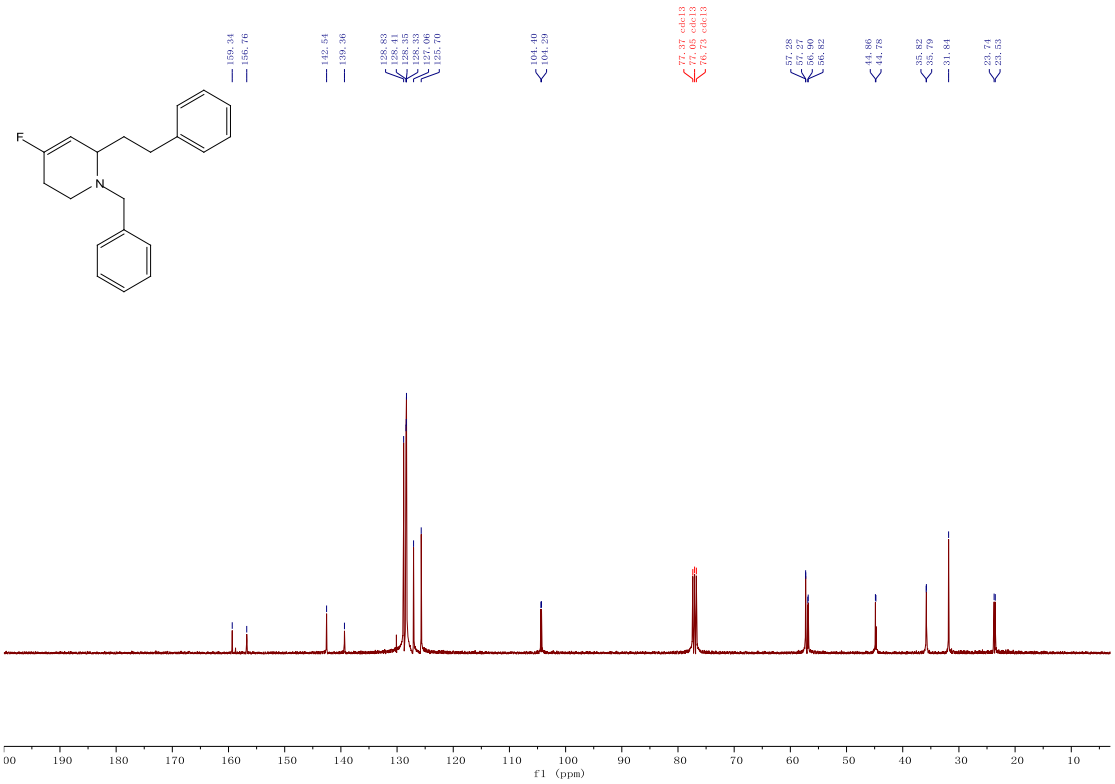
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **8**



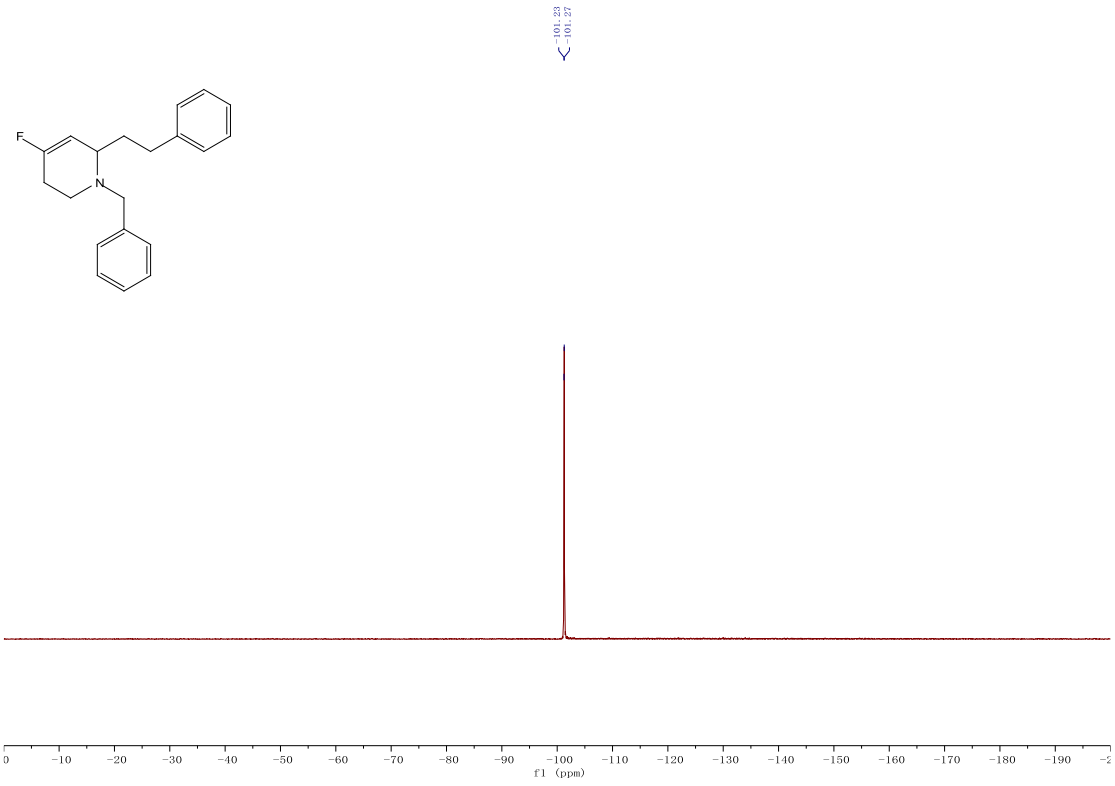
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**



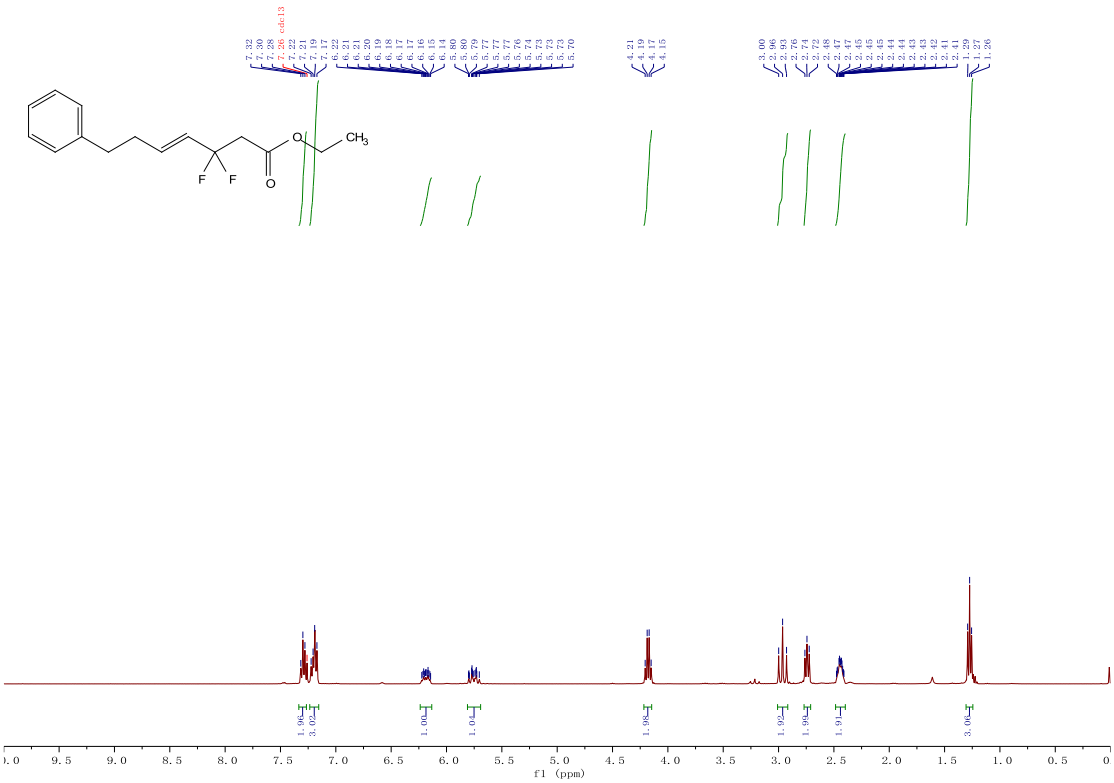
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **10**



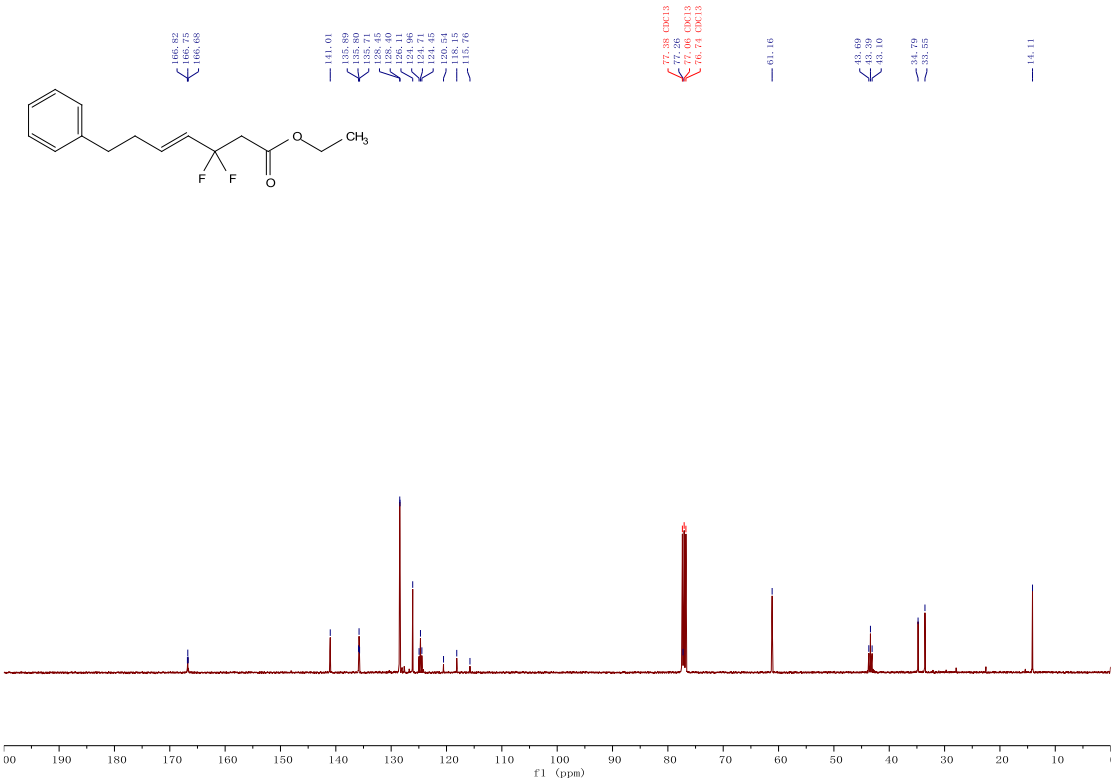
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **10**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **11**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **11**