Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Organic Photoredox Catalytic Decarboxylative Cross-Coupling of *gem*-Difluoroalkenes with Unactivated Carboxylic Acids

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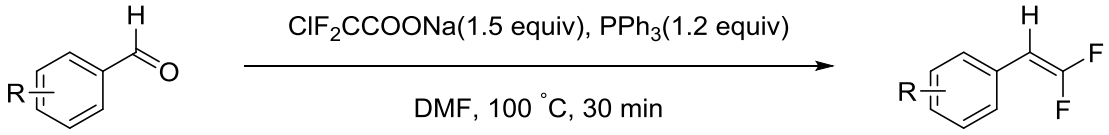
1. General procedures

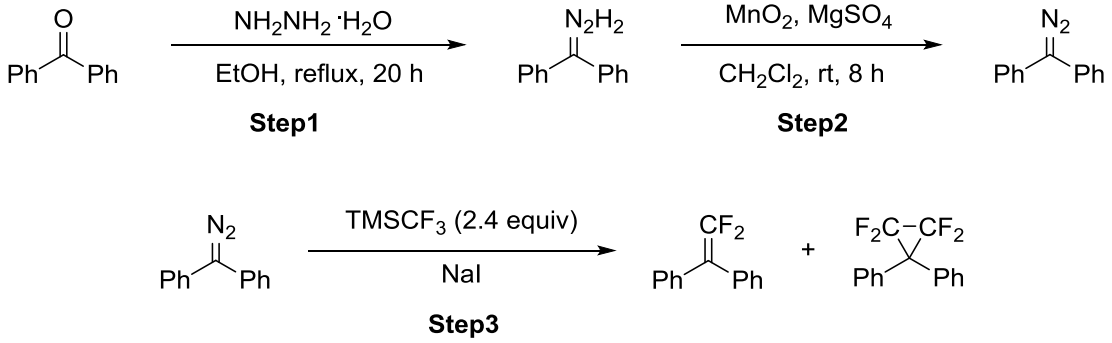
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The reaction product was isolated by column chromatography on a silica gel (236 – 400 mesh) column using petroleum ether (PE) with a boiling range from 60 to 90 ℃ and EtOAc. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on 400, 101, 376 MHz NMR spectrometers using $CDCl_3$ as solvent. In addition, ^{1}H, and ^{13}C NMR spectra used tetramethylsilane as the internal standard and the ^{19}F NMR spectra used trifluoroacetic acid as the internal standard. HRMS were made by means of ESI. EPR spectra were recorded on a Bruker EMXplus. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were performed under argon atmosphere. All the *gem*-difluoroalkenes were prepared with the Wittig reaction according to the literature.

2. General procedure for synthesis of asymmetric *gem*-difluoroalkenes



The preparation followed literature methods.[1] To a two-necked round-bottom flask equipped with a magnetic stir bar and charged with aldehyde (1 equiv), PPh_3 (1.2 equiv), and DMF (0.5 mol/L for aldehyde) was added a solution of sodium chlorodifluoroacetate (1.5 equiv) in DMF (2 mol/L) dropwisely at 100 ℃ over 30 min (**caution**: During the course of the reaction, internal pressure increased due to vigorous liberation of CO_2 gas.). After the addition was completed, the reaction mixture was heated additionally at the same temperature for 30 min. After cooling to 0 ℃ to the reaction mixture was added water and extracted with Et_2O. The combined organic extract was washed with water and brine, and then dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give the corresponding *gem*-difluoroalkene.

3. General procedure for synthesis of symmetric *gem*-difluoroalkenes



The preparation followed literature methods.[2]

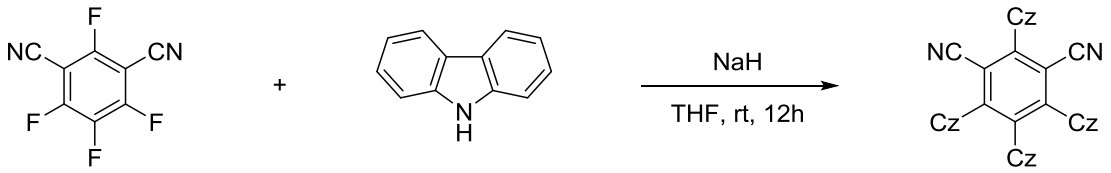
Step 1: Hydrazine monohydrate (80% purity, 18.2 mL, 300 mmol) was added to benzophenone (5.46 g, 30 mmol) in ethanol (60 mL). Then HOAc (0.5 mL) was added and the mixture was heated at reflux for 20 h. After cooling to room temperature, benzophenone hydrazone precipitated as white needle-shaped crystals. Filtration of the crude mixture gave pure benzophenone hydrazone (4.7 g, 80%) as a white solid.

Step 2: Benzophenone hydrazone (4.5 g, 23 mmol), anhydrous $MgSO_4$ (2 g), and 60 mL CH_2Cl_2 was cooled to 0 °C. To this rapidly stirring mixture was added activated MnO_2 (7.0 g, 80.5 mmol) in one portion. The reaction mixture was warmed to room temperature and kept stirring for 8 h, then the solid was filtered off and washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was purified by silica gel (pretreated with Et_3N and PE (Et_3N/PE = 1:10)) with PE/Et_3N = 20:1 as eluent to afford diphenyldiazomethane as a purple solid (3.8 g, 85% yield), which was kept at -20 °C**.**

Step 3: To an oven-dried 10 mL pressure tube equipped with a stir bar were added NaI (30 mg, 0.4 mmol), diphenyldiazomethane (**4a**) (97 mg, 0.5 mmol) and $TMSCF_3$ (170 μL, 1.2 mmol) and THF (5 mL) under Ar. Then the tube was sealed and stirred at rt for 18 h until the color of the reaction mixture was changed from purple to light yellow. The reaction mixture was extracted with EtOAc/H_2O (50 mL/20 mL). The organic extract was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography.

4. Synthesis of donor-acceptor fluorophores

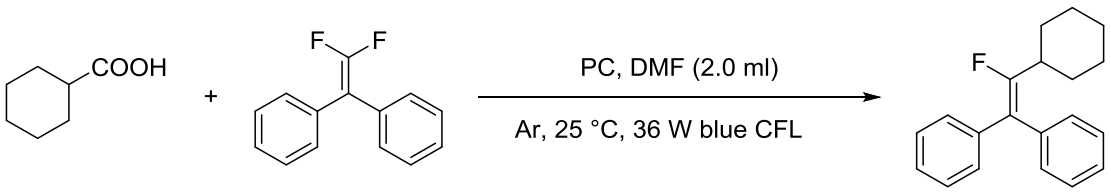
2,4,5,6-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene(4CzIPN), 1,2,4,5-tetrakis(car-bazol-9-yl)-3,6-dicyanobenzene(4CzTPN), and 1,2,3,4-tetrakis(carbazol-9-yl)-5,6-dicyanobenzene (4CzPN) were synthesized using an adapted procedure.[3]



NaH (60% in oil, 0.60 g, 15 mmol) was added slowly to a stirred solution of carbazole (1.67 g, 10.0 mmol). in dry THF (40 mL) under a nitrogen atmosphere at room temperature. After 30 min, tetrafluoroisophthalonitrile (0.40 g, 2.00 mmol), tetrafluoroterephthalonitrile (0.40 g, 2.00 mmol), tetrafluorophthalonitrile (0.40 g, 2.00 mmol), was added. After stirred at room temperature for 12 h, 2 mL water was added to the reaction mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure and washed by water and EtOH to yield the crude product, which was purified by recrystalization from hexane/CH_2Cl_2 or acetone/$CHCl_3$ to give 1.51 g (96%, 4CzIPN), 1.53 g (97%, 4CzTPN), 1.48 g (94%, 4CzPN) corresponding products.

5. Optimization of conditions for decarboxylative monofluoroalkenylation

Table S1: Screening of photocatalyst[a]

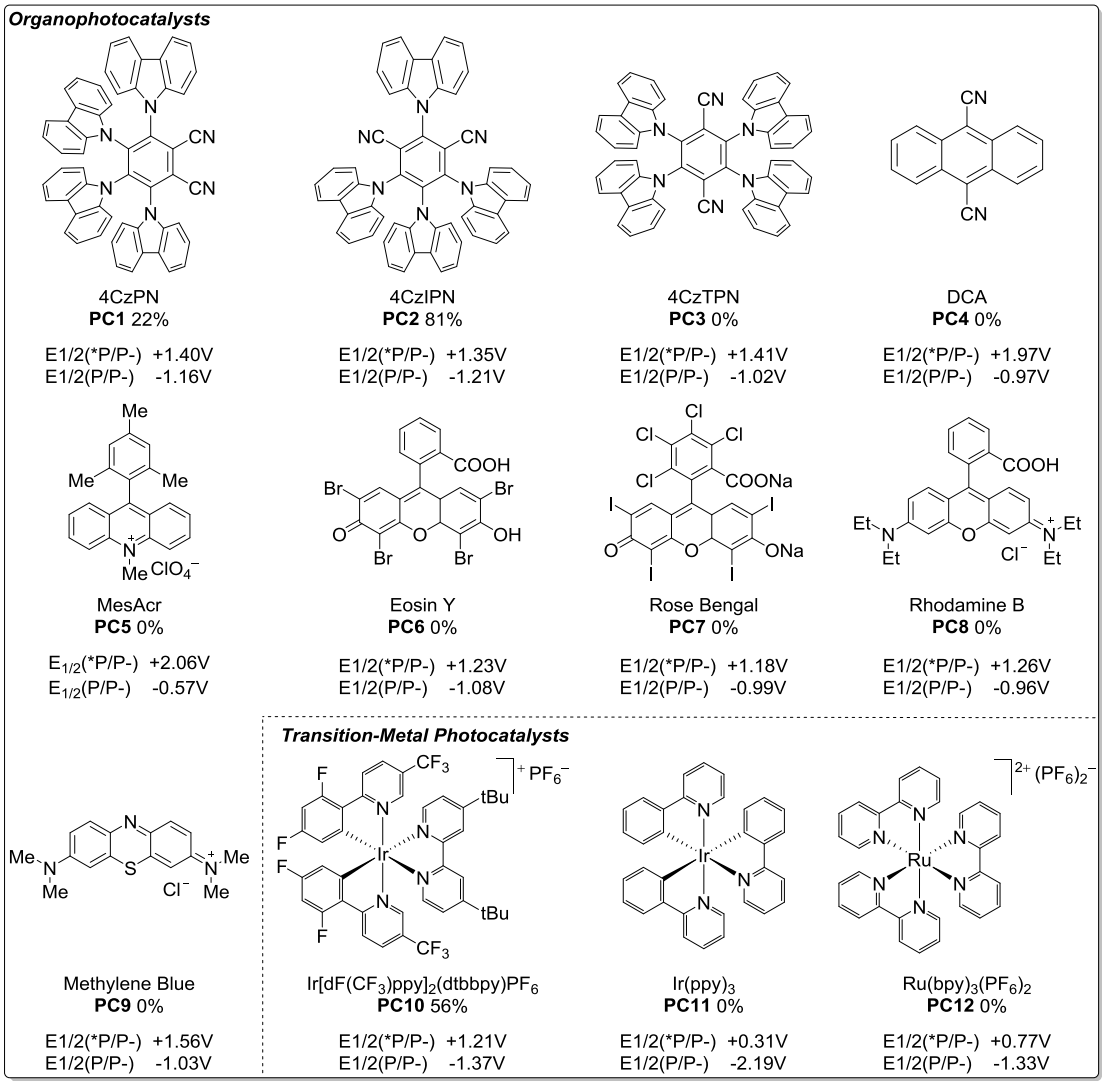


1a **2a** **3a**

Entry	Photocatalyst	Yield (%)[b]
1	PC1	22
2	PC2	81
3	PC3	0
4	PC4	0
5	PC5	0

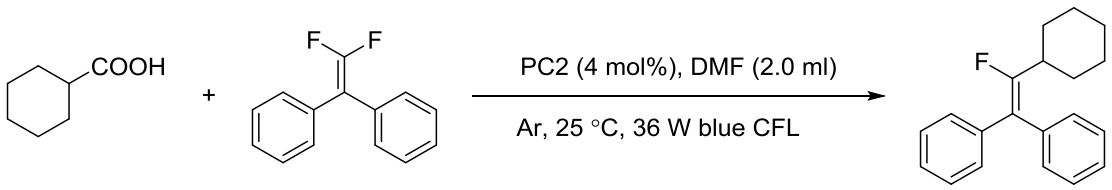
6	PC6	0
7	PC7	0
8	PC8	0
9	PC9	0
10	PC10	56
11	PC11	0
12	PC12	0
13[c]	PC2	32
14[d]	PC2	60

[a]Reaction conditions: 1a (0.1 mmol, 1 equiv), 2a (4 equiv), catalyst (4 mol %), and Cs_2CO_3 (6 equiv) in DMF (2.0 mL) under Ar reaction 24 h. [b]All reaction yields are of isolated products. [c]Under LED. [d]Under sunlight for 72 hours.



Sheme S1. Photocatalysts.

Table S2*:* Screening of bases[a]

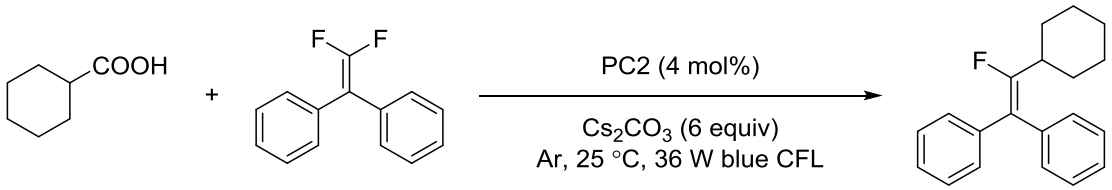


1a **2a** **3a**

Entry	Base	Yield (%)[b]
1	Cs_2CO_3	81
2	Na_2CO_3	52
3	K_2CO_3	34
4	K_3PO_4	20
5	$(CH_3)_3SiOK$	25
6	Na_2HPO_4	29
7	NaH_2PO_4	30
8	K_2HPO_4	23
9	CH_3CH_2ONa	0
10	CsOAc	26
11[c]	Cs_2CO_3	43

[a]Reaction conditions: 1a (0.1 mmol, 1 equiv), 2a (4 equiv), catalyst (4 mol %), and base (6 equiv) in DMF (2.0 mL) under Ar reaction 24 h. [b]All reaction yields are of isolated products. [c]2 equiv base were employed.

Table S3: Screening of solvent[a]



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

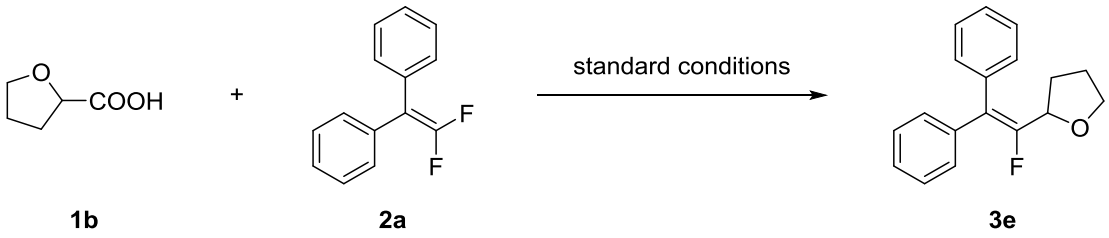
Entry	Solvent	Yield (%)[b]
1	DMF	81
2	MeOH	0
3	DCE	12
4	MeCN	15
5	DMSO	80
6	PhCl	10

[a]Reaction conditions: 1a (0.1 mmol, 1 equiv), 2a (4 equiv), catalyst (4 mol %), and base (6 equiv) in solvent (2.0 mL) under Ar reaction 24 h. [b]All reaction yields are of isolated products.

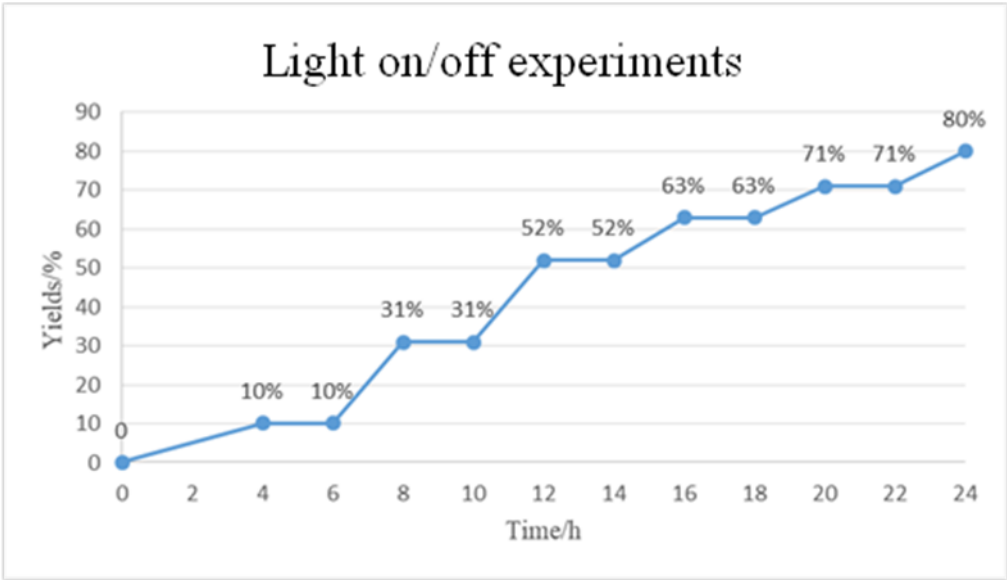
6. General procedures for synthesis of compounds

Carboxylic acids (1) (0.1 mmol), substituted *gem*-difluoroalkene (2) (0.4 mmol), 4CzIPN (0.04 mmol, 3.2 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), DMF (2.0 mL) were added to a 10-mL Schlenk tube. The tube was filled with argon and then sealed, and irradiated with two 36 W blue CFLs (approximately 4 cm away from the light source). After the complete conversion of the substrates (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product.

7. Reaction light on/off experiments



1b **2a** **3e**



Scheme S2. Reaction light on/off experiments

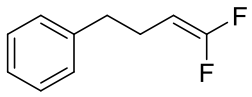
From the light on/off experiments, we found that the reaction needed continual irradiation of light, and thus it is a photocatalyzed rather than a photo-initiated reaction. Finding suggest that a radical chain pathway is unlikely.

8. Procedure For EPR Studies

Carboxylic acids (**1h**) (0.1 mmol), substituted *gem*-difluoroalkene (**2a**) (0.4 mmol), 4CzIPN (0.04 mmol, 3.2 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg) and DMF (2.0 mL) were added to a 10-mL Schlenk tube. The tube was filled with argon and then sealed, and irradiated with two 36 W blue CFL for 2h or or under darkness. At 25 ℃ DMPO (TCI chemicals) (0.1 M) (0.5 equiv) was added and the reaction mixture was stirred for 5 min. A filtered sample was transferred to a capillary and directly measured. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.842807 GHz. Typical spectrometer parameters are shown as follows, scan range: 200 G; center field set: 3500.00 G; time constant: 0.01 ms; scan time: 30 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; microwave power: 2.0 mW.[4]

9. Investigation of aliphatic difluoroalkenes

Aliphatic difluoroalkene (**2u**) was synthesized according to corresponding references.[5]

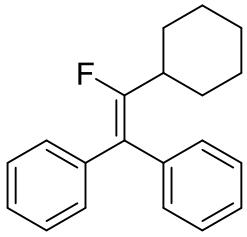


2u:^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.26 – 7.15 (m, 3H), 4.17 (dtd, *J* = 25.4, 7.8, 2.5 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.32 (qt, *J* = 7.5, 1.9 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -12.96 (d, *J* = 47.6 Hz), -14.62 – -15.48 (m).

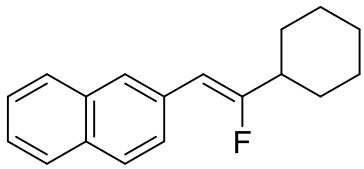
Reaction conditions for aliphatic difluoroalkene (**2u**) with **1a**:

Carboxylic acids (**1a**) (0.1 mmol), substituted *gem*-difluoroalkene (**2u**) (0.4 mmol), 4CzIPN (0.04 mmol, 3.2 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg) and DMF (2.0 mL) were added to a 10-mL Schlenk tube. The tube was filled with argon and then sealed, and irradiated with two 36 W blue CFLs (approximately 4 cm away from the light source). After 72 hours, no desired products have been obtained.

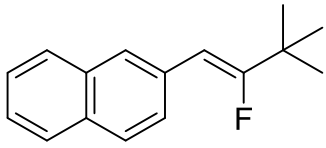
10. Characterization data of compounds



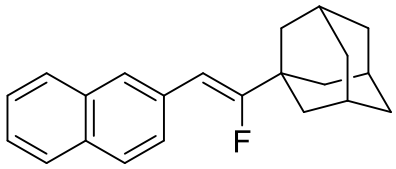
(2-cyclohexyl-2-fluoroethene-1,1-diyl)dibenzene (3a): Eluent: 100% petroleum ether (PE). Rf: 0.63; White solid (81%); m.p. 80.4–80.7 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 7.24 – 7.18 (m, 5H), 2.55 – 2.16 (m, 1H), 1.77 (d, *J* = 12.1 Hz, 4H), 1.72 – 1.55 (m, 3H), 1.29 – 1.03 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.89 (d, *J* = 245.7 Hz), 139.15 (d, *J* = 8.2 Hz), 137.88, 130.14 (d, *J* = 3.0 Hz), 129.66 (d, *J* = 5.1 Hz), 128.40, 127.88, 127.09, 126.64, 118.83 (d, *J* = 15.5 Hz), 39.22 (d, *J* = 25.4 Hz), 29.54, 25.81, 25.65. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.98 (d, *J* = 31.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{22}F^+$, 281.1700; found,281.1704.



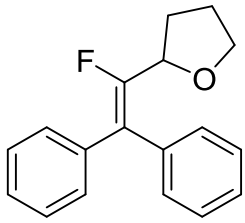
2-(2-cyclohexyl-2-fluorovinyl)naphthalene (3b): Eluent: 100% PE. Rf: 0.75; Colorless oil (60%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.79 (td, *J* = 8.9, 8.4, 4.4 Hz, 4H), 7.68 – 7.57 (m, 1H), 7.53 – 7.38 (m, 3H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 0.5H), 6.24 (d, *J* = 22.1 Hz, 0.5H), 5.60 (d, *J* = 40.6 Hz, 1H), 2.85 – 2.63 (m, 0.5H), 2.41 – 2.21 (m, 1H), 2.01 (d, *J* = 10.7 Hz, 2H), 1.93 – 1.58 (m, 7H), 1.47 – 1.24 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.52 (d, *J* = 268.6 Hz), 133.55, 132.19, 131.63, 127.93, 127.80, 127.50, 127.04 (d, *J* = 7.7 Hz), 126.73 (d, *J* = 7.4 Hz), 125.98, 125.58, 103.71 (d, *J* = 8.7 Hz), 41.68 (d, *J* = 24.5 Hz), 30.11 (d, *J* = 2.4 Hz), 29.54 (d, *J* = 32.7 Hz), 25.96 (d, *J* = 5.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -28.52 (dd, *J* = 40.6, 15.7 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{20}F^+$, 255.1544; found, 255.1547.



2-(2-fluoro-3,3-dimethylbut-1-en-1-yl)naphthalene (3c): Eluent: 100% PE. Rf: 0.65; Colorless oil (75%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.85 – 7.73 (m, 4H), 7.70 – 7.62 (m, 1H), 7.51 – 7.38 (m, 2H), 6.39 (d, *J* = 26.7 Hz, 0.2H), 5.70 (d, *J* = 40.7 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 164.78 (d, *J* = 252.5 Hz), 133.56, 132.20, 131.65, 127.94, 127.79, 127.50, 127.21 (d, *J* = 7.8 Hz), 126.82 (d, *J* = 7.8 Hz), 125.98, 125.61, 102.43 (d, *J* = 9.5 Hz), 35.60 (d, *J* = 23.9 Hz), 27.52 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -32.84 (d, *J* = 40.8 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{18}F^+$, 229.1387; found, 229.1384.

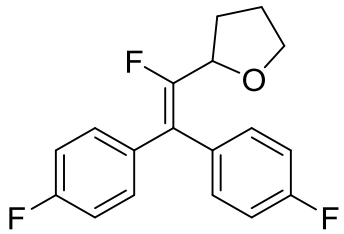


(3*R*,5*R*)-1-((*Z*)-1-fluoro-2-(naphthalen-2-yl)vinyl)adama-ntine (3d): Eluent: 100% PE. Rf: 0.65; white solid (65%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 0.6H), 7.87 – 7.74 (m, 3.6H), 7.69 – 7.63 (m, 1H), 7.53 – 7.39 (m, 2.6H), 7.35 – 7.31 (m, 0.5H), 6.37 (d, *J* = 27.5 Hz, 0.6H), 5.59 (d, *J* = 41.4 Hz, 1H), 2.09 (s, 2H), 1.96 – 1.84 (m, 6H), 1.77 (d, *J* = 3.2 Hz, 7H), 1.58 (d, *J* = 15.6 Hz, 7H). ^{13}C NMR (101 MHz, Chloroform-d) δ 163.86 (d, *J* = 262.3 Hz), 161.04 (d, *J* = 252.5 Hz), 133.57, 132.87, 132.18 (d, *J* = 1.9 Hz), 131.78 (d, *J* = 2.0 Hz), 128.47 (d, *J* = 2.3 Hz), 127.93, 127.77, 127.64, 127.49, 127.23, 127.11, 126.89 (d, *J* = 7.8 Hz), 126.09, 125.95, 125.73, 125.55, 106.45 (d, *J* = 34.2 Hz), 102.44 (d, *J* = 9.5 Hz), 39.89 (d, *J* = 3.8 Hz), 39.33, 37.46, 37.23, 36.68, 36.51, 27.97 (d, *J* = 10.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -31.43 (d, *J* = 27.5 Hz), -37.47 (d, *J* = 41.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{24}F^+$, 307.1857; found, 307.1860.

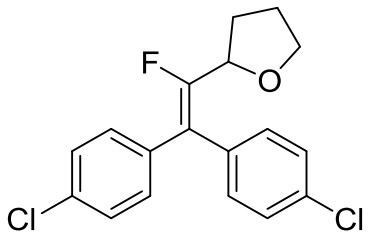


2-(1-fluoro-2,2-diphenylvinyl)tetrahydrofuran (3e): Eluent: PE/ethyl acetate (EA) (9:1). Rf: 0.65; White solid (90%); m.p. 91–92 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 7H), 7.26 – 7.21 (m, 3H), 4.54 (dt, *J* = 29.5, 7.0 Hz, 1H), 3.98 (q, *J* = 7.0 Hz, 1H), 3.82 (td, *J*

= 7.6, 5.0 Hz, 1H), 2.26 – 1.98 (m, 3H), 1.95 – 1.83 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.84 (d, *J* = 265.6 Hz), 137.85 (d, *J* = 7.3 Hz), 137.07, 130.46 (d, *J* = 3.0 Hz), 129.77 (d, *J* = 4.8 Hz), 128.34, 127.96, 127.59, 127.33, 123.20 (d, *J* = 14.1 Hz), 74.92 (d, *J* = 26.3 Hz), 69.23, 28.86 (d, *J* = 2.0 Hz), 26.84. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -50.33 (d, *J* = 29.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{18}FO^+$, 269.1336; found,269.1339.

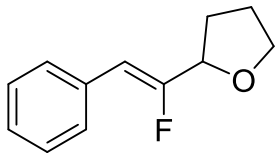


2-(1-fluoro-2,2-bis(4-fluorophenyl)vinyl)tetrahydrofuran (3f): Eluent: PE/EA (15:1). Rf: 0.42; White solid (98%); m.p. 67.9–68.3 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (dtd, *J* = 14.1, 5.8, 2.9 Hz, 4H), 7.12 – 6.94 (m, 4H), 4.51 (dq, *J* = 29.4, 6.7 Hz, 1H), 3.99 (q, *J* = 6.9 Hz, 1H), 3.83 (td, *J* = 7.6, 5.4 Hz, 1H), 2.22 – 1.99 (m, 3H), 1.91 (ddddt, *J* = 13.0, 9.2, 5.7, 3.6, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ162.39 (d, *J* = 247.6 Hz),161.94 (d, *J* = 247.6 Hz), 155.97 (d, *J* = 266.2 Hz), 133.56 (dd, *J* = 7.4, 3.4 Hz), 132.85 (d, *J* = 3.2 Hz), 132.08 (dd, *J* = 8.1, 3.1 Hz), 131.45 (dd, *J* = 8.1, 5.0 Hz), 130.40 (d, *J* = 2.9 Hz), 129.70 (d, *J* = 4.8 Hz), 128.23 (d, *J* = 41.0 Hz), 121.38 (d, *J* = 14.8 Hz), 115.96 – 114.63 (m), 74.83 (dd, *J* = 26.1, 5.3 Hz), 69.23, 28.75 (d, *J* = 2.3 Hz), 26.83. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -37.95 (dtd, *J* = 65.4, 8.7, 4.3 Hz), -49.61 (d, *J* = 29.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{16}F_3O^+$, 305.1148; found, 305.1143.

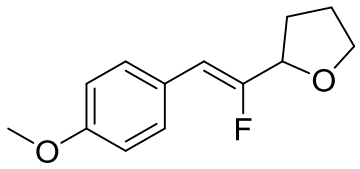


2-(2,2-bis(4-chlorophenyl)-1-fluorovinyl)tetrahydrofuran (3g): Eluent: PE/EA (15:1). Rf: 0.5; White solid (99%); m.p. 90.0–91.1 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.21 – 7.15 (m, 4H), 4.49 (dt, *J* = 29.5, 7.0 Hz, 1H),

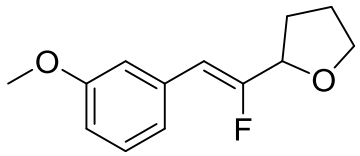
3.97 (q, *J* = 6.9 Hz, 1H), 3.81 (td, *J* = 7.6, 5.4 Hz, 1H), 2.28 – 1.98 (m, 3H), 1.97 – 1.81 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.48 (d, *J* = 267.8 Hz), 135.83 (d, *J* = 7.3 Hz), 135.08, 133.99, 133.42 (d, *J* = 1.1 Hz), 131.78 (d, *J* = 3.1 Hz), 131.07 (d, *J* = 5.1 Hz), 128.75, 128.29, 121.27 (d, *J* = 14.7 Hz), 74.78 (d, *J* = 26.2 Hz), 69.28, 28.78 (d, *J* = 2.3 Hz), 26.85. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -47.86 (d, *J* = 29.3 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{16}Cl_2FO^+$, 337.0557; found, 337.0560.



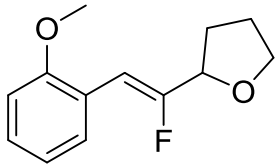
(*Z*)-2-(1-fluoro-2-phenylvinyl)tetrahydrofuran (3h): Eluent: PE/EA (15:1). Rf: 0.6; Yellow oil (90%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.19 (m, 1H), 5.78 (d, *J* = 39.4 Hz, 1H), 4.53 (ddd, *J* = 13.5, 7.5, 5.4 Hz, 1H), 4.20 – 3.97 (m, 1H), 3.95 – 3.77 (m, 1H), 2.34 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.34 (d, *J* = 269.2 Hz), 133.07 (d, *J* = 2.7 Hz), 128.66 (d, *J* = 7.3 Hz), 128.43, 127.19 (d, *J* = 2.4 Hz), 106.04 (d, *J* = 6.4 Hz), 69.00, 29.54, 25.79. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.80 (dd, *J* = 39.4, 14.3 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{14}FO^+$, 193.1023; found, 193.1027.



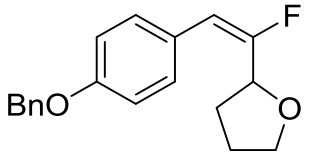
(*Z*)-2-(1-fluoro-2-(4-methoxyphenyl)vinyl)tetrahydrofuran (3i): Eluent: PE/EA (15:1). Rf: 0.23; Colorless oil (40%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 39.6 Hz, 1H), 4.50 (ddd, *J* = 15.2, 7.3, 5.5 Hz, 1H), 4.01 (dt, *J* = 8.3, 6.4 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.82 (s, 3H), 2.38 – 1.87 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ158.68 (d, *J* = 2.7 Hz), 157.86 (d, *J* = 266.5 Hz), 129.94 (d, *J* = 7.2 Hz), 125.77 (d, *J* = 2.5 Hz), 113.87, 105.76 (d, *J* = 7.0 Hz), 77.23 (d, *J* = 31.2 Hz), 68.94, 55.24, 29.43, 25.86. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -44.93 (dd, *J* = 39.5, 15.5 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{16}FO_2^+$, 223.1129; found,223.1132.



(*Z*)-2-(1-fluoro-2-(3-methoxyphenyl)vinyl)tetrahydrofuran (3j): Eluent: PE/EA (15:1). Rf: 0.25; Yellow oil (76%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (t, *J* = 8.4 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.85 – 6.77 (m, 1H), 5.76 (d, *J* = 39.1 Hz, 1H), 4.52 (ddd, *J* = 13.5, 7.5, 5.4 Hz, 1H), 4.15 – 3.98 (m, 1H), 3.91 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.42 – 1.83 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ159.58, 159.53 (d, *J* = 269.4 Hz), 134.32 (d, *J* = 2.6 Hz), 129.35, 121.32 (d, *J* = 6.7 Hz), 113.89 (d, *J* = 7.9 Hz), 113.17 (d, *J* = 2.1 Hz), 105.97 (d, *J* = 6.2 Hz), 69.01, 55.19, 29.56, 25.79. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.92 (dd, *J* = 38.9, 14.0 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{16}FO_2^+$, 223.1129; found,223.1131.

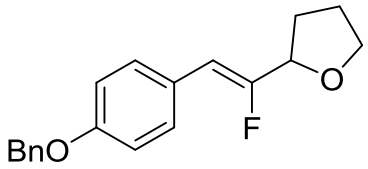


(*Z*)-2-(1-fluoro-2-(2-methoxyphenyl)vinyl)tetrahydrofuran (3k): Eluent: PE/EA (15:1). Rf: 0.24; Yellow oil (89%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.02 – 6.80 (m, 2H), 6.20 (d, *J* = 40.3 Hz, 1H), 4.54 (ddd, *J* = 16.2, 7.3, 5.7 Hz, 1H), 4.03 (dt, *J* = 8.3, 6.5 Hz, 1H), 3.89 (dddd, *J* = 8.0, 6.7, 5.6, 1.0 Hz, 1H), 3.84 (s, 3H), 2.39 – 1.81 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ160.46, 157.53 (d, *J* = 263.7 Hz), 129.93 (d, *J* = 12.3 Hz), 128.39 (d, *J* = 1.8 Hz), 121.82 (d, *J* = 3.0 Hz), 120.57, 110.46, 100.03 (d, *J* = 5.3 Hz), 77.69, 68.96, 55.52, 29.43, 25.92. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -44.08 (dd, *J* = 40.2, 16.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{16}FO_2^+$, 223.1129; found,223.1133.

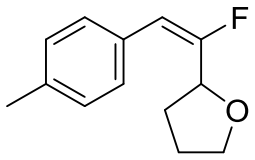


(*E*)-2-(2-(4-(benzyloxy)phenyl)-1-fluorovinyl)tetrahydrofuran (3la): Eluent: PE/EA (15:1). Rf: 0.37; Colorless oil (30%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.30 (m, 5H), 7.19

(d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 20.2 Hz, 1H), 5.07 (s, 2H), 4.76 (dt, *J* = 30.2, 6.7 Hz, 1H), 4.00 (dt, *J* = 8.8, 6.4 Hz, 1H), 3.85 (td, *J* = 7.6, 5.0 Hz, 1H), 2.32 – 1.98 (m, 3H), 1.94 (p, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.47 (d, *J* = 257.4 Hz), 158.08, 136.88, 130.07 (d, *J* = 2.6 Hz), 128.62, 128.02, 127.45, 125.85, 114.89, 110.80 (d, *J* = 26.9 Hz), 73.50 (d, *J* = 26.5 Hz), 70.06, 69.10, 28.28 (d, *J* = 2.7 Hz), 26.75. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -45.50 (dd, *J* = 30.2, 20.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{20}FO_2^+$, 299.1442; found,299.1446.

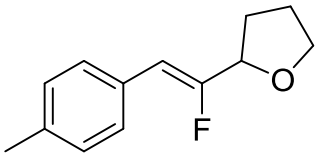


(*Z*)-2-(2-(4-(benzyloxy)phenyl)-1-fluorovinyl)tetrahydrofuran (3lb): Eluent: PE/EA (15:1). Rf: 0.13; White solid (68%); m.p. 62.6–62.8 ℃; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.29 (m, 7H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.72 (d, *J* = 39.5 Hz, 1H), 5.08 (s, 2H), 4.51 (ddd, *J* = 15.1, 7.3, 5.5 Hz, 1H), 4.02 (dt, *J* = 8.3, 6.4 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 1H), 2.32 – 1.85 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.98 (d, *J* = 266.6 Hz), 157.91 (d, *J* = 2.8 Hz), 136.96, 129.97 (d, *J* = 7.3 Hz), 128.60, 127.98, 127.47, 126.05 (d, *J* = 2.5 Hz), 114.85, 105.74 (d, *J* = 6.9 Hz), 69.99, 68.95, 29.45, 25.86. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -44.67 (dd, *J* = 39.5, 15.5 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{20}FO_2^+$, 299.1442; found,299.1445.

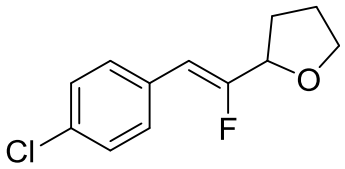


(*E*)-2-(1-fluoro-2-(p-tolyl)vinyl)tetrahydrofuran (3ma): Eluent: PE/EA (15:1). Rf: 0.52; Light yello w oil (22%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (s, 4H), 6.34 (d, *J* = 20.1 Hz, 1H), 4.77 (dt, *J* = 30.3, 6.7 Hz, 1H), 4.00 (q, *J* = 6.9 Hz, 1H), 3.85 (td, *J* = 7.5, 4.9 Hz, 1H), 2.35 (s, 3H), 2.19 – 1.97 (m, 3H), 1.94 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.82 (d, *J* = 258.3 Hz), 137.03, 130.20 (d, *J* = 12.5 Hz), 129.15, 128.77 (d, *J* = 2.7 Hz), 111.12 (d, *J* = 26.4 Hz), 73.48 (d, *J* = 26.5 Hz), 69.12, 28.34 (d, *J* = 2.7 Hz), 26.74, 21.14. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -44.90 (dd, *J* = 30.3, 20.2 Hz). HRMS

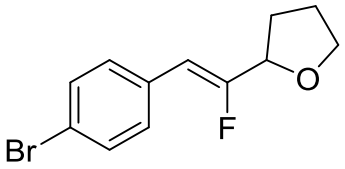
ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{16}FO^+$, 207.1180; found,207.1183



(*Z*)-2-(1-fluoro-2-(p-tolyl) vinyl)tetrahydrofuran (3mb): Eluent: PE/EA (15:1). Rf: 0.35; Light yellow oil (76%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.75 (d, *J* = 39.5 Hz, 1H), 4.51 (dt, *J* = 14.0, 6.4 Hz, 1H), 4.02 (q, *J* = 7.0 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 1H), 2.35 (s, 3H), 2.05 (dddd, *J* = 35.9, 29.2, 14.4, 6.6 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.70 (d, *J* = 267.9 Hz), 137.00 (d, *J* = 2.4 Hz), 130.20 (d, *J* = 2.7 Hz), 129.14, 128.58 (d, *J* = 7.2 Hz), 106.06 (d, *J* = 6.7 Hz), 68.97, 29.48, 25.83, 21.23. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.99 (dd, *J* = 39.5, 15.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{16}FO^+$, 207.1180; found,207.1184

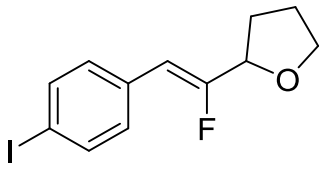


(*Z*)-2-(2-(4-chlorophenyl)-1-fluorovinyl)tetrahydrofuran (3n): Eluent: PE/EA (15:1). Rf: 0.2; Light yellow solid (54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.24 (m, 2H), 5.74 (d, *J* = 38.9 Hz, 1H), 4.51 (ddd, *J* = 13.3, 7.6, 5.3 Hz, 1H), 4.02 (dt, *J* = 8.6, 6.4 Hz, 1H), 3.96 – 3.80 (m, 1H), 2.36 – 1.79 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.86 (d, *J* = 269.9 Hz), 132.79 (d, *J* = 3.0 Hz), 131.54 (d, *J* = 2.6 Hz), 129.87 (d, *J* = 7.4 Hz), 128.60, 104.94 (d, *J* = 6.4 Hz), 69.05, 29.56, 25.77. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.64 (dd, *J* = 38.8, 13.7 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{13}ClFO^+$, 277.0633; found,277.0636.

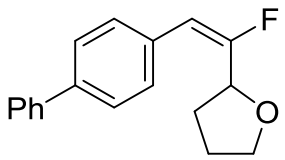


(*Z*)-2-(2-(4-bromophenyl)-1-fluorovinyl)tetrahydrofuran (3o): Eluent: PE/EA (15:1). Rf:

0.4; Light yellow solid (50%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 38.9 Hz, 1H), 4.51 (ddd, *J* = 13.3, 7.5, 5.3 Hz, 1H), 4.02 (dd, *J* = 8.1, 6.5 Hz, 1H), 3.99 – 3.82 (m, 1H), 2.33 – 1.84 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.01 (d, *J* = 270.3 Hz), 131.98 (d, *J* = 2.2 Hz), 131.57, 130.18 (d, *J* = 7.5 Hz), 120.96 (d, *J* = 3.5 Hz), 104.98 (d, *J* = 6.3 Hz), 69.06, 29.55, 25.77. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.21 (dd, *J* = 38.8, 13.6 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{13}BrFO^+$, 271.0128; found,271.0125.

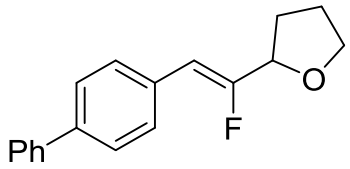


(*Z*)-2-(1-fluoro-2-(4-iodophenyl)vinyl)tetrahydrofuran (3p): Eluent: PE/EA (15:1). Rf: 0.33; Light yellow oil (45%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.71 (d, *J* = 38.9 Hz, 1H), 4.50 (ddd, *J* = 13.2, 7.6, 5.3 Hz, 1H), 4.01 (dt, *J* = 8.7, 6.4 Hz, 1H), 3.94 – 3.82 (m, 1H), 2.28 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.22 (d, *J* = 270.4 Hz), 137.88, 137.55, 132.56 (d, *J* = 2.6 Hz), 130.38 (d, *J* = 7.4 Hz), 105.06 (d, *J* = 6.3 Hz), 69.05, 29.56, 25.76. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -39.70 (dd, *J* = 38.9, 13.5 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{13}FIO^+$, 318.9990; found,318.9992.

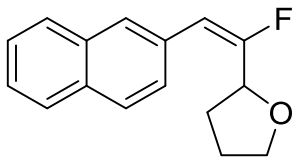


(*E*)-2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)tetrahydrofuran (3qa): Eluent: PE/EA (20:1). Rf: 0.4; Yellow oil (16%); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.55 (m, 4H), 7.51 – 7.41 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 3H), 6.41 (d, *J* = 20.0 Hz, 1H), 4.83 (dt, *J* = 30.1, 6.7 Hz, 1H), 4.02 (q, *J* = 6.9 Hz, 1H), 3.88 (td, *J* = 7.7, 5.1 Hz, 1H), 2.11 (tq, *J* = 15.0, 7.2 Hz, 3H), 2.01 – 1.87 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.90 (d, *J* = 256.8 Hz), 140.58, 140.11, 132.19 (d, *J* = 12.9 Hz), 129.31 (d, *J* = 2.6 Hz), 128.82, 127.41, 127.16, 127.00, 110.94 (d, *J* = 26.9 Hz), 73.53 (d, *J* = 26.3 Hz), 69.20, 28.37 (d, *J* = 2.7 Hz), 26.78. ^{19}F NMR

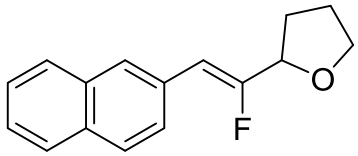
(376 MHz, Chloroform-*d*) δ -43.34 (dd, *J* = 30.1, 20.0 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{18}FO^+$, 269.1336; found,269.1333.



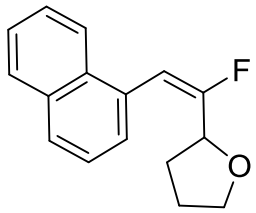
(*Z*)-2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)tetrahydrofuran (3qb): Eluent: PE/EA (20:1). Rf: 0.32; White solid (80%); m.p. 82.9-83.5 ℃; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 – 7.57 (m, 6H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 5.84 (d, *J* = 39.4 Hz, 1H), 4.56 (ddd, *J* = 13.5, 7.4, 5.5 Hz, 1H), 4.05 (q, *J* = 6.9, 6.5 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 1H), 2.43 – 1.90 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.58 (d, *J* = 269.3 Hz), 140.71, 139.88 (d, *J* = 2.3 Hz), 132.15 (d, *J* = 2.6 Hz), 129.09 (d, *J* = 7.3 Hz), 128.80, 127.32, 127.11, 126.97, 105.71 (d, *J* = 6.5 Hz), 77.09 (d, *J* = 31.9 Hz), 69.04, 29.59, 25.82. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.15 (dd, *J* = 39.4, 14.2 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{18}FO^+$, 269.1336; found,269.1339.



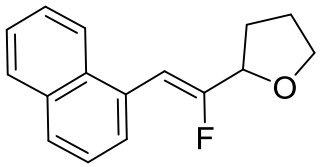
(*E*)-2-(1-fluoro-2-(naphthalen-2-yl)vinyl)tetrahydrofuran (3ra): Eluent: PE/EA (15:1). Rf: 0.5; White solid (38%); m.p. 62.6–62.9 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.77 (m, 3H), 7.73 (s, 1H), 7.53 – 7.43 (m, 2H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.52 (d, *J* = 20.0 Hz, 1H), 4.85 (dt, *J* = 30.2, 6.9 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.94 – 3.83 (m, 1H), 2.21 – 2.02 (m, 3H), 1.98 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.51 (d, *J* = 260.0 Hz), 133.30, 132.43, 130.66 (d, *J* = 12.4 Hz), 128.06, 127.90, 127.67 (d, *J* = 3.0 Hz), 127.63, 126.98 (d, *J* = 2.2 Hz), 126.33, 126.06, 111.31 (d, *J* = 26.9 Hz), 73.55 (d, *J* = 26.5 Hz), 69.21, 28.44 (d, *J* = 2.6 Hz), 26.76. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -43.33 (dd, *J* = 30.2, 19.9 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{16}FO^+$, 243.1180; found,243.1182.



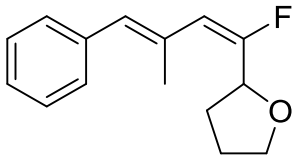
(*Z*)-2-(1-fluoro-2-(naphthalen-2-yl)vinyl)tetrahydrofuran (3rb): Eluent: PE/EA (15:1). Rf: 0.32; White solid (50%); m.p. 72.5–73 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.87 – 7.76 (m, 3H), 7.67 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.40 (m, 2H), 5.94 (d, *J* = 39.3 Hz, 1H), 4.62 – 4.52 (m, 1H), 4.05 (q, *J* = 7.4, 6.6 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 1H), 2.25 – 1.93 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.68 (d, *J* = 269.6 Hz), 133.45, 132.49 (d, *J* = 1.8 Hz), 130.64 (d, *J* = 3.2 Hz), 128.05, 127.95, 127.72 (d, *J* = 7.2 Hz), 127.55, 126.64 (d, *J* = 7.4 Hz), 126.11, 125.94, 106.19 (d, *J* = 6.4 Hz), 69.06, 29.60, 25.84. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.24 (dd, *J* = 39.3, 14.3 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{16}FO^+$, 243.1180; found,243.1183.



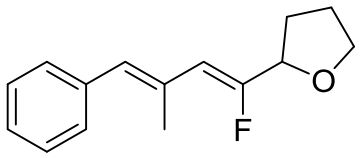
(*E*)-2-(1-fluoro-2-(naphthalen-1-yl)vinyl)tetrahydrofuran (3sa): Eluent: PE/EA (15:1). Rf: 0.4; Light yellow oil (21%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.94 (m, 1H), 7.90 – 7.78 (m, 2H), 7.62 – 7.39 (m, 4H), 6.77 (d, *J* = 19.1 Hz, 1H), 4.62 (dt, *J* = 29.8, 7.0 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 1H), 3.82 (td, *J* = 7.6, 5.1 Hz, 1H), 2.39 – 1.94 (m, 3H), 1.88 (dt, *J* = 10.4, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.96 (d, *J* = 274.1 Hz), 133.46, 132.15 (d, *J* = 2.7 Hz), 130.11 (d, *J* = 1.8 Hz), 128.39, 128.14, 127.27 (d, *J* = 1.9 Hz), 126.29, 126.08, 125.41, 124.87, 108.66 (d, *J* = 25.7 Hz), 73.47 (d, *J* = 26.2 Hz), 69.21, 28.60 (d, *J* = 1.8 Hz), 26.74. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -43.08 (dd, *J* = 29.8, 19.2 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{16}FO^+$, 243.1180; found,243.1181.



(*Z*)-2-(1-fluoro-2-(naphthalen-1-yl)vinyl)tetrahydrofuran (3sb): Eluent: PE/EA (15:1). Rf: 0.3; Light yellow oil (68%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 3H), 7.79 (d, *J* = 7.8 Hz, 3H), 6.47 (d, *J* = 37.0 Hz, 1H), 4.68 (ddd, *J* = 13.0, 7.5, 5.5 Hz, 1H), 4.10 (q, *J* = 7.0, 6.5 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 2.76 – 1.81 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.02 (d, *J* = 267.8 Hz), 133.64, 131.36, 129.09, 128.59, 127.76, 127.30 (d, *J* = 8.3 Hz), 126.06, 125.67, 125.47, 124.05, 102.66 (d, *J* = 7.9 Hz), 69.10, 29.71, 25.82. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -42.63 (dd, *J* = 36.9, 13.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{16}H_{16}FO^+$, 243.1180; found,243.1184.

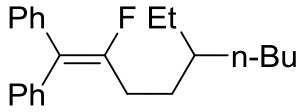


2-((1*E*,3*E*)-1-fluoro-3-methyl-4-phenylbuta-1,3-dien-1-yl)tetrahy-drofuran (3ta): Eluent: PE/EA (15:1). Rf: 0.39; Yellow oil (22%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.4 Hz, 4H), 7.27 – 7.17 (m, 1H), 6.34 (s, 1H), 5.82 (d, *J* = 41.2 Hz, 1H), 4.39 (dt, *J* = 16.0, 6.3 Hz, 1H), 3.88 (dq, *J* = 39.1, 7.1 Hz, 2H), 2.17 (dd, *J* = 3.7, 1.5 Hz, 3H), 2.11 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.19 (d, *J* = 260.3 Hz), 137.78, 131.00 (d, *J* = 3.2 Hz), 129.92 (d, *J* = 3.4 Hz), 129.08, 128.12, 126.58, 105.05 (d, *J* = 6.5 Hz), 68.91, 29.42, 25.85, 23.72, 23.65. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -40.61 (ddd, *J* = 41.3, 16.0, 3.9 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{18}FO^+$, 233.1336; found,233.1339.

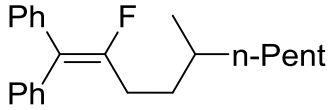


2-((1*Z*,3*E*)-1-fluoro-3-methyl-4-phenylbuta-1,3-dien-1-yl)tet-rahydrofuran (3tb): Eluent: PE/EA (15:1). Rf: 0.2; Yellow oil (21%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.26 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.52 (s, 1H), 5.52 (d, *J* = 39.4 Hz, 1H), 4.43 (dt, *J* = 15.2, 6.4 Hz, 1H), 3.99 (q, *J* = 6.9 Hz, 1H), 3.87 (q, *J* = 7.0 Hz, 1H), 2.15 (d, *J* = 1.6 Hz, 3H), 2.12 – 1.91 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.07 (d, *J* = 268.5 Hz), 137.62, 132.02 (d, *J* = 4.2 Hz), 130.69 (d, *J* = 5.3 Hz), 129.15, 128.08, 126.54, 110.79 (d, *J* = 5.9 Hz),

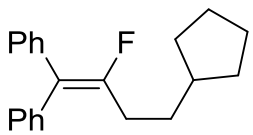
68.93, 29.49, 25.88, 17.06, 16.99. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -43.34 (dd, *J* = 39.3, 15.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{18}FO^+$, 233.1336; found,233.1338.



(5-ethyl-2-fluoronon-1-ene-1,1-diyl)dibenzene (4a): Eluent: 100% PE. Rf: 0.48; Yellow oil (41%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 7H), 7.26 – 7.16 (m, 3H), 2.41 – 2.11 (m, 2H), 1.57 (dd, *J* = 10.5, 5.3 Hz, 2H), 1.31 – 1.09 (m, 9H), 0.83 (dt, *J* = 26.5, 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.33 (d, *J* = 239.5 Hz), 139.17 (d, *J* = 8.3 Hz), 137.75, 130.24 (d, *J* = 3.2 Hz), 129.54 (d, *J* = 5.1 Hz), 128.32, 127.90, 127.13, 126.68, 120.12 (d, *J* = 1.9 Hz), 38.41, 32.44, 30.10, 28.73, 27.88 (d, *J* = 27.1 Hz), 25.61, 23.05, 14.09, 10.74. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -29.70 (t, *J* = 23.4 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{30}F^+$, 325.2326; found,325.2329.

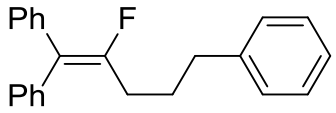


(2-fluoro-5-methyldec-1-ene-1,1-diyl)dibenzene (4b): Eluent: 100% PE. Rf: 0.65; Yellow oil (38%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.25 (m, 7H), 7.20 (d, *J* = 6.6 Hz, 3H), 2.38 – 2.21 (m, 2H), 1.63 (ddd, *J* = 9.5, 7.6, 6.0 Hz, 1H), 1.42 (td, *J* = 9.9, 9.5, 5.7 Hz, 2H), 1.32 – 1.18 (m, 8H), 1.05 (d, *J* = 8.2 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.79 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.17 (d, *J* = 271.0 Hz), 139.17 (d, *J* = 8.3 Hz), 137.77, 130.26 (d, *J* = 2.9 Hz), 129.57 (d, *J* = 5.1 Hz), 128.33, 127.91, 127.13, 126.69, 109.98 (d, *J* = 3.6 Hz), 41.95, 36.55, 33.85, 32.24 (d, *J* = 17.6 Hz), 28.18 (d, *J* = 27.1 Hz), 26.55, 22.68, 19.41, 14 .11. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -29.78 (t, *J* = 23.0 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{30}F^+$, 325.2326; found,325.2330.

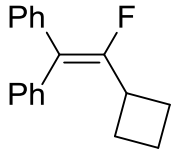


(4-cyclopentyl-2-fluorobut-1-ene-1,1-diyl)dibenzene (4c): Eluent: 100% PE. Rf: 0.56; Yellow oil (30%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.33

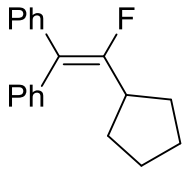
(m, 2H), 7.29 (d, *J* = 3.1 Hz, 3H), 7.20 (d, *J* = 6.4 Hz, 4H), 2.32 (dt, *J* = 23.2, 7.7 Hz, 2H), 1.70 – 1.44 (m, 8H), 1.27 (s, 1H), 1.02 (dq, *J* = 15.3, 7.3 Hz, 2 H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.21 (d, *J* = 261.0 Hz), 139.49 (d, *J* = 4.5 Hz), 137.76, 130.26 (d, *J* = 2.9 Hz), 129.55 (d, *J* = 5.1 Hz), 128.45, 127.90, 127.11, 126.68, 120.92 (d, *J* = 9.4 Hz), 39.63, 33.19, 32.47, 29.83 (d, *J* = 27.1 Hz), 25.13.^{19}F NMR (376 MHz, Chloroform-*d*) δ -29.60 (t, *J* = 23.2 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{24}F^+$, 295.1857; found,295.1857.



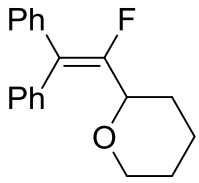
(2-fluoropent-1-ene-1,1,5-triyl)tribenzene (4d): Eluent: 100% PE. Rf: 0.56; Light yellow oil (42%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 7H), 7.27 – 7.07 (m, 8H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.37 (dt, *J* = 22.7, 7.5 Hz, 2H), 1.94 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.91 (d, *J* = 261.0 Hz), 141.71, 138.98 (d, *J* = 8.2 Hz), 137.64, 130.24 (d, *J* = 3.1 Hz), 129.57 (d, *J* = 5.0 Hz), 128.37, 128.36, 128.31, 127.93, 127.15, 126.80, 125.84, 120.69 (d, *J* = 15.1 Hz), 35.16, 30.00 (d, *J* = 27.4 Hz), 28.43. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -30.09 (t, *J* = 22.7 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{22}F^+$, 317.1700; found,317.1703.



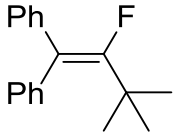
(2-cyclobutyl-2-fluoroethene-1,1-diyl)dibenzene (4e): Eluent: 100% PE. Rf: 0.78; Yellow oil (60%); 1H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 6H), 7.28 – 7.17 (m, 2H), 7.18 – 7.12 (m, 2H), 3.29 (dp, *J* = 31.2, 8.8 Hz, 1H), 2.39 (pd, *J* = 9.4, 2.6 Hz, 2H), 2.02 (tdd, *J* = 11.3, 7.1, 2.9 Hz, 2H), 1.83 (dtd, *J* = 20.7, 9.1, 8.3, 4.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.41 (d, *J* = 259.2 Hz), 139.04 (d, *J* = 7.9 Hz), 137.82, 130.37 (d, *J* = 3.0 Hz), 129.76 (d, *J* = 4.9 Hz), 128.25, 127.89, 127.15, 126.75, 119.39 (d, *J* = 16.7 Hz), 35.42 (d, *J* = 30.9 Hz), 25.78, 18.00. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -41.04 (d, *J* = 31.2 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{18}F^+$, 253.1387; found,253.1390.



(2-cyclopentyl-2-fluoroethene-1,1-diyl)dibenzene (4f): Eluent: 100% PE. Rf: 0.78**;** Light yellow oil (50%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 5H), 7.21 (t, *J* = 7.0 Hz, 5H), 2.80 (dp, *J* = 33.7, 8.3 Hz, 1H), 1.97 – 1.67 (m, 6H), 1.53 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.58 (d, *J* = 258.8 Hz), 139.34 (d, *J* = 8.3 Hz), 137.94, 130.38 (d, *J* = 3.0 Hz), 129.67 (d, *J* = 5.0 Hz), 128.32, 127.87, 127.05, 126.63, 113.61 (d, *J* = 2.9 Hz), 41.96, 39.91 (d, *J* = 26.8 Hz), 30.31, 26.33. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -43.79 (d, *J* = 33.8 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{20}F^+$, 267.1544; found,267.1545.

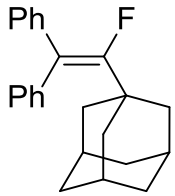


2-(1-fluoro-2,2-diphenylvinyl)tetrahydro-2H-pyran (4g): Eluent: PE/EA (9:1). Rf: 0.63**;** White solid (61%)**;** m.p. 66.5–66.6 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 6.8 Hz, 3H), 7.29 (d, *J* = 6.5 Hz, 4H), 7.29 – 7.19 (m, 3H), 4.11 – 3.92 (m, 2H), 3.38 (t, *J* = 11.3 Hz, 1H), 2.03 – 1.84 (m, 2H), 1.66 (ddt, *J* = 17.3, 13.0, 6.1 Hz, 2H), 1.54 – 1.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.65 (d, *J* = 232.8 Hz), 138.04 (d, *J* = 7.1 Hz), 137.02, 130.19 (d, *J* = 3.0 Hz), 129.82 (d, *J* = 4.9 Hz), 128.30, 127.94, 127.61, 127.32, 123.08 (d, *J* = 14.3 Hz), 74.70 (d, *J* = 26.0 Hz), 68.52, 27.84, 25.42, 22.99. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -46.51 (d, *J* = 26.0 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{20}FO^+$, 283.1493; found,283.1496.

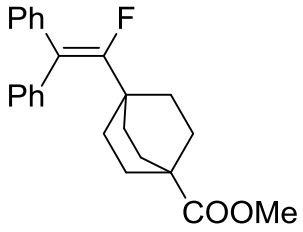


(2-fluoro-3,3-dimethylbut-1-ene-1,1-diyl)dibenzene (4h): Eluent: 100% PE. Rf: 0.63; Colorless oil (52%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 6H), 7.25 – 7.15

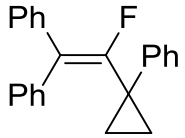
(m, 4H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.55 (d, *J* = 258.8 Hz), 139.40 (d, *J* = 2.3 Hz), 139.00, 130.76 (d, *J* = 3.1 Hz), 129.31 (d, *J* = 4.4 Hz), 128.95, 127.88 (d, *J* = 3.7 Hz), 127.15, 126.51, 119.61 (d, *J* = 21.2 Hz), 36.78 (d, *J* = 26.1 Hz), 29.20 (d, *J* = 4.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -27.98. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{20}F^+$, 255.1544; found,255.1546.



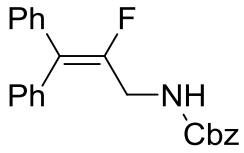
(3*r*,5*r*,7*r*)-1-(1-fluoro-2,2-diphenylvinyl)adamantane (4i): Eluent: PE/EA (20:1). Rf: 0.73; White solid (51%); m.p. 108.4–109.4 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.6 Hz, 3H), 7.24 (dd, *J* = 7.2, 2.9 Hz, 6H), 7.20 – 7.12 (m, 1H), 1.89 (s, 3H), 1.74 (d, *J* = 3.0 Hz, 6H), 1.67 – 1.56 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.41 (d, *J* = 254.5 Hz), 138.52 (d, *J* = 28.5 Hz), 135.31, 130.86 (d, *J* = 3.1 Hz), 129.28 (d, *J* = 4.3 Hz), 127.84, 127.74, 127.06, 126.43, 115.51 (d, *J* = 56.1 Hz), 40.10 (d, *J* = 4.0 Hz), 36.52, 28.15. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -34.07. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{24}H_{26}F^+$, 333.2013; found,333.2016.



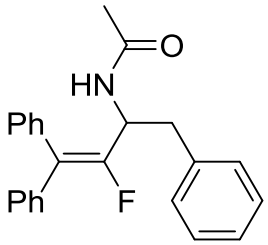
methyl4-(1-fluoro-2,2-diphenylvinyl)bicyclo[2.2.2]octane-1-carbox-ylate (4j): Eluent: PE/EA (15:1). Rf: 0.45; White solid (39%); m.p. 99.7–102.1 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 7H), 7.22 – 7.13 (m, 3H), 3.61 (s, 3H), 1.76 – 1.51 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.06, δ 160.17 (d, *J* = 267.9 Hz), 139.27 (d, *J* = 1.9 Hz), 138.41, 130.82 (d, *J* = 3.0 Hz), 129.24 (d, *J* = 4.5 Hz), 127.95, 127.89, 127.28, 126.62, 120.76 (d, *J* = 21.7 Hz), 51.65, 38.13, 36.99 (d, *J* = 25.3 Hz), 28.74 (d, *J* = 3.9 Hz), 27.94. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -28.82. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{24}H_{26}FO_2^+$, 365.1911; found,365.1914.



(2-fluoro-2-(1-phenylcyclopropyl)ethene-1,1-diyl)dibenzene (4k): Eluent: PE/EA (20:1). Rf: 0.69; White solid (44%); m.p. 74.6–75 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 8H), 7.27 – 7.18 (m, 5H), 7.14 – 7.07 (m, 2H), 1.10 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.19 (d, *J* = 254.4 Hz), 152.88, 149.37 (d, *J* =38.38), 143.04 (d, *J* = 3.4 Hz), 137.92, 130.15 (d, *J* = 2.9 Hz), 129.98 (d, *J* = 4.4 Hz), 128.47, 127.93 (d, *J* = 2.7 Hz), 127.28, 127.15, 125.95, 125.75, 112.84 (d, *J* = 4.0 Hz), 26.15 (d, *J* = 45.0 Hz), 19.36 (d, *J* = 5.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -19.30. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{20}F^+$, 315.1544; found, 315.1547.

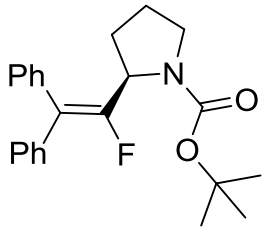


benzyl (2-fluoro-3,3-diphenylallyl)carbamate (4l): Eluent: PE/EA (9:1). Rf: 0.39; White solid (40%); m.p. 66.1–66.6 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 12H), 7.27 – 7.19 (m, 3H), 5.12 (s, 2H), 5.00 (s, 1H), 4.09 (dd, *J* = 19.1, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ, 156.01, 152.67 (d, *J* = 261.9 Hz), 138.83, 137.40 (d, *J* = 6.9 Hz), 136.44 (d, *J* = 25.5 Hz), 130.12 (d, *J* = 3.0 Hz), 129.58 (d, *J* = 5.0 Hz), 128.60, 128.55, 128.17 (d, *J* = 6.3 Hz), 128.05, 127.89, 127.50, 123.16 (d, *J* = 13.1 Hz), 119.02, 67.04, 40.51 (d, *J* = 27.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -38.01 (t, *J* = 19.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{21}FNO_2^+$, 362.1551; found,362.1553.

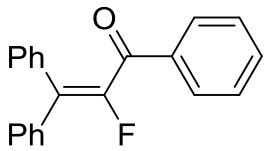


***N*-(3-fluoro-1,4,4-triphenylbut-3-en-2-yl)acetamide (4m)**: Eluent: PE/EA (5:1). Rf: 0.2; Yellow oil (38%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (s, 5H), 7.26 – 7.08 (m, 8H),

6.72 (d, *J* = 6.0 Hz, 2H), 5.81 (d, *J* = 8.7 Hz, 1H), 4.97 (dtd, *J* = 28.6, 9.1, 6.3 Hz, 1H), 3.04 – 2.89 (m, 2H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.67, 153.90 (d, *J* = 246.3 Hz), 136.72 (t, *J* = 3.7 Hz), 136.60, 133.64, 129.91 (d, *J* = 2.9 Hz), 129.54, 129.29 (d, *J* = 4.8 Hz), 128.43, 128.19, 127.98, 127.53, 127.32, 126.81, 111.96 (d, *J* = 209.2 Hz), 50.39 (d, *J* = 24.9 Hz), 39.20, 23.36. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -49.44 (d, *J* = 28.6 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{24}H_{23}FNO^+$, 360.1758; found,360.1762.

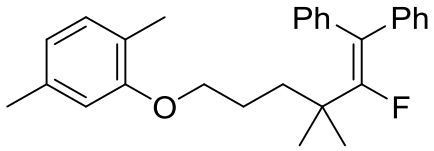


***tert*-butyl(*R*)-2-(1-fluoro-2,2-diphenylvinyl)pyrrolidine-1-carboxyla-te (4n)**: Eluent: PE/EA (15:1). Rf: 0.3; White solid (89%); m.p. 125–126 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 21.5, 7.1 Hz, 6H), 7.23 (d, *J* = 13.4 Hz, 4H), 4.42 (d, *J* = 26.0 Hz, 1H), 3.51 (d, *J* = 24.9 Hz, 2H), 2.51 – 1.91 (m, 3H), 1.77 (dt, *J* = 13.2, 7.1 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.62 (d, *J* = 265.2 Hz), 154.13, 137.83, 137.44, 130.57 (d, *J* = 2.9 Hz), 129.63 (d, *J* = 5.0 Hz), 128.28, 128.00, 127.49, 127.09, 119.90 (d, *J* = 10.5 Hz), 79.74, 55.49 (d, *J* = 24.5 Hz), 47.30, 33.16, 28.63, 23.71. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -46.07 (d, *J* = 25.8 Hz), -46.75 (d, *J* = 26.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{27}FNO_2^+$, 368.2020; found,368.2024.

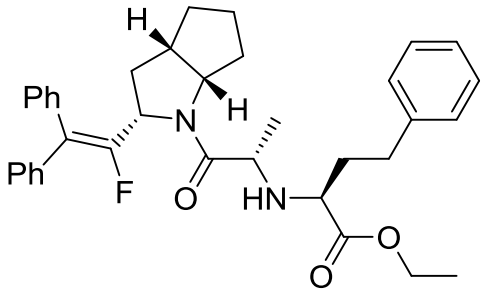


2-fluoro-1,3,3-triphenylprop-2-en-1-one (4o): Eluent: PE/EA (9:1). Rf: 0.67; Colorless oil (31%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.78 (m, 3H), 7.63 – 7.57 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 3H), 7.44 – 7.32 (m, 5H), 7.24 – 7.17 (m, 2H), 7.17 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.07 (d, *J* = 31.1 Hz), 149.85 (d, *J* = 268.8 Hz), 136.44 (d, *J* = 5.3 Hz), 136.08 (d, *J* = 8.5 Hz), 133.29, 130.94 (d, *J* = 11.7 Hz), 130.46 (d, *J* = 3.1 Hz), 130.31 (d, *J* = 5.0 Hz), 129.49 (d, *J* = 2.7 Hz), 128.86, 128.52, 128.34 (d, *J* = 1.4 Hz), 128.27,

128.24, 119.79 (d, *J* = 7.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -35.15. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{16}FO^+$, 303.1180; found,303.1184.

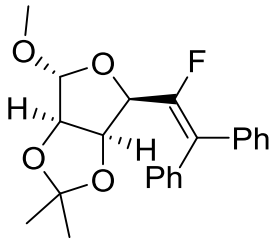


(6-(2,5-dimethylphenoxy)-2-fluoro-3,3-dimethylhex-1-ene-1,1-diyl)dibenzene (4p): Eluent: PE/EA (15:1). Rf: 0.63; Light yellow oil (47%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 7.1 Hz, 5H), 7.28 – 7.14 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.76 – 6.57 (m, 2H), 3.94 (t, *J* = 6.3 Hz, 2H), 2.27 (d, *J* = 46.4 Hz, 6H), 2.01 – 1.86 (m, 2H), 1.74 – 1.63 (m, 2H), 1.02 (d, *J* = 1.5 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.00 (d, *J* = 253.9 Hz), 157.03, 139.36, 138.72 (d, *J* = 8.6 Hz), 136.46, 130.66 (d, *J* = 3.1 Hz), 130.32, 129.21 (d, *J* = 4.3 Hz), 127.93 (d, *J* = 3.5 Hz), 127.21, 126.61, 123.67, 121.40 (d, *J* = 21.4 Hz), 120.70, 116.00, 112.10, 68.15, 39.95 (d, *J* = 25.1 Hz), 38.38 (d, *J* = 3.0 Hz), 27.55 (d, *J* = 4.7 Hz), 25.36, 21.42, 15.79. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -28.02. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{28}H_{32}FO^+$, 403.2432; found,403.2435.

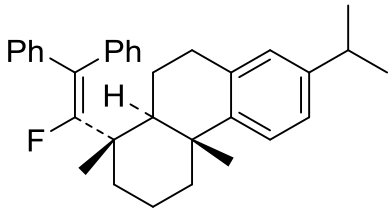


ethyl(*S*)-2-(((*S*)-1-((2*S*,3a*S*,6a*S*)-2-(1-fluoro-2,2-diphenylvinyl)hexahydrocyclopenta[*b*]pyrrol-1(2*H*)-yl)-1-oxopropan-2-yl)amino)-4-phenylbutanoate (4q): Eluent: PE/EA (9:1). Rf: 0.2; Colorless oil (61%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.25 (m, 6H), 7.24 – 7.06 (m, 9H), 4.92 – 4.55 (m, 1H), 4.40 (dtd, *J* = 30.3, 7.9, 3.7 Hz, 1H), 4.29 – 4.01 (m, 1H), 3.92 – 3.52 (m, 1H), 3.41 – 2.87 (m, 2H), 2.80 – 2.39 (m, 2H), 2.34 – 1.40 (m, 12H), 1.35 – 1.02 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.69, 174.37, 174.33, 173.99, 157.56 (d, *J* = 55.1 Hz), 154.92 (d, *J* = 54.0 Hz), 141.47, 141.19, 138.05 (d, *J* = 7.5 Hz), 137.30, 137.06 (d, *J* = 7.3 Hz), 136.28, 130.52 (d, *J* = 3.2 Hz), 130.35 (d, *J* = 2.8 Hz), 129.67 (d, *J* =

2.8 Hz), 129.63 (d, *J* = 2.7 Hz), 129.00, 128.59, 128.54, 128.50, 128.45, 128.26, 128.14, 128.04, 127.98, 127.74, 127.54, 127.15, 126.02 (d, *J* = 5.3 Hz), 120.53 (d, *J* = 13.7 Hz), 120.36 (d, *J* = 12.8 Hz), 65.38, 64.06, 60.86, 60.59, 59.98, 59.46, 58.23 (d, *J* = 24.5 Hz), 57.66 (d, *J* = 24.6 Hz), 53.50, 52.88, 43.47, 41.19, 38.40, 36.34, 35.55, 35.06, 34.93, 32.74, 32.45, 32.08, 31.15, 31.00, 24.59, 23.86, 19.56, 19.44, 14.42, 14.34. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.81 – -121.12 (m), -121.37 (d, *J* = 30.1 Hz), -122.93 (d, *J* = 26.9 Hz), -126.42 (d, *J* = 25.8 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{36}H_{42}FN_2O_3^+$, 569.3174; found,569.3177.

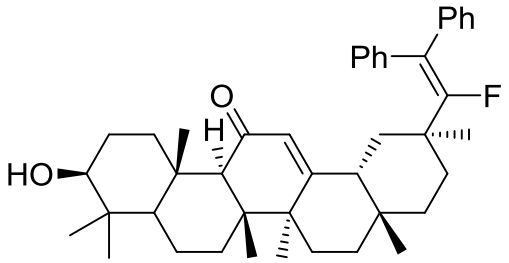


(3a*S*,4*R*,6*R*,6a*R*)-4-(1-fluoro-2,2-diphenylvinyl)-6-methoxy-2,2-di-methyltetrahydrofuro[3,4-d][1,3]dioxole (4r): Eluent: PE/EA (9:1). Rf: 0.6; Light yellow solid (49%); m.p. 78.3–78.7 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.23 (m, 10H), 5.07 – 4.98 (m, 2H), 4.81 (dd, *J* = 34.1, 1.9 Hz, 1H), 4.67 (d, *J* = 5.8 Hz, 1H), 3.40 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.57 (d, *J* = 269.9 Hz), 137.36 (d, *J* = 6.6 Hz), 136.77, 130.70 (d, *J* = 3.1 Hz), 129.97 (d, *J* = 4.8 Hz), 128.46, 128.06 (d, *J* = 9.6 Hz), 127.76, 125.67 (d, *J* = 13.5 Hz), 112.77, 109.33, 86.26, 83.13 (d, *J* = 25.1 Hz), 81.50 (d, *J* = 4.3 Hz), 55.14, 26.68, 25.13. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.26 (d, *J* = 34.1 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{24}FO_4^+$, 371.1653; found,371.1654.

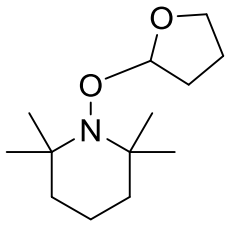


(1*S*,4a*R*,10a*S*)-1-(1-fluoro-2,2-diphenylvinyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-e (4s): Eluent: PE/EA (9:1). Rf: 0.45; Light yellow oil (37%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.53 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.44 (q, *J* = 7.2 Hz, 2H), 7.37 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.26 – 7.13 (m, 4H), 7.02 – 6.89

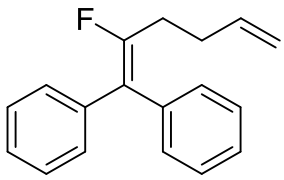
(m, 4H), 3.02 – 2.93 (m, 2H), 2.84 (p, *J* = 6.9 Hz, 1H), 2.33 – 2.19 (m, 2H), 2.00 (dd, *J* = 12.4, 5.0 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.68 (dt, *J* = 26.1, 13.2 Hz, 3H), 1.44 (d, *J* = 5.7 Hz, 1H), 1.28 – 1.20 (m, 7H), 1.16 (s, 3H), 0.78 (d, *J* = 2.1 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.58 (d, *J* = 199.9 Hz), 140.16 (d, *J* = 4.0 Hz), 139.39 (d, *J* = 8.5 Hz), 139.05 (d, *J* = 3.8 Hz), 134.77, 130.42 (d, *J* = 3.0 Hz), 130.10 (d, *J* = 4.4 Hz), 129.23 (d, *J* = 4.0 Hz), 128.86 (d, *J* = 3.3 Hz), 128.38, 128.06 (d, *J* = 5.0 Hz), 127.90, 126.90 (d, *J* = 6.5 Hz), 126.49, 126.29, 124.05 (d, *J* = 3.1 Hz), 123.86, 121.28, 120.19, 110.91 (d, *J* = 1.3 Hz), 45.44 (d, *J* = 21.3 Hz), 43.84 (d, *J* = 4.3 Hz), 37.94, 37.30, 36.72, 33.45, 30.10, 29.72 (d, *J* = 2.9 Hz), 25.39, 23.99, 21.06, 19.33 (d, *J* = 5.1 Hz), 18.52. ^{19}F NMR (376 MHz, Chloroform-*d*) δ-15.22, -29.53. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{33}H_{38}F^+$, 453.2952; found,453.2955.



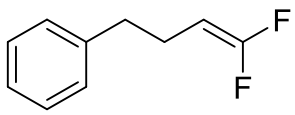
(2*S*,4a*S*,6a*S*,6b*R*,10*S*,12a*S*,12b*R*,14b*R*)-2-(1-fluoro-2,2-diphenylvinyl)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2*H*)-one (4t): Eluent: PE/EA (9:1). Rf: 0.22; Colorless oil (66%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 3H), 7.27 – 7.13 (m, 7H), 5.50 (s, 1H), 3.25 (dd, *J* = 10.4, 5.9 Hz, 1H), 2.79 (dt, *J* = 13.5, 3.6 Hz, 1H), 2.26 (s, 1H), 1.98 (ddd, *J* = 27.3, 13.6, 5.1 Hz, 3H), 1.82 – 1.56 (m, 7H), 1.50 – 1.34 (m, 4H), 1.34 – 1.28 (m, 1H), 1.19 – 1.07 (m, 14H), 1.02 (s, 3H), 1.00 – 0.87 (m, 2H), 0.81 (s, 6H), 0.69 (d, *J* = 10.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.14, 169.43, 162.34 (d, *J* = 258.1 Hz), 139.43 (d, *J* = 2.6 Hz), 138.64 (d, *J* = 8.4 Hz), 130.55 (d, *J* = 3.1 Hz), 129.26 (d, *J* = 4.3 Hz), 128.32, 128.14, 127.91, 127.18, 126.64, 120.31 (d, *J* = 22.0 Hz), 78.74, 61.74, 60.41, 54.91, 46.41, 45.39, 43.20, 40.80, 40.56, 40.22 (d, *J* = 4.4 Hz), 39.15, 37.06, 35.47, 32.72, 32.02, 29.97 (d, *J* = 5.0 Hz), 28.41, 28.11, 27.32, 26.36 (d, *J* = 12.5 Hz), 23.41, 20.73 (d, *J* = 2.9 Hz), 18.65, 17.49, 16.37, 15.60, 14.22. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -30.61. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{43}H_{56}FO_2^+$, 623.4259; found,623.4261.



2,2,6,6-tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine (5): Colorless oil (13%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.36 (dd, *J* = 5.4, 1.9 Hz, 1H), 3.98 – 3.78 (m, 2H), 2.07 – 1.88 (m, 3H), 1.85 – 1.73 (m, 1H), 1.49 (d, *J* = 4.0 Hz, 4H), 1.37 – 1.17 (m, 5H), 1.15 – 0.97 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 109.66, 66.64, 60.21, 58.67, 40.17, 39.76, 33.91, 33.37, 31.24, 23.91, 20.49, 20.08, 17.27. HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{26}NO_2^+$, 228.1958; found, 228.1961.



(2-fluorohexa-1,5-diene-1,1-diyl)dibenzene (7): Colorless oil (10%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.26 (m, 5H), 7.20 (td, *J* = 5.5, 4.8, 2.0 Hz, 5H), 5.78 (ddd, *J* = 16.8, 10.4, 5.3 Hz, 1H), 5.15 – 4.90 (m, 2H), 2.52 – 2.30 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.27 (d, *J* = 255.1 Hz), 141.11, 137.60, 137.02, 130.27 (d, *J* = 3.1 Hz), 129.54 (d, *J* = 5.0 Hz), 128.93, 128.41 (d, *J* = 7.3 Hz), 127.91, 127.19, 126.80, 126.05, 115.23 (d, *J* = 51.7 Hz), 30.49 (d, *J* = 66.6 Hz), 29.79 (d, *J* = 19.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -30.74 (t, *J* = 21.6 Hz). HRMS ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{18}F^+$, 253.1387; found, 253.1389.



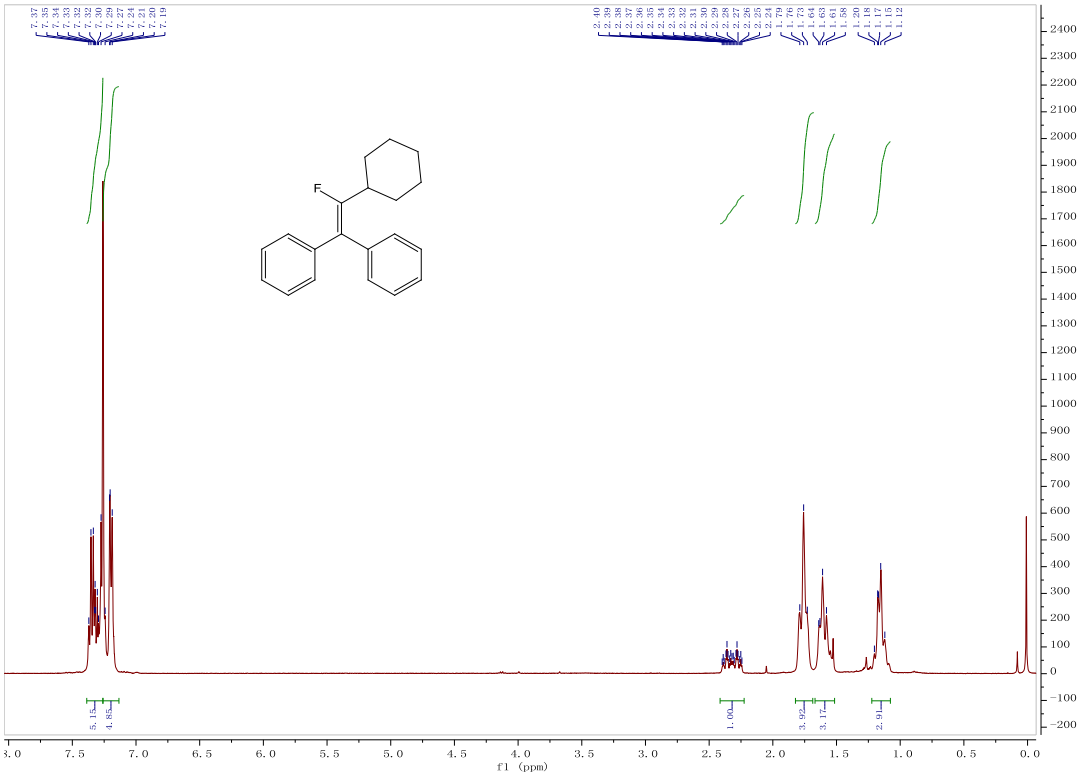
(4,4-difluorobut-3-en-1-yl)benzene (2u): Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.26 – 7.15 (m, 3H), 4.17 (dtd, *J* = 25.4, 7.8, 2.5 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.32 (qt, *J* = 7.5, 1.9 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -12.96 (d, *J* = 47.6 Hz), -14.62 – -15.48 (m).

11. References:

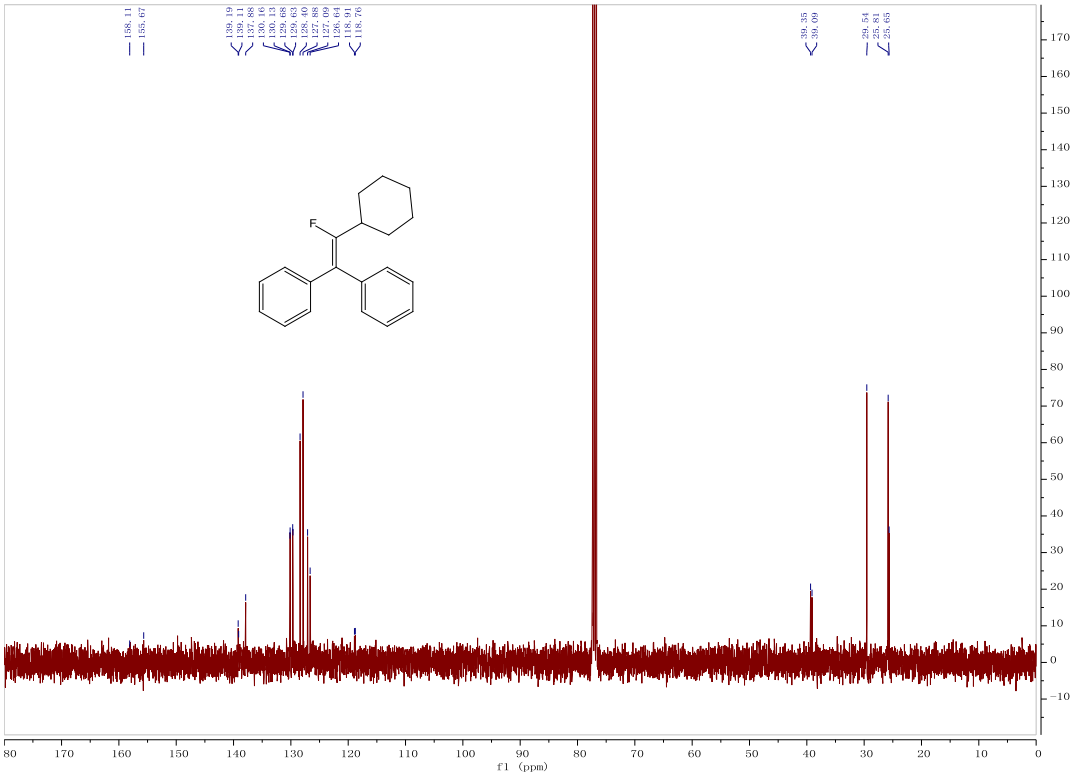
1. S. A. Fuqua, W. G. Duncan and R. M. Silverstein, *J. Org. Chem.*, 1965, **30**, 1027.
2. M. Hu, C. Ni, L. Li, Y. Han and J. Hu, *J. Am. Chem. Soc.*, 2015, **137**, 14496.
3. J. Luo and J. Zhang, *ACS Catal.*, 2016, **6**, 873.
4. F. Fumagalli, S. Warratz, S. Zhang, T. Rogge, C. Zhu, A. C. Steckl and L. Ackermann, *Chem. Eur. J.*, 2018, **24**, 3984.
5. J. Hu, X. Han, Y. Yuan and Z. Shi, *Angew. Chem. Int. Ed.*, 2017, **56**, 13342.

12. NMR spectra:

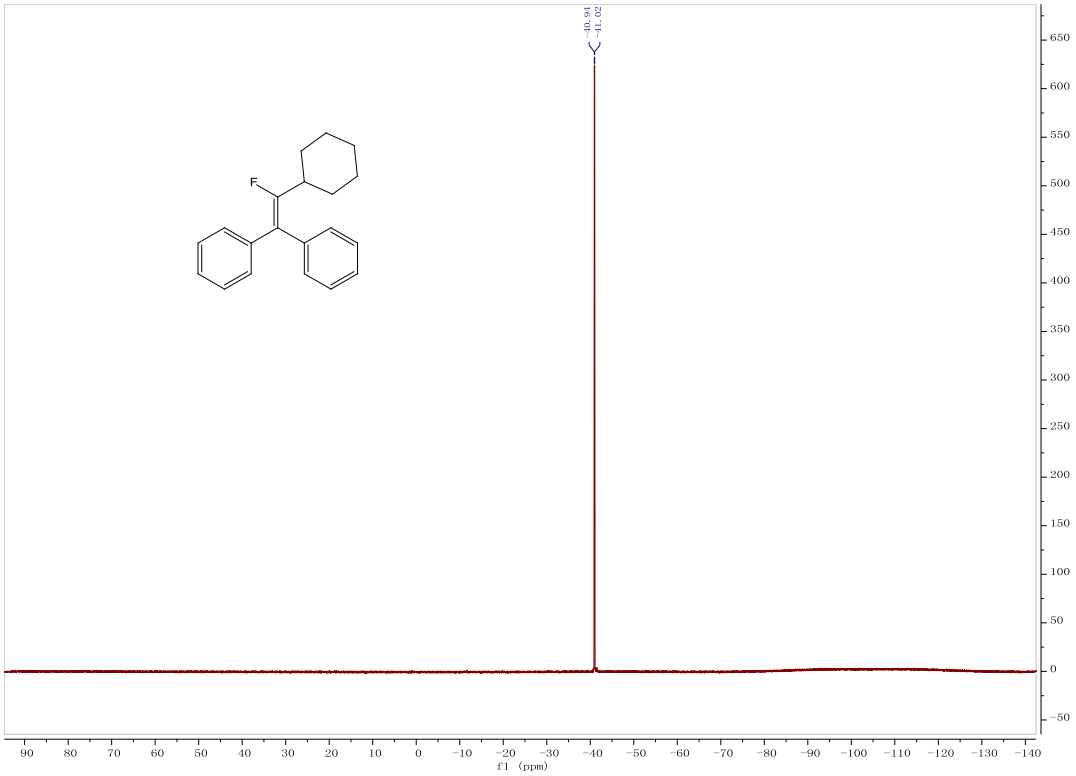
^{1}H NMR spectrum of **3a**



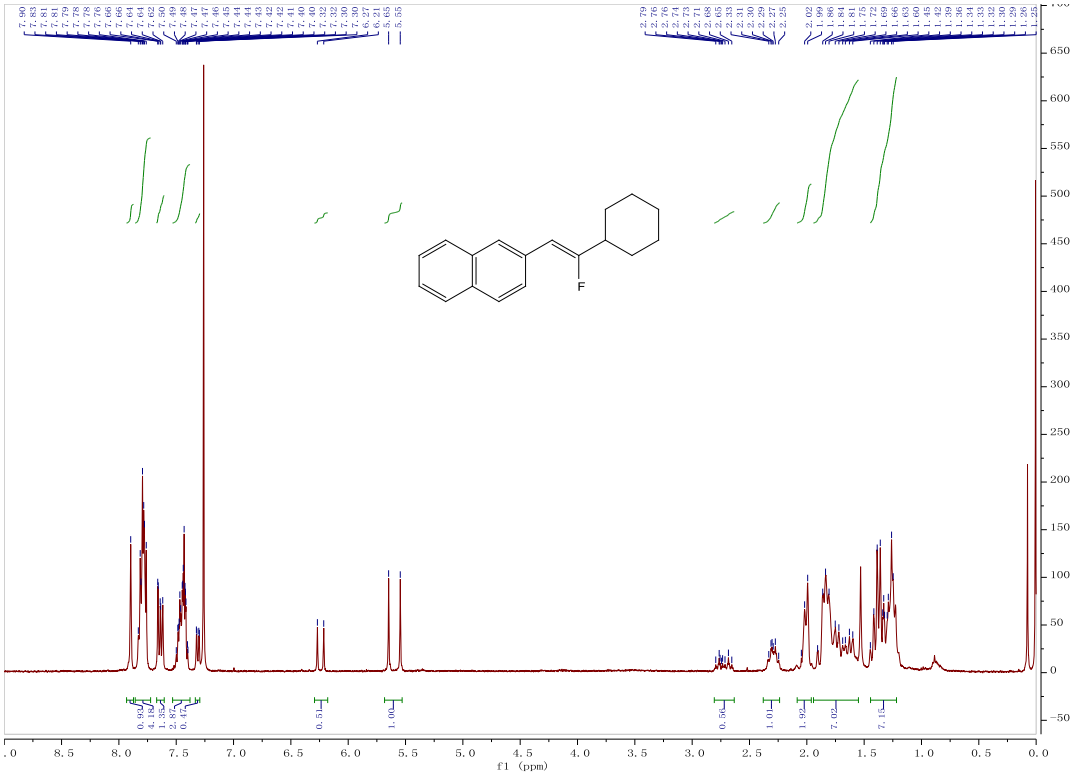
^{13}C NMR spectrum of **3a**



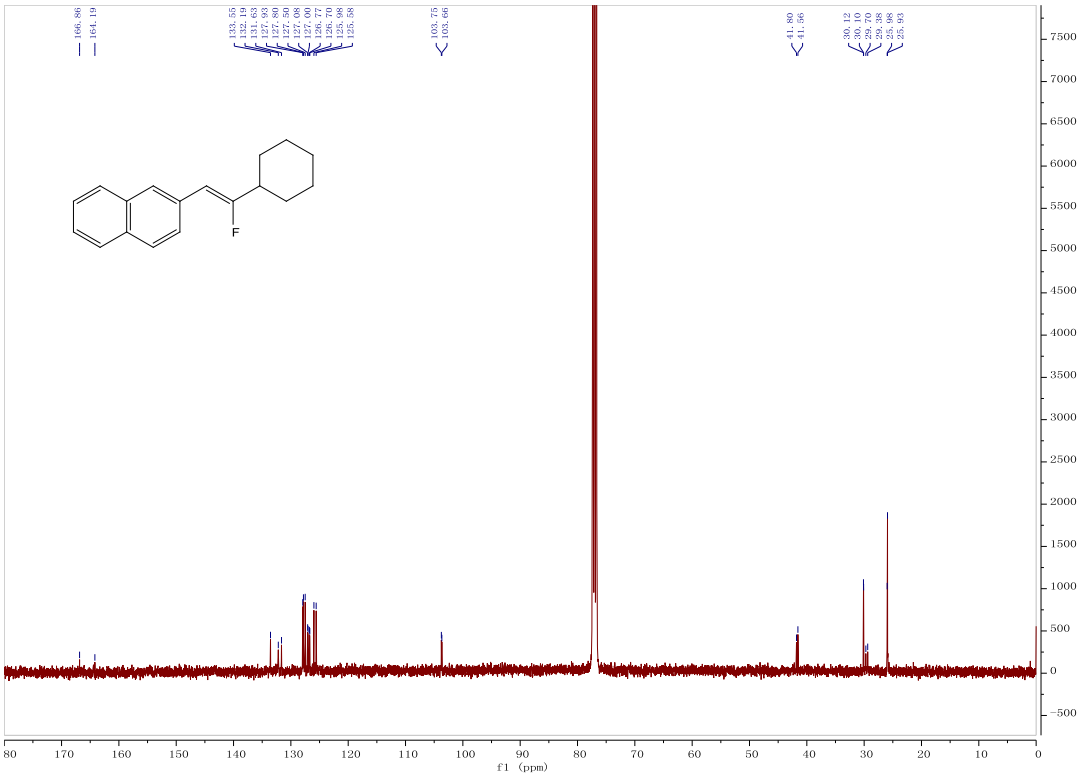
^{19}F NMR spectrum of **3a**



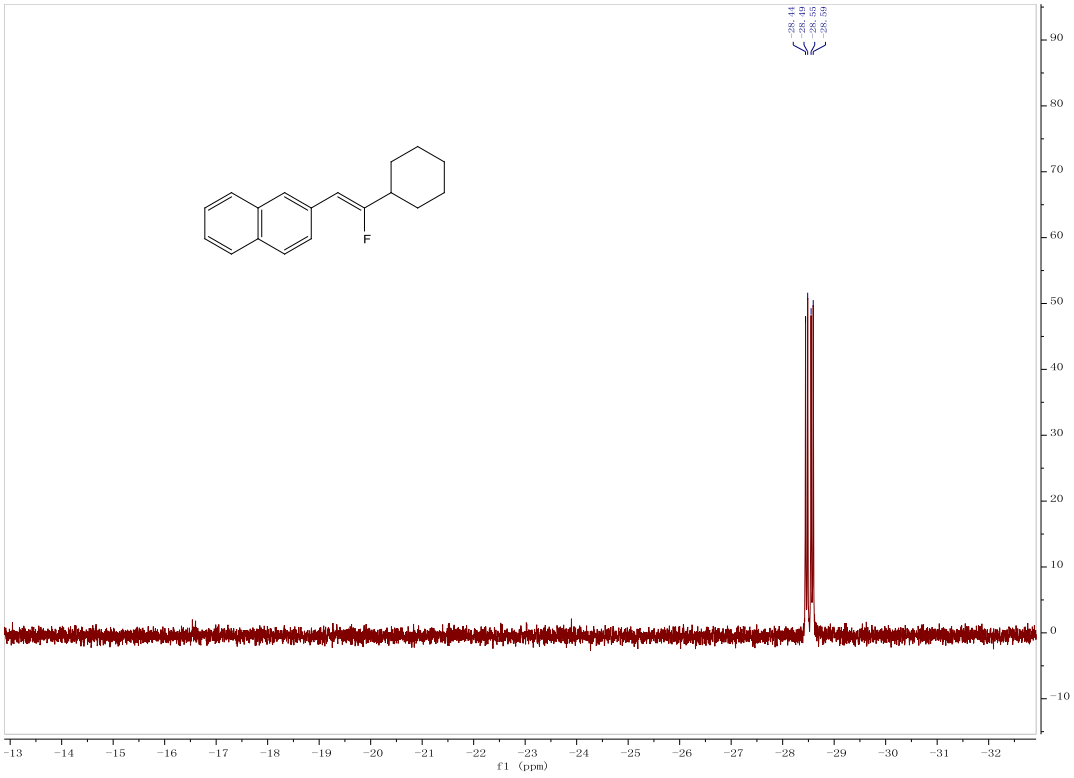
^{1}H NMR spectrum of **3b**



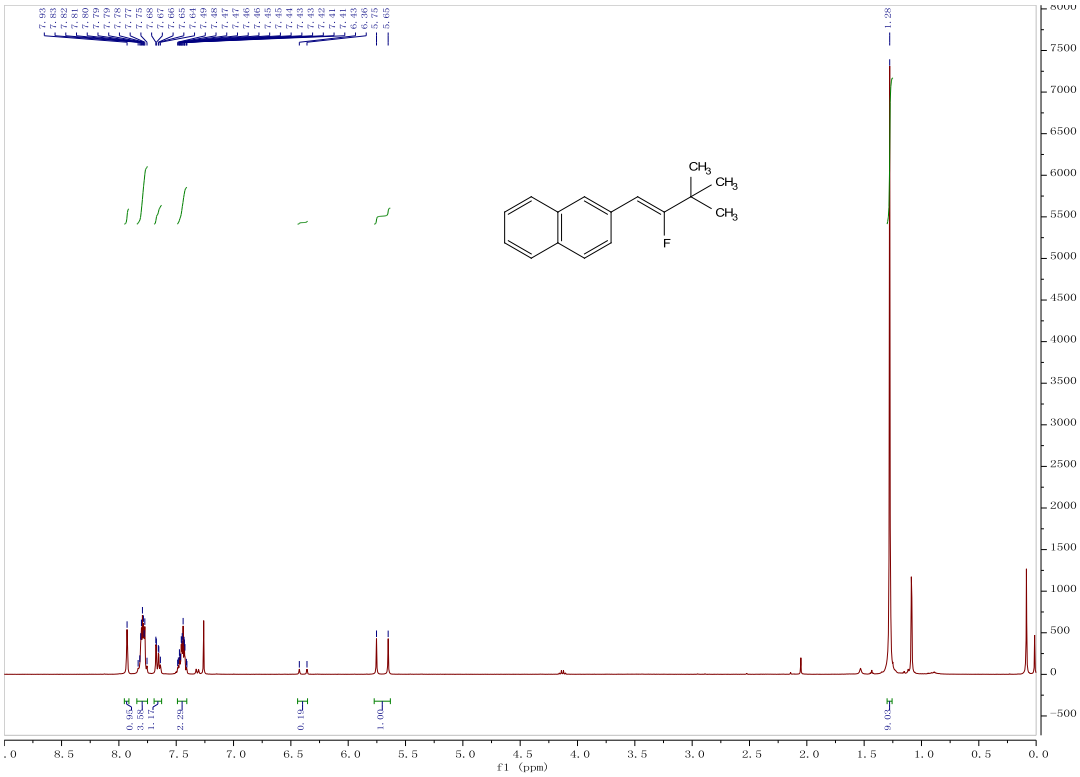
^{13}C NMR spectrum of **3b**



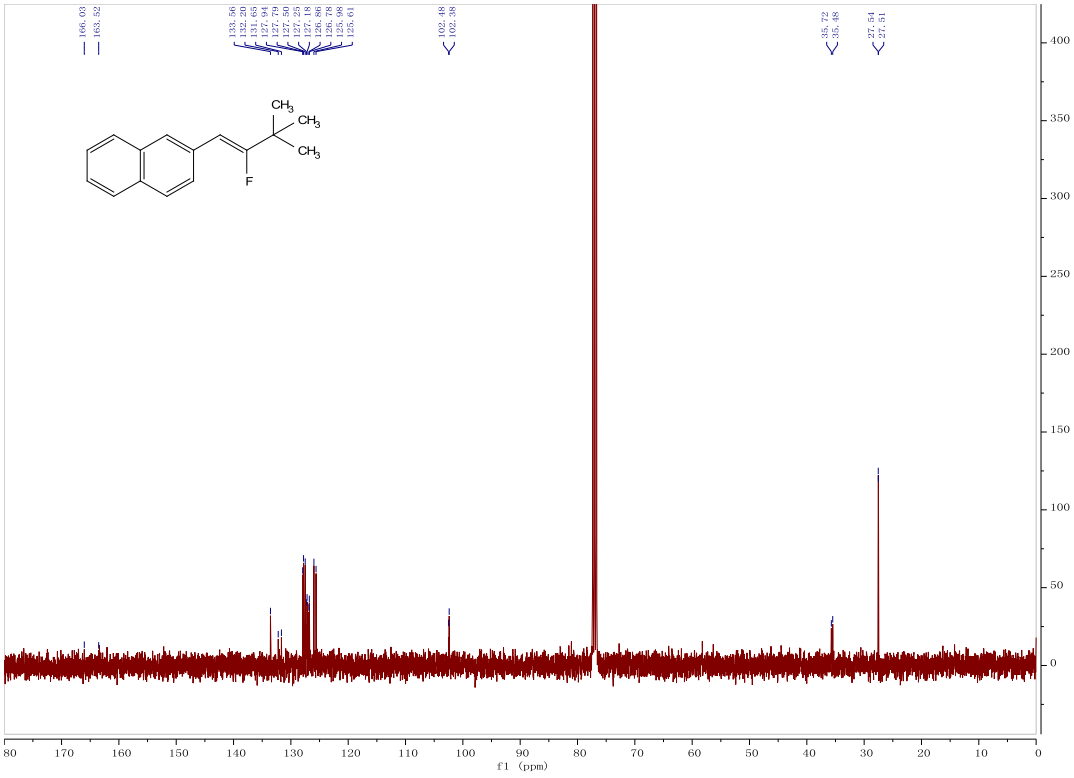
^{19}F NMR spectrum of **3b**



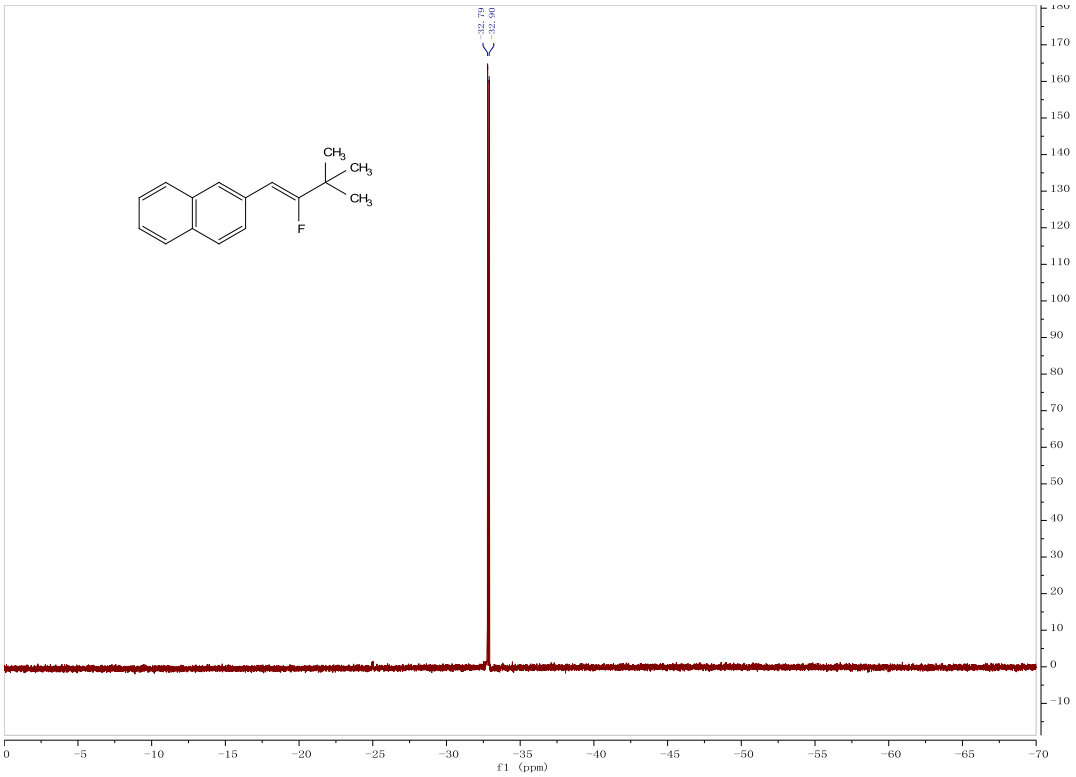
^{1}H NMR spectrum of **3c**



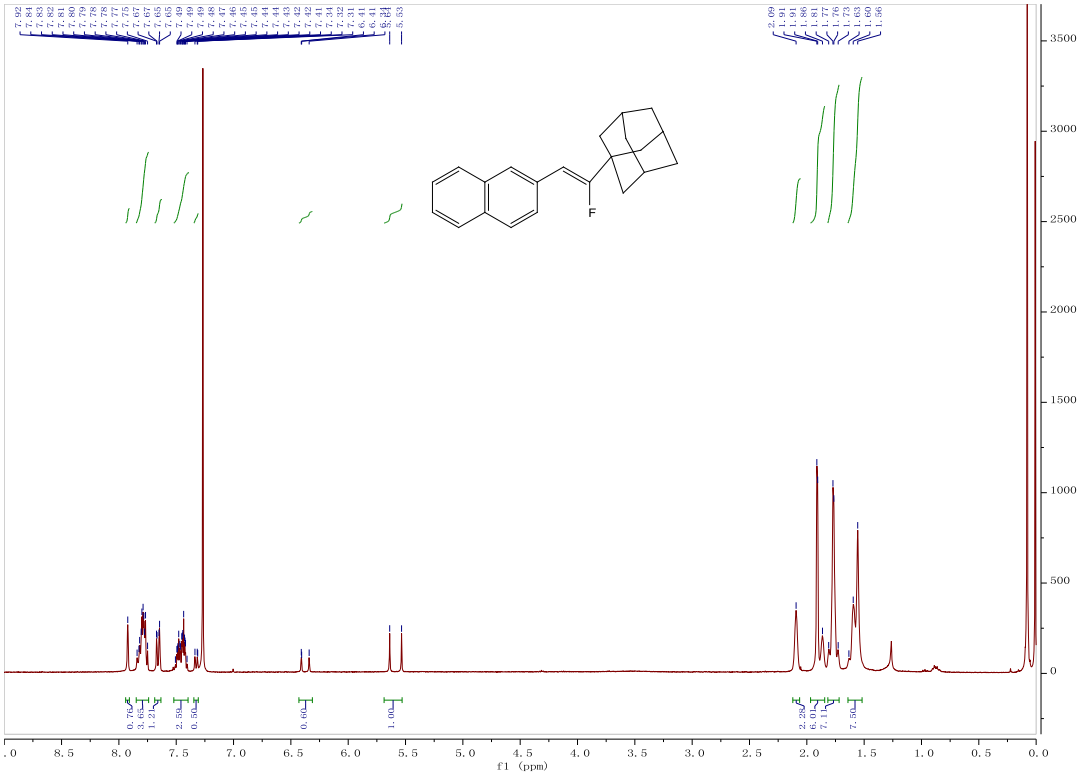
^{13}C NMR spectrum of **3c**



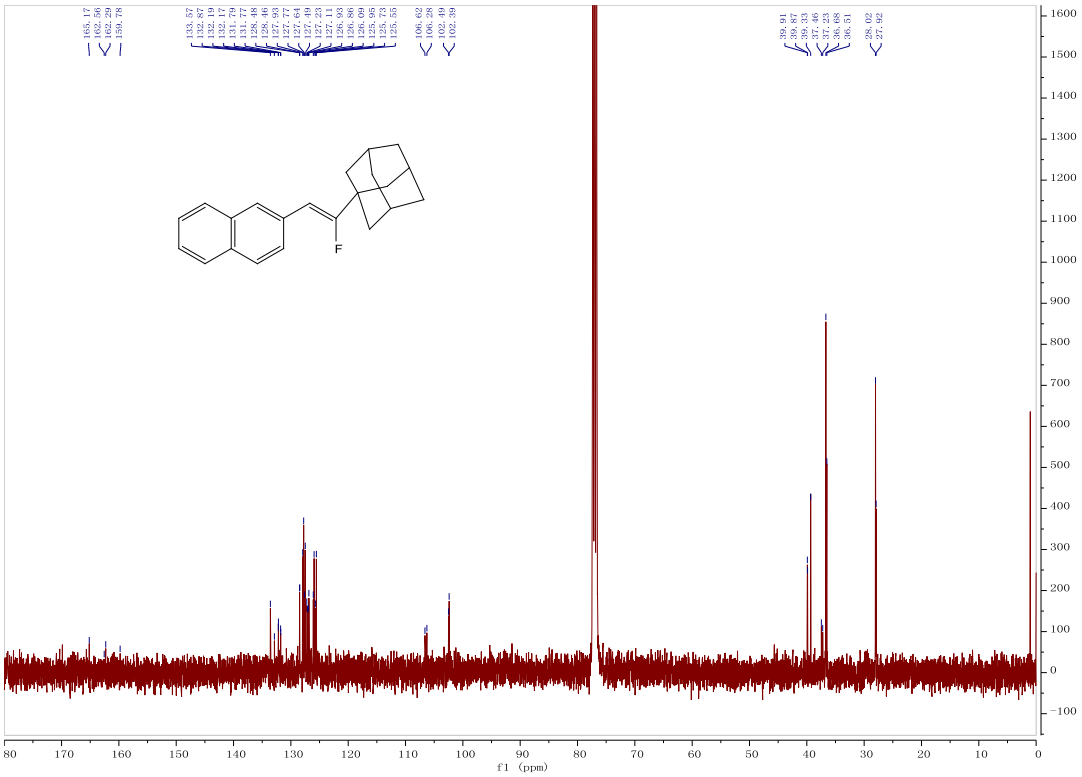
^{19}F NMR spectrum of **3c**



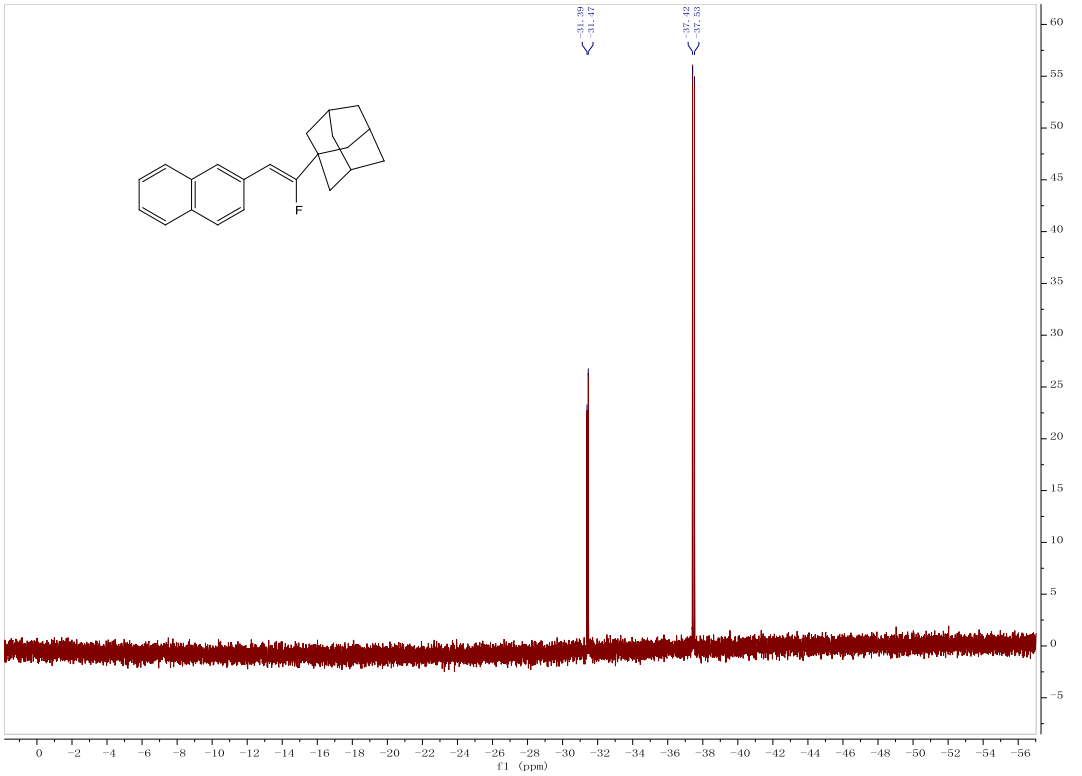
^{1}H NMR spectrum of **3d**



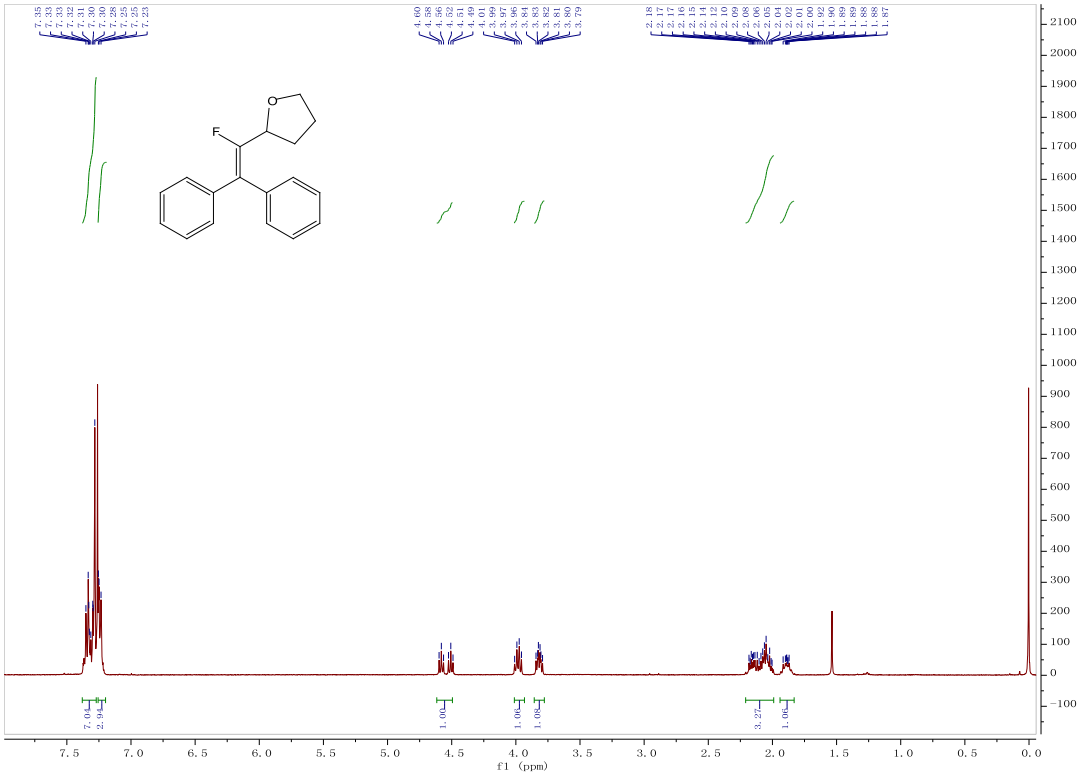
^{13}C NMR spectrum of **3d**



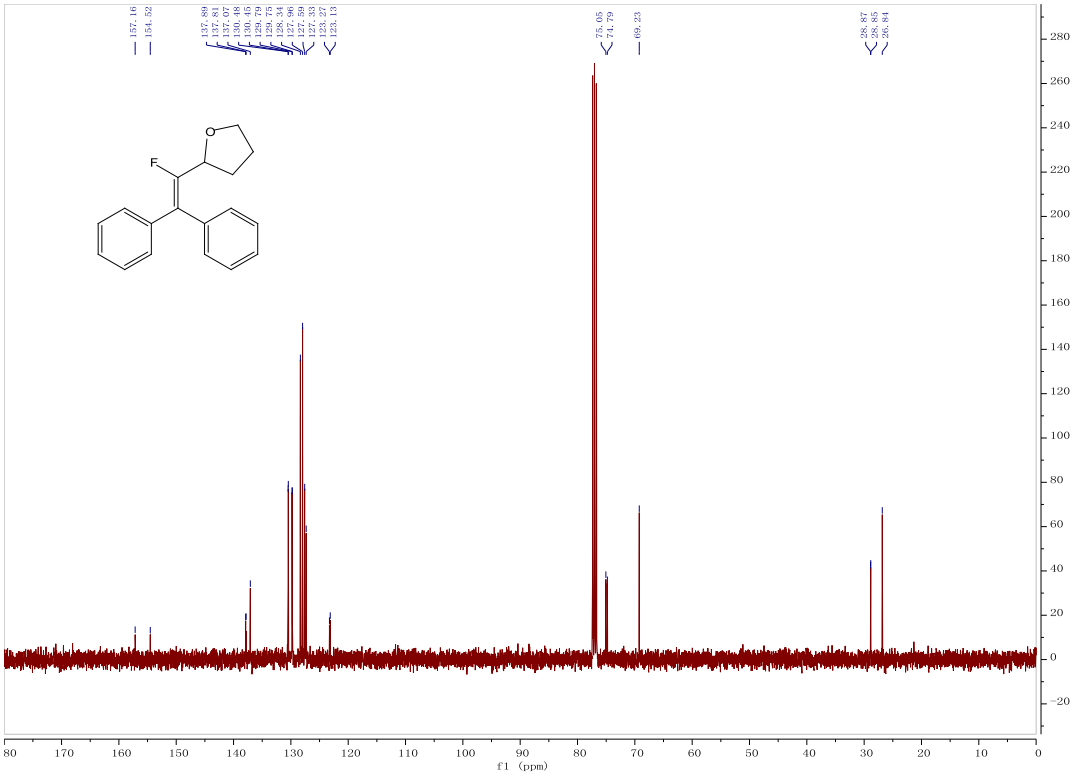
^{19}F NMR spectrum of **3d**



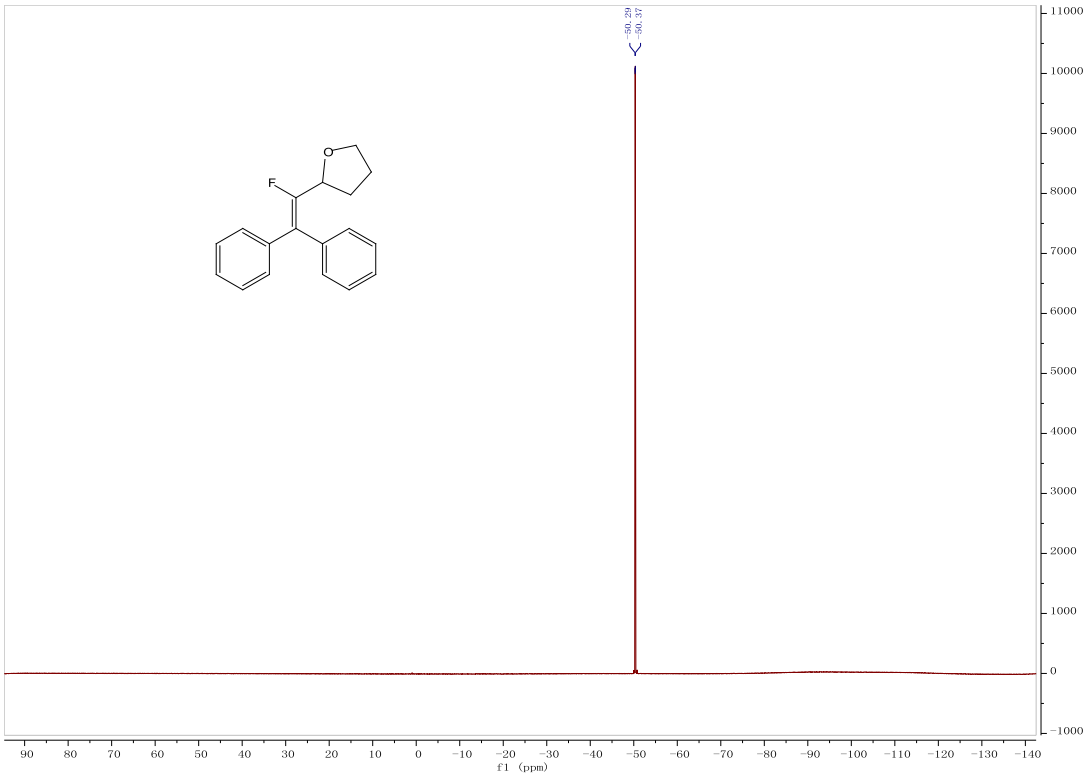
^{1}H NMR spectrum of **3e**



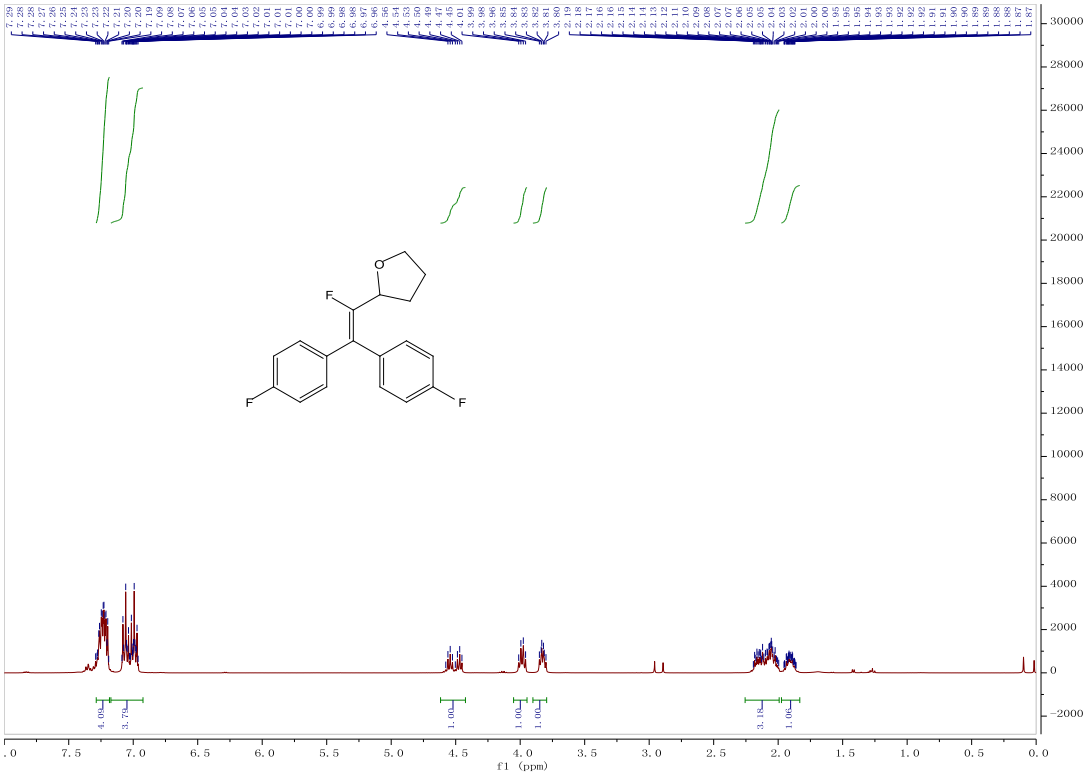
^{13}C NMR spectrum of **3e**



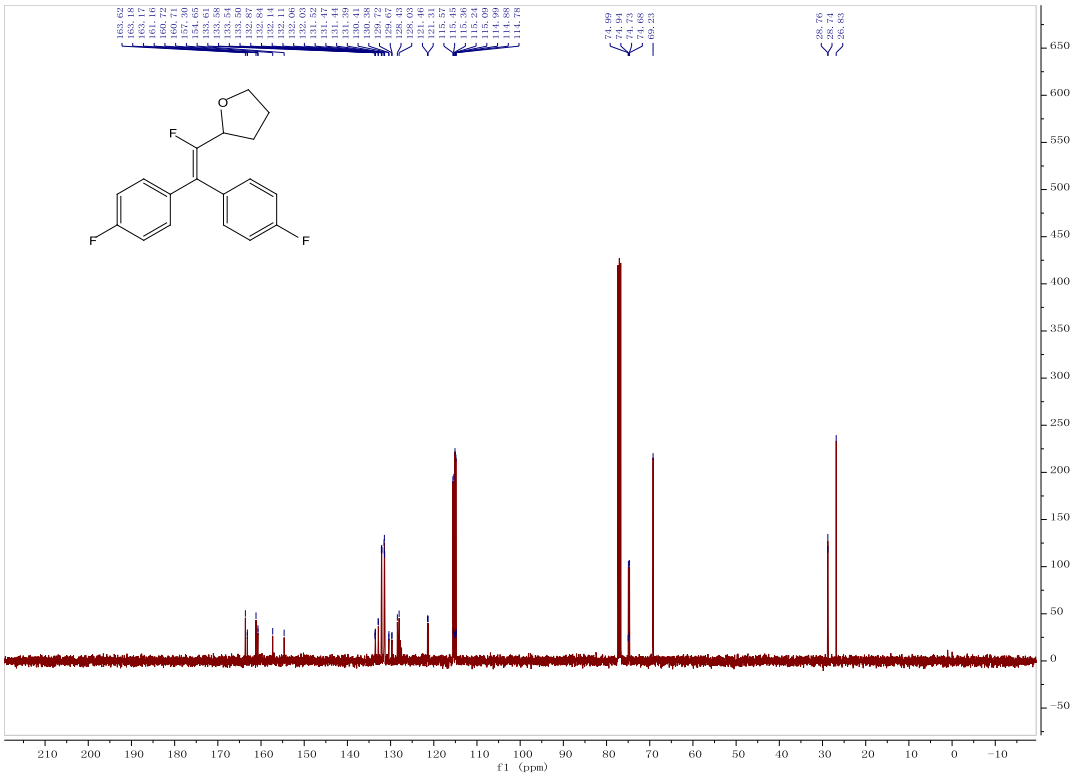
^{19}F NMR spectrum of **3e**



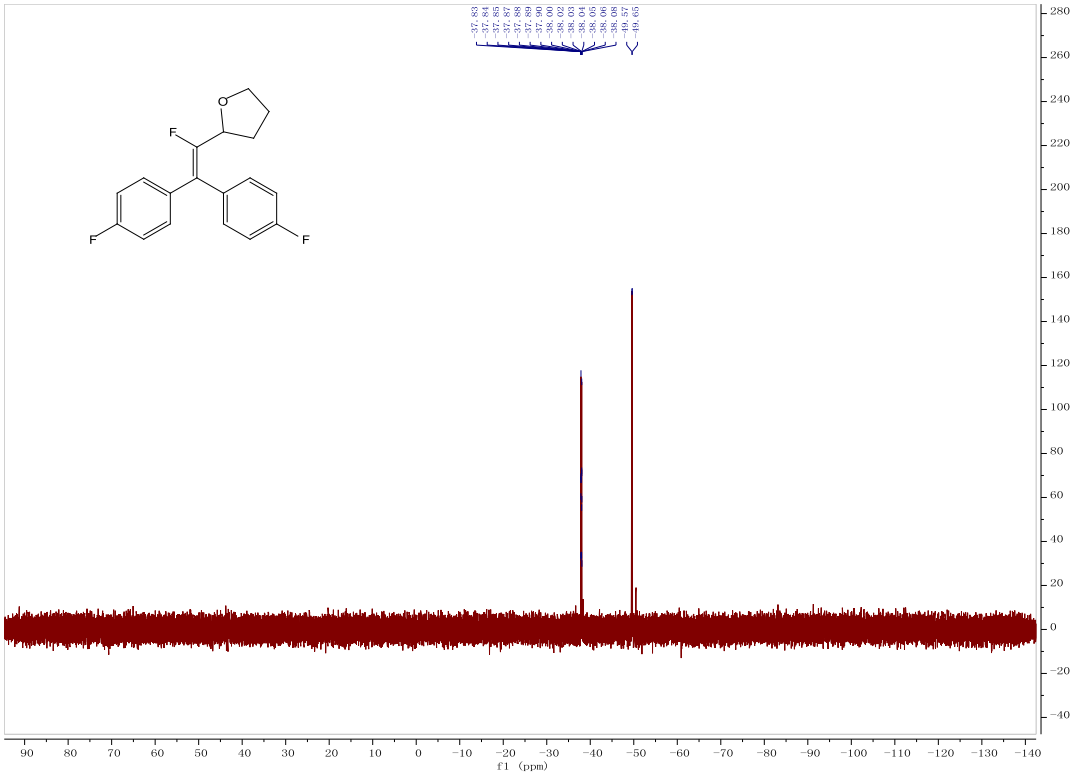
^{1}H NMR spectrum of **3f**



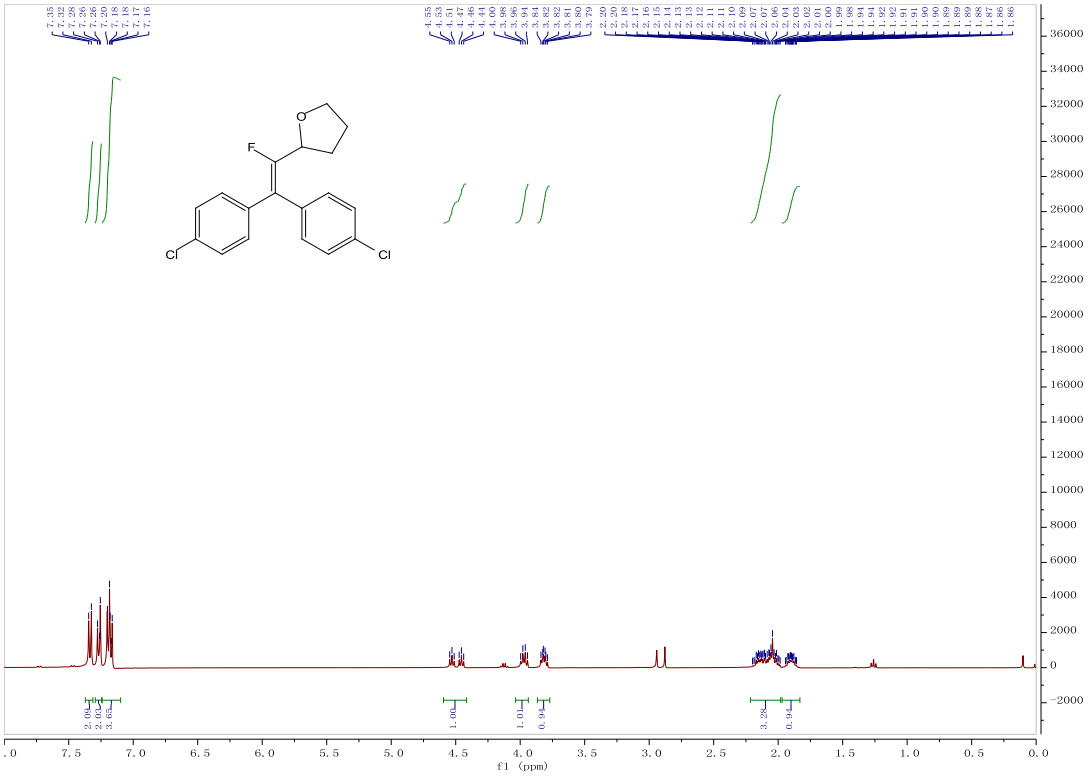
^{13}C NMR spectrum of **3f**



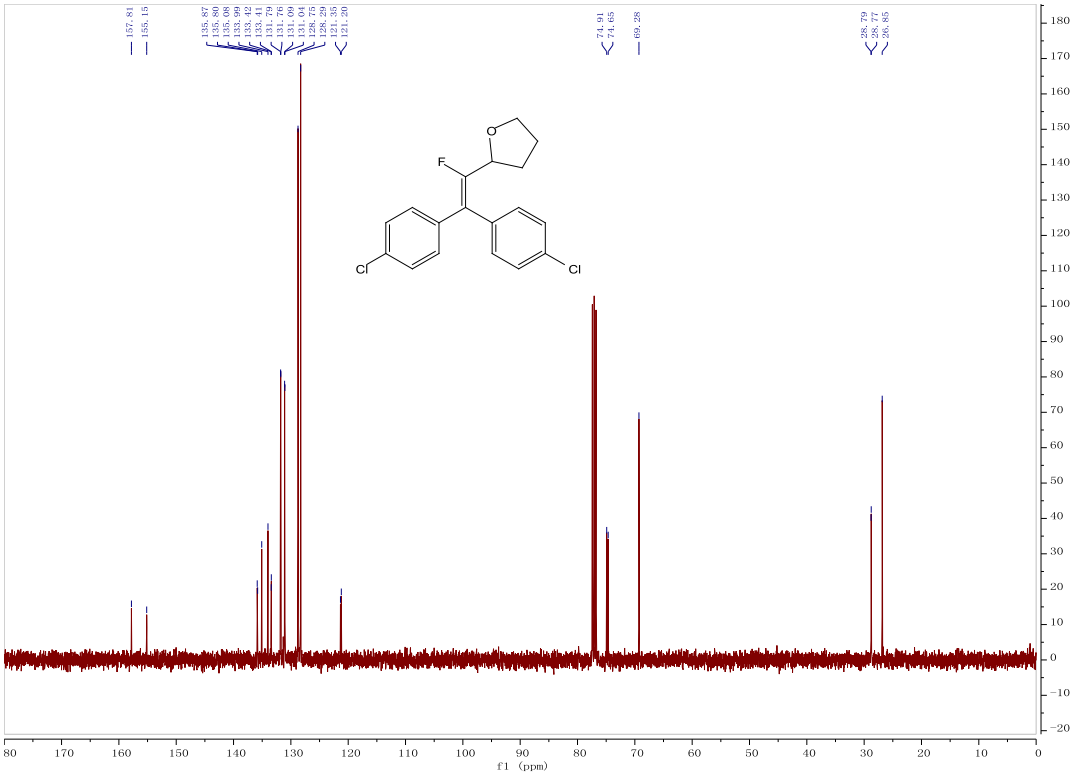
^{19}F NMR spectrum of **3f**



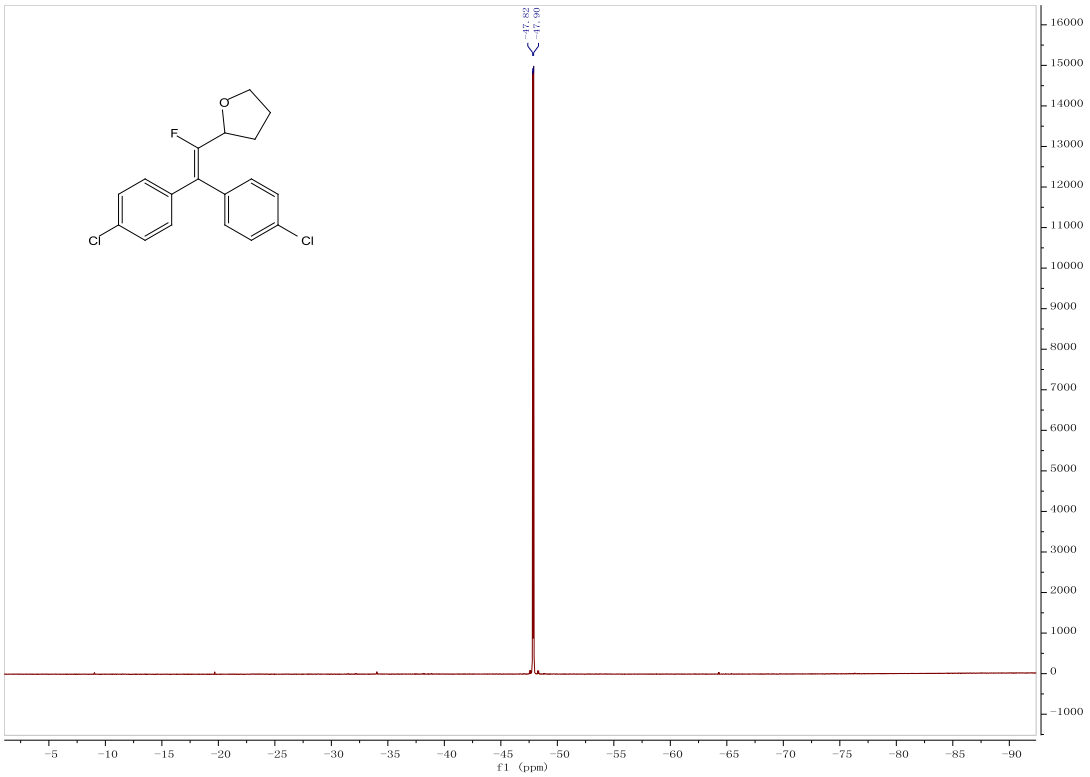
^{1}H NMR spectrum of **3g**



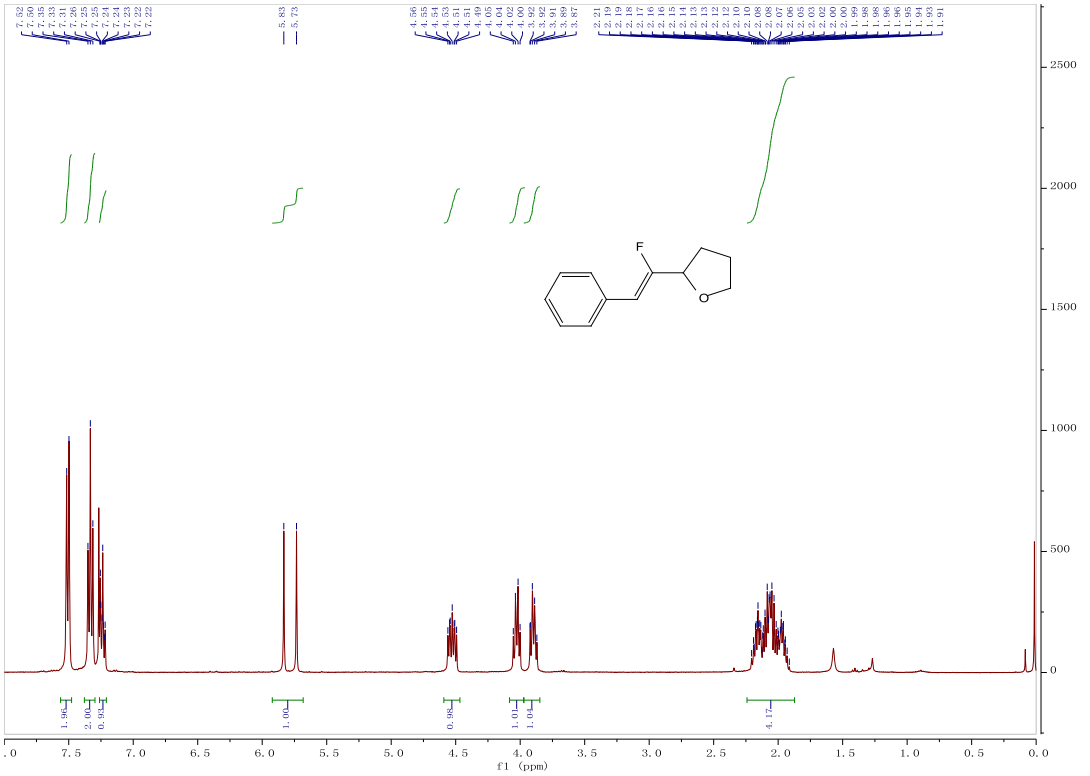
^{13}C NMR spectrum of **3g**



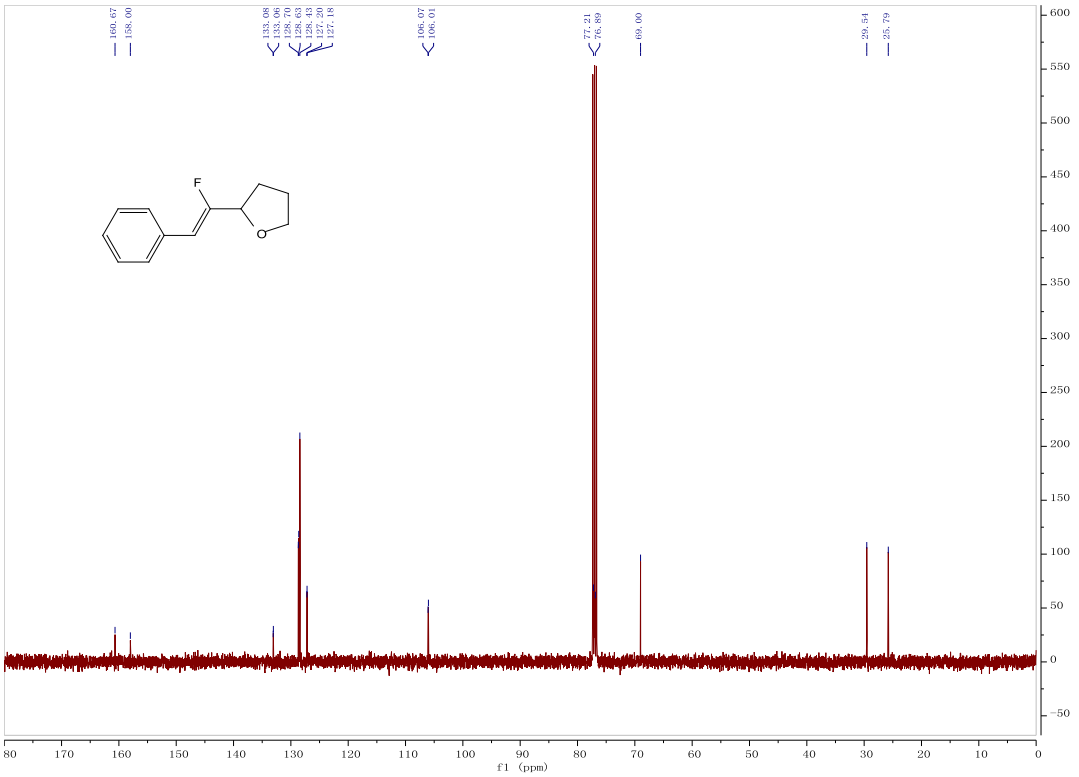
^{19}F NMR spectrum of **3g**



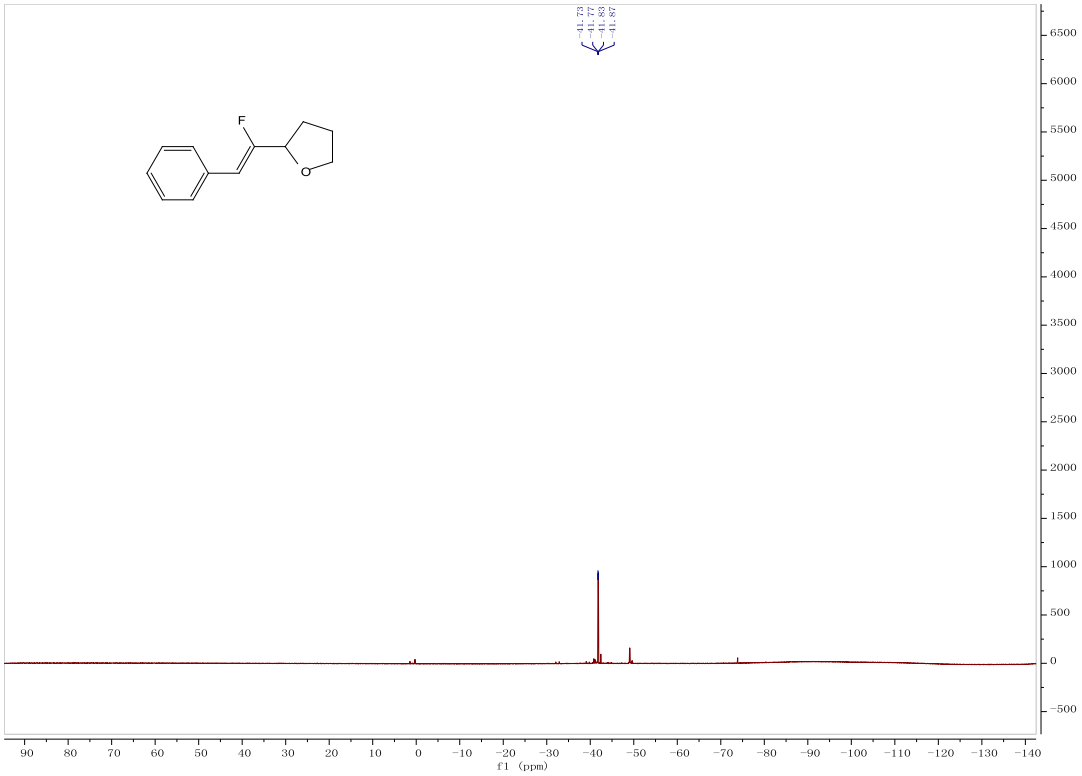
^{1}H NMR spectrum of **3h**



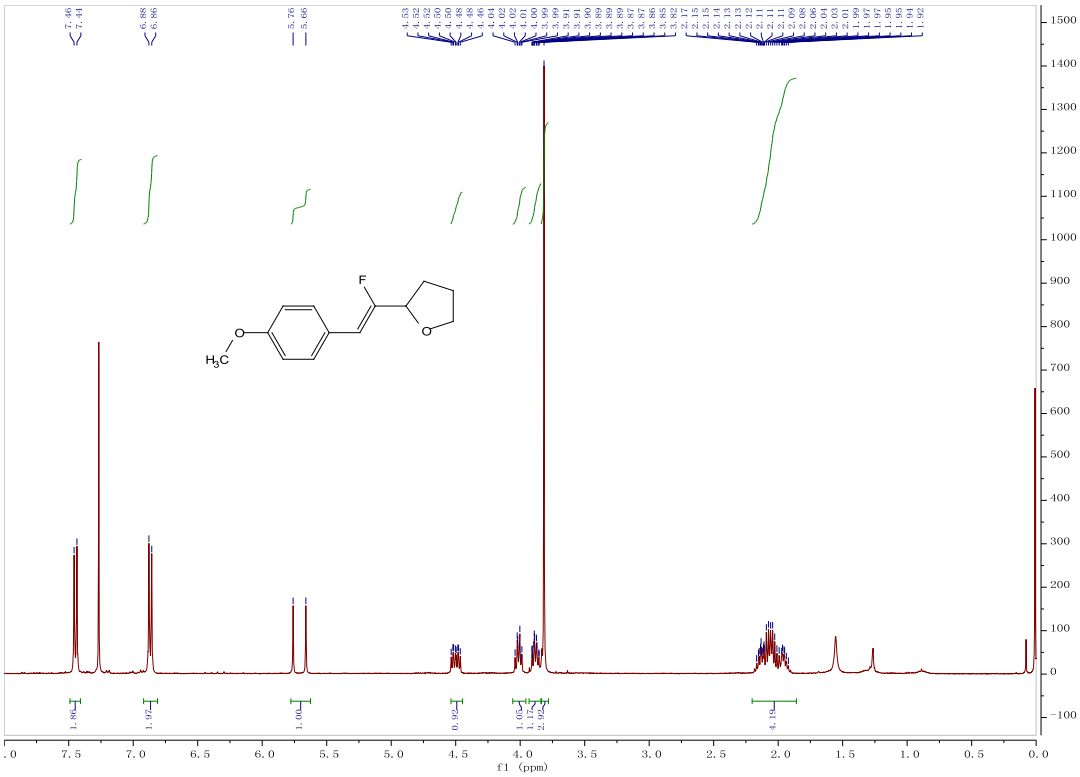
^{13}C NMR spectrum of **3h**



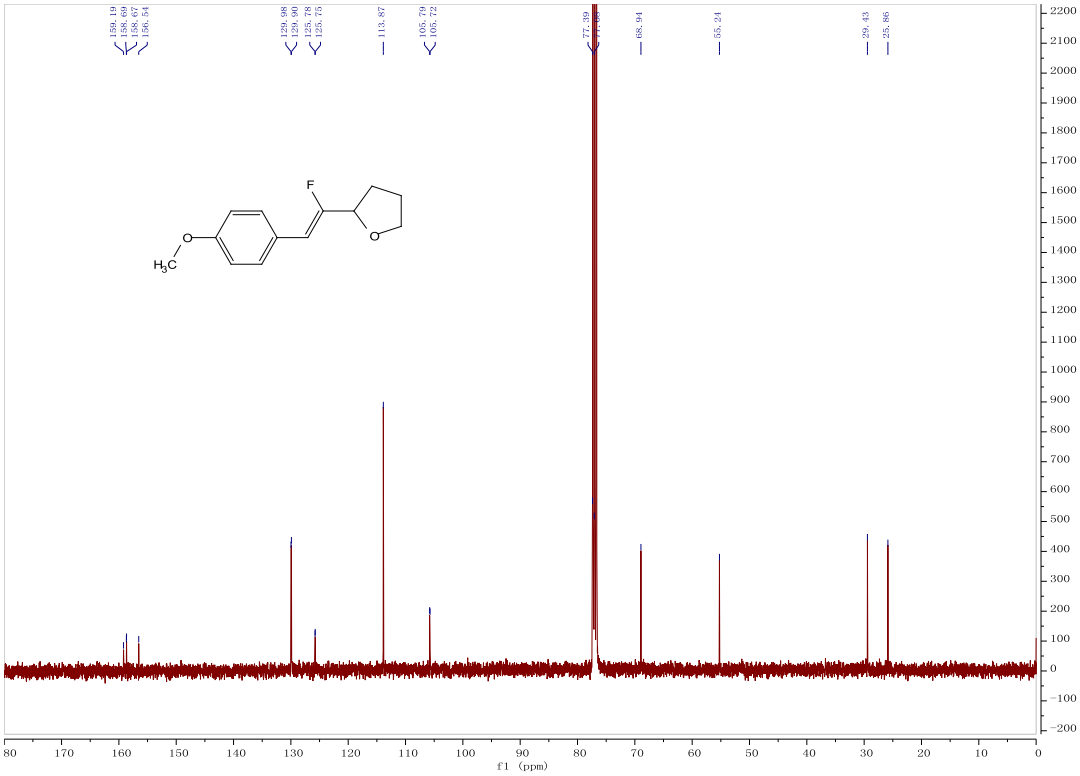
^{19}F NMR spectrum of **3h**



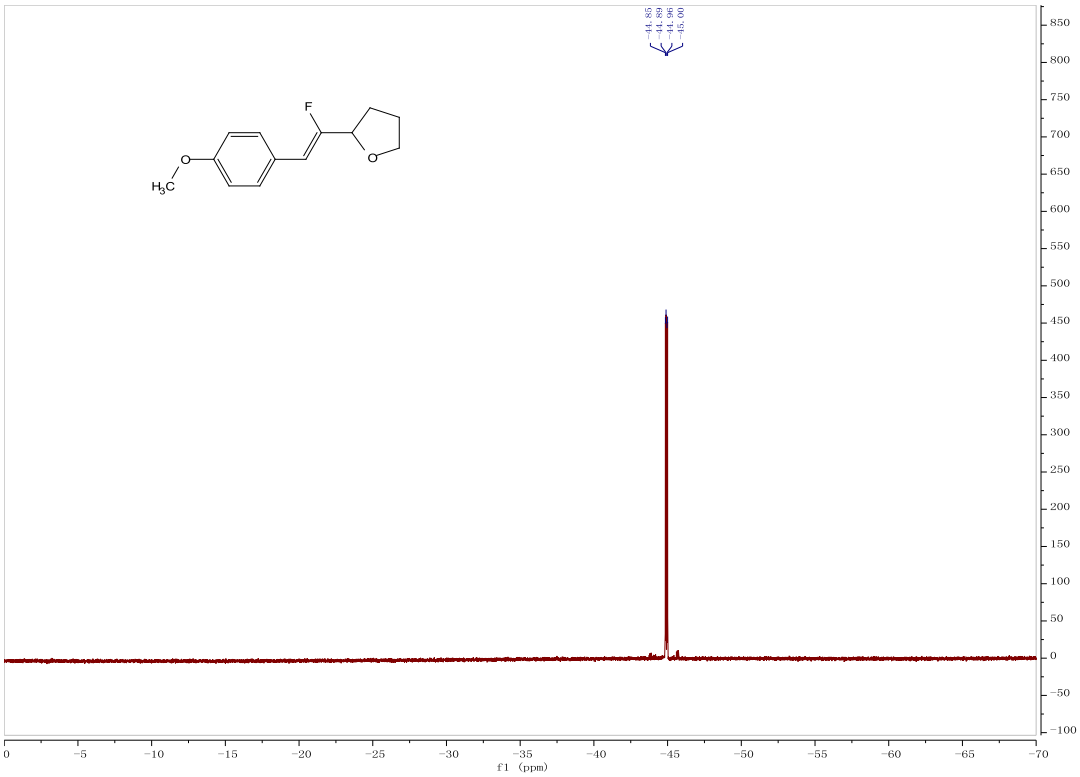
^{1}H NMR spectrum of **3i**



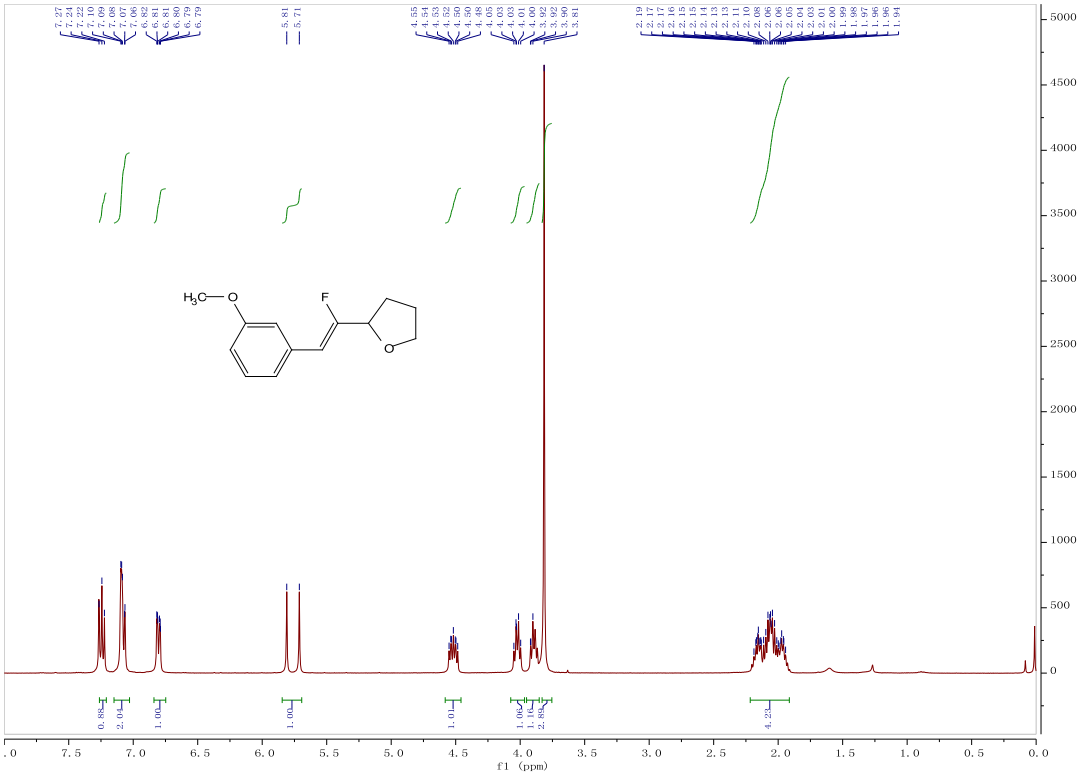
^{13}C NMR spectrum of **3i**



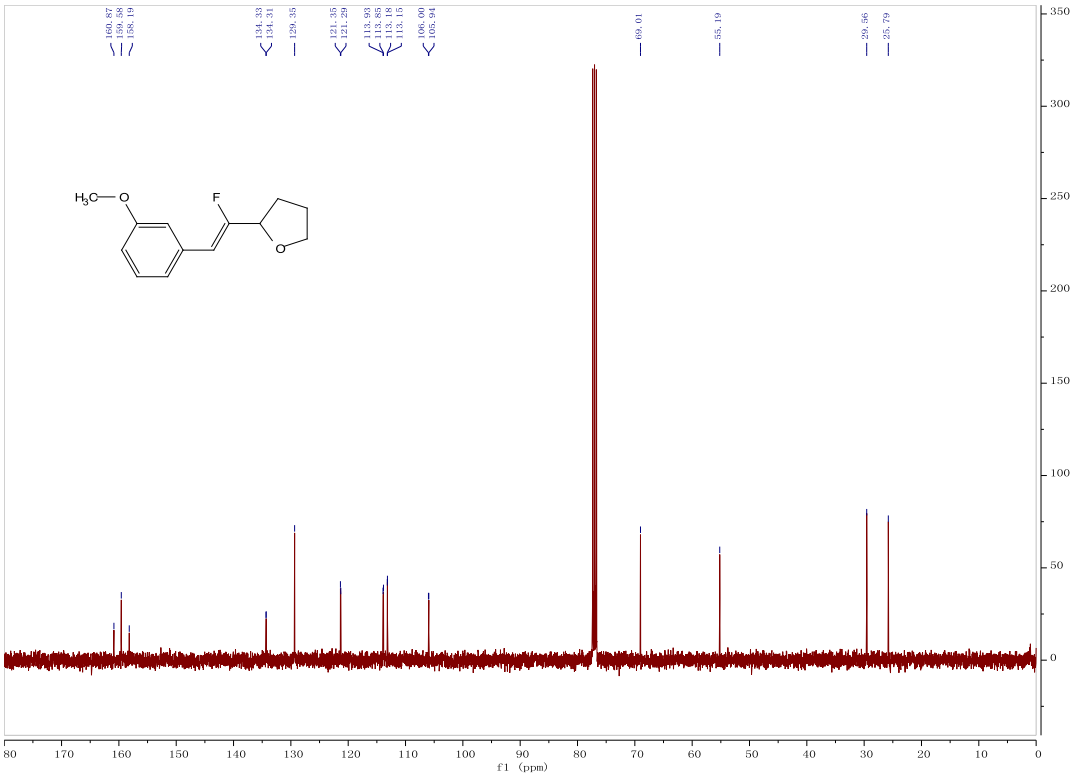
^{19}F NMR spectrum of **3i**



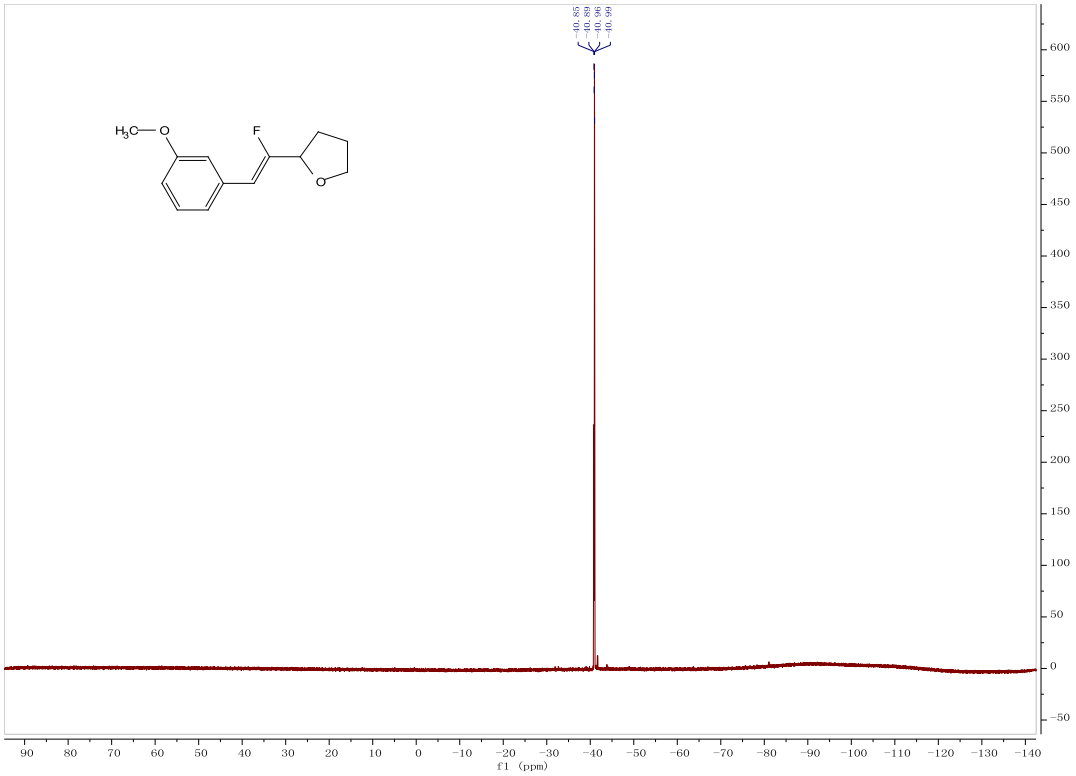
^{1}H NMR spectrum of **3j**



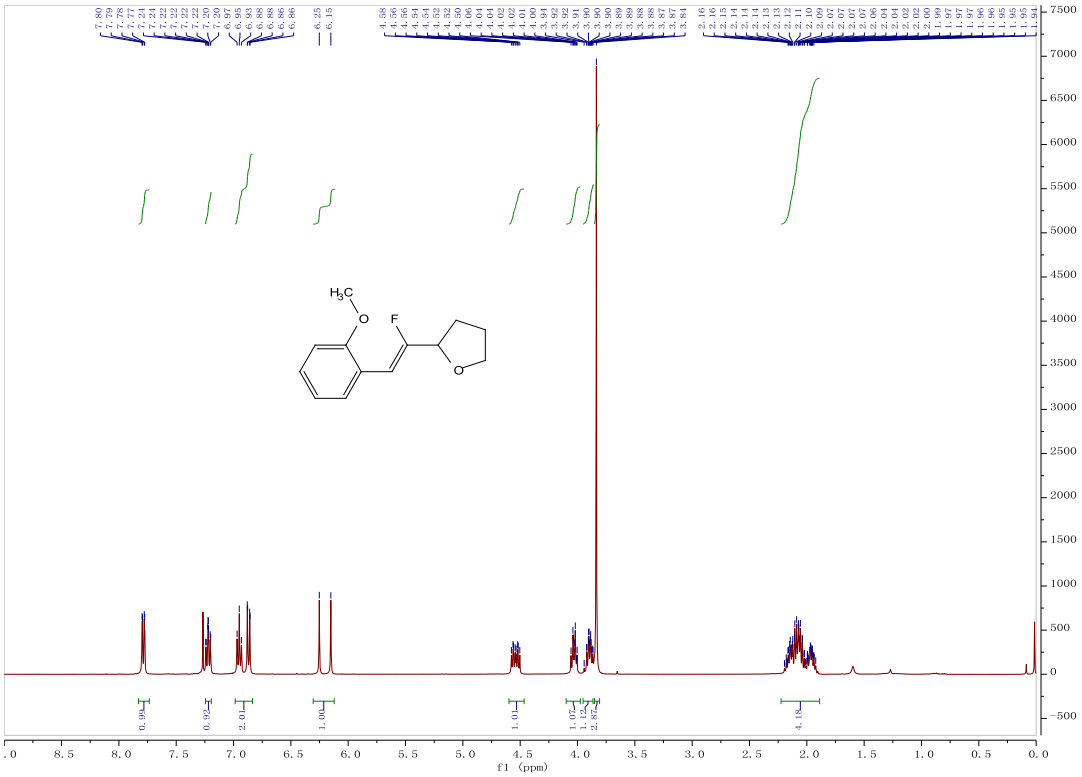
^{13}C NMR spectrum of **3j**



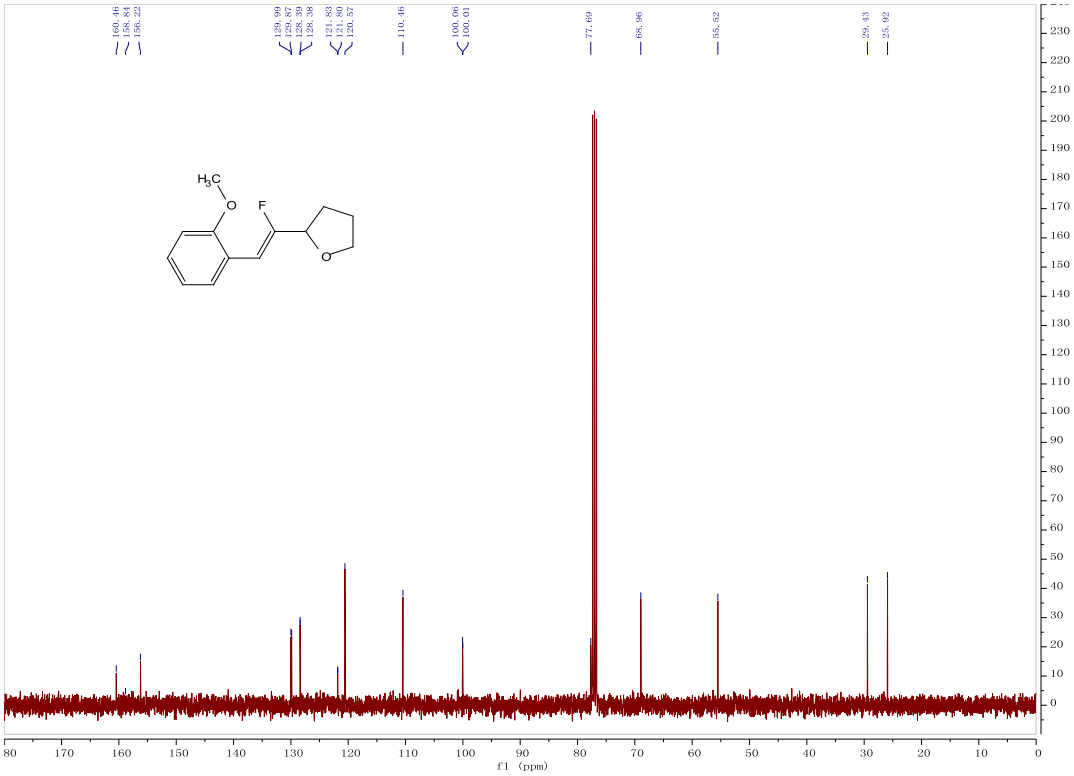
^{19}F NMR spectrum of **3j**



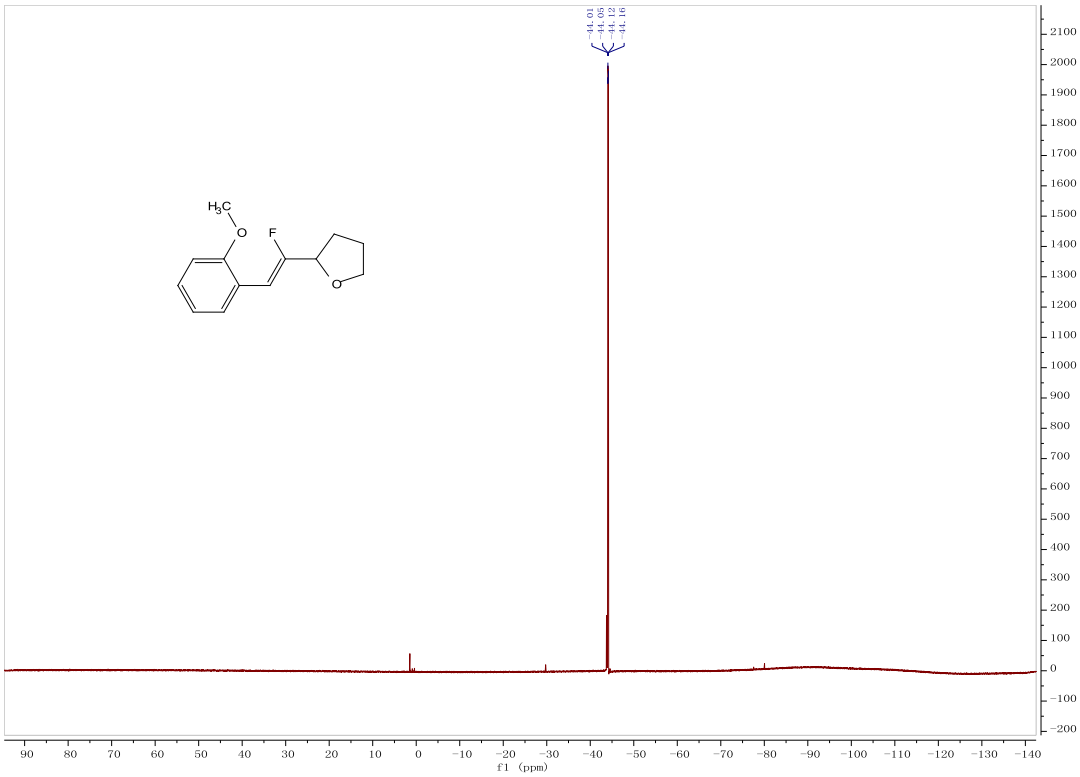
^{1}H NMR spectrum of **3k**



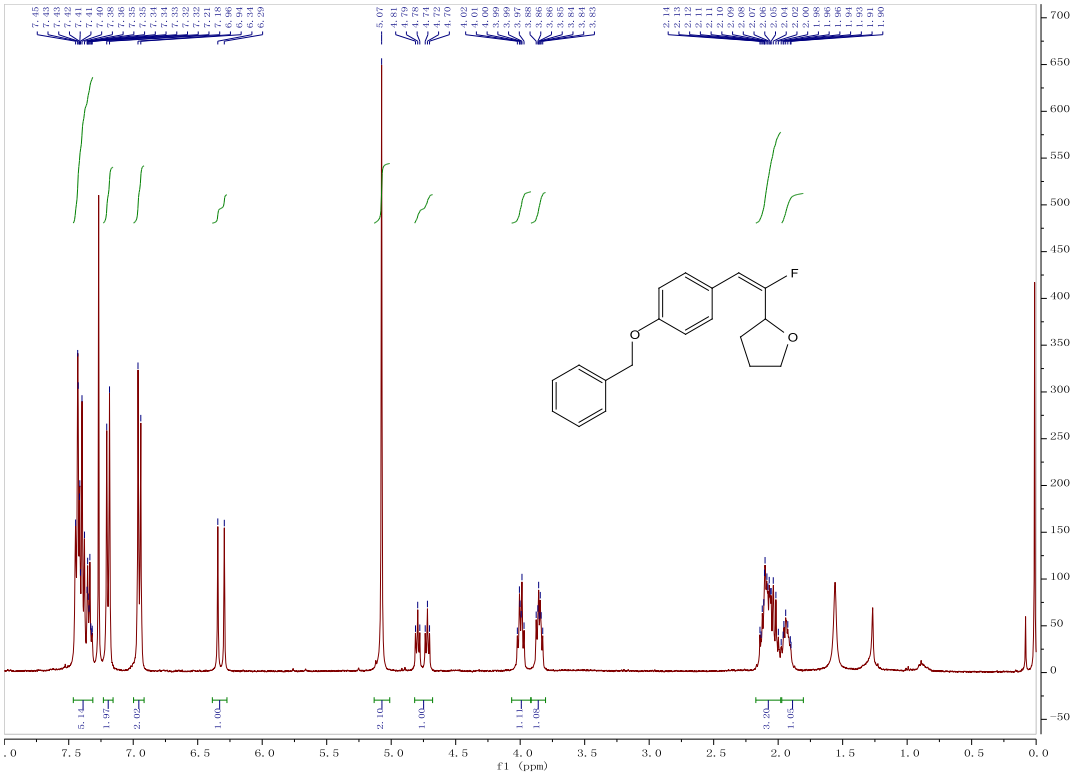
^{13}C NMR spectrum of **3k**



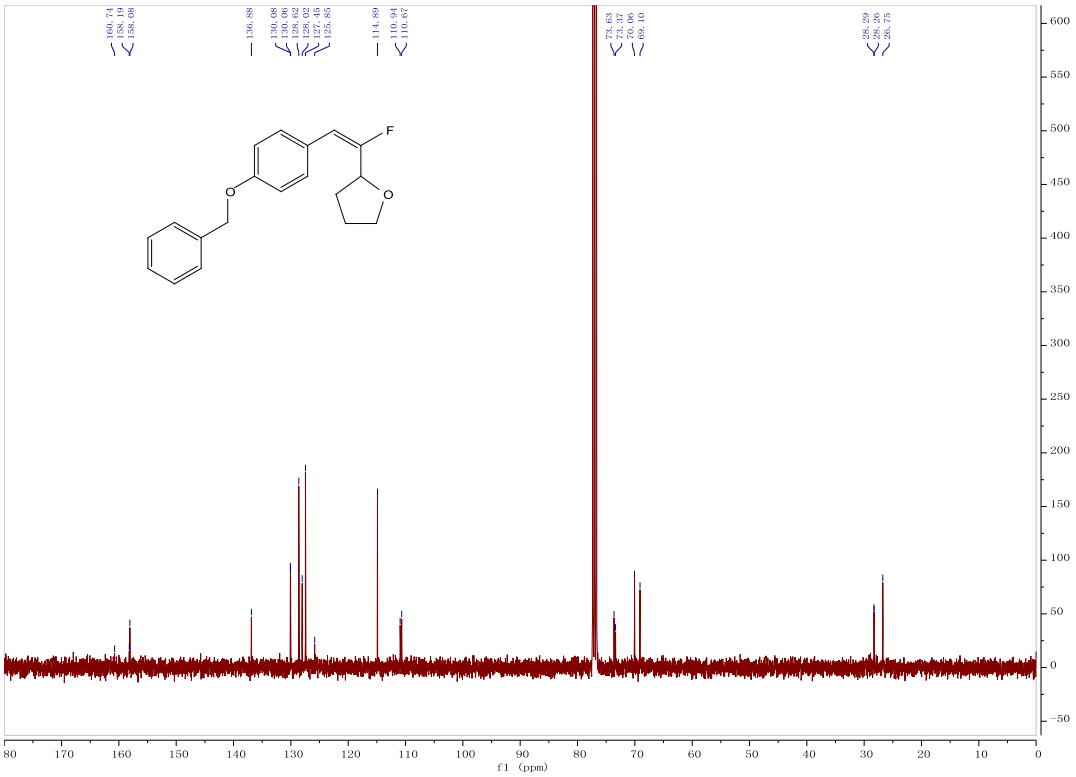
^{19}F NMR spectrum of **3k**



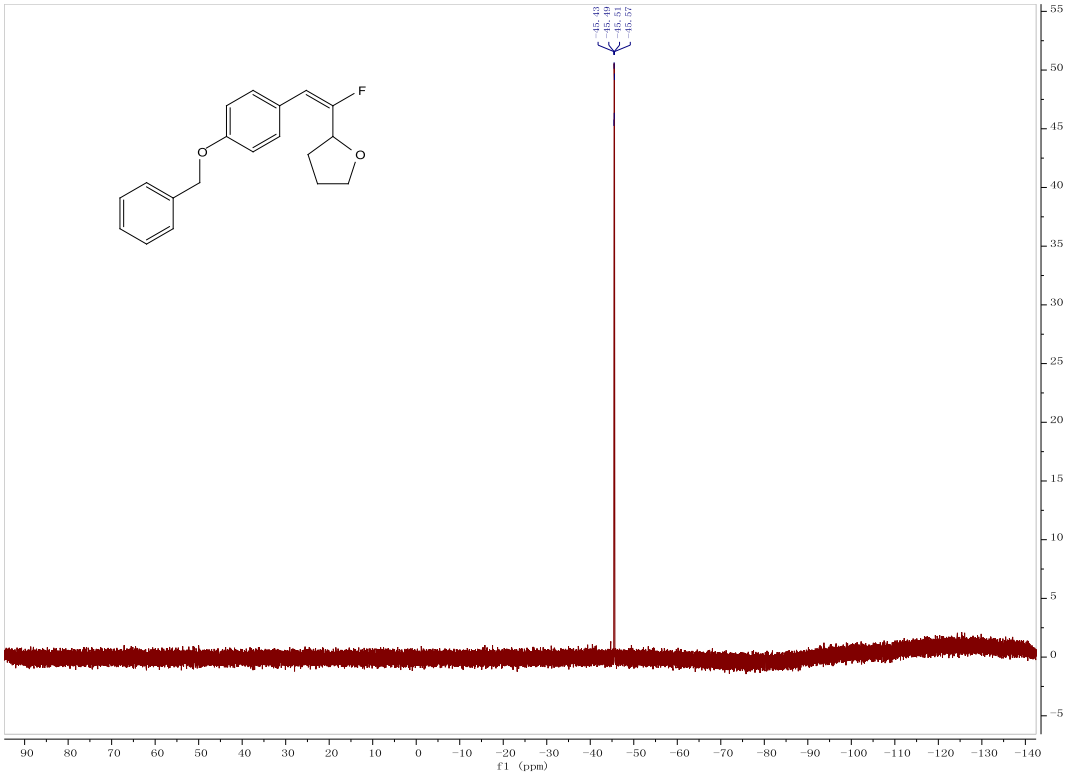
^{1}H NMR spectrum of **3la**



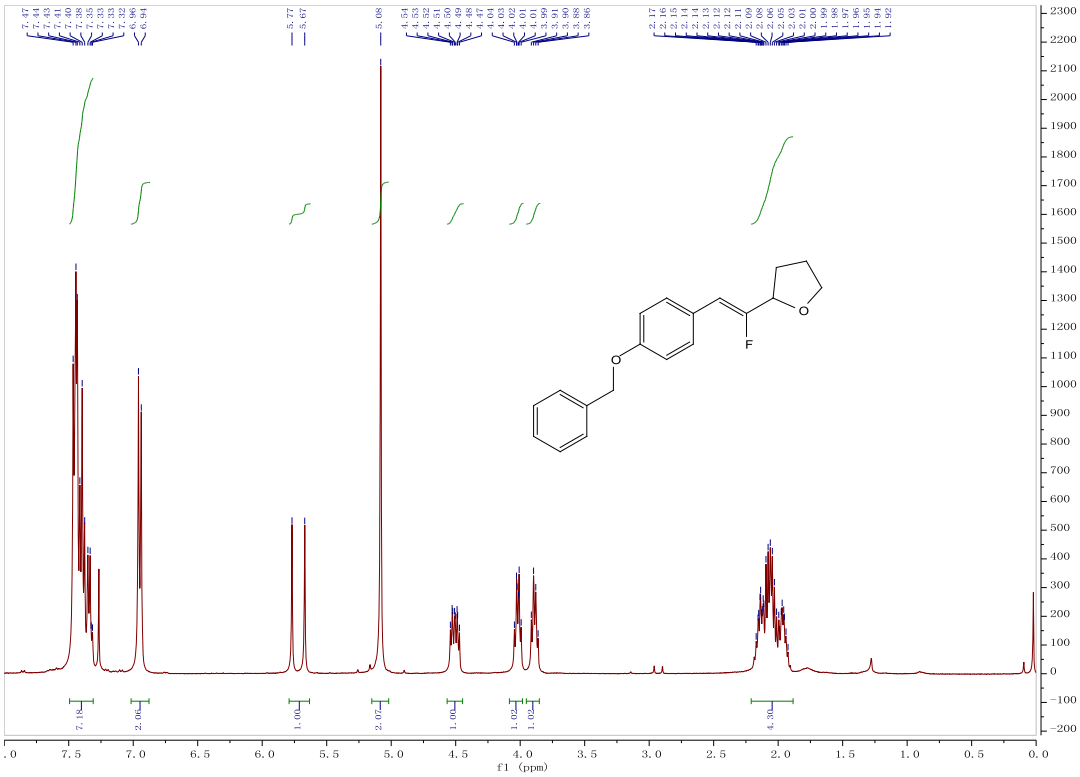
^{13}C NMR spectrum of **3la**



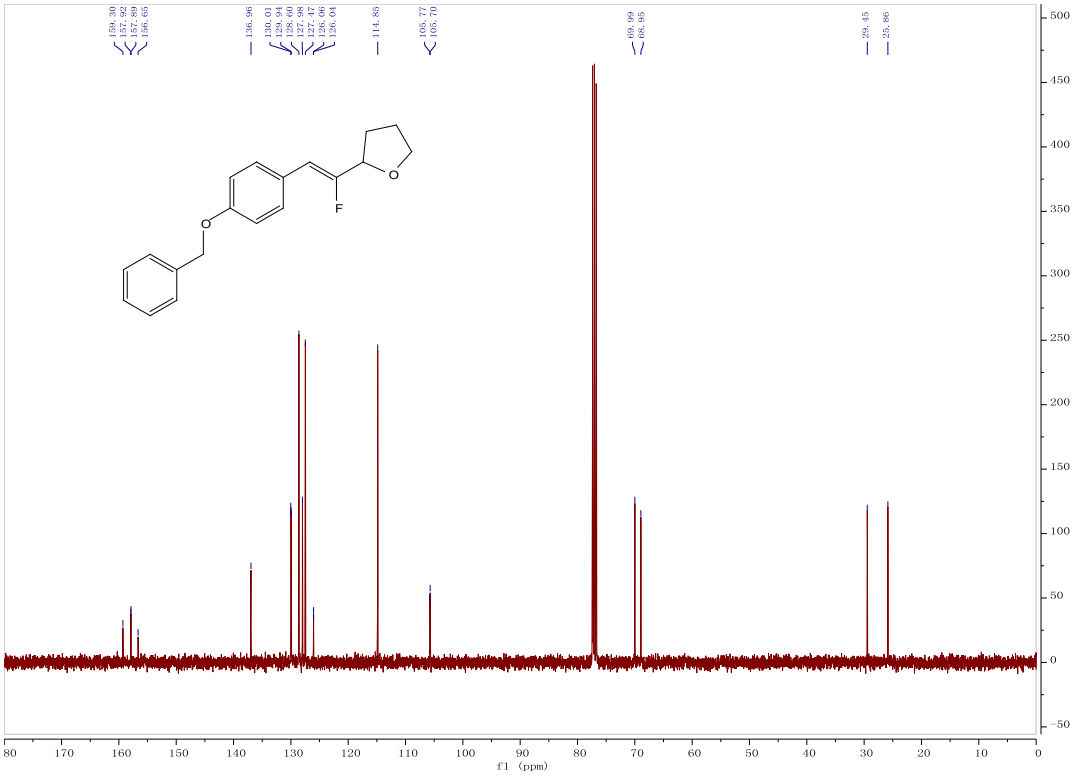
^{19}F NMR spectrum of **3la**



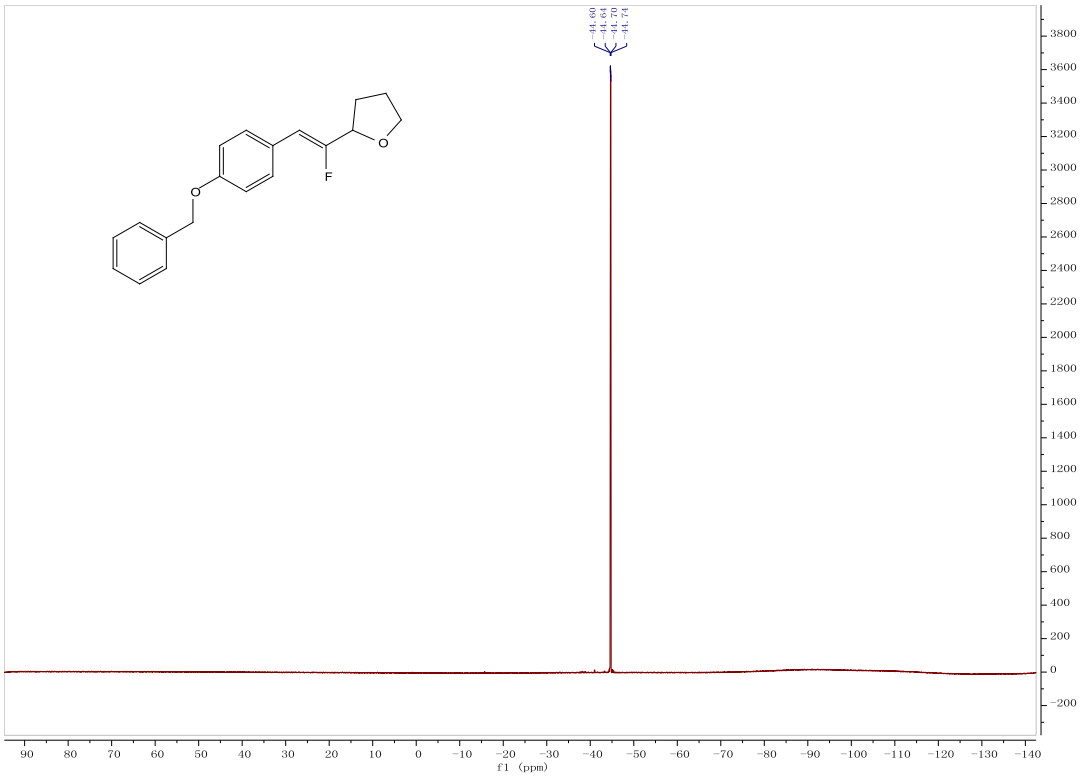
^{1}H NMR spectrum of **3lb**



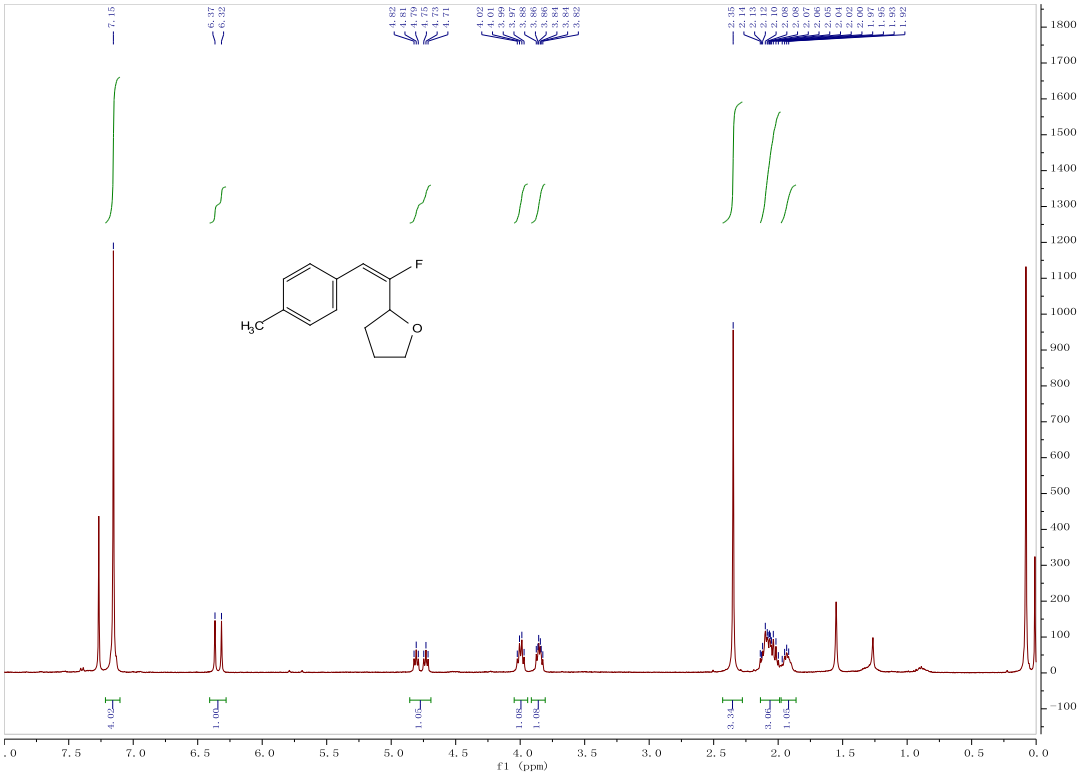
^{13}C NMR spectrum of **3lb**



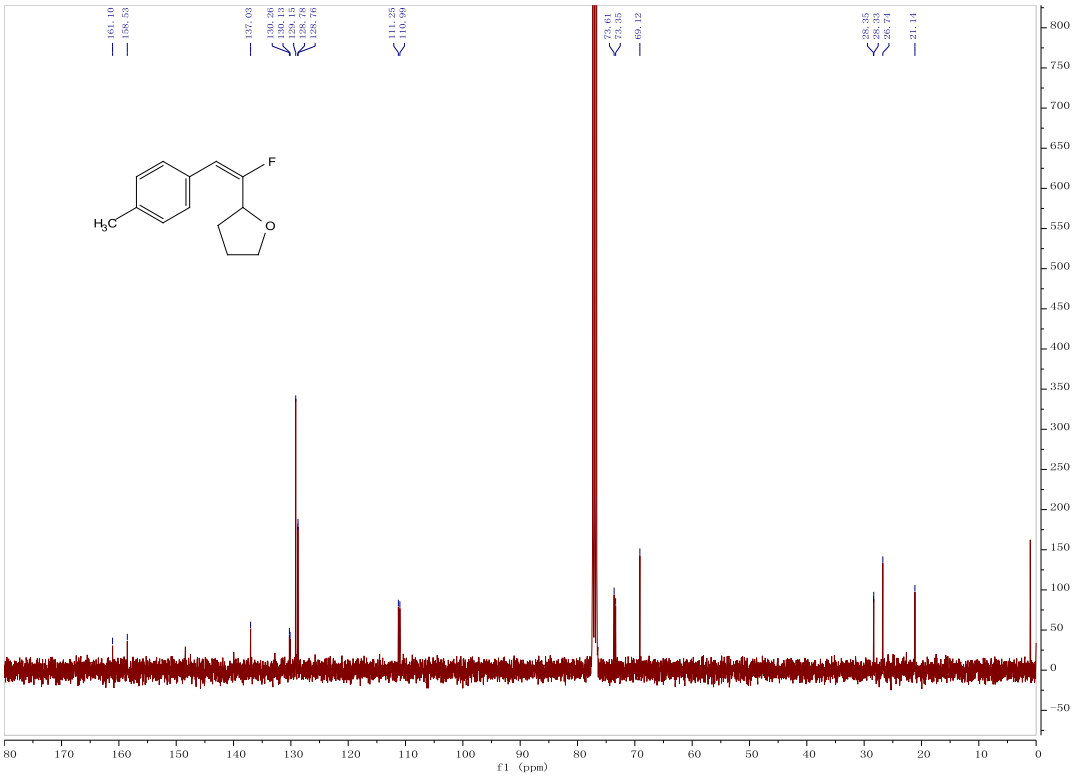
^{19}F NMR spectrum of **3lb**



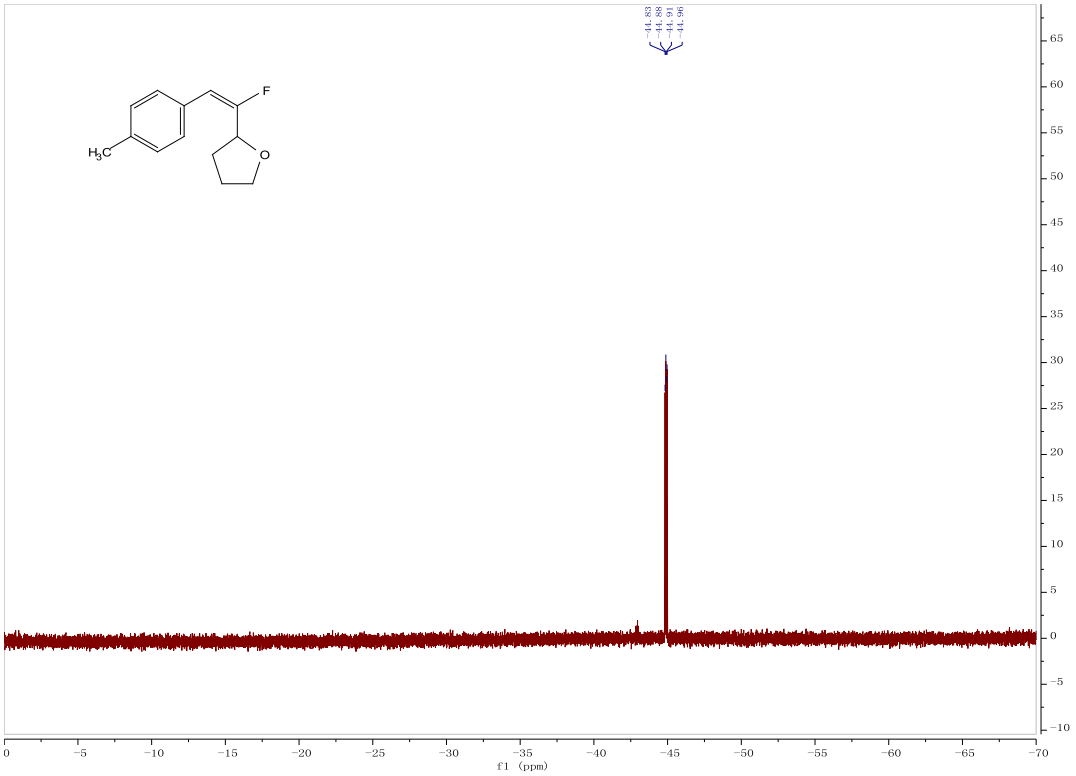
^{1}H NMR spectrum of **3ma**



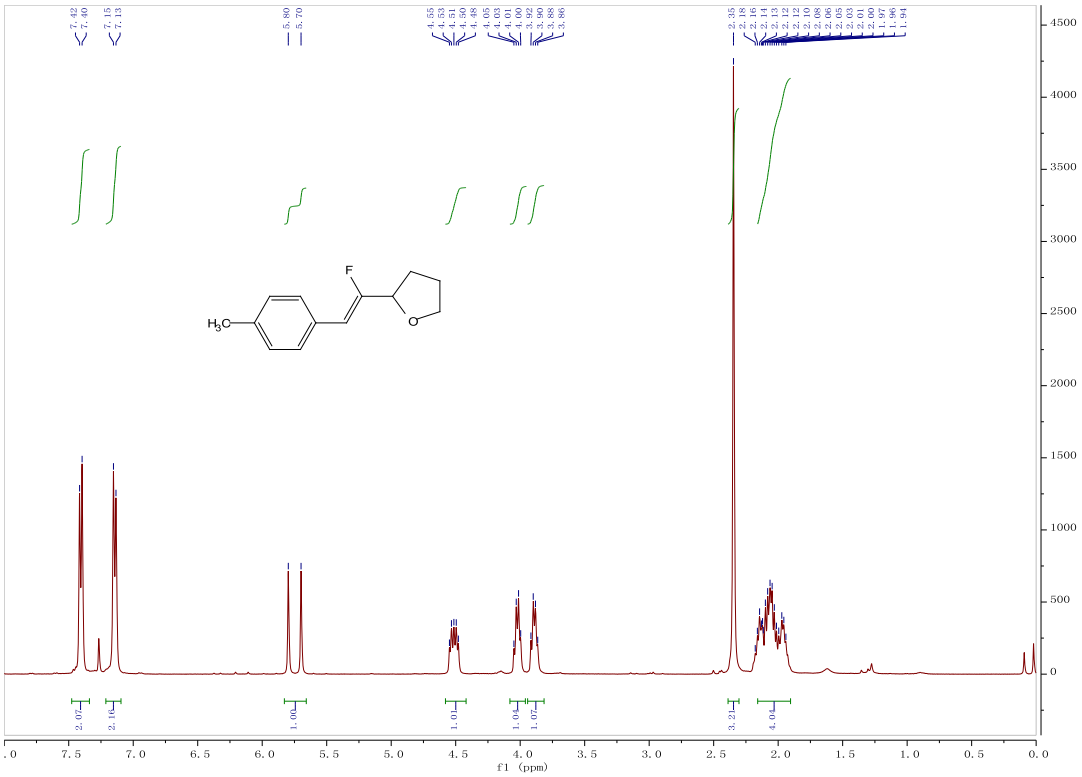
^{13}C NMR spectrum of **3ma**



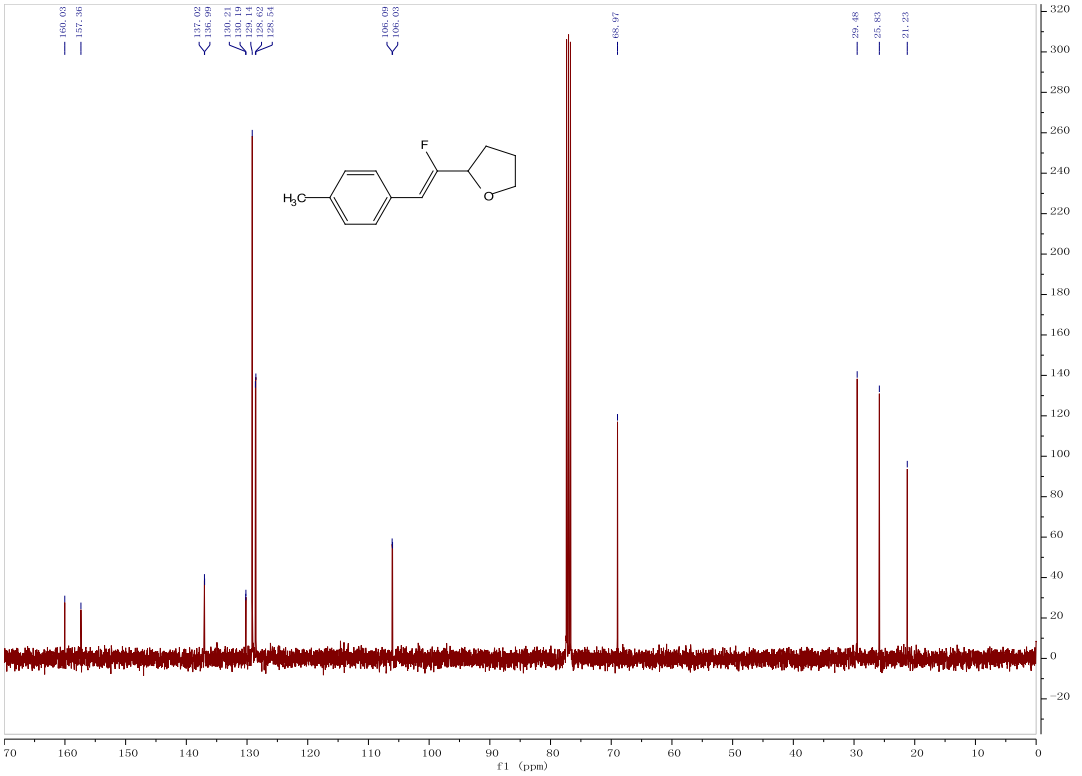
^{19}F NMR spectrum of **3ma**



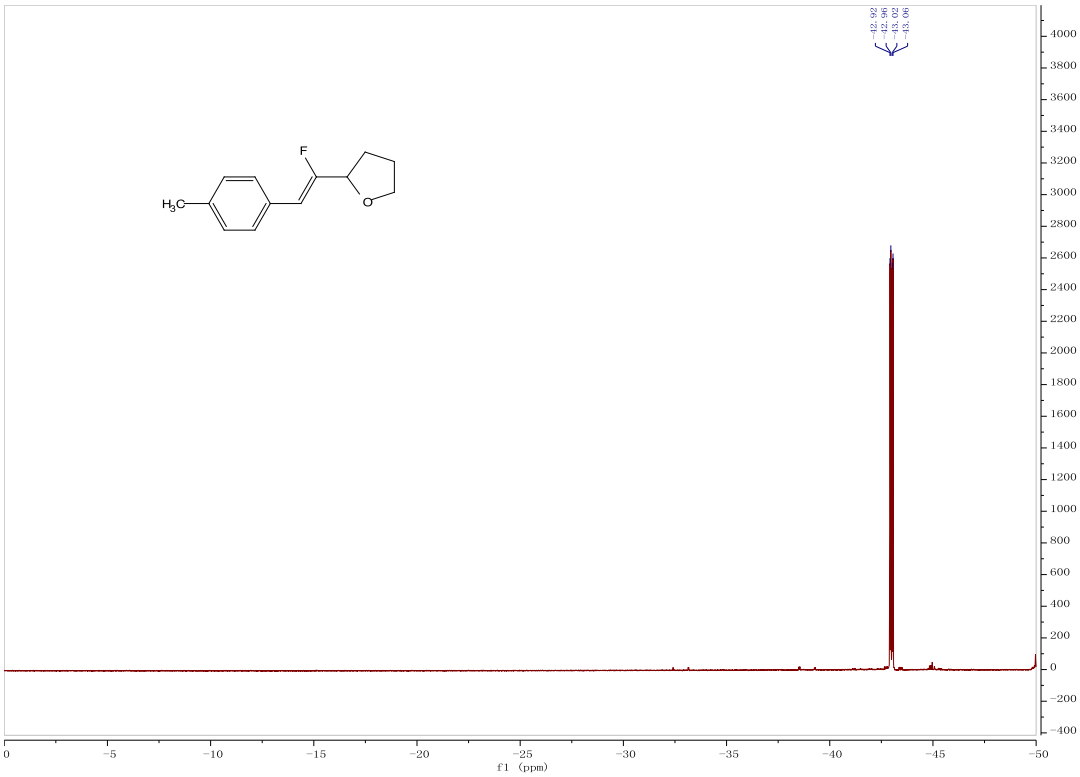
^{1}H NMR spectrum of **3mb**



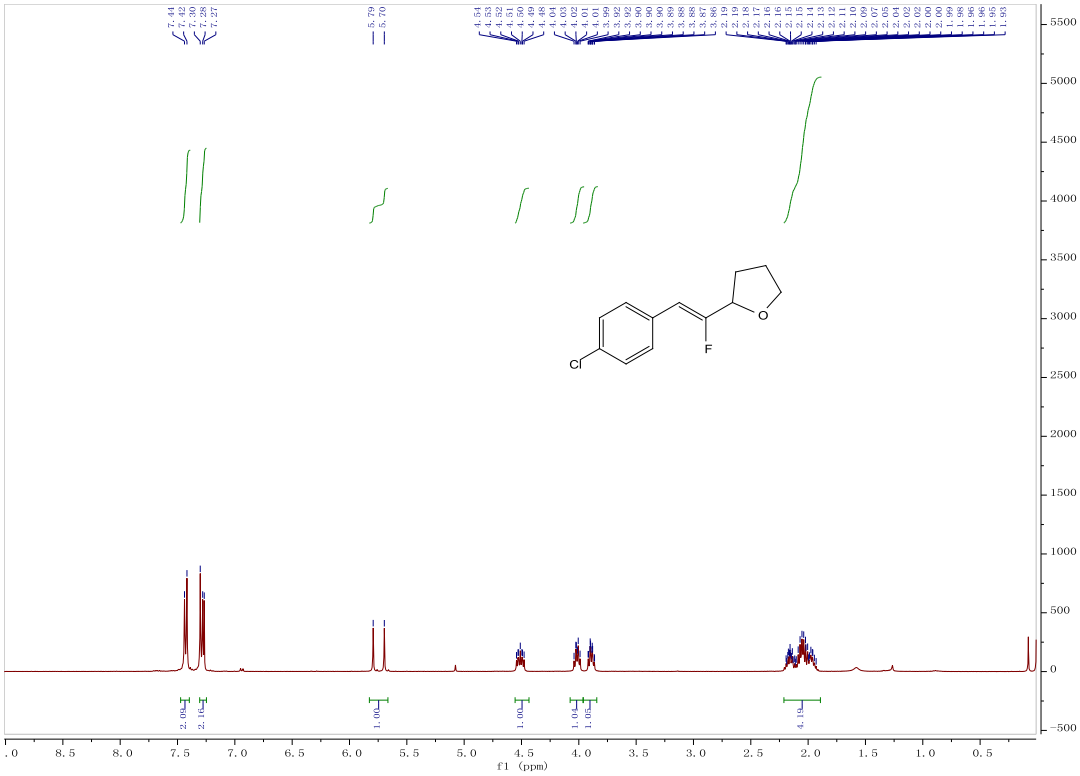
^{13}C NMR spectrum of **3mb**



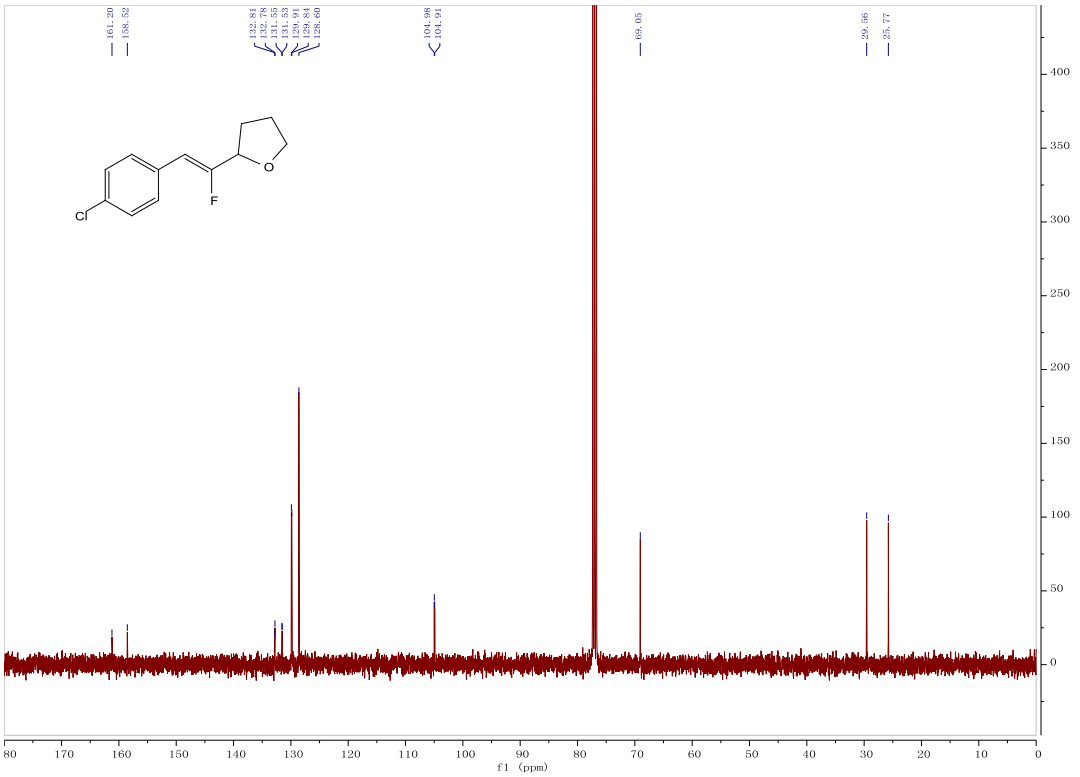
^{19}F NMR spectrum of **3mb**



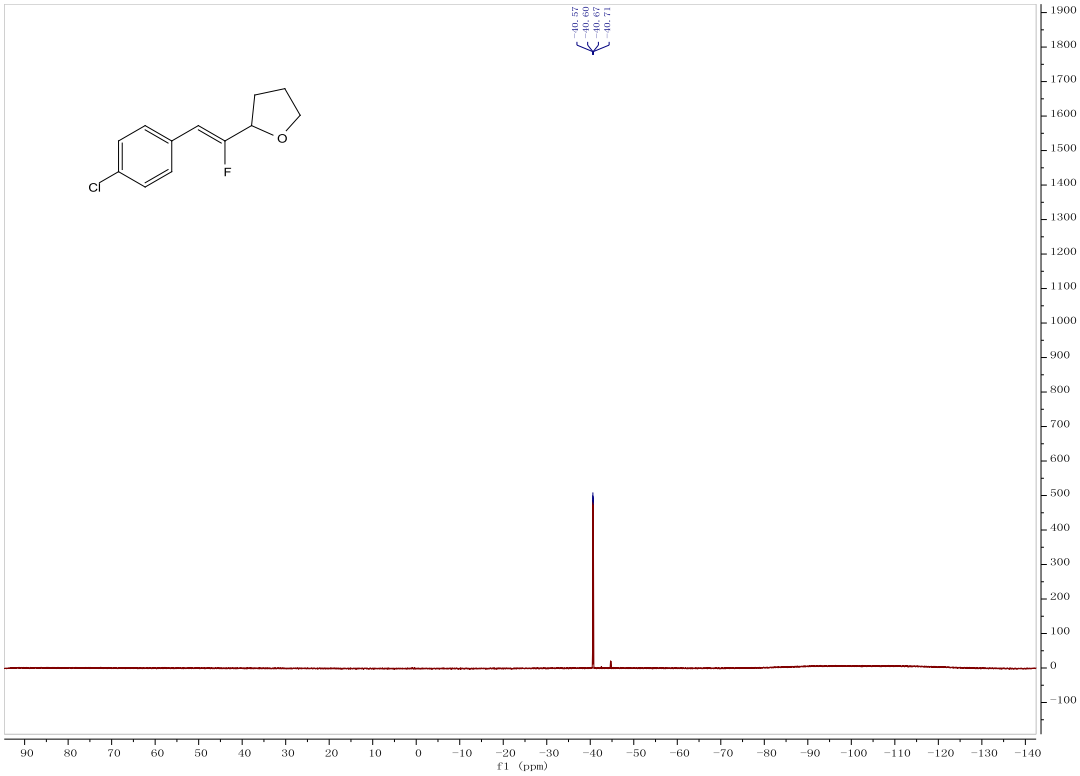
^{1}H NMR spectrum of **3n**



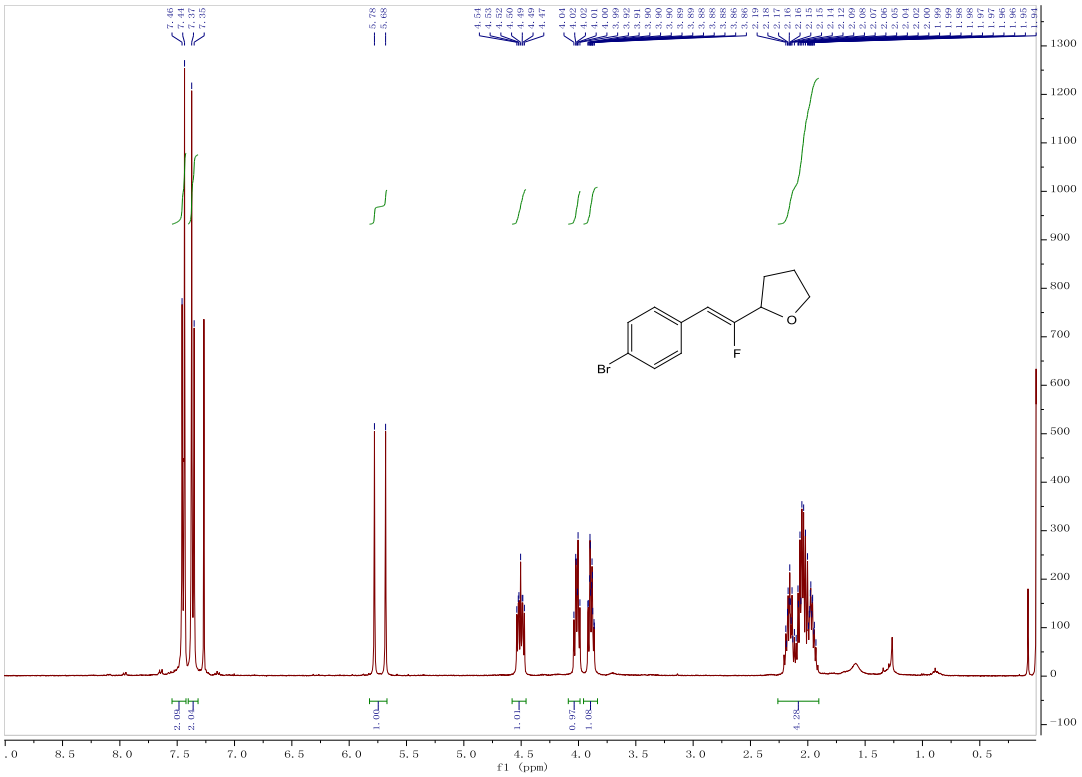
^{13}C NMR spectrum of **3n**



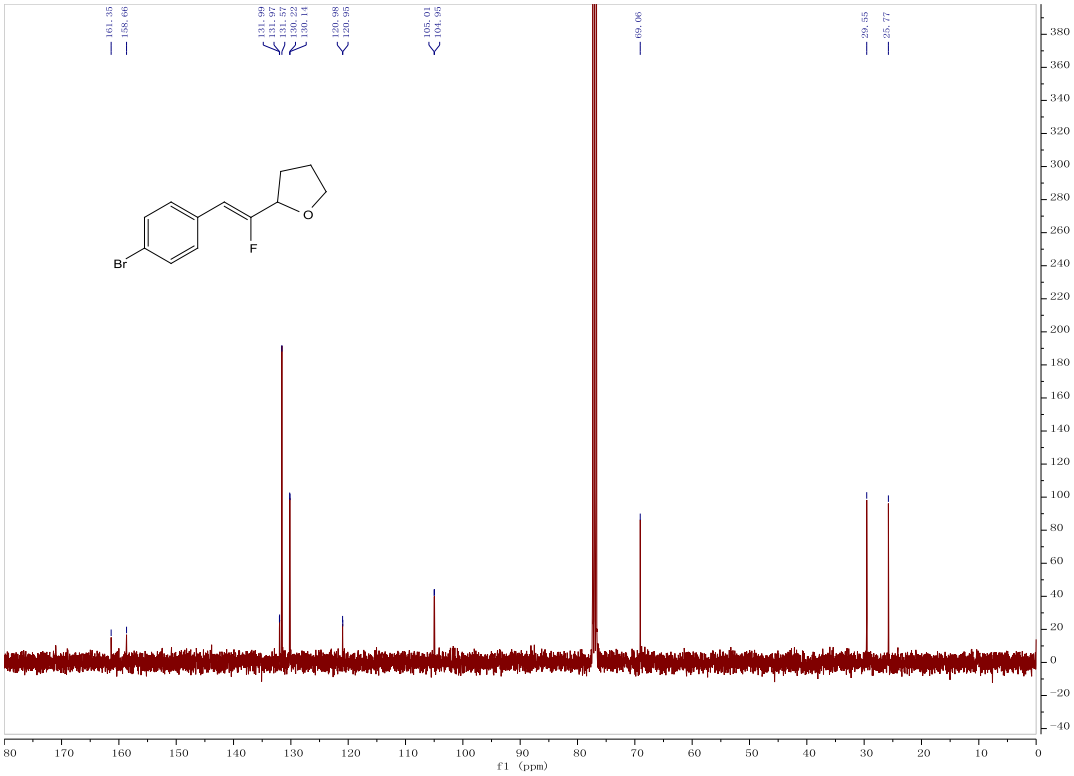
^{19}F NMR spectrum of **3n**



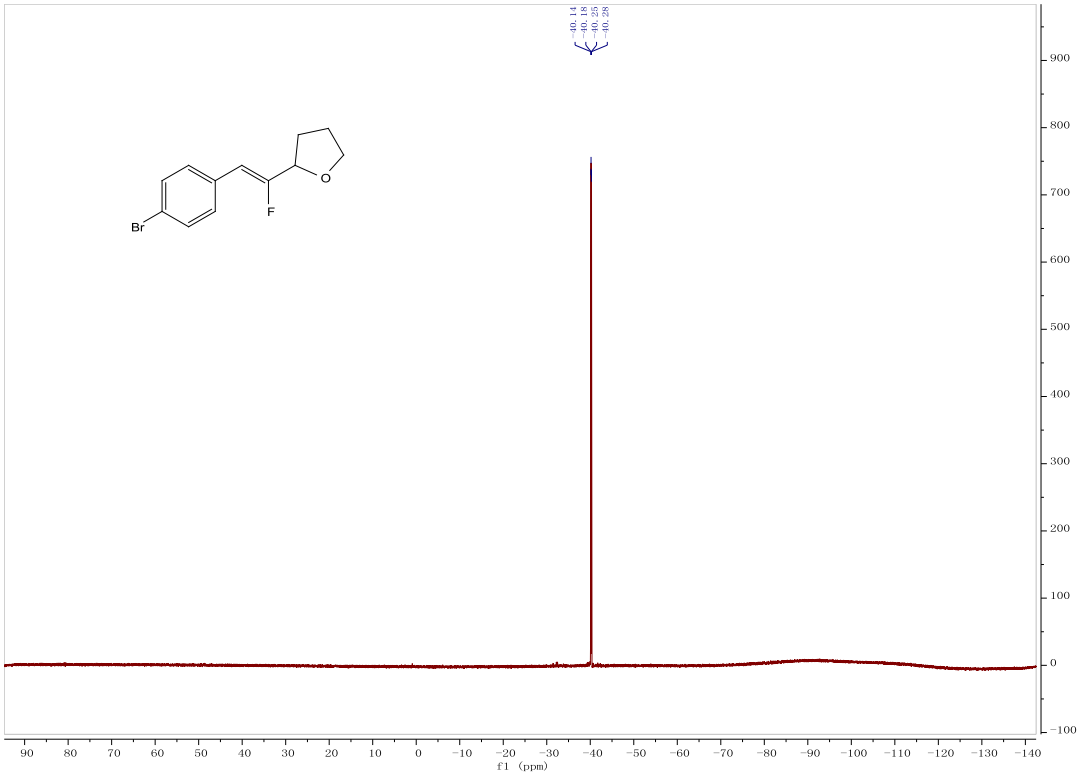
^{1}H NMR spectrum of **3o**



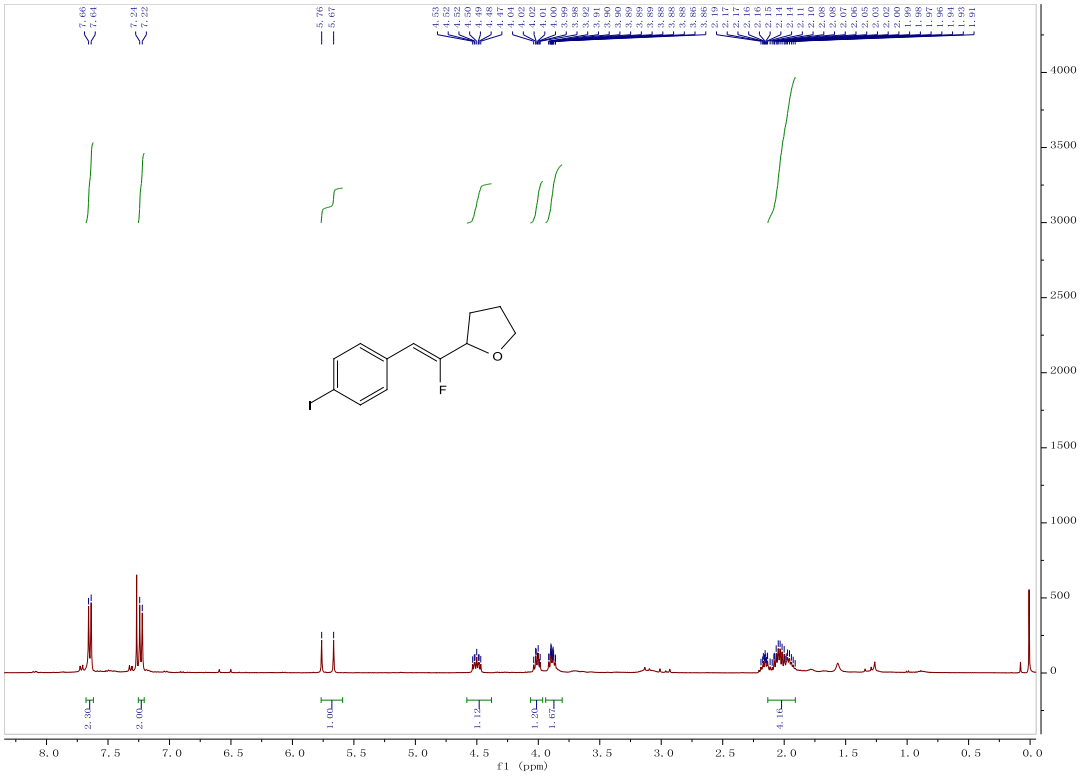
^{13}C NMR spectrum of **3o**



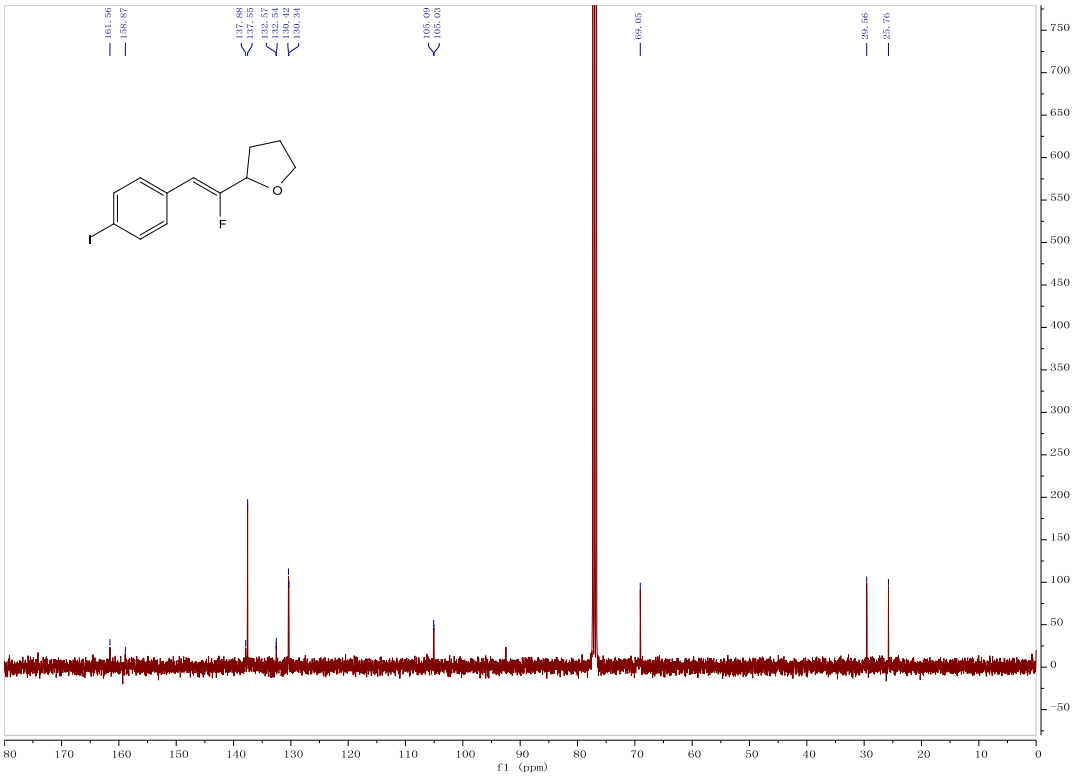
^{19}F NMR spectrum of **3o**



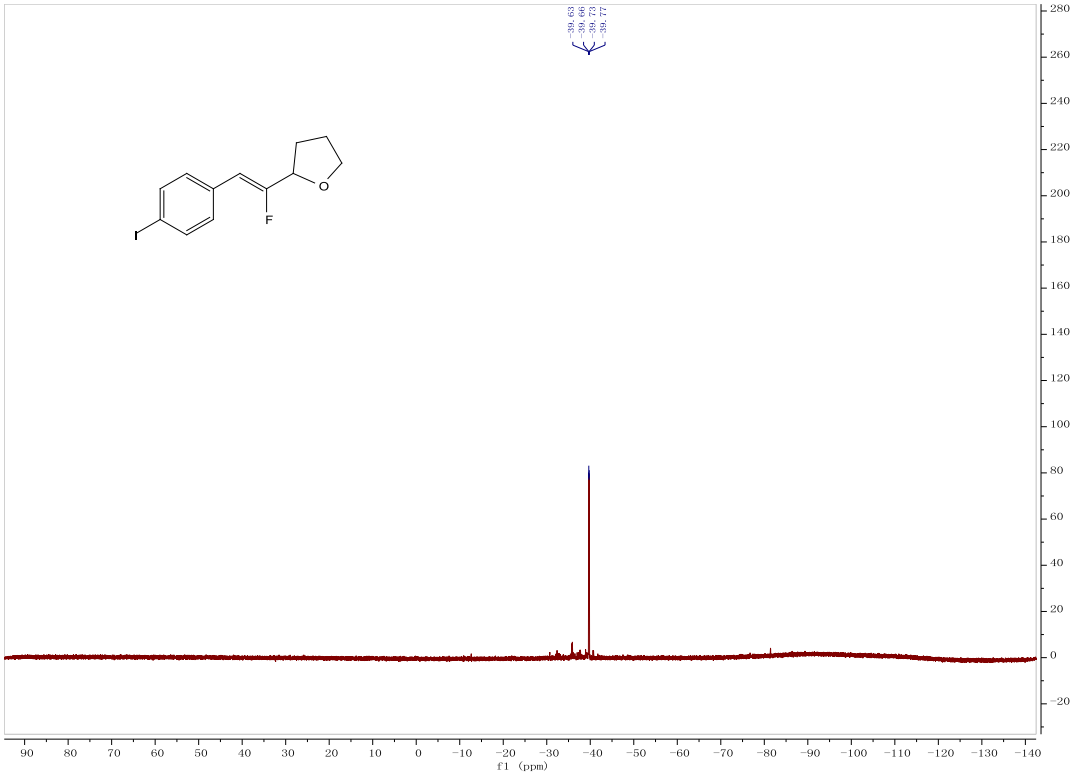
^{1}H NMR spectrum of **3p**



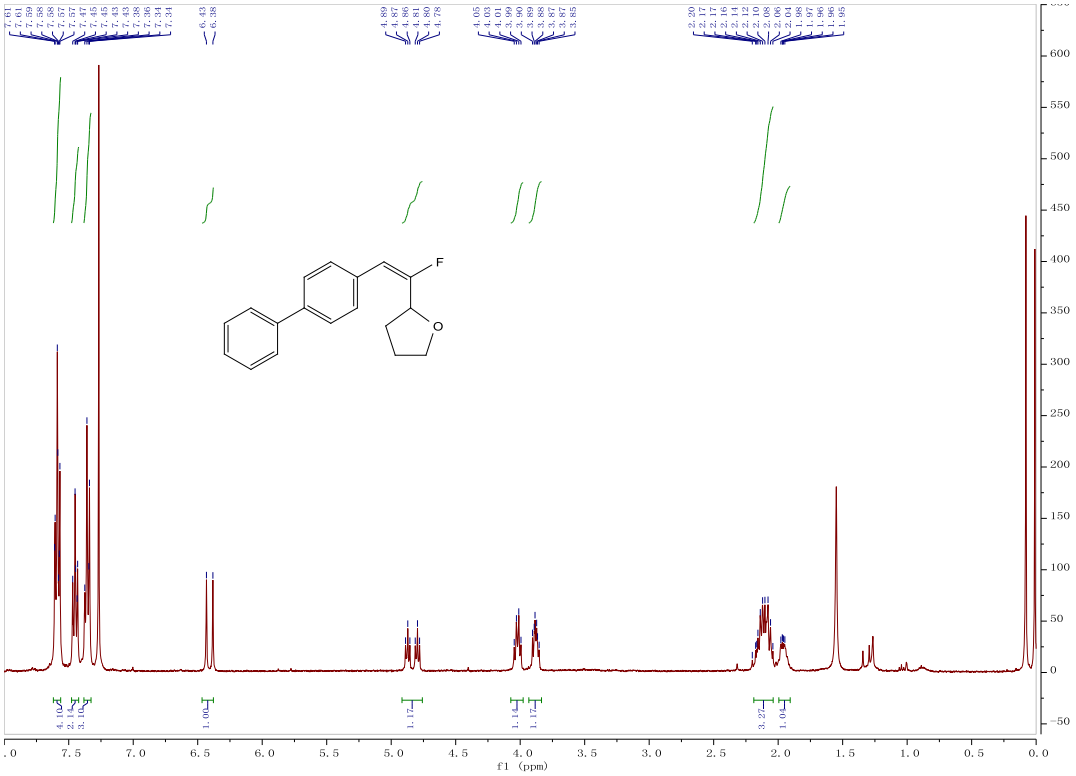
^{13}C NMR spectrum of **3p**



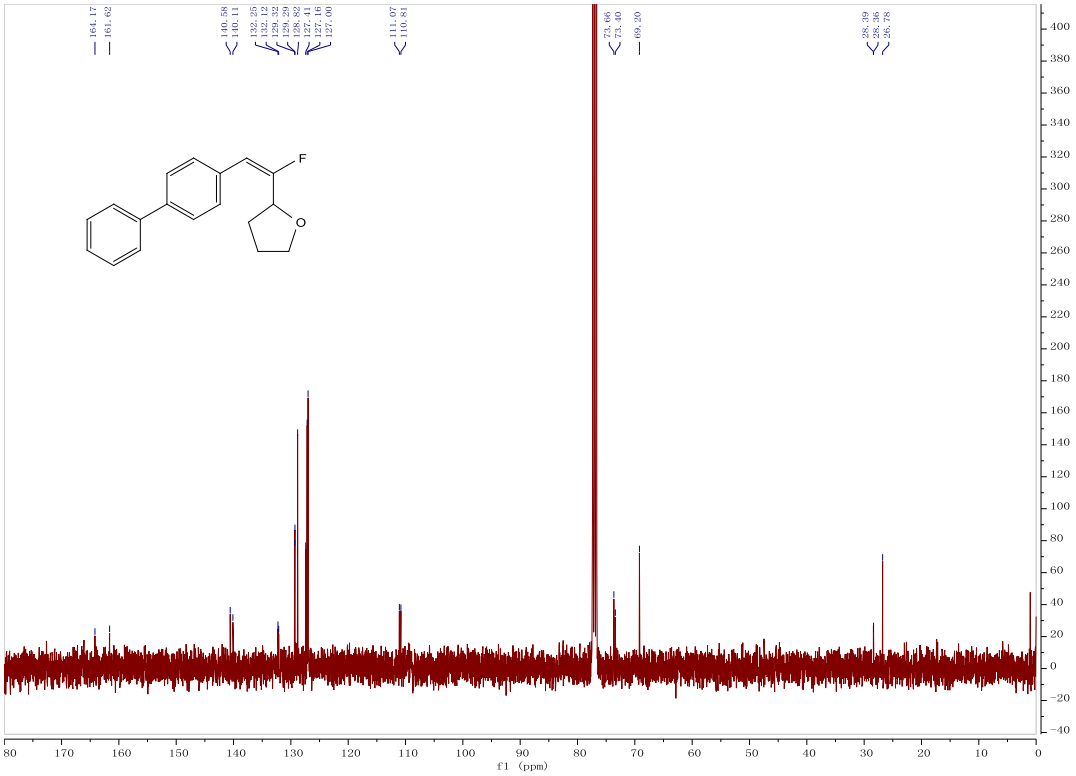
^{19}F NMR spectrum of **3p**



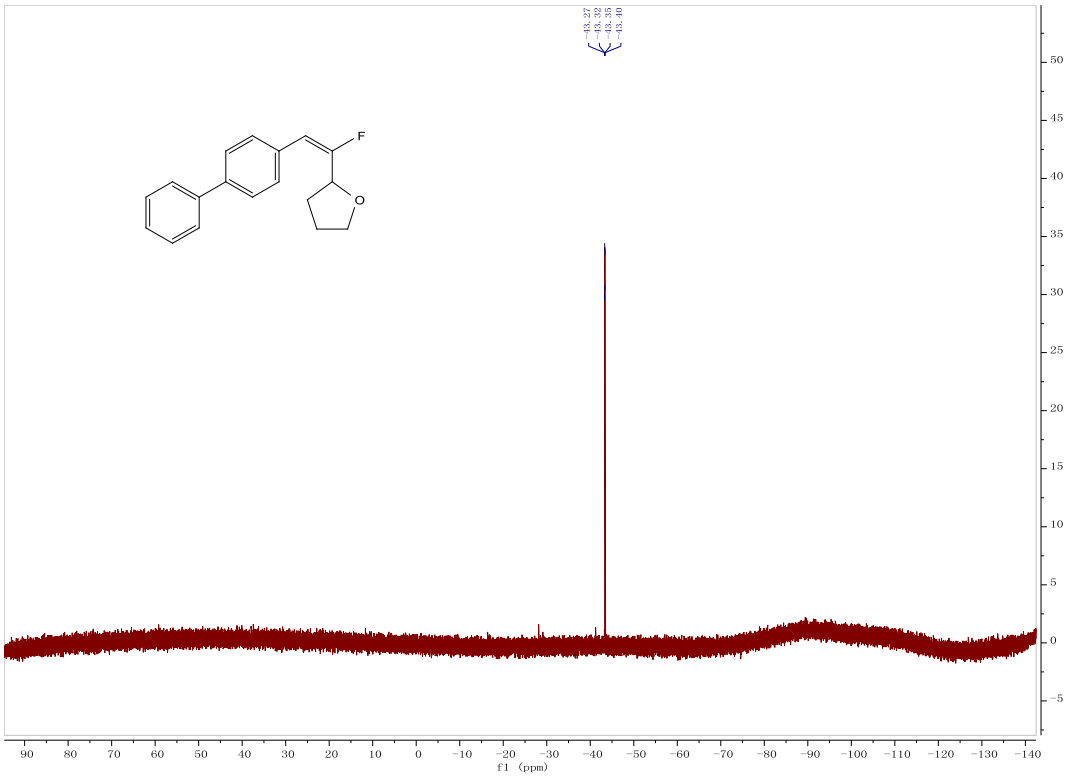
^{1}H NMR spectrum of **3qa**



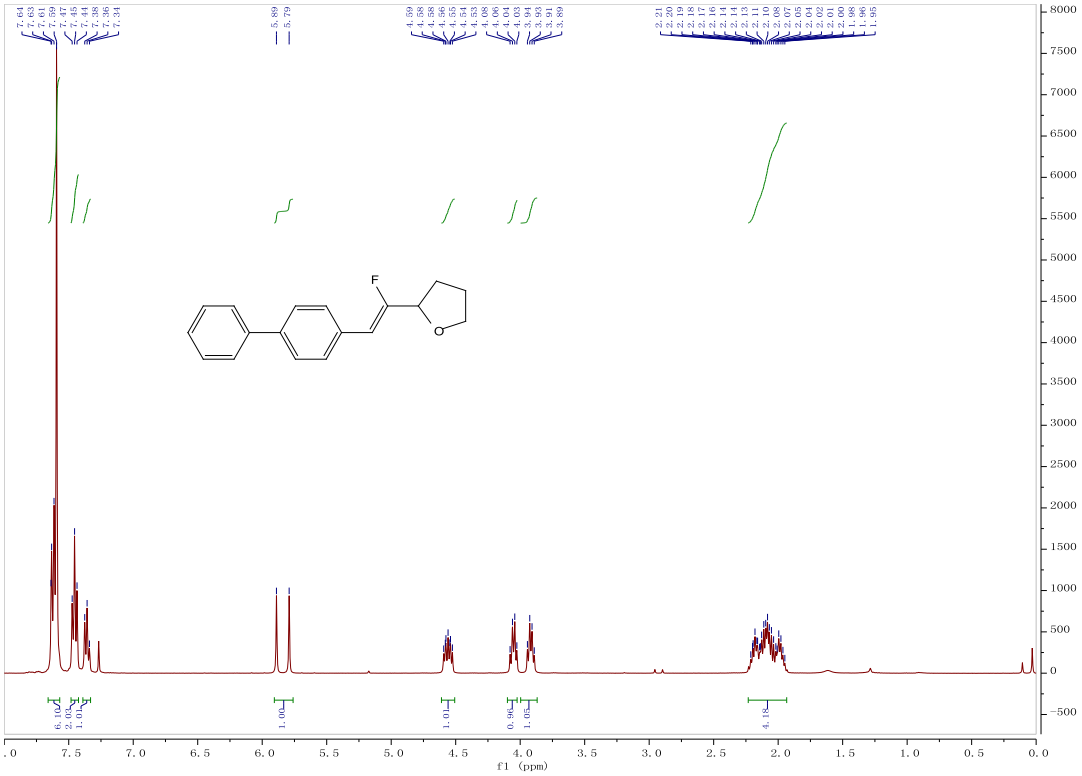
^{13}C NMR spectrum of **3qa**



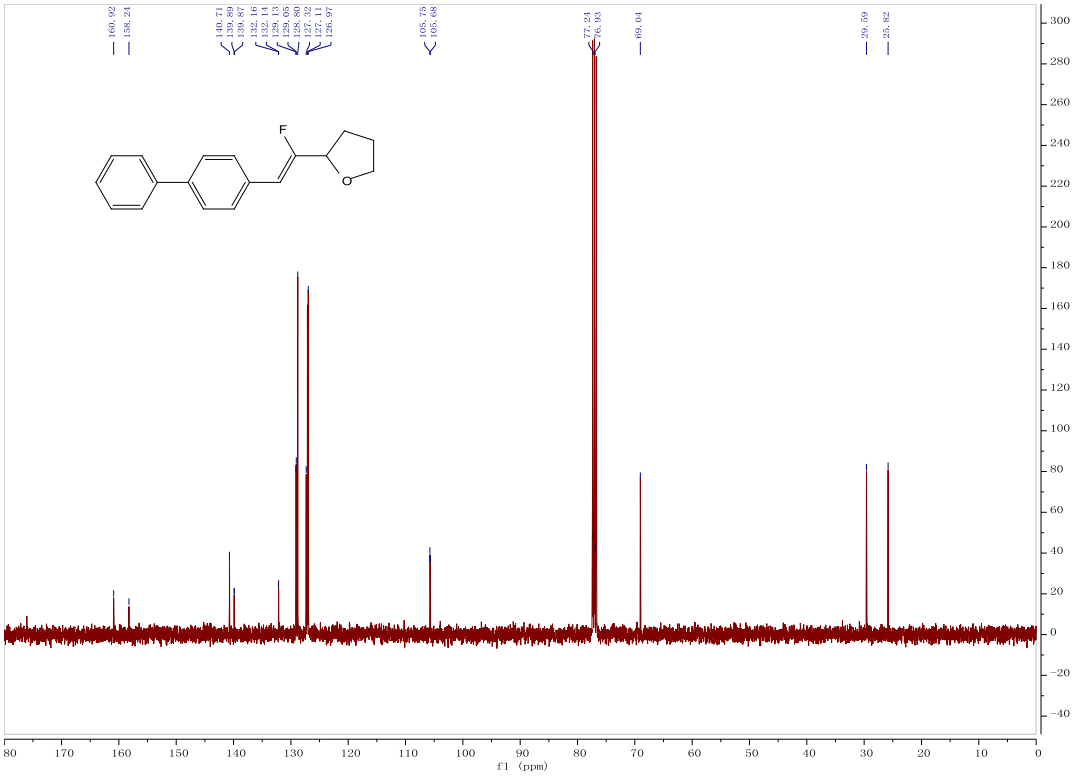
^{19}F NMR spectrum of **3qa**



^{1}H NMR spectrum of **3qb**

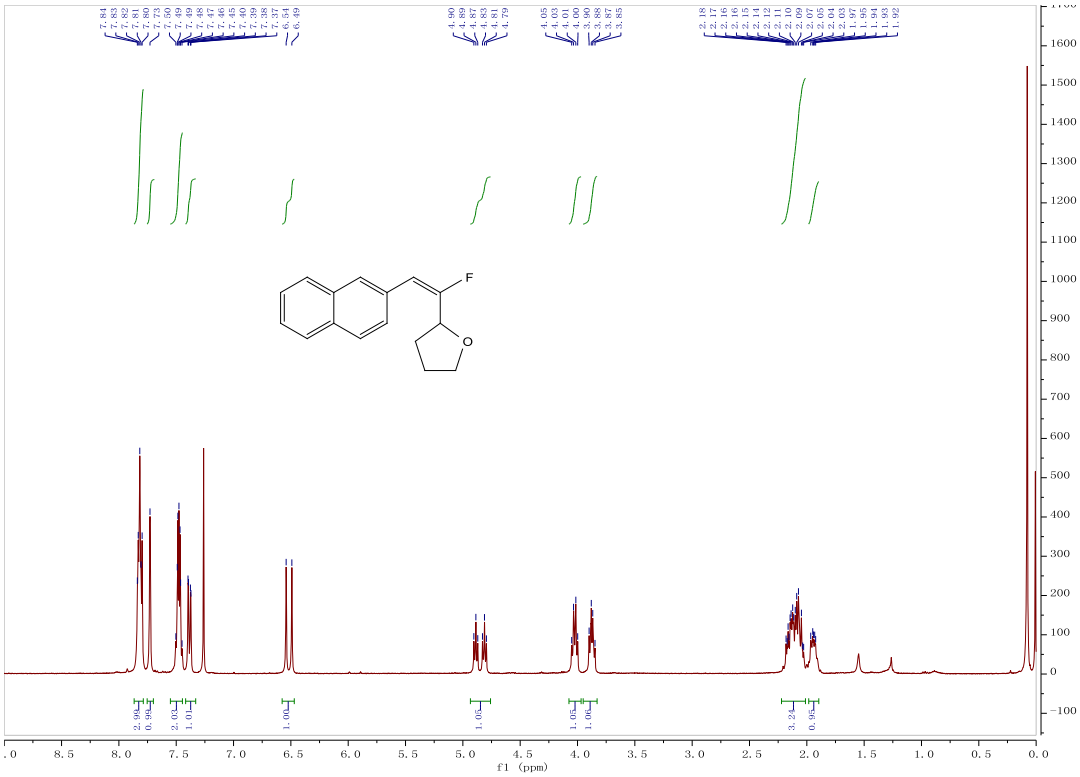


^{13}C NMR spectrum of **3qb**

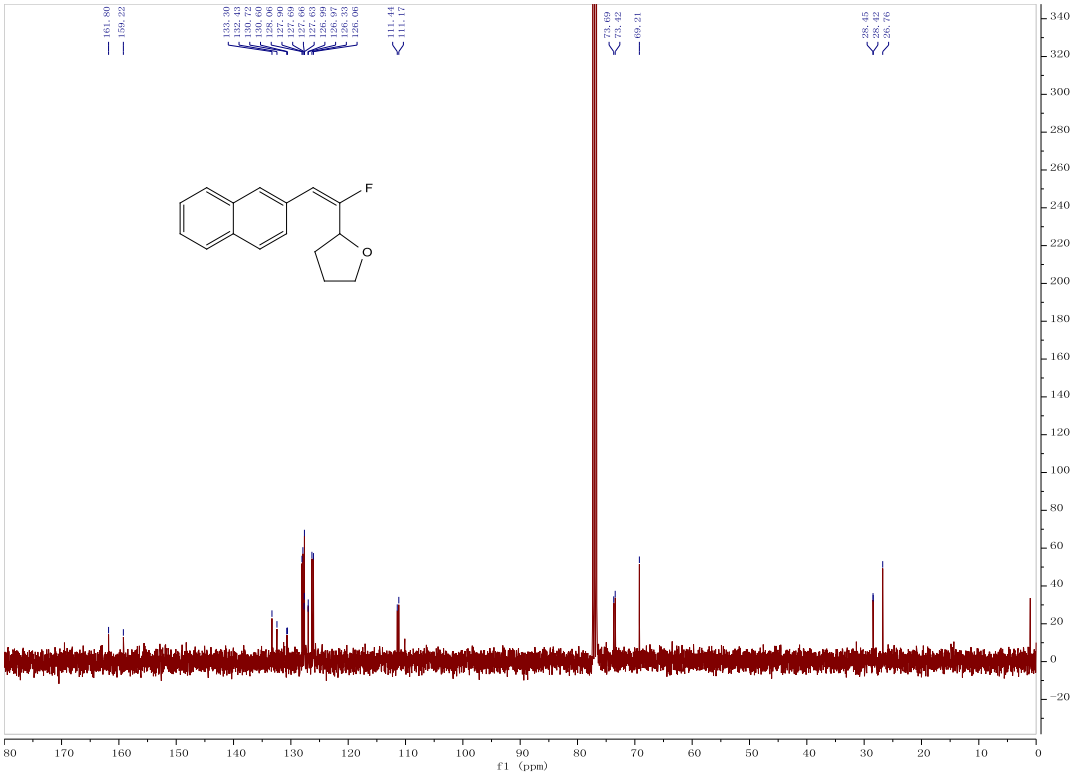


^{19}F NMR spectrum of **3qb**

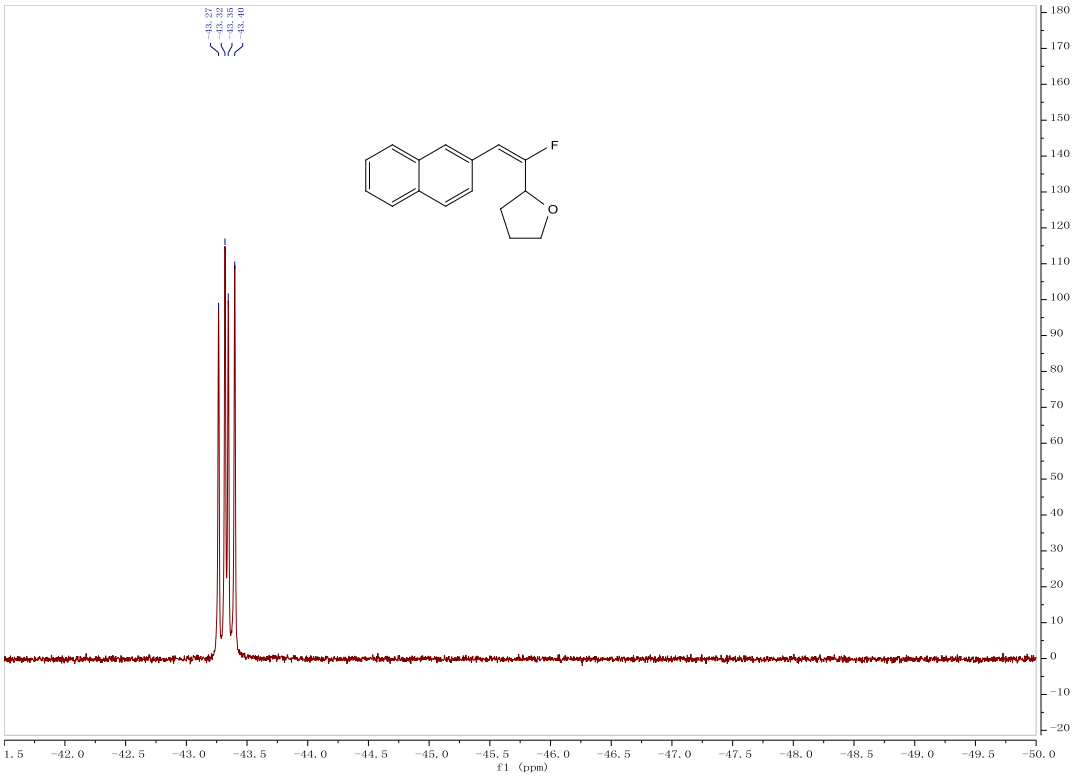
^{1}H NMR spectrum of **3ra**



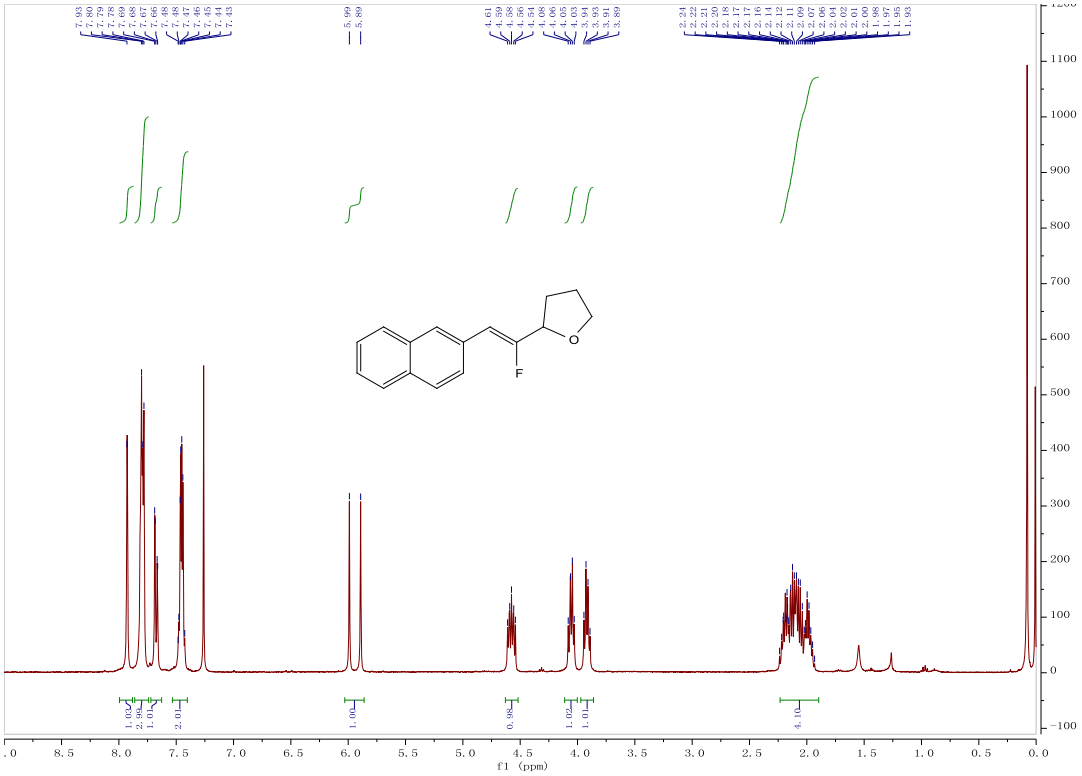
^{13}C NMR spectrum of **3ra**



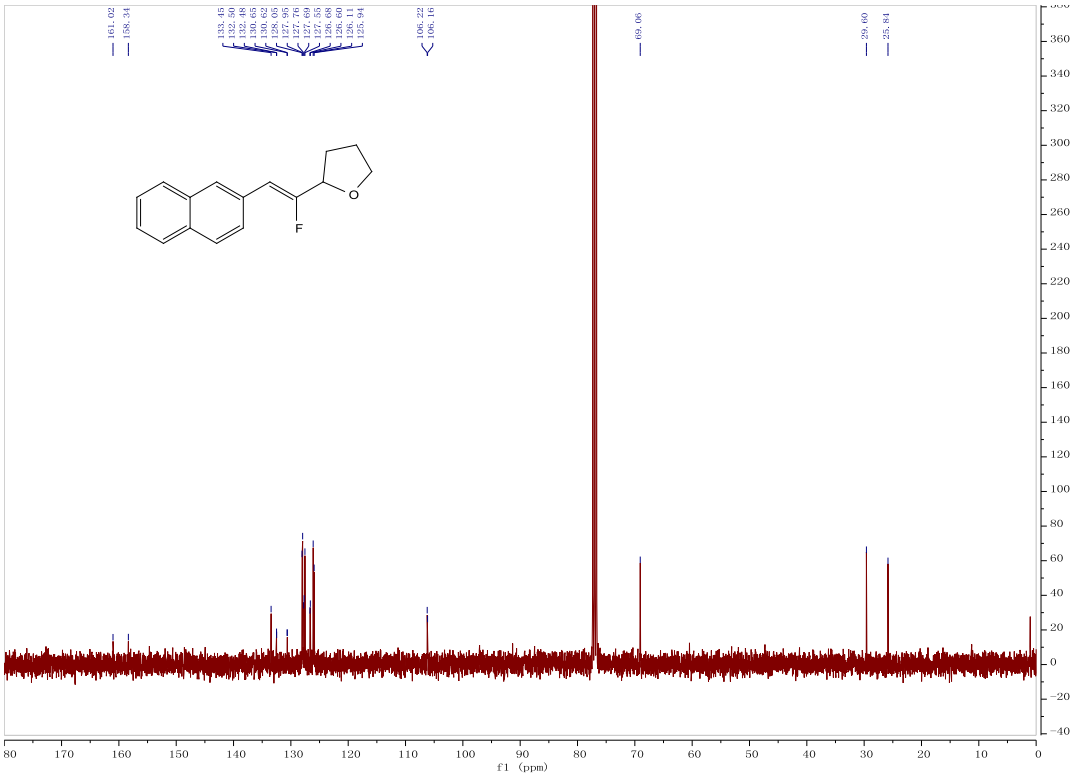
^{19}F NMR spectrum of **3ra**



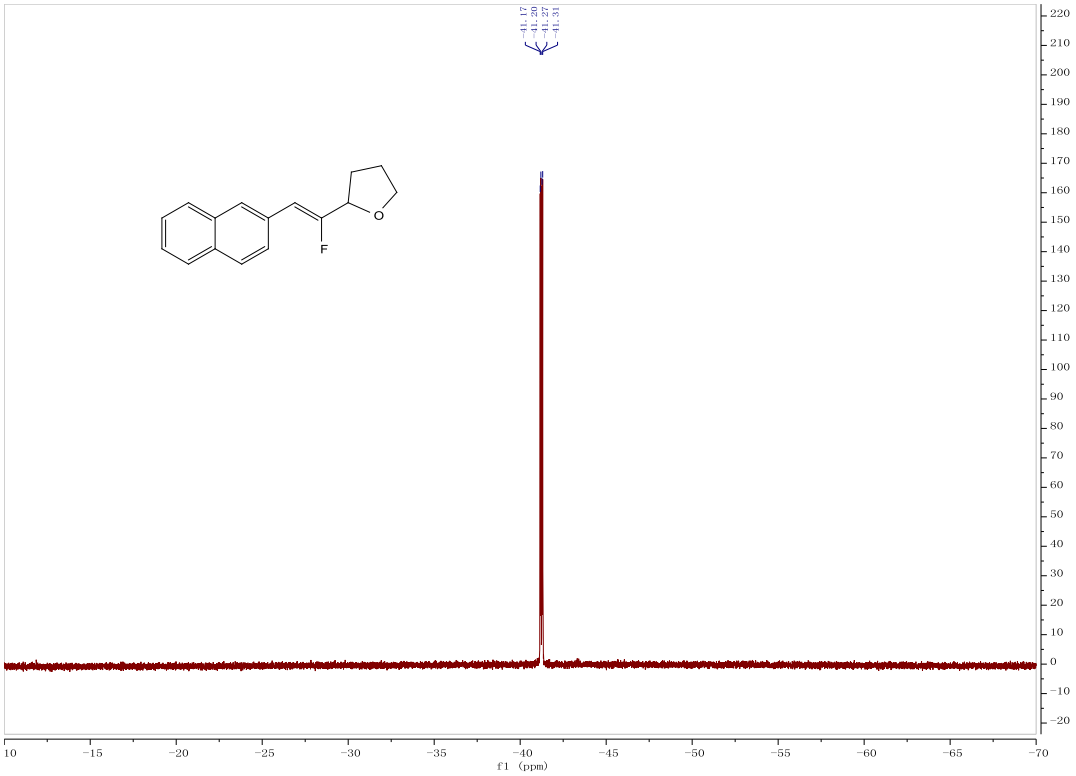
^{1}H NMR spectrum of **3rb**



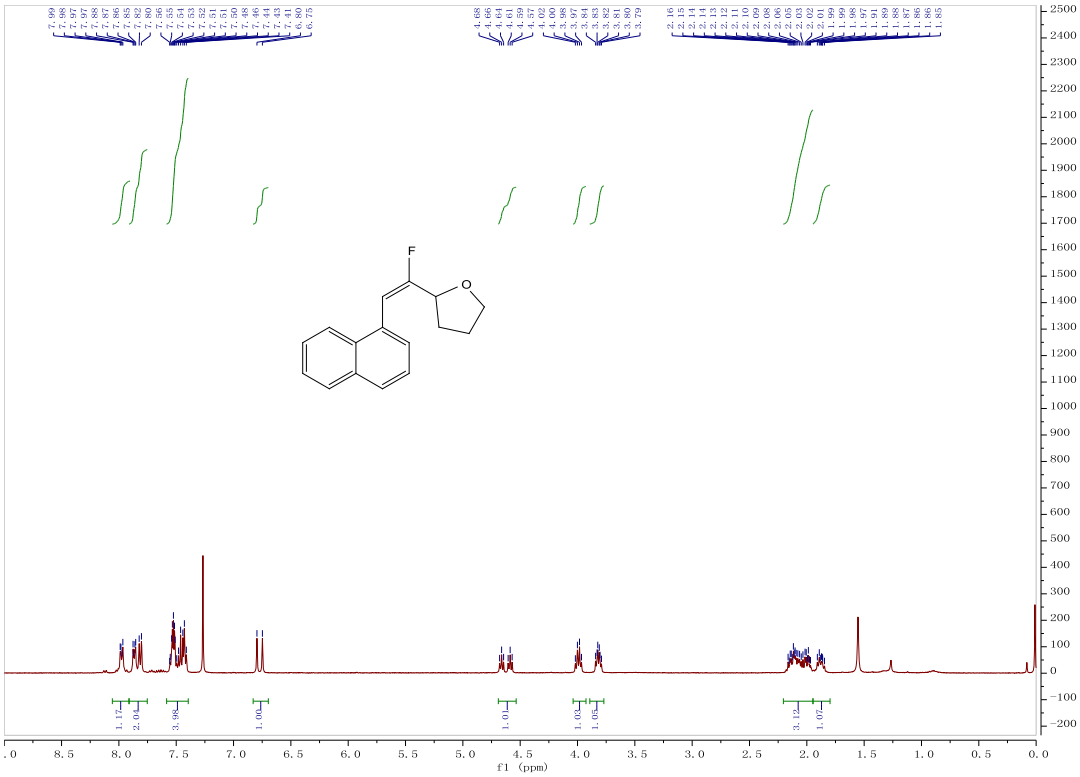
^{13}C NMR spectrum of **3rb**



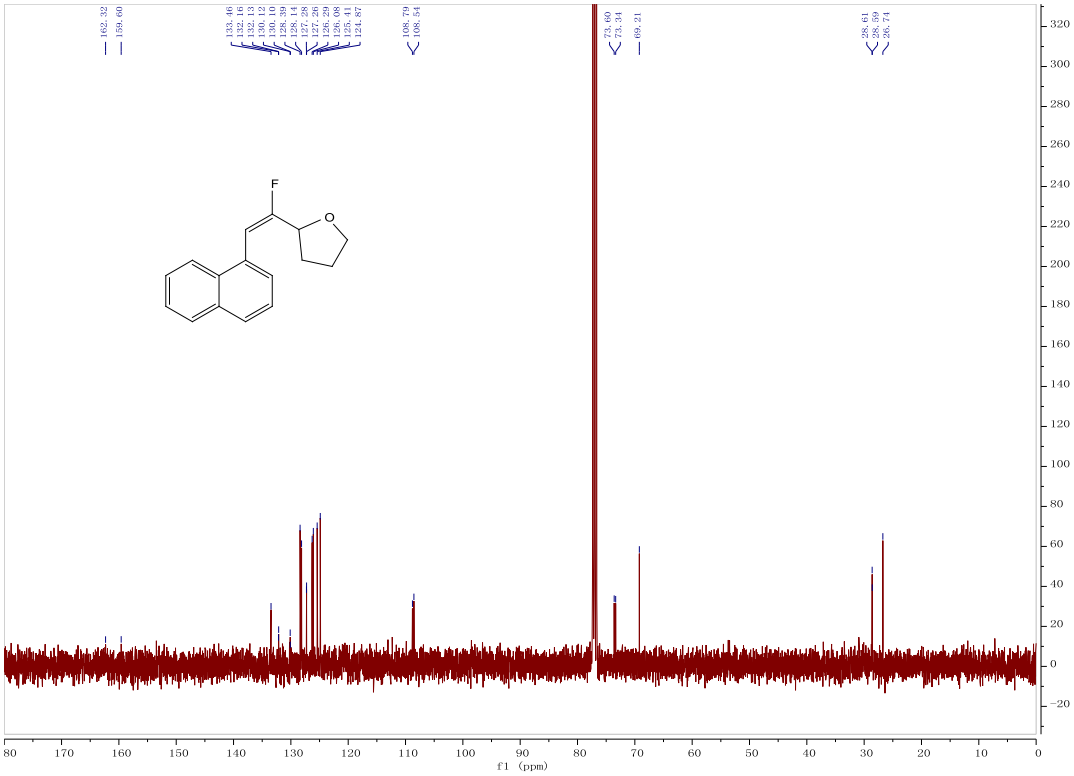
^{19}F NMR spectrum of **3rb**



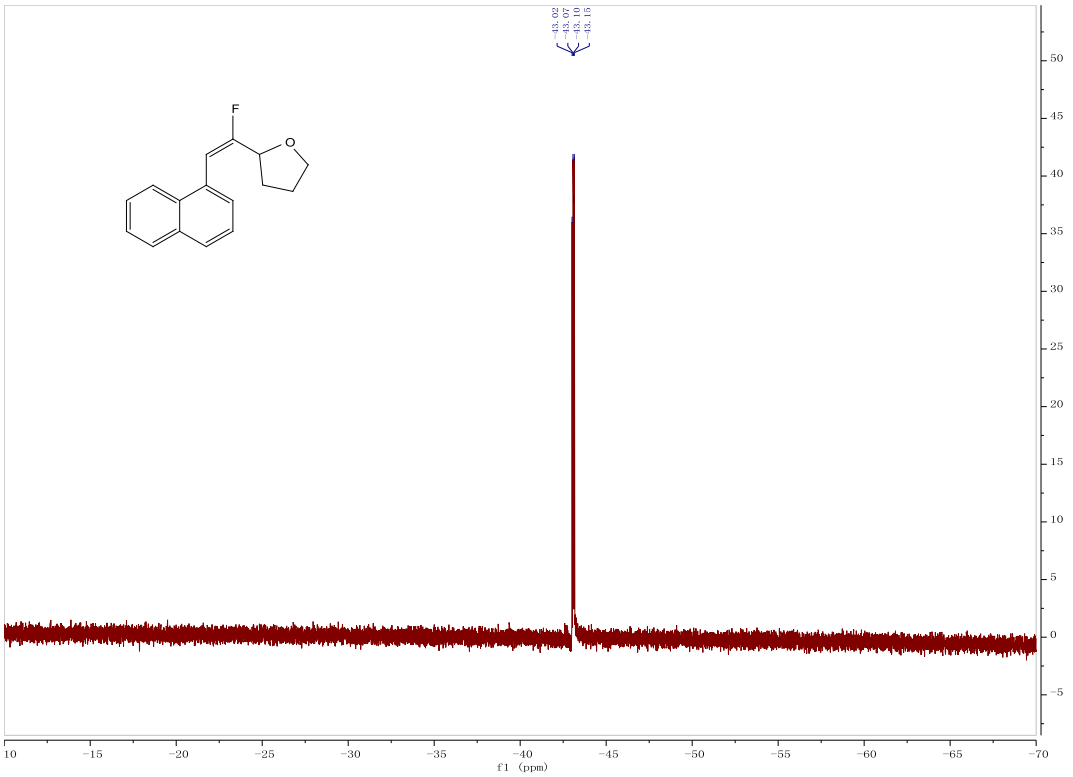
^{1}H NMR spectrum of **3sa**



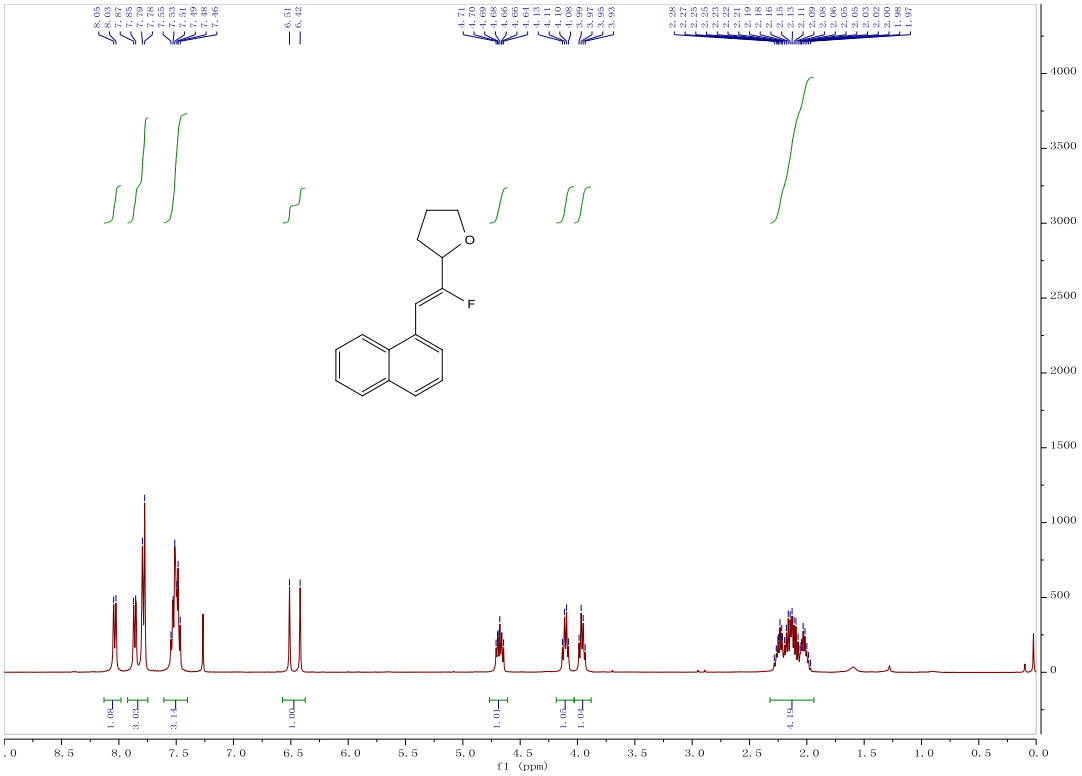
^{13}C NMR spectrum of **3sa**



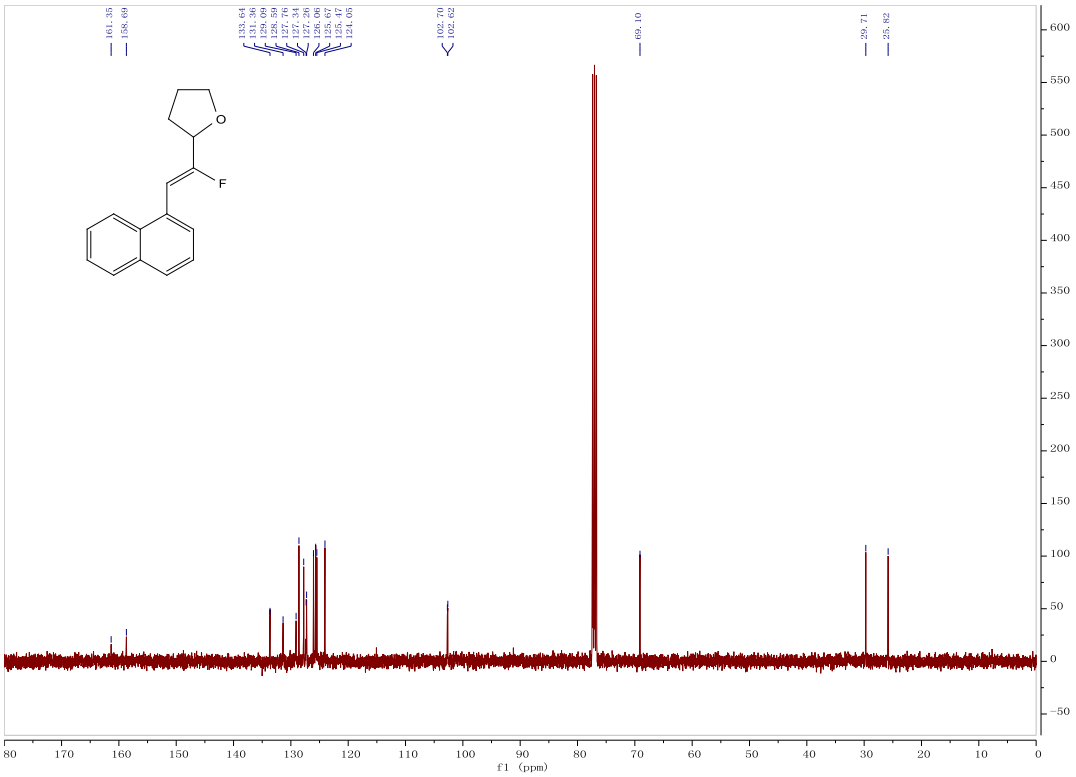
^{19}F NMR spectrum of **3sa**



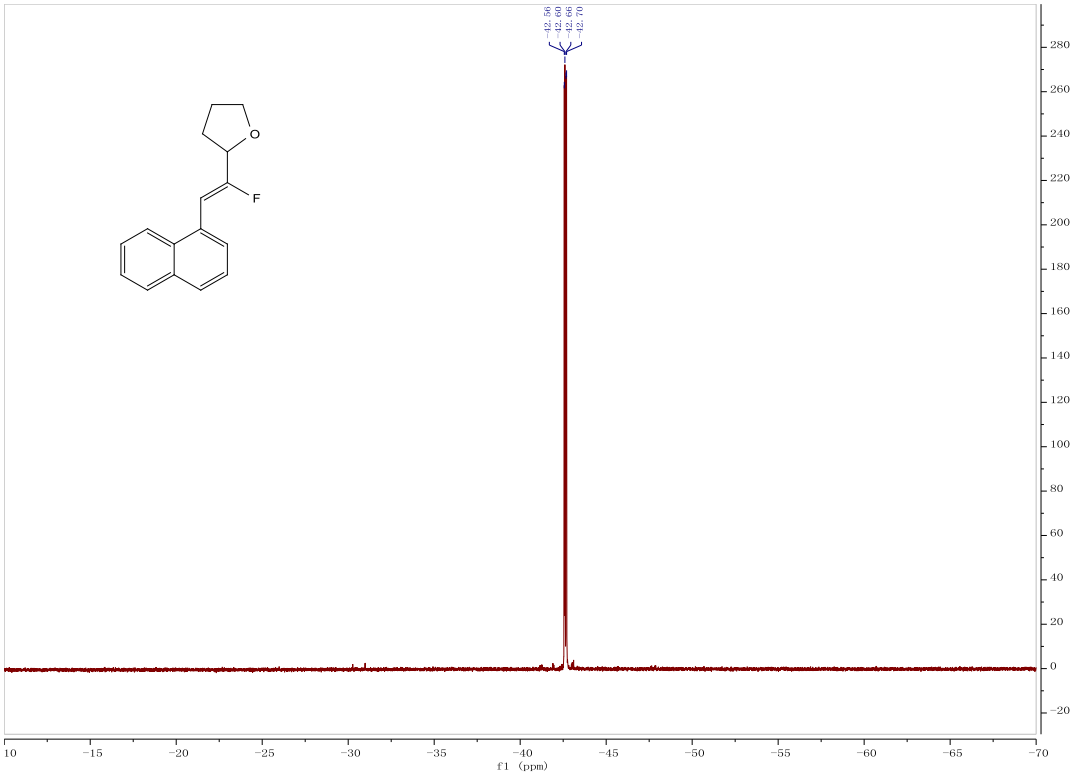
^{1}H NMR spectrum of **3sb**



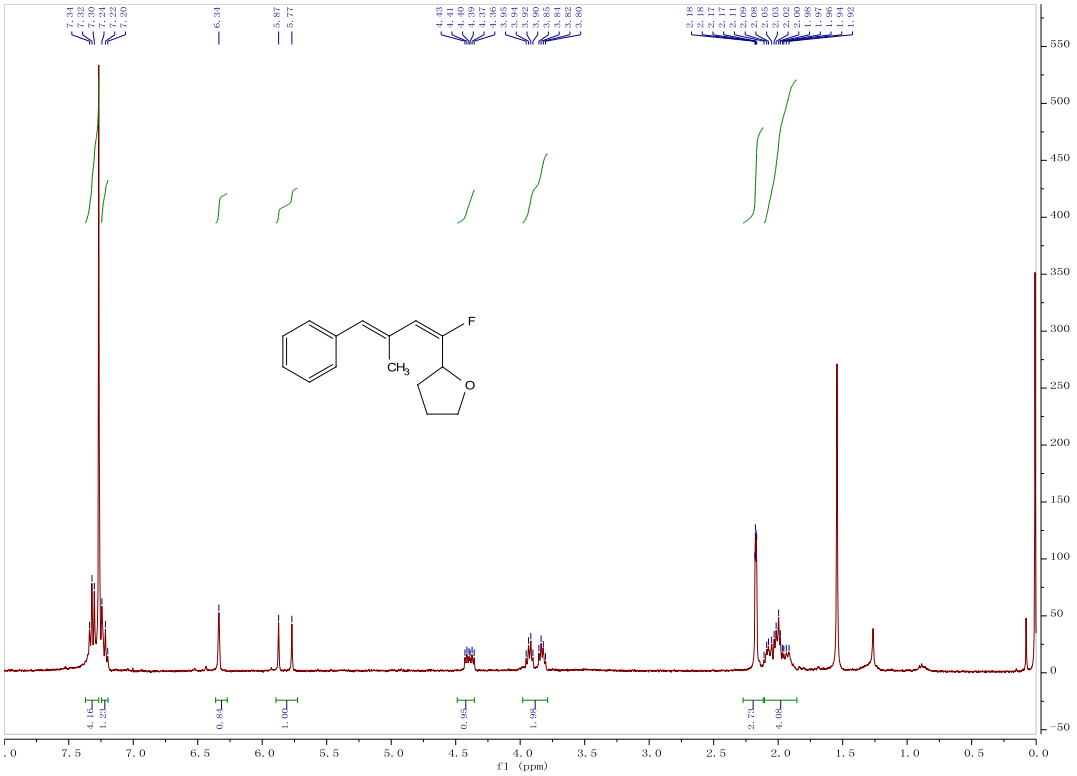
^{13}C NMR spectrum of **3sb**



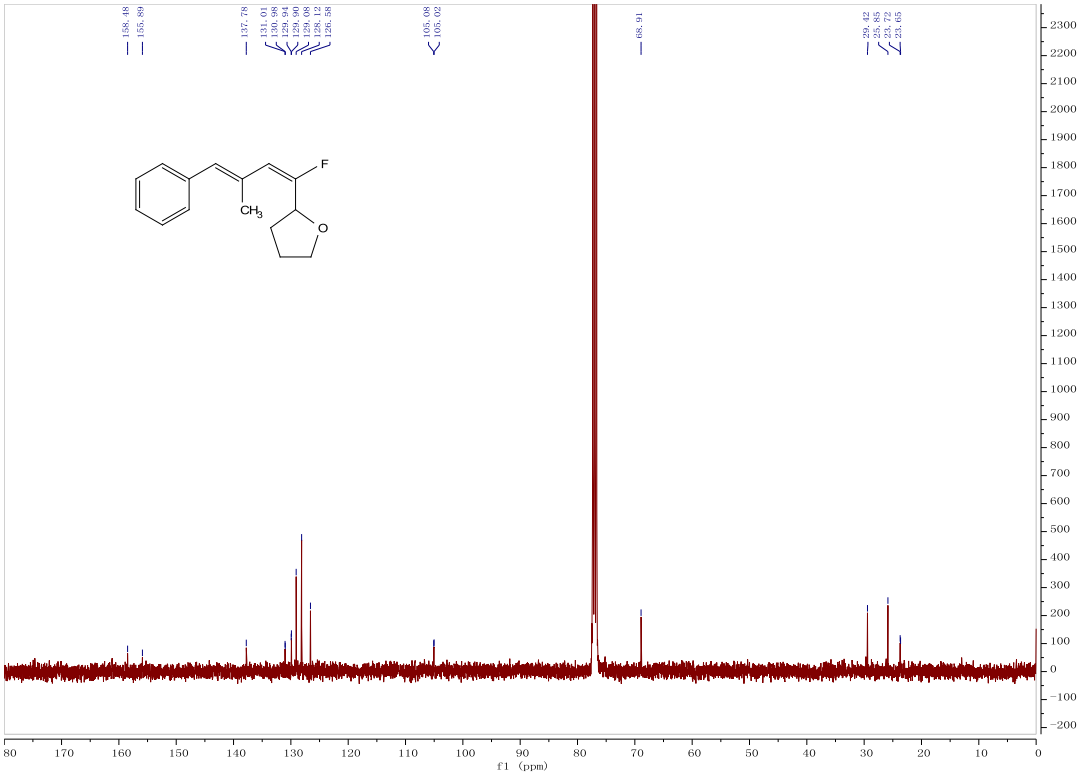
^{19}F NMR spectrum of **3sb**



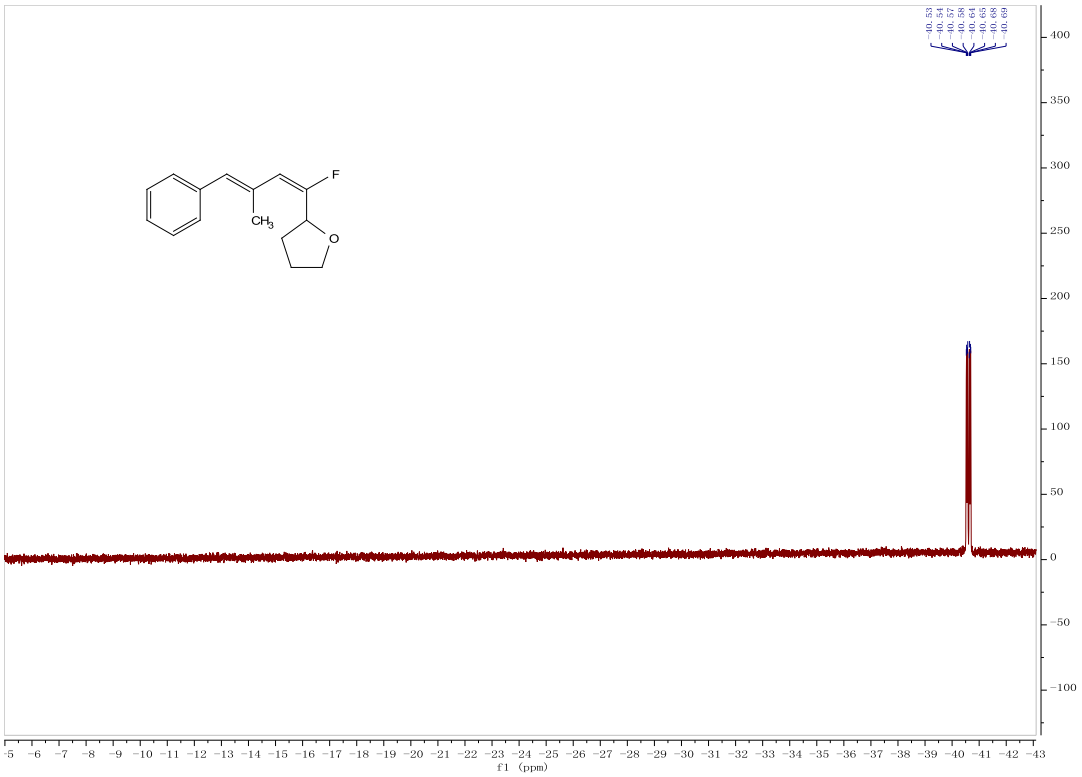
^{1}H NMR spectrum of **3ta**



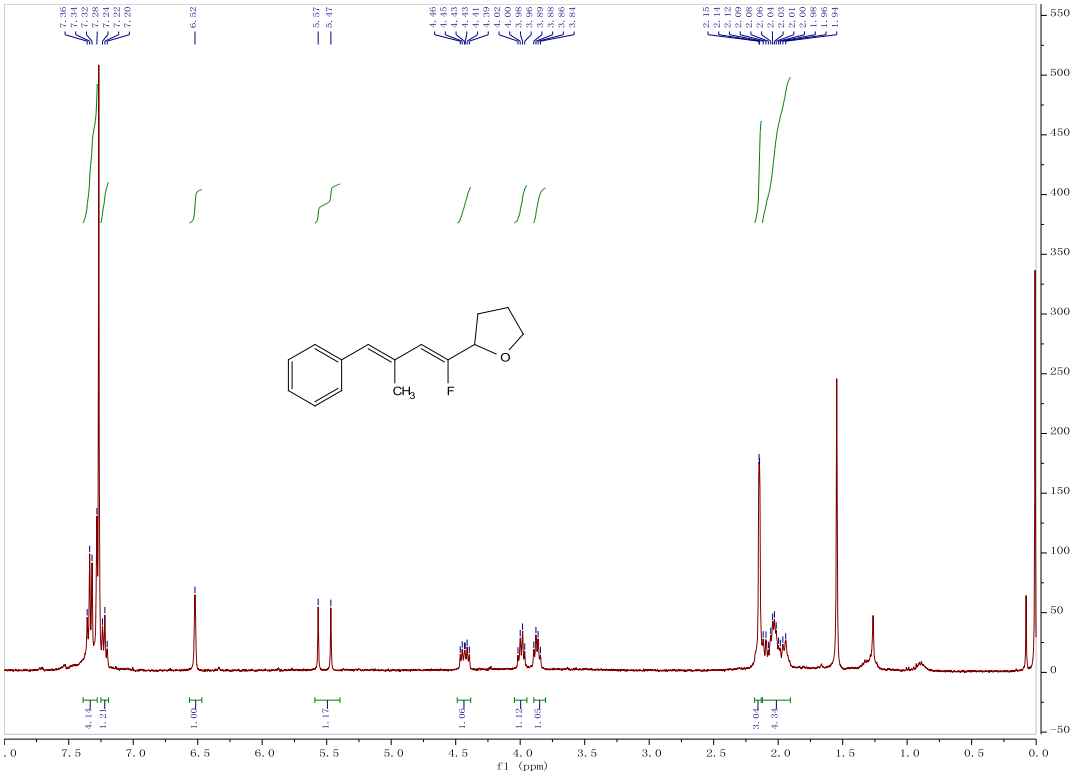
^{13}C NMR spectrum of **3ta**



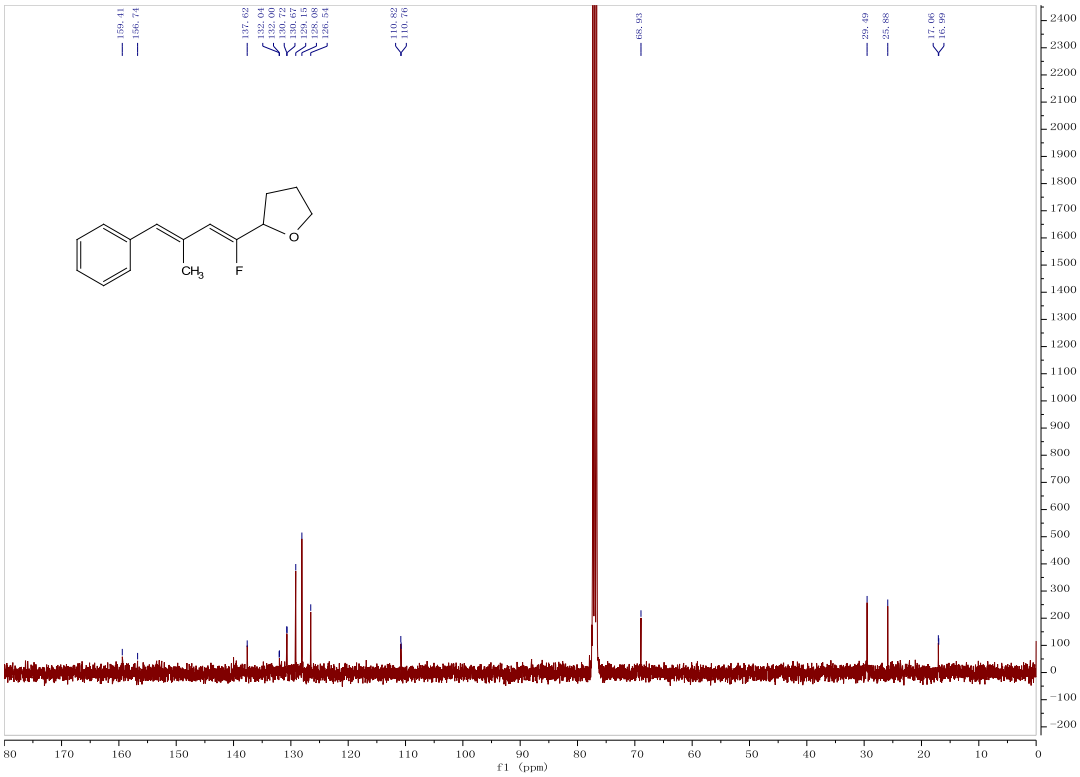
^{19}F NMR spectrum of **3ta**



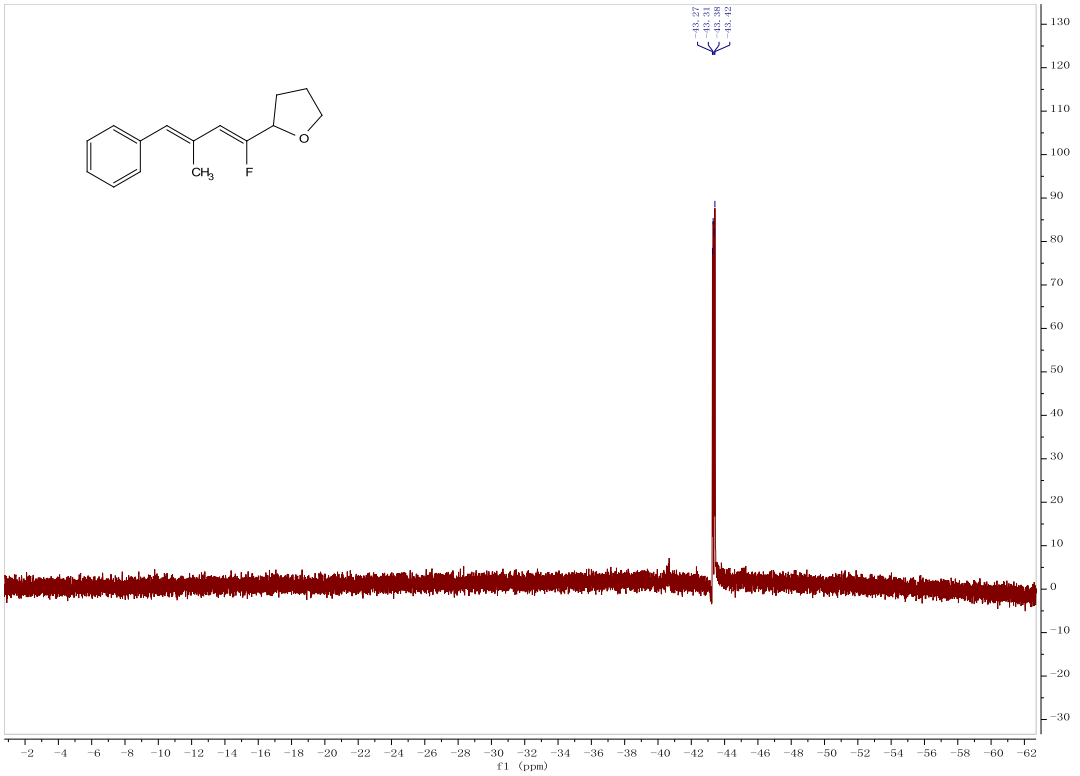
^{1}H NMR spectrum of **3tb**



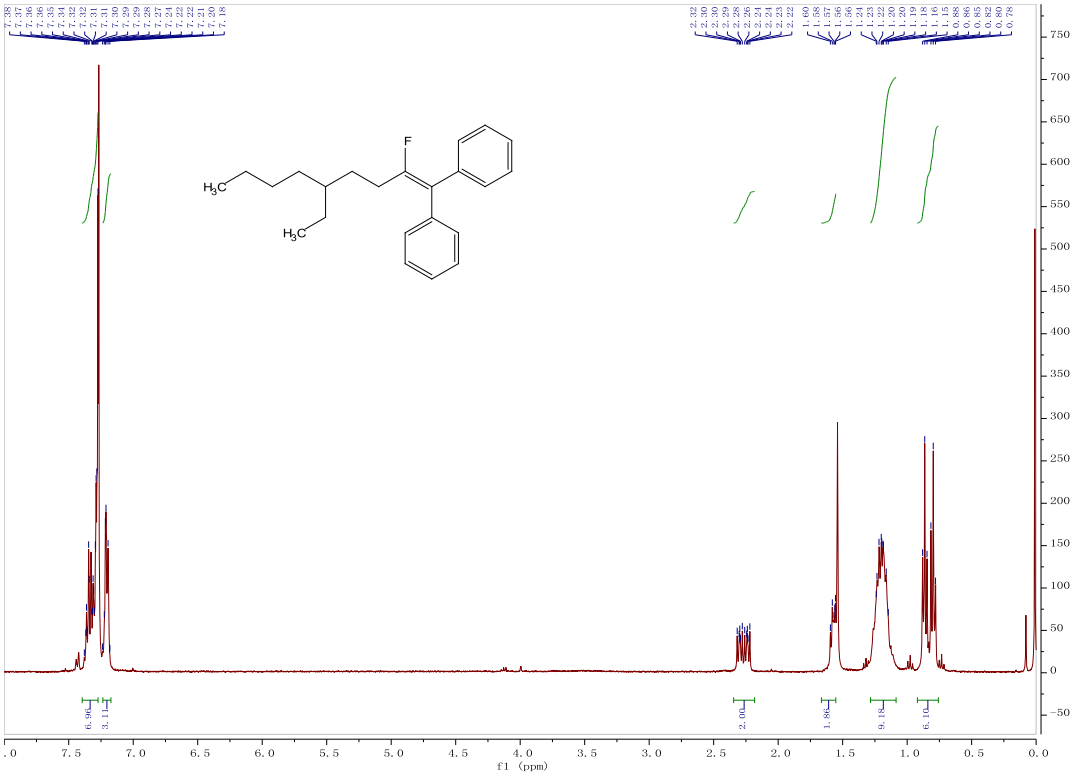
^{13}C NMR spectrum of **3tb**



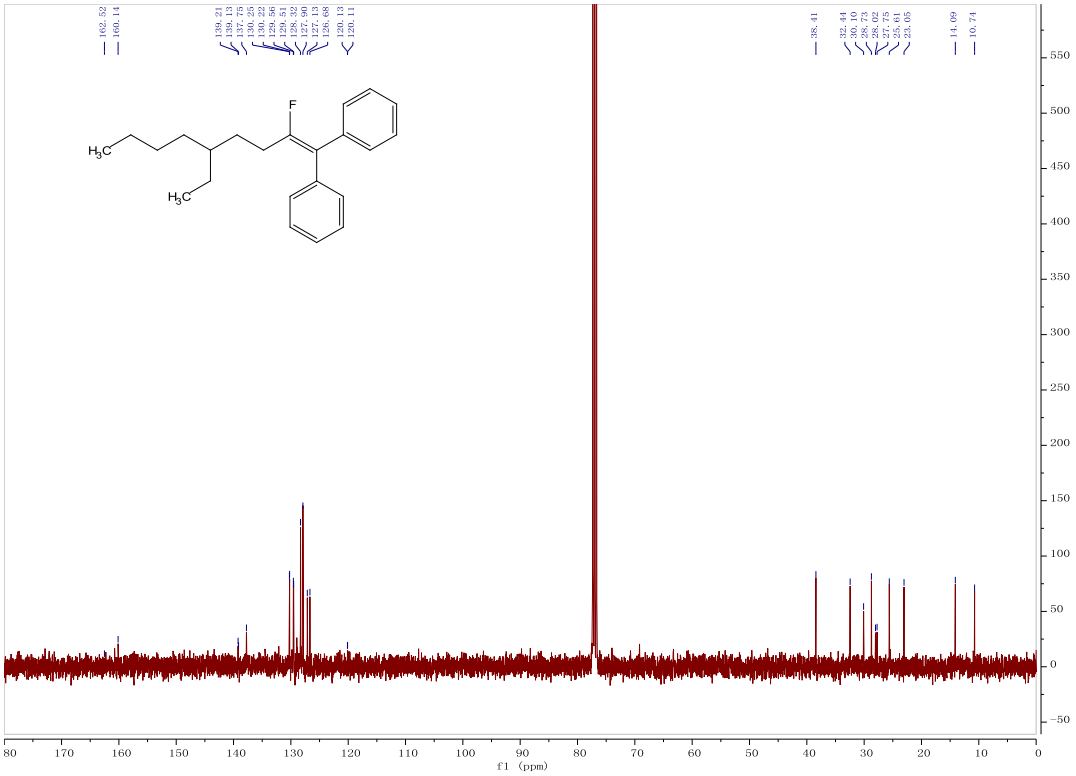
^{19}F NMR spectrum of **3tb**



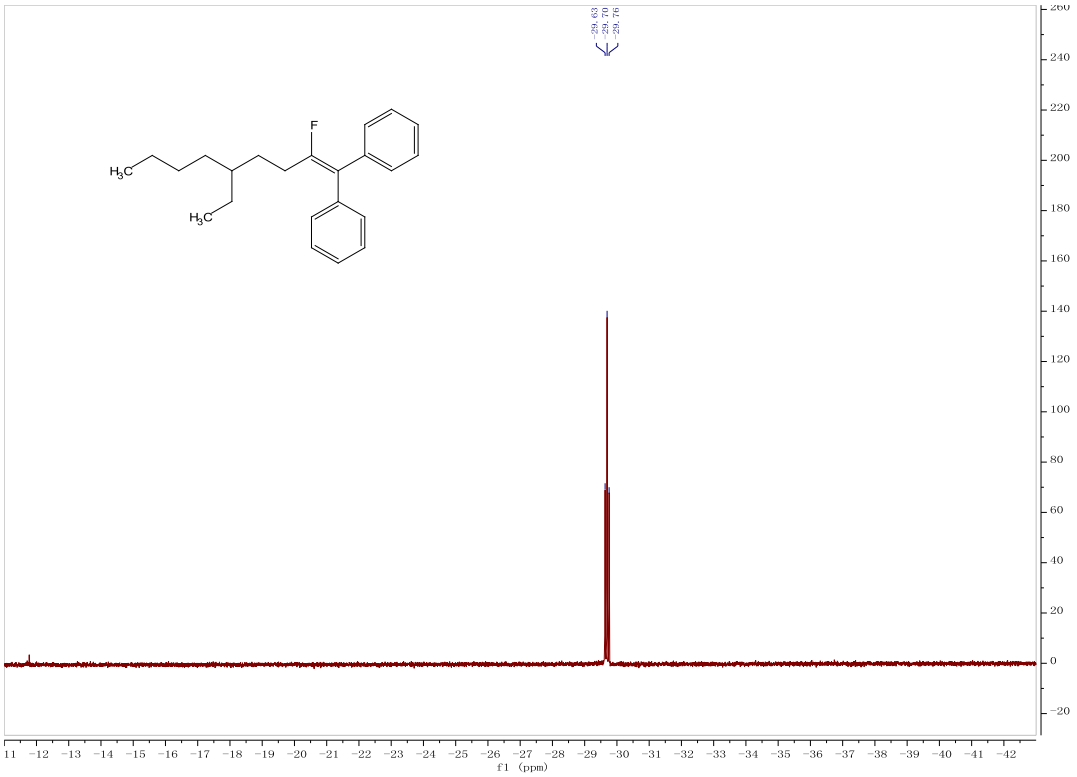
^{1}H NMR spectrum of **4a**



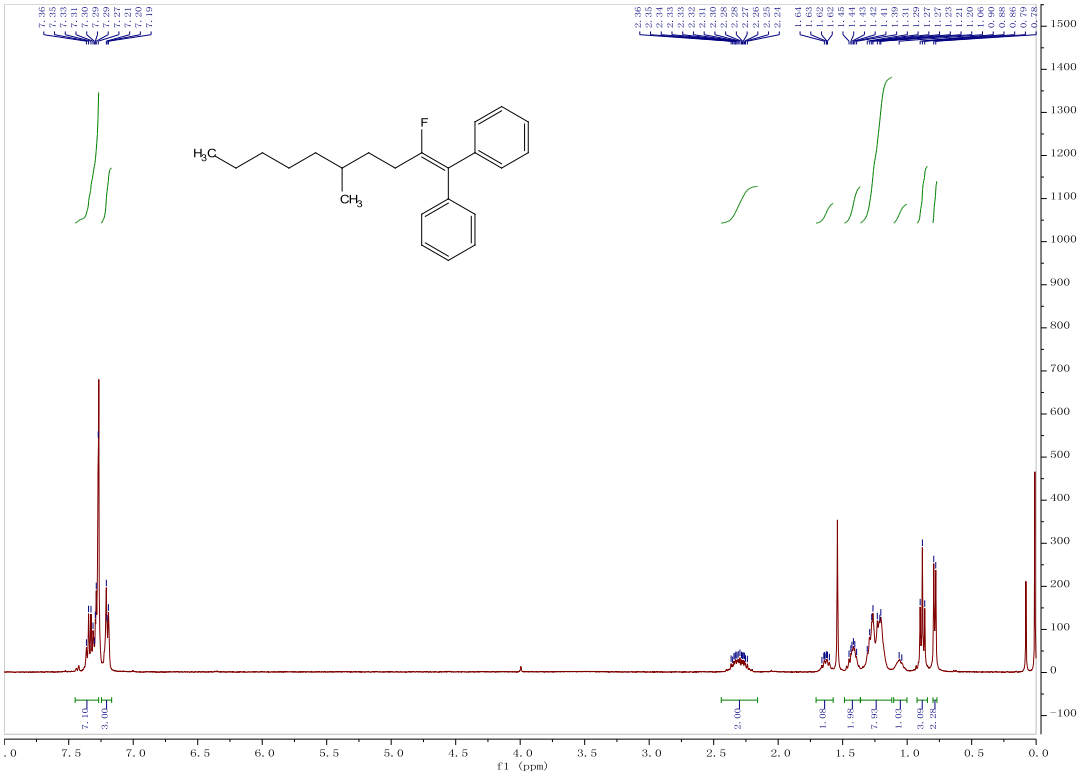
^{13}C NMR spectrum of **4a**



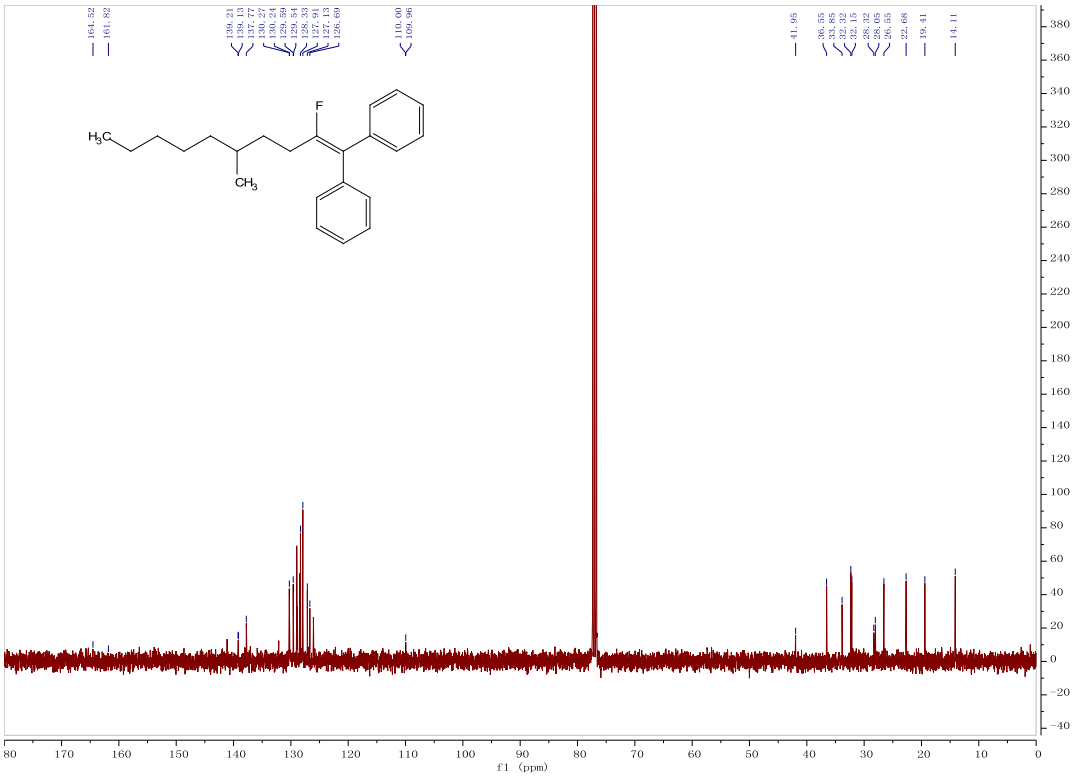
^{19}F NMR spectrum of **4a**



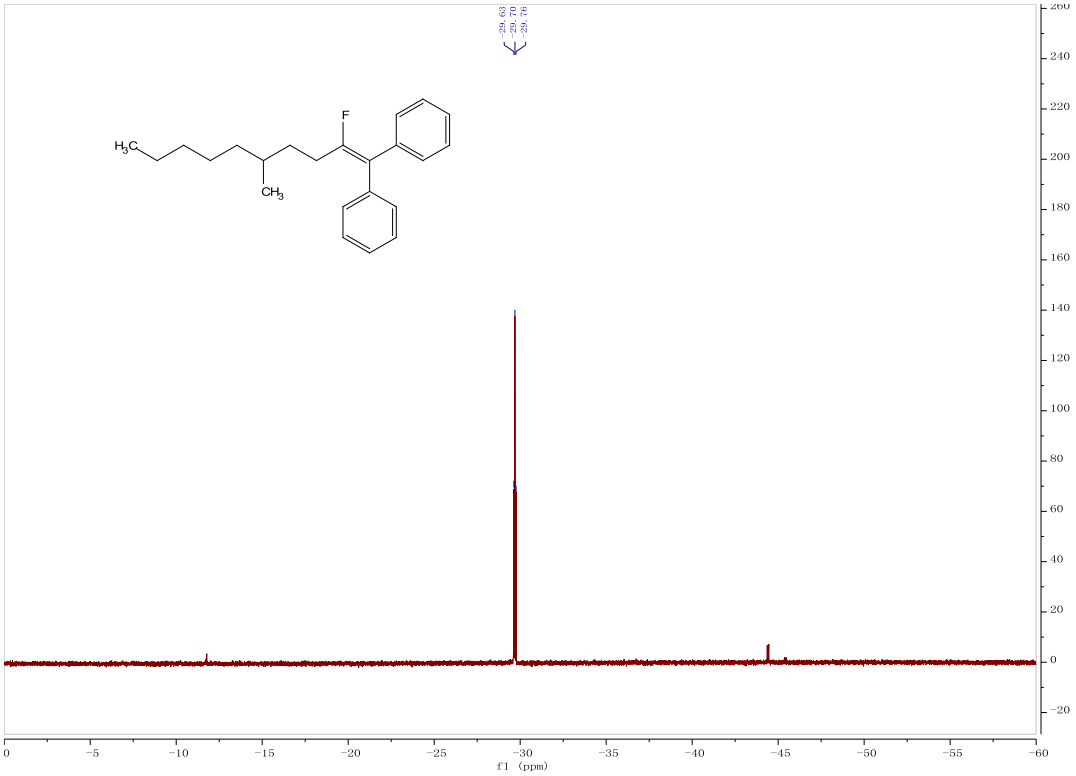
^{1}H NMR spectrum of **4b**



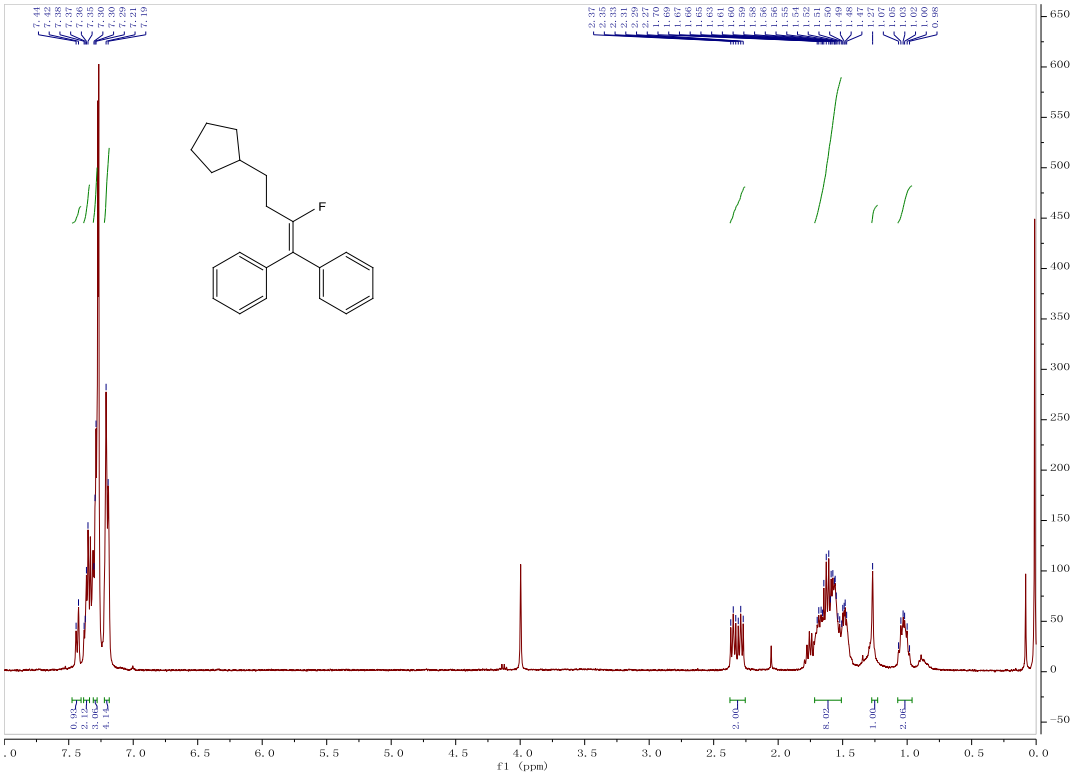
^{13}C NMR spectrum of **4b**



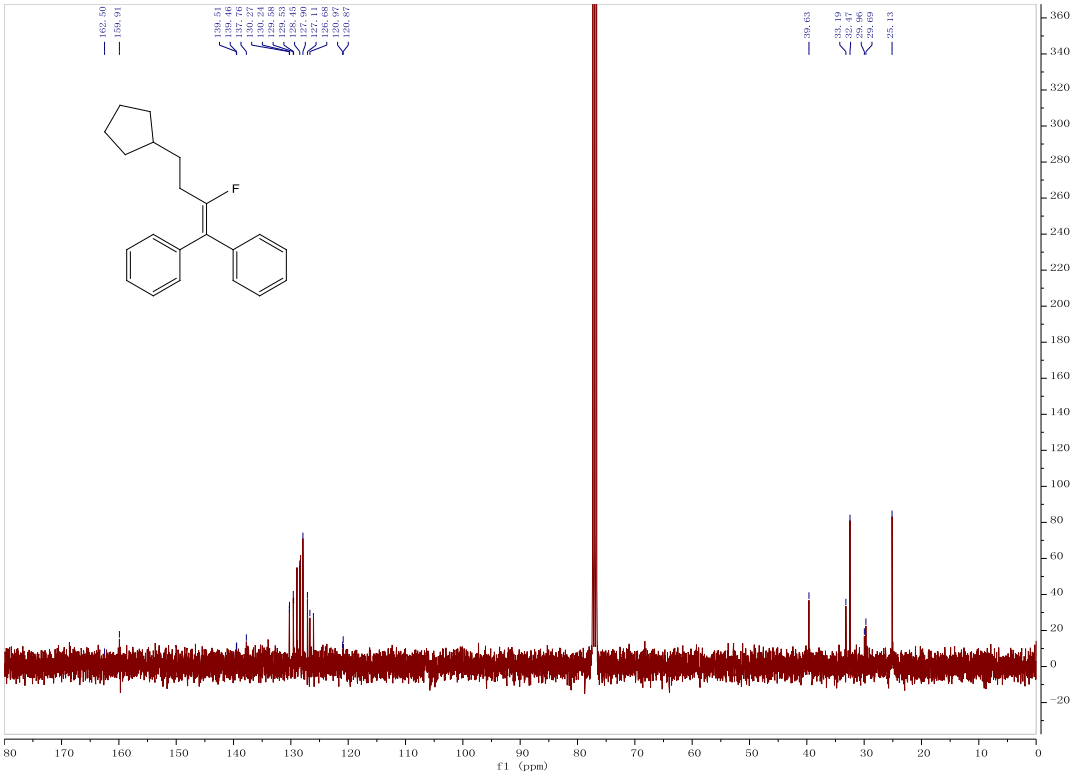
^{19}F NMR spectrum of **4b**



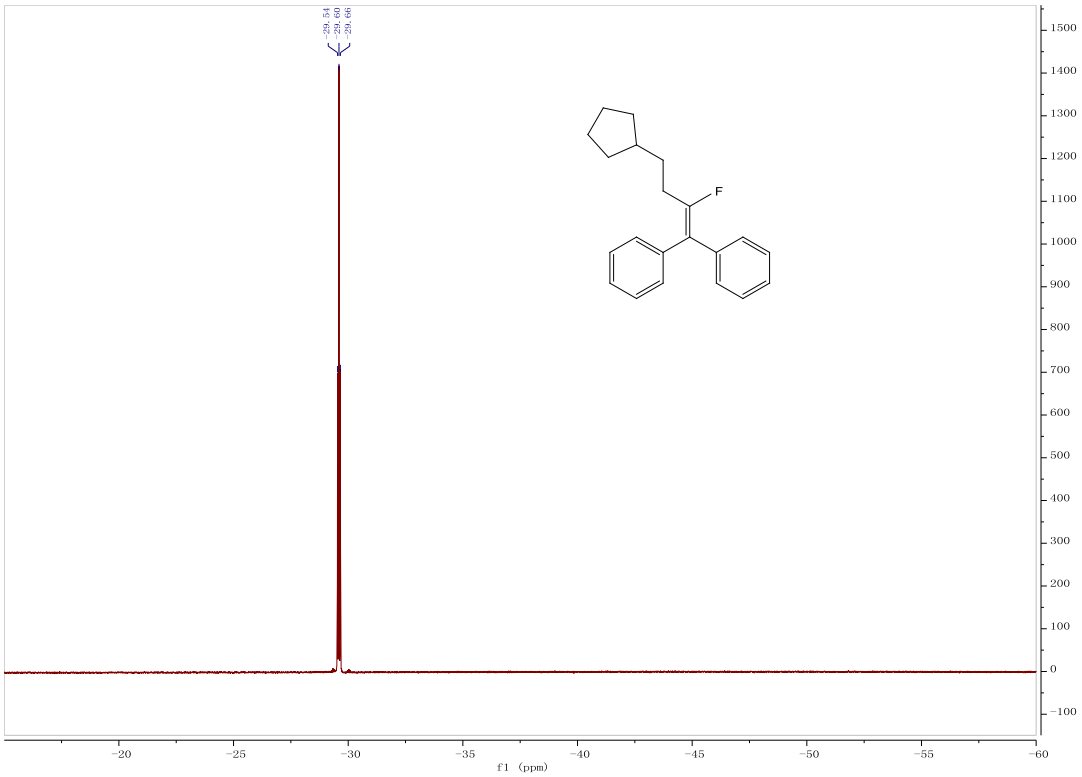
^{1}H NMR spectrum of **4c**



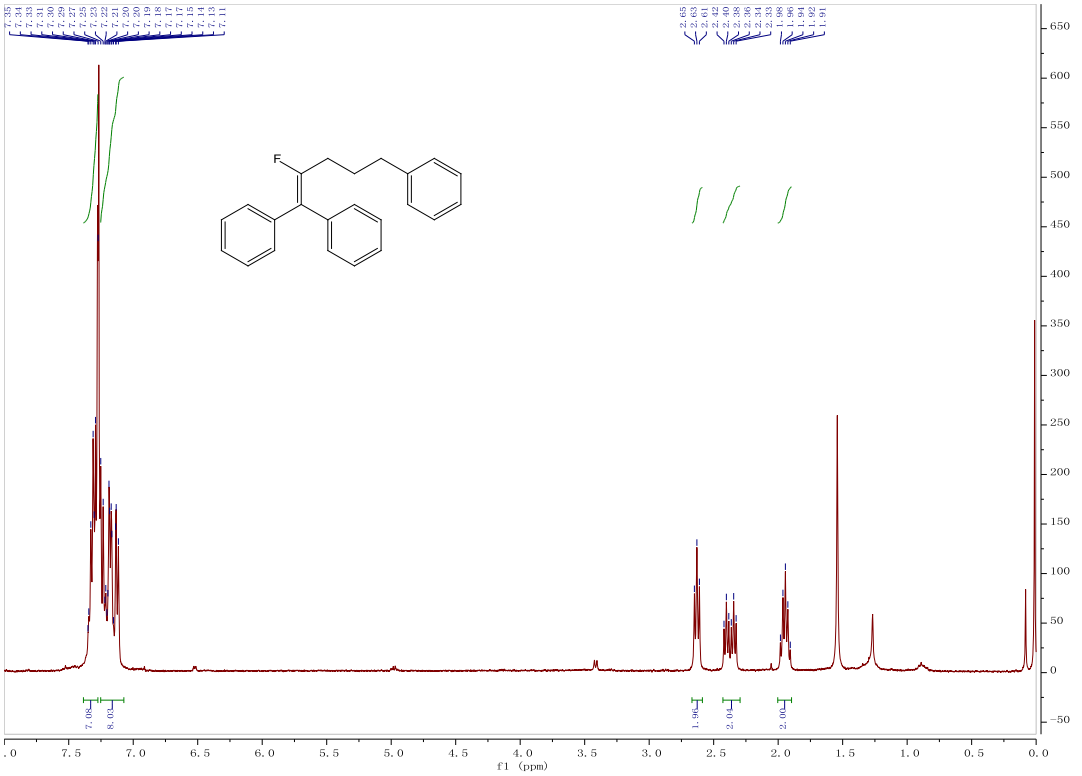
^{13}C NMR spectrum of **4c**



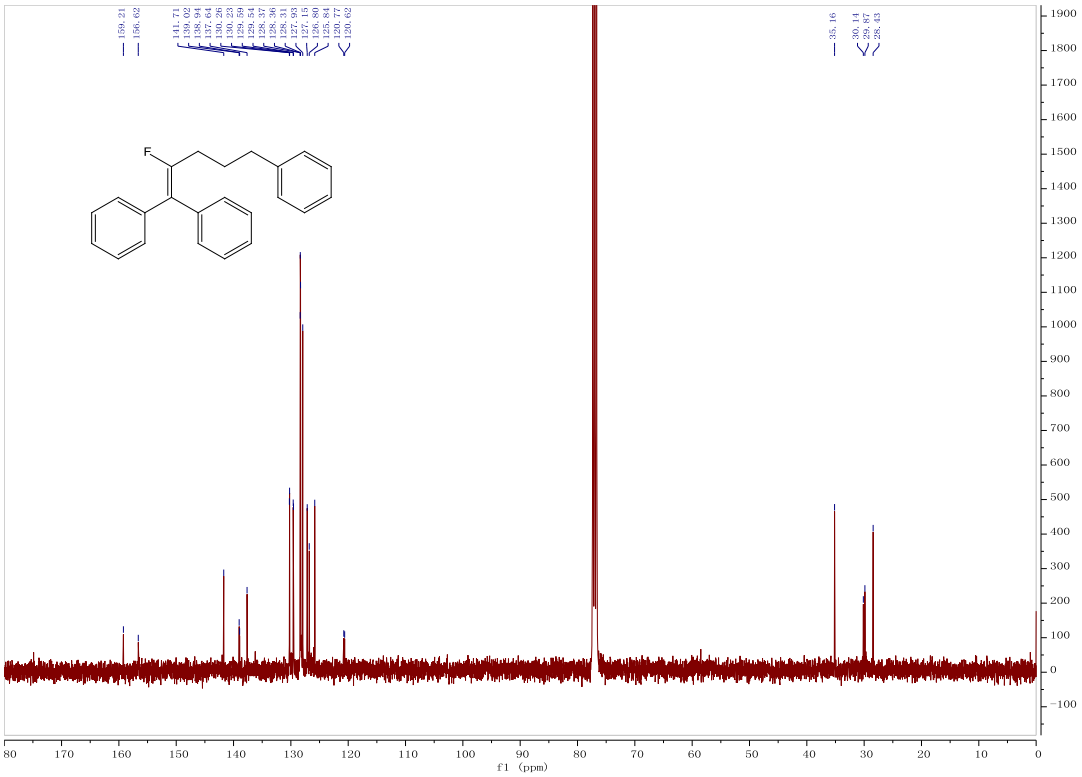
^{19}F NMR spectrum of **4c**



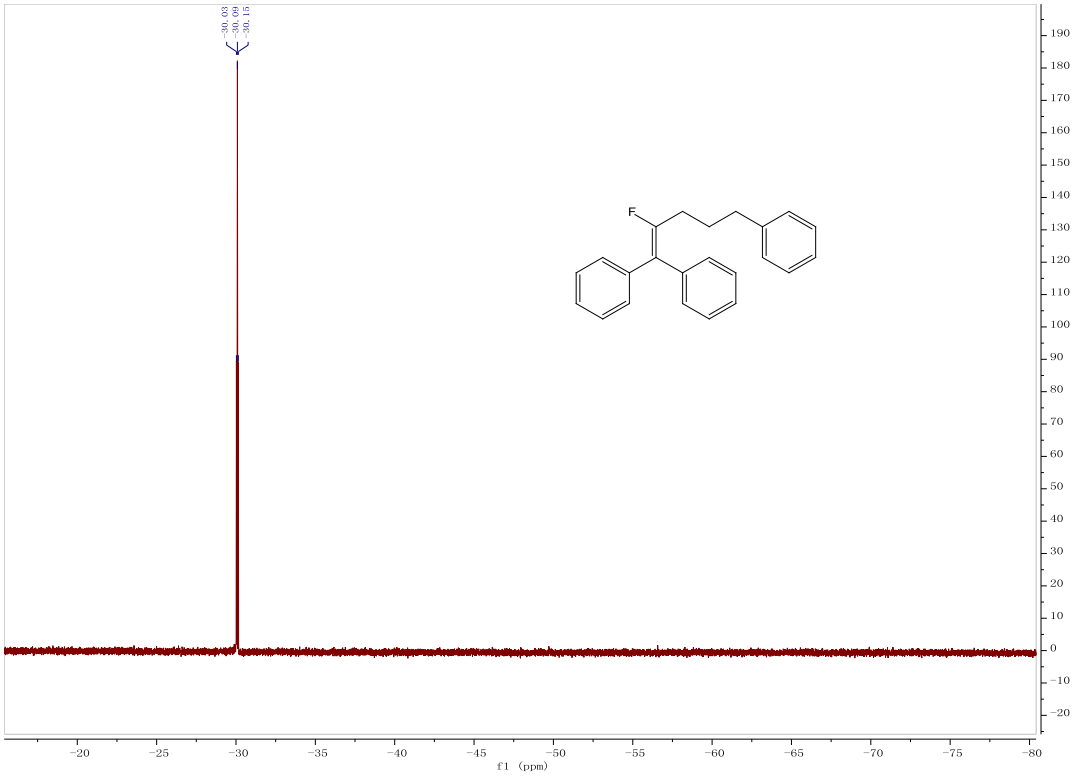
^{1}H NMR spectrum of **4d**



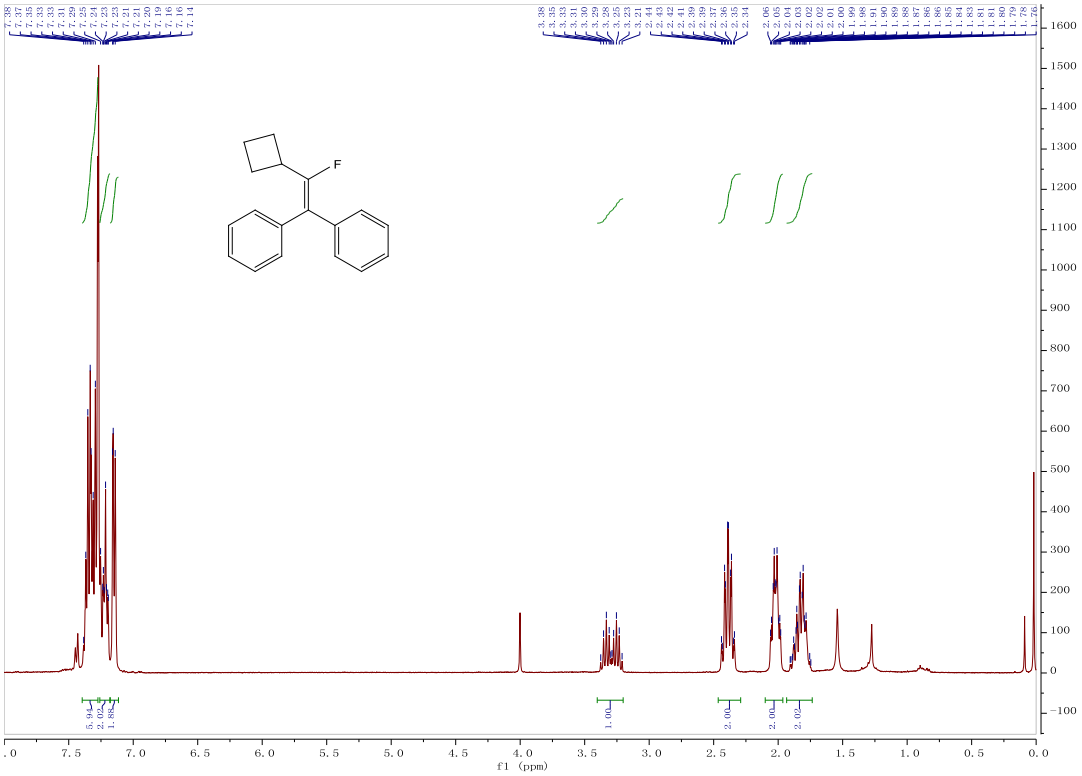
^{13}C NMR spectrum of **4d**



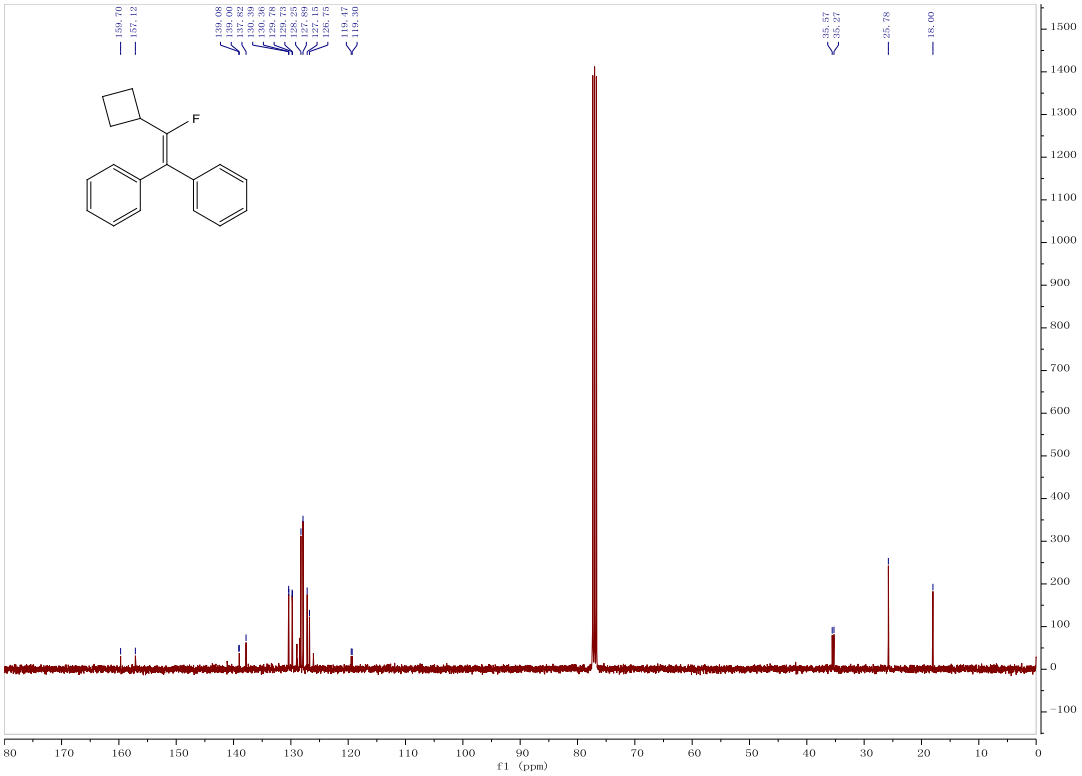
^{19}F NMR spectrum of **4d**



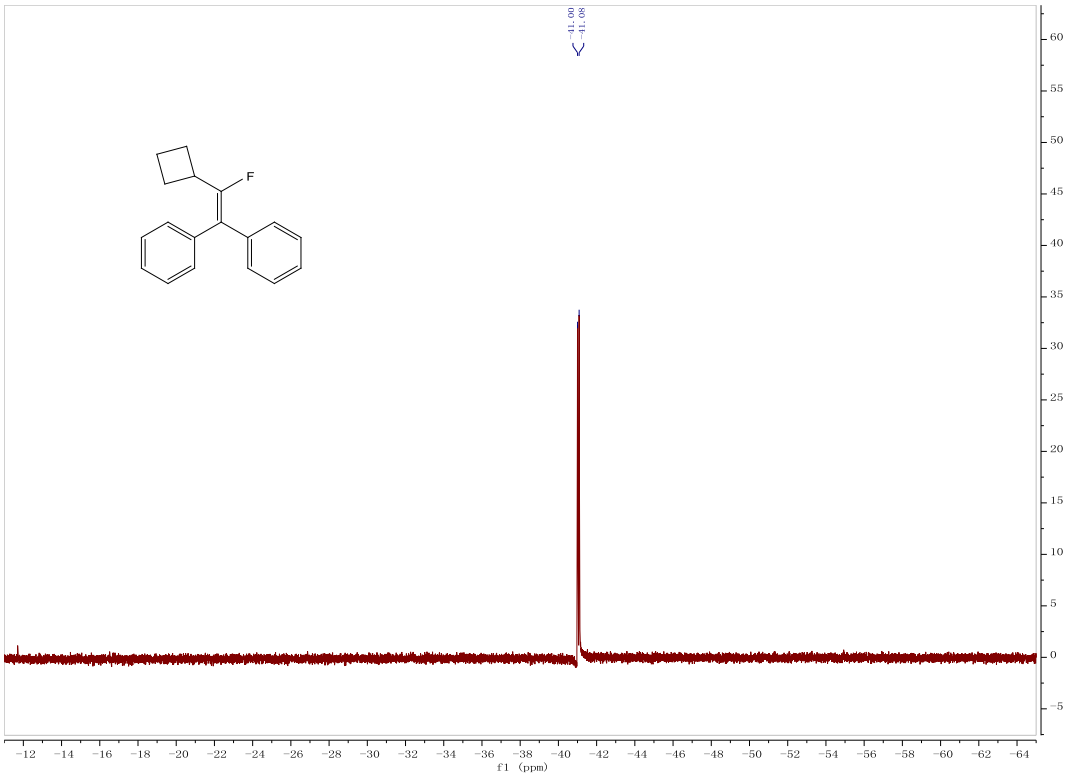
^{1}H NMR spectrum of **4e**



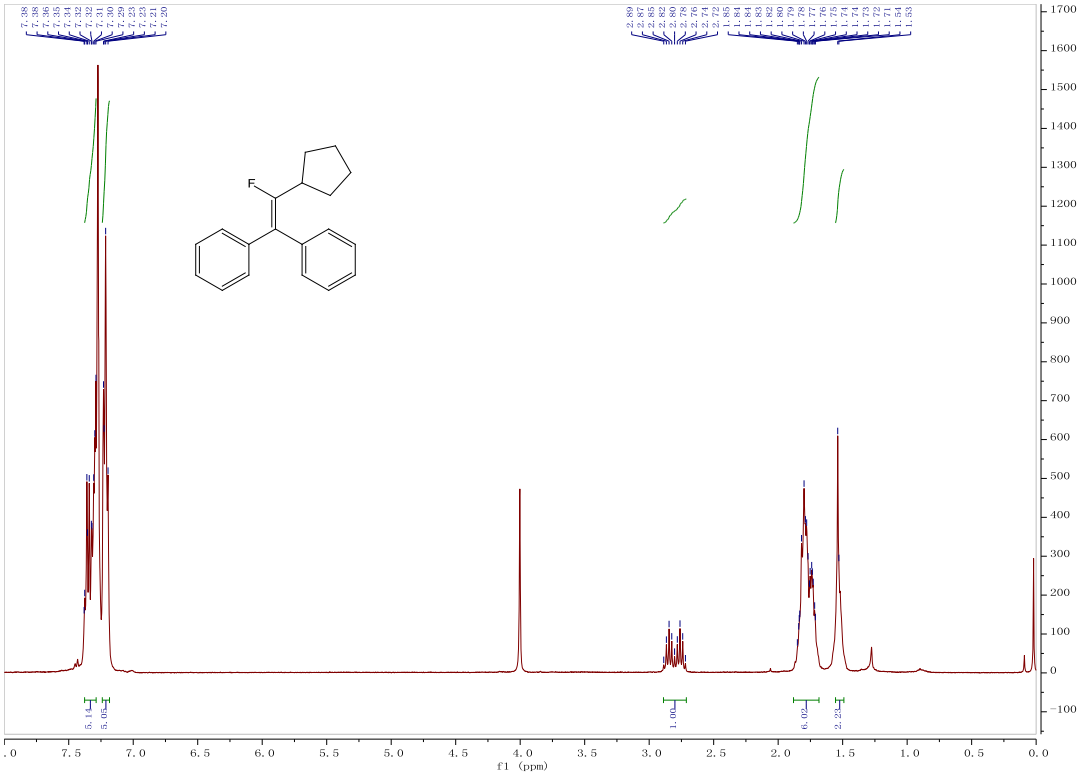
^{13}C NMR spectrum of **4e**



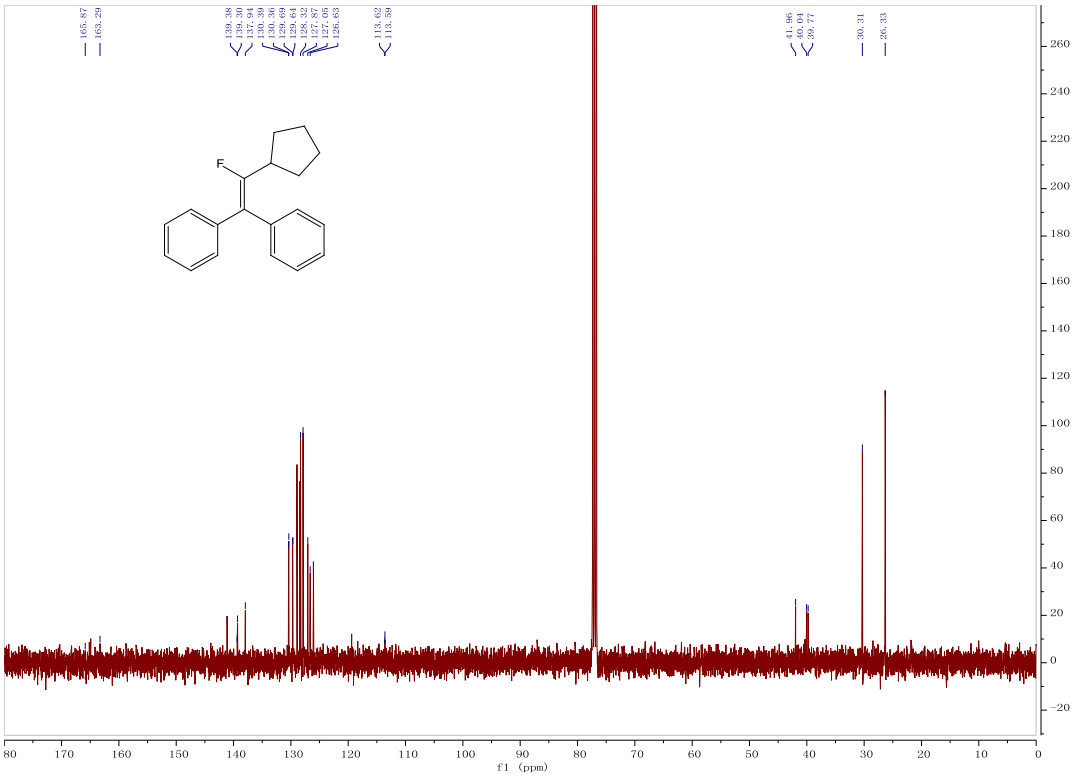
^{19}F NMR spectrum of **4e**



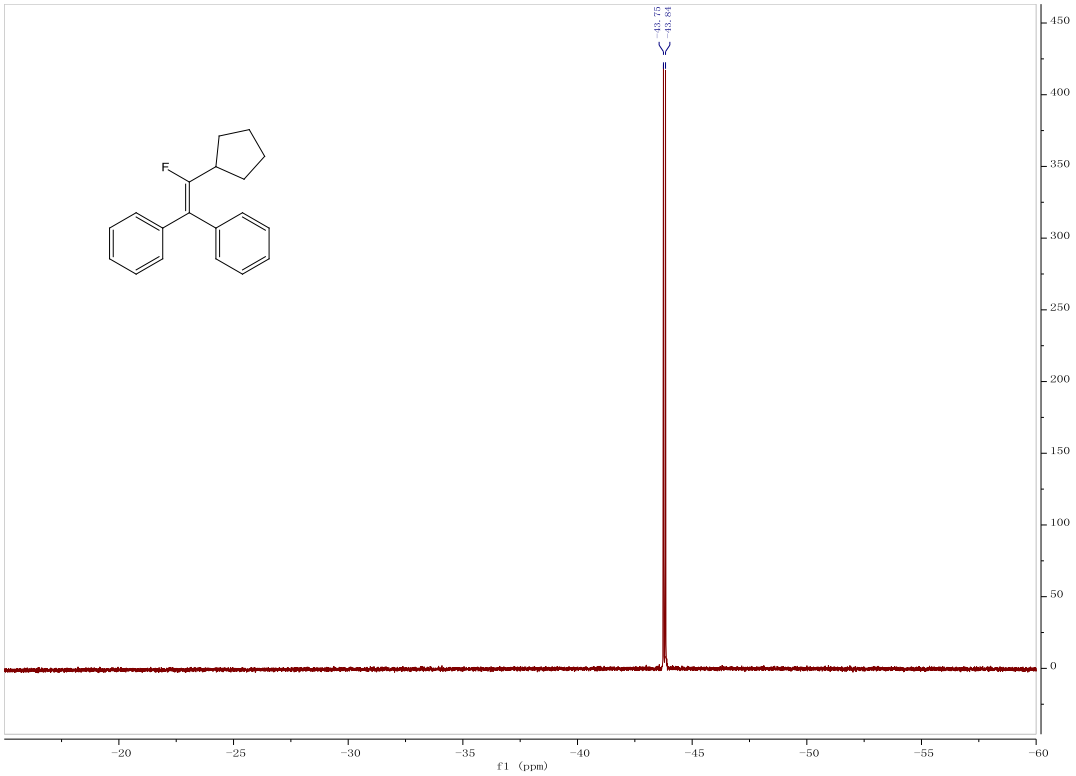
^{1}H NMR spectrum of **4f**



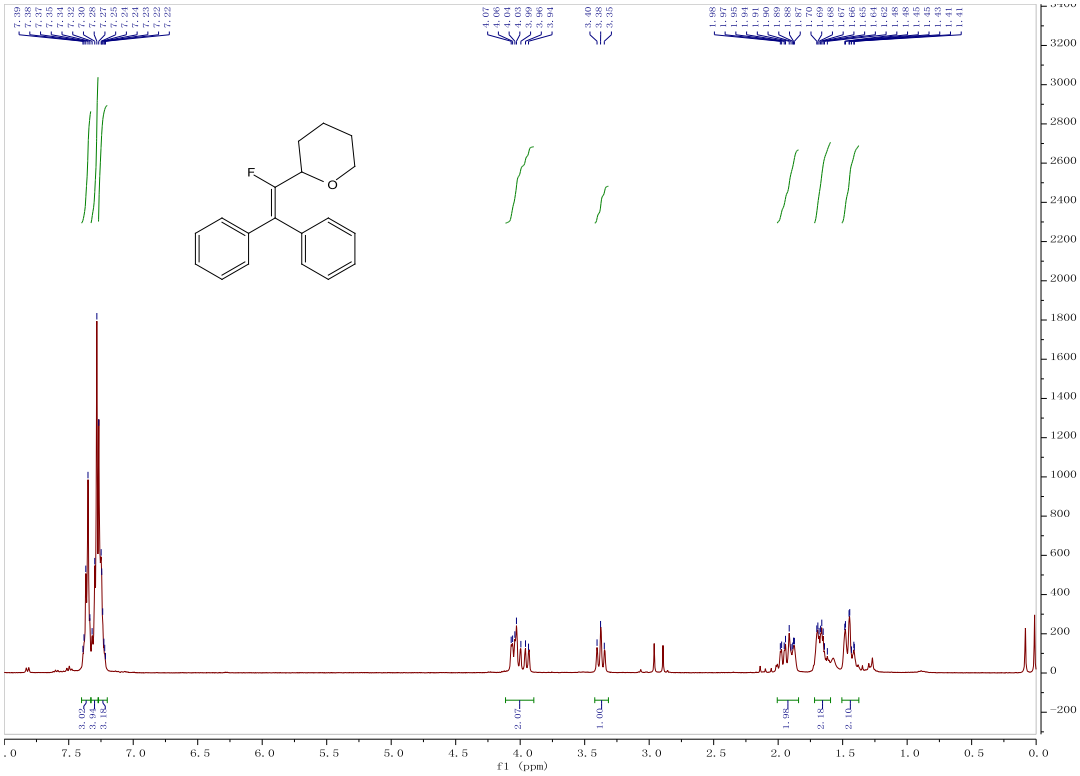
^{13}C NMR spectrum of **4f**



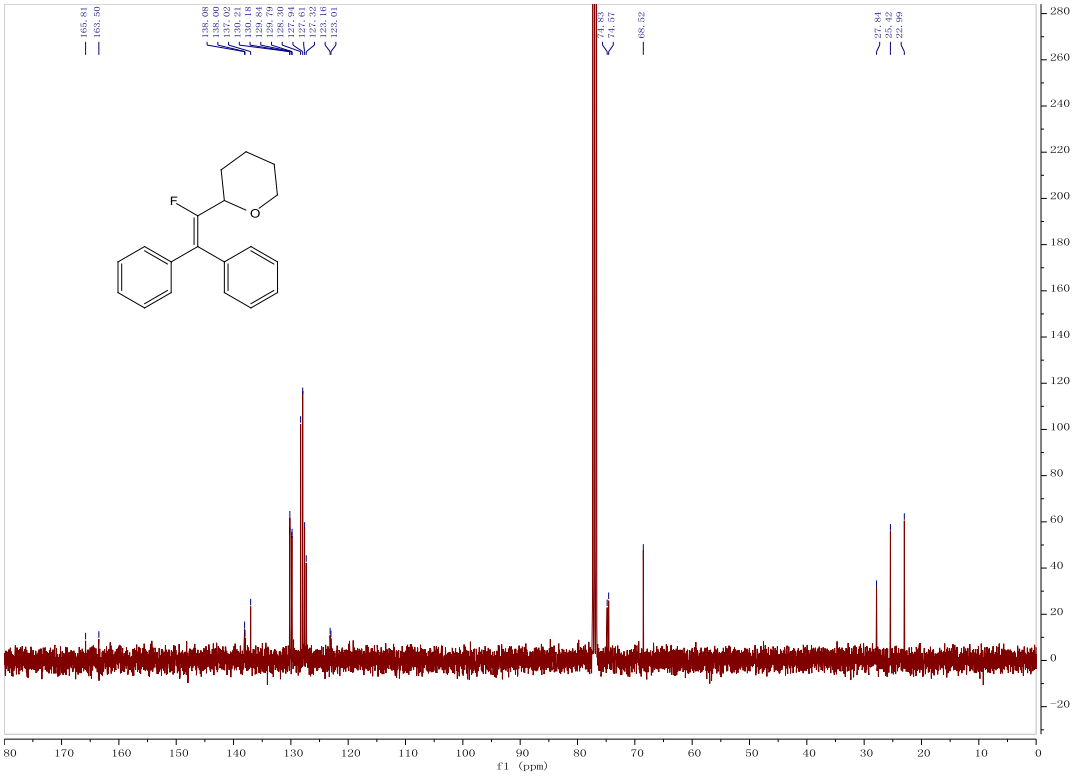
^{19}F NMR spectrum of **4f**



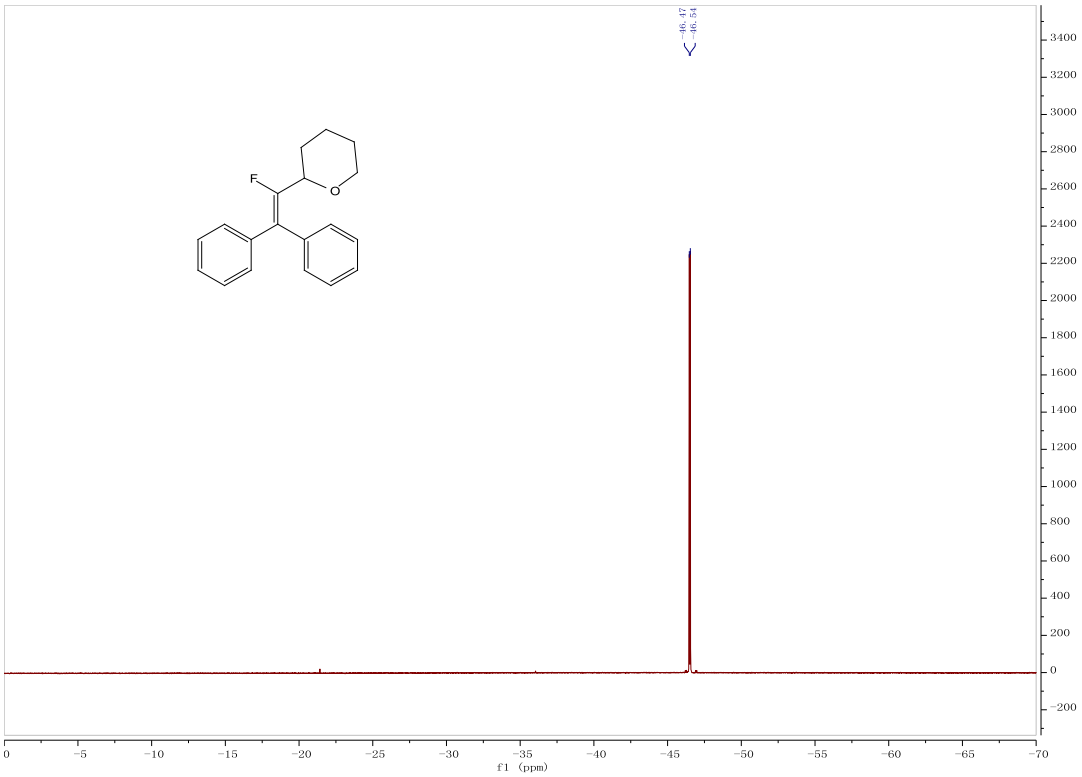
^{1}H NMR spectrum of **4g**



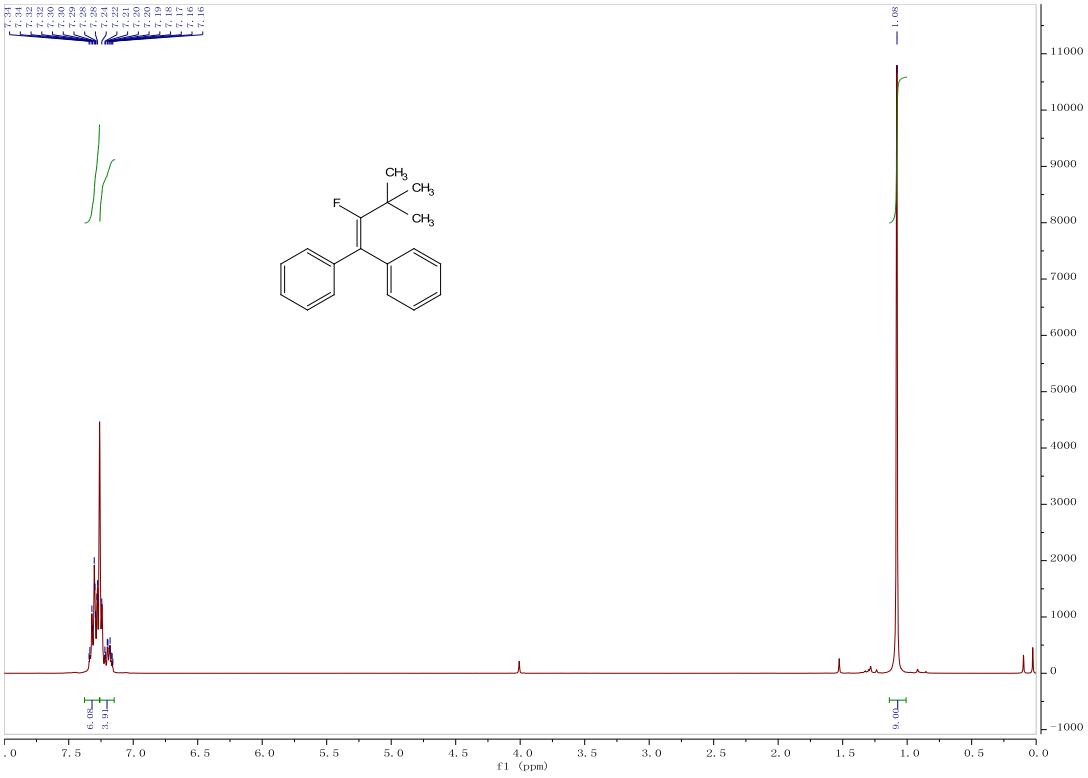
^{13}C NMR spectrum of **4g**



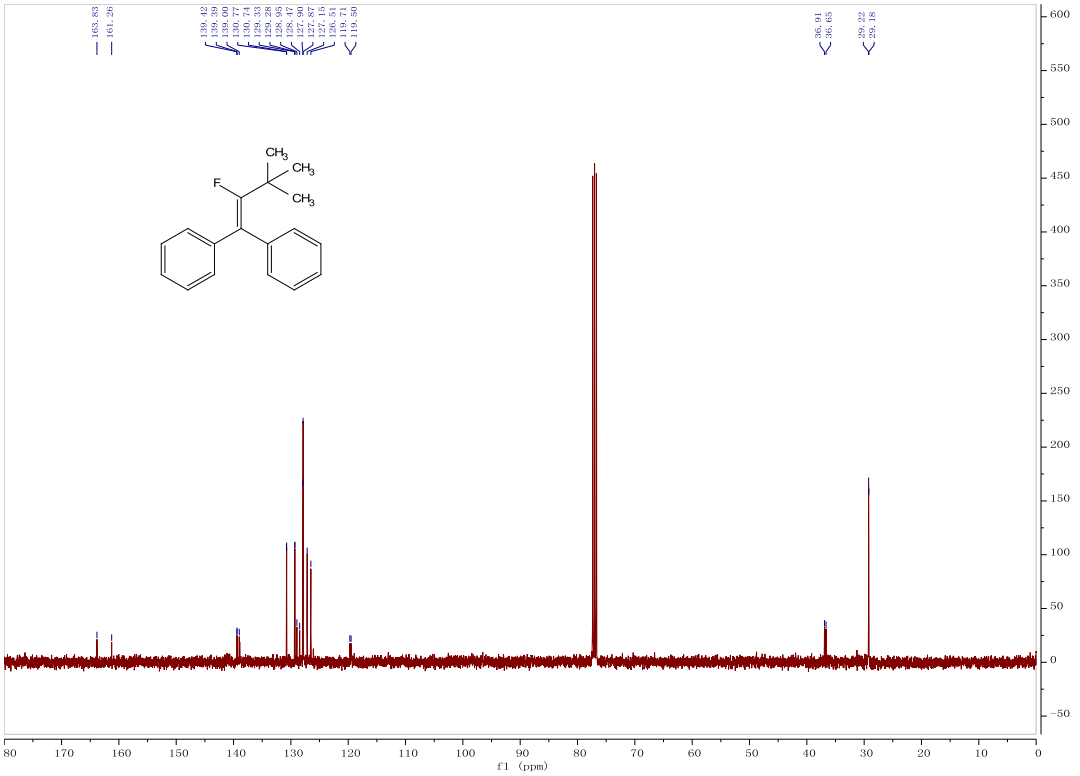
^{19}F NMR spectrum of **4g**



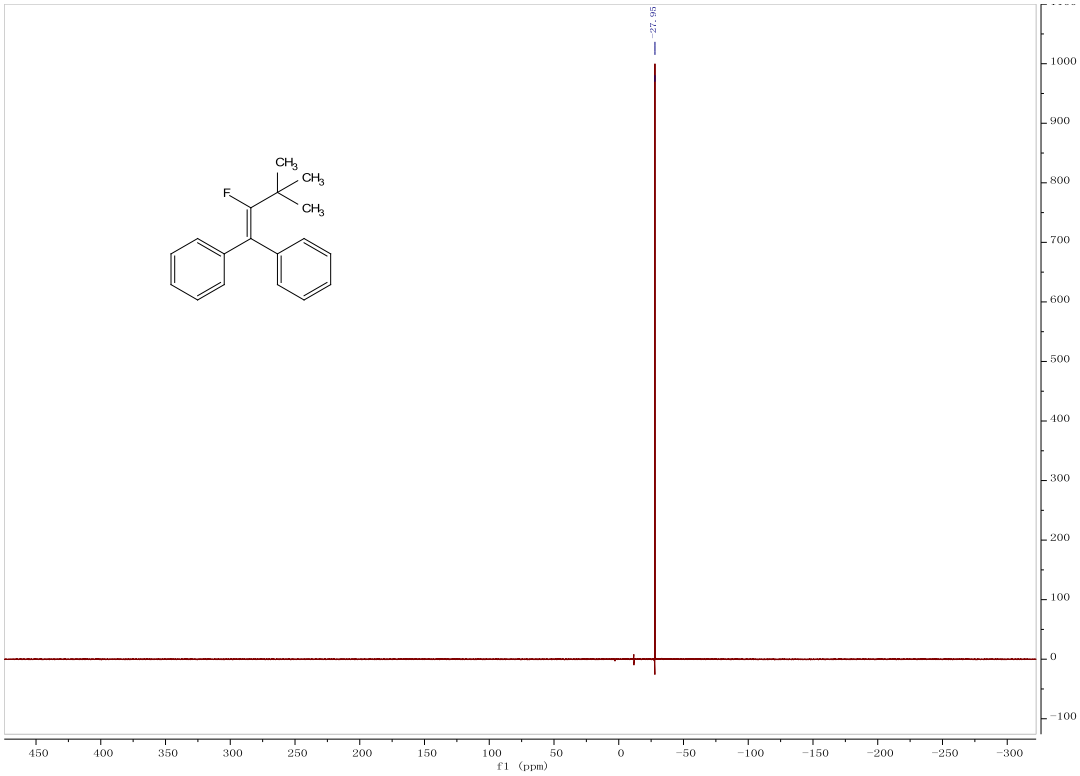
^{1}H NMR spectrum of **4h**



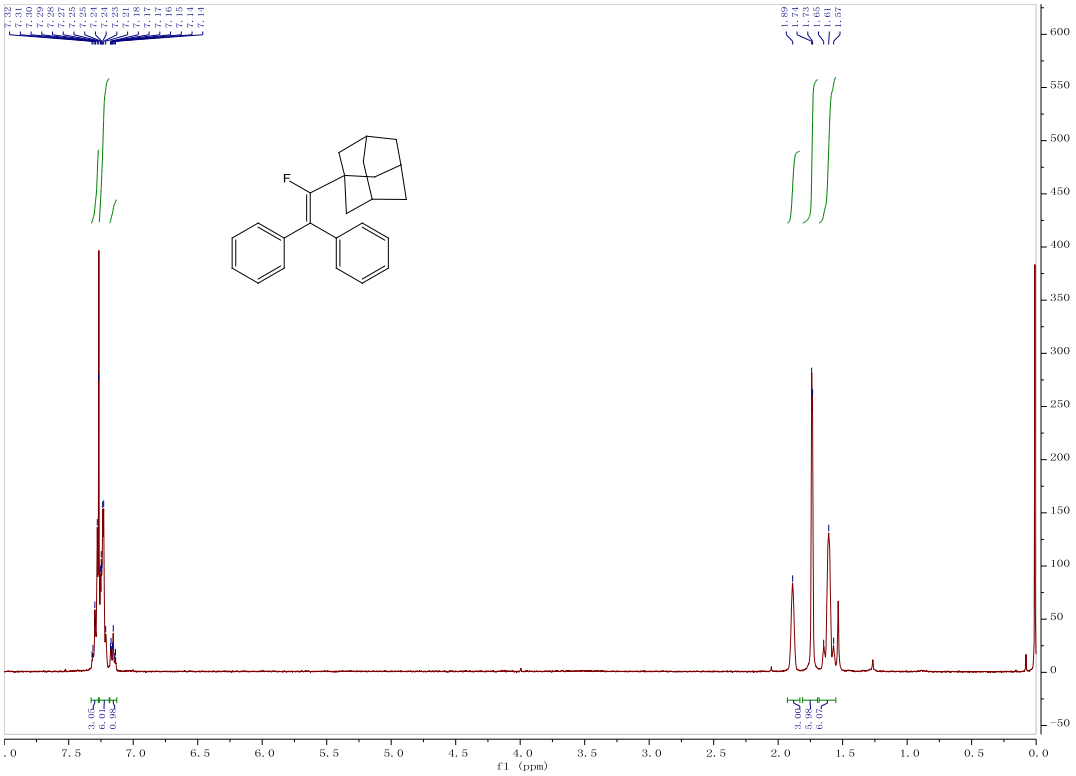
^{13}C NMR spectrum of **4h**



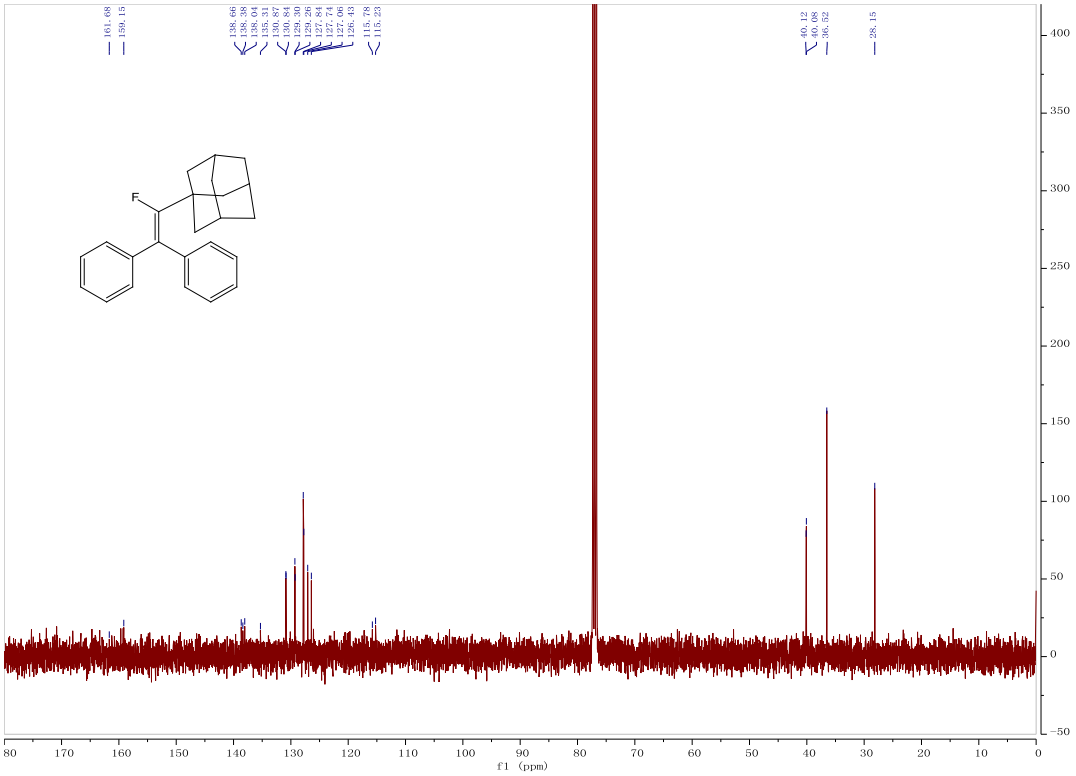
^{19}F NMR spectrum of **4h**



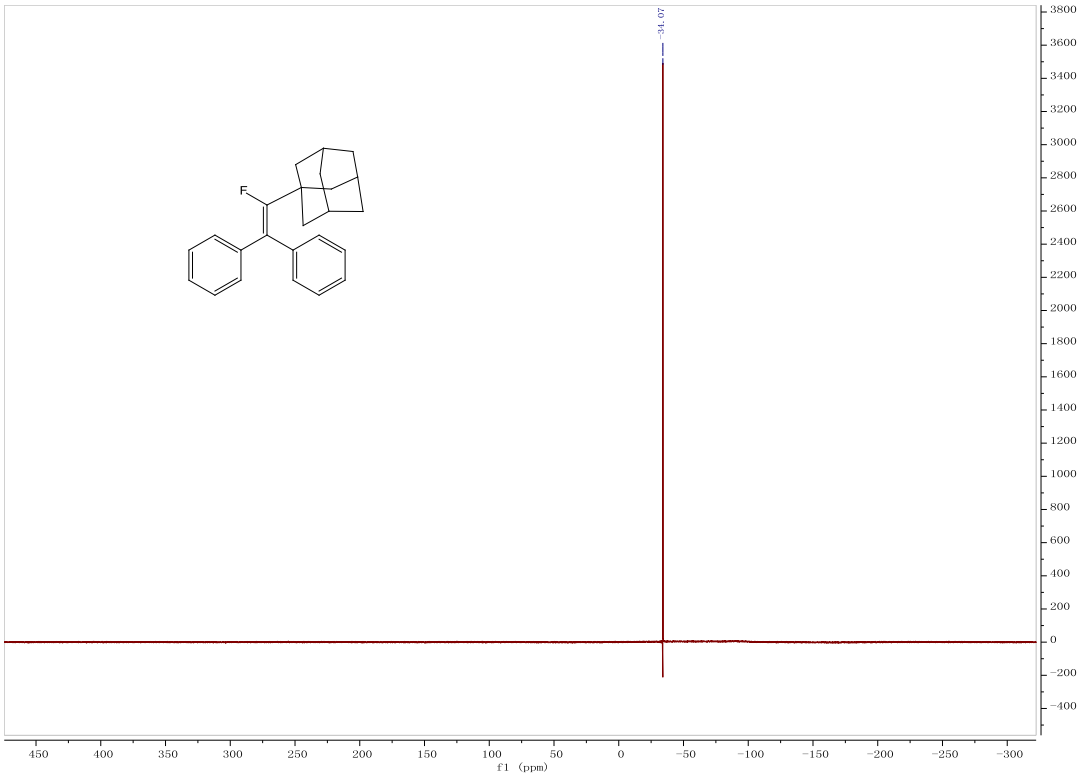
^{1}H NMR spectrum of **4i**



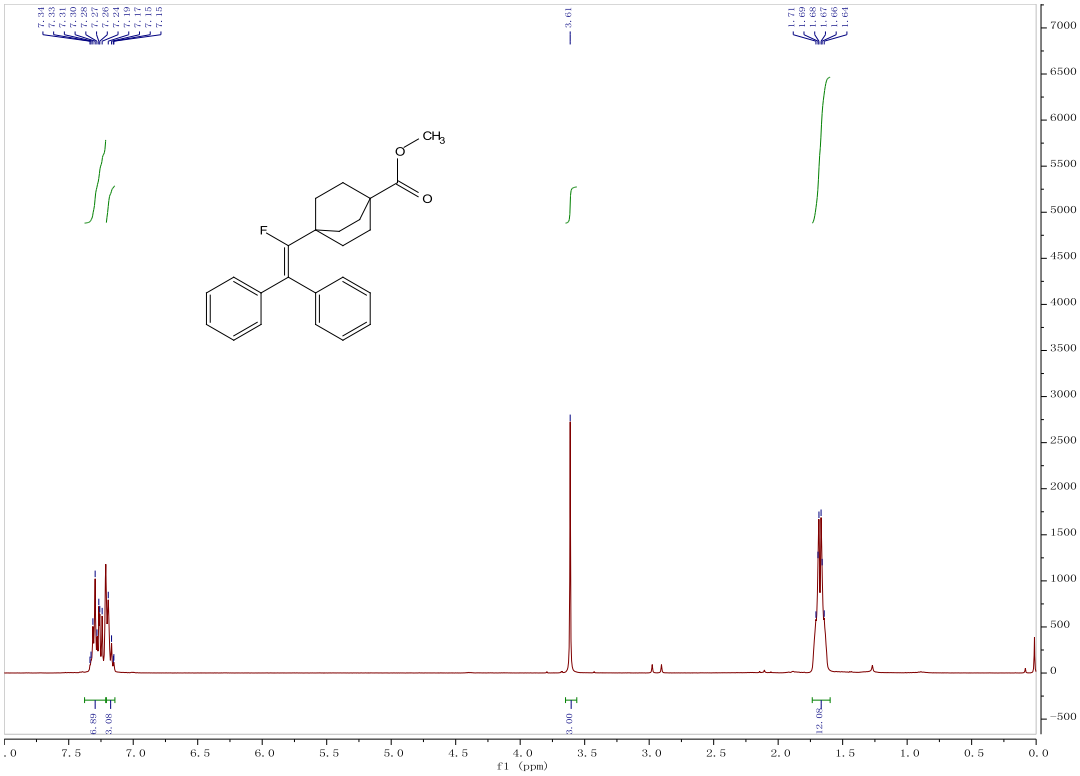
^{13}C NMR spectrum of **4i**



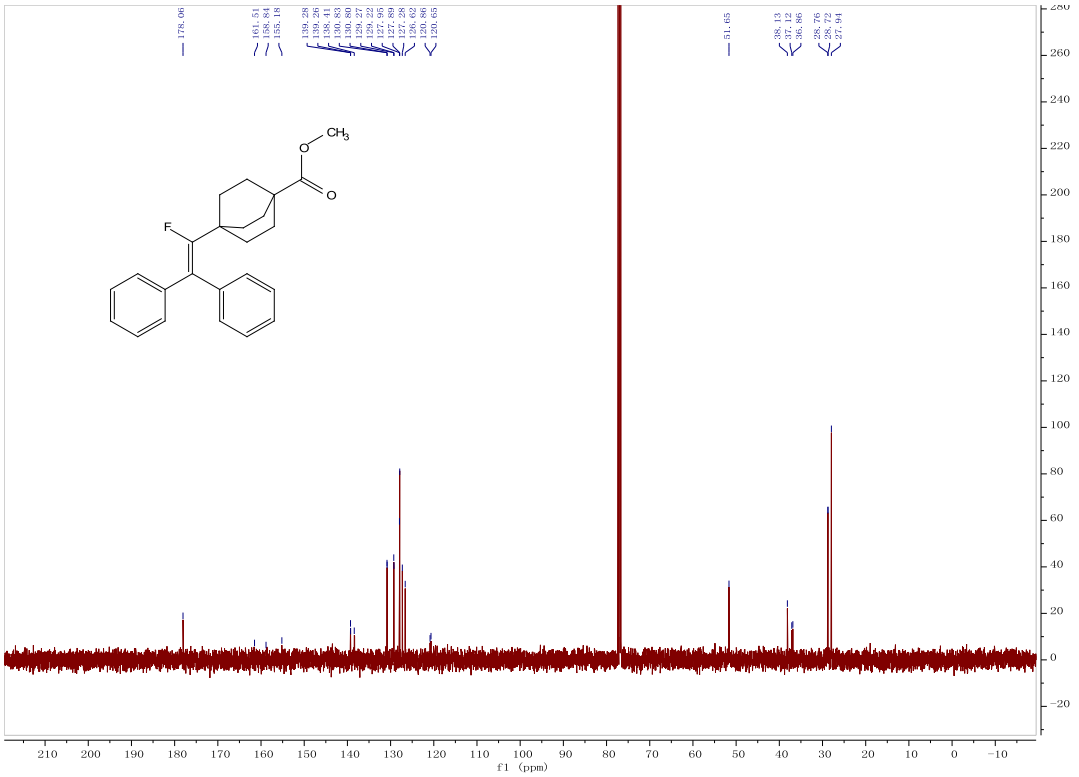
^{19}F NMR spectrum of **4i**



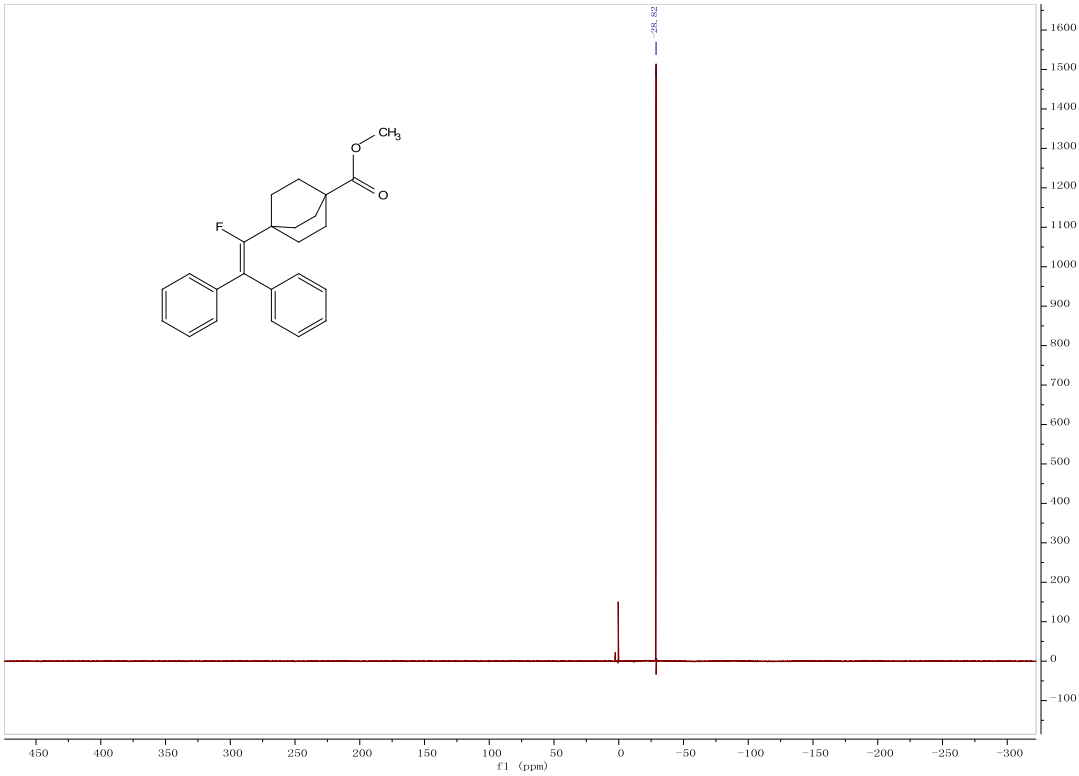
^{1}H NMR spectrum of **4j**



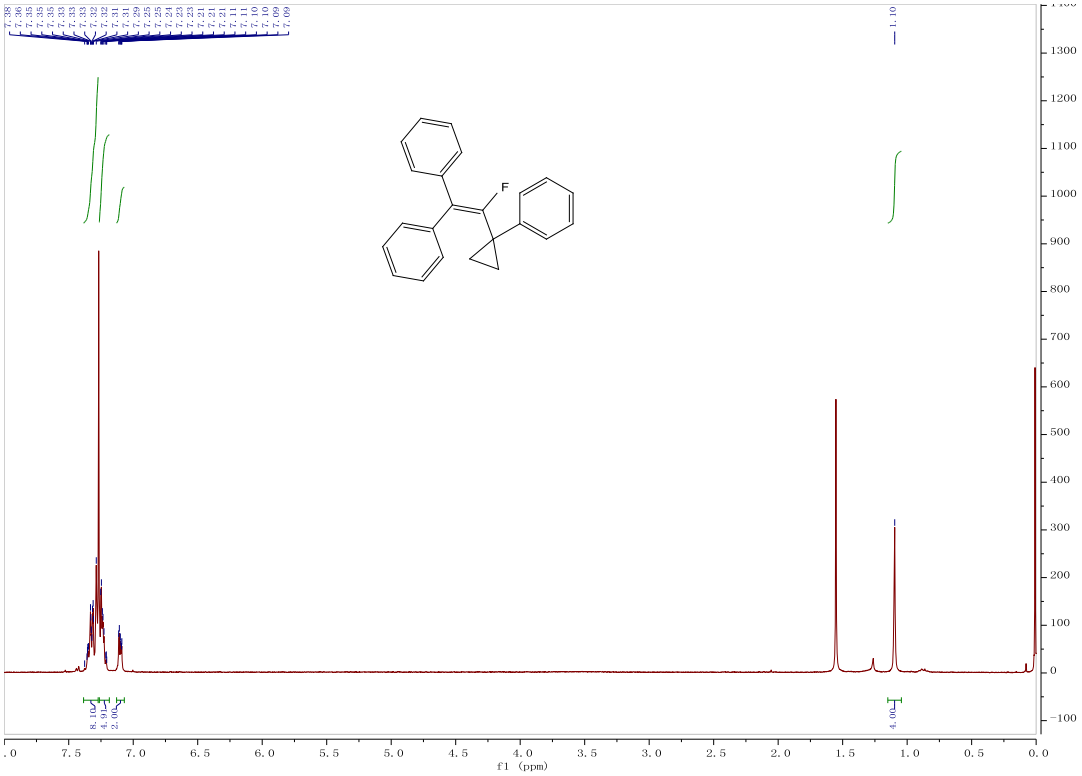
^{13}C NMR spectrum of **4j**



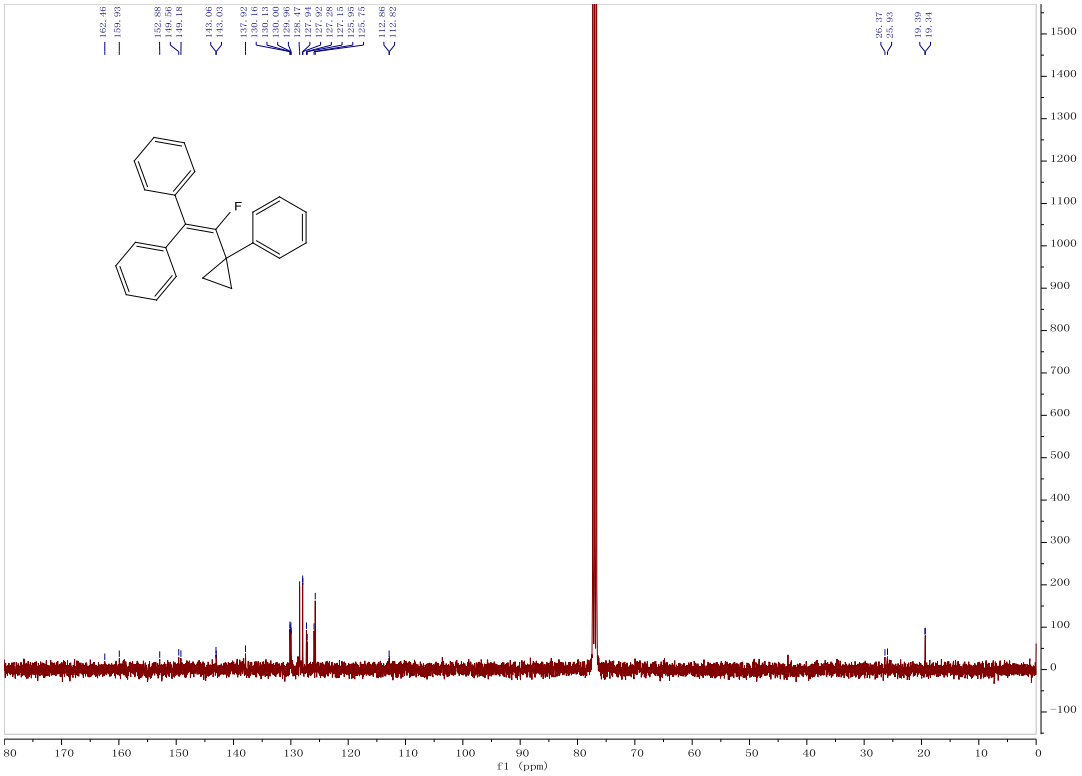
^{19}F NMR spectrum of **4j**



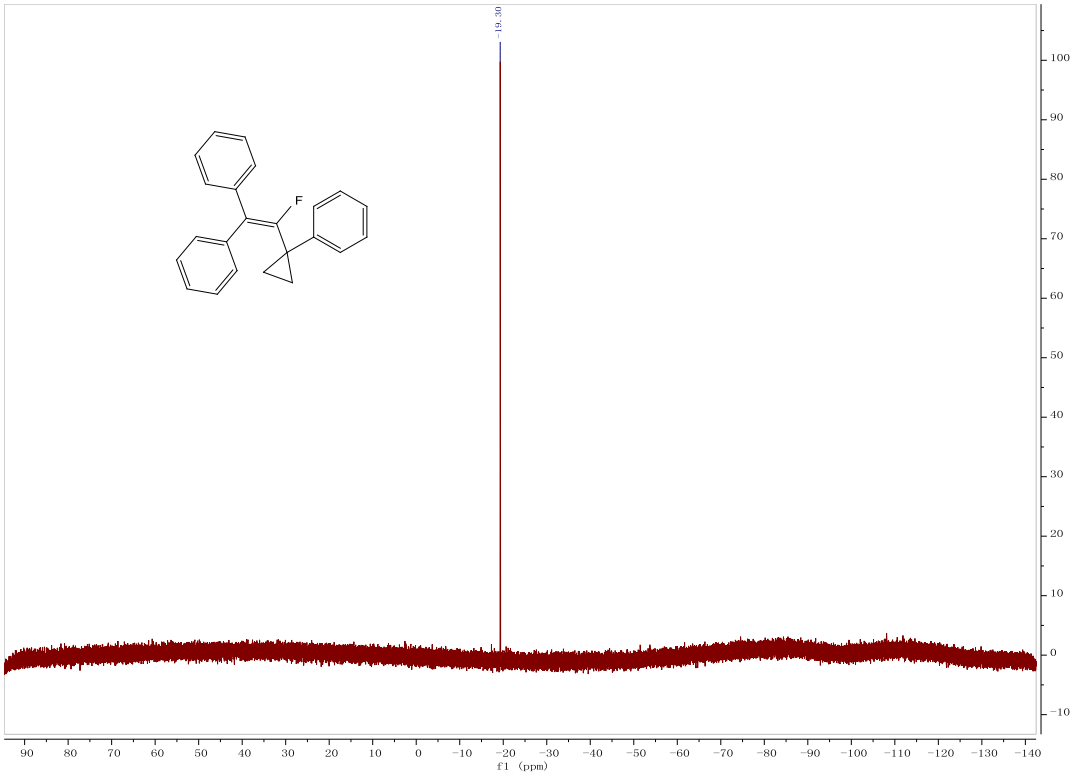
^{1}H NMR spectrum of **4k**



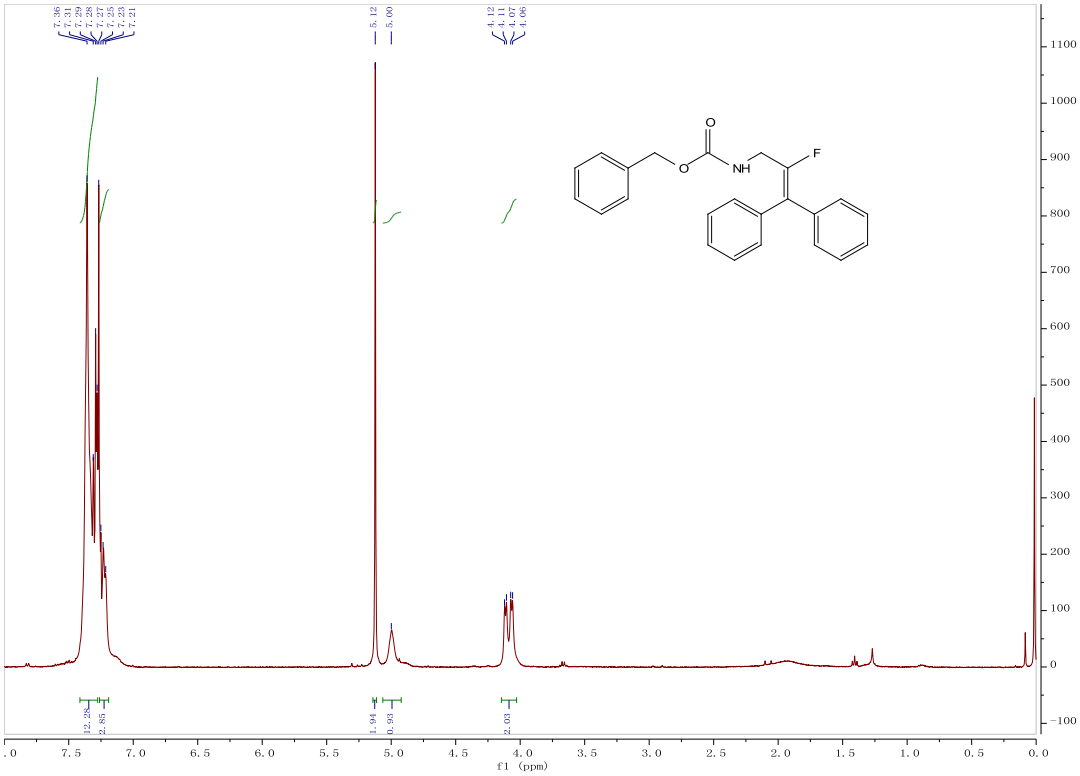
^{13}C NMR spectrum of **4k**



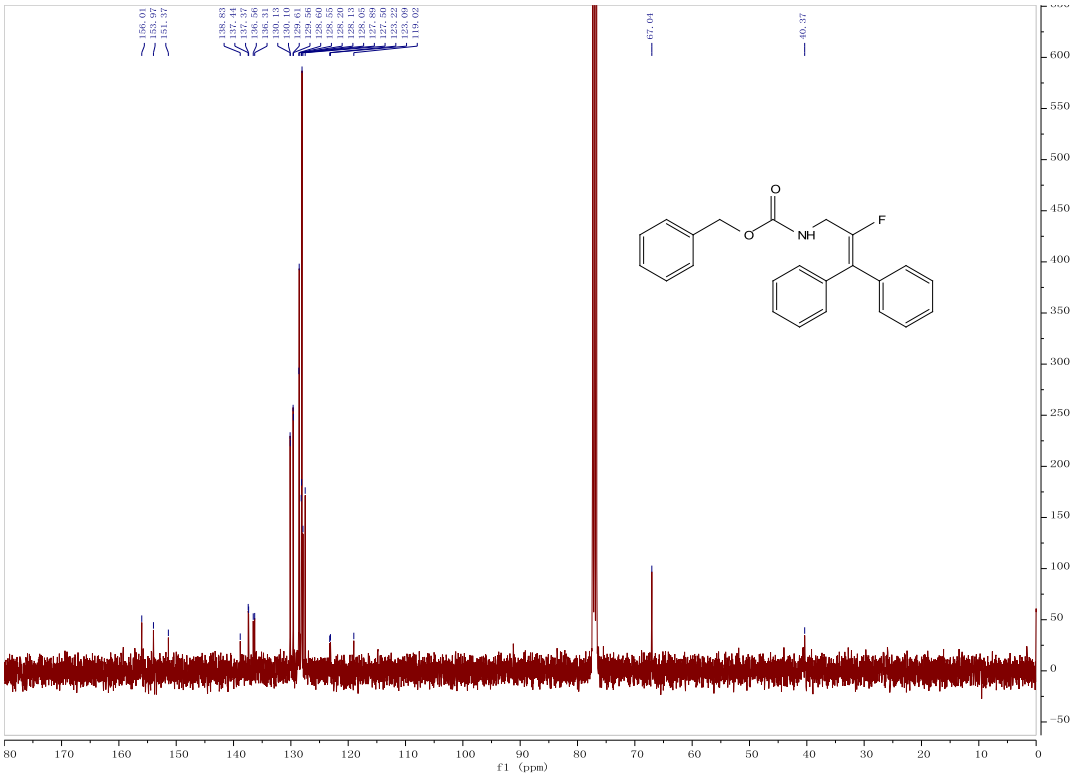
^{19}F NMR spectrum of **4k**



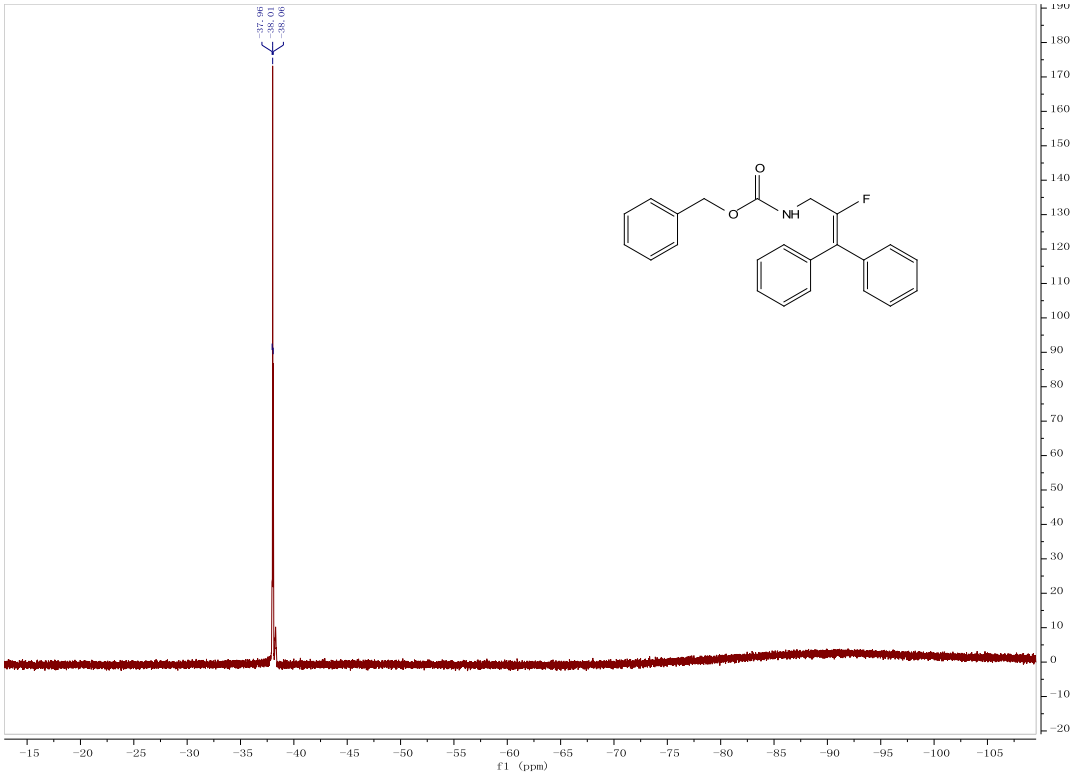
^{1}H NMR spectrum of **4l**



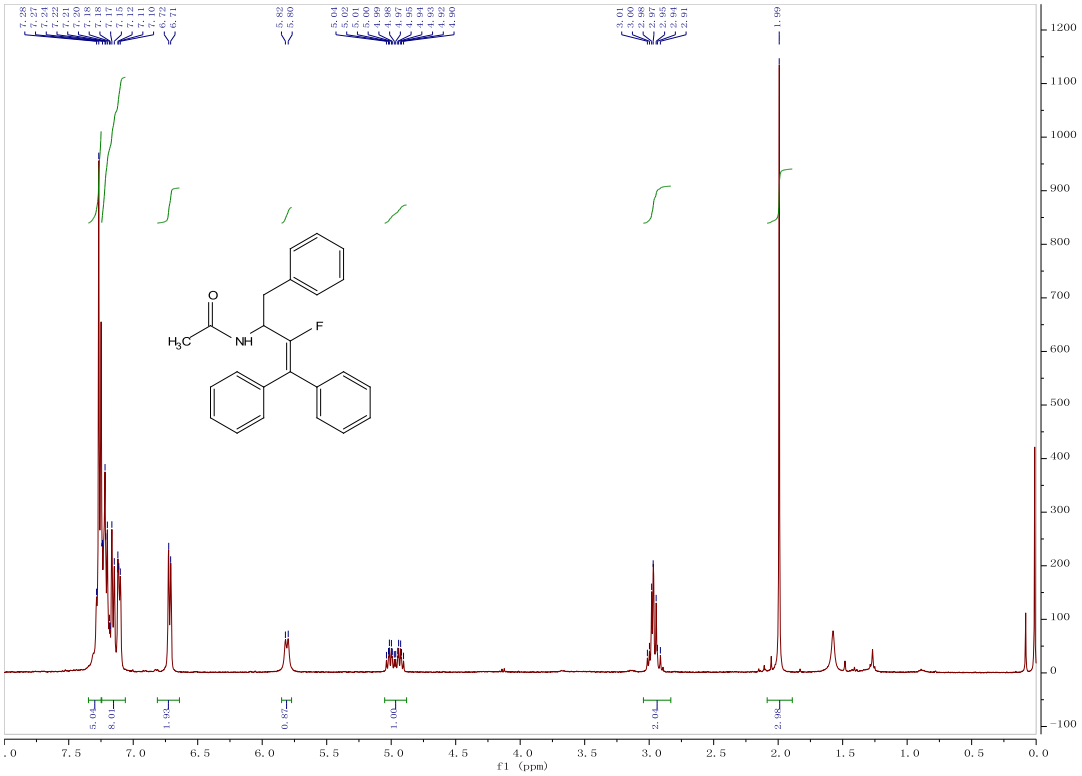
^{13}C NMR spectrum of **4l**



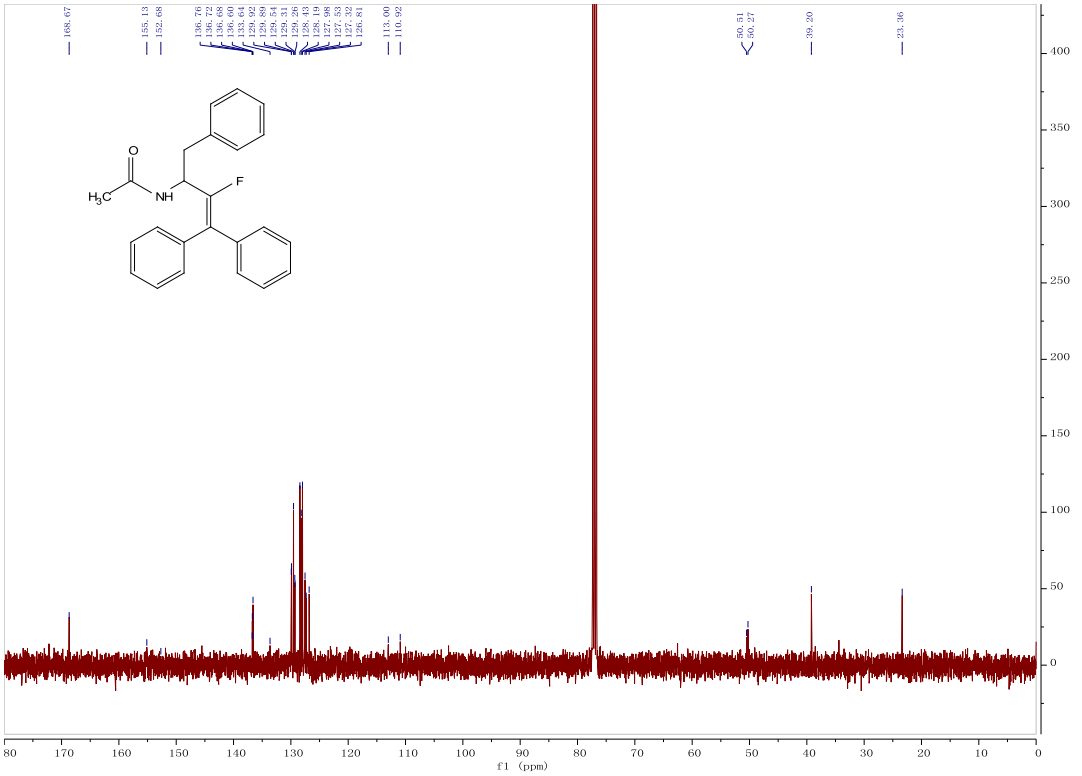
^{19}F NMR spectrum of **4l**



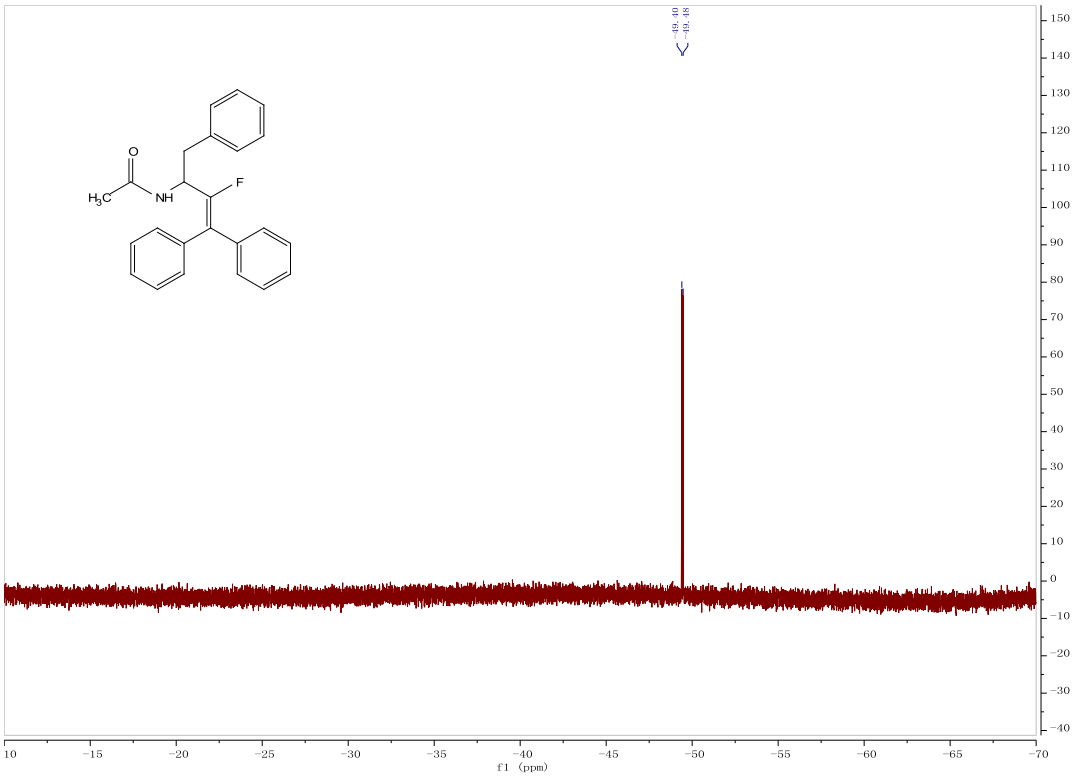
^{1}H NMR spectrum of **4m**



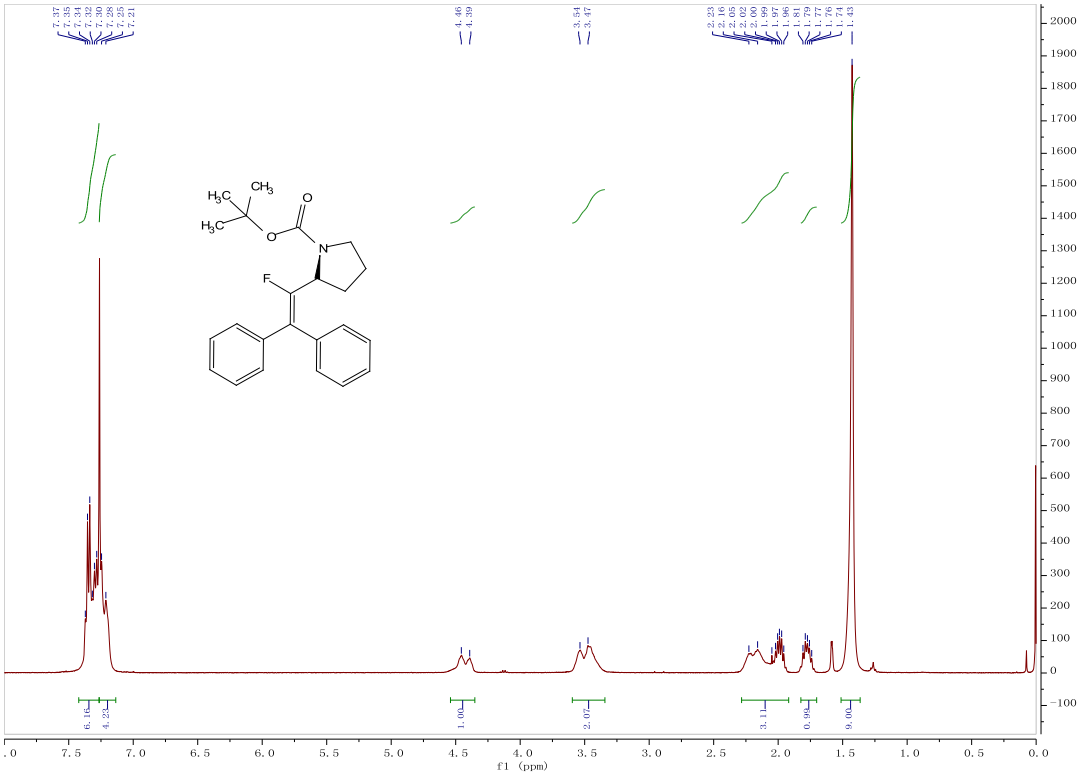
^{13}C NMR spectrum of **4m**



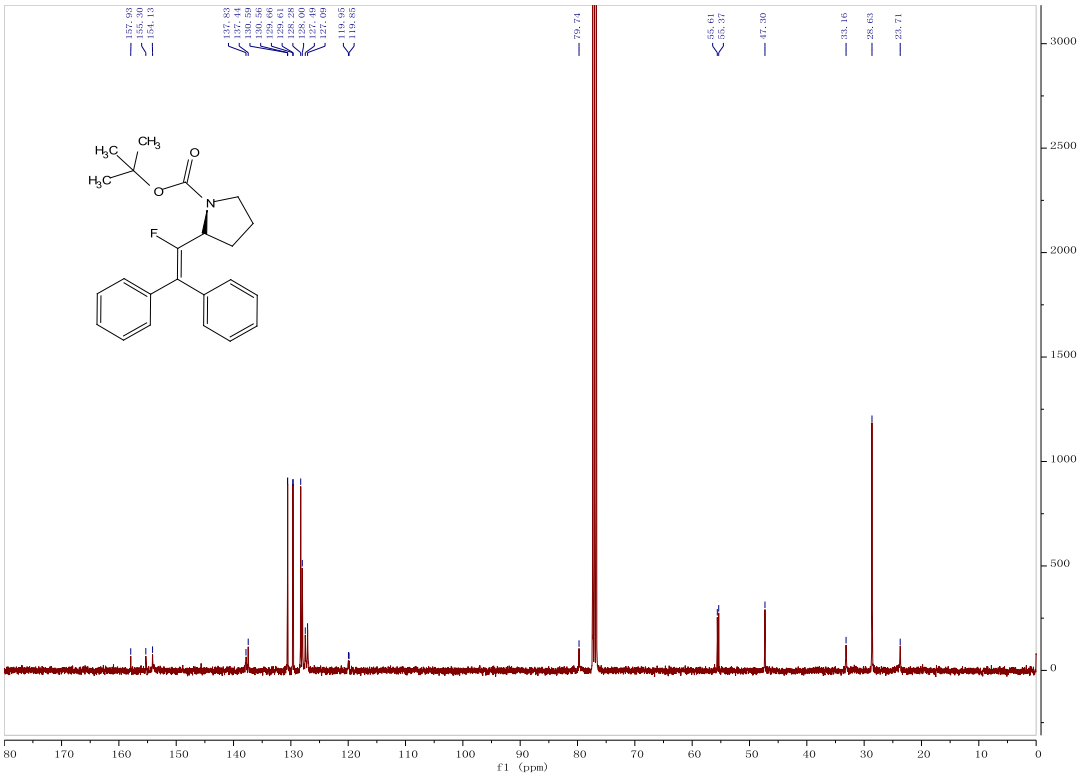
^{19}F NMR spectrum of **4m**



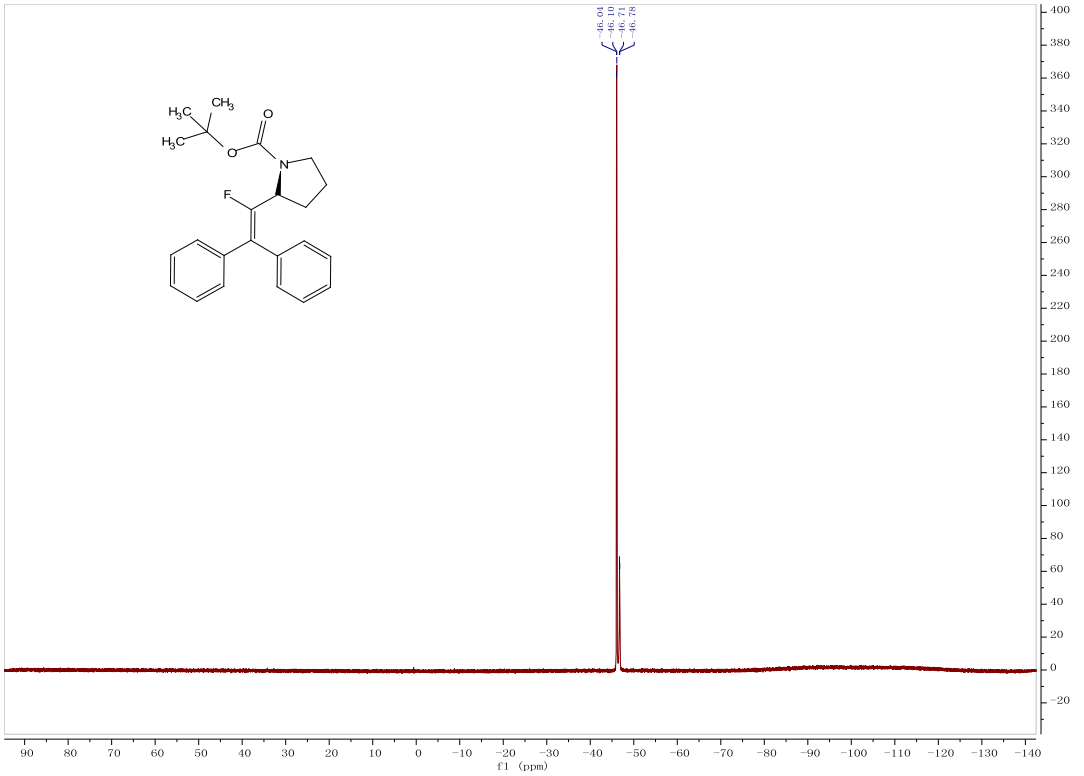
^{1}H NMR spectrum of **4n**



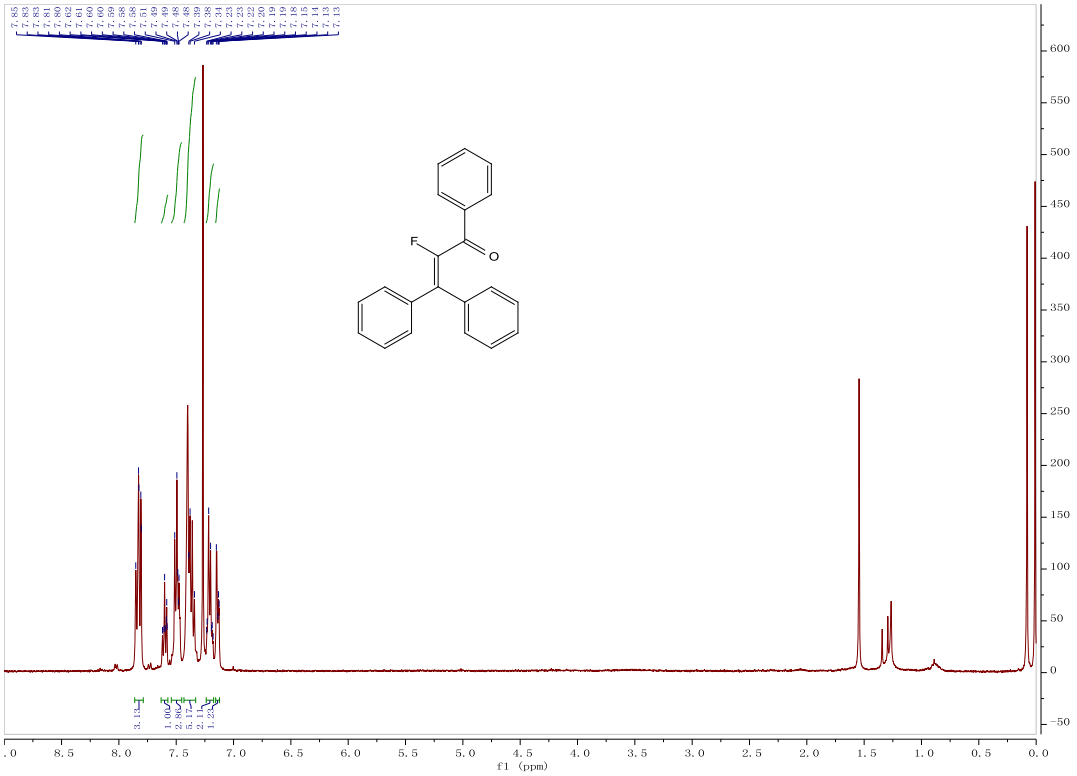
^{13}C NMR spectrum of **4n**



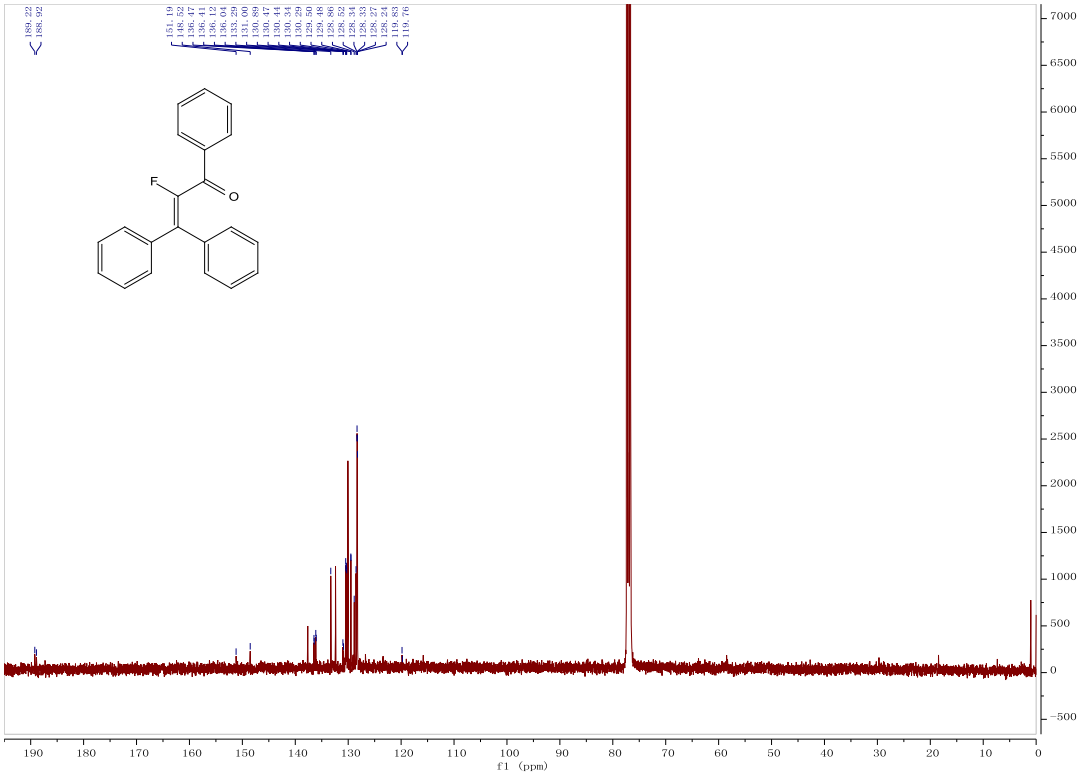
^{19}F NMR spectrum of **4n**



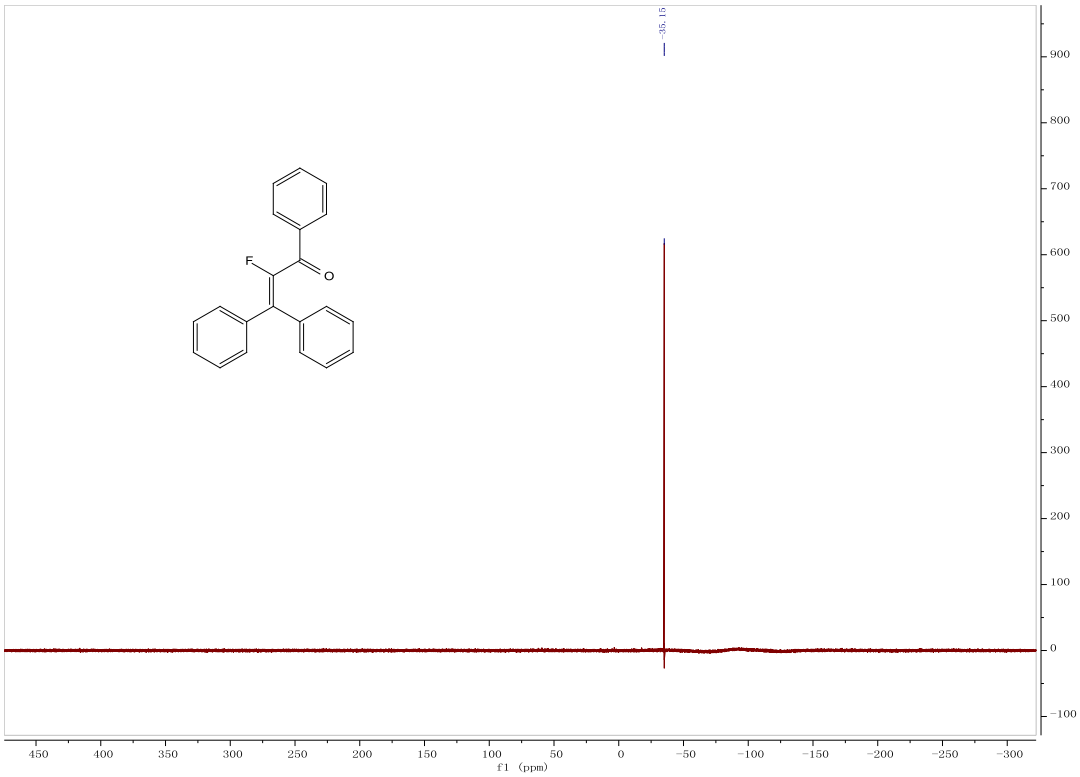
^{1}H NMR spectrum of **4o**



^{13}C NMR spectrum of **4o**

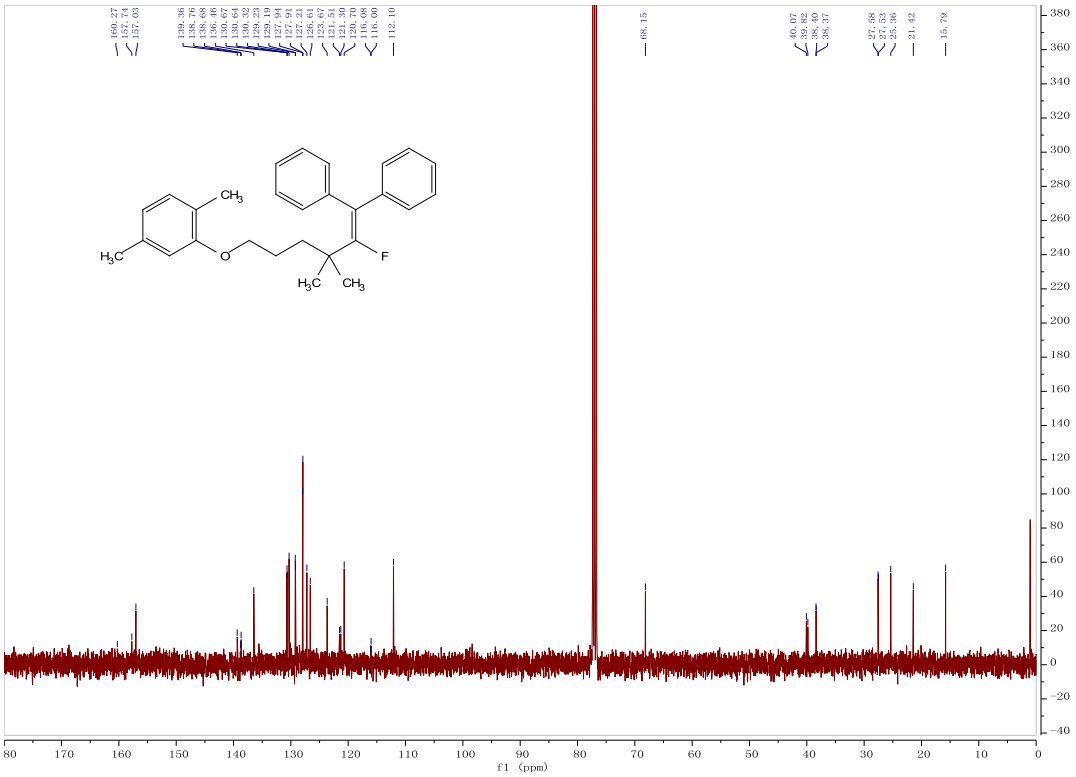


^{19}F NMR spectrum of **4o**

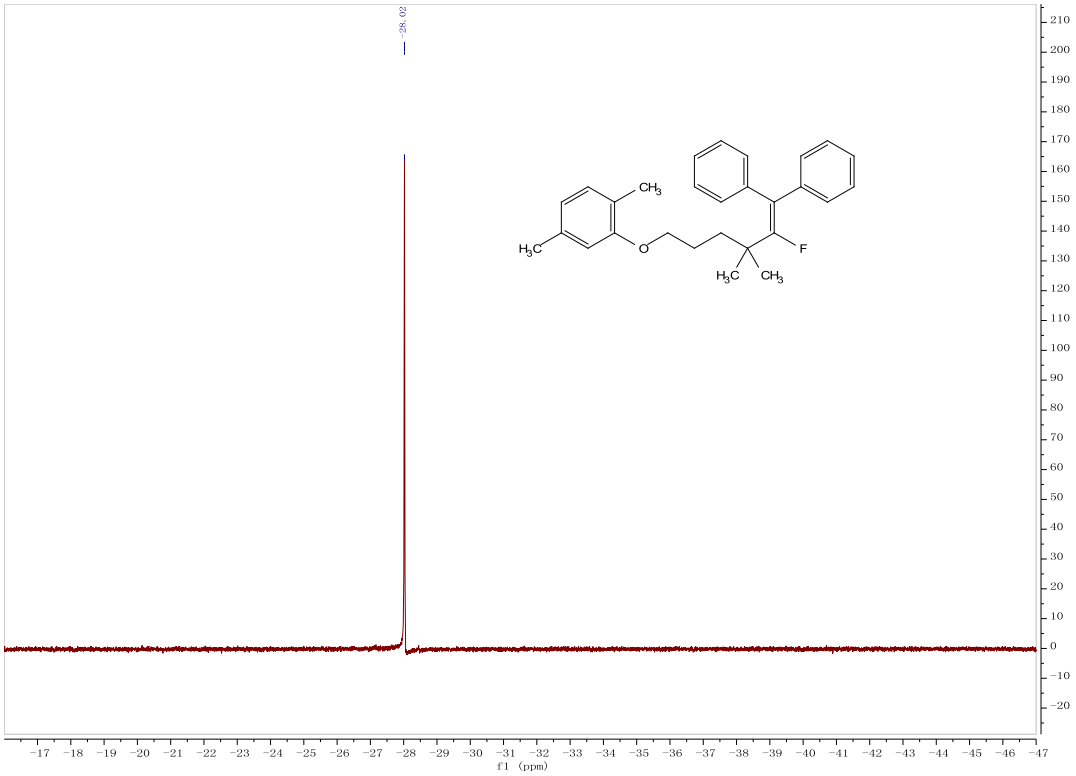


^{1}H NMR spectrum of **4p**

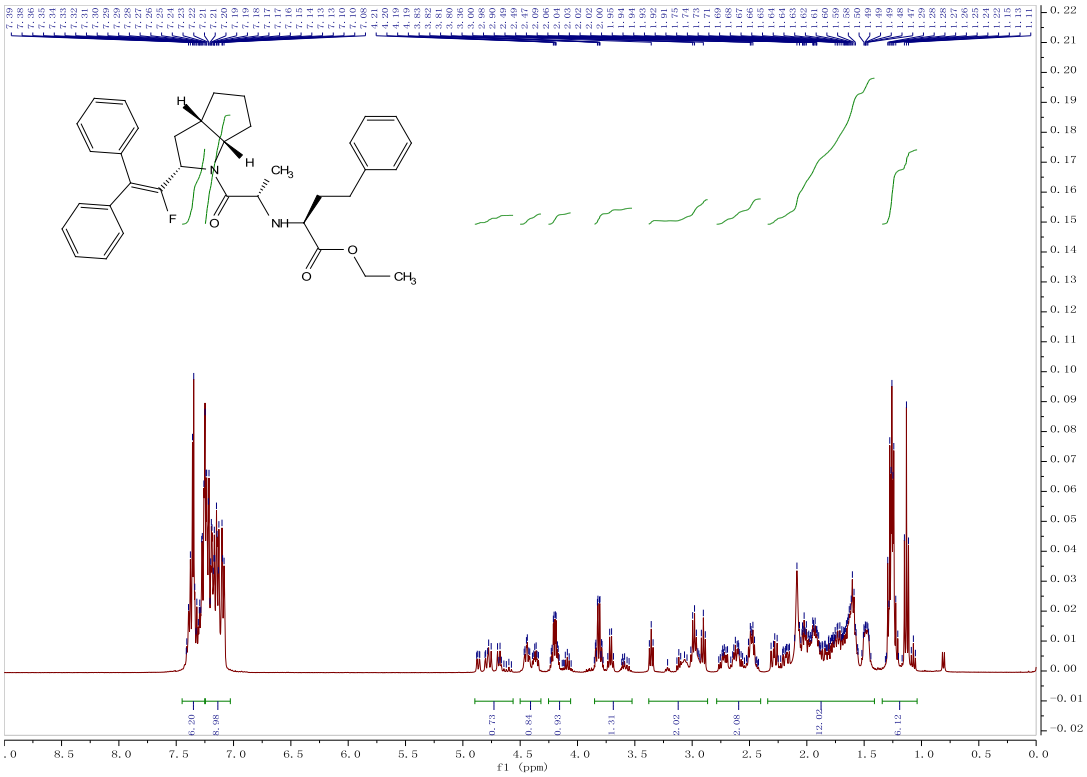
^{13}C NMR spectrum of **4p**



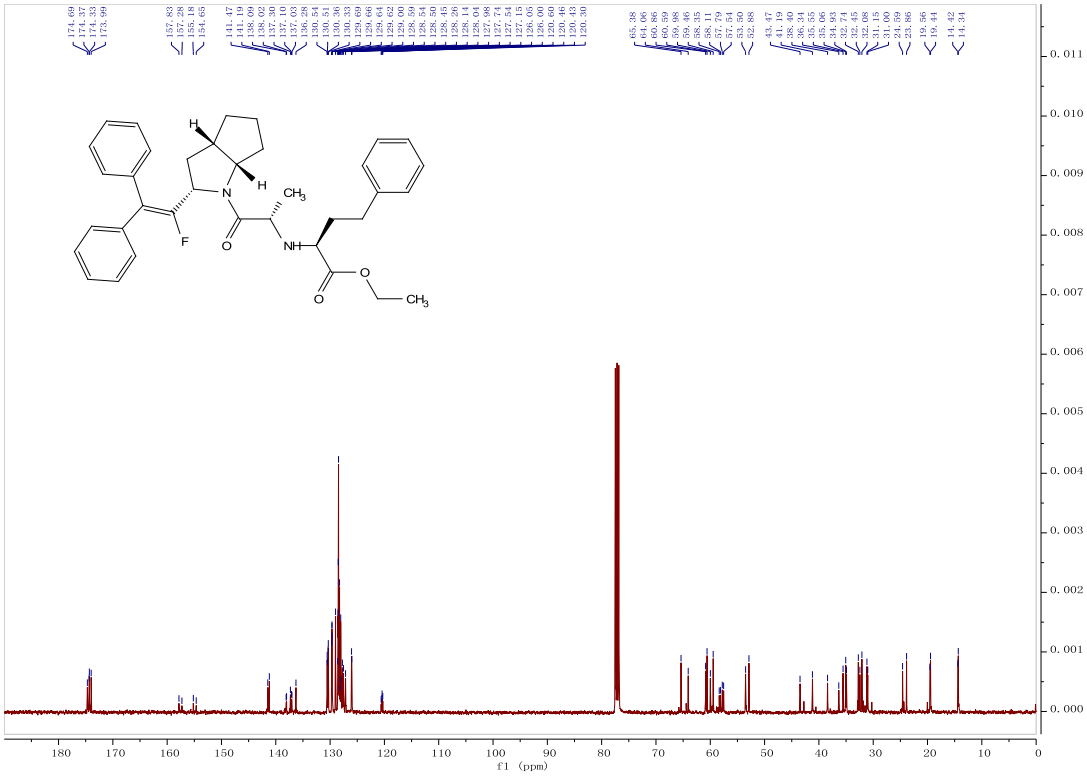
^{19}F NMR spectrum of **4p**



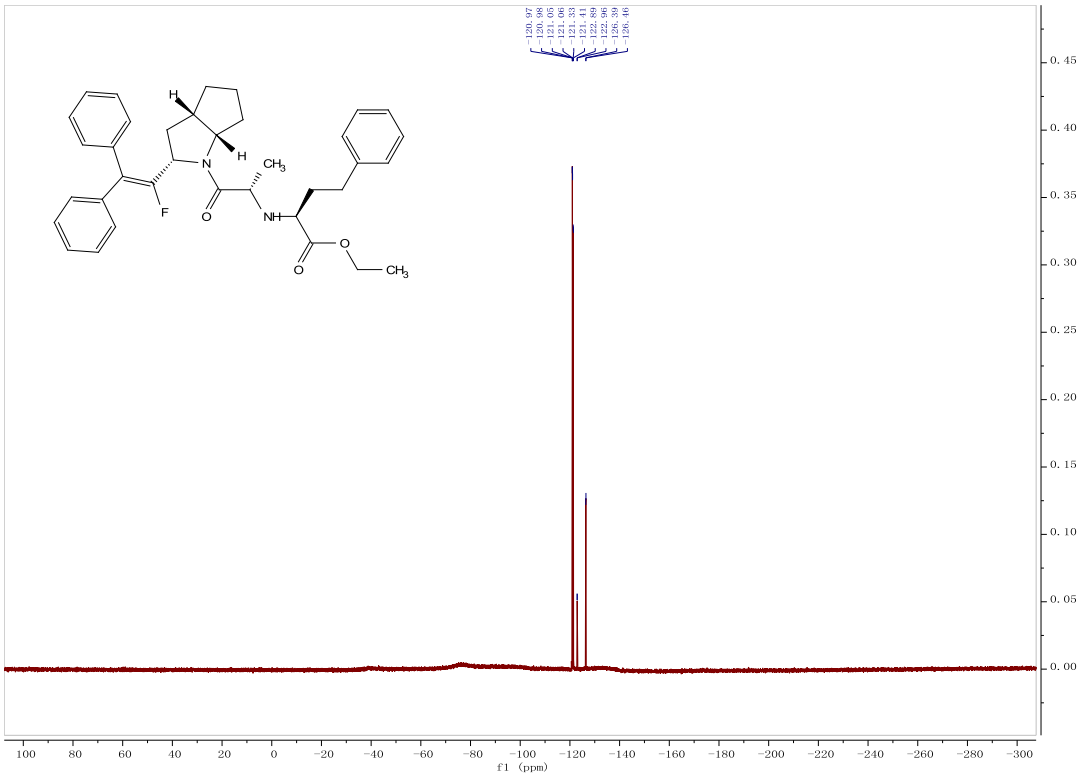
^{1}H NMR spectrum of **4q**



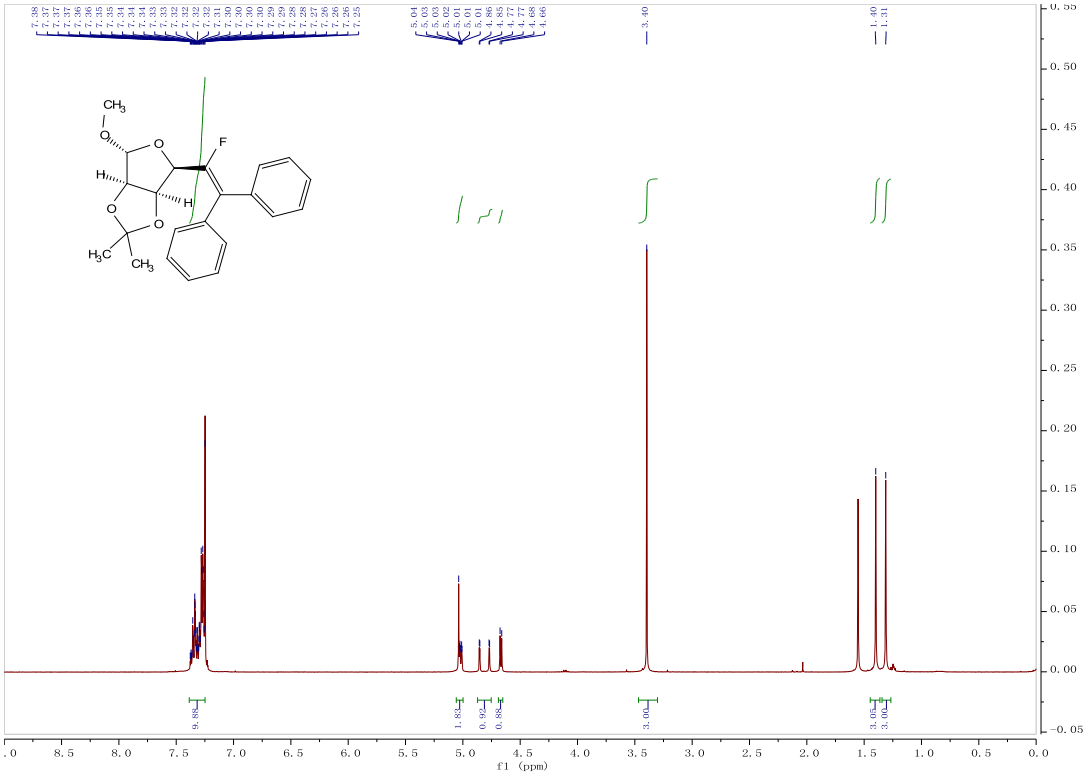
^{13}C NMR spectrum of **4q**



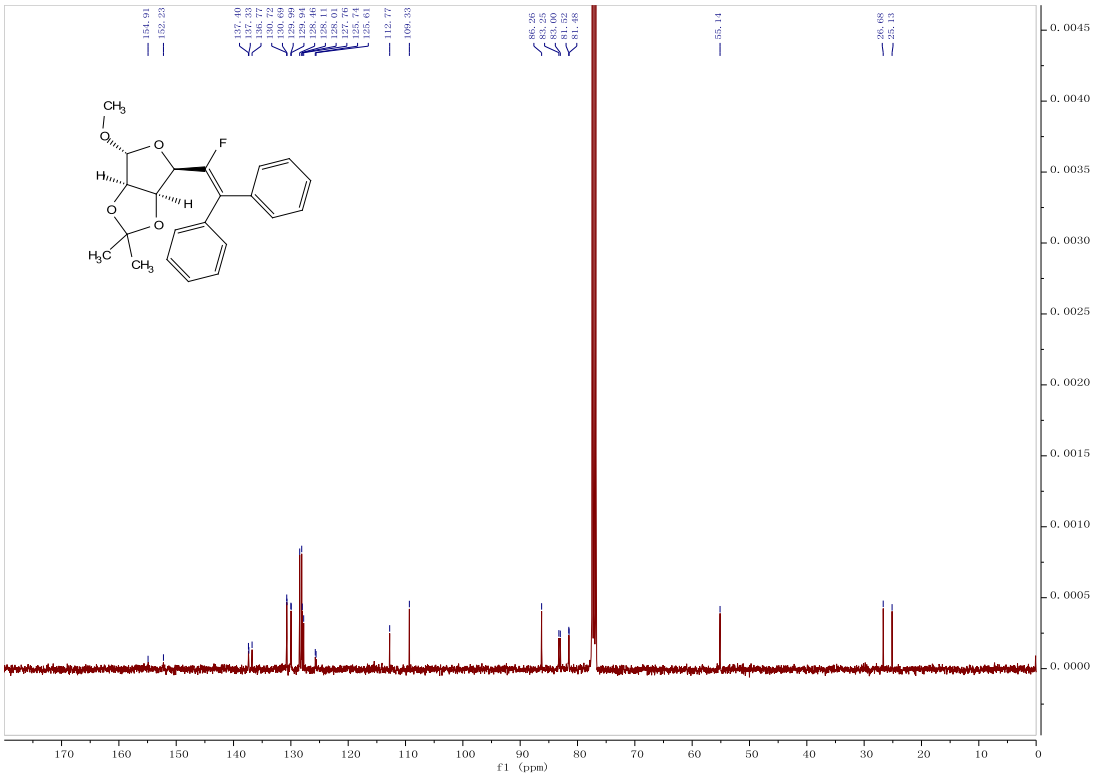
^{19}F NMR spectrum of **4q**



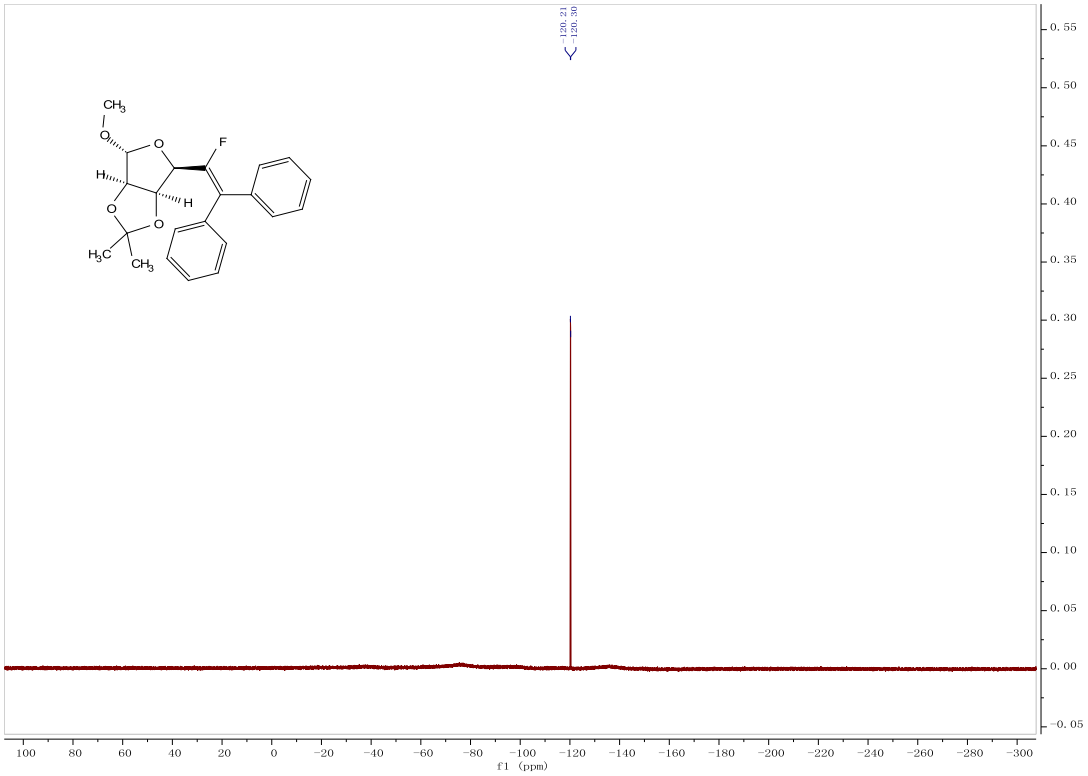
^{1}H NMR spectrum of **4r**



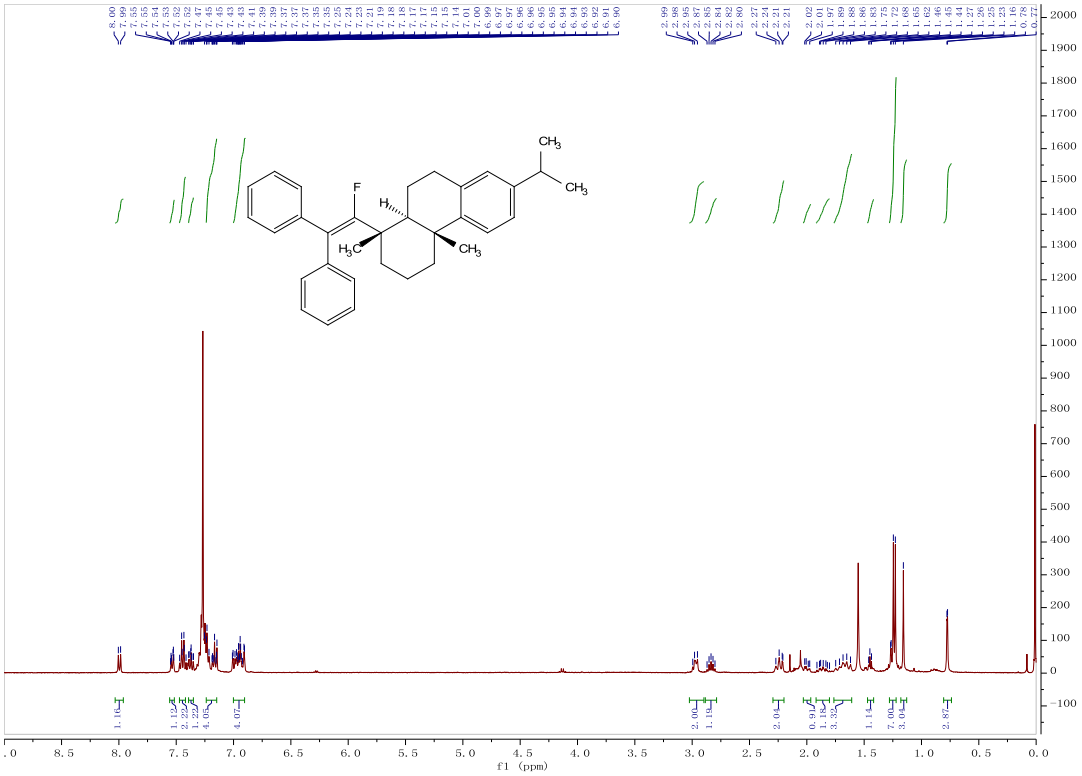
^{13}C NMR spectrum of **4r**



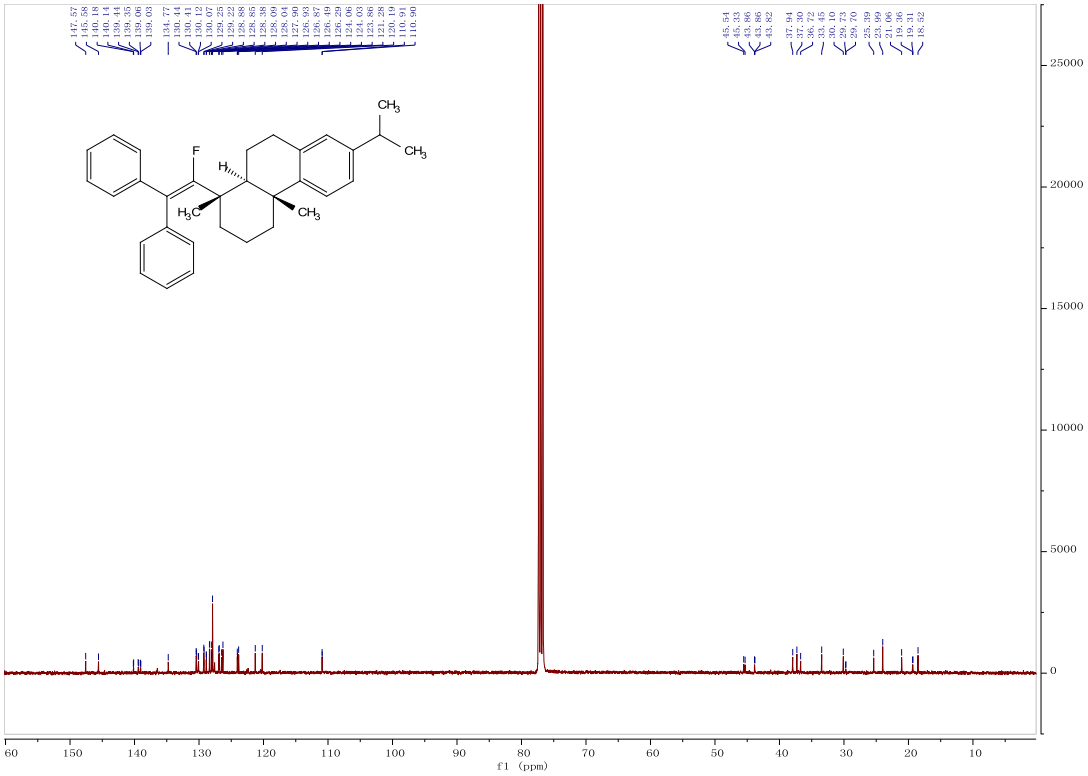
^{19}F NMR spectrum of **4r**



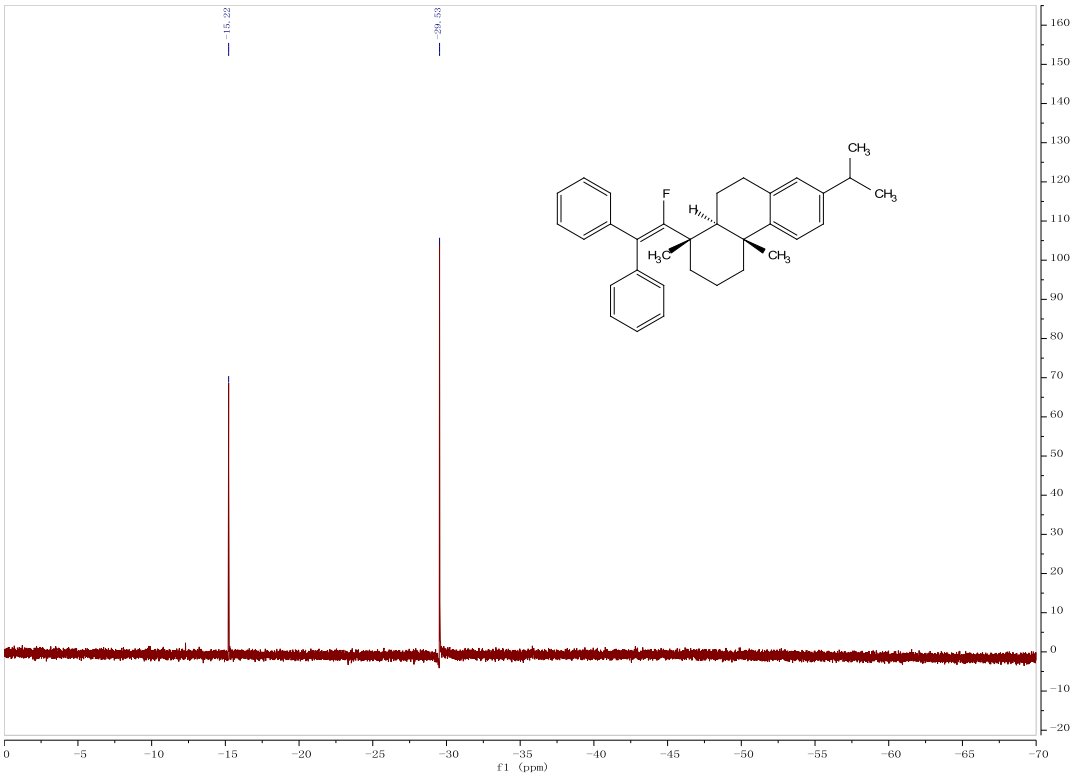
^{1}H NMR spectrum of **4s**



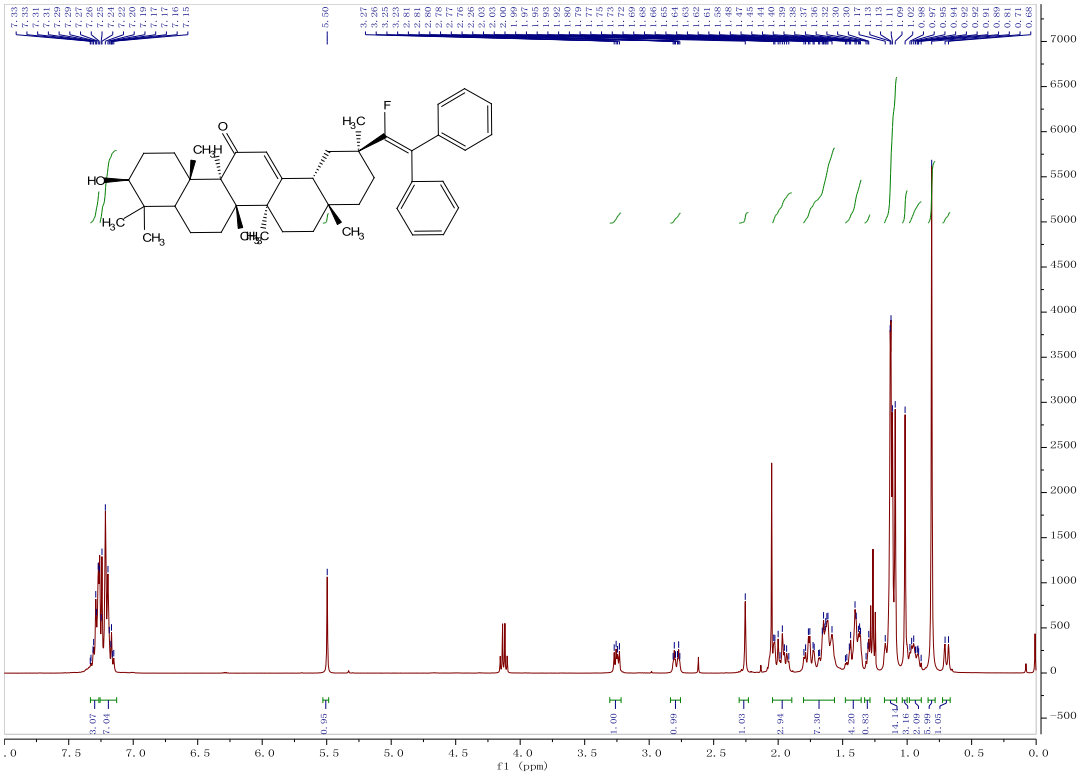
^{13}C NMR spectrum of **4s**



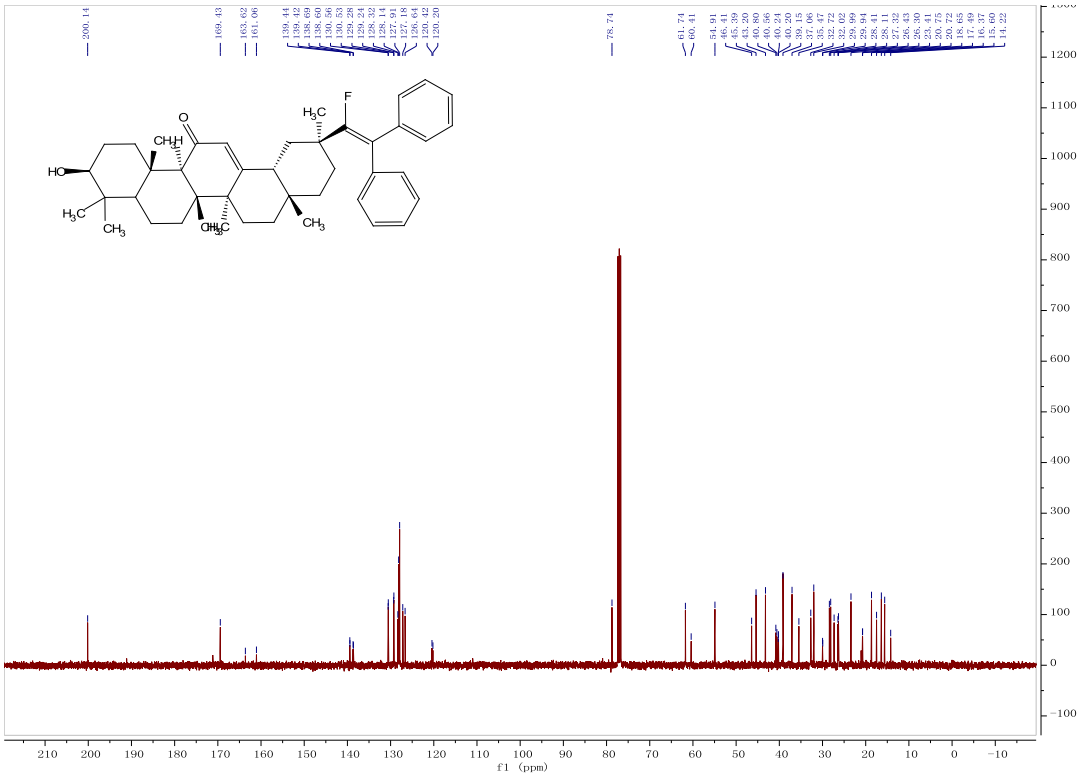
^{19}F NMR spectrum of **4s**



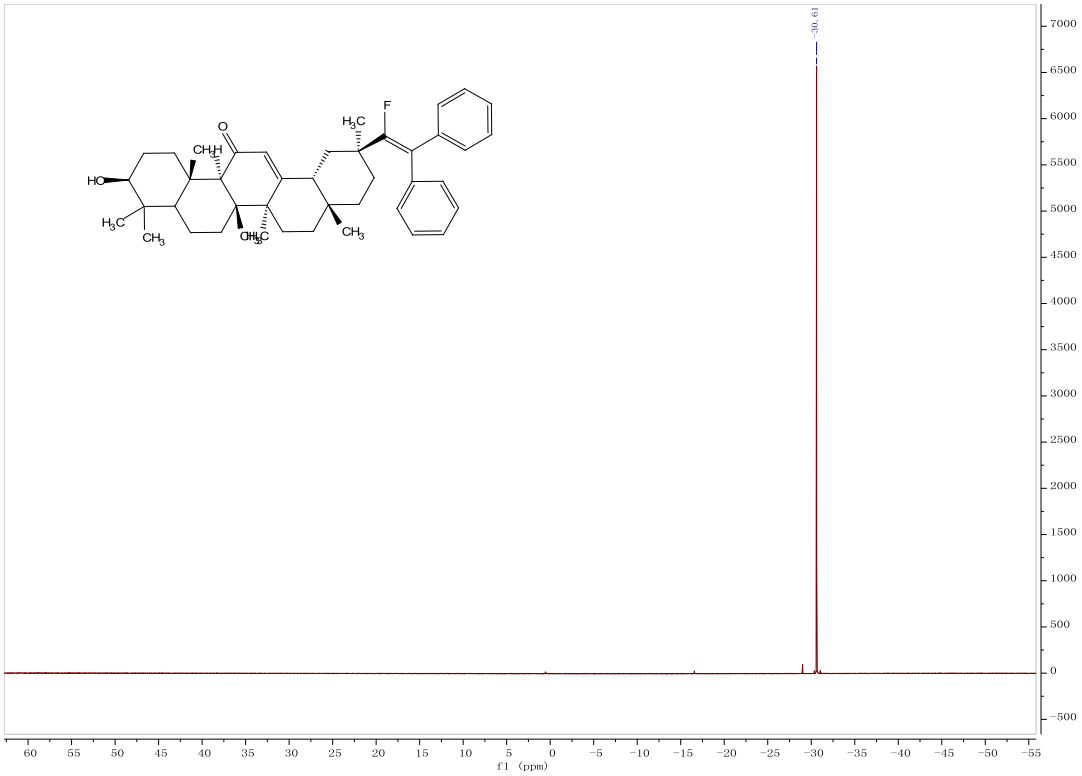
^{1}H NMR spectrum of **4t**



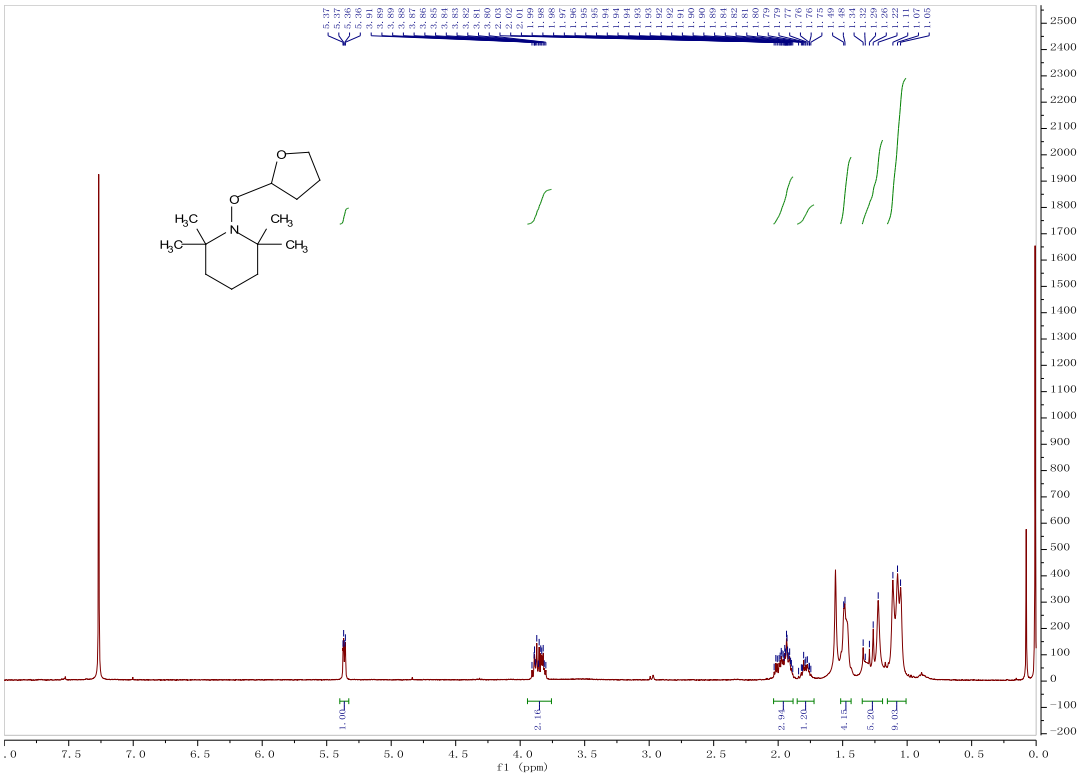
^{13}C NMR spectrum of **4t**



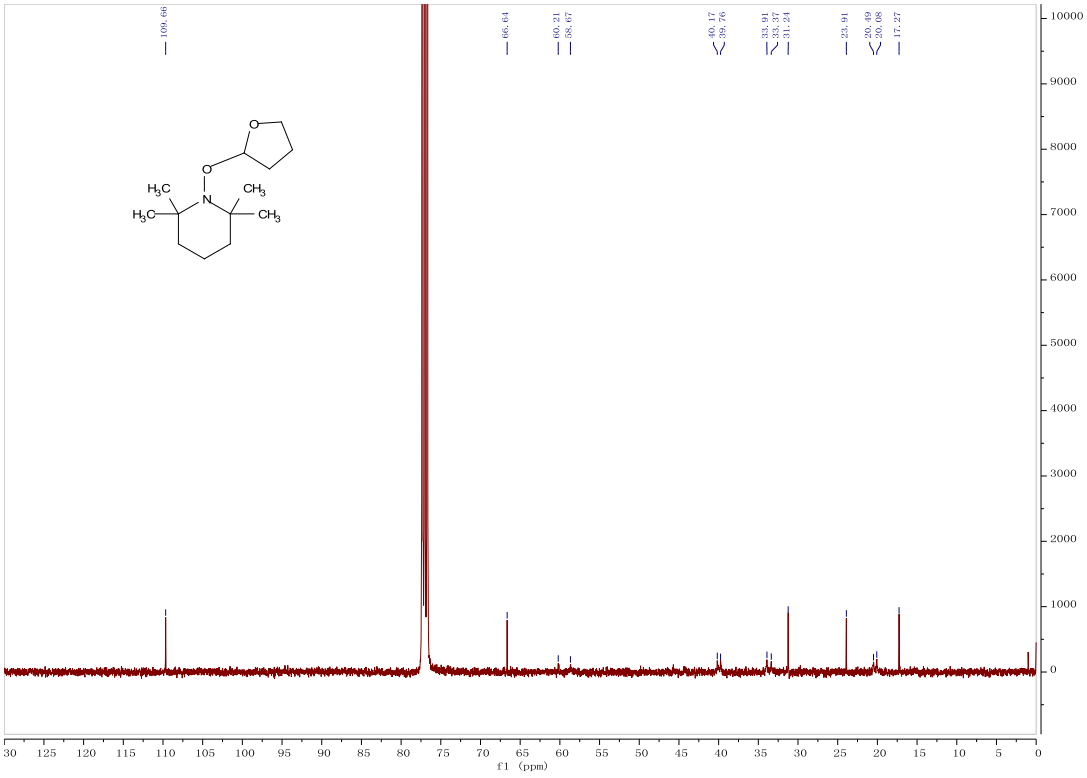
^{19}F NMR spectrum of **4t**



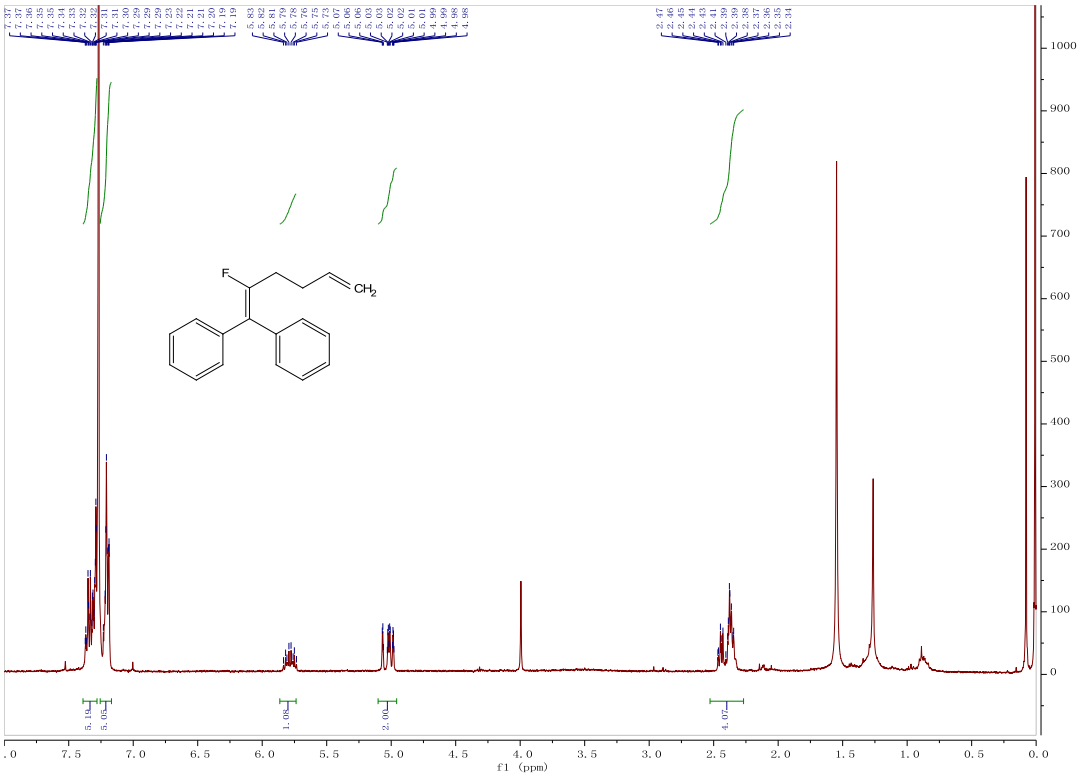
^{1}H NMR spectrum of **5**



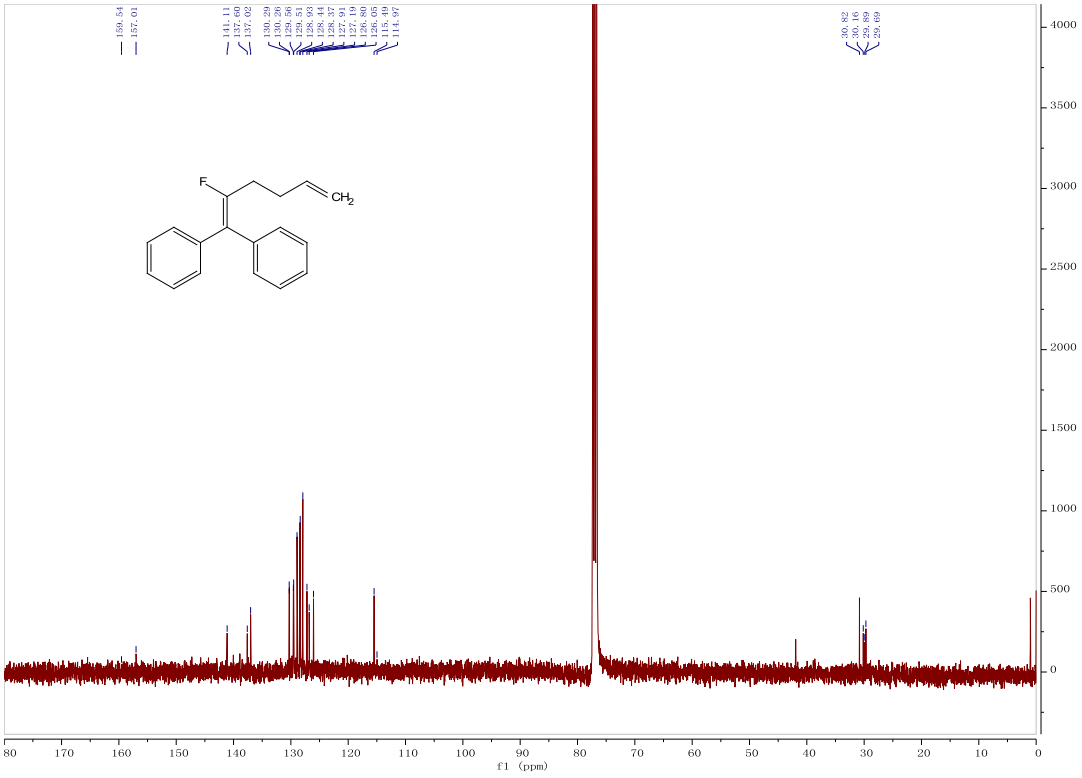
^{13}C NMR spectrum of **5**



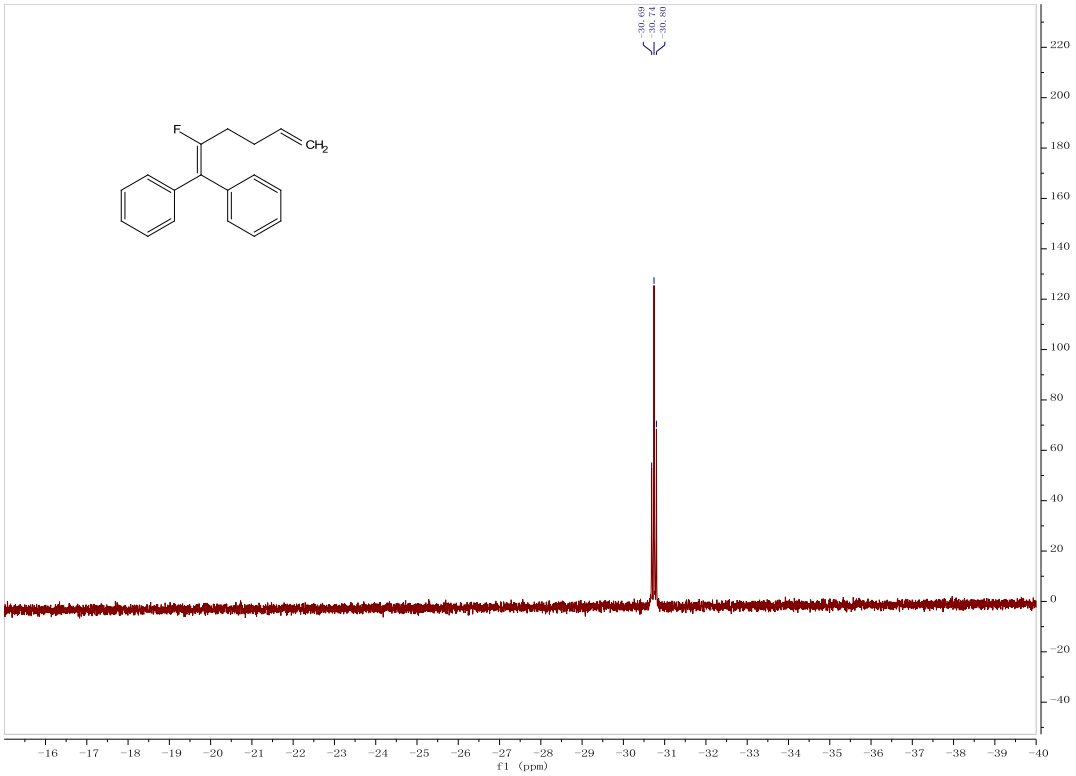
^{1}H NMR spectrum of **7**



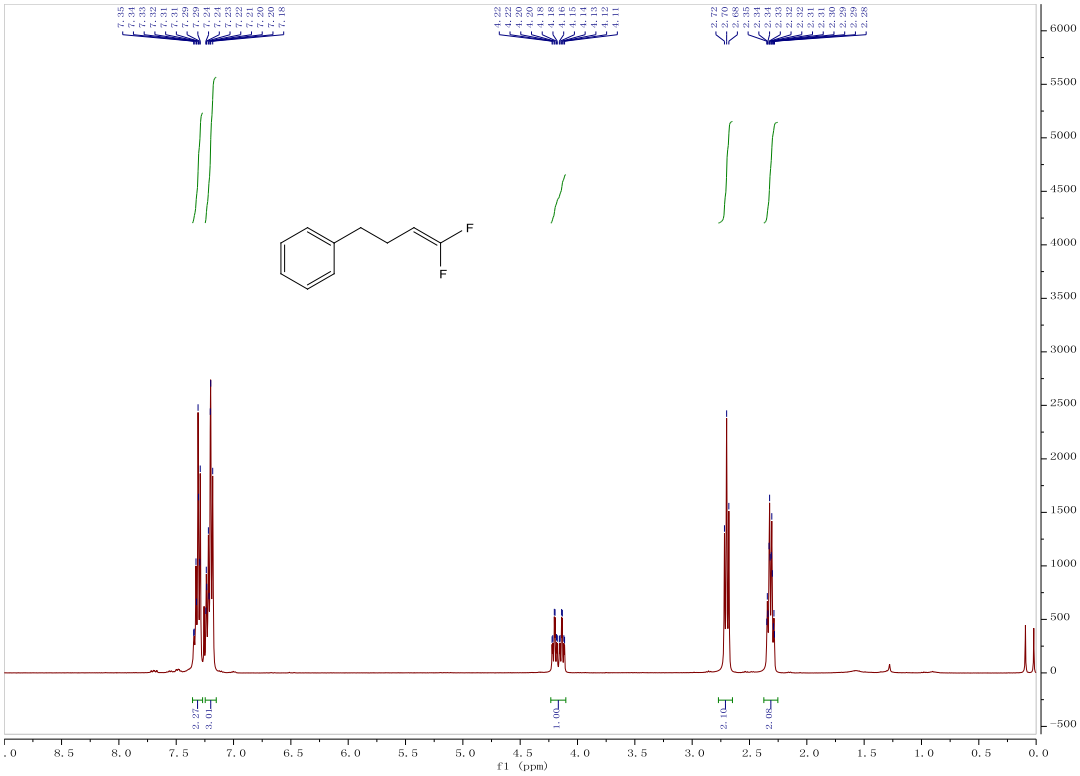
^{13}C NMR spectrum of **7**



^{19}F NMR spectrum of **7**



^{1}H NMR spectrum of **2u**



^{19}F NMR spectrum of **2u**